APPENDIX

Pd Catalyzed Asymmetric Allylic Alkylation. A Short Route to the Cyclopentyl Core of Viridenomycin

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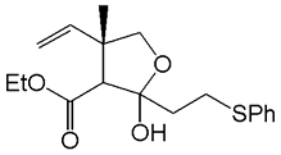
Experimental session

General

All reactions were performed in oven-dried glassware. Solvents were dried and distilled using standard procedures. Dichloromethane and triethylamine were distilled from calcium hydride; tetrahydrofuran and toluene were distilled from sodium/ benzophenone, while benzene was distilled from sodium metal.

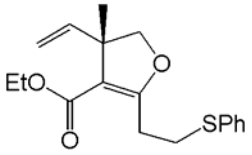
NMR spectra were recorded using a Varian Gemini 300 spectrometer using TMS (0.00 ppm), residue $CHCl_3$ (7.26 ppm) and $CDCl_3$ (77.0 ppm) as the internal standard. IR spectra were recorded on liquid films (NaCl plates) employing a Perkin-Elmer Paragon 500 FTIR spectrophotometer. Optical rotations were measured in a Jasco DIP-360 digital polarimeter in 5-cm cells at room temperature. Elemental analyses were obtained from M-H-W Laboratories, Phoenix, Arizona. Chiral HPLC was performed on a Thermo Separation Products Spectra Series P100 HPLC using Chiralpak OC columns with detection at 254 nm.

4-(S)-2-Hydroxy-4-methyl-2-(2-phenylsulfanyl-ethyl)-4-vinyl-tetrahydro-furan-3-carboxylic acid ethyl ester (**7**)



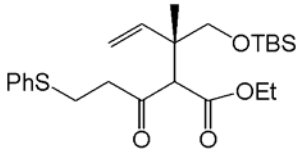
To an oven-dried round-bottom flask were added $Pd_2dba_3.CHCl_3$ (156 mg, 15 mmol), (*S,S*)-**2** (312 mg, 45 mmol) and a stirbar. The flask was then placed under reduced pressure (vacuum pump) for 10 seconds and refilled with Ar; this purging procedure was repeated five times to ensure no oxygen remained in the reaction vessel. After being placed under an Ar atmosphere, freshly distilled CH_2Cl_2 (150 mL) was added and the resulting dark purple solution was stirred at room temperature until it turned a deep orange color (10 min). During this time, ethyl 3-oxo-5-phenylsulfanylpentanoate (3.78 g, 15.0 mmol) was added. Finally, 2-methyl-2-vinyloxirane (1.91 mL, 19.5 mmol) was added to the reaction mixture and the solution turned bright yellow. Stirring was continued for 26 h at room temperature, at which point the orange color returned. The solvent was removed in vacuo. The crude product was purified by flash chromatography (19:1 petroleum ether: ethyl acetate) on silica gel to afford the desired compound **7** 3.56 g (71 %) as colorless oil. Two diastereomers (dr ~ 1:1) were not separated. IR: 3434, 3083, 1708, 1584, 1482, 1440, 1376, 1345, 1210, 1184, 1051, 1026, 924, 739 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, mixture of 1:1 diastereomers): δ 7.29 (m, 8H), 7.16 (m, 2H), 6.09 (dd, *J* = 11.0, 17.3 Hz, 1H), 5.92 (dd, *J* = 10.5, 17.3 Hz, 1H), 5.47 (s, 1H), 5.39 (s, 1H), 5.08 (m, 4H), 4.18 (m, 4H), 4.07 (d, *J* = 8.5 Hz, 1H), 3.88 (d, *J* = 8.5 Hz, 1H), 3.84 (d, *J* = 8.5 Hz, 1H), 3.67 (d, *J* = 8.8 Hz, 1H), 3.11 (m, 4H), 2.83 (s, 1H), 2.70 (s, 1H), 2.04 (m, 4H), 1.37 (s, 3H), 1.26 (m, 9H). ^{13}C NMR (75 MHz, $CDCl_3$, 1:1 diastereomers): δ 172.9, 172.6, 144.1, 141.0, 137.3, 136.2, 128.9, 128.7, 125.7, 114.4, 112.7, 105.2, 105.1, 77.8, 77.7, 61.4, 61.4, 61.3, 58.9, 47.8, 47.7, 40.3, 40.0, 27.3, 24.7, 20.4, 14.1. Anal. Calc d for $C_{18}H_{24}O_4S$: C64.26, H 7.19; found C 64.15, H 7.33.

4-(S)-4-Methyl-2-(2-phenylsulfanyl-ethyl)-4-vinyl-4,5-dihydro-furan-3-carboxylic acid ethyl ester (**8**)



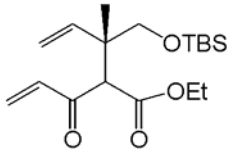
To a stirred solution of **7** (25 mg, 0.074 mmol, mixture of the two diastereomers) and DMAP (2 mg, 0.015 mmol) in THF (1.0 mL) under N_2 atmosphere and room temperature were added triethylamine (260 μL, 1.85 mmol) and methanesulfonyl chloride (58 μL, 0.74 mmol) subsequently. After the reaction was complete (monitored by TLC), water was added to quench the reaction. The reaction mixture was extracted with Et_2O and the organic layers were dried over $MgSO_4$. After the solvent was removed in vacuo, the residue was purified by flash chromatography (30:1 petroleum ether: ethyl ether) on silica gel to afford **8** 23 mg (94 %) as colorless oil in 94 % ee (separated by chiral HPLC: OC column, 99.5:0.5 heptane: isopropanol, 1.0 mL/min, (-)-isomer: 14.65 min, (+)-isomer: 16.65 min). $[\alpha]_D^{24}$ = +21.01 (c = 3.4, $CHCl_3$). IR: 3067, 1696, 1629, 1071 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.37 (m, 2H), 7.29 (m, 2H), 7.18 (m, 1H), 6.00 (dd, *J* = 10.9, 17.2 Hz, 1H), 5.06 (d, *J* = 10.3 Hz, 1H), 5.04 (d, *J* = 18.1 Hz, 1H), 4.24 (d, *J* = 8.8 Hz, 1H), 4.10 (q, *J* = 7.1 Hz, 2H), 4.03 (d, *J* = 8.8 Hz, 1H), 3.14 (t, *J* = 7.3 Hz, 2H), 2.97 (t, *J* = 7.2 Hz, 2H), 1.40 (s, 3H), 1.19 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 169.3, 165.1, 143.0, 135.9, 129.5, 128.9, 126.1, 112.6, 110.8, 82.1, 59.3, 48.9, 30.6, 28.7, 23.4, 14.2. Anal. Calc d for $C_{18}H_{22}O_3S$: C 67.89, H 6.96; found C 67.69, H 7.06.

3-(S)-3-(tert-Butyl-dimethyl-silanyloxymethyl)-3-methyl-2-(3-phenylsulfanyl-propionyl)-pent-4-enoic acid ethyl ester (**9**)



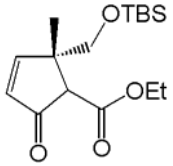
To a solution of **7** (4.337 g, 12.9 mmol) in DMF (13.0 mL) at 0 ^oC were added imidazole (4.39 g, 64.5 mmol) and TBDMSCl (4.86 g, 32.3 mmol) consequently and the reaction mixture was slowly warmed to room temperature and stirred overnight. Water was added and the mixture was extracted with Et_2O. The organic layers were dried over $MgSO_4$ and the solvent was removed in vacuo. The residue was purified by column chromatography (30 :1 => 20:1 petroleum ether: ethyl acetate) on silica gel to afford **9** 5.26 g (91 %) as colorless oil. Two diastereomers (dr ~ 1:1) were not separated. IR: 3085, 1750, 1715, 1473, 1253, 1093, 938, 778, 739 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, 1:1 diastereomers): δ 7.30 (m, 8H), 7.19 (m, 2H), 6.17 (dd, *J* = 11.0, 17.6 Hz, 1H), 6.12 (dd, *J* = 11.0, 17.3 Hz, 1H), 5.04 (m, 4H), 4.10 (m, 4H), 3.84 (s, 1H), 3.83 (s, 1H), 3.45 (m, 4H), 3.10 (m, 4H), 2.85 (m, 4H), 1.19 (m, 12H), 0.87 (s, 18H), 0.00 (s, 6H), -0.01 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$, 1:1 diastereomers): δ 203.3, 203.1, 168.3, 168.2, 141.3, 141.1, 135.8, 129.3, 129.3, 128.9, 126.2, 114.4, 114.3, 69.2, 69.2, 61.6, 61.3, 61.0, 44.6, 44.5, 44.2, 43.7, 27.3, 27.2, 25.8, 18.7, 18.2, 14.0, -5.6, -5.7. Anal. Calc d for $C_{24}H_{38}O_4SSi$: C 63.96, H 8.50, found C 64.16, H 8.66.

3-(S)-2-Acryloyl-3-(tert-butyl-dimethyl-silanyloxymethyl)-3-methyl-pent-4-enoic acid ethyl ester (**10**)



A solution of compound **9** (116 mg, 0.257 mmol) in methanol (1.4 mL) was immersed in an ice bath with stirring while a solution of $NaIO_4$ (61 mg, 0.297 mmol) in 0.4 mL water was added dropwise. The ice bath was removed after 10 min and stirring was continued at room temperature for 21 h. The reaction mixture was diluted with water, and extracted with ethyl acetate. The combined organic layers were washed with brine and dried over $MgSO_4$ and the solvent was removed in vacuo. The crude product was re-dissolved in 2.6 mL benzene containing ethyl vinyl ketone (31 L, 0.308 mmol) under N_2 atmosphere and heated at 75 ^oC for 22 h. After cooled to room temperature, the reaction mixture was filtered and the solvent was removed in vacuo. The residue was purified by column chromatography on silica gel (30:1 petroleum ether: ethyl ether) to afford the desired product **10** 74 mg (84%) as colorless oil. The 1:1 diastereomers were not separable. IR: 3088, 1738, 1692, 1611, 1470, 1401, 1253, 1092, 838, 777 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, 1:1 diastereomers): δ 6.50 (dd, *J* = 10.5, 20.4 Hz, 1H), 6.44 (dd, *J* = 10.4, 20.4 Hz, 1H), 6.21 (m, 4H), 5.75 (d, *J* = 10.3 Hz, 2H), 5.05 (m, 4H), 4.14 (s, 2H), 4.12 (q, *J* = 7.0 Hz, 2H), 4.11 (q, *J* = 7.2 Hz, 2H), 3.57 (d, *J* = 9.5 Hz, 1H), 3.56 (d, *J* = 9.5 Hz, 1H), 3.45 (d, *J* = 9.3 Hz, 1H), 3.42 (d, *J* = 9.3 Hz, 1H), 1.21 (m, 12H), 0.88 (s, 18H), 0.01 (s, 6H), 0.00 (s, 3H), -0.01 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$, 1:1 diastereomers): δ 194.7, 194.5, 168.5, 141.4, 141.2, 136.7, 136.4, 128.5, 128.3, 114.2, 114.2, 69.2, 69.0, 60.9, 60.9, 59.1, 59.0, 44.6, 25.8, 19.1, 18.4, 18.2, 14.1, -5.6. Anal. Calc d for $C_{18}H_{32}O_4Si$: C 63.49, H 9.47; found C 63.60, H 9.43.

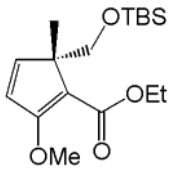
2-(S)-2-(tert-Butyl-dimethyl-silanyloxymethyl)-2-methyl-5-oxo-cyclopent-3-enecarboxylic acid ethyl ester (**12**)



In a solution of Grubbs-II catalyst (127 mg, 0.15 mmol) in CH_2Cl_2 (100 mL) under Ar atmosphere was added compound **10** (1.56 g, 4.59 mmol) with 50 mL CH_2Cl_2. The reaction mixture was refluxed for 3.5 days and then cooled to room temperature and stirred open to air overnight. After removing solvent in vacuo, the residue was purified by column chromatography on silica gel (30:1 petroleum ether: ethyl ether -> 19:1 petroleum ether: ethyl acetate) to afford the desired product **12** 989 mg (69%) as colorless oil and recover starting material **10** 309 mg (20%). Two diastereomers (dr ~ 4:1) were not separated. IR: 1742, 1712, 1666, 1254, 1137, 1098, 1036, 829, 778 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): major diastereomer: δ 7.38 (d, *J* = 5.6 Hz, 1H), 6.15 (d, *J* = 5.6 Hz, 1H), 4.19 (q, *J* = 7.2 Hz, 2H), 3.58 (s, 2H), 3.36 (s, 1H), 1.27 (t, *J* = 7.2 Hz, 3H), 1.15 (s, 3H), 0.85 (s, 9H), 0.04 (s, 3H), 0.03 (s, 3H); minor diastereomer: δ 7.46 (d, *J* = 5.6 Hz, 1H), 6.15 (d, *J* = 5.6 Hz, 1H), 4.19 (q, *J* = 7.2 Hz, 2H), 3.64 (s, 2H), 3.06 (s, 1H), 1.36 (s,

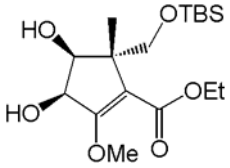
3H), 1.28 (t, *J* = 7.1 Hz, 3H), 0.87 (s, 9H), 0.01 (s, 3H), 0.00 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$, 4:1 diastereomers): δ 203.6, 169.1, 169.0, 132.4, 132.0, 68.7, 66.5, 61.0, 60.2, 57.4, 50.8, 25.6, 23.4, 18.1, 14.2, 14.0, -5.6, -5.7. Anal. Calc d for $C_{16}H_{28}O_4Si$: C 61.50, H 9.03; found C 61.62, H 9.17.

5-(S)-5-(tert-Butyl-dimethyl-silanyloxymethyl)-2-methoxy-5-methyl-cyclopenta-1,3-dienecarboxylic acid ethyl ester (**13**)



To a solution of **12** (382 mg, 1.22 mmol) in THF (12 mL) at 0 ^{o}C was added NaH (60% in mineral oil, 63 mg, 1.59 mmol) and Me_2SO_4 (139 μL, 1.46 mmol). The reaction mixture was slowly warmed to room temperature and stirred overnight, then quenched by Et_3N and saturated $NaHCO_3$ solution, extracted with Et_2O, and the organic layers were washed with brine and dried over Na_2SO_4. After removing solvent in vacuo, the residue was purified by column chromatography on silica gel (38:1:2 petroleum ether: ethyl acetate: Et_3N) to afford the desired product **31** 367 mg (92%) as colorless oil. $[\alpha]_D$ = +56.78 (c 3.52, $CHCl_3$). IR: 1677, 1607, 1408, 1255, 1212, 1078, 1054, 838 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.91 (d, *J* = 5.9 Hz, 1H), 6.46 (d, *J* = 5.9 Hz, 1H), 4.20 (q, *J* = 7.1 Hz, 2H), 4.10 (d, *J* = 9.0 Hz, 1H), 3.95 (s, 3H), 3.25 (d, *J* = 9.3 Hz, 1H), 1.31 (s, 3H), 1.31 (t, *J* = 7.1 Hz, 3H), 0.88 (s, 9H), 0.03 (s, 3H), 0.00 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 168.5, 163.6, 154.8, 121.2, 111.2, 67.4, 59.0, 58.4, 56.1, 25.8, 18.2, 16.4, 14.5, -5.5, -5.6.

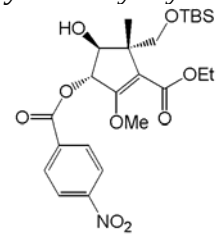
3-(S)-4-(S)-5-(S)-5-(tert-Butyl-dimethyl-silanyloxymethyl)-3,4-dihydroxy-2-methoxy-5-methyl-cyclopent-1-enecarboxylic acid ethyl ester (**14**)



To a solution of **13** (454 mg, 1.39 mmol) in acetone (10 mL) at 0 ^{o}C under N_2 were added NMO (199 mg, 1.71 mmol) in water (4 mL) and OsO_4 (4% aq, 0.98 mL, 0.15 mmol) dropwise. The reaction mixture was warmed to room temperature and stirred for 2.7 days, then quenched with saturated $NaHSO_3$ aqueous solution 2 mL. After stirring for 2 h, the reaction mixture was diluted with water and brine, extracted with EtOAc, and the organic layers were washed with brine and dried over $MgSO_4$. After removing solvent in vacuo, the residue was purified by column chromatography on silica gel (4:1 => 3:1 petroleum ether: ethyl acetate) to afford the desired product **14** 398 mg (79%) as colorless oil. Rf = 0.25 (2:1 petroleum ether: ethyl acetate). $[\alpha]_D$ = -28.76 (c 5.70, $CHCl_3$). IR: 3449, 1692, 1625, 1465, 1376, 1250, 1186, 1093, 1046, 838, 776 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.72 (dd, *J* = 4.4, 6.1 Hz, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 4.05 (dd, *J* = 4.7, 6.1 Hz, 1H), 3.99 (s, 3H), 3.74 (d, *J* = 9.3 Hz, 1H), 3.61 (d, *J* = 9.3 Hz, 1H), 2.83 (d, *J* = 4.4 Hz, 1H), 2.48 (d, *J* = 4.6 Hz, 1H), 1.28 (t, *J* = 7.1 Hz, 3H), 1.21 (s, 3H), 0.88 (s, 9H), 0.04 (s, 3H), 0.02 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 165.1, 110.4, 72.7, 71.3,

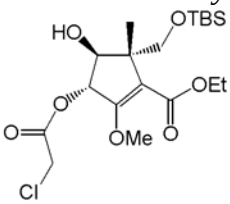
68.7, 59.6, 57.8, 50.2, 25.8, 18.1, 17.9, 14.2, -5.7. Anal. Calc d for $C_{17}H_{32}O_6Si$: C 56.64, H 8.95, found C 56.49, H 8.74.

1-(R)-4-(S)-5-(S)-4-Nitro-benzoic acid 4-(tert-butyl-dimethyl-silanyloxymethyl)-3-ethoxycarbonyl-5-hydroxy-2-methoxy-4-methyl-cyclopent-2-enyl ester (**15a**)



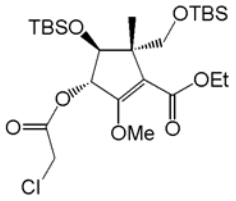
To a solution of **14** (20 mg, 0.555 mmol), Ph_3P (16 mg, 0.61mmol) and 4-nitrobenzoic acid (14 mg, 0.83 mmol) in toluene (0.5 mL) was added DIAD (12 L, 0.61 mmol) dropwise at room temperature and stirred at 40 ^oC for 24 h. After removing solvent, the residue was purified by column chromatography on silica gel (6:1 petroleum ether: ethyl acetate) to afford the desired product **15a** 14.6 mg (52%) as colorless oil. Rf = 0.50 (4:1 petroleum ether: ethyl acetate). $[\alpha]_D^{24}$ = +50.70 (c 0.7, $CHCl_3$). IR: 3528, 1734, 1709, 1638, 1608, 1531, 1465, 1349, 1261, 1100, 1047, 838, 778, 720 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 8.30 (d, *J* = 9.0 Hz, 2H), 8.25 (d, *J* = 9.3 Hz, 2H), 5.96 (d, *J* = 6.1 Hz, 1H), 4.29 (dd, *J* = 2.4, 6.1 Hz, 1H), 4.21 (q, *J* = 7.1 Hz, 2H), 3.82 (s, 3H), 3.70 (s, 2H), 2.85 (d, *J* = 2.7 Hz, 1H), 1.31 (t, *J* = 7.1 Hz, 3H), 1.21 (s, 3H), 0.85 (s, 9H), 0.022 (s, 3H), 0.015 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 164.7, 164.0, 158.8, 150.8, 134.7, 131.0, 123.6, 114.1, 81.0, 78.2, 68.2, 60.2, 59.2, 48.5, 25.8, 18.1, 17.0, 14.2, -5.7. Anal. Calc d for $C_{24}H_{35}NO_9Si$: C 56.56, H 6.92, N 2.75, found C 56.77, H 7.05, N 2.56.

3-(R)-4-(S)-5-(S)-5-(tert-Butyl-dimethyl-silanyloxymethyl)-3-(2-chloro-acetoxy)-4-hydroxy-2-methoxy-5-methyl-cyclopent-1-enecarboxylic acid ethyl ester (**15b**)



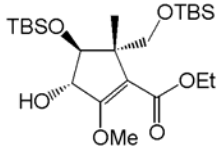
To a solution of **14** (149 mg, 0.413 mmol), Ph_3P (119 mg, 0.453 mmol) and chloroacetic acid (78 mg, 0.824 mmol) in toluene (2.0 mL) was added DIAD (90 μL, 0.453 mmol) dropwise at room temperature and stirred at 40 ^oC for 40 h. After removing solvent, the residue was purified by column chromatography on silica gel (5:1 => 4:1 =>3:1 petroleum ether: ethyl acetate) to afford the desired product **15b** 102 mg (57%) as colorless oil and recovered starting material **14** 10 mg (7%). $[\alpha]_D^{25}$ = +20.98 (c 3.5, $CHCl_3$). Rf = 0.68 (2:1 petroleum ether: ethyl acetate). IR: 3490, 1745, 1702, 1636, 1465, 1376, 1349, 1252, 1186, 1099, 1048, 982, 839, 778 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 5.75 (d, *J* = 6.1 Hz, 1H), 4.18 (m, 5H), 3.81 (s, 3H), 3.67 (AB, 2H), 1.30 (t, *J* = 7.1 Hz, 3H), 1.17 (s, 3H), 0.87 (s, 9H), 0.04 (s, 3H), 0.03 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 167.5, 164.0, 158.5, 114.0, 81.4, 77.7, 68.1, 60.2, 59.4, 48.4, 40.7, 25.8, 18.1, 16.9, 14.1, -5.7. Anal. Calc d for $C_{19}H_{33}ClO_7Si$: C 52.22, H 7.61; found C 52.50, H 7.86.

3-(R)-4-(S)-5-(S)-4-(tert-Butyl-dimethyl-silanyloxy)-5-(tert-butyl-dimethyl-silanyloxymethyl)-3-(2-chloro-acetoxy)-2-methoxy-5-methyl-cyclopent-1-enecarboxylic acid ethyl ester (**17a**)



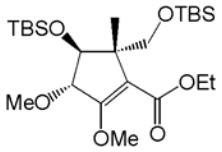
To a solution of **15b** (130 mg, 0.297 mmol) in CH_2Cl_2 at 0 ^oC under N_2 were added 2,6-lutidine (144 μL, 1.19 mmol) and TBDMSOTf (213 μL, 0.891 mmol). After the reaction was complete in 15 min, the reaction mixture was quenched by water, extracted by Et_2O, and the organic layers were dried over $MgSO_4$. After removing solvent in vacuo, the residue was purified by column chromatography (24:1 petroleum ether: ethyl acetate) on silica gel to afford the desired product **17a** 160 mg (98%) as colorless oil. $[\alpha]_D^{23}$ = +52.74 (c 1.37, $CHCl_3$). IR: 1774, 1746, 1709, 1638, 1473, 1376, 1253, 1166, 1101, 1051, 837, 777 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 5.81 (d, *J* = 6.1 Hz, 1H), 4.30 (d, *J* = 6.1 Hz, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 4.12 (AB, 2H), 3.76 (s, 3H), 3.73 (d, *J* = 9.8 Hz, 1H), 3.32 (d, *J* = 9.8 Hz, 1H), 1.30 (t, *J* = 7.1 Hz, 3H), 1.05 (s, 3H), 0.88 (s, 9H), 0.86 (s, 9H), 0.63 (s, 3H), 0.21 (s, 6H), -0.01 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.7, 164.2, 158.7, 114.5, 81.0, 74.7, 64.1, 60.1, 59.9, 49.8, 40.8, 25.7, 25.6, 18.1, 17.9, 16.9, 14.1, -4.6, -4.9, -5.5, -5.8. Anal. Calc d for $C_{25}H_{47}ClO_7Si_2$: C 54.47, H 8.59; found C 54.61, H 8.79.

3-(R)-4-(S)-5-(S)-4-(tert-Butyl-dimethyl-silanyloxy)-5-(tert-butyl-dimethyl-silanyloxymethyl)-3-hydroxy-2-methoxy-5-methyl-cyclopent-1-enecarboxylic acid ethyl ester (**17b**)



The suspension of K_2CO_3 (1 mg, 0.007 mmol) in a solution of **17a** (13 mg, 0.0236 mmol) in EtOH (0.3 mL) was stirred at room temperature overnight, then diluted with water, extracted with Et_2O, and the organic layers were washed with brine and dried over $MgSO_4$. After removing solvent in vacuo, the residue was purified by column chromatography (19:1 => 9:1 petroleum ether: ethyl acetate) on silica gel to afford the desired product **17b** 11 mg (100%) as white solid. M.P. 77.5 — 78.0^oC. Rf = 0.28 (9:1 petroleum ether: ethyl acetate). $[\alpha]_D^{24}$ = -17.48 (c 6.0, $CHCl_3$). IR: 3462, 1695, 1627, 1464, 1376, 1350, 1254, 1232, 1189, 1100, 896, 837, 778 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 4.24 (d, *J* = 11.5 Hz, 1H), 4.19 (m, 2H), 4.05 (d, *J* = 11.5 Hz, 1H), 3.97 (s, 3H), 3.95 (d, *J* = 9.8 Hz, 1H), 3.69 (s, 1H), 3.35 (d, *J* = 9.5 Hz, 1H), 1.29 (t, *J* = 7.2 Hz, 3H), 1.06 (s, 3H), 0.89 (s, 9H), 0.88 (s, 9H), 0.12 (s, 3H), 0.09 (s, 3H), 0.07 (s, 3H), 0.05 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.9, 165.1, 107.5, 81.1, 78.1, 68.1, 59.5, 57.4, 51.5, 25.8, 25.7, 18.4, 18.1, 16.4, 14.3, -4.7, -5.1, -5.6, -5.7. Anal. Calc d for $C_{23}H_{46}O_6Si_2$: C 58.18, H 9.77, found C 58.30, H 9.88.

3-(R)-4-(S)-5-(S)-4-(tert-Butyl-dimethyl-silanyloxy)-5-(tert-butyl-dimethyl-silanyloxymethyl)-2,3-dimethoxy-5-methyl-cyclopent-1-enecarboxylic acid ethyl ester (**18**)



To a solution of **17b** (99 mg, 0.21 mmol) in THF (2.0 mL) at 0 ^{o}C was added NaH (60% in mineral oil, 11 mg, 0.27 mmol) and MeI (31 L, 0.50 mmol) subsequently. The reaction mixture was warmed to room temperature with stirring and after 7 h quenched by water and extracted by Et_2O. The organic layers were washed with brine and dried over $MgSO_4$. After removing solvent, the residue was purified by column chromatography (30:1 petroleum ether: ethyl acetate) on silica gel to afford the desired product **18** 92 mg (90 %) as colorless oil. Rf = 0.50 (9:1 petroleum ether: ethyl acetate). $[\alpha]_D^{24}$ = +23.83 (c 4.4, $CHCl_3$). IR: 1706, 1631, 1472, 1374, 1350, 1255, 1215, 1190, 1100, 1048, 837, 776 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.32 (s, 2H), 4.17 (m, 2H), 3.90 (s, 3H), 3.74 (d, *J* = 9.8 Hz, 1H), 3.41 (s, 3H), 3.35 (d, *J* = 9.8 Hz, 1H), 1.29 (t, *J* = 7.1 Hz, 3H), 1.01 (s, 3H), 0.91 (s, 9H), 0.85 (s, 9H), 0.12 (s, 3H), 0.09 (s, 3H), 0.02 (s, 3H), -0.01 (s, 3H). ^{1}H NMR (300 MHz, C_6D_6): δ 4.54 (d, *J* = 6.1 Hz, 1H), 4.29 (d, *J* = 6.1 Hz, 1H), 4.07 (m, 3H), 3.59 (s, 3H), 3.52 (d, *J* = 9.8 Hz, 1H), 3.33 (s, 3H), 1.31 (s, 3H), 1.05 (t, *J* = 7.1 Hz, 3H), 1.03 (s, 9H), 0.98 (s, 9H), 0.25 (s, 3H), 0.22 (s, 3H), 0.10 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 164.6, 162.6, 112.6, 86.1, 72.8, 65.0, 59.6, 58.4, 54.9, 49.0, 25.8, 25.7, 18.1, 16.9, 14., -4.4, -4.9, -5.6, -5.7. Anal. Calc d for $C_{24}H_{48}O_6Si_2$: C 58.97, H 9.90, found C 59.18, H 10.02.