Supporting Information

Total Synthesis of (±)-Clavubicyclone

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A solution of **7** (13.2 g, 64.1 mmol) in CH₂Cl₂ (50 mL) was added to a solution of 2-triphenylphosphoranylidene-γ-butyrolactone (27.0 g, 76.1 mmol) in CH₂Cl₂ (250 mL) at ambient temperature and the resulting mixture was stirred at same temperature for 1 h. Water 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, 2 : 1) to afford **21** (15.3 g, 55.8 mmol) as a colorless crystals in 87% yield.

21: mp 74-76 °C (from hexane-AcOEt). IR (KBr) ν cm⁻¹; 1734, 1511. ¹H NMR (300 MHz, CDCl₃) δ ; 2.95 (2H, dt, J = 2.4, 7.5 Hz), 3.78 (3H, s), 4.12 (2H, br d, J = 4.6 Hz), 4.36 (2H, dt, J = 0.6, 7.4 Hz), 4.47 (2H, s), 6.21 (1H, td, J = 4.8, 15.3 Hz), 6.38 (1H, tdd, J = 1.7, 11.3, 15.3 Hz), 6.84-6.92 (2H, m), 7.08 (1H, td, J = 2.8, 11.2 Hz), 7.22-7.30 (2H, m). ¹³C NMR (75 MHz, CDCl₃) δ ; 25.3, 55.1, 65.3, 69.2, 72.3, 113.7, 124.3, 126.3, 129.3, 129.7, 134.9, 140.0, 159.2, 171.8. HRESIMS calcd for C₁₆H₁₉O₄ (M+H)⁺ 275.1283, found 275.1284. Anal. Calcd for C₁₆H₁₈O₄: C, 70.06 H, 6.61. Found: C, 69.92 H, 6.61.

To a solution of **21** (14.2 g, 51.8 mmol) in CH₂Cl₂ (200 mL) was added a solution of DIBAL-H (0.94 M in hexane, 127 mL, 120 mmol) at -78 °C and the mixture was stirred at same temperature

for 1 h and at 0 °C for 10 min. A solution of Rochelle salt was added to the reaction mixture and the resulting mixture was stirred at ambient temperature for 1 h. The mixture was extracted with AcOEt and the organic layer was washed with brine, dried with MgSO₄, and concentrated under vacuum. The resulting residue was purified by silica gel column chromatography (hexane : AcOEt, 1 : 3-1 : 6) to afford **22** (14.0 g, 50.3 mmol) as a colorless oil in 97% yield.

22: IR (film) ν cm⁻¹; 3306, 1513, 1246. ¹H NMR (300 MHz, CDCl₃) δ ; 2.47 (2H, t, *J* = 5.9 Hz), 3.55 (2H, br s), 3.66 (2H, t, *J* = 5.9 Hz), 3.79 (3H, s), 4.00-4.07 (2H, m), 4.03 (2H, s), 4.44 (2H, s), 5.81 (1H, td *J* = 6.1, 15.1 Hz), 6.13 (1H, d, *J* = 11.1 Hz), 6.45 (1H, dd, *J* = 11.1, 15.1 Hz), 6.82-6.92 (2H, m), 7.20-7.29 (2H, m). ¹³C NMR (75 MHz, CDCl₃) δ ; 32.5, 55.2, 61.7, 67.6, 70.1, 71.9, 113.8, 127.8, 127.9, 129.4, 130.1, 130.9, 138.7, 159.2. HRESIMS calcd for C₁₆H₂₃O₄ (M+H)⁺ 279.1596, found 279.1581.

To a solution of **22** (14.0 g, 50.3 mmol) in CH₂Cl₂ (400 mL) was added MnO₂ (43.7 g, 503 mmol) at ambient temperature and the mixture was stirred at same temperature for 5 h. The mixture was filtered and the filtrate was concentrated under vacuum to obtain crude **23**. A solution of methyl acetoacetate (17.4 g, 150 mmol) in THF (30 mL) was added to the suspension of NaH (60% in mineral oil, 6.0 g, 150 mmol) in THF (200 mL) at 0 °C. After being stirred at same temperature for 15 min, a solution of n-BuLi (1.5 M in hexane, 100 mL, 150 mmol) was added to the mixture and the mixture was stirred for additional 15 min. To the resulting solution was added a solution of crude **23** in THF (30 mL) at -40 °C and the mixture was stirred for 30 min. 1M HCl was added to the reaction mixture and the mixture was extracted with AcOEt. The organic layer was washed with brine, dried with MgSO₄, and concentrated under vacuum. The resulting residue was purified by silica gel column chromatography (hexane : AcOEt, 1 : 2-1 : 5) to afford **8** (12.4 g, 31.6 mmol) as an yellow oil in 63% yield.

8: IR (film) ν cm⁻¹; 3368, 1718, 1216. ¹H NMR (300 MHz, CDCl₃) δ ; 2.39-2.58 (2H, m), 2.74 (1H,

dd, $J = 3.3, 17.0$ Hz), 2.89 (1H, dd, $J = 9.4, 17.0$ Hz), 3.52 (2H, s), 3.62-3.80 (3H, m), 3.74 (3H, s), 3.81 (3H, s), 4.05 (2H, dd, $J = 1.2, 5.9$ Hz), 4.45 (2H, s), 4.61 (1H, dd, $J = 2.9, 9.4$ Hz), 5.85 (1H, td, $J = 5.9, 15.1$ Hz), 6.17 (1H, d, $J = 11.0$ Hz), 6.43 (1H, dd, $J = 11.0, 15.1$ Hz), 6.83-6.95 (2H, m), 7.20-7.33 (2H, m). ^{13}C NMR (75 MHz, CDCl_3) δ ; 29.7, 30.6, 48.4, 49.7, 52.5, 55.3, 62.4, 70.0, 72.0, 113.8, 127.2, 128.1, 129.4, 130.2, 132.1, 139.2, 159.3, 167.3, 202.8. HRESIMS calcd for $\text{C}_{21}\text{H}_{28}\text{O}_7\text{Na}$ ($\text{M}+\text{Na}$) $^+$ 415.1733, found 415.1719.

To a solution of **8** (13.0 g, 33.2 mmol) in acetonitrile (200 mL) was added a solution of TsN_3 (9.80 g, 49.7 mmol) in acetonitrile (20 mL) and triethylamine (13.8 mL, 99.3 mmol) at ambient temperature and the mixture was stirred at same temperature for 4 h. The mixture was concentrated under vacuum and the resulting residue was purified by silica gel column chromatography (hexane : AcOEt, 1 : 2) to afford **24** (12.3 g, 29.4 mmol) as a yellow oil in 89% yield.

24: IR (film) ν cm^{-1} ; 3419, 2141, 1716, 1514. ^1H NMR (300 MHz, CDCl_3) δ ; 2.45 (2H, br s), 3.01 (1H, td $J = 3.7, 16.3$ Hz), 3.12 (1H, ddd, $J = 1.3, 9.0, 16.3$ Hz), 3.50-3.75 (3H, m), 3.75 (3H, s), 3.78 (3H, s), 4.00 (2H, br d, $J = 6.0$ Hz), 4.24 (1H, br s), 4.40 (2H, s), 4.57 (1H, br d, $J = 6.7$ Hz), 5.79 (1H, dtd, $J = 1.8, 6.0, 15.0$ Hz), 6.13 (1H, d, $J = 11.0$ Hz), 6.41 (1H, ddd, $J = 1.2, 11.1, 15.0$ Hz), 6.79-6.90 (2H, m), 7.16-7.29 (2H, m). ^{13}C NMR (75 MHz, CDCl_3) δ ; 30.4, 45.6, 52.1, 55.0, 62.0, 69.9, 71.6, 71.9, 76.4, 113.5, 127.3, 127.5, 129.2, 130.0, 131.2, 139.9, 159.0, 161.3, 191.4. HRESIMS calcd for $\text{C}_{21}\text{H}_{26}\text{N}_2\text{O}_7\text{Na}$ ($\text{M}+\text{Na}$) $^+$ 441.1638, found 441.1618.

To a solution of **24** (12.3 g, 29.4 mmol) in DMF (100 mL) was added imidazole (10.0 g, 147 mmol) and TBDPSCl (19.1 mL, 73.5 mmol) at ambient temperature and the mixture was stirred at same temperature for 24 h. Water was added to the mixture and the resulting mixture was extracted with ether. The organic layer was washed with brine, dried with MgSO_4 , and concentrated under

vacuum. The resulting residue was purified by silica gel column chromatography (hexane : AcOEt, 10 : 1) to afford **5** (23.7 g, 26.5 mmol) as an yellow oil in 90% yield.

5: IR (film) ν cm^{-1} ; 2138, 1722, 1513, 1111. ^1H NMR (300 MHz, CDCl_3) δ ; 0.99 (9H, s), 1.03 (9H, s), 2.31-2.55 (2H, m), 2.85 (1H, dd, $J = 4.3, 15.0$ Hz), 3.12 (1H, dd, $J = 7.9, 15.0$ Hz), 3.41-3.66 (2H, m), 3.75 (3H, s), 3.81 (3H, s), 3.92 (2H, d, $J = 6.3$ Hz), 4.39 (2H, s), 4.65 (1H, dd, $J = 4.3, 7.8$ Hz), 5.62 (1H, td, $J = 6.4, 14.7$ Hz), 6.02 (1H, d, $J = 11.2$ Hz), 6.13 (1H, dd, $J = 11.2, 14.6$ Hz), 6.86-6.93 (2H, m), 7.20-7.45 (14H, m), 7.50-7.69 (8H, m). ^{13}C NMR (75 MHz, CDCl_3) δ ; 18.9, 19.1, 26.7, 26.8, 31.1, 47.1, 51.8, 54.9, 63.1, 70.1, 71.4, 73.9, 76.1, 113.6, 127.1, 127.5, 127.5, 127.6, 128.2, 129.2, 129.3, 129.4, 130.2, 130.4, 133.1, 133.5, 133.5, 133.6, 135.3, 135.8, 135.8, 138.9, 159.0, 161.1, 189.1. HRESIMS calcd for $\text{C}_{53}\text{H}_{62}\text{N}_2\text{O}_7\text{NaSi}_2$ ($\text{M}+\text{Na}$) $^+$ 917.3993, found 917.4016.

A solution of **5** (17.0 g, 19.0 mmol) in benzene (50 mL) was added slowly to a solution of rhodium acetate dimer (90.8 mg, 0.19 mmol) in benzene (200 mL) at 80 °C during 30 min and the mixture was stirred at same temperature for additional 30 min. The mixture was concentrated under vacuum and the resulting residue was purified by silica gel column chromatography (hexane : AcOEt, 5 : 1- 3 : 1) to afford two diastereomers **9-1** (11.3 g, 13.0 mmol) and **9-2** (3.48 g, 4.02 mmol) as a colorless oil in 90% yield.

9-1 IR (film) ν cm^{-1} ; 1734, 1513, 1111. ^1H NMR (300 MHz, CDCl_3) δ ; 1.04 (9H, s), 1.06 (9H, s), 1.99 (1H, dd, $J = 3.2, 5.7$ Hz), 2.04-2.20 (1H, m), 2.08 (2H, br d, $J = 2.7$ Hz), 2.81-2.94 (1H, m), 3.65-3.91 (4H, m), 3.81 (3H, s), 3.84 (3H, s), 4.27 (2H, s), 4.30 (1H, t, $J = 2.4$ Hz), 5.63-5.69 (2H, m), 6.84-6.91 (2H, m), 7.17-7.23 (2H, m), 7.31-7.48 (12H, m), 7.56-7.68 (8H, m). ^{13}C NMR (75 MHz, CDCl_3) δ ; 19.1, 19.3, 26.0, 26.8, 26.8, 37.6, 42.7, 47.1, 47.9, 52.4, 55.2, 60.7, 69.8, 70.6, 71.3, 113.7, 125.0, 127.6, 127.6, 127.7, 127.9, 129.3, 129.6, 129.6, 129.9, 130.0, 130.3, 132.4, 133.4, 133.6, 133.7, 135.5, 135.7, 159.1, 166.2, 204.4. HRESIMS calcd for $\text{C}_{53}\text{H}_{62}\text{O}_7\text{NaSi}_2$ ($\text{M}+\text{Na}$) $^+$ 889.3932, found 889.3898.

9-2 IR (film) ν cm^{-1} ; 1734, 1511, 1111. ^1H NMR (300 MHz, CDCl_3) δ ; 0.96 (9H, s), 1.02 (9H, s),

2.10 (2H, d, $J = 7.7$ Hz), 2.14-2.25 (2H, m), 2.72 (1H, d, $J = 8.9$ Hz), 3.50-3.69 (2H, m), 3.51 (3H, s), 3.81 (3H, s), 4.04 (2H, d, $J = 5.6$ Hz), 4.45 (2H, s), 4.63 (1H, t, $J = 7.7$ Hz), 5.88 (1H, dd, $J = 9.0$, 15.5 Hz), 6.01 (1H, td, $J = 5.8$, 15.5 Hz), 6.86-6.94 (2H, m), 7.25-7.45 (14H, m), 7.49-7.66 (8H, m). ^{13}C NMR (75 MHz, CDCl_3) δ : 19.0, 19.1, 26.7, 26.8, 28.0, 36.8, 42.7, 47.0, 49.9, 51.9, 55.1, 61.0, 69.8, 70.2, 71.4, 113.7, 124.9, 127.5, 127.6, 127.8, 127.8, 129.4, 129.5, 129.5, 130.0, 130.2, 132.3, 132.9, 133.2, 133.3, 133.4, 135.3, 135.4, 135.5, 159.1, 165.6, 202.8. HRESIMS calcd for $\text{C}_{53}\text{H}_{62}\text{O}_7\text{NaSi}_2$ ($\text{M}+\text{Na}$) $^+$ 889.3932, found 889.3944.

To a solution of **9** (diasteremeric mixture, 15.2 g, 17.5 mmol) in toluene (150 mL) was added a solution of DBU (4.0 g, 26.3 mmol) in toluene (10 mL) at ambient temperature and the mixture was stirred at 70 °C for 24 h. The mixture was concentrated under vacuum and the resulting residue was purified by silica gel column chromatography (hexane : AcOEt, 4 : 1) to afford **4** (9.53 g, 15.6 mmol) as a colorless oil in 89% yield.

4: IR (film) ν cm^{-1} : 1706, 1513, 1248, 1112. ^1H NMR (300 MHz, CDCl_3) δ : 1.05 (9H, s), 2.20-2.37 (2H, m), 2.52 (1H, d, $J = 9.7$ Hz), 3.64-3.74 (1H, m), 3.71 (3H, s), 3.75-3.85 (1H, m), 3.80 (3H, s), 3.97 (2H, d, $J = 5.6$ Hz), 4.40 (2H, s), 5.74 (1H, d, $J = 5.7$ Hz), 5.87 (1H, td, $J = 5.7$, 15.5 Hz), 6.04 (1H, dd, $J = 9.8$, 15.5 Hz), 6.84-6.91 (2H, m), 7.21-7.28 (2H, m), 7.34-7.47 (6H, m), 7.59-7.69 (4H, m), 7.79 (1H, d, $J = 5.7$ Hz). ^{13}C NMR (75 MHz, CDCl_3) δ : 19.0, 26.7, 27.5, 45.1, 45.5, 52.3, 55.2, 61.4, 62.1, 69.5, 71.6, 113.7, 125.6, 127.2, 127.7, 129.4, 129.7, 130.1, 133.1, 133.1, 133.5, 135.4, 159.2, 165.6, 166.4, 199.2. HRESIMS calcd for $\text{C}_{37}\text{H}_{43}\text{O}_6\text{Si}$ ($\text{M}+\text{H}$) $^+$ 611.2829, found 611.2855.

A solution of **4** (9.53 g, 15.6 mmol) in diphenyl ether (40 mL) was stirred at 180 °C for 30 min. The mixture was purified by silica gel column chromatography (hexane : AcOEt, 5 : 1) to afford **3** (5.53 g, 9.06 mmol) as a colorless oil in 58% yield.

3: IR (film) ν cm⁻¹; 1772, 1734, 1514, 1285, 1088. ¹H NMR (300 MHz, CDCl₃) δ ; 1.04 (9H, s), 2.36-2.55 (2H, m), 2.95-3.05 (1H, m), 3.21 (1H, br t, J = 3.5 Hz), 3.34 (1H, s), 3.36 (1H, d, J = 2.4 Hz), 3.66-3.82 (2H, m), 3.74 (3H, s), 3.79 (3H, s), 4.34 (1H, d, J = 11.6 Hz), 4.41 (1H, d, J = 11.6 Hz), 5.40 (1H, br d, J = 9.6 Hz), 5.76-5.82 (1H, m), 6.40 (1H, dd, J = 2.4, 9.6 Hz), 6.84-6.90 (2H, m), 7.18-7.24 (2H, m), 7.34-7.47 (6H, m), 7.61-7.68 (4H, m). ¹³C NMR (75 MHz, CDCl₃) δ ; 19.1, 26.8, 33.5, 42.7, 50.7, 52.3, 55.2, 61.8, 62.0, 68.5, 72.5, 113.7, 123.2, 127.2, 127.6, 129.1, 129.7, 129.9, 132.8, 133.5, 133.5, 135.5, 152.1, 159.2, 168.4, 203.7. HRESIMS calcd for C₃₇H₄₃O₆Si (M+H)⁺ 611.2829, found 611.2848.

To a solution of **3** (745 mg, 1.22 mmol) in THF (15 mL) was added a solution of LiAlH(Ot-Bu)₃ (1.0 M in THF, 1.83 mL, 1.83 mmol) at -50 °C and the mixture was stirred at same temperature for 3 h. A solution of Rochelle salt was added to the reaction mixture and the resulting mixture was stirred at ambient temperature for 30 min. The mixture was extracted with AcOEt and the organic layer was washed with brine, dried with MgSO₄, and concentrated under vacuum. The resulting residue was purified by silica gel column chromatography (hexane : AcOEt, 1 : 3) to afford two diastereomers **25-1** (620 mg, 1.01 mmol) and **25-2** (57.3 mg, 0.0936 mmol) as a colorless oil in 91% yield.

25-1: IR (film) ν cm⁻¹; 3504, 1734, 1513. ¹H NMR (300 MHz, CDCl₃) δ ; 1.04 (9H, s), 2.31 (2H, t, J = 6.7 Hz), 2.38 (1H, d, J = 10.9 Hz), 2.53-2.64 (1H, m), 2.75 (1H, br q, J = 4.4 Hz), 3.31 (2H, d, J = 7.8 Hz), 3.61-3.77 (2H, m), 3.70 (3H, s), 3.80 (3H, s), 4.35 (1H, d, J = 11.5 Hz), 4.41 (1H, d, J =

11.5 Hz), 4.64 (1H, dd, $J = 4.7, 10.7$ Hz), 5.32-5.37 (1H, m), 5.63 (1H, td, $J = 2.0, 10.0$ Hz), 6.29 (1H, d, $J = 10.0$ Hz), 6.84-6.90 (2H, m), 7.19-7.25 (2H, m), 7.34-7.47 (6H, m), 7.62-7.70 (4H, m). ^{13}C NMR (75 MHz, CDCl_3) δ : 19.2, 26.8, 32.8, 33.8, 43.2, 52.1, 55.2, 59.1, 62.2, 69.0, 72.6, 78.3, 113.8, 124.1, 127.6, 128.4, 129.0, 129.1, 129.6, 130.3, 133.7, 133.8, 135.5, 152.7, 159.2, 172.5. HRESIMS calcd for $\text{C}_{37}\text{H}_{45}\text{O}_6\text{Si}$ ($\text{M}+\text{H}$) $^+$ 613.2985, found 613.2985.

25-2: IR (film) ν cm^{-1} ; 3448, 1734, 1512. ^1H NMR (300 MHz, CDCl_3) δ : 1.04 (9H, s), 2.37-2.57 (2H, m), 2.65-2.75 (1H, m), 2.94 (1H, br s), 2.98 (1H, d, $J = 7.6$ Hz), 3.20 (2H, d, $J = 7.8$ Hz), 3.66-3.79 (2H, m), 3.72 (3H, s), 3.79 (3H, s), 4.26 (1H, d, $J = 7.3$ Hz), 4.32 (1H, d, $J = 11.5$ Hz), 4.38 (1H, d, $J = 11.5$ Hz), 5.23 (1H, ddd, $J = 1.9, 2.2, 9.7$ Hz), 5.28 (1H, br s), 6.20 (1H, dd, $J = 2.4, 9.7$ Hz), 6.82-6.89 (2H, m), 7.17-7.24 (2H, m), 7.34-7.47 (6H, m), 7.62-7.70 (4H, m). ^{13}C NMR (75 MHz, CDCl_3) δ : 19.2, 26.9, 32.4, 39.4, 48.5, 52.1, 55.3, 61.6, 62.7, 69.1, 72.6, 84.4, 113.8, 122.6, 126.2, 127.6, 129.2, 129.6, 130.3, 133.8, 133.8, 132.3, 135.6, 150.4, 159.2, 172.7. HRESIMS calcd for $\text{C}_{37}\text{H}_{45}\text{O}_6\text{Si}$ ($\text{M}+\text{H}$) $^+$ 613.2985, found 613.2970.

To a solution of **25-1** (614 mg, 1.00 mmol) in DMF (5 mL) was added imidazole (204 mg, 3.00 mmol) and TBDMSCl (227 mg, 1.50 mmol) at ambient temperature and the mixture was stirred at same temperature for 24 h. Water was added to the mixture and the resulting mixture was extracted with ether. The organic layer was washed with brine, dried with MgSO_4 , and concentrated under vacuum. The resulting residue was purified by silica gel column chromatography (hexane : AcOEt, 20 : 1) to afford **26** (698 mg, 0.961 mmol) as a colorless oil in 96% yield.

26: IR (film) ν cm^{-1} ; 1743, 1508, 1249, 1112. ^1H NMR (300 MHz, CDCl_3) δ : -0.02 (3H, s), 0.04 (3H, s), 0.84 (9H, s), 1.03 (9H, s), 2.27 (2H, t, $J = 6.7$ Hz), 2.52-2.67 (2H, m), 3.28 (2H, d, $J = 7.8$ Hz), 3.60-3.75 (2H, m), 3.65 (3H, s), 3.79 (3H, s), 4.34 (1H, d, $J = 11.6$ Hz), 4.41 (1H, d, $J = 11.6$ Hz), 4.62 (1H, dd, $J = 1.2, 5.1$ Hz), 5.22-5.29 (1H, m), 5.42 (1H, ddd, $J = 1.9, 2.2, 10.0$ Hz), 6.21 (1H, ddd, $J = 1.5, 2.1, 10.0$ Hz), 6.83-6.90 (2H, m), 7.19-7.26 (2H, m), 7.33-7.46 (6H, m), 7.61-7.69 (4H, m). ^{13}C NMR (75 MHz, CDCl_3) δ : -5.1, -4.8, 17.9, 19.2, 25.6, 26.8, 32.7, 34.3, 44.3, 51.7, 55.2, 59.3, 62.2, 69.5, 72.6, 79.0, 113.7, 123.2, 126.8, 127.6, 128.1, 129.2, 129.6, 130.5, 133.8, 133.8, 135.5, 152.6, 159.1, 173.0. HRESIMS calcd for $\text{C}_{43}\text{H}_{59}\text{O}_6\text{Si}_2$ ($\text{M}+\text{H}$) $^+$ 727.3850, found 727.3832.

To a solution of **26** (1.61 g, 2.22 mmol) in MeOH (25 mL) and water (3 mL) was added lithium hydroxide mono hydrate (466 mg, 11.1 mmol) was added and the mixture was stirred at 60 $^\circ\text{C}$ for

30 h. 1M HCl was added to the mixture at ambient temperature until pH became 2 and the mixture was extracted with AcOEt. The organic layer was washed with brine, dried with MgSO₄, and concentrated under vacuum. The resulting residue was purified by silica gel column chromatography (hexane : AcOEt, 20 : 1) to afford **27** (890 mg, 1.88 mmol) as a colorless oil in 85% yield.

27: IR (film) ν cm⁻¹; 3388, 2929, 1700, 1513, 1249. ¹H NMR (300 MHz, CDCl₃) δ ; 0.01 (3H, s), 0.05 (3H, s), 0.84 (9H, s), 2.24-2.42 (2H, m), 2.51-2.61 (1H, m), 2.61-2.68 (1H, m), 3.36 (2H, d, J = 6.1 Hz), 3.53-3.70 (2H, m), 3.81 (3H, s), 4.39 (1H, d, J = 12.1 Hz), 4.43 (1H, d, J = 12.1 Hz), 4.67 (1H, dd, J = 1.0, 4.9 Hz), 5.45 (1H, d, J = 3.0 Hz), 5.50 (1H, ddd, J = 1.7, 2.1, 10.2 Hz), 6.24 (1H, ddd, J = 0.8, 2.4, 10.2 Hz), 6.85-6.94 (2H, m), 7.20-7.33 (2H, m). ¹³C NMR (75 MHz, CDCl₃) δ ; -5.0, -4.8, 17.9, 25.6, 33.2, 34.7, 45.4, 55.3, 58.7, 60.1, 69.8, 72.7, 79.4, 113.7, 126.8, 128.1, 130.0, 130.1, 150.6, 159.2, 178.1. HRESIMS calcd for C₂₆H₃₉O₆Si (M+H)⁺ 475.2516, found 475.2536.

To a solution of **27** (225 mg, 0.475 mmol) in DMF (1.5 mL) was added imidazole (161 mg, 2.37 mmol) and TBDMSCl (179 mg, 1.19 mmol) at ambient temperature and the mixture was stirred at same temperature for 30 min. Water was added to the mixture and the resulting mixture was extracted with ether. The organic layer was washed with brine, dried with MgSO₄, and concentrated under vacuum. MeOH (2 mL) and K₂CO₃ (78.8 mg, 0.570 mmol) was added to the residue and the mixture was stirred at ambient temperature for 20 min. 1M HCl was added to the mixture at ambient temperature until pH became 2 and the mixture was extracted with ether. The organic layer was washed with brine, dried with MgSO₄, and concentrated under vacuum. The resulting residue was purified by silica gel column chromatography (hexane : AcOEt, 10 : 1) to afford **10** (270 mg, 0.459 mmol) as a colorless oil in 97% yield.

10: IR (film) ν cm⁻¹; 2930, 1703, 1514, 1250. ¹H NMR (300 MHz, CDCl₃) δ ; 0.02 (3H, s), 0.03 (6H, s), 0.07 (3H, s), 0.85 (9H, s), 0.87 (9H, s), 2.29 (2H, t, J = 7.0 Hz), 2.55-2.73 (2H, m), 3.31 (2H, d, J = 8.5 Hz), 3.55-3.70 (2H, m), 3.81 (3H, s), 4.39 (1H, d, J = 11.7 Hz), 4.48 (1H, d, J = 11.7 Hz), 4.66 (1H, d, J = 4.9 Hz), 5.25-5.33 (1H, m), 5.43 (1H, d, J = 10.0 Hz), 6.20 (1H, d, J = 10.0 Hz), 6.89 (2H, d, J = 8.4 Hz), 7.26 (2H, d, J = 8.4 Hz), 11.3 (1H, br s). ¹³C NMR (75 MHz, CDCl₃) δ ; -5.3, -4.9, 4.8, 17.9, 18.3, 25.7, 25.9, 32.9, 34.2, 44.4, 55.2, 59.3, 61.7, 69.4, 72.6, 79.1, 113.8, 123.5, 127.0, 127.7, 129.2, 130.5, 152.4, 159.2, 178.9. HRESIMS calcd for C₃₂H₅₃O₆Si₂ (M+H)⁺ 589.3381, found 589.3354.

To a solution of **10** (270 mg, 0.459 mmol) in CH₂Cl₂ (10 mL) and THF (5 mL) was added EDC (132 mg, 0.689 mmol) at ambient temperature and followed by addition of a solution of 2-mercaptopyridine-*N*-oxide (85.5 mg, 0.689 mmol) in CH₂Cl₂ (1 mL) under the dark condition. After being stirred for 2 h, oxygen gas was introduced to the mixture and the mixture was stirred at ambient temperature for 1.5 h under fluorescent light. Triphenylphosphine (241 mg, 0.918 mmol) was added to the mixture and the resulting mixture was stirred for 1 h. Sat. aqueous NH₄Cl was added to the mixture and the mixture was extracted with ether. The organic layer was washed with brine, dried with MgSO₄, and concentrated under vacuum. The resulting residue was purified by silica gel column chromatography (hexane : AcOEt, 30 :1-20 : 1) to afford **28** (159 mg, 0.284 mmol) as a colorless oil in 62% yield.

28: IR (film) ν cm^{-1} ; 3429, 1514, 1249. ^1H NMR (300 MHz, CDCl_3) δ ; 0.09 (12H, s), 0.89 (9H, s), 0.91 (9H, s), 2.26-2.44 (2H, m), 2.56-2.69 (2H, m), 3.22-3.34 (2H, m), 3.51-3.60 (1H, m), 3.52 (1H, s), 3.74-3.81 (1H, m), 3.81 (3H, s), 3.99 (1H, dd, $J = 1.8, 4.9$ Hz), 4.38 (1H, d, $J = 11.6$ Hz), 4.46 (1H, d, $J = 11.6$ Hz), 5.20 (1H, br d, $J = 3.2$ Hz), 5.31 (1H, td, $J = 2.2, 10.1$ Hz), 5.80 (1H, ddd, $J = 1.8, 2.0, 10.1$ Hz), 6.85-6.92 (2H, m), 7.22-7.30 (2H, m). ^{13}C NMR (75 MHz, CDCl_3) δ ; -5.5, -4.8, -4.5, 18.1, 18.3, 25.9, 26.0, 30.8, 34.6, 44.0, 55.3, 64.1, 70.0, 72.6, 79.9, 81.3, 113.7, 121.0, 126.0, 129.2, 130.7, 134.8, 156.2, 159.1. HRESIMS calcd for $\text{C}_{31}\text{H}_{53}\text{O}_5\text{Si}_2$ ($\text{M}+\text{H}$) $^+$ 561.3432, found 561.3425.

To a solution of **28** (97.8 mg, 0.175 mmol) in THF (3 mL) was added triethylamine (0.245 mL, 1.75 mmol), acetic anhydride (0.165 mL, 1.75 mmol), and DMAP (21.3 mg, 0.175 mmol) at ambient temperature and the mixture was stirred at 60 °C for 24 h. Water was added to the mixture and the resulting mixture was extracted with ether. The organic layer was washed with brine, dried with MgSO₄, and concentrated under vacuum. The resulting residue was purified by silica gel column chromatography (hexane : AcOEt, 25 : 1) to afford **11** (96.9 mg, 0.161 mmol) as a colorless oil in 92% yield.

11: IR (film) ν cm^{-1} ; 1740, 1513, 1249. ^1H NMR (300 MHz, CDCl_3) δ ; 0.02 (3H, s), 0.04 (9H, s),

0.87 (9H, s), 0.88 (9H, s), 2.06 (3H, s), 2.21 (2H, t, $J = 7.4$ Hz), 2.54-2.72 (2H, m), 3.21-3.31 (2H, m), 3.55-3.72 (2H, m), 3.81 (3H, s), 4.37 (1H, d, $J = 11.6$ Hz), 4.46 (1H, d, $J = 11.6$ Hz), 5.06 (1H, dd, $J = 1.6, 5.5$ Hz), 5.15-5.22 (1H, m), 5.37 (1H, ddd, $J = 2.1, 2.3, 10.2$ Hz), 5.83 (1H, td, $J = 2.0, 10.2$ Hz), 6.85-6.92 (2H, m), 7.21-7.30 (2H, m). ^{13}C NMR (75 MHz, CDCl_3) δ : -5.3, -5.3, -4.9, -4.8, 18.0, 18.3, 21.9, 25.7, 25.9, 31.7, 34.7, 43.1, 55.2, 61.9, 69.4, 72.6, 75.8, 88.9, 113.8, 120.0, 126.6, 129.2, 130.5, 130.7, 152.1, 159.2, 170.3. HRESIMS calcd for $\text{C}_{33}\text{H}_{55}\text{O}_6\text{Si}_2$ ($\text{M}+\text{H}$) $^+$ 603.3537, found 603.3535.

To a solution of **11** (81.3 mg, 0.135 mmol) in MeOH (1.5 mL) was added diluted H_2SO_4 (1M, 0.015 mL, 0.015 mmol) and the mixture was stirred at ambient temperature for 20 min. Sat. aqueous NaHCO_3 was added to the mixture and the mixture was extracted with ether. The organic layer was washed with brine, dried with MgSO_4 , and concentrated under vacuum. The resulting residue was purified by silica gel column chromatography (hexane : AcOEt, 3 : 1) to afford **29** (63.3 mg, 0.130 mmol) as a colorless oil in 96% yield.

29: IR (film) ν cm^{-1} : 3437, 1738, 1513, 1248. ^1H NMR (300 MHz, CDCl_3) δ : 0.01 (3H, s), 0.03 (3H, s), 0.86 (9H, s), 2.06 (3H, s), 2.12-2.36 (3H, m), 2.51-2.60 (1H, m), 2.61-2.68 (1H, m), 3.28-3.37 (2H, m), 3.56-3.72 (2H, m), 3.80 (3H, s), 4.37 (1H, d, $J = 12.0$ Hz), 4.42 (1H, d, $J = 12.0$ Hz), 5.06 (1H, dd, $J = 1.7, 5.5$ Hz), 5.35 (1H, br d, $J = 3.5$ Hz), 5.41 (1H, td, $J = 2.3, 10.2$ Hz), 5.91 (1H, td, $J = 2.1, 10.2$ Hz), 6.84-6.92 (2H, m), 7.19-7.28 (2H, m). ^{13}C NMR (75 MHz, CDCl_3) δ : -4.9, -4.8, 18.0, 21.9, 25.7, 31.8, 35.2, 44.2, 55.3, 60.1, 69.8, 72.8, 76.2, 77.2, 88.7, 113.8, 122.5, 127.6, 130.0, 130.1, 131.1, 150.4, 159.3, 170.4. HRESIMS calcd for $\text{C}_{27}\text{H}_{41}\text{O}_6\text{Si}$ ($\text{M}+\text{H}$) $^+$ 489.2672, found 489.2637.

To a solution of **29** (58.6 mg, 0.120 mmol) in CH_2Cl_2 (2 mL) was added NaHCO_3 (50.4 mg, 0.600 mmol) and Dess-Martin periodinane (76.4 mg, 0.18 mmol) at 0 $^\circ\text{C}$ and the mixture was stirred at ambient temperature for 30 min. A solution of sodium thiosulfate was added to the mixture and the resulting mixture was extracted with ether. The organic layer was washed with brine, dried

with MgSO_4 , and concentrated under vacuum to afford crude **30**. A solution of crude **30** in ether (2 mL) was added to the solution of hexylidenetriphenylphosphorane, which was prepared from hexyltriphenylphosphonium bromide (205 mg, 0.48 mmol) with NaHMDS (1 M in THF, 0.420 mL, 0.420 mmol), at $-78\text{ }^\circ\text{C}$ and the resulting mixture was stirred at ambient temperature for 2 h. Sat. aqueous NH_4Cl was added to the mixture and the mixture was extracted with ether. The organic layer was washed with brine, dried with MgSO_4 , and concentrated under vacuum. The resulting residue was purified by silica gel column chromatography (hexane : AcOEt, 25 : 1) to afford **12** (45.9 mg, 0.0828 mmol) as a colorless oil in 69% yield (2 steps, $Z/E = >95 : 5$).

12: IR (film) $\nu\text{ cm}^{-1}$; 1739, 1513, 1247. ^1H NMR (300 MHz, CDCl_3) δ ; 0.02 (3H, s), 0.05 (3H, s), 0.87 (9H, s), 0.88 (3H, t, $J = 6.7\text{ Hz}$), 1.19-1.38 (6H, m), 1.95 (2H, br q, $J = 3.7\text{ Hz}$), 2.07 (3H, s), 2.55-2.82 (4H, m), 3.19-3.31 (2H, m), 3.80 (3H, s), 4.36 (1H, d, $J = 11.6\text{ Hz}$), 4.47 (1H, d, $J = 11.6\text{ Hz}$), 5.05 (1H, dd, $J = 1.7, 5.5\text{ Hz}$), 5.10-5.15 (1H, m), 5.26-5.50 (3H, m), 5.88 (1H, td, $J = 2.1, 10.2\text{ Hz}$), 6.84-6.93 (2H, m), 7.21-7.30 (2H, m). ^{13}C NMR (75 MHz, CDCl_3) δ ; -4.9, -4.8, 14.1, 18.0, 21.9, 22.5, 25.7, 25.9, 27.0, 29.2, 31.5, 34.7, 42.9, 55.2, 69.3, 72.6, 75.9, 88.9, 113.7, 118.8, 125.2, 126.5, 129.2, 130.5, 130.9, 131.7, 154.2, 159.1, 170.3. HRESIMS calcd for $\text{C}_{33}\text{H}_{51}\text{O}_5\text{Si}$ ($\text{M}+\text{H}$) $^+$ 555.3506, found 555.3479.

To a solution of **12** (40.0 mg, 0.0722 mmol) in CH_2Cl_2 (1.5 mL) and water (0.1 mL) was added DDQ (21.3 mg, 0.0939 mmol) at $0\text{ }^\circ\text{C}$ and the mixture was stirred at ambient temperature for 3 h. Sat. aqueous NaHCO_3 was added to the mixture and the mixture was extracted with ether. The organic layer was washed with brine, dried with MgSO_4 , and concentrated under vacuum. The resulting residue was purified by silica gel column chromatography (hexane : AcOEt, 15 : 1) to afford **31** (29.7 mg, 0.0684 mmol) as a colorless oil in 95% yield.

31: IR (film) $\nu\text{ cm}^{-1}$; 3307, 1741, 1248. ^1H NMR (300 MHz, CDCl_3) δ ; 0.03 (3H, s), 0.05 (3H, s), 0.83-0.92 (3H, m), 0.87 (9H, s), 1.20-1.40 (6H, m), 1.98 (2H, br q, $J = 7.1\text{ Hz}$), 2.08 (3H, s), 2.43-2.53 (1H, m), 2.63-2.85 (3H, m), 3.52 (2H, d, $J = 7.4\text{ Hz}$), 5.07 (1H, dd, $J = 1.7, 5.6\text{ Hz}$), 5.27 (1H, td, $J = 1.7, 3.5\text{ Hz}$), 5.30-5.51 (3H, m), 5.95 (1H, td, $J = 2.1, 10.2\text{ Hz}$). ^{13}C NMR (75 MHz, CDCl_3) δ ; -4.9, -4.8, 14.1, 18.0, 21.9, 22.6, 25.7, 26.0, 27.0, 29.2, 31.5, 37.3, 43.0, 62.9, 76.1, 88.8, 118.6,

125.1, 126.0, 131.8, 131.8, 154.7, 170.4. HRESIMS calcd for $C_{25}H_{43}O_4Si$ (M+H)⁺ 435.2931, found 435.2914.

To a solution of **31** (11.0 mg, 0.0253 mmol) in CH_2Cl_2 (0.5 mL) was added $NaHCO_3$ (17.1 mg, 0.203 mmol) and Dess-Martin periodinane (16.2 mg, 0.0381 mmol) at 0 °C and the mixture was stirred at ambient temperature for 30 min. A solution of sodium thiosulfate was added to the mixture and the resulting mixture was extracted with ether. The organic layer was washed with brine, dried with $MgSO_4$, and concentrated under vacuum to afford crude **32**. To a solution of crude **32** in ether (0.5 mL) was added the solution of (3-*t*-butyldimethylsilyloxy)propylmagnesium bromide (0.5 M in THF, 0.10 mL, 0.051 mmol), which was prepared from 1-bromo-(3-*t*-butyldimethylsilyloxy)propane with magnesium, at -10 °C and the resulting mixture was stirred at same temperature for 20 min. Sat. aqueous NH_4Cl was added to the mixture and the mixture was extracted with ether. The organic layer was washed with brine, dried with $MgSO_4$, and concentrated under vacuum. The resulting residue was purified by silica gel column chromatography (hexane : AcOEt, 15 : 1) and reverse phase HPLC (methanol : water, 30 : 1) to afford two diastereomers **33-1** (5.9 mg, 0.00973 mmol) and **33-2** (5.6 mg, 0.00924 mmol) as a colorless oil in 75% yield (2 steps).

33-1: IR (film) ν cm^{-1} ; 3401, 1734, 1252. 1H NMR (300 MHz, $CDCl_3$) δ ; 0.03 (3H, s), 0.04 (3H, s), 0.06 (6H, s), 0.83-0.91 (3H, m), 0.88 (9H, s), 0.90 (9H, s), 1.20-1.40 (6H, m), 1.46-1.56 (1H, m), 1.60-1.79 (3H, m), 1.98 (2H, br q, J = 7.0 Hz), 2.07 (3H, s), 2.23-2.32 (1H, m), 2.51 (1H, br d, J = 5.1 Hz), 2.52-2.60 (1H, m), 2.64-2.85 (2H, m), 3.41-3.52 (1H, m), 3.60-3.73 (2H, m), 5.04 (1H, dd, J = 1.7, 5.7 Hz), 5.19-5.24 (1H, m), 5.30-5.51 (2H, m), 5.73 (1H, td, J = 2.1, 10.3 Hz), 5.92 (1H, td, J = 1.9, 10.3 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ ; -5.4, -4.9, -4.8, 14.1, 18.0, 18.3, 21.9, 22.6, 25.7, 25.9, 26.0, 27.0, 28.5, 29.2, 29.7, 31.5, 32.2, 40.2, 43.8, 63.4, 71.1, 76.3, 88.9, 118.6, 125.2, 126.6, 130.8, 131.8, 154.5, 170.4. HRESIMS calcd for $C_{34}H_{63}O_5Si_2$ (M+H)⁺ 607.4214, found 607.4178.

33-2: IR (film) ν cm^{-1} ; 3447, 1741, 1250. 1H NMR (300 MHz, $CDCl_3$) δ ; 0.03 (3H, s), 0.05 (3H, s), 0.06 (6H, s), 0.83-0.91 (3H, m), 0.87 (9H, s), 0.90 (9H, s), 1.20-1.40 (6H, m), 1.46-1.57 (1H, m), 1.60-1.79 (3H, m), 1.98 (2H, br q, J = 6.9 Hz), 2.07 (3H, s), 2.26-2.34 (1H, m), 2.46 (1H, br d, J = 4.3 Hz), 2.65-2.84 (2H, m), 2.81-2.89 (1H, m), 3.45-3.57 (1H, m), 3.62-3.74 (2H, m), 5.04 (1H, dd, J = 1.8, 5.7 Hz), 5.30-5.51 (4H, m), 5.97 (1H, td, J = 2.1, 10.3 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ ; -5.4, -4.9, -4.8, 14.1, 18.0, 18.3, 21.9, 22.6, 25.7, 25.9, 26.0, 27.1, 28.9, 29.2, 31.5, 32.6, 40.5, 42.5, 63.4, 71.0, 76.5, 88.9, 120.3, 125.3, 126.5, 131.7, 132.4, 153.5, 170.3. HRESIMS calcd for $C_{34}H_{63}O_5Si_2$ (M+H)⁺ 607.4214, found 607.4185.

To a solution of **33-1** (5.0 mg, 0.00825 mmol) in THF (0.3 mL) was added triethylamine (0.0035 mL, 0.0248 mmol), acetic anhydride (0.0012 mL, 0.0124 mmol), and DMAP (0.1 mg, 0.0008 mmol) at ambient temperature and the mixture was stirred at same temperature for 30 min. Water was added to the mixture and the resulting mixture was extracted with ether. The organic layer was washed with brine, dried with MgSO_4 , and concentrated under vacuum. The resulting residue was purified by silica gel column chromatography (hexane : AcOEt, 25 : 1) to afford **2** (5.2 mg, 0.008 mmol) as a colorless oil in 97% yield.

2: IR (film) ν cm^{-1} ; 1741, 1241. ^1H NMR (300 MHz, CDCl_3) δ ; 0.03 (3H, s), 0.04 (6H, s), 0.05 (3H, s), 0.83-0.90 (3H, m), 0.88 (9H, s), 0.88 (9H, s), 1.20-1.40 (6H, m), 1.42-1.63 (3H, m), 1.67-1.82 (1H, m), 1.99 (2H, br q, $J = 6.9$ Hz), 2.03 (3H, s), 2.07 (3H, s), 2.41-2.51 (1H, m), 2.54-2.63 (1H, m), 2.63-2.85 (2H, m), 3.59 (2H, t, $J = 6.0$ Hz), 4.77-4.88 (1H, m), 5.04 (1H, dd, $J = 1.8, 5.6$ Hz), 5.19 (1H, td $J = 1.7, 3.3$ Hz), 5.29-5.57 (3H, m), 5.89 (1H, td, $J = 2.1, 10.3$ Hz). ^{13}C NMR (75 MHz, CDCl_3) δ ; -5.3, -4.9, -4.8, 14.1, 18.0, 18.3, 21.2, 21.9, 22.6, 25.7, 25.9, 26.0, 27.1, 27.9, 28.4, 29.2, 31.5, 37.2, 43.5, 62.6, 73.7, 76.1, 88.7, 118.2, 125.1, 131.2, 131.9, 154.6, 170.3, 170.7. HRESIMS calcd for $\text{C}_{36}\text{H}_{65}\text{O}_6\text{Si}_2$ ($\text{M}+\text{H}$) $^+$ 649.4320, found 649.4313.

To a solution of **2** (5.0 mg, 0.0771 mmol) in acetone (0.5 mL) was added Jones reagent (0.01 mL) at ambient temperature and the mixture was stirred at same temperature for 15 min. Isopropyl alcohol and water was added to the mixture and the resulting mixture was extracted with AcOEt. The organic layer was washed with brine, dried with MgSO₄, and concentrated under vacuum to obtain crude carboxylic acid. To a solution of crude carboxylic acid in ether (0.5 mL) was added a solution of excess of diazomethane in ether at 0 °C. After completed the reaction, the mixture was concentrated under vacuum. The resulting residue was purified by silica gel column chromatography (hexane : AcOEt, 25 : 1) to afford **33** (3.8 mg, 0.00676 mmol) as a colorless oil in 88% yield (2 steps).

33: IR (film) ν cm⁻¹; 1741, 1234. ¹H NMR (300 MHz, CDCl₃) δ ; 0.03 (3H, s), 0.05 (3H, s), 0.83-0.94 (3H, m), 0.88 (9H, s), 1.20-1.40 (6H, m), 1.74-1.89 (1H, m), 1.92-2.12 (3H, m), 2.04 (3H, s), 2.07 (3H, s), 2.26-2.35 (2H, m), 2.40-2.49 (1H, m), 2.54-2.64 (1H, m), 2.64-2.84 (2H, m), 3.68 (3H, s), 4.85 (1H, dt, J = 3.4, 8.7 Hz), 5.04 (1H, dd, J = 1.8, 5.7 Hz), 5.21 (1H, td, J = 1.8, 3.4 Hz), 5.28-5.41 (2H, m), 5.41-5.53 (1H, m), 5.91 (1H, td, J = 2.3, 10.3 Hz). ¹³C NMR (75 MHz, CDCl₃) δ ; -4.9, -4.8, 14.1, 18.0, 21.2, 21.8, 22.5, 25.7, 26.0, 27.1, 27.4, 29.2, 29.7, 31.5, 37.4, 43.4, 51.7, 72.9, 76.1, 88.6, 118.0, 124.7, 125.0, 131.5, 132.0, 154.8, 170.3, 170.6, 173.4. HRESIMS calcd for C₃₁H₅₁O₇Si (M+H)⁺ 563.3404, found 563.3412.

To a solution of **33** (3.8 mg, 0.00676 mmol) in THF (0.5 mL) was added excess of HF•pyridine complex at ambient temperature and the mixture was stirred at same temperature for 12 h. Water was added to the mixture and the mixture was extracted with ether. The organic layer was washed with brine, dried with MgSO₄, and concentrated under vacuum. The resulting residue was purified by silica gel column chromatography (hexane : AcOEt, 3 : 1) to afford **34** (2.8 mg, 0.00625 mmol) as a colorless oil in 92% yield.

34: IR (film) ν cm⁻¹; 3469, 1739, 1236. ¹H NMR (300 MHz, CDCl₃) δ ; 0.89 (3H, t, J = 6.6 Hz), 1.17-1.41 (6H, m), 1.76-1.91 (1H, m), 1.95-2.12 (3H, m), 2.04 (3H, s), 2.14 (3H, s), 2.33 (2H, dd, J = 7.2, 7.9 Hz), 2.57-2.67 (1H, m), 2.75-2.84 (1H, m), 2.86 (2H, br d, J = 7.0 Hz), 3.67 (3H, s), 4.30-4.36 (1H, m), 4.56 (1H, br d, J = 2.4 Hz), 4.87 (1H, dt, J = 3.3, 8.5 Hz), 5.27-5.33 (1H, m), 5.29-5.55 (2H, m), 5.88 (1H, td, J = 2.3, 10.3 Hz). ¹³C NMR (150 MHz, CDCl₃) δ ; 14.1, 21.0, 21.5, 22.6, 25.6, 27.1, 27.3, 29.2, 29.7, 31.5, 37.1, 44.0, 51.7, 72.6, 78.6, 90.0, 120.1, 125.0, 125.9, 130.4, 132.1, 154.4, 170.7, 172.6, 173.3. HRESIMS calcd for C₂₅H₃₇O₇ (M+H)⁺ 449.2539, found 449.2523.

A solution of DMSO (0.027 mL, 0.380 mmol) in CH_2Cl_2 (0.1 mL) was added to a solution of oxalyl chloride (0.0132 mL, 0.154 mmol) in CH_2Cl_2 (0.2 mL) at $-78\text{ }^\circ\text{C}$ and the mixture was stirred at same temperature for 20 min. A solution of **34** (2.0 mg, 0.00446 mmol) in CH_2Cl_2 (0.2 mL) was added to the mixture at same temperature and the mixture was stirred at same temperature for 30 min. Triethylamine (0.112 mL, 0.80 mmol) was added to the mixture at same temperature and the resulting mixture was stirred at ambient temperature for 30 min. Water was added to the mixture and the mixture was extracted with ether. The organic layer was washed with brine, dried with MgSO_4 , and concentrated under vacuum. The resulting residue was purified by silica gel column chromatography (hexane : AcOEt, 5 : 1) to afford ($\pm$)-**1** (1.8 mg, 0.00403 mmol) as a colorless oil in 90% yield.

1: IR (film) $\nu\text{ cm}^{-1}$; 1741, 1234. ^1H NMR (300 MHz, CDCl_3) δ ; 0.88 (3H, t, $J = 6.9\text{ Hz}$), 1.20-1.42 (6H, m), 1.82 (1H, dt, $J = 8.6, 14.7\text{ Hz}$), 1.99-2.13 (1H, m), 2.01 (2H, br q, $J = 7.3\text{ Hz}$), 2.05 (3H, s), 2.16 (3H, s), 2.27-2.39 (2H, m), 2.80 (1H, dd, $J = 6.8, 17.0\text{ Hz}$), 2.80-2.85 (1H, m), 2.91 (1H, dd, $J = 7.8, 17.0\text{ Hz}$), 3.19 (1H, br s), 3.68 (3H, s), 4.97 (1H, dt, $J = 3.1, 8.6\text{ Hz}$), 5.37 (1H, ddd, $J = 6.8, 7.8, 10.7\text{ Hz}$), 5.40 (1H, td, $J = 2.2, 10.0\text{ Hz}$), 5.54 (1H, td, $J = 7.3, 10.7\text{ Hz}$), 5.70 (1H, dd, $J = 1.6, 3.1\text{ Hz}$), 6.17 (1H, dd, $J = 2.5, 10.0\text{ Hz}$). ^{13}C NMR (150 MHz, CDCl_3) δ ; 14.0, 20.7, 20.9, 22.5, 26.5, 26.9, 27.1, 29.1, 29.5, 31.5, 45.2, 49.5, 51.4, 72.4, 82.7, 118.0, 123.6, 125.1, 133.1, 135.0, 154.6, 168.8, 170.4, 173.0, 203.0. HRESIMS calcd for $\text{C}_{25}\text{H}_{35}\text{O}_7$ ($\text{M}+\text{H}$) $^+$ 447.2383, found 447.2349.