SUPPORTING INFORMATION

THE PAECILIN PUZZLE – ENANTIOSELECTIVE SYNTHESES OF THE PROPOSED STRUCTURES OF PAECILIN A AND B

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Contents

General methods

Experimental methods: All reactions (except reactions with HF reagent) were carried out in pre-dried round bottom flasks. All solvents were reagent grade and stored over molecular sieves. If it was not mentioned otherwise the commercially available reagents were used without further purification. Degasing was subsequently done by freezing the solvent or respectively the solution and evaporation for a number of times. Due to the necessary reaction temperature short-term cooling was performed either with an ice/water or with a dry ice/acetone bath. Long-term cooling was performed by using the cryostat EK 90 from the *Haake* company. All reactions were magnetically stirred and monitored by thin layer chromatography (TLC) on silica plates Si 60 F_{254} from the *Merck* company. Flash chromatography was performed under increased pressure (p = 0.2–0.4 bar) with silica gel 60 (mesh: 0.032–0.063 mm) from the *Merck* company. Staining was accomplished using VSS (900 mL MeOH, 100 mL acetic acid, 30 mL conc. H_2SO_4 and 5 g vanilline). For high performance liquid chromatography (HPLC) the samples were membrane-filtered (0.2 μm) and the used solvents were HPLC grade. Both used columns Chiralpak® IA (250 × 4.6 mm, 5 μm) and Chiralcel® OD (250 × 4.6 mm, particle size: 10 μm) were from *Daicel Chemical Industries Ltd.*. Yields refer to isolated and purified compounds, unless otherwise stated.

NMR spectroscopy: NMR spectra were recorded with a *Varian* Mercury-300, Unity-300, Inova-500 and Inova-600 spectrometer and a *Bruker* AMX-300 spectrometer in $CDCl_3$; chemical shifts are given in ppm relative to tetramethylsilane (TMS), coupling constants J in Hertz. The solvent signals were used as references and the chemical shifts converted to the TMS scale ($CHCl_3$: δ_H = 7.24 ppm, δ_C = 77.36 ppm). The multiplicities of first order were assigned as: s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublets), etc. Signals of higher orders were assigned as m (multiplet) or m_c (centred multiplet).

ORP: Optical rotation values were measured on a *Perkin-Elmer* Lambda 2 and a *JASCO* P-2000 polarimeter. The used solvent and the sample concentration are mentioned in all cases.

IR spectroscopy: IR spectra were recorded with a *Bruker* Vector 22 spectrometer (Liquids were gauged on NaCl plates and solids in a KBr matrix) and *JASCO* FT/IR-4100 spectrometer (substances were applied neat on an ATR unit).

UV spectroscopy: UV spectra were recorded with a *Perkin-Elmer* Lambda 2 spectrometer and *JASCO* V-630 spectrometer.

Mass spectrometry: ESI-MS and ESI-HRMS spectra were recorded with a *Bruker* Daltronik Apex IV, EI-MS and EI-HRMS spectra were recorded with a *Thermo Finnigan* MAT 95.

Ultrasonic reactor: Reactions using ultrasonic irradiation were performed in a ultrasonic bath RK 102 H from the *Bandelin electronic* company.

Experimental procedures

Synthesis of the vinylchroman 20

(*S*)-2-(Benzyloxymethyl)-5-methoxy-2-vinylchroman (20): A solution of $Pd(OTFA)_2$ (121 mg, 365 µmol, 10 mol%) and (*S,S*)-*i*Pr-BOXAX (**9b**) (174 mg, 365 µmol, 10 mol%) in MeOH (3.6 mL) was stirred at RT for 30 min. After addition of a solution of phenol *E*/*Z*-1**9** (*E*/*Z* = 1:1.7, 1.14 g, 3.65 mmol, 1.00 eq.) in MeOH (5.4 mL) and *p*-benzoquinone (1.58 g, 14.6 mmol, 4.00 eq.) the mixture was heated at 60 °C for 24 h and then cooled to RT. Filtration over a pad of silica gel (15 × 6 cm, washing with petroleum ether/EtOAc = 10:1, TLC monitoring), evaporation of the solvent *in vacuo* and column chromatography on silica gel (petroleum ether/EtOAc = 30:1) provided vinylchroman **20** as a colorless oil (900 mg, 2.90 mmol, 79%, 96% *ee*). Analytical HPLC (column: *Daicel* Chiralcel® OD): wavelength: 205 nm, flow: 0.8 mL/min, eluent: *n*-hexane/*i*-PrOH = 99:1; t_R = 12.0 min, (–)-(*S*)-**20**, 98.0%; t_R = 17.0 min, (+)-(*R*)-**20**, 2.0%; 96% *ee*, α = 1.83. **Optical Rotation**: $[\alpha]_D^{23}$ = –75.2 (*c* = 0.19, $CHCl_3$). **TLC**: R_f = 0.35 (petroleum ether/EtOAc = 20:1). **^{1}H-NMR** (300 MHz, $CDCl_3$): δ = 1.87–2.08 (m, 2 H, 3-H_2), 2.44 (ddd, *J* = 17.1, 10.8, 6.6 Hz, 1 H, 4-H_a), 2.73 (ddd, *J* = 17.1, 4.8, 3.9 Hz, 1 H, 4-H_b), 3.53 (d, *J* = 16.5 Hz, 1 H, CH_aOBn), 3.57 (d, *J* = 16.5 Hz, 1 H, CH_bOBn), 3.79 (s, 3 H, 5-OCH_3), 4.59 (d, *J* = 12.3 Hz, 1 H, OCH_aPh), 4.63 (d, *J* = 12.3 Hz, 1 H, OCH_bPh), 5.17 (dd, *J* = 10.8, 1.5 Hz, 1 H, 2'-H_a), 5.25 (dd, *J* = 17.4, 1.5 Hz, 1 H, 2'-H_b), 5.85 (dd, *J* = 17.4, 10.8 Hz, 1 H, 1'-H), 6.40 (d, *J* = 8.1 Hz, 1 H, 6-H), 6.58 (d, *J* = 8.1 Hz, 1 H, 8-H), 7.06 (t, *J* = 8.1 Hz, 1 H, 7-H), 7.23–7.38 (m, 5 H, 5 × Ph-H) ppm. **^{13}C-NMR** (125 MHz, $CDCl_3$): δ = 16.4 (C-4), 26.6 (C-3), 55.5 (5-OCH_3), 73.7 (OCH_2Ph), 75.6 (CH_2OBn), 78.8 (C-2), 101.6 (C-6), 109.8 (C-8), 110.8 (C-4a), 116.2 (C-2'), 126.9 (C-7), 127.5 (Ph-C_p), 127.6 (Ph-C_o), 128.3 (Ph-C_m), 137.8 (C-1'), 138.3 (Ph-C_i), 154.4 (C-8a), 157.5 (C-5) ppm. **IR** (film): ν(cm^{-1}) = 2934, 2856, 1592, 1468, 1409, 1345, 1315, 1267, 1250, 1193, 1167, 1096, 1028, 929, 773, 738, 698. **UV** (CH_3OH): λ_{max} (lg ε) = 204.0 nm (4.701), 271.5 (3.113), 279.0 (3.121). **MS** (ESI): *m*/*z* (%) = 643.3 (53) $[2M+Na]^+$, 333.2 (100) $[M+Na]^+$, 311.2 (25) $[M+H]^+$. Calcd for $\mathbf{C_{20}H_{22}O_3}$: 311.1642 $[M+H]^+$, Found: 311.1641 $[M+H]^+$ (ESI-HRMS).

Synthesis of the methyl ester 31

Methyl (*S*, *E*)-4-[(*R*)-2-(Benzyloxymethyl)-5-methoxychroman-2-yl]-4-(*tert*-butyldimethylsilyloxy)but-2-enoate (27): A solution of trimethyl phosphonoacetate (1.40 g, 7.70 mmol, 1.70 eq.) in THF (30 mL) was treated with sodium hydride (236 mg, 60% (w/w) in mineral oil, 5.89 mmol, 1.30 eq.) at 0 °C. The resulting mixture was stirred at 0 °C for 45 min before a solution of aldehyde **25** (2.07 g, 4.53 mmol, 1.00 eq.) in THF (15 mL) was added dropwise at 0 °C. Then the slurry was stirred at RT for further 1.5 h before being quenched by addition of a sat. aq. NH_4Cl solution (15 mL). The mixture was poured into sat. aq. NH_4Cl solution (260 mL) and extracted with *t*BuOMe (2 × 130 mL). The combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. Chromatographic separation on silica gel (petroleum ether/*t*BuOMe = 20:1 → 4:1) provided compound **27** (2.18 g, 4.26 mmol, 94%) and the corresponding *Z*-isomer (140 mg, 270 µmol, 6%) as colorless oils. Characterization data for **27**: **TLC**: R_f = 0.22 (petroleum ether/*t*BuOMe = 15:1). **^{1}H-NMR** (300 MHz, $CDCl_3$): δ = –0.01 (s, 3 H, $Si(CH_3)_a$), 0.06 (s, 3 H, $Si(CH_3)_b$), 0.91 (s, 9 H, $SiC(CH_3)_3$), 1.74 (ddd, *J* = 14.1, 10.5, 6.6 Hz, 1 H, 3'-H_a), 2.04 (ddd, *J* = 14.1, 6.3, 4.8 Hz, 1 H, 3'-H_b), 2.45 (ddd, *J* = 17.4, 10.5, 6.3 Hz, 1 H, 4'-H_a), 2.67 (ddd, *J* = 17.4, 6.6, 4.8 Hz, 1 H, 4'-H_b), 3.54 (d, *J* = 10.2 Hz, 1 H, CH_aOBn), 3.63 (d, *J* = 10.2 Hz, 1 H, CH_bOBn), 3.69 (s, 3 H, $COOCH_3$), 3.78 (s, 3 H, 5'-OCH_3), 4.44 (d, *J* = 12.0 Hz, 1 H, OCH_aPh), 4.49 (d, *J* = 12.0 Hz, 1 H, OCH_bPh), 4.64 (dd, *J* = 5.4, 1.5 Hz, 1 H, 4-H), 6.04 (dd, *J* = 15.6, 1.5 Hz, 1 H, 2-H), 6.39 (dd, *J* = 8.1, 0.9 Hz, 1 H, 6'-H), 6.50 (dd, *J* = 8.1, 0.9 Hz, 1 H, 8'-H), 7.05 (t, *J* = 8.1 Hz, 1 H, 7'-H), 7.11 (dd, *J* = 15.6, 5.4 Hz, 1 H, 3-H), 7.17–7.31 (m, 5 H, 5 × Ph-H) ppm. **^{13}C-NMR** (125 MHz, $CDCl_3$): δ = –4.9 ($Si(CH_3)_a$), –4.3 ($Si(CH_3)_b$), 15.9 (C-4'), 18.3 ($Si\underline{C}(CH_3)_3$), 22.8 (C-3'), 26.0 ($SiC(\underline{C}H_3)_3$), 51.5 ($COO\underline{C}H_3$), 55.4 (5'-OCH_3), 68.6 (CH_2OBn), 73.4 (OCH_2Ph), 73.8 (C-4), 79.9 (C-2'), 101.6 (C-6'), 110.0 (C-8'), 110.3 (C-4a'), 121.7 (C-2), 126.9 (C-7'), 127.3, 127.3 (Ph-C_o, Ph-C_p), 128.1 (Ph-C_m), 138.2 (Ph-C_i), 147.5 (C-3), 153.7 (C-8a'), 157.5 (C-5'), 166.6 ($\underline{C}OOCH_3$) ppm. **IR** (neat): $\tilde{\nu}$ (cm^{-1}) = 2953, 2857, 1726, 1659, 1592, 1469, 1438, 1347, 1251, 1192, 1167, 1096, 1029, 838, 776, 737, 699. **UV** (CH_3OH): λ_{max} (lg ε) = 204.0 nm (4.807), 264.0 (3.274), 270.0 (3.276), 279.0 (3.238). **MS** (ESI): *m*/*z* (%) = 1047.6 (79) $[2M+Na]^+$, 535.3 (100) $[M+Na]^+$. Calcd for **$C_{29}H_{40}O_6Si$:** 535.2492 $[M+Na]^+$, Found: 535.2486 $[M+Na]^+$ (ESI-HRMS). Characterization data for *Z*-isomer: **TLC**: R_f = 0.31 (petroleum ether/*t*BuOMe = 15:1). **^{1}H-NMR** (300 MHz, $CDCl_3$): δ = 0.00 (s, 3 H, $Si(CH_3)_a$), 0.09 (s, 3 H, $Si(CH_3)_b$), 0.87 (s, 9 H, $SiC(CH_3)_3$), 1.80 (ddd, *J* = 13.8, 11.1, 6.3 Hz, 1 H, 3'-H_a), 2.04 (ddd, *J* = 13.8, 6.0, 3.6 Hz, 1 H, 3'-H_b), 2.45 (ddd, *J* = 17.1, 11.1, 6.0 Hz, 1 H, 4'-H_a), 2.67 (ddd,

J = 17.1, 6.3, 3.6 Hz, 1 H, 4'-H$_b$), 3.43 (d, J = 9.6 Hz, 1 H, CH$_a$OBn), 3.67 (s, 3 H, COOCH$_3$), 3.78 (s, 3 H, 5'-OCH$_3$), 3.79 (d, J = 9.6 Hz, 1 H, CH$_b$OBn), 4.45 (d, J = 12.0 Hz, 1 H, OCH$_a$Ph), 4.51 (d, J = 12.0 Hz, 1 H, OCH$_b$Ph), 5.63 (d, J = 9.9 Hz, 1 H, 4-H), 5.81 (dd, J = 11.7, 0.9 Hz, 1 H, 2-H), 6.31–6.45 (m, 3 H, 3-H, 6'-H, 8'-H), 7.00 (t, J = 8.1 Hz, 1 H, 7'-H), 7.20–7.35 (m, 5 H, 5 × Ph-H) ppm. **^{13}C-NMR** (125 MHz, CDCl$_3$): δ = –4.8 (Si(CH$_3$)$_a$), –4.7 (Si(CH$_3$)$_b$), 16.0 (C-4'), 18.3 (Si$\underline{\text{C}}$(CH$_3$)$_3$), 22.7 (C-3'), 25.9 (SiC($\underline{\text{C}}$H$_3$)$_3$), 51.3 (COO$\underline{\text{C}}$H$_3$), 55.5 (5'-OCH$_3$), 68.2 (CH$_2$OBn), 71.0 (C-4), 73.5 (OCH$_2$Ph), 79.6 (C-2'), 101.4 (C-6'), 109.8 (C-8'), 110.6 (C-4a'), 119.8 (C-2), 126.7 (C-7'), 127.2 (Ph-C$_o$), 127.3 (Ph-C$_p$), 128.2 (Ph-C$_m$), 138.4 (Ph-C$_i$), 147.0 (C-3), 154.1 (C-8a'), 157.5 (C-5'), 166.2 ($\underline{\text{C}}$OOCH$_3$) ppm. **IR** (film): $\tilde{\nu}$ (cm^{-1}) = 2951, 2928, 2855, 1723, 1591, 1468, 1438, 1251, 1198, 1088, 834, 770, 697. **UV** (CH$_3$OH): $\lambda_{\max}$ (lg ε) = 271.0 nm (3.214), 280.0 (3.162). **MS** (ESI): m/z (%) = 1047.6 (100) [2M+Na]$^+$, 535.3 (96) [M+Na]$^+$. Calcd for **C$_{29}$H$_{40}$O$_6$Si**: 535.2492 [M+Na]$^+$, Found: 535.2489 [M+Na]$^+$ (ESI-HRMS).

Methyl (3*S*, 4*S*)-4-[(*R*)-2-(Benzyloxymethyl)-5-methoxychroman-2-yl]-4-(*tert*-butyldimethylsilyloxy)-3-methylbutanoate (29a): To a suspension of CuBr·Me$_2$S (5.44 g, 26.5 mmol, 6.00 eq.) in THF (40 mL) was added MeLi (33.1 mL of a 1.6 M solution in Et$_2$O, 52.9 mmol, 12.0 eq.) at –35 °C and the resulting mixture was stirred for 40 min at –35 °C. Then TMSCl (3.38 mL, 2.87 g, 26.5 mmol, 6.00 eq.) and a solution of ester **27** (2.26 g, 4.41 mmol, 1.00 eq.) in THF (50 mL) were added and stirring was continued at –35 °C for 60 min. Afterwards the reaction was quenched by carefully addition of NEt$_3$ (75 mL) and water (190 mL). The aqueous layer was extracted with *t*BuOMe (2 × 100 mL) and the combined organic layers were washed with water (150 mL), dried over Na$_2$SO$_4$ and concentrated *in vacuo*. Column chromatography on silica gel (petroleum ether/EtOAc = 20:1 → 10:1) provided ester **29a** as a colorless oil (2.19 g, 4.14 mmol, 94%). **TLC**: R_f = 0.56 (petroleum ether/*t*BuOMe = 6:1). **^{1}H-NMR** (300 MHz, CDCl$_3$): δ = 0.07 (s, 3 H, Si(CH$_3$)$_a$), 0.14 (s, 3 H, Si(CH$_3$)$_b$), 0.92 (s, 9 H, SiC(CH$_3$)$_3$), 1.05 (d, J = 6.9 Hz, 3 H, 3-CH$_3$), 1.73 (ddd, J = 13.5, 10.5, 6.0 Hz, 1 H, 3'-H$_a$), 2.07 (dd, J = 16.2, 10.2 Hz, 1 H, 2-H$_a$), 2.24 (ddd, J = 13.5, 6.0, 4.2 Hz, 1 H, 3'-H$_b$), 2.42–2.59 (m, 2 H, 3-H, 4'-H$_a$), 2.69 (ddd, J = 17.1, 6.0, 4.2 Hz, 1 H, 4'-H$_b$), 2.87 (dd, J = 16.2, 2.4 Hz, 1 H, 2-H$_b$), 3.39 (d, J = 9.9 Hz, 1 H, CH$_a$OBn), 3.54 (s, 3 H, COOCH$_3$), 3.74 (d, J = 9.9 Hz, 1 H, CH$_b$OBn), 3.75 (s, 1 H, 4-H), 3.80 (s, 3 H, 5'-OCH$_3$), 4.44 (s, 2 H, OCH$_2$Ph), 6.38 (d, J = 8.4 Hz, 1 H, 6'-H), 6.45 (d, J = 8.4 Hz, 1 H, 8'-H), 7.03 (t, J = 8.4 Hz, 1 H, 7'-H), 7.18–7.33 (m, 5 H, 5 × Ph-H) ppm. **^{13}C-NMR** (125 MHz, CDCl$_3$): δ = –4.5 (Si(CH$_3$)$_a$), –4.0 (Si(CH$_3$)$_b$), 16.1 (C-4'), 18.7 (Si$\underline{\text{C}}$(CH$_3$)$_3$), 21.2 (3-CH$_3$), 23.8 (C-3'), 26.3 (SiC(CH$_3$)$_3$), 30.8 (C-3), 36.1 (C-2), 51.2 (COOCH$_3$), 55.4 (5'-OCH$_3$), 67.8 (CH$_2$OBn), 73.4

(OCH_2Ph), 80.5 (C-4), 80.8 (C-2'), 101.4 (C-6'), 109.8 (C-8'), 110.6 (C-4a'), 126.9 (C-7'), 127.4, 127.4 (Ph-C_o, Ph-C_p), 128.2 (Ph-C_m), 138.1 (Ph-C_i), 153.8 (C-8a'), 157.6 (C-5'), 174.5 ($\underline{C}OOCH_3$) ppm. **IR** (neat): $\tilde{\nu}$ (cm^{-1}) = 2951, 2929, 2855, 1736, 1591, 1468, 1250, 1165, 1091, 1040, 832, 768, 697. **UV** (CH_3OH): λ_{max} (lg ε) = 204.0 nm (4.759), 273.0 (3.188), 280.0 (3.186), 299.0 (2.574), 308.0 (2.603). **MS** (ESI): *m*/*z* (%) = 1079.6 (20) $[2M+Na]^+$, 551.3 (100) $[M+Na]^+$. Calcd for **$C_{30}H_{44}O_6Si$**: 551.2805 $[M+Na]^+$, Found: 551.2802 $[M+Na]^+$ (ESI-HRMS).

Methyl (3*S*,4*S*)-4-(*tert*-Butyldimethylsilyloxy)-4-[(*R*)-2-(hydroxymethyl)-5-methoxychroman-2-yl]-3-methylbutanoate (29b): Pd/C (73.4 mg, 10% Pd, 69.0 µmol, 10 mol%) was added to a solution of ester **29a** (365 mg, 690 µmol, 1.00 eq.) in EtOAc (10 mL). Hydrogen was passed through the resulting mixture for 1 h at RT. The catalyst was removed by filtration over Celite (washing with EtOAc) and the solvent was evaporated *in vacuo*. Column chromatography on silica gel (petroleum ether/EtOAc = 4:1) furnished the alcohol **29b** as a colorless oil (303 mg, 690 µmol, 100%). **TLC**: R_f = 0.33 (petroleum ether/EtOAc = 3:1). **^{1}H-NMR** (300 MHz, $CDCl_3$): δ = 0.04 (s, 3 H, $Si(CH_3)_a$), 0.17 (s, 3 H, $Si(CH_3)_b$), 0.93 (s, 9 H, $SiC(CH_3)_3$), 1.06 (d, *J* = 6.9 Hz, 3 H, 3-CH_3), 1.75 (ddd, *J* = 15.6, 9.0, 6.6 Hz, 1 H, 3'-H_a), 2.04–2.19 (m, 2 H, 2-H_a, 3'-H_b), 2.42–2.73 (m, 4 H, $CH_2O\underline{H}$, 3-H, 4'-H_2), 2.86 (t, *J* = 6.3 Hz, 1 H, 2-H_b), 3.66 (s, 3 H, $COOCH_3$), 3.73 (t, *J* = 6.3 Hz, 2 H, $C\underline{H}_2OH$), 3.78 (d, *J* = 2.7 Hz, 1 H, 4-H), 3.79 (s, 3 H, 5'-OCH_3), 6.39 (dd, *J* = 8.1, 0.6 Hz, 1 H, 6'-H), 6.49 (dd, *J* = 8.1, 0.6 Hz, 1 H, 8'-H), 7.04 (t, *J* = 8.1 Hz, 1 H, 7'-H) ppm. **^{13}C-NMR** (125 MHz, $CDCl_3$): δ = –4.4 ($Si(CH_3)_a$), –4.3 ($Si(CH_3)_b$), 16.1 (C-4'), 18.6 ($Si\underline{C}(CH_3)_3$), 21.4 (3-CH_3), 23.4 (C-3'), 26.2 ($SiC(\underline{C}H_3)_3$), 30.9 (C-3), 36.9 (C-2), 51.6 ($COO\underline{C}H_3$), 55.4 (5'-OCH_3), 62.2 (CH_2OH), 80.1 (C-4), 80.3 (C-2'), 101.7 (C-6'), 110.0 (C-8'), 110.4 (C-4a'), 127.1 (C-7'), 153.5 (C-8a'), 157.7 (C-5'), 174.5 ($\underline{C}OOCH_3$) ppm. **IR** (neat): $\tilde{\nu}$ (cm^{-1}) = 2953, 2930, 2855, 1736, 1591, 1468, 1438, 1249, 1168, 1091, 1040, 1005, 833, 779, 712, 551. **UV** (CH_3OH): λ_{max} (lg ε) = 204.0 nm (4.651), 273.0 (3.086), 280.0 (3.076). **MS** (ESI): *m*/*z* (%) = 899.6 (100) $[2M+Na]^+$, 461.3 (42) $[M+Na]^+$, 439.3 (4) $[M+H]^+$. Calcd for **$C_{23}H_{38}O_6Si$:** 461.2335 $[M+Na]^+$, Found: 461.2333 $[M+Na]^+$ (ESI-HRMS).

Methyl (3*S*,4*S*)-4-(*tert*-Butyldimethylsilyloxy)-4-[(*S*)-2-formyl-5-methoxychroman-2-yl]-3-methylbutanoate (29c): A solution of alcohol **29b** (1.80 g, 4.12 mmol, 1.00 eq.) in CH_2Cl_2 (35 mL) was treated with DMP (2.62 g, 6.18 mmol, 1.50 eq.) at RT and the reaction mixture was stirred at RT for 2 h. After addition of silica gel (9 g) the solvent was evaporated *in vacuo*.

Column chromatography on silica gel (petroleum ether/EtOAc = 12:1) furnished aldehyde **29c** as a colorless oil (1.65 g, 3.78 mmol, 92%). **TLC**: R_f = 0.29 (petroleum ether/EtOAc = 10:1). **^{1}H-NMR** (300 MHz, $CDCl_3$): δ = 0.11 (s, 3 H, $Si(CH_3)_a$), 0.24 (s, 3 H, $Si(CH_3)_b$), 0.90 (s, 9 H, $SiC(C\underline{H}_3)_3$), 1.02 (d, J = 6.9 Hz, 3 H, 3-CH_3), 1.73–1.88 (m, 1 H, 3'-H_a), 2.07 (dd, J = 15.9, 10.2 Hz, 1 H, 2-H_a), 2.25–2.52 (m, 3 H, 3-H, 3'-H_b, 4'-H_a), 2.59–2.71 (m, 1 H, 4'-H_b), 2.74 (dd, J = 15.9, 3.3 Hz, 1 H, 2-H_b), 3.67 (s, 3 H, $COOCH_3$), 3.76 (s, 3 H, 5'-OCH_3), 3.89 (d, J = 1.2 Hz, 1 H, 4-H), 6.41 (d, J = 8.1 Hz, 1 H, 6'-H), 6.62 (d, J = 8.1 Hz, 1 H, 8'-H), 7.07 (t, J = 8.1 Hz, 1 H, 7'-H), 9.63 (s, 1 H, CHO) ppm. **^{13}C-NMR** (125 MHz, $CDCl_3$): δ = –4.5 ($Si(CH_3)_a$), –3.7 ($Si(CH_3)_b$), 16.1 (C-4'), 18.5 ($Si\underline{C}(CH_3)_3$), 20.0 (3-CH_3), 23.3 (C-3'), 26.1 ($SiC(\underline{C}H_3)_3$), 32.0 (C-3), 35.4 (C-2), 51.5 ($COO\underline{C}H_3$), 55.4 (5'-OCH_3), 81.5 (C-4), 86.1 (C-2'), 102.4 (C-6'), 109.6 (C-8'), 110.6 (C-4a'), 127.3 (C-7'), 153.7 (C-8a'), 157.7 (C-5'), 173.8 ($\underline{C}OOCH_3$), 204.5 (CHO) ppm. **MS** (ESI): m/z (%) = 959.5 (19) $[2M+2MeOH+Na]^+$, 927.4 (70) $[2M+MeOH+Na]^+$, 895.4 (100) $[2M+Na]^+$, 491.2 (28) $[M+MeOH+Na]^+$, 459.2 (50) $[M+Na]^+$. Calcd for **$C_{23}H_{36}O_6Si$**: 459.2179 $[M+Na]^+$, Found: 459.2173 $[M+Na]^+$ (ESI-HRMS).

Methyl (*S*)-2-[(1*S*,2*S*)-1-(*tert*-Butyldimethylsilyloxy)-4-methoxy-2-methyl-4-oxobutyl]-5-methoxychroman-2-carboxylate (31): A solution of KOH (1.70 g, 30.2 mmol, 8.00 eq.) and iodine (3.55 g, 14.0 mmol, 3.70 eq.) in MeOH (35 mL) was stirred for 5 min at RT and then added to a stirred solution of aldehyde **31b** (1.65 g, 3.78 mmol, 1.00 eq.) in MeOH (35 mL) before the reaction was stirred for 75 min at RT. A second solution of KOH (1.70 g, 30.2 mmol, 8.00 eq.) and iodine (3.55 g, 14.0 mmol, 3.70 eq.) in MeOH (35 mL) was stirred for 5 min at RT before being added to the reaction mixture. Stirring was continued at RT for 55 min and a third solution of KOH (1.70 g, 30.2 mmol, 8.00 eq.) and iodine (3.55 g, 14.0 mmol, 3.70 eq.) in MeOH (35 mL) which was stirred for 5 min at RT was added to the reaction mixture. Stirring was continued for further 20 min and the reaction was quenched with sat. aq. $Na_2S_2O_3$ solution (24 mL) and water (140 mL). The aqueous layer was extracted with CH_2Cl_2 (3 × 70 mL), the combined organic layers dried over Na_2SO_4 and concentrated *in vacuo*. Column chromatography on silica gel (petroleum ether/EtOAc = 12:1) provided chroman **31** as a pale-yellow oil (1.73 g, 3.70 mmol, 98%). **TLC**: R_f = 0.28 (petroleum ether/EtOAc = 10:1). **^{1}H-NMR** (300 MHz, $CDCl_3$): δ = 0.11 (s, 3 H, $Si(CH_3)_a$), 0.16 (s, 3 H, $Si(CH_3)_b$), 0.89 (s, 9 H, $SiC(CH_3)_3$), 1.07 (d, J = 6.9 Hz, 3 H, 2'-CH_3), 1.82–1.97 (m, 1 H, 3-H_a), 2.08 (dd, J = 16.2, 10.2 Hz, 1 H, 3'-H_a), 2.20–2.40 (m, 2 H, 3-H_b, 4-H_a), 2.41–2.55 (m_c, 1 H, 2'-H), 2.71–2.85 (m, 1 H, 4-H_b), 2.74 (dd, J = 16.2, 3.0 Hz, 1 H, 3'-H_b), 3.62 (s, 3 H, 2-$COOCH_3$), 3.66 (s, 3 H, 4'-OCH_3), 3.77 (s, 3 H, 5-OCH_3), 3.90 (d, J = 2.1 Hz, 1 H, 1'-H), 6.37 (dd, *J* = 8.4, 0.9 Hz, 1 H, 8-H), 6.53 (dd, *J* = 8.4, 0.9 Hz, 1 H, 6-H), 7.03 (t, *J* = 8.4 Hz, 1 H, 7-H) ppm. **^{13}C-NMR** (125 MHz, $CDCl_3$): δ = –4.0, –4.0 ($Si(CH_3)_2$), 16.7 (C-4), 18.5 ($Si\underline{C}(CH_3)_3$), 20.6 (2'-CH_3), 25.8 (C-3), 26.1 ($SiC(\underline{C}H_3)_3$), 32.3 (C-2'), 36.1 (C-3'), 51.4 (4'-OCH_3), 52.2 (2-$COO\underline{C}H_3$), 55.4 (5-OCH_3), 80.1 (C-1'), 84.8 (C-2), 101.9 (C-6), 109.5 (C-8), 109.9 (C-4a), 127.0 (C-7), 154.3 (C-8a), 157.4 (C-5), 172.3 (2-$\underline{C}OOCH_3$), 174.2 (C-4') ppm. **IR** (neat): $\tilde{\nu}$ (cm^{-1}) = 2952, 2931, 2856, 1731, 1592, 1470, 1437, 1247, 1191, 1167, 1109, 1090, 1042, 833, 770, 672. **UV** (CH_3OH): λ_{max} (lg ε) = 203.0 nm (4.628), 273.0 (3.107), 279.0 (3.110). **MS** (ESI): *m*/*z* (%) = 955.5 (100) $[2M+Na]^+$, 489.3 (64) $[M+Na]^+$. Calcd for **$C_{24}H_{38}O_7Si$**: 489.2284 $[M+Na]^+$, Found: 489.2281 $[M+Na]^+$ (ESI-HRMS).

Syntheses of the lactonyl chromanones *ent*-3c and *ent*-3d

Methyl (*S*)-5-Methoxy-2-[(2*S*,3*S*)-3-methyl-5-oxotetrahydrofuran-2-yl]chroman-2-carboxylate (33): A solution of chroman **31** (318 mg, 681 µmol, 1.00 eq.) in THF (9.5 mL) was treated with TBAF·3 H_2O (430 mg, 1.36 mmol, 2.00 eq.) at RT and the reaction mixture was stirred at RT for 1 h. After addition of silica gel (1.5 g) the solvent was evaporated *in vacuo*. Column chromatography on silica gel (petroleum ether/EtOAc = 4:1) furnished chroman **33** as a colorless foam (187 mg, 584 µmol, 86%). **TLC**: R_f = 0.22 (petroleum ether/EtOAc = 4:1). **^{1}H-NMR** (300 MHz, $CDCl_3$): δ = 1.07 (d, *J* = 7.2 Hz, 3 H, 3'-CH_3), 2.11 (dd, *J* = 17.7, 3.6 Hz, 1 H, 4'-H_a), 2.19–2.34 (m, 3 H, 3-H_2, 4-H_a), 2.66–2.79 (m_c, 1 H, 3'-H), 2.81–2.93 (m, 1 H, 4-H_b), 3.02 (dd, *J* = 17.7, 9.3 Hz, 1 H, 4'-H_b), 3.72 (s, 3 H, $COOCH_3$), 3.77 (s, 3 H, 5-OCH_3), 4.44 (d, *J* = 3.0 Hz, 1 H, 2'-H), 6.41 (dd, *J* = 8.4, 0.9 Hz, 1 H, 6-H), 6.49 (dd, *J* = 8.4, 0.9 Hz, 1 H, 8-H), 7.05 (t, *J* = 8.4 Hz, 1 H, 7-H) ppm. **^{13}C-NMR** (125 MHz, $CDCl_3$): δ = 16.5 (C-4), 20.8 (3'-CH_3), 25.5 (C-3), 30.3 (C-3'), 36.4 (C-4'), 52.8 ($COO\underline{C}H_3$), 55.4 (5-OCH_3), 82.1 (C-2), 87.7 (C-2'), 102.6 (C-6), 109.4 (C-8), 109.8 (C-4a), 127.3 (C-7), 153.8 (C-8a), 157.4 (C-5), 171.0 ($\underline{C}OOCH_3$), 176.5 (C-5') ppm. **IR** (neat): $\tilde{\nu}$ (cm^{-1}) = 2949, 1777, 1757, 1731, 1605, 1591, 1467, 1449, 1440, 1344, 1284, 1272, 1247, 1171, 1131, 1086, 1018, 965, 773. **UV** (CH_3OH): λ_{max} (lg ε) = 272.0 nm (3.132), 279.0 (3.127). **MS** (ESI): *m*/*z* (%) = 663.3 (100) $[2M+Na]^+$, 343.1 (26) $[M+Na]^+$. Calcd for **$C_{17}H_{20}O_6$**: 343.1158 $[M+Na]^+$, Found: 343.1152 $[M+Na]^+$ (ESI-HRMS).

Methyl (*S*)-5-Methoxy-2-[(2*R*,3*R*)-3-methyl-5-oxotetrahydrofuran-2-yl]chroman-2-carboxylate (35): A solution of chroman **32** (900 mg, 1.93 mmol, 1.00 eq.) in THF (27 mL) was treated with TBAF·3 H_2O (1.22 g, 3.86 mmol, 2.00 eq.) at RT and the reaction mixture was stirred at RT for 100 min. After addition of silica gel (3.9 g) the solvent was evaporated *in vacuo*. Column chromatography on silica gel (petroleum ether/EtOAc = 4:1 → 3:1) furnished chroman **35** as a colorless foam (542 mg, 1.69 mmol, 88%). **TLC**: R_f = 0.19 (petroleum ether/EtOAc = 4:1). **^{1}H-NMR** (300 MHz, $CDCl_3$): δ = 1.23 (d, J = 7.2 Hz, 3 H, 3'-CH_3), 1.76–1.90 (m, 1 H, 3-H_a), 2.12 (dd, J = 17.7, 3.9 Hz, 1 H, 4'-H_a), 2.22–2.41 (m, 2 H, 3-H_b, 4-H_a), 2.61–2.76 (m_c, 1 H, 3'-H), 2.81–2.92 (m, 1 H, 4-H_b), 2.90 (dd, J = 17.7, 9.3 Hz, 1 H, 4'-H_b), 3.70 (s, 3 H, $COOCH_3$), 3.77 (s, 3 H, 5-OCH_3), 4.45 (d, J = 3.3 Hz, 1 H, 2'-H), 6.42 (dd, J = 8.1, 0.6 Hz, 1 H, 6-H), 6.54 (dd, J = 8.1, 0.6 Hz, 1 H, 8-H), 7.07 (t, J = 8.1 Hz, 1 H, 7-H) ppm. **^{13}C-NMR** (125 MHz, $CDCl_3$): δ = 16.2 (C-4), 21.2 (3'-CH_3), 25.0 (C-3), 29.7 (C-3'), 36.4 (C-4'), 52.9 ($COO\underline{C}H_3$), 55.4 (5-OCH_3), 81.8 (C-2), 89.0 (C-2'), 102.6 (C-6), 109.4 (C-8), 109.5 (C-4a), 127.5 (C-7), 153.6 (C-8a), 157.4 (C-5), 170.8 ($\underline{C}OOCH_3$), 176.1 (C-5') ppm. **IR** (neat): $\tilde{\nu}$ (cm^{-1}) = 2956, 1772, 1751, 1733, 1606, 1591, 1470, 1347, 1268, 1248, 1170, 1145, 1082, 972, 769, 710, 514. **UV** (CH_3CN): λ_{max} (lg ε) = 203.0 nm (4.630), 273.0 (3.150), 279.0 (3.148), 300.0 (2.433). **MS** (ESI): *m*/*z* (%) = 663.3 (100) $[2M+Na]^+$, 343.1 (34) $[M+Na]^+$. Calcd for **$C_{17}H_{20}O_6$**: 343.1158 $[M+Na]^+$, Found: 343.1155 $[M+Na]^+$ (ESI-HRMS).

Methyl (*S*)-5-Methoxy-2-[(2*S*,3*S*)-3-methyl-5-oxotetrahydrofuran-2-yl]-4-oxochroman-2-carboxylate (34): Method A (Mn-catalysed oxidation): A solution of chroman **33** (40.0 mg, 125 µmol, 1.00 eq.) and *tert*-butyl hydroperoxide (230 µL of a 5.5 M solution in decane, 1.25 mmol, 10.0 eq.) in EtOAc (0.45 mL) was treated with powdered molecular sieves 3 Å (45 mg) and the resulting mixture was stirred at RT for 30 min. After addition of $Mn(OAc)_3$·2 H_2O (6.70 mg, 25.0 µmol, 20 mol%) stirring was continued for 2 d before additional $Mn(OAc)_3$·2 H_2O (3.40 mg, 12.7 µmol, 10 mol%), *tert*-butyl hydroperoxide (115 µL of a 5.5 M solution in decane, 633 µmol, 5.06 eq.) and EtOAc (0.2 mL) were added. The mixture was stirred for further 24 h at RT and filtered over silica gel (eluting with EtOAc). After concentration *in vacuo* and column chromatography on silica gel (petroleum ether/EtOAc = 3:2) chromanone **34** was obtained as a colorless solid (29.3 mg, 87.6 µmol, 70%). Method B (Rh-catalysed oxidation): A solution of chroman **33** (40.0 mg, 125 µmol, 1.00 eq.) and dirhodium-tetrakiscaprolactamate (**36**) (410 µg, 625 nmol, 0.5 mol%) in dichloroethane (0.5 mL) was treated with $NaHCO_3$ (5.30 mg, 62.5 µmol, 0.50 eq.). *tert*-Butyl hydroperoxide (114 µL of a 5.5 M solution in decane, 625 µmol, 5.00 eq.) was added and the resulting deep-red solution was heated with stirring at 40 °C. After 3 h the mixture was treated with additional dirhodium-tetrakiscaprolactamate (**36**) (410 µg, 625 nmol, 0.5 mol%) and *tert*-butyl hydroperoxide (114 µL of a 5.5 M solution in decane, 625 µmol, 5.00 eq.). Stirring was continued at 40 °C for 19 h before additional dirhodium-tetrakiscaprolactamate (**36**) (820 µg, 1.25 µmol, 1 mol%) and *tert*-butyl hydroperoxide (228 µL of a 5.5 M solution in decane, 1.25 mmol, 10.0 eq.) were added. After stirring at 40 °C for further 8 h the solids were removed by filtration over silica gel (eluting with EtOAc). After evaporation of the solvent *in vacuo* and column chromatography on silica gel (petroleum ether/EtOAc = 3:2) chromanone **34** was obtained as a colorless solid (28.0 mg, 83.7 µmol, 67%). Method C ($KMnO_4$ oxidation): A suspension of chroman **33** (50.0 mg, 156 µmol, 1.00 eq.), potassium permanganate (99.0 mg, 624 µmol, 4.00 eq.), 15% aq. $MgSO_4$ solution (0.25 mL) and acetone (1 mL) in a sealed tube was kept for 4 h at 60 °C in ultrasonic bath. A second portion of potassium permanganate (99.0 mg, 624 µmol, 4.00 eq.), 15% aq. $MgSO_4$ solution (0.25 mL) and acetone (0.5 mL) was added before the irradiation was continued for 3 h at 60 °C. After addition of a third portion of potassium permanganate (150 mg, 949 µmol, 8.00 eq.) and 15% aq. $MgSO_4$ solution (0.38 mL) the reaction mixture was irradiated for further 3 h bei 60 °C, cooled to RT and passed through silica gel in column (6 × 3 cm, washing with EtOAc, TLC monitoring). After evaporation of the solvent *in vacuo* column chromatography on silica gel (petroleum ether/EtOAc = 3:2) furnished chromanone **34** as a colorless solid (35.5 mg, 106 µmol, 68%, 73% brsm). **Optical Rotation**: $[\alpha]_D^{24}$ = –36.3 (c = 0.60, $CHCl_3$). **TLC**: R_f = 0.24 (petroleum ether/EtOAc = 1:1). **^{1}H-NMR** (300 MHz, $CDCl_3$): δ = 1.14 (d, J = 7.2 Hz, 3 H, 3'-CH_3), 2.18 (dd, J = 17.7, 4.2 Hz, 1 H, 4'-H_a), 2.71–2.85 (m_c, 1 H, 3'-H), 2.93 (d, J = 16.2 Hz, 1 H, 3-H_a), 2.98 (dd, J = 17.7, 9.3 Hz, 1 H, 4'-H_b), 3.35 (d, J = 16.2 Hz, 1 H, 3-H_b), 3.68 (s, 3 H, $COOCH_3$), 3.85 (s, 3 H, 5-OCH_3), 4.34 (d, J = 3.3 Hz, 1 H, 2'-H), 6.51 (dd, J = 8.4, 0.9 Hz, 1 H, 6-H), 6.58 (dd, J = 8.4, 0.9 Hz, 1 H, 8-H), 7.38 (t, J = 8.4 Hz, 1 H, 7-H) ppm. **^{13}C-NMR** (125 MHz, $CDCl_3$): δ = 20.5 (3'-CH_3), 29.6 (C-3'), 36.3 (C-4'), 42.4 (C-3), 53.3 ($COO\underline{C}H_3$), 56.2 (5-OCH_3), 84.1 (C-2), 86.5 (C-2'), 104.7 (C-6), 109.8 (C-8), 110.6 (C-4a), 136.4 (C-7), 160.3 (C-5), 161.0 (C-8a), 169.1 ($\underline{C}OOCH_3$), 175.7 (C-5'), 187.4 (C-4) ppm. **IR** (neat): $\tilde{\nu}$ (cm^{-1}) = 2973, 1779, 1747, 1694, 1601, 1578, 1471, 1441, 1291, 1259, 1199, 1164, 1012, 788, 742, 580, 529. **UV** (CH_3CN): λ_{max} (lg ε) = 214.0 nm (4.187), 265.0 (3.907), 327.0 (3.564). **MS** (ESI): m/z (%) = 691.2 (100) $[2M+Na]^+$, 357.1 (28) $[M+Na]^+$. Calcd for **$C_{17}H_{18}O_7$**: 357.0950 $[M+Na]^+$, Found: 357.0946 $[M+Na]^+$ (ESI-HRMS).

Methyl (*S*)-5-Methoxy-2-[(2*R*,3*R*)-3-methyl-5-oxotetrahydrofuran-2-yl]-4-oxochroman-2-carboxylate (37): A solution of chroman **35** (90.0 mg, 281 µmol, 1.00 eq.) and dirhodium-tetrakiscaprolactamate (1.84 mg, 2.81 µmol, 1 mol%) in dichloroethane (1.1 mL) was treated with $NaHCO_3$ (11.8 mg, 141 µmol, 0.50 eq.). *tert*-Butyl hydroperoxide (510 µL of a 5.5 M solution in decane, 2.81 mmol, 10.0 eq.) was added and the resulting deep-red solution was heated with stirring at 40 °C. After 4 h the mixture was treated with additional dirhodium-tetrakiscaprolactamate (1.84 mg, 2.81 µmol, 1 mol%) and *tert*-butyl hydroperoxide (510 µL of a 5.5 M solution in decane, 2.81 mmol, 10.0 eq.). Stirring was continued at 40 °C for 15 h before additional dirhodium-tetrakiscaprolactamate (1.84 mg, 2.81 µmol, 1 mol%) and *tert*-butyl hydroperoxide (510 µL of a 5.5 M solution in decane, 2.81 mmol, 10.0 eq.) were added. After stirring at 40 °C for further 6.5 h the solids were removed by filtration over silica gel (eluting with EtOAc). After evaporation of the solvent *in vacuo* and column chromatography on silica gel (petroleum ether/EtOAc = 1:1) chromanone **37** was obtained as a colorless solid (59.0 mg, 176 µmol, 63%). Mn-catalysed oxidation (51% yield, 64% brsm) and $KMnO_4$ oxidation (47% yield) were performed according to the described procedure for synthesis of **34**. **TLC**: $R_f = 0.21$ (petroleum ether/EtOAc = 1:1). **^{1}H-NMR** (300 MHz, $CDCl_3$): $\delta = 1.25$ (d, $J = 6.9$ Hz, 3 H, 3'-CH_3), 2.19 (dd, $J = 17.1$, 3.6 Hz, 1 H, 4'-H_a), 2.74–2.89 (m_c, 1 H, 3'-H), 2.88 (dd, $J = 17.1$, 9.3 Hz, 1 H, 4'-H_b), 2.93 (d, $J = 16.2$ Hz, 1 H, 3-H_a), 3.06 (d, $J = 16.2$ Hz, 1 H, 3-H_b), 3.68 (s, 3 H, $COOCH_3$), 3.88 (s, 3 H, 5-OCH_3), 4.41 (d, $J = 3.6$ Hz, 1 H, 2'-H), 6.54 (dd, $J = 8.4$, 0.9 Hz, 1 H, 6-H), 6.65 (dd, $J = 8.4$, 0.9 Hz, 1 H, 8-H), 7.41 (t, $J = 8.4$ Hz, 1 H, 7-H) ppm. **^{13}C-NMR** (125 MHz, $CDCl_3$): $\delta = 21.0$ (3'-CH_3), 29.8 (C-3'), 36.1 (C-4'), 41.6 (C-3), 53.4 ($COO\underline{C}H_3$), 56.2 (5-OCH_3), 84.1 (C-2), 87.7 (C-2'), 104.9 (C-6), 110.1 (C-8), 110.9 (C-4a), 136.8 (C-7), 160.5 (C-5), 161.2 (C-8a), 168.9 ($\underline{C}OOCH_3$), 175.4 (C-5'), 186.4 (C-4) ppm. **IR** (neat): $\tilde{\nu}$ (cm^{-1}) = 1767, 1755, 1674, 1601, 1574, 1471, 1440, 1336, 1257, 1178, 1100, 1076, 1001, 790, 742, 650, 576, 520. **UV** (CH_3CN): λ_{max} (lg ε) = 265.0 nm (3.995), 328.0 (3.677). **MS** (ESI): *m/z* (%) = 691.2 (100) $[2M+Na]^+$, 357.1 (40) $[M+Na]^+$. Calcd for **$C_{17}H_{18}O_7$**: 357.0950 $[M+Na]^+$, Found: 357.0945 $[M+Na]^+$ (ESI-HRMS).

Methyl (*S*)-5-Hydroxy-2-[(2*S*,3*S*)-3-methyl-5-oxotetrahydrofuran-2-yl]-4-oxochroman-2-carboxylate (*ent*-3c): A solution of BBr_3 (7.78 mL of a 1.0 M solution in CH_2Cl_2, 7.78 mmol, 10.0 eq.) was added slowly to a stirred solution of chromanone **34** (260 mg, 778 µmol, 1.00 eq.) in CH_2Cl_2 (40 mL) at –78 °C. Stirring was continued for 30 min at –78 °C before being quenched with sat. aq. $NaHCO_3$ solution (7 mL) at –78 °C. The organic layer was separated and the aqueous layer was extracted with EtOAc (3 × 40 mL). The combined organic layers were dried over Na_2SO_4 and the solvent was evaporated *in vacuo*. After column chromatography on silica gel (petroleum ether/EtOAc = 2:1) chromanone ***ent*-3c** was obtained as a colorless solid (209 mg, 653 µmol, 84%). **Optical Rotation**: $[\alpha]_D^{24}$ = –68.1 (c = 1.20, $CHCl_3$). **TLC**: R_f = 0.31 (petroleum ether/EtOAc = 2:1). **^{1}H-NMR** (300 MHz, $CDCl_3$): δ = 1.16 (d, J = 7.2 Hz, 3 H, 3'-CH_3), 2.20 (dd, J = 17.7, 3.9 Hz, 1 H, 4'-H_a), 2.76–2.90 (m_c, 1 H, 3'-H), 2.99 (dd, J = 17.7, 9.6 Hz, 1 H, 4'-H_b), 3.05 (d, J = 17.1 Hz, 1 H, 3-H_a), 3.46 (d, J = 17.1 Hz, 1 H, 3-H_b), 3.72 (s, 3 H, $COOCH_3$), 4.34 (d, J = 3.6 Hz, 1 H, 2'-H), 6.47 (dd, J = 8.4, 0.9 Hz, 1 H, 8-H), 6.52 (dd, J = 8.4, 0.9 Hz, 1 H, 6-H), 7.37 (t, J = 8.4 Hz, 1 H, 7-H), 11.42 (s_{br}, 1 H, 5-OH) ppm. **^{13}C-NMR** (125 MHz, $CDCl_3$): δ = 20.5 (3'-CH_3), 29.6 (C-3'), 36.3 (C-4'), 40.5 (C-3), 53.5 ($COO\underline{C}H_3$), 84.2 (C-2), 86.4 (C-2'), 107.4 (C-8, C-4a), 110.4 (C-6), 138.8 (C-7), 159.2 (C-8a), 161.8 (C-5), 169.0 ($\underline{C}OOCH_3$), 175.5 (C-5'), 194.8 (C-4) ppm. **IR** (neat): $\tilde{\nu}$ (cm^{-1}) = 2976, 2955, 1779, 1738, 1639, 1623, 1577, 1466, 1342, 1293, 1201, 1179, 1156, 1048, 1008, 840, 802, 728, 637, 579, 515. **UV** (CH_3CN): λ_{max} (lg ε) = 271.0 nm (3.930), 347.0 (3.485). **MS** (ESI): m/z (%) = 663.2 (100) $[2M+Na]^+$, 343.1 (31) $[M+Na]^+$. Calcd for **$C_{16}H_{16}O_7$**: 343.0794 $[M+Na]^+$, Found: 343.0796 $[M+Na]^+$ (ESI-HRMS).

Methyl (*S*)-5-Hydroxy-2-[(2*R*,3*R*)-3-methyl-5-oxotetrahydrofuran-2-yl]-4-oxochroman-2-carboxylate (*ent*-3d): A solution of BBr_3 (18.5 mL of a 1.0 M solution in CH_2Cl_2, 18.5 mmol, 10.0 eq.) was added slowly to a stirred solution of chromanone **37** (620 mg, 1.85 mmol, 1.00 eq.) in CH_2Cl_2 (90 mL) at –78 °C. Stirring was continued for 30 min at –78 °C before being quenched with sat. aq. $NaHCO_3$ solution (170 mL) at –78 °C. The organic layer was separated and the aqueous layer was extracted with EtOAc (3 × 80 mL). The combined organic layers were dried over Na_2SO_4 and the solvent was evaporated *in vacuo*. After column chromatography on silica gel (petroleum ether/EtOAc = 2:1) chromanone ***ent*-3d** was obtained as a pale-yellow foam (492 mg, 1.54 mmol, 83%). **Optical Rotation**: $[\alpha]_D^{23}$ = –39.1 (c = 1.02, $CHCl_3$). **TLC**: R_f = 0.61 (petroleum ether/EtOAc = 1:1). **^{1}H-NMR** (300 MHz, $CDCl_3$): δ = 1.26 (d, J = 6.9 Hz, 3 H, 3'-CH_3), 2.20 (dd, J = 17.1, 3.9 Hz, 1 H, 4'-H_a), 2.74–2.89 (m_c, 1 H, 3'-H), 2.87 (dd, J = 17.1, 9.3 Hz, 1 H, 4'-H_b), 3.01 (d, J = 17.1 Hz, 1 H, 3-H_a), 3.17 (d, J = 17.1 Hz, 1 H, 3-H_b), 3.70 (s, 3 H, $COOCH_3$), 4.42 (d, J = 3.9 Hz, 1 H, 2'-H), 6.51 (d, J = 8.4 Hz, 1 H, 8-H), 6.54 (d, J = 8.4 Hz, 1 H, 6-H), 7.39 (t, J = 8.4 Hz, 1 H, 7-H), 11.41 (s_{br}, 1 H, 5-OH) ppm. **^{13}C-NMR** (125 MHz, $CDCl_3$): δ = 20.8 (3'-CH_3), 29.9 (C-3'), 36.0 (C-4'), 39.7 (C-3), 53.6 ($COO\underline{C}H_3$), 84.2 (C-2), 87.5 (C-2'), 107.6 (C-4a), 107.6 (C-8), 110.6 (C-6), 139.0 (C-7), 159.1 (C-8a), 161.9 (C-5), 168.8 ($\underline{C}OOCH_3$), 175.1 (C-5'), 193.9 (C-4) ppm. **IR**

(neat): $\tilde{\nu}$ (cm^{-1}) = 2957, 1784, 1738, 1646, 1626, 1579, 1461, 1354, 1228, 1202, 1171, 1051, 1008, 796, 731, 638. **UV** (CH_3OH): λ_{max} (lg ε) = 206.0 nm (4.246), 272.0 (3.945), 349.0 (3.471). **MS** (ESI): *m*/*z* (%) = 663.2 (100) [2M+Na]$^+$, 343.1 (20) [M+Na]$^+$. Calcd for $\mathbf{C_{16}H_{16}O_7}$: 343.0794 [M+Na]$^+$, Found: 343.0790 [M+Na]$^+$ (ESI-HRMS).

Synthesis of the dimeric compound 41

Methyl (*S*)-8-Bromo-2-[(1*S*,2*S*)-1-(*tert*-butyldimethylsilyloxy)-4-methoxy-2-methyl-4-oxo-butyl]-5-methoxy-4-oxochroman-2-carboxylate (38): *n*Bu_4NBr_3 (145 mg, 301 µmol, 1.02 eq.) was added to a solution of chromanone **31** (142 mg, 295 µmol, 1.00 eq.) in THF/H_2O (1:1, 1.4 mL) at RT and the reaction mixture was stirred for 23 h at RT. After concentration *in vacuo* and column chromatography on silica gel (petroleum ether/EtOAc = 3:1) chromanone **38** was obtained as a colorless oil (150 mg, 268 µmol, 91%). **Optical Rotation**: $[\alpha]_D^{25}$ = +12.5 (*c* = 1.70, $CHCl_3$). **TLC**: R_f = 0.31 (petroleum ether/EtOAc = 2:1). **^{1}H-NMR** (300 MHz, $CDCl_3$): δ = 0.10 (s, 3 H, $Si(CH_3)_a$), 0.15 (s, 3 H, $Si(CH_3)_b$), 0.89 (s, 9 H, $SiC(CH_3)_3$), 1.11 (d, *J* = 6.9 Hz, 3 H, 2'-CH_3), 2.19 (dd, *J* = 16.5, 10.5 Hz, 1 H, 3'-H_a), 2.38–2.53 (m_c, 1 H, 2'-H), 2.88 (d, *J* = 16.2 Hz, 1 H, 3-H_a), 3.23 (dd, *J* = 16.5, 3.0 Hz, 1 H, 3'-H_b), 3.25 (d, *J* = 16.2 Hz, 1 H, 3-H_b), 3.64 (s, 3 H, 2-$COOCH_3$), 3.65 (s, 3 H, 4'-OCH_3), 3.86 (s, 3 H, 5-OCH_3), 4.00 (d, *J* = 2.1 Hz, 1 H, 1'-H), 6.43 (d, *J* = 9.0 Hz, 1 H, 6-H), 7.60 (d, *J* = 9.0 Hz, 1 H, 7-H) ppm. **^{13}C-NMR** (125 MHz, $CDCl_3$): δ = –4.2, –3.2 ($Si(CH_3)_2$), 18.5 ($\mathrm{Si\underline{C}(CH_3)_3}$), 19.9 (2'-$CH_3$), 26.1 ($\mathrm{SiC(\underline{C}H_3)_3}$), 32.7 (C-2'), 36.6 (C-3'), 43.1 (C-3), 51.5 (4'-OCH_3), 53.1 (2-$\mathrm{COO\underline{C}H_3}$), 56.3 (5-$OCH_3$), 78.1 (C-1'), 88.4 (C-2), 102.2 (C-8), 105.4 (C-6), 111.8 (C-4a), 139.1 (C-7), 157.8 (C-8a), 159.4 (C-5), 170.2 (2-$\mathrm{\underline{C}OOCH_3}$), 173.6 (C-4'), 188.2 (C-4) ppm. **IR** (neat): $\tilde{\nu}$ (cm^{-1}) = 2953, 2931, 1735, 1639, 1587, 1471, 1436, 1315, 1251, 1099, 1054, 832, 776, 734, 528. **UV** (CH_3CN): λ_{max} (lg ε) = 194.0 nm (4.426), 268.0 (3.813), 336.0 (3.592). **MS** (ESI): *m*/*z* (%) = 1141.3 (100) [2M+Na]$^+$, 1063.4 (9) [2M–Br+Na]$^+$, 583.1 (29) [M+Na]$^+$, 561.2 (48) [M+H]$^+$, 481.3 (6) [M–Br+H]$^+$. Calcd for $\mathbf{C_{24}H_{35}BrO_8Si}$: 581.1182 [M+Na]$^+$, Found: 581.1177 [M+Na]$^+$ (ESI-HRMS).

Methyl (*S*)-8-Bromo-2-[(1*R*,2*R*)-1-(*tert*-butyldimethylsilyloxy)-4-methoxy-2-methyl-4-oxo-butyl]-5-methoxy-4-oxochroman-2-carboxylate (42): *n*Bu_4NBr_3 (147 mg, 305 µmol, 1.02 eq.) was added to a solution of chromanone **32** (144 mg, 300 µmol, 1.00 eq.) in

THF/H_2O (1:1, 6.4 mL) at RT and the reaction mixture was stirred for 22 h at RT. After concentration *in vacuo* and column chromatography on silica gel (petroleum ether/EtOAc = 2:1) chromanone **42** was obtained as a colorless oil (140 mg, 250 µmol, 83%). **Optical Rotation**: $[\alpha]^{25}_{D}$ = –42.8 (*c* = 0.48, $CHCl_3$). **TLC**: R_f = 0.26 (petroleum ether/EtOAc = 2:1). **^{1}H-NMR** (300 MHz, $CDCl_3$): δ = 0.09 (s, 3 H, $Si(CH_3)_a$), 0.22 (s, 3 H, $Si(CH_3)_b$), 0.88 (s, 9 H, $SiC(CH_3)_3$), 1.04 (d, *J* = 6.6 Hz, 3 H, 2'-CH_3), 2.04–2.23 (m, 2 H, 2'-H, 3'-H_a), 2.62 (d, *J* = 12.9 Hz, 1 H, 3'-H_b), 3.08 (d, *J* = 16.8 Hz, 1 H, 3-H_a), 3.23 (d, *J* = 16.8 Hz, 1 H, 3-H_b), 3.64 (s, 3 H, 4'-OCH_3), 3.65 (s, 3 H, 2-$COOCH_3$), 3.86 (s, 3 H, 5-OCH_3), 4.18 (d, *J* = 1.5 Hz, 1 H, 1'-H), 6.45 (d, *J* = 9.0 Hz, 1 H, 6-H), 7.59 (d, *J* = 9.0 Hz, 1 H, 7-H) ppm. **^{13}C-NMR** (125 MHz, $CDCl_3$): δ = –4.7, –3.8 ($Si(CH_3)_2$), 18.7 ($Si\underline{C}(CH_3)_3$), 19.9 (2'-CH_3), 26.1 ($SiC(\underline{C}H_3)_3$), 32.1 (C-2'), 35.7 (C-3'), 41.0 (C-3), 51.6 (4'-OCH_3), 53.1 (2-$COO\underline{C}H_3$), 56.4 (5-OCH_3), 79.6 (C-1'), 88.9 (C-2), 102.4 (C-8), 106.0 (C-6), 111.8 (C-4a), 139.1 (C-7), 156.9 (C-8a), 159.7 (C-5), 169.8 (2-$\underline{C}OOCH_3$), 173.0 (C-4'), 188.3 (C-4) ppm. **IR** (neat): $\tilde{\nu}$ (cm^{-1}) = 2953, 2930, 1737, 1692, 1587, 1471, 1436, 1312, 1250, 1097, 1054, 833, 777, 523. **UV** (CH_3CN): λ_{max} (lg ε) = 193.0 nm (4.452), 210.0 (4.310), 266.0 (3.849), 336.0 (3.631). **MS** (ESI): *m*/*z* (%) = 1141.3 (100) $[2M+Na]^+$, 1063.4 (65) $[2M–Br+Na]^+$, 983.5 (21) $[2M–Br+Na]^+$, 583.1 (60) $[M+Na]^+$, 561.2 (26) $[M+H]^+$, 503.2 (34) $[M–Br+Na]^+$, 481.2 (23) $[M–Br+H]^+$. Calcd for **$C_{24}H_{35}BrO_8Si$**: 581.1182 $[M+Na]^+$, Found: 581.1177 $[M+Na]^+$ (ESI-HRMS).

Dimethyl (2*S*,2'*S*)-2,2'-bis[(1*S*,2*S*)-1-(*tert*-Butyldimethylsilyloxy)-4-methoxy-2-methyl-4-oxobutyl]-5,5'-dimethoxy-4,4'-dioxo-[8,8'-bichroman]-2,2'-dicarboxylate (39): A solution of chromanone **38** (127 mg, 227 µmol, 1.00 eq.) in THF (8.5 mL) was added to a mixture of $Pd(OAc)_2$ (5.10 mg, 22.7 µmol, 10 mol%), S-Phos (23.3 mg, 56.8 µmol, 25 mol%), Cs_2CO_3 (148 mg, 454 µmol, 2.00 eq.), bis(pinacolato)diboron (115 mg, 454 µmol, 2.00 eq.) and water (16.4 µL, 16.4 mg, 908 µmol, 4.00 eq.) at RT and the reaction mixture was stirred at 50 °C for 21 h. The catalyst was removed by filtration over silica gel (washing with EtOAc) and the solvent was evaporated *in vacuo*. Column chromatography on silica gel (petroleum ether/EtOAc = 2:1 → 1:1) provided biaryl **39** as a colorless solid (35.0 mg, 36.5 µmol, 32%) and a inseparable mixture of chromanonen **31** and **38** as a pale-yellow oil (77.0 mg, 141 µmol, 62%, **31**:**38** = 1:5). **Optical Rotation**: $[\alpha]^{26}_{D}$ = –24.6 (*c* = 0.92, $CHCl_3$). **TLC**: R_f = 0.11 (petroleum ether/EtOAc = 2:1). **^{1}H-NMR** (300 MHz, $CDCl_3$): δ = 0.06 (s, 6 H, 2 × $Si(CH_3)_a$), 0.09 (s, 6 H, 2 × $Si(CH_3)_b$), 0.84–0.96 (m, 24 H, 2 × $SiC(CH_3)_3$, 2''-CH_3, 2'''-CH_3), 1.88 (dd,

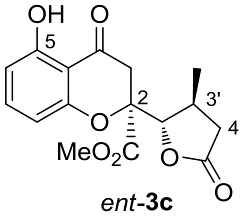
J = 16.8, 10.8 Hz, 2 H, 3''-H$_a$, 3'''-H$_a$), 2.05–2.22 (m, 2 H, 2''-H, 2'''-H), 2.38 (d, J = 16.8 Hz, 2 H, 3''-H$_b$, 3'''-H$_b$), 2.87 (dd, J = 15.6 Hz, 2 H, 3-H$_a$, 3'-H$_a$), 3.25 (d, J = 15.6 Hz, 2 H, 3-H$_b$, 3'-H$_b$), 3.47 (s, 6 H, 4''-OCH$_3$, 4'''-OCH$_3$), 3.63 (s$_{br}$, 6 H, 2-COOCH$_3$, 2'-COOCH$_3$), 3.85 (d, J = 1.8 Hz, 2 H, 1''-H, 1'''-H), 3.92 (s, 6 H, 5-OCH$_3$, 5'-OCH$_3$), 6.55 (d, J = 9.0 Hz, 2 H, 6-H, 6'-H), 7.54 (d, J = 9.0 Hz, 2 H, 7-H, 7'-H) ppm. **^{13}C-NMR** (125 MHz, CDCl$_3$): δ = –4.4, –3.4 (Si(CH$_3$)$_2$), 18.4 ($\mathrm{Si\underline{C}(CH_3)_3}$), 19.1 (2''-CH$_3$, 2'''-CH$_3$), 26.1 ($\mathrm{SiC(\underline{C}H_3)_3}$), 32.9 (C-2'', C-2'''), 35.7 (C-3'', C-3'''), 43.3 (C-3, C-3'), 51.1 (4''-OCH$_3$, 4'''-OCH$_3$), 52.9 (2-COO$\mathrm{\underline{C}H_3}$, 2'-COO$\mathrm{\underline{C}H_3}$), 56.0 (5-OCH$_3$, 5'-OCH$_3$), 78.1 (C-1'', C-1'''), 87.6 (C-2, C-2'), 104.0 (C-6, C-6') , 110.8 (C-4a, C-4a'), 118.0 (C-8, C-8'), 139.4 (C-7, C-7'), 158.7 (C-8a, C-8a'), 159.8 (C-5, C-5'), 171.0 (2-$\mathrm{\underline{C}OOCH_3}$, 2'-$\mathrm{\underline{C}OOCH_3}$), 173.2 (C-4'', C-4'''), 189.1 (C-4, C-4') ppm. **IR** (neat): $\tilde{\nu}$ (cm^{-1}) = 2923, 1728, 1690, 1593, 1572, 1474, 1255, 1166, 1119, 1099, 1039, 827, 772. **UV** (CH$_3$CN): λ_{max} (lg ε) = 193.0 nm (4.679), 247.0 (4.261), 338.0 (3.818). **MS** (ESI): m/z (%) = 981.4 (100) [M+Na]$^+$. Calcd for **$\mathbf{C_{48}H_{70}O_{16}Si_2}$**: 981.4100 [M+Na]$^+$, Found: 981.4095 [M+Na]$^+$ (ESI-HRMS).

Dimethyl (2*S*,2'*S*)-5,5'-Dimethoxy-2,2'-bis[(2*S*,3*S*)-3-methyl-5-oxotetrahydrofuran-2-yl]-4,4'-dioxo-[8,8'-bichroman]-2,2'-dicarboxylate (40): NEt$_3$·3 HF (120 µL, 118 mg, 730 µmol, 25.0 eq.) was added to a solution of biaryl **39** (28.0 mg, 29.2 µmol, 1.00 eq.) in 1,4-dioxane (1 mL) at RT and the reaction mixture was stirred at 60 °C for 3 d. After a second addition of NEt$_3$·3 HF (120 µL, 118 mg, 730 µmol, 25.0 eq.) stirring was continued for further 4 d at 60 °C before being quenched by carefully addition of sat. aq. NaHCO$_3$ solution (8 mL) at 0 °C. The aqueous layer was extracted with EtOAc (3 × 15 mL), the combined organic layers were dried over Na$_2$SO$_4$ and the solvent was evaporated *in vacuo*. Column chromatography on silica gel (petroleum ether/EtOAc = 1:5) furnished compound **40** as a colorless foam (19.0 mg, 28.5 µmol, 98%). **Optical Rotation**: $[\alpha]_D^{25}$ = +11.4 (c = 0.47, CHCl$_3$). **TLC**: R_f = 0.12 (petroleum ether/EtOAc = 1:3). **^{1}H-NMR** (300 MHz, CDCl$_3$): δ = 1.00 (d, J = 7.2 Hz, 6 H, 3''-CH$_3$, 3'''-CH$_3$), 1.55–1.86 (m, 4 H, 4''-H$_2$, 4'''-H$_2$), 2.47–2.65 (m$_c$, 2 H, 3''-H, 3'''-H), 2.74 (d, J = 15.9 Hz, 2 H, 3-H$_a$, 3'-H$_a$), 3.42 (d, J = 15.9 Hz, 2 H, 3-H$_b$, 3'-H$_b$), 3.60 (s$_{br}$, 6 H, 2-COOCH$_3$, 2'-COOCH$_3$), 3.90 (s, 6 H, 5-OCH$_3$, 5'-OCH$_3$), 4.28 (s$_{br}$, 2 H, 2''-H, 2'''-H), 6.61 (d, J = 8.7 Hz, 2 H, 6-H, 6'-H), 7.13–7.29, 7.43–7.64 (2 × m, 2 H, 7-H, 7'-H) ppm. **^{13}C-NMR** (125 MHz, CDCl$_3$): δ = 21.0 (3''-CH$_3$, 3'''-CH$_3$), 29.6 (C-3'', C-3'''), 35.3 (C-4'', C-4'''), 42.3 (C-3, C-3'), 52.5 (2-COO$\mathrm{\underline{C}H_3}$, 2'-COO$\mathrm{\underline{C}H_3}$), 56.4 (5-OCH$_3$, 5'-OCH$_3$), 84.2 (C-2, C-2'), 85.9 (C-2'', C-2'''), 104.0 (C-6, C-6'), 110.6 (C-8, C-8'), 118.1 (C-4a, C-4a'), 138.2 (C-7, C-7'), 158.4 (C-8a, C-8a'), 159.6 (C-5, C-5'), 167.9 (2-$\mathrm{\underline{C}OOCH_3}$, 2'-$\mathrm{\underline{C}OOCH_3}$), 176.9 (C-5'', C-5'''), 188.0

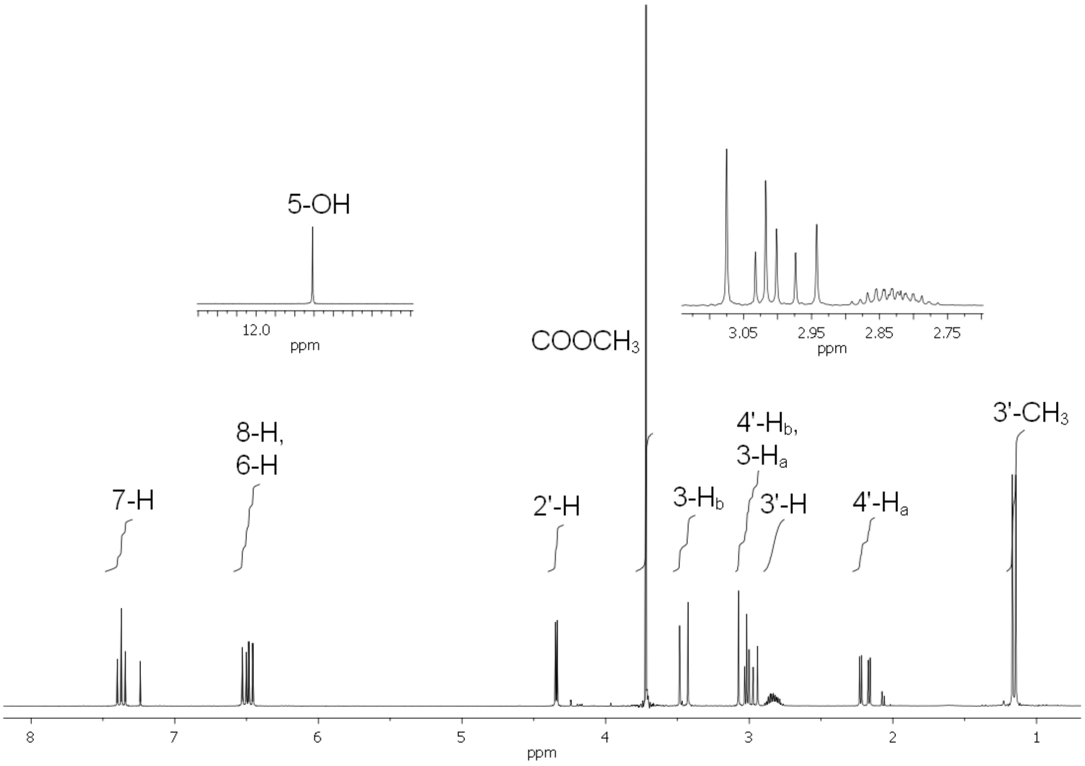
(C-4, C-4') ppm. **IR** (neat): $\tilde{\nu}$ (cm^{-1}) = 2958, 1783, 1748, 1684, 1569, 1474, 1254, 1160, 1091, 1011, 749. **UV** (CH_3CN): λ_{max} (lg ε) = 194.0 nm (4.628), 254.0 (4.251), 336.0 (3.899). **MS** (ESI): *m*/*z* (%) = 1355.4 (71) $[2M+Na]^+$, 689.2 (100) $[M+Na]^+$, 667.2 (60) $[2M+H]^+$. Calcd for $\mathbf{C_{34}H_{34}O_{14}}$: 689.1846 $[M+Na]^+$, Found: 689.1841 $[M+Na]^+$ (ESI-HRMS).

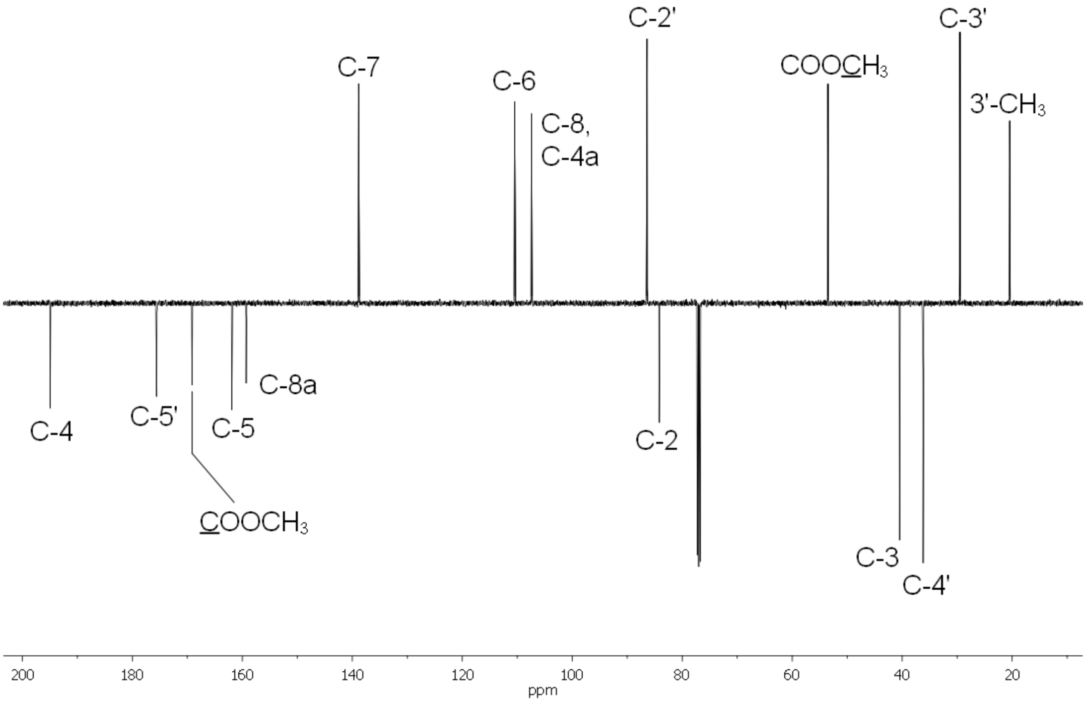
Dimethyl (2*S*,2'*S*)-5,5'-Dihydroxy-2,2'-bis[(2*S*,3*S*)-3-methyl-5-oxotetrahydrofuran-2-yl]-4,4'-dioxo-[8,8'-bichroman]-2,2'-dicarboxylate (41): A solution of BBr_3 (590 µL of a 1.0 M solution in CH_2Cl_2, 590 µmol, 19.9 eq.) was added slowly to a stirred solution of biaryl **40** (19.0 mg, 29.7 µmol, 1.00 eq.) in CH_2Cl_2 (3 mL) at –78 °C. The resulting solution was stirred for 30 min at –78 °C before being quenched with sat. aq. $NaHCO_3$ solution (10 mL) at –78 °C. The organic layer was separated and the aqueous layer was extracted with EtOAc (3 × 10 mL). The combined organic layers were dried over Na_2SO_4 and the solvent was evaporated *in vacuo*. After column chromatography on silica gel (petroleum ether/EtOAc = 1:1) biaryl **41** was obtained as a colorless foam (12.7 mg, 19.9 µmol, 67%). **Optical Rotation**: $[\alpha]_D^{24}$ = +78.3 (*c* = 0.64, $CHCl_3$). **TLC**: R_f = 0.28 (petroleum ether/EtOAc = 1:1). **^{1}H-NMR** (300 MHz, $CDCl_3$): δ = 1.05 (d, *J* = 6.9 Hz, 6 H, 3''-CH_3, 3'''-CH_3), 1.82 (dd, *J* = 18.0, 3.6 Hz, 2 H, 4''-H_a, 4'''-H_a), 2.06 (dd, *J* = 18.0, 9.0 Hz, 2 H, 4''-H_b, 4'''-H_b), 2.39–2.57 (m_c, 2 H, 3''-H, 3'''-H), 3.03 (d, *J* = 17.4 Hz, 2 H, 3-H_a, 3'-H_a), 3.59 (d, *J* = 17.4 Hz, 2 H, 3-H_b, 3'-H_b), 3.76 (s_{br}, 6 H, 2-$COOCH_3$, 2'-$COOCH_3$), 4.26 (d, *J* = 3.0 Hz, 2 H, 2''-H, 2'''-H), 6.60 (d, *J* = 8.7 Hz, 2 H, 6-H, 6'-H), 7.47–7.82 (m, 2 H, 7-H, 7'-H), 11.61 (s_{br}, 2 H, 5-OH, 5'-OH) ppm. **^{13}C-NMR** (125 MHz, $CDCl_3$): δ = 20.7 (3''-CH_3, 3'''-CH_3), 29.7 (C-3'', C-3'''), 35.4 (C-4'', C-4'''), 40.5 (C-3, C-3'), 53.5 (2-$COO\underline{C}H_3$, 2'-$COO\underline{C}H_3$), 84.9 (C-2, C-2'), 85.9 (C-2'', C-2'''), 107.5 (C-4a, C-4a'), 109.9 (C-6, C-6'), 115.0 (C-8, C-8'), 140.8 (C-7, C-7'), 156.4 (C-8a, C-8a'), 161.6 (C-5, C-5'), 168.9 (2-$\underline{C}OOCH_3$, 2'-$\underline{C}OOCH_3$), 175.3 (C-5'', C-5'''), 195.3 (C-4, C-4') ppm. **IR** (neat): $\tilde{\nu}$ (cm^{-1}) = 2960, 1787, 1748, 1646, 1465, 1343, 1152, 1008, 733. **UV** (CH_3CN): λ_{max} (lg ε) = 196.0 (4.534), 256.0 (4.361), 359.0 (3.756). **MS** (ESI): *m*/*z* (%) = 1299.3 (100) $[2M+Na]^+$, 661.2 (59) $[M+Na]^+$. Calcd for $\mathbf{C_{32}H_{30}O_{14}}$: 661.1533 $[M+Na]^+$, Found: 661.1530 $[M+Na]^+$ (ESI-HRMS).

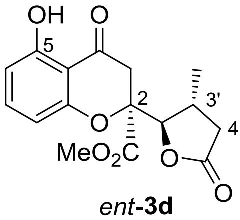
^{1}H- and ^{13}C-NMR spectras of *ent*-3c, *ent*-3d and 41



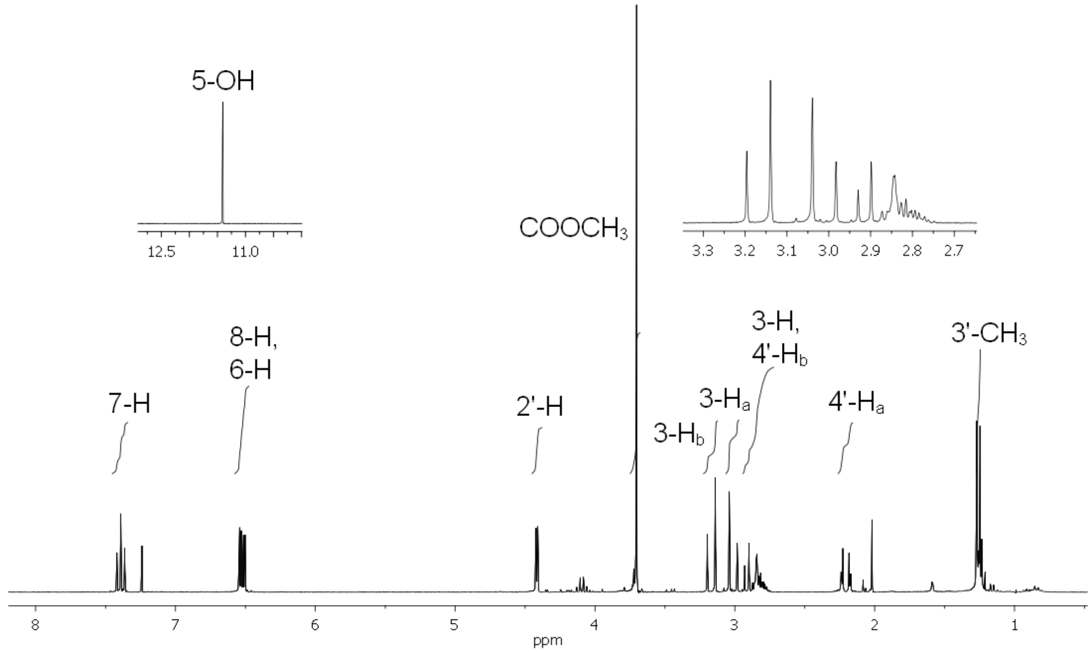
ent-**3c**






OH
5
O
2
3'
4'
O
MeO2C
O
O

ent-**3d**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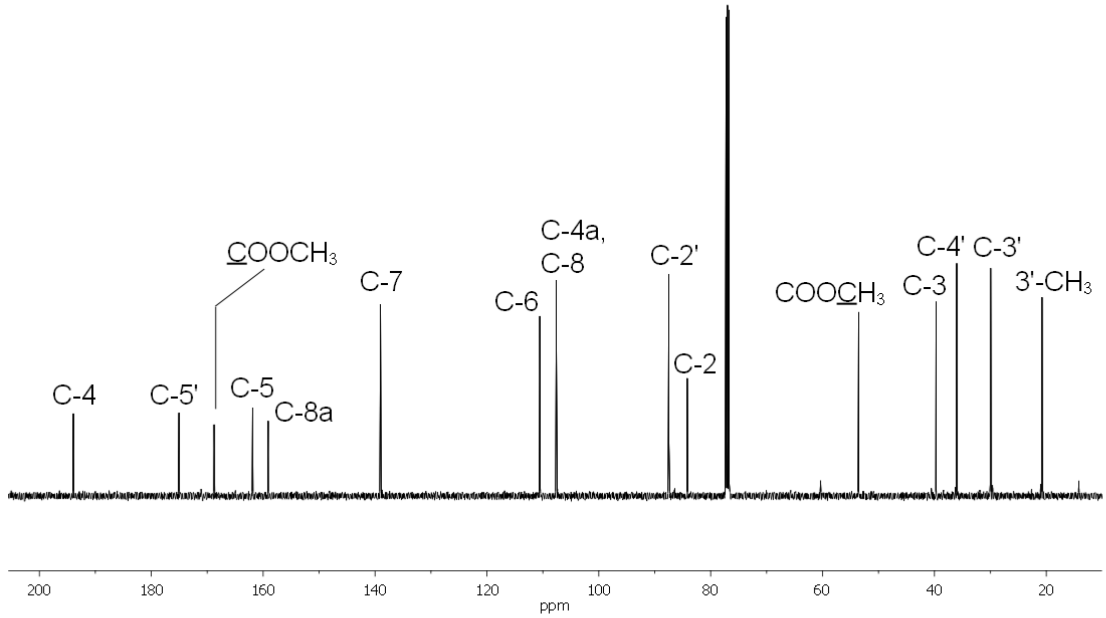
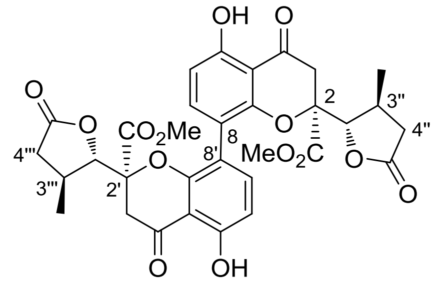
12.5
11.0
COOCH3
3.3
3.2
3.1
3.0
2.9
2.8
2.7
8-H,
6-H
7-H
2'-H
3-H,
4'-Hb
3-Ha
3-Hb
4'-Ha
3'-CH3
8
7
6
5
4
3
2
1
ppm


C-4
C-5'
COOCH3
C-5
C-8a
C-7
C-6
C-4a,
C-8
C-2'
C-2
COOCH3
C-3
C-4'
C-3'
3'-CH3
200
180
160
140
120
100
80
60
40
20
ppm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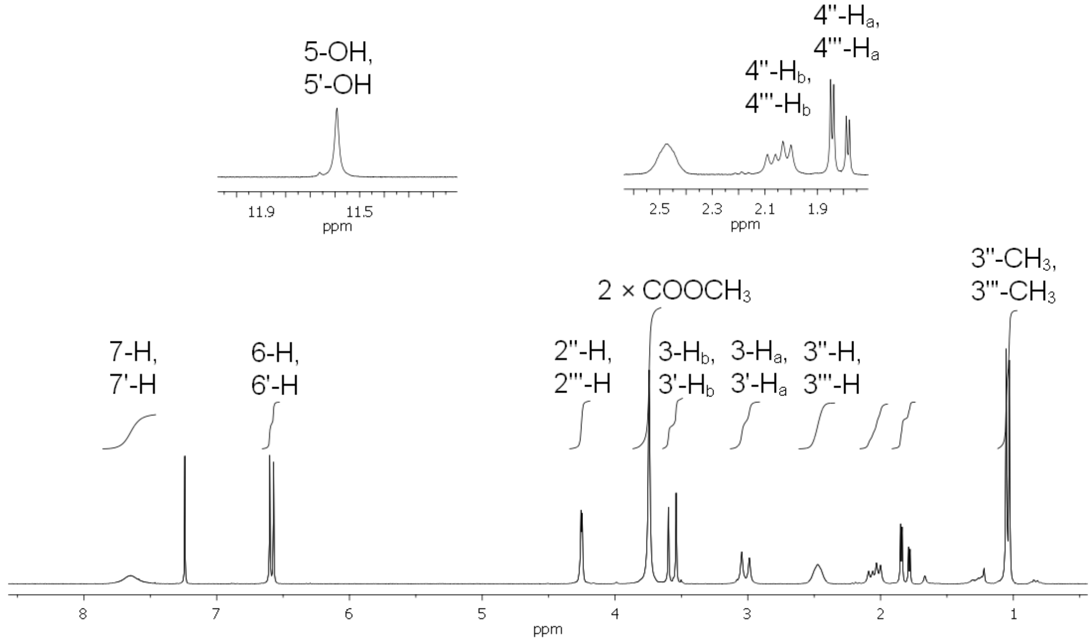
O
O
O
CO2Me
2
3''
4''
8
8'
MeO2C
O
O
O
4'''
3'''
2'
O
OH

41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5'-OH
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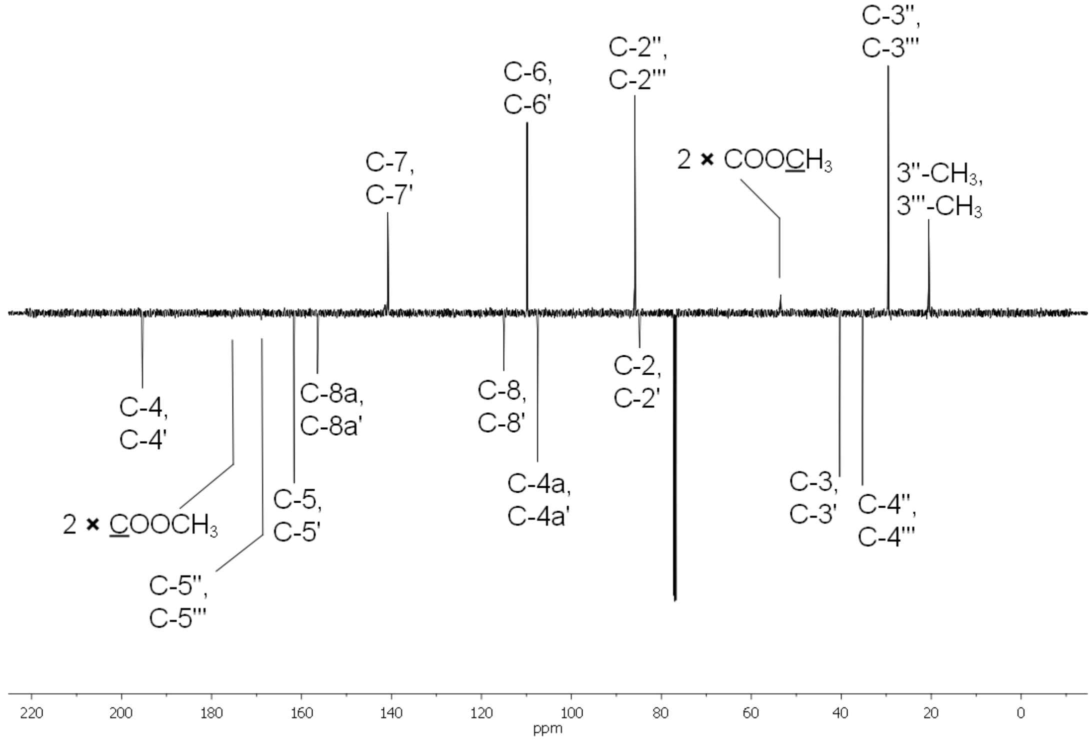
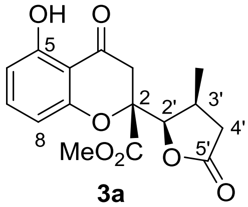
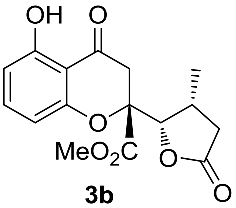
11.5
ppm
4''-Ha,
4'''-Ha
4''-Hb,
4'''-Hb
2.5
2.3
2.1
1.9
ppm
3''-CH3,
3'''-CH3
2 × COOCH3
7-H,
7'-H
6-H,
6'-H
2''-H,
2'''-H
3-Hb,
3'-Hb
3-Ha,
3'-Ha
3''-H,
3'''-H
8
7
6
5
4
3
2
1
ppm

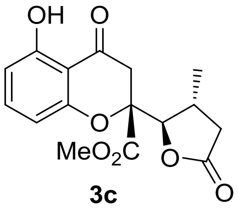

C-3'',
C-3'''
C-6,
C-6'
C-2'',
C-2'''
C-7,
C-7'
2 × COOCH3
3''-CH3,
3'''-CH3
C-4,
C-4'
C-8a,
C-8a'
C-8,
C-8'
C-2,
C-2'
2 × COOCH3
C-5,
C-5'
C-4a,
C-4a'
C-3,
C-3'
C-4'',
C-4'''
C-5'',
C-5'''
220
200
180
160
140
120
100
80
60
40
20
0
ppm



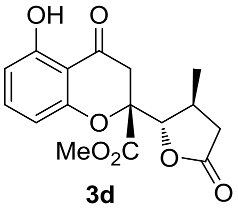
3a



3b



3c



3d

^{1}H-NMR:

	Synthetic (Porco) (500 MHz, $CDCl_3$)		Synthetic (this work) (300 MHz, $CDCl_3$)		Natural Product Paecilin B (**3**) (500 MHz, $CDCl_3$)
	rac-**3a**	*rac*-**3b**	*ent*-**3c**	*ent*-**3d**	
5-OH	11.38 (s, 1H)	11.44 (s, 1H)	11.42 (s, 1H)	11.41 (s, 1H)	11.49 (s, 1H)
7-H	7.40 (t, *J* = 8.3, 1H)	7.41 (t, *J* = 8.3, 1H)	7.37 (t, *J* = 8.4, 1H)	7.39 (t, *J* = 8.4, 1H)	7.46 (t, *J* = 8.4, 8.1, 1H)
6-H	6.54 (dd, *J* = 8.4, 0.9, 1H)	6.55 (dd, *J* = 8.3, 0.8, 1H)	6.52 (dd, *J* = 8.4, 0.9, 1H)	6.54 (d, *J* = 8.4, 1H)	6.61 (d, *J* = 8.1, 1H)
8-H	6.46 (dd, *J* = 8.2, 0.9, 1H)	6.54 (dd, *J* = 8.2, 0.9, 1H)	6.47 (dd, *J* = 8.4, 0.9, 1H)	6.51 (d, *J* = 8.4, 1H)	6.51 (d, *J* = 7.8, 1H)
2’-H	4.84 (d, *J* = 7.9, 1H)	4.79 (d, *J* = 6.8, 1H)	4.34 (d, *J* = 3.6, 1H)	4.42 (d, *J* = 3.9, 1H)	4.97 (d, *J* = 6.6, 1H)
$COOCH_3$	3.73 (s, 3H)	3.73 (s, 3H)	3.72 (s, 3H)	3.70 (s, 3H)	3.72 (s, 3H)
3-H_b	3.65 (d, *J* = 17.4, 1H)	3.25 (d, *J* = 17.3, 1H)	3.46 (d, *J* = 17.1, 1H)	3.17 (d, *J* = 17.1, 1H)	3.53 (d, *J* = 17.4, 1H)
3-H_a	2.89 (d, *J* = 17.4, 1H)	3.18 (d, *J* = 17.3, 1H)	3.05 (d, *J* = 17.1, 1H)	3.01 (d, *J* = 17.1, 1H)	3.16 (d, *J* = 17.4, 1H)
4’-H_b	2.60 (dd, *J* = 11.0, 2.0, 1H)	2.69 (dd, *J* = 17.3, 8.3, 1H)	2.99 (dd, *J* = 17.7, 9.6, 1H)	2.87 (dd, *J* = 17.1, 9.3, 1H)	2.73 (dd, *J* = 17, 7, 1H)
3’-H	2.98 (m, 1H)	2.96 (m, 1H)	2.83 (m, 1H)	2.81 (m, 1H)	2.87 (m, 1H)
4’-H_a	2.60 (dd, *J* = 11.0, 2.0, 1H)	2.46 (dd, *J* = 17.3, 7.9, 1H)	2.20 (dd, *J* = 17.7, 3.9, 1H)	2.20 (dd, *J* = 17.1, 3.9, 1H)	2.41 (dd, *J* = 17, 7, 1H)
3’-CH_3	1.25 (d, *J* = 7.1, 3H)	1.32 (d, *J* = 7.2, 3H)	1.16 (d, *J* = 7.2, 3H)	1.26 (d, *J* = 6.9, 3H)	1.34 (d, *J* = 6.9, 3H)

^{13}C-NMR:

	Synthetic (Porco) (100/125 MHz, $CDCl_3$)		Synthetic (this work) (125 MHz, $CDCl_3$)		Natural Product Paecilin B (**3**) (125 MHz, $CDCl_3$)
	rac-**3a**	*rac*-**3b**	*ent*-**3c**	*ent*-**3d**	
C-4	194.5	193.9	194.8	193.9	195.00
C-5’	175.5	174.8	175.5	175.1	174.66
$\underline{C}OOCH_3$	169.6	169.0	169.0	168.8	169.30
C-5	161.7	161.9	161.8	161.9	161.89
C-8a	159.3	158.8	159.2	159.1	155.38
C-7	138.7	139.0	138.8	139.0	138.97
C-6	110.3	110.5	110.4	110.6	109.77
C-8	107.3	107.5	107.4	107.6	107.80
C-4a	107.1	107.5	107.4	107.6	130.42
C-2’	84.5	84.3	86.4	87.5	82.63
C-2	82.0	82.7	84.2	84.2	84.87
$COO\underline{C}H_3$	53.3	53.6	53.5	53.6	53.10
C-3	41.4	39.8	40.5	39.7	39.98
C-4’	35.8	36.7	36.3	36.0	36.80
C-3’	33.5	33.4	29.6	29.9	33.58
3’-CH_3	13.4	14.8	20.5	20.8	14.63