# Chiral Bimetallic Boronic Esters: A Donor–Acceptor Coexisting Receptor for Amines

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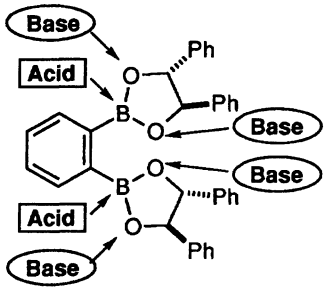
A chiral bimetallic Lewis acid, 2,2′-(1,2-phenylene)bis[(4*R*,5*R*)-4,5-diphenyl-1,3,2-dioxaborolane] (**1a**), has been synthesized. The exceptionally strong binding of **1a** with benzylamine was demonstrated by titrations. The complex formation ratio of **1a** : amine=1 : 2 was determined by a Job plot. The binding constants, $K_1$ and $K_2$, were determined by non-linear curve fitting to be $K_1 \ll K_2$. The results can be explained in terms of an allosteric effect. The first amine molecule coordinates with one of the two boron atoms of **1a**; at the same time, one NH proton interacts with one of the two oxygen atoms in the other dioxaborolane ring to form a hydrogen bond. As a result, the two dioxaborolane rings are conformationally fixed by two-point binding to provide a preferable binding site for the second amine molecule. Although only a small chiral recognition of 1-phenylethylamine has been obtained with **1a**, the clear separation of the peaks of the amine provides the possibility to use **1a** as an NMR chiral-shift reagent.

Nature uses a donor–acceptor combination in molecular recognition. A unit with both proton-donor sites and proton-acceptor sites plays essential roles in biological functions. For example, nucleic bases and peptides have protic N–H bonds and basic C=O or C=N bonds to perform their functions. A large number of studies have been reported which mimic these kinds of molecular recognitions by combining multiple hydrogen bondings. Lately, the hypothesis has been elegantly extended to supramolecular chemistry in building nano-scale molecular assemblies with well-characterized structures.[1] Compared to the use of multiple proton donor–acceptor bindings, however, fewer have been reported concerning multiple electron donor–acceptor (Lewis base–Lewis acid) attractions. Recently, some intensive studies have been reported on the synthesis of multimetallic organic compounds.[2,3] Although most conventional Lewis acid receptors, however, have only Lewis-acidic sites, there are no efficiently working basic sites in the molecule. One of the few examples of a combination of electron-acceptor metal and electron-donor hetero atoms in one molecule has been reported by Aoyama and Ogoshi using a rhodium(III)–porphyrin system. In their elegant system, the Lewis basic substituent on the porphyrin ring works cooperatively with the rhodium center.[4] Reetz et al. have prepared another system in which a molecule with a boronic ester and a crown ether-type poly ether coexist. In their study, the electron donor–acceptor feature of the compound was used in its complex formation with an amine molecule.[5]

Concerning the use of organoboron compounds as a Lewis acid, pioneering studies have been reported by Brown et al. on the interaction of various boranes with amines.[6] Bidentate binding of two Lewis acidic boron centers to one methoxide anion was first reported in 1967 by Shriver.[7] Recently, bidentate Lewis acids with two boron centers, developed by Katz,[8] have provided a new orientation in this field. Narasaka et al.[2f] also reported a bidentate diboronate which recognized the location of two amino groups of diamines.[9] However, all of those studies focused on the crab-like bidentate capture of Lewis basic guest molecules. Moreover, the molecules have only Lewis-acidic sites, which are electron-pair acceptor sites, but do not have any efficiently working electron donor sites (Lewis basic sites). The idea that a combination of multiple electron donor-acceptor bonds would provide the more "sophisticated" functions prompted us to synthesize a diboronate, 2,2′-(1,2-phenylene)bis[(4*R*,5*R*)-4,5-diphenyl-1,3,2-dioxaborolane] (**1a**).[10]

The present compound has the following two characteristic features. First, the molecule has four basic oxygen sites in addition to the two Lewis-acidic centers. The basic sites play essential roles in the binding properties of **1a** (Chart 1). Second, the compound has chirality. In sharp contrast to the rapid growing of newly designed chiral Lewis acids as




**1a**

Chart 1.

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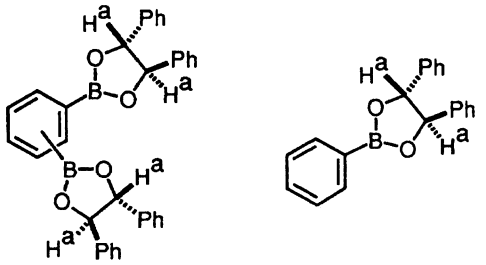


**1a**: *ortho-*
**1b**: *meta-*
**1c**: *para-*

**2**

Chart 2.

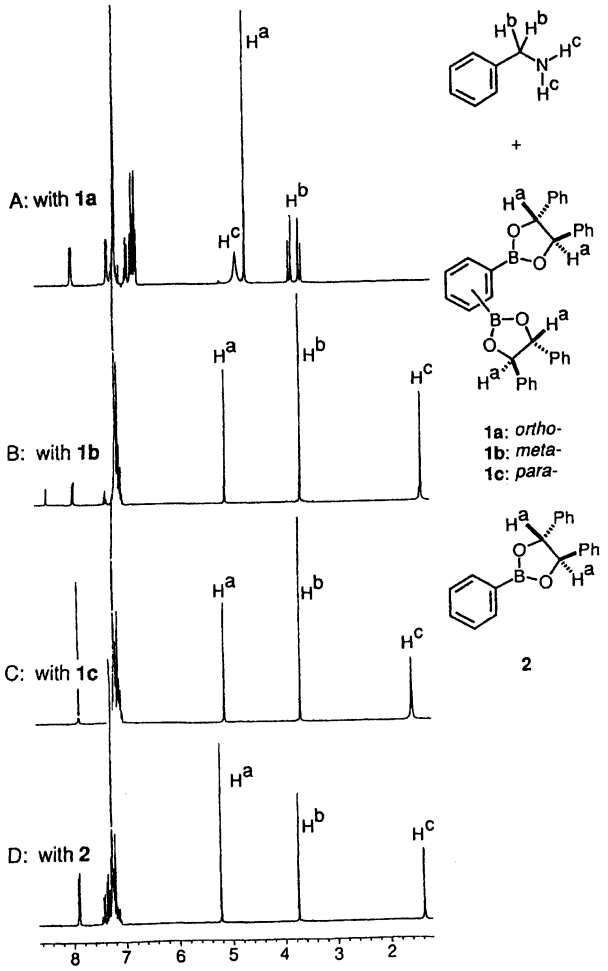



Fig. 1. $^1$H NMR spectra at 20 °C in $CDCl_3$ of A: benzylamine (0.20 M) with *ortho*-isomer **1a** (0.10 M), B: with *meta*-isomer **1b** (0.10 M), C: with *para*-isomer **1c** (0.10 M), and D: with monoboronate **2** (0.20 M). The benzylic $H^b$ protons of the amine are shown in a diastereotopic AB qurtet pattern only in the presence of *ortho*-isomer **1a**.

catalysts for asymmetric transformations,[11] to the best of our knowledge, this is the first study on a chiral bimetallic Lewis acid, expecting the two metal centers to "help each other".[12–14]

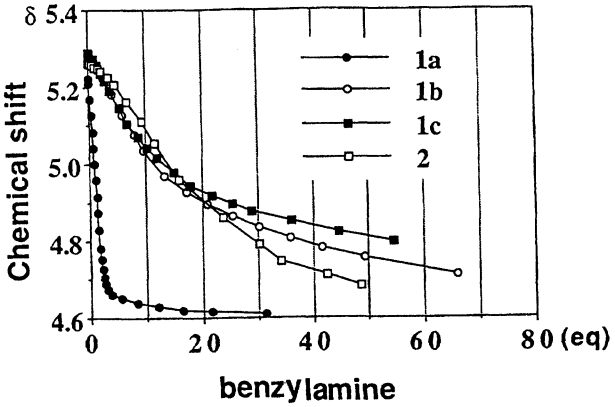



Fig. 2. Titration of **1a**—**c** and **2** with benzylamine at 20 °C (0.10 M of **1a**—**c** or **2** in $CDCl_3$). Chemical shifts of the singlets due to methine protons ($H^a$) of boronic esters are plotted against the molar equivalents of the added benzylamine.

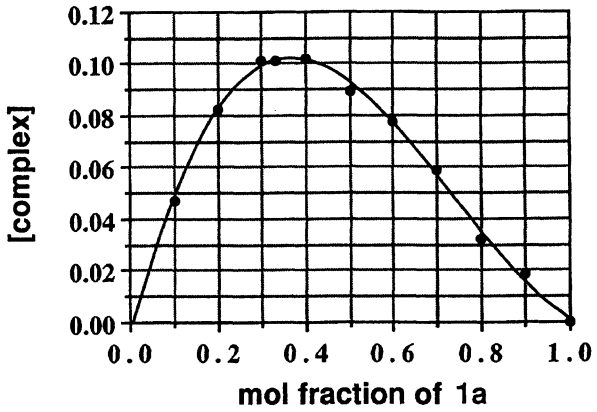



Fig. 3. Job's plot of **1a**-benzylamine. Mol fraction of **1a** has been changed continously and by keeping the sum of [**1a**] and [benzylamine] equals 0.05 M. The *Y* axis represents the value [**1a**]·[$\Delta\delta_{observed}$] which equals [complex]·[$\Delta\delta_{complex}$] where $\Delta\delta_{complex}$ is a constant. The maximum of the complex concentration is observed at the mol fraction of **1a** is 0.33 that means the complex consists of **1a** : amine=1 : 2.

## Results and Discussion

**Synthesis of Four Lewis Acids (1a—c and 2) Having Common Dioxaborolane Frameworks.** The chiral *ortho*-diboronate **1a** as well as the *meta*-isomer **1b**, the *para*-isomer **1c**, and the monometallic analog **2** were synthesized as follows (Chart 2). A treatment of 1,2-bis(trimethylsilyl)benzene with $BCl_3$ gave a mixture of 1,2- and 1,3-bis(dichloroboryl)benzene in a 1 : 1 ratio. The addition of this mixture to a chloroform solution of (*R*,*R*)-1,2-diphenyl-1,2-ethanediol, followed by the removal of the generated HCl in vacuo and the subsequent purification by column chromatography and/or recrystallization, gave pure **1a** and **1b**. Other compounds, **1c** and **2**, were prepared from the corresponding boronic acids and the diol.

**Comparison of 1a—c and 2 in their Complex Formation with Benzylamine at 20 °C.** First, the interactions be-

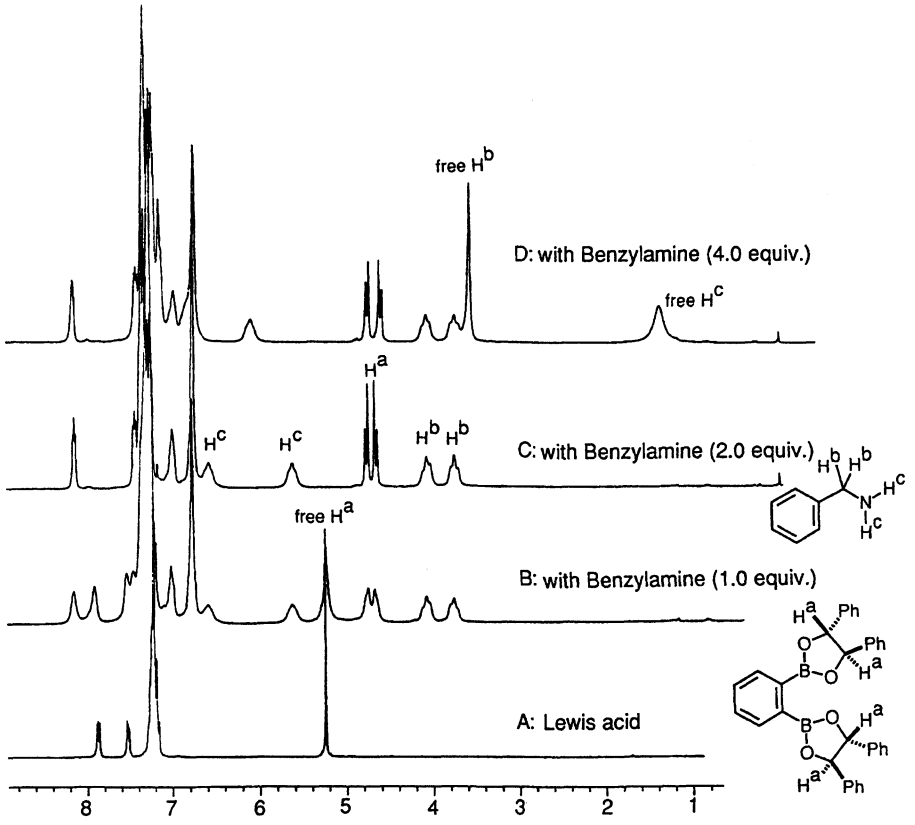
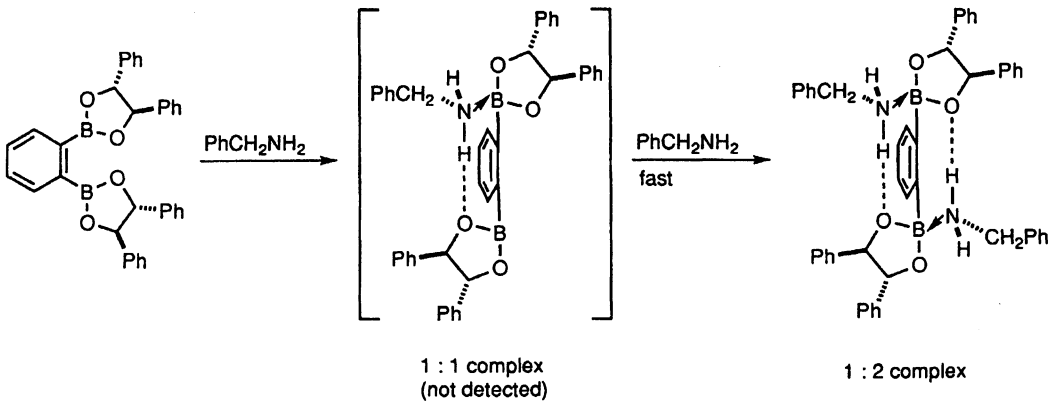



Fig. 4. Low temperature $^1$H NMR spectra of a mixture of **1a** (0.10 M) and benzylamine at −50 °C in $CDCl_3$, A: free **1a** only without amine added, B: with 1.0 equiv of amine; the 1 : 2 complex and free **1a** are present, C: with 2.0 equiv of amine; only the 1 : 2 complex is present, D: with 4 equiv of amine; the 1 : 2 complex and free benzylamine are present.




Scheme 1.

tween benzylamine and each of the boronic esters, **1a**—**c** and **2**, were investigated based on the $^1$H NMR spectra in $CDCl_3$ at 20 °C. The results are summarized in Fig. 1. Among the four boronic esters, the *ortho*-diboronate **1a** behaves uniquely (Fig. 1, A). Two originally enantiotopic benzylic protons ($H^b$) of the amine appear as a diastereotopic AB quartet only in the presence of **1a**. In addition, a marked down-field shift is observed for the NH protons ($H^c$) compared with the free amine. Those results indicate that benzylamine is complexed with **1a** and fairly influenced by the chiral surrounding. At the same time, however, the signal due to the methine protons ($H^a$) of the dioxaborolane frameworks of **1a** remained as a singlet with a slight up-field shift. This observation suggests that the complex formation equilibrium is rapid compared with the NMR time scale, so that the methine signal due to **1a** is observed as the averaged singlet. In sharp contrast to the *ortho*-diboronate **1a**, *meta*- and *para*-diboronates, **1b** and **1c**, and monoboronate **2** showed only small changes on the whole signal pattern upon admixture with benzylamine under the same conditions. In those cases, the benzylic protons ($H^b$) of the amine are shown as singlets, and the chemical shifts of peaks due to amino protons ($H^c$) are hardly influenced by the boronates (Fig. 1, B—D).

Figure 2 shows the result of titration of the boronic esters

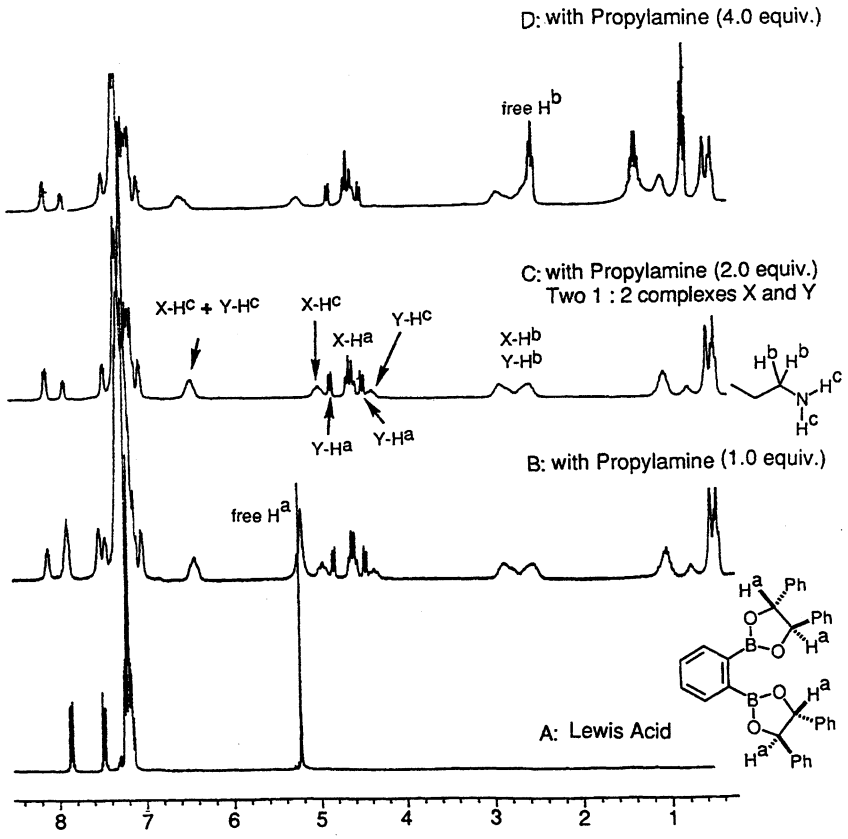



Fig. 5. Low temperature $^1$H NMR spectra of a mixture of **1a** (0.10 M) and propylamine at −50 °C in $CDCl_3$, A: free **1a** only without amine added, B: with 1.0 equiv of amine; the two 1 : 2 complexes (X and Y) and free **1a** are present, C: with 2.0 equiv of amine; the two 1 : 2 complexes (X and Y) are present, D: with 4 equiv of amine; the two 1 : 2 complexes (X and Y) and free benzylamine are present.

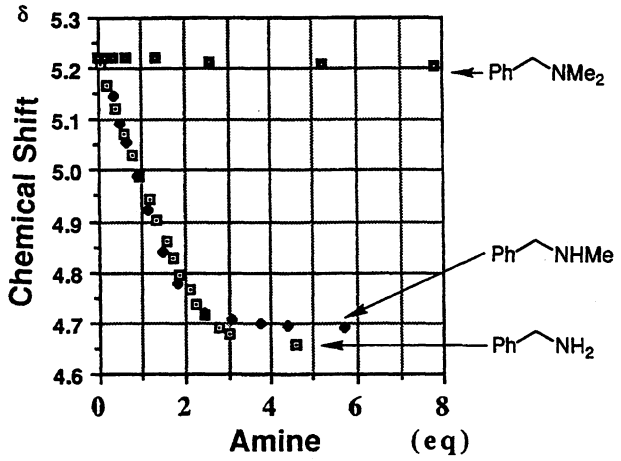



Fig. 6. Titration of **1a** with benzylamine, *N*-methylbenzylamine, and *N*,*N*-dimethylbenzylamine at 20 °C (0.10 M of **1a** in $CDCl_3$). Chemical shifts of the singlet due to methine protons ($H^a$) of **1a** are plotted against the molar equivalents of the added amine.

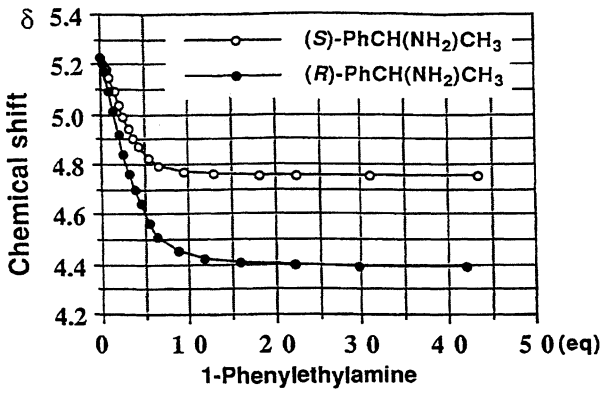



Fig. 7. Titration of **1a** with (*S*)- and (*R*)-1-phenylethylamine at 20 °C (0.10 M of **1a** in $CDCl_3$). Chemical shifts of the singlet due to methine protons of **1a** are plotted against the molar equivalents of the added benzylamine.

(**1a**, **1b**, **1c**, and **2**) with benzylamine at 20 °C. The chemical-shift changes of the singlets due to methine protons (around $\delta = 5.3$) were monitored by $^1$H NMR, and are plotted against the concentration of the amine. Clear saturation is particular for **1a**, which demonstrates the exceptionally strong binding of **1a** with benzylamine. Since the system is under rapid equilibrium, the complex formation ratios could not be estimated from this titration experiment.

**Determination of the Ratio of 1a vs. Benzylamine in the Complex.** The complex formation ratio of **1a** : benzylamine=1 : 2 has been revealed by a Job plot.[15] The experiment was carried out by using $^1$H NMR at 20 °C while keeping $[\mathbf{1a}]_{initial}+[amine]_{initial}=0.05$ M in $CDCl_3$ (M=mol dm$^{-3}$).

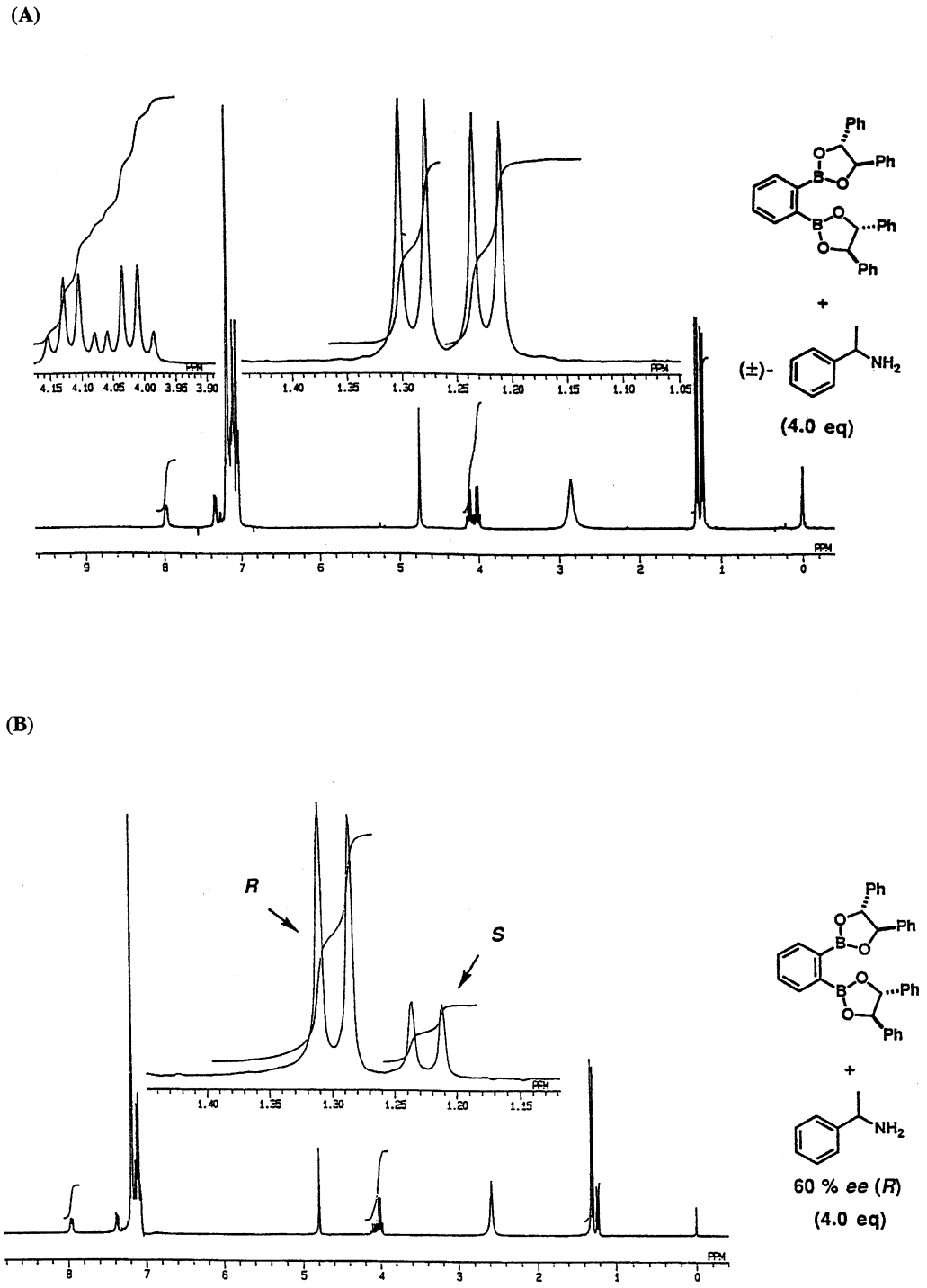



Fig. 8. A: $^1$H NMR spectra at 20 °C in $CDCl_3$ of (±)-1-phenylethylamine (0.40 M) in the presence of **1a** (0.10 M). B: $^1$H NMR spectra at 20 °C in $CDCl_3$ of (*R*)-1-phenylethylamine (60% ee, 0.40 M) in the presence of **1a** (0.10 M).

The result is shown in Fig. 3. The maximum of complex formation occurred at $[\mathbf{1a}]_{initial}/([\mathbf{1a}]_{initial}+[amine]_{initial})=0.33$. Thus, the complex-formation equilibrium of **1a** with benzylamine is given in Eqs. 1 and 2. Based on this result, each of the two boron centers is suggested to accept one amine molecule. The association constants ($K_1$ and $K_2$) are discussed in later in this paper.

$$\mathbf{1a} + (amine) \overset{K_1}{\rightleftharpoons} \mathbf{1a}\cdot(amine) \quad (1)$$

$$\mathbf{1a}\cdot(amine) + (amine) \overset{K_2}{\rightleftharpoons} \mathbf{1a}\cdot(amine)_2 \quad (2)$$

**Low-Temperature $^1$H NMR Studies Concerning the Complex Formation of 1a with Benzylamine.** The rapid equilibrium between the complex and the free Lewis acid–free amine system has been frozen at −50 °C. Low-temperature $^1$H NMR spectroscopy has clearly revealed that only the 1 : 2 complex consisting of **1a** and benzylamine is formed, regardless of the initial ratios. As shown in Fig. 4,

Table 1. Association Constants and Hill Coefficients in the Complex Formation of **1a** with Various Amines[a)]

| Run | Amines | Initial [**1a**] $M^{-1}$ | $K_1$ $M^{-1}$ | $K_2$ $M^{-1}$ | Hill coefficients |
|---|---|---|---|---|---|
| 1 | $PhCH_2NH_2$ | 0.100 | 0.64 (0.32) | 75 (52) | 1.50 |
| 2 | $PhCH_2NHMe$ | 0.094 | 0.13 (0.03) | 530 (210) | 2.23[b)] |
| 3 | (*R*)-PhCH(Me)$NH_2$ | 0.100 | 0.59 (0.09) | 15 (2) | 1.76 |
| 4 | (*R*)-PhCH(Me)$NH_2$ | 0.011 | 0.66 ($0.1\times10^{-2}$) | 22 ($0.5\times10^{-2}$) | 1.80 |
| 5 | (*S*)-PhCH(Me)$NH_2$ | 0.100 | 0.50 (0.05) | 19 (3) | 1.79 |
| 6 | (*R*)-NapCH(Me)$NH_2$ | 0.041 | 0.13 (0.11) | 120 (98) | 2.09[b)] |
| 7 | (*S*)-NapCH(Me)$NH_2$ | 0.041 | 0.19 (0.20) | 80 (81) | 1.32 |

a) Standard deviations are written in the parentheses. All the association constants have been calculated base data points. b) Hill coefficients should be within the range of 1 to 2 in this system. The larger statistic errors caused from the large standard deviations of $K_2$ in Runs 2 and 6.

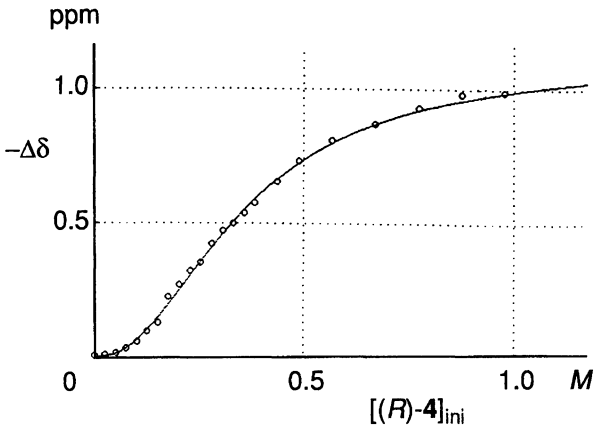
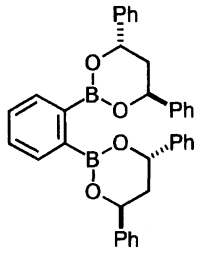



Fig. 9. A calculated curve superimposed over the titration data for (*R*)-**4**. $\Delta\delta$ values of the singlet due to $H^a$ of **1a** are plotted as *Y*-axis against the initial concentration of (*R*)-**4**. The sigmoidal curve is unique for a cooperative binding of multiple guest molecules to one host molecule.




**5**

Chart 3.

when the Lewis acid and the amine were mixed in a 1 : 2 initial ratio (Fig. 4, C), the 1 : 2 complex was observed as a single species. Thus, at −50 °C, the dissociation of the 1 : 2 complex to free diboronate **1a** and benzylamine was slow relative to the NMR time scale. More importantly, when **1a** and benzylamine were mixed 1 : 1 (Fig. 4, B)) and 1 : 4 (Fig. 4, D)) initial ratios, free diboronate **1a** and free amine were observed, respectively, in addition to the 1 : 2 complex. In no case was any 1 : 1 complex detected. Here, the absence of any 1 : 1 complex suggests that the two amine molecules bind to **1a** cooperatively at this temperature. In other words, when the first amine molecule binds to **1a**, the second amine does so rapidly, or when the first amine molecule dissociates from the 1 : 2 complex, fast dissociation of the second amine takes place.

The low-temperature $^1H$ NMR study also provided information about the structure of the 1 : 2 complex. There are two significant structural features in this 1 : 2 complex, as shown in Fig. 4, C: (1) The dioxaborolane methine protons of **1a** appear as only one AB quartet, indicating that the two methine protons on each dioxaborolane ring are magnetically nonequivalent, and that the two dioxaborolane moieties are equivalent. The $C_2$ symmetric chiral structure of the 1 : 2 complex can thus be deduced. (2) A remarkable difference in the chemical shift of the two NH protons of benzylamine and one of the two NH protons is significantly down-field shifted. These observations strongly suggest that the down-field NH proton is involved in some kind of hydrogen bonding. Thus the complex seems to be constructed by hydrogen bondings in addition to the normal Lewis acid–Lewis base complex formation.

**Possible Model for the 1 : 2 Complex of 1a and Benzylamine.** All of the results described above clearly accounted for in terms of an "allosteric effect", as shown in Scheme 1. The first amine molecule coordinates to one of the two boron atoms of the diboronate **1a**; at the same time, one NH proton interacts with one of the two oxygen atoms in the other dioxaborolane ring to form a hydrogen bond.[16,17)] As a result of this steric restriction, the two dioxaborolane rings are conformationally fixed by two-point binding to provide a preferable binding site for the second amine molecule. Additionally, the hydrogen bonding resulting from the first amine binding reduces the electron density on the sencond boron center. This strengthened Lewis acidity may also contribute to the higher affinity of the second amine to **1a**. It should be noted that this allosteric effect can be realized only with the *ortho*-diboronate **1a**, which has a Lewis base acceptor (boron atom) and a proton acceptor (oxygen atom) at a nearby site. In the *meta*- and *para*-isomers, **1b** and **1c**, and the monoboronate counterpart **2**, the Lewis-acidic centers do not possess any helpful basic sites at their proper positions.

In the 1 : 2 complex described in Scheme 1, two nitrogen

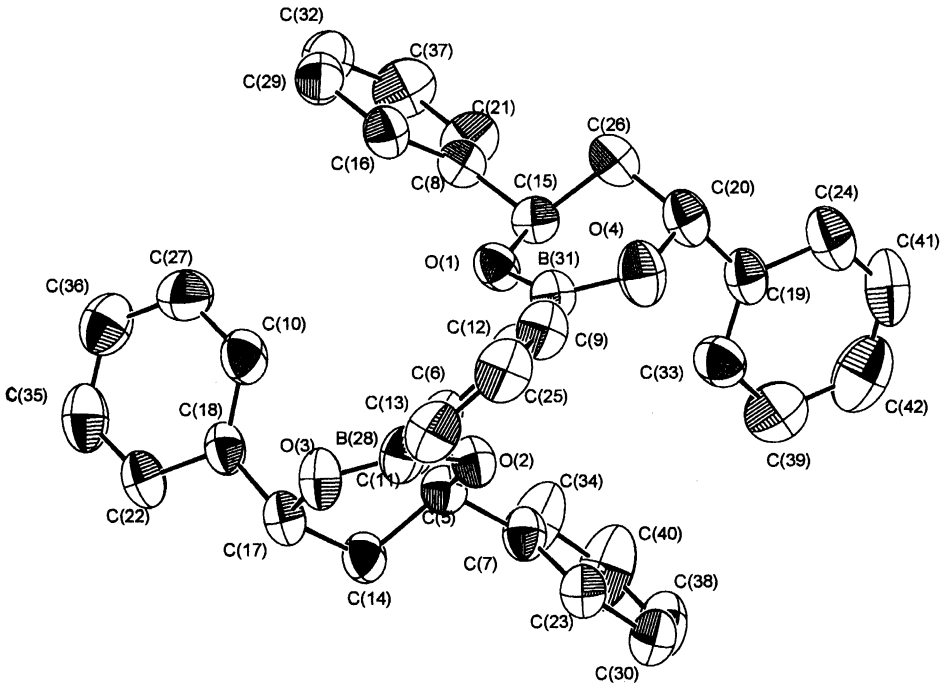



Fig. 10. An ORTEP drawing of the chiral bimetallic Lewis acid **5**.

atoms are chiral and the two benzyl groups of the amines can occupy either "*exo*" or "*endo*" position. We assume that the observation of a single 1 : 2 complex is due to either (1) the strongly preferred configuration of "*exo*" or "*endo*" over the other, or, (2) the existence of a rapid equilibrium between the two configurations.

**Complex Formation from 1a with Other Amines.** Propylamine, an aliphatic amine, exhibited a similar spectral behavior to benzylamine against **1a**. For example, the methylene protons at the $\alpha$-position of the $-NH_2$ group appeared as a diastereotopic pattern in the $^1$H NMR spectrum upon mixing with **1a** at 20 °C. On the other hand, at −50 °C, two 1 : 2 complexes (X and Y) were observed while only one 1 : 2 complex was detectable with benzylamine. As shown in Fig. 5, only the two 1 : 2 complexes (X and Y) are formed regardless of the initial ratios. Free diboronate **1a** and free amine were observed in addition to X and Y, under the existence of excess **1a** or amine, respectively. In no case was any 1 : 1 complex detected. The two 1 : 2 complexes could be assigned as "*exo*" and "*endo*" isomers.

The interaction of **1a** with secondary and tertiary amines was also investigated by $^1$H NMR; the chemical shift due to the methine protons of **1a** are plotted against the amount of added amine in Fig. 6. Although a secondary amine, *N*-methylbenzylamine, showed a quite similar behavior in an interaction with **1a**, the tertiary amine *N*,*N*-benzylamine, did not affect the signals, due to **1a**.

Further, chiral amines were added to a $CDCl_3$ solution of the bimetallic Lewis acid **1a**. Titration was carried out at 20 °C for (*R*)- and (*S*)-1-phenylethylamine **3** and (*R*)- and (*S*)-1-(2-naphthyl)ethylamine **4** (Fig. 7). Strong bindings were indicated by titration with all of the amines. The possibilities of chiral recognition are discussed in combination with the association constants in the next paragraph. Here, we describe the possibility of using **1a** as an NMR chiral shift reagent. The clear separation of the peaks due to each enantiomer of **3** is shown in Fig. 8 (A). Racemic **3** (0.40 M in $CDCl_3$) exhibited a pair of doublets ($PhCH(NH_2)C\underline{H}_3$) and a pair of quartets ($PhC\underline{H}(NH_2)CH_3$) in the presence of **1a** (0.10 M) at 20 °C.[18] A sample of (*R*)-**3** (60% ee) showed the two pairs of doublets and quartets for **3** in the ratio of 80 : 20, as shown in Fig. 8 (B).

**Calculation of the Association Constants and Hill Coefficients.** The association constants for some primary and secondary amine bindings to the Lewis acid **1a** were calculated at 20 °C using a nonlinear curve-fitting method.[19] The results are summarized in Table 1. In all of the runs, the second association constants ($K_2$) are larger by at least two orders of magnitude than the first association constants ($K_1$). A secondary amine, benzyl(methyl)amine, forms a more stable complex compared to the corresponding primary amine, benzylamine (Runs 1 and 2). The stronger basicity of the secondary amine may explain the result. A small change was observed in the association constant under different concentrations of **1a**, although theoretically the constants should not vary with the concentration (Runs 3 and 4). The difference of $K_1$ and $K_2$ between that for (*R*)-1-phenylethylamine ((*R*)-**3**) and that for its (*S*)-isomer ((*S*)-**3**) cannot be regarded as being significant (Runs 3 and 5). In other words, the chiral discrimination is negligible in the present system.[20] A similar discussion is applicable to complex formation with (*R*)- and (*S*)-1-(2-naphthyl)ethylamine ((*R*)- and (*S*)-**4**) (Runs 6 and 7). Figure 9 shows a typical calculated curve superimposed over the experimental results. The curve fits nicely to the tetration data for (*R*)-**4**. The sigmoidal curve is unique for a cooperative binding of multiple guest molecules to one host

molecule; also one of the well-known examples of this phenomenon may be an allosteric binding of oxygen molecules to hemoglobin. Hill coefficients[21] for the titration have also been estimated (Table 1).

Cooperative binding of multiple guest molecules to one host molecule has been one of the most attractive phenomena in both biochemistry and molecular recognition chemistry.[22] It is of great interest that cooperativity has been accomplished by such a simple molecule **1a**.

**A Chiral Bimetallic Lewis Acid with Six-membered Rings: An Analog to 1a.** A chiral bimetallic Lewis acid with six-membered 1,3,2-dioxaborinane **5** was prepared as an analog to **1a** (Chart 3). In sharp contrast to the five-membered 1,3,2-dioxaborolane **1a**, the six-membered **5** did not show any significant interaction with benzylamine in $^1$H NMR studies. As shown in the ORTEP drawing of **5** in Fig. 10, the two boron atoms of **5** are rather crowded with the six-membered ring, which seems to prevent the coordination of nitrogen atoms. In addition, the ring strain in the five-membered ring of dioxaborolane has been released in the six-membered ring. Since the dioxaborolane five-membered ring contains two $sp^2$ oxygen atoms and one $sp^2$ boron atom, the ring should possess a potential strain energy to accelerate the $sp^2 \rightarrow sp^3$ orbital change of the boron atom. This may cause a greater acidic character of the boron atom in the five-membered ring.

**Conclusion.** We synthesized chiral bimetallic Lewis acid **1a**, and elucidated its unique binding properties to various amines. In our study, the two basic sites in **1a** played significant roles, as important as the two Lewis acidic sites. Here, we conclude that not only the cooperativity of the two metal centers, but also the cooperativity of the metal center and basic oxygen center is the essential character of this bimetallic Lewis acid. We believe that the molecular design to arrange basic sites close to the Lewis-acidic centers should become a versatile strategy for capturing primary and secondary amines, alcohols, and thiols. Although the compound has chirality, its chiral-recognition ability is not satisfactory at this moment. Further molecular designs are required for this purpose.

## Experimental

**Preparation of 2,2′-(1,2-Phenylene)bis[(4*R*,5*R*)-4,5-diphenyl-1,3,2-dioxaborolane] (1a) and Its *meta*-Isomer (1b):** In an 80-mL Schlenk tube under an argon atmosphere was placed a 1 : 1 mixture of 1,2-bis(dichloroboryl)benzene and 1,3-bis(dichloroboryl)benzene (1.6 g, 6.7 mmol, total), which was obtained from 1,2-bis(trimethylsilyl)benzene.[23] (*R*,*R*)-1,2-Diphenyl-1,2-ethanediol[24] (2.4 g, 13.4 mmol) was added, and the mixture was dissolved in $CHCl_3$ (40 mL). After the resulting clear solution was heated at 60 °C for 2 h, the generated HCl as well as the solvent were removed under reduced pressure. Recrystallization from $CH_3CN$ afforded **1b** in 35% yield. The mother liquor was concentrated and purified by column chromatography on reversed-phase silica gel (Wakogel LP140C18, $CH_3CN$, $R_f$=0.75). Recrystallization from ether–hexane gave **1a** in 33% yield. **1a**: Mp 85.2—86.0 °C (ether–hexane). $^1$H NMR ($CDCl_3$, 0.10 M) $\delta$=5.22 (s, 4 H), 7.12—7.33 (m, 20 H), 7.47 (dd, $J$=3.3, 5.6 Hz, 2 H), 7.86 (dd, $J$=3.3, 5.3 Hz, 2 H); $^{13}$C NMR ($CDCl_3$) $\delta$=87.46, 126.09, 128.25, 128.66, 129.94, 133.84, 139.96 (carbon atoms bound to boron atoms were not observed); $^{11}$B NMR ($CDCl_3$, an external reference of $B(OMe)_3$ in $CDCl_3$ was used for $^{11}$B NMR spectra) $\delta$=20.5; $[\alpha]_D^{26.0}$ −15.8 (*c* 0.79, $CHCl_3$). Found: C, 77.94; H, 5.44%. Calcd for $C_{34}H_{28}B_2O_4$: C, 78.20; H, 5.40%.

2, 2′- (1, 3- Phenylene)bis[(4*S*, 5*S*)- 4, 5- diphenyl- 1, 3, 2- dioxaborolane] (the enantiomer of **1b**): Mp 151.4—152.0 °C ($CH_3CN$). $^1$H NMR ($CDCl_3$, 0.10 M) $\delta$=5.27 (s, 4 H), 7.26—7.35 (bs, 20 H), 7.46 (t, $J$=7.6 Hz, 1 H), 8.09 (d, $J$=7.6 Hz, 2 H), 8.59 (s, 1H); $^{13}$C NMR ($CDCl_3$) $\delta$=86.94, 125.84, 127.60, 128.37, 128.81, 138.56, 140.23, 142.30; $^{11}$B NMR ($CDCl_3$) $\delta$=18.3; $[\alpha]_D^{21.0}$ 102.8 (*c* 1.0, $CHCl_3$). Found: C, 78.00; H, 5.49%. Calcd for $C_{34}H_{28}B_2O_4$: C, 78.20; H, 5.40%.[25]

**Preparation of 2,2′-(1,4-Phenylene)bis[(4*R*,5*R*)-4,5-diphenyl-1,3,2-dioxaborolane] (1c):** 1,4-Phenylenediboronic acid was prepared according to Ref. 26. To a solution of *p*-phenylenediboronic acid (83 mg, 0.50 mmol) in $CHCl_3$ (5.0 mL) was added (*R*,*R*)-1,2-diphenyl-1,2-ethanediol (214 mg, 1.0 mmol) under an argon atmosphere. The removal of water by azeotropic distillation followed by recrystallization from $CH_2Cl_2$–hexane gave **1c** in 67% yield.

**1c**: Mp 177.0—177.4 °C ($CH_2Cl_2$–hexane). $^1$H NMR ($CDCl_3$) $\delta$=5.37 (s, 4 H), 7.39 (bs, 20 H), 8.07 (s, 4 H); $^{13}$C NMR ($CDCl_3$) $\delta$=87.01, 125.88, 128.45, 128.84, 134.54, 140.16 (carbon atoms bound to boron atoms were not observed); $^{11}$B NMR ($CDCl_3$) $\delta$=21.4; $[\alpha]_D^{21.0}$ −105.4 (*c* 1.0, $CHCl_3$). Found: C, 78.15; H, 5.31%. Calcd for $C_{34}H_{28}B_2O_4$: C, 78.20; H, 5.40%.

**(4*S*,5*S*)-2,4,5-Triphenyl-2-phenyl-1,3,2-dioxaborolane** (the enantiomer of **2**): 80% yield. Mp 106.9—107.8 °C ($CH_2Cl_2$–hexane). $^1$H NMR ($CDCl_3$) $\delta$=5.25 (s, 2 H), 7.20—7.47 (m, 13 H), 7.90—7.93 (m, 2 H); $^{13}$C NMR ($CDCl_3$) $\delta$=86.93, 125.84, 127.96, 128.37, 128.81, 131.86, 135.22, 140.32 (carbon atom bound to boron atom was not observed); $^{11}$B NMR ($CDCl_3$) $\delta$=19.6; $[\alpha]_D^{22.8}$ 91.6 (*c* 1.0, $CHCl_3$). Found: C, 79.81; H, 5.45%. Calcd for $C_{20}H_{17}BO_2$: C, 80.03; H, 5.71%.

**Preparation of 2,2′-(1,2-Phenylene)bis[(4*S*,6*S*)-4,6-diphenyl-1,3,2-dioxaborinane-2-yl]benzene (5):** A similar procedure as that for **1a** provided **5** in 44% yield. Mp 190.0—191.3 °C ($CH_2Cl_2$–$CH_3CN$). $^1$H NMR ($CDCl_3$, 0.10 M) $\delta$=2.21 (t, $J$=5.3 Hz, 4 H), 5.10 (t, $J$=5.3 Hz, 4 H), 7.12—7.33 (m, 20 H), 7.47 (dd, $J$=3.1, 5.4 Hz, 2 H), 7.78 (dd, $J$=3.1, 5.4 Hz, 2 H); $^{13}$C NMR ($CDCl_3$) $\delta$=41.85, 70.53, 125.32, 127.30, 128.34, 128.90, 132.70, 142.14 (carbon atoms bound to boron atoms were not observed); $^{11}$B NMR ($CDCl_3$) $\delta$=41.3; $[\alpha]_D^{23.0}$ 19.8 (*c* 1.0, $CHCl_3$). Found: C, 78.53; H, 5.82%. Calcd for $C_{36}H_{32}B_2O_4$: C, 78.58; H, 5.86%.

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