Carbon-Carbon Bond-Forming Enantioselective synthesis of Chiral Organosilicon Compounds by Rhodium-Chiral Diene-Catalyzed Asymmetric 1,4-Addition Reaction

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Supporting Information

I. General

All air- and moisture-sensitive manipulations were carried out with standard Schlenk techniques under nitrogen or in a glove box under argon.

THF, 1,4-dioxane, and benzene were distilled over benzophenone ketyl under nitrogen. Dichloromethane was distilled over CaH₂ under nitrogen.

(Dimethylphenylsilyl)acetylene (Aldrich), benzaldehyde (Wako Chemicals), propionaldehyde (Wako Chemicals), *n*-BuLi (Kanto Chemicals; 1.60 M solution in hexane), LiAlH₄ (Wako Chemicals), MnO₂ (Aldrich), tetrafluoroboric acid diethyl ether complex (Fluka), KF (Wako Chemicals), KHCO₃ (Nacalai Tesque), H₂O₂ (Wako Chemicals), *p*-toluenesulfonic acid monohydrate (Nacalai Tesque), and phenylboronic acid (TCI) were used as received. Other arylboronic acids were synthesized from the corresponding aryl bromides with B(OMe)₃ (Wako Chemicals). 4-Dimethylphenylsilyl-3-butyne-2-ol,¹ 4-(*t*-butyl)dimethylsilyl-3-butyne-2-ol,¹ 4-triphenylsilyl-3-butyne-2-ol,¹ ethyl (*E*)-3-dimethylphenylsilyl-2-propenoate,² [RhCl(C₂H₄)₂]₂,³ (1*R*, 4*R*)-2,5-diphenylbicyclo[2.2.2]octa-2,5-diene ((*R,R*)-Ph-bod*)⁴, and (1*R*, 4*R*)-2,5-dibenzylbicyclo[2.2.2]octa-2,5-diene ((*R,R*)-Bn-bod*)⁴ were prepared following the literature procedures.

All other chemicals and solvents were purchased from Aldrich, Wako Chemicals, TCI, Nacalai Tesque, or Kanto Chemicals and used as received.

II. Synthesis of Substrates

The yields have not been optimized.

(*E*)-3-Dimethylphenylsilyl-1-phenyl-2-propen-1-one (1c)

¹ Jung, M. E.; Pizzi, G. J. *Org. Chem.* **2002**, 67, 3911.

² Flemig, I.; Marangon, E.; Roni, C.; Russel, M. G.; Chamudis, S. T. *Chem. Commun.* **2003**, 200.

³ Cramer, R. *Inorg. Synth.* **1974**, 15, 16.

⁴ (a) Tokunaga, N.; Otomaru, Y.; Okamoto, K.; Ueyama, K.; Hayashi, T. *J. Am. Chem. Soc.* **2004**, 126, 13584. (b) Otomaru, Y.; Okamoto, K.; Shintani, R.; Hayashi, T. *J. Org. Chem.* **2005**, 70, 2503.

n-BuLi (4.04 mL, 6.3 mmol; 1.60 M solution in hexane) was added to a solution of (dimethylphenylsilyl)acetylene (1.17 mL, 6.60 mmol) in THF (18 mL) at $-50\text{ }^{\circ}\text{C}$ and the mixture was stirred for 20 min. Benzaldehyde (582 μL , 6.00 mmol) was then added to this, and the resulting solution was stirred for 1 h at room temperature. The reaction was quenched with water, poured into NaCl (aqueous, saturated), and extracted with Et₂O. The organic layer was dried over MgSO₄, filtered, and concentrated under vacuum. The residue was chromatographed on silica gel with Et₂O/hexane = 1/3 to afford 1-phenyl-3-dimethylphenylsilyl-2-propyn-1-ol (CAS 103024-10-8) as a pale yellow oil (1.59 g, 6.00 mmol; 99% yield).

¹H NMR (CDCl₃): δ 7.65-7.61 (m, 2H), 7.58-7.54 (m, 2H), 7.41-7.31 (m, 6H), 5.50 (d, ³*J*_{HH} = 6.3 Hz, 1H), 2.19 (d, ³*J*_{HH} = 6.5 Hz, 1H), 0.45 (s, 6H). ¹³C NMR (CDCl₃): δ 140.2, 136.5, 133.7, 129.5, 128.6, 128.4, 127.9, 126.8, 106.7, 89.7, 65.1, -1.0 .

A solution of 1-phenyl-3-dimethylphenylsilyl-2-propyn-1-ol (1.59 g, 6.00 mmol) in THF (5 mL) was added to a suspension of LiAlH₄ (137 mg, 3.60 mmol) in THF (15 mL) at $0\text{ }^{\circ}\text{C}$, and the mixture was stirred for 36 h at $30\text{ }^{\circ}\text{C}$. After quenching with water, the precipitate was removed by filtration. The resulting solution was dried over MgSO₄, filtered, and concentrated under vacuum to afford 1-phenyl-3-dimethylphenylsilyl-2-propen-1-ol as a colorless oil quantitatively.

This oil was dissolved in dichloromethane (40 mL) and MnO₂ (2.79 g, 32.1 mmol) was added to it at $0\text{ }^{\circ}\text{C}$. After stirring for 12 h at room temperature, the mixture was filtered through celite. The resulting solution was dried over MgSO₄, filtered, and concentrated under vacuum. The residue was chromatographed on silica gel with Et₂O/hexane = 1/20 to afford (*E*)-1-phenyl-3-dimethylphenylsilyl-2-propen-1-one (**1c**) as a pale yellow oil (1.03 g, 3.90 mmol; 65% yield).

¹H NMR (CDCl₃): δ 7.93-7.89 (m, 2H), 7.58-7.53 (m, 3H), 7.46 (t, ³*J*_{HH} = 7.8 Hz, 2H), 7.41 (d, ³*J*_{HH} = 18.8 Hz, 1H), 7.41-7.36 (m, 3H), 7.28 (d, ³*J*_{HH} = 18.7 Hz, 1H), 0.48 (s, 6H). ¹³C NMR (CDCl₃): δ 190.4, 147.5, 139.4, 137.4, 136.6, 133.9, 132.8, 129.5, 128.8, 128.6, 128.0, -3.0 . Anal. Calcd for C₁₇H₁₈OSi: C, 76.64; H, 6.81. Found: C, 76.92; H, 7.00.

(*E*)-5-Dimethylphenylsilyl-4-penten-3-one (**1b**)

1b

This was synthesized using propionaldehyde instead of benzaldehyde, following the procedure for compound **1c**. Colorless oil. 34% overall yield from propionaldehyde.

¹H NMR (CDCl₃): δ 7.52-7.48 (m, 2H), 7.42-7.34 (m, 3H), 7.15 (d, ³*J*_{HH} = 19.2 Hz, 1H), 6.52 (d, ³*J*_{HH} = 19.1 Hz, 1H), 2.62 (q, ³*J*_{HH} = 7.3 Hz, 2H), 1.10 (t, ³*J*_{HH} = 7.3 Hz, 3H), 0.42 (s, 6H). ¹³C NMR (CDCl₃): δ 200.7, 144.0, 143.2, 136.5, 133.8, 129.5, 128.0, 32.7, 7.9,

–3.2. Anal. Calcd for C₁₃H₁₈OSi: C, 71.50; H, 8.31. Found: C, 71.70; H, 8.31.

(E)-4-Dimethylphenylsilyl-3-buten-2-one (1a) (CAS 144823-72-3)

1a

This was synthesized from 4-dimethylphenylsilyl-3-butyne-2-ol, following the procedure for compound **1c**. Colorless oil. 70% overall yield from 4-dimethylphenylsilyl-3-butyne-2-ol.

¹H NMR (CDCl₃): δ 7.56-7.48 (m, 2H), 7.43-7.35 (m, 3H), 7.11 (d, ³J_{HH} = 19.2 Hz, 1H), 6.49 (d, ³J_{HH} = 19.1 Hz, 1H), 2.28 (s, 3H), 0.43 (s, 6H). ¹³C NMR (CDCl₃): δ 198.5, 145.5, 144.1, 136.3, 133.8, 129.6, 128.0, 26.3, –3.2.

(E)-4-(*t*-Butyl)dimethylsilyl-3-buten-2-one (1i) (CAS 172534-56-4)

1i

This was synthesized from 4-(*t*-butyl)dimethylsilyl-3-butyne-2-ol, following the procedure for compound **1c**. Colorless oil. 43% overall yield from 4-(*t*-butyl)dimethylsilyl-3-butyne-2-ol.

¹H NMR (CDCl₃): δ 7.04 (d, ³J_{HH} = 19.3 Hz, 1H), 6.48 (d, ³J_{HH} = 19.3 Hz, 1H), 2.29 (s, 3H), 0.91 (s, 9H), 0.11 (s, 6H). ¹³C NMR (CDCl₃): δ 198.3, 145.4, 144.2, 26.31, 26.29, 16.5, –6.5.

(E)-4-Triphenylsilyl-3-buten-2-one (1j)

1j

This was synthesized from 4-triphenylsilyl-3-butyne-2-ol, following the procedure for compound **1c**. Colorless oil. 76% overall yield from 4-triphenylsilyl-3-butyne-2-ol.

¹H NMR (CDCl₃): δ 7.53-7.47 (m, 7H), 7.45 (t, ³J_{HH} = 7.1 Hz, 3H), 7.39 (t, ³J_{HH} = 7.5 Hz, 6H), 6.54 (d, ³J_{HH} = 19.0 Hz, 1H), 2.33 (s, 3H). ¹³C NMR (CDCl₃): δ 198.2, 146.9, 141.5, 135.9, 132.6, 130.1, 128.1, 26.8. Anal. Calcd for C₂₂H₂₀OSi: C, 80.44; H, 6.14. Found: C, 80.46; H, 6.27.

III. 1,4-Addition Reactions

General Procedure for Equation 1, Table 1, and Table 2.

A solution of [RhCl(C₂H₄)₂]₂ (1.2 mg, 6.2 μmol Rh) and ligand (6.6 μmol) in 1,4-dioxane (0.50 mL) was stirred for 5 min at room temperature. KOH (0.10 mL, 60 μmol; 0.6 M aqueous) was then added to it, and the resulting solution was stirred for additional 5 min at room temperature. ArB(OH)₂ (0.30 mmol) and substrate (0.20 mmol) were added to it with additional 1,4-dioxane (0.50 mL), and the resulting mixture was stirred for 6 h at 50 °C. The reaction mixture was directly passed

through a pad of silica gel with Et₂O, and the solvent was removed under vacuum. The residue was purified by silica gel preparative TLC with Et₂O/hexane to afford the desired 1,4-adduct.

2a

Table 1, entry 1. (CAS 100103-32-0) Pale yellow oil. 94% yield. The ee was determined on a Daicel Chiralpak AD-H column with hexane : 2-propanol = 200 : 1, flow = 1.0 mL/min. Retention times: 10.3 min [(S)-enantiomer], 16.6 min [(R)-enantiomer]. 99% ee. $[\alpha]_D^{20}$ -9.3 (c 1.19, CHCl₃). The absolute configuration was determined by comparison of the optical rotation with that reported in the literature.⁵

¹H NMR (CDCl₃): δ 7.41-7.30 (m, 5H), 7.18 (t, ³J_{HH} = 7.5 Hz, 2H), 7.07 (t, ³J_{HH} = 7.3 Hz, 1H), 6.93 (d, ³J_{HH} = 7.2 Hz, 2H), 2.93-2.85 (m, 2H), 2.67-2.58 (m, 1H), 1.93 (s, 3H), 0.23 (s, 3H), 0.21 (s, 3H). ¹³C NMR (CDCl₃): δ 208.0, 142.0, 136.6, 134.1, 129.3, 128.1, 127.7, 127.6, 124.9, 44.0, 31.4, 29.9, -4.1, -5.4.

2b

Table 1, entry 2. Pale yellow oil. 89% yield. The ee was determined on a Daicel Chiralpak AD-H column with hexane : 2-propanol = 200 : 1, flow = 1.0 mL/min. Retention times: 8.5 min [(S)-enantiomer], 13.3 min [(R)-enantiomer]. 98% ee. $[\alpha]_D^{20}$ +0.68 (c 1.74, CHCl₃). The absolute configuration was assigned by analogy with Table 1, entry 1.

¹H NMR (CDCl₃): δ 7.41-7.29 (m, 5H), 7.17 (t, ³J_{HH} = 7.7 Hz, 2H), 7.06 (t, ³J_{HH} = 7.3 Hz, 1H), 6.93 (d, ³J_{HH} = 7.1 Hz, 2H), 2.94-2.84 (m, 2H), 2.64-2.55 (m, 1H), 2.22 (dq, ²J_{HH} = 17.6 Hz and ³J_{HH} = 7.3 Hz, 2H), 2.18 (dq, ²J_{HH} = 17.6 Hz and ³J_{HH} = 7.2 Hz, 2H), 0.85 (t, ³J_{HH} = 7.3 Hz, 3H), 0.23 (s, 3H), 0.20 (s, 3H). ¹³C NMR (CDCl₃): δ 210.5, 142.2, 136.7, 134.1, 129.3, 128.1, 127.7, 127.6, 124.8, 42.8, 36.0, 31.2, 7.6, -4.0 -5.3. Anal. Calcd for C₁₉H₂₈O₅: C, 76.97; H, 8.16. Found: C, 77.20; H, 8.30.

2c

Table 1, entry 3. (CAS 118356-60-8) Pale yellow oil. 94% yield. The ee was determined on a Daicel Chiralpak AD-H column with hexane : 2-propanol = 95 : 5, flow = 1.0 mL/min. Retention times: 5.6 min [(S)-enantiomer], 8.0 min [(R)-enantiomer]. 97% ee. $[\alpha]_D^{20}$ -30.7 (c 1.01, CHCl₃). The absolute configuration was determined by comparison of the optical rotation with that reported in the literature.⁵

¹H NMR (CDCl₃): δ 7.79-7.75 (m, 2H), 7.49 (t, ³J_{HH} = 7.4 Hz, 1H), 7.45-7.41 (m, 2H), 7.40-7.30 (m, 5H), 7.16 (t, ³J_{HH} = 7.4 Hz, 2H), 7.05 (t, ³J_{HH} = 7.3 Hz, 1H), 6.97 (d, ³J_{HH} =

⁵ Matsumoto, Y.; Hayashi, T.; Ito, Y. *Tetrahedron* **1994**, 50, 335.

7.0 Hz, 2H), 3.47 (dd, $^2J_{\text{HH}} = 17.1$ Hz and $^3J_{\text{HH}} = 10.1$ Hz, 1H), 3.20 (dd, $^2J_{\text{HH}} = 17.1$ Hz and $^3J_{\text{HH}} = 4.4$ Hz, 1H), 3.09 (dd, $^3J_{\text{HH}} = 10.1$ and 4.4 Hz, 1H), 0.29 (s, 3H), 0.23 (s, 3H). ^{13}C NMR (CDCl_3): δ 199.0, 142.4, 137.1, 136.8, 134.1, 132.7, 129.3, 128.4, 128.0, 127.9, 127.73, 127.67, 124.8, 39.0, 31.1, -3.9, -5.2.

2d

Table 1, entry 4. Pale yellow oil. 95% yield. The ee was determined on a Daicel Chiralpak AD-H column with hexane : 2-propanol = 95 : 5, flow = 1.0 mL/min. Retention times: 4.9 min [(*S*)-enantiomer], 5.7 min [(*R*)-enantiomer]. 96% ee. $[\alpha]_{\text{D}}^{20}$ -0.9 (*c* 0.96, CHCl_3). The absolute configuration was assigned by analogy with Table 1, entry 1.

^1H NMR (CDCl_3): δ 7.41-7.30 (m, 5H), 6.84 (d, $^3J_{\text{HH}} = 8.6$ Hz, 2H), 6.74 (d, $^3J_{\text{HH}} = 8.8$ Hz, 2H), 3.75 (s, 3H), 2.88-2.77 (m, 2H), 2.65-2.55 (m, 1H), 1.92 (s, 3H), 0.23 (s, 3H), 0.20 (s, 3H). ^{13}C NMR (CDCl_3): δ 208.4, 157.1, 136.8, 134.1, 133.8, 129.2, 128.4, 127.7, 113.7, 55.1, 44.2, 30.4, 29.9, -4.1, -5.4. Anal. Calcd for $\text{C}_{19}\text{H}_{24}\text{O}_2\text{Si}$: C, 73.03; H, 7.74. Found: C, 72.92; H, 7.59.

2e

Table 1, entry 5. Pale yellow oil. 94% yield. The ee was determined on a Daicel Chiralpak AD-H column with hexane : 2-propanol = 98 : 2, flow = 1.0 mL/min. Retention times: 4.7 min [(*S*)-enantiomer], 5.8 min [(*R*)-enantiomer]. 95% ee. $[\alpha]_{\text{D}}^{20}$ -9.8 (*c* 1.35, CHCl_3). The absolute configuration was assigned by analogy with Table 1, entry 1.

^1H NMR (CDCl_3): δ 7.43 (d, $^3J_{\text{HH}} = 8.2$ Hz, 2H), 7.41-7.31 (m, 5H), 7.01 (d, $^3J_{\text{HH}} = 8.2$ Hz, 2H), 2.98 (dd, $^3J_{\text{HH}} = 10.9$ and 3.4 Hz, 1H), 2.92 (dd, $^2J_{\text{HH}} = 16.6$ Hz and $^3J_{\text{HH}} = 11.0$ Hz, 1H), 2.68 (dd, $^2J_{\text{HH}} = 16.6$ Hz and $^3J_{\text{HH}} = 3.4$ Hz, 1H), 1.96 (s, 3H), 0.24 (s, 3H), 0.23 (s, 3H). ^{13}C NMR (CDCl_3): δ 207.2, 146.8, 135.8, 134.1, 129.6, 127.9, 127.6, 127.1 (q, $^2J_{\text{CF}} = 32.6$ Hz), 125.1 (q, $^3J_{\text{CF}} = 3.6$ Hz), 124.4 (q, $^1J_{\text{CF}} = 271.2$ Hz), 43.6, 31.6, 30.0, -4.3, -5.4. Anal. Calcd for $\text{C}_{19}\text{H}_{21}\text{F}_3\text{OSi}$: C, 65.12; H, 6.04. Found: C, 64.92; H, 6.05.

2f

Table 1, entry 6. Pale yellow oil. 92% yield. The ee was determined on a Daicel

Chiralpak AD-H column with hexane : 2-propanol = 100 : 1, flow = 1.0 mL/min. Retention times: 6.6 min [(*S*)-enantiomer], 7.0 min [(*R*)-enantiomer]. 95% ee. $[\alpha]_D^{20}$ -11.8 (*c* 1.23, CHCl₃). The absolute configuration was assigned by analogy with Table 1, entry 1.

¹H NMR (CDCl₃): δ 7.42-7.31 (m, 5H), 7.10 (t, ³*J*_{HH} = 7.8 Hz, 1H), 7.05 (dt, ³*J*_{HH} = 7.9 Hz and ⁴*J*_{HH} = 1.2 Hz, 1H), 6.87 (t, ⁴*J*_{HH} = 1.8 Hz, 1H), 6.80 (d, ³*J*_{HH} = 6.6 Hz, 1H), 2.91-2.82 (m, 2H), 2.67-2.59 (m, 1H), 1.96 (s, 3H), 0.24 (s, 3H), 0.22 (s, 3H). ¹³C NMR (CDCl₃): δ 207.3, 144.5, 136.0, 134.1, 134.0, 129.5, 129.3, 127.8, 127.4, 125.8, 125.0, 43.7, 31.1, 30.0, -4.2, -5.4. Anal. Calcd for C₁₈H₂₁ClOSi: C, 68.22; H, 6.68. Found: C, 68.41; H, 6.68.

2g

Table 1, entry 7. White solid. 96% yield. The ee was determined on a Daicel Chiralpak AD-H column with hexane : 2-propanol = 98 : 2, flow = 1.0 mL/min. Retention times: 7.2 min [(*S*)-enantiomer], 8.4 min [(*R*)-enantiomer]. 93% ee. $[\alpha]_D^{20}$ +0.98 (*c* 0.82, CHCl₃). The absolute configuration was assigned by analogy with Table 1, entry 1.

¹H NMR (CDCl₃): δ 7.75 (d, ³*J*_{HH} = 7.8 Hz, 1H), 7.67 (d, ³*J*_{HH} = 8.3 Hz, 2H), 7.43-7.30 (m, 8H), 7.10 (d, ³*J*_{HH} = 8.4 Hz, 1H), 3.07-2.97 (m, 2H), 2.76-2.66 (m, 1H), 1.93 (s, 3H), 0.25 (s, 3H), 0.24 (s, 3H). ¹³C NMR (CDCl₃): δ 208.0, 139.8, 136.5, 134.2, 133.6, 131.5, 129.4, 127.8, 127.6, 127.5, 127.3, 127.1, 125.8, 125.1, 124.8, 44.1, 31.7, 30.0, -4.0, -5.3. Anal. Calcd for C₂₂H₂₄OSi: C, 79.47; H, 7.28. Found: C, 79.55; H, 7.20.

2h

Table 1, entry 8. Pale yellow oil. 90% yield. The ee was determined on a Daicel Chiralcel OD-H column with hexane : 2-propanol = 90 : 10, flow = 1.0 mL/min. Retention times: 7.1 min [(*S*)-enantiomer], 7.7 min [(*R*)-enantiomer]. 93% ee. $[\alpha]_D^{20}$ -14.4 (*c* 0.95, CHCl₃). The absolute configuration was assigned by analogy with Table 1, entry 1.

¹H NMR (CDCl₃): δ 7.40-7.29 (m, 5H), 7.09-7.03 (m, 2H), 6.97 (t, ³*J*_{HH} = 7.2 Hz, 1H), 6.84 (d, ³*J*_{HH} = 8.2 Hz, 1H), 3.13 (dd, ³*J*_{HH} = 10.9 and 4.0 Hz, 1H), 2.93 (dd, ²*J*_{HH} = 16.8 Hz and ³*J*_{HH} = 11.0 Hz, 1H), 2.65 (dd, ²*J*_{HH} = 16.8 Hz and ³*J*_{HH} = 4.1 Hz, 1H), 2.22 (s, 3H), 1.90 (s, 3H), 0.27 (s, 3H), 0.19 (s, 3H). ¹³C NMR (CDCl₃): δ 208.0, 140.8, 137.0, 135.8, 134.1, 130.3, 129.3, 127.7, 126.0, 125.7, 124.6, 44.9, 30.0, 25.7, 20.4, -3.9, -5.2. Anal. Calcd for C₁₉H₂₄OSi: C, 76.97; H, 8.16. Found: C, 77.27; H, 8.30.

Table 2, entry 1. (CAS 118356-59-5) Pale yellow oil. 95% yield. The ee was determined on a Daicel Chiralcel OJ-H column with hexane : 2-propanol = 200 : 1, flow = 0.3 mL/min. Retention times: 24.3 min [(S)-enantiomer], 25.9 min [(R)-enantiomer]. >99% ee. $[\alpha]_D^{20} +2.0$ (c 1.55, CHCl₃). The absolute configuration was assigned by analogy with Table 1, entry 1.

¹H NMR (CDCl₃): δ 7.21 (t, ³J_{HH} = 7.7 Hz, 2H), 7.10-7.04 (m, 3H), 2.98 (dd, ²J_{HH} = 16.1 Hz and ³J_{HH} = 11.6 Hz, 1H), 2.81 (dd, ³J_{HH} = 11.6 and 3.3 Hz, 1H), 2.70 (dd, ²J_{HH} = 16.1 Hz and ³J_{HH} = 3.3 Hz, 1H), 1.97 (s, 3H), 0.82 (s, 9H), 0.04 (s, 3H), -0.18 (s, 3H). ¹³C NMR (CDCl₃): δ 208.3, 143.5, 128.3, 127.9, 124.9, 45.6, 30.2, 29.1, 27.0, 17.6, -6.7, -7.0.

Table 2, entry 2. White solid. 91% yield. The ee was determined on a Daicel Chiralpak AD-H column with hexane : 2-propanol = 98 : 2, flow = 0.5 mL/min. Retention times: 10.4 min [(S)-enantiomer], 11.9 min [(R)-enantiomer]. 97% ee. $[\alpha]_D^{20} -62.2$ (c 1.55, CHCl₃). The absolute configuration was assigned by analogy with Table 1, entry 1.

¹H NMR (CDCl₃): δ 7.40 (t, ³J_{HH} = 7.2 Hz, 3H), 7.36 (d, ³J_{HH} = 6.5 Hz, 6H), 7.31 (t, ³J_{HH} = 7.3 Hz, 6H), 7.12-7.06 (m, 3 H), 6.88-6.83 (m, 2 H), 3.63 (dd, ³J_{HH} = 11.7 and 2.5 Hz, 1H), 3.07 (dd, ²J_{HH} = 16.7 Hz and ³J_{HH} = 11.8 Hz, 1H), 2.94 (dd, ²J_{HH} = 16.7 Hz and ³J_{HH} = 2.6 Hz, 1H), 1.93 (s, 3H). ¹³C NMR (CDCl₃): δ 207.5, 141.2, 136.3, 133.2, 129.7, 129.2, 128.1, 127.8, 125.4, 45.8, 30.5, 29.4. Anal. Calcd for C₂₈H₂₆OSi: C, 82.71; H, 6.45. Found: C, 82.66; H, 6.55.

Table 2, entry 3. (CAS 67263-05-2) Pale yellow oil. 88% yield. The ee was determined on a Daicel Chiralpak AD-H column with hexane : 2-propanol = 100 : 1, flow = 0.5 mL/min. Retention times: 10.6 min [(S)-enantiomer], 12.1 min [(R)-enantiomer]. 95% ee. $[\alpha]_D^{20} -3.2$ (c 1.23, CHCl₃). The absolute configuration was assigned by analogy with Table 1, entry 1.

¹H NMR (CDCl₃): δ 7.42-7.30 (m, 5H), 7.18 (t, ³J_{HH} = 7.5 Hz, 2H), 7.07 (t, ³J_{HH} = 7.3 Hz, 1H), 6.94 (d, ³J_{HH} = 7.2 Hz, 2H), 3.92 (dq, ²J_{HH} = 10.9 Hz and ³J_{HH} = 7.2 Hz, 1H), 3.88 (dq, ²J_{HH} = 10.9 Hz and ³J_{HH} = 7.2 Hz, 1H), 2.83 (dd, ³J_{HH} = 11.3 and 4.7 Hz, 1H), 2.73 (dd, ²J_{HH} = 15.8 Hz and ³J_{HH} = 11.4 Hz, 1H), 2.54 (dd, ²J_{HH} = 15.7 Hz and ³J_{HH} = 4.7 Hz, 1H), 1.03 (t, ³J_{HH} = 7.3 Hz, 3H), 0.25 (s, 3H), 0.21 (s, 3H). ¹³C NMR (CDCl₃): δ. 172.3 141.7, 136.5, 134.1, 129.3, 128.0, 127.7, 127.6, 124.9, 60.2, 34.9, 32.3, 14.0, -4.1, -5.5.

Table 2, entry 4. Pale yellow oil. 86% yield. The ee was determined on a Daicel Chiralcel OD-H column with hexane : 2-propanol = 100 : 1, flow = 1.0 mL/min. Retention times: 9.1 min [(S)-enantiomer], 10.2 min [(R)-enantiomer]. 93% ee. $[\alpha]_D^{20}$ +5.6 (c 0.80, CHCl₃). The absolute configuration was assigned by analogy with Table 1, entry 1.

¹H NMR (CDCl₃): δ 7.41-7.30 (m, 5H), 6.85 (t, ³J_{HH} = 8.8 Hz, 2H), 6.74 (d, ³J_{HH} = 8.8 Hz, 2H), 3.92 (dq, ²J_{HH} = 10.7 Hz and ³J_{HH} = 7.1 Hz, 1H), 3.90 (dq, ²J_{HH} = 10.7 Hz and ³J_{HH} = 7.0 Hz, 1H), 3.76 (s, 3H), 2.77 (dd, ³J_{HH} = 11.2 and 5.0 Hz, 1H), 2.67 (dd, ²J_{HH} = 15.6 Hz and ³J_{HH} = 11.2 Hz, 1H), 2.59 (dd, ²J_{HH} = 15.6 Hz and ³J_{HH} = 5.0 Hz, 1H), 1.04 (t, ³J_{HH} = 7.1 Hz, 3H), 0.24 (s, 3H), 0.21 (s, 3H). ¹³C NMR (CDCl₃): δ 173.1, 157.1, 136.7, 134.1, 133.6, 129.2, 128.5, 127.7, 113.5, 60.2, 55.1, 35.2, 31.3, 14.0, -4.1, -5.4. Anal. Calcd for C₂₀H₂₆O₃Si: C, 70.13; H, 7.65. Found: C, 70.18; H, 7.72.

Procedure for Equation 2.

This reaction was performed according to the literature procedure.⁵ Tetrafluoroboric acid diethyl ether complex (54.0 μL, 0.39 mmol) was added dropwise to a solution of **2a** (46.0 mg, 0.16 mmol; 99% ee) in dichloromethane (1.0 mL) at 0 °C. The mixture was stirred for 1 h at 0 °C and then the solvent was removed under vacuum. The residue was dissolved in methanol (1.0 mL) and THF (1.0 mL). KF (18.4 mg, 0.32 mmol) and KHCO₃ (150 mg, 1.5 mmol) were then added to this solution at 0 °C. After stirring for 15 min at 0 °C, H₂O₂ (240 μL, 2.1 mmol; 30 wt% aqueous) was added to it, and the mixture was stirred for 12 h at room temperature. The reaction was quenched with Na₂S₂O₃ (10 mL, 2.0 M aqueous), poured into HCl (0.5 M aqueous), and then extracted with Et₂O. The organic layer was dried over MgSO₄, filtered, and concentrated under vacuum. The residue was purified by silica gel preparative TLC with Et₂O/hexane = 2/1 to afford **3** (CAS 86734-69-2 for (S)-enantiomer) as a colorless oil (21.8 mg, 0.13 mmol, 82% yield).

The ee was determined on a Daicel Chiralpak AD-H column with hexane : 2-propanol = 98 : 2, flow = 1.0 mL/min. Retention times: 28.8 min [(R)-enantiomer], 35.5 min [(S)-enantiomer]. 98% ee. $[\alpha]_D^{20}$ -76.6 (c 0.80, CHCl₃).

The absolute configuration was determined by comparison of the optical rotation with that reported in the literature.⁵

¹H NMR (CDCl₃): δ 7.39-7.32 (m, 4H), 7.31-7.24 (m, 1H), 5.15 (dt, ³J_{HH} = 9.2 and 3.1 Hz, 1H), 3.29 (d, ³J_{HH} = 3.2 Hz, 1H), 2.88 (dd, ²J_{HH} = 17.4 Hz and ³J_{HH} = 9.1 Hz, 1H), 2.80 (dd, ²J_{HH} = 17.5 Hz and ³J_{HH} = 3.2 Hz, 1H), 2.18 (s, 3H). ¹³C NMR (CDCl₃): δ 209.0, 142.7, 128.5, 127.6, 125.6, 69.8, 51.9, 30.7.

Procedure for Equation 3.

PhMgBr (156 μ L, 0.21 mmol; 1.33 M in Et₂O) was added to a solution of **2c** (59.5 mg, 0.17 mmol; 97% ee) in THF (1.0 mL) at 0 °C, and the mixture was stirred for 5 h at room temperature. The reaction was quenched with water, and extracted with Et₂O. The organic layer was dried over MgSO₄, filtered, and concentrated under vacuum. The residue was dissolved in benzene (2.0 mL), and *p*-toluenesulfonic acid (32.9 mg, 0.17 mmol; monohydrate) was added to the solution. After stirring for 4 h at 50 °C, the reaction was quenched with NaHCO₃ (saturated, aqueous) and extracted with Et₂O. The organic layer was dried over MgSO₄, filtered, and concentrated under vacuum. The residue was purified by silica gel preparative TLC with Et₂O/hexane = 1/10 to afford **4** as a white solid (56.7 mg, 0.14 mmol, 82% yield).

The ee was determined on a Daicel Chiralcel OD-H column with hexane : 2-propanol = 200 : 1, flow = 0.5 mL/min. Retention times: 8.7 min [(*R*)-enantiomer], 11.5 min [(*S*)-enantiomer]. 97% ee. $[\alpha]_D^{20} +174.4$ (*c* 2.00, CHCl₃).

¹H NMR (CDCl₃): δ 7.37-7.06 (m, 16H), 7.31-7.24 (m, 4H), 6.40 (d, ³*J*_{HH} = 12.3 Hz, 1H), 3.38 (d, ³*J*_{HH} = 12.3 Hz, 1H), 0.24 (s, 3H), 0.19 (s, 3H). ¹³C NMR (CDCl₃): δ 143.2, 142.4, 140.7, 140.1, 136.7, 134.3, 130.1, 129.2, 128.4, 128.3, 128.1, 128.0, 127.5, 127.3, 127.2, 126.8, 126.7, 124.7, 40.1, -4.1, -4.7. Anal. Calcd for C₂₉H₂₈Si: C, 86.08; H, 6.98. Found: C, 85.84; H, 7.21.