Total Synthesis of Viridicatumtoxin B and Analogues Thereof: Strategy Evolution, Structural Revision, and Biological Evaluation

K. C. Nicolaou, Christopher R. H. Hale, Christian Nilewski, Heraklidia A. Ioannidou, Abdelatif ElMarrouni, Lizanne G. Nilewski, Kathryn Beabout, Tim T. Wang, and Yousif Shamoo

†Department of Chemistry
Rice University
6100 Main Street, Houston, Texas 77005, United States

‡Department of Chemistry
The Scripps Research Institute
10550 North Torrey Pines Road, La Jolla, California 92037, United States

§Department of Biochemistry and Cell Biology
Rice University
6100 Main Street, Houston, Texas 77005, United States

∥Department of Ecology and Evolutionary Biology
Rice University
6100 Main Street, Houston, Texas 77005, United States

†Present addresses: Department of Chemistry, Rice University, 6100 Main Street, Houston, Texas 77005, United States
‡These authors contributed equally.

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I. General Methods

All reactions were carried out under an argon atmosphere unless otherwise noted. Methylene chloride, tetrahydrofuran, toluene, methanol, dimethylformamide, acetonitrile, diisopropylamine, and triethylamine were dried prior to use by passage through an activated alumina column unless otherwise noted.[1] Anhydrous acetone, ethyl acetate, and 1,2-dichloroethane were purchased from commercial suppliers and stored under argon. Yields refer to chromatographically and spectroscopically (1H NMR) homogenous material, unless otherwise stated.

Reactions were monitored by thin-layer chromatography (TLC) carried out on 0.25 mm E. Merck silica gel plates (60F-254) and were visualized using UV light and an ethanolic solution of phosphomolybdic acid and cerium sulfate or an aqueous solution of potassium permanganate. Flash column chromatography using E. Merck silica gel (60, particle size 0.040–0.063 mm) was performed as described by Still.[2] NMR spectra were recorded on a Bruker DRX-600 equipped with a 5 mm DCH cryoprobe, Bruker DRX-500, Bruker AV-400, or Varian INOVA-400 instrument and calibrated using residual undeuterated solvent for 1H NMR [δH = 7.26 (CHCl3), 7.16 (C6D5H), 2.05 (D5H-acetone), 2.50 (D5H-DMSO), and 5.32 (CDCl2) ppm] and 13C deuterated solvent for 13C NMR [δC = 77.16 (CDCl3), 128.06 (C6D6), 206.68 (d6-acetone), and 53.84 (CD2Cl2) ppm] as an internal reference at 298 K.[3] The following abbreviations were used to designate the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, b = broad, ap = apparent.

ATR-Infrared (IR) spectra were recorded on a Perkin-Elmer 100 series FT-IR spectrometer. High-resolution mass spectra (HRMS) were recorded on an Agilent LC/MSD/TOF mass spectrometer using ESI (electrospray ionization) or a Shimadzu Ion Trap-TOF using ESI.
Melting points were recorded on a Fisher-Johns 12-144 melting point apparatus or a Thomas Hoover uni-melt capillary melting point apparatus. X-Ray crystallographic structures were collected using a Bruker Smart-APEX instrument (CCD detector) or a Bruker Kappa APEX-II instrument (CCD detector).

Preparative HPLC separations were performed using a Waters 2767 prep LC system equipped with a Waters Atlantis prep T3 OBD column (16 × 150 mm, 5 µm particle size) and monitored using a Waters 2996 photodiode array detector.
II. Experimental Procedures and Physical Data of Compounds

Allylic alcohol 47: Allylic alcohol 47 was prepared using the following modification of a published four-step procedure.\(^{[4]}\) Geranic acid 45 (30.98 g, 184.2 mmol, 1.0 equiv) was dissolved in toluene (450 mL, not dried prior to use) and H\(_3\)PO\(_4\) (~2 mL) was added. The mixture was heated to reflux and vigorously stirred at that temperature for 90 minutes. After cooling to room temperature, water (100 mL) was added, the layers were separated, and the toluene layer was concentrated to give crude cyclogeranic acid (S1) as a solid. The crude residue was then dissolved in acetone (600 mL, technical grade) and K\(_2\)CO\(_3\) (50.0 g, 362 mmol, 2.0 equiv) and MeI (45 mL, 100 g, 0.72 mol, 3.9 equiv) were added. The suspension was vigorously stirred at room temperature for 15 hours, and the solids were then removed by filtration through a short pad of silica gel (rinsed with Et\(_2\)O). The filtrate was concentrated to give cyclogeranic acid methyl ester (46). The crude methyl ester was dissolved in CH\(_2\)Cl\(_2\) (500 mL, HPLC grade) and cooled to 0 °C using an ice bath. A solution of mCPBA (70–75%, 51.0 g, ~220 mmol, ~1.2 equiv) in CH\(_2\)Cl\(_2\) (900 mL, HPLC grade) was added to the stirred substrate solution via addition funnel over ca. 1 hour. The ice bath was then removed, and the resulting mixture was allowed to stir at room temperature for 2 hours. The reaction was then quenched with a saturated solution of aq. Na\(_2\)S\(_2\)O\(_3\) (1 L) and stirred for an additional 30 minutes. The layers were separated, and the organic layer was then washed with saturated aq. NaHCO\(_3\) solution (2 \(\times\) 500 mL). The organic phase was dried over Na\(_2\)SO\(_4\), filtered, and concentrated to give crude epoxide S2. The crude epoxide was dissolved in anhydrous methanol (600 mL), NaOMe (15 g, 0.28 mol,
1.5 equiv) was added, and the resulting mixture was refluxed for 17 hours. It was then cooled to room temperature, acidified to pH = 1 with 1 N aq. HCl, diluted with water (1 L) and extracted with EtOAc (1 L). The organic phase was dried over Na₂SO₄, filtered, and concentrated. The crude product was purified by flash column chromatography (10→20→30→50% EtOAc:hexanes) to give allylic alcohol 47 (25.7 g, 130 mmol, 70% yield for four steps). The physical and spectroscopic data matched those reported in the literature.⁴

**TBS ether 48**: Allylic alcohol 47 (15.6 g, 78.8 mmol, 1.0 equiv) was dissolved in CH₂Cl₂ (800 mL, HPLC grade) at room temperature. Imidazole (10.6 g, 156 mmol, 2.0 equiv) and TBSCl (18.9 g, 126 mmol, 1.6 equiv) were added sequentially, and the suspension was stirred at room temperature for 12 hours. The reaction was quenched with saturated NaHCO₃ solution (500 mL), and the phases were separated. The organic phase was dried over Na₂SO₄, filtered, and concentrated. Residual volatiles were then azeotropically removed with toluene (twice). The crude TBS ether was dissolved in CH₂Cl₂ (700 mL, HPLC grade) and cooled to −78 °C. DIBAL-H (210 mL, 1.0 M solution in hexanes, 210 mmol, 2.7 equiv) was added to the reaction mixture over 20 minutes, and the cooling bath was then allowed to warm to 0 °C. The reaction mixture was stirred at this temperature for 70 minutes, and the reaction was then cautiously quenched with methanol (100 mL). The mixture was allowed to warm to room temperature, and saturated aq. Rochelle’s salt solution (800 mL) was added. The resulting thick emulsion was vigorously stirred at room temperature for 5 hours. The phases were separated, and the organic phase was dried over Na₂SO₄, filtered, and concentrated to give the crude allylic alcohol. The residue was
purified by flash column chromatography (5→10→15% EtOAc:hexanes) to give allylic alcohol 48 (20.5 g, 72.2 mmol, 91% for two steps) as a colorless oil that slowly solidified. **48**: R$_f$ = 0.2 (silica gel, EtOAc:hexanes 1:9); FT-IR (neat) $\nu_{\text{max}}$ = 3337, 2951, 2930, 2857, 1472, 1361, 1251, 1084, 1049, 1004, 935, 888, 834, 772, 671 cm$^{-1}$; $^1$H NMR (CDCl$_3$, 600 MHz) $\delta$ = 4.14 (d, $J$ = 11.4 Hz, 1 H), 4.09 (d, $J$ = 11.4 Hz, 1 H), 4.00 (dd, $J$ = 6.0, 6.0 Hz, 1 H), 1.80 (m, 1 H), 1.79 (s, 3 H), 1.65 – 1.57 (m, 2 H), 1.37 (ddd, $J$ = 13.2, 10.5, 2.8 Hz, 1 H), 1.06 (s, 3 H), 1.02 (s, 3 H), 0.90 (s, 9 H), 0.10 (s, 3 H), 0.08 (s, 3 H) ppm; $^{13}$C NMR (CDCl$_3$, 151 MHz) $\delta$ = 140.1, 136.1, 71.3, 59.4, 35.5, 34.6, 29.5, 28.2, 28.0, 26.1, 18.3, 16.3, –4.1, –4.5 ppm; HRMS (ESI) calcd for C$_{16}$H$_{32}$O$_2$SiH$^+$ [M+H$^+$] 285.2244, found 285.2245.

Allylic chloride **27**: To a solution of allylic alcohol 48 (3.00 g, 10.5 mmol, 1.0 equiv) in CH$_2$Cl$_2$ (50 mL) was added Et$_3$N (2.2 mL, 16 mmol, 1.5 equiv), MsCl (1.0 mL, 13 mmol, 1.2 equiv), and DMAP (64 mg, 0.52 mmol, 0.05 equiv), and the mixture was stirred at room temperature for 14 hours. Then, LiCl (445 mg, 10.5 mmol, 1.0 equiv) was added, and the mixture was stirred for another 42 hours. The reaction was then quenched with saturated aq. NaHCO$_3$ solution (50 mL), the phases were separated, and the organic phase was dried over Na$_2$SO$_4$, filtered, and concentrated. The residue was purified by flash column chromatography (5% Et$_2$O:hexanes) to give allylic chloride 27 (1.52 g, 5.03 mmol, 48%) as a colorless oil. **27**: R$_f$ = 0.7 (silica gel, Et$_2$O:hexanes 1:19); FT-IR (neat) $\nu_{\text{max}}$ = 2956, 2926, 2857, 1472, 1360, 1256, 1084, 1053, 888, 835, 773 cm$^{-1}$; $^1$H NMR (CDCl$_3$, 500 MHz) $\delta$ = 4.13 (d, $J$ = 11.2 Hz, 1 H), 4.05 – 4.00 (m, 2 H),
1.81 (m, 1 H), 1.79 (s, 3 H), 1.66 – 1.56 (m, 2 H), 1.41 (ddd, J = 13.5, 10.9, 2.7 Hz, 1 H), 1.074 (s, 3 H), 1.066 (s, 3 H), 0.90 (s, 9 H), 0.10 (s, 3 H), 0.09 (s, 3 H) ppm; \(^{13}\)C NMR (CDCl\(_3\), 126 MHz) \(\delta = 139.0, 136.5, 71.3, 41.5, 35.7, 35.1, 29.4, 28.4, 28.0, 26.0, 18.3, 16.4, –4.0, –4.6\) ppm; HRMS (ESI) calcd for C\(_{16}\)H\(_{31}\)OSiClNa\(^+\) [M+Na\(^+\)] 325.1725, found 325.1726.

Juglone derivative 51: Bromojuglone derivative 51 was prepared according to a literature procedure.\(^5\) To a stirred solution of juglone (50, 6.0 g, 34 mmol, 1.0 equiv) in glacial AcOH (90 mL) at room temperature was added dropwise Br\(_2\) (1.8 mL, 35 mmol, 1.03 equiv). The reaction mixture was allowed to stir for 30 minutes and was then poured into ice water. The pale orange solid was collected by filtration, redissolved in EtOH (40 mL), and heated to reflux. After 15 minutes of refluxing, the resulting solution was allowed to cool to room temperature, the resulting solid was filtered off and used in the next step without further purification. To a suspension of the so-obtained bromojuglone (8.6 g, 34 mmol, 1.0 equiv) in CH\(_2\)Cl\(_2\) (200 mL) was added sequentially Ag\(_2\)O (16.2 g, 70.1 mmol, 2.1 equiv) and BnBr (12 g, 8.6 mL, 70 mmol, 2.1 equiv), and the resulting mixture was stirred for 18 hours at room temperature. The mixture was then filtered through Celite\(^\text{\textregistered}\) and concentrated. Purification of the residue by flash column chromatography (5→10→20% EtOAc:hexanes) yielded benzyl-bromojuglone 51 (7.65 g, 22.3 mmol, 66% yield for two steps) as a yellow solid. The physical and spectroscopic data of this compound matched those reported in the literature.\(^5\)
**Diene 53:** This compound was prepared starting from readily available (Z)-methyl 3-methoxybut-2-enoate by a literature procedure.\[^6\] To a solution of diisopropylamine (2.37 mL, 16.9 mmol, 1.1 equiv) in THF (51 mL) at –78 °C was added n-BuLi (2.5 M in hexanes, 6.46 mL, 16.1 mmol, 1.05 equiv), and the resulting mixture was stirred for 15 minutes at that temperature and then allowed to warm to 0 °C. After stirring for 15 minutes at 0 °C, the reaction mixture was recooled to –78 °C, and a solution of (Z)-methyl 3-methoxybut-2-enoate (2.00 g, 15.4 mmol, 1.0 equiv) in THF (15 mL) was added dropwise. After stirring at that temperature for 1 hour, a solution of TMSCl (2.34 mL, 18.4 mmol, 1.2 equiv) in THF (15 mL) was added. The mixture was stirred for 10 minutes at that temperature and was then gradually allowed to warm to room temperature over 1.5 hours. The mixture was concentrated, and the resulting residue was resuspended in hexanes, filtered through a sintered funnel, and concentrated to give analytically pure diene 53 (3.08 g, 15.2 mmol, 99%). The physical and spectroscopic data of this compound matched those reported in the literature.\[^6\]

**Anthraquinone 56:** To a solution of benzyl-bromojuglone 51 (3.23 g, 9.42 mmol, 1.0 equiv) in CH\(_2\)Cl\(_2\) (60 mL) cooled to –30 °C was added a solution of diene 53 (5.71 g, 28.2 mmol, 3.0 equiv) in CH\(_2\)Cl\(_2\) (30 mL) dropwise. The reaction mixture was warmed to ambient temperature over 25 minutes and was stirred at that temperature for another 45 minutes. A large
excess of silica gel was then added, and the mixture was stirred for 1 hour. [In some cases, the addition of silica gel did not induce the elimination of HBr (intermediate visible by TLC analysis). In these instances, several equivalents of Et₃N can be added to induce the elimination.] The mixture was then concentrated, and the silica gel (with material adsorbed) was loaded onto a silica gel column (20% Et₂O:hexanes, then 100% CH₂Cl₂) to give anthraquinone 56 (3.04 g, 8.44 mmol, 90%) as a yellow powder. 56: Rₛ = 0.6 (silica gel, EtOAc:hexanes 3:7); FT-IR (neat) νₑₓₘₐₓ = 3065, 3012, 2921, 2850, 1671, 1631, 1583, 1490, 1388, 1326, 1296, 1244, 1198, 1165, 1149, 1031, 979, 842, 752 cm⁻¹; ¹H NMR (CDCl₃, 600 MHz) δ = 13.36 (s, 1 H), 7.96 (dd, J = 7.7, 1.1 Hz, 1 H), 5.36 (s, 2 H), 3.93 (s, 3 H) ppm; ¹³C NMR (CDCl₃, 151 MHz) δ = 187.5, 182.9, 165.6, 165.4, 159.8, 136.2, 135.9, 135.2, 134.3, 128.9, 128.2, 126.9, 121.6, 120.7, 120.4, 111.9, 107.5, 106.6, 71.4, 56.1 ppm; HRMS (ESI) calcd for C₂₂H₁₆O₅H⁺ [M+H⁺] 361.1070, found 361.1070.

Anthrone 28: Anthraquinone 56 (3.04 g, 8.44 mmol, 1.0 equiv) was dissolved in DMF (100 mL), and K₂CO₃ (5.8 g, 42 mmol, 5.0 equiv) and MeI (2.7 mL, 42 mmol, 5.0 equiv) were added sequentially. The resulting mixture was heated to 65 °C and stirred for 14 hours. The mixture was allowed to cool to ambient temperature, diluted with water (400 mL), and extracted with CH₂Cl₂ (300 mL). The organic phase was washed with water (2 × 300 mL). The organic layer was dried over Na₂SO₄, filtered, and concentrated to give the crude methylated anthraquinone 57. The crude residue was dissolved in glacial AcOH (155 mL) and conc. HCl
(15 mL) was added. The solution was heated to 50 °C, and SnCl₂ (11.2 g, 59.1 mmol, 7.0 equiv) was added. The mixture was stirred at this temperature for 15 minutes and then allowed to cool to ambient temperature. The mixture was then cautiously poured into water (400 mL) and extracted with CH₂Cl₂ (300 mL). The organic phase was dried over Na₂SO₄, filtered, and concentrated to give crude product, which was purified by flash column chromatography (33→66% Et₂O:hexanes) to give anthrone 28 (1.96 g, 7.26 mmol, 86% yield for two steps) as a yellow solid. 28: R₂F = 0.4 (silica gel, Et₂O:hexanes 3:2); FT-IR (neat) νₘₐₓ = 3002, 2939, 2839, 1624, 1594, 1567, 1492, 1452, 1428, 1353, 1327, 1251, 1222, 1161, 1092, 1058, 951, 909, 897, 829, 779, 728 cm⁻¹; ¹H NMR (CDCl₃, 500 MHz) δ = 13.35 (s, 1 H), 7.36 (ap t, J = 7.9 Hz, 1 H), 6.84 (dd, J = 8.3, 1.0 Hz, 1 H), 6.78 (dd, J = 7.6, 1.0 Hz, 1 H), 6.45 (d, J = 2.3 Hz, 1 H), 6.42 (d, J = 2.3 Hz, 1 H), 4.26 (s, 2 H), 3.96 (s, 3 H), 3.88 (s, 3 H) ppm; ¹³C NMR (CDCl₃, 126 MHz) δ = 189.1, 164.5, 163.5, 163.0, 146.2, 140.1, 134.5, 117.63, 117.57, 115.4, 114.7, 104.3, 97.9, 56.3, 55.7, 34.1 ppm; HRMS (ESI) calcd for C₁₆H₁₄O₄H⁺ [M+H⁺] 271.0965, found 271.0972.

**Alkylated anthrone 58:** A solution of anthrone 28 (2.2 g, 8.1 mmol, 1.0 equiv) and allylic chloride 27 (2.46 g, 8.14 mmol, 1.0 equiv) in anhydrous acetone (80 mL) was degassed with argon for 15 minutes while the reaction vessel was shielded from light with aluminum foil. After the degassing period, Na₂CO₃ (2.15 g, 20.3 mmol, 2.5 equiv) and KI (67 mg, 0.40 mmol, 0.05 equiv) were added, and the reaction mixture was heated to 50 °C and stirred for 12 hours.
Additional KI (67 mg, 0.40 mmol, 0.05 equiv) was added, and the reaction mixture was stirred for an additional 6 hours. The mixture was then allowed to cool to room temperature, and the reaction was quenched with saturated aq. NH₄Cl solution (100 mL) and water (100 mL), and extracted with CH₂Cl₂ (200 mL). The organic phase was dried over Na₂SO₄, filtered, and concentrated. The residue was purified by flash column chromatography (5→10→20% EtOAc:hexanes) to give product **58** (2.23 g, 4.16 mmol, 51%, d.r. ca. 1:1) as a yellow foam. **58**: 

Rᵣ = 0.65 (silica gel, Et₂O:hexanes 7:3); FT-IR (neat) νₘₐₓ = 2951, 2934, 2855, 1629, 1599, 1457, 1359, 1330, 1245, 1222, 1161, 1042, 834, 774, 732 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ = 13.01 (s, 1 H), 13.00 (s, 1 H), 7.33 (ap t, J = 7.9 Hz, 1 H), 7.30 (ap t, J = 8.0 Hz, 1 H), 6.85 (bs, 1 H), 6.83 (bs, 1 H), 6.78 – 6.74 (m, 2 H), 6.44 – 6.42 (m, 2 H), 6.41 – 6.39 (m, 2 H), 4.30 – 4.24 (m, 2 H), 3.97 (s, 3 H), 3.96 (s, 3 H), 3.97 – 3.87 (m, 2 H), 3.90 (s, 3 H), 3.89 (s, 3 H), 2.50 – 2.39 (m, 2 H), 2.32 – 2.18 (m, 2 H), 1.82 – 1.74 (m, 2 H), 1.63 – 1.46 (m, 6 H), 1.34 (bs, 3 H), 1.28 (bs, 3 H), 0.91 (ap s, 18 H), 0.80 (bs, 3 H), 0.74 (bs, 3 H), 0.67 (bs, 3 H), 0.56 (bs, 3 H), 0.084 (s, 3 H), 0.076 (s, 3 H), 0.07 (ap s, 6 H) ppm; ¹³C NMR (CDCl₃, 101 MHz)* δ = 188.70, 188.68, 164.3, 164.2, 163.31, 163.29, 162.5, 151.2, 150.8, 145.6, 144.8, 136.4, 134.6, 134.4, 134.1, 118.8, 118.0, 117.4, 117.1, 115.8, 115.7, 114.1, 114.0, 105.7, 105.3, 97.9, 97.6, 72.0, 71.6, 56.3, 55.74, 55.65, 44.6, 44.54, 44.49, 44.0, 35.9, 35.8, 35.7, 35.5, 31.7, 29.6, 29.4, 28.7, 28.6, 27.8, 27.0, 26.0, 18.3, 18.1, –4.07, –4.10, –4.61, –4.64 ppm; HRMS (ESI) calcd for C₃₂H₄₄O₅SiH⁺ [M+H⁺] 537.3031, found 537.3045.

*Due to signal broadening, not all the ¹³C signals could be identified.
Spirocycle 25: To a solution of alkylated anthrone 58 (2.23 g, 4.16 mmol, 1.0 equiv) in CH₂Cl₂ (60 mL) was added ZnI₂ (663 mg, 2.08 mmol, 0.5 equiv), and the resulting solution was heated to reflux. After 8 hours and 14 hours, additional portions of ZnI₂ (280 mg, 0.878 mmol, 0.2 equiv; then 100 mg, 0.313 mmol, 0.08 equiv) were added. After 17 hours of total reflux time, the reaction mixture was allowed to cool to room temperature. The reaction mixture was washed with water (40 mL), and the organic phase was dried over Na₂SO₄, filtered, and concentrated. Purification of the residue by flash column chromatography (20→50% Et₂O:hexanes) gave spirocycle 25 (572 mg, 1.41 mmol, 34%) as a yellow solid. 25: R_f = 0.3 (silica gel, Et₂O:hexanes 2:1); FT-IR (neat) ν_max = 2962, 2942, 2835, 1627, 1601, 1567, 1455, 1333, 1310, 1268, 1243, 1215, 1130, 1109, 998, 830, 780 cm⁻¹; ¹H NMR (CDCl₃, 600 MHz) δ = 13.14 (s, 1 H), 7.36 (dd, J = 8.3, 7.4 Hz, 1 H), 6.85 (d, J = 8.3 Hz, 1 H), 6.74 (d, J = 7.4 Hz, 1 H), 6.37 (s, 1 H), 5.46 (m, 1 H), 4.38 (dd, J = 11.2, 7.9 Hz, 1 H), 4.03 (s, 3 H), 3.86 (s, 3 H), 2.80 (dd, J = 12.9, 7.9 Hz, 1 H), 2.22 (m, 1 H), 2.19 (dd, J = 12.9, 11.2 Hz, 1 H), 2.04 (m, 1 H), 1.89 (ddd, J = 12.6, 12.6, 6.1 Hz, 1 H), 1.39 (dd, J = 13.2, 6.1 Hz, 1 H), 1.32 (s, 3 H), 1.02 (s, 3 H) ppm; ¹³C NMR (CDCl₃, 151 MHz) δ = 189.3, 163.0, 162.3, 162.2, 155.1, 145.3, 137.9, 134.6, 123.1, 121.5, 117.8, 115.9, 115.7, 111.9, 94.3, 59.6, 56.4, 55.2, 43.5, 42.4, 38.7, 34.8, 27.5, 24.7, 23.1, 20.6 ppm; HRMS (ESI) calcd for C₂₆H₅₈O₄H⁺ [M+H⁺] 405.2060, found 405.2063.
**Quinomethide 62:** To a solution of spirocycle 25 (15 mg, 0.037 mmol, 1.0 equiv) in MeOH (1 mL) at room temperature was added PhI(OAc)$_2$[7] (36 mg, 0.11 mmol, 3.0 equiv). The reaction mixture was allowed to stir at that temperature for 43 hours. The reaction mixture was then diluted with water (2 mL), extracted with EtOAc (2 × 2 mL), and the combined organics were concentrated. Purification of the crude product by preparative TLC (silica gel, 40% EtOAc:hexanes) provided quinomethide 62 (5.5 mg, 0.014 mmol, 37%) and recovered starting material 25 (3.9 mg, 0.0097 mmol, 26%). 62: $R_f = 0.6$ (silica gel, EtOAc:hexanes 2:3); FT-IR (neat) $v_{\text{max}} = 2962, 2931, 2840, 1623, 1573, 1466, 1435, 1335, 1263, 1236, 1218, 1161, 1037, 908, 830, 784, 731$ cm$^{-1}$; $^1$H NMR (CDCl$_3$, 600 MHz) δ = 13.94 (s, 1 H), 7.48 (ap t, $J = 7.7$ Hz, 1 H), 7.40 (d, $J = 7.7$ Hz, 1 H), 7.15 (s, 1 H), 6.98 (d, $J = 8.1$ Hz, 1 H), 6.41 (s, 1 H), 5.75 (bs, 1 H), 4.08 (s, 3 H), 3.93 (s, 3 H), 2.30 – 2.25 (m, 2 H), 1.92 (ddd, $J = 13.0, 6.2, 6.2$ Hz, 1 H), 1.64 (ddd, $J = 13.0, 6.9, 6.9$ Hz, 1 H), 1.15 (s, 3 H), 0.88 (s, 3 H), 0.85 (s, 3 H) ppm; $^{13}$C NMR (CDCl$_3$, 151 MHz) δ = 188.8, 163.8, 162.4, 160.2, 150.6, 145.3, 134.3, 133.9, 132.4, 131.1, 124.9, 124.5, 117.7, 116.9, 114.6, 109.7, 93.8, 67.1, 56.5, 55.6, 37.2, 35.9, 27.0, 26.8, 23.2, 19.7 ppm; HRMS (ESI) calcd for C$_{26}$H$_{26}$O$_4$H$^+$ [M+H$^+$] 403.1904, found 403.1918.

Quinomethide 62 was produced in varying quantities under the conditions shown in Table S1 and could be isolated by standard flash column chromatography (30% EtOAc:hexanes) or preparative TLC (silica gel, 30% EtOAc:hexanes).
Table S1. Conditions screened for phenolic oxidation (25→61 or 64, see Scheme 6 in the article).

| entry | conditions | observation |
|-------|------------|-------------|
| 1[8]  | PIFA, MeCN/H2O, 25 °C | slow decomposition |
| 2[8]  | PIDA, MeOH, 25 °C | 62 (37%) |
| 3[8]  | PIFA, MeOH, 25 °C | 62a |
| 4[8]  | PIFA, DMF/H2O, 0→25 °C | C6-hydroxylation |
| 5[8]  | NaIO4, EtOH/H2O, 25 °C | 62a + complex mixture |
| 6[8]  | PhICl2, CH2Cl2/MeOH, 0 °C | C17-chlorination/C16,21 olefin |
| 7[9]  | O2, salcomine, DMF, 25 °C | rapid decomposition |
| 8     | O2, aq. NaOH, 25 °C | decomposition |
| 9[10] | O2, hv, methylene blue, MeOH/CH2Cl2, 25 °C | 1O2-ene reaction involving C17,16,21 |
| 10[11]| CAN, MeCN/H2O, 25 °C | n.r.o. |
| 11[12]| cat. RuCl3•H2O, H2O2, MeOH/HCl, 25 °C | C16,17 epoxidation |
| 12[13]| Mn(OAc)2, H2O2, AcOH, 25→50 °C | decomposition |
| 13[14]| cat. MeReO3, H2O2, AcOH, 25→55 °C | C16,17 epoxidation |
| 14[15]| Ag2CO3, Celite®, C6H6, reflux | slow formation of 62a |
| 15[16]| Ag2O, Na2SO4, Et2O, reflux | slow formation of 62a |
| 16[17]| PhSeO2H, CH2Cl2, 25 °C | 62a |
| 17[18]| Fremy’s salt, MeOH/H2O, 25 °C | n.r.o. |

n.r.o. = no reaction observed; a as evidenced by TLC analysis

Anthracene derivative 63: To a stirred solution of spirocyclic compound 25 (20 mg, 0.050 mmol) in MeOH was added K2CO3 (17 mg, 0.12 mmol, 2.4 equiv). After stirring for 10 minutes at room temperature, the reaction mixture was filtered through a plug of Celite® and concentrated. Purification by preparative TLC (silica gel, 30% acetone:toluene) provided the title compound (10.9 mg, 0.0270 mmol, 54%) as a yellow foam. 63: Rf = 0.4 (silica gel, EtOAc:hexanes 1:1); FT-IR (neat) νmax = 3550, 2960, 2919, 1627, 1607, 1561, 1455, 1338, 1218, 1021, 902, 825, 780 cm⁻¹, 1H NMR (C6D6, 600 MHz) δ = 13.72 (s, 1 H), 7.02 – 7.00 (m, 2 H), 6.85 (s, 1 H), 6.81 (dd, J = 5.5, 3.0 Hz, 1 H), 5.86 (s, 1 H), 5.54 (bs, 1 H), 3.37 (s, 3 H), 3.06 (s,
3 H), 2.92 (d, J = 15.5 Hz, 1 H), 2.71 (d, J = 15.5 Hz, 1 H), 2.21 (m, 1 H), 2.03 (m, 1 H), 2.01 (s, 3 H), 1.64 (ddd, J = 13.0, 10.4, 6.2 Hz, 1 H), 1.32 (m, 1 H), 0.95 (s, 3 H), 0.44 (s, 3 H) ppm; 

$^{13}$C NMR (C$_6$D$_6$, 151 MHz) \( \delta = 188.8, 163.6, 162.63, 162.59, 150.2, 140.4, 137.9, 134.1, 125.7, 120.8, 119.5, 119.0, 117.6, 112.8, 97.2, 88.1, 60.4, 55.9, 54.4, 43.4, 38.6, 34.4, 26.1, 25.6, 23.4, 21.8 \) ppm; HRMS (ESI) calcd for C$_{26}$H$_{28}$O$_4$H$^+ [M+H$^+$] 405.2060, found 405.2045.

**Quinone 64:** To a vigorously stirred solution of 63 (29 mg, 0.072 mmol, 1.0 equiv) in CH$_2$Cl$_2$:H$_2$O (7:1, 0.8 mL) at 0 °C was added PhI(OAc)$_2$[7] (58 mg, 0.18 mmol, 2.5 equiv). The resulting reaction mixture was stirred for 10 minutes at 0 °C, during which time a red color evolved. The mixture was then allowed to warm to room temperature and stirred for an additional 45 minutes. During this time, the reaction mixture turned deeply purple. The entire reaction mixture was loaded onto two preparative TLC plates and eluted (silica gel, 15% acetone:toluene) which provided the title compound (1.2 mg, 2.9 µmol, 4%) as a purple solid along with 62 (3.7 mg, 9.2 µmol, 13%) and recovered starting material 63 (13 mg, 0.032 mmol, 45%). 64: \( R_y = 0.65 \) (silica gel, EtOAc:hexanes 2:3); FT-IR (neat) \( \nu_{max} = 2961, 2918, 1624, 1591, 1570, 1487, 1434, 1338, 1281, 1218, 1154, 1134, 1100, 1049, 919, 853 \) cm$^{-1}$; \( ^1$H NMR (C$_6$D$_6$, 600 MHz) \( \delta = 16.41 \) (s, 1 H), 6.43 (d, J = 10.2 Hz, 1 H), 6.36 (d, J = 10.2 Hz, 1 H), 6.13 (s, 1 H), 5.58 (bs, 1 H), 4.25 (d, J = 20.3 Hz, 1 H), 3.45 (d, J = 20.3 Hz, 1 H), 3.43 (s, 3 H), 3.18 (s, 3 H), 2.25 (m, 1 H), 2.00 (m, 1 H), 1.88 (td, J = 12.3, 6.0 Hz, 1 H), 1.64 (s, 3 H), 1.24 (dd, J = 13.3,
6.1 Hz, 1 H), 1.08 (s, 3 H), 0.52 (s, 3 H) ppm; $^{13}$C NMR (C$_6$D$_6$, 151 MHz) δ = 187.3, 184.9, 167.1, 161.1, 159.4, 147.9, 143.2, 139.54, 139.49, 136.8, 127.0, 121.8, 121.6, 110.6, 109.5, 97.8, 60.2, 55.9, 54.8, 46.1, 38.5, 34.3, 25.6, 24.6, 23.4, 21.1 ppm; HRMS (ESI) calcd for C$_{26}$H$_{26}$O$_5$H$^+$ [$M+H^+]$ 419.1853, found 419.1857.

**Acyl malonate 69:**\(^{[19]}\) Dimethyl malonate (68) (30.2 mL, 34.8 g, 0.264 mol, 1.0 equiv) was added to a suspension of magnesium chloride (25.3 g, 0.266 mol, 1.0 equiv) in acetonitrile (265 mL). The suspension was cooled to 0 °C and Et$_3$N (74 mL, 54 g, 0.53 mol, 2.0 equiv) was added. After stirring for 15 minutes, freshly distilled acetyl chloride (19 mL, 21 g, 0.27 mol, 1.0 equiv) was added, and the reaction mixture was stirred for one hour at 0 °C and then allowed to warm to room temperature. After stirring for 23 hours at room temperature, the reaction mixture was cooled to 0 °C, quenched with 5 N aq. HCl solution (200 mL) and extracted with Et$_2$O (4 × 200 mL). The combined organic layers were washed with brine, dried over MgSO$_4$, filtered, and concentrated to give crude 69 as a light yellow-green liquid. The crude product was purified by distillation under reduced pressure to yield 44.3 g (0.254 mol, 96%, keto:enol = 1:3.4) of 69 as a colorless oil. 69: R$_f$ = 0.5 (silica gel, EtOAc:hexanes 1:3); FT-IR (neat) $\nu_{\text{max}}$ = 2957, 1721, 1650, 1604, 1437, 1241, 1148, 1087 cm$^{-1}$; $^1$H NMR (CDCl$_3$, 400 MHz) δ = 13.53 (s, 1 H, enol tautomer), 4.46 (s, 1 H, keto tautomer), 3.81 – 3.76 (m, 6 H, keto tautomer + 6 H, enol tautomer), 2.32 (s, 3 H, keto tautomer), 2.19 (s, 3 H, enol tautomer) ppm; $^{13}$C NMR (CDCl$_3$, 101 MHz) δ = 196.5, 181.6, 171.7, 166.5, 165.0, 99.3, 65.6, 53.2, 52.4, 52.1, 29.2, 21.1 ppm; HRMS (ESI) calcd for C$_7$H$_{10}$O$_5$Na$^+$ [$M+Na^+]$ 197.0420, found 197.0425.
Diester 70: To a solution of 69 (8.7 g, 50 mmol) in DMF (255 mL) at 0 °C was added K₂CO₃ (9.3 g, 67 mmol, 1.3 equiv). After stirring for 20 minutes, dimethyl sulfate (6.3 mL, 8.4 g, 67 mmol, 1.3 equiv) was added dropwise. After 17 hours, saturated aq. NH₄Cl solution (90 mL) was carefully added, the phases were separated, and the aqueous layer was extracted with EtOAc (6 × 100 mL). The combined organic phases were washed with brine, dried over MgSO₄, filtered, and concentrated. The crude product was purified by flash column chromatography (25→50% EtOAc:hexanes) to yield 70 (5.0 g, 27 mmol, 54%) of a colorless solid.* 70: Rf = 0.5 (silica gel, EtOAc:hexanes 1:1); FT-IR (neat) νmax = 2954, 1709, 1615, 1434, 1379, 1309, 1220, 1095, 1064 cm⁻¹; ¹H NMR (CDCl₃, 500 MHz) δ = 3.76 (s, 3 H), 3.75 (s, 3 H), 3.67 (s, 3 H), 2.42 (s, 3 H) ppm; ¹³C NMR (CDCl₃, 126 MHz) δ = 171.3, 167.0, 165.5, 106.9, 55.6, 52.4, 51.7, 14.1 ppm; HRMS (ESI) calcd for C₈H₁₂O₅Na⁺ [M+Na⁺] 211.0577, found 211.0579.

*On multidecagram scale, column chromatographic purification could be replaced by distillation under reduced pressure. The so-obtained product was less pure, but could be used in the next step without additional purification.

Isoxazole 71: A solution of sodium methoxide was prepared by treating sodium (2.80 g, 122 mmol, 3.1 equiv, cut into small pieces) with methanol (28 mL). A solution of hydroxylamine
hydrochloride (3.70 g, 53.2 mmol, 1.4 equiv) in dry methanol (30 mL) and, subsequently, a solution of diester 70 (7.30 g, 38.8 mmol, 1.0 equiv) in dry methanol (21 mL) were slowly added to the sodium methoxide solution at 0 °C. The reaction was allowed to warm to room temperature and stirred for 24 hours. The reaction was quenched with saturated aq. NH₄Cl solution (20 mL) and concentrated by rotary evaporation to remove most of the methanol. The residue was acidified to pH 4 with 5% aq. HCl solution, extracted with chloroform (6 × 100 mL), dried over MgSO₄, filtered, and concentrated to give isoxazole 71 (2.94 g, 18.7 mmol, 48%) as a colorless solid. 71: R₇ = 0.3 (silica gel, EtOAc:hexanes 1:1); FT-IR (neat) νₘₐₓ = 2959, 2826, 2611, 1704, 1630, 1535, 1430, 1312, 1187, 1121, 1082, 954, 812, 783 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ = 8.41 (bs, 1 H), 3.94 (s, 3 H), 2.60 (s, 3 H) ppm; ¹³C NMR (CDCl₃, 101 MHz) δ = 175.2, 169.6, 164.3, 98.9, 52.5, 14.1 ppm; HRMS (ESI) calcd for C₆H₇NO₄H⁺ [M+H⁺] 158.0448, found 158.0451.

Benzyl isoxazole 26: To a stirred solution of isoxazole 71 (8.16 g, 51.9 mmol, 1.0 equiv) in DMF (500 mL) was added Ag₂O (18.2 g, 78.5 mmol, 1.5 equiv). After stirring for 5 minutes, benzyl bromide (7.6 mL, 11 g, 64 mmol, 1.2 equiv) was added and the reaction mixture was shielded from light with aluminum foil and stirred at room temperature for 18 hours. The reaction mixture was then filtered through a silica gel pad and rinsed with EtOAc. The filtrate was concentrated to give the crude product as a thick dark orange-brown oil. Purification by flash column chromatography (20% EtOAc:hexanes) yielded 26 (8.58 g, 34.7 mmol, 67%) as a colorless solid. 26: R₇ = 0.3 (silica gel, EtOAc:hexanes 1:5); FT-IR (neat) νₘₐₓ = 3033, 2953,
1732, 1715, 1621, 1510, 1319, 1117, 784, 738, 697 cm−1; 1H NMR (CDCl3, 600 MHz) δ = 7.49 – 7.46 (m, 2 H), 7.40 – 7.37 (m, 2 H), 7.34 (m, 1 H), 5.35 (s, 2 H), 3.84 (s, 3 H), 2.61 (s, 3 H) ppm; 13C NMR (CDCl3, 151 MHz) δ = 177.2, 169.2, 162.0, 135.8, 128.7, 128.4, 127.9, 100.7, 71.7, 51.8, 14.1 ppm; HRMS (ESI) calcd for C13H13NO4H+ [M+H+] 248.0917, found 248.0906.

1,2-Addition Product 72: To a solution of isoxazole 26 (30.6 mg, 0.124 mmol, 1.0 equiv) in THF (0.7 mL) at −78 °C was added LiHMDS (1.0 M in THF, 0.18 mL, 0.18 mmol, 1.4 equiv), and the mixture was stirred at −78 °C for 40 minutes. A solution of quinone monoketal 67 (19.7 mg, 0.128 mmol, 1.0 equiv) in THF (0.7 mL) was added. After stirring for 15 minutes at −78 °C, the mixture was allowed to warm to −30 °C over 30 minutes. Then, the reaction was quenched with phosphate buffered saline solution (3 mL) and extracted with CH2Cl2 (3 × 15 mL). The combined organic phases were dried over MgSO4, filtered, and concentrated. Purification of the crude product by flash column chromatography (50% EtOAc:hexanes, 0.1% Et3N) yielded the 1,2-adduct 72 (30.8 mg, 0.0767 mmol, 62%) as a colorless oil. 72: Rf = 0.40 (silica gel, EtOAc:hexanes 1:1); FT-IR (neat) νmax = 3413, 2950, 2829, 1716, 1618, 1510, 1451, 1366, 1324, 1031, 957, 737, 696 cm−1; 1H NMR (C6D6, 600 MHz) δ = 7.32 (d, J = 7.4 Hz, 2 H), 7.13 – 7.09 (m, 2 H), 7.05 (m, 1 H), 5.96 (d, J = 10.5 Hz, 2 H), 5.80 (d, J = 10.5 Hz, 2 H), 5.21 (s, 2 H), 3.35 (s, 3 H), 3.25 (s, 2 H), 3.09 (s, 3 H), 3.01 (s, 3 H), 2.71 (bs, 1 H) ppm; 13C NMR (C6D6, 151 MHz) δ = 175.8, 169.2, 162.5, 136.3, 135.6, 128.7, 128.5, 128.4, 127.6, 103.0, 51.8, 14.1 ppm; HRMS (ESI) calcd for C13H13NO4H+ [M+H+] 248.0917, found 248.0906.
Isoxazole 73: Isoxazole 26 (11.3 g, 45.5 mmol, 1.0 equiv) was dissolved in THF (225 mL) and cooled to –78 °C. LiHMDS (1.0 M in THF, 100 mL, 100 mmol, 2.2 equiv) was added, and the mixture was stirred at –78 °C for 30 minutes. Then a solution of methyl chloroformate (3.6 mL, 4.4 g, 46 mmol, 1.0 equiv) in THF (35 mL) was added (the flask was rinsed with THF, 2 × 10 mL), and the mixture was stirred at –78 °C for another 45 minutes. Then the reaction was quenched with saturated aq. NH₄Cl solution (ca. 400 mL). The mixture was extracted with EtOAc (3 × 200 mL), and the combined organic layers were dried over MgSO₄, filtered, and concentrated. Purification by column chromatography (50% EtOAc:hexanes) afforded 73 (13.4 g, 43.8 mmol, 96%) as a slightly yellowish oil that solidified upon standing. 73: Rf = 0.61 (silica gel, EtOAc:hexanes 1:1); FT-IR (neat) v_max = 2955, 1743, 1715, 1629, 1512, 1326, 1201, 1117, 1084, 737 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ = 7.50 – 7.46 (m, 2 H), 7.42 – 7.31 (m, 3 H), 5.36 (s, 2 H), 4.07 (s, 2 H), 3.83 (s, 3 H), 3.74 (s, 3 H) ppm; ¹³C NMR (CDCl₃, 101 MHz) δ = 172.3, 169.1, 167.1, 161.4, 135.6, 128.7, 128.5, 128.0, 102.4, 72.0, 52.9, 52.0, 33.9 ppm; HRMS (ESI) calcd for C₁₅H₁₅NO₆H⁺ [M+H⁺] 306.0972, found 306.0973.
Michael adduct 74: To a solution of isoxazole 73 (13.4 g, 43.8 mmol, 1.0 equiv) in MeOH (300 mL) was added a solution of quinone monoketal 67 (6.80 g, 44.1 mmol, 1.0 equiv) in MeOH (130 mL). A freshly prepared solution of NaOMe in MeOH (1.0 M, 44 mL, 44 mmol, 1.0 equiv) was added, and the mixture was stirred at room temperature for ca. 18 hours. Then saturated aq. NH₄Cl solution (300 mL) was added, and the mixture was extracted with EtOAc (3 × 200 mL). The combined organic phases were dried over MgSO₄, filtered, and concentrated. The crude product was purified by flash column chromatography (33% EtOAc:hexanes, 0.1% Et₃N) to afford 74 (14.2 g, 31.0 mmol, 71%, d.r. ca. 3:1 by ¹H NMR analysis). 74: Rᵢ = 0.42 (silica gel, EtOAc:hexanes 1:1); FT-IR (neat) νₑₑₑ = 2953, 2837, 1736, 1691, 1618, 1511, 1452, 1365, 1297, 1221, 1195, 1114, 1056, 915, 733 cm⁻¹; ¹H NMR (CDCl₃, 600 MHz) δ = 7.49 – 7.44 (m, 4 H, major + minor), 7.41 – 7.31 (m, 6 H, major + minor), 6.78 (d, J = 10.6 Hz, 1 H, minor), 6.71 (d, J = 10.6 Hz, 1 H, major), 6.14 (d, J = 10.6 Hz, 1 H, minor), 5.95 (d, J = 10.6 Hz, 1 H, major), 5.35 (s, 2 H, minor), 5.32 (s, 2 H, major), 5.00 (d, J = 7.0 Hz, 1 H, major), 4.92 (d, J = 8.9 Hz, 1 H, minor), 3.83 (s, 3 H, minor), 3.82 (s, 3 H, major), 3.70 (s, 3 H, major), 3.67 (s, 3 H, minor), 3.59 (m, 1 H, major), 3.46 (m, 1 H, minor), 3.31 (s, 3 H, major), 3.28 (s, 3 H, major), 3.18 (s, 3 H, minor), 3.12 (s, 3 H, minor), 2.82 (dd, J = 17.2, 4.9 Hz, 1 H, minor), 2.70 – 2.61 (m, 2 H, major + minor), 2.43 (dd, J = 17.3, 5.2 Hz, 1 H, major) ppm; ¹³C NMR (CDCl₃, 151 MHz) δ = 196.44 (minor), 196.35 (major), 174.2 (minor), 173.2 (major), 169.1 (minor), 168.9 (major), 168.7 (major), 168.4 (minor), 161.4 (minor), 161.2 (major), 146.1 (minor), 145.1 (major), 135.6 (minor), 135.5 (major), 131.9 (minor), 131.5 (major), 128.6 (major + minor), 128.48 (major),
128.45 (minor), 128.0 (major), 127.9 (minor), 103.5 (major), 101.5 (minor), 98.3 (minor), 98.2 (major), 72.0 (major), 71.9 (minor), 53.0 (major), 52.8 (minor), 52.1 (major), 52.0 (minor), 50.6 (minor), 50.4 (major), 49.6 (minor), 49.5 (major), 44.3 (minor), 43.1 (major), 41.6 (major), 40.7 (minor), 38.9 (minor), 37.5 (major) ppm; HRMS (ESI) calcd for C$_{23}$H$_{25}$NO$_9$Na$^+$ [M$+$Na$^+$] 482.1421, found 482.1428.

**Dieckmann product 75:** To a solution of Michael adduct 74 (13.9 g, 30.3 mmol, 1.0 equiv, d.r. ca. 3:1) in toluene (500 mL) at 0 °C was added carefully NaH (60% in mineral oil, 4.86 g, 117 mmol, 3.9 equiv). The mixture was then warmed to 80 – 90 °C and stirred at this temperature for 2.5 hours. Then the mixture was cooled to 0 °C, and the reaction was carefully quenched with an excess of saturated aq. NH$_4$Cl solution (200 mL). The phases were separated, and the aqueous phase was extracted with EtOAc (100 mL) and subsequently CH$_2$Cl$_2$ (3 × 100 mL). The combined organic phases were dried over MgSO$_4$, filtered, and concentrated. Recrystallization of the crude product from Et$_2$O (200–300 mL) afforded 75 (6.70 g, 15.7 mmol, 52%) as a greenish powder. Alternatively, the crude product could be used directly in the next step without further purification. 75: R$_f$ = 0.46 (silica gel, EtOAc:hexanes 1:1); FT-IR (neat) $\nu$$_{max}$ = 3400, 2952, 1743, 1646, 1511, 1488, 1453, 1292, 1215, 1143, 1087, 1067, 911, 729 cm$^{-1}$; $^1$H NMR (CDCl$_3$, 600 MHz) $\delta$ = 14.83 (s, 1 H), 7.51 – 7.46 (m, 2 H), 7.42 – 7.31 (m, 3 H), 6.54 (d, $J$ = 10.2 Hz, 1 H), 6.37 (d, $J$ = 10.2 Hz, 1 H), 5.37 (s, 2 H), 4.56 (d, $J$ = 11.2 Hz, 1 H), 4.07 (d, $J$ = 11.2 Hz, 1 H), 3.86 (s, 3 H), 3.30 (s, 3 H), 3.24 (s, 3 H) ppm; $^{13}$C NMR (CDCl$_3$, 151 MHz) $\delta$ =
181.9, 175.8, 169.5, 169.3, 167.9, 169.3, 167.9, 128.6, 105.9, 101.8, 98.9, 72.6, 53.3, 52.2, 51.0, 41.3, 39.4 ppm; HRMS (ESI) calcld for C_{22}H_{21}NO_{8}H^{+} [M+H^{+}] 428.1340, found 428.1354.

**AB-ring system 76** (via methyl ester route from Scheme 9): Crude product 75 obtained by Dieckmann condensation of 74 (114 mg, 0.248 mmol) according to the experimental procedure described above was dissolved in DCE (2.8 mL) and treated with Me$_3$SnOH (205 mg, 1.13 mmol, 4.6 equiv). The mixture was stirred at 80 °C for 12 hours, after which another portion of Me$_3$SnOH (100 mg, 0.553 mmol, 2.2 equiv) was added. Stirring was continued at 80 °C for another 7 hours, and another portion of Me$_3$SnOH (100 mg, 0.553 mmol, 2.2 equiv) was added. After another 2 hours aq. KHSO$_4$ solution (0.015 M, ca. 20 mL) was added. The phases were separated, and the aqueous phase was extracted with CH$_2$Cl$_2$ (3 × 50 mL). The combined organic layers were then washed with brine, dried over MgSO$_4$, filtered, and concentrated. Purification of the residue by flash column chromatography (40% EtOAc:hexanes) yielded 76 (35.7 mg, 97.2 µmol, 39% yield for two steps) as a yellowish oil. 76: R$_f$ = 0.60 (silica gel, acetone:toluene 1:9); FT-IR (neat) $\nu_{\text{max}}$ = 2942, 2833, 1651, 1509, 1494, 1277, 1146, 1061, 906, 861, 810, 754, 704, 648 cm$^{-1}$; $^1$H NMR (C$_6$D$_6$, 600 MHz) δ = 15.49 (s, 1 H), 7.40 (d, $J = 7.2$ Hz, 2 H), 7.12 (t, $J = 7.4$ Hz, 2 H), 7.05 (m, 1 H), 6.00 (d, $J = 10.2$ Hz, 1 H), 5.72 (d, $J = 10.2$ Hz, 1 H), 5.27 (d, $J = 12.3$ Hz, 1 H, AB system), 5.23 (d, $J = 12.3$ Hz, 1 H, AB system), 3.00 (dd, $J = 17.1$, 12.5 Hz, 1 H), 2.93 (dd, $J = 12.5$, 6.5 Hz, 1 H), 2.89 (s, 3 H), 2.79 (s, 3 H),
2.59 (dd, $J = 17.1, 6.5$ Hz, 1 H) ppm; $^{13}$C NMR (C$_6$D$_6$, 151 MHz) $\delta = 183.4, 180.3, 168.44,$ 
$168.37, 137.1, 136.1, 129.3, 128.7, 128.51, 128.46, 105.9, 103.0, 98.2, 72.1, 50.8, 50.3, 38.2,$
$21.1$ ppm; HRMS (ESI) calcd for C$_{20}$H$_{19}$NO$_6$H$^+$ [M+H$^+$] $370.1285$, found $370.1280$.

**Phenol 79:** To a solution of PhSeCl (321 mg, 1.68 mmol) in CH$_2$Cl$_2$ (32 mL) at 0 °C was added
pyridine (0.15 mL, 0.15 g, 1.9 mmol), and the mixture was stirred for 15 minutes. Separately,
intermediate 76 (314 mg, 0.850 mmol, 1.0 equiv) was dissolved in CH$_2$Cl$_2$ (9 mL) at 0 °C to
which was added dropwise 17.5 mL of the previously prepared PhSeCl–pyridine solution. After
stirring at 0 °C for 30 min, another 9 mL PhSeCl–pyridine solution were added, followed by
another 4 mL portion after another 30 minutes. After a total reaction time of 1.5 hours, the
mixture was washed with water (2 × 10 mL) and concentrated. The crude product was dissolved
in CH$_2$Cl$_2$ (9 mL) and cooled to 0 °C. Then, H$_2$O$_2$ (70 µL, 30% in H$_2$O) was added, and after 10,
20, and 30 minutes, additional portions of H$_2$O$_2$ (70 µL, 30% in water) were added. Then the
reaction was quenched with saturated aq. NaHCO$_3$ solution (10 mL), and the phases were
separated. The aqueous phase was extracted with CH$_2$Cl$_2$ (3 × 10 mL), dried over MgSO$_4$,
filtered, and concentrated. Purification of the residue by flash column chromatography (50%
Et$_2$O:hexanes, 0.1% Et$_3$N) afforded phenol 79 (170 mg, 0.463 mmol, 54%) as a yellow oil. **79:** R$_f$
= 0.37 (silica gel, EtOAc:hexanes 1:1); FT-IR (neat) $\nu_{\text{max}} = 2943, 2832, 1660, 1610, 1530, 1412,$
1364, 1309, 1279, 1153, 1101, 1075, 908, 844, 733, 696 cm$^{-1}$; $^1$H NMR (CDCl$_3$, 600 MHz) $\delta =$
13.70 (s, 1 H), 7.57 – 7.52 (m, 2 H), 7.44 – 7.34 (m, 3 H), 7.28 (s, 1 H), 6.96 (d, $J = 10.4$ Hz,
1 H), 6.57 (d, J = 10.4 Hz, 1 H), 5.50 (s, 2 H), 3.20 (s, 6 H) ppm; $^{13}$C NMR (CDCl$_3$, 151 MHz) δ = 188.8, 169.1, 166.6, 160.4, 145.2, 143.6, 135.3, 132.2, 128.8, 128.7, 128.4, 110.4, 104.3, 101.7, 95.3, 72.6, 51.4 ppm; HRMS (ESI) calcd for C$_{20}$H$_{17}$NO$_6$H$^+$ [M+H$^+$] 368.1129, found 368.1123.

**AB-enone fragment 65**: To a solution of phenol 79 (3.41 g, 9.29 mmol, 1.0 equiv) in anhydrous acetone (100 mL) were added sequentially K$_2$CO$_3$ (2.57 g, 18.6 mmol, 2.0 equiv) and BnBr (1.65 mL, 13.9 mmol, 1.5 equiv). The resulting slurry was warmed to 50 °C and stirred for 2.75 hours. Then, additional portions of K$_2$CO$_3$ (2.57 g, 18.6 mmol, 2.0 equiv) and BnBr (1.65 mL, 13.9 mmol, 1.5 equiv) were added, and the mixture was warmed to 65 °C and stirred for another 3.75 hours. The mixture was then allowed to cool to room temperature, filtered through a plug of Celite®, and concentrated. Purification of the residue by flash column chromatography (10→20→30% EtOAc:hexanes, 0.1% Et$_3$N) provided AB-enone 65 (3.97 g, 8.69 mmol, 94%).

65: $R_f = 0.61$ (silica gel, Et$_2$O:hexanes 1:1); FT-IR (neat) $\nu_{\text{max}} = 3034, 2914, 2831, 1671, 1606, 1528, 1356, 1335, 1312, 1275, 1097, 1074, 960, 914, 733, 695$ cm$^{-1}$; $^1$H NMR (CDCl$_3$, 600 MHz) δ = 7.63 (s, 1 H), 7.52 – 7.47 (m, 2 H), 7.44 – 7.36 (m, 5 H), 7.26 (m, 1 H), 7.23 – 7.18 (m, 2 H), 6.86 (d, J = 10.5 Hz, 1 H), 6.54 (d, J = 10.5 Hz, 1 H), 5.49 (s, 2 H), 5.17 (s, 2 H), 3.22 (s, 6 H) ppm; $^{13}$C NMR (CDCl$_3$, 151 MHz) δ = 182.6, 167.2, 166.1, 156.1, 145.3, 140.8, 136.2, 135.1, 134.6, 129.2, 129.02, 129.00, 128.9, 128.44, 128.39, 120.7, 110.5, 105.4, 95.6, 77.9, 73.0, 51.4 ppm; HRMS (ESI) calcd for C$_{27}$H$_{23}$NO$_6$H$^+$ [M+H$^+$] 458.1598, found 458.1602.
Isoxazole 81: To a solution of isoxazole 26 (10.3 g, 41.7 mmol, 1.0 equiv) in THF (200 mL) at –78 °C was added LiHMDS (1.0 M in THF, 93 mL, 93 mmol, 2.2 equiv), and the mixture was stirred at –78 °C for 30 minutes. Then, a solution of TeocCl[20] (8.2 g, 45 mmol, 1.1 equiv) in THF (100 mL) was added via cannula, and stirring was continued for another hour. The reaction was quenched with excess saturated aq. NH₄Cl solution (100 mL), and the mixture was extracted with Et₂O (3 × 100 mL), dried over MgSO₄, filtered and concentrated. Purification by flash column chromatography (33% EtOAc:hexanes) furnished product 81 (14.4 g, 36.8 mmol, 88%) as a yellowish oil. 81: Rf = 0.78 (silica gel, EtOAc:hexanes 1:1); FT-IR νmax = 2954, 1737, 1716, 1628, 1512, 1248, 1174, 1115, 857, 835, 734, 695 cm⁻¹; ¹H NMR (CDCl₃, 500 MHz) δ = 7.50 – 7.46 (m, 2 H), 7.41 – 7.37 (m, 2 H), 7.34 (m, 1 H), 5.36 (s, 2 H), 4.26 – 4.21 (m, 2 H), 4.04 (s, 2 H), 3.83 (s, 3 H), 1.01 – 0.97 (m, 2 H), 0.03 (s, 9 H) ppm; ¹³C NMR (CDCl₃, 126 MHz) δ = 172.5, 169.0, 166.8, 161.4, 135.6, 128.7, 128.5, 128.0, 102.3, 71.9, 64.4, 52.0, 34.3, 17.4, –1.5 ppm; HRMS (ESI) calcd for C₁₉H₂₅NO₆SiH⁺ [M+H⁺] 392.1524, found 392.1522.
Michael adduct 82: To a solution of 81 (416 mg, 1.06 mmol, 1.0 equiv) and quinone monoketal 67 (163 mg, 1.06 mmol, 1.0 equiv) in toluene (10.6 mL) was added tBuOK (23 mg, 0.21 mmol, 0.2 equiv) and the mixture was stirred at room temperature for 4 hours. Then, the reaction was quenched with saturated aq. NH₄Cl solution (10 mL), and the mixture was extracted with EtOAc (3 × 10 mL), dried over MgSO₄, filtered, and concentrated. Purification of the residue by flash column chromatography (50% Et₂O:hexanes, 0.1% Et₃N) afforded Michael adduct 82 (411 mg, 0.753 mmol, 71%, d.r. ca. 2.4:1 by ¹H NMR analysis). The reaction could be scaled up to multigram scale (> 10 g). In such large scale reactions, the diastereomeric product mixture was obtained in comparable yields but in lower purity, which, however, did not have any negative effect on the following deprotection/decarboxylation sequence. 82: Rᵓ = 0.45 (silica gel, EtOAc:hexanes 1:1); FT-IR (neat) νmax = 2953, 1732, 1691, 1619, 1511, 1451, 1249, 1112, 1054, 914, 857, 836, 730, 695 cm⁻¹; ¹H NMR (CDCl₃, 500 MHz) δ = 7.50 – 7.42 (m, 4 H, major + minor), 7.42 – 7.30 (m, 6 H, major + minor), 6.77 (dd, J = 10.4, 0.8 Hz, 1 H, minor), 6.68 (dd, J = 10.5, 1.3 Hz, 1 H, major), 6.14 (d, J = 10.4 Hz, 1 H, minor), 5.92 (d, J = 10.5 Hz, 1 H, major), 5.35 (s, 2 H, minor), 5.32 (s, 2 H, major), 4.97 (d, J = 6.6 Hz, 1 H, major), 4.87 (d, J = 9.3 Hz, 1 H, minor), 4.24 – 4.12 (m, 4 H, major + minor), 3.83 (s, 3 H, minor), 3.82 (s, 3 H, major), 3.62 – 3.52 (m, 1 H, major), 3.49 – 3.43 (m, 1 H, minor), 3.30 (s, 3 H, major), 3.28 (s, 3 H, major), 3.17 (s, 3 H, minor), 3.10 (s, 3 H, minor), 2.83 (dd, J = 17.2, 4.7 Hz, 1 H, minor), 2.68 (dd, J = 17.7, 5.4 Hz, 1 H, major), 2.65 (dd, J = 17.2, 6.9 Hz, 1 H, minor), 2.45 (dd, J = 17.7, 5.1 Hz, 1 H, major), 0.98 – 0.90 (m, 4 H, major + minor), 0.00 (s, 9 H, minor), –0.01 (s, 9 H, major) ppm; ¹³C NMR (CDCl₃, 126 MHz) δ = 196.5 (minor), 196.4 (major), 174.4 (minor), 173.5 (major), 169.1
(minor), 168.9 (major), 168.3 (major), 168.0 (minor), 161.3 (minor), 161.1 (major), 146.2 (minor), 145.1 (major), 135.7 (minor), 135.6 (major), 131.9 (minor), 131.5 (major), 128.6 (major + minor), 128.44 (major), 128.42 (minor) 128.0 (major), 127.9 (minor), 103.5 (major), 101.4 (minor), 98.4 (minor), 98.2 (major), 72.0 (major), 71.8 (minor), 64.6 (minor), 64.5 (major), 52.0 (major), 51.9 (minor), 50.5 (minor), 50.3 (major), 49.5 (minor), 49.4 (major), 44.7 (minor), 43.3 (major), 41.5 (major), 40.8 (minor), 39.0 (minor), 37.5 (major), 17.26 (major), 17.25 (minor), – 1.5 (major + minor) ppm; HRMS (ESI) calcd for C_{27}H_{35}NO_{9}SiNa^+ [M+Na^+] 568.1973, found 568.1963.

**Intermediate 83:** To a solution of Michael adduct 82 (16.8 g, 30.8 mmol, 1.0 equiv) in THF (300 mL) was added TBAF (1.0 M in THF, 37 mL, 37 mmol, 1.2 equiv), and the mixture was stirred at room temperature for 45 minutes. Then, the reaction was quenched with saturated aq. NH₄Cl solution (150 mL). The aqueous phase was extracted with EtOAc (3 × 100 mL), and the combined organic phases were dried over MgSO₄, filtered, and concentrated. Purification by flash column chromatography (33→50% EtOAc: hexanes, 0.1% Et₃N; then 50% EtOAc:CH₂Cl₂, 0.1% Et₃N) afforded compound 83 (10.5 g, 26.2 mmol, 85%) as a colorless amorphous solid. 83: Rᵣ = 0.38 (silica gel, EtOAc:hexanes 1:1); FT-IR (neat) νₘₐₓ = 2958, 2927, 2837, 1712, 1688, 1618, 1511, 1461, 1367, 1315, 1106, 1068, 1047, 913, 740, 696 cm⁻¹; ¹H NMR (CDCl₃, 600 MHz) δ = 7.48 – 7.45 (m, 2 H), 7.40 – 7.36 (m, 2 H), 7.33 (m, 1 H), 6.77 (dd, J = 10.4, 1.6 Hz, 1 H), 6.12 (d, J = 10.4 Hz, 1 H), 5.33 (s, 2 H), 3.79 (s, 3 H), 3.35 (s, 3 H), 3.31 (s, 3 H), 3.14 (dd, J = 14.8, 4.0 Hz, 1 H), 3.05 (dd, J = 14.8, 11.1 Hz, 1 H), 2.95 (m, 1 H), 2.70 (dd, J =
17.4, 4.8 Hz, 1 H), 2.32 (dd, J = 17.4, 4.0 Hz, 1 H) ppm; $^{13}$C NMR (CDCl$_3$, 151 MHz) $\delta$ = 197.1, 177.8, 169.2, 161.5, 146.6, 135.6, 131.6, 128.7, 128.5, 127.9, 101.7, 98.4, 71.9, 51.9, 50.2, 48.4, 39.2, 38.7, 27.3 ppm; HRMS (ESI) calcd for C$_{21}$H$_{23}$NO$_7$Na$^+$ [M+Na$^+$] 424.1367, found 424.1365.

![AB ring system 76](image)

**AB ring system 76** (via Teoc ester route from Scheme 10): To a solution of 83 (10.5 g, 26.2 mmol, 1.0 equiv) in toluene (500 mL) at 0 °C was carefully added NaH (60% in mineral oil, 4.37 g, 105 mmol, 4.0 equiv). The mixture was warmed up to 80 °C and stirred for 2 hours, and then at 110 °C for a further 2 hours. The mixture was allowed to cool to room temperature, and the reaction was carefully quenched by addition of saturated aq. NH$_4$Cl solution (200 mL). The phases were separated, and the aqueous phase was extracted with EtOAc (3 × 100 mL). The combined organic phases were then dried over MgSO$_4$, filtered, and concentrated. Purification by flash column chromatography (50% EtOAc:hexanes, 0.1% Et$_3$N) afforded 76 (7.72 g, 20.9 mmol, 80%) as a yellowish solid. The physical and spectroscopic data matched those reported above.
**ABCD tetracycle 88:** AB-enone 65 (2.00 g, 4.38 mmol, 1.0 equiv) was dissolved in MeCN (40 mL) and DBU (2.0 mL, 13 mmol, 3.0 equiv) was added. Separately, a solution of cyclic anhydride 66 (1.26 g, 5.68 mmol, 1.3 equiv) in MeCN (40 mL) was prepared, and the cyclic anhydride solution was added via addition funnel to the solution of AB enone 65 and DBU over 1 hour. The reaction mixture was then heated to 60 °C for 18 hours. The mixture was concentrated, and the crude residue was purified by flash column chromatography (10→20→30→40% EtOAc:hexanes) to give pentacycle 88 (2.27 g, 3.57 mmol, 82%) as an orange foam. **88:** Rf = 0.4 (silica gel, EtOAc:hexanes 2:3); FT-IR (neat) νmax = 2940, 1602, 1526, 1453, 1321, 1282, 1197, 1156, 1092, 1070, 959, 913, 893, 733, 697 cm⁻¹; ¹H NMR (CDCl₃, 600 MHz) δ = 7.51 – 7.48 (m, 2 H), 7.44 (s, 1 H), 7.41 – 7.38 (m, 3 H), 7.33 – 7.32 (m, 2 H), 7.24 (m, 1 H), 7.20 – 7.17 (m, 2 H), 6.40 (ap s, 2 H), 5.51 (d, J = 11.4 Hz, 1 H, AB system), 5.47 (d, J = 11.4 Hz, 1 H, AB system), 5.20 (d, J = 9.3 Hz, 1 H, AB system), 5.13 (d, J = 9.3 Hz, 1 H, AB system), 3.93 (s, 3 H), 3.88 (s, 3 H), 3.49 (s, 3 H), 3.41 (ap t, J = 14.3 Hz, 1 H), 3.34 (dd, J = 14.1, 4.2 Hz, 1 H), 3.03 (s, 3 H), 2.81 (dd, J = 14.8, 4.2 Hz, 1 H) ppm; ¹³C NMR (CDCl₃, 151 MHz) δ = 183.7, 174.6, 166.3, 166.0, 164.1, 161.9, 155.1, 145.0, 141.5, 136.4, 135.2, 129.3, 128.99, 128.95, 128.86, 128.3, 128.2, 120.8, 113.7, 110.6, 105.6, 104.9, 104.7, 99.8, 97.7, 78.4, 72.9, 56.3, 55.6, 52.9, 50.5, 36.5, 27.9 ppm; HRMS (ESI) calcd for C₃₇H₃₅NO₉H⁺ [M+H⁺] 636.2228, found 636.2231.
Pentacycle 89: Pentacycle 88 (1.0 g, 1.6 mmol, 1.0 equiv) was dissolved in CH₂Cl₂ (120 mL) at room temperature, and TFA (0.61 mL, 7.9 mmol, 4.9 equiv) was added. The reaction mixture was stirred for 20 minutes, and the reaction was then quenched with saturated aq. NaHCO₃ solution (40 mL). The layers were separated, and the aqueous phase was extracted with CH₂Cl₂ (40 mL). The combined organics were dried over Na₂SO₄, filtered, and concentrated to give pentacycle 89 (0.98 g, 1.6 mmol, quant) as a red foam which was analytically pure. 89: Rᵣ = 0.5 (silica gel, EtOAc:hexanes 2:3); FT-IR (neat) νₑₑₐₙ₉ₑₙₑ₉ₑₙₑₑₑₑ₉ₑ₉ₑ₉ₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑᵉₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑ={`}
Allylic bromide 91: To a solution of allylic alcohol 48 (23.9 g, 84.2 mmol, 1.0 equiv) in CH₂Cl₂ (450 mL) was added Et₃N (23.3 mL, 168 mmol, 2.0 equiv). The solution was cooled to –50 °C, and methanesulfonyl chloride (11.0 mL, 143 mmol, 1.7 equiv) was added dropwise. The solution was stirred at this temperature for 1 hour, during which a thick white suspension formed. A solution of lithium bromide (25.6 g, 294 mmol, 3.5 equiv) in THF (98 mL) was then transferred to the reaction flask via cannula over 10 minutes. The mixture was allowed to warm to –20 °C and was stirred at this temperature for 1 hour. The reaction was quenched by pouring the slurry into water (1 L). The mixture was extracted with hexanes (1 L), and the organic layer was dried over Na₂SO₄, filtered, and concentrated to give the allylic bromide 91 (29.1 g, 84.1 mmol, quant.) as a pale yellow oil which was used crude for further reactions. The material was analytically pure and could be stored neat at –38 °C for several months with no signs of decomposition. 91: R_f = 0.8 (silica gel, EtOAc:hexanes 1:10); FT-IR (neat) ν_max = 2955, 2929, 2856, 1471, 1362, 1251, 1204, 1083, 1051, 1027, 936, 887, 834, 772, 678 cm⁻¹; ¹H NMR (CDCl₃, 600 MHz) δ = 4.05 (d, J = 10.2 Hz, 1 H), 4.02 (ap t, J = 6.6 Hz, 1 H), 3.95 (d, J = 10.2 Hz, 1 H), 1.83 – 1.76 (m, 4 H), 1.65 – 1.54 (m, 2 H), 1.42 (m, 1 H), 1.12 (s, 3 H), 1.09 (s, 3 H), 0.90 (s, 9 H), 0.10 (s, 3 H), 0.08 (s, 3 H) ppm; ¹³C NMR (CDCl₃, 151 MHz) δ = 139.7, 136.3, 71.5, 35.9, 35.3, 30.3, 29.3, 28.6, 28.1, 26.0, 18.3, 16.6, –4.0, –4.6 ppm; HRMS (ESI) calcd for C₂₆H₅₁BrOSiNa⁺ [M+Na⁺] 369.1220, found 369.1231.
Intermediate 90: Pentacycle 89 (0.95 g, 1.6 mmol, 1.0 equiv) was dissolved in DMF (100 mL) at room temperature. A solution of allylic bromide 91 (0.84 g, 2.4 mmol, 1.5 equiv) in DMF (50 mL) was added. The reaction mixture was degassed by bubbling argon for 30 minutes while it was shielded from light with aluminum foil. Na₂CO₃ (1.55 g, 14.6 mmol, 9.1 equiv) was added, and the reaction mixture was stirred for 45 minutes in the dark with continuous degassing. The mixture was diluted with water (100 mL) and extracted with EtOAc (3 × 100 mL). The combined organic layers were washed with water (50 mL), dried over Na₂SO₄, filtered, and concentrated. The crude residue was purified by flash column chromatography (5→10→20% EtOAc:hexanes) to give the alkylated product 90 (1.09 g, 1.25 mmol, 78%, d.r. ca. 6:1) as a red foam. 90: Rƒ = 0.45 (silica gel, EtOAc:hexanes 1:4); FT-IR (neat) ν_max = 2935, 2855, 1597, 1455, 1339, 1298, 1252, 1160, 1101, 1083, 1013, 918, 835, 733, 697 cm⁻¹; ¹H NMR (CDCl₃, 600 MHz, major isomer)* δ = 15.97 (s, 1 H), 7.75 (s, 1 H), 7.55 – 7.52 (m, 2 H), 7.44 – 7.38 (m, 5 H), 7.29 (m, 1 H), 7.23 – 7.20 (m, 2 H), 6.45 (d, J = 2.2 Hz, 1 H), 6.38 (d, J = 2.2 Hz, 1 H), 5.54 (d, J = 11.5 Hz, 1 H, AB system), 5.52 (d, J = 11.5 Hz, 1 H, AB system), 5.19 (bs, 2 H), 4.59 (m, 1 H), 3.98 (s, 3 H), 3.96 (s, 3 H), 3.93 (s, 3 H), 3.84 (m, 1 H), 2.64 (dd, J = 14.2, 5.3 Hz, 1 H), 2.25 (m, 1 H), 1.80 (m, 1 H), 1.68 – 1.64 (m, 2 H), 1.39 (m, 1 H), 0.88 (s, 9 H), 0.03 (s, 3 H), −0.01 (s, 3 H) ppm; ¹³C NMR (CDCl₃, 151 MHz)* δ = 188.5, 166.0, 164.2, 163.5, 163.2, 155.8, 142.5, 136.5, 136.2, 135.5, 135.3, 129.4, 129.0, 128.9, 128.8, 128.4, 128.2, 116.6, 114.3, 109.2, 109.1, 106.1, 98.4, 96.4, 79.1, 72.8, 71.6, 61.8, 56.4, 55.7, 41.2, 36.0, 29.7, 29.0, 18.4,
16.8, –4.15, –4.72 ppm; HRMS (ESI) calcd for C_{52}H_{59}NO_{9}H^{+} [M+H^{+}] 870.4032, found 870.4046.

*Due to signal broadening, not all the signals could be identified.

Spirocycle 24: Substrate 90 (453 mg, 0.521 mmol, 1.0 equiv) was dissolved in CH_{2}Cl_{2} (52 mL) and cooled to 0 °C. BF_{3}•OEt_{2} (0.05 M in CH_{2}Cl_{2}, 1.0 mL, 0.052 mmol, 0.1 equiv) was added, and the reaction mixture was stirred at 0 °C. Five additional portions of BF_{3}•OEt_{2} (0.05 M in CH_{2}Cl_{2}, 1.0 mL, 0.052 mmol, 0.1 equiv) were added, one every 10 minutes. The reaction was then quenched with saturated aq. NaHCO_{3} solution (20 mL). The layers were separated, and the aqueous phase was extracted with CH_{2}Cl_{2} (3 × 20 mL). The organics were combined and concentrated, and the crude residue was purified by flash column chromatography (25% EtOAc:hexanes) to give spirocycle 24 (211 mg, 0.286 mmol, 55%) as a red foam. 24: R_{f} = 0.6 (silica gel, EtOAc:hexanes 2:3); FT-IR (neat) ν_{max} = 2922, 2840, 1615, 1594, 1567, 1452, 1328, 1302, 1254, 1217, 1145, 1104, 1031, 1001, 913, 735, 696 cm^{-1}; ^{1}H NMR (CDCl_{3}, 600 MHz) δ = 16.37 (s, 1 H), 7.76 (s, 1 H), 7.54 – 7.52 (m, 2 H), 7.44 – 7.37 (m, 5 H), 7.27 (m, 1 H), 7.21 – 7.18 (m, 2 H), 6.40 (s, 1 H), 5.53 (d, J = 11.3 Hz, 1 H, AB system), 5.50 (d, J = 11.3 Hz, 1 H, AB system), 5.46 (bs, 1 H), 5.17 (d, J = 9.0 Hz, 1 H, AB system), 5.14 (d, J = 9.0 Hz, 1 H, AB system), 4.57 (dd, J = 11.7, 7.3 Hz, 1 H), 4.06 (s, 3 H), 3.87 (s, 3 H), 3.84 (s, 3 H), 3.18 (dd, J = 13.7, 7.3 Hz, 1 H), 2.53 (ap t, J = 12.7 Hz, 1 H), 2.23 (m, 1 H), 2.10 – 1.97 (m, 2 H), 1.42 (dd, J
= 12.9, 6.0 Hz, 1 H), 1.33 (s, 3 H), 1.04 (s, 3 H), 0.99 (s, 3 H) ppm; $^{13}$C NMR (CDCl$_3$, 151 MHz)
$\delta$ = 189.3, 166.1, 164.3, 164.2, 162.7, 162.3, 155.7, 153.6, 142.8, 137.8, 136.5, 136.4, 135.3,
129.5, 129.3, 129.1, 128.89, 128.85, 128.4, 128.3, 123.5, 121.5, 116.7, 111.7, 109.6, 109.3, 96.3,
94.5, 79.1, 72.8, 59.9, 58.7, 56.5, 55.2, 44.6, 41.5, 38.9, 35.0, 27.8, 24.8, 23.1, 20.6 ppm; HRMS
(ESI) calcd for C$_{46}$H$_{43}$NO$_8$H$^+$ [M$+$H$^+$] 738.3061, found 738.3047.

**Benzoate 92:** Substrate 24 (91.7 mg, 0.124 mmol, 1 equiv) was dissolved in CH$_2$Cl$_2$ (8 mL) at
room temperature. Et$_3$N (0.43 mL, 3.1 mmol, 25 equiv), BzCl (0.22 mL, 1.9 mmol, 15 equiv),
and DMAP (1 mg, 0.008 mmol, 0.06 equiv) were added sequentially, and the reaction mixture
was stirred for 45 minutes. The reaction was then quenched with saturated aq. NH$_4$Cl solution
(5 mL), and the layers were separated. The aqueous phase was extracted with CH$_2$Cl$_2$ (3 ×
10 mL), and the combined organic phases were dried over Na$_2$SO$_4$, filtered, and concentrated.
The residue was purified by flash column chromatography (33% EtOAc:hexanes) to provide
benzoate ester 92 (83 mg, 0.099 mmol, 79%) as an orange foam. 92: R$_f$ = 0.5 (silica gel,
EtOAc:hexanes 2:3); FT-IR (neat) $\nu_{\text{max}}$ = 2941, 2921, 1740, 1669, 1629, 1599, 1576, 1537, 1452,
1355, 1327, 1262, 1241, 1217, 1138, 1101, 1056, 1025, 998, 912, 731, 699 cm$^{-1}$; $^1$H NMR
(CDCl$_3$, 600 MHz, ca. 3:1 mixture of rotamers) $\delta$ = 8.05 – 8.03 (m, 2 H, minor), 7.97 – 7.95 (m,
2 H, major), 7.91 (ap s, 2 H, major + minor), 7.40 – 7.36 (m, 2 H, major + minor), 7.32 – 7.26
(m, 6 H, major + minor), 7.24 – 7.18 (m, 4 H, major + minor), 7.00 – 6.97 (m, 2 H, major +
minor), 6.93 – 6.91 (m, 2 H, minor), 6.91 – 6.89 (m, 2 H, major), 6.84 – 6.81 (m, 4 H, major + minor),
6.36 (s, 1 H, major), 6.29 (s, 1 H, minor), 5.48 – 5.45 (m, 2 H, major + minor), 5.42 – 5.37 (m, 4 H, major + minor), 5.22 (d, \( J = 10.5 \) Hz, 1 H, minor, AB system), 5.11 (d, \( J = 10.8 \) Hz, 1 H, major, AB system), 5.07 (d, \( J = 10.8 \) Hz, 1 H, major, AB system), 5.06 (d, \( J = 10.5 \) Hz, 1 H, minor, AB system), 4.57 (dd, \( J = 11.5, 7.3 \) Hz, 1 H, major), 4.52 (dd, \( J = 11.5, 7.3 \) Hz, 1 H, minor), 3.97 (s, 3 H, major), 3.95 (s, 3 H, minor), 3.91 (s, 3 H, major), 3.83 (s, 3 H, major), 3.80 (s, 3 H, minor), 3.77 (s, 3 H, minor), 3.22 – 3.15 (m, 2 H, major + minor), 2.54 – 2.46 (m, 2 H, major + minor), 2.27 – 2.19 (m, 2 H, major + minor), 2.10 – 1.98 (m, 4 H, major + minor), 1.46 – 1.41 (m, 2 H, major + minor), 1.34 (ap s, 6 H, major + minor), 1.02 (s, 3 H, major), 1.01 (s, 3 H, minor), 0.99 (s, 3 H, minor), 0.98 (s, 3 H, major) ppm; \(^{13}\)C NMR (CDCl\(_3\), 151 MHz, ca. 3:1 mixture of rotamers)* \( \delta = 183.9 \) (minor), 182.5 (major), 166.7 (major), 166.4 (minor), 165.4 (major), 165.3 (minor), 163.00 (major), 162.99 (minor), 161.27 (minor), 161.25 (major), 160.2 (minor), 160.1 (major), 153.4 (major + minor), 152.1 (major), 151.8 (minor), 150.2 (minor), 150.1 (major), 144.7 (major), 144.1 (minor), 138.1 (minor), 137.8 (major), 135.86 (major), 135.83 (minor), 134.93 (major), 134.87 (minor), 134.53 (major), 134.46 (minor), 132.8 (minor), 132.5 (minor), 130.8, 130.67, 130.62, 130.4, 130.2, 130.1, 128.9, 128.8, 128.74, 128.68, 128.63, 128.61, 128.1, 128.0, 127.72, 127.71, 127.27, 127.25, 127.14, 127.09, 125.0 (minor), 123.8 (major), 122.9 (major), 122.8 (minor), 121.5 (major), 121.3 (minor), 119.3 (major), 119.0 (minor), 115.0 (minor), 114.8 (major), 109.9 (major), 109.7 (minor), 96.3 (major + minor), 95.0 (minor), 94.6 (major), 79.8 (minor), 79.5 (major), 73.0 (minor), 72.8 (major), 60.7 (minor), 60.5 (major), 59.01 (minor), 58.96 (major), 56.6 (minor), 56.4 (major), 55.15 (major), 55.13 (minor), 44.63 (major), 44.56 (minor), 40.8 (minor), 40.7 (major), 38.89 (minor), 38.86 (major), 34.95 (minor), 34.91 (major), 27.7 (minor), 27.6 (major), 24.7 (major + minor), 23.1 (major + minor),
20.8 (minor), 20.6 (major) ppm; HRMS (ESI) calcd for C_{53}H_{47}NO_{9}H^+ [M+H^+] 842.3323, found 842.3331.

*Due to overlapping $^{13}$C signals of each rotamer with each other, some of the $^{13}$C NMR signals could not be assigned to the major or minor rotamer.

Amide 93: Intermediate 92 (20 mg, 0.024 mmol, 1.0 equiv) was dissolved in MeOH:1,4-dioxane (4 mL, 1:1), and Pd black (13 mg, 0.12 mmol, 5.0 equiv) was added. The flask was flushed with argon, and then H\textsubscript{2} gas was bubbled through the reaction mixture for 20 minutes. The hydrogen atmosphere was removed by flushing the flask with argon. The mixture was then filtered through a plug of Celite® and concentrated to afford amide 93 (16 mg, 0.024 mmol, quant) as a red solid which was typically used without purification in subsequent endoperoxide formation attempts.

93: R\textsubscript{f} = 0.5 (silica gel, acetone:toluene 1:4); FT-IR (neat) \nu_{\text{max}} = 3503, 3326, 3189, 2919, 2840, 1749, 1663, 1610, 1593, 1448, 1421, 1400, 1376, 1328, 1237, 1216, 1176, 1141, 1103, 1053, 1019, 997, 907, 727, 700 cm\textsuperscript{-1}; $^1$H NMR (CDCl\textsubscript{3}, 600 MHz, ca. 1:1 mixture of rotamers) \delta = 16.18 (s, 1 H), 16.05 (s, 1 H), 12.91 (s, 1 H), 12.80 (s, 1 H), 8.25 – 8.23 (m, 4 H), 7.72 – 7.69 (m, 2 H), 7.58 – 7.54 (m, 4 H), 7.43 (s, 1 H), 7.42 (s, 1 H), 6.34 (s, 1 H), 6.33 (s, 1 H), 5.85 (bs, 2 H), 5.44 (bs, 2 H), 4.52 – 4.45 (m, 2 H), 3.97 (s, 3 H), 3.96 (s, 3 H), 3.84 (s, 6 H), 3.811 (s, 3 H), 3.806 (s, 3 H), 3.15 – 3.11 (m, 2 H), 2.51 – 2.42 (m, 2 H), 2.23 – 2.16 (m, 2 H), 2.07 – 2.02 (m, 2 H), 2.00 – 1.93 (m, 2 H), 1.41 – 1.38 (m, 2 H), 1.31 (s, 3 H), 1.29 (s, 3 H), 1.00 (s, 6 H), 0.95
(s, 3 H), 0.94 (s, 3 H) ppm; $^{13}$C NMR (CDCl$_3$, 151 MHz, ca. 1:1 mixture of rotamers) $\delta$ = 189.1, 188.9, 170.84, 170.81, 164.6, 164.0, 162.7, 162.6, 162.34, 162.28, 162.2, 161.8, 161.7, 153.71, 153.66, 151.13, 151.11, 142.2, 142.0, 137.71, 137.65, 136.6, 136.4, 134.22, 131.4, 131.2, 130.7, 129.5, 129.4, 129.04, 129.00, 123.58, 123.56, 121.52, 121.46, 112.0, 111.9, 111.4, 110.2, 109.9, 109.7, 109.4, 105.53, 105.48, 94.5, 94.4, 60.1, 60.0, 58.70, 58.68, 56.4, 55.2, 44.40, 44.36, 41.6, 41.5, 38.89, 38.87, 34.9, 27.7, 24.8, 23.1, 20.6, 20.5 ppm; HRMS (ESI) calcd for C$_{39}$H$_{37}$NO$_9$H$^+$ [M+H$^+$] 664.2541, found 664.2544.

**Amide 98:** Substrate 24 (0.10 g, 0.14 mmol, 1.0 equiv) was dissolved in MeOH:1,4-dioxane (20 mL, 1:1), and Pd black (72 mg, 0.67 mmol, 5.0 equiv) was added. The headspace was flushed with argon and then H$_2$ gas. The mixture was stirred under a H$_2$ atmosphere for 30 minutes. The headspace was then flushed with argon, and the mixture was filtered through a pad of Celite® to give the amide 98 (83 mg, 0.14 mmol, quant.) which was used without further purification. 98: $R_f$ = 0.5 (silica gel, EtOAc:hexanes 3:2); FT-IR (neat) $\nu_{\text{max}}$ = 3444, 3338, 2920, 2851, 1656, 1615, 1568, 1458, 1431, 1409, 1329, 1297, 1221, 1185, 1145, 1102 cm$^{-1}$; $^1$H NMR (CDCl$_3$, 600 MHz) $\delta$ = 14.08 (bs, 1 H), 13.66 (bs, 1 H), 8.49 (bs, 1 H), 6.86 (bs, 1 H), 6.38 (s, 1 H), 5.88 (bs, 1 H), 5.45 (bs, 1 H), 4.49 (dd, $J$ = 11.4, 7.3 Hz, 1 H), 4.05 (s, 3 H), 3.88 (s, 3 H), 3.77 (s, 3 H), 3.12 (dd, $J$ = 13.7, 7.3 Hz, 1 H), 2.46 (ap t, $J$ = 13.0 Hz, 1 H), 2.21 (m, 1 H), 2.05 (m, 1 H), 1.97 (ddd, $J$ = 12.8, 12.8, 6.2 Hz, 1 H), 1.40 (dd, $J$ = 12.8, 6.2 Hz, 1 H), 1.32 (s, 3 H),
1.02 (s, 3 H), 0.96 (s, 3 H) ppm; $^{13}$C NMR (CDCl$_3$, 151 MHz) δ = 186.0, 173.3, 170.3, 165.8, 163.6, 162.9, 162.8, 154.4, 142.2, 137.44, 137.40, 129.9, 124.3, 121.6, 109.4, 107.3, 106.8, 100.3, 99.2, 94.6, 59.8, 58.9, 56.6, 55.3, 44.2, 42.1, 38.9, 34.9, 27.7, 24.9, 23.0, 20.6 ppm; HRMS (ESI) calcd for C$_{32}$H$_{33}$NO$_8$H$^+$ [M+H$^+$] 560.2279, found 560.2286.

**Quinone S3**: Substrate 24 (100 mg, 0.136 mmol, 1.0 equiv) was dissolved in DMF:H$_2$O (10 mL, 9:1), and PIFA (64 mg, 0.15 mmol, 1.1 equiv) was added. The reaction mixture was heated to 40 °C for 2 hours, and was then allowed to cool to room temperature. Water (20 mL) and EtOAc (20 mL) were added. The layers were separated, and the organic phase was washed with water (2 × 10 mL). The organic phase was dried over Na$_2$SO$_4$, filtered, and concentrated to give the crude quinone intermediate. The crude quinone was dissolved in CH$_2$Cl$_2$ (10 mL) and Et$_3$N (0.18 mL, 1.3 mmol, 10 equiv), BzCl (0.07 mL, 0.6 mmol, 4.4 equiv), and DMAP (1 mg, 0.008 mmol, 0.06 equiv) were added sequentially. The reaction mixture was stirred for 5 minutes at room temperature and was then concentrated. Purification of the residue by flash column chromatography (10→20→30% EtOAc:hexanes) gave the benzyolated quinone S3 (72 mg, 0.087 mmol, 65% yield for two steps) as a red solid. S3: R$_f$ = 0.7 (silica gel, EtOAc:hexanes 2:3); FT-IR (neat) $\nu$$_{\text{max}}$ = 2939, 1740, 1668, 1597, 1529, 1453, 1408, 1353, 1312, 1247, 1209, 1184, 1056, 1024, 909, 733, 700 cm$^{-1}$; $^1$H NMR (CDCl$_3$, 600 MHz, ca. 1.3:1 mixture of rotamers) δ = 8.37 – 8.34 (m, 4 H, major + minor), 8.11 (ap s, 2 H, major + minor), 7.74 – 7.71 (m, 2 H, major
+ minor), 7.60 – 7.56 (m, 4 H, major + minor), 7.51 – 7.49 (m, 4 H, major + minor), 7.44 – 7.39 (m, 6 H, major + minor), 7.15 – 7.13 (m, 2 H, major + minor), 7.10 – 7.07 (m, 4 H, major + minor), 6.89 – 6.86 (m, 4 H, major + minor), 6.74 (ap s, 2 H, major + minor), 5.57 (m, 2 H, major + minor), 5.51 – 5.46 (m, 4 H, major + minor), 5.16 (d, J = 9.1 Hz, 1 H, minor, AB system), 5.14 (d, J = 9.1 Hz, 1 H, major, AB system), 5.02 (ap bd, J = 9.1 Hz, 2 H, major + minor), 4.19 (d, J = 20.0 Hz, 1 H, minor), 4.08 (d, J = 20.0 Hz, 1 H, major), 3.91 (ap s, 6 H, major + minor), 3.77 (s, 3 H, major), 3.76 (s, 3 H, minor), 3.49 (d, J = 20.0 Hz, 1 H, major), 3.43 (d, J = 20.0 Hz, 1 H, minor), 2.30 – 2.22 (m, 2 H, major + minor), 2.15 – 2.08 (m, 2 H, major + minor), 1.96 (ap ddd, J = 12.2, 12.2, 6.0 Hz, 2 H, major + minor), 1.53 (s, 3 H, major), 1.51 (s, 3 H, minor), 1.43 (dd, J = 12.5, 6.5 Hz, 1 H, minor), 1.38 (dd, J = 13.3, 6.3 Hz, 1 H, major), 0.972 (s, 3 H, minor), 0.966 (s, 3 H, major), 0.49 (s, 3 H, minor), 0.41 (s, 3 H, major) ppm; 13C NMR (CDCl3, 151 MHz, ca. 1.3:1 mixture of rotamers)* δ = 183.56 (major), 183.54 (minor), 181.85 (minor), 181.82 (major), 166.56 (major), 166.55 (minor) 166.24 (minor), 166.22 (major), 166.03 (major), 166.00 (minor), 157.61 (major), 157.55 (minor), 157.08 (major), 157.03 (minor), 155.91 (major), 155.88 (minor), 148.9 (major), 148.8 (minor), 146.7 (minor), 146.6 (major), 146.0 (major), 145.9 (minor), 138.56 (major), 138.53 (minor), 136.4 (major), 136.3 (minor), 136.2 (major + minor), 135.1 (major + minor), 133.20 (major), 133.16 (minor), 130.61, 130.59, 130.50, 129.39, 129.37, 129.1, 129.0, 128.9, 128.7, 128.5, 128.2, 128.1, 126.0 (minor), 125.9 (major), 124.70 (major), 124.67 (minor), 123.5 (minor), 123.4 (major), 121.8, 121.67, 121.63, 121.58, 114.2 (minor), 114.1 (major), 113.4 (minor), 113.3 (major), 105.14 (minor), 105.10 (major), 99.3 (major + minor), 78.00 (major), 77.98 (minor), 73.1 (major + minor), 59.9 (minor), 59.8 (major), 56.47 (major), 56.43 (minor), 55.78 (minor), 55.75 (major), 46.7 (major), 46.6 (minor), 38.5 (major), 38.4 (minor), 34.17 (minor), 34.13 (major), 25.7 (minor), 25.6 (major),
24.4 (minor), 24.3 (major), 23.1 (major + minor), 21.1 (major), 21.0 (minor) ppm; HRMS (ESI) calcd for C_{52}H_{43}NO_{9}H^{+} [M+H^{+}] 826.3010, found 826.3017.

*Due to overlapping $^{13}$C signals of each rotamer with each other, some of the $^{13}$C NMR signals could not be assigned to the major or minor rotamer.

Phenol 101: Benzoate ester S3 (72 mg, 0.087 mmol, 1.0 equiv) was dissolved in Et$_2$O:benzene (8 mL, 1:7) and MgBr$_2$•OEt$_2$ (23 mg, 0.089 mmol, 1.0 equiv) was added. The reaction mixture was stirred at room temperature for 2 hours. The mixture was then concentrated and purified by preparative TLC (silica gel, CH$_2$Cl$_2$) to provide phenol 101 (48 mg, 0.065 mmol, 75%) as a red solid. 101: $R_f$ = 0.65 (silica gel, EtOAc:hexanes 2:3); FT-IR (neat) $v_{max}$ = 2934, 1744, 1634, 1597, 1530, 1406, 1354, 1275, 1258, 1203, 1114, 1053, 1022, 908, 868, 778, 703 cm$^{-1}$; $^1$H NMR (CDCl$_3$, 600 MHz, ca. 1:1 mixture of rotamers) $\delta$ = 14.86 (s, 1 H), 14.84 (s, 1 H), 8.33 – 8.31 (m, 4 H), 7.79 (s, 1 H), 7.74 (s, 1 H), 7.71 – 7.67 (m, 2 H), 7.60 – 7.56 (m, 4 H), 7.54 – 7.52 (m, 4 H), 7.41 – 7.37 (m, 4 H), 7.37 – 7.33 (m, 2 H), 6.73 (s, 1 H), 6.71 (s, 1 H), 5.58 (bs, 2 H), 5.49 (s, 4 H), 4.14 (d, $J$ = 20.2 Hz, 1 H), 4.13 (d, $J$ = 20.2 Hz, 1 H), 3.92 (ap s, 6 H), 3.75 (s, 3 H), 3.72 (s, 3 H), 3.48 (d, $J$ = 20.2 Hz, 1 H), 3.47 (d, $J$ = 20.2 Hz, 1 H), 2.29 – 2.22 (m, 2 H), 2.14 – 2.08 (m, 2 H), 1.98 – 1.92 (m, 2 H), 1.53 (s, 3 H), 1.52 (s, 3 H), 1.42 – 1.36 (m, 2 H), 0.96 (s, 3 H), 0.95 (s, 3 H), 0.44 (s, 3 H), 0.40 (s, 3 H) ppm; $^{13}$C NMR (CDCl$_3$, 151 MHz, ca. 1:1 mixture of rotamers) $\delta$ = 187.82, 187.76, 182.98, 182.93, 168.54, 168.48, 166.79, 165.76, 165.74, 161.59,
Hydroxy compounds 103 and 12a-epi-103: Starting material 76 (21.6 mg, 58.4 µmol, 1.0 equiv) was dissolved in acetone:water (0.5 mL, 9:1). DMDO\textsuperscript{21} (ca. 0.08 M in acetone, 0.94 mL, 0.08 mmol, 1.3 equiv) was added, and the mixture was stirred at room temperature for 70 minutes. Another portion of DMDO was then added (ca. 0.08 M in acetone, 0.31 mL, 0.03 mmol, 0.4 equiv). After 1.5 hours total reaction time, the solvent was largely removed \textit{in vacuo} at room temperature, and the residue was treated with CH\textsubscript{2}Cl\textsubscript{2} (5 mL) and water (5 mL). The organic phase was dried over MgSO\textsubscript{4}, filtered, and concentrated to yield a diastereomeric mixture of products 103 + 12a-epi-103 (22 mg, d.r. ca. 1:2.3) as an orange oil. Purification by preparative TLC (silica gel, 50% EtOAc:hexanes, 0.1% Et\textsubscript{3}N) afforded 103 (6.7 mg, 17 µmol, 29%) and 12a-epi-103 (11.3 mg, 29.3 µmol, 50%).
**103**: $R_f = 0.38$ (silica gel, EtOAc:hexanes 1:1); FT-IR (neat) $\nu_{\text{max}} = 3418, 3034, 2944, 2836, 1709, 1686, 1616, 1511, 1487, 1370, 1097, 1087, 1031, 970, 911, 727 \text{ cm}^{-1}$; $^1\text{H NMR (CDCl}_3$, 600 MHz) $\delta = 7.46$ (d, $J = 7.6$ Hz, 2 H), 7.38 – 7.30 (m, 3 H), 6.92 (d, $J = 10.6$ Hz, 1 H), 6.34 (d, $J = 10.6$ Hz, 1 H), 5.35 (d, $J = 11.8$ Hz, AB system, 1 H), 5.32 (d, $J = 11.8$ Hz, AB system, 1 H), 4.67 (s, 1 H), 3.35 (s, 3 H), 3.26 (s, 3 H), 3.20 – 3.13 (m, 2 H), 3.06 (m, 1 H); $^{13}\text{C NMR (CDCl}_3$, 151 MHz) $\delta = 194.2, 185.8, 181.2, 167.9, 145.8, 135.2, 129.9, 128.63, 128.62, 128.3, 105.6, 97.6, 78.3, 72.4, 50.8, 49.8, 46.0, 22.3$ ppm; HRMS (ESI) calcd for C$_{20}$H$_{19}$NO$_7$H$^+$ $[\text{M+H}^+]$ 386.1234, found 386.1239.

**12a-epi-103**: $R_f = 0.25$ (silica gel, EtOAc:hexanes 1:1); FT-IR (neat) $\nu_{\text{max}} = 3428, 2945, 1720, 1615, 1511, 1486, 1454, 1367, 1117, 1063, 911, 736 \text{ cm}^{-1}$; $^1\text{H NMR (CDCl}_3$, 600 MHz) $\delta = 7.47$ (d, $J = 7.5$ Hz, 2 H), 7.39 – 7.31 (m, 3 H), 7.06 (d, $J = 10.6$ Hz, 1 H), 6.37 (d, $J = 10.6$ Hz, 1 H), 5.34 (d, $J = 12.0$ Hz, AB system, 1 H), 5.31 (d, $J = 12.0$ Hz, AB system, 1 H), 4.23 (s, 1 H), 3.46 (s, 3 H), 3.38 (dd, $J = 17.7, 11.0$ Hz, 1 H), 3.35 (s, 3 H), 3.09 (dd, $J = 11.0, 4.5$ Hz, 1 H), 3.02 (dd, $J = 17.7, 4.5$ Hz, 1 H) ppm; $^{13}\text{C NMR (CDCl}_3$, 151 MHz) $\delta = 192.0, 183.4, 180.4, 168.6, 145.8, 135.3, 133.2, 128.7, 128.6, 128.2, 105.7, 97.9, 73.8, 72.2, 51.6, 51.5, 45.3, 19.9$ ppm; HRMS (ESI) calcd for C$_{20}$H$_{19}$NO$_7$H$^+$ $[\text{M+H}^+]$ 386.1234, found 386.1296.
**BCD Tricycle 107**: To a solution of quinone monoketal 67 (12.4 g, 80.4 mmol, 3.0 equiv) in MeCN (250 mL) were added sequentially DBU (11.9 mL, 12.1 g, 79.8 mmol, 3.0 equiv) followed by cyclic anhydride 66 (5.95 g, 26.8 mmol, 1.0 equiv). The mixture was stirred at 60 °C for 15 hours. The reaction was then quenched with saturated aq. NH₄Cl solution (100 mL) and extracted with EtOAc (3 × 50 mL). The combined organic phases were dried over MgSO₄, filtered, and concentrated. Purification of the residue by flash column chromatography (50% EtOAc:hexanes, 0.1% Et₃N) provided the title compound 107 (4.43 g, 13.3 mmol, 50%) as a yellow foam. **107**: R<sub>f</sub> = 0.5 (silica gel, EtOAc:hexanes 1:1); FT-IR (neat) \( \nu_{\text{max}} = 2940, 2836, 1598, 1456, 1372, 1322, 1278, 1221, 1202, 1161, 1138, 1086, 970, 882, 816 \text{ cm}^{-1} \); \(^1\text{H NMR (C}_{6}\text{D}_{6}, 600 \text{ MHz}) \delta = 17.29 (s, 1 \text{ H}), 6.20 (m, 1 \text{ H}), 6.19 (d, J = 10.3 \text{ Hz}, 1 \text{ H}), 6.16 (m, 1 \text{ H}), 5.93 (d, J = 10.3 \text{ Hz}, 1 \text{ H}), 3.35 (s, 3 \text{ H}), 3.29 (ap t, J = 14.9 \text{ Hz}, 1 \text{ H}), 3.22 (s, 3 \text{ H}) 3.06 (dd, J = 14.9, 4.5 Hz, 1 \text{ H}), 3.05 (s, 3 \text{ H}), 3.01 (s, 3 \text{ H}), 2.88 (dd, J = 15.4, 4.5 Hz, 1 \text{ H}) \text{ ppm}; \(^{13}\text{C NMR (C}_{6}\text{D}_{6}, 151 \text{ MHz}) \delta = 183.8, 174.2, 164.3, 162.7, 146.3, 137.9, 130.8, 114.2, 105.4, 105.2, 98.1 (2 \text{ C}), 55.5, 54.9, 50.5, 50.2, 38.2, 29.4 \text{ ppm}; \) HRMS (ESI) calcd for C₁₈H₂₀O₆H⁺ [M+H⁺] 333.1333, found 333.1337.
Anthrone 108: BCD tricycle 107 (7.78 g, 23.4 mmol, 1.0 equiv) was dissolved in CH₂Cl₂ (200 mL) at room temperature, and freshly crystallized CSA (109 mg, 0.469 mmol, 0.02 equiv) was added. The resulting solution was stirred for 30 minutes, and the reaction was then quenched with saturated aq. NaHCO₃ solution (200 mL). The layers were separated, and the organic phase was dried over Na₂SO₄, filtered, and concentrated to give anthrone 108 (7.03 g, 23.4 mmol, quant) as an orange solid. 108: Rᵥ = 0.3 (silica gel, EtOAc:hexanes 3:7); FT-IR (neat) νₘₐₓ = 2937, 2838, 1637, 1601, 1475, 1449, 1332, 1269, 1230, 1163, 1098, 1059, 1027, 970, 816, 733 cm⁻¹; ¹H NMR (CDCl₃, 600 MHz) δ = 12.89 (s, 1 H), 7.03 (d, J = 8.9 Hz, 1 H), 6.85 (d, J = 8.9 Hz, 1 H), 6.54 (m, 1 H), 6.43 (d, J = 2.4 Hz, 1 H), 4.16 (s, 2 H), 3.97 (s, 3 H), 3.89 (s, 3 H), 3.86 (s, 3 H) ppm; ¹³C NMR (CDCl₃, 151 MHz) δ = 189.1, 164.44, 163.41, 156.3, 147.8, 146.5, 127.4, 117.5, 116.9, 114.7, 114.6, 104.4, 97.9, 56.3, 56.2, 55.7, 29.1 ppm; HRMS (ESI) calcd for C₁₇H₁₆O₅Na⁺ [M+Na⁺] 323.0890, found 323.0897.

Alkylated anthrone 109: A solution of anthrone 108 (7.9 g, 26 mmol, 1.0 equiv) and allylic bromide 91 (10.9 g, 31.5 mmol, 1.2 equiv) in DMF (1 L) was degassed for 35 minutes by bubbling argon through the solution. During this time, the reaction flask was shielded from light
using aluminum foil. After the degassing period, sodium carbonate (27.9 g, 263 mmol, 10 equiv) was added to the reaction flask, and the mixture was vigorously stirred for 1 hour in the dark. During this time, the reaction mixture typically turned very dark. The reaction was quenched by the addition of water (1 L) and diluted with EtOAc (2 L). The layers were separated, and the organic phase was washed with additional water (2 × 2 L), dried over Na₂SO₄, filtered, and concentrated to give a crude oil which was purified by flash column chromatography (5→10→20% EtOAc:hexanes) to give pure alkylated anthrone 109 (11.11 g, 19.63 mmol, 75%, d.r. ca. 1:1) as a yellow foam. 109: R<sub>f</sub> = 0.7 (silica gel, EtOAc:hexanes 3:7); FT-IR (neat) ν<sub>max</sub> = 2932, 2855, 1637, 1599, 1471, 1329, 1266, 1228, 1199, 1162, 1104, 1036, 1002, 964, 833, 773, 738 cm<sup>-1</sup>; This compound exhibited extremely broad NMR signals (both in ¹H NMR and ¹³C NMR) on the NMR timescale due to hindered bond rotation of the newly-formed C–C bond. An improved ¹H NMR spectrum could be obtained at 65 °C in d₆-DMSO (d.r. ca. 1:1). ¹H NMR (d₆-DMSO, 500 MHz, 65 °C) δ = 12.32 (s, 1 H), 12.31 (s, 1 H), 7.26 – 7.22 (m, 2 H), 6.805 (d, J = 9.1 Hz, 1 H), 6.80 (d, J = 9.1 Hz, 1 H), 6.60 (d, J = 2.2 Hz, 1 H), 6.54 (d, J = 2.1 Hz, 1 H), 6.39 (bs, 1 H), 6.34 (d, J = 2.2 Hz, 1 H), 4.57 – 4.52 (m, 2 H), 3.96 (m, 1 H), 3.93 – 3.84 (m, 19 H), 2.60 – 2.56 (m, 2 H), 1.96 – 1.86 (m, 2 H), 1.84 – 1.72 (m, 2 H), 1.64 – 1.15 (m, 18 H), 0.91 – 0.86 (m, 18 H), 0.72 (bs, 3 H), 0.50 (bs, 3 H), 0.09 – 0.05 (m, 12 H) ppm; ¹H NMR (CDCl₃, 600 MHz, 23 °C) δ = 12.543 (bs, 1 H), 12.537 (s, 1 H), 7.05 (d, J = 9.0 Hz, 1 H), 7.045 (d, J = 9.0 Hz, 1 H), 6.843 (d, J = 9.0 Hz, 1 H), 6.840 (d, J = 9.0 Hz, 1 H), 6.43 – 6.37 (m, 3 H), 6.30 (d, J = 2.3 Hz, 1 H), 4.68 – 4.54 (m, 2 H), 4.00 – 3.85 (m, 20 H), 2.74 – 2.64 (m, 2 H), 2.01 – 1.71 (m, 6 H), 1.69 – 1.12 (m, 12 H), 0.97 – 0.54 (m, 25 H), 0.32 – 0.03 (m, 15 H) ppm; ¹³C NMR (CDCl₃, 151 MHz, 23 °C)* δ = 188.79, 188.74, 164.0, 163.9, 163.24, 163.15, 156.24, 156.22, 147.7, 147.6, 133.6, 133.5, 117.8, 117.7, 117.6, 117.66, 117.6, 115.13, 115.09, 114.6, 114.5, 106.2,
106.1, 98.23, 71.7, 56.3, 56.09, 56.05, 55.9, 55.6, 41.1, 40.6, 36.0, 35.9, 29.8, 29.7, 29.1, 28.9, 26.10, 26.07, 18.39, 18.37, 16.6, –3.96, –4.11, –4.61, –4.63 ppm; HRMS (ESI) calcd for C_{33}H_{46}O_{6}SiH^{+} [M+H^{+}] 567.3136, found 567.3137.

*Due to signal broadening, not all the $^{13}$C signals could be identified.

![Chemical structure of spirocycle 60](image)

**BCDEF Spirocycle 60**: Alkylated anthrone **109** (3.07 g, 5.42 mmol, 1.0 equiv, d.r. ca. 1:1) was dissolved in CH$_2$Cl$_2$ (500 mL, HPLC grade) and cooled to 0 °C. A freshly prepared solution of BF$_3$•OEt$_2$ (21.6 mL of a 0.05 M in CH$_2$Cl$_2$, 1 mmol, 0.2 equiv) was added dropwise, and the reaction mixture was allowed to stir for 20 minutes. The reaction was quenched with saturated aq. NaHCO$_3$ solution (300 mL), and the phases were separated. The aqueous phase was extracted with CH$_2$Cl$_2$ (200 mL), and the combined organics were dried over Na$_2$SO$_4$, filtered, and concentrated. The residue was purified by flash column chromatography (50% EtOAc:hexanes) to give spirocycle **60** (1.92 g, 4.42 mmol, 82%) as a yellow foam. A portion of this material was crystallized from chloroform:EtOAc (1:1) to give crystals suitable for X-ray crystallographic analysis (m.p. = 114–115 °C). **60**: R$_f$ = 0.5 (silica gel, EtOAc:hexanes 3:7); FT-IR (neat) $v_{\text{max}}$ = 2940, 2916, 2835, 1632, 1600, 1567, 1471, 1438, 1329, 1302, 1257, 1217, 1137, 1107, 1039, 1002, 922, 825, 730 cm$^{-1}$; $^1$H NMR (CDCl$_3$, 600 MHz) $\delta$ = 13.01 (s, 1 H), 7.05 (d, $J = 9.0$ Hz, 1 H), 6.85 (d, $J = 9.0$ Hz, 1 H), 6.38 (s, 1 H), 5.44 (bs, 1 H), 4.38 (dd, $J = 11.8$, 7.5 Hz, 1 H), 4.04 (s, 3 H), 3.86 (s, 3 H), 3.81 (s, 3 H), 3.13 (dd, $J = 13.7$, 7.5 Hz, 1 H), 2.25 – 2.17 (m, 2 H), 2.04 (m, 1 H), 1.95 (ddd, $J = 12.5$, 12.5, 6.1 Hz, 1 H), 1.38 (dd, $J = 12.5$, 6.0 Hz, 1 H), 1.29 (s, 3 H), 1.27 (s, 3 H), 1.24 (s, 3 H), 1.18 (s, 3 H), 1.11 (s, 3 H), 0.99 (s, 3 H), 0.89 (s, 3 H), 0.87 (s, 3 H), 0.85 (s, 3 H), 0.79 (s, 3 H), 0.77 (s, 3 H), 0.75 (s, 3 H), 0.73 (s, 3 H), 0.71 (s, 3 H), 0.69 (s, 3 H), 0.67 (s, 3 H), 0.65 (s, 3 H), 0.63 (s, 3 H), 0.61 (s, 3 H), 0.59 (s, 3 H), 0.57 (s, 3 H), 0.55 (s, 3 H), 0.53 (s, 3 H), 0.51 (s, 3 H), 0.49 (s, 3 H), 0.47 (s, 3 H), 0.45 (s, 3 H), 0.43 (s, 3 H), 0.41 (s, 3 H), 0.39 (s, 3 H), 0.37 (s, 3 H), 0.35 (s, 3 H), 0.33 (s, 3 H), 0.31 (s, 3 H), 0.29 (s, 3 H), 0.27 (s, 3 H), 0.25 (s, 3 H), 0.23 (s, 3 H), 0.21 (s, 3 H), 0.19 (s, 3 H), 0.17 (s, 3 H), 0.15 (s, 3 H), 0.13 (s, 3 H), 0.11 (s, 3 H), 0.09 (s, 3 H), 0.07 (s, 3 H), 0.05 (s, 3 H), 0.03 (s, 3 H), 0.01 (s, 3 H).
1.01 (s, 3 H), 0.96 (s, 3 H) ppm; $^{13}$C NMR (CDCl$_3$, 151 MHz) $\delta$ = 189.1, 162.4, 162.3, 157.3, 155.6, 149.2, 138.3, 131.0, 123.5, 121.3, 119.3, 118.1, 115.8, 112.1, 94.3, 58.7, 56.6, 56.5, 55.2, 44.8, 41.7, 38.8, 34.9, 27.8, 24.9, 23.1, 20.6 ppm; HRMS (ESI) calcd for C$_{27}$H$_{30}$O$_5$H$^+$ [M+H$^+$] 435.2166, found 435.2162.

Desired quinone 111 and undesired side-product 112: Starting material 60 (2.0 g, 4.6 mmol, 1.0 equiv) was dissolved in MeOH (230 mL). PhI(OAc)$_2$[7] (1.77 g, 5.50 mmol, 1.2 equiv) was added in one portion, and the reaction mixture was stirred at room temperature for 50 minutes. Then, additional PhI(OAc)$_2$ (1.77 g, 5.50 mmol, 1.2 equiv) was added, and the reaction mixture was stirred for an additional 1 hour. Finally, a third portion of PhI(OAc)$_2$ (885 mg, 2.25 mmol, 0.6 equiv) was added, and the mixture was stirred for a further 1 hour. The reaction was then quenched with saturated aq. NaHCO$_3$ solution (300 mL) and extracted with EtOAc (2 x 300 mL). The combined organics were dried over Na$_2$SO$_4$, filtered, and concentrated. Purification by flash column chromatography (20% acetone:toluene, 0.1% Et$_3$N, then 25% MeOH:toluene, 0.1% Et$_3$N) gave the desired quinone monoketal 111 (1.16 g, 2.50 mmol, 54%) as a dark red foam and the undesired side-product 112 (507 mg, 1.03 mmol, 22%) as an orange foam. A sample of the undesired product 112 was crystallized from CH$_2$Cl$_2$:EtOAc (1:1) which gave crystals suitable for X-ray analysis (m.p. = 201–203 °C).
111: \( R_f = 0.3 \) (silica gel, EtOAc:hexanes 7:3); FT-IR (neat) \( \nu_{\text{max}} = 2938, 2835, 1682, 1618, 1582, 1461, 1435, 1367, 1330, 1283, 1221, 1095, 1069, 846, 826, 730 \text{ cm}^{-1}; \) \(^1\)H NMR (CDCl\(_3\), 600 MHz) \( \delta = 7.81 (s, 1 \text{ H}), 6.63 (d, J = 10.3 \text{ Hz}, 1 \text{ H}), 6.57 (d, J = 10.3 \text{ Hz}, 1 \text{ H}), 6.38 (s, 1 \text{ H}), 5.77 (m, 1 \text{ H}), 3.99 (s, 3 \text{ H}), 3.89 (s, 3 \text{ H}), 3.26 (s, 3 \text{ H}), 3.17 (s, 3 \text{ H}), 2.31 – 2.21 (m, 2 \text{ H}), 1.94 (ddd, \( J = 13.1, 6.3, 6.3 \text{ Hz}, 1 \text{ H}), 1.62 (ddd, \( J = 13.1, 6.6, 6.6 \text{ Hz}, 1 \text{ H}), 1.15 – 1.13 (m, 3 \text{ H}), 0.88 (s, 3 \text{ H}), 0.83 (s, 3 \text{ H}) \text{ ppm}; \) \(^{13}\)C NMR (CDCl\(_3\), 151 MHz) \( \delta = 183.1, 179.7, 161.7, 161.5, 159.4, 148.5, 146.7, 140.7, 135.1, 130.8, 130.2, 130.0, 125.0, 123.2, 111.9, 96.7, 94.6, 68.6, 56.5, 55.6, 51.7, 51.6, 37.5, 35.6, 27.1, 26.9, 23.1, 19.9 \text{ ppm}; \) HRMS (ESI) calcd for \( \text{C}_{28}\text{H}_{30}\text{O}_{6}\text{H}^+ \) [\( M+\text{H}^+ \)] 463.2115, found 463.2117.

112: \( R_f = 0.4 \) (silica gel, acetone:toluene 1:4); FT-IR (neat) \( \nu_{\text{max}} = 2939, 2838, 1690, 1613, 1568, 1462, 1436, 1334, 1315, 1272, 1215, 1131, 1068, 1012, 819 \text{ cm}^{-1}; \) \(^1\)H NMR (C\(_6\)D\(_6\), 600 MHz) \( \delta = 6.10 (d, J = 10.4 \text{ Hz}, 1 \text{ H}), 6.01 (d, J = 10.4 \text{ Hz}, 1 \text{ H}), 5.96 (s, 1 \text{ H}), 5.57 (bs, 1 \text{ H}), 3.82 (d, J = 15.8 \text{ Hz}, 1 \text{ H}), 3.38 (s, 3 \text{ H}), 3.10 (s, 3 \text{ H}), 3.00 (s, 3 \text{ H}), 2.84 (s, 3 \text{ H}), 2.81 (s, 3 \text{ H}), 2.68 (d, J = 15.8 \text{ Hz}, 1 \text{ H}), 2.25 (m, 1 \text{ H}), 2.08 (m, 1 \text{ H}), 1.97 (s, 3 \text{ H}), 1.81 (m, 1 \text{ H}), 1.54 (bs, 1 \text{ H}), 1.11 (s, 3 \text{ H}), 0.79 (s, 3 \text{ H}) \text{ ppm}; \) \(^{13}\)C NMR (C\(_6\)D\(_6\), 151 MHz) \( \delta = 181.7, 179.6, 161.9, 160.3, 152.7, 149.3, 139.6, 138.6 (b), 136.4, 132.5, 124.8, 120.5, 114.7, 96.8, 96.5, 80.3, 60.2, 55.9, 54.3, 51.3,
50.7, 50.6, 46.7 (b), 38.8, 35.0, 26.5, 26.2, 23.6, 22.2 ppm; HRMS (ESI) calcd for C_{29}H_{34}O_{7}H^+ [M+H^+] 495.2377, found 495.2384.

Optimized three-step protocol for the conversion of 60 to 111: BCDEF spirocycle 60 (4.70 g, 10.8 mmol, 1.0 equiv) was dissolved in MeOH:CH_{2}Cl_{2} (1:1, 220 mL), and the solution was cooled to 0 °C. PhI(OAc)$_2$ [7] (4.2 g, 13 mmol, 1.2 equiv) was added and the reaction mixture was stirred for 30 minutes at 0 °C and 30 minutes at room temperature. The reaction was quenched with saturated aq. NaHCO$_3$ solution (200 mL) and diluted with CH$_2$Cl$_2$ (200 mL). The layers were separated, and the aqueous layer was extracted with CH$_2$Cl$_2$ (200 mL). The combined organics were dried over Na$_2$SO$_4$, filtered, and concentrated to give the crude ketal 61 which was used without purification in the next step. A sample of this material could be purified by flash column chromatography (30% EtOAc:hexanes, 0.1% Et$_3$N) for characterization purposes.

61: R$_f$ = 0.4 (silica gel, EtOAc:hexanes 3:7); FT-IR (neat) $\nu_{\text{max}}$ = 2937, 2838, 1655, 1591, 1463, 1412, 1339, 1271, 1214, 1095, 1071, 841, 529 cm$^{-1}$; $^1$H NMR (C$_6$D$_6$, 600 MHz) $\delta$ = 16.00 (s, 1 H), 6.30 (d, $J$ = 10.3 Hz, 1 H), 6.18 (s, 1 H), 6.15 (d, $J$ = 10.3 Hz, 1 H), 5.61 (bs, 1 H), 4.03 (d, $J$ = 18.1 Hz, 1 H), 3.50 (s, 3 H), 3.37 (d, $J$ = 18.1 Hz, 1 H), 3.28 (s, 3 H), 2.96 (s, 3 H), 2.84 (s,
3 H), 2.32 (m, 1 H), 2.06 – 1.97 (m, 2 H), 1.79 (s, 3 H), 1.35 (m, 1 H), 1.18 (s, 3 H), 0.73 (s, 3 H) ppm; $^{13}$C NMR (C$_6$D$_6$, 151 MHz) δ = 188.6, 165.7, 160.7, 158.4, 148.4, 142.9, 137.9, 134.3, 133.2, 126.4, 122.9, 121.2, 109.9, 109.6, 97.3, 95.9, 59.5, 54.8, 51.0, 50.5, 43.6, 38.5, 34.5, 26.1, 24.5, 23.5, 21.5 ppm; HRMS (ESI) calcd for C$_{28}$H$_{32}$O$_6$H$^+$ [M+H$^+$] 465.2272, found 465.2279.

The so-obtained crude ketal 61 was dissolved in CH$_2$Cl$_2$ (220 mL) and freshly crystallized CSA (175 mg, 0.753 mmol, 0.07 equiv) was added. The reaction mixture was stirred at room temperature for 30 minutes, and the reaction was then quenched with saturated aq. NaHCO$_3$ solution (100 mL). The layers were separated, and the organic phase was dried over Na$_2$SO$_4$, filtered, and concentrated to give the crude product 110. A sample of this material could be purified by flash column chromatography (30% EtOAc:hexanes) for characterization purposes.

110: R$_f$ = 0.35 (silica gel, EtOAc:hexanes 3:7); FT-IR (neat) $v_{max}$ = 2937, 2840, 1625, 1573, 1479, 1432, 1331, 1258, 1237, 1218, 1181, 1037, 931, 829, 804, 732 cm$^{-1}$; $^1$H NMR (CDCl$_3$, 600 MHz) δ = 13.85 (s, 1 H), 7.61 (s, 1 H), 7.19 (d, $J = 9.1$ Hz, 1 H), 6.98 (d, $J = 9.1$ Hz, 1 H), 6.42 (s, 1 H), 5.75 (m, 1 H), 4.08 (s, 3 H), 3.97 (s, 3 H), 3.93 (s, 3 H), 2.30 – 2.26 (m, 2 H), 1.90 (ddd, $J = 12.5$, 6.0, 6.0 Hz, 1 H), 1.68 (ddd, $J = 13.5$, 6.9, 6.9 Hz, 1 H), 1.16 – 1.14 (m, 3 H), 0.89 (s, 3 H), 0.84 (s, 3 H) ppm; $^{13}$C NMR (CDCl$_3$, 151 MHz) δ = 188.7, 162.3, 160.1, 157.9, 152.7, 151.8, 150.5, 131.7, 130.6, 124.18, 124.15, 120.2, 118.2, 117.4, 116.8, 109.7, 93.5, 66.9,
56.4, 56.2, 55.5, 37.1, 35.9, 27.0, 26.9, 23.3, 19.8 ppm; HRMS (ESI) calcd for C_{27}H_{28}O_{5}H^+ [M+H^+] 433.2009, found 433.2008.

The crude product 110 from above was dissolved in methanol (220 mL), and PhI(OAc)$_2$ [7] (4.2 g, 13 mmol, 1.2 equiv) was added. The reaction mixture was stirred for 90 minutes, and the reaction was then quenched with saturated aq. NaHCO$_3$ solution (200 mL). CH$_2$Cl$_2$ (200 mL) was added, and the layers were separated. The aqueous phase was extracted with CH$_2$Cl$_2$ (2 × 200 mL), and the combined organic layers were dried over Na$_2$SO$_4$, filtered, and concentrated. The crude residue was purified by flash column chromatography (5→10→20% acetone:toluene, 0.1% Et$_3$N, then 10% MeOH:CH$_2$Cl$_2$, 0.1% Et$_3$N) to give the diketone ketal 111 (3.9 g, 8.4 mmol, 78% yield for the three steps) as a red foam. The physical and spectroscopic data of 111 matched those reported above.

Michael addition product 113: To a solution of quinone monoketal 111 (119 mg, 0.258 mmol, 1.0 equiv) and methyl ester isoxazole 81 (111 mg, 0.284 mmol, 1.1 equiv) in toluene (6 mL) was added tBuOK (6 mg, 0.05 mmol, 0.2 equiv) at room temperature, and the reaction mixture was stirred at this temperature for 45 minutes. The reaction was quenched with saturated aq. NH$_4$Cl solution (5 mL), and the layers were separated. The organic phase was dried over Na$_2$SO$_4$, filtered, and concentrated. The residue was purified by flash column chromatography (30→50→70% EtOAc:hexanes, 0.2% Et$_3$N) to give product 113 (163 mg, 0.191 mmol, 74%,
mixture of four diastereomers) as a solid. **113: R_f = 0.5** (silica gel, EtOAc:hexanes 4:1); FT-IR (neat) ν_max = 2954, 1735, 1698, 1615, 1582, 1512, 1459, 1435, 1364, 1327, 1251, 1223, 1123, 1092, 1058, 914, 858, 837, 732, 696 cm⁻¹; ¹H NMR (CDCl₃, 600 MHz) δ = 7.73 (s), 7.72 (s), 7.58 (s), 7.45 – 7.43 (m), 7.38 – 7.29 (m), 6.39 (s), 6.38 (s), 6.34 (s), 6.31 (s), 5.77 – 5.73 (m), 5.72 – 5.70 (m), 5.36 – 5.31 (m), 5.14 (d, J = 11.9 Hz, AB system), 5.08 – 5.06 (m), 4.95 (d, J = 12.0 Hz, AB system), 4.94 – 4.93 (m), 4.88 – 4.85 (m), 4.80 (d, J = 9.1 Hz), 4.23 – 4.01 (m), 3.97 (s), 3.89 (s), 3.88 (s, 3.87 (s), 3.86 (s), 3.84 (s), 3.81 – 3.78 (m), 3.66 (s), 3.63 (s), 3.49 (s), 3.42 (s), 3.40 (s), 3.23 (s), 3.20 (s), 3.13 (s), 3.10 (s), 3.05 (s), 3.00 (s), 2.99 – 2.94 (m), 2.75 – 2.64 (m), 2.31 – 2.20 (m), 2.01 – 1.91 (m), 1.87 – 1.82 (m), 1.63 – 1.45 (m), 1.17 (bs), 1.12 (bs), 1.06 (bs), 1.00 (bs), 0.92 – 0.74 (m), 0.69 (s), –0.025 (s), –0.028 (s), –0.06 (s), –0.07 (s) ppm; ¹³C NMR (CDCl₃, 151 MHz) δ = 194.68, 194.65, 194.34, 179.80, 179.40, 178.84, 178.46, 173.73, 173.70, 173.47, 173.42, 169.31, 169.15, 168.88, 168.73, 168.29, 168.22, 167.81, 167.77, 162.50, 162.30, 161.66, 161.55, 161.50, 161.41, 161.35, 161.11, 161.09, 160.55, 160.51, 159.17, 158.99, 158.96, 149.05, 148.82, 148.80, 148.73, 144.90, 144.39, 135.70, 135.66, 135.62, 132.83, 132.71, 132.69, 132.64, 132.54, 132.49, 132.29, 131.06, 130.77, 130.39, 130.16, 128.60, 128.57, 128.47, 128.45, 128.41, 128.37, 128.29, 128.26, 128.11, 127.96, 127.88, 127.87, 125.32, 125.03, 124.44, 124.36, 123.11, 122.95, 122.90, 111.80, 111.78, 111.71, 111.69, 103.18, 103.08, 101.65, 101.60, 101.48, 101.47, 101.43, 101.37, 94.53, 94.44, 94.32, 72.01, 71.90, 71.80, 71.77, 68.08, 67.93, 67.91, 67.89, 65.02, 64.96, 64.68, 56.47, 56.42, 56.37, 56.33, 55.54, 55.50, 55.47, 55.40, 51.98, 51.92, 51.85, 51.74, 51.65, 51.44, 51.38, 51.28, 48.85, 48.66, 48.64, 45.91, 45.88, 45.82, 44.52, 44.33, 40.05, 40.01, 39.86, 39.81, 39.08, 38.02, 38.00, 37.84, 37.69, 37.33, 37.13, 35.93, 35.72, 35.59, 35.49, 27.22, 27.17, 27.13, 26.97, 26.92, 26.85, 26.82, 23.18, 23.12, 23.10, 23.07, 20.14,
20.09, 19.77, 19.72, 17.42, 17.21, 17.18, –1.50, –1.55 ppm; HRMS (ESI) calcd for C_{47}H_{55}NO_{12}SiH^{+} [M+H^{+}] 854.3566, found 854.3564.

**Compound 115 (+ 15-epi-115):** To a solution of compound 113 (212 mg, 0.249 mmol, 1.0 equiv, mixture of four diastereomers) in THF (8 mL) at room temperature was added TBAF (1 M in THF, 0.3 mL, 0.3 mmol, 1.2 equiv), and the reaction mixture was stirred for 10 minutes. Then, saturated aq. NH_{4}Cl solution (8 mL), water (10 mL), and EtOAc (20 mL) were added. The layers were separated, and the organic phase was dried over Na_{2}SO_{4}, filtered, and concentrated. The residue was purified by flash column chromatography (10 → 30 → 50 → 80 → 90% EtOAc:hexanes, 0.2% Et_{3}N) to give the compound 115 (+ 15-epi-115) (105 mg, 0.148 mmol, 60%, d.r. ca. 2:1) as a yellow foam. 115 (+ 15-epi-115): R_{f} = 0.4 (silica gel, EtOAc:hexanes 4:1); FT-IR (neat) ν_{max} = 2954, 2840, 1734, 1697, 1615, 1582, 1513, 1464, 1435, 1366, 1327, 1282, 1221, 1153, 1122, 1055, 912, 823, 732 cm^{-1}; ^{1}H NMR (CDCl_{3}, 600 MHz) δ = 7.87 (s, 1 H, major), 7.86 (s, 1 H, minor), 7.48 – 7.46 (m, 4 H, major + minor), 7.40 – 7.37 (m, 4 H, major + minor), 7.35 – 7.32 (m, 2 H, major + minor), 6.404 (s, 1 H, major), 6.397 (s, 1 H, minor), 5.80 – 5.77 (m, 2 H, major + minor), 5.34 (s, 2 H, minor), 5.33 (s, 2 H, major), 3.984 (s, 3 H, major), 3.980 (s, 3 H, minor), 3.89 (ap s, 6 H, major + minor), 3.80 (s, 3 H, minor), 3.78 (s, 3 H, major), 3.48 (s, 3 H, minor), 3.47 (s, 3 H, major), 3.20 (s, 3 H, major), 3.14 – 3.09 (m, 6 H, major + minor), 3.11 (s, 3 H, minor), 2.83 – 2.77 (m, 2 H, major + minor), 2.52 – 2.47 (m, 2 H, major + minor), 2.30 – 2.25 (m, 4 H, major + minor), 1.99 – 1.90 (m, 2 H, major + minor), 1.65 – 1.59
(m, 2 H, major + minor), 1.14 (bs, 3 H, major), 1.10 (bs, 3 H, minor), 0.86 – 0.84 (m, 3 H, major + 6 H, minor), 0.82 (s, 3 H, major) ppm; $^{13}$C NMR (CDCl$_3$, 151 MHz) $\delta$ = 194.57 (major), 194.53 (minor), 179.7 (minor), 179.5 (major), 177.4 (major), 177.3 (minor), 169.4 (minor), 169.3 (major), 162.7 (minor), 162.6 (major), 161.8 (major), 161.6 (minor), 161.3 (major), 161.2 (minor), 159.3 (major), 159.2 (minor), 149.0 (major), 148.9 (minor), 145.34 (major), 145.29 (minor), 135.63 (major + minor), 132.6 (minor), 132.50 (major), 132.47 (major), 132.3 (minor), 130.6 (major), 130.4 (minor), 128.7 (major + minor), 128.5 (major + minor), 128.0 (major + minor), 125.1 (minor), 124.8 (major), 123.0 (major), 122.9 (minor), 111.85 (major), 111.80 (minor), 102.11 (major), 102.08 (minor), 101.9 (minor), 101.8 (major), 94.7 (major), 94.4 (minor), 71.9 (major + minor), 68.11 (minor), 68.05 (major), 56.5 (major), 56.4 (minor), 55.55 (major), 55.52 (minor), 52.25 (minor), 52.21 (major), 51.6 (major), 51.4 (minor), 48.2 (major + minor), 38.83 (major), 38.78 (minor), 37.61 (major), 37.55 (minor), 37.4 (minor), 37.3 (major), 35.8 (major), 35.7 (minor), 28.41 (minor), 28.37 (major), 27.2 (major), 27.0 (major), 26.94 (minor), 26.85 (minor), 23.19 (minor), 23.16 (major), 19.96 (major), 19.92 (minor) ppm; HRMS (ESI) calcd for C$_{41}$H$_{43}$NO$_{10}$H$^+$ [M+H$^+$] 710.2960, found 710.2961.

**Naphthalene 117 (+ 15-epi-117):** To a solution of substrate 115 (+ 15-epi-115) (20 mg, 0.028 mmol, 1.0 equiv, d.r. ca. 2:1) in THF (1.0 mL) at 0 °C was added NaCNBH$_3$ (9.0 mg, 0.14 mmol, 5.0 equiv). The reaction mixture was stirred for 2 minutes, and the reaction was then quenched with saturated aq. NH$_4$Cl solution (2 mL). The mixture was warmed to room
temperature, diluted with water (5 mL), and extracted with EtOAc (5 mL). The organic layer was
concentrated, and the residue purified by preparative TLC (silica gel, 35% EtOAc:hexanes) to
provide product 117 (+ 15-epi-117) (16 mg, 0.023 mmol, 82%, d.r. ca. 2:1) as a yellow powder.

117 (+ 15-epi-117): R_f = 0.5 (silica gel, EtOAc:hexanes 3:7); FT-IR (neat) ν_max = 2940, 2839,
1735, 1717, 1596, 1512, 1465, 1435, 1406, 1343, 1324, 1265, 1209, 1150, 1112, 1057, 1012,
941, 811, 746 cm⁻¹; ^1H NMR (C₆D₆, 600 MHz) δ = 16.64 (s, 1 H, minor), 16.47 (s, 1 H, major),
7.38 – 7.35 (m, 4 H, major + minor), 7.13 – 7.10 (m, 4 H, major + minor), 7.06 – 7.03 (m, 2 H,
major + minor), 6.22 (s, 1 H, major), 6.21 (s, 1 H, minor), 5.65 (bs, 1 H, minor), 5.61 (bs, 1 H,
major), 5.26 – 5.19 (m, 4 H, major + minor), 4.09 (d, J = 18.0 Hz, 1 H, minor), 3.76 (d, J =
18.6 Hz, 1 H, major), 3.56 (d, J = 18.6 Hz, 1 H, major), 3.52 (s, 6 H, major + minor), 3.51 (m,
1 H, minor), 3.33 (s, 3 H, major), 3.32 (s, 3 H, minor), 3.31 (s, 3 H, minor), 3.30 (s, 3 H, major),
3.17 (s, 3 H, minor), 3.15 (s, 3 H, major), 3.14 – 3.08 (m, 2 H, major + minor), 2.97 (s, 3 H,
major), 2.95 – 2.89 (m, 2 H, major + minor), 2.87 – 2.81 (m, 2 H, major + minor), 2.71 – 2.66
(m, 2 H, major + minor), 2.69 (s, 3 H, minor), 2.61 – 2.55 (m, 2 H, major + minor), 2.41 – 2.33
(m, 2 H, major + minor), 2.14 – 2.05 (m, 1 H, major + 2 H, minor), 2.02 (m, 1 H, major), 1.82 (s,
3 H, minor), 1.81 (s, 3 H, major), 1.42 – 1.38 (m, 2 H, major + minor), 1.21 (s, 3 H, major), 1.16
(s, 3 H, minor), 0.72 (s, 3 H, minor), 0.66 (s, 3 H, major) ppm; ^13C NMR (C₆D₆, 151 MHz) δ =
201.6 (major), 201.3 (minor), 178.31 (major), 178.26 (minor), 169.57 (minor), 169.52 (major),
167.0 (minor), 166.5 (major), 161.10 (major), 161.07 (minor), 160.92 (minor), 160.90 (major),
158.59 (minor), 158.53 (major), 148.56 (major), 148.52 (minor), 138.6 (major), 138.1 (minor),
136.4 (major + minor), 133.5 (minor), 133.1 (major), 128.67 (minor), 128.66 (major), 128.42
(minor), 128.39 (major), 128.35*, 128.33*, 125.6 (major), 125.5 (minor), 122.7 (major), 122.5
(minor), 121.3 (minor), 120.7 (major), 110.0 (major), 109.9 (major), 109.71 (minor), 109.68
(minor), 102.33 (major), 102.28 (minor), 101.98 (minor), 101.82 (major), 95.9 (major), 95.8 (minor), 71.8 (major + minor), 58.73 (major), 58.68 (minor), 55.97 (major), 55.93 (minor), 54.81 (minor), 54.74 (major), 51.20 (major), 51.16 (minor), 50.0 (major), 49.3 (minor), 46.99 (major), 46.96 (minor), 45.7 (major), 45.5 (minor), 38.9 (major + minor), 38.6 (minor), 38.4 (major), 38.1 (major), 37.7 (minor), 34.62 (major), 34.55 (minor), 27.7 (minor), 27.5 (major), 26.1 (major), 26.0 (minor), 25.0 (major), 24.3 (minor), 23.56 (minor), 23.53 (major), 21.6 (major), 21.5 (minor) ppm; HRMS (ESI) calcd for C_{41}H_{45}NO_{10}H^+ [M+H^+] 712.3116, found 712.3109.

*Due to overlap with the NMR solvent signal, these peaks could not be assigned to the major or minor diastereomer.

Benzyl ether 119 (+ 15-epi-119): To a stirred solution of substrate 117 (+15-epi-117) (37 mg, 0.052 mmol, 1.0 equiv, d.r. ca. 2:1) in toluene (1.5 mL) at room temperature was added sequentially NaH (10 mg, 60 wt% in mineral oil, 0.25 mmol, 5.0 equiv), BnBr (30 µL, 0.25 mmol, 5.0 equiv), and nBu₄NI (3 mg, 0.008 mmol, 0.15 equiv). The reaction mixture was then heated to 100 °C. After 1 hour, additional NaH (10 mg, 60 wt%, 0.25 mmol, 5.0 equiv) and BnBr (30 µL, 0.25 mmol, 5.0 equiv) was added. After 2.75 hours, the reaction mixture was allowed to cool to room temperature, and the reaction was quenched with saturated aq. NH₄Cl solution (2 mL). The layers were separated, the organic phase was concentrated, and the residue was purified by preparative TLC (silica gel, 30% EtOAc:hexanes, Et₃N buffered) to provide benzyl ether 119 (+ 15-epi-119) (35 mg, 0.044 mmol, 85%, d.r. ca. 2:1). For analytical purposes,
a small portion of this material was subjected to further preparative TLC (silica gel, 50% EtOAc:hexanes, Et3N buffered) to provide diastereomERICALLY pure benzyl ethers 119-A and 119-B, whose relative configurations were not assigned.

**119-A:** $R_f = 0.45$ (silica gel, EtOAc:hexanes 3:7); FT-IR (neat) $\nu_{\text{max}} = 2924, 2855, 1734, 1714, 1687, 1600, 1512, 1454, 1355, 1325, 1211, 1112, 1057, 1016, 978, 735, 700 \text{ cm}^{-1}$; $^1$H NMR (C$_6$D$_6$, 600 MHz) $\delta = 7.89 – 7.87$ (m, 2 H), 7.35 – 7.30 (m, 4 H), 7.19 (m, 1 H), 7.11 –7.08 (m, 2 H), 7.03 (m, 1 H), 6.32 (s, 1 H), 5.78 (d, $J = 9.8$ Hz, 1 H), 5.66 (bs, 1 H), 5.27 (d, $J = 9.8$ Hz, 1 H), 5.22 (d, $J = 12.2$ Hz, 1 H, AB system), 5.19 (d, $J = 12.2$ Hz, 1 H, AB system), 3.90 (d, $J = 18.6$ Hz, 1 H), 3.65 (d, $J = 18.6$ Hz, 1 H), 3.36 (s, 3 H), 3.34 (s, 3 H), 3.32 (s, 3 H), 3.16 (s, 3 H), 3.09 – 3.02 (m, 2 H), 3.01 (s, 3 H), 2.85 (dd, $J = 14.5, 4.4$ Hz, 1 H), 2.59 (dd, $J = 14.5, 10.3$ Hz, 1 H), 2.57 (d, $J = 17.5$ Hz, 1 H), 2.38 (m, 1 H), 2.13 – 2.02 (m, 2 H), 1.89 (s, 3 H), 1.38 (m, 1 H), 1.25 (s, 3 H), 0.67 (s, 3 H) ppm; $^{13}$C NMR (C$_6$D$_6$, 151 MHz)* $\delta = 195.3, 178.6, 169.4, 161.2, 158.0, 155.8, 154.7, 147.1, 139.7, 138.6, 138.5, 136.3, 129.0, 128.7, 128.6, 128.5, 128.4, 124.5, 122.7, 121.0, 114.6, 103.1, 101.7, 97.0, 78.7, 71.8, 58.9, 55.9, 55.0, 51.2, 49.9, 47.3, 45.8, 40.5, 38.5, 37.0, 34.5, 29.2, 26.1, 24.6, 23.5, 21.7 ppm; HRMS (ESI) calcd for C$_{48}$H$_{51}$NO$_{10}$H$^+$ [M+H$^+$] 802.3586, found 802.3582.

*Due to overlap with the NMR solvent signal, not all the $^{13}$C signals could be identified.
**119-B**: $R_f = 0.4$ (silica gel, EtOAc:hexanes 3:7); FT-IR (neat) $\nu_{\text{max}} = 2921, 2850, 1737, 1716, 1683, 1600, 1512, 1463, 1355, 1319, 1254, 1115, 1049, 1014, 736, 695 \text{ cm}^{-1}$; $^1$H NMR ($\text{C}_6\text{D}_6, 600 \text{ MHz}$) $\delta = 7.89 - 7.86$ (m, 2 H), $7.37 - 7.34$ (m, 2 H), $7.33 - 7.29$ (m, 2 H), $7.19$ (m, 1 H), $7.12 - 7.09$ (m, 2 H), $7.04$ (m, 1 H), $6.33$ (s, 1 H), $5.72$ (d, $J = 9.9$ Hz, 1 H), $5.66$ (bs, 1 H), $5.25$ (d, $J = 9.9$ Hz, 1 H), $5.23$ (s, 2 H), $4.20$ (d, $J = 18.3$ Hz, 1 H), $3.370$ (d, $J = 18.3$ Hz, 1 H), $3.368$ (s, 3 H), $3.34$ (s, 3 H), $3.30$ (s, 3 H), $3.20$ (s, 3 H), $3.14$ (dd, $J = 14.7$, $3.2$ Hz, 1 H), $3.10 - 3.01$ (m, 2 H), $2.88$ (dd, $J = 14.7$, $11.3$ Hz, 1 H), $2.78$ (s, 3 H), $2.57$ (d, $J = 17.4$ Hz, 1 H), $2.38$ (m, 1 H), $2.17 - 2.08$ (m, 2 H), $1.85$ (s, 3 H), $1.43$ (dd, $J = 12.0$, $6.0$ Hz, 1 H), $1.21$ (s, 3 H), $0.72$ (s, 3 H) ppm; $^{13}$C NMR ($\text{C}_6\text{D}_6, 151 \text{ MHz}$)* $\delta = 194.5, 178.6, 169.5, 161.3, 158.2, 155.9, 155.2, 147.0, 139.6, 138.8, 138.1, 136.3, 128.67, 128.66, 128.4, 124.0, 122.6, 121.3, 114.5, 103.1, 101.9, 97.0, 78.2, 71.8, 58.7, 56.0, 55.0, 51.2, 49.5, 47.3, 45.7, 40.5, 38.9, 36.6, 34.6, 29.3, 26.2, 24.3, 23.6, 21.7 ppm; HRMS (ESI) calcd for $\text{C}_{48}\text{H}_{51}\text{NO}_{10}\text{H}^+ [\text{M+H}^+] 802.3586$, found 802.3582.

*Due to overlap with the NMR solvent signal, not all the $^{13}$C signals could be identified.

**Isoxazole carboxylic acid 121**: To a solution of methyl ester 26 (11.96 g, 48.38 mmol, 1.0 equiv) in EtOH (100 mL) was added a solution of NaOH (3.7 g, 92 mmol, 1.9 equiv) in water (30 mL), and the reaction mixture was stirred at room temperature for 3 hours. The reaction
mixture was acidified to pH ~1 with 5% aq. HCl solution and extracted with EtOAc (2 × 500 mL). The combined organic phases were washed with brine (300 mL), dried over Na₂SO₄, and concentrated to afford the acid **121** (11.14 g, 47.77 mmol, 99%) as a white solid. **121**: R<sub>f</sub> = 0.7 (silica gel, MeOH:CH₂Cl₂ 1:3); FT-IR (neat) ν<sub>max</sub> = 3061, 3036, 2934, 1732, 1617, 1523, 1474, 1456, 1367, 1318, 1284, 1242, 1220, 1112, 1093, 1025, 986, 970, 953, 922, 909, 843, 782, 751, 738, 699 cm⁻¹; <sup>1</sup>H NMR (d₆-acetone, 600 MHz) δ = 7.54 – 7.51 (m, 2 H), 7.42 – 7.38 (m, 2 H), 7.35 (m, 1 H), 5.32 (s, 2 H), 2.61 (s, 3 H) ppm; <sup>13</sup>C NMR (d₆-acetone, 151 MHz) δ = 178.6, 170.6, 162.7, 137.6, 129.7, 129.5, 129.3, 101.7, 72.5, 14.3 ppm; HRMS (ESI) calcd for C₁₂H₁₀NO₄H⁺ [M+H⁺] 234.0761, found 234.0762.

Phenyl ester isoxazole **122**: To a solution of carboxylic acid **121** (11.0 g, 47.2 mmol, 1.0 equiv) in THF (220 mL) were added PPh₃ (13.0 g, 49.6 mmol, 1.05 equiv) and phenol (4.67 g, 49.6 mmol, 1.05 equiv), and the resulting mixture was stirred at room temperature for 10 minutes. Then diisopropyl azodicarboxylate (DIAD, 9.8 mL, 49 mmol, 1.05 equiv) was added and the resulting mixture was heated at reflux for 3 hours. The reaction mixture was then allowed to cool to room temperature and concentrated. The crude residue was purified by flash column chromatography (5% acetone:toluene) to give the phenyl ester **122** (11.4 g, 36.9 mmol, 78%) as a colorless oil that slowly solidified. The residue was recrystallized from CH₂Cl₂:pentane (1:8) in the fridge (4 °C) to give colorless needles (m.p. = 70–72 °C). **122**: R<sub>f</sub> = 0.7 (silica gel, 5% acetone:toluene); FT-IR (neat) ν<sub>max</sub> = 3067, 2931, 1952, 1801, 1720, 1682, 1620, 1587, 1515, 1494, 1468, 1453, 1445, 1368, 1308, 1295, 1270, 1192, 1163, 1111, 1066.
1033, 1024, 999, 978, 924, 910, 852, 833, 809, 776, 742, 729, 687 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ = 7.51 – 7.48 (m, 2 H), 7.44 – 7.27 (m, 6 H), 7.20 – 7.18 (m, 2 H), 5.40 (s, 2 H), 2.70 (s, 3 H) ppm; ¹³C NMR (CDCl₃, 101 MHz) δ = 178.1, 169.3, 159.8, 150.3, 135.7, 129.6, 128.6, 128.4, 127.7, 126.2, 121.8, 100.5, 71.7, 14.3 ppm; HRMS (ESI) calcd for C₁₈H₁₅NO₄H⁺ [M+H⁺] 310.1074, found 310.1067.

Teoc isoxazole 123: A solution of phenyl ester isoxazole 122 (5.0 g, 16 mmol, 1.0 equiv) in THF (100 mL) was cooled to –78 °C and LiHMDS (1 M solution in THF:ethylbenzene, 35.6 mL, 35.6 mmol, 2.2 equiv) was added dropwise. The resulting red solution was stirred at –78 °C for 30 minutes. A separately prepared solution of TeocCl [20] (6.43 g, 35.6 mmol, 2.2 equiv) in THF (50 mL) was added dropwise and the mixture was stirred at –78 °C for 2 hours. The reaction was then quenched with saturated aq. NH₄Cl solution (100 mL). The mixture was diluted with water (100 mL) and extracted with Et₂O (3 × 200 mL). The combined organic phases were dried over Na₂SO₄, concentrated, and purified by flash column chromatography (20% Et₂O:hexanes) to give the product 123 (6.30 g, 13.9 mmol, 86%) as a pale yellow oil. 123: Rᵢ = 0.4 (silica gel, Et₂O:hexanes 1:4); FT-IR (neat) νmax = 3293, 2984, 2940, 2840, 2163, 2051, 1981, 1738, 1663, 1628, 1592, 1515, 1476, 1442, 1389, 1368, 1330, 1290, 1266, 1241, 1223, 1192, 1165, 1135, 1104, 1056, 1027, 963, 897, 883, 866, 856, 798, 778, 750, 723, 690 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ = 7.51 – 7.48 (m, 2 H), 7.42 – 7.33 (m, 5 H), 7.26 (m, 1 H), 7.18 – 7.15 (m, 2 H),
5.41 (s, 2 H), 4.25 – 4.20 (m, 2 H), 4.12 (s, 2 H), 0.99 – 0.94 (m, 2 H), 0.02 (s, 9 H) ppm; \(^{13}\)C NMR (CDCl\(_3\), 101 MHz) \(\delta = 173.3, 169.2, 166.6, 159.3, 150.1, 135.6, 129.6, 128.7, 128.5, 127.8, 126.3, 121.7, 102.1, 72.0, 64.5, 34.5, 17.4, -1.5\) ppm; HRMS (ESI) calcd for C\(_{24}\)H\(_{27}\)NO\(_6\)SiH\(^{+}\) \([M+H]^{+}\) 454.1680, found 454.1685.

**Heptacycle 114 (+ 15-epi-114):** To a solution of pentacycle 111 (4.05 g, 8.76 mmol, 1.0 equiv) and phenyl ester isoxazole 123 (4.34 g, 9.57 mmol, 1.1 equiv) in toluene (175 mL) was added \(t\)BuOK (1.17 g, 10.4 mmol, 1.2 equiv), and the resulting solution was stirred for 15 minutes at room temperature. The reaction was quenched with saturated aq. NH\(_4\)Cl solution (100 mL). The phases were separated, and the organic phase was dried over Na\(_2\)SO\(_4\), filtered, and concentrated. The crude residue was purified by flash column chromatography (0→5→10% MeOH:CH\(_2\)Cl\(_2\)) to give the product 114 (+ 15-epi-114) (6.78 g, 8.26 mmol, 94%, d.r. ca. 1:1) as an orange solid. Alternative batches of material displayed varying ratios of diastereomeric purity ranging from 1:1 to 3:1, favoring the desired spirocycle configuration, albeit in reduced yield, indicating some levels of diastereomeric enhancement during chromatography. 114 (+ 15-epi-114): \(R_f = 0.6\) (silica gel, EtOAc:hexanes 8:2); FT-IR (neat) \(\nu_{\text{max}} = 2952, 1736, 1656, 1618, 1581, 1510, 1488, 1453, 1367, 1307, 1250, 1218, 1155, 1054, 1025, 933, 858, 838, 735, 695 \text{ cm}^{-1}\); \(^1\)H NMR (C\(_6\)D\(_6\), 600 MHz) \(\delta = 16.73\) (s, 1 H, major), 16.72 (s, 1 H, major), 7.59 (s, 1 H, minor), 7.56 (s, 1 H, major), 7.38 – 7.35 (m, 4 H, major + minor), 7.13 – 7.10 (m, 4 H, major + minor), 7.07 – 7.03...
(m, 2 H, major + minor), 6.05 (s, 1 H, minor), 6.03 (s, 1 H, major), 5.73 (bs, 1 H, minor), 5.70
(bs, 1 H, major), 5.20 – 5.15 (m, 4 H, major + minor), 4.74 (d, J = 9.8 Hz, 1 H, major), 4.72 (d, J
= 9.9 Hz, 1 H, minor), 4.41 – 4.34 (m, 2 H, major + minor), 4.33 – 4.27 (m, 2 H, major + minor),
4.26 (d, J = 9.8 Hz, 1 H, major), 4.21 (d, J = 9.9 Hz, 1 H, minor), 3.54 (s, 3 H, minor), 3.51 (s,
3 H, major), 3.20 (bs, 6 H, major + minor), 3.13 (s, 3 H, major), 3.06 (s, 3 H, minor), 3.01 (s, 3
H, minor), 2.96 (s, 3 H, major), 2.27 – 2.20 (m, 2 H, major + minor), 2.14 – 2.07 (m, 2 H, major
+ minor), 1.95 (ddd, J = 13.4, 6.6, 6.6 Hz, 1 H, major), 1.90 (ddd, J = 13.2, 6.7, 6.7 Hz, 1 H,
minor), 1.47 (ddd, J = 13.2, 6.5, 6.5 Hz, 2 H, major + minor), 1.27 (bs, 3 H, minor), 1.19 (bs,
3 H, major), 1.03 – 0.99 (m, 4 H, major + minor), 0.95 (s, 3 H, major), 0.92 (s, 3 H, minor), 0.87
(s, 3 H, major), 0.82 (s, 3 H, minor), –0.09 (s, 9 H, major), –0.11 (s, 9 H, minor) ppm; 13C NMR
(C6D6, 151 MHz) δ = 181.4 (major), 181.3 (minor), 178.5 (major), 178.1 (minor), 175.5 (major),
175.4 (minor), 171.6 (minor), 171.4 (major), 169.2 (major), 169.1 (minor), 168.5 (major +
minor), 162.1 (minor), 161.6 (major), 159.2 (minor), 159.0 (major), 157.02 (major), 156.95
(minor), 148.8 (minor), 148.5 (major), 139.83 (minor), 139.78 (major), 136.0 (major + minor),
135.0 (minor), 134.9 (major), 132.5 (major), 132.4 (minor), 130.9 (minor), 130.8 (major), 128.7,
128.5, 125.1 (minor), 125.0 (major), 122.9 (minor), 122.8 (major), 112.9 (major), 112.8 (minor),
106.4 (major + minor), 103.31 (major), 103.26 (minor), 102.6 (major), 102.5 (minor), 95.6
(minor), 95.1 (major), 72.2 (major + minor), 68.3 (minor), 68.2 (major), 64.8 (major + minor),
56.2 (minor), 56.0 (major), 54.9 (major + minor), 54.2 (major), 53.7 (minor), 52.8 (minor), 52.5
(major), 40.7 (major + minor), 40.2 (major + minor), 37.7 (major), 37.5 (minor), 35.90 (major),
35.86 (minor), 27.20 (major), 27.17 (minor), 27.13 (minor), 27.09 (major), 23.4 (major + minor),
20.3 (minor), 20.2 (major), 17.4 (major + minor), –1.66 (major), –1.67 (minor) ppm; HRMS
(ESI) calcd for C46H51NO11SiH+ [M+H]+ 822.3304, found 822.3305.
C12a alcohol 124/15-epi-124 and lactone product 125/15-epi-125: To a solution of substrate 114 (+ 15-epi-114) (10.6 mg, 12.8 µmol, 1.0 equiv, d.r. ca. 2:1) in acetone (0.20 mL) at –78 °C was added DMDO[21] (ca. 0.08 M in acetone, 0.24 mL, 0.02 mmol, 1.6 equiv). The mixture was stirred at that temperature for 1 hour 15 minutes, and then another portion of DMDO was added (ca. 0.08 M in acetone, 0.12 mL, 0.01 mmol, 0.8 equiv), followed by a final portion of DMDO (ca. 0.08 M in acetone, 0.06 mL, 0.005 mmol, 0.4 equiv) after 2 hours 10 minutes total reaction time. After 3.5 hours of total reaction time, the reaction was quenched by addition of excess of saturated aq. Na2SO3 solution (2 mL). The mixture was extracted with CH2Cl2 (3 × 5 mL), and the combined organic phases were dried over MgSO4, filtered, and concentrated. Purification by preparative TLC (silica gel, 66% EtOAc:hexanes) furnished lactone 125 (+ 15-epi-125) (2.3 mg, 2.7 µmol, 21%, d.r. ca. 2:1) and C12a alcohol 124 (+ 15-epi-124) (1.0 mg, 1.2 µmol, 9%, d.r. ca. 2:1).

Procedure with mCPBA: To a stirred solution of compound 114 (+ 15-epi-114) (10 mg, 0.012 mmol, 1.0 equiv, d.r. ca. 2:1) in CH2Cl2 (1 mL) at –78 °C was added mCPBA (6.0 mg, 0.026 mmol, 2.2 equiv) and the reaction mixture was stirred for 30 minutes at the same temperature. Additional mCPBA (1.5 mg, 0.0065 mmol, 0.5 equiv) was added and the reaction mixture was stirred for an additional 1 hour. The reaction was then quenched with saturated aq. Na2SO3 solution (2 mL) and allowed to warm to room temperature. The mixture was extracted
with CH$_2$Cl$_2$ (2 × 5 mL), and the combined organics were dried over Na$_2$SO$_4$, filtered, and concentrated. The crude material was purified by preparative TLC (silica gel, 60% EtOAc:hexanes) to give recovered starting material $\text{114}$ (2.4 mg, 2.8 µmol, 24%) and product $\text{124}$ (+15-epi-$\text{124}$) (5.5 mg, 6.6 µmol, 55%, 71% brsm, d.r. ca. 2:1) as an orange solid.

$\text{124}$ (+15-epi-$\text{124}$): $R_f = 0.43$ (silica gel, EtOAc:hexanes 3:2); FT-IR (neat) $\nu_{\text{max}} = 3430, 2953, 2849, 1736, 1716, 1616, 1582, 1513, 1483, 1460, 1367, 1335, 1316, 1252, 1130, 1050, 985, 838, 697, 569 \text{ cm}^{-1}$; $^1$H NMR (C$_6$D$_6$, 600 MHz) $\delta = 7.59$ (s, 1 H, minor), 7.58 (s, 1 H, major), 7.28 – 7.25 (m, 4 H, major + minor), 7.06 – 6.99 (m, 6 H, major + minor), 5.955 (s, 1 H, minor), 5.948 (s, 1 H, major), 5.75 (m, 1 H, minor), 5.66 (m, 1 H, major), 5.164 (ap d, $J = 12.1$ Hz, 2 H, major + minor, AB system), 5.160 (bs, 2 H, major + minor), 5.100 (d, $J = 12.1$ Hz, 1 H, minor, AB system), 5.095 (d, $J = 12.1$ Hz, 1 H, major, AB system), 4.43 (d, $J = 1.3$ Hz, 1 H, minor), 4.39 (d, $J = 1.2$ Hz, 1 H, major), 4.20 – 4.13 (m, 4 H, major + minor), 4.03 (d, $J = 1.2$ Hz, 1 H, major), 4.00 (d, $J = 1.3$ Hz, 1 H, minor), 3.44 (ap s, 6 H, major + minor), 3.15 (s, 3 H, minor), 3.14 (s, 3 H, major), 2.96 (s, 3 H, minor), 2.92 (s, 3 H, major), 2.84 (s, 3 H, major), 2.81 (s, 3 H, minor), 2.27 – 2.19 (m, 2 H, major + minor), 2.15 – 2.07 (m, 2 H, major + minor), 1.88 (ddd, $J = 13.3, 6.4, 6.4$ Hz, 2 H, major + minor), 1.52 (ddd, $J = 13.3, 6.9, 6.9$ Hz, 1 H, major), 1.46 (ddd, $J = 13.3, 6.9, 6.9$ Hz, 1 H, minor), 1.22 (bs, 3 H, minor), 1.11 (bs, 3 H, major), 0.95 (s, 3 H, major), 0.91 – 0.84 (m, 4 H, major + minor), 0.84 (s, 3 H, minor), 0.79 (s, 3 H, major), 0.76 (s, 3 H, minor), –0.15 (s, 9 H, minor), –0.16 (s, 9 H, major) ppm; $^{13}$C NMR (C$_6$D$_6$, 151 MHz)* $\delta = 192.9$
(major + minor), 184.5 (major + minor), 177.5 (major + minor), 177.0 (major + minor), 168.79 (major), 168.77 (minor), 168.50 (minor), 168.49 (major), 162.3 (major), 161.9 (minor), 159.9 (major + minor), 159.2 (major + minor), 148.5 (major + minor), 144.6 (major + minor), 135.88 (minor), 135.87 (major), 133.29 (major + minor), 132.7 (major + minor), 130.76 (major), 130.67 (minor), 128.6 (major + minor), 128.46 (major + minor), 125.1 (major + minor), 122.7 (major + minor), 112.2 (major + minor), 107.2 (major + minor), 101.5 (major + minor), 95.5 (major + minor), 81.5 (major + minor), 72.39 (major), 72.36 (minor), 68.4 (minor), 68.2 (major), 65.3 (major + minor), 56.06 (major), 56.03 (minor), 54.78 (major), 54.75 (minor), 52.2 (major + minor), 51.8 (major + minor), 51.3 (major + minor), 40.0 (major + minor), 37.7 (major + minor), 36.0 (major), 35.9 (minor), 27.11 (major), 27.09 (minor), 23.4 (major + minor), 20.2 (major + minor), 17.22 (major), 17.21 (minor), −1.73 (major + minor) ppm; HRMS (ESI) calcd for $\text{C}_{46}\text{H}_{51}\text{NO}_{12}\text{SiH}^+ [M+H]^+$ 838.3253, found 838.3252.

*Due to overlap with the NMR solvent, not all the $^{13}$C signals could be identified.

![Teoc lactone product 125 (+ 15-epi-125)](image)

**Teoc lactone product 125 (+ 15-epi-125):** $R_f = 0.60$ (silica gel, EtOAc:hexanes 3:2); FT-IR (neat) $\nu_{\text{max}} = 2954, 1745, 1693, 1614, 1577, 1517, 1452, 1366, 1336, 1256, 1222, 1169, 1116, 1075, 1001, 839, 770, 696 \text{ cm}^{-1}$; $^1$H NMR (C$_6$D$_6$, 600 MHz) $\delta = 12.31$ (s, 1 H, minor), 12.27 (s, 1 H, major), 7.81 (s, 1 H, major), 7.79 (s, 1 H, minor), 7.31 − 7.28 (m, 4 H, major + minor), 7.08 − 7.05 (m, 4 H, major + minor), 7.03 − 6.99 (m, 2 H, major + minor), 5.92 (s, 1 H, major), 5.91 (s, 1 H, minor), 5.77 − 5.74 (m, 2 H, major + minor), 5.09 (bd, $J = 12.4$ Hz, 2 H, major + minor, AB system), 5.043 (d, $J = 12.4$ Hz, 1 H, minor, AB system), 5.038 (d, $J = 12.4$ Hz, 1 H, major,
AB system), 4.21 – 4.15 (m, 1 H, major + 3 H, minor), 4.11 (d, $J = 10.7$ Hz, 1 H, major), 4.06 (ddd, $J = 11.3, 11.3, 6.0$ Hz, 1 H, major), 3.77 (d, $J = 10.9$ Hz, 1 H, minor), 3.75 (d, $J = 10.7$ Hz, 1 H, major), 3.41 (ap s, 6 H, major + minor), 3.17 (bs, 6 H, major + minor), 3.01 (s, 3 H, major), 2.96 (s, 3 H, minor), 2.86 (s, 3 H, major), 2.75 (s, 3 H, minor), 2.32 – 2.23 (m, 2 H, major + minor), 2.21 – 2.12 (m, 2 H, major + minor), 1.99 – 1.90 (m, 2 H, major + minor), 1.68 (ddd, $J = 13.4, 6.8, 6.8$ Hz, 1 H, minor), 1.56 (ddd, $J = 13.3, 6.7, 6.7$ Hz, 1 H, major), 1.37 (bs, 3 H, major), 1.21 (bs, 3 H, minor), 1.04 (s, 3 H, minor), 1.03 (s, 3 H, minor), 0.96 – 0.85 (m, 4 H, major + minor), 0.92 (s, 3 H, major), 0.82 (s, 3 H, major), –0.10 (s, 9 H, minor), –0.13 (s, 9 H, major) ppm; $^{13}$C NMR (C$_6$D$_6$, 151 MHz)* $\delta = 186.21$ (major), 186.18 (minor), 171.9 (major), 171.7 (minor), 170.4 (major + minor), 167.5 (minor), 167.4 (major), 162.81 (minor), 162.75 (major), 159.87 (major), 159.84 (minor), 159.3 (minor), 159.1 (major), 156.5 (major + minor), 150.1 (major + minor), 141.3 (minor), 141.2 (major), 135.9 (major + minor), 134.6 (major), 134.5 (minor), 133.0 (minor), 132.8 (major), 131.1 (major), 131.0 (minor), 128.6 (major + minor), 126.82 (major), 126.79 (minor), 125.2 (minor), 125.0 (major), 123.01 (major), 122.99 (minor), 110.94 (major), 110.90 (minor), 103.4 (major), 103.3 (minor), 101.2 (major), 101.1 (minor), 94.19 (minor), 94.16 (major), 71.9 (major + minor), 67.9 (minor), 67.8 (major), 64.3 (major + minor), 55.71 (major), 55.69 (minor), 54.9 (major + minor), 51.6 (major), 51.3 (minor), 49.50 (minor), 49.45 (major), 45.91 (major), 45.85 (minor), 43.06 (major), 43.04 (minor), 37.7 (minor), 37.5 (major), 36.0 (minor), 35.9 (major), 27.22 (major), 27.15 (major), 27.09 (2C minor), 23.5 (minor), 23.4 (major), 20.13 (major), 20.08 (minor), 17.64 (minor), 17.56 (major), –1.70 (minor), –1.75 (major) ppm; HRMS (ESI) calcd for C$_{46}$H$_{51}$NO$_{12}$SiH$^+$ [M+H$^+$] 838.3253, found 838.3255.

*Due to overlap with the NMR solvent, not all the $^{13}$C signals could be identified.
**Lactone 127 (+ 15-epi-127):** A biphasic mixture of HF•Et₃N in DMSO was prepared from 1.0 mL DMSO, 1.6 mL Et₃N, and 0.25 mL HF (aq. 49%). Under vigorous stirring 0.4 mL (ca. 1 mmol HF) of this mixture were taken out with a syringe and subsequently added to a solution of intermediate 124 (+ 15-epi-124) (8.7 mg, 0.010 mmol, 1.0 equiv, d.r. ca. 2:1) in DMSO (0.3 mL). After 10 min, the mixture was warmed up to 60 °C and stirred at this temperature for 2 hours. The mixture was allowed to cool to room temperature, diluted with EtOAc (10 mL), and washed with saturated aq. NH₄Cl solution (5 mL) and brine (2 × 5 mL). The organic phase was dried over MgSO₄, filtered, and concentrated. Purification by preparative TLC (silica gel, 20% acetone:toluene, Et₃N buffered) afforded lactone 127 (+ 15-epi-127) (3.0 mg, 4.3 μmol, 43%, d.r. ca. 2:1) as an inseparable mixture of diastereomers. 127 (+ 15-epi-127): R_f = 0.58 (silica gel, acetone:toluene 1:4); FT-IR (neat) ν_max = 2928, 1737, 1696, 1576, 1461, 1335, 1259, 1118, 1077, 1017, 829 cm⁻¹; ¹H NMR (C₆D₆, 600 MHz) data for major diastereomer: δ = 12.21 (s, 1 H), 7.76 (s, 1 H), 7.47 – 7.43 (m, 2 H), 7.16 – 7.08 (m, 3 H), 5.91 (s, 1 H), 5.75 (bs, 1 H), 5.31 (d, J = 12.6 Hz, 1 H, AB system), 5.21 (d, J = 12.6 Hz, 1 H, AB system), 3.39 (s, 3 H), 3.15 (s, 3 H), 2.86 (s, 3 H), 2.74 (dd, J = 12.4, 5.3 Hz, 1 H), 2.60 (s, 3 H), 2.43 (dd, J = 17.8, 12.4 Hz, 1 H), 2.33 (dd, J = 17.8, 5.3 Hz, 1 H), 2.29 (m, 1 H), 2.20 (m, 1 H), 1.89 (m, 1 H), 1.64 (m, 1 H), 1.28 (s, 3 H), 0.96 (s, 3 H), 0.81 (s, 3 H) ppm; ¹³C NMR (C₆D₆, 151 MHz)* data for major diastereomer: δ = 187.1, 174.6, 171.3, 163.3, 160.4, 159.2, 157.3, 150.9, 140.3, 136.9, 134.2,
133.5, 131.7, 129.8, 127.6, 125.6, 123.6, 111.6, 103.5, 101.5, 94.9, 72.4, 68.3, 56.4, 55.4, 51.6, 48.1, 39.5, 38.2, 36.7, 30.7, 27.7, 27.4, 24.1, 20.6 ppm; HRMS (ESI) calcd for C₄₀H₃₉NO₁₀H⁺ [M+H⁺] 694.2647, found 694.2644.

*Due to overlap with the NMR solvent, not all the ¹³C signals could be identified.

Desired product 116 (+ 15-epi-16) and product 131: To a solution of substrate 114 (+ 15-epi-114) (9.1 mg, 0.011 mmol, 1.0 equiv, d.r. ca. 2:1) in DMSO (0.3 mL) was added a solution of HF•Et₃N in DMSO (0.44 mL, ca. 1.1 mmol HF, prepared as described above, cf. 127), and the mixture was stirred at room temperature for 1 hour. It was then warmed up to 60 °C and stirred at this temperature for another 2 hours. Then, the mixture was diluted with EtOAc (10 mL) and washed with saturated aq. NH₄Cl solution (5 mL) and brine (2 × 5 mL). The organic phase was dried over MgSO₄, filtered, and concentrated. NMR and TLC analysis indicated significant decomposition, and therefore only the two major products were isolated. Purification by preparative TLC (silica gel, 20% acetone:toluene) afforded aromatized product 131 (2.7 mg, 3.3 µmol, 30%) and desired product 116 (+ 15-epi-116) (2.1 mg, 3.1 µmol, 28%, d.r. ca. 2:1).
Desired product 116 (+ 15-epi-116): $R_f = 0.36$ (silica gel, toluene:acetone 4:1); FT-IR (neat) $v_{\text{max}} = 3526, 2939, 2840, 1655, 1618, 1582, 1509, 1464, 1333, 1218, 1156, 1053, 1028, 1003, 911, 843, 736, 696 \text{ cm}^{-1}$; $^1H$ NMR (d$_6$-acetone, 600 MHz) data for major diastereomer: $\delta = 7.79$ (s, 1 H), 7.55 – 7.53 (m, 2 H), 7.44 – 7.41 (m, 2 H), 7.39 – 7.36 (m, 1 H), 6.72 (s, 1 H), 5.78 (m, 1 H), 5.37 (s, 2 H), 4.16 (dd, $J = 10.9, 8.2$ Hz, 1 H), 3.98 (s, 3 H), 3.97 (s, 3 H), 3.60 (s, 3 H), 3.37 (dd, $J = 17.8, 10.9$ Hz, 1 H), 3.31 (s, 3 H), 3.17 (dd, $J = 17.8, 8.2$ Hz, 1 H), 2.31 – 2.26 (m, 2 H), 2.06 (m, 1 H), 1.66 (m, 1 H), 1.15 (s, 3 H), 0.97 (s, 3 H), 0.86 (s, 3 H) ppm; $^{13}C$ NMR (d$_6$-acetone, 151 MHz)* data for major diastereomer: $\delta = 183.3, 181.1, 179.6, 168.8, 161.9, 160.3, 159.3, 148.9, 142.2, 136.8, 133.7, 131.1, 129.3, 129.2, 129.1, 125.6, 123.3, 112.2, 105.9, 105.0, 102.8, 96.0, 72.6, 68.8, 56.4, 56.0, 53.9, 52.4, 38.2, 37.7, 36.2, 27.4, 27.1, 23.7, 21.0, 20.2 ppm; HRMS (ESI) calcd for C$_{40}$H$_{39}$NO$_9$H$^+$ [M+H$^+$] 678.2697, found 678.2696.

*Two $^{13}C$ signals of the major diastereomer could not be unambiguously identified.

Product 131: $R_f = 0.45$ (silica gel, toluene:acetone 4:1); FT-IR (neat) $v_{\text{max}} = 2953, 1734, 1671, 1620, 1583, 1535, 1350, 1314, 1252, 1236, 1220, 1155, 1082, 835 \text{ cm}^{-1}$; $^1H$ NMR (C$_6$D$_6$, 600 MHz) $\delta = 15.19$ (s, 1 H), 8.13 (s, 1 H), 7.39 (d, $J = 7.5$ Hz, 2 H), 7.16 – 7.12 (m, 2 H), 7.07
(m, 1 H), 6.01 (s, 1 H), 5.72 (bs, 1 H), 5.24 (s, 2 H), 4.58 – 4.49 (m, 2 H), 3.52 (s, 3 H), 3.18 (s, 3 H), 2.79 (s, 3 H), 2.73 (s, 3 H), 2.21 (m, 1 H), 2.02 (m, 1 H), 1.78 (m, 1 H), 1.48 (m, 1 H), 1.32 (s, 3 H), 1.14 – 1.09 (m, 2 H), 1.02 (s, 3 H), 0.85 (s, 3 H), –0.14 (s, 9 H) ppm; $^{13}$C NMR (C$_6$D$_6$, 151 MHz) δ = 187.8, 177.6, 166.9, 166.4, 164.0, 162.1, 161.8, 161.4, 159.4, 148.9, 148.0, 138.4, 135.8, 132.0, 130.5, 129.7, 128.8, 128.5, 125.3, 123.1, 112.8, 112.6, 109.9, 105.5, 99.6, 95.1, 72.5, 68.7, 64.4, 56.0, 54.8, 51.9, 51.7, 37.6, 35.7, 27.2, 27.0, 23.4, 20.1, 17.5, –1.70 ppm; HRMS (ESI) calcd for C$_{46}$H$_{49}$NO$_{11}$SiH$^+$ [M+H$^+$] 820.3147, found 820.3151.

**Heptacycle 116 (+ 15-epi-116):** To a solution of Teoc-heptacycle 114 (+ 15-epi-114) (6.78 g, 8.26 mmol, 1.0 equiv, d.r. ca. 2:1) in THF (900 mL) was added NH$_4$F (6.07 g, 164 mmol, 20 equiv), and the solution was degassed with argon for 1 hour. The degassing was discontinued, and the reaction flask was shielded from light using aluminum foil. Tetrabutylammonium fluoride (82 mL, 1 M solution in THF, freshly prepared from TBAF•3H$_2$O salt, 82 mmol, 10 equiv) was added in one portion. The reaction mixture was stirred for 5 minutes, and the reaction was then quenched with brine (500 mL) and diluted with EtOAc (600 mL). The layers were separated, and the organic phase was washed with water (3 × 500 mL), dried over Na$_2$SO$_4$, and concentrated. The crude residue was purified by flash column chromatography (2→10% MeOH:CH$_2$Cl$_2$) to give the deprotected heptacycle 116 (+ 15-epi-116) (5.5 g, 8.1 mmol, 98%, d.r. ca. 2:1) as a red foam. The data of the so-obtained material matched those reported above.
Intermediate 132 (+ 15-epi-132): A solution of substrate 116 (+ 15-epi-116) (4.5 g, 6.6 mmol, 1.0 equiv, d.r. ca. 2:1) in anhydrous acetone (170 mL) was cooled to –78 °C, and Ni(acac)$_2$ (340 mg, 1.32 mmol, 0.2 equiv) was added followed by DMDO$^{[21]}$ (170 mL of a ~0.08 M solution in acetone, 14 mmol, 2.1 equiv). Three additional portions of DMDO (150 mL each, 12 mmol each, 1.8 equiv each) were added, one every 2 hours, and the reaction was maintained between –78 and –65 °C for a total of 6.5 hours. The reaction was then quenched by the addition of dimethylsulfide (5 mL, 0.1 mol, 15 equiv), and stirred at the same temperature for 15 minutes. Saturated aq. NH$_4$Cl solution (100 mL) was added, and the mixture was allowed to warm to room temperature. The mixture was diluted with water (400 mL) and EtOAc (600 mL). The layers were separated, and the organic phase was washed with water (300 mL) and brine (300 mL), dried over Na$_2$SO$_4$, and concentrated. Purification by flash column chromatography (10–20–30% acetone:toluene) gave the hydroxylated product 132 (+ 15-epi-132) (2.8 g, 4.0 mmol, 61%, d.r. ca. 2:1) as a red foam. 132 (+ 15-epi-132): $R_f$ = 0.3 (silica gel, acetone:toluene 1:4); FT-IR (neat) $v_{\text{max}}$ = 3443, 2938, 2845, 1719, 1616, 1581, 1514, 1487, 1369, 1331, 1259, 1221, 1155, 1130, 1102, 1055, 991, 821, 735, 697 cm$^{-1}$; $^1$H NMR (C$_6$D$_6$, 600 MHz) $\delta$ = 7.63 (s, 1 H, major), 7.62 (s, 1 H, minor), 7.30 – 7.27 (m, 4 H, major + minor), 7.09 – 7.05 (m, 4 H, major + minor), 7.03 – 7.00 (m, 2 H, major + minor), 5.92 (s, 1 H, minor), 5.91 (s, 1 H, major), 5.73 (bs, 1 H, minor), 5.69 (bs, 1 H, major), 5.19 (s, 1 H, major), 5.18 (s, 1 H, minor), 5.12 – 5.03 (m, 4 H, major + minor), 3.405 (s, 3 H, major), 3.401 (s, 3 H, minor), 3.14 (s, 3 H, minor), 3.13 (s, 3 H, major), 2.96 – 2.91 (m, 2 H, major + minor), 2.79 (s,
3 H, minor), 2.73 (s, 3 H, major), 2.69 (s, 3 H, major), 2.65 – 2.61 (m, 2 H, major + minor), 2.60 (s, 3 H, minor), 2.48 (dd, \( J = 18.7, 8.8 \) Hz, 1 H, minor), 2.44 (dd, \( J = 18.7, 8.7 \) Hz, 1 H, major), 2.29 – 2.22 (m, 2 H, major + minor), 2.18 – 2.12 (m, 2 H, major + minor), 1.90 – 1.86 (m, 2 H, major + minor), 1.60 – 1.54 (m, 2 H, major + minor), 1.24 – 1.22 (m, 3 H, minor), 1.17 – 1.16 (m, 3 H, major), 0.96 (s, 3 H, major), 0.90 (s, 3 H, minor), 0.80 (s, 3 H, major), 0.795 (s, 3 H, minor) ppm; \(^{13}\)C NMR (C\(_6\)D\(_6\), 151 MHz)* \( \delta = 192.29 \) (major), 192.23 (minor), 184.64 (minor), 184.58 (major), 180.46 (major), 180.43 (minor), 177.1 (minor), 176.9 (major), 168.3 (major + minor), 162.3 (major), 162.1 (minor), 159.84 (minor), 159.75 (major), 159.24 (major), 159.17 (minor), 148.9 (major + minor), 145.3 (major + minor), 135.9 (major + minor), 133.76 (major), 133.71 (minor), 132.79 (major), 132.75 (minor), 131.0 (major), 130.9 (minor), 128.6, 125.2 (minor), 125.0 (major), 122.8 (major), 122.7 (minor), 112.19 (minor), 112.16 (major), 106.6 (major + minor), 102.34 (major), 102.30 (minor), 95.4 (major), 95.2 (minor), 81.4 (minor), 81.3 (major), 72.3 (major + minor), 68.2 (minor), 68.1 (major), 56.01 (major), 55.96 (minor), 54.76 (major), 54.74 (minor), 51.3 (major), 51.1 (minor), 49.3 (major), 49.2 (minor), 45.4 (minor), 45.3 (major), 37.61 (major), 37.59 (minor), 36.1 (major), 35.9 (minor), 27.09 (major), 27.04 (major), 27.00 (minor), 26.97 (minor), 23.5 (major + minor), 21.8 (minor), 21.7 (major), 20.15 (minor), 20.13 (major); ppm; HRMS (ESI) calcd for C\(_{40}\)H\(_{39}\)NO\(_{10}\)H\(^+\) [M+H\(^+\)] 694.2647, found 694.2639.

*Due to overlap with the NMR solvent, not all the \(^{13}\)C signals could be identified.
133 and 15-epi-133: Substrate 132 (+ 15-epi-132) (53 mg, 0.076 mmol, 1.0 equiv, d.r. ca. 2:1) was dissolved in THF (2 mL) and cooled to −78 °C. Sodium cyanoborohydride (46 mg, 0.78 mmol, 10 equiv) was added in one portion, and the solution was vigorously stirred for 1.5 hours at that temperature. The reaction was quenched with saturated aq. NH₄Cl solution (2 mL), and the mixture was allowed to warm to room temperature and stirred for 20 minutes. Brine (5 mL) and EtOAc (10 mL) were added, and the layers were separated. The organic phase was dried over Na₂SO₄, filtered, and concentrated. The residue was purified by flash column chromatography (5–10–15–20% EtOAc:toluene) to give 133 (27 mg, 0.039 mmol, 51%) and 15-epi-133 (10 mg, 0.014 mmol, 19%) as amorphous yellow solids. 15-epi-133 could be crystallized by slow evaporation from EtOAc to give crystals suitable for X-ray crystallographic analysis (m.p. = 213–215 °C dec.).

133: R_f = 0.5 (silica gel, acetone:toluene 1:4); FT-IR (neat) ν_max = 3414, 2938, 2840, 1715, 1591, 1513, 1483, 1405, 1344, 1308, 1215, 1131, 1106, 1059, 989, 903, 812, 736, 697, 534 cm⁻¹; 
¹H NMR (CD₆D₆, 600 MHz) δ = 16.14 (s, 1 H), 7.30 (d, J = 7.3 Hz, 2 H), 7.08 – 7.04 (m, 2 H), 7.01 (m, 1 H), 6.14 (s, 1 H), 5.56 (bs, 1 H), 5.25 (d, J = 12.2 Hz, 1 H, AB system), 5.13 (d, J = 12.2 Hz, 1 H, AB system), 5.12 (bs, 1 H), 3.52 (d, J = 18.7 Hz, 1 H), 3.43 (s, 3 H), 3.26 (d, J =
18.7 Hz, 1 H), 3.25 (s, 3 H), 2.83 – 2.80 (m, 4 H), 2.72 (s, 3 H), 2.66 (m, 1 H), 2.65 (m, 1 H), 2.32 (m, 1 H), 2.04 (m, 1 H), 1.87 (ddd, J = 12.5, 12.5, 6.1 Hz, 1 H), 1.65 (s, 3 H), 1.36 (m, 1 H), 1.17 (s, 3 H), 0.59 (s, 3 H) ppm; $^{13}$C NMR (C$_6$D$_6$, 151 MHz)* $\delta = 196.8, 184.3, 179.8, 168.9, 168.7, 161.2, 159.3, 148.6, 138.0, 136.0, 132.9, 128.6, 128.5, 124.8, 122.5, 121.0, 109.5, 108.8, 106.5, 102.1, 95.9, 78.5, 72.2, 58.6, 55.9, 54.8, 51.1, 48.8, 45.6, 44.9, 38.4, 34.5, 26.1, 25.0, 23.4, 21.8, 21.4 ppm; HRMS (ESI) calcd for C$_{40}$H$_{41}$NO$_{10}$H$^+$ [M+H$^+$] 696.2803, found 696.2784.

*Due to overlap with the NMR solvent, not all the $^{13}$C signals could be identified.

15-epi-133: R$_f = 0.4$ (silica gel, acetone:toluene 1:4); FT-IR (neat) $\nu_{max} = 3413, 2926, 1716, 1593, 1514, 1484, 1406, 1370, 1344, 1308, 1216, 1184, 1130, 1104, 1049, 998, 903, 735$ cm$^{-1}$; $^1$H NMR (C$_6$D$_6$, 600 MHz) $\delta = 16.27$ (s, 1 H), 7.34 (d, J = 6.8 Hz, 2 H), 7.10 – 7.06 (m, 2 H), 7.02 (m, 1 H), 6.13 (s, 1 H), 5.62 (bs, 1 H), 5.45 (s, 1 H), 5.24 (d, J = 12.2 Hz, 1 H, AB system), 5.13 (d, J = 12.2 Hz, 1 H, AB system), 3.84 (d, J = 18.1 Hz, 1 H), 3.43 (s, 3 H), 3.26 (s, 3 H), 3.06 (d, J = 18.1 Hz, 1 H), 2.83 (s, 3 H), 2.78 (dd, J = 7.9, 7.9 Hz, 1 H), 2.63 – 2.52 (m, 5 H), 2.34 (m, 1 H), 2.07 (m, 1 H), 1.96 (ddd, J = 12.5, 12.5, 5.9 Hz, 1 H), 1.75 (s, 3 H), 1.36 (dd, J = 12.5, 6.1 Hz, 1 H), 1.11 (s, 3 H), 0.55 (s, 3 H) ppm; $^{13}$C NMR (C$_6$D$_6$, 151 MHz) $\delta = 196.4, 184.7, 180.0, 170.0, 169.1, 161.7, 159.9, 149.1, 138.4, 136.5, 134.5, 129.2, 129.13, 129.06, 125.0, 123.1, 122.0, 110.0, 108.8, 107.4, 102.8, 96.5, 79.3, 72.8, 59.2, 56.5, 55.3, 50.6, 48.5, 46.0, 44.9, 39.3, 35.0, 26.6, 25.1, 24.1, 23.7, 22.0 ppm; HRMS (ESI) calcd for C$_{40}$H$_{41}$NO$_{10}$Na$^+$ [M+Na$^+$] 718.2623, found 718.2608.
Table S2. Conditions screened for the desired methyl enolether formation (133→134, see Scheme 23 in the article).

| entry | conditions | observation |
|-------|------------|-------------|
| 1     | PPTS, C₆H₆, MS 3Å, 80 °C | Ketone 137\(^a\) |
| 2\(^{[22]}\) | BF₃•OEt₂, CH₂Cl₂, 25 °C | Ketone 137\(^a\) |
| 3     | toluene, 110 °C | Ketone 137\(^a\) |
| 4\(^{[23]}\) | Al₂Bu₃, CH₂Cl₂, 25 °C | r.s.m. + decomposition |
| 5     | TsOH, C₆H₆, MS 4Å, 25 °C | Ketone 137\(^a\) |
| 6     | CSA, CH₂Cl₂, MS 4Å, 25 °C | Ketone 137\(^a\) |
| 7\(^{[24]}\) | TMSOTf, iPr₂EtN, CH₂Cl₂, 0→25 °C | C₁₂a 3°-OH silylation\(^b\) |

\(^a\)as evidenced by TLC or \(^1\)H NMR analysis; \(^b\)15-epi-133 was used in this experiment

**Triketone 137:** Ketal 133 (56 mg, 0.081 mmol, 1.0 equiv) was dissolved in THF (5 mL) at room temperature and 2 M aq. HCl solution (0.5 mL) was added. The resulting red solution was stirred at room temperature for 3.5 hours, after which it was diluted with water (10 mL) and EtOAc (20 mL). The layers were separated and the organic phase was washed with water (20 mL) and brine (20 mL), dried over Na₂SO₄, filtered, and concentrated to give analytically pure triketone 137 (51 mg, 0.079 mmol, 98%). **Triketone 137:** \(R_f = 0.6\) (silica gel, acetone:toluene 1:4); FT-IR (neat) \(\nu_{\text{max}} = 3447, 2959, 2922, 2841, 1698, 1612, 1587, 1514, 1482, 1401, 1344, 1294, 1260, 1217, 1189, 1161, 1109, 1037, 906, 827, 734, 697, 532 \text{ cm}^{-1}\); \(^1\)H NMR (CDCl₃, 600 MHz) \(\delta = 13.99\) (s, 1 H), 7.41 – 7.38 (m, 2 H), 7.33 – 7.28 (m, 3 H), 6.72 (s, 1 H), 5.49 (bs, 1 H), 5.29 (d, \(J = 12.0\) Hz, 1 H, AB system), 5.26 (d, \(J = 12.0\) Hz, 1 H, AB system), 4.90 (s, 1 H), 4.09 (s, 3 H), 3.93 (s, 3 H), 3.87 – 3.83 (m, 2 H), 3.65 (d, \(J = 20.1\) Hz, 1 H), 3.32 (dd, \(J = 17.3, 4.7\) Hz, 1 H), 3.14 (d, \(J = 20.1\) Hz, 1 H), 2.19 (m, 1 H), 2.03 (m, 1 H), 1.80 (ddd, \(J = 12.6, 12.6, 6.1\) Hz, 1 H), 1.46 (s, 3 H), 1.29 (dd, \(J = 12.6, 6.1\) Hz, 1 H), 0.89 (s, 3 H), 0.29 (s, 3 H) ppm; \(^13\)C NMR.
(CDCl₃, 151 MHz) δ = 195.5, 192.0, 184.7, 181.7, 168.2, 164.5, 160.3, 159.6, 147.8, 142.5, 136.2, 135.0, 128.6, 128.3, 126.9, 121.5, 109.7, 107.8, 105.3, 98.1, 78.5, 72.4, 59.6, 56.8, 55.6, 53.1, 45.5, 38.4, 34.1, 25.5, 24.3, 22.9, 20.9, 20.8 ppm; HRMS (ESI) calcd for C₃₈H₃₅NO₉H⁺ [M+H⁺] 650.2384, found 650.2386.

**Aromatic A-ring compound 138**: This compound was observed during a number of attempted enolate oxidations and appeared as a red-purple spot on TLC (see Table S3 below and Scheme 23). As a control experiment to determine the base sensitivity of 137: To a solution of ketone 137 (9.0 mg, 14 µmol, 1.0 equiv) in MeOH:toluene (2 mL, 1:1) was added DBU (10 µL, 66 µmol, 4.7 equiv), and the solution immediately turned red-purple. The reaction mixture was concentrated, and the residue was purified by preparative TLC (silica gel, 10% acetone:toluene) to provide the elimination product 138 (4.0 mg, 6.5 µmol, 45%). 138: R_f = 0.7 (silica gel, acetone:toluene 1:4); FT-IR (neat) ν_max = 2921, 2845, 1615, 1529, 1452, 1433, 1402, 1342, 1307, 1259, 1205, 1137, 1051, 913 cm⁻¹; ¹H NMR (CDCl₃, 600 MHz) δ = 15.25 (s, 1 H), 13.99 (s, 1 H), 7.85 (s, 1 H), 7.58 – 7.56 (m, 2 H), 7.45 – 7.41 (m, 2 H), 7.38 (m, 1 H), 6.73 (s, 1 H), 5.55 (bs, 1 H), 5.53 (s, 2 H), 4.12 (s, 3 H), 3.98 (d, J = 20.3 Hz, 1 H), 3.96 (s, 3 H), 3.31 (d, J = 20.3 Hz, 1 H), 2.24 (m, 1 H), 2.09 (m, 1 H), 1.92 (ddd, J = 12.7, 12.7, 6.5 Hz, 1 H), 1.50 (s, 3 H), 1.36 (dd, J = 12.7, 6.1 Hz, 1 H), 0.94 (s, 3 H), 0.39 (s, 3 H) ppm; ¹³C NMR (CDCl₃, 151 MHz) δ = 190.0, 183.1, 169.4, 167.5, 167.3, 161.28, 161.25, 160.5, 148.5, 146.1, 138.1, 136.8, 136.0,
129.52, 129.49, 129.1, 122.4, 122.1, 112.7, 110.7, 108.6, 107.9, 98.9, 73.4, 60.5, 57.5, 56.4, 47.2, 39.1, 34.9, 26.2, 25.2, 23.7, 21.6 ppm; HRMS (ESI) calcd for C$_{38}$H$_{33}$NO$_8$H$^+$ [M+H$^+$] 632.2279, found 632.2252.

Table S3. Conditions screened for the desired ketone oxidation (137$\rightarrow$136, see Scheme 23 in the article).

| entry | conditions                  | observation            |
|-------|-----------------------------|-------------------------|
| 1$^{[25]}$ | Mn$^{III}$(OAc)$_3$, C$_6$H$_6$, AcOH, reflux | decomposition          |
| 2     | TsOH, C$_6$H$_6$, O$_2$, 50 °C | slow formation of 138$^a$ |
| 3$^{[26]}$ | Co(OAc)$_2$, AcOH, O$_2$, 75 °C | slow formation of 138$^a$ |
| 4     | DBU, toluene:MeOH 1:1, 25 °C | rapid formation of 138 (45%) |

$^a$as evidenced by TLC analysis

Methyl ethers 140 and 5-epi-140: To a flask containing solid substrate 133 (10 mg, 14 µmol, 1.0 equiv) and NaCNBH$_3$ (4 mg, 0.06 mmol, 4.3 equiv) was added glacial AcOH (1 mL), and the reaction mixture was vigorously stirred at room temperature for 40 minutes. The reaction was then quenched with pH 7.4 buffer (3 mL) and diluted with water (2 mL). The mixture was extracted with EtOAc (5 mL), and the organic phase was dried over Na$_2$SO$_4$, filtered, and concentrated. Purification by preparative TLC (silica gel, 20% acetone:toluene) provided methyl ether 140 (3.7 mg, 5.6 µmol, 40%) and 5-epi-140 (3.0 mg, 4.5 µmol, 32%).
**140**: $R_f = 0.6$ (silica gel, acetone:toluene 1:4); FT-IR (neat) $\nu_{\text{max}} = 3437, 2920, 2840, 1703, 1608, 1592, 1513, 1481, 1404, 1342, 1255, 1214, 1185, 1141, 1081, 1034, 1010, 813, 735 \text{ cm}^{-1}$; 
$^1\text{H NMR (C}_6\text{D}_6, 600 \text{ MHz}) \delta = 14.98 \text{ (s, 1 H), 7.27 – 7.25 (m, 2 H), 7.05 – 7.02 (m, 2 H), 6.99 (m, 1 H), 6.10 (s, 1 H), 5.56 (bs, 1 H), 5.13 (d, } J = 12.2 \text{ Hz, 1 H, AB system), 5.10 (d, } J = 12.2 \text{ Hz, 1 H, AB system), 4.86 (s, 1 H), 4.29 (d, } J = 8.7 \text{ Hz, 1 H), 3.54 (d, } J = 17.5 \text{ Hz, 1 H), 3.44 (s, 3 H), 3.26 (s, 3 H), 2.85 (s, 3 H), 2.83 (d, } J = 17.5 \text{ Hz, 1 H), 2.74 – 2.68 (m, 2 H), 2.62 (m, 1 H), 2.31 (m, 1 H), 2.04 (m, 1 H), 1.91 (ddd, } J = 13.0, 13.0, 6.1 \text{ Hz, 1 H), 1.56 (s, 3 H), 1.37 (dd, } J = 13.0, 6.0 \text{ Hz, 1 H), 1.15 (s, 3 H), 0.68 (s, 3 H) \text{ ppm; } ^{13}\text{C NMR (C}_6\text{D}_6, 151 \text{ MHz}) \delta = 196.9, 185.4, 180.3, 168.6, 166.5, 161.0, 158.9, 149.2, 137.9, 135.7, 132.4, 128.7, 128.49, 128.45, 127.6, 127.0, 122.0, 121.0, 108.92, 108.88, 106.2, 95.5, 78.6, 75.4, 72.3, 59.3, 55.8, 54.8, 42.7, 42.6, 38.6, 34.4, 26.0, 24.5, 23.5, 22.8, 21.5 \text{ ppm; HRMS (ESI) calcd for C}_{39}\text{H}_{39}\text{NO}_{9}\text{H}^+ [M+H^+] 666.2697, found 666.2685.}

**5-epi-140**: $R_f = 0.7$ (silica gel, acetone:toluene 1:4); FT-IR (neat) $\nu_{\text{max}} = 3443, 2925, 2845, 1709, 1593, 1514, 1485, 1451, 1405, 1345, 1317, 1259, 1215, 1138, 1086, 994 \text{ cm}^{-1}$; 
$^1\text{H NMR (C}_6\text{D}_6, 600 \text{ MHz, 298 K}) \delta = 15.31 \text{ (s, 1 H), 7.33 – 7.31 (m, 2 H), 7.09 – 7.07 (m, 2 H), 7.03 (m, 1 H), 6.10 (s, 1 H), 5.60 (bs, 1 H), 5.23 (d, } J = 12.0 \text{ Hz, 1 H, AB system), 5.09 (d, } J = 12.0 \text{ Hz, 1 H,}}$
AB system, 4.94 (bs, 1 H), 4.71 (bs, 1 H), 3.44 (s, 3 H), 3.39 – 3.33 (m, 2 H), 3.24 (s, 3 H), 2.90 (bs, 3 H), 2.60 – 2.55 (m, 2 H), 2.34 (m, 1 H), 2.27 (m, 1 H), 2.10 – 1.98 (m, 2 H), 1.81 (s, 3 H), 1.38 (dd, \( J = 12.9, 6.2 \) Hz, 1 H), 1.13 (s, 3 H), 0.59 (s, 3 H) ppm; \(^{13}\)C NMR (C\(_6\)D\(_6\), 151 MHz, 298 K)* \( \delta = 167.6, 161.0, 159.0, 138.1, 135.8, 132.4, 128.7, 128.6, 128.5, 127.6, 126.4, 122.0, 121.1, 108.8, 108.6, 106.7, 95.3, 72.4, 59.1, 56.3, 55.8, 54.7, 38.5, 34.4, 26.0, 24.3, 23.5, 21.5 ppm; HRMS (ESI) calcd for C\(_{39}\)H\(_{39}\)NO\(_9\)H\(^{+}\) \([M+H^{+}]\) 666.2697, found 666.2686.

*Due to signal broadening, not all the \(^{13}\)C signals could be identified.

**Table S4.** Conditions screened for the benzylic methyl ether elimination (140 or 5-epi-140→141, see Scheme 24 in the article).

| entry | isomer | conditions | observation |
|-------|--------|------------|-------------|
| 1     | 140    | TsOH, 75 °C | 143 (54%)   |
| 2\([27]\) |        | TFA, 0 °C   | complex mixture |
| 3     |        | ZnBr\(_2\), 25 °C | decomposition |
| 4\([28]\) |        | HFIP, 25→50 °C | n.r.o. |
| 5\([29]\) |        | KI, DMSO, 75 °C | partial decomposition |
| 6     |        | Super-hydride, THF, –78 °C | decomposition |
| 7     |        | AlBr\(_3\), EtSH, CH\(_2\)Cl\(_2\), 0 °C | lactone formation involving C12a-OH |
| 8     |        | TMSI, py, CHCl\(_3\), 25 °C | decomposition |
| 9     |        | L-Selectride, THF, 25 °C | 143\(^a\) and r.s.m |
| 10    | 5-epi-140 | TsOH, 50 °C | n.r.o. |
| 11\([22]\) |        | BF\(_3\)•OEt\(_2\), 25 °C | unstable adduct tentatively formed |
| 12\([30]\) |        | BBr\(_3\), –78→25 °C | decomposition |
| 13    |        | NaH, THF, 0 °C | decomposition |
| 14\([31]\) |        | AlCl\(_3\), CH\(_2\)Cl\(_2\), 60 °C | decomposition |
| 15    |        | AlCl\(_3\), NaI, MeCN, 0→25 °C | decomposition |
| 16\([32]\) |        | InCl\(_3\), MeCN, 25 °C | unstable adduct tentatively formed |
| 17\([23]\) |        | Al\(_i\)Bu\(_3\), CH\(_2\)Cl\(_2\), 25 °C | n.r.o. |
| 18    |        | TMSOTf, Et\(_3\)N, CH\(_2\)Cl\(_2\), 25 °C | 143\(^a\) |
| 19    |        | \(t\)Bu-py\(\cdot\)PF\(_6\), TsOH, 120 °C | 143\(^a\) |
| 20    |        | DBU, THF, 25 °C | lactone formation involving C12a-OH |
| 21    |        | SiO\(_2\), THF, 25 °C | n.r.o. |
| 22\([28]\) |        | TFE, 75 °C | 144 (70%) |
| 23\([33]\) |        | Amberlyst 15, 80 °C | n.r.o. |
| 24\([34]\) |        | FeCl\(_3\), 25 °C | decomposition |
| 25    |        | MgBr\(_2\), 90 °C | partial decomposition |
| 26    |        | PPTS, 65 °C | n.r.o. |
| 27    |        | Sc(OTf)\(_3\), CH\(_2\)Cl\(_2\), 25→50 °C | 143\(^a\) |

n.r.o. = no reaction observed; \(^a\)as evidenced from TLC or \(^1\)H NMR analysis
**Compound 143**: To a solution of 140 (3.7 mg, 5.6 µmol, 1.0 equiv) in toluene (1 mL) at room temperature was added TsOH•H₂O (1 small crystal). The reaction mixture was stirred at this temperature for 1.5 hours, and no reaction was observed at this point. The mixture was then gradually warmed to 75 °C. Upon stirring at that temperature for 10 minutes, a strong red color evolved. The mixture was allowed to cool to room temperature, and the reaction was quenched by the addition of aq. pH 7.4 buffer solution (1 mL). The layers were separated, and the organic phase was concentrated and purified by preparative TLC (silica gel, 20% acetone:toluene) to yield elimination product 143 (2 mg, 3 µmol, 54%) as a red solid. 143: Rᵥ = 0.7 (silica gel, acetone:toluene 1:4); FT-IR (neat) νmax = 2922, 2845, 1623, 1591, 1456, 1413, 1328, 1270, 1219, 1150, 1028, 869, 733 cm⁻¹; ¹H NMR (CDCl₃, 600 MHz) δ = 12.29 (s, 1 H), 7.59 – 7.57 (m, 3 H), 7.44 – 7.42 (m, 2 H), 7.36 (m, 1 H), 7.22 (s, 1 H), 7.10 (s, 1 H), 6.40 (s, 1 H), 5.76 (bs, 1 H), 5.53 (s, 2 H), 4.09 (s, 3 H), 3.94 (s, 3 H), 2.32 – 2.26 (m, 2 H), 1.91 (ddd, J = 12.8, 6.2, 6.2 Hz, 1 H), 1.67 (ddd, J = 12.8, 6.9, 6.9 Hz, 1 H), 1.17 (s, 3 H), 0.90 (s, 3 H), 0.88 (s, 3 H) ppm; ¹³C NMR (CDCl₃, 151 MHz) δ = 186.5, 173.0, 166.7, 165.8, 162.7, 161.2, 157.2, 151.3, 144.8, 140.2, 135.8, 133.8, 130.8, 128.76, 128.75, 128.6, 128.3, 125.5, 124.6, 113.0, 109.6, 107.7, 107.2, 101.6, 96.3, 93.8, 72.3, 67.3, 56.5, 55.6, 37.3, 35.9, 27.1, 26.8, 23.2, 19.8 ppm; HRMS (ESI) calcd for C₃₈H₃₃NO₇H⁺ [M+H⁺] 616.2330, found 616.2333.
Trifluoroethyl ester 144: 5-epi-140 (8 mg, 0.01 mmol, 1.0 equiv) was dissolved in trifluoroethanol (1 mL) and heated to 70 °C for 2 hours. The solution was then allowed to cool to room temperature and concentrated. Purification of the residue by preparative TLC (silica gel, 10% acetone:CH₂Cl₂) provided the trifluoroethyl ester 144 (5 mg, 0.007 mmol, 70%). 144: R<sub>f</sub> = 0.3 (silica gel, EtOAc:CH₂Cl₂ 1:9); FT-IR (neat) ν<sub>max</sub> = 3503, 2962, 2924, 2845, 1736, 1594, 1514, 1466, 1405, 1345, 1302, 1272, 1215, 1181, 1110, 734, 696 cm⁻¹; <sup>1</sup>H NMR (C<sub>₆</sub>D<sub>₆</sub>, 600 MHz) δ = 15.17 (s, 1 H), 7.35 – 7.33 (m, 2 H), 7.16 – 7.13 (m, 2 H), 7.06 (m, 1 H), 6.11 (s, 1 H), 5.59 (bs, 1 H), 5.21 (s, 2 H), 4.72 (d, J = 11.5 Hz, 1 H), 4.50 (d, J = 2.0 Hz, 1 H), 4.06 (q, J = 8.5 Hz, 2 H), 3.78 (dd, J = 15.2, 5.5 Hz, 1 H), 3.49 – 3.43 (m, 5 H), 3.40 (s, 1 H), 3.25 (s, 3 H), 3.05 (d, J = 16.8 Hz, 1 H), 2.96 (s, 3 H), 2.69 (dddd, J = 11.5, 7.9, 5.6, 2.0 Hz, 1 H), 2.28 (m, 1 H), 2.01 (m, 1 H), 1.81 (ddd, J = 12.9, 12.9, 6.4 Hz, 1 H), 1.74 (s, 3 H), 1.28 (dd, J = 12.9, 6.1 Hz, 1 H), 1.08 (s, 3 H), 0.54 (s, 3 H) ppm; <sup>1</sup>C NMR (C<sub>₆</sub>D<sub>₆</sub>, 151 MHz) δ = 202.1, 180.9, 169.4, 166.8, 161.0, 159.5, 158.7, 148.0, 137.6, 136.2, 132.2, 128.6, 128.4, 128.0, 127.4, 123.7 (q, J<sub>C-F</sub> = 277.7 Hz), 122.3, 121.5, 109.3, 108.0, 100.1, 95.6, 75.7, 71.9, 71.8, 59.8 (q, J<sub>C-F</sub> = 36.3 Hz), 59.3, 57.0, 55.8, 54.8, 45.6, 42.5, 38.6, 34.2, 28.4, 25.9, 24.2, 23.4, 21.5 ppm; HRMS (ESI) calcd for C₄₁H₄₂F₃NO₁₀H⁺ [M+H⁺] 766.2833, found 766.2835.
Phenyl Selenide 149: The starting material 133 (55 mg, 0.079 mmol, 1.0 equiv) was azeotropically dried with toluene (2 × 1 mL) before it was dissolved in THF (0.8 mL) and cooled to –78 °C. KHMDS (0.5 M in toluene, 0.55 mL, 0.26 mmol, 3.3 equiv) was added dropwise, and the mixture was stirred for 1 hour. Then, a solution of PhSeCl (52.6 mg, 0.275 mmol, 3.5 equiv) in THF (0.6 mL) was slowly added, and the mixture was allowed to warm to –40 °C over 1 hour. Then, the reaction was quenched with MeOH (0.2 mL), stirred for 5 minutes at –40 °C, and treated with saturated aq. NH₄Cl solution (2 mL). After warming to room temperature, the mixture was extracted with CH₂Cl₂ (3 × 5 mL). The combined organic layers were dried over MgSO₄, filtered, and concentrated. Purification by preparative TLC (silica gel, 50% EtOAc:hexanes) yielded selenide 149 (31.1 mg, 36.6 µmol, 46%, 62% brsm) and recovered starting material 133 (14.1 mg, 20.3 µmol, 26%). 149: Rᶠ = 0.6 (silica gel, acetone:toluene 1:19); FT-IR (neat) ν_max = 3461, 2938, 2839, 1713, 1607, 1591, 1476, 1404, 1344, 1300, 1211, 1182, 1142, 1109, 1046, 1000, 914, 886, 739, 694 cm⁻¹; ¹H NMR (C₆D₆, 600 MHz) δ = 15.90 (s, 1 H), 7.90 – 7.88 (m, 2 H), 7.23 – 7.21 (m, 2 H), 7.09 – 6.97 (m, 6 H), 6.14 (s, 1 H), 5.51 (bs, 1 H), 5.17 (d, J = 12.1 Hz, 1 H, AB system), 5.08 (d, J = 12.1 Hz, 1 H, AB system), 4.97 (s, 1 H), 4.74 (s, 1 H), 3.64 (s, 1 H), 3.46 (s, 3 H), 3.36 (d, J = 18.5 Hz, 1 H), 3.26 (s, 3 H), 3.02 (d, J = 18.5 Hz, 1 H), 2.95 (s, 3 H), 2.64 (s, 3 H), 2.31 (m, 1 H), 2.03 (m, 1 H), 1.77 (m, 1 H), 1.53 (s, 3 H), 1.36 (m, 1 H), 1.17 (s, 3 H), 0.57 (s, 3 H) ppm; ¹³C NMR (C₆D₆, 151 MHz)* δ = 197.4, 184.0, 181.9, 168.9, 168.5, 161.2, 159.2, 148.5, 137.8, 136.0, 134.8, 132.7, 131.9, 129.7, 128.6,
128.4, 124.7, 122.4, 121.0, 109.41, 109.37, 104.7, 102.1, 95.8, 78.1, 72.2, 58.4, 55.8, 55.3, 54.8, 52.9, 50.4, 45.2, 38.5, 34.4, 31.8, 26.2, 25.0, 23.4, 21.3 ppm; HRMS (ESI) calcd for C_{46}H_{45}NO_{10}SeH^+ [M+H^+] 852.2281, found 852.2242.

*Due to overlap with the NMR solvent, not all the $^{13}$C signals could be identified.

Lactone 152: To a solution of phenyl selenide 149 (5 mg, 6 µmol, 1.0 equiv) in THF (1 mL) at −78 °C was added DMDO (73 µL of ~0.08 M solution, 6 µmol, 1.0 equiv) and the mixture was stirred for 20 minutes at that temperature. The reaction was then quenched with DMS (50 µL, 0.68 mmol), and the mixture was allowed to warm to room temperature over 3 hours and concentrated. Purification by preparative TLC (silica gel, 5% acetone:toluene) gave the title compound (1.9 mg, 2.7 µmol, 46%) as yellow solid. 152: R$_f$ = 0.7 (silica gel, acetone:toluene 1:19); FT-IR (neat) $\nu_{\text{max}}$ = 2920, 2840, 1593, 1534, 1474, 1433, 1416, 1362, 1342, 1215, 1176, 1144, 1059, 1011, 923 cm$^{-1}$; $^1$H NMR (C$_6$D$_6$, 600 MHz) $\delta$ = 15.40 (s, 1 H), 7.83 (s, 1 H), 7.32 – 7.29 (m, 2 H), 7.12 – 7.08 (m, 2 H), 7.05 (m, 1 H), 6.20 (s, 1 H), 5.88 (s, 1 H), 5.64 (s, 1 H), 5.24 (s, 2 H), 3.88 (d, $J$ = 18.2 Hz, 1 H), 3.47 (s, 3 H), 3.38 (d, $J$ = 18.2 Hz, 1 H), 3.27 (s, 3 H), 3.12 (s, 3 H), 2.82 (s, 3 H), 2.33 (m, 1 H), 2.11 – 2.01 (m, 2 H), 1.81 (s, 3 H), 1.34 (m, 1 H), 1.15 (s, 3 H), 0.68 (s, 3 H) ppm; $^{13}$C NMR (C$_6$D$_6$, 151 MHz) $\delta$ = 191.9, 165.8, 165.4, 161.0, 160.5, 158.3, 147.5, 141.4, 137.9, 136.1, 133.84, 133.79, 133.3, 128.7, 128.6, 128.5, 125.7, 123.0, 121.4, 117.0, 113.1, 109.7, 107.0, 102.3, 96.3, 72.3, 58.7, 56.0, 54.8, 50.3, 49.9, 45.6, 38.7, 34.4,
26.0, 24.4, 23.5, 21.5 ppm; HRMS (ESI) calcd for C_{40}H_{39}NO_{10}H^+ [M+H^+] 694.2647, found 694.2631.

**TMS Phenyl Selenide 154**: To a solution of alcohol 149 (28 mg, 0.033 mmol, 1.0 equiv) in CH₂Cl₂ (3 mL) at 0 °C were added Et₃N (0.18 mL, 1.3 mmol, 40 equiv) and freshly distilled TMSOTf (0.18 mL, 0.99 mmol, 30 equiv). After stirring for 5 minutes, the reaction was quenched with aq. pH 7.4 buffer solution (3 mL) and allowed to warm to room temperature. The layers were separated, and the organic phase was dried over Na₂SO₄, filtered, and concentrated. The residue was purified by preparative TLC (silica gel, 5% acetone:toluene) to give the silylated alcohol 154 (18.9 mg, 0.0205 mmol, 62%). 154: \( R_f = 0.7 \) (silica gel, acetone:toluene 1:19); FT-IR (neat) \( \nu_{\text{max}} = 2941, 2914, 2838, 1717, 1609, 1591, 1509, 1475, 1404, 1342, 1296, 1250, 1210, 1180, 1140, 1064, 1054, 1032, 1003, 987, 888, 875, 841, 812, 736, 692 \text{ cm}^{-1}; \)

\(^1\)H NMR (C₆D₆, 600 MHz) \( \delta = 16.46 \) (s, 1 H), 7.90 – 7.88 (m, 2 H), 7.27 – 7.24 (m, 2 H), 7.07 – 7.02 (m, 5 H), 6.99 (m, 1 H), 6.16 (s, 1 H), 5.51 (bs, 1 H), 5.26 (d, \( J = 12.2 \) Hz, 1 H, AB system), 5.10 (d, \( J = 12.2 \) Hz, 1 H, AB system), 4.98 (s, 1 H), 3.85 (s, 1 H), 3.46 (s, 3 H), 3.35 (d, \( J = 18.5 \) Hz, 1 H), 3.27 (s, 3 H), 3.02 (d, \( J = 18.5 \) Hz, 1 H), 2.96 (s, 3 H), 2.62 (s, 3 H), 2.30 (m, 1 H), 2.02 (m, 1 H), 1.76 (ddd, \( J = 12.6, 12.6, 6.2 \) Hz, 1 H), 1.53 (s, 3 H), 1.34 (dd, \( J = 12.6, 6.2 \) Hz, 1 H), 1.18 (s, 3 H), 0.57 (s, 3 H), 0.54 (s, 9 H) ppm; \(^{13}\)C NMR (C₆D₆, 151 MHz)* \( \delta = 197.9, 184.9, 182.2, 168.8, 168.7, 161.2, 159.0, 148.3, 138.0, 136.0, 134.5, 133.2, 131.6, 129.7,
128.6, 128.3, 124.5, 120.9, 109.9, 109.8, 104.8, 102.4, 95.9, 81.8, 72.1, 58.4, 58.3, 55.9, 
54.8, 52.9, 50.5, 45.4, 38.5, 34.4, 32.0, 26.3, 25.1, 23.4, 21.4, 3.0 ppm; HRMS (ESI) calcd for 
C_{49}H_{53}NO_{10}SeSiH^+ [M+H^+] 924.2677, found 924.2684.

*Due to overlap with the NMR solvent, not all the $^{13}$C signals could be identified.

**Triketone 155:** To a solution of substrate 149 (20.4 mg, 0.0240 mmol, 1.0 equiv) in CH$_2$Cl$_2$
(0.8 mL) at 0 °C was added TFA (0.4 mL), and the mixture was stirred at 0 °C for 40 minutes.
Then, water (2 mL) was added, and the aqueous phase was extracted with CH$_2$Cl$_2$ (3 x 5 mL).
The combined organic phases were dried over MgSO$_4$, filtered, and concentrated. Purification of
the residue by preparative TLC (silica gel, 50% EtOAc:hexanes) afforded triketone 155
(10.0 mg, 0.0124 mmol, 52%). 155: R$_f$ = 0.33 (silica gel, EtOAc:hexanes 1:1); FT-IR (neat) $\nu_{\max}$
= 3434, 2921, 1701, 1587, 1513, 1475, 1400, 1343, 1327, 1216, 1170, 1135, 1107, 1037, 823,
739, 693 cm$^{-1}$; $^1$H NMR (C$_6$D$_6$, 600 MHz) $\delta$ = 14.49 (s, 1 H), 7.85 – 7.81 (m, 2 H), 7.09 – 6.92
(m, 8 H), 6.11 (s, 1 H), 5.52 (bs, 1 H), 5.46 (bs, 1 H), 4.95 (s, 1 H), 4.89 (d, $J$ = 12.1 Hz, 1 H, AB
system), 4.79 (d, $J$ = 12.1 Hz, 1 H, AB system), 3.96 (d, $J$ = 19.8 Hz, 1 H), 3.60 (s, 1 H), 3.39 (s,
3 H), 3.31 (d, $J$ = 19.8 Hz, 1 H), 3.15 (s, 3 H), 2.19 (m, 1 H), 1.92 (m, 1 H), 1.83 (m, 1 H), 1.43
(s, 3 H), 1.23 (m, 1 H), 1.04 (s, 3 H), 0.47 (s, 3 H) ppm; $^{13}$C NMR (C$_6$D$_6$, 151 MHz)* $\delta$ = 195.9,
191.1, 183.6, 182.8, 168.5, 165.3, 161.0, 159.5, 148.0, 142.1, 136.6, 135.6, 134.8, 131.7, 129.8,
126.2, 122.1, 121.7, 110.5, 108.5, 104.1, 97.9, 79.4, 72.1, 60.1, 59.8, 55.9, 54.8, 45.8, 38.6, 34.2,
31.9, 25.6, 24.3, 23.2, 21.1 ppm; HRMS (ESI) calcd for C_{38}H_{34}NO_{9}^{+} [M–PhSe\textsuperscript{-}] 648.2228, found 648.2218.

*Due to overlap with the NMR solvent, not all the $^{13}$C signals could be identified.

**Lactone 158:** To a solution of intermediate 155 (8.8 mg, 0.011 mmol, 1.0 equiv) in CH$_2$Cl$_2$ (1.5 mL) at 0 °C was added H$_2$O$_2$ solution (30% in water, 0.05 mL, 0.06 g solution, 0.02 g H$_2$O$_2$, 0.05 mmol H$_2$O$_2$, 4.5 equiv) and the mixture was stirred for 10 minutes. Then, the mixture was diluted with water (2 mL) and extracted with CH$_2$Cl$_2$ (3 × 5 mL). The combined organic phases were dried over MgSO$_4$ and concentrated. Purification by preparative TLC (silica gel, 50% EtOAc:hexanes) afforded lactone 158 (2.5 mg, 3.9 µmol, 35%). 158: $R_f = 0.33$ (silica gel, EtOAc:hexanes 1:1); FT-IR (neat) $\nu_{\text{max}} = 3376, 2921, 1623, 1597, 1534, 1470, 1430, 1362, 1342, 1302, 1259, 1210, 1186, 1142, 1130, 1097, 1049, 1008, 909, 821, 740, 696 \text{ cm}^{-1}$; $^1$H NMR (CD$_2$Cl$_2$, 600 MHz) $\delta = 13.00$ (s, 1 H), 7.54 (d, $J = 7.4$ Hz, 2 H), 7.46 – 7.37 (m, 3 H), 7.09 (s, 1 H), 6.74 (s, 1 H), 5.54 (bs, 1 H), 5.46 (s, 2 H), 4.06 (s, 3 H), 3.93 (s, 3 H), 3.59 (d, $J = 19.3$ Hz, 1 H), 3.15 (d, $J = 19.3$ Hz, 1 H), 2.24 (m, 1 H), 2.08 (m, 1 H), 1.88 (m, 1 H), 1.51 (s, 3 H), 1.35 (m, 1 H), 0.92 (s, 3 H), 0.34 (s, 3 H) ppm; $^{13}$C NMR (CD$_2$Cl$_2$, 151 MHz) $\delta = 191.7, 171.3, 167.2, 166.3, 162.9, 160.0, 159.9, 146.8, 143.0, 141.2, 138.0, 136.7, 135.8, 131.5, 129.1, 129.0, 128.8, 127.4, 126.1, 121.9, 109.4, 106.5, 99.7, 99.5, 98.3, 72.9, 59.1, 57.0, 55.9, 45.8, 38.7, 34.3, 25.5, 24.1, 23.2, 20.9 ppm; HRMS (ESI) calcd for C$_{38}$H$_{33}$NO$_9$H$^+$ [M+H$^+$] 648.2228, found 648.2220.
Iodide 159: To a stirred solution of intermediate 133 (6.8 mg, 9.8 µmol, 1.0 equiv) in THF (0.3 mL) at –78 °C was added KHMDS (0.5 M in toluene, 0.07 mL, 0.004 mmol, 3.6 equiv), and the reaction mixture was stirred for 80 minutes. Then, a solution of NIS (7.7 mg, 34 µmol, 3.5 equiv) in THF (100 µL) was added, and the mixture was allowed to warm to –35 °C over 1 hour. Then, the reaction was quenched with MeOH (0.1 mL), followed by a mixture of saturated aq. NH₄Cl:saturated aq. Na₂S₂O₃ (3 mL, 1:1). The resulting mixture was extracted with CH₂Cl₂ (3 × 10 mL), and the combined organic phases were dried over MgSO₄, filtered, and concentrated. Purification by preparative TLC (silica gel, 50% EtOAc:hexanes) afforded iodide 159 (3.0 mg, 3.7 µmol, 37%). 159: Rf = 0.58 (silica gel, EtOAc:hexanes 1:1); FT-IR (neat) vmax = 3461, 2920, 1716, 1591, 1512, 1474, 1404, 1344, 1322, 1291, 1210, 1183, 1139, 1112, 1046, 998, 912, 734 cm⁻¹; ¹H NMR (CDCl₃, 600 MHz) δ = 15.27 (s, 1 H), 7.47 – 7.44 (m, 2 H), 7.38 – 7.30 (m, 3 H), 6.62 (s, 1 H), 5.87 (bs, 1 H), 5.47 (bs, 1 H), 5.38 (d, J = 11.9 Hz, 1 H, AB system), 5.31 (d, J = 11.9 Hz, 1 H, AB system), 4.83 (s, 1 H), 4.08 (s, 3 H), 3.92 (s, 3 H), 3.77 (s, 1 H), 3.53 (s, 3 H), 3.45 (d, J = 18.6 Hz, 1 H), 3.01 (d, J = 18.6 Hz, 1 H), 2.89 (s, 3 H), 2.23 (m, 1 H), 2.05 (m, 1 H), 1.80 (m, 1 H), 1.41 (s, 3 H), 1.24 (m, 1 H), 0.94 (s, 3 H), 0.48 (s, 3 H) ppm; ¹³C NMR (CDCl₃, 151 MHz) δ = 195.5, 183.9, 178.5, 168.4, 167.8, 160.6, 159.6, 148.2, 137.1, 135.2, 133.0, 128.64, 128.60, 128.2, 123.17, 122.8, 121.1, 108.5, 108.3, 104.5, 102.6, 96.1, 78.3, 72.3,
58.3, 56.7, 56.2, 55.5, 53.5, 50.7, 44.8, 38.4, 34.2, 32.1, 25.8, 24.7, 23.0, 21.0 ppm; HRMS (ESI) calcd for C$_{40}$H$_{40}$INO$_{10}$Na$^+$ [M+Na$^+$] 844.1589, found 844.1599.

C$_4$-alcohol 160: To a stirred solution of intermediate 133 (12.8 mg, 18.4 µmol, 1.0 equiv) in THF (0.36 mL) at –78 °C was added KHMDS (0.5 M in toluene, 0.13 mL, 0.07 mmol, 3.8 equiv), and the mixture was stirred for 1 hour. A solution of Davis oxaziridine$^{[35]}$ (16.8 mg, 64.3 µmol, 3.5 equiv) in THF (0.1 mL) was added, and the mixture was allowed to warm to –40 °C over 1 hour. Then, the reaction was quenched with MeOH (0.05 mL) followed by saturated aq. NH$_4$Cl solution (2 mL). The mixture was extracted with CH$_2$Cl$_2$ (3 × 5 mL), and the combined organic phases were dried over MgSO$_4$, filtered, and concentrated. Purification by preparative TLC (silica gel, 50% EtOAc:hexanes) afforded the intermediate alcohol (6.8 mg, 9.6 µmol, 52%). This material was dissolved in CH$_2$Cl$_2$ (0.3 mL) and TFA (0.1 mL) was added at 0 °C. The mixture was stirred at this temperature for 30 minutes and then was allowed to warm to room temperature and stirred for another 15 minutes. Then H$_2$O (3 mL) was added, the phases were separated, and the aqueous phase was extracted with CH$_2$Cl$_2$ (3 × 5 mL). The combined organic phases were dried over MgSO$_4$, filtered, and concentrated. Purification by preparative TLC (silica gel, 10% acetone:toluene) yielded triketone 160 (4.0 mg, 6.0 µmol, 63%). 160: R$_f$ = 0.22 (silica gel, acetone:toluene 1:9); FT-IR (neat) $\nu_{\text{max}}$ = 3417, 2924, 1708, 1587, 1514, 1473, 1400, 1343, 1289, 1218, 1189, 1065, 1048, 858, 732 cm$^{-1}$; $^1$H NMR (CDCl$_3$,
δ = 13.83 (s, 1 H), 7.42 – 7.39 (m, 2 H), 7.35 – 7.30 (m, 3 H), 6.73 (s, 1 H), 5.71 (dd, J = 11.8, 2.0 Hz, 1 H), 5.49 (bs, 1 H), 5.32 (d, J = 11.9 Hz, AB system, 1 H), 5.293 (d, J = 11.9 Hz, AB system, 1 H), 5.289 (s, 1 H), 4.09 (s, 3 H), 3.99 (d, J = 2.0 Hz, 1 H), 3.94 (s, 3 H), 3.80 (d, J = 11.8 Hz, 1 H), 3.62 (d, J = 20.3 Hz, 1 H), 3.10 (d, J = 20.3 Hz, 1 H), 2.19 (m, 1 H), 2.03 (m, 1 H), 1.79 (m, 1 H), 1.45 (s, 3 H), 1.29 (m, 1 H), 0.89 (s, 3 H), 0.29 (s, 3 H) ppm; $^{13}$C NMR (CDCl$_3$, 151 MHz) δ = 193.9, 190.2, 183.9, 180.2, 167.9, 164.7, 160.4, 159.9, 147.8, 143.3, 136.0, 134.9, 128.8, 128.7, 128.4, 127.1, 121.6, 121.3, 109.5, 107.6, 105.0, 98.2, 79.4, 72.7, 61.4, 59.7, 58.4, 56.8, 55.6, 45.5, 38.5, 34.0, 25.4, 24.3, 22.9, 20.9 ppm; HRMS (ESI) calcd for C$_{38}$H$_{35}$NO$_{10}$H$^+$ [M+H$^+$] 666.2334, found 666.2333.

**Diol 164:** Triketone 137 (99 mg, 0.15 mmol, 1.0 equiv) was dissolved in anhydrous EtOAc:acetone (1:1, 16 mL) and sodium triacetoxyborohydride (39 mg, 0.18 mmol, 1.2 equiv) was added. The reaction mixture was heated to 40 °C for 3.5 hours and was allowed to cool to room temperature and diluted with water (30 mL) and EtOAc (30 mL). The layers were separated, and the organic phase was washed with water (30 mL) and brine (30 mL), dried over Na$_2$SO$_4$, filtered, and concentrated. The residue was purified by flash column chromatography (5→10% acetone:toluene) to give product 164 (53 mg, 0.082 mmol, 53%) 164: R$_f$ = 0.5 (silica gel, acetone:toluene 1:4); FT-IR (neat) $\nu_{max}$ = 3498, 3179, 2927, 2855, 1651, 1574, 1452, 1403, 1352, 1257, 1216, 1170, 1148, 1087, 1019, 950, 897, 844, 830, 811, 741, 682, 661 cm$^{-1}$; $^1$H NMR (CDCl$_3$, 600 MHz) δ = 14.51 (s, 1 H), 7.40 – 7.31 (m, 5 H), 6.69 (s, 1 H), 5.49 (bs, 1 H),
5.27 (d, \( J = 11.7 \) Hz, 1 H, AB system), 5.23 (d, \( J = 11.7 \) Hz, 1 H, AB system), 4.59 (d, \( J = 4.1 \) Hz, 1 H), 4.15 (s, 1 H), 4.09 (s, 3 H), 3.93 (s, 3 H), 3.83 (d, \( J = 17.7 \) Hz, 1 H), 3.66 (d, \( J = 6.6 \) Hz, 1 H), 3.54 (d, \( J = 19.6 \) Hz, 1 H), 3.24 (d, \( J = 19.6 \) Hz, 1 H), 2.92 (dd, \( J = 17.7, 6.6 \) Hz, 1 H), 2.19 (m, 1 H), 2.04 (m, 1 H), 1.82 (ddd, \( J = 12.7, 12.7, 6.1 \) Hz, 1 H), 1.68 (d, \( J = 4.1 \) Hz, 1 H), 1.48 (s, 3 H), 1.29 (dd, \( J = 12.7, 6.1 \) Hz, 1 H), 0.89 (s, 3 H), 0.31 (s, 3 H) ppm; \(^{13}\)C NMR (CDCl\(_3\), 151 MHz) \( \delta = 201.1, 192.9, 169.6, 169.3, 164.7, 160.4, 159.6, 148.0, 138.9, 136.4, 135.7, 128.70, 128.69, 128.5, 126.2, 124.2, 121.5, 109.9, 109.3, 103.8, 97.4, 77.1, 71.8, 68.5, 59.6, 56.7, 55.6, 50.5, 44.9, 38.5, 34.0, 25.5, 24.2, 23.0, 21.0, 18.7 ppm; HRMS (ESI) calcd for C\(_{38}\)H\(_{37}\)NO\(_{9}\)H\(^{+}\)\([M+H^{+}]\) 652.2541, found 652.2535.

**TBS ether 165:** To a solution of diol 164 (43 mg, 0.066 mmol, 1.0 equiv) in 1,2-dichloroethane (2.1 mL) was added freshly distilled 2,6-lutidine (0.12 mL, 1.0 mmol, 15 equiv). The reaction mixture was cooled to 5 °C, and freshly distilled TBSOTf (0.15 mL, 0.67 mmol, 10 equiv) was added. The reaction mixture was allowed to warm to room temperature and stirred for 20 minutes. Three additional portions of 2,6-lutidine (2 \( \times \) 0.12 mL, then 1 \( \times \) 0.06 mL) and TBSOTf (2 \( \times \) 0.15 mL, then 1 \( \times \) 0.08 mL) were added to the reaction flask in 20 minute intervals, and the mixture was stirred for an additional 30 minutes. The reaction was then quenched with saturated aq. NaHCO\(_3\) solution (5 mL) (vigorous bubbling) and extracted with CH\(_2\)Cl\(_2\) (2 \( \times \) 5 mL). The combined organics were dried over Na\(_2\)SO\(_4\), filtered, and concentrated. Residual volatiles were then azeotropically removed with toluene (twice). The crude material was then purified by
preparative TLC (silica gel, 10% acetone:toluene) to give the TBS ether 165 (32 mg, 0.042 mmol, 64%) as a yellow solid. 165: Rf = 0.53 (silica gel, acetone:toluene 1:9); FT-IR (neat) νmax = 3474, 2951, 2856, 1697, 1605, 1588, 1472, 1402, 1342, 1296, 1215, 1134, 1081, 912, 838, 779, 734 cm⁻¹; ¹H NMR (CDCl₃, 600 MHz) δ = 14.65 (s, 1 H), 7.42 – 7.40 (m, 2 H), 7.38 – 7.32 (m, 3 H), 6.69 (s, 1 H), 5.50 (s, 1 H), 5.29 (d, J = 11.3 Hz, 1 H, AB system), 5.22 (d, J = 11.3 Hz, 1 H, AB system), 4.55 (s, 1 H), 4.09 (s, 3 H), 3.99 (s, 1 H), 3.93 (s, 3 H), 3.92 (d, J = 18.0 Hz, 1 H), 3.59 (d, J = 7.6 Hz, 1 H), 3.56 (d, J = 19.8 Hz, 1 H), 3.21 (d, J = 19.8 Hz, 1 H), 2.87 (dd, J = 18.0, 7.6 Hz, 1 H), 2.20 (m, 1 H), 2.03 (m, 1 H), 1.84 (m, 1 H), 1.46 (s, 3 H), 1.27 (m, 1 H), 0.90 (s, 3 H), 0.32 (s, 3 H), 0.30 (s, 9 H), −0.26 (s, 3 H), −0.55 (s, 3 H) ppm; ¹³C NMR (CDCl₃, 151 MHz) δ = 202.2, 191.8, 169.5, 169.4, 164.9, 160.3, 159.5, 148.0, 138.5, 136.5, 135.6, 128.9, 128.7, 128.6, 126.0, 124.5, 121.4, 110.3, 109.0, 104.5, 97.3, 77.8, 71.9, 69.1, 59.5, 56.8, 55.5, 50.2, 45.1, 38.5, 34.0, 25.5, 25.2, 24.2, 23.0, 20.8, 18.3, 17.6, −5.5 ppm; HRMS (ESI) calcd for C₄₄H₅₁NO₉SiH⁺ [M+H⁺] 766.3406, found 766.3414.

**Diol 167:** To a solution of TBS ether 165 (28.8 mg, 37.6 µmol, 1.0 equiv) in THF (0.38 mL) at −78 °C was added KHMDS (1.0 M in THF, 0.13 mL, 0.13 mmol, 3.5 equiv), and the mixture was stirred for 1 hour 5 minutes. A solution of Davis oxaziridine[^35] (40 mg, 0.15 mmol, 4.0 equiv) in THF (0.2 mL) was added, and stirring was continued for another 40 minutes. The reaction was then quenched by the sequential addition of MeOH (0.05 mL), dimethyl sulfide (0.1 mL, 1 mmol), and saturated aq. NH₄Cl solution (5 mL). The reaction mixture was allowed
to warm to room temperature and was extracted with CH$_2$Cl$_2$ (3 × 10 mL), and the combined organic phases were dried over MgSO$_4$, filtered, and concentrated. Purification by preparative TLC (silica gel, 10% acetone:toluene) afforded recovered starting material 165 (11.2 mg, 14.6 µmol, 39%) and product 167 (8.5 mg, 11 µmol, 29%, 47% brsm). 167: $R_f = 0.22$ (silica gel, acetone:toluene 1:9); FT-IR (neat) $\nu_{\text{max}} = 3443, 2928, 2857, 1702, 1607, 1589, 1472, 1401, 1342, 1322, 1265, 1217, 1186, 1135, 1052, 839$ cm$^{-1}$; $^1$H NMR (CDCl$_3$, 600 MHz) $\delta = 14.20$ (s, 1 H), 7.43 – 7.39 (m, 2 H), 7.38 – 7.32 (m, 3 H), 6.70 (s, 1 H), 5.50 (bs, 1 H), 5.28 (d, $J = 11.4$ Hz, 1 H, AB system), 5.20 (d, $J = 11.4$ Hz, 1 H, AB system), 4.61 (s, 1 H), 4.27 (s, 1 H), 4.14 (d, $J = 17.5$ Hz, 1 H), 4.08 (s, 3 H), 3.93 (s, 3 H), 3.54 (d, $J = 19.5$ Hz, 1 H), 3.22 (d, $J = 19.5$ Hz, 1 H), 2.99 (s, 1 H), 2.68 (d, $J = 17.5$, 1 H), 2.20 (m, 1 H), 2.03 (m, 1 H), 1.85 (m, 1 H), 1.47 (s, 3 H), 1.28 (m, 1 H), 0.90 (s, 3 H), 0.35 (s, 3 H), 0.31 (s, 9 H), −0.27 (s, 3 H), −0.56 (s, 3 H) ppm; $^{13}$C NMR (CDCl$_3$, 151 MHz) $\delta = 200.9$, 190.2, 169.6, 169.1, 164.1, 160.3, 159.4, 147.9, 140.4, 136.4, 135.4, 129.0, 128.8, 128.6, 126.0, 123.2, 121.5, 110.5, 109.1, 104.3, 97.5, 80.8, 77.5, 72.0, 68.5, 59.6, 56.8, 55.5, 44.9, 38.6, 34.0, 28.7, 25.4, 25.2, 24.2, 23.0, 20.9, 17.7, −5.3, −5.7 ppm; HRMS (ESI) calcd for C$_{44}$H$_{51}$NO$_{10}$SiH$^+$ [$M$+H$^+$] 782.3355, found 782.3357.

**Bis-TBS Ether 168**: To a solution of substrate 164 (13 mg, 0.020 mmol, 1.0 equiv) in CH$_2$Cl$_2$ (0.8 mL) at 0 °C was added iPr$_2$EtN (104 µL, 0.597 mmol, 30 equiv) followed by freshly distilled TBSOTf (91 µL, 0.40 mmol, 20 equiv). The reaction mixture was allowed to stir for 3
minutes at 0 °C and was then allowed to warm to room temperature and stirred for 30 additional minutes. The reaction was then quenched with saturated aq. NaHCO₃ solution (2 mL) and extracted with CH₂Cl₂ (2 × 4 mL). The combined organics were dried over Na₂SO₄, filtered, and concentrated. Purification by preparative TLC (silica gel, 10% EtOAc:toluene) afforded the bis-silylated product 168 (10 mg, 0.011 mmol, 57%) as a yellow solid. 168: Rf = 0.8 (silica gel, acetone:toluene 1:9); FT-IR (neat) νmax = 3416, 2929, 2857, 1696, 1663, 1594, 1509, 1472, 1463, 1373, 1341, 1250, 1209, 1183, 1166, 1139, 1081, 1065, 1050, 911, 831, 779, 734, 700 cm⁻¹; ¹H NMR (CDCl₃, 600 MHz) δ = 7.42 – 7.40 (m, 2 H), 7.37 – 7.31 (m, 3 H), 6.65 (s, 1 H), 5.49 (bs, 1 H), 5.28 (d, J = 11.4 Hz, 1 H, AB system), 5.22 (d, J = 11.4 Hz, 1 H, AB system), 4.55 (s, 1 H), 4.49 (s, 1 H), 3.96 (s, 3 H), 3.93 (d, J = 17.9 Hz, 1 H), 3.91 (s, 3 H), 3.58 (d, J = 19.6 Hz, 1 H), 3.46 (d, J = 7.6 Hz, 1 H), 3.32 (d, J = 19.6 Hz, 1 H), 2.85 (dd, J = 17.9, 7.6 Hz, 1 H), 2.20 (m, 1 H), 2.03 (m, 1 H), 1.86 (ddd, J = 12.3, 12.3, 6.2 Hz, 1 H), 1.50 (s, 3 H), 1.27 (m, 1 H), 1.18 (s, 9 H), 0.90 (s, 3 H), 0.29 (s, 9 H), 0.27 (s, 3 H), 0.05 (s, 3 H), 0.03 (s, 3 H), –0.31 (s, 3 H), –0.50 (s, 3 H) ppm; ¹³C NMR (CDCl₃, 151 MHz) δ = 197.2, 192.6, 169.8, 169.4, 158.9, 157.3, 155.7, 147.2, 140.3, 136.9, 135.6, 128.9, 128.62, 128.56, 127.2, 124.8, 121.1, 118.2, 114.3, 105.2, 97.4, 78.2, 71.8, 68.7, 59.0, 55.6, 55.4, 50.6, 45.9, 38.5, 33.9, 26.4, 25.5, 25.4, 24.2, 23.0, 21.0, 18.8, 18.7, 17.8, –3.0, –3.6, –5.0, –5.6 ppm; HRMS (ESI) calcd for C₅₀H₆₅NO₉Si₂H⁺ [M+H⁺] 880.4270, found 880.4265.
**Aromatized product 172:** To a solution of *bis*-TBS ether 168 (10 mg, 0.011 mmol, 1.0 equiv) in THF (0.36 mL) at −78 °C was added KHMDS (0.5 M in toluene, 0.06 mL, 0.03 mmol, 2.5 equiv). The reaction mixture instantly turned red and was stirred for 45 minutes. The reaction was quenched with MeOH (0.5 mL) followed by saturated aq. NH₄Cl solution (1 mL) and was then allowed to warm to room temperature. Water (2 mL) was added, and the mixture was extracted with EtOAc (2 × 2 mL). The combined organics were dried over Na₂SO₄, filtered, and concentrated. The crude residue was purified by preparative TLC (silica gel, 10% EtOAc:toluene) to give the aromatized product 172 (3 mg, 0.005 mmol, 43%) as a red-orange solid. 172: Rᵣ = 0.6 (silica gel, EtOAc:toluene 1:9); FT-IR (neat) νₓmax = 2956, 2937, 1660, 1625, 1595, 1538, 1474, 1433, 1410, 1336, 1281, 1211, 1190, 1132, 1075, 911 cm⁻¹; ¹H NMR (CDCl₃, 600 MHz) δ = 16.66 (s, 1 H), 8.83 (s, 1 H), 8.35 (s, 1 H), 7.56 – 7.54 (m, 2 H), 7.47 – 7.40 (m, 3 H), 6.74 (s, 1 H), 5.55 (bs, 1 H), 5.53 (s, 2 H), 4.13 (s, 3 H), 4.01 (d, J = 20.3 Hz, 1 H), 3.96 (s, 3 H), 3.33 (d, J = 20.3 Hz, 1 H), 2.24 (m, 1 H), 2.09 (m, 1 H), 1.94 (ddd, J = 12.5, 12.5, 6.3 Hz, 1 H), 1.51 (s, 3 H), 1.37 (dd, J = 12.5, 5.9 Hz, 1 H), 0.95 (s, 3 H), 0.40 (s, 3 H) ppm; ¹³C NMR (CDCl₃, 151 MHz) δ = 184.6, 182.8, 167.7, 167.0, 165.9, 160.5, 159.6, 147.8, 144.7, 136.7, 136.3, 135.1, 130.4, 129.0, 128.9, 128.6, 127.4, 122.3, 121.7, 121.6, 118.9, 110.2, 109.1, 108.7, 98.0, 72.7, 59.8, 56.8, 55.6, 46.4, 38.4, 34.2, 25.5, 24.5, 23.0, 20.9 ppm; HRMS (ESI) calcd for C₃₈H₃₃NO₇H⁺ [M+H⁺] 616.2330, found 616.2324.
Triol 173/173': The starting material 167 (11 mg, 14 µmol, 1.0 equiv) was dissolved in MeCN (0.3 mL) in a plastic vial and cooled to 0 °C. Then, HF•pyridine (70% HF, 0.02 mL, 0.02 g, 0.8 mmol HF) was added, and the mixture was stirred at room temperature for 35 minutes, then warmed up to 50–55 °C. After 5 hours at this temperature, another portion of HF•pyridine (70% HF, 0.05 mL, 0.06 g, 2 mmol HF) was added, followed by a final portion of HF•pyridine (70% HF, 0.05 mL, 0.06 g, 2 mmol HF) after another 16 hours. After 25 hours total reaction time, the mixture was allowed to cool to room temperature, and the reaction was quenched with saturated aq. NaHCO₃ solution (2 mL). The mixture was extracted with CH₂Cl₂ (10 mL) and EtOAc (10 mL), and the combined organic phases were dried over MgSO₄, filtered, and concentrated. Purification by preparative TLC (silica gel, 20% acetone:toluene) yielded product 173/173' (6.2 mg, 9.3 µmol, 66%).* 173/173': Rₚ = 0.30 (silica gel, acetone:toluene 1:4); FT-IR (neat) νₘₚₓ = 3474, 2922, 1700, 1590, 1483, 1400, 1341, 1267, 1216, 1185, 1134, 1120, 1044, 913, 818, 735 cm⁻¹; ¹H NMR (CDCl₃, 600 MHz) δ = 14.08 (s, 1 H), 7.47 – 7.29 (m, 5 H), 6.69 (s, 1 H), 5.50 (bs, 1 H), 5.31 – 5.16 (m, 2 H), 4.06 (s, 3 H), 3.93 (s, 3 H), 3.20 (bs, 1 H), 2.76 (d, J = 17.4 Hz, 1 H), 2.19 (m, 1 H), 2.04 (m, 1 H), 1.84 (m, 1 H), 1.48 (s, 3 H), 1.32 (m, 1 H), 0.89 (s, 3 H), 0.36 (m, 1 H) ppm; ¹³C NMR (CDCl₃, 151 MHz) δ = 199.8, 169.3, 160.4, 147.8, 142.0, 136.2, 133.0, 129.3, 128.7, 128.6, 128.4, 126.6, 121.6, 97.7, 71.8, 59.7, 56.8, 55.6, 44.6, 38.5, 34.0, 25.5, 24.2, 23.0, 21.0 ppm; HRMS (ESI) calcd for C₃₈H₃₇NO₁₀H⁺ [M+H⁺] 668.2490, found 668.2491.
*We surmise that hydroxy ketone 173 exists in equilibrium with its cyclic hemiacetal isomer 173'. At T = 298 K, slow interconversion between these two species is observed in CDCl₃, which results in broad signals in the ¹H and ¹³C NMR spectra. Due to signal broadening, not all the ¹³C signals could be identified. For further analysis, see the corresponding benzyl ether product 194/194'.

![Triketone 136](image)

**Triketone 136**: To a solution of starting material 173/173' (6.2 mg, 9.3 µmol, 1.0 equiv) in DCE (0.3 mL) at 0 °C was added DMP[36] (13 mg, 30 µmol, 3.2 equiv) and the mixture was warmed to 40 °C and stirred at that temperature for 3 hours. Another portion of DMP (4 mg, 9 µmol, 1.0 equiv) was then added, followed by a final portion (4 mg, 9 µmol, 1.0 equiv) after 3 hours 45 minutes total reaction time. After a total reaction time of 4 hours, the mixture was allowed to cool to room temperature, and a mixture of saturated aq. NaHCO₃:saturated aq. Na₂S₂O₃ (1:1, 5 mL) was added. The mixture was extracted with CH₂Cl₂ (3 × 10 mL), and the combined organic phases were dried over MgSO₄, filtered, and concentrated. Purification by preparative TLC (silica gel, 5% acetone:CH₂Cl₂) afforded triketone 136 (2.0 mg, 3.0 µmol, 32%). 136: Rₜ = 0.39 (silica gel, EtOAc:hexanes 1:1); FT-IR (neat) νₘₐₓ = 3447, 2918, 1705, 1609, 1580, 1484, 1403, 1342, 1270, 1220, 1189, 908, 731 cm⁻¹; ¹H NMR (CD₂Cl₂, 600 MHz) δ = 14.10 (s, 1 H), 7.55 – 7.50 (m, 2 H), 7.47 – 7.39 (m, 3 H), 6.77 (s, 1 H), 5.53 (bs, 1 H), 5.37 (s, 2 H), 4.60 (s, 1 H), 4.27 (s, 1 H), 4.06 (s, 3 H), 4.04 (d, J = 19.8 Hz, 1 H), 3.94 (s, 3 H), 3.41 (d, J = 18.3 Hz,
1 H), 3.15 (d, \( J = 18.3 \) Hz, 1 H), 3.05 (d, \( J = 19.8 \) Hz, 1 H), 2.24 (m, 1 H), 2.08 (m, 1 H), 1.88 (m, 1 H), 1.49 (s, 3 H), 1.40 (m, 1 H), 0.94 (s, 3 H), 0.45 (s, 3 H) ppm; \(^{13}\)C NMR (CD\(_2\)Cl\(_2\), 151 MHz) \( \delta = 194.8, 194.7, 185.1, 179.2, 167.9, 166.8, 161.0, 160.6, 147.9, 143.7, 136.4, 135.4, 129.2, 129.1, 129.0, 127.1, 122.0, 118.1, 109.9, 108.5, 106.4, 98.7, 83.9, 80.9, 73.1, 60.1, 57.0, 55.9, 44.5, 38.6, 34.8, 34.4, 25.6, 24.4, 23.3, 20.8 ppm; HRMS (ESI) calcd for C\(_{38}\)H\(_{35}\)NO\(_{10}\)H\(^+\) \([M+H^+]\) 666.2334, found 666.2328.

**Methyl viridicatumtoxin B (176):** Starting material 136 (2.0 mg, 3.0 \( \mu \)mol, 1.0 equiv) was dissolved in MeOH:1,4-dioxane (0.4 mL, 1:1). Pd-black (1.7 mg, 16 \( \mu \)mol, 5.3 equiv) was added, and the suspension was degassed, then placed under an atmosphere of argon, and finally hydrogen. After 8 minutes, the hydrogen was removed by flushing the flask with argon for 30 seconds. The palladium was then removed by filtration through Celite\(^\circledR\) using EtOAc and then MeOH:CH\(_2\)Cl\(_2\) (1:9) as eluents. The crude product was purified by preparative RP-TLC (C\(_{18}\), MeOH:H\(_2\)O:AcOH, 95:5:0.1) to yield methyl viridicatumtoxin B (176, 1.0 mg, 1.7 \( \mu \)mol, 57%). 176: \( R_f = 0.03 \) (silica gel, acetone:toluene: 1:4); FT-IR (neat) \( \nu_{\text{max}} = 3404, 2925, 1586, 1399, 1342, 1267, 1186, 1141, 1095 \) cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\), 600 MHz) \( \delta = 17.92 \) (s, 1 H), 14.24 (s, 1 H), 9.21 (s, 1 H), 6.74 (s, 1 H), 5.92 (s, 1 H), 5.53 (bs, 1 H), 4.86 (s, 1 H), 4.16 (s, 1 H), 4.09 (s, 3 H), 4.05 (d, \( J = 19.8 \) Hz, 1 H), 3.95 (s, 3 H), 3.12 (d, \( J = 18.9 \) Hz, 1 H), 3.04 (d, \( J = 19.8 \) Hz, 1 H), 2.80 (d, \( J = 18.9 \) Hz, 1 H), 2.23 (m, 1 H), 2.08 (m, 1 H), 1.88 (m, 1 H), 1.47 (s, 3 H), 1.39
(m, 1 H), 0.93 (s, 3 H), 0.45 (s, 3 H) ppm; $^{13}$C NMR (CDCl$_3$, 151 MHz) $\delta = 195.2$, 194.8, 192.8, 189.2, 173.1, 166.1, 160.5, 160.0, 147.6, 143.2, 136.0, 127.0, 121.8, 118.0, 109.9, 108.2, 99.8, 98.2, 81.0, 77.7, 59.9, 56.8, 55.7, 44.4, 42.1, 38.5, 34.1, 25.7, 24.4, 22.9, 20.9 ppm; HRMS (ESI) calcd for C$_{31}$H$_{31}$NO$_{10}$H$^+$ [M+H$^+$] 578.2021, found 578.2015.

**Diester 178**: Substrate 85 for this reaction was prepared by a literature procedure.$^{[37]}$ To two separate batches of substrate 85 (19.0 g each, 64.1 mmol each, 1.0 equiv each) in CH$_2$Cl$_2$ (570 mL) at –78 °C was added a freshly prepared solution of BBr$_3$ (1 M in CH$_2$Cl$_2$, 86.6 mL, 86.6 mmol, 1.35 equiv) dropwise over 15 minutes. The reaction mixture was stirred for an additional 15 minutes at –78 °C and was then allowed to warm to room temperature. The two batches were combined and poured into ice water, extracted with CH$_2$Cl$_2$ (2 × 500 mL), washed with brine (200 mL), dried over Na$_2$SO$_4$, and concentrated to afford an off-white solid (33.1 g). To a solution of the previous crude residue in DMF (840 mL) were added Ag$_2$O (57.4 g, 248 mmol, 1.9 equiv) and benzyl bromide (16.7 mL, 141 mmol, 1.1 equiv). The reaction mixture was shielded from light using aluminum foil and was stirred for 15 hours at room temperature. The solution was then filtered through a pad of silica gel, rinsed with EtOAc, and concentrated. The residue was then diluted with water (500 mL) and extracted with diethyl ether (1 L). The organic phase was dried over Na$_2$SO$_4$, filtered, and concentrated to give a crude oil which was purified by flash column chromatography (2→5→10% EtOAc:hexanes) to give benzylated product 178 (31.4 g, 84.3 mmol, 66% for two steps) as a colorless oil. 178: R$_f = 0.4$ (silica gel, EtOAc:hexanes 1:4); FT-IR (neat) $\nu_{\text{max}} = 2981$, 1727, 1603, 1583, 1463, 1455, 1434, 1366, 1317,
Cyclic anhydride 177: A solution of NaOH (20 g, 0.50 mol, 27 equiv) in water (50 mL) was added to a solution of diester 178 (6.80 g, 18.2 mmol, 1.0 equiv) in EtOH (70 mL) at room temperature. The resulting mixture was stirred for 15 hours at reflux. The EtOH was then removed under reduced pressure, and the remaining aqueous phase was acidified to pH 1 with 12 N aq. HCl. The aqueous phase was extracted with EtOAc (200 mL), and the organic phase was dried over Na₂SO₄, filtered, and concentrated to obtain the crude diacid (179) as a white solid (5.48 g). Acetic anhydride (1.74 mL, 18.4 mmol, 1.1 equiv) was added via syringe to a slurry of the diacid in toluene (42 mL), and the resulting mixture was heated at reflux for 1 hour. The flask was then cooled in an ice bath, the solid product was filtered, and the filter cake was washed with pentane. The solids were collected and dried to afford 177 as light yellow crystals (4.90 g, 16.4 mmol, 90%). 177: Rᵥ = 0.3 (silica gel, EtOAc:hexanes 1:4); FT-IR (neat) ν_max = 1785, 1746, 1605, 1584, 1345, 1274, 1226, 1196, 1175, 1154, 998, 738 cm⁻¹; ¹H NMR (CDCl₃, 600 MHz) δ = 7.55 – 7.53 (m, 2 H), 7.42 – 7.38 (m, 2 H), 7.32 (m, 1 H), 6.50 (d, J = 2.2 Hz, 1 H), 6.42 (d, J = 2.1 Hz, 1 H), 5.07 (s, 2 H), 4.31 (q, J = 7.1 Hz, 2 H), 4.15 (q, J = 7.1 Hz, 2 H), 3.78 (s, 3 H), 3.69 (s, 2 H), 1.28 (t, J = 7.1 Hz, 3 H), 1.25 (t, J = 7.1 Hz, 3 H) ppm; ¹³C NMR (CDCl₃, 151 MHz) δ = 170.9, 167.5, 161.6, 158.1, 136.7, 135.3, 128.6, 128.0, 127.2, 117.0, 107.9, 99.3, 70.7, 61.1, 61.0, 55.5, 39.7, 14.3, 14.2 ppm; HRMS (ESI) calcd for C₂₁H₂₄O₆H⁺ [M+H⁺] 373.1646, found 373.1643.
1 H), 6.34 (m, 1 H), 5.25 (s, 2 H), 3.99 (s, 2 H), 3.85 (s, 3 H) ppm; $^{13}$C NMR (CDCl$_3$, 151 MHz) δ = 165.8, 165.4, 162.8, 156.8, 138.8, 135.8, 128.9, 128.2, 126.8, 104.4, 104.1, 99.9, 70.8, 56.0, 35.6 ppm; HRMS (ESI) calcd for C$_{17}$H$_{14}$O$_5$H$^+$ [M+H$^+$] 299.0914, found 299.0918.

**BCD Tricycle 180:** To a solution of quinone monoketal 67 (3.10 g, 20.1 mmol, 3.0 equiv) in THF (45 mL) at 0 °C was added NaH (57–63% oil dispersion, 804 mg, 20.1 mmol, 3.0 equiv). Separately, a slurry of cyclic anhydride 177 (2.00 g, 6.71 mmol, 1.0 equiv) in THF (45 mL) was prepared, and the cyclic anhydride solution was added to the quinone solution dropwise over 45 minutes, during which time a strong yellow color evolved. The cyclic anhydride flask was rinsed with additional THF (2 × 10 mL). The reaction flask was allowed to warm to room temperature and stirred for 1 hour. The reaction mixture was then re-cooled to 0 °C, and the reaction was quenched by cautious addition of saturated aq. NH$_4$Cl solution (50 mL). The mixture was diluted with EtOAc (200 mL) and brine (100 mL) was added. The organic phase was separated, dried over Na$_2$SO$_4$, and concentrated. The crude residue was slurried in toluene (120 mL) and heated to 65 °C with vigorous stirring. DBU (3.0 mL, 20 mmol, 3.0 equiv) was injected into the reaction vessel while maintaining vigorous stirring. After 2 hours, an additional portion of DBU (2.0 mL, 13 mmol, 2 equiv) was added. After an additional 2.5 hours, the dark solution was cooled to room temperature and washed with brine (2 × 100 mL). The organic phase was concentrated, and the crude residue was purified by flash column chromatography (5→10→20→25→30% EtOAc:hexanes, 0.1% Et$_3$N) to give tricyclic product 180 (1.48 g, 3.62 mmol, 54%) as a yellow...
foam. Alternatively, the reaction can be performed using the following “one-pot” protocol, which was run in two batches in parallel. Quinone monoketal 67 (3.90 g, 25.2 mmol, 3.0 equiv) was dissolved in MeCN (55 mL), and DBU (3.8 mL, 25 mmol, 3.0 equiv) was added. Separately, cyclic anhydride 177 (2.50 g, 8.39 mmol, 1.0 equiv) was slurried in MeCN (55 mL) and added to the quinone solution at room temperature over 1 hour using a syringe pump with constant agitation. After the addition was complete, the mixture was heated to 65 °C for 3 hours. The dark mixture was then cooled to room temperature and concentrated. Purification by column chromatography (same gradient as above) gave the BCD tricycle 180 (2.80 g from two batches, 6.86 mmol, 41%). 180: \( R_f = 0.3 \) (silica gel, EtOAc:hexanes 1:4); FT-IR (neat) \( \nu_{\text{max}} = 2939, 2833, 1598, 1456, 1439, 1371, 1322, 1278, 1223, 1196, 1163, 1139, 1087, 1074 \text{ cm}^{-1} \); \( ^1 \text{H NMR} \) (C\(_6\)D\(_6\), 600 MHz) \( \delta = 17.31 \) (s, 1 H), 7.59 – 7.56 (m, 2 H), 7.20 – 7.17 (m, 2 H), 7.07 (m, 1 H), 6.33 (d, \( J = 2.2 \) Hz, 1 H), 6.19 (d, \( J = 10.4 \) Hz, 1 H), 6.17 (m, 1 H), 5.93 (d, \( J = 10.4 \) Hz, 1 H), 4.87 (d, \( J = 12.5 \) Hz, 1 H, AB system), 4.79 (d, \( J = 12.5 \) Hz, 1 H, AB system), 3.31 (ap t, \( J = 15.0 \) Hz, 1 H), 3.19 (s, 3 H), 3.09 (dd, \( J = 14.4, 4.5 \) Hz, 1 H), 3.05 (s, 3 H), 3.01 (s, 3 H), 2.89 (dd, \( J = 15.3, 4.5 \) Hz, 1 H) ppm; \( ^{13} \text{C NMR} \) (C\(_6\)D\(_6\), 151 MHz) \( \delta = 183.8, 174.2, 164.2, 161.4, 146.3, 138.0, 137.4, 130.8, 128.7, 127.8, 127.1, 114.6, 105.8, 105.3, 99.8, 98.1, 70.6, 54.9, 50.5, 50.2, 38.2, 29.4 ppm; HRMS (ESI) calcd for C\(_{24}\)H\(_{24}\)O\(_6\)H\(^+\) \([M+H^+]\) 409.1646, found 409.1658.

**Anthrone S4:** BCD tricycle 180 (3.6 g, 8.8 mmol, 1.0 equiv) was dissolved in CH\(_2\)Cl\(_2\) (88 mL) at room temperature, and freshly crystallized CSA (41 mg, 0.18 mmol, 0.02 equiv) was added.
The resulting solution was stirred for 30 minutes, and the reaction was then quenched with saturated aq. NaHCO₃ solution (80 mL). The layers were separated, and the organic phase was dried over Na₂SO₄, filtered, and concentrated to give anthrone S₄ (3.28 g, 8.72 mmol, 99%) as an orange foam. S₄: Rₚ = 0.3 (silica gel, EtOAc:hexanes 3:7); FT-IR (neat) vₘₐₓ = 2936, 2836, 1636, 1599, 1583, 1475, 1432, 1384, 1330, 1267, 1228, 1195, 1170, 1096, 1059, 1027, 817, 733 cm⁻¹; ¹H NMR (CDCl₃, 600 MHz) δ = 13.03 (s, 1 H), 7.62 – 7.59 (m, 2 H), 7.43 – 7.39 (m, 2 H), 7.32 (m, 1 H), 7.02 (d, J = 8.9 Hz, 1 H), 6.85 (d, J = 8.9 Hz, 1 H), 6.51 (m, 1 H), 6.45 (m, 1 H), 5.24 (s, 2 H), 4.14 (s, 2 H), 3.85 (s, 3 H), 3.82 (s, 3 H) ppm; ¹³C NMR (CDCl₃, 151 MHz) δ = 188.6, 164.2, 162.2, 156.4, 147.8, 146.3, 136.7, 128.8, 127.8, 127.4, 126.8, 117.7, 116.9, 115.2, 114.7, 105.0, 99.6, 70.7, 56.1, 55.6, 29.1 ppm; HRMS (ESI) calcd for C₂₃H₂₀O₅H⁺ [M+H⁺] 377.1389, found 377.1386.

Alkylated anthrone 181: A solution of anthrone S₄ (4.69 g, 12.5 mmol, 1.0 equiv) and allylic bromide 91 (4.75 g, 13.7 mmol, 1.1 equiv) in DMF (250 mL) was degassed for 40 minutes by bubbling argon through the solution. During this time, the reaction flask was shielded from light using aluminum foil. After the degassing period, Na₂CO₃ (13.3 g, 125 mmol, 10 equiv) was added to the reaction flask, and the mixture was vigorously stirred for 1 hour in the dark. During this time, the reaction mixture typically turned very dark. The reaction was quenched by the addition of brine (1 L) and diluted with EtOAc (800 mL). The aqueous phase was extracted with
EtOAc (500 mL), and the combined organics were washed with brine (1 L). The organic layer was dried over Na₂SO₄, filtered, and concentrated to give a crude oil which was purified by flash column chromatography (2→5→10% EtOAc:hexanes) to give pure alkylated anthrone 181 (6.19 g, 9.64 mmol, 77%) as a yellow foam (d.r. ca. 1:1 as judged by ¹H NMR analysis). 181: Rᵥ = 0.5 (silica gel, EtOAc:hexanes 1:4); FT-IR (neat) $\nu_{\text{max}} = 2932, 2856, 1636, 1599, 1583, 1568, 1472, 1432, 1328, 1265, 1227, 1196, 1164, 1148, 1101, 1034, 1002, 907, 832, 772, 728 \text{ cm}^{-1}$; This compound exhibited broad NMR signals (both in ¹H NMR and ¹³C NMR) on the NMR timescale due to hindered bond rotation of the newly-formed C–C bond. ¹H NMR (CDCl₃, 600 MHz, 298 K) $\delta = 12.72$ (bs, 1 H), 12.71 (s, 1 H), 7.58 – 7.56 (m, 4 H), 7.41 – 7.37 (m, 4 H), 7.32 – 7.28 (m, 2 H), 7.05 (d, $J = 9.0 \text{ Hz}$, 1 H), 7.045 (d, $J = 9.0 \text{ Hz}$, 1 H), 6.86 (d, $J = 9.0 \text{ Hz}$, 1 H), 6.85 (d, $J = 9.0 \text{ Hz}$, 1 H), 6.44 (d, $J = 2.3 \text{ Hz}$, 1 H), 6.43 (d, $J = 2.3 \text{ Hz}$, 1 H), 6.39 (bs, 1 H), 6.29 (m, 1 H), 5.28 (d, $J = 12.9 \text{ Hz}$, 2 H, AB system), 5.25 – 5.20 (m, 2 H), 4.64 (bs, 1 H), 4.56 (bs, 1 H), 3.98 – 3.95 (m, 2 H), 3.91 – 3.88 (m, 6 H), 3.85 – 3.82 (m, 6 H), 3.75 – 2.65 (m, 2 H), 2.04 – 0.88 (m, 40 H), 0.83 – 0.59 (m, 3 H), 0.32 – 0.00 (m, 15 H) ppm; ¹³C NMR (CDCl₃, 151 MHz, 298 K)* $\delta = 188.6, 188.5, 163.7, 163.6, 161.9, 161.8, 156.23, 156.20, 150.3$ (b), 129.6 (b), 147.7, 147.6, 136.68, 136.65, 133.6, 133.4, 128.7, 127.74, 127.73, 126.70, 126.69, 117.70, 117.67, 117.65, 117.61, 115.05, 115.0, 114.99, 114.9, 106.6, 106.4, 100.1, 71.6, 70.7, 56.02, 55.99, 55.7, 55.5, 41.1, 40.6, 38.6, 38.6, 37.1, 35.9, 34.4, 29.74, 29.66, 29.1, 28.9, 26.6, 26.1, 26.0, 25.8, 18.32, 18.31, 16.6, 16.4, 11.6, −4.0, −4.2, −4.66, −4.68 ppm; HRMS (ESI) calcd for C₉₉H₅₆O₆SiH⁺ [M+H⁺] 643.3449, found 643.3441.

*Due to signal broadening, not all the ¹³C signals could be identified.
**BCDEF Spirocycle 182**: Alkylated anthrone 181 (2.30 g, 3.58 mmol, 1.0 equiv, d.r. ca. 1:1) was dissolved in CH$_2$Cl$_2$ (180 mL) and cooled to 0 °C. A freshly prepared solution of BF$_3$•OEt$_2$ (3.6 mL of a 0.1 M in CH$_2$Cl$_2$, 0.36 mmol, 0.1 equiv) was added dropwise, and the reaction mixture was allowed to stir for 20 minutes. The reaction was quenched with saturated aq. NaHCO$_3$ solution (100 mL), and the phases were separated. The aqueous phase was extracted with CH$_2$Cl$_2$ (100 mL), and the combined organic layers were dried over Na$_2$SO$_4$, filtered, and concentrated. The residue was purified by flash column chromatography (5→10% EtOAc:hexanes) to give spirocycle 182 (1.34 g, 2.62 mmol, 73%) as a yellow foam. **182**: R$_f$ = 0.5 (silica gel, EtOAc:hexanes 1:4); FT-IR (neat) $v_{\text{max}}$ = 2919, 2838, 1633, 1598, 1567, 1472, 1441, 1384, 1327, 1301, 1270, 1257, 1221, 1200, 1139, 1106, 1039, 1001, 909, 825, 732 cm$^{-1}$; $^1$H NMR (CDCl$_3$, 600 MHz) $\delta = 13.15$ (s, 1 H), 7.62 – 7.59 (m, 2 H), 7.43 – 7.40 (m, 2 H), 7.32 (m, 1 H), 7.06 (d, $J = 9.0$ Hz, 1 H), 6.86 (d, $J = 9.0$ Hz, 1 H), 6.40 (s, 1 H), 5.43 (bs, 1 H), 5.37 (d, $J = 12.7$ Hz, 1 H, AB system), 5.28 (d, $J = 12.7$ Hz, 1 H, AB system), 4.39 (dd, $J = 11.8$, 7.5 Hz, 1 H), 3.81 (s, 3 H), 3.75 (s, 3 H), 3.13 (dd, $J = 13.7$, 7.5 Hz, 1 H), 2.25 – 2.16 (m, 2 H), 2.04 (m, 1 H), 1.95 (ddd, $J = 12.7$, 12.7, 6.0 Hz, 1 H), 1.37 (dd, $J = 12.7$, 5.8 Hz, 1 H), 1.26 (s, 3 H), 1.00 (s, 3 H), 0.96 (s, 3 H) ppm; $^{13}$C NMR (CDCl$_3$, 151 MHz) $\delta = 188.9, 162.1, 161.2$, 157.4, 155.4, 149.2, 138.3, 136.9, 131.1, 128.8, 128.0, 127.0, 124.0, 121.3, 119.2, 118.1, 115.7, 112.7, 96.9, 71.5, 58.7, 56.6, 55.2, 44.9, 41.7, 38.8, 34.9, 27.8, 24.9, 23.1, 20.5 ppm; HRMS (ESI) calcd for C$_{33}$H$_{34}$O$_5$H$^+$ [M+H$^+$] 511.2479, found 511.2467.

![Spirocycle 182](image-url)
Quinomethide 184: Spirocycle 182 (200 mg, 0.392 mmol, 1.0 equiv) was dissolved in MeOH:CH₂Cl₂ (1:1, 8 mL), and the solution was cooled to 0 °C. PhI(OAc)₂ (151 mg, 0.469 mmol, 1.2 equiv) was added and the reaction mixture was stirred for 30 minutes at 0 °C and 30 minutes at room temperature. The reaction was quenched with saturated aq. NaHCO₃ solution (20 mL) and extracted with EtOAc (2 × 20 mL). The combined organics were washed with brine (10 mL), dried over Na₂SO₄, and concentrated. The so-obtained crude ketal 183 was dissolved in CH₂Cl₂ (8 mL), and freshly crystallized CSA (6 mg, 0.03 mmol, 0.07 equiv) was added at 0 °C. The reaction mixture was stirred at that temperature for 5 minutes, and the reaction was then quenched with saturated aq. NaHCO₃ solution (10 mL). The layers were separated, and the organic phase was dried over Na₂SO₄, filtered, and concentrated to give the crude product 184. Flash column chromatography (2% EtOAc:toluene) gave intermediate 184 (169 mg, 0.332 mmol, 85% yield for two steps) as a red solid. 184: R_f = 0.7 (silica gel, EtOAc:hexanes 1:9); FT-IR (neat) ν_max = 2936, 2324, 2162, 2050, 1981, 1625, 1574, 1479, 1442, 1429, 1384, 1363, 1331, 1311, 1259, 1238, 1222, 1180, 1163, 1128, 1029, 931, 874, 829, 806, 735, 716, 696 cm⁻¹; ¹H NMR (CDCl₃, 600 MHz) δ = 13.98 (s, 1 H), 7.65 – 7.63 (m, 2 H), 7.60 (s, 1 H), 7.45 – 7.41 (m, 2 H), 7.34 (m, 1 H), 7.20 (d, J = 6.0 Hz, 1 H), 7.00 (d, J = 6.0 Hz, 1 H), 6.44 (s, 1 H), 5.74 (bs, 1 H), 5.38 (d, J = 12.8 Hz, 1 H, AB system), 5.35 (d, J = 12.8 Hz, 1 H, AB system), 3.97 (s, 3 H), 3.81 (s, 3 H), 2.31 – 2.22 (m, 2 H), 1.90 (ddd, J = 12.9, 5.6, 5.6 Hz, 1 H), 1.66 (ddd, J = 12.9, 6.5, 6.5 Hz, 1 H), 1.14 (s, 3 H), 0.85 (s, 6 H) ppm; ¹³C NMR (CDCl₃,
Ketal 185: Quinomethide 184 (2.60 g, 5.09 mmol, 1.0 equiv) was dissolved in a mixture of
CH$_2$Cl$_2$:MeOH (1:10; 101 mL), and PhI(OAc)$_2$ (2.0 g, 6.2 mmol, 1.2 equiv) was added. The
reaction mixture was stirred for 1.5 hours and was then quenched with saturated aq. NaHCO$_3$
solution (100 mL). The mixture was diluted with water and extracted with CH$_2$Cl$_2$ (200 mL),
dried over Na$_2$SO$_4$, filtered, and concentrated. The crude residue was purified by flash column
chromatography (4% acetone:toluene, 0.1% Et$_3$N) to give diketone ketal 185 (2.47 g, 4.58 mmol,
90% yield) as a yellow foam. 185: R$_f$ = 0.3 (silica gel, acetone:toluene 1:9); FT-IR (neat) $v_{\text{max}}$ =
2937, 2835, 1681, 1618, 1582, 1456, 1435, 1373, 1328, 1282, 1224, 1094, 1082, 1067, 846,
733 cm$^{-1}$; $^1$H NMR (CDCl$_3$, 600 MHz) $\delta$ = 7.83 (s, 1 H), 7.65 – 7.62 (m, 2 H), 7.43 – 7.39 (m,
2 H), 7.32 (m, 1 H), 6.64 (d, $J$ = 10.4 Hz, 1 H), 6.59 (d, $J$ = 10.4 Hz, 1 H), 6.43 (s, 1 H), 5.76 (bs,
1 H), 5.30 (d, $J$ = 12.0 Hz, 1 H, AB system), 5.26 (d, $J$ = 12.0 Hz, 1 H, AB system), 3.82 (s,
3 H), 3.26 (s, 3 H), 3.17 (s, 3 H), 2.28 – 2.23 (m, 2 H), 1.94 (ddd, $J$ = 13.1, 6.3, 6.3 Hz, 1 H),
1.61 (m, 1 H), 1.13 (bs, 3 H), 0.88 (s, 3 H), 0.82 (s, 3 H) ppm; $^{13}$C NMR (CDCl$_3$, 151 MHz) $\delta$ =
183.3, 179.6, 161.6, 160.6, 159.2, 148.4, 147.1, 140.9, 136.7, 135.2, 130.5, 130.1, 130.0, 128.7,
127.9, 127.1, 125.0, 123.5, 96.7, 96.5, 71.1, 68.6, 56.0, 51.7, 51.6, 37.5, 35.5, 27.1, 26.9,
23.1, 19.9 ppm; HRMS (ESI) calcd for C_{34}H_{34}O_{6}H^{+} [M+H^{+}] 539.2428, found 539.2433.

**Heptacyle 186 (+15-epi-186):** To a solution of pentacyle 185 (2.5 g, 4.6 mmol, 1.0 equiv) and
phenyl ester isoxazole 123 (2.3 g, 5.1 mmol, 1.1 equiv) in toluene (90 mL) was added potassium
tert-butoxide (0.62 g, 5.6 mmol, 1.2 equiv), and the resulting solution was stirred for 15 minutes.
The reaction was quenched with saturated aq. NH_{4}Cl solution (100 mL). The phases were
separated, and the organic phase was dried over Na_{2}SO_{4}, filtered, and concentrated. The crude
residue was purified by flash column chromatography (2→5% acetone:toluene) to give the
product 186 (+15-epi-186) (3.8 g, 4.2 mmol, 91%, d.r. ca. 2:1) as a yellow foam. 186 (+15-epi-
186): R_{f} = 0.6 (silica gel, EtOAc:hexanes 3:7); FT-IR (neat) \nu_{max} = 2952, 1737, 1656, 1618,
1582, 1511, 1489, 1454, 1385, 1366, 1308, 1250, 1223, 1157, 1054, 1025, 932, 859, 838, 736,
696 cm^{-1}; ^{1}H NMR (C_{6}D_{6}, 600 MHz) \delta = 16.78 (s, 1 H, major), 16.77 (s, 1 H, minor), 7.70 –
7.64 (m, 4 H, major + minor), 7.61 (s, 1 H, minor), 7.58 (s, 1 H, major), 7.39 – 7.35 (m, 4 H,
major + minor), 7.21 – 7.17 (m, 4 H, major + minor), 7.12 – 7.07 (m, 6 H, major + minor), 7.06
– 7.02 (m, 2 H, major + minor), 6.22 – 6.19 (m, 2 H, major + minor), 5.72 (bs, 1 H, minor), 5.69
(bs, 1 H, major), 5.19 – 5.17 (m, 4 H, major + minor), 5.06 – 5.01 (m, 4 H, major + minor), 4.73
(d, J = 10.0 Hz, 1 H, major), 4.72 (m, 1 H, minor), 4.42 – 4.35 (m, 2 H, major + minor), 4.34 –
4.26 (m, 2 H, major + minor), 4.22 (d, J = 10.0 Hz, 1 H, major), 4.20 (m, 1 H, minor), 3.19 (s,
3 H, major), 3.18 (s, 3 H, minor), 3.13 (s, 3 H, major), 3.08 (s, 3 H, minor), 3.02 (s, 3 H, minor),
2.96 (s, 3 H, major), 2.26 – 2.18 (m, 2 H, major + minor), 2.14 – 2.07 (m, 2 H, major + minor),
1.96 (dd, J = 13.2, 6.6, 6.6 Hz, 1 H, major), 1.89 (dd, J = 13.2, 6.7, 6.7 Hz, 1 H, minor), 1.47
(ap ddd, J = 13.2, 6.7, 6.7 Hz, 2 H, major + minor), 1.24 (bs, 3 H, minor), 1.18 (bs, 3 H, major),
1.03 – 0.98 (m, 4 H, major + minor), 0.93 (s, 3 H, major), 0.91 (s, 3 H, minor), 0.87 (s, 3 H, major),
0.82 (s, 3 H, minor), −0.09 (s, 9 H, major), −0.11 (s, 9 H, minor) ppm; $^{13}$C NMR (C$_6$D$_6$,
151 MHz) δ = 181.5 (major), 181.4 (minor), 178.7 (major), 178.3 (minor), 175.5 (major), 175.4
(minor), 171.6 (minor), 171.4 (major), 169.2 (major), 169.1 (minor), 168.4 (major + minor),
161.0 (minor), 160.5 (major), 159.1 (minor), 158.9 (major), 157.2 (major), 157.1 (minor), 148.7
(minor), 148.5 (major), 140.01 (minor), 139.95 (major), 137.4 (minor), 137.3 (major), 135.9
(major + minor), 134.9 (minor), 134.8 (major), 132.5 (major), 132.4 (minor), 130.8 (minor),
130.7 (major), 128.9*, 128.7*, 128.51*, 128.47*, 127.3*, 127.2*, 125.12 (minor), 125.08
(major), 123.5 (minor), 123.3 (major), 113.3 (major), 113.2 (minor), 106.3 (major + minor),
103.30 (major), 103.27 (minor), 102.6 (major), 102.5 (minor), 97.7 (minor), 97.4 (major), 72.3
(major + minor), 71.6 (minor), 71.4 (major), 68.4 (minor), 68.3 (major), 64.8 (major + minor),
54.9 (major + minor), 54.2 (major), 53.7 (minor), 52.8 (minor), 52.5 (major), 40.61 (minor),
40.58 (major), 40.2 (major + minor), 37.7 (major), 37.5 (minor), 35.8 (major + minor), 27.22
(major), 27.16 (minor), 27.14 (minor), 27.07 (major), 23.4 (major + minor), 20.3 (minor), 20.2
(major), 17.4 (major + minor), −1.66 (major), −1.67 (minor) ppm; HRMS (ESI) calcd for
C$_{52}$H$_{55}$NO$_{11}$SiH$^+$ [M+H$^+$] 898.3617, found 898.3612.

*Due to overlapping $^{13}$C resonances of each diastereomer with each other as well as with the
NMR solvent, not all of the signals could be assigned.
Heptacycle 187 (+15-epi-187): To a solution of Teoc-heptacycle 186 (+15-epi-186) (3.2 g, 3.6 mmol, 1.0 equiv, d.r. ca. 2:1) in THF (400 mL) was added NH4F (2.7 g, 71 mmol, 20 equiv), and the solution was degassed with argon for 1 hour. The degassing was discontinued, and the reaction flask was shielded from light using aluminum foil. A freshly prepared solution of tetrabutylammonium fluoride (36 mL, 1 M solution in THF, 36 mmol, 10 equiv, prepared from TBAF•3H2O) was added in one portion. The reaction mixture was stirred for 5 minutes. The reaction was then quenched with brine (250 mL) and extracted with EtOAc (250 mL). The layers were separated, and the organic phase was washed with water (3×200 mL), dried over Na2SO4, and concentrated. The crude residue was purified by flash column chromatography (2→5% acetone:toluene) to give heptacycle 187 (+15-epi-187) (2.3 g, 3.1 mmol, 86%, d.r. ca. 2:1) as an orange solid. 187 (+15-epi-187): Rf = 0.5 (silica gel, acetone:toluene 1:9); FT-IR (neat) νmax = 2956, 2927, 2855, 1711, 1653, 1618, 1582, 1509, 1455, 1365, 1311, 1258, 1219, 1157, 1075, 1052, 1027, 912, 814, 736, 697 cm–1; 1H NMR (CDCl3, 600 MHz) δ = 15.60 (s, 1 H, major), 15.59 (s, 1 H, minor), 7.72 (s, 1 H, major), 7.70 (s, 1 H, minor), 7.61 – 7.57 (m, 4 H, major + minor), 7.52 – 7.49 (m, 4 H, major + minor), 7.41 – 7.36 (m, 8 H, major + minor), 7.35 – 7.29 (m, 4 H, major + minor), 6.45 (s, 1 H, minor), 6.44 (s, 1 H, major), 5.77 (bs, 1 H, minor), 5.76 (bs, 1 H, major), 5.40 (ap s, 4 H, major + minor), 5.33 (d, J = 12.7 Hz, 1 H, major, AB system), 5.30 – 5.25 (m, 3 H, major + minor), 3.91 (dd, J = 11.0, 8.4 Hz, 1 H, major), 3.86 (dd, J = 11.0, 8.5 Hz, 1 H, minor), 3.80 (s, 3 H, minor), 3.79 (s, 3 H, major), 3.46 – 3.40 (m, 2 H, major + minor), 3.45 (s, 3 H, major), 3.40 (s, 3 H, minor), 3.34 (s, 3 H, minor), 3.27 (s, 3 H, major), 3.03
– 2.94 (m, 2 H, major + minor), 2.26 (ap s, 4 H, major + minor), 1.99 (ap ddd, \(J = 13.2, 6.6, 6.6\) Hz, 2 H, major + minor), 1.58 – 1.52 (m, 2 H, major + minor), 1.13 (s, 3 H, minor), 1.09 (s, 3 H, major), 0.92 (s, 3 H, major), 0.88 (s, 3 H, minor), 0.79 (s, 3 H, major), 0.77 (s, 3 H, minor) ppm; \(^{13}\)C NMR (CDCl\(_3\), 151 MHz) \(\delta = 182.1\) (major), 181.0 (minor), 180.1 (major), 179.8 (minor), 179.09 (major), 179.06 (minor), 169.9 (minor), 168.1 (major), 160.7 (minor), 160.3 (major), 159.39 (major), 159.35 (minor), 159.2 (minor), 159.1 (major), 148.2 (minor), 148.1 (major), 141.14 (minor), 141.13 (major), 136.79 (major), 136.77 (minor), 135.5 (major + minor), 132.89 (minor), 132.86 (major), 132.60 (major), 132.55 (minor), 130.0 (major + minor), 128.8*, 128.7*, 128.6*, 128.4*, 127.9*, 127.2 (minor), 127.1 (major), 125.24 (minor), 125.22 (major), 123.4 (minor), 123.2 (major), 112.3 (major), 112.2 (minor), 105.7 (major + minor), 103.42 (major), 103.37 (minor), 102.18 (major), 102.15 (minor), 97.1 (minor), 97.0 (major), 72.4 (major + minor), 71.4 (minor), 71.3 (major), 68.4 (minor), 68.3 (major), 55.6 (minor), 55.5 (major), 53.6 (major), 53.1 (minor), 52.9 (minor), 52.6 (major), 37.8 (major), 37.6 (minor), 37.0 (minor), 36.9 (major), 35.64 (major), 35.60 (minor), 27.30 (minor), 27.25 (major), 26.9 (minor), 26.8 (major), 23.13 (major), 23.10 (minor), 20.5 (major + minor), 20.03 (major), 20.00 (minor) ppm; HRMS (ESI) calcd for C\(_{46}\)H\(_{43}\)NO\(_9\)H\(^+\) [M+H\(^+\)] 754.3010, found 754.3000.

*Due to overlapping \(^{13}\)C resonances of each diastereomer with each other, not all of the signals could be assigned.
Alcohol 188 (+ 15-epi-188): A solution of substrate 187 (+ 15-epi-187) (1.6 g, 2.1 mmol, 1.0 equiv, d.r. ca. 2:1) in CH₂Cl₂ (100 mL) was cooled to -78 °C, and Ni(acac)₂ (109 mg, 0.424 mmol, 0.2 equiv) was added. Then, DMDO[21] (56 mL of a ~0.08 M solution in acetone, 4.5 mmol, 2.1 equiv) was added. The reaction mixture was allowed to warm to -60 °C over 6.5 hours, during which two additional portions of DMDO (40 mL, 3.2 mmol, 1.5 equiv) and CH₂Cl₂ (20 mL each) were added, one every 2 hours. The reaction was then quenched by the addition of dimethylsulfide (5.0 mL, 4.2 g, 68 mmol, 32 equiv), and the mixture was stirred at the same temperature for 15 minutes. Saturated aq. NH₄Cl solution (100 mL) was added, and the mixture was allowed to warm to room temperature. The mixture was diluted with water (150 mL) and extracted with CH₂Cl₂ (150 mL). The layers were separated, and the organic phase was washed with water (250 mL) and brine (250 mL), dried over Na₂SO₄, and concentrated. Purification by flash column chromatography (3→5→10% acetone:toluene) gave the hydroxylated product 188 (+ 15-epi-188) (575 mg, 0.747 mmol, 36%, 60% brsm, d.r. ca. 2:1) as an orange solid and recovered starting material 187 (+ 15-epi-187) (630 mg, 0.837 mmol, 40%). The recovered starting material could be resubjected to the reaction conditions to give hydroxylated product 188 (+ 15-epi-188) (800 mg combined, 1.04 mmol, 50% combined, d.r. ca. 2:1) as an orange foam. 188 (+ 15-epi-188): Rf = 0.25 (silica gel, acetone:toluene 1:9); FT-IR (neat) νmax = 3425, 2931, 2850, 1719, 1618, 1582, 1514, 1488, 1455, 1366, 1313, 1259, 1224, 1132, 1103, 1055, 991, 829, 735, 696 cm⁻¹; ¹H NMR (CDCl₃, 600 MHz) δ = 7.862 (s, 1 H, major), 7.855 (s, 1 H, minor), 7.61 – 7.58 (m, 4 H, major + minor), 7.44 – 7.37 (m, 8 H, major +
minor), 7.35 – 7.29 (m, 8 H, major + minor), 6.45 (s, 1 H, major), 6.44 (s, 1 H, minor), 5.79 (bs, 2 H, major + minor), 5.28 – 5.20 (m, 8 H, major + minor), 5.04 (bs, 2 H, major + minor), 3.83 (s, 6 H, major + minor), 3.45 (s, 3 H, minor), 3.42 (s, 3 H, major), 3.39 (dd, \( J = 9.3, 6.2 \) Hz, 2 H, major + minor), 3.25 (s, 3 H, major), 3.24 – 3.19 (m, 2 H, major + minor), 3.16 (s, 3 H, minor), 2.95 (dd, \( J = 19.1, 6.4 \) Hz, 1 H, minor), 2.89 (dd, \( J = 19.1, 6.3 \) Hz, 1 H, major), 2.28 (bs, 4 H, major + minor), 1.96 – 1.87 (m, 2 H, major + minor), 1.64 – 1.58 (m, 2 H, major + minor), 1.10 (s, 3 H, major), 1.09 (s, 3 H, minor), 0.84 (bs, 6 H, major + minor), 0.83 (s, 3 H, minor), 0.82 (s, 3 H, major) ppm; \(^{13}\text{C}\) NMR (CDCl\(_3\), 151 MHz) \( \delta = 191.7 \) (major), 191.5 (minor), 184.0 (minor), 183.9 (major), 180.0 (major), 179.9 (minor), 177.5 (minor), 177.3 (major), 167.81 (major), 167.79 (minor), 162.94 (minor), 162.87 (major), 160.9 (major), 160.7 (minor), 159.5 (major), 159.4 (minor), 148.6 (major), 148.5 (minor), 146.7 (major), 146.6 (minor), 136.5 (major + minor), 135.0 (major + minor), 132.6 (major), 132.4 (minor), 132.2 (major + minor), 130.1 (major), 129.9 (minor), 128.8*, 128.62*, 128.56*, 128.21*, 128.19*, 127.9*, 127.0*, 125.4 (minor), 125.2 (major), 123.5 (major), 123.4 (minor), 111.62 (major), 111.57 (minor), 106.4 (minor), 106.3 (major), 102.47 (major), 102.45 (minor), 96.8 (major), 96.6 (minor), 80.6 (minor), 80.4 (major), 72.5 (minor), 72.4 (major), 71.3 (major), 71.2 (minor), 68.50 (minor), 68.46 (major), 55.59 (major), 55.57 (minor), 51.9 (major), 51.7 (minor), 49.4 (major), 49.3 (minor), 44.4 (major + minor), 37.84 (major), 37.75 (minor), 35.8 (major), 35.6 (minor), 27.1 (major + minor), 26.93 (major), 26.90 (minor), 23.1 (major + minor), 22.7 (minor), 22.6 (major), 20.1 (major), 19.9 (minor) ppm; HRMS (ESI) calcd for C\(_{46}\)H\(_{43}\)NO\(_{10}\)H\(^+\) [M+H\(^+\)] 770.2960, found 770.2953.

*Due to overlapping \(^{13}\text{C}\) resonances of each diastereomer with each other, not all of the signals could be assigned.
Alcohol **189** and **15-epi-189**: A solution of alcohol **188** (+ **15-epi-188**) (225 mg, 0.292 mmol, 1.0 equiv, d.r. ca. 2:1) in THF (16 mL) was cooled to −78 °C and NaCNBH₃ (182 mg, 2.90 mmol, 10 equiv) was added. The solution was allowed to stir for 1.5 hours as it gradually warmed to −60 °C. The reaction was quenched with saturated aq. NH₄Cl solution (10 mL) and allowed to warm to room temperature. The mixture was diluted with water (20 mL) and extracted with EtOAc (30 mL). The layers were separated, and the aqueous phase was extracted once with EtOAc (20 mL). The combined organics were dried over Na₂SO₄, filtered, and concentrated. The crude residue was passed through a short column of silica (5–10% acetone:toluene) to remove residual cyanoborohydride reagent. The crude material was then purified by preparative TLC (silica gel, 10% acetone:toluene) to give naphthol **189** (88 mg, 0.11 mmol, 39%) and **15-epi-189** (43 mg, 0.056 mmol, 19%) as yellow powders.

**189**: Rₚ = 0.6 (silica gel, acetone:toluene 1:4); FT-IR (neat) ν_max = 3409, 2939, 1715, 1592, 1514, 1484, 1448, 1407, 1344, 1307, 1219, 1131, 1105, 1049, 994, 905, 735, 696 cm⁻¹; ¹H NMR (CDCl₃, 600 MHz) δ = 15.40 (s, 1 H), 7.62 – 7.56 (m, 2 H), 7.49 – 7.45 (m, 2 H), 7.42 – 7.39 (m, 2 H), 7.38 – 7.30 (m, 4 H), 6.66 (s, 1 H), 5.62 (bs, 1 H), 5.49 (bs, 1 H), 5.35 – 5.28 (m, 4 H), 3.84
(s, 3 H), 3.49 (d, $J = 18.8$ Hz, 1 H), 3.38 – 3.31 (m, 1 H), 3.35 (s, 3 H), 3.34 (s, 3 H), 3.16 (d, $J = 18.8$ Hz, 1 H), 3.09 (dd, $J = 18.8$, 7.4 Hz, 1 H), 2.82 (dd, $J = 18.8$, 8.4 Hz, 1 H), 2.23 (m, 1 H), 2.06 (m, 1 H), 1.79 (dd, $J = 12.3$, 12.3, 6.2 Hz, 1 H), 1.46 (s, 3 H), 1.36 (dd, $J = 12.3$, 5.9 Hz, 1 H), 0.94 (s, 3 H), 0.48 (s, 3 H) ppm; $^{13}$C NMR (CDCl$_3$, 151 MHz) $\delta = 193.8$, 184.3, 179.3, 168.4, 168.0, 159.5, 159.3, 148.3, 137.4, 136.5, 135.2, 134.5, 128.8, 128.60, 128.55, 128.2, 128.0, 126.9, 123.6, 123.2, 120.8, 109.0, 107.7, 106.3, 102.4, 98.1, 78.3, 72.4, 71.5, 58.5, 55.5, 51.2, 48.2, 45.1, 43.8, 38.1, 34.2, 25.8, 24.7, 23.5, 23.0, 21.1 ppm; HRMS (ESI) calcd for C$_{46}$H$_{45}$NO$_{10}$Na$^+$ [M$+$Na$^+$] 794.2936, found 794.2919.

15-epi-189: $R_f = 0.5$ (silica gel, acetone:toluene 1:4); FT-IR (neat) $\nu_{\text{max}} = 3400, 2940, 2921, 1717, 1593, 1514, 1485, 1448, 1408, 1370, 1345, 1306, 1235, 1219, 1130, 1104, 1048, 998, 904, 820, 735, 696$ cm$^{-1}$; $^1$H NMR (CDCl$_3$, 600 MHz) $\delta = 15.55$ (s, 1 H), 7.60 – 7.57 (m, 2 H), 7.49 – 7.47 (m, 2 H), 7.42 – 7.30 (m, 6 H), 6.65 (s, 1 H), 5.70 (s, 1 H), 5.52 (bs, 1 H), 5.33 (s, 2 H), 5.30 (s, 2 H), 3.85 – 3.80 (m, 4 H), 3.44 (s, 3 H), 3.35 (m, 1 H), 3.16 (dd, $J = 19.0$, 7.5 Hz, 1 H), 3.13 (s, 3 H), 2.97 (d, $J = 18.3$ Hz, 1 H), 2.87 (dd, $J = 19.0$, 10.0 Hz, 1 H), 2.23 (m, 1 H), 2.05 (m, 1 H), 1.84 (ddd, $J = 12.6$, 12.6, 6.1 Hz, 1 H), 1.51 (s, 3 H), 1.34 (dd, $J = 12.6$, 5.5 Hz, 1 H), 0.88 (s, 3 H), 0.42 (s, 3 H) ppm; $^{13}$C NMR (CDCl$_3$, 151 MHz) $\delta = 193.4$, 184.3, 179.2, 168.9, 168.0, 159.5, 159.3, 148.2, 137.2, 136.6, 135.14, 135.12, 128.8, 128.62, 128.60, 128.3, 128.0, 126.9, 123.5, 122.9, 121.3, 108.8, 107.3, 106.5, 102.5, 98.2, 78.4, 72.4, 71.6, 58.5, 55.5, 50.5, 48.0,
45.1, 43.4, 38.6, 34.1, 25.7, 24.01, 23.99, 23.0, 21.1 ppm; HRMS (ESI) calcd for C_{46}H_{45}NO_{10}Na^+ [M+Na^+] 794.2936, found 794.2944.

**Triketone 190:** To a solution of ketal 189 (23 mg, 0.029 mmol, 1.0 equiv) in THF (2.3 mL) was added 2 N aq. HCl (0.25 mL). The reaction mixture was stirred at room temperature for 5 hours and was then diluted with water (5 mL) and extracted with EtOAc (10 mL). The organic phase was washed with water (10 mL) and brine (10 mL), and then dried over Na$_2$SO$_4$, filtered, and concentrated to give analytically pure triketone 190 (21 mg, 0.029 mmol, quant.) as a yellow solid. Triketone 190 was found to be unstable on silica gel and was used without further purification. 190: $R_f = 0.7$ (silica gel, EtOAc:hexanes 2:3); FT-IR (neat) $\nu_{\text{max}} = 3448, 2962, 2918, 1696, 1609, 1585, 1513, 1481, 1446, 1402, 1344, 1327, 1292, 1258, 1199, 1158, 1132, 1108, 1037, 908, 825, 731, 696 \text{ cm}^{-1}$; $^1$H NMR (CDCl$_3$, 600 MHz) $\delta = 13.91$ (s, 1 H), 7.62 – 7.59 (m, 2 H), 7.46 – 7.42 (m, 2 H), 7.41 – 7.39 (m, 2 H), 7.36 (m, 1 H), 7.34 – 7.28 (m, 3 H), 6.77 (s, 1 H), 5.49 (bs, 1 H), 5.33 (s, 2 H), 5.29 (d, $J = 12.0$ Hz, 1 H, AB system), 5.26 (d, $J = 12.0$ Hz, 1 H, AB system), 4.94 (s, 1 H), 3.89 – 3.82 (m, 5 H), 3.66 (d, $J = 20.0$ Hz, 1 H), 3.33 (dd, $J = 17.3$, 4.8 Hz, 1 H), 3.15 (d, $J = 20.0$ Hz, 1 H), 2.19 (m, 1 H), 2.03 (m, 1 H), 1.80 (ddd, $J = 12.7$, 12.7, 6.2 Hz, 1 H), 1.45 (s, 3 H), 1.30 (dd, $J = 12.7$, 5.6 Hz, 1 H), 0.88 (s, 3 H), 0.30 (s, 3 H) ppm; $^{13}$C NMR (CDCl$_3$, 151 MHz) $\delta = 195.4, 192.0, 184.8, 181.7, 168.2, 164.6, 159.4, 159.2, 147.7, 142.4, 136.3, 136.2, 135.0, 128.9, 128.61, 128.60, 128.24, 128.21, 127.2, 127.1, 121.8,
Diol 191: To a solution of triketone 190 (98 mg, 0.14 mmol, 1.0 equiv) in anhydrous EtOAc:acetone (1:1, 13.4 mL) at room temperature was added sodium triacetoxyborohydride (34 mg, 0.16 mmol, 1.2 equiv) and the solution was warmed to 40 °C for 1 hour 45 minutes. The reaction mixture was then allowed to cool to room temperature, diluted with water (15 mL) and extracted with EtOAc (20 mL). The organic phase was washed with water (10 mL) and brine (10 mL), dried over Na₂SO₄, filtered, and concentrated. The residue was purified by preparative TLC (silica gel, 30% EtOAc:hexanes) to give the diol 191 (46 mg, 0.063 mmol, 47%) as a yellow foam. 191: Rᵥ = 0.5 (silica gel, EtOAc:hexanes 3:7); FT-IR (neat) νmax = 3475, 2961, 2920, 2855, 1693, 1662, 1586, 1512, 1483, 1446, 1403, 1341, 1293, 1260, 1199, 1162, 1132, 1113, 1036, 908, 732, 696 cm⁻¹; ¹H NMR (CDCl₃, 600 MHz) δ = 14.41 (s, 1 H), 7.62 – 7.60 (m, 2 H), 7.46 – 7.43 (m, 2 H), 7.40 – 7.31 (m, 6 H), 6.73 (s, 1 H), 5.49 (bs, 1 H), 5.36 (d, J = 12.1 Hz, 1 H, AB system), 5.33 (d, J = 12.1 Hz, 1 H, AB system), 5.27 (d, J = 11.7 Hz, 1 H, AB system), 5.23 (d, J = 11.7 Hz, 1 H, AB system), 4.59 (d, J = 3.9 Hz, 1 H), 4.17 (s, 1 H), 3.85 (s, 3 H), 3.82 (d, J = 17.6 Hz, 1 H), 3.67 (d, J = 6.9 Hz, 1 H), 3.54 (d, J = 19.5 Hz, 1 H), 3.24 (d, J = 19.5 Hz, 1 H), 2.92 (dd, J = 17.6, 6.9 Hz, 1 H), 2.19 (m, 1 H), 2.03 (m, 1 H), 1.82 (ddd, J = 12.7, 12.7, 6.0 Hz, 1 H), 1.68 (d, J = 3.9 Hz, 1 H), 1.46 (s, 3 H), 1.29 (dd, J = 12.7, 6.0 Hz, 1 H), 0.87 (s, 3 H), 0.31 (s, 3 H) ppm; ¹³C NMR (CDCl₃, 151 MHz) δ = 201.0, 193.0, 169.6, 169.3, 164.8,
159.4, 159.3, 148.0, 138.8, 136.5, 136.4, 135.7, 128.9, 128.70, 128.68, 128.5, 128.2, 127.1, 126.5, 124.2, 121.5, 110.0, 109.9, 103.8, 99.5, 77.1, 71.8, 71.7, 68.5, 59.6, 55.6, 50.5, 44.9, 38.5, 34.0, 25.5, 24.2, 23.0, 21.0, 18.7 ppm; HRMS (ESI) calcd for C_{44}H_{41}NO_{9}H^{+} [M+H^{+}] 728.2854, found 728.2828.

TBS ether 192: To a solution of diol 191 (33 mg, 0.045 mmol, 1.0 equiv) in CH$_2$Cl$_2$ (1.7 mL) was added freshly distilled 2,6-lutidine (80 µL, 0.68 mmol, 15 equiv). The reaction mixture was cooled to 0 °C, and freshly distilled TBSOTf (0.10 mL, 0.45 mmol, 10 equiv) was added. The reaction mixture was allowed to warm to room temperature and stirred for 15 minutes. Three additional portions of 2,6-lutidine (80 µL, each) and TBSOTf (0.10 mL, each) were added to the reaction flask in 15 minute intervals and the mixture was stirred for an additional 30 minutes. The reaction was then quenched with saturated aq. NaHCO$_3$ solution (5 mL) (vigorous bubbling) and extracted with CH$_2$Cl$_2$ (2 × 5 mL). The combined organics were dried over Na$_2$SO$_4$, filtered, and concentrated. Residual volatiles were then azeotropically removed with toluene (twice). The crude material was then purified by preparative TLC (silica gel, 5% acetone:toluene) to give the TBS ether 192 (23 mg, 0.027 mmol, 61%) as a yellow solid. 192: R$_f$ = 0.4 (silica gel, 5% acetone:toluene); FT-IR (neat) $v_{\text{max}}$ = 3479, 2927, 2856, 1697, 1656, 1605, 1589, 1510, 1473, 1448, 1405, 1343, 1295, 1260, 1205, 1166, 1135, 1082, 1048, 838, 779, 736, 697 cm$^{-1}$; $^1$H NMR (CDCl$_3$, 600 MHz) $\delta$ = 14.52 (s, 1 H), 7.61 – 7.57 (m, 2 H), 7.44 – 7.39 (m, 4 H), 7.37 – 7.31 (m, 4 H), 6.72 (s, 1 H), 5.49 (bs, 1 H), 5.35 (d, $J$ = 12.1 Hz, 1 H, AB system), 5.32 (d, $J$ = 12.1 Hz,
1 H, AB system), 5.28 (d, J = 11.5 Hz, 1 H, AB system), 5.21 (d, J = 11.5 Hz, 1 H, AB system),
4.55 (s, 1 H), 4.01 (s, 1 H), 3.91 (d, J = 17.9 Hz, 1 H), 3.84 (s, 3 H), 3.59 (d, J = 7.4 Hz, 1 H),
3.56 (d, J = 19.9 Hz, 1 H), 3.20 (d, J = 19.9 Hz, 1 H), 2.86 (dd, J = 17.9, 7.4 Hz, 1 H), 2.19 (m,
1 H), 2.03 (m, 1 H), 1.84 (m, 1 H), 1.44 (s, 3 H), 1.27 (m, 1 H), 0.88 (s, 3 H), 0.31 (s, 3 H), 0.30
(s, 9 H), –0.27 (s, 3 H), –0.54 (s, 3 H) ppm; $^{13}$C NMR (CDCl$_3$, 151 MHz) $\delta$ = 202.2, 191.8,
169.5, 169.4, 165.1, 159.3, 159.2, 147.9, 138.5, 136.6, 136.4, 135.5, 129.0, 128.8, 128.7, 128.6,
128.1, 127.1, 126.4, 124.5, 121.4, 110.4, 109.7, 104.5, 99.8, 77.8, 71.9, 71.8, 69.2, 59.6, 55.5,
50.2, 45.1, 38.5, 34.0, 25.5, 25.2, 24.2, 23.0, 20.9, 18.4, 17.7, –5.47, –5.50 ppm; HRMS (ESI)
calcd for C$_{50}$H$_{55}$NO$_9$SiH$^+$ [M+H$^+$] 842.3719, found 842.3705.

**Diol 193**: A solution of TBS ether 192 (50 mg, 0.059 mmol, 1.0 equiv) in THF (1.1 mL) was
cooled to –78 °C, and KHMDS solution (1 M in THF, 0.20 mL, 0.20 mmol, 3.4 equiv) was
added dropwise. After stirring for 1 hour at –78 °C, freshly recrystallized (from EtOAc) Davis
oxaziridine$^{[35]}$ (60 mg, 0.23 mmol, 3.9 equiv) in THF (0.3 mL) was added, and the mixture was
stirred for 1 hour 40 minutes at –78 °C. The reaction was quenched by addition of MeOH
(0.2 mL), followed by dimethyl sulfide (0.1 mL) and saturated aq. NH$_4$Cl solution (2.0 mL). The
mixture was extracted with CH$_2$Cl$_2$ (3 × 15 mL), and the combined organic layers were dried
over MgSO$_4$, filtered, and concentrated. Purification by preparative TLC (silica gel, 10%
acetone:toluene, then 1.25% acetone:CH$_2$Cl$_2$ for the recovered starting material and 5%
acetone:CH$_2$Cl$_2$ for the product) afforded diol 193 (10 mg, 0.012 mmol, 20%) as an orange solid
and recovered starting material 192 (23 mg, 0.027 mmol, 45%). 193: \( R_f = 0.4 \) (silica gel, acetone:toluene 1:9); FT-IR (neat) \( \nu_{\text{max}} = 3460, 2921, 2856, 1702, 1606, 1588, 1509, 1473, 1447, 1403, 1340, 1320, 1267, 1205, 1136, 1050, 910, 838, 780, 734, 696 \text{ cm}^{-1}; \) \(^1\)H NMR (CDCl\(_3\), 600 MHz) \( \delta = 14.10 \) (s, 1 H), 7.59 – 7.57 (m, 2 H), 7.45 – 7.39 (m, 4 H), 7.38 – 7.33 (m, 4 H), 6.72 (s, 1 H), 5.50 (bs, 1 H), 5.36 (d, \( J = 12.4 \) Hz, 1 H, AB system), 5.33 (d, \( J = 12.4 \) Hz, 1 H, AB system), 5.28 (d, \( J = 11.4 \) Hz, 1 H, AB system), 5.20 (d, \( J = 11.4 \) Hz, 1 H, AB system), 4.62 (s, 1 H), 4.30 (s, 1 H), 4.15 (d, \( J = 17.6 \) Hz, 1 H), 3.84 (s, 3 H), 3.55 (d, \( J = 19.4 \) Hz, 1 H), 3.22 (d, \( J = 19.4 \) Hz, 1 H), 3.01 (s, 1 H), 2.68 (d, \( J = 17.6 \) Hz, 1 H), 2.19 (m, 1 H), 2.03 (m, 1 H), 1.84 (m, 1 H), 1.46 (s, 3 H), 1.28 (m, 1 H), 0.88 (s, 3 H), 0.35 (s, 3 H), 0.31 (s, 9 H), −0.26 (s, 3 H), −0.54 (s, 3 H) ppm; \(^{13}\)C NMR (CDCl\(_3\), 151 MHz) \( \delta = 200.8, 190.2, 169.7, 169.1, 164.2, 159.2, 159.1, 147.8, 140.4, 136.6, 136.4, 135.4, 129.1, 128.81, 128.76, 128.6, 128.1, 127.1, 126.5, 123.2, 121.4, 110.6, 109.8, 104.3, 100.1, 80.8, 77.5, 72.0, 71.8, 68.5, 59.7, 55.5, 44.9, 38.6, 34.0, 28.7, 25.4, 25.2, 24.2, 23.0, 20.9, 17.7, −5.4, −5.6 ppm; HRMS (ESI) calcd for C\(_{50}H_{55}NO_{10}SiH^+\) \([M+H^+]\) 858.3668, found 858.3664.

**Triol 194/194'**: Diol 193 (13.3 mg, 15.5 \( \mu \)mol, 1.0 equiv) was dissolved in MeCN (0.4 mL) in a plastic vial and cooled to 0 °C. HF•pyridine (70% HF in pyridine, 0.02 mL) was added, and the mixture was warmed to 50–55 °C. After 1 hour, 14 hours, and 20 hours, an additional portion of HF•pyridine (70% HF in pyridine, 0.05 mL each) was added. After 25 hours the reaction was
allowed to cool to room temperature, diluted with EtOAc (5 mL), and carefully quenched with saturated aq. NaHCO₃ solution (5 mL). The organic phase was separated, and the aqueous phase was extracted with EtOAc (2 × 15 mL). The combined organic phases were dried over MgSO₄, filtered, and concentrated. Purification by preparative TLC (silica gel, 20% acetone:toluene) afforded triol 194/194' (7.1 mg, 9.5 µmol, 61%) as a yellow solid.* 194/194': Rᶠ = 0.4 (silica gel, acetone:toluene 1:9); FT-IR (neat) νₑₘₐₓ = 3460, 2923, 1698, 1590, 1513, 1483, 1448, 1403, 1341, 1323, 1264, 1205, 1134, 1044, 816, 738, 697 cm⁻¹; ¹H NMR (CDCl₃, 600 MHz, 298 K) δ = 14.01 (bs, 1 H), 7.61 – 7.58 (m, 2 H), 7.46 – 7.28 (m, 8 H), 6.73 (s, 1 H), 5.49 (bs, 1 H), 5.34 (d, J = 12.1 Hz, 1 H, AB system), 5.31 (d, J = 12.1 Hz, 1 H, AB system), 5.35 – 5.10 (m, 2 H), 4.68 (bs, 1 H), 4.43 (bs, 1 H), 3.99 (bs, 1 H), 3.85 (s, 3 H), 3.52 (bs, 1 H), 3.22 (bs, 1 H), 3.08 (bs, 1 H), 2.76 (d, J = 17.3 Hz, 1 H), 2.19 (m, 1 H), 2.03 (m, 1 H), 1.83 (m, 1 H), 1.46 (s, 3 H), 1.29 (m, 1 H), 0.87 (s, 3 H), 0.35 (bs, 3 H) ppm; ¹H NMR (CDCl₃, 500 MHz, 233 K) δ = 14.27 (s, 1 H, B), 14.02 (s, 1 H, A), 7.62 – 7.28 (m, 10 H, A + 10 H, B), 6.76 (s, 1 H, B), 6.68 (s, 1 H, A), 5.50 (bs, 1 H, B), 5.45 (bs, 1 H, A), 5.40 – 4.40 (m), 4.01 (d, J = 17.6 Hz, 1 H, A), 3.97 (d, J = 19.7 Hz, 1 H, B), 3.91 (s, 3 H, B), 3.83 (s, 3 H, A), 3.48 (d, J = 19.8 Hz, 1 H, A), 3.34 (bs), 3.23 (d, J = 19.8 Hz, 1 H, A), 3.05 (d, J = 18.5 Hz, 1 H, B), 2.99 (d, J = 19.7 Hz, 1 H, B), 2.88 (bs), 2.80 (d, J = 18.5 Hz, 1 H, B), 2.77 (d, J = 17.6 Hz, 1 H, A), 2.24 – 1.70 (m), 1.57 – 1.52 (m), 1.45 (s, 3 H, B), 1.39 (s, 3 H, A), 1.34 – 1.28 (m), 0.89 (s, 3 H, B), 0.82 (s, 3 H, A), 0.37 (s, 3 H, B), 0.27 (s, 3 H, A) ppm; ¹³C NMR (151 MHz, CDCl₃, 298 K) δ = 199.7, 169.3, 159.2, 147.7, 136.4, 128.9, 128.7, 128.5, 128.2, 127.0, 121.6, 109.9, 99.7, 71.8, 71.6, 59.7, 55.6, 44.6, 38.5, 33.9, 33.5, 32.1, 29.6, 29.5, 29.4, 29.2, 25.5, 24.8, 24.2, 22.93, 22.85, 21.0 ppm; HRMS (ESI) calcd for C₄₄H₄₁NO₁₀H⁺ [M+H⁺] 744.2803, found 744.2794.
We surmise that hydroxy ketone 194 exists in equilibrium with its cyclic hemiacetal isomer 194'. At T = 298 K, slow interconversion between these two species is observed in CDCl₃, which results in broad signals in the ¹H and ¹³C NMR spectra. Due to signal broadening, not all the ¹³C signals could be identified. The signals become sharper and split into two sets when the sample is cooled to T = 233 K. Wherever possible, the signals observed in the ¹H NMR at T = 233 K are reported with their corresponding integrals and assigned to signal set A or B.

Triketone 195: A solution of triol 194/194' (7.1 mg, 9.6 µmol, 1.0 equiv) in DCE (0.5 mL) was cooled to 0 °C, and Dess–Martin periodinane[36] (4.6 mg, 11 µmol, 1.2 equiv) was added. After stirring for 30 minutes at 0 °C, the mixture was stirred at room temperature for 1.5 hours. The reaction mixture was then warmed up to 50 °C, and three additional portions of Dess–Martin periodinane (2.3 mg, 5.4 µmol, 0.6 equiv each) were added in 1 hour intervals. After 5 hours at 50 °C, TLC analysis indicated complete conversion. The reaction mixture was allowed to cool to room temperature, and the reaction was then quenched with saturated aq. NaHCO₃:saturated aq. Na₂S₂O₃ solution (1:1). The phases were separated, and the aqueous phase was extracted with CH₂Cl₂ (2 × 10 mL). The combined organic phases were washed with brine (10 mL), dried over MgSO₄, filtered, and concentrated. Purification by preparative TLC (silica gel, 5% acetone:CH₂Cl₂) afforded triketone 195 (4.7 mg, 6.3 µmol, 66%) as a yellow powder. 195: R₇ = 0.5 (silica gel, acetone:toluene 1:9); FT-IR (neat) νmax = 3451, 2919, 1715, 1613, 1586, 1516,
1485, 1447, 1342, 1274, 1203, 1186, 1140, 1091, 1027, 965, 737, 696 cm⁻¹; ¹H NMR (CD₂Cl₂, 600 MHz) δ = 14.11 (s, 1 H), 7.61 – 7.58 (m, 2 H), 7.54 – 7.42 (m, 2 H), 7.47 – 7.39 (m, 5 H), 7.36 (m, 1 H), 6.85 (s, 1 H), 5.54 (bs, 1 H), 5.40 – 5.35 (m, 2 H), 5.35 – 5.30 (m, 2 H), 4.63 (bs, 1 H), 4.29 (bs, 1 H), 4.04 (d, J = 19.8 Hz, 1 H), 3.90 (s, 3 H), 3.42 (d, J = 18.4 Hz, 1 H), 3.16 (d, J = 18.4 Hz, 1 H), 3.06 (d, J = 19.8 Hz, 1 H), 2.24 (m, 1 H), 2.08 (m, 1 H), 1.89 (ddd, J = 12.9, 12.9, 6.2 Hz, 1 H), 1.49 (s, 3 H), 1.40 (dd, J = 12.9, 5.7 Hz, 1 H), 0.94 (s, 3 H), 0.46 (s, 3 H) ppm; ¹³C NMR (CD₂Cl₂, 151 MHz) δ = 194.9, 194.7, 185.1, 179.1, 167.9, 166.8, 160.4, 159.8, 147.8, 143.7, 136.7, 136.4, 135.4, 129.2, 129.04, 129.03, 128.96, 128.4, 127.5, 127.4, 122.0, 118.2, 110.4, 108.6, 106.4, 100.6, 83.9, 81.0, 73.1, 71.9, 60.2, 56.0, 44.5, 38.6, 34.8, 34.4, 25.6, 24.4, 23.3, 20.9 ppm; HRMS (ESI) calcd for C₄₄H₃₉NO₁₀H⁺ [M+H⁺] 742.2647, found 742.2648.

**Synthetic viridicatumtoxin B [(±)-1]:** Using a procedure similar to the one reported by Myers,³⁸ trikетone 195 (4.7 mg, 6.3 µmol, 1.0 equiv) was dissolved in freshly distilled 1,4-dioxane:MeOH (1:1, 1.2 mL) under argon and Pd black (3.3 mg, 31 µmol, 4.9 equiv) was added. The suspension was degassed, placed under a hydrogen atmosphere, and stirred for 8 minutes at room temperature, after which the hydrogen was removed by flushing the flask with argon. The suspension was then filtered (Celite®, MeOH:CH₂Cl₂ 1:9), and the filtrate was concentrated to afford analytically pure synthetic viridicatumtoxin B [(±)-1] (3.5 mg, 6.2 µmol, 98%) as a yellow solid. (±)-1: R_f = 0.1 (silica gel, MeOH:CH₂Cl₂ 1:9); FT-IR (neat) ν_max = 3423, 2921, 2855,
1623, 1587, 1491, 1449, 1400, 1260, 1190, 1142, 1089, 798 cm⁻¹; ¹H NMR (CDCl₃, 600 MHz) δ = 17.92 (s, 1 H), 14.72 (s, 1 H), 9.20 (s, 1 H), 8.74 (s, 1 H), 6.80 (s, 1 H), 5.97 (s, 1 H), 5.53 (s, 1 H), 4.89 (s, 1 H), 4.18 (s, 1 H), 4.03 (d, J = 19.8 Hz, 1 H), 3.90 (s, 3 H), 3.11 (bd, J = 18.8 Hz, 1 H), 3.04 (d, J = 19.8 Hz, 1 H), 2.81 (bd, J = 18.8 Hz, 1 H), 2.22 (m, 1 H), 2.07 (m, 1 H), 1.86 (m, 1 H), 1.46 (s, 3 H), 1.40 (m, 1 H), 0.93 (s, 3 H), 0.46 (s, 3 H) ppm; ¹³C NMR (CDCl₃, 151 MHz) δ = 195.2, 194.3, 192.8, 188.7, 173.0, 165.4, 161.3, 158.4, 146.4, 144.8, 135.8, 127.3, 122.0, 117.0, 107.3, 106.8, 102.6, 99.7, 80.7, 77.7, 60.6, 55.8, 44.6, 42.1, 38.5, 34.2, 25.6, 24.4, 23.0, 20.9 ppm; HRMS (ESI) calcd for C₃₀H₂₉NO₁₀H⁺ [M+H⁺] 564.1864, found 564.1865.
Comparison of NMR Spectroscopic Data of Natural and Synthetic Viridicatumtoxin B [(±)-1]

$^1$H NMR spectroscopic data from reference 39 compared to those of synthetic 1:

| Proton  | Natural viridicatumtoxin B (CDCl$_3$, 500 MHz)$^{[39]}$ | Synthetic viridicatumtoxin B [CDCl$_3$, 600 MHz, $\delta$(CHCl$_3$) = 7.26 ppm] | $\Delta$ (ppm) |
|---------|-------------------------------------------------|--------------------------------------------------------------------------------|----------------|
| C3-OH   | –                                               | 17.92 (bs, 1 H)                                                              | –              |
| C11-OH  | –                                               | 14.72 (bs, 1 H)                                                              | –              |
| C13-NH  | –                                               | 9.20 (bs, 1 H)                                                               | –              |
| C10-OH  | –                                               | 8.74 (bs, 1 H)                                                               | –              |
| H9      | 6.79 (s, 1 H)                                   | 6.80 (s, 1 H)                                                                | –0.01          |
| C13-NH' | –                                               | 5.97 (bs, 1 H)                                                               | –              |
| H17     | 5.52 (m, 1 H)                                   | 5.53 (bs, 1 H)                                                               | –0.01          |
| C12a-OH | –                                               | 4.89 (bs, 1 H)                                                               | –              |
| C4a-OH  | –                                               | 4.18 (bs, 1 H)                                                               | –              |
| H14     | 4.02 (d, $J$ = 19.8 Hz, 1 H)                    | 4.03 (d, $J$ = 19.8 Hz, 1 H)                                                 | –0.01          |
| H24     | 3.89 (s, 3 H)                                   | 3.90 (s, 3 H)                                                                | –0.01          |
| H4      | 3.12 (d, $J$ = 20.4 Hz, 1 H)                    | 3.11 (bd, $J$ = 18.8 Hz, 1 H)                                                | 0.01           |
| H14'    | 3.01 (d, $J$ = 19.8 Hz, 1 H)                    | 3.04 (d, $J$ = 19.8 Hz, 1 H)                                                 | –0.03          |
| H4'     | 2.84 (d, $J$ = 20.4 Hz, 1 H)                    | 2.81 (bd, $J$ = 18.8 Hz, 1 H)                                                | 0.03           |
| H18     | 2.25 (m, 1 H)                                   | 2.22 (m, 1 H)                                                                | 0.03           |
| H18'    | 2.08 (m, 1 H)                                   | 2.07 (m, 1 H)                                                                | 0.01           |
| H19     | 1.88 (m, 1 H)                                   | 1.86 (m, 1 H)                                                                | 0.02           |
| H21     | 1.46 (s, 3 H)                                   | 1.46 (s, 3 H)                                                                | 0.00           |
| H19'    | 1.41 (m, 1 H)                                   | 1.40 (m, 1 H)                                                                | 0.01           |
| H22     | 0.92 (s, 3 H)                                   | 0.93 (s, 3 H)                                                                | –0.01          |
| H23     | 0.46 (s, 3 H)                                   | 0.46 (s, 3 H)                                                                | 0.00           |

*The chemical shifts of hydroxyl and amide protons are not reported in reference 39. For a comparison of $^1$H NMR spectra of natural viridicatumtoxin B (CDCl$_3$, 300 MHz, kindly provided by Professor W.-G. Kim) and synthetic viridicatumtoxin B (CDCl$_3$, 600 MHz), see S258–S259.
$^{13}$C NMR spectroscopic data from reference 39 compared to those of synthetic 1:

| Carbon | Natural viridicatumtoxin B (CDCl$_3$, 226 MHz)$^{[39]}$ | Synthetic viridicatumtoxin B (CDCl$_3$, 151 MHz) $\delta$(CDCl$_3$) = 77.16 ppm | \( \Delta \) (ppm) |
|--------|-------------------------------------------------|---------------------------------------------------------------------------------|-----------------|
| C12    | 195.1                                          | 195.2                                                                          | –0.1            |
| C5 (observed) | –                              | 194.3                                                                          | –               |
| C3     | 192.9                                          | 192.8                                                                          | 0.1             |
| C1     | 188.6                                          | 188.7                                                                          | –0.1            |
| C13    | 172.9                                          | 173.0                                                                          | –0.1            |
| C11    | 165.3                                          | 165.4                                                                          | –0.1            |
| C8     | 161.2                                          | 161.3                                                                          | –0.1            |
| C10    | 158.4                                          | 158.4                                                                          | 0.0             |
| C6a    | 146.0                                          | 146.4                                                                          | –0.4            |
| C5a    | 144.8                                          | 144.8                                                                          | 0.0             |
| C16    | 135.7                                          | 135.8                                                                          | –0.1            |
| C10a   | 127.2                                          | 127.3                                                                          | –0.1            |
| C17    | 121.9                                          | 122.0                                                                          | –0.1            |
| C6     | 116.9                                          | 117.0                                                                          | –0.1            |
| C5 (reported) | 116.4                            | –                                                                              | –               |
| C7     | 106.8                                          | 107.3                                                                          | –0.5            |
| C11a   | 106.6                                          | 106.8                                                                          | –0.2            |
| C9     | 102.5                                          | 102.6                                                                          | –0.1            |
| C2     | 99.9                                           | 99.7                                                                           | 0.2             |
| C12a   | 80.7                                           | 80.7                                                                           | 0.0             |
| C4a    | 77.8                                           | 77.7                                                                           | 0.1             |
| C15    | 60.6                                           | 60.6                                                                           | 0.0             |
| C24    | 55.7                                           | 55.8                                                                           | –0.1            |
| C14    | 44.5                                           | 44.6                                                                           | –0.1            |
| C4     | 42.1                                           | 42.1                                                                           | 0.0             |
| C20    | 38.4                                           | 38.5                                                                           | –0.1            |
| C19    | 34.1                                           | 34.2                                                                           | –0.1            |
| C23    | 25.5                                           | 25.6                                                                           | –0.1            |
| C22    | 24.3                                           | 24.4                                                                           | –0.1            |
| C18    | 22.8                                           | 23.0                                                                           | –0.2            |
| C21    | 21.0                                           | 20.9                                                                           | 0.1             |
**$^{13}$C NMR spectroscopic data from the authentic spectrum compared to those of synthetic 1:**

| Carbon | Natural viridicatumtoxin B (CDCl$_3$, 226 MHz)$^\dagger$ | Synthetic viridicatumtoxin B (CDCl$_3$, 151 MHz) $\delta$(CDCl$_3$) = 77.018 ppm | $\Delta$ (ppm) |
|--------|----------------------------------------------------------|-----------------------------------------------------------------|----------------|
| C12    | 195.10$^\ast$                                           | 195.08                                                          | 0.0           |
| C5     | not reported                                             | 194.13                                                          | –             |
| C3     | 192.9                                                   | 192.70                                                          | 0.2           |
| C1     | 188.62$^\ast$                                           | 188.61                                                          | 0.0           |
| C13    | 172.90$^\ast$                                           | 172.89                                                          | 0.0           |
| C11    | 165.3                                                  | 165.23                                                          | 0.1           |
| C8     | 161.20$^\ast$                                           | 161.18                                                          | 0.0           |
| C10    | 158.26$^\ast$                                           | 158.23                                                          | 0.0           |
| C6a    | 146.28$^\ast$                                           | 146.27                                                          | 0.0           |
| C5a    | 144.8                                                   | 144.66                                                          | 0.1           |
| C16    | 135.62$^\ast$                                           | 135.61                                                          | 0.0           |
| C10a   | 127.21$^\ast$                                           | 127.18                                                          | 0.0           |
| C17    | 121.86$^\ast$                                           | 121.83                                                          | 0.0           |
| C6     | 116.9                                                   | 116.90                                                          | 0.0           |
| C7     | 107.18$^\ast$                                           | 107.15                                                          | 0.0           |
| C11a   | 106.73$^\ast$                                           | 106.71                                                          | 0.0           |
| C9     | 102.46$^\ast$                                           | 102.44                                                          | 0.0           |
| C2     | 99.9                                                    | 99.55                                                           | 0.4           |
| C12a   | 80.54$^\ast$                                           | 80.53                                                           | 0.0           |
| C4a    | 77.8                                                    | 77.58                                                           | 0.2           |
| C15    | 60.50$^\ast$                                           | 60.47                                                           | 0.0           |
| C24    | 55.70$^\ast$                                           | 55.70                                                           | 0.0           |
| C14    | 44.5                                                    | 44.47                                                           | 0.0           |
| C4     | 42.03$^\ast$                                           | 42.00                                                           | 0.0           |
| C20    | 38.32$^\ast$                                           | 38.31                                                           | 0.0           |
| C19    | 34.1                                                    | 34.03                                                           | 0.1           |
| C23    | 25.48$^\ast$                                           | 25.48                                                           | 0.0           |
| C22    | 24.32$^\ast$                                           | 24.30                                                           | 0.0           |
| C18    | 22.84$^\ast$                                           | 22.83                                                           | 0.0           |
| C21    | 20.76$^\ast$                                           | 20.77                                                           | 0.0           |

$^\dagger$Chemical shifts marked with $^\ast$ were taken from a scanned authentic $^{13}$C NMR spectrum of viridicatumtoxin B kindly provided by Prof. W.-G. Kim (see S260). The provided spectrum was referenced to 77.018 ppm and contained a partial peak listing. Chemical shifts without $^\ast$ were not included in this peak listing and are taken from reference 39. Some discrepancies between the tabulated data in reference 39 and the chemical shifts in the authentic $^{13}$C NMR spectrum were observed. In particular, although the crucial $^{13}$C NMR signal of C5 near 194 ppm was visible in the authentic $^{13}$C NMR spectrum, its chemical shift was not reported.
Viridicatumtoxin analogs **V2–V4** were prepared via hydrogenation of their isoxazole, dimethyl ketal precursors, the latter moieties of which were found to undergo ketal hydrolysis during reverse phase HPLC purification.

**Viridicatumtoxin analog V2**: To a stirred solution of **189** (30 mg, 0.048 mmol, 1.0 equiv) in 1,4-dioxane:MeOH (4 mL, 1:1) was added Pd black (28 mg, 0.27 mmol, 5.6 equiv) under argon. The flask headspace was exchanged for H₂, and the reaction mixture was stirred for 10 minutes at room temperature. The flask headspace was re-exchanged for argon, and the mixture was filtered through Celite® and concentrated to give crude **V2** (30 mg). A portion of this material was purified by reverse-phase prep-HPLC [Waters Atlantis prep T3 OBD, 16 × 150 mm, 5 µm particle size, 20 mL/min, 50% MeCN in H₂O (0→15 min), then ramp to 70% MeCN (15→25 min), 0.07% TFA buffer, λ = 288 nm]: t<sub>R</sub> = 17.59 min, to provide pure **V2** (9.5 mg, 17 µmol). **V2**: R<sub>f</sub> = 0.1 (silica gel, MeOH:CH₂Cl₂ 1:19); FT-IR (neat) ν<sub>max</sub> = 3435, 2921, 1685, 1623, 1585, 1492, 1448, 1399, 1281, 1259, 1198, 1162, 1133, 1069, 904, 733 cm<sup>−1</sup>; <sup>1</sup>H NMR (CDCl₃, 600 MHz) δ = 18.21 (s, 1 H), 14.49 (s, 1 H), 9.02 (s, 1 H), 8.71 (s, 1 H), 6.79 (s, 1 H), 5.73 (s, 1 H), 5.50 (s, 1 H), 4.82 (s, 1 H), 3.88 (s, 3 H), 3.71 (d, J = 20.1 Hz, 1 H), 3.56 (t, J = 4.4 Hz, 1 H), 3.35 (dd, J = 18.0, 3.9 Hz, 1 H), 3.20 (d, J = 20.1 Hz, 1 H), 3.15 (dd, J = 18.0, 5.0 Hz, 1 H), 2.20 (m, 1 H), 2.04 (m, 1 H), 1.81 (td, J = 12.6, 6.1 Hz, 1 H), 1.45 (s, 3 H), 1.32 (dd, J = 12.6, 6.1 Hz, 1 H), 0.90 (s, 3 H), 0.34 (s, 3 H) ppm; <sup>13</sup>C NMR (CDCl₃, 151 MHz) δ = 196.6, 196.5, 192.6, 189.8, 173.7, 163.5, 160.9, 158.1, 146.7, 143.6, 135.9, 127.0, 121.7, 120.7, 106.9,
106.9, 102.4, 99.8, 77.4, 60.4, 55.8, 50.4, 45.6, 38.5, 34.1, 29.3, 25.5, 24.3, 22.9, 21.0 ppm; HRMS (ESI) calcd for C$_{30}$H$_{29}$NO$_9$H$^+$ [M+H$^+$] 548.1915, found 548.1902.

**Viridicatumtoxin analog V3:** To a stirred solution of 15-epi-189 (44 mg, 0.057 mmol, 1.0 equiv) in 1,4-dioxane:MeOH (5 mL, 1:1) was added Pd black (42 mg, 0.40 mmol, 7 equiv) under argon. The flask headspace was exchanged for H$_2$, and the reaction mixture was stirred for 10 minutes at room temperature. The flask headspace was re-exchanged for argon, and the mixture was filtered through Celite® and concentrated to give crude V3 (40 mg). A portion of this material was purified by reverse-phase prep-HPLC [Waters Atlantis prep T3 OBD, 16 × 150 mm, 5 µm particle size, 20 mL/min, 50% MeCN in H$_2$O (0→15 min), then ramp to 70% MeCN (15→25 min), 0.07% TFA buffer, $\lambda = 288$ nm]: $t_R = 17.51$ min, to provide pure V3 (11 mg, 20 µmol). **V3:** $R_f = 0.1$ (silica gel, MeOH:CH$_2$Cl$_2$ 1:19); FT-IR (neat) $\nu_{max} = 3414, 2923, 1681, 1622, 1585, 1452, 1401, 1283, 1261, 1203, 1134, 1070, 909, 730$ cm$^{-1}$; $^1$H NMR (CDCl$_3$, 600 MHz) $\delta = 18.22$ (s, 1 H), 14.60 (s, 1 H), 9.05 (s, 1 H), 8.74 (s, 1 H), 6.79 (s, 1 H), 5.73 (s, 1 H), 5.49 (s, 1 H), 5.47 (bs, 1 H), 3.88 (s, 3 H), 3.85 (m, 1 H), 3.44 (t, $J = 4.6$ Hz, 1 H), 3.36 (dd, $J = 18.1, 2.3$ Hz, 1 H), 3.14 (dd, $J = 18.1, 5.0$ Hz, 1 H), 3.08 (d, $J = 20.0$ Hz, 1 H), 2.19 (m, 1 H), 2.04 (m, 1 H), 1.83 (td, $J = 12.6, 6.2$ Hz, 1 H), 1.41 (s, 3 H), 1.36 (dd, $J = 12.6, 5.9$ Hz, 1 H), 0.91 (s, 3 H), 0.39 (s, 3 H) ppm; $^{13}$C NMR (CDCl$_3$, 151 MHz) $\delta = 196.5, 196.3, 192.6, 189.8, 173.6, 164.0, 161.0, 158.1, 146.9, 143.6, 135.9, 127.1, 121.8, 120.6, 107.0, 106.9, 102.4, 99.9,
77.3, 60.4, 55.8, 50.5, 45.4, 38.5, 34.1, 29.5, 25.5, 24.6, 23.0, 20.8 ppm; HRMS (ESI) calcd for C\textsubscript{30}H\textsubscript{29}NO\textsubscript{9}H\textsuperscript{+} [M+H\textsuperscript{+}] 548.1915, found 548.1894.

**Viridicatumtoxin analog V4**: To a stirred solution of 15-*epi*-133 (40 mg, 0.058 mmol, 1.0 equiv) in 1,4-dioxane:MeOH (5 mL, 1:1) was added Pd black (43 mg, 0.40 mmol, 7 equiv) under argon. The flask headspace was exchanged for H\textsubscript{2}, and the reaction mixture was stirred for 10 minutes at room temperature. The flask headspace was re-exchanged for argon, and the mixture was filtered through Celite® and concentrated to give crude V4 (44 mg). A portion of this material was purified by reverse-phase prep-HPLC [Waters Atlantis prep T3 OBD, 16 × 150 mm, 5 µm particle size, 20 mL/min, 50% MeCN in H\textsubscript{2}O (0 → 15 min), then ramp to 70% MeCN (15 → 25 min), 0.07% TFA buffer, λ = 288 nm]: t\textsubscript{R} = 14.25 min, to provide pure V4 (8.8 mg, 16 µmol). V4: R\textsubscript{f} = 0.1 (silica gel, MeOH:CH\textsubscript{2}Cl\textsubscript{2} 1:19); FT-IR (neat) \nu\textsubscript{max} = 3400, 2939, 1683, 1585, 1466, 1400, 1342, 1285, 1216, 1187, 1163, 1132, 1068, 914, 824, 731 cm\textsuperscript{-1}; ¹H NMR (CDCl\textsubscript{3}, 600 MHz) \delta = 18.19 (s, 1 H), 14.20 (s, 1 H), 9.06 (s, 1 H), 6.72 (s, 1 H), 5.72 (s, 1 H), 5.49 (s, 1 H), 4.93 (s, 1 H), 4.09 (s, 3 H), 3.94 (s, 3 H), 3.86 (d, J = 19.9 Hz, 1 H), 3.44 (t, J = 4.5 Hz, 1 H), 3.36 (dd, J = 18.1, 4.0 Hz, 1 H), 3.13 (dd, J = 18.1, 5.1 Hz, 1 H), 3.08 (d, J = 19.9 Hz, 1 H), 2.20 (m, 1 H), 2.05 (m, 1 H), 1.85 (td, J = 12.5, 6.1 Hz, 1 H), 1.42 (s, 3 H), 1.34 (dd, J = 12.5, 6.2 Hz, 1 H), 0.91 (s, 3 H), 0.37 (s, 3 H) ppm; ¹³C NMR (CDCl\textsubscript{3}, 151 MHz) \delta = 196.2, 196.1, 193.1, 190.0, 173.6, 165.0, 160.4, 159.6, 148.1, 142.1, 136.2, 126.9, 121.6, 121.5,
110.0, 107.9, 99.9, 98.1, 77.2, 56.8, 55.6, 50.5, 45.2, 38.5, 34.0, 29.4, 25.5, 24.5, 23.0, 20.8 ppm; HRMS (ESI) calcd for C$_{31}$H$_{31}$NO$_9$H$^+$ [M+H$^+$] 562.2072, found 562.2082.

Viridicatumtoxin analogs V5 and V6 were prepared according to Scheme S-1 shown below.

Scheme S-1: Synthesis of viridicatumtoxin analogs V5 and V6.$^a$

$^a$Reagents and conditions: a) NaCNBH$_3$ (4.0 equiv), AcOH, 25 °C, 25 minutes, 31% for S5, 27% for 5-epi-S5; b) H$_2$ balloon, Pd black (4.1 equiv), THF:MeOH 1:1, 25 °C, 10 min, 96%; c) H$_2$, Pd black (4.5 equiv), THF:MeOH 1:1, 25 °C, 10 min, quant.

S5 and 5-epi-S5: This reaction was run twice in parallel. To two separate batches of substrate 189 (25 mg each, 0.032 mmol each, 1.0 equiv each) was added solid NaCNBH$_3$ (8 mg each, 0.13 mmol each, 4.0 equiv each). Then, AcOH (2.5 mL each) was rapidly injected into the reaction vessel, and the mixture was vigorously stirred at room temperature for 25 minutes. The two reaction mixtures were combined for work up by pouring them into water (25 mL). Brine
(5 mL) was added, and the mixture was extracted with EtOAc (35 mL). The organic phase was washed with additional brine (2 × 25 mL), and the organic layer was dried over Na₂SO₄, filtered and concentrated. The crude residue was purified by preparative TLC (silica gel, 10% acetone:toluene) to provide S₅ (26 mg, not pure) and isomer 5-epi-S₅ (13 mg, 0.017 mmol, 27%, yellow foam). Product S₅ was further purified by preparative TLC (silica gel, 5% EtOAc:CH₂Cl₂) to give pure compound S₅ (15 mg, 0.020 mmol, 31%) as a yellow foam.

S₅: R_f = 0.6 (silica gel, acetone:toluene 3:17); FT-IR (neat) ν_max = 3397, 2916, 1702, 1591, 1512, 1481, 1448, 1405, 1371, 1339, 1319, 1254, 1195, 1143, 1109, 1081, 1032, 986, 914, 812, 734, 695 cm⁻¹; ¹H NMR (C₆D₆, 500 MHz) δ = 15.00 (s, 1 H), 7.58 – 7.55 (m, 2 H), 7.28 – 7.25 (m, 2 H), 7.24 – 7.20 (m, 2 H), 7.12 (m, 1 H), 7.05 – 6.98 (m, 3 H), 6.26 (s, 1 H), 5.56 (s, 1 H), 5.14 (d, J = 12.2 Hz, 1 H, AB system), 5.10 (d, J = 12.2 Hz, 1 H, AB system), 4.89 (ap s, 3 H), 4.34 (d, J = 8.6 Hz, 1 H), 3.56 (d, J = 17.6 Hz, 1 H), 3.26 (s, 3 H), 2.85 (s, 3 H), 2.83 (m, 1 H), 2.77 – 2.64 (m, 3 H), 2.31 (m, 1 H), 2.04 (m, 1 H), 1.91 (ddd, J = 12.3, 12.3, 6.1 Hz, 1 H), 1.65 (s, 3 H), 1.37 (dd, J = 13.2, 6.0 Hz, 1 H), 1.15 (s, 3 H), 0.69 (s, 3 H) ppm; ¹³C NMR (C₆D₆, 126 MHz) δ = 197.0, 185.4, 180.3, 168.6, 166.3, 159.7, 158.8, 149.2, 137.9, 137.2, 135.7, 132.5, 128.9, 128.7, 128.6, 128.51, 128.48, 127.2, 127.0, 122.5, 121.1, 109.2, 109.0, 106.2, 97.5, 78.6, 75.3, 72.3, 71.2, 59.3, 54.9, 54.7, 42.8, 42.6, 38.7, 34.4, 26.1, 24.6, 23.4, 22.7, 21.5 ppm; HRMS (ESI) calcd for C₄₅H₄₃NO₉Na⁺ [M+Na⁺] 764.2830, found 764.2853.
5-epi-S5: $R_f = 0.7$ (silica gel, acetone:toluene 3:17); FT-IR (neat) $\nu_{\text{max}} = 3447, 2917, 1708, 1593, 1514, 1485, 1449, 1407, 1373, 1345, 1317, 1259, 1192, 1138, 1115, 1086, 994, 913, 813, 735, 696 \text{ cm}^{-1}; ^1\text{H NMR (C}_6\text{D}_6, 500 MHz)^* \delta = 15.33 \text{ (s, 1 H)}, 7.57 - 7.54 \text{ (m, 2 H)}, 7.35 - 7.32 \text{ (m, 2 H)}, 7.22 - 7.18 \text{ (m, 2 H)}, 7.12 - 7.06 \text{ (m, 3 H)}, 7.04 \text{ (m, 1 H)}, 6.25 \text{ (s, 1 H)}, 5.59 \text{ (s, 1 H)}, 5.25 \text{ (d, } J = 12.1 \text{ Hz, 1 H, AB system)}, 5.13 \text{ (d, } J = 12.1 \text{ Hz, 1 H, AB system)}, 4.91 \text{ (s, 2 H)}, 4.75 \text{ (bs, 1 H)}, 3.44 \text{ (bs, 1 H)}, 3.36 \text{ (m, 1 H)}, 3.24 \text{ (s, 3 H)}, 2.91 \text{ (bs, 3 H)}, 2.64 - 2.56 \text{ (m, 2 H)}, 2.38 - 2.25 \text{ (m, 2 H)}, 2.10 - 1.97 \text{ (m, 2 H)}, 1.78 \text{ (s, 3 H)}, 1.38 \text{ (dd, } J = 12.5, 6.0 \text{ Hz, 1 H)}, 1.12 \text{ (s, 3 H)}, 0.59 \text{ (s, 3 H) ppm}; ^{13}\text{C NMR (C}_6\text{D}_6, 126 MHz)^* \delta = 167.5, 159.7, 158.9, 138.0, 137.3, 135.8, 132.5, 128.9, 128.7, 128.63, 128.56, 127.1, 126.4, 122.5, 121.2, 108.6, 106.7, 97.5, 72.4, 71.2, 59.1, 56.3, 54.8, 38.5, 34.4, 26.0, 24.3, 23.5, 21.5 \text{ ppm; HRMS (ESI) calcd for C}_{45}\text{H}_{43}\text{NO}_{9}\text{Na}^+ [M+Na^+] 764.2830, \text{ found 764.2832.}

^*\text{Due to signal broadening, 1 proton signal and 12 carbon signals could not be identified.}

Viridicatumtoxin analog V5: Following conditions similar to those of Stork,[40] Pd black (12 mg, 0.11 mmol, 4.1 equiv) was added to a stirred solution of S5 (20 mg, 0.027 mmol, 1.0 equiv) in THF:MeOH (1.2 mL, 1:1) under argon. The flask headspace was exchanged for H$_2$,
and the reaction mixture was stirred for 10 minutes at room temperature. The flask headspace was re-exchanged for argon, and the mixture was filtered through cotton and concentrated to give V5 (15 mg, 0.026 mmol, 96%) as a yellow powder. V5: Rf = 0.1 (silica gel, MeOH:CH2Cl2 1:19); FT-IR (neat) νmax = 3399, 2917, 1625, 1595, 1490, 1471, 1451, 1401, 1309, 1273, 1200, 1084, 909, 732 cm⁻¹; ¹H NMR (CDCl₃, 600 MHz) δ = 18.00 (s, 1 H), 15.12 (s, 1 H), 9.25 (bs, 1 H), 8.80 (s, 1 H), 6.63 (s, 1 H), 5.91 (bs, 1 H), 5.49 (bs, 1 H), 5.16 (bs, 1 H), 4.39 (d, J = 4.5 Hz, 1 H), 3.85 (s, 3 H), 3.57 (s, 3 H), 3.36 (d, J = 17.5 Hz, 1 H), 3.13 (m, 1 H), 2.88 (d, J = 17.5 Hz, 1 H), 2.85 (dd, J = 18.9, 5.4 Hz, 1 H), 2.58 (dd, J = 18.9, 10.0 Hz, 1 H), 2.22 (m, 1 H), 2.04 (m, 1 H), 1.77 (ddd, J = 12.7, 12.7, 6.1 Hz, 1 H), 1.48 (s, 3 H), 1.38 (dd, J = 12.7, 6.2 Hz, 1 H), 0.93 (s, 3 H), 0.50 (s, 3 H) ppm; ¹³C NMR (CDCl₃, 151 MHz) δ = 195.0, 194.0, 191.5, 173.2, 166.1, 160.5, 158.2, 147.6, 137.1, 135.7, 123.5, 122.5, 121.2, 106.4, 105.7, 100.6, 99.7, 76.7, 76.5, 60.0, 57.1, 55.6, 41.9, 38.4, 38.0, 34.2, 32.8, 25.8, 24.3, 23.0, 21.1 ppm; HRMS (ESI) calcd for C₃₁H₃₃NO₉Na⁺ [M+Na⁺] 586.2048, found 586.2045.

Viridicatumtoxin analog V6: Following conditions similar to those of Stork,⁴⁰ Pd black (8.6 mg, 0.081 mmol, 4.5 equiv) was added to a stirred solution of 5-epi-S5 (13 mg, 0.018 mmol, 1.0 equiv) in THF:MeOH (1.0 mL, 1:1) under argon. The flask headspace was exchanged for H₂, and the reaction mixture was stirred for 10 minutes at room temperature. The flask headspace was re-exchanged for argon, and the mixture was filtered through cotton and concentrated to
give V6 (10 mg, 0.018 mmol, quant.) as a yellow powder. **V6**: R$_f$ = 0.1 (silica gel, MeOH:CH$_2$Cl$_2$ 1:19); FT-IR (neat) $\nu_{\text{max}}$ = 3419, 2921, 1626, 1594, 1490, 1471, 1450, 1404, 1301, 1201, 1139, 1088, 907, 733 cm$^{-1}$; $^1$H NMR (CDCl$_3$, 600 MHz) $\delta$ = 17.94 (s, 1 H), 15.34 (s, 1 H), 9.11 (s, 1 H), 8.84 (s, 1 H), 6.60 (s, 1 H), 5.85 (s, 1 H), 5.49 (s, 1 H), 5.00 (s, 1 H), 4.86 (s, 1 H), 3.85 (s, 3 H), 3.52 (bs, 3 H), 3.22 (d, J = 17.9 Hz, 1 H), 3.13 (d, J = 17.9 Hz, 1 H), 3.10 (m, 1 H), 2.92 (m, 1 H), 2.60 (dd, J = 19.6, 10.9 Hz, 1 H), 2.22 (m, 1 H), 2.03 (m, 1 H), 1.82 (td, J = 12.6, 6.1 Hz, 1 H), 1.54 (s, 3 H), 1.32 (dd, J = 12.6, 6.1 Hz, 1 H), 0.89 (s, 3 H), 0.42 (s, 3 H) ppm; $^{13}$C NMR (CDCl$_3$, 151 MHz) $\delta$ = 195.2, 194.8 (b), 192.1, 173.0, 166.6, 160.6, 158.1, 148.2, 137.6, 134.2, 124.2, 122.1, 120.8, 106.9, 105.3, 100.7, 99.2, 76.6, 75.6, 59.4, 57.0, 55.6, 43.9, 39.2 (b), 38.3, 34.1, 30.8 (b), 25.7, 24.1, 23.0, 21.2 ppm; HRMS (ESI) calcd for C$_{31}$H$_{33}$NO$_9$Na$^+$ [M+Na$^+$] 586.2048, found 586.2036.
III. Biological Materials and Methods

**Bacterial Strains and Growth Media:** Four clinical strains were used for these studies, *Enterococcus faecalis* S613, *Enterococcus faecium* isolate 105, Methicillin-Resistant *Staphylococcus aureus* 371 (MRSA 371) and *Acinetobacter baumannii* AB210. *Enterococcus* strains were cultured in 80% Lysogeny Broth (LB) & 20% Brain Heart Infusion (BHI). MRSA 371 and AB210 were cultured in 100% LB.

**Minimal Inhibitory Concentration (MIC) Assays:** Micro-broth MIC assays were performed in triplicate using 96-well plates. Wells were filled with 150 µL of broth media and inoculated with 2 µL of stationary phase culture. The concentration of the test antibiotics increased in 2-fold increments and ranged from 0.25 – 128 µg/mL. Plates were incubated overnight at 37 °C and the MICs were defined as the lowest drug concentration that had no growth after 16 – 24 hours.
**Time-Kill Assay:** We performed time-kill assays using *E. faecalis* S613 cultures. Cells were taken at early exponential phase and diluted to $9 \times 10^5 - 1 \times 10^6$ CFU/mL. Cells were then treated with 2x the MIC of tigecycline (9), viridicatumtoxin A (2), or V6. A growth control with no antibiotic was also included and CFUs were determined at 0, 2, 4 and 6 hours after the addition of antibiotic. The time-kill assay was setup in triplicate with error bars displaying the standard deviation. See graph below.
IV. References

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V. $^1$H, $^{13}$C, and Selected 2D NMR Spectra

$^1$H NMR spectrum (CDCl$_3$, 600 MHz) of compound 48.

$^{13}$C NMR spectrum (CDCl$_3$, 151 MHz) of compound 48.
$^1$H NMR spectrum (CDCl$_3$, 500 MHz) of compound 27.

$^{13}$C NMR spectrum (CDCl$_3$, 126 MHz) of compound 27.
$^1$H NMR spectrum (CDCl$_3$, 600 MHz) of compound 56.

$^{13}$C NMR spectrum (CDCl$_3$, 151 MHz) of compound 56.
$^1$H NMR spectrum (CDCl$_3$, 500 MHz) of compound 28.

$^{13}$C NMR spectrum (CDCl$_3$, 126 MHz) of compound 28.
$^1$H NMR spectrum (CDCl$_3$, 400 MHz) of compound 58 (d.r. ca. 1:1).

$^{13}$C NMR spectrum (CDCl$_3$, 101 MHz) of compound 58 (d.r. ca. 1:1).
$^1$H NMR spectrum (CDCl$_3$, 600 MHz) of compound 25.

$^{13}$C NMR spectrum (CDCl$_3$, 151 MHz) of compound 25.
$^1$H NMR spectrum (CDCl$_3$, 600 MHz) of compound 62.

$^{13}$C NMR spectrum (CDCl$_3$, 151 MHz) of compound 62.
$^1$H NMR spectrum ($\text{C}_6\text{D}_6$, 600 MHz) of compound 63.

$^{13}$C NMR spectrum ($\text{C}_6\text{D}_6$, 151 MHz) of compound 63.
$^1$H NMR spectrum (C$_6$D$_6$, 600 MHz) of compound 64.

$^{13}$C NMR spectrum (C$_6$D$_6$, 151 MHz) of compound 64.
$^1$H NMR spectrum (CDCl$_3$, 400 MHz) of compound 69.

$^{13}$C NMR spectrum (CDCl$_3$, 101 MHz) of compound 69.
$^1$H NMR spectrum (CDCl$_3$, 500 MHz) of compound 70.

$^{13}$C NMR spectrum (CDCl$_3$, 126 MHz) of compound 70.
$^1$H NMR spectrum (CDCl$_3$, 400 MHz) of compound 71.

$^{13}$C NMR spectrum (CDCl$_3$, 101 MHz) of compound 71.
$^1$H NMR spectrum (CDCl$_3$, 600 MHz) of compound 26.

$^{13}$C NMR spectrum (CDCl$_3$, 151 MHz) of compound 26.
$^1$H NMR spectrum (C$_6$D$_6$, 600 MHz) of compound 72.

$^{13}$C NMR spectrum (C$_6$D$_6$, 151 MHz) of compound 72.
$^1$H NMR spectrum (CDCl$_3$, 400 MHz) of compound 73.

$^{13}$C NMR spectrum (CDCl$_3$, 101 MHz) of compound 73.
$^1$H NMR spectrum (CDCl$_3$, 600 MHz) of compound 74 (d.r. ca. 3:1).

$^{13}$C NMR spectrum (CDCl$_3$, 151 MHz) of compound 74 (d.r. ca. 3:1).
$^1$H NMR spectrum (CDCl$_3$, 600 MHz) of compound 75.

$^{13}$C NMR spectrum (CDCl$_3$, 151 MHz) of compound 75.
$^1$H NMR spectrum (C$_6$D$_6$, 600 MHz) of compound 76.

$^{13}$C NMR spectrum (C$_6$D$_6$, 151 MHz) of compound 76.
$^1$H NMR spectrum (CDCl$_3$, 600 MHz) of compound 79.

$^{13}$C NMR spectrum (CDCl$_3$, 151 MHz) of compound 79.
$^1$H NMR spectrum (CDCl$_3$, 600 MHz) of compound 65.

$^{13}$C NMR spectrum (CDCl$_3$, 151 MHz) of compound 65.
$^1$H NMR spectrum (CDCl$_3$, 500 MHz) of compound 81.

$^{13}$C NMR spectrum (CDCl$_3$, 126 MHz) of compound 81.
$^1$H NMR spectrum (CDCl$_3$, 500 MHz) of compound 82 (d.r. ca. 2.4:1).

$^{13}$C NMR spectrum (CDCl$_3$, 126 MHz) of compound 82 (d.r. ca. 2.4:1).
$^1$H NMR spectrum (CDCl$_3$, 600 MHz) of compound 83.

$^{13}$C NMR spectrum (CDCl$_3$, 151 MHz) of compound 83.
$^1$H NMR spectrum (CDCl$_3$, 600 MHz) of compound 88.

$^{13}$C NMR spectrum (CDCl$_3$, 151 MHz) of compound 88.
$^1$H NMR spectrum (CDCl$_3$, 500 MHz) of compound 89.

$^{13}$C NMR spectrum (CDCl$_3$, 151 MHz) of compound 89.
$^1$H NMR spectrum (CDCl$_3$, 600 MHz) of compound 91.

$^{13}$C NMR spectrum (CDCl$_3$, 151 MHz) of compound 91.
$^1$H NMR spectrum (CDCl$_3$, 600 MHz) of compound 90 (d.r. ca. 6:1).

$^{13}$C NMR spectrum (CDCl$_3$, 151 MHz) of compound 90 (d.r. ca. 6:1).
$^1$H NMR spectrum (CDCl$_3$, 600 MHz) of compound 24.

$^{13}$C NMR spectrum (CDCl$_3$, 151 MHz) of compound 24.
HSQC spectrum (CDCl₃, 600 MHz/151 MHz) of compound 24.

HMBC spectrum (CDCl₃, 600 MHz/151 MHz) of compound 24.
NOESY spectrum (CDCl₃, 600 MHz/600 MHz) of compound 24.

Expansion of NOESY spectrum of compound 24:
\(^1\text{H NMR spectrum (CDCl}_3, 600 \text{ MHz)} \text{ of compound 92 (ca. 3:1 mixture of rotamers).}

\[^{13}\text{C NMR spectrum (CDCl}_3, 151 \text{ MHz)} \text{ of compound 92 (ca. 3:1 mixture of rotamers).}
\(^1\)H NMR spectrum (CDCl\(_3\), 600 MHz) of compound 93 (ca. 1:1 mixture of rotamers).

\(^{13}\)C NMR spectrum (CDCl\(_3\), 151 MHz) of compound 93 (ca. 1:1 mixture of rotamers).
$^1$H NMR spectrum (CDCl$_3$, 600 MHz) of compound 98.

$^{13}$C NMR spectrum (CDCl$_3$, 151 MHz) of compound 98.
$^1$H NMR spectrum (CDCl₃, 600 MHz) of compound S3 (ca. 1.3:1 mixture of rotamers).

$^{13}$C NMR spectrum (CDCl₃, 151 MHz) of compound S3 (ca. 1.3:1 mixture of rotamers).
$^1$H NMR spectrum (CDCl$_3$, 600 MHz) of compound **101** (ca. 1:1 mixture of rotamers).

$^{13}$C NMR spectrum (CDCl$_3$, 151 MHz) of compound **101** (ca. 1:1 mixture of rotamers).
$^1$H NMR spectrum (CDCl$_3$, 600 MHz) of compound 103.

$^{13}$C NMR spectrum (CDCl$_3$, 151 MHz) of compound 103.
$^1$H NMR spectrum (CDCl$_3$, 600 MHz) of compound $12a$-$e$$t$-$103$.

$^{13}$C NMR spectrum (CDCl$_3$, 151 MHz) of compound $12a$-$e$$t$-$103$. 
$^1$H NMR spectrum (C$_6$D$_6$, 600 MHz) of compound 107.

$^{13}$C NMR spectrum (C$_6$D$_6$, 151 MHz) of compound 107.
$^1$H NMR spectrum (CDCl$_3$, 600 MHz) of compound 108.

$^{13}$C NMR spectrum (CDCl$_3$, 151 MHz) of compound 108.
$^1$H NMR spectrum (d$_6$-DMSO, 500 MHz, 338 K) of compound 109 (d.r. ca. 1:1).

$^1$H NMR spectra (d$_6$-DMSO, 500 MHz, 298–338 K) of compound 109 (d.r. ca. 1:1).
$^1$H NMR spectrum (CDCl$_3$, 600 MHz, 298 K) of compound 109 (d.r. ca. 1:1).

$^{13}$C NMR spectrum (CDCl$_3$, 151 MHz, 298 K) of compound 109 (d.r. ca. 1:1).
$^1$H NMR spectrum (CDCl$_3$, 600 MHz) of compound 60.

$^{13}$C NMR spectrum (CDCl$_3$, 151 MHz) of compound 60.
\(^1\)H NMR spectrum (C\(_6\)D\(_6\), 600 MHz) of compound 61.

\(^{13}\)C NMR spectrum (C\(_6\)D\(_6\), 151 MHz) of compound 61.
$^1$H NMR spectrum (CDCl$_3$, 600 MHz) of compound 110.

$^{13}$C NMR spectrum (CDCl$_3$, 151 MHz) of compound 110.
$^1$H NMR spectrum (CDCl$_3$, 600 MHz) of compound 111.

$^{13}$C NMR spectrum (CDCl$_3$, 151 MHz) of compound 111.
$^1$H NMR spectrum (C$_6$D$_6$, 600 MHz) of compound 112.

$^{13}$C NMR spectrum (C$_6$D$_6$, 151 MHz) of compound 112.
HMBC spectrum (C₆D₆, 600 MHz/151 MHz) of compound 112.

Expansion of HMBC spectrum of compound 112:
NOESY spectrum (C₆D₆, 600 MHz/600 MHz) of compound 112.

Expansion of NOESY spectrum of compound 112:

S187
$^1$H NMR spectrum (CDCl$_3$, 600 MHz) of compound 113 (mixture of 4 diastereomers).

$^{13}$C NMR spectrum (CDCl$_3$, 151 MHz) of compound 113 (mixture of 4 diastereomers).
$^1$H NMR spectrum (CDCl$_3$, 600 MHz) of compound 115 + 15-epi-115 (d.r. ca. 2:1).

$^{13}$C NMR spectrum (CDCl$_3$, 151 MHz) of compound 115 + 15-epi-115 (d.r. ca. 2:1).
$^1$H NMR spectrum (C$_6$D$_6$, 600 MHz) of compound 117 + 15-epi-117 (d.r. ca. 2:1).

$^{13}$C NMR spectrum (C$_6$D$_6$, 151 MHz) of compound 117 + 15-epi-117 (d.r. ca. 2:1).
$^1$H NMR spectrum (C$_6$D$_6$, 600 MHz) of compound **119-A**.

$^{13}$C NMR spectrum (C$_6$D$_6$, 151 MHz) of compound **119-A**.
COSY spectrum (C₆D₆, 600 MHz/600 MHz) of compound 119-A.
$^1$H NMR spectrum (C$_6$D$_6$, 600 MHz) of compound 119-B.

$^{13}$C NMR spectrum (C$_6$D$_6$, 151 MHz) of compound 119-B.
$^1$H NMR spectrum (d$_6$-acetone, 600 MHz) of compound 121.

$^13$C NMR spectrum (d$_6$-acetone, 151 MHz) of compound 121.
$^1$H NMR spectrum (CDCl$_3$, 400 MHz) of compound 122.

$^{13}$C NMR spectrum (CDCl$_3$, 101 MHz) of compound 122.
\(^1\)H NMR spectrum (CDCl\(_3\), 400 MHz) of compound 123.

\(^13\)C NMR spectrum (CDCl\(_3\), 101 MHz) of compound 123.
$^1$H NMR spectrum ($\text{C}_6\text{D}_6$, 600 MHz) of compound 114 + 15-epi-114 (d.r. ca. 2:1).

$^{13}$C NMR spectrum ($\text{C}_6\text{D}_6$, 151 MHz) of compound 114 + 15-epi-114 (d.r. ca. 2:1).
$^1$H NMR spectrum (C$_6$D$_6$, 600 MHz) of compound 124 + 15-epi-124 (d.r. ca. 2:1).

$^{13}$C NMR spectrum (C$_6$D$_6$, 151 MHz) of compound 124 + 15-epi-124 (d.r. ca. 2:1).
$^{1}$H NMR spectrum (C$_6$D$_6$, 600 MHz) of compound 125 + 15-epi-125 (d.r. ca. 2:1).

$^{13}$C NMR spectrum (C$_6$D$_6$, 151 MHz) of compound 125 + 15-epi-125 (d.r. ca. 2:1).
$^1$H NMR spectrum (C$_6$D$_6$, 600 MHz) of compound 127 + 15-epi-127 (d.r. ca. 2:1).

$^{13}$C NMR spectrum (C$_6$D$_6$, 151 MHz) of compound 127 + 15-epi-127 (d.r. ca. 2:1).
$^1$H NMR spectrum (d$_6$-acetone, 600 MHz) of compound 116 + 15-epi-116 (d.r. ca. 2:1).

$^{13}$C NMR spectrum (d$_6$-acetone, 151 MHz) of compound 116 + 15-epi-116 (d.r. ca. 2:1).
$^1$H NMR spectrum (C$_6$D$_6$, 600 MHz) of compound 131.

$^{13}$C NMR spectrum (C$_6$D$_6$, 151 MHz) of compound 131.
$^1$H NMR spectrum (C$_6$D$_6$, 600 MHz) of compound 132 + 15-epi-132 (d.r. ca. 2:1).

$^{13}$C NMR spectrum (C$_6$D$_6$, 151 MHz) of compound 132 + 15-epi-132 (d.r. ca. 2:1).
$^1$H NMR spectrum (C$_6$D$_6$, 600 MHz) of compound 133.

$^{13}$C NMR spectrum (C$_6$D$_6$, 151 MHz) of compound 133.
$^1$H NMR spectrum (C$_6$D$_6$, 600 MHz) of compound 15-epi-133.

$^{13}$C NMR spectrum (C$_6$D$_6$, 151 MHz) of compound 15-epi-133.
$^1$H NMR spectrum (CDCl$_3$, 600 MHz) of compound 137.

$^{13}$C NMR spectrum (CDCl$_3$, 151 MHz) of compound 137.

*negative peak at ~177 ppm is an NMR artifact.
$^1$H NMR spectrum (CDCl$_3$, 600 MHz) of compound 138.

$^{13}$C NMR spectrum (CDCl$_3$, 151 MHz) of compound 138.
$^1$H NMR spectrum (C$_6$D$_6$, 600 MHz) of compound 140.

$^{13}$C NMR spectrum (C$_6$D$_6$, 151 MHz) of compound 140.
HSQC spectrum (C₆D₆, 600 MHz/151 MHz) of compound **140**.

![HSQC Spectrum](image)

HMBC spectrum (C₆D₆, 600 MHz/151 MHz) of compound **140**.

![HMBC Spectrum](image)
NOESY spectrum (C₆D₆, 600 MHz/600 MHz) of compound **140**.

Expansion of NOESY spectrum of compound **140**: 
$^1$H NMR spectrum ($C_6D_6$, 600 MHz, 298 K) of compound 5-epi-140.

$^{13}$C NMR spectrum ($C_6D_6$, 151 MHz, 298 K) of compound 5-epi-140.
$^1$H NMR spectrum ($\text{C}_6\text{D}_6$, 500 MHz, 323 K) of compound 5-epi-140.

$^1$H NMR spectra ($\text{C}_6\text{D}_6$, 500 MHz, 298, 313, and 323 K) of compound 5-epi-140.
$^1$H NMR spectrum (CDCl$_3$, 600 MHz) of compound 143.

$^{13}$C NMR spectrum (CDCl$_3$, 151 MHz) of compound 143.
$^1$H NMR spectrum (C$_6$D$_6$, 600 MHz) of compound 144.

$^{13}$C NMR spectrum (C$_6$D$_6$, 151 MHz) of compound 144.
HSQC spectrum (C$_6$D$_6$, 600 MHz/151 MHz) of compound 144.

HMBC spectrum (C$_6$D$_6$, 600 MHz/151 MHz) of compound 144.
$^1$H NMR spectrum (C$_6$D$_6$, 600 MHz) of compound 149.

$^{13}$C NMR spectrum (C$_6$D$_6$, 151 MHz) of compound 149.
HSQC spectrum ($\text{C}_6\text{D}_6$, 600 MHz/151 MHz) of compound 149.

[Image of HSQC spectrum]

HMBC spectrum ($\text{C}_6\text{D}_6$, 600 MHz/151 MHz) of compound 149.

[Image of HMBC spectrum]
$^1$H NMR spectrum (C$_6$D$_6$, 600 MHz) of compound 152.

$^{13}$C NMR spectrum (C$_6$D$_6$, 151 MHz) of compound 152.
$^1$H NMR spectrum (C$_6$D$_6$, 600 MHz) of compound 154.

$^{13}$C NMR spectrum (C$_6$D$_6$, 151 MHz) of compound 154.
$^1$H NMR spectrum (C$_6$D$_6$, 600 MHz) of compound 155.

$^{13}$C NMR spectrum (C$_6$D$_6$, 151 MHz) of compound 155.
$^1$H NMR spectrum (CD$_2$Cl$_2$, 600 MHz) of compound 158.

$^{13}$C NMR spectrum (CD$_2$Cl$_2$, 151 MHz) of compound 158.
\(^1\)H NMR spectrum (CDCl\(_3\), 600 MHz) of compound \textbf{159}.

\(^{13}\)C NMR spectrum (CDCl\(_3\), 151 MHz) of compound \textbf{159}.
$^1$H NMR spectrum (CDCl$_3$, 600 MHz) of compound 160.

$^{13}$C NMR spectrum (CDCl$_3$, 151 MHz) of compound 160.
$^1$H NMR spectrum (CDCl$_3$, 600 MHz) of compound 164.

$^{13}$C NMR spectrum (CDCl$_3$, 151 MHz) of compound 164.
HSQC spectrum (CDCl₃, 600 MHz/151 MHz) of compound 164.

HMBC spectrum (CDCl₃, 600 MHz/151 MHz) of compound 164.
$^1$H NMR spectrum (CDCl$_3$, 600 MHz) of compound 165.

$^{13}$C NMR spectrum (CDCl$_3$, 151 MHz) of compound 165.
$^1$H NMR spectrum (CDCl$_3$, 600 MHz) of compound 167.

$^{13}$C NMR spectrum (CDCl$_3$, 151 MHz) of compound 167.

*peak at ~177 ppm is an NMR artifact.
\(^1\)H NMR spectrum (CDCl\(_3\), 600 MHz) of compound 168.

\(^1\)C NMR spectrum (CDCl\(_3\), 151 MHz) of compound 168.
$^1$H NMR spectrum (CDCl$_3$, 600 MHz) of compound 172.

$^{13}$C NMR spectrum (CDCl$_3$, 151 MHz) of compound 172.
HSQC spectrum (CDCl₃, 600 MHz/151 MHz) of compound 172.
$^1$H NMR spectrum (CDCl$_3$, 600 MHz, 298 K) of compound 173/173$'$.

$^{13}$C NMR spectrum (CDCl$_3$, 151 MHz, 298 K) of compound 173/173$'$. 
$^1$H NMR spectrum (CD$_2$Cl$_2$, 600 MHz) of compound 136.

$^{13}$C NMR spectrum (CD$_2$Cl$_2$, 151 MHz) of compound 136.
$^1$H NMR spectrum (CDCl$_3$, 600 MHz) of compound 176.

$^{13}$C NMR spectrum (CDCl$_3$, 151 MHz) of compound 176.
$^1$H NMR spectrum (CDCl$_3$, 600 MHz) of compound 178.

$^{13}$C NMR spectrum (CDCl$_3$, 151 MHz) of compound 178.
$^1$H NMR spectrum (CDCl$_3$, 600 MHz) of compound 177.

$^{13}$C NMR spectrum (CDCl$_3$, 151 MHz) of compound 177.
$^1$H NMR spectrum (C$_6$D$_6$, 600 MHz) of compound 180.

$^{13}$C NMR spectrum (C$_6$D$_6$, 151 MHz) of compound 180.
$^1$H NMR spectrum (CDCl$_3$, 600 MHz) of compound S4.

$^{13}$C NMR spectrum (CDCl$_3$, 151 MHz) of compound S4.
$^1$H NMR spectrum (CDCl$_3$, 600 MHz) of compound 181 (d.r. ca. 1:1).

$^{13}$C NMR spectrum (CDCl$_3$, 151 MHz) of compound 181 (d.r. ca. 1:1).
$^1$H NMR spectrum (CDCl$_3$, 600 MHz) of compound 182.

$^{13}$C NMR spectrum (CDCl$_3$, 151 MHz) of compound 182.
$^1$H NMR spectrum (CDCl$_3$, 600 MHz) of compound 184.

$^{13}$C NMR spectrum (CDCl$_3$, 151 MHz) of compound 184.
$^1$H NMR spectrum (CDCl$_3$, 600 MHz) of compound 185.

$^{13}$C NMR spectrum (CDCl$_3$, 151 MHz) of compound 185.
\(^1\)H NMR spectrum (\(\text{C}_6\text{D}_6\), 600 MHz) of compound 186 + 15-\textit{epi}-186 (d.r. ca. 2:1).

\(^{13}\)C NMR spectrum (\(\text{C}_6\text{D}_6\), 151 MHz) of compound 186 + 15-\textit{epi}-186 (d.r. ca. 2:1).
$^1$H NMR spectrum (CDCl$_3$, 600 MHz) of compound 187 + 15-epi-187 (d.r. ca. 2:1).

$^{13}$C NMR spectrum (CDCl$_3$, 151 MHz) of compound 187 + 15-epi-187 (d.r. ca. 2:1).
\(^1\)H NMR spectrum (CDCl\(_3\), 600 MHz) of compound 188 + 15-epi-188 (d.r. ca. 2:1).

\(^{13}\)C NMR spectrum (CDCl\(_3\), 151 MHz) of compound 188 + 15-epi-188 (d.r. ca. 2:1).
$^1$H NMR spectrum (CDCl$_3$, 600 MHz) of compound 189.

$^{13}$C NMR spectrum (CDCl$_3$, 151 MHz) of compound 189.
$^1$H NMR spectrum (CDCl$_3$, 600 MHz) of compound 15-epi-189.

$^{13}$C NMR spectrum (CDCl$_3$, 151 MHz) of compound 15-epi-189.
$^1$H NMR spectra (C$_6$D$_6$, 600 MHz) of compounds 189, 15-epi-189, and 15-epi-133 (0–8 ppm).

$^1$H NMR spectra (C$_6$D$_6$, 600 MHz) of compounds 189, 15-epi-189, and 15-epi-133 (2.5–4 ppm).
$^1$H NMR spectrum (CDCl$_3$, 600 MHz) of compound 190.

$^{13}$C NMR spectrum (CDCl$_3$, 151 MHz) of compound 190.
$^1$H NMR spectrum (CDCl$_3$, 600 MHz) of compound 191.

$^{13}$C NMR spectrum (CDCl$_3$, 151 MHz) of compound 191.
$^1$H NMR spectrum (CDCl$_3$, 600 MHz) of compound 192.

$^{13}$C NMR spectrum (CDCl$_3$, 151 MHz) of compound 192.
$^1$H NMR spectrum (CDCl$_3$, 600 MHz) of compound 193.

$^{13}$C NMR spectrum (CDCl$_3$, 151 MHz) of compound 193.
HSQC spectrum (CDCl₃, 600 MHz/151 MHz) of compound 193.

HMBC spectrum (CDCl₃, 600 MHz/151 MHz) of compound 193.
NOESY spectrum (CDCl$_3$, 600 MHz/600 MHz) of compound 193.

Expansion of NOESY spectrum of compound 193:
$^1$H NMR spectrum (CDCl$_3$, 600 MHz, 298 K) of compound 194/194'.

$^{13}$C NMR spectrum (CDCl$_3$, 151 MHz, 298 K) of compound 194/194'.
\(^1\text{H NMR spectrum (CDCl}_3, 500 \text{ MHz, 233 K) of compound 194/194'}\).
$^1$H NMR spectrum (CD$_2$Cl$_2$, 600 MHz) of compound 195.

$^{13}$C NMR spectrum (CD$_2$Cl$_2$, 151 MHz) of compound 195.
$^1$H NMR spectrum (CDCl$_3$, 600 MHz) of synthetic viridicatumtoxin B [(±)-1].

$^{13}$C NMR spectrum (CDCl$_3$, 151 MHz) of synthetic viridicatumtoxin B [(±)-1].
$^1$H NMR spectra of natural (CDCl$_3$, 300 MHz) and synthetic (CDCl$_3$, 600 MHz) viridicatumtoxin B (1) (0–15 ppm).
$^1$H NMR spectra of natural (CDCl$_3$, 300 MHz) and synthetic (CDCl$_3$, 600 MHz) viridicatumtoxin B (1) (0–8 ppm).
$^{13}$C NMR spectra of natural (CDCl$_3$, 226 MHz) and synthetic (CDCl$_3$, 151 MHz) viridicatumtoxin B (I).
$^1$H NMR spectrum (CDCl$_3$, 600 MHz) of compound V2.

$^{13}$C NMR spectrum (CDCl$_3$, 151 MHz) of compound V2.
$^1$H NMR spectrum (CDCl$_3$, 600 MHz) of compound V3.

$^{13}$C NMR spectrum (CDCl$_3$, 151 MHz) of compound V3.
$^1$H NMR spectrum (CDCl$_3$, 600 MHz) of compound V4.

$^{13}$C NMR spectrum (CDCl$_3$, 151 MHz) of compound V4.
$^1$H NMR spectrum (C$_6$D$_6$, 500 MHz) of compound S5.

$^{13}$C NMR spectrum (C$_6$D$_6$, 126 MHz) of compound S5.
$^1$H NMR spectrum (C$_6$D$_6$, 500 MHz) of compound 5-epi-S5.

$^{13}$C NMR spectrum (C$_6$D$_6$, 126 MHz) of compound 5-epi-S5.
$^1$H NMR spectrum (CDCl$_3$, 600 MHz) of compound V5.

$^{13}$C NMR spectrum (CDCl$_3$, 151 MHz) of compound V5.
$^1$H NMR spectrum (CDCl$_3$, 600 MHz) of compound V6.

$^{13}$C NMR spectrum (CDCl$_3$, 151 MHz) of compound V6.