Supporting Information

Experimental Data for Compounds

General Procedures.

$^1$H NMR were measured in CDCl$_3$ solution and referenced to TMS (0.00 ppm) or in C$_6$D$_6$ solution and referenced to C$_6$D$_3$H (7.16 ppm) using JEOL GSX400 (400 MHz), Bruker AV400N (400 MHz) and Bruker AV500 (500 MHz) spectrometers. $^{13}$C NMR were measured in CDCl$_3$ solution and referenced to CDCl$_3$ (77.0 ppm) or in C$_6$D$_6$ solution and referenced to C$_6$D$_6$ (128.0 ppm) using JEOL GSX400 (100 MHz), Bruker AV400N (100MHz), Bruker AV500 (125 MHz) spectrometers. Chemical shifts are reported in ppm (from TMS). When peak multiplicities are reported, the following abbreviations are used: s, singlet; d, doublet; t, triplet; q, quartet; quint, quintet; m, multiplet; br, broadened. Optical rotations were determined on JAS.CO P-1010-GT. IR spectra were measured on JAS.CO FT/IR-410 spectrometer. Mass spectra were recorded on Waters MICRO MASS LCT-Premier spectrometers. Column chromatography was performed on silica gel 60N (KANTO CHEMICAL, spherical neutral, 63-210 mesh), and flash column chromatography was performed on silica gel (FUJI SILISIA CHEMICAL, spherical neutral, 40-50 µm) using indicated solvent. Thin layer chromatography was performed on precoated plates (0.25 mm, silica gel Merck Kieselgel 60F$_{254}$), and compounds were visualized with UV light and $p$-anisaldehyde stain. All melting points were measured with BÜCHI 535 and Yanaco MP-500D melting point apparatus and are uncorrected. All non-aqueous reactions were performed in oven-dried glassware under positive pressure of argon or nitrogen, unless otherwise noted. Reaction mixture was stirred magnetically. Solvents were freshly distilled prior to use or purchased from Kanto Kagaku or Aldrich: tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl or purchased from Kanto Kagaku (Tetrahydrofuran, Dehydrated Stabilizer free): methylene chloride (CH$_2$Cl$_2$) was distilled from calcium hydride or purchased from Kanto Kagaku (Methylene chloride, Dehydrated): ether (Et$_2$O) was purchased from Kanto Kagaku (Diethyl ether, Dehydrated): acetonitrile (CH$_3$CN) was distilled from calcium hydride and kept over 4Å molecular sieves: pyridine and triethylamine (Et$_3$N) were distilled from KOH and kept over KOH tablets.
To a stirred solution of 5 (302 mg, 0.834 mmol) in 1,2-dichloroethane (15.0 mL) was added DDQ (410 mg, 1.81 mmol) at room temperature, and then the mixture was heated to reflux. After being stirred for 2 h, the reaction mixture was cooled to room temperature and added saturated aq. NaHCO₃. After being stirred for 2 h at room temperature, resultant mixture was extracted with CH₂Cl₂. The combined extracts were washed with saturated aq. NaHCO₃, brine, dried over MgSO₄, filtered and concentrated in vacuo. The residue was purified by silica gel chromatography (hexane / AcOEt = 70 / 30) to afford 7 (214 mg, 94%) as a colorless oil.

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\begin{align*}
\text{[4-(t-BuDimethylsilyloxy)-6,8-dioxabicyclo[3.2.1]oct-2-en-7-yl]methanol (7)}
\end{align*}
\]

\[\alpha\]$_D^{28}$ +135.5 (c 1.81, CHCl₃); IR (neat) 3420, 2955, 2885, 2857, 1089, 1064 cm$^{-1}$; $^1$H-NMR (400 MHz, CDCl₃) $\delta$ 6.25 (ddd, $J = 10.0, 4.8, 1.2$ Hz, 1H), 5.72 (dq, $J = 10.0, 2.0$ Hz, 1H), 5.45 (t, $J = 1.5$ Hz, 1H), 4.51 (d, $J = 4.8$ Hz, 1H), 3.91 (t, $J = 6.0$ Hz, 1H), 3.74 (dt, $J = 3.6, 1.2$ Hz, 1H), 3.63–3.53 (m, 2H), 1.75 (dd, $J = 6.4, 5.0$ Hz, OH, D₂O exchangeable, 1H), 0.91 (s, 9H), 0.12 (s, 3H), 0.12 (s, 3H); $^{13}$C-NMR (100 MHz, CDCl₃) $\delta$ 129.6, 127.2, 103.5, 80.4, 71.5, 66.5, 63.9, 25.8, 18.3, −4.6, −4.7; HRMS (ESI) Calcd for C₁₃H₂₅O₄Si ([M+H]$^+$) 273.1522, Found 273.1521.

**tert-Butyl-(7-iodomethyl-6,8-dioxabicyclo[3.2.1]oct-2-en-4-yloxy)dimethylsilane (8)**

To a stirred solution of 7 (493 mg, 1.81 mmol) in CH$_2$Cl$_2$ (15.0 mL) were added Et$_3$N (0.76 mL, 5.46 mmol) and MsCl (0.28 mL, 3.62 mmol) at 0 °C. After being stirred at room temperature for 0.5 h, the reaction mixture was quenched with saturated aq. NaHCO$_3$ and extracted with Et$_2$O. The combined extracts were washed with brine, dried over MgSO$_4$, filtered and concentrated in vacuo to give crude as a colorless oil, which was used to the next reaction without further purification.

To a stirred solution of crude in THF (10.0 mL) was added LiI (2.45 g, 18.3 mmol) at room temperature, and then the mixture was heated to reflux. After being stirred for 4 h, the reaction mixture was diluted with Et$_2$O and added with saturated aq. NaHCO$_3$/ saturated aq. Na$_2$S$_2$O$_3$ (5/1, v/v). The resultant mixture was stirred at room temperature for 0.5 h, and then extracted with Et$_2$O. The combined extracts were washed with brine, dried over MgSO$_4$, filtered and concentrated in vacuo. The residue was purified by silica gel column chromatography (hexane / AcOEt = 95 / 5) to afford 8 (633 mg, 92% for 2 steps) as a colorless solid.

Mp: 104.5–105.5 °C; [α]$_D^{28}$ +112.5 (c 1.22, CHCl$_3$); IR (neat) 2926, 2879, 2855, 1255, 1088 cm$^{-1}$; $^1$H-NMR (400 MHz, CDCl$_3$) $\delta$ 6.18 (ddd, $J$ = 10.0, 4.8, 1.0 Hz, 1H), 5.74 (ddd, $J$ = 9.8, 4.0, 2.0 Hz, 1H), 5.48 (t, $J$ = 5.6 Hz, 1H), 4.63 (d, $J$ = 4.8 Hz, 1H), 4.06 (dd, $J$ = 9.2, 5.6 Hz, 1H), 3.71 (dt, $J$ = 3.6, 1.2 Hz, 1H), 3.17 (dd, $J$ = 9.6, 5.6 Hz, 1H), 3.10 (dd, $J$ = 10.2, 9.8 Hz, 1H), 0.91 (s, 9H), 0.12 (s, 3H) 0.11 (s, 3H); $^{13}$C-NMR (100 MHz, CDCl$_3$) $\delta$ 129.3, 127.4, 104.1, 80.6, 73.3, 65.9, 25.8, 18.3, 6.6, −4.6, −4.7; HRMS (ESI) Calcd for C$_{13}$H$_{23}$O$_3$NaSi$^+$ ([M+Na]$^+$) 405.0359, Found 405.0354.
3-(tert-Butyldimethylsilyloxy)-6-vinyl-3,6-dihydro-2H-pyran-2-ol (3)

![Chemical Structure of 3](image)

To a stirred solution of 8 (633 mg, 1.66 mmol) in EtOH (19.0 mL) was added Zn powder (1.07 g, 16.6 mmol) at room temperature, and then the mixture was heated to reflux. After being stirred for 2.5 h, the resultant solution was filtered and concentrated in vacuo. The residue was purified by silica gel column chromatography (hexane / AcOEt = 80 / 20) to afford 3 (427 mg, quant., ca. 2.7 : 1 mixture of diastereomers; 1H NMR) as a colorless oil.

IR (neat) 3421, 2954, 2929, 2886, 2857, 1472, 1361, 1113, 877, 838, 780 cm⁻¹; 1H-NMR (400 MHz, CDCl₃) δ 5.90–5.77 (m, 1.27H), 5.71–5.59 (m, 1.73H), 5.33 (dt, J = 17.2, 1.6 Hz, 0.73H), 5.31 (dt, J = 17.2, 1.6 Hz, 0.27H), 5.22 (dt, J = 12.8, 1.2 Hz, 0.27H), 5.19 (dt, J = 10.4, 1.2 Hz, 0.73H), 5.15 (dd, J = 5.6, 3.6 Hz, 0.27H), 4.82–4.80 (m, 0.27H), 4.76 (dd, J = 5.6, 4.0 Hz, 0.73H) 4.77–4.74 (m, 0.73H), 4.22–4.20 (m, 0.27H), 4.09–4.08 (m, 0.73H), 3.41 (d, J = 6.0 Hz, OH, D₂O exchangeable, 0.27H), 2.79 (dd, J = 5.6, 2.0 Hz, OH, D₂O exchangeable, 0.73H), 0.93 (s, 2.4H), 0.92 (s, 6.6H), 0.13 (s, 1.6H), 0.11 (s, 4.4H); 13C-NMR (100 MHz, CDCl₃) δ 136.5, 136.0, 130.3, 128.8, 128.6, 125.3, 116.7, 97.0, 90.6, 75.8, 70.3, 69.4, 64.8, 25.8, 18.2, −4.5, −4.7, −4.8; HRMS (ESI) Calcd for C₁₃H₂₄O₃NaSi ([M+Na]⁺) 279.1392, Found 279.1394.
6-[5-(tert-Butyldimethylsilyloxy)-6-hydroxy-5,6-dihydro-2H-pyran-2-yl]-1-methylhex-5-enyl acetate (10)

To a stirred solution of 3 (10.8 mg, 42.1 µmol) and 4 (32.9 mg, 0.211 mmol) in CH₂Cl₂ (0.5 mL) was added Grubbs’ 2nd generation catalyst 9 (1.7 mg, 2.00 µmol) at room temperature, and then the reaction mixture was heated to reflux. After being stirred for 1 h, the reaction mixture was concentrated in vacuo and purified by silica gel column chromatography (hexane / AcOEt = 90 / 10) to afford 10 (13.6 mg, 84%, ca. 4 : 1 mixture of diastereomers; ¹H NMR) as a yellow oil.

IR (neat) 3520, 2931, 2860, 1733, 1383, 1249, 839, 781 cm⁻¹; ¹H-NMR (400 MHz, CDCl₃) δ 5.80 (dt, J = 10.4, 1.6 Hz, 0.2H), 5.74 (dt, J = 15.2, 6.4 Hz, 0.8H), 5.66–5.54 (m, 2H), 5.49–5.39 (m, 1H), 5.13 (dd, J = 5.2, 4.0 Hz, 0.2H), 4.94–4.83 (m, 1H), 4.78–4.64 (m, 1.8H), 4.22–4.18 (m, 0.2H), 4.09–4.03 (m, 0.8H), 3.38 (d, J = 5.6 Hz, OH, D₂O exchangeable, 0.2H), 2.76 (d, J = 5.6 Hz, OH, D₂O exchangeable, 0.8H), 2.08–2.03 (m, 2H), 2.02 (s, 3H), 1.63–1.33 (m, 4H), 1.20 (d, J = 6.4 Hz, 3H), 0.92 (d, J = 2.4 Hz, 9H), 0.13 (s, 6H); ¹³C-NMR (100 MHz, CDCl₃) δ 170.7, 133.8, 133.5, 130.9, 129.4, 128.8, 128.4, 128.2, 125.0, 97.0, 90.6, 75.6, 70.8, 70.0, 69.4, 64.8, 35.4, 32.0, 31.9, 25.8, 25.7, 24.7, 24.6, 21.3, 19.9, 18.2, 18.1, −4.5, −4.7, −4.8; HRMS (ESI) Calcd for C₂₀H₃₆NaO₅Si ([M+Na⁺]) 407.2230, Found 407.2227.
13-Acetoxy-4-(tert-butyldimethylsilyloxy)-7-hydroxytetradeca-2,5,8-trienoic acid methyl ester (11)

To a stirred solution of 10 (9.7 mg, 25.2 µmol) in toluene (0.3 mL) was added methyl (triphenylphosphoranylidene) acetate (42.2 mg, 0.126 mmol) at room temperature, and then the mixture was heated to reflux. After being stirred for 2 h, the resultant mixture was concentrated in vacuo. The residue was purified by silica gel column chromatography (hexane / AcOEt = 90 / 10) to afford the \textit{Z}-isomer (1.2 mg, 10%) as a colorless oil and 11 (9.2 mg, 84%) as a colorless oil;

\textit{Z}-isomer

\([\alpha]_{D}^{21} = -91.4 (c 1.03, \text{CHCl}_3); \text{IR (neat)} 3476, 2931, 2857, 1722, 1257, 1059, 826 \text{ cm}^{-1}; \text{^1H-NMR (400 MHz, CDCl}_3) \delta 6.28 (dd, J = 9.2, 7.2 Hz, 1H), 6.14 (dd, J = 11.2, 8.8 Hz, 1H), 5.69 (dd, J = 11.2, 1.2 Hz, 1H), 5.60 (dt, J = 15.2, 7.6 Hz, 1H), 5.52–5.41 (m, 3H), 5.10 (t, J = 5.6 Hz, 1H), 4.94–4.83 (m, 1H), 3.72 (s, 3H), 2.23 (d, J = 3.2 Hz, OH, D\textsubscript{2}O exchangeable, 1H), 2.03–1.98 (m, 5H), 1.56–1.30 (m, 4H), 1.19 (d, J = 6.8 Hz, 3H), 0.89 (s, 9H), 0.09 (s, 3H), 0.08 (s, 3H); \textit{^13C-NMR (100 MHz, CDCl}_3) \delta 170.7, 166.2, 149.7, 132.8, 131.3, 131.2, 130.7, 116.9, 70.8, 68.7, 65.0, 51.4, 35.4, 32.0, 25.8, 25.0, 21.3, 19.9, 18.1, -4.7; \text{HRMS (ESI) Calcd for C}_{23}H_{41}O_{6}Si ([M+H]^+) 441.2672, Found 441.2677.}

\textit{E}-enoate (11)

\([\alpha]_{D}^{32} = +64.7 (c 0.34, \text{CHCl}_3); \text{IR (neat)} 3496, 2931 2858, 1730, 1252 \text{ cm}^{-1}; \text{^1H-NMR (400 MHz, CDCl}_3) \delta 6.77 (dd, J = 15.6, 4.0 Hz, 1H), 6.02 (dd, J = 15.2, 1.2 Hz, 1H), 5.68 (dt, J = 15.2, 3.2 Hz, 1H), 5.54–5.49 (m, 1H), 5.49 (ddd, J = 10.8, 8.0, 0.8 Hz, 1H), 5.35 (ddd, J = 10.8, 8.0, 0.8 Hz, 1H), 5.19–5.16 (m, 1H), 4.92–4.87 (m, 2H), 3.73 (s, 3H), 2.06 (q, J = 6.8 Hz, 2H), 2.03 (s, 3H), 1.72 (s, OH, D\textsubscript{2}O exchangeable, 1H), 1.53–1.39 (m, 4H), 1.21 (d, J = 6.4 Hz, 3H), 0.91 (s, 9H), 0.09 (s, 3H), 0.08 (s, 3H); \textit{^13C-NMR (100 MHz, CDCl}_3) \delta 170.7, 167.0, 148.8, 132.2, 131.7, 131.4, 131.2, 119.3, 70.7, 69.3, 68.4, 51.5, 35.4, 31.9, 25.7, 24.7, 21.3, 19.9, 18.2, -4.6, -4.9; \text{HRMS (ESI) Calcd for C}_{23}H_{41}O_{6}Si ([M+H]^+) 441.2672, Found 441.2677.}
4,7-Bis-(tert-butyldimethylsilyloxy)-13-hydroxytetradeca-2,5,8-trienoic acid (13)

To a stirred solution of 11 (5.4 mg, 12.2 µmol) in CH₂Cl₂ (0.3 mL) were added imidazole (2.5 mg, 36.8 µmol), TBSCl (3.7 mg, 24.5 µmol) and 4-DMAP (0.14 mg, 1.22 µmol) at 0 °C. After being stirred at room temperature for 1 h, the reaction mixture was quenched with H₂O and extracted with CHCl₃. The combined extracts were washed with brine, dried over MgSO₄, filtered and concentrated in vacuo to give 12 as a colorless oil, which was used to the next reaction without further purification.

To a stirred solution of crude 12 in MeOH/H₂O (0.04 mL, 3/1, v/v) was added NaOH (2.5 mg, 61.3 µmol) at room temperature. After being stirred at room temperature for 24 h, the reaction mixture was quenched with H₂O and extracted with AcOEt. The combined extracts were washed with brine, dried over MgSO₄, filtered and concentrated. The residue was purified by silica gel column chromatography (CHCl₃ / MeOH = 99 / 1) to afford 13 (4.2 mg, 69%) as a colorless oil.

[α]_{D}^{26} +73.4 (c 2.08, CHCl₃); IR (neat) 3379, 2953, 2927, 2856, 1699, 1654, 1255, 1075, 837, 776 cm⁻¹; ¹H-NMR (400 MHz, CDCl₃) δ 6.86 (dd, J = 15.2, 4.0 Hz, 1H), 6.01 (d, J = 15.2 Hz, 1H), 5.57 (dt, J = 15.2, 6.8 Hz, 1H), 5.52−5.40 (m, 2H), 5.25 (ddd, J = 11.2, 7.6, 1.2 Hz, 1H), 5.20−5.12 (m, 1H), 4.85 (t, J = 7.2 Hz, 1H), 3.83−3.82 (m, 1H), 2.06−2.05 (m, 2H), 1.51−1.42 (m, 4H), 1.17 (d, J = 4.4 Hz, 3H), 0.91 (s, 9H), 0.88 (s, 9H), 0.09 (d, J = 1.6 Hz, 6H), 0.09 (s, 3H), 0.07 (s, 3H), OH protons were not detected; ¹³C-NMR (100 MHz, CDCl₃) δ 170.4, 150.6, 133.3, 132.2, 131.3, 129.3, 118.9, 70.9, 68.7, 68.2, 38.7, 32.1, 25.8, 25.4, 22.9, 18.2, −4.2, −4.5, −4.6, −4.8; HRMS (ESI) Calcd for C₂₆H₅₁O₅Si₂ ([M+H]+) 499.3275, Found 499.3278.
5,8-Bis-(tert-butyldimethylsilyloxy)-14-methyloxacyclotetradeca-3,6,9-trien-2-one (14)

To a stirred solution of 13 (37.0 mg, 74.2 µmol) in CH₂Cl₂ (5.0 mL) were taken up and added dropwise to a solution of 2-methyl-6-nitro benzoic acid anhydride (30.6 mg, 89.0 µmol) and 4-DMAP (21.7 mg, 0.178 mmol) in CH₂Cl₂ (45.0 mL) over a period of 18 h at room temperature. After being stirred at the same temperature for 1 h, the reaction mixture was quenched with saturated aq. NaHCO₃, and then extracted with CH₂Cl₂. The combined extracts were washed with brine, dried over MgSO₄, filtered and concentrated in vacuo. The residue was purified by silica gel column chromatography (hexane / AcOEt = 95 / 5) to afford 14 (32.8 mg, 92%) as a colorless oil.

[α]D31 +92.8 (c 1.50, CHCl₃); IR (neat) 2930, 2857, 1720, 1254, 1127, 1060, 837, 778 cm⁻¹; ¹H-NMR (400 MHz, CDCl₃) δ 7.05 (dd, J = 15.2, 3.6 Hz, 1H), 5.87 (dd, J = 15.2, 1.6 Hz, 1H), 5.68 (dt, J = 15.6, 6.8 Hz, 1H), 5.45 (dd, J = 15.6, 6.4 Hz, 1H), 5.41–5.33 (m, 2H), 5.15 (s, 1H), 4.77 (t, J = 6.8 Hz, 1H), 4.72–4.64 (m, 1H), 2.15–1.88 (m, 2H), 1.87–1.66 (m, 2H), 1.53–1.42 (m, 2H), 1.26 (d, J = 6.4 Hz, 3H), 0.92 (s, 9H), 0.90 (s, 9H), 0.09 (s, 3H), 0.09 (s, 3H), 0.08 (s, 3H), 0.07 (s, 3H); ¹³C-NMR (100 MHz, CDCl₃) δ 166.4, 149.5, 132.2, 131.9, 131.8, 131.5, 117.5, 72.0, 71.0, 69.0, 34.6, 32.9, 25.9, 25.8, 24.5, 20.3, 18.3, 18.2, −4.4, −5.0; HRMS (ESI) Calcd for C₂₆H₄₆NaO₄Si₂ ([M+Na]⁺) 503.2989, Found 503.2993.
To a stirred solution of 14 (6.5 mg, 13.5 µmol) in THF (0.5 mL) at 0 °C was added HF·pyridine (70.0 µL). After being stirred for 15 min at room temperature, the reaction mixture was quenched with saturated aq. NaHCO₃ at 0 °C, and then extracted with AcOEt. The combined extracts were washed with saturated aq. CuSO₄, brine, and dried over MgSO₄, filtered and concentrated in vacuo. The residue was purified by silica gel column chromatography (hexane / AcOEt = 50 / 50) to afford 2 (3.4 mg, quant.) as a colorless oil.

[α]D²⁸ +188.2 (c 0.68, CHCl₃); IR (neat) 3362, 2974, 2931, 1698, 1261, 1008, 976 cm⁻¹; ¹H-NMR (400 MHz, CDCl₃) δ 7.03 (dd, J = 15.6, 4.4 Hz, 1H), 5.90 (dd, J = 15.6, 2.0 Hz, 1H), 5.86 (ddd, J = 15.6, 9.2, 5.6 Hz, 1H), 5.54 (dd, J = 11.2, 4.4 Hz, 1H), 5.49 (dd, J = 15.2, 7.6 Hz, 1H), 5.46 (ddd, J = 10.8, 9.6, 2.4 Hz, 1H), 5.26–5.25 (m, 1H), 4.82 (t, J = 8.4 Hz, 1H), 4.75 (dt, J = 16.0, 6.0, 2.0 Hz, 1H), 2.32 (brs, OH, D₂O exchangeable, 1H), 2.13–1.95 (m, 2H), 1.80 (brs, OH, D₂O exchangeable, 1H), 1.87–1.73 (m, 2H), 1.54–1.48 (m, 1H), 1.26 (d, J = 6.0, 3H), 1.15–1.08 (m, 1H); ¹³C-NMR (100 MHz, CDCl₃) δ 166.1, 148.3, 134.4, 132.1, 131.2, 130.3, 118.3, 72.0, 70.6, 68.4, 34.5, 32.8, 24.4, 20.2; HRMS (ESI) Calcd for C₁₄H₂₀O₄Na ([M+Na]+) 275.1259, Found 275.1262.
Aspergillide C (1)

To a stirred suspension of KH (1.7 mg, 30% in oil, 12.5 µmol) in THF (0.1 mL) were added 18-Crown-6 (7.9 mg, 29.7 µmol) and 2 (1.5 mg, 5.95 µmol) in THF (0.2 mL) at 0 °C. After being stirred at the same temperature for 10 min, the reaction mixture was quenched with saturated aq. NH₄Cl and extracted with AcOEt. The combined extracts were washed with brine, dried over MgSO₄, filtered and concentrated in vacuo. The residue was purified by silica gel column chromatography (hexane / AcOEt = 70 / 30) to afford 1 (1.3 mg, 86%) as a colorless solid.

Mp: 104.5−105.5 °C; (lit.² mp: 115.5−116 °C); [α]D²⁹ +83.8 (c 0.33, MeOH) {lit.³ [α]D²⁵ +66.2 (c 0.19, MeOH), lit.² [α]D²⁵ +83.0 (c 0.14, MeOH), lit.⁴ [α]D²⁵ +77.5 (c 0.11, MeOH)}; IR (neat) 3411, 2924, 2852, 1732, 1456, 1375, 1193 cm⁻¹; ¹H-NMR (500 MHz, C₆D₆) δ 5.94 (dddd, J = 15.5, 9.5, 6.0, 2.0 Hz, 1H), 5.74 (ddd, J = 10.5, 6.0, 2.0 Hz, 1H), 5.41 (dd, J = 15.5, 9.5, 6.0, 2.0 Hz, 1H), 5.18 (dd, J = 15.5, 4.0 Hz, 1H), 5.15−5.13 (m, 1H), 4.46−4.45 (m, 1H), 4.03 (dt, J = 11.5, 1.5 Hz, 1H), 3.22 (dd, J = 10.5, 5.0 Hz, 1H), 2.87 (dd, J = 13.5, 11.5 Hz, 1H), 2.25 (dd, J = 13.5, 2.0 Hz, 1H), 1.96 (ddddd, J = 13.0, 9.5, 6.0, 2.0 Hz, 1H), 1.63−1.54 (m, 2H), 1.45−1.36 (m, 1H), 1.32−1.25 (m, 1H), 1.24 (brs, OH, D₂O exchangeable, 1H), 1.20−1.12 (m, 1H), 0.99 (d, J = 6.5 Hz, 3H); ¹³C-NMR (100 MHz, CDCl₃) δ 170.0, 135.0, 131.8, 128.5, 126.2, 72.0, 69.8, 69.5, 64.5, 38.8, 32.0, 31.0, 23.7, 18.7; HRMS (ESI) Calcd for C₁₄H₂₁O₄ ([M+H]+) 253.1440, Found 253.1444.

3-epi-Aspergillide C (15)

To a stirred solution of 4 (3.0 mg, 1.20 µmol) in MeCN (0.2 mL) were added LiCl (5.0 mg, 11.9 µmol) and DBU (16.7 µL, 11.9 µmol) at room temperature. After being stirred at the same temperature for 15 min, the reaction mixture was quenched with saturated aq. NH₄Cl and extracted with AcOEt. The combined extracts were washed with brine, dried over MgSO₄, filtered and concentrated in vacuo. The residue was purified by silica gel column chromatography (hexane / AcOEt = 60 / 40) to afford 15 (2.9 mg, 97%) as a colorless oil.

[α]$_{31}^{D}$ +80.2 ($c$ 0.49, CHCl₃); IR (neat) 3366, 2926, 2853, 1732, 1263, 1066, 1028 cm$^{-1}$; $^1$H-NMR (500 MHz, CDCl₃) $\delta$ 6.07 (dddd, $J$ = 10.0, 6.0, 2.5, 1.0 Hz, 1H), 5.99 (dd, $J$ = 10.0, 3.0 Hz, 1H), 5.82 (ddddd, $J$ = 15.5, 7.0, 6.0, 1.5 Hz, 1H), 5.58 (ddt, $J$ = 16.0, 6.5, 1.5 Hz, 1H), 5.08–5.04 (m, 1H), 4.67 (d, $J$ = 4.5 Hz, 1H), 4.59 (dd, $J$ = 12.5, 3.0 Hz, 1H), 3.67 (dd, $J$ = 10.0, 9.5 Hz, 1H), 2.53 (dd, $J$ = 16.0, 11.5 Hz, 1H), 2.37 (dd, $J$ = 16.5, 3.5 Hz, 1H), 2.23-2.03 (m, 2H), 2.00 (d, $J$ = 9.6 Hz, OH, D₂O exchangeable, 1H), 1.86–1.78 (m, 1H), 1.75–1.56 (m, 3H), 1.20 (d, $J$ = 6.6 Hz, 3H); $^{13}$C-NMR (100 MHz, CDCl₃) $\delta$ 170.0, 134.8, 131.8, 130.1, 124.2, 73.6, 70.9, 69.7, 64.2, 38.7, 32.7, 30.8, 21.6, 18.8; HRMS (ESI) Calcd for C₁₄H₂₁O₄ ([M+H]$^+$) 253.1440, Found 253.1435.
Interconversion of 3-epi-aspergillide C (15) to aspergillide C (1)

To a stirred suspension of KH (0.9 mg, 30% in oil, 6.66 µmol) in THF (0.1 mL) were added 18-Crown-6 (4.2 mg, 15.9 µmol) and 3-epi-aspergillide C (15) (0.8 mg, 3.17 µmol) in THF (0.2 mL) at 0 °C. After being stirred for 15 min, the reaction mixture was quenched with saturated aq. NH₄Cl and extracted with AcOEt. The combined extracts were washed with brine, dried over MgSO₄, filtered and concentrated in vacuo. The residue was purified by silica gel column chromatography (hexane / AcOEt = 60 / 40) to afford aspergillide C (1) (0.6 mg, 75%) as a colorless solid.
$^1$H NMR (400 MHz) in CDCl$_3$
$^{13}$C NMR (100 MHz) in CDCl$_3$
$^1$H NMR (400MHz) in CDCl$_3$
$^1^3$C NMR (100MHz) in CDCl$_3$
TBSO

\[
3 (\sigma_r = 2.7 : 1)
\]

\[\text{\textsuperscript{1}H NMR (400 MHz) in CDCl}_3\]
TBSO

H

3 (dr = 2.7 : 1)

$^{13}$C NMR (100MHz) in CDCl$_3$
10 (dr = 4 : 1)

$^1$H NMR (400MHz) in CDCl$_3$
$^{13}$C NMR (100MHz) in CDCl$_3$
\[ ^{13}\text{C} \text{NMR (100MHz) in CDCl}_3 \]

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TBSCO
MeO₂C
HO
Ac
Me
11-Z

$^1$H NMR (400MHz) in CDCl₃
1H NMR (400 MHz) in CDCl₃
Electronic Supplementary Material (ESI) for Chemical Communications
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$^{13}$C NMR (100MHz) in CDCl$_3$
$^1$H NMR (400 MHz) in CDCl$_3$
$^{13}$C NMR (100MHz) in CDCl$_3$
$^1$H NMR (400 MHz) in CDCl$_3$
$^{13}$C NMR (100MHz) in CDCl$_3$
$^1$H NMR (400 MHz) in CDCl$_3$
$^{13}$C NMR (100MHz) in CDCl$_3$
$^1$H NMR (500MHz) in C$_6$D$_6$
$^{13}$C NMR (125MHz) in C$_6$D$_6$
$^1$H NMR (500MHz) in CDCl$_3$
Electronic Supplementary Material (ESI) for Chemical Communications
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1H NMR (100MHz) in CDCl₃