A novel manganese(III) acetate mediated reaction between 2-benzoyl-1,4-naphthoquinones and 1,3-dicarbonyl compounds

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A manganese(III)-mediated reaction between 2-benzoyl-1,4-naphthoquinones and 1,3-dicarbonyl compounds is described. This reaction provides an effective method for the synthesis of naphtho[2,3-*c*]furan-4,9-diones and naphthacene-5,12-diones, and it shows fair to high chemoselectivity depending on the electronic effect of the benzoyl group substituent on the reactants. With ethyl benzoylacetate and 1,3-diketones, the novel naphtho[2,3-*c*]furan-4,9-diones were produced effectively with high selectivity.

Introduction

Carbon–carbon bond-forming reactions mediated by radicals have received considerable attention in organic synthesis during the last two decades.[1,2] Compounds containing the quinone group represent an important class of biologically active molecules that are widespread in nature.[3] Oxidative free-radical reaction mediated by metal salts has received considerable attention in organic synthesis for the construction of carbon–carbon bonds. Among these, manganese(III) acetate and cerium(IV) ammonium nitrate have been used most efficiently.[2,4–6] The free-radical reaction of 1,4-naphthoquinones has been reported.[6,7] Previously, we found that the manganese(III) acetate mediated oxidative free-radical reaction of 2-benzyl-(3-ethoxycarbonylmethyl)-1,4-naphthoquinones produced naphthacene-5,12-diones effectively. In contrast, with 2-benzoyl-(3-ethoxycarbonylmethyl)-1,4-naphthoquinones, in addition to the expected 6-hydroxynaphthacene-5,12-diones, the novel naphtho[2,3-*c*]furan-4,9-diones were also produced as the major products. This is presumably due to the electron deficiency of the benzoyl group, which disfavours the intramolecular cyclization of the electrophilic radical intermediate onto the C–C double bond of the benzoyl group.[6g] These naphthacene-5,12-diones can also be generated directly from the intermolecular oxidative free-radical reaction of 2-benzyl-1,4-naphthoquinones with 1,3-dicarbonyl compounds.[6d] This report describes our results of the manganese(III) acetate mediated reactions between 2-benzoyl-1,4-naphthoquinones and 1,3-dicarbonyl compounds.

Results and discussion

Table 1 Reaction with β-ketoesters

Entry	Quinone	β-Ketoester	Products (yield (%))
1	**1a**: R^1 = H, R^2 = H	**2a**: R^3 = ^{n}PrCO	**3a** (46), **4a** (20)
2	**1b**: R^1 = H, R^2 = Me	**2a**: R^3 = ^{n}PrCO	**3b** (41), **4b** (22)
3	**1c**: R^1 = H, R^2 = Br	**2a**: R^3 = ^{n}PrCO	**3c** (48), **4c** (3)
4	**1d**: R^1 = H, R^2 = Cl	**2a**: R^3 = ^{n}PrCO	**3d** (54), **4d** (3)
5	**1e**: R^1 = Me, R^2 = H	**2a**: R^3 = ^{n}PrCO	**3e** (51), **4e** (15)
6	**1f**: R^1 = Me, R^2 = Me	**2a**: R^3 = ^{n}PrCO	**3f** (53), **4f** (16)
7	**1g**: R^1 = Br, R^2 = H	**2a**: R^3 = ^{n}PrCO	**3g** (50), **4g** (5)
8	**1h**: R^1 = Cl, R^2 = H	**2a**: R^3 = ^{n}PrCO	**3h** (45), **4h** (6)
9	**1i**: R^1 = Cl, R^2 = Cl	**2a**: R^3 = ^{n}PrCO	**3i** (46), **4i** (6)
10	**1a**: R^1 = H, R^2 = H	**2b**: R^3 = ^{i}PrCO	**3a** (50), **4a** (12)
11	**1b**: R^1 = H, R^2 = Cl	**2b**: R^3 = ^{i}PrCO	**3d** (50), **4d** (2)
12	**1a**: R^1 = H, R^2 = H	**2c**: R^3 = PhCO	**3a** (54), **4a** (3)
13	**1b**: R^1 = H, R^2 = Me	**2c**: R^3 = PhCO	**3b** (48), **4b** (3)
14	**1c**: R^1 = H, R^2 = Br	**2c**: R^3 = PhCO	**3c** (48), **4c** (2)
15	**1d**: R^1 = H, R^2 = Cl	**2c**: R^3 = PhCO	**3d** (52), **4d** (2)
16	**1e**: R^1 = Me, R^2 = H	**2c**: R^3 = PhCO	**3e** (68), **4e** (6)
17	**1f**: R^1 = Me, R^2 = Me	**2c**: R^3 = PhCO	**3f** (65), **4f** (5)
18	**1g**: R^1 = Br, R^2 = H	**2c**: R^3 = PhCO	**3g** (42), **4g** (3)
19	**1h**: R^1 = Cl, R^2 = H	**2c**: R^3 = PhCO	**3h** (45), **4h** (5)
20	**1i**: R^1 = Cl, R^2 = Cl	**2c**: R^3 = PhCO	**3i** (44), **4i** (2)

We first tried the manganese(III)-mediated reaction of 2-benzoyl-1,4-naphthoquinones **1** with β-ketoesters **2** (Scheme 1). When 2-benzoyl-1,4-naphthoquinone (**1a**) was treated with ethyl butyrylacetate (**2a**, R^3 = ^{n}PrCO) and manganese(III) acetate in acetic acid at 70 °C, in addition to the expected naphthacene 5,12-dione **4a** (20%), the novel naphtho[2,3-*c*]furan-4,9-dione **3a** was also obtained in 46% yield (Table 1, entry 1). Although the mechanistic details of this reaction are unclear, **3a** and **4a** may be formed by the reaction route presented in Scheme 1. Manganese(III) acetate oxidation of **2a** produces radical **5a**. This radical intermediate **5a** undergoes intermolecular addition to the quinone ring followed by oxidation to give **6a**,[8] which was then oxidized by manganese(III) acetate to generate **7a**. Radical **7a** undergoes either a six-membered-ring free-radical cyclization and subsequent aromatization to give **8a**, which undergoes a further retro-Claisen condensation to produce **4a** (path a)[9] or oxidation to give **9a** (path b). This cation intermediate **9a** undergoes a five-membered-ring cyclization followed by retro-Claisen condensation to generate **3a**.[10] Analogous results were obtained with other 2-benzoyl-1,4-naphthoquinones **1**, and the results are summarized in Table 1 (entries 1–9). In all cases, naphtho[2,3-*c*]furan-4,9-dione **3** and naphthacene-5,12-dione **4** were obtained in fair yields. Contrary to the reactions of 2-benzyl-1,4-naphthoquinones with β-ketoesters,[6d] **3** is the major product. It indicates that the electron deficiency of the benzoyl group disfavours the intramolecular cyclization of electrophilic radical **7** onto the C–C double bond of benzoyl group (path a). Interestingly,

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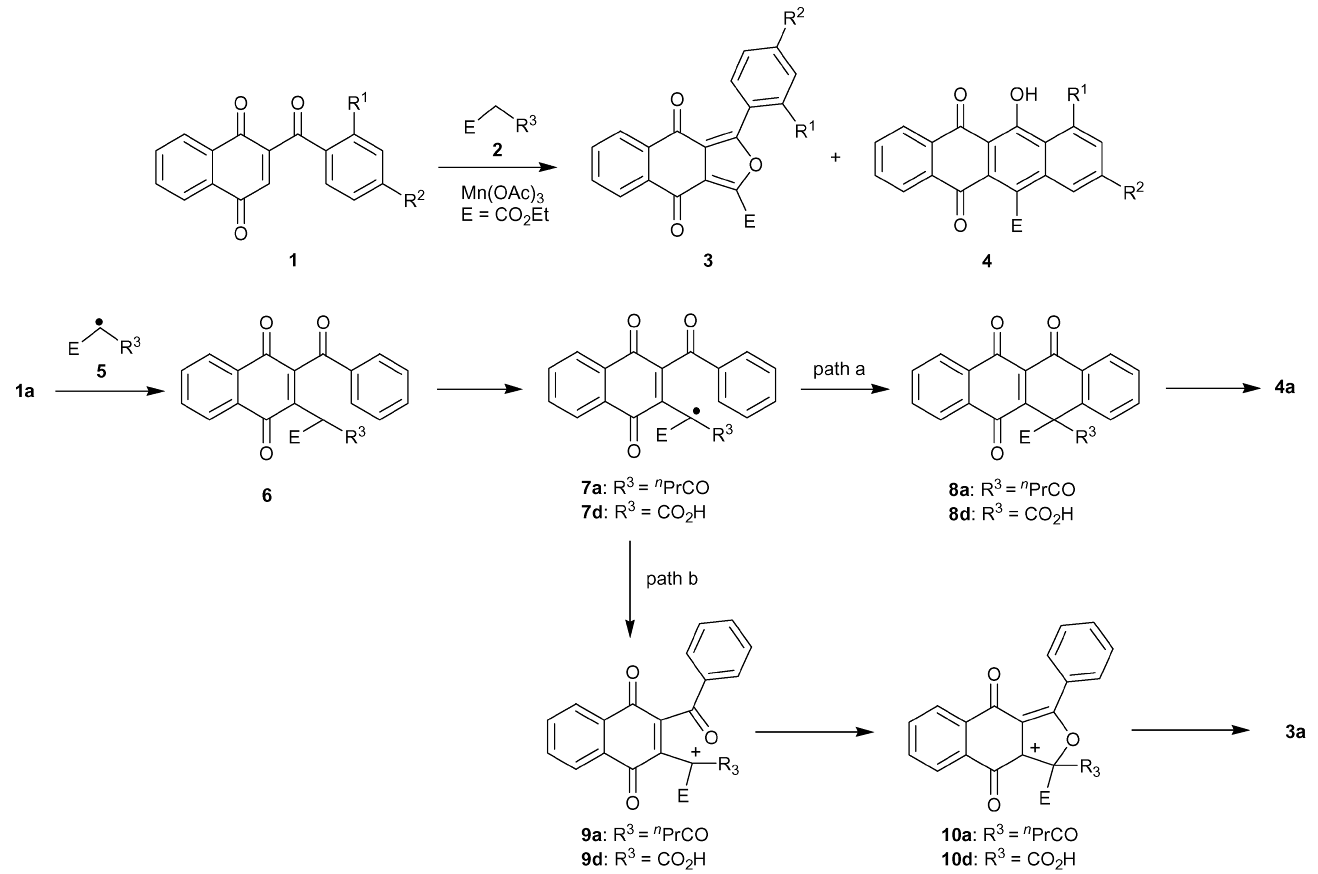


Scheme 1

the reaction of **1** bearing an additional electron-withdrawing halogeno group gave the corresponding products **3** and **4** with an excellent **3**/**4** ratio (entries 3, 4, 7–9). These results can be rationalized by considering that the electron deficiency of radical intermediate **7** makes the rate of six-membered-ring cyclization to the benzene ring bearing an electron-withdrawing halogeno group much slower (path a), making the competitive oxidation of **7** the major route (path b). The formation of naphtho[2,3-*c*]furan-4,9-diones is interesting, because they are one of the subsets of natural products containing a *c*-fused furan ring.[3c] To improve the chemoselectivity, reaction of 2-benzoyl-1,4-naphthoquinone **1a** with other β-ketoesters was next investigated. Reaction of 2-benzoyl-1,4 naphthoquinone **1a** with ethyl isobutyrylacetate (**2b**, $\mathrm{R^3 = {}^iPrCO}$) and manganese(III) acetate in acetic acid afforded **3a** and **4a** in 50% and 12% yields, respectively (entry 10). The **3a**/**4a** ratio rose to 54 : 3 when ethyl benzoylacetate (**2c**, $\mathrm{R^3 = PhCO}$) was employed (entry 12). The selectivity of this reaction increases as the size of substituents ($\mathrm{R^3}$) increases. This can be attributed to the steric effect exerted by $\mathrm{R^3}$ group – the cyclization of **7** (path a) is retarded by the larger $\mathrm{R^3}$ group and the oxidation of **7** becomes the major route (path b). On the basis of this finding, by choosing ethyl benzoylacetate (**2c**) as the radical precursor, the generalities of this reaction were examined with a variety of 2-benzoyl-1,4-naphthoquinones **1**. The results are summarized in Table 1 (entries 12–20). In all cases, 2-benzoyl-1,4-naphthoquinone **1** was converted to the corresponding product **3** with high selectivity.

Next, we investigated this manganese(III)-mediated reaction with ethyl hydrogen malonate (**2d**). Treatment of 2-benzoyl-1,4-naphthoquinone (**1a**) with **2d** and manganese(III) acetate under the above conditions led to the formation of **3a** and **4a** in 19% and 38% yields, respectively (Table 2, entry 1). These two products **3a** and **4a** were presumably generated by the decarboxylation of **8d** and **10d**, respectively. Compounds **8d** and **10d** were formed by a route similar to that for **8a** and **10a** (Scheme 1). The scope of this reaction is shown in Table 2 (entries 1–9). In contrast to the reaction between 2-benzoyl-1,4-naphthoquinones **1** and β-ketoesters, this reaction is less selective, particularly for 2-benzoyl-1,4-naphthoquinones **1a** and **1b**, for which naphthacene-5,12-diones **4a** and **4b** are the major products (entries 1 and 2). It can be rationalized that the radical intermediate **7d** bearing a weaker electron-withdrawing $\mathrm{CO_2H}$ group is less electron-deficient, and this makes the intramolecular cyclization of **7d** (path a) faster than that of **7a**. Similar to the results shown above for ethyl butyrylacetate (**2a**), the presence of an additional electron-withdrawing halogeno group on the benzoyl group appears to increase the ratio of **3**/**4**, producing naphtho[2,3-*c*]furan-4,9-dione **3** as the major product. In particular, naphtho[2,3-*c*]furan-4,9-diones **3g–i** were produced with high selectivities from the corresponding quinone **1** bearing an *ortho*-halogeno group (entries 7–9).

We have continued to study this manganese(III) mediated reaction with 1,3-diketones **11** (Eq. 1). When 2-benzoyl-1,4-naphthoquinone **1a** was treated with pentanedione (**11a**) and manganese(III) acetate, **12a** and **13a** were obtained in 41% and 8% yields, respectively (Table 3, entry 1). Other examples were also summarized in Table 3. In most cases, 2-benzoyl-1,4-naphthoquinone **1** was converted to the corresponding furan

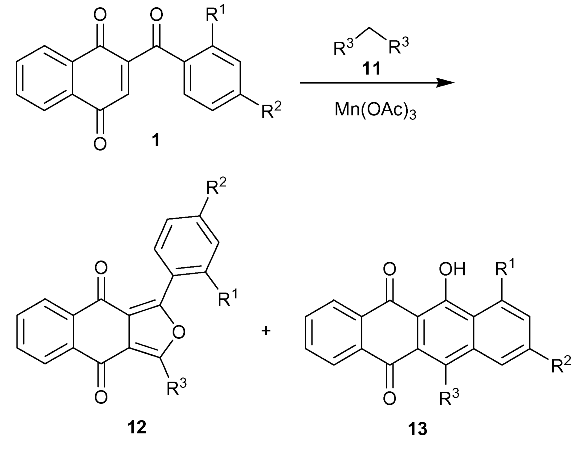
Table 2 Reaction with ethyl hydrogen malonate

Entry	Quinone	Malonate	Products (yield (%))
1	**1a**: R^1 = H, R^2 = H	**2d**: R^3 = CO_2H	**3a** (19), **4a** (38)
2	**1b**: R^1 = H, R^2 = Me	**2d**: R^3 = CO_2H	**3b** (12), **4b** (39)
3	**1c**: R^1 = H, R^2 = Br	**2d**: R^3 = CO_2H	**3c** (26), **4c** (16)
4	**1d**: R^1 = H, R^2 = Cl	**2d**: R^3 = CO_2H	**3d** (32), **4d** (16)
5	**1e**: R^1 = Me, R^2 = H	**2d**: R^3 = CO_2H	**3e** (30), **4e** (14)
6	**1f**: R^1 = Me, R^2 = Me	**2d**: R^3 = CO_2H	**3f** (34), **4f** (19)
7	**1g**: R^1 = Br, R^2 = H	**2d**: R^3 = CO_2H	**3g** (50), **4g** (5)
8	**1h**: R^1 = Cl, R^2 = H	**2d**: R^3 = CO_2H	**3h** (51), **4h** (4)
9	**1i**: R^1 = Cl, R^2 = Cl	**2d**: R^3 = CO_2H	**3i** (57), **4i** (2)

Table 3 Reaction with 1,3-diketones

Entry	Quinone	1,3-Diketone	Products (yield (%))
1	**1a**: R^1 = H, R^2 = H	**11a**: R^3 = MeCO	**12a** (41), **13a** (8)
2	**1b**: R^1 = H, R^2 = Me	**11a**: R^3 = MeCO	**12b** (42), **13b** (9)
3	**1c**: R^1 = H, R^2 = Br	**11a**: R^3 = MeCO	**12c** (43)
4	**1d**: R^1 = H, R^2 = Cl	**11a**: R^3 = MeCO	**12d** (47)
5	**1e**: R^1 = Me, R^2 = H	**11a**: R^3 = MeCO	**12e** (40), **13c** (9)
6	**1f**: R^1 = Me, R^2 = Me	**11a**: R^3 = MeCO	**12f** (47), **13d** (7)
7	**1g**: R^1 = Br, R^2 = H	**11a**: R^3 = MeCO	**12g** (52)
8	**1h**: R^1 = Cl, R^2 = H	**11a**: R^3 = MeCO	**12h** (56)
9	**1i**: R^1 = Cl, R^2 = Cl	**11a**: R^3 = MeCO	**12i** (65)
10	**1a**: R^1 = H, R^2 = H	**11b**: R^3 = ^{i}PrCO	**12j** (47)
11	**1b**: R^1 = H, R^2 = Me	**11b**: R^3 = ^{i}PrCO	**12k** (38)
12	**1c**: R^1 = H, R^2 = Br	**11b**: R^3 = ^{i}PrCO	**12l** (38)
13	**1a**: R^1 = H, R^2 = H	**11c**: R^3 = PhCO	**12m** (70)
14	**1b**: R^1 = H, R^2 = Me	**11c**: R^3 = PhCO	**12n** (71)
15	**1c**: R^1 = H, R^2 = Br	**11c**: R^3 = PhCO	**12o** (65)
16	**1d**: R^1 = H, R^2 = Cl	**11c**: R^3 = PhCO	**12p** (70)
17	**1e**: R^1 = Me, R^2 = H	**11c**: R^3 = PhCO	**12q** (74)
18	**1f**: R^1 = Me, R^2 = Me	**11c**: R^3 = PhCO	**12r** (70)
19	**1g**: R^1 = Br, R^2 = H	**11a**: R^3 = PhCO	**12s** (82)
20	**1h**: R^1 = Cl, R^2 = H	**11a**: R^3 = PhCO	**12t** (74)
21	**1i**: R^1 = Cl, R^2 = Cl	**11a**: R^3 = PhCO	**12u** (76)

product **12** in high selectivity. Again, the selectivity of this reaction increases as the size of 1,3-diketone increases.



(1)

Conclusions

1,4-Naphthquinone **6**, generated by the free-radical addition of radical intermediate **5** to the C–C double bond of the quinone ring, undergoes efficient manganese(III)-mediated cyclization reactions. This reaction provides a method for the synthesis of naphtho[2,3-*c*]furan-4,9-diones and naphthacene-5,12-diones from readily available 2-benzoyl-1,4-naphthoquinones and 1,3-dicarbonyl compounds. The product distributions are highly dependent on the 1,3-dicarbonyl compounds used and the electronic effect of the substituents on benzoyl groups. With ethyl benzoylacetate and 1,3-diketones, the novel naphtho[2,3-*c*]furan-4,9-diones were produced effectively in high selectivities.

Experimental

General considerations

Melting points are uncorrected. Infrared spectra were taken with a Hitachi 260-30 spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AVANCE-300, AMX-400 or AVANCE-500 spectrometer. Chemical shifts are reported in ppm relative to TMS as internal reference. Elemental analyses were performed with Heraeus CHN-Rapid Analyzer. Mass spectra were recorded on a Jeol JMS-SX 102 A mass spectrometer. Analytical thin-layer chromatography was performed with precoated silica gel 60 F-254 plates (0.25 mm thick) from EM Laboratories and visualized by UV. The reaction mixture was purified by column chromatography over silica gel (70–230 mesh) from EM Laboratories. The starting 2-benzoyl-1,4-naphthoquinones **1** were synthesized by the CAN oxidative demethylation[11] of the corresponding 2-benzoyl-1,4-dimethoxynaphthalenes.[12] The spectral data of **3a–h** and **4a–f** have been reported.[6g]

Typical experimental procedure for the reaction between 2-benzoyl-1,4-naphthoquinones and β-ketoesters

A mixture of 2-benzoyl-1,4-naphthoquinone (**1a**) (162 mg, 0.62 mmol), ethyl butyrylacetate (**2a**) (385 mg, 2.43 mmol) and manganese(III) acetate (654 g, 2.44 mmol) in acetic acid (10 cm^3) was heated at 70 °C for 30 min. The reaction mixture was diluted with ethyl acetate (100 cm^3), washed with saturated aqueous sodium bisulfite (50 cm^3), water (3 × 50 cm^3), aqueous saturated sodium bicarbonate (3 × 50 cm^3), dried (Na_2SO_4), and concentrated *in vacuo.* The crude product was purified by column chromatography over silica gel (20 g) (eluting with 2 : 1 dichloromethane–hexane) followed by recrystallization ($CHCl_3$–hexane) to give **3a** (98 mg, 46%) and **4a** (42 mg, 20%).

Typical experimental procedure for the reaction between 2-benzoyl-1,4-naphthoquinones and ethyl hydrogen malonate

A mixture of 2-benzoyl-1,4-naphthoquinone (**1a**) (153 mg, 0.57 mmol), ethyl hydrogen malonate (**2d**) (307 mg, 2.32 mmol) and manganese(III) acetate (614 mg, 2.29 mmol) in acetic acid (10 cm^3) was heated at 70 °C for 1 h, and more ethyl hydrogen malonate (**2d**) (153 mg, 1.15 mmol) and manganese(III) acetate (309 mg, 1.15 mmol) was then added. After being stirred for 1 h, the reaction mixture was worked up as described above and the crude product was purified by column chromatography over silica gel (20 g) (eluting with 2 : 1 dichloromethane–hexane) followed by recrystallization ($CHCl_3$–hexane) to give **3a** (39 mg, 19%) and **4a** (76 mg, 38%).

3-(2,4-Dichlorophenyl)-4,9-dioxo-4,9-dihydronaphtho[2,3-*c*]-furan-1-carboxylic acid ethyl ester 3i. Yellow needles; mp 179–180 °C (from $CHCl_3$–hexane); (Found: C, 60.78; H, 2.96.

$C_{21}H_{12}Cl_2O_5$ requires C, 60.74; H, 2.91%); $\nu_{max}(CHCl_3)/cm^{-1}$ 3020, 1730, 1685, 1585 and 1285; δ_H(400 MHz; $CDCl_3$; Me_4Si) 1.49 (3 H, t, *J* 7.1, CH_3), 4.54 (2 H, q, *J* 7.1, OCH_2), 7.43 (1 H, dd, *J* 8.3 and 1.9, ArH), 7.60 (1 H, d, *J* 1.9, ArH), 7.65 (1 H, d, *J* 8.3, ArH), 7.77–7.85 (2 H, m, ArH), 8.20–8.26 (1 H, m, ArH) and 8.31–8.37 (1 H, m, ArH); δ_C(100.6 MHz; $CDCl_3$; Me_4Si) 14.2 (q), 62.6 (t), 120.9 (s), 124.7 (s), 125.6 (s), 127.11 (d), 127.16 (d), 128.0 (d), 130.2 (d), 133.0 (d), 134.2 (d), 134.4 (d), 134.6 (s), 135.5 (s), 135.6 (s), 138.0 (s), 144.0 (s), 154.5 (s), 157.2 (s), 177.5 (s) and 178.6 (s).

1-Bromo-12-hydroxy-6,11-dioxo-6,11-dihydronaphthacene-5-carboxylic acid ethyl ester 4g. Orange crystals; mp 246–247 °C (from $CHCl_3$–hexane); $\nu_{max}(CHCl_3)/cm^{-1}$ 3420, 1715, 1670, 1560, 1250 cm^{-1}; δ_H (400 MHz; $CDCl_3$; Me_4Si) 1.49 (3 H, t, *J* 7.1, CH_3), 4.66 (2 H, q, *J* 7.1, OCH_2), 7.54 (1 H, t, *J* 7.8, ArH), 7.81–7.89 (3 H, m, ArH), 8.03 (1 H, d, *J* 7.8, ArH), 8.30–8.35 (1 H, m, ArH), 8.40–8.45 (1 H, m, ArH) and 16.05 (1 H, s, OH); δ_C(100.6 MHz; $CDCl_3$; Me_4Si) 14.1 (q), 62.4 (t), 109.0 (s), 120.9 (s), 125.3 (s), 125.5 (s), 127.0 (d), 127.20 (d), 127.27 (s), 127.8 (d), 131.7 (d), 133.5 (s), 133.8 (s), 134.6 (d), 134.8 (d), 136.0 (s), 137.0 (d), 166.0 (s), 169.0 (s), 181.5 (s) and 187.8 (s); *m/z* (EI) 423.9950 (M^+. $C_{21}H_{13}BrO_5$ requires 423.9946), 381 (100%), 379 (99), 354 (36), 352 (38), 346 (16), 325 (21) and 323 (19).

1-Chloro-12-hydroxy-6,11-dioxo-6,11-dihydronaphthacene-5-carboxylic acid ethyl ester 4h. Orange crystals; mp 250–251 °C (from $CHCl_3$–hexane); $\nu_{max}(CHCl_3)/cm^{-1}$ 2980, 1715, 1665, 1390, 1280 and 1250; δ_H(400 MHz; $CDCl_3$; Me_4Si) 1.49 (3 H, t, *J* 7.2, CH_3), 4.66 (2 H, q, *J* 7.2, OCH_2), 7.64 (1 H, t, *J* 8.0, ArH), 7.75 (1 H, d, *J* 8.0, ArH), 7.79 (1 H, d, *J* 8.0, ArH), 7.80–7.89 (2 H, m, ArH), 8.27–8.34 (1 H, m, ArH), 8.37–8.44 (1 H, m, ArH) and 16.01 (1 H, s, OH); δ_C(100.6 MHz; $CDCl_3$; Me_4Si) 14.1 (q), 62.4 (t), 109.1 (s), 124.6 (s), 125.3 (s), 126.4 (d), 127.17 (d), 127.25 (s), 127.8 (d), 131.5 (d), 132.9 (d), 133.4 (s), 133.8 (s), 134.2 (s), 134.6 (d), 134.8 (d), 135.9 (s), 166.3 (s), 169.0 (s), 181.4 (s) and 187.8 (s); *m/z* (EI) 380.0453 (M^+. $C_{21}H_{13}ClO_5$ requires 380.0452), 345 (16%), 335 (100), 308 (16), 223 (18) and 187 (26).

1,3-Dichloro-12-hydroxy-6,11-dioxo-6,11-dihydronaphthacene-5-carboxylic acid ethyl ester 4i. Orange crystals; mp 214–215 °C (from $CHCl_3$–hexane); $\nu_{max}(CHCl_3)/cm^{-1}$ 3015, 1730, 1595, 1565 and 1250; δ_H(400 MHz; $CDCl_3$; Me_4Si) 1.49 (3 H, t, *J* 7.2, CH_3), 4.67 (2 H, q, *J* 7.2, OCH_2), 7.72 (1 H, d, *J* 2.0, ArH), 7.74 (1 H, d, *J* 2.0, ArH), 7.81–7.90 (2 H, m, ArH), 8.28–8.34 (1 H, m, ArH), 8.38–8.44 (1 H, m, ArH) and 15.96 (1 H, s, OH); δ_C(100.6 MHz; $CDCl_3$; Me_4Si) 14.0 (q), 62.6 (t), 109.3 (s), 122.9 (s), 125.4 (d), 126.1 (s), 126.4 (s), 127.2 (d), 127.8 (d), 132.8 (d), 133.3 (s), 133.7 (s), 134.8 (d), 135.0 (d), 135.3 (s), 136.3 (s), 137.6 (s), 166.1 (s), 168.5 (s), 181.3 (s) and 187.8 (s); *m/z* (EI) 414.0062 (M^+. $C_{21}H_{12}Cl_2O_5$ requires 414.0062), 369 (62%), 344 (26), 335 (10), 315 (24) and 285 (100).

Typical experimental procedure for the reaction between 2-benzoyl-1,4-naphthoquinones and 1,3-diketones

A mixture of 2-benzoyl-1,4-naphthoquinone (**1a**) (162 mg, 0.62 mmol), 2,4-pentanedione (**11a**) (251 mg, 2.51 mmol) and manganese(III) acetate (664 mg, 2.48 mmol) in acetic acid (10 cm^3) was heated at 70 °C for 30 min. After work-up as described above, the crude product was purified by column chromatography over silica gel (20 g) (eluting with 2 : 1 dichloromethane–hexane) followed by recrystallization ($CHCl_3$–hexane) to give **12a** (80 mg, 41%) and **13a** (16 mg, 8%).

1-Acetyl-4,9-dioxo-3-phenyl-4,9-dihydronaphtho[2,3-*c*]furan 12a. Pale yellow needles; mp 159–160 °C (from $CHCl_3$–hexane); (Found: C, 75.82; H, 3.83. $C_{20}H_{12}O_4$ requires C, 75.94; H, 3.82%); $\nu_{max}(CHCl_3)/cm^{-1}$ 3010, 1675, 1530, 1490, 1390 and 1250; δ_H(400 MHz; $CDCl_3$; Me_4Si) 2.89 (3 H, s, CH_3), 7.49–7.58 (3 H, m, ArH), 7.74–7.84 (2 H, m, ArH), 8.24–8.33 (2 H, m, ArH) and 8.41–8.49 (2 H, m, ArH); δ_C(100.6 MHz; $CDCl_3$; Me_4Si) 29.5 (q), 118.3 (s), 124.7 (s), 127.4 (d), 127.5 (d), 128.6 (2 × d), 128.9 (2 × d), 132.0 (d), 134.0 (d), 134.4 (d), 134.8 (s), 135.1 (s), 148.9 (s), 158.7 (s), 178.9 (s), 179.2 (s) and 187.3 (s).

1-Acetyl-3-(4-methylphenyl)-4,9-dioxo-4,9-dihydronaphtho[2,3-*c*]-furan 12b. Yellow needles; mp 183–184 °C (from $CHCl_3$–hexane); (Found: C, 76.08; H, 4.26. $C_{21}H_{14}O_4$ requires C, 76.35; H, 4.27%); $\nu_{max}(CHCl_3)/cm^{-1}$ 3015, 1680, 1495, 1390, 1270 and 1250; δ_H(400 MHz; $CDCl_3$; Me_4Si) 2.45 (3 H, s, CH_3), 2.89 (3 H, s, CH_3), 7.34 (2 H, d, *J* 8.2, ArH), 7.75–7.84 (2 H, m, ArH), 8.26–8.34 (2 H, m, ArH) and 8.37 (2 H, d, *J* 8.2, ArH); δ_C(100.6 MHz; $CDCl_3$; Me_4Si) 21.8 (q), 29.5 (q), 117.9 (s), 124.75 (s), 124.82 (s), 127.44 (d), 127.52 (d), 128.9 (2 × d), 129.3 (2 × d), 134.0 (d), 134.4 (d), 134.8 (s), 135.2 (s), 142.9 (s), 148.6 (s), 159.2 (s), 178.9 (s), 179.3 (s) and 187.4 (s).

1-Acetyl-3-(4-bromophenyl)-4,9-dioxo-4,9-dihydronaphtho[2,3-*c*]-furan 12c. Pale orange powder; mp 200–201 °C (from $CHCl_3$–hexane); (Found: C, 60.49; H, 2.81. $C_{20}H_{11}BrO_4$ requires C, 60.78; H, 2.81%); $\nu_{max}(CHCl_3)/cm^{-1}$ 2925, 1675, 1595, 1480 and 1265; δ_H(400 MHz; $CDCl_3$; Me_4Si) 2.91 (3 H, s, CH_3), 7.69 (2 H, d, *J* 8.7, ArH), 7.80–7.87 (2 H, m, ArH), 8.28–8.35 (2 H, m, ArH) and 8.39 (2 H, d, *J* 8.7, ArH); δ_C(100.6 MHz; $CDCl_3$; Me_4Si) 29.6 (q), 118.7 (s), 124.8 (s), 126.4 (s), 126.9 (s), 127.6 (d), 127.7 (d), 130.3 (2 × d), 132.0 (2 × d), 134.3 (d), 134.6 (d), 134.8 (s), 135.0 (s), 149.0 (s), 157.6 (s), 179.0 (s), 179.1 (s) and 187.4 (s).

1-Acetyl-3-(4-chlorophenyl)-4,9-dioxo-4,9-dihydronaphtho[2,3-*c*]-furan 12d. Yellow needles; mp 207–208 °C (from $CHCl_3$–hexane); (Found: C, 68.31; H, 3.22. $C_{20}H_{11}ClO_4$ requires C, 68.49; H, 3.16%); $\nu_{max}(CHCl_3)/cm^{-1}$ 3030, 1680, 1485, 1270 and 1250; δ_H(400 MHz; $CDCl_3$; Me_4Si) 2.90 (3 H, s, CH_3), 7.52 (2 H, d, *J* 8.6, ArH), 7.78–7.86 (2 H, m, ArH), 8.27–8.33 (2 H, m, ArH) and 8.46 (2 H, d, *J* 8.6, ArH); δ_C(100.6 MHz; $CDCl_3$; Me_4Si) 29.6 (q), 118.6 (s), 124.7 (s), 125.9 (s), 127.5 (d), 127.6 (d), 129.0 (2 × d), 130.2 (2 × d), 134.2 (d), 134.5 (d), 134.8 (s), 135.0 (s), 138.3 (s), 148.9 (s), 157.5 (s), 179.0 (s), 179.1 (s) and 187.3 (s).

1-Acetyl-3-(2-methylphenyl)-4,9-dioxo-4,9-dihydronaphtho[2,3-*c*]-furan 12e. Pale yellow needles; mp 179–180 °C (from $CHCl_3$–hexane); (Found: C, 76.30; H, 4.27. $C_{21}H_{14}O_4$ requires C, 76.35; H, 4.27%); $\nu_{max}(CHCl_3)/cm^{-1}$ 3020, 1680, 1595, 1540, 1400 and 1250; δ_H(400 MHz; $CDCl_3$; Me_4Si) 2.41 (3 H, s, CH_3), 2.88 (3 H, s, CH_3), 7.31–7.39 (2 H, m, ArH), 7.47 (1 H, t, *J* 7.5, ArH), 7.68 (1 H, d, *J* 7.5, ArH), 7.76–7.86 (2 H, m, ArH), 8.21–8.28 (1 H, m, ArH) and 8.30–8.37 (1 H, m, ArH); δ_C(100.6 MHz; $CDCl_3$; Me_4Si) 20.3 (q), 29.4 (q), 119.6 (s), 123.8 (s), 125.6 (d), 127.11 (s), 127.18 (d), 127.8 (d), 130.8 (d), 130.9 (d), 131.3 (d), 134.2 (d), 134.4 (d), 134.8 (s), 135.3 (s), 138.5 (s), 149.5 (s), 159.7 (s), 178.8 (s), 179.1 (s) and 187.3 (s).

1-Acetyl-3-(2,4-dimethylphenyl)-4,9-dioxo-4,9-dihydronaphtho-[2,3-*c*]furan 12f. Yellow needles; mp 204–205 °C (from $CHCl_3$–hexane); (Found: C, 76.68; H, 4.68. $C_{22}H_{16}O_4$ requires C, 76.73; H, 4.68%); $\nu_{max}(CHCl_3)/cm^{-1}$ 3010, 1680, 1595, 1540 and 1250; δ_H(400 MHz; $CDCl_3$; Me_4Si) 2.38 (3 H, s, CH_3), 2.42 (3 H, s, CH_3), 2.87 (3 H, s, CH_3), 7.16 (1 H, d, *J* 7.9, ArH), 7.18 (1 H, s, ArH), 7.60 (1 H, d, *J* 7.9, ArH), 7.76–7.85 (2 H, m, ArH), 8.22–8.28 (1 H, m, ArH) and 8.31–8.36 (1 H, m, ArH); δ_C(100.6 MHz; $CDCl_3$; Me_4Si) 20.3 (q), 21.5 (q), 29.4 (q), 119.3 (s), 123.9 (s), 124.2 (s), 126.4 (d), 127.2 (d), 127.8 (d), 130.9 (d), 131.6 (d), 134.1 (d), 134.4 (d), 134.9 (s), 135.4 (s), 138.4 (s), 141.8 (s), 149.3 (s), 160.1 (s), 178.8 (s), 179.2 (s) and 187.3 (s).

1-Acetyl-3-(2-bromophenyl)-4,9-dioxo-4,9-dihydronaphtho[2,3-*c*]-furan 12g. Pale orange powder; mp 194–195 °C (from $CHCl_3$–hexane); (Found: C, 60.64; H, 2.78. $C_{20}H_{11}BrO_4$ requires C, 60.78; H, 2.81%); $\nu_{max}(CHCl_3)/cm^{-1}$ 3010, 1680, 1595, 1400 and 1250; δ_H(400 MHz; $CDCl_3$; Me_4Si) 2.89 (3 H, s, CH_3), 7.44 (1 H, td, *J* 7.4 and 1.6, ArH), 7.50 (1 H, td, *J* 7.4 and 1.6, ArH), 7.67 (1 H, dd, *J* 7.4 and 1.6, ArH), 7.76 (1 H, dd, *J* 7.4 and 1.6, ArH), 7.78–7.87 (2 H, m, ArH), 8.21–8.26 (1 H, m, ArH) and 8.32–8.37 (m, 1H, ArH); δ_C(125.6 MHz; $CDCl_3$; Me_4Si) 29.3 (q), 120.4 (s), 123.5 (s), 127.1 (2 × d), 127.9 (d), 129.1 (s), 132.4 (2 × d), 133.4 (d), 134.31 (d), 134.37 (d), 134.6 (s), 135.5 (s), 149.8 (s), 157.0 (s), 178.61 (s), 178.66 (s) and 187.2 (s).

1-Acetyl-3-(2-chlorophenyl)-4,9-dioxo-4,9-dihydronaphtho[2,3-*c*]-furan 12h. Pale yellow needles; mp 236–237 °C (from $CHCl_3$–hexane); (Found: C, 68.37; H, 3.12. $C_{20}H_{11}ClO_4$ requires C, 68.49; H, 3.16%); $\nu_{max}(CHCl_3)/cm^{-1}$ 3030, 1685, 1580, 1540, 1400 and 1250; δ_H(400 MHz; $CDCl_3$; Me_4Si) 2.90 (3 H, s, CH_3), 7.45 (1 H, t, *J* 7.5, ArH), 7.48–7.61 (2 H, m, ArH), 7.71 (1 H, d, *J* 7.5, ArH), 7.76–7.87 (2 H, m, ArH), 8.25 (1 H, dd, *J* 6.5 and 1.8, ArH) and 8.35 (1 H, dd, *J* 6.5 and 1.8, ArH); δ_C(100.6 MHz; $CDCl_3$; Me_4Si) 29.3 (q), 120.6 (s), 123.6 (s), 126.6 (d), 127.0 (s), 127.2 (d), 127.9 (d), 130.2 (d), 132.2 (d), 132.4 (d), 134.33 (d), 134.42 (d), 134.44 (s), 134.6 (s), 135.4 (s), 149.9 (s), 155.9 (s), 178.6 (s), 178.7 (s) and 187.3 (s).

1-Acetyl-3-(2,4-dichlorophenyl)-4,9-dioxo-4,9-dihydronaphtho-[2,3-*c*]furan 12i. Yellow needles; mp 191–192 °C (from $CHCl_3$–hexane); (Found: C, 62.26; H, 2.56. $C_{20}H_{10}Cl_2O_4$ requires C, 62.36; H, 2.62%); $\nu_{max}(CHCl_3)/cm^{-1}$ 3020, 1685, 1470, 1410, 1250; δ_H(400 MHz; $CDCl_3$; Me_4Si) 2.89 (3 H, s, CH_3), 7.44 (1 H, dd, *J* 8.5 and 1.6, ArH), 7.60 (1 H, d, *J* 1.6, ArH), 7.67 (1 H, d, *J* 8.5, ArH), 7.77–7.89 (2 H, m, ArH), 8.24 (1H, dd, *J* 7.2 and 2.2, ArH) and 8.35 (1 H, dd, *J* 7.2 and 2.2, ArH); δ_C(100.6 MHz; $CDCl_3$; Me_4Si) 29.4 (q), 120.9 (s), 123.6 (s), 125.5 (s), 127.14 (d), 127.19 (d), 128.0 (d), 130.3 (d), 133.1 (d), 134.46 (d), 134.48 (d), 135.34 (s), 135.36 (s), 138.1 (s), 150.1 (s), 154.7 (s), 178.6 (2 × s) and 187.2 (s).

1-Isobutyryl-3-phenyl-4,9-dioxo-4,9-dihydronaphtho[2,3-*c*]furan 12j. Orange needles; mp 156–157 °C (from $CHCl_3$–hexane); (Found: C, 76.66; H, 4.67. $C_{22}H_{16}O_4$ requires C, 76.73; H, 4.68%); $\nu_{max}(CHCl_3)/cm^{-1}$ 2980, 1660, 1530, 1485 and 1315; δ_H(300 MHz; $CDCl_3$; Me_4Si) 1.31 (6 H, d, *J* 6.8, 2 × CH_3), 3.98 (1 H, septet, *J* 6.8, CH), 7.53–7.61 (3 H, m, ArH), 7.78–7.86 (2 H, m, ArH), 8.29–8.37 (2 H, m, ArH) and 8.43–8.51 (2 H, m, ArH); δ_C(125.7 MHz; $CDCl_3$; Me_4Si) 18.4 (2 × q), 38.3 (d), 118.3 (s), 124.6 (s), 127.4 (d), 127.6 (d), 128.6 (2 × d), 128.8 (2 × d), 131.9 (d), 134.1 (d), 134.3 (d), 135.0 (s), 135.1 (s), 149.0 (s), 158.6 (s), 179.1 (2 × s) and 194.5 (s).

1-Isobutyryl-3-(4-methylphenyl)-4,9-dioxo-4,9-dihydronaphtho-[2,3-*c*]furan 12k. Orange needles; mp 140–141 °C (from $CHCl_3$–hexane); (Found: C, 77.15; H, 5.09. $C_{23}H_{18}O_4$ requires 77.08; H, 5.06); $\nu_{max}(CHCl_3)/cm^{-1}$ 2980, 1660, 1540, 1495 and 1315; δ_H(300 MHz; $CDCl_3$; Me_4Si) 1.30 (6 H, d, *J* 6.8, 2 × CH_3), 2.46 (3 H, s, CH_3), 3.97 (1 H, septet, *J* 6.8, CH), 7.36 (2 H, d, *J* 8.1, ArH), 7.74–7.86 (2 H, m, ArH), 8.27–8.35 (2 H, m, ArH) and 8.38 (2 H, d, *J* 8.1, ArH); δ_C(75.5 MHz; $CDCl_3$; Me_4Si) 18.5 (2 × q), 21.7 (q), 38.3 (d), 117.9 (s), 124.6 (s), 124.9 (s), 127.4 (d), 127.6(d), 128.8 (2 × d), 129.4 (2 × d), 134.0 (d), 134.3 (d), 135.0 (s), 135.2 (s), 142.7 (s), 148.6 (s), 159.0 (s), 179.1 (s), 179.2 (s) and 194.5 (s).

1-(4-bromophenyl)-3-isobutyryl-4,9-dioxo-4,9-dihydronaphtho-[2,3-*c*]furan 12l. Orange needles; mp 177–178 °C (from $CHCl_3$–hexane); (Found: C, 62.40; H, 3.59. $C_{22}H_{15}BrO_4$ requires C, 62.43; H, 3.57); $\nu_{max}(CHCl_3)/cm^{-1}$ 1660, 1595, 1480 and 1385; δ_H(300 MHz; $CDCl_3$; Me_4Si) 1.30 (6 H, d, *J* 6.8, 2 × CH_3), 3.99 (1 H, septet, *J* 6.8, CH), 7.69 (2 H, d, *J* 8.4, ArH), 7.77–7.88 (2 H, m, ArH), 8.28–8.34 (2 H, m, ArH) and 8.39 (2 H, d, *J* 8.4, ArH); δ_C(100.6 MHz; $CDCl_3$; Me_4Si) 18.4 (2 × q), 38.4 (d), 118.7 (s), 124.5 (s), 126.5 (s), 126.7 (s), 127.5 (d), 127.7 (d), 130.2 (2 × d), 132.0 (2 × d), 134.2 (d), 134.5 (d), 134.9 (s), 135.0 (s), 149.1 (s), 157.4 (s), 179.0 (s), 179.1 (s) and 194.6 (s).

1-Benzoyl-3-phenyl-4,9-dioxo-4,9-dihydronaphtho[2,3-*c*]furan 12m. Yellow needles; mp 196–197 °C (from $CHCl_3$–hexane); (Found: C, 79.08; H, 3.71. $C_{25}H_{14}O_4$ requires C, 79.36; H, 3.73%); $\nu_{max}(CHCl_3)/cm^{-1}$ 3015, 1675, 1595, 1270 and 1250; δ_H(400 MHz; $CDCl_3$; Me_4Si) 7.47–7.58 (5 H, m, ArH), 7.68 (1 H, t, *J* 7.6, ArH), 7.77 (1 H, td, *J* 7.4 and 1.3, ArH), 7.82 (1 H, td, *J* 7.4 and 1.3, ArH), 8.01 (2 H, d, *J* 7.6, ArH), 8.22 (1 H, d, *J* 7.4, ArH), 8.36 (1 H, d, *J* 7.4, ArH) and 8.42–8.52 (2 H, m, ArH); δ_C(100.6 MHz; $CDCl_3$; Me_4Si) 117.7 (s), 125.1 (s), 127.4 (d), 127.7 (d), 128.6 (2 × d), 128.7 (4 × d), 129.9 (2 × d), 131.8 (d), 134.0 (d), 134.2 (d), 134.3 (d), 134.7 (s), 135.6 (s), 136.1 (s), 149.4 (s), 158.5 (s), 178.5 (s), 179.0 (s) and 184.0 (s).

1-Benzoyl-3-(4-methylphenyl)-4,9-dioxo-4,9-dihydronaphtho-[2,3-*c*]furan 12n. Yellow needles; mp 225–226 °C (from $CHCl_3$–hexane); (Found: C, 79.52; H, 4.19. $C_{26}H_{16}O_4$ requires C, 79.58; H, 4.11%); $\nu_{max}(CHCl_3)/cm^{-1}$ 3015, 1680, 1595, 1500 and 1270; δ_H(400 MHz, $CDCl_3$; Me_4Si) 2.45 (3 H, s, CH_3), 7.35 (2 H, d, *J* 8.2, ArH), 7.53 (2 H, t, *J* 7.6, ArH), 7.68 (1 H, t, *J* 7.6, ArH), 7.76 (1 H, t, *J* 7.4, ArH), 7.81 (1 H, t, *J* 7.4, ArH), 8.01 (2 H, d, *J* 7.6, ArH), 8.21 (1 H, d, *J* 7.4, ArH), 8.36 (1 H, d, *J* 7.4, ArH) and 8.40 (2 H, d, *J* 8.2, ArH); δ_C(100.6 MHz, $CDCl_3$; Me_4Si) 21.7 (q), 117.2 (s), 125.0 (s), 125.2 (s), 127.4 (d), 127.6 (d), 128.6 (2 × d), 128.7 (2 × d), 129.4(2 × d), 129.9 (2 × d), 133.9 (d), 134.1 (d), 134.3 (d), 134.8 (s), 135.7 (s), 136.2 (s), 142.6 (s), 149.1 (s), 159.0 (s), 178.6 (s), 179.0 (s) and 184.0 (s).

1-Benzoyl-3-(4-bromophenyl)-4,9-dioxo-4,9-dihydronaphtho-[2,3-*c*]furan 12o. Yellow powder; mp 215–216 °C (from $CHCl_3$–hexane); (Found: C, 65.55; H, 2.81. $C_{25}H_{13}BrO_4$ requires C, 65.66; H, 2.87%); $\nu_{max}(CHCl_3)/cm^{-1}$ 3015, 1675, 1595, 1270 and 1250; δ_H(400 MHz; $CDCl_3$; Me_4Si) 7.54 (2 H, t, *J* 7.7, ArH), 7.64–7.71 (3 H, m, ArH), 7.74–7.85 (2 H, m, ArH), 7.99 (2 H, d, *J* 7.7, ArH), 8.21 (1 H, d, *J* 7.6, ArH), 8.35 (1 H, d, *J* 7.6, ArH) and 8.40 (2 H, d, *J* 8.2, ArH); δ_C(125.6 MHz; $CDCl_3$; Me_4Si) 118.0 (s), 125.1 (s), 126.6 (2 × s), 127.5 (d), 127.7 (d), 128.7 (2 × d), 129.87 (2 × d), 129.93 (2 × d), 132.0 (2 × d), 134.1 (d), 134.3 (d), 134.4 (d), 134.7

(s), 135.5 (s), 136.0 (s), 149.5 (s), 157.3 (s), 178.4 (s), 179.0 (s) and 183.9 (s).

1-Benzoyl-3-(4-chlorophenyl)-4,9-dioxo-4,9-dihydr naphtho[2,3-*c*]-furan 12p. Yellow needles; mp 208–209 °C (from CHCl$_3$–hexane); (Found: C, 72.71; H, 3.27. $C_{25}H_{13}ClO_4$ requires C, 72.74; H, 3.17%); ν_{max}(CHCl$_3$)/cm^{-1} 3015, 1680, 1595, 1490, 1270 and 1250; δ_H(400 MHz; CDCl$_3$; Me$_4$Si) 7.50 (2 H, d, *J* 8.7, ArH), 7.54 (2 H, t, *J* 7.6, ArH), 7.69 (1 H, t, *J* 7.6, ArH), 7.76 (1 H, t, *J* 7.4, ArH), 7.81 (1 H, t, *J* 7.4, ArH), 8.00 (2 H, d, *J* 7.6, ArH), 8.20 (1 H, d, *J* 7.4, ArH), 8.34 (1 H, d, *J* 7.4, ArH) and 8.47 (2 H, d, *J* 8.7, ArH); δ_C(100.6 MHz; CDCl$_3$; Me$_4$Si) 117.9 (s), 125.0 (s), 126.1 (s), 127.4 (d), 127.7 (d), 128.7 (2 × d), 129.0 (2 × d), 129.81 (2 × d), 129.85 (2 × d), 134.1 (d), 134.3 (d), 134.4 (d), 134.6 (s), 135.4 (s), 136.0 (s), 138.0 (s), 149.4 (s), 157.3 (s), 178.4 (s), 179.0 (s) and 183.9 (s).

1-Benzoyl-3-(2-methylphenyl)-4,9-dioxo-4,9-dihydronaphtho-[2,3-*c*]furan 12q. Yellow crystals; mp 175–176 °C (from CHCl$_3$–hexane); (Found: C, 79.50; H, 4.15. $C_{26}H_{16}O_4$ requires C, 79.58; H, 4.11%); ν_{max}(CHCl$_3$)/cm^{-1} 3035, 1675, 1590, 1270 and 1250; δ_H(400 MHz; CDCl$_3$; Me$_4$Si) 2.42 (3 H, s, CH$_3$), 7.34 (1 H, t, *J* 6.5, ArH), 7.35 (1 H, d, *J* 6.5, ArH), 7.45 (1 H, t, *J* 7.6, ArH), 7.51 (2 H, t, *J* 7.6, ArH), 7.65 (1 H, td, *J* 6.5 and 1.0, ArH), 7.70–7.79 (3 H, m, ArH), 7.99 (2 H, dd, *J* 7.6 and 1.1, ArH) and 8.19–8.28 (2 H, m, ArH); δ_C(100.6 MHz; CDCl$_3$; Me$_4$Si) 20.4 (q), 118.8 (s), 124.2 (s), 125.5 (d), 127.1 (s), 127.2 (d), 127.5 (d), 128.5 (2 × d), 129.8 (2 × d), 130.7 (d), 130.9 (d), 131.2 (d), 133.98 (d), 134.02 (d), 134.2 (d), 135.09 (s), 135.11 (s), 136.0 (s), 138.4 (s), 149.9 (s), 159.2 (s), 178.3 (s), 178.7 (s) and 183.8 (s).

1-Benzoyl-3-(2,4-dimethylphenyl)-4,9-dioxo-4,9-dihydronaphtho-[2,3-*c*]furan 12r. Yellow crystals; mp 167–168 °C (from CHCl$_3$–hexane); (Found: C, 79.67; H, 4.52. $C_{27}H_{18}O_4$ requires C, 79.79; H, 4.46%); ν_{max}(CHCl$_3$)/cm^{-1} 3015, 1660, 1585, 1490 and 1270; δ_H(400 MHz; CDCl$_3$; Me$_4$Si) 2.39 (3 H, s, CH$_3$), 2.41 (3 H, s, CH$_3$), 7.165 (1 H, d, *J* 6.2, ArH), 7.173 (1 H, s, ArH), 7.51 (2 H, t, *J* 7.8, ArH), 7.60–7.69 (2 H, m, ArH), 7.71–7.81 (2 H, m, ArH), 8.00 (2 H, dd, *J* 7.8 and 1.1, ArH) and 8.20–8.29 (2 H, m, ArH); δ_C(100.6 MHz; CDCl$_3$; Me$_4$Si) 20.4 (q), 21.5 (q), 118.6 (s), 124.3 (s), 124.4 (s), 126.4 (d), 127.3 (d), 127.6 (d), 128.6 (2 × d), 129.9 (2 × d), 131.0 (d), 131.6 (d), 133.97 (d), 134.03 (d), 134.2 (d), 135.2 (s), 135.3 (s), 136.1 (s), 138.3 (s), 141.7 (s), 149.7 (s), 159.7 (s), 178.4 (s), 178.8 (s) and 183.9 (s).

1-Benzoyl-3-(2-bromophenyl)-4,9-dioxo-4,9-dihydronaphtho-[2,3-*c*]furan 12s. Yellow crystals; mp 208–209 °C; (from CHCl$_3$–hexane); (Found: C, 65.60; H, 2.81. $C_{25}H_{13}BrO_4$ requires C, 65.66; H, 2.87%); ν_{max}(CHCl$_3$)/cm^{-1} 3015, 1680, 1600, 1270 and 1250; δ_H(400 MHz; CDCl$_3$; Me$_4$Si) 7.43 (1 H, td, *J* 7.6 and 1.6, ArH), 7.29–7.51 (3 H, m, ArH), 7.67 (1 H, t, *J* 7.3, ArH), 7.69 (1 H, dd, *J* 7.6 and 1.6, ArH), 7.54–7.77 (3 H, m, ArH), 8.05 (2 H, d, *J* 7.3, ArH) and 8.20–8.31 (2 H, m, ArH); δ_C(100.6 MHz; CDCl$_3$; Me$_4$Si) 119.8 (s), 123.4 (s), 124.1 (s), 127.21 (d), 127.26 (d), 127.8 (d), 128.6 (2 × d), 129.2 (s), 130.0 (2 × d), 132.4 (d), 132.6 (d), 133.4 (d), 134.18 (d), 134.24 (2 × d), 135.0 (s), 135.3 (s), 135.8 (s), 150.4 (s), 156.5 (s), 178.0 (s), 178.7 (s) and 183.5 (s).

1-Benzoyl-3-(2-chlorophenyl)-4,9-dioxo-4,9-dihydronaphtho-[2,3-*c*]furan 12t. Yellow crystals; mp 201–202 °C (from CHCl$_3$–hexane); (Found: C, 72.70; H, 3.13. $C_{25}H_{13}ClO_4$ requires C, 72.74; H, 3.17%); ν_{max}(CHCl$_3$)/cm^{-1} 3015, 1680, 1595, 1270 and 1250; δ_H(400 MHz; CDCl$_3$; Me$_4$Si) 7.44 (1 H, td, *J* 7.6 and 1.4, ArH), 7.47–7.60 (4 H, m, ArH), 7.67 (1 H, t, *J* 7.6, ArH), 7.75 (1 H, dd, *J* 7.6 and 1.4, ArH), 7.76–7.83 (2 H, m, ArH), 8.04 (2 H, dd, *J* 7.6 and 1.4, ArH) and 8.21–8.30 (2 H, m, ArH); δ_C(100.6 MHz; CDCl$_3$; Me$_4$Si) 120.0 (s), 124.2 (s), 126.6 (d), 127.1 (s), 127.3 (d), 127.8 (d), 128.6 (2 × d), 130.0 (2 × d), 130.3 (d), 132.3 (d), 132.5 (d), 134.19 (d), 134.21 (d), 134.25 (d), 134.31 (s), 135.0 (s), 135.3 (s), 135.8 (s), 150.6 (s), 155.4 (s), 178.1 (s), 178.7 (s) and 183.5 (s).

1-Benzoyl-3-(2,4-dichlorophenyl)-4,9-dihydro-4,9-dioxonaphtho-[2,3-*c*]furan 12u. Yellow crystals; mp 179–180 °C (from CHCl$_3$–hexane); (Found: C, 66.98; H, 2.63. $C_{25}H_{12}Cl_2O_4$ requires C, 67.13; H, 2.70%); ν_{max}(CHCl$_3$)/cm^{-1} 3015, 1680, 1585, 1270 and 1250; δ_H(400 MHz; CDCl$_3$; Me$_4$Si) 7.43 (1 H, dd, *J* 8.4 and 2.1, ArH), 7.53 (2 H, t, *J* 7.7, ArH), 7.59 (1 H, d, *J* 2.1, ArH), 7.68 (1 H, t, *J* 7.7, ArH), 7.71 (1 H, d, *J* 8.4, ArH), 7.73–7.83 (2 H, m, ArH), 8.02 (2 H, d, *J* 7.7, ArH) and 8.21–8.28 (2 H, m, ArH); δ_C(100.6 MHz; CDCl$_3$; Me$_4$Si) 120.2 (s), 124.1 (s), 125.5 (s), 127.2 (d), 127.3 (d), 127.8 (d), 128.7 (2 × d), 130.0 (2 × d), 130.3 (d), 133.3 (d), 134.30 (d), 134.34 (2 × d), 134.9 (s), 135.2 (s), 135.3 (s), 135.8 (s), 138.0 (s), 150.7 (s), 154.2 (s), 177.9 (s), 178.7 (s) and 183.5 (s).

6-Acetyl-11-hydroxy-5,12-dioxo-5,12-dihydronaphthacene 13a. Orange needles; mp 249–250 °C (from CHCl$_3$–hexane); (Found: C, 75.79; H, 3.77. $C_{20}H_{12}O_4$ requires C, 75.94; H, 3.82%); ν_{max}(CHCl$_3$)/cm^{-1} 3010, 1670, 1595, 1430, 1295 and 1260; δ_H(400 MHz; CDCl$_3$; Me$_4$Si) 2.70 (3 H, s, CH$_3$), 7.71–7.89 (5 H, m, ArH), 8.27–8.34 (1 H, m, ArH), 8.35–8.43 (1 H, m, ArH), 8.61 (1 H, dd, *J* 7.1 and 1.7, ArH) and 14.82 (1 H, s, OH); δ_C(75.5 MHz; CDCl$_3$; Me$_4$Si) 31.9 (q), 108.4 (s), 124.1 (s), 125.3 (d), 126.8 (d), 127.1 (d), 127.8 (d), 129.4 (d), 132.0 (d), 132.4 (s), 133.6 (s), 133.9 (s), 134.6 (d), 134.7 (d), 136.5 (s), 164.0 (s), 182.7 (s), 187.9 (s) and 205.2 (s).

6-Acetyl-11-hydroxy-8-methyl-5,12-dioxo-5,12-dihydronaphthacene 13b. Orange needles; mp 294–295 °C (from CHCl$_3$–hexane); (Found: C, 76.23; H, 4.27. $C_{21}H_{14}O_4$ requires C, 76.35; H, 4.27%) ν_{max}(KBr)/cm^{-1} 3405, 2915, 1700, 1660, 1590 and 1255; δ_H(400 MHz; CDCl$_3$; Me$_4$Si) 2.56 (3 H, s, CH$_3$), 2.69 (3 H, s, CH$_3$), 7.54–7.59 (2 H, m, ArH), 7.79–7.88 (2 H, m, ArH), 8.28–8.33 (1 H, m, ArH), 8.36–8.41 (1 H, m, ArH), 8.49 (1 H, d, *J* 8.9, ArH) and 14.81 (1 H, s, OH); δ_C(100.6 MHz; CDCl$_3$; Me$_4$Si) 22.2 (q), 32.0 (q), 107.9 (s), 125.2 (d), 125.8 (s), 126.1 (d), 127.0 (d), 127.8 (d), 131.4 (d), 132.7 (s), 133.7 (s), 133.9 (s), 134.55 (d), 134.59 (d), 136.1 (s), 143.1 (s), 164.1 (s), 182.8 (s), 187.7 (s) and 205.6 (s).

11-Acetyl-6-hydroxy-7-methyl-5,12-dioxo-5,12-dihydronaphthacene 13c. Orange needles; mp 233–234 °C (from CHCl$_3$–hexane); (Found: C, 76.35; H, 4.25.$C_{21}H_{14}O_4$ requires C, 76.35; H, 4.27); ν_{max}(CHCl$_3$)/cm^{-1} 3395, 2930, 1700, 1670, 1595 and 1580; δ_H(400 MHz; CDCl$_3$; Me$_4$Si) 2.68 (3 H, s, CH$_3$), 3.05 (3 H, s, CH$_3$), 7.43–7.50 (1 H, m, ArH), 7.57–7.65 (2 H, m, ArH), 7.77–7.87 (2 H, m, ArH), 8.28 (1 H, dd, *J* 7.0 and 1.7, ArH), 8.39 (1 H, dd, *J* 7.3 and 1.7, ArH) and 15.83 (1 H, s, OH); δ_C(100.6 MHz; CDCl$_3$; Me$_4$Si) 25.3 (q), 31.9 (q), 108.5 (s), 123.7 (s), 125.2 (d), 127.0 (d), 127.2 (s), 127.6 (d), 131.6 (d), 132.8 (d), 133.7 (s), 133.8 (s), 134.1 (s), 134.49 (d), 134.54 (d), 137.0 (s), 140.9 (s), 168.3 (s), 182.6 (s), 187.6 (s) and 205.8 (s).

11-Acetyl-6-hydroxy-7,9-dimethyl-5,12-dioxo-5,12-dihydronaphthacene 13d. Orange needles; mp 276–277 °C (from $CHCl_3$–hexane); $\nu_{max}(CHCl_3)/cm^{-1}$ 3425, 2925, 1695, 1595, 1580 and 1270; δ_H(400 MHz; $CDCl_3$; Me_4Si) 2.48 (3 H, s, CH_3), 2.67 (3 H, s, CH_3), 3.01 (3 H, s, CH_3), 7.31 (1 H, s, ArH), 7.39 (1 H, s, ArH), 7.76–7.87 (2 H, m, ArH), 8.28 (1 H, dd, *J* 7.5 and 1.6, ArH), 8.39 (1 H, dd, *J* 7.5 and 1.6, ArH) and 15.83 (1 H, s, OH); δ_C (100.6 MHz; $CDCl_3$; Me_4Si) 21.9 (q), 25.1 (q), 32.0 (q), 108.1 (s), 123.8 (s), 124.7 (d), 125.1 (s), 127.0 (d), 127.6 (d), 133.7 (s), 133.9 (s), 134.3 (d), 134.45 (s), 134.49 (d), 134.8 (d), 136.6 (s), 140.6 (s), 142.5 (s), 168.3 (s), 182.7 (s), 187.3 (s) and 206.1 (s); *m/z* (EI) 344.1053 (M^+. $C_{22}H_{16}O_4$ requires 344.1048), 329 (100%), 318 (4), 245 (5), 215 (16) and 202 (18).

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