Supporting Information

Nickel-Catalyzed *trans*-Alkynylboration of Alkynes via Activation of a Boron-Chlorine Bond

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1. General

All reactions were carried out under an atmosphere of nitrogen or argon with magnetic stirring. ^1H and ^{13}C NMR spectra were recorded on a Varian Mercury vx400 or a Gemini-2000 spectrometer at ambient temperature. ^1H NMR data are reported as follows: chemical shift in ppm downfield from tetramethylsilane (δ scale), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sex = sextet, m = multiplet, and br = broad), coupling constant (Hz), and integration. ^{13}C NMR chemical shifts are reported in ppm downfield from tetramethylsilane (δ scale). All ^{13}C NMR spectra were obtained with complete proton decoupling. High-resolution mass spectra were recorded on a JEOL JMS-HX110A (FAB) or a JEOL JMS-SX102A (EI) spectrometer. IR spectra were recorded on a FTIR SHIMADZU DR-8000 spectrometer. Preparative TLC was performed with silica gel 60PF₂₅₄ (Merck). Column chromatography was performed with Ultra Pure Silca Gel 230-400 mesh (SILICYCLE).

Anhydrous dioxane (Wako) was purchased from the commercial source. Toluene was dried and deoxygenized using an alumina/catalyst column system (GlassContour Co.). Ni(cod)₂ (Aldrich), iodobenzene (Wako), pinacol (TCI), KF (Wako), tricyclohexylphosphine (Aldrich), trimethylphosphine (Aldrich), triphenylphosphine (Wako), tris(4-methoxyphenyl)phosphine (Aldrich), tris(p-trifluoromethylphenyl)phosphine (Strem), and 1,4-bis(diphenylphosphino)ethane (dppe, Kanto) trimethylphosphine (Aldrich) and DMAP (Wako) were used as received from the commercial sources. Tributylalkynylstannanes (**2a-2c**) were prepared from tributyltin chloride (Wako) and lithium acetylides. Tributylvinylstannane (Aldrich), pyridine (Wako), acetic anhydride (Wako), were purchased from the commercial sources and distilled before use. Pd(PPh₃)₄¹ and chloro boryl ethers² (**1a-1f**) were prepared according to the literature methods.

2. Experimental Procedures

Procedures for the synthesis of chloro(diisopropylamino)boryl ethers of alkynols

Representative Procedure 1 (chloro(diisopropylamino)boryl ethers of primary alkynols)

Synthesis of 1c (entry 5): A mixture of boric acid (415 mg, 6.71 mmol) and 6-methyl-5-hepten-3-yn-1-ol (3.0 g, 24.2 mmol) in toluene (15 mL) was stirred under reflux for 12 h with removal of water by a Dean-Stark trap. Evaporation of the solvent followed by bulb-to-bulb distillation (180-230 °C/0.5 mmHg) yielded tris(6-methyl-5-hepten-3-yn-1-oxy)borane (2.90 g, 99% based on boric acid). A mixture of the trialkoxyborane (2.9 g, 7.62 mmol), boron trichloride dimethylsulfide complex (737 mg, 4.11 mmol), and chlorobis(diisopropylamino)borane (2.89 g, 11.7 mmol) was heated in toluene (3 mL) with stirring at 80 °C for 16 h. Bulb-to-bulb distillation (120-150 °C/1 mmHg) yielded **1c** (5.21g, 85%).

Representative Procedure 2 (chloro(diisopropylamino)boryl ethers of secondary alkynols)

Synthesis of 1e (entry 7): A solution of dichloro(diisopropylamino)borane 1.50 g (8.24 mmol) and triethylamine 1.23 mL (8.80 mmol) in THF (16 mL) was cooled to -78 °C. 4-heptyne-2-ol (897 mg, 8.0 mmol) was added dropwise to the solution over 10 min at -78 °C. The reaction mixture was stirred for 5 h, while the reaction temperature was gradually raised to room temperature. After further stirring for 7 h at room temperature, hexane (10 mL) was added, resulting in precipitation of ammonium salt, which was washed twice with hexane. The combined filtrate

⁽¹⁾ Coulson, D. R. *Inorg. Synth.* **1972**, *13*, 121.

⁽²⁾ Suginome, M.; Yamamoto, A.; Murakami, M. J. *Organomet. Chem.* **2005**, accessible on the web.

and washings were evaporated in vacuo. Bulb-to-bulb distillation (100–150 °C/5.0 mmHg) gave **1e** 1.80 g (87% yield).

General procedure for the trans-alkynylboration of alkyne (Table 1)

To a solution of Ni(cod)₂ (1.1 mg, 0.004 mmol), triphenylphosphine (4.2 mg, 0.016 mmol), and dibenzylether (internal standard) in toluene (250 µL) were added chloroboryl ether **1** (0.20 mmol) and alkynyltributylstannane (0.20 mmol) at room temperature. The mixture was heated at 80 °C for 24 h and cooled to room temperature. An aliquot (ca 5 µL) of the solution was taken from the mixture by syringe and subjected to a ¹H NMR measurement for determination of NMR yields of **3** after evaporation of the volatile materials under vacuum. To the rest of the solution were added pinacol (200 µL, 2.0 M THF solution), acetic anhydride (50 µL, 0.53 mmol), pyridine (50 µL, 0.62 mmol) and DMAP (3.0 mg, 0.024 mmol). The mixture was stirred at 50 °C for 24 h and cooled to room temperature. To the mixture were added 4.0 M KF aq (1.0 mL) and then ether (300 µL). The resulting biphasic suspension was filtered through Celite and extracted with ether 4 times. The organic layer was dried over magnesium sulfate and evaporated. The crude product was purified by preparative TLC (hexane/ether = 3/1) to give **4**. The products **4** are stable under an inert atmosphere, but gradually decomposes on storage in air at room temperature for days.

Procedure for the trans-alkynylboration on a larger scale (2.5 mmol scale)

Synthesis of **4aa** (Table 1, entry 1): To a solution of Ni(cod)₂ (13.8 mg, 0.05 mmol) and triphenylphosphine (52.5 mg, 0.20 mmol) in toluene (1.0 mL) were added chloroboryl ether **1a** (609 mg, 2.5 mmol) and tributyl(phenylethynyl)stannane **2a** (978 mg, 2.5 mmol) at room temperature. The mixture was heated at 80 °C for 22 h and cooled to room temperature. To the solution were added pinacol (5.0 mmol, 2.5 mL, 2.0 M THF solution), acetic anhydride (625 µL, 6.63 mmol), pyridine (625 µL, 7.75 mmol) and DMAP (30 mg, 0.24 mmol). The mixture was stirred at 50 °C for 10 h and cooled to room temperature. To the mixture were added water (3.0 mL) and KF (145 mg, 2.5 mmol). The resulting biphasic suspension was filtered through Celite and extracted with ether 2 times. The organic layer was dried over magnesium sulfate and evaporated. The crude product was purified by column chromatography (hexane/ether = 9/1) to give **4aa** (781 mg, 85%).

General procedure for the alkynylboration-Suzuki-Miyaura coupling sequence (Scheme 3)

Compound **3ea** was prepared in a 0.15 mmol scale according to the general procedure given above. To the crude reaction mixture containing **3ea** were added Pd(PPh₃)₄ (8.7 mg, 0.0075 mmol),

organic halide (0.225 mmol), 5N NaOH aq (100 μ L) and dioxane (100 μ L). The reaction mixture was stirred at 50 °C for 24 h and cooled to room temperature. A solution of 4N KF aq (100 μ L) was added, and the resulting biphasic suspension was filtered through a pad of celite. The organic layer was washed with water and dried over magnesium sulfate. Crude material was subjected to preparative TLC (hexane/ether = 8/3) to afford a coupling product.

Synthesis of the nickel complex *trans*-8 (eq 2)

To a solution of Ni(cod)₂ (55 mg, 0.20 mmol) and trimethylphosphine (45.5 μ L, 0.44 mmol) in toluene (200 μ L) was added chloroboryl ether **1g** (63.9 mg, 0.20 mmol) at room temperature. The reaction mixture was stirred at room temperature for 24 h. Volatile materials were removed under reduced pressure. Residual solid was washed with pentane (300 μ L) four times and dried in vacuo, affording nickel complex *trans*-**8** as yellow solid (32 mg, 30 % yield).

3. Detail of the single-crystal X-ray analysis

A single-crystal of *trans*-**8** suitable for X-ray analysis was obtained from the reaction mixture (toluene solution), which was left undisturbed after the reaction. The single crystal was mounted on a glass fiber. All measurements were made on a Rigaku-RAXIS imaging plate area detector with graphite-monochromated MoK α (λ = 0.7107 Å) radiation. Details of crystal and data collection parameters are shown in Table.

Recryst. solvent	toluene
Formula	C ₂₄ H ₄₅ BCINONiP ₂
Crystal size [mm]	0.40•0.30•0.30
FW	530.54
Crystal system	triclinic
Space group	P-1 (no. 2)
<i>a</i> [Å]	10.031(4)
<i>b</i> [Å]	11.740(5)
<i>c</i> [Å]	14.711(7)
α [deg]	103.30(2)
β [deg]	103.09(2)
γ [deg]	111.77(1)
<i>V</i> [Å ³]	1469.5(1)
<i>Z</i>	2
ρ_{calcd} [g cm ⁻³]	1.199
$2\theta_{\text{max}}$ [deg]	27.48

μ [cm ⁻¹]	0.875
Independent refl.	6650
Observed refl.	5162
No. of parameters	434
GOF	2.297
<i>R</i> 1	0.028
<i>wR</i> 2	0.032

4. Spectral data for new compounds

(Z)-1-Acetoxy-3-(4,4,5,5-tetramethyl[1,3,2]dioxaborolan-2-yl)-4-ethyl-6-phenylhex-3-en-5-yne (4aa): ¹H NMR (CDCl₃) δ 1.17 (t, *J* = 7.2 Hz, 3H), 1.29 (s, 12H), 2.02 (s, 3H), 2.60 (q, *J* = 7.2 Hz, 2H), 2.81 (t, *J* = 6.8 Hz, 2H), 4.18 (t, *J* = 6.8 Hz, 2H), 7.30-7.35 (m, 3H), 7.42-7.48 (m, 2H), ¹³C NMR (CDCl₃) δ 14.4, 21.2, 24.8, 28.9, 33.7, 64.1, 83.3, 89.3, 96.6, 123.5, 128.2, 128.3, 131.6, 141.4, 171.2, ¹¹B NMR (CDCl₃) δ 30.0, IR (neat) 2197, 1740 cm⁻¹. FABHRMS calcd. for C₂₂H₂₉BO₄ (M⁺): 368.2159. Found: 368.2160.

(Z)-1-Acetoxy-3-(4,4,5,5-tetramethyl[1,3,2]dioxaborolan-2-yl)-4-ethylnon-3-en-5-yne (4ab): ¹H NMR (CDCl₃) δ 0.90 (t, *J* = 7.2 Hz, 3H), 0.96 (t, *J* = 7.2 Hz, 3H), 1.15 (s, 12H), 1.46 (sex, *J* = 7.2 Hz, 3H), 1.92 (s, 3H), 2.25 (t, *J* = 7.2 Hz, 2H), 2.36 (q, *J* = 7.2 Hz, 2H), 2.58 (t, *J* = 7.2 Hz, 2H), 3.98 (t, *J* = 7.2 Hz, 2H) ¹³C NMR (CDCl₃) δ 13.5, 14.2, 21.1, 21.6, 22.3, 24.7, 29.2, 33.2, 64.2, 80.6, 83.1, 98.0, 142.4, 171.1 ¹¹B NMR (CDCl₃) δ 30.2, IR (neat) 2209, 1742 cm⁻¹. Anal. calcd. for C₁₉H₃₂BO₄: C, 68.27; H, 9.35. Found: C, 68.06; H, 9.13.

(Z)-1-Acetoxy-3-(4,4,5,5-tetramethyl[1,3,2]dioxaborolan-2-yl)-4-ethyl-6-trimethylsilylhex-3-en-5-yne (4ac): ^1H NMR (CDCl_3) δ 0.19 (s, 9H), 1.08 (t, J = 7.6 Hz, 3H), 1.26 (s, 12H), 2.02 (s, 3H), 2.47 (q, J = 7.6 Hz, 2H), 2.71 (t, J = 7.2 Hz, 2H), 4.10 (t, J = 7.2 Hz, 2H) ^{13}C NMR (CDCl_3) δ -0.22, 14.2, 21.1, 24.7, 28.6, 33.5, 64.0, 83.2, 101.8, 104.7, 141.3, 171.0 ^{11}B NMR (CDCl_3) δ 29.7, IR (neat) 2137, 1742 cm^{-1} . HRMS(FAB) calcd. for $\text{C}_{19}\text{H}_{34}\text{BO}_4\text{Si}$ ($\text{M}+\text{H}^+$): 365.2319. Found: 365.2319.

(Z)-1-Acetoxy-3-(4,4,5,5-tetramethyl[1,3,2]dioxaborolan-2-yl)-4,6-diphenylhex-3-en-5-yne (4ba): ^1H NMR (CDCl_3) δ 1.18 (s, 12H), 2.06 (s, 3H), 3.00 (t, J = 6.8 Hz, 2H), 4.33 (t, J = 6.8 Hz, 2H), 7.30-7.36 (m, 3H), 7.45-7.50 (m, 2H) ^{13}C NMR (CDCl_3) δ 21.1, 24.6, 34.4, 63.4, 83.7, 88.6, 97.0, 123.2, 127.8, 128.2, 128.3, 128.5, 131.6, 135.6, 140.3, 171.1 ^{11}B NMR (CDCl_3) δ 30.4, IR (neat) 2197, 1740 cm^{-1} . HRMS(EI) calcd. for $\text{C}_{26}\text{H}_{29}\text{BO}_4$ (M^+): 416.2159. Found: 416.2157.

(Z)-1-Acetoxy-3-(4,4,5,5-tetramethyl[1,3,2]dioxaborolan-2-yl)-4-(2-phenyl-1-ethyn-1-yl)-6-methylhept-3,5-diene (4ca): ^1H NMR (CDCl_3) δ 1.30 (s, 12H), 1.84 (s, 3H), 2.02 (s, 3H), 2.06 (s, 3H), 2.89 (t, J = 6.8 Hz, 2H), 4.22 (t, J = 6.8 Hz, 2H), 6.42 (s, 1H), 7.30-7.35 (m, 3H), 7.44-7.48 (m,

2H) ^{13}C NMR (CDCl_3) δ 19.7, 21.1, 24.8, 27.5, 33.1, 64.0, 83.4, 88.7, 97.6, 123.5, 123.8, 128.2, 128.3, 131.3, 134.2, 137.7, 171.1 ^{11}B NMR (CDCl_3) δ 30.2, IR (neat) 2195, 1740 cm^{-1} . HRMS (FAB) calcd. for $\text{C}_{24}\text{H}_{31}\text{BO}_4$ (M^+): 394.2315. Found: 394.2325.

(Z)-1-Acetoxy-3-(4,4,5,5-tetramethyl[1,3,2]dioxaborolan-2-yl)-1,4,6-triphenylhex-3-en-5-yne (4da): ^1H NMR (CDCl_3) δ 1.18 (s, 12H), 2.09 (s, 3H), 3.13 (dd, J = 13.2, 5.6 Hz, 1H), 3.25 (dd, J = 13.2, 8.4 Hz, 1H), 6.12 (dd, J = 8.4, 5.6 Hz, 1H), 7.25-7.38 (m, 10H), 7.39-7.48 (m, 5H) ^{13}C NMR (CDCl_3) δ 21.4, 24.6, 24.7, 42.3, 75.8, 83.6, 89.1, 97.1, 123.3, 126.5, 127.69, 127.74, 128.2, 128.3, 128.6, 131.5, 136.0, 140.4, 140.8, 170.1 ^{11}B NMR (CDCl_3) δ 30.2, IR (neat) 2195, 1732 cm^{-1} . HRMS(FAB) calcd. for $\text{C}_{32}\text{H}_{33}\text{BO}_4$ (M^+): 492.2472. Found: 492.2474.

(Z)-2-Acetoxy-4-(4,4,5,5-tetramethyl[1,3,2]dioxaborolan-2-yl)-5-ethyl-7-phenylhept-4-en-6-yne (4ea): ^1H NMR (CDCl_3) δ 1.16 (t, J = 7.2 Hz, 3H), 1.26 (d, J = 6.0 Hz, 3H), 1.30 (s, 12H), 2.00 (s, 3H), 2.54 (dq, J = 13.2, 7.2 Hz, 1H), 2.62 (dq, J = 13.2, 7.2 Hz, 1H), 2.70 (dd, J = 12.8, 6.0 Hz, 1H), 2.79 (dd, J = 12.8, 7.2 Hz, 1H), 5.12 (sex, J = 6.4 Hz, 1H), 7.29-7.35 (m, 3H), 7.43-7.48 (m, 2H) ^{13}C NMR (CDCl_3) δ 14.4, 20.0, 21.5, 24.76, 24.82, 29.0, 40.6, 71.1, 83.3, 89.8, 96.3, 123.6, 128.1, 128.3, 131.5, 140.6, 170.6 ^{11}B NMR (CDCl_3) δ 30.6, IR (neat) 2195, 1736 cm^{-1} . HRMS(FAB) calcd. for $\text{C}_{23}\text{H}_{32}\text{BO}_4$ ($\text{M}+\text{H}^+$): 383.2394. Found: 383.2390.

(Z)-1-Acetoxy-4-(4,4,5,5-tetramethyl[1,3,2]dioxaborolan-2-yl)-5-methyl-7-phenylhept-4-en-6-yne (4fa): ^1H NMR (CDCl_3) δ 1.29 (s, 12H), 1.80 (quint, $J = 7.2$ Hz, 2H), 1.98 (s, 3H), 2.20 (s, 3H) 2.55 (t, $J = 7.2$ Hz, 2H), 4.09 (t, $J = 7.2$ Hz, 2H), 7.29-7.35 (m, 3H), 7.42-7.47 (m, 2H) ^{13}C NMR (CDCl_3) δ 21.0, 22.3, 24.8, 28.7, 30.8, 64.6, 83.2, 90.5, 95.5, 123.5, 128.1, 128.2, 131.5, 132.1, 171.2 ^{11}B NMR (CDCl_3) δ 30.2, IR (neat) 2195, 1740 cm^{-1} . HRMS (FAB) calcd. for $\text{C}_{22}\text{H}_{29}\text{BO}_4$ (M^+): 368.2159. Found: 368.2163.

(E)-1-Acetoxy-1,4-diphenyl-3-(4,4,5,5-tetramethyl[1,3,2]dioxaborolan-2-yl)hex-3,5-diene (5): ^1H NMR (CDCl_3) δ 0.98 (s, 12H), 2.08 (s, 3H), 2.82 (dd, $J = 13.2, 6.0$ Hz, 1H), 3.06 (dd, $J = 13.2, 8.4$ Hz), 4.78 (d, $J = 17.2$ Hz, 1H), 5.22 (d, $J = 10.4$ Hz, 1H), 5.94 (dd, $J = 8.4, 6.0$ Hz, 1H), 7.00 (dd, $J = 17.2, 10.4$ Hz, 1H), 7.06-7.11 (m, 2H), 7.21-7.30 (m, 4H), 7.32-7.37 (m, 2H), 7.38-7.42 (m, 2H) ^{13}C NMR (CDCl_3) δ 21.3, 24.5, 37.7, 75.9, 83.0, 119.9, 126.5, 126.7, 127.4, 127.7, 128.3, 129.8, 134.6, 140.6, 141.3, 151.3, 170.1 ^{11}B NMR (CDCl_3) δ 30.5, IR (neat) 1740 cm^{-1} . HRMS(FAB) calcd. for $\text{C}_{26}\text{H}_{32}\text{BO}_4$ ($\text{M}+\text{H}^+$): 419.2394. Found: 419.2395.

(E)-5-Ethyl-4,7-diphenylhept-4-en-6-yn-2-ol (6) ^1H NMR (CDCl_3) δ 1.13 (t, $J = 7.2$ Hz, 3H), 1.24 (d, $J = 6.0$ Hz, 3H), 2.16 (q, $J = 7.2$ Hz, 2H), 2.87 (dd, $J = 13.2, 5.2$ Hz), 3.04 (dd, $J = 13.2, 8.0$ Hz, 1H), 3.77-3.85 (m, 1H), 7.15-7.20 (m, 2H), 7.26-7.39 (m, 6H), 7.47-7.52 (m, 2H) ^{13}C NMR (CDCl_3) δ 13.8, 23.3, 26.6, 47.4, 66.9, 89.4, 94.1,

123.6, 124.3, 127.1, 128.0, 128.1, 128.3, 131.4, 140.8, 144.4 IR (neat) 3350, 2199 cm^{-1} . HRMS(EI) calcd. for $\text{C}_{21}\text{H}_{22}\text{O}$ (M^+): 290.1671 Found: 290.1671.

(1E, 3E)-4-Ethyl-1,6-diphenyl-3-(2-hydroxypropyl)hex-1,3-dien-5-yne (7): yellow solid, m.p. 85.5 – 87.0; ^1H NMR (CDCl_3) δ 1.26 (t, J = 7.2 Hz, 3H), 1.35 (d, J = 6.4 Hz, 3H), 2.58 (q, J = 7.2 Hz, 2H), 2.92-3.02 (m, 2H), 4.19 (sex, J = 7.2 Hz, 1H), 6.79 (d, J = 16.4 Hz, 1H), 7.23-7.30 (m, 2H), 7.30-7.38 (m, 5H), 7.44-7.50 (m, 4H) ^{13}C NMR (CDCl_3) δ 13.9, 23.6, 25.4, 41.0, 68.3, 91.4, 96.9, 123.6, 125.2, 126.2, 126.6, 127.8, 128.1, 128.3, 128.7, 130.5, 131.3, 137.4, 139.4. HRMS(EI) calcd. for $\text{C}_{23}\text{H}_{24}\text{O}$ (M^+): 316.1827 Found: 316.1827.

Nickel complex trans-8: ^1H NMR (C_6D_6) δ 1.05 (t, J = 3.6 Hz, 18H), 1.45 (s, 6H), 3.11 (sep, J = 6.4 Hz, 2H), 3.32 (s, 2H), 7.01 (t, J = 7.6 Hz, 1H), 7.13 (d, J = 7.6 Hz, 2H), 7.68 (d, J = 7.6 Hz, 2H) ^{13}C NMR (C_6D_6) δ 14.6 (t, $J_{\text{C-P}}$ = 13.9 Hz) 23.1, 23.9, 31.1, 56.2, 78.2, 126.0, 128.3, 128.5, 148.4, ^{11}B NMR (CDCl_3) δ 26.6 (br), Anal. calcd. for $\text{C}_{24}\text{H}_{45}\text{BClNiOP}_2$: C, 54.33; H, 8.55, N, 2.64. Found: C, 54.10; H, 8.37, N, 2.75.

5. Summary of the nOe experiments

NOe experiments were carried out for the stereochemical assignment of the alkynylboration products. The curved arrows indicate the observed nOe, and the dotted arrows indicate the protons between which no nOe was observed. Only selected nOes are shown.

Compound 3ea. The following result suggested cis orientation of the ethyl group and the diisopropylaminoboryl group.

Compounds 4. No nOes were observed between allylic protons of **4**. Relatively weak nOes were found for the pinacol methyls and H²s. These also indicate that *trans*-addition took place, although not being decisive.

Compound 5. NOe was observed for the allylic protons, strongly indicating that *trans*-addition had taken place.

Compounds 6 and 7. The compounds derived from Suzuki-Miyaura coupling show NOEs between the protons of the ethyl group and incoming organic groups. These results also indicate *trans*-alkynylboration had taken place.

STANDARD 18 OBSERVE

Pulse Sequence: zgpg1
Solvent: CDCl3
Acidant Temperature
Nucleus: 400MHz 13C/variant

Relax. delay 1.500 sec
Pulse 45.0 degrees
Acq. time 3.500 sec
Relax. 6000.0 Hz
1.00000000
OBSERVE: RL 400.447677 MHz
DATA PROCESSING
FT also 55536
Total time 1 min, 31 sec

1.294
1.185
1.166
2.019
1.564
2.809
2.610
2.592
4.196
4.178
4.161
7.479
7.459
7.455
7.325
7.313
7.308
7.260

12.35
3.27
3.07
2.00
1.96
2.16
3.29

ppm

CC(C)(C)OC(=O)C(C)(C)C#CC1=CC=CC=C1

S11

¹³C OBSERVE
 Pulse Sequence: zgpg30
 Solvent: CDCl₃
 Ambient Temperature
 GMSINVT-300WB "gamma2"
 Relax. delay 1.158 sec
 Pulse 45.0 degrees
 Acq. time 0.842 sec
 Width 19000.0 Hz
 3800 repetitions
 OBSERVE CH: 13-451961 MHz
 PROCESSOR: 13-300-007335 MHz
 Power 16 dB
 continuously on
 WATER-16 modulated
 DATA PROCESSING
 Line broadening 1.0 Hz
 FT size 32768
 Total time 638 hr, 20 min, 1 sec

NMR of Compound **4aa** (entry 1 in Table 1)

CC(C)OC(=C(C#CSi(C)(C)C)C)B1OC(C)(C)OC1(C)C

¹³C NMR of Compound **4ac** (entry 3 in Table 1)

¹H NMR of Compound **4ba** (entry 4 in Table 1)

```
Pulse Sequence: szpul
Solvent: CDCl3
Ambient temperature
GEMINI-300BH "varian2"
```

Pulse delay 1.188 nsec
 Pulse 45.0 degrees
 Acq. time 0.842 sec
 Width 19000.0 Hz
 208 repetitions
 OBSERVE CH1, 75.413698 MHz
 DECOUPLE CH1, 300.068735 MHz
 Power: 36 dB
 continuously on
 WALTZ16 modulated
 DAPA PROCESSING
 Line broadening 1.0 Hz
 gamma alias 33768
 Total time 39 min, 13 sec

S16

¹H NMR of Compound **4ca** (entry 5 in Table 1)

13C OBSERVE

Pulse Sequence: zgpg30

Solvent: CDCl3

Acquire Temperature: 300.2 K

Offset: 300.137 MHz

Relax. delay: 1.158 sec

Pulse 45.0 degrees

Acquire Time: 0.450 sec

Relax. delay: 0.450 sec

Width: 13000.0 Hz

1144 experiments

OBSERVE: CL3, 75.451975 MHz

PROBHD: H1, 300.0687338 MHz

Power: 36 dB

continuously on

WALTZ-16 modulated

DATA PROCESSING

Line broadening: 1.0 Hz

Gamma: 1.000000

Gamma2: 1.000000

Total time: 8 hr, 23 min, 0 sec

^{13}C NMR of Compound **4ca** (entry 5 in Table 1)

¹H NMR of Compound **4da** (entry 6 in Table 1)

¹³C NMR of Compound **4da** (entry 6 in Table 1)

¹H NMR of Compound **4ea** (entry 7 in Table 1)

¹³C NMR of Compound **4ea** (entry 7 in Table 1)

STANDARD 1H OBSERVE

Pulse Sequence: #2pul.

Solvent: CDCl₃
Ambient temperature

ANDREAS TEMPERALURE
Mercury-400BB "Varian"

Relax. delay 1.500 sec
Pulse 45.0 degrees

Acq. time 3.500 sec

Width 6006.0 Hz
16 repetitions

OBSERVE H1, 400.44376
DATA PROCESSINGDATA PROCESSING
RT 0120 65536

Total time 1 min, 31 sec

¹H NMR of Compound **4fa** (entry 8 in Table 1)

¹³C NMR of Compound **4fa** (entry 8 in Table 1)

¹H NMR of Compound 5 (a mixture of *E*- and *Z*-isomers (83:17) after isolation)

^{13}C NMR of Compound **5** (pure (*E*)-isomer after purification by HPLC)

¹³C NMR of Compound 6 (Scheme 3)

¹H NMR of Compound 7 (Scheme 3)

^{13}C NMR of Compound 7 (Scheme 3)