Supporting Information

Enantioselective Total Synthesis of (+)-Tricycloclavulone

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Compound **5**.

To a suspension of copper(II) chloride (1.3 g, 9.7 mmol) and ligand **8** (5.76 g, 11.6 mmol) in CH_2Cl_2 (110 mL) was stirred at ambient temperature for 30 min and silver hexafluoroantimonate (7.0 g, 20.4 mmol) was added to the resulting mixture. After being stirred for 1 h at ambient temperature, a solution of 2-methoxycarbonyl-2-cyclohexen-1-one (**6**) (6.40 g, 45.7 mmol) and phenylthioacetylene (**7**) (7.24 g, 54.8 mmol) in CH_2Cl_2 (130 mL) was added to the mixture at -78°C . After being stirred for 1.5 h at same temperature, phosphate buffer (pH 6.86, 150 mL) was added to the mixture and the resulting mixture was extracted with AcOEt. The organic layer was washed with brine and dried over MgSO_4 . Filtration and concentration of the mixture under reduced pressure gave crude material, which was purified by silica gel column chromatography (hexane : AcOEt, 7 : 1) to afford compound **5** (8.44 g, 30.8 mmol) in 67% yield. 73% ee (Chiralcel OJ-H, hexane : IPA = 95 : 5). $[\alpha]_{\text{D}}^{22} = +499^\circ$ (c 1.33, CHCl_3). IR (neat) cm^{-1} : 1746, 1731, 1294, 747. ^1H NMR (300 MHz, CDCl_3) δ : 1.89 (1H, bdd, $J = 9.1, 13.5$ Hz), 2.13 (1H, dddd, $J = 6.9, 8.7, 11.9, 13.5$ Hz), 2.39 (1H, ddd, $J = 1.0, 8.7, 18.3$ Hz), 3.02 (1H, ddd, $J = 9.1, 11.9, 18.3$ Hz), 3.67 (1H, d, $J = 6.9$ Hz), 3.75 (3H, s), 5.88 (1H, s), 7.26-7.38 (3H, m), 7.49-7.53 (2H, m). ^{13}C NMR (75 MHz, CDCl_3) δ : 22.4 (CH_2), 34.9 (CH_2), 48.3 (CH), 52.3 (CH_3), 66.2 (C), 128.8 (CH), 129.4 (CH), 129.7 (C), 133.0 (CH), 133.8 (CH), 140.5 (C), 167.6 (C), 208.4 (C). EI-MS m/z : 274 (M^+). Anal. Calcd for $\text{C}_{15}\text{H}_{14}\text{O}_3\text{S}$: C, 65.67; H, 5.14. Found: C, 65.55; H, 5.11.

Ligand **8**.

To the mixture of (R)-BINOL (8.0 g, 27.9 mmol), picolinic acid (7.56 g, 61.4 mmol), and 4-

dimethylaminopyridine (684 mg, 5.6 mmol) in CH₂Cl₂ (80 mL) was added a solution of dicyclohexylcarbodiimide (13.2 g, 64.2 mmol) at ambient temperature. After being stirred for 15 h at same temperature, the mixture was filtered through celite and the filtrate was concentrated under reduced pressure. The residue was purified by silica gel column chromatography (hexane : AcOEt, 1 : 5) to afford the ligand **8** (12.9 g, 26.0 mmol) in 93% yield. mp 90-95 °C. $[\alpha]_D^{28} +80.1^\circ$ (*c* 1.59, CHCl₃). IR (KBr) $\nu_{\text{cm}^{-1}}$: 1752, 1685, 1654, 1582, 745. ¹H NMR (300 MHz, CDCl₃) δ : 7.31-7.48 (14H, m), 7.56-7.61 (4H, m), 7.90 (2H, d, *J* = 8.1 Hz), 8.00 (2H, d, *J* = 8.9 Hz), 8.63 (2H, d, *J* = 4.6 Hz). ¹³C NMR (75 MHz, CDCl₃) δ : 121.5, 123.5, 125.4, 125.9, 126.1, 126.9, 127.1, 127.9, 129.8, 131.6, 133.3, 136.9, 146.8, 147.0, 150.0, 162.8. HRESIMS calcd for C₃₂H₂₁N₂O₄: 497.1501 (M+H)⁺, Found: 497.1496. Anal. Calcd for C₃₂H₂₀N₂O₄: C, 77.41; H, 4.06; N, 5.64. Found: C, 77.20; H, 4.15; N, 5.58.

Compound **9**.

A solution of vinylmagnesium chloride (1.38 M in THF, 0.28 mL, 0.38 mmol) was added to a solution of compound **5** (100 mg, 0.36 mmol) in THF (1.5 mL) at -20 °C and the mixture was stirred at same temperature for 10 min. Saturated aq. NH₄Cl was added to the reaction mixture and the mixture was extracted with ether. Organic layer was washed with brine, dried over MgSO₄, and concentrated under reduced pressure. The resulting residue was purified by silica gel column chromatography (hexane : AcOEt, 8 : 1) to afford the allyl alcohol derivative (109 mg, 0.36 mmol) in 99% yield. $[\alpha]_D^{22} = +16.9^\circ$ (*c* 1.27, CHCl₃). IR (neat) $\nu_{\text{cm}^{-1}}$: 3519, 1731, 1165, 923, 748. ¹H NMR (300 MHz, CDCl₃) δ : 1.47 (1H, dd, *J* = 6.9, 13.4 Hz), 1.70 (1H, tt, *J* = 6.6, 13.2 Hz), 1.85 (1H, dd, *J* = 6.4, 12.3 Hz), 2.37 (1H, dt, *J* = 6.8, 12.7 Hz), 2.62 (1H, s), 3.46 (1H, d, *J* = 6.8 Hz), 3.66 (3H, s), 5.15 (1H, dd, *J* = 1.3, 10.9 Hz), 5.38 (1H, dd, *J* = 1.3, 17.2 Hz), 5.80 (1H, d, *J* = 0.8 Hz), 6.00 (1H, dd, *J* = 10.9, 17.2 Hz), 7.32-7.37 (3H, m), 7.50-7.53 (2H, m). ¹³C NMR (75 MHz, CDCl₃) δ : 23.6 (CH₂), 36.3 (CH₂), 46.7 (CH), 51.8 (CH₃), 68.5 (C), 79.6 (C), 113.3 (CH₂), 128.3 (CH), 129.3 (CH), 130.8 (C), 132.7 (CH), 133.1 (CH), 138.3 (C), 138.8 (CH), 171.0 (C). EI-MS *m/z*: 302 (M⁺). HREIMS calcd for C₁₇H₁₈O₃S (M⁺) 302.0977, found 302.0990.

To the mixture of the allyl alcohol derivative (3.44 g, 11.4 mmol) and lutidine (2.7 mL, 22.8 mmol) in CH₂Cl₂ (40 mL) was added a solution of TESOTf (3.9 mL, 17.1 mmol) at -10 °C and the mixture was stirred at same temperature for 1 h. Water was added to the reaction mixture and the mixture was extracted with ether. The organic layer was washed with brine, dried over MgSO₄, and concentrated under reduced pressure. The resulting residue was purified by silica gel column chromatography (hexane : AcOEt, 15 : 1) to afford the allyl silyl ether derivative (4.74 g, 11.4 mmol) in 100% yield. $[\alpha]_D^{22} = +6.8^\circ$ (*c* 1.07, CHCl₃). IR (neat) $\nu_{\text{cm}^{-1}}$: 2951, 2874, 1731, 1237, 1048, 922, 745, 691. ¹H NMR (300 MHz, CDCl₃) δ : 0.63-0.72 (6H, m), 1.00-1.05 (9H, m), 1.46

(1H, dd, $J = 7.0, 13.3$ Hz), 1.67 (1H, tt, $J = 6.6, 13.1$ Hz), 2.01 (1H, dd, $J = 6.4, 12.3$ Hz), 2.36 (1H, dt, $J = 7.0, 12.7$ Hz), 3.32 (1H, d, $J = 6.9$ Hz), 3.69 (3H, s), 5.14 (1H, dd, $J = 1.4, 10.8$ Hz), 5.31 (1H, dd, $J = 1.4, 17.4$ Hz), 5.62 (1H, d, $J = 0.8$ Hz), 5.91 (1H, dd, $J = 10.8, 17.4$ Hz), 7.28-7.37 (3H, m), 7.49-7.52 (2H, m). ^{13}C NMR (75 MHz, CDCl_3) δ : 6.6 (CH_2), 7.1 (CH_3), 24.5 (CH_2), 35.5 (CH_2), 46.1 (CH_3), 51.3 (CH), 70.3 (C), 81.4 (C), 114.1 (CH_2), 127.9 (CH), 129.1 (CH), 129.5 (CH), 131.9 (C), 133.3 (CH), 139.3 (CH), 140.5 (C), 171.1 (C). EI-MS m/z : 416 (M^+). HREIMS calcd for $\text{C}_{23}\text{H}_{32}\text{O}_3\text{SiS}$ (M^+) 416.1841, found 416.1830.

To a solution of allyl silyl ether derivative (51.0 mg, 0.12 mmol) in ether (0.4 mL) was added LiAlH_4 (4.6 mg, 0.12 mmol) at 0 °C and the reaction mixture was stirred at same temperature for 10 min. To the reaction mixture was added a solution of Rochelle salt and the mixture was stirred for 30 min. The reaction mixture was extracted with ether and the organic layer was washed with brine, dried over MgSO_4 , and concentrated under reduced pressure. The resulting residue was purified by silica gel column chromatography (hexane : AcOEt, 7 : 1) to afford the alcohol derivative (45.6 g, 0.12 mmol) in 100% yield. $[\alpha]_{\text{D}}^{22} = +32.9^\circ$ (c 1.27, CHCl_3). IR (neat) vcm^{-1} : 3582, 2950, 2873, 1035, 920, 743, 690. ^1H NMR (300 MHz, CDCl_3) δ : 0.67-0.76 (6H, m), 1.00-1.06 (9H, m), 1.50 (1H, dd, $J = 7.4, 13.2$ Hz), 1.58 (1H, tt, $J = 6.7, 13.2$ Hz), 1.92 (1H, dd, $J = 5.9, 13.7$ Hz), 1.95 (1H, dd, $J = 3.7, 8.1$ Hz), 2.38 (1H, dt, $J = 7.4, 12.2$ Hz), 2.69 (1H, d, $J = 6.3$ Hz), 3.74 (1H, dd, $J = 8.1, 11.2$ Hz), 4.01 (1H, dd, $J = 3.7, 11.2$ Hz), 5.19 (1H, dd, $J = 1.4, 10.8$ Hz), 5.35 (1H, dd, $J = 1.4, 17.4$ Hz), 5.60 (1H, s), 6.00 (1H, dd, $J = 10.8, 17.4$ Hz), 7.32-7.36 (3H, m), 7.53-7.56 (2H, m). ^{13}C NMR (75 MHz, CDCl_3) δ : 6.6 (CH_2), 7.2 (CH_3), 25.3 (CH_2), 35.6 (CH_2), 44.3 (CH), 64.0 (CH_2), 66.1 (C), 82.2 (C), 113.5 (CH_2), 127.2 (CH), 128.0 (CH), 129.1 (CH), 132.0 (C), 133.2 (CH), 139.4 (CH), 143.1 (C). HRESIMS calcd for $\text{C}_{22}\text{H}_{32}\text{O}_2\text{SSi}$: 389.1985 ($\text{M}+\text{H}^+$), found: 389.1971.

To a solution of alcohol (1.80 g, 4.63 mmol) in CH_2Cl_2 (25 mL) was added Dess-Martin periodinane (2.36 g, 5.56 mmol) at room temperature. After being stirred for 20 min at same temperature, the mixture was diluted with ether and poured onto saturated aqueous NaHCO_3 . After filtration of the mixture, the filtrate was washed with saturated aqueous NaHCO_3 , brine, and dried over MgSO_4 . The mixture was filtered and concentrated under vacuum. The residue was purified by silica gel column chromatography (hexane : AcOEt, 9 : 1) to afford the aldehyde (1.57 g, 4.06 mmol) in 88% yield. $[\alpha]_{\text{D}}^{22} = -24.7^\circ$ (c 1.29, CHCl_3). IR (neat) vcm^{-1} : 2954, 2875, 1714, 1053, 1008, 744. ^1H NMR (300 MHz, CDCl_3) δ : 0.67-0.76 (6H, m), 1.00-1.06 (9H, m), 1.53 (1H, dd, $J = 7.3, 13.4$ Hz), 1.63 (1H, tt, $J = 6.6, 13.0$ Hz), 1.97 (1H, dd, $J = 6.2, 12.5$ Hz), 2.42 (1H, dt, $J = 7.3, 12.5$ Hz), 3.25 (1H, d, $J = 6.7$ Hz), 5.22 (1H, dd, $J = 1.1, 10.9$ Hz), 5.32 (1H, dd, $J = 1.1, 17.4$ Hz), 5.72 (1H, d, $J = 0.6$ Hz), 5.98 (1H, dd, $J = 10.9, 17.4$ Hz), 7.29-7.37 (3H, m), 7.48-7.51 (2H, m), 9.85 (1H, s). ^{13}C NMR (75 MHz, CDCl_3) δ : 6.6 (CH_2), 7.2 (CH_3), 24.7 (CH_2), 35.8 (CH_2), 43.6 (CH), 74.4 (C), 81.4 (C), 115.0 (CH_2), 128.2 (CH), 129.2 (CH), 130.2 (CH), 131.6 (C), 133.2 (CH), 138.9 (CH), 140.8 (C), 201.1 (CH). HRESIMS calcd for $\text{C}_{22}\text{H}_{30}\text{O}_2\text{SSi}$: 387.1824 ($\text{M}+\text{H}^+$), found: 387.1814.

A solution of *n*-butyllithium (1.58 M in hexane, 5.1 mL, 8.06 mmol) was added a solution of tetravinyltin (569 mg, 2.5 mmol) in THF (3.1 mL) at -78 °C and the mixture was stirred at same temperature for 20 min and at room temperature for 75 min. A solution of the aldehyde (1.96 g, 5.0 mmol) in THF (15 mL) was added to the reaction mixture at -78 °C. After being stirred for 1 h at same temperature, saturated aqueous NH_4Cl was added to the reaction mixture. The mixture was extracted with ether and organic layer was washed with brine, dried over MgSO_4 , and concentrated

under reduced pressure. The resulting mixture was purified by silica gel column chromatography (hexane : AcOEt, 12 : 1 – 9 : 1) to afford the compound **9** (1.89 g, 4.56 mmol, 92%) as a diastereomeric mixture (2 : 1). Less polar isomer (minor isomer). IR (neat) vcm^{-1} ; 3441, 2951, 2875, 1557, 1478, 1440, 1415, 1300, 1239, 1048, 1008, 921, 854, 744, 691. ^1H NMR (300 MHz, CDCl_3) δ ; 0.65-0.84 (6H, m), 1.00-1.05 (9H, m), 1.46 (1H, dd, $J = 7.0, 13.2$ Hz), 1.60 (1H, tt, $J = 6.4, 13.0$ Hz), 1.91 (1H, dd, $J = 6.1, 11.9$ Hz), 2.43 (1H, dt, $J = 7.1, 12.3$ Hz), 2.49 (1H, d, $J = 6.5$ Hz), 3.25 (1H, d, $J = 1.8$ Hz), 4.46 (1H, dd, $J = 0.9, 6.9$ Hz), 5.17 (1H, td, $J = 1.0, 10.3$ Hz), 5.28 (1H, dd, $J = 1.2, 10.9$ Hz), 5.33 (1H, td, $J = 1.0, 17.1$ Hz), 5.43 (1H, dd, $J = 1.2, 17.3$ Hz), 5.48 (1H, s), 6.04 (1H, ddd, $J = 6.9, 10.3, 17.1$ Hz), 6.16 (1H, dd, $J = 10.9, 17.3$ Hz), 7.31-7.39 (3H, m), 7.52-7.56 (2H, m). ^{13}C NMR (75 MHz, CDCl_3) δ ; 6.6 (CH_2), 7.2 (CH_3), 25.2 (CH_2), 35.2 (CH_2), 43.9 (CH), 67.1 (C), 74.9 (CH), 83.6 (C), 114.1 (CH_2), 116.6 (CH_2), 125.9 (CH), 128.1 (CH), 129.1 (CH), 131.9 (C), 133.5 (CH), 137.5 (CH), 138.9 (CH), 141.2 (C).

More polar isomer (major isomer). IR (neat) vcm^{-1} ; 3540, 2951, 2874, 1557, 1476, 1439, 1412, 1298, 1230, 1136, 1044, 1008, 921, 851, 743, 691. ^1H NMR (300 MHz, CDCl_3) δ ; 0.64-0.75 (6H, m), 0.99-1.04 (9H, m), 1.47 (1H, dd, $J = 7.1, 13.3$ Hz), 1.59 (1H, tt, $J = 6.3, 13.0$ Hz), 1.90-1.97 (2H, m), 2.40 (1H, dt, $J = 7.16, 12.3$ Hz), 2.94 (1H, d, $J = 6.6$ Hz), 4.34 (1H, brs), 5.18 (1H, dd, $J = 1.5, 10.8$ Hz), 5.20 (1H, td, $J = 1.7, 10.5$ Hz), 5.33 (1H, dd, $J = 1.5, 17.4$ Hz), 5.38 (1H, td, $J = 1.7, 17.4$ Hz), 5.62 (1H, d, $J = 0.8$ Hz), 6.05 (1H, dd, $J = 10.8, 17.4$ Hz), 6.37 (1H, ddd, $J = 5.3, 10.5, 17.4$ Hz), 7.30-7.38 (3H, m), 7.48-7.53 (2H, m). ^{13}C NMR (75 MHz, CDCl_3) δ ; 6.7 (CH_2), 7.3 (CH_3), 24.9 (CH_2), 36.6 (CH_2), 44.7 (CH), 69.5 (C), 71.4 (CH), 81.7 (C), 113.6 (CH_2), 115.3 (CH_2), 127.9 (CH), 128.7 (CH), 129.1 (CH), 132.1 (C), 133.3 (CH), 138.3 (C), 139.9 (CH), 140.8 (C).

Anal. Calcd for $\text{C}_{24}\text{H}_{34}\text{O}_2\text{SSi}$: C, 69.51 H, 8.26. Found: C, 69.38 H, 8.32. (mixture of isomers)

Compound **11**.

To a solution compound **9** (1.89 g, 4.56 mmol) in toluene (40 mL) was added [1,3-bis-(2,4,6-trimethylphenyl)-2-imidazolidinylidene]dichloro(phenylmethylene)-(tricyclohexylphosphine)ruthenium (**10**) (390 mg, 0.46 mmol) at 50 °C and the mixture was stirred at same temperature for 2 h. The mixture was poured onto water and the resulting mixture was extracted with AcOEt. The organic layer was washed with brine, dried over MgSO_4 , and concentrated under vacuum. The residue was purified by silica gel column chromatography (hexane : AcOEt, 9 : 1 - 7 : 1) to afford the allylic alcohol derivative (1.40 g, 3.62 mmol) as diastereomeric mixture (2 : 1) in 79% yield. Data for major isomer: IR (neat) vcm^{-1} ; 3406, 3055, 2952, 2874, 1769, 1583, 1552, 1236, 1112, 1000, 743. ^1H NMR (300 MHz, CDCl_3) δ ; 0.58 (6H, q, $J = 8.0$ Hz), 0.97 (9H, t, $J = 7.7$ Hz), 1.23-1.45 (2H, m), 1.94 (1H, dd, $J = 6.7, 12.6$ Hz), 2.29 (1H, td, $J = 7.3, 12.9$ Hz), 3.12 (1H, d, $J = 6.7$ Hz), 5.14 (1H, s), 5.75 (1H, d, $J = 2.4$ Hz), 5.78 (1H, d, $J = 0.8$ Hz), 6.02 (1H, dd, $J = 1.4, 5.8$ Hz), 7.24-7.36 (3H, m), 7.52-7.56 (3H, m). ^{13}C NMR (75 MHz, CDCl_3) δ ; 6.4 (CH_2), 7.0 (CH_3), 24.2 (CH_2), 36.6 (CH_2), 45.2 (CH), 71.7 (C), 75.7 (CH), 89.3 (C), 127.5 (CH), 128.9 (CH), 130.1 (CH), 132.5 (CH), 132.7 (C), 135.0 (CH), 138.4 (C), 138.7 (CH). HRESIMS calcd for $\text{C}_{22}\text{H}_{30}\text{O}_2\text{SSi}$: 387.1801 ($\text{M}+\text{H}^+$), found: 387.1814. Data for minor isomer: IR (neat) vcm^{-1} ; 2952, 2874, 1722, 1547, 1477, 1439, 1236, 1114, 1007, 864, 849, 743. ^1H NMR (300 MHz, CDCl_3) δ ; 0.64 (6H, q, $J = 7.8$ Hz), 1.00 (9H, t, $J = 7.8$ Hz), 1.18-1.27 (1H, m), 1.34-1.43 (1H, m), 1.71 (1H, d, $J = 10.6$ Hz), 1.96 (1H, dd, $J = 6.5, 12.3$ Hz), 2.24 (1H, td, $J = 7.1, 12.7$ Hz), 2.53 (1H, d, J

= 6.7 Hz), 4.58 (1H, dd, J = 2.4, 10.5 Hz), 5.64 (1H, s), 5.96 (1H, d, J = 5.8 Hz), 6.26 (1H, dd, J = 2.6, 5.8 Hz), 7.28-7.90 (3H, m), 7.57-7.60 (2H, m). ^{13}C NMR (75 MHz, CDCl_3) δ : 6.4 (CH_2), 7.1 (CH_3), 23.8 (CH_2), 33.8 (CH_2), 48.5 (CH), 68.6 (C), 78.9 (CH) 90.0 (C), 126.8 (CH), 127.9 (CH), 129.0 (CH), 132.2 (CH), 133.3 (CH), 137.0 (CH), 139.2 (CH), 140.4 (C). HRESIMS calcd for $\text{C}_{22}\text{H}_{30}\text{O}_2\text{SSi}$: 409.1632 ($\text{M}+\text{Na}$) $^+$, found: 409.1634.

To a solution of allylic alcohol (700 mg, 1.80 mmol) in CH_2Cl_2 (20 mL) was added NaHCO_3 (530 mg, 6.3 mmol) and Dess-Martin periodinane (5.73 g, 13.5 mmol) at ambient temperature and the mixture was stirred at the same temperature for 2 h. Aqueous 10% $\text{Na}_2\text{S}_2\text{O}_3$ solution was added to the reaction mixture at 0 °C and the mixture was extracted with CH_2Cl_2 and AcOEt. The organic layer was washed with saturated NaHCO_3 , brine, dried over MgSO_4 , and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (hexane : AcOEt, 5 : 1 - 4 : 1) to afford the enone **11** (530 mg, 1.27 mmol, 71%). $[\alpha]_{\text{D}}^{22} = +29.4^\circ$ (c 1.34, CHCl_3). IR (neat) vcm^{-1} : 2955, 2876, 1721, 1446, 1321, 1155, 1004, 731. ^1H NMR (300 MHz, CDCl_3) δ : 0.63-0.71 (6H, m), 0.95-1.00 (9H, m), 1.44 (1H, tt, J = 7.4, 14.0 Hz), 1.72 (1H, dd, J = 7.6, 14.1 Hz) 2.10 (1H, dd, J = 7.0, 13.3 Hz), 2.38 (1H, dt, J = 7.6, 13.3 Hz), 2.86 (1H, d, J = 7.6 Hz), 6.20 (1H, d, J = 5.9 Hz), 6.83 (1H, d, J = 0.9 Hz), 7.38 (1H, d, J = 5.9 Hz), 7.51 (2H, t, J = 7.1 Hz), 7.61 (1H, t, J = 7.1 Hz), 7.99 (2H, d, J = 7.1 Hz). ^{13}C NMR (75 MHz, CDCl_3) δ : 6.3 (CH_2), 6.8 (CH_3), 22.2 (CH_2), 35.1 (CH_2), 51.5 (CH), 72.4 (C), 85.1 (C), 128.9 (CH), 133.5 (CH), 135.0 (CH), 140.0 (C), 143.9 (C), 146.9 (CH), 160.2 (CH), 201.3 (C). EI-MS m/z : 387. HRESIMS calcd for $\text{C}_{22}\text{H}_{23}\text{O}_4\text{SSi}$ ($\text{M}^+ - \text{CH}_2\text{CH}_3$) 387.1086, found 387.1085.

Compound **12**.

To a solution of compound **11** (133 mg, 0.32 mmol) in CH_2Cl_2 (1.2 mL) and ether (0.4 mL) was added a solution of DIBAL-H (0.93 M in hexane, 0.41 mL, 0.38 mmol) was added at -78 °C. After being stirred at same temperature for 2 h and 1h at -30 °C, the mixture was diluted with ether and a solution of Rochelle salt was added to the mixture. After being stirred for 30 min, the mixture was extracted with AcOEt and the organic layer was washed with brine, dried over MgSO_4 , and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (hexane : AcOEt, 4 : 1 – 2 : 1) to afford the allylic alcohol **12** (98 mg, 0.23 mmol, 72%) and its diastereomer (25 mg, 0.06 mmol, 19%). Data for major isomer: $[\alpha]_{\text{D}}^{22} = +17.4^\circ$ (c 1.43, CHCl_3). IR (neat) vcm^{-1} : 3500, 2952, 2874, 1564, 1446, 1306, 1147, 1121, 1085, 1004, 725. ^1H NMR (300 MHz, CDCl_3) δ : 0.59 (6H, q, J = 7.8 Hz), 0.95 (9H, t, J = 8.0 Hz), 1.24-1.37 (1H, m), 1.49 (1H, dd, J = 6.9, 13.5 Hz), 2.01 (1H, dd, J = 6.9, 12.8 Hz), 2.14 (1H, td, J = 7.1, 13.0 Hz), 2.63 (1H, d, J = 7.5 Hz) 3.25 (1H, d, J = 8.0 Hz), 4.54 (1H, dd, J = 2.4, 7.7 Hz), 5.94 (1H, d, J = 5.8 Hz), 6.21 (1H, dd, J = 2.6, 5.8 Hz), 6.71 (1H, s), 7.51-7.64 (3H, m), 8.02-8.05 (2H, m). ^{13}C NMR (75 MHz, CDCl_3) δ : 6.2 (CH_2), 6.9 (CH_3), 22.0 (CH_2), 34.7 (CH_2), 50.4 (CH), 73.5 (C), 77.1 (CH) 88.0 (C), 128.1 (CH), 128.9 (CH), 133.2 (CH), 137.0 (CH), 137.7 (CH), 140.9 (C), 146.6 (C), 148.0 (CH). HRESIMS calcd for $\text{C}_{22}\text{H}_{30}\text{O}_4\text{SSi}$: 441.1537 ($\text{M}+\text{Na}$) $^+$, found: 441.1532. Data for minor isomer: $[\alpha]_{\text{D}}^{22} = +63.6^\circ$ (c 1.35, CHCl_3). IR (neat) vcm^{-1} : 3450, 2953, 2875, 1710, 1568, 1446, 1305, 1151, 1115, 1000, 963, 841, 792, 727. ^1H NMR (300 MHz, CDCl_3) δ : 0.47 (6H, q, J = 8.0

Hz), 0.86 (9H, t, $J = 8.0$ Hz), 1.25-1.37 (1H, m), 1.42-1.49 (1H, m), 1.90 (1H, dd, $J = 6.7, 12.7$ Hz), 2.10 (1H, td, $J = 7.1, 13.0$ Hz), 3.16 (2H, d, $J = 7.5$ Hz), 5.20 (1H, s), 5.70 (1H, dt, $J = 1.9, 6.8$ Hz), 5.95 (1H, dt, $J = 1.5, 5.9$ Hz), 6.61 (1H, s), 7.45-7.59 (3H, m), 7.88-7.92 (2H, m). ^{13}C NMR (75 MHz, CDCl_3) δ : 5.9 (CH_2), 6.7 (CH_3), 22.4 (CH_2), 36.5 (CH_2), 45.8 (CH), 73.7 (C), 74.7 (CH), 87.8 (CH), 127.8 (CH), 128.8 (CH), 133.2 (CH), 134.2 (CH), 139.0 (CH), 140.1 (C), 143.3 (C), 147.9 (CH). HRESIMS calcd for $\text{C}_{22}\text{H}_{30}\text{O}_4\text{SSi}$: 419.1724 ($\text{M}+\text{H}$) $^+$, found: 419.1712. Anal. Calcd for $\text{C}_{22}\text{H}_{30}\text{O}_4\text{SSi}$: C, 63.12; H, 7.22. Found: C, 62.94; H, 7.03.

Compound 4.

To a solution of allylic alcohol **12** (98 mg, 0.23 mmol) in THF (2.3 mL) was added a solution of methylmagnesium bromide (0.93 M, 0.57 mL, 0.53 mmol) at 0 °C and the resulting mixture was stirred at ambient temperature for 1h. After the addition of methyl chloroformate (54.8 mg, 0.04 mL, 0.58 mmol) to the mixture at 0 °C, the mixture was stirred at same temperature for 40 min. Saturated aqueous NH_4Cl was added to the reaction mixture and the mixture was extracted with AcOEt. Organic layer was washed with brine, dried over MgSO_4 , and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (hexane : AcOEt, 3 : 1) to afford the compound **4** (88 mg, 0.18 mmol) in 80% yield. $[\alpha]_{\text{D}}^{22} = +8.44^\circ$ (c 1.41, CHCl_3). IR (neat) vcm^{-1} : 2952, 2874, 1742, 1443, 1319, 1269. ^1H NMR (300 MHz, CDCl_3) δ : 0.56 (6H, q, $J = 7.8$ Hz), 0.93 (9H, t, $J = 7.8$ Hz), 1.28 (1H, tt, $J = 7.2, 13.5$ Hz), 1.47 (1H, dd, $J = 7.0, 13.5$ Hz), 1.99 (1H, dd, $J = 7.0, 13.0$ Hz), 2.13 (1H, dt, $J = 7.1, 13.2$ Hz), 2.70 (1H, d, $J = 7.5$ Hz), 3.78 (3H, s), 5.46 (1H, d, $J = 2.4$ Hz), 6.08 (1H, d, $J = 5.9$ Hz), 6.12 (1H, dd, $J = 2.5, 5.9$ Hz), 6.54 (1H, s), 7.49 (2H, t, $J = 7.1$ Hz), 7.58 (1H, t, 7.1 Hz), 7.99 (2H, d, $J = 7.1$ Hz). ^{13}C NMR (75 MHz, CDCl_3) δ : 6.1 (CH_2), 6.8 (CH_3), 21.7 (CH_2), 34.9 (CH_2), 50.5 (CH_3), 54.8 (CH), 70.5 (C), 80.8 (CH), 87.7 (C), 128.5 (CH), 128.7 (CH), 131.8 (CH), 132.9 (CH), 140.3 (CH), 141.3 (CH), 145.8 (C), 146.9 (C), 155.6 (C). HRESIMS calcd for $\text{C}_{24}\text{H}_{32}\text{NaO}_6\text{SSi}$: 499.1588 ($\text{M}+\text{Na}$) $^+$, found: 499.1587.

Compound 13.

To a suspension of CuI (451 mg, 2.37 mmol) in ether (6.0 mL) was added a solution of *n*-butyllithium (1.57 M in hexane, 2.5 mL, 3.95 mmol) at -23 °C and the resulting mixture was stirred for 5 min. Then, a solution of **4** (377 mg, 0.79 mmol) in ether (4.6 mL) was added to the reaction mixture and the resulting mixture was stirred at same temperature for 1.5 h. Saturated aqueous NH_4Cl was added to the reaction mixture and the mixture was extracted with ether. Organic layer was washed with brine, dried over MgSO_4 , and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (hexane : AcOEt, 5 : 1) to afford the compound **13** (349 mg, 0.65 mmol) in 83% yield. $[\alpha]_{\text{D}}^{22} = +0.73^\circ$ (c 1.23, CHCl_3). IR (neat) vcm^{-1} : 2952, 2874, 1744, 1726, 1445, 1324, 1243, 1147, 1083. ^1H NMR (300 MHz, CDCl_3) δ : 0.62-0.74 (6H, m), 0.84 (3H, t, $J = 6.8$ Hz), 0.96 (9H, t, $J = 7.7$ Hz), 1.14-1.32 (5H, m), 1.46-1.60 (3H, m), 1.89 (1H, bs), 1.96 (1H, dd, $J = 6.2, 12.5$ Hz), 2.23 (1H, dd, $J = 6.5, 7.0$ Hz), 3.01 (1H, dt, $J = 7.3, 12.5$ Hz), 3.16 (1H, ddd, $J = 2.7, 7.6, 10.8$ Hz), 3.64 (3H, s), 4.37 (1H, brs), 5.87 (1H, d, $J = 5.9$ Hz), 6.05 (1H, dd, $J = 2.9, 5.9$ Hz), 7.44 (2H, t, $J = 7.2$ Hz), 7.53 (1H, t, $J = 7.2$ Hz), 7.98 (2H, d, $J = 7.2$ Hz). ^{13}C NMR (75 MHz, CDCl_3) δ : 6.2 (CH_2), 7.0 (CH_3), 13.9 (CH_3), 22.6 (CH_2), 29.5 (CH_2), 29.6

(CH₂), 30.8 (CH₂), 35.0 (CH₂), 41.1 (CH), 47.0 (CH) 51.7 (CH₃), 67.2 (C), 77.1 (C), 80.2 (CH), 93.6 (C), 127.8 (CH), 130.4 (CH), 132.8 (CH), 133.1 (CH), 141.9 (CH), 142.9 (C), 167.7 (C). HRESIMS calcd for C₂₈H₄₂NaO₆SSi: 557.2385 (M+Na)⁺, found: 557.2369.

Compound **3**.

To a solution of **13** (321 mg, 0.60 mmol) in THF (3.0 mL) was added a solution of TBAF (1M in THF, 0.84 mL, 0.84 mmol) at ambient temperature. After being stirred for 1.5 h, water was added to the reaction mixture and the mixture was extracted with AcOEt. The organic layer was washed with brine, dried over MgSO₄, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (hexane : AcOEt, 4 : 1) to afford the sulfonyllactone (195 mg, 0.50 mmol) in 84% yield. $[\alpha]_D^{23} = -8.21^\circ$ (*c* 1.29, CHCl₃). IR (neat) vcm⁻¹; 3498, 2957, 2857, 1768, 1447, 1352, 1148, 1082. ¹H NMR (300 MHz, CDCl₃) δ : 0.81 (3H, t, *J* = 7.0 Hz), 1.10-1.40 (6H, m), 1.51 (1H, dt, *J* = 6.0, 13.7 Hz), 2.13 (1H, ddd, *J* = 4.2, 7.4, 9.9 Hz), 2.24 (1H, dd, *J* = 5.5, 13.2 Hz), 2.33 (1H, td, *J* = 6.8, 13.1 Hz), 2.48-2.61 (1H, m), 3.05 (1H, td, *J* = 4.5, 8.9 Hz), 4.46 (1H, s), 4.95 (1H, t, *J* = 1.6 Hz), 5.84 (1H, dd, *J* = 1.6, 5.8 Hz), 6.26 (1H, dd, *J* = 1.6, 5.8 Hz), 7.54 (2H, t, *J* = 7.5 Hz), 7.68 (1H, t, *J* = 7.5 Hz), 7.92 (2H, d, *J* = 7.5 Hz). ¹³C NMR (75 MHz, CDCl₃) δ : 13.8 (CH₃), 22.1 (CH₂), 28.3 (CH₂), 31.2 (CH₂), 33.7 (CH₂), 42.7 (CH₂), 45.8 (CH), 46.7 (CH), 68.9 (C), 72.9 (C), 90.4 (CH), 93.5 (C), 126.6 (CH), 128.6 (CH), 130.5 (CH), 134.5 (CH), 136.7 (C), 142.6 (CH), 169.0 (C). HRESIMS calcd for C₂₁H₂₄NaO₅S: 411.1277 (M+Na)⁺, found: 411.1242. Anal. Calcd for C₂₁H₂₄O₅S: C, 64.93; H, 6.23. Found: C, 65.12; H, 6.49.

To a solution of sulfonyllactone (195 mg, 0.50 mmol) in THF (3.4 mL) was added a solution of SmI₂ (0.1 M in THF, 20.0 mL, 2.00 mmol) at -78 °C. After being stirred for 1 h at same temperature, water was added to the reaction mixture. The resulting mixture was extracted with AcOEt, and the organic layer was washed with brine, dried over MgSO₄, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (hexane : AcOEt, 3 : 1) to afford the lactone **3** (124 mg, 0.50 mmol) in 100% yield. $[\alpha]_D^{22} = -12.0^\circ$ (*c* 1.07, CHCl₃). mp 105-110 °C. After recrystallization using hexane and AcOEt (7.5 : 1), optically pure compound (>99% ee) was obtained in 32% yield. $[\alpha]_D^{22} = -20.3^\circ$ (*c* 1.33, CHCl₃). mp 150-156 °C. IR (KBr) vcm⁻¹; 3440, 2929, 1751, 1170, 974. ¹H NMR (300 MHz, CDCl₃) δ : 0.89 (3H, t, *J* = 6.7 Hz), 1.25-1.36 (5H, m), 1.45-1.53 (1H, m), 1.74-1.77 (1H, m), 1.96-2.13 (2H, m), 2.14-2.35 (4H, m), 3.35 (1H, d, *J* = 9.4 Hz), 5.05 (1H, t, *J* = 1.5 Hz), 5.89 (1H, dd, *J* = 2.0, 5.6 Hz), 6.13 (1H, dd, *J* = 1.1, 5.6 Hz). ¹³C NMR (75 MHz, CDCl₃) δ : 14.0 (CH₃), 22.5 (CH₂), 28.9 (CH₂), 31.8 (CH₂), 34.8 (CH₂), 38.5 (CH), 40.0 (CH), 41.9 (CH₂), 46.3 (CH), 61.6 (C), 90.2 (CH), 91.4 (C), 130.3 (CH), 141.2 (CH), 178.0 (C). HRESIMS calcd for C₁₅H₂₁O₃: 249.1481 (M+H)⁺, found: 249.1491.

Compound 2.

To the mixture of lactone (20.1 mg, 0.08 mmol) and lutidine (25.7 mg, 0.030 mL, 0.24 mmol) in CH_2Cl_2 (0.3 mL) was added TESOTf (31.7 mg, 0.03 mL, 0.12 mmol) at -5°C . After being stirred for 30 min at same temperature, water was added to the reaction mixture. The mixture was extracted with ether and the organic layer was washed with brine, dried over MgSO_4 , and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (hexane : AcOEt, 9 : 1) to afford the TES-lactone (31.2 mg, 0.08 mmol) in 100% yield. $[\alpha]_D^{23} = +22.4^\circ$ (*c* 2.08, CHCl_3). IR (neat) vcm^{-1} : 2955, 2874, 1789, 1460, 1163, 1077, 1022, 965, 727. ^1H NMR (300 MHz, CDCl_3) δ : 0.59 (6H, q, $J = 8.0$ Hz), 0.87-0.97 (12H, m), 1.18-1.42 (6H, m), 1.72-1.82 (1H, m), 1.90-2.28 (5H, m), 3.37 (1H, d, $J = 9.4$ Hz), 4.99 (1H, s), 5.86 (1H, d, $J = 5.6$ Hz), 6.16 (1H, d, $J = 5.6$ Hz). ^{13}C NMR (75 MHz, CDCl_3) δ : 6.3 (CH_2), 7.0 (CH_3), 14.0 (CH_3), 22.5 (CH_3), 29.0 (CH_2), 31.9 (CH_2), 34.7 (CH_2), 38.7 (CH), 40.2 (CH), 43.4 (CH_2), 45.9 (CH), 62.3 (C), 89.6 (CH), 92.4 (C), 129.9 (CH), 141.1 (CH), 178.2 (C). HRESIMS calcd for $\text{C}_{21}\text{H}_{35}\text{O}_3\text{Si}$: 363.2332 ($\text{M}+\text{H}$) $^+$, found: 363.2355. Anal. Calcd for $\text{C}_{21}\text{H}_{34}\text{O}_3\text{Si}$: C, 69.56; H, 9.45. Found: C, 69.63; H, 9.49.

To a solution of TES-lactone (31.2 mg, 0.09 mmol) in THF (1.0 mL) was added LiAlH_4 (7.2 mg, 0.19 mmol) at -5°C and the mixture was stirred for 10 min. After dilution of the mixture with ether, aqueous Rochelle salt was added to the mixture and the resulting mixture was stirred at same temperature for 30 min. The mixture was extracted with ether and the organic layer was washed with brine, dried over MgSO_4 , and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (hexane : AcOEt, 6 : 1) to afford the diol (28.0 mg, 0.08 mmol) in 89% yield. $[\alpha]_D^{22} = +34.8^\circ$ (*c* 1.87, CHCl_3). IR (neat) vcm^{-1} : 3279, 2931, 1456, 1121, 1032, 857, 741. ^1H NMR (300 MHz, CDCl_3) δ : 0.55-0.65 (6H, m), 0.87 (3H, t, $J = 6.9$ Hz), 0.95 (9H, t, $J = 7.9$ Hz), 1.03-1.42 (8H, m), 1.49-1.61 (1H, m), 1.77 (1H, t, $J = 5.9$ Hz), 1.84-1.96 (2H, m), 2.12 (1H, td, $J = 8.1, 12.0$ Hz), 2.73 (1H, dt, $J = 3.6, 9.8$ Hz), 3.79 (1H, dd, $J = 3.7, 11.9$ Hz), 4.11 (1H, dd, $J = 9.9, 11.8$ Hz), 4.52 (1H, d, $J = 2.6$ Hz), 5.85 (1H, d, $J = 5.7$ Hz), 6.11 (1H, dd, $J = 2.6, 5.7$ Hz). ^{13}C NMR (75 MHz, CDCl_3) δ : 6.4 (CH_2), 7.0 (CH_3), 14.1 (CH_3), 22.8 (CH_2), 28.6 (CH_2), 29.7 (CH_2), 30.1 (CH_2), 35.6 (CH_2), 35.8 (CH), 38.4 (CH), 47.7 (CH), 59.1 (C), 61.4 (CH_2), 80.9 (CH), 92.0 (C), 135.0 (CH), 140.7 (CH). HRESIMS calcd for $\text{C}_{21}\text{H}_{38}\text{NaO}_3\text{Si}$: 389.2517 ($\text{M}+\text{Na}$) $^+$, found: 389.2488.

To a solution of DMSO (117.5 mg, 0.11 mL, 1.50 mmol) in CH_2Cl_2 (2.5 mL) was added to a solution of oxalyl chloride (63.5 mg, 0.04 mL, 0.5 mmol) in CH_2Cl_2 (2.5 mL) at -45°C and the mixture was stirred at same temperature for 30 min. A solution of diol (38.0 mg, 0.10 mmol) in CH_2Cl_2 (0.5 mL) was added to the mixture. After being stirred at same temperature for 40 min, triethylamine (121.4 mg, 0.17 mL, 1.2 mmol) was added to the mixture and the reaction

temperature was raised to ambient temperature. Water was added to the reaction mixture and the mixture was extracted with CH_2Cl_2 . The organic layer was washed with brine, dried over MgSO_4 , and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (hexane : AcOEt, 9 : 1) to afford the ketoaldehyde (27.0 mg, 0.074 mmol) in 74% yield. $[\alpha]_{\text{D}}^{22} = -30.0^\circ$ (*c* 0.71, CHCl_3). IR (neat) vcm^{-1} : 2956, 1713, 1454, 1338, 1260, 1136, 1014, 813, 727. ^1H NMR (300 MHz, CDCl_3) δ : 0.56 (6H, q, $J = 7.9$ Hz), 0.87 (3H, t, $J = 7.2$ Hz), 0.92 (9H, t, $J = 7.9$ Hz) 1.10-1.32 (6H, m) 1.50-1.73 (2H, m), 2.08 (1H, dd, $J = 6.6, 13.5$ Hz), 2.18-2.33 (2H, m) 2.68 (1H, t, $J = 6.6$ Hz) 3.15 (1H, dd, $J = 5.3, 9.2$ Hz), 6.15 (1H, d, $J = 5.8$ Hz), 7.34 (1H, d, $J = 5.8$ Hz), 10.46 (1H, d, $J = 5.3$ Hz). ^{13}C NMR (75 MHz, CDCl_3) δ : 6.3 (CH_2), 6.8 (CH_3), 14.0 (CH_3), 22.5 (CH_2), 27.8 (CH_2), 29.3 (CH_2), 31.2 (CH_2), 35.6 (CH) 36.9 (CH_2), 47.6 (CH), 51.4 (CH), 60.8 (C), 89.2 (C), 134.1 (CH), 162.3 (CH), 204.1 (CH), 206.5 (C). HRESIMS calcd for $\text{C}_{21}\text{H}_{34}\text{NaO}_3\text{Si}$: 363.2332 ($\text{M}+\text{Na}$) $^+$, found: 363.2355.

A solution of 5-(dimethoxyphosphoryl)-4-oxopentanoic acid methyl ester (**14**) (31.4 mg, 0.13 mmol) in THF (0.6 mL) was added to a suspension of NaH (60% in mineral oil, 5.2 mg, 0.13 mmol) in THF (0.6 mL) at -30°C and the mixture was stirred at same temperature for 30 min. Then, 0.6 mL of the phosphonate reagent was added to a solution of ketoaldehyde (4.6 mg, 0.013 mmol) in THF (0.3 mL) at -30°C . After being stirred for 5 h at ambient temperature, saturated aqueous NH_4Cl was added to the reaction mixture. The mixture was extracted with AcOEt and the organic layer was washed with brine, dried over MgSO_4 , and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (hexane : AcOEt, 6 : 1) to afford the compound **2** (4.3 mg, 0.009 mmol) in 72% yield. $[\alpha]_{\text{D}}^{22} = -67.3^\circ$ (*c* 0.65, CHCl_3). IR (neat) vcm^{-1} : 2953, 2931, 2874, 1741, 1707, 1674, 1622, 1436, 1337, 1212, 1129, 1006, 814, 744. ^1H NMR (300 MHz, CDCl_3) δ : 0.53 (6H, q, $J = 7.6$ Hz), 0.86 (3H, t, $J = 7.3$ Hz), 0.92 (9H, t, $J = 7.6$ Hz) 1.08-1.30 (6H, m) 1.39-1.60 (2H, m), 2.07 (1H, dd, $J = 6.2, 13.3$ Hz), 2.17-2.33 (2H, m) 2.49 (1H, t, $J = 6.4$ Hz), 2.56-2.70 (2H, m), 3.06 (2H, dt, $J = 2.2, 6.9$ Hz), 3.39 (1H, dd, $J = 9.9, 10.5$ Hz), 3.69 (3H, s), 5.94 (1H, d, $J = 16.0$ Hz), 6.07 (1H, d, $J = 5.8$ Hz), 7.30 (1H, d, $J = 5.8$ Hz), 7.87 (1H, dd, $J = 11.2, 16.0$ Hz). ^{13}C NMR (75 MHz, CDCl_3) δ : 6.5 (CH_2), 6.9 (CH_3), 14.0 (CH_3), 22.6 (CH_2), 27.6 (CH_2), 28.0 (CH_2), 29.1 (CH_2), 31.4 (CH_2), 33.4 (CH_2) 36.9 (CH_2), 37.0 (CH_2), 40.4 (CH), 50.4 (CH), 51.7 (CH_3), 60.7 (C), 89.6 (C), 131.3 (CH), 134.6 (CH), 146.8 (CH), 161.8 (CH), 173.5 (C), 198.5 (C), 206.6 (C). HRESIMS calcd for $\text{C}_{27}\text{H}_{42}\text{NaO}_6\text{Si}$: 497.2686 ($\text{M}+\text{Na}$) $^+$, found: 497.2699.

Compound **16**.

To a solution of **2** (4.3 mg, 9.1 μmol) in isopropanol (0.1 mL) was added [(1*R*,2*R*)-*N*-(*p*-toluenesulfonyl)-1,2-diphenylethanediamine](*p*-cymene)ruthenium(II) (**15**) (0.5 mg, 0.83 μmol) at 0 °C. After being stirred at ambient temperature for 7 h, the mixture was recooled at 0 °C. The ruthenium catalyst (2.0 mg, 3.3 μmol) and isopropanol (0.5 mL) and the reaction mixture was stirred at ambient temperature for 20 h. Water was added to the reaction mixture and the mixture was extracted with AcOEt. The organic layer was washed with brine, dried over MgSO_4 , and concentrated under reduced pressure. The residue was unstable and it was purified roughly by silica gel short column chromatography (hexane : AcOEt, 4 : 1) to afford **16** as a diastereomeric mixture (4.3 mg, 9.1 μmol ,) in 100% yield. $[\alpha]_D^{22} = -30.3^\circ$ (*c* 0.29, CHCl_3). IR (neat) vcm^{-1} : 3474, 2954, 1738, 1708, 1455, 1336, 1239, 1166, 1128, 1006, 972, 817, 745. ^1H NMR (300 MHz, CDCl_3) δ : 0.51-0.61 (6H, m), 0.86 (3H, t, $J = 7.6$ Hz), 0.92 (9H, t, $J = 7.6$ Hz), 1.08-1.32 (6H, m), 1.33-1.55 (3H, m), 1.78-1.87 (2H, m), 1.99-2.16 (2H, m), 2.17-2.44 (4H, m), 3.29 (1H, dd, $J = 9.8, 10.5$ Hz), {3.66 (s), 3.67 (s), 3H}, 4.18-4.24 (1H, m), 5.33-5.42 (1H, m), 6.06 (1H, d, $J = 5.7$ Hz), 6.60 (1H, dd, $J = 11.0, 15.0$ Hz), 7.29 (1H, d, $J = 5.7$ Hz). HRESIMS calcd for $\text{C}_{27}\text{H}_{44}\text{NaO}_5\text{Si}$: 499.2818 ($\text{M}+\text{Na}$) $^+$, found: 499.2856.

Compound **1**.

The mixture of **16** (4.3 mg, 9.0 μmol) and pyridine (3.9 mg, 0.050 mmol) and 4-dimethylaminopyridine (0.2 mg, 1.8 μmol), and Ac_2O (4.6 mg, 0.045 mmol) in CH_2Cl_2 (0.2 mL) was stirred at 0 °C for 1.5 h. Water was added to the mixture and the mixture was extracted with AcOEt. The organic layer was washed with sat. NaHCO_3 , brine, dried over MgSO_4 , and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (hexane : AcOEt, 5 : 1). The resulting diastereomeric mixture was separated by silica gel HPLC (hexane : AcOEt, 7 : 1) to afford two diastereomers (major isomer; 4.3 mg, 8.3 μmol , minor isomer; 0.39 mg, 0.75 μmol) in 99% yield. Major isomer: $[\alpha]_D^{22} = -4.5^\circ$ (*c* 0.3, CHCl_3). IR (neat) vcm^{-1} : 3358, 2954, 1738, 1710, 1598, 1369, 1237, 1125. ^1H NMR (300 MHz, CDCl_3) δ : 0.55 (6H, q, $J = 7.9$ Hz), 0.85 (3H, t, $J = 7.3$ Hz), 0.92 (9H, t, $J = 7.9$ Hz), 1.07-1.16 (2H, m), 1.20-1.30 (3H, m), 1.32-1.53 (4H, m), 1.86-2.38 (7H, m), 2.04 (3H, s), 3.25 (1H, dd, $J = 9.9,$

10.5 Hz), 3.66 (3H, s), 5.23-5.34 (2H, m), 6.06 (1H, d, $J = 5.8$ Hz), 6.64-6.76 (1H, m), 7.26 (1H, d, $J = 5.8$ Hz), ^{13}C NMR (75 MHz, CDCl_3) δ : 6.5, 6.9, 14.1, 21.2, 22.7, 27.5, 29.3, 29.6, 29.9, 31.1, 36.9, 37.1, 40.0, 50.4, 51.6, 60.5, 73.9, 89.8, 128.5, 132.4, 134.9, 161.3, 170.0, 173.6, 206.4. HRESIMS calcd for $\text{C}_{29}\text{H}_{46}\text{NaO}_6\text{Si}$: 541.2984 ($\text{M}+\text{Na}$) $^+$, found: 541.2961. Minor isomer: $[\alpha]_{\text{D}}^{23} = -36.7^\circ$ (c 0.03, CHCl_3). IR (neat) vcm^{-1} : 3357, 2954, 1742, 1711, 1594, 1370, 1237, 1126. ^1H NMR (300 MHz, CDCl_3) δ : 0.55 (6H, q, $J = 7.8$ Hz), 0.86 (3H, t, $J = 7.1$ Hz), 0.92 (9H, t, $J = 7.8$ Hz), 1.08-1.17 (2H, m), 1.18-1.55 (7H, m), 1.94-2.12 (3H, m), 2.03 (3H, s), 2.15-2.39 (4H, m), 3.27 (1H, t, $J = 10.1$ Hz), 3.67 (3H, s), 5.28 (1H, td, $J = 6.2, 12.6$ Hz), 5.37 (1H, dd, $J = 6.4, 15.0$ Hz), 6.07 (1H, d, $J = 5.7$ Hz), 6.67 (1H, dd, $J = 11.0, 15.0$ Hz), 7.26 (1H, d, $J = 5.7$ Hz). ^{13}C NMR (75 MHz, CDCl_3) δ : 6.5, 6.9, 14.0, 21.2, 22.7, 27.7, 29.2, 29.4, 29.7, 29.9, 31.2, 37.1, 39.9, 50.3, 51.6, 60.5, 73.0, 89.9, 128.8, 131.2, 134.9, 161.2, 170.1, 173.5, 206.8. HRESIMS calcd for $\text{C}_{29}\text{H}_{46}\text{NaO}_6\text{Si}$: 541.2984 ($\text{M}+\text{Na}$) $^+$, found: 541.2961.

To a solution of major isomer of mono-acetate (4.7 mg, 9.1 μmol) in THF (0.1 mL) was added a solution of TBAF (1M in THF, 10.8 μL , 10.8 μmol) at 0 $^\circ\text{C}$ and the mixture was stirred at same temperature for 5 min. Then, water was added to the mixture and the mixture was extracted with AcOEt. The organic layer was washed with sat. NaHCO_3 , brine, dried over MgSO_4 , and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (hexane : AcOEt, 1 : 1) to afford the alcohol (3.7 mg, 9.1 μmol) in 99% yield. $[\alpha]_{\text{D}}^{22} = -32.4^\circ$ (c 0.25, CHCl_3). IR (neat) vcm^{-1} : 3416, 2926, 2855, 1738, 1704, 1440, 1371, 1238, 1167, 1079, 973, 824. ^1H NMR (300 MHz, CDCl_3) δ : 0.86 (3H, t, $J = 7.1$ Hz), 1.06-1.17 (2H, m), 1.20-1.32 (4H, m), 1.34-1.54 (3H, m), 2.07 (3H, s), 1.90-2.46 (7H, m), 3.24 (1H, t, $J = 10.0$ Hz), 3.66 (3H, s), 5.26 (1H, td, $J = 6.6, 13.4$ Hz), 5.32 (1H, dd, $J = 7.0, 14.8$ Hz), 6.08 (1H, d, $J = 5.7$ Hz), 6.70 (1H, dd, $J = 11.0, 14.6$ Hz), 7.30 (1H, d, $J = 5.7$ Hz), ^{13}C NMR (75 MHz, CDCl_3) δ : 14.1, 21.2, 22.6, 27.6, 29.2, 29.4, 30.0, 31.0, 35.4, 37.1, 40.0, 50.8, 51.6, 59.7, 73.6, 88.6, 128.5, 131.7, 135.1, 161.3, 170.2, 173.7, 206.4. HRESIMS calcd for $\text{C}_{23}\text{H}_{32}\text{NaO}_6$: 427.2105 ($\text{M}+\text{Na}$) $^+$, Found: 427.2097.

To a solution of alcohol (3.7 mg, 9.1 μmol) and pyridine (7.9 mg, 0.1 mmol) was added 4-dimethylaminopyridine (0.22 mg, 1.8 μmol) and followed by addition of a solution of Ac_2O (9.2 mg, 0.09 mmol) in CH_2Cl_2 (0.1 mL) at 0 $^\circ\text{C}$. After being stirred for 1 h at ambient temperature, water was added to the reaction mixture and the mixture was extracted with AcOEt. The organic layer was washed with sat. NaHCO_3 , brine, dried over MgSO_4 , and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (hexane : AcOEt, 4 : 1) to afford (+)-tricycloclovulone (**1**) (4.05 mg, 9.1 μmol) in 99% yield. $[\alpha]_{\text{D}}^{23} = +9.5^\circ$ (c 0.19, CHCl_3). IR (neat) vcm^{-1} : 3021, 2918, 2849, 1738, 1713, 1440, 1369, 1237, 1061, 1020, 972, 756. ^1H NMR (500 MHz, CDCl_3) δ : 0.86 (3H, t, $J = 5.3$ Hz), 1.10-1.15 (2H, m), 1.23-1.29 (3H, m), 1.37-1.47 (2H, m), 1.50-1.63 (2H, m), 1.93-1.98 (2H, m), 1.97 (3H, s), 2.07 (3H, s), 2.25 (1H, td, $J = 7.8, 13.2$ Hz), 2.34-2.38 (2H, m), 2.43 (1H, t, $J = 6.8$ Hz), 2.64 (1H, dd, $J = 6.8, 13.9$ Hz), 3.17 (1H, t, $J = 10.0$ Hz), 3.66 (3H, s), 5.29-5.34 (2H, m), 6.14 (1H, d, $J = 5.9$ Hz), 6.66-6.72 (1H, m), 7.61 (1H, d, $J = 5.9$ Hz), ^{13}C NMR (125 MHz, CDCl_3) δ : 14.1 (CH_3), 21.2 (CH_2), 21.5 (CH_3), 22.6 (CH_2), 27.9 (CH_2), 29.3 (CH_2), 29.5 (CH_2), 29.9 (CH_2), 30.9 (CH_2), 34.2 (CH_2), 37.1 (CH), 40.5 (CH), 49.5 (CH), 51.6 (CH_3), 60.2 (C), 73.7 (CH), 93.9 (C), 129.0 (CH), 131.2 (CH), 136.8 (CH), 156.7 (CH), 170.0 (C), 170.1 (C), 173.6 (C), 205.0 (C). HRESIMS calcd for $\text{C}_{25}\text{H}_{34}\text{NaO}_7$: 469.2209 ($\text{M}+\text{Na}$) $^+$, Found: 469.2202.

Determination of the absolute stereochemistry of compound **5**.

The **ent-5** was prepared by the enantioselective [2+2]-cycloaddition reaction using **enat-8** ligand and converted to known **31** as shown in above Scheme.

To a solution of **ent-5** (60% ee) (135 mg, 0.429 mmol) in CH_2Cl_2 (2 mL) was added titanium tetrachloride (53 μL , 0.428 mmol) at 0 °C. After being stirred for 30 min at same temperature, neutral phosphate buffer solution (pH 6.86, 1 mL) was added to the reaction mixture. The resulting mixture was extracted with AcOEt and the organic layer was dried over MgSO_4 and concentrated under vacuum. The residue was purified by silica gel column chromatography (hexane : AcOEt, 5 : 1) to afford compound **30** (140 mg, 0.45 mmol) in 91% yield. $[\alpha]_{\text{D}}^{28} +267^\circ$ (*c* 0.51, CHCl_3). IR (neat) vcm^{-1} ; 1760, 1730, 1584. ^1H NMR (300 MHz, CDCl_3) δ ; 1.68-1.79 (1H, m), 2.25-2.23 (3H, m), 3.08 (1H, d, $J = 11.3$ Hz), 3.73 (3H, s), 3.88-3.98 (1H, m), 6.15 (1H, d, $J = 9.5$ Hz), 7.30-7.39 (5H, m). ^{13}C NMR (75 MHz, CDCl_3) δ ; 27.5, 37.8, 42.8, 52.6, 60.6, 127.8, 129.2, 129.5, 130.5, 132.1, 139.1, 168.4, 209.3. HRESIMS calcd for $\text{C}_{15}\text{H}_{15}\text{O}_3\text{NaSCl}$: 333.0328 ($\text{M}+\text{Na}$) $^+$, Found: 333.0302.

The mixture of compound **30** (60 mg, 0.193 mmol) and concentrated HCl (0.1 mL) in MeOH (1 mL) was heated at 60 °C. After being stirred for 12 h at same temperature, the mixture was concentrated under reduced pressure. The residue was purified by silica gel column chromatography (hexane : isopropanol, 1 : 5) to afford compound **31** (9 mg, 0.063 mmol) in 33% yield. $[\alpha]_{\text{D}}^{28} +65.1^\circ$ (*c* 0.45, CHCl_3). IR (neat) vcm^{-1} ; 1737. ^1H NMR (300 MHz, CDCl_3) δ ; 1.20-1.25 (1H, m), 1.53-1.70 (1H, m), 1.86-1.96 (1H, m), 2.14-2.39 (3H, m), 2.48-2.68 (3H, m). ^{13}C NMR (75 MHz, CDCl_3) δ ; 29.1, 33.1, 38.3, 39.3, 44.5, 177.7, 218.3.

Determination of the stereochemistry of hydroxyl group on the α -chain of compound **16**.

To a solution of **16** (0.9 mg, 1.9 mmol) in CH₂Cl₂ (50 mL) was added a solution of pyridine (0.83 mg, 10.5 mmol) in CH₂Cl₂ (50 mL), a solution of (*R*)-(-)- α -methoxy- α -trifluoromethylphenylacetyl chloride (2.4 mg, 9.5 mmol) in CH₂Cl₂ (50 mL), and dimethylaminopyridine (0.2 mg, 1.6 mmol) at 0 °C. After being stirred for 30 min at same temperature, a solution of pyridine (0.83 mg, 10.5 mmol) in CH₂Cl₂ (50 mL), a solution of (*R*)-(-)- α -methoxy- α -trifluoromethylphenylacetyl chloride (2.4 mg, 9.5 mmol) in CH₂Cl₂ (50 mL) were added to the reaction mixture and the mixture was stirred at ambient temperature for 11 h. The mixture was concentrated under reduced pressure and the residue was purified by silica gel column chromatography (hexane : AcOEt, 1 : 1), followed by HPLC (silica gel, hexane : AcOEt, 5 : 1) to afford the ester **32** (0.4 mg, 0.58 mmol, 31%). ¹H NMR (500 MHz, CDCl₃) δ ; 0.54 (6H, q, *J* = 7.9 Hz), 0.81-0.92 (12H, m), 1.10-1.21 (4H, m) 1.37-1.97 (4H, m) 2.00-2.05 (2H, m), 2.08-2.15 (1H, m), 2.22-2.38 (5H, m), 3.24 (1H, t, *J* = 10.3 Hz), 3.55 (3H, s), 3.66 (3H, s), 5.20 (1H, dd, *J* = 8.1, 15.3 Hz), 5.55 (1H, q, *J* = 7.4 Hz), 6.07 (1H, d, *J* = 5.7 Hz), 6.82 (1H, dd, *J* = 11.2, 15.2 Hz), 7.35-7.39 (3H, m), 7.52-7.53 (2H, m).

To a solution of **16** (0.5mg, 1.0 mmol) in CH₂Cl₂ (30 mL) was added a solution of pyridine (0.83 mg, 10.5 mmol) in CH₂Cl₂ (100 mL), a solution of (*S*)-(+)- α -methoxy- α -trifluoromethylphenylacetyl chloride (2.5 mg, 10.0 mmol) in CH₂Cl₂ (50 mL), and dimethylaminopyridine (0.2 mg, 1.6 mmol) at 0 °C. After being to same temperature for 30 min, a solution of pyridine (0.83 mg, 10.5 mmol) in CH₂Cl₂ (50 mL), a solution of (*S*)-(-)- α -methoxy- α -trifluoromethylphenylacetyl chloride (2.5 mg, 10.0 mmol) in CH₂Cl₂ (50 mL) were added to the reaction mixture and the mixture was stirred at ambient temperature for 12 h. Water was added to the reaction mixture and the mixture was extracted with AcOEt. The organic layer was washed with brine, dried over MgSO₄, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (hexane : AcOEt, 1 : 1), followed by HPLC (silica gel, hexane : AcOEt, 5 : 1) to afford the ester **33** (0.4 mg, 0.58 mmol, 58%). ¹H NMR (500 MHz, CDCl₃) δ ; 0.55 (6H, q, *J* = 7.9 Hz), 0.81 (3H, t, *J* = 7.2 Hz) 0.92 (9H, t, *J* = 7.9 Hz), 1.05-1.14 (2H, m), 1.20-1.22 (2H, m) 1.36-1.40 (2H, m), 1.44-1.48 (2H, m), 1.97-2.02 (2H, m), 2.11 (1H, t, *J* = 8.0 Hz), 2.17-2.29 (4H, m), 2.36-2.39 (1H, m), 3.27 (1H, t, *J* = 10.3 Hz), 3.56 (3H, s), 3.64 (3H, s), 5.32 (1H, dd, *J* = 8.0, 15.3 Hz), 5.57 (1H, q, *J* = 7.0 Hz), 6.08 (1H, d, *J* = 5.7 Hz), 6.87 (1H, dd, *J* = 11.2, 15.2 Hz), 7.28-7.39 (3H, m), 7.53-7.55 (2H, m).

$\Delta\delta$ values for MTPA ester (**32-33**)

¹H NMR spectrum

¹H

Current Data Parameters
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EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
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