Supporting Information

Feigrisolide C : Structural Revision and Synthesis

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General Information

^1H - and ^{13}C -NMR spectra were obtained on the 300 MHz, 500 MHz, and 600 MHz spectrometer. Chemical shift values were recorded as parts per million relative to tetramethylsilane as an internal standard unless otherwise indicated, and coupling constants as hertz. Mass spectra were recorded using electron impact (EI, 70 eV), chemical ionization (CI, methane), and fast atom bombardment (FAB, *m*-nitrobenzyl alcohol) method. Significant fragments are reported as followed: m/z (relative intensity). Optical rotation data were obtained on a automatic polarimeter.

The progress of reaction was checked on TLC plates, and the spots were

visualized under 254 nm UV light and/or charring after dipping the TLC plate into vanillin solution (9.0 g of vanillin and 1.5 mL of concentrated sulfuric acid in 300 mL of methanol), KMnO₄ solution (3 g of KMnO₄, 20 g of K₂CO₃, and 5 mL of 5% NaOH solution on 300 mL of water), or phosphomolybdic acid solution (250 mg phosphomolybdic acid in 50 mL ethanol). Column chromatography was performed on silica gel using hexane-EtOAc (v/v). The solvents were simple distilled unless otherwise noted.

Unless otherwise specified, all reactions were conducted under a slight positive pressure of dry nitrogen. The usual work-up refers to washing the quenched reaction mixture with brine, drying the organic extracts over anhydrous MgSO₄ and evaporating under reduced pressure using a rotary evaporator.

All solvents used in reaction were dried under nitrogen atmosphere. THF was distilled from Na-benzophenone and DCM was distilled from P₂O₅. Benzene was washed with conc. H₂SO₄, distilled from Na-benzophenone, and stored over 4 Å molecular sieves. Ethyl ether was distilled from LAH. CH₃CN was distilled from CaH₂ and stored over 4 Å molecular sieves. Pyridine and TEA was distilled over KOH and stored over 4 Å molecular sieves.

Aldehyde **7**

To a solution of methyl (*R*)-3-hydroxypentanoate (**6**, 1.1 g, 8.47 mmol) and benzyl 2,2,2-trichloroacetimidate (1.8 mL, 10.16 mmol) in cyclohexane (11 mL) and DCM (5.5 mL) was added trifluoromethanesulfonic acid (0.11 mL, 1.27 mmol) within 5 min. The mixture was stirred until the starting material had completely reacted as monitored by TLC. The crystalline trichloroacetamide was removed by filtration and the filtrate was washed with sat. NaHCO₃ solution (50 mL) and water (50 mL). The organic layer was dried over MgSO₄, and concentrated. Purification of the residue by flash column chromatography (Hex-EtOAc, 4:1) gave the benzyl ether **6A** (1.53 g, 81.4%). *R_f* 0.42 (Hex-EtOAc, 4:1). ¹H-NMR (300 MHz, CDCl₃): δ 7.34-7.23 (m, 5H), 4.53 (s, 2H), 3.89-3.79 (m, 1H), 3.65 (s, 3H), 2.59 and 2.47 (ABX, 2H, *J*_{AB} = 15.1 Hz, *J*_{AX} = 7.5 Hz, *J*_{BX} = 5.3 Hz), 1.66-1.57 (m, 2H), 0.94 (t, 3H, *J* = 7.4 Hz). ¹³C-NMR (75 MHz, CDCl₃): δ 172.1, 138.4, 128.1, 127.5, 127.4, 76.9, 71.3, 51.4, 39.1, 26.7, 9.2.

To a stirred suspension of LAH (101 mg, 2.7 mmol) in ether (10 mL) was added a solution of the benzyl ether **6A** (198 mg, 0.89 mmol) in ether (10 mL) at 0 °C. The reaction mixture was stirred for 1 h, and the reaction was quenched by addition of water (0.4 mL) and 15% NaOH solution (0.1 mL). The white precipitate that had formed was removed by filtration. Concentration and purification of the residue by flash column chromatography (Hex-EtOAc, 1:3) gave alcohol **6B** (168 mg, 97%). R_f 0.35 (Hex-EtOAc, 1:3).

To a stirred solution of alcohol **6B** (255 mg, 1.3 mmol) in DCM (1.5 mL) and DMSO (1.5 mL) were added TEA (0.91 mL, 6.5 mmol) and sulfur trioxide pyridine complex (623 mg, 3.9 mmol) at 0 °C. After 30 min at room temperature, the reaction was quenched by addition of sat. NH_4Cl solution (5 mL), and the reaction mixture was extracted with DCM (10 mL $\times$ 2). The organic extracts were dried over MgSO_4 , filtered, and concentrated. Purification by flash column chromatography (Hex-EtOAc, 4:1) gave aldehyde **7** (150 mg, 60%). R_f 0.47 (Hex-EtOAc, 4:1). $^1\text{H-NMR}$ (300 MHz, CDCl_3): δ 9.78-9.76 (m, 1H), 7.35-7.27 (m, 5H), 4.55 and 4.49 (AB q, 2H, $J = 11.5$ Hz), 3.96-3.85 (m, 1H), 2.64 and 2.52 (ABX, 2H, $J_{AB} = 16.3$ Hz, $J_{AX} = 7.4$ Hz, $J_{BX} = 4.7$ Hz), 1.73-1.57 (m, 2H), 0.94 (t, 3H, $J = 7.5$ Hz). $^{13}\text{C-NMR}$ (75 MHz, CDCl_3): δ 201.6, 138.1, 128.2, 127.6, 127.6, 75.2, 71.0, 47.7, 26.6, 9.2.

Alcohol **8**

To a solution of aldehyde **7** (150 mg, 0.78 mmol) in DCM (40 mL) was added TiCl_4 (0.78 mL, 1.0 M in toluene) at -78 °C. After 10 min, allyltrimethylsilane (0.15 mL, 0.94 mmol) was added and the reaction mixture was stirred under nitrogen for 2 h at -78 °C. The reaction was quenched by addition of water (100 mL) and the reaction mixture was extracted with ether (50 mL $\times$ 2). The organic extracts were washed with sat. NaHCO_3 solution (40 mL) and brine (40 mL), dried over MgSO_4 , filtered, concentrated, and purified by flash column chromatography to give alcohol **8** (155 mg, 85%). R_f 0.44 (Hex-EtOAc, 4:1). $^1\text{H-NMR}$ (300 MHz, CDCl_3): δ 7.36-7.28 (m, 5H), 5.90-5.76 (m, 1H), 5.14-5.06 (m, 2H), 4.59 and 4.52 (AB q, 2H, $J = 11.5$ Hz), 3.99-3.91 (m, 1H), 3.70-3.62 (m, 1H), 2.73 (d, 1H, $J = 3.5$ Hz), 2.25-2.20 (m, 2H), 1.77-1.54 (m, 4H), 0.92 (t, 3H, $J = 7.5$ Hz). $^{13}\text{C-NMR}$ (75 MHz, CDCl_3): δ 138.4, 135.0, 128.4, 127.8,

127.7, 117.5, 78.0, 71.2, 67.6, 42.2, 38.9, 26.0, 9.6. IR (neat): ν_{max} = 3435, 3066, 3030, 2966, 2935, 2877, 1641, 1497, 1454, 1354, 1207, 1146, 1066, 1028 cm^{-1} .

β -Alkoxymethacrylate **10**

The secondary alcohol **8** (159 mg, 0.68 mmol) was dissolved in DCM (30 mL). To the solution was bubbled a stream of O_3 at -78°C until no starting material was detected by TLC. Dimethyl sulfide (0.15 mL, 2.04 mmol) was added to the solution at room temperature and the reaction mixture was stirred for 2 h. After evaporation of DCM and dimethyl sulfide, the residue was dissolved in MeOH (20 mL) and NaBH_4 (129 mg, 3.40 mmol) was added at 0°C . The resulting mixture was stirred for 1 h at room temperature. The reaction was quenched by addition of sat. NH_4Cl solution (70 mL) and the reaction mixture was extracted with EtOAc (50 mL $\times$ 3). The organic extracts were washed with brine (50 mL), dried over MgSO_4 , filtered, concentrated, and purified by flash column chromatography (only EtOAc) to give diol **8B** (126 mg, 78%). R_f 0.38 (only EtOAc).

A solution of diol **8B** (913 mg, 3.83 mmol) and TEA (0.8 mL, 5.75 mmol) in DCM (3.83 mL) was treated with *p*-toluenesulfonyl chloride (876 mg, 4.6 mmol). The reaction mixture was stirred for 8 h at 0°C . The reaction was quenched by addition of sat. NH_4Cl solution (5 mL), and the reaction mixture was extracted with DCM (10 mL $\times$ 3). The organic extracts were dried over MgSO_4 , filtered, concentrated under reduced pressure, and the residue was purified by flash column chromatography (Hex-EtOAc, 1:1) to give the secondary alcohol **8C** (1.35 g, 89.7%). R_f 0.56 (Hex-EtOAc, 1:1). ^1H -NMR (300 MHz, CDCl_3): δ 7.78 (d, 2H, J = 8.3 Hz), 7.36-7.27 (m, 7H), 4.56 and 4.46 (AB q, 2H, J = 11.5 Hz), 4.21-4.13 (m, 2H), 4.01-3.93 (m, 1H), 3.64-3.57 (m, 1H), 2.93 (s, 1H), 2.42 (s, 3H), 1.91-1.48 (m, 6H), 0.90 (t, 3H, J = 7.4 Hz). ^{13}C -NMR (75 MHz, CDCl_3): δ 144.6, 138.1, 132.9, 129.7, 128.4, 127.8, 127.8, 127.7, 76.6, 71.0, 67.8, 64.7, 39.0, 36.5, 25.7, 21.5, 9.5. MS m/z (FAB, relative intensity): 393 ($\text{M}^+ + 1$, 4), 145 (74), 109 (24), 91 (74), 69 (68), 55 (100), 43 (60). HRMS (FAB) calcd. for $\text{C}_{21}\text{H}_{29}\text{O}_5\text{S}$ ($\text{M}^+ + 1$) 393.1735, found 393.1740. $[\alpha]_D^{25}$ -11.5 (c 2.01, CHCl_3).

To a solution of the secondary alcohol **8C** (1.43 g, 3.64 mmol) and PPTS (183

mg, 0.73 mmol) in benzene (20 mL) was added **9** (1.7 g, 10.48 mmol), and the mixture was heated under reflux for 4 h. After removal of the solvent in *vacuo*, flash column chromatography (Hex-EtOAc, 2:1) afforded β -alkoxymethacrylate **10** (1.23 g, 69.1%). R_f 0.54 (Hex-EtOAc, 2:1). $^1\text{H-NMR}$ (300 MHz, CDCl_3): δ 7.74 (d, 2H, $J = 8.3$ Hz), 7.38-7.27 (m, 8H), 4.55 and 4.30 (AB q, 2H, $J = 11.1$ Hz), 4.25-4.19 (m, 1H), 4.16-4.09 (m, 1H), 4.06-3.98 (m, 1H), 3.65 (s, 3H), 3.48-3.40 (m, 1H), 2.41 (s, 3H), 1.99-1.86 (m, 2H), 1.68-1.56 (m, 7H), 0.88 (t, 3H, $J = 7.5$ Hz). $^{13}\text{C-NMR}$ (75 MHz, CDCl_3): δ 168.9, 157.1, 144.8, 138.3, 132.6, 129.7, 128.3, 127.7, 127.7, 127.5, 105.4, 76.6, 75.3, 70.4, 66.1, 50.9, 39.5, 34.6, 25.5, 21.5, 9.0, 8.4. $[\alpha]_D^{25} -45.6$ (c 3.59, CHCl_3).

Benzyl ether **11**

To a solution of β -alkoxymethacrylate **10** (132 mg, 0.27 mmol) in acetone (8 mL) was added NaI (123 mg, 0.82 mmol) at room temperature. The reaction mixture was heated under reflux for 3 h. The mixture was added to brine (5 mL). The organic layer was separated, and the aqueous layer was extracted with ether (10 mL $\times$ 3). The combined organic extracts were dried over MgSO_4 , filtered, concentrated, and purified by flash column chromatography (Hex-EtOAc, 4:1) to give iodide **10A** (94 mg, 78.4%). R_f 0.56 (Hex-EtOAc, 4:1).

To a stirred solution of iodide **10A** (103 mg, 0.23 mmol) in toluene (0.01 M, 23 mL) were added TTMSS (0.074 mL, 0.28 mmol) and Et_3B (1 M in Hexane, 0.35 mL, 0.35 mmol) in sequence at -20 $^\circ\text{C}$. The reaction mixture was stirred for 1 h under air at -20 $^\circ\text{C}$. Concentration and purification by flash column chromatography (Hex-EtOAc, 4:1) furnished the benzyl ether **11** (69 mg, 94%). R_f 0.46 (Hex-EtOAc, 4:1). $^1\text{H-NMR}$ (300 MHz, CDCl_3): δ 7.34-7.27 (m, 5H), 4.54 and 4.49 (AB q, 2H, $J = 11.4$ Hz), 4.09-3.98 (m, 2H), 3.67 (s, 3H), 3.57-3.44 (m, 1H), 2.58-2.48 (m, 1H), 2.03-1.93 (m, 2H), 1.73-1.42 (m, 6H), 1.12 (d, 3H, $J = 7.0$ Hz), 0.92 (t, 3H, $J = 7.4$ Hz). $^{13}\text{C-NMR}$ (75 MHz, CDCl_3): δ 175.4, 139.0, 128.3, 127.8, 127.4, 80.3, 78.1, 76.6, 71.5, 51.6, 45.6, 40.9, 31.5, 28.6, 27.1, 13.4, 9.3. $[\alpha]_D^{25} -19.5$ (c 0.57, CHCl_3).

(+)-Methyl homononactate (12**)**

The benzyl ether **11** (135 mg, 0.42 mmol) was dissolved in MeOH (5 mL) and palladium on activated carbon (10% w/w, 90 mg) was added. The mixture was stirred under hydrogen atmosphere for 30 min and then filtered through a filter paper. After solvent evaporation, flash column chromatography (Hex-EtOAc, 2:1) yielded (+)-methyl homononactate (**12**, 88 mg, 91%). R_f 0.12 (Hex-EtOAc, 4:1). $^1\text{H-NMR}$ (300 MHz, CDCl_3): δ 4.16-4.12 (m, 1H), 4.02-3.94 (m, 1H), 3.72-3.68 (m, 1H), 3.69 (s, 3H), 2.75-2.73 (br. s, 1H), 2.60-2.50 (m, 1H), 2.06-1.93 (m, 3H), 1.79-1.35 (m, 5H), 1.13 (d, 3H, $J = 7.0$ Hz), 0.94 (t, 3H, $J = 7.4$ Hz). $^{13}\text{C-NMR}$ (75 MHz, CDCl_3): δ 175.2, 81.0, 70.5, 51.6, 45.2, 40.6, 30.6, 30.0, 30.0, 28.8, 13.4, 10.1. $[\alpha]_D^{25} +8.6$ (c 0.15, CHCl_3).

Diacetate **13**

To a solution of (+)-methyl homononactate (**12**, 3 mg, 0.013 mmol) in ether (0.013 mL) was added LiBH_4 (2 M in THF, 0.013 mL, 0.026 mmol) at 0 °C. The reaction mixture was stirred for 1 h at room temperature. After evaporation of ether, the residue was dissolved in DCM (0.013 mL). TEA (0.027 mL, 0.195 mmol), DMAP (7.9 mg, 0.065 mmol), and acetic anhydride (0.012 mL, 0.13 mmol) were added at room temperature. The reaction mixture was stirred for 1 h, and the reaction was quenched by addition of sat. NH_4Cl solution (1 mL). The reaction mixture was extracted with DCM (3 mL $\times$ 3), and the organic extracts were dried over MgSO_4 . Filtration, concentration, and purification of the residue by flash column chromatography (Pentane-Ether, 1:1) provided diacetate **13** (2.5 mg, 66%). R_f 0.49 (Pentane-Ether, 1:1). $^1\text{H-NMR}$ (600 MHz, CDCl_3): δ 4.95-4.91 (m, 1H), 4.20 and 3.96 (ABX, 2H, $J_{AB} = 10.8$ Hz, $J_{AX} = 4.7$ Hz, $J_{BX} = 7.0$ Hz), 3.87-3.82 (m, 1H), 3.66 (dt, 1H, $J = 7.3, 7.3$ Hz), 2.05 (s, 3H), 2.04 (s, 3H), 1.94-1.21 (m, 9H), 0.91 (d, 3H, $J = 7.0$ Hz), 0.89 (t, 3H, $J = 7.6$ Hz).

Diacetate **15**

To a solution of (+)-methyl nonactate (**14**, 5.6 mg, 0.026 mmol) in ether (0.026 mL) was added LiBH₄ (2 M in THF, 0.026 mL, 0.052 mmol) at 0 °C. The reaction mixture was stirred for 1 h at room temperature. After evaporation of ether, the residue was dissolved in DCM (0.026 mL). TEA (0.054 mL, 0.39 mmol), DMAP (15.8 mg, 0.130 mmol), and acetic anhydride (0.024 mL, 0.26 mmol) were added at room temperature. The reaction mixture was stirred for 1 h, and the reaction was quenched by addition of sat. NH₄Cl solution (3 mL). The reaction mixture was extracted with DCM (6 mL × 3), and the organic extracts were dried over MgSO₄. Filtration, concentration, and purification of the residue by flash column chromatography (Pentane-Ether, 1:1) provided diacetate **15** (5.4 mg, 75%). R_f 0.47 (Pentane-Ether, 1:1). ¹H-NMR (600 MHz, CDCl₃): δ 5.02-4.97 (m, 1H), 4.20 and 3.96 (ABX, 2H, J_{AB} = 10.8 Hz, J_{AX} = 4.6 Hz, J_{BX} = 7.0 Hz), 3.88-3.83 (m, 1H), 3.66 (dt, 1H, J = 7.3, 7.3 Hz), 2.05 (s, 3H), 2.02 (s, 3H), 1.97-1.47 (m, 7H), 1.25 (d, 3H, J = 6.3 Hz), 0.91 (d, 3H, J = 6.8 Hz).

(+)-Methyl 8-*epi*-nonactate (**16**)

R_f 0.17 (Hex-EtOAc, 2:1). ¹H-NMR (600 MHz, CDCl₃): δ 4.10-4.05 (m, 1H), 4.02-3.96 (m, 2H), 3.70 (s, 3H), 3.65 (s, 1H), 2.57-2.52 (m, 1H), 2.07-1.97 (m, 2H), 1.70-1.52 (m, 4H), 1.17 (d, 3H, J = 6.2 Hz), 1.13 (d, 3H, J = 7.0 Hz). ¹³C-NMR (75 MHz, CDCl₃): δ 175.1, 81.5, 80.1, 67.7, 51.6, 45.2, 44.5, 31.6, 28.5, 23.3, 13.4. IR (neat): ν_{max} = 3457, 2969, 2929, 2879, 1739, 1461, 1375, 1263, 1199, 1081 cm⁻¹. MS *m/z* (FAB, relative intensity): 217 (M⁺+1, 100), 199 (15), 157 (36), 129 (12), 71 (12). HRMS (FAB) calcd. for C₁₁H₂₁O₄ (M⁺+1) 217.1440, found 217.1447. [α]_D²⁵ +36.1 (c 1.78, CHCl₃).

Diacetate **3**

To a solution of (+)-methyl 8-*epi*-nonactate (**16**, 9 mg, 0.042 mmol) in ether (0.042 mL) was added LiBH₄ (2 M in THF, 0.042 mL, 0.084 mmol) at 0 °C. The reaction mixture was stirred for 1 h at room temperature. After evaporation of ether, the residue was dissolved in DCM (0.042 mL). TEA (0.087 mL, 0.626 mmol), DMAP (25.4

mg, 0.209 mmol), and acetic anhydride (0.039 mL, 0.42 mmol) were added at room temperature. The reaction mixture was stirred for 1 h, and the reaction was quenched by addition of sat. NH_4Cl solution (3.2 mL). The reaction mixture was extracted with DCM (9.6 mL $\times$ 3), and the organic extracts were dried over MgSO_4 . Filtration, concentration, and purification of the residue by flash column chromatography (Pentane-Ether, 1:1) provided diacetate **3** (8.0 mg, 70%). R_f 0.45 (Pentane-Ether, 1:1). ^1H -NMR (300 MHz, CDCl_3): δ 5.05-5.00 (m, 1H), 4.21 and 3.98 (ABX, 2H, $J_{AB} = 10.8$ Hz, $J_{AX} = 4.6$ Hz, $J_{BX} = 6.9$ Hz), 3.89-3.84 (m, 1H), 3.66 (dt, 1H, $J = 7.4, 7.4$ Hz), 2.05 (s, 3H), 2.02 (s, 3H), 1.93-1.87 (m, 2H), 1.61-1.43 (m, 5H), 1.25 (d, 3H, $J = 6.3$ Hz), 0.91 (d, 3H, $J = 6.9$ Hz).

Acid **19**

To a stirred solution of the benzyl ether **11** (103 mg, 0.32 mmol) in MeOH (3.5 mL) was added lithium hydroxide hydrate (201 mg, 4.8 mmol) in H_2O (1 mL). The reaction mixture was stirred for 5 h at room temperature and acidified with 2 N HCl (pH 5), and extracted with DCM (10 mL $\times$ 5). Drying organic extracts over MgSO_4 , filtration, concentration, and purification of the residue by flash column chromatography (Hex-EtOAc-AcOH, 2:1:0.05) provided acid **19** (89 mg, 91%). R_f 0.29 (Hex-EtOAc, 2:1). ^1H -NMR (300 MHz, CDCl_3): δ 7.46-7.27 (m, 5H), 4.56 and 4.47 (AB q, 2H, $J = 11.4$ Hz), 4.25-4.08 (m, 1H), 4.02-3.95 (m, 1H), 3.58-3.51 (m, 1H), 2.66-2.46 (m, 1H), 2.08-1.97 (m, 2H), 1.76-1.50 (m, 7H), 1.17 (d, 3H, $J = 7.1$ Hz), 0.91 (t, 3H, $J = 7.4$ Hz). ^{13}C -NMR (75 MHz, CDCl_3): δ 178.7, 139.0, 128.3, 127.8, 127.5, 80.1, 77.0, 76.6, 71.4, 45.1, 40.7, 31.4, 29.1, 26.9, 13.3, 9.2. $[\alpha]_D^{25} -18.6$ (c 1.90, CHCl_3).

Ester **20**

To a mixture of acid **19** (25 mg, 0.082 mmol) and TEA (0.026 mL, 0.19 mmol) in THF (1 mL) was added 2,4,6-trichlorobenzoyl chloride (0.02 mL, 0.14 mmol). The reaction mixture was stirred for 2 h at room temperature. The white precipitate that had formed was removed by filtration under N₂ via cannula transfer to a glass pipet equipped with a septum and a plug of glass wool. The THF filtrate was evaporated by a stream of N₂. The residue was diluted with benzene (2 mL) and DMAP (30 mg, 0.25 mmol) was added. To this mixture was added alcohol **14** (26 mg, 0.12 mmol) in benzene (1 mL). The reaction mixture was stirred for 2 h at room temperature and the reaction was quenched by addition of sat. NH₄Cl solution (3 mL). The reaction mixture was extracted with DCM (10 mL × 3), and the organic extracts were dried over MgSO₄, filtered, and concentrated. Purification by flash column chromatography (Hex-EtOAc, 4:1) gave ester **20** (41 mg, 99%). R_f 0.54 (Hex-EtOAc, 2:1). ¹H-NMR (300 MHz, CDCl₃): δ 7.34-7.27 (m, 5H), 5.02-4.96 (m, 1H), 4.54 and 4.48 (AB q, 2H, *J* = 11.2 Hz), 4.05-3.86 (m, 4H), 3.69 (s, 3H), 3.57-3.52 (m, 1H), 2.52-2.45 (m, 2H), 2.01-1.90 (m, 4H), 1.78-1.72 (m, 2H), 1.69-1.47 (m, 8H), 1.24 (d, 3H *J* = 6.3 Hz), 1.10 (d, 3H, *J* = 7.0 Hz), 1.09 (d, 3H, *J* = 7.0 Hz), 0.92 (t, 3H, *J* = 7.4 Hz)

Alcohol **21**

Ester **20** (12 mg, 0.023 mmol) was dissolved in MeOH (1 mL) and palladium on activated carbon (10% w/w, 5 mg) was added. The mixture was stirred under hydrogen atmosphere for 30 min and then filtered through a filter paper. After solvent evaporation, flash column chromatography (Hex-EtOAc, 2:1) yielded alcohol **21** (9 mg, 94%). R_f 0.43 (Hex-EtOAc, 1:3). ¹H-NMR (300 MHz, CDCl₃): δ 5.03-4.92 (m, 1H), 4.15-4.11 (m, 1H), 4.01-3.84 (m, 3H), 3.72-3.64 (m, 1H), 3.68 (s, 3H), 2.88 (d, 1H *J* = 4.9 Hz), 2.54-2.42 (m, 2H), 2.00-1.94 (m, 4H), 1.77-1.42 (m, 10H), 1.23 (d, 3H *J* = 6.1 Hz), 1.09 (d, 6H, *J* = 7.0 Hz), 0.92 (t, 3H, *J* = 7.4 Hz). ¹³C-NMR (75 MHz, CDCl₃): δ 175.4, 174.4, 81.2, 80.4, 76.6, 76.4, 70.5, 69.4, 51.7, 45.5, 45.4, 42.4, 40.6, 31.3, 30.6, 29.9, 28.8, 28.5, 20.6, 13.4, 13.4, 10.3.

(2'*S*, 3'*S*, 6'*R*, 8'*R*)-homononactoyl (2*S*, 3*S*, 6*R*, 8*R*)-nonactic acid (**17**)

To a solution of alcohol **21** (5.0 mg, 0.012 mmol) in HMPA (0.048 mL) was added lithium *n*-propyl mercaptide (0.48 M in HMPA, 0.0048 mL). The reaction mixture was stirred for 2 h at room temperature. The reaction was quenched by addition of sat. NaHCO₃ (0.026 mL) solution and water (0.020 mL). The reaction mixture was extracted with CHCl₃ (0.020 mL × 6). The aqueous phase was acidified to pH 1 with 2 N HCl and extracted with CHCl₃ (0.040 mL × 8). The organic extracts were dried over MgSO₄, filtered, and concentrated. Purification by flash column chromatography (CHCl₃-MeOH, 9:1) gave (2'*S*, 3'*S*, 6'*R*, 8'*R*)-homononactoyl (2*S*, 3*S*, 6*R*, 8*R*)-nonactic acid (**17**, 3.3 mg, 69%). *R*_f 0.43 (CHCl₃-MeOH, 9:1). ¹H-NMR (300 MHz, CDCl₃): δ 5.09-5.00 (m, 1H), 4.17-4.14 (m, 1H), 4.03-3.90 (m, 3H), 3.77-3.72 (m, 1H), 2.54-2.44 (m, 2H), 2.10-1.98 (m, 4H), 1.86-1.40 (m, 11H), 1.26 (d, 3H *J* = 6.2 Hz), 1.18 (d, 3H, *J* = 7.1 Hz), 1.11 (d, 3H, *J* = 7.0 Hz), 0.93 (t, 3H, *J* = 7.4 Hz). ¹³C-NMR (75 MHz, CDCl₃): δ 176.0, 174.2, 81.2, 80.5, 77.2, 77.1, 76.8, 70.5, 68.9, 45.6, 44.8, 42.1, 40.5, 31.0, 30.5, 29.9, 29.4, 28.8, 20.3, 13.5, 10.2. [α]²⁵_D +22.1 (*c* 0.1, CHCl₃).

(-)-Methyl nonactate (**ent-14**)

*R*_f 0.17 (Hex-EtOAc, 2:1). ¹H-NMR (600 MHz, CDCl₃): δ 4.19-4.11 (m, 1H), 4.04-3.95 (m, 2H), 3.70 (s, 3H), 2.94 (s, 1H), 2.59-2.49 (m, 1H), 2.07-1.94 (m, 2H), 1.80-1.59 (m, 4H), 1.21 (d, 3H, *J* = 6.3 Hz), 1.13 (d, 3H, *J* = 7.0 Hz). ¹³C-NMR (75 MHz, CDCl₃): δ 175.3, 81.1, 77.3, 65.1, 51.7, 45.3, 42.5, 30.4, 28.8, 23.2, 13.6. [α]²⁵_D -22.1 (*c* 0.18, CHCl₃).