FIRST SYNTHESIS AND CRYSTAL STRUCTURES OF CHIRAL 1,3-DIENYLBORATES

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Abstract — We report on the synthesis of bicyclic 1,3-dienylborates (**1a/1b** and **2a/2b**), wherein the boron and nitrogen atoms are chiral. The absolute configuration of these molecules was established by single X-Ray diffraction studies and qualitative homonuclear NOE difference spectroscopy. The conformational stability of these molecules is low at ambient or subambient temperature. The diastereomeric borates (**2a/2b**) were found to be very reactive toward dienophiles in the Diels-Alder reaction.

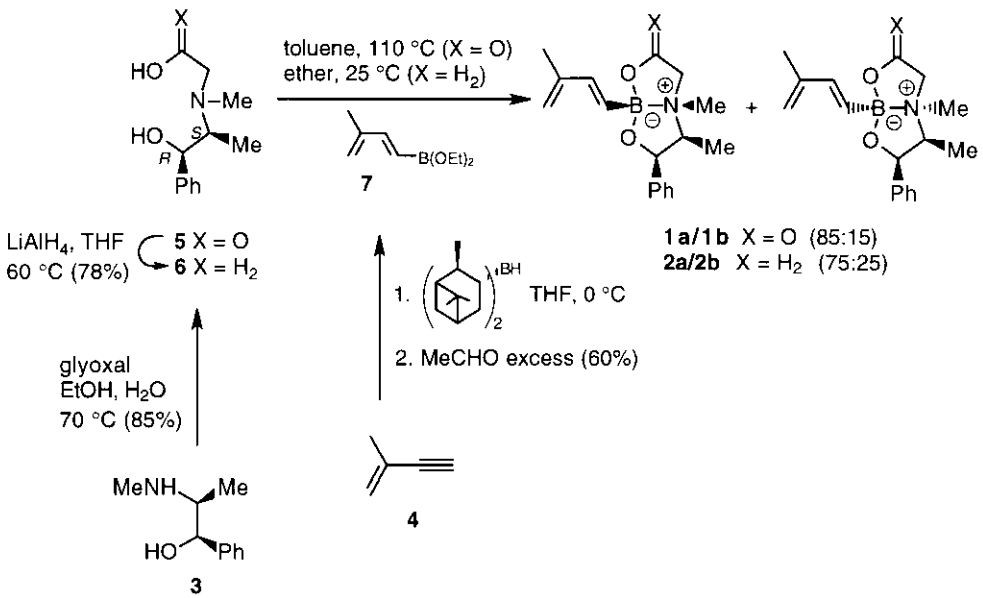
In this paper details are presented of the preparation, separation, and structural assignments of the first 1,3-dienylborates containing chiral boron and nitrogen atoms. Preliminary studies show that these chiral molecules undergo Diel-Alder cycloaddition as donor-activated 1,3-dienes with electron-poor dienophiles. Treatment of (–)-ephedrine (**3**) with glyoxal in ethanol-water at –70 °C[1] led to the formation of chiral *N*-[1(*S*)-methyl-2(*R*)-phenyl-2-hydroxyethyl]sarcosine (**5**) in 85% yield (Scheme 1). The carboxylic acid function was reduced with lithium aluminum hydride in THF at 60 °C[2] to give *N*-[1(*S*)-methyl-2(*R*)-phenyl-2-hydroxyethyl]-*N*-(2-hydroxyethyl)methylamine (**6**) in good yield. 3-Methylbuta-1(*E*),3-dienyldiethoxyboronate (**7**) may be prepared by hydroboration of 3-methyl-3-buten-1-yne (**4**)[3] with (+)-diisopinocampheylborane in THF at 0 °C.[4] The hydroborated product was not isolated but directly treated with an excess of acetaldehyde (10 equiv.) affording **7** which was purified by distillation (60%). The reaction of the diene (**7**) with **5** in refluxing toluene led to a couple of diastereomers (**1a** and **1b**) possessing a *cis*-ring fusion in a 85:15 *ratio*.[5] The diastereomers with a *trans*-ring fusion were not formed probably because of severe ring strain.[5d,6] Crude **1a/1b** was dissolved in dichloromethane-heptane at room temperature, and the solution was allowed to slowly evaporate. Filtration of the suspension gave pure **1a** (30%). By chromatography on neutral silica of the crude reaction mixture, **1a** mainly decomposed and only about 2% of the pure material could be obtained. The minor isomer (**1b**) was more stable and could be isolated in 9% yield.

When each pure diastereomer was solubilized in $CDCl_3$ or C_6D_6 and stirred for 1 h at ambient temperature, the original 85:15 solution equilibrium *ratio* of **1a/1b** was restored. The most likely mechanism involves reversible B···N bond dissociation.[7] Heated at 70 °C in the same solvents, a total

decomposition of **1a/1b** occured. Clearly the substituents are not sufficiently electronegative to stabilize the ate complex.

The 1,3-dienylboronate (**7**) was heated with the chiral diethanolamine (**6**) in refluxing toluene. This gave a crude product that was found to be a 75:25 mixture of diastereomers (**2a**) and (**2b**) according to NMR analysis. However, important degradation of the products was also observed. In ether at ambient temperature[8] the reaction was cleaner and provided **2a** and **2b** which could be purified, but not separated, by recrystallization in toluene-acetone (**2a/2b** 75:25, 64%). These two epimers decomposed during chromatography on acidic, neutral or basic silica.

Scheme 1



^{1}H-, ^{13}C-, ^{11}B-NMR and X-Ray Structures of the Chiral 1,3-Dienylborates (1a/1b and 2a/2b)

^{1}H-, ^{13}C-, ^{11}B-NMR spectra permit the complete structural assignment of the two couples of diastereomers (**1a/1b**) and (**2a/2b**). The ^{11}B-NMR spectra ($CDCl_3$) of **1a** and **1b** at room temperature with BF_3-ether as external standard showed single signals at δ = 11.2 and 11.7 ppm, respectively, which are characteristic of compounds with tetracoordinated boron.[9]

Crude **1a/1b** was dissolved in toluene at ambient temperature, and the solution was allowed to slowly evaporate providing suitable crystals for X-Ray diffraction studies.[10] The structure determination establishes that the two diastereomers are incorporated in the same unit cell (Figure 1). The N → B bond length of 1.67 Å is comparable to the N → B bond length in analogous compounds.[6c,11] The proton H^{α} was not modified when the *N*-methyl signal of **1a** at 2.56 ppm was irradiated (Figure 2). However, an enhancement of 7% could be measured at the signal of the neighboring proton H^{1} of the diene. These observations are consistant with a *trans* relationship between H^{α} and the *N*-methyl group. A NOE of 2% was also measured at the phenyl group. Accordingly, the first molecular structure displayed in Figure 3 is compatible with the structure of the major isomer (**1a**), whereas the second diagram may be

ascribed to **1b**.

Single crystals of the major isomer (**2a**) could be obtained by fractional crystallization of the crude reaction mixture from toluene-acetone (1:1). The X-Ray diffraction analysis established that the ring fusion of the bicyclic borate is *cis* and that the B-diene and C-Ph groups have the same orientation (Figure 4).[10] This stereochemistry was expected for the major product on the basis of steric considerations. The stereochemistry of the minor isomer was deduced. This compound also possesses a *cis*-ring fusion but the B-diene and C-Ph groups are oriented in the opposite way. When the pure isomer (**2a**) was solubilized in $CDCl_3$, appearance of the minor isomer (**2b**) was observed until the thermodynamic *ratio* of epimers (**2a/2b** 75:25) was attained in the reaction mixture.

Figure 1. Unit cell containing the two co-crystallized diastereomers (1a) and (1b)

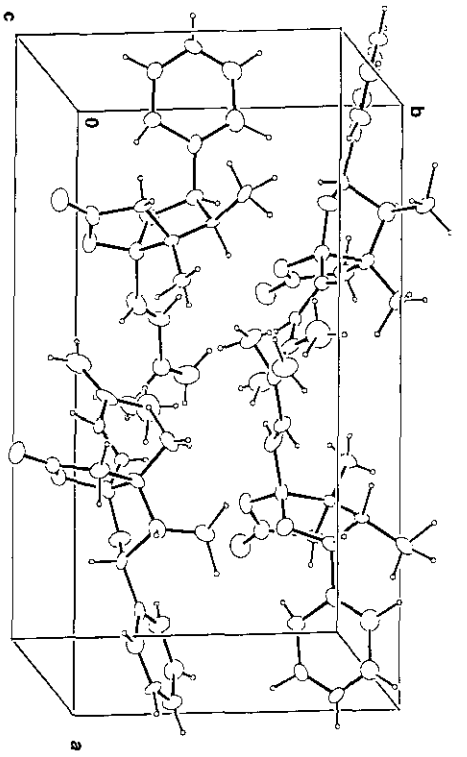
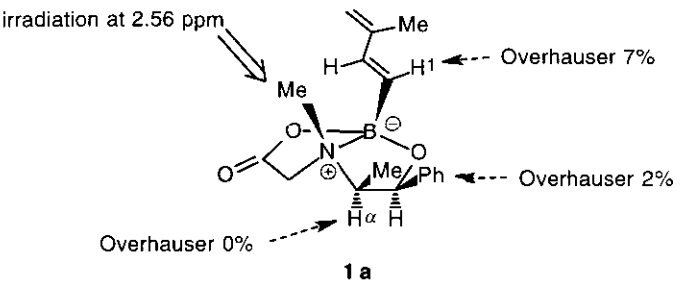
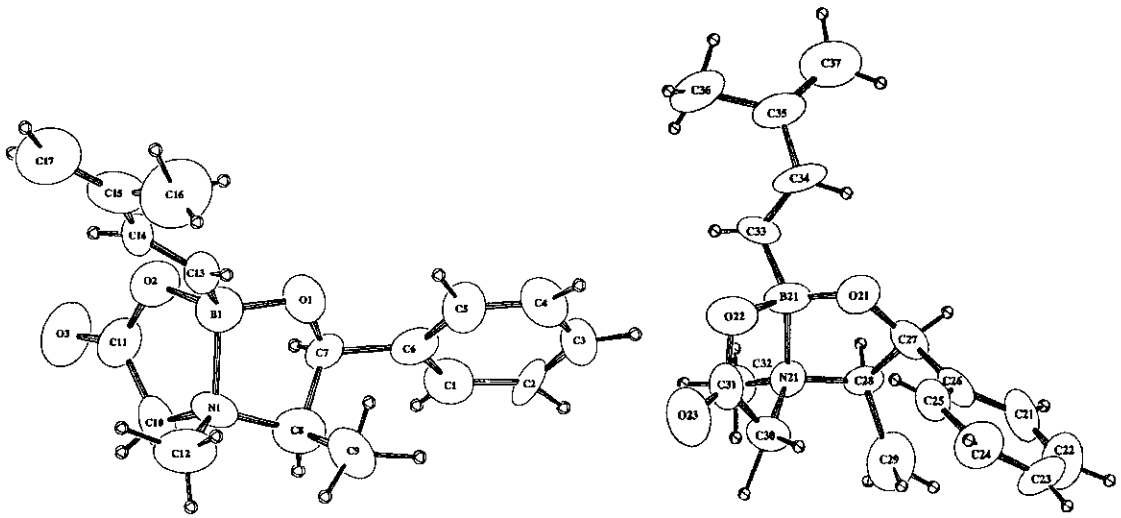


Figure 2



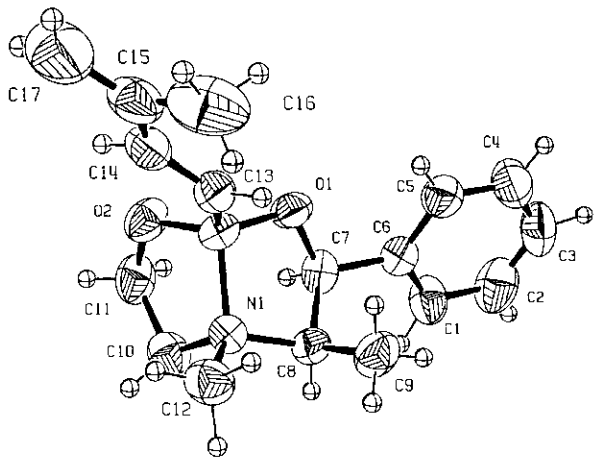
1a

Figure 3. Molecular structure of 1a and 1b



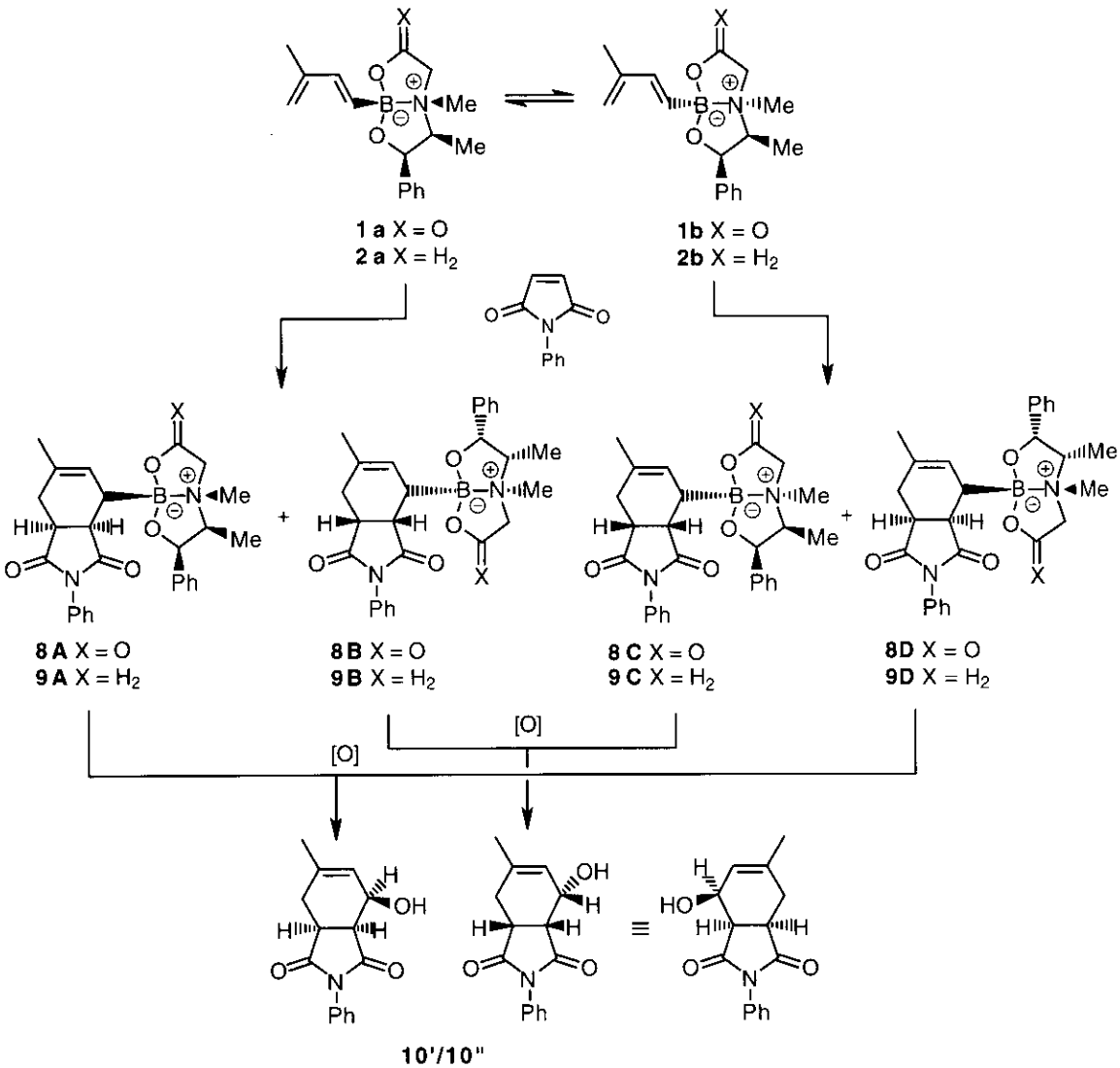
1a **1b**

Figure 4. Molecular structure of 2a



We present now our preliminary results of Diels-Alder reactions on chiral 1,3-dienylborates (**1a/1b**) and (**2a/2b**). Each couple of diastereomers is expected to give four diastereomeric cycloadducts (**8A-D**) and (**9A-D**) derived from an *endo* transition state (Scheme 2).[12] After oxidation of the carbon-boron bond, chiral alcohols (**10'**) and (**10"**) are potentially at hand. Although it has been shown that the conformational stability of the chiral couple of dienes (**1a/1b**) and (**2a/2b**) is low, if the cycloaddition rate runs faster for one of the dienes, a kinetic dynamic resolution could occured and one chiral Diels-Alder adduct could be preferentially formed, provided that interconversion of diastereomers occurs on the time scale for cycloaddition.

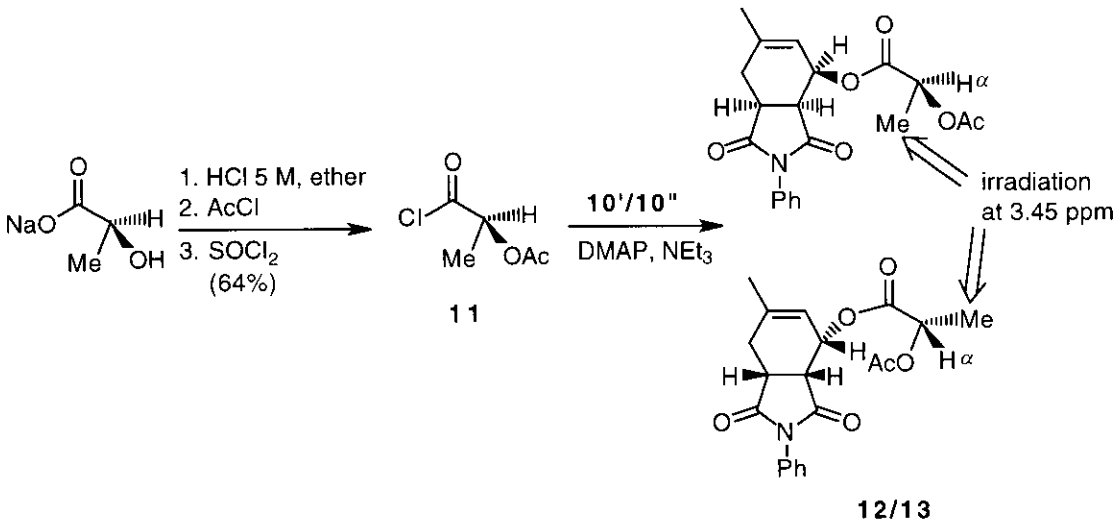
Scheme 2



When the pure diene (**1a**) was reacted with *N*-phenylmaleimide in $CDCl_3$ at ambient temperature for 12 h or at 70 °C for 1 h, ^{1}H-NMR analysis of the crude reaction mixture showed that the original 85:15 solution equilibrium *ratio* of **1a/1b** was restored. After 12 h at 70 °C, a complete degradation of the diene was observed. The Diels-Alder reaction of the mixture of dienes (**2a/2b**) (75:25 *ratio*) proceeded in refluxing toluene for 12 h as followed by the disappearance of the vinylic peaks of the diene and the dienophile. Oxidation of the reaction mixture with hydrogen peroxide in 3M sodium acetate afforded the alcohol (**10'/10"**) in 63% yield.[13] The coupling constant J_{H^2,H^3} = 3.7 Hz of **10'/10"** is in agreement with a *cis* relationship between the H^2 and H^3 protons. Since the oxidation of boranes into alcohols always takes place with retention of configuration at the carbon atom,[14] it may be assumed that the Diels-Alder cycloadducts result from an *endo* approach of the diene and the dienophile. The specific rotation of the alcohol (**10'/10"**) was measured ($[\alpha]_{589}^{25}$ (c = 6.78, chloroform) –7.4 °) and the enantiomeric excess was

determined by the NMR method of Singer *et al.* (Scheme 3).[15] The acid chloride (**11**) derived from (*S*)-lactic acid was treated with the crude alcohol (**10'/10"**) affording the diastereomeric esters (**12/13**). The selective irriadiation of the proton signal at 3.45 ppm transformed the two quartets at 5.00 ppm attributed to H^{α} into two singlets which could be easily integrated. The alcohol (**10'/10"**) was obtained with 12% ee.

Scheme 3



In this work we have described for the first time a method for the preparation of chiral 1,3-dienylborates by reaction of a chiral *N*-substituted amino acid or diethanolamine with a 1,3-dienylboronate. The conformational stability of the dienes is low and the equilibration of the diastereomers is observed at ambient or subambiente temperature. The replacement of the methyl group at the nitrogen atom by a hydrogen should increase the conformational stability of these molecules.[6d] The deprotonation of the corresponding borates should allow the convertion of the dative N → B bond into a covalente bond. We are proceeding with complete study of the stereoselectivity and asymmetric induction in these reactions.

EXPERIMENTAL

General. Elemental analyses were performed by CNRS in Gif-sur-Yvette. Melting points were taken on a Büchi 510 apparatus and are uncorrected. NMR spectra were recorded in $CDCl_3$ on a 200- or 300-MHz spectrometer operating in the Fourrier transform mode. Chemical shifts were recorded relative to the internal TMS (tetramethylsilane) reference signal. ^{13}C-NMR spectra were obtained with broadband proton decoupling. MS were obtained with a Varian MAT 311 mass spectrometer. Chromatography solvents were ACS grade and were used as commercially supplied.

(N → B)-3-Methylbuta-1(*E*),3-dienyl[*N*-methyl-*N*-(1(*S*)-methyl-2(*R*)-phenyl-2-oxyethyl)amino-acetate-*O,O',N*]boron (1a/1b). A solution of the sarcosine derivative (**5**)[1] (1.42 g, 6,4 mmol) in benzene (25 mL) was introduced in a round-bottom flask equipped with a Dean-Stark trap. 3-Methylbuta-1(*E*),3-

dienyldiethoxyboronate (**7**) (1 g, 6.4 mmol) in benzene (5 mL) was added and the mixture was refluxed for 8 h. Concentration *in vacuo* gave the crude 1,3-dienylborates (**1a/1b**) (85:15). Crude **1a/1b** was dissolved in dichloromethane-heptane at rt, and the solution was allowed to slowly evaporate. Filtration of the suspension gave pure **1a** as a solid which was stored under argon at 0 °C (0.57 g, 30%). ^{1}H-NMR (300 MHz) δ ppm: 7.39-7.26 (m, 5 H), 6.88 (d, 1H, J = 17.9 Hz), 5.69 (d, 1H, J = 17.9 Hz), 5.39 (d, 1H, J = 5.7 Hz), 5.07 (br s, 2H), 3.89 (d, 1H, J = 16.8 Hz), 3.59 (d, 1H, J = 16.8 Hz), 3.59 (m, 1H), 2.56 (s, 3H), 1.91 (s, 3H), 0.96 (d, 3H, J = 7 Hz). ^{13}C-NMR (75.5 MHz) δ ppm: 169.4, 145.0, 143.3, 138.7, 128.4, 127.8, 126.2, 117.1, 76.9, 69.3, 62.2, 42.1, 18.4, 11.3. ^{11}B-NMR (96.3 MHz) δ ppm: 11.2. HRMS calcd for $C_{17}H_{22}NO_3{}^{11}B$: 299.1693. Found: 299.167. MS (*m/z*, relative intensity %): 299 (49), 298 (12), 233 (2), 232 (14), 204 (7), 193 (12), 178 (10), 142 (100), 141 (20), 113 (31), 105 (43). The minor isomer (**1b**) was purified by chromatography (dichloromethane-ethyl acetate 95:5 → 80:20) (180 mg, 9%). The yellow (non-crystalline) powder was stored under nitrogen at 0 °C. ^{1}H-NMR (300 MHz) δ ppm: 7.37-7.26 (m, 5H), 6.87 (d, 1H, J = 17.8 Hz), 5.71 (d, 1H, J =17.8 Hz), 5.49 (d, 1H, J = 7.5 Hz), 5.04 (s, 2H), 3.65 (m, 1H, J = 7 Hz, J = 7.5 Hz), 3.52 (d, 1H, J = 16.6 Hz), 2.98 (d, 1H, J = 16.6 Hz), 2.66 (s, 3H), 1.89 (s, 3H), 1.14 (d, 3H, J = 7.0 Hz). ^{13}C-NMR (50.3 MHz) δ ppm: 169.9, 145.3, 143.3, 138.6, 128.6, 127 9, 126.1, 116.9, 78.6, 65.9, 55.4, 46.0, 18.4, 10.9. ^{11}B-NMR (96.3 MHz) δ ppm: 11.7.

(N → B)-3-Methylbuta-1(*E*),3-dienyl[*N*-methyl-*N*-(1(*S*)-methyl-2(*R*)-phenyl-2-oxyethyl)-*N*-(2-oxyethyl)-*O*,*O*',*N*]boron (2a/2b). To a solution of 3-methylbuta-1(*E*),3-dienyldiethoxyboronate (**7**) (0.72 g, 4.6 mmol) in dry ether (10 mL) was added the aminodiol (**6**) (1.03 g, 4.9 mmol) in dry ether (10 mL). The mixture was stirred for 1 h at ambient temperature. The reaction mixture was filtered and the filtrate was concentrated *in vacuo*. The diastereomers (**2a/2b**) (75:25 *ratio*) were purified by recrystallization from toluene (0.83 g, 64%). White crystals of the major isomer (**2a**) could be obtained by recrystallization from toluene-acetone (mp 128-130 °C). HRMS calcd for $C_{17}H_{24}NO_2{}^{11}B$: 285.1900. Found: 285.189. MS (*m/z*, relative intensity %): 285 (34), 244 (2), 218 (53), 164 (15), 128 (100), 127 (20), 117 (23), 94 (56), 91 (55), 58 (52). Anal. Calcd for $C_{17}H_{24}NO_2B$: C, 71.60, H, 8.48. Found: C, 71.53, H, 8.45. **2a:** ^{1}H-NMR (300 MHz) δ ppm: 7.47-7.22 (m, 5H), 6.87 (d, 1H, J = 17.8 Hz), 5.71 (d, 1H, J = 17.8 Hz), 5.49 (d, 1H, J = 4.7 Hz), 4.98 (d, 2H, J = 10.3 Hz), 4.16 (m, 1H), 3.99 (m, 1H), 3.37 (m, 1H), 3.35 (m, 1H), 3.04 (m, 1H), 2.50 (s, 3H), 1.90 (s, 3H), 1.01 (d, 3H, J = 7.1 Hz). ^{13}C-NMR (75.5 MHz) δ ppm: 144.1, 142.5, 140.3, 128.1, 127.0, 126.0, 114.9, 76.3, 68.4, 61.6, 61.0, 41.8, 18.6, 11.5. ^{11}B-NMR (96.3 MHz) δ ppm: 11.7. **2b**: ^{1}H-NMR (300 MHz) δ ppm: 7.47-7.22 (m, 5H), 6.82 (d, 1H, J = 17.5 Hz), 5.77 (d, 1H, J = 17.5 Hz), 5.37 (d, 1H, J = 8.2 Hz), 4.98 (d, 2H, J = 10.3 Hz), 4.31 (m, 1H), 4.08 (m, 1H), 3.53 (m, 1H), 3.24 (m, 1H), 2.55 (s, 3H), 2.44 (m, 1H), 1.90 (s, 3H), 0.83 (d, 3H, J = 7.0 Hz). ^{13}C-NMR (75.5 MHz) δ ppm: 143.0, 141.1, 127.9, 127.1, 126.6, 115.0, 75.1, 64.5, 62.5, 52.8, 43.7, 18.6, 11.1. ^{11}B-NMR (96.3 MHz) δ ppm: 11.7.

4-Hydroxy-6-methyl-2-phenyl-2,3,3a,4,7,7a-hexahydro-1*H*-1,3-isoindoledione (10'/10"). In a 100 mL-round-bottom flask equipped with a condenser and a Dean-Stark trap, a mixture of **2a/2b** (4.0 g, 14 mmol) and *N*-phenylmaleimide (2.42 g, 14 mmol) in toluene (50 mL) was heated at 110 °C for 12 h. Concentration *in vacuo* gave a yellow solid. HRMS calcd for $C_{27}H_{32}N_2O_4{}^{11}B$ $[M+H]^+$: 459.2455.

Found: 459.246. The crude Diels-Alder cycloadducts (0.5 g, 1.09 mmol) were solubilized in THF (10 mL) and cooled at –10 °C. An aqueous solution of 3 M sodium acetate (0.54 mL, 0.54 mmol) was added dropwise and the temperature was maintained below 0 °C. Hydrogen peroxide (0.33 mL, 3.6 mmol) was added and the mixture was stirred at 0 °C for 2 h. Water (10 mL) was added and the aqueous layer was extracted with ether (2 × 20 mL). The ether layers were joined, washed with saturated ammonium chloride (15 mL), separated, and dried with $MgSO_4$. Filtration and concentration *in vacuo* gave a residue which was washed with ether (30 mL). The alcohol (**10'/10"**) (177 mg, 63%) was obtained as a white solide (mp 118-120 °C). ^{1}H-NMR (300 MHz) δ ppm: 7.49-7.40 (m, 3H), 7.26-7.21 (m, 2H), 5.80 (ddd, 1H, J = 3.6, 2.0 and 2.0 Hz), 4.54 (d, 1H, J = 3.6 Hz), 3.37 (dd, 1H, J = 9.1 and 3.6 Hz), 3.29 (br ddd, 1H, J = 9.1, 3.0 and 8.0 Hz), 2.66 (dd, 1H, J = 15.8 and 3.0 Hz), 2.34 (dd, 1H, J = 15.8 and 8.0 Hz), 1.81 (br s, 3H), 1.62 (br s, 1H). ^{13}C-NMR (50.3 MHz) δ ppm: 178.8, 178.5, 136.7, 131.5, 129.2, 128.4, 126.5, 126.4, 66.3, 44.5, 38.1, 28.4, 23.2. HRMS calcd for $C_{15}H_{15}NO_3$: 257.1052. Found: 257.105. MS (*m/z*, relative intensity %): 257 (49), 242 (12), 229 (17), 187 (11), 174 (100), 146 (5), 119 (12), 109 (30), 93 (50), 84 (81). $[\alpha]_{589}^{25}$ = –7.4 ° (c = 6.78, chloroform).

Dimethyl-2,3,3a,4,7,7a-hexahydro-6-methyl-1,3-dioxo-2-phenyl-1*H*-isoindol-4-propanedioate (12/13). In a 20 mL-round bottom flask, the alcohol (**10'/10"**) (80 mg, 0.31 mmol) and 2 crystals of DMAP were solubilized in dry ether (5 mL). Triethylamine (65 μL, 0.46 mmol) and the acid chloride (**11**) (47 mg, 0.31 mmol) were successively added and the reaction mixture was stirred at ambient temperature for 12 h. The precipitate which was formed was dissolved by addition of 1 M HCl (1 mL). The aqueous layer was extracted with ether (2 × 3 mL) and the organic layers were joined, washed with a saturated solution of sodium hydrogenocarbonate (3 mL) and water (3 × 3 mL), dried ($MgSO_4$), and filtered. The solvent was removed *in vacuo* affording the ester (**12/13**) as a yellow oil (82 mg, 71%, de = 12%). ^{1}H-NMR (200 MHz, major isomer) δ ppm: 7.49-7.28 (m, 5H), 5.89 (m, 1H), 5.53 (m, 1H), 5.00 (q, 1H, J = 7.1 Hz), 3.49-3.24 (m, 2H), 2.73-2.35 (m, 2H), 1.99 (s, 3H), 1.63 (br s, 3H), 1.41 (d, 3H, J = 7.1 Hz). ^{13}C-NMR (50.3 MHz, major isomer) δ ppm: 178.5, 174,.5, 170.2, 169.6, 141.9, 131.8, 129.1, 128.6, 126.6, 119.8, 68.6, 68.1, 43.2, 36.9, 26.9, 23.4, 20.5, 17.0. ^{1}H-NMR (200 MHz, minor isomer) δ ppm: 7.49-7.28 (m, 5H), 6.06 (m, 1H), 5.01 (q, 1H, J = 7.1 Hz), 1.63 (br s). ^{13}C-NMR (50.3 MHz, minor isomer) δ ppm: 174.3, 178.3, 120.4, 68.4, 42.8, 37.6, 27.7, 16.7. HRMS calcd for $C_{20}H_{21}NO_6$: 371.1369. Found: 371.137. MS (*m/z*, relative intensity %): 371 (4), 256 (44), 255 (9), 240 (18), 239 (30), 237 (71), 224 (3), 193 (39), 120 (13), 119 (26), 118 (13), 115 (24), 109 (15), 93 (100), 87 (26).

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