Chiral 2,3-Dihydro-1*H*-1,3,2-diazaboroles

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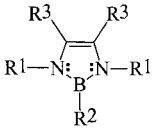
A series of differently substituted chiral 2,3-dihydro-1*H*-1,3,2-diazaboroles has been prepared by various methods. 2-Bromo-1-*tert*-butyl-3-[(*S*)-1-phenylethyl]-2,3-dihydro-1*H*-1,3,2-diazaborole (**3a**), 2-bromo-1,3-di[(*S*)-1-phenylethyl]-2,3-dihydro-1*H*-1,3,2-diazaborole (**3b**) and 2-bromo-1,3-di[(*S*)-1-cyclohexylethyl]-2,3-dihydro-1*H*-1,3,2-diazaborole (**3c**) were formed from the reaction of the corresponding 1,4-diazabutadienes and boron tribromide and the subsequent reduction of the resulting borolium salts [R^1N^a = CH–CH=$N^b(R^2)BBr_2$]Br(N^a–*B*) [**2a**: R^1 = *t*Bu, R^2 = CH(Me)Ph; **2b**: R^1 = R^2 = CH(Me)Ph; **2c**: R^1 = R^2 = CH(Me)(*c*C_6H_{11})] with sodium amalgam. Treatment of (*S*)-**3a** with $LiAlH_4$ or methyllithium afforded 1-*tert*-butyl-2-hydro-3-[(*S*)-1-phenylethyl]-2,3-dihydro-1*H*-1,3,2-diazaborole [(*S*)-**6**] and 1-*tert*-butyl-2-methyl-3-[(*S*)-1-phenylethyl]-2,3-dihydro-1*H*-1,3,2-diazaborole [(*S*)-**7**], respectively. Aminolysis of the BBr bond of (*S*)-**3a** by *tert*-butylamine or (*S*)-1-phenylethylamine gave the corresponding 2-*tert*-butylamino- and 2-[1-phenylethylamino]-2,3-dihydro-1*H*-1,3,2-diazaboroles (*S*)-**8** and (*S,S*)-**9**, respectively. Similarly, (*S,S*)-**3b** and (*S,S*)-**3c** were reacted with *tert*-butylamine to furnish the 2-*tert*-butylamino-2,3-dihydro-1*H*-1,3,2-diazaborole derivatives (*S,S*)-**11** and (*S,S*)-**12**, respectively. The 2-trimethylstannyl-2,3-dihydro-1*H*-1,3,2-diazaboroles (*S,S*)-**10** and (*S,S*)-**14** were accessible from **3b** or **3c** and trimethylstannyllithium. The transformation of achiral 2-bromo-1,3-di-*tert*-butyl-2,3-dihydro-1*H*-1,3,2-diazaborole into the chiral (*S*)-2-[1-phenylethylamino]- and (*S*)-2-[1-cyclohexyl-ethylamino] derivatives (*S*)-**15** and (*S*)-**16** was effected by aminolysis with enantiomerically pure (*S*)-1-phenylethylamine or (*S*)-1-cyclohexylethylamine. The novel compounds were characterized by ^1H, ^{11}B, ^{13}C, and ^{119}Sn NMR spectroscopy as well as mass spectrometry and determination of the optical rotation. The molecular structure of compound **3c** was confirmed by X-ray structural analysis.

Introduction

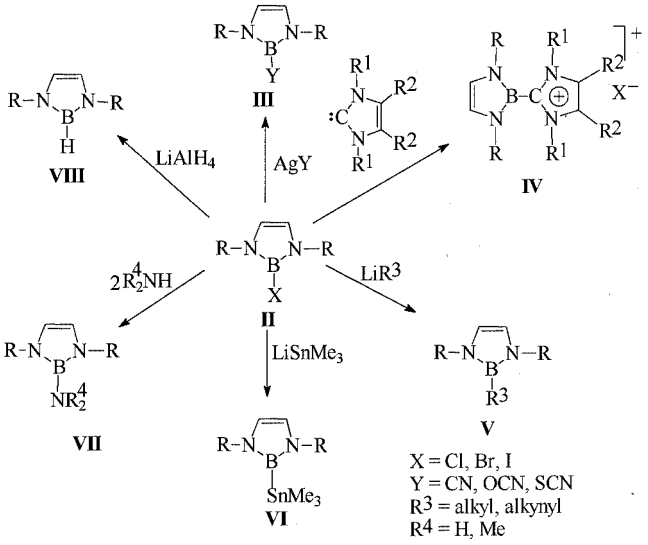
The synthesis of the first 2,3-dihydro-1*H*-1,3,2-diazaboroles **I** dates back to the early 1970s,[1,2] and since then a series of contributions concerning the synthesis, structure, and bonding of such heterocycles has been published.[3–6]



I

I	R1	R2	R3
a	Me	Ph	H
b	Ph	Me	Me
c	Me	*t*Bu	H
d	H/Me	Ph	H

Recently, we started a program investigating the synthesis of 2-halo-2,3-dihydro-1*H*-1,3,2-diazaboroles **II** as starting materials for further chemical transformations.[7,8] Treatment of **II** with organolithium compounds,[9] $LiSnMe_3$,[9] $LiAlH_4$,[9] imidazol-2-ylidenes,[7] amines[10] and silver salts[8] afforded a series of novel 1,3,2-diazaboroles **III**–**VIII** (Scheme 1).



Scheme 1. Chemical transformations of **II**

Terminal as well as internal alkynes are inserted regioselectively into the B–Sn bond of **VI** in a reaction catalyzed by low-valent Pd species (Scheme 2).[11]

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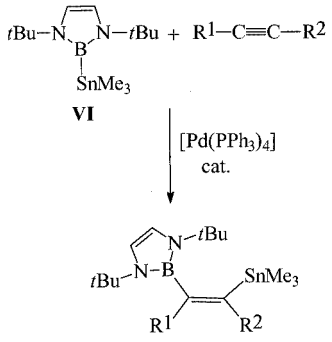
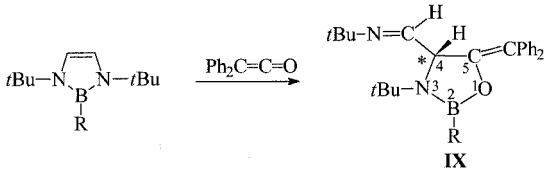


Scheme 2. Insertion of alkynes into the B−Sn bond of **VI**

Moreover, it was demonstrated that 1,3,2-diazaboroles are smoothly converted into 1,3,2-oxazaborolidines **IX** upon reaction with an equimolar amount of diphenylketene (Scheme 3).[12]



Scheme 3. Conversion of 2,3-dihydro-1*H*-diazaboroles into 1,3,2-oxazaborolidines by treatment with diphenylketene

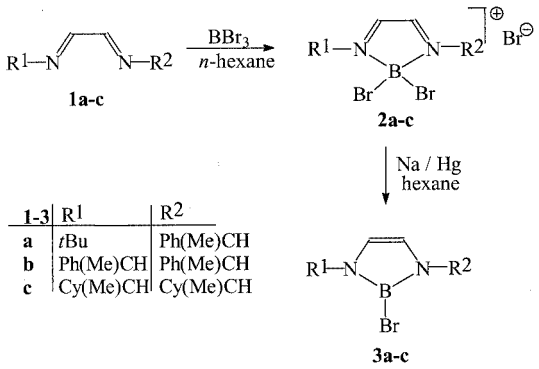
Here a stereogenic center was created at C(4), and it was challenging to elaborate conditions that would allow the stereoselective synthesis of these compounds.

Results and Discussion

The intention of the work described herein is to provide efficient syntheses of chiral 2,3-dihydro-1*H*-1,3,2-diazaboroles as the required precursors for such transformations. The most obvious way to introduce chirality into 1,3,2-diazaboroles is the use of chiral substituents at the heteroatoms of the ring. This target may be achieved by the employment of chiral 1,4-diazabutadienes as starting materials. The latter are available from the condensation of glyoxal and chiral primary amines such as (*S*)-1-phenylethylamine or (*S*)-1-cyclohexylethylamine. The combined condensation of glyoxal with *tert*-butylamine and (*S*)-phenylethylamine in a molar ratio of 4:7:1 leads to the formation of a 3:1 mixture of 1,4-di-*tert*-butyl-1,4-diazabutadiene and Ph(Me)CHN=CH−CH=N*t*Bu (**1a**). The former product is easily removed in vacuo at ambient temperature. The residue of crude **1a** was purified by distillation to give a light yellow oil (43% yield). This compound is thermolabile and has to be stored at −30 °C. According to NMR spectroscopic data **1a** is a 1:2 mixture of two isomers.

The diazabutadienes (*S*,*S*)-Ph(Me)CHN=CH−CH=NCH(Me)Ph (**1b**)[13] and (*S*,*S*)-*c*-C_6H_{11}(Me)CHN=CH−CH=N−CH(Me)(*c*-C_6H_{11}) (**1c**) were prepared from an aqueous glyoxal solution and the respective amines in a molar ratio of 1:2. Compound **1c** was isolated as colorless crystals in 82% yield, whereas **1b** was obtained as a colorless oil as described previously.

Combination of equimolar amounts of **1a** and BBr_3 in hexane at 20 °C led to the precipitation of the orange borolium salt **2a**. Its moisture sensitivity and low volatility precluded reliable elemental analyses and useful mass spectra. The reduction of compound **2a** with sodium amalgam in hexane afforded 1,3,2-diazaborole **3a** as a yellow oil in 66% yield after distillation (Scheme 4).



Scheme 4. Preparation of 1,3,2-diazaboroles **3a**−**c** (Cy = cyclohexyl)

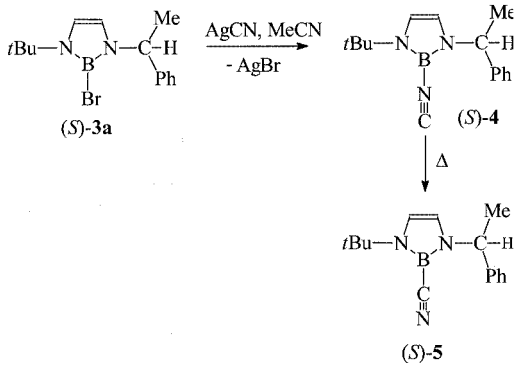
Neat **3a** decomposes to a brown oil after 24 h at 20 °C, therefore it is recommended to store the reaction mixture and to isolate the compound only prior to use.

The preparation of the yellow borolium salt **2b** was achieved by reaction of diazabutadiene (**1b**) and boron tribromide under similar conditions. Sodium amalgam reduction of **2b** over a period of two days led to a 32% yield of crude oily **3b**. Like **3a**, compound **3b** should only be isolated immediately before subsequent transformations.

In contrast to this, the reduction of analogously prepared orange moisture-sensitive **2c** with sodium amalgam led to the formation of colorless crystalline **3c** (60.5%), which separated upon concentrating the hexane reaction solution. Further purification of the thermostable product was achieved by sublimation at 80 °C and 5×10^{-6} bar.

In the $^{11}B\{^1H\}$ NMR spectra the 2-bromo-1,3,2-diazaboroles **3a**−**c** show singlets at δ = 17.3 (**3a**), 19.0 (**3b**) and 18.2 ppm (**3c**), which are very similar to the ^{11}B resonance in *t*BuN^{a}CH=CHN^b(*t*Bu)BBr(N^a−*B*) (δ = 16.2 ppm).[7] The ^1H and ^{13}C NMR resonances of the CH=CH building block (δ_H = 6.13−6.41 ppm and δ_C = 111.9−114.9 ppm are also very similar to the corresponding data for *t*BuN^a-CH=CHN^b(*t*Bu)BBr (δ_H = 6.27 ppm, δ_C = 113.6 ppm).

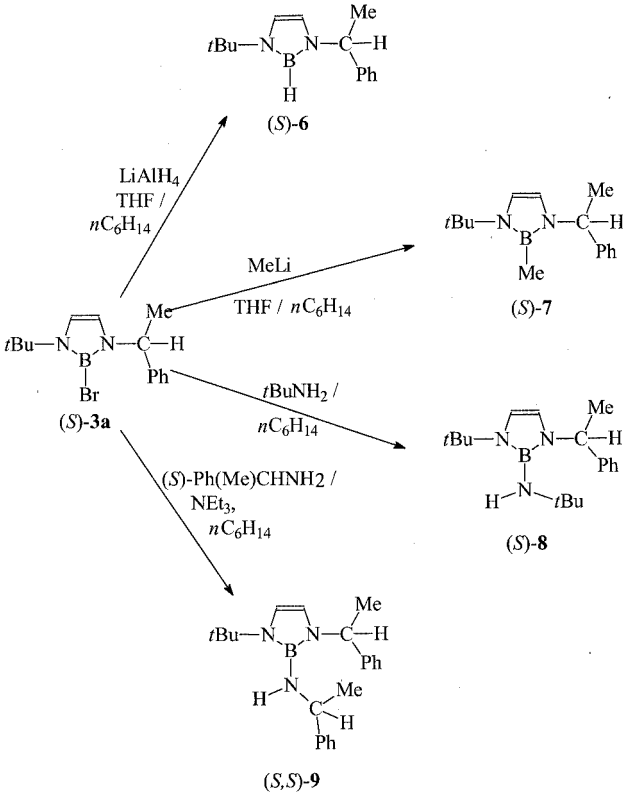
A series of chiral 1,3,2-diazaboroles were derived from **3a** by nucleophilic substitution at the boron center. Reaction of **3a** with silver cyanide in acetonitrile for 1 h furnished a liquid mixture of 2-isocyano-1,3,2-diazaborole (**4**) and 2-cyano-1,3,2-diazaborole (**5**) (Scheme 5)



Scheme 5. Reaction of (*S*)-**3a** with AgCN

The presence of both isomers was confirmed by the ^{1}H, ^{13}C NMR and IR spectra of a freshly prepared sample. Particularly informative is the IR spectrum where sharp bands at $\tilde{\nu}$ = 2113 and 2206 cm^{-1} are attributed to the ν(CN) vibrations of the isocyano function in **4** and the cyano group in **5**, respectively. Storing the product mixture at −30 °C for two weeks or vacuum distillation at 200 °C led to the complete disappearance of the band at 2113 cm^{-1}. After the rearrangement **4** → **5** the pure cyano derivative was obtained as a colorless solid (57% yield). In contrast to precursor **3a**, compound **5** is stable at room temperature. A similar rearrangement was not observed during the preparation of *t*BuN^{a}−CH=CH−N^{b}(*t*Bu)BCN(*N^{a}*−*B*) from the corresponding 2-bromo-1,3,2-diazaborole and AgCN. To the best of our knowledge stable boryl isocyanides are still undocumented. The $^{11}B\{^{1}H\}$ NMR spectrum of **5** is characterized by a singlet at δ = 11.6 ppm. In the ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra the HC=CH unit gives rise to two doublets at δ = 6.25 and 6.40 ppm ($^{3}J_{H,H}$ = 2.3 Hz) and two singlets at δ = 114.8 and 116.1 ppm, respectively. In *t*BuN^{a}−CH=CH−N^{b}(*t*Bu)BCN(*N^{a}*−*B*) the corresponding resonances were observed at δ_B = 12.0 ppm (s), δ_H = 6.14 ppm (s) and δ_C = 114.6 ppm (s).

Reduction of (*S*)-**3a** with lithium aluminium hydride in a THF/hexane mixture (Scheme 6) afforded the 2-hydro-1,3,2-diazaborole (*S*)-**6** as a yellow oil (95%). Purification by vacuum distillation to give (*S*)-**6** as a colorless liquid was accompanied by considerable loss of product (47%). At room temperature decomposition of a pure sample to a brown oil was complete within 24 h. In the IR spectrum a strong band at $\tilde{\nu}$ = 2621 cm^{-1} is due to the ^{11}B-H stretching mode. In the proton-coupled ^{11}B NMR spectrum ($CDCl_3$ solution) compound (*S*)-**6** exhibits a doublet at δ = 19.4 ppm ($^{1}J_{B,H}$ = 146 Hz). These values compare well with the result given for *t*BuN^{a}CH=CH−N^{b}(*t*Bu)BH(*N^{a}*−*B*) [δ_B = 18.9 ppm (d, $^{1}J_{B,H}$ = 149 Hz)].[9] In contrast to the latter compound, where the boron-ligated hydrogen atom appears in the ^{1}H NMR spectrum as a quadruplet resonance (δ = 4.78 ppm, $^{1}J_{B,H}$ = 150 Hz) no such signal was detected in the ^{1}H NMR spectrum of (*S*)-**6**.



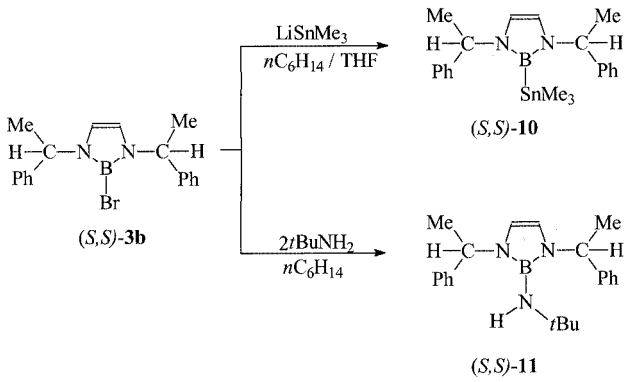
Scheme 6. Reaction of (*S*)-**3a** with $LiAlH_4$, MeLi, *t*$BuNH_2$ and (*S*)-Ph(Me)CH−NH_2

The reaction of 2-bromo-1,3,2-diazaborole (*S*)-**3a** with methyllithium in a mixture of hexane and THF (Scheme 6) cleanly afforded (*S*)-**7** as a colorless oil after distillation at 200 °C and 10^{-5} bar (51%). The $^{11}B\{^{1}H\}$ NMR spectrum of (*S*)-**7** shows a singlet at δ = 26.2 ppm, which is identical with that of *t*BuN^{a}CH=CHN^{b}(*t*Bu)BCH$_3$(*N^{a}*−*B*).[3] The CH=CH unit appears as two doublets at δ = 6.32 and 6.48 ppm ($^{3}J_{H,H}$ = 2.5 Hz) in the ^{1}H NMR spectrum and two singlets at δ = 111.1 and 113.5 ppm in the $^{13}C\{^{1}H\}$ NMR spectrum of the compound.

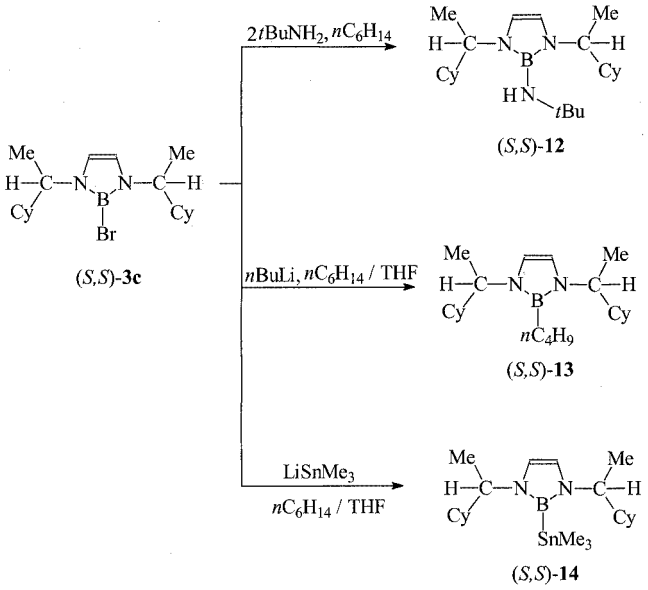
To increase the steric demand of chiral 1,3,2-diazaboroles we introduced bulky amino substituents at the boron atom of the ring. Reaction of (*S*)-**3a** with an excess of *tert*-butylamine in hexane gave (*S*)-**8** (Scheme 6), which was isolated as a yellow oil by vacuum distillation (300 °C, 10^{-5} bar, 74%). Compound (*S*,*S*-**9**) resulted from the treatment of (*S*)-**3a** with an equimolar amount of (*S*)-1-phenylethylamine in the presence of triethylamine. The heterocycle was isolated as a colorless liquid in 48% yield by vacuum distillation. The ^{11}B NMR signals of (*S*)-**8** (δ = 22.3 ppm) and (*S*,*S*)-**9** (δ = 21.6 ppm) are similar to those of the amino-functionalized 1,3,2-diazaboroles *t*BuN^{a}CH=CHN^{b}(*t*Bu)BN(H)*t*Bu(N^{a}−B) (δ = 22.9 ppm) and *t*BuN^{a}-CH=CHN^{b}(*t*Bu)BNH(2,6-$Me_2C_6H_3$)(*N^{a}*−*B*) (δ = 21.6 ppm).[10]

It was also intended to convert the chiral 1,3,2-diazaborole (*S*,*S*)-**3b** into more stable and sterically more congested

derivatives. A hexane solution of (*S*,*S*)-**3b** was combined with a solution of a slight excess of $LiSnMe_3$ in THF at room temperature, whereupon the stannylated heterocycle (*S*,*S*)-**10** was generated. Analytically pure colorless (*S*,*S*)-**10** was obtained by crystallizing the crude material from toluene (67% yield). (Scheme 7)



Scheme 7. Conversion of (*S*,*S*-**3b**) into (*S*,*S*-**10**) and (*S*,*S*-**11**)



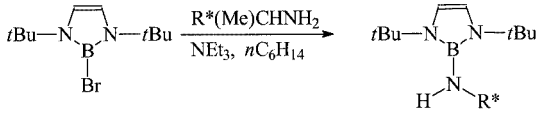
Scheme 8. Synthesis of (*S*,*S*)-**12**, (*S*,*S*)-**13** and (*S*,*S*)-**14** from (*S*,*S*)-**3c**

Compound **10** can be stored at room temperature under an inert atmosphere without discernible decomposition. The singlet at δ = 28.2 ppm in the $^{11}B\{^1H\}$ NMR spectrum is accompanied by ^{119}Sn satellites ($^1J_{Sn,B}$ = 994 Hz). Similarly, the $^{119}Sn\{^1H\}$ NMR spectrum of **10** features a quadruplet at δ = 150.0 ppm ($^1J_{Sn,B}$ = 994 Hz). The $^{11}B\{^1H\}$ NMR spectrum of 2,6-$Me_2C_6H_3N^aCH{=}CHN^b$(2,6-$Me_2C_6H_3$)$BSnMe_3$(*N*^{a}−*B*) is characterized by a singlet at δ = 28.2 ppm with ^{119}Sn satellites ($^1J_{Sn,B}$ = 960 Hz). The $^{119}Sn\{^1H\}$ NMR resonance of this molecule appears as a quadruplet at δ = 146 ppm with $^1J_{Sn,B}$ = 960 Hz.

The stable amino-functionalized 1,3,2-diazaborole (*S*,*S*)-**11** was isolated as a yellow liquid from the reaction of **3b** with a twofold equimolar amount of *tert*-butylamine in hexane at 20 °C (50%). Similarly, the colorless liquid diazaborole (*S*,*S*)-**12** was synthesized from (*S*,*S*)-**3c** and *tert*-butylamine (58% after distillation at 300 °C, 4 × 10^{-6} bar; Scheme 8). Preparation of the 2-butyl-1,3,2-diazaborole (*S*,*S*)-**13** was accomplished by reaction of **3c** with an excess of *n*-butyllithium in a hexane/THF mixture at −15 to 20 °C. Pure colorless oily **13** was obtained by distillation (250 °C, 5 × 10^{-6} bar, 47%).

Analogously to the preparation of (*S*,*S*)-**10** the stannylated diazaborole (*S*,*S*)-**14** was synthesized as a colorless liquid from **3c** and $LiSnMe_3$ in a THF/hexane mixture (58% yield).

A different approach to chiral 1,3,2-diazaboroles was based upon the reaction of achiral *t*$BuN^aCH{=}CHN^b$(*t*Bu)BBr(*N*^{a}−*B*) with the chiral auxiliaries (*S*)-Ph(Me)$CHNH_2$ and (*S*)-Cy(Me)$CHNH_2$ in the presence of triethylamine (Scheme 9). Heterocycle **15** was isolated as a pale yellow oil in 74% yield by distillation (200 °C, 10^{-5} bar). The same holds for **16**, which was isolated as a colorless oil after distillation (150 °C, 2 × 10^{-6} bar, 72%). The $^{11}B\{^1H\}$ spectra of the 2-amino-1,3,2-diazaboroles (*S*,*S*)-**11** [δ = 22.5 (s)], (*S*,*S*)-**12** [δ = 22.1 (s)], (*S*)-**15** [δ = 22.3 (s)] and (*S*)-**16** [δ = 22.0 (s)] resemble those of **8** and **9** and do not show any marked influence of the substituent at the nitrogen atom.



Scheme 9. Preparation of (*S*)-**15** and (*S*)-**16**

X-ray Structural Analysis of (*S*,*S*)-3c

The molecular structure of (*S*,*S*)-**3c** (Figure 1) features a planar 1,3,2-diazaborole ring with two nearly orthogonally oriented 1-cyclohexylethyl substituents at the nitrogen atoms. A C_2 axis bisects the molecule along the B(1)−Br(1) vector. The bond length B(1)−Br(1) [1.930(2) Å] is close to the sum of the covalent radii of boron (0.81 Å) and bromine (1.14)[14] and compares well with the B−Br distances in [(2,4,6-$Me_3C_6H_2$)(Br)B]$_2$ [1.928(4) and 1.932(4) Å].[15] B−Br bond lengths involving sp^2-hybridized boron atoms range from 1.87(1) Å in [*i*$Pr_3P{=}N^a{-}B^a$(Br)N^b-(=P*i*Pr$_3$)B^bBr_2]Br(*N*^{a}−*B*^{b})[16] or 1.902(5) Å in 2,6-$Mes_2C_6H_3BBr_2$ (Mes = 2,4,6-$Me_3C_6H_2$)[17] to 2.00(1) Å in the triborane [(Me_2N)(Br)B]$_2$$BNMe_2$.[18] Atomic distances and valence angles within the diazaborole ring are in good agreement with the corresponding data for (2,6-$Me_2C_6H_3$)$N^a{-}CH{=}CH{-}N^b$(2,6-$Me_2C_6H_3$)BI(*N*^{a}−*B*).[18] In (*S*,*S*)-**3c** the B−N bond length [1.417(1) Å] indicates multiple bond character. In a series of diazaboroles the B−N bond lengths range from 1.407(5) to 1.450(2) Å. The atomic distance C(1)−C(1A) [1.350(3) Å] and the

N−C(sp^2) bond length [1.403(2) Å] also indicate multiple bonding. For the N(sp^2)−C(sp^3) single bond N(1)−C(2) a length of 1.471(2) Å was determined. The endocyclic angles in (*S*)-**3c** — N(1)−B(1)−N(1A) [107.7(1)°] B(1)−N(1)−C(1) [106.6(1)°], and N(1)−C(1)−C(1A) [109.5(1)°] — are similar to those in 2,6-$Me_2C_6H_3N^a$CH=CHN^b(2,6-$Me_2C_6H_3$)BI(N^a−*B*) [106.9(4)°, 107.5(3)°, and 109.1(2)°, respectively].[8] This also applies to the exocyclic angle N(1)−B(1)−Br(1) [126.1(1)°] in (*S*)-**3c** and the N(1)−B(1)−I(1) angle [126.6(2)°] in 2,6-$Me_2C_6H_3N^a$−CH=CHN^b(2,6-$Me_2C_6H_3$)BI(N^a−*B*).

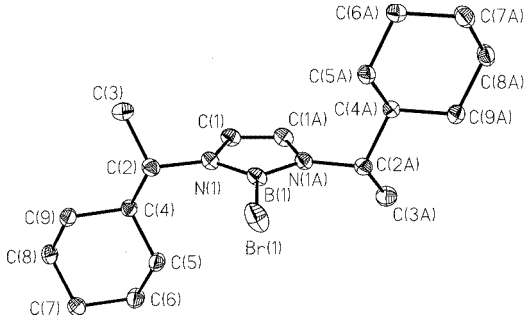


Figure 1. Molecular structure of (*S*,*S*)-**3c** in the crystal; selected bond lengths [Å] and bond angles [°]: B(1)−Br(1) 1.930(2), B(1)−N(1) 1.417(1), N(1)−C(1) 1.403(2), N(1)−C(2) 1.471(2), C(1)−C(1A) 1.350(3); N(1)−B(1)−N(1A) 107.7(1), Br(1)−B(1)−N(1) 126.1(1), B(1)−N(1)−C(1) 106.6(1), B(1)−N(1)−C(2) 131.0(1), N(1)−C(1)−C(1A) 109.5(1); B(1)−N(1)−C(2)−C(3) 124.3, B(1)−N(1)−C(2)−C(4) −110.0

Experimental Section

General: All manipulations were performed under dry argon. Solvents were rigorously dried with an appropriate drying agent and freshly distilled before use. The following compounds were prepared as described in the literature: (*S*,*S*)-Ph(Me)CHN=CH−CH=NCH(Me)Ph (**1b**),[13] *t*BuN^{a}CH=CHN^b(*t*Bu)BBr(N^a−*B*).[7]

An aqueous glyoxal solution (40%) of *tert*-butylamine, boron tribromide, silver cyanide, trimethyltin chloride, *n*-butyllithium, methyllithium, triethylamine, (*S*)-1-phenylethylamine and (*S*)-1-cyclohexylethylamine were purchased commercially. IR spectra Bruker FTIR Vector 22, Bruker FTIR IFS66. ^{1}H, ^{11}B, ^{13}C NMR spectra: Bruker AC 100 (^{1}H, 100.13 MHz, ^{11}B (32.13 MHz); Bruker Avance DRX 500 (^{1}H, 500.13 MHz, ^{11}B, 160.46 MHz, ^{13}C, 125.75 MHz); references: $SiMe_4$ (^{1}H, ^{13}C), BF_3·OEt_2 (^{11}B). Mass spectra EI (70 eV), CI (NH_3): Autospec sector-field mass spectrometer (Micromass). Optical rotations were measured with a Jasco DIP-360 in CH_2Cl_2 solution [c = 0.01 g·mL^{-1}, d = 1 dm].

Preparation of the 1,4-Diazabutadienes. (*S*)-*t*BuN=CH−CH=N−CH(Me)Ph (1a): Solutions of (*S*)-1-phenylethylamine (28.8 g, 0.24 mol) in hexane (200 mL) and *tert*-butylamine (121.7 g, 1.90 mol) in hexane (200 mL) were simultaneously added dropwise to a well-stirred chilled mixture of an aqueous solution of glyoxal 114.3 mL (114.2 mL, 1.0 mol, 0 °C) and 400 mL of hexane. Then stirring was continued at room temp. for 30 min. The liquid content of the flask separated into two phases. The aqueous phase was extracted with hexane (30 mL) and then discarded. The combined hexane phases were dried (Na_2SO_4) and then freed from solvent. The remaining yellow oil was kept at 5 × 10^{-6} bar and 20 °C to remove *t*BuN=CH−CH=N*t*Bu (49.0 g crude **1a**). The brown oily residue (10.0 g) was distilled at (5 × 10^{-6} bar, and 70 °C) to give 4.5 g (43%) of **1a** as a light-yellow liquid. This purification step could not be scaled up because of serious loss of product. IR (film): $\tilde{\nu}$ = 3062 cm^{-1} w, 3029 m, 2981 s, 2864 s, 1629 s [ν(C=N)], 1493 m, 1451 m, 1361 s, 1213 s, 759 s, 699 s. ^{1}H NMR ($CDCl_3$): δ = 1.21 and 1.23 (2s, 9 H, *t*Bu), 1.55 and 1.56 (2d, $^3J_{H,H}$ = 6.4, 6.8 Hz, 3 H, CH_3), 4.48 [q, $^3J_{H,H}$ = 6.8 Hz, 1 H, C*H*Me], 7.23−7.33 (m, 5 H, *H*−Ph), 7.92−8.02 (m, 2 H, N=CH) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 23.9 (s, CH*C*H$_3$), 29.27 and 29.34 [2s, C(*C*H$_3$)], 58.2 and 58.3 [2s, *C*(CH$_3$)$_3$], 69.66 and 69.71 (2s, *C*HCH$_3$), 126.6, 126.7, 127.2, 128.5, 128.6, 143.6, 143.7 (7s, *C*−Ph), 157.0, 157.8, 160.7, 161.5 (4s, H*C*=N) ppm. MS/EI: *m*/*z* (%) = 216 (6) [M$^+$], 201 (36) [M$^+$ − CH$_3$], 159 (33) [M$^+$ − *t*Bu], 145 (100) [M$^+$ − CH$_3$ − CH$_2$=CMe$_2$]. [α]$_D^{24}$ = −97. $C_{14}H_{20}N_2$ (216.33): calcd. C 77.73, H 9.32, N 12.95; found C 77.40, H 9.56, N 12.86.

(*S*,*S*)-Cy(Me)CH−N=CH−CH=N−CH(Me)Cy (1c): A solution of (*S*)-1-cyclohexylethylamine (17.8 g, 140 mmol) in 80 mL of hexane was added during 30 min to a vigorously stirred mixture of 8 mL of aqueous glyoxal (70 mmol) and 50 mL of hexane. Both phases were separated and the aqueous layer was extracted with 50 mL of hexane. The combined organic phases were dried twice with Na_2SO_4. Solvent was removed in vacuo to afford 16.1 g (82%) of **1c** as colorless crystals. ^{1}H NMR ($CDCl_3$): δ = 0.85 (m, 2 H, Cy), 0.93 (m, 2 H, Cy), 1.15 (m, 8 H, Cy), 1.23 (m, 4 H, Cy), 1.42 (m, 2 H, Cy), 1.63 (m, 4 H, Cy), 1.75 (m, 6 H, CH$_3$), 2.97 (q, $^3J_{H,H}$ = 6.6 Hz, 2 H, C*H*CH$_3$), 7.85 (s, 2 H, N=CH) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 19.6 (s, CH$_3$), 26.2, 26.3, 26.5, 29.5, 29.8, 43.4 (6s, Cy), 71.6 (s, *C*HCH$_3$), 160.2 (s, CH=N) ppm. MS/EI: *m*/*z* (%) = 276 (7) [M$^+$], 193 (100) [M$^+$ − Cy]. [α]$_D^{24}$ = +34. $C_{18}H_{32}N_2$ (276.47): calcd. C 78.20, H 11.67, N 10.13; found C 77.40, H 11.94, N 10.30.

Preparation of the 2,3-Dihydro-1*H*-1,3,2-diazaboroles. (*S*)-*t*BuN^a-CH=CHN^b {CH(Ph)Me}BBr(N^a−*B*) (3a): A solution of 1,4-diazabutadiene **1a** (3.3 g, 15.3 mmol) in 50 mL of hexane and a solution of boron tribromide (3.85 g, 15.5 mmol) in 50 mL of hexane were added dropwise and simultaneously at 20 °C to a volume of 100 mL of hexane. The resulting orange slurry was stirred for another 30 min and filtered. The filter cake was washed with pentane (50 mL) and dried at 5 × 10^{-3} bar. The borolium salt (*S*)-*t*BuN^a=CH−CH=N^b{CH(Ph)Me}BBr$_2$]Br(N^a−*B*) **2a** was obtained as an orange powder (6.4 g, 90%). ^{1}H NMR ($CDCl_3$): δ = 1.75 (s, 9 H, *t*Bu), 2.02 (d, $^3J_{H,H}$ = 6.9 Hz, 3 H, CHC*H*$_3$), 5.35 (q, $^3J_{H,H}$ = 6.9 Hz, 1 H, C*H*CH$_3$), 7.40 (m, 3 H, Ph), 7.57 (m, 2 H, Ph), 8.40 (d, $^3J_{H,H}$ = 7.9 Hz, 1 H, *C*H=N−CH), 8.68 (d, $^3J_{H,H}$ = 7.9 Hz, 1 H, *C*H=N*t*Bu) ppm. ^{11}B{^{1}H} NMR ($CDCl_3$): δ = −1.2 (s) ppm. Compound **2a** (11.5 g, 24.6 mmol) was added to a mixture of sodium amalgam (from 2.5 g, 108 mmol Na and 240 g Hg) and hexane (200 mL) and vigorously stirred for two days. The yellow hexane solution was then decanted and the solvent evaporated. The remaining brown oil was distilled by means of a hot air gun to afford **3a** as a yellow oil (5.1 g, 66%). As pure diazaborole **3a** decomposes markedly at ambient temp. within one day, it is recommended to store the compound in the hexane solution over sodium amalgam and to use the freshly isolated material. IR (film): $\tilde{\nu}$ = 3030 cm^{-1} m, 2985 s, 2873 s, 1603 w, 1495 m, 1450 s, 1147 m, 962 m, 755 m, 700 s, 610 m. ^{1}H NMR ($CDCl_3$): δ = 1.51 (s, 9 H, *t*Bu), 1.66 (d, $^3J_{H,H}$ = 7.1 Hz, 3 H, C*H*$_3$), 5.19 (q, $^3J_{H,H}$ = 7.1 Hz, 1 H, C*H*CH$_3$), 6.19 (d, $^3J_{H,H}$ = 2.4 Hz, 1 H, *H*C=NCHMe), 6.41 (d, $^3J_{H,H}$ = 2.4 Hz, 1 H, *H*C=N*t*Bu), 7.26 (m, 3 H, Ph), 7.3 (m, 2 H,

Ph) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 21.4 (s, CH*C*H_3), 31.2 [s, C(*C*H_3)$_3$], 52.8 [s, *C*(CH$_3$)$_3$], 58.3 (s, *C*HCH$_3$), 111.9 (s, H*C*=NCHMe), 114.9 (s, H*C*=N*t*Bu), 126.5, 126.8, 128.3, 144.0 (4s, Ph) ppm. $^{11}B\{^1H\}$ NMR ($CDCl_3$): δ = 17.3 s ppm. MS/EI: *m*/*z* (%) = 308 (6) [M^+ with ^{81}Br], 306 (7). [M^+ with ^{79}Br]. $[\alpha]_D^{24}$ = −104. $C_{14}H_{20}BBrN_2$ (307.04): calcd. C 54.77, H 6.57, N 9.12; found C 55.40, H 6.89, N 8.62.

(*S*,*S*)-Me(Ph)HCN^a−CH=CH−N^b\|CH(Ph)Me\|BBr(*N*^{a}−*B*) (3b): A solution of (*S*,*S*)−Me(Ph)HC−N=CH−CH=N−CH(Ph)Me (**1b**) (7.04 g, 27.0 mmol) in 50 mL of hexane and a solution of BBr_3 (6.67 g, 27.0 mmol) in 50 mL of hexane were added slowly at 20 °C to 300 mL of hexane, whereupon a yellow precipitate separated. Stirring was continued for two days. The mixture was then filtered, the filter cake was washed with hexane (50 mL) and then dried in vacuo. Yield: 11.2 g (81.4%) [(*S*,*S*)−Me(Ph)HC−N^a=CH−CH=N^b−CH(Ph)MeBBr$_2$]Br(*N*^{a}−*B*) (**2b**).

A slurry of **2b** (8.0 g, 18.4 mmol) and sodium amalgam (from 230 g Hg and 2.4 g Na) in 200 mL of hexane was stirred vigorously for two days. The yellow organic phase was decanted and the solvents evaporated to dryness to afford 2.1 g (32%) of crude **3b**. The marked thermolability of this compound thwarted reliable elemental analyses. As in the case of **3a** it is recommended to store the reaction mixture and to isolate the required amount of compound prior to use. ^1H NMR (C_6D_6): δ = 1.38 (d, $^3J_{H,H}$ = 7.1 Hz, 6 H, CH$_3$), 5.13 (q, $^3J_{H,H}$ = 7.1 Hz, 2 H, C*H*CH$_3$), 6.13 (s, 2 H, CH=N), 7.01−7.17 (m, 10 H, Ph) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 21.5 (s, CH*C*H$_3$), 53.9 (s, *C*HCH$_3$), 114.6 (s, CH=N), 126.7, 127.1, 128.5, 144.3 (4s, Ph). $^{11}B\{^1H\}$ NMR (C_6D_6): δ = 19.0 (s) ppm.

(*S*,*S*)-Me(Cy)HC−N^{a}CH=CH−N^b\|CH(Cy)Me\|BBr(*N*^{a}−*B*) (3c): A solution of 1,4-diazabutadiene **1c** (8.0 g, 29.0 mmol) in 100 mL of hexane and a solution of BBr_3 (7.52 g, 30.0 mmol) in 100 mL of hexane were added simultaneously at 0 °C to 100 mL of hexane. The resulting slurry was allowed to stir for 1 h at 20 °C and was then filtered. The filter cake was washed with 100 mL of pentane and dried in vacuo. The borolium salt (*S*,*S*)-[Me(Cy)CH−N^a=CH−CH=N^b{CH(Cy)Me}BBr$_2$]Br(*N*^{a}−*Br*) (**2c**) was obtained as an orange solid (14.5 g, 93%). ^1H NMR (C_6D_6): δ = 0.69−2.00 (m, 22 H, C_6H_{11}), 1.41 (d, $^3J_{H,H}$ = 6.8 Hz, 6 H, CH$_3$), 3.76 (m, 2 H, C*H*CH$_3$), 9.12 (s, 2 H, HC=CH) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 18.4 (s, CH$_3$), 26.2, 26.3 (2s, 3,5-*C*−Cy), 29.0, 31.5 (2s, 2,6-*C*−Cy), 42.2 (s, 1-*C*−Cy), 60.9 (s, *C*HCH$_3$), 146.7 (s, HC=CH) ppm. $^{11}B\{^1H\}$ NMR (C_6D_6): δ = 0.6 (s, BBr_2), −23.8 (s, BBr_4^-) ppm.

Solid borolium salt **2c** (9.5 g, 18.0 mmol) was combined with sodium amalgam [from Na (1.3 g, 55.0 mmol) and 130 g of Hg]. After the addition of 200 mL of hexane the resulting slurry was stirred at room temp. for three days. The yellow hexane phase was decanted and concentrated to ca 10 mL, whereby crystalline colorless **3c** precipitated (4.0 g, 60.5%). The purity of the sample was satisfactory for most chemical transformations. Analytically pure **3c** was obtained by sublimation at 80 °C and 5 × 10^{-6} bar. ^1H NMR ($CDCl_3$): δ = 0.79−1.81 (m, 22 H, C_6H_{11}), 1.25 (d, $^3J_{H,H}$ = 6.8 Hz, 6 H, CH$_3$), 3.46 (m, 2 H, C*H*CH$_3$), 6.17 (s, 2 H, HC=CH) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 19.6 (s, CH$_3$), 26.15, 26.22 (2s, 3,5-*C*−Cy), 26.3 (s, 4-*C*−Cy), 29.9, 30.3 (2s, 2,6-*C*−Cy), 44.1 (s, 1-*C*−Cy), 55.6 (s, *C*HCH$_3$), 113.5 (s, HC=CH) ppm. $^{11}B\{^1H\}$ NMR: δ = 18.2 (s) ppm. MS/CI (toluene): *m*/*z* (%) = 367 (9) [MH^+]. $[\alpha]_D^{24}$ = −29. $C_{18}H_{32}BBrN_2$ (367.18): calcd. C 58.88, H 8.78, N 7.63; found C 58.44, H 9.17, N 7.48.

(*S*)-*t*BuN^{a}CH=CHN^b\|CH(Ph)Me\|B−NC(*N*^{a}−*B*) (4) and (*S*)-*t*BuN^{a}CH=CHN^b\|CH(Ph)Me\|BCN(*N*^{a}−*B*) (5): A solution of **3a** (0.65 g, 2.1 mmol) in 5 mL of acetonitrile was added to a slurry of silver cyanide (0.3 g, 2.2 mmol) in hexane (70 mL) and the mixture was stirred for 1 h. The supernatant yellow solution was decanted, and the residue was extracted with pentane (2 × 20 mL). The combined organic phases were evaporated to dryness to afford a mixture of isocyanide **4** and cyanide **5** as a yellow oil (0.41 g). This mixture was dissolved in hexane (30 mL) and stored at −30 °C for two weeks. The solvent was then removed and the solid brown residue was distilled by means of a hot air gun (200 °C, 5 × 10^{-3} bar) to give 0.3 g (57%) of the 2-cyano derivative **5** as a colorless solid. IR (KBr): $\tilde{\nu}$ = 2976 cm^{-1} (s), 2206 w [ν(C≡N)], 1455 s, 1414 m, 1372 w, 1336 w, 1259 w, 1228 m, 1156 m, 704 s, 647 m. ^1H NMR ($CDCl_3$): δ = 1.49 (s, 9 H, *t*Bu), 1.74 (d, $^3J_{H,H}$ = 7.1 Hz, 3 H, CH$_3$), 5.19 (q, $^3J_{H,H}$ = 7.1 Hz, 1 H, C*H*CH$_3$), 6.25 (d, $^3J_{H,H}$ = 2.3 Hz, 1 H, =C*H*−NCH), 6.40 (d, $^3J_{H,H}$ = 2.3 Hz, 1 H, =C*H*N*t*Bu), 7.27 (m, 3 H, Ph), 7.31 (m, 2 H, Ph) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 22.1 (s, CH*C*H$_3$), 31.6 [s, C(*C*H$_3$)$_3$], 53.6 [s, *C*(CH$_3$)$_3$], 55.1 (s, *C*HCH$_3$), 114.8 (s, =*C*NCH), 116.1 (s, =*C*N*t*Bu), 126.3 (s, C≡N), 126.4, 127.3, 128.5, 143.4 (4s, Ph) ppm. $^{11}B\{^1H\}$ NMR ($CDCl_3$): δ = 11.6 (s) ppm. MS/EI: *m*/*z* (%) = 253 (40) [M^+], 252 (10) [M^+ with ^{10}B]. $[\alpha]_D^{24}$ = −140. $C_{15}H_{20}BN_3$ (253.16): calcd. C 71.17, H 7.96, N 16.60; found C 71.16, H 7.93, N 16.41.

4: IR (KBr): $\tilde{\nu}$ = 2113 cm^{-1} w [ν(B−N≡C)]. ^1H NMR ($CDCl_3$): δ = 1.51 (s, 9 H, *t*Bu), 1.78 (d, $^3J_{H,H}$ = 7.0 Hz, 3 H, CH$_3$), 5.10 (q, $^3J_{H,H}$ = 7.0 Hz, 1 H, C*H*CH$_3$), 6.22 (d, $^3J_{H,H}$ = 2.3 Hz, 1 H, =C*H*NCH), 6.37 (d, $^3J_{H,H}$ = 2.3 Hz, 1 H, =C*H*N*t*Bu) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 22.5 (s, CH$_3$), 31.6 [s, C(*C*H$_3$)$_3$], 53.7 [s, *C*(CH$_3$)$_3$], 55.7 (s, *C*HCH$_3$], 114.7 (s, =*C*N*t*Bu), 116.0 (s, =*C*N−CH), 126.3, 127.2, 128.4, 143.3 (4s, Ph).

(*S*)-*t*BuN^{a}CH=CHN^b\|CH(Ph)Me\|BH(*N*^{a}−*B*) (6): At 0 °C a quantity of $LiAlH_4$ (0.05 g, 1.3 mmol) was added to a slurry of **3a** (0.4 g, 1.3 mmol) in a mixture of 20 mL of hexane and 5 mL of THF. After a few minutes of stirring the reaction mixture became clear. It was then filtered, and the filtrate was evaporated to dryness. The residue was triturated with pentane (6 mL), and filtered again. Removal of pentane afforded 0.28 g (95%) of crude **6** as a yellow oil. Distillation with a hot air gun at 150 °C and 2 × 10^{-5} bar afforded pure **6** as a colorless liquid (0.14 g, 47%). This product is temperature-sensitive at room temp.; decomposition to a brown oil was complete after 24 h (NMR control). IR (film): $\tilde{\nu}$ = 3086 m, 3063 m, 3027 m, 2973 s, 2868 s, 2621 s [ν(BH)], 1603 m, 1494 m, 1151 m, 920 m, 753 m, 664 s. ^1H NMR ($CDCl_3$): δ = 1.44 (s, 9 H, *t*Bu), 1.71 (d, $^3J_{H,H}$ = 7.0 Hz, 3 H, CH$_3$), 4.88 (q, $^3J_{H,H}$ = 7.0 Hz, 1 H, C*H*CH$_3$), 6.15 (d, $^3J_{H,H}$ = 2.0 Hz, 1 H, =C*H*NCH), 6.40 (d, $^3J_{H,H}$ = 2.0 Hz, 1 H, =C*H*N*t*Bu), 7.27 (m, 3 H, Ph), 7.30 (m, 2 H, Ph) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 24.0 (s, CH$_3$), 31.8 [s, C(*C*H$_3$)$_3$], 51.5 [s, *C*(CH$_3$)$_3$], 56.5 (s, *C*HCH$_3$), 114.4 (s, =*C*NCH), 116.2 (s, =*C*N*t*Bu), 126.1, 126.7, 128.3, 146.1 (4s, Ph) ppm. ^{11}B NMR ($CDCl_3$): δ = 19.4 (d, $^1J_{B,H}$ = 146 Hz) ppm. MS/EI: *m*/*z* (%) = 228 (7) [M^+], 213 (7) [$M^+ - CH_3$]. $[\alpha]_D^{24}$ = +94. $C_{14}H_{21}BN_2$ (228.15): calcd. C 73.70, H 9.28, N 12.28; found C 73.44, H 9.39, N 12.21.

(*S*)-*t*BuN^{a}CH=CHN^b\|CH(Ph)Me\|BCH$_3$(*N*^{a}−*B*) (7): A sample of **3a** (0.57 g, 1.8 mmol) was suspended in a mixture of hexane (40 mL) and THF (2.5 mL). An ethereal solution of methyllithium was then added (2 mL, 1.6 M), and the resulting mixture was stirred at 20 °C for two days. The volatile components were removed in vacuo, and the residue was extracted twice with 2.5 mL of hexane.

After filtration it was evaporated to dryness to give crude **7** (0.4 g, 92%) as a red oil. Purification was achieved by hot air distillation (200 °C, 1.5×10^{-5} bar) to yield 0.23 g (51%) of **7** as a colorless liquid. IR (film): $\tilde{\nu}$ = 3027 s, 2972 s, 1602 m, 1401 s, 1253 s, 1152 m, 1029 m, 758 m, 700 s, 665 m. ^{1}H NMR ($CDCl_3$): δ = 0.75 (s, 3 H, BCH_3), 1.56 (s, 9 H, *t*Bu), 1.80 (d, $^3J_{H,H}$ = 7.1 Hz, 3 H, $CHCH_3$), 5.12 (q, $^3J_{H,H}$ = 7.1 Hz, 1 H, $CHCH_3$), 6.32 (d, $^3J_{H,H}$ = 2.5 Hz, 1 H, =C*H*−NCH), 6.48 (d, $^3J_{H,H}$ = 2.5 Hz, 1 H, =C*H*N*t*Bu), 7.34 (m, 3 H, Ph), 7.41 (m, 2 H, Ph) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 22.2 ($CHCH_3$), 31.6 [s, $C(CH_3)_3$], 52.4 [s, $C(CH_3)_3$], 55.7 (s, $CHCH_3$), 111.1 (s, =*C*HNCH), 113.5 (s, =*C*HN*t*Bu), 126.2, 126.3, 128.4, 145.7, (4 s, Ph) ppm. ^{11}B{^{1}H} NMR ($CDCl_3$): δ = 26.2 (s) ppm. MS/EI: *m*/*z* (%) = 242 (75) [M^+], 241 (19) [M^+ with ^{10}B], 227 (54) [$M^+ - CH_3$]. $[\alpha]_D^{24}$ = −111. $C_{15}H_{23}BN$ (242.17): calcd. C 73.06, H 10.07, N 12.17; found C 73.28, H 9.85, N 12.19.

(*S*)-*t*BuN^{a}CH=CHN^b[CH(Ph)Me]BNH*t*Bu(*N^a*−*B*) (8): *tert*-Butylamine (1 mL, 0.66 g, 9.0 mmol) was added at room temp. to a well stirred slurry of **3a** (1.3 g, 4.2 mmol) in hexane (10 mL). A colorless precipitate was formed immediately. After filtration the filtrate was freed from solvent to yield 1.17 g of a brown oil, which was subsequently purified by distillation with a hot air gun (300 °C, 10^{-5} bar). Compound **8** was obtained as a yellow oil (yield 0.93 g, 74%). IR (film): $\tilde{\nu}$ = 3443 cm^{-1} w [ν(NH)], 3061 m, 3027 m, 2986 s, 2865 s, 1602 w, 1494 s, 1135 m, 1028 m, 817 m, 789 m, 753 m, 699 s, 647 m. ^{1}H NMR ($CDCl_3$): δ = 1.28 (s, 9 H, NH*t*Bu), 1.47 (s, 9 H, =CHN−*t*Bu), 1.69 (d, $^3J_{H,H}$ = 7.0 Hz, 3 H, CH_3), 5.22 (q, $^3J_{H,H}$ = 7.0 Hz, 1 H, $CHCH_3$), 5.93 (d, $^3J_{H,H}$ = 2.8 Hz, 1 H, =C*H*−NCH), 6.24 (d, $^3J_{H,H}$ = 2.8 Hz, 1 H, =C*H*−N*t*Bu), 7.21 (m, 1 H, Ph), 7.29 (m, 4 H, Ph) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 21.9 (s, CH_3), 31.6 [s, $NC(CH_3)_3$], 33.6 [s, $NHC(CH_3)_3$], 49.2 [s, $NHC(CH_3)_3$], 51.8 [s, =CH−N$C(CH_3)_3$], 52.2 (s, $CHCH_3$), 109.6 (s, =H*C*N−CH), 113.0 (s, =*C*HN*t*Bu), 126.1, 126.4, 128.3, 144.0 (4s, Ph) ppm. ^{11}B{^{1}H} NMR ($CDCl_3$): δ = 22.3 (s) ppm. $[\alpha]_D^{24}$ = −125. $C_{18}H_{30}BN_3$ (299.27): calcd. C 72.24, H 10.10, N 14.04; found C 71.91, H 10.20, N 13.87.

(*S*,*S*)−*t*BuN^a−CH=CHN^b−[CH(Ph)Me]BNH[CH(Ph)Me]-(*N^a*−*B*) (9): Triethylamine (0.12 g, 1.2 mmol) was added to a slurry of (*S*)-**3a** (0.38 g, 1.2 mmol) in hexane (15 mL) at ambient temp. followed by the addition of (*S*)-1-phenylethylamine (0.16 g, 1.3 mmol). The reaction mixture spontaneously turned cloudy with separation of a colorless precipitate. The mixture was stirred for 15 min and then filtered. The filtrate was evaporated to dryness to yield (*S*,*S*)-**9** as a red-brown oil (yield 0.38 g, 92%). Distillation of the product (hot air gun, 150 °C, 2×10^{-6} bar) gave 0.2 g (48%) of **9** as a colorless liquid. IR (film): $\tilde{\nu}$ = 3463 cm^{-1} w [ν(NH)], 3061 m, 3026 m, 2961 s, 2865 s, 1601 w, 1478 w, 1332 s, 1137 m, 1028 m, 908 w, 758 m, 700 s, 636 m. ^{1}H NMR ($CDCl_3$): δ = 1.24 (d, $^3J_{H,H}$ = 6.9 Hz, 3 H, BNHCC*H*$_3$), 1.33 (d, $^3J_{H,H}$ = 6.7 Hz, = HC−NCHC*H*$_3$), 1.46 (s, 9 H, *t*Bu), 2.27 (d, $^3J_{H,H}$ = 8.8 Hz, 1 H, *NH*), 4.37 [m, 1 H, N(H)C*H*CH_3], 4.72 (q, $^3J_{H,H}$ = 7.0 Hz, 1 H, CH=NC*H*CH_3), 5.86 (d, $^3J_{H,H}$ = 2.6 Hz, 1 H, =C*H*NCH), 6.13 (d, $^3J_{H,H}$ = 2.6 Hz, 1 H, =C*H*N*t*Bu), 7.20 (m, 4 H, Ph), 7.34 (m, 6 H, Ph) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 22.1 (s, CNCH*C*H_3), 28.2 (s, HNCH*C*H_3), 31.1 [s, $C(CH_3)_3$], 51.5 [s, $C(CH_3)_3$], 51.9 (s, $CHCH_3$), 52.0 (s, $CHCH_3$), 109.2 (s, =*C*HNCH), 111.9 (s, =*C*HN*t*Bu), 125.3, 125.9, 126.1, 126.15, 128.1, 128.2, 146.5, 148.8 (8s, Ph) ppm. ^{11}B{^{1}H} NMR ($CDCl_3$): δ = 21.6 (s) ppm. MS/EI: *m*/*z* (%) = 347 (37) [M^+], 346 (9) [M^+ with ^{10}B]. $[\alpha]_D^{24}$ = −99. $C_{22}H_{30}BN_3$ (347.31): calcd. C 76.08, H 8.71, N 12.10; found C 76.10, H 8.77, N 11.86.

(*S*)-Me(Ph)CH−N^a−CH=CH−N^b[CH(Ph)Me]BSnMe$_3$(*N^a*−*B*) (10): Trimethyltin chloride (1.68 g, 8.45 mmol) was added to a slurry of lithium sand (0.13 g, 18.6 mmol) in THF (80 mL) and stirred at 20 °C until a green solution was formed (ca. 2 h). A solution of **3b** (1.31 g, 5.6 mmol) in hexane (30 mL) was then added dropwise to this mixture and stirring was continued for another 2 h. The volatile components were removed in vacuo and the residue was extracted with pentane (3 × 10 mL). The filtrate was evaporated to dryness. Recrystallization of the residue from toluene gave 1.66 g (67%) of **10** as colorless crystals. ^{1}H NMR (C_6D_6): δ = 0.22 (t, $^2J_{Sn,H}$ = 47.3 Hz, 9 H, $SnMe_3$), 1.51 (d, $^3J_{H,H}$ = 7.1 Hz, 6 H, $CHCH_3$), 5.15 (q, $^3J_{H,H}$ = 7.1 Hz, 2 H, $CHCH_3$), 6.38 (s, 2 H, HC=CH), 7.01 (t, $^3J_{H,H}$ = 7.3 Hz, 2 H, *p*-H−Ph), 7.09 (m, 4 H, Ph), 7.16 (m, 4 H, Ph) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ = −9.4 [t, $^1J_{Sn,C}$ = 298.9 Hz, $Sn(CH_3)_3$], 23.0 (s, $CHCH_3$), 55.9 (s, $CHCH_3$), 116.4 (s, HC=CH), 126.5, 126.7, 128.6, 145.5 (4s, Ph) ppm. ^{11}B{^{1}H} NMR (C_6D_6): δ = 28.2 (t, $^1J_{Sn,B}$ = 994 Hz). ^{119}Sn{^{1}H} NMR (C_6D_6): δ = −150.0 (q, $^1J_{Sn,B}$ = 994 Hz) ppm. MS/EI: *m*/*z* (%) = 440 (2) [M^+]. $[\alpha]_D^{24}$ = −119. $C_{21}H_{29}BN_2Sn$ (439.00): calcd. C 56.62, H 6.58, N 6.28; found C 57.46, H 6.66, N 6.38.

(*S*,*S*)-Me(Ph)CH−N^a−CH=CH−N^b[CH(Ph)Me]B(NH*t*Bu)-(*N^a*−*B*) (11): A slurry of **3b** (1.80 g, 5.0 mmol) in hexane (50 mL) was treated with *tert*-butylamine (0.74 g, 1.1 mL, 10 mmol) and stirred for 5 min at room temperature. The mixture was then filtered. The filtrate was evaporated to dryness to give a red oil (1.75 g), which was distilled at 200 °C (hot air gun) and 2×10^{-6} bar to afford **11** as a pale yellow liquid (0.86 g, 50%). IR (film): $\tilde{\nu}$ = 3414 cm^{-1} w [ν(NH)], 3060 m, 3026 m, 2969 s, 2871 m, 1946 w, 1602 m, 1493 s, 1243 m, 1167 m, 1027 m, 757 m, 699 s. ^{1}H NMR ($CDCl_3$): δ = 1.15 (s, 9 H, *t*Bu), 1.70 (d, $^3J_{H,H}$ = 7.0 Hz, 6 H, CH_3), 5.04 (q, $^3J_{H,H}$ = 7.0 Hz, 2 H, $CHCH_3$), 6.12 (s, 2 H, CH=CH), 7.30 (m, 4 H, Ph), 7.34 (m, 6 H, Ph) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 22.4 (s, CH_3), 33.2 [s, $C(CH_3)_3$], 49.1 [s, $C(CH_3)_3$], 111.9 (s, H*C*=*C*H), 126.1, 126.4, 128.2, 145.7, (4s, Ph) ppm. ^{11}B{^{1}H} NMR ($CDCl_3$): δ = 22.5 (s) ppm. $[\alpha]_D^{24}$ = −165. $C_{22}H_{30}BN_3$ (347.31): calcd. C 76.08, H 8.71, N 12.10; found C 75.90, H 8.93, N 11.66.

(*S*,*S*)-Me(Cy)CHN^a−CH=CH−N^b[CH(Cy)Me]BN(H)*t*Bu (12): A solution of **3c** (0.70 g, 1.9 mmol) in hexane (25 mL) was treated at 20 °C with *tert*-butylamine (0.29 g, 4.0 mmol). After stirring for 10 min this mixture was filtered, and the filtrate was evaporated to dryness. The residual yellow oil was distilled by means of a hot air gun (300 °C, 4×10^{-6} bar) to afford 0.40 g (58%) of **12** as a colorless oil. IR (film): $\tilde{\nu}$ = 3419 cm^{-1} w [ν(NH)], 2923 s, 2843 s, 2658 w, 1446 s, 1229 s, 890 s, 657 s. ^{1}H NMR ($CDCl_3$): δ = 0.87−1.80 (m, 22 H, C_6H_{11}), 1.20 (d, $^3J_{H,H}$ = 6.8 Hz, 6 H, $CHCH_3$), 1.21 (s, 9 H, *t*Bu), 3.25 (m, 2 H, $CHCH_3$), 5.95 (s, 2 H, HC=CH) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 22.7 (s, $CHCH_3$), 26.4 (s, 3,5-*C*−Cy), 26.5 (s, 4-*C*−Cy), 30.4, 30.8 (2s, 2,6-*C*−Cy), 31.6 [s, $C(CH_3)_3$], 33.6 [s, $C(CH_3)_3$], 44.5 (s, 1-*C*−Cy), 54.4 (s, $CHCH_3$), 110.6 (s, HC=CH) ppm. ^{11}B{^{1}H} NMR ($CDCl_3$): δ = 22.1 (s) ppm. MS/CI (NH_3): *m*/*z* (%) = 360 (87) [MH^+], 359 (100) [MH^+ with ^{10}B and M^+ with ^{11}B], 358 (22) [M^+, ^{10}B]. $[\alpha]_D^{24}$ = −55. $C_{22}H_{42}BN_3$ (359.41): calcd. C 73.52, H 11.78, N 11.69; found C 73.23, H 12.06, N 11.40.

(*S*,*S*)−Me(Cy)CHN^a−CH=CH−N^b[CH(Cy)Me]B−*n*C$_4$H$_9$(*N^a*-*B*) (13): A hexane solution of *n*-butyllithium (12%, 2.0 g, 3.8 mmol) was added dropwise at −15 °C to a solution of **3c** (0.76 g, 2.1 mmol) in a mixture of 50 mL of hexane and 10 mL of THF. After stirring for one day at 20 °C the solvent and volatile components were removed in vacuo. The residue was extracted with 30 mL of pentane. Removal of solvent gave a yellow oil (0.75 g) which was

distilled at 250 °C and 5×10^{-6} bar to give 0.32 g (47%) of **13** as a colorless oil. ^{1}H NMR (C_6D_6): δ = 0.80−1.70 (m, 31 H, C_6H_{11} and C_4H_9), 1.24 (d, $^3J_{H,H}$ = 6.8 Hz, 6 H, CHCH_3), 3.37 (m, 2 H, CHCH$_3$), 6.19 (s, 2 H, HC=CH) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ = 14.4 (s, CH_2CH_3), 20.9 (s, CHCH$_3$), 26.5 (s, CH_2CH_3), 26.7 (s, 3,5-C−Cy), 26.8 (s, 4-C−Cy), 30.3 (s, $CH_2CH_2CH_3$), 30.7, 30.9 (2s, 2,6-C−Cy), 44.5 (s, 1-C−Cy), 55.6 (s, CHCH$_3$), 112.4 (s, HC=CH) ppm. ^{11}B{^{1}H} NMR (C_6D_6): δ = 26.4 (s) ppm. MS/EI: *m*/*z* (%) = 344 (50) [M$^+$, ^{11}B], 343 (14) [M$^+$, ^{10}B], 262 (20) [M$^+$ − C_6H_{10}], 261 (100) [M$^+$ − C_6H_{11}]. $[\alpha]_D^{24}$ = −18. $C_{22}H_{41}BN_2$ (344.39): calcd. C 76.73, H 12.00, N 8.13; found C 76.47, H 12.12, N 7.88.

(*S*,*S*)-Me(Cy)CHN^a−CH=CH−N^b\|CH(Cy)Me\|BSnMe$_3$(*N*^{a}−*B*) (14): Lithium sand (0.14 g, 20 mmol) was added to a solution of trimethyltin chloride (0.77 g, 3.9 mmol) in 40 mL of THF and the slurry was stirred at ambient temp. with sonification. The resulting mixture was combined with a solution of (*S*,*S*)-**3c** (1.45 g, 3.95 mmol) in hexane (20 mL). Stirring was continued for 1 h. The mixture was then evaporated to dryness, and 30 mL of hexane was added to the residue. It was filtered, and the filtrate was freed from solvent to give crude (*S*,*S*)-**14** as a cloudy yellow oil (1.7 g). Distillation (250 °C, 1×10^{-5} bar) gave 1.02 g (58%) of pure (*S*,*S*)-**14** as colorless liquid. IR (film): $\tilde{\nu}$ = 2979 cm^{-1} m, 2924 s, 2853 s, 2651 w, 2348 w, 1643 s, 1449 s, 1398 s, 1225 m [δ(SnMe$_3$)], 891 w, 764 s, [(SnMe$_3$)], 513 s. ^{1}H NMR (C_6D_6): δ = 0.4 (s, $^2J_{Sn,H}$ = 45.2 Hz, 9 H, SnMe$_3$), 0.78−1.74 (m, 22 H, C_6H_{11}), 1.22 (d, $^3J_{H,H}$ = 6.3 Hz, 6 H, CHCH_3), 3.49 (m, 2 H, CHCH$_3$), 6.37 (s, $^4J_{Sn,H}$ = 12.6 Hz, 2 H, CH=CH) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ = −9.7 (s, $^1J_{Sn,C}$ = 269 Hz, $SnCH_3$), 20.9 (s, CHCH$_3$), 26.6 (s, 4-C−Cy), 26.6, 26.7 (2s, 3,5-C−Cy), 30.68/31.72 (2s, 2,6-C−Cy), 44.7 (s, 1-C−Cy), 58.4 (s, CHCH$_3$), 115.4 (s, $^3J_{Sn,C}$ = 37.9 Hz, HC=CH) ppm. ^{11}B{^{1}H} NMR (C_6D_6): δ = 30.8 (s, $^1J_{Sn,B}$ = 986 Hz) ppm. ^{119}Sn{^{1}H} NMR (C_6D_6): δ = −149.1 (q, $^1J_{Sn,B}$ = 986 Hz) ppm. MS/CI (NH_3): *m*/*z* = 453 (100) [M$^+$ + H]. $[\alpha]_D^{24}$ = −44. $C_{21}H_{41}BN_2Sn$ (451.08): calcd. C 55.92, H 9.16, N 6.21; found C 56.11, H 9.05, N 6.21.

(*S*)-*t*BuN^a−CH=CH−N^b(*t*Bu)B−N(H)CH(Ph)Me(*N*^{a}−*B*) (15): Equimolar amounts of 1,3,2-diazaborole *t*BuN^{a}CH=CHN^b(*t*Bu)BBr(*N*^{a}−*B*) (2.33 g, 9.0 mmol) and triethylamine (1.25 mL, 9.0 mmol) were dissolved in hexane (70 mL). At room temperature (*S*)-1-phenylethylamine (1.1 g, 9.0 mmol) was then added. After 15 min of stirring the mixture was filtered, and the filtrate was freed from solvent and volatile components to afford a cloudy oil (2.27 g). Pure compound **14** (2.02 g, 74%) was obtained as a pale yellow oil by distillation (200 °C, hot air gun, 10^{-5} bar). IR (film): $\tilde{\nu}$ = 3443 cm^{-1} w [ν(NH)], 2971 s, 2930 m, 2862 m, 1601 s, 1395 s, 1365 s, 1233 s, 1133 m, 1021 w, 821 w, 699 m, 631 m. ^{1}H NMR (C_6D_6): δ = 1.31 (s, 18 H, *t*Bu), 1.47 (d, $^3J_{H,H}$ = 6.7 Hz, 3 H, CHCH_3), 1.90 (d, $^3J_{H,H}$ = 11.3 Hz, 1 H, NH), 4.64 (m, 1 H, CHCH$_3$), 6.19 (s, 2 H, CH=CH), 7.01 (m, 1 H, *p*-*H*−Ph), 7.18 (m, 2 H, *m*-*H*−Ph), 7.36 (d, $^3J_{H,H}$ = 7.2 Hz, 2 H, *o*-*H*−Ph) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ = 26.4 (s, CHCH$_3$), 31.8 [s, C(CH$_3$)$_3$], 51.9 [s, C(CH$_3$)$_3$], 54.6 (s, CHCH$_3$), 111.3 (s, HC=CH), 126.3, 128.6, 148.3 (3s, Ph) ppm. ^{11}B{^{1}H} NMR (C_6D_6): δ = 22.3 (s) ppm. MS/CI (NH_3): *m*/*z* (%) = 300 (100) [MH$^+$], 299 (45) [M$^+$]. $[\alpha]_D^{24}$ = −29. $C_{18}H_{30}BN_3$ (299.27): calcd. C 72.24, H 10.10, N 10.04; found C 71.88, H 10.18, N 13.85.

(*S*)-*t*BuN^a−CH=CH−N^b(*t*Bu)BN(H)CH(Cy)Me(*N*^{a}−*B*) (16): Analogously 1.1 g of crude **16** were prepared from *t*BuN^{a}CH=CHN^b(*t*Bu)BBr(*N*^{a}−*B*) (0.93 g, 3.6 mmol), triethylamine (0.37 g, 5.0 mmol) and (*S*)-1-cyclohexylethylamine (0.46 g, 3.6 mmol). Purification to afford a colorless oil (0.23 g, 72%) was achieved by vacuum distillation (150 °C, hot air gun, 2×10^{-6} bar). IR (film): $\tilde{\nu}$ = 3450 cm^{-1} w [ν(NH)], 2925 s, 2853 m, 1396 s, 1365 s, 1233 s, 1133 m, 821 w, 625 m. ^{1}H NMR ($CDCl_3$): δ = 0.85−1.84 (m, 11 H, C_6H_{11}), 1.04 (d, $^3J_{H,H}$ = 6.6 Hz, 3 H, CHCH_3), 1.40 (s, 18 H, *t*Bu), 3.29 (m, 1 H, CHCH$_3$), 6.06 (s, 2 H, HC=CH) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 21.5 (s, CHCH$_3$), 26.6, 26.7 (2s, 3,5-C−Cy), 28.6 (s, 4-C−Cy), 30.1 (s, 2,6-C−Cy), 31.4 [s, C(CH$_3$)], 46.5 (s, 1-C−Cy), 51.7 [s, C(CH$_3$)$_3$], 110.0 (s, CH=CH) ppm. ^{11}B{^{1}H} NMR ($CDCl_3$): δ = 22.0 (s) ppm. MS/EI: *m*/*z* (%) = 305 (62) [M$^+$]. $[\alpha]_D^{24}$ = −6. $C_{18}H_{36}BN_3$ (305.32): calcd. C 70.81, H 11.89, N 13.76; found C 70.75, H 12.04, N 13.73.

X-ray Structural Analysis of (*S*,*S*)-3c: Colorless single crystals were grown from *n*-hexane; 0.27 × 0.24 × 0.15 mm, T = 100 K; Nonius Kappa CCD Mo-K_α (graphite monochromator, λ = 0.71073 Å) empirical formula $C_{18}H_{30}BBrN_2$, tetragonal space group $P4_12_12$; unit cell dimensions: $a = b$ = 10.8870(1), c = 16.0510(1) Å; V = 1902.47(3) Å^3, $d_{calcd.}$ = 1.275 g·cm^{-3}, Z = 4; μ = 2.16 mm^{-1}; range for data collection: 2.9 < θ < 30.0°; index ranges −15 < h < 15, −10 < k < 10, −22 < l < 22; reflection collected 56253; unique reflections 2761 (R_{int} = 0.049); parameters 102; absorption correction multi-scan, min/max transmission 0.738/0.593: Program used: SHELXL-97; structure refinement: full-matrix least-squares on F^2, wR_{F^2} = 0.064 (all data) R_F = 0.024, wR_F = 0.063 based on 2651 unique reflections with $I > 2\sigma(I)$, GOOF (F^2) = 1.057, maximum residual electron density 0.561 e Å^{-3}; hydrogen atoms treated as riding group.

CCDC-180671 [(*S*,*S*)-**3c**] contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Center, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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