Concise Total Synthesis of Vicenistatin

Supporting Information

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General.

NMR spectra were measured on JEOL JNM-AL400 (400 MHz), JEOL ECP-500 (500 MHz), and JEOL ECA-600 (600 MHz). Chemical shifts were reported in the $\delta$ scale relative to tetramethylsilane (TMS) as 0.00 ppm for $^1$H (CDCl$_3$) and residual CHCl$_3$ (7.26 ppm for $^1$H and 77.00 ppm for $^{13}$C), pyridine (7.19 ppm for $^1$H and 123.5 ppm for $^{13}$C) as internal reference. The infrared (IR) spectra were recorded on JASCO FT/IR-700. Mass spectra (MS) were measured on JEOL JMS-DX303 (EI), JEOL JMS-700 (EI), JEOL JMS-T100GC (EI), and JEOL JMS 700 (FAB). Melting points were taken with Yazawa BY-2 and are uncorrected. The optical rotations were determined on JASCO DIP-370 Digital Polarimeter at room temperature, using the sodium D line.

Silica gel column chromatography, flash column chromatography, and amine silica gel column chromatography were carried out with silica gel 60N (Kanto Chemical Co., Inc., spherical, neutral, 63-210 µm), silica gel (Kanto Chemical Co., Inc., spherical, neutral, 40-50 µm), and Chromatorex NHDM 1020 (Fuji Silysia Chemical Co., Ltd., 100-200 mesh), respectively. All reactions were carried out under an argon atmosphere using flame-dried or oven-dried glassware, unless otherwise noted, and monitored with analytical TLC (Merck Kieselgel 60 F$_{254}$) or NH-TLC (FUJI SILYSIA CHEMICAL Co., Ltd.).

**(4R,5R,6R)-5,6-Epoxyhept-1-en-4-ol [(+)-8]**

To a stirred solution of (±)-7 (30.0 g, 268 mmol), (−)-diisopropyl L-tartrate (9.39 g, 40.1 mmol) and MS3Å (9.00 g) in CH$_2$Cl$_2$ (39 mL) was added titanium tetraisopropoxide (7.93 mL, 26.8 mmol) at −20 °C. After the reaction mixture was stirred at that temperature for 30 min, to the mixture was added $t$-butyl hydroperoxide (3.42 M in CH$_2$Cl$_2$, 39.2 mL, 134 mmol) dropwise. The mixture was stirred for 4 hr, then quenched by addition of iron(II) sulfate heptahydrate (18.0 g) and citric acid monohydrate (6.00 g) in ion-exchanged water (150 mL) and warmed to room temperature. The resulting mixture was filtered through Celite and the filtrate was extracted twice with ether. The combined organic extracts were washed with brine, dried (MgSO$_4$), and concentrated. The residue was purified by silica gel column chromatography (EtOAc-hexane = 1 : 4) to give (−)-7 (14.9 g, 133 mmol, 50%, 71% ee) as a colorless oil, and a mixture of (+)-8 and (−)-diisopropyl L-tartrate. The mixture was distilled (45 mmHg, 150 °C) to give (+)-8 (11.1 g, 86.6 mmol, 32%, 99% ee) as a colorless oil.

(+)-8: $[\alpha]_D^{23}$ +3.0° (c 1.28, CH$_2$Cl$_2$); IR (neat) 3436, 2979, 2927, 1642, 1437, 1288, 873 cm$^{-1}$; $^1$H-NMR (400 MHz, CDCl$_3$) $\delta$ 5.87 (1H, ddt, $J$ = 17.1, 9.9, 7.2 Hz), 5.17 (2H, m), 3.80 (1H, m), 2.76 (1H, dd, $J$ = 2.2, 5.3 Hz), 2.76 (1H, dd, $J$ = 2.3, 3.7 Hz), 2.27-2.46 (2H, m), 1.95 (1H, d, $J$ = 2.7 Hz), 1.35 (3H, d, $J$ = 5.3 Hz); $^{13}$C-NMR (100 MHz, CDCl$_3$) $\delta$ 133.6, 118.2, 68.3, 61.3, 51.4, 38.1, 17. ; LRMS (EI) $m/z$ 128 (M$^+$), 87 (100%).

Optical purity of (−)-7 was determined by chiral HPLC analysis of the benzyoyl derivative (−)-7′
(HPLC conditions: column; CHIRALCEL AD-H, eluent; hexane-i-PrOH = 40 : 1, flow rate; 0.5 mL/min, detection; UV 254 nm, retention time; 8.8 min for (+)-7' and 10.0 min for (−)-7').

**4S,5R,6R)-5,6-Epoxyhept-1-en-4-ol ([+]-9)**

To a stirred solution of (+)-8 (1.63 g, 12.5 mmol) in THF (42 mL) were added 4-nitrobenzoic acid (3.13 g, 18.7 mmol) and Ph3P (4.90 g, 18.8 mmol) at 0 °C. After the reaction mixture was stirred at that temperature for 30 min, to the mixture was added diisopropyl azodicarboxylate (3.68 mL, 19.5 mmol) dropwise. The resulting mixture was added sat. NaHCO3 aq. and extracted twice with ether. The combined organic extracts were washed with brine, dried (MgSO4), and concentrated. The residue was purified by silica gel column chromatography (EtOAc-hexane = 1 : 8) to give ester (+)-8' (3.46 g, 12.5 mmol, 100%) as a pale yellow oil.

(+)-8': [α]D27 +26.4° (c 0.44, CHCl3); IR (neat) 2980, 1725, 1607, 1529, 1348, 1273, 1103 cm⁻¹; 1H-NMR (400 MHz, CDCl3) δ 8.3 (2H, d, J = 8.9 Hz), 8.22 (2H, d, J = 8.7 Hz), 5.82 (1H, ddt, J = 17.1, 9.9, 7.2 Hz), 5.13-5.21 (2H, m), 5.00 (1H, q, J = 6.4 Hz), 2.98 (2H, m), 2.60 (2H, m), 1.35 (3H, d, J = 4.8 Hz); 13C-NMR (100 MHz, CDCl3) δ 164.0, 150.7, 135.4, 132.0, 130.9, 123.6, 119.0, 74.3, 59.5, 52.9, 36.2, 17.2; LRMS (EI) m/z 262 [M–CH3]+, 150 (100%).; HRMS Calcd. C13H12NO5: 262.0715. Found: 262.0693.

Optical purity of (+)-8' was determined by chiral HPLC analysis (HPLC conditions: column; CHIRALCEL AD-H, eluent; hexane-i-PrOH = 10 : 1, flow rate; 0.5 mL/min, detection; UV 254 nm, retention time; 21.4 min for (+)-8' and 32.3 min for (−)-8').

To a stirred solution of ester (3.19 g, 11.5 mmol) in MeOH (29 mL) was added NaOMe (311 mg, 5.75 mmol) at room temperature. After stirring for 3 hr, the reaction was quenched with sat. NH4Cl aq., and the resulting mixture was extracted twice with EtOAc. The combined organic extracts were washed with brine, dried (MgSO4), and concentrated. The residue was purified by silica gel column chromatography (EtOAc-hexane = 1 : 2) to give ester (+)-9 (1.24 g, 9.68 mmol, 84%) as a colorless oil.

(+)-9: [α]D29 +32.7° (c 0.30, CHCl3); IR (neat) 3436, 2979, 2927, 1642, 1437, 1288, 873 cm⁻¹; 1H-NMR (400 MHz, CDCl3) δ5.84 (1H, ddt, 17.3, 10.0, 7.1 Hz, H2), 5.16 (2H, m, H1), 3.57 (1H, dt, J = 5.3, 5.3 Hz, H4), 3.00 (1H, m, H6), 2.74 (1H, dd, J = 2.4, 2.3 Hz, H5), 2.38 (2H, m, H3), 2.01 (1H, br, OH), 1.32 (3H, d, J = 5.3 Hz, H7); 13C-NMR (100 MHz, CDCl3) δ 133.4, 118.2, 70.2, 62.0, 52.6, 39.2, 17.2; LRMS (EI) m/z 113 [M+–CH3]+, 41 (100%).

**4S,5S,1'R)-4-(1'-Benzoyloxyethyl)-5-(prop-2'-enyl)oxazolidin-2-one [(-)-10]**

To a stirred solution of (+)-9 (1.00 g, 7.81 mmol) in CH2Cl2 (26 mL) was added benzoyl isocyanate (1.18 mL, 9.37 mmol) at room temperature. After the reaction completed, the reaction mixture was concentrated. The residue was purified by
silica gel column chromatography (EtOAc-hexane = 1 : 2) to give carbamate (2.14 g, 7.78 mmol, 100%) as a colorless oil.

carbamate: $[\alpha]_D^{27} +22.7^\circ$ (c 0.16, CHCl$_3$); IR (neat) 3276, 3000, 1758, 1517, 1491, 1195 cm$^{-1}$; $^1$H-NMR (400 MHz, CDCl$_3$) $\delta$ 8.05 (1H, s, NH), 7.81 (2H, d, $J = 7.3$ Hz), 7.59 (1H, t, $J = 7.3$ Hz), 7.48 (2H, t, $J = 7.6$ Hz), 5.80 (1H, ddd, $J = 17.1, 9.9, 7.2$ Hz), 5.17 (2H, m), 4.83 (1H, brq, $J = 4.2$ Hz), 2.98 (1H, m), 2.87 (1H, dd, $J = 2.0, 5.6$ Hz), 2.54 (2H, m), 1.33 (3H, d, $J = 5.1$); $^{13}$C-NMR (100 MHz, CDCl$_3$) $\delta$ 165.0, 150.2, 132.8, 131.9, 128.6, 127.7, 118.7, 74.7, 59.2, 52.7, 35.9, 16.9; LRMS (EI) m/z 275 (M$^+$), 105 (100%).

To a stirred solution of carbamate (429 mg, 1.56 mmol) in CH$_2$Cl$_2$ (5 mL) was added 1,8-diazabicyclo[5.4.0]undec-7-ene (58.3 µL, 390 µmol) at room temperature. After the reaction mixture was refluxed for 2 hr, the mixture was concentrated. The residue was purified by silica gel column chromatography (EtOAc-hexane = 1 : 3) to give (−)-10 (384 mg, 1.40 mmol, 90%) as a colorless oil.

(−)-10: $[\alpha]_D^{29} -19.1^\circ$ (c 2.97, CHCl$_3$); IR (neat) 3269, 2980, 1758, 1601, 1451, 1381, 1268, 1112 cm$^{-1}$; $^1$H-NMR (400 MHz, CDCl$_3$) $\delta$ 8.03 (2H, d, $J = 7.3$ Hz), 7.57 (1H, t, $J = 7.4$ Hz), 7.45 (2H, t, $J = 7.7$ Hz), 5.83 (1H, ddt, $J = 17.1, 10.2, 6.6$ Hz), 5.64 (1H, s), 5.29 (1H, dt, $J = 6.1, 6.1$ Hz), 5.25 (2H, m), 4.76 (1H, m), 4.09 (1H, t, $J = 6.7$ Hz), 2.58 (1H, m), 2.46 (1H, m), 1.43 (3H, d, $J = 6.4$ Hz); $^{13}$C-NMR (100 MHz, CDCl$_3$) $\delta$ 165.1, 159.6, 133.2, 132.2, 129.5, 128.4, 118.5, 78.7, 69.4, 58.4, 33.5, 16.4; LRMS (EI) m/z 276 [M+H]$^+$, 105 (100%); HRMS (EI) Calcd. C$_{15}$H$_{18}$NO$_4$: 276.1236. Found: 276.1222.

(4S,5S,1’R)-5-(Prop-2’-enyl)-N-methyloxazolidin-2-one [(+)-11]

To a stirred solution of NaH (60% in mineral oil, 69.8 mg, 2.91 mmol), which was washed by hexane (1 mL) twice, in THF (2 mL) was added (−)-10 (668 mg, 2.43 mmol), which was used after azeotropic removal of water, in THF (2 mL) via cannula at room temperature. After the reaction mixture was stirred for 30 min, MeI (227 µL, 3.65 mmol) was added to the mixture dropwise and the mixture was stirred for another 3 hr. After the reaction completed, sat. NH$_4$Cl aq. was added to the reaction mixture. The resulting mixture was concentrated in vacuo, and extracted twice with EtOAc. The combined organic extracts were washed with brine, dried (MgSO$_4$), and concentrated. The residue was purified by silica gel column chromatography (Et$_2$O-hexane = 2 : 1) to give methylated compound (665 mg, 2.30 mmol, 95%) as a colorless oil.

methylated compound: $[\alpha]_D^{29} +24.5^\circ$ (c 0.40, CHCl$_3$); IR (neat) 2980, 2360, 1759, 1719, 1434, 1401, 1274 cm$^{-1}$; $^1$H-NMR (400 MHz, CDCl$_3$) $\delta$ 8.01 (2H, d, $J = 8.5$ Hz), 7.61 (1H, t, $J = 7.6$ Hz), 7.47 (2H, t, 7.9 Hz), 5.90 (1H, ddt, $J = 17.1, 10.4, 6.6$ Hz), 5.47 (1H, dq, $J = 6.5, 1.4$ Hz), 5.26 (2H, m), 4.63 (1H, dt, $J = 8.2, 7.2$ Hz), 3.92 (1H, dd, $J = 1.4, 7.7$ Hz), 3.08 (3H, s), 2.61 (2H, m), 1.42 (3H, d,
\( J = 6.5 \text{ Hz} \); \(^{13}\text{C-NMR} \) (100 MHz, CDCl\(_3\)) \( \delta \) 165.5, 158.0, 133.5, 132.1, 129.6, 128.6, 119.0, 76.0, 70.2, 62.7, 33.5, 31.3, 15.2; LRMS (EI) \( m/z \): 290 [M+H]\(^+\), 140 (100%); HRMS (EI) Calcd. C\(_{16}\)H\(_{19}\)NO\(_4\) : 290.1392. Found : 290.1372.

To a stirred solution of methylated compound (600 mg, 2.08 mmol) in MeOH (7 mL) was added NaOMe (56.2 mg, 1.04 mmol) at room temperature. The reaction mixture was stirred at the same temperature for 1 hr and then quenched by an addition of sat. NH\(_4\)Cl aq. The mixture was extracted twice with EtOAc. The combined organic extracts were washed with water and brine, dried (MgSO\(_4\)), and concentrated. The residue was purified by silica gel column chromatography (EtOAc) to give \((+)-11\) (329 mg, 1.78 mmol, 90%) as a colorless oil.

\((+)-11\) : [\( \alpha \)]\(_D\)\(^{33}\) +4.16° (c 0.89, CHCl\(_3\)); IR (neat) 3336, 1721, 1409, 1144 cm\(^{-1}\); \(^1\text{H-NMR} \) (400 MHz, CDCl\(_3\)) \( \delta \) 5.82 (1H, ddt, \( J = 17.4, 10.4, 6.6 \) Hz, H\(_2\)), 5.17 (2H, m), 4.57 (1H, dt, \( J = 5.7, 8.4 \) Hz), 4.14 (1H, m), 3.71 (1H, dd, \( J = 2.7, 7.7 \) Hz), 3.02 (3H, s), 2.52 (2H, m), 1.28 (3H, d, \( J = 6.3 \) Hz); \(^{13}\text{C-NMR} \) (100 MHz, CDCl\(_3\)) \( \delta \) 158.6, 132.8, 129.0, 128.2, 125.2, 118.3, 66.7, 64.6, 33.4, 31.5, 18.7; LRMS (EI) \( m/z \) 185 (M\(^+\)), 140 (100%); HRMS (EI) Calcd. C\(_9\)H\(_{15}\)NO\(_3\) : 185.1052. Found : 185.1053.

(3S,4R,5R)-6-Methoxy-3,4-dimethyl-tetrahydro-pyrano[3,4]oxazol-2-one (12)

O\(_3\) gas was bubbled through a cooled (−20 °C) solution of \((+)-11\) (637 mg, 3.44 mmol) in MeOH (8.6 mL) for 15 min. N\(_2\) gas was then bubbled through the mixture for 15 min at the same temperature. To the reaction mixture were added Me\(_2\)S and \( p\)-TsOH•H\(_2\)O, and the mixture was refluxed. After the reaction completed, the reaction mixture was allowed to cool to room temperature and concentrated. The residue was extracted twice with EtOAc. The combined organic extracts were washed with water and brine, dried (MgSO\(_4\)), and concentrated. The residue was purified by silica gel column chromatography (EtOAc) to give 12 (616 mg, 3.06 mmol, 89%, \( \alpha : \beta = 1 : 1 \)) as a colorless oil.

12 : [\( \alpha \)]\(_D\)\(^{31}\) +38.5° (c 0.13, CHCl\(_3\)); IR (neat) ; 2937, 1755, 1430, 1395 cm\(^{-1}\); \(^1\text{H-NMR} \) (400 MHz, CDCl\(_3\)) \( \delta \) 4.75 (1H, t, \( J = 6.3 \) Hz), 4.72 (1H, m), 4.64 (1H, dd, \( J = 8.2, 2.7 \) Hz), 4.57 (1H, ddd, \( J = 5.6, 8.5, 9.7 \) Hz), 3.92 (1H, ddd, \( J = 6.3, 8.7, 12.3 \) Hz), 3.68 (1H, ddd, \( J = 6.3, 8.2, 12.6 \) Hz), 3.47 (3H, s), 4.41 (1H, t, \( J = 8.6 \) Hz), 3.72 (3H, s), 3.25 (1H, dd, \( J = 8.2, 6.8 \) Hz), 2.96 (3H, s), 2.90 (3H, s), 2.27-2.34 (2H, m), 1.89-1.97 (2H, m), 1.41 (3H, d, \( J = 6.3 \) Hz), 1.38 (3H, d, \( J = 6.3 \) Hz); \(^{13}\text{C-NMR} \) (100 MHz, CDCl\(_3\)) \( \delta \) 158.3, 157.8, 98.9, 96.9, 96.6, 72.6, 71.1, 69.6, 65.2, 61.7, 60.3, 56.1, 55.0, 31.8, 31.1, 31.0, 30.9, 20.8, 20.5; LRMS (EI) \( m/z \) 201 (M\(^+\)), 99 (100%); HRMS (EI) Calcd. C\(_9\)H\(_{15}\)NO\(_4\) : 201.1052. Found : 201.1053.

(3S,4R,5R)-2,4,6-Trideoxy-4-methylamino-3,4-(internalcarbamate)-\( D\)-ribo-hexopyranosyl fluoride (3)

To a stirred solution of 12 (74.5 mg, 370 µmol) and phenyl trimethylsilyl sulfide
(350 µL, 1.86 mmol) in CH₂Cl₂ (1.2 mL) was added trimethylsilyl trifluoromethanesulfonate (110 µL, 614 µmol) at 0 °C. The reaction mixture was warmed to room temperature and stirred for 30 min. The mixture was quenched with sat. NaHCO₃ aq. and extracted twice with EtOAc. The combined organic extracts were washed with brine, dried (MgSO₄), and concentrated. The residue was purified by silica gel column chromatography (EtOAc-hexane = 2 : 1) to give thioglycoside (93.7 mg, 336 µmol, 90.7%) as a colorless oil.

thioglycoside: [α]D27 +114° (c 1.87, CHCl₃); IR (neat) 3487, 2934, 1768, 1583 cm⁻¹; ¹H-NMR (400 MHz, CDCl₃) δ 7.47 (4H, m), 7.33-7.24 (6H, m), 5.46 (1H, dd, J = 8.3, 6.6 Hz), 4.95 (1H, dd, J = 12.0, 2.4 Hz), 4.64 (2H, m), 4.19 (1H, dq, J = 8.5, 6.2 Hz), 3.60 (1H, dq, J = 8.8, 6.1 Hz), 3.47 (1H, t, J = 8.4 Hz), 3.20 (1H, dd, J = 8.8, 6.3 Hz), 2.93 (3H, s), 2.91 (3H, s), 2.54-2.44 (2H, m), 2.12-1.98 (2H, m), 1.42 (3H, d, J = 6.3 Hz), 1.38 (3H, d, J = 6.1 Hz); ¹³C-NMR (100 MHz, CDCl₃) δ 157.9, 157.5, 134.3, 133.0, 131.6, 131.4, 128.8, 128.7, 127.5, 127.3, 80.9, 80.0, 74.9, 72.8, 70.0, 66.2, 61.8, 59.6, 32.2, 31.3, 31.1, 31.0, 21.2, 20.5; LRMS (EI) m/z 279 (M⁺), 170 (100%); HRMS (EI) Calcd. C₁₄H₁₇NO₃S : 279.0929. Found : 279.0910.

To a stirred solution of thioglycoside (32.7 mg, 117 µmol) in CH₂Cl₂ (1.2 mL) were added N-bromosuccinimide (46.0 mg, 258 µmol) and (diethylamino)sulfur trifluoride (100 µL, 756 µmol) at −15 °C. The reaction mixture was stirred for 1 hr. After the reaction was quenched with sat. NaHCO₃ aq., the mixture was allowed to warm to room temperature, and then extracted twice with EtOAc. The combined organic extracts were washed with brine, dried (Na₂SO₄), and concentrated. The residue was purified by amine silica gel column chromatography (NH-silica gel, EtOAc-hexane = 2 : 3) to give 3 (15.8 mg, 83.6 µmol, 71%, α : β = 1 : 1) as a colorless oil.

3: [α]D29 +3.4° (c 0.79, CHCl₃); IR (neat) 2981, 1767, 1433, 1400 cm⁻¹; ¹H-NMR (400 MHz, CDCl₃) δ 5.79 (1H, ddd, J = 59.9, 4.1, 2.9 Hz), 5.67 (1H, dt, J = 57.7, 5.8 Hz), 4.87 (1H, dd, J = 7.7, 7.0 Hz), 4.54 (1H, ddd, J = 8.9, 8.9, 5.6 Hz), 4.11 (1H, ddq, J = 14.7, 1.9, 6.3 Hz), 3.94 (1H, dq, J = 13.8, 6.5 Hz), 3.57 (1H, dt, J = 2.2, 8.2 Hz), 3.45 (1H, t, J = 8.5 Hz), 1.45 (3H, d, J = 6.3 Hz), 1.44 (3H, d, J = 6.3 Hz); LRMS (EI) m/z 189 (M⁺), 99 (100%); HRMS (EI) Calcd. C₈H₁₁NO₃S : 188.0723. Found : 188.0719.

(3E,6E)-4,6-Dimethyl-7-iodo-hepta-3,6-dien-1-ol (15)

To a stirred solution of bis(cyclopentadienyl)zirconium(IV) dichloride (589 mg, 2.02 mmol) in CH₂Cl₂ (6 mL) was added trimethylaluminium (2.0 M in heptane, 6.05 mL, 12.1 mmol) at room temperature. The reaction mixture was cooled to 0 °C and to the mixture was added a solution of 14 (500 mg, 4.03 mmol) in CH₂Cl₂ (4 mL) via cannula. After stirring at room temperature for 3 hr, the reaction mixture was cooled to 0 °C and to the mixture was added a solution of iodine (1.23 g, 4.84 mmol) in THF (5 mL) using a syringe. The reaction mixture was stirred at room temperature for 2 hr and then quenched by slow
addition of water at 0 °C. The mixture was extracted twice with ether. The combined organic extracts were washed with brine, dried (MgSO₄), and concentrated. The residue was purified by flash chromatography (EtOAc-hexane = 1 : 15) to give 15 (688 mg, 2.59 mmol, 64%) as a pale yellow oil. 

**15**: IR (neat): 3341, 2913, 1433, 1376, 1267, 1139, 1045, 753 cm⁻¹; ¹H-NMR (400 MHz, CDCl₃) δ 5.93 (s, 1H), 5.22 (t, 1H, J = 7.0 Hz), 3.64 (t, 2H, J = 6.6 Hz), 2.87 (s, 2H), 2.31 (dd, 2H, J = 7.0, 6.6 Hz), 1.76 (s, 3H), 1.57 (s, 3H), 1.42 (s, 1H); ¹³C-NMR (100 MHz, CDCl₃) δ 145.7, 134.4, 122.9, 76.0, 62.1, 49.6, 31.5, 23.2, 15.6; LRMS (EI) m/z 266 (M⁺), 93 (100%); HRMS (EI) Calcd. C₉H₁₅OI: 266.0166. Found: 266.0176.

(3S,4S)-(6E,9E)-10-Iodo-3,7,9-trimethyl-dec-1,6,9-trien-4-ol [(-)-16]

To a stirred solution of 15 (2.06 g, 7.74 mmol) in CH₂Cl₂ (35 mL) was added Dess-Martin periodinane (3.60 g, 8.52 mmol) at room temperature. The reaction mixture was stirred at room temperature for 1 hr and then concentrated. To the residue was added hexane and the mixture was filtered through Celite. The filtrate was concentrated in vacuo to give crude aldehyde (1.86 g, <7.05 mmol) as pale yellow oil. This material was used without further purification.

To a stirred solution of potassium t-butoxide (1.58 g, 14.1 mmol, freshly dried by heating with a heatgun under vacuum) in THF (12 mL) was added cis-2-butene (ca. 4 ml) at –78 °C. Then n-butyllithium (1.56 M in hexane, 7.68 mL, 12.0 mmol) was added dropwise to the reaction mixture at –78 °C. The reaction mixture was stirred to –50 °C for 10 min. To the mixture was added (+)-B-methoxydiisopinocamphenylborane (3.78 g, 12.0 mmol) in THF (20 mL) via cannula at –78 °C and the resulting mixture was stirred at the same temperature for 30 min. After boron trifluoride diethyl etherate (1.48 mL, 12.0 mL) was added to the reaction mixture at –78 °C, crude aldehyde (1.86 g, <7.05 mmol) prepared above was added to the mixture via a syringe at the same temperature. The resulting mixture was slowly warmed to 0 °C, then cooled again to –78 °C. After MeOH (4.5 mL), sat. NaHCO₃ aq. (45 mL), and 30% aq. H₂O₂ (22 mL) were added, the resulting mixture was stirred at room temperature overnight. The resulting mixture was extracted twice with ether. The combined organic extracts were washed with brine, dried (MgSO₄), and concentrated. The residue was purified by flash chromatography (EtOAc-hexane = 1 : 20) to give (-)-16 (1.16 g, 3.63 mmol, 47% for 2 steps, 100 %de, 94%ee) as pale yellow oil. 

**(-)-16**: [α]D²⁹ = -21.6° (c 1.24, CHCl₃); IR (neat): 3419, 2972, 2911, 1638, 1434, 1375, 1267, 1139, 1094, 1040, 998, 915, 884, 758, 667 cm⁻¹; ¹H-NMR (396 MHz, CDCl₃) δ 5.94 (s, 1H), 5.80 (m, 1H), 5.28 (t, 1H, J = 6.7 Hz), 5.09 (d, 1H, J = 17.6 Hz), 5.08 (d, 1H, J = 10.4 Hz), 3.55-3.49 (m, 1H), 2.88 (s, 2H), 2.32-2.12 (m, 3H), 1.76 (s, 3H), 1.55 (s, 3H), 1.49 (d, 1H, J = 4.4 Hz), 1.05 (d, 3H, J = 4.1 Hz); ¹³C-NMR (99 MHz, CDCl₃) δ 145.9, 140.9, 134.7, 123.6, 115.2, 76.0, 74.5, 49.9, 43.1, 33.1, 23.2, 15.7, 14.4; LRMS (EI) m/z 320 (M⁺), 109 (100%); HRMS (EI) Calcd. C₁₃H₂₁O₁: 320.0635.
Optical purity of (–)-16 was determined by chiral HPLC analysis (HPLC conditions: column; CHIRALCEL OD-H, eluent; hexane-i-PrOH = 199 : 1, flow rate; 0.5 mL/min, detection; UV 254 nm, retention time; 21.5 min for (–)-16 and 69.6 min for (+)-16).

(4S,5S)-(2E,7E,10E)-11-Iodo-4,8,10-trimethyl-5-trimethylsilyloxy-undec-2,7,10-trienal [(–)-5]
To a stirred solution of 16 (113 mg, 353 µmol) in CH₂Cl₂ (3.5 mL) were added acrolein (236 µL, 3.53 mmol) and Hoveyda-Grubbs 2nd generation catalyst (22 mg, 35.3 µmol) at room temperature. The reaction mixture was stirred at room temperature for 3 hr and then concentrated. The residue was purified by silica gel column chromatography (EtOAc-hexane = 1 : 2) to give crude 17 (37 mg) as a pale yellow oil.

To a stirred solution of crude 17 (37 mg, <102 µmol) in CH₂Cl₂ (1 mL) were added 2,6-lutidine (71 µL, 613 µmol) and trimethylsilyl chloride (39 µL, 307 µmol) at room temperature. The reaction mixture was stirred at room temperature for 40 min, then quenched with water. The resulting mixture was extracted twice with ether. The combined organic extracts were washed with brine, dried (MgSO₄), and concentrated. The residue was purified by silica gel column chromatography (EtOAc-hexane = 1 : 10) to give (–)-5 (43 mg, 102 µmol, 29% for 2 steps) as a pale yellow oil.

(–)-5: [α]D⁡₂⁵⁻⁴⁶.⁹° (c 0.89, CHCl₃); IR (neat): 2959, 1693, 1250, 1142, 840 cm⁻¹; ¹H-NMR (396 MHz, CDCl₃) δ 9.53 (d, 1H, J = 7.9 Hz), 6.88 (dd, 1H, J = 15.9, 7.2 Hz), 6.11 (dd, 1H, J = 15.9, 7.9 Hz), 5.93 (s, 1H), 5.21 (t, 1H, J = 6.9 Hz), 3.52 (dt, 1H, J = 6.5, 5.2 Hz), 2.85 (s, 2H), 2.59-2.54 (m, 1H), 2.24-2.10 (m, 2H), 1.76 (s, 3H), 1.52 (s, 3H), 1.09 (d, 3H, J = 4.1 Hz), 0.11 (s, 9H); ¹³C-NMR (99 MHz, CDCl₃) δ 160.5, 145.4, 133.5 132.0, 122.8, 75.7, 74.7, 49.4, 42.0, 32.9, 23.0, 15.4, 13.5, 0.00; LRMS (EI) m/z 420 (M⁺), 185 (100%); HRMS (EI) Calcd. C₁₇H₂₉OSiI: 420.0979. Found : 420.0963.

(2S)-2-Methyl-5-yn-1-ol [(–)-20]
To a stirred solution of (–)-19 (87 mg, 473 µmol) in MeOH (2 mL) was added K₂CO₃ (131 mg, 946 µmol) at room temperature. The reaction mixture was stirred for 6 hr. After quenched with H₂O, the mixture was extracted twice with ether. The combined organic extracts were washed with brine, dried (MgSO₄), and concentrated. The residue was purified by silica gel column chromatography (EtOAc-hexane = 1 : 2) to give (–)-20 (51 mg, 455 µmol, 96%) as a colorless oil.

(–)-20: [α]D⁡₂⁵⁻¹₃.₉° (c 0.82, CHCl₃); IR (neat): 3300, 2929, 2874, 1040 cm⁻¹; ¹H-NMR (396 MHz, CDCl₃) δ 3.55-3.47 (m, 2H), 2.34-2.17 (m, 2H), 1.95 (t, 1H, J = 2.7 Hz), 1.84-1.76 (m, 1H), 1.75-1.65 (m, 1H), 1.43-1.34 (m, 1H), 0.95 (d, 3H, J = 6.7 Hz); ¹³C-NMR (99 MHz, CDCl₃) δ 84.4,
(2S)-(5E)-2-Methyl-6-tributylstanyl-hexa-5-ene-1-ol [(−)-21]  
To a stirred solution of Pd$_2$(dba)$_3$•CHCl$_3$ (10.4 mg, 100 µmol) and Cy$_3$P•HBF$_4$ (15 mg, 407 µmol) in degassed CH$_2$Cl$_2$ (10 mL) was added i-Pr$_2$NEt (36 µL, 202 µmol) at room temperature. The reaction mixture was stirred for 20 min. A solution of (−)-20 (100 mg, 893 µmol) in degassed CH$_2$Cl$_2$ (2 mL) and Bu$_3$SnH (323 µL, 1.20 mmol) were added dropwise to the mixture. The resulting mixture was stirred for 2 hr, and then concentrated. The residue was purified by silica gel column chromatography (EtOAc-hexane = 1 : 10) to give (−)-21 (266 mg, 658 µmol, 74%, gem isomer : trans isomer = 1 : 20) as a colorless oil. This material was used in the next reaction without further purification. Small amount of this material was purified further to give pure (−)-21.

(−)-21: [α]$_D$$^{25}$−5.0° (c 0.68, CHCl$_3$); IR (neat): 3328, 2956, 2925, 2871, 2852, 1598, 1462, 1376, 1042, 989 cm$^{-1}$; $^1$H-NMR (400 MHz, CDCl$_3$) δ 6.02-5.77 (m, 2H), 3.52 (ddd, 1H, $J$ = 10.5, 5.9, 5.6 Hz), 3.44 (ddd, 1H, $J$ = 10.5, 6.1, 5.9 Hz), 2.26-2.08 (m, 2H), 1.69-1.61 (m, 1H), 1.56-1.38 (m, 7H), 1.35-1.18 (m, 18H); $^{13}$C-NMR (100 MHz, CDCl$_3$) δ 149.2, 127.3, 68.2, 35.3, 32.4, 29.3, 29.2, 27.1, 16.6, 13.8, 9.5; LRMS (EI) m/z 347 [M–n-Bu]$^+$, 347 (100%); HRMS (EI) Calcd. C$_{15}$H$_{31}$OSn: 347.1396. Found: 347.1397.

(2S)-(5E)-2-Methyl-6-tributylstanyl-hexa-5-ene-1-azide [(+)-22]  
To a stirred solution of Ph$_3$P (345 mg, 1.32 mmol) in THF (4 mL) was added diisopropyl azodicarboxylate (259 µL, 1.32 mmol) at 0 °C. The reaction mixture was stirred at the same temperature for 20 min. A solution of (−)-21 (266 mg, 658 µmol) in THF (1.5 mL) and diphenyl phosphoryl azide (295 µL, 1.32 mmol) were added to the mixture. The resulting mixture was allowed to warm to room temperature over 2 hr, and then quenched with H$_2$O. The mixture was extracted twice with hexane. The combined organic extracts were washed with brine, dried (MgSO$_4$), and concentrated. The residue was purified by silica gel column chromatography (EtOAc-hexane = 1 : 10) to give (+)-22 (232 mg, 651 µmol, 82%, gem isomer : trans isomer = 1 : 20) as a colorless oil. Analytical sample was prepared from pure (−)-21.

(+)-22: [α]$_D$$^{27}$+24.6° (c 0.64, CHCl$_3$); IR (neat): 2957, 2925, 2871, 2852, 2097, 1598, 1461, 1376, 1283, 990 cm$^{-1}$; $^1$H-NMR (400 MHz, CDCl$_3$) δ 5.99-5.81 (m, 2H), 3.22 (dd, 1H, $J$ = 12.0, 6.8 Hz), 3.12 (dd, 1H, $J$ = 12.0, 6.8 Hz), 2.22-2.09 (m, 2H), 1.76-1.69 (m, 1H), 1.55-1.39 (m, 7H), 1.33-1.22 (m, 7H), 0.96 (d, 3H, $J$ = 6.8 Hz), 0.95-0.78 (m, 15H); $^{13}$C-NMR (100 MHz, CDCl$_3$) δ 148.7, 127.3, 57.8, 35.1, 33.3, 33.0, 29.2, 27.4, 17.6, 13.8, 9.5; LRMS (EI) m/z 372 [M–n-Bu]$^+$, 344 (100%); HRMS (EI) Calcd. C$_{15}$H$_{30}$N$_3$Sn: 372.1460. Found: 372.1458.
diethyl [(2S)-(5E)-2-Methyl-hex-5-enylcarbamoylmethyl]phosphonate [(–)-6]

A solution of (+)-22 (1.27 g, 2.97 mmol), 5% Lindlar catalyst (255 mg, 20% w/w) and quinoline (526 µl, 4.45 mmol) in MeOH (15 mL) was stirred for 2 h under H₂ atmosphere at room temperature. The reaction mixture was filtered through Celite. The filtrate was concentrated to give crude amine as a pale yellow oil, which was used without further purification.

To a stirred solution of crude amine and 23 (1.46 g, 7.42 mmol) in CH₂Cl₂ were added N-(3-dimethylaminopropyl)-N’-ethylcarbodiimide hydrochloride (1.42 g, 7.42 mmol) and 1-hydroxybenzotriazole hydrate (1.00 g, 7.42 mmol) at room temperature. After stirred at the same temperature for 5 min, the reaction was cooled to 0 °C, Et₃N (2.07 mmol, 14.8 mmol) was added. The resulting mixture was allowed to warm to room temperature and stirred for 10 hr. The reaction was quenched with H₂O, and the mixture was extracted twice with EtOAc. The combined organic extracts were washed with brine, dried (MgSO₄), and concentrated. The residue was purified by silica gel column chromatography (EtOAc) to give (–)-6 (1.39 g, 2.39 mmol, 80% for 2 steps, gem isomer : trans isomer = 1 : 20) as a colorless oil. Analytical sample was prepared from pure (–)-22.

(–)-6: [α]D²⁷ = -2.7° (c 0.48, CHCl₃); IR (neat): 3296, 2957, 2925, 2871, 2852, 1654, 1557, 1457, 1245, 1029, 968 cm⁻¹; ¹H-NMR (400 MHz, CDCl₃) δ 6.77 (br t, 1H), 5.98-5.80 (m, 2H), 4.14 (dq, 4H, J = 7.6, 7.1 Hz), 3.23 (ddd, 1H, J = 13.3, 5.9, 5.6 Hz), 3.11 (ddd, 1H, J = 13.3, 6.6, 6.4 Hz), 2.84 (d, 2H, J = 20.2 Hz), 2.23-2.08 (m, 2H), 1.71-1.63 (m, 1H), 1.52-1.44 (m, 7H), 1.36-1.25 (m, 13H), 0.93 (d, 3H, J = 6.6 Hz), 0.92-0.77 (m, 15H); ¹³C-NMR (100 MHz, CDCl₃) δ 163.7, 148.9, 127.5, 62.7, 45.7, 35.7, 35.3, 34.4, 33.5, 32.9, 29.2, 27.3, 17.5, 16.4, 13.8, 9.5; LRMS (EI) m/z 524 [M–n-Bu]⁺, 524 (100%); HRMS (EI) Calcd. C₂₁H₄₃NO₄PSn: 524.1952. Found: 524.1953.

(6S,7S)-(2E,4E,9E,12E)-N-[(2'S)-(5'E)-2'-Methyl-6'-tributylstanyl-hex-5'-enyl]-6,10,12-trimethyl-13-iodo-7-trimethylsilyloxy-2,4,9,12-tetraen-amide [(–)-24]

To a cooled (–78 °C) solution of (–)-6 (56 mg, 96.9 µmol) in THF (1 mL) was added potassium bis(trimethylsilyl)amide (211 µL, 106 µmol). Then, a solution of (–)-5 (37 mg, 88.1 µmol) in THF (2 mL) was added via a syringe at the same temperature. The resulting mixture was allowed to warm to 0 °C over 20 min. Sat. NH₄Cl aq. was added, and the mixture was allowed to warm to room temperature. The resulting mixture was extracted twice with ether and the combined organic extracts were washed with brine, dried (MgSO₄), and concentrated. The residue was purified by silica gel column chromatography (EtOAc-hexane = 1 : 6) to give (–)-24 (53 mg, 62.6 µmol, 71%, gem isomer : trans isomer = 1 : 20) as a colorless oil. Analytical sample was prepared from pure (–)-6.

(–)-24: [α]D₂⁷ = -37.5° (c 0.38, CHCl₃); IR (neat): 3282, 2956, 2924, 2870, 2852, 1656, 1627, 1551,
1461, 1375, 1250, 998, 839 cm⁻¹; ¹H-NMR (396 MHz, CDCl₃) δ 7.19 (dd, 1H, J = 14.9, 10.5 Hz), 6.10 (dd, 1H, J = 15.4, 10.5 Hz), 6.00 (dd, 1H, J = 15.4, 7.6 Hz), 5.92-5.84 (m, 3H), 5.77 (d, 1H, J = 14.9 Hz), 5.43 (brt, 1H), 5.23 (t, 1H, J = 7.0 Hz), 3.57 (dt, 1H, J = 5.8, 5.6 Hz), 3.28 (ddd, 1H, J = 13.6, 6.8, 5.8 Hz), 3.18 (ddd, 1H, J = 13.6, 6.3 Hz), 2.85 (s, 2H), 2.37-2.29 (m, 1H), 2.26-2.08 (m, 4H), 1.77 (s, 3H), 1.72-1.63 (m, 1H), 1.52-1.45 (m, 10H), 1.35-1.26 (m, 7H), 1.02 (d, 3H, J = 6.8 Hz), 0.93-0.84 (m, 15H); ¹³C-NMR (99 MHz, CDCl₃) δ 163.7, 148.9, 127.5, 62.7, 45.7, 35.7, 35.3, 34.4, 33.5, 32.9, 29.2, 27.3, 17.5, 16.4, 13.8, 9.5; LRMS (FAB) m/z 524 [M+H]⁺, 73 (100%); HRMS (FAB) Calcd. C₃₈H₇₁NO₂SiSn: 848.3316. Found: 848.3367.

(6S,7S,18S)-(2E,4E,9E,12E,14E)-20-Aza-6,10,12,18-tetramethyl-7-(trimethylsilyloxy)cycloicosa-2,4,9,12,14-pentaenone (4)

A solution of 24 (27 mg, 31.9 µmol), Pd₂(dba)₃•CHCl₃ (6.6 mg, 6.38 µmol), Ph₃As (9.8 mg, 31.9 µmol) and i-Pr₂NEt (56 µl, 319 µmol) in DMF (15 mL) was stirred at room temperature for 2 hr. The resulting mixture was extracted twice with ether and the combined organic extracts were washed with brine, dried (MgSO₄), and concentrated. The residue was purified by silica gel column chromatography (EtOAc-hexane = 1 : 4) to give crude 4 (3.1 mg, 7.23 µmol, < 23%) as a white powder.

4: [α]D²⁶ +56.8° (c 0.12, CHCl₃); IR (neat): 3316, 2955, 1656, 1627, 1616, 1262, 1251, 1070, 992, 887, 841; ¹H-NMR (396 MHz, pyridine-d₅) δ 8.40 (1H, brs), 7.56 (1H, dd, J = 14.6, 11.5 Hz), 6.75 (1H, dd, J = 14.1, 11.5 Hz), 6.23 (1H, d, J = 15.1 Hz), 6.21 (1H, m), 5.93 (2H, m), 5.68 (1H, ddd, 1H, J = 14.6, 8.5, 6.1 Hz), 5.20 (1H, t, J = 7.4 Hz), 3.93 (1H, m), 3.47 (1H, m), 3.09 (1H, brd, J = 13.4 Hz), 2.70 (1H, d, J = 14.1 Hz), 2.63 (1H, d, J = 14.4 Hz), 2.41-2.32 (4H, m), 2.15-2.07 (1H, m), 1.91 (3H, s), 1.81 (3H, m), 1.55 (3H, s), 1.08 (3H, d, J = 6.6 Hz), 0.85 (3H, d, J = 6.8 Hz), 0.20 (9H, s); ¹³C-NMR (151 MHz, pyridine-d₅) δ 166.3, 143.3, 140.3, 134.6, 134.0, 132.5, 128.3, 127.7, 124.5, 121.9, 77.2, 49.7, 47.4, 43.3, 38.2, 33.6, 33.1, 28.2, 19.3, 18.3, 17.4, 17.2, 0.5.

(6S,7S,18S)-20-Aza-6,10,12,18-dimethyl-7-O-(2’4’6’-trideoxy-4’-methylamino-ß-ribo-hexopyranosyl)cycloicosa-2,4,9,12,14-pentaenone (vicenistatin) (1)

A solution of 3 (9.3 mg, 49.0 µmol), 4 (4.2 mg, 9.79 µmol) and activated MS4Å (50 mg) in CH₂Cl₂ (1 mL) was stirred at room temperature for 30 min. To the mixture was added trimethylsilyl trifluoromethanesulfonate (0.294 M in CH₂Cl₂, 100 µL, 29.4 µmol) at -78 °C. After the reaction mixture was warmed to 0 °C, sat. NaHCO₃ aq. was added to the mixture. The resulting mixture was allowed to warm to room temperature and extracted twice with CHCl₃. The combined organic
extracts were dried (MgSO₄), and concentrated. The residue was purified by silica gel column chromatography (EtOAc-hexane = 2 : 1) to give crude glycoside (2.8 mg).

A solution of crude glycoside (2.8 mg) in 5.0 M KOH aq. (2 mL) and MeOH (3 mL) was stirred at room temperature for 1 week. After the reaction mixture was neutralized with 10% HCl aq., the residue was concentrated. The residue was purified by silica gel column chromatography (MeOH-CHCl₃ = 1 : 9) to give 1 (0.5 mg, 1.0 µmol 10% for 2 steps) as a white powder and α-anomer isomer of 1 (0.9 mg, 1.8 µmol 18% for 2 steps) as a white powder.

1: [α]D Twenty-six –1.2° (c 0.06, MeOH); lit. 1 [α]D Twenty-two –3° (c 0.1, MeOH); IR (neat): 3294, 2923, 1655, 1625, 1459, 1377, 1158, 1098, 993 cm⁻¹; ¹H-NMR (500 MHz, pyridine-d₅) δ 8.52 (1H, brd), 7.59 (1H, dd, J = 14.7, 11.0 Hz), 6.79 (1H, dd, J = 14.7, 11.5 Hz), 6.24 (1H, d, J = 15.1 Hz), 6.21 (1H, dd, J = 15.1, 11.0 Hz), 5.95 (1H, d, J = 10.5 Hz), 5.86 (1H, dd, J = 14.7, 10.1 Hz), 5.69 (1H, ddd, J = 14.2, 9.2, 5.0 Hz), 5.29 (1H, dd, J = 9.5, 3.0 Hz), 5.21 (1H, t, J = 7.5 Hz), 4.38 (1H, m), 4.00 (2H, m), 3.37 (1H, m), 3.05 (1H, m), 2.74 (1H, d, J = 15.1 Hz), 2.62 (1H, d, J = 15.1 Hz), 2.43 (3H, s), 2.23 (1H, dd, J = 9.5, 3.0 Hz), 1.94 (3H, s), 1.90 (1H, m), 1.69 (3H, s), 1.51 (3H, d, J = 6.4 Hz), 1.08 (3H, d, J = 6.4 Hz), 0.83 (3H, d, J = 6.9 Hz).

¹³C-NMR (151 MHz, pyridine-d₅) δ 166.1, 143.1, 140.1, 133.8, 132.4, 128.3, 128.2, 124.4, 121.8, 100.6, 85.8, 70.2, 64.9, 63.0, 49.1, 46.1, 42.9, 39.2, 36.4, 33.6, 33.3, 32.6, 27.4, 19.4, 18.5, 17.7, 17.5, 17.2; LRMS (FAB) m/z 501 [M+H]+, 154 (100%); HRMS (FAB) Calcd. C₃₀H₄₉N₂O₄: 501.3690. Found: 501.3680.  

α-vicenistatin: [α]D Twenty-nine +36.9° (c 0.09, MeOH); IR (neat): 3307, 2926, 1655, 1625, 1543, 1458, 1379, 1119, 1085, 1018, 993 cm⁻¹; ¹H-NMR (500 MHz, pyridine-d₅) δ 8.52 (1H, brd), 7.53 (1H, dd, J = 14.7, 11.0 Hz), 6.79 (1H, dd, J = 14.7, 11.5 Hz), 6.24 (1H, d, J = 15.1 Hz), 6.21 (1H, dd, J = 15.1, 11.0 Hz), 5.95 (1H, d, J = 10.5 Hz), 5.86 (1H, dd, J = 14.7, 10.1 Hz), 5.69 (1H, ddd, J = 14.2, 9.2, 5.0 Hz), 5.24 (1H, d, J = 3.7 Hz), 5.12 (1H, t, J = 6.9 Hz), 4.25 (1H, m), 4.17 (1H, m), 3.83 (1H, dt, J = 13.3, 8.7 Hz), 3.63 (1H, m), 3.17 (1H, dt, J = 13.7, 4.1 Hz), 2.69 (1H, d, J = 14.2 Hz), 2.58 (1H, d, J = 14.7 Hz), 2.44 (3H, s), 2.37 (1H, dd, J = 13.7, 6.0 Hz), 1.88 (3H, s), 1.81 (1H, m), 1.55 (3H, s), 1.50 (3H, d, J = 6.4 Hz), 1.17 (3H, d, J = 6.4 Hz), 0.84 (3H, d, J = 6.9 Hz). ¹³C-NMR (151 MHz, pyridine-d₅) δ 166.3, 143.0, 140.1, 134.9, 134.0, 132.6, 128.5, 128.4, 127.7, 124.8, 121.6, 94.3, 80.0, 65.4, 64.6, 62.6, 49.6, 45.0, 43.3, 36.5, 34.0, 33.5, 33.1, 31.7, 28.3, 19.2, 18.8, 18.3, 17.3, 17.2; LRMS (FAB) m/z 501 [M+H]+, 144 (100%); HRMS (FAB) Calcd. C₃₀H₄₉N₂O₄: 501.3690. Found: 501.3684.

Reference: