Supporting Information-I

Sustainable construction of value-added naphthoquinones for pharmaceuticals

Sibani Rath, Pinki Lamba, P. Sravan Kumar Reddy, Anugam V. Krishna, and

Dhevalapally B. Ramachary*

Catalysis Laboratory, School of Chemistry, University of Hyderabad, Hyderabad-500 046, India;

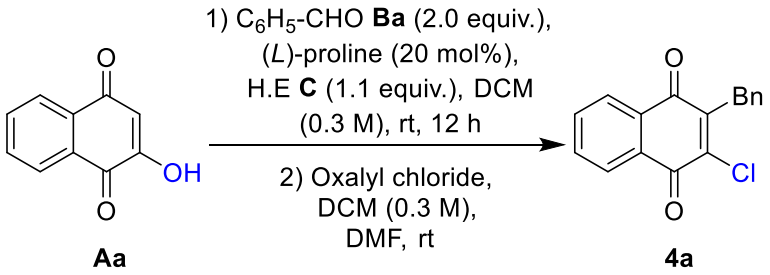
E-mail: ramsc@uohyd.ac.in and ramchary.db@gmail.com

CONTENTS **Page No**

General Methods: The ^{1}H NMR and ^{13}C NMR spectra were recorded at 400 MHz and 500 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. Elemental analyses were recorded on a Thermo Finnigan Flash EA 1112 analyzer. 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 ($\lambda = 0.71073$ 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. All the microwave irradiation reactions were performed in a "Monowave 200 Anton Paar microwave reactor".

Materials: All solvents and commercially available chemicals were used as received. 3-Alkyllawsones **1**, 2-alkyl-3-chloronaphthalene-1,4-diones **4** and other key intermediates for the total synthesis of deoxyneocryptotanshinone and miltirone are synthesized by using literature protocols and gave corresponding references.

Table S1: Reaction optimization for the one-pot synthesis of 2-benzyl-3-chloronaphthalene-1,4-dione **4a** [a]

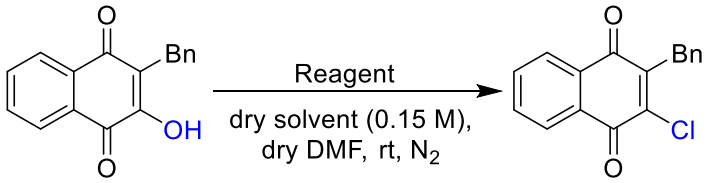


Entry	Oxalyl Chloride	DMF	*t* (h)	Yield (%)[b]
1	2	1.3	3	71
2	2	-	18	0
3[c]	2	1.3	4.5	59
4	3	1.5	3	75
5[d]	3	1.5	4	31

[a] Reaction was carried out taking **Aa** (0.3 mmol), C_6H_5CHO (2.0 equiv.), proline (20 mol%), Hantzsch ester (H. E, 1.1 equiv.), DCM (0.3 M) followed by addition of oxalyl chloride, again DCM (0.3 M) and DMF at rt. [b] Yields refer to the column purified product. [c] After step-1, DCM (0.3 M) was not added in the step-2. [d] 300 mg 4 Aº MS was added to the reaction mixture after reductive alkylation.

Discussion for Table S1: Initially, lawsone **Aa** (0.3 mmol) was taken and treated with 2.0 equiv. of benzaldehyde **Ba**, 20 mol% of proline, and 1.1 equiv. of Hantzsch ester (HE) in DCM (0.3 M) and stirred at rt for 12 h. After completion of reductive alkylation reaction, again DCM (0.3 M), 2.0 equiv. of oxalyl chloride and 1.3 equiv. of DMF was added and stirred at rt for 3 h to furnishing **4a** in 71% yield (Table S1, entry 1). Next, the one-pot synthesis was performed without adding DMF which resulted in no product **4a** formation (Table S1, entry 2). Without extra addition of DCM (0.3 M) in the chlorination step resulting **4a** in only 59% yield with a long reaction time of 4.5 h (Table S1, entry 3). On increasing the oxalyl chloride amount to 3.0 equiv., product **4a** obtained in 75% yield in 3 h (Table S1, entry 4). Lastly, 300 mg of 4 Aº MS was added after step-1 to reduce the H_2O content and stirred for 15 minutes followed by addition of DCM (0.3 M), 3.0 equiv. of oxalyl chloride and 1.5 equiv. of DMF. Surprisingly, the reaction took 4 h for completion furnishing **4a** in 31% yield (Table S1, entry 5). Thus, we came to the conclusion that, one-pot synthesis of 2-benzyl-3-chloronaphthalene-1,4-dione **4a** from the lawsone **Aa** is not a very good protocol.

Table S2: Reaction optimization for the high-yielding synthesis of 2-benzyl-3-chloronaphthalene-1,4-dione **4a** [a]



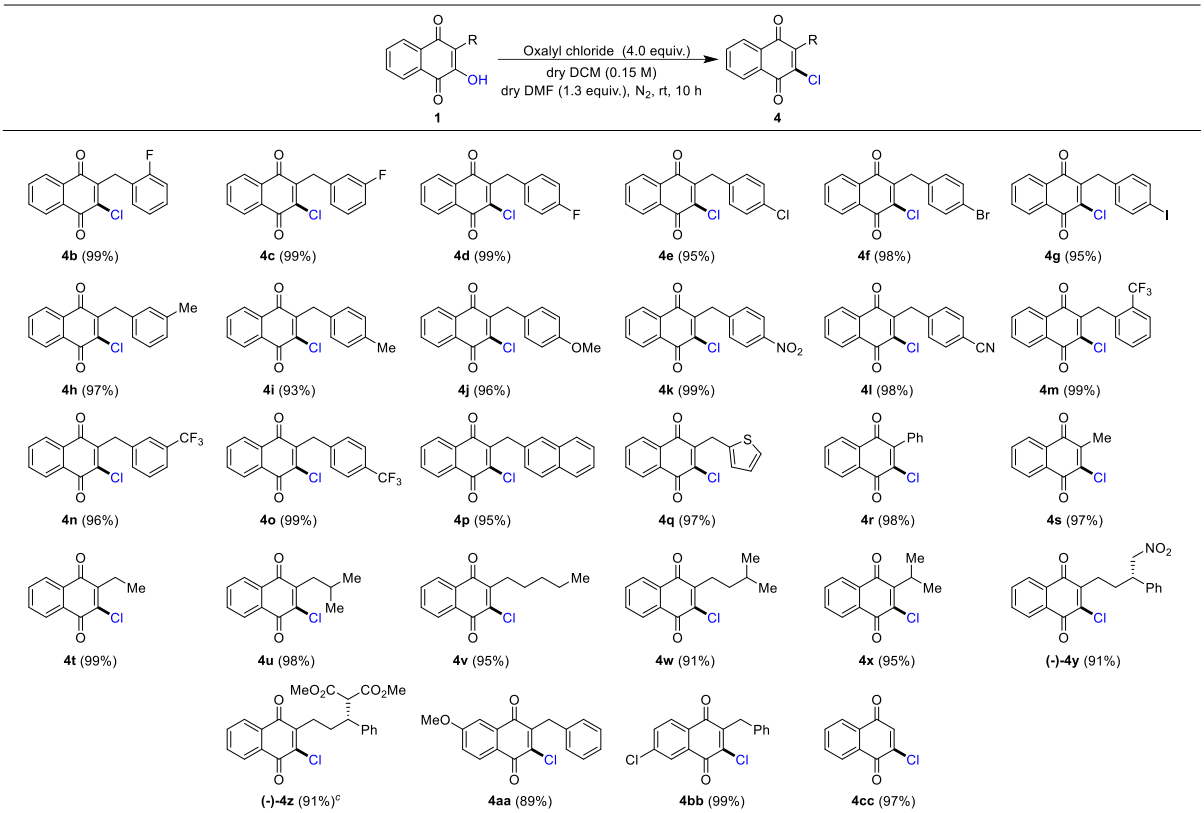
1a **4a**

Entry	Reagent	(equiv.)	Solvent	DMF	*t* (h)	Yield (%)[b]
1	Oxalyl chloride	(2)	DCM	1.3	10	70
2	Oxalyl chloride	(4)	DCM	1.3	10	95
3[c]	Thionyl Chloride	(2)	DCM	-	10	-
4	Oxalyl chloride	(4)	AcCN	1.3	10	18

[a] Reaction was carried out taking **1a** (0.3 mmol), oxalyl chloride, dry DCM (0.15 M) and dry DMF (1.3 equiv.) under nitrogen atmosphere. [b] Yields refer to the column purified product. [c] 92% of unreacted **1a** was recovered after the reaction.

Discussion for Table S2: With this pre-knowledge, we performed the chlorination reaction by taking pure isolated 3-benzyllawsone **1a** (0.3 mmol), 2.0 equiv. of oxalyl chloride, dry DCM (0.15 M) and 1.3 equiv. of dry DMF at room temperature under nitrogen atmosphere for 10 h furnished the product **4a** in 70% yield (Table S2, entry 1). On increasing the amount of oxalyl chloride up to 4.0 equiv. furnished the product **4a** in 95% yield in 10 h (Table S2, entry 2). When oxalyl chloride was replaced by 2.0 equiv. of thionyl chloride, reaction did not proceed at all and 92% of unreacted starting material **1a** was recovered back from the reaction mixture (Table S2, entry 3). Lastly, on changing the solvent from dry DCM to dry acetonitrile, **4a** obtained in just 18% yield after 10 h (Table S2, entry 4). Thus, reacting 3-benzyllawsone **1a** with 4.0 equiv. of oxalyl chloride, 1.3 equiv. of dry DMF and dry DCM (0.15 M) at room temperature under nitrogen atmosphere for 10 h was finalized as the best optimized condition for the synthesis of 2-alkyl-3-chloronaphthalene-1,4-diones **4**.

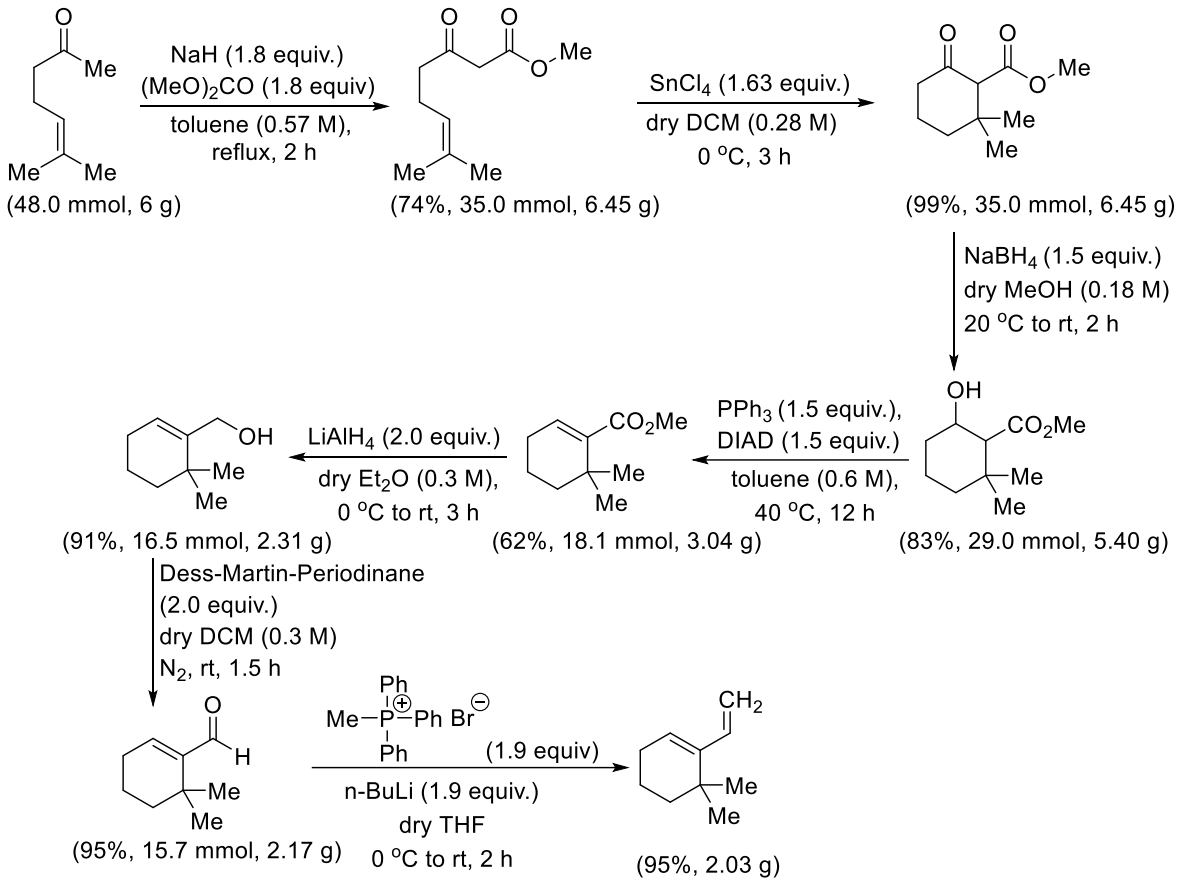
Table S3: Substrate scope for the synthesis of 2-alkyl-3-chloronaphthalene-1,4-diones **4** [a]



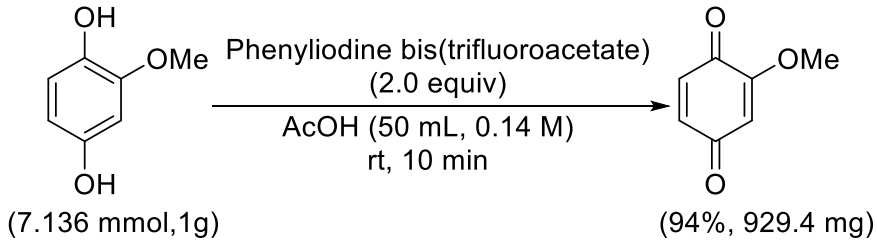
[a] Reaction was carried out taking **1** (0.3 mmol), oxalyl chloride (4.0 equiv.), dry DCM (0.15 M), dry DMF (1.3 equiv.) under nitrogen condition. [b] Yields refer to the column purified product. [c] Reaction completed within 2 h.

Discussion for Table S3: After successful optimization, we generated a huge library of 2-alkyl-3-chloronaphthalene-1,4-diones **4** from the corresponding 3-alkyllawsones **1** (Table S3). Interestingly, all the three-component reductive *C*-alkylated products containing aromatic, biaryl, heteroaromatic, aliphatic group **1b-x** performed excellently resulting in **4b-x** in 91-99% yield in 10 h (Table S3). Chiral substrates such as (-)-**1y** and (-)-**1z** also resulted in product (-)-**4y** and (-)-**4z** in 91% yield in 10 h and 2 h respectively (Table S3). More functionalized reductive *C*-alkylated products such as **1aa** and **1bb** also afforded **4aa** and **4bb** in 89% and 99% yield respectively. When simple lawsone was subjected in the optimized reaction condition, **4cc** was obtained in 97% yield in 10 h (Table S3).

Synthesis of key-intermediates for the total synthesis of deoxyneocryptotanshinone and miltirone:[1,2]

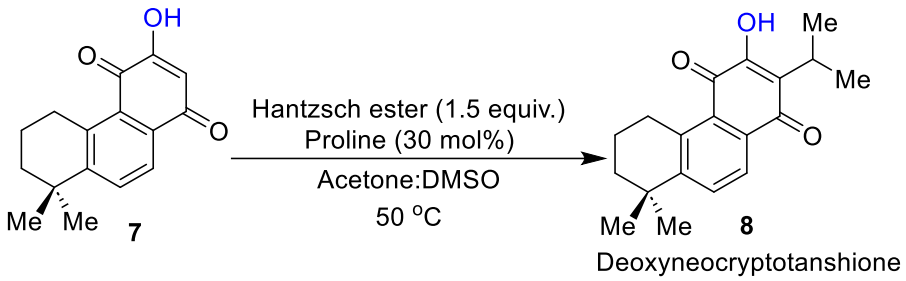


Scheme S1. Synthesis of 6, 6-dimethyl-1-vinylcyclohex-1-ene.[1]



Scheme S2. Synthesis of 2-methoxycyclohexa-2,5-diene-1,4-dione.[2]

Table-S4: Optimization for the reductive *C*-alkylation of 3-hydroxy-8,8-dimethyl-5,6,7,8-tetrahydrophenanthrene-1,4-dione **7** with acetone [a]



Entry	Solvent	*t* (h)	Yield (%)[b]
1[c]	2:3	24	27
2[d]	2:3	24	17
3	2:3	48	30
4[e]	1:2	48	35
5[e,f]	1:2	48	45

[a] Reactions were carried out in solvent (0.3 M) with 1.5 equiv. of Hantzsch ester (added portion-wise) with relative to **7** (0.2 mmol) in presence of 30 mol% of proline as catalyst at 50 ºC. [b] Yield refers to the column purified product of **8**. [c] 1.1 equiv. of Hantzsch ester was taken with relative to **7** (0.1 mmol). [d] 3.0 equiv. of Hantzsch ester was taken. [e] Acetone : DMSO (1:2) in 0.26 M was taken. [f] 1.0 equiv. of proline was taken.

Discussion for Table S4: In the beginning, key intermediate **7** was treated with 30 mol% of proline, 1.1 equiv. of Hantzsch ester and a solvent combination of acetone and DMSO in 2:3 ratio (0.3 M) resulting in the desired natural product deoxyneocryptotanshinone **8** with 27% yield in 24 h through reductive alkylation reaction (Table S4, entry 1). On performing the reductive *C*-alkylation reaction using 3.0 equiv. of Hantzsch ester, yield dropped to 17% in 24 h (Table S4, entry 2). Increasing the reaction time up to 48 h did not contribute to any betterment of the reductive alkylation with acetone (Table S4, entry 3). On taking acetone and DMSO in 1:2 ratio (0.26 M), reductive alkylation product **8** was obtained in 35% yield in 48 h (Table S4, entry 4). On increasing the catalyst loading up to 1.0 equiv., the natural product **8** was obtained with 45% in 48 h (Table S4, entry 5).

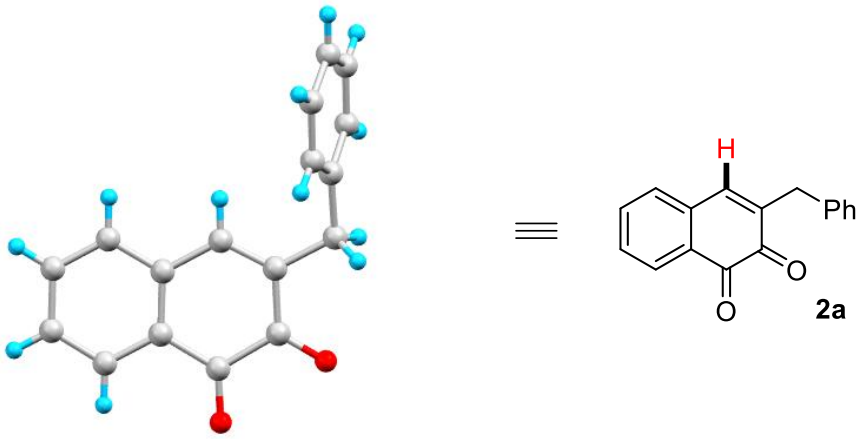


Figure S1: Crystal structure of 3-benzylnaphthalene-1,2-dione (**2a**).

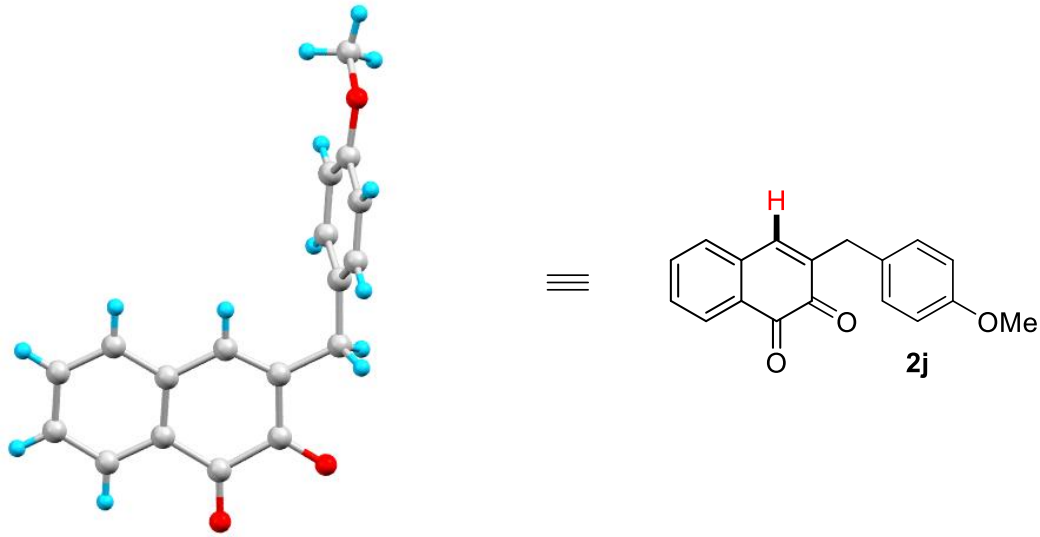


Figure S2: Crystal structure of 3-(4-methoxybenzyl)-naphthalene-1,2-dione (**2j**).

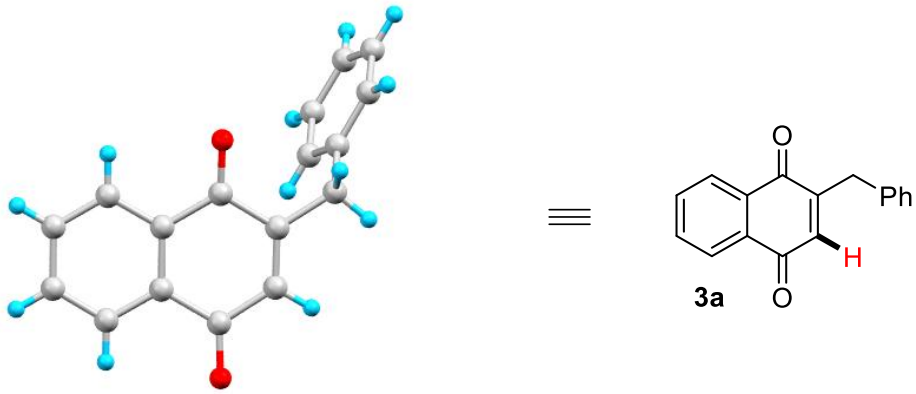


Figure S3: Crystal structure of 2-benzylnaphthalene-1,4-dione (**3a**).

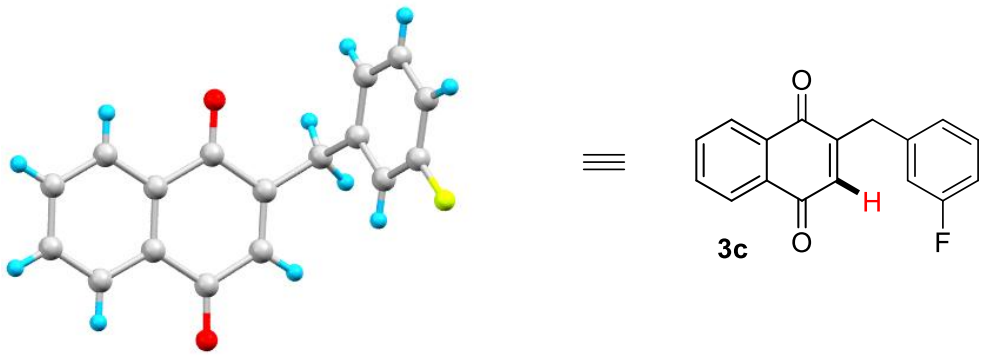


Figure S4: Crystal structure of 2-(3-fluorobenzyl)-naphthalene-1,4-dione (**3c**).

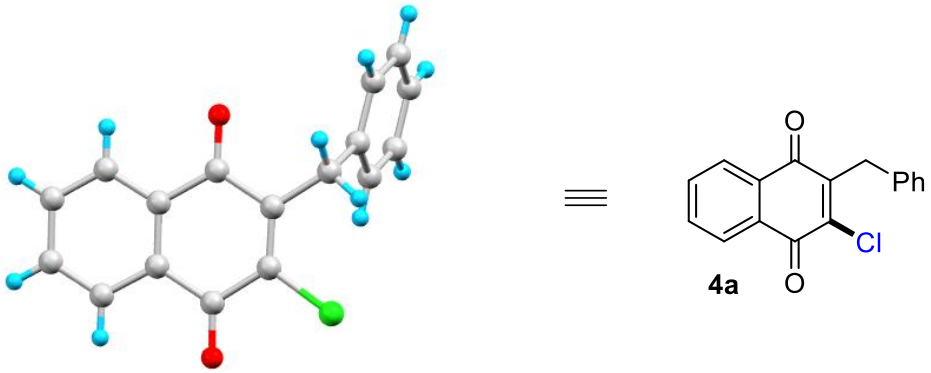


Figure S5: Crystal structure of 2-benzyl-3-chloronaphthalene-1,4-dione (**4a**).

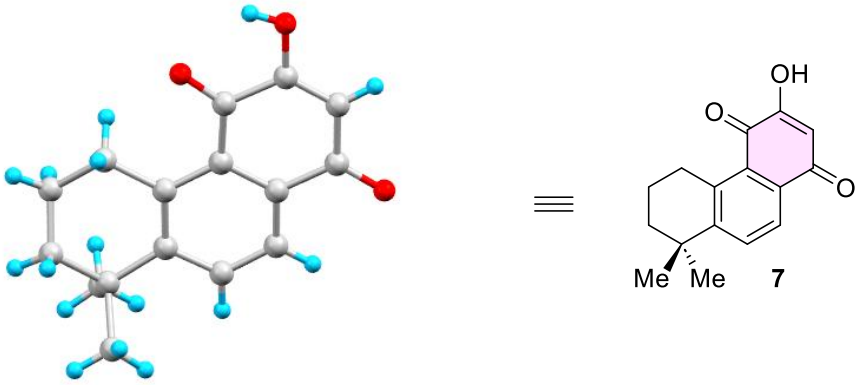
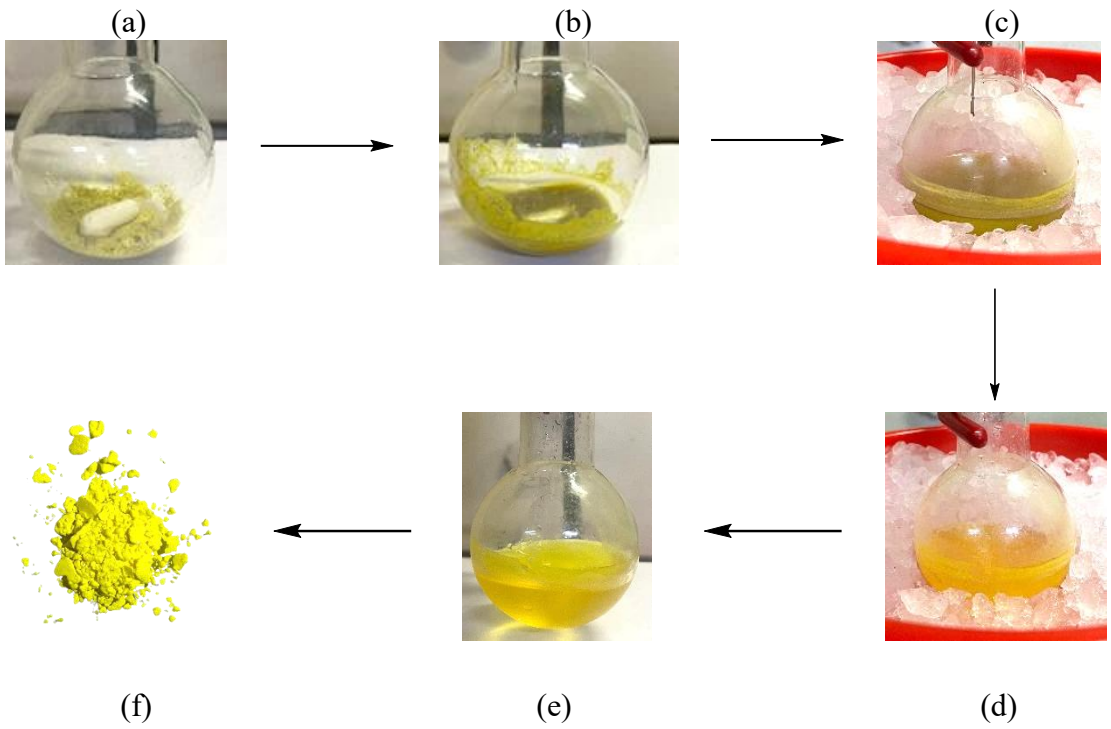
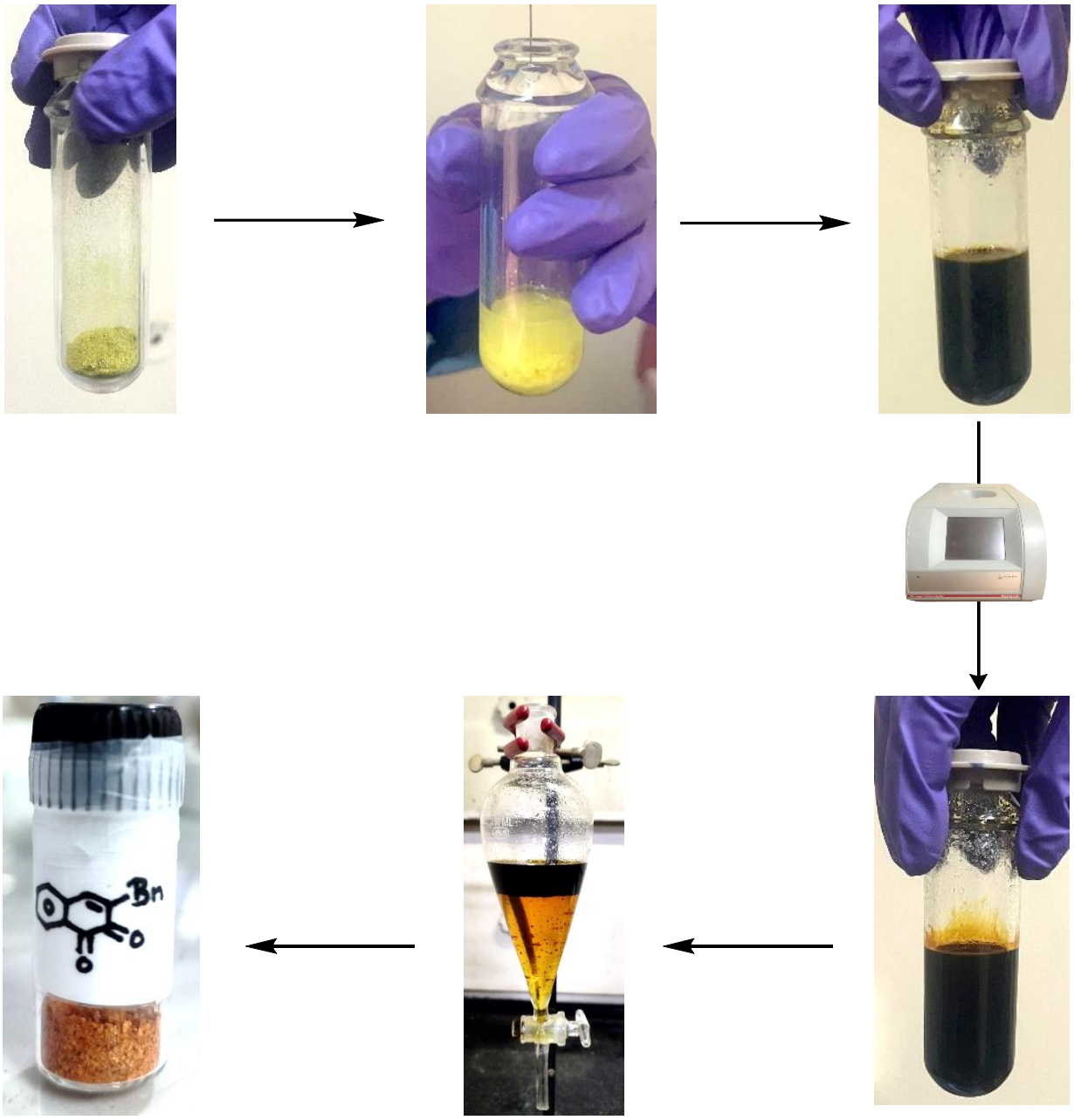


Figure S6: Crystal structure of 3-hydroxy-8,8-dimethyl-5,6,7,8-tetrahydrophenanthrene-1,4-dione (**7**).



(a) 3.8 mmol of 2-benzyl-3-hydroxynaphthalene-1,4-dione **1a** was taken in a round bottom flask equipped with a magnetic stirring bar. (b) Then, 25 mL of dry DCM was added and N_2 atmosphere was maintained. (c) The reaction temperature was brought to 0 ºC and 2.8 mL of oxalyl chloride was added drop-wise. (d) Then, 0.4 mL of dry DMF was added drop wise to the reaction mixture and stirred at 0 ºC for 5 minutes. (e) The ice bath was removed and the reaction mixture was stirred for 10 h at rt. (f) Pure 2-benzyl-3-chloronaphthalene-1,4-dione **4a** was obtained with 91% yield after flash column chromatography.

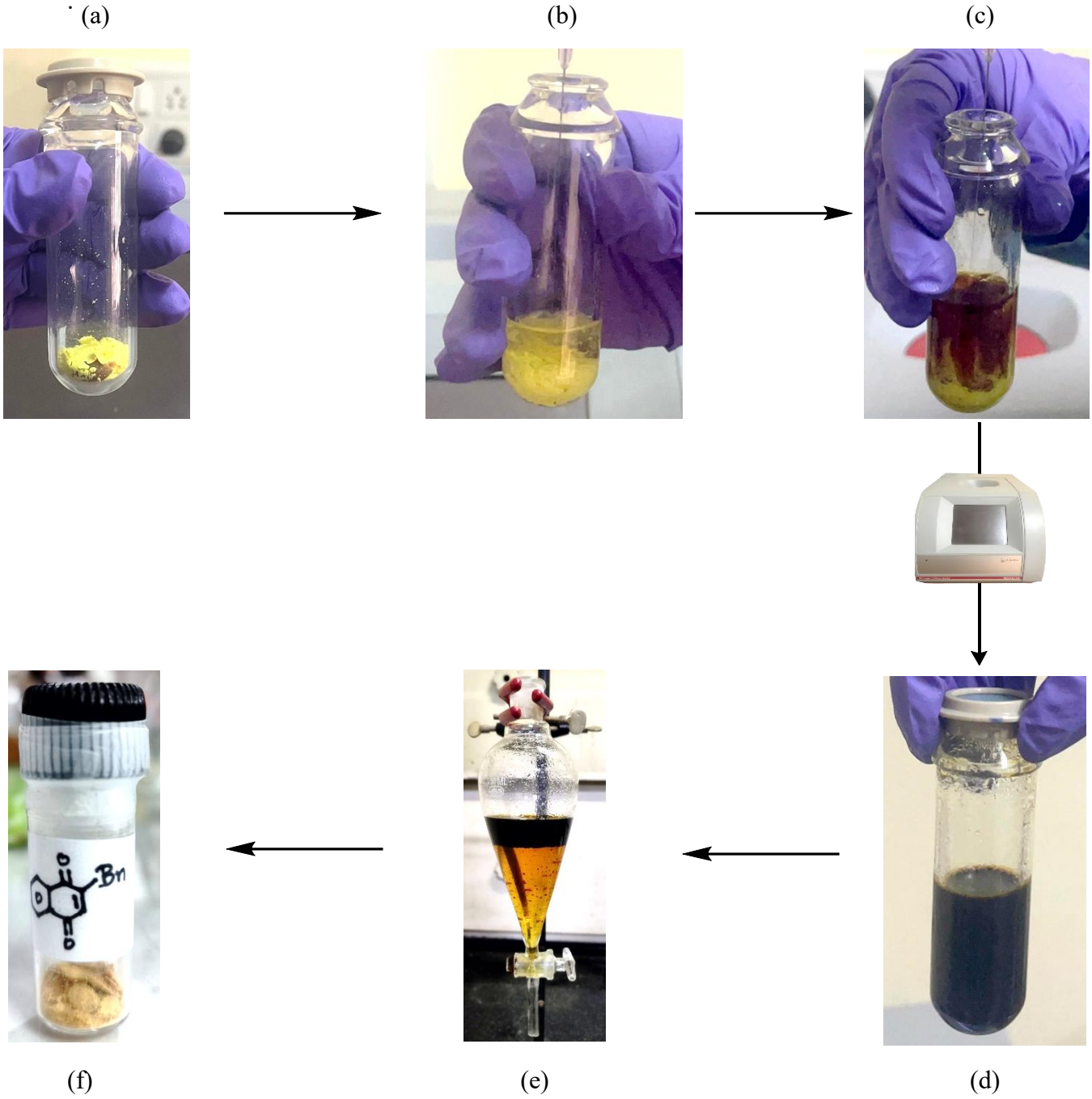
Figure S7: Pictorial representation for the gram-scale synthesis of 2-benzyl-3-chloronaphthalene-1,4-dione (**4a**).



(f) (e) (d)

(a) 3.8 mmol of 2-benzyl-3-hydroxynaphthalene-1,4-dione **1a** was taken in a microwave reaction tube equipped with a magnetic stirring bar. (b) 9.5 mL of AcOH was added to it. (c) Then, hydroiodic acid (57 wt.% in H_2O, 6.0 mL, 7.0 equiv.) was added to the reaction mixture and allowed to stirred at 90 °C in the Monowave 200 microwave reactor. (d) After 1 h the reaction mixture was taken out of the microwave reactor. (e) The reaction mixture was diluted with water and organic phase was separated using EtOAc (3 x 25 mL) and concentrated using rotary evaporator. (f) Pure 3-benzylnaphthalene-1,2-dione **2a** was obtained with 90% yield after column purification.

Figure S8: Pictorial representation of gram-scale synthesis of 3-benzylnaphthalene-1,2-dione **2a**.



(a) 3.54 mmol of 2-benzyl-3-chloronaphthalene-1,4-dione **4a** was taken in a microwave reaction tube equipped with a magnetic stirring bar. (b) 9.0 mL of AcOH was added to it. (c) Then, hydroiodic acid (57 wt.% in H_2O, 4.0 mL, 5.0 equiv.) was added to the reaction mixture and allowed to stirred at 90 ºC in mono-wave 200 microwave reactor. (d) After 1 h the reaction mixture was taken out of the microwave reactor. (e) The reaction mixture was diluted with water and organic phase was separated using EtOAc (3 x 25 mL) and concentrated using rota evaporator. (f) Pure 2-benzylnaphthalene-1,4-dione **3a** was obtained with 95% yield after column purification.

Figure S9: Pictorial representation for the gram-scale synthesis of 2-benzylnaphthalene-1,4-dione **3a**.

General Experimental Procedures

Procedure A: General Procedure for Hydrodehydroxylation: In an oven dried microwave reaction vial equipped with a magnetic stirring bar was taken 3-alkyllawsone (0.2 mmol, 1.0 equiv.), to which acetic acid (0.5 mL, 0.4 M) followed by hydroiodic acid (57 wt.% in H_2O, 0.31 mL, 1.4 mmol, 7.0 equiv.) was added and allowed to stirred at 90 ºC in Monowave 200 microwave reactor. The completion of the reaction was monitored by thin layer chromatography. The reaction mixture was diluted with water and organic layer was extracted with ethyl acetate (3 x 10 mL). The combined organic layer was dried over Na_2SO_4 and concentrated. Pure 1,2-naphthoquinones were obtained by column chromatography (silica gel, hexane/ethyl acetate).

Procedure B: General Procedure for Hydrodechlorination: In an oven dried microwave reaction vial equipped with a magnetic stirring bar was taken 2-alkyl-3-chloronaphthalene-1,4-dione (0.2 mmol, 1.0 equiv.), to which acetic acid (0.5 mL, 0.4 M) followed by hydroiodic acid (57 wt.% in H_2O, 0.22 mL, 1.0 mmol, 5.0 equiv.) was added and allowed to stirred at 90 ºC in Monowave 200 microwave reactor. The completion of the reaction was monitored by thin layer chromatography. The reaction mixture was diluted with water and organic layer was extracted with ethyl acetate (3 x 10 mL). The combined organic layer was dried over Na_2SO_4 and concentrated. Pure 1,4-naphthoquinones were obtained by column chromatography (silica gel, hexane/ethyl acetate).

Procedure C: General Procedure for Synthesis of 2-Alkyl-3-chloronaphthalene-1,4-diones: In an oven dried round bottom flask equipped with a magnetic stirring bar was taken 3-alkyllawsone (0.3 mmol, 1.0 equiv.) to which dry DCM (2 mL, 0.15 M) was added under nitrogen atmosphere. Then, oxalyl chloride (103 µL, 1.2 mmol, 4.0 equiv.) and dry DMF (30 µL, 0.39 mmol, 1.3 equiv.) was added respectively and the reaction mixture was allowed to stirred at room temperature for 10 h followed by flash column chromatography (silica gel, mixture of hexane/ethyl acetate) to obtain the pure 2-alkyl-3-chloronaphthalene-1,4-dione.

Procedure D: General Procedure for Proline Catalyzed Three Component Reductive Alkylation (TCRA) Reaction: In an oven dried round bottom flask equipped with a magnetic stirring bar, 2-hydroxy-1,4-naphthoquinone (52.2 mg, 0.3 mmol, 1.0 equiv.) was taken, to which proline (6.9 mg, 0.06 mmol, 20 mol%), Hantzsch ester (83.6 mg, 0.33 mmol, 1.1 equiv.) and DCM (1.0 mL, 0.3 M) was added and stirred for 10 seconds. Then, aldehyde (0.6 mmol, 2.0 equiv.) was added and allowed to stirred for 12-24 h at 35 ºC. After completion of reaction,

the reaction mixture was concentrated under reduced pressure and purified by column chromatography (silica gel, mixture of hexanes/ethyl acetate) to afford pure 3-alkyl-2-hydroxy-1,4-naphthoquinone.

Procedure E: General Procedure for the Synthesis of Phthiocol 1s: In an oven dried round bottom flask equipped with a magnetic stirring bar at 0 ºC was taken 2-ethyl-3-hydroxy-1,4-naphthoquinone (500 mg, 2.47 mmol, 1.0 equiv.), to which ice-cold $KMnO_4$ (4.69 mmol, 1.9 equiv. in 86 mL of H_2O) and 173 mL of ice-cold NaOH solution (2% NaOH in H_2O) was added and stirred vigorously for 20 seconds and stood still at 0 ºC for 2 h followed by at 25 ºC for 20 h. After 20 h, the reaction mixture was filtered in order to remove the precipitated MnO_2. The filtrate was acidified with 20% HCl and then extracted with ethyl acetate thrice (3 x 25 mL). The combined organic layers were dried over Na_2SO_4 and concentrated. Pure phthiocol **1s** was obtained by column chromatography (silica gel, hexane/ethyl acetate).

Procedure F: General Procedure for the Synthesis of 2-Hydroxy-3-isopropylnaphthalene-1,4-dione (1x): In an oven dried round bottom flask equipped with a magnetic stirring bar was taken 2-hydroxy-1,4-naphthoquinone (52.2 mg, 0.3 mmol, 1.0 equiv.). To this proline (10.4 mg, 0.09 mmol, 30 mol%), Hantzsch ester (114.0 mg, 0.45 mmol, 1.5 equiv.) in two portion and solvent combination of acetone + DMSO in 1:2 (1.0 mL, 0.3 M) was added and stirred for 24 h at 50 ºC. After completion of reaction, the reaction mixture was diluted with water and organic layer was extracted with ethyl acetate thrice (3 x 10 mL). The combined organic layers were dried over sodium sulphate and concentrated. Pure product (**1x**) was afforded via column chromatography (silica gel, mixture of hexanes/ethyl acetate).

Procedure G: Modified procedure for the synthesis of 3-Hydroxy-8,8-dimethyl-5,6,7,8-tetrahydrophenanthrene-1,4-dione 7:[1,2]

Step-1: [4+2]-cycloaddition reaction: In an oven dried round bottom flask equipped with a magnetic stirring bar was taken hot ethanol (6 mL). To it, 2-methoxycyclohexa-2,5-diene-1,4-dione (349.4 mg, 2.53 mmol, 1.0 equiv.) was added and stirred for 10 seconds. In another round bottom flask, the solution of 6,6-dimethyl-1-vinylcyclohex-1-ene (690 mg, 5.06 mmol, 2.0 equiv.) in ethanol (3 mL) was taken and drop-wise added to the solution of dienophile. The reaction was stirred for 12 h at room temperature.

Step-2: Aromatization through air-oxidation followed by deprotection of OMe: After completion of cycloaddition reaction, the solvent was evaporated to remove any excess diene from the reaction media. Then, ethanol (2.5 mL, 1.0 M) was added to the reaction mixture and

KOH pellets (1.41 g, 25.2 mmol, 14.0 equiv.) was added. Air was bubbled into the reaction mixture and stirred for 24 h at room temperature. Then, reaction mixture was acidified with HCl (1.0 N) and organic layer was extracted with ethyl acetate thrice (3 x 25 mL). The combined organic layers were dried over Na_2SO_4 and concentrated. Pure product **7** was obtained by column chromatography (silica gel, hexane/ethyl acetate).

Procedure H: General Procedure for the synthesis of Deoxyneocyptotanshione 8: In an oven dried round bottom flask equipped with a magnetic stirring bar was taken compound **7** (51.3 mg, 0.2 mmol, 0.2 equiv.). To this proline (23 mg, 0.2 mmol, 1.0 equiv.), Hantzsch ester (76 mg, 0.3 mmol, 1.5 equiv.) in two portion and solvent combination of acetone + DMSO in 1:2 (0.26 mL, 0.77 M) was added and stirred for 48 h at 50 ºC. After completion of reaction, the reaction mixture was diluted with water and organic layer was extracted with ethyl acetate thrice (3 x 5 mL). The combined organic layers were dried over sodium sulphate and concentrated. Pure natural product **8** was afford via column chromatography (silica gel, mixture of hexanes/ethyl acetate).

Procedure I: General Procedure for the synthesis of Miltirone 9: In an oven dried round bottom flask vial equipped with a magnetic stirring bar was taken compound **8** (60 mg, 0.2 mmol, 1.0 equiv.), to which acetic acid (0.9 mL, 0.22 M) followed by hydroiodic acid (57 wt.% in H_2O, 0.31 mL, 1.4 mmol, 7.0 equiv.) was added and allowed to stirred at 90 ºC in an oil bath. After reaction completion, the reaction mixture was diluted with water and organic layer was extracted with ethyl acetate (3 x 10 mL). The combined organic layer was dried over Na_2SO_4 and concentrated. Pure natural product **9** was obtained by column chromatography (silica gel, hexane/ethyl acetate).

Procedure J: General Procedure for the synthesis of analogue of Deoxyneocryptotanshinone 11: In an oven dried round bottom flask equipped with a magnetic stirring bar was taken compound **7** (50.0 mg, 0.2 mmol, 0.2 equiv.). To this proline (4.5 mg, 0.04 mmol, 20 mol%), Hantzsch ester (53.2 mg, 0.21 mmol, 1.1 equiv.) and DCM (0.66 mL, 0.3 M) was added and stirred for 10 seconds. Then, acetaldehyde (56 µL, 1.0 mmol, 5.0 equiv.) was added and stirred for 15 h at room temperature. After completion of reaction, the reaction mixture was concentrated under reduced pressure and pure product **11** was afford via column chromatography (silica gel, mixture of hexanes/ethyl acetate).

Procedure K: General Procedure for the synthesis of analogue of Miltirone 12: In an oven dried round bottom flask vial equipped with a magnetic stirring bar was taken compound **11**

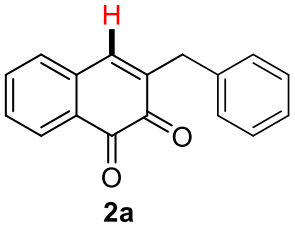
(31 mg, 0.11 mmol, 1.0 equiv.), to which acetic acid (0.5 mL, 0.22 M) followed by hydroiodic acid (57 wt.% in H_2O, 0.17 mL, 0.77 mmol, 7.0 equiv.) was added and allowed to stirred at 90 ºC in an oil bath. After reaction completion, the reaction mixture was diluted with water and organic layer was extracted with ethyl acetate (3 x 5 mL). The combined organic layer was dried over Na_2SO_4 and concentrated. Pure product **12** was obtained by column chromatography (silica gel, hexane/ethyl acetate).

Procedure L: Modified procedure for the synthesis of (6,6-dimethylcyclohex-1-en-1-yl)-methanol: **Step-1**: In an oven dried round bottom flask methyl 6,6-dimethylcyclohex-1-ene-1-carboxylate (3.0 g, 18.0 mmol, 1.0 equiv.) was taken and dry ether (27 mL) was added to it in nitrogen atmosphere and stirred for 10 seconds.

Step-2: In a separate oven dried round bottom flask $LiAlH_4$ (1.37 g, 36 mmol, 2.0 equiv.) was taken and to it dry ether (27 mL) was added at 0 ºC under nitrogen atmosphere. Then, the previously prepared ester solution (in step-1) was added to it drop-wise at 0 ºC. The reaction mixture was stirred for 3 h at 0 ºC to rt. After the completion of reaction, half saturated solution of ammonium chloride was added to the reaction mixture and stirred for 5 minutes. The organic layer was extracted using diethyl ether thrice (3 x 80 mL). The organic layers were washed with water followed by washing with brine. The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. The crude product (6,6-dimethylcyclohex-1-en-1-yl)-methanol (2.31 g, 91%) was obtained as a viscous colourless oil and was pure enough to use directly in the next step without further purification.

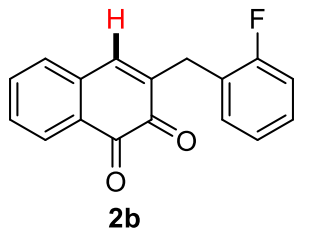
Procedure M: Modified procedure for the synthesis of 6,6-dimethylcyclohex-1-ene-1-carbaldehyde: In an oven dried round bottom flask was taken (6,6-dimethylcyclohex-1-en-1-yl)-methanol (2.31 g, 16.5 mmol, 1.0 equiv.) and dry DCM (50 mL, 0.3 M) was added to the reaction mixture under nitrogen atmosphere. The reaction mixture was brought to 0 ºC and Dess-Martin-Periodinane (14 g, 33 mmol, 2.0 equiv.) was added to it slowly. Then, reaction was stirred for 1.5 h at room temperature. The slightly volatile product 6,6-dimethylcyclohex-1-ene-1-carbaldehyde (2.17 g, 95%) was obtained by flash column chromatography (silica gel, hexane/ethyl acetate) and was immediately used in the next step.

3-Benzylnaphthalene-1,2-dione (2a): Prepared by following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.4:9.6 to 0.8:9.2) and isolated as orange solid. Yield: 99% (49 mg). MP: 149-151 ºC. IR (Neat): ν_{max} 2917, 1657, 1584, 1451, 1380, 1256, 938, 753 and 699 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 8.03 (1H, d, *J* = 8.0 Hz), 7.56 (1H, dt, *J* = 7.5, 1.5 Hz), 7.41 (1H, dt, *J* = 7.5, 1.0 Hz), 7.35-7.32 (2H, m), 7.27-7.24 (3H, m), 7.19 (1H, d, *J* = 7.0 Hz), 6.98 (1H, br s, olefinic-*H*), 3.77 (2H, s); $^{13}C\{^1H\}$ NMR ($CDCl_3$, DEPT-135, 125 MHz): δ 180.8 (C, *C*=O), 179.1 (C, *C*=O), 141.6 (CH), 140.0 (C), 137.7 (C), 135.8 (CH), 135.2 (C), 130.6 (C), 130.0 (CH), 129.9 (CH), 129.4 (CH), 129.3 (2 x CH), 128.7 (2 x CH), 126.7 (CH), 35.1 (CH_2); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{17}H_{13}O_2$ 249.0916; Found 249.0920.



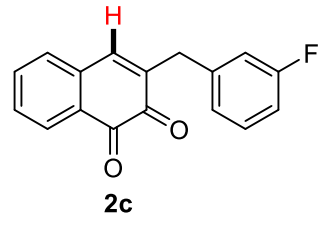
2a

3-(2-Fluorobenzyl)naphthalene-1,2-dione (2b): Prepared by following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.2:9.8 to 0.5:9.5) and isolated as orange solid. Yield: 99% (52.7 mg). MP:156-158 ºC. IR (Neat): ν_{max} 2960, 1657, 1584, 1450, 1257, 1096, 937 and 754 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 8.03 (1H, d, *J* = 7.5 Hz), 7.57 (1H, dt, *J* = 7.5, 1.0 Hz), 7.42 (1H, t, *J* = 7.5 Hz), 7.32 (1H, td, *J* = 7.2, 1.5 Hz), 7.28-7.23 (1H, m), 7.22 (1H, d, *J* = 7.5 Hz), 7.11 (1H, dt, *J* = 7.5, 1.0 Hz), 7.07 (1H, t, *J* = 9.5 Hz), 7.03 (1H, s, olefinic-*H*), 3.80 (2H, s); $^{13}C\{^1H\}$ NMR ($CDCl_3$, DEPT-135, 100 MHz): δ 180.6 (C, *C*=O), 179.0 (C, *C*=O), 161.2 (C, d, *J* = 245 Hz, *C*-F), 141.7 (CH), 138.2 (C), 135.8 (CH), 135.1 (C), 131.8 (CH, d, *J* = 4.0 Hz), 130.6 (C), 130.0 (CH), 129.9 (CH), 129.6 (CH), 128.7 (CH, d, *J* = 8.0 Hz), 124.6 (C, d, *J* = 15.0 Hz), 124.3 (CH, d, *J* = 3.0 Hz), 115.5 (CH, d, *J* = 21.0 Hz), 28.6 (CH_2, d, *J* = 3.0 Hz); ^{19}F NMR ($CDCl_3$, 375 MHz): δ -117.3; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{17}H_{12}FO_2$ 267.0821; Found 267.0818.



2b

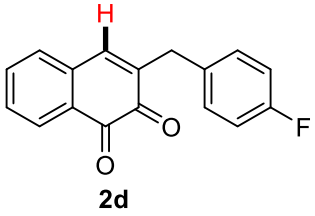
3-(3-Fluorobenzyl)naphthalene-1,2-dione (2c): Prepared by following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.2:9.8 to 0.5:9.5) and isolated as orange solid. Yield: 99% (52.7 mg). MP: 139-141 ºC. IR (Neat): ν_{max} 2915, 1659, 1584, 1450, 1381, 1257, 1097, 938 and 753 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 8.03 (1H, d, *J* = 7.0 Hz), 7.59 (1H, t, *J* = 8.0 Hz), 7.43 (1H, t, *J* = 7.5 Hz), 7.29 (1H, q, *J* = 6.5 Hz), 7.24 (1H, d, *J* = 7.5 Hz), 7.05 (2H, d, *J* = 9.5 Hz), 6.96 (2H, br q), 3.76 (2H, s); $^{13}C\{^1H\}$ NMR ($CDCl_3$, DEPT-135, 100 MHz): δ 180.6 (C, *C*=O), 178.9 (C, *C*=O), 162.9 (C, d, *J* = 245 Hz,



2c

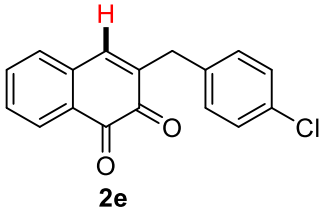
C-F), 141.9 (CH), 140.2 (C, d, *J* = 7.0 Hz), 139.1 (C), 135.9 (CH), 134.9 (C), 130.6 (C), 130.15 (CH, d, *J* = 8.3 Hz), 130.1 (CH), 130.0 (CH), 129.5 (CH), 124.9 (CH, d, *J* = 3.0 Hz), 116.1 (CH, d, *J* = 21 Hz), 113.7 (CH, d, *J* = 21 Hz), 34.9 (CH_2, d, *J* = 1.0 Hz); ^{19}F NMR ($CDCl_3$, 470 MHz): δ -112.9; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{17}H_{11}FO_2Na$ 289.0641; Found 289.0642.

3-(4-Fluorobenzyl)naphthalene-1,2-dione (**2d**): Prepared by following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.4:9.6 to 0.8:9.2) and isolated as orange solid. Yield: 94% (50 mg). MP: 140-141 °C. IR (Neat): ν_{max} 2922, 1657, 1504, 1216, 1153, 1094, 933 and 761 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 8.03 (1H, d, *J* = 7.5 Hz), 7.60 (1H, dt, *J* = 7.5, 1.0 Hz), 7.42 (1H, dt, *J* = 7.5, 1.0 Hz), 7.23 (3H, m), 7.01 (3H, m), 3.74 (2H, s); $^{13}C\{^1H\}$ NMR ($CDCl_3$, DEPT-135, 100 MHz): δ 180.7 (C, *C*=O), 179.0 (C, *C*=O), 161.7 (C, d, *J* = 243 Hz, *C*-F), 141.7 (CH), 139.7 (C), 135.9 (CH), 135.0 (C), 133.3 (C, d, *J* = 3.0 Hz), 130.8 (CH), 130.7 (CH), 130.6 (C), 130.0 (2 x CH, d, *J* = 8 Hz), 129.5 (CH), 115.5 (2 x CH, d, *J* = 21 Hz), 34.5 (CH_2); ^{19}F NMR ($CDCl_3$, 375 MHz): δ -116.1; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{17}H_{12}FO_2$ 267.0821; Found 267.0819.



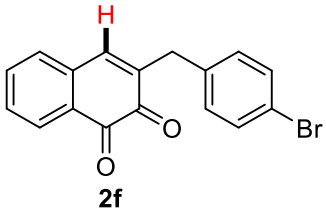
2d

3-(4-Chlorobenzyl)naphthalene-1,2-dione (**2e**): Prepared by following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.2:9.8 to 0.5:9.5) and isolated as orange solid. Yield: 93% (52.5 mg). MP: 142-144 °C. IR (Neat): ν_{max} 2922, 1656, 1584, 1452, 1383, 1255, 1089, 934, 804, and 763 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 8.04 (1H, d, *J* = 7.0 Hz), 7.59 (1H, t, *J* = 7.5 Hz), 7.43 (1H, t, *J* = 7.5 Hz), 7.30 (2H, d, *J* = 7.5 Hz), 7.23-7.19 (3H, m), 6.99 (1H, s, olefinic-*H*), 3.73 (2H, s); $^{13}C\{^1H\}$ NMR ($CDCl_3$, DEPT-135, 100 MHz): δ 180.7 (C, *C*=O), 179.0 (C, *C*=O), 141.8 (CH), 139.4 (C), 136.2 (C), 135.9 (CH), 135.0 (C), 132.6 (C), 130.6 (2 x CH, C), 130.2 (CH), 130.1 (CH), 129.5 (CH), 128.8 (2 x CH), 34.6 (CH_2); HRMS (ESI-TOF) *m/z*: $[M + NH_4]^+$ Calcd for $C_{17}H_{15}NClO_2$ 300.0791; Found 300.0792.



2e

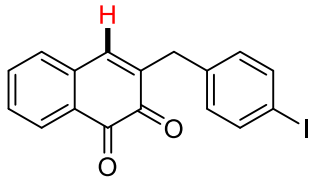
3-(4-Bromobenzyl)naphthalene-1,2-dione (**2f**): Prepared by following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.2:9.8 to 0.5:9.5) and isolated as orange solid. Yield: 93% (61 mg). MP: 144-146 °C. IR (Neat): ν_{max} 3036, 1656, 1584, 1452, 1383, 1255, 1089, 934, and 763 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 8.04 (1H,



2f

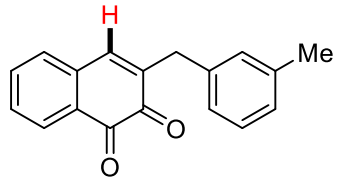
d, J = 7.5 Hz), 7.59 (1H, dt, J = 7.5, 1.0 Hz), 7.43 (1H, dt, J = 7.5, 1.0 Hz), 7.30 (2H, td, J = 8.5, 2.5 Hz), 7.23-7.19 (3H, m), 6.99 (1H, s, olefinic-*H*), 3.73 (2H, s); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, DEPT-135, 100 MHz): δ 180.6 (C, *C*=O), 178.9 (C, *C*=O), 141.8 (CH), 139.3 (C), 136.1 (C), 135.9 (CH), 134.9 (C), 132.6 (C), 130.5 (2 x CH, C), 130.1 (CH), 130.0 (CH), 129.5 (CH), 128.8 (2 x CH), 34.6 (CH_2); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{17}H_{12}BrO_2$ 327.0021; Found 327.0020.

2-Chloro-3-(4-iodobenzyl)naphthalene-1,4-dione (2g): Prepared by following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.4:9.6 to 0.8:9.2) and isolated as orange solid. Yield: 95% (71 mg). MP: 159-161 ºC. IR (Neat): ν_{max} 1664, 1480, 1305, 1256, 1003, 938 and 766 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.03 (1H, d, J = 7.5 Hz), 7.64 (2H, d, J = 8.5 Hz), 7.58 (1H, dt, J = 8.5, 1.5 Hz), 7.42 (1H, dt, J = 7.5, 1.0 Hz), 7.22 (1H, d, J = 7.5 Hz), 7.02 (1H, s, olefinic-*H*), 7.00 (2H, d, J = 6.0 Hz), 3.70 (2H, CH_2); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, DEPT-135, 100 MHz): δ 180.6 (C, *C*=O), 178.9 (C, *C*=O), 141.8 (CH), 139.2 (C), 137.8 (2 x CH), 137.4 (C), 135.9 (CH), 134.9 (C), 131.3 (2 x CH), 130.6 (C), 130.1 (CH), 130.0 (CH), 129.5 (CH), 92.1 (C), 34.8 (CH_2); HRMS (ESI-TOF) *m/z*: $[M + NH_4]^+$ Calcd for $C_{17}H_{15}NIO_2$ 392.0147; Found 392.0147.



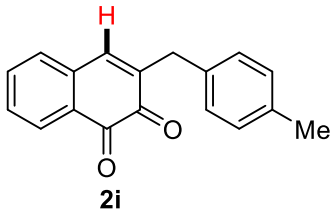
2g

3-(3-Methylbenzyl)naphthalene-1,2-dione (2h): Prepared by following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.4:9.6 to 0.8:9.2) and isolated as orange solid. Yield: 95% (50 mg). MP: 142-144 ºC. IR (Neat): ν_{max} 2919, 1658, 1583, 1377, 1257, 940 and 752 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.01 (1H, d, J = 7.0 Hz), 7.56 (1H, t, J = 7.5 Hz), 7.40 (1H, t, J = 7.5 Hz), 7.21 (2H, m), 7.06 (3H, m), 6.99 (1H, br s, olefinic-*H*), 3.72 (2H, s), 2.34 (3H, s, Ar-CH_3); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, DEPT-135, 125 MHz): δ 180.8 (C, *C*=O), 179.1 (C, *C*=O), 141.6 (CH), 140.0 (C), 138.3 (C), 137.6 (CH), 135.7 (C), 135.2 (C), 130.6 (C), 130.0 (CH), 129.9 (2 x CH), 129.4 (CH), 128.6 (CH), 127.4 (CH), 126.3 (CH), 35.0 (CH_2), 21.3 (CH_3); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{18}H_{15}O_2$ 263.1072; Found 263.1070.



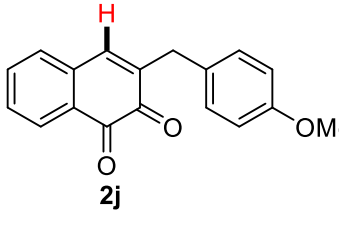
2h

3-(4-Methylbenzyl)naphthalene-1,2-dione (2i): Prepared by following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.4:9.6 to 0.8:9.2) and isolated as orange solid. Yield: 95% (50 mg). MP: 139-141 ºC. IR (Neat): ν_{max} 2918, 1654, 1583, 1514, 1375, 1252, 942 and 767 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 8.02 (1H, d, *J* = 7.5 Hz), 7.56 (1H, dt, *J* = 7.5, 1.5 Hz), 7.40 (1H, dt, *J* = 7.5, 1.0 Hz), 7.19 (1H, d, *J* = 7.5 Hz), 7.14 (4H, s), 6.97 (1H, br s, olefinic-*H*), 3.72 (2H, br s), 2.34 (3H, s, Ar-CH_3); $^{13}C\{^1H\}$ NMR ($CDCl_3$, DEPT-135, 125 MHz): δ 180.8 (C, *C*=O), 179.2 (C, *C*=O), 141.5 (CH), 140.2 (C), 136.3 (C), 135.7 (CH), 135.2 (C), 134.5 (C), 130.5 (C), 129.9 (2 x CH), 129.4 (3 x CH), 129.2 (2 x CH), 34.7 (CH_2), 21.0 (CH_3); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{18}H_{15}O_2$ 263.1072; Found 263.1062.



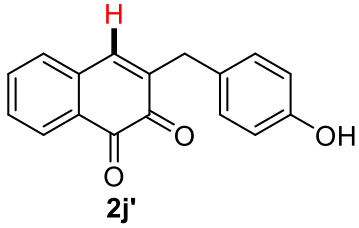
2i

3-(4-Methoxybenzyl)naphthalene-1,2-dione (2j): Prepared by following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.8:9.2 to 1.1:8.9) and isolated as orange solid. Yield: 70% (39 mg). MP: 154-156 ºC. IR (Neat): ν_{max} 2904, 1658, 1510, 1451, 1300, 1244, 1030, 938, 814 and 760 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 8.03 (1H, d, *J* = 7.5 Hz), 7.56 (1H, t, *J* = 7.5 Hz), 7.41 (1H, t, *J* = 7.5 Hz), 7.18 (3H, t, *J* = 9.5 Hz), 6.96 (1H, s, olefinic-*H*), 6.87 (2H, d, *J* = 8.5 Hz), 3.81 (3H, s, OCH_3), 3.71 (2H, s); $^{13}C\{^1H\}$ NMR ($CDCl_3$, DEPT-135, 125 MHz): δ 180.9 (C, *C*=O), 179.3 (C, *C*=O), 158.5 (C), 141.4 (CH), 140.4 (C), 135.8 (CH), 135.3 (C), 130.6 (C), 130.4 (2 x CH), 130.0 (CH), 129.9 (CH), 129.7 (C), 129.4 (CH), 114.2 (2 x CH), 55.3 (CH_3, OCH_3), 34.3 (CH_2); HRMS (ESI-TOF) *m/z*: $[M + NH_4]^+$ Calcd for $C_{18}H_{18}NO_3$ 296.1287; Found 296.1283.



2j

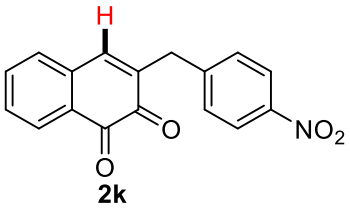
3-(4-Hydroxybenzyl)naphthalene-1,2-dione (2j'): Prepared by following the procedure **A** and purified by column chromatography using EtOAc/hexane (2.6:7.4 to 3.6:6.4) and isolated as wine-red solid. Yield: 20% (10.5 mg). MP: 170-172 ºC. IR (Neat): ν_{max} 3372, 2926, 1661, 1510, 1245, 1176, 1031, 760 cm^{-1}; ^1H NMR (DMSO-d_6, 500 MHz): δ 9.25 (1H, s, O*H*), 7.88 (1H, d, *J* = 8.0 Hz), 7.67 (1H, dt, *J* = 7.0, 1.0 Hz), 7.49 (1H, d, *J* = 7.5 Hz), 7.45 (1H, d, *J* = 8.0 Hz), 7.26 (1H, s, olefinic-*H*), 7.06 (2H, d, *J* = 8.5 Hz), 6.69 (2H, d, *J* = 8.5 Hz), 3.55 (2H, s); $^{13}C\{^1H\}$ NMR (DMSO-d_6, DEPT-135, 100 MHz): δ 180.2 (C, *C*=O), 178.6 (C, *C*=O), 155.8 (C), 140.7 (CH), 139.6 (C), 135.6 (CH), 135.1 (C), 130.8



2j'

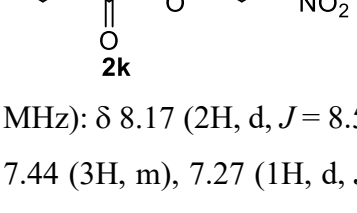
(C), 129.9 (2 x CH), 129.7 (CH), 129.6 (CH), 128.7 (CH), 128.5 (C), 115.2 (2 x CH), 33.8 (CH_2); HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{17}H_{12}NaO_3$ 287.0684; Found 287.0689.

3-(4-Nitrobenzyl)naphthalene-1,2-dione (2k): Prepared by following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.8:9.2 to 1.1:8.9) and isolated as orange solid. Yield: 90% (53 mg). MP: 149-151 ºC. IR (Neat): ν_{max} 2922, 1736, 1661, 1516, 1455, 1343, 1257, 1107 and 760 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 8.17 (2H, d, *J* = 8.5 Hz), 8.05 (1H, d, *J* = 8.0 Hz), 7.62 (1H, dt, *J* = 7.5, 1.0 Hz), 7.48-7.44 (3H, m), 7.27 (1H, d, *J* = 8.0 Hz), 7.12 (1H, s, olefinic-*H*), 3.87 (2H, s); $^{13}C\{^1H\}$ NMR ($CDCl_3$, DEPT-135, 125 MHz): δ 180.5 (C, *C*=O), 178.7 (C, *C*=O), 147.0 (C), 145.6 (C), 142.5 (CH), 138.1 (C), 136.0 (CH), 134.7 (C), 130.8 (C), 130.5 (CH), 130.2 (CH), 130.0 (2 x CH), 129.7 (CH), 124.0 (2 x CH), 35.4 (CH_2); HRMS (ESI-TOF) *m/z*: $[M + NH_4]^+$ Calcd for $C_{17}H_{15}N_2O_4$ 311.1032; Found 311.1031.



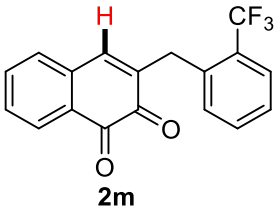
2k

4-((3,4-Dioxo-3,4-dihydronaphthalen-2-yl)methyl)benzonitrile (2l): Prepared by following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.8:9.2 to 1.1:8.9) and isolated as pale yellow solid. Yield: 93% (51 mg). MP: 151-152 ºC. IR (Neat): ν_{max} 2924, 2226, 1662, 1589, 1381, 1257, 907 and 729 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 8.06 (1H, d, *J* = 7.5 Hz), 7.63-7.60 (3H, m), 7.47 (1H, dt, *J* = 7.5, 1.0 Hz), 7.40 (2H, d, *J* = 8.5 Hz), 7.27 (1H, t, *J* = 4.0 Hz), 7.09 (1H, s, olefinic-*H*), 3.83 (2H, s); $^{13}C\{^1H\}$ NMR ($CDCl_3$, DEPT-135, 125 MHz): δ 180.5 (C, *C*=O), 178.7 (C, *C*=O), 143.5 (C), 142.4 (CH), 138.3 (C), 136.0 (CH), 134.8 (C), 132.5 (2 x CH), 130.8 (C), 130.5 (CH), 130.2 (2 x CH), 130.0 (CH), 129.6 (CH), 118.7 (C), 110.8 (C), 35.6 (CH_2); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{18}H_{12}NO_2$ 274.0868; Found 274.0866.



2l

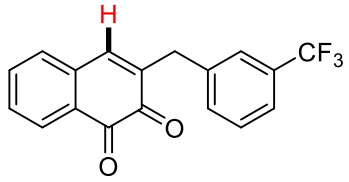
3-(2-(Trifluoromethyl)benzyl)naphthalene-1,2-dione (**2m**): Prepared by following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.8:9.2 to 1.1:8.9) and isolated as orange solid. Yield: 95% (60 mg). MP: 148-150 °C. IR (Neat): ν_{max} 1696, 1588, 1453, 1309, 1110, 1036 and 762 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 8.03 (1H, d, *J* = 8.0 Hz), 7.71 (1H, d, *J* = 7.5 Hz), 7.57-7.51 (2H, m), 7.41 (2H, q, *J* = 7.5 Hz), 7.35 (1H, d, *J* = 7.5 Hz), 7.14 (1H, d, *J* = 7.5 Hz), 6.72 (1H, s, olefinic-*H*), 3.97 (2H, s); $^{13}C\{^1H\}$ NMR ($CDCl_3$, DEPT-135, 125 MHz): δ 180.5 (C, *C*=O), 179.0 (C, *C*=O), 142.1 (CH), 139.1 (C),



2m

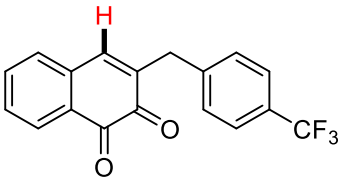
136.0 (C), 135.9 (CH), 134.9 (C), 132.3 (CH), 132.1 (CH), 130.5 (C), 130.1 (CH), 130.0 (CH), 129.6 (CH), 129.2 (C, q, J = 30 Hz), 127.1 (CH), 126.3 (CH, q, J = 5.0 Hz), 124.3 (C, q, J = 272.5 Hz, CF$_3$), 31.6 (CH$_2$); ^{19}F NMR (CDCl$_3$, 375 MHz): δ -62.4; HRMS (ESI-TOF) m/z: [M + NH$_4$]$^+$ Calcd for $C_{18}H_{15}F_3NO_2$ 334.1055; Found 334.1053.

3-(3-(Trifluoromethyl)benzyl)naphthalene-1,2-dione (2n): Prepared by following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.8:9.2 to 1.1:8.9) and isolated as orange solid. Yield: 99% (62.6 mg). MP: 154-156 ºC. IR (Neat): ν_{max} 2930, 1652, 1589, 1448, 1325, 1258, 1110, 953, 832 and 760 cm^{-1}; ^{1}H NMR (CDCl$_3$, 500 MHz): δ 8.04 (1H, d, J = 7.5 Hz), 7.60 (1H, t, J =7.5 HZ), 7.52 (2H, d, J = 9.5 Hz), 7.46 (3H, m), 7.25 (1H, d, J = 9.0 Hz), 7.06 (1H, s, olefinic-H), 3.82 (2H, s); ^{13}C{^{1}H} NMR (CDCl$_3$, DEPT-135, 100 MHz): δ 180.6 (C, C=O), 178.8 (C, C=O), 142.1 (CH), 138.9 (C), 138.8 (C), 135.9 (CH), 134.9 (C), 132.7 (CH), 131.0 (C, q, J = 32.0 Hz), 130.7 (C), 130.3 (CH), 130.1 (CH), 129.6 (CH), 129.2 (CH), 125.8 (CH, q, J = 4.0 Hz), 124.0 (C, q, J = 270.0 Hz, CF$_3$), 123.7 (CH, q, J = 4.0 Hz), 35.2 (CH$_2$); ^{19}F NMR (CDCl$_3$, 375 MHz): δ -62.5; HRMS (ESI-TOF) m/z: [M + NH$_4$]$^+$ Calcd for $C_{18}H_{15}F_3NO_2$ 334.1055; Found 334.1057.



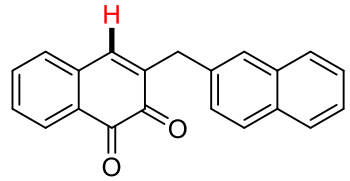
2n

3-(4-(Trifluoromethyl)benzyl)naphthalene-1,2-dione (**2o**): Prepared by following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.8:9.2 to 1.1:8.9) and isolated as yellow solid. Yield: 95% (60 mg). MP: 140-142 °C. IR (Neat): ν_{max} 2923, 1666, 1586, 1417, 1319, 1256, 1102, 966 and 766 cm^{-1}; ^{1}H NMR (CDCl$_3$, 500 MHz): δ 8.05 (1H, d, J = 8.0 Hz), 7.61-7.57 (3H, m), 7.44 (1H, t, J = 7.5 Hz), 7.40 (2H, d, J = 8.0 Hz), 7.25 (1H, d, J = 7.5 Hz), 7.05 (1H, s, olefinic-H), 3.83 (2H, s); ^{13}C{^{1}H} NMR (CDCl$_3$, DEPT-135, 100 MHz): δ 180.6 (C, C=O), 178.8 (C, C=O), 142.1 (CH), 142.0 (C), 138.9 (C), 135.9 (CH), 134.9 (C), 130.7 (C), 130.3 (CH), 130.1 (CH), 129.6 (3 x CH), 129.1 (C, q, J = 33 Hz), 125.6 (2 x CH, q, J = 4.0 Hz), 124.1 (C, q, J = 271 Hz, CF$_3$), 35.2 (CH$_2$); ^{19}F NMR (CDCl$_3$, 375 MHz): δ -62.5; HRMS (ESI-TOF) m/z: [M + NH$_4$]$^+$ Calcd for $C_{18}H_{15}F_3NO_2$ 334.1055; Found 334.1058.



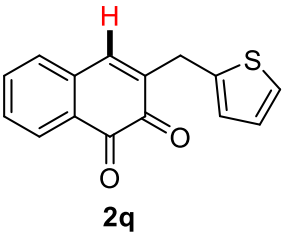
2o

3-(Naphthalen-1-ylmethyl)naphthalene-1,2-dione (2p): Prepared by following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.4:9.6 to 0.8:9.2) and isolated as yellow solid. Yield: 95% (56.7 mg). MP: 139-141 ºC. IR (Neat): ν_{max} 3014, 2923, 1658, 1591, 1364, 1256, 940 and 748 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 8.03 (1H, d, *J* = 7.5 Hz), 7.82 (3H, m), 7.72 (1H, s), 7.54 (1H, dt, *J* = 7.5, 1.0 Hz), 7.50-7.45 (2H, m), 7.40 (1H, t, *J* = 8.0 Hz), 7.36 (1H, d, *J* = 8.5 Hz), 7.14 (1H, d, *J* = 7.5 Hz), 6.98 (1H, br s, olefinic-*H*), 3.93 (2H, s); $^{13}C\{^1H\}$ NMR ($CDCl_3$, DEPT-135, 125 MHz): δ 180.8 (C, *C*=O), 179.1 (C, *C*=O), 141.8 (CH), 139.9 (C), 135.8 (CH), 135.1 (2 x C), 133.6 (C), 132.3 (C), 130.6 (C), 130.0 (CH), 129.9 (CH), 129.4 (CH), 128.4 (CH), 127.9 (CH), 127.6 (CH), 127.5 (2 x CH), 126.2 (CH), 125.7 (CH), 35.2 (CH_2); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{21}H_{15}O_2$ 299.1072; Found 299.1073.



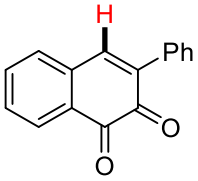
2p

3-(Thiophen-2-ylmethyl)naphthalene-1,2-dione (**2q**): Prepared by following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.4:9.6 to 0.8:9.2) and isolated as orange solid. Yield: 92% (47 mg); MP: 108-110 °C. IR (Neat): ν_{max} 2920, 2850, 1709, 1459, 1258, 1011 and 789 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 8.05 (1H, d, *J* = 8.0 Hz), 7.59 (1H, dt, *J* = 7.5, 1.0 Hz), 7.44 (1H, br t, *J* = 7.5 Hz), 7.25 (1H, d, *J* = 7.5 Hz), 7.21 (1H, d, *J* = 5.0 Hz), 7.12 (1H, s, olefinic-*H*), 6.98 (1H, dd, *J* = 5, 5 Hz), 6.93 (1H, d, *J* = 2.5 Hz), 3.98 (2H, s); $^{13}C\{^1H\}$ NMR ($CDCl_3$, DEPT-135, 100 MHz): δ 180.4 (C, *C*=O), 179.0 (C, *C*=O), 141.8 (CH), 139.5 (C), 139.0 (C), 135.9 (CH), 134.9 (C), 130.6 (C), 130.2 (CH), 130.0 (CH), 129.6 (CH), 127.2 (CH), 126.7 (CH), 124.6 (CH), 29.1 (CH_2); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{15}H_{11}O_2S$ 255.0480; Found 255.0482.



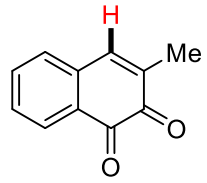
2q

3-Phenylnaphthalene-1,2-dione (**2r**): Prepared by following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.4:9.6 to 0.8:9.2) and isolated as red solid. Yield: 94% (44 mg). MP: 110-112 °C. IR (Neat): ν_{max} 1652, 1588, 1357, 1271 and 758 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 8.10 (1H, d, *J* = 7.6 Hz), 7.66 (1H, d, *J* = 7.2 Hz), 7.54-7.46 (4H, m), 7.45-7.37 (4H, m); $^{13}C\{^1H\}$ NMR ($CDCl_3$, DEPT-135, 100 MHz): δ 180.3 (C, *C*=O), 179.2 (C, *C*=O), 141.5 (CH), 139.2 (C), 135.8 (CH), 135.6 (C), 134.4 (C), 131.2 (C), 130.3 (CH), 130.0 (2 x CH), 128.9 (CH), 128.6 (2 x CH), 128.4 (2 x CH); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{16}H_{11}O_2$ 235.0759; Found 235.0760.



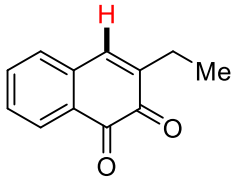
2r

3-Methylnaphthalene-1,2-dione (2s): Prepared by following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.2:9.8 to 0.5:9.5) and isolated as orange solid. Yield: 99% (34 mg). MP: 149-151 ºC. IR (Neat): ν_{max} 2924, 1643, 1381, 1263, 1064, 942 and 761 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 8.02 (1H, td, *J* = 8.0, 1.0 Hz), 7.59 (1H, dt, *J* = 7.5, 1.5 Hz), 7.41 (1H, dt, *J* = 7.5, 1.0 Hz), 7.25 (1H, d, *J* = 7.5 Hz), 7.20 (1H, br s, olefinic-*H*), 2.05 (3H, s, C*H*$_3$); $^{13}C\{^1H\}$ NMR ($CDCl_3$, DEPT-135, 125 MHz): δ 181.5 (C, *C*=O), 179.1 (C, *C*=O), 141.5 (CH), 136.5 (C), 135.8 (CH), 135.4 (C), 130.7 (C), 129.9 (CH), 129.7 (CH), 128.9 (CH), 15.7 (CH_3); HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{11}H_8O_2Na$ 195.0422; Found 195.0422.



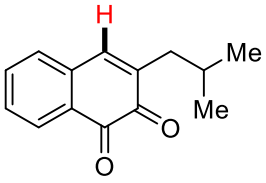
2s

3-Ethylnaphthalene-1,2-dione (2t): Prepared by following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.2:9.8 to 0.5:9.5) and isolated as orange solid. Yield: 99% (37 mg). MP: 150-152 ºC. IR (Neat): ν_{max} 2923, 1647, 1458, 1377, 1259, 1089 and 750 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 7.99 (1H, d, *J* = 7.5 Hz), 7.57 (1H, dt, *J* = 7.5, 0.5 Hz), 7.38 (1H, t, *J* = 8.0 Hz), 7.25 (1H, d, *J* = 7.5 Hz), 7.13 (1H, s, olefinic-*H*), 2.44 (2H, q, *J* = 7.5 Hz), 1.14 (3H, t, *J* = 7.5 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$, DEPT-135, 125 MHz): δ 181.1 (C, *C*=O), 179.4 (C, *C*=O), 142.0 (C), 140.0 (CH), 135.8 (CH), 135.5 (C), 130.6 (C), 129.8 (CH), 129.7 (CH), 129.1 (CH), 22.4 (CH_2), 12.3 (CH_3); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{12}H_{11}O_2$ 187.0759; Found 187.0754.



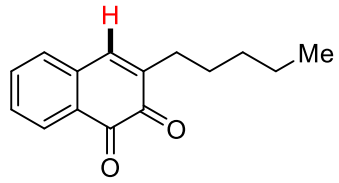
2t

3-Isobutylnaphthalene-1,2-dione (**2u**): Prepared by following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.4:9.6 to 0.8:9.2) and isolated as brown liquid. Yield: 94% (40 mg). IR (Neat): ν_{max} 2922, 1739, 1665, 1461, 1264, 1158, 967 and 774 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 8.04 (1H, d, *J* = 7.5 Hz), 7.61 (1H, dt, *J* = 7.5, 1.0 Hz), 7.42 (1H, dt, *J* = 8.0, 1.0 Hz), 7.28 (1H, d, *J* = 7.5 Hz), 7.14 (1H, s, olefinic-*H*), 2.30 (2H, d, *J* = 7.0 Hz), 1.89 (1H, septet, *J* = 7.0 Hz), 0.94 (6H, d, *J* = 6.5 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$, DEPT-135, 125 MHz): δ 181.4 (C, *C*=O), 179.4 (C, *C*=O), 141.8 (CH), 139.8 (C), 135.8 (CH), 135.4 (C), 130.8 (C), 130.0 (CH), 129.8 (CH), 129.1 (CH), 38.7 (CH_2), 27.5 (CH), 22.5 (2 x CH_3); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{14}H_{15}O_2$ 215.1072; Found 215.1070.



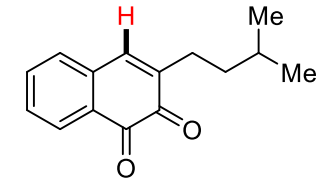
2u

3-Pentylnaphthalene-1,2-dione (2v): Prepared by following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.4:9.6 to 0.8:9.2) and isolated as orange solid. Yield: 92% (42 mg). MP: 151-153 ºC. IR (Neat): ν_{max} 2924, 1651, 1585, 1452, 1256, 939 and 763 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 8.02 (1H, td, *J* = 7.5, 1.0 Hz), 7.59 (1H, dt, *J* = 7.5, 1.0 Hz), 7.40 (1H, dt, *J* = 8.0, 1.0 Hz), 7.27 (1H, d, *J* = 7.5 Hz), 7.15 (1H, br s, olefinic-*H*), 2.41 (2H, t, *J* = 7.5, 1.0 Hz), 1.56-1.50 (2H, m), 1.35-1.32 (4H, m), 0.89 (3H, br t, *J* = 7.5 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$, DEPT-135, 125 MHz): δ 181.2 (C, *C*=O), 179.4 (C, *C*=O), 140.9 (C), 140.6 (CH), 135.8 (CH), 135.5 (C), 130.7 (C), 129.9 (CH), 129.6 (CH), 129.1 (CH), 31.5 (CH_2), 29.3 (CH_2), 27.9 (CH_2), 22.4 (CH_2), 13.9 (CH_3); HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{15}H_{16}O_2Na$ 251.1048; Found 251.1054.



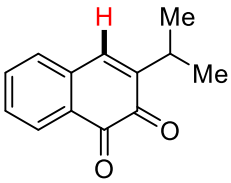
2v

3-Isopentylnaphthalene-1,2-dione (2w): Prepared by following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.4:9.6 to 0.8:9.2) and isolated as orange solid. Yield: 99% (45.6 mg). MP: 151-153 ºC. IR (Neat): ν_{max} 2921, 1650, 1586, 1451, 1263, 936 and 762 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 8.02 (1H, d, *J* = 8.0 Hz), 7.59 (1H, dt, *J* = 7.5, 1.5 Hz), 7.40 (1H, dt, *J* = 7.5, 1.0 Hz), 7.26 (1H, d, *J* = 7.0 Hz), 7.15 (1H, s, olefinic-*H*), 2.44-2.41 (2H, m), 1.62 (1H, septet, *J* = 6.5 Hz), 1.44-1.39 (2H, m), 0.94 (6H, d, *J* = 6.5 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$, DEPT-135, 125 MHz): δ 181.2 (C, *C*=O), 179.4 (C, *C*=O), 141.1 (C), 140.4 (CH), 135.8 (CH), 135.5 (C), 130.7 (C), 129.9 (CH), 129.6 (CH), 129.1 (CH), 37.3 (CH_2), 27.8 (CH), 27.2 (CH_2), 22.4 (2 x CH_3); HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{15}H_{16}O_2Na$ 251.1048; Found 251.1050.



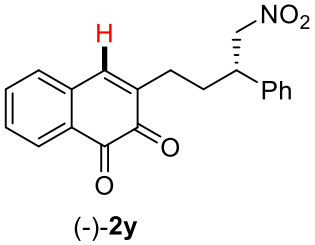
2w

3-Isopropylnaphthalene-1,2-dione (2x): Prepared by following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.4:9.6 to 0.8:9.2) and isolated as orange solid. Yield: 95% (38 mg). MP: 155-157 ºC. IR (Neat): ν_{max} 2926, 1658, 1456, 1262, 935 and 733 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 8.02 (1H, d, *J* = 7.5 Hz), 7.60 (1H, dt, *J* = 7.5, 1.5 Hz), 7.40 (1H, dt, *J* = 7.5, 1.0 Hz), 7.29 (1H, d, *J* = 7.5 Hz), 7.13 (1H, s, olefinic-*H*), 3.06 (1H, septet, *J* = 7.0 Hz), 1.17 (6H, d, *J* = 7.0 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$, DEPT-135, 125 MHz): δ 180.8 (C, *C*=O), 179.5 (C, *C*=O), 146.4 (C), 138.3 (CH), 135.8 (CH), 135.5 (C), 130.5 (C), 129.8 (CH), 129.7 (CH), 129.3 (CH), 27.1 (CH), 21.5 (2 x CH_3); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{13}H_{13}O_2$ 201.0916; Found 201.0915.



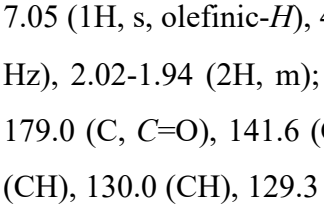
2x

(*S*)-3-(4-Nitro-3-phenylbutyl)naphthalene-1,2-dione (2y): Prepared by following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.8:9.2 to 1.1:8.9) and isolated as red solid. Yield: 89% (59.7 mg). MP: 154-156 ºC. $[\alpha]_D^{25}$ = -30.5° [*c* = 0.1, $CHCl_3$]; IR (Neat): ν_{max} 2924, 1657, 1546, 1453, 1379, 1259, 910 and 701 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 8.01 (1H, d, *J* = 7.5 Hz), 7.60 (1H, dt, *J* = 7.5, 1.0 Hz), 7.42 (1H, t, *J* = 7.5 Hz), 7.34 (2H, t, *J* = 7.5 Hz), 7.28-7.22 (4H, m), 7.05 (1H, s, olefinic-*H*), 4.61-4.53 (2H, m), 3.51 (1H, quintet, *J* = 7.0 Hz), 2.33 (2H, t, *J* = 7.5 Hz), 2.02-1.94 (2H, m); $^{13}C\{^1H\}$ NMR ($CDCl_3$, DEPT-135, 125 MHz): δ 180.9 (C, *C*=O), 179.0 (C, *C*=O), 141.6 (CH), 139.1 (C), 138.4 (C), 135.9 (CH), 135.0 (C), 130.7 (C), 130.1 (CH), 130.0 (CH), 129.3 (CH), 129.2 (2 x CH), 128.0 (CH), 127.7 (2 x CH), 80.9 (CH_2), 44.1 (CH), 31.1 (CH_2), 27.5 (CH_2); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{20}H_{18}NO_4$ 336.1236; Found 336.1242.



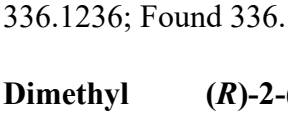
(-)-**2y**

Dimethyl (*R*)-2-(3-(3,4-dioxo-3,4-dihydronaphthalen-2-yl)-1-phenylpropyl)malonate (2z): Prepared by following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.8:9.2 to 1.1:8.9) and isolated as brown liquid. Yield: 93% (76 mg). MP: 142-144 °C. $[\alpha]_D^{25}$ = -41.0° [*c* = 0.1, $CHCl_3$]; IR (Neat): ν_{max} 2952, 1732, 1665, 1434, 1249, 1151 and 761 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 8.01 (1H, d, *J* = 7. 5 Hz), 7.59 (1H, t, *J* = 7. 5 Hz), 7.41 (1H, t, *J* = 8.0 Hz), 7.30-7.26 (2H, m), 7.24-7.16 (4H, m), 7.04 (1H, s, olefinic-*H*), 3.76 (3H, s), 3.66 (1H, d, *J* = 10.5 Hz), 3.42 (4H, br s), 2.30-2.20 (2H, m), 1.97 (2H, q, *J* = 7.5 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$, DEPT-135, 100 MHz): δ 181.0 (C, *C*=O), 179.2 (C, *C*=O), 168.7 (C, *O-C*=O), 168.1 (C, O-*C*=O), 141.3 (CH), 139.8 (C), 139.5 (C), 135.8 (CH), 135.3 (C), 130.7 (C), 130.0 (CH), 129.9 (CH), 129.2 (CH), 128.7 (2 x CH), 128.4 (2 x CH), 127.4 (CH), 58.7 (CH), 52.8 (CH_3), 52.3 (CH_3), 45.3 (CH), 31.6 (CH_2), 27.7 (CH_2); HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{24}H_{22}NaO_6$ 429.1314; Found 429.1315.



(-)-**2z**

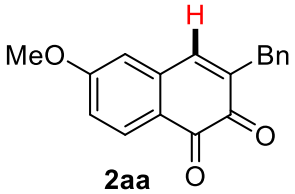
3-Benzyl-6-hydroxynaphthalene-1,2-dione (2aa'): Prepared by following the procedure **A** and purified by column chromatography using EtOAc/hexane (1.4:8.6 to 1.7:8.3) and isolated as wine-red solid. Yield: 85% (45 mg). MP: 185-187 °C. IR (Neat): ν_{max} 3295, 2923, 1698, 1653, 1449, 1212, 1028, 833 and 699 cm^{-1}; ^1H NMR (DMSO-d_6, 500 MHz): δ 10.40 (1H, s, O*H*),



2aa'

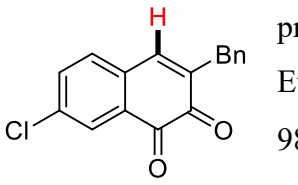
7.30-7.25 (7H, m), 7.21-7.18 (1H, m), 7.01 (1H, dd, J = 8.5, 3.0 Hz), 3.61 (2H, s); $^{13}C\{^{1}H\}$ NMR (DMSO-d_6 , DEPT-135, 125 MHz): δ 180.3 (C, *C*=O), 178.6 (C, *C*=O), 159.2 (C), 142.2 (CH), 139.1 (C), 135.0 (C), 132.4 (C), 131.7 (CH), 128.8 (2 x CH), 128.3 (2 x CH), 126.6 (C), 126.1 (CH), 121.7 (CH), 115.7 (CH), 34.5 (CH_2); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{17}H_{12}NaO_3$ 287.0684; Found 287.0683.

2-Benzyl-7-methoxynaphthalene-1,4-dione (**2aa**): Prepared by following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.8:9.2 to 1.0:9.0) and isolated as orange solid. Yield: 14% (8 mg). MP: 140-142 °C. IR (Neat): ν_{max} 2918, 1654, 1593, 1426, 1215, 1015, 831 and 698 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.53 (1H, d, J = 2.5 Hz), 7.34-7.31 (2H, m), 7.26-7.23 (3H, m), 7.10 (1H, d, J = 8.5 Hz), 7.04 (1H, dd, J = 8.5, 3.0 Hz), 6.92 (1H, s, olefinic-*H*), 3.87 (3H, s), 3.73 (2H, s); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, DEPT-135, 125 MHz): δ 180.8 (C, *C*=O), 179.2 (C, *C*=O), 161.2 (C), 141.9 (CH), 138.1 (C), 137.1 (C), 132.0 (C), 131.1 (CH), 129.3 (2 x CH), 128.7 (2 x CH), 128.3 (C), 126.6 (CH), 121.8 (CH), 114.3 (CH), 55.8 (CH_3), 35.0 (CH_2); HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{18}H_{14}NaO_3$ 301.0841; Found 301.0842.



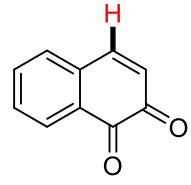
2aa

2-Benzyl-6-chloro-3-hydroxynaphthalene-1,4-dione (**2bb**): Prepared by following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.2:9.8 to 0.5:9.5) and isolated as orange solid. Yield: 98% (55.6 mg). MP: 129-131 °C. IR (Neat): ν_{max} 3028, 1660, 1585, 1413, 1254, 1078, 907 and 699 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.98 (1H, br s), 7.53 (1H, dd, J = 8.0, 2.0 Hz), 7.34 (2H, t, J = 7.5 Hz), 7.26 (3H, t, J = 8.0 Hz), 7.16 (1H, d, J = 8.0 Hz), 6.96 (1H, s, olefinic-*H*), 3.76 (2H, s); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, DEPT-135, 125 MHz): δ 179.9 (C, *C*=O), 178.1 (C, *C*=O), 140.5 (CH), 140.1 (C), 137.3 (C), 136.6 (C), 135.5 (CH), 133.4 (C), 131.5 (C), 130.6 (CH), 129.8 (CH), 129.3 (2 x CH), 128.8 (2 x CH), 126.8 (CH), 35.2 (CH_2); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{17}H_{12}ClO_2$ 283.0526; Found 283.0525.



2bb

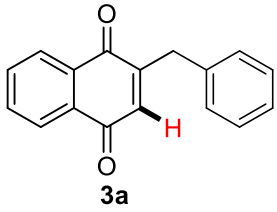
Naphthalene-1,2-dione (2cc): Prepared by following the procedure **A** and purified by column chromatography using EtOAc/hexane (0.4:9.6 to 0.8:9.2) and isolated as wine red solid. Yield: 32% (10 mg). MP: 145-147 ºC. IR (Neat): ν_{max} 2921, 1650, 1589, 1301, 1136, 938, 811, 752 and 661 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.11 (1H, d, J = 7.5 Hz), 7.65 (1H, dt, J = 7.5, 1.0 Hz), 7.51 (1H, t, J = 7.5



2cc

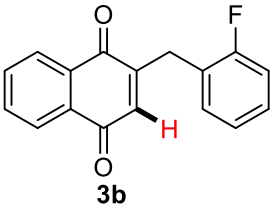
Hz), 7.44 (1H, d, J = 10.5 Hz), 7.36 (1H, d, J = 7.5 Hz), 6.43 (1H, d, J = 10.0 Hz); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, DEPT-135, 125 MHz): δ 180.9 (C, *C*=O), 178.9 (C, *C*=O), 145.3 (CH), 135.8 (CH), 134.8 (C), 131.6 (C), 130.9 (CH), 130.2 (CH), 129.8 (CH), 127.9 (CH); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{10}H_7O_2$ 159.0446; Found 159.0452.

2-Benzylnaphthalene-1,4-dione (**3a**): Prepared by following the procedure **B** and purified by column chromatography using EtOAc/hexane (0.2:9.8 to 0.5:9.5) and isolated as yellow solid. Yield: 99% (49 mg). MP: 82-84 ºC. IR (Neat): ν_{max} 2923, 1660, 1593, 1298, 1262, 939 and 701 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.12-8.08 (1H, m), 8.05-8.02 (1H, m), 7.74-7.70 (2H, m), 7.33 (2H, t, J = 7.5 Hz), 7.26 (3H, m), 6.60 (1H, t, J = 1.5 Hz, olefinic-*H*), 3.90 (2H, d, J = 1.5 Hz, CH_2); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, DEPT-135, 125 MHz): δ 185.1 (C, *C*=O), 184.9 (C, *C*=O), 150.8 (C), 136.7 (C), 135.6 (CH), 133.7 (CH), 133.6 (CH), 132.1 (C), 132.0 (C), 129.4 (2 x CH), 128.8 (2 x CH), 126.9 (CH), 126.6 (CH), 126.0 (CH), 35.7 (CH_2); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{17}H_{13}O_2$ 249.0916; Found 249.0913.



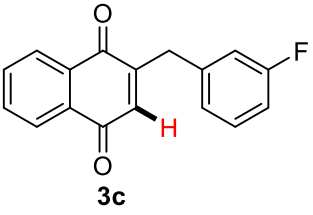
3a

2-(2-Fluorobenzyl)naphthalene-1,4-dione (**3b**): Prepared by following the procedure **B** and purified by column chromatography using EtOAc/hexane (0.2:9.8 to 0.5:9.5) and isolated as pale yellow solid. Yield: 93% (49.5 mg). MP: 94-96 ºC. IR (Neat): ν_{max} 2922, 1663, 1593, 1491, 1300, 1232 and 759 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.14-8.10 (1H, m), 8.06-8.03 (1H, m), 7.75-7.70 (2H, m), 7.29-7.25 (2H, m), 7.12 (1H, t, J = 7.5 Hz), 7.08 (1H, t, J = 9.5 Hz), 6.57 (1H, s, olefinic-*H*), 3.94 (2H, s); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, DEPT-135, 125 MHz): δ 185.1 (C, *C*=O), 184.8 (C, *C*=O), 161.2 (C, d, J = 245 Hz, *C*-F), 149.4 (C), 135.5 (CH), 133.8 (CH), 133.7 (CH), 132.1 (C, d, J = 4.5 Hz), 131.8 (CH, d, J = 4.0 Hz), 129.1 (CH, d, J = 8.12 Hz), 126.7 (CH), 126.2 (CH), 124.5 (CH, d, J = 3.5 Hz), 123.8 (C), 123.7 (C), 115.7 (CH, d, J = 21.2 Hz), 29.1 (CH_2, d, J = 2.5 Hz); ^{19}F NMR ($CDCl_3$, 470 MHz): δ -117.0; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{17}H_{12}FO_2$ 267.0821; Found 267.0819.



3b

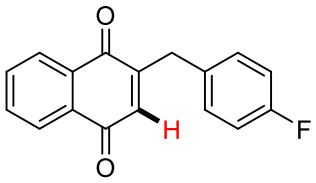
2-(3-Fluorobenzyl)naphthalene-1,4-dione (**3c**): Prepared by following the procedure **B** and purified by column chromatography using EtOAc/hexane (0.2:9.8 to 0.5:9.5) and isolated as pale yellow solid. Yield: 99% (52.7 mg). MP: 90-92 ºC. IR (Neat): ν_{max} 2923, 1659, 1585, 1482, 1242, 1137, 961 and 748 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.11-8.10 (1H, m), 8.06-8.04 (1H, m), 7.74-7.73 (2H, m), 7.30 (1H, m), 7.03 (1H, d, J = 7.5 Hz), 6.96 (2H, br



3c

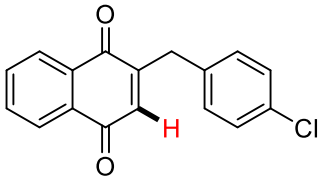
d, J = 9.5 Hz), 6.62 (1H, s, olefinic-*H*), 3.89 (2H, s); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, DEPT-135, 100 MHz): δ 185.5 (C, *C*=O), 185.3 (C, *C*=O), 163.5 (C, d, J = 245 Hz, *C*-F), 150.6 (C), 139.7 (C, d, J = 8.0 Hz), 136.3 (CH), 134.36 (CH), 134.30 (CH), 132.5 (2 x C), 130.8 (CH, d, J = 8.0 Hz), 127.2 (CH), 126.6 (CH), 125.5 (CH, d, J = 3.0 Hz), 116.8 (CH, d, J = 21.0 Hz), 114.5 (CH, d, J = 21.0 Hz), 35.9 (CH_2, d, J = 2.0 Hz); ^{19}F NMR ($CDCl_3$, 470 MHz): δ -112.6; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{17}H_{12}FO_2$ 267.0821; Found 267.0823.

2-(4-Fluorobenzyl)naphthalene-1,4-dione (**3d**): Prepared by following the procedure **B** and purified by column chromatography using EtOAc/hexane (0.2:9.8 to 0.5:9.5) and isolated as yellow solid. Yield: 95% (50.5 mg). MP: 94-96 °C. IR (Neat): ν_{max} 2920, 1654, 1505, 1301, 1244, 1134, 933 and 776 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.11-8.09 (1H, m), 8.06-8.04 (1H, m), 7.75-7.72 (2H, m), 7.21 (2H, dd, J = 8.0, 5.5 Hz), 7.02 (2H, t, J = 8.5 Hz), 6.60 (1H, s, olefinic-*H*), 3.87 (2H, s); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, DEPT-135, 125 MHz): δ 185.0 (C, *C*=O), 184.9 (C, *C*=O), 161.9 (C, d, J = 243.7 Hz, *C*-F), 150.6 (C), 135.6 (CH), 133.8 (CH), 133.7 (CH), 132.4 (C, d, J = 2.5 Hz), 132.13 (C), 132.08 (C), 130.9 (2 x CH, d, J = 8.75 Hz), 126.7 (CH), 126.1 (CH), 115.8 (2 x CH, d, J = 21.2 Hz), 35.0 (CH_2); ^{19}F NMR ($CDCl_3$, 470 MHz): δ -116.2; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{17}H_{12}FO_2$ 267.0821; Found 267.0820.



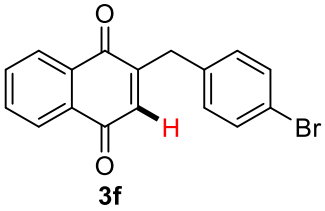
3d

2-(4-Chlorobenzyl)naphthalene-1,4-dione (3e): Prepared by following the procedure **B** and purified by column chromatography using EtOAc/hexane (0.2:9.8 to 0.5:9.5) and as yellow solid. Yield: 99% (56 mg). MP: 85-87 °C. IR (Neat): ν_{max} 2921, 1662, 1461, 1298, 1184, 1082, 966 and 775 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.11-8.08 (1H, m), 8.05-8.03 (1H, m), 7.75-7.72 (2H, m), 7.30 (2H, d, J = 8.5 Hz), 7.19 (2H, d, J = 8.0 Hz), 6.61 (1H, s, olefinic-*H*), 3.86 (2H, s); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, DEPT-135, 125 MHz): δ 185.0 (C, *C*=O), 184.8 (C, *C*=O), 150.3 (C), 135.7 (CH), 135.3 (C), 133.9 (CH), 133.8 (CH), 132.9 (C), 132.1 (C), 132.0 (C), 130.7 (2 x CH), 129.0 (2 x CH), 126.7 (CH), 126.1 (CH), 35.2 (CH_2); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{17}H_{12}ClO_2$ 283.0526; Found 283.0526.



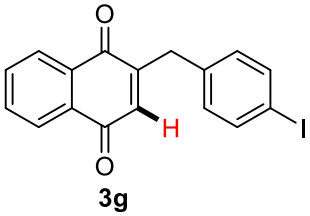
3e

2(4-Bromobenzyl)naphthalene-1,4-dione (**3f**): Prepared by following the procedure **B** and purified by column chromatography using EtOAc/hexane (0.2:9.8 to 0.5:9.5) and isolated as yellow solid. Yield: 99% (65 mg). MP: 93-95 °C. IR (Neat): ν_{max} 2924, 1740, 1654, 1366, 1222, 1088 and 779 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 8.11-8.08 (1H, m), 8.06-8.03 (1H, m), 7.77-7.72 (2H, m), 7.30 (2H, dd, *J* = 8.5, 1.5 Hz), 7.19 (2H, dd, *J* = 7.5, 1.0 Hz), 6.61 (1H, s, olefinic-*H*), 3.86 (2H, s); $^{13}C\{^1H\}$ NMR ($CDCl_3$, DEPT-135, 125 MHz): δ185.0 (C, *C*=O), 184.8 (C, *C*=O), 150.2 (C), 135.7 (CH), 135.2 (C), 133.8 (2 x CH), 132.9 (C), 132.0 (2 x C), 130.7 (2 x CH), 129.0 (2 x CH), 126.7 (CH), 126.1 (CH), 35.2 (CH_2); HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{17}H_{11}BrO_2Na$ 348.9840; Found 348.9841.



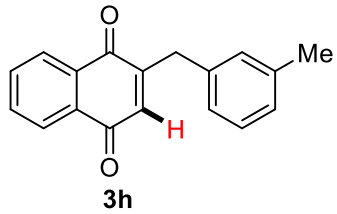
3f

2-(4-Iodobenzyl)naphthalene-1,4-dione (3g): Prepared by following the procedure **B** and purified by column chromatography using EtOAc/hexane (0.2:9.8 to 0.5:9.5) and isolated as yellow solid. Yield: 99% (74 mg). MP: 140-142 °C. IR (Neat): ν_{max} 2918, 1657, 1588, 1482, 1294, 1244, 1005, 937, 857 and 781 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ 8.10-8.07 (1H, m), 8.05-8.02 (1H, m), 7.75-7.71 (2H, m), 7.65 (2H, d, *J* = 8.0 Hz), 7.01 (2H, d, *J* = 8.5 Hz), 6.61 (1H, s, olefinic-*H*), 3.83 (2H, s); $^{13}C\{^1H\}$ NMR ($CDCl_3$, DEPT-135, 100 MHz): δ 184.9 (C, *C*=O), 184.8 (C, *C*=O), 150.1 (C), 137.9 (2 x CH), 136.4 (C), 135.7 (CH), 133.9 (CH), 133.8 (CH), 132.0 (2 x C), 131.4 (2 x CH), 126.7 (CH), 126.1 (CH), 92.4 (C), 35.3 (CH_2); HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{17}H_{11}IO_2Na$ 396.9701; Found 396.9701.



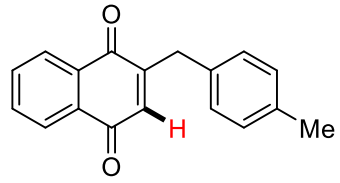
3g

2-(3-Methylbenzyl)naphthalene-1,4-dione (**3h**): Prepared by following the procedure **B** and purified by column chromatography using EtOAc/hexane (0.2:9.8 to 0.5:9.5) and isolated as yellow solid. Yield: 92% (48 mg). MP: 98-100 °C. IR (Neat): ν_{max} 2919, 1659, 1587, 1298, 1262, 954, 895 and 742 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ 8.12-8.09 (1H, m), 8.06-8.03 (1H, m), 7.74-7.70 (2H, m), 7.22 (1H, t, *J* = 7.5 Hz), 7.05 (3H, m), 6.61 (1H, br s, olefinic-*H*), 3.86 (2H, s), 2.34 (3H, s); $^{13}C\{^1H\}$ NMR ($CDCl_3$, DEPT-135, 125 MHz): δ 185.2 (C, *C*=O), 185.0 (C, *C*=O), 151.0 (C), 138.5 (C), 136.6 (C), 135.6 (CH), 133.7 (2 x CH), 132.2 (C), 132.1 (C), 130.1 (CH), 128.7 (CH), 127.7 (CH), 126.6 (CH), 126.4 (CH), 126.1 (CH), 35.6 (CH_3), 21.3 (CH_2); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{18}H_{15}O_2$ 263.1072; Found 263.1076.



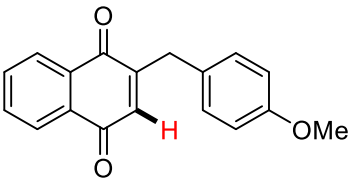
3h

2-(4-Methylbenzyl)naphthalene-1,4-dione (**3i**): Prepared by following the procedure **B** and purified by column chromatography using EtOAc/hexane (0.2:9.8 to 0.5:9.5) and isolated as yellow solid. Yield: 92% (48 mg). MP: 96-98 ºC. IR (Neat): ν_{max} 2921, 1657, 1589, 1510, 1298, 1263, 807 and 751 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ 8.11-8.09 (1H, m), 8.05-8.03 (1H, m), 7.74-7.70 (2H, m), 7.14 (4H, s), 6.60 (1H, br s, olefinic-*H*), 3.86 (2H, br s), 2.33 (3H, s); $^{13}C\{^1H\}$ NMR ($CDCl_3$, DEPT-135, 100 MHz): δ 185.2 (C, *C*=O), 185.1 (C, *C*=O), 151.1 (C), 136.6 (C), 135.5 (CH), 133.7 (2 x CH), 133.6 (C), 132.2 (C), 132.1 (C), 129.5 (2 x CH), 129.3 (2 x CH), 126.6 (CH), 126.1 (CH), 35.3 (CH_2), 21.0 (CH_3); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{18}H_{15}O_2$ 263.1072; Found 263.1075.



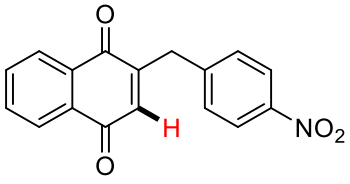
3i

2-(4-Methoxybenzyl)naphthalene-1,4-dione2 (**3j**): Prepared by following the procedure **B** and purified by column chromatography using EtOAc/hexane (0.2:9.8 to 0.5:9.5) and isolated as yellow solid. Yield: 90% (50 mg). MP: 110-112 ºC. IR (Neat): ν_{max} 2904, 1658, 1510, 1451, 1244, 1030, 938 and 760 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ 8.10-8.08 (1H, m), 8.03-8.02 (1H, m), 7.73-7.69 (2H, m), 7.16 (2H, d, *J* = 8.5 Hz), 6.86 (2H, d, *J* = 8.5 Hz), 6.60 (1H, br s, olefinic-*H*), 3.83 (2H, s), 3.79 (3H, s); $^{13}C\{^1H\}$ NMR ($CDCl_3$, DEPT-135, 100 MHz): δ 185.2 (C, *C*=O), 185.1 (C, *C*=O), 158.5 (C), 151.2 (C), 135.4 (CH), 133.7 (CH), 133.6 (CH), 132.1 (C), 132.0 (C), 130.4 (2 x CH), 128.5 (C), 126.6 (CH), 126.0 (CH), 114.2 (2 x CH), 55.2 (CH_3), 34.9 (CH_2); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{18}H_{15}O_3$ 279.1021; Found 279.1024.



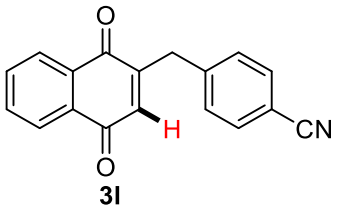
3j

2-(4-Nitrobenzyl)naphthalene-1,4-dione (**3k**): Prepared by following the procedure **B** and purified by column chromatography using EtOAc/hexane (0.2:9.8 to 0.5:9.5) and isolated as yellow solid. Yield: 94% (55 mg). MP: 112-114 ºC. IR (Neat): ν_{max} 3070, 1660, 1513, 1343, 1264, 1105, 905 and 726 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ 8.20 (2H, d, *J* = 9.0 Hz), 8.11-8.09 (1H, m), 8.08-8.06 (1H, m), 7.77-7.74 (2H, m), 7.45 (2H, d, *J* = 8.5 Hz), 6.70 (1H, s, olefinic-*H*), 4.00 (2H, s); $^{13}C\{^1H\}$ NMR ($CDCl_3$, DEPT-135, 100 MHz): δ 184.7 (C, *C*=O), 184.6 (C, *C*=O), 149.0 (C), 147.1 (C), 144.6 (C), 136.2 (CH), 134.1 (CH), 134.0 (CH), 132.0 (C), 131.9 (C), 130.2 (2 x CH), 126.8 (CH), 126.3 (CH), 124.1 (2 x CH), 35.8 (CH_2); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{17}H_{12}NO_4$ 294.0766; Found 294.0763.



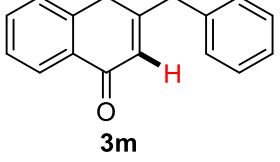
3k

4-((1,4-Dioxo-1,4-dihydronaphthalen-2-yl)methyl)benzonitrile (**3l**): Prepared by following the procedure **B** and purified by column chromatography using EtOAc/hexane (0.2:9. 8 to 0.5:9.5) and isolated as yellow solid. Yield: 99% (54 mg). MP: 111-113 ºC. IR (Neat): ν_{max} 3069, 1660, 1592, 1299, 1264, 905 and 727 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ 8.10-8.08 (1H, m), 8.07-8.04 (1H, m), 7.77-7.73 (2H, m), 7.63 (2H, d, *J* = 8.0 Hz), 7.40 (2H, d, *J* = 8.0 Hz), 6.67 (1H, br s, olefinic-*H*), 3.95 (2H, s); $^{13}C\{^1H\}$ NMR ($CDCl_3$, DEPT-135, 100 MHz): δ 184.7 (C, *C*=O), 184.6 (C, *C*=O), 149.2 (C), 142.6 (C), 136.1 (CH), 134.1 (CH), 133.9 (CH), 132.6 (2 x CH), 132.0 (C), 131.9 (C), 130.1 (2 x CH), 126.8 (CH), 126.3 (CH), 118.6 (C), 111.1 (C), 36.0 (CH_2); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{18}H_{12}NO_2$ 274.0868; Found 274.0868.



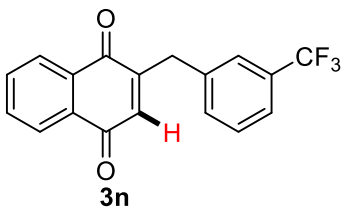
3l

2-(2-(Trifluoromethyl)benzyl)naphthalene-1,4-dione (**3m**): Prepared by following the procedure **B** and purified by column chromatography using EtOAc/hexane (0.2:9.8 to 0.5:9.5) and isolated as yellow solid. Yield: 98% (62 mg). MP: 87-89 °C. IR (Neat): ν_{max} 2922, 1658, 1592, 1302, 1100, 1034, 938 and 766 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ 8.14 (1H, d, *J* = 7.0 Hz), 8.03 (1H, d, *J* = 6.0 Hz), 7.74-7.71 (3H, m), 7.53 (1H, t, *J* = 7.5 Hz), 7.42 (1H, t, *J* = 7.5 Hz), 7.29 (1H, d, *J* = 7.5 Hz), 6.25 (1H, s, olefinic-*H*), 4.11 (2H, s); ^{13}C $\{^1H\}$ NMR ($CDCl_3$, DEPT-135, 125 MHz): δ 184.8 (C, *C*=O), 184.6 (C, *C*=O), 150.5 (C), 135.8 (CH), 135.0 (C), 133.8 (2 x CH), 132.4 (CH), 132.2 (CH), 132.0 (2 x C), 129.5 (C, q, *J* = 30 Hz), 127.4 (CH), 126.7 (CH), 126.5 (CH, q, *J* = 5.0 Hz), 126.2 (CH), 124.2 (C, q, *J* = 271 Hz, *C*F_3), 32.4 (CH_2); ^{19}F NMR ($CDCl_3$, 470 MHz): δ -60.0; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{18}H_{12}F_3O_2$ 317.0789; Found 317.0783.



3m

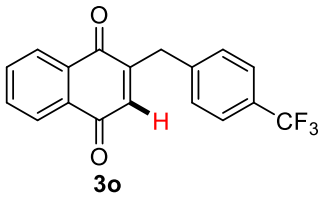
2-(3-(Trifluoromethyl)benzyl)naphthalene-1,4-dione (**3n**): Prepared by following the procedure **B** and purified by column chromatography using EtOAc/hexane (0.2:9.8 to 0.5:9.5) and isolated as yellow solid. Yield: 95% (60 mg). MP: 90-92 ºC. IR (Neat): ν_{max} 1661, 1593, 1329, 1265, 1101, 1071, 920 and 785 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 8.13-8.10 (1H, m), 8.07-8.04 (1H, m), 7.76-7.72 (2H, m), 7.53 (2H, m), 7.46 (2H, m), 6.62 (1H, br s, olefinic-*H*), 3.96 (2H, br s); $^{13}C\{^1H\}$ NMR ($CDCl_3$, DEPT-135, 125 MHz): δ 184.9 (C, *C*=O), 184.7 (C, *C*=O), 149.8 (C), 137.8 (C), 135.9 (CH), 133.9 (CH), 133.8 (CH), 132.8 (CH), 132.08 (C), 132.05 (C), 131.3 (C, q, *J* = 32.5 Hz), 129.3 (CH), 126.7 (CH), 126.2



3n

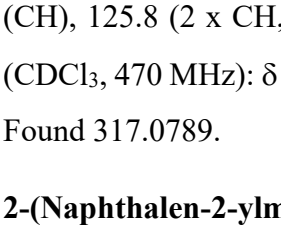
(CH), 126.1 (CH, q, J = 3.75 Hz), 124.0 (C, q, J = 271.2 Hz, CF$_3$), 123.9 (CH, q, J = 3.75 Hz), 35.6 (CH$_2$); ^{19}F NMR (CDCl$_3$, 470 MHz): δ -62.6; HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for $C_{18}H_{12}F_3O_2$ 317.0789; Found 317.0792.

2-(4-(Trifluoromethyl)benzyl)naphthalene-1,4-dione (**3o**): Prepared by following the procedure **B** and purified by column chromatography using EtOAc/hexane (0.2:9.8 to 0.5:9.5) and isolated as orange solid. Yield: 99% (63 mg). MP: 85-87 °C. IR (Neat): ν_{max} 2925, 1654, 1320, 1105, 1063 and 734 cm^{-1}. ^{1}H NMR (CDCl$_3$, 500 MHz): δ 8.12-8.09 (1H, m), 8.07-8.04 (1H, m), 7.76-7.72 (2H, m), 7.59 (2H, d, J = 8.0 Hz), 7.39 (2H, d, J = 8.5 Hz), 6.64 (1H, t, J = 1.5 Hz, olefinic-H), 3.96 (2H, s); ^{13}C{^{1}H} NMR (CDCl$_3$, DEPT-135, 125 MHz): δ 184.8 (C, C=O), 184.7 (C, C=O), 149.7 (C), 141.0 (C), 135.9 (CH), 133.9 (CH), 133.8 (CH), 132.0 (2 x C), 129.7 (2 x CH), 129.4 (C, q, J = 32.5 Hz), 126.7 (CH), 126.2 (CH), 125.8 (2 x CH, q, J = 3.75 Hz), 124.1 (C, q, J = 270 Hz, CF$_3$), 35.6 (CH$_2$); ^{19}F NMR (CDCl$_3$, 470 MHz): δ -62.5; HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for $C_{18}H_{12}F_3O_2$ 317.0789; Found 317.0789.



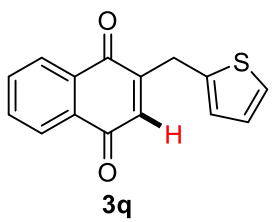
3o

2-(Naphthalen-2-ylmethyl)naphthalene-1,4-dione (**3p**): Prepared by following the procedure **B** and purified by column chromatography using EtOAc/hexane (0.2:9.8 to 0.5:9.5) and isolated as yellow solid. Yield: 99% (59 mg). MP: 136-138 ºC. IR (Neat): ν_{max} 2925, 1650, 1589, 1302, 1136, 939, 811 and 752 cm^{-1}. ^{1}H NMR (CDCl$_3$, 500 MHz): δ 8.13-8.10 (1H, m), 8.05-8.02 (1H, m), 7.83-7.79 (3H, m), 7.73-7.69 (3H, m), 7.49-7.44 (2H, m), 7.35 (1H, dd, J = 8.5, 1.5 Hz), 6.64 (1H, br s, olefinic-H), 4.06 (2H, s); ^{13}C{^{1}H} NMR (CDCl$_3$, DEPT-135, 125 MHz): δ 185.0 (C, C=O), 184.9 (C, C=O), 150.7 (C), 135.7 (CH), 134.2 (C), 133.7 (CH), 133.6 (CH), 133.6 (C), 132.3 (C), 132.1 (2 x C), 128.5 (CH), 128.1 (CH), 127.6 (CH), 127.5 (CH), 127.4 (CH), 126.6 (CH), 126.2 (CH), 126.1 (CH), 125.8 (CH), 35.8 (CH$_2$); HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for $C_{21}H_{15}O_2$ 299.1072; Found 299.1069.



3p

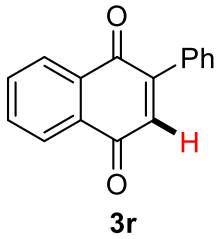
2-(Thiophen-2-ylmethyl)naphthalene-1,4-dione (**3q**): Prepared by following the procedure **B** and purified by column chromatography using EtOAc/hexane (0.2:9.8 to 0.5:9.5) and isolated as pale yellow solid. Yield: 95% (48 mg). MP: 95-97 °C. IR (Neat): ν_{max} 2923, 1658, 1590, 1297, 749 and 695 cm^{-1}. ^{1}H NMR (CDCl$_3$, 500 MHz): δ 8.14-8.10 (1H, m), 8.07-8.04 (1H, m), 7.76-



3q

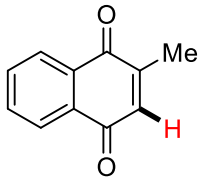
7.71 (2H, m), 7.21 (1H, dd, J = 5.0, 1.0 Hz), 6.99-6.97 (1H, m), 6.93-6.92 (1H, m), 6.72 (1H, br s, olefinic-*H*), 4.11 (2H, s); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, DEPT-135, 100 MHz): δ 185.1 (C, *C*=O), 184.7 (C, *C*=O), 149.8 (C), 138.2 (C), 135.5 (CH), 133.9 (CH), 133.8 (CH), 132.1 (C), 132.0 (C), 127.3 (CH), 127.0 (CH), 126.7 (CH), 126.1 (CH), 125.0 (CH), 29.6 (CH_2); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{15}H_{11}O_2S$ 255.0480; Found 255.0482.

2-Phenylnaphthalene-1,4-dione (**3r**): Prepared by following the procedure **B** and purified by column chromatography using EtOAc/hexane (0.2:9.8 to 0.5:9.5) and isolated as yellow solid. Yield: 93% (43.6 mg). MP: 97-99 °C. IR (Neat): ν_{max} 2969, 1738, 1366, 1215 and 759 cm^{-1}. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.21-8.17 (1H, m), 8.14-8.10 (1H, m), 7.80-7.75 (2H, m), 7.60-7.55 (2H, m), 7.49-7.46 (3H, m), 7.08 (1H, s, olefinic-*H*); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, DEPT-135, 125 MHz): δ 185.1 (C, *C*=O), 184.4 (C, *C*=O), 148.1 (C), 135.2 (CH), 133.9 (CH), 133.8 (CH), 133.4 (C), 132.4 (C), 132.1 (C), 130.0 (CH), 129.4 (2 x CH), 128.4 (2 x CH), 127.0 (CH), 126.0 (CH); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{16}H_{11}O_2$ 235.0759; Found 235.0760.



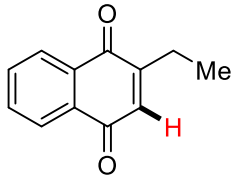
3r

2-Methylnaphthalene-1,4-dione [**Vitamin K$_3$ or Menadione**, **3s**]: Prepared by following the procedure **B** and purified by column chromatography using EtOAc/hexane (0.2:9.8 to 0.5:9.5) and isolated as yellow solid. Yield: 92% (31.7 mg). MP: 105-107 ºC. IR (Neat): ν_{max} 2921, 1660, 1589, 1352, 1261, 1155, 939 and 777 cm^{-1}. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.10-8.07 (1H, m), 8.06-8.03 (1H, m), 7.73-7.70 (2H, m), 6.83 (1H, q, J = 1.5 Hz, olefinic-*H*), 2.19 (3H, d, J = 1.5 Hz, CH_3); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, DEPT-135, 125 MHz): δ 185.5 (C, *C*=O), 184.9 (C, *C*=O), 148.1 (C), 135.6 (CH), 133.6 (CH), 133.5 (CH), 132.2 (C), 132.1 (C), 126.5 (CH), 126.1 (CH), 16.4 (CH_3); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{11}H_9O_2$ 173.0603; Found 173.0603.



3s

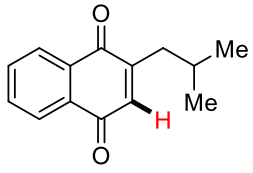
2-Ethylnaphthalene-1,4-dione (**3t**): Prepared by following the procedure **B** and purified by column chromatography using EtOAc/hexane (0.2:9.8 to 0.5:9.5) and isolated as pale yellow solid. Yield: 99% (37 mg). MP: 110-112 ºC. IR (Neat): ν_{max} 2921, 1660, 1590, 1415, 1298, 1248, 1142, 893, 765 and 656 cm^{-1}. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.12-8.09 (1H, m), 8.08-8.05 (1H, m), 7.74-7.71 (2H, m), 6.79 (1H, t, J = 1.5 Hz, olefinic-*H*), 2.62 (2H, dq, J = 7.5, 1.5 Hz), 1.21 (3H, t, J = 7.0 Hz); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, DEPT-135, 125 MHz): δ 185.31 (C, *C*=O), 185.27 (C, *C*=O), 153.2 (C), 134.0 (CH), 133.64 (CH), 133.62 (CH), 132.3 (C), 132.1 (C), 126.6 (CH),



3t

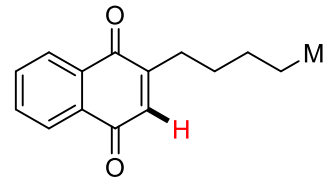
126.0 (CH), 22.6 (CH_2), 11.9 (CH_3); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{12}H_{11}O_2$ 187.0759; Found 187.0762.

2-Isobutylnaphthalene-1,4-dione (**3u**): Prepared by following the procedure **B** and purified by column chromatography using EtOAc/hexane (0.2:9.8 to 0.5:9.5) and isolated as orange solid. Yield: 98% (42 mg). MP: 94-96 °C. IR (Neat): ν_{max} 2953, 1652, 1586, 1455, 1377, 1255, 1103, 919 and 758 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ 8.03 (1H, d, *J* = 7.5 Hz), 7.60 (1H, dt, *J* = 7.5, 1.0 Hz), 7.41 (1H, dt, *J* = 8.0, 1.0 Hz), 7.27 (1H, d, *J* = 7.5 Hz), 7.13 (1H, s, olefinic-*H*), 2.29 (2H, d, *J* = 7.5 Hz), 1.88 (1H, septet, *J* = 7.0 Hz), 0.93 (6H, td, *J* = 7.0, 1.5 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$, DEPT-135, 125 MHz): δ 181.3 (C, *C*=O), 179.4 (C, *C*=O), 141.8 (CH), 139.7 (C), 135.8 (CH), 135.4 (C), 130.7 (C), 129.9 (CH), 129.7 (CH), 129.1 (CH), 38.7 (CH_2), 27.5 (CH), 22.4 (2 x CH_3); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{14}H_{15}O_2$ 215.1072; Found 215.1071.



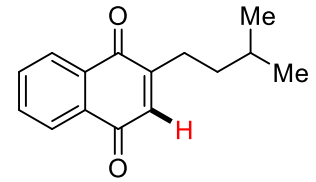
3u

2-Pentylnaphthalene-1,4-dione (**3v**): Prepared by following the procedure **B** and purified by column chromatography using EtOAc/hexane (0.2:9.8 to 0.5:9.5) and isolated as yellow solid. Yield: 95% (43 mg). MP: 120-122 °C. IR (Neat): ν_{max} 2927, 1659, 1593, 1299, 896, 750 and 661 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ 8.10-8.08 (1H, m), 8.06-8.03 (1H, m), 7.73-7.70 (2H, m), 6.78 (1H, br s, olefinic-*H*), 2.55 (2H, dt, *J* = 7.5, 1.0 Hz), 1.58 (2H, quintet, *J* = 7.5 Hz), 1.40-1.31 (4H, m), 0.90 (3H, t, *J* = 7.0 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$, DEPT-135, 125 MHz): δ 185.2 (2 x C, 2 x *C*=O), 152.0 (C), 134.7 (CH), 133.6 (CH), 133.5 (CH), 132.3 (C), 132.1 (C), 126.6 (CH), 126.0 (CH), 31.5 (CH_2), 29.5 (CH_2), 27.7 (CH_2), 22.4 (CH_2), 13.9 (CH_3); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{15}H_{17}O_2$ 229.1229; Found 229.1229.



3v

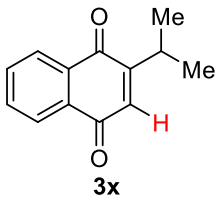
2-Isopentylnaphthalene-1,4-dione (3w): Prepared by following the procedure **B** and purified by column chromatography using EtOAc/hexane (0.2:9.8 to 0.5:9.5) and isolated as yellow solid. Yield: 97% (45.6 mg). MP: 132-134 °C. IR (Neat): ν_{max} 2953, 1651, 1592, 1467, 1304, 1141, 933, 753 and 662 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ 8.09-8.07 (1H, m), 8.05-8.03 (1H, m), 7.72-7.70 (2H, m), 6.78 (1H, br s, olefinic-*H*), 2.56 (2H, t, *J* = 8.0 Hz), 1.65 (1H, septet, *J* = 6.5 Hz), 1.44 (2H, br q, *J* = 6.5 Hz), 0.95 (6H, d, *J* = 6.5 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$, DEPT-135, 100 MHz): δ 185.2 (2 x C, 2 x *C*=O), 152.3 (C), 134.6 (CH), 133.6 (2 x



3w

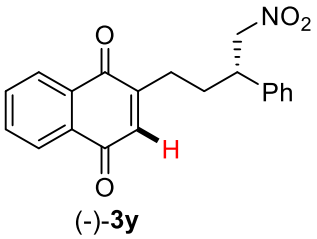
CH), 132.3 (C), 132.0 (C), 126.5 (CH), 126.0 (CH), 37.0 (CH_2), 27.9 (CH), 27.5 (CH_2), 22.4 (2 x CH_3); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{15}H_{17}O_2$ 229.1229; Found 229.1224.

2-Isopropylnaphthalene-1,4-dione (3x): Prepared by following the procedure **B** and purified by column chromatography using EtOAc/hexane (0.2:9.8 to 0.5:9.5) and isolated as yellow solid. Yield: 99% (39.6 mg). MP: 96-98 ºC. IR (Neat): ν_{max} 2964, 1658, 1593, 1327, 1250, 932 and 717 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 8.11-8.08 (1H, m), 8.06-8.03 (1H, m), 7.73-7.69 (2H, m), 6.76 (1H, d, *J* = 1.0 Hz, olefinic-*H*), 3.28-3.20 (1H, m), 1.19 (6H, d, *J* = 7.0 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$, DEPT-135, 100 MHz): δ 185.5 (C, *C*=O), 184.8 (C, *C*=O), 157.3 (C), 133.6 (CH), 133.5 (CH), 132.6 (CH), 132.5 (C), 131.9 (C), 126.6 (CH), 125.9 (CH), 27.0 (CH), 21.5 (2 x CH_3); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{13}H_{13}O_2$ 201.0916; Found 201.0915.



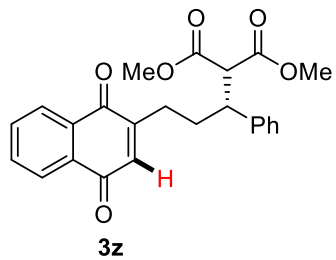
3x

(*S*)-2-(4-Nitro-3-phenylbutyl)naphthalene-1,4-dione (3y): Prepared by following the procedure **B** and purified by column chromatography using EtOAc/hexane (0.2:9.8 to 0.5:9.5) and isolated as red solid. Yield: 99% (66 mg). MP: 118-120 ºC. $[\alpha]_D^{25}$ = -32.0° [*c* = 0.1, $CHCl_3$]. IR (Neat): ν_{max} 2929, 1701, 1547, 1374, 1280, 734 and 697 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 8.72-8.03 (2H, m), 7.75-7.70 (2H, m), 7.38-7.33 (2H, m), 7.29-7.26 (1H, m), 7.24-7.21 (2H, m), 6.68 (1H, t, *J* = 1.5 Hz, olefinic-*H*), 4.62-4.54 (2H, m), 3.55 (1H, quintet, *J* = 8.0 Hz), 2.49-2.42 (2H, m), 2.05-2.00 (2H, m); $^{13}C\{^1H\}$ NMR ($CDCl_3$, DEPT-135, 125 MHz): δ 184.9 (C, *C*=O), 184.8 (C, *C*=O), 150.3 (C), 138.2 (C), 135.3 (CH), 133.8 (CH), 133.7 (CH), 132.1 (C), 130. (C), 129.2 (2 x CH), 128.1 (CH), 127.7 (2 x CH), 126.6 (CH), 126.1 (CH), 80.7 (CH_2), 44.2 (CH), 31.1 (CH_2), 27.7 (CH_2); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{20}H_{18}NO_4$ 336.1236; Found 336.1236.



(-)-**3y**

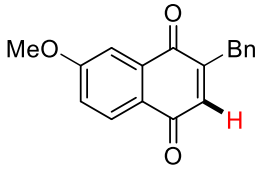
Dimethyl (*R*)-2-(3-(1,4-dioxo-1,4-dihydronaphthalen-2-yl)-1-phenylpropyl)malonate (3z): Prepared by following the procedure **B** and purified by column chromatography using EtOAc/hexane (0.4:9.6 to 0.8:9.2) and isolated as brown solid. Yield: 94% (76 mg). MP: 120-122 °C. $[\alpha]_D^{25}$ = -15.0° [*c* = 0.1, $CHCl_3$]. IR (Neat): ν_{max} 2921, 1731, 1661, 1455, 1259, 1152 and 700 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ 8.05-8.02 (2H, m), 7.71-7.69 (2H, m), 7.29 (2H, t, *J* = 7.5 Hz), 7.22-7.18 (3H, m), 6.67 (1H, s, olefinic-*H*), 3.76 (3H, s), 3.68 (1H, d, *J* = 10.5 Hz), 3.47-3.42 (4H, m), 2.39-2.36 (2H, m), 2.04-1.96 (2H, m); $^{13}C\{^1H\}$ NMR ($CDCl_3$, DEPT-135, 100 MHz): δ 185.0 (2 x C, 2 x *C*=O),



3z

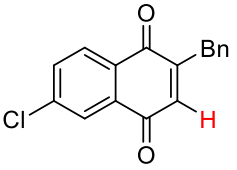
168.6 (C, O-*C*=O), 167.9 (C, O-*C*=O), 150.8 (C), 139.5 (C), 135.0 (CH), 133.6 (2 x CH), 132.2 (C), 132.0 (C), 128.7 (2 x CH), 128.3 (2 x CH), 127.4 (CH), 126.5 (CH), 126.0 (CH), 58.5 (CH), 52.7 (CH_3), 52.3 (CH_3), 45.3 (CH), 31.6 (CH_2), 27.8 (CH_2); HRMS (ESI-TOF) *m/z*: [M + Na]$^+$ Calcd for $C_{24}H_{22}O_6Na$ 429.1314; Found 429.1319.

2-Benzyl-7-methoxynaphthalene-1,4-dione (**3aa**): Prepared by following the procedure **B** and purified by column chromatography using EtOAc/hexane (0.2:9.8 to 0.5:9.5) and isolated as yellow solid. Yield: 93% (52 mg). MP: 92-93 °C. IR (Neat): ν_{max} 2921, 1743, 1654, 1591, 1492, 1313, 1067, 841 and 705 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.99 (1H, d, *J* = 8.5 Hz), 7.53 (1H, br s), 7.34 (2H, t, *J* = 7.5 Hz), 7.26 (3H, t, *J* = 7.5 Hz), 7.18 (1H, dd, *J* = 8.5, 2.0), 6.55 (1H, s, olefinic-*H*), 3.94 (3H, s) 3.88 (2H, s); ^{13}C{^{1}H} NMR ($CDCl_3$, DEPT-135, 125 MHz): δ 185.1 (C, *C*=O), 184.3 (C, *C*=O), 164.0 (C), 150.3 (C), 136.8 (C), 135.9 (CH), 134.2 (C), 129.4 (2 x CH), 128.8 (2 x CH), 128.5 (CH), 126.9 (CH), 125.7 (C), 120.3 (CH), 110.0 (CH), 55.9 (CH_3), 35.7 (CH_2); HRMS (ESI-TOF) *m/z*: [M + H]$^+$ Calcd for $C_{18}H_{15}O_3$ 279.1021; Found 279.1027.



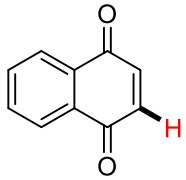
3aa

2-Benzyl-6-chloronaphthalene-1,4-dione (**3bb**): Prepared by following the procedure **B** and purified by column chromatography using EtOAc/hexane (0.2:9.8 to 0.5:9.5) and isolated as yellow solid. Yield: 95% (54 mg). MP: 94-96 °C. IR (Neat): ν_{max} 3030, 1663, 1586, 1494, 1287, 1067, 841 and 700 cm^{-1}. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.05 (1H, d, *J* = 8.5 Hz), 8.00 (1H, d, *J* = 2.0 Hz), 7.68 (1H, dd, *J* = 8.2, 2.0 Hz), 7.34 (2H, t, *J* = 7.0 Hz), 7.28-7.23 (3H, m), 6.61 (1H, s, olefinic-*H*), 3.90 (2H, CH_2); ^{13}C{^{1}H} NMR ($CDCl_3$, DEPT-135, 125 MHz): δ 184.0 (2 x C, 2 x *C*=O), 151.2 (C), 140.8 (C), 136.4 (C), 135.4 (CH), 133.7 (CH), 133.2 (C), 130.3 (C), 129.4 (2 x CH), 128.9 (2 x CH), 128.4 (CH), 127.1 (CH), 126.2 (CH), 35.7 (CH_2); HRMS (ESI-TOF) *m/z*: [M + H]$^+$ Calcd for $C_{17}H_{12}ClO_2$ 283.0526; Found 283.0519.



3bb

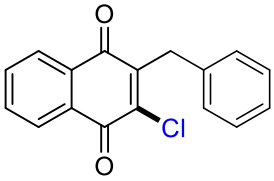
Naphthalene-1,4-dione (**3cc**): Prepared by following the procedure **B** and purified by column chromatography using EtOAc/hexane (0.2:9.8 to 0.5:9.5) and isolated as yellow solid. Yield: 95% (30 mg). MP: 121-122 ºC. IR (Neat): ν_{max} 2923, 1655, 1586, 1327, 1298, 1144, 1054, 861 and 764 cm^{-1}. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.08-8.06 (2H, m), 7.76-7.74 (2H, m), 6.97 (2H, s, olefinic-*H*); ^{13}C{^{1}H} NMR ($CDCl_3$, DEPT-135, 100 MHz): δ 185.0 (2 x C, 2 x *C*=O), 138.6 (2 x CH), 133.9



3cc

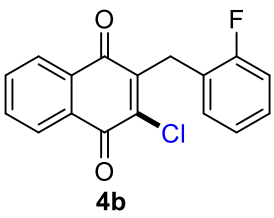
(2 x CH), 131.8 (2 x C), 126.4 (2 x CH); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{10}H_7O_2$ 159.0446; Found 159.0445.

2-Benzyl-3-chloronaphthalene-1,4-dione (4a): Prepared by following the procedure **C** and purified by column chromatography using EtOAc/hexane (0.2:9.8 to 0.5:9.5) and isolated as yellow solid. Yield: 95% (80.6 mg). MP: 159-161 ºC. IR (Neat): ν_{max} 1668, 1592, 1277, 1150, 951, 845 and 711 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ 8.17-8.14 (1H, m), 8.13-8.10 (1H, m), 7.77-7.72 (2H, m), 7.37 (2H, d, *J* = 8.0 Hz), 7.28 (2H, t, *J* = 7.5 Hz), 7.21 (1H, t, *J* = 7.5 Hz), 4.18 (2H, s); $^{13}C\{^1H\}$ NMR ($CDCl_3$, DEPT-135, 125 MHz): δ 182.3 (C, *C*=O), 177.9 (C, *C*=O), 146.4 (C), 143.7 (C), 136.7 (C), 134.2 (CH), 133.9 (CH), 131.6 (C), 131.3 (C), 129.2 (2 x CH), 128.6 (2 x CH), 127.1 (2 x CH), 126.8 (CH), 33.9 (CH_2); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{17}H_{12}ClO_2$ 283.0526; Found 283.0526.



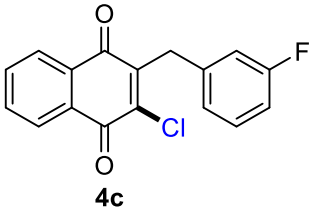
4a

2-Chloro-3-(2-fluorobenzyl)naphthalene-1,4-dione (**4b**): Prepared by following the procedure **C** and purified by column chromatography using EtOAc/hexane (0.2:9.8 to 0.5:9.5) and isolated as pale yellow solid. Yield: 99% (89.5 mg). MP: 141-143 ºC. IR (Neat): ν_{max} 2921, 1664, 1588, 1489, 1275, 1092, 954 and 705 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ 8.18-8.16 (1H, m), 8.13-8.11 (1H, m), 7.78-7.74 (2H, m), 7.22-7.18 (2H, m), 7.05-7.01 (2H, m), 4.21 (2H, s); $^{13}C\{^1H\}$ NMR ($CDCl_3$, DEPT-135, 100 MHz): δ 182.1 (C, *C*=O), 177.8 (C, *C*=O), 160.5 (C, d, *J* = 245 Hz, *C*-F), 145.6 (C), 144.7 (C), 134.3 (CH), 134.0 (CH), 131.6 (C), 131.4 (C), 130.4 (CH, d, *J* = 4.0 Hz), 128.5 (CH, d, *J* = 8.0 Hz), 127.3 (CH), 127.2 (CH), 124.1 (CH, d, *J* = 3.0 Hz), 123.7 (C, d, *J* = 16.0 Hz), 115.6 (CH, d, *J* = 22.0 Hz), 27.2 (CH_2, d, *J* = 4.0 Hz); ^{19}F NMR ($CDCl_3$, 375 MHz): δ -115.7; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{17}H_{10}ClFO_2Na$ 323.0251; Found 323.0256.



4b

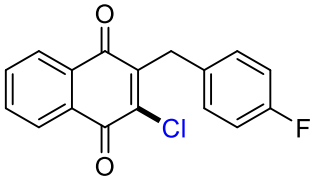
2-Chloro-3-(3-fluorobenzyl)naphthalene-1,4-dione (**4c**): Prepared by following the procedure **C** and purified by column chromatography using EtOAc/hexane (0.2:9.8 to 0.5:9.5) and isolated as pale yellow solid. Yield: 99% (89 mg). MP: 135-136 ºC. IR (Neat): ν_{max} 3069, 1670, 1589, 1485, 1279, 1137, 955, 844 and 712 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ 8.18-8.15 (1H, m), 8.14-8.11 (1H, m), 7.79-7.74 (2H, m), 7.23 (1H, br dt, *J* = 8.5, 2.0 Hz), 7.15 (1H, br d, *J* = 7.5 Hz), 7.07 (1H, br d, *J* = 10.0 Hz), 6.91 (1H, br dt, *J* = 8.5, 2.0 Hz), 4.17 (2H, s); $^{13}C\{^1H\}$ NMR ($CDCl_3$, DEPT-135, 125 MHz):



4c

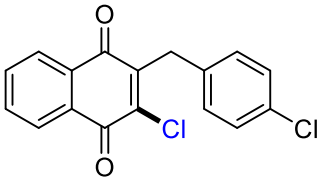
δ 182.3 (C, *C*=O), 177.8 (C, *C*=O), 162.8 (C, d, *J* = 243.7 Hz, *C*-F), 145.7 (C), 144.0 (C), 139.0 (C, d, *J* = 7.5 Hz), 134.4 (CH), 134.1 (CH), 131.5 (C), 131.3 (C), 130.0 (CH, d, *J* = 8.75 Hz), 127.3 (CH), 127.2 (CH), 124.8 (CH, d, *J* = 2.5 Hz), 116.1 (CH, d, *J* = 21.2 Hz), 113.8 (CH, d, *J* = 20.0 Hz), 33.6 (CH_2, d, *J* = 1.25 Hz); ^{19}F NMR ($CDCl_3$, 470 MHz): δ -112.8; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{17}H_{10}ClFO_2Na$ 323.0251; Found 323.0250.

2-Chloro-3-(4-fluorobenzyl)naphthalene-1,4-dione (**4d**): Prepared by following the procedure **C** and purified by column chromatography using EtOAc/hexane (0.2:9.8 to 0.5:9.5) and isolated as yellow solid. Yield: >99% (90 mg). MP: 121-122 °C. IR (Neat): ν_{max} 2968, 1739, 1661, 1368, 1217, 844 and 704 cm^{-1}. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.15-8.13 (1H, m), 8.12-8.10 (1H, m), 7.77-7.72 (2H, m), 7.34 (2H, dd, *J* = 8.5, 5.5 Hz), 6.96 (2H, t, *J* = 9.0 Hz), 4.14 (2H, s); $^{13}C\{^1H\}$ NMR ($CDCl_3$, DEPT-135, 125 MHz): δ 182.3 (C, *C*=O), 177.8 (C, *C*=O), 161.8 (C, d, *J* = 244 Hz, *C*-F), 146.2 (C), 143.6 (C), 134.3 (CH), 134.1 (CH), 132.3 (C, d, *J* = 2.5 Hz), 131.5 (C), 131.3 (C), 130.7 (2 x CH, d, *J* = 7.5 Hz), 127.2 (CH), 127.1 (CH), 115.4 (2 x CH, d, *J* = 21.2 Hz), 33.1 (CH_2); ^{19} F NMR ($CDCl_3$ 470 MHz): δ -115.7; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{17}H_{10}ClFO_2Na$ 323.0251; Found 323.0251.



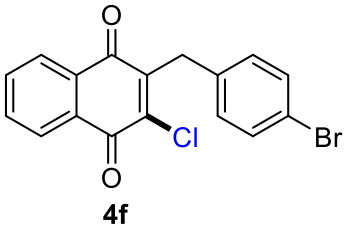
4d

2-Chloro-3-(4-Chlorobenzyl)naphthalene-1,4-dione (**4e**): Prepared by following the procedure **C** and purified by column chromatography using EtOAc/hexane (0.2:9.8 to 0.5:9.5) and isolated as yellow solid. Yield: 95% (90 mg). MP: 131-133 °C. IR (Neat): ν_{max} 1671, 1588, 1486, 1321, 1280, 1149, 1088, 953, 845, and 787 cm^{-1}. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.17-8.14 (1H, m), 8.12-8.10 (1H, m), 7.78-7.73 (2H, m), 7.31 (2H, d, *J* = 8.5 Hz), 7.24 (2H, d, *J* = 8.5 Hz), 4.14 (2H, s); $^{13}C\{^1H\}$ NMR ($CDCl_3$, DEPT-135, 125 MHz): δ 182.3 (C, *C*=O), 177.7 (C, *C*=O), 145.9 (C), 143.8 (C), 135.1 (C), 134.3 (CH), 134.1 (CH), 132.8 (C), 131.5 (C), 131.3 (C), 130.5 (2 x CH), 128.8 (2 x CH), 127.2 (CH), 127.1 (CH), 33.3 (CH_2); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{17}H_{11}Cl_2O_2$ 317.0136; Found 317.0134.



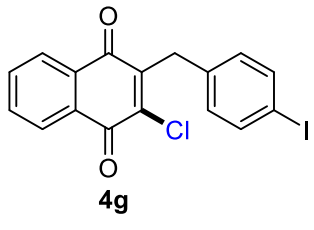
4e

2-(4-Bromobenzyl)-3-chloronaphthalene-1,4-dione (**4f**): Prepared by following the procedure **C** and purified by column chromatography using EtOAc/hexane (0.2:9.8 to 0.5:9.5) and isolated as yellow solid. Yield: 98% (106 mg). MP: 135-137 °C. IR (Neat): ν_{max} 2923, 1670, 1588, 1486, 1321, 1279, 1088, 844 and 702 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ 8.16-8.13 (1H, m), 8.12-8.08 (1H, m), 7.81-7.72 (2H, m), 7.31 (2H, d, *J* = 8.0 Hz), 7.24 (2H, d, *J* = 8.0 Hz), 4.13 (2H, s); $^{13}C\{^1H\}$ NMR ($CDCl_3$, DEPT-135, 100 MHz): δ 182.3 (C, *C*=O), 177.8 (C, *C*=O), 145.9 (C), 143.8 (C), 135.1 (C), 134.3 (CH), 134.1 (CH), 132.8 (C), 131.5 (C), 131.3 (C), 130.5 (2 x CH), 128.8 (2 x CH), 127.2 (CH), 127.1 (CH), 33.3 (CH_2); HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{17}H_{10}BrClO_2Na$ 382.9450; Found 382.9452.



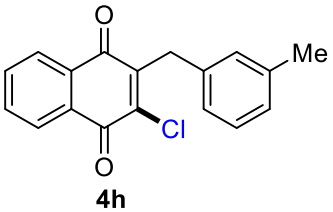
4f

2-Chloro-3-(4-iodobenzyl)naphthalene-1,4-dione (4g): Prepared by following the procedure **C** and purified by column chromatography using EtOAc/hexane (0.2:9.8 to 0.5:9.5) and isolated as yellow solid. Yield: 95% (116 mg). MP: 161-163 ºC. IR (Neat): ν_{max} 2922, 1670, 1587, 1479, 1276, 1002, 845 and 750 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ 8.17-8.13 (1H, m), 8.12-8.09 (1H, m), 7.77-7.72 (2H, m), 7.59 (2H, td, *J* = 8.5, 2.5 Hz), 7.12 (2H, td, *J* = 8.0, 2.5 Hz), 4.10 (2H, CH_2); $^{13}C\{^1H\}$ NMR ($CDCl_3$, DEPT-135, 100 MHz): δ 182.3 (C, *C*=O), 177.7 (C, *C*=O), 145.8 (C), 143.9 (C), 137.7 (2 x CH), 136.3 (C), 134.3 (CH), 134.1 (CH), 131.5 (C), 131.2 (C, 2 x CH), 127.2 (CH), 127.1 (CH), 92.3 (C), 33.4 (CH_2); HRMS (ESI-TOF) *m/z*: $[M + NH_4]^+$ Calcd for $C_{17}H_{14}NClIO_2$ 425.9758; Found 425.9757.



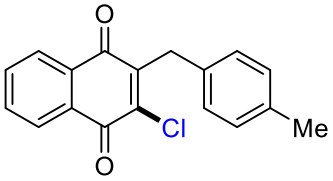
4g

2-Chloro-3-(3-methylbenzyl)naphthalene-1,4-dione (4h): Prepared by following the procedure **C** and purified by column chromatography using EtOAc/hexane (0.2:9.8 to 0.5:9.5) and isolated as yellow solid. Yield: 97% (86 mg). MP: 157-160 ºC. IR (Neat): ν_{max} 2919, 1668, 1590, 1489, 1275, 1149, 954, 846 and 781 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ 8.17-8.14 (1H, m), 8.13- 8.10 (1H, m), 7.77-7.72 (2H, m), 7.17-7.16 (3H, m), 7.03-7.01 (1H, m), 4.15 (2H, s), 2.31 (3H, s); $^{13}C\{^1H\}$ NMR ($CDCl_3$, DEPT-135, 125 MHz): δ 182.4 (C, *C*=O), 178.0 (C, *C*=O), 146.5 (C), 143.7 (C), 138.3 (C), 136.6 (C), 134.2 (CH), 134.0 (CH), 131.7 (C), 131.3 (C), 129.8 (CH), 128.5 (CH), 127.6 (CH), 127.2 (2 x CH), 126.2 (CH), 33.8 (CH_2), 21.4 (CH_3); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{18}H_{14}ClO_2$ 297.0682; Found 297.0682.



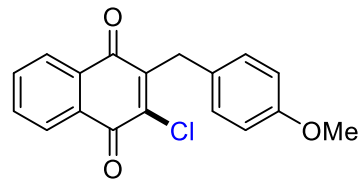
4h

2-Chloro-3-(4-methylbenzyl)naphthalene-1,4-dione (4i): Prepared by following the procedure **C** and purified by column chromatography using EtOAc/hexane (0.2:9.8 to 0.5:9.5) and isolated as yellow solid. Yield: 93% (83 mg). MP: 156-158 ºC. IR (Neat): ν_{max} 2918, 1666, 1592, 1280, 1150, 955, 847 and 703 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ 8.16-8.13 (1H, m), 8.12-8.09 (1H, m), 7.76-7.71 (2H, m), 7.26 (2H, d, *J* = 8.0 Hz), 7.08 (2H, d, *J* = 7.5 Hz), 4.14 (2H, s), 2.29 (3H, s); $^{13}C\{^1H\}$ NMR ($CDCl_3$, DEPT-135, 125 MHz): δ 182.4 (C, *C*=O), 178.0 (C, *C*=O), 146.6 (C), 143.5 (C), 136.5 (C), 134.2 (CH), 134.0 (CH), 133.6 (C), 131.7 (C), 131.3 (C), 129.3 (2 x CH), 129.1 (2 x CH), 127.1 (2 x CH), 33.5 (CH_2), 21.0 (CH_3); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{18}H_{14}ClO_2$ 297.0682; Found 297.0679.



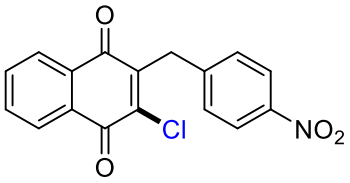
4i

2-Chloro-3-(4-methoxybenzyl)naphthalene-1,4-dione (4j): Prepared by following the procedure **C** and purified by column chromatography using EtOAc/hexane (0.2:9.8 to 0.5:9.5) and isolated as yellow solid. Yield: 96% (89.7 mg). MP: 161-163 ºC. IR (Neat): ν_{max} 2924, 1660, 1510, 1276, 1153, 1031, 845 and 705 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ 8.15-8.13 (1H, m), 8.11-8.09 (1H, m), 7.75-7.71 (2H, m), 7.30 (2H, d, *J* = 8.5 Hz), 6.81 (2H, d, *J* = 8.5 Hz), 4.11 (2H, s), 3.75 (3H, s); $^{13}C\{^1H\}$ NMR ($CDCl_3$, DEPT-135, 100 MHz): δ 182.4 (C, *C*=O), 178.0 (C, *C*=O), 158.5 (C), 146.6 (C), 143.3 (C), 134.2 (CH), 133.9 (CH), 131.6 (C), 131.3 (C), 130.3 (2 x CH), 128.6 (C), 127.1 (2 x CH), 114.0 (2 x CH), 55.2 (CH_3), 33.0 (CH_2); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{18}H_{14}ClO_3$ 313.0631; Found 313.0631.



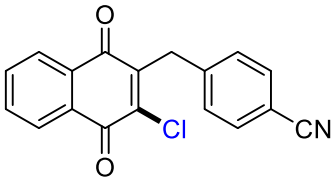
4j

2-Chloro-3-(4-nitrobenzyl)naphthalene-1,4-dione (4k): Prepared by following the procedure **C** and purified by column chromatography using EtOAc/hexane (0.2:9.8 to 0.5:9.5) and isolated as yellow solid. Yield: 99% (97 mg). MP: 141-143 ºC. IR (Neat): ν_{max} 2922, 1677, 1521, 1343, 1282, 1102 and 720 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ 8.18-8.15 (2H, m), 8.13-8.11 (2H, m), 7.78 (2H, m), 7.53 (2H, d, *J* = 8.5 Hz), 4.27 (2H, s); $^{13}C\{^1H\}$ NMR ($CDCl_3$, DEPT-135, 125 MHz): δ 182.2 (C, *C*=O), 177.5 (C, *C*=O), 147.0 (C), 144.9 (C), 144.6 (C), 144.2 (C), 134.6 (CH), 134.4 (CH), 131.4 (C), 131.3 (C), 130.0 (2 x CH), 127.4 (CH), 127.3 (CH), 123.9 (2 x CH), 33.8 (CH_2); HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{17}H_{10}ClNO_4Na$ 350.0196; Found 350.0199.



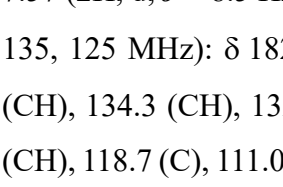
4k

4-((3-Chloro-1,4-dioxo-1,4-dihydronaphthalen-2-yl)methyl)benzonitrile (**4l**): Prepared by following the procedure **C** and purified by column chromatography using EtOAc/hexane (0.2:9.8 to 0.5:9.5) and isolated as yellow solid. Yield: 98% (90 mg). MP: 141-143 ºC. IR (Neat): ν_{max} 2921, 1659, 1591, 1280, 1147, 943, 838 and 707 cm^{-1}. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.17-8.15 (1H, m), 8.13-8.10 (1H, m), 7.79-7.75 (2H, m), 7.57 (2H, d, *J* = 8.5 Hz), 7.48 (2H, d, *J* = 8.0 Hz), 4.22 (2H, s); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, DEPT-135, 125 MHz): δ 182.2 (C, *C*=O), 177.5 (C, *C*=O), 145.0 (C), 144.5 (C), 142.2 (C), 134.5 (CH), 134.3 (CH), 132.5 (2 x CH), 131.4 (C), 131.3 (C), 130.0 (2 x CH), 127.4 (CH), 127.3 (CH), 118.7 (C), 111.0 (C), 34.0 (CH_2); HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{18}H_{10}ClNO_2Na$ 330.0298; Found 330.0296.



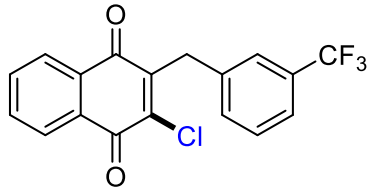
4l

2-Chloro-3-(2-(trifluoromethyl)benzyl)naphthalene-1,4-dione (**4m**): Prepared by following the procedure **C** and purified by column chromatography using EtOAc/hexane (0.2:9.8 to 0.5:9.5) and isolated as yellow solid. Yield: 99% (104 mg). MP: 144-147 °C. IR (Neat): ν_{max} 2969, 1739, 1369, 1212, 1104 and 762 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.23-8.21 (1H, m), 8.14-8.12 (1H, m), 7.81-7.77 (2H, m), 7.71 (1H, d, *J* = 8.0 Hz), 7.38 (1H, t, *J* = 7.5 Hz), 7.32 (1H, t, *J* = 7.5 Hz), 6.98 (1H, d, *J* = 7.5 Hz), 4.40 (2H, s); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, DEPT-135, 125 MHz): δ 182.0 (C, *C*=O), 177.6 (C, *C*=O), 145.8 (C), 145.4 (C), 135.2 (C), 134.5 (CH), 134.2 (CH), 132.0 (CH), 131.5 (C), 131.4 (C), 128.6 (C, q, *J* = 30 Hz), 128.0 (CH), 127.4 (CH), 127.3 (CH), 126.7 (CH), 126.4 (CH, q, *J* = 5.0 Hz), 124.4 (C, q, *J* = 272.5 Hz, CF_3), 30.5 (CH_2, br d, *J* = 2.5 Hz); ^{19}F NMR ($CDCl_3$, 470 MHz): δ -60.8. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{18}H_{11}ClF_3O_2$ 351.0400; Found 351.0405.



4m

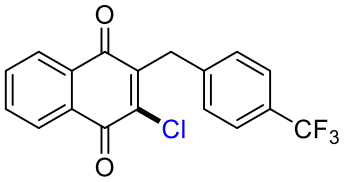
2-Chloro-3-(3-(trifluoromethyl)benzyl)naphthalene-1,4-dione (4n): Prepared by following the procedure **C** and purified by column chromatography using EtOAc/hexane (0.2:9.8 to 0.5:9.5) and isolated as yellow solid. Yield: 95% (84 mg). MP: 149-151 ºC. IR (Neat): ν_{max} 1657, 1593, 1328, 1282, 1117, 952, 845 and 787 cm^{-1}. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.18-8.14 (1H, m), 8.14-8.10 (1H, m), 7.78-7.73 (2H, m), 7.64 (1H, s), 7.56 (1H, d, *J* = 7.5 Hz), 7.48 (1H, d, *J* = 7.5 Hz), 7.40 (1H, t, *J* = 8.0 Hz), 4.23 (2H, s); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, DEPT-135, 125 MHz): δ 182.2 (C, *C*=O), 177.7 (C, *C*=O), 145.5 (C), 144.2 (C), 137.6 (C), 134.4 (CH), 134.2 (CH), 132.6 (CH), 131.5 (C), 131.3 (C), 131.0 (C, q, *J* = 32.5



4n

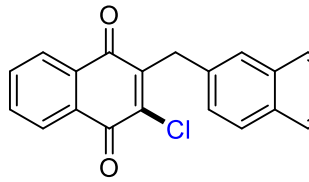
Hz), 129.1 (CH), 127.3 (CH), 127.2 (CH), 126.0 (CH, q, J = 3.75 Hz), 124.0 (C, q, J = 270 Hz, CF_3), 123.8 (CH, q, J = 3.75 Hz), 33.7 (CH_2); ^{19}F NMR ($CDCl_3$, 470 MHz): δ -62.6; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{18}H_{10}ClF_3O_2Na$ 373.0219; Found 373.0216.

2-Chloro-3-(4-(trifluoromethyl)benzyl)naphthalene-1,4-dione (**4o**): Prepared by following the procedure **C** and purified by column chromatography using EtOAc/hexane (0.2:9.8 to 0.5:9.5) and isolated as yellow solid. Yield: 99% (104 mg). MP: 130-132 °C. IR (Neat): ν_{max} 2922, 1663, 1588, 1421, 1278, 1038, 839 and 692 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ 8.17-8.15 (1H, m), 8.12-8.10 (1H, m), 7.78-7.74 (2H, m), 7.53 (2H, d, J = 8.0 Hz), 7.49 (2H, d, J = 8.5 Hz), 4.23 (2H, s); $^{13}C\{^1H\}$ NMR ($CDCl_3$, DEPT-135, 100 MHz): δ 182.2 (C, *C*=O), 177.7 (C, *C*=O), 145.5 (C), 144.2 (C), 140.7 (C), 134.4 (CH), 134.2 (CH), 131.5 (C), 131.3 (C), 129.5 (2 x CH), 129.2 (C, q, J = 32 Hz), 127.3 (CH), 127.2 (CH), 125.6 (2 x CH, q, J = 4.0 Hz), 124.1 (C, q, J = 270 Hz, CF_3), 33.7 (CH_2); ^{19}F NMR ($CDCl_3$, 375 MHz): δ -62.5; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{18}H_{11}ClF_3O_2$ 351.0400; Found 351.0395.



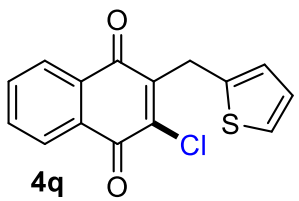
4o

2-Chloro-3-(naphthalen-2-ylmethyl)naphthalene-1,4-dione (4p): Prepared by following the procedure **C** and purified by column chromatography using EtOAc/hexane (0.2:9.8 to 0.5:9.5) and isolated as yellow solid. Yield: 99% (59 mg). MP: 149-151 °C. IR (Neat): ν_{max} 2932, 1663, 1589, 1277, 1146, 947, 851 and 742 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 8.16-8.15 (1H, m), 8.12-8.10 (1H, m), 7.80-7.72 (6H, m), 7.50 (1H, dd, J = 8.5, 1.5 Hz), 7.46-7.40 (2H, m), 4.34 (2H, s); $^{13}C\{^1H\}$ NMR ($CDCl_3$, DEPT-135, 100 MHz): δ182.4 (C, *C*=O), 177.8 (C, *C*=O), 146.5 (C), 144.0 (C), 134.3 (CH), 134.2 (CH), 133.9 (C), 133.8 (C), 132.6 (C), 132.0 (C), 131.7 (C), 128.4 (CH), 127.8 (CH), 127.7 (CH), 127.6 (CH), 127.4 (CH), 127.2 (2 x CH), 126.1 (CH), 125.7 (CH), 34.2 (CH_2); HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{21}H_{14}O_2Cl$ 333.0682; Found 333.0688.



4p

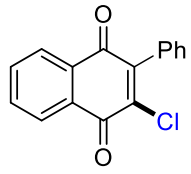
2-Chloro-3-(thiophen-2-ylmethyl)naphthalene-1,4-dione (**4q**): Prepared by following the procedure **C** and purified by column chromatography using EtOAc/hexane (0.2:9.8 to 0.5:9.5) and isolated as yellow solid. Yield: 97% (84 mg). MP: 100-102 °C. IR (Neat): ν_{max} 2922, 1663, 1588, 1276, 1118, 1037, 839 and 694 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 8.14 (2H, m), 7.77-7.73 (2H, m), 7.14 (1H, d, J = 5.0 Hz), 7.02 (1H, br d, J = 5.0 Hz),



4q

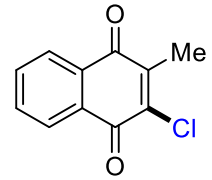
6.91 (1H, br q, J = 5.0 Hz), 4.35 (2H, s); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, DEPT-135, 100 MHz): δ 182.0 (C, *C*=O), 177.8 (C, *C*=O), 145.1 (C), 143.4 (C), 137.6 (C), 134.3 (CH), 134.0 (CH), 131.5 (C), 131.3 (C), 127.2 (CH), 127.1 (CH), 126.8 (2 x CH), 124.7 (CH), 28.2 (CH_2); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{15}H_{10}ClO_2S$ 289.0090; Found 289.0093.

2-Chloro-3-phenylnaphthalene-1,4-dione (**4r**): Prepared by following the procedure **C** and purified by column chromatography using EtOAc/hexane (0.2:9.8 to 0.5:9.5) and isolated as yellow solid. Yield: 98% (79 mg). MP: 102-104 °C. IR (Neat): ν_{max} 2923, 1672, 1584, 1492, 1302, 1086, 1019, 816 and 692 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.25-8.21 (1H, m), 8.18-8.15 (1H, m), 7.82-7.78 (2H, m), 7.52-7.46 (3H, m), 7.36 (2H, dd, J = 7.5, 1.5 Hz); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, DEPT-135, 125 MHz): δ 182.1 (C, *C*=O), 178.2 (C, *C*=O), 146.0 (C), 143.1 (C), 134.4 (CH), 134.1 (CH), 131.8 (C), 131.7 (C), 131.3 (C), 129.5 (2 x CH), 129.4 (CH), 128.1 (2 x CH), 127.3 (CH), 127.2 (CH); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{16}H_{10}ClO_2$ 269.0369; Found 269.0367.



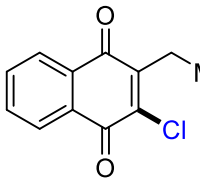
4r

2-Methylnaphthalene-1,4-dione (4s): Prepared by following the procedure **C** and purified by column chromatography using EtOAc/hexane (0.2:9.8 to 0.5:9.5) and isolated as yellow solid. Yield: 97% (60 mg). MP: 92-94 ºC. IR (Neat): ν_{max} 2923, 1670, 1587, 1279, 1028, 845 and 701 cm^{-1}. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.16-8.13 (1H, m), 8.12-8.10 (1H, m), 7.76-7.72 (2H, m), 2.34 (3H, s); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, DEPT-135, 125 MHz): δ 182.6 (C, *C*=O), 177.5 (C, *C*=O), 144.8 (C), 143.3 (C), 134.1 (CH), 133.9 (CH), 131.7 (C), 131.4 (C), 127.1 (CH), 127.0 (CH), 14.4 (CH_3); HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{11}H_7ClO_2Na$ 229.0032; Found 229.0032.



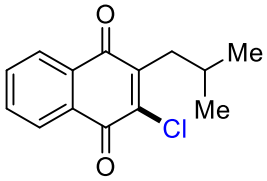
4s

2-Chloro-3-ethylnaphthalene-1,4-dione (**4t**): Prepared by following the procedure **C** and purified by column chromatography using EtOAc/hexane (0.2:9.8 to 0.5:9.5) and isolated as yellow solid. Yield: 99% (65.5 mg). MP: 95-97 ºC. IR (Neat): ν_{max} 2927, 1656, 1588, 1453, 1327, 1276, 1176, 1053, 829 and 711 cm^{-1}. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.17-8.14 (1H, m), 8.14-8.11 (1H, m), 7.77-7.72 (2H, m), 2.84 (2H, q, J = 7.5 Hz), 1.91 (3H, t, J = 7.5 Hz); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, DEPT-135, 125 MHz): δ 182.2 (C, *C*=O), 177.9 (C, *C*=O), 149.6 (C), 142.8 (C), 134.2 (CH), 133.9 (CH), 131.8 (C), 131.4 (C), 127.1 (CH), 127.0 (CH), 22.0 (CH_2), 12.0 (CH_3); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{12}H_{10}ClO_2$ 221.0369; Found 221.0369.



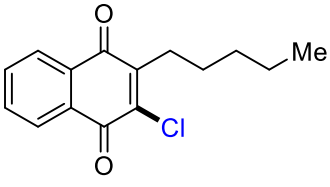
4t

2-Chloro-3-isobutylnaphthalene-1,4-dione (**4u**): Prepared by following the procedure **C** and purified by column chromatography using EtOAc/hexane (0.2:9.8 to 0.5:9.5) and isolated as yellow solid. Yield: 98% (73 mg). MP: 96-98 °C. IR (Neat): ν_{max} 2955, 1658, 1589, 1276, 1163, 1079, 840 and 711 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ 8.16-8.14 (1H, m), 8.12-8.10 (1H, m), 7.77-7.72 (2H, m), 2.73 (2H, d, *J* = 7.5 Hz), 2.07 (1H, septet, *J* = 7.0 Hz), 0.98 (6H, d, *J* = 6.5 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$, DEPT-135, 125 MHz): δ 182.6 (C, *C*=O), 177.8 (C, *C*=O), 148.0 (C), 143.7 (C), 134.1 (CH), 133.8 (CH), 131.7 (C), 131.4 (C), 127.1 (2 x CH), 37.0 (CH_2), 28.4 (CH), 22.8 (2 x CH_3); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{14}H_{14}ClO_2$ 249.0682; Found 249.0684.



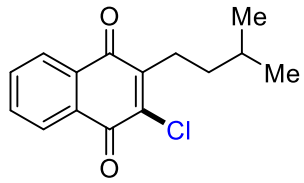
4u

2-Chloro-3-pentylnaphthalene-1,4-dione (4v): Prepared by following the procedure **C** and purified by column chromatography using EtOAc/hexane (0.2:9.8 to 0.5:9.5) and isolated as yellow solid. Yield: 95% (75 mg). MP: 134-136 ºC. IR (Neat): ν_{max} 2957, 1657, 1589, 1457, 1328, 1275, 1106, 836 and 710 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 8.16-8.14 (1H, m), 8.13-8.11 (1H, m), 7.77-7.72 (2H, m), 2.80 (2H, t, *J* = 7.5 Hz), 1.57-1.53 (2H, m), 1.44-1.33 (4H, m), 0.91 (3H, t, *J* = 7.5 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$, DEPT-135, 100 MHz): δ 182.4 (C, *C*=O), 177.9 (C, *C*=O), 148.7 (C), 143.0 (C), 134.1 (CH), 133.8 (CH), 131.8 (C), 131.4 (C), 127.1 (CH), 127.0 (CH), 31.9 (CH_2), 28.5 (CH_2), 27.5 (CH_2), 22.4 (CH_2), 13.9 (CH_3); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{15}H_{16}ClO_2$ 263.0839; Found 263.0838.



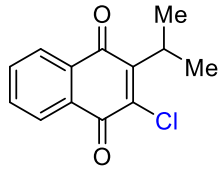
4v

2-Chloro-3-isopentylnaphthalene-1,4-dione (4w): Prepared by following the procedure **C** and purified by column chromatography using EtOAc/hexane (0.2:9.8 to 0.5:9.5) and isolated as yellow solid. Yield: 91% (72 mg). MP: 137-139 ºC. IR (Neat): ν_{max} 2957, 1658, 1590, 1325, 1275, 1172, 1082, 847 and 711 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ 8.17-8.13 (1H, m), 8.13-8.09 (1H, m), 7.77-7.72 (2H, m), 2.81-2.78 (2H, m), 1.69 (1H, septet, *J* = 6.5 Hz), 1.44-1.39 (2H, m), 0.98 (6H, d, *J* = 6.5 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$, DEPT-135, 125 MHz): δ 182.4 (C, *C*=O), 177.8 (C, *C*=O), 149.0 (C), 142.8 (C), 134.1 (CH), 133.8 (CH), 131.8 (C), 131.4 (C), 127.1 (CH), 127.0 (CH), 36.6 (CH_2), 28.6 (CH), 26.6 (CH_2), 22.3 (2 x CH_3); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{15}H_{16}ClO_2$ 263.0839; Found 263.0834.



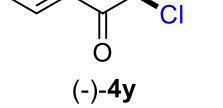
4w

2-Chloro-3-isopropylnaphthalene-1,4-dione (4x): Prepared by following the procedure **C** and purified by column chromatography using EtOAc/hexane (0.2:9.8 to 0.5:9.5) and isolated as yellow solid. Yield: 95% (67 mg). MP: 149-151 ºC. IR (Neat): ν_{max} 2961, 1657, 1565, 1278, 1061, 812 and 713 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ 8.13-8.11 (1H, m), 8.09-8.07 (1H, m), 7.76-7.70 (2H, m), 3.60 (1H, septet, *J* = 7.0 Hz), 1.39 (6H, d, *J* = 7.0 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$, DEPT-135, 125 MHz): δ 182.5 (C, *C*=O), 178.0 (C, *C*=O), 151.9 (C), 142.6 (C), 134.1 (CH), 133.6 (CH), 132.4 (C), 131.0 (C), 126.9 (2 x CH), 30.6 (CH), 19.7 (2 x CH_3); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{13}H_{12}ClO_2$ 235.0526; Found 235.0530.



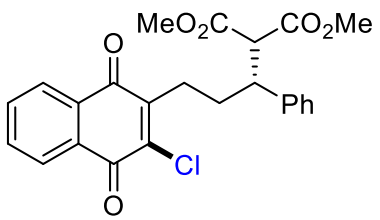
4x

(*S*)-2-Chloro-3-(4-nitro-3-phenylbutyl)naphthalene-1,4-dione (**4y**): Prepared by following the procedure **C** and purified by column chromatography using EtOAc/hexane (0.2:9.8 to 0.5:9.5) and isolated as red solid. Yield: 91% (101 mg). MP: 144-146 ºC. $[\alpha]_D^{25}$ = -32.0° [*c* = 0.1, $CHCl_3$]. IR (Neat): ν_{max} 2925, 1670, 1548, 1377, 1280, 838 and 702 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ 8.12-8.10 (1H, m), 8.09-8.06 (1H, m), 7.77-7.72 (2H, m), 7.32-7.29 (2H, m), 7.26-7.20 (3H, m), 4.62-4.53 (2H, m), 3.62-3.56 (1H, m), 2.79-2.73 (1H, m), 2.72-2.66 (1H, m), 2.10-2.02 (1H, m), 1.99-1.92 (1H, m); $^{13}C\{^1H\}$ NMR ($CDCl_3$, DEPT-135, 100 MHz): δ 182.2 (C, *C*=O), 177.4 (C, *C*=O), 147.1 (C), 143.4 (C), 138.2 (C), 134.2 (CH), 134.0 (CH), 131.6 (C), 131.2 (C), 129.1 (2 x CH), 128.0 (CH), 127.6 (2 x CH), 127.2 (CH), 127.0 (CH), 80.8 (CH_2), 44.5 (CH), 30.2 (CH_2), 26.4 (CH_2); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{20}H_{17}ClNO_4$ 370.0846; Found 370.0848.



(-)-**4y**

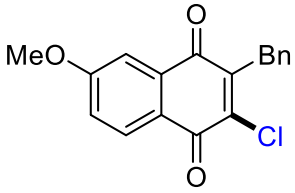
Dimethyl-(*R*)-2-(3-(3-chloro-1,4-dioxo-1,4-dihydronaphthalen-2-yl)-1-phenylpropyl)malonate (**4z**): Prepared by following the procedure **C** and purified by column chromatography using EtOAc/hexane (0.4:9.6 to 0.8:9.2) and isolated as yellow solid. Yield: 91% (120 mg). MP: 140-142 ºC. $[\alpha]_D^{25}$ = -68° [*c* = 0.1, $CHCl_3$]. IR (Neat): ν_{max} 2951, 1733, 1669, 1594, 1453, 1279, 1143, 840 and 699 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ 8.08-8.07 (1H, m), 8.05-8.03 (1H, m), 7.73-7.68 (2H, m), 7.24 (4H, d, *J* = 4.5 Hz), 7.17-7.12 (1H, m), 3.74 (3H, s), 3.64 (1H, d, *J* = 10.5 Hz), 3.49 (1H, dt, *J* = 10.5 , 3.5 Hz), 3.43 (3H, s), 2.69-2.64 (1H, m), 2.60-2.54 (1H, m), 2.06-1.99 (1H, m), 1.98-1.91 (1H, m); $^{13}C\{^1H\}$ NMR ($CDCl_3$, DEPT-135, 125 MHz): δ 182.0 (C, *C*=O), 177.5 (C, *C*=O), 168.4 (C, *C*=O), 167.9 (C, *C*=O), 147.6 (C), 143.1 (C), 139.5 (C),



(-)-**4z**

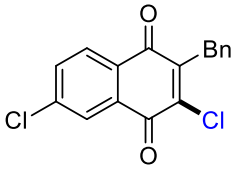
134.0 (CH), 133.8 (CH), 131.6 (C), 131.2 (C), 128.5 (2 x CH), 128.3 (2 x CH), 127.4 (CH), 127.0 (CH), 126.9 (CH), 58.6 (CH), 52.6 (CH_3), 52.2 (CH_3), 45.7 (CH), 31.0 (CH_2), 26.8 (CH_2); HRMS (ESI-TOF) *m/z*: $[M + NH_4]^+$ Calcd for $C_{24}H_{25}ClNO_6$ 458.1370; Found 458.1367.

3-Benzyl-2-chloro-6-methoxynaphthalene-1,4-dione (**4aa**): Prepared by following the procedure **C** and purified by column chromatography using EtOAc/hexane (0.2:9.8 to 0.5:9.5) and isolated as yellow solid. Yield: 89% (84 mg). MP: 140-142 °C. IR (Neat): ν_{max} 2968, 1738, 1672, 1583, 1454, 1352, 1228, 1071, 816 and 692 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ 8.05 (1H, d, *J* = 8.5 Hz), 7.50 (1H, d, *J* = 3.0 Hz), 7.33 (2H, d, *J* = 7.5 Hz), 7.25 (2H, t, *J* = 7.5 Hz), 7.19-7.14 (2H, m), 4.13 (2H, s), 3.91 (3H, s); $^{13}C\{^1H\}$ NMR ($CDCl_3$, DEPT-135, 100 MHz): δ 182.5 (C, *C*=O), 176.9 (C, *C*=O), 164.4 (C), 145.9 (C), 144.1 (C), 136.8 (C), 133.7 (C), 129.7 (CH), 129.1 (2 x CH), 128.6 (2 x CH), 126.8 (CH), 124.7 (C), 120.5 (CH), 110.5 (CH), 55.9 (CH_3), 33.9 (CH_2); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{18}H_{14}ClO_3$ 313.0631; Found 313.0636.



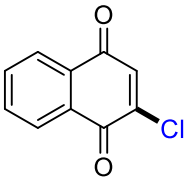
4aa

2-Benzyl-3,6-dichloronaphthalene-1,4-dione (**4bb**): Prepared by following the procedure **C** and purified by column chromatography using EtOAc/hexane (0.2:9.8 to 0.5:9.5) and isolated as yellow solid. Yield: 99% (94 mg). MP: 145-147 °C. IR (Neat): ν_{max} 2921, 1671, 1585, 1276, 1151, 952 and 729 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ 8.10 (1H, br s), 8.05 (1H, dd, *J* = 8.0, 0.5 Hz), 7.70 (1H, qd, *J* = 7.0, 1.0 Hz), 7.36 (2H, d, *J* = 7.5 Hz), 7.28 (2H, t, *J* = 7.0 Hz), 7.21 (1H, t, *J* = 8.0 Hz), 4.17 (2H, s); $^{13}C\{^1H\}$ NMR ($CDCl_3$, DEPT-135, 125 MHz): δ 181.4 (C, *C*=O), 177.0 (C, *C*=O), 146.7 (C), 143.5 (C), 141.1 (C), 136.4 (C), 134.3 (CH), 132.4 (C), 129.8 (C), 129.2 (2 x CH), 128.8 (CH), 128.7 (2 x CH), 127.1 (CH), 127.0 (CH), 33.9 (CH_2); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{17}H_{11}Cl_2O_2$ 317.0136; Found 317.0133.



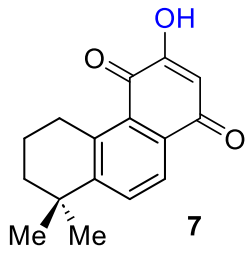
4bb

2-Chloronaphthalene-1,4-dione (4cc): Prepared by following the procedure **C** and purified by column chromatography using EtOAc/hexane (0.2:9.8 to 0.5:9.5) and isolated as yellow solid. Yield: 97% (60 mg). MP: 125-130 ºC. IR (Neat): ν_{max} 3047, 1738, 1660, 1573, 1367, 1294, 1216, 1117, 857 and 779 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ 8.19-8.15 (1H, m), 8.11-8.07 (1H, m), 7.81-7.76 (2H, m), 7.22 (1H, s); $^{13}C\{^1H\}$ NMR ($CDCl_3$, DEPT-135, 125 MHz): δ 182.6 (C, *C*=O), 177.9 (C, *C*=O), 146.3 (C), 135.9 (CH), 134.5 (CH), 134.1 (CH), 131.7 (C), 131.3 (C), 127.5 (CH), 126.7 (CH); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{10}H_6ClO_2$ 193.0056; Found 193.0049.



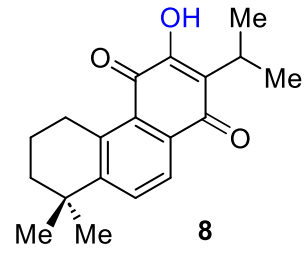
4cc

3-Hydroxy-8,8-dimethyl-5,6,7,8-tetrahydrophenanthrene-1,4-dione (**7**): Prepared by following the procedure **G** and purified by column chromatography using EtOAc/hexane (0.6:9.4 to 0.8:9.2) and isolated as yellow solid. Yield: 31% (200 mg). MP: 161-163 ºC. IR (Neat): ν_{max} 3361, 2924, 1650, 1566, 1374, 1204 and 845 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ 8.00 (1H, d, *J* = 8.5 Hz), 7.78 (1H, d, *J* = 8.0 Hz), 7.65 (1H, s, O*H*), 6.27 (1H, s, olefinic-*H*), 3.27 (2H, t, *J* = 6.5 Hz), 1.88-1.83 (2H, m), 1.70-1.68 (2H, m), 1.33 (6H, s, 2 x CH_3); $^{13}C\{^1H\}$ NMR ($CDCl_3$, DEPT-135, 125 MHz): δ 185.1 (C, *C*=O), 183.4 (C, *C*=O), 156.8 (C), 153.1 (C), 141.4 (C), 133.8 (CH), 132.6 (C), 126.6 (C), 124.8 (CH), 108.3 (CH), 37.7 (CH_2), 34.9 (C), 31.8 (2 x CH_3), 30.0 (CH_2), 19.1 (CH_2); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{16}H_{17}O_3$ 257.1178; Found 257.1178.



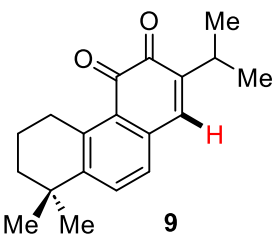
7

3-Hydroxy-2-isopropyl-8,8-dimethyl-5,6,7,8-tetrahydrophenanthrene-1,4-dione [**Deoxyneocryptotanshinone 8**]: Prepared by following the procedure **H** and purified by column chromatography using EtOAc/hexane (0.2:9.8 to 0.5:9.5) and isolated as yellow solid. Yield: 45% (27 mg). MP: 110-112 ºC. IR (Neat): ν_{max} 3346, 2929, 1642, 1564, 1377, 1288, 1198, 985 and 797 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ 8.00 (1H, d, *J* = 8.0 Hz), 7.73 (1H, d, *J* = 8.0 Hz, and 1H, s, O*H*), 3.36 (1H, septet, *J* = 7.0 Hz), 3.26 (2H, t, *J* = 6.5 Hz), 1.86-1.81 (2H, m), 1.68-1.66 (2H, m), 1.32 (6H, s, 2 x CH_3), 1.29 (6H, d, *J* = 7.0 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$, DEPT-135, 125 MHz): δ 184.6 (C, *C*=O), 183.4 (C, *C*=O), 153.2 (C), 152.5 (C), 140.6 (C), 133.3 (CH), 132.7 (C), 126.4 (C), 126.1 (C), 125.0 (CH), 37.7 (CH_2), 34.8 (C), 31.8 (2 x CH_3), 29.9 (CH_2), 24.4 (CH), 19.8 (2 x CH_3), 19.1 (CH_2); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{19}H_{23}O_3$ 299.1647; Found 299.1649.



8

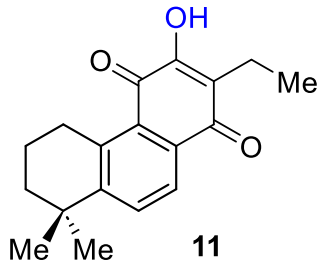
2-Isopropyl-8,8-dimethyl-5,6,7,8-tetrahydrophenanthrene-3,4-dione [**Miltirone 9**]: Prepared by following the procedure **I** and purified by column chromatography using EtOAc/hexane (0.2:9.8 to 0.5:9.5) and isolated as orange solid. Yield: 53% (30 mg). MP: 99-101 ºC. IR (Neat): ν_{max} 2923, 1655, 1460, 1260, 1173, 941 and 808 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ 7.59 (1H, d, *J* = 8.0 Hz), 7.10 (1H, d, *J* = 8.0 Hz), 7.07 (1H, s, olefinic-*H*), 3.18 (2H, t, *J* = 6.5 Hz), 3.02 (1H, septet, *J* = 7.0 Hz), 1.82-1.77 (2H, m), 1.66-1.64 (2H, m), 1.30 (6H, s, 2 x CH_3), 1.16 (6H, d, *J* = 7.0 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$, DEPT-135, 125 MHz): δ 182.4 (C, *C*=O), 181.6 (C, *C*=O), 149.7 (C), 145.1 (C), 144.5 (C),



9

139.8 (CH), 134.4 (C), 133.7 (CH), 128.3 (C), 127.8 (CH), 37.9 (CH_2), 34.5 (C), 31.8 (2 x CH_3), 29.8 (CH_2), 26.9 (CH), 21.5 (2 x CH_3), 19.1 (CH_2); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{19}H_{23}O_2$ 283.1698; Found 283.1697.

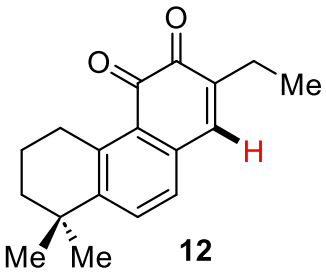
2-Ethyl-3-hydroxy-8,8-dimethyl-5,6,7,8-tetrahydrophenanthrene-1,4-dione (**11**): Prepared



11

by following the procedure **J** and purified by column chromatography using EtOAc/hexane (0.2:9.8 to 0.5:9.5) and isolated as orange semi-solid. Yield: 62% (34 mg). IR (Neat): ν_{max} 3359, 2930, 1643, 1564, 1377, 1329, 1263, 1195, 1097, 980 and 755 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ 8.00 (1H, d, *J* = 8.5 Hz), 7.73 (1H, d, *J* = 8.5 Hz), 7.62 (1H, s, OH), 3.26 (2H, t, *J* = 6.5 Hz), 2.59-2.55 (2H, m), 1.85-1.80 (2H, m), 1.68-1.66 (2H, m), 1.31 (6H, s), 1.12 (3H, t, *J* = 7.5 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$, DEPT-135, 125 MHz): δ 184.7 (C, *C*=O), 183.1 (C, *C*=O), 153.2 (C), 152.7 (C), 140.8 (C), 133.2 (CH), 132.5 (C), 126.5 (C), 124.8 (CH), 123.2 (C), 37.7 (CH_2), 34.8 (C), 31.8 (2 x CH_3), 29.9 (CH_2), 19.1 (CH_2), 16.5 (CH_2), 12.6 (CH_3); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{18}H_{21}O_3$ 285.1491; Found 285.1491.

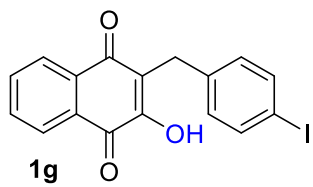
2-Ethyl-8,8-dimethyl-5,6,7,8-tetrahydrophenanthrene-3,4-dione (**12**): Prepared by



12

following the procedure **K** and purified by column chromatography using EtOAc/hexane (0.2:9.8 to 0.5:9.5) and isolated as orange semi-solid. Yield: 68% (20 mg). IR (Neat): ν_{max} 2927, 1656, 1457, 1259, 1143 and 905 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ 7.58 (1H, d, *J* = 8.0 Hz), 7.08 (2H, d, *J* = 7.5 Hz), 3.17 (2H, t, *J* = 6.5 Hz), 2.46-2.41 (2H, m), 1.82-1.77 (2H, m), 1.66-1.63 (2H, m), 1.29 (6H, s), 1.15 (3H, t, *J* =7.5 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$, DEPT-135, 125 MHz): δ 182.2 (C, *C*=O), 181.8 (C, *C*=O), 149.6 (C), 144.6 (C), 141.4 (CH), 140.6 (C), 134.4 (C), 133.7 (CH), 128.3 (C), 127.7 (CH), 37.8 (CH_2), 34.5 (C), 31.7 (2 x CH_3), 29.9 (CH_2), 22.0 (CH_2), 19.0 (CH_2), 12.4 (CH_3); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{18}H_{21}O_2$ 269.1542; Found 269.1541.

2-Hydroxy-3-(4-iodobenzyl)naphthalene-1,4-dione (**1g**): Prepared by following the

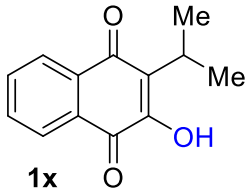


1g

procedure **D** and purified by column chromatography using EtOAc/hexane (0.2:9.8 to 0.5:9.5) and isolated as yellow solid. Yield: 90% (105 mg). MP: 193-195 ºC. IR (Neat): ν_{max} 3379, 1633, 1592, 1365, 1274, 1226, 1043 and 726 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ 8.10 (1H, dd, *J* = 7.5, 1.0 Hz), 8.07 (1H, d, *J* = 7.5, 1.0 Hz), 7.75 (1H, dt, *J* = 7.5, 1.0

Hz), 7.67 (1H, dt, *J* = 7.5, 1.0 Hz), 7.57 (2H, br d, *J* = 7.5 Hz), 7.14 (2H, br d, *J* = 7.5 Hz), 3.87 (2H, s); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, DEPT-135, 100 MHz): δ 184.2 (C, *C*=O), 181.5 (C, *C*=O), 153.1 (C), 138.5 (C), 137.5 (2 x CH), 135.1 (CH), 133.1 (CH), 132.7 (C), 131.3 (2 x CH), 129.3 (C), 126.9 (CH), 126.2 (CH), 122.4 (C), 91.6 (C), 28.6 (CH_2); HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ Calcd for $C_{17}H_{12}IO_3$ 390.9831; Found 390.9833.

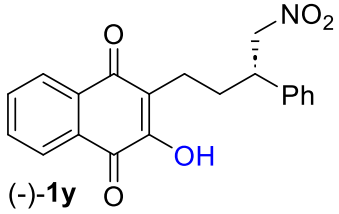
2-Hydroxy-3-isopropylnaphthalene-1,4-dione (**1x**): Prepared by following the procedure **F**



1x

and purified by column chromatography using EtOAc/hexane (0.2:9.8 to 0.5:9.5) and isolated as yellow solid. Yield: 40% (26 mg). MP: 101-103 ºC. IR (Neat): ν_{max} 3367, 2923, 1644, 1586, 1359, 1259, 1009, 793 and 662 cm^{-1}. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.11 (1H, dd, *J* = 7.5 Hz, 1.0 Hz), 8.06 (1H, dd, *J* = 7.5, 1.0 Hz), 7.74 (1H, dt, *J* = 7.5, 1.5 Hz), 7.66 (1H, dt, *J* = 7.5, 1.0 Hz), 7.42 (1H, s, O*H*), 3.42 (1H, septet, *J* = 7.0 Hz), 1.31 (6H, d, *J* = 7.0 Hz); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, DEPT-135, 100 MHz): δ 184.4 (C, *C*=O), 181.9 (C, *C*=O), 152.7 (C), 134.9 (CH), 133.2 (C), 132.7 (CH), 129.2 (C), 128.8 (C), 126.9 (CH), 125.9 (CH), 24.6 (CH), 19.8 (2 x CH_3); HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ Calcd for $C_{13}H_{13}O_3$ 217.0865; Found 217.0868.

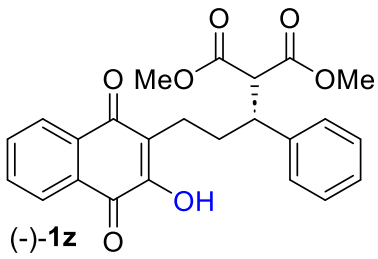
(*S*)-2-Hydroxy-3-(4-nitro-3-phenylbutyl)naphthalene-1,4-dione (**1y**): Prepared by



(-)-**1y**

following the procedure **D** and purified by column chromatography using EtOAc/hexane (2.0:8.0 to 3.0:7.0) and isolated as yellow solid. Yield: 95% (100 mg). MP: 130-132 ºC. $[\alpha]_D^{25}$ = -19.5° [*c* = 0.1, $CHCl_3$]; IR (Neat): ν_{max} 3338, 1640, 1544, 1371, 1272, 1214, 1004 and 728 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.08 (1H, dd, *J* = 7.5, 1.0 Hz), 8.05 (1H, dd, *J* = 7.5, 1.0 Hz), 7.75 (1H, dt, *J* = 7.5, 1.0 Hz), 7.67 (1H, dt, *J* = 7.5, 1.5 Hz), 7.32-7.28 (3H, m), 7.25-7.18 (3H, m), 4.65-4.61 (1H, m), 4.57-4.53 (1H, m), 3.57-3.51 (1H, m), 2.60-2.49 (2H, m), 2.10-2.02 (1H, m), 1.97-1.90 (1H, m); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, DEPT-135, 100 MHz): δ 184.5 (C, *C*=O), 181.1 (C, *C*=O), 153.1 (C), 138.9 (C), 135.0 (CH), 133.0 (CH), 132.8 (C), 129.3 (C), 128.9 (2 x CH), 127.8 (CH), 127.6 (2 x CH), 126.8 (CH), 126.2 (CH), 122.9 (C), 80.9 (CH_2), 44.4 (CH), 30.8 (CH_2), 21.2 (CH_2); HRMS (ESI-TOF) *m*/*z*: $[M + Na]^+$ Calcd for $C_{20}H_{17}NO_5Na$ 374.1004; Found 374.1009.

Diethyl (*R*)-2-(3-(3-hydroxy-1,4-dioxo-1,4-dihydronaphthalen-2-yl)-1-phenylpropyl)malonate (**1z**): Prepared by following the procedure **D** and purified by column chromatography using EtOAc/hexane (2.0:8.0 to 3.0:7.0) and isolated as yellow solid. Yield: 95% (120 mg). MP: 140-142 ºC. $[\alpha]_D^{25} = -68^{\circ}$ [*c* = 0.1, $CHCl_3$]; IR (Neat): ν_{max} 2921, 1735, 1264, 1147, 1020, 735 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 8.07 (1H, d, *J* = 7.5 Hz), 8.03 (1H, d, *J* = 7.5 Hz), 7.73 (1H, t, *J* = 7.5 Hz), 7.66 (1H, m, *J* = 7.5 Hz), 7.30-7.23 (4H, m), 7.19-7.15 (2H, m), 3.74 (3H, s), 3.66 (1H, d, *J* = 10.5 Hz), 3.47-3.45 (1H, m), 3.43 (3H, s), 2.52-2.46 (1H, m), 2.42-2.37 (1H, m), 2.08-2.00 (1H, m), 1.96-1.90 (1H, m); $^{13}C\{^1H\}$ NMR ($CDCl_3$, DEPT-135, 125 MHz): δ 184.3 (C, *C*=O), 181.2 (C, *C*=O), 168.4 (C, O-*C*=O), 168.1 (C, O-*C*=O), 152.9 (C), 146.8 (C), 140.1 (C), 134.8 (CH), 132.9 (C), 132.8 (CH), 128.3 (4 x CH), 127.1 (CH), 126.6 (CH), 126.0 (CH), 123.6 (C), 58.8 (CH), 52.5 (CH_3), 52.2 (CH_3), 45.8 (CH), 31.4 (CH_2), 21.5 (CH_2); HRMS (ESI-TOF) *m*/*z*: $[M + Na]^+$ Calcd for $C_{24}H_{22}O_7Na$ 445.1263; Found 445.1262.



2-Iodonaphthalene-1,4-dione (**21cc**):[6] Prepared by using literature procedure and purified by column chromatography using EtOAc/hexane (0.2:9.8 to 0.5:9.5) and isolated as orange solid. Yield: 35% (630 mg). MP.: 108-110 ºC. IR (Neat): ν_{max} 3040, 1647, 1584, 1560, 1293, 1243, 1113, 1054, 907, 773, 687 and 663 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 8.17 (1H, dd, *J* = 7.5, 2.0 Hz), 8.08 (1H, dd, *J* = 7.25, 2.0 Hz), 7.90 (1H, s), 7.79 (1H, dt, *J* = 7.5, 1.5 Hz), 7.74 (1H, dt, *J* = 7.5, 1.5 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$, DEPT-135, 100 MHz): δ 182.0 (C, *C*=O), 178.7 (C, *C*=O), 148.4 (CH), 134.3 (CH), 133.9 (CH), 131.7 (C), 129.7 (C), 128.2 (CH), 127.0 (CH), 123.0 (C, *C*-I); HRMS (ESI-TOF) *m*/*z*: $[M + Na]^+$ Calcd for $C_{10}H_5NaIO_2$ 306.9232; Found 306.9232.

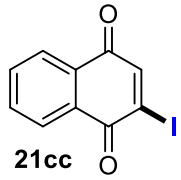


Table S5: Correlation NMR data for the compound **8** (Deoxyneocryptotanshinone):[3]

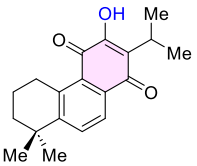
 3-Hydroxy-2-isopropyl-8,8-dimethyl-5,6,7,8-tetrahydrophenanthrene-1,4-dione [Deoxyneocryptotanshinone **8**]		Isolated compound ^{13}C NMR (125 MHz, $CDCl_3$)	Present synthetic compound ^{13}C NMR (125 MHz, $CDCl_3$)
		184.6 (C-14)	184.6 (C, *C*=O)
		183.4 (C-11)	183.4 (C, *C*=O)
Isolated compound ^{1}H NMR (500 MHz, $CDCl_3$)	Present synthetic compound ^{1}H NMR (500 MHz, $CDCl_3$)	153.3 (C-12)	153.2 (C)
		152.5 (C-10)	152.5 (C)
7.97 (1H, d, *J* = 8.2 Hz)	8.00 (1H, d, *J* = 8.0 Hz)	140.7 (C-4)	140.6 (C)
		133.4 (C-6)	133.3 (CH)
7.82 (1H, s, *OH*)	7.73 (1H, d, *J* = 8.0 Hz) and	132.8 (C-8)	132.7 (C)
7.71 (1H, d, *J* = 8.2 Hz)	7.73 (1H, s, *OH*)	126.5 (C-9)	126.4 (C)
3.37 (1H, septet, *J* = 6.5 Hz)	3.36 (1H, septet, *J* = 7.0 Hz)	125.1 (C-7)	126.1 (C)
		123.8 (C-13)	125.0 (CH)
3.20 (2H, t, *J* = 6.4 Hz)	3.26 (2H, t, *J* = 6.5 Hz)	37.8 (C-3)	37.7 (CH_2)
1.79 (4H, m)	1.86-1.81 (2H, m)	- (C-5)	34.8 (C)
	1.68-1.66 (2H, m)	31.8 (C-18 and C-19)	31.8 (2 x CH_3)
1.30 (6H, s)	1.32 (6H, s)	30.0 (C-1)	29.9 (CH_2)
1.29 (6H, d, *J* = 7.0 Hz)	1.29 (6H, d, *J* = 7.0 Hz)	24.5 (C-15)	24.4 (CH)
		19.9 (C-16 and C-17)	19.8 (2 x CH_3)
		19.2 (C-2)	19.1 (CH_2)

Table S6: Correlation NMR data for the compound **9** (Miltirone):[4]

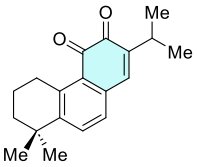
 2-Isopropyl-8,8-dimethyl-5,6,7,8-tetrahydrophenanthrene-3,4-dione [Miltirone **9**]		Isolated compound ^{13}C NMR (100 MHz, $CDCl_3$)	Present synthetic compound ^{13}C NMR (125 MHz, $CDCl_3$)
		182.3	182.4 (C, *C*=O)
		181.4	181.6 (C, *C*=O)
Isolated compound ^{1}H NMR (400 MHz, $CDCl_3$)	Present synthetic compound ^{1}H NMR (500 MHz, $CDCl_3$)	149.6	149.7 (C)
		144.9	145.1 (C)
7.56 (1H, d, *J* = 7.8 Hz)	7.59 (1H, d, *J* = 8.0 Hz)	144.4	144.5 (C)
7.08 (1H, d, *J* = 7.8 Hz)	7.10 (1H, d, *J* = 8.0 Hz)	139.9	139.8 (CH)
7.05 (1H, s)	7.07 (1H, s, olefinic-*H*)	134.3	134.4 (C)
3.14 (2H, t, *J* = 6.6 Hz)	3.18 (2H, t, *J* = 6.5 Hz)	133.7	133.7 (CH)
2.98 (1H, septet, *J* = 6.9 Hz)	3.02 (1H, septet, *J* = 7.0 Hz)	128.1	128.3 (C)
1.75 (2H, m)	1.82-1.77 (2H, m)	127.9	127.8 (CH)
1.61 (2H, m)	1.66-1.64 (2H, m)	37.7	37.9 (CH_2)
1.26 (6H, s)	1.30 (6H, s)	34.4	34.5 (C)
1.13 (6H, d, *J* = 6.9 Hz)	1.16 (6H, d, *J* = 7.0 Hz)	31.7 (2 x C)	31.8 (2 x CH_3)
		29.8	29.8 (CH_2)
		26.8	26.9 (CH)
		21.5 (2 x C)	21.5 (2 x CH_3)
		19.0	19.1 (CH_2)

Table S7: Correlation NMR data for the compound **3s** (Vitamin K_3):[5]

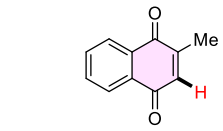
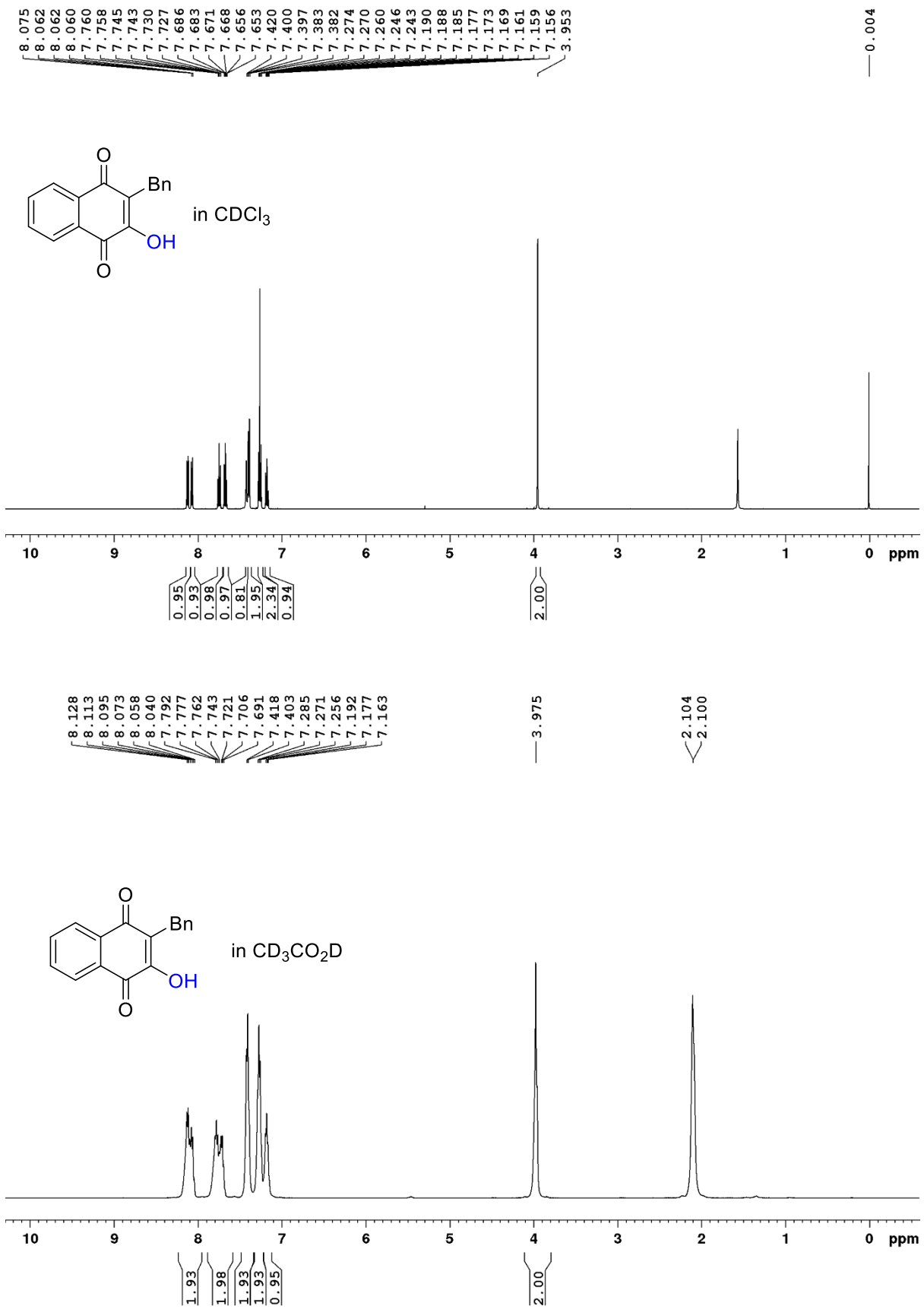
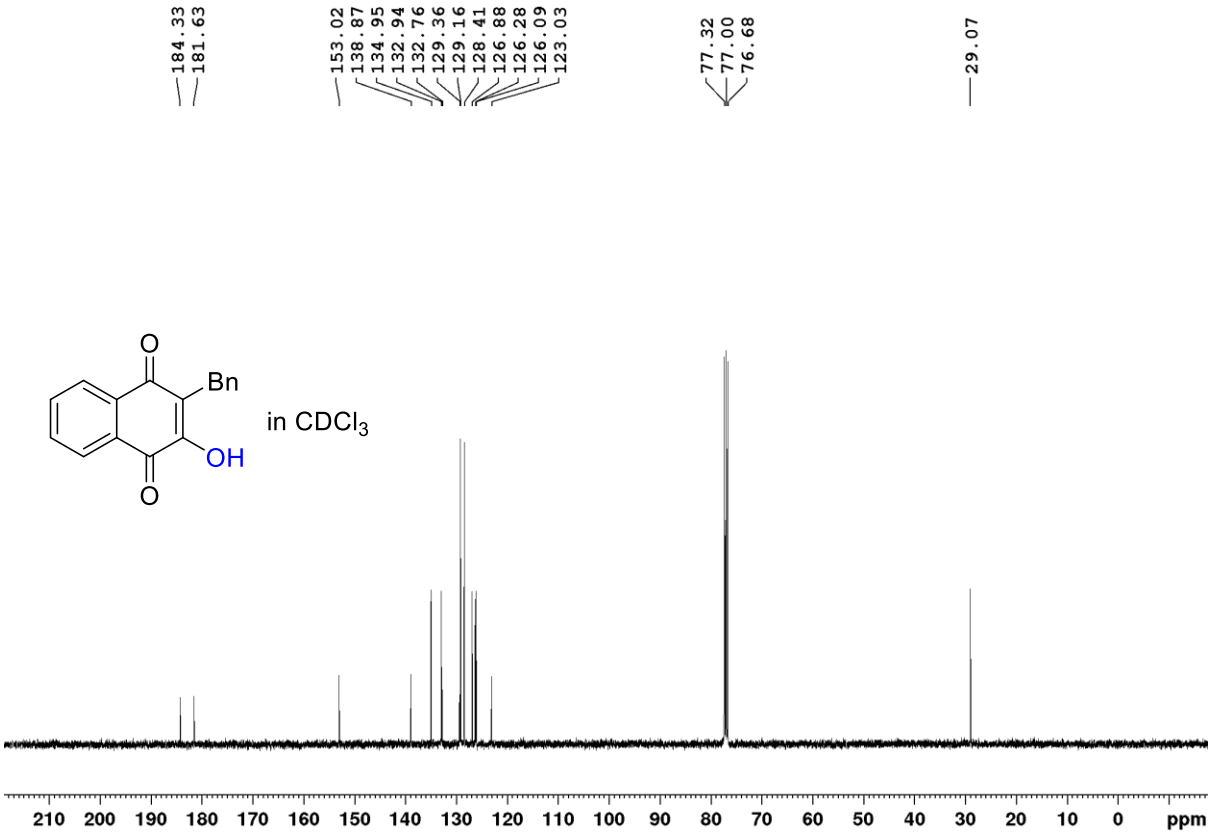
 2-Methylnaphthalene-1,4-dione (**3s**) Vitamin-K_3		Isolated compound ^{13}C NMR (67.9 MHz, $CDCl_3$)	Present synthetic compound ^{13}C NMR (125 MHz, $CDCl_3$)
		185.5	185.5 (C, *C*=O)
		184.9	184.9 (C, *C*=O)
Isolated compound ^{1}H NMR (270 MHz, $CDCl_3$)	Present synthetic compound ^{1}H NMR (500 MHz, $CDCl_3$)	148.2	148.1 (C)
		135.7	135.6 (CH)
8.07 (1H, dd, *J* = 10.4, 5.9 Hz)	8.10-8.07 (1H, m)	133.6	133.6 (CH)
8.06 (1H, dd, *J* = 10.4, 5.61 Hz)	8.06-8.03 (1H, m)	133.5	133.5 (CH)
7.72 (1H, d, *J* = 5.6 Hz)	7.73-7.70 (2H, m)	132.3	132.2 (C)
7.71 (1H, d, *J* = 5.9 Hz)			
6.84 (1H, q, *J* = 1.5 Hz)	6.83 (1H, br s)	132.2	132.1 (C)
2.19 (3H, d, *J* = 1.5 Hz)	2.19 (3H, br s)	126.5	126.5 (CH)
		126.1	126.1 (CH)
		16.4	16.4 (CH_3)

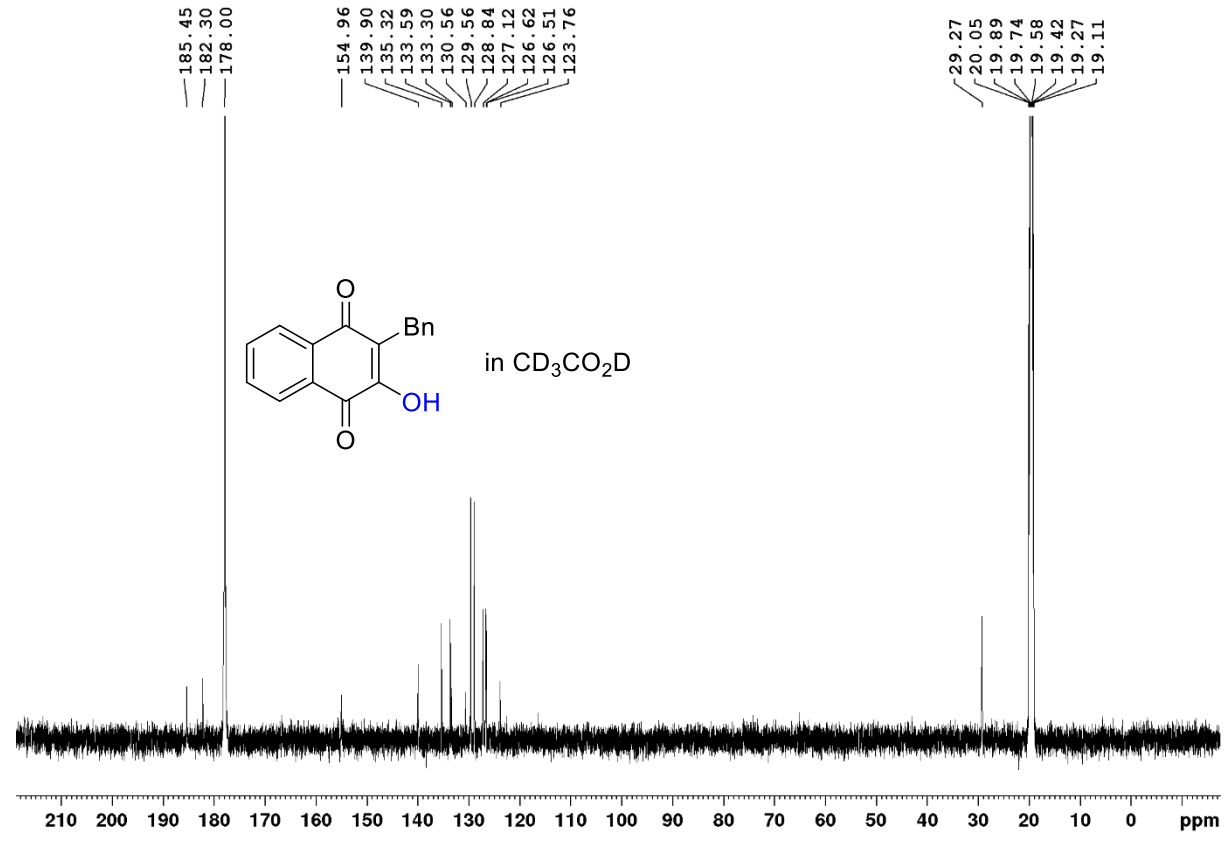
Figure S10: NMR experiment to study the effect of solvent in inducing enol-enol tautomerism of **1a** at 25 ºC. ^{1}H NMR spectra (500 MHz):



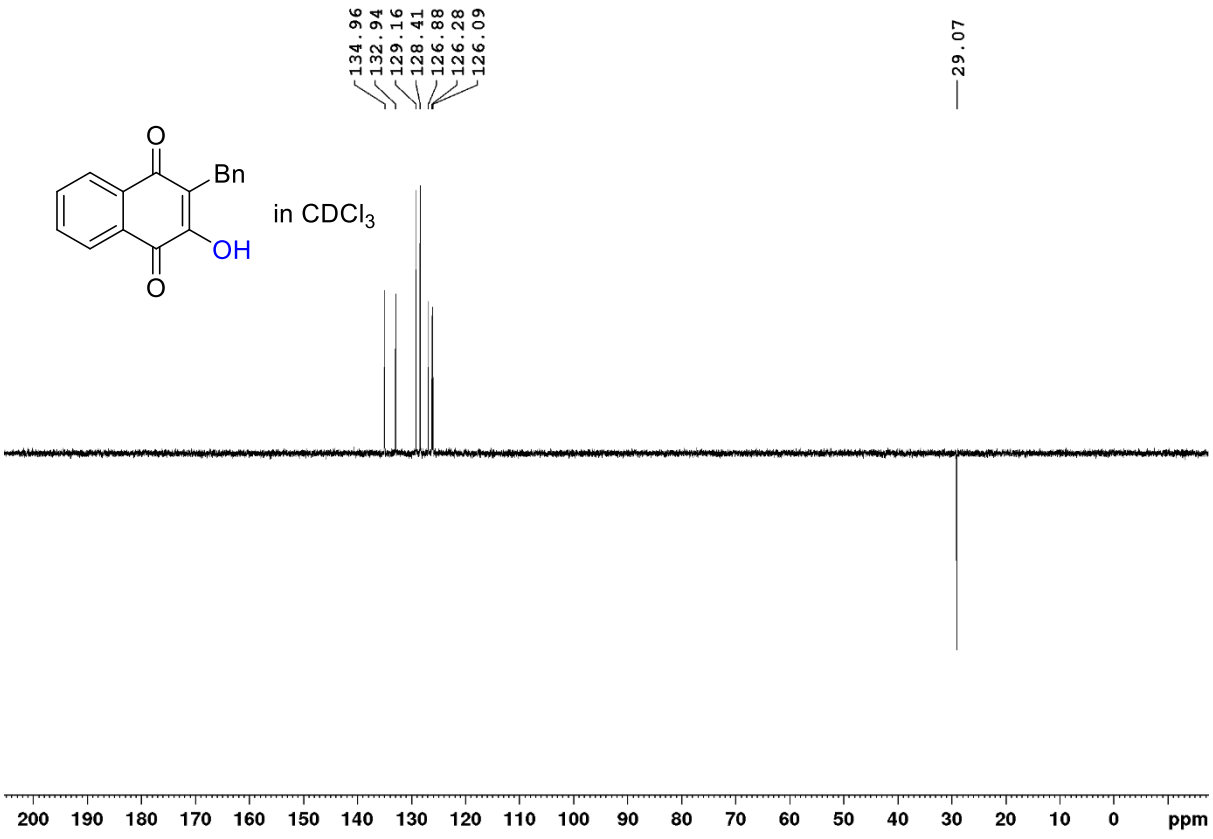
^{13}C NMR spectra (100 MHz):



^{13}C NMR spectra (125 MHz):



DEPT-135 Spectra (100 MHz):



DEPT-135 Spectra (125 MHz):

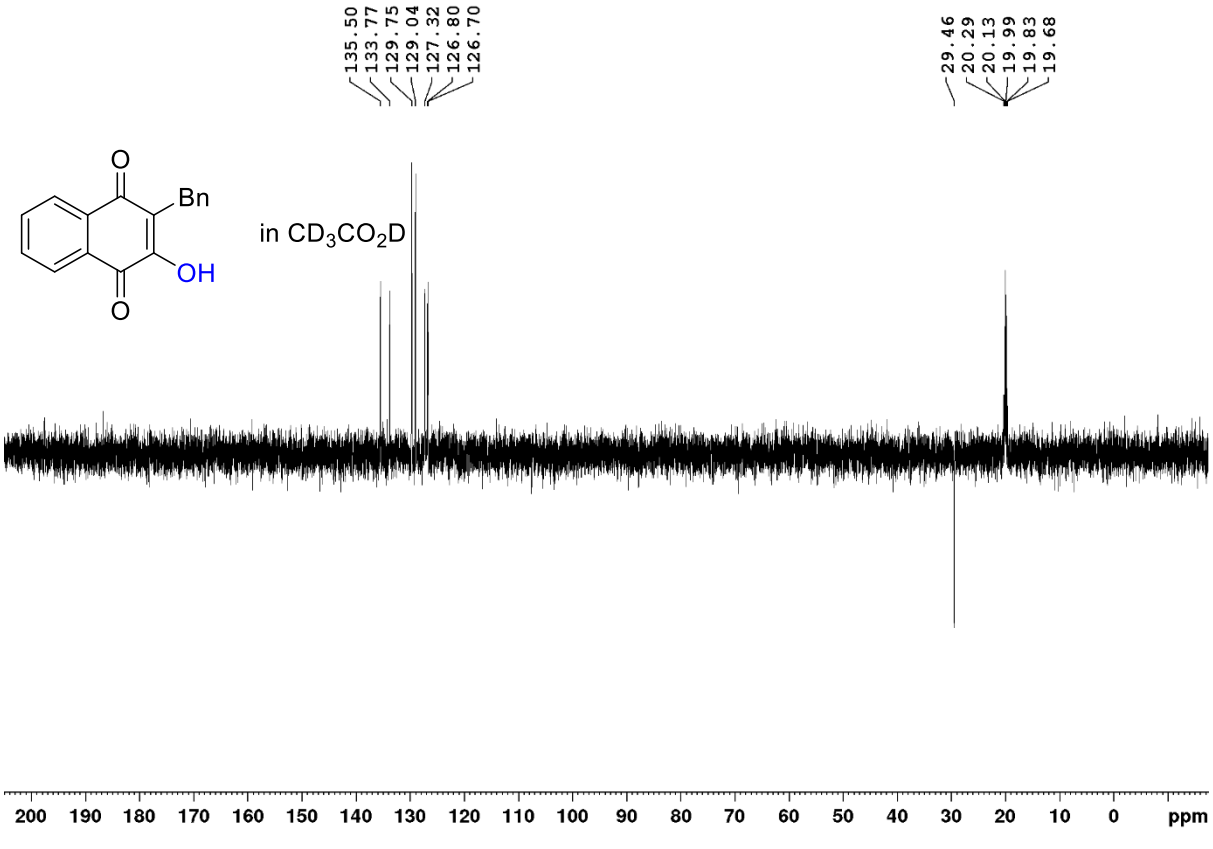
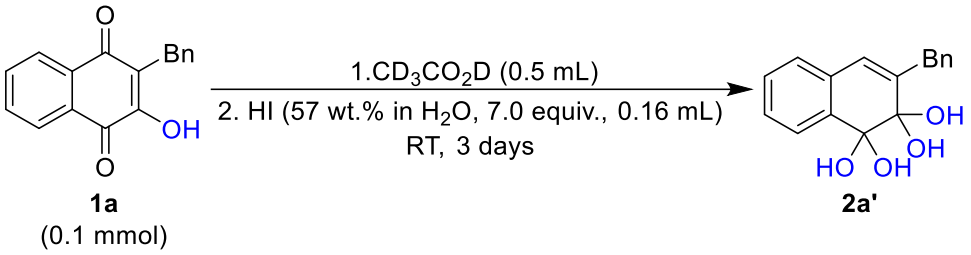
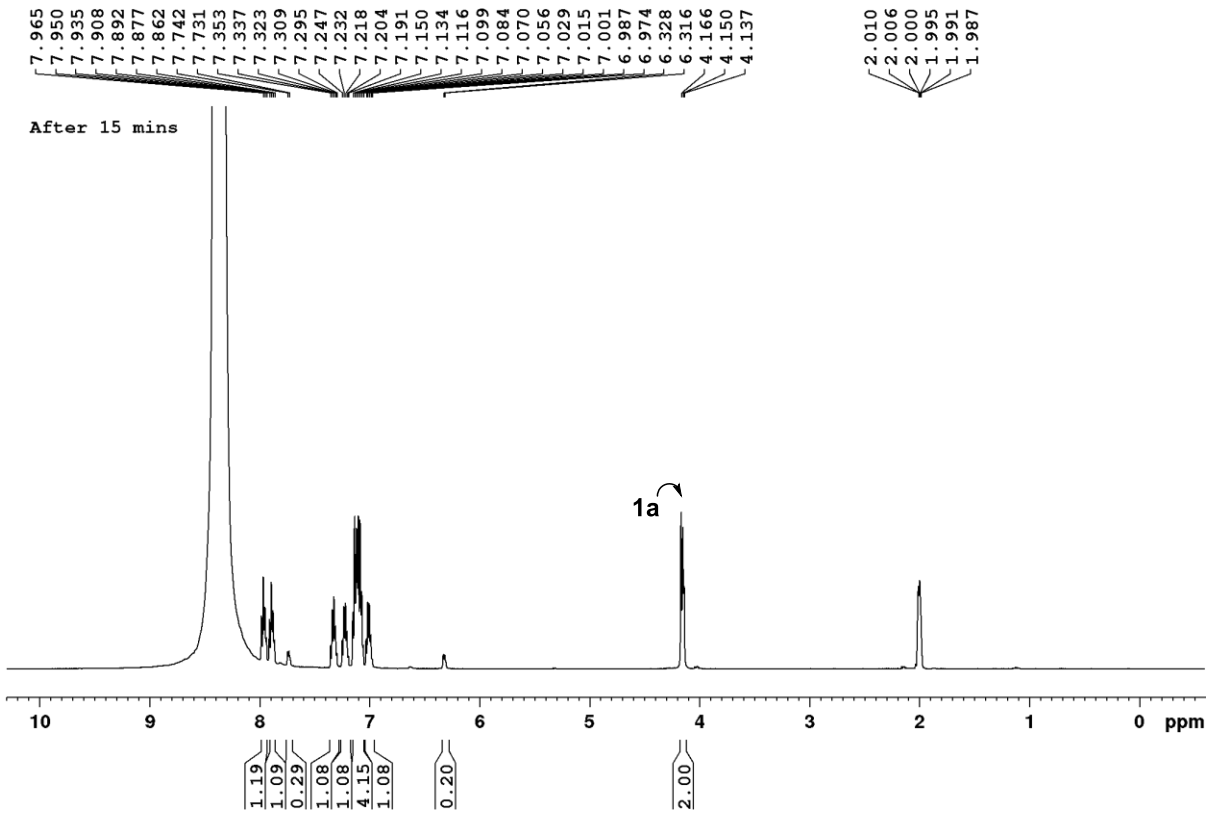


Figure S11: Online experiment to study the role of HI (57 wt.% in H_2O) in HDH reaction of **1a** in CD_3CO_2D at 25 ºC.

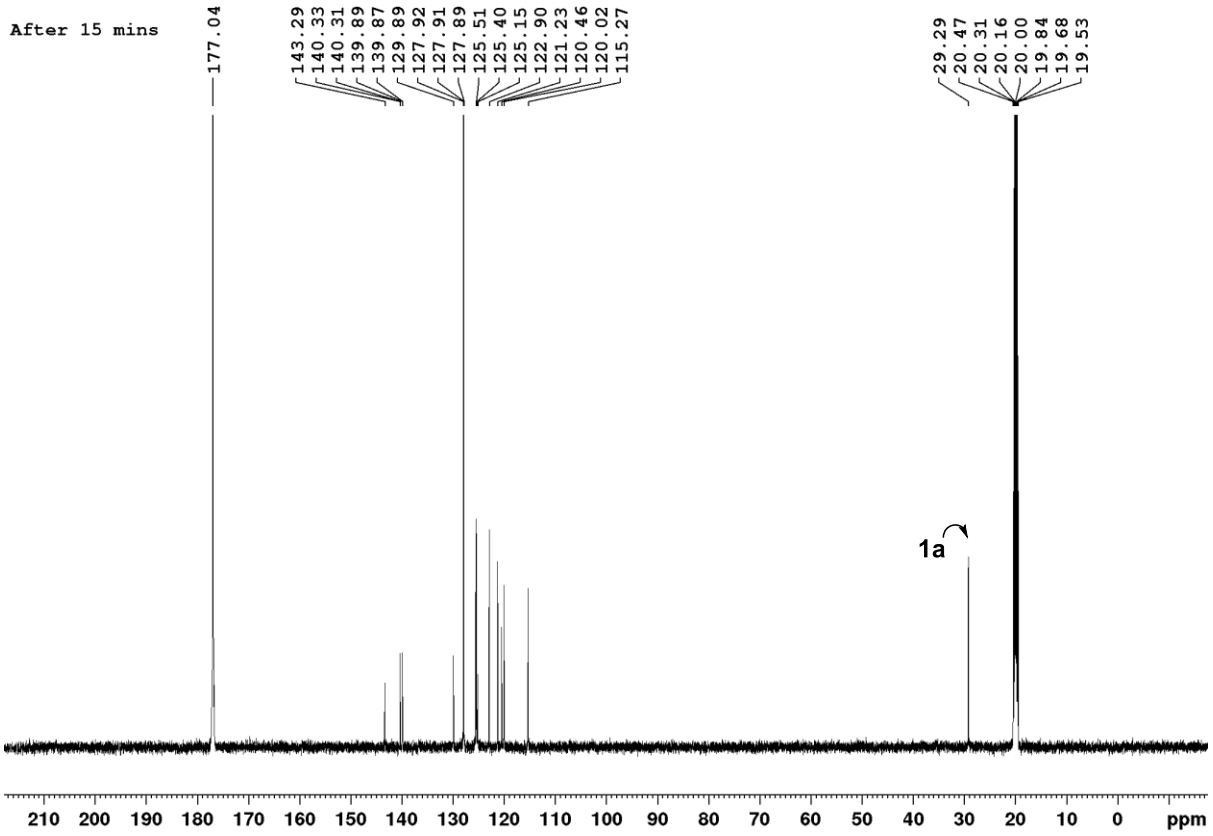


Procedure: For the online NMR experiment to study the effect of aq. HI in HDH reaction of **1a**: The ^1H and ^{13}C NMR spectra of the on-going reactions of **1a** (0.1 mmol) in presence of HI (57 wt.% in H_2O, 7.0 equiv., 0.16 mL) in CD_3CO_2D (0.5 mL) at 25 ºC were reported in Figure S11. Spectra were recorded after 15 minutes, 2 h 15 minutes and 3 days intervals (**spectra-1, 2, 3**) for the reaction course. It was observed that the aq. HI is facilitating the enol-enol tautomerism and in its presence the reactant and product were completely in acetal form.

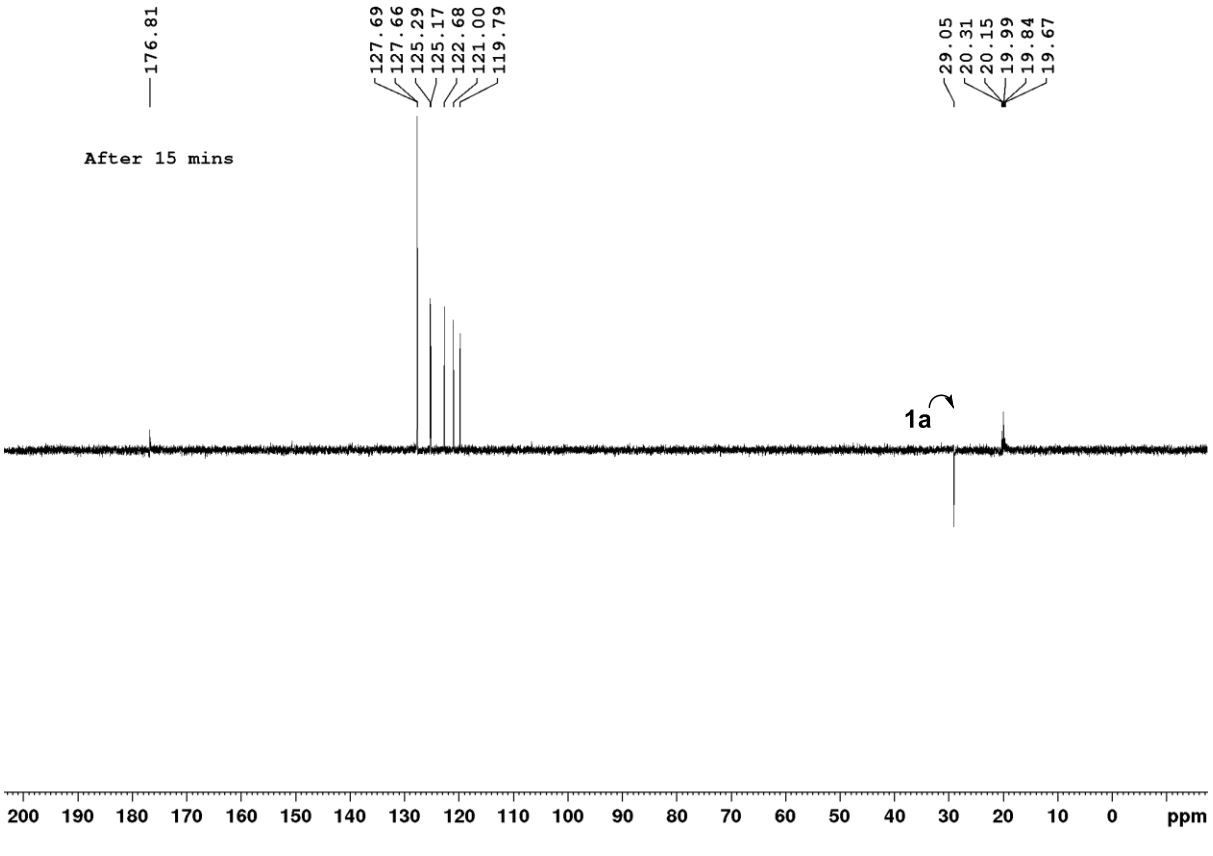
Spectra-1: ^1H NMR (500 MHz, CD_3CO_2D):



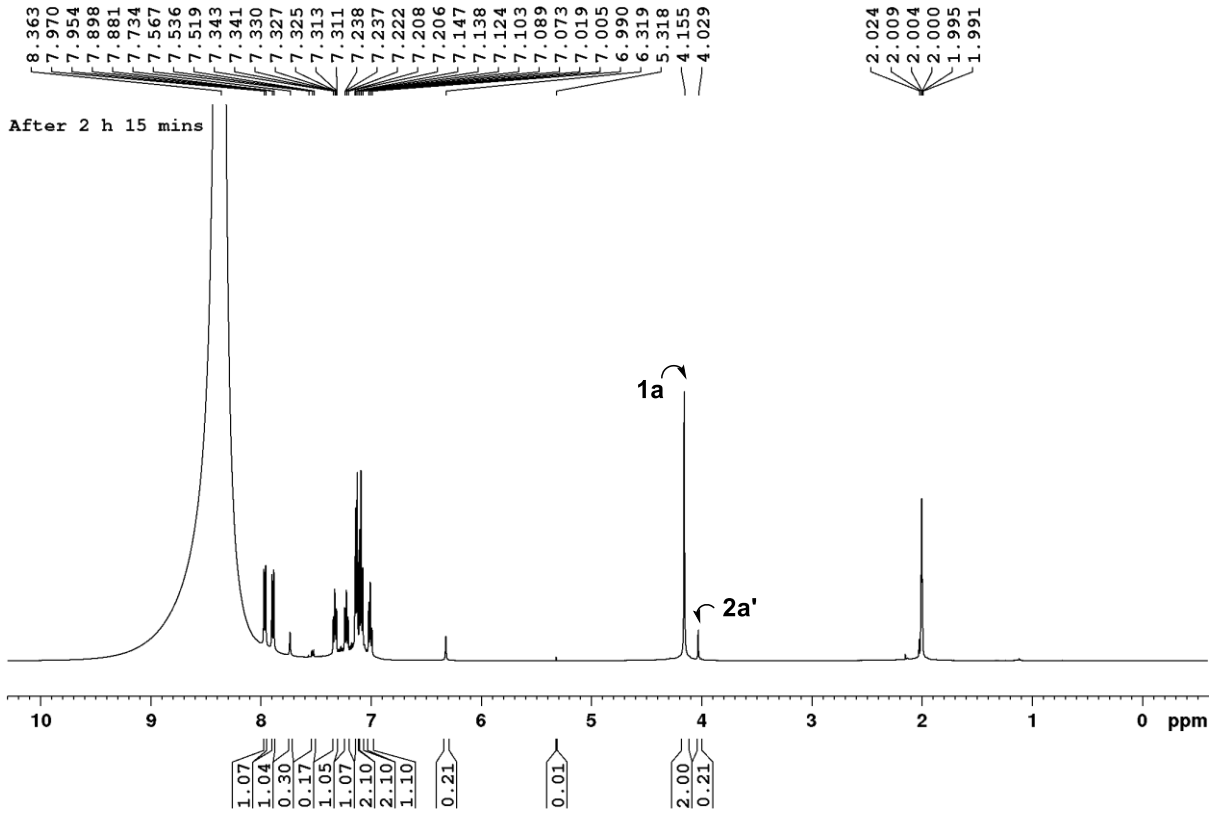
Spectra-1: ^{13}C NMR (125 MHz, CD_3CO_2D):



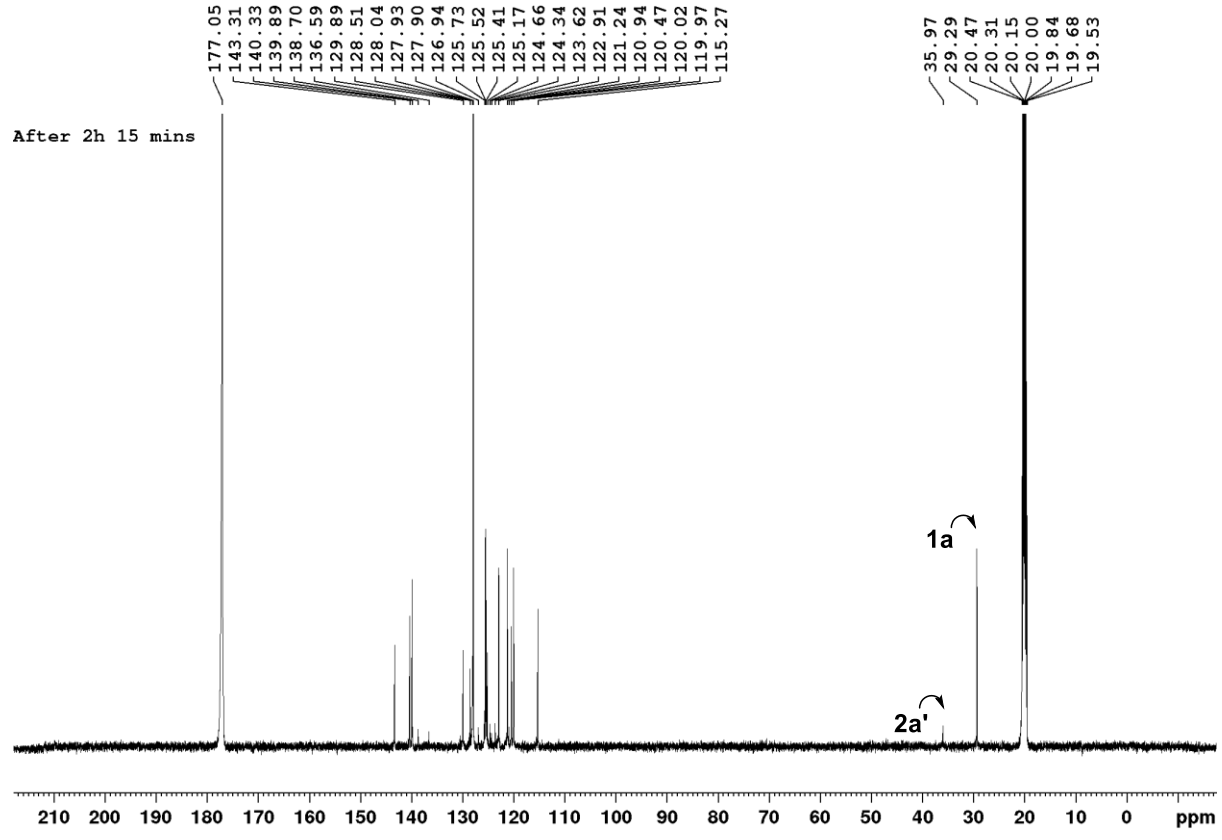
Spectra-1: DEPT-135 (125 MHz, CD_3CO_2D):



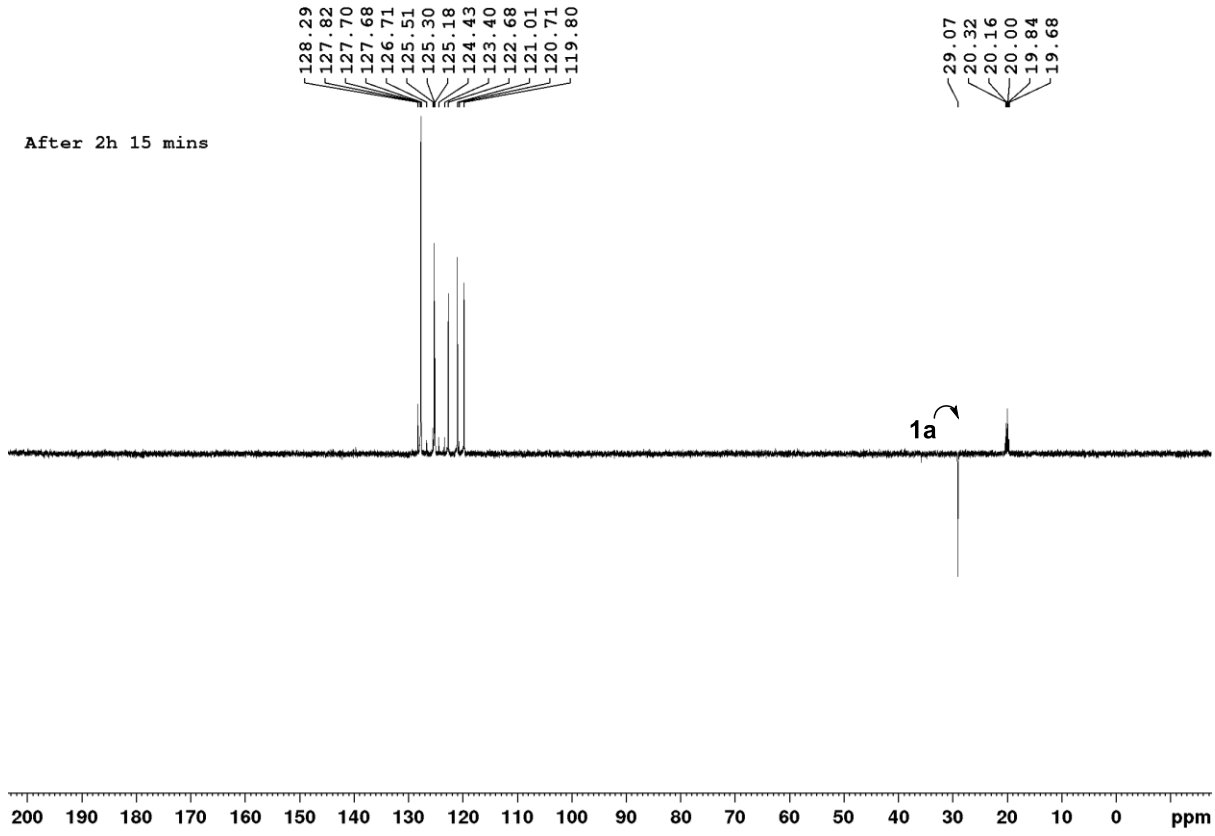
Spectra-2: ^{1}H NMR (500 MHz, CD_3CO_2D):



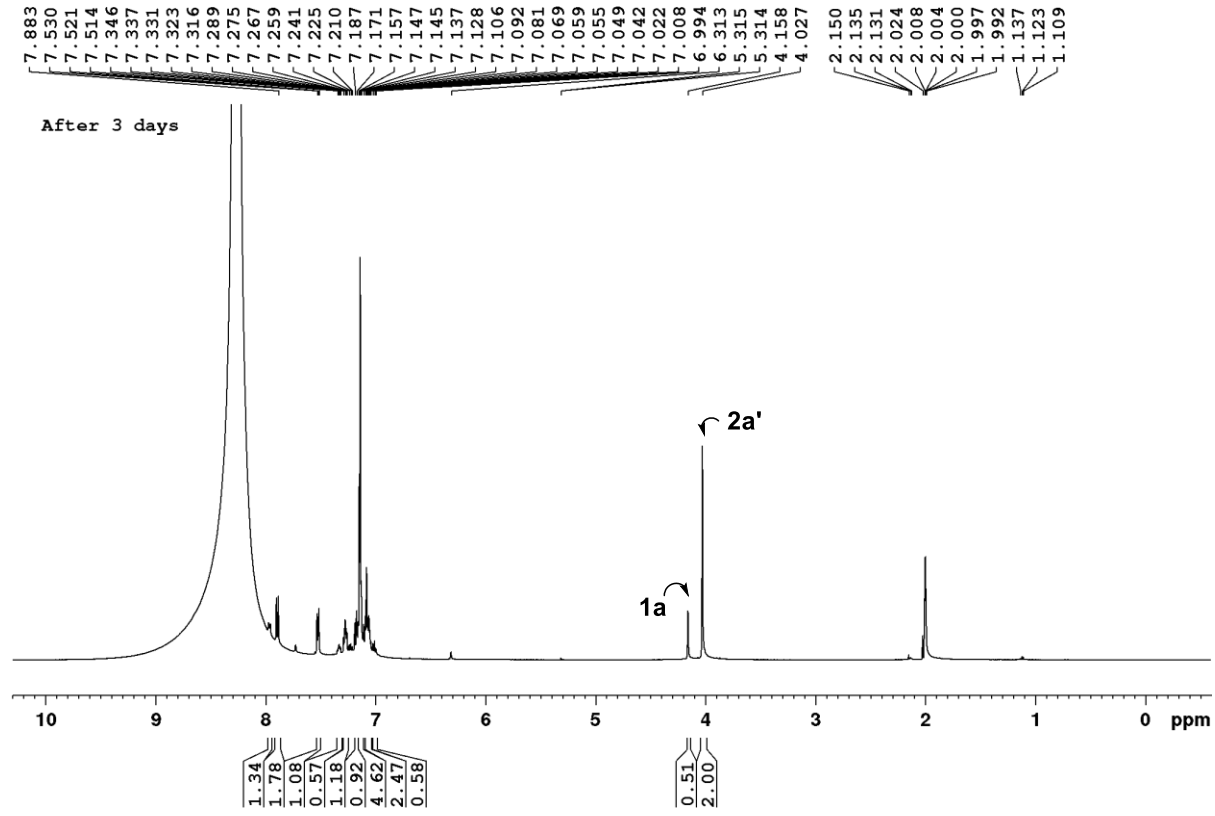
Spectra-2: ^{13}C NMR (125 MHz, CD_3CO_2D):



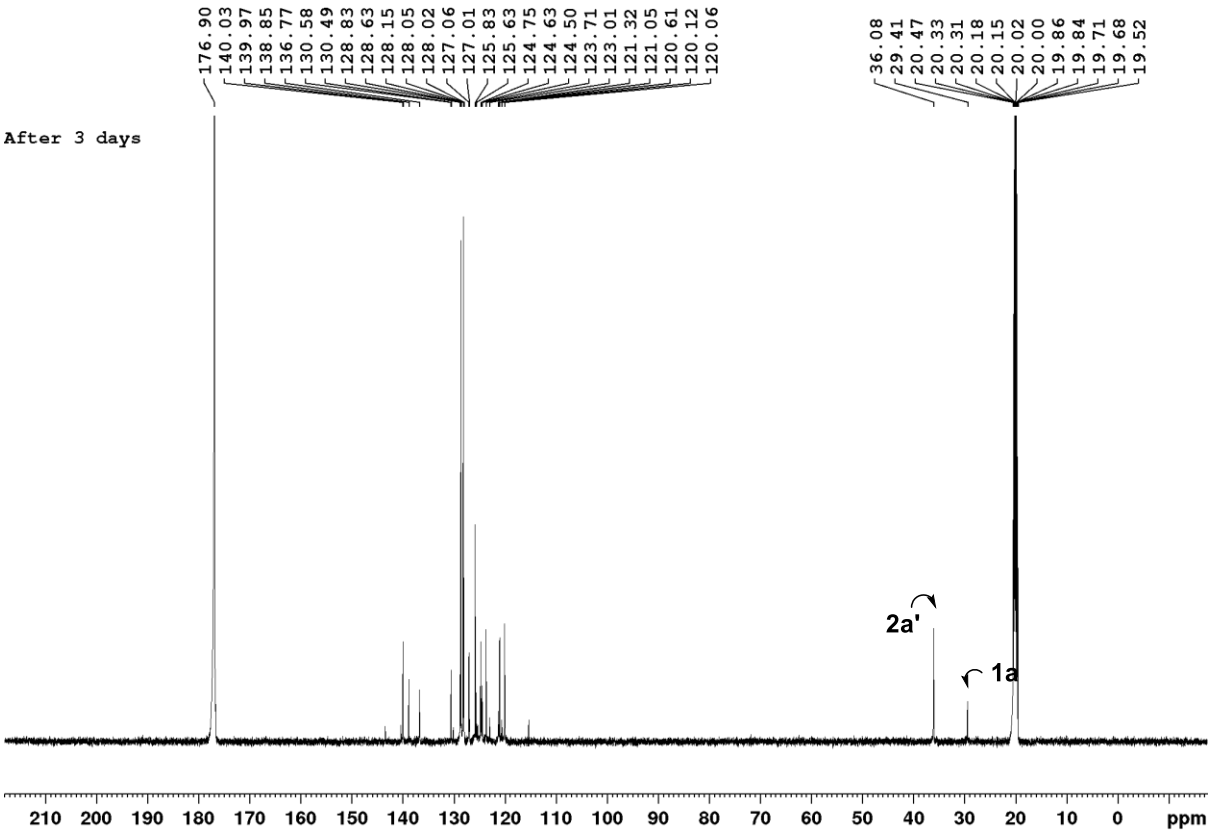
Spectra-2: DEPT-135 (125 MHz, CD_3CO_2D):



Spectra-3: ^1H NMR (500 MHz, CD_3CO_2D):



Spectra-3: ^{13}C NMR (125 MHz, CD_3CO_2D):



Spectra-3: DEPT-135 (125 MHz, CD_3CO_2D):

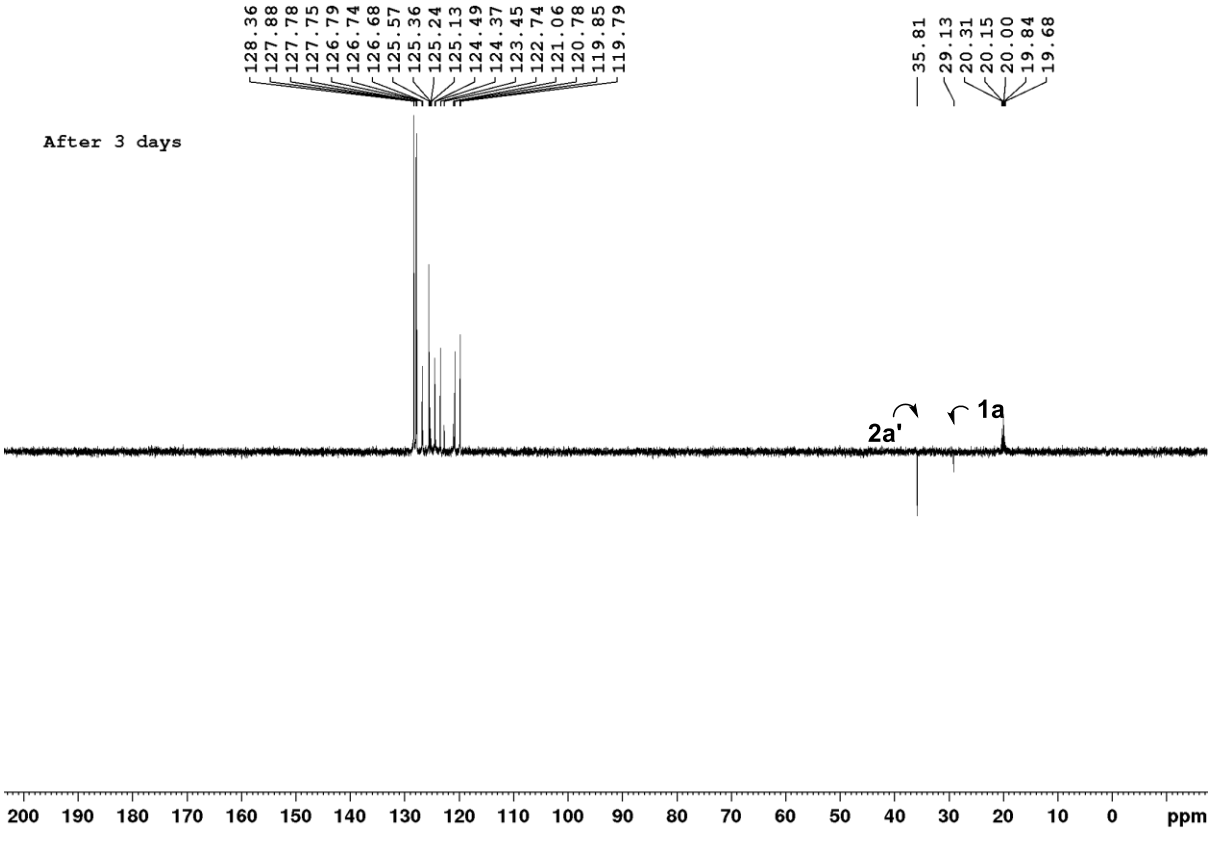
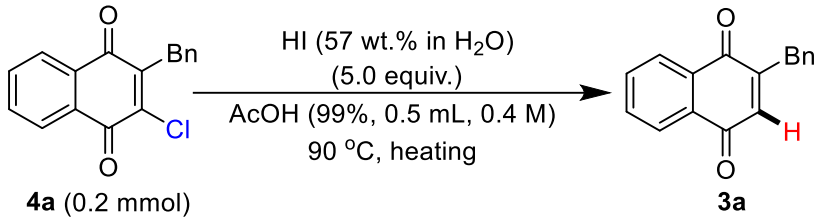
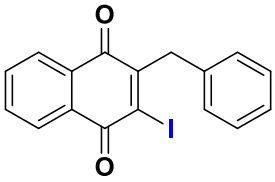


Figure S12: The on-line ESI-HRMS analysis of on-going reaction between **4a** and aq. HI (57 wt.% in H_2O) in AcOH at 90 °C under thermal condition.



4a (0.2 mmol) **3a**

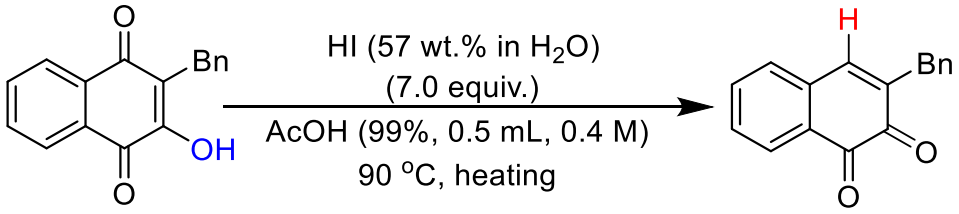
Experimentally observed key-intermediate by using on-line ESI-HRMS analysis:



Formula [M]: $C_{17}H_{11}IO_2$

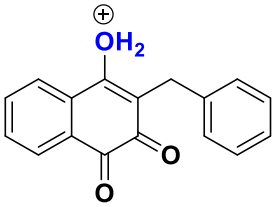
Exact Mass [M + H] = 374.9882

Figure S13: The on-line ESI-HRMS of an on-going reaction of **1a** with aq. HI (57 wt.% in H_2O) and in AcOH at 90 °C under thermal condition.



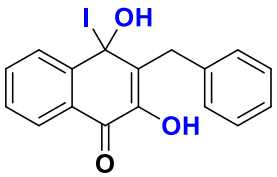
1a (0.2 mmol) **2a**

Experimentally observed key-intermediates by using on-line ESI-HRMS analysis:



Formula [M]: $C_{17}H_{13}O_3^+$

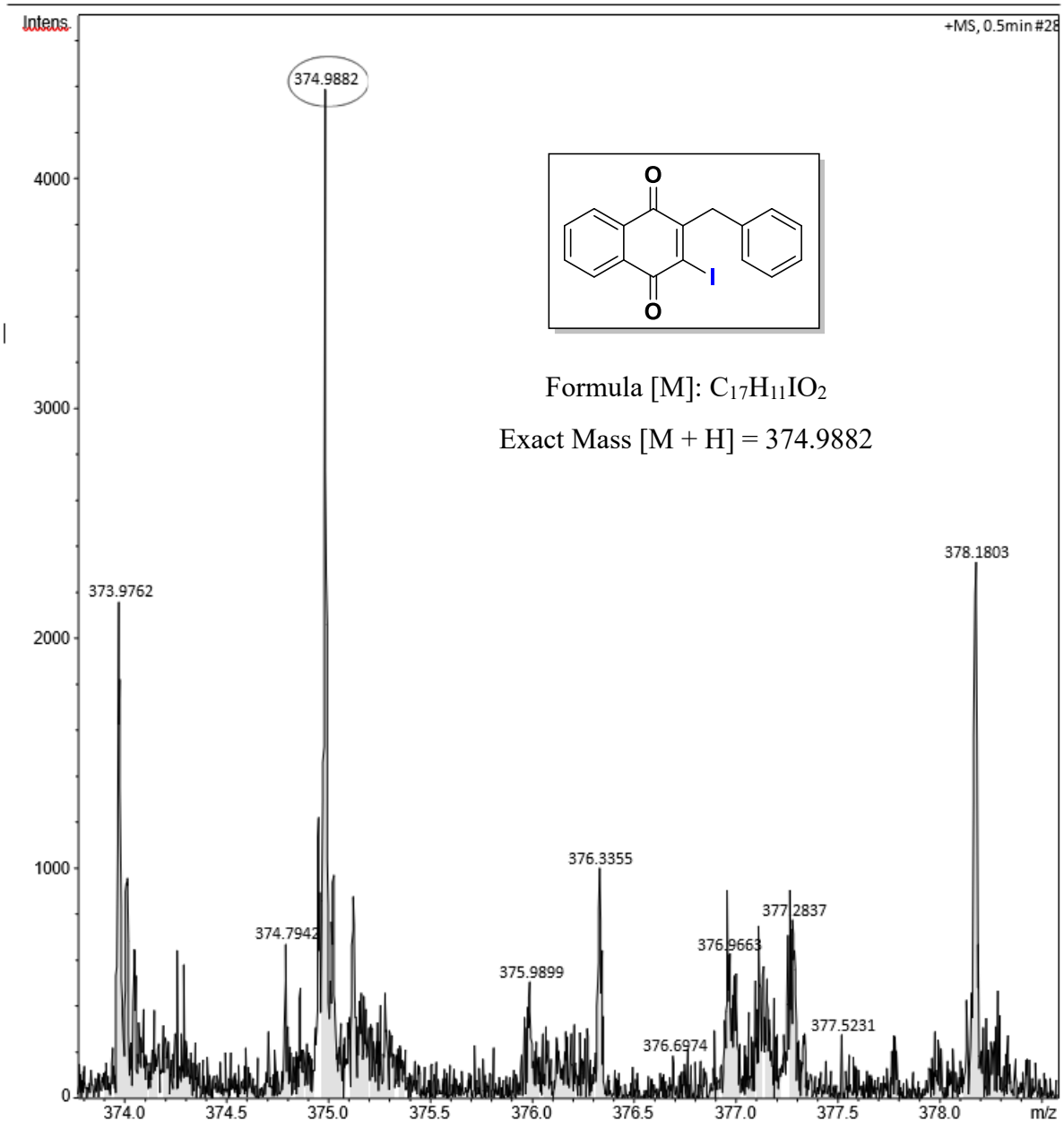
Exact Mass [M+NH_4] = 283.1203



Formula [M] = $C_{17}H_{13}IO_3$

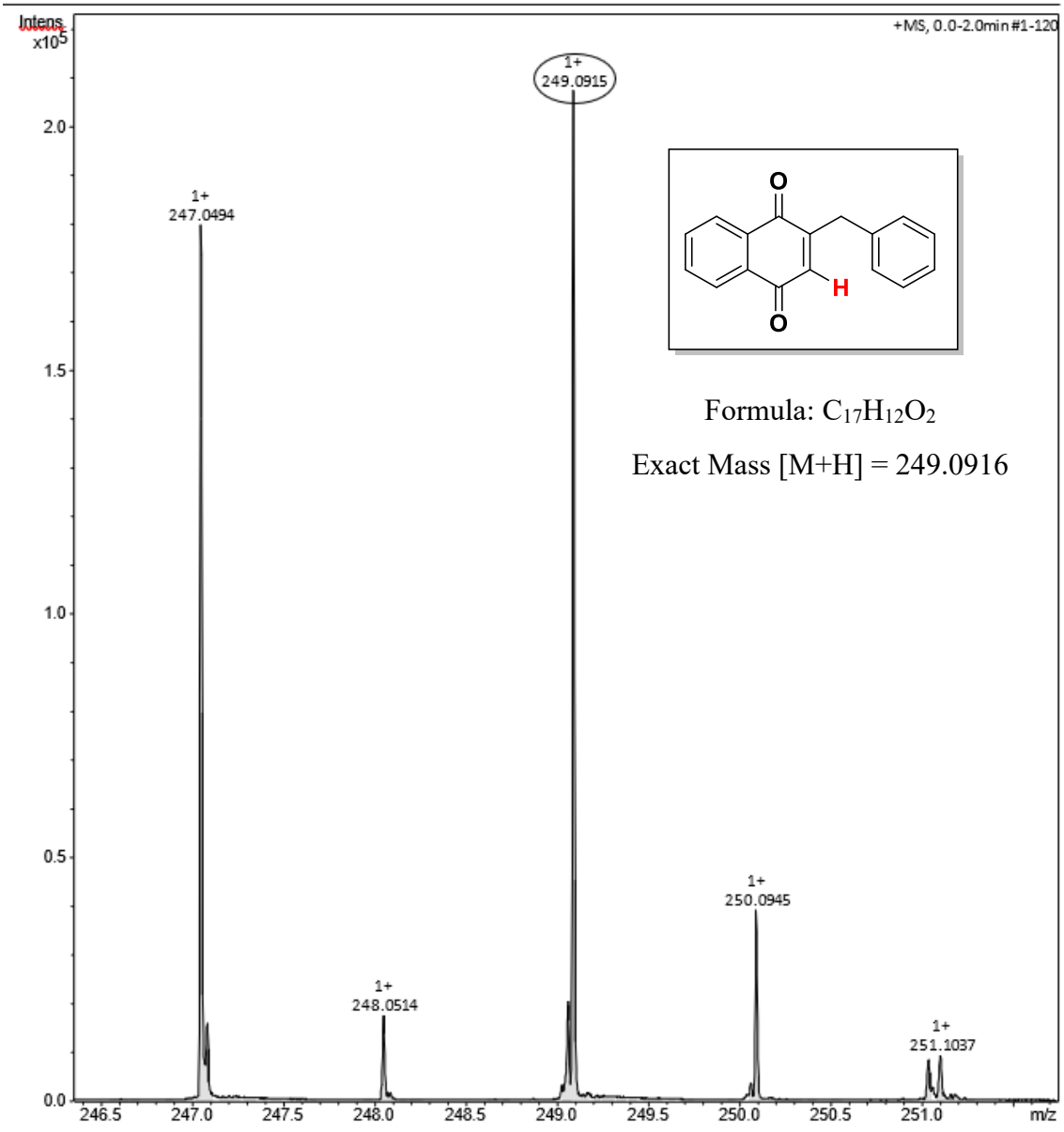
Exact Mass [M] = 391.9909

Exact Mass [M+H] = 392.9988



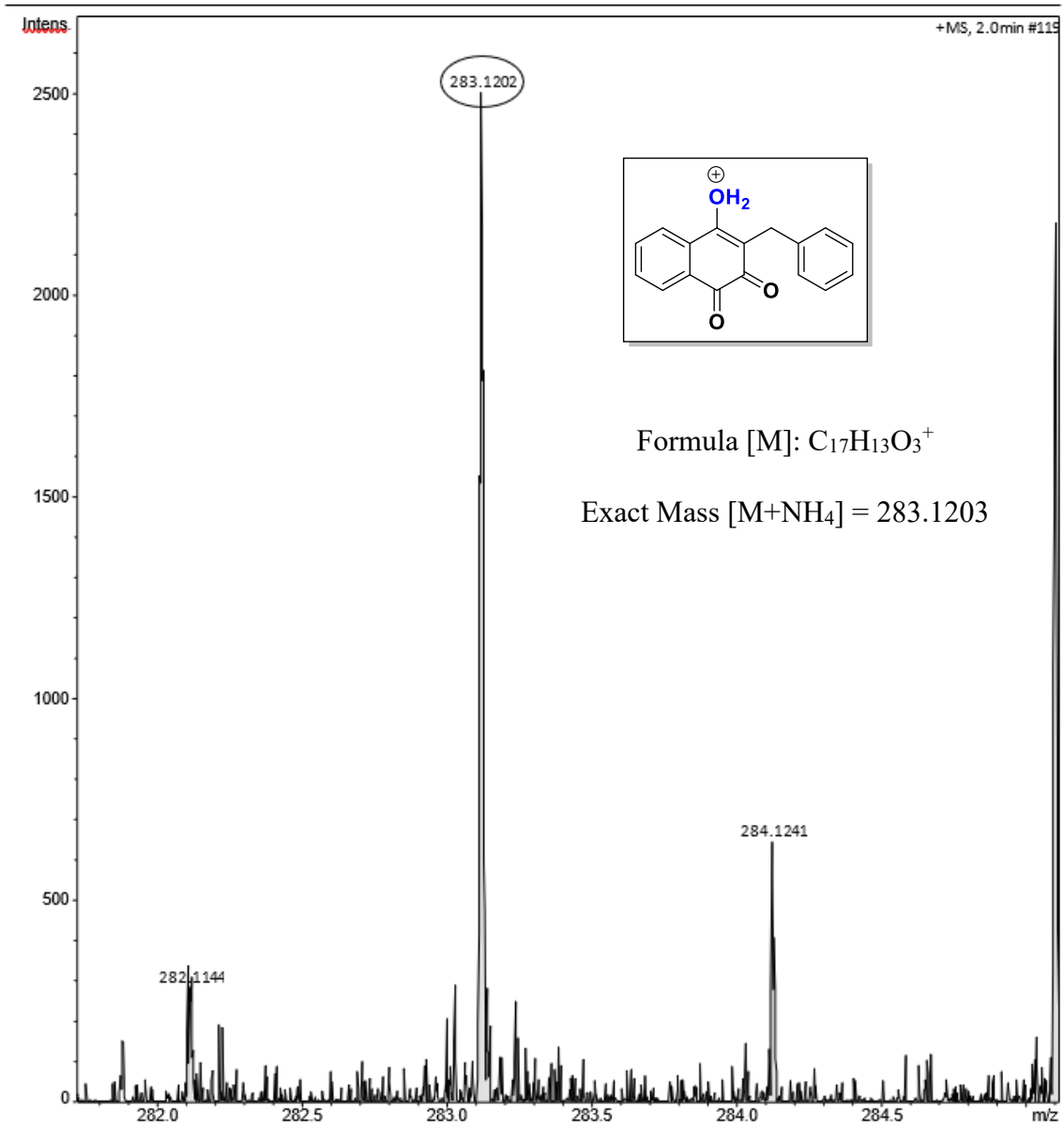
Formula [M]: $C_{17}H_{11}IO_2$

Exact Mass [M + H] = 374.9882



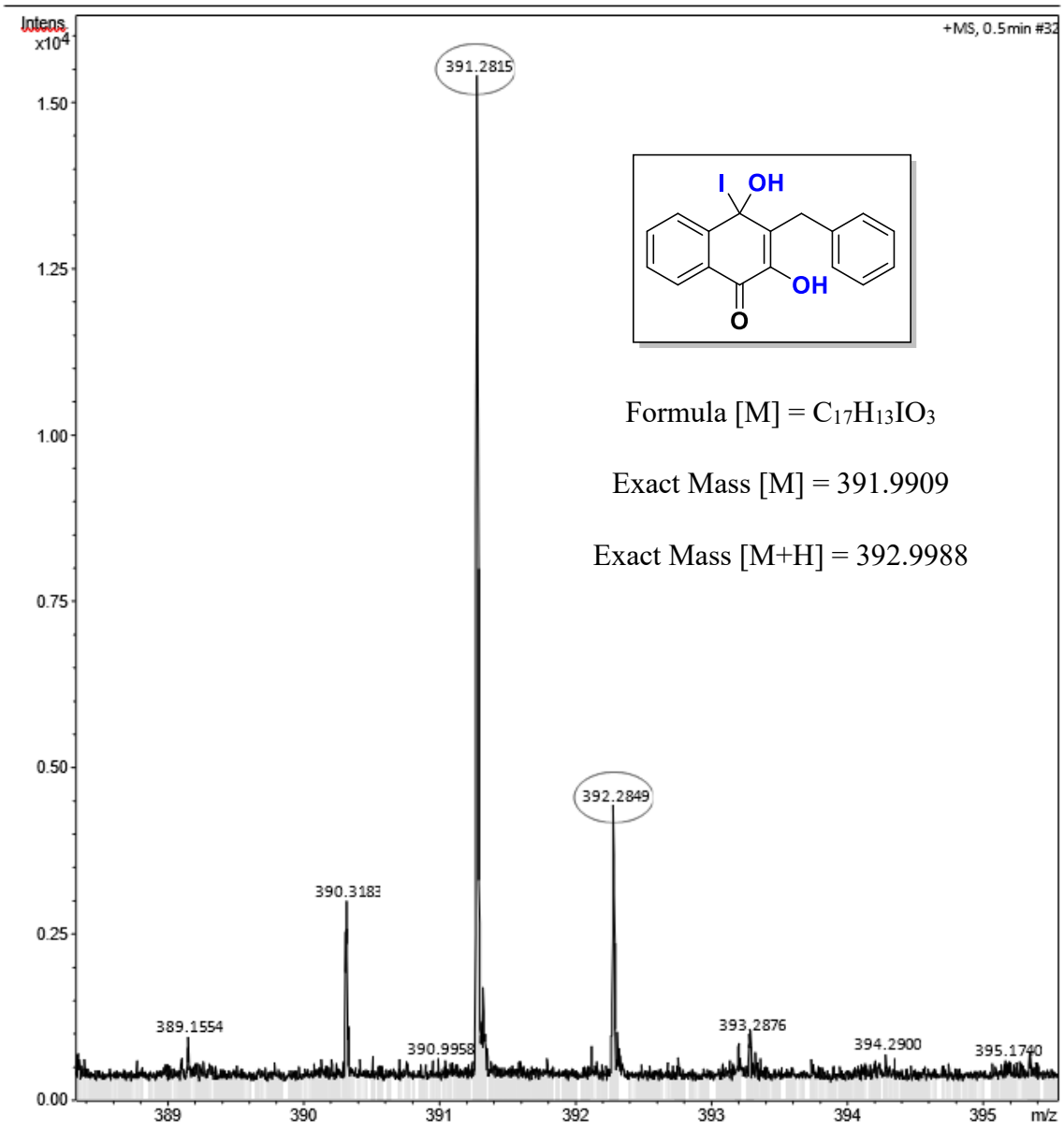
Formula: $C_{17}H_{12}O_2$

Exact Mass [M+H] = 249.0916



Formula [M]: $C_{17}H_{13}O_3^+$

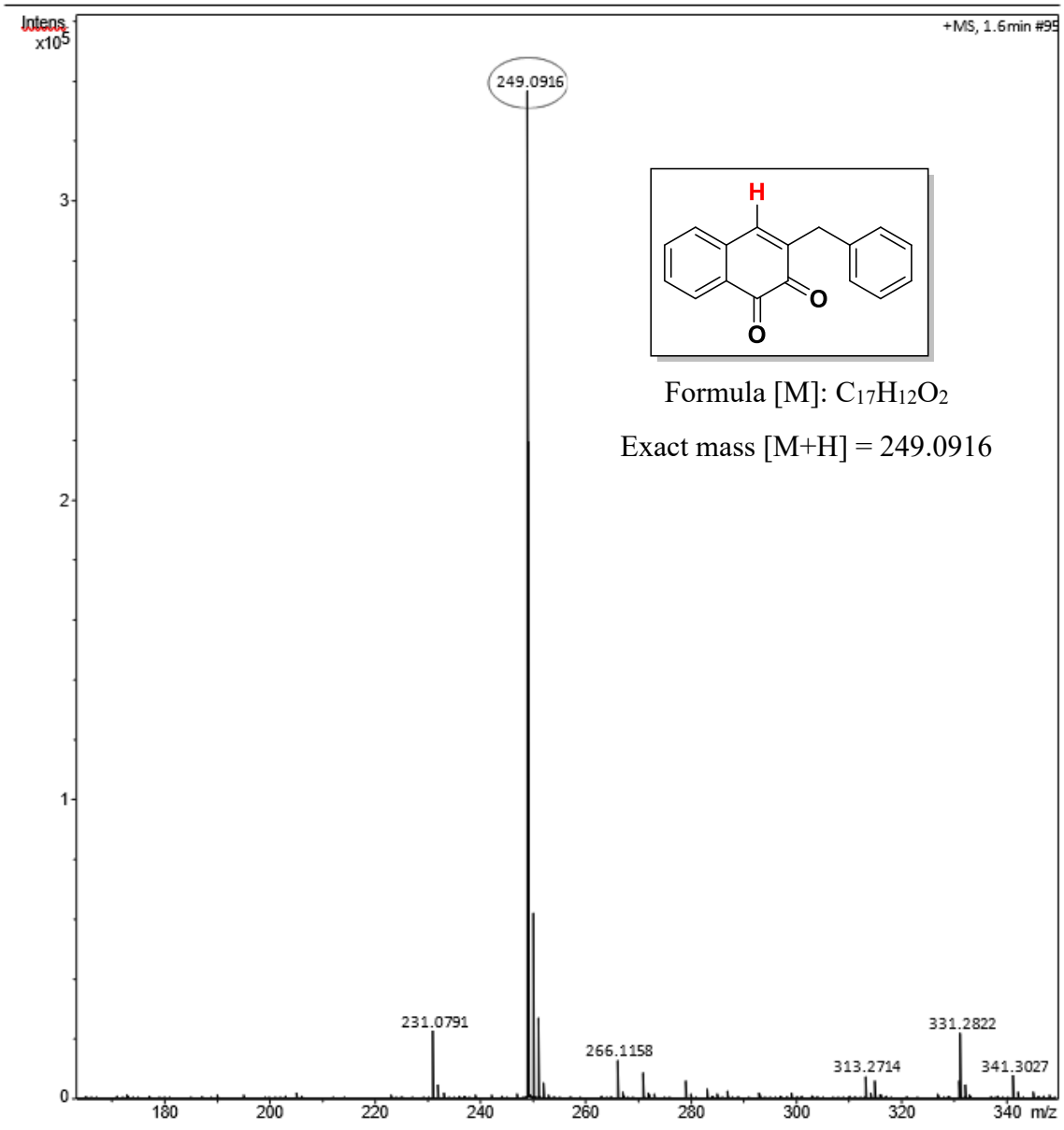
Exact Mass [M+NH_4] = 283.1203



Formula [M] = $C_{17}H_{13}IO_3$

Exact Mass [M] = 391.9909

Exact Mass [M+H] = 392.9988



Formula [M]: $C_{17}H_{12}O_2$

Exact mass [M+H] = 249.0916

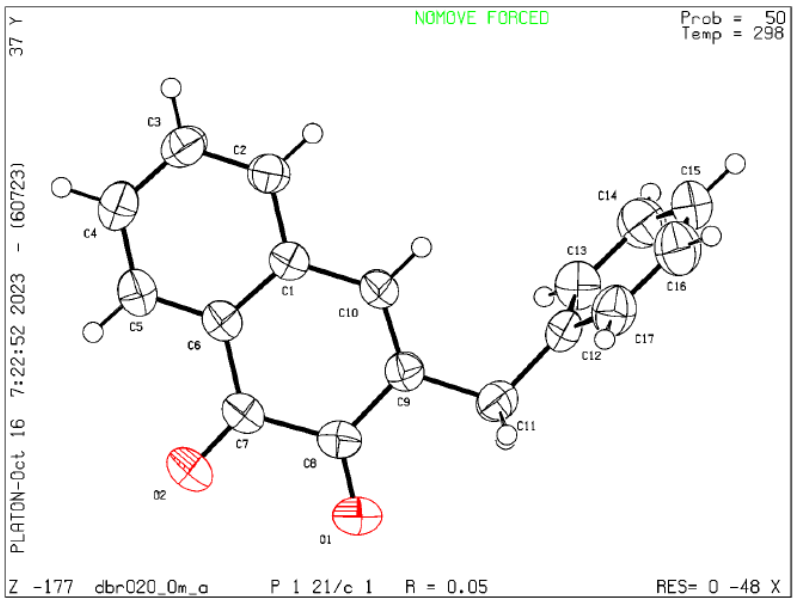
X-Ray Single Crystal Data for 3-benzylnaphthalene-1,2-dione (2a). The Ellipsoid Contour % Probability Levels are 50%

Crystalized from $CHCl_3$-EtOAc; $C_{17}H_{12}O_2$; Mr = 248.27; monoclinic; space group = P_1 21/C_1; A metallic orangish orange crystal of 0.21x0.12x0.11 mm^3 was used.

Table S8. Crystal data for 3-benzylnaphthalene-1,2-dione **2a** (CCDC-2395504)

```
Bond precision:   C-C = 0.0022 A          Wavelength=0.71073

Cell:             a=17.742(4)     b=5.4248(11)       c=12.764(2)
                  alpha=90        beta=95.498(8)     gamma=90
Temperature:      298 K

                  Calculated                Reported
Volume            1222.8(4)                 1222.8(4)
Space group       P 21/c                    P 1 21/c 1
Hall group        -P 2ybc                   -P 2ybc
Moiety formula    C17 H12 O2                C17 H12 O2
Sum formula       C17 H12 O2                C17 H12 O2
Mr                248.27                    248.27
Dx,g cm-3         1.349                     1.349
Z                 4                         4
Mu (mm-1)         0.088                     0.088
F000              520.0                     520.0
F000'             520.25
h,k,lmax          23,7,16                   23,7,16
Nref              2833                      2779
Tmin,Tmax         0.987,0.990               0.586,0.746
Tmin'             0.982

Correction method= # Reported T Limits: Tmin=0.586 Tmax=0.746
AbsCorr = MULTI-SCAN

Data completeness= 0.981          Theta(max)= 27.612

R(reflections)= 0.0502( 2192)                wR2(reflections)=
                                             0.1350( 2779)
S = 1.066                 Npar= 172
```

Ellipsoid plot for 3-benzylnaphthalene-1,2-dione (**2a**):



X-Ray Single Crystal Data for 3-(4-methoxybenzyl)-naphthalene-1,2-dione (2j). The Ellipsoid Contour % Probability Levels are 50%

Crystalized from $CHCl_3$-EtOAc; $C_{18}H_{14}O_3$; Mr = 278.29; monoclinic; space group = P_1 21/C_1; A metallic orangish orange crystal of 0.20x0.19x0.17 mm^3 was used.

Table S9. Crystal data for 3-(4-methoxybenzyl)-naphthalene-1,2-dione **2j** (CCDC-2395505)

Bond precision: C-C = 0.0027 A Wavelength=0.71073

Cell: a=19.0585(16) b=5.6006(5) c=13.1682(9)
alpha=90 beta=104.843(3) gamma=90
Temperature: 298 K

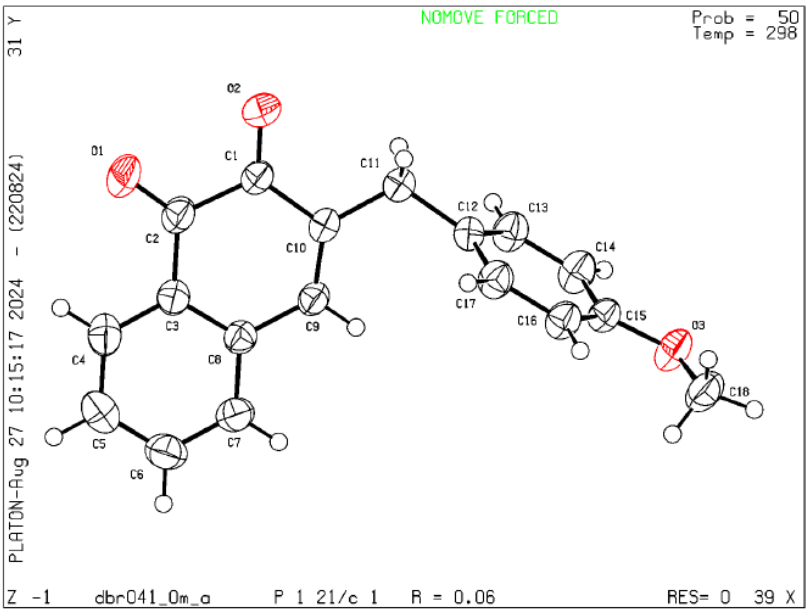
	Calculated	Reported
Volume	1358.66(19)	1358.66(19)
Space group	P 21/c	P 1 21/c 1
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C18 H14 O3	C18 H14 O3
Sum formula	C18 H14 O3	C18 H14 O3
Mr	278.29	278.29
Dx,g cm-3	1.360	1.360
Z	4	4
Mu (mm-1)	0.092	0.092
F000	584.0	584.0
F000'	584.30	
h,k,lmax	26,7,18	26,7,18
Nref	3684	3677
Tmin,Tmax	0.982,0.984	0.624,0.746
Tmin'	0.982	

Correction method= # Reported T Limits: Tmin=0.624 Tmax=0.746
AbsCorr = MULTI-SCAN

Data completeness= 0.998 Theta(max)= 29.188

R(reflections)= 0.0613(2012) wR2(reflections)= 0.1622(3677)
S = 0.976 Npar= 191

Ellipsoid plot for 3-(4-methoxybenzyl)-naphthalene-1,2-dione (**2j**):



X-Ray Single Crystal Data for 2-benzylnaphthalene-1,4-dione (3a). The Ellipsoid Contour % Probability Levels are 50%

Crystalized from $CHCl_3$-EtOAc; $C_{17}H_{12}O_2$; Mr = 248.27; monoclinic; space group = $P_1\ 21/n_1$; A metallic yellowish yellow crystal of 0.22x0.20x0.11 mm^3 was used.

Table S10. Crystal data for 2-benzylnaphthalene-1,4-dione **3a** (CCDC-2395506)

Bond precision:	C-C = 0.0019 A	Wavelength=0.71073	
Cell:	a=5.4268(1)	b=10.2243(2)	c=22.7209(5)
	alpha=90	beta=94.593(2)	gamma=90
Temperature:	299 K		
	Calculated	Reported	
Volume	1256.63(4)	1256.63(4)	
Space group	P 21/n	P 1 21/n 1	
Hall group	-P 2yn	-P 2yn	
Moiety formula	C17 H12 O2	C17 H12 O2	
Sum formula	C17 H12 O2	C17 H12 O2	
Mr	248.27	248.27	
Dx,g cm-3	1.312	1.312	
Z	4	4	
Mu (mm-1)	0.085	0.085	
F000	520.0	520.0	
F000'	520.25		
h,k,lmax	6,13,28	6,12,28	
Nref	2701	2616	
Tmin,Tmax	0.982,0.991	0.486,1.000	
Tmin'	0.982		

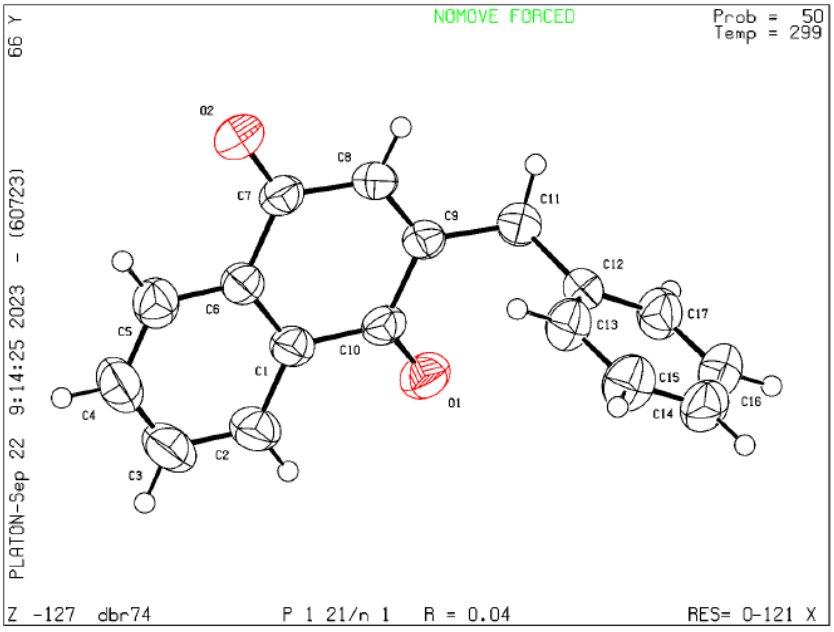
Correction method= # Reported T Limits: Tmin=0.486 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 0.969 Theta(max)= 26.881

R(reflections)= 0.0447(2057) wR2(reflections)= 0.1265(2616)

S = 1.068 Npar= 172

Ellipsoid plot for 2-benzylnaphthalene-1,4-dione (**3a**):



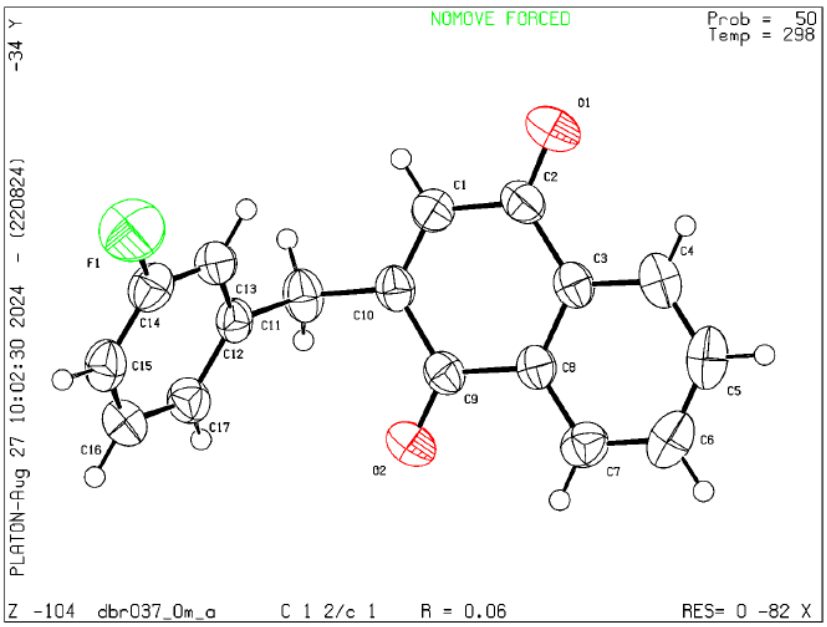
X-Ray Single Crystal Data for 2-(3-fluorobenzyl)-naphthalene-1,4-dione (3c). The Ellipsoid Contour % Probability Levels are 50%

Crystalized from $CHCl_3$-EtOAc; $C_{17}H_{11}FO_2$; Mr = 266.26; monoclinic; space group = C 12/c_1; A metallic yellowish yellow crystal of 0.22x0.2x0.18 mm^3 was used.

Table S11. Crystal data for 2-(3-fluorobenzyl)-naphthalene-1,4-dione **3c** (CCDC-2395507)

```
Bond precision:   C-C = 0.0024 A          Wavelength=0.71073

Cell:             a=15.4575(11)     b=7.5249(6)       c=21.8542(18)
                  alpha=90          beta=93.640(3)    gamma=90
Temperature:      298 K

                  Calculated                Reported
Volume            2536.9(3)                 2536.9(3)
Space group       C 2/c                     C 1 2/c 1
Hall group        -C 2yc                    -C 2yc
Moiety formula    C17 H11 F O2              C17 H11 F O2
Sum formula       C17 H11 F O2              C17 H11 F O2
Mr                266.26                    266.26
Dx,g cm-3         1.394                     1.394
Z                 8                         8
Mu (mm-1)         0.101                     0.101
F000              1104.0                    1104.0
F000'             1104.63
h,k,lmax          20,9,28                   20,9,28
Nref              3058                      3052
Tmin,Tmax         0.978,0.982               0.614,0.746
Tmin'             0.978

Correction method= # Reported T Limits: Tmin=0.614 Tmax=0.746
AbsCorr = NONE

Data completeness= 0.998          Theta(max)= 27.971

R(reflections)= 0.0630( 2054)                  wR2(reflections)=
                                               0.1642( 3052)
S = 1.099                 Npar= 181
```

Ellipsoid plot for 2-(3-fluorobenzyl)-naphthalene-1,4-dione (**3c**):



X-Ray Single Crystal Data for 2-benzyl-3-chloronaphthalene-1,4-dione (4a). The Ellipsoid Contour % Probability Levels are 50%

Crystalized from $CHCl_3$-EtOAc; $C_{17}H_{11}ClO_2$; Mr =282.71; triclinic; space group = P_1;

A metallic yellowish yellow crystal of 0.19x0.17x0.11 mm^3 was used.

Table S12. Crystal data for 2-benzyl-3-chloronaphthalene-1,4-dione **4a** (CCDC-2395508)

Bond precision:	C-C = 0.0047 A	Wavelength=0.71073	
Cell:	a=4.9955(2)	b=5.9148(3)	c=11.7073(7)
	alpha=103.743(2)	beta=98.978(2)	gamma=97.252(2)
Temperature:	298 K		
	Calculated	Reported	
Volume	327.06(3)	327.06(3)	
Space group	P 1	P 1	
Hall group	P 1	P 1	
Moiety formula	C17 H11 Cl O2	C17 H11 Cl O2	
Sum formula	C17 H11 Cl O2	C17 H11 Cl O2	
Mr	282.71	282.71	
Dx,g cm-3	1.435	1.435	
Z	1	1	
Mu (mm-1)	0.289	0.289	
F000	146.0	146.0	
F000'	146.21		
h,k,lmax	6,7,15	6,7,15	
Nref	2944[1472]	2920	
Tmin,Tmax	0.947,0.969	0.650,0.746	
Tmin'	0.947		

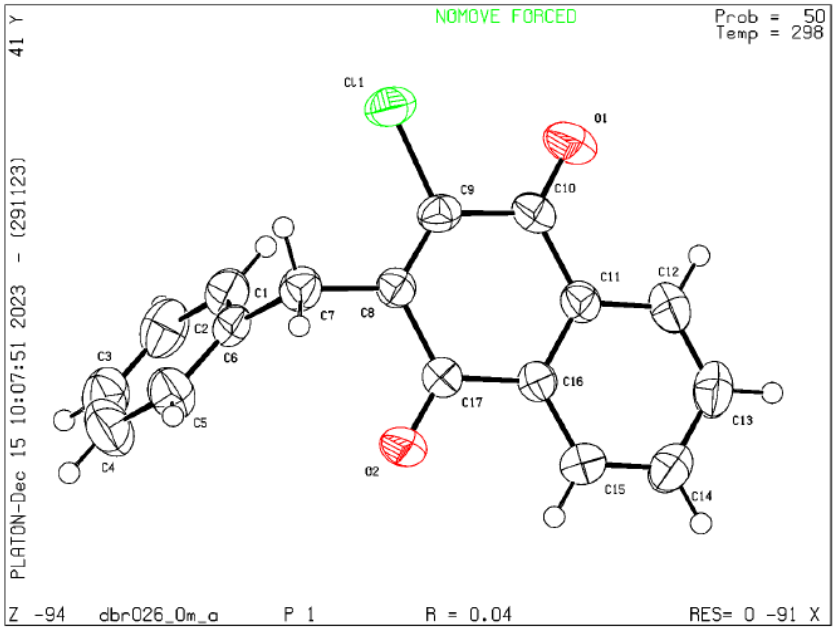
Correction method= # Reported T Limits: Tmin=0.650 Tmax=0.746
AbsCorr = MULTI-SCAN

Data completeness= 1.98/0.99 Theta(max)= 27.227

R(reflections)= 0.0375(2512) wR2(reflections)= 0.0880(2920)

S = 1.021 Npar= 181

Ellipsoid plot for 2-benzyl-3-chloronaphthalene-1,4-dione (**4a**):



X-Ray Single Crystal Data for 3-hydroxy-8,8-dimethyl-5,6,7,8-tetrahydrophenanthrene-1,4-dione (7). The Ellipsoid Contour % Probability Levels are 50%

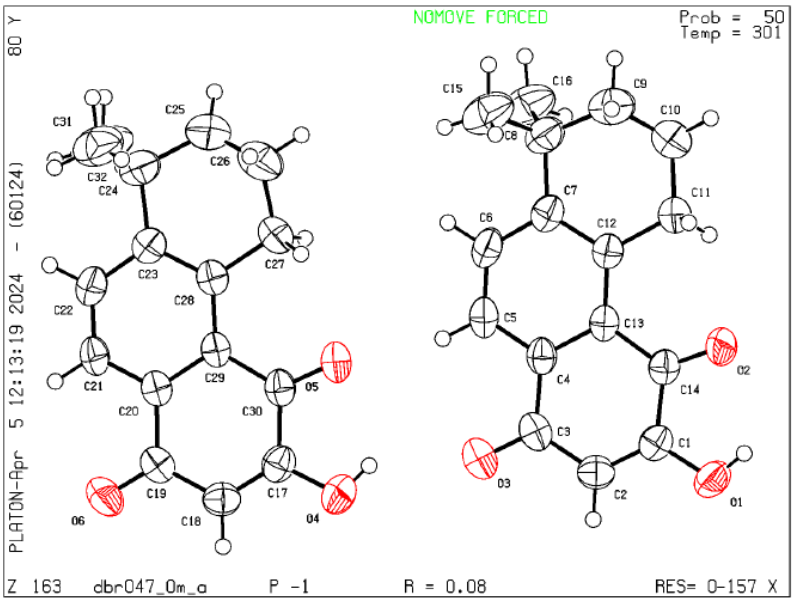
Crystalized from $CHCl_3$-EtOAc; $C_{16}H_{16}O_3$; Mr =511.57; triclinic; space group = P_{-1};

A metallic yellowish yellow crystal of 0.20x0.19x0.14 mm^3 was used.

Table S13. Crystal data for 3-hydroxy-8,8-dimethyl-5,6,7,8-tetrahydrophenanthrene-1,4-dione **7** (CCDC-2395509)

```
Bond precision:   C-C = 0.0036 A          Wavelength=0.71073

Cell:          a=6.8522(5)       b=12.7911(11)     c=15.3647(12)
               alpha=94.719(3)   beta=102.333(3)   gamma=90.643(3)
Temperature:   301 K

                Calculated                Reported
Volume          1310.56(18)               1310.56(18)
Space group     P -1                      P -1
Hall group      -P 1                      -P 1
Moiety formula  C16 H16 O3, C16 H15 O3    C16 H16 O3, C16 H15 O3
Sum formula     C32 H31 O6                C32 H31 O6
Mr              511.57                    511.57
Dx,g cm-3       1.296                     1.296
Z               2                         2
Mu (mm-1)       0.089                     0.089
F000            542.0                     542.0
F000'           542.28
h,k,lmax        9,17,20                   9,17,20
Nref            6584                      6530
Tmin,Tmax       0.982,0.988               0.660,0.746
Tmin'           0.982

Correction method= # Reported T Limits: Tmin=0.660 Tmax=0.746
AbsCorr = MULTI-SCAN

Data completeness= 0.992          Theta(max)= 28.385

R(reflections)= 0.0795( 3965)                wR2(reflections)=
                                             0.2523( 6530)
S = 1.079              Npar= 349
```

Ellipsoid plot for 3-hydroxy-8,8-dimethyl-5,6,7,8-tetrahydrophenanthrene-1,4-dione (**7**):



References:

1. D. R. Laplace, B. Verbraeken, K. V. Hecke and J. M. Winne, *Chem. Eur. J.*, 2014, **20**, 253-262.
2. Q. -Y. Wei, Z. Zhou, M. -L. Yao, J. -K. Liu, B. Wu and J. -M. Yang, *Chem. Commun.*, 2023, **59**, 11520-11523.
3. (*a*) For the first reported synthesis of deoxyneocryptotanshinone, see: T. Hayashi, H. Kakisawa, H. -Y. Hsu and Y. P. Chen, *J. Chem. Soc. D*, 1970, 299a-299a; (*b*) For the first reported isolation of deoxyneocryptotanshinone in nature, see: Y. Ikeshiro, I. Hashimoto, Y. Iwamoto, I. Mase and Y. Tomita, *Phytochemistry* 1991, **30**, 2791-2792; (*c*) For the correlation NMR data of deoxyneocryptotanshinone, see: F. Eghtesadi, M. M. Farimani, N. Hazeri and J. Valizadeh, *SpringerPlus* 2016, **5**, 1068.
4. (*a*) For the first reported isolation of miltirone, see: T. Hayashi, H. Kakisawa, H. -Y. Hsu and Y. P. Chen, *J. Chem. Soc. D*, 1970, 299a-299a; (*b*) For the first reported synthesis of miltirone, see: D. Nasipuri and A. K. Mitra, *J. Chem. Soc., Perkin Trans. 1*, 1973, 285-287; (*c*) For the correlation of NMR data, see: J. Lee, H. S. Mei and J. K. Snyder, *J. Org. Chem.*, 1990, **55**, 5013-5016.
5. For the correlation NMR data of vitamin K_3, see: S. -I. Murahashi, N. Miyaguchi, S. Noda, T. Naota, A. Fujii, Y. Inubushi and N. Komiya, *Eur. J. Org. Chem.*, 2011, 5355-5365.
6. A. L. Perez, G. Lamoureux and A. Herrera, *Synth. Commun.*, 2004, **34**, 3389-3397.