Palladium-Catalyzed Asymmetric Hydrosilylation of 4-Substituted 1-Buten-3-ynes. Catalytic Asymmetric Synthesis of Axially Chiral Allenylsilanes

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Supporting Data

General. All manipulations were carried out under a nitrogen atmosphere. Nitrogen gas was dried by passage through P_2O_5. NMR spectra were recorded on a JEOL JNM LA-500 spectrometer (500 MHz for ^{1}H, 125 MHz for ^{13}C, and 202 MHz for ^{31}P). Chemical shifts are reported in δ ppm referenced to an internal tetramethylsilane standard for ^{1}H NMR and chloroform-*d* (δ 77.00) or benzene-d_6 (δ 128.39) for ^{13}C NMR, and external 85% H_3PO_4 standard for ^{31}P NMR. Optical rotations were measured with a JASCO DIP-370 polarimeter. HPLC analysis was performed on a JASCO PU-980 liquid chromatograph system with a chiral stationary phase column, Daicel Chiralpak OD-H. GLC analysis was performed on a Hewlett Packard HP6890 system with a chiral stationary phase column, CP-Chiralsil-Dex CB.

Preparation of 4-Substituted 1-Buten-3-ynes: 5,5-Dimethyl-1-hexen-3-yne (1a): The procedure of Sonogashira[1] has been modified slightly as follows: To a solution of 1.7 mL (24.4 mmol) of vinyl bromide, 0.57 g (0.8 mmol) of $PdCl_2(Ph_3P)_2$, and 0.08 g (0.4 mmol) of copper(I) iodide in 30 mL of triethylamine was added 2 mL of (16.2 mmol) of 3,3-dimethyl-1-butyne in an ice-bath, then temperature was raised to room temperature. After stirring for 12 h, the reaction mixture was diluted with pentane, filtered through celite, and the filter cake was washed with pentane. To an aqueous solution of 10% hydrochloric acid was added dropwise the resulting pentane solution in an ice-bath to remove triethylamine from organic layer. The organic layer was washed with aqueous ammonium chloride and water, pentane was evaporated under reduced pressure in an ice-bath. The crude

product was distilled under reduced pressure to give 1.0 g (59% yield) of the titled compound as a clear oil. ^{1}H NMR ($CDCl_3$) δ 1.25 (s, 9H), 5.36 (d, *J* = 11.3 Hz, 1H), 5.53 (d, *J* = 17.6 Hz, 1H), 5.79 (dd, *J* = 17.6, 11.3 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 27.83, 30.91, 77.74, 99.21, 117.64, 125.21. Anal. Calcd for C_8H_{12}: C, 88.82; H, 11.18. Found: C, 88.70; H, 11.43. **4-(2,4,6-Trimethylphenyl)-1-buten-3-yne (1b):** The titled compound was prepared in a manner similiar to that described above for the preparation of **1a**. The starting acetylene, 2-ethynyl-1,3,5-trimethylbenzene was prepared from 2',4',6'-trimethylacetophenone by Negishi's method[2] and used without further purification. An analytically pure sample was obtained by column chromatography (silica gel, hexane) as a clear oil. ^{1}H NMR ($CDCl_3$) δ 2.31 (s, 3H), 2.45 (s, 6H), 3.49 (s, 1H), 6.90 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 20.85, 21.27, 81.34, 84.49, 118.91, 127.54, 138.07, 140.78. Anal. Calcd for $C_{11}H_{12}$: C, 91.61; H, 8.39. Found: C, 91.60; H, 8.53. Yield of **1b** was 79% starting from 2',4',6'-trimethylacetophenone. A clear oil. ^{1}H NMR ($CDCl_3$) δ 2.31 (s, 3H), 2.43 (s, 6H), 5.52 (d, *J* = 11.2 Hz, 1H), 5.73 (d, *J* = 17.5 Hz, 1H), 6.13 (dd, *J* = 17.5, 11.2 Hz, 1H), 6.89 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 20.90, 21.28, 87.83, 95.68, 117.63, 119.84, 125.65, 127.54, 137.76, 140.15. Anal. Calcd for $C_{13}H_{14}$: C, 91.71; H, 8.29. Found: C, 92.00; H, 8.52. **4-(*tert*-Butyldimethylsilyl)-1-buten-3-yne (1c):** To a solution of 100 mL (200 mmol) of EtMgCl in THF was added 13.5 g (260 mmol) of 1-buten-3-yne in an ice-bath, and then a solution of 30.1 g (200 mmol) of *tert*-butyldimethylsilyl chloride in 50 mL of THF was added dropwise to the resulting reaction mixture in an ice-bath. After stirring for 1 h, 100 mL of 1 M hydrochloric acid was added. The mixture was extracted with ether, and the ether extracts were washed with water and dried over anhydrous magnesium sulfate. The crude product was purified by distillation (95 °C/15 mmHg) to give 18.3 g (55% yield) of the titled compound as a clear oil. ^{1}H NMR ($CDCl_3$) δ 0.14 (s, 6H), 0.96 (s, 9H), 5.50 (d, *J* = 11.3 Hz, 1H), 5.69 (d, *J* = 17.6 Hz, 1H), 5.83 (dd, *J* =17.6, 11.3 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ –4.68, 16.61, 26.07, 93.35, 104.37, 117.32, 127.83. Anal. Calcd for $C_{10}H_{18}Si$: C, 72.21; H, 10.91. Found: C, 72.01; H, 10.92.

Preparation of Chiral Ferrocenyl Compounds: (*S*)-*N*,*N*-Dimethyl-1-((*R*)-2-bromoferrocenyl)ethylamine: To a solution of 2.3 g (8.9 mmol) of (*S*)-*N*,*N*-dimethyl-1-ferrocenylethylamine[3] in 30 mL of ether was added dropwise 11.1 mL (10.7 mmol, 0.96 M in cyclohexane/hexane) of *sec*-butyllithium at room temperature. After stirring at room temperature for 2 h, the reaction mixture was cooled to –78 °C and then 2.1 mL (17.8 mmol) of 1,2-dibromotetrafluoroethane was added slowly. After 1 h, excess *sec*-butyllithium was quenched with aqueous sodium hydrogen carbonate. The mixture was extracted with ether, and the ether extracts were washed with water and dried over anhydrous magnesium sulfate. The crude product was purified by column chromatography (silica gel, hexane/ether/triethylamine (5/3/0.8)) to give 2.82 g (95% yield) of the titled compound as a yellow solid (diastereomeric ratio was 98/2). The diastereomerically pure compound was obtained by recrystallization from acetonitrile (2.52 g, 85% yield). $[\alpha]_D^{20}$ –8.6 (*c* 1.0, chloroform). ^{1}H NMR ($CDCl_3$) δ 1.52 (d, *J* = 6.6 Hz, 3H), 2.13 (s, 6H), 3.75 (q, *J* = 6.8 Hz, 1H), 4.09 (s, 1H), 4.13 (s, 1H), 4.15 (s, 5H), 4.45 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 16.73, 41.10, 56.04, 65.13, 65.63, 69.77, 71.16, 79.75, 87.33. Anal. Calcd for $C_{14}H_{18}BrFeN$: C, 50.04; H, 5.40; N, 4.17. Found: C, 49.91; H, 5.18; N, 4.25. **(*R*)-1-Bromo-2-((*S*)-1-methoxyethyl)ferrocene:** To a solution of 2.4 g (7.3 mmol) of (*S*)-*N*,*N*-dimethyl-1-((*R*)-2-bromoferrocenyl)ethylamine in 15 mL of acetonitrile was added 2 mL of methyl iodide. The reaction mixture was stirred at room temperature for 2 h, and then all volatiles were evaporated under reduced pressure. The remaining yellow residue was dissolved in 15 mL of methanol. After refluxing for 30 min, the reaction mixture was cooled to room temperature, and methanol was removed under reduced pressure. The mixture was extracted with ether, and the ether extracts were washed with aqueous ammonium chloride and dried over anhydrous magnesium sulfate. The crude product was purified by column chromatography (silica gel, hexane/ethyl acetate (10/1)) to give 2.2 g (94% yield) of the titled compound as an orange oil. $[\alpha]_D^{20}$ +13.4 (*c* 1.0, chloroform). ^{1}H NMR ($CDCl_3$) δ 1.63 (d, *J* = 6.3 Hz, 3H), 3.24 (s, 3H), 4.16 (s, 6H), 4.22 (s, 1H), 4.44 (q, *J* = 6.4 Hz, 1H), 4.48 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 19.82, 55.86, 64.66, 66.39, 70.23, 71.19, 72.68, 79.83, 87.33. Anal. Calcd for $C_{13}H_{15}BrFeO$: C, 48.34; H, 4.68. Found: C,

48.32; H, 4.71. **Bis[(*R*)-2-((*S*)-1-methoxyethyl)ferrocenyl]phenylphosphine ((*S*)-(*R*)-bisPPFOMe):** To a solution of 1.7 g (5.3 mmol) of (*R*)-1-bromo-2-((*S*)-1-methoxyethyl)ferrocene in 20 mL of THF was added dropwise 3.4 mL (5.3 mmol, 1.55 M in hexane) of *n*-butyllithium at –78 °C. After stirring at –78 °C for 1 h, 0.36 mL (2.65 mmol) of dichlorophenylphosphine was added slowly. The reaction mixture was refluxed for 2 h, and then hydrolyzed with aqueous ammonium chloride at room temperature. The mixture was extracted with ether, and the ether extracts were washed with water and dried over anhydrous magnesium sulfate. The crude product was purified by column chromatography (silica gel, hexane/ethyl acetate (10/1)) to give 1.13 g (72% yield) of the titled compound as an orange solid. $[\alpha]_D^{20}$ +447.4 (*c* 1.1, benzene). ^{1}H NMR (C_6D_6) δ 1.54 (d, *J* = 6.5 Hz, 3H), 1.70 (d, *J* = 6.4 Hz, 3H), 2.78 (s, 3H), 3.44 (s, 3H), 3.61 (s, 5H), 4.07 (s, 5H), 4.13 (t, *J* = 2.4 Hz, 1H), 4.16 (t, *J* = 2.4 Hz, 1H), 4.29 (m, 1H), 4.35 (m, 1H), 4.39 (m, 1H), 4.40 (m, 1H), 4.68 (qd, *J* = 6.5, 2.8 Hz, 1H), 4.95 (qd, *J* = 6.4, 2.9 Hz, 1H), 7.03-7.11 (m, 3H), 7.76-7.79 (m, 2H); ^{13}C NMR (C_6D_6) δ 20.20 (d, *J* = 3.1 Hz), 20.29, 54.90, 56.33, 68.71 (d, *J* = 6.2 Hz), 68.91, 69.45 (d, *J* = 4.1 Hz), 69.81, 70.31, 70.54, 71.40 (d, *J* = 4.2 Hz), 72.94 (d, *J* = 5.1 Hz), 73.68 (d, *J* = 8.3 Hz), 74.12 (d, *J* = 10.4 Hz), 77.84 (d, *J* = 16.5 Hz), 80.59 (d, *J* = 9.3 Hz), 95.12 (d, *J* = 23.8 Hz), 97.36 (d, *J* = 32.1 Hz), 128.06 (d, *J* = 9.3 Hz), 128.82 (d, *J* = 33.1 Hz), 135.09 (d, *J* = 23.8 Hz), 142.39 (d, *J* = 8.2 Hz); ^{31}P{^{1}H} NMR (C_6D_6) δ –44.27 (s). Anal. Calcd for $C_{32}H_{35}Fe_2O_2P$: C, 64.67; H, 5.94. Found: C, 64.68; H, 6.04.

Palladium-Catalyzed Asymmetric Hydrosilylation of 4-Substituted 1-Buten-3-ynes: The reaction conditions and results are summarized in Table 1. A typical procedure is given for entry 3. To a mixture of 3.7 mg (0.010 mmol) of $[PdCl(\pi\text{-}C_3H_5)]_2$, 18.8 mg (0.044 mmol) of chiral ligand (*S*)-(*R*)-PPFOMe, and 216 mg (2.0 mmol) of 5,5-dimethyl-1-hexen-3-yne (**1a**) was added 0.45 mL (4.4 mmol) of trichlorosilane at 20 °C. After the reaction mixture was stirred for 9 h, excess trichlorosilane was evaporated under reduced pressure. The crude product was distilled (bulb-to-bulb, 150 °C/15 mmHg) under reduced pressure to give 386 mg (79% yield) of allenyltrichlorosilane **2a** as a clear oil. **(*S*)-5,5-Dimethyl-4-trichlorosilyl-2,3-hexadiene (2a):** ^{1}H NMR ($CDCl_3$) δ 1.22 (s, 9H), 1.71

(d, J = 7.3 Hz, 3H), 5.32 (q, J = 7.3 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 12.98, 30.85, 35.29, 88.32, 105.59, 210.54. **(*S*)-1-(2,4,6-Trimethylphenyl)-1-trichlorosilyl-1,2-butadiene (2b):** ^{1}H NMR ($CDCl_3$) δ 1.80 (d, J = 7.3 Hz, 3H), 2.31 (br s, 6H), 2.36 (s, 3H), 5.41 (q, J = 7.3 Hz, 1H), 6.94 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 11.93, 22.90, 20.99 (br s), 21.23, 85.30, 96.21, 128.60, 129.53, 136.15 (br s), 136.38 (br s), 137.18, 211.56. **(*S*)-1-(*tert*-Butyldimethylsilyl)-1-trichlorosilyl-1,2-butadiene (2c):** ^{1}H NMR ($CDCl_3$) δ 0.22 (s, 3H), 0.24 (s, 3H), 0.96 (s, 9H), 1.69 (d, J = 7.3 Hz, 3H), 4.95 (q, J = 7.3 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ –4.67, –4.56, 11.53, 18.13, 26.51, 77.14, 86.69, 218.57.

Reaction of Allenyltrichlorosilanes 2 with Methyl Grignard Reagent: To a solution of 120 mg (0.5 mmol) of allenyl(trichloro)silane **2a** in 5 mL of ether was added dropwise 1 mL (3.0 mmol, 3.0 M in ether) of MeMgBr in an ice-bath, and then the reaction mixture was refluxed for 6 h. After cooling to room temperature, excess MeMgBr was hydrolyzed with aqueous ammonium chloride. The mixture was extracted with ether, and the extracts were washed with water and dried over anhydrous magnesium sulfate. The crude product was purified by preparative TLC (silica gel, hexane) to give 62 mg (68% yield) of allenyl(trimethyl)silane **3a** as a clear oil. **(*S*)-5,5-Dimethyl-4-trimethylsilyl-2,3-hexadiene (3a):** $[\alpha]_D^{20}$ +27.8 (c 1.0, chloroform) for 72% ee. ^{1}H NMR ($CDCl_3$) δ 0.15 (s, 9H), 1.09 (s, 9H), 1.61 (d, J = 6.8 Hz, 3H), 4.76 (q, J = 6.8 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 1.26, 13.96, 31.36, 34.70, 80.64, 106.75, 206.25. Anal. Calcd for $C_{11}H_{22}Si$: C, 72.44; H, 12.16. Found: C, 72.22; H, 12.45. **(*S*)-1-(2,4,6-Trimethylphenyl)-1-trimethylsilyl-1,2-butadiene (3b):** $[\alpha]_D^{20}$ –8.2 (c 1.4, chloroform) for 56% ee. ^{1}H NMR ($CDCl_3$) δ 0.13 (s, 9H), 1.68 (d, J = 7.0 Hz, 3H), 2.22 (br s, 3H), 2.27 (br s, 3H), 2.28 (s, 3H), 4.84 (q, J = 7.1 Hz, 1H), 6.88 (s, 2H); ^{13}C NMR ($CDCl_3$) δ –0.60, 12.83, 20.86, 20.88 (br s), 21.14 (br s), 78.20, 97.21, 128.09, 134.51, 134.77 (br s), 134.84, 134.98 (br s), 206.42. Anal. Calcd for $C_{16}H_{24}Si$: C, 78.62; H, 9.90. Found: C, 78.59; H, 9.80. **(*S*)-1-(*tert*-Butyldimethylsilyl)-1-trimethylsilyl-1,2-butadiene (3c):** $[\alpha]_D^{20}$ –5.8 (c 1.0, chloroform) for 61% ee. ^{1}H NMR ($CDCl_3$) δ 0.07 (s, 3H), 0.08 (s, 3H), 0.11 (s, 9H), 0.90 (s, 9H), 1.57 (d, J = 6.8 Hz, 3H), 4.31 (q, J = 6.8 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ

–4.22, –4.05, 0.50, 12.40, 17.96, 26.71, 69.87, 85.18, 213.25. Anal. Calcd for $C_{13}H_{28}Si_2$: C, 64.91; H, 11.73. Found: C, 65.09; H, 11.98.

Reaction of Allenyl(trichloro)silane 2 with Benzaldehyde in DMF: A mixture of 0.40 mmol of allenyl(trichloro)silane **2** and 30 μL (0.30 mmol) of benzaldehyde in 1 mL of DMF was stirred at 0 °C for 2 h, and then aqueous 1 M hydrochloric acid was added to quench the reaction. The aqueous layer was extracted with ether and dried over anhydrous magnesium sulfate. The crude product was purified by preparative TLC (silica gel, hexane/ethyl acetate (4/1)) to give a high yield of homopropargylic alcohols **4** and **5**. The diastereomeric ratio (**4**/**5**) was determined by ^{1}H NMR of the crude product. **(1*R*, 2*S*)-*syn*-1-Phenyl-2,5,5-trimethyl-3-hexyn-1-ol (4a):** $[\alpha]_D^{20}$ +22.4 (*c* 0.81, chloroform) for 72% ee. ^{1}H NMR ($CDCl_3$) δ 1.04 (d, *J* = 7.0 Hz, 3H), 1.16 (s, 9H), 2.06 (br s, 1H), 2.82 (qd, *J* = 7.0, 5.5 Hz, 1H), 4.65 (d, *J* = 5.5 Hz, 1H), 7.26-7.38 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 16.15, 27.32, 31.21, 34.32, 76.53, 79.57, 92.16, 126.58, 127.46, 127.87, 141.57. Anal. Calcd for $C_{15}H_{20}O$: C, 83.29; H, 9.32. Found: C, 83.54; H, 9.55. **(1*S*, 2*S*)-*anti*-1-Phenyl-2,5,5-trimethyl-3-hexyn-1-ol (5a):** $[\alpha]_D^{20}$ –30.7 (*c* 0.49, chloroform) for 72% ee. ^{1}H NMR ($CDCl_3$) δ 1.04 (d, *J* = 7.0 Hz, 3H), 1.22 (s, 9H), 2.73 (m, 1H), 4.40 (d, *J* = 7.1 Hz, 1H), 7.25-7.36 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 17.73, 27.40, 31.27, 35.65, 77.64, 78.95, 92.91, 126.72, 127.74, 128.11, 141.67. **(1*R*, 2*S*)-*syn*-2-Methyl-1-phenyl-4-(2,4,6-trimethylphenyl)-3-hexyn-1-ol (4b):** $[\alpha]_D^{20}$ +2.2 (*c* 1.2, chloroform) for 56% ee. ^{1}H NMR ($CDCl_3$) δ 1.28 (d, *J* = 6.9 Hz, 3H), 2.25 (s, 9H), 2.28 (br s, 1H), 3.19 (qd, *J* = 6.9, 6.3 Hz, 1H), 4.76 (d, *J* = 6.3 Hz, 1H), 6.81 (s, 2H), 7.29 (d, *J* = 7.2, 1H), 7.34 (t, *J* = 7.1 Hz, 2H), 7.43 (d, *J* = 7.0 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 16.57, 20.87, 21.21, 35.28, 76.88, 80.94, 98.62, 119.98, 126.67, 127.41, 127.72, 128.15, 137.13, 140.00, 141.73. Anal. Calcd for $C_{20}H_{22}O$: C, 86.29; H, 7.97. Found: C, 86.17; H, 8.24. **(1*S*, 2*S*)-*anti*-2-Methyl-1-phenyl-4-(2,4,6-trimethylphenyl)-3-hexyn-1-ol (5b):** $[\alpha]_D^{20}$ –51.5 (*c* 0.40, chloroform) for 56% ee. ^{1}H NMR ($CDCl_3$) δ 1.23 (d, *J* = 7.0 Hz, 3H), 2.26 (s, 3H), 2.33 (s, 6H), 2.61 (br s, 1H), 3.11 (qd, *J* = 7.0, 6.8 Hz, 1H), 4.58 (d, *J* = 6.8 Hz, 1H), 6.84 (s, 2H), 7.26 (d, *J* = 7.4, 1H), 7.35 (t, *J* = 7.6 Hz, 2H), 7.41 (d, *J* = 7.1 Hz,

2H); ^{13}C NMR ($CDCl_3$) δ 18.00, 21.02, 21.25, 36.57, 77.64, 81.56, 97.91, 119.78, 126.63, 127.52, 127.86, 128.26, 137.39, 140.05, 141.63. **(1*R*, 2*S*)-*syn*-4-(*tert*-Butyldimethylsilyl)-2-methyl-1-phenyl-3-hexyn-1-ol (4c):** $[\alpha]_D^{20}$ +13.6 (*c* 1.0, chloroform) for 61% ee. ^{1}H NMR ($CDCl_3$) δ 0.05 (s, 6H), 0.86 (s, 9H), 1.11 (d, *J* = 7.0 Hz, 3H), 2.26 (br s, 1H), 2.88 (qd, *J* = 7.0, 5.9 Hz, 1H), 4.67 (d, *J* = 5.7 Hz, 1H), 7.24-7.37 (m, 5H); ^{13}C NMR ($CDCl_3$) δ –4.57, 15.91, 16.41, 26.01, 35.33, 76.32, 85.58, 108.71, 126.55, 127.64, 128.02, 141.29. Anal. Calcd for $C_{17}H_{26}OSi$: C, 74.39; H, 9.55. Found: C, 74.22; H, 9.73. **(1*S*, 2*S*)-*anti*-4-(*tert*-Butyldimethylsilyl)-2-methyl-1-phenyl-3-hexyn-1-ol (5c):** $[\alpha]_D^{20}$ –36.4 (*c* 1.0, chloroform) for 61% ee. ^{1}H NMR ($CDCl_3$) δ 0.09 (s, 6H), 0.91 (s, 9H), 1.08 (d, *J* = 7.0 Hz, 3H), 2.80 (dq, *J* = 7.1, 7.0 Hz, 1H), 4.46 (d, *J* = 7.1 Hz, 1H), 7.24-7.34 (m, 5H); ^{13}C NMR ($CDCl_3$) δ –4.51, 16.46, 17.36, 26.05, 36.56, 77.35, 86.28, 108.17, 126.67, 127.89, 128.20, 141.29.

Desilylation of (1*R*, 2*S*)-*syn*-4-(*tert*-Butyldimethylsilanyl)-2-methyl-1-phenyl-3-hexyn-1-ol (4c) with TBAF: A mixture of 1.0 mL (1.0 mmol, 1 M in THF) of tetrabutylammonium fluoride and 50 mg (0.18 mmol) of **4c**, which was derived from hydrosilylation of **1c** with (*S*)-(*R*)-PPFOMe as a chiral ligand at 20 °C, in 2 mL of THF was stirred for 12 h. The reaction mixture was diluted with ether, washed with water, and dried with anhydrous magnesium sulfate. The crude product was purified by preparative TLC (silica gel, hexane/ethyl acetate (5/1)) to give 27 mg (95% yield) of (1*R*, 2*S*)-*syn*-2-methyl-1-phenyl-3-butyn-1-ol (**6**). $[\alpha]_D^{20}$ +22.6 (*c* 0.88, chloroform). The optical rotation value of **6** reported in the literature is +12.0 (c 1.0, chloroform) for 34% ee.[4] The enantioselectivity of **6** was 55% ee by HPLC analysis with a stationary phase column (Daicel Chiralcel OD-H).

Preparation of (*S*)-MTPA Ester of *syn*-1-Phenyl-2,5,5-trimethyl-3-hexyn-1-ol (4a):[5] A mixture of 70 mg (0.30 mmol) of (*S*)-2-methoxy-2-(trifluoromethyl)phenylacetic acid and 87 μL (1.0 mmol) of oxalyl chloride in 1.0 mL of dichloromethane was stirred at room temperature for 3 h, and then all volatiles were evaporated under reduced pressure. To the resulting material was added 1 mL of dichloromethane, 32 μL of pyridine, 2 mg of 4-(dimethylamino)pyridine, and 22 mg of **4a**, which was derived from

hydrosilylation of **1a** with (*S*)-(*R*)-PPFOMe as a chiral ligand at 20 °C, successively. After stirring at room temperature for 12 h, the reaction mixture was diluted with dichloromethane, washed with aqueous 1 M hydrochloric acid, and dried over anhydrous magnesium sulfate. The crude product was purified by preparative TLC (silica gel, hexane/ethyl acetate (10/1)) to give 14 mg of (*S*)-MTPA ester. The ratio of diastereomers was 5.9/1. Major isomer: ^{1}H NMR ($CDCl_3$) δ 1.08 (s, 9H), 1.14 (d, *J* = 7.0 Hz, 3H), 2.98 (m, 1H), 3.59 (s, 3H), 5.83 (d, *J* = 6.5 Hz, 1H), 7.21-7.46 (m, 10H). Minor isomer: ^{1}H NMR ($CDCl_3$) δ 1.03 (s, 9H), 1.06 (d, *J* = 7.0 Hz, 3H), 2.96 (m, 1H), 3.47 (s, 3H), 5.80 (d, *J* = 6.5 Hz, 1H), 7.21-7.46 (m, 10H).

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