

## Supporting Information

### **Rhodium-Catalyzed Asymmetric Rearrangement of Alkynyl Alkenyl Carbinols: Synthetic Equivalent to Asymmetric Conjugate Alkynylation of Enones**

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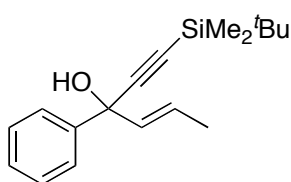
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**General.** All anaerobic and moisture-sensitive manipulations were carried out with standard Schlenk techniques under predried nitrogen or glovebox techniques under argon. NMR spectra were recorded on a JEOL JNM LA-500 spectrometer (500 MHz for  $^1\text{H}$ , 125 MHz for  $^{13}\text{C}$ ). Chemical shifts are reported in  $\delta$  ppm referenced to an internal  $\text{SiMe}_4$  standard for  $^1\text{H}$  NMR, chloroform-*d* ( $\delta$  77.00) for  $^{13}\text{C}$  NMR: the following abbreviations are used; s: singlet, d: doublet, t: triplet, q: quartet, m: multiplet. Elemental analyses were performed at the Microanalytical Center, Kyoto University. High-resolution mass spectra were obtained with a Bruker micrOTOF spectrometer.

**Materials.** Toluene and THF were purified by passing through a neutral alumina column under  $\text{N}_2$ . Rhodium complexes,  $[\text{Rh}(\text{OH})(\text{cod})]_2$ <sup>1</sup> was prepared according to the reported procedure. The starting alcohols **3** were prepared by the reaction of (*t*-butyldimethylsilyl)ethynyllithium with the corresponding enones, 1-phenyl-2-penten-1-one,<sup>2</sup> 1-(2-furanyl)-2-buten-1-one,<sup>3</sup> 1-phenyl-1,4-hexadien-3-one,<sup>4</sup> 3-penten-2-one,<sup>5</sup> and 1-indenone,<sup>6</sup> according to the reported procedures. 1-Phenyl-2-buten-1-one was purchased and used after purification by column chromatography (silica gel, hexane/ethyl acetate = 20/1).

**Preparation of compound 3a.** To a solution of (*t*-butyldimethylsilyl)ethynyllithium prepared from (*t*-butyldimethylsilyl)acetylene (934  $\mu\text{L}$ , 5.0 mmol) and *n*-butyllithium (3.2 mL, 5.1 mmol) in THF (5 mL) was added (*E*)-1-phenyl-2-buten-1-one (**1a**) (0.71 mL, 5.0 mmol) at  $-78^\circ\text{C}$  and the mixture was slowly warmed up to room temperature. After stirring overnight, the mixture was quenched with aqueous  $\text{NH}_4\text{Cl}$  and extracted with EtOAc. The EtOAc extracts were washed with brine, dried over  $\text{MgSO}_4$ , and concentrated on a rotary evaporator. The residue was subjected to silica gel column chromatography (eluent, hexane/ethyl acetate = 20/1) to give compound **3a** (1.0 g, 3.5 mmol, 70% yield).



Compound **3a**: Colorless oil;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  0.15 (s, 3H), 0.16 (s, 3H), 0.97 (s, 9H), 1.72 (dd,  $J$  = 6.6, 1.6 Hz, 3H), 2.44 (s, 1H), 5.69 (dq,  $J$  = 15.2, 1.6 Hz, 1H), 6.03 (dq,  $J$  = 15.2, 6.6 Hz, 1H), 7.25–7.29 (m, 1H), 7.32–7.36 (m, 2H), 7.60–7.63 (m, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  –4.63, –4.61, 16.6, 17.4,

<sup>1</sup> Uson, R.; Oro, L. A.; Cabeza, J. A. *Inorg. Synth.* **1985**, 23, 126.

<sup>2</sup> Resek, J. E.; Meyers, A. I. *Tetrahedron Lett.* **1995**, 36, 7051.

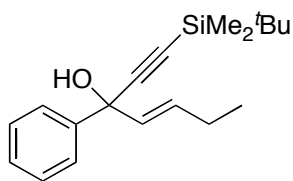
<sup>3</sup> Kondo, T.; Mukai, T.; Watanabe, Y. *J. Org. Chem.* **1991**, 56, 487.

<sup>4</sup> Lee, P. H.; Park, J.; Lee, K.; Kim, H.-C. *Tetrahedron Lett.* **1999**, 40, 7109.

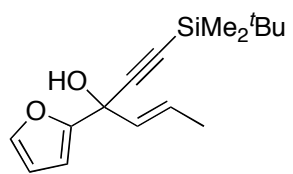
<sup>5</sup> Arisawa, M.; Torisawa, Y.; Kawahara, M.; Yamanaka, M.; Nishida, A.; Nakagawa, M. *J. Org. Chem.* **1997**, 62, 4327.

<sup>6</sup> Nicolaou, K. C.; Montagnon, T.; Baran, P. S. *Angew. Chem. Int. Ed.* **2002**, 41, 1386.

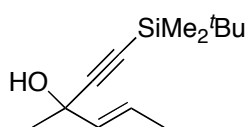
26.1, 73.1, 90.0, 107.3, 125.7, 125.7, 127.7, 128.2, 135.0, 143.8. HRMS (ESI) calcd for  $C_{18}H_{26}NaOSi$  ( $M+Na$ )<sup>+</sup> 309.1645, found 309.1653.



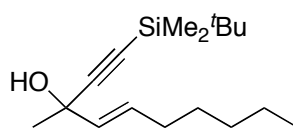
Compound **3b**: Colorless oil;  $^1H$  NMR ( $CDCl_3$ )  $\delta$  0.15 (s, 3H), 0.16 (s, 3H), 0.97 (s, 9H), 0.99 (t,  $J = 7.5$  Hz, 3H), 2.08 (qdd,  $J = 7.5, 6.4, 1.6$  Hz, 2H), 2.46 (s, 1H), 5.67 (dt,  $J = 15.3, 1.6$  Hz, 1H), 6.08 (dt,  $J = 15.3, 6.4$  Hz, 1H), 7.25–7.29 (m, 1H), 7.31–7.37 (m, 2H), 7.60–7.65 (m, 2H);  $^{13}C$  NMR ( $CDCl_3$ )  $\delta$  -4.7, -4.6, 13.2, 16.6, 24.8, 26.1, 73.1, 90.1, 107.4, 125.6, 127.6, 128.2, 132.5, 132.8, 143.9. Anal. Calcd for  $C_{19}H_{28}OSi$ : C, 75.94; H, 9.39. Found: C, 75.68; H, 9.23.



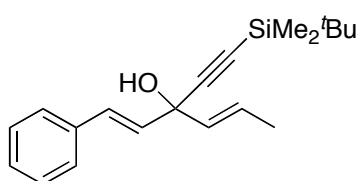
Compound **3c**: Colorless oil;  $^1H$  NMR ( $CDCl_3$ )  $\delta$  0.15 (s, 6H), 0.96 (s, 9H), 1.77 (dd,  $J = 6.6, 1.7$  Hz, 3H), 2.53 (s, 1H), 5.86 (dq,  $J = 15.2, 1.7$  Hz, 1H), 6.12 (dq,  $J = 15.2, 6.6$  Hz, 1H), 6.32 (dd,  $J = 3.3, 1.8$  Hz, 1H), 6.27 (dd,  $J = 3.3, 0.9$  Hz, 1H), 7.39 (dd,  $J = 1.8, 0.9$  Hz, 1H);  $^{13}C$  NMR ( $CDCl_3$ )  $\delta$  -4.71, -4.70, 16.6, 17.4, 26.1, 68.4, 89.6, 104.7, 106.9, 110.2, 127.9, 131.0, 142.8, 155.0. HRMS (ESI) calcd for  $C_{16}H_{24}NaOSi$  ( $M+Na$ )<sup>+</sup> 299.1438, found 299.1439.



Compound **3d**: Colorless oil;  $^1H$  NMR ( $CDCl_3$ )  $\delta$  0.11 (s, 3H), 0.12 (s, 3H), 0.94 (s, 9H), 1.52 (s, 3H), 1.72 (dd,  $J = 6.6, 1.4$  Hz, 3H), 2.09 (s, 1H), 5.59 (dq,  $J = 15.3, 1.4$  Hz, 1H), 5.99 (dq,  $J = 15.3, 6.6$  Hz, 1H);  $^{13}C$  NMR ( $CDCl_3$ )  $\delta$  -4.62, -4.61, 16.5, 17.3, 26.1, 30.5, 68.2, 86.9, 108.8, 125.4, 135.2. Anal. Calcd for  $C_{13}H_{24}OSi$ : C, 69.58; H, 10.78. Found: C, 69.37; H, 11.02.

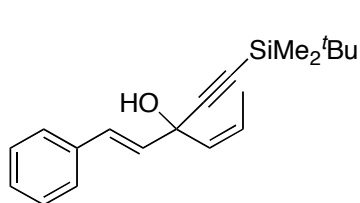


Compound **3e**: Colorless oil;  $^1H$  NMR ( $CDCl_3$ )  $\delta$  0.12 (s, 6H), 0.89 (t,  $J = 6.9$  Hz, 3H), 0.94 (s, 9H), 1.24–1.43 (m, 6H), 1.53 (s, 3H), 2.00 (s, 1H), 2.05 (tdd,  $J = 7.3, 6.9, 1.4$  Hz, 2H), 5.57 (dt,  $J = 15.3, 1.4$  Hz, 1H), 5.99 (dt,  $J = 15.3, 6.9$  Hz, 1H);  $^{13}C$  NMR ( $CDCl_3$ )  $\delta$  -4.7, 14.0, 16.5, 22.5, 26.1, 28.7, 30.5, 31.3, 31.7, 68.2, 86.9, 108.9, 130.9, 133.9. HRMS (ESI) calcd for  $C_{17}H_{32}NaOSi$  ( $M+Na$ )<sup>+</sup> 303.2115, found 303.2116.

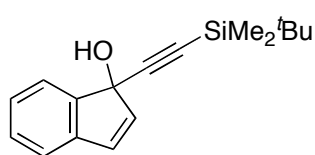


Compound (*E,E*)-**3f**: Colorless oil;  $^1H$  NMR ( $CDCl_3$ )  $\delta$  0.17 (s, 6H), 0.99 (s, 9H), 1.75 (dd,  $J = 6.7, 1.6$  Hz, 3H), 2.31 (s, 1H), 5.63 (dq,  $J = 15.3, 1.6$  Hz, 1H), 6.07 (dq,  $J = 15.3, 6.7$  Hz, 1H), 6.23 (d,  $J = 15.9$  Hz, 1H), 6.89 (d,  $J = 15.9$  Hz, 1H), 7.22–7.26 (m, 1H), 7.28–7.33 (m, 2H), 7.28–7.33 (m, 2H);  $^{13}C$  NMR ( $CDCl_3$ )  $\delta$  -4.6, 16.5, 17.4, 26.1, 71.4, 90.1, 105.9, 126.6, 126.8, 127.8, 128.5, 129.5, 131.6, 133.0, 136.3. HRMS (ESI) calcd for  $C_{20}H_{28}NaOSi$  ( $M+Na$ )<sup>+</sup> 335.1802,

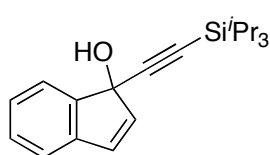
found 335.1804.



Compound (*E,Z*)-**3f**: Colorless oil;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  0.15 (s, 3H), 0.16 (s, 3H), 0.98 (s, 9H), 1.85 (d,  $J = 6.7$  Hz, 3H), 2.32 (s, 1H), 5.60–5.68 (m, 2H), 6.27 (d,  $J = 15.8$  Hz, 1H), 6.96 (d,  $J = 15.8$  Hz, 1H), 7.23–7.26 (m, 1H), 7.32 (t,  $J = 7.5$  Hz, 2H), 7.37–7.42 (m, 2H);  $^{13}\text{C}$  NMR  $\delta$  ( $\text{CDCl}_3$ ) –4.68, –4.66, 14.1, 16.6, 26.1, 70.0, 89.4, 106.6, 126.8, 127.9, 128.2, 128.6, 129.5, 131.6, 133.0, 136.3. Anal. Calcd for  $\text{C}_{20}\text{H}_{28}\text{OSi}$ : C, 76.86; H, 9.03. Found: C, 76.47; H, 8.81.



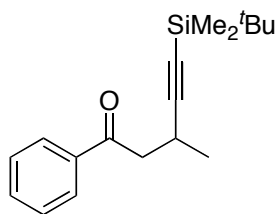
Compound **3g**: Colorless oil;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  0.08 (s, 3H), 0.09 (s, 3H), 0.90 (s, 9H), 2.28 (s, 1H), 6.32 (d,  $J = 5.5$  Hz, 1H), 6.68 (d,  $J = 5.5$  Hz, 1H), 7.19 (d,  $J = 6.5$  Hz, 1H), 7.20–7.29 (m, 2H), 7.53 (d,  $J = 7.0$  Hz, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  –4.79, –4.77, 16.6, 26.0, 77.0, 85.9, 104.2, 121.7, 122.6, 127.1, 129.1, 132.3, 139.0, 141.3, 146.7. HRMS (ESI) calcd for  $\text{C}_{17}\text{H}_{22}\text{NaOSi}$  ( $\text{M}+\text{Na}$ ) $^+$  293.1332, found 293.1339.



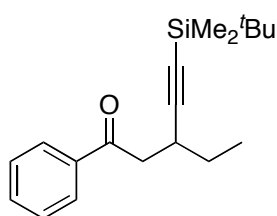
Compound **3h**: Colorless oil;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  0.90–1.10 (m, 21H), 2.32 (s, 1H), 6.32 (d,  $J = 5.5$  Hz, 1H), 6.67 (d,  $J = 5.5$  Hz, 1H), 7.17–7.27 (m, 3H), 7.53 (d,  $J = 7.0$  Hz, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  11.1, 18.5, 18.6, 77.0, 83.9, 105.8, 121.7, 122.5, 127.0, 129.0, 132.2, 139.1, 141.3, 146.9. Anal. Calcd for  $\text{C}_{20}\text{H}_{28}\text{OSi}$ : C, 76.86; H, 9.03. Found: C, 76.57; H, 8.89.

**General procedure for rhodium-catalyzed asymmetric rearrangement of alkynyl alkenyl carbinols (Table 1).** A mixture of  $[\text{Rh}(\text{OH})(\text{cod})]_2$  (2.3 mg, 0.005 mmol) and (*R*)-BINAP (7.5 mg, 0.012 mmol) in toluene (0.5 mL) was heated at 60 °C for 5 min. To the mixture was added alcohol **3** (0.20 mmol) and toluene (0.5 mL), and it was stirred at 60 °C for 3 h. The mixture was passed through a short column of silica gel with ethyl acetate as eluent. After evaporation of the solvent, the residue was subjected to a preparative TLC ( $\text{SiO}_2$ , hexane/ethyl acetate) to give compound **2**. The enantiomeric excess of the product **2** was measured by HPLC. The absolute configuration of **2a** produced by use of (*R*)-binap was determined to be *S*-(–), which is assigned by comparison of the specific rotation ( $[\alpha]_{\text{D}}^{20}$  –15 ( $c$  1.50,  $\text{Et}_2\text{O}$ )) of (*R*)-3-methyl-1-phenyl-1-pentanone (**4**), derived from **2a** in two steps, with the reported value (vide infra).<sup>7</sup> For others, they were assigned by consideration of the stereochemical pathway.

<sup>7</sup> Soai, K.; Okudo, M.; Okamoto, M. *Tetrahedron Lett.* **1991**, 32, 95.

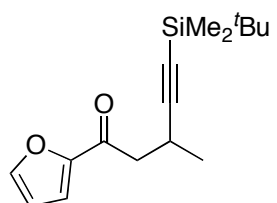


Compound **2a** (88% yield, 94% ee (*S*)): Colorless oil. The ee was measured by HPLC (Chiralcel OJ-H column  $\times$  2, 0.2 mL/min, hexane/2-propanol = 500/1, 224 nm,  $t_1$  = 44.1 min (*S*),  $t_2$  = 46.0 min (*R*));  $[\alpha]_D^{20}$  -4 (*c* 0.90, CHCl<sub>3</sub>) for 94% ee. <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  0.04 (s, 6H), 0.88 (s, 9H), 1.27 (d, *J* = 6.8 Hz, 3H), 3.01 (dd, *J* = 15.8, 7.3 Hz, 1H), 3.21 (dq, *J* = 7.3, 6.8, 5.8 Hz, 1H), 3.26 (dd, *J* = 15.8, 5.8 Hz, 1H), 7.46 (t, *J* = 7.5 Hz, 2H), 7.56 (t, *J* = 7.5 Hz, 1H), 7.96 (d, *J* = 7.3 Hz, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  -4.5, 16.5, 21.1, 23.0, 26.0, 45.4, 82.7, 111.2, 128.2, 128.6, 133.1, 137.1, 198.0. Anal. Calcd for C<sub>18</sub>H<sub>26</sub>OSi: C, 75.46; H, 9.15. Found: C, 75.36; H, 9.24.



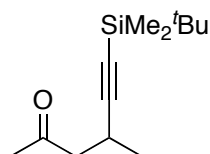
Compound **2b** (91% yield, 98% ee (*S*)): Colorless oil. The ee was measured by HPLC (Chiralcel OJ-H column  $\times$  2, 0.2 mL/min, hexane/2-propanol = 500/1, 224 nm,  $t_1$  = 41.7 min (*S*),  $t_2$  = 43.9 min (*R*));  $[\alpha]_D^{20}$  -9 (*c* 0.75, CHCl<sub>3</sub>) for 98% ee. <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  0.03 (s, 6H), 0.88 (s, 9H), 1.06 (t, *J* = 7.4 Hz, 3H), 1.42–1.52 (m, 1H), 1.57–1.69 (m, 1H),

2.98–3.10 (m, 2H), 3.24 (dd, *J* = 15.2, 5.4 Hz, 1H), 7.46 (t, *J* = 7.5 Hz, 2H), 7.56 (t, *J* = 7.5 Hz, 1H), 7.96 (d, *J* = 7.4 Hz, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  -4.5, 11.6, 16.5, 26.1, 27.9, 30.1, 43.5, 84.0, 109.8, 128.2, 128.6, 133.1, 137.2, 198.2. HRMS (ESI) calcd for C<sub>19</sub>H<sub>28</sub>NaOSi (M+Na)<sup>+</sup> 323.1802, found 323.1814.



Compound **2c** (89% yield, 91% ee (*S*)): Colorless oil. The ee was measured by HPLC (Chiralpak AD-H column  $\times$  2, 0.2 mL/min, hexane/2-propanol = 500/1, 224 nm,  $t_1$  = 71.7 min (*S*),  $t_2$  = 78.5 min (*R*));  $[\alpha]_D^{20}$  -17 (*c* 1.28, CHCl<sub>3</sub>) for 91% ee. <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  0.03 (s, 6H),

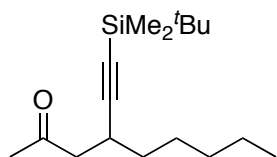
0.87 (s, 9H), 1.25 (d, *J* = 6.8 Hz, 3H), 2.85 (dd, *J* = 15.4, 7.6 Hz, 1H), 3.08 (dd, *J* = 15.4, 6.6 Hz, 1H), 3.16 (dq, *J* = 7.6, 6.8, 6.6 Hz, 1H), 6.53 (dd, *J* = 3.5, 1.7 Hz, 1H), 7.21 (dd, *J* = 3.5, 0.7 Hz, 1H), 7.58 (dd, *J* = 1.7, 0.7 Hz, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) -4.5, 16.4, 21.0, 23.1, 26.0, 45.1, 82.9, 110.7, 112.3, 117.5, 146.5, 152.9, 187.1. HRMS (ESI) calcd for C<sub>16</sub>H<sub>24</sub>NaOSi (M+Na)<sup>+</sup> 299.1438, found 299.1441.



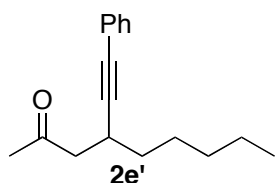
Compound **2d** (78% yield, 98% ee (*S*)): Colorless oil. The ee was measured by HPLC (Chiralpak AD-H column, 0.5 mL/min, hexane/2-propanol = 4/1, 200 nm,  $t_1$  = 6.2 min (*S*),  $t_2$  = 7.0 min (*R*));  $[\alpha]_D^{20}$  +19 (*c* 1.01, CHCl<sub>3</sub>) for 98% ee.

<sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  0.06 (s, 6H), 0.91 (s, 9H), 1.19 (d, *J* = 6.9 Hz, 3H), 2.17 (s, 3H), 2.49 (dd, *J* = 16.4, 7.2 Hz, 1H), 2.67 (dd, *J* = 16.4, 6.9 Hz, 1H), 2.98 (dq, *J* = 7.2, 6.9, 6.9 Hz, 1H); <sup>13</sup>C NMR

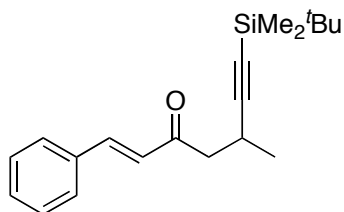
(CDCl<sub>3</sub>)  $\delta$  -4.5, 16.5, 20.9, 22.7, 26.1, 30.5, 50.4, 82.8, 110.8, 206.5. Anal. Calcd for C<sub>13</sub>H<sub>24</sub>OSi: C, 69.58; H, 10.78. Found: C, 69.80; H, 10.93.



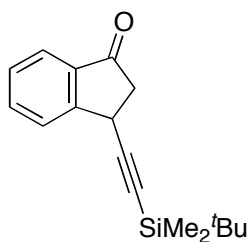
Compound **2e** (78% yield, 81% ee (*S*)): Colorless oil. The enantiomeric purity of **2e** was determined by HPLC analysis of 4-(phenylethynyl)-2-nonanone (**2e'**), which was obtained by Sonogashira coupling reaction of 4-ethynyl-2-nonanone with iodobenzene after deprotection of the silyl group on **2e** with tetrabutylammonium fluoride (TBAF).  $[\alpha]_D^{20}$  -9 (*c* 1.08, CHCl<sub>3</sub>) for 81% ee. <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  0.06 (s, 3H), 0.07 (s, 3H), 0.89 (t, *J* = 6.8 Hz, 3H), 0.91 (s, 9H), 1.20–1.55 (m, 8H), 2.18 (s, 3H), 2.49 (dd, *J* = 16.0, 6.6 Hz, 1H), 2.64 (dd, *J* = 16.0, 7.4 Hz, 1H), 2.84–2.92 (m, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  -4.51, -4.50, 13.9, 16.5, 22.5, 26.0, 26.7, 28.3, 30.5, 31.4, 34.7, 48.9, 83.9, 109.7, 206.7. HRMS (ESI) calcd for C<sub>17</sub>H<sub>32</sub>NaOSi (M+Na)<sup>+</sup> 303.2115, found 303.2118. Compound **2e'**



[CAS#:146491-95-4]: Colorless oil (95% from **2e**). The ee was measured by HPLC (Chiralcel OD-H column, 0.5 mL/min, hexane/2-propanol = 200/1, 254 nm, *t*<sub>1</sub> = 18.6 min (*S*), *t*<sub>2</sub> = 24.1 min (*R*));  $[\alpha]_D^{20}$  -12 (*c* 0.70, CHCl<sub>3</sub>) for 81% ee. <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  0.90 (t, *J* = 6.9 Hz, 3H), 1.25–2.60 (m, 8H), 2.21 (s, 3H), 2.59 (dd, *J* = 16.2, 6.4 Hz, 1H), 2.74 (dd, *J* = 16.2, 7.6 Hz, 1H), 3.02–3.12 (m, 1H), 7.25–7.30 (m, 3H), 7.35–7.39 (m, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  14.0, 22.5, 26.9, 27.8, 30.5, 31.5, 34.8, 49.0, 81.9, 92.0, 123.7, 127.7, 128.1, 131.6, 206.8.



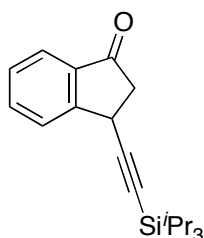
Compound **2f** (78% yield with 96% ee (*S*) from (*E,E*)-**3f**, 88% yield with 81% ee (*R*) from (*E,Z*)-**3f**): Colorless oil. The ee was measured by HPLC (Chiralcel OJ-H column, 0.5 mL/min, hexane/2-propanol = 500/1, 224 nm, *t*<sub>1</sub> = 15.8 min (*S*), *t*<sub>2</sub> = 19.0 min (*R*));  $[\alpha]_D^{20}$  -14 (*c* 0.81, CHCl<sub>3</sub>) for 96% ee (*S*);  $[\alpha]_D^{20}$  +13 (*c* 1.29, CHCl<sub>3</sub>) for 81% ee (*R*). <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  0.05 (s, 6H), 0.89 (s, 9H), 1.24 (d, *J* = 6.9 Hz, 3H), 2.72 (dd, *J* = 15.8, 7.6 Hz, 1H), 2.94 (dd, *J* = 15.8, 6.4 Hz, 1H), 3.11 (dq, *J* = 7.6, 6.9, 6.4 Hz, 1H), 6.77 (d, *J* = 16.2 Hz, 1H), 7.36–7.42 (m, 3H), 7.52–7.57 (m, 2H), 7.56 (d, *J* = 16.2 Hz, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  -4.5, 16.5, 21.0, 23.1, 26.0, 47.5, 82.8, 111.1, 126.4, 128.3, 129.0, 130.5, 134.5, 143.0, 198.0. HRMS (ESI) calcd for C<sub>20</sub>H<sub>28</sub>NaOSi (M+Na)<sup>+</sup> 335.1802, found 335.1804.



Compound **2g** (86% yield, 71% ee (*S*)): White solid. The ee was measured by HPLC (Chiralpak AD-H column, 0.5 mL/min, hexane/2-propanol = 500/1, 224 nm, *t*<sub>1</sub> = 23.4 min (*S*), *t*<sub>2</sub> = 27.2 min (*R*));  $[\alpha]_D^{20}$  +48 (*c* 0.86, CHCl<sub>3</sub>) for 71% ee. <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  0.09 (s, 3H), 0.10 (s, 3H), 0.92 (s, 9H), 2.78 (dd, *J* = 18.9, 4.8 Hz, 1H), 3.10 (dd, *J* = 18.9, 8.0 Hz, 1H), 4.27

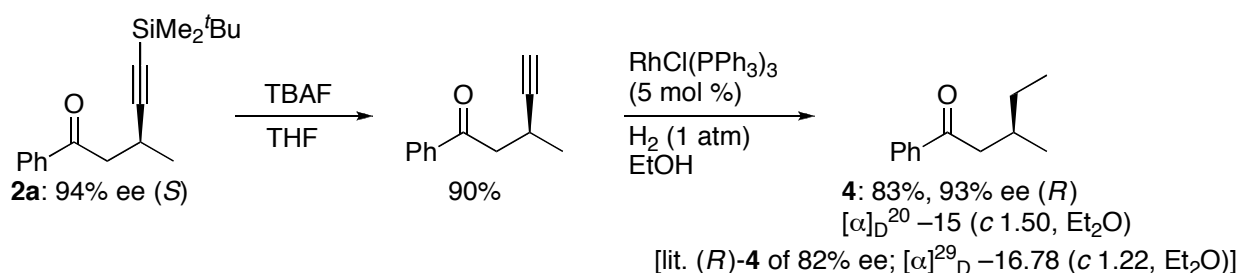
(dd,  $J = 8.0, 4.8$  Hz, 1H), 7.41–7.47 (m, 1H), 7.67–7.70 (m, 2H), 7.75 (d,  $J = 7.6$  Hz, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  –4.6, 16.5, 26.1, 30.6, 44.4, 84.6, 106.4, 123.6, 126.3, 128.3, 135.3, 135.6, 154.2, 203.8. HRMS (ESI) calcd for  $\text{C}_{17}\text{H}_{22}\text{NaOSi}$  ( $\text{M}+\text{Na}$ ) $^+$  293.1332, found 293.1338.

**Procedure for rhodium-catalyzed asymmetric rearrangement of **3h** with a chiral diene ligand [(*S,S*)-Ph-bod\*] (eq 3).** A mixture of (*S,S*)-Ph-bod\*<sup>3</sup> (3.1 mg, 0.012 mmol) and  $[\text{RhCl}(\text{C}_2\text{H}_4)_2]_2$  (1.9 mg, 0.005 mmol) in toluene (0.5 mL) was stirred at room temperature for 10 min. To this solution were added  $\text{Cs}_2\text{CO}_3$  (6.5 mg, 0.020 mmol), alcohol **3h** (62.4 mg, 0.20 mmol) and toluene (0.5 mL), and the mixture was heated at 80 °C for 15 h. The reaction mixture was passed through a short column of silica gel with ethyl acetate as eluent. After evaporation of the solvent, the residue was subjected to a preparative TLC (eluent, hexane/ ethyl acetate = 10/1) to give compound **2h** (57.0 mg, 0.18 mmol, 91% yield).



Compound **2h** (91% yield, 97% ee (*R*)): White solid. The ee was measured by HPLC (Chiralpak AD-H column, 0.2 mL/min, hexane/2-propanol = 200/1, 224 nm,  $t_1 = 28.1$  min (*R*),  $t_2 = 30.8$  min (*S*));  $[\alpha]_{\text{D}}^{20} -46$  ( $c$  1.11,  $\text{CHCl}_3$ ) for 97% ee.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.05 (s, 21H), 2.78 (dd,  $J = 18.7, 4.9$  Hz, 1H), 3.12 (dd,  $J = 18.7, 8.0$  Hz, 1H), 4.29 (dd,  $J = 8.0, 4.9$  Hz, 1H), 7.44 (t,  $J = 6.8$  Hz, 1H), 7.65–7.70 (m, 2H), 7.75 (d,  $J = 7.7$  Hz, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  11.2, 18.6, 30.6, 44.6, 82.4, 107.6, 123.5, 126.2, 128.3, 135.2, 135.5, 154.5, 203.9. Anal. Calcd for  $\text{C}_{20}\text{H}_{28}\text{OSi}$ : C, 76.86; H, 9.03. Found: C, 76.65 ; H, 9.01.

#### Transformation of compound **2a** into **4**.



To a solution of **2a** (106.4 mg, 0.37 mmol) in THF (1.0 mL) was added tetrabutylammonium fluoride (TBAF) solution (0.37 mL, 1.0 M in THF), and the mixture was stirred at room temperature for 2 h. The mixture was quenched with  $\text{H}_2\text{O}$  and extracted with ethyl acetate. The combined organic layer was washed with brine, dried over  $\text{MgSO}_4$ , filtered, and concentrated on a rotary evaporator. The residue was subjected to a preparative TLC ( $\text{SiO}_2$ , hexane/ethyl acetate = 10/1) to give 3-methyl-1-phenyl-4-pentyn-1-one (56.8 mg, 0.33 mmol, 90%). A mixture of this acetylenic ketone (56.8 mg, 0.33 mmol) and  $\text{RhCl}(\text{PPh}_3)_3$  (17.0 mg, 0.018 mmol) in ethanol (2.0

mL) was stirred at room temperature for 12 h under H<sub>2</sub> (1 atm). The mixture was filtered through a pad of celite and the filtrate was concentrated on a rotary evaporator. The residue was subjected to a preparative TLC (SiO<sub>2</sub>, hexane/ethyl acetate = 20/1) to give compound **4** (48.0 mg, 0.27 mmol, 83%). Compound **4**<sup>7</sup> (93% ee (*R*)): Colorless oil. The ee was measured by HPLC (Chiralcel OD-H column × 3, 0.2 mL/min, hexane/2-propanol = 500/1, 224 nm *t*<sub>1</sub> = 106.0 min (*R*), *t*<sub>2</sub> = 110.4 min (*S*)); [α]<sub>D</sub><sup>20</sup> −15 (*c* 1.50, Et<sub>2</sub>O) for 93% ee. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 0.93 (t, *J* = 7.3 Hz, 3H), 0.96 (d, *J* = 6.7 Hz, 3H), 1.21–1.34 (m, 1H), 1.39–1.49 (m, 1H), 2.01–2.14 (m, 1H), 2.75 (dd, *J* = 15.7, 8.0 Hz, 1H), 2.95 (dd, *J* = 15.7, 5.6 Hz, 1H), 7.46 (t, *J* = 7.8 Hz, 2H), 7.55 (t, *J* = 7.1 Hz, 1H), 7.95 (d, *J* = 7.6 Hz, 2H).



