Supporting Information-I

High-yielding Total Synthesis of Embelin, Rapanone, and Irisoquin A, D, F

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General Methods: The ^{1}H NMR and ^{13}C NMR spectra were recorded at 500, 400, 125 and 100 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 silica gel (particle size: 0.063−0.200 mm). High-resolution mass spectra were recorded on a micromass ESI-TOF MS. IR spectra were recorded on FT/IR-5300 and FT/IR-5700. Mass spectra were recorded on either VG7070H mass spectrometer using EI technique or Shimadzu-LCMS-2010 A mass spectrometer. The X-ray diffraction measurements were carried out at 298 K on an automated Enraf-Nonious $MACH_3$ diffractometer using graphite monochromated, Mo−Kα (λ = 0.71073 Å) radiation with CAD4 software, or the X-ray intensity data were measured at 298 K on a SMART

APEX CCD area detector system equipped with a graphite monochromator and a Mo−Kα fine-focus sealed tube (λ = 0.71073 Å). For thin-layer chromatography (TLC), silica gel plates 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. For the synthesis of key intermediate 2-hydroxy-5-methoxycyclohexa-2,5-diene-1,4-dione **8** and chiral aldehydes **10**, **13** and **15** were prepared according to the literature procedures.[1-3]

Procedure A: Preparation of 2,5-didecyl-3,6-dihydroxycyclohexa-2,5-diene-1,4-dione (6a): In an ordinary glass vial equipped with a magnetic stirring bar, 0.6 mmol of the decanal **2a**, 0.3 mmol of 2,5-dihydroxycyclohexa-2,5-diene-1,4-dione **1** and 0.39 mmol of Hantzsch ester **4** were added sequentially in 1.0 mL of DCM followed by 0.03 mmol of proline **3a** and the reaction mixture was stirred at room temperature for 9 h. The crude reaction mixture was directly loaded onto a silica gel column without aqueous workup and pure cascade product **6a** was obtained in 26% yield (silica gel, mixture of hexane/ethyl acetate).

Procedure B: Preparation of 2,5-dibenzyl-3,6-dihydroxycyclohexa-2,5-diene-1,4-dione (6p): In an ordinary glass vial equipped with a magnetic stirring bar, to 0.6 mmol of the benzaldehyde **2p**, 0.3 mmol of 2,5-dihydroxycyclohexa-2,5-diene-1,4-dione **1** and 0.33 mmol of Hantzsch ester **4** was added in 1.0 mL of DCM, followed by 0.03 mmol of proline **3a** and the reaction mixture was stirred at 50 ^{o}C for 24 h. The crude reaction mixture was directly loaded onto a silica gel column without aqueous workup and pure cascade product **6p** was obtained in 30% yield (silica gel, mixture of hexane/ethyl acetate).

Procedure C: **Benzylamine Catalysed Cascade Three-Component Reductive Alkylation (TCRA) Reaction with 2-hydroxy-5-methoxycyclohexa-2,5-diene-1,4-dione for Table 2 and Table 3:** In an ordinary glass vial equipped with a magnetic stirring bar, to 0.3 mmol of the aldehyde **2**, 0.3 mmol of 2-hydroxy-5-methoxycyclohexa-2,5-diene-1,4-dione **8** and 0.33 mmol of Hantzsch ester **4** was added in 1.0 mL of DCM and then 10 mol% of the benzylamine **3d** was added and the reaction mixture was stirred at room temperature for 1-24 h. The crude reaction mixture was directly loaded onto a silica gel column without aqueous workup, and pure cascade products **9a-9aa** were obtained in 74-88% yield (silica gel, mixture of hexane/ethyl acetate).

Procedure D: **Synthesis of 3-alkyl-2,5-dihydroxycyclohexa-2,5-diene-1,4-dione for Table 4**: In a round bottom flask equipped with a magnetic stirring bar, 0.2 mmol of **9** was added to 8.8 mL of ethanol followed by the addition of 4.4 mL of 2.0 M aqueous NaOH solution. The reaction mixture was stirred at 70 ºC for 2 h and was allowed to cool to room temperature and diluted with hydrochloric acid (2.0 M, 22 mL) then extracted with ethyl acetate (3 x 20 mL). The combined organic phases were washed with brine solution and followed by dried over Na_2SO_4 and concentrated in vaccum to give pure products **5c-5h** in 89-93% yield.

Procedure E: **Synthesis of 6-benzyl-3-alkyl-2,5-dihydroxycyclohexa-2,5-diene-1,4-dione for Table 5**: In an ordinary glass vial equipped with a magnetic stirring bar, to 0.3 mmol of the aldehyde **2**, 0.3 mmol of 3-alkyl-2,5-dihydroxycyclohexa-2,5-diene-1,4-dione **5**, 0.33 mmol of Hantzsch ester **4** was added in 1.0 mL of DCM and then 10 mol% of the benzylamine **3d** was added and the reaction mixture was stirred at room temperature for 1-8 h. The crude reaction mixture was directly loaded onto a silica gel column without aqueous workup, and pure products **6fp-6ad** were obtained in 78-91% yield (silica gel, mixture of hexane/ethyl acetate).

Procedure F: Synthesis of 2-hydroxy-5-methoxy-3-(2-((1*R*,2*S*)-1,3,3-trimethyl-2-(3-oxobutyl)cyclohexyl)ethyl)cyclohexa-2,5-diene-1,4-dione (11) and 2-Hydroxy-3-(2-((1*R*,2*R*,4a*S*,8a*S*)-2-hydroxy-2,5,5,8a-tetramethyldecahydronaphthalen-1-yl)ethyl)-5-methoxycyclohexa-2,5-diene-1,4-dione (16): In an ordinary glass vial equipped with a magnetic stirring bar, to 0.3 mmol of the aldehyde **10/15**, 0.3 mmol of 2-hydroxy-5-methoxycyclohexa-2,5-diene-1,4-dione **8** and 0.33 mmol of Hantzsch ester **4** was added in 1.0 mL of DCM and 0.03 mmol of benzylamine **3d** was added and the corresponding reaction mixture was stirred at room temperature for 10-12 h. The crude reaction mixture was directly loaded onto a silica gel column without aqueous workup, and pure cascade chiral products (+)-**11** and (+)-**16** were obtained in 75% and 82% yield, respectively (silica gel, mixture of hexane/ethyl acetate).

Procedure G: Preparation of 2-*n*-undecyl-4-methoxy-3,6-dioxocyclohexa-1,4-dien-1-yl acetate (22f): In an oven dried 10 mL round bottom flask equipped with a magnetic stirring bar, to the compound **9f** (0.3 mmol) in dry DCM (1.0 mL), acetyl chloride (3.0 equiv.) and con. H_2SO_4 (30 mol%) were added sequentially. The resulting reaction mixture was stirred at room temperature for 5 h. The crude reaction mixture was directly loaded onto a silica gel column without aqueous workup to obtain **22f** in 86% yield.

Procedure H: Preparation of (1*R*,2*R*,8a*S*)-2,5,5,8a-tetramethyl-2-((trimethylsilyl)oxy)decahydronaphthalene-1-carbaldehyde [(-)-13]: In a round bottom flask equipped with a magnetic stirring bar, 0.1 mmol (23.8 mg) of the chiral aldehyde (+)-**10** was added to DCM (0.1 M, 1.0 mL) under argon atmosphere at 0 °C. The reaction mixture was stirred for 5 min and then DMAP (1.5 equiv, 18.3 mg), DIPEA (3.0 equiv, 52 µL), was added to the reaction mixture. After 5 min, TMS-OTf (3.0 equiv, 66.6 µL) was added to the reaction mixture drop by drop and stirred at 25 °C for 12 h. The reaction mixture was quenched with saturated aqueous $NaHCO_3$ solution and extracted with DCM, concentrtaed in vacuo, purified by flash column chromatography to give (-)-**13** in 93% yield.

Procedure I: Preparation of 2-Hydroxy-5-methoxy-3-(2-((1*S*,4a*S*,8a*S*)-5,5,8a-trimethyl-2-methylenedecahydronaphthalen-1-yl)ethyl)cyclohexa-2,5-diene-1,4-dione (17), 2-Hydroxy-5-methoxy-3-(2-((1*S*,4a*S*,8a*S*)-2,5,5,8a-tetramethyl-1,4,4a,5,6,7,8,8a-octahydronaphthalen-1-yl)ethyl)cyclohexa-2,5-diene-1,4-dione (18), and 2-Hydroxy-5-methoxy-3-(2-((4a*S*,8a*S*)-2,5,5,8a-tetramethyl-3,4,4a,5,6,7,8,8a-octahydronaphthalen-1-yl)ethyl)cyclohexa-2,5-diene-1,4-dione (19): In a round bottom flask equipped with a magnetic stirring bar, 0.13 mmol (65.0 mg) of (+)-**16** was added to DCM (0.13 M, 1.0 mL) at 25 °C. The reaction mixture was stirred for 5 min and then *p*-TSA (0.2 equiv, 4.9 mg) was added to the reaction mixture and stirred at 25 °C. Upon completion of reaction after 2 h monitored by TLC the reaction mixture was directly loaded on to the column (silica gel, 10-15% ethyl acetate/ hexane) to give mixture of (+)-**17**, **18**, and **19** in 88% yield in a 1:1:1 ratio.

Procedure J: Preparation of 2-hydroxy-5-methoxy-3-(2-((4a*S*,8a*S*)-2,5,5,8a-tetramethyl-3,4,4a,5,6,7,8,8a-octahydronaphthalen-1-yl)ethyl)cyclohexa-2,5-diene-1,4-dione (19): In a round bottom flask equipped with a magnetic stirring bar, 0.05 mmol (18.6 mg) of (+)-**17**, **18**, and **19** was added to DCM (0.05 M, 1.0 mL) at 0 °C under argon atmosphere. The reaction mixture was stirred for 5 min and $BF_3.OEt_2$ (1.0 equiv, 6.9 µL) was added to the reaction mixture and was stirred at the same temperature for 1 h. The reaction mixture was quenched with saturated aqueous NH_4Cl solution and extracted with DCM, concentrated in vacuo, purified by flash column chromatography column (silica gel, 10-15% ethyl acetate/ hexane) to give (+)-**19** in 81% yield.

Procedure K: Preparation of 2,5-dihydroxy-3-(2-((8a*S*)-2,5,5,8a-tetramethyl-3,4,4a,5,6,7,8,8a-octahydronaphthalen-1-yl)ethyl)cyclohexa-2,5-diene-1,4-dione [(-)-21]: In a round bottom flask equipped with a magnetic stirring bar, 0.025 mmol (9.3 mg) of (+)-**19** was added to toluene (0.025 M, 1.0 mL) at 25 °C. The reaction mixture was stirred for 5 min

and then *p*-TSA (0.5 equiv, 2.4 mg) was added to the reaction mixture and was stirred at 100 °C. Upon completion of reaction after 6 h monitored by TLC the reaction mixture was quenched with water and extracted with DCM, concentrated in *vacuo* to give product (-)-**21** in 89% yield.

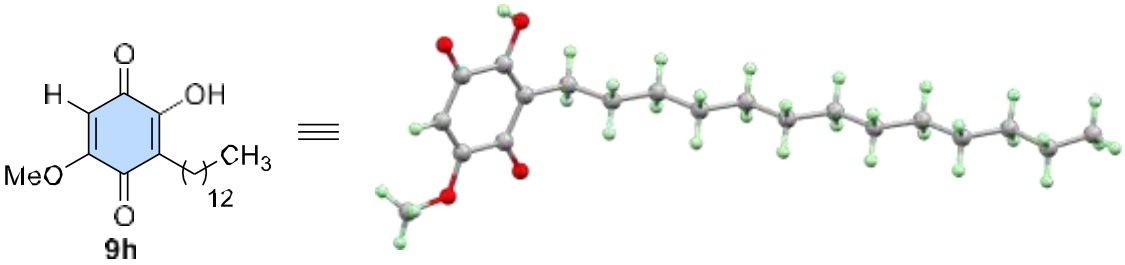
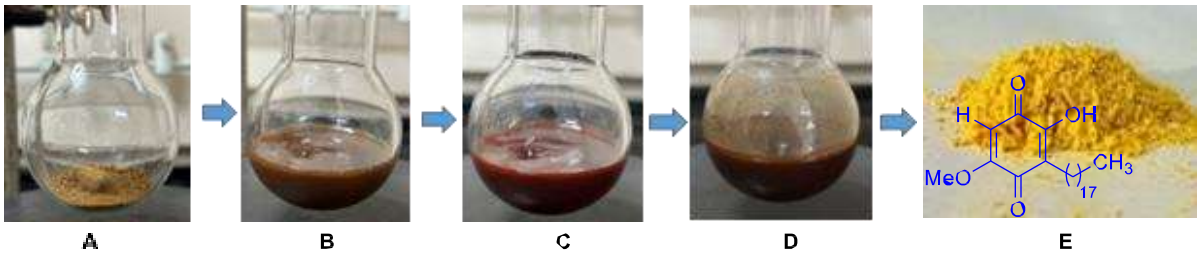


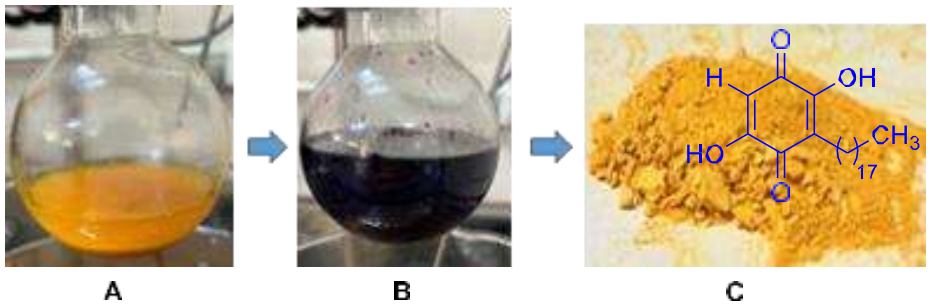
Figure S1: X-Ray crystal structure of 5-*O*-methylrapanone **9h.**

Step-1: **Organocatalytic Reductive Coupling of 8 with 2l to give Natural Product Irisoquin 9l**



A: Addition of compound **8** in DCM at room temperature; **B**: Addition of aldehyde **2l**; **C**: Addition of catalyst, benzylamine **3d** to the reaction mixture; **D**: Addition of Hantzsch ester **4** to the reaction mixture at room temperature and appearance of the reaction mixture after 2 h; **E**: The column purification of the crude reaction mixture yielded irisoquin **9l** as a yellow solid.

Step-2: **Synthesis of Demethylated-Irisoquin 5l through Hydrolysis of 9l**



A: Compound **9l** is added to ethanol at room temperature; **B**: Appearance of the reaction mixture after the addition of aqueous 2.0 M sodium hydroxide solution and kept heating at 70 °C for 2 h; **C**: The reaction mixture is acidified with 2.0 N aqueous HCl solution and extracted with ethyl acetate and washed with brine to give demethylated-irisoquin (**5l**) as orange solid without further purification.

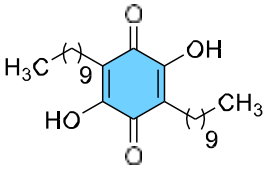
Figure S2. Pictorial representation for gram-scale synthesis of irisoquin **9l** and demethylated-irisoquin **5l**.

General Observations during the Recording of NMR Samples:

[1] Because of the keto-enol/enol-enol tautomerism in compounds like 2,5-dihydroxy-3-alkylcyclohexa-2,5-diene-1,4-diones **5**, 2,5-dialkyl-3,6-dihydroxycyclohexa-2,5-diene-1,4-diones **6** and 3-alkyl-2-hydroxy-5-methoxycyclohexa-2,5-diene-1,4-diones **9**, many numbers of isomers are existed and they are in equilibrium in the solution. Due to this reason, we observed that total number of protons integration in aliphatic region is bit more compared to the actual number for few compounds [**9j**, **9k**, **9l**, **9m**, **9n**, **5a**, **5e**, **5f**, and **5h**] of ^{1}H NMR spectra in the $CDCl_3$ or CD_3OD or DMSO-D_6 as a reference solvent.

[2] Because of the keto-enol/enol-enol tautomerism in compounds like 2,5-dihydroxy-3-alkylcyclohexa-2,5-diene-1,4-diones **5** and 2,5-dialkyl-3,6-dihydroxycyclohexa-2,5-diene-1,4-diones **6**, ^{13}C NMR resulted in the poor resolution of two sets of 1,3-dicarbonyl carbons [2 x (2 x C=O)] even after more than 2000 scans in the $CDCl_3$ or CD_3OD or DMSO-D_6 as a reference solvent for NMR.

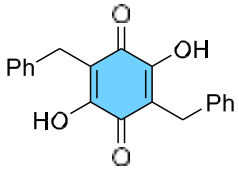
2,5-Didecyl-3,6-dihydroxycyclohexa-2,5-diene-1,4-dione (6a):



6a

The title compound was prepared following the procedure **A**, purified by column chromatography using EtOAc/hexane (2.0:8.0 to 3.0:7.0), and was isolated as orange solid. Yield: 26% (33.0 mg), Mp.: 105-107 ºC; IR (Neat): ν_{max} 3317, 2919, 2849, 1610, 1460, 1308, 1279, 1129, 764, 711, and 595 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.62 (2H, br s, *OH*), 2.41 (4H, t, *J* = 7.5 Hz), 1.46 (4H, pentet, *J* = 7.5 Hz), 1.25 (28H, br s), 0.87 (6H, t, *J* = 7.0 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz, DEPT-135): δ 116.0 (2 x C), 31.9 (2 x CH_2), 29.6 (2 x CH_2), 29.5 (4 x CH_2), 29.4 (2 x CH_2), 29.3 (2 x CH_2), 28.1 (2 x CH_2), 22.7 (2 x CH_2), 22.4 (2 x CH_2), 14.1 (2 x CH_3); HRMS (ESI-TOF) *m*/*z*: [M + Na]$^{+}$ Calcd for $C_{26}H_{44}O_4Na$ 443.3137; Found 443.3138.

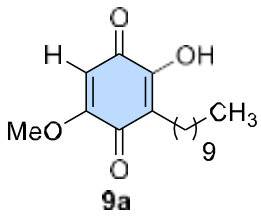
2,5-Dibenzyl-3,6-dihydroxycyclohexa-2,5-diene-1,4-dione (6p): The title compound was prepared following the procedure **B**, purified by column chromatography using EtOAc/hexane (2.0:8.0 to 3.0:7.0), and was isolated yellow semi solid. Yield: 30% (28.8 mg); IR (Neat): ν_{max} 3298, 2922, 2852, 1729, 1616, 1451, 1373, 1294, 1252, 1182, 1077, 1017, 860, 761, 699, 620, and 447 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.71



6p

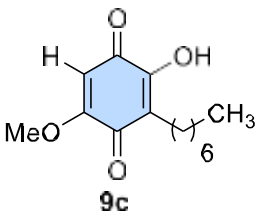
(2H, br s, *OH*), 7.29-7.28 (4H, m), 7.25-7.23 (4H, m), 7.19-7.16 (2H, tt, *J* = 7.0, 1.5 Hz), 3.74 (4H, s); ^{13}C NMR ($CDCl_3$, 125 MHz, DEPT-135): δ 138.5 (2 x C), 128.9 (4 x CH), 128.5 (4 x CH), 126.5 (2 x CH), 115.1 (2 x C), 28.4 (2 x CH_2); HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ Calcd for $C_{20}H_{17}O_4$ 321.1127; Found 321.1127.

3-Decyl-2-hydroxy-5-methoxycyclohexa-2,5-diene-1,4-dione (9a): The title compound was prepared following the procedure **C**, purified by column chromatography using EtOAc/hexane (1.0:9.0 to 1.5:8.5), and was isolated as yellow solid. Yield: 82% (72.4 mg). Mp.: 105-107 ºC; IR (Neat): ν_{max} 3349, 2953, 2915, 2848, 1632, 1594, 1467, 1442, 1307, 1196, 1111, 1030, 837 and 682 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 5.83 (1H, s, olefinic-*H*), 3.85 (3H, s, OC*H*$_3$), 2.43 (2H, t, *J* = 7.6 Hz), 1.44 (2H, pentet, *J* = 7.6 Hz), 1.28-1.24 (14H, m), 0.86 (3H, t, *J* = 6.8 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, DEPT-135): δ 182.8 (C, *C*=*O*), 181.7 (C, *C*=*O*), 161.1 (C), 151.5 (C), 119.3 (C), 102.1 (CH), 56.7 (O*C*H$_3$), 31.9 (CH_2), 29.6 (CH_2), 29.5 (2 x CH_2), 29.4 (CH_2), 29.3 (CH_2), 28.0 (CH_2), 22.6 (CH_2), 22.6 (CH_2), 14.1 (CH_3); HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ Calcd for $C_{17}H_{27}O_4$ 295.1909; Found 295.1907.



9a

2-Hydroxy-5-methoxy-3-pentylcyclohexa-2,5-diene-1,4-dione (9b): The title compound was prepared following the procedure **C**, purified by column chromatography using EtOAc/hexane (1.0:9.0 to 1.5:8.5), and was isolated yellow solid. Yield: 80% (53 mg). Mp.: 90-92 ºC; IR (Neat): ν_{max} 3345, 2925, 1630, 1590, 1441, 1463, 1296, 1197, 1108, 1039, 837 and 683 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.28 (1H, br s, O*H)*, 5.83 (1H, s, olefinic-*H*), 3.84 (3H, s, OC*H*$_3$), 2.42 (2H, t, *J* = 7.5 Hz), 1.45 (2H, quintet, *J* = 7.0 Hz), 1.29 (4H, br s), 0.86 (3H, t, *J* = 6.0 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, DEPT-135): δ 182.8 (C, *C*=O), 181.7 (C, *C*=O), 161.1 (C), 151.6 (C), 119.3 (C), 102.2 (CH), 56.7 (OC*H*$_3$), 31.7 (CH_2), 27.7 (CH_2), 22.6 (CH_2), 22.4 (CH_2), 13.9 (CH_3); HRMS (ESI-TOF) *m*/*z*: $[M + Na]^+$ Calcd for $C_{12}H_{16}O_4Na$ 247.0946; Found 247.0948.

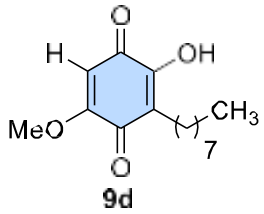


9c

3-Heptyl-2-hydroxy-5-methoxycyclohexa-2,5-diene-1,4-dione (9c): The title compound was prepared following the procedure **C**, purified by column chromatography using EtOAc/hexane (1.0:9.0 to 1.5:8.5), and was isolated yellow semi solid. Yield: 80% (60 mg). IR (Neat): ν_{max} 3337, 2922, 2845, 1630, 1594, 1462, 1442, 1442, 1355,

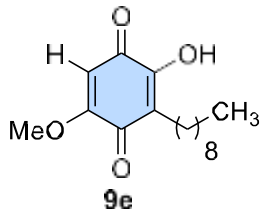
1234, 1203, 1111, 837 and 688 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 7.26 (1H br s, *OH*), 5.84 (1H, s, olefinic-*H*), 3.86 (3H, s, *OCH_3*), 2.44 (2H, t, *J* = 7.5 Hz), 1.46 (2H, pentet, *J* = 7.5 Hz), 1.31-1.26 (8H, m), 0.88 (3H, t, *J* = 6.5 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, DEPT-135): δ 182.8 (C, *C*=O), 181.6 (C, *C*=O), 161.1 (C), 151.5 (C), 119.3 (C), 102.1 (CH), 56.7 (*OCH_3*), 31.7 (CH_2), 29.5 (CH_2), 29.0 (CH_2), 28.0 (CH_2), 22.6 (2 x CH_2), 14.0 (CH_3), HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ Calcd for $C_{14}H_{21}O_4$ 253.1440; Found 253.1436.

2-Hydroxy-5-methoxy-3-octylcyclohexa-2,5-diene-1,4-dione (9d): The title compound was prepared following the procedure **C**, purified by column chromatography using EtOAc/hexane (1.0:9.0 to 1.5:8.5), and was isolated yellow solid. Yield: 87% (69 mg). Mp.: 128-130 ºC IR (Neat): ν_{max} 3338, 2915, 2847, 1630, 1595, 1463, 1442, 1352, 1383, 1304, 1202, 1113 1024, 983, 838, and 689 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 7.24 (1H, br s, *OH*), 5.83 (1H, s, olefinic-*H*), 3.85 (3H, s, *OCH_3*), 2.43 (2H, t, *J* = 7.5 Hz), 1.44 (2H, quintet, *J* = 7.5 Hz), 1.29-1.25 (10H, m), 0.86 (3H, t, *J* = 7.0 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz, DEPT-135): δ 182.8 (C, *C*=O), 181.7 (C, *C*=O), 161.1 (C), 151.5 (C), 119.3 (C), 102.1 (CH), 56.7 (*OCH_3*), 31.8 (CH_2), 29.5 (CH_2), 29.3 (CH_2), 29.2 (CH_2), 28.0 (CH_2), 22.6 (CH_2), 22.6 (CH_2), 14.0 (CH_3); HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ Calcd for $C_{15}H_{23}O_4$ 267.1596; Found 267.1594.



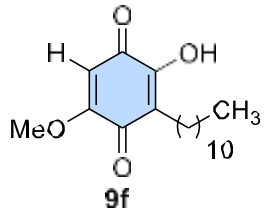
9d

2-Hydroxy-5-methoxy-3-nonylcyclohexa-2,5-diene-1,4-dione (9e): The title compound was prepared following the procedure **C**, purified by column chromatography using EtOAc/hexane (1.0:9.0 to 1.5:8.5), and was isolated yellow solid. Yield: 80% (67.3 mg). Mp.: 110-112 ºC; IR (Neat): ν_{max} 3337, 2917, 2849, 1659, 1630, 1593, 1463, 1442, 1382, 1200, 1113, 838 and 688 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 5.83 (1H, s, olefinic-*H*), 3.85 (3H, s, *OCH_3*), 2.42 (2H, t, *J* = 7.5 Hz), 1.44 (2H, quintet, *J* = 7.0 Hz), 1.28-1.24 (12H, m), 0.87 (3H, t, *J* = 3.5 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz, DEPT-135): δ 182.8 (C, *C*=O), 181.6 (C, *C*=O), 161.1 (C), 151.5 (C), 119.3 (C), 102.1 (CH), 56.7 (*OCH_3*), 31.8 (CH_2), 29.5 (CH_2), 29.5 (CH_2), 29.4 (CH_2), 29.3 (CH_2), 28.0 (CH_2), 22.6 (CH_2), 22.60 (CH_2), 14.1 (CH_3); HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ Calcd for $C_{16}H_{25}O_4$ 281.1753; Found 281.1753.



9e

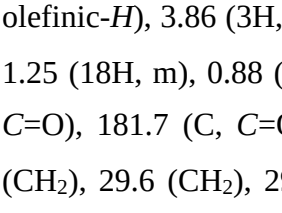
2-Hydroxy-5-methoxy-3-undecylcyclohexa-2,5-diene-1,4-dione 9f [5-*O*-Methylembelin]:



9f

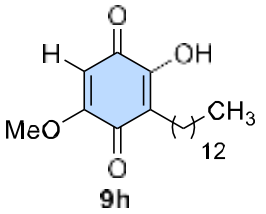
The title compound was prepared following the procedure **C**, purified by column chromatography using EtOAc/hexane (1.0:9.0 to 1.5:8.5), and was isolated yellow solid. Yield: 80% (74 mg). Mp.: 104-106 ºC; IR (Neat): ν_{max} 3348, 2916, 2849, 1632, 1595, 1465, 1444, 1196, 1111, 1036, 839 and 682 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.23 (1H, br s, *OH*), 5.83 (1H, s, olefinic-*H*), 3.85 (3H, s, *OCH₃*), 2.4 (2H, t, *J* = 8.0 Hz), 1.43 (2H, pent, *J* = 7.2 Hz), 1.24 (17H, s). 0.87 (3H, t, *J* = 6.4 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, DEPT-135): δ 182.8 (C, *C*=O), 181.6 (C, *C*=O), 161.1 (C), 151.5 (C), 119.3 (C), 102.1 (CH), 56.7 (*OCH₃*), 31.9 (CH_2), 29.63 (CH_2), 29.6 (CH_2), 29.5 (2 x CH_2), 29.4 (CH_2), 29.3 (CH_2), 28.0 (CH_2), 22.6 (CH_2) 22.61 (CH_2); HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ Calcd for $C_{18}H_{29}O_4$ 309.2066; Found 309.2066.

3-Dodecyl-2-hydroxy-5-methoxycyclohexa-2,5-diene-1,4-dione (9g): The title compound was prepared following the procedure **C**, purified by column chromatography using EtOAc/hexane (1.0:9.0 to 1.5:8.5), and was isolated yellow solid. Yield: 88% (85 mg). Mp.: 102-104 ºC; IR (Neat): ν_{max} 3351, 2914, 2848, 1632, 1596, 1468, 1442, 1304, 1198, 1111, 837 and 680 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 5.84 (1H, s, olefinic-*H*), 3.86 (3H, s, *OCH₃*), 2.44 (2H, t, *J* = 7.5 Hz), 1.45 (2H, pentet, *J* = 7.0 Hz), 1.29-1.25 (18H, m), 0.88 (3H, t, *J* = 6.5); ^{13}C NMR ($CDCl_3$, 125 MHz, DEPT-135): δ 182.8 (C, *C*=O), 181.7 (C, *C*=O), 161.1 (C), 151.5 (C), 119.3 (C), 102.1 (CH), 56.7 (*OCH₃*), 31.9 (CH_2), 29.6 (CH_2), 29.6 (2 x CH_2), 29.6 (CH_2), 29.5 (CH_2), 29.4 (CH_2), 29.3 (CH_2), 28.0 (CH_2), 22.7 (CH_2), 22.6 (CH_2), 14.1 (CH_3); HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ Calcd for $C_{19}H_{31}O_4$ 323.2222; Found 323.2220.



9g

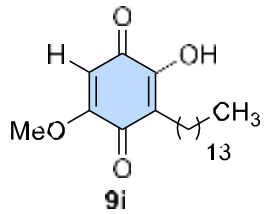
2-Hydroxy-5-methoxy-3-tridecylcyclohexa-2,5-diene-1,4-dione 9h [5-*O*-Methylrapanone]: The title compound was prepared following the procedure **C**, purified by column chromatography using EtOAc/hexane (1.0:9.0 to 1.5:8.5), and was isolated yellow solid. Yield: 80% (80 mg). Mp.: 98-100 ºC; IR (Neat): ν_{max} 3349, 2916, 2849, 1717, 1632, 1594, 1443, 1377, 1287, 1199, 1109, 1041, 885 and 683 cm^{-1}. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.25 (1H, br s, O*H*), 5.83 (1H, s, olefinic-*H*), 3.85 (3H, s, *OCH₃*), 2.43 (2H, t, *J* = 7.5 Hz), 1.44 (2H, pentet, *J* = 7.5 Hz), 1.30-1.24 (20H, m),



9h

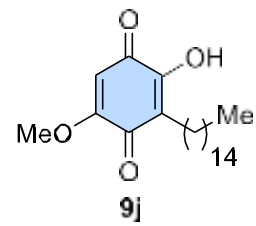
0.87 (3H, t, *J* = 7.0 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz, DEPT-135): δ 182.8 (C, *C*=O), 181.7 (C, *C*=O), 161.1 (C), 151.5 (C), 119.3 (C), 102.1 (CH), 56.7 (O*C*H$_3$), 31.9 (CH_2), 29.6 (4 x CH_2), 29.5 (2 x CH_2), 29.4 (CH_2), 29.3 (CH_2), 28.0 (CH_2), 22.7 (CH_2), 22.6 (CH_2), 14.1 (CH_3); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{20}H_{33}O_4$ 337.2379; Found 337.2377.

2-Hydroxy-5-methoxy-3-tetradecylcyclohexa-2,5-diene-1,4-dione (9i): The title compound was prepared following the procedure **C**, purified by column chromatography using EtOAc/hexane (1.0:9.0 to 1.5:8.5), and was isolated yellow solid. Yield: 85% (89 mg). Mp.: 98-100 ºC; IR (Neat): ν_{max} 3351, 2913, 2848, 1633, 1596, 1470, 1378, 1199, 1110, 1037, 837 and 681 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.22 (1H, br s, O*H*), 5.83 (1H, s, olefinic-*H*), 3.85 (3H, s, O*CH*$_3$), 2.43 (2H, t, *J* = 7.5 Hz), 1.45 (2H, pentet, *J* = 7.0 Hz), 1.29-1.24 (22H, m), 0.87 (3H, t, *J* = 6.5 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz, DEPT-135): δ 182.8 (C, *C*=O), 181.7 (C, *C*=O), 161.1 (C), 151.5 (C), 119.3 (C), 102.1 (CH), 56.7 (O*C*H$_3$), 31.9 (CH_2), 29.6 (5 x CH_2), 29.6 (2 x CH_2), 29.4 (CH_2), 29.3 (CH_2), 28.0 (CH_2), 22.7 (CH_2), 22.6 (CH_2), 14.1 (CH_3); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{21}H_{35}O_4$ 351.2534; Found 351.2531.

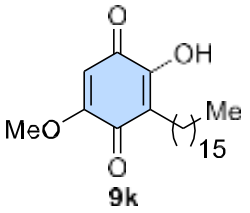


9i

2-Hydroxy-5-methoxy-3-pentadecylcyclohexa-2,5-diene-1,4-dione 9j [Sorgoleone-364]: The title compound was prepared following the procedure **C**, purified by column chromatography using EtOAc/hexane (1.0:9.0 to 1.5:8.5), and was isolated yellow solid. Yield: 81% (88.7 mg). Mp.: 96-98 ºC. IR (Neat): ν_{max} 3349, 2915, 2848, 1634, 1596, 1466, 1303, 1230, 1198 1111, 1032, 839 and 684 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 5.83 (1H, s, olefinic-*H*), 3.85 (3H, s, O*CH*$_3$), 2.43 (2H, t, *J* = 7.5 Hz), 1.44 (2H, pentet, *J* = 7.5 Hz), 1.29-1.24 (24H, m), 0.87 (3H, t, *J* = 7.0 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz, DEPT-135): δ 182.8 (C, *C*=O), 181.7 (C, *C*=O), 161.1 (C), 151.5 (C), 119.3 (C), 102.1 (CH), 56.7 (O*C*H$_3$), 31.9 (CH_2), 29.7 (2 x CH_2), 29.7 (2 x CH_2), 29.6 (2 x CH_2), 29.5 (2 x CH_2), 29.4 (CH_2), 29.3 (CH_2), 28.0 (CH_2), 22.7 (CH_2), 22.6 (CH_2), 14.1 (CH_3); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{22}H_{37}O_4$ 365.2692; Found 365.2692.



9j

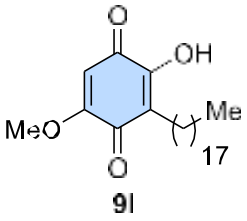


9k

3-Hexadecyl-2-hydroxy-5-methoxycyclohexa-2,5-diene-1,4-dione 9k [Irisoquin A]: The title compound was prepared following the procedure **C**, purified by column chromatography using EtOAc/hexane (1.0:9.0 to 1.5:8.5), and was isolated yellow solid. Yield: 87% (99 mg).

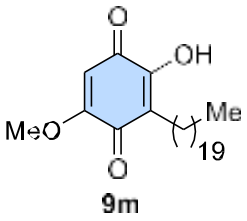
Mp.: 142-144 ºC. IR (Neat): ν_{max} 3351, 2913, 2848, 1633, 1595, 1469, 1443, 1378, 1357, 1306, 1197, 1111, 1031, 837 and 681 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.25 (1H, br s, *OH*), 5.84 (1H, s, olefinic-*H*), 3.86 (3H, s, *OCH₃*), 2.44 (2H, t, *J* = 7.6 Hz), 1.45 (2H, pentet, *J* = 7.5 Hz), 1.25 (26H, br s), 0.88 (3H, t, *J* = 6.4 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, DEPT-135): δ 182.8 (C, *C*=O), 181.6 (C, *C*=O), 161.1 (C), 151.5 (C), 119.3 (C), 102.1 (CH), 56.7 (O*C*H_3), 31.9 (CH_2), 29.7 (3 x CH_2), 29.7 (2 x CH_2), 29.6 (2 x CH_2), 29.5 (2 x CH_2), 29.4 (CH_2), 29.3 (CH_2), 28.0 (CH_2), 22.7 (CH_2), 22.6 (CH_2), 14.1 (CH_3); HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ Calcd for $C_{23}H_{39}O_4$ 379.2848; Found 379.2848.

2-Hydroxy-5-methoxy-3-octadecylcyclohexa-2,5-diene-1,4-dione 9l [Irisoquin]: The title compound was prepared following the procedure **C**, purified by column chromatography using EtOAc/hexane (1.0:9.0 to 1.5:8.5), and was isolated yellow solid. Yield: 81% (95.4 mg). Mp.: 130-132 ºC. IR (Neat): ν_{max} 3351, 2913, 2848, 1633, 1596, 1471, 1442, 1378, 1310, 1197, 1111, 1035, 842 and 682 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 5.84 (1H, s, olefinic-*H*), 3.86 (3H, s, *OCH₃*), 2.44 (2H, t, *J* = 7.6 Hz), 1.44 (2H, quintet, *J* = 7.2 Hz), 1.30-1.25 (30H, m), 0.88 (3H, t, *J* = 6.4 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, DEPT-135): δ 182.8 (C, *C*=O), 181.6 (C, *C*=O), 162.1 (C), 151.5 (C), 119.3 (C), 102.1 (CH), 56.7 (O*C*H_3), 31.9 (CH_2), 29.7 (6 x CH_2), 29.6 (3 x CH_2), 29.5 (2 x CH_2), 29.4 (CH_2), 29.3 (CH_2), 28.0 (CH_2), 22.7 (CH_2), 22.6 (CH_2), 14.1 (CH_3); HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ Calcd for $C_{25}H_{43}O_4$ 407.3161; Found 407.3161.



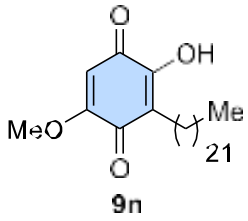
9l

2-Hydroxy-3-icosyl-5-methoxycyclohexa-2,5-diene-1,4-dione 9m [Irisoquin D]: The title compound was prepared following the procedure **C**, purified by column chromatography using EtOAc/hexane (1.0:9.0 to 1.5:8.5), and was isolated yellow solid. Yield: 84% (109 mg). Mp.: 138-140 ºC. IR (Neat): ν_{max} 3350, 2912, 2848, 1633, 1595, 1470, 1378, 1308, 1198, 1111, 1033, 837 and 682 cm^{-1}; ^{1}H NMR ($CDCl_3$, 125 MHz, 500 MHz): δ 7.22 (1H, br s, *OH*), 5.84 (1H, s, olefinic-*H*), 3.86 (3H, s, *OCH₃*), 2.44 (2H, t, *J* = 7.5 Hz), 1.48-1.42 (2H, pentet, *J* = 7.5 Hz), 1.30-1.24 (34H, m), 0.88 (3H, t, *J* = 7.0 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz, DEPT-135): δ 182.8 (C, *C*=O), 181.6 (C, *C*=O), 161.1 (C), 151.5 (C), 119.2 (C), 102.1 (CH), 56.7 (O*C*H_3), 31.9 (CH_2), 29.7 (9 x CH_2), 29.6 (2 x CH_2), 29.5 (2 x CH_2), 29.4 (CH_2), 29.3 (CH_2), 28.0 (CH_2), 22.7 (CH_2), 22.6 (CH_2), 14.1 (CH_3); HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ Calcd for $C_{27}H_{47}O_4$ 435.3474; Found 435.3472.



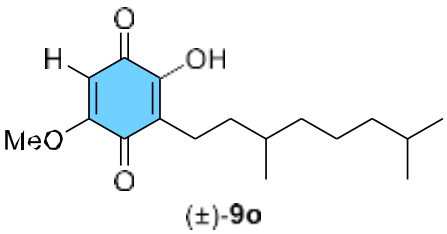
9m

3-Docosyl-2-hydroxy-5-methoxycyclohexa-2,5-diene-1,4-dione 9n [Irisoquin F]: The title compound was prepared following the procedure **C**, purified by column chromatography using EtOAc/hexane (1.0:9.0 to 1.5:8.5), and was isolated yellow solid. Yield: 78% (108.3 mg). Mp.: 120-122 ºC; IR (Neat): ν_{max} 3352, 2913, 2848, 1635, 1596, 1471, 1439, 1378, 1308, 1199, 1111, 1033, 837, 715 and 683 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.25 (1H, br s, *OH*), 5.84 (1H, s, olefinic-*H*), 3.86 (3H, s, OC*H*$_3$), 2.44 (2H, t, *J* = 7.5 Hz), 1.44 (2H, septet, *J* = 7.0 Hz), 1.25 (38H, br s), 0.88 (3H, t, *J* = 6.5 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz, DEPT-135): δ 182.8 (C, *C*=O), 181.7 (C, *C*=O), 161.1 (C), 151.5 (C), 119.3 (C), 102.1 (CH), 56.7 (O*C*H$_3$), 31.9 (CH_2), 29.7 (10 x CH_2), 29.6 (3 x CH_2), 29.5 (2 x CH_2), 29.4 (CH_2), 29.3 (CH_2), 28.0 (CH_2), 22.7 (CH_2), 22.6 (CH_2), 14.1 (CH_3); HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ Calcd for $C_{29}H_{51}O_4$ 463.3787; Found 463.3788.



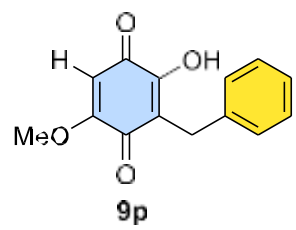
9n

3-(3,7-Dimethyloctyl)-2-hydroxy-5-methoxycyclohexa-2,5-diene-1,4-dione (±)-9o: The title compound was prepared following the procedure **C**, purified by column chromatography using EtOAc/hexane (1.0:9.0 to 1.5:8.5), and was isolated yellow solid. Yield: 85% (75 mg). Mp.: 90-92 ºC; IR (Neat): ν_{max} 3342, 2952, 1633, 1593, 1444, 1360, 1283, 1196, 1115, 837, 760 and 688 cm^{-1}. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.31 (1H, br s, *OH*), 5.84 (1H, s, olefinic-*H*), 3.86 (3H, s, *OCH*$_3$), 2.46-2.41 (2H, m), 1.52-1.40 (3H, m), 1.33-1.20 (4H, m), 1.15-1.08 (3H, m), 0.92 (3H, d, *J* = 6.5 Hz), 0.86 (6H, d, *J* = 7.0 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, DEPT-135): δ 182.8 (C, *C*=O), 181.6 (C, *C*=O), 161.1 (C), 151.4 (C), 119.6 (C), 102.2 (CH), 56.7 (O*C*H$_3$), 39.3 (CH_2), 36.9 (CH_2), 35.0 (CH_2), 32.9 (CH), 29.9 (CH), 24.6 (CH_2), 22.7 (CH_3), 22.6 (CH_3), 20.3 (CH_2), 19.4 (CH_3); HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ Calcd for $C_{17}H_{27}O_4$ 295.1909; Found 295.1909.



(±)-**9o**

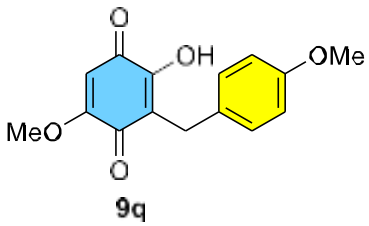
3-Benzyl-2-hydroxy-5-methoxycyclohexa-2,5-diene-1,4-dione (9p): The title compound was prepared following the procedure **C**, purified by column chromatography using EtOAc/hexane (1.2:8.8 to 2.0:8.0), and was isolated yellow solid. Mp.: 155-157 ºC. Yield: 83% (60.7 mg). IR (Neat): ν_{max} 3341, 2922, 1640, 1596, 1356, 1221, 1034, 978, 865, 742, 695 and 626 cm^{-1}. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.32 (2H, d, *J* = 7.5 Hz), 7.24, (2H, t, *J* = 7.5 Hz), 7.16 (1H, t, *J* = 7.5 Hz), 5.83 (1H, s, olefinic-*H*), 3.83



9p

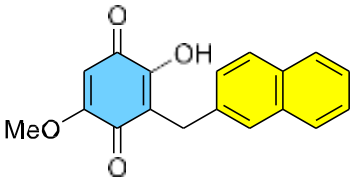
(3H, s, *OCH*$_3$), 3.78 (2H, s); ^{13}C NMR ($CDCl_3$, 100 MHz, DEPT-135): δ 182.7 (C, *C*=O), 181.3 (C, *C*=O), 161.1 (C), 151.6 (C), 138.7 (C), 129.0 (2 x CH), 128.4 (2 x CH), 126.3 (CH), 117.9 (C), 102.3 (CH), 56.7 (*OCH*$_3$), 28.4 (CH_2); HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ Calcd for $C_{14}H_{13}O_4$ 245.0814; Found 245.0814.

2-Hydroxy-5-methoxy-3-(4-methoxybenzyl)cyclohexa-2,5-diene-1,4-dione (9q): The title compound was prepared following the procedure **C**, purified by column chromatography using EtOAc/hexane (1.0:9.0 to 2.0:8.0), and was isolated yellow semi solid. Yield: 80% (65.6 mg). IR (Neat): ν_{max} 3315, 2812, 1612, 1577, 1556, 1382, 1260, 1066, 1031, 952, 924, 814 and 612 cm^{-1}. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.43 (1H, br s, *OH*), 7.24 (2H, d, *J* = 8.5 Hz), 6.78 (2H, d, *J* = 8.5 Hz), 5.82 (1H, s, olefinic-*H*), 3.83 (3H, s, *OCH*$_3$), 3.75 (3H, s, *OCH*$_3$), 3.71 (2H, s); ^{13}C NMR ($CDCl_3$, 100 MHz, DEPT-135): δ 182.8 (C, *C*=O), 181.4 (C, *C*=O), 161.0 (C), 158.0 (C), 151.3 (C), 130.8 (C), 130.0 (2 x CH), 118.2 (C), 113.7 (2 x CH), 102.2 (CH), 56.7 (O*C*H$_3$), 55.2 (O*C*H$_3$), 27.4 (CH_2); HRMS (ESI-TOF) *m*/*z*: $[M + Na]^+$ Calcd for $C_{15}H_{14}O_5Na$ 297.0739; Found 297.0741.



9q

2-Hydroxy-5-methoxy-3-(4-nitrobenzyl)cyclohexa-2,5-diene-1,4-dione (9r): The title compound was prepared following the procedure **C**, purified by column chromatography using EtOAc/hexane (2.0:8.0 to 1.0:1.0), and was isolated yellow solid. Mp.: 148-150 ºC Yield: 82% (71.0 mg). IR (Neat): ν_{max} 3321, 1647, 1597, 1512, 1376, 1346, 1304, 1210, 1166, 1041, 982, 934, 849 and 708 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.12 (2H, d, *J* = 8.5 Hz), 7.49 (2H, d, *J* = 8.5 Hz), 5.91 (1H, s, olefinic-*H*), 3.88 (3H, s, O*CH*$_3$); ^{13}C NMR ($CDCl_3$, 125 MHz, DEPT-135): δ 182.2 (C, *C*=O), 181.0 (C, *C*=O), 161.1 (C), 152.0 (C), 146.6 (C), 146.3. (C), 129.9 (2 x CH), 123.7 (2 x CH), 116.2 (C), 102.5 (CH), 56.9 (O*C*H$_3$), 28.4 (CH_2); HRMS (ESI-TOF) *m*/*z*: $[M + Na]^+$ Calcd for $C_{14}H_{11}NO_6Na$ 312.0484; Found 312.0489.

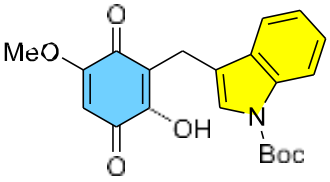


9s

2-Hydroxy-5-methoxy-3-(naphthalen-2-ylmethyl)cyclohexa-2,5-diene-1,4-dione (9s): The title compound was prepared following the procedure **C**, purified by column chromatography using EtOAc/hexane (1.8:8.2 to 2.8:7.2), and was isolated yellow solid. Yield: 76% (67 mg). Mp.: 190-192

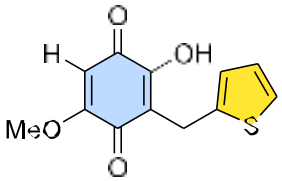
ºC; IR (Neat): ν_{max} 3328, 3066, 1656, 1595, 1356, 1310, 1211, 1032, 992, 867, 806 and 638 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 7.76 (2H, s), 7.73 (1H, d, *J* = 8.5 Hz), 7.47-7.40 (4H, m), 5.84 (1H, s, olefinic-*H*), 3.94 (2H, s), 3.80 (3H, s, *OCH*$_3$); ^{13}C NMR ($CDCl_3$, 125 MHz, DEPT-135): δ 182.7 (C, *C*=O), 181.3 (C, *C*=O), 161.1 (C), 151.6 (C), 136.2 (C), 133.5 (C), 132.1 (C), 128.0 (CH), 127.6 (CH), 127.6 (CH), 127.5 (CH), 127.4 (CH), 125.9 (CH), 125.4 (CH), 117.8 (C), 102 (CH), 56.8 (O*C*H$_3$), 28.5 (CH_2); HRMS (ESI-TOF) *m*/*z*: $[M + Na]^+$ Calcd for $C_{18}H_{14}O_4Na$ 317.0790; Found 317.0792.

***tert*-Butyl 3-((2-hydroxy-5-methoxy-3,6-dioxocyclohexa-1,4-dien-1-yl)methyl)-1*H*-indole-1-carboxylate (9t):** The title compound was prepared following the procedure **C**, purified by column chromatography using EtOAc/hexane (1.8:8.2 to 2.8:7.2), and was isolated yellow solid. Yield: 88% (101 mg). Mp.: 142-144 ºC; IR (Neat): ν_{max} 3331, 2926, 1726, 1646, 1605, 1452, 1360, 1308, 1254, 1214, 1155, 1081, 1036 and 750 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 7.72 (1H, d, *J* = 7.5 Hz), 7.72 (1H, d, *J* = 7.5 Hz), 7.48 (1H, s), 7.29-7.28 (1H, m), 7.21 (1H, dt, *J* = 7.7, 1.0 Hz), 5.83 (1H, s, olefinic-*H*), 3.85-3.84 (2H, m), 3.84 (3H, s, O*CH*$_3$), 1.65 (9H, s, 3 x *CH*$_3$); ^{13}C NMR ($CDCl_3$, 100 MHz, DEPT-135): δ 182.5 (C, *C*=O), 181.0 (C, *C*=O), 161.3 (C), 151.5 (C), 149.7 (C), 135.5. (C), 130.3 (C), 124.4 (CH), 124.1 (CH), 122.4 (CH), 119.3 (CH), 117.1 (C), 116.8 (C), 115.1 (CH), 102.3 (CH), 83.3 (C), 56.6 (O*C*H$_3$), 28.2 (3 x CH_3), 18.0 (CH_2); HRMS (ESI-TOF) *m*/*z*: $[M + Na]^+$ Calcd for $C_{21}H_{21}NO_6Na$ 406.1267; Found 406.1270.



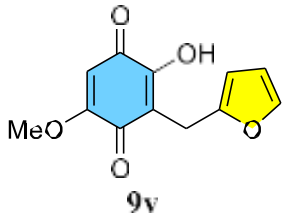
9t

2-Hydroxy-5-methoxy-3-(thiophen-2-ylmethyl)cyclohexa-2,5-diene-1,4-dione (9u): The title compound was prepared following the procedure **C**, purified by column chromatography using EtOAc/hexane (1.2:8.8 to 2.0:8.0), and was isolated yellow solid. Yield: 83% (62.3 mg). Mp.: 118-120 ºC; IR (Neat): ν_{max} 3318, 2921, 1645, 1603, 1384, 1358, 1308, 1213, 1119, 1040, 844 and 704 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 7.09 (1H, dd, *J* = 5.0, 1.0 Hz), 6.92 (1H, d, *J* = 2.5 Hz), 6.89 (1H, dd, *J* = 5.0, 3.5 Hz), 5.86 (1H, s, olefinic-*H*), 3.97 (2H, s), 3.85 (3H, s, *OCH*$_3$); ^{13}C NMR ($CDCl_3$, 100 MHz, DEPT-135): δ 182.6 (C, *C*=O), 180.9 (C, *C*=O), 161.1 (C), 151.4 (C), 140.3 (C), 126.7 (CH), 125.9 (CH), 123.9 (CH), 116.9 (C), 102.4 (CH), 56.8 (O*C*H$_3$), 22.5 (CH_2); HRMS (ESI-TOF) *m*/*z*: $[M + Na]^+$ Calcd for $C_{12}H_{10}O_4SNa$ 273.0197; Found 273.0196.



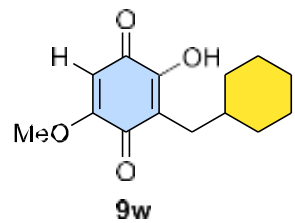
9u

3-(Furan-2-ylmethyl)-2-hydroxy-5-methoxycyclohexa-2,5-diene-1,4-dione (9v): The title compound was prepared following the procedure **C**, purified by column chromatography using EtOAc/hexane (1.2:8.8 to 2.0:8.0), and was isolated yellow solid. Yield: 86% (60.4 mg). Mp.: 110-112 ºC. IR (Neat): ν_{max} 3331, 1642, 1595, 1382, 1355, 1304, 1203, 1117, 1038, 841and 698 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.46 (1H, br s), 6.25 (1H, dd, *J* = 3.0 Hz, 2.0 Hz), 6.07 (1H, dd, *J* = 3.0, 0.5 Hz), 5.87 (1H, s, olefinic-*H*), 3.86 (3H, s, OC*H*$_3$), 3.82 (2H, s); ^{13}C NMR ($CDCl_3$, 100 MHz, DEPT-135): δ 182.5 (C, *C*=O), 180.8 (C, *C*=O), 161.1 (C), 152.1 (C), 151.4 (C), 141.2 (CH), 114.6 (C), 110.3 (CH), 106.3 (CH), 102.4 (CH), 56.8 (O*C*H$_3$), 21.3 (CH_2); HRMS (ESI-TOF) *m*/*z*: $[M + K]^+$ Calcd for $C_{12}H_{10}O_5K$ 273.0165; Found 273.0169.



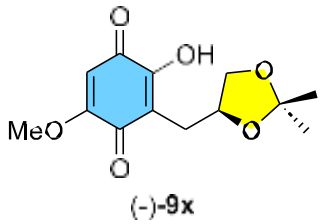
9v

3-(Cyclohexylmethyl)-2-hydroxy-5-methoxycyclohexa-2,5-diene-1,4-dione (9w): The title compound was prepared following the procedure **C**, purified by column chromatography using EtOAc/hexane (1.0:9.0 to 1.5:8.0), and was isolated yellow solid. Mp.: 160-162 ºC. Yield: 74% (55.5 mg). IR (Neat): ν_{max} 3368, 2926, 1628, 1590, 1448, 1379, 1298, 1245, 1202, 1120, 1029, 969, 835, and 675 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.30 (1H, br s, *OH*), 5.85 (1H, s, olefinic-*H*), 3.86 (3H, s), 2.35 (2H, d, *J* = 7.0 Hz), 1.72-1.49 (6H, m), 1.22-1.09 (3H, m), 1.01-0.94 (2H, m); ^{13}C NMR ($CDCl_3$, 125 MHz, DEPT-135): δ 182.8 (C, *C*=O), 181.9 (C, *C*=O), 161.1 (C), 152.0 (C), 118.1 (C), 102.2 (CH), 56.8 (O*C*H$_3$), 37.1 (CH), 33.2 (2 x CH_2), 30.1 (CH_2), 26.4 (CH_2), 26.2 (2 x CH_2); HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ Calcd for $C_{14}H_{19}O_4$ 251.1283; Found 251.1285.



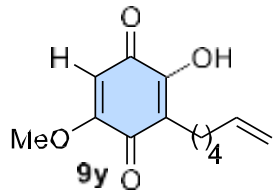
9w

(*S*)-3-((2,2-Dimethyl-1,3-dioxolan-4-yl)methyl)-2-hydroxy-5-methoxycyclohexa-2,5-diene-1,4-dione [(-)-9x]: The title compound was prepared following the procedure **C**, purified by column chromatography using EtOAc/hexane (1.2:8.8 to 2.0:8.0), and was isolated yellow semi solid. Yield: 88% (70.8 mg). IR (Neat): ν_{max} 3296, 2926, 1648, 1605, 1380, 1305, 1213, 1152, 1064, and 842 cm^{-1}; $[\alpha]_D^{25}$ = -2.50° [c = 0.100 g/100 mL, $CHCl_3$]; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.65 (1H, br s, *OH*), 5.86 (1H, s, olefinic-*H*), 4.32 (1H, sextet, *J* = 6.0 Hz), 4.02 (1H, dd, *J* = 8.5, 6.0 Hz), 3.85 (3H, s, *OCH*$_3$), 3.68 (1H, dd, *J* = 8.0, 6.0 Hz), 2.84 (1H, dd, *J* = 13.5, 7.5 Hz), 2.65 (1H, dd, *J* = 13.5, 6.0 Hz), 1.43 (3H, s), 1.31 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz, DEPT-135): δ 182.3

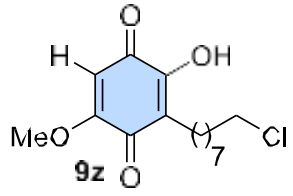


(-)-9x

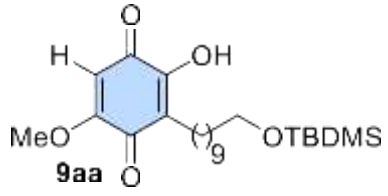
(C, *C*=O), 181.4 (C, *C*=O), 161.0 (C), 153.1 (C), 114.6 (C), 109.3 (C), 102.6 (CH), 74.2 (CH), 69.2 (CH_2), 56.8 (O*C*H_3), 27.5 (CH_2), 26.8 (CH_3), 25.6 (CH_3); HRMS (ESI-TOF) *m*/*z*: $[M + Na]^+$ Calcd for $C_{13}H_{16}O_6Na$ 291.0845; Found 291.0847.



3-(Hex-5-en-1-yl)-2-hydroxy-5-methoxycyclohexa-2,5-diene-1,4-dione (9y): The title compound was prepared following the procedure **C**, purified by column chromatography using EtOAc/hexane (1.0:9.0 to 1.5:8.5), and was isolated yellow solid. Yield: 83% (58 mg). Mp.: 78-80 ºC; IR (Neat): ν_{max} 3332, 2927, 2852, 1658, 1633, 1597, 1242, 1206, 1112, 909, 839 and 693 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ 5.84 (1H, s), 5.83-5.75 (1H, m), 4.99 (1H, qd, *J* = 17.0, 2.0 Hz), 4.92 (1H, pd, *J* = 10.0, 1.0 Hz), 3.85 (3H, s, OC*H*$_3$), 2.45 (2H, t, *J* = 8.0 Hz), 2.06 (2H, tq, *J* = 7.0, 1.5 Hz), 1.51-1.38 (4H, m); ^{13}C NMR ($CDCl_3$, 125 MHz, DEPT-135): δ 182.7 (C, *C*=O), 181.6 (C, *C*=O), 161.1 (C), 151.6 (C), 138.7 (CH), 119.0 (C), 114.4 (CH_2), 102.2 (CH), 56.7 (O*C*H_3), 33.5 (CH_2), 28.7 (CH_2), 27.4 (CH_2), 22.4 (CH_2); HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{13}H_{16}O_4Na$ 259.0946; Found 259.0942.



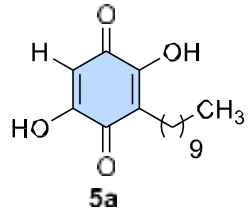
3-(8-Chlorooctyl)-2-hydroxy-5-methoxycyclohexa-2,5-diene-1,4-dione (9z): The title compound was prepared following the procedure **C**, purified by column chromatography using EtOAc/hexane (1.0:9.0 to 1.5:8.5), and was isolated yellow solid. Yield: 81% (56 mg). Mp.: 76-78 ºC; IR (Neat): ν_{max} 3352, 2922, 2852, 1636, 1594, 1465, 1313, 1201, 1117, and 650 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 7.24 (1H, br s, O*H*), 5.83 (1H, s), 3.85 (3H, s, OC*H*$_3$), 3.52 (2H, t, *J* = 7.0 Hz), 2.43 (2H, t, *J* = 7.0 Hz), 1.75 (2H, p, *J* = 7.0 Hz), 1.45-1.39 (4H, m), 1.30 (6H, m); ^{13}C NMR ($CDCl_3$, 100 MHz, DEPT-135): δ 182.7 (C, *C*=O), 181.6 (C, *C*=O), 161.1 (C), 151.5 (C), 119.1 (C), 102.1 (CH), 56.7 (O*C*H_3), 45.1 (CH_2), 32.6 (CH_2), 29.3 (CH_2), 29.1 (CH_2), 28.7 (CH_2), 27.9 (CH_2), 26.8 (CH_2), 22.5 (CH_2); HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{15}H_{21}ClO_4Na$ 323.1026; Found 323.1028.



3-(10-((*tert*-Butyldimethylsilyl)oxy)decyl)-2-hydroxy-5-methoxycyclohexa-2,5-diene-1,4-dione (9aa): The title compound was prepared following the procedure **C**, purified by column chromatography using EtOAc/hexane (1.0:9.0 to 1.5:8.5), and was isolated yellow solid. Yield: 80% (101.5 mg). Mp.: 82-84 ºC; IR (Neat): ν_{max} 3359, 2927, 2855, 1646, 1607, 1461, 1358, 1211, 1098, and 836 cm^{-1}; ^1H NMR ($CDCl_3$,

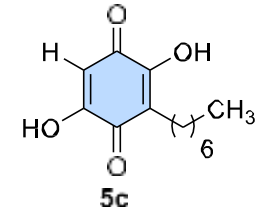
500 MHz): δ 7.24 (1H, br s, O*H*), 5.83 (1H, s), 3.85 (3H, s, OC*H*$_3$), 3.58 (2H, t, *J* = 7.0 Hz), 2.43 (2H, t, *J* = 7.5 Hz), 1.50-1.41 (4H, m), 1.28-1.26 (12H, m), 0.88 (9H, s), 0.04 (6H, s); ^{13}C NMR ($CDCl_3$, 100 MHz, DEPT-135): δ 182.8 (C, *C*=O), 181.6 (C, *C*=O), 161.1 (C), 151.5 (C), 119.2 (C), 102.1 (CH), 63.3 (CH_2), 56.7 (O*C*H$_3$), 32.9 (CH_2), 29.6 (CH_2), 29.5 (CH_2), 29.4 (CH_2), 29.4 (CH_2), 29.3 (CH_2), 28.0 (CH_2), 26.0 (3 x *C*H$_3$), 25.8 (CH_2), 22.6 (CH_2), 18.4 (C), -5.2 (2 x Si*CH*$_3$); HRMS (ESI-TOF) *m/z*: [M + Na]$^+$ Calcd for $C_{23}H_{40}O_5SiNa$ 447.2543; Found 447.2540.

3-Decyl-2,5-dihydroxycyclohexa-2,5-diene-1,4-dione (5a): The title compound was prepared following the procedure **D**, purified by column chromatography using EtOAc/hexane (3.0:7.0 to 4.0:6.0), and was isolated semi solid. Yield: 89% (74.8 mg). IR (Neat): ν_{max} 3302, 2919, 2850, 1699, 1612, 1331, 1318, 1181, 1117, 767 and 709 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.71 (2H, br s, 2 x *OH*), 6.00 (1H, s, olefinic-*H*), 2.44 (2H, t, *J* = 7.5 Hz), 1.47 (2H, quintet, 7.5 Hz), 1.29-1.25 (14H, m), 0.87 (3H, t, *J* = 7.0 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz, DEPT-135): δ 117.0 (C), 102.2 (CH), 31.9 (CH_2), 29.6 (CH_2), 29.5 (2 x CH_2), 29.3 (CH_2), 29.3 (CH_2), 27.9 (CH_2), 22.7 (CH_2), 22.5 (CH_2), 14.1 (CH_3); HRMS (ESI-TOF) *m/z*: [M + Na]$^+$ Calcd for $C_{16}H_{24}O_4Na$ 303.1572; Found 303.1573.

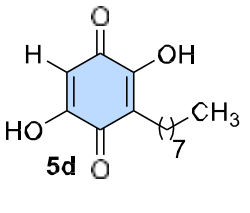


5a

3-Heptyl-2,5-dihydroxycyclohexa-2,5-diene-1,4-dione (5c): The title compound was prepared following the procedure **D**, purified by column chromatography using EtOAc/hexane (3.0:7.0 to 4.0:6.0), and was isolated yellow solid. Yield: 91%. Mp.: 112-114 ºC; IR (Neat): ν_{max} 3304, 2954, 2922, 2854, 1611, 1393, 1346, 1322, 1188, 1113, 944, 884, 767 and 693 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.71 (2H, br s, 2 x O*H*), 6.00 (1H, s, olefinic-*H*), 2.44 (2H, t, *J* = 7.5 Hz), 1.47 (2H, quintet, *J* = 7.5 Hz), 1.31-1.27 (8H, m), 0.87 (3H, t, *J* = 6.5 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz, DEPT-135): δ 117.0 (C), 102.2 (CH), 31.7 (CH_2), 29.5 (CH_2), 29.0 (CH_2), 27.9 (CH_2), 22.6 (CH_2), 22.5 (CH_2), 14.0 (CH_3); HRMS (ESI-TOF) *m/z*: [M + H]$^+$ Calcd for $C_{13}H_{19}O_4$ 239.1283; Found 239.1283.



5c

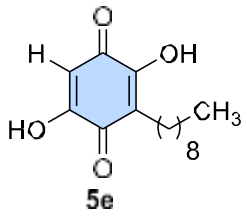


5d

2,5-Dihydroxy-3-octylcyclohexa-2,5-diene-1,4-dione (5d): The title compound was prepared following the procedure **D**, purified by column chromatography using EtOAc/hexane (3.0:7.0 to 4.0:6.0), and was isolated red solid. Yield: 93%. Mp.: 150-152 ºC; IR (Neat): ν_{max} 3301,

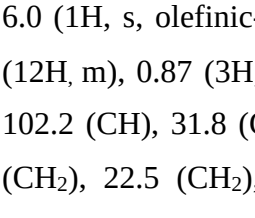
2920, 2851, 1611, 1460, 1330, 1272, 1184, 956, 904, 767 and 694 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 7.72 (2H, br s, 2 x O*H*), 6.01 (1H, s, olefinic-*H*), 2.45 (2H, t, *J* = 7.5 Hz), 1.47 (2H, quintet, *J* = 7.0 Hz), 1.30-1.26 (10H, m), 0.88 (3H, t, *J* = 7.0 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz, DEPT-135): δ 117.0 (C), 102.2 (CH), 31.8 (CH_2), 29.5 (CH_2), 29.3 (CH_2), 29.2 (CH_2), 27.9 (CH_2), 22.6 (CH_2), 22.5 (CH_2), 14.1 (CH_3); HRMS (ESI-TOF) *m*/*z*: $[M + Na]^+$ Calcd for $C_{14}H_{20}O_4Na$ 275.1529; Found 275.1259.

2,5-Dihydroxy-3-nonylcyclohexa-2,5-diene-1,4-dione (5e): The title compound was prepared following the procedure **D**, purified by column chromatography using EtOAc/hexane (3.0:7.0 to 4.0:6.0), and was isolated yellow solid. Yield: 90% (72 mg). Mp.: 145-147 ºC; IR (Neat): ν_{max} 3303, 2918, 2848, 1610, 1460, 1323, 1262, 1181, 965, 859, 767 and 694 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 7.23 (2H, br s, 2 x O*H*), 6.0 (1H, s, olefinic-*H*), 2.44 (2H, t, *J* = 7.5 Hz), 1.47 (2H, quintet, *J* = 7.5 Hz), 1.29-1.25 (12H, m), 0.87 (3H, t, *J* = 6.5 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz, DEPT-135): δ 117.0 (C), 102.2 (CH), 31.8 (CH_2), 29.5 (CH_2), 29.5 (CH_2), 29.4 (CH_2), 29.3 (CH_2), 27.9 (CH_2), 22.6 (CH_2), 22.5 (CH_2), 14.1 (CH_3); HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ Calcd for $C_{15}H_{23}O_4$ 267.1596; Found 267.1591.



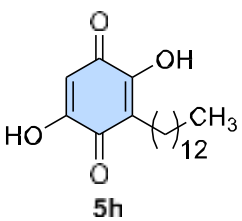
5e

2,5-Dihydroxy-3-undecylcyclohexa-2,5-diene-1,4-dione 5f [Embelin]: The title compound was prepared following the procedure **D**, purified by column chromatography using EtOAc/hexane (2.0:8.0 to 3.0:7.0), and was isolated yellow solid. Mp.: 150-152 ºC. Yield: 89% (52.4 mg). IR (Neat): ν_{max} 3304, 2918, 2848, 1713, 1641, 1612, 1461, 1324, 1190, 1116, 943, 901, 859, 767, 707 and 693 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 6.01 (1H, s, olefinic-*H*), 2.45 (2H, t, *J* = 7.5 Hz), 1.45 (2H, quintet, *J* = 7.0 Hz), 1.29-1.25 (16H, m), 0.88 (3H, *J* = 6.0 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz, DEPT-135): δ 117.1 (C), 102.2 (CH), 31.9 (CH_2), 29.6 (CH_2), 29.6 (CH_2), 29.5 (2 x CH_2), 29.4 (CH_2), 29.3 (CH_2), 27.9 (CH_2), 22.7 (CH_2), 22.5 (CH_2), 14.1 (CH_3); HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ Calcd for $C_{17}H_{27}O_4$ 295.1909; Found 295.1900.



5f

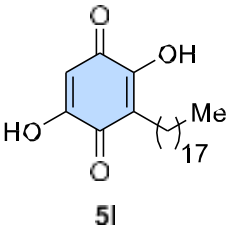
2,5-Dihydroxy-3-tridecylcyclohexa-2,5-diene-1,4-dione 5h [Rapanone]: The title compound was prepared following the procedure **D**, purified by column chromatography using EtOAc/hexane (2.0:8.0 to 3.0:7.0), and was isolated yellow solid. Yield: 93% (60 mg). Mp.: 105-



5h

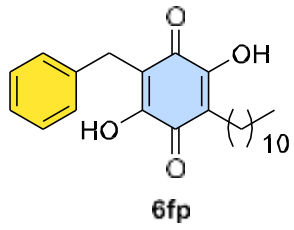
107 ºC; IR (Neat): ν_{max} 3316, 2917, 2847, 1736, 1607, 1370, 1305, 1233, 1042, 769, 722 and 553 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 7.69 (2H, br s, 2 x O*H*), 6.0 (1H, s, olefinic-*H*), 2.44 (2H, t, *J* =7.5 Hz), 1.47 (2H, pentet, *J* = 7.5 Hz), 1.29-1.25 (20H, m), 0.88 (3H, t, *J* = 6.5 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, DEPT-135): δ 117.0 (C), 102.2 (CH), 31.9 (CH_2), 29.7 (CH_2), 29.6 (3 x CH_2), 29.5 (2 x CH_2), 29.4 (CH_2), 29.3 (CH_2), 27.9 (CH_2), 22.7 (CH_2), 22.5 (CH_2), 14.1 (CH_3); HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{19}H_{30}O_4Na$ 345.2042; Found 345.2042.

2,5-Dihydroxy-3-octadecylcyclohexa-2,5-diene-1,4-dione (5l): The title compound was prepared following the procedure **D** and was isolated as an orange solid. Yield: 93% (900 mg). Mp.: 140-142 °C; IR (Neat): ν_{max} 3304, 2919, 2847, 1612, 1358, 1325, 1218, 1188, 904, 768 and 711 cm^{-1}; ^1H NMR ($CDCl_3$ + CD_3OD, 500 MHz): δ 2.31 (2H, t, *J* = 7.5 Hz), 1.34 (2H, p, *J* = 7.5 Hz), 1.21-1.15 (30H, m), 0.77 (3H, t, *J* = 7.0 Hz); ^{13}C NMR ($CDCl_3$ + CD_3OD, 125 MHz, DEPT-135): δ 117.5 (C), 102.8 (CH), 31.7 (CH_2), 29.5 (8 x CH_2), 29.43 (CH_2), 29.40 (CH_2), 29.37 (CH_2), 29.2 (CH_2), 29.1 (CH_2), 27.8 (CH_2), 22.4 (CH_2), 22.3 (CH_2), 13.8 (CH_3); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{24}H_{40}O_4$ 393.3005; Found 393.3007.



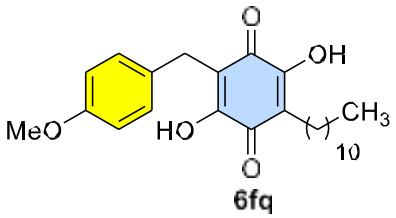
5l

2-Benzyl-3,6-dihydroxy-5-undecylcyclohexa-2,5-diene-1,4-dione (6fp): The title compound was prepared following the procedure **E**, purified by column chromatography using EtOAc/hexane (1.5:8.5 to 2.5:7.5), and was isolated yellow solid. Mp.: 120-122 ºC. Yield: 78% (90 mg). IR (Neat): ν_{max} 3306, 2917, 2849, 1612, 1493, 1463, 1362, 1301, 1165, 1118, 1077, 1030, 1000, 893, 765, 696, 662 and 613 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 7.67 (2H, br s, 2 x OH), 7.30 (2H, d, *J* = 7.0 Hz), 7.28-7.26 (2H, m), 7.19 (1H, m), 3.76 (2H, s), 2.40 (2H, t, *J* = 7.5 Hz), 1.43 (2H, d, *J* = 6.5 Hz), 1.25 (16H, m), 0.87 (3H, t, *J* = 6.5 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, DEPT-135): δ 138.7 (C), 128.9 (2 x CH), 128.5 (2 x CH), 126.4 (CH), 116.4 (C), 114.7 (C), 31.9 (CH_2), 29.6 (CH_2), 29.6 (CH_2), 29.5 (2 x CH_2), 29.4 (CH_2), 29.3 (CH_2), 28.3 (CH_2), 28.0 (CH_2), 22.7 (CH_2), 22.4 (CH_2), 14.1 (CH_3); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{24}H_{33}O_4$ 385.2379; Found 385.2378.



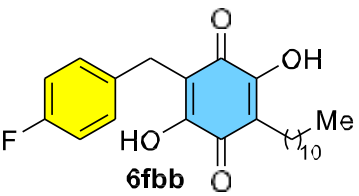
6fp

2,5-Dihydroxy-3-(4-methoxybenzyl)-6-undecylcyclohexa-2,5-diene-1,4-dione (6fq): The title compound was prepared following the procedure **E**, purified by column chromatography using EtOAc/hexane (1.5:8.5 to 2.5:7.5), and was isolated yellow solid. Yield: 91% (113 mg). Mp.: 110-112 ºC. IR (Neat): ν_{max} 3322, 2917, 2846, 1608, 1511, 1460, 1302, 1239, 1177, 1120, 1029, 1005, 804, 764, 699, 676 and 593 cm^{-1}; ^{1}H NMR (DMSO-D_6, 500 MHz): δ 10.83 (1H, br s, *OH*), 7.10 (2H, d, *J* = 8.5 Hz), 6.80 (2H, d, *J* = 8.5 Hz), 3.69 (3H, s, O*CH*$_3$), 3.55 (2H, s), 2.28 (2H, t, *J* = 7.0 Hz), 1.35 (2H, br s), 1.22 (16H, s), 0.85 (3H, t, *J* = 6.5 Hz); ^{13}C NMR (DMSO-D_6, 100 MHz, DEPT-135): δ 157.5 (C), 131.4 (C), 129.3 (2 x CH), 116.4 (C), 115.5 (C), 113.7 (2 x CH), 54.9 (O*C*H$_3$), 31.3 (CH_2), 29.0 (CH_2), 29.0 (CH_2), 28.9 (2 x CH_2), 28.8 (CH_2), 28.7 (CH_2), 27.6 (CH_2), 26.8 (CH_2), 22.1 (CH_2), 21.8 (CH_2), 13.9 (CH_3); HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ Calcd for $C_{25}H_{35}O_5$ 415.2484; Found 415.2484.



6fq

2,5-Dihydroxy-3-(4-nitrobenzyl)-6-undecylcyclohexa-2,5-diene-1,4-dione (6fr): The title compound was prepared following the procedure **E**, purified by column chromatography using EtOAc/hexane (1.5:8.5 to 2.5:7.5), and was isolated yellow solid. Yield: 81% (104 mg). Mp.: 98-100 ºC. IR (Neat): ν_{max} 3310, 2918, 2846, 1607, 1527, 1460, 1342, 1299, 1187, 1119, 1029, 1005, 796, 765, 718, 686 and 578 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.12 (2H, d, *J* = 8.5 Hz), 7.72 (1H, br s, *OH*), 7.46 (2H, d, *J* = 8.5 Hz), 3.85 (2H, s), 2.41 (2H, t, *J* = 7.5 Hz), 1.45 (2H, quintet, *J* = 6.0 Hz), 1.24 (16H, s), 0.87 (3H, t, *J* = 6.5 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz, DEPT-135): δ 146.7 (C), 146.2 (C), 129.7 (2 x CH), 123.7 (2 x CH), 116.9 (C), 113.1 (C), 31.9 (CH_2), 29.6 (CH_2), 29.6 (CH_2), 29.5 (CH_2), 29.5 (CH_2), 29.3 (CH_2), 29.3 (CH_2), 28.3 (CH_2), 27.9 (CH_2), 22.7 (CH_2), 22.5 (CH_2), 14.1 (CH_3); HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ Calcd for $C_{24}H_{32}NO_6$ 430.2230; Found 430.2229.

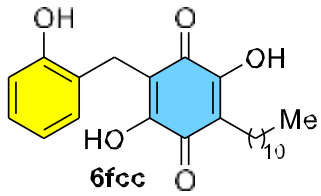


6fbb

2-(4-Fluorobenzyl)-3,6-dihydroxy-5-undecylcyclohexa-2,5-diene-1,4-dione (6fbb): The title compound was prepared following the procedure **E**, purified by column chromatography using EtOAc/hexane (3.0:7.0 to 4.0:6.0), and was isolated yellow solid. Mp.: 175-177 ºC. Yield: 86% (103.8 mg). IR (Neat): ν_{max} 3307, 2917, 2847, 1608, 1509, 1461, 1363, 1319, 1299, 1230, 1161, 1118, 1027, 1000, 760, 708, 662 and

595 cm^{-1}; ^{1}H NMR (DMSO d_6, 500 MHz): δ 10.90 (2H, br s, 2 x *OH*), 7.20 (2H, t, *J* = 8.0 Hz), 7.05 (2H, t, *J* = 9.0 Hz), 3.60 (2H, s), 2.28 (2H, t, *J* = 7.5 Hz), 1.21 (18H, s), 0.84 (3H, t, *J* = 7.0 Hz); ^{13}C NMR (DMSO-d_6, 125 MHz, DEPT-135): δ 161.6 (C, d, *J* = 240.0 Hz, *C*-F), 135.7 (C, d, *J* = 2.5 Hz), 130.0 (2 x CH, d, *J* = 7.5 Hz), 116.6 (C), 114.9 (2 x CH, d, *J* = 20.0 Hz), 114.9 (C), 31.3 (CH_2), 29.0 (CH_2), 29.0 (CH_2), 28.9 (CH_2), 28.9 (CH_2), 28.8 (CH_2), 28.7 (CH_2), 27.5 (CH_2), 26.9 (CH_2), 22.1 (CH_2), 21.9 (CH_2), 13.9 (CH_3); ^{19}F NMR (DMSO-d_6, 375 MHz): δ -117.3; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{24}H_{32}FO_4$ 403.2285; Found 403.2284.

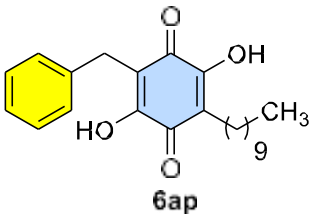
2,5-Dihydroxy-3-(2-hydroxybenzyl)-6-undecylcyclohexa-2,5-diene-1,4-dione (6fcc): The



6fcc

title compound was prepared following the procedure **E**, purified by column chromatography using EtOAc/hexane (3.0:7.0 to 4.0:6.0), and was isolated yellow solid. Mp.: 110-112 ºC. Yield: 52% (62 mg). IR (Neat): ν_{max} 3324, 2917, 2849, 1647, 1623, 1491, 1458, 1346, 1289, 1239, 1177, 1120, 1079, 960, 899, 750, and 698 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.25-7.21 (2H, m), 7.19-7.17 (1H, m), 7.16 (1H, br s, O*H*), 7.14-7.11 (1H, m), 3.73 (2H, s), 2.47 (2H, t, *J* = 8.0 Hz), 1.48 (2H, quintet, *J* = 7.5 Hz), 1.30-1.25 (16H, m), 0.87 (3H, t, *J* = 7.5 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz, DEPT-135): δ 182.5 (C, *C*=O), 180.5 (C, *C*=O), 151.1 (C), 151.1 (C), 149.4 (C), 129.5 (CH), 128.5 (CH), 125.7 (CH), 118.9 (C), 118.4 (C), 117.9 (CH), 112.2 (C), 31.9 (CH_2), 29.6 (CH_2), 29.6 (CH_2), 29.5 (2 x CH_2), 29.4 (CH_2), 29.3 (CH_2), 28.1 (CH_2), 22.7 (CH_2), 22.5 (CH_2), 21.0 (CH_2), 14.1 (CH_3); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{24}H_{33}O_5$ 401.2328; Found 401.2332.

2-Benzyl-5-decyl-3,6-dihydroxycyclohexa-2,5-diene-1,4-dione (6ap): The title compound

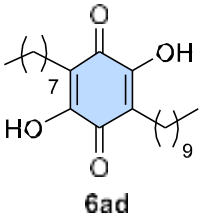


6ap

was prepared following the procedure **E**, purified by column chromatography using EtOAc/hexane (3.0:7.0 to 4.0:6.0), and was isolated yellow solid. Mp.: 132-134 ºC. Yield: 80% (89 mg). IR (Neat): ν_{max} 3324, 2919, 2848, 1741, 1611, 1494, 1461, 1362, 1306, 1210, 1192, 1119, 1027, 999, 764, 711, 699 and 664 cm^{-1}. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.68 (2H, br s, 2 x O*H*), 7.32-7.30 (2H, m), 7.26 (2H, dt, *J* = 6.25, 2.0 Hz), 7.19 (1H, tt, *J* = 7.0 Hz, 2.0 Hz), 3.76 (2H, s), 2.40 (2H, t, *J* = 7.5 Hz), 1.44 (2H, quintet, *J* = 7.5 Hz), 1.29-1.25 (14H, m), 0.87 (3H, t, *J* = 7.0 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz, DEPT-135): δ 138.7 (C), 128.9 (2 x CH), 128.5 (2 x CH), 126.4 (CH), 116.4 (C), 114.7 (C), 31.9 (CH_2), 29.6 (CH_2), 29.5 (CH_2), 29.5 (CH_2), 29.4 (CH_2), 29.3 (CH_2), 28.3 (CH_2),

28.0 (CH_2), 22.7 (CH_2), 22.4 (CH_2), 14.1 (CH_3); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{23}H_{31}O_4$ 371.2222; Found 371.2225.

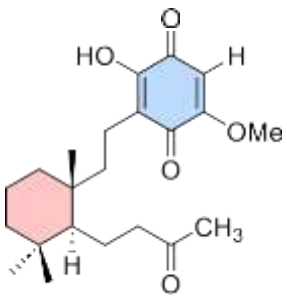
2-Decyl-3,6-dihydroxy-5-octylcyclohexa-2,5-diene-1,4-dione (6ad): The title compound



6ad

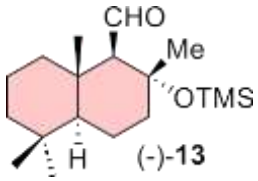
was prepared following the procedure **E**, purified by column chromatography using EtOAc/hexane (2.0:8.0 to 3.0:7.0) and was isolated as a slight red solid. Mp.: 140-142 ºC. Yield: 83% (97.7 mg). IR (Neat): ν_{max} 3314, 2956, 2918, 2849, 1608, 1467, 1284, 1126, 763, 716 and 603 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 7.61 (2H, br s, 2 x O*H*), 2.41 (4H, t, *J* = 8.0 Hz), 1.46 (4H, quintet, *J* = 7.5 Hz), 1.29-1.25 (24H, m), 0.87 (6H, t, *J* = 7.0 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, DEPT-135): δ 116.0 (2 x C), 31.9 (2 x CH_2), 29.5 (4 x CH_2), 29.4 (CH_2), 29.3 (2 x CH_2), 29.2 (CH_2), 28.0 (2 x CH_2), 22.7 (2 x CH_2), 22.4 (2 x CH_2), 14.0 (2 x CH_3); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{24}H_{41}O_4$ 393.3005; Found 393.3005.

2-Hydroxy-5-methoxy-3-(2-((1*R*,2*S*)-1,3,3-trimethyl-2-(3-oxobutyl)cyclohexyl)ethyl)cyclohexa-2,5-diene-1,4-dione [(+)-11]: The title compound was

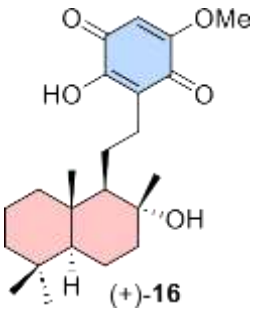


(+)-**11**

prepared following the procedure **F**, purified by column chromatography using EtOAc/hexane (4.0:6.0 to 5.0:5.0), and was isolated as a yellow semi solid. Yield: 75% (84.7 mg). IR (Neat): ν_{max} 3334 (OH), 2924, 1709 (C=O), 1647 (C=O), 1605 (C=O), 1458, 1380, 1358, 1222, 1039, 841 and 647 cm^{-1}; $[\alpha]_D^{25}$ = +1.5° [c = 0.100 g/100 mL, $CHCl_3$]. ^1H NMR ($CDCl_3$, 500 MHz): δ 5.83 (1H, s, olefinic-*H*), 3.85 (3H, s, OCH_3), 2.66-2.59 (1H, m), 2.49-2.42 (1H, m), 2.40-2.34 (2H, m), 2.12 (3H, s, COCH_3), 1.53-1.48 (4H, m), 1.41-1.38 (1H, m), 1.28-1.24 (5H, m), 1.13 (1H, tt, *J* = 13.5, 3.5 Hz), 0.91 (3H, s, CH_3), 0.90 (3H, s, CH_3), 0.85 (3H, s, CH_3); ^{13}C NMR ($CDCl_3$, 125 MHz, DEPT-135): δ 209.4 (C, *C*=*O*), 182.7 (C, *C*=*O*), 181.6 (C, *C*=*O*), 161.2 (C), 151.3 (C), 119.8 (C), 102.2 (CH), 56.7 (OCH_3), 53.3 (CH), 47.4 (CH_2), 42.1 (CH_2), 41.8 (CH_2), 37.7 (C), 37.6 (CH_2), 35.3 (C), 33.5 (CH_3), 29.8 (CH_3), 21.8 (CH_3), 20.4 (CH_2), 19.4 (CH_3), 18.7 (CH_2), 17.0 (CH_2); HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{22}H_{32}O_5Na$ 399.2147; Found 399.2148.

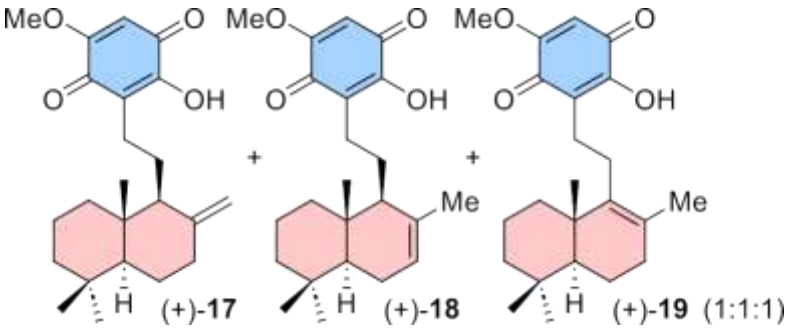
(1*R*,2*R*,4a*S*,8a*S*)-2,5,5,8a-Tetramethyl-2-((trimethylsilyl)oxy)decahydronaphthalene-1-carbaldehyde [(-)-13]: 

The title compound was prepared following the procedure-**H**, purified by column chromatography using hexane and was isolated as a white solid. Yield: 93% (29 mg). Mp.: 58-60 ºC; IR (Neat): ν_{max} 2949, 2869, 1718, 1386, 1251, 1134, 1158, 1084, 1057, 1041, 907, 840 and 732 cm^{-1}; $[\alpha]_D^{25}$ = -36.0° [c = 0.100 g/100 mL, $CHCl_3$]. ^1H NMR ($CDCl_3$, 500 MHz): δ 9.96 (1H, d, *J* = 3.5 Hz), 2.12 (1H, d, *J* = 3.5 Hz), 1.90 (1H, td, *J* = 12.0, 3.5 Hz), 1.75 (1H, td, *J* = 13.5, 3.5 Hz), 1.69-1.65 (1H, m), 1.60 (2H, td, *J* = 13.5, 3.5 Hz), 1.50 (3H, s), 1.43-1.41 (1H, m), 1.37-1.35 (1H, m), 1.30 (1H, dt, *J* = 14.0, 3.0 Hz), 1.15 (2H, dt, *J* = 14.0, 4.0 Hz), 1.10 (3H, s), 1.06 (1H, dd, *J* = 13.0, 4.0 Hz), 0.86 (3H, s), 0.80 (3H, s), 0.09 (9H, s); ^{13}C NMR ($CDCl_3$, 125 MHz, DEPT-135): δ 206.9 (C, *C*=O), 76.7 (C), 72.3 (CH), 55.4 (CH), 44.6 (CH_2), 41.8 (CH_2), 39.8 (CH_2), 38.2 (C), 33.4 (CH_3), 33.2 (C), 26.1 (CH_3), 21.4 (CH_3), 20.4 (CH_2), 18.1 (CH_2), 16.8 (CH_3), 2.71 (3 x CH_3); HRMS (ESI-TOF) *m/z*: $[M + K]^+$ Calcd for $C_{18}H_{34}O_2SiK$ 349.1965; Found 349.1962.

2-Hydroxy-3-(2-((1*R*,2*R*,4a*S*,8a*S*)-2-hydroxy-2,5,5,8a-tetramethyldecahydronaphthalen-1-yl)ethyl)-5-methoxycyclohexa-2,5-diene-1,4-dione [(+)-16]: 

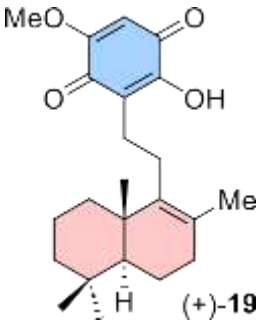
The title compound was prepared following the procedure-**F**, purified by column chromatography using EtOAc/hexane (3.0:7.0 to 4.0:6.0), and was isolated yellow semi solid. Yield: 82% (96 mg). IR (Neat): ν_{max} 3332 (O-H), 2924, 2852, 1645 (C=O), 1604 (C=O), 1457, 1383, 1361, 1313, 1213, 1123, 1039, 937, 842, 736 and 559 cm^{-1}. $[\alpha]_D^{25}$ = +23.0° [*c* = 0.100 g/100 mL, $CHCl_3$]. ^1H NMR ($CDCl_3$, 500 MHz): δ 5.82 (1H, s, olefinic-*H*), 3.84 (3H, s, OC*H*$_3$), 2.62-2.50 (2H, m), 1.84 (1H, td, *J* = 12.5, 3.0 Hz), 1.75 (1H, br d, *J* = 12.5 Hz), 1.65-1.59 (1H, m), 1.55 (1H, tt, *J* = 14.0, 3.5 Hz), 1.49-1.40 (4H, m), 1.38-1.33 (1H, m), 1.26-1.21 (2H, m), 1.15 (3H, s), 1.11 (2H, quintet, *J* = 4.5 Hz), 0.90 (2H, dd, *J* = 12.5, 2.0 Hz), 0.85 (3H, s), 0.76 (3H, s), 0.72 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz, DEPT-135): δ 182.9 (C, *C*=*O*), 182.1 (C, *C*=*O*), 160.8 (C), 151.9 (C), 119.5 (C), 102.5 (CH), 74.6 (C), 60.8 (CH), 56.7 (O*C*H$_3$), 56.0 (CH), 43.8 (CH_2), 41.9 (CH_2), 39.3 (CH_2), 38.8 (C), 33.3 (CH_3), 33.2 (C), 25.3 (CH_2), 24.0 (CH_3), 23.6 (CH_2), 21.4 (CH_3), 20.3 (CH_2), 18.4 (CH_2), 15.3 (CH_3); HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{23}H_{34}O_5Na$ 413.2304; Found 413.2306.

2-Hydroxy-5-methoxy-3-(2-((1*S*,4a*S*,8a*S*)-5,5,8a-trimethyl-2-methylenedecahydronaphthalen-1-yl)ethyl)cyclohexa-2,5-diene-1,4-dione [(+)-17], 2-Hydroxy-5-methoxy-3-(2-((1*S*,4a*S*,8a*S*)-2,5,5,8a-tetramethyl-1,4,4a,5,6,7,8,8a-octahydronaphthalen-1-yl)ethyl)cyclohexa-2,5-diene-1,4-dione [(+)-18], and 2-Hydroxy-5-methoxy-3-(2-((4a*S*,8a*S*)-2,5,5,8a-tetramethyl-3,4,4a,5,6,7,8,8a-octahydronaphthalen-1-yl)ethyl)cyclohexa-2,5-diene-1,4-dione [(+)-19]: The title compound mixture was prepared following the procedure-**I**, purified by column chromatography using EtOAc/hexane (1.0:9.0 to 1.5:8.5), and was isolated as a yellow semi-solid. Yield: 88% (42 mg); IR (Neat): ν_{max} 3349, 2925, 1643, 1604, 1457, 1383, 1353, 1317, 1237, 1206 and 840 cm^{-1}; $[\alpha]_D^{25}$ = +16.8° [c = 0.167g/100 mL, $CHCl_3$]; IR (Neat): ν_{max} 3348, 2924, 2846, 1643, 1604, 1457, 1383, 1353, 1316, 1236, 1206, 1053 and 839 cm^{-1}; for product-**17**: ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.23 (1H, br s, O*H*), 5.83 (1H, s, olefinic-*H*), 4.89 (1H, s, olefinic-*H*), 4.80 (1H, s, olefinic-*H*), 3.85 (3H, s, OCH_3), 2.66-2.56 (2H, m), 1.97-1.93 (3H, m), 1.88-1.83 (2H, m), 1.74-1.71 (1H, m), 1.60-1.56 (3H, m), 1.40-1.39 (2H, m), 1.18-1.15 (3H, m), 0.84 (3H, s), 0.88 (3H, s), 0.78 (3H, s); ^{13}C NMR ($CDCl_3$, 125 MHz, DEPT-135): δ 182.9 (C, *C*=O), 182.8 (C, *C*=O), 161.1 (C), 151.5 (C), 148.1 (C), 119.8 (C), 106.7 (CH_2), 102.2 (CH), 57.0 (CH), 56.8 (O*C*H_3), 55.5 (CH), 42.3 (CH_2), 39.1 (C), 39.0 (CH_2), 38.3 (CH_2), 33.6 (C), 33.2 (CH_3), 24.4 (CH_2), 22.5 (CH_2), 21.9 (CH_3), 19.4 (CH_2), 19.2 (CH_2), 14.4 (CH_3); for product-**18**: ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.23 (1H, br s, O*H*), 5.83 (1H, s, olefinic-*H*), 5.39 (1H, d, *J* = 1.5 Hz, olefinic-*H*), 3.85 (3H, s, OCH_3), 2.53-2.46 (2H, m), 2.27-2.21 (1H, m), 2.05-1.99 (2H, m), 1.81 (3H, s), 1.55-1.52 (3H, m), 1.50-1.45 (3H, m), 1.22-1.19 (2H, m), 1.05-0.98 (1H, m), 0.93 (3H, s), 0.83 (3H, s), 0.70 (3H, s); ^{13}C NMR ($CDCl_3$, 125 MHz, DEPT-135): δ 182.9 (C, *C*=O), 181.8 (C, *C*=O), 161.1 (C), 151.5 (C), 135.3 (C), 122.2 (CH), 119.4 (C), 102.2 (CH), 56.7 (O*C*H_3), 54.7 (CH), 50.1 (CH), 42.2 (CH_2), 39.0 (CH_2), 33.4 (CH_3), 33.4 (C), 33.0 (C), 25.7 (CH_2), 24.9 (CH_2), 23.8 (CH_2), 21.9 (CH_3), 21.7 (CH_3), 19.1 (CH_2), 13.4 (CH_3); for product-**19**: ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.23 (1H, br s, O*H*), 5.83 (1H, s, olefinic-*H*), 3.85 (3H, s, OCH_3), 2.45-2.38 (2H, m), 2.13-2.06 (2H, m), 2.04-1.99 (2H, m), 1.67-1.64 (3H, m), 1.44-1.41 (2H, m), 1.36-1.32 (2H, m), 1.13-1.07 (2H, m), 0.93 (3H, s), 0.88 (3H, s), 0.86 (3H, s), 0.78 (3H,

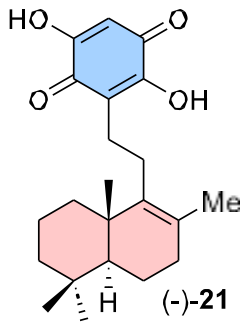


s); ^{13}C NMR ($CDCl_3$, 125 MHz, DEPT-135): δ 182.8 (C, *C*=O), 181.7 (C, *C*=O), 161.1 (C), 151.4 (C), 139.7 (C), 127.2 (C), 119.3 (C), 102.2 (CH), 56.7 (O*C*H$_3$), 39.7 (C), 39.0 (CH_2), 33.7 (C), 33.6 (CH_2), 33.4 (CH), 33.0 (CH_3), 26.5 (CH_3), 25.6 (CH_2), 25.4 (CH_2), 24.9 (CH_2), 20.0 (CH_3), 19.4 (CH_2), 18.4 (CH_2), 14.4 (CH_3); HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{23}H_{32}O_4Na$ 395.2198; Found 395.2192.

2-Hydroxy-5-methoxy-3-(2-((4a*S*,8a*S*)-2,5,5,8a-tetramethyl-3,4,4a,5,6,7,8,8a-octahydronaphthalen-1-yl)ethyl)cyclohexa-2,5-diene-1,4-dione [(+)-19]: The title compound was prepared following the procedure-**J**, purified by column chromatography using EtOAc/hexane (1.0:9.0 to 1.5:8.5), and was isolated as orange semi-solid. Yield: 81% (15 mg); IR (Neat): ν_{max} 3400, 2921, 1732, 1643, 1604, 1494, 1457, 1378, 1299, 1229, 1123, 1033, 725, 691 and 567 cm^{-1}; $[\alpha]_D^{25}$ = +4.0° [c = 0.050 g/100 mL, $CHCl_3$]; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.19 (1H, br s, O*H*), 5.81 (1H, s, olefinic-*H*), 3.85 (3H, s, OC*H*$_3$), 2.36-2.30 (1H, m), 2.15-2.08 (2H, m), 1.99-1.95 (2H, m), 1.80-1.74 (1H, m), 1.67-1.61 (2H, m), 1.53-1.49 (1H, m), 1.47-1.43 (3H, m), 1.41-1.37 (2H, m), 1.37-1.31 (1H, m), 0.98 (3H, s), 0.96 (3H, s), 0.89 (3H, d, *J* = 7.0 Hz), 0.80 (3H, s); ^{13}C NMR ($CDCl_3$, 125 MHz, DEPT-135): δ 182.8 (C, *C*=O), 181.7 (C, *C*=O), 161.1 (C), 151.2 (C), 137.0 (C), 132.5 (C), 120.1 (C), 102.1 (CH), 56.7 (O*C*H$_3$), 40.8 (C), 39.9 (CH_2), 34.5 (C), 34.5 (CH_2), 33.5 (CH), 29.2 (CH_3), 27.7 (CH_3), 27.2 (CH_2), 25.4 (CH_2), 25.2 (CH_2), 21.0 (CH_3), 20.0 (CH_2), 17.7 (CH_2), 16.1 (CH_3); HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{23}H_{32}O_4Na$ 395.2198; Found 395.2197.

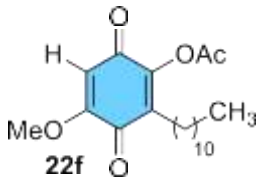


2,5-Dihydroxy-3-(2-((4a*S*,8a*S*)-2,5,5,8a-tetramethyl-3,4,4a,5,6,7,8,8a-octahydronaphthalen-1-yl)ethyl)cyclohexa-2,5-diene-1,4-dione [(-)-21]: The title compound was prepared following the procedure-**K**, and was isolated as violet solid. Yield: 89% (8 mg). Mp.: 148-150 ºC; IR (Neat): ν_{max} 3313, 2923, 2855, 1613, 1356, 1327, 1181, 902 and 726 cm^{-1}; $[\alpha]_D^{25}$ = -9.0° [c = 0.233 g/100 mL, $CHCl_3$]; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.66 (2H, br s, 2 x O*H*), 5.98 (1H, s, olefinic-*H*), 2.38-2.28 (1H, m), 2.17-2.11 (1H, m), 2.04-2.00 (1H, m), 1.79-1.72 (1H, m), 1.66-1.60 (3H, m), 1.53-1.46 (5H, m), 1.41 (1H, dd, *J* = 12.0, 3.5 Hz), 1.35 (2H, dt, *J* = 11.0, 5.0 Hz), 0.99 (3H, s), 0.97 (3H, s), 0.90 (3H, d, *J* = 7.0 Hz), 0.82 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz, DEPT-135): δ 137.3 (C), 132.3 (C), 117.8 (C), 102.1 (CH), 40.8 (C), 40.0 (CH_2), 34.5 (C),



34.4 (CH_2), 33.6 (CH), 29.2 (CH_3), 27.7 (CH_3), 27.2 (CH_2), 25.4 (CH_2), 25.2 (CH_2), 21.0 (CH_3), 20.0 (CH_2), 17.5 (CH_2), 16.1 (CH_3); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{22}H_{31}O_4$ 359.2222; Found 359.2224.

2-*n*-Undecyl-4-methoxy-3,6-dioxocyclohexa-1,4-dien-1-yl acetate (22f): The title compound was prepared following the procedure **G**, purified by column chromatography using EtOAc/hexane (1.0:9.0 to 1.5:8.5), and was isolated yellow solid. Mp.: 85-87 ºC. Yield: 84% (88 mg). IR (Neat): ν_{max} 2916, 2848, 1770, 1667, 1647, 1605, 1463, 1331, 1370, 1241, 1176, 1140, 1079, 1050, 1006, 962, 844, 718, 581 and 438 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 5.88 (1H, s, olefinic-*H*), 3.83 (3H, s, OC*H*$_3$), 2.40 (2H, t, *J* = 7.5 Hz), 2.35 (3H, s), 1.42 (2H, quintet, *J* = 7.0 Hz), 1.31-1.24 (16H, m), 0.87 (3H, t, *J* = 7.5 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, DEPT-135): δ 181.7 (C, *C*=O), 179.8 (C, *C*=O), 168.0 (C), 159.0 (C), 149.3 (C), 135.1 (C), 105.5 (CH), 56.5 (O*C*H$_3$), 31.9 (CH_2), 29.6 (CH_2), 29.6 (CH_2), 29.5 (CH_2), 29.4 (CH_2), 29.3 (CH_2), 29.2 (CH_2), 28.2 (CH_2), 23.6 (CH_2), 22.6 (CH_2), 20.3 (CH_3), 14.1 (CH_3); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{20}H_{31}O_5$ 351.2171; Found 351.2171.



22f

Table S1. Correlation NMR data for the compound **9l** (Irisoquin):[4]

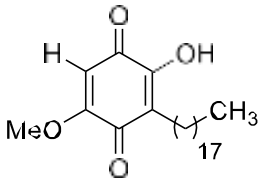
		Isolated compound ^{13}C NMR (75 MHz, $CDCl_3$)	Present synthetic compound ^{13}C NMR (100 MHz, $CDCl_3$)
 Irisoquin (**9l**) 2-Hydroxy-5-methoxy-3-octadecylcyclohexa-2,5-diene-1,4-dione		182.8 (C, *C*=*O*)	182.8 (C, *C*=*O*)
		181.6 (C, *C*=*O*)	181.6 (C, *C*=*O*)
		161.1 (C)	161.1 (C)
		151.5 (C)	151.5 (C)
		119.2 (C)	119.3 (C)
Isolated compound ^{1}H NMR (300 MHz, $CDCl_3$)	Present synthetic compound ^{1}H NMR (400 MHz, $CDCl_3$)	102.1 (CH)	102.1 (CH)
7.27 (brs, OH)	-		
5.84 (1H, s)	5.84 (1H, s)	56.7 (OCH_3)	56.7 (OCH_3)
3.86 (3H, s)	3.86 (3H, s)	31.9 (CH_2)	31.9 (CH_2)
2.44 (2H, t, *J* = 6.5 Hz)	2.44 (2H, t, *J* = 7.6 Hz)	29.6-29.4 (CH_2)	29.7 (6 x CH_2) 29.6 (3 x CH_2) 29.5 (2 x CH_2) 29.4 (CH_2) 29.3 (CH_2)
1.42 (2H, m)	1.49-1.40 (2H, m)	28.0 (CH_2)	28.0 (CH_2)
1.25 (30H, m)	1.30-1.26 (30H, m)		22.7 (CH_2)
0.88 (3H, t, *J* = 6.5 Hz)	0.88 (3H, t, *J* = 6.4 Hz)	22.6 (CH_2)	22.6 (CH_2)
		14.1 (CH_3)	14.1 (CH_3)

Table S2. Correlation NMR data for the compound **9k** (Irisoquin A):[5]

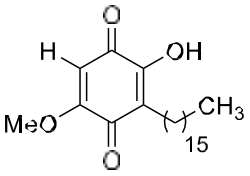
		Isolated compound ^{13}C NMR (75 MHz, $CDCl_3$)	Present synthetic compound ^{13}C NMR (100 MHz, $CDCl_3$)
 Irisoquin A (**9k**) 3-Hexadecyl-2-hydroxy-5-methoxycyclohexa-2,5-diene-1,4-dione		182.8 (C, *C*=*O*)	182.8 (C, *C*=*O*)
		181.7 (C, *C*=*O*)	181.6 (C, *C*=*O*)
		161.1 (C)	161.1 (C)
		151.5 (C)	151.5 (C)
		119.3 (C)	119.3 (C)
Isolated compound ^{1}H NMR (300 MHz, $CDCl_3$)	Present synthetic compound ^{1}H NMR (400 MHz, $CDCl_3$)	102.2 (CH)	102.1 (CH)
7.29 (br s, OH)	7.25 (br s, OH)	56.8 (OCH_3)	56.7 (OCH_3)
5.86 (1H, s)	5.84 (1H, s)	31.9 (CH_2)	31.9 (CH_2)
3.86 (3H, s)	3.86 (3H, s)	29.7-29.4 (CH_2)	29.7 (3 x CH_2)
2.43 (2H, t, *J* = 6.5 Hz)	2.44 (2H, t, *J* = 7.6 Hz)		29.7 (2 x CH_2)
1.44 (2H, m)	1.49-1.40 (2H, m)		29.6 (2 x CH_2)
1.24 (br s)	1.25 (26H, m)		29.5 (2 x CH_2)
0.87 (3H, t, *J* = 6.5 Hz)	0.88 (3H, t, *J* = 6.4 Hz)		29.4 (CH_2)
			29.3 (CH_2)
		28.0 (CH_2)	28.0 (CH_2)
		28.0 (CH_2)	-
		22.7 (CH_2)	22.7 (CH_2)
		-	22.6 (CH_2)
		14.1 (CH_3)	14.1 (CH_3)

Table S3. Correlation NMR data for the compound **9m** (Irisoquin D):[5]

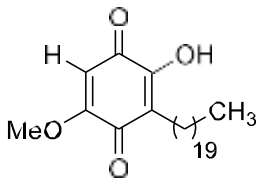
		Isolated compound ^{13}C NMR (75 MHz, $CDCl_3$)	Present synthetic compound ^{13}C NMR (125 MHz, $CDCl_3$)
 Irisoquin D (**9m**) 2-Hydroxy-3-icosyl-5-methoxycyclohexa-2,5-diene-1,4-dione		182.8 (C, *C*=*O*)	182.8 (C, *C*=*O*)
		181.7 (C, *C*=*O*)	181.6 (C, *C*=*O*)
		161.1 (C)	161.1 (C)
		151.5 (C)	151.5 (C)
		119.3 (C)	119.2 (C)
Isolated compound ^{1}H NMR (300 MHz, $CDCl_3$)	Present synthetic compound ^{1}H NMR (500 MHz, $CDCl_3$)	102.2 (CH)	102.1 (CH)
7.29 (br s, OH)	7.23 (br s, OH)	56.8 (OCH_3)	56.7 (OCH_3)
5.86 (1H, s)	5.84 (1H, s)	31.9 (CH_2)	31.9 (CH_2)
3.86 (3H, s)	3.86 (3H, s)	29.7-29.3 (CH_2)	29.7 (9 x CH_2)
2.43 (2H, t, *J* = 6.5 Hz)	2.44 (2H, t, *J* = 7.5 Hz)		29.6 (2 x CH_2)
1.44 (2H, m)	1.48-1.42 (2H, m)		29.5 (2 x CH_2)
1.24 (br s)	1.30-1.26 (34H, m)		29.4 (CH_2)
0.87 (3H, t, *J* = 6.5 Hz)	0.88 (3H, t, *J* = 7.0 Hz)		29.3 (CH_2)
		28.0 (CH_2)	28.0 (CH_2)
		28.0 (CH_2)	-
		22.7 (CH_2)	22.7 (CH_2)
		-	22.6 (CH_2)
		14.1 (CH_3)	14.1 (CH_3)

Table S4: Correlation NMR data for the compound **9n** (Irisoquin F):[5]

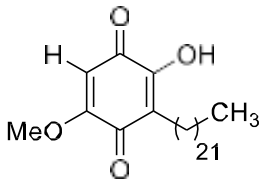
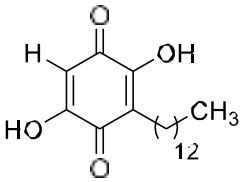
<table>
<tr><td colspan="2" rowspan="5"> 
Irisoquin F (9n)
3-Docosyl-2-hydroxy-5-methoxycyclohexa-2,5-diene-1,4-dione</td><td>Isolated compound ^{13}C NMR (75 MHz, $CDCl_3$)</td><td>Present synthetic compound ^{13}C NMR (125 MHz, $CDCl_3$)</td></tr>
<tr><td>182.8 (C, C=O)</td><td>182.8 (C, C=O)</td></tr>
<tr><td>181.7 (C, C=O)</td><td>181.7 (C, C=O)</td></tr>
<tr><td>161.1 (C)</td><td>161.1 (C)</td></tr>
<tr><td>151.5 (C)</td><td>151.5 (C)</td></tr>
<tr><td>Isolated compound ^{1}H NMR (300 MHz, $CDCl_3$)</td><td>Present synthetic compound ^{1}H NMR (500 MHz, $CDCl_3$)</td><td>119.3 (C)</td><td>119.3 (C)</td></tr>
<tr><td>7.29 (br s, OH)</td><td>7.25 (br s, OH)</td><td>102.2 (CH)</td><td>102.1 (CH)</td></tr>
<tr><td>5.86 (1H, s)</td><td>5.84 (1H, s)</td><td>56.8 (OCH$_3$)</td><td>56.7 (OCH$_3$)</td></tr>
<tr><td>3.86 (3H, s)</td><td>3.86 (3H, s)</td><td>31.9 (CH_2)</td><td>31.9 (CH_2)</td></tr>
<tr><td>2.43 (2H, t, J = 6.5 Hz)</td><td>2.44 (2H, t, J = 7.5 Hz)</td><td rowspan="5">29.7-29.3 (CH_2)</td><td>29.7 (10 x CH_2)</td></tr>
<tr><td>1.44 (2H, m)</td><td>1.48-1.42 (2H, m)</td><td>29.6 (3 x CH_2)</td></tr>
<tr><td>1.24 (br s)</td><td>1.30-1.26 (38H, m)</td><td>29.5 (2 x CH_2)</td></tr>
<tr><td>0.87 (3H, t, J = 6.5 Hz)</td><td>0.88 (3H, t, J = 7.0 Hz)</td><td>29.4 (CH_2)</td></tr>
<tr><td></td><td></td><td>29.3 (CH_2)</td></tr>
<tr><td></td><td></td><td>28.0 (CH_2)</td><td>28.0 (CH_2)</td></tr>
<tr><td></td><td></td><td>28.0 (CH_2)</td><td>-</td></tr>
<tr><td></td><td></td><td>22.7 (CH_2)</td><td>22.7 (CH_2)</td></tr>
<tr><td></td><td></td><td>-</td><td>22.6 (CH_2)</td></tr>
<tr><td></td><td></td><td>14.1 (CH_3)</td><td>14.1 (CH_3)</td></tr>
</table>

Table S5: Correlation NMR data for the compound **5h** (Rapanone):[6]

<table>
<tr><td colspan="2"> 
Rapanone (5h)
2,5-Dihydroxy-3-tridecylcyclohexa-2,5-diene-1,4-dione</td><td>Isolated compound ^{13}C NMR (125 MHz, $CDCl_3$)</td><td>Present synthetic compound ^{13}C NMR (100 MHz, $CDCl_3$)</td></tr>
<tr><td colspan="2" rowspan="2"></td><td>117.1 (C)</td><td>117.0 (C)</td></tr>
<tr><td>102.2 (CH)</td><td>102.2 (CH)</td></tr>
<tr><td>Isolated compound ^{1}H NMR (500 MHz, $CDCl_3$)</td><td>Present synthetic compound ^{1}H NMR (400 MHz, $CDCl_3$)</td><td rowspan="13">32.0-22.6 (12 x CH_2)

14.2 (CH_3)</td><td>31.9 (CH_2)</td></tr>
<tr><td>7.60 (2H, br s, OH)</td><td>7.70 (2H, br s, OH)</td><td>29.7 (CH_2)</td></tr>
<tr><td>5.90 (1H, s)</td><td>6.0 (1H, s)</td><td>29.6 (3 x CH_2)</td></tr>
<tr><td>2.45 (2H, t)</td><td>2.44 (2H, t, J = 6.0 Hz)</td><td>29.5 (2 x CH_2)</td></tr>
<tr><td>1.48 (2H, t)</td><td>1.47 (2H, t, J = 7.5 Hz)</td><td>29.4 (CH_2)</td></tr>
<tr><td>1.26 (20H, m)</td><td>1.27 (20H, m)</td><td>29.3 (CH_2)</td></tr>
<tr><td>0.87 (3H, t)</td><td>0.88 (3H, t, J = 6.5 Hz)</td><td>27.9 (CH_2)</td></tr>
<tr><td rowspan="3"></td><td rowspan="3"></td><td>22.7 (CH_2)</td></tr>
<tr><td>22.5 (CH_2)</td></tr>
<tr><td>14.1 (CH_3)</td></tr>
</table>

Table S6: Correlation NMR data for the compound **5f** (Embelin):[7]

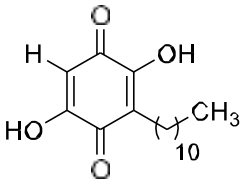
<table>
<tr><td colspan="2"> 
Embelin (5f)
2,5-Dihydroxy-3-undecylcyclohexa-2,5-diene-1,4-dione</td><td>Isolated compound ^{13}C NMR (100 MHz, $CDCl_3$)</td><td>Present synthetic compound ^{13}C NMR (125 MHz, $CDCl_3$)</td></tr>
<tr><td colspan="2" rowspan="2"></td><td>117.4 (C)</td><td>117.1 (C)</td></tr>
<tr><td>103.9 (CH)</td><td>102.2 (CH)</td></tr>
<tr><td rowspan="2">Isolated compound ^{1}H NMR (400 MHz, $CDCl_3$)</td><td rowspan="2">Present synthetic compound ^{1}H NMR (500 MHz, $CDCl_3$)</td><td rowspan="12">31.3-22.0 (10 x CH_2)</td><td>31.9 (CH_2)</td></tr>
<tr><td>29.62 (CH_2)</td></tr>
<tr><td>7.69 (2H, s)</td><td>-</td><td>29.6 (CH_2)</td></tr>
<tr><td>6.00 (1H, s)</td><td>6.01 (1H, s)</td><td>29.5 (2 x CH_2)</td></tr>
<tr><td>2.46-2.43 (2H, m)</td><td>2.45 (2H, t, J = 7.5 Hz)</td><td rowspan="2">29.36 (CH_2)</td></tr>
<tr><td>1.49-1.45 (2H, m)</td><td>1.50-1.44 (2H, m)</td><td>29.3 (CH_2)</td></tr>
<tr><td>1.29-1.26 (16H, m)</td><td>1.29-1.25 (16H, m)</td><td>27.9 (CH_2)</td></tr>
<tr><td rowspan="2">0.90 (3H, t, J = 8.0 Hz)</td><td rowspan="2">0.88 (3H, t, J = 6.5 Hz)</td><td>22.7 (CH_2)</td></tr>
<tr><td>22.5 (CH_2)</td></tr>
<tr><td colspan="2"></td><td>14.0 (CH_3)</td><td>14.1 (CH_3)</td></tr>
</table>

Table S7: Correlation NMR data for the compound **9f** (5-*O*-Methylembelin):[8,4]

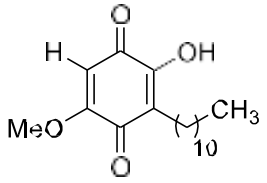
		Isolated compound ^{13}C NMR (100 MHz, $CDCl_3$)	Present synthetic compound ^{13}C NMR (100 MHz, $CDCl_3$)
 5-*O*-Methylembelin (**9f**) 2-Hydroxy-5-methoxy-3-undecylcyclohexa-2,5-diene-1,4-dione		182.8 (C, *C*=*O*)	182.8 (C, C=O)
		181.6 (C, *C*=*O*)	181.6 (C, C=O)
		161.0 (C)	161.1 (C)
		151.6 (C)	151.5 (C)
		119.2 (C)	119.3 (C)
Isolated compound ^{1}H NMR (400 MHz, $CDCl_3$)	Present synthetic compound ^{1}H NMR (400 MHz, $CDCl_3$)	102.1 (CH)	102.1 (CH)
7.26 (1H, br s, OH)	7.23 (1H, br s, OH)	56.6 (O*C*H_3)	56.7 (O*C*H_3)
5.85 (1H, s)	5.83 (1H, s)	31.8 (CH_2)	31.9 (CH_2)
3.86 (3H, s)	3.85 (3H, s)	29.5-29.1 (7 x CH_2)	29.63 (CH_2)
			29.59 (CH_2)
			29.53 (2 x CH_2)
2.44 (2H, t)	2.43 (2H, t, *J* = 8.0 Hz)		29.38 (CH_2)
			29.3 (CH_2)
1.45 (2H, m)	1.43 (2H, m)	27.9 (CH_2)	28.0 (CH_2)
1.25 (16H, m)	1.29-1.24 (16H, m)	22.6 (CH_2)	22.65 (CH_2)
			22.61 (CH_2)
0.88 (3H, t)	0.87 (3H, t, *J* = 6.4 Hz)	14.0 (CH_3)	14.1 (CH_3)

Table S8. Correlation NMR data for the compound **9h** (5-*O*-methylrapanone):[4]

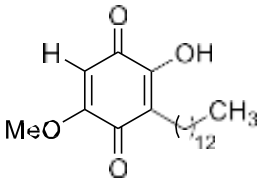
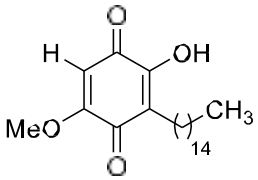
		Isolated compound ^{13}C NMR (75 MHz, $CDCl_3$)	Present synthetic compound ^{13}C NMR (125 MHz, $CDCl_3$)
 *O-Methylrapanone* 2-Hydroxy-5-methoxy-3-tridecylcyclohexa-2,5-diene-1,4-dione (**9h**)		182.8 (C, *C*=O)	182.8 (C, *C*=O)
		181.6 (C, *C*=O)	181.7 (C, *C*=O)
		161.0 (C)	161.1 (C)
		151.6 (C)	151.5 (C)
		119.2 (C)	119.3 (C)
Isolated compound ^{1}H NMR (300 MHz, $CDCl_3$)	Present synthetic compound ^{1}H NMR (500 MHz, $CDCl_3$)	102.1 (CH)	102.1 (CH)
7.26 (1H, br s)	7.25 (1H, br s, O*H*)	56.6 (O*C*H_3)	56.7 (O*C*H_3)
5.86 (1H, s)	5.83 (1H, s)	31.8 (CH_2)	31.9 (CH_2)
3.86 (3H, s)	3.85 (3H, s)	29.5-29.1 (CH_2)	29.6 (4 x CH_2) 29.5 (2 x CH_2) 29.4 (CH_2) 29.3 (CH_2)
2.44 (2H, t)	2.43 (2H, t, *J* = 7.5 Hz)	27.9 (CH_2)	28.0 (CH_2)
1.44 (2H, m)	1.44 (2H, p, *J* = 7.5 Hz)	-	22.7 (CH_2)
1.25 (20H, m)	1.30-1.24 (20H, m)	22.6 (CH_2)	22.6 (CH_2)
0.88 (3H, t)	0.87 (3H, t, *J* = 7.0 Hz)	14.0 (CH_3)	14.1 (CH_3)

Table S9. Correlation NMR data for the compound **9j** (Sorgoleone-364):[9]

		Isolated compound ^{13}C NMR (75 MHz, $CDCl_3$)	Present synthetic compound ^{13}C NMR (125 MHz, $CDCl_3$)
 *Sorgoleone-364* 2-Hydroxy-5-methoxy-3-pentadecylcyclohexa-2,5-diene-1,4-dione (**9j**)		183.1 (C, *C*=O)	182.8 (C, *C*=O)
		182.0 (C, *C*=O)	181.7 (C, *C*=O)
		161.5 (C)	161.1 (C)
		151.9 (C)	151.5 (C)
		119.6 (C)	119.3 (C)
Isolated compound ^{1}H NMR (300 MHz, $CDCl_3$)	Present synthetic compound ^{1}H NMR (500 MHz, $CDCl_3$)	102.5 (CH)	102.1 (CH)
5.83 (1H, s)	5.83 (1H, s)	56.7 (OCH_3)	56.7 (OCH_3)
3.85 (3H, s)	3.85 (3H, s)	31.9 (CH_2)	31.9 (CH_2)
2.43 (2H, dd, *J* = 7.6, 7.5 Hz)	2.43 (2H, t, *J* = 7.5 Hz)	29.6-29.3 (CH_2)	29.7 (2 x CH_2) 29.7 (2 x CH_2) 29.6 (2 x CH_2) 29.5 (2 x CH_2) 29.4 (CH_2) 29.3 (CH_2)
1.42 (2H, m)	1.44 (2H, p, *J* = 7.5 Hz)	28.0 (CH_2)	28.0 (CH_2)
1.24 (24H, m)	1.29-1.24 (24H, m)	-	22.7 (CH_2)
0.87 (3H, t, *J* = 7.6 Hz)	0.87 (3H, t, *J* = 7.0 Hz)	22.6 (CH_2)	22.6 (CH_2)
		22.5 (CH_2)	-
		14.2 (CH_3)	14.1 (CH_3)

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X-Ray Single Crystal Data for 9h. The Ellipsoid Counter% Probability Levels are 50%

Crystallized from DCM-Hexane; $C_{20}H_{32}O_4$; Mr = 336.45; triclininc; space group = *P*-1; A clear orange crystal of 0.25×0.17×0.11 mm^3 was used.

Table S10. Crystal data and structure refinement for *O*-methylrapanone **9h** (CCDC-2386997)

Bond precision: C-C = 0.0049 A Wavelength=0.71073

Cell: a=5.1617(1) b=9.9928(3) c=19.9937(5)
alpha=86.035(2) beta=83.345(2) gamma=80.582(2)

Temperature: 299 K

	Calculated	Reported
Volume	1009.19(4)	1009.19(4)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	C20 H32 O4	C20 H32 O4
Sum formula	C20 H32 O4	C20 H32 O4
Mr	336.46	336.45
Dx,g cm-3	1.107	1.107
Z	2	2
Mu (mm-1)	0.075	0.075
F000	368.0	368.0
F000'	368.18	
h,k,lmax	6,12,25	6,12,25
Nref	4442	4247
Tmin,Tmax	0.985,0.992	0.403,1.000
Tmin'	0.981	

Correction method= # Reported T Limits: Tmin=0.403 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 0.956 Theta(max)= 27.041

R(reflections)= 0.0657(2116) wR2(reflections)= 0.2476(4247)

S = 1.034 Npar= 223

Ellipsoid plot for *O*-methylrapanone 9h: