Rapid Stereocontrolled Assembly of the Fully Substituted *C*-Aryl Glycoside of Kendomycin with a Prins Cyclization: A Formal Synthesis

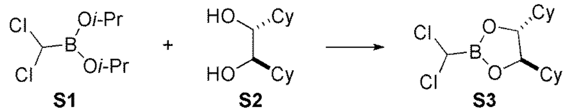
Supporting Information

Experimental procedures and characterization for all compounds

Kevin B. Bahnck and Professor Scott D. Rychnovsky
Department of Chemistry, University of California, Irvine, Irvine, CA, U.S.A.

General Experimental Details. Unless otherwise stated, all reactions were carried out under an inert argon atmosphere using standard syringe/septa techniques. All glassware was flame-dried and cooled under argon prior to use. Yields refer to isolated and spectroscopically homogeneous compounds unless otherwise stated. All commercially available reagents were used as received with the following exceptions. Tetrahydrofuran, diethyl ether, and dichloromethane were degassed with argon and dried by vacuum filtration through activated alumina according to the Grubbs procedure.[1] Benzene and 2,6-lutidine were distilled from calcium hydride under argon at atmospheric pressure. Boron trifluoride diethyl etherate was distilled from calcium hydride under 1 atm of argon and stored in a Schlenk flask. Acetic acid was heated for 1 h with CrO_3 and Ac_2O at 100 ºC prior to collection of the distillate at 115–118 ºC under 1 atm of argon. Zinc chloride from Aldrich was received as a 99.99% anhydrous powder, dissolved in dry argon-degassed THF, and stored in a Schlenk flask as a THF solution. Tributylphosphine was fractionally distilled under reduced pressure and stored under argon in a Schlenk flask. Concentrations of organolithium solutions were determined by titration with recrystallized (–)-menthol and 1,10-phenanthroline. Flash chromatography was performed using forced flow with Fisher silica gel (60 mesh). Thin layer chromatography (TLC) was performed on Whatman 250 μm layer 6Å glass-backed silica gel plates. Eluted plates were examined under UV light then developed using cerric ammonium molybdate, *p*-anisaldehyde, and potassium permanganate TLC stains.

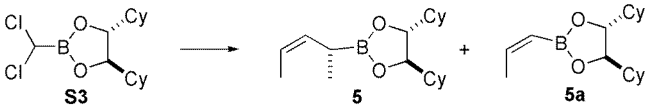
Instrumentation: Optical rotations were measured using a JASCO DIP–370 digital polarimeter. Infrared spectra were recorded on a MIDAC Grams/Prospect FTIR spectrometer. IR samples were analyzed as thin films on NaCl plates (oils) or as KBr pellets (solids). Melting points were obtained on a Thomas-Hoover apparatus and are uncorrected. ^{1}H NMR spectra were recorded at 400, 500, or 600 MHz on Bruker NMR spectrometers and were referenced to TMS (δ 0.00) in $CDCl_3$, unless otherwise indicated. Coupling constants refer to apparent multiplicities, indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet), sext (sextet), sept (septet); m (multiplet); dd (doublet of doublets); etc. ^{13}C NMR spectra were recorded at 100, 125, or 150 MHz and referenced to $CDCl_3$ (δ 77.23), unless otherwise indicated. Mass spectra were measured on a MicroMass Analytical 7070E, a MicroMass AutoSpec E or a MicroMass LCT Electrospray spectrometer. Chiral HPLC analysis was performed on an HP model 1050 Series with a 0.46 cm x 25 cm CHIRALCEL OD-H column.



---

[1] Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518-1520

(4*R*,5*R*)-4,5-Dicyclohexyl-2-dichloromethyl[1,3,2]dioxaborolane (S3). Known isopropyl ester **S1**[2] (9.50 g, 44.6 mmol) was added dropwise with an addition funnel to a suspension of known (*R*,*R*)-diol **S2**[3] (10.10 g, 44.6 mmol) in 170 mL of *n*-hexane at rt. Following an initial endotherm, the reaction mixture attained homogeneity after 30 min, at which time it was heated at reflux. Transesterification was complete after collecting of an azeotrope of hexanes and *i*-PrOH (bp = 57° C / 1 atm), and the residual solvent was removed *in vacuo* at 60 °C. The pale yellow oil was dissolved in 50 mL of pentane and passed through a 45 µm teflon filter. The clear colorless filtrate was concentrated and placed under vacuum (ca. 20 Torr) overnight. The resulting oil solidified after 1 d at 0 °C to provide boronate **S3** as a white paste (14.16 g, 99%): $[\alpha]^{20}_{D}$ +6.0 (*c* 1.06, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 5.39 (s, 1H), 4.06 (dd, *J* = 8.5, 3.8, 2H), 1.80–1.77 (m, 6H), 1.70–1.61 (m, 4H), 1.43 (tq, *J* = 11.6, 3.8, 2H), 1.27–0.97 (m, 10H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 85.2, 43.0, 28.3, 27.3, 26.5, 26.1, 26.0; IR (thin film) 2927, 2855, 1450, 1414, 1362, 998, 727 cm^{-1}; HRMS (EI) *m* / *z* calcd for $C_{15}H_{25}BCl_2O_2$ $(M)^+$ 318.1325, found 318.1328.



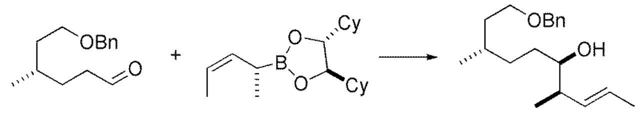
(4*R*,5*R*)-4,5-Dicyclohexyl-2-((*Z*)-(*R*)-1-methylbut-2-enyl[1,3,2]dioxaborolane (5).[4] Boronate **S3** (3.19 g, 10.0 mmol) was azeotroped with benzene (4 x 30 mL) then dissolved in 30 mL of THF. The flask was fitted with a thermocouple to monitor the internal temperature. After cooling to –78 °C, the solution was treated dropwise over 20 min with MeLi (1.27 M in pentane, 8.3 mL, 10.5 mmol, 1.05 equiv.), at such a rate that the internal temperature did not exceed –70 °C. The mixture was stirred at –78 °C for 30 min prior to the dropwise addition of solution of $ZnCl_2$ (0.61 M in THF, 14.1 mL, 8.5 mmol, 0.85 equiv.). The reaction mixture was held at –78 °C for 1 h before removing the cooling bath and allowing it to reach ambient temperature over 3 h. During this warming time, a vinyl Grignard reagent was prepared separately as follows: A dry 100 mL pear flask was flushed with argon and charged with Mg powder (0.27 g, 11.0 mmol, 1.10 equiv.). THF (50 mL) was added, and the suspension was treated with 100 µL of dibromoethane and stirred vigorously for 10 min. To this activated suspension was added neat *cis*-bromopropene (1.4 mL, 16.5 mmol, 1.50 equiv.) portionwise at such a rate to maintain a gentle exotherm. The Grignard formation was driven to completion by heating at 50 °C for 2 h. The original reaction mixture was cooled to –78 °C before adding the Grignard solution (0.21 M in THF) dropwise using an addition funnel over 20 min. (Care was taken to ensure the internal reaction temperature during the Grignard addition did not exceed –70 °C). The cooling bath was allowed to expire overnight, and the reaction mixture thus warmed to 0 °C over 10 h. Saturated aq. NH_4Cl (20 mL) was added and the mixture was extracted with Et_2O (2 x 20 mL). The organic layers were washed with brine, dried over Na_2SO_4, and concentrated *in vacuo*. The residue was purified by flash chromatography with hexanes to provide Hoffmann's boronate **5**[4] as a colorless oil (1.79 g, 59%), contaminated with 0.41 g (15%) of the inseparable (but inconsequential) byproduct **5a** : (Approximate ratios of **5** and **5a** were calculated by comparing the integrations of their unique proton signals at δ 2.19 (app. q) for the allylic methine of **5** and δ 1.98 (dd, *J* = 1.2, 7.2, 3H) for the methyl of **5a**. Boronate **5a**: ^1H NMR (500 MHz, $CDCl_3$) δ 5.41–5.33 (m, 2H), 3.87 (d, *J* = 4.8, 2H), 2.19 (app. q, *J* = 7.8, 1H), 180–1.55 (m, 14H), 1.35–0.91 (m, 14H).

---

[2] Rathke, M. W.; Chao, E.; Wu, G. *J. Organomet. Chem.* **1976**, `*122*, 145.

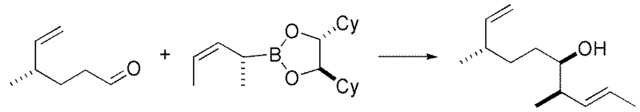
[3] Hiscox, W. C.; Matteson, D. S. *J. Org. Chem.* **1996**, *61*, 8315.

[4] Hoffmann, R. W.; Ditrich, K.; Koster, G. *Chem. Ber.* **1989**, *122*, 1783.



4 **5** **7**

(*E*)-(4*R*,5*R*,8*S*)-10-Benzyloxy-4,8-dimethyldec-2-en-5-ol (7). A solution of aldehyde **4**[5] (0.89 g, 4.03 mmol) and Hoffmann's boronate **5**[4] (1.29 g, 4.24 mmol, 1.1 equiv.) were combined in 5 mL of *n*-hexane. The flask was capped, sealed with Teflon tape, and held at 0 ºC for 36 h. The hexane was removed *in vacuo* and the residue was dissolved in 20 mL of THF and 5 mL of aq. NaOH (3.0 M). After the addition of H_2O_2 (4 mL, 30% w/w), the mixture was heated at reflux (ca. 80 ºC) for 2 h. Upon reaching ambient temperature, the organic layer was washed with aq. NaOH and brine and dried over Na_2SO_4 to afford a white paste containing desired alcohol **7** and the chiral auxiliary diol **S2**. The majority of diol **S2** was separated from alcohol **7** by trituration of the residue with pentane (3 x 30 mL). The solid residue was dried overnight under vacuum (ca. 20 Torr) to afford feathery white flakes of pure diol **S2** (1.38 g, 96% recovery). The pentane triturate was filtered, concentrated, and subjected to flash chromatography (40 mL of silica) with hexanes:Et_2O (1:19) to provide alcohol **7** as a pale oil (1.06 g, 91%): $[\alpha]^{24}{}_{D}$ +18.1 (*c* 1.00, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.35–7.33 (m, 4H), 7.29–7.25 (m, 1H), 5.53–5.46 (m, 1H), 5.40–5.35 (m, 1H), 4.49 (s, 2H), 3.54–3.46 (m, 2H), 3.42–3.36 (m, 1H), 2.21 (m, 1H), 171–1.27 (m, 6H), 1.68 (d, *J* = 6.8, 3H), 1.15–1.11 (m, 1H), 0.97 (d, *J* = 6.9, 3H), 0.89 (d, *J* = 6.6, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.8, 133.7, 128.5, 127.8, 127.7, 126.2, 75.6, 73.1, 68.9, 42.5, 36.8, 33.6, 31.4, 30.3, 20.0, 18.3, 14.8; IR (thin film) 3367, 3077, 1640, 1453, 1376, 968, 910 cm^{-1}; HRMS (EI) *m* / *z* calcd for $C_{19}H_{30}NaO_2$ $(M + Na)^+$ 313.2144, found 313.2139.



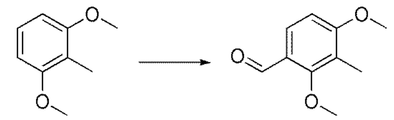
S4 **5** **S5**

(*E*)-(4*R*,5*R*,8*S*)-4,8-Dimethyldeca-2,9-dien-5-ol (S5). A solution of known aldehyde **S4**[6] (0.20 g, 1.80 mmol, 2.4 equiv) and boronate **5**[4] (0.23g, 0.75 mmol) were combined in 1.5 mL of *n*-hexane. The flask was capped, sealed with Teflon tape, and held at 0 ºC for 36 h. The hexane was removed *in vacuo* and the residue was dissolved in 4.0 mL of THF and 1.0 mL of aq. NaOH (3.0 M). After the addition of H_2O_2 (1.5 mL), the mixture was heated at reflux (ca. 80 ºC) for 2 h. Upon reaching ambient temperature, the organic layer was washed with aq. NaOH and brine and dried over Na_2SO_4 to afford a white paste containing desired alcohol **S5** and the chiral auxiliary diol **S2**. The majority of diol **S2** was separated from alcohol **S5** by trituration of the residue with pentane (3 x 10 mL). The pentane triturate was filtered, concentrated, and subjected to flash chromatography (15 mL of silica) with hexanes:Et_2O (1:19) to provide alcohol **S5** as a pale oil (0.13 g, 95%): ^1H NMR (500 MHz, $CDCl_3$) δ 5.67 (ddd, *J* = 17.5, 10.3, 7.6, 1H), 5.53–5.47 (m, 1H), 5.38–5.34 (m, 1H), 4.97–4.90 (m, 2H), 3.44–3.40 (m, 1H), 2.21 (app. sext., *J* = 6.8, 1H), 2.16–2.08 (m, 1H), 1.68 (d, *J* = 6.3, 3H), 1.51–1.43 (m, 3H), 1.35–1.28 (m, 2H), 1.00 (d, *J* = 6.8, 3H), 0.98 (d, *J* = 6.9, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.7, 133.7, 126.1, 112.9, 75.2, 42.7, 38.0, 33.0, 31.6, 20.6, 18.2, 15.0; IR (thin film) 3367, 3077, 1640, 1453, 1376, 968, 910 cm^{-1}; HRMS (EI) *m* / *z* calcd for $C_{12}H_{22}NaO$ $(M +Na)^+$ 205.1568, found 205.1560.

---

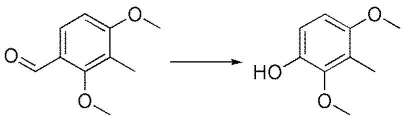
[5] Breitenbach, R.; Chiu, C. K.-F.; Massett, S. S.; Meltz, M.; Murtiashaw, C. W.; Pezzullo, S. L.; Staigers, T. *Tetrahedron Asym.* **1996**, *7*, 435.

[6] Kocienski, P. J.; Cernigliaro, G. J. *J. Org. Chem.* **1977**, *42*, 3622.



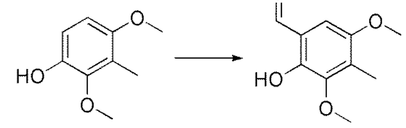
S6

2,4-Dimethoxy-3-methylbenzaldehyde (S6). A dry two-necked flask (1L), fitted with a mechanical stirrer and addition funnel, was charged with a solution of 2,6-dimethoxytoluene (76.1 g, 500 mmol) in 70 mL of CH_2Cl_2. After cooling to 0° C, a 550.0 mL (550 mmol, 1.10 equiv.) solution of $TiCl_4$ (1.0 M in CH_2Cl_2) was added dropwise over 1 h. Freshly distilled CH_3OCHCl_2 (47.5 mL, 525 mmol, 1.05 equiv.) was added dropwise over 1h using a syringe pump. After this addition, 200 mL of aq. HCl (3.0 M) was added and the maroon mixture was stirred vigorously for 30 min. Upon separation the dark violet organic layer was concentrated, then dissolved in 500 mL of Et_2O and washed sequentially with aq. HCl (1.0 M) and brine. Drying over Na_2SO_4, filtration, and concentration afforded a dark red oil. After 24 h under vacuum (ca. 20 Torr), the red-orange paste was recrystallized from petroleum ether (4 crops) to deliver benzaldehyde **S6** as off-white needles (77.9 g, 86%): mp = 51–54° C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.24 (s, 1H), 7.75 (d, *J* = 8.8, 1H), 6.75 (d, *J* = 8.8, 1H), 3.91 (s, 3H), 3.86 (s, 3H), 2.17 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 189.6, 164.5, 163.0, 128.4, 123.3, 120.6, 107.0, 63.6, 56.3, 8.9; IR (KBr) 3000, 2753, 1686, 1597, 1280, 1108 cm^{-1}; HRMS (EI) *m* / *z* calcd for $C_{10}H_{12}O_3$ $(M)^+$ 180.0786, found 180.0780.



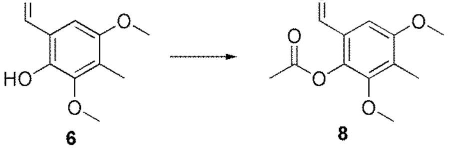
S6 **S7**

2,4-Dimethoxy-3-methylphenol (S7). A solution of peracetic acid (32% w/w in AcOH, 84.0 mL, 400 mmol, 1.2 equiv) was added dropwise with an addition funnel to a solution of benzaldehyde **S6** (60.0 g, 333 mmol) in 200 mL of CH_2Cl_2 at 0 °C. After 1 h, the mixture was stirred for 30 min with 100 mL of H_2O. The organic layer was washed with aq. $NaHCO_3$ and brine, and the aqueous layers were back-extracted with 100 mL of CH_2Cl_2. The combined organic layers were concentrated and dissolved in 200 mL of MeOH. K_2CO_3 (50.6 g, 366.3 mmol, 1.1 equiv.) was added in two portions over 5 min (a moderate exotherm was observed), and after 30 min the majority of MeOH was removed *in vacuo*. The residue was partitioned between 200 mL of Et_2O and H_2O and the aqueous layer acidified to pH 1.0 by the slow addition of conc. HCl. The organic layer was washed with brine, dried over Na_2SO_4, and concentrated to afford a dark red oil. Flash chromatography through a 500 mL silica plug with 1:1 hexanes:CH_2Cl_2 as the eluant afforded an orange oil that solidified after 24 h under vacuum (ca. 20 Torr) to afford a whitish-orange wax (51.3 g, 93%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.74 (d, *J* = 8.8, 1H), 6.53 (d, *J* = 8.8, 1H), 5.35 (s, 1H), 3.77 (s, 6H), 2.17 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.1, 146.2, 143.1, 120.2, 111.9, 106.9, 61.0, 56.3, 9.5; IR (KBr) 3505–3299 (br), 3006, 2948, 2832, 1617, 1490, 1262, 1105, 1015, 861, 798 cm^{-1}; HRMS (EI) *m* / *z* calcd for $C_9H_{12}O_3$ $(M)^+$ 168.0786, found 168.0785.

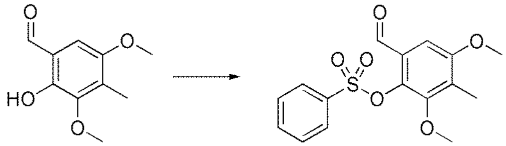


S7 **6**

2-Hydroxy-3,5-dimethoxy-4-methylbenzaldehyde (6).[7] To a solution of phenol **S7** (5.00 g, 29.7 mmol) in 200 mL of distilled acetic acid at 100° C was added hexamethylenetetraamine (25.0 g, 178.4 mmol, 6.0 equiv.) in three portions over 10 min. After stirring for 25 min and cooling to ambient temperature, H_2O (200 mL) was added and the mixture was stirred vigorously for 1 h to ensure complete imine hydrolysis. The mixture was extracted with CH_2Cl_2, and the organic layers were washed with $NaHCO_3$ and brine, and dried over Na_2SO_4. The crude brown solid was chromatographed through a 200 mL plug of silica with 1:1 hexane:CH_2Cl_2 to afford Kubo's hydroxybenzaldehyde **6**[7] as yellow needles (4.12 g, 71%): mp = 106–108 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.84 (s, 1H), 9.82 (s, 1H), 6.70 (s, 1H), 3.88 (s, 3H), 3.83 (s, 3H), 2.22 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 195.9, 151.5, 150.2, 147.0, 131.5, 118.3, 107.3, 60.5, 56.1, 20.9, 10.1; IR (KBr) 3432 (br), 1656, 1625, 1472, 1317, 1135, 947 cm^{-1}; HRMS (EI) *m* / *z* calcd for $C_{10}H_{12}NaO_4$ $(M + Na)^+$ 219.0633, found 219.0636.



2-Acetoxy-3,5-dimethoxy-4-methylbenzaldehyde (8). A mixture of phenol **6** (0.80 g, 4.08 mmol), NEt_3 (1.71 mL, 12.23 mmol, 3.0 equiv), and freshly distilled AcCl (0.44 mL, 6.12 mmol, 1.5 equiv) in 50 mL of CH_2Cl_2 at rt was stirred for 2 h. The mixture was diluted with Et_2O (5 mL) and washed sequentially with saturated aqueous solutions of NH_4Cl, $NaHCO_3$, and brine. Treatment with Na_2SO_4, filtration, and concentration afforded a yellow oil that was purified by flash chromatography (50 mL of SiO_2) with 9:1 hexanes:Et_2O to deliver acetate **8** as a light yellow powder (0.93 g, 96%): mp = 82–84 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.04 (s, 1H), 7.09 (s, 1H), 3.88 (s, 3H), 3.78 (s, 3H), 2.41 (s, 3H), 2.22 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 188.1, 169.6, 156.6, 151.3, 140.4, 129.5, 126.7, 104.8, 61.2, 56.1, 20.7, 10.2; IR (KBr) 2968, 2872, 1769, 1685, 1470, 1201, 856, 738 cm^{-1}; HRMS (EI) *m* / *z* calcd for $C_{12}H_{14}NaO_5$ $(M + Na)^+$ 261.0739, found 261.0746.

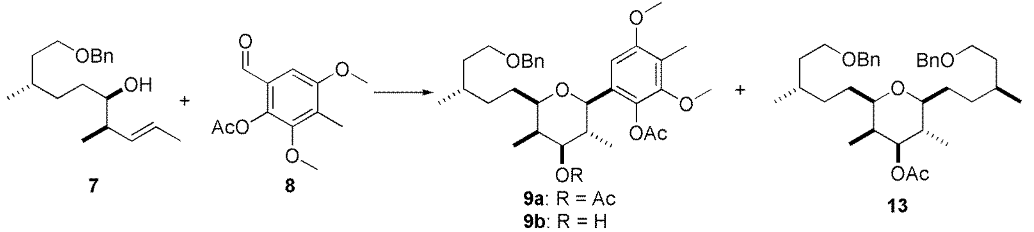


Benzenesulfonic acid 6-formyl-2,4-dimethoxy-3-methylphenyl ester (10). To a solution of phenol **6** (2.50 g, 12.74 mmol) and freshly distilled $PhSO_2Cl$ (1.95 mL, 15.29 mmol, 1.2 equiv) in 50 mL of CH_2Cl_2 was added NEt_3 (4.44 mL, 31.86 mmol, 2.5 equiv) dropwise using an addition funnel, and the mixture was stirred at rt overnight before the addition of 10 mL of aq. HCl (3.0 M). The organic layer was separated and washed aq. $NaHCO_3$ and brine, dried over Na_2SO_4, filtered, and concentrated to an orange solid. Flash chromatography through 80 mL of silica with 1:1 hexanes:CH_2Cl_2 afforded sulfonate **10** as an off-white powder (3.86 g, 90%): mp = 136–138 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.96 (s, 1H), 7.95–7.93 (m, 2H), 7.74–7.71 (m, 1H), 7.59–7.56 (m, 2H), 7.12 (s, 1H), 3.87 (s, 3H), 3.61 (s, 3H), 2.14 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 187.5, 157.2, 152.2, 139.4, 135.7, 134.8, 129.6, 129.4, 128.7, 128.6, 103.2, 61.0,

---

[7] Kubo, A.; Kitahara, Y.; Nakahara, S.; Numata, R. *Chem. Pharm. Bull.* **1985**, *33*, 2122.

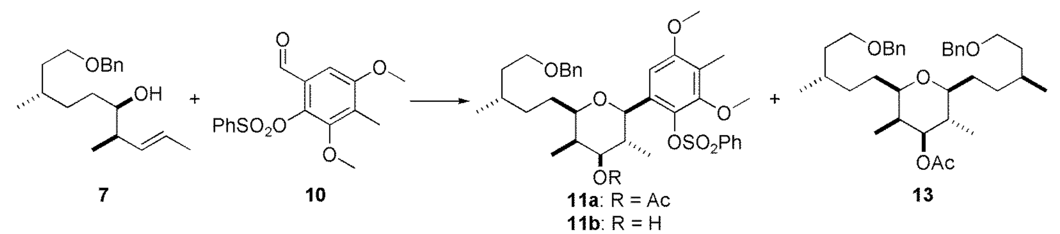
56.1, 10.1; IR (KBr) 3854, 1694, 1584, 1465, 1366, 1178 cm^{-1}; HRMS (EI) *m* / *z* calcd for $C_{16}H_{17}NaO_6S$ (M + H)$^+$ 337.0746, found 337.0742;



7 8 9a: R = Ac 9b: R = H 13

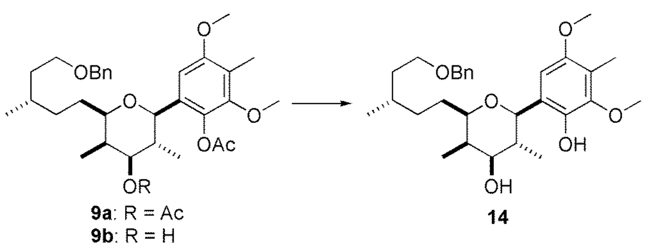
Acetic acid 6-[(2*R*,3*R*,4*S*,5*S*,6*R*)-4-acetoxy-6-((*S*)-5-benzyloxy-3-methylpentyl)- 3,5-dimethyltetrahydropyran-2-yl]-2,4-dimethoxy-3-methylphenyl ester (9a). To a heterogeneous mixture of alcohol **7** (60 mg, 207 µmol), benzaldehyde **8** (49 mg, 108 µmol, 1.05 equiv.), and AcOH (59 µL, 1033 mmol, 5.0 equiv.) in 3.0 mL of *n*-hexane at 0 ºC was added $BF_3{\cdot}OEt_2$ (65 µmol, 2.5 equiv.). An orange precipitate formed immediately, and the stirred mixture was allowed to reach rt overnight. Et_2O (5 mL) was added and the mixture became homogeneous. After stirring for 5 min, 2 mL of aq. $NaHCO_3$ was added. The organic layer was washed with additional aqueous $NaHCO_3$ and brine. Drying over Na_2SO_4, filtering, and removing the solvent *in vacuo* left an oily yellow residue, which was purified by preparatory TLC with 1:1 hexanes:Et_2O to afford THP **9a** (59 mg, 50%), THP **9b** (16 mg, 15%), and THP **13** (5 mg, 9%), all as pale oils; **THP 9a**: $[\alpha]^{24}_{D}$ +14.7 (*c* 1.00, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.35–7.24 (m, 5H), 6.63 (br. s, 1H), 4.78 (dd, *J* = 11.0, 4.8), 1H), 4.74 (s, 2H), 4.13–4.08 (m, 1H), 3.82 (s, 3H), 3.71 (s, 3H), 3.52–3.44 (m, 3H), 2.30 (s, 3H), 2.13 (s, 3H), 2.16–2.12 (m, 1H), 2.10 (s, 3H), 1.68–1.52 (m, 4H), 1.48–1.33 (m, 4H), 0.99 (d, *J* = 6.9, 3H), 0.86 (d, *J* = 6.6, 3H), 0.65 (d, *J* = 6.5); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.8, 169.1, 157.0, 150.8, 144.0, 138.9, 136.4, 130.3, 128.5, 127.8, 127.6, 121.1, 79.6, 79.2, 73.1, 73.0, 68.8, 60.9, 55.9, 36.8, 35.4, 32.9, 30.1, 29.8, 21.3, 21.1, 20.8, 19.7, 13.4, 9.4, 6.5; IR (thin film) 2934, 1771, 1732, 1558, 1457, 1241, 1195, 1129 cm^{-1}; HRMS (EI) *m* / *z* calcd for $C_{33}H_{46}O_8$ (M + Na)$^+$ 593.3090, found 593.3090.
THP 9b: $[\alpha]^{24}_{D}$ +14.2 (*c* 1.00, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.38–7.30 (m, 4H), 7.28–7.25 (m, 1H), 6.63 (br. s, 1H), 4.48 (s, 2H), 4.01 (app. d, *J* = 10.0, 1H), 3.80 (s, 3H), 3.70 (s, 3H), 3.53–3.45 (m, 3H), 3.42 (td, *J* = 7.1, 1.6, 1H), 2.30 (s, 3H), 2.13 (s, 3H), 1.96–1.92 (m, 1H), 1.90–1.84 (m, 1H), 1.67–1.60 (m, 3H), 1.51–1.34 (m, 4H), 1.10–1.03 (m, H), 1.00 (d, *J* = 6.9, 3H), 0.87 (d, *J* = 6.6, 3H), 0.76 (d, *J* = 6.6, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.4, 151.0, 138.9, 136.5, 130.7, 128.6, 128.5, 127.8, 127.7, 120.9, 82.0, 79.9, 77.4, 73.1, 68.8, 60.9, 55.9, 38.0, 37.8, 36.9, 32.9, 30.0, 29.8, 20.8, 19.7, 13.5, 9.4, 5.9; IR (thin film) 3481 (br), 2931, 1771, 1457, 1365, 1196, 1129, 908, 734 cm^{-1}; HRMS (EI) *m* / *z* calcd for $C_{31}H_{44}NaO_7$ (M + Na)$^+$ 551.2985, found 551.2979.

THP 13: $[\alpha]^{24}_{D}$ +18.5 (*c* 1.00, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.35–7.25 (m, 10H), 4.60 (dd, *J* = 11.1, 4.8, 1H), 4.50–4.48 (m, 4H), 3.56–3.44 (m, 4H), 3.29 (ddd, *J* = 7.4, 5.5, 1.7, 1H), 2.91 (m, 1H), 2.08 (s, 3H), 2.04–1.97 (m, 1H), 1.72–1.32 (m, 15H), 0.87 (d, *J* = 6.6, 3H), 0.86 (d, *J* = 6.5, 3H), 0.83 (d, *J* = 6.8, 3H), 0.78 (d, *J* = 6.4, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.9, 138.9, 138.8, 128.5, 128.1, 127.81, 127.80, 127.71, 127.67, 82.0, 79.4, 78.6, 73.1, 73.0, 68.93, 68.90, 37.2, 37.0, 35.7, 35.0, 33.4, 32.9, 30.5, 30.1, 30.08, 30.04, 21.4, 19.8, 19.7, 13.4, 6.5; IR (thin film) 2927, 1741, 1456, 1241, 1101, 1027, 736, 698 cm^{-1}; HRMS (EI) *m* / *z* calcd for $C_{35}H_{52}NaO_5$ (M + Na)$^+$ 575.3712, found 575.3723.

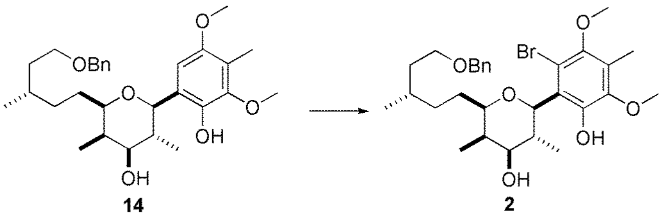


Acetic acid (2*R*,3*R*,4*S*,5*S*,6*R*)-2-(2-benzenesulfonyloxy-3,5-dimethoxy-4-methylphenyl)-6-((*S*)-5-benzyloxy-3-methylpentyl)-3,5-dimethyltetrahydropyran-4-yl ester (11a). To a heterogeneous mixture of alcohol **7** (60 mg, 207 µmol), benzaldehyde **10** (69 mg, 207 µmol, 1.00 equiv.), and AcOH (59 µL, 1033 µmol, 5.0 equiv.) in 3.0 mL of *n*-hexane at 0 °C was added $BF_3{\cdot}OEt_2$ (65 µmol, 2.5 equiv.). A dark orange precipitate formed immediately and after 6 h, 2 mL of aq. $NaHCO_3$ and 3 mL of Et_2O were added. The organic layer was washed with aq. $NaHCO_3$ and brine. Drying over Na_2SO_4, filtering, and removing the solvent *in vacuo* left an oil, which was purified by preparatory TLC with 1:1 hexanes:Et_2O to afford THP **11a** (105 mg, 76%), THP **11b** (13 mg, 10%), and THP **13** (5 mg, 9%), all as pale oils. **THP 11a**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04–8.01 (m, 2H), 7.68–7.65 (m, 1H), 7.58–7.54 (m, 2H), 7.34–7.24 (m, 5H), 6.67 (s, 1H), 4.64 (dd, *J* = 10.9, 4.7, 1H), 4.48 (s, 2H), 4.17 (d, *J* = 10.3, 1H), 3.83 (s, 3H), 3.53–3.47 (m, 2H), 3.44 (s, 3H), 3.25 (td, *J* = 6.6, 1.1, 1H), 2.09 (s, 3H), 2.08 (s, 3H), 1.99–1.92 (m, 1H), 1.70–1.50 (m, 4H), 1.48–1.40 (m, 2H), 1.38–1.32 (m, 1H), 1.08–1.02 (m, 1H), 0.97 (d, *J* = 6.9, 3H), 0.89 (d, *J* = 6.5, 3H), 0.64 (d, *J* = 6.5, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.6, 157.3, 151.4, 138.8, 137.9, 135.8, 134.0, 132.4, 129.1, 128.5, 128.3, 127.8, 127.6, 121.4, 103.8, 79.1, 79.0, 73.1, 68.8, 60.4, 55.8, 36.9, 36.2, 35.0, 32.7, 30.2, 29.8, 21.3, 19.7, 14.4, 13.0, 9.4, 6.4; IR (thin film) 2934, 1739, 1455, 1373, 1240, 1130, 884, 794 cm^{-1}; HRMS (EI) *m* / *z* calcd for $C_{37}H_{48}NaO_9S$ $(M + Na)^+$ 691.2917, found 691.2909.

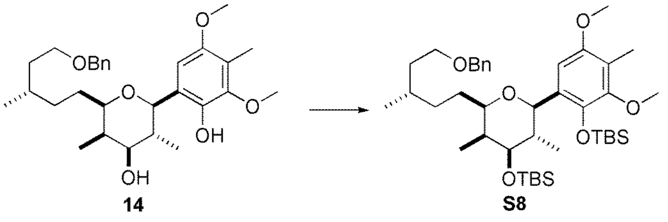
THP 11b: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04–8.01 (m, 2H), 7.66–7.63 (m, 1H), 7.55–7.52 (m, 2H), 7.33–7.25 (m, 5H), 6.67 (s, 1H), 4.48 (s, 2H), 4.15 (d, *J* = 10.0, 1H), 3.82 (s, 3H), 3.52–3.48 (m, 2H), 3.45–3.38 (m, 4H), 3.24 (td, *J* = 6.8, 1.5, 1H), 2.07 (s, 3H), 1.89–1.87 (m, 1H), 1.80–1.74 (m, 1H), 1.67–1.54 (m, 4H), 1.48–1.43 (m, 2H), 1.39–1.35 (m, 1H), 1.09–1.04 (m, 1H), 0.97 (d, *J* = 6.9, 3H), 0.90 (d, *J* = 6.5, 3H), 0.77 (d, *J* = 6.5, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.3, 151.4, 138.9, 138.0, 136.0, 134.4, 133.9, 129.0, 128.6, 128.4, 127.8, 127.7, 121.2, 104.0, 79.6, 77.81, 77.85, 73.1, 68.9, 60.4, 55.8, 38.7, 37.8, 37.0, 32.8, 30.1, 29.8, 19.7, 13.1, 9.4, 5.8; IR (thin film) 3445(br), 2928, 2871, 1586, 1456, 1371, 1776, 1130 cm^{-1}; HRMS (EI) *m* / *z* calcd for $C_{35}H_{46}NaO_8S$ $(M + Na)^+$ 649.2811, found 649.2826.



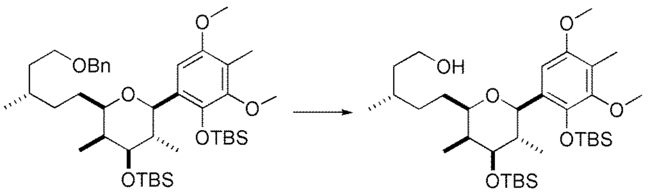
(2*R*,3*R*,4*S*,5*R*,6*R*)-2-((*S*)-5-Benzyloxy-3-methylpentyl)-6-(2-hydroxy-3,5-dimethoxy-4-methylphenyl)-3,5-dimethyltetrahydropyran-4-ol (14). A solution of acetate **9a** (59 mg, 103 µmol) and alcohol **9b** (16 mg, 30 µmol) in 1.0 mL of $CHCl_3$ at –78 °C was treated with DIBAL (1.0 M in hexanes, 401 µL, 401 µmol, 3.0 equiv.) and stirred for 1 h. To the reaction mixture was added 5 mL of saturated aqueous sodium potassium tartrate. After 1 h of vigorous stirring and dilution with 5 mL of Et_2O, the organic layer was washed with brine and dried over Na_2SO_4. The solvent was removed *in vacuo*, and the residue was purified by preparatory TLC (1:2 hexanes:Et_2O) to afford THP **14** as a pale oil (59 mg, 91%): $[\alpha]^{24}_{D}$ +37.9 (*c* 1.00, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.35–7.24 (m, 5H), 6.89 (s, 1H), 6.34 (s, 1H), 4.48 (br. s, 2H), 4.15 (d, *J* = 10.3, 1H), 3.81 (s, 3H), 3.76 (s, 3H), 3.60–3.45 (m, 4H), 2.14 (s, 3H), 1.97 (ddq, *J* = 1.8, 4.8, 6.6, 1H), 1.93 (qdd, *J* = 6.6, 9.6, 10.3, 1H), 1.68–1.58 (m, 3H), 1.65 (br. s, 1H), 1.54–1.47 (m, 1H), 1.46–1.37 (m, 2H), 1.34–1.25 (m, 1H), 1.01 (d, *J* = 6.9, 3H), 0.88 (d, *J* = 6.4, 3H), 0.83 (d, *J* = 6.5, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.1, 147.0, 142.3, 138.8, 128.5, 127.8, 127.7, 122.8, 120.2, 106.2, 83.7, 80.4, 77.0, 73.1, 68.7, 60.6, 56.3, 38.2, 37.6, 36.9, 33.0, 30.0, 29.9, 19.6, 13.7, 9.2, 5.9; IR (thin film) 3368 (br), 2928, 2870, 1462, 1367, 1121, 1092, 738, 699 cm^{-1}; HRMS (EI) *m* / *z* calcd for $C_{29}H_{42}NaO_6$ $(M + Na)^+$ 509.2879, found 509.2863.



(2*R*,3*R*,4*S*,5*R*,6*R*)-2-((*S*)-5-Benzyloxy-3-methylpentyl)-6-(2-bromo-6-hydroxy-3,5-dimethoxy-4-methylphenyl)-3,5-dimethyltetrahydropyran-4-ol (2). Diol **14** (35 mg, 72 μmol) was dissolved in 1.5 mL of $CHCl_3$, and a 1.0 mL solution of Br_2 (4 μL, 86 μmol, 1.2 equiv.) in $CHCl_3$ was added dropwise over 10 min. After 2 h, aqueous $Na_2S_2O_3$ (2 mL) and Et_2O (3 mL) were added. The organic layer was washed with brine and dried over Na_2SO_4. Concentration afforded a residue that was purified by preparatory TLC (1:1 hexanes:Et_2O) to afford THP **2** as a yellow film (26 mg, 65%): $[\alpha]^{24}_{D}$ +46.1 (*c* 1.00, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 8.32 (s, 1H), 7.38–7.25 (m, 5H), 4.83 (d, *J* = 10.6, 1H), 4.48 (s, 2H), 3.84 (s, 3H), 3.72 (s, 3H), 3.62–3.55 (m, 2H), 3.53–3.43 (m, 2H), 2.25 (s, 3H), 2.12 (qdd, *J* = 6.6, 9.9, 10.4, 1H), 2.02 (ddq, *J* = 1.8, 4.8, 6.6, 1H), 1.68–1.50 (m, 5H), 1.47–1.38 (m, 2H), 1.18–1.08 (m, 1H), 1.00 (d, *J* = 7.0, 3H), 0.91 (d, *J* = 6.6, 3H), 0.88 (d, *J* = 6.5, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.5, 147.0, 146.6, 138.8, 128.6, 127.8, 127.7, 126.6, 123.0, 113.3, 84.4, 81.2, 76.6, 73.1, 68.7, 60.6, 60.4, 38.0, 37.1, 36.9, 32.8, 30.0, 29.9, 19.9, 13.6, 10.4, 6.0; IR (thin film) 3297 (br), 2934, 1559, 1457, 1464, 1089 cm^{-1}; HRMS (EI) *m* / *z* calcd for $C_{29}H_{45}BrNO_6$ $(M + NH_4)^+$ 582.2430, found 582.2429.

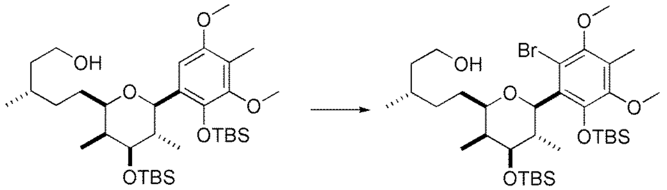


(2*R*,3*S*,4*S*,5*S*,6*R*)-2-((*S*)-5-Benzyloxy-3-methylpentyl)-4-(*tert*-butyldimethylsilanyloxy)-6-[2-(*tert*-butyldimethylsilanyloxy)-3,5-dimethoxy-4-methylphenyl]-3,5-dimethyltetrahydropyran (S8). A solution of diol **14** (44 mg, 90 μmol) and 2,6-lutidine (126 μL, 1085 μmol, 12.0 equiv.) in 1.0 mL of CH_2Cl_2 was cooled to 0 °C. Over 1 min, TBSOTf (125 μL, 542 μmol, 6.0 equiv.) was added dropwise. The solution was allowed to reach rt and stirred for 24 h. The reaction mixture was quenched with 2 mL of saturated aq. $NaHCO_3$ and diluted with 5 mL of Et_2O. The organic layer was separated, washed with brine, and dried over Na_2SO_4. The residue was purified by preparatory TLC (4:1 hexanes:Et_2O) to afford bis-silylether **S8** as a thin film (52 mg, 80%): $[\alpha]^{24}_{D}$ +29.0 (*c* 1.00, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.34–7.30 (m, 4H), 7.28–7.24 (m, 1H), 6.61 (s, 1H), 4.48 (s, 2H), 4.39 (d, *J* = 10.3, 1H), 3.79 (s, 3H), 3.62 (s, 3H), 3.51–3.45 (m, 3H), 3.38–3.35 (m, 1H), 2.10 (s, 3H), 1.80 (ddq, *J* = 1.7, 4.8, 6.6, 1H), 1.71 (qt, *J* = 6.6, 10.2, 1H), 1.67–1.54 (m, 4H), 1.48–1.38 (m, 3H), 1.03 (s, 9H), 1.01 (d, *J* = 6.7, 3H), 0.91 (s, 9H), 0.87 (d, *J* = 6.6, 3H), 0.62 (d, *J* = 6.6, 3H), 0.20 (s, 3H), 0.10 (s, 3H), 0.08 (s, 3H), 0.07 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.0, 149.8, 140.3, 138.9, 130.4, 128.5, 127.8, 127.7, 119.8, 104.1, 79.6, 78.5, 77.3, 73.1, 68.9, 60.1, 55.8, 39.8, 39.4, 37.1, 33.4, 30.3, 30.1, 26.4, 26.1, 19.7, 18.8, 18.4, 13.6, 9.3, 6.2, –3.8, –3.9, –4.6, –4.7; IR (thin film) 3735, 2930, 1457, 1252, 1129, 1076, 837 cm^{-1}; HRMS (EI) *m* / *z* calcd for $C_{41}H_{70}NaO_6Si_2$ $(M + Na)^+$ 737.4609, found 737.4603.



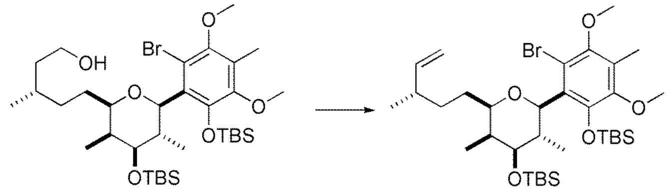
S8 **S9**

(*S*)-5-{(2*R*,3*S*,4*S*,5*S*,6*R*)-4-(*tert*-Butyldimethylsilanyloxy)-6-[2-(*tert*-butyldimethylsilanyloxy)-3,5-dimethoxy-4-methylphenyl]-3,5-dimethyltetrahydropyran-2-yl}-3-methylpentan-1-ol (S9). A suspension of benzyl ether **S8** (55 mg, 77 μmol) and 10% $Pd(OH)_2/C$ (8 mg) in 2.0 mL of EtOAc was subjected to 1 atm of H_2 for 2 h, when TLC analysis indicated complete hydrogenolysis. Filtration through celite, concentration, and purification of the residue by flash chromatography (3:1 hexanes:Et_2O) afforded alcohol **S9** as a thin film (43 mg, 89%): $[\alpha]^{24}_{D}$ +32.9 (*c* 1.00, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.61 (s, 1H), 4.41 (d, *J* = 10.4, 1H), 3.79 (s, 3H), 3.68–3.59 (m, 2H), 3.62 (s, 3H), 3.47 (dd, *J* = 4.6, 10.0, 1H), 3.38 (app. t, *J* = 5.6, 1H), 2.10 (s, 3H), 1.80 (ddq, *J* = 1.7, 4.8, 6.6, 1H), 1.71 (qdd, *J* = 6.6, 9.9, 10.2, 1H), 1.62–1.51 (m, 4H), 1.48–1.36 (m, 4H), 1.03 (s, 9H), 1.01 (d, *J* = 6.9, 3H), 0.92 (s, 9H), 0.88 (d, *J* = 6.5, 3H), 0.63 (d, *J* = 6.5, 3H), 0.21 (s, 3H), 0.11 (s, 3H), 0.08 (s, 3H), 0.07 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.0, 149.9, 140.3, 130.3, 119.9, 104.2, 79.6, 78.5, 77.4, 61.3, 60.0, 55.8, 40.3, 39.8, 39.5, 33.4, 30.4, 29.8, 26.4, 26.1, 19.6, 18.8, 18.4, 13.6, 9.3, 6.2, -3.8, -3.9, -4.6, -4.7; IR (thin film) 3420 (br), 2930, 1558, 1457, 1253, 1130, 836 cm^{-1}; HRMS (EI) *m* / *z* calcd for $C_{34}H_{64}NaO_6Si_2$ $(M + Na)^+$ 647.4139, found 647.4142.



S9 **S10**

(*S*)-5-[(2*R*,3*S*,4*S*,5*S*,6*R*)-6-[2-Bromo-6-(*tert*-butyldimethylsilanyloxy)-3,5-dimethoxy-4-methylphenyl]-4-(*tert*-butyldimethylsilanyloxy)-3,5-dimethyltetrahydropyran-2-yl]-3-methylpentan-1-ol (S10). To a solution of alcohol **S9** (20 mg, 32.0 μmol) and 20 μL of propylene oxide (288.0 μmol, 9.0 equiv.) in 1.0 mL of CH_2Cl_2 was added 2.5 μL of neat Br_2 (48.0 μmol, 1.50 equiv.) dropwise over 1 min at rt. The mixture was stirred for 1 h until TLC indicated complete consumption of the starting material, at which time 2 mL of Et_2O and 2 mL of aqueous $Na_2S_2O_3$ were added. After stirring vigorously for 30 min, the organic layer was washed with brine and dried over Na_2SO_4. Concentration afforded a residue that was purified by column chromatography (2:1 hexanes:Et_2O) to afford aryl bromide **S10** as a yellow film (17 mg, 75%): $[\alpha]^{24}_{D}$ +26.7 (*c* 1.00, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.65 (d, *J* = 10.6, 1H), 3.69–3.61 (m, 2H), 3.75 (s, 3H), 3.59 (s, 3H), 3.41 (dd, *J* = 4.5, 9.9, 1H), 3.39 (dt, *J* = 1.8, 6.7, 1H), 2.49 (qdd, J = 6.6, 9.9, 10.5, 1H), 2.25 (s, 3H), 1.79 (ddq, J = 1.4, 4.6, 6.7, 1H), 1.65–1.37 (m, 8H), 1.10 (d, J = 6.8, 3H), 1.04 (s, 9H), 0.91 (s, 9H), 0.90 (d, J = 6.6, 3H), 0.57 (d, J = 6.6, 3H), 0.24 (s, 3H), 0.11 (s, 3H), 0.07 (s, 3H), 0.06 (s, 3H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 150.9, 149.4, 144.5, 129.3, 125.7, 112.9, 80.1, 78.8, 78.0, 61.4, 60.4, 59.9, 40.3, 39.6, 34.8, 33.3, 30.2, 29.8, 26.3, 26.1, 19.6, 18.8, 18.4, 13.5, 10.6, 7.0, -3.6, -4.0, -4.6, -4.8; IR (thin film) 3335 (br), 2930, 2858, 1447, 1253, 1106, 836 cm^{-1}; HRMS (EI) m / z calcd for $\mathrm{C_{34}H_{63}BrNaO_6Si_2}$ (M + Na)$^+$ 725.3244, found 725.3239.



S10 **15**

(2*R*,3*S*,4*S*,5*S*,6*R*)-2-[2-Bromo-6-(*tert*-butyldimethylsilanyloxy)-3,5-dimethoxy-4-methylphenyl]-4-(*tert*-butyldimethylsilanyloxy)-3,5-dimethyl-6-((*S*)-3-methylpent-4-enyl)-tetrahydropyran (15).[8] To a mixture of alcohol **S10** (15 mg, 21 μmol) and 19 mg of 2-nitrophenyl selenocyanate (85 μmol, 4.0 equiv.) in 0.5 mL of THF at rt was added freshly distilled PBu$_3$ (40 μL, 160 μmol, 7.5 equiv.). After 1 h of stirring, a second portion of PBu$_3$ (40 μL) was added to drive the reaction to completion. The reaction mixture was concentrated *in vacuo* and passed through a 5 mL plug silica gel with 1% Et$_2$O in hexanes to provide a yellow oil. This crude selenide was dissolved in 0.5 mL of THF and 21 μL of aqueous $\mathrm{H_2O_2}$ (30% w/w) (213 μmol, 10.0 equiv.) was added. After 2 h of stirring, the reaction mixture was concentrated and purified by preparatory TLC (4:1 hexanes:Et$_2$O) to afford olefin **15** as a colorless film (11 mg, 73 %): $[\alpha]^{24}_{\mathrm{D}}$ +27.1 (c 1.00, CHCl$_3$); **CDCl$_3$**: ^{1}H NMR (600 MHz,) δ 5.70 (ddd, J = 7.3, 10.3, 17.5, 1H), 4.94 (app. td, J = 1.5, 17.5, 1H), 4.89 (ddd, J = 0.9, 1.8, 10.3, 1H), 4.65 (d, J = 10.6, 1H), 3.75 (s, 3H), 3.59 (s, 3H), 3.41 (dd, J = 4.6, 9.9, 1H), 3.40 (dt, J = 1.8, 6.6, 1H), 2.48 (qt, J = 6.6, 10.6, 1H), 2.22 (s, 3H), 2.10 (app. sept, J = 6.9, 1H), 1.78 (ddq, J = 1.8, 4.5, 6.6, 1H), 1.68–1.60 (m, 1H), 1.46–1.37 (m, 2H), 1.25–1.17 (m, 1H), 1.10 (d, J = 6.9, 3H), 1.05 (s, 9H), 0.98 (d, J = 6.8, 3H), 0.91 (s, 9H), 0.57 (d, J = 6.6, 3H), 0.24 (s, 3H), 0.12 (s, 3H), 0.07 (s, 3H), 0.05 (s, 3H); ^{13}C NMR (125 MHz) δ 150.9, 149.4, 145.0, 144.5, 129.3, 125.6, 112.9, 112.6, 79.9, 78.9, 78.0, 60.4, 59.9, 39.7, 38.9, 34.8, 32.8, 30.4, 26.3, 26.1, 20.1, 18.8, 18.4, 10.6, 7.0, -3.6, -4.0 -4.6, -4.8;
C$_6$D$_6$: **^{1}H** NMR (600 MHz,) δ (PhH = 7.15) 5.64 (ddd, J = 7.5, 10.3, 17.5), 4.97 (app. td, J = 1.3, 17.5, 1H), 4.95 (d, J = 10.6, 1H), 4.92 (app. d, J = 10.3, 1H), 3.70 (dd, J = 4.6, 9.9, 1H), 3.64 (app. ddd, J = 2.0, 4.5, 8.5, 1H), 3.41 (s, 3H), 3.35 (s, 3H), 2.95 (qt, J = 6.6, 10.6, 1H), 2.15 (s, 3H), 2.09 (app. sept, J = 6.9, 1H), 2.01–1.95 (m, 1H), 1.95–1.88 (m, 1H), 1.68–1.62 (m, 1H), 1.49–142 (m, 1H), 1.45 (d, J = 6.9, 3H), 1.38–1.25 (m, H), 1.10 (s, 9H), 1.02 (s, 9H), 0.97 (d, J = 6.7, 3H), 0.92 (d, J = 6.6, 3H), 0.30 (s, 3H), 0.19 (s, 3H), 0.15 (s, 6H);
^{13}C NMR (125 MHz) δ (PhH = 128.0) 151.8, 149.6, 144.8, 144.2, 129.8, 126.0, 113.7, 112.8, 80.3, 79.4, 78.4, 59.7, 59.4, 41.0, 38.2, 35.3, 33.6, 31.3, 26.3, 26.1, 20.2, 18.7, 18.4, 13.8, 10.5, 7.6, -3.6, -4.0, -4.7, -4.8; IR (thin film) 2956, 2929, 2857, 1447, 1386, 1256, 1108, 1076, 837 cm^{-1}; HRMS (EI) m / z calcd for $\mathrm{C_{34}H_{61}BrNaO_5Si_2}$ (M + Na)$^+$ 707.3139, found 707.3141.

---

[8] NOTE – The spectroscopic data for olefin **15** matches the set reported for an intermediate in Smith's total synthesis of kendomycin: Smith, A. B.; Mesaros, E. F.; Meyer, E. A. *J. Am. Chem. Soc.* **2005**, *127*, 6948.