**Rhodium-Catalyzed Asymmetric Synthesis of 3,3-Disubstituted 1-Indanones**

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I. General

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

1,4-Dioxane was distilled over benzophenone ketyl under nitrogen. Dichloromethane was distilled over CaH$_2$ under nitrogen. THF was purified by passing through a neutral alumina column under nitrogen.

LiAlH$_4$ (Wako Chemicals), $p$-toluenesulfonic acid (Nacalai Tesque; monohydrate), diisobutylaluminum hydride (Kanto Chemicals; 0.95 M solution in hexane), N,N-diisopropylethylamine (Wako Chemicals), chloromethyl methyl ether (Wako Chemicals), and tetrabutylammonium fluoride (Aldrich; 1.0 M solution in THF) were used as received.

Aryl alkynyl ketones 1 were all synthesized following the literature procedure for 1a.$^1$ Arylboronates 2a–2g were synthesized following the literature procedure for 2a.$^2$ Methylboronate 2h,$^3$ [Rh(OH)(cod)]$_2$,$^4$ (R)-binap,$^5$ and (R)-segphos$^6$ were prepared following the literature procedure.

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II. Analytical Data for New Aryl Alkynyl Ketones

1-(2-Methylphenyl)-3-triethylsilyl-2-propyn-1-one (1b)

1H NMR (CDCl₃): δ 8.26 (d, J_HH = 7.6 Hz, 1H), 7.44 (t, J_HH = 7.5 Hz, 1H), 7.33 (t, J_HH = 7.5 Hz, 1H), 7.24 (d, J_HH = 7.6 Hz, 1H), 2.63 (s, 3H), 1.06 (t, J_HH = 7.9 Hz, 9H), 0.74 (q, J_HH = 7.9 Hz, 6H). 13C NMR (CDCl₃): δ 179.4, 140.7, 135.5, 133.5, 133.0, 132.2, 126.0, 103.8, 97.2, 22.1, 7.5, 4.1. Anal. Calcd for C₁₆H₂₂OSi: C, 74.36; H, 8.58. Found: C, 74.35; H, 8.59.

1-(3-Methylphenyl)-3-triethylsilyl-2-propyn-1-one (1c)

1H NMR (CDCl₃): δ 7.98-7.96 (m, 2H), 7.42 (d, J_HH = 7.3 Hz, 1H), 7.37 (t, J_HH = 7.9 Hz, 1H), 2.42 (s, 3H), 1.08 (t, J_HH = 7.9 Hz, 9H), 0.76 (q, J_HH = 7.9 Hz, 6H). 13C NMR (CDCl₃): δ 177.9, 138.5, 136.8, 135.0, 130.1, 128.6, 127.2, 102.4, 98.6, 21.4, 7.5, 4.1. Anal. Calcd for C₁₆H₂₂OSi: C, 74.36; H, 8.58. Found: C, 74.32; H, 8.63.

1-(4-Methylphenyl)-3-triethylsilyl-2-propyn-1-one (1d)

1H NMR (CDCl₃): δ 8.05 (d, J_HH = 8.2 Hz, 2H), 7.28 (d, J_HH = 8.5 Hz, 2H), 2.43 (s, 3H), 1.07 (t, J_HH = 7.9 Hz, 9H), 0.75 (q, J_HH = 7.8 Hz, 6H). 13C NMR (CDCl₃): δ 177.5, 145.3, 134.6, 129.9, 129.4, 102.4, 98.3, 21.9, 7.5, 4.1. Anal. Calcd for C₁₆H₂₂OSi: C, 74.36; H, 8.58. Found: C, 74.57; H, 8.62.

1-(4-Methoxyphenyl)-3-triethylsilyl-2-propyn-1-one (1e)
1H NMR (CDCl$_3$): $\delta$ 8.13 (d, $^{3}J_{HH} = 9.2$ Hz, 2H), 6.96 (d, $^{3}J_{HH} = 8.8$ Hz, 2H), 3.88 (s, 3H), 1.07 (t, $^{3}J_{HH} = 7.9$ Hz, 9H), 0.75 (q, $^{3}J_{HH} = 7.8$ Hz, 6H). 13C NMR (CDCl$_3$): $\delta$ 176.4, 164.6, 132.1, 130.2, 113.9, 102.4, 97.8, 55.7, 7.5, 4.1. Anal. Calcd for C$_{16}$H$_{22}$O$_{2}$Si: C, 70.03; H, 8.08. Found: C, 69.96; H, 8.01.

1-(4-Fluorophenyl)-3-triethylsilyl-2-propyn-1-one (1f)

1H NMR (CDCl$_3$): $\delta$ 8.19 (dd, $^{3}J_{HH} = 8.8$ Hz and $^{4}J_{HF} = 5.5$ Hz, 2H), 7.16 (t, $^{3}J = 8.7$ Hz, 2H), 1.08 (t, $^{3}J_{HH} = 7.9$ Hz, 9H), 0.76 (q, $^{3}J_{HH} = 7.9$ Hz, 6H). 13C NMR (CDCl$_3$): $\delta$ 176.0, 166.6 (d, $^{1}J_{CF} = 256$ Hz), 133.3 (d, $^{4}J_{CF} = 2.1$ Hz), 132.3 (d, $^{3}J_{CF} = 10.3$ Hz), 115.9 (d, $^{2}J_{CF} = 21.7$ Hz), 101.9, 99.2, 7.5, 4.0. Anal. Calcd for C$_{15}$H$_{19}$FOSi: C, 68.66; H, 7.30. Found: C, 68.87; H, 7.49.

1-Phenyl-3-dimethylethylsilyl-2-propyn-1-one (1g)

1H NMR (CDCl$_3$): $\delta$ 8.15 (d, $^{3}J_{HH} = 7.3$ Hz, 2H), 7.61 (tt, $^{3}J_{HH} = 7.3$ Hz and $^{4}J_{HH} = 1.2$ Hz, 1H), 7.49 (t, $^{3}J_{HH} = 7.9$ Hz, 2H), 1.08 (t, $^{3}J_{HH} = 7.9$ Hz, 3H), 0.75 (q, $^{3}J_{HH} = 7.9$ Hz, 2H), 0.29 (s, 6H). 13C NMR (CDCl$_3$): $\delta$ 177.9, 136.8, 134.3, 129.8, 128.8, 101.5, 100.2, 7.7, 7.4, -2.6. Anal. Calcd for C$_{13}$H$_{16}$OSi: C, 72.17; H, 7.45. Found: C, 72.32; H, 7.57.

1-Phenyl-3-triethylgermyl-2-propyn-1-one (1i)

1H NMR (CDCl$_3$): $\delta$ 8.17 (d, $^{3}J_{HH} = 7.3$ Hz, 2H), 7.59 (t, $^{3}J_{HH} = 7.3$ Hz, 1H), 7.47 (t, $^{3}J_{HH}$
= 7.6 Hz, 2H), 1.17 (t, \( J_{HH} = 7.6 \) Hz, 9H), 1.01 (q, \( J_{HH} = 7.8 \) Hz, 6H). \(^{13}\)C NMR (CDCl\(_3\)): \( \delta \) 177.7, 137.0, 134.1, 129.8, 128.7, 102.7, 101.2, 9.2, 5.9. HRMS (ESI) calcd for C\(_{15}\)H\(_{21}\)GeO (M+H\(^+\)) 291.0801, found 291.0791.

1-(3-Chlorophenyl)-3-triethylsilyl-2-propyn-1-one (1j)

\[ \text{Cl} \quad \begin{array}{c} \text{O} \\ \text{SiEt}_3 \end{array} \]

\(^1\)H NMR (CDCl\(_3\)): \( \delta \) 8.13 (t, \( J_{HH} = 1.8 \) Hz, 1H), 8.04 (ddd, \( J_{HH} = 7.6 \) Hz and \( J_{HH} = 1.5 \) and 1.2 Hz, 1H), 7.58 (ddd, \( J_{HH} = 7.9 \) Hz and \( J_{HH} = 2.1 \) and 1.2 Hz, 1H), 7.44 (t, \( J_{HH} = 7.8 \) Hz, 1H), 1.08 (t, \( J_{HH} = 7.9 \) Hz, 9H), 0.76 (q, \( J_{HH} = 7.9 \) Hz, 6H). \(^{13}\)C NMR (CDCl\(_3\)): \( \delta \) 176.2, 138.2, 135.0, 134.1, 130.0, 129.6, 127.8, 101.7, 100.1, 7.5, 4.0. Anal. Calcd for C\(_{15}\)H\(_{19}\)ClOSi: C, 64.61; H, 6.87. Found: C, 64.88; H, 6.87.

### III. Catalytic Reactions

**General Procedure for Table 2, Table 3, and Equation 3.**

A solution of [Rh(OH)(cod)]\(_2\) (2.3 mg, 10 \( \mu \)mol Rh) and (R)-segphos (6.2 mg, 10 \( \mu \)mol) in 1,4-dioxane (0.5 mL) was stirred for 5 min at room temperature. Arylboronate 2 (0.24 mmol) and aryl alkynyl ketone 1 (0.20 mmol) were added successively with additional 1,4-dioxane (0.5 mL). The resulting mixture was stirred for 12 h at 50 °C, and the reaction was quenched with water (60 \( \mu \)L). This was then passed through a pad of silica gel with Et\(_2\)O. After removing the solvent under vacuum, the residue was chromatographed on silica gel with Et\(_2\)O/hexane to afford indanone 3.

**Table 2, Entry 1.** Eluant for chromatography: Et\(_2\)O/hexane = 1/10. Pale yellow oil. 89% yield. The ee value was determined on a Daicel Chiralcel OJ-H column with hexane : 2-propanol = 90 : 10, flow = 0.4 mL/min. Retention times: 12.3 min [(R)-enantiomer], 17.9
min [(S)-enantiomer]. 98% ee. [$\alpha$]$^D_{20}$ – 176 (c 1.16, CHCl$_3$). The absolute configuration was assigned by analogy with 3jg (equation 3).

$^1$H NMR (CDCl$_3$): $\delta$ 7.82 (d, $^3J_{HH}$ = 7.3 Hz, 1H), 7.77 (d, $^3J_{HH}$ = 7.9 Hz, 1H), 7.67 (td, $^3J_{HH}$ = 7.9 Hz and $^4J_{HH}$ = 1.2 Hz, 1H), 7.40 (td, $^3J_{HH}$ = 7.5 Hz and $^4J_{HH}$ = 0.9 Hz, 1H), 7.35 (d, $^3J_{HH}$ = 8.2 Hz, 2H), 7.28 (t, $^3J_{HH}$ = 7.3 Hz, 2H), 7.16 (tt, $^3J_{HH}$ = 7.9 Hz and $^4J_{HH}$ = 1.2 Hz, 1H), 3.37 (d, $^2J_{HH}$ = 19.8 Hz, 1H), 2.98 (d, $^2J_{HH}$ = 19.5 Hz, 1H), 0.74 (t, $^3J_{HH}$ = 7.8 Hz, 9H), 0.62 (dq, $^2J_{HH}$ = 15.2 Hz and $^3J_{HH}$ = 7.0 Hz, 3H), 0.56 (dq, $^2J_{HH}$ = 15.2 Hz and $^3J_{HH}$ = 8.5 Hz, 3H).

$^{13}$C NMR (CDCl$_3$): $\delta$ 205.6, 159.0, 144.9, 136.7, 134.0, 128.4, 128.3, 126.8, 126.7, 125.4, 124.2, 50.4, 43.5, 7.6, 3.1. Anal. Calcd for C$_{22}$H$_{28}$O$_2$Si: C, 78.21; H, 8.13. Found: C, 78.19; H, 8.35.

Table 2, Entry 2. The reaction was conducted for 24 h in the presence of 8 mol% Rh/(R)-segphos with 1.5 equiv of 2b. Eluant for chromatography: Et$_2$O/hexane = 1/7.5. Pale yellow oil. 71% yield. The ee value was determined on a Daicel Chiralcel OJ-H column with hexane : 2-propanol = 90 : 10, flow = 0.8 mL/min. Retention times: 10.2 min [(R)-enantiomer], 20.7 min [(S)-enantiomer]. 98% ee. [$\alpha$]$^D_{20}$ – 147 (c 0.62, CHCl$_3$). The absolute configuration was assigned by analogy with 3jg (equation 3).

$^1$H NMR (CDCl$_3$): $\delta$ 7.81 (d, $^3J_{HH}$ = 7.6 Hz, 1H), 7.72 (d, $^3J_{HH}$ = 7.9 Hz, 1H), 7.65 (t, $^3J_{HH}$ = 7.1 Hz, 1H), 7.39 (t, $^3J_{HH}$ = 7.3 Hz, 1H), 7.24 (d, $^3J_{HH}$ = 8.9 Hz, 2H), 6.82 (d, $^3J_{HH}$ = 8.9 Hz, 2H), 3.78 (s, 3H), 3.33 (d, $^2J_{HH}$ = 19.5 Hz, 1H), 2.92 (d, $^2J_{HH}$ = 19.7 Hz, 1H), 0.76 (t, $^3J_{HH}$ = 7.8 Hz, 9H), 0.62 (dq, $^2J_{HH}$ = 14.9 Hz and $^3J_{HH}$ = 7.2 Hz, 3H), 0.55 (dq, $^2J_{HH}$ = 15.1 Hz and $^3J_{HH}$ = 7.9 Hz, 3H). $^{13}$C NMR (CDCl$_3$): $\delta$ 206.1, 159.8, 157.6, 137.3, 136.9, 134.3, 128.4, 128.1, 126.9, 124.4, 113.9, 55.4, 50.9, 42.8, 7.9, 3.4. Anal. Calcd for C$_{22}$H$_{28}$O$_2$Si: C, 74.95; H, 8.01. Found: C, 74.86; H, 7.89.
Table 2, Entry 3. Eluant for chromatography: Et$_2$O/hexane = 1/10. Pale yellow oil. 83% yield. The ee value was determined on a Daicel Chiralcel OJ-H column with hexane : 2-propanol = 90 : 10, flow = 0.5 mL/min. Retention times: 10.3 min [(R)-enantiomer], 15.4 min [(S)-enantiomer]. 99% ee. [α]$^D_{20}$ $-164$ (c 0.86, CHCl$_3$). The absolute configuration was assigned by analogy with 3jg (equation 3).

$^1$H NMR (CDCl$_3$): δ 7.81 (d, $^3$J$_{HH}$ = 7.5 Hz, 1H), 7.74 (d, $^3$J$_{HH}$ = 7.9 Hz, 1H), 7.65 (td, $^3$J$_{HH}$ = 7.9 Hz and $^4$J$_{HH}$ = 1.3 Hz, 1H), 7.39 (t, $^3$J$_{HH}$ = 7.1 Hz, 1H), 7.22 (d, $^3$J$_{HH}$ = 8.3 Hz, 2H), 7.08 (d, $^3$J$_{HH}$ = 8.1 Hz, 2H), 3.34 (d, $^2$J$_{HH}$ = 19.7 Hz, 1H), 2.95 (d, $^2$J$_{HH}$ = 19.6 Hz, 1H), 2.30 (s, 3H), 0.75 (t, $^3$J$_{HH}$ = 7.8 Hz, 9H), 0.61 (dq, $^2$J$_{HH}$ = 14.9 Hz and $^3$J$_{HH}$ = 7.2 Hz, 3H), 0.55 (dq, $^2$J$_{HH}$ = 15.1 Hz and $^3$J$_{HH}$ = 8.2 Hz, 3H). $^{13}$C NMR (CDCl$_3$): δ 206.0, 159.6, 142.1, 136.9, 135.2, 134.2, 129.2, 128.5, 127.0, 126.9, 124.4, 50.8, 43.3, 21.0, 7.9, 3.4. Anal. Calcd for C$_{22}$H$_{28}$OSi: C, 78.51; H, 8.39. Found: C, 78.31; H, 8.29.

Table 2, Entry 4. The reaction was conducted in the presence of 8 mol% Rh/(R)-segphos. Eluant for chromatography: Et$_2$O/hexane = 1/10. Pale yellow solid. 88% yield. The ee value was determined on a Daicel Chiralpak AD-H column with hexane : 2-propanol = 90 : 10, flow = 0.4 mL/min. Retention times: 24.8 min [(S)-enantiomer], 26.5 min [(R)-enantiomer]. 98% ee. [α]$^D_{20}$ $-130$ (c 1.12, CHCl$_3$). The absolute configuration was assigned by analogy with 3jg (equation 3).

$^1$H NMR (CDCl$_3$): δ 7.82 (d, $^3$J$_{HH}$ = 7.6 Hz, 1H), 7.72 (d, $^3$J$_{HH}$ = 7.9 Hz, 1H), 7.68 (td,
$^3J_{HH} = 7.9$ Hz and $^4J_{HH} = 1.2$ Hz, 1H), 7.41 (td, $^3J_{HH} = 7.5$ Hz and $^4J_{HH} = 0.9$ Hz, 1H), 7.39 (d, $^3J_{HH} = 8.8$ Hz, 2H), 7.22 (d, $^3J_{HH} = 8.8$ Hz, 2H), 3.35 (d, $^2J_{HH} = 19.5$ Hz, 1H), 2.90 (d, $^2J_{HH} = 19.5$ Hz, 1H), 0.75 (t, $^3J_{HH} = 7.8$ Hz, 9H), 0.61 (dq, $^2J_{HH} = 15.2$ Hz and $^3J_{HH} = 7.0$ Hz, 3H), 0.54 (dq, $^2J_{HH} = 15.2$ Hz and $^3J_{HH} = 8.2$ Hz, 3H). $^{13}$C NMR (CDCl$_3$): $\delta$ 205.2, 158.5, 144.2, 136.9, 134.5, 131.5, 128.6, 128.3, 127.1, 124.6, 119.4, 50.4, 43.3, 7.8, 3.2. Anal. Calcd for C$_{21}$H$_{25}$BrOSi: C, 62.83; H, 6.28. Found: C, 63.06; H, 6.09.

Table 2, Entry 5. Eluant for chromatography: Et$_2$O/hexane = 1/10. Pale yellow oil. 89% yield. The ee value was determined on a Daicel Chiralcel OD-H column with hexane : 2-propanol = 97 : 3, flow = 0.4 mL/min. Retention times: 15.2 min [(R)-enantiomer], 16.0 min [(S)-enantiomer]. 98% ee. $[\alpha]^{20}_D$ –166 (c 0.78, CHCl$_3$). The absolute configuration was assigned by analogy with 3jg (equation 3).

$^1$H NMR (CDCl$_3$): $\delta$ 7.84 (d, $^3J_{HH} = 7.7$ Hz, 1H), 7.77 (d, $^3J_{HH} = 7.8$ Hz, 1H), 7.71 (td, $^3J_{HH} = 7.2$ Hz and $^4J_{HH} = 1.2$ Hz, 1H), 7.54 (d, $^3J_{HH} = 8.3$ Hz, 2H), 7.47 (d, $^3J_{HH} = 8.4$ Hz, 2H), 7.44 (t, $^3J_{HH} = 7.1$ Hz, 1H), 3.40 (d, $^2J_{HH} = 19.4$ Hz, 1H), 2.95 (d, $^2J_{HH} = 19.6$ Hz, 1H), 0.75 (t, $^3J_{HH} = 7.8$ Hz, 9H), 0.62 (dq, $^2J_{HH} = 15.1$ Hz and $^3J_{HH} = 7.8$ Hz, 3H), 0.55 (dq, $^2J_{HH} = 15.3$ Hz and $^3J_{HH} = 8.0$ Hz, 3H). $^{13}$C NMR (CDCl$_3$): $\delta$ 205.0, 158.1, 149.4, 136.9, 134.5, 128.5, 128.0 (q, $^2J_{CF} = 32.6$ Hz), 127.4, 127.2, 125.5 (q, $^3J_{CF} = 3.6$ Hz), 124.8, 124.4 (q, $^1J_{CF} = 271$ Hz), 50.3, 44.1, 7.8, 3.2. Anal. Calcd for C$_{22}$H$_{25}$F$_3$OSi: C, 67.66; H, 6.45. Found: C, 67.61; H, 6.50.
Table 2, Entry 6. Eluant for chromatography: Et$_2$O/hexane = 1/11. White solid. 91% yield. The ee value was determined on a Daicel Chiralcel OJ-H column with hexane : 2-propanol = 90 : 10, flow = 0.3 mL/min. Retention times: 20.6 min [(R)-enantiomer], 24.7 min [(S)-enantiomer]. 96% ee. [α]$^0_D$ –199 (c 0.56, CHCl$_3$). The absolute configuration was assigned by analogy with 3jg (equation 3).

$^1$H NMR (CDCl$_3$): δ 7.83 (d, $^3$J$_{HH}$ = 7.7 Hz, 1H), 7.75 (d, $^3$J$_{HH}$ = 7.4 Hz, 1H), 7.70 (t, $^3$J$_{HH}$ = 7.1 Hz, 1H), 7.43 (t, $^3$J$_{HH}$ = 7.1 Hz, 1H), 7.33 (s, 1H), 7.23-7.20 (m, 2H), 7.17-7.13 (m, 1H), 3.36 (d, $^2$J$_{HH}$ = 19.5 Hz, 1H), 2.93 (d, $^2$J$_{HH}$ = 19.4 Hz, 1H), 0.75 (t, $^3$J$_{HH}$ = 7.5 Hz, 9H), 0.62 (dq, $^2$J$_{HH}$ = 15.0 Hz and $^3$J$_{HH}$ = 7.2 Hz, 3H), 0.55 (dq, $^2$J$_{HH}$ = 15.4 Hz and $^3$J$_{HH}$ = 7.4 Hz, 3H).

$^{13}$C NMR (CDCl$_3$): δ 205.2, 158.3, 147.4, 136.9, 134.6, 134.5, 125.9, 125.3, 124.7, 50.4, 43.7, 7.8, 3.3. Anal. Calcd for C$_{21}$H$_{25}$ClOSi: C, 70.66; H, 7.06. Found: C, 70.42; H, 7.15.

Table 2, Entry 7. Eluant for chromatography: Et$_2$O/hexane = 1/10. Pale yellow oil. 91% yield. The ee value was determined on a Daicel Chiralcel OD-H column with hexane : 2-propanol = 97 : 3, flow = 0.8 mL/min. Retention times: 9.7 min [(S)-enantiomer], 10.7 min [(R)-enantiomer]. 98% ee. [α]$^0_D$ –146 (c 0.73, CHCl$_3$). The absolute configuration was assigned by analogy with 3jg (equation 3).

$^1$H NMR (CDCl$_3$): δ 7.86 (d, $^3$J$_{HH}$ = 7.7 Hz, 2H), 7.79-7.77 (m, 3H), 7.74-7.71 (m, 2H), 7.46-7.41 (m, 4H), 3.45 (d, $^2$J$_{HH}$ = 19.5 Hz, 1H), 3.06 (d, $^2$J$_{HH}$ = 19.7 Hz, 1H), 0.77 (t, $^3$J$_{HH}$ = 7.8 Hz, 9H), 0.67 (dq, $^2$J$_{HH}$ = 14.8 Hz and $^3$J$_{HH}$ = 8.0 Hz, 3H), 0.61 (dq, $^2$J$_{HH}$ = 15.1 Hz and $^3$J$_{HH}$ = 8.2 Hz, 3H). $^{13}$C NMR (CDCl$_3$): δ 205.8, 159.2, 142.7, 137.1, 134.4, 133.4, 131.7, 128.7, 128.3, 128.0, 127.6, 127.1, 126.41, 126.40, 125.7, 124.8, 124.6, 50.6, 44.0, 8.0, 3.5. Anal. Calcd for C$_{25}$H$_{28}$OSi: C, 80.59; H, 7.57. Found: C, 80.36; H, 7.63.
**Table 2, Entry 8.** The reaction was conducted for 24 h in the presence of 8 mol% Rh/(R)-segphos with 3.0 equiv of 2h. Eluant for chromatography: Et₂O/hexane = 1/10. Pale yellow oil. 51% yield. The ee value was determined on a Daicel Chiralcel OJ-H column with hexane : 2-propanol = 97 : 3, flow = 0.3 mL/min. Retention times: 17.3 min [(S)-enantiomer], 19.3 min [(R)-enantiomer]. 87% ee. [α]²⁰ºD –120 (c 0.50, CHCl₃). The absolute configuration was assigned by analogy with 3jg (equation 3).

¹H NMR (CDCl₃): δ 7.70 (d, ³JHH = 7.6 Hz, 1H), 7.56 (t, ³JHH = 7.7 Hz, 1H), 7.41 (d, ³JHH = 7.8 Hz, 1H), 7.28 (t, ³JHH = 7.5 Hz, 1H), 2.95 (d, ²JHH = 19.3 Hz, 1H), 2.34 (d, ²JHH = 19.4 Hz, 1H), 1.50 (s, 3H), 0.84 (t, ³JHH = 8.0 Hz, 9H), 0.59 (dq, ²JHH = 15.1 Hz and ³JHH = 7.7 Hz, 3H), 0.54 (dq, ²JHH = 15.1 Hz and ³JHH = 8.1 Hz, 3H). ¹³C NMR (CDCl₃): δ 206.6, 163.8, 136.1, 134.7, 126.3, 125.1, 123.9, 50.2, 32.4, 24.0, 8.0, 2.2. Anal. Calcd for C₁₆H₂₄OSi: C, 73.79; H, 9.29. Found: C, 73.90; H, 9.40.

**Table 3, Entry 1.** Eluant for chromatography: Et₂O/hexane = 1/14. Pale yellow oil. 86% yield. The ee value was determined on a Daicel Chiralcel OJ-H column with hexane : 2-propanol = 90 : 10, flow = 0.4 mL/min. Retention times: 10.0 min [(R)-enantiomer], 13.0 min [(S)-enantiomer]. 94% ee. [α]²⁰ºD –183 (c 0.84, CHCl₃). The absolute configuration was assigned by analogy with 3jg (equation 3).

¹H NMR (CDCl₃): δ 7.54 (d, ³JHH = 7.6 Hz, 1H), 7.49 (t, ³JHH = 7.5 Hz, 1H), 7.33-7.31 (m, 2H), 7.26 (tt, ³JHH = 7.9 Hz and ⁴JHH = 1.8 Hz, 2H), 7.14 (tt, ³JHH = 7.0 Hz and ⁴JHH = 1.2 Hz, 1H), 7.12 (dt, ³JHH = 7.3 Hz and ⁴JHH = 0.9 Hz, 1H), 3.32 (d, ²JHH = 19.2 Hz, 1H), 2.95 (d, ²JHH = 19.2 Hz, 1H), 2.66 (s, 3H), 0.75 (t, ³JHH = 7.8 Hz, 9H), 0.63 (dq, ²JHH = 15.2 Hz and ³JHH = 7.0 Hz, 3H), 0.57 (dq, ²JHH = 14.9 Hz and ³JHH = 8.5 Hz, 3H). ¹³C NMR (CDCl₃): δ
Table 3, Entry 2. Eluant for chromatography: Et₂O/hexane = 1/10. Pale yellow oil. 84% yield. The ee value was determined on a Daicel Chiralcel OD-H column with hexane : 2-propanol = 90 : 10, flow = 0.4 mL/min. Retention times: 10.6 min [(R)-enantiomer], 14.0 min [(S)-enantiomer]. 98% ee. [α]$_D^{20}$ -176 (c 1.37, CHCl₃). The absolute configuration was assigned by analogy with 3jg (equation 3).

$^1$H NMR (CDCl₃): δ 7.66 (d, $^3$J$_{HH} = 8.2$ Hz, 1H), 7.61 (d, $^4$J$_{HH} = 1.8$ Hz, 1H), 7.49 (dd, $^3$J$_{HH} = 7.9$ Hz and $^4$J$_{HH} = 1.8$ Hz, 1H), 7.33 (dd, $^3$J$_{HH} = 8.5$ Hz and $^4$J$_{HH} = 1.2$ Hz, 2H), 7.26 (t, $^3$J$_{HH} = 8.7$ Hz, 2H), 7.14 (tt, $^3$J$_{HH} = 7.3$ Hz and $^4$J$_{HH} = 0.9$ Hz, 1H), 3.36 (d, $^2$J$_{HH} = 19.5$ Hz, 1H), 2.97 (d, $^2$J$_{HH} = 19.8$ Hz, 1H), 2.43 (s, 3H), 0.75 (t, $^3$J$_{HH} = 7.9$ Hz, 9H), 0.61 (dq, $^2$J$_{HH} = 14.9$ Hz and $^3$J$_{HH} = 7.3$ Hz, 3H), 0.54 (dq, $^2$J$_{HH} = 14.9$ Hz and $^3$J$_{HH} = 8.5$ Hz, 3H).

$^{13}$C NMR (CDCl₃): δ 206.1, 156.7, 145.5, 137.3, 137.0, 135.7, 128.6, 128.5, 127.2, 125.7, 124.6, 51.0, 43.4, 21.3, 8.0, 3.5. Anal. Calcd for C$_{22}$H$_{28}$OSi: C, 78.51; H, 8.39. Found: C, 78.30; H, 8.54.

Table 3, Entry 3. Eluant for chromatography: Et₂O/hexane = 1/10. Pale yellow solid. 83% yield. The ee value was determined on a Daicel Chiralpak AS column with hexane : 2-propanol = 95 : 5, flow = 0.5 mL/min. Retention times: 34.3 min [(R)-enantiomer], 47.6 min [(S)-enantiomer]. 98% ee. [α]$_D^{20}$ -174 (c 1.41, CHCl₃). The absolute configuration was assigned by analogy with 3jg (equation 3).

$^1$H NMR (CDCl₃): δ 7.70 (d, $^3$J$_{HH} = 7.9$ Hz, 1H), 7.52 (s, 1H), 7.34 (dd, $^3$J$_{HH} = 8.5$ Hz and $^4$J$_{HH} = 1.2$ Hz, 2H), 7.28 (t, $^3$J$_{HH} = 7.8$ Hz, 2H), 7.20 (d, $^3$J$_{HH} = 7.9$ Hz, 1H), 7.15 (tt, $^3$J$_{HH} = 7.3$ Hz and $^4$J$_{HH} = 1.2$ Hz, 1H), 3.34 (d, $^2$J$_{HH} = 19.5$ Hz, 1H), 2.96 (d, $^2$J$_{HH} = 19.5$ Hz, 1H),
2.52 (s, 3H), 0.75 (t, $^3J_{HH} = 7.9$ Hz, 9H), 0.62 (dq, $^2J_{HH} = 14.9$ Hz and $^3J_{HH} = 7.3$ Hz, 3H), 0.55 (dq, $^2J_{HH} = 14.9$ Hz and $^3J_{HH} = 8.2$ Hz, 3H). $^{13}$C NMR (CDCl$_3$): δ 205.2, 159.7, 145.24, 145.19, 134.7, 128.8, 128.4, 128.2, 127.0, 125.6, 124.2, 50.8, 43.4, 22.6, 7.8, 3.3. Anal. Calcd for C$_{22}$H$_{28}$OSi: C, 78.51; H, 8.39. Found: C, 78.66; H, 8.58.

Table 3, Entry 4. Eluant for chromatography: Et$_2$O/hexane = 1/6. Pale yellow oil. 82% yield. The $ee$ value was determined on a Daicel Chiralcel OD-H column with hexane : 2-propanol = 90 : 10, flow = 0.4 mL/min. Retention times: 13.8 min [(R)-enantiomer], 23.1 min [(S)-enantiomer]. 98% $ee$. [α]$^{20}_{D}$ –185 (c 1.03, CHCl$_3$). The absolute configuration was assigned by analogy with 3jg (equation 3).

$^1$H NMR (CDCl$_3$): δ 7.76 (d, $^3J_{HH} = 8.5$ Hz, 1H), 7.36-7.33 (m, 2H), 7.28 (t, $^3J_{HH} = 7.9$ Hz, 2H), 7.158 (d, $^4J_{HH} = 2.1$ Hz, 1H), 7.156 (tt, $^3J_{HH} = 7.3$ Hz and $^4J_{HH} = 1.2$ Hz, 1H), 6.94 (dd, $^3J_{HH} = 8.5$ Hz and $^4J_{HH} = 2.1$ Hz, 1H), 3.93 (s, 3H), 3.33 (d, $^2J_{HH} = 19.2$ Hz, 1H), 2.95 (d, $^2J_{HH} = 19.2$ Hz, 1H), 0.78 (t, $^3J_{HH} = 7.9$ Hz, 9H), 0.64 (dq, $^2J_{HH} = 14.9$ Hz and $^3J_{HH} = 7.3$ Hz, 3H), 0.58 (dq, $^2J_{HH} = 15.2$ Hz and $^3J_{HH} = 8.2$ Hz, 3H). $^{13}$C NMR (CDCl$_3$): δ 203.8, 164.7, 161.6, 144.9, 130.3, 128.4, 126.9, 125.9, 125.5, 113.5, 112.9, 55.7, 50.8, 43.4, 7.7, 3.2. Anal. Calcd for C$_{22}$H$_{28}$O$_2$Si: C, 74.95; H, 8.01. Found: C, 74.89; H, 8.26.

Table 3, Entry 5. The reaction was conducted in the presence of 8 mol% Rh/(R)-segphos. Eluant for chromatography: Et$_2$O/hexane = 1/10. Pale yellow oil. 79% yield. The $ee$ value was determined on a Daicel Chiralpak AS column with hexane : 2-propanol = 90 : 10, flow = 0.4 mL/min. Retention times: 17.0 min [(R)-enantiomer], 19.8 min [(S)-enantiomer]. 99% $ee$. [α]$^{20}_{D}$ –158 (c 0.81, CHCl$_3$). The absolute configuration was assigned by analogy with 3jg (equation 3).
$^1$H NMR (CDCl$_3$): δ 7.82 (dd, $^3J_{HH} = 8.5$ Hz and $^4J_{HF} = 5.6$ Hz, 1H), 7.41 (dd, $^3J_{HF} = 9.5$ Hz and $^4J_{HH} = 1.9$ Hz, 1H), 7.33-7.28 (m, 4H), 7.18 (tt, $^3J_{HH} = 6.8$ Hz and $^4J_{HH} = 1.7$ Hz, 1H), 7.10 (td, $^3J = 8.4$ Hz and $^4J_{HH} = 2.2$ Hz, 1H), 3.37 (d, $^2J_{HH} = 19.5$ Hz, 1H), 0.77 (t, $^3J_{HH} = 7.8$ Hz, 9H), 0.63 (dq, $^2J_{HH} = 15.1$ Hz and $^3J_{HH} = 7.1$ Hz, 3H), 0.56 (dq, $^2J_{HH} = 15.1$ Hz and $^3J_{HH} = 8.3$ Hz, 3H). $^{13}$C NMR (CDCl$_3$): δ 203.7, 166.8 (d, $^1J_{CF} = 255$ Hz), 162.0 (d, $^3J_{CF} = 9.3$ Hz), 144.3, 133.4, 128.7, 126.8, 126.5 (d, $^3J_{CF} = 10.3$ Hz), 125.9, 115.2 (d, $^2J_{CF} = 22.7$ Hz), 115.1 (d, $^2J_{CF} = 22.7$ Hz), 50.7, 43.8, 7.8, 3.2. Anal. Calcd for C$_{21}$H$_{25}$FOSi: C, 74.07; H, 7.40. Found: C, 73.85; H, 7.48.

Table 3, Entry 6. Eluant for chromatography: Et$_2$O/hexane = 1/10. Pale yellow oil. 90% yield. The ee value was determined on a Daicel Chiralcel OD-H column with hexane : 2-propanol = 97 : 3, flow = 0.5 mL/min. Retention times: 12.9 min [(R)-enantiomer], 16.8 min [(S)-enantiomer]. 94% ee. [α]$^2_D$ = −178 (c 1.10, CHCl$_3$). The absolute configuration was assigned by analogy with 3jg (equation 3).

$^1$H NMR (CDCl$_3$): δ 7.81 (d, $^3J_{HH} = 7.6$ Hz, 1H), 7.69 (t, $^3J_{HH} = 7.7$ Hz, 1H), 7.65 (d, $^3J_{HH} = 7.7$ Hz, 1H), 7.39 (t, $^3J_{HH} = 7.5$ Hz, 1H), 7.35 (d, $^3J_{HH} = 8.1$ Hz, 2H), 7.29 (t, $^3J_{HH} = 8.0$ Hz, 2H), 7.17 (t, $^3J_{HH} = 7.3$ Hz, 1H), 3.27 (d, $^2J_{HH} = 19.6$ Hz, 1H), 3.00 (d, $^2J_{HH} = 19.4$ Hz, 1H), 0.75 (t, $^3J_{HH} = 7.9$ Hz, 3H), 0.48 (dq, $^2J_{HH} = 14.9$ Hz and $^3J_{HH} = 7.9$ Hz, 1H), 0.36 (dq, $^2J_{HH} = 15.1$ Hz and $^3J_{HH} = 7.8$ Hz, 1H), −0.035 (s, 3H), −0.044 (s, 3H). $^{13}$C NMR (CDCl$_3$): δ 205.7, 159.3, 144.8, 136.8, 134.4, 128.6, 128.1, 127.0, 126.9, 125.7, 124.4, 50.2, 43.2, 7.5, 5.6, −4.6, −4.9. Anal. Calcd for C$_{19}$H$_{22}$OSi: C, 77.50; H, 7.53. Found: C, 77.47; H, 7.53.

Table 3, Entry 7. The reaction was conducted for 24 h in the presence of 8 mol% Rh/(R)-
segphos with 1.5 equiv of 2a. Eluant for chromatography: Et₂O/hexane = 1/10. Pale yellow oil. 75% yield. The ee value was determined on a Daicel Chiralcel OD-H column with hexane : 2-propanol = 97 : 3, flow = 0.6 mL/min. Retention times: 12.2 min [(R)-enantiomer], 14.5 min [(S)-enantiomer]. 98% ee. \([\alpha]^{20}_D – 153 \) (c 0.67, CHCl₃). The absolute configuration was assigned by analogy with 3jg (equation 3).

\(^1\)H NMR (CDCl₃): \(\delta\) 7.89 (d, \(^3\)J\(_{HH}\) = 7.9 Hz, 1H), 7.81 (d, \(^3\)J\(_{HH}\) = 7.6 Hz, 1H), 7.66 (t, \(^3\)J\(_{HH}\) = 7.7 Hz, 1H), 7.46 (d, \(^3\)J\(_{HH}\) = 7.8 Hz, 2H), 7.40 (t, \(^3\)J\(_{HH}\) = 7.3 Hz, 1H), 7.31 (t, \(^3\)J\(_{HH}\) = 7.5 Hz, 2H), 7.17 (t, \(^3\)J\(_{HH}\) = 7.3 Hz, 1H), 3.46 (d, \(^2\)J\(_{HH}\) = 19.5 Hz, 1H), 3.16 (d, \(^2\)J\(_{HH}\) = 19.5 Hz, 1H), 0.57 (s, 9H), 0.19 (s, 3H), –0.04 (s, 3H). \(^13\)C NMR (CDCl₃): \(\delta\) 205.7, 159.2, 144.8, 136.8, 134.3, 129.1, 128.4, 127.3, 127.1, 125.8, 124.5, 49.9, 44.0, 28.1, 19.8, –5.2, –6.0. Anal. Calcd for C\(_{21}\)H\(_{26}\)OSi: C, 78.21; H, 8.13. Found: C, 77.95; H, 8.33.

Table 3, Entry 8. The reaction was conducted in the presence of 8 mol% Rh/(R)-segphos. Eluant for chromatography: Et₂O/hexane = 1/11. Pale yellow oil. 88% yield. The ee value was determined on a Daicel Chiralcel OD-H column with hexane : 2-propanol = 97 : 3, flow = 0.3 mL/min. Retention times: 20.8 min [(R)-enantiomer], 24.3 min [(S)-enantiomer]. 98% ee. \([\alpha]^{20}_D – 157 \) (c 0.77, CHCl₃). The absolute configuration was assigned by analogy with 3jg (equation 3).

\(^1\)H NMR (CDCl₃): \(\delta\) 7.81 (d, \(^3\)J\(_{HH}\) = 7.6 Hz, 1H), 7.68-7.63 (m, 2H), 7.36 (t, \(^3\)J\(_{HH}\) = 8.0 Hz, 1H), 7.32-7.25 (m, 4H), 7.15 (t, \(^3\)J\(_{HH}\) = 7.3 Hz, 1H), 3.32 (d, \(^2\)J\(_{HH}\) = 19.8 Hz, 1H), 2.99 (d, \(^2\)J\(_{HH}\) = 19.8 Hz, 1H), 0.83 (dd, \(^3\)J\(_{HH}\) = 7.0 and 4.0 Hz, 9H), 0.80-0.69 (m, 6H). \(^13\)C NMR (CDCl₃): \(\delta\) 205.8, 160.0, 145.7, 136.5, 134.4, 128.7, 127.7, 126.73, 126.68, 125.7, 124.3, 51.1, 45.2, 9.2, 4.9. Anal. Calcd for C\(_{21}\)H\(_{26}\)OGe: C, 68.72; H, 7.14. Found: C, 68.99; H, 7.28.
Equation 3. The reaction was conducted with $1j/2g = 1.2/1.0$ in the presence of 8 mol% Rh/(R)-segphos. Eluant for chromatography: Et$_2$O/hexane = 1/10. Pale yellow solid. 71% yield. The $ee$ value was determined on a Daicel Chiralcel OD-H column with hexane : 2-propanol = 100 : 1, flow = 0.6 mL/min. Retention times: 14.5 min [(S)-enantiomer], 18.4 min [(R)-enantiomer]. 97% $ee$. $[\alpha]_D^{20} – 114$ (c 1.20, CHCl$_3$). Recrystallization from pentane afforded single crystals and the absolute configuration was determined to be (R) by X-ray analysis.

$^1$H NMR (CDCl$_3$): $\delta$ 7.81 (d, $^3J_{HH} = 2.1$ Hz, 1H), 7.79-7.77 (m, 3H), 7.73 (d, $^3J_{HH} = 7.9$ Hz, 1H), 7.70 (s, 1H), 7.68 (dd, $^3J_{HH} = 8.2$ Hz and $^4J_{HH} = 1.8$ Hz, 1H), 7.47-7.41 (m, 2H), 7.39 (dd, $^3J_{HH} = 8.5$ Hz and $^4J_{HH} = 1.8$ Hz, 1H), 3.46 (d, $^2J_{HH} = 19.8$ Hz, 1H), 3.07 (d, $^2J_{HH} = 19.8$ Hz, 1H), 0.78 (t, $^3J_{HH} = 7.9$ Hz, 9H), 0.66 (dq, $^2J_{HH} = 14.9$ Hz and $^3J_{HH} = 7.9$ Hz, 3H), 0.60 (dq, $^2J_{HH} = 15.5$ Hz and $^3J_{HH} = 7.9$ Hz, 3H). $^{13}$C NMR (CDCl$_3$): $\delta$ 204.3, 157.4, 142.1, 138.5, 134.3, 133.4, 133.3, 131.6, 129.6, 128.4, 127.9, 127.5, 126.5, 126.1, 125.8, 124.6, 124.3, 50.8, 43.7, 7.9, 3.4. Anal. Calcd for C$_{25}$H$_{27}$ClOSi: C, 73.77; H, 6.69. Found: C, 73.85; H, 6.78.

Procedures for Scheme 3.

LiAlH$_4$ (79.4 mg, 2.09 mmol) was added to a solution of 3aa (345 mg, 1.07 mmol; 98% $ee$ (R)) in THF (3.0 mL) at room temperature, and the mixture was stirred for 1.5 h at room temperature. The reaction was quenched with water (0.16 mL) and filtered through celite with Et$_2$O. After removal of the solvent, the residue was dissolved in benzene (15 mL) and $p$-toluenesulfonic acid (5.0 mg, 26 µmol; monohydrate) was added to it. The resulting mixture was refluxed for 1 h with a Dean–Stark trap and the solvent was removed under
vacuum. The residue was chromatographed on silica gel with Et₂O/hexane = 1/1 to afford compound 4 as a pale orange oil (316 mg, 1.03 mmol; 96% yield).

The ee value was determined on a Daicel Chiralcel OD-H column with hexane : 2-propanol = 200 : 1, flow = 0.4 mL/min. Retention times: 10.5 min [(S)-enantiomer], 14.4 min [(R)-enantiomer]. 98% ee. [α]⁰₂₀⁻D –82.4 (c 1.03, CHCl₃).

¹H NMR (CDCl₃): δ 7.66 (d, 3 J_HH = 7.6 Hz, 1H), 7.60 (dd, 3 J_HH = 7.9 Hz and 4 J_HH = 1.5 Hz, 2H), 7.49 (d, 3 J_HH = 7.6 Hz, 1H), 7.44 (t, 3 J_HH = 7.6 Hz, 2H), 7.34 (tt, 3 J_HH = 7.3 Hz and 4 J_HH = 1.2 Hz, 1H), 7.28 (t, 3 J_HH = 7.3 Hz, 1H), 7.21 (td, 3 J_HH = 7.5 Hz and 4 J_HH = 1.2 Hz, 1H), 6.72 (d, 3 J_HH = 1.8 Hz, 1H), 3.76 (d, 3 J_HH = 2.1 Hz, 1H), 0.89 (t, 3 J_HH = 7.9 Hz, 9H), 0.59-0.51 (m, 6H). ¹³C NMR (CDCl₃): δ 146.7, 143.0, 142.2, 136.9, 133.3, 128.7, 128.0, 127.2, 124.9, 124.0, 123.3, 120.4, 42.8, 7.6, 3.2. Anal. Calcd for C₂₁H₂₆Si: C, 82.29; H, 8.55. Found: C, 82.05; H, 8.53.

Diisobutylaluminum hydride (0.21 mL, 0.20 mmol; 0.95 M solution in hexane) was added to a solution of 3aa (32.0 mg, 0.10 mmol; 98% ee (R)) in THF (1.8 mL) at –78 °C, and the mixture was stirred for 1 h at –78 °C. The reaction was quenched with water and this was 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 = 1/3 to afford compound 5 as a colorless oil (31.3 mg, 97 µmol; 97% yield (dr = 93/7)).

The ee value of the major diastereomer was determined on a Daicel Chiralcel OJ-H column with hexane : 2-propanol = 95 : 5, flow = 0.5 mL/min. Retention times: 11.1 min [(1R,3R)-enantiomer], 13.2 min [(1S,3S)-enantiomer]. 98% ee. [α]⁰₂₀⁻D –70.3 (c 1.18, CHCl₃). The relative configuration was determined to be cis by NOE.

¹H NMR (CDCl₃): δ 7.47 (d, 3 J_HH = 7.6 Hz, 1H), 7.38 (d, 3 J_HH = 7.3 Hz, 1H), 7.33 (t, 3 J_HH = 7.1 Hz, 1H), 7.28 (td, 3 J_HH = 7.3 Hz and 4 J_HH = 0.9 Hz, 1H), 7.21–7.16 (m, 4H), 7.09–7.05 (m, 1H), 5.10 (t, 3 J_HH = 7.8 Hz, 1H), 3.03 (dd, 2 J_HH = 12.8 Hz and 3 J_HH = 6.7 Hz, 1H), 2.32 (dd, 2 J_HH = 12.8 Hz and 3 J_HH = 8.8 Hz, 1H), 1.96 (bs, 1H), 0.80 (t, 3 J_HH = 7.8 Hz, 9H), 0.67
(dq, $^2J_{HH} = 15.2$ Hz and $^3J_{HH} = 7.3$ Hz, 3H), 0.61 (dq, $^2J_{HH} = 15.2$ Hz and $^3J_{HH} = 7.9$ Hz, 3H).

$^{13}$C NMR (CDCl$_3$): $\delta$ 146.3, 145.7, 145.2, 128.4, 128.1, 127.4, 126.9, 126.7, 124.9, 124.1, 75.4, 48.6, 46.5, 8.1, 3.5. Anal. Calcd for C$_{21}$H$_{28}$OSi: C, 77.72; H, 8.70. Found: C, 77.63; H, 8.79.

$N,N$-Diisopropylethylamine (312 mg, 2.41 mmol) and chloromethyl methyl ether (212 mg, 2.64 mmol) were added to a solution of compound 5 (374 mg, 1.15 mmol; dr = 93/7) in dichloromethane (10 mL) at room temperature and the mixture was stirred for 19 h at room temperature. The reaction was quenched with water and this was extracted with Et$_2$O. The organic layer was dried over MgSO$_4$, filtered, and concentrated under vacuum. The residue was chromatographed on silica gel with Et$_2$O/hexane = 1/10 to afford compound 6 as a white solid (380 mg, 1.03 mmol; 90% yield (single diastereomer)).

The ee value was determined on a Daicel Chiralcel OJ-H column with hexane : 2-propanol = 15 : 1, flow = 0.4 mL/min. Retention times: 17.4 min [(1R,3R)-enantiomer], 20.7 min [(1S,3S)-enantiomer]. 98% ee. $[\alpha]^{20}_D$ –50.7 (c 1.28, CHCl$_3$).

$^1$H NMR (CDCl$_3$): $\delta$ 7.46 (d, $^3J_{HH} = 7.6$ Hz, 1H), 7.38 (d, $^3J_{HH} = 7.6$ Hz, 1H), 7.32 (td, $^3J_{HH} = 7.0$ Hz and $^4J_{HH} = 0.6$ Hz, 1H), 7.26 (t, $^3J_{HH} = 7.3$ Hz, 1H), 7.21-7.15 (m, 4H), 7.09-7.03 (m, 1H), 5.01 (t, $^3J_{HH} = 7.6$ Hz, 1H), 4.84 (d, $^2J_{HH} = 6.7$ Hz, 1H), 4.79 (d, $^2J_{HH} = 6.7$ Hz, 1H), 3.45 (s, 3H), 3.04 (dd, $^2J_{HH} = 12.5$ Hz and $^3J_{HH} = 6.7$ Hz, 1H), 2.45 (dd, $^2J_{HH} = 12.5$ Hz and $^3J_{HH} = 8.8$ Hz, 1H), 0.80 (t, $^3J_{HH} = 7.8$ Hz, 9H), 0.67 (dq, $^2J_{HH} = 14.9$ Hz and $^3J_{HH} = 7.3$ Hz, 3H), 0.62 (dq, $^2J_{HH} = 15.2$ Hz and $^3J_{HH} = 8.2$ Hz, 3H). $^{13}$C NMR (CDCl$_3$): $\delta$ 146.0, 145.3, 144.0, 128.1, 127.34, 127.27, 126.8, 126.7, 124.8, 124.7, 96.6, 81.2, 55.6, 46.6, 46.1, 8.0, 3.5. Anal. Calcd for C$_{23}$H$_{32}$O$_2$Si: C, 74.95; H, 8.75. Found: C, 75.16; H, 9.02.
TBAF (0.21 mL, 0.21 mmol; 1.0 M solution in THF) was added to a solution of compound 6 (76.4 mg, 0.207 mmol) in THF (0.80 mL) at 0 °C and the mixture was stirred for 5.5 h at 0 °C. The reaction was quenched with water and this was 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 = 1/5 to afford compound 7 as a pale yellow oil (51.7 mg, 0.203 mmol; 98% yield (dr = 91/9)).

The ee value of the major diastereomer was determined on a Daicel Chiralcel OD-H column with hexane : 2-propanol = 100 : 1, flow = 0.5 mL/min. Retention times: 21.6 min [(1S,3S)-enantiomer], 37.9 min [(1R,3R)-enantiomer]. 98% ee. [α]²⁰ D –21.3 (c 1.05, CHCl₃). The relative configuration was determined to be cis by NOE.

¹H NMR (CDCl₃): δ 7.46 (d, 3J_HH = 7.6 Hz, 1H), 7.30 (t, 3J_HH = 7.9 Hz, 2H), 7.28 (d, 3J_HH = 7.6 Hz, 1H), 7.25-7.20 (m, 4H), 6.94 (d, 3J_HH = 7.6 Hz, 1H), 5.18 (t, 3J_HH = 7.0 Hz, 1H), 4.87 (s, 2H), 4.18 (t, 3J_HH = 8.4 Hz, 1H), 3.45 (s, 3H), 3.00 (dt, 2J_HH = 12.8 Hz and 3J_HH = 7.3 Hz, 1H), 2.06 (ddd, 2J_HH = 13.1 Hz and 3J_HH = 9.1 and 7.3 Hz, 1H). ¹³C NMR (CDCl₃): δ 145.8, 144.7, 143.5, 128.6, 128.50, 128.45, 127.2, 126.6, 125.2, 124.4, 96.4, 80.4, 55.7, 48.7, 44.6. Anal. Calcd for C₁₇H₁₈O₂: C, 80.28; H, 7.13. Found: C, 80.57; H, 7.35.

IV. X-ray Crystal Structure of Compound 3jg

Data Collection

A pale yellow pentane solution of compound 3jg was prepared. Crystals suitable for X-ray analysis were obtained by cooling the solution to –20 °C overnight.

A colorless prism crystal of C₁₂₅H₁₃₅O₅Cl₅Si₅ having approximate dimensions of 0.40 x 0.20 x 0.10 mm was mounted on a glass fiber. All measurements were made on a Rigaku RAXIS RAPID imaging plate area detector with graphite monochromated Mo-Kα radiation.

Indexing was performed from 3 oscillations that were exposed for 45 seconds. The crystal-to-detector distance was 127.40 mm.

Cell constants and an orientation matrix for data collection corresponded to a primitive monoclinic cell with dimensions:

\[
\begin{align*}
a &= 22.698(4) \text{ Å} \\
b &= 11.599(3) \text{ Å} \\
\beta &= 117.781(6)^\circ
\end{align*}
\]
c = 23.188(4) Å
V = 5401.0(21) Å³

For Z = 2 and F.W. = 2035.13, the calculated density is 1.251 g/cm³. Based on the systematic absences of:

0k0: k ± 2n

packing considerations, a statistical analysis of intensity distribution, and the successful solution and refinement of the structure, the space group was determined to be:

P2₁ (#4)

The data were collected at a temperature of −150 ± 1 °C to a maximum 2θ value of 55.0°. A total of 44 oscillation images were collected. A sweep of data was done using ω scans from 130.0 to 190.0° in 5.0° step, at χ = 45.0° and φ = 30.0°. The exposure rate was 150.0 [sec./°]. A second sweep was performed using ω scans from 0.0 to 160.0° in 5.0° step, at χ = 45.0° and φ = 180.0°. The exposure rate was 150.0 [sec./°]. The crystal-to-detector distance was 127.40 mm. Readout was performed in the 0.100 mm pixel mode.

Data Reduction

Of the 7909 reflections that were collected, 2452 were unique (Rint = 0.065).

The linear absorption coefficient, µ, for Mo-Kα radiation is 2.450 cm⁻¹. An empirical absorption correction was applied which resulted in transmission factors ranging from 0.548 to 0.976. The data were corrected for Lorentz and polarization effects.

Structure Solution and Refinement

The structure was solved by direct methods⁷ and expanded using Fourier techniques.⁸ The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the

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The final cycle of full-matrix least-squares refinement on F was based on 36290 observed reflections (I > 2.00σ(I)) and 1397 variable parameters and converged (largest parameter shift was 0.00 times its esd) with unweighted and weighted agreement factors of:

$$R = \sum |F_o| - |F_c| / \sum |F_o| = 0.0631$$

$$R_w = [\sum w (|F_o| - |F_c|)^2 / \sum w F_o^2]^{1/2} = 0.0676$$

The standard deviation of an observation of unit weight was 0.80. A Sheldrick weighting scheme was used. Plots of Σ w (|Fol − |Fc|)² versus |Fol, reflection order in data collection, sin θ/λ and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to 1.84 and −1.38 e⁻ /Å³, respectively. The absolute structure was deduced based on Flack parameter 0.01(3).

Neutral atom scattering factors were taken from Cromer and Waber. Anomalous dispersion effects were included in Fcalc; the values for Δf' and Δf'' were those of Creagh and McAuley. The values for the mass attenuation coefficients are those of Creagh and Hubbell. All calculations were performed using the CrystalStructure crystallographic software package.

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9 Least Squares function minimized:
$$\sum w (|F_o| - |F_c|)^2$$ where w = Least Squares weights.
10 Standard deviation of an observation of unit weight:
$$[\sum w (|F_o| - |F_c|)^2/(N_o - N_v)]^{1/2}$$ where: N₀ = number of observations, Nᵥ = number of variables
The crystal structure has been deposited at the Cambridge Crystallographic Data Centre (deposition number: CCDC 631569). The data can be obtained free of charge via the Internet at www.ccdc.cam.ac.uk/conts/retrieving.html.

Experimental Details

A. Crystal Data

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical Formula</td>
<td>C$<em>{125}$H$</em>{135}$O$_5$Cl$_5$Si$_5$</td>
</tr>
<tr>
<td>Formula Weight</td>
<td>2035.13</td>
</tr>
<tr>
<td>Crystal Color, Habit</td>
<td>colorless, prism</td>
</tr>
<tr>
<td>Crystal Dimensions</td>
<td>0.40 X 0.20 X 0.10 mm</td>
</tr>
<tr>
<td>Crystal System</td>
<td>monoclinic</td>
</tr>
<tr>
<td>Lattice Type</td>
<td>Primitive</td>
</tr>
<tr>
<td>Indexing Images</td>
<td>3 oscillations @ 45.0 seconds</td>
</tr>
<tr>
<td>Detector Position</td>
<td>127.40 mm</td>
</tr>
<tr>
<td>Pixel Size</td>
<td>0.100 mm</td>
</tr>
<tr>
<td>Lattice Parameters</td>
<td></td>
</tr>
<tr>
<td>a</td>
<td>22.698(4) Å</td>
</tr>
<tr>
<td>b</td>
<td>11.599(3) Å</td>
</tr>
<tr>
<td>c</td>
<td>23.188(4) Å</td>
</tr>
<tr>
<td>β</td>
<td>117.781(6) °</td>
</tr>
<tr>
<td>V</td>
<td>5401.0(21) Å$^3$</td>
</tr>
<tr>
<td>Space Group</td>
<td>P2$_1$ (#4)</td>
</tr>
<tr>
<td>Z value</td>
<td>2</td>
</tr>
<tr>
<td>Dcalc</td>
<td>1.251 g/cm$^3$</td>
</tr>
<tr>
<td>F000</td>
<td>2160.00</td>
</tr>
<tr>
<td>μ(MoKα)</td>
<td>2.450 cm$^{-1}$</td>
</tr>
</tbody>
</table>
B. Intensity Measurements

Diffractometer: Rigaku RAXIS-RAPID

Radiation: MoKα (λ = 0.71075 Å) graphite monochromated

Detector Aperture: 280 mm x 256 mm

Data Images: 44 exposures

ω oscillation Range (χ=45.0, φ=30.0): 130.0 - 190.0°
Exposure Rate: 150.0 sec./°

ω oscillation Range (χ=45.0, φ=180.0): 0.0 - 160.0°
Exposure Rate: 150.0 sec./°

Detector Position: 127.40 mm

Pixel Size: 0.100 mm

2θmax: 55.0°

No. of Reflections Measured: Total: 7909

Corrections: Lorentz-polarization Absorption (trans. factors: 0.548 - 0.976)
C. Structure Solution and Refinement

Structure Solution  Direct Methods (SIR92)
Refinement  Full-matrix least-squares on F
Function Minimized  \( \Sigma w (|F_o| - |F_c|)^2 \)
Least Squares Weights  \( 1/ [0.0010F_o^2 + 3.0000\sigma(F_o^2) + 0.5000] \)
2\(\theta\)max cutoff  55.0°
Anomalous Dispersion  All non-hydrogen atoms
No. Observations (I>2.00\(\sigma(I)\))  36290
No. Variables  1397
Reflection/Parameter Ratio  25.98
Residuals: R (I>2.00\(\sigma(I)\))  0.0631
Residuals: Rw (I>2.00\(\sigma(I)\))  0.0676
Goodness of Fit Indicator  0.801
Flack Parameter  0.01(3)
Max Shift/Error in Final Cycle  0.000
Maximum peak in Final Diff. Map  1.84 e\(^-\)/Å\(^3\)
Minimum peak in Final Diff. Map  −1.38 e\(^-\)/Å\(^3\)