Synthetic Study of the C’D’E’ Ring System of Maitotoxin
via Furan Based Strategy

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### Abbreviations

<table>
<thead>
<tr>
<th>Ac</th>
<th>acetyl</th>
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<tr>
<td>acac</td>
<td>acetylacetonate</td>
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<td>AD</td>
<td>asymmetric dihydroxylation</td>
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<td>9-BBN</td>
<td>9-borabicyclo[3.3.1]nonane</td>
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<td>Bn</td>
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<td>DDQ</td>
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<td>(DHQ)$_2$PHAL</td>
<td>hydroquinine 1,4-phthalazinediyl diether</td>
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<td>DMAP</td>
<td>4-($N$-$N$-dimethylamino)pyridine</td>
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<td>DMDO</td>
<td>dimethyldioxirane</td>
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<td>$N$-$N$-dimethylformamide</td>
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<td>dr</td>
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<tr>
<td>MCPBA</td>
<td>meta-chloroperbenzoic acid</td>
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Me  methyl
MS  mass spectrometry
MS4A  molecular sieves 4 angstrom
n  normal
NAP  2-naphthylmethyl
NBS  N-bromosuccinimide
NMR  nuclear magnetic resonance
NOE  nuclear Overhauser effect
NOESY  nuclear Overhauser effect spectroscopy
p  para
pin  pinacolate
Ph  phenyl
PPTS  pyridinium para-toluenesulfonate
quant  quantitative
rt  room temperature
t  tertiary
TBAF  tetra-n-butylammonium fluoride
TBHP  tert-butyl hydroperoxide
TBS  tert-butyldimethylsilyl
TEMPO  2,2,6,6-tetramethylpiperidin-1-oxyl
TES  triethylsilyl
THF  tetrahydrofuran
TLC  thin-layer chromatography
TMS  trimethylsilyl
**General methods for organic syntheses.** All reactions sensitive to air or moisture were performed under argon atmosphere with dry glassware unless otherwise noted. The dehydrated solvents, CH₂Cl₂, tetrahydrofuran (THF), toluene, N,N-dimethylformamide (DMF) were used without further dehydration. TMSCl, pyridine, and 2,6-lutidine were distilled before use. Molecular sieves 4A (MS4A) were preactivated by heating in vacuo. PPTS and CuCO₃·Cu(OH)₂ were prepared according to the literature.⁠¹ All other chemicals were obtained from local vendors, and used as supplied unless otherwise stated. Thin-layer chromatography (TLC) was performed using precoated TLC glass plates (silica gel 60 F₂₅₄, 0.25-mm thickness) for the reaction analyses. For normal phase column chromatography, silica gel 60N (Kanto Chemical Co., Ltd., spherical, neutral, 100–210 μm) was used. For normal phase flash column chromatography, silica gel 60N (Kanto Chemical Co., Ltd., spherical, neutral, 40–50 μm) was used. Optical rotations were recorded on a JASCO P-1010 polarimeter. IR spectra were recorded on a FT/IR-4000 spectrometer (JASCO). ¹H NMR spectra were recorded on JNM ECA-600 or JNM ECS-400 spectrometer (JEOL) in 600 or 400 MHz, and ¹³C NMR spectra were recorded at 150 or 100 MHz. Chemical shifts were reported in ppm from tetramethylsilane (TMS) with reference to internal residual solvent [¹H NMR: CHCl₃ (7.26), C₆D₆H (7.16); ¹³C NMR: CDCl₃ (77.16), C₆D₆ (128.06)]. The following abbreviations are used to designate the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, brs = broad singlet. High resolution mass spectra (HRMS) were recorded on micrOTOF II (Bruker) ESI-TOF equipment.
**Bis-TBS ether 2.** Imidazole (1.02 g, 14.9 mmol) and TBSCl (2.02 g, 13.4 mmol) were added to a solution of diol **1** (2.02 g, 5.90 mmol) in DMF (6 mL) at 0 °C under argon atmosphere. The mixture was stirred at rt for 12 h. Additional imidazole (1.00 g, 15.9 mmol) and TBSCl (1.96 g, 13.0 mmol) were added to the mixture, and after stirring for 4 h, further imidazole (1.09 g, 16.0 mmol) and TBSCl (2.67 g, 17.7 mmol) were added. After stirring at rt for 2 h, the reaction mixture was warmed to 70 °C, stirred for 2 h, then warmed to 90 °C. The mixture was stirred for 50 min at 90 °C, quenched with MeOH, saturated aqueous NH4Cl, and H2O, diluted with EtOAc, and extracted with Et2O. The organic layer was washed with saturated aqueous NaCl, dried over anhydrous Na2SO4, filtered, and concentrated under reduced pressure. The residue was purified by flash silica gel column chromatography to give bis-TBS ether **2** (3.43 g, 6.16 mmol, quant).

**2:** [α]D15 +2.5 (c 1.16, CHCl3); Rf = 0.77 (hexane/EtOAc = 10/1); IR (neat) 3724, 3057, 2953, 2928, 2885, 2857, 2360, 1123, 1098, 853, 836 cm⁻1; ¹H NMR (400 MHz, CDCl3) δ 7.86–7.84 (m, 3H), 7.79 (s, 1H), 7.52–7.46 (m, 3H), 6.03 (dd, J = 17.4, 11.0 Hz, 1H), 5.39 (dd, J = 17.4, 1.8 Hz, 1H), 5.09 (dd, J = 11.0, 1.8 Hz, 1H), 4.75 (d, J = 11.7 Hz, 1H), 4.70 (J = 11.7 Hz, 1H), 3.99 (dd, J = 11.9, 4.6 Hz, 1H), 3.47 (d, J = 10.5 Hz, 1H), 3.44 (d, J = 10.5 Hz, 1H), 3.33 (dd, J = 11.9, 4.1 Hz, 1H), 1.99 (ddd, J = 11.9, 4.6, 4.1 Hz, 1H), 1.84 (ddd, J = 11.9, 11.9, 11.9, 1H), 1.43 (s, 3H), 1.12 (s, 3H), 0.93 (m, 9H), 0.88 (m, 9H), 0.09 (s, 3H), 0.08 (s, 3H), 0.04 (s, 3H), 0.02 (s, 3H). ¹³C NMR (100 MHz, CDCl3) δ 145.2, 136.2, 133.4, 133.1, 128.2, 128.0, 127.8, 126.3, 126.2, 125.9 (×2), 112.7, 80.5, 78.1, 76.1, 72.2, 68.0, 67.0, 31.2, 26.1, 25.8, 20.4, 18.41, 18.35, 18.0, −4.1, −4.95, −4.97, −5.2; HRESIMS m/z [M + Na]+ calcd for C33H54O4Si2Na+ 593.3453, found 593.3465.

**Alcohol 3.** A solution of bisTBS ether **2** (1.86 g, 3.27 mmol) in THF (6.0 mL) was added to a solution of 9-BBN dimer (1.68 g, 6.94 mmol) in THF (18 mL) at 0 °C under argon atmosphere
and washed with THF (4.0 mL + 5.0 mL). The mixture was stirred at rt for 3 h, then cooled to 0 °C. Saturated aqueous NaHCO₃ (10 mL) and 30% aqueous H₂O₂ (7.0 mL, 68.6 mmol) were added to reaction solution. The resulting mixture was stirred at rt for 30 min, quenched with saturated aqueous Na₂S₂O₃, and extracted with EtOAc. The organic layer was washed with saturated aqueous NaCl, dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography to give alcohol 3 (1.81 g, 3.08 mmol, 94%).

3: [α]D²⁰ = −12.2 (c 1.10, CHCl₃); Rf = 0.67 (hexane/EtOAc = 10/1); IR (neat) 3501, 2952, 2928, 2885, 2856, 1123, 1089, 850, 837 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.84–7.82 (m, 3H), 7.75 (s, 1H), 7.51–7.42 (m, 3H), 4.77 (d, J = 11.7 Hz, 1H), 4.64 (d, J = 11.7 Hz, 1H), 3.81 (dd, J = 11.9, 4.6 Hz, 1H), 3.72–3.70 (m, 2H), 3.47 (dd, J = 11.9, 4.1 Hz, 1H), 3.40 (d, J = 10.1, 1H), 3.36 (d, J = 10.1 Hz, 1H), 2.02 (ddd, J = 12.2, 4.6, 4.1 Hz, 1H), 1.89 (ddd, J = 15.4, 6.4, 4.1 Hz, 1H), 1.83–1.73 (m, 2H), 1.34 (s, 3H), 1.10 (s, 3H), 0.90 (m, 9H), 0.84 (m, 9H), 0.04 (s, 3H), 0.04 (s, 3H), 0.00 (m, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 135.9, 133.3, 133.1, 128.3, 128.0, 127.8, 126.5, 126.3, 126.1, 125.9, 78.7, 78.2 (×2), 71.7, 68.3, 67.7, 59.3, 42.3, 30.4, 26.2, 25.8, 21.5, 18.4, 18.1, 17.9, −3.7, −4.8, −5.3, −5.4; HRESIMS m/z [M + Na]⁺ calcd for C₃₃H₆₀O₇Si₂Na⁺ 611.3558, found 611.3572.

Aldehyde 4. TEMPO (26.7 mg, 171 mmol), 0.5 M aqueous KBr (1.2 mL, 0.6 mmol) were added to the solution of alcohol 3 (1.76g, 3.00 mmol) in CH₂Cl₂ (38 mL) at 0 °C. A aqueous solution of NaOCl-NaHCO₃ (8.8 mL, prepared from NaOCl•5H₂O (2.14 g, 13.0 mmol), H₂O (7.2 mL), and saturated aqueous NaHCO₃ (31 mL)) was added to the reaction mixture. The mixture was stirred at 0 °C for 1 h. Additional aqueous solution of NaOCl-NaHCO₃ (0.8 mL) was added to the reaction mixture, and after stirring for 15 min, the solution (0.6 mL) was added at 0 °C. The reaction mixture was stirred for 15 min, quenched with saturated aqueous Na₂S₂O₃, extracted with EtOAc, washed with saturated aqueous NaCl, dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure to give a crude aldehyde 4 (1.72 g) which was used for the next reaction without further purification.
Alkyne 5. n-BuLi (1.6 M in hexane, 11.0 mL, 17.6 mmol) was added to a solution of TMS diazomethane (2.0 M solution in hexane, 9.0 mL, 18.0 mmol) in THF (10 mL) at −78 °C under argon atmosphere. The solution was stirred for 35 min. A solution of crude aldehyde 4 (1.72 g) in THF (5 mL) was added to the solution via canula and washed with THF (5 + 5 + 5 mL). The reaction mixture was stirred at −78 °C for 40 min, warmed to 0 °C. The mixture was stirred for 1 h, quenched with saturated aqueous NH₄Cl, and extracted with EtOAc. The organic layer was washed with saturated aqueous NaCl, dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography to give alkyne 5 (1.44 g, 2.47 mmol, 82%, 2 steps).

5: [α]D¹⁹−4.8 (c 1.13, CHCl₃); Rf = 0.83 (hexane/EtOAc = 7/1); IR (neat) 3312, 2953, 2928, 2885, 2856, 1125, 1099, 852, 837 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.90–7.84 (m, 3H), 7.79 (s, 1H), 7.52–7.47 (m, 3H), 4.81 (d, J = 11.7 Hz, 1H), 4.69 (d, J = 11.7 Hz, 1H), 3.88 (dd, J = 11.9, 4.6 Hz, 1H), 3.46 (dd, J = 11.9, 4.1 Hz, 1H), 3.42 (s, 2H), 2.56 (dd, J = 16.6, 2.4 Hz, 1H), 2.35 (dd, J = 16.6, 2.4 Hz, 1H), 2.03–1.97 (m, 2H), 1.77 (ddd, J = 11.9, 11.9, 11.9 Hz, 1H), 1.36 (s, 3H), 1.08 (s, 3H), 0.90 (m, 9H), 0.87 (m, 9H), 0.07 (s, 3H), 0.07 (s, 3H), 0.04 (s, 3H), 0.02 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 136.1, 133.4, 133.1, 128.3, 128.0, 127.8, 126.5, 126.2, 125.99, 125.96, 81.9, 79.0, 78.2, 75.5, 71.6, 70.3, 68.3, 67.2, 32.5, 30.6, 26.2, 25.8, 20.9, 18.6, 17.9, 17.8, −4.2, −4.9, −5.0, −5.2; HRESIMS m/z [M + Na]⁺ calcd for C₃₄H₅₄O₄Si₂Na⁺ 605.3453, found 605.3453.

Alkene 6. [Cp*Ru(MeCN)₃]PF₆ (135 mg, 0.267 mmol) and Et₃SiH (3.1 mL, 19.5 mmol) were added to a solution of alkyne 5 (1.44 g, 2.47 mmol) in CH₂Cl₂ (25 mL) at 0 °C. After the reaction mixture was stirred at rt for 3 h, [Cp*Ru(MeCN)₃]PF₆ (39.7 mg, 78.7 µmol) was
added to the mixture. The mixture was stirred for 30 min, and filtered through a short pad of silica gel. The filtrate was concentrated under reduced pressure to give a crude alkene 6 (1.91 g) which was used for the next reaction without further purification.

![Image](https://example.com/image.png)

**Iodide 7.** 2,6-lutidine (2.0 mL, 17.3 mmol) and I₂ (6.37 g, 25.1 mmol) were added to a solution of crude alkene 6 (1.91 g) in CH₂Cl₂ (25 mL) at 0 °C. The reaction mixture was stirred at rt for 2 h. Additional I₂ (10.6 g, 41.6 mmol) was added to the mixture. The mixture was stirred at rt for 1.5 h, quenched with saturated aqueous Na₂S₂O₃/Et₃N, extracted with EtOAc, dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography to give iodide 7 (1.36 g, 1.91 mmol, 77%, 2 steps).

**7:** [α]D¹⁸ −2.6 (c 1.23, CHCl₃); IR (neat) 2952, 2927, 2885, 2856, 1122, 1100, 1086, 852, 836, 776 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.84–7.82 (m, 3H), 7.78 (s, 1H), 7.49–7.46 (m, 3H), 6.37 (d, J = 1.4 Hz, 1H), 5.91 (d, J = 1.4 Hz, 1H), 4.77 (d, J = 11.9 Hz, 1H), 4.66 (d, J = 11.9 Hz, 1H), 3.84 (dd, J = 11.9, 4.7 Hz, 1H), 3.38 (s, 2H), 3.33 (J = 11.9, 4.3 Hz, 1H) 2.89 (d, J = 15.1 Hz, 1H), 2.65 (d, J = 15.1 Hz, 1H) 2.00 (ddd, J = 11.9, 4.7, 4.3 Hz, 1H), 1.75 (ddd, J = 11.9, 11.9, 11.9 Hz, 1H), 1.34 (s, 3H), 1.06 (s, 3H), 0.87 (m, 9H), 0.83 (m, 9H), 0.02 (s, 3H), 0.01 (s, 3H), 0.00 (s, 3H), −0.01 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 136.1, 133.4, 133.1, 130.7, 128.3, 128.0, 127.8, 126.4, 126.2, 126.0, 125.9, 103.3, 79.1, 78.2, 77.3, 71.3, 68.4, 67.2, 55.6, 30.3, 26.1, 25.8, 20.5, 18.4, 18.1, 18.0, −3.9, −4.9, −5.0, −5.1; HRESIMS m/z [M + Na]⁺ calcd for C₃₄H₅₅IO₄Si₂Na⁺ 733.2576, found 733.2610.
**Furanylborate 9.** A solution of furan 8 (421 mg, 2.08 mmol) in octane (1.0 mL) was added to a solution of [IrCl(COD)]2 (21.9 mg, 32.6 µmol), dtbpy (17.3 mg, 64.5 µmol), and B2pin2 (809 mg, 3.19 mmol) in octane (2.0 mL) under argon atmosphere and washed with octane (1.0 + 1.0 mL). The mixture was stirred at 80 °C for 18 h and purified by silica gel column chromatography to give furanylborate 9 (481 mg, 1.47 mmol, 70%).

9: IR (neat) 2978, 2928, 2863 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.35–7.22 (m, 5H), 7.01 (d, J = 3.2 Hz, 1H), 6.15 (d, J = 3.2 Hz, 1H), 4.52 (s, 2H), 3.75 (t, J = 7.1 Hz, 2H), 3.03 (t, J = 7.1 Hz, 2H), 1.34 (s, 12H); ¹³C NMR (100 MHz, CDCl₃) δ 158.7, 138.4, 128.5, 127.8, 127.7, 124.9, 107.4, 84.2, 73.1, 68.2, 29.3, 24.9; HRESIMS m/z [M + Na]⁺ calcd for C₁₉H₂₅BO₄Na⁺ 351.1738, found 351.1744.

**Olefin 10.** Na₂CO₃ (4.4 mg, 41.5 µmol) and Pd(PPh₃)₂Cl₂ (4.0 mg, 5.70 µmol) were added to a solution of iodide 7 (20.8 mg, 29.3 µmol) and furanylborate 9 (13.6 mg, 41.4 µmol) in DMF (degassed, 1.20 mL) and H₂O (degassed, 0.24 mL) at rt under argon atmosphere. The mixture was stirred for 30 min, warmed to 95 °C. After stirring for 3 h, the mixture was diluted with Et₂O, extracted with Et₂O dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography to give olefin 10 (17.5 mg, 22.3 µmol, 76%).

10: [α]D17 −1.8 (c 1.23, CHCl₃); IR (neat) 2952, 2927, 2884, 2856, 1119, 1100, 853, 775 cm⁻¹; ¹H NMR (400 MHz, C₆D₆) δ 7.73–7.64 (m, 4H), 7.43–7.41 (m, 1H), 7.32–7.08 (m, 7H), 6.55 (d, J = 3.0 Hz, 1H), 6.07 (s, 1H), 6.02 (d, J = 3.0 Hz, 1H), 5.50 (s, 1H), 4.57 (d, J = 11.9 Hz, 1H), 4.35 (d, J = 11.9 Hz, 1H), 4.22 (s, 2H), 3.99 (dd, J = 11.9, 4.1 Hz, 1H), 3.53–3.45 (m,
5H), 3.01 (d, J = 14.2 Hz, 1H), 2.80 (t, J = 6.9 Hz, 2H), 2.71 (d, J = 14.2 Hz, 1H), 2.09 (ddd, J = 11.9, 4.6, 4.1 Hz, 1H), 1.86 (ddd, J = 11.9, 11.9, 11.9 Hz, 1H), 1.47 (s, 3H), 1.17 (s, 3H), 1.06 (m, 9H), 0.94 (m, 9H), 0.19 (s, 3H), 0.15 (s, 3H), 0.07 (s, 3H), 0.03 (s, 3H); 13C NMR (100 MHz, C₆D₆) δ 155.2, 153.1, 139.2, 137.0, 134.2, 133.9, 133.5, 128.6, 128.5, 127.7, 127.6, 126.4, 126.1, 126.0, 112.9, 108.9, 108.3, 80.0, 78.3, 77.3, 72.9, 71.2, 69.1, 68.6, 68.2, 44.8, 31.0, 29.5, 26.3, 25.9, 20.7, 18.7, 18.3, 18.1, −3.8, −4.8, −5.0 (×2). The 13C NMR signals of 10 is partially overlapped with the signal of C₆D₆; HRESIMS m/z [M + Na]⁺ calcd for C₄₇H₆₈O₆Si₂Na⁺ 807.4447, found 807.4463.

Diol 11. K₂CO₃ (127 mg, 0.915 mmol), K₃Fe(CN)₆ (302 mg, 0.917 mmol), (DHQD)₂PHAL (46.7 mg, 60.0 µmol), MeSO₂NH₂ (21.8 mg, 0.229 mmol), and K₂OsO₄·2H₂O (8.9 mg, 24.2 µmol) were dissolved in t-BuOH (3.8 mL) and H₂O (3.8 mL). The suspension was stirred at rt for 30 min then cooled to 0 °C. Olefine 10 (120 mg, 0.153 mmol) in t-BuOMe (2.0 mL) was added to the suspension and washed with t-BuOMe (2.0 + 2.0 + 1.6 mL). The mixture was stirred at rt for 2 h, quenched with solid Na₂S₂O₃, extracted with EtOAc, washed with saturated aqueous NaCl, dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography to give diol 11 (113 mg, 0.138 mmol, 90%, dr > 20:1).

11: [α]D²¹ +41.3 (c 1.03, C₆H₆); IR (neat) 3405, 2953, 2928, 2884, 2857, 1120, 1091, 834, 777 cm⁻¹; ¹H NMR (600 MHz, C₆D₆) δ 7.72 (s, 1H), 7.70–7.63 (m, 3H), 7.45–7.44 (m, 1H), 7.29–7.23 (m, 2H), 7.17–7.13 (m, 5H), 6.58 (d, J = 3.1 Hz, 1H), 6.00 (d, J = 3.1 Hz, 1H), 5.96 (s, 1H), 4.39 (d, J = 12.0 Hz, 1H), 4.26 (d, J = 12.0 Hz, 1H), 4.11 (s, 2H), 4.05 (ddd, J = 12.0, 4.8, 4.1 Hz, 1H), 3.87 (ddd, J = 12.0, 4.8, 4.1 Hz, 1H), 3.83–3.81 (m, 2H), 3.58 (d, J = 10.0 Hz, 1H), 3.49 (d, J = 10.0 Hz, 1H), 3.38–3.31 (m, 2H), 2.66 (d, J = 12.4 Hz, 1H), 2.65 (d, J = 12.4 Hz, 1H), 2.60 (d, J = 15.1 Hz, 1H), 2.61–2.56 (m, 1H), 2.50 (d, J = 15.1 Hz, 1H), 2.00 (ddd, J = 12.0, 4.8, 4.1 Hz, 1H), 1.72 (ddd, J = 12.0, 12.0, 12.0 Hz, 1H), 1.35 (s, 3H), 1.09 (m, 9H), 1.08 (s, 3H), 0.88 (m, 9H), 0.23 (s, 3H), 0.20 (s, 3H), 0.03 (s, 3H), −0.08 (s, 3H); ¹³C NMR (150 MHz, C₆D₆) δ 158.3, 152.8, 139.1, 137.4, 133.9, 133.5, 128.6, 128.5, 128.40, 128.35,
127.7, 127.6, 126.4, 126.0, 125.9, 125.8, 107.4, 107.1, 79.8, 79.0, 76.9, 74.4, 72.8, 71.22, 71.17, 68.4, 68.2, 67.4, 42.4, 31.3, 29.2, 26.6, 25.9, 24.1, 18.9, 18.4, 18.0, −3.6, −4.8, −5.0, −5.1; HRESIMS m/z [M + Na]+ calcd for C_{47}H_{70}O_{8}Si_{2}Na^+ 841.4501, found 841.4536.

Enone 12. 0.132 M aqueous Oxone (0.65 mL, 85.9 µmol) was added to a solution of diol 11 (28.2 mg, 34.4 µmol) and NaHCO₃ (29.3 mg, 0.3488 mmol) in acetone (2.2 mL) at 0 °C. The mixture was stirred at rt for 3 h. Aqueous Oxone (0.32 mL, 42.3 µmol) was added to the reaction mixture. After stirring for 25 min, further aqueous Oxone (0.32 mL, 42.3 µmol) was added. The resulting mixture was stirred at rt for 1 h, extracted with EtOAc, washed with saturated aqueous Na₂S₂O₃ and saturated aqueous NaCl, dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure. PPTS (67.8 mg, 0.2698 mmol) was added to a solution of the residue (31.6 mg) in CH₂Cl₂ (3.0 mL) at 0 °C. The mixture was stirred for 1 h, quenched with saturated aqueous NaHCO₃, extracted with EtOAc, washed with saturated aqueous NaCl, dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography to give enone 12 (20.9 mg, 74%, 2 steps).

12: [α]D¹⁶ −25.1 (c 0.95, CHCl₃); IR (neat) 3058, 2954, 2928, 2883, 2856, 1119, 1100, 853, 837, 776 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.82–7.79 (m, 3H), 7.75 (s, 1H), 7.47–7.43 (m, 3H), 7.36–7.28 (m, 5H), 6.96 (d, J = 9.8 Hz, 1H), 5.93 (d, J = 9.8 Hz, 1H), 4.92 (d, J = 8.7 Hz, 1H), 4.75 (d, J = 11.9 Hz, 1H), 4.64 (d, J = 11.9 Hz, 1H), 4.43 (s, 2H), 3.72–3.59 (m, 4H), 3.45 (m, 1H), 3.44 (d, J = 9.8 Hz, 1H), 3.38 (d, J = 9.8 Hz, 1H), 2.45 (d, J = 15.1 Hz, 1H), 2.30–2.19 (m, 2H), 2.15 (d, J = 15.1 Hz, 1H), 1.99 (ddd, J = 12.4, 4.6, 4.1 Hz, 1H), 1.75 (ddd, J = 12.4, 12.4, 12.4 Hz, 1H), 1.33 (s, 3H), 1.10 (s, 3H), 0.89 (s, 9H), 0.85 (s, 9H), 0.03 (s, 6H), 0.01 (s, 3H), 0.00 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 196.7, 148.6, 138.2, 136.4, 133.4, 133.1, 131.0, 128.5, 128.2, 128.0, 127.8, 127.7, 126.3, 126.1, 125.95, 125.87, 103.4, 86.8, 78.4, 78.3, 76.4, 73.3, 71.3, 69.7, 68.5, 66.0, 65.7, 38.1, 35.9, 30.7, 26.2, 25.8, 22.9, 18.6, 18.01, 17.96, −3.7, −4.8, −5.1, −5.2. The one ¹³C NMR signal of 12 overlapped in the aromatic region; HRESIMS m/z [M + Na]+ calcd for C₄₇H₆₈O₈Si₂Na⁺ 839.4345, found 839.4374.
Hydroxyketone 14. B₂pin₂ (29.1 mg, 0.115 mmol), PPh₃ (28.7 mg, 0.109 mmol), CuCO₃·Cu(OH)₂ (9.6 mg, 43.4 µmol) were added to a solution of enone 12 (29.0 mg, 35.5 µmol) in THF (0.50 mL) and H₂O (0.50 mL) at 0 °C. The mixture was stirred at rt for 2.5 h. Saturated aqueous NaHCO₃ (0.60 mL, 0.68 mmol) and 30% aqueous H₂O₂ (0.20 mL, 1.96 mmol) were added to the reaction mixture at 0 °C. The resulting mixture was stirred at rt for 20 min, quenched with saturated aqueous NH₄Cl and saturated aqueous Na₂S₂O₃, extracted with EtOAc, washed with saturated aqueous NaCl, dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography to give hydroxyketone 14 (28.1 mg, 336 µmol, 95%).

14: [α]₀²³ −2.4 (c 1.33, CHCl₃); IR (neat) 3471, 3058, 2953, 2928, 2883, 2856, 1732, 1104, 1089, 854, 837, 775 cm⁻¹; ¹H NMR (600 MHz, CDCl₃) δ 7.84–7.82 (m, 3H), 7.77 (s, 1H), 7.49–7.45 (m, 3H), 7.37–7.29 (m, 5H), 4.75 (d, J = 11.7 Hz, 1H), 4.66 (d, J = 11.7 Hz, 1H), 4.56 (d, J = 12.0 Hz, 1H), 4.53 (d, J = 12.0 Hz, 1H), 3.90–3.88 (m, 1H), 3.80 (s, 2H), 3.74 (td, J = 9.6, 2.8 Hz, 1H), 3.70–3.67 (m, 1H), 3.56 (dd, J = 12.0, 4.1 Hz, 1H), 3.35 (dd, J = 12.0, 3.8 Hz, 1H), 3.29 (d, J = 10.0 Hz, 1H), 2.81 (dd, J = 15.1, 5.50 Hz, 1H), 2.74 (dd, J = 15.1, 6.9 Hz, 1H), 2.51 (ddd, J = 14.7, 10.0, 4.5 Hz, 1H), 2.28 (d, J = 14.1 Hz, 1H), 2.02 (d, J = 14.1 Hz, 1H), 1.95–1.90 (m, 2H), 1.74 (ddd, J = 12.0, 12.0, 12.0 Hz, 1H), 1.37 (s, 3H), 1.09 (s, 3H), 0.91 (s, 9H), 0.83 (s, 9H), 0.74 (s, 3H), 0.07 (s, 3H), −0.04 (s, 3H), −0.04 (s, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 208.7, 137.4, 136.2, 133.4, 133.1, 128.7, 128.3, 128.1, 128.0, 127.9, 127.8, 126.5, 126.2, 126.01, 125.97, 109.4, 87.6, 81.5, 78.9, 75.9, 73.7, 72.3, 72.2, 71.8, 69.8, 68.8, 65.9, 42.9, 41.4, 34.7, 30.6, 26.3, 25.8, 21.6, 18.6, 17.9, 17.8, −3.8, −4.9, −5.1, −5.2; HRESIMS m/z [M + Na]⁺ calcd for C₄₇H₇₀O₉Si₂Na⁺ 857.4451, found 857.4450.
**Hemiacetal 15.** DDQ (19.5 mg, 85.7 µmol) was added to a solution of ketone 14 (35.8 mg, 42.9 µmol) in CH₂Cl₂ (1.42 mL) and pH 7 buffer (0.72 mL) at 0 °C. The mixture was stirred at rt for 35 min, quenched with saturated aqueous NaHCO₃ and saturated aqueous Na₂S₂O₃, extracted with EtOAc, washed with saturated aqueous NaCl, dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography to give hemiacetal 15 (24.8 mg, 35.7 µmol, 83%).

15: [α]D₁⁹ +26.1 (c 1.20, CHCl₃); IR (neat) 3384, 2953, 2929, 2894, 2857, 1099, 1037, 837 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.40–7.29 (m, 5H), 4.54 (s, 2H), 4.45 (brs, 1H), 4.20 (dd, J = 8.0, 5.7 Hz, 1H), 4.12 (d, J = 7.8 Hz, 1H), 4.10 (dd, J = 12.4, 3.2 Hz, 1H), 3.83 (m, 1H), 3.76 (ddd, J = 10.0, 7.8, 3.4 Hz, 1H), 3.61 (ddd, J = 10.0, 6.9, 3.7 Hz, 1H), 3.51 (d, J = 7.8 Hz, 1H), 3.34 (s, 2H), 2.36 (d, J = 11.9 Hz, 1H), 2.20–2.07 (m, 3H), 1.92–1.86 (m, 2H), 1.79–1.71 (m, 2H), 1.18 (s, 3H), 1.10 (s, 3H), 0.91 (s, 9H), 0.85 (s, 9H), 0.07 (s, 6H), 0.05 (s, 3H), 0.04 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 137.1, 128.7, 128.2, 128.1, 107.1, 94.4, 82.7, 79.0, 73.6, 73.1, 72.2, 70.4, 70.1, 68.6, 68.4, 65.7, 41.8, 36.4, 35.8, 30.7, 26.1, 25.8, 20.8, 19.1, 18.5, 18.0, −3.9, −4.7, −5.1, −5.2; HRESIMS m/z [M + Na]⁺ calcd for C₃₆H₆₂O₉Si₂Na⁺ 717.3825, found 717.3860.

**Triol 16.** Et₃SiH (0.27 mL, 1.69 mmol) and TiCl₄ (50 µL, 0.456 mmol) were added to a solution of hemiacetal 15 (19.4 mg, 27.9 µmol) in CH₂Cl₂ (5.4 mL) at −40 °C under argon atmosphere. The mixture was stirred for 25 min, warmed to 0 °C, then stirred for 50 min. After warming to rt, the mixture was stirred for 1 h, quenched with saturated aqueous NaHCO₃, filtered through a thin Celite® pad. The filtrate was dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure to give a crude triol 16 (12.8 mg) which was used for the next reaction without further purification.
Triacetate 17. DMAP (8.6 mg, 70.4 µmol) and Ac₂O (0.20 mL, 2.12 mmol) were added to a solution of crude triol 16 (12.8 mg, 27.9 µmol) in pyridine (2.5 mL) at 0 °C under argon atmosphere. The mixture was stirred at rt for 3 h, concentrated under reduced pressure. The residue was purified by silica gel column chromatography to give triacetate 17 (7.0 mg, 11.7 µmol, 42%, 2 steps).

17: [α]D²⁴ +76.8 (c 1.28, CHCl₃); IR (neat) 2954, 2929, 2887, 2857, 1740, 1372, 1248, 1100, 1073, 1051 cm⁻¹; ¹H NMR (600 MHz, CDCl₃) δ 4.59 (dd, J = 4.8, 1.5 Hz, 1H), 4.31 (ddd, J = 11.0, 7.9, 5.8 Hz, 1H), 4.20 (d, J = 11.3 Hz, 1H), 4.16 (ddd, J = 11.0, 7.8, 6.6 Hz, 1H), 4.06 (dd, J = 12.3, 3.7 Hz, 1H), 3.90 (dd, J = 11.4, 4.7 Hz, 1H), 3.73 (d, J = 7.8 Hz, 1H), 3.70 (d, J = 11.3 Hz, 1H), 3.64 (dd, J = 4.8, 1.5 Hz, 1H), 3.36 (d, J = 7.8 Hz, 1H), 2.18 (ddd, J = 14.0, 7.8, 5.8 Hz, 1H), 2.13–2.07 (m, 7H), 2.06–1.99 (m, 4H), 1.97 (ddd, J = 15.9, 1.5, 1.5 Hz, 1H), 1.90 (m, 2H), 1.84 (d, J = 14.9 Hz, 1H), 1.74 (ddd, J = 11.9, 11.9, 11.9 Hz, 1H), 1.31 (s, 3H), 1.17 (s, 3H), 0.86 (s, 9H), 0.08 (s, 3H), 0.06 (s, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 171.2, 171.1, 170.5, 107.2, 81.4, 77.5, 72.6, 71.4, 70.9, 69.1, 68.9, 68.4, 67.5, 59.3, 44.9, 32.6, 31.3, 29.4, 25.8, 24.3, 21.3, 21.2, 21.1, 18.7, 17.9, −4.0, −5.0; HRESIMS m/z [M + Na]⁺ caleed for C₂₉H₄₈O₁₁SiNa⁺ 623.2858, found 623.2884.

References


$^1$H NMR (400 Hz, CDCl$_3$)
$^1$H NMR (500 MHz, CDCl$_3$)
$^1$H NMR (400 Hz, CDCl$_3$)
$^{13}$C NMR (100 Hz, CDCl$_3$)
$^1$H NMR (400 Hz, CDCl$_3$)
$^{13}$C NMR (100 Hz, CDCl$_3$)
$^{1}\text{H NMR (400 Hz, CDCl$_3$)}$

X : parts per Million : H
$^{13}$C NMR (100 Hz, CDCl$_3$)

The spectrum shows resonances at various chemical shifts, indicating the presence of different carbon atoms with varying chemical environments. The specific positions and intensities of the peaks provide information about the molecular structure and functional groups present in the compound.
13C NMR (150 MHz, C6D6)
$^{1}$H NMR (400 MHz, CDCl$\textsubscript{3}$)
$^{1}$H NMR (600 MHz, CDCl$_3$)
$^{13}$C NMR (150 MHz, CDCl$_3$)
$^{1}H$ NMR (600 MHz, CDCl$_3$)
$^{1}$H NMR (150 MHz, CDCl$_3$)
1D and 2D NMR spectra of 17

COSY

HMOCQ
13C NMR (top) and DEPT135 (bottom)
$^1$H NMR (top) and 1D NOESY (bottom, irradiation of H-124, 3.64 ppm)