Palladium-Catalyzed Asymmetric Silaboration of Allenes

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1. General

All reactions were performed in a drybox or using Schlenk technique under an atmosphere of nitrogen or argon with magnetic stirring. Column chromatography was performed with Ultra Pure Silica Gel (SILICYCLE, pH 7.0, 40–63 μm , 60Å). PTLC was performed with Silica gel 60 PF₂₅₄ (Merck). ¹H NMR spectra were recorded on a Varian Mercury-400 (400.44 MHz) spectrometer. ¹³C NMR spectra were recorded on a Varian GEMINI-2000 (75.45 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-MS700 spectrometer. Optical rotation was measured by JASCO P-1020 polarimeter.

2. Materials

Toluene was dried and degassed by The Ultimate Solvent System (GlassContour). Silylboranes **1a**¹, **1b-c**², and **1d**¹ were synthesized by the method reported previously. Allenes **2a**, **2d-g**, **2i** were prepared by the reaction of methyl propargyl ether with corresponding Grignard reagents in the presence of catalytic amount of CuBr.³ **2c** was synthesized from propargyl alcohol and isobutyl aldehyde via 3,3-sigmatropic rearrangements.⁴ **2b** and **2j** were prepared by silylation or acetylation of 4,4-dimethyl-1,2-pentadien-5-ol that was obtained by reduction of **2c** with LiAlH₄. **2h** was purchased from TCI. (*R*)-**2k** (>99% ee) and (*S*)-**2k** (>99% ee) were prepared by silylation of the corresponding (*R*)- and (*S*)-4,4-dimethyl-7-phenyl-1,2-heptadien-6-yn-5-ol, which was obtained by optical resolution of the racemate [column: DAICEL OD-H (10 mm x 250 mm); eluent: hexane/2-propanol = 95:5; flow rate: 2.0 mL/min; detection wavelength: 220 nm; T_R = 19.3 (*R*), 28.2 (*S*) min]. Pd(dba)₂⁵ and CpPd(η^3 -allyl)⁶ were prepared according to the literature methods. (+)-NMDPP, (*S*)-MONOPHOS, (*R,R*)-**4**, (*S*)-QUINAP, and (*S*)-MOP were purchased from STREM. Ligands (*R*)-**5a-m** were synthesized from (*S*)-BINOL (KANTO) by the reported

procedure.⁷ Ethyl 4-bromobenzoate (TCI), Me₃SiOTf (TCI), Pd(OAc)₂ (Mitsunaga), S-PHOS (STREM), and K₃PO₄ (NACALAI TESQUE) were used as received from the commercial sources.

3. Screening of chiral ligands for palladium-catalyzed asymmetric silaboration of cyclohexylallene (Table 1)

A ligand (9.6 μmol) and Pd(dba)₂ (4.6 mg, 8.0 μmol) were dissolved in 200 μL of toluene in a screw-capped vial. The mixture was stirred at room temperature for 5 min. **2a** (59 mg, 0.48 mmol) and **1a** (105 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 (3–15 h), the volatile materials were evaporated. The product was isolated by bulb-to-bulb distillation to give **3a** as colorless viscous liquid (67–99%). The enantiomeric excess of **3a** was determined by HPLC analysis [column: DAICEL OD-H (4.6 mm x 250 mm); eluent: hexane; flow rate: 0.6 mL/min; detection wavelength: 220 nm; T_R = 7.3 (*R*), 8.9 (*S*) min]. Absolute configuration of the major isomer was assumed to *S* based on that of **6a** (See below).

(*S*)-3-Cyclohexyl-3-(dimethylphenylsilyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-propene [(*S*)-**3a**].⁸ ¹H NMR (400 MHz, CDCl₃) δ 7.45–7.54 (m, 2H), 7.29–7.32 (m, 3H), 5.77 (d, *J* = 3.6 Hz, 1H), 5.42 (d, *J* = 3.6 Hz, 1H), 1.96 (d, *J* = 10.0 Hz, 1H), 1.56–1.80 (m, 6H), 1.232 (s, 6H), 1.226 (s, 6H), 1.04–1.17 (m, 3H), 0.71–0.85 (m, 2H), 0.37 (s, 3H), 0.20 (s, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 140.8, 134.0 (2C), 128.2, 127.6, 127.3 (2C), 83.2 (2C), 41.6, 38.9, 34.3, 33.6, 26.7, 26.6 (2C), 24.8 (2C), 24.6 (2C), -1.2, -3.6. The boron-bound carbon was not detected due to quadrupolar relaxation.

4. Screening of silylboranes for asymmetric silaboration of **2a** using Pd/(*R*)-**5g** catalyst (Figure 1)

According to the procedure described for Table 1, silylboranes **1b-e** were reacted in the asymmetric

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silaboration of **2a** using Pd/(*R*)-**5g** catalyst. The β -borylallylsilanes produced from **1b** and **1c** were isolated and analyzed after converting to pinacol ester **3a** by the reaction with pinacol (1.2 equiv) at room temperature (68% yield with 27% ee from **1b**, 86% yield with 40% ee from **1c**, respectively). No reaction was observed in the reaction of **1e** under the conditions reported.

(S)-3-Cyclohexyl-3-(diphenylmethylsilyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-propene [(S)-6a]. According to the procedure described for Table 1, the silaboration **2a** with **1d** was carried out at room temperature in the presence of the Pd/(*R*)-**5g** catalyst. The product **6a** was isolated by bulb-to-bulb distillation in 99% yield. The enantiomeric excess was determined to be 89% by the procedure described below (see Scheme S1). (*S*)-**6a** (89% ee): $[\alpha]_D^{26}$ -106.0 (*c* 1.01, CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ 7.64-7.69 (m, 2H), 7.46-7.50 (m, 2H), 7.37-7.40 (m, 3H), 7.25-7.29 (m, 3H), 5.81 (d, *J* = 3.0 Hz, 1H), 5.44 (d, *J* = 3.0 Hz, 1H), 2.46 (d, *J* = 9.6 Hz, 1H), 1.82-1.91 (m, 2H), 1.63-1.70 (m, 2H), 1.57-1.59 (m, 2H), 1.20 (s, 6H), 1.19 (s, 6H), 1.11-1.13 (m, 3H), 0.81-0.91 (m, 2H), 0.65 (s, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 138.5, 137.7, 135.2 (2C), 134.9 (2C), 128.7, 128.6, 128.3, 127.5 (2C), 127.2 (2C), 83.2 (2C), 39.4 (2C), 34.9, 33.4, 26.8, 26.7, 26.5, 24.8 (2C), 24.5 (2C), -4.3. The boron-bound carbon was not detected due to quadrupolar relaxation. HRMS (CI) *m/z* calcd for C₂₈H₄₀BO₂Si (MH⁺): 447.2891, found: 447.2891.

Scheme S1. Transformation of **6a** for determination of the ee

Determination of the enantiomeric excess of 6a (Scheme S1): To determine the enantiomeric excess, **6a** was transformed to alcohol **12** via the reactions shown in Scheme S1. A 1,4-dioxane (2.0 mL) solution of **6a** (74 mg, 0.17 mmol), TsNHNH₂ (373 mg, 2.0 mmol), and Et₃N (0.42 mL, 3.0 mmol) was heated at 100 °C for 4 h. After the mixture was cooled to room temperature, aqueous NaOH solution (3 N, 1.8 mL) and H₂O₂ solution (30%, 1.8 mL) were added to the mixture. The mixture was stirred for 24 h at room temperature. The resulting mixture was extracted with ether and the extracts were washed with water. After drying with anhydrous MgSO₄, the concentrated mixture was purified by PTLC (hexane/AcOEt = 9:1) to give **12** as a mixture of diastereomers (47 mg, 84% from **6a**). HPLC analysis of the mixture indicated the enantiomeric excess of 89% [column: DAICEL OD-H (4.6 mm x 250 mm); eluent: hexane/2-propanol = 99:1; flow rate: 0.6 mL/min; detection wavelength: 220 nm; T_R = 12.0 (minor enantiomer of diastereomer A), 13.4 (major enantiomer of diastereomer

A), 14.8 (minor enantiomer of diastereomer B), 18.1 (major enantiomer of diastereomer B) min]. **12**: A 61:39 mixture of diastereomers A and B. ¹H NMR (400 MHz, CDCl₃) δ 7.56-7.63 (m, 4H for A and 4H for B), 7.34-7.36 (m, 6H for A and 6H for B), 4.15-4.25 (m, 1H for A and 1H for B), 1.01-1.80 (m, 13H for A and 13H for B), 1.24 (d, *J* = 6.4 Hz, 3H for B), 1.17 (d, *J* = 6.4 Hz, 3H for A), 0.78 (s, 3H for A), 0.77 (s, 3H for B). Anal. Calcd for C₂₂H₃₀OSi: C, 78.05; H, 8.93. Found: C, 77.78; H, 8.82.

Scheme S2. Assignment of the absolute configuration of **6a**

Assignment of the absolute configuration of 6a (Scheme S2): The diastereomers *anti*- and *syn*-**12** were separated by PTLC. The relative configuration of each diastereomer was assigned by base-mediated, stereospecific Peterson elimination, which produced (*Z*)-**13** from *anti*-**12** and (*E*)-**13** from *syn*-**12**. The absolute configuration of *syn*-**12** was assigned by the method reported by Trost.⁹ Thus, condensation of *syn*-**12** with (*S*)- α -methoxyphenylacetic acid was carried out in the presence of *N,N'*-dicyclohexylcarbodiimide (DCC) and 4-dimethylaminopyridine (DMAP). The resulted ester **14** was subjected to the ¹H NMR analysis. The observed downfield shift of the signal for the terminal methyl group of the major diastereomers as well as upfield shift of same proton of minor diastereomers indicated that the major isomer has a 2*S*,3*S* configuration. Accordingly, it was concluded that the silaboration of **2a** with **1d** in the presence of (*R*)-**5g** produced (*S*)-**6a** as a major enantiomer.

5. Asymmetric silaboration of allenes **2** with **1d** in the presence of Pd/(*R*)-**5g** catalyst (Table 2 and eqs 1 and 2)

A typical procedure is given for the reaction of entry 1 in Table 2. (*R*)-**5g** (4.8 mg, 9.6 μ mol) and Pd(dba)₂ (4.6 mg, 8.0 μ mol) were dissolved in 100 μ L of toluene and stirred at room temperature for 5 min. To the solution was added

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2a (59 mg, 0.48 mmol) and the mixture was cooled to 0 °C. A toluene (200 μ L) solution of **1d** (131 mg, 0.40 mmol) were added slowly to the reaction mixture, and the resulting mixture was then stirred at 0 °C. The reaction was monitored by GC. After the reaction was completed (22 h), the volatile materials were evaporated. The product was isolated by bulb-to-bulb distillation to give **6a** as colorless viscous liquid (90%). Enantiomeric excess was determined as 91% by the procedure described above (see Scheme S1).

(S)-4,4-Dimethyl-5-(dimethylphenylsilyloxy)-3-(diphenylmethylsilyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-propene [(R)-6b, entry 2]. According to the procedure described for entry 1, **2b** (118 mg) and **1d** (130 mg) were reacted at 0 °C for 50 h. The product **6b** was isolated by bulb-to-bulb distillation (392 mg, 97%). The enantiomeric excess was determined to be 92% by the procedure described below (see Scheme S3). **(R)-6b** (92% ee): $[\alpha]_D^{24}$ -55.1 (*c* 1.17, CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ 7.72-7.74 (m, 2H), 7.56-7.62 (m, 4H), 7.40-7.45 (m, 3H), 7.34-7.37 (m, 3H), 7.26-7.29 (m, 3H), 5.95 (br s, 1H), 5.68 (br s, 1H), 3.34-3.36 (m, 1H), 3.19-3.21 (m, 1H), 3.02 (br s, 1H), 1.23 (s, 12H), 0.97 (s, 3H), 0.95 (s, 3H), 0.91 (br s, 3H), 0.33 (s, 3H), 0.32 (s, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 139.7 (br), 138.7, 138.5, 135.0 (2C), 134.7 (2C), 133.4 (2C), 132.8 (br), 129.2, 128.5, 128.2, 127.6 (2C), 127.5 (2C), 127.1 (2C), 83.4 (2C), 71.8 (br), 40.1 (br), 25.4, 24.7 (4C), 24.5 (2C), -1.7, -1.8, -2.5. The boron-bound carbon was not detected due to quadrupolar relaxation. HRMS (CI) *m/z* calcd for C₃₄H₄₈BO₃Si₂ (MH⁺): 571.3235, found: 571.3235.

Scheme S3. Transformation of **6b** for determination of the ee

Determination of the enantiomeric excess of 6b (Scheme S3): To determine the enantiomeric excess, **6b** was transformed to diol **15** via the reactions shown in Scheme S3. **6b** (76 mg, 0.13 mmol) was added to MeOH solution of HCl (0.5 M) and stirred for 3 h at room temperature. Removal of the volatile materials by rotary evaporator gave alcohol **13**. According to the procedure described for Scheme S1, **13** was transformed into diol **15** (28 mg, 64% from **6b**), which was isolated as a mixture of diastereomers by PTLT (hexane/AcOEt = 1:2). HPLC analysis of the diastereomers mixture indicated the enantiomeric excess of 92% [column: DAICEL OD-H (4.6 mm x 250 mm); eluent: hexane/2-propanol = 98:2; flow rate: 0.6 mL/min; detection wavelength: 220 nm; T_R = 21.2 (minor enantiomer of

diastereomer A), 22.9 (major enantiomer of diastereomer A), 26.9 (minor enantiomer of diastereomer B), 31.4 (major enantiomer of diastereomer B) min]. **15** (major diastereomer): ¹H NMR (400 MHz, CDCl₃) δ 7.64-7.69 (m, 4H), 7.31-7.37 (m, 6H), 4.40 (dq, *J* = 6.8, 1.2 Hz, 1H), 3.52 (d, *J* = 11.4 Hz, 1H), 3.16 (d, *J* = 11.4 Hz, 1H), 2.54 (br s, 2H), 1.87 (d, *J* = 1.2 Hz, 1H), 1.03 (d, *J* = 6.8 Hz, 3H), 1.00 (s, 3H), 0.91 (s, 3H), 0.89 (s, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 139.6, 139.3, 135.3 (2C), 134.7 (2C), 128.74, 128.66, 127.8 (2C), 127.6 (2C), 71.4, 68.8, 42.9, 39.5, 27.2, 26.5, 25.4, -0.2. HRMS (EI) *m/z* calcd for C₂₀H₂₆BOSi (M⁺-H₂O): 310.1753, found: 310.1751. **15** (minor diastereomer): ¹H NMR (400 MHz, CDCl₃) δ 7.59-7.65 (m, 4H), 7.31-7.35 (m, 6H), 4.25 (dq, *J* = 6.8, 2.4 Hz, 1H), 3.54 (d, *J* = 11.2 Hz, 1H), 3.27 (d, *J* = 11.2 Hz, 1H), 2.67 (br s, 2H), 1.90 (d, *J* = 2.4 Hz, 1H), 1.38 (d, *J* = 6.8 Hz, 3H), 1.07 (s, 3H), 0.94 (s, 3H), 0.89 (s, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 139.3, 138.5, 134.7 (2C), 134.5 (2C), 128.9, 128.8, 127.9 (2C), 127.8 (2C), 72.0, 69.0, 41.5, 39.7, 28.8, 28.1, 26.2, -2.0.

(R)-4,4-Dimethyl-3-(diphenylmethylsilyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-penten-5-ol [(R)-6c, entry 3]. According to the procedure described for entry 1, **2c** (106 mg) and **1d** (259 mg) were reacted at 0 °C for 90 h. The product **6c** was isolated by bulb-to-bulb distillation (329 mg, 95%). The enantiomeric excess was determined to be 93% by the procedure described below (see Scheme S4). **(R)-6c** (93% ee): $[\alpha]_D^{24}$ -61.0 (*c* 1.20, CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ 9.36 (s, 1H), 7.62-7.66 (m, 2H), 7.58-7.61 (m, 2H), 7.32-7.36 (m, 3H), 7.26-7.31 (m, 3H), 5.97 (d, *J* = 2.6 Hz, 1H), 5.63 (d, *J* = 2.6 Hz, 1H), 3.04 (s, 1H), 1.21 (s, 6H), 1.18 (s, 6H), 1.033 (s, 3H), 1.028 (s, 3H), 0.81 (s, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 205.6, 137.6, 137.0, 135.0 (2C), 134.9 (2C), 133.7, 129.2, 128.8, 127.8 (2C), 127.5 (2C), 83.8 (2C), 50.1, 37.3 (br), 24.7 (4C), 22.8, 22.7, -2.6. The boron-bound carbon was not detected due to quadrupolar relaxation. Anal. Calcd for C₂₆H₃₅BO₃Si: C, 71.88; H, 8.12. Found: C, 71.60; H, 7.89.

Scheme S4. Transformation of **6c** for determination of the ee

Determination of the enantiomeric excess of 6c (Scheme S4): To determine the enantiomeric excess, **6c** was transformed to diol **15** via the reactions shown in Scheme S4. **6c** was added to a suspension of LiAlH₄ (1.0 equiv.) in ether and stirred for 3 h at room temperature. Water and aqueous NaOH solution was sequentially added to the reaction mixture. The mixture was extracted with ether and dried with anhydrous Na₂SO₄. Removal of the volatile materials afforded alcohol **13**. Transformation of **13** to **15** was carried out by similar procedure to that described for

6b (Scheme S3). HPLC analysis of resulting **15** indicated the enantiomeric excess of 93%.

(R)-3-(Diphenylmethylsilyl)-3-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-propene [(R)-6d, entry 4]. According to the procedure described for entry 1, **2d** (56 mg) and **1d** (125 mg) were reacted at 0 °C for 24 h. The product **6d** was isolated by bulb-to-bulb distillation (158 mg, 93%). The enantiomeric excess was determined to be 88% by HPLC analysis [column: DAICEL OD-H (4.6 mm x 250 mm); eluent: hexane; flow rate: 0.6 mL/min; detection wavelength: 220 nm; T_R = 16.0 (major), 27.6 (minor) min]. (*R*)-**6d** (88% ee): $[\alpha]_D^{26} +12.0$ (*c* 1.07, CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ 7.48-7.50 (m, 2H), 7.22-7.37 (m, 8H), 7.02-7.15 (m, 5H), 5.91 (d, *J* = 2.4 Hz, 1H), 5.63 (d, *J* = 2.4 Hz, 1H), 3.94 (s, 1H), 1.14 (s, 6H), 1.11 (s, 6H), 0.59 (s, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 142.2, 136.5, 136.2, 135.4 (2C), 135.3 (2C), 130.5, 129.4 (2C), 129.0, 128.9, 127.7 (2C), 127.5 (2C), 127.3 (2C), 124.8, 83.5 (2C), 40.3, 24.7 (2C), 24.6 (2C), -4.0. The boron-bound carbon was not detected due to quadrupolar relaxation. Anal. Calcd for C₂₈H₃₃BO₂Si: C, 76.35; H, 7.55. Found: C, 76.31; H, 7.65.

(R)-3-(Diphenylmethylsilyl)-3-(4-methylphenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-propene [(R)-6e, entry 5]. According to the procedure described for entry 1, **2e** (63 mg) and **1d** (130 mg) were reacted at 0 °C for 50 h. The product **6e** was isolated by bulb-to-bulb distillation (171 mg, 94%). The enantiomeric excess was determined to be 89% by HPLC analysis [column: DAICEL OD-H (4.6 mm x 250 mm); eluent: hexane; flow rate: 0.6 mL/min; detection wavelength: 220 nm; T_R = 15.5 (major), 20.9 (minor) min]. (*R*)-**6e** (89% ee): $[\alpha]_D^{24} -6.9$ (*c* 1.19, CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ 7.48-7.51 (m, 2H), 7.24-7.41 (m, 8H), 6.95 (s, 4H), 5.90 (d, *J* = 2.4 Hz, 1H), 5.62 (d, *J* = 2.4 Hz, 1H), 3.93 (s, 1H), 2.28 (s, 3H), 1.15 (s, 6H), 1.13 (s, 6H), 0.59 (s, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 139.1, 136.7, 136.4, 135.4 (2C), 135.3 (2C), 134.2, 130.3, 129.3 (2C), 129.0, 128.9, 128.5 (2C), 127.5 (2C), 127.3 (2C), 83.5 (2C), 39.7, 24.7 (2C), 24.6 (2C), 20.9, -3.9. The boron-bound carbon was not detected due to quadrupolar relaxation. Anal. Calcd for C₂₉H₃₅BO₂Si: C, 76.64; H, 7.76. Found: C, 76.37; H, 7.79.

(R)-3-(Diphenylmethylsilyl)-3-(2-methylphenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-propene [(R)-6f, entry 6]. According to the procedure described for entry 1, **2f** (63 mg) and **1d** (130 mg) were reacted at 0 °C for 50 h. The product **6f** was isolated by bulb-to-bulb distillation (169 mg, 93%). The enantiomeric excess was determined to be 90% by HPLC analysis [column: DAICEL OD-H (4.6 mm x 250 mm); eluent: hexane; flow rate: 0.6 mL/min; detection wavelength: 220 nm; T_R = 14.6 (major), 19.7 (minor) min]. (*R*)-**6f** (90% ee): $[\alpha]_D^{24} +5.7$ (*c* 1.08, CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ 7.57-7.59 (m, 2H), 7.30-7.43 (m, 6H), 7.18-7.26 (m, 3H), 7.04-7.10 (m, 3H), 5.93 (d, *J* = 2.4 Hz, 1H), 5.63 (d, *J* = 2.4 Hz, 1H), 4.20 (s, 1H), 2.16 (s, 3H), 1.17 (s, 6H), 1.11 (s, 6H), 0.70 (s, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 141.1, 137.0, 136.6, 136.4, 135.4 (2C), 135.2 (2C), 130.2, 130.1, 130.0, 129.0, 128.9, 127.5 (2C), 127.3 (2C), 125.2, 125.1, 83.4 (2C), 34.9, 24.9 (2C), 24.4 (2C), 20.2, -3.8. The boron-bound carbon was not detected due to quadrupolar relaxation. Anal. Calcd for C₂₉H₃₅BO₂Si: C, 76.64; H, 7.76. Found: C, 76.41; H, 7.85.

(R)-3-(Diphenylmethylsilyl)-3-(1-naphthyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-propene [(R)-6g, entry 7]. According to the procedure described for entry 1, **2g** (80 mg) and **1d** (130 mg) were reacted at 0 °C for 50 h. The product **6g** was isolated by bulb-to-bulb distillation (168 mg, 86%). The enantiomeric excess was determined to be 90% by HPLC analysis [column: DAICEL OD-H (4.6 mm x 250 mm); eluent: hexane; flow rate: 0.6 mL/min; detection wavelength: 220 nm; T_R = 14.9 (major), 21.5 (minor) min]. (*R*)-**6f** (90% ee): $[\alpha]_D^{26} -134.0$ (*c* 1.05, CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ 8.42-8.45 (m, 1H), 7.85-7.89 (m, 1H), 7.70 (d, *J* = 8.4 Hz, 1H), 7.60-7.62 (m, 2H), 7.26-7.54 (m, 12H), 6.01 (d, *J* = 2.4 Hz, 1H), 5.60 (d, *J* = 2.4 Hz, 1H), 4.90 (s, 1H), 1.20 (s, 12H), 0.82 (s, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 139.8, 136.64, 136.58, 135.5 (2C), 135.4 (2C), 134.3, 132.6, 130.9, 129.03, 128.95, 128.5, 127.7, 127.6 (2C), 127.5 (2C), 126.1, 125.4, 125.2, 124.9, 124.8, 83.6 (2C), 33.9, 25.1 (2C), 24.3 (2C), -3.4. The boron-bound carbon was not detected due to quadrupolar relaxation. HRMS (EI) *m/z* calcd for C₃₂H₃₅BO₂Si (*M*⁺): 490.2499, found: 490.2502.

(S)-3-(Diphenylmethylsilyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-butene [(S)-6h, entry 8]. According to the procedure described for entry 1, **2h** (26 mg) and **1d** (130 mg) were reacted at 0 °C for 28 h. The product **6h** was isolated by bulb-to-bulb distillation (146 mg, 96%). The enantiomeric excess was determined to be 80% by the procedure described below (see Scheme S5). (S)-**6h** (80% ee): $[\alpha]_D^{24}$ -71.4 (*c* 1.25, CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ 7.59-7.61 (m, 2H), 7.52-7.56 (m, 2H), 7.29-7.41 (m, 6H), 5.85 (d, *J* = 3.2 Hz, 1H), 5.40 (dd, *J* = 3.2, 0.8 Hz, 1H), 2.68 (dq, *J* = 7.2, 0.8 Hz, 1H), 1.21 (d, *J* = 7.2 Hz, 3H), 1.14 (s, 6H), 1.11 (s, 6H), 0.55 (s, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 136.8, 135.8, 135.2 (4C), 129.0, 128.9, 127.5 (4C), 126.6, 83.2 (2C), 24.7 (4C), 24.4, 15.4, -5.9. The boron-bound carbon was not detected due to quadrupolar relaxation. Anal. Calcd for C₂₃H₃₁BO₂Si: C, 73.01; H, 8.26. Found: C, 72.86; H, 8.30.

Scheme S5. Transformation of **6h** for determination of the ee

Determination of the enantiomeric excess of 6h (Scheme S5): To determine the enantiomeric excess, **6h** was transformed to an alcohol **17** via the reactions shown in Scheme S5. According to the procedure described for the transformation of **6a** (Scheme S1), **6h** (72 mg, 0.19 mmol) was hydrogenated by the reaction with TsNHNH₂ in the presence of Et₃N, and the resulting alkylboron compounds **16** was oxidized by H₂O₂ under basic conditions. Isolation by PTLC (hexane/AcOEt = 4:1) gave **17** as a mixture of diastereomers (47 mg, 92 % from **6h**). HPLC analysis of the mixture indicated the enantiomeric excess of 80% [column: DAICEL OD-H (4.6 mm x 250 mm); eluent: hexane/2-propanol = 98:2; flow rate: 0.6 mL/min; detection wavelength: 220 nm; T_R = 13.5 (minor enantiomer of diastereomer A), 15.0 (major enantiomer of diastereomer A), 19.5 (both enantiomers of diastereomer B) min]. **17**: A 62:38 mixture of diastereomers A and B. ¹H NMR (400 MHz, CDCl₃) δ 7.58-7.61 (m, 4H for A and 4H for B), 7.35-7.41 (m, 6H for A and 6H for B), 4.08 (dq, *J* = 6.4, 4.0 Hz, 1H for A), 3.96 (quintet, *J* = 4.0 Hz, 1H for B), 1.68 (dq, *J* = 7.6, 6.4 Hz, 1H for B), 1.51 (dq, *J* = 7.6, 4.0 Hz, 1H for A), 1.24-1.39 (br s, 1H for A and 1H for B), 1.21 (d, *J* = 6.4 Hz, 3H for A), 1.16 (d, *J* = 6.4 Hz, 3H for B), 1.12 (d, *J* = 7.6 Hz, 3H for A), 1.07 (d, *J* = 7.6 Hz, 3H for B), 0.67 (s, 3H for A), 0.66 (s, 3H for B). HRMS (EI) *m/z* calcd for C₁₇H₂₀Si (M⁺-H₂O): 252.1334, found: 252.1336.

(S)-3-(Diphenylmethylsilyl)-5-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-pentene [(S)-6i, entry 9]. According to the procedure described for entry 1, **2i** (69 mg) and **1d** (130 mg) were reacted at 0 °C for 28 h. The product **6i** was isolated by bulb-to-bulb distillation (170 mg, 91%). The enantiomeric excess was determined to be 82% by the procedure described below (see Scheme S6). (S)-**6i** (82% ee): $[\alpha]_D^{24}$ -47.2 (*c* 1.28, CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ 7.50-7.54 (m, 2H), 7.25-7.45 (m, 10H), 7.17-7.21 (m, 1H), 7.11-7.13 (m, 2H), 5.97 (d, *J* = 3.2 Hz, 1H), 5.48 (d, *J* = 3.2 Hz, 1H), 2.75 (ddd, *J* = 13.6, 9.0, 4.4 Hz, 1H), 2.63 (dd, *J* = 12.4, 2.8 Hz, 1H), 2.47 (ddd, *J* = 13.6, 8.4, 8.0 Hz, 1H), 2.00-2.10 (m, 1H), 1.88-1.97 (m, 1H), 1.18 (s, 6H), 1.17 (s, 6H), 0.54 (s, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 142.7, 136.7, 135.8, 135.2 (2C), 135.1 (2C), 129.0, 128.8, 128.7 (2C), 128.1 (2C), 128.0, 127.5 (2C), 127.4 (2C), 125.5, 83.2 (2C), 35.0, 31.5, 30.7, 24.8 (2C), 24.7 (2C), -5.68. The boron-bound carbon was not detected due to quadrupolar relaxation. HRMS (CI) *m/z* calcd for C₃₀H₃₈BO₂Si (MH⁺): 469.2734, found: 469.2737.

Scheme S6. Transformation of **6i** for determination of the ee

Determination of the enantiomeric excess of 6i (Scheme S6): To determine the enantiomeric excess, **6i** was transformed to urethane **20** via the reactions shown in Scheme S6. According to the procedure described for the transformation of **6a** (Scheme S1), **6i** (97 mg, 0.21 mmol) was hydrogenated by the reaction with TsNHNH₂ in the presence of Et₃N, and the resulting alkylboron compounds **18** was oxidized by H₂O₂ under basic conditions. Isolation by PTLC (hexane/AcOEt = 3:1) gave **19** as a mixture of diastereomers (56 mg, 75 % from **6i**). **19**: A 59:41 mixture of diastereomers A and B. ¹H NMR (400 MHz, CDCl₃) δ 7.56-7.63 (m, 4H for A and 4H for B), 7.34-7.44 (m, 6H for A and 6H for B), 7.16-7.28 (m, 3H for A and 3H for B), 7.00-7.04 (m, 2H for A and 2H for B), 4.14-4.20 (m, 1H for A and 1H for B), 2.49-2.73 (m, 2H for A and 2H for B), 1.84-2.00 (m, 2H for A and 2H for B), 1.65 (dt, *J* = 7.2, 4.8 Hz, 1H for B), 1.56 (dt, *J* = 5.6, 4.0 Hz, 1H for A), 1.22-1.38 (br s, 1H for A and 1H for B), 1.26 (d, *J* = 6.4 Hz, 3H for A), 1.20 (d, *J* = 6.4 Hz, 3H for B), 0.74 (s, 3H for A), 0.72 (s, 3H for B). HRMS (EI) *m/z* calcd for C₂₄H₂₆Si (M⁺-H₂O): 342.1804, found: 342.1806.

Then **19** (5.1 mg, 0.014 mmol) was reacted with 3,5-dinitrophenyl isocyanide (4.4 mg, 0.021 mmol) in pyridine (0.20 mL) at 80 °C. After cooling the mixture to room temperature, volatile materials were removed in vacuo and then the residue was extracted with hexane to give **20** as a mixture of diastereomers. HPLC analysis of the product indicated the enantiomeric excess of 82% [column: Sumichiral OA-4000 (4.6 mm x 250 mm); eluent: hexane/ $\text{ClCH}_2\text{CH}_2\text{Cl}$ /EtOH = 15:5:1; flow rate: 0.6 mL/min; detection wavelength: 220 nm; T_R = 17.3 (major enantiomer of diastereomer A), 20.1 (minor enantiomer of diastereomer A), 21.0 (minor enantiomer of diastereomer B), 22.8 (major enantiomer of diastereomer B) min].

(R)-5-Acetoxy-3-(dimethylphenylsilyl)-4,4-dimethyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-pentene [(R)-3j, entry 10]. According to the procedure described for entry 1, **2j** (37 mg) and **1a** (69 mg) were reacted at -10 °C for 96 h. The product **3j** was isolated by bulb-to-bulb distillation (99 mg, 91%). The enantiomeric excess was determined to be 90% by 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 = 7.9 (minor), 8.5 (major) min]. **(R)-3j**: ^1H NMR (400 MHz, CDCl_3) δ 7.52-7.54 (m, 2H), 7.29-7.32 (m, 3H), 5.95 (br s, 1H), 5.59 (br s, 1H), 3.80 (d, J = 10.6 Hz, 1H), 3.67 (d, J = 10.6 Hz, 1H), 2.35 (br s, 1H), 2.00 (s, 3H), 1.22 (s, 6H), 1.21 (s, 6H), 0.93 (s, 3H), 0.91 (s, 3H), 0.49 (br s, 3H), 0.29 (br s, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ 171.0, 134.0 (2C), 132.0 (br), 128.4, 127.4 (3C), 83.4 (2C), 72.7, 37.8 (br), 26.3, 24.9, 24.8 (2C), 24.5 (3C), 20.9, -0.3, -0.9. The boron-bound carbon was not detected due to quadrupolar relaxation. Anal. Calcd for $\text{C}_{23}\text{H}_{37}\text{BO}_4\text{Si}$: C, 66.34; H, 8.96. Found: C, 66.55; H, 9.04.

(3S,5R)-4,4-dimethyl-5-(diphenylmethylsilyl)-1-phenyl-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(trimethylsilyloxy)-6-hepten-1-yne [(3S,5R)-6k, eq 1]. According to the procedure described for entry 1 in Table 2, **(R)-2k** (>99% ee, 100 mg) and **1d** (94 mg) were reacted at 20 °C for 90 h in the presence of 5.0 mol% of $\text{Pd}(\text{dba})_2$ and 6.0 mol% of **(R)-5g**. Column chromatography (hexane/ Et_2O = 14:1) following bulb-to-bulb distillation afforded **6k** (163 mg, 92%). The diastereomers ratio was determined to be 94:6 by HPLC analysis [column: NACALAI TESQUE COSMOSIL 5SL-II (4.6 mm x 250 mm); eluent: hexane/ $\text{ClCH}_2\text{CH}_2\text{Cl}$ = 85:15; flow rate: 0.6 mL/min;

detection wavelength: 220 nm; T_R = 26.9 (minor), 29.0 (major) min]. **(3S,5R)-6k**: ^1H NMR (400 MHz, CDCl_3) δ 7.71-7.74 (m, 2H), 7.59-7.61 (m, 2H), 7.46-7.52 (m, 2H), 7.30-7.33 (m, 6H), 7.19-7.24 (m, 3H), 5.90 (br s, 1H), 5.71 (br s, 1H), 4.14 (br s, 1H), 3.52 (br s, 1H), 1.16 (s, 12H), 1.08 (s, 3H), 1.02 (s, 3H), 0.91 (s, 3H), 0.08 (br s, 9H). ^{13}C NMR (75 MHz, CDCl_3) δ 141.7 (br, C-B), 139.6, 138.5, 135.0 (2C), 134.9 (2C), 132.9 (br), 131.5 (2C), 128.7, 128.2, 128.1 (2C), 127.8, 127.5 (2C), 127.1 (2C), 123.7, 90.4, 86.2, 83.4 (2C), 70.2 (br), 43.7 (br), 24.7 (3C), 24.5 (2C), 23.7, 22.0 (br), 0.21 (3C), -2.9. Anal. Calcd for $\text{C}_{37}\text{H}_{49}\text{BO}_3\text{Si}_2$: C, 73.00; H, 8.11. Found: C, 72.96; H, 8.29 (A mixture of diastereomers was used for elemental analysis).

(3R,5R)-4,4-dimethyl-5-(diphenylmethylsilyl)-1-phenyl-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(trimethylsilyloxy)-6-hepten-1-yne [(3R,5R)-6k, eq 2]. According to the procedure described for entry 1 in Table 2, **(S)-2k** (>99% ee, 100 mg) and **1d** (94 mg) were reacted at 20 °C for 90 h in the presence of 5.0 mol% of $\text{Pd}(\text{dba})_2$ and 6.0 mol% of **(R)-5g**. Column chromatography (hexane/ Et_2O = 14:1) following bulb-to-bulb distillation afforded **6k** (161 mg, 91%). The diastereomers ratio was determined to be 88:12 by HPLC analysis [column: NACALAI TESQUE COSMOSIL 5SL-II (4.6 mm x 250 mm); eluent: hexane/ $\text{ClCH}_2\text{CH}_2\text{Cl}$ = 85:15; flow rate: 0.6 mL/min; detection wavelength: 220 nm; T_R = 27.4 (major), 30.4 (minor) min]. **(3R,5R)-6k**: ^1H NMR (300 MHz, CDCl_3) δ 7.73-7.76 (m, 2H), 7.49-7.54 (m, 4H), 7.35-7.39 (m, 3H), 7.25-7.30 (m, 3H), 7.18-7.20 (m, 3H), 5.81 (br s, 1H), 5.69 (d, J = 3.3 Hz, 1H), 4.28 (br s, 1H), 3.42 (br s, 1H), 1.16 (br s, 6H), 1.13 (s, 6H), 0.992 (s, 3H), 0.987 (s, 3H), 0.89 (br s, 3H), 0.13 (s, 9H). ^{13}C NMR (75 MHz, CDCl_3) δ 138.7, 135.2 (2C), 134.7 (2C), 133.1 (br), 131.6 (2C), 128.5, 128.2 (2C), 128.1, 127.9, 127.5 (2C), 127.0 (2C), 123.7, 90.5, 85.9, 83.4 (2C), 70.7, 65.9, 42.9 (br), 24.8 (2C), 24.4 (2C), 23.4 (br), 22.9, 15.3, 0.26 (3C), -2.6 (br). 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 **(3S,5R)-6k**.

6. Synthetic utility of (*R*)-**6c**: Asymmetric synthesis of **8** by cyclization/Suzuki-Miyaura cross coupling (eq. 3).

A CH_2Cl_2 solution of Me_3SiOBn (50 mg, 0.28 mmol) and (*R*)-**6c** (93% ee, 93 mg, 0.21 mmol) was cooled to -78°C . To the mixture was added Me_3SiOTf (62 mg, 0.28 mmol) slowly and the resulting solution was stirred at -78°C for 6 h. Aqueous NaHCO_3 solution was added to the mixture at -78°C , and resulting mixture was warmed to room temperature. The organic layer was extracted with ether and the extract was washed with water. After drying with anhydrous MgSO_4 , crude **7** was obtained by removal of the volatile materials. Crude **7** was applied to next Suzuki-Miyaura cross coupling without purification. **7**: ^1H NMR (400 MHz, CDCl_3) δ 7.31–7.35 (m, 4H), 7.23–7.28 (m, 1H), 6.28 (dd, $J = 2.0, 1.6$ Hz, 1H), 4.62 (d, $J = 12.2$ Hz, 1H), 4.50 (d, $J = 12.2$ Hz, 1H), 3.74 (t, $J = 6.6$ Hz, 1H), 2.74 (ddd, $J = 11.8, 6.6, 1.6$ Hz, 1H), 2.47 (ddd, $J = 11.8, 6.6, 2.0$ Hz, 1H), 1.28 (s, 12H), 1.09 (s, 3H), 1.08 (s, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ 156.6, 139.1, 128.2 (2C), 127.3 (2C), 127.2, 87.4, 83.2 (2C), 71.6, 48.6, 38.6, 26.7, 24.9 (2C), 20.4. The boron-bound carbon was not detected due to quadrupolar relaxation.

A toluene (0.29 mL) solution of **7**, ethyl 4-bromobenzoate (74 mg, 0.32 mmol), $\text{Pd}(\text{OAc})_2$ (0.96 mg, 0.0043 mmol), 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl (S-PHOS, 3.5 mg, 0.0086 mmol), K_3PO_4 (91 mg, 0.43 mmol), and H_2O (0.29 mL) was heated at 100°C for 1 h. After cooling of the mixture to room temperature, the mixture was filtrated by passing through celite and resulting solution was concentrated. The mixture was then purified by PTLTLC (hexane/ $\text{Et}_2\text{O} = 85:15$) to give **8** (44 mg, 58% from **6c**). HPLC analysis indicated the enantiomeric excess of 93% [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; $T_R = 18.7$ (*R*, minor), 24.1 (*S*, major) min]. Absolute configuration of the product was assigned to *S* by the method described below (see Scheme S7). **8**: ^1H NMR (400 MHz, CDCl_3) δ 7.97–8.00 (m, 2H), 7.34–7.45 (m, 6H), 7.27–7.31 (m, 1H), 6.09 (dd, $J = 2.0, 1.2$ Hz, 1H), 4.69 (d, $J = 12.0$ Hz, 1H), 4.61 (d, $J = 12.0$ Hz, 1H), 4.38 (q, $J = 6.8$ Hz, 2H), 3.93 (t, $J = 6.8$ Hz, 1H), 3.01 (ddd, $J = 15.6, 6.8, 1.2$ Hz, 1H), 2.78 (ddd, $J = 15.6, 6.8, 2.0$ Hz, 1H), 1.41 (t, $J = 6.8$ Hz, 3H), 1.22 (s, 3H), 1.19 (s, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ 166.4, 140.6, 138.8, 137.8, 135.8, 129.6 (2C), 128.8, 128.3

(2C), 127.4, 127.3 (2C), 125.1 (2C), 86.3, 72.0, 60.9, 47.9, 37.6, 27.4, 21.1, 14.4. HRMS (CI) m/z calcd for $\text{C}_{23}\text{H}_{26}\text{O}_3$ (M^+): 350.1882, found: 350.1885.

Scheme S7. Assignment of the absolute configuration of **8**

Assignment of the absolute configuration of **8 (Scheme S7):** A EtOH (1.0 mL) solution of Pd/C (5.0 mg) was stirred for 30 minutes at room temperature under hydrogen atmosphere. The EtOH solution of **8** (15 mg, 0.043 mmol) was added to the mixture and heated at 65°C for 10 h. After removal of the catalyst by filtration, the clued mixture was purified by PTLTLC (hexane/ $\text{Et}_2\text{O} = 1:1$) affording saturated alcohol **21** (6.3 mg, 56%). The absolute configuration of **21** was assigned by the method reported by Trost.⁹ According to the similar procedure described for Scheme S2, **21** was transformed to ester **22** which was subjected to the ^1H NMR analysis. The observed upfield shift of the signals for the methyl groups at C2 position of the major diastereomers as well as that for the proton on C5 of minor diastereomers indicated that the major isomer had a 1*S*,4*S* configuration. Accordingly, the absolute configuration of **8** was assigned as *S*. The stereochemistry also indicated that the proposed transition state (**T1**) is reasonable for the cyclization of (*R*)-**6c**.

7. Synthetic utility of (*R*)-**6b**: Asymmetric synthesis of **10** by cyclization/Suzuki-Miyaura cross coupling (eq. 4).

Benzaldehyde (38 mg, 0.36 mmol) and **6b** (92% ee, 157 mg, 0.27 mmol) were dissolved in CH_2Cl_2 and the mixture

was cooled to -78 °C. Me₃SiOTf (79 mg, 0.36 mmol) was slowly added to the mixture and the resulting mixture was stirred at -78 °C for 4 h. Aqueous NaHCO₃ solution was added to the mixture and the resulting mixture was extracted with ether. After drying with anhydrous MgSO₄, removal of the volatile materials afforded crude **9** that was applied to next Suzuki-Miyaura cross coupling without purification. **9**: ¹H NMR (400 MHz, CDCl₃) δ 7.38-7.40 (m, 2H), 7.30-7.34 (m, 2H), 7.22-7.26 (m, 1H), 6.48 (br s, 1H), 4.47 (dd, *J* = 9.6, 2.6 Hz, 1H), 3.72 (dd, *J* = 12.0, 0.8 Hz, 1H), 3.52 (d, *J* = 12.0 Hz, 1H), 2.74 (ddd, *J* = 16.4, 9.6, 2.4 Hz, 1H), 2.67 (dd, *J* = 16.4, 2.6 Hz, 1H), 1.26 (s, 6H), 1.24 (s, 6H), 1.21 (s, 3H), 1.07 (s, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 155.6, 144.0, 128.2 (2C), 127.1, 126.0 (2C), 83.44, 83.38 (2C), 78.7, 41.2, 38.8, 26.7, 24.9 (2C), 24.7 (2C), 24.4. The boron-bound carbon was not detected due to quadrupolar relaxation.

A toluene solution of **9**, ethyl 4-bromobenzoate (94 mg, 0.41 mmol), Pd(dba)₂ (3.2 mg, 5.5 μmol), S-PHOS (4.5 mg, 0.011 mmol), K₃PO₄ (117 mg, 0.55 mmol), and H₂O (0.037 mL) was heated at 100 °C for 10 h. After cooling of the mixture to room temperature, the mixture was filtrated by passing through celite and resulting solution was concentrated. The mixture was then purified by PTLC (hexane/Et₂O = 85:15) to give **10** (68 mg, 71% from **6b**). HPLC analysis indicated the enantiomeric excess of 92% [column: DAICEL OD-H (4.6 mm x 250 mm); eluent: hexane/2-propanol = 95:5; flow rate: 0.6 mL/min; detection wavelength: 220 nm; T_R = 11.3 (major), 19.8 (minor) min]. Absolute configuration of the major isomer was assumed to *R* based on the transition state **T2**, which was made on the basis of (1) well-established *anti*-S_E' stereochemical course of the reaction of α-chiral allylsilanes and (2) assumed trans configuration of the intermediary oxonium ion. **10**: ¹H NMR (400 MHz, CDCl₃) δ 7.93-7.96 (m, 2H), 7.40-7.43 (m, 2H), 7.34-7.37 (m, 2H), 7.26-7.31 (m, 3H), 5.89-5.90 (m, 1H), 4.72 (dd, *J* = 10.0, 2.0 Hz, 1H), 4.37 (q, *J* = 7.2 Hz, 2H), 3.82 (dd, *J* = 12.0, 0.8 Hz, 1H), 3.68 (d, *J* = 12.0 Hz, 1H), 3.25 (ddd, *J* = 16.4, 10.0, 2.4 Hz, 1H), 2.80 (dd, *J* = 16.4, 2.0 Hz, 1H), 1.40 (t, *J* = 7.2 Hz, 3H), 1.32 (s, 3H), 1.13 (s, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 166.4, 150.0, 143.6, 141.5, 136.9, 129.5 (2C), 128.5, 128.4 (2C), 127.4, 125.9 (2C), 125.7 (2C), 82.4, 78.9, 60.9, 42.4, 39.3, 27.4, 24.9, 14.4. HRMS (EI) *m/z* calcd for C₂₃H₂₆O₃ (M⁺): 350.1882, found: 350.1883.

8. ¹H and ¹³C NMR spectra of the compounds that do not have elemental analysis data

¹H and ¹³C NMR spectra of **6a**, **6b**, **6g**, **6i**, **8**, and **10** are shown in following pages.

STANDARD IN OBSERVE

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature

Mercury-400BB "varian"

Relax. delay 1.500 sec

Pulse width 12.0000 sec

Acq. time 1.500 sec

Width 6006.0 Hz

16 repetitions

OBSERVE H1, 400.4437673 MHz

DATA PROCESSING

FT size 65536

Total time 1 min, 31 sec

13C OBSERVE

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature

GEMINI-300BB "varian2"

Relax. delay 1.158 sec

Time 45.000000 sec

Acq. 0.843 sec

Width 19000.0 Hz

52 repetitions

OBSERVE CH3, 75.4515698 MHz

DECOUPLE H1, 300.0687335 MHz

Power 35 dB

continuously on

WALTZ16 Modulated

DATA PROCESSING

Line Resolving 1.000

FT size 32768

Total time 43 min, 45 sec

STANDARD 11 OBSERVE

Pulse sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-400MB "varian"
Relax. delay 1.500 sec
Pulse 45.0 degrees
Acq. time 3.900 sec
Width 6008.0 Hz
F1 400.1463664 MHz
OBSERVE F1 400.4437664 MHz
DATA PROCESSING
PT size 65536
Total time 1 min, 31 sec

13C OBSERVE

Pulse Sequence: a2pul
Solvent: CDCl3
Ambient temperature
GEMINI-300DB "varian2"

Relax. delay 1.158 sec
Pulse 45.0 degrees
Acq. time 0.842 sec
Nuc 13C
Nuc 1H 400.136 MHz
192 repetitions

OBSERVE C13, 75.4519721 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 43 min, 45 sec

STANDARD 1H OBSERVE
 Pulse Sequence: #2pul
 Solvent: CDCl3
 Ambient temperature
 Mercury-400BB "varian"
 Relax. delay 1.500 sec
 Acq. time 3.500 sec
 Width 6006.0 Hz
 16 repetitions
 OBSERVE M1, 400.4437666 MHz
 DATA PROCESSING
 FT size 65536
 Total time 1 min, 42 sec

13C OBSERVE

Pulse sequence: s2pul
Solvent: CDCl₃
Ambient temperature
GEMINI-300DB "varian2"

Relax. delay 1.158 sec
Pulse 45.0 degrees
Acq. time 0.042 sec
Width 19000.0 Hz
376 repetitions

OBSERVE C13, 75.4519721 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 43 min, 45 sec

STANDARD 1H OBSERVE

Pulse Sequence: #2pul
Solvent: CDCl3
Ambient temperature
File: phenetp1
Mercury-400BB "varian"

Relax. delay 1.500 sec
Pulse 45.0 degrees
Acq. time 0.300 sec
Mk1 6006 Hz
16 repetitions

OBSERVE H1, 400.4437671 MHz
DATA PROCESSING
FT size 65536
Total time 1 min, 42 sec

13C OBSERVE

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature

GEMINI-300DB "varian2"

Relax. delay 1.158 sec

Pulse 45.0 degrees

Acq. time 0.842 sec

NUC1 13C

NUC2 13C

204

OBSERVE C13, 75.4515688 MHz

DECOUPLE H1, 300.0687355 MHz

Power 36 dB

continuously on

HALT-16 modules

DATA PROCESSING

Line broadening 1.00 Hz

FT size 32768

Total time 52 min, 51 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

Width 6006.0 Hz

16 repetitions

OBSERVE H1, 400.4437671 MHz

DATA PROCESSING

FT size 65536

Total time 1 min, 42 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

Width 6000.0 Hz

1638400000

OBSERVE IN 400.4437675 MHz

DATA PROCESSING

FT size 65536

Total time 1 min, 42 sec

13C OBSERVE

Pulse Sequence: s2pul

Solvent: CDCl3

Ambient temperature

GBMIN-300SB "varia2"

Relax. delay 1.158 sec

Pulse 45.0 degrees

Acq. time 0.842 sec

Width 19000.0 Hz

904 repetitions

OBSERVE C13, 75.4519675 MHz

PROCPROF F4, 300.0687335 MHz

Relax. delay 1.158 sec

continuously on

WALTZ-16 modulated

DATA PROCESSING

Line broadening 1.0 Hz

FT size 32768

Total time 43 min, 45 sec