Supporting Information-I

A Seven-step, One-pot Regioselective Synthesis of Biologically Important 3-Aryllawsones: Scope and Applications

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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. GCMS mass spectrometry was performed on Shimadzu GCMS-QP2010 mass spectrometer. 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 (λ = 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 (λ = 0.71073 Å). For thin-layer chromatography (TLC), silica gel plates Merck 60 F254 were used and compounds were visualized by irradiation with UV light and/or by treatment with a solution of *p*-anisaldehyde (23 mL), conc. H_2SO_4 (35 mL), acetic acid (10 mL), and ethanol (900 mL) followed by heating.

Materials: All solvents and commercially available chemicals were used as received. 3-Alkyllawsones **1/3** were prepared according to the literature procedure.[1]

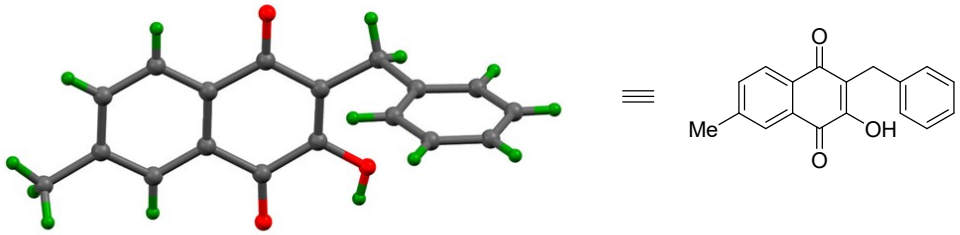


Figure S1: X-Ray crystal structure of 2-benzyl-3-hydroxy-6-methylnaphthalene-1,4-dione (**3b**).

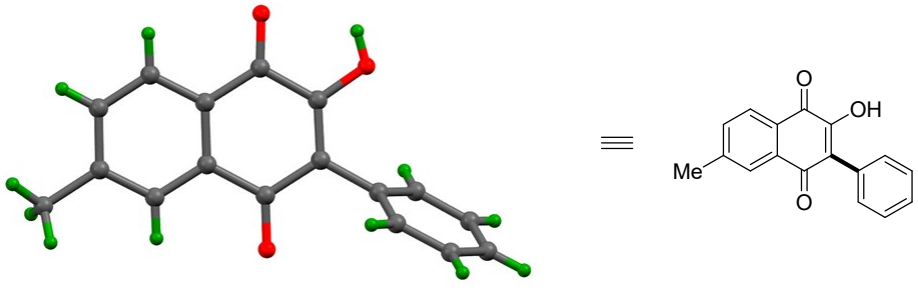


Figure S2: X-Ray crystal structure of 2-hydroxy-6-methyl-3-phenylnaphthalene-1,4-dione (**4b**).

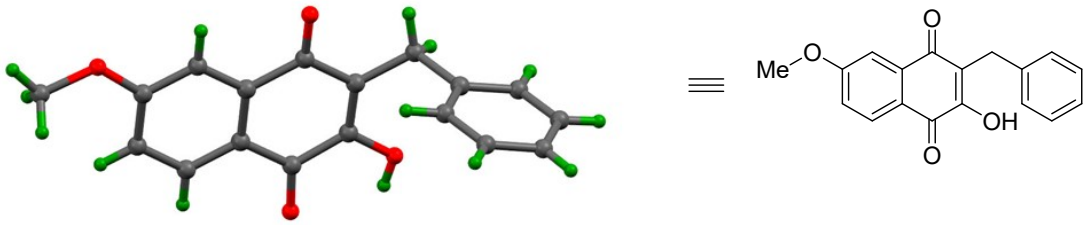


Figure S3: X-Ray crystal structure of 3-benzyl-2-hydroxy-6-methoxynaphthalene-1,4-dione (**3d**).

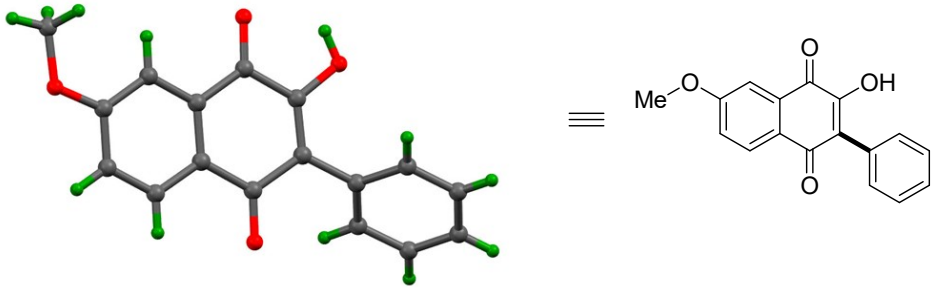


Figure S4: X-Ray crystal structure of 3-hydroxy-6-methoxy-2-phenylnaphthalene-1,4-dione (**4d**).

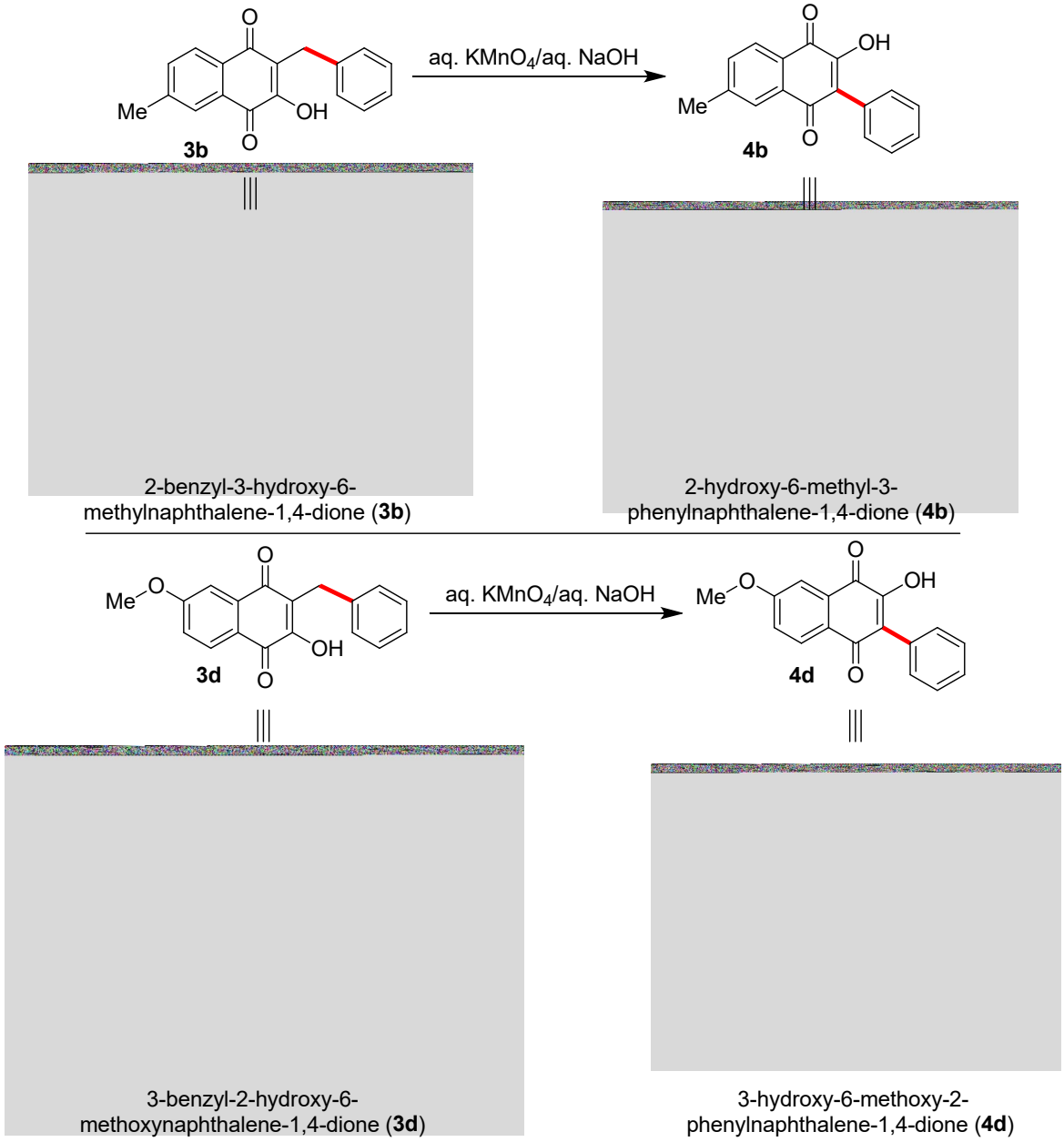
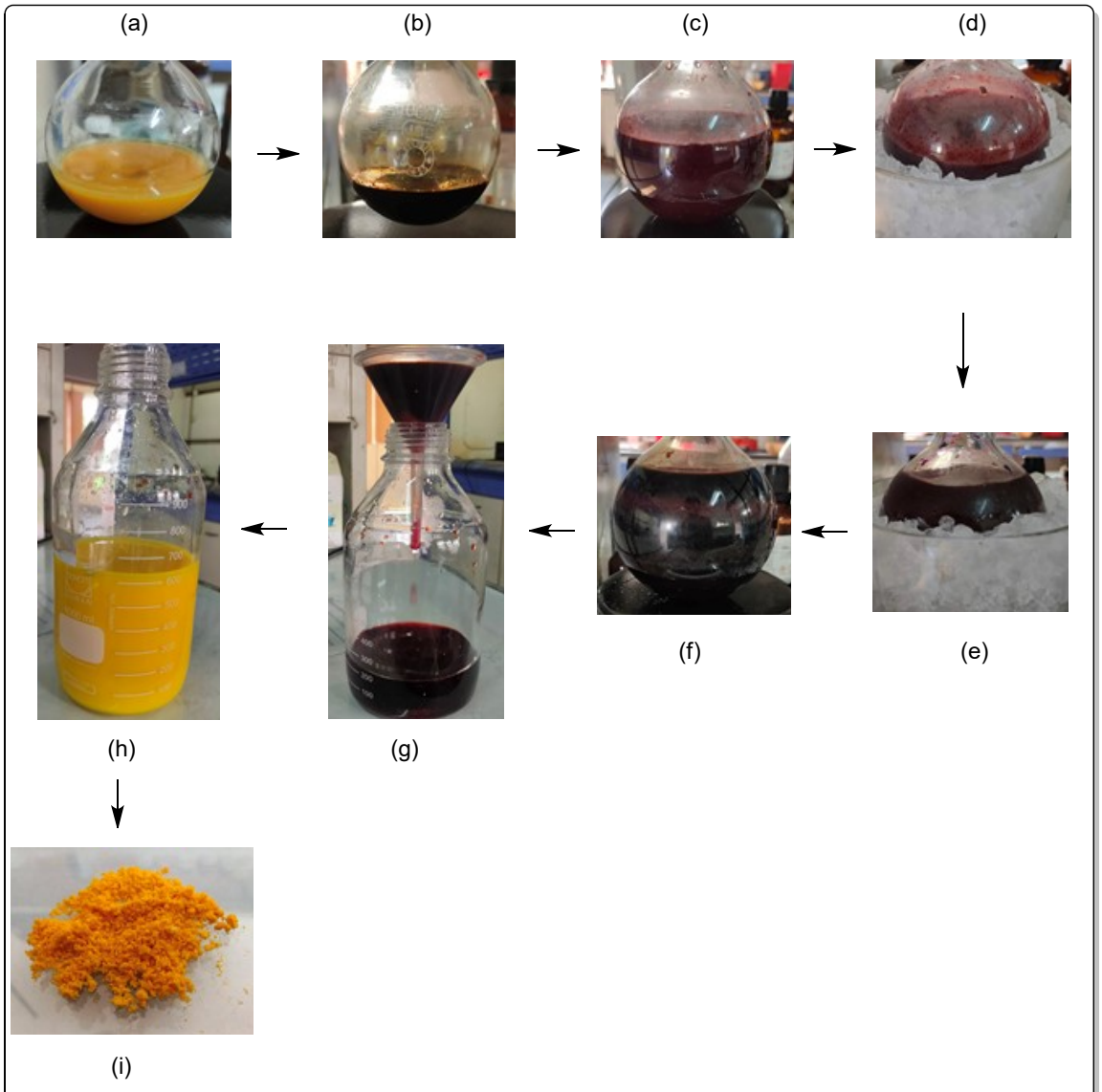
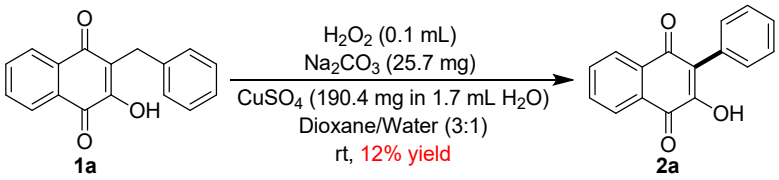


Figure S5: Providing proof for the alkyl 1,4-migratory insertion into the lawsones through correlation of X-ray crystal structures of OrgRC and OD products **3b**, **4b**, **3d** and **4d**.

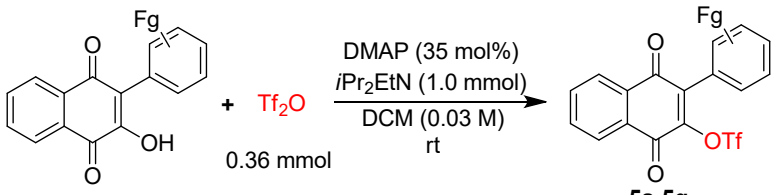


(a) 5.74 mmol Lawsone is treated with 11.48 mmol benzaldehyde in the presence of 20 mol% L-proline and 6.31 mmol Hantzsch ester for 12 h (b) RRC was sucessfully completed and then DCM was evapourated. (c) After evaporating DCM, 322 mL of 2% aq. NaOH was added (d) reaction mixture was then cooled to zero degree (e) Then, 8.68 mmol of potassium permanganate in 161 mL of water which was already cooled to zero degree was added and stirred for 30 seconds and maintained undisturbed at 0 oC for 2 h (f) Then, the reaction mixture was allowed to stay undisturbed for 15 h at room temperature (g) The reaction mixture was filtered in order to remove manganese dioxide (h) Then, the filtrate was acidified with 20% HCl (i) After neutralising this way, workup should be done using ethyl acetate, combined organic layers were dried and concentrated, purified through colom chromatography to achieve pure 3-phenyllawsone.

Figure-S6: Pictorial representation of gram-scale sequential one-pot OrgRC/OD reactions.



Scheme S1: Performing oxidative decarboxylation (OD) through Fieser's modified conditions (H_2O_2 / $CuSO_4$).

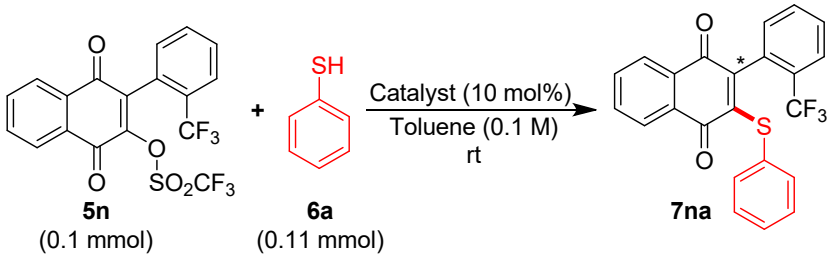


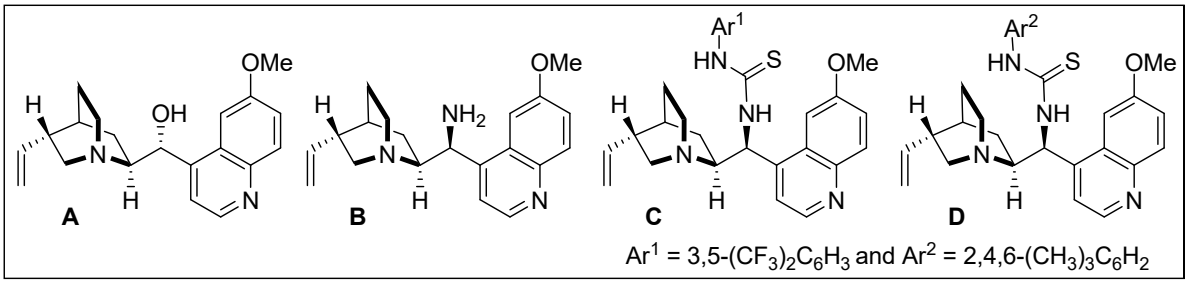
entry	Fg	Time	yield (%)[a]
1	H (**2a**)	40	**5a**: 82
2	4-F (**2d**)	30	**5d**: 70
3	4-CF_3 (**2p**)	30	**5p**: 74
4	4-Me (**2i**)	40	**5i**: 76
5	3-Me (**2h**)	40	**5h**: 75
6	2-Me (**2g**)	30	**5g**: 72
7	2-CF_3 (**2n**)	30	**5n**: 70
8	2-methoxynaphthalen-1-yl (**2q**)	60	**5q**: 62

[a] Yield refers to the column purified products.

Scheme S2: Synthesis of 3-aryllawsone-trifluoromethanesulfonates **5**.

Table-S1: Optimization for the asymmetric synthesis of 2,3-diaryl-naphthalene-1,4-diones [a]





entry	catalyst	time (h)	yield (%)[c]	*ee* (%)
1[b]	**A**	12	77	10
2[b]	**B**	48	77	1
3	**C**	6	80	1
4	**D**	3	82	2

[a]Reactions were carried out in 0.1 mmol scale. [b]Reaction was carried out at 0 °C. [c]Yield refers to the overall yield of the column purified products.

General Experimental Procedures:

Procedure A: **General Procedure for Oxidative Decarboxylation**: In an oven dried round bottomed flask equipped with a magnetic stirring bar at 0 °C was taken 3-alkyllawsones **1** or **3** (0.2 mmol, 1.0 equiv.), to which $KMnO_4$ (0.38 mmol, 1.9 equiv. in 7.0 mL of H_2O) and 14.0 mL of 2% NaOH in H_2O was added and stirred vigorously for 20 seconds and left unstirred at 0 °C for 2 h followed by 25 °C for 15 h. The aq. $KMnO_4$ and aq. NaOH should be cooled to 0 °C prior to its addition to 3-alkyllawsones **1** or **3**. After 15 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. The combined organic layers were dried (Na_2SO_4), and concentrated. Pure products of 3-aryllawsones **2** or **4** were obtained by column chromatography (silica gel, mixture of hexane/ethyl acetate).

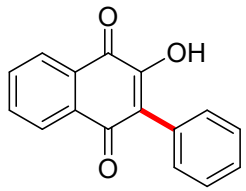
Procedure B: **General Procedure for the OTf Protection of 2/4**: In an oven dried round bottom flask was taken the mixture of 3-aryllawsones **2/4** (0.2 mmol, 1.0 equiv.) and DMAP (0.07 mmol, 35 mol%) in DCM (0.03 M) and cooled to 0 °C. To this (iPr)$_2$EtN (1.0 mmol, 5.0 equiv.) and triflic anhydride (0.36 mmol, 1.8 equiv.) were added respectively and allowed to stir for 1 h at 0 °C. Then the reaction mixture was diluted with DCM and washed with saturated aq. NH_4Cl twice. The organic layer was separated and dried (Na_2SO_4), and concentrated. Pure products 3-aryllawsone-triflates **5** were obtained by column chromatography (silica gel, mixture of hexane/ethyl acetate).

Procedure C: **General Procedure for the thia-Michael Reaction**: In an oven dried round bottom flask was taken the mixture of 3-aryllawsone-triflates **5** (0.065 mmol, 1.0 equiv.) and thiophenol **6** (0.06565 mmol, 1.01 equiv.) in DCM (0.0065 M). The reaction mixture was stirred for 30 min. and then added Et_3N (0.21 mmol, 3.2 equiv.) and further stirred for another 30 min. Then the reaction mixture was diluted with DCM and washed with saturated aq. NH_4Cl twice. The organic layer was separated and dried (Na_2SO_4), and concentrated. Pure thia-Michael products **7** were obtained by column chromatography (silica gel, mixture of hexane/ethyl acetate).

Procedure D: **General Procedure for the Preparation of 2-Arylnaphthalene-1,4-diones 8**: In an oven dried round bottom flask was taken 3-aryllawsone-triflates **5** (0.115 mmol, 1.0 equiv.). To this 0.44 mL HI and 0.44 mL AcOH were added and stirred at 130 °C for respective times. Then, the reaction mixture was cooled to 0 °C and added water (7.0 mL) slowly and extracted with ethyl acetate thrice. The combined organic layers were dried (Na_2SO_4), and concentrated. Pure products **8** was obtained by column chromatography (silica gel, mixture of hexane/ethyl acetate).

Procedure E: **General Procedure for aza-Michael Reaction**: In an oven dried round bottom flask was taken the mixture of 2-arylnaphthalene-1,4-diones **8** (0.15 mmol, 1.0 equiv.) and chiral (*R*)-*tert*-butylsulfinamide or (*S*)-*tert*-butylsulfinamide **9** (0.3 mmol, 2.0 equiv.) in DMF (0.15 M). To this, potassium *tert*-butoxide (0.3 mmol, 2.0 equiv.) was added and allowed to stir for 2 h under air atmosphere. Allow it to stir for 30 min. and then added Et_3N (0.21 mmol, 3.2 equiv.) and further stir for another 30 min. Then the reaction mixture is diluted with DCM and washed with saturated aq. NH_4Cl twice. The organic layer was separated and dried (Na_2SO_4), and concentrated. Pure chiral products **10** were obtained by column chromatography (silica gel, mixture of hexane/ethyl acetate).

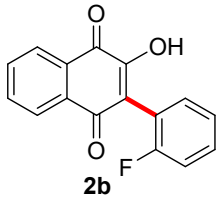
2-Hydroxy-3-phenylnaphthalene-1,4-dione (2a): Prepared by following the procedure **A** and purified by column chromatography using EtOAc/hexane and isolated as yellow solid. Yield: 78% (39.0 mg);



2a

Mp.: 116-118 °C; IR (Neat): ν_{max} 3339, 2931, 1640, 1587, 1428, 1366, 1344, 1309, 1217, 1019, 756 and 724 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.21 (1H, dd, *J* = 7.75, 1.0 Hz), 8.16 (1H, dd, *J* = 7.5, 1.0 Hz), 7.82 (1H, dt, *J* = 7.5, 1.5 Hz), 7.74 (1H, dt, *J* = 7.5, 1.0 Hz), 7.59 (1H, s, O*H*), 7.53-7.50 (2H, m), 7.46 (2H, dt, *J* = 6.75, 1.5 Hz), 7.40 (1H, tt, *J* = 7.5, 1.5 Hz); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 183.7 (C, *C*=O), 181.8 (C, *C*=O), 152.2 (C, *C*-OH), 135.3 (CH), 133.1 (CH), 132.8 (C), 130.6 (2 x CH), 129.9 (C), 129.3 (C), 128.7 (CH), 127.9 (2 x CH), 127.3 (CH), 126.1 (CH), 122.1 (C); HRMS m/z 251.0706 ($M + H^+$), calcd for $C_{16}H_{10}O_3H$ 251.0708.

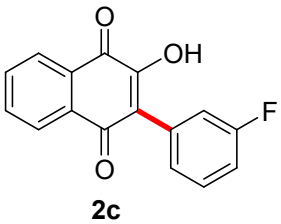
(2-(2-Fluorophenyl)-3-hydroxynaphthalene-1,4-dione (2b): Prepared by following the procedure **A**



2b

and purified by column chromatography using EtOAc/hexane and isolated as yellow solid. Yield: 84% (45.0 mg); Mp 110-112 °C; IR (Neat): ν_{max} 3343, 2924, 1660, 1610, 1592, 1337, 1264, 1214, 1117, 1001, 790, 756, and 724 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.20 (1H, dd, *J* = 7.75, 1.0 Hz), 8.18 (1H, dd, *J* = 7.5, 1.0 Hz), 7.82 (1H, dt, *J* = 7.75, 1.0 Hz), 7.75 (1H, dt, *J* = 7.75, 1.0 Hz), 7.63 (1H, s, O*H*), 7.44-7.40 (1H, m), 7.37 (1H, dt, *J* = 7.25, 1.5 Hz), 7.26-7.23 (1H, m), 7.20-7.16 (1H, m); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 182.7 (C, *C*=O), 181.4 (C, *C*=O), 160.1 (C, d, *J* = 248.75 Hz, *C*-F), 153.2 (C, *C*-OH), 135.4 (CH), 132.2 (CH), 132.8 (C), 132.0 (CH, d, *J* = 3.75 Hz), 130.7 (CH, d, *J* = 8.75 Hz), 129.3 (C), 127.3 (CH), 126.4 (CH), 123.7 (CH, d, *J* = 3.75 Hz), 117.9 (C, d, *J* = 16.25 Hz), 117.6 (C), 115.7 (CH, d, *J* = 21.25 Hz); ^{19}F NMR ($CDCl_3$, 375 MHz): δ −110.6; HRMS m/z 269.0617 ($M + H^+$), calcd for $C_{16}H_9FO_3H$ 269.0614.

2-(3-Fluorophenyl)-3-hydroxynaphthalene-1,4-dione (2c): Prepared by following the procedure **A** and purified by column chromatography using EtOAc/hexane and isolated as orange solid. Yield: 90% (48.3

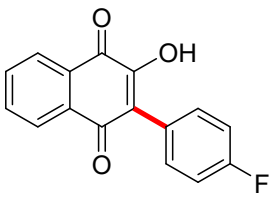


2c

mg); Mp 138-140 °C; IR (Neat): ν_{max} 3219, 2921, 2360, 2340, 1668, 1644, 1580, 1331, 1242, 1170, 1100, 1003, 893, 879, and 713 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.20 (1H, d, *J* = 8.0 Hz), 8.16 (1H, d, *J* = 7.5 Hz), 7.83 (1H, t, *J* = 7.0 Hz), 7.75 (1H, t, *J* = 7.5 Hz), 7.70 (1H, s, O*H*), 7.44-7.40 (1H, m), 7.30 (1H, d, *J* = 8.0 Hz), 7.25 (1H, d, *J* = 7.5 Hz), 7.10 (1H, dt, *J* = 8.5, 1.5 Hz); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 183.3 (C, *C*=O), 181.6 (C, *C*=O), 163.3 (C, d, *J* = 243.75 Hz, *C*-F),

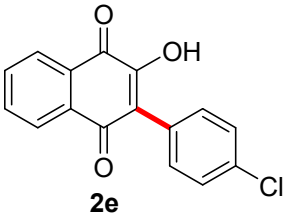
153.4 (C, *C*-OH), 135.4 (CH), 132.3 (CH), 132.7 (C), 131.9 (C, d, J = 8.75 Hz), 129.3 (CH, d, J = 8.75 Hz), 129.2 (C), 127.3 (CH), 126.5 (CH, d, J = 3.75 Hz), 126.2 (CH), 120.8 (C, d, J = 2.5 Hz), 117.8 (CH, d, J = 22.5 Hz), 115.5 (CH, d, J = 21.25 Hz); ^{19}F NMR ($CDCl_3$, 375 MHz): δ −113.4; HRMS m/z 269.0613 (M + H^+), calcd for $C_{16}H_9FO_3H$ 269.0614.

2-(4-Fluorophenyl)-3-hydroxynaphthalene-1,4-dione (2d): Prepared by following the procedure **A** and purified by column chromatography using EtOAc/hexane and isolated as yellow solid. Yield: 84% (45.0 mg); Mp 180-182 °C; IR (Neat): ν_{max} 3330, 2926, 1664, 1645, 1593, 1352, 1233, 1079, 823 and 570 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.20 (1H, dd, J = 7.75, 1.0 Hz), 8.15 (1H, dd, J = 7.5, 1.0 Hz), 7.82 (1H, dt, J = 7.5, 1.0 Hz), 7.75 (1H, dt, J = 7.5, 1.0 Hz), 7.65 (1H, s, O*H*), 7.54-7.50 (2H, m), 7.15 (2H, t, J = 9.0 Hz); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 183.6 (C, *C*=O), 181.7 (C, *C*=O), 162.7 (C, d, J = 247.5 Hz, *C*-F), 152.2 (C, *C*-OH), 135.3 (CH), 133.2 (CH), 132.7 (C), 132.66 (2 x CH, d, J = 8.75 Hz), 129.2 (C), 127.3 (CH), 126.2 (CH), 125.8 (C, d, J = 3.75 Hz), 121.1 (C), 115.0 (2 x CH, d, J = 21.25 Hz); ^{19}F NMR ($CDCl_3$, 375 MHz): δ −112.2; HRMS m/z 269.0615 (M + H^+), calcd for $C_{16}H_9FO_3H$ 269.0614.

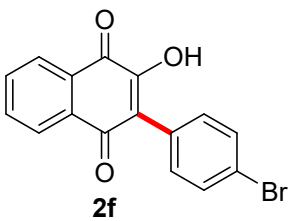


2d

2-(4-Chlorophenyl)-3-hydroxynaphthalene-1,4-dione (2e): Prepared by following the procedure **A** and purified by column chromatography using EtOAc/hexane and isolated as yellow solid. Yield: 56% (31.9 mg); Mp.: 160-162 °C; IR (Neat): ν_{max} 3327, 2922, 2852, 1664, 1592, 1491, 1357, 1336, 1280, 1235 and 725 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.20 (1H, d, J = 7.5 Hz), 8.16 (1H, d, J = 7.5 Hz), 7.82 (1H, t, J = 7.5 Hz), 7.75 (1H, t, J = 7.5 Hz), 7.67 (1H, s, O*H*), 7.47 (2H, d, J = 8.5 Hz), 7.43 (2H, d, J = 8.0 Hz); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 183.4 (C, *C*=O), 181.6 (C, *C*=O), 152.3 (C, *C*-OH), 135.4 (CH), 134.7 (C), 133.3 (CH), 132.7 (C), 132.1 (2 x CH), 129.2 (C), 128.3 (C), 128.2 (2 x CH), 127.3 (CH), 126.2 (CH), 120.9 (C); HRMS m/z 285.0317 (M + H^+), calcd for $C_{16}H_9ClO_3H$ 285.0318.



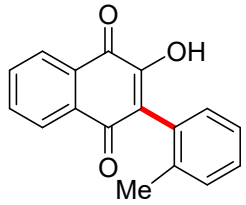
2e



2f

2-(4-Bromophenyl)-3-hydroxynaphthalene-1,4-dione (2f): Prepared by following the procedure **A** and purified by column chromatography using EtOAc/hexane and isolated as orange solid. Yield: 17% (11.9 mg); Mp.: 168-170 °C; IR (Neat): ν_{max} 3357, 2923, 2852, 2188, 2163, 1730, 1659, 1459, 1364, 1281, 1072 and 727 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.20 (1H, d, J = 7.5 Hz), 8.16 (1H, d, J =

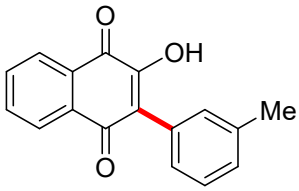
7.0 Hz), 7.82 (1H, dt, *J* = 7.5, 1.0 Hz), 7.75 (1H, dt, *J* = 7.5, 1.0 Hz), 7.65 (1H, s, O*H*), 7.59 (2H, d, *J* = 8.5 Hz), 7.41 (2H, d, *J* = 8.5 Hz); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 183.4 (C, *C*=O), 181.6 (C, *C*=O), 152.2 (C, *C*-OH), 135.4 (CH), 133.3 (CH), 132.8 (C), 132.4 (2 x CH), 131.2 (2 x CH), 129.2 (C), 128.8 (C), 127.3 (CH), 126.2 (CH), 123.0 (C), 120.9 (C); HRMS m/z 328.9814 ($M + H^+$), calcd for $C_{16}H_9BrO_3H$ 328.9813.



2g

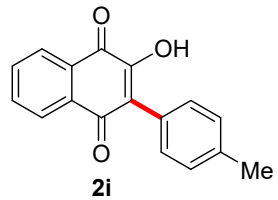
2-Hydroxy-3-(o-tolyl)naphthalene-1,4-dione (2g): Prepared by following the procedure **A** and purified by column chromatography using EtOAc/hexane and isolated as orange solid. Yield: 80% (42.3 mg); Mp.: 104-106 °C; IR (Neat): ν_{max} 3271, 2918, 2849, 1664, 1647, 1632, 1590, 1457, 1333, 1295, 1273, 1236, 1206, 1127, 1097, 997 and 720 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.18 (2H, dt, *J* = 7.4, 1.2 Hz), 7.82 (1H, dt, *J* = 7.8, 1.2 Hz), 7.75 (1H, dt, *J* = 7.6, 1.2 Hz), 7.46 (1H, s, O*H*), 7.35-7.26 (3H, m), 7.18 (1H, d, *J* = 7.2 Hz), 2.21 (3H, s, CH_3); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 183.6 (C, *C*=O), 181.7 (C, *C*=O), 152.5 (C, *C*-OH), 137.0 (C), 135.3 (CH), 133.1 (CH), 132.9 (C), 130.1 (CH), 129.9 (CH), 129.8 (C), 129.4 (C), 128.8 (CH), 127.2 (CH), 126.2 (CH), 125.5 (CH), 123.1 (C), 20.0 (CH_3); HRMS m/z 265.0867 ($M + H^+$), calcd for $C_{17}H_{12}O_3H$ 265.0865.

2-Hydroxy-3-(m-tolyl)naphthalene-1,4-dione (2h): Prepared by following the procedure **A** and purified by column chromatography using EtOAc/hexane and isolated as orange solid. Yield: 83% (43.8 mg);



2h

Mp.: 110-112 °C; IR (Neat): ν_{max}3270, 2920, 1710, 1644, 1458, 1232, 777, 714, 663 and 527 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.20 (1H, td, *J* = 7.0, 0.5 Hz), 8.15 (1H, td, *J* = 7.5, 0.5 Hz), 7.81 (1H, dt, *J* = 7.75, 1.5 Hz), 7.73 (1H, dt, *J* = 7.5, 1.5 Hz), 7.60 (1H, s, O*H*), 7.36 (1H, t, *J* = 8.0 Hz), 7.31-7.29 (2H, m), 7.23-7.21 (1H, m), 2.41 (3H, s, CH_3); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 183.7 (C, *C*=O), 181.8 (C, *C*=O), 152.2 (C, *C*-OH), 137.5 (C), 135.2 (CH), 133.1 (CH), 132.8 (C), 131.1 (CH), 129.8 (C), 129.5 (CH), 129.3 (C), 127.8 (CH), 127.6 (CH), 127.2 (CH), 126.1 (CH), 122.4 (C), 21.5 (CH_3); HRMS m/z 265.0864 ($M + H^+$), calcd for $C_{17}H_{12}O_3H$ 265.0865.

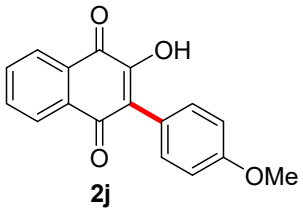


2i

2-Hydroxy-3-(p-tolyl)naphthalene-1,4-dione (2i): Prepared by following the procedure **A** and purified by column chromatography using EtOAc/hexane and isolated as orange solid. Yield: 72% (38.0 mg); Mp.: 142-144 °C; IR (Neat): ν_{max} 3361, 2922, 2360, 2340, 1648, 1591, 1512, 1360, 1334, 1280, 1001, 820 and 725 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.20 (1H, dd, *J* = 7.6, 0.8 Hz), 8.15 (1H, dd, *J* = 7.6, 1.2 Hz),

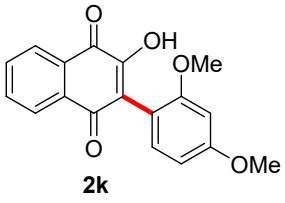
7.81 (1H, dt, *J* = 7.6, 1.6 Hz), 7.74 (1H, dt, *J* = 7.6, 1.2 Hz), 7.56 (1H, s, O*H*), 7.42 (2H, d, *J* = 8.4 Hz), 7.28 (2H, d, *J* = 8.0 Hz), 2.40 (3H, s, CH_3); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 183.8 (C, *C*=O), 181.8 (C, *C*=O), 152.0 (C, *C*-OH), 138.7 (C), 135.2 (CH), 133.1 (CH), 132.9 (C), 130.5 (2 x CH), 129.3 (C), 128.7 (2 x CH), 127.2 (CH), 126.9 (C), 126.1 (CH), 122.3 (C), 21.4 (CH_3); HRMS m/z 265.0869 (M + H^+), calcd for $C_{17}H_{12}O_3H$ 265.0865.

2-Hydroxy-3-(4-methoxyphenyl)naphthalene-1,4-dione (2j): Prepared by following the procedure **A** and purified by column chromatography using EtOAc/hexane and isolated as red solid. Yield: 73% (40.9 mg); Mp.: 134-136 °C; IR (Neat): ν_{max} 3360, 2922, 2851, 1648, 1605, 1590, 1359, 1277, 1251, 1180, 1028, 819 and 723 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.19 (1H, d, *J* = 7.6 Hz), 8.13 (1H, d, *J* = 7.6 Hz), 7.80 (1H, t, *J* = 7.6 Hz), 7.72 (1H, t, *J* = 7.2 Hz), 7.61 (1H, s, O*H*), 7.51 (2H, d, *J* = 8.8 Hz), 7.00 (2H, d, *J* = 8.8 Hz), 3.86 (3H, s, OCH_3); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 184.0 (C, *C*=O), 181.7 (C, *C*=O), 159.8 (C), 151.8 (C, *C*-OH), 135.1 (CH), 133.1 (CH), 132.8 (C), 132.2 (2 x CH), 129.3 (C), 127.2 (CH), 126.0 (CH), 122.1 (C), 121.8 (C), 113.4 (2 x CH), 55.3 (CH_3, O*C*H_3); HRMS m/z 281.0815 (M + H^+), calcd for $C_{17}H_{12}O_4H$ 281.0814.



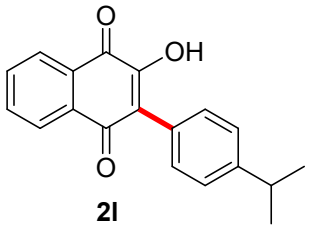
2j

2-(2,4-Dimethoxyphenyl)-3-hydroxynaphthalene-1,4-dione (2k): Prepared by following the procedure **A** and purified by column chromatography using EtOAc/hexane and isolated as yellow solid. Yield: 73% (45.3 mg); Mp.: 178-180 °C; IR (Neat): ν_{max} 3308, 2924, 1663, 1648, 1608, 1507, 1367, 1333, 1302, 1256, 1207, 1037, 998 and 724 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.17 (1H, dd, *J* = 7.5, 1.5 Hz), 8.14 (1H, dd, *J* = 7.75, 1.5 Hz), 7.78 (1H, dt, *J* = 7.5, 1.5 Hz), 7.72 (1H, dt, *J* = 7.5, 1.5 Hz), 7.39 (1H, s, O*H*), 7.17 (1H, d, *J* = 8.5 Hz), 6.60 (1H, dd, *J* = 8.25, 2.5 Hz), 6.58 (1H, d, *J* = 2.5 Hz), 3.85 (3H, s, OCH_3), 3.77 (3H, s, OCH_3); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 183.4 (C, *C*=O), 181.8 (C, *C*=O), 161.6 (C), 158.4 (C), 152.8 (C, *C*-OH), 135.0 (CH), 133.2 (C), 132.9 (CH), 131.9 (CH), 129.6 (C), 127.2 (CH), 126.1 (CH), 120.8 (C), 111.9 (C), 104.7 (CH), 99.1 (CH), 55.7 (CH_3, O*C*H_3), 55.4 (CH_3, O*C*H_3); HRMS m/z 311.0920 (M + H^+), calcd for $C_{18}H_{14}O_5H$ 311.0919.



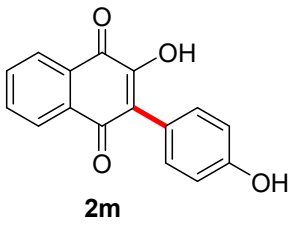
2k

2-Hydroxy-3-(4-isopropylphenyl)naphthalene-1,4-dione (2l): Prepared by following the procedure **A** and purified by column chromatography using EtOAc/hexane and isolated as yellow solid. Yield: 60% (35.1 mg); Mp.: 130-132 °C; IR (Neat): ν_{max} 2919, 2850, 1697, 1610, 1462, 1423, 1283, 935 and 777 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 8.20 (1H, d, *J* = 7.6 Hz), 8.15 (1H, d, *J* = 7.6 Hz), 7.82-7.79 (1H, m), 7.73 (1H, t, *J* = 7.60 Hz), 7.47 (2H, d, *J* = 8.0 Hz), 7.33 (2H, d, *J* = 8.4 Hz), 2.96 (1H, septet, *J* = 7.2 Hz), 1.29 (6H, d, *J* = 7.2 Hz); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 183.9 (C, *C*=O), 181.8 (C, *C*=O), 152.0 (C, *C*-OH), 149.4 (C), 135.2 (CH), 133.1 (CH), 132.8 (C), 130.6 (2 x CH), 129.3 (C), 127.3 (CH), 127.2 (C), 126.1 (2 x CH), 126.0 (CH), 122.2 (C), 34.4 (CH), 23.8 (2 x CH_3); HRMS m/z 315.0998 ($M + Na^+$), calcd for $C_{19}H_{16}O_3Na$ 315.0997.



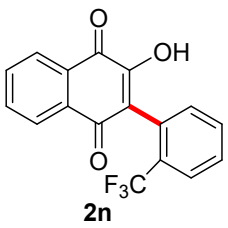
2l

2-Hydroxy-3-(4-hydroxyphenyl)naphthalene-1,4-dione (2m): Prepared by following the procedure **A** and purified by column chromatography using EtOAc/hexane and isolated as brown solid. Yield: 55% (29.3 mg); Mp.: 200-202 °C; IR (Neat): ν_{max} 3338, 2480, 2012, 1655, 1578, 1513, 1340, 1234, 1174, 1084, 1002 824 and 713 cm^{-1}; ^1H NMR (CD_3OD, 500 MHz) δ 8.10 (2H, d, *J* = 6.5 Hz), 7.79 (2H, td, *J* = 22.0, 7.0 Hz), 7.35 (2H, d, *J* = 8.0 Hz), 6.87 (2H, d, *J* = 8.5 Hz); ^{13}C NMR (CD_3OD, DEPT-135) δ 186.3 (C, *C*=O), 183.0 (C, *C*=O), 158.5 (C, *C*-OH), 155.7 (C), 135.7 (CH), 134.3 (CH), 134.2 (C), 133.6 (2 x CH), 131.7 (C), 127.7 (CH), 126.8 (CH), 123.9 (C), 123.4 (C), 115.6 (2 x CH); HRMS m/z 289.0485 ($M + Na^+$), calcd for $C_{16}H_{10}O_4Na$ 289.0477.



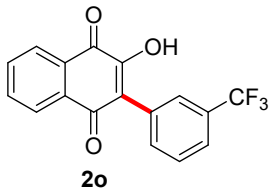
2m

2-Hydroxy-3-(2-(trifluoromethyl)phenyl)naphthalene-1,4-dione (2n): Prepared by following the procedure **A** and purified by column chromatography using EtOAc/hexane and isolated as yellow solid. Yield: 67% (42.6 mg); Mp.: 172-174 °C; IR (Neat): ν_{max} 3376, 1641, 1586, 1368, 1352, 1308, 1231, 1145, 1037, 792 and 727 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 8.19 (1H, dd, *J* = 4.25, 1.0 Hz), 8.18 (1H, dd, *J* = 4.0, 1.0 Hz), 7.83 (1H, dt, *J* = 7.5, 1.0 Hz), 7.80 (1H, d, *J* = 8.0 Hz), 7.77 (1H, dt, *J* = 8.0, 1.5 Hz), 7.64 (1H, t, *J* = 7.5 Hz), 7.56 (1H, t, *J* = 7.5 Hz), 7.46 (1H, s, O*H*), 7.30 (1H, d, *J* = 7.5 Hz); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 183.3 (C, *C*=O), 181.4 (C, *C*=O), 152.7 (C, *C*-OH), 135.4 (CH), 133.3 (CH), 132.7 (C), 131.7 (CH), 131.3 (CH), 129.4 (C, q, *J* = 30.0 Hz), 129.3 (C), 128.8 (C), 127.3 (C), 126.47 (2 x CH, q, *J* = 15.0 Hz), 126.5 (2 x CH), 123.9 (C, q, *J* = 268.75 Hz, *C*F_3); ^{19}F NMR ($CDCl_3$, 375 MHz): δ –60.8; HRMS m/z 341.0405 ($M + Na^+$), calcd for $C_{17}H_9F_3O_3Na$ 341.0401.



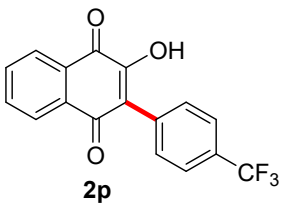
2n

(2-Hydroxy-3-(3-(trifluoromethyl)phenyl)naphthalene-1,4-dione (2o): Prepared by following the procedure **A** and purified by column chromatography using EtOAc/hexane and isolated as yellow solid. Yield: 66% (42.0 mg); Mp.: 90-92 °C; IR (Neat): ν_{max} 3356, 2922, 2564, 1686, 1420, 1331, 1265, 1168, 1119, 1091, 1070, 919 and 683 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 8.21 (1H, dd, *J* = 7.75, 1.0 Hz), 8.17 (1H, dd, *J* = 7.5, 1.0 Hz), 7.84 (1H, dt, *J* = 7.5, 1.5 Hz), 7.81 (1H, s), 7.76 (1H, dt, *J* = 7.5, 1.5 Hz), 7.71 (1H, d, *J* = 8.0 Hz), 7.65 (1H, d, *J* = 7.5 Hz), 7.58 (1H, t, *J* = 8.0 Hz); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 183.3 (C, *C*=O), 181.6 (C, *C*=O), 152.6 (C, *C*-OH), 135.5 (CH), 134.1 (CH), 133.4 (CH), 132.7 (C), 130.8 (C), 130.5 (C), 130.4 (C, q, *J* = 32.5 Hz), 129.2 (C), 128.3 (CH), 127.7 (CH, q, *J* = 3.75 Hz), 127.4 (CH), 126.3 (CH), 125.3 (CH, q, *J* = 3.75 Hz), 124.1 (C, q, *J* = 270.0 Hz, *C*F_3); ^{19}F NMR ($CDCl_3$, 375 MHz): δ –62.6; HRMS m/z 319.0579 (M + H^+), calcd for $C_{17}H_9F_3O_3H$ 319.0582.



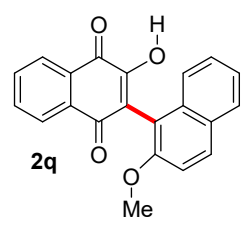
2o

2-Hydroxy-3-(4-(trifluoromethyl)phenyl)naphthalene-1,4-dione (2p): Prepared by following the procedure **A** and purified by column chromatography using EtOAc/hexane and isolated as yellow solid. Yield: 71% (45.2 mg); Mp.: 208-210 °C; IR (Neat): ν_{max} 3330, 3116, 2918, 2849, 1666, 1632, 1591, 1359, 1327, 1280, 1079, 1064, 1002, 887 and 723 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 8.22 (1H, dd, *J* = 7.5, 1.0 Hz), 8.18 (1H, dd, *J* = 7.5, 1.0 Hz), 7.84 (1H, dt, *J* = 7.5, 1.0 Hz), 7.77 (1H, dt, *J* = 7.5, 1.5 Hz), 7.72 (2H, d, *J* = 8.0 Hz), 7.64 (2H, d, *J* = 8.0 Hz); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 183.2 (C, *C*=O), 181.6 (C, *C*=O), 152.6 (C, *C*-OH), 135.6 (CH), 133.7 (C), 133.4 (CH), 132.7 (C), 131.1 (2 x CH), 130.6 (C), 130.5 (C, q, *J* = 32.5 Hz), 129.2 (C), 127.4 (CH), 126.3 (CH), 124.8 (2 x CH, q, *J* = 3.75 Hz), 124.1 (C, q, *J* = 271.2 Hz, *C*F_3); ^{19}F NMR ($CDCl_3$, 375 MHz): δ –62.8; HRMS m/z 319.0586 (M + H^+), calcd for $C_{17}H_9F_3O_3H$ 319.0582.



2p

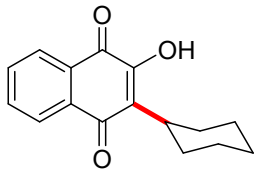
(3'-Hydroxy-2-methoxy-[1,2'-binaphthalene]-1',4'-dione (2q): Prepared by following the procedure **A** and purified by column chromatography using EtOAc/hexane and isolated as yellow solid. Yield: 30% (19.8 mg); Mp.: 128-130 °C; IR (Neat): ν_{max} 3351, 2923, 2859, 2125, 1736, 1666, 1593, 1509, 1266, 1073, 1043, 993, and 727 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 8.21 (2H, dt, *J* = 7.25, 1.0 Hz), 7.95 (1H, d, *J* = 9.0 Hz), 7.84 (1H, d, *J* = 8.0 Hz), 7.82 (1H, dt, *J* = 7.25, 1.5 Hz), 7.76 (1H, dt, *J* = 7.5, 1.5 Hz), 7.48 (1H, d, *J* = 8.5 Hz), 7.41-7.39 (2H, m), 7.37 (1H, s, O*H*), 7.34 (1H, dt, *J* = 8.0, 1.5 Hz), 3.88 (3H, s, OCH_3); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 183.2 (C, *C*=O), 181.5 (C, *C*=O), 154.9 (C), 153.7 (C, *C*-OH), 135.1 (CH), 133.3 (C), 133.0 (CH), 132.4 (C), 130.9 (CH), 129.7 (C), 129.1 (C), 128.4 (CH), 127.3 (CH),



2q

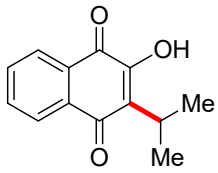
126.8 (CH), 126.3 (CH), 124.2 (CH), 123.7 (CH), 119.3 (C), 113.4 (C), 113.37 (CH), 56.7 (CH_3, O*C*H_3); HRMS m/z 331.0972 (M + H^+), calcd for $C_{21}H_{14}O_4H$ 331.0970.

2-Cyclohexyl-3-hydroxynaphthalene-1,4-dione (2r): Prepared by following the procedure **A** and purified by column chromatography using EtOAc/hexane and isolated as yellow solid. Yield: 74% (37.9 mg); Mp.: 98-100 °C; IR (Neat): ν_{max} 3360, 2923, 2851, 2360, 1646, 1595, 1382, 1338, 1274, 1238, 1056, 1003, 939 and 724 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 8.10 (1H, d, *J* = 7.5 Hz), 8.05 (1H, d, *J* = 7.5 Hz), 7.74 (1H, dt, *J* = 7.5, 1.5 Hz), 7.66 (1H, dt, *J* = 7.5, 1.0 Hz), 7.50 (1H, s, O*H*), 3.08 (1H, tt, *J* = 12.5, 5.0 Hz), 2.01-1.94 (2H, m), 1.81 (2H, d, *J* = 12.5 Hz), 1.73 (1H, d, *J* = 11.0 Hz), 1.61 (1H, d, *J* = 13.0 Hz), 1.42-1.25 (4H, m); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 184.5 (C, *C*=O), 181.9 (C, *C*=O), 152.8 (C, *C*-OH), 134.8 (CH), 133.2 (C), 132.6 (CH), 129.2 (C), 127.9 (C), 126.9 (CH), 125.9 (CH), 35.2 (CH), 29.2 (2 x CH_2), 26.7 (2 x CH_2), 25.9 (CH_2); HRMS m/z 257.1177 (M + H^+), calcd for $C_{16}H_{16}O_3H$ 257.1178.



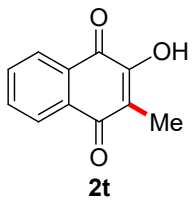
2r

2-Hydroxy-3-isopropylnaphthalene-1,4-dione (2s): Prepared by following the procedure **A** and purified by column chromatography using EtOAc/hexane and isolated as yellow solid. Yield: 81% (35.0 mg); Mp.: 145-147 °C; IR (Neat): ν_{max} 3368, 2921, 2851, 1710, 1661, 1595, 1269, 1121, 1013 and 725 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 8.11 (1H, dd, *J* = 8.0, 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, 1.5 Hz), 7.43 (1H, d, *J* = 2.0 Hz, O*H*), 3.42 (1H, septet, *J* = 7.5 Hz), 1.31 (6H, d, *J* = 7.0 Hz); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 184.4 (C, *C*=O), 181.9 (C, *C*=O), 152.7 (C, *C*-OH), 134.9 (CH), 133.1 (C), 132.7 (CH), 129.2 (C), 128.7 (C), 126.9 (CH), 125.9 (CH), 24.6 (C), 19.8 (2 x CH_3); HRMS m/z 217.0858 (M + H^+), calcd for $C_{13}H_{12}O_3H$ 217.0865.



2s

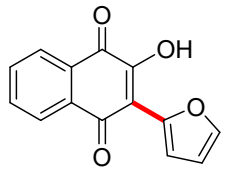
2-Hydroxy-3-methylnaphthalene-1,4-dione (2t): Prepared by following the procedure **A** and purified by column chromatography using EtOAc/hexane and isolated as brown solid. Yield: 53% (19.9 mg); Mp.: 128-130 °C; IR (Neat): ν_{max} 3321, 2920, 1738, 1651, 1588, 1457, 1390, 1339, 1302, 1274, 1204, 1178, 1069, 1026, 935 and 721 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 8.12 (1H, dd, *J* = 7.75, 0.5 Hz), 8.07 (1H, dd, *J* = 7.25, 0.5 Hz), 7.75 (1H, dt, *J* = 7.5, 1.0 Hz), 7.68 (1H, dt, *J* = 7.5, 1.5 Hz), 7.32 (1H, s, O*H*), 2.11 (3H, s, CH_3); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 185.0 (C, *C*=O), 181.2 (C, *C*=O), 153.1 (C, *C*-OH), 134.8 (CH),



2t

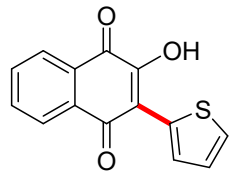
132.9 (C), 132.88 (CH), 129.4 (C), 126.7 (CH), 126.1 (CH), 120.5 (C), 8.6 (CH_3); HRMS m/z 189.0553 ($M + H^+$), calcd for $C_{11}H_8O_3H$ 189.0552.

2-(Furan-2-yl)-3-hydroxynaphthalene-1,4-dione (2u): Prepared by following the procedure **A** and purified by column chromatography using EtOAc/hexane and isolated as brown solid. Yield: 44% (21.1 mg); Mp.: 128-130 °C; IR (Neat): ν_{max} 3326, 1656, 1620, 1591, 1458, 1394, 1357, 1331, 1282, 1039, 1008, 874 and 746 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 8.17 (1H, d, *J* = 7.5 Hz), 8.14 (1H, s), 8.11 (1H, d, *J* = 7.5 Hz), 7.79 (1H, dt, *J* = 7.5, 0.5 Hz), 7.72 (1H, dt, *J* = 7.5, 0.5 Hz), 7.69 (1H, s, O*H*), 7.43 (1H, d, *J* = 3.5 Hz), 6.62 (1H, q, *J* = 1.5 Hz); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 182.3 (C, *C*=O), 181.0 (C, *C*=O), 150.0 (C, *C*-OH), 145.9 (C), 143.9 (CH), 135.1 (CH), 133.3 (CH), 132.8 (C), 129.2 (C), 127.1 (CH), 126.1 (CH), 117.0 (CH), 112.3 (C), 112.1 (CH); HRMS m/z 263.0324 ($M + Na^+$), calcd for $C_{14}H_8O_4Na$ 263.0320.



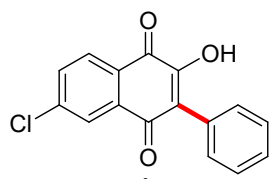
2u

2-Hydroxy-3-(thiophen-2-yl)naphthalene-1,4-dione (2v): Prepared by following the procedure **A** and purified by column chromatography using EtOAc/hexane and isolated as brown solid. Yield: 47% (24.1 mg); Mp 138-140 °C; IR (Neat): ν_{max} 3316, 2920, 1647, 1589, 1375, 1352, 1325, 1281, 1229, 877 and 701 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 8.24 (1H, dd, *J* = 4.0, 1.0 Hz), 8.21 (1H, dd, *J* = 7.5, 1.0 Hz), 8.11 (1H, dd, *J* = 7.5, 1.0 Hz), 7.79 (1H, dt, *J* = 7.5, 1.0 Hz), 7.72 (1H, dt, *J* = 7.75, 1.5 Hz), 7.62 (1H, dd, *J* = 5.5, 1.0 Hz), 7.20 (1H, dd, *J* = 5.5, 4.0 Hz); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 183.7 (C, *C*=O), 180.9 (C, *C*=O), 150.1 (C, *C*-OH), 135.2 (CH), 133.4 (CH), 132.6 (C), 132.5 (CH), 131.1 (C), 131.1 (CH), 129.1 (C), 127.5 (CH), 126.8 (CH), 126.1 (CH), 116.0 (C); HRMS m/z 257.0276 ($M + H^+$), calcd for $C_{14}H_8O_3SH$ 257.0272.



2v

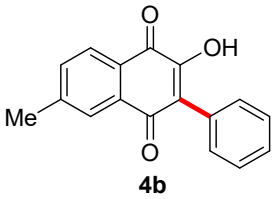
6-Chloro-2-hydroxy-3-phenylnaphthalene-1,4-dione (4a): Prepared by following the procedure **A** and purified by column chromatography using EtOAc/hexane and isolated as red solid. Mp 106-108 °C; Yield: 70% (39.8 mg); IR (Neat): ν_{max} 3336, 2921, 2851, 2359, 1701, 1663, 1639, 1620, 1308, 1285, 1119, 768 and 743 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 8.16 (1H, d, *J* = 2.0 Hz), 8.10 (1H, d, *J* = 8.0 Hz), 7.70 (1H, dd, *J* = 8.5, 2.0 Hz), 7.61 (1H, s, O*H*), 7.51-7.45 (4H, m), 7.41 (1H, tt, *J* = 4.5, 1.5 Hz); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 182.5 (C, *C*=O), 180.9 (C, *C*=O), 152.3 (C, *C*-OH), 142.4



4a

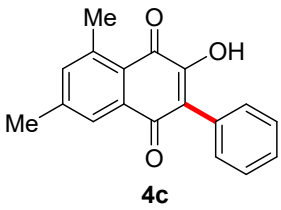
(C), 134.1 (C), 133.2 (CH), 130.6 (2 x CH), 129.6 (C), 128.8 (CH), 128.0 (2 x CH), 127.7 (CH), 127.5 (C), 127.49 (CH), 122.3 (C); HRMS m/z 285.0316 ($M + H^+$), calcd for $C_{16}H_9ClO_3H$ 285.0318.

2-Hydroxy-6-methyl-3-phenylnaphthalene-1,4-dione (4b): Prepared by following the procedure **A** and purified by column chromatography using EtOAc/hexane and isolated as orange solid. Yield: 70% (37.0 mg); Mp.: 140-142 °C; IR (Neat): ν_{max} 3348, 2961, 2150, 2031, 1652, 1595, 1366, 1259, 1089, 1015, 797 and 739 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 8.04 (1H, d, *J* = 7.5 Hz), 8.00 (1H, brs), 7.62 (1H, s, O*H*), 7.54-7.50 (3H, m), 7.48-7.45 (2H, m), 7.40 (1H, tt, *J* = 7.5, 1.0 Hz), 2.53 (3H, s, CH_3); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 184.0 (C, *C*=O), 181.5 (C, *C*=O), 152.3 (C, *C*-OH), 146.9 (C), 133.7 (CH), 132.8 (C), 130.6 (2 x CH), 130.1 (C), 128.5 (CH), 127.9 (2 x CH), 127.8 (CH), 127.0 (C), 126.4 (CH), 121.8 (C), 22.1 (CH_3); HRMS m/z 265.0865 ($M + H^+$), calcd for $C_{17}H_{12}O_3H$ 265.0865.



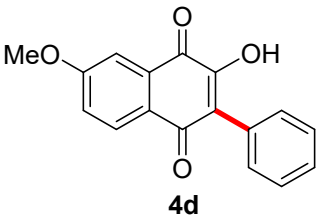
4b

3-Hydroxy-5,7-dimethyl-2-phenylnaphthalene-1,4-dione (4c): Prepared by following the procedure **A** and purified by column chromatography using EtOAc/hexane and isolated as orange solid. Yield: 54% (30.0 mg); Mp.: 160-162 °C; IR (Neat): ν_{max} 3326, 3045, 2918, 1738, 1644, 1596, 1362, 1342, 1232, 1073, 1040, 999 and 682 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.94 (1H, d, *J* = 0.5 Hz), 7.91 (1H, s), 7.53-7.51 (2H, m), 7.45 (2H, tt, *J* = 7.5, 1.0 Hz), 7.38 (1H, tt, *J* = 7.5, 1.5 Hz), 7.32 (1H, s, O*H*), 2.77 (3H, s, CH_3), 2.47 (3H, s, CH_3); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 184.1 (C, *C*=O), 182.5 (C, *C*=O), 152.7 (C, *C*-OH), 145.9 (C), 142.0 (C), 137.3 (CH), 134.4 (C), 130.6 (2 x CH), 130.2 (C), 128.4 (CH), 127.9 (2 x CH), 126.8 (CH), 124.5 (C), 120.3 (C), 22.6 (CH_3), 21.9 (CH_3); HRMS m/z 279.1022 ($M + H^+$), calcd for $C_{18}H_{14}O_3H$ 279.1021.



4c

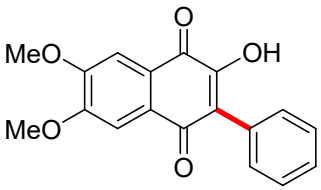
3-Hydroxy-6-methoxy-2-phenylnaphthalene-1,4-dione (4d): Prepared by following the procedure **A** and purified by column chromatography using EtOAc/hexane and isolated as red solid. Yield: 62% (34.7 mg); Mp.: 197-199 °C; IR (Neat): ν_{max} 3373, 2947, 1656, 1588, 1366, 1319, 1260, 1166, 1033, 925, 877 and 754 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 8.13 (1H, d, *J* = 8.5 Hz), 7.58 (1H, d, *J* = 3.0 Hz), 7.51-7.44 (5H, m), 7.39 (1H, tt, *J* = 7.5, 1.5 Hz), 7.26 (1H, dd, *J* = 8.5, 2.5 Hz), 3.96 (3H, s, OCH_3); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 183.1 (C, *C*=O), 182.0 (C, *C*=O), 163.5 (C), 151.9 (C, *C*-OH), 131.0 (C), 130.7 (2 x CH), 130.1 (C), 129.6 (CH), 128.6 (CH), 127.9 (2 x CH),



4d

126.1 (C), 121.9 (C), 121.3 (CH), 109.7 (CH), 56.0 (CH_3, OCH_3); HRMS m/z 281.0818 (M + H^+), calcd for $C_{17}H_{12}O_4H$ 281.0814.

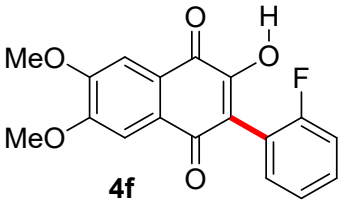
2-Hydroxy-6-methoxy-7-methyl-3-phenylnaphthalene-1,4-dione (4e): Prepared by following the procedure **A** and purified by column chromatography using EtOAc/hexane and isolated as red solid.



4e

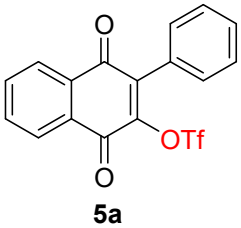
Yield: 60% (35.2 mg); Mp.: 200-202 °C; IR (Neat): ν_{max} 3319, 2362, 1640, 1573, 1506, 1312, 1270, 1219, 1154, 1071, 977 and 737 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.62 (1H, s), 7.59 (1H, s), 7.53 (1H, s, O*H*), 7.50 (1H, t, *J* = 1.5 Hz), 7.49 (1H, d, *J* = 1.0 Hz), 7.45 (2H, tt, *J* = 7.5, 1.5 Hz), 7.39 (1H, tt, *J* = 7.0, 1.5 Hz), 4.04 (3H, s, OCH_3), 4.03 (3H, s, OCH_3); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 183.4 (C, *C*=O), 181.0 (C, *C*=O), 154.8 (C), 152.8 (C, *C*-OH), 152.1 (C), 130.6 (2 x CH), 130.2 (C), 128.4 (CH), 128.1 (C), 127.8 (2 x CH), 123.4 (C), 121.0 (C), 109.0 (CH), 107.5 (CH), 56.6 (CH_3, OCH_3), 56.52 (CH_3, OCH_3); HRMS m/z 311.0919 (M + H^+), calcd for $C_{18}H_{14}O_5H$ 311.0919.

2-(3-Fluorophenyl)-3-hydroxy-6,7-dimethoxynaphthalene-1,4-dione (4f): Prepared by following the procedure **A** and purified by column chromatography using EtOAc/hexane and isolated as dark orange solid.



4f

Yield: 82% (53.8 mg); Mp.: 208-210 °C; IR (Neat): ν_{max} 3318, 2923, 2174, 2037, 1989, 1646, 1580, 1510, 1362, 1325, 1303, 1280, 1213, 1041, 891 and 784 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.70 (1H, s, O*H*), 7.60 (1H, s), 7.52 (1H, s), 7.42-7.38 (1H, m), 7.28 (1H, d, *J* = 7.5 Hz), 7.23 (1H, td, *J* = 10.0, 1.0 Hz), 7.08 (1H, dt, *J* = 8.5, 2.0 Hz), 4.03 (3H, s, OCH_3), 4.026 (3H, s, OCH_3); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 183.0 (C, *C*=O), 180.6 (C, *C*=O), 162.2 (C, d, *J* = 243.75 Hz, *C*-F), 154.8 (C, *C*-OH), 152.8 (C), 152.3 (C), 132.1 (C, d, *J* = 8.75 Hz), 129.2 (CH, d, *J* = 7.5 Hz), 127.9 (C), 126.4 (CH, d, *J* = 2.5 Hz), 123.2 (C), 119.6 (C, d, *J* = 2.5 Hz), 117.7 (CH, d, *J* = 22.5 Hz), 115.3 (CH, d, *J* = 21.25 Hz), 109.0 (CH), 107.5 (CH), 56.6 (CH_3, OCH_3), 56.5 (CH_3, OCH_3); ^{19}F NMR ($CDCl_3$, 375 MHz): δ −113.6; HRMS m/z 329.0828 (M + H^+), calcd for $C_{18}H_{13}FO_5H$ 329.0825.

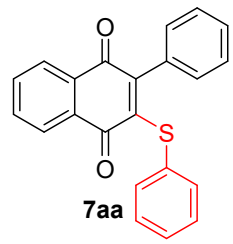


5a

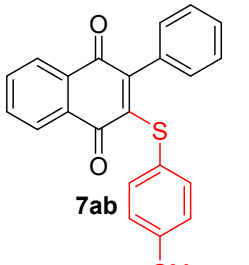
1,4-Dioxo-3-phenyl-1,4-dihydronaphthalen-2-yl trifluoromethanesulfonate (5a): Prepared by following the procedure **B** and purified by column chromatography using EtOAc/hexane and isolated as light yellow solid. Yield: 82% (62.7 mg); Mp.: 150-152 °C; IR (Neat): ν_{max} 2920, 2851, 1742, 1671, 1621, 1592, 1493, 1267, 1046, 968, 846 and 756 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 8.25 (1H, dd, *J* = 5.75, 3.0 Hz), 8.14 (1H, dd, *J* = 5.5, 4.0 Hz), 7.86 (2H, dd, *J* = 5.5, 3.5 Hz), 7.51 (3H, d,

J = 7.0 Hz), 7.40 (2H, dd, *J* = 7.25, 1.5 Hz); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 182.9 (C, *C*=O), 177.7 (C, *C*=O), 148.2 (C), 138.2 (C), 135.1 (CH), 134.7 (CH), 131.6 (C), 130.5 (CH), 130.3 (2 x CH), 130.0 (C), 128.2 (2 x CH), 127.5 (CH), 127.05 (C), 127.03 (CH), 118.0 (C, q, *J* = 318.75 Hz, *C*F_3); ^{19}F NMR ($CDCl_3$, 375 MHz): δ –74.51; HRMS m/z 405.0022 ($M + Na^+$), calcd for $C_{17}H_9F_3O_5SNa$ 405.0020.

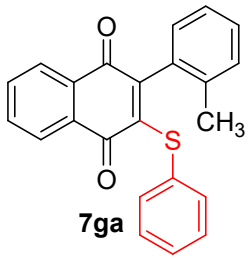
2-Phenyl-3-(phenylthio)naphthalene-1,4-dione (7aa): Prepared by following the procedure **C** and purified by column chromatography using EtOAc/hexane and isolated as orange solid. Yield: 92% (20.5 mg); Mp.: 124-126 °C; IR (Neat): ν_{max} 3052, 1669, 1650, 1584, 1492, 1470, 1312, 1278, 1253, 1121, 1067, 1023, 807 and 747 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.14 (1H, dd, *J* = 7.25, 1.5 Hz), 8.06 (1H, dd, *J* = 7.5, 1.0 Hz), 7.76 (1H, dt, *J* = 7.5, 1.5 Hz), 7.72 (1H, dt, *J* = 7.5, 1.5 Hz), 7.37-7.35 (3H, m), 7.24-7.19 (4H, m), 7.17-7.14 (3H, m); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 182.1 (C, *C*=O), 181.4 (C, *C*=O), 148.1 (C), 147.9 (C), 134.0 (CH), 133.65 (CH), 133.6 (C), 133.4 (C), 132.6 (C), 132.1 (C), 131.6 (2 x CH), 129.7 (2 x CH), 128.9 (2 x CH), 128.9 (CH), 127.8 (2 x CH), 127.5 (CH), 126.93 (CH), 126.9 (CH); HRMS m/z 343.0791 ($M + H^+$), calcd for $C_{22}H_{14}O_2SH$ 343.0793.



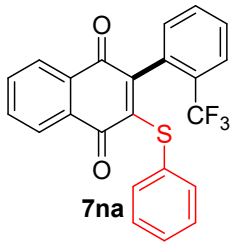
2-((4-Methoxyphenyl)thio)-3-phenylnaphthalene-1,4-dione (7ab): Prepared by following the procedure **C** and purified by column chromatography using EtOAc/hexane and isolated as red solid. Yield: 90% (21.8 mg); Mp.: 120-122 °C; IR (Neat): ν_{max} 2988, 1731, 1372, 1222, 1036, 829, 662, and 608 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.12-8.10 (1H, m), 8.06-8.04 (1H, m), 7.74 (1H, dt, *J* = 7.25, 1.5 Hz), 7.71 (1H, dt, *J* = 7.0, 1.0 Hz), 7.36-7.34 (3H, m), 7.19-7.17 (2H, m), 7.15 (1H, d, *J* = 2.0 Hz), 7.14 (1H, d, *J* = 2.0 Hz), 6.67 (1H, d, *J* = 2.0 Hz), 6.66 (1H, d, *J* = 2.0 Hz), 3.75 (3H, s, OC*H*$_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 182.1 (C, *C*=O), 181.9 (C, *C*=O), 159.5 (C), 148.8 (C), 146.6 (C), 134.3 (2 x CH), 133.9 (CH), 133.5 (CH), 133.47 (C), 132.6 (C), 132.1 (C), 129.7 (2 x CH), 128.7 (CH), 127.8 (2 x CH), 126.9 (CH), 126.8 (CH), 123.4 (C), 114.5 (2 x CH), 55.3 (CH_3, O*C*H_3); HRMS m/z 373.0896 ($M + H^+$), calcd for $C_{23}H_{16}O_3SH$ 373.0898.



2-(Phenylthio)-3-(o-tolyl)naphthalene-1,4-dione (7ga): Prepared by following the procedure **C** and purified by column chromatography using EtOAc/hexane and isolated as red semi-solid. Yield: 90% (20.8 mg); IR (Neat): ν_{max} 2921, 2852, 2360, 2337, 1668, 1591, 1276, 1255, 1128, 1084, 1128, 819, 748 and 716 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.13-8.11 (1H, m), 8.07-8.05 (1H, m), 7.75 (1H, dt, *J* = 7.25, 1.5 Hz), 7.72

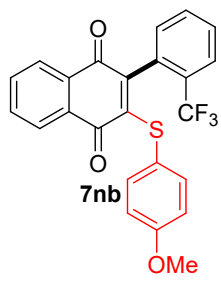


(1H, dt, J = 7.5, 1.5 Hz), 7.27 (1H, dt, J = 7.5, 1.5 Hz), 7.24-7.21 (2H, m), 7.20-7.17 (5H, m), 7.04 (1H, d, J = 1.5 Hz), 2.13 (3H, s); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 181.7 (C, *C*=O), 181.2 (C, *C*=O), 148.5 (C), 148.4 (C), 135.8 (C), 134.0 (CH), 133.6 (CH), 133.59 (C), 132.9 (C), 132.7 (C), 132.2 (C), 131.9 (2 x CH), 130.3 (CH), 128.93 (CH), 128.9 (2 x CH), 128.8 (CH), 127.7 (CH), 127.0 (CH), 126.9 (CH), 125.6 (CH), 20.0 (CH_3); HRMS m/z 357.0948 ($M + H^+$), calcd for $C_{23}H_{16}O_2SH$ 357.0949.

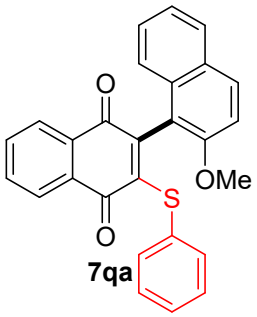


2-(Phenylthio)-3-(2-(trifluoromethyl)phenyl)naphthalene-1,4-dione (7na): Prepared by following the procedure **C** and purified by column chromatography using EtOAc/hexane and isolated as red solid. Yield: 93% (24.8 mg); Mp.: 141-143 °C; The enantiomers of **7na** were seperated by chiral stationary phase HPLC using a Daicel chiralpak ID column (hexane/2-propanol = 90:10, flow rate 1.0 mL/min, λ = 254 nm), t_R = 8.72 min (enantiomer I), t_R = 9.45 min (enantiomer II); IR (Neat): ν_{max} 3072, 2964, 2167, 1730, 1660, 1591, 1315, 1277, 1170, 1127, 1074, 768 and 747 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.12 (1H, dd, J = 7.5, 1.5 Hz), 8.06 (1H, dd, J = 7.5, 2.0 Hz), 7.77-7.71 (3H, m), 7.58 (1H, t, J = 7.5 Hz), 7.52 (1H, t, J = 7.5 Hz), 7.29-7.27 (2H, m), 7.23-7.19 (4H, m); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 181.6 (C, *C*=O), 180.5 (C, *C*=O), 148.1 (C), 146.9 (C), 134.1 (CH), 133.8 (CH), 132.7 (C), 132.68 (C), 132.2 (C), 131.93 (C), 131.87 (2 x CH), 131.7 (CH), 130.4 (CH), 129.1 (2 x CH), 129.0 (CH), 128.5 (C, q, J = 30.0 Hz), 127.9 (CH), 127.1 (CH), 126.9 (CH), 126.6 (CH, q, J = 5.0 Hz), 123.9 (C, q, J = 271.25 Hz, *C*F_3); ^{19}F NMR ($CDCl_3$, 375 MHz): δ −59.6; HRMS m/z 411.0666 ($M + H^+$), calcd for $C_{23}H_{13}F_3O_2SH$ 411.0667.

2-((4-Methoxyphenyl)thio)-3-(2-(trifluoromethyl)phenyl)naphthalene-1,4-dione (7nb): Prepared by following the procedure **C** and purified by column chromatography using EtOAc/hexane and isolated as red semi solid; Yield: 92% (26.3 mg); The enantiomers of **7nb** were seperated by chiral stationary phase HPLC using a Daicel chiralpak ID column (hexane/2-propanol = 90:10, flow rate 1.0 mL/min, λ = 254 nm), t_R = 16.07 min (enantiomer I), t_R = 16.94 min (enantiomer II); IR (Neat): ν_{max} 2929, 1658, 1591, 1493, 1314, 1277, 1249, 1170, 1126, 1075, 1050, 767 and 716 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.10-8.08 (1H, m), 8.06-8.04 (1H, m), 7.76-7.71 (2H, m), 7.70-7.68 (1H, m), 7.55 (1H, t, J = 7.5 Hz), 7.49 (1H, t, J = 8.0 Hz), 7.28 (1H, d, J = 2.0 Hz), 7.22 (1H, d, J = 2.0 Hz), 7.20 (1H, d, J = 8.0 Hz), 6.72 (1H, d, J = 2.0 Hz), 6.71 (1H, d, J = 2.0 Hz), 3.76 (3H, s, O*C*H_3); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 181.6 (C, *C*=O), 181.1 (C, *C*=O), 159.8 (C), 149.0 (C), 145.2 (C), 134.7 (2 x CH), 134.0 (CH), 133.7 (CH), 132.6 (CH), 132.1 (C), 131.9 (C), 131.6 (C), 130.6 (CH), 128.9 (CH), 128.3 (C, q, J =



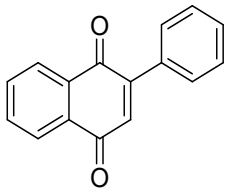
30.0 Hz), 127.0 (CH), 126.8 (CH), 126.6 (CH, q, J = 5.0 Hz), 123.9 (C, q, J = 272.5 Hz, CF_3), 122.1 (C), 114.6 (2 x CH), 55.3 (CH_3, OCH_3); ^{19}F NMR ($CDCl_3$, 375 MHz): δ –59.6; HRMS m/z 441.0773 ($M + H^+$), calcd for $C_{24}H_{15}F_3O_3SH$ 441.0772.



7qa

2-Methoxy-3'-(phenylthio)-[1,2'-binaphthalene]-1',4'-dione (7qa): Prepared by following the procedure **C** and purified by column chromatography using EtOAc/hexane and isolated as orange solid. Yield: 95% (26.08 mg); Mp.: 146-148 °C; The enantiomers of **7qa** were seperated by chiral stationary phase HPLC using a Daicel chiralpak ID column (hexane/2-propanol = 90:10, flow rate 1.0 mL/min, λ = 254 nm), t_R = 20.94 min (enantiomer I), t_R = 25.67 min (enantiomer II); IR (Neat): ν_{max} 2982, 2001, 1736, 1462, 1446, 1235, 1044, 934, 846, 787 and 723 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 8.14-8.12 (2H, m), 7.81 (1H, d, J = 9.0 Hz), 7.78 (1H, d, J = 8.5 Hz), 7.76-7.73 (2H, m), 7.48 (1H, d, J = 8.5 Hz), 7.42 (1H, dt, J = 6.75, 1.5 Hz), 7.35-7.32 (1H, m), 7.14 (1H, d, J = 9.0 Hz), 7.07-7.04 (3H, m), 7.01-6.98 (2H, m), 3.83 (3H, s, OCH_3); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 181.46 (C, *C*=O), 181.40 (C, *C*=O), 154.0 (C), 149.8 (C), 144.4 (C), 133.9 (CH), 133.4 (CH), 132.8 (C), 132.7 (C), 132.14 (C), 132.1 (2 x CH), 131.8 (C), 131.0 (CH), 128.7 (C), 128.4 (CH), 128.3 (2 x CH), 127.6 (CH), 127.06 (CH), 127.04 (CH), 126.99 (CH), 123.8 (CH), 123.6 (CH), 116.4 (C), 112.5 (CH), 56.1 (CH_3, OCH_3); HRMS m/z 423.1054 ($M + H^+$), calcd for $C_{27}H_{18}O_3SH$ 423.1055.

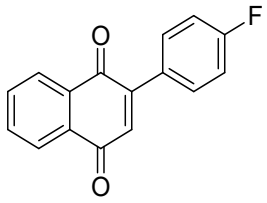
2-Phenylnaphthalene-1,4-dione (8a): Prepared by following the procedure **D** and purified by column chromatography using EtOAc/hexane and isolated as yellow solid; Yield: 76% (20.5 mg); Mp.: 97-99 °C;



8a

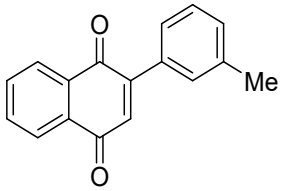
IR (Neat): ν_{max} 2922, 2852, 1662, 1587, 1331, 1304, 1242, 1081, 898 and 756 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 8.19-8.18 (1H, m), 8.13-8.11 (1H, m), 7.80-7.76 (2H, m), 7.57 (2H, dd, J = 7.5, 2.5 Hz), 7.47 (3H, dd, J = 5.0, 1.5 Hz), 7.08 (1H, s); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 185.1 (C, *C*=O), 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), 125.9 (CH); HRMS m/z 235.0755 ($M + H^+$), calcd for $C_{16}H_{10}O_2H$ 235.0759.

2-(4-Fluorophenyl)naphthalene-1,4-dione (8d): Prepared by following the procedure **D** and purified by column chromatography using EtOAc/hexane and isolated as yellow solid; Yield: 70% (20.3 mg); Mp.: 116-118 °C; IR (Neat): ν_{max} 2921, 2851, 1667, 1589, 1545, 1505, 1327, 1252, 1226, 1160, 1111, 1001, 793 and 726 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 8.19-8.17 (1H, m), 8.13-8.11 (1H, m), 7.80-7.78 (2H, m), 7.60-7.57 (2H, m), 7.17 (2H, tt, *J* = 8.5, 2.5 Hz), 7.06 (1H, s); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 185.0 (C, *C*=O), 184.3 (C, *C*=O), 163.9 (C, d, *J* = 250.0 Hz, *C*-F), 147.0 (C), 135.0 (CH), 133.9 (2 x CH, d, *J* = 1.25 Hz), 132.3 (C), 132.10 (C), 131.5 (2 x CH, d, *J* = 7.5 Hz), 129.4 (C, d, *J* = 3.75 Hz), 127.1 (CH), 126.0 (CH), 115.6 (2 x CH, d, *J* = 21.25 Hz); ^{19}F NMR ($CDCl_3$, 375 MHz): δ –110.28; HRMS m/z 253.0659 ($M + H^+$), calcd for $C_{16}H_9FO_2H$ 253.0665.



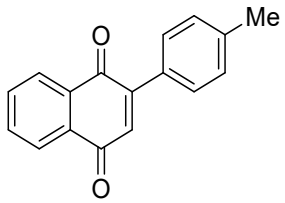
8d

2-(m-Tolyl)naphthalene-1,4-dione (8h): Prepared by following the procedure **D** and purified by column chromatography using EtOAc/hexane and isolated as yellow solid; Yield: 70% (20.0 mg); Mp.: 126-128 °C; IR (Neat): ν_{max} 3301, 2920, 1663, 1589, 1480, 1457, 1325, 1307, 1260, 1245, 1219, 1119, 1082, 910 and 778 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 8.19-8.17 (1H, m), 8.12-8.10 (1H, m), 7.79-7.45 (2H, m), 7.38-7.34 (3H, m), 7.30-7.26 (1H, m), 7.06 (1H, s), 2.42 (3H, s, C*H*$_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 185.1 (C, *C*=O), 184.4 (C, *C*=O), 148.3 (C), 138.1 (C), 135.1 (CH), 133.8 (CH), 133.7 (CH), 133.2 (C), 132.5 (C), 132.0 (C), 130.8 (CH), 130.0 (CH), 128.3 (CH), 127.0 (CH), 126.5 (CH), 125.9 (CH), 21.4 (CH_3); HRMS m/z 249.0913 ($M + H^+$), calcd for $C_{17}H_{12}O_2H$ 249.0916.



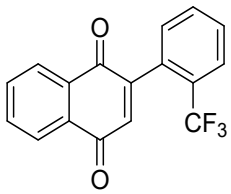
8h

2-(p-Tolyl)naphthalene-1,4-dione (8i): Prepared by following the procedure **D** and purified by column chromatography using EtOAc/hexane and isolated as yellow solid; Yield: 76% (21.7 mg); Mp.: 130-132 °C; IR (Neat): ν_{max} 3459, 2922, 2854, 1688, 1651, 1593, 1510, 1346, 1301, 1247, 1208, 1187, 1047, 966, 828, 796 and 773 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 8.19-8.17 (1H, m), 8.12-8.10 (1H, m), 7.79-7.56 (2H, m), 7.49 (2H, d, *J* = 8.0 Hz), 7.28 (2H, d, *J* = 8.0 Hz), 7.06 (1H, s), 2.42 (3H, s, C*H*$_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 185.2 (C, *C*=O), 185.1 (C, *C*=O), 148.0 (C), 140.4 (C), 134.6 (CH), 133.8 (CH), 133.7 (CH), 132.5 (C), 132.1 (C), 130.5 (C), 129.4 (2 x CH), 129.2 (2 x CH), 127.0 (CH), 125.9 (CH), 21.4 (CH_3); HRMS m/z 249.0914 ($M + H^+$), calcd for $C_{17}H_{12}O_2H$ 249.0916.



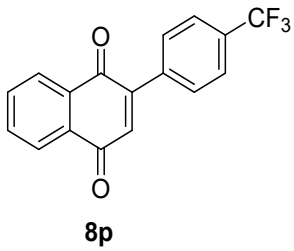
8i

2-(2-(Trifluoromethyl)phenyl)naphthalene-1,4-dione (8n): Prepared by following the procedure **D** and purified by column chromatography using EtOAc/hexane and isolated as yellow solid; Yield: 60% (20.8 mg); Mp.: 122-124 °C; IR (Neat): ν_{max} 2921, 2851, 2359, 1666, 1619, 1594, 1447, 1344, 1313, 1254, 1169, 1109, 1068, 1035, 1020, 767 and 716 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 8.16-8.14 (2H, m), 7.81-7.77 (3H, m), 7.63 (1H, t, *J* = 7.5 Hz), 7.58 (1H, t, *J* = 8.0 Hz), 7.31 (1H, d, *J* = 7.5 Hz), 6.94 (1H, s); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 184.6 (C, *C*=O), 183.8 (C, *C*=O), 148.4 (C), 136.70 (C), 136.69 (CH), 134.08 (CH), 134.04 (CH), 132.1 (C), 131.58 (C), 131.5 (CH), 130.6 (CH), 129.3 (CH), 128.9 (C, q, *J* = 30.0 Hz), 127.0 (CH), 126.5 (CH, q, *J* = 3.75 Hz), 126.3 (CH), 126.0 (C, q, *J* = 272.5 Hz, *C*F_3); ^{19}F NMR ($CDCl_3$, 375 MHz): δ –57.96; HRMS m/z 303.0635 (M + H^+), calcd for $C_{17}H_9F_3O_2H$ 303.0633.



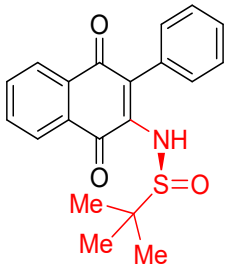
8n

2-(4-(Trifluoromethyl)phenyl)naphthalene-1,4-dione (8p): Prepared by following the procedure **D** and purified by column chromatography using EtOAc/hexane and isolated as yellow solid; Yield: 74% (25.7 mg); Mp.: 132-134 °C; IR (Neat): ν_{max} 3069, 2361, 1664, 1618, 1593, 1343, 1312, 1299, 1269, 1209, 1107, 1068, 1035, 810 and 766 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 8.21-8.19 (1H, m), 8.15-8.13 (1H, m), 7.83-7.99 (2H, m), 7.74 (2H, d, *J* = 8.5 Hz), 7.69 (2H, d, *J* = 8.0 Hz), 7.11 (1H, s); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 184.8 (C, *C*=O), 183.9 (C, *C*=O), 146.9 (C), 136.9 (C), 136.1 (CH), 134.14 (CH), 134.12 (CH), 132.2 (C), 132.0 (C), 131.8 (C, q, *J* = 32.5 Hz), 129.8 (2 x CH), 127.2 (CH), 126.0 (C, q, *J* = 270.0 Hz, *C*F_3), 126.2 (CH), 125.4 (2 x CH, q, *J* = 3.75 Hz); ^{19}F NMR ($CDCl_3$, 375 MHz): δ –62.89; HRMS m/z 303.0638 (M + H^+), calcd for $C_{17}H_9F_3O_2H$ 303.0633.



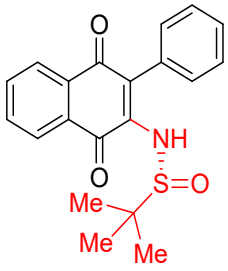
8p

(*S*)-N-(1,4-Dioxo-3-phenyl-1,4-dihydronaphthalen-2-yl)-2-methylpropane-2-sulfinamide (+)-10a: Prepared by following the procedure **E** and purified by column chromatography using EtOAc/hexane and isolated as orange solid; Yield: 70% (37.1 mg); Mp.: 138-140 °C; The enantiomeric excess (*ee*) was determined by chiral stationary phase HPLC using a Daicel chiralpak AD-H column (hexane/2-propanol = 90:10, flow rate 1.0 mL/min, λ = 254 nm), t_R = 32.38 min (major), t_R = 47.92 min (minor); $[\alpha]_D^{25}$ = +110.0° [c = 0.1, $CHCl_3$, 99.6% *ee*]; IR (Neat): ν_{max} 2921, 2851, 1734, 1663, 1615, 1328, 1291, 1173, 1085, 1042, 997, 843, 721 and 704 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 8.12 (2H, dd, *J* = 7.75, 1.0 Hz), 7.77 (1H, dt, *J* = 7.5, 1.0 Hz), 7.72 (1H, dt, *J* = 7.5,



(+)-10a

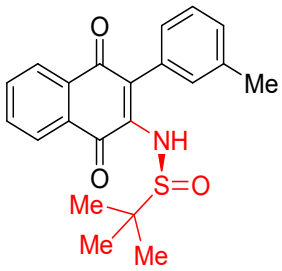
1.0 Hz), 7.47 (2H, t, *J* = 7.0 Hz), 7.43 (1H, t, *J* = 7.5 Hz), 7.32 (2H, d, *J* = 7.0 Hz), 6.94 (1H, s, N*H*), 1.13 (9H, s, 3 x C*H*$_3$) ; ^{13}C NMR ($CDCl_3$, DEPT-135) δ 182.9 (C, *C*=O), 181.6 (C, *C*=O), 142.1 (C), 134.8 (CH), 133.2 (CH), 132.3 (C), 131.8 (C), 130.3 (C), 130.2 (2 x CH), 128.9 (CH), 128.7 (2 x CH), 126.8 (CH), 126.6 (C), 126.5 (CH), 57.7 (C), 22.0 (3 x *C*H$_3$); HRMS m/z 354.1164 (M + H$^+$), calcd for $C_{20}H_{19}NO_3SH$ 354.1164.



(-)-10a

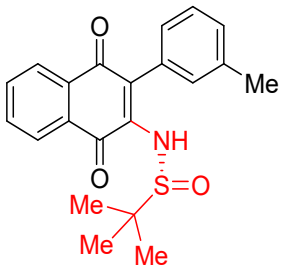
(*R*)-N-(1,4-Dioxo-3-phenyl-1,4-dihydronaphthalen-2-yl)-2-methylpropane-2-sulfinamide (-)-10a: Prepared by following the procedure **E** and purified by column chromatography using EtOAc/hexane and isolated as orange solid; Yield: 70% (37.1 mg); Mp.: 138-140 °C; The enantiomeric excess (*ee*) was determined by chiral stationary phase HPLC using a Daicel chiralpak AD-H column (hexane/2-propanol = 90:10, flow rate 1.0 mL/min, λ = 254 nm), t_R = 32.70 min (minor), t_R = 46.29 min (major); $[\alpha]_D^{25}$ = -97.0^o [c = 0.1, $CHCl_3$, 99.6% *ee*].

(*S*)-N-(1,4-Dioxo-3-(m-tolyl)-1,4-dihydronaphthalen-2-yl)-2-methylpropane-2-sulfinamide (+)-10h: Prepared by following the procedure **E** and purified by column chromatography using EtOAc/hexane and isolated as orange solid; Yield: 75% (41.3 mg); Mp.: 138-140 °C; The enantiomeric excess (*ee*) was determined by chiral stationary phase HPLC using a Daicel chiralpak AD-H column (hexane/2-propanol = 90:10, flow rate 1.0 mL/min, λ = 254 nm), t_R = 32.15 min (major), t_R = 46.11 min (minor); $[\alpha]_D^{25}$ = +103.0^o [c = 0.1, $CHCl_3$, 99.6% *ee*]; IR (Neat): ν_{max} 2922, 2852, 1735, 1664, 1595, 1460, 1406, 1362, 1292, 1237, 1185, 1091, 1042, 1005, 782 and 719 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.14 (2H, d, *J* = 8.0 Hz), 7.78 (1H, dt, *J* = 7.5, 1.5 Hz), 7.73 (1H, dt, *J* = 7.5, 1.0 Hz), 7.36 (1H, t, *J* = 8.0 Hz), 7.24 (1H, d, *J* = 7.5 Hz), 7.12 (2H, d, *J* = 7.5 Hz), 6.89 (1H, s, N*H*), 2.39 (3H, s, C*H*$_3$), 1.13 (9H, s, 3 x C*H*$_3$) ; ^{13}C NMR ($CDCl_3$, DEPT-135) δ 183.0 (C, *C*=O), 181.7 (C, *C*=O), 142.2 (C), 138.4 (C), 134.8 (CH), 133.2 (CH), 132.4 (C), 131.7 (C), 130.8 (CH), 130.4 (C), 129.7 (CH), 128.7 (CH), 127.3 (CH), 127.0 (C), 126.9 (CH), 126.5 (CH), 57.6 (C), 22.1 (3 x *C*H$_3$), 21.4 (*C*H$_3$); HRMS m/z 368.1320 (M + H$^+$), calcd for $C_{21}H_{21}NO_3SH$ 368.1320.



(+)-10h

(*R*)-N-(1,4-Dioxo-3-(m-tolyl)-1,4-dihydronaphthalen-2-yl)-2-methylpropane-2-sulfinamide (-)-10h:



(-)-10h

Prepared by following the procedure **E** and purified by column chromatography using EtOAc/hexane and isolated as orange solid; Yield: 75% (41.3 mg); Mp.: 138-140 °C; The enantiomeric excess (*ee*) was determined by chiral stationary phase HPLC using a Daicel chiralpak AD-H column (hexane/2-propanol = 90:10, flow rate 1.0 mL/min, λ = 254 nm), t_R = 33.37 min (minor), t_R = 45.65 min (major); $[\alpha]_D^{25}$ = -124.0° [c = 0.1, $CHCl_3$, 99.6% *ee*].

References:

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