Supporting Information

Stereoselective 1,4-Silaboration of 1,3-Dienes Catalyzed by Nickel Complexes

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General. All reactions were carried out under a nitrogen atmosphere. All materials were obtained from commercial suppliers. Toluene and methylene chloride (CH_2Cl_2) were distilled under nitrogen from calcium hydride. Bis(acetylacetonato)nickel(II), $Ni(acac)_2$, was dried in vacuo (110 °C/1.0 mmHg) before use. Column chromatography was performed with aluminium oxide 90 (70–230 mesh, E. Merck, Darmstadt). The ^{1}H and ^{13}C NMR spectra were recorded on Varian VXR-200 and Gemini 2000 equipped with 4.7 T and 7.0 T magnets, respectively. The proton chemical shifts were referenced to internal residual $CHCl_3$. The carbon chemical shifts were referenced to the carbon signal of $CDCl_3$. The ^{11}B and ^{29}Si NMR spectra were recorded on a JEOL JNM-A400 equipped with 9.4 T magnet. The boron and silicon chemical shifts were referenced to the external standards trimethoxyborane ($B(OMe)_3$) and tetramethylsilane ($SiMe_4$), respectively. Mass spectra were recorded on a JEOL JMS-HX110A.

(*Z*)-2,3-Dimethyl-1-(dimethylphenylsilyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-butene (3a). To a mixture of $Ni(acac)_2$ (25.7 mg, 0.10 mmol) and 2,3-dimethyl-1,3-butadiene (330 mg, 4.0 mmol) in a Schlenk tube was added DIBAH 0.2 M solution in toluene (1.0 mL) at 0 °C, and then the mixture was stirred for 30 min. To the mixture was added **1** (521 mg, 2.0 mmol), and then the mixture was heated at 80 °C for 24 h. Evaporation of volatile materials remained residue, which was subjected to bulb-to-bulb distillation to afford **3a** (619 mg, 90%). **3a**: ^{1}H NMR

($CDCl_3$) δ 0.29 (s, 6H), 1.23 (s, 12H), 1.52-1.56 (m, 3H), 1.60 (s, 2H), 1.65-1.68 (m, 3H), 1.77 (s, 2H), 7.30-7.37 (m, 3H), 7.49-7.57 (m, 2H); ^{13}C NMR ($CDCl_3$) δ –2.3, 19.5 (br), 20.1, 21.1, 24.7, 24.8, 82.9, 122.0, 123.5, 127.7, 128.7, 133.6, 140.2; ^{11}B NMR ($CDCl_3$) δ 14.7; ^{29}Si NMR ($CDCl_3$) δ –4.3. HRMS Calcd for $C_{20}H_{33}BO_2Si$: 344.2343. Found: 344.2330.

(*Z*)-2-Methyl-1-(dimethylphenylsilyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-butene (3b). ^{1}H NMR ($CDCl_3$) δ 0.31 (s, 6H), 1.25 (s, 12H), 1.52 (d J = 7.5 Hz, 2H), 1.57-1.64 (m, 3H), 1.75 (s, 2H), 5.11-5.22 (m, 1H), 7.32-7.40 (m, 3H), 7.50-7.58 (m, 2H); ^{13}C NMR ($CDCl_3$) δ –2.4, 12.8 (br), 22.1, 24.7, 26.1, 83.1, 116.8, 127.7, 128.9, 132.5, 133.6, 139.8. HRMS Calcd for $C_{19}H_{31}BO_2Si$: 330.2186. Found: 330.2176.

(*Z*)-2-Methyl-4-(dimethylphenylsilyl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-butene (4b). ^{1}H NMR ($CDCl_3$) δ 0.27 (s, 6H), 1.24 (s, 12H), 1.60-1.71 (m, 5H), 1.75 (d, J = 1.2 Hz, 2H), 5.09-5.20 (m, 1H), 7.32-7.40 (m, 3H), 7.49-7.57 (m, 2H); ^{13}C NMR ($CDCl_3$) δ –3.3, 16.3 (br), 17.4, 24.7, 25.5, 83.0, 118.4, 127.7, 128.8, 130.4, 133.6, 139.6. HRMS Calcd for $C_{19}H_{31}BO_2Si$: 330.2186. Found: 330.2199.

(*Z*)-2-Methyl-1-(dimethylphenylsilyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-pentene (3c). ^{1}H NMR ($CDCl_3$) δ 0.31 (s, 6H), 0.97 (d, J = 7.5 Hz, 3H), 1.23 (s, 12H), 1.59 (d, J = 1.1 Hz, 3H), 1.65-1.98 (m, 3H), 5.01 (d, J = 10.2 Hz, 1H), 7.31-7.40 (m, 3H), 7.49-7.61 (m, 2H); ^{13}C NMR ($CDCl_3$) δ –2.4, 16.2, 17.9 (br), 22.2, 24.5, 24.6, 26.2, 82.8, 125.3, 127.7, 128.8, 130.5, 133.6, 139.9. HRMS Calcd for $C_{20}H_{33}BO_2Si$: 344.2343. Found: 344.2351.

(*Z*)-2-Methyl-4-(dimethylphenylsilyl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-pentene (4c). ^{1}H NMR ($CDCl_3$) δ 0.23 (s, 3H), 0.25 (s, 3H), 0.95 (d, J = 7.2 Hz, 3H), 1.23 (s,

12H), 1.42-1.73 (m, 2H), 1.75 (d, J = 1.5 Hz, 3H), 1.84-1.97 (m, 1H), 4.90-4.99 (m, 1H), 7.31-7.39 (m, 3H), 7.48-7.57 (m, 2H); ^{13}C NMR ($CDCl_3$) δ –5.7, –4.3, 15.3, 16.5 (br), 21.7, 24.6, 24.7, 25.8, 83.0, 126.5, 127.5, 128.7, 129.1, 134.1, 138.5. HRMS Calcd for $C_{20}H_{33}BO_2Si$: 344.2343. Found: 344.2354.

(*Z*)-1-(Dimethylphenylsilyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-butene (3d). A Schlenk tube equipped with a glass tube (500 mL) was charged with $Ni(acac)_2$ (20.6 mg, 0.080 mmol) and toluene (0.80 mL). The reaction vessel was evacuated and flushed with gaseous 1,3-butadiene. To the mixture was added DIBAH 0.2 M solution in toluene (0.80 mL), and then the mixture was stirred for 30 min. To the mixture was added **1** (521 mg, 2.0 mmol), and then the mixture was heated at 80 °C for 24 h. Evaporation of volatile materials remained residue, which was subjected to bulb-to-bulb distillation to afford **3d** (619 mg, 90%). **3d**: ^{1}H NMR ($CDCl_3$) δ 0.28 (s, 6H), 1.25 (s, 12H), 1.55-1.80 (m, 4H), 5.33-5.52 (m, 2H), 7.32-7.40 (m, 3H), 7.49-7.58 (m, 2H); ^{13}C NMR ($CDCl_3$) δ –3.4, 11.2 (br), 17.0, 24.7, 83.1, 122.6, 124.7, 127.7, 128.9, 133.6, 139.2. HRMS Calcd for $C_{18}H_{29}BO_2Si$: 316.2030. Found: 316.2034.

(1*R,2*R**)-2,3-Dimethyl-2-(dimethylphenylsilyl)methyl-1-phenyl-3-buten-1-ol (5a).** A mixture of **3a** (341 mg, 0.99 mmol), benzaldehyde (105 mg, 0.99 mmol), and CH_2Cl_2 (5.0 mL) was stirred at room temperature for 24 h. To the mixture was added triethanolamine (148 mg, 0.99 mmol), and then the mixture was stirred at room temperature for 24 h. The mixture was purified by column chromatography on alumina (activity II–III) with CH_2Cl_2 to afford **5a** (281 mg, 87%). **5a**: ^{1}H NMR ($CDCl_3$) δ 0.29-0.33 (m, 6H), 1.00 (s, 3H), 1.08-1.19 (m, 1H), 1.47 (d, J = 14.8 Hz, 1H), 1.74 (s, 3H), 2.08-2.36 (br, 1H), 4.47 (d, J = 1.6 Hz, 1H), 4.80-4.85 (m, 1H), 4.97-5.04 (m, 1H), 7.23-7.40 (m, 8H), 7.45-7.54 (m, 2H); ^{13}C NMR ($CDCl_3$) δ –0.6, –0.4, 21.0, 21.6, 21.7, 47.2, 79.5,

114.3, 127.2, 127.3, 127.7, 128.0, 128.6, 133.5, 140.6, 140.9, 149.3. Anal. Calcd for $C_{21}H_{28}OSi$: C, 77.72; H, 8.70. Found: C, 77.46; H, 8.75.

(1*S,2*R**)-2-(Dimethylphenylsilyl)methyl-1-phenyl-3-buten-1-ol (5d).** ^{1}H NMR ($CDCl_3$) δ 0.24 (s, 3H), 0.26 (s, 3H), 0.74 (dd, J = 14.7, 11.4 Hz, 1H), 1.06 (dd, J = 14.7, 3.0 Hz, 1H), 2.08 (d, J = 4.7 Hz, 1H), 2.48-2.66 (m, 1H), 4.55 (t, J = 4.7 Hz, 1H), 4.92-5.08 (m, 2H), 5.54 (ddd, J = 17.0, 10.3, 9.0 Hz, 1H), 7.17-7.45 (m, 10H); ^{13}C NMR ($CDCl_3$) δ –2.5, –1.9, 13.2, 16.5, 25.4, 46.1, 78.8, 126.9, 127.1, 127.7, 127.8, 128.7, 130.2, 133.7, 134.7, 139.7, 142.4. Anal. Calcd for $C_{19}H_{24}OSi$: C, 76.97; H, 8.16. Found: C, 76.92; H, 8.36.

(1*R,4*S**)-1-(Dimethylphenylsilyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-cyclohexene (7a).** To a mixture of $Ni(acac)_2$ (15.47 mg, 0.060 mmol), **6a** (192 mg, 2.4 mmol), and P(*c*-Hex)Ph_2 (32.2 mg, 0.12 mmol) in a Schlenk tube was added DIBAH 0.2 M solution in toluene (0.60 mL) at 0 °C, and then the mixture was stirred for 30 min. To the mixture was added **1** (309 mg, 1.2 mmol), and then the mixture was stirred at 80 °C for 24 h. Evaporation of volatile materials remained residue, which was subjected to bulb-to-bulb distillation to give **7a** (400 mg, 99%). **7a**: ^{1}H NMR ($CDCl_3$) δ 0.28 (s, 3H), 0.29 (s, 3H), 1.21 (s, 6H), 1.22 (s, 6H), 1.48-1.66 (m, 2H), 1.69-1.86 (m, 4H), 5.56-5.68 (m, 1H), 5.68-5.83 (m, 1H), 7.30-7.40 (m, 3H), 7.47-7.58 (m, 2H); ^{13}C NMR (CDCl3) δ –5.0, –4.9, 21.8 (br), 23.2, 23.7, 24.6, 24.7, 25.4, 83.0, 125.8, 126.6, 127.6, 128.8, 134.0, 138.4; ^{11}B NMR ($CDCl_3$) δ 14.6; ^{29}Si NMR ($CDCl_3$) δ –2.5. HRMS Calcd for $C_{20}H_{31}BO_2Si$: 342.2186. Found: 342.2178.

(1*R,4*R**)-1-(Dimethylphenylsilyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-cyclohexene (7a').** ^{1}H NMR ($CDCl_3$) δ 0.34 (s, 3H), 0.35 (s, 3H), 1.18 (s, 6H), 1.19 (s, 6H), 1.46-1.54 (m, 1H), 1.61-1.81 (m, 2H), 1.95-2.11 (m, 3H), 5.52-5.61 (m, 1H), 5.67-5.75 (m, 1H), 7.28-

7.36 (m, 3H), 7.51-7.58 (m, 2H); ^{13}C NMR ($CDCl_3$) δ –2.5, –2.4, 20.8 (br), 24.2, 24.8, 25.0, 25.1, 27.4, 82.9, 124.9, 127.6, 128.6, 129.8, 134.1, 140.1. HRMS Calcd for $C_{20}H_{31}BO_2Si$: 342.2186. Found: 342.2183.

(1*R,4*S**)-1-(Dimethylphenylsilyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-cycloheptene (7b).** ^{1}H NMR ($CDCl_3$) δ 0.29 (s, 6H), 1.25 (s, 12H), 1.35-2.08 (m, 8H), 5.67 (ddd, *J* = 10.9, 4.2, 1.8 Hz, 1H), 5.84 (ddd, *J* = 10.9, 5.8, 2.4 Hz, 1H), 7.30-7.42 (m, 3H), 7.47-7.59 (m, 2H); ^{13}C NMR ($CDCl_3$) δ –4.6, –4.5, 24.6, 24.7, 24.8 (br), 28.1, 28.2, 28.7, 32.1, 83.1, 127.6, 128.8, 131.4, 133.1, 133.9, 138.4. HRMS Calcd for $C_{21}H_{33}BO_2Si$: 356.2343.