

# The Asymmetric Silaboration of Terminal Allenes Bearing $\alpha$ -Stereogenic Centers: Stereoselection Based on “Reagent Control”

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## 1. General

All reactions were performed in a drybox or using Schlenk technique under a nitrogen atmosphere with magnetic stirring. Column chromatography was performed with Ultra Pure Silica Gel (SILICYCLE, pH 7.0, 40–63  $\mu$ m, 60 Å).  $^1\text{H}$  NMR spectra were recorded on a Varian Mercury-400 (400.44 MHz) spectrometer.  $^{13}\text{C}$  NMR spectra were recorded on a Varian GEMINI-2000 (75.45 MHz), JEOL JNM-A500 (125.65 MHz), or JEOL ECA-600 (150.92 MHz) spectrometers. Chemical shifts were reported in ppm downfield from tetramethylsilane. Elemental analyses were performed by Elemental Analysis Center of Kyoto University. High resolution mass spectra were recorded on a JEOL JMS-700 spectrometer.

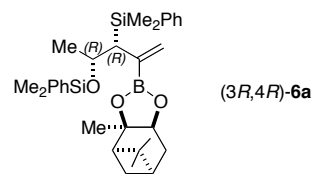
## 2. Materials

Toluene was dried and degassed by The Ultimate Solvent System (GlassContour). Silylboranes **1**, (–)-**2**, and (+)-**2** were synthesized by the method reported previously.  $\text{CpPd}(\eta^3\text{-allyl})^3$  and (R)-**3**<sup>4</sup> were prepared according to the literature methods. (R)- and (S)-**4a** were synthesized from commercially available (R)- and (S)-1-butyn-3-ol via (i) silylation ( $\text{Me}_2\text{PhSiCl}$ , imidazole, DMF), and then (ii) Crabbé reaction<sup>5</sup>. Allenes **4b–4g** were prepared from coresponding propargylic alcohols by a procedure similar to **4a**. (R)- and (S)-**7** were synthesized by silylation of (R)- and (S)-4-methyl-1,2-pentadien-5-ol<sup>6</sup>.

## 3. Silaboration of (R)-**4a** with silylboranes **1** or **2** (Table 1)

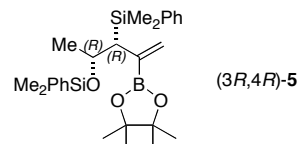
A typical procedure is given for the reaction of entry 4 in Table 1. In a drybox, (R)-**3** (2.1 mg, 4.8  $\mu$ mol) and  $\text{CpPd}(\eta^3\text{-allyl})$  (0.85 mg, 4.0  $\mu$ mol) were dissolved in 200  $\mu$ L of toluene in a screw-capped vial. The mixture was stirred at room temperature for 15 min. (R)-**4a** (105 mg, 0.48 mmol) and (–)-**2** (126 mg, 0.40 mmol) were added sequentially to the reaction mixture. The reaction mixture

was stirred at room temperature and the reaction was monitored by GC. After the reaction was completed (15 h), the volatile materials were evaporated.  $^1\text{H}$  NMR analysis of the residual crude mixture indicated the ratio of (3R,4R)-**6a** : (3S,4R)-**6a** to be 98 : 2. Absolute configuration of the allylic carbon in major isomer was assumed to R based on the previous report.<sup>2</sup> The product was isolated by bulb-to-bulb distillation to give **6a** as colorless viscous liquid (208 mg, 98%).



(3R,4R)-**6a**.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.49–7.54 (m, 4H), 7.27–7.39 (m, 6H), 5.72 (d,  $J$  = 3.2 Hz, 1H), 5.38 (d,  $J$  = 3.2 Hz, 1H), 4.25 (dq,  $J$  = 9.6, 6.0 Hz, 1H), 4.17 (dd,  $J$  = 8.8, 2.0 Hz, 1H), 2.31 (d,  $J$  = 8.8 Hz, 1H), 2.27 (dt,  $J$  = 8.8, 2.4 Hz, 1H), 2.11 (ddt,  $J$  = 10.8, 6.4, 2.0 Hz, 1H), 1.99 (t,  $J$  = 5.6 Hz, 1H), 1.84–1.88 (m, 1H), 1.80 (ddd,  $J$  = 14.4, 5.6, 2.0 Hz, 1H), 1.28 (s, 6H), 1.04 (d,  $J$  = 6.0 Hz, 3H), 0.98 (d,  $J$  = 10.8 Hz, 1H), 0.83 (s, 3H), 0.343 (s, 3H), 0.335 (s, 3H), 0.32 (s, 3H), 0.27 (s, 3H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  140.0, 138.9, 134.4 (2C), 133.5 (2C), 129.2, 128.4, 128.2, 127.6 (2C), 127.1 (2C), 85.7, 77.8, 72.2, 51.3, 45.1, 39.5, 38.1, 35.4, 28.6, 27.1, 26.3, 24.7, 24.0, –0.1, –1.2, –2.0, –2.4. The boron-bound carbon was not detected due to quadrupolar relaxation. Anal. Calcd for  $\text{C}_{31}\text{H}_{45}\text{BO}_3\text{Si}_2$ : C, 69.90; H, 8.52. Found: C, 69.90; H, 8.59.

(3R,4R)-**5** (entry 2). According to the typical procedure, **5** was obtained as a diastereomeric mixture [(3R,4R)-**5** : (3S,4R)-**5** = 89 : 11] by the reaction of (R)-**4a** (108 mg) with **1** (106 mg). The product was isolated by bulb-to-bulb distillation (190 mg, 98%).



(3R,4R)-**5**.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.49–7.54 (m, 4H), 7.26–7.37 (m, 6H), 5.73 (d,  $J$  = 3.6 Hz, 1H), 5.38 (d,  $J$  = 3.6 Hz, 1H), 4.23 (dq,  $J$  = 8.8, 6.0 Hz, 1H), 2.30 (d,  $J$  = 8.8 Hz, 1H), 1.17 (s, 6H), 1.16 (s, 6H), 1.03 (d,  $J$  = 6.0, 3H), 0.34 (s, 3H), 0.33 (s, 3H), 0.32 (s, 3H), 0.27 (s, 3H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  140.0, 138.9, 134.5 (2C), 133.5 (2C), 129.2,

(1) Suginome, M.; Matsuda, T.; Ito, Y. *Organometallics* **2000**, *19*, 4647.  
(2) Suginome, M.; Ohmura, T.; Miyake, Y.; Mitani, S.; Ito, Y.; Murakami, M. *J. Am. Chem. Soc.* **2003**, *125*, 11175.

(3) Tatsuno, Y.; Yoshida, T.; Otsuka, S. *Inorg. Synth.* **1979**, *19*, 220.

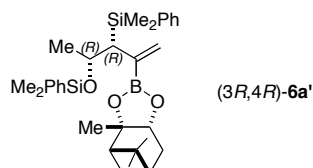
(4) Uozumi, Y.; Suzuki, N.; Ogiwara, A.; Hayashi, T. *Tetrahedron* **1994**, *50*, 4293.

(5) (a) Crabbé, P.; Nassim, B.; Robert-Lopes, M.-T. *Org. Synth. Collect. Vol. VII* **1990**, pp. 276. (b) Trost, B. M.; Pinkerton, A. B.; Seidel, M. *J. Am. Chem. Soc.* **2001**, *123*, 12466.

(6) Konegawa, T.; Ohtsuka, Y.; Ikeda, H.; Sugai, T.; Ohta, H. *Synlett* **1997**, 1297.

128.5, 128.2, 127.6 (2C), 127.1 (2C), 83.2 (2C), 72.3, 44.6, 24.8 (2C), 24.6 (2C), 24.6, -0.1, -1.2, -2.1, -2.3. The boron-bound carbon was not detected due to quadrupolar relaxation. Anal. Calcd for  $C_{27}H_{41}BO_3Si_2$ : C, 67.48; H, 8.60. Found: C, 67.71; H, 8.49.

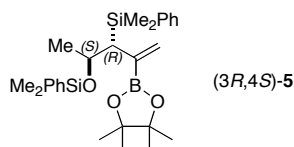
**(3*R*,4*R*)-6a' (entry 5).** According to the typical procedure, **6a'** was obtained as a mixture of four diastereomers [(3*R*,4*R*)-**6a'** : (3*S*,4*R*)-**6a'** : (3*R*,4*S*)-**6a'** : (3*S*,4*S*)-**6a'** = 37 : 14 : 21 : 28 (determined by  $^1H$  NMR on the basis of the integrations of the vinylic protons)] by the reaction of *rac*-**4a** (55 mg) with (+)-**2** (61 mg). The product was isolated by bulb-to-bulb distillation (100 mg, 97%).



Because of low selectivity, the diastereomers were not separable or identifiable by  $^1H$  NMR. Only characteristic  $^1H$  NMR chemical shifts of (3*R*,4*R*)-**6a'** are shown;  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  5.76 (d,  $J$  = 3.0 Hz, 1H), 5.41 (d,  $J$  = 3.0 Hz, 1H).

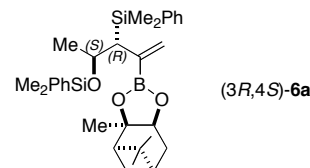
#### 4. Silaboration of (*S*)-**4a** (Table 2)

**(3*R*,4*S*)-5 (entry 2).** According to the typical procedure described above, **5** was obtained as a diastereomeric mixture [(3*R*,4*S*)-**5** : (3*S*,4*S*)-**5** = 78:22] by the reaction of (*S*)-**4a** (109 mg) with **1** (110 mg). The product was isolated by bulb-to-bulb distillation (195 mg, 97%).



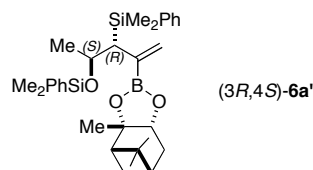
**(3*R*,4*S*)-5.**  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.49-7.52 (m, 4H), 7.28-7.35 (m, 6H), 5.96 (d,  $J$  = 3.6 Hz, 1H), 5.80 (d,  $J$  = 3.6 Hz, 1H), 4.23 (quint,  $J$  = 6.4 Hz, 1H), 2.31 (d,  $J$  = 6.4 Hz, 1H), 1.184 (s, 6H), 1.180 (s, 6H), 1.04 (d,  $J$  = 6.4 Hz, 3H), 0.34 (s, 3H), 0.300 (s, 3H), 0.295 (s, 3H), 0.23 (s, 3H).  $^{13}C$  NMR (75 MHz,  $CDCl_3$ )  $\delta$  139.5, 139.1, 134.1 (2C), 133.4 (2C), 130.3, 129.1, 128.5, 127.5 (2C), 127.4 (2C), 83.3 (2C), 71.0, 42.4, 24.7 (4C), 24.0, -0.2, -0.9, -2.1, -4.0. The boron-bound carbon was not detected due to quadrupolar relaxation. Anal. Calcd for  $C_{27}H_{41}BO_3Si_2$ : C, 67.48; H, 8.60. Found: C, 67.39; H, 8.46.

**(3*R*,4*S*)-6a (entry 4).** According to the typical procedure described above, **6a** was obtained as a diastereomeric mixture [(3*R*,4*S*)-**6a** : (3*S*,4*S*)-**6a** = 94 : 6] by the reaction of (*S*)-**4a** (106 mg) with (–)-**2** (125 mg). The product was isolated by bulb-to-bulb distillation (208 mg, 98%).



**(3*R*,4*S*)-6a.**  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.49-7.52 (m, 4H), 7.29-7.33 (m, 6H), 5.93 (d,  $J$  = 3.2 Hz, 1H), 5.77 (d,  $J$  = 3.2 Hz, 1H), 4.26 (quint,  $J$  = 6.0 Hz, 1H), 4.21 (dd,  $J$  = 8.8, 2.0 Hz, 1H), 2.31 (d,  $J$  = 6.4 Hz, 1H), 2.28-2.34 (m, 1H), 2.14 (ddt,  $J$  = 10.8, 6.4, 2.4 Hz, 1H), 2.04 (t,  $J$  = 5.4 Hz, 1H), 1.80-1.89 (m, 2H), 1.30 (s, 3H), 1.28 (s, 3H), 1.05 (d,  $J$  = 6.0 Hz, 3H), 1.04-1.07 (m, 1H), 0.83 (s, 3H), 0.36 (s, 3H), 0.30 (s, 6H), 0.24 (s, 3H).  $^{13}C$  NMR (75 MHz,  $CDCl_3$ )  $\delta$  139.5, 139.1, 134.1 (2C), 133.4 (2C), 130.0, 129.1, 128.5, 127.5 (2C), 127.4 (2C), 85.5, 77.9, 70.8, 51.4, 43.2, 39.5, 38.1, 35.5, 28.6, 27.1, 26.4, 24.1, 24.0, -0.2, -0.9, -2.1, -3.9. The boron-bound carbon was not detected due to quadrupolar relaxation. HRMS (FAB)  $m/z$  calcd for  $C_{31}H_{45}BO_3Si_2$  ( $M^+$ ): 532.3000, found: 532.3008.

**(3*R*,4*S*)-6a' (entry 5).** The results were obtained in the same experiment described for entry 5 in Table 1.



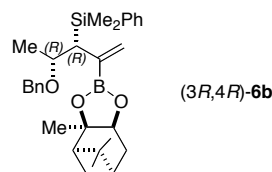
Only characteristic  $^1H$  NMR chemical shifts of (3*R*,4*S*)-**6a'** are shown;  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  5.97 (d,  $J$  = 3.6 Hz, 1H), 5.83 (d,  $J$  = 3.6 Hz, 1H).

#### 5. Silaboration of $\alpha$ -alkoxyallenes **4b-g** with (–)-**2** in the presence of Pd/(*R*)-**3** catalyst (Table 3)

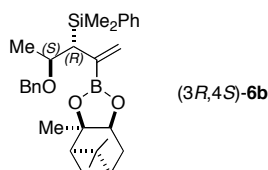
All reactions shown in Table 3 were carried out using racemic allenes **4b-g** by a procedure similar to the typical procedure described above. The ratios of diastereomers were determined by  $^1H$  NMR, on the basis of the integrations of the vinylic protons. The vinylic signals were assigned based on the chemical shifts of the diastereomers of **6a**, which were prepared from the enantiopure allenes. The chemical shifts of vinylic protons of **6a-g** are summarized in Table S1 (see p. S7). For **6b-f**, the strong signals observed at 5.74-5.79 and 5.40-5.48 ppm were assigned to (3*R*,4*R*)-isomer on the basis of the signals of (3*R*,4*R*)-**6a** (5.72 and 5.38 ppm). Similarly, another strong signals appeared at 5.88-5.93 and 5.67-5.86 ppm were assigned to (3*R*,4*S*)-isomer. Signals of minor diastereomers could also be assigned to (3*S*,4*R*)-**6** (5.94-5.98 and 5.82-5.92 ppm), and to (3*S*,4*S*)-**6** (5.76-5.81 and 5.42-5.56 ppm). To determine the diastereomers ratio of **6g**,  $^1H$  NMR measurement was carried out using  $C_6D_6$  as solvent.

**(3*R*,4*R*)-6b and (3*R*,4*S*)-6b (entry 1).** According to the typical procedure described above, **6b** was obtained as a diastereomeric mixture [(3*R*,4*R*)-**6b** : (3*S*,4*R*)-**6b** : (3*R*,4*S*)-**6b** : (3*S*,4*S*)-**6b** = 54.6 : 1.6 : 41.8 : 2.0] in the reaction of *rac*-**4b** (88 mg) with (–)-**2** (126 mg). The product was

isolated by bulb-to-bulb distillation (184 mg, 94%). The two major diastereomers were isolated by silica gel column chromatography (hexane : Et<sub>2</sub>O = 97 : 3).

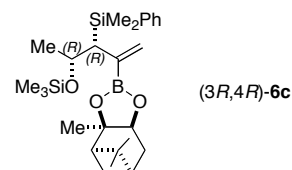


(3*R*,4*R*)-**6b**. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.45-7.48 (m, 2H), 7.22-7.31 (m, 8H), 5.78 (d, *J* = 3.2 Hz, 1H), 5.44 (d, *J* = 3.2 Hz, 1H), 4.55 (d, *J* = 11.2 Hz, 1H), 4.25 (d, *J* = 11.2 Hz, 1H), 4.23 (dd, *J* = 8.8, 1.6 Hz, 1H), 3.89 (dq, *J* = 10.0, 6.0 Hz, 1H), 2.37 (d, *J* = 10.0 Hz, 1H), 2.33 (ddt, *J* = 14.8, 8.8, 2.4 Hz, 1H), 2.18 (ddt, *J* = 10.8, 6.0, 2.4 Hz, 1H), 2.05 (t, *J* = 5.6 Hz, 1H), 1.88-1.92 (m, 1H), 1.84 (ddd, *J* = 14.4, 3.2, 2.0 Hz, 1H), 1.32 (s, 3H), 1.29 (s, 3H), 1.17 (d, *J* = 6.0 Hz, 3H), 1.06 (d, *J* = 10.8 Hz, 1H), 0.85 (s, 3H), 0.32 (s, 3H), 0.28 (s, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 139.7, 139.0, 134.4 (2C), 128.5, 128.2, 128.0 (2C), 127.6 (2C), 127.1 (2C), 127.0, 85.7, 77.8, 77.4, 70.2, 51.3, 43.4, 39.5, 38.1, 35.4, 28.6, 27.1, 26.4, 24.0, 19.5, -2.2, -2.4. The boron-bound carbon was not detected due to quadrupolar relaxation. Anal. Calcd for C<sub>30</sub>H<sub>41</sub>BO<sub>3</sub>Si: C, 73.75; H, 8.46. Found: C, 73.50; H, 8.34 (A mixture of diastereomers was used for elemental analysis).

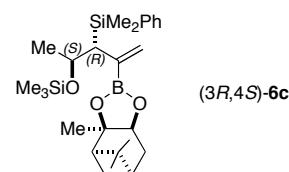


(3*R*,4*S*)-**6b**. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.51-7.54 (m, 2H), 7.21-7.34 (m, 8H), 5.92 (d, *J* = 3.6 Hz, 1H), 5.74 (d, *J* = 3.6 Hz, 1H), 4.50 (d, *J* = 11.2 Hz, 1H), 4.23 (dd, *J* = 8.8, 2.0 Hz, 1H), 4.22 (d, *J* = 11.2 Hz, 1H), 3.95 (dq, *J* = 7.2, 6.0 Hz, 1H), 2.41 (d, *J* = 7.2 Hz, 1H), 2.28-2.35 (m, 1H), 2.10-2.17 (m, 1H), 2.05 (t, *J* = 6.0 Hz, 1H), 1.81-1.89 (m, 2H), 1.30 (s, 3H), 1.28 (s, 3H), 1.14 (d, *J* = 6.0 Hz, 3H), 1.09 (d, *J* = 10.8 Hz, 1H), 0.83 (s, 3H), 0.38 (s, 3H), 0.27 (s, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 139.4, 139.3, 134.1 (2C), 129.8, 128.6, 128.0 (2C), 127.5 (2C), 127.3 (2C), 126.9, 85.6, 77.9, 76.1, 69.7, 51.4, 42.6, 39.5, 38.1, 35.5, 28.6, 27.1, 26.3, 24.0, 19.0, -2.1, -3.8. The boron-bound carbon was not detected due to quadrupolar relaxation. Elemental analysis was carried out for a mixture of diastereomers. See characterization data of (3*R*,4*R*)-**6b**.

(3*R*,4*R*)-**6c** and (3*R*,4*S*)-**6c** (entry 2). According to the typical procedure described above, **6c** was obtained as a diastereomeric mixture [(3*R*,4*R*)-**6c** : (3*S*,4*R*)-**6c** : (3*R*,4*S*)-**6c** : (3*S*,4*S*)-**6c** = 56.8 : 1.3 : 38.9 : 3.0] in the reaction of *rac*-**4c** (75 mg) with (–)-**2** (122 mg). The product was isolated by bulb-to-bulb distillation (158 mg, 87%).

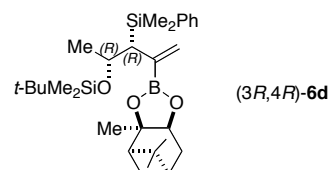


(3*R*,4*R*)-**6c**. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.51-7.54 (m, 2H), 7.27-7.32 (m, 3H), 5.74 (d, *J* = 3.2 Hz, 1H), 5.40 (d, *J* = 3.2 Hz, 1H), 4.17-4.27 (m, 2H), 2.25-2.35 (m, 1H), 2.28 (d, *J* = 9.2 Hz, 1H), 2.12-2.19 (m, 1H), 2.02 (t, *J* = 5.6 Hz, 1H), 1.86-1.90 (m, 1H), 1.79-1.84 (m, 1H), 1.29 (s, 3H), 1.28 (s, 3H), 1.14 (d, *J* = 5.6 Hz, 3H), 1.02 (d, *J* = 10.8 Hz, 1H), 0.83 (s, 3H), 0.36 (s, 3H), 0.31 (s, 3H), 0.08 (s, 9H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 140.0, 134.5 (2C), 128.2 (2C), 127.1 (2C), 85.7, 77.7, 71.6, 51.3, 45.1, 39.5, 38.1, 35.4, 28.5, 27.1, 26.3, 24.6, 24.0, 0.8 (3C), -1.9, -2.6. The boron-bound carbon was not detected due to quadrupolar relaxation. Anal. Calcd for C<sub>26</sub>H<sub>43</sub>BO<sub>3</sub>Si<sub>2</sub>: C, 66.36; H, 9.21. Found: C, 66.12; H, 8.95 (A mixture of diastereomers was used for elemental analysis).



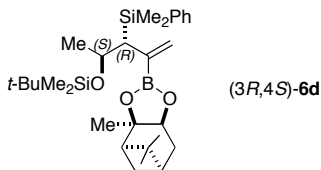
(3*R*,4*S*)-**6c**. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.51-7.54 (m, 2H), 7.27-7.32 (m, 3H), 5.90 (d, *J* = 3.6 Hz, 1H), 5.75 (d, *J* = 3.6 Hz, 1H), 4.17-4.27 (m, 2H), 2.25-2.35 (m, 1H), 2.26 (d, *J* = 6.4 Hz, 1H), 2.12-2.19 (m, 1H), 2.04 (t, *J* = 5.4 Hz, 1H), 1.86-1.90 (m, 1H), 1.79-1.84 (m, 1H), 1.33 (s, 3H), 1.28 (s, 3H), 1.10 (d, *J* = 6.4 Hz, 3H), 1.06 (d, *J* = 10.8 Hz, 1H), 0.84 (s, 3H), 0.38 (s, 3H), 0.25 (s, 3H), 0.04 (s, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 139.6, 134.1 (2C), 130.0, 128.5, 127.4 (2C), 85.5, 77.9, 70.2, 51.4, 43.4, 39.4, 38.1, 35.5, 28.6, 27.1, 26.3, 24.04, 23.99, 0.7 (3C), -2.1, -3.8. The boron-bound carbon was not detected due to quadrupolar relaxation. Elemental analysis was carried out for a mixture of diastereomers. See characterization data of (3*R*,4*R*)-**6c**.

(3*R*,4*R*)-**6d** and (3*R*,4*S*)-**6d** (entry 3). According to the typical procedure described above, **6d** was obtained as a diastereomeric mixture [(3*R*,4*R*)-**6d** : (3*S*,4*R*)-**6d** : (3*R*,4*S*)-**6d** : (3*S*,4*S*)-**6d** = 57.0 : 0.8 : 38.9 : 3.3] in the reaction of *rac*-**4d** (98 mg) with (–)-**2** (129 mg). The product was isolated by bulb-to-bulb distillation (191 mg, 90%).



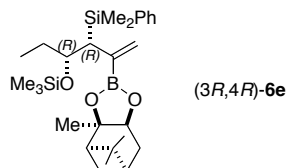
(3*R*,4*R*)-**6d**. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.51-7.54 (m, 2H), 7.26-7.32 (m, 3H), 5.77 (d, *J* = 3.2 Hz, 1H), 5.51 (d, *J* = 3.2 Hz, 1H), 4.21-4.29 (m, 1H), 4.15 (dd, *J* = 8.6, 1.8 Hz, 1H), 2.32 (d, *J* = 7.6 Hz, 1H), 2.26-2.30 (m, 1H), 2.14 (ddt, *J* = 10.8, 6.4, 2.4 Hz, 1H), 2.01 (t, *J* = 5.2 Hz, 1H), 1.78-1.89 (m, 2H), 1.274 (s, 3H), 1.267 (s, 3H), 1.15 (d, *J* = 6.0 Hz, 3H), 1.00 (d, *J* = 10.8 Hz, 1H), 0.85 (s, 9H), 0.82 (s,

3H), 0.41 (s, 3H), 0.29 (s, 3H), 0.04 (s, 3H), 0.01 (s, 3H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  140.2, 134.4 (2C), 128.7, 128.2, 127.2 (2C), 85.7, 77.8, 72.2, 51.3, 44.4, 39.5, 38.1, 35.4, 28.5, 27.1, 26.3 (3H), 26.2, 25.3, 24.0, 18.3, -1.9, -2.7, -3.6, -4.0. The boron-bound carbon was not detected due to quadrupolar relaxation. Anal. Calcd for  $\text{C}_{29}\text{H}_{49}\text{BO}_3\text{Si}_2$ : C, 67.94; H, 9.63. Found: C, 67.75; H, 9.83 (A mixture of diastereomers was used for elemental analysis).

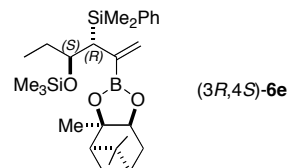


(3*R*,4*S*)-**6d**.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.51-7.54 (m, 2H), 7.26-7.32 (m, 3H), 5.90 (d,  $J$  = 3.2 Hz, 1H), 5.69 (d,  $J$  = 3.2 Hz, 1H), 4.21-4.29 (m, 1H), 4.21 (dd,  $J$  = 8.6, 1.8 Hz, 1H), 2.32 (d,  $J$  = 7.6 Hz, 1H), 2.26-2.30 (m, 1H), 2.14 (ddt,  $J$  = 10.8, 6.4, 2.4 Hz, 1H), 2.03 (t,  $J$  = 5.2 Hz, 1H), 1.78-1.89 (m, 2H), 1.30 (s, 3H), 1.28 (s, 3H), 1.11 (d,  $J$  = 6.0 Hz, 3H), 1.05 (d,  $J$  = 10.8 Hz, 1H), 0.84 (s, 9H), 0.83 (s, 3H), 0.38 (s, 3H), 0.25 (s, 3H), 0.00 (s, 3H), -0.02 (s, 3H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  139.7, 134.1 (2C), 129.7, 128.5, 127.5, 85.5, 77.9, 70.4, 51.3, 43.8, 39.5, 38.1, 35.4, 28.6, 27.1, 26.3, 26.1 (3C), 24.7, 24.0, 18.1, -2.0, -3.6, -3.8, -4.3. The boron-bound carbon was not detected due to quadrupolar relaxation. Elemental analysis was carried out for a mixture of diastereomers. See characterization data of (3*R*,4*R*)-**6d**.

(3*R*,4*R*)-**6e** and (3*R*,4*S*)-**6e** (entry 4). According to the typical procedure described above, **6e** was obtained as a diastereomeric mixture [(3*R*,4*R*)-**6e** : (3*S*,4*R*)-**6e** : (3*R*,4*S*)-**6e** : (3*S*,4*S*)-**6e** = 52.1 : 1.0 : 43.8 : 3.1] in the reaction of *rac*-**4e** (76 mg) with (-)-**2** (123 mg). The product was isolated by bulb-to-bulb distillation (185 mg, 98%).

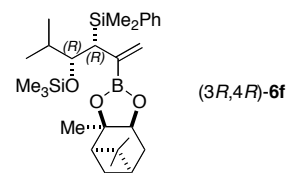


(3*R*,4*R*)-**6e**.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.51-7.55 (m, 2H), 7.27-7.32 (m, 3H), 5.75 (d,  $J$  = 3.2 Hz, 1H), 5.41 (d,  $J$  = 3.2 Hz, 1H), 4.15-4.22 (m, 2H), 2.49 (d,  $J$  = 9.2 Hz, 1H), 2.27-2.33 (m, 1H), 2.11-2.17 (m, 1H), 2.00-2.04 (m, 1H), 1.86-1.89 (m, 1H), 1.78-1.84 (m, 1H), 1.32-1.68 (m, 2H), 1.28 (s, 6H), 1.02 (d,  $J$  = 10.8 Hz, 1H), 0.83 (s, 3H), 0.81 (t,  $J$  = 7.6 Hz, 3H), 0.36 (s, 3H), 0.30 (s, 3H), 0.06 (s, 9H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  140.1, 134.5 (2C), 128.4, 128.2, 127.1 (2C), 85.7, 77.7, 75.3, 51.3, 39.5, 39.3, 38.1, 35.5, 28.5, 28.1, 27.1, 26.3, 24.0, 6.7, 0.7 (3C), -1.9, -2.8. The boron-bound carbon was not detected due to quadrupolar relaxation. Anal. Calcd for  $\text{C}_{27}\text{H}_{45}\text{BO}_3\text{Si}_2$ : C, 66.92; H, 9.36. Found: C, 66.68; H, 9.26 (A mixture of diastereomers was used for elemental analysis).

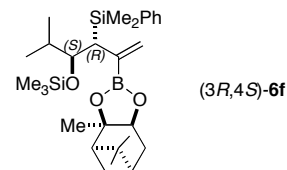


(3*R*,4*S*)-**6e**.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.51-7.55 (m, 2H), 7.27-7.32 (m, 3H), 5.93 (d,  $J$  = 3.8 Hz, 1H), 5.86 (d,  $J$  = 3.8 Hz, 1H), 4.15-4.22 (m, 1H), 3.91 (dt,  $J$  = 7.6, 5.4 Hz, 1H), 2.38 (d,  $J$  = 5.2 Hz, 1H), 2.27-2.33 (m, 1H), 2.11-2.17 (m, 1H), 2.00-2.04 (m, 1H), 1.86-1.89 (m, 1H), 1.78-1.84 (m, 1H), 1.32-1.68 (m, 2H), 1.29 (s, 3H), 1.28 (s, 3H), 1.04 (d,  $J$  = 10.8 Hz, 1H), 0.83 (s, 3H), 0.73 (t,  $J$  = 7.6 Hz, 3H), 0.37 (s, 3H), 0.25 (s, 3H), 0.04 (s, 9H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  139.5, 134.5 (2C), 130.7, 128.5, 127.4 (2C), 85.5, 77.9, 76.2, 51.3, 39.4, 38.2, 38.1, 35.5, 28.8, 28.5, 27.1, 26.3, 24.0, 10.1, 0.9 (3C), -2.3, -4.0. The boron-bound carbon was not detected due to quadrupolar relaxation. Elemental analysis was carried out for a mixture of diastereomers. See characterization data of (3*R*,4*R*)-**6e**.

(3*R*,4*R*)-**6f** and (3*R*,4*S*)-**6f** (entry 5). According to the typical procedure described above, **6f** was obtained as a diastereomeric mixture [(3*R*,4*R*)-**6f** : (3*S*,4*R*)-**6f** : (3*R*,4*S*)-**6f** : (3*S*,4*S*)-**6f** = 54.1 : 1.4 : 41.2 : 3.3] in the reaction of *rac*-**4f** (89 mg) with (-)-**2** (126 mg). The product was isolated by bulb-to-bulb distillation (188 mg, 94%). The diastereomers were isolated by silica gel column chromatography (hexane :  $\text{Et}_2\text{O}$  = 100 : 1).



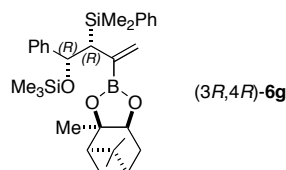
(3*R*,4*R*)-**6f**.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.49-7.52 (m, 2H), 7.25-7.28 (m, 3H), 5.74 (d,  $J$  = 2.8 Hz, 1H), 5.48 (d,  $J$  = 2.8 Hz, 1H), 4.16 (dd,  $J$  = 8.4, 3.2 Hz, 1H), 4.09 (dd,  $J$  = 8.4, 2.0 Hz, 1H), 2.62 (d,  $J$  = 8.4 Hz, 1H), 2.28 (ddt,  $J$  = 14.4, 8.4, 2.4 Hz, 1H), 2.12 (ddt,  $J$  = 10.4, 6.4, 2.0 Hz, 1H), 1.99 (t,  $J$  = 5.6 Hz, 1H), 1.81-1.88 (m, 2H), 1.78 (ddd,  $J$  = 14.4, 3.2, 2.0 Hz, 1H), 1.26 (s, 3H), 1.21 (s, 3H), 0.96 (d,  $J$  = 10.8 Hz, 1H), 0.90 (d,  $J$  = 6.8 Hz, 3H), 0.81 (s, 3H), 0.78 (d,  $J$  = 6.8 Hz, 3H), 0.38 (s, 3H), 0.29 (s, 3H), 0.09 (s, 9H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  140.8, 134.6 (2C), 128.0, 127.6, 127.0 (2C), 85.6, 81.5, 77.6, 51.3, 39.5, 38.1, 37.5, 35.5, 34.9, 28.5, 27.1, 26.3, 24.0, 18.2, 16.6, 1.0 (3C), -1.4, -3.1. The boron-bound carbon was not detected due to quadrupolar relaxation. Anal. Calcd for  $\text{C}_{28}\text{H}_{47}\text{BO}_3\text{Si}_2$ : C, 67.44; H, 9.50. Found: C, 67.17; H, 9.26 (A mixture of diastereomers was used for elemental analysis).



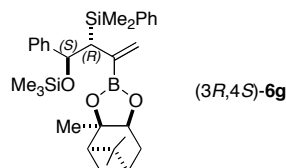
(3*R*,4*S*)-**6f**.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.49-7.52 (m, 2H), 7.30-7.32 (m, 3H), 5.88 (d,  $J$  = 3.2 Hz, 1H), 5.67 (d,  $J$

= 3.2 Hz, 1H), 4.27 (dd,  $J$  = 8.8, 2.0 Hz, 1H), 3.99 (dd,  $J$  = 8.8, 2.4 Hz, 1H), 2.47 (d,  $J$  = 8.8 Hz, 1H), 2.30-2.37 (m, 1H), 2.017 (ddt,  $J$  = 10.8, 6.0, 2.0 Hz, 1H), 2.06 (t,  $J$  = 5.4 Hz, 1H), 1.86-1.92 (m, 2H), 1.71 (ddt,  $J$  = 13.6, 6.4, 2.0 Hz, 1H), 1.34 (s, 3H), 1.29 (s, 3H), 1.12 (d,  $J$  = 10.8 Hz, 1H), 0.86 (d,  $J$  = 6.4 Hz, 3H), 0.85 (s, 3H), 0.56 (d,  $J$  = 6.4 Hz, 3H), 0.39 (s, 3H), 0.21 (s, 3H), 0.05 (s, 9H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  139.5, 134.1 (2C), 129.7, 128.5, 127.4 (2C), 85.4, 78.6, 78.1, 51.4, 39.9, 39.5, 38.2, 35.4, 33.4, 28.6, 27.1, 26.4, 24.1, 21.3, 15.6, 1.1 (3C), -1.6, -4.1. The boron-bound carbon was not detected due to quadrupolar relaxation. Elemental analysis was carried out for a mixture of diastereomers. See characterization data of (3*R*,4*R*)-**6f**.

**(3*R*,4*R*)-6g and (3*R*,4*S*)-6g (entry 6).** According to the typical procedure described above, **6g** was obtained as a diastereomeric mixture [(3*R*,4*R*)-**6g** : (3*S*,4*R*)-**6g** : (3*R*,4*S*)-**6g** : (3*S*,4*S*)-**6g** = 52.5 : 1.5 : 42.1 : 3.9] in the reaction of *rac*-**4g** (111 mg) with (–)-**2** (130 mg). The product was isolated by bulb-to-bulb distillation (185 mg, 84%). The diastereomers were isolated by silica gel column chromatography (hexane :  $\text{Et}_2\text{O}$  = 50 : 1).



**(3*R*,4*R*)-6g.**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.57-7.61 (m, 2H), 7.29-7.33 (m, 3H), 7.10-7.22 (m, 5H), 5.59 (d,  $J$  = 3.2 Hz, 1H), 5.25 (d,  $J$  = 3.2 Hz, 1H), 4.96 (d,  $J$  = 10.8 Hz, 1H), 4.15 (dd,  $J$  = 8.8, 2.0 Hz, 1H), 2.78 (d,  $J$  = 10.8 Hz, 1H), 2.26 (ddt,  $J$  = 14.4, 8.8, 2.4 Hz, 1H), 2.07 (ddt,  $J$  = 10.8, 6.0, 2.0 Hz, 1H), 1.97 (t,  $J$  = 5.6 Hz, 1H), 1.81-1.86 (m, 1H), 1.71 (ddd,  $J$  = 14.4, 3.2, 2.0 Hz, 1H), 1.26 (s, 3H), 1.23 (s, 3H), 0.81 (s, 3H), 0.78 (d,  $J$  = 10.8 Hz, 1H), 0.44 (s, 3H), 0.41 (s, 3H), -0.16 (s, 9H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  145.1, 139.9, 134.5 (2C), 129.9, 128.3, 127.6 (2C), 127.5 (2C), 127.2 (2C), 126.8, 85.6, 77.9, 77.7, 51.3, 45.1, 39.4, 38.1, 35.3, 28.5, 27.1, 26.3, 24.0, 0.4 (3C), -1.7, -2.4. The boron-bound carbon was not detected due to quadrupolar relaxation. Anal. Calcd for  $\text{C}_{31}\text{H}_{45}\text{BO}_3\text{Si}_2$ : C, 69.90; H, 8.52. Found: C, 70.17; H, 8.76 (A mixture of diastereomers was used for elemental analysis).

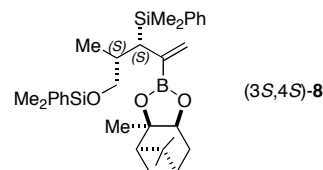


**(3*R*,4*S*)-6g.**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.37-7.39 (m, 2H), 7.09-7.27 (m, 8H), 5.92 (d,  $J$  = 3.2 Hz, 1H), 5.78 (d,  $J$  = 3.2 Hz, 1H), 5.05 (d,  $J$  = 6.0 Hz, 1H), 4.13 (dd,  $J$  = 8.8, 2.0 Hz, 1H), 2.58 (d,  $J$  = 6.8 Hz, 1H), 2.24 (ddt,  $J$  = 14.4, 8.8, 2.4 Hz, 1H), 2.08 (ddt,  $J$  = 10.8, 6.0, 2.0 Hz, 1H), 1.98 (t,  $J$  = 5.6 Hz, 1H), 1.81-1.85 (m, 1H), 1.67 (ddt,  $J$  = 14.4, 3.2, 2.0 Hz, 1H), 1.26 (s, 3H), 1.21 (s, 3H), 0.87 (d,  $J$  = 10.8 Hz, 1H), 0.80 (s, 3H), 0.173 (s, 3H), 0.167 (s, 3H), -0.12 (s,

9H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  144.9, 138.9, 134.1 (2C), 130.8, 128.4, 127.4 (2C), 127.3 (2C), 127.2 (2C), 126.8, 85.4, 77.8, 76.0, 51.3, 44.2, 39.4, 38.1, 35.4, 28.5, 27.1, 26.3, 24.0, 0.4 (3C), -2.9, -3.3. The boron-bound carbon was not detected due to quadrupolar relaxation. Elemental analysis was carried out for a mixture of diastereomers. See characterization data of (3*R*,4*R*)-**6g**.

## 6. Silaboration of **7** and cyclization of **8** (Scheme 1)

In a drybox, (*R*)-**3** (2.1 mg, 4.8  $\mu\text{mol}$ ) and  $\text{CpPd}(\eta^3\text{-allyl})$  (0.85 mg, 4.0  $\mu\text{mol}$ ) were dissolved in 200  $\mu\text{L}$  of toluene in a screw-capped vial. A small magnetic stirbar was added, and the mixture was stirred at room temperature for 15 min. (*R*)-**7** (112 mg, 0.48 mmol) and (–)-**2** (127 mg, 0.40 mmol) were added to the reaction mixture. The reaction mixture was stirred at room temperature and the reaction was monitored by GC. After the reaction was completed (12 h), the volatile materials were evaporated.  $^1\text{H}$  NMR analysis of the residual crude mixture indicated the ratio of (3*S*,4*S*)-**8** : (3*R*,4*S*)-**8** to be 96:4. The product was isolated by bulb-to-bulb distillation to give **8** as colorless liquid (194 mg, 88%).

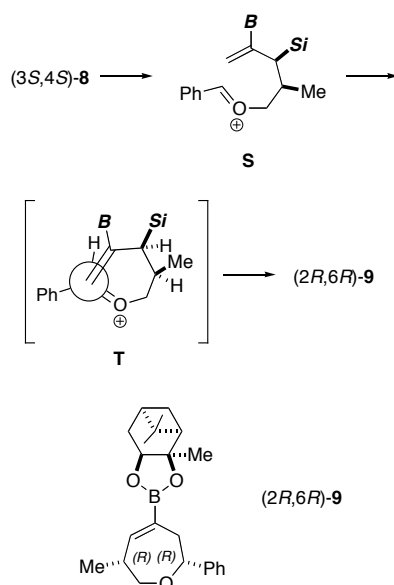


**(3*S*,4*S*)-8.**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.28-7.47 (m, 10H), 5.84 (d,  $J$  = 3.2 Hz, 1H), 5.47 (d,  $J$  = 3.2 Hz, 1H), 4.26 (dd,  $J$  = 8.8, 1.8 Hz, 1H), 3.55 (dd,  $J$  = 10.0, 4.4 Hz, 1H), 2.97 (dd,  $J$  = 10.0, 8.8 Hz, 1H), 2.34 (ddt,  $J$  = 14.4, 8.8, 2.2 Hz, 1H), 2.08-2.21 (m, 2H), 2.06 (t,  $J$  = 5.4 Hz, 1H), 2.01 (d,  $J$  = 9.2 Hz, 1H), 1.82-1.92 (m, 2H), 1.34 (s, 3H), 1.30 (s, 3H), 1.09 (d,  $J$  = 10.8 Hz, 1H), 0.89 (d,  $J$  = 6.4 Hz, 3H), 0.85 (s, 3H), 0.32 (s, 3H), 0.252 (s, 3H), 0.249 (s, 3H), 0.17 (s, 3H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  140.2, 138.1, 133.8 (2C), 133.4 (2C), 129.3, 129.0, 128.4, 127.7 (2C), 127.5 (2C), 85.7, 77.8, 68.4, 51.4, 39.5, 38.1, 37.6, 36.8, 35.5, 28.6, 27.1, 26.4, 24.0, 17.4, -1.5, -1.8, -2.0, -4.1. The boron-bound carbon was not detected due to quadrupolar relaxation. HRMS (FAB)  $m/z$  calcd for  $\text{C}_{32}\text{H}_{48}\text{BO}_3\text{Si}_2$  ( $\text{MH}^+$ ): 547.3235, found: 547.3225.

Under an argon atmosphere, benzaldehyde (21 mg, 0.20 mmol) and (4*S*)-**8** [(3*S*,4*S*) : (3*R*,4*S*) = 96:4, 99 mg, 0.18 mmol] were dissolved in 500  $\mu\text{L}$  of  $\text{CH}_2\text{Cl}_2$  in a Schlenk tube. The mixture was cooled to  $-78^\circ\text{C}$ .  $\text{Me}_3\text{SiOTf}$  (44 mg, 0.20 mmol) was slowly added and the resulting solution was stirred at that temperature for 3 h. The mixture was diluted with ether and quenched with aqueous  $\text{NaHCO}_3$ . The organic materials were extracted with ether, washed with water, and dried over anhydrous  $\text{MgSO}_4$ . The product was isolated by bulb-to-bulb distillation to give **9** (59 mg, 0.16 mmol, 89%). HPLC analysis [column: DAICEL OD-H (4.6 mm x 250 mm); eluent: hexane/2-propanol = 99.5 : 0.5; flow rate: 0.6 mL/min; detection wavelength: 220 nm;  $T_R$  = 10.1 (2*R*,6*R*), 29.7 (2*S*,6*R*) min] indicated the ratio of

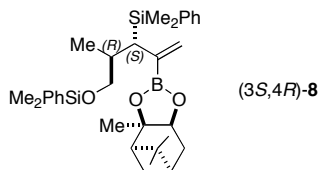
(2*R*,6*R*)-**9** : (2*S*,6*R*)-**9** to be 96 : 4. Absolute configuration of the stereogenic carbon center formed in this reaction was predicted to be *R* because rigid transition state **T** was expected in the cyclization step of oxonium intermediate **S** (Scheme S1).

**Scheme S1.** Expected Reaction Path via Chirality Transfer



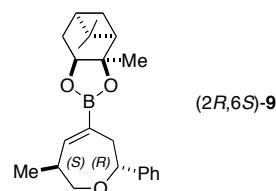
(2*R*,6*R*)-**9**. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.21-7.40 (m, 5H), 6.70 (dd, *J* = 6.0, 2.4 Hz, 1H), 4.62 (dd, *J* = 9.6, 2.0 Hz, 1H), 4.30 (dd, *J* = 8.8, 2.0 Hz, 1H), 3.94 (dd, *J* = 12.0, 5.2 Hz, 1H), 3.75 (dd, *J* = 12.0, 2.4 Hz, 1H), 2.80 (dddd, *J* = 16.8, 9.6, 2.4, 1.6 Hz, 1H), 2.70 (dd, *J* = 16.8, 2.4 Hz, 1H), 2.65-2.76 (m, 1H), 2.33 (ddt, *J* = 14.4, 8.8, 2.4 Hz, 1H), 2.22 (ddt, *J* = 10.8, 6.4, 2.4 Hz, 1H), 2.05 (t, *J* = 5.6 Hz, 1H), 1.89-1.93 (m, 1H), 1.84 (ddd, *J* = 14.4, 3.2, 2.0 Hz, 1H), 1.40 (s, 3H), 1.29 (s, 3H), 1.17 (d, *J* = 7.2 Hz, 3H), 1.15 (d, *J* = 9.6 Hz, 1H), 0.85 (s, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 150.9, 143.8, 128.2 (2C), 127.1, 126.1 (2C), 85.9, 81.8, 78.1, 72.9, 51.4, 39.5, 38.6, 38.2, 35.6, 29.7, 28.7, 27.1, 26.5, 24.0, 16.6. The boron-bound carbon was not detected due to quadrupolar relaxation. HRMS (EI) *m/z* calcd for C<sub>23</sub>H<sub>31</sub>BO<sub>3</sub> (M<sup>+</sup>): 366.2366, found: 366.2366.

The reaction of (*S*)-**7** (112 mg, 0.48 mmol) with (–)-**2** (124 mg, 0.39 mmol) was carried out according to the procedure similar to that of (*R*)-**7**. <sup>1</sup>H NMR analysis of crude mixture indicated the ratio of (3*S*,4*R*)-**8** : (3*R*,4*R*)-**8** to be 94:6. The product was isolated by bulb-to-bulb distillation to give **8** as colorless liquid (174 mg, 81%).



(3*S*,4*R*)-**8**. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.49-7.53 (m, 4H), 7.29-7.36 (m, 6H), 5.75 (d, *J* = 2.8 Hz, 1H), 5.40 (d, *J* = 2.8 Hz, 1H), 4.21 (dd, *J* = 8.8, 2.0 Hz, 1H), 3.63 (dd, *J* = 9.6, 3.4 Hz, 1H), 3.12 (dd, *J* = 9.6, 8.4 Hz, 1H), 2.31 (ddt, *J* = 14.4, 8.8, 2.4 Hz, 1H), 2.11-2.14 (m, 2H), 2.03 (t, *J* = 5.6 Hz, 1H), 1.98 (d, *J* = 11.2 Hz, 1H), 1.86-1.90 (m, 1H), 1.80 (ddd, *J* = 14.4, 3.2, 2.0 Hz, 1H), 1.29 (s, 3H), 1.28 (s, 3H), 1.03 (d, *J* = 11.2 Hz, 1H), 0.91 (d, *J* = 6.4 Hz, 3H), 0.84 (s, 3H), 0.37 (s, 3H), 0.31 (s, 6H), 0.22 (s, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 140.1, 138.3, 134.0 (2C), 133.4 (2C), 129.3, 128.4, 127.7, 127.6 (2C), 127.4 (2C), 85.6, 77.8, 67.9, 51.3, 39.5, 38.1, 37.7, 36.7, 35.5, 28.6, 27.1, 26.4, 24.0, 18.5, -1.5, -1.67, -1.73, -3.4. The boron-bound carbon was not detected due to quadrupolar relaxation. Anal. Calcd for C<sub>32</sub>H<sub>47</sub>BO<sub>3</sub>Si<sub>2</sub>: C, 70.30; H, 8.67. Found: C, 70.35; H, 8.71.

According to the procedure described for the reaction of (4*S*)-**8**, cyclization of (4*R*)-**8** [(3*S*,4*R*) : (3*R*,4*R*) = 94:6, 84 mg, 0.15 mmol] was carried out with benzaldehyde (21 mg, 0.20 mmol) and Me<sub>3</sub>SiOTf (44 mg, 0.20 mmol). The product was isolated by bulb-to-bulb distillation to give **9** (44 mg, 0.12 mmol, 77%). HPLC analysis [column: DAICEL OD-H (4.6 mm x 250 mm); eluent: hexane/2-propanol = 99.5 : 0.5; flow rate: 0.6 mL/min; detection wavelength: 220 nm; T<sub>R</sub> = 9.4 (2*R*,6*S*), 18.6 (2*S*,6*S*) min] indicated the ratio of (2*R*,6*R*)-**9** : (2*S*,6*R*)-**9** to be 94 : 6.

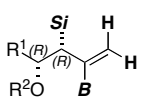
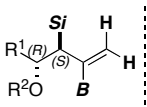
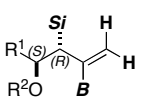
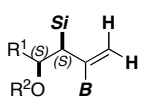


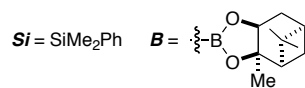
(2*R*,6*S*)-**9**. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.21-7.38 (m, 5H), 6.57 (broad d, *J* = 2.0 Hz, 1H), 4.34 (dd, *J* = 6.4, 4.8 Hz, 1H), 4.31 (dd, *J* = 8.4, 1.6 Hz, 1H), 3.93 (ddd, *J* = 11.6, 3.4, 1.0 Hz, 1H), 3.38 (dd, *J* = 11.6, 10.0 Hz, 1H), 2.84-2.91 (m, 1H), 2.72-2.73 (m, 2H), 2.33 (ddt, *J* = 14.4, 8.8, 2.4 Hz, 1H), 2.23 (ddt, *J* = 10.8, 6.2, 2.4 Hz, 1H), 2.07 (t, *J* = 5.6 Hz, 1H), 1.89-1.93 (m, 1H), 1.84 (ddd, *J* = 14.4, 3.0, 2.0 Hz, 1H), 1.40 (s, 3H), 1.29 (s, 3H), 1.14 (d, *J* = 10.8 Hz, 1H), 1.07 (d, *J* = 7.6 Hz, 3H), 0.85 (s, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 153.5, 144.0, 128.2 (2C), 127.1, 125.9 (2C), 86.0, 82.5, 78.1, 75.3, 51.4, 40.3, 39.5, 38.8, 38.2, 35.6, 28.7, 27.1, 26.5, 24.0, 17.6. The boron-bound carbon was not detected due to quadrupolar relaxation. HRMS (EI) *m/z* calcd for C<sub>23</sub>H<sub>31</sub>BO<sub>3</sub> (M<sup>+</sup>): 366.2366, found: 366.2363.

## 7. <sup>1</sup>H and <sup>13</sup>C NMR spectra of the compounds that do not have elemental analysis data

<sup>1</sup>H and <sup>13</sup>C NMR spectra of (3*R*,4*S*)-**6**, (3*S*,4*S*)-**8**, (2*R*,6*R*)-**9**, and (2*S*,6*R*)-**9** are shown in following pages.

**Table S1.**  $^1\text{H}$  NMR Chemical Shifts of Vinylic Protons (400 MHz,  $\text{CDCl}_3$ )

$\text{R}^1$	$\text{R}^2$	 $(3R,4R)\text{-6}$ <i>major</i>	 $(3S,4R)\text{-6}$ <i>minor</i>	 $(3R,4S)\text{-6}$ <i>major</i>	 $(3S,4S)\text{-6}$ <i>minor</i>
Me	$\text{Me}_2\text{PhSi}$ ( <b>6a</b> )	5.72, 5.38	5.97, 5.82	5.93, 5.77	5.75, 5.41
Me	Bn ( <b>6b</b> )	5.78, 5.44	5.97, 5.82	5.92, 5.74	5.81, 5.46
Me	$\text{Me}_3\text{Si}$ ( <b>6c</b> )	5.74, 5.40	5.95, 5.82	5.90, 5.75	5.77, 5.42
Me	<i>t</i> -Bu $\text{Me}_2\text{Si}$ ( <b>6d</b> )	5.77, 5.51	5.94, 5.85	5.90, 5.69	5.81, 5.56
Et	$\text{Me}_3\text{Si}$ ( <b>6e</b> )	5.75, 5.41	5.98, 5.92	5.93, 5.86	5.78, 5.43
<i>i</i> -Pr	$\text{Me}_3\text{Si}$ ( <b>6f</b> )	5.74, 5.48	5.95, 5.88	5.88, 5.67	5.76, 5.51
Ph	$\text{Me}_3\text{Si}$ ( <b>6g</b> )	5.59, 5.25	5.95, 5.82	5.92, 5.78	5.58, 5.25
	<b>6g</b> in $\text{C}_6\text{D}_6$	5.99, 5.39	6.44, 6.09	6.42, 6.05	6.01, 5.39



STANDARD IN OBSERVE

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature

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Pulse 45.0 degrees

Acq. time 3.500 sec

Width 6006.0 Hz

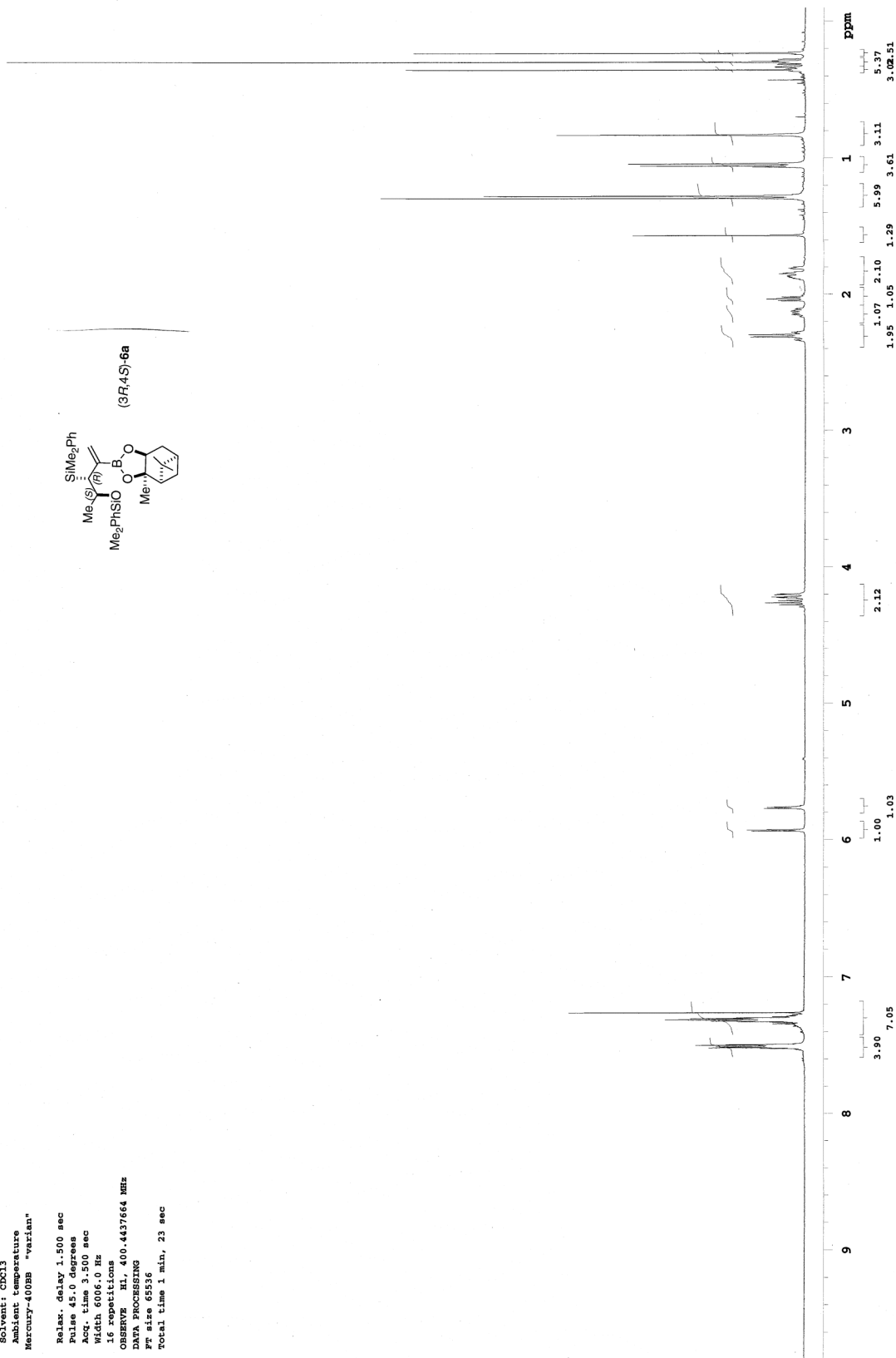
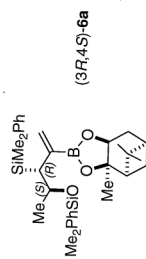
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DATA PROCESSING

FT size 65536

Total time 1 min, 23 sec





13C OBSERVE

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature

QNP-300B "varian2"

Relax. delay 1.158 sec

Pulse 45.0 degrees

Acq. time 0.842 sec

Width 19000.0 Hz

384 repetitions

OBSERVE C13, 75.4519675 MHz

DECOUPLE H1, 300.0687335 MHz

Power 36 dB

continuously on

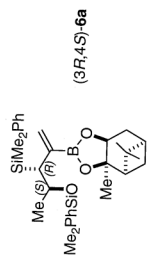
WALTZ-16 modulated

DATA PROCESSING

Line broadening 1.0 Hz

FF size 32768

Total time 6 hr, 48 sec



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130.044  
129.075  
128.507  
127.492  
127.431

139.451  
139.112

-0.237  
-0.883  
-2.051  
-3.849

51.347  
43.200  
39.465  
38.143  
35.484  
28.598  
27.107  
26.354  
24.125  
24.018

70.790

77.413  
77.000  
76.570

77.922

85.531

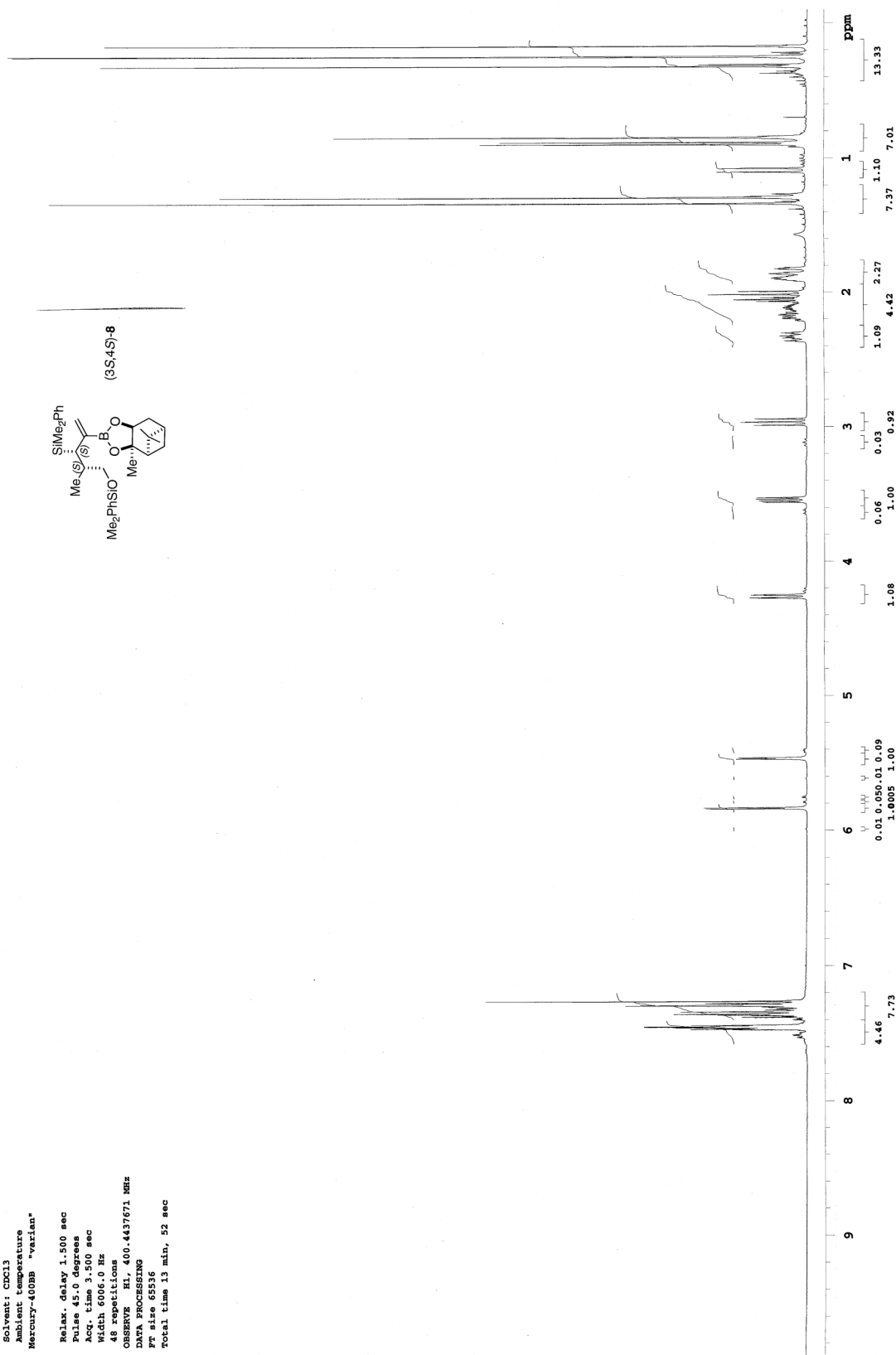
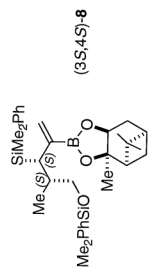
ppm

STANDARD 1H OBSERVE

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Solvent: CDCl3  
Ambient temperature  
Mercury-400MB "varian"

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Pulse 45.0 degrees  
Acq. time 3.500 sec  
Width 6006.0 Hz  
48 repetitions

OBSERVE H1, 400.4437671 MHz  
DATA PROCESSING  
FT size 65536  
Total time 13 min, 52 sec



13C OBSERVE

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature

GBMHI-300NB "varian2"

Relax. delay 1.158 sec

Pulse 45.0 degrees

Acq. time 0.842 sec

Width 19000.0 Hz

256 repetitions

OBSERVE C13, 75.4519705 MHz

DECOUPLE H1, 300.0687335 MHz

Power 36 dB

continuously on

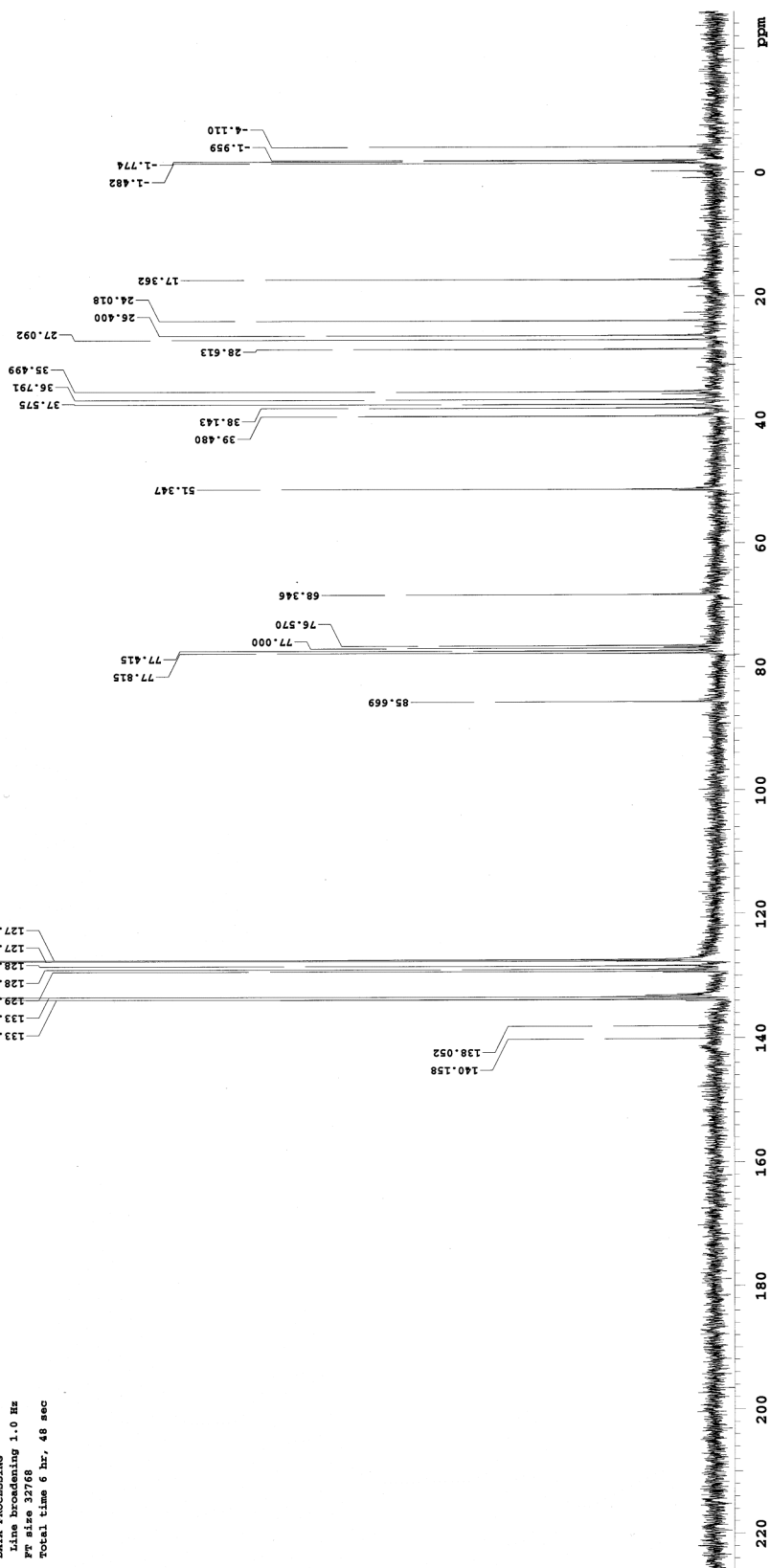
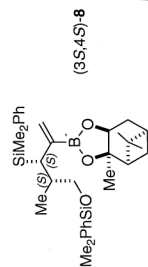
WALTZ-16 modulated

DATA PROCESSING

Line broadening 1.0 Hz

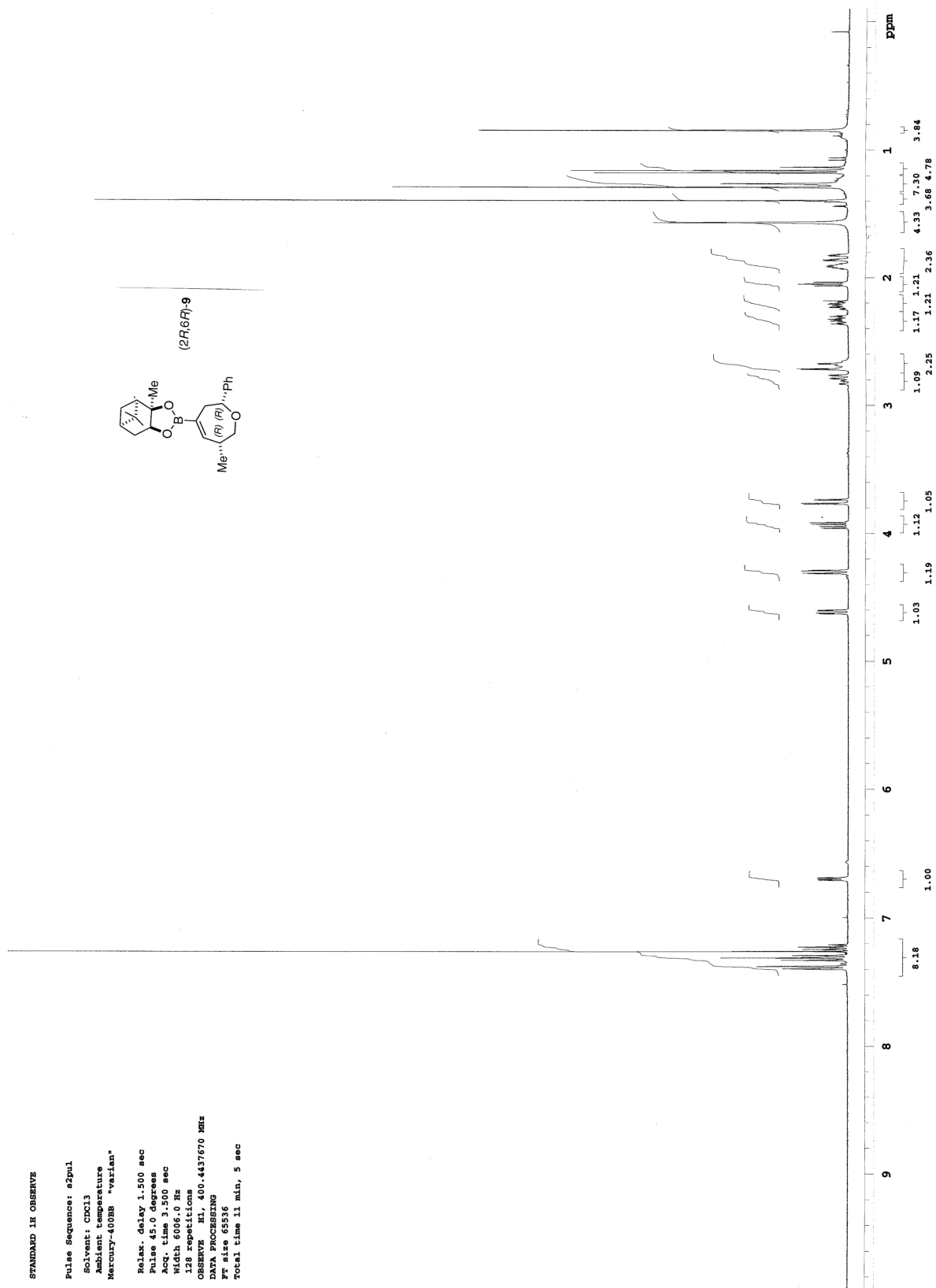
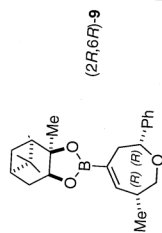
Pr size 32768

Total time 6 hr, 48 sec



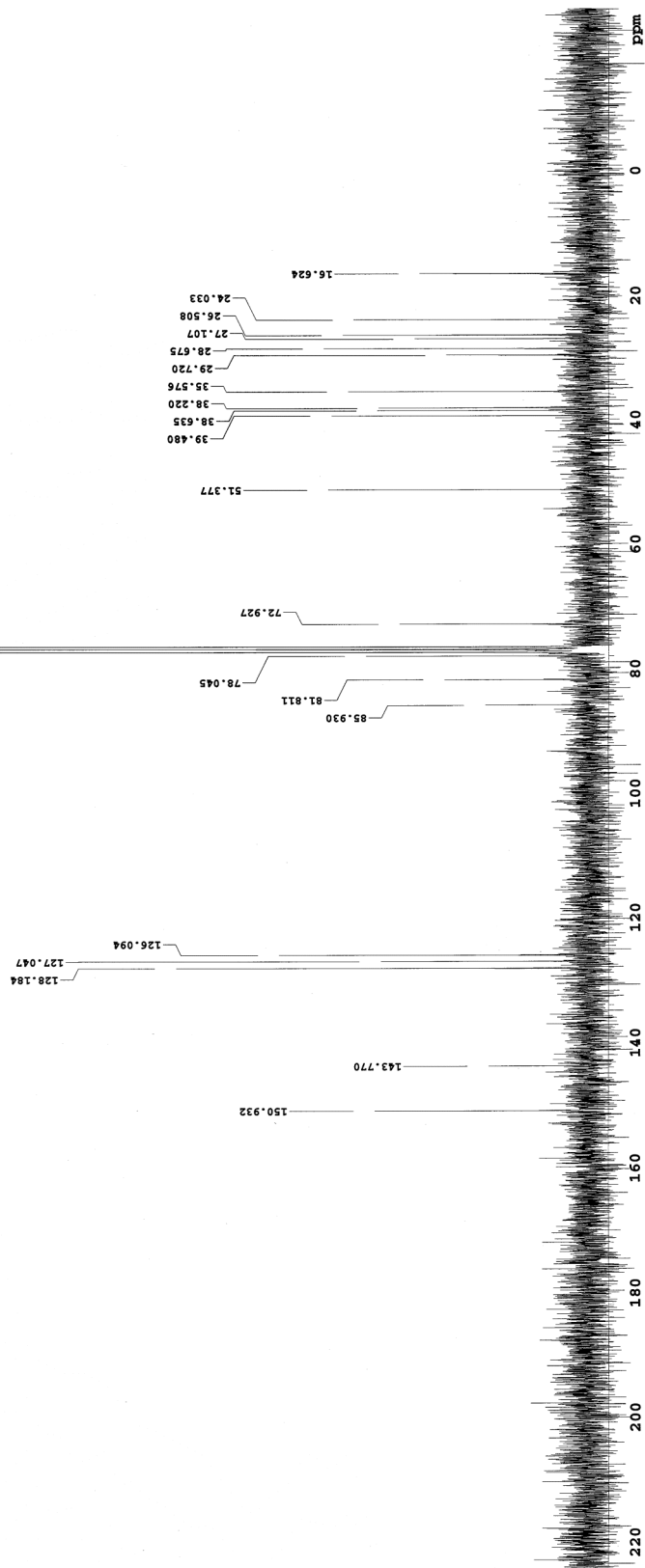
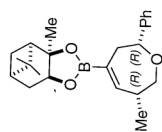
STANDARD 1H OBSERVE

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 Ambient temperature  
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 FT size 65536  
 Total time 11 min, 5 sec



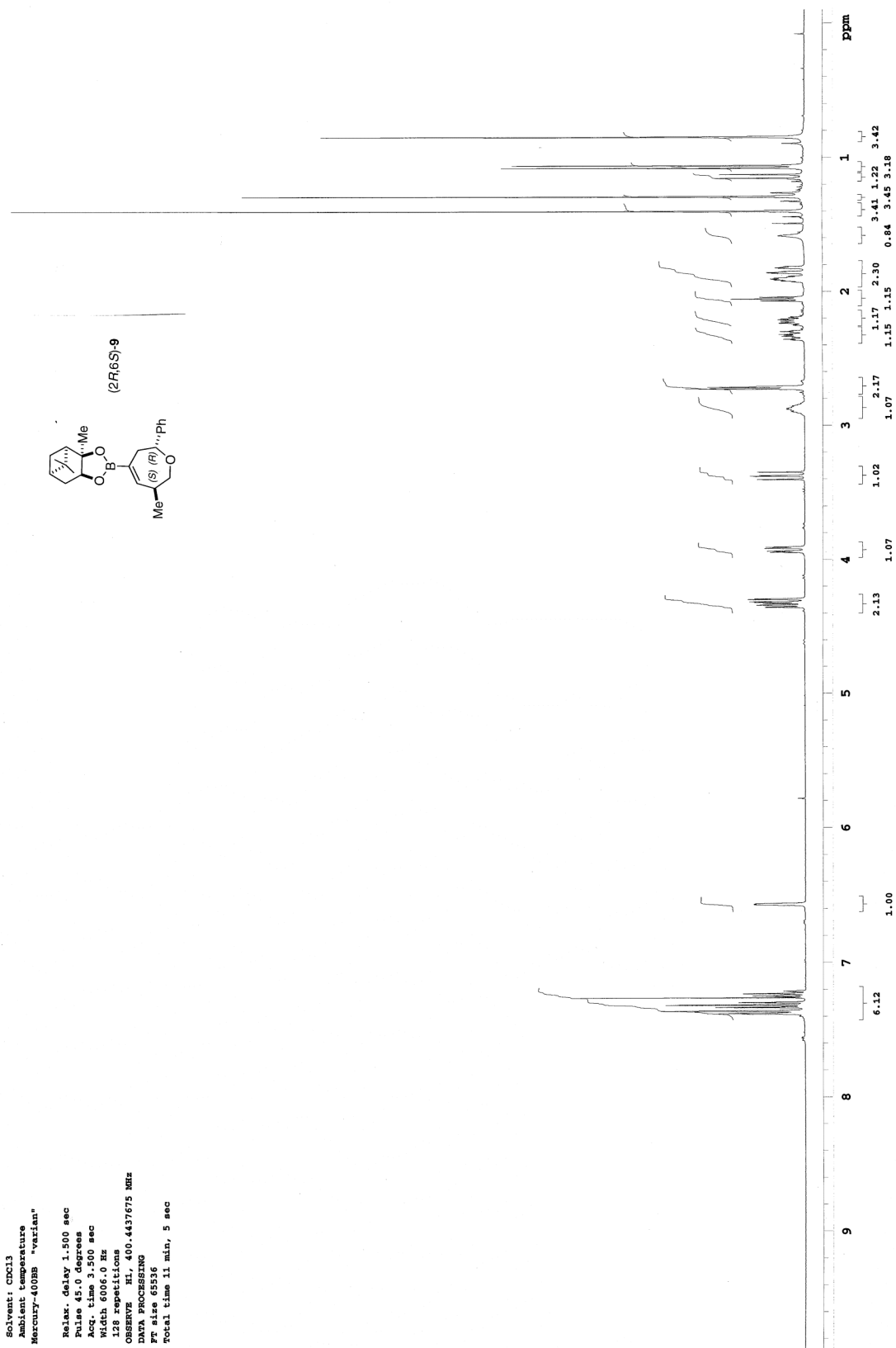
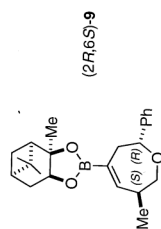
13C OBSERVE

Pulse Sequence: s2pul  
 Solvent: CDCl3  
 Ambient temperature  
 GEMINI-300SB "varian2"  
 Relax. delay 1.158 sec  
 Pulse 45.0 degrees  
 Acq. time 0.842 sec  
 Width 19000.0 Hz  
 1008 repetitions  
 OBSERVE C13, 75.4519663 MHz  
 DECOUPLE H1, 300.0687335 MHz  
 Power 36 dB  
 continuously on  
 WALTZ-16 modulated  
 DATA PROCESSING  
 Line broadening 1.0 Hz  
 FT size 32768  
 Total time 6 hr, 48 sec



STANDARD 1H OBSERVE

Pulse Sequence: s2pul  
 Solvent: CDCl3  
 Ambient temperature  
 Mercury-400DB "varian"  
 Relax. delay 1.500 sec  
 Pulse 45.0 degrees  
 Acq. time 3.500 sec  
 MHz 600.0 Hz  
 320 Spectral width  
 OBSERVE F1 400.4437675 MHz  
 DATA PROCESSING  
 FT size 65536  
 Total time 11 min, 5 sec



13C OBSERVE

Pulse Sequence: s2pul  
 Solvent: CDCl3  
 Ambient temperature  
 GEMINI-300HS "varian2"  
 Relax delay 1.158 sec  
 Pulse 45.0 degrees  
 Acq. time 0.842 sec  
 Width 19000.0 Hz  
 304 repetitions  
 OBSERVE C13, 75.4515663 MHz  
 DECOUPLE H1, 300.0687335 MHz  
 Power 36 dB  
 continuously on  
 WALTZ-16 modulated  
 DATA PROCESSING  
 Line broadening 1.0 Hz  
 FT size 32768  
 Total time 6 hr, 48 sec

