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Preparation of some organo-bis(diisopropylamino)boranes and their application to the synthesis of oxazaborolidines

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Abstract

The reactivity of $ClB(NEt_2)_2$ and $ClB(N^iPr_2)_2$ towards organomagnesium or organolithium derivatives was studied. $ClB(N^iPr_2)_2$ proved to be an excellent reagent for the preparation of pure boronic derivatives $RB(N^iPr_2)_2$, which can be used for an efficient synthesis of oxazaborolidines, including Corey's CBS catalyst.

1. Introduction

The boronic acid derivatives RBXY (X, Y = N, O, S etc.) have continued to receive interest in relation to organic synthesis [1]. The most striking recent examples are Corey's developments of the oxazaborolidine-catalysed asymmetric reduction of ketones [2–4] and [4 + 2] cycloadditions [5].

Most of the cyclic boronic derivatives involved were prepared from boronic acids $RB(OH)_2$ or esters $RB(OR')_2$ [6]. These compounds were generally obtained by addition of an organometallic derivative to a trialkoxyborane [7].

$$R{-}M + B(OR')_3 \longrightarrow RB(OR')_2$$

M = MgX, Li

Scheme 1.

A severe drawback of this method is the formation of borinic derivatives R_2BOR' as by-products. This side-reaction takes place to a large extent when organomagnesium compounds are used [7a]. An interesting alternative is the reaction of organolithium or organomagnesium reagents with chlorobis(dialkylamino)borane **1**.

$$R{-}M + ClB(NR'_2)_2 \longrightarrow RB(NR'_2)_2$$

1a: R' = Me
1b: R' = Et
1c: R' = ^{i}Pr

2

M = MgX, Li

Scheme 2.

The borylation of organolithium derivatives with the chloroborane **1a** was first described by Nöth and Fritz [8]. It was applied to alkenylmagnesium halides by Braun and Normant [9]. Hoffmann *et al.* [10,11] used it for the preparation of allylboronates, essentially from the corresponding organoalkali metal compounds.

But there is no general study of the scope of this reaction, from the preparative point of view. In particular, reactions with simple organomagnesium compounds are poorly documented. Moreover, the possible importance of the dialkylamino moiety has not been well defined. Nöth *et al.* used chlorobis(dimethylamino)borane **1a** and Normant *et al.* chlorobis(diethylamino)borane **1b**, while a few examples of borylation with chlorobis(diisopropylamino)borane **1c** have been reported [12].

In order to gain more insight, and because we met with difficulties in using these reagents, we decided to study this problem more systematically. For example, we found that the nature of the R' group in chloroboranes **1** has a dramatic influence on the course of the reaction. We describe in this paper the reaction condi-

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tions that allow an efficient and easy access to organobis(dialkylamino)boranes **2** (boronic amides) in excellent yields and purity, from both organomagnesium and organolithium compounds.

We also demonstrate the use of these boronic amides as precursors of cyclic boronic derivatives such as oxazaborolidines.

2. Results and discussion

2.1. Preparation of chlorobis(dialkylamino)boranes

Our first concern was to re-examine the syntheses of the aminochloroboranes **1**, in order to optimize their preparation. **1a** was prepared by Hoffmann *et al.* [11] (following reported methods [13]) in a 73% yield according to the following scheme.

$$BCl_3 + 2\ Me_2NH + 2\ Et_3N \xrightarrow[60°C,\ 1\ h]{\text{petroleum ether}} Cl\text{–}B(NMe_2)_2$$

1a: 73%

Scheme 3.

The stoichiometry must be carefully controlled to avoid the formation of dichloromono(dimethylamino) borane **5a** or tris(dimethylamino)borane **4a**. This is experimentally difficult, since it requires handling gaseous BCl_3 and anhydrous dimethylamine (b.p. 7°C). Another way to prepare **1a** is to use a comproportionation reaction: mixing 1 equivalent of BCl_3 with 2 equivalents of $B(NMe_2)_3$ **4a** leads to the formation of **1a** [13,14].

$$BCl_3 + 2\ B(NMe_2)_3 \longrightarrow 3\ ClB(NMe_2)_2$$

4a **1a**

Scheme 4.

$ClB(NEt_2)_2$ (**1b**) is prepared using the latter method [15] from BCl_3 and $B(NEt_2)_3$ (**4b**). We met again with the difficulty of controlling the exact amount of BCl_3. An excess of this reagent produces dichloromono(diethylamino)borane **5b** [16], which is not easily removed. We solved this problem by using the solid $BCl_3 \cdot Me_2S$ (air-stable enough for rapid handling) as a source of trichloroborane. **1b** is then quantitatively obtained, free (< 0.5 %, 300MHz ^{1}H-NMR) of **5b**.

$$BCl_3 \cdot S(CH_3)_2 + 2\ B(NEt_2)_3 \xrightarrow[20°C,\ 1\ h]{\text{ether}} 3\ ClB(NEt_2)_2$$

4b **1b**: 85%

Scheme 5.

1b can be distilled and stored under N_2 for months. We set up a convenient procedure for the synthesis of tris(diethylamino)borane **4b** [15].

$$BCl_3 \cdot S(CH_3)_2 \xrightarrow[\text{cyclohexane}\ \text{reflux, 2 h}]{6.5\ Et_2NH} B(NEt_2)_3$$

2b: 85%

Scheme 6.

The chlorobis(diisopropylamino)borane **1c** was easily prepared [17] by the reaction of BCl_3 or $BCl_3 \cdot Me_2S$ with diisopropylamine. It has been shown that diisopropylamine does not react with **1c** even at 300°C [18]. Thus, an excess of diisopropylamine can be used to ensure complete transformation of boron trichloride to **1c**. Under these conditions, no dichloromono(diisopropylamino)borane **5c** could be detected.

$$\begin{matrix} BCl_3 \\ \text{or} \\ BCl_3 \cdot S(CH_3)_2 \end{matrix} \xrightarrow[\text{toluene}\ \text{reflux, 3 h}]{4.5\ {}^iPr_2NH} ClB(N{}^iPr_2)_2$$

1c: 80%

Scheme 7.

2.2. Borylation of organomagnesium and organolithium derivatives with 1b and 1c

A large majority of the examples of borylation with chlorobis(dialkylamino)boranes **1** involves **1a**; the use of **1b** or **1c** is poorly documented. We report here the utility of **1b** and **1c** for the preparation of boronic acid derivatives. Most of the work was devoted to organomagnesium derivatives, since these are not efficiently borylated by trialkoxyboranes [7a].

The reaction conditions used in the case of **1a** [8] (ether or THF, −78°C to 20°C) appeared inefficient. We found that very good yields could be obtained with organomagnesium compounds if the solution of the organometallic compound was added to a cyclohexane solution of **1b** or **1c** at room temperature and the reaction mixture heated under reflux for 2 h [19*]. When organolithium derivatives were used, the reagents were mixed at 0°C and the reaction was complete within 2 h at room temperature. In both cases, a slight excess (1.2 eq) of organometallic compound was used. The results are shown in Table 1.

It appears from Table 1 that **1b** always gave noticeable amounts of dialkyl(diethylamino)borane **3b** [20*]. More polar solvents such as THF or dioxane led to poorer results in terms of purity and yields. Mixing LiBu or BuMgBr with **1b** below −30°C and slow

* Reference number with an asterisk indicates a note in the list of references.

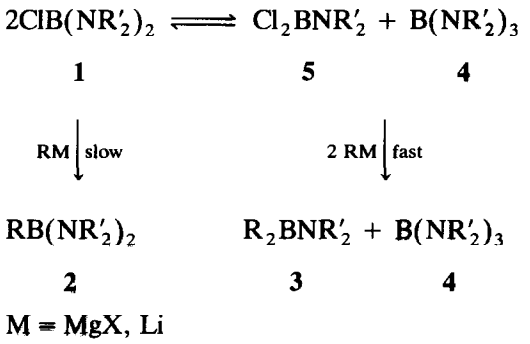
raising of the temperature did not change the results [21*].

On the other hand, the formation of borinic amide did not take place when **1c** was used as the borylating agent and therefore yields from primary organolithium and organomagnesium derivatives were good-to-excellent.

With the less reactive vinylmagnesium derivatives (entries 6, 7), the reaction becomes sluggish and unchanged **1c** was recovered, together with the product **2c** (more severe conditions, such as refluxing toluene for 16 h, did not improve the results).

The scope of the reaction also appears limited by steric hindrance in **1c**. In reactions of isopropylmagnesium bromide (entry 9), **1b** led to the expected product in moderate yield [22*]. The reaction of isopropylmagnesium bromide with **1c** produced only trace amounts of the expected secondary boronic amide **2c**, the main product being the borane $HB(N^iPr_2)_2$ (64% yield).

The formation of borinic compounds may be explained by Scheme 8.



Scheme 8.

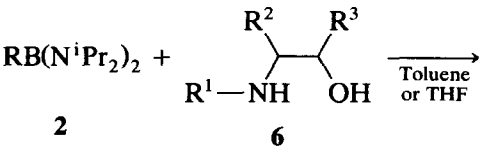
For steric and electronic reasons, dichloro(diethylamino)borane (**5b**) reacts faster with the organometallic reagent than the monochloro-compound **1b**. Displacement of the disproportionation equilibrium then occurs, leading to the formation of the borinic derivative **3** [23*]. With **1c**, the disproportionation is not possible since tris(diisopropylamino)borane **4c** cannot be formed [18]. Therefore, the desired boronic compound is the only observed product.

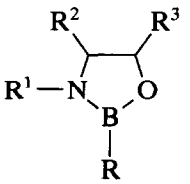
From a preparative point of view, chlorobis(diisopropylamino)borane **1c** appears to be an easily available and efficient reagent for the preparation of boronic derivatives from aromatic or primary aliphatic organomagnesium and organolithium compounds, with excellent yields and purities under very mild conditions. The boronic amides **2c** are interesting, stable reagents that can be stored under N_2 for months and handled rapidly in air.

2.3. *Application of organobis(diisopropylamino)boranes to the synthesis of various boraheterocycles*

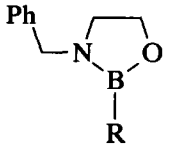
As compared to the more classical reaction of organolithium derivatives with trialkoxyboranes, the use of **1c** offers another major advantage. The organobis(diisopropylamino)boranes (**2c**) are more versatile derivatives than the corresponding boronic acids or esters because they can be easily transformed into a variety of RBXY (X, Y = N, O, Hal etc.) compounds [1,24].

An important illustration of this is the synthesis of 1,3,2-oxazaborolidines. A few examples of the synthesis of oxazaborolidines from organobis(dialkylamino)-boranes have been reported [25]. By analogy with these results, we found that heating the diaminoboranes **2c** with β-aminoalcohols **6** in refluxing toluene, with removal of diisopropylamine by distillation, provides an efficient, clean access to oxazaborolidines **7**, even from 2-anilinoethanol (**7e**).

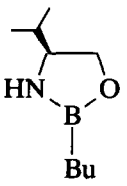




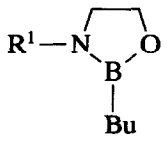
7



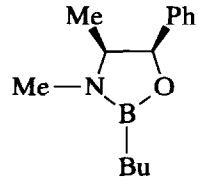
7a: R = Me 86% [a]
7b: R = Bu 90% [a]
7c: R = Ph 92% [a]



7f: 95% [a]



7d: R^1 = t-Bu 96% [a]
7e: R^1 = Ph 90% [a]

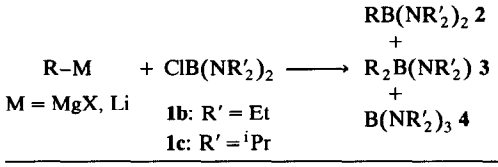


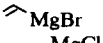
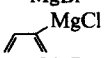
7g: quant [b]

[a] After distillation. [b] Crude product.

Scheme 9.

TABLE 1. Borylation of organomagnesium and organolithium derivatives with **1b** and **1c**



Entry	R–M	Overall yield [a]	Mol. ratio [a]	Yield (%) [b]
		2b + 3b + 4b (%)	**2b:3b:4b**	
1	MeMgI	–	– – –	87
2	EtMgBr	73	81 14 5	84
3	^{n}BuMgBr	70	80 20 0	84
4	^{n}HeptMgBr	77	78 22 0	%
5	PhMgBr	95	79 12 9	73
6		68	71 15 14	40 [c]
7		89	81 6 13	low [d]
8		–	– – –	78
9		56	82 18 0	traces [e]
10	Li^{n}Bu	91	85 12 3	94
11	LiMe	72	88 12 0	87
12	LiPh	86	85 14 1	87

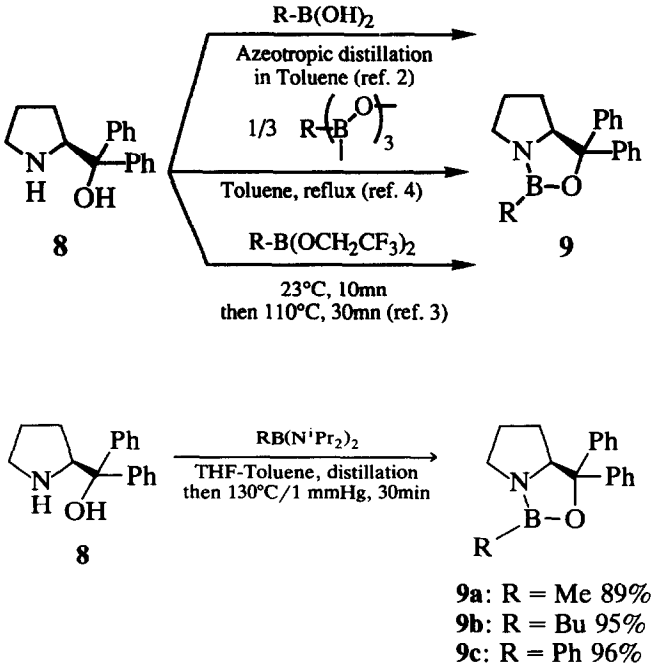
[a] A mixture of **2b** + **3b** + **4b** was obtained after distillation. The values are the overall yields in **2b** + **3b** + **4b** from chloroborane (**1c**), calculated from the mass of the mixture and the **2b**:**3b**:**4b** ratios; the latter were determined from ^{1}H-NMR spectra of the distilled mixture. [b] Isolated yields from chloroborane **1c**, after distillation; no **3c** was detected in the 300MHz-NMR spectra. [c] A 50:50 mixture of **1c** and **2c** was obtained. [d] A mixture of several unidentified compounds was obtained. [e] The main product is HB(N^{i}Pr$_2$)$_2$ (64% yield).

2.4. Access to Corey's enantioselective reduction catalysts

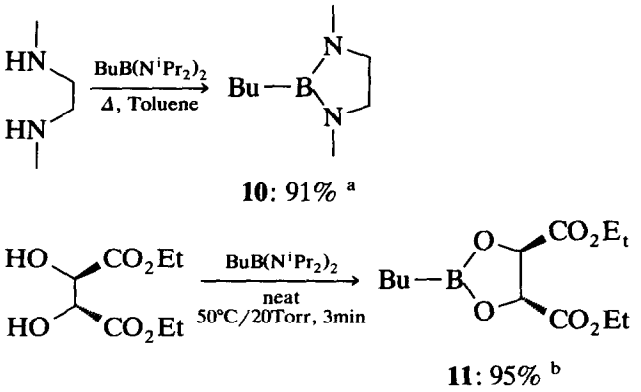
We then turned to the preparation of the oxazaborolidine catalyst **9** (CBS). It has been shown [4] that the purity of the catalyst is essential for the reproducibility of the reductions. The first synthesis by Corey *et al.* started from boronic acids [2]. It was then found [4] that boronic anhydrides permit a more efficient control of the reagent stoichiometries, giving purer **9**. More recently, Corey's group has developed another method, using a boronic trifluoroethylester [3].

Application of the reaction conditions used for **7** led to unsatisfactory purities when applied to **8**. We found that the use of a toluene-THF mixture allows easy access to catalysts **9a, 9b, 9c** in crude yields of 89, 95, 96%, respectively, in an excellent state of purity, as shown by the 300MHz ^{1}H-NMR spectra [26] (Fig. 1).

The transformation of organobis(dimethylamino)-boranes (**2a**) into 1,3,2-diazaborolanes [27] (**10**) or 1,3,2-dioxaborolanes [10,11] (**11**) has already been described. The organobis(diisopropylamino)boranes (**2c**) also react easily and cleanly under similar conditions with ethylenediamine and diethyl tartrate to give **10** and **11** in 91 and 95% yields, respectively.



Scheme 10.



[a] Distilled compound. [b] Crude product.

Scheme 11.

Another important feature of the reactivity of organobis(diisopropylamino)boranes is their reaction with mandelic acid. Only one equivalent of diisopropylamine is evolved, and a solid is formed. The second molecule of amine can be efficiently displaced by addition of an excess of anhydrous hydrochloric acid in ether. This leads cleanly to the dioxaborolane **12**.

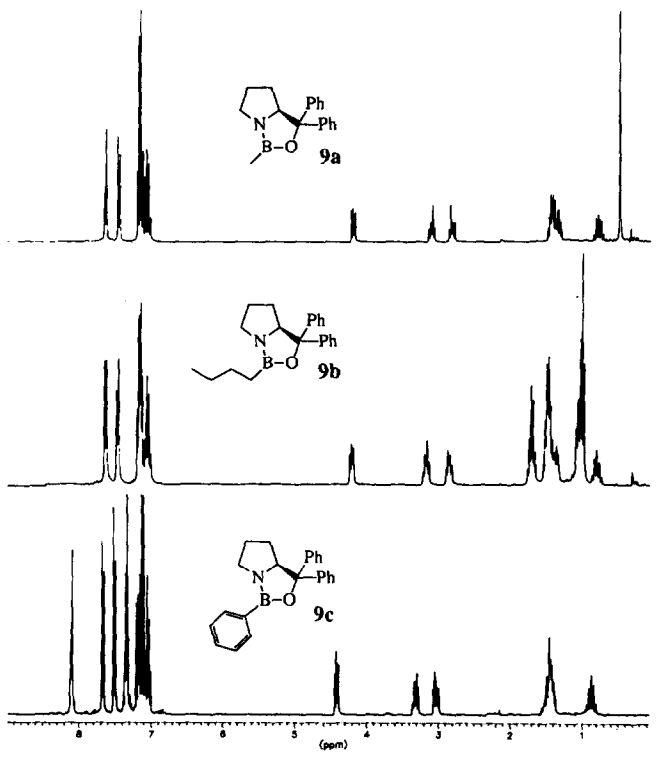
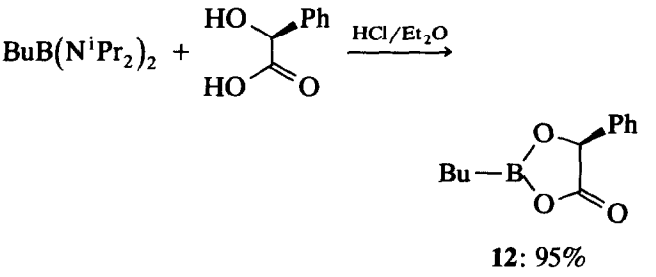


Fig. 1. 300 MHz ^{1}H NMR spectra of **9a–9c** (C_6D_6).



Scheme 12.

3. Conclusion

The present work shows that the use of the easily available chlorobis(diisopropylamino)borane **1c** allows an efficient transformation of organomagnesium or organolithium compounds into boronic derivatives under very simple conditions. Furthermore, the boronic amides **2c** were obtained free from borinic species. The organobis(diisopropylamino)boranes **2c** so obtained appear to be excellent reagents for the preparation of various boraheterocycles, particularly the valuable oxazaborolidines.

4. Experimental section

^{1}H and ^{13}C NMR spectra were recorded on a Bruker WP 80 CW and a Bruker AM 300 (75.5 MHz for ^{13}C). Mass spectra were measured at 70 eV on a Varian MAT 311 Spectrometer (Centre Régional de Mesures Physiques de l'Ouest). BCl_3 (99.9%) was purchased from Matheson Gas Products. Diethylamine, diisopropylamine and (*S*)-α,α-diphenyl-2-pyrrolidinemethanol (**8**) were purchased from Aldrich (reagent grade) and used as received. Other reagents and solvents were dried by the usual techniques and distilled.

4.1. Tris(diethylamino)borane (2b) [15]

Into a 1-L, three-necked flask fitted with a mechanical stirrer and a reflux condenser, under N_2 atmosphere, were introduced 350 ml (3.38 mol) of diethylamine and 350 ml of cyclohexane. The reaction mixture was heated to 40°C, and 89.6 g (0.502 mol) of solid $BCl_3 \cdot Me_2S$ were added in *ca.* 5g-portions over 1 h. The temperature of the reaction mixture rose to reflux temperature and a thick precipitate appeared. After completion of the addition, the reflux was maintained for 1.5 h. After cooling, the precipitate of hydrochloride was rapidly filtered off and washed with 100 ml of cyclohexane. Concentration and distillation of the filtrate yielded pure **2b**: 89.2 g, 78% yield, b.p. 121°C/30 mmHg (litt. 50–53°C/0.4 mmHg [15]); NMR ($CDCl_3$,

δ): ^{1}H 0.94 (t, 3H, J = 7.1 Hz), 2.81 (q, 2H); ^{13}C($CDCl_3$) 14.82, 40.06; ^{11}B(Et_2O) 28.7.

4.2. Chlorobis(diethylamino)borane (1b) [15]

The complex $BCl_3 \cdot Me_2S$ (5.69 g, 31.7 mmol) and tris(diethylamino)borane **2b** (14.34 g, 63.1 mmol) were stirred without solvent for 2 h at room temperature. The solid dissolved and an oil was formed. Distillation yielded 15.26 g, 85% yield of **1b**, b.p. 84°C/20 mmHg (litt. 83–7°C/16 mmHg [15]); NMR ($CDCl_3$, δ): ^{1}H 0.91 (t, 3H, J = 7.0 Hz), 2.90 (q, 2H); ^{13}C($CDCl_3$) 15.23, 42.60; ^{11}B($CDCl_3$) 28.3.

4.3. Chlorobis(diisopropylamino)borane (1c) [15]

Into a 1-L, three-necked flask fitted with a reflux condenser, and a magnetic stirrer under N_2, were introduced 223 g (2.20 mol) of $^iPr_2NH$ and 500 ml of dry toluene. The flask was held at 20°C. Gaseous BCl_3 was briskly bubbled through the solution (15–30 min), until 47 g (0.4 mol) of BCl_3 had been added (as determined by weighing the apparatus). A precipitate formed and the temperature of the reaction mixture was raised to about 40°C. The mixture was then heated under reflux for 4 h. After cooling, the precipitate was rapidly filtered off and washed with 2 × 100 ml of cyclohexane. Concentration and distillation of the filtrate yielded pure **2c**: 73.4 g (80% yield from BCl_3) b.p. 127°C/17 mmHg (litt. [17] 55–65/0.2–0.5); NMR ($CDCl_3$, δ): ^{1}H 1.20 (d, 12H, J = 6.9 Hz); 3.46 (heptet., 2H); ^{13}C($CDCl_3$) 23.44; 47.02; ^{11}B($CDCl_3$) 30.06.

4.4. Borylation of organomagnesium halides with $ClB(NEt_2)_2$ (1b)

The synthesis of $BuB(NEt_2)_2$ is typical. Into a 100 ml, double-necked flask fitted with a short distillation head and a magnetic stirrer under N_2, were introduced 3.71 g (19.5 mmol) of **1b** in 50 ml of cyclohexane. At 20°C were added 10.5 ml (24 mmol) of BuMgBr (2.28 M ethereal solution). The temperature was raised to the boiling point of the solvent and a precipitate formed. When the temperature at the top of the column reached 70°C, the distillation was stopped, the distillation head replaced by a reflux condenser, and the reaction mixture heated under reflux for 2 h. After cooling to 20°C, 2 ml of dry Et_2NH were added, and stirring was continued for 30 min. The reaction mixture was filtered over Celite. The precipitate was washed with 2 × 20 ml of cyclohexane, and the combined organic phases combined. The products were distilled in one fraction (overheating of the boiling vessel was necessary at the end of distillation). 2.96 g of a mixture of **2b**, **3b** and **4b** was obtained. The relative percentages were determined by ^{1}H-NMR spectroscopy and the yields were calculated from these data.

4.5. Borylation of organolithium derivatives by $ClB(NEt_2)_2$ (1b)

The reaction with butyllithium is representative. Into a 100 ml flask with a magnetic stirrer under N_2 were introduced 5.31 g (27.9 mmol) of **1b** in 50 ml cyclohexane. 21 ml (34 mmol) of a 1.6 M hexane solution of Li^{n}Bu were added dropwise at 0°C. A white precipitate slowly appeared. Stirring was continued for 2 h at 20°C. 2 ml of dry diethylamine were added and the reaction mixture was stirred for 30 min. It was then filtered and distilled as above, yielding 5.34 g of a mixture of **2b, 3b** and **4b**. The data below were extracted from the spectra of the mixtures.

4.5.1. Ethylbis(diethylamino)borane

B.p. 75–80°C/10 mmHg; NMR (CCl_4, δ): ^{1}H 0.91 (t, 3H, J = 8.0 Hz), 0.71 (q, 2H), 1.01 (t, 12H, J = 7.0 Hz), 2.94 (q, 8H); ^{13}C(CCl_4) 7.96 (broad), 10.11, 16.07, 49.09; ^{11}B($CDCl_3$) 35.6; high resolution mass spectrum (HRMS) $C_{10}H_{25}N_2{}^{11}B$ m/z calc. 184.2111, found 184.212.

4.5.2. Diethyldiethylaminoborane

NMR ($CDCl_3$, δ): ^{1}H 0.79 (t, 4H, J = 7.4 Hz), 0.91 (t, 6H), 1.03 (t, 6H, J = 7.1 Hz), 3.03 (q, 4H); ^{13}C($CDCl_3$) 9.46, 10.2 (broad), 16.32, 42.38; ^{11}B($CDCl_3$) 46.9.

4.5.3. Butylbis(diethylamino)borane

B.p. 100°C/30 mmHg; NMR ($CDCl_3$, δ): ^{1}H 0.70 (t, 2H, J = 7.0 Hz), 0.89 (t, 3H, J = 7.1 Hz), 1.01 (t, 12H, J = 7.0 Hz), 1.21–1.35 (m, 4H), 2.95 (q, 8H); ^{13}C($CDCl_3$) 14.03, 15.66 (NEt_2), 15.5 (broad), 26.36, 28.79, 41.79; ^{11}B($CDCl_3$) 34.7; HRMS $C_{12}H_{29}N_2{}^{11}B$ m/z calc. 212.2424, found 212.243.

4.5.4. Dibutyldiethylaminoborane

NMR ($CDCl_3$, δ): ^{1}H 0.79 (t, 4H, J = 7.0 Hz), 0.94 (t, 6H, J = 7.1 Hz), 1.13 (t, 6H, J = 7.0 Hz), 1.2–1.5 (m, 8H), 3.05 (q, 4H); ^{13}C($CDCl_3$) 14.06, 16.14, 18 (broad), 26.36, 28.18, 42.28; ^{11}B($CDCl_3$) 45.5.

4.5.5. Heptylbis(diethylamino)borane

B.p. 110–120°C/1 mmHg; NMR ($CDCl_3$, δ): ^{1}H 0.69 (t, 2H, J = 7.1 Hz), 0.88 (t, 3H, J = 7.0 Hz), 1.01 (t, 12H, J = 7.0 Hz), 1.29 (s, 10H), 2.94 (q, 8H); ^{13}C($CDCl_3$) 13.15, 15.78, 16 (broad), 22.87, 26.57, 29.49, 32.12, 33.54, 41.86; ^{11}B (Et_2O) 34.7; HRMS $C_{15}H_{35}N_2{}^{11}B$ m/z calc. 254.2893, found 254.290.

4.5.6. Diheptyldiethylaminoborane

NMR ($CDCl_3$, δ): ^{1}H 0.77 (t, 4H, J = 7.1 Hz), 0.88 (t, 6H, J = 7.0 Hz), 1.02 (t, 6H, J = 7.0 Hz), 1.29 (s, 20H), 3.04 (q, 4H); ^{13}C($CDCl_3$) 13.15, 16.26, 19 (broad), 22.87, 25.96, 29.84, 32.09, 33.52, 42.37; ^{11}B (Et_2O) 43.4.

4.5.7. Phenylbis(diethylamino)borane

B.p. 110°C/30 mmHg; NMR (CCl_4, δ): ^1H 0.98 (t, 12H, $J = 7.0$ Hz), 2.91 (q, 8H), 7.15–7.30 (m, 5H); $^{13}C(CDCl_3)$ 15.74, 42.33, 126.98, 127.38, 132.43, 142 (broad); ^{11}B (Et_2O) 33.2; HRMS $C_{14}H_{25}N_2{}^{11}B$ m/z calc. 232.2111, found 232.211.

4.5.8. Diphenyldiethylaminoborane

NMR (CCl_4, δ): ^1H 1.08 (t, 3H, $J = 7.1$ Hz), 3.27 (q, 2H); ^{13}C 15.40, 44.08; aromatic signals overlapped those of **2b** ^1H and ^{13}C. ^{11}B (Et_2O) 42.1.

4.5.9. Vinylbis(diethylamino)borane

B.p. 70–80°C/22 mmHg; NMR ($CDCl_3$, δ): ^1H 0.99 (t, 12H, $J = 7.0$ Hz), 2.98 (q, 8H), 5.40 (dd, 1H, $^2J = 19.9$ Hz, $^3J_{cis} = 4.4$ Hz), 5.58 (dd, broad, 1H), 6.13 (dd, 1H, $^3J_{trans} = 14.2$ Hz); $^{13}C(CDCl_3)$ 15.40, 42.02, 125.83, 140 (broad); $^{11}B(CDCl_3)$ 31.1; HRMS $C_{10}H_{23}N_2{}^{11}B$ m/z calc. 182.1954, found 182.195.

4.5.10. Divinyldiethylaminoborane

NMR ($CDCl_3$, δ): ^1H 1.12 (t, 6H, $J = 7.0$ Hz), 3.10 (q, 4H), 5.7 (m, 2H), 6.30 (dd, 1H, $^2J = 19.2$ Hz, $^3J_{trans} = 13.8$ Hz); $^{13}C(CDCl_3)$ 16.50, 44.10, 131.05, 151 (broad); $^{11}B(CDCl_3)$ 36.9.

4.5.11. 1,3-Butadiene-2-ylbis(diethylamino)-borane

B.p. 53°C/0.5 mmHg; NMR ($CDCl_3$, δ): ^1H 1.11 (t, 12H, $J = 7.0$ Hz), 2.94 (q, 8H), 5.00 (dd, H_a, $^2J_{ac} = 2.6$Hz, $^3J_{ae} = 10.3$ Hz), 5.07 (broad d, H_b, $^2J_{bd} = 3.3$ Hz), 5.13 (dd, H_c, $^3J_{ce} = 17.6$ Hz), 5.36 (broad d, H_d), 6.42 (dd, H_e); $^{13}C(CDCl_3)$ 16.03, 42.54, 115.46(CH_2), 121.86(CH_2), 143.13(CH), 153 (broad, C–B); $^{11}B(CDCl_3)$ 31.5; HRMS $C_{12}H_{25}N_2{}^{11}B$ m/z calc. 208.2111, found 202.213.

4.5.12. Bis(1,3-Butadiene-2-yl)-diethylaminoborane

NMR ($CDCl_3$, δ): ^1H 1.12 (t, 6H, 7.0 Hz), 3.13 (q, 4H), the signals of ethylenic protons overlapped those of the major boronic compound; $^{13}C(CDCl_3)$ 15.71, 43.92, 115.87, 120.97, 141.80, *C*–B not detected; $^{11}B(CDCl_3)$ 41.1.

4.5.13. 2-Propylbis(diethylamino)borane

B.p. 80–85°C/15 mmHg; NMR ($CDCl_3$, δ): ^1H 0.98 (broad s, 7H), 0.98 (t, 12H, overlapped), 2.92 (q, 8H, $J = 7.0$ Hz); $^{13}C(CDCl_3)$ 15 (broad), 15.47, 19.44, 41.54; $^{11}B(CDCl_3)$ 36.3; HRMS $C_{12}H_{15}N_2{}^{11}B$ m/z calc. 198.2267, found 198.227.

4.5.14. Bis(2-propyl)diethylaminoborane

NMR ($CDCl_3$, δ): ^1H Signals overlapped those of the major boronic compound, except 3.03 (q, $J = 7.0$ Hz); $^{13}C(CDCl_3)$ 15 (broad), 16.24, 19.18, 43.96; $^{11}B(CDCl_3)$ 46.0.

4.5.15. Methylbis(diethylamino)borane

B.p. 78°C/17 mmHg; NMR (CCl_4, δ): ^1H 0.23 (s, 3H), 1.03 (t, 12H, $J = 7.0$ Hz), 2.93 (q, 8H); $^{13}C(CCl_4)$ 0 (broad), 15.50, 42.10; $^{11}B(CDCl_3)$ 36.2; HRMS $C_9H_{23}N_2{}^{11}B$ m/z calc. 170.1954, found 170.195.

4.5.16. Dimethyldiethylaminoborane

NMR (CCl_4, δ): ^1H 0.21 (s, 6H), 1.08 (t, 6H, $J = 7.0$ Hz), 3.00 (q, 3H); $^{13}C(CCl_4)$ 15.94, 43.83 (CH_3–B not found); $^{11}B(CDCl_3)$ 45.7.

4.6. Borylation of organomagnesium or organolithium derivatives with 1c

The synthesis of $^nBuB(N^iPr_2)_2$ is typical. Into a 250 ml, three-necked flask fitted with a reflux condenser under N_2 atmosphere were introduced 7.88 g (32 mmol) of **1c** in 120 ml cyclohexane. The temperature was lowered to 0°C, and 17.0 ml (39 mmol, 1.2 eq) of a 2.28 M solution in ether of BuMgBr were added over 10 min. The reaction mixture was then heated under reflux for 2 h (when dilute solutions of organometallic compound in ether were used, the ether was distilled off to allow the reflux temperature to reach 60°C). A precipitate formed. After cooling to 20°C, 3 ml of dry diisopropylamine were added, and the stirring was continued for 30 min. After filtration through Celite and washing the precipitate with cyclohexane, the combined organic phases were concentrated. A rapid short-path distillation gave an oil which was redistilled on a 10 cm Krismer column, yielding 7.79 g (84%) of $BuB(N^iPr_2)_2$.

4.6.1. Methylbis(diisopropylamino)borane

B.p. 118°C/27 mmHg; NMR ($CDCl_3$, δ): ^1H 0.39 (s, 3H), 1.13 (d, 24H, $J = 6.5$ Hz), 3.50 (hept, 4H); $^{13}C(CDCl_3)$: 6.8 (broad), 24.07, 45.97; ^{11}B (C_6D_6) 39.3; HRMS $C_{13}H_{31}N_2{}^{11}B$ m/z calc. 226.2580, found 226.258.

4.6.2. Ethylbis(diisopropylamino)borane

B.p. 121°C/19 mmHg; NMR ($CDCl_3$, δ): ^1H 1.37–1.48 (m, 5H), 1.09 (d, 24H, $J = 6.8$ Hz), 3.47 (hept, 4H); $^{13}C(CDCl_3)$ 10.92, 12 (broad), 24.57, 46.39; $^{11}B(CDCl_3)$ 39.2; HRMS $C_{14}H_{32}N_2{}^{11}B$ m/z calc. 240.2737, found 240.272.

4.6.3. Butylbis(diisopropylamino)borane

B.p. 130°C/15 mmHg; NMR ($CDCl_3$, δ): ^1H 0.82–0.95 (m, 5H), 1.13 (d, 24H, 6.8 Hz), 3.48 (hept, 4H); $^{13}C(CDCl_3)$ 14.11, 21.3 (broad), 24.64, 26.61, 29.36, 46.49; $^{11}B(CDCl_3)$ 39.3; HRMS $C_{16}H_{37}N_2{}^{11}B$ m/z calc. 268.3050, found 268.306.

4.6.4. Phenylbis(diisopropylamino)borane

B.p. 84–85°C/0.01 mmHg; NMR ($CDCl_3$, δ): ^1H 1.01 (d, 24H, $J = 6.8$ Hz), 3.49 (hept, 4H), 7.18 (m, 3H), 7.36 (m, 2H); $^{13}C(CDCl_3)$ 25.07, 47.23, 125.99, 126.59, 134.60; $^{11}B(CDCl_3)$ 37.5; HRMS $C_{18}H_{33}N_2{}^{11}B$ *m/z* calc. 288.2737, found 288.272.

4.6.5. Vinylbis(diisopropylamino)borane

B.p. 51°C/0.05 mmHg; NMR ($CDCl_3$, δ): ^1H 1.12 (d, 2H, $J = 6.8$ Hz), 3.46 (hept, 4H), 5.41 (dd, 1H, $J_{gem} = 4.5$ Hz, $J_{trans} = 19.8$ Hz), 5.61 (broad dd, 1H), 6.38 (dd, 1H, $J_{cis} = 14.2$ Hz); $^{13}C(CDCl_3)$ 24.57, 46.60, 126.62, 146 (broad); $^{11}B(CDCl_3)$ 37.1; HRMS $C_{14}H_{31}N_2{}^{11}B$ *m/z* calc. 238.2580, found 238.259.

4.6.6. (2-propen-1-yl)bis(diisopropylamino)borane

B.p.: 80°C/0.2 mmHg; NMR ($CDCl_3$, δ): ^1H 1.16 (d, 24H, $J = 6.8$ Hz), 1.19 (d, 2H, $J = 7.1$ Hz), 3.51 (hept, 4H), 4.80–4.94 (m, 2H), 5.85–6.05 (m, 1H) $^{13}C(CDCl_3)$ 23 (broad), 24.55, 46.54, 112.68, 140.14; $^{11}B(CDCl_3)$ 36.9; HRMS $C_{15}H_{33}N_2{}^{11}B$ *m/z* calc. 252.2737, found 253.273.

4.6.7. Bis(diisopropylamino)borane

B.p. 45–7°C/0.1 mmHg; NMR ($CDCl_3$, δ): 0.90 (broad s, 1H), 1.10 (d, 12H, $J = 6.7$ Hz), 3.37 (hept, 4H); $^{13}C(CDCl_3)$ 24.69, 45.65; ^{11}B (C_6D_6) 26.8 (d, $J = 113$ Hz); HRMS $C_{12}H_{29}B_2{}^{11}B$ *m/z* calc. 212.2424, found 212.242.

4.7. Synthesis of oxazaborolidines 7

Into a 20 ml double-necked flask fitted with a short distillation head under N_2 were introduced 5 mmol of the β-aminoalcohol **7** and 5.5 mmol of the organobis(diisopropylamino)borane **2c** in 5 ml dry toluene. The flask was heated to 150°C until 4 ml of toluene had distilled. 5 ml of fresh toluene was added and distillation continued further. The crude **7** was then distilled *in vacuo*.

4.7.1. 3-benzyl-2-methyl-1,3,2-oxazaborolidine (7a)

B.p. 75–80°C/15 mmHg; NMR (CCl_4, δ): ^1H 0.26 (s, 3H), 2.99 (t, 2H, $J = 8.1$ Hz), 4.03 (t, 2H), 4.03 (s, 2H), 7.10–7.24 (m, 5H); $^{13}C(CCl_4)$ 48.52, 50.32, 65.62, 127.52, 127.88, 128.87, 140.06 (CH_3–B not detected; ^{11}B ($CDCl_3$) 34.1; HRMS $C_{10}H_{14}NO^{11}B$ *m/z* calc. 185.1951, found 185.195.

4.7.2. 3-benzyl-2-butyl-1,3,2-oxazaborolidine (7b)

B.p. 109–110°C/15 mmHg; NMR (CCl_4, δ) ^1H 0.82 (t, 2H, $J = 7.5$ Hz), 0.91 (t, 3H, $J = 7.1$ Hz), 1.25–1.30 (m, 4H); 3.01 (t, 2H, $J = 8.1$ Hz), 4.05 (t, 2H), 4.07 (s, 2H), 7.05–7.30 (m, 5H); ^{13}C (CCl_4) 13.2 (broad), 14.31, 25.81, 27.45, 47.37, 50.13, 64.73, 127.46, 127.81, 128.79, 139.97; ^{11}B (ether) 34.3; HRMS $C_{13}H_{20}NO^{11}B$ *m/z* calc. 217.1638, found 217.164.

4.7.3. 3-benzyl-2-phenyl-1,3,2-oxazaborolidine (7c) [25]

B.p.: 130–140°C/0.1 mmHg (lit. [25], 128°C/0.2 mmHg); NMR (CCl_4, δ) ^1H 3.17 (t, 2H, $J = 8.3$ Hz), 4.17 (t, 2H), 4.35 (s, 2H), 7.10–7.35 (m, 8H), 7.60–7.70 (m, 2H); $^{13}C(CCl_4)$ 50.22, 50.73, 65.64, 127.63, 128.34, 129.21, 130.29, 134.30, 139.79 (only 6 lines are observed in the aromatic region); ^{11}B ($CDCl_3$) 31.7; HRMS $C_{15}H_{16}NO^{11}B$ *m/z* calc. 237.1325, found 237.132.

4.7.4. 2-butyl-3-(tertiorybutyl)-1,3,2-oxazaborolidine (7d)

B.p. 65–70°C/15 mmHg; NMR (CCl_4, δ) ^1H 0.81 (t, 2H, $J = 7.4$ Hz), 0.89 (t, 3H, $J = 7.0$ Hz), 1.21 (s, 9H), 1.20–1.40 (m, 4H), 3.24 (t, 2H, $J = 8.1$ Hz), 3.95 (t, 2H); ^{13}C (CCl_4) 14.16 15.2 (broad), 25.83, 27.54, 30.20, 46.23, 50.34, 64.00; ^{11}B (ether) 33.1; HRMS $C_{10}H_{22}NO^{11}B$ *m/z* calc. 183.1794, found 183.180.

4.7.5. 2-butyl-3-phenyl-1,3,2-oxazaborolidine (7e)

B.p. 95°C/15 mmHg; NMR (CCl_4, δ) ^1H 0.92 (t, 3H, $J = 7.2$ Hz), 1.07 (t, 2H, $J = 7.7$ Hz), 1.20–1.45 (m, 4H), 3.43 (t, 2H, $J = 7.9$ Hz), 4.03 (t, 2H), 6.75–6.80 (m, 3H), 7.05–7.15 (m, 2H); $^{13}C(CCl_4)$ 14 (broad), 14.04, 25.51, 26.62, 48.67, 64.31, 118.12, 121.06, 128.72, 144.56; ^{11}B (ether) 33.7; HRMS $C_{12}H_{18}NO^{11}B$ *m/z* calc. 203.1481, found 203.148.

4.7.6. (S)-2-butyl-4-(1'-methyl-ethyl)-1,3,2-oxazaborolidine (7f)

B.p. 82–86°C/10 mmHg; NMR ($CDCl_3$, δ). ^1H 0.73 (t, 2H, $J = 7.1$ Hz), 0.74 (d, 3H, $J = 6.7$ Hz), 0.79 (d, 3H, $J = 6.7$ Hz), 0.91 (t, 3H, $J = 7.1$ Hz), 1.25–1.45 (m, 4H), 3.13–3.22 (m, 1H), 3.24 (broad s, 1H), 3.75 (dd, 1H, $J = 6.0$ Hz, $J = 9.3$ Hz), 4.09 (dd, 1H, $J = 8.6$ Hz); $^{13}C(CCl_4)$ 11.4 (broad), 14.06, 18.07, 18.10, 25.64, 27.21, 34.19, 60.95, 70.15; ^{11}B (ether) 34.6; HRMS $C_9H_{20}NO^{11}B$ *m/z* calc. 169.1638, found 169.163.

4.7.7. (4S,5R)-2-butyl-3,4-dimethyl-5-phenyl-1,3,2-oxazaborolidine (7g)

NMR (CCl_4, δ) ^1H 0.52 (d, 3H, $J = 6.5$ Hz), 0.87 (t, 2H, $J = 7.6$ Hz), 0.95 (t, 3H, $J = 7.1$ Hz), 1.34–1.55 (m, 4H), 2.56 (s, 3H), 5.34 (d, 1H, $J = 8.3$ Hz), 7.10–7.30 (m, 5H); $^{13}C(CCl_4)$ 10.6 (broad), 14.24, 15.44, 25.78, 26.85, 29.83, 60.32, 126.26, 126.82, 127.72, 142.23; ^{11}B (ether) 34.2; HRMS $C_{14}H_{22}NO^{11}B$ *m/z* calc. 231.1794, found 231.179.

4.8. Synthesis of catalysts 9

Into a 20 ml Schlenk flask under Ar were introduced (*S*)-α,α-diphenyl-2-pyrrolidinemethanol (132 mg,

0.521 mmol) and 1.05 equivalents of **2c** in 3 ml THF and 4 ml toluene. The reaction mixture was heated under reflux for 30 min, then concentrated and heated under vacuum (130°C/1 mmHg for 30 min) to remove the remaining solvent, yielding crude **9** in excellent purity (see Fig. 1).

4.8.1. (S)-tetrahydro-1-methyl-3,3-diphenyl-1H,3H-pyrrolo(1,2-c)(1,3,2)oxazaborole (9a)

NMR (C_6D_6, δ) ^{1}H 0.44 (s, 3H), 0.65–0.70 (m, 1H), 1.25–1.45 (m, 3H), 2.75–2.85 (m, 1H), 3.05–3.15 (m, 1H), 4.24 (dd, 1H, $J = 5.4$ Hz, $J = 9.7$ Hz), 7.00–7.65 (m, 10H); ^{13}C(C_6D_6)-5 (broad), 26.60, 30.49, 43.01, 73.07, 88.10, 126.64, 126.85, 127.76, 128.05, 128.39, 144.81, 148.38; ^{11}B ($CDCl_3$) 34.4.

4.8.2. (S)-tetrahydro-1-butyl-3,3-diphenyl-1H,3H-pyrrolo(1,2-c)(1,3,2)oxazaborole (9b)

NMR (C_6D_6, δ) ^{1}H 0.70–0.75 (m, 1H), 0.95–1.10 (m, 5H), 1.25–1.50 (m, 5H), 1.67 (quint, 2H, $J = 7.7$ Hz), 2.80–2.85 (m, 1H), 3.05–3.20 (m, 1H), 4.18 (dd, 1H, $J = 5.2$ Hz, $J = 9.7$ Hz), 7.00–7.65 (m, 10H); ^{13}C (C_6D_6) 11.7 (broad), 14.34, 26.17, 26.70, 27.40, 30.52, 42.95, 73.38, 87.85, 126.59, 126.80, 127.32, 127.76, 128.05, 128.38, 144.86, 148.48; ^{11}B ($CDCl_3$) 34.6.

4.8.3. (S)-tetrahydro-1-phenyl-3,3-diphenyl-1H,3H-pyrrolo(1,2-c)(1,3,2)oxazaborole (9c)

NMR (C_6D_6, δ) ^{1}H 0.75–0.90 (m, 1H), 1.30–1.45 (m, 3H), 2.95–3.05 (m, 1H), 3.20–3.35 (m, 1H), 4.39 (dd, 1H, $J = 5.1$ Hz, $J = 9.6$ Hz), 6.95–8.15 (m, 10H); ^{13}C (C_6D_6) 27.78, 30.17, 43.75, 74.75, 88.17, 126.84, 126.98, 127.42, 127.78, 128.13, 128.28, 128.46, 130.75, 135.20, 144.50, 148.00; ^{11}B (C_6D_6) 31.5.

4.8.4. Synthesis of 2-butyl-1,3-dimethyl-1,3,2-diazaborolane (10)

Into a two-necked flask fitted with a short distillation head under N_2 were introduced 2.208 g (8.23 mmol of BuB (N^iPr_2)$_2$ and 0.682 g (7.74 mmol) of *N,N'*-dimethylethylenediamine. The flask was heated at 110°C for 2 h while 1.13 g of $^iPr_2NH$ were recovered. After cooling, distillation under reduced pressure yielded 1.083 g (91%) of **10**, b.p. 79–82°C/37 mmHg; NMR (CCl_4, δ) ^{1}H 0.67 (t, 2H, $J = 7.4$ Hz), 0.89 (t, 3H, $J = 7.0$ Hz), 1.30 (m, 4H), 2.59 (s, 6H), 3.06 (s, 4H); ^{13}C (CCl_4) 11 (broad), 14.74, 26.49, 28.2, 34.39, 51.95; ^{11}B ($CDCl_3$) 32.7; HRMS $C_8H_{19}N_2{}^{11}B$ m/z calc. 154.1641, found 154.164.

4.8.5. Synthesis of (4R,5S)-2-butyl-4,5-dicarboxyethyl-1,3,2-dioxaborolane (11)

In a 50 ml Schlenk flask with N_2 atmosphere were introduced 0.923 g (4.48 mmol) of diethyl tartrate and 1.215 g (4.52 mmol) of BuB(N^iPr_2)$_2$ in 10 ml of ether. After 30 min at 20°C, removal of ether gave a solid. This solid was heated at 50°C under vacuum (20 mmHg) for 3 min, which caused melting and frothing. Removal of the remaining amine at 20°C/0.05 mmHg yielded 1.22 g (95% yield) of crude **11** of $\approx$ 93% purity (mixed with 7% diethyl tartrate, as shown by ^{1}H and ^{13}C NMR); NMR ($CDCl_3$, δ) ^{1}H 0.90 (t, 3H, $J = 7.2$ Hz), 0.98 (t, 2H, $J = 7.7$ Hz), 1.25–1.55 (m, 10H), 4.26 (q, 4H, $J = 7.1$ Hz), 4.85 (s, 2H); ^{13}C ($CDCl_3$) 10 (broad), 13.68, 13.95, 25.03, 25.64, 61.96, 77.36, 169.48; ^{11}B ($CDCl_3$) 35.7; HRMS $C_{12}H_{21}O_6{}^{11}B$ m/z calc. 273.1431, found 273.143.

4.8.6. Synthesis of (S)-2-butyl-3-phenyl-4-oxo-1,3,2-dioxaborolane (12b)

Into a 50 ml Schlenk flask under N_2 were introduced 0.760 g (5.00 mmol) of (S)-mandelic acid and 1.338 g (4.99 mmol) of Bu(N^iPr_2)$_2$ in 5 ml ether. A gel formed almost immediately. After 15 min at 20°C, 7 ml (11.2 mmol) of a 1.6 M solution of dry HCl in ether were added at 20°C. A white precipitate was formed immediately. After stirring for 2 h at 20°C, the reaction mixture was filtered under N_2. Concentration of the filtrate yielded **12** (purity > 98% by ^{1}H and ^{13}C NMR), 0.880 g, 81% yield; NMR ($CDCl_3$, δ). ^{1}H 0.93 (t, 3H, $J = 7.3$ Hz), 1.18 (t, 2H, $J = 7.7$ Hz), 1.39 (sext, 2H, $J = 7.3$ Hz), 1.55 (quint, 2H, $J = 7.3$ Hz), 5.45 (s, 1H), 7.39 (broad s, 5H); ^{13}C ($CDCl_3$) 11 (broad), 13.80, 25.00, 25.22, 76.74, 125.65, 128.90, 129.13, 133.75, 174.30; ^{11}B ($CDCl_3$) 37.7; HRMS $C_{12}H_{15}O_3{}^{11}B$ m/z calc. 218.1114, found 218.111.

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20 Not isolated, but identified in the mixtures by ^{11}B, ^{1}H and ^{13}C NMR spectroscopy, and comparison with an authentic sample in one case (Et_2BNEt_2).

21 Indeed, when reagents were mixed at low temperature, it seemed that no reaction took place (no evolution of heat, no precipitate) below 0°C (LiBu) or 20°C (BuMgBr); if the temperature of the reaction mixture was raised to these values a mild exothermic precipitation of salts started.

22 Hoffmann *et al.* obtained the corresponding ^{i}Pr–$B(NMe_2)_2$ in 95% yield (ref. 11).

23 On this hypothesis, yields in **4b** and **5b** should be equal. Note that the Table indicates recovered yields, after a distillative work-up. Since the global recovery of boron is not quantitative, the proportions in the crude reaction mixture may be different. Moreover, some **4b** can be formed from unreacted **1b** during diethylaminolysis, see note 19.

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