Supporting Information
(Experimental Procedures and NMR Spectra Data)

Stereoselective Construction of 2-Vinyl 3-Hydroxybenzopyran Rings:
Total Syntheses of Teadenols A and B

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Analysis Instruments

Nuclear magnetic resonance \(^1\text{H} \text{NMR (500 MHz)}, \text{ } ^{13}\text{C} \text{NMR (125 MHz)}\) spectra were determined on JEOL ECA-500 instrument. Chemical shifts for \(^1\text{H} \text{NMR were reported in parts per million downfields from tetramethylsilane (δ) as the internal standard and coupling constants were in hertz (Hz). The following abbreviations are used for spin multiplicity: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. Chemical shifts for } ^{13}\text{C NMR were reported in ppm relative to the centerline of a triplet at 77.0 ppm for deuteriochloroform.}

High-resolution mass spectra (HRMS) were obtained on a BRUKER DALTONICS micrOTOF (ESI).

Infrared (IR) spectra were recorded on a SHIMADZU IRPrestige-21.

Optical rotations were measured on a JASCO P-1030 Polarimeter at RT using the sodium D line.

Analytical thin layer chromatography (TLC) was performed on Merck precoated analytical plates, 0.25 mm thick, silica gel 60 F\(_{254}\). Preparative TLC separations were made on 7 x 20 cm plates prepared with a 0.25 mm layer of Merck silica gel 60 F\(_{254}\). Compounds were eluted from the adsorbent with 10% methanol in chloroform. Column chromatography separations were performed on KANTO CHEMICAL Silica Gel 60 (spherical) 40–50 µm, Silica Gel 60 (spherical) 63–210 µm or Silica Gel 60 N (spherical, neutral) 63–210 µm.

Reagents and solvents were commercial grades and were used as supplied with the following exceptions.

1) Dichloromethane, tetrahydrofuran and toluene: dried over molecular sieves 4A.

2) Methanol and acetonitrile: dried over molecular sieves 3A.

All reactions sensitive to oxygen and/or moisture were conducted under an argon atmosphere.

Numbering System

Based on a numbering system employed in Ishimaru’s paper,\(^1\) we employ the following numbering system in the main text and Supporting Information. The numbers assigned for early synthetic intermediates to specify positions of interest are in accord with the corresponding carbons in Teadenol A and B.

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I. Synthesis of Common Intermediate 9

Synthesis of Lactone 12

To a solution of phloroglucinol (10, 100 g, 793 mmol) in CH$_3$CN (800 mL) were added acrylic acid (11, 60 mL, 872 mmol) and Amberlyst 15 (32 g) at room temperature. The resulting mixture was stirred at 100 °C for 24 hours. Then the reaction mixture was filtered through a pad of Celite and evaporated under reduced pressure. The crude material including S1 was applied to the following reaction without further purification.

To a solution of the crude material including S1 in DMF (800 mL) were added K$_2$CO$_3$ (329 g, 2.38 mol) and benzyl bromide (283 mL, 2.38 mol) at 0 °C. The resulting mixture was stirred at room temperature for 4 hours. Then the reaction mixture was quenched with saturated aqueous NH$_4$Cl and extracted with EtOAc. The organic layer was washed with brine, dried over anhydrous MgSO$_4$ and evaporated under reduced pressure. The residue was purified by column chromatography (silica gel, n-hexane/EtOAc = 20/1) to afford 12 (188 g, 66%, 2 steps) as a colorless solid.

IR (film, cm$^{-1}$): 3032, 2912, 1770, 1624, 1595.

$^1$H NMR (500 MHz, CDCl$_3$, δ): 7.41-7.32 (m, 10H), 6.41 (d, $J = 2.3$ Hz, 1H), 6.32 (d, $J = 2.3$ Hz, 1H), 5.03 (s, 2H), 5.02 (s, 2H), 2.93 (t, $J = 7.7$ Hz, 2H), 2.72 (t, $J = 7.7$ Hz, 2H).

$^{13}$C NMR (125 MHz, CDCl$_3$, δ): 168.6, 159.0, 156.3, 153.1, 136.4, 136.3, 128.61, 128.57, 128.11, 128.09, 127.5, 127.2, 104.0, 96.7, 95.2, 70.31, 70.26, 28.7, 17.2.

Synthesis of Ester S3

To a solution of 12 (188 g, 26.4 mmol) in EtOH (1.0 L) was added Amberlyst 15 (10 g) at room temperature. The resulting mixture was refluxed for 3.5 hours. After cooling, the reaction mixture was filtered through a pad of Celite and evaporated under reduced pressure. The crude material including S2 was applied to the following reaction without further purification.

To a solution of the crude material including S2 in DMF (1.0 L) were added imidazole (53.3 g, 783 mmol) and TBSCl (94.4 g, 626 mmol) at 0 °C. The resulting mixture was stirred at room temperature for 15 hours. The reaction mixture was quenched with saturated aqueous NH₄Cl and extracted with EtOAc. The organic layer was washed with brine, dried over anhydrous MgSO₄ and evaporated under reduced pressure. The residue was purified by column chromatography (silica gel, n-hexane/EtOAc = 19/1) to afford S3 (209 g, 77%, 2 steps) as a colorless oil.

IR (ATR, cm⁻¹): 2953, 2930, 2859, 1732, 1605, 1586, 1431.

¹H NMR (500 MHz, CDCl₃, δ): 7.42-7.35 (m, 8H), 7.28-7.24 (m, 2H), 6.25 (d, J = 2.3 Hz, 1H), 6.07 (d, J = 2.3 Hz, 1H), 5.02 (s, 2H), 4.98 (s, 2H), 4.10 (q, J = 7.4 Hz, 2H), 2.94 (t, J = 8.2 Hz, 2H), 2.46 (t, J = 8.2 Hz, 2H), 1.22 (t, J = 7.4 Hz, 3H), 0.99 (s, 9H), 0.18 (s, 6H).

¹³C NMR (125 MHz, CDCl₃, δ): 173.4, 158.1, 158.0, 154.7, 137.1, 136.9, 128.5, 128.4, 127.9, 127.6, 127.3, 126.8, 112.6, 98.3, 93.7, 70.0, 69.9, 59.9, 34.0, 25.6, 19.3, 18.1, 14.2, -4.3.

HRMS (ESI): Calcd for C₃₁H₄₀O₅SiNa [(M+Na)⁺], 543.2558, found 543.2537.
Synthesis of Diol 16

To a solution of S3 (106 g, 203 mmol) in CH$_2$Cl$_2$ (1.0 L) was added DIBAL (239 mL, 244 mmol, 1.02 M solution in n-hexane) over 1 hour at –78 °C. The resulting mixture was stirred at the same temperature for 1.5 hours. Then the reaction mixture was quenched with MeOH (6.0 mL). The resulting mixture was diluted with 1 M HCl (1.4 L) and extracted with EtOAc. The organic layer was washed with brine, dried over anhydrous Na$_2$SO$_4$ and evaporated under reduced pressure. The crude material including 13 was applied to the following reaction without further purification.

To a solution of the crude material including 13 in CH$_3$CN (660 mL) were added nitrosobenzene (21.7 g, 203 mmol), L-proline (5.85 mg, 50.8 mmol) and urea 14 at –20 °C. After 2.5 hours, MeOH (35 mL) and NaBH$_4$ (2.37 g, 81.3 mmol) were added at the same temperature. The resulting mixture was stirred at –20 °C for 1.5 hours. Then the reaction mixture was quenched with saturated aqueous NaHCO$_3$ and extracted with EtOAc. The organic layer was washed with brine, dried over anhydrous Na$_2$SO$_4$ and evaporated under reduced pressure. The crude material including 15 was applied to the following reaction without further purification.

To a solution of the crude material including 15 in EtOH (500 mL) were added AcOH (500 mL) and zinc powder (133 g, 2.03 mol). The resulting mixture was stirred at room temperature for 6 hours. Then the reaction mixture was filtered through a pad of Celite and evaporated under reduced pressure. The residue was purified by column chromatography (silica gel, n-hexane/EtOAc = 4/1 to 2/1) to afford diol 16 (66 g, 66% 3 steps, 98% ee) as a yellow oil. The enantiomeric excess value (ee) of 16 was determined by chiral HPLC analysis.

HPLC: (DAICEL CHIRALCEL OD-H, n-hexane/IPA = 10/1, 1.0 mL/min, 254 nm, $\tau$ major 11.7 min, $\tau$ minor 8.6 min).

$[\alpha]_D^{25}$ +2.2 ($c$ 1.00, CHCl$_3$, 98% ee).

IR (film, cm$^{-1}$): 3412, 2954, 2930, 2884, 2859, 1608, 1586, 1431, 1387.

$^1$H NMR (500 MHz, CDCl$_3$, $\delta$): 7.41-7.30 (m, 10H), 6.32 (d, $J = 2.3$ Hz, 1H), 6.11 (d, $J = 2.3$ Hz, 1H), 5.01 (s, 2H), 3.86 (quintet, $J = 2.8$ Hz, 1H), 3.52 (dd, $J = 11.3$, 2.8 Hz, 1H), 3.42 (dd, $J = 11.3$, 6.2 Hz, 1H), 2.87 (dd, $J = 13.6$, 6.2 Hz, 1H), 2.83 (dd, $J = 13.6$, 6.2 Hz, 1H), 2.63 (brs, 1H), 2.21 (brs, 1H), 0.99 (s, 9H), 0.192 (s, 3H), 0.186 (s, 3H).

$^{13}$C NMR (125 MHz, CDCl$_3$, $\delta$): 158.3, 158.2, 155.1, 136.8, 136.3, 128.7, 128.6, 128.1, 128.0, 127.4, 127.2, 126.8, 109.7, 94.0, 72.1, 70.5, 70.1, 65.9, 27.2, 25.7, 18.2, –4.17, –4.25.

HRMS (ESI): Calcd for C$_{29}$H$_{38}$O$_5$SiNa [(M+Na)$^+$] 517.2399, found 517.2381.

The racemic diol (±)-16 was prepared by similar procedure to prepare optical active compound exception for employment with racemic catalyst.

Optically Active: Diol (±)-16

![Graph showing chromatogram of optically active diol (±)-16](image)

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DAICEL CHIRALCEL OD-H, n-hexane/i-PrOH = 10/1, Flow rate 1.0 mL/min, 254 nm

Racemic: Diol (±)-16

![Graph showing chromatogram of racemic diol (±)-16](image)

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DAICEL CHIRALCEL OD-H, n-hexane/i-PrOH = 10/1, Flow rate 1.0 mL/min, 254 nm
Since a determination of the absolute configuration of 16 by the modified Mosher method was difficult, we decided to prepare the authentic sample (R)-S8 from chiral epoxide S6 as shown in the following scheme. After transmetalation of bromide S5, copper catalyzed epoxide opening reaction of S6 with the Grignard reagent proceeded smoothly to provide S6. Removal trityl group by TFA, the desired diol S8 was obtained in optical active form.

Synthesis of (R)-S8 from S5

To a suspension of magnesium ribbon (29 mg, 1.2 mmol) in THF (1.3 mL) were added I2 (1 small amount) and a solution of S5 (300 mg, 1.21 mmol) in THF (0.5 mL). After 0.5 hours, CuI (23 mg, 0.12 mmol) and a solution of S6 (383 mg, 1.21 mmol) in THF (0.5 mL) were added at –30 °C. The resulting mixture was stirred at the same temperature for 3 hours. Then the reaction mixture was quenched with saturated aqueous NH4Cl and extracted with EtOAc. The organic layer was dried over anhydrous Na2SO4 and evaporated under reduced pressure. The crude material including S7 was applied to the following reaction without further purification.

To a solution of the crude material including S7 in CH2Cl2 (1.0 mL) was added TFA (0.1 mL) at room temperature. The resulting mixture was stirred at the same temperature for 10 minutes. Then the reaction mixture was quenched with Et3N and evaporated under reduced pressure. The residue was purified by column chromatography (silica gel, n-hexane/EtOAc = 1/4) to afford (R)-S8 (from S5, 30 mg, 23% 2 steps, 99% ee) as a colorless solid. The enantiomeric excess value (ee) of (R)-S8 was determined by chiral HPLC analysis.

HPLC: (DAICEL CHIRALCEL AS-H, n-hexane/IPA = 9/1, 1.0 mL/min, 254 nm, τmajor 18.5 min, τminor 16.7 min).

[α]D25 −1.7 (c 1.00, CHCl3, 99% ee).

IR (film, cm⁻¹): 3311, 2941, 2890, 2837, 1594, 1495, 1452, 1415.

1H NMR (500 MHz, CDC13, δ): 6.16 (s, 2H), 3.87 (quintet, J = 4.5 Hz, 1H), 3.82 (s, 6H), 3.81 (s, 3H), 3.51 (dd, J = 11.3, 3.4, 1H), 3.44 (dd, J = 11.3, 5.1 Hz, 1H), 2.88 (dd, J = 13.6, 6.2 Hz, 1H), 2.83 (dd, J = 13.6, 6.2 Hz, 1H), 2.60 (brs, 1H), 2.39 (brs, 1H).

13C NMR (125 MHz, CDC13, δ): 159.8, 158.8, 106.3, 90.7, 72.0, 65.8, 55.6, 55.3, 26.3.

HRMS (ESI): Calcd for C12H18O5Na [(M+Na)+] 265.1052, found 265.1046.
Conversion from our synthetic intermediate 16 to the diol S8 was performed by changing the protecting group from benzyl and TBS to the methyl ethers as shown in the following scheme.

Synthesis of S8 from 16

To a solution of 16 (1.00 g, 2.02 mmol) in CH₂Cl₂ (20 mL) were added 2,2-dimethoxy propane (0.37 mL, 3.0 mmol) and 10-camphor sulfonic acid (CSA, 47 mg, 0.20 mmol) at room temperature. The resulting mixture was stirred at the same temperature for 8 hours. Then the reaction mixture was quenched with saturated aqueous NaHCO₃ and extracted with CH₂Cl₂. The organic layer was dried over anhydrous Na₂SO₄ and evaporated under reduced pressure. The residue was filtered through a pad of Celite and evaporated under reduced pressure. The crude material including S9 was applied to the following reaction without further purification.

To a solution of the crude material including S9 in THF (10 mL) was added TBAF (2.0 mL, 2.0 mmol, 1 M solution in THF) at room temperature. The resulting mixture was stirred at the same temperature for 1 hour. Then the reaction mixture was quenched with saturated aqueous NH₄Cl and extracted with CH₂Cl₂. The organic layer was dried over anhydrous Na₂SO₄ and evaporated under reduced pressure. The residue was filtered through a pad of silica gel (Eluted with EtOAc) and evaporated under reduced pressure. The crude material including S10 was applied to the following reaction without further purification.

To a solution of the crude material including S10 in MeOH (20 mL) was added 5% Pd/C (215 mg) at room temperature. The resulting mixture was stirred at the same temperature under ordinary hydrogen pressure (balloon) for 1 hour. Then the reaction mixture was filtered through a pad of Celite and evaporated under reduced pressure. The crude material including S11 was applied to the following reaction without further purification.

To a solution of the crude material including S11 in acetone (10 mL) were added K₂CO₃ (838 mg, 6.06 mmol) and Me₂SO₄ (0.57 mL, 6.1 mmol) at room temperature. The resulting mixture was stirred at the same temperature for 8 hours. Then the reaction mixture was quenched with saturated aqueous NaHCO₃ and extracted with CH₂Cl₂. The organic layer was dried over anhydrous Na₂SO₄ and evaporated under reduced pressure. The crude material including S12 was applied to the following reaction without further purification.

To a solution of the crude material including S12 in THF (10 mL) was added 2 M HCl (2.0 mL) at room temperature. The resulting mixture was stirred at the same temperature for 3 hours. Then the reaction mixture was diluted with H₂O and extracted with CH₂Cl₂. The organic layer was dried over anhydrous Na₂SO₄ and evaporated under reduced pressure. The residue was purified by column chromatography (silica gel, n-hexane/EtOAc = 1/4) to afford S8 (from 16, 97 mg, 20% 5 steps, 98% ee) as a colorless solid.

Since the all spectral data ([α]D, ¹H NMR, ¹³C NMR, IR, HRMS and HPLC) of S8 derived from 16, were in full agreement with (R)-S8, which was prepared from S5 and S6, the absolute configuration of 16 was concluded to 3R.
According to the preparation of optical active S8, racemic diol S8 was synthesized from racemic 16, described in above. Confirmation of the absolute configuration and enantio excess of 16 was accomplished by comparison with the chiral HPLC analysis of racemic as well as optical active S8 derived from 16 and 6S, as shown in the following.

Optically Active: Diol (R)-S8 Derived from 5S and 6S

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DAICEL CHIRALCEL AS-H, n-hexane/i-PrOH = 9/1, Flow rate 1.0 mL/min, 230 nm

Optically Active: Diol S8 Derived from 16

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DAICEL CHIRALCEL AS-H, n-hexane/i-PrOH = 9/1, Flow rate 1.0 mL/min, 230 nm

Racemic: Diol (t)-S8

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DAICEL CHIRALCEL AS-H, n-hexane/i-PrOH = 9/1, Flow rate 1.0 mL/min, 230 nm
Synthesis of PMB Ether 18

To a solution of 16 (23.9 g, 48.3 mmol) in CH$_2$Cl$_2$ (120 mL) were added p-anisaldehyde dimethyl acetal (17, 12.3 mL, 72.5 mmol) and PPTS (1.21 g, 4.83 mmol) at room temperature. The resulting mixture was stirred at the same temperature for 5 hour. Then the reaction mixture was quenched with saturated aqueous NH$_4$Cl and extracted with EtOAc. The organic layer was washed with brine, dried over anhydrous Na$_2$SO$_4$ and evaporated under reduced pressure. The crude material including S4 was applied to the following reaction without further purification.

To a solution of the crude material including S4 in CH$_2$Cl$_2$ (500 mL) was added DIBAL (104 mL, 106 mmol, 1.02 M solution in CH$_2$Cl$_2$) over 1 hour at –78 °C. The resulting mixture was stirred at the same temperature for 4 hours. Then the reaction mixture was quenched with MeOH (10 mL). The resulting mixture was diluted with 1 M HCl (1.0 L) and extracted with CH$_2$Cl$_2$. The organic layer was washed with brine, dried over anhydrous Na$_2$SO$_4$ and evaporated under reduced pressure. The residue was purified by column chromatography (silica gel, n-hexane/EtOAc = 9/1) to afford 18 (26.6 g, 90%, 2 steps) as a colorless oil.

$[^a]_D^{24}$ –5.8 (c 1.05, CHCl$_3$).

IR (film, cm$^{-1}$): 2955, 2932, 2859, 1605, 1587, 1512, 1431.

$^1$H NMR (500 MHz, CDCl$_3$, δ): 7.45-7.30 (m, 10H), 7.11 (d, $J = 8.5$ Hz, 2H), 6.80 (d, $J = 8.5$ Hz, 2H), 6.29 (d, $J = 2.3$ Hz, 1H), 6.08 (d, $J = 2.3$ Hz, 1H), 5.02-4.95 (m, 4H), 4.49 (d, $J = 11.3$ Hz, 1H), 4.30 (d, $J = 11.3$ Hz, 1H), 3.78 (s, 3H), 3.67 (m, 1H), 3.52 (m, 1H), 3.44 (m, 1H), 2.98 (dd, $J = 13.0, 4.5$ Hz, 1H), 2.74 (dd, $J = 13.0, 9.3$ Hz, 1H), 2.17 (m, 1H), 0.98 (s, 9H), 0.19 (s, 3H), 0.18 (s, 3H).

$^{13}$C NMR (125 MHz, CDCl$_3$, δ): 158.9, 158.3, 158.1, 155.0, 136.8, 136.6, 130.9, 129.1, 128.50, 128.46, 128.0, 127.8, 127.6, 127.2, 113.5, 109.6, 98.4, 93.6, 79.4, 70.8, 70.3, 70.0, 64.1, 55.0, 25.8, 24.8, 18.2, –4.14, –4.22.

HRMS (ESI): Calcd for C$_{37}$H$_{46}$O$_6$SiNa [(M+Na)$^+$] 637.2975, found 637.2956
To a solution of oxalyl chloride (0.70 mL, 8.2 mmol) in CH$_2$Cl$_2$ (20 mL) was added dropwise a solution of DMSO (0.86 mL, 12 mmol) in CH$_2$Cl$_2$ (10 mL) at −78 °C. After 15 minutes, a solution of 18 (3.36 g, 5.47 mmol) in CH$_2$Cl$_2$ (10 mL) was added at −78 °C. After 15 minutes, Et$_3$N (4.6 mL, 33 mmol) was added at −78 °C. The resulting mixture was stirred at the same temperature for 15 minutes. Then the reaction mixture was quenched with saturated aqueous NH$_4$Cl and extracted with CH$_2$Cl$_2$. The organic layer was washed with brine, dried over anhydrous Na$_2$SO$_4$ and evaporated under reduced pressure. The residue was purified by column chromatography (silica gel, n-hexane/EtOAc = 9/1) to afford S13 (3.17 g, 95%) as a colorless oil.

[$\alpha$]$_D$$^{24}$ +22.5 (c 0.96, CHCl$_3$).

IR (film, cm$^{-1}$): 2955, 2932, 2859, 1734, 1609, 1589, 1512, 1431.

$^1$H NMR (500 MHz, CDCl$_3$, δ): 9.48 (d, $J = 2.8$ Hz, 1H), 7.42-7.28 (m, 10H), 7.12 (d, $J = 8.5$ Hz, 2H), 6.79 (d, $J = 8.5$ Hz, 2H), 6.24 (d, $J = 2.3$ Hz, 1H), 6.06 (d, $J = 2.3$ Hz, 1H), 4.98 (s, 2H), 4.96 (d, $J = 11.3$ Hz, 1H), 4.93 (d, $J = 11.3$ Hz, 1H), 4.46 (d, $J = 11.3$ Hz, 1H), 4.36 (d, $J = 11.3$ Hz, 1H), 3.96-3.91 (m, 1H), 3.77 (s, 3H), 3.08-2.98 (m, 2H), 0.97 (s, 9H), 0.17 (s, 3H), 0.16 (s, 3H).

$^{13}$C NMR (125 MHz, CDCl$_3$, δ): 202.4, 159.1, 158.5, 158.3, 155.1, 136.8, 136.7, 129.5, 129.4, 128.5, 128.4, 127.9, 127.8, 127.2, 113.6, 107.5, 98.2, 93.5, 82.3, 71.8, 70.0, 69.9, 55.0, 25.7, 24.7, 18.1, −4.28, −4.32.

HRMS (ESI): Calcd for C$_{37}$H$_{44}$O$_6$SiNa [(M+Na)$^+$] 635.2794, found 635.2799.
Synthesis of Diester 9

To a solution of S13 (2.56 g, 4.18 mmol) in toluene (4.0 mL) was added 19 (5.09 g, 12.5 mmol). The resulting mixture was stirred at 100 °C for 24 hours. Then the reaction mixture was evaporated under reduced pressure. The residue was purified by column chromatography (silica gel, n-hexane/EtOAc = 9/1) to afford 9 (2.74 g, 86%, 98% ee) as a colorless oil. The enantiomeric excess value (ee) of 9 was determined by chiral HPLC analysis.

HPLC: (DAICEL CHIRALCEL OD-H, n-hexane/IPA = 100/1, 1.0 mL/min, 220 nm, τmajor 26.1 min, τminor 23.3 min). 
[α]D24 +11.9 (c 1.05, CHCl3, 98% ee).

IR (film, cm⁻¹): 2953, 2932, 2859, 1742, 1719, 1609, 1587, 1512, 1436.

1H NMR (500 MHz, CDCl3, δ): 7.40-7.29 (m, 10H), 7.12 (d, J = 9.1 Hz, 1H), 6.88 (d, J = 9.1 Hz, 2H), 6.78 (d, J = 9.1 Hz, 2H), 6.19 (d, J = 2.3 Hz, 1H), 6.01 (d, J = 2.3 Hz, 1H), 5.85 (ddt, J = 17.0, 10.2, 5.7 Hz, 1H), 5.26 (ddt, J = 17.0, 1.7, 1.1 Hz, 1H), 5.19 (ddt, J = 10.2, 1.7, 1.1 Hz, 1H), 4.99 (s, 2H), 4.91 (d, J = 11.9 Hz, 1H), 4.86 (d, J = 11.9 Hz, 1H), 4.59 (ddt, J = 13.0, 5.7, 1.1 Hz, 1H), 4.53 (ddt, J = 13.0, 5.7, 1.1 Hz, 1H), 4.44 (d, J = 11.3 Hz, 1H), 4.41 (td, J = 9.1, 6.2 Hz, 1H), 4.23 (d, J = 11.3 Hz, 1H), 3.77 (s, 3H), 3.55 (s, 3H), 3.04 (dd, J = 13.0, 5.7 Hz, 1H), 2.91 (dd, J = 13.0, 9.1 Hz, 1H), 2.81 (s, 2H), 0.98 (s, 9H), 0.16 (s, 3H), 0.14 (s, 3H).

13C NMR (125 MHz, CDCl3, δ): 170.8, 166.1, 159.0, 158.5, 158.3, 155.3, 145.8, 136.9, 136.8, 132.1, 130.4, 129.3, 128.6, 128.4, 127.9, 127.7, 127.3, 127.1, 117.9, 113.6, 108.5, 98.2, 93.4, 74.2, 70.6, 70.0, 65.4, 55.2, 55.1, 51.7, 31.8, 28.8, 25.8, 18.2, –4.29, –4.37.

HRMS (ESI): Calcd for C45H54O9SiNa [(M+Na)+] 789.3401, found 789.3429.

Optically Active: Diester (+)-9

<Peak Report>
PDA Chart 220 nm
Peak Retention time  Area    Height  Area%
1    23.265    6422.76    9432    0.617
2    26.131    103514073   1472524    99.383

DAICEL CHIRALCEL OD-H, n-hexane/i-PrOH = 100/1, Flow rate 1.0 mL/min, 220 nm

Racemic: Diester (+)-9

<Peak Report>
PDA Chart 220 nm
Peak Retention time  Area    Height  Area%
1    22.287    58026440    981596    40.916
2    26.120    57299635    891929    50.184

DAICEL CHIRALCEL OD-H, n-hexane/i-PrOH = 100/1, Flow rate 1.0 mL/min, 220 nm
II. Total Synthesis of Teadenol A (1)

Synthesis of Alcohol S14

To a solution of 9 (7.00 mg, 9.13 mmol) in a mixture of CH$_2$Cl$_2$ (180 mL) and phosphate buffer (pH 7, 60 mL) was added DDQ (4.14 g, 18.3 mmol) at 0 °C. The resulting mixture was stirred at room temperature for 1.5 hours. Then the reaction mixture was quenched with saturated aqueous NaHCO$_3$ and extracted with CH$_2$Cl$_2$. The organic layer was washed with brine, dried over anhydrous Na$_2$SO$_4$ and evaporated under reduced pressure. The residue was purified by column chromatography (silica gel, n-hexane/EtOAc = 4/1 to 3/1) to afford S14 (760 mg, 98%) as a colorless oil.

[$\alpha$]$_D^{25}$ = –13.1 (c 1.05, CHCl$_3$).

IR (film, cm$^{-1}$): 2953, 2932, 2859, 1742, 1719, 1701, 1605, 1589, 1431.

$^1$H NMR (500 MHz, CDCl$_3$, $\delta$): 7.41-7.29 (m, 10H), 6.97 (d, $J$ = 7.9 Hz, 1H), 6.27 (d, $J$ = 2.3 Hz, 1H), 6.07 (d, $J$ = 2.3 Hz, 1H), 5.87 (dtt, $J$ = 11.3, 10.2, 5.7 Hz, 1H), 5.28 (dd, $J$ = 17.0, 1.1 Hz, 1H), 5.19 (dd, $J$ = 10.2, 1.1 Hz, 1H), 4.99 (s, 2H), 4.98 (s, 2H), 4.67-4.51 (m, 3H), 3.59 (s, 3H), 3.21 (d, $J$ = 16.4 Hz, 1H), 3.16 (d, $J$ = 16.4 Hz, 1H), 2.96 (dd, $J$ = 13.0, 6.5 Hz, 1H), 2.92 (dd, $J$ = 13.0, 5.7 Hz, 1H), 2.63 (brs 1H), 0.99 (s, 9H), 0.20 (s, 3H), 0.18 (s, 3H).

$^{13}$C NMR (125 MHz, CDCl$_3$, $\delta$): 171.3, 166.4, 158.5, 158.4, 155.3, 146.81, 146.75, 136.8, 136.6, 132.0, 128.6, 127.9, 127.2, 125.6, 117.9, 117.8, 108.6, 98.2, 93.4, 70.2, 70.1, 68.9, 68.8, 65.4, 52.0, 51.9, 32.1, 30.4, 25.7, 18.2, –4.14, –4.30.

HRMS (ESI): Calcd for C$_{37}$H$_{46}$O$_8$SiNa [(M+Na)$^+$] 669.2864, found 669.2854.
Synthesis of Dihydropyranone 20

To a solution of S14 (11.1 g, 17.2 mmol) in CH$_2$Cl$_2$ (340 mL) was added TsOH·H$_2$O (326 mg, 1.72 mmol) at room temperature. The resulting mixture was stirred at the same temperature for 1 hour. Then the reaction mixture was quenched with saturated aqueous NaHCO$_3$ and extracted with CH$_2$Cl$_2$. The organic layer was washed with brine, dried over anhydrous Na$_2$SO$_4$ and evaporated under reduced pressure. The crude material including S15 was applied to the following reaction without further purification.

To a solution of the crude material including S15 in THF (170 mL) were added Pd(PPh$_3$)$_4$ (1.99 g, 1.72 mmol) and morpholine (1.6 mL, 19 mmol) at 0 °C. The resulting mixture was stirred at room temperature for 4 hours. Then the reaction mixture was quenched with 2 M HCl and extracted with EtOAc. The organic layer was dried over anhydrous Na$_2$SO$_4$ and evaporated under reduced pressure. The residue was purified by column chromatography (silica gel, n-hexane/EtOAc = 3/1 to 3/2) to afford carboxylic acid 20 (8.80 g, 89%, 2 steps) as a colorless solid.

[$\alpha$]$_D^{25}$ $-$45.6 (c 1.13, CHCl$_3$).

IR (film, cm$^{-1}$): 3034, 2955, 2932, 2885, 1742, 1719, 1605, 1589, 1431.

$^1$H NMR (500 MHz, CDCl$_3$, $\delta$): 7.41-7.29 (m, 10H), 7.00 (d, $J$ = 2.8 Hz, 1H), 6.29 (d, $J$ = 2.3 Hz, 1H), 6.09 (d, $J$ = 2.3 Hz, 1H), 5.30-5.24 (1H, m), 5.00 (s, 2H), 4.99 (s, 2H), 3.23-3.14 (m, 2H), 3.11-3.03 (m, 2H), 0.96 (s, 9H), 0.20 (s, 3H), 0.18 (s, 3H).

$^{13}$C NMR (125 MHz, CDCl$_3$, $\delta$): 169.5, 168.1, 159.1, 158.6, 155.5, 138.8, 136.7, 136.6, 128.63, 128.57, 128.04, 127.97, 127.3, 127.2, 123.8, 106.2, 98.20, 98.18, 93.6, 93.5, 78.4, 70.20, 70.17, 70.13, 29.1, 28.6, 25.7, 18.2, $-$4.28.

HRMS (ESI): Calcd for C$_{33}$H$_{38}$O$_7$SiNa [(M+Na)$^+$] 597.2304, found 597.2279.
Synthesis of Allyl Carbonate S17

To a solution of 20 (8.80 g, 15.3 mmol) in THF (150 mL) were added Et$_3$N (3.2 mL, 17 mmol) and methyl chloroformate (1.3 mL, 17 mmol) at 0 °C. After 1 hour, the reaction mixture was filtered through a pad of Celite and washed with THF (50 mL). To the resulting filtrate was added MeOH (50 mL) and NaBH$_4$ (2.32 g, 61.2 mmol) at −78 °C. After 0.5 hours, the resulting mixture was warmed up to −40 °C and stirred at the same temperature for 0.5 hours. The reaction mixture was quenched with saturated aqueous NH$_4$Cl and extracted with EtOAc. The organic layer was washed with brine, dried over anhydrous Na$_2$SO$_4$ and evaporated under reduced pressure. The crude material including S16 was applied to the following reaction without further purification.

To a solution of the crude material including S16 in CH$_2$Cl$_2$ (150 mL) were added pyridine (7.4 mL, 92 mmol) and methyl chloroformate (3.5 mL, 46 mmol) at −20 °C. The resulting mixture was stirred at the same temperature for 4 hours. The reaction mixture was quenched with saturated aqueous NH$_4$Cl and extracted with EtOAc. The organic layer was washed with brine, dried over anhydrous Na$_2$SO$_4$ and evaporated under reduced pressure. The residue was purified by column chromatography (silica gel, n-hexane/EtOAc = 4/1) to afford S17 (9.20 g, 97%, 2 steps) as a colorless oil.

[α]$_D^{26}$ −21.5 (c 1.18, CHCl$_3$).

IR (film, cm$^{-1}$): 2955, 2932, 2859, 1742, 1605, 1589, 1431.

$^1$H NMR (500 MHz, CDCl$_3$, δ): 7.42-7.30 (m, 10H), 6.28 (d, $J$ = 2.3 Hz, 1H), 6.08 (d, $J$ = 2.3 Hz, 1H), 5.86-5.82 (m, 1H), 5.17 (brs, 1H), 5.00 (s, 2H), 4.98 (s, 2H), 4.47 (d, $J$ = 13.0 Hz, 1H), 4.41 (d, $J$ = 13.0 Hz, 1H), 3.76 (s, 3H), 2.96 (dd, $J$ = 13.0, 6.2 Hz, 1H), 3.00 (dd, $J$ = 13.0, 8.5 Hz, 1H), 2.94 (d, $J$ = 21.0 Hz 1H), 2.83 (d, $J$ = 21.0 Hz 1H), 0.96 (s, 9H), 0.18 (s, 3H), 0.16 (s, 3H).

$^{13}$C NMR (125 MHz, CDCl$_3$, δ): 168.6, 158.8, 158.6, 155.4, 155.3, 136.8, 136.7, 128.6, 128.5, 127.95, 127.86, 127.3, 127.2, 124.9, 107.1, 98.2, 93.5, 78.2, 70.1, 68.4, 54.9, 30.6, 29.5, 25.6, 18.1, −4.23, −4.33.

HRMS (ESI): Calcd for C$_{35}$H$_{42}$O$_8$SiNa [(M+Na)$^+$] 641.2511, found 641.2541.
Synthesis of Lactone 21

To a solution of S17 (980 mg, 1.58 mmol) in THF (16 mL) were added AcOH (0.18 mL, 3.2 mmol) and TBAF (1.7 mL, 1 M solution in THF) at 0 °C. The resulting mixture was stirred at the same temperature for 0.5 hours. Then the reaction mixture was quenched with saturated aqueous NH₄Cl and extracted with EtOAc. The organic layer was washed with 1 M HCl, dried over anhydrous Na₂SO₄ and evaporated under reduced pressure. The crude material including 7 was applied to the following reaction without further purification.

To a solution of the crude material including 7 in CH₂Cl₂ (80 mL) was added Pd(PPh₃)₄ (183 mg, 0.158 mmol) at room temperature. The resulting mixture was stirred at the same temperature for 4 hours. Then the reaction mixture was evaporated under reduced pressure. The residue was purified by column chromatography (silica gel, n-hexane/CHCl₃/EtOAc = 5/4/1) to afford 21 (400 mg, 59%, 2 steps) as a colorless solid.

\[ [\alpha]\]_D^{25} +88.8 (c 0.94, CHCl₃).

IR (ATR, cm⁻¹): 1725, 1621, 1594, 1500.

¹H NMR (500 MHz, CDCl₃, δ): 7.43-7.29 (m, 10H), 6.25 (d, J = 2.3 Hz, 1H), 6.14 (d, J = 2.3 Hz, 1H), 5.93 (d, J = 1.7 Hz, 1H), 5.01 (s, 2H), 4.98 (s, 2H), 4.08 (quintet, J = 2.8 Hz, 1H), 4.34 (d, J = 1.7 Hz, 1H), 3.16 (dd, J = 17.6, 2.3 Hz, 1H), 2.97 (dd, J = 17.6, 5.7 Hz, 1H), 2.16 (d, J = 1.7 Hz, 3H).

¹³C NMR (125 MHz, CDCl₃, δ): 163.6, 158.7, 157.8, 154.5, 154.1, 136.7, 128.54, 128.52, 128.0, 127.9, 127.5, 127.2, 119.3, 99.7, 94.4, 94.2, 71.1, 70.1, 70.0, 69.1, 23.9, 20.7.

Synthesis of Ester 22

To a solution of 21 (450 mg, 1.05 mmol) in THF (10 mL) were added HMPA (0.37 mL, 2.1 mmol) and KHMDS (4.2 mL, 2.1 mmol, 0.5 M solution in toluene) at −78 °C. After 1 hour, Tf₂NPh (563 mg, 1.58 mmol) was added at −78 °C. After 1 hour, the resulting mixture was warm up to 0 °C and stirred at the same temperature for 1 hour. Then the reaction mixture was quenched with saturated aqueous NH₄Cl and extracted with EtOAc. The organic layer was dried over anhydrous Na₂SO₄ and evaporated under reduced pressure. The crude material including S18 was applied to the following reaction without further purification.

To a solution of the crude material including S18 in a 9:1 mixture of MeOH and DMF (total 10 mL) were added Pd(PPh₃)₄ (121 mg, 0.105 mmol) and Et₃N (440 µL, 3.15 mmol) at room temperature. The resulting mixture was stirred at the same temperature under ordinary carbon monoxide pressure (balloon) for 2 hours. Then the reaction mixture was quenched with saturated aqueous NH₄Cl and extracted with EtOAc. The organic layer was dried over anhydrous Na₂SO₄ and evaporated under reduced pressure. The residue was purified by column chromatography (n-hexane/CHCl₃/EtOAc = 50/50/1 to 10/10/1) to afford 22 (323 mg, 65%) as a colorless solid.

[α]D²² +320.5 (c 0.50, CHCl₃).

IR (film, cm⁻¹): 2922, 2851, 1734, 1719, 1595, 1499, 1458.

¹H NMR (500 MHz, CDCl₃, δ): 7.46-7.28 (m, 10H), 6.64 (s, 1H), 6.24 (d, J = 2.3 Hz, 1H), 6.17 (d, J = 2.3 Hz, 1H), 5.38 (s, 1H), 5.31 (s, 1H), 4.99 (s, 2H), 4.96 (s, 2H), 4.56 (brs, 1H), 4.50-4.46 (m, 1H), 3.79 (s, 3H), 3.18 (dd, J = 17.8, 2.3 Hz, 1H), 2.94 (dd, J = 17.8, 5.2 Hz, 1H).

¹³C NMR (125 MHz, CDCl₃, δ): 163.6, 158.7, 157.8, 154.5, 154.1, 136.7, 128.54, 128.52, 128.0, 127.9, 127.5, 127.2, 119.3, 99.7, 94.4, 94.2, 71.1, 70.1, 70.0, 69.1, 23.9, 20.7.

Synthesis of Teadenol A (1)

To a solution of 22 (160 mg, 0.340 mmol) in CH$_2$Cl$_2$ (10 mL) was added BCl$_3$ (1.4 mL, 1.4 mmol, 1 M solution in CH$_2$Cl$_2$) at –78 °C. The resulting mixture was stirred at the same temperature for 1 hour. Then the reaction mixture was quenched with saturated aqueous NaHCO$_3$ and extracted with EtOAc. The organic layer was washed with brine, dried over anhydrous Na$_2$SO$_4$ and evaporated under reduced pressure. The crude material including S19 was applied to the following reaction without further purification.

To a solution of the crude material including S19 in THF (3.5 mL) was added TMSOK (131 mg, 1.02 mmol) at room temperature. The resulting mixture was stirred at the same temperature for 15 minutes. The reaction mixture was quenched with 1 M HCl and extracted with EtOAc. The organic layer was dried over anhydrous Na$_2$SO$_4$ and evaporated under reduced pressure. The residue (124 mg) was purified by column chromatography (ODS, H$_2$O/CH$_3$CN = 1/0 to 1/1) and preparative HPLC (Cosmosil 20D x 250 mm, gradient, 0% to 50% MeOH in H$_2$O, for 120 min, minute ramp, λ = 254 nm, flow rate; 3 mL/min) to afford 1 (7.3 mg, 8%, 2 steps) as a colorless solid.

[α]$_D^{22}$ +451 (c 0.12, DMSO). Lit: [α]$_D^{21}$ +468 (c 0.15, DMSO). 4.

IR (ATR, cm$^{-1}$): 3608, 3496, 3261, 1721, 1623, 1613, 1525, 1476.

$^1$H NMR (500 MHz, DMSO-d$_6$, δ): 9.37 (s, 1H), 9.03 (s, 1H), 5.69 (s, 1H), 6.57 (s, 1H), 5.97 (d, J = 2.3 Hz, 1H), 5.70 (d, J = 2.3 Hz, 1H), 5.45 (brs, 1H), 5.33 (brs, 1H), 4.63 (s, 1H), 4.43 (t, J = 3.4 Hz, 1H), 2.81 (d, J = 3.4 Hz, 2H).

$^{13}$C NMR (125 MHz, DMSO-d$_6$, δ): 163.1, 156.5, 156.3, 154.6, 144.0, 136.5, 118.0, 110.1, 96.8, 95.5, 94.2, 70.9, 70.8, 24.0.

HRMS (ESI): Calcd for C$_{14}$H$_{13}$O$_6$ [(M+H)$^+$] 277.0712, found 277.0707.

III. Total Synthesis of Teadenol B (2)

Synthesis of Carboxylic Acid S20

To a solution of 9 (19.5 g, 25.4 mmol) in THF (100 mL) were added Pd(PPh₃)₄ (2.94 g, 2.54 mmol) and pyrrolidine (2.3 mL, 28 mmol) at 0 °C. The resulting mixture was stirred at room temperature for 1 hour. Then the reaction mixture was quenched with 1 M HCl and extracted with EtOAc. The organic layer was washed with brine, dried over anhydrous Na₂SO₄ and evaporated under reduced pressure. The residue was purified by column chromatography (silica gel, n-hexane/EtOAc = 1/1) to afford S20 (18.0 g, 97%) as a yellow amorphous.

\[ \alpha_d^{24} +15.9 (c 1.12, \text{CHCl}_3) \]

IR (ATR, cm⁻¹): 2950, 2929, 2855, 1739, 1690, 1701, 1603, 1584, 1511, 1432.

\(^1\text{H NMR (500 MHz, CDCl}_3, \delta)\): 7.41-7.29 (m, 10H), 7.11 (d, \(J = 8.5\) Hz, 2H), 6.99 (d, \(J = 9.1\) Hz, 1H), 6.79 (d, \(J = 8.5\) Hz, 2H), 6.20 (d, \(J = 2.3\) Hz, 1H), 6.03 (d, \(J = 2.3\) Hz, 1H), 4.99 (s, 2H), 4.89 (q, \(J = 11.3\) Hz, 2H), 4.44 (d, \(J = 11.3\) Hz, 1H), 4.50-4.39 (m, 1H), 4.23 (d, \(J = 11.3\) Hz, 1H), 3.76 (s, 3H), 3.55 (s, 3H), 3.06 (dd, \(J = 13.0, 5.7\) Hz, 1H), 2.91 (dd, \(J = 13.0, 9.1\) Hz, 1H), 2.80 (s, 2H), 0.98 (s, 9H), 0.17 (s, 3H), 0.15 (s, 3H).

\(^{13}\text{C NMR (125 MHz, CDCl}_3, \delta)\): 171.9, 170.7, 159.0, 158.5, 158.3, 155.3, 148.2, 136.9, 136.8, 130.3, 129.3, 128.6, 128.5, 127.94, 127.85, 127.4, 127.3, 126.6, 113.6, 108.4, 98.2, 93.4, 74.3, 70.7, 70.1, 70.0, 55.2, 51.8, 31.4, 28.7, 25.8, 18.2, −4.25, −4.38.

HRMS (ESI): Calcd for C₄₂H₅₀O₉SiNa [(M+Na)^+] 749.3095, found 749.3116.
Synthesis of Alcohol S21

To a solution of S20 (18.0 g, 1.95 mmol) in THF (250 mL) were added Et3N (5.2 mL, 37 mmol) and methyl chloroformate (2.1 mL, 27 mmol) at 0 °C. The resulting mixture was stirred at the same temperature for 1 hour. The reaction mixture was filtered through a pad of Celite and washed with THF (100 mL). To the resulting filtrate was added MeOH (80 mL) and NaBH4 (3.75 g, 99.2 mmol) at –78 °C. After 0.5 hours, the resulting mixture was warmed up to –40 °C and stirred at the same temperature for 0.5 hours. The reaction mixture was quenched with saturated aqueous NH4Cl and extracted with EtOAc. The organic layer was washed with brine, dried over anhydrous Na2SO4 and evaporated under reduced pressure. The residue was purified by column chromatography (silica gel, n-hexane/EtOAc = 3/1) to afford S21 (14.9 g, 84%) as a colorless oil.

[α]D25 +39.3 (c 1.26, CHCl3).

IR (film, cm⁻¹): 3450, 3032, 2953, 2930, 2859, 1736, 1605, 1589, 1512, 1435.

1H NMR (500 MHz, CDCl3, δ): 7.41–7.29 (m, 10H), 7.13 (d, J = 8.5 Hz, 2H), 6.79 (d, J = 8.5 Hz, 2H), 6.22 (d, J = 2.3 Hz, 1H), 6.03 (d, J = 2.3 Hz, 1H), 5.58 (d, J = 9.1 Hz, 1H), 4.99 (s, 2H), 4.95 (d, J = 11.3 Hz, 1H), 4.91 (d, J = 11.3 Hz, 1H), 4.40 (d, J = 11.3 Hz, 1H), 4.32 (ddd, J = 9.3, 9.1, 5.1 Hz, 1H), 4.22 (d, J = 11.3 Hz, 1H), 3.97 (s, 2H), 3.76 (s, 3H), 3.53 (s, 3H), 3.01 (dd, J = 13.0, 5.1 Hz, 1H), 2.83 (dd, J = 13.0, 9.3 Hz, 1H), 2.73 (d, J = 16.2 Hz, 1H), 2.55 (d, J = 16.2, Hz, 1H), 0.99 (s, 9H), 0.17 (s, 3H), 0.16 (s, 3H).

13C NMR (125 MHz, CDCl3, δ): 172.1, 158.8, 158.5, 158.1, 155.2, 137.0, 136.9, 134.3, 132.5, 130.9, 129.2, 128.5, 128.4, 127.9, 127.8, 127.25, 127.17, 113.5, 109.6, 98.3, 93.6, 74.1, 70.1, 70.0, 69.9, 67.4, 55.1, 51.7, 33.0, 29.3, 25.8, 18.1, –4.29, –4.34.

HRMS (ESI): Calcd for C42H52O8SiNa [(M+Na)⁺] 735.3353, found 735.3324.
Synthesis of Phenol 8

To a solution of S21 (14.9 g, 20.9 mmol) in CH2Cl2 (200 mL) were added pyridine (10.0 mL, 125 mmol) and methyl chloroformate (4.8 mL, 63 mmol) at −20 °C. The resulting mixture was stirred at the same temperature for 4 hours. Then the reaction mixture was quenched with saturated aqueous NH4Cl and extracted with EtOAc. The organic layer was washed with brine, dried over anhydrous Na2SO4 and evaporated under reduced pressure. The crude material including S22 was applied to the following reaction without further purification.

To a solution of crude material including S22 in THF (200 mL) were added AcOH (2.3 mL, 39 mmol) and TBAF (22.0 mL, 22 mmol, 1 M solution in THF) at 0 °C. The resulting mixture was stirred at the same temperature for 0.5 hours. Then the reaction mixture was quenched with 1 M HCl and extracted with EtOAc. The organic layer was dried over anhydrous Na2SO4 and evaporated under reduced pressure. The residue was purified by column chromatography (silica gel, n-hexane/EtOAc = 4/1 to 3/2) to afford 8 (11.1 g, 86%, 2 steps) as a colorless oil.

[α]D^25 +57.4 (c 1.20, CHCl3).

IR (film, cm⁻¹): 3290, 2955, 2395, 1736, 1611, 1589, 1512, 1456.

1H NMR (500 MHz, CDCl3, δ): 7.93 (s, 1H), 7.41-7.29 (m, 10H), 7.14 (d, J = 8.5 Hz, 2H), 6.82 (d, J = 8.5 Hz, 2H), 6.27 (d, J = 2.3 Hz, 1H), 6.21 (d, J = 2.3 Hz, 1H), 5.75 (d, J = 8.5 Hz, 1H), 5.00 (s, 2H), 4.95 (s, 2H), 4.63 (d, J = 12.5 Hz, 1H), 4.58 (d, J = 12.5 Hz, 1H), 4.51 (d, J = 11.3 Hz, 1H), 4.33 (ddd, J = 8.5, 8.5, 2.3 Hz, 1H), 4.27 (d, J = 11.3 Hz, 1H), 3.79 (s, 3H), 3.78 (s, 3H), 3.57 (s, 3H), 3.09 (d, J = 15.9 Hz, 1H), 2.97 (dd, J = 13.0, 2.3 Hz, 1H), 2.84 (dd, J = 13.0, 8.5 Hz, 1H), 2.80 (d, J = 15.9, Hz, 1H).

13C NMR (125 MHz, CDCl3, δ): 170.4, 159.2, 159.1, 157.8, 157.4, 155.3, 136.93, 136.89, 133.6, 130.2, 129.5, 129.0, 128.5, 128.4, 127.9, 127.8, 127.5, 127.2, 113.7, 106.2, 95.8, 93.0, 70.74, 70.68, 70.0, 69.9, 55.1, 54.8, 51.9, 33.2, 29.4.

Synthesis of Chromane 24

To a solution of 8 (9.20 g, 14.0 mmol) in THF (280 mL) were added AcOH (0.80 mL, 14 mmol) and Pd(PPh₃)₄ (1.62 g, 1.40 mmol) at room temperature. The resulting mixture was stirred at 60 °C for 1 hour. Then the reaction mixture was evaporated under reduced pressure. The residue was purified by column chromatography (silica gel, n-hexane/EtOAc = 4/1) to afford 24 (7.94 g, total 98%, dr = 6:1) as a colorless solid. The diastereomer ratio (dr) of 24 was determined by ¹H NMR spectrum.

[α]D 24 −45.6 (c 0.78, CHCl₃).
IR (film, cm⁻¹): 2920, 2853, 2395, 1736, 1612, 1593, 1508, 1431.
¹H NMR (500 MHz, CDCl₃, δ): 7.41-7.30 (m, 10H), 7.25 (d, J = 8.5 Hz, 2H), 6.86 (d, J = 8.5 Hz, 2H), 6.21 (d, J = 2.3 Hz, 1H), 6.15 (d, J = 2.3 Hz, 1H), 5.35 (s, 1H), 5.25 (s, 1H) 5.00 (d, J = 1.1 Hz, 2H), 4.97 (s, 2H), 4.62 (d, J = 11.3 Hz, 1H), 4.52 (d, J = 11.3 Hz, 1H), 4.51 (d, J = 6.8 Hz, 1H), 3.79 (ddd, J = 7.9, 5.1 Hz, 1H), 3.79 (s, 3H), 3.65 (s, 3H), 3.14 (d, J = 15.6 Hz, 1H), 3.09 (d, J = 15.6 Hz, 1H), 3.03 (dd, J = 16.4, 5.1 Hz, 1H), 2.63 (dd, J = 16.4, 7.9 Hz, 1H).
¹³C NMR (125 MHz, CDCl₃, δ): 171.5, 159.2, 158.7, 157.6, 154.7, 139.3, 137.0, 136.9, 130.1, 129.4, 128.6, 128.5, 127.95, 127.86, 127.5, 127.2, 117.9, 113.8, 101.7, 94.3, 93.6, 79.8, 71.3, 70.6, 70.1, 69.9, 55.3, 51.9, 38.3, 24.9.
HRMS (ESI) Calcd for C₃₆H₃₆O₇Na [(M+Na)⁺] 603.2351, found 603.2364.

500 MHz NMR spectrum of Chromane 26 (dr = 6:1)
Synthesis of Lactone 25

To a suspension of MgBr₂·OEt₂ (8.89 g, 34.4 mmol) in a mixture of Et₂O (25 mL) and CH₂Cl₂ (10 mL) were added a solution of 24 (2.00 g, 3.44 mmol) and Me₂S (7.5 mL, 100 mmol) at room temperature. The resulting mixture was stirred at the same temperature for 12 hours. Then the reaction mixture was quenched with saturated aqueous NH₄Cl and extracted with Et₂O. The organic layer was washed with brine, dried over anhydrous Na₂SO₄ and evaporated under reduced pressure. The crude material including S²₃ was applied to the following reaction without further purification.

To a solution of the crude material including S²₃ in toluene (20 mL) was added TsOH·H₂O (65.0 mg, 0.344 mmol). The resulting mixture was stirred at 100 °C for 1 hour. Then the reaction mixture was quenched with saturated aqueous NaHCO₃ and extracted with EtOAc. The organic layer was washed with brine, dried over anhydrous Na₂SO₄ and evaporated under reduced pressure. The residue was purified by column chromatography (silica gel, n-hexane/EtOAc = 4/1) to afford 25 (965 mg, 65%, 2 steps) as a colorless solid.

$\left[\alpha\right]_D^{24} = -139.9 \ (c \ 0.68, \ CHCl₃)$.

IR (ATR, cm⁻¹): 1720, 1585, 1489, 1435, 1381.

¹H NMR (500 MHz, CDCl₃, δ): 7.30-7.24 (m, 10H), 6.29 (d, J = 2.3 Hz, 1H), 6.21 (d, J = 1.7 Hz, 1H), 5.89 (t, J = 1.7 Hz, 1H), 5.05 (d, J = 11.9 Hz, 1H), 5.02 (d, J = 11.9 Hz, 1H), 5.01 (s, 2H), 4.50 (td, J = 10.8, 5.7 Hz, 1H), 4.23 (d, J = 10.8 Hz, 1H), 3.29 (dd, J = 15.9, 6.2 Hz, 1H), 2.83 (dd, J = 15.9, 10.8 Hz, 1H), 2.17 (s, 3H).

¹³C NMR (125 MHz, CDCl₃, δ): 162.7, 159.1, 157.8, 157.3, 154.4, 136.60, 136.58, 128.6, 128.5, 128.0, 127.9, 127.4, 126.9, 116.8, 101.6, 94.6, 94.5, 74.0, 72.3, 70.1, 69.9, 26.5, 17.5.

To a solution of HMPA (0.78 mL, 4.5 mmol) in THF (20 mL) were added KHMSD (9.0 mL, 4.5 mmol, 0.5 M solution in toluene) and a solution of 25 (965 mg, 2.25 mmol) in THF (20 mL) at –78 °C. After 1 hour, a solution of PhNTf₂ (1.21 g, 3.38 mmol) in THF (5 mL) was added at –78 °C. After 1 hour, the resulting mixture was warmed up to 0 °C and stirred at the same temperature for 1 hour. Then the reaction mixture was quenched with phosphate buffer (pH 6.4) and extracted with EtOAc. The organic layer was dried over anhydrous Na₂SO₄ and evaporated under reduced pressure. The crude material including S24 was applied to the following reaction without further purification.

To a solution of the crude material including S24 in a 9:1 mixture of MeOH and DMF (total 20 mL) were added Pd(PPh₃)₄ (260 mg, 0.225 mmol) and Et₃N (0.94 mL, 0.68 mmol) at room temperature. The resulting mixture was stirred at the same temperature under ordinary hydrogen pressure (balloon) for 15 hours. Then the reaction mixture was quenched with saturated aqueous NH₄Cl and extracted with EtOAc. The organic layer was washed with brine, dried over anhydrous Na₂SO₄ and evaporated under reduced pressure. The residue was purified by column chromatography (silica gel, n-hexane/CHCl₃/EtOAc = 1/1/0.1) to afford 26 (338 mg, 32%, 2 steps) as a colorless solid.

[a]D² = –16.9 (c 0.42, CHCl₃).

IR (ATR, cm⁻¹): 2921, 2852, 1720, 1618, 1592, 1500, 1434.

¹H NMR (500 MHz, CDCl₃, δ): 7.45-7.30 (m, 10H), 6.65 (s, 1H), 6.29 (d, J = 2.3 Hz, 1H), 6.25 (d, J = 2.3 Hz, 1H), 5.60 (brs, 1H), 5.25 (brs, 1H), 5.02 (s, 1H), 5.02 (d, J = 11.3 Hz, 1H), 4.99 (d, J = 11.3 Hz, 1H), 4.43 (dt, J = 10.8, 2.3 Hz, 1H), 4.12 (td, J = 10.2, 6.2 Hz, 1H), 3.84 (s, 3H), 3.40 (dd, J = 16.5, 6.2 Hz, 1H), 2.83 (dd, J = 16.5, 10.2 Hz, 1H).

¹³C NMR (125 MHz, CDCl₃, δ): 162.8, 159.0, 157.7, 154.6, 143.0, 136.8, 136.7, 136.3, 128.6, 128.5, 128.0, 127.9, 127.5, 127.2, 113.7, 112.9, 101.8, 94.5, 94.1, 73.5, 72.0, 70.2, 70.0, 52.5, 26.2.

Synthesis of Teadenol B (2)

To a solution of 26 (300 mg, 0.638 mmol) in CH₂Cl₂ (30 mL) were added PhMe₅ (567 mg, 3.83 mmol) and BCl₃ (2.6 mL, 2.6 mmol, 1 M solution in CH₂Cl₂) at -78 °C. The resulting mixture was stirred for 5 hours at the same temperature. Then the reaction mixture was quenched with saturated aqueous NaHCO₃, acidified with 2 M HCl and extracted with EtOAc. The organic layer was dried over anhydrous Na₂SO₄ and evaporated under reduced pressure. The crude material including S25 was applied to the following reaction without further purification.

To a solution of the crude material including S25 in MeOH (15 mL) was added a solution of LiOH·H₂O (268 mg, 6.38 mmol) in H₂O (15 mL) at room temperature. The resulting mixture was stirred at the same temperature for 15 minutes. The reaction mixture was quenched with 2 M HCl and extracted with EtOAc. The residue (202 mg) was purified by preparative HPLC (Cosmosil 20D x 250 mm, gradient, 20% to 80% MeOH in H₂O, for 120 min, minute ramp, λ = 254 nm, flow rate; 3 mL/min) to afford 2 (8.4 mg, 5%, 2 steps) as a colorless solid.

[α]D₂₀ –27.0 (c 0.20, CHCl₃). Lit: [α]D₂₀ –27.7 (c 0.18, MeOH)

IR (ATR, cm⁻¹): 3431, 1677, 1598, 1454.

¹H NMR (500 MHz, CD₃OD, δ): 6.62 (s, 1H), 5.95 (d, J = 2.3, 1H), 5.90 (d, J = 2.3 Hz, 1H), 5.51 (brs, 1H), 5.32 (brs, 1H), 4.43 (dt, J = 10.8, 2.3 Hz, 1H), 4.35 (td, J = 10.8, 2.3 Hz, 1H), 4.00 (td, J = 10.2, 6.2 Hz, 1H), 3.19 (dd, J = 15.9, 6.2 Hz, 1H), 2.65 (dd, J = 15.9, 10.2 Hz, 1H).

¹³C NMR (125 MHz, CD₃OD, δ): 164.2, 156.9, 156.5, 154.7, 143.2, 137.3, 112.2, 112.1, 98.7, 95.6, 94.3, 73.7, 71.9, 25.7.

HRMS (ESI) Calculated for C₁₄H₁₂O₆Na [(M+Na)⁺] 299.0532, found 299.0526.


500 MHz NMR spectrum of crude material of teadenol B (2)
IV. NMR Spectra Data
Filename         = HOo-140702-1-H-5.jdf
Author           = delta
Experiment       = single_pulse.ex2
Sample_Id        = 1
Solvent          = CHLOROFORM-D
Creation_Time    =  2-JUL-2014 13:05:25
Revision_Time    = 10-SEP-2015 17:37:30
Current_Time     = 10-SEP-2015 17:38:24
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X_Points         = 16384
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X_Sweep          = 9.28677563[kHz]
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Irr_Freq         = 495.13191398[MHz]
Irr_Offset       = 5[ppm]
Tri_Domain       = 1H
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Tri_Offset       = 5[ppm]
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Irr_Mode         = Off
Tri_Mode         = Off
Dante_Presat     = FALSE
Initial_Wait     = 1[s]
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Author           = delta
Experiment       = single_pulse.ex2
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Creation_Time    = 30-AUG-2014 22:41:06
Revision_Time    = 29-DEC-2015 12:57:44
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X_Acq_Duration   = 1.76422912[s]
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X_Freq           = 495.13191398[MHz]
X_Offset         = 5[ppm]
X_Points         = 16384
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X_Resolution     = 0.5668198[Hz]
X_Sweep          = 9.28677563[kHz]
Irr_Domain       = 1H
Irr_Freq         = 495.13191398[MHz]
Irr_Offset       = 5[ppm]
Tri_Domain       = 1H
Tri_Freq         = 495.13191398[MHz]
Tri_Offset       = 5[ppm]
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Irr_Mode         = Off
Tri_Mode         = Off
Dante_Presat     = FALSE
Initial_Wait     = 1[s]
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MeO
OMe
OH
OMe
OH
S8
(from
S5)
R
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OPMB
CO
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CO
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Me
S20

S
O

Abundance
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Author           = delta
Experiment       = single_pulse.ex2
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Creation_Time    = 21-NOV-2014 17:18:13
Revision_Time    = 29-DEC-2015 17:55:44
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X_Acq_Duration   = 1.76422912[s]
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Irr_Freq         = 495.13191398[MHz]
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**Experiment Details**

- **Filename**: HOo-141225-1-6.jdf
- **Author**: delta
- **Experiment**: single_pulse.ex2
- **Sample_Id**: S#596102
- **Solvent**: CHLOROFORM-D
- **Creation_Time**: 25-DEC-2014 16:16:56
- **Revision_Time**: 17-SEP-2015 15:46:37
- **Current_Time**: 17-SEP-2015 15:47:21
- **Comment**: single_pulse
- **Data_Format**: 1D COMPLEX
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- **Dim_Title**: 1H
- **Dim_Units**: [ppm]
- **Dimensions**: X
- **Site**: ECA 500
- **Spectrometer**: DELTA2_NMR
- **Field_Strength**: 11.62926421[T] (500[MHz])
- **X_Acq_Duration**: 1.76422912[s]
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- **X_Freq**: 495.13191398[MHz]
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- **X_Points**: 16384
- **X_Prescans**: 1
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- **X_Sweep**: 9.28677563[kHz]
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- **Irr_Freq**: 495.13191398[MHz]
- **Irr_Offset**: 5[ppm]
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- **Tri_Freq**: 495.13191398[MHz]
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- **Clipped**: FALSE
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- **Temp_Get**: 24.9[dC]
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- **X_Acq_Time**: 1.76422912[s]
- **X_Angle**: 45[deg]
- **X_Atn**: 4[dB]
- **X_Pulse**: 4.08[us]
- **Irr_Mode**: Off
- **Tri_Mode**: Off
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- **Repetition_Time**: 6.76422912[s]

**Chemical Structures**

![Chemical Structures Diagram]
Filename         = HOo-150319-2-5.jdf
Author           = delta
Experiment       = single_pulse.ex2
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Solvent          = METHANOL-D3
Creation_Time    = 19-MAR-2015 17:40:43
Revision_Time    = 25-SEP-2015 13:34:24
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X_Resolution     = 0.5668198[Hz]
X_Sweep          = 9.28677563[kHz]
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Irr_Freq         = 495.13191398[MHz]
Irr_Offset       = 5[ppm]
Tri_Domain       = 1H
Tri_Freq         = 495.13191398[MHz]
Tri_Offset       = 5[ppm]
Clipped          = FALSE
Scans            = 8
Total_Scans      = 8
Relaxation_Delay = 5[s]
Recvr_Gain       = 46
Temp_Get         = 24.9[dC]
X_90_Width       = 8.16[us]
X_Acq_Time       = 1.76422912[s]
X_Angle          = 45[deg]
X_Atn            = 4[dB]
X_Pulse          = 4.08[us]
Irr_Mode         = Off
Tri_Mode         = Off
Dante_Presat     = FALSE
Initial_Wait     = 1[s]
Repetition_Time  = 6.76422912[s]