Supporting Information-I

Two-step, High-yielding Total Synthesis of Antibiotic Pyrones

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General Experimental Procedures for the Total Synthesis of Bioactive 3,6-Dialkyl-4-Hydroxy-2*H*-Pyran-2-ones:

General Methods: The ^{1}H NMR and ^{13}C NMR spectra were recorded at 400, 500 MHz and 100, 125 MHz, respectively. The chemical shifts are reported in ppm downfield to TMS ($\delta = 0$) for ^{1}H NMR and relative to the central $CDCl_3$ resonance ($\delta = 77.0$) for ^{13}C NMR. In the ^{13}C NMR spectra, the nature of the carbons (C, CH, CH_2 or CH_3) was determined by recording the DEPT-135 experiment, and is given in parentheses. The coupling constants *J* are given in Hz. Column chromatography was performed using Acme's silica gel (particle size 0.063-0.200 mm). High-resolution mass spectra were recorded on micromass ESI-TOF MS. IR spectra were recorded on JASCO FT/IR-5300 and Thermo Nicolet FT/IR-5700. The X-ray diffraction measurements were carried out at 298 K on an automated Enraf-Nonious MACH 3 diffractometer using graphite monochromated, Mo-Kα ($\lambda = 0.71073$ Å) radiation with CAD4 software or the X-ray intensity data were measured at 298 K on a Bruker SMART APEX CCD area detector system equipped with a graphite monochromator and a Mo-Kα fine-focus sealed tube ($\lambda = 0.71073$ Å). For thin-layer chromatography (TLC), silica gel plates Merck 60 F254 were used and compounds were visualized by irradiation with UV light and/or by treatment with a solution of *p*-anisaldehyde (23 mL), conc. H_2SO_4 (35 mL), acetic acid (10 mL), and ethanol (900 mL) followed by heating.

Materials: All solvents and commercially available chemicals were used as received without further purification unless otherwise stated. Compound **1** was commercially purchased and used for the preparation of starting materials **3a** to **3l**.

Modified Procedure for the Preparation of Starting Materials 6-Alkylated-4-hydroxy-pyran-2-one 3a-3l (Procedure A): Starting materials **3a-3l** were prepared by using modified procedure reported by Hsung and co-workers.[1] 4-Hydroxy-6-methyl-2*H*-pyran-2-one **1** (0.63 g, 5 mmol, 1.0 equiv.) was added to an oven dried round bottom flask. To this flask dry THF (15 mL) and HMPA (2.5 mL) were added and the resulting solution was cooled to –78 °C; 1.6 M *n*-BuLi in hexanes (7.2 mL, 2.3 equiv.) was added dropwise. After stirring at –78 °C for 1 h, R-I/R-Br (2.0 equiv.) was added dropwise. The resulting mixture was warmed to room temperature and stirred for 15 h. The solution was carefully quenched with 3.0 M HCl with the final pH being ~ 2. After

partitioning, the aqueous layer was extracted with ethyl acetate (3 × 25 mL), washed with brine, and dried over Na_2SO_4. After concentrating under reduced pressure, the crude dark oil was purified via flash column chromatography (silica gel, gradient: 20-30% EtOAc–hexanes) to give the desired **3** as light-yellow solids (see Scheme 2).

Organocatalytic Reductive Alkylation of Alkyl Aldehydes 5 with 3 (Procedure B): To an ordinary glass vial equipped with a magnetic stirring bar were added 0.02 mmol of catalyst **4**, 0.24 mmol of aldehyde **5** and 1.0 mL of anhydrous DCM. Then, 0.22 mmol of Hantzsch ester **6** and 0.2 mmol of pyrone compound **3** were added sequentially to a well-stirred solution and the resulting mixture was allowed to stir for 1.0 h at 25 °C as mentioned in Table 1, Schemes 3-6, 9 and 11. The crude reaction mixture was directly loaded onto a silica gel column, and pure coupling products **7** were obtained in 80-97% yield (eluent: mixture of hexanes/ethyl acetate).

***C*-3 Alkylation Reaction of 3 with Paraformaldehyde 5h and Thiophenol 8 (Procedure C):** Compound **3** (0.5 mmol, 1.0 equiv.) in ethanol (1 mL) was slowly added into a stirred solution of paraformaldehyde **5h** (0.5 mmol), thiophenol **8** (1.5 mmol), acetic acid (40 mol%) and piperidine (24 mol%) in ethanol (1 mL) at 55 °C. The solution was allowed to stir for 6 h and upon completion the solvent is evaporated. The residue was purified by column chromatography to obtain product **9** in 75-90% yield (see Scheme 7).

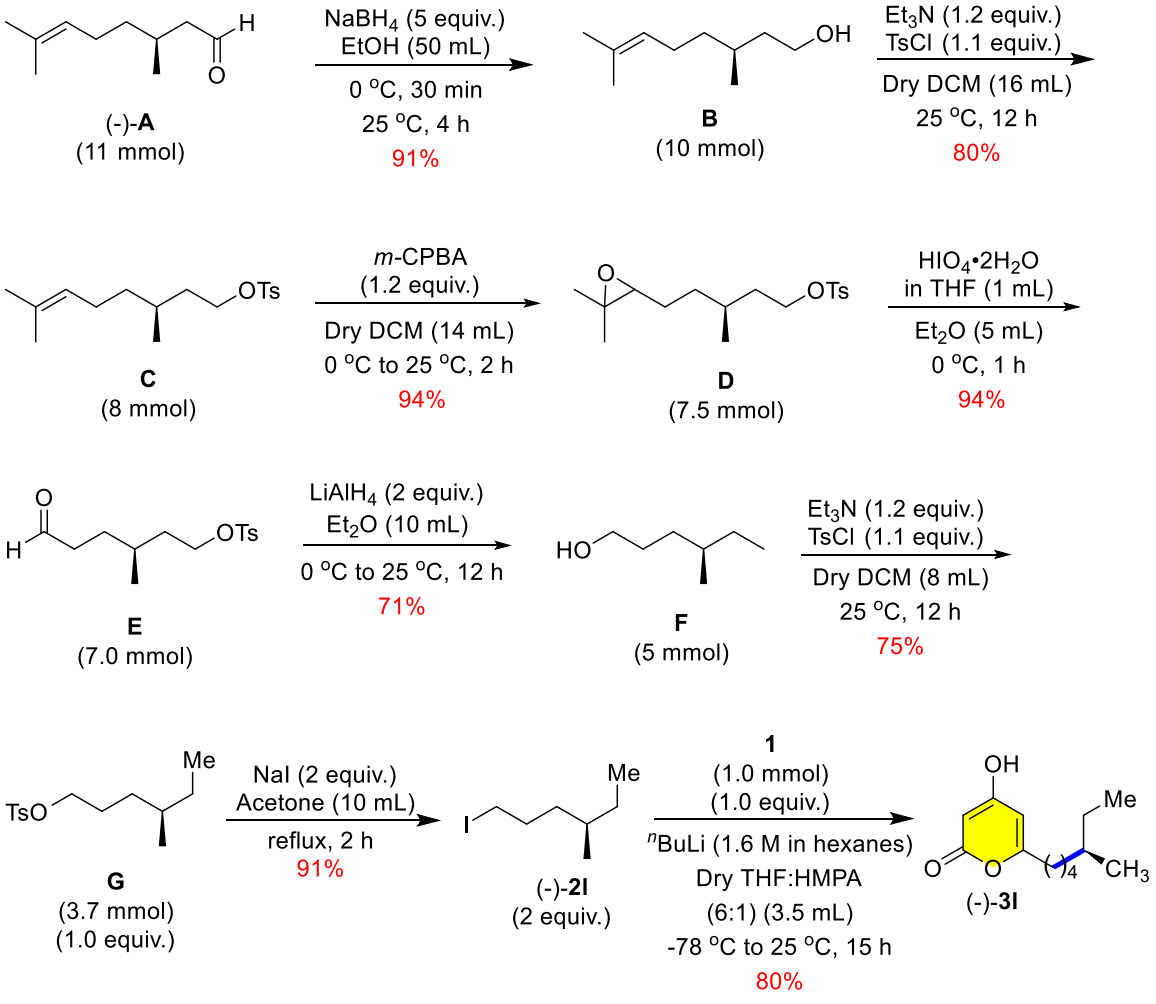
Synthesis of Violapyrones by Desulphurization of 9 (Procedure D): To a solution of **9** (0.2 mmol, 1.0 equiv.) in ethanol (1 mL) was added freshly prepared Raney-nickel (200 mg) and reaction was stirred for 1 h at 25 °C. After completion, reaction mixture was filtered through celite and evaporated to give crude mixture. This crude mixture was purified by column chromatography and product **7** obtained in 78-86% yield (see Schemes 8 and 9).

Acetylation of the Compound 7bc (Procedure E): To a solution of the product **7bc** (0.8 mmol, 1.0 equiv.) in CH_2Cl_2 (8 mL) was added NEt_3 (0.11 mL, 0.8 mmol) and acetic anhydride (0.11 mL, 1.2 mmol). The solution was allowed to stir at room temperature under nitrogen for 0.5 h, then the solution was diluted with dichloromethane and washed with 1N HCl (4 mL), saturated $NaHCO_3$ (4 mL) and brine (4 mL). The organic layer was dried over Na_2SO_4 and concentrated.

The crude oil was purified via flash chromatography (hexane/EtOAc 9:1) to yield **10bc** (93%) as a colorless oil (Scheme 10).

Methylation of Violapyrones 7 (Procedure F): To an ordinary glass vial equipped with a magnetic stirring bar was added **7** (0.1 mmol), in 0.5 mL of methanol. Then, the reaction mixture was cooled to 0 °C and 1.0 mmol in situ prepared ethereal diazomethane from *N*-methyl-*N*-nitroso urea was added and the resulting mixture was allowed to stir for 0.5 h. The solvent was evaporated under reduced pressure and the crude reaction mixture was directly loaded onto a silica gel column, and purified to obtain pure products **11/12** as pale-yellow liquids (eluent: mixture of hexanes/ethyl acetate) (Scheme 10).

Scheme S1. Synthesis of Chiral *C*-6 Alkylated Pyrone (-)-**3l** [1-3]



Discussion for Scheme S1: To synthesize the chiral (-)-violapyrone C, we have to obtain the corresponding chiral alkyl iodide compound (-)-**2l** for coupling with 4-hydroxy-6-methyl-2*H*-pyran-2-one **1**. For the synthesis of (-)-**2l** derivative we have to commence our total synthesis from the commercially available aldehyde (-)-citronellal **A** as a starting material and obtained the key intermediate **F** in about 5 steps by following the reported methodology by Mori and coworkers.[2]

In the first step, compound **A** is reduced by $NaBH_4$ to get compound **B**. The obtained alcohol is further tosylated to give compound **C**. And then epoxidation of compound **C** using *m*-CPBA was performed to get compound **D**, which on oxidative cleavage with $HIO_4{\cdot}2H_2O$ gave corresponding aldehyde **E**, which on double reduction with $LiAlH_4$ gave alcohol **F**. Further tosylation of alcohol **F** gave compound **G**. The halogenation of compound **G** by refluxing in acetone with NaI gave chiral alkyl iodide (-)-**2l**.[3]

The obtained chiral alkyl iodide (-)-**2l** is employed in *C*-7 alkylation with 6-methyl-4-hydroxy-pyrone-2-one (**1**) using ^{n}BuLi to obtain the compound (-)-**3l** by following the procedure A. An overall yield of 25% yield is obtained for 8 steps starting from compound (-)-**A** to compound (-)-**3l** (see Scheme S1).

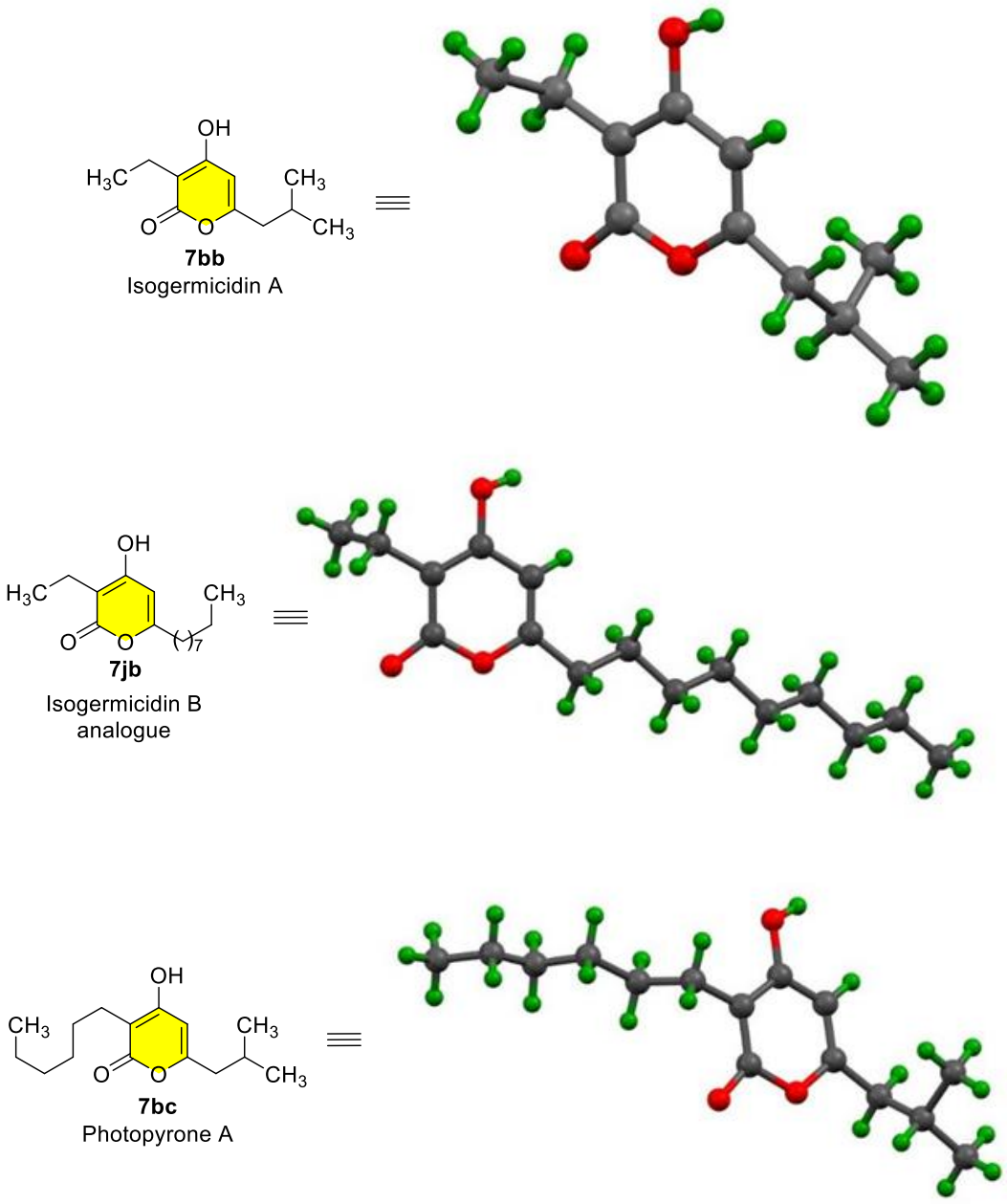
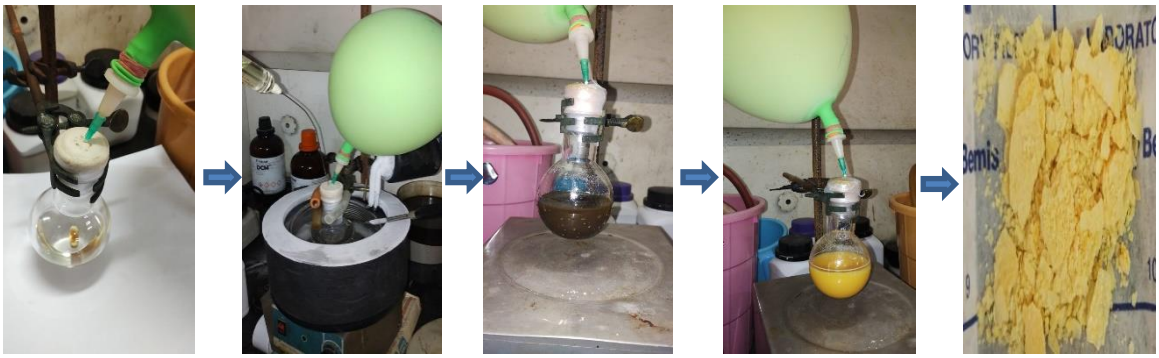


Figure S1. X-ray crystal structure of compounds isogermicidin A (**7bb**), isogermicidin B analogue (**7jb**) and photopyrone A (**7bc**).

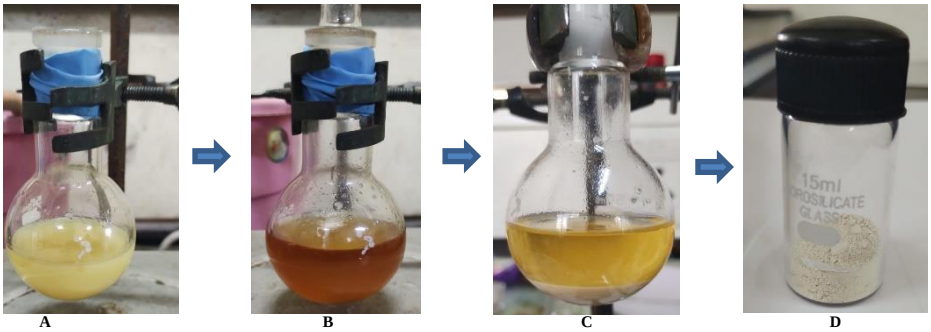
Step-1: C-7 Alkylation of Triacetate Lactone with Isopropyl Iodide using ^{n}BuLi



A **B** **C** **D** **E**

A: Triacetate lactone is dissolved in dry THF and HMPA at room temperature; **B**: Addition of ^{n}BuLi at -78^{o} C followed by stirring for 1.0 h and added isopropyl iodide; **C**: After addition of isopropyl iodide the reaction is brought to room temperature and allowed to stir for 15 h; **D**: After 15 h, the color change can be observed and reaction mixture is acidified with 2N HCl and then extracted with ethyl acetate and washed with brine; **E**: The column purification of the reaction mixture yielded C-7 alkylated compound **3b**.

Step-2: C-3 Alkylation using Three-component Reductive Alkylation

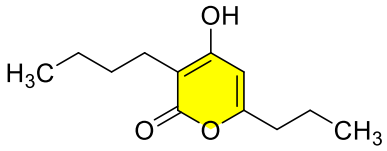


A **B** **C** **D**

A: Compound **3b** obtained in C-7 alkylation is added to a mixture of hexanal **5c**, proline **4a** and Hantzsch ester **6** in DCM at rt; **B**: Product formed after stirring the reaction mixture for 1.0 h at room temperature; **C**: Evaporation of the DCM solvent and addition of hexanes to the reaction mixture gave a solid precipitate; **D**: After filteration and washing with cold hexanes, product **7bc** is obtained as a fine off-white solid.

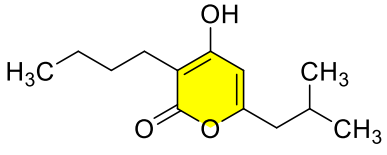
Figure S2: Pictorial representation of grams-scale reactions for **3b** and **7bc** synthesis.

3-Butyl-4-hydroxy-6-propyl-2*H*-pyran-2-one (**7aa**): The compound was prepared following the procedure **B** and purified by column chromatography using EtOAc/hexanes (1:9 to 2:8) and isolated as a white solid (Mp = 120-122 °C); Yield: 97% (41 mg); IR (Neat): ν_{max} 2957, 2929, 2871, 2647, 1627, 1566, 1406, 1252, 981 and 834 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 10.35 (1H, br s, O*H*), 6.22 (1H, s), 2.46 (2H, t, *J* = 7.5 Hz), 2.42 (2H, t, *J* = 7.5 Hz), 1.66 (2H, sext, *J* = 7.5 Hz), 1.49 (2H, quint, *J* = 8.0 Hz), 1.36 (2H, sext, *J* = 7.5 Hz), 0.95 (3H, t, *J* = 7.5 Hz), 0.91 (3H, t, *J* = 7.5 Hz); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz, DEPT-135): δ 168.4 (C), 167.2 (C), 163.3 (C), 103.4 (C), 101.0 (CH), 35.4 (CH_2), 30.2 (CH_2), 22.8 (CH_2), 22.7 (CH_2), 20.2 (CH_2), 13.9 (CH_3), 13.4 (CH_3); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{12}H_{19}O_3$ 211.1334; Found 211.1337.



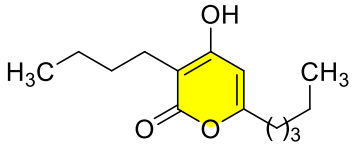
7aa

3-Butyl-4-hydroxy-6-isobutyl-2*H*-pyran-2-one (7ba): The compound was prepared following the procedure **B** and purified by column chromatography using EtOAc/hexanes (1:9 to 2:8) and isolated as a white solid (Mp = 123-125 °C); Yield: 96% (43 mg); IR (Neat): ν_{max} 2954, 1661, 1553, 1408, 1218, 998, and 782 cm^{-1} ;^{1}H NMR ($CDCl_3$, 500 MHz): δ 10.43 (1H, br s, O*H*), 6.20 (1H, s), 2.46 (2H, t, *J* = 8.0 Hz), 2.30 (2H, d, *J* = 7.0 Hz), 2.04 (1H, nonet, *J* = 7.0 Hz), 1.49 (2H, quint, *J* = 7.0 Hz), 1.36 (2H, sext, *J* = 7.0 Hz), 0.93 (6H, d, *J* = 7.0 Hz), 0.91 (3H, t, *J* = 7.0 Hz); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz, DEPT-135): δ 168.5 (C), 167.3 (C), 162.7 (C), 103.5 (C), 101.9 (CH), 42.6 (CH_2), 30.2 (CH_2), 26.9 (CH), 22.8 (CH_2), 22.7 (CH_2), 22.2 (2 x CH_3), 14.0 (CH_3); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{13}H_{21}O_3$ 225.1491; Found 225.1489.



7ba

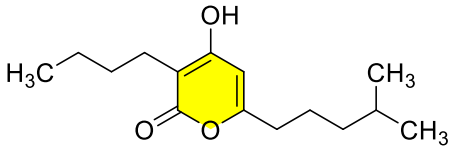
3-Butyl-4-hydroxy-6-pentyl-2*H*-pyran-2-one (7ca): The compound was prepared following the procedure **B** and purified by column chromatography using EtOAc/hexanes (1:9 to 2:8) and isolated as a white solid (Mp = 93-95 °C); Yield: 97% (46.5 mg); IR (Neat): ν_{max} 2954, 2924, 2858, 2662, 1631, 1569, 1434, 1405, 1245, 1126, 990, and 831 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 10.46 (1H, s), 6.22 (1H, s), 2.60-2.27 (4H, m), 1.63 (2H, quint, *J* = 7.5 Hz), 1.50 (2H, quint, *J* = 7.0 Hz), 1.36 (2H, sext, *J* = 7.5 Hz), 1.41-1.24 (4H, m), 0.95-0.82 (6H, m); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz, DEPT-135): δ 167.5 (C), 166.0 (C), 163.8 (C), 103.7 (C), 100.4 (CH), 33.6 (CH_2), 31.2 (CH_2), 30.3 (CH_2), 26.5 (CH_2), 22.9 (CH_2), 22.6 (CH_2), 22.2



7ca

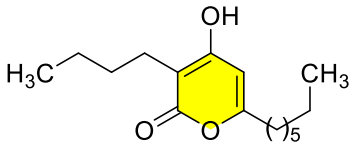
(CH_2), 13.8 (CH_3), 13.6 (CH_3); HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{14}H_{22}O_3Na$ 261.1467; Found 261.1467.

3-Butyl-4-hydroxy-6-(4-methylpentyl)-2*H*-pyran-2-one (7fa): The compound was prepared following the procedure **B** and purified by column chromatography using EtOAc/hexanes (1:9 to 2:8) and isolated as a white solid; Yield: 92% (46.5 mg); IR (Neat): ν_{max} 2953, 2928, 2870, 1631, 1570, 1406, 1290, 1125, and 758 cm^{-1} ;^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.50 (1H, br s, O*H*), 6.02 (1H, s), 2.49-2.37 (4H, m), 1.65-1.60 (2H, m), 1.54 (1H, nonet, *J* = 6.5 Hz), 1.49 (2H, quint, *J* = 6.5 Hz), 1.36 (2H, sext, *J* = 7.5 Hz), 1.20 (2H, q, *J* = 7.0 Hz), 0.91 (3H, t, *J* = 7.5 Hz), 0.87 (6H, d, *J* = 7.0 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz, DEPT-135): δ 168.5 (C), 167.4 (C), 163.5 (C), 103.4 (C), 100.9 (CH), 38.2 (CH_2), 33.7 (CH_2), 30.2 (CH_2), 27.7 (CH), 24.7 (CH_2), 22.8 (CH_2), 22.7 (CH_2), 22.4 (2 x CH_3), 14.0 (CH_3); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{15}H_{25}O_3$ 253.1804; Found 253.1803.



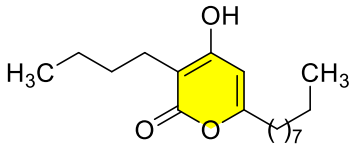
7fa

3-Butyl-6-heptyl-4-hydroxy-2*H*-pyran-2-one (7ga) : The compound was prepared following the procedure **B** and purified by column chromatography using EtOAc/hexanes (1:9 to 2:8) and isolated as a white solid (Mp = 65-67 °C); Yield: 97% (52 mg); IR (Neat): ν_{max} 2927, 2857, 1720, 1667, 1590, 1406, 1227, 1102, 1043, and 771 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 9.46 (1H, s), 6.14 (1H, s), 2.51-2.41 (4H, m), 1.62 (2H, quint, *J* = 7.5 Hz), 1.49 (2H, quint, *J* = 8.0 Hz), 1.36 (2H, sext, *J* = 7.5 Hz), 1.33-1.21 (8H, m), 0.91 (3H, t, *J* = 7.5 Hz), 0.87 (3H, t , *J* = 7.0 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz, DEPT-135): δ 168.2 (C), 167.0 (C), 163.6 (C), 103.4 (C), 100.8 (CH), 33.5 (CH_2), 31.6 (CH_2), 30.2 (CH_2), 28.96 (CH_2), 28.91 (CH_2), 26.8 (CH_2), 22.8 (CH_2), 22.7 (CH_2), 22.5 (CH_2), 13.99 (CH_3), 13.97 (CH_3); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{16}H_{27}O_3$ 267.1960; Found 267.1960.



7ga

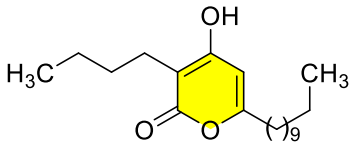
3-Butyl-4-hydroxy-6-nonyl-2*H*-pyran-2-one (**7ja**): The compound was prepared following the procedure **B** and purified by column chromatography using EtOAc/hexanes (1:9 to 2:8) and isolated as a white solid (Mp = 77-79 °C); Yield: 92% (54 mg); IR (Neat): ν_{max} 2954, 2924, 2854, 1663, 1573, 1407, 1249, 995, and 834 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 10.29 (1H, br s, O*H*), 6.21 (1H, s), 2.54-2.36 (4H, m), 1.62 (2H, quint, *J* = 7.5 Hz), 1.49 (2H,



7ja

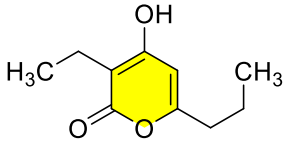
quint, *J* = 7.5 Hz), 1.41-1.22 (14H, m), 0.91 (3H, t, *J* = 7.5 Hz), 0.87 (3H, t, *J* = 7.0 Hz); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz, DEPT-135) δ 168.3 (C), 167.2 (C), 163.6 (C), 103.3 (C), 100.8 (CH), 33.5 (CH_2), 31.8 (CH_2), 30.2 (CH_2), 29.4 (CH_2), 29.3 (CH_2), 29.2 (CH_2), 29.0 (CH_2), 26.8 (CH_2), 22.8 (CH_2), 22.7 (CH_2), 22.6 (CH_2), 14.0 (CH_3), 13.9 (CH_3); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{18}H_{31}O_3$ 295.2273; Found 295.2274.

3-Butyl-4-hydroxy-6-undecyl-2*H*-pyran-2-one (**7ka**): The compound was prepared following the procedure **B** and purified by column chromatography using EtOAc/hexanes (1:9 to 2:8) and isolated as a white solid (Mp = 78-80 °C); Yield: 90% (58 mg); IR (Neat): ν_{max} 2953, 2921, 2852, 2680, 1661, 1631, 1569, 1406, 1244, 995, and 835 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 10.38 (1H, br s, O*H*), 6.22 (1H, s), 2.54-2.34 (4H, m), 1.62 (2H, quint, *J* = 7.0 Hz), 1.49 (2H, quint, *J* = 7.5 Hz), 1.41-1.21 (18H, m), 0.91 (3H, t, *J* = 7.0 Hz), 0.87 (3H, t, *J* = 7.0 Hz); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz, DEPT-135) δ 168.4 (C), 167.3 (C), 163.6 (C), 103.3 (C), 100.9 (CH), 33.5 (CH_2), 31.9 (CH_2), 30.2 (CH_2), 29.6 (CH_2), 29.58 (CH_2), 29.5 (CH_2), 29.32 (CH_2), 29.3 (CH_2), 29.0 (CH_2), 26.8 (CH_2), 22.8 (CH_2), 22.7 (CH_2), 22.6 (CH_2), 14.1 (CH_3), 13.9 (CH_3); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{20}H_{35}O_3$ 323.2586; Found 323.2584.



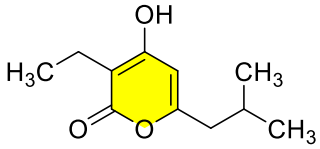
7ka

3-Ethyl-4-hydroxy-6-propyl-2*H*-pyran-2-one (or) Isogermicidin B (7ab): The compound was prepared following the procedure **B** and purified by column chromatography using EtOAc/hexanes (1:9 to 2:8) and isolated as a white solid (Mp = 96-98 °C); Yield: 96% (35 mg); IR (Neat): ν_{max} 2961, 2928, 2871, 2656, 1665, 1628, 1572, 1411, 1279, 975, and 835 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 9.85 (1H, br s, O*H*), 6.16 (1H, s), 2.49 (2H, q, *J* = 7.5 Hz), 2.42 (2H, t, *J* = 8.0 Hz), 1.66 (2H, sext, *J* = 7.5 Hz), 1.10 (3H, t, *J* = 7.5 Hz), 0.95 (3H, t, *J* = 7.5 Hz); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz, DEPT-135) δ 167.9 (C), 166.5 (C), 163.4 (C), 104.7 (C), 100.9 (CH), 35.4 (CH_2), 20.1 (CH_2), 16.4 (CH_2), 13.4 (CH_3), 12.5 (CH_3); HRMS (ESI-TOF) *m/z*: [M + H] Calcd for $C_{10}H_{15}O_3$ 183.1021; Found 183.1020.



7ab

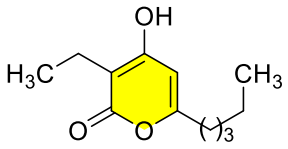
3-Ethyl-4-hydroxy-6-isobutyl-2*H*-pyran-2-one (or) Isogermicidin A (**7bb**): The compound was prepared following the procedure **B** and purified by column chromatography using EtOAc/hexanes (1:9 to 2:8) and isolated as a white solid (Mp = 111-113 °C); Yield: 93% (36.5 mg); IR (Neat): ν_{max} 2958, 2929, 2871, 2666, 1664, 1628, 1571, 1410, 1276, 984, 852, and



7bb

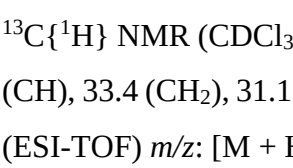
771 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 10.37 (1H, br s, O*H*), 6.19 (1H, s), 2.49 (2H, q, *J* = 7.5 Hz), 2.30 (2H, d, *J* = 7.5 Hz), 2.04 (1H, nonet, *J* = 7.0 Hz), 1.10 (3H, t, *J* = 7.5 Hz), 0.93 (6H, d, *J* = 7.0 Hz); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz, DEPT-135) δ 168.3 (C), 167.0 (C), 162.7 (C), 104.7 (C), 101.9 (CH), 42.6 (CH_2), 26.8 (CH), 22.2 (2 x CH_3), 16.4 (CH_2), 12.5 (CH_3); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{11}H_{17}O_3$ 197.1178; Found 197.1176.

3-Ethyl-4-hydroxy-6-pentyl-2*H*-pyran-2-one (**7cb**): The compound was prepared following the procedure **B** and purified by column chromatography using EtOAc/hexanes (1:9 to 2:8) and isolated as a white solid (Mp = 84-86 °C); Yield: 95% (40 mg); IR (Neat): ν_{max} 2963, 2927, 2870, 2647, 1661, 1626, 1571, 1401, 1277, 1168, 989, 853, and 728 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 10.61 (1H, br s, O*H*), 6.25 (1H, s), 2.50 (2H, q, *J* = 7.5 Hz), 2.44 (2H, t, *J* = 8.0 Hz), 1.63 (2H, quint, *J* = 7.5 Hz), 1.37-1.26 (4H, m), 1.10 (3H, t, *J* = 7.5 Hz), 0.88 (3H, t, *J* = 6.5 Hz); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz, DEPT-135) δ 168.5 (C), 167.4 (C), 163.6 (C), 104.7 (C), 101.1 (CH), 33.4 (CH_2), 31.1 (CH_2), 26.5 (CH_2), 22.3 (CH_2), 16.4 (CH_2), 13.8 (CH_3), 12.5 (CH_3); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{12}H_{19}O_3$ 211.1334; Found 211.1332.



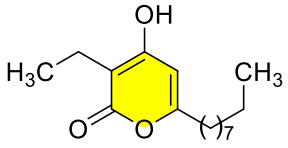
7cb

3-Ethyl-6-heptyl-4-hydroxy-2*H*-pyran-2-one (**7gb**): The compound was prepared following the procedure **B** and purified by column chromatography using EtOAc/hexanes (1:9 to 2:8) and isolated as a white solid (Mp = 74-76 °C); Yield: 95% (45.5 mg); IR (Neat): ν_{max} 2957, 2921, 2852, 2654, 1665, 1629, 1569, 1406, 1276, 1174, 948, 855, and 769 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 10.37 (1H, br s, O*H*), 6.22 (1H, s), 2.50 (2H, q, *J* = 7.5 Hz), 2.44 (2H, t, *J* = 7.5 Hz), 1.62 (2H, quint, *J* = 7.0 Hz), 1.36-1.22 (8H, m), 1.10 (3H, t, *J* = 7.5 Hz), 0.87 (3H, t, *J* = 7.0 Hz); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz, DEPT-135) δ 168.3 (C), 167.2 (C), 163.6 (C), 104.6 (C), 100.9 (CH), 33.5 (CH_2), 31.6 (CH_2), 28.95 (CH_2), 28.92 (CH_2), 26.8 (CH_2), 22.6 (CH_2), 16.4 (CH_2), 13.9 (CH_3), 12.5 (CH_3); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{14}H_{23}O_3$ 239.1647; Found 239.1648.



7gb

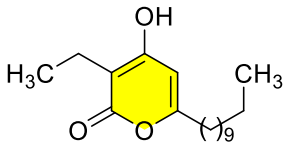
3-Ethyl-4-hydroxy-6-nonyl-2*H*-pyran-2-one (**7jb**): The compound was prepared following the procedure **B** and purified by column chromatography using EtOAc/hexanes (1:9 to 2:8) and isolated as a white solid (Mp = 80-82 °C); Yield: 90% (48 mg); IR (Neat): ν_{max} 2917, 2850, 2646, 1665, 1629, 1569, 1407, 1270, 1175, 947, 857, and 767 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz):



7jb

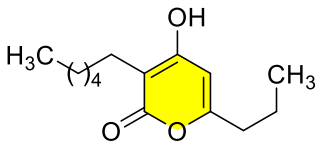
δ 10.49 (1H, br s, O*H*), 6.24 (1H, s), 2.50 (2H, q, *J* = 7.0 Hz), 2.44 (2H, t, *J* = 7.5 Hz), 1.62 (2H, quint, *J* = 7.5 Hz), 1.36-1.19 (12H, m), 1.10 (3H, t, *J* = 7.5 Hz), 0.87 (3H, t, *J* = 7.0 Hz); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz, DEPT-135) δ 168.3 (C), 167.2 (C), 163.6 (C), 104.6 (C), 100.9 (CH), 33.5 (CH_2), 31.8 (CH_2), 29.4 (CH_2), 29.26 (CH_2), 29.23 (CH_2), 29.0 (CH_2), 26.8 (CH_2), 22.6 (CH_2), 16.4 (CH_2), 14.0 (CH_3), 12.5 (CH_3); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{16}H_{27}O_3$ 267.1960; Found 267.1958.

3-Ethyl-4-hydroxy-6-undecyl-2*H*-pyran-2-one (**7kb**): The compound was prepared following the procedure **B** and purified by column chromatography using EtOAc/hexanes (1:9 to 2:8) and isolated as a white solid (Mp = 84-86 °C); Yield: 89% (52.5 mg); IR (Neat): ν_{max} 2916, 2849, 2645, 1665, 1628, 1569, 1406, 1274, 1175, 949, 861, and 767 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 10.60 (1H, br s, O*H*), 6.25 (1H, s), 2.50 (2H, q, *J* = 7.5 Hz), 2.44 (2H, t, *J* = 7.5 Hz), 1.62 (2H, quint, *J* = 7.0 Hz), 1.35-1.21 (16H, m), 1.11 (3H, t, *J* = 7.5 Hz), 0.87 (3H, t, *J* = 7.0 Hz); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz, DEPT-135) δ 168.4 (C), 167.3 (C), 163.7 (C), 104.6 (C), 101.0 (CH), 33.5 (CH_2), 31.9 (CH_2), 29.6 (2 x CH_2), 29.5 (CH_2), 29.33 (CH_2), 29.31 (CH_2), 29.0 (CH_2), 26.8 (CH_2), 22.7 (CH_2), 16.4 (CH_2), 14.1 (CH_3), 12.5 (CH_3); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{18}H_{31}O_3$ 295.2273; Found 295.2277.



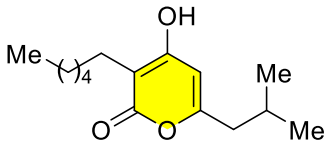
7kb

3-Hexyl-4-hydroxy-6-propyl-2*H*-pyran-2-one (**7ac**): The compound was prepared following the procedure **B** and purified by column chromatography using EtOAc/hexanes (1:9 to 2:8) and isolated as a white solid (Mp = 86-88 °C); Yield: 91% (43.5 mg); IR (Neat): ν_{max} 2957, 2925, 2854, 2646, 1672, 1571, 1408, 1261, 1100, 996, and 829 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 9.94 (1H, br s, O*H*), 6.17 (1H, s), 2.51-2.34 (4H, m), 1.66 (2H, sext, *J* = 7.5 Hz), 1.49 (2H, quint, *J* = 7.5 Hz), 1.38-1.25 (6H, m), 0.95 (3H, t, *J* = 7.5 Hz), 0.86 (3H, t, *J* = 6.5 Hz); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz, DEPT-135) δ 168.1 (C), 166.7 (C), 163.4 (C), 103.5 (C), 100.8 (CH), 35.4 (CH_2), 31.8 (CH_2), 29.3 (CH_2), 28.0 (CH_2), 23.1 (CH_2), 22.7 (CH_2), 20.2 (CH_2), 14.1 (CH_3), 13.5 (CH_3); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{14}H_{23}O_3$ 239.1647; Found 239.1648.



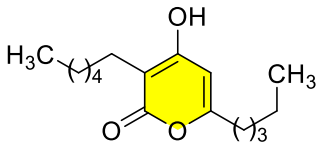
7ac

3-Hexyl-4-hydroxy-6-isobutyl-2*H*-pyran-2-one (or) Photopyrone A (7bc): The compound was prepared following the procedure **B** and purified by column chromatography using EtOAc/hexanes (1:9 to 2:8) and isolated as a white solid (Mp = 117-119 °C); Yield: 96% (48.5 mg); IR (Neat): ν_{max} 2952, 2921, 2855, 2648, 1626, 1558, 1404, 1261, 1128, 998, and 850 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 10.24 (1H, br s, O*H*), 6.18 (1H, s), 2.45 (2H, t, *J* = 8.0 Hz), 2.30 (2H, d, *J* = 7.0 Hz), 2.04 (1H, nonet, *J* = 7.0 Hz), 1.49 (2H, quint, *J* = 8.0 Hz), 1.38-1.24 (6H, m), 0.93 (6H, d, *J* = 6.5 Hz), 0.86 (3H, t, *J* = 7.0 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz, DEPT-135): δ 167.0 (C), 165.3 (C), 162.7 (C), 103.5 (C), 101.0 (CH), 42.7 (CH_2), 31.6 (CH_2), 29.1 (CH_2), 27.9 (CH_2), 26.7 (CH), 23.1 (CH_2) 22.4 (CH_2), 22.0 (2 x CH_3), 13.7 (CH_3); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{15}H_{25}O_3$ 253.1804; Found 253.1805.



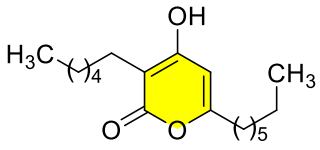
7bc

3-Hexyl-4-hydroxy-6-pentyl-2*H*-pyran-2-one (or) Pseudopyronine A (**7cc**): The compound was prepared following the procedure **B** and purified by column chromatography using EtOAc/hexanes (1:9 to 2:8) and isolated as a white solid (Mp = 86-88 °C); Yield: 94% (50 mg); IR (Neat): ν_{max} 2953, 2922, 2855, 2656, 1663, 1630, 1553, 1406, 1256, 1130, 992, and 855 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 10.07 (1H, br s, O*H*), 6.18 (1H, s), 2.49-2.39 (4H, m), 1.63 (2H, quint, *J* = 7.5 Hz), 1.49 (2H, quint, *J* = 8.0 Hz), 1.37-1.26 (10H, m), 0.88 (3H, t, *J* = 7.0 Hz), 0.86 (3H, t, *J* = 7.0 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz, DEPT-135) δ 168.2 (C), 166.9 (C), 163.6 (C), 103.4 (C), 100.8 (CH), 33.5 (CH_2), 31.8 (CH_2), 31.1 (CH_2), 29.3 (CH_2), 28.0 (CH_2), 26.5 (CH_2), 23.1 (CH_2), 22.7 (CH_2), 22.3 (CH_2), 14.1 (CH_3), 13.8 (CH_3); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{16}H_{27}O_3$ 267.1960; Found 267.1963.



7cc

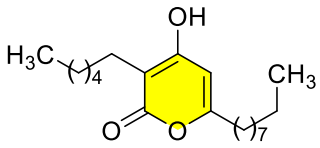
6-Heptyl-3-hexyl-4-hydroxy-2*H*-pyran-2-one (or) Pseudopyronine B (**7gc**): The compound was prepared following the procedure **B** and purified by column chromatography using EtOAc/hexanes (1:9 to 2:8) and isolated as a white solid (Mp = 70-72 °C); Yield: 96% (56.5 mg); IR (Neat): ν_{max} 2955, 2921, 2850, 2647, 1663, 1630, 1558, 1406, 1255, 1129, 997, and 857 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 10.43 (1H, br s, O*H*), 6.22 (1H, s), 2.49-2.38 (4H, m), 1.62 (2H, quint, *J* = 7.5 Hz), 1.50 (2H, quint, *J* = 8.0 Hz), 1.38-1.23 (14H, m), 0.91-0.83 (6H, m); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz, DEPT-135) δ 168.5 (C), 167.4 (C), 163.6 (C), 103.4 (C), 100.9 (CH), 33.5 (CH_2), 31.8 (CH_2), 31.6 (CH_2), 29.3 (CH_2), 29.0 (CH_2), 28.9 (CH_2), 28.1 (CH_2), 26.8



7gc

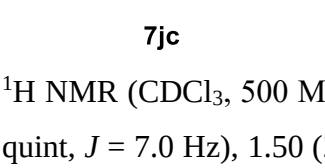
(CH_2), 23.1 (CH_2), 22.7 (CH_2), 22.6 (CH_2), 14.1 (CH_3), 14.0 (CH_3); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{18}H_{31}O_3$ 295.2273; Found 295.2270.

3-Hexyl-4-hydroxy-6-nonyl-2*H*-pyran-2-one (or) Pseudopyronine C (**7jc**): The compound was prepared following the procedure **B** and purified by column chromatography using EtOAc/hexanes (1:9 to 2:8) and isolated as a white solid (Mp = 70-72 °C); Yield: 92% (59 mg); IR (Neat): ν_{max} 2954, 2919, 2851, 2652, 1631, 1560, 1407, 1258, 1131, 998, and 857 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 10.31 (1H, br s, O*H*), 6.21 (1H, s), 2.51-2.37 (4H, m), 1.62 (2H, quint, *J* = 7.0 Hz), 1.50 (2H, quint, *J* = 7.5 Hz), 1.37-1.23 (18H, m), 0.91-0.83 (6H, m); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz, DEPT-135) δ 168.4 (C), 167.3 (C), 163.6 (C), 103.4 (C), 100.9 (CH), 33.5 (CH_2), 31.8 (2 x CH_2), 29.4 (CH_2), 29.36 (CH_2), 29.31 (CH_2), 29.3 (CH_2), 29.0 (CH_2), 28.1 (CH_2), 26.8 (CH_2), 23.1 (CH_2), 22.7 (CH_2), 22.6 (CH_2), 14.1 (CH_3), 14.07 (CH_3); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{20}H_{35}O_3$ 323.2586; Found 323.2588.



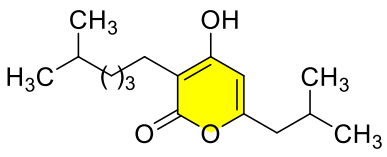
7jc

3-Hexyl-4-hydroxy-6-undecyl-2*H*-pyran-2-one (**7kc**): The compound was prepared following the procedure **B** and purified by column chromatography using EtOAc/hexanes (1:9 to 2:8) and isolated as a white solid (Mp = 71-73 °C); Yield: 90% (63 mg); IR (Neat): ν_{max} 2953, 2917, 2850, 2648, 1630, 1559, 1406, 1255, 1131, 998, and 835 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 9.79 (1H, br s, O*H*), 6.16 (1H, s), 2.49-2.39 (4H, m), 1.62 (2H, quint, *J* = 7.5 Hz), 1.50 (2H, quint, *J* = 7.5 Hz), 1.36-1.24 (22H, m), 0.91-0.83 (6H, m); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz, DEPT-135) δ 168.1 (C), 166.8 (C), 163.6 (C), 103.4 (C), 100.7 (CH), 33.5 (CH_2), 31.9 (CH_2), 31.8 (CH_2), 29.61 (CH_2), 29.60 (CH_2), 29.5 (CH_2), 29.34 (CH_2), 29.33 (CH_2), 29.31 (CH_2), 29.0 (CH_2), 28.0 (CH_2), 26.8 (CH_2), 23.1 (CH_2), 22.7 (2 x CH_2), 14.1 (2 x CH_3); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{22}H_{39}O_3$ 351.2899; Found 351.2897.



7kc

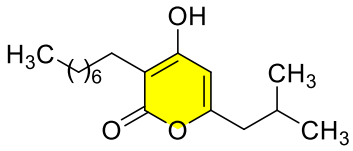
4-Hydroxy-6-isobutyl-3-(5-methylhexyl)-2*H*-pyran-2-one (or) Photopyrone B (7bd): The compound was prepared following the procedure **B** and purified by column chromatography using EtOAc/hexanes (1:9 to 2:8) and isolated as a white solid; Yield: 86% (46 mg); IR (Neat): ν_{max} 2954, 2929, 2865, 1665, 1572, 1408, 1260, 1101, and 801 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 9.30 (1H, br s, O*H*), 6.08 (1H, d, *J* = 7.5 Hz), 2.44 (2H, t, *J* = 8.0



7bd

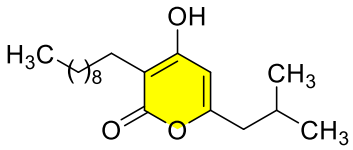
Hz), 2.29 (2H, d, J = 7.5 Hz), 2.05 (1H, nonet, J = 7.0 Hz), 1.55-1.45 (3H, m), 1.37-1.30 (2H, m), 1.17 (2H, q, J = 7.0 Hz), 0.93 (6H, d, J = 6.5 Hz), 0.85 (6H, d, J = 7.0 Hz); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz, DEPT-135): δ 167.7 (C), 166.0 (C), 162.7 (C), 103.4 (C), 101.4 (CH), 42.7 (CH_2), 38.9 (CH_2), 28.3 (CH_2), 27.9 (CH), 27.5 (CH_2), 26.8 (CH), 23.2 (CH_2), 22.6 (2 x CH_3), 22.2 (2 x CH_3); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{16}H_{27}O_3$ 267.1960; Found 267.1963.

4-Hydroxy-6-isobutyl-3-octyl-2*H*-pyran-2-one (or) Photopyrone C (7be): The compound was prepared following the procedure **B** and purified by column chromatography using EtOAc/hexanes (1:9 to 2:8) and isolated as a white solid (Mp = 108-110 °C); Yield: 92% (52 mg); IR (Neat): ν_{max} 2953, 2918, 2851, 2655, 1661, 1624, 1556, 1404, 1295, 1127, 1002, and 858 cm^{-1} ; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 10.16 (1H, br s, O*H*), 6.18 (1H, s), 2.45 (2H, t, J = 8.0 Hz), 2.30 (2H, d, J = 7.0 Hz), 2.04 (1H, nonet, J = 6.5 Hz), 1.50 (2H, quint, J = 7.5 Hz), 1.39-1.19 (10H, m), 0.93 (6H, d, J = 6.5 Hz), 0.86 (3H, t, J = 7.0 Hz); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz, DEPT-135): δ 168.4 (C), 167.0 (C), 162.6 (C), 103.5 (C), 101.9 (CH), 42.6 (CH_2), 31.9 (CH_2), 29.7 (CH_2), 29.6 (CH_2), 29.3 (CH_2), 28.1 (CH_2), 26.8 (CH), 23.1(CH_2), 22.6 (CH_2), 22.2 (2 x CH_3), 14.1 (CH_3); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{17}H_{29}O_3$ 281.2117; Found 281.2113.



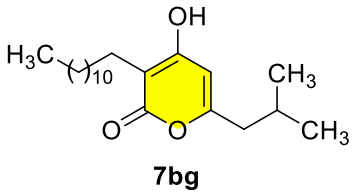
7be

3-Decyl-4-hydroxy-6-isobutyl-2*H*-pyran-2-one (or) Photopyrone E (7bf): The compound was prepared following the procedure **B** and purified by column chromatography using EtOAc/hexanes (1:9 to 2:8) and isolated as a white solid (Mp = 70-72 °C); Yield: 92% (57 mg); IR (Neat): ν_{max} 2952, 2918, 2850, 2662, 1625, 1555, 1404, 1256, 1104, 994, and 860 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 10.43 (1H, br s, O*H*), 6.20 (1H, s), 2.45 (2H, t, J = 8.0 Hz), 2.30 (2H, d, J = 7.0 Hz), 2.03 (1H, nonet, J = 7.0 Hz), 1.50 (2H, quint, J = 8.0 Hz), 1.40-1.21 (14H, m), 0.93 (6H, d, J = 6.5 Hz), 0.85 (3H, t, J = 7.0 Hz); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz, DEPT-135): δ 168.5 (C), 167.2 (C), 162.6 (C), 103.5 (C), 102.0 (CH), 42.6 (CH_2), 31.9 (CH_2), 29.75 (CH_2), 29.73 (CH_2), 29.7 (CH_2), 29.67 (CH_2), 29.3 (CH_2), 28.1 (CH_2), 26.8 (CH), 23.1 (CH_2), 22.7 (CH_2), 22.2 (2 x CH_3), 14.1 (CH_3); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{19}H_{33}O_3$ 309.2430; Found 309.2426.



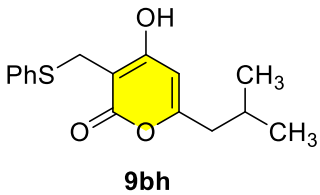
7bf

3-Dodecyl-4-hydroxy-6-isobutyl-2*H*-pyran-2-one (or) Photopyrone G (7bg): The compound was prepared following the procedure **B** and purified by column chromatography using EtOAc/hexanes (1:9 to 2:8) and isolated as a white solid (Mp = 65-67 °C); Yield: 90% (60 mg); IR (Neat): ν_{max} 2925, 2853, 1721, 1594, 1441, 1370, 1283, 1252, 1229, 1103, 1044, and 772 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 10.52 (1H, br s, O*H*), 6.21 (1H, s), 2.45 (2H, t, *J* = 7.5 Hz), 2.30 (2H, d, *J* = 7.5 Hz), 2.04 (1H, nonet, *J* = 7.0 Hz), 1.50 (2H, quint, *J* = 8.0 Hz), 1.38-1.21 (18H, m), 0.93 (6H, d, *J* = 6.5 Hz), 0.87 (3H, t, *J* = 7.0 Hz); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz, DEPT-135): δ 168.5 (C), 167.3 (C), 162.6 (C), 103.5 (C), 102.0 (CH), 42.6 (CH_2), 31.9 (CH_2), 29.8 (4 x CH_2), 29.7 (2 x CH_2), 29.4 (CH_2), 28.1 (CH_2), 26.9 (CH), 23.1 (CH_2), 22.7 (CH_2), 22.2 (2 x CH_3), 14.1(CH_3); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{21}H_{37}O_3$ 337.2743; Found 337.2739.



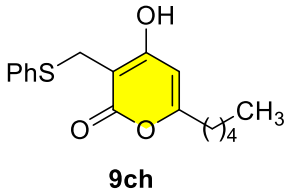
7bg

4-hydroxy-6-isobutyl-3-((phenylthio)methyl)-2*H*-pyran-2-one (**9bh**): The compound was prepared following the procedure **C** and purified by column chromatography using EtOAc/hexanes (1:9 to 2:8) and isolated as a white solid (Mp = 139-141 °C); Yield: 76% (110 mg); IR (Neat): ν_{max} 3062, 2956, 2869, 2645, 1626, 1567, 1409, 1260, 1139, 995, and 861 cm^{-1}; ^{1}H NMR (CD_3OD, 500 MHz): δ 7.41 (2H, dd, *J* = 8.5, 1.0 Hz), 7.24 (2H, t, *J* = 8.0 Hz), 7.18 (1H, t, *J* = 7.5 Hz), 5.94 (1H, s), 3.93 (2H, s, C*H*$_2$), 2.33 (2H, d, *J* = 7.0 Hz), 2.03 (1H, nonet, *J* = 7.0 Hz), 0.95 (6H, d, *J* = 7.0 Hz); $^{13}C\{^{1}H\}$ NMR (CD_3OD, 125 MHz, DEPT-135) δ 168.9 (C), 167.6 (C), 165.8 (C), 137.9 (C), 132.3 (2 x CH), 129.8 (2 x CH), 127.6 (CH), 101.9 (CH), 100.3 (C), 43.6 (CH_2), 28.9 (CH_2), 28.3 (CH), 22.6 (2 x CH_3); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{16}H_{19}O_3S$ 291.1055; Found 291.1057.



9bh

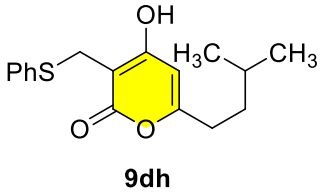
4-Hydroxy-6-pentyl-3-((phenylthio)methyl)-2*H*-pyran-2-one (**9ch**): The compound was prepared following the procedure **C** and purified by column chromatography using EtOAc/hexanes (1:9 to 2:8) and isolated as a white solid (Mp = 140-142 °C); Yield: 82% (125 mg); IR (Neat): ν_{max} 2952, 2926, 2867, 2576, 1622, 1550, 1411, 1253, 1185, 993, and 874 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 10.29 (1H, br s, O*H*), 7.39 (2H, d, *J* = 8.0 Hz), 7.24 (2H, t, *J* = 8.0 Hz), 7.16 (1H, t, *J* = 7.5 Hz), 6.15 (1H, s), 4.06 (2H, s, C*H*$_2$), 2.39 (2H, t, *J* = 8.0 Hz), 1.59 (2H, quint, *J* = 7.5 Hz), 1.33-1.23 (4H, m), 0.86 (3H, t, *J* = 7.0 Hz); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz,



9ch

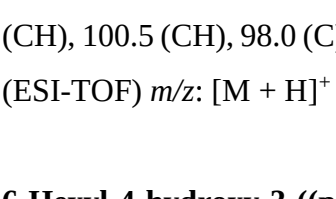
DEPT-135) δ 168.4 (C), 166.7 (C), 165.4 (C), 135.5 (C), 129.8 (2 x CH), 128.8 (2 x CH), 126.4 (CH), 100.7 (CH), 98.3 (C), 33.5 (CH_2), 31.0 (CH_2), 27.7 (CH_2), 26.3 (CH_2), 22.2 (CH_2), 13.8 (CH_3); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{17}H_{21}O_3S$ 305.1211; Found 305.1212.

4-Hydroxy-6-isopentyl-3-((phenylthio)methyl)-2*H*-pyran-2-one (9dh): The compound was prepared following the procedure **C** and purified by column chromatography using EtOAc/hexanes (1:9 to 2:8) and isolated as a white solid; Yield: 80% (122 mg); IR (Neat): ν_{max} 2955, 2929, 2868, 2626, 1626, 1556, 1432, 1412, 1260, 1182, 990, and 733 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 8.49 (1H, br s, O*H*), 7.38 (2H, td, *J* = 8.5, 1.5 Hz), 7.28 (2H, tt, *J* = 7.5, 1.5 Hz), 7.22 (1H, tt, *J* = 8.5, 1.0 Hz), 5.80 (1H, s), 4.12 (2H, s, C*H*$_2$), 2.40 (2H, t, *J* = 8.0 Hz), 1.56-1.52 (1H, m), 1.51-1.46 (2H, m), 0.89 (6H, d, *J* = 6.5 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz, DEPT-135): δ 168.2 (C), 166.3 (C), 165.6 (C), 134.9 (C), 129.9 (2 x CH), 128.9 (2 x CH), 126.6 (CH), 100.5 (CH), 98.0 (C), 35.5 (CH_2), 31.5 (CH_2), 27.8 (CH_2), 27.5 (CH), 22.2 (2 x CH_3); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{17}H_{21}O_3S$ 305.1211; Found 305.1211.



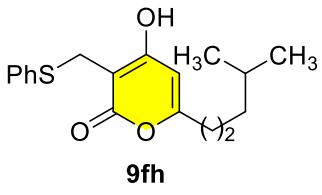
9dh

6-Hexyl-4-hydroxy-3-((phenylthio)methyl)-2*H*-pyran-2-one (**9eh**): The compound was prepared following the procedure **C** and purified by column chromatography using EtOAc/hexanes (1:9 to 2:8) and isolated as a white solid (Mp = 132-134 °C); Yield: 90% (143 mg); IR (Neat): ν_{max} 2925, 2855, 2643, 1623, 1553, 1409, 1262, 1184, 996, and 732 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 9.79 (1H, br s, O*H*), 7.39 (2H, dd, *J* = 8.0, 1.5 Hz), 7.25 (2H, t, *J* = 8.0 Hz), 7.17 (1H, t, *J* = 8.0 Hz), 6.05 (1H, s), 4.08 (2H, s, C*H*$_2$), 2.39 (2H, t, *J* = 7.5 Hz), 1.58 (2H, quint, *J* = 8.0 Hz), 1.32-1.24 (6H, m), 0.86 (3H, t, *J* = 7.0 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz, DEPT-135) δ 168.3 (C), 166.6 (C), 165.4 (C), 135.3 (C), 129.8 (2 x CH), 128.8 (2 x CH), 126.5 (CH), 100.7 (CH), 98.2 (C), 33.5 (CH_2), 31.3 (CH_2), 28.6 (CH_2), 27.7 (CH_2), 26.6 (CH_2), 22.4 (CH_2), 13.9 (CH_3); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{18}H_{23}O_3S$ 319.1368; Found 319.1366.



9eh

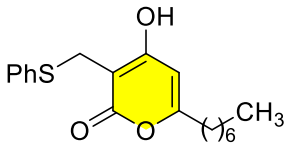
4-Hydroxy-6-(4-methylpentyl)-3-((phenylthio)methyl)-2*H*-pyran-2-one (9fh): The compound was prepared following the procedure **C** and purified by column chromatography using EtOAc/hexanes (1:9 to 2:8) and isolated as a white solid; Yield: 89% (142 mg); IR (Neat): ν_{max} 2958, 2919, 2846, 1675, 1588, 1464, 1419, and 1255 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz):



9fh

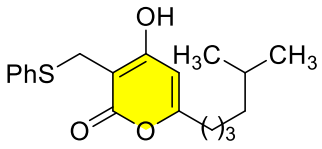
δ 9.02 (1H, br s, O*H*), 7.39 (2H, td, *J* = 8.5, 1.5 Hz), 7.31-7.24 (2H, m), 7.20 (1H, tt, *J* = 8.0, 2.0 Hz), 5.90 (1H, s), 4.10 (2H, s, CH_2), 2.38 (2H, t, *J* = 8.0 Hz), 1.65-1.57 (2H, m), 1.52 (1H, nonet, *J* = 7.0 Hz), 1.17 (2H, q, *J* = 6.5 Hz), 0.86 (6H, d, *J* = 7.0 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz, DEPT-135): δ 167.7 (C), 165.5 (2 x C), 133.8 (C), 130.0 (2 x CH), 129.1 (2 x CH), 127.1 (CH), 100.3 (CH), 97.4 (C), 38.1 (CH_2), 33.8 (CH_2), 28.1 (CH_2), 27.7 (CH), 24.5 (CH_2), 22.4 (2 x CH_3); HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{18}H_{22}O_3SNa$ 341.1187; Found 341.1185.

6-Heptyl-4-hydroxy-3-((phenylthio)methyl)-2*H*-pyran-2-one (**9gh**): The compound was prepared following the procedure **C** and purified by column chromatography using EtOAc/hexanes (1:9 to 2:8) and isolated as a white solid (Mp = 121-123 °C); Yield: 78% (130 mg); IR (Neat): ν_{max} 3056, 2924, 2854, 2580, 1624, 1550, 1409, 1249, 1183, 993, and 732 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 9.99 (1H, br s, O*H*), 7.39 (2H, dd, *J* = 9.5, 1.5 Hz), 7.24 (2H, t, *J* = 7.5 Hz), 7.16 (1H, t, *J* = 7.5 Hz), 6.09 (1H, s), 4.07 (2H, s, CH_2), 2.39 (2H, t, *J* = 8.0 Hz), 1.58 (2H, quint, *J* = 7.0 Hz), 1.31-1.21 (8H, m), 0.86 (3H, t, *J* = 7.5 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz, DEPT-135) δ 168.3 (C), 166.5 (C), 165.4 (C), 135.2 (C), 129.8 (2 x CH), 128.8 (2 x CH), 126.5 (CH), 100.6 (CH), 98.1 (C), 33.5 (CH_2), 31.6 (CH_2), 28.9 (2 x CH_2), 27.7 (CH_2), 26.7 (CH_2), 22.5 (CH_2), 14.0 (CH_3); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{19}H_{25}O_3S$ 333.1524; Found 333.1523.



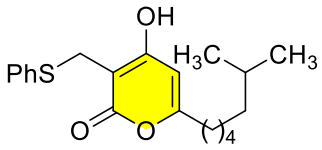
9gh

4-Hydroxy-6-(5-methylhexyl)-3-((phenylthio)methyl)-2*H*-pyran-2-one (9hh): The compound was prepared following the procedure **C** and purified by column chromatography using EtOAc/hexanes (1:9 to 2:8) and isolated as a white solid; Yield: 80% (133 mg); IR (Neat): ν_{max} 2954, 2924, 2865, 2591, 1622, 1551,1431, 1408, 1249, 1183, 989, and 733 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 9.03 (1H, br s, O*H*), 7.39 (2H, d, *J* = 7.0 Hz), 7.29-7.25 (2H, m), 7.20 (1H, t, *J* = 8.0 Hz), 5.90 (1H, s), 4.10 (2H, s, CH_2), 2.40 (2H, t, *J* = 7.5 Hz), 1.59 (2H, quint, *J* = 7.5 Hz), 1.50 (1H, nonet, *J* = 6.5 Hz), 1.28 (2H, quint, *J* = 7.5 Hz), 1.15 (2H, q, *J* = 7.0 Hz), 0.85 (6H, d, *J* = 7.0 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz, DEPT-135): δ 168.2 (C), 166.4 (C), 165.4 (C), 135.1 (C), 129.9 (2 x CH), 128.9 (2 x CH), 126.6 (CH), 100.6 (CH), 98.1 (C), 38.5 (CH_2), 33.6 (CH_2), 27.8 (CH_2), 27.78 (CH), 26.9 (CH_2), 26.7 (CH_2), 22.5 (2 x CH_3); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{19}H_{25}O_3S$ 333.1524; Found 333.1526.



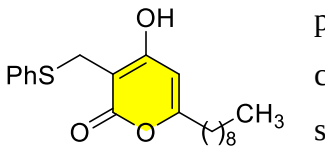
9hh

4-Hydroxy-6-(6-methylheptyl)-3-((phenylthio)methyl)-2*H*-pyran-2-one (9ih): The compound was prepared following the procedure **C** and purified by column chromatography using EtOAc/hexanes (1:9 to 2:8) and isolated as a white solid; Yield: 75% (130 mg); IR (Neat): ν_{max} 2957, 2923, 2857, 1721, 1677, 1581, 1462, and 1366 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.40 (1H, br s, O*H*), 7.42-7.34 (2H, m), 7.32-7.27 (2H, m), 7.23 (1H, tt, *J* = 8.0, 2.0 Hz), 5.78 (1H, s), 4.13 (2H, s, C*H*$_2$), 2.39 (2H, t, *J* = 7.5 Hz), 1.65-1.60 (2H, m), 1.48 (1H, nonet, *J* = 6.5 Hz) 1.27 (4H, quint, *J* = 3.5 Hz), 1.14 (2H, q, *J* = 7.0 Hz), 0.86 (6H, d, *J* = 6.5 Hz); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz, DEPT-135): δ 168.2 (C), 167.4 (C), 165.4 (C), 135.4 (C), 129.8 (2 x CH), 128.8 (2 x CH), 126.5 (CH), 100.6 (CH), 98.2 (C), 38.7 (CH_2), 33.6 (CH_2), 29.2 (CH_2), 27.86 (CH), 27.8 (CH_2), 26.9 (CH_2), 26.7 (CH_2), 22.5 (2 x CH_3); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{20}H_{27}O_3S$ 347.1681; Found 347.1680.



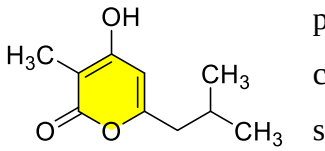
9ih

4-Hydroxy-6-nonyl-3-((phenylthio)methyl)-2*H*-pyran-2-one (**9jh**): The compound was prepared following the procedure **C** and purified by column chromatography using EtOAc/hexanes (1:9 to 2:8) and isolated as a white solid (Mp = 107-109 °C); Yield: 76% (137 mg); IR (Neat): ν_{max} 2954, 2922, 2852, 2591, 1626, 1550, 1407, 1252, 1184, 998, and 732 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 9.98 (1H, br s, O*H*), 7.39 (2H, dd, *J* = 8.0, 1.0 Hz), 7.24 (2H, t, *J* = 8.0 Hz), 7.16 (1H, t, *J* = 7.5 Hz), 6.09 (1H, s), 4.07 (2H, s, C*H*$_2$), 2.39 (2H, t, *J* = 8.0 Hz), 1.57 (2H, quint, *J* = 7.0 Hz), 1.31-1.21 (12H, m), 0.87 (3H, t, *J* = 7.0 Hz); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz, DEPT-135) δ 168.2 (C), 166.3 (C), 165.5 (C), 134.9 (C), 129.9 (2 x CH), 128.9 (2 x CH), 126.6 (CH), 100.6 (CH), 98.0 (C), 33.6 (CH_2), 31.8 (CH_2), 29.4 (CH_2), 29.2 (2 x CH_2), 28.9 (CH_2), 27.9 (CH_2), 26.7 (CH_2), 22.7 (CH_2), 14.1 (CH_3); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{21}H_{29}O_3S$ 361.1837; Found 361.1836.



9jh

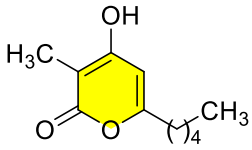
4-Hydroxy-6-isobutyl-3-methyl-2*H*-pyran-2-one (or) Germicidin I (**7bh**): The compound was prepared following the procedure **D** and purified by column chromatography using EtOAc/hexanes (1:9 to 2:8) and isolated as a white solid (Mp = 148-150 °C); Yield: 82% (30 mg); IR (Neat): ν_{max} 2956, 2923, 2868, 2658, 1630, 1574, 1405, 1254, 1127, 1003, and 856 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 10.05 (1H, br s, O*H*), 6.16 (1H, s), 2.31 (2H, d, *J* = 7.0 Hz), 2.04 (1H, nonet,



7bh

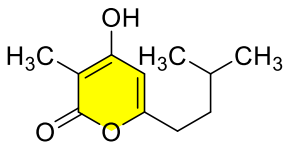
J = 7.0 Hz), 1.97 (3H, s, C*H*$_3$), 0.93 (6H, d, *J* = 6.5 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz, DEPT-135) δ 168.4 (C), 166.7 (C), 162.6 (C), 101.7 (CH), 98.7 (C), 42.6 (CH_2), 26.9 (CH), 22.2 (2 x CH_3), 8.1 (CH_3); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{10}H_{15}O_3$ 183.1021; Found 183.1021.

4-Hydroxy-3-methyl-6-pentyl-2*H*-pyran-2-one (or) Violapyrone L (**7ch**): The compound was prepared following the procedure **D** and purified by column chromatography using EtOAc/hexanes (1:9 to 2:8) and isolated as a white solid; Yield: 80% (31.5 mg); IR (Neat): ν_{max} 3232, 2958, 2926, 2857, 2668, 1664, 1578, 1408, 1246, 1123, 997, and 753 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 10.39 (1H, br s, O*H*), 6.22 (1H, s), 2.45 (2H, t, *J* = 7.5 Hz), 1.97 (3H, s, C*H*$_3$), 1.63 (2H, quint, *J* = 7.5 Hz), 1.34-1.28 (4H, m), 0.88 (3H, t, *J* = 7.0 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz, DEPT-135) δ 168.7 (C), 167.3 (C), 163.4 (C), 100.8 (CH), 98.6 (C), 33.4 (CH_2), 31.0 (CH_2), 26.5 (CH_2), 22.3 (CH_2), 13.8 (CH_3), 8.1 (CH_3); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{11}H_{17}O_3$ 197.1178; Found 197.1178.



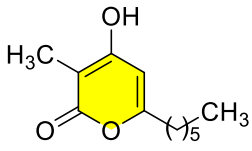
7ch

4-Hydroxy-6-isopentyl-3-methyl-2*H*-pyran-2-one (or) Violapyrone J1 (7dh): The compound was prepared following the procedure **D** and purified by column chromatography using EtOAc/hexanes (1:9 to 2:8) and isolated as a white solid (Mp = 80-82 °C); Yield: 81% (32 mg); IR (Neat): ν_{max} 2960, 2921, 2851,1675, 1576, 1462, 1246, and 803 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 6.10 (1H, s), 2.44 (2H, t, *J* = 8.0 Hz), 1.96 (3H, s, C*H*$_3$), 1.58 (1H, nonet, *J* = 6.5 Hz), 1.51 (2H, q, *J* =8.0 Hz), 0.90 (6H, d, *J* = 6.5 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz, DEPT-135): δ 167.8 (C), 166.0 (C), 163.7 (C), 100.1 (CH), 98.5 (C), 35.7 (CH_2), 31.5 (CH_2), 27.5 (CH), 22.2 (2 x CH_3), 8.1 (CH_3); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{11}H_{17}O_3$ 197.1178; Found 197.1175.



7dh

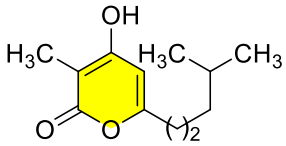
6-Hexyl-4-hydroxy-3-methyl-2*H*-pyran-2-one (or) Violapyrone J (**7eh**): The compound was prepared following the procedure **D** and purified by column chromatography using EtOAc/hexanes (1:9 to 2:8) and isolated as a white solid (Mp = 76-78 °C); Yield: 79% (33 mg); IR (Neat): ν_{max} 2954, 2926, 2856, 2674, 1658, 1575, 1406, 1240, 1122, 1001, and 831 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 10.56 (1H, br s, O*H*), 6.23 (1H, s), 2.45 (2H, t, *J* = 8.0 Hz), 1.97 (3H, s, C*H*$_3$), 1.62 (2H, quint, *J* = 7.5 Hz), 1.39-1.22 (6H, m), 0.87 (3H, t, *J* = 7.0 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz, DEPT-135) δ 168.8 (C), 167.4 (C), 163.4 (C), 100.9 (CH), 98.6 (C), 33.4 (CH_2), 31.4 (CH_2), 28.6 (CH_2),



7eh

26.7 (CH_2), 22.4 (CH_2), 13.9 (CH_3), 8.1 (CH_3); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{12}H_{19}O_3$ 211.1334; Found 211.1333.

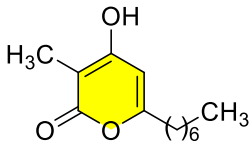
4-Hydroxy-3-methyl-6-(4-methylpentyl)-2*H*-pyran-2-one (or) Violapyrone A (7fh): The



7fh

compound was prepared following the procedure **D** and purified by column chromatography using EtOAc/hexanes (1:9 to 2:8) and isolated as a white solid; Yield: 78% (33 mg); IR (Neat): ν_{max} 2952, 2676, 1634, 1573, 1406, 1248, 1174, 1124, 1002, and 751 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 9.70 (1H, br s, O*H*), 6.15 (1H, s), 2.43 (2H, t, *J* = 7.5 Hz), 1.97 (3H, s, C*H*$_3$), 1.67-1.59 (2H, m), 1.54 (1H, nonet, *J* = 6.5 Hz), 1.24-1.17 (2H, m), 0.86 (6H, d, *J* = 7.0 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz, DEPT-135): δ 168.2 (C), 166.5 (C), 163.5 (C), 100.5 (CH), 98.6 (C), 38.1 (CH_2), 33.7 (CH_2), 27.7 (CH), 24.7 (CH_2), 22.4 (2 x CH_3), 8.1 (CH_3); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{12}H_{19}O_3$ 211.1334; Found 211.1336.

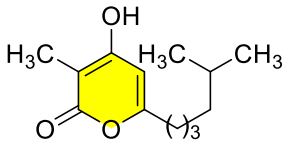
6-Heptyl-4-hydroxy-3-methyl-2*H*-pyran-2-one (or) Violapyrone I (**7gh**): The compound was



7gh

prepared following the procedure **D** and purified by column chromatography using EtOAc/hexanes (1:9 to 2:8) and isolated as a white solid (Mp = 92-94 °C); Yield: 80% (36 mg); IR (Neat): ν_{max} 3097, 2922, 2853, 2668, 2359, 1634, 1572, 1407, 1251, 1126, 1002, and 834 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 9.46 (1H, br s, O*H*), 6.13 (1H, s), 2.44 (2H, t, *J* = 8.0 Hz), 1.97 (3H, s, C*H*$_3$), 1.62 (2H, quint, *J* = 7.5 Hz), 1.37-1.19 (8H, m), 0.87 (3H, t, *J* = 7.0 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz, DEPT-135) δ 168.4 (C), 166.9 (C), 163.5 (C), 100.7 (CH), 98.6 (C), 33.4 (CH_2), 31.6 (CH_2), 28.9 (2 x CH_2), 26.8 (CH_2), 22.6 (CH_2), 14.0 (CH_3), 8.1 (CH_3); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{13}H_{21}O_3$ 225.1491; Found 225.1491.

4-Hydroxy-3-methyl-6-(5-methylhexyl)-2*H*-pyran-2-one (or) Violapyrone B (7hh): The

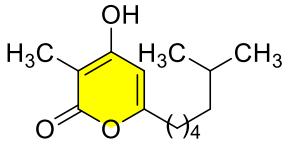


7hh

compound was prepared following the procedure **D** and purified by column chromatography using EtOAc/hexanes (1:9 to 2:8) and isolated as a white solid; Yield: 80% (36 mg); IR (Neat): ν_{max} 2928, 1637, 1575, 1407, 1242, 1124, and 832 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 6.03 (1H, s), 2.44 (2H, t, *J* = 8.0 Hz), 1.96 (3H, s, C*H*$_3$), 1.61 (2H, quint, *J* = 7.5 Hz), 1.51 (1H, nonet, *J* = 6.5 Hz), 1.36-1.27 (2H, m), 1.17 (2H, q, *J* = 6.5 Hz), 0.85 (6H, d, *J* = 6.5 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$,125 MHz, DEPT-135): δ 167.5 (C), 165.5 (C), 163.5 (C), 100.0 (CH), 98.5 (C), 38.5

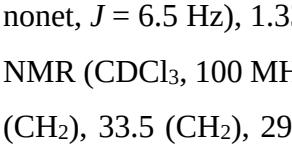
(CH_2), 33.5 (CH_2), 27.8 (CH), 27.0 (CH_2), 26.7 (CH_2), 22.5 (2 x CH_3), 8.1 (CH_3); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{13}H_{21}O_3$ 225.1491; Found 225.1493.

4-Hydroxy-3-methyl-6-(6-methylheptyl)-2*H*-pyran-2-one (or) Violapyrone H (7ih): The compound was prepared following the procedure **D** and purified by column chromatography using EtOAc/hexanes (1:9 to 2:8) and isolated as a white solid; Yield: 79% (37.5 mg); IR (Neat): ν_{max} 3358, 2961, 2923, 2853, 1639, 1588, 1410, 1256, 1169, and 1027 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 5.91 (1H, s), 2.44 (2H, t, *J* = 7.5 Hz), 1.96 (3H, s, C*H*$_3$), 1.67-1.62 (2H, m), 1.51 (1H, nonet, *J* = 6.5 Hz), 1.33-1.28 (4H, m), 1.15 (2H, q, *J* = 7.5 Hz), 0.86 (6H, d, *J* = 6.5 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz, DEPT-135): δ 166.7 (C), 164.3 (C), 163.7 (C), 99.5 (CH), 98.4 (C), 38.8 (CH_2), 33.5 (CH_2), 29.2 (CH_2), 27.9 (CH), 27.0 (CH_2), 26.8 (CH_2), 22.6 (2 x CH_3), 8.0 (CH_3); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{14}H_{23}O_3$ 239.1647; Found 239.1647.



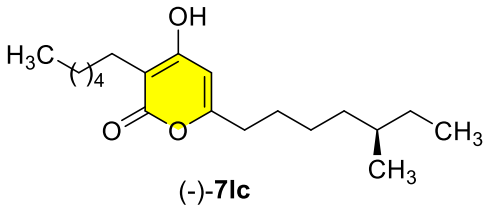
7ih

4-Hydroxy-3-methyl-6-nonyl-2*H*-pyran-2-one (**7jh**): The compound was prepared following the procedure **D** and purified by column chromatography using EtOAc/hexanes (1:9 to 2:8) and isolated as a white solid (Mp = 88-90 °C); Yield: 86% (43.5 mg); IR (Neat): ν_{max} 2954, 2920, 2851, 2685, 1634, 1572, 1406, 1247, 1127, 1002, and 840 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 6.06 (1H, s), 2.43 (2H, t, *J* = 7.5 Hz), 1.95 (3H, s, C*H*$_3$), 1.61 (2H, quint, *J* = 7.0 Hz), 1.33-1.22 (12H, m), 0.87 (3H, t, *J* = 7.0 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz, DEPT-135) δ 167.9 (C), 166.6 (C), 163.5 (C), 100.5 (CH), 98.4 (C), 33.4 (CH_2), 31.8 (CH_2), 29.4 (CH_2), 29.26 (CH_2), 29.24 (CH_2), 28.9 (CH_2), 26.8 (CH_2), 22.6 (CH_2), 14.1 (CH_3), 8.1 (CH_3); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{15}H_{25}O_3$ 253.1804; Found 253.1805.



7jh

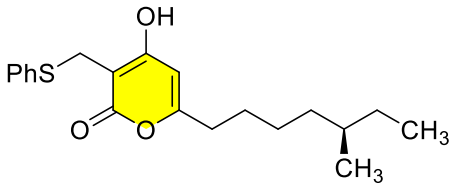
(*R*)-3-Hexyl-4-hydroxy-6-(5-methylheptyl)-2*H*-pyran-2-one (-)-**7lc**: The compound was prepared following the procedure **B** and purified by column chromatography using EtOAc/hexanes (1:9 to 2:8) and isolated as a white solid; Yield: 87% (54 mg); $[\alpha]_D^{25}$ = –7.0° (*c* = 0.1, MeOH); IR (Neat): ν_{max} 3142, 2963, 2924, 2855, 1663, 1576, 1407, 1260, 1125, 995, and 836 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 10.20 (1H, br s, O*H*), 6.20 (1H, s), 2.48-2.41 (4H, m), 1.67-1.56 (2H, m), 1.50 (2H, quint, *J* = 8.0 Hz), 1.37-1.25 (11H, m), 1.17-1.06 (2H, m), 0.88-0.82 (9H, m); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz, DEPT-135) δ 167.7 (C), 166.2 (C), 163.6 (C), 103.4 (C), 100.4 (CH), 36.2 (CH_2), 34.2 (CH),



(-)-**7lc**

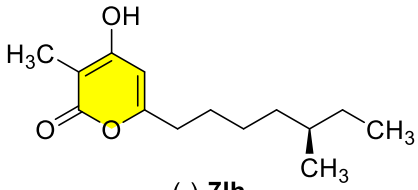
33.6 (CH_2), 31.8 (CH_2), 29.4 (CH_2), 29.3 (CH_2), 28.0 (CH_2), 27.1 (CH_2), 26.5 (CH_2), 23.1 (CH_2), 22.6 (CH_2), 19.1 (CH_3), 14.1 (CH_3), 11.3 (CH_3); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{19}H_{33}O_3$ 309.2430; Found 309.2432.

(*R*)-4-Hydroxy-6-(5-methylheptyl)-3-((phenylthio)methyl)-2*H*-pyran-2-one (-)-**9lh**: The compound was prepared following the procedure **C** and purified by column chromatography using EtOAc/hexanes (1:9 to 2:8) and isolated as a white solid (Mp = 104-106 °C); Yield: 83% (144 mg); $[\alpha]_D^{25}$ = –5.7° (*c* = 0.1, $CHCl_3$); IR (Neat): ν_{max} 2956, 2925, 2853, 1670, 1579, 1410, 1257, 1182, 998, and 738 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 7.39 (2H, d, *J* = 8.0 Hz), 7.26 (2H, t, *J* = 8.0 Hz), 7.18 (1H, t, *J* = 7.5 Hz), 5.96 (1H, s), 4.09 (2H, s, C*H*$_2$), 2.40 (2H, t, *J* = 7.5 Hz), 1.64-1.52 (2H, m), 1.34-1.23 (5H, m), 1.16-1.12 (2H, m), 0.87-0.79 (6H, m); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz, DEPT-135) δ 167.8 (C), 165.8 (C), 165.5 (C), 134.3 (C), 129.9 (2 x CH), 129.0 (2 x CH), 126.8 (CH), 100.3 (CH), 97.7 (C), 36.1 (CH_2), 34.2 (CH), 33.6 (CH_2), 29.4 (CH_2), 28.0 (CH_2), 26.9 (CH_2), 26.4 (CH_2), 19.1 (CH_3), 11.3 (CH_3); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{20}H_{27}O_3S$ 347.1681; Found 347.1680.



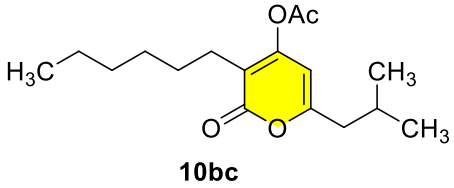
(-)-**9lh**

(*R*)-4-Hydroxy-3-methyl-6-(5-methylheptyl)-2*H*-pyran-2-one (or) (-)-Violapyrone C (-)-**7lh**: The compound was prepared following the procedure **D** and purified by column chromatography using EtOAc/hexanes (1:9 to 2:8) and isolated as a white solid (Mp = 80-82 °C); Yield: 80% (38 mg); $[\alpha]_D^{25}$ = –31.0° (*c* = 0.1, MeOH); IR (Neat): ν_{max} 2956, 2923, 2854, 1661, 1582, 1409, 1240, 1171, 1050, and 756 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 10.10 (1H, br s, O*H*), 6.20 (1H, s), 2.45 (2H, t, *J* = 7.5 Hz), 1.97 (3H, s, C*H*$_3$), 1.68-1.55 (2H, m), 1.38-1.24 (5H, m), 1.17-1.04 (2H, m), 0.87-0.80 (6H, m); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz, DEPT-135) δ 168.5 (C), 167.1 (C), 163.5 (C), 100.7 (CH), 98.6 (C), 36.2 (CH_2), 34.2 (CH), 33.5 (CH_2), 29.4 (CH_2), 27.1 (CH_2), 26.4 (CH_2), 19.1 (CH_3), 11.3 (CH_3), 8.1 (CH_3); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{14}H_{23}O_3$ 239.1647; Found 239.1644.



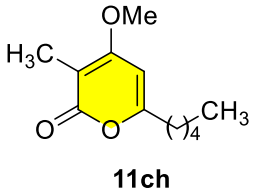
(-)-**7lh**

3-Hexyl-6-isobutyl-2-oxo-2*H*-pyran-4-yl acetate (**10bc**): The compound was prepared following the procedure **E** and purified by column chromatography using EtOAc/hexanes (0.5:9.5 to 1:9) and isolated as a white liquid; Yield: 93% (220 mg); IR (Neat): ν_{max} 2956, 2927, 2868, 2358, 2339, 1775, 1716, 1649, 1590, 1369, 1181, 1012, and 885 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 5.90 (1H, s), 2.37 (2H, t, *J* = 7.5 Hz), 2.33-2.29 (5H, m), 2.07 (1H, nonet, *J* = 7.0 Hz), 1.48 (2H, quint, *J* = 8.0 Hz), 1.32-1.26 (6H, m), 0.95 (6H, d, *J* = 6.5 Hz), 0.87 (3H, t, *J* = 7.0 Hz); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz, DEPT-135) δ 167.3 (C), 164.9 (C), 162.2 (C), 158.1 (C), 115.6 (C), 102.3 (CH), 42.7 (CH_2), 31.5 (CH_2), 29.1 (CH_2), 27.6 (CH_2), 26.8 (CH), 24.3 (CH_2), 22.5 (CH_2), 22.2 (2 x CH_3), 20.8 (CH_3), 14.0 (CH_3); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{17}H_{27}O_4$ 295.1909; Found 295.1910.



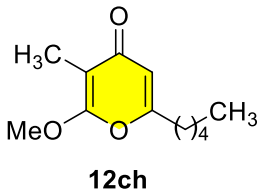
10bc

4-Methoxy-3-methyl-6-pentyl-2*H*-pyran-2-one (or) Childinin G (**11ch**): The compound was prepared following the procedure **F** and purified by column chromatography using EtOAc/hexanes (1:9 to 2:8) and isolated as a pale yellow liquid; Yield: 63% (16 mg, 0.12 mmol); IR (Neat): ν_{max} 2958, 2927, 2865, 1697, 1645, 1569, 1463, 1246, 1133, and 754 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 5.99 (1H, s), 3.87 (3H, s, OC*H*$_3$), 2.48 (2H, t, *J* = 8.0 Hz), 1.90 (3H, s, C*H*$_3$), 1.67 (2H, quint, *J* = 7.5 Hz), 1.37-1.29 (4H, m), 0.90 (3H, t, *J* = 7.0 Hz); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz, DEPT-135) δ 165.9 (C), 165.8 (C), 164.4 (C), 100.8 (C), 94.1 (CH), 56.1 (CH_3, O*C*H$_3$), 34.1 (CH_2), 31.1 (CH_2), 26.7 (CH_2), 22.3 (CH_2), 13.8 (CH_3), 8.3 (CH_3); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{12}H_{19}O_3$ 211.1334; Found 211.1333.



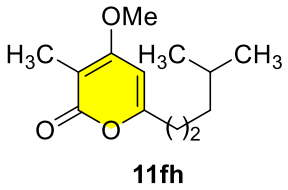
11ch

2-Methoxy-3-methyl-6-pentyl-4*H*-pyran-4-one (**12ch**): The compound was prepared following the procedure **F** and purified by column chromatography using EtOAc/hexanes (1:9 to 2:8) and isolated as a pale yellow liquid; Yield: 34% (8.5 mg, 0.12 mmol); IR (Neat): ν_{max} 2954, 2926, 2856, 1666, 1629, 1591, 1461, 1406, 1257, 1179, 1141, and 747 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 6.05 (1H, s), 3.97 (3H, s, OC*H*$_3$), 2.49 (2H, t, *J* = 7.5 Hz), 1.83 (3H, s, C*H*$_3$), 1.65 (2H, quint, *J* = 7.5 Hz), 1.38-1.32 (4H, m), 0.91 (3H, t, *J* = 7.0 Hz); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz, DEPT-135) δ 181.3 (C), 162.9 (2 x C), 111.7 (CH), 100.9 (C), 55.5 (CH_3, O*C*H$_3$), 32.6 (CH_2), 30.9 (CH_2), 26.2 (CH_2), 22.2 (CH_2), 13.8 (CH_3), 6.5 (CH_3); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{12}H_{19}O_3$ 211.1334; Found 211.1332.



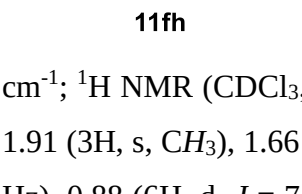
12ch

4-Methoxy-3-methyl-6-(4-methylpentyl)-2*H*-pyran-2-one (or) Violapyrone Q (**11fh**): The compound was prepared following the procedure **F** and purified by column chromatography using EtOAc/hexanes (1:9 to 2:8) and isolated as a pale yellow liquid; Yield: 56% (15 mg, 0.12 mmol); IR (Neat): ν_{max} 2952, 2923, 2867, 1691, 1644, 1567, 1461, 1246, 1132, 1015, and 753 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 5.99 (1H, s), 3.87 (3H, s, OC*H*$_3$), 2.46 (2H, t, *J* = 8.0 Hz), 1.91 (3H, s, C*H*$_3$), 1.66 (2H, quint, *J* = 8.0 Hz), 1.56 (1H, nonet, *J* = 6.5 Hz), 1.21 (2H, q, *J* = 6.5 Hz), 0.88 (6H, d, *J* = 7.0 Hz); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz, DEPT-135) δ 165.9 (C), 165.8 (C), 164.4 (C), 100.9 (C), 94.1 (CH), 56.1 (CH_3, O*C*H$_3$), 38.2 (CH_2), 34.4 (CH_2), 27.7 (CH), 24.9 (CH_2), 22.5 (2 x CH_3), 8.4 (CH_3); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{13}H_{21}O_3$ 225.1491; Found 225.1493.



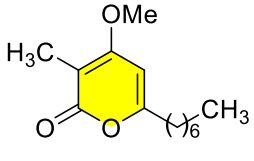
11fh

2-Methoxy-3-methyl-6-(4-methylpentyl)-4*H*-pyran-4-one (**12fh**): The compound was prepared following the procedure **F** and purified by column chromatography using EtOAc/hexanes (1:9 to 2:8) and isolated as a pale yellow liquid; Yield: 31% (8.2 mg, 0.12 mmol); IR (Neat): ν_{max} 2953, 2923, 2852, 1665, 1587, 1461, 1408, 1260, 1180, 1143, and 743 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 6.05 (1H, s), 3.97 (3H, s, OC*H*$_3$), 2.48 (2H, t, *J* = 7.5 Hz), 1.84 (3H, s, C*H*$_3$), 1.66-1.61 (2H, m), 1.57 (1H, nonet, *J* = 6.5 Hz), 1.26-1.22 (2H, m), 0.89 (6H, d, *J* = 6.5 Hz); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz, DEPT-135) δ 181.3 (C), 162.94 (C), 162.92 (C), 111.7 (CH), 100.9 (C), 55.6 (CH_3, O*C*H$_3$), 38.0 (CH_2), 32.9 (CH_2), 27.7 (CH), 24.4 (CH_2), 22.4 (2 x CH_3), 6.6 (CH_3); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{13}H_{21}O_3$ 225.1491; Found 225.1489.



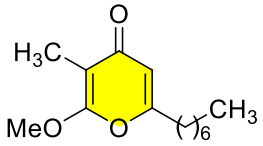
12fh

6-Heptyl-4-methoxy-3-methyl-2*H*-pyran-2-one (or) Violapyrone S (**11gh**): The compound was prepared following the procedure **F** and purified by column chromatography using EtOAc/hexanes (1:9 to 2:8) and isolated as a pale yellow liquid; Yield: 50% (21.5 mg, 0.18 mmol); IR (Neat): ν_{max} 2954, 2924, 2855, 1691, 1644, 1568, 1461, 1247, 1132, 1028, and 753 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 5.99 (1H, s), 3.87 (3H, s, OC*H*$_3$), 2.48 (2H, t, *J* = 8.0 Hz), 1.90 (3H, s, C*H*$_3$), 1.66 (2H, quint, *J* = 7.5 Hz), 1.35-1.24 (8H, m), 0.88 (3H, t, *J* = 7.0 Hz); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz, DEPT-135) δ 165.9 (C), 165.8 (C), 164.4 (C), 100.9 (C), 94.1 (CH), 56.1 (CH_3, O*C*H$_3$), 34.1 (CH_2), 31.6 (CH_2), 28.9 (CH_2), 28.87 (CH_2), 27.0 (CH_2), 22.5 (CH_2), 13.9 (CH_3), 8.3 (CH_3); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{14}H_{23}O_3$ 239.1647; Found 239.1646.



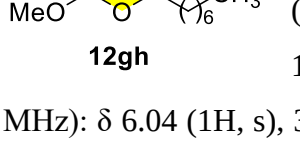
11gh

6-Heptyl-2-methoxy-3-methyl-4*H*-pyran-4-one (**12gh**): The compound was prepared following the procedure **F** and purified by column chromatography using EtOAc/hexanes (1:9 to 2:8) and isolated as a pale yellow liquid; Yield: 31% (13.5 mg, 0.18 mmol); IR (Neat): ν_{max} 2954, 2925, 2855, 1665, 1629, 1590, 1460, 1404, 1263, 1180, 1141, 1002, and 856 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 6.04 (1H, s), 3.97 (3H, s, OC*H*$_3$), 2.49 (2H, t, *J* = 7.5 Hz), 1.83 (3H, s, C*H*$_3$), 1.64 (2H, quint, *J* = 7.5 Hz), 1.38-1.27 (8H, m), 0.89 (3H, t, *J* = 7.0 Hz); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz, DEPT-135) δ 181.3 (C), 162.8 (2 x C), 111.7 (CH), 100.8 (C), 55.5 (CH_3, O*C*H$_3$), 32.7 (CH_2), 31.6 (CH_2), 28.9 (CH_2), 28.8 (CH_2), 26.5 (CH_2), 22.5 (CH_2), 13.9 (CH_3), 6.5 (CH_3); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{14}H_{23}O_3$ 239.1647; Found 239.1647.



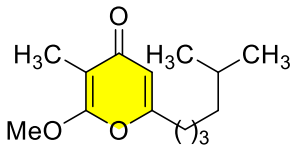
12gh

4-Methoxy-3-methyl-6-(5-methylhexyl)-2*H*-pyran-2-one (or) Violapyrone R (**11hh**): The compound was prepared following the procedure **F** and purified by column chromatography using EtOAc/hexanes (1:9 to 2:8) and isolated as a pale yellow liquid; Yield: 50% (12 mg, 0.1 mmol); IR (Neat): ν_{max} 2926, 1696, 1646, 1570, 1465, 1245, 1134, 1019, and 609 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 6.00 (1H, s), 3.88 (3H, s, OC*H*$_3$), 2.48 (2H, t, *J* = 7.5 Hz), 1.91 (3H, s, C*H*$_3$), 1.64 (2H, quint, *J* = 7.5 Hz), 1.53 (1H, nonet, *J* = 6.5 Hz), 1.33 (2H, quint, *J* = 7.5 Hz), 1.19 (2H, q, *J* = 7.0 Hz), 0.87 (6H, d, *J* = 7.0 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz, DEPT-135) δ 165.9 (C), 165.8 (C), 164.4 (C), 100.8 (C), 94.1 (CH), 56.1 (CH_3, O*C*H$_3$), 38.5 (CH_2), 34.2 (CH_2), 27.8 (CH), 27.2 (CH_2), 26.7 (CH_2), 22.5 (2 x CH_3), 8.4 (CH_3); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{14}H_{23}O_3$ 239.1647; Found 239.1643.



11hh

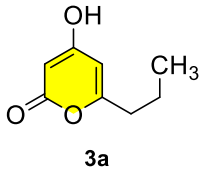
2-Methoxy-3-methyl-6-(5-methylhexyl)-4*H*-pyran-4-one (**12hh**): The compound was prepared following the procedure **F** and purified by column chromatography using EtOAc/hexanes (1:9 to 2:8) and isolated as a pale yellow liquid; Yield: 30% (7.2 mg, 0.1 mmol); IR (Neat): ν_{max} 2922, 2852, 1706, 1665, 1567, 1462, 1246, 1177, and 616 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 6.05 (1H, s), 3.97 (3H, s, OC*H*$_3$), 2.49 (2H, t, *J* = 7.5 Hz), 1.83 (3H, s, C*H*$_3$), 1.62 (2H, quint, *J* = 7.5 Hz), 1.53 (1H, nonet, *J* = 6.5 Hz), 1.36 (2H, quint, *J* = 7.5 Hz), 1.20 (2H, q, *J* = 7.0 Hz), 0.87 (6H, d, *J* = 7.0 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz, DEPT-135) δ 181.3 (C), 162.9 (2 x C), 111.7 (CH), 100.9 (C), 55.6 (CH_3, O*C*H$_3$), 38.5 (CH_2), 32.7 (CH_2), 27.9 (CH), 26.8



12hh

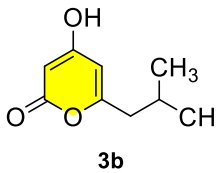
(CH_2), 26.6 (CH_2), 22.5 (2 x CH_3), 6.6 (CH_3); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{14}H_{23}O_3$ 239.1647; Found 239.1652.

4-Hydroxy-6-propyl-2*H*-pyran-2-one (**3a**): The compound was prepared following the procedure **A** and purified by column chromatography using EtOAc/hexanes (2:8 to 3:7) and isolated as a pale yellow solid (Mp = 84-86 °C); Yield: 85% (650 mg); IR (Neat): ν_{max} 2962, 2873, 2608, 1656, 1551, 1490, 1440, 1241, 1141, 991, and 826 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 6.01 (1H, s), 5.60 (1H, s), 2.46 (2H, t, *J* = 7.5 Hz), 1.67 (2H, sext, *J* = 7.5 Hz), 0.96 (3H, t, *J* = 7.5 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz, DEPT-135) δ 172.6 (C), 168.4 (C), 167.0 (C), 101.4 (CH), 89.8 (CH), 33.5 (CH_2), 20.0 (CH_2), 13.4 (CH_3); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz, DEPT-135) δ 172.7 (C), 168.4 (C), 167.1 (C), 101.5 (CH), 89.8 (CH), 33.5 (CH_2), 20.0 (CH_2), 13.4 (CH_3); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_8H_{11}O_3$ 155.0708; Found 155.0708.



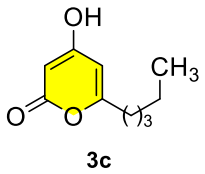
3a

4-Hydroxy-6-isobutyl-2*H*-pyran-2-one (3b): The compound was prepared following the procedure **A** and purified by column chromatography using EtOAc/hexanes (2:8 to 3:7) and isolated as a light yellow solid; Yield: 80% (673 mg); IR (Neat): ν_{max} 2958, 2926, 1696, 1661, 1563, 1489,1444, 1253, 1142, 995, and 823 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 5.97 (1H, d, *J* = 2.0 Hz), 5.59 (1H, d, *J* = 2.0 Hz), 2.34 (2H, d, *J* = 7.0 Hz), 2.11-2.02 (1H, m), 0.94 (6H, d, *J* = 6.5 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz, DEPT-135) δ 172.3 (C), 168.2 (C), 166.5 (C), 102.3 (CH), 89.9 (CH), 42.8 (CH_2), 26.9 (CH), 22.2 (2 x CH_3); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_9H_{13}O_3$ 169.0865; Found 169.0866.



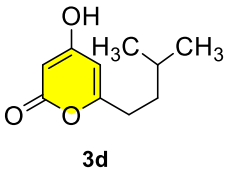
3b

4-Hydroxy-6-pentyl-2*H*-pyran-2-one (**3c**): The compound was prepared following the procedure **A** and purified by column chromatography using EtOAc/hexanes (2:8 to 3:7) and isolated as a pale yellow solid (Mp = 64-66 °C); Yield: 87% (795 mg); IR (Neat): ν_{max} 2955, 2930, 2861, 2634, 1660, 1563, 1490, 1443, 1249, 1141, 991, and 829 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 11.23 (1H, br s, O*H*), 6.01 (1H, d, *J* = 2.0 Hz), 5.59 (1H, d, *J* = 2.0 Hz), 2.47 (2H, t, *J* = 8.0 Hz), 1.64 (2H, quint, *J* = 7.5 Hz), 1.35-1.28 (4H, m), 0.89 (3H, t, *J* = 7.0 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz, DEPT-135) δ 172.7 (C), 168.5 (C), 167.3 (C), 101.3 (CH), 89.8 (CH), 33.6 (CH_2), 31.0 (CH_2), 26.3 (CH_2), 22.2 (CH_2), 13.8 (CH_3); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{10}H_{15}O_3$ 183.1021; Found 183.1024.



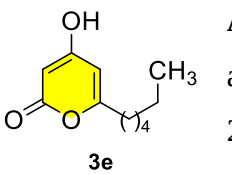
3c

4-Hydroxy-6-isopentyl-2*H*-pyran-2-one [Fistupyrone] (3d): The compound was prepared following the procedure **A** and purified by column chromatography using EtOAc/hexanes (2:8 to 3:7) and isolated as a light yellow solid; Yield: 81% (738 mg); IR (Neat): ν_{max} 2954, 2869, 1738, 1657, 1551, 1439, 1367, 1234, 1140 and 825 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 5.99 (1H, s), 5.58 (1H, d, *J* = 1.5 Hz), 2.48 (2H, t, *J* = 7.5 Hz), 1.59 (1H, nonet, *J* = 6.5 Hz), 1.52 (2H, q, *J* = 8.0 Hz), 0.91 (6H, d, *J* = 6.5 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz, DEPT-135) δ 172.6 (C), 168.3 (C), 167.5 (C), 101.1 (CH), 89.6 (CH), 35.5 (CH_2), 31.5 (CH_2), 27.4 (CH), 22.1 (2 x CH_3); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{10}H_{15}O_3$ 183.1021; Found 183.1021.



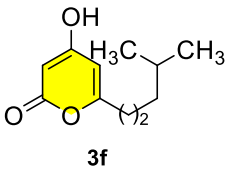
3d

6-Hexyl-4-hydroxy-2*H*-pyran-2-one (**3e**): The compound was prepared following the procedure **A** and purified by column chromatography using EtOAc/hexanes (2:8 to 3:7) and isolated as a pale yellow liquid; Yield: 80% (785 mg); IR (Neat): ν_{max} 2954, 2923, 2855, 2591, 1694, 1643, 1610, 1561, 1542, 1486, 1294, 1245, 1138, 839, and 603 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 11.24 (1H, br s, O*H*), 6.00 (1H, s), 5.59 (1H, s), 2.48 (2H, t, *J* = 8.0 Hz), 1.63 (2H, quint, *J* = 7.5 Hz), 1.37-1.26 (6H, m), 0.88 (3H, t, *J* = 7.0 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz, DEPT-135) δ 172.7 (C), 168.4 (C), 167.4 (C), 101.3 (CH), 89.7 (CH), 33.6 (CH_2), 31.3 (CH_2), 28.6 (CH_2), 26.6 (CH_2), 22.4 (CH_2), 13.9 (CH_3); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{11}H_{17}O_3$ 197.1178; Found 197.1176.



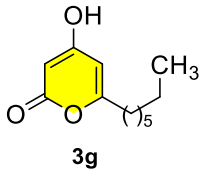
3e

4-Hydroxy-6-(4-methylpentyl)-2*H*-pyran-2-one (**3f**): The compound was prepared following the procedure **A** and purified by column chromatography using EtOAc/hexanes (2:8 to 3:7) and isolated as a pale yellow solid; Yield: 81% (795 mg); IR (Neat): ν_{max} 2953, 2869, 1658, 1562, 1489, 1442, 1249, 1141, 829, and 630 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 11.29 (1H, br s, O*H*), 6.00 (1H, d, *J* = 2.0 Hz), 5.59 (1H, d, *J* = 2.5 Hz), 2.46 (2H, t, *J* = 8.0 Hz), 1.63 (2H, quint, *J* = 8.0 Hz), 1.55 (1H, nonet, *J* = 6.5 Hz), 1.21 (2H, q, *J* = 7.0 Hz), 0.87 (6H, d, *J* = 6.5 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz, DEPT-135) δ 172.6 (C), 168.4 (C), 167.3 (C), 101.3 (CH), 89.7 (CH), 38.1 (CH_2), 33.8 (CH_2), 27.7 (CH), 24.5 (CH_2), 22.4 (CH_3), 22.38 (CH_3); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{11}H_{17}O_3$ 197.1178; Found 197.1180.



3f

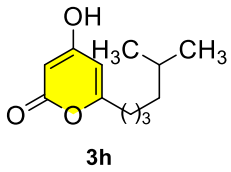
6-Heptyl-4-hydroxy-2*H*-pyran-2-one (**3g**): The compound was prepared following the procedure



3g

A and purified by column chromatography using EtOAc/hexanes (2:8 to 3:7) and isolated as a pale yellow solid (Mp = 56-58 °C); Yield: 90% (950 mg); IR (Neat): ν_{max} 2951, 2924, 2852, 2568, 2360, 2339, 1680, 1648, 1609, 1561, 1540, 1490, 1290, 1247, 1141, 836, and 606 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 11.29 (1H, br s, O*H*), 6.01 (1H, d, *J* = 1.5 Hz), 5.59 (1H, d, *J* = 2.0 Hz), 2.47 (2H, t, *J* = 7.5 Hz), 1.63 (2H, quint, *J* = 7.5 Hz), 1.36-1.21 (8H, m), 0.87 (3H, t, *J* = 7.0 Hz); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz, DEPT-135) δ 172.7 (C), 168.4 (C), 167.4 (C), 101.3 (CH), 89.8 (CH), 33.6 (CH_2), 31.6 (CH_2), 28.9 (2 x CH_2), 26.7 (CH_2), 22.6 (CH_2), 14.0 (CH_3); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{12}H_{19}O_3$ 211.1334; Found 211.1337.

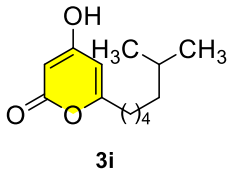
4-Hydroxy-6-(5-methylhexyl)-2*H*-pyran-2-one (3h) : The compound was prepared following



3h

the procedure **A** and purified by column chromatography using EtOAc/hexanes (2:8 to 3:7) and isolated as a light yellow solid; Yield: 80% (841 mg); IR (Neat): ν_{max} 3088, 2953, 2952, 2866, 2614, 1658, 1558, 1442, 1245, 1141, 994, and 830 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 5.99 (1H, s), 5.58 (1H, s), 2.47 (2H, t, *J* = 8.0 Hz), 1.62 (2H, quint, *J* = 7.5 Hz), 1.53 (1H, nonet, *J* = 6.5 Hz) 1.32 (2H, quint, *J* = 7.5 Hz), 1.17 (2H, q, *J* = 7.0 Hz), 0.85 (6H, d, *J* = 6.0 Hz); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz, DEPT-135): δ 172.6 (C), 168.3 (C), 167.4 (C), 101.3 (CH), 89.8 (CH), 38.5 (CH_2), 33.6 (CH_2), 27.8 (CH), 26.9 (CH_2), 26.7 (CH_2), 22.5 (2 x CH_3); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{12}H_{19}O_3$ 211.1334; Found 211.1334.

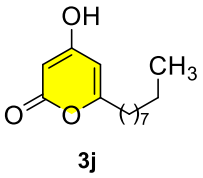
4-Hydroxy-6-(6-methylheptyl)-2*H*-pyran-2-one (3i): The compound was prepared following



3i

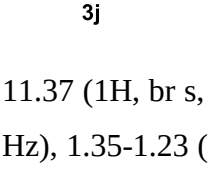
the procedure **A** and purified by column chromatography using EtOAc/hexanes (2:8 to 3:7) and isolated as a light yellow solid; Yield: 81% (908 mg); IR (Neat): ν_{max} 2992, 2934, 2867, 1658, 1564, 1442, 1275, 1259, 994, and 750 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz, DEPT-135): δ 10.90 (1H, br s, O*H*), 5.98 (1H, s), 5.58 (1H, s), 2.48 (2H, t, *J* = 7.5 Hz), 1.64 (2H, quint, *J* = 7.5 Hz), 1.51 (1H, nonet, *J* = 6.5 Hz), 1.39-1.22 (4H, m), 1.15 (2H, q, *J* = 6.5 Hz), 0.86 (6H, d, *J* = 6.5 Hz); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz, DEPT-135): δ 172.7 (C), 168.4 (C), 167.3 (C), 101.3 (CH), 89.7 (CH), 38.7 (CH_2), 33.6 (CH_2), 29.1 (CH_2), 27.8 (CH), 26.9 (CH_2), 26.7 (CH_2), 22.5 (2 x CH_3); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{13}H_{21}O_3$ 225.1491; Found 225.1495.

4-Hydroxy-6-nonyl-2*H*-pyran-2-one (**3j**): The compound was prepared following the procedure **A** and purified by column chromatography using EtOAc/hexanes (2:8 to 3:7) and isolated as a pale yellow solid (Mp = 70-72 °C); Yield: 82% (976 mg); IR (Neat): ν_{max} 2953, 2919, 2850, 2564, 2360, 2339, 1681, 1649, 1610, 1560, 1541, 1491, 1294, 1255, 1141, 836, and 606 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 11.37 (1H, br s, O*H*), 6.01 (1H, s), 5.60 (1H, s), 2.47 (2H, t, *J* = 8.0 Hz), 1.63 (2H, quint, *J* = 7.5 Hz), 1.35-1.23 (12H, m), 0.87 (3H, t, *J* = 7.0 Hz); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz, DEPT-135) δ 172.7 (C), 168.5 (C), 167.4 (C), 101.3 (CH), 89.8 (CH), 33.6 (CH_2), 31.8 (CH_2), 29.4 (CH_2), 29.2 (2 x CH_2), 28.9 (CH_2), 26.7 (CH_2), 22.6 (CH_2), 14.1 (CH_3); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{14}H_{23}O_3$ 239.1647; Found 239.1646.



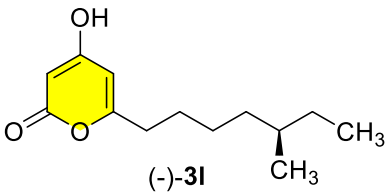
3j

4-Hydroxy-6-undecyl-2*H*-pyran-2-one (**3k**): The compound was prepared following the procedure **A** and purified by column chromatography using EtOAc/hexanes (2:8 to 3:7) and isolated as a pale yellow solid (Mp = 79-81 °C); Yield: 80% (1.07 g); IR (Neat): ν_{max} 2954, 2918, 2849, 2561, 1683, 1649, 1610, 1563, 1540, 1491, 1298, 1249, 1142, 836, and 606 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 11.27 (1H, br s, O*H*), 6.00 (1H, d, *J* = 1.5 Hz), 5.59 (1H, d, *J* = 2.0 Hz), 2.47 (2H, t, *J* = 8.0 Hz), 1.63 (2H, quint, *J* = 7.5 Hz), 1.35-1.23 (16H, m), 0.88 (3H, t, *J* = 7.0 Hz); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz, DEPT-135) δ 172.7 (C), 168.4 (C), 167.4 (C), 101.3 (CH), 89.8 (CH), 33.7 (CH_2), 31.9 (CH_2), 29.6 (2 x CH_2), 29.4 (CH_2), 29.3 (CH_2), 29.2 (CH_2), 28.9 (CH_2), 26.7 (CH_2), 22.7 (CH_2), 14.1 (CH_3); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{16}H_{27}O_3$ 267.1960; Found 267.1963.



3k

(*R*)-4-Hydroxy-6-(5-methylheptyl)-2*H*-pyran-2-one (-)-**3l**: The compound was prepared following the procedure **A** and purified by column chromatography using EtOAc/hexanes (2:8 to 3:7) and isolated as a white solid (Mp = 60-62 °C); Yield: 80% (180 mg, 1.0 mmol); $[\alpha]_D^{25}$ = –8.0° (*c* = 0.1, MeOH); IR (Neat): ν_{max} 2955, 2926, 2858, 1657, 1553, 1441, 1240, 1140, 993, and 828 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 5.98 (1H, d, *J* = 1.5 Hz), 5.58 (1H, d, *J* = 2.0 Hz), 2.48 (2H, t, *J* = 8.0 Hz), 1.67-1.57 (2H, m), 1.35-1.25 (5H, m), 1.17-1.06 (2H, m), 0.87-0.82 (6H, m); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz, DEPT-135) δ 172.6 (C), 168.3 (C), 167.4 (C), 101.2 (CH), 89.8 (CH), 36.1 (CH_2), 34.2 (CH), 33.7 (CH_2), 29.4 (CH_2), 26.9 (CH_2), 26.4 (CH_2), 19.1 (CH_3), 11.3 (CH_3); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{13}H_{21}O_3$ 225.1491; Found 225.1490.



(-)-**3l**

X-Ray Single Crystal Data for 7bb. The Ellipsoid Counter % Probability Levels are 50%
Crystallized from Hexane-Ethyl acetate; $C_{11}H_{16}O_3$; Mr = 196.24; orthorhombic; space group = *P b c n*; A clear whitish white crystal of 0.15x0.14x0.11 mm^3 was used.
Table S1. Crystal data and structure refinement for **7bb** (CCDC-2292620)

Bond precision: C-C = 0.0066 A Wavelength=0.71073

Cell: a=13.5552(4) b=7.1623(3) c=23.1013(8)
alpha=90 beta=90 gamma=90
Temperature: 299 K

	Calculated	Reported
Volume	2242.82(14)	2242.82(14)
Space group	P b c n	P b c n
Hall group	-P 2n 2ab	-P 2n 2ab
Moiety formula	C11 H16 O3	C11 H16 O3
Sum formula	C11 H16 O3	C11 H16 O3
Mr	196.24	196.24
Dx,g cm-3	1.162	1.162
Z	8	8
Mu (mm-1)	0.083	0.083
F000	848.0	848.0
F000'	848.45	
h,k,lmax	16,8,27	16,8,27
Nref	1990	1989
Tmin,Tmax	0.988,0.991	0.553,1.000
Tmin'	0.988	

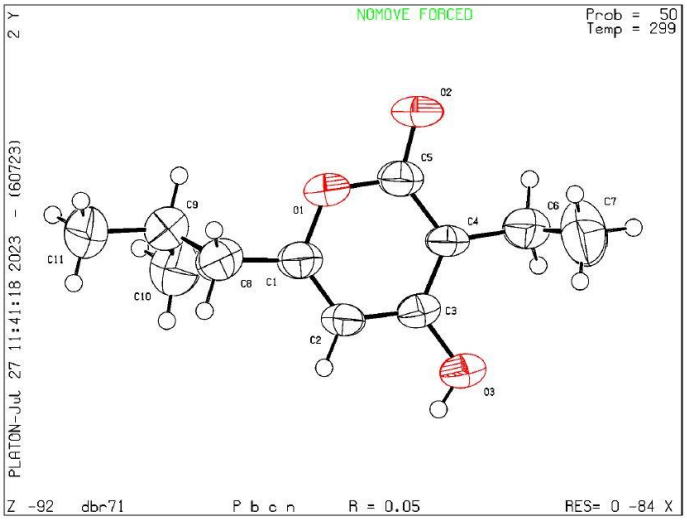
Correction method= # Reported T Limits: Tmin=0.553 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 0.999 Theta(max)= 25.024

R(reflections)= 0.0542(932) wR2(reflections)= 0.2085(1989)

S = 1.151 Npar= 131

Ellipsoid plot for 7bb:



X-Ray Single Crystal Data for 7jb. The Ellipsoid Counter % Probability Levels are 50%
Crystallized from Hexane-Ethyl acetate; $C_{16}H_{26}O_3$; Mr = 266.38; triclinic; space group = *P-1*; A metallic white crystal of 0.2x0.2x0.1 mm^3 was used.

Table S2. Crystal data and structure refinement for **7jb** (CCDC-2292622)

Bond precision: C-C = 0.0062 A Wavelength=0.71073

Cell: a=9.1560(2) b=10.2227(2) c=17.7959(4)
alpha=81.850(2) beta=88.334(2) gamma=87.904(2)
Temperature: 298 K

	Calculated	Reported
Volume	1647.27(6)	1647.27(6)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	C16 H26 O3, C14 H21 O3, C2 H5	2(C16 H26 O3)
Sum formula	C32 H52 O6	C32 H52 O6
Mr	532.74	532.73
Dx,g cm-3	1.074	1.074
Z	2	2
Mu (mm-1)	0.072	0.072
F000	584.0	584.0
F000'	584.27	
h,k,lmax	11,13,22	11,12,22
Nref	7153	6897
Tmin,Tmax	0.983,0.992	0.423,1.000
Tmin'	0.983	

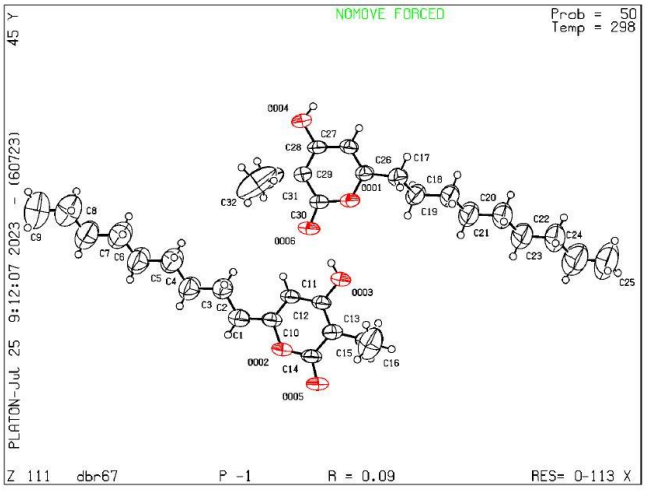
Correction method= # Reported T Limits: Tmin=0.423 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 0.964 Theta(max)= 26.954

R(reflections)= 0.0884(3313) wR2(reflections)= 0.3129(6897)

S = 1.051 Npar= 343

Ellipsoid plot for 7jb:



X-Ray Single Crystal Data for 7bc. The Ellipsoid Counter % Probability Levels are 50%
Crystallized from Hexane-Ethyl acetate; $C_{15}H_{24}O_3$; Mr = 252.34; triclinic; space group = *P 1*; A metallic white crystal of 0.2x0.2x0.1 mm^3 was used.

Table S3. Crystal data and structure refinement for **7bc** (CCDC-2292621)

Bond precision: C-C = 0.0304 A Wavelength=0.71073

Cell: a=5.2134(6) b=9.7698(10) c=15.9903(12)
alpha=96.982(7) beta=91.685(8) gamma=96.327(9)
Temperature: 298 K

	Calculated	Reported
Volume	802.73(14)	802.73(14)
Space group	P 1	P 1
Hall group	P 1	P 1
Moiety formula	C15 H24 O3	C15 H24 O3
Sum formula	C15 H24 O3	C15 H24 O3
Mr	252.34	252.34
Dx,g cm-3	1.044	1.044
Z	2	2
Mu (mm-1)	0.071	0.071
F000	276.0	276.0
F000'	276.13	
h,k,lmax	6,11,18	6,11,18
Nref	5276[2638]	4989
Tmin,Tmax	0.983,0.992	0.478,1.000
Tmin'	0.983	

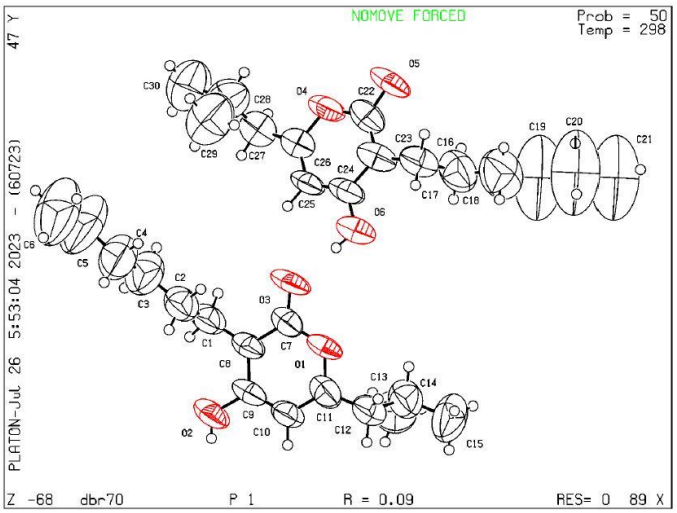
Correction method= # Reported T Limits: Tmin=0.478 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 1.89/0.95 Theta(max)= 24.406

R(reflections)= 0.0860(1329) wR2(reflections)= 0.2236(4989)

S = 0.851 Npar= 321

Ellipsoid plot for 7bc:



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