Supporting Information

A concise total synthesis of the purported structure of flossonol

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General Experimental Methods

Purification procedures were in accordance with the instructions in D. D. Perrin and W. L. F. Armarego, “Purification of Laboratory Chemicals”, Fourth Edition, The Bath Press, Bath, 2002. All reactions were carried out under dry, oxygen free nitrogen. Flash chromatography was performed on silica gel (SDS, 60 Å C. C. 40-63 mm) as the stationary phase. Thin Layer Chromatography (TLC) was performed on alumina plates pre-coated with silica gel (Merck silica gel, 60 F254), which were visualized by the quenching of UV fluorescence when applicable (λmax = 254 nm and/or 366 nm) and/or by staining with vanillin or anisadehyde in acidic ethanol followed by heating. Infrared spectra were recorded as solutions in CCl₄ using KCl cells, on a Perkin-Elmer FT 2000. Absorption maxima (nmax) are reported in wavenumbers (cm⁻¹) and only selected peaks are reported. Magnetic resonance spectra were recorded at room temperature on a Bruker Avance DPX 400 instrument. Proton magnetic resonance spectra (1H NMR) were recorded at 400 MHz and coupling constants (J) are reported to ± 0.5 Hz. The following abbreviations were utilized to describe peak patterns when appropriate: b = broad, s = singlet, d = doublet, t = triplet, q = quartet, quint = quintuplet, hex = hexuplet, hept = heptuplet, oct = octuplet and m = multiplet. Carbon magnetic resonance spectra (13C NMR) were recorded in the same instrument at 100.6 MHz. Chemical shifts (δH, δC) are quoted in parts per million (ppm) and are referenced to TMS (0 ppm). Low-resolution mass spectra (m/z) were recorded by chemical ionization (CI/NH3) on a Hewlett-Packard HP 5989B and only report molecular species ([M+H]+, [M+NH4]+) and other major fragments. High-resolution mass spectra were recorded by positive electron impact ionization (EI+) at 70 e.V. on a JEOL JMS-GCmate II mass spectrometer. The quoted masses are accurate to ± 5 ppm. The names of the molecules that appear in the following pages were generated using either Beilstein AutoNom 2000 (CAS) or ChemBioDraw Ultra 10.0.
<table>
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<th>Abbreviation</th>
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<tr>
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Experimental Procedures and Spectroscopic Data

Compound 4: 2-bromo-1-(4-methoxy-3-methylphenyl)propan-1-one

2-Methylanisole (4.92 g, 40.3 mmol, 1.0 eq.) in distilled dichloroethane (100 mL) was cooled to 0°C under a nitrogen atmosphere and 2-bromopropionyl bromide (5.1 mL, 48.4 mmol, 1.2 eq.) was added. Aluminium trichloride (8.06 g, 60.45 mmol, 1.5 eq.) was then added portionwise and the solution stirred for 10 min at 0°C then 3 h at RT. Ice (100 g) was added to the reaction mixture which was extracted three times with DCM. The combined organic layers were washed with NaHCO₃ (sat. aq.), dried over MgSO₄ and evaporated under reduced pressure. The crude was triturated with pentane (50 mL) and filtrated. The desired product was obtained as a white solid (8.49 g, 33.0 mmol, 82 %).

$^1$H NMR (δ, ppm) (CDCl₃, 400 MHz): 7.90 (dd, 1H, J₁ = 2.3 Hz, J₂ = 8.6 Hz, C₉H); 7.84 (d, 1H, J = 2.0 Hz, C₅H); 6.87 (d, 1H, J = 8.6 Hz, C₈H); 5.28 (q, 1H, J = 6.6 Hz, C₂H); 3.91 (s, 3H, OCH₃); 2.26 (s, 3H, CH₃); 1.88 (d, 3H, J = 6.6 Hz, CH₃).

$^{13}$C NMR (δ, ppm) (CDCl₃, 100.6 MHz): 192.26 (CO); 162.24 (OC); 131.50 (C₅H); 129.13 (C₆H); 127.16 (C₇H); 126.30 (CIV); 109.35 (C₈H); 55.58 (OCH₃); 41.48 (C₂H); 20.30 (CH₃); 16.28 (CH₃). IR (cm⁻¹) (CCl₄): 2962, 2840, 1682, 1602, 1258. HRMS (EI⁺) calcd for: C₁₁H₁₃BrO₂: 256.0099, found: 256.0097.

Compound 2: O-ethyl S-1-(4-methoxy-3-methylphenyl)-1-oxopropan-2-yl carbonodithioate

To a solution of compound 4 (6.38 g, 24.8 mmol, 1.0 eq) in acetone (50 mL) at 0 °C under a nitrogen atmosphere was added potassium O-ethylxanthate (4.77 g, 29.8 mmol, 1.2 eq) portionwise. The mixture was stirred for 60 min and evaporated to dryness under reduced pressure. Water was added and the mixture was extracted three times with DCM. The combined organic layers were dried over magnesium sulfate and concentrated under reduced pressure. The desired product was obtained as
a transparent oil (7.35 g, 24.7 mmol, 99%). $^1$H NMR (δ, ppm) (CDCl$_3$, 400 MHz): 7.90 (dd, 1H, J1 = 2.3 Hz, J2 = 8.6 Hz, C$_9$H); 7.83 (d, 1H, J = 2.3 Hz, C$_5$H); 6.86 (d, 1H, J = 8.6 Hz, C$_6$H); 5.45 (q, 1H, J = 7.1 Hz, C$_2$H); 4.62 (q, 2H, J = 7.1 Hz, OC$_{13}$H$_2$); 3.90 (s, 3H, OC$_{11}$H$_3$); 2.24 (s, 3H, C$_{10}$H$_3$); 1.60 (d, 3H, J = 7.1 Hz, C$_3$H); 1.37 (t, 3H, J = 7.1 Hz, C$_{14}$H$_3$). $^{13}$C NMR (δ, ppm) (CDCl$_3$, 100.6 MHz): 213.26 (C$_{12}$S); 195.56 (C$_4$O); 162.26 (OCC$_7$); 131.22 (C$_5$H); 128.84 (C$_9$H); 127.25 (C$_{10}$H); 127.09 (C$_{11}$H); 109.35 (C$_8$H); 70.46 (OC$_{13}$H$_2$); 55.54 (OC$_{11}$H$_3$); 49.72 (C$_2$H); 17.34 (C$_3$H); 16.27 (C$_{10}$H$_3$); 13.69 (C$_{14}$H$_3$). IR (cm$^{-1}$) (CCl$_4$): 2933, 2839, 1677, 1602, 1256, 1225, 1055. HRMS (EI+) calcd for C$_{14}$H$_{18}$O$_3$S$_2$ 298.0697, found: 298.0695.

Compound 5: 1-(ethoxycarbonothioylthio)-4-(4-methoxy-3-methylphenyl)-3-methyl-4-oxobutyl acetate

Compound 2 (596 mg, 2.00 mmol, 1.0 eq.) and vinyl acetate (690 mg, 8.00 mmol, 4.0 eq.) were dissolved in AcOEt (2.0 mL). The solution was refluxed under nitrogen atmosphere for 15 min. Dilauroyl peroxide was then added in 5 mol% portions every 90 min until complete consumption of the starting material which took 20 mol% of dilauroyl peroxide. Purification by two column chromatographies (EP/AcOEt: from 100/0 to 90/10 then Pentane/diethyl ether: from 100/0 to 0/100) yielded the desired product as a slightly yellow oil in a 1 : 1 mixture of diastereoisomers (506 mg, 1.32 mmol, 66 %). $^1$H NMR (δ, ppm) (CDCl$_3$, 400 MHz): 7.84 – 7.80 (m, 1H, C$_{16}$H); 7.77 – 7.7 (m, 1H, C$_{12}$H); 6.85 (dd, 1H, J$_1$ = 3.0, J$_2$ = 8.6 Hz, C$_{15}$H); 6.68 (t$_{app}$, 1H, J = 6.5 Hz, SC$_4$H) & 6.64 (dd, 1H, J$_1$ = 6.1 Hz, J$_2$ = 8.2 Hz, SC$_4$H); 4.68 – 4.42 (m, 2H, OC$_8$H$_2$); 3.89 (s, 3H, OC$_{18}$H$_3$); 3.64 – 3.55 (m, 1H, C$_3$H); 2.62 – 2.53 (m, 1H, C$_3$H); 2.25 & 2.24 (s, 3H, C$_{13}$H$_3$); 2.04 – 1.97 (m, 1H, C$_2$H$_2$); 1.96 & 1.95 (s, 3H, C$_8$H$_3$); 1.39 (t, 3H, J = 7.1 Hz, C$_3$H$_3$) & 1.33 (t, 3H, J = 7.1 Hz, C$_3$H$_3$); 1.24 (d, 3H, J = 7.0 Hz, C$_9$H$_3$) & 1.23 (d, 3H, J = 7.0 Hz, C$_9$H$_3$). $^{13}$C NMR (δ, ppm) (CDCl$_3$, 100.6 MHz): 209.89 (C$_7$S); 201.01 (C$_4$O); 169.20 & 169.11 (C$_4$O); 161.88 & 161.82 (OC$_{14}$H); 130.97 & 130.94 (C$_{12}$H); 128.45 & 128.40 (C$_{14}$H); 126.98 (C$_{15}$H); 109.29 (C$_{16}$H); 79.51 & 79.12 (SC$_4$H); 70.26 & 70.15 (OC$_8$H$_2$); 55.53 & 55.51 (OC$_{18}$H$_3$); 37.83 & 37.10 (C$_3$H); 37.05 & 36.81 (C$_2$H); 20.77 & 20.71 (C$_8$H$_3$); 18.48 & 18.44 (C$_{13}$H$_3$); 16.31 & 16.28 (C$_9$H$_3$); 13.61 & 13.50 (C$_9$H$_3$). IR (cm$^{-1}$) (CCl$_4$): 2965, 2934, 1752, 1678, 1602, 1256, 1225, 1055. HRMS (EI+) calcd for C$_{14}$H$_{18}$O$_3$S$_2$ 298.0697, found: 298.0695.
Compound 7: 1-(ethoxycarbonothioylthio)-4-(4-methoxy-3-methylphenyl)-3-methyl-4-oxobutyl pivalate

Compound 5 (500 mg, 1.68 mmol, 1.0 eq) and vinyl pivalate (500 μL, 3.36 mmol, 2.0 eq) were dissolved in AcOEt (1.7 mL). The solution was refluxed under nitrogen atmosphere for 15 min. Dilauroyl peroxide was then added in 5 mol% portions every 90 min until complete consumption of the starting material which took 20 mol% of dilauroyl peroxide. The solution was then cooled to room temperature, the solvent evaporated under reduced pressure and the residues purified by column chromatography (EP/AcOEt: from 98/2 to 92/8). The desired product was obtained as a transparent oil in a 1:0.9 mixture of diastereoisomers (486 mg, 1.14 mmol, 68%).

**1H NMR** (δ, ppm) (CDCl3, 400 MHz): Diastereoisomer n°1: 7.83 – 7.78 (m, 1H, C17H); 7.76 – 7.74 (m, 1H, C13H); 6.84 (d, 1H, J = 8.6 Hz, C16H); 6.68 – 6.62 (m, 1H, SC1H); 4.68 – 4.44 (m, 2H, OC9H2); 3.89 (s, 3H, OC19H3); 3.62 – 3.53 (m, 1H, C3H); 2.60 – 2.51 (m, 1H, C2H2); 2.23 (s, 3H, C18H3); 2.05 – 1.97 (m, 1H, C2H2); 1.34 (t, 3H, J = 7.1 Hz, C10H3); 1.25 (d, 3H, J = 6.9 Hz, C11H3); 1.17 (s, 9H, C6(C7H3)3). Diastereoisomer n°2: 7.83 – 7.78 (m, 1H, C17H); 7.76 – 7.74 (m, 1H, C13H); 6.85 (d, 1H, J = 8.6 Hz, C16H); 6.68 – 6.62 (m, 1H, SC1H); 4.68 – 4.44 (m, 2H, OC9H2); 3.89 (s, 3H, OC19H3); 3.62 – 3.53 (m, 1H, C3H); 2.60 – 2.51 (m, 1H, C2H2); 2.25 (s, 3H, C18H3); 2.05 – 1.97 (m, 1H, C2H2); 1.40 (t, 3H, J = 7.1 Hz, C10H3); 1.24 (d, 3H, J = 7.0 Hz, C11H3); 1.12 (s, 9H, C6(C7H3)3).

**13C NMR** (δ, ppm) (CDCl3, 100.6 MHz): Diastereoisomer n°1: 210.11 (C8S); 200.96 (C4O); 176.60 (C6O); 161.85 (OC15); 131.03 (C13H); 128.46 (C17H); 128.21 (C9O); 126.94 (C7O); 109.29 (C16H); 79.09 (SC1H); 70.11 (OC9H2); 55.53 (OC19H3); 38.81 (C6); 37.80 (C2H2); 36.97 (C3H2); 26.90 (C6(C7H3)3); 18.04 (C11H3); 16.25(C18H3); 13.53 (C10H3). Diastereoisomer n°2: 209.98 (C8S); 200.89 (C6O); 176.58 (C6O); 161.82 (OC15); 131.00 (C13H); 128.46 (C17H); 128.17 (C9O); 126.91 (C7O); 109.28 (C16H); 79.65 (SC1H); 70.21 (OC9H2); 55.51 (OC19H3); 38.74 (C6); 37.18 (C2H2); 36.83 (C3H2); 26.88 (C6(C7H3)3); 18.51 (C11H3); 16.28(C18H3); 13.65 (C10H3). **IR** (cm⁻¹) (CCl4): 2975, 2935, 2873, 1740, 1678, 1602, 1257, 1231, 1135, 1047. **HRMS** (El+) calcd for C21H30O5S2 305.1753, found: 305.1760 (loss of the O-ethylcarbonodithioate).
Compound *cis*-8: 7-methoxy-3,6-dimethyl-4-oxo-1,2,3,4-tetrahydronaphthalen-1-yl pivalate

Compound 7 (450 mg, 1.05 mmol, 1.0 eq) was dissolved in AcOEt (10.5 mL). The solution was refluxed under nitrogen atmosphere for 15 min. Dilauroyl peroxide was then added in 20 mol% portions every 60 min until complete consumption of the starting material which took 140 mol% of dilauroyl peroxide. The solution was then cooled to room temperature, the solvent evaporated under reduced pressure and the residues purified by column chromatography (EP/AcOEt: from 100/0 to 95/5). The desired product was obtained as a white solid in a 1 : 0.6 mixture of separable diastereoisomers (189 mg, 0.62 mmol, 59%). $^1$H NMR (δ, ppm) (CDCl₃, 400 MHz): 7.84 (s, 1H, C₈H); 6.68 (s, 1H, C₆H); 6.15 (dd, 1H, J₁ = 4.5 Hz, J₂ = 10.6 Hz, OC₄H); 3.85 (s, 3H, OC₁₃H₃); 2.66 (ddq, 1H, J₁ = 4.5 Hz, J₂ = 6.7 Hz, J₃ = 13.4 Hz, C₂H); 2.45 (ddd, 1H, J₁ = 4.4 Hz, J₂ = 5.1 Hz, J₃ = 12.2 Hz, C₃H₂); 2.22 (s, 3H, C₁₄H₃); 1.89 (ddd, 1H, J₁ = 10.8 Hz, J₂ = 12.0 Hz, J₃ = 13.0 Hz, C₃H₂); 1.31 (s, 9H, C₁₁(C₁₂H₃)₃); 1.29 (d, 3H, J = 6.8 Hz, C₉H₃). $^{13}$C NMR (δ, ppm) (CDCl₃, 100.6 MHz): 197.92 (C₁O); 178.00 (C₁₀O) 162.05 (C₈); 142.71 (C₈a); 129.73 (C₆H); 127.19 (C₄IV); 124.42(C₄IV); 105.78 (C₆H); 69.39 (OC₄H); 55.38 (OC₁₃H₃); 40.24 (C₂H); 38.95 (C₁₁); 37.62 (C₃H₂); 27.14 (3C, C₁₁(C₁₂H₃)₃); 15.87 (C₁₄H₃); 15.58 (C₉H₃). IR (cm⁻¹) (CCl₄): 2969, 2934, 2872, 1731, 1686, 1609, 1270, 1250, 1151. HRMS (EI+) calcd for C₁₉H₂₄O₄ 304.1675, found: 304.1679.
Compound trans-8: 7-methoxy-3,6-dimethyl-4-oxo-1,2,3,4-tetrahydronaphthalen-1-yl pivalate

$^1$H NMR (δ, ppm) (CDCl$_3$, 400 MHz): 7.84 (s, 1H, C$_8$H); 6.78 (s, 1H, C$_5$H); 6.05 (dd, 1H, $J_1 = 3.1$ Hz, $J_2 = 3.5$ Hz, OC$_4$H); 3.87 (s, 3H, OC$_{13}$H$_3$); 2.95 (ddq, 1H, $J_1 = 4.7$ Hz, $J_2 = 7.0$ Hz, $J_3 = 11.6$ Hz, C$_2$H); 2.32 (ddd, 1H, $J_1 = 4.4$ Hz, $J_2 = 4.4$ Hz, $J_3 = 14.1$ Hz, C$_3$H$_2$); 2.23 (s, 3H, C$_14$H$_3$); 2.14 (ddd, 1H, $J_1 = 3.3$ Hz, $J_2 = 11.6$ Hz, $J_3 = 14.6$ Hz, C$_1$H$_2$); 1.27 (d, 3H, $J = 7.0$ Hz, C$_9$H$_3$); 1.18 (s, 9H, C$_{11}$H$_3$)$_3$. $^{13}$C NMR (δ, ppm) (CDCl$_3$, 100.6 MHz): 198.89 (C$_1$O); 178.08 (C$_{10}$O) 162.07 (C$_6$); 140.11 (C$_{8a}$H); 129.64 (C$_8$H); 128.22 (CIV$_H$); 109.42 (C$_3$H); 68.47 (OC$_4$H); 55.68 (OC$_{13}$H$_3$); 38.99 (C$_{11}$); 36.94 (C$_2$H); 36.51 (C$_3$H$_2$); 27.07 (3C, C$_{11}$H$_3$)$_3$); 16.04 (C$_{14}$H$_3$); 15.51 (C$_9$H$_3$). IR (cm$^{-1}$) (CCl$_4$): 2977, 2934, 2870, 1725, 1683, 1606, 1278, 1261, 1148. HRMS (EI+) calcd for C$_{18}$H$_{24}$O$_4$ 304.1675, found: 304.1665.

Compound 9a: 4-hydroxy-6-methoxy-2,7-dimethyl-3,4-dihydro-2H-naphtalen-1-one

Compound 8 (100 mg, 0.33 mmol, 1eq.) and potassium hydroxide (184 mg, 3.3 mmol, 10 eq.) were dissolved in ethanol (3.3 mL). The reaction mixture was stirred at 50 °C under a nitrogen atmosphere for 1 h. Then, water was added, the pH was neutralized with HCl (1M) and the solution was extracted three times with DCM. The combined organic layers were dried over MgSO$_4$, evaporated under reduced pressure and the crude was purified by column chromatography (EP/Ether: from 50/50 to 0/100). The desired product was obtained a white solid in a 1 : 0.4 mixture of separable diastereoisomers (65 mg, 0.29 mmol, 90 %). $^1$H NMR (δ, ppm) (CDCl$_3$, 400 MHz): 7.78 (s, 1H, C$_8$H); 7.11 (s, 1H, C$_5$H); 4.96 (dd, 1H, $J_1 = 4.6$ Hz, $J_2 = 11.3$ Hz, OC$_4$H); 3.89 (s, 3H, OC$_{10}$H$_3$); 2.54 (ddq, 1H, $J_1 = 4.3$ Hz, $J_2 = 6.7$ Hz, $J_3 = 13.4$ Hz, C$_2$H); 2.44 (ddd, 1H, $J_1 = 4.2$ Hz, $J_2 = 4.8$ Hz, $J_3 = 12.1$ Hz, C$_3$H$_2$); 2.20 (s, 3H, C$_{11}$H$_3$); 1.81 (ddd, 1H, $J_1 = 11.4$ Hz, $J_2 = 12.1$ Hz, $J_3 = 13.4$ Hz, C$_9$H$_3$); 1.26 (d, 3H, $J = 6.7$ Hz, C$_9$H$_3$).
\[ ^{13}\text{C NMR} (\delta, \text{ppm}) \text{ (CDCl}_3, \text{ 100.6 MHz}): \delta_{198.59} (\text{C}_1\text{O}); \delta_{162.39} (\text{C}_6); \delta_{147.08} (\text{C}_{6\text{a}}); \delta_{129.49} (\text{C}_8\text{H}); \delta_{126.68} (\text{C}_7); \delta_{123.75} (\text{C}_7\text{H}); \delta_{105.91} (\text{C}_6\text{H}); \delta_{68.34} (\text{OC}_4\text{H}); \delta_{55.59} (\text{OC}_{10}\text{H}_3); \delta_{42.32} (\text{C}_3\text{H}_2); \delta_{40.78} (\text{C}_2\text{H}); \delta_{15.85} (\text{C}_{11}\text{H}_3); \delta_{15.47} (\text{C}_9\text{H}_3). \]

\[ \text{IR} (\text{cm}^{-1}) \text{ (CCl}_4): \text{3597, 2933, 2859, 1683, 1607, 1267, 1247, 1148.} \]

\[ \text{HRMS (EI+) calcd for } \text{C}_{13}\text{H}_{16}\text{O}_3 \text{ 220.1099, found: 220.1091.} \]

Compound 9b: 4-hydroxy-6-methoxy-2,7-dimethyl-3,4-dihydro-2H-naphtalen-1-one

\[ ^{1}\text{H NMR} (\delta, \text{ppm}) \text{ (CDCl}_3, \text{ 400 MHz}): \delta_{7.79} (\text{s, 1H, C}_8\text{H}); \delta_{6.84} (\text{s, 1H, C}_5\text{H}); \delta_{4.93} (\text{bt, 1H, J = 4.2 Hz, O}_4\text{H}); \delta_{3.90} (\text{s, 3H, O}_10\text{H}_3); \delta_{3.01} (\text{ddq, 1H, J1 = 4.8 Hz, J2 = 7.0 Hz, J3 = 10.3 Hz, C}_2\text{H}); \delta_{2.29} (\text{ddd, 1H, J1 = 4.9 Hz, J3 = 13.6 Hz, C}_3\text{H}_2); \delta_{2.21} (\text{s, 3H, C}_{11}\text{H}_3); \delta_{2.13} (\text{ddd, 1H, J1 = 3.5 Hz, J2 = 10.3 Hz, J3 = 13.7 Hz, C}_3\text{H}_2); \delta_{1.25} (\text{d, 3H, J = 7.0 Hz, C}_9\text{H}_3). \]

\[ ^{13}\text{C NMR} (\delta, \text{ppm}) \text{ (CDCl}_3, \text{ 100.6 MHz}): \delta_{199.36} (\text{C}_1\text{O}); \delta_{162.33} (\text{C}_6); \delta_{143.99} (\text{C}_{6\text{a}}); \delta_{129.77} (\text{C}_7\text{H}); \delta_{127.69} (\text{C}_7\text{H}); \delta_{123.81} (\text{C}_7\text{H}); \delta_{108.32} (\text{C}_5\text{H}); \delta_{66.84} (\text{OC}_4\text{H}); \delta_{55.61} (\text{OC}_{10}\text{H}_3); \delta_{39.37} (\text{C}_3\text{H}_2); \delta_{36.80} (\text{C}_2\text{H}); \delta_{15.93} (\text{C}_{11}\text{H}_3); \delta_{15.46} (\text{C}_9\text{H}_3). \]

\[ \text{IR} (\text{cm}^{-1}) \text{ (CCl}_4): \text{3617, 2931, 2873, 1683, 1606, 1261, 1143.} \]

\[ \text{HRMS (EI+) calcd for } \text{C}_{13}\text{H}_{16}\text{O}_3 \text{ 220.1099, found: 220.1101.} \]

Compound 12: 2-chloro-N-methoxy-N-methylacetamide

A solution of N,O-Dimethylhydroxylamine hydrochloride (4.88 g, 50.0 mmol, 1.0 eq.) and triethylamine (15.2 mL, 110 mmol, 2.2 eq.) in distillated dichloroethane (200 mL) was cooled to 0°C under a nitrogen atmosphere and 2-chloropropionyl chloride (4.9 mL, 51.0 mmol, 1.02 eq.) was added dropwise. Then, the solution was stirred for 4 h at RT. Water was added to the reaction mixture which was extracted three times with DCM. The combined organic layers were washed with HCl (1M), NaHCO₃ (sat. aq.), dried over MgSO₄ and evaporated under reduced pressure (100 mbar at 40 °C). The desired product was obtained as an orange oil (6.64 g, 43.8 mmol, 87 %). \[ ^{1}\text{H NMR} (\delta, \text{ppm}) \text{ (CDCl}_3, \text{ 400 MHz): \delta_{4.95} – 4.82} (\text{m, 1H, C}_2\text{H}); \delta_{3.77} (\text{s, 3H, NC}_4\text{H}_3); \delta_{3.22} (\text{s, 3H, OC}_5\text{H}_3); \delta_{1.63} (\text{d, 3H, J = 6.8 Hz, C}_3\text{H}_2). \]

\[ ^{13}\text{C NMR} (\delta, \text{ppm}) \text{ (CDCl}_3, \text{ 100.6 MHz): \delta_{61.68} (\text{NC}_4\text{H}_3); \delta_{48.53} (\text{C}_3\text{H}); \delta_{32.42} (\text{OC}_5\text{H}_3); \delta_{20.73} \]
10

\( \text{IR (cm}^{-1}) \text{ (CCl}_4\text{): 2979, 2939, 1682, 1557, 1378, 1263. HRMS (EI+) calcd for: C}_{11}\text{H}_{13}\text{BrO}_2 \\
151.0400, \text{found: 151.0398.} \)

\[ \begin{array}{c}
\text{Compound 15: 2-chloro-1-(3-methoxy-4-methylphenyl)propan-1-one}
\end{array} \]

\( \text{Compound 12 (5.15 g, 25.9 mmol, 1.0 eq.) in distilled THF (260 mL) was cooled to -78 °C under a nitrogen atmosphere and n-BuLi (31.1 mmol, 1.2 eq.) was added dropwise. After 30 min, a solution of compound XX (5.49 g, 36.3 mmol, 1.4 eq.) in THF (20 mL) was added dropwise and the solution stirred for 1 h at -78 °C then 1 h at 0 °C. NH}_4\text{Cl (sat. aq.) and water were added, the water layer was extracted three times with diethyl ether, the organic layer was washed with NaCl (sat. aq.), dried over MgSO}_4\text{ and evaporated under reduced pressure. The crude was purified by column chromatography (EP/AcOEt: from 100/0 to 90/10). The desired product was obtained as white solid (4.15 g, 19.5 mmol, 75 %).} \)

\[ \begin{array}{c}
\text{\textsuperscript{1}H NMR (δ, ppm) (CDCl}_3\text{, 400 MHz): 7.51 (dd, 1H, J}_1\text{ = 1.5 Hz, J}_2\text{ = 7.7 Hz, C}_9\text{H); 7.48 (d, 1H, J = 1.5 Hz, C}_5\text{H); 7.23 (d, 1H, J = 7.7 Hz, C}_8\text{H); 5.26 (q, 1H, J = 6.7 Hz, C}_2\text{H); 3.89 (s, 3H, OC}_1\text{H}_3\text{); 2.28 (s, 3H, C}_1\text{H}_3\text{); 1.74 (d, 3H, J = 6.7 Hz, C}_3\text{H).} \)
\end{array} \]

\[ \begin{array}{c}
\text{\textsuperscript{13}C NMR (δ, ppm) (CDCl}_3\text{, 100.6 MHz): 193.34 (C}_1\text{O); 158.07 (OC}_4\text{); 134.00 (C}_4\text{); 133.06 (C}_7\text{); 130.47 (C}_8\text{H); 121.52 (C}_9\text{H); 109.43 (C}_5\text{H); 55.43 (OC}_6\text{H}_2\text{); 52.73 (C}_2\text{H); 20.16 (C}_3\text{H}_3\text{); 16.63 (C}_1\text{H}_3\text{). IR (cm}^{-1}) \text{ (CCl}_4\text{): 2936, 1689, 1410, 1268. HRMS (EI+) calcd for C}_{11}\text{H}_{13}\text{O}_2\text{Cl 212.0604, found: 212.0601.} \)
\end{array} \]

\[ \begin{array}{c}
\text{Compound 16: O-ethyl S-1-(3-methoxy-4-methylphenyl)-1-oxopropan-2-yl carbonodithioate}
\end{array} \]

\[ \begin{array}{c}
\text{Compound 15 (4.05 g, 19.0 mmol, 1.0 eq.) in acetone (38 mL) was cooled to 0 °C under a nitrogen atmosphere and potassium O-ethylxanthate (22.8 mmol, 1.2 eq.) was added portionwise. After 2 h at RT, the solvent was removed under reduced pressure and water was added to the residue which was extracted three times with DCM. The combined organic layers were dried over MgSO}_4\text{ and evaporated under reduced pressure. The crude was purified by column chromatography (EP/AcOEt:}
\end{array} \]
90/10). The desired product was obtained as slightly yellow solid (5.29 g, 17.8 mmol, 93%). $^1$H NMR (δ, ppm) (CDCl$_3$, 400 MHz): 7.54 (d, 1H, J = 7.7 Hz, C$_9$H); 7.46 (s, 1H, C$_{10}$H); 7.22 (d, 1H, J = 7.7 Hz, C$_{11}$H); 5.48 (q, 1H, J = 7.1 Hz, C$_2$H); 4.63 (q, 2H, J = 7.1 Hz, OC$_{13}$H$_2$); 3.87 (s, 3H, OC$_{10}$H$_3$); 2.27 (s, 3H, C$_{11}$H$_3$); 1.61 (d, 3H, J = 7.1 Hz, C$_3$H$_3$); 1.37 (t, 3H, J = 7.1 Hz, C$_{14}$H$_3$). $^{13}$C NMR (δ, ppm) (CDCl$_3$, 100.6 MHz): 213.23 (C$_{12}$S); 196.42 (C$_1$O); 158.01 (OC$_8$H$_6$); 133.91 (C$_{IV}$); 133.77 (C$_{IV}$); 130.55 (C$_8$H); 121.19 (C$_9$H); 109.15 (C$_5$H); 70.66 (OC$_{13}$H$_2$); 55.47 (OC$_{11}$H$_3$); 49.90 (C$_2$H); 17.21 (C$_3$H$_3$); 16.62 (C$_{11}$H$_3$); 13.72 (C$_{14}$H$_3$). IR (cm$^{-1}$) (CCl$_4$): 2982, 2959, 2935, 1681, 1227, 1112, 1055. HRMS (EI+) calcd for C$_{14}$H$_{18}$O$_3$S$_2$: 298.0697, found: 289.0689.

Compound 17: 1-(ethoxycarbonothioylthio)-4-(3-methoxy-4-methylphenyl)-3-methyl-4-oxobutyl pivalate

A stirred solution of xanthate 16 (1.00 g, 3.35 mmol, 1.0 eq.) and vinyl pivalate (860 mg, 6.71 mmol, 2.0 eq.) in ethyl acetate (3.4 mL) was refluxed for 10 minutes under a nitrogen atmosphere. DLP was then added in 5 mol% portions every 90 minutes until complete consumption of the starting material was observed, which took 10 mol% DLP. The reaction mixture was then cooled to room temperature and evaporated to dryness under reduced pressure. Purification by column chromatography (EP/AcOEt: from 100/0 to 96/4) yielded the desired product as a transparent oil in a 1 : 0.8 mixture of inseparable diastereoisomers (696 mg, 1.63 mmol, 48%). $^1$H NMR (δ, ppm) (CDCl$_3$, 400 MHz):

Diastereoisomer n°1: 7.45 – 7.40 (m, 1H, C$_{13}$H & C$_{17}$H); 7.20 (d, 1H, J = 7.5 Hz, C$_{18}$H); 6.67 (t, 1H, J = 6.7 Hz, SC$_{16}$H); 4.66– 4.57 (m, 2H, OC$_{18}$H$_2$); 3.89 (s, 3H, OC$_{12}$H$_3$); 3.60 (sextapp, 1H, J = 6.9 Hz, C$_2$H); 2.56 (ddd, 1H, J$_1$ = 7.1 Hz, J$_2$ = 7.1 Hz, J$_3$ = 14.3 Hz, C$_3$H$_3$); 2.26 (s, 3H, C$_{13}$H$_3$); 2.07 – 1.98 (m, 1H, C$_3$H$_2$); 1.40 (t, 3H, J = 7.1 Hz, C$_{19}$H$_3$); 1.26 (d, 3H, J = 7.0 Hz, C$_{14}$H$_3$); 1.12 (s, 9H, C$_{15}$(C$_{16}$H$_3$)$_3$). Diastereoisomer n°2: 7.45 – 7.40 (m, 1H, C$_{13}$H & C$_{17}$H); 7.19 (d, 1H, J = 7.5 Hz, C$_{18}$H); 6.64 (dd, 1H, J$_1$ = 5.8 Hz, J$_2$ = 8.2 Hz, SC$_{16}$H); 4.59– 4.44 (m, 2H, OC$_{18}$H$_2$); 3.88 (s, 3H, OC$_{12}$H$_3$); 3.60 (sextapp, 1H, J = 6.9 Hz, C$_2$H); 2.58 (ddd, 1H, J$_1$ = 6.8 Hz, J$_2$ = 8.3 Hz, J$_3$ = 14.6 Hz, C$_3$H$_3$); 2.26 (s, 3H, C$_{13}$H$_3$); 2.07 – 1.98 (m, 1H, C$_3$H$_2$); 1.34 (t, 3H, J = 7.1 Hz, C$_{19}$H$_3$); 1.27 (d, 3H, J = 7.0 Hz, C$_{14}$H$_3$); 1.16 (s, 9H, C$_{15}$(C$_{16}$H$_3$)$_3$). $^{13}$C NMR (δ, ppm) (CDCl$_3$, 100.6 MHz): Diastereoisomer n°1: 210.03 (C$_{27}$S); 201.75 (C$_1$O); 176.63 (C$_{16}$O); 158.08 (OC$_6$); 134.85 (C$_3$); 133.20 (C$_6$); 130.43 (C$_{10}$H); 120.93 (C$_{11}$H); 109.03 (C$_7$H); 79.66 (SC$_{14}$H); 70.25 (OC$_{18}$H$_2$); 55.41
(OC₂H₅₃); 38.74 (C₁₅); 37.32 (C₅H₂); 37.16 (C₁₅(C₁₆H₃)₃); 26.87 (C₁₅(C₁₆H₃)₃); 18.47 (C₇H₃); 16.52 (C₁₅H₃); 13.64 (C₁₅H₃). Diastereoisomer n°2: 209.93 (C₁₇S); 201.82 (C₁O); 176.63 (C₆O); 158.05 (OC₈H₂); 134.80 (C₉H₃); 133.12 (C₆H); 130.43 (C₁₀H); 120.91 (C₁₁H); 108.97 (C₇H); 79.10 (SC₄H); 70.15 (OC₁₈H₂); 55.41 (OC₁₂H₃); 38.82 (C₁₅); 37.74 (C₃H₂); 37.20 (C₂H₂); 26.87 (C₁₅(C₁₆H₃)₃); 18.07 (C₉H₃); 16.52 (C₁₅H₃); 13.53 (C₁₉H₃). IR (cm⁻¹) (CCl₄): 2975, 2936, 2873, 1739, 1682, 1228, 1136, 1046. HRMS (EI+) calcd for C₁₈H₂₅O₄ 305.1753, found: 305.1746 (loss of the O-ethylcarbonodithioate).

Compound 18: 6-methoxy-3,7-dimethyl-4-oxo-1,2,3,4-tetrahydronaphthalen-1-yl pivalate

A stirred solution of xanthate 17 (660 mg, 1.55 mmol, 1.0 eq) in ethyl acetate (16 mL) was refluxed for 10 minutes under a nitrogen atmosphere. DLP was then added in 20 mol% portions every 60 minutes until complete consumption of the starting material was observed Which toof 160 mol% of DLP. The reaction mixture was then cooled to room temperature and evaporated to dryness under reduced pressure. Purification by column chromatography (EP/AcOEt: 95/5) yielded the desired product as a white solid in a 1 : 0.5 mixture of inseparable diastereoisomers (301 mg, 0.99 mmol, 64 %). ¹H NMR (δ, ppm) (CDCl₃, 400 MHz): Diastereoisomer n°1: 7.45 (s, 1H, C₈H); 7.06 (s, 1H, C₅H); 6.13 (dd, 1H, J₁ = 4.9 Hz, J₂ = 10.4 Hz, OC₄H); 3.88 (s, 3H, OC₁₄H₃); 2.68 (ddq, 1H, J₁ = 4.4 Hz, J₂ = 6.7 Hz, J₃ = 13.4 Hz, ᵃC₂H); 2.46 (ddd, 1H, J₁ = 4.6 Hz, J₂ = 4.6 Hz, J₃ = 12.4 Hz, C₃H₂); 2.26 (s, 3H, C₁₃H₃); 1.88 (ddd, 1H, J₁ = 10.6 Hz, J₂ = 12.7 Hz, J₃ = 12.7 Hz, C₉H₃); 1.31 – 1.29 (m, 3H, C₉H₃); 1.30 (s, 9H, C₁₁(C₁₂H₃)₃). Diastereoisomer n°2: 7.45 (s, 1H, C₈H); 7.18 (s, 1H, C₅H); 6.01 (bt, 1H, J = 3.5 Hz, OC₄H); 3.89 (s, 3H, OC₁₄H₃); 3.03 – 2.93 (m, 1H, ᵃC₂H); 2.33 (ddd, 1H, J₁ = 4.2 Hz, J₂ = 4.2 Hz, J₃ = 13.9 Hz, ᵃC₃H₂); 2.25 (s, 3H, C₁₃H₃); 2.12 (ddd, 1H, J₁ = 3.2 Hz, J₂ = 12.1 Hz, J₃ = 14.2 Hz, C₇H₂); 1.28 (d, 3H, J = 7.2 Hz, C₉H₃); 1.17 (s, 9H, C₁₁(C₁₂H₃)₃). ¹³C NMR (δ, ppm) (CDCl₃, 100.6 MHz): Diastereoisomer n°1: 198.87 (C₁O); 178.17 (C₁₀O) 157.67 (C₈); 134.81 (C₆O); 133.86 (C₈); 130.70 (C₉O); 128.00 (C₈H); 106.95 (C₉O); 69.04 (OC₄H); 55.58 (OC₁₄H₂); 40.49 (C₉H); 38.92 (C₁₁); 37.60 (C₇H₂); 27.15 (3C, C₁₁(C₁₂H₃)₃); 16.87 (C₁₄H₂); 15.65 (C₉H₃). Diastereoisomer n°2: 198.79 (C₁O); 178.02 (C₁₀O) 158.41 (C₈); 133.88 (C₆); 132.42 (C₉O); 131.61 (C₇H₃); 131.20 (C₉O); 106.90 (C₈H); 68.08 (OC₄H); 55.56 (OC₁₄H₂); 38.97 (C₁₁); 36.94 (C₉H₃); 36.55 (C₉H₃); 27.07 (3C, C₁₁(C₁₂H₃)₃); 16.62 (C₁₄H₂); 15.43 (C₉H₃). IR (cm⁻¹) (CCl₄): 2969, 2934, 1730, 1687, 1147. HRMS (EI+) calcd for C₂₀H₂₄O₄ 304.1675, found: 304.1669.
Compound 19: 7-methoxy-2,6-dimethylnaphthalen-1-ol

Compound 18 (200 mg, 0.657 mmol, 1.0 eq.) and KOH (368 mg, 6.57 mmol, 10 eq.) in EtOH (6.6 mL) were stirred at 50 °C for 1 h. The reaction mixture was cooled to RT and HCl (1M) was added until the pH was neutral. The water layer was extracted three times with DCM, the combined organic layers were dried over MgSO₄ and the solvent evaporated under reduced pressure. The crude was purified by column chromatography (EP/AcOEt: from 80/20 to 50/50). The product was obtained as white solid (92 mg, 0.45 mmol, 69 %). ¹H NMR (δ, ppm) (CDCl₃, 400 MHz): 7.53 (s, 1H, C₅H); 7.38 (s, 1H, C₈H); 7.27 (d, 1H, J = 8.2 Hz, C₄H); 7.09 (d, 1H, J = 8.2 Hz, C₃H); 5.06 (bs, 1H, OH); 3.98 (s, 3H, OC₁₁H₃); 2.40 (s, 3H, C₉H₃ or C₁₀H₃); 2.39 (s, 3H, C₉H₃ or C₁₀H₃). ¹³C NMR (δ, ppm) (CDCl₃, 100.6 MHz): 156.63 (C₇O); 147.51 (C₁O); 128.80 (C₁₁O); 128.56 (C₁H); 127.82 (C₁₁H); 126.28 (C₉H); 123.88 (C₄); 119.21 (C₄H); 115.66 (C₂); 98.11 (C₆H); 55.28 (OC₁₁H₃); 16.76 (C₁₀H₃); 15.64 (C₉H₃). IR (cm⁻¹) (CCl₄): 36.17, 2955, 2926, 1742. HRMS (EI+) calcd for C₁₃H₁₄O₂ 202.0994, found: 202.0984.

Compound 21: 1-(ethoxycarbonothioylthio)-4-(3-methoxy-4-methylphenyl)-3-methyl-4-oxobutyl acetate

A stirred solution of xanthate 16 (596 mg, 2.00 mmol, 1.0 eq) and vinyl acetate (430 mg, 5.00 mmol, 2.5 eq) in ethyl acetate (2 mL) was refluxed for 10 minutes under a nitrogen atmosphere. DLP was then added in 5 mol% portions every 90 minutes until complete consumption of the starting material was observed, which took 17.5 mol% of DLP. The reaction mixture was then cooled to room temperature and evaporated to dryness under reduced pressure. Purification by column chromatography (EP/AcOEt: from 192/8 to 80/20) yielded the desired product as a transparent oil in a 1 : 1 mixture of inseparable diastereoisomers (550 mg, 1.43 mmol, 71 %). ¹H NMR (δ, ppm) (CDCl₃, 400 MHz): 7.45 – 7.43 (m, 3H, 2*C₇H & C₁₁H); 7.42 – 7.41 (m, 1H, C₁₁H); 7.21 (d, 1H, J = 8.5 Hz, C₁₅H);
7.20 (d, 1H, J = 7.4 Hz, C10H); 6.69 (t, 1H, J = 6.5 Hz, SC4H); 6.65 (dd 1H, J1 = 6.1 Hz, J2 = 8.1 Hz, SC4H); 4.67–4.43 (m, 4H, OC18H2); 3.89 (s, 6H, OC12H3); 3.66–3.57 (m, 2H, C2H); 2.64–2.55 (m, 1H, C3H2); 2.27 (s, 6H, C13H3); 2.07–1.98 (m, 1H, C3H2); 1.96 (s, 3H, C15H3); 1.95 (s, 3H, C15H3); 1.39 (t, 3H, J = 7.1 Hz, C19H3); 1.33 (t, 3H, J = 7.1 Hz, C19H3); 1.26 (d, 3H, J = 7.0 Hz, C5H3); 1.25 (d, 3H, J = 7.0 Hz, C5H3).

13C NMR (δ, ppm) (CDCl3, 100.6 MHz): 209.82 (2*C17S); 201.88 (2*C1O); 169.20 & 169.13 (C14O); 158.09 (2*OC8); 134.91 & 134.85 (C6); 133.25 & 133.13 (C9); 130.49 & 130.47 (C10H); 120.92 & 120.89 (C11H); 108.94 & 108.81 (C7H); 79.52 & 79.11 (SC4H); 70.29 & 79.19 (OC18H2); 55.42 (2*OC12H3); 37.83 & 37.38 (C3H2); 37.14 (2*C2H2); 20.76 & 20.71 (C13H3); 18.43 & 18.41 (C5H3); 16.53 (2*C13H3); 13.62 & 13.51 (2*C19H3).

IR (cm−1) (CCl4): 2961, 2936, 1754, 1682, 1223, 1113, 1048.

HRMS (EI+) calcd for C18H24O5S2 384.1065, found: not found.

Compound 22: 6-methoxy-3,7-dimethyl-4-oxo-1,2,3,4-tetrahydronaphthalen-1-yl acetate

A stirred solution of xanthate 21 (532 mg, 1.38 mmol, 1.0 eq) in ethyl acetate (14 mL) was refluxed for 10 minutes under a nitrogen atmosphere. DLP was then added in 20 mol% portions every 60 minutes until complete consumption of the starting material was observed, which took 160 mol% of DLP. The reaction mixture was then cooled to room temperature and evaporated to dryness under reduced pressure. Purification by column chromatography (EP/AcOEt: from 100/0 to 95/5) yielded the desired product as a white solid in a 1:0.6 mixture of inseparable diastereoisomers (220 mg, 0.84 mmol, 60%).

1H NMR (δ, ppm) (CDCl3, 400 MHz): Diastereoisomer n°1: 7.45 (s, 1H, C8H); 7.10 (s, 1H, C5H); 6.15 (dd, 1H, J1 = 4.9 Hz, J2 = 10.5 Hz, OC4H); 3.87 (s, 3H, OC13H3); 2.66 (ddq, 1H, J1 = 4.5 Hz, J2 = 6.7 Hz, J3 = 13.3 Hz, C2H); 2.50 (dt, 1H, J1 = 4.6 Hz, J2 = 12.4 Hz, C12H2); 2.27 (s, 3H, C12H3); 2.21 (s, 3H, C11H3); 1.90 (ddd, 1H, J1 = 10.6 Hz, J2 = 12.7 Hz, J3 = 12.7 Hz, C12H2); 1.29 (d, 3H, J = 6.8 Hz, C9H3). Diastereoisomer n°2: 7.44 (s, 1H, C8H); 7.22 (s, 1H, C5H); 6.05 (dd, 1H, J1 = 4.9 Hz, J2 = 10.5 Hz, OC4H); 3.88 (s, 3H, OC13H3); 3.01 (ddq, 1H, J1 = 4.7 Hz, J2 = 6.8 Hz, J3 = 12.4 Hz, C12H2); 2.36 (ddd, 1H, J1 = 3.7 Hz, J2 = 4.5 Hz, J3 = 14.2 Hz, C12H2); 2.25 (s, 3H, C12H3); 2.11 (ddd, 1H, J1 = 3.2 Hz, J2 = 12.5 Hz, J3 = 14.5 Hz, C12H2); 2.07 (s, 3H, C12H3); 1.27 (d, 3H, J = 6.8 Hz, C9H3).

13C NMR (δ, ppm) (CDCl3, 100.6 MHz): Diastereoisomer n°1: 198.77 (C1O); 170.81 (C10O) 157.72 (C7); 133.89 (CIV); 131.84 (CIV); 130.67 (CIV); 128.00 (CIV); 106.96 (C6H); 69.55 (OC4H); 55.56 (OC13H3); 40.47 (C10H); 37.70 (C12H2); 21.31 (C11H3);
16.75 (C_{12}H_{3}); 15.60 (C_{6}H_{3}). Diastereoisomer n°2: 199.63 (C_{7}O); 170.62 (C_{10}O) 158.52 (C_{7}); 134.32 (C_{4}); 132.09 (C_{6}); 131.33 (C_{6}); 128.00 (C_{8}H); 106.92 (C_{6}H); 69.40 (OC_{4}H); 55.56 (OC_{13}H_{3}); 36.78 (C_{2}H); 36.52 (C_{6}H_{3}); 21.38 (C_{11}H_{3}); 16.57 (C_{12}H_{3}); 15.28 (C_{9}H_{3}). IR (cm^{-1}) (CCl_{4}): 2963, 2933, 1744, 1687, 1234. HRMS (EI+) calcd for C_{15}H_{18}O_{4} 262.1205, found: 262.1202.

Compound 20a: 4-hydroxy-7-methoxy-2,6-dimethyl-3,4-dihydronaphthalen-1(2H)-one

Compound 22 (128 mg, 0.49 mmol, 1.0 eq.) and NaOH (40 mg, 1.0 mmol, 2 eq.) in EtOH (10 mL) were stirred at RT for 2 h. Water was added and the water layer was extracted three times with DCM. The combined organic layers were washed with NH_{4}Cl (aq. sat.), dried over MgSO_{4} and the solvent evaporated under reduced pressure. The crude was purified by column chromatography (pentane/diethyl ether: from 80/20 to 60/40). The product was obtained as a white solid in a 1:0.7 mixture of separable diastereoisomers (96 mg, 0.44 mmol, 89 %). ^{1}H RMN (δ, ppm) (CDCl_{3}, 400 MHz): 7.44 (s, 1H, C_{5}H); 7.21 (s, 1H, C_{6}H); 4.92 (tapp, 1H, J = 3.6 Hz, OC_{4}H); 3.88 (s, 3H, OC_{11}H_{3}); 3.10 (ddq, 1H, J_{1} = 4.7 Hz, J_{2} = 6.9 Hz, J_{3} = 11.5 Hz, C_{2}H); 2.31 (dtapp, 1H, J_{1} = 4.4 Hz, J_{2} = 13.7 Hz, C_{3}H_{2}); 2.27 (s, 3H, C_{10}H_{3}); 2.12 (ddd, 1H, J_{1} = 3.3 Hz, J_{2} = 11.4 Hz, J_{3} = 13.8 Hz, C_{3}H_{2}); 1.27 (d, 3H, J = 6.9 Hz, C_{9}H_{3}). ^{13}C RMN (δ, ppm) (CDCl_{3}, 100.6 MHz): 200.21 (C_{1}O); 158.21 (C_{7}); 136.11 (C_{4a}); 134.12 (C_{6}); 130.72 (C_{5}H); 128.05 (C_{8a}); 107.13 (C_{4}H); 66.49 (OC_{4}H); 55.65 (OC_{11}H_{3}); 39.36 (C_{2}H); 36.57 (C_{2}H); 16.67 (C_{10}H_{3}); 15.37 (C_{9}H_{3}). IR (cm^{-1}) (CCl_{4}): 3616, 2933, 1686, 1609, 1269. HRMS (EI+) calcd for C_{13}H_{16}O_{3} 220.1099, found: 220.1097.

Compound 20b: 4-hydroxy-7-methoxy-2,6-dimethyl-3,4-dihydronaphthalen-1(2H)-one

^{1}H RMN (δ, ppm) (CDCl_{3}, 400 MHz): 7.47 (s, 1H, C_{5}H); 7.42 (s, 1H, C_{6}H); 5.00 – 4.94 (m, 1H, OC_{4}H); 3.87 (s, 3H, OC_{11}H_{3}); 2.59 (ddq, 1H, J_{1} = 4.3 Hz, J_{2} = 6.7 Hz, J_{3} = 13.4 Hz, C_{2}H); 2.46 (ddd, 1H, J_{1} = 4.4 Hz,
$J_2 = 4.6$ Hz, $J_3 = 12.3$ Hz, $C_3H_2$); 2.28 (s, 3H, $C_{10}H_3$); 1.95 (bd, 1H, $J = 6.5$ Hz, OH); 1.80 (ddd, 1H, $J_1 = 11.4$ Hz, $J_2 = 12.2$ Hz, $J_3 = 13.4$ Hz, $C_3H_2$); 1.29 (d, 3H, $J = 6.7$ Hz, $C_9H_3$). $^{13}$C RMN ($\delta$, ppm) (CDCl$_3$, 100.6 MHz): 199.30 ($C_1$O); 157.45 ($C_7$); 138.96 ($C_{4a}$); 133.98 ($C_6$); 130.04 ($C_{8a}$); 127.99 ($C_5$H); 106.72 ($C_9$H); 67.99 (OC$_4$H); 55.55 (OC$_{11}$H$_3$); 42.39 ($C_3H_2$); 41.07 ($C_2$H); 16.76 ($C_{10}H_3$); 15.48 ($C_9H_3$). IR (cm$^{-1}$) (CCl$_4$): 3598, 2933, 1686, 1265. HRMS (El+) calcd for C$_{13}$H$_{16}$O$_3$ 220.1099, found: 220.1095.
Comparative table of spectroscopical data of original flossoinol, compound 9a and compound 9b

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<th>IH NMR</th>
<th>IR (cm⁻¹)</th>
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<td>7.83 (s, 1H, C₆H₃); 6.77 (s, 1H, C₆H₃); 4.33 (dd, 1H, J₁ = 5 Hz, J₂ = 12 Hz, OCH₃); 3.91 (s, 3H, OCH₃)</td>
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<td>3.17 (ddq, 1H, J₁ = 5 Hz, J₂ = 5 Hz, J₃ = 12 Hz, C₆H₅); 2.48 (dd, 1H, J₁ = 5 Hz, J₂ = 5 Hz, J₃ = 12 Hz, C₆H₅); 2.21 (s, 3H, C₆H₃); 1.78 (dd, 1H, J₁ = 12 Hz, J₂ = 12 Hz, C₆H₃); 1.45 (d, 3H, J = 5 Hz, C₆H₃)</td>
<td>3490, 2930, 1670, 1610, 1565, 1490, 1250</td>
<td>220 (38), 202 (62), 189 (6), 176 (100), 159 (40), 148 (85), 133 (37), 115 (24)</td>
</tr>
<tr>
<td><strong>Compound 9a</strong></td>
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<td></td>
<td>7.78 (s, 1H, C₆H₃); 7.11 (s, 1H, C₆H₃); 4.96 (dd, 1H, J₁ = 4.6 Hz, J₂ = 11.3 Hz, OCH₃); 3.89 (s, 3H, OCH₃)</td>
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<td>2.54 (ddq, 1H, J₁ = 4.3 Hz, J₂ = 6.7 Hz, J₃ = 13.4 Hz, C₆H₅); 2.44 (dd, 1H, J₁ = 4.3 Hz, J₂ = 4.8 Hz, J₃ = 12.1 Hz, C₆H₅); 2.20 (s, 3H, C₆H₃); 1.81 (dd, 1H, J₁ = 11.4 Hz, J₂ = 12.1 Hz, J₃ = 13.4 Hz, C₆H₃); 1.26 (d, 3H, J = 5.7 Hz, C₆H₃)</td>
<td>3597, 2933, 1683, 1607, 1562, 1497, 1257, 1247, 1148</td>
<td>220 (45), 202 (40), 191 (16), 178 (52), 162 (24), 159 (24), 149 (100), 115 (13)</td>
</tr>
<tr>
<td><strong>Compound 9b</strong></td>
<td></td>
<td></td>
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</tr>
<tr>
<td></td>
<td>7.79 (s, 1H, C₆H₃); 6.84 (s, 1H, C₆H₃); 4.98 (bt, 1H, J = 4.2 Hz, OCH₃); 3.90 (s, 3H, OCH₃)</td>
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<tr>
<td></td>
<td>3.01 (ddq, 1H, J₁ = 4.8 Hz, J₂ = 7.0 Hz, J₃ = 10.3 Hz, C₆H₅); 2.29 (dd, 1H, J₁ = 4.9 Hz, J₂ = 4.9 Hz, J₃ = 13.6 Hz, C₆H₅); 2.21 (s, 3H, C₆H₃); 2.13 (dd, 1H, J₁ = 3.5 Hz, J₂ = 10.3 Hz, J₃ = 13.7 Hz, C₆H₃); 1.25 (d, 3H, J = 7.0 Hz, C₆H₃)</td>
<td>3617, 2931, 1683, 1606, 1556, 1490, 1261, 1143</td>
<td>220 (49), 202 (25), 191 (13), 178 (61), 169 (16), 159 (25), 149 (100), 131 (29), 119 (34)</td>
</tr>
</tbody>
</table>

(a) Sun N., Chang C., Cassady J. M. *Phytochemistry* 1997, 25, 3051-3053

NMR 470 MHz in CDCl₃ using TMS as internal standard; IR: KBr, EIMS (70 eV)

(b) NMR 400 MHz in CDCl₃ using TMS as internal standard; IR: CCl₄, EIMS (70 eV)