

Supplementary information

for

Free radical reaction between 2-benzoyl-1,4-benzoquinones and 1,3-dicarbonyl compounds

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Contents

1) Experimental and characterization data of compounds

2) Copies of ¹H and ¹³C NMR spectra of compounds

1) Experimental

General considerations

Melting points are uncorrected. Infrared spectra were taken with a Hitachi 260-30 spectrometer. ¹H and ¹³C NMR spectra were recorded on a Bruker AVANCE-300 or AMX-400 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 102A 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 EM Laboratories silica gel (70-230 mesh).

Typical experimental procedure for the manganese(III) mediated reaction of 2-benzoyl-1,4-benzoquinones with β -ketoesters, β -ketoamide and 1,3-diketones.

A mixture of 5-benzoyl-2,3-dimethyl-1,4-benzoquinone (**7b**) (143 mg, 0.60 mmol), ethyl butyrylacetate (**8a**) (391 mg, 2.47 mmol) and manganese(III) acetate (671 mg, 2.50 mmol) in acetic acid (10 cm³) was heated at 70 °C for 30 min. The reaction mixture was diluted with ethyl acetate (100 cm³), washed with saturated aqueous sodium bisulfite (50 cm³), water (3 $\times$ 50 cm³), aqueous saturated sodium bicarbonate (3 $\times$ 50 cm³), dried (Na₂SO₄), and concentrated in vacuo. The crude product was purified by column chromatography over silica gel (20g) (eluted with 2:1 dichloromethane-hexane) followed by recrystallization (CHCl₃-hexane) to give **9b** (68 mg, 35%) and **10b** (56 mg, 29%).

4,7-Dihydro-5,6-dimethyl-3-(4-methylphenyl)-4,7-dioxobenzoc[furan-1-carboxylic acid ethyl ester 9a. Yellow crystals; mp 161-162 °C (from CHCl₃-hexane); (Found: C, 70.89; H, 5.42. C₂₀H₁₈O₅ requires C, 70.99; H, 5.36%); $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$ 3010, 1730, 1665, 1610 and 1280; $\delta_{\text{H}}(300 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$ 1.47 (3 H, t, *J* 7.1, CH₃), 2.14 (6 H, s, 2 $\times$ CH₃), 2.42 (3 H, s, CH₃), 4.50 (2 H, q, *J* 7.1, OCH₂), 7.30 (2 H, d, *J* 8.2, ArH) and 8.32 (2 H, d, *J* 8.2, ArH); $\delta_{\text{C}}(75.4 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$ 13.0 (q), 13.2 (q), 14.1 (q), 21.6 (q), 62.1 (t), 116.7 (s), 124.75 (s), 124.81 (s), 128.4 (2 $\times$ d), 129.2 (2 $\times$ d), 141.4 (s), 142.3 (s), 145.0 (s), 145.4 (s), 157.4 (s), 157.6 (s), 179.3 (s) and 180.1 (s).

4,7-Dihydro-5,6-dimethyl-4,7-dioxo-3-phenylbenzo[c]furan-1-carboxylic acid ethyl ester 9b. Yellow crystals; mp 161-162 °C (from CHCl₃-hexane); (Found: C, 70.27; H, 4.93. C₁₉H₁₆O₅ requires C, 70.36; H, 4.97%); $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$ 3015, 1730, 1665, 1400, 1375 and 1280; $\delta_{\text{H}}(400 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$ 1.48 (3 H, t, *J* 7.1, CH₃), 2.17 (6 H, s, 2 $\times$ CH₃), 4.51 (2 H, q, *J* 7.1, OCH₂), 7.49-7.56 (3 H, m, ArH) and 8.39-8.46 (2 H, m, ArH); $\delta_{\text{C}}(75.4 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$ 13.18 (q), 13.25 (q), 14.2 (q), 62.3 (t), 117.3 (s), 124.9 (s), 127.6 (s), 128.52 (2 $\times$ d), 128.55 (2 $\times$ d), 131.7 (d), 141.8 (s), 145.3 (s), 145.5 (s), 157.4 (s), 157.5 (s), 179.4 (s) and 180.3 (s).

3-(4-Chlorophenyl)-4,7-dihydro-5,6-dimethyl-4,7-dioxobenzo[c]furan-1-carboxylic acid ethyl ester 9c. Yellow crystals; mp 146-147 °C (from CHCl₃-hexane); (Found: C, 63.51; H, 4.20. C₁₉H₁₅ClO₅ requires C, 63.61; H, 4.21%); $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$ 2990, 1730, 1665, 1485 and 1275; $\delta_{\text{H}}(400 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$ 1.48 (3 H, t, *J* 7.1, CH₃), 2.17 (6 H, s, 2 × CH₃), 4.51 (2 H, q, *J* 7.1, OCH₂), 7.50 (2 H, d, *J* 8.7, ArH) and 8.43 (2 H, d, *J* 8.7, ArH); $\delta_{\text{C}}(100.6 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$ 13.16 (q), 13.20 (q), 14.1 (q), 62.3 (t), 117.5 (s), 124.8 (s), 126.0 (s), 128.9 (2 × d), 129.7 (2 × d), 137.8 (s), 141.9 (s), 145.4 (2 × s), 156.1 (s), 157.4 (s), 179.2 (s) and 180.3 (s).

3-(4-Bromophenyl)-4,7-dihydro-5,6-dimethyl-4,7-dioxobenzo[c]furan-1-carboxylic acid ethyl ester 9d. Yellow needles; mp 154-155 °C (from CHCl₃-hexane); (Found: C, 56.31; H, 3.72. C₁₉H₁₅BrO₅ requires C, 56.59; H, 3.75%); $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$ 3010, 1730, 1670, 1595 and 1485; $\delta_{\text{H}}(400 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$ 1.48 (3 H, t, *J* 7.1, CH₃), 2.16 (6 H, s, 2 × CH₃), 4.51 (2 H, q, *J* 7.1, OCH₂), 7.64 (2 H, d, *J* 7.8, ArH) and 8.34 (2 H, d, *J* 7.8, ArH); $\delta_{\text{C}}(100.6 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$ 13.17 (q), 13.22 (q), 14.2 (q), 62.3 (t), 117.7 (s), 124.8 (s), 126.4 (2 × s), 129.8 (2 × d), 131.8 (2 × d), 142.0 (s), 145.4 (2 × s), 156.1 (s), 157.3 (s), 179.1 (s) and 180.2 (s).

4,7-Dihydro-5,6-dimethyl-3-(2-methylphenyl)-4,7-dioxobenzo[c]furan-1-carboxylic acid ethyl ester 9e. Yellow crystals; mp 142-143 °C (from CHCl₃-hexane); (Found: C, 70.88; H, 5.43. C₂₀H₁₈O₅ requires C, 70.99; H, 5.36%); $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$ 2990, 1730, 1670, 1605, 1555 and 1280; $\delta_{\text{H}}(400 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$ 1.45 (3 H, t, *J* 7.2, CH₃), 2.11 (3 H, s, CH₃), 2.17 (3 H, s, CH₃), 2.36 (3 H, s, CH₃), 4.49 (2 H, q, *J* 7.2, OCH₂), 7.27-7.35 (2 H, m, ArH), 7.43 (1 H, t, *J* 7.5, ArH) and 7.63 (1 H, d, *J* 7.5, ArH); $\delta_{\text{C}}(100.6 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$ 12.8 (q), 13.3 (q), 14.2 (q), 20.3 (q), 62.2 (t), 118.5 (s), 124.0 (s), 125.5 (d), 127.1 (s), 130.72 (d), 130.77 (d), 131.1 (d), 138.5 (s), 142.2 (s), 145.0 (s), 145.9 (s), 157.4 (s), 158.2 (s), 179.3 (s) and 180.1 (s).

4,7-Dihydro-5,6-dimethyl-3-(2,4-dimethylphenyl)-4,7-dioxobenzo[c]furan-1-carboxylic acid ethyl ester 9f. Yellow powders; mp 121-122 °C (from CHCl₃-hexane); (Found: C, 71.39; H, 5.72. C₂₁H₂₀O₅ requires C, 71.58; H, 5.72%); $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$ 2990, 1730, 1670, 1375 and 1285; $\delta_{\text{H}}(300 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$ 1.45 (3 H, t, *J* 7.1, CH₃), 2.10 (3 H, s, CH₃), 2.16 (3 H, s, CH₃), 2.33 (3 H, s, CH₃), 2.38 (3 H, s, CH₃), 4.48 (2 H, q, *J* 7.1, OCH₂), 7.12 (1 H, d, *J* 7.8, ArH), 7.14 (1 H, s, ArH) and 7.55 (1 H, d, *J* 7.8, ArH); $\delta_{\text{C}}(75.4 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$ 12.8 (q), 13.2 (q), 14.2 (q), 20.2 (q), 21.5 (q), 62.1 (t), 118.2 (s), 124.0 (s), 124.2 (s), 126.3 (d), 130.7 (d), 131.5 (d), 138.3 (s), 141.5 (s), 142.0 (s), 145.1 (s), 145.7 (s), 157.5 (s), 158.6 (s), 179.4 (s) and 180.1 (s).

4,7-Dihydro-*N,N*,5,6-tetramethyl-3-(4-methylphenyl)-4,7-dioxobenzo[c]furan-1-carboxamide 9g. Yellow crystals; mp 211-212 °C (from CHCl₃-hexane); (Found: C, 71.21; H, 5.69; N, 4.16. C₂₀H₁₉NO₄ requires C, 71.20; H, 5.68; N, 4.15%); $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 2925, 1645, 1545, 1500 and 1410; $\delta_{\text{H}}(400 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$ 2.13 (3 H, s, CH₃), 2.18 (3 H, s, CH₃), 2.43 (3 H, s, CH₃), 3.07 (3 H, s, NCH₃), 3.21 (3 H, s, NCH₃), 7.30 (2 H, d, *J* 8.3, ArH) and 8.35 (2 H, d, *J* 8.3, ArH); $\delta_{\text{C}}(75.4 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$ 12.6 (q), 13.4 (q), 21.6 (q), 35.1 (q), 37.6 (q), 114.8 (s), 120.3 (s), 124.9 (s), 127.9 (2 × d), 129.2 (2 × d), 142.0 (s), 144.1 (s), 146.0 (s), 146.9 (s), 157.1 (s), 159.8 (s), 180.1 (s) and 180.5 (s).

4,7-Dihydro-*N,N*,5,6-tetramethyl-4,7-dioxo-3-phenylbenzo[c]furan-1-carboxamide 9h. Yellow crystals; mp 200-201 °C (from CHCl₃-hexane); (Found: C, 70.67; H, 5.29; N, 4.31. C₁₉H₁₇NO₄ requires C, 70.58; H, 5.30; N, 4.33%); $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 2920, 1650, 1545, 1490 and 1400; $\delta_{\text{H}}(400 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$ 2.13 (3 H, s, CH₃), 2.18 (3 H, s, CH₃), 3.07 (3 H, s, NCH₃), 3.21 (3 H, s, NCH₃), 7.32-7.61 (3 H, m, ArH) and 8.30-8.50 (2 H, m, ArH); $\delta_{\text{C}}(75.4 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$ 12.6 (q), 13.4 (q), 35.1 (q), 37.6 (q), 115.4 (s), 120.3 (s), 127.6 (s), 127.9 (2 × d), 128.5 (2 × d), 131.3 (d), 144.2 (s), 146.3 (s), 146.9 (s), 156.7 (s), 159.7 (s), 180.1 (s) and 180.4 (s).

3-(4-Chlorophenyl)-4,7-dihydro-*N,N*,5,6-tetramethyl-4,7-dioxobenzo[c]furan-1-carboxamide 9i. Yellow crystals; mp 231-232 °C (from CHCl₃-hexane); (Found: C, 63.59; H, 4.50; N, 3.87. C₁₉H₁₆ClNO₄ requires C, 63.78; H, 4.51; N, 3.91%); $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 2915, 1650, 1540, 1485 and 1415; $\delta_{\text{H}}(400 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$ 2.13 (3 H, s, CH₃), 2.18 (3 H, s, CH₃), 3.07 (3 H, s, NCH₃), 3.21 (3 H, s, NCH₃), 7.47 (2 H, d, *J* 8.6, ArH) and 8.43 (2 H, d, *J* 8.6, ArH); $\delta_{\text{C}}(75.4 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$ 12.7 (q), 13.5 (q), 35.1 (q), 37.7 (q), 115.7 (s), 120.3 (s), 126.1 (s), 128.8 (2 × d), 129.2 (2 × d), 137.4 (s), 144.4 (s), 146.4 (s), 146.9 (s), 155.5 (s), 159.6 (s), 180.2 (s) and 180.3 (s).

4,7-Dihydro-*N,N*,5,6-tetramethyl-3-(2,4-dimethylphenyl)-4,7-dioxobenzo[c]furan-1-carboxamide 9j. Yellow liquid; $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 2925, 1655, 1410, 1270 and 1240; $\delta_{\text{H}}(400 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$ 2.11 (3 H, s, CH₃), 2.12 (3 H, s, CH₃), 2.35 (3 H, s, CH₃), 2.38 (3 H, s, CH₃), 3.07 (3 H, s, NCH₃), 3.19 (3 H, s, NCH₃), 7.11 (1 H, d, *J* 8.1, ArH), 7.13 (1 H, s, ArH) and 7.58 (1 H, d, *J* 8.1, ArH); $\delta_{\text{C}}(75.4 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$ 12.4 (q), 12.8 (q), 20.1 (q), 21.2 (q), 34.8 (q), 37.4 (q), 116.1 (s), 119.3 (s), 124.0 (s), 126.0 (d), 130.4 (d), 131.3 (d), 137.9 (s), 141.0 (s), 144.4 (s), 146.20 (s), 146.23 (s), 157.4 (s), 159.5 (s), 179.8 (s) and 180.2 (s); *m/z* (EI) 351.1466 (M⁺. C₂₁H₂₁NO₄ requires 351.1471), 308 (100%), 296 (22), 291 (61), 280 (55), 265 (20) and 252 (81).

1-Acetyl-4,7-dihydro-5,6-dimethyl-3-(4-methylphenyl)-4,7-dioxobenzo[c]furan 9k. Orange crystals; mp 167-168 °C (from CHCl₃-hexane); (Found: C, 73.83; H, 5.24. C₁₉H₁₆O₄ requires C, 74.01; H, 5.23%); $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$ 3010, 1665, 1500, 1375 and 1270; $\delta_{\text{H}}(300 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$ 2.17 (6 H, s, 2 × CH₃), 2.44 (3 H, s, CH₃), 2.82 (3 H, s, CH₃), 7.32 (2 H, d, *J* 8.1, ArH) and

8.34 (2 H, d, *J* 8.1, ArH); δ_{C} (75.4 MHz; CDCl₃; Me₄Si) 13.1 (q), 13.3 (q), 21.7 (q), 29.4 (q), 116.8 (s), 123.8 (s), 124.7 (s), 128.6 (2 × d), 129.3 (2 × d), 142.7 (s), 144.8 (s), 145.9 (s), 147.7 (s), 158.0 (s), 180.3 (s), 180.6 (s) and 187.3 (s).

1-Acetyl-4,7-dihydro-5,6-dimethyl-4,7-dioxo-3-phenylbenzo[c]furan 9l. Yellow crystals; mp 154-155 °C (from CHCl₃-hexane); (Found: C, 73.35; H, 4.76. C₁₈H₁₄O₄ requires C, 73.46; H, 4.79%); ν_{max} (CHCl₃)/cm⁻¹ 3015, 1665, 1535, 1375 and 1270; δ_{H} (400 MHz; CDCl₃; Me₄Si) 2.19 (6 H, s, 2 × CH₃), 2.84 (3 H, s, CH₃), 7.50-7.56 (3 H, m, ArH) and 8.40-8.45 (2 H, m, ArH); δ_{C} (100.6 MHz; CDCl₃; Me₄Si) 13.2 (q), 13.3 (q), 29.4 (q), 117.3 (s), 123.8 (s), 127.4 (s), 128.58 (2 × d), 128.65 (2 × d), 131.9 (d), 145.0 (s), 145.9 (s), 147.9 (s), 157.6 (s), 180.3 (s), 180.5 (s) and 187.3 (s).

1-Acetyl-3-(4-chlorophenyl)-4,7-dihydro-5,6-dimethyl-4,7-dioxobenzo[c]furan 9m. Orange crystals; mp 147-148 °C (from CHCl₃-hexane); (Found: C, 65.58; H, 4.03. C₁₈H₁₃ClO₄ requires C, 65.76; H, 3.99%); ν_{max} (CHCl₃)/cm⁻¹ 3015, 1660, 1535, 1485, 1375 and 1270; δ_{H} (300 MHz; CDCl₃; Me₄Si) 2.19 (6 H, s, 2 × CH₃), 2.84 (3 H, s, CH₃), 7.50 (2 H, d, *J* 8.7, ArH) and 8.43 (2 H, d, *J* 8.7, ArH); δ_{C} (100.6 MHz; CDCl₃; Me₄Si) 13.17 (q), 13.25 (q), 29.4 (q), 117.5 (s), 123.7 (s), 125.9 (s), 128.9 (2 × d), 129.9 (2 × d), 138.1 (s), 145.2 (s), 145.8 (s), 147.9 (s), 156.3 (s), 180.3 (s), 180.4 (s) and 187.2 (s).

1-Acetyl-3-(4-bromophenyl)-4,7-dihydro-5,6-dimethyl-4,7-dioxobenzo[c]furan 9n. Orange crystals (from CHCl₃-hexane); mp 133-134 °C; (Found: C, 57.96; H, 3.51. C₁₈H₁₃BrO₄ requires C, 57.93; H, 3.51%); ν_{max} (CHCl₃)/cm⁻¹ 3015, 1665, 1595, 1485 and 1270; δ_{H} (300 MHz; CDCl₃; Me₄Si) 2.18 (6 H, s, 2 × CH₃), 2.84 (3 H, s, CH₃), 7.66 (2 H, d, *J* 8.7, ArH) and 8.36 (2 H, d, *J* 8.7, ArH); δ_{C} (100.6 MHz; CDCl₃; Me₄Si) 13.16 (q), 13.23 (q), 29.4 (q), 117.6 (s), 123.7 (s), 126.3 (s), 126.7 (s), 130.0 (2 × d), 131.9 (2 × d), 145.1 (s), 145.8 (s), 147.9 (s), 156.2 (s), 180.27 (s), 180.34 (s) and 187.2 (s).

1-Acetyl-4,7-dihydro-5,6-dimethyl-3-(2-methylphenyl)-4,7-dioxobenzo[c]furan 9o. Yellow crystals; mp 128-129 °C (from CHCl₃-hexane); (Found: C, 73.89; H, 5.29. C₁₉H₁₆O₄ requires C, 74.01; H, 5.23%); ν_{max} (CHCl₃)/cm⁻¹ 3015, 1670, 1610, 1375 and 1270; δ_{H} (400 MHz; CDCl₃; Me₄Si) 2.12 (3 H, s, CH₃), 2.18 (3 H, s, CH₃), 2.37 (3 H, s, CH₃), 2.81 (3 H, s, CH₃), 7.31 (1 H, t, *J* 7.7, ArH), 7.33 (1 H, d, *J* 7.7, ArH), 7.44 (1 H, t, *J* 7.7, ArH) and 7.62 (1 H, d, *J* 7.7, ArH); δ_{C} (100.6 MHz; CDCl₃; Me₄Si) 12.9 (q), 13.3 (q), 20.3 (q), 29.2 (q), 118.5 (s), 122.8 (s), 125.5 (d), 127.0 (s), 130.76 (d), 130.80 (d), 131.2 (d), 138.4 (s), 145.4 (s), 145.6 (s), 148.5 (s), 158.5 (s), 180.2 (s), 180.4 (s) and 187.2 (s).

1-Acetyl-4,7-dihydro-5,6-dimethyl-3-(2,4-dimethylphenyl)-4,7-dioxobenzo[c]furan 9p. Yellow needles; mp 147-148 °C (from CHCl₃-hexane); (Found: C, 74.26; H, 5.66. C₂₀H₁₈O₄ requires C, 74.52; H, 5.63%); ν_{max} (CHCl₃)/cm⁻¹ 3015, 1670, 1545, 1375 and 1270; δ_{H} (300 MHz; CDCl₃; Me₄Si) 2.12 (3 H, s, CH₃), 2.17 (3 H, s, CH₃), 2.34 (3 H, s, CH₃), 2.39 (3 H, s, CH₃), 2.80 (3 H, s, CH₃), 7.13 (1 H, d, *J* 7.7, ArH), 7.14 (1 H, s, ArH), and 7.54 (1 H, d, *J* 7.7, ArH); δ_{C} (100.6 MHz; CDCl₃; Me₄Si) 12.9 (q), 13.3 (q), 20.3 (q), 21.5 (q), 29.2 (q), 118.2 (s), 122.9 (s), 124.1 (s), 126.3 (d), 130.8 (d), 131.6 (d), 138.3 (s), 141.7 (s), 145.45 (s), 145.52 (s), 148.3 (s), 158.9 (s), 180.2 (s), 180.5 (s) and 187.2 (s).

1-Benzoyl-4,7-dihydro-5,6-dimethyl-3-(4-methylphenyl)-4,7-dioxobenzo[c]furan 9q. Yellow crystals; mp 183-184 °C (from CHCl₃-hexane); (Found: C, 77.73; H, 4.90. C₂₄H₁₈O₄ requires C, 77.82; H, 4.90%); ν_{max} (CHCl₃)/cm⁻¹ 3015, 1660, 1605, 1500 and 1275; δ_{H} (300 MHz; CDCl₃; Me₄Si) 2.10 (3 H, s, CH₃), 2.18 (3 H, s, CH₃), 2.43 (3 H, s, CH₃), 7.32 (2 H, d, *J* 8.2, ArH), 7.51 (2 H, t, *J* 7.5, ArH), 7.66 (1 H, t, *J* 7.5, ArH), 7.96 (2 H, d, *J* 7.5, ArH) and 8.34 (2 H, d, *J* 8.2, ArH); δ_{C} (75.4 MHz; CDCl₃; Me₄Si) 12.9 (q), 13.4 (q), 21.7 (q), 116.3 (s), 124.4 (s), 124.9 (s), 128.3 (2 × d), 128.6 (2 × d), 129.4 (2 × d), 129.8 (2 × d), 134.0 (d), 136.2 (s), 142.5 (s), 144.8 (s), 146.2 (s), 148.1 (s), 157.7 (s), 179.9 (s), 180.4 (s) and 183.8 (s).

1-Benzoyl-4,7-dihydro-5,6-dimethyl-4,7-dioxo-3-phenylbenzo[c]furan 9r. Yellow crystals; mp 183-184 °C (from CHCl₃-hexane); (Found: C, 77.57; H, 4.54. C₂₃H₁₆O₄ requires C, 77.52; H, 4.53%); ν_{max} (CHCl₃)/cm⁻¹ 3015, 1660, 1600, 1490, 1450 and 1275; δ_{H} (400 MHz; CDCl₃; Me₄Si) 2.10 (3 H, s, CH₃), 2.18 (3 H, s, CH₃), 7.48-7.56 (5H, m, ArH), 7.66 (1 H, t, *J* 7.6, ArH), 7.97 (2 H, d, *J* 7.6, ArH) and 8.40-8.46 (2 H, m, ArH); δ_{C} (100.6 MHz; CDCl₃; Me₄Si) 12.9 (q), 13.4 (q), 116.7 (s), 124.3 (s), 127.6 (s), 128.3 (2 × d), 128.6 (4 × d), 129.8 (2 × d), 131.7 (d), 134.0 (d), 136.1 (s), 144.9 (s), 146.2 (s), 148.4 (s), 157.2 (s), 179.8 (s), 180.4 (s) and 183.8 (s).

1-Benzoyl-3-(4-chlorophenyl)-4,7-dihydro-5,6-dimethyl-4,7-dioxobenzo[c]furan 9s. Yellow crystals; mp 191-192 °C (from CHCl₃-hexane); (Found: C, 70.75; H, 3.92. C₂₃H₁₅ClO₄ requires C, 70.68; H, 3.87%); ν_{max} (CHCl₃)/cm⁻¹ 3015, 1660, 1600, 1490 and 1275; δ_{H} (400 MHz; CDCl₃; Me₄Si) 2.10 (3 H, s, CH₃), 2.18 (3 H, s, CH₃), 7.45 (2 H, d, *J* 8.7, ArH), 7.52 (2 H, t, *J* 7.6, ArH), 7.67 (1 H, t, *J* 7.6, ArH), 7.95 (2 H, d, *J* 7.6, ArH) and 8.42 (2 H, d, *J* 8.7, ArH); δ_{C} (100.6 MHz; CDCl₃; Me₄Si) 12.9 (q), 13.3 (q), 116.9 (s), 124.2 (s), 126.1 (s), 128.6 (2 × d), 129.0 (2 × d), 129.5 (2 × d), 129.8 (2 × d), 134.1 (d), 136.0 (s), 137.8 (s), 145.1 (s), 146.1 (s), 148.4 (s), 156.0 (s), 179.6 (s), 180.3 (s) and 183.7 (s).

1-Benzoyl-3-(4-bromophenyl)-4,7-dihydro-5,6-dimethyl-4,7-dioxobenzo[c]furan 9t. Yellow crystals; mp 192-193 °C (from CHCl₃-hexane); (Found: C, 63.39; H, 3.43. C₂₃H₁₅BrO₄ requires C, 63.47; H, 3.47%); ν_{max} (CHCl₃)/cm⁻¹ 3015, 1665, 1600, 1485 and 1280; δ_{H} (400 MHz; CDCl₃; Me₄Si) 2.10 (3 H, s, CH₃), 2.18 (3 H, s, CH₃), 7.52 (2 H, t, *J* 7.8, ArH), 7.64 (2 H, d, *J* 8.6, ArH), 7.67 (1 H, t, *J* 7.8, ArH), 7.95 (2 H, d, *J* 7.8, ArH) and 8.34 (2 H, d, *J* 8.6, ArH); δ_{C} (100.6 MHz; CDCl₃; Me₄Si) 12.9 (q), 13.4 (q),

117.0 (s), 124.2 (s), 126.4 (s), 126.5 (s), 128.6 (2 × d), 129.6 (2 × d), 129.8 (2 × d), 131.9 (2 × d), 134.1 (d), 136.0 (s), 145.1 (s), 146.1 (s), 148.4 (s), 156.0 (s), 179.6 (s), 180.3 (s) and 183.7 (s).

1-Benzoyl-4,7-dihydro-5,6-dimethyl-3-(2-methylphenyl)-4,7-dioxobenzo[c]furan 9u. Yellow crystals; mp 135-136 °C (from CHCl₃-hexane); (Found: C, 77.77; H, 4.90. C₂₄H₁₈O₄ requires C, 77.82; H, 4.90%); $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$ 3030, 1665, 1600, 1480 and 1275; $\delta_{\text{H}}(400 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$ 2.11 (3 H, s, CH₃), 2.12 (3 H, s, CH₃), 2.38 (3 H, s, CH₃), 7.27-7.35 (2 H, m, ArH), 7.42 (1 H, t, *J* 7.4, ArH), 7.49 (2 H, t, *J* 7.4, ArH), 7.64 (1 H, t, *J* 7.4, ArH), 7.68 (1 H, d, *J* 7.4, ArH) and 7.95 (2 H, d, *J* 7.4, ArH); $\delta_{\text{C}}(100.6 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$ 12.9 (q), 13.0 (q), 20.5 (q), 117.9 (s), 123.4 (s), 125.5 (d), 127.0 (s), 128.5 (2 × d), 129.8 (2 × d), 130.75 (d), 130.84 (d), 131.1 (d), 133.9 (d), 136.0 (s), 138.3 (s), 145.5 (s), 145.6 (s), 148.9 (s), 158.0 (s), 179.6 (s), 180.2 (s) and 183.6 (s).

1-Benzoyl-4,7-dihydro-5,6-dimethyl-3-(2,4-dimethylphenyl)-4,7-dioxobenzo[c]furan 9v. Yellow crystals; mp 163-164 °C (from CHCl₃-hexane); (Found: C, 78.01; H, 5.24. C₂₅H₂₀O₄ requires C, 78.11; H, 5.24%); $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$ 3015, 1665, 1600, 1375 and 1275; $\delta_{\text{H}}(400 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$ 2.11 (3 H, s, CH₃), 2.12 (3 H, s, CH₃), 2.34 (3 H, s, CH₃), 2.39 (3 H, s, CH₃), 7.137 (1 H, d, *J* 8.3, ArH), 7.142 (1 H, s, ArH), 7.50 (2 H, t, *J* 7.5, ArH), 7.60 (1 H, d, *J* 8.3, ArH), 7.64 (1 H, t, *J* 7.5, ArH) and 7.95 (2 H, d, *J* 7.5, ArH); $\delta_{\text{C}}(100.6 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$ 12.9 (q), 13.0 (q), 20.4 (q), 21.4 (q), 117.6 (s), 123.5 (s), 124.1 (s), 126.3 (d), 128.5 (2 × d), 129.8 (2 × d), 130.8 (d), 131.6 (d), 133.9 (d), 136.1 (s), 138.2 (s), 141.5 (s), 145.4 (s), 145.6 (s), 148.7 (s), 158.4 (s), 179.7 (s), 180.2 (s) and 183.6 (s).

1,4-Dihydro-9-hydroxy-2,3,6-trimethyl-1,4-dioxoanthracene-10-carboxylic acid ethyl ester 10a. Red needles; mp 168-169 °C (from CHCl₃-hexane); (Found: C, 70.91; H, 5.36. C₂₀H₁₆O₅ requires C, 70.99; H, 5.36%); $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$ 2925, 1720, 1655, 1500 and 1265; $\delta_{\text{H}}(300 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$ 1.47 (3 H, t, *J* 7.1, CH₃), 2.17 (3 H, s, CH₃), 2.19 (3 H, s, CH₃), 2.54 (3 H, s, CH₃), 4.63 (2 H, q, *J* 7.1, OCH₂), 7.50 (1 H, d, *J* 8.4, ArH), 7.57 (1 H, s, ArH), 8.37 (1 H, d, *J* 8.4, ArH) and 14.31 (1 H, s, OH); $\delta_{\text{C}}(75.4 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$ 12.4 (q), 13.2 (q), 14.1 (q), 22.1 (q), 62.0 (t), 107.1 (s), 124.1 (s), 124.7 (d), 125.2 (s), 126.2 (d), 126.4 (s), 131.1 (d), 133.0 (s), 142.5 (s), 144.3 (s), 145.9 (s), 162.6 (s), 169.2 (s), 183.1 (s) and 188.8 (s).

1,4-Dihydro-9-hydroxy-2,3-dimethyl-1,4-dioxoanthracene-10-carboxylic acid ethyl ester 10b. Red crystals; mp 169-170 °C (from CHCl₃-hexane); (Found: C, 70.26; H, 4.96. C₁₉H₁₆O₅ requires C, 70.36; H, 4.97%); $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$ 2990, 1660, 1605, 1300 and 1270; $\delta_{\text{H}}(300 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$ 1.47 (3 H, t, *J* 7.2, CH₃), 2.20 (3 H, s, CH₃), 2.22 (3 H, s, CH₃), 4.63 (2 H, q, *J* 7.2, OCH₂), 7.66-7.80 (2 H, m, ArH), 7.83 (1 H, d, *J* 8.0, ArH), 8.52 (1 H, d, *J* 8.0, ArH) and 14.35 (1 H, s, OH); $\delta_{\text{C}}(75.4 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$ 12.5 (q), 13.3 (q), 14.1 (q), 62.1 (t), 107.6 (s), 123.9 (s), 124.9 (d), 126.9 (s), 127.0 (d), 127.3 (s), 129.1 (d), 131.7 (d), 132.8 (s), 144.4 (s), 146.1 (s), 162.6 (s), 169.1 (s), 183.1 (s) and 189.1 (s).

6-Chloro-1,4-dihydro-9-hydroxy-2,3-dimethyl-1,4-dioxoanthracene-10-carboxylic acid ethyl ester 10c. Red crystals; mp 189-190 °C (from CHCl₃-hexane); (Found: C, 63.61; H, 4.23. C₁₉H₁₅ClO₅ requires C, 63.61; H, 4.21%); $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$ 2990, 1725, 1660, 1605, 1425 and 1255; $\delta_{\text{H}}(300 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$ 1.47 (3 H, t, *J* 7.2, CH₃), 2.18 (3 H, s, CH₃), 2.19 (3 H, s, CH₃), 4.62 (2 H, q, *J* 7.2, OCH₂), 7.59 (1 H, dd, *J* 8.9 and 1.7, ArH), 7.76 (1 H, d, *J* 1.7, ArH), 8.39 (1 H, d, *J* 8.9, ArH) and 14.24 (1 H, s, OH); $\delta_{\text{C}}(75.4 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$ 12.4 (q), 13.3 (q), 14.0 (q), 62.3 (t), 107.7 (s), 125.1 (s), 125.3 (s), 125.6 (s), 126.0 (d), 126.4 (d), 129.7 (d), 133.6 (s), 138.3 (s), 144.4 (s), 146.2 (s), 162.1 (s), 168.5 (s), 182.8 (s) and 188.9 (s).

6-Bromo-1,4-dihydro-9-hydroxy-2,3-dimethyl-1,4-dioxoanthracene-10-carboxylic acid ethyl ester 10d. Red crystals; mp 211-212 °C (from CHCl₃-hexane); (Found: C, 56.60; H, 3.69. C₁₉H₁₅BrO₅ requires C, 56.59; H, 3.75%); $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$ 2925, 1725, 1660, 1605, 1425 and 1370; $\delta_{\text{H}}(300 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$ 1.47 (3 H, t, *J* 7.1, CH₃), 2.19 (3 H, s, CH₃), 2.20 (3 H, s, CH₃), 4.63 (2 H, q, *J* 7.1, OCH₂), 7.75 (1 H, dd, *J* 8.9 and 1.4, ArH), 7.94 (1 H, d, *J* 1.4, ArH), 8.32 (1 H, d, *J* 8.9, ArH) and 14.24 (1 H, s, OH); $\delta_{\text{C}}(75.4 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$ 12.5 (q), 13.3 (q), 14.0 (q), 62.3 (t), 107.8 (s), 125.0 (s), 125.5 (s), 125.6 (s), 126.3 (d), 126.9 (s), 129.2 (d), 132.4 (d), 133.8 (s), 144.4 (s), 146.2 (s), 162.2 (s), 168.5 (s), 182.8 (s) and 188.9 (s).

1,4-Dihydro-9-hydroxy-2,3,8-trimethyl-1,4-dioxoanthracene-10-carboxylic acid ethyl ester 10e. Red crystals; mp 177-178 °C (from CHCl₃-hexane); (Found: C, 70.87; H, 5.41. C₂₀H₁₈O₅ requires C, 70.99; H, 5.36%); $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$ 2925, 1720, 1655, 1630, 1600 and 1295; $\delta_{\text{H}}(300 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$ 1.46 (3 H, t, *J* 7.1, CH₃), 2.18 (3 H, s, CH₃), 2.21 (3 H, s, CH₃), 3.00 (3 H, s, CH₃), 4.61 (2 H, q, *J* 7.1, OCH₂), 7.42 (1 H, d, *J* 7.6, ArH), 7.57 (1 H, t, *J* 7.6, ArH), 7.65 (1 H, d, *J* 7.6, ArH) and 15.34 (1 H, s, OH); $\delta_{\text{C}}(75.4 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$ 12.6 (q), 13.2 (q), 14.1 (q), 25.0 (q), 62.0 (t), 107.8 (s), 123.6 (s), 125.4 (d), 126.6 (s), 127.6 (s), 131.2 (d), 132.5 (d), 134.5 (s), 140.3 (s), 144.6 (s), 145.6 (s), 166.7 (s), 169.5 (s), 183.0 (s) and 188.8 (s).

1,4-Dihydro-9-hydroxy-2,3,6,8-tetramethyl-1,4-dioxoanthracene-10-carboxylic acid ethyl ester 10f. Red crystals; mp 218-219 °C (from CHCl₃-hexane); (Found: C, 71.56; H, 5.70. C₂₁H₂₀O₅ requires C, 71.58; H, 5.72%); $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$ 2985, 1725, 1630, 1600 and 1260; $\delta_{\text{H}}(300 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$ 1.46 (3 H, t, *J* 7.2, CH₃), 2.16 (3 H, s, CH₃), 2.19 (3 H, s, CH₃), 2.46 (3 H, s, CH₃), 2.95 (3 H, s, CH₃), 4.62 (2 H, q, *J* 7.2, OCH₂), 7.24 (1 H, s, ArH), 7.39 (1 H, s, ArH) and 15.30 (1 H, s, OH); $\delta_{\text{C}}(75.4 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$ 12.6 (q), 13.1 (q), 14.0 (q), 21.8 (q), 24.8 (q), 62.0 (t), 107.3 (s), 123.7 (s), 124.5 (s), 124.9 (d), 127.1 (s), 134.5 (d), 134.8 (s), 140.0 (s), 141.9 (s), 144.6 (s), 145.4 (s), 166.7 (s), 169.6 (s), 183.0 (s) and 188.6 (s).

10-Acetyl-1,4-dihydro-9-hydroxy-2,3,6-trimethyl-1,4-dioxanthracene 10k. Red crystals; mp 206-207 °C (from CHCl₃-hexane); $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$ 2960, 1630, 1600, 1300 and 1255; $\delta_{\text{H}}(300 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$ 2.18 (3 H, s, CH₃), 2.22 (3 H, s, CH₃), 2.53 (3 H, s, CH₃), 2.62 (3 H, s, CH₃), 7.50 (1 H, s, ArH), 7.53 (1 H, d, *J* 8.5, ArH), 8.41 (1 H, d, *J* 8.5, ArH) and 14.29 (1 H, s, OH); $\delta_{\text{C}}(100.6 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$ 12.6 (q), 13.2 (q), 22.2 (q), 31.8 (q), 107.0 (s), 123.2 (s), 125.0 (d), 125.6 (s), 126.1 (d), 131.2 (d), 132.2 (s), 135.5 (s), 142.6 (s), 144.9 (s), 145.6 (s), 162.5 (s), 184.0 (s), 188.9 (s) and 205.6 (s); *m/z* (EI) 308.1056 (M^+). C₁₉H₁₆O₄ requires 308.1048), 292 (100%), 279 (2), 237 (2), 209 (2) and 166 (4).

9-Acetyl-1,4-dihydro-10-hydroxy-2,3-dimethyl-1,4-dioxanthracene 10l. Red crystals; mp 215-216 °C (from CHCl₃-hexane); $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$ 3010, 1630, 1600, 1435, 1300 and 1260; $\delta_{\text{H}}(300 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$ 2.19 (3 H, s, CH₃), 2.22 (3 H, s, CH₃), 2.62 (3 H, s, CH₃), 7.67-7.78 (3 H, m, ArH), 8.53 (1 H, d, *J* 7.3, ArH) and 14.30 (1 H, s, OH); $\delta_{\text{C}}(100.6 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$ 12.5 (q), 13.2 (q), 31.8 (q), 107.4 (s), 123.1 (s), 125.1 (d), 126.7 (d), 127.6 (s), 129.2 (d), 131.7 (d), 131.9 (s), 135.9 (s), 144.9 (s), 145.8 (s), 162.3 (s), 183.9 (s), 189.0 (s) and 205.3 (s); *m/z* (EI) 294.0888 (M^+). C₁₈H₁₄O₄ requires 294.0892), 279 (100%), 266 (3), 223 (2) and 165 (10).

Typical experimental procedure for the nucleophilic reaction between 2-benzoyl-1,4-benzoquinones and ethyl butyrylacetate.

A solution of 5-(4-methylbenzoyl)-2,3-dimethyl-1,4-benzoquinone (**7a**) (174 mg, 0.69 mmol), ethyl butyrylacetate (**8a**) (221 mg, 1.40 mmol) and sodium acetate (171 mg, 2.09 mmol) in acetonitrile (10 cm³) was heated at 70 °C for 1 h. The reaction mixture was diluted with ethyl acetate (100 cm³), washed with water (3 × 50 cm³), dried (Na₂SO₄), and concentrated in vacuo. The crude product was purified by column chromatography over silica gel (20g) (eluted with 1:15 ethyl acetate-hexane) to give **19a** (225 mg, 82%) as a mixture of isomeric products in 11:1 ratio. The major isomer can be obtained in pure form by recrystallization (ethyl acetate-hexane)

rel-(2S,3R)-2,3-Dihydro-2,5-dihydroxy-6,7-dimethyl-4-(4-methylbenzoyl)-2-propylbenzo[b]furan-3-carboxylic acid ethyl ester 19a. Yellow crystals; mp 88-89 °C; $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 3445, 2965, 1730, 1615 and 1335; $\delta_{\text{H}}(400 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$ 1.00 (3 H, t, *J* 7.5, CH₃), 1.08 (3 H, t, *J* 7.1, CH₃), 1.53 (2 H, sextet, *J* 7.5, CH₂), 1.85-1.95 (2 H, m, CH₂), 2.22 (6 H, s, 2 × CH₃), 2.44 (3 H, s, CH₃), 3.73-3.97 (2 H, m, OCH₂), 3.88 (1 H, s, CH), 7.25 (2 H, d, *J* 7.6, ArH), 7.49 (2 H, d, *J* 7.6, ArH) and 10.42 (1 H, s, OH); $\delta_{\text{C}}(75.4 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$ 11.7 (q), 13.1 (q), 13.6 (q), 14.1 (q), 16.6 (t), 21.7 (q), 40.9 (t), 57.2 (d), 61.5 (t), 109.4 (s), 115.6 (s), 118.0 (s), 127.1 (s), 127.8 (s), 129.12 (2 × d), 129.20 (2 × d), 136.5 (s), 143.3 (s), 149.8 (s), 153.8 (s), 169.8 (s) and 199.6 (s); *m/z* (EI) 412.1896 (M^+). C₂₄H₂₈O₆ requires 412.1885), 394 (13%), 348 (19), 324 (35), 296 (100) and 283 (39).

rel-(2S,3R)-4-Benzoyl-2,3-dihydro-2,5-dihydroxy-6,7-dimethyl-2-propylbenzo[b]furan-3-carboxylic acid ethyl ester 19b. Yellow crystals; mp 120-121 °C (from CHCl₃-hexane); (Found: C, 69.28; H, 6.60. C₂₃H₂₆O₆ requires C, 69.33; H, 6.58%); $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 3445, 2960, 1735, 1620 and 1335; $\delta_{\text{H}}(400 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$ 0.99 (3 H, t, *J* 7.5, CH₃), 1.08 (3 H, t, *J* 7.2, CH₃), 1.45-1.58 (2 H, m, CH₂), 1.85-1.92 (2 H, m, CH₂), 2.22 (3 H, s, CH₃), 2.23 (3 H, s, CH₃), 3.73-3.86 (1 H, m, OCH), 3.83 (1 H, s, CH), 3.86-3.98 (1 H, m, OCH), 7.45 (2 H, t, *J* 7.7, ArH), 7.53-7.62 (3 H, m, ArH) and 10.55 (1 H, s, OH); $\delta_{\text{C}}(75.4 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$ 11.7 (q), 13.1 (q), 13.6 (q), 14.0 (q), 16.7 (t), 41.0 (t), 57.2 (d), 61.5 (t), 109.4 (s), 115.3 (s), 118.0 (s), 127.2 (s), 128.2 (s), 128.4 (2 × d), 129.0 (2 × d), 132.4 (d), 139.3 (s), 149.8 (s), 154.2 (s), 169.7 (s) and 199.9 (s).

rel-(2S,3R)-2,3-Dihydro-2,5-dihydroxy-6,7-dimethyl-4-(2,4-dimethylbenzoyl)-2-propylbenzo[b]furan-3-carboxylic acid ethyl ester 19f. Yellow crystals; mp 103-104 °C; (Found: C, 70.37; H, 7.13; C₂₅H₃₀O₆ requires C, 70.40; H, 7.09%); $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 3440, 2960, 1730, 1615 and 1335; $\delta_{\text{H}}(300 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$ 0.98 (3 H, t, *J* 7.3, CH₃), 1.07 (3 H, t, *J* 7.1, CH₃), 1.48 (2 H, sextet, *J* 7.3, CH₂), 1.75-1.97 (2 H, m, CH₂), 2.21 (3 H, s, CH₃), 2.23 (3 H, s, CH₃), 2.33 (3 H, s, CH₃), 2.39 (3 H, s, CH₃), 3.44 (1 H, s, OH), 3.65-3.86 (1 H, m, OCH), 3.76 (1 H, s, CH), 3.89-3.92 (1 H, m, OCH), 7.01 (1 H, d, *J* 8.0, ArH), 7.07 (1 H, s, ArH), 7.09 (1 H, d, *J* 8.0, ArH) and 11.64 (1 H, s, OH); $\delta_{\text{C}}(75.4 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$ 11.6 (q), 13.2 (q), 13.7 (q), 14.1 (q), 16.7 (t), 20.0 (q), 21.5 (q), 41.3 (t), 58.2 (d), 61.1 (t), 108.9 (2 × s), 115.5 (s), 118.0 (s), 126.1 (d), 127.3 (s), 128.7 (s), 129.2 (d), 132.3 (d), 141.6 (s), 149.8 (s), 155.8 (s), 169.6 (s) and 201.4 (s).

Manganese(III) mediated oxidation reaction of nucleophilic adduct 19a.

A mixture of **19a** (150 mg, 0.36 mmol) and manganese(III) acetate (195 mg, 0.73 mmol) in acetonitrile (10 cm³) was stirred at RT for 3 h. The reaction mixture was diluted with ethyl acetate (100 cm³), washed with saturated aqueous sodium bisulfite (50 cm³), water (3 × 50 cm³), dried (Na₂SO₄), and concentrated in vacuo. The crude product was purified by column chromatography over silica gel (20g) (eluted with 1:15 ethyl acetate-hexane) to give **12a** (108 mg, 72%).

2-[1,4-Dihydro-3-(4-methylbenzoyl)-1,4-dioxo-naphthalen-2-yl]-3-oxo-hexanoic acid ethyl ester 12a. Yellow oil; $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 3270, 1650, 1605, 1455, 1285, 825; $\delta_{\text{H}}(300 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$ 0.86 (3 H, t, J 7.3, CH_3), 1.19 (3 H, t, J 7.1, CH_3), 1.42-1.57 (2 H, m, CH_2), 2.00-2.21 (2 H, m, CH_2), 2.09 (3 H, s, CH_3), 2.13 (3 H, s, CH_3), 2.39 (3 H, s, CH_3), 3.93-4.22 (2 H, m, OCH_2), 7.19 (2 H, d, J 8.0, ArH), 7.70 (2 H, d, J 8.0, ArH), 12.96 (1 H, s, OH); $\delta_{\text{C}}(75.4 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$ 12.2 (q), 12.7 (q), 13.7 (q), 14.1 (q), 19.1 (t), 21.7 (q), 35.4 (t), 60.8 (t), 94.1 (s), 129.1 (2 $\times$ d), 129.2 (2 $\times$ d), 133.0 (s), 137.6 (s), 140.9 (s), 141.7 (s), 143.4 (s), 145.3 (s), 170.3 (s), 178.9 (s), 185.8 (s), 185.9 (s), 191.6 (s); m/z (EI) 410.1734 (M^+ , $\text{C}_{24}\text{H}_{26}\text{O}_6$ requires 410.1739), 393 (58%), 347 (66) and 321 (100).

Typical experimental procedure for the manganese(III) mediated radical reaction of 12a.

A mixture of **12a** (178 mg, 0.43 mmol) and manganese(III) acetate (290 mg, 1.08 mmol) in acetic acid (10 cm^3) was heated at 70 $^{\circ}\text{C}$ 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 $\times$ 50 cm^3), aqueous saturated sodium bicarbonate (3 $\times$ 50 cm^3), dried (Na_2SO_4), and concentrated in vacuo. The crude product was purified by column chromatography over silica gel (20g) (eluted with 2:1 dichloromethane-hexane) followed by recrystallization (CHCl_3 -hexane) to give **9a** (57 mg, 39%) and **10a** (44 mg, 30%).

Typical experimental procedure for the manganese(III) mediated radical reaction of nucleophilic adduct 19.

A mixture of **19a** (151 mg, 0.37 mmol) and manganese(III) acetate (486 mg, 1.81 mmol) in acetonitrile (10 cm^3) was heated at 70 $^{\circ}\text{C}$ for 4 h. The reaction mixture was diluted with ethyl acetate (100 cm^3), washed with saturated aqueous sodium bisulfite (50 cm^3), water (3 $\times$ 50 cm^3), dried (Na_2SO_4), and concentrated in vacuo. The crude product was purified by column chromatography over silica gel (20g) (eluted with 2:1 dichloromethane-hexane) followed by recrystallization (CHCl_3 -hexane) to give **9a** (60 mg, 48%).

Typical experimental procedure for the one-pot reaction.

A solution of 5-(4-methylbenzoyl)-2,3-dimethyl-1,4-benzoquinone (**7a**) (150 mg, 0.59 mmol), ethyl butyrylacetate (**8a**) (186 mg, 1.18 mmol) and sodium acetate (145 mg, 1.77 mmol) in acetonitrile (5 cm^3) was heated at 70 $^{\circ}\text{C}$ for 1 h. To the reaction mixture manganese(III) acetate (791 mg, 2.95 mmol) and formic acid (15 cm^3) were then added. After heated at 70 $^{\circ}\text{C}$ for another 30 min, the reaction mixture was diluted with ethyl acetate (100 cm^3), washed with saturated aqueous sodium bisulfite (50 cm^3), water (3 $\times$ 50 cm^3), aqueous saturated sodium bicarbonate (3 $\times$ 50 cm^3), dried (Na_2SO_4), and concentrated in vacuo. The crude product was purified by column chromatography over silica gel (20g) (eluted with 2:1 dichloromethane-hexane) followed by recrystallization (CHCl_3 -hexane) to give **10a** (115 mg, 58%).

Typical experimental procedure for the manganese(III) mediated reaction of 2-alkyl-5-benzoyl-1,4-benzoquinones.

A mixture of 2-benzoyl-5-methyl-1,4-benzoquinone (**20b**) (144 mg, 0.64 mmol), ethyl butyrylacetate (**8a**) (412 mg, 2.61 mmol) and manganese(III) acetate (712 mg, 2.66 mmol) in acetic acid (10 cm^3) was heated at 70 $^{\circ}\text{C}$ 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 $\times$ 50 cm^3), aqueous saturated sodium bicarbonate (3 $\times$ 50 cm^3), dried (Na_2SO_4), and concentrated in vacuo. The crude product was purified by column chromatography over silica gel (20g) (eluted with 2:1 dichloromethane-hexane) followed by recrystallization (CHCl_3 -hexane) to give **21b** (70 mg, 36%) and **22b** (44 mg, 22%).

4,7-Dihydro-6-methyl-3-(4-methylphenyl)-4,7-dioxobenzo[c]furan-1-carboxylic acid ethyl ester 21a. Yellow powder; mp 117-118 $^{\circ}\text{C}$ (from CHCl_3 -hexane); $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 2985, 1730, 1670, 1500 and 1280; $\delta_{\text{H}}(400 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$ 1.48 (3 H, t, J 7.1, CH_3), 2.17 (3 H, d, J 1.4, CH_3), 2.44 (3 H, s, CH_3), 4.51 (2 H, q, J 7.1, OCH_2), 6.78 (1 H, q, J 1.4, CH), 7.33 (2 H, d, J 8.2, ArH) and 8.36 (2 H, d, J 8.2, ArH); $\delta_{\text{C}}(75.4 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$ 14.2 (q), 16.2 (q), 21.7 (q), 62.3 (t), 117.1 (s), 124.6 (s), 124.7 (s), 128.4 (2 $\times$ d), 129.3 (2 $\times$ d), 138.1 (d), 142.0 (s), 142.7 (s), 149.4 (s), 157.4 (s), 157.7 (s), 180.0 (s) and 180.2 (s); m/z (EI) 324.0992 (M^+ , $\text{C}_{19}\text{H}_{16}\text{O}_5$ requires 324.0998), 267 (7%), 252 (42) and 228 (69).

4,7-Dihydro-6-methyl-4,7-dioxo-3-phenylbenzo[c]furan-1-carboxylic acid ethyl ester 21b. Yellow crystals; mp 115-116 $^{\circ}\text{C}$ (from CHCl_3 -hexane); (Found: C, 69.62; H, 4.56. $\text{C}_{18}\text{H}_{14}\text{O}_5$ requires C, 69.67; H, 4.55%); $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 2985, 1715, 1675, 1535 and 1215; $\delta_{\text{H}}(400 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$ 1.48 (3 H, t, J 7.1, CH_3), 2.17 (3 H, d, J 1.4, CH_3), 4.51 (2 H, q, J 7.1, OCH_2), 6.78 (1 H, q, J 1.4, CH), 7.32-7.59 (3 H, m, ArH) and 8.38-8.49 (2 H, m, ArH); $\delta_{\text{C}}(75.4 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$ 14.1 (q), 16.2 (q), 62.3 (t), 117.6 (s), 124.7 (s), 127.3 (s), 128.4 (2 $\times$ d), 128.6 (2 $\times$ d), 131.9 (d), 138.0 (d), 142.3 (s), 149.6 (s), 157.2 (s), 157.3 (s), 179.9 (s) and 180.2 (s).

3-(4-Chlorophenyl)-4,7-dihydro-6-methyl-4,7-dioxobenzo[c]furan-1-carboxylic acid ethyl ester 21c. Yellow crystals; mp 121-122 °C (from CHCl₃-hexane); (Found: C, 62.65; H, 3.75. C₁₈H₁₃ClO₅ requires C, 62.71; H, 3.80%); $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 2980, 1715, 1675, 1485 and 1280; $\delta_{\text{H}}(400 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$ 1.48 (3 H, t, J 7.1, CH₃), 2.18 (3 H, s, CH₃), 4.52 (2 H, q, J 7.1, OCH₂), 6.79 (1 H, s, CH), 7.50 (2 H, d, J 8.7, ArH) and 8.44 (2 H, d, J 8.7, ArH); $\delta_{\text{C}}(100.6 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$ 14.1 (q), 16.3 (q), 62.4 (t), 117.8 (s), 124.6 (s), 125.7 (s), 129.0 (2 × d), 129.6 (2 × d), 137.9 (d), 138.0 (s), 142.3 (s), 149.8 (s), 156.0 (s), 157.2 (s), 179.4 (s) and 180.2 (s).

6-Ethyl-4,7-dihydro-3-(4-methylphenyl)-4,7-dioxobenzo[c]furan-1-carboxylic acid ethyl ester 21d. Yellow crystals; mp 137-138 °C (from CHCl₃-hexane); (Found: C, 70.82; H, 5.35. C₂₀H₁₈O₅ requires C, 70.99; H, 5.36%); $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 2980, 1720, 1670, 1505 and 1185; $\delta_{\text{H}}(400 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$ 1.20 (3 H, t, J 7.3, CH₃), 1.48 (3 H, t, J 7.4, CH₃), 2.44 (3 H, s, CH₃), 2.60 (2 H, q, J 7.3, CH₂), 4.51 (2 H, q, J 7.4, OCH₂), 6.72 (1 H, s, CH), 7.33 (2 H, d, J 8.1, ArH) and 8.36 (2 H, d, J 8.1, ArH); $\delta_{\text{C}}(75.4 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$ 12.1 (q), 14.2 (q), 21.7 (q), 22.4 (t), 62.3 (t), 117.0 (s), 124.7 (s), 125.0 (s), 128.4 (2 × d), 129.4 (2 × d), 136.6 (d), 142.0 (s), 142.7 (s), 154.5 (s), 157.5 (s), 157.6 (s), 179.8 (s) and 180.5 (s).

6-tert-Butyl-4,7-dihydro-3-(4-methylphenyl)-4,7-dioxobenzo[c]furan-1-carboxylic acid ethyl ester 21e. Yellow liquid; $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 2970, 1730, 1680, 1505 and 1185; $\delta_{\text{H}}(400 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$ 1.37 (9 H, s, 3 × CH₃), 1.47 (3 H, t, J 7.1, CH₃), 2.44 (3 H, s, CH₃), 4.50 (2 H, q, J 7.1, OCH₂), 6.79 (1 H, s, CH), 7.33 (2 H, d, J 8.3, ArH) and 8.37 (2 H, d, J 8.3, ArH); $\delta_{\text{C}}(75.4 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$ 14.1 (q), 21.6 (q), 29.3 (3 × q), 35.7 (s), 62.1 (t), 116.7 (s), 124.6 (s), 126.4 (s), 128.1 (2 × d), 129.3 (2 × d), 136.6 (d), 142.2 (s), 142.5 (s), 157.0 (s), 157.4 (s), 160.0 (s), 179.7 (s) and 180.7 (s); m/z (EI) 366.1466 (M⁺. C₂₂H₂₂O₅ requires 366.1468), 324 (17%), 319 (55), 305 (22), 277 (40) and 262 (14).

6-Benzyl-4,7-dihydro-3-(4-methylphenyl)-4,7-dioxobenzo[c]furan-1-carboxylic acid ethyl ester 21f. Yellow crystals; mp 113-114 °C (from CHCl₃-hexane); (Found: C, 74.92; H, 5.04. C₂₅H₂₀O₅ requires C, 74.99; H, 5.03%); $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 2920, 1730, 1670, 1505 and 1280; $\delta_{\text{H}}(400 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$ 1.48 (3 H, t, J 7.1, CH₃), 2.43 (3 H, s, CH₃), 3.87 (2 H, s, CH₂), 4.51 (2 H, q, J 7.1, OCH₂), 6.54 (1 H, s, CH), 7.21-7.37 (7 H, m, ArH) and 8.33 (2 H, d, J 8.3, ArH); $\delta_{\text{C}}(75.4 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$ 14.2 (q), 21.7 (q), 35.3 (t), 62.3 (t), 117.0 (s), 124.6 (s), 124.9 (s), 127.0 (d), 128.4 (2 × d), 128.8 (2 × d), 129.4 (2 × d), 129.5 (2 × d), 136.8 (s), 138.3 (d), 142.1 (s), 142.7 (s), 152.2 (s), 157.4 (s), 157.8 (s), 179.5 (s) and 180.3 (s).

4,7-Dihydro-*N,N*,6-trimethyl-3-(4-methylphenyl)-4,7-dioxobenzo[c]furan-1-carboxamide 21g. Yellow crystals; mp 205-206 °C (from CHCl₃-hexane); (Found: C, 70.44; H, 5.30; N, 4.33. C₁₉H₁₇NO₄ requires C, 70.58; H, 5.30; N, 4.33%); $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 2935, 1645, 1610, 1540 and 1505; $\delta_{\text{H}}(400 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$ 2.13 (3 H, d, J 1.3, CH₃), 2.43 (3 H, s, CH₃), 3.07 (3 H, s, NCH₃), 3.21 (3 H, s, NCH₃), 6.80 (1 H, q, J 1.3, CH), 7.31 (2 H, d, J 8.1, ArH) and 8.35 (2 H, d, J 8.1, ArH); $\delta_{\text{C}}(75.4 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$ 15.5 (q), 21.5 (q), 34.9 (q), 37.4 (q), 115.0 (s), 120.1 (s), 124.6 (s), 127.6 (2 × d), 129.2 (2 × d), 139.3 (d), 142.1 (s), 146.4 (s), 148.4 (s), 156.9 (s), 159.5 (s), 180.0 (s) and 181.0 (s).

4,7-Dihydro-*N,N*,6-trimethyl-3-phenyl-4,7-dioxobenzo[c]furan-1-carboxamide 21h. Yellow crystals; mp 195-196 °C (from CHCl₃-hexane); (Found: C, 69.84; H, 4.92; N, 4.49. C₁₈H₁₅NO₄ requires C, 69.89; H, 4.89; N, 4.53%); $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 2920, 1650, 1545, 1495 and 1405; $\delta_{\text{H}}(400 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$ 2.14 (3 H, d, J 1.5, CH₃), 3.08 (3 H, s, NCH₃), 3.22 (3 H, s, NCH₃), 6.82 (1 H, q, J 1.5, CH), 7.44-7.58 (3 H, m, ArH) and 8.38-8.49 (2 H, m, ArH); $\delta_{\text{C}}(75.4 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$ 15.7 (q), 35.1 (q), 37.6 (q), 115.7 (s), 120.3 (s), 127.4 (s), 127.8 (2 × d), 128.6 (2 × d), 131.5 (d), 139.4 (d), 146.9 (s), 148.7 (s), 156.6 (s), 159.5 (s), 180.1 (s) and 181.0 (s).

3-(4-Chlorophenyl)-4,7-dihydro-*N,N*,6-trimethyl-4,7-dioxobenzo[c]furan-1-carboxamide 21i. Yellow crystals; mp 220-221 °C (from CHCl₃-hexane); (Found: C, 62.61; H, 4.12; N, 4.03. C₁₈H₁₄ClNO₄ requires C, 62.89; H, 4.10; N, 4.07%); $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 2920, 1650, 1610, 1540 and 1485; $\delta_{\text{H}}(400 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$ 2.15 (3 H, d, J 0.9, CH₃), 3.08 (3 H, s, NCH₃), 3.22 (3 H, s, NCH₃), 6.82 (1 H, q, J 0.9, CH), 7.48 (2 H, d, J 8.7, ArH) and 8.43 (2 H, d, J 8.7, ArH); $\delta_{\text{C}}(75.4 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$ 15.7 (q), 35.1 (q), 37.7 (q), 116.0 (s), 120.3 (s), 125.9 (s), 129.0 (2 × d), 129.1 (2 × d), 137.7 (s), 139.3 (d), 147.1 (s), 148.9 (s), 155.5 (s), 159.4 (s), 180.2 (s) and 180.9 (s).

6-Ethyl-4,7-dihydro-*N,N*-dimethyl-3-(4-methylphenyl)-4,7-dioxobenzo[c]furan-1-carboxamide 21j. Yellow crystals; mp 186-187 °C (from CHCl₃-hexane); (Found: C, 71.06; H, 5.67; N, 4.11. C₂₀H₁₉NO₄ requires C, 71.20; H, 5.68; N, 4.15%); $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 2920, 1645, 1610, 1540 and 1505; $\delta_{\text{H}}(400 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$ 1.19 (3 H, t, J 7.4, CH₃), 2.43 (3 H, s, CH₃), 2.55 (2 H, qd, J 7.4 and 1.4, CH₂), 3.07 (3 H, s, NCH₃), 3.21 (3 H, s, NCH₃), 6.75 (1 H, t, J 1.4, CH), 7.31 (2 H, d, J 8.4, ArH) and 8.36 (2 H, d, J 8.4, ArH); $\delta_{\text{C}}(75.4 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$ 11.8 (q), 21.5 (q), 21.9 (t), 34.9 (q), 37.4 (q), 114.9 (s), 120.4 (s), 124.6 (s), 127.6 (2 × d), 129.1 (2 × d), 137.7 (d), 142.0 (s), 146.4 (s), 153.3 (s), 156.7 (s), 159.5 (s), 180.1 (s) and 180.6 (s).

6-tert-Butyl-4,7-dihydro-*N,N*-dimethyl-3-(4-methylphenyl)-4,7-dioxobenzo[c]furan-1-carboxamide 21k. Orange crystals; mp 175-176 °C (from CHCl₃-hexane); (Found: C, 72.23; H, 6.35; N, 3.77. C₂₂H₂₃NO₄ requires C, 72.31; H, 6.34; N, 3.83%); $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 2955, 1650, 1580, 1505 and 1400; $\delta_{\text{H}}(400 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$ 1.35 (9 H, s, 3 × CH₃), 2.43 (3 H, s, CH₃), 3.06 (3

H, s, NCH₃), 3.22 (3 H, s, NCH₃), 6.81 (1 H, s, CH), 7.31 (2 H, d, *J* 8.3, ArH) and 8.36 (2 H, d, *J* 8.3, ArH); δ_C (75.4, MHz; CDCl₃; Me₄Si) 21.7 (q), 29.2 (3 $\times$ q), 35.1 (q), 35.5 (s), 37.6 (q), 114.8 (s), 121.8 (s), 124.8 (s), 127.7 (2 $\times$ d), 129.4 (2 $\times$ d), 137.9 (d), 142.2 (s), 146.9 (s), 156.5 (s), 158.6 (s), 159.9 (s), 180.8 (s) and 180.9 (s).

6-Benzyl-4,7-dihydro-*N,N*-dimethyl-3-(4-methylphenyl)-4,7-dioxobenzo[*c*]furan-1-carboxamide 21l. Yellow crystals; mp 190–191 °C (from CHCl₃-hexane); (Found: C, 74.97; H, 5.31; N, 3.43. C₂₅H₂₁NO₄ requires C, 75.17; H, 5.30; N, 3.51%); $\nu_{\max}$ (KBr)/cm⁻¹ 2915, 1650, 1555, 1505 and 1455; δ_H (400 MHz; CDCl₃; Me₄Si) 2.42 (3 H, s, CH₃), 3.06 (3 H, s, NCH₃), 3.21 (3 H, s, NCH₃), 3.83 (2 H, s, CH₂), 6.59 (1 H, s, CH), 7.18–7.38 (7 H, m, ArH) and 8.32 (2 H, d, *J* 8.2, ArH); δ_C (75.4 MHz; CDCl₃; Me₄Si) 21.6(q), 34.9 (t), 35.1 (q), 37.6 (q), 115.0 (s), 120.4 (s), 124.7 (s), 126.9 (d), 127.7 (2 $\times$ d), 128.8 (2 $\times$ d), 129.2 (2 $\times$ d), 129.3 (2 $\times$ d), 136.7 (s), 139.6 (d), 142.3 (s), 146.7 (s), 151.2 (s), 157.0 (s), 159.5 (s), 180.1 (s) and 180.4 (s).

1,4-Dihydro-9-hydroxy-3,6-dimethyl-1,4-dioxoanthracene-10-carboxylic acid ethyl ester 22a. Red crystals; mp 191–192 °C (from CHCl₃-hexane); (Found: C, 70.33; H, 4.96. C₁₉H₁₆O₅ requires C, 70.36; H, 4.97%); $\nu_{\max}$ (KBr)/cm⁻¹ 2980, 1715, 1645, 1600 and 1260; δ_H (400 MHz; CDCl₃; Me₄Si) 1.48 (3 H, t, *J* 7.2, CH₃), 2.20 (3 H, d, *J* 1.5, CH₃), 2.56 (3 H, s, CH₃), 4.64 (2 H, q, *J* 7.2, OCH₂), 6.90 (1 H, q, *J* 1.5, CH), 7.54 (1 H, d, *J* 8.5, ArH), 7.59 (1 H, s, ArH), 8.40 (1 H, d, *J* 8.5, ArH) and 14.11 (1 H, s, OH); δ_C (75.4 MHz; CDCl₃; Me₄Si) 14.1 (q), 16.8 (q), 22.2 (q), 62.2 (t), 107.5 (s), 123.8 (s), 124.8 (d), 125.3 (s), 126.4 (d), 127.0 (s), 131.4 (d), 133.0 (s), 136.4 (d), 142.8 (s), 150.5 (s), 162.7 (s), 169.1 (s), 184.0 (s) and 189.0 (s).

1,4-Dihydro-9-hydroxy-3-methyl-1,4-dioxoanthracene-10-carboxylic acid ethyl ester 22b. Red crystals; mp 143–144 °C (from CHCl₃-hexane); (Found: C, 69.65; H, 4.56. C₁₈H₁₄O₅ requires C, 69.67; H, 4.55%); $\nu_{\max}$ (KBr)/cm⁻¹ 2990, 1730, 1645, 1600 and 1225; δ_H (400 MHz; CDCl₃; Me₄Si) 1.47 (3 H, t, *J* 7.2, CH₃), 2.21 (3 H, d, *J* 1.4, CH₃), 4.63 (2 H, q, *J* 7.2, OCH₂), 6.91 (1 H, q, *J* 1.4, CH), 7.66–7.81 (2 H, m, ArH), 7.84 (1 H, d, *J* 7.8, ArH), 8.52 (1 H, d, *J* 7.8, ArH) and 14.13 (1 H, s, OH); δ_C (100.6 MHz; CDCl₃; Me₄Si) 14.1 (q), 16.8 (q), 62.2 (t), 107.9 (s), 123.6 (s), 124.9 (d), 127.1 (d), 127.3 (s), 127.4 (s), 129.3 (d), 131.8 (d), 132.7 (s), 136.4 (d), 150.6 (s), 162.5 (s), 168.8 (s), 183.8 (s) and 189.1 (s).

6-Chloro-1,4-dihydro-9-hydroxy-3-methyl-1,4-dioxoanthracene-10-carboxylic acid ethyl ester 22c. Red crystals; mp 220–221 °C (from CHCl₃-hexane); $\nu_{\max}$ (KBr)/cm⁻¹ 2920, 1720, 1640, 1595 and 1260; δ_H (300 MHz; CDCl₃; Me₄Si) 1.48 (3 H, t, *J* 7.0, CH₃), 2.21 (3 H, s, CH₃), 4.64 (2 H, q, *J* 7.0, OCH₂), 6.92 (1 H, s, CH), 7.66 (1 H, d, *J* 8.7, ArH), 7.80 (1 H, s, ArH), 8.46 (1 H, d, *J* 8.7, ArH) and 14.08 (1 H, s, OH); δ_C (100.6 MHz; CDCl₃; Me₄Si) 14.0 (q), 16.8 (q), 62.5 (t), 108.1 (s), 124.9 (s), 125.5 (s), 126.20 (d), 126.23 (s), 126.5 (d), 130.1 (d), 133.7 (s), 136.4 (d), 138.5 (s), 150.8 (s), 162.3 (s), 168.4 (s), 183.7 (s) and 189.1 (s); *m/z* (EI) 344.0456 (M⁺. C₁₈H₁₃ClO₅ requires 344.0451), 299 (100%), 272 (16), 255 (23) and 241 (18).

3-Ethyl-1,4-dihydro-9-hydroxy-6-methyl-1,4-dioxoanthracene-10-carboxylic acid ethyl ester 22d. Orange needles; mp 184–185 °C (from CHCl₃-hexane); (Found: C, 70.66; H, 5.30. C₂₀H₁₈O₅: C, 70.99; H, 5.36%); $\nu_{\max}$ (KBr)/cm⁻¹ 2975, 1720, 1640, 1600 and 1260; δ_H (400 MHz; CDCl₃; Me₄Si) 1.20 (3 H, t, *J* 7.4, CH₃), 1.47 (3 H, t, *J* 7.1, CH₃), 2.54 (3 H, s, CH₃), 2.61 (2 H, qd, *J* 7.4 and 1.5, CH₂), 4.63 (2 H, q, *J* 7.1, OCH₂), 6.82 (1 H, t, *J* 1.5, CH), 7.52 (1 H, d, *J* 8.4, ArH), 7.58 (1 H, s, ArH), 8.38 (1 H, d, *J* 8.4, ArH) and 14.10 (1 H, s, OH); δ_C (75.4 MHz; CDCl₃; Me₄Si) 11.6 (q), 14.0 (q), 22.2 (q), 22.8 (t), 62.1 (t), 107.3 (s), 124.1 (s), 124.7 (d), 125.3 (s), 126.4 (d), 126.9 (s), 131.3 (d), 133.0 (s), 134.6 (d), 142.7 (s), 155.4 (s), 162.6 (s), 169.0 (s), 183.6 (s) and 189.2 (s).

3-*tert*-Butyl-1,4-dihydro-9-hydroxy-6-methyl-1,4-dioxoanthracene-10-carboxylic acid ethyl ester 22e. Red crystals; mp 141–142 °C (from CHCl₃-hexane); (Found: C, 71.95; H, 6.03. C₂₂H₂₂O₅ requires C, 72.12; H, 6.05%); $\nu_{\max}$ (KBr)/cm⁻¹ 2965, 1730, 1630, 1505 and 1250; δ_H (400 MHz; CDCl₃; Me₄Si) 1.37 (9 H, s, 3 $\times$ CH₃), 1.45 (3 H, t, *J* 7.2, CH₃), 2.56 (3 H, s, CH₃), 4.62 (2 H, q, *J* 7.2, OCH₂), 6.89 (1 H, s, CH), 7.53 (1 H, d, *J* 8.5, ArH), 7.64 (1 H, s, ArH), 8.39 (1 H, d, *J* 8.5, ArH) and 14.00 (1 H, s, OH); δ_C (75.4 MHz; CDCl₃; Me₄Si) 14.0 (q), 22.2 (q), 29.3 (3 $\times$ q), 36.1 (s), 62.0 (t), 107.3 (s), 124.7 (d), 124.9 (s), 126.0 (s), 126.3 (d), 126.9 (s), 131.2 (d), 133.3 (s), 134.6 (d), 142.7 (s), 160.9 (s), 162.4 (s), 169.1 (s), 183.6 (s) and 189.5 (s).

3-Benzyl-1,4-dihydro-9-hydroxy-6-methyl-1,4-dioxoanthracene-10-carboxylic acid ethyl ester 22f. Red crystals; mp 154–155 °C (from CHCl₃-hexane); (Found: C, 74.75; H, 5.02. C₂₅H₂₀O₅ requires C, 74.99; H, 5.03%); $\nu_{\max}$ (KBr)/cm⁻¹ 2980, 1730, 1635, 1600 and 1260; δ_H (400 MHz; CDCl₃; Me₄Si) 1.46 (3 H, t, *J* 7.2, CH₃), 2.56 (3 H, s, CH₃), 3.90 (2 H, s, CH₂), 4.64 (2 H, q, *J* 7.2, OCH₂), 6.58 (1 H, s, CH), 7.23 (2 H, d, *J* 7.1, ArH), 7.28 (1 H, t, *J* 7.1, ArH), 7.35 (2 H, t, *J* 7.1, ArH), 7.54 (1 H, d, *J* 8.4, ArH), 7.61 (1 H, s, ArH), 8.40 (1 H, d, *J* 8.4, ArH) and 14.07 (1 H, s, OH); δ_C (75.4 MHz; CDCl₃; Me₄Si) 14.0 (q), 22.2 (q), 35.7 (t), 62.1 (t), 107.3 (s), 124.0 (s), 124.8 (d), 125.3 (s), 126.4 (d), 127.0 (d), 127.1 (s), 128.8 (2 $\times$ d), 129.5 (2 $\times$ d), 131.4 (d), 133.0 (s), 136.4 (d), 142.8 (s), 153.3 (s), 162.7 (s), 168.9 (s), 183.3 (s) and 189.0 (s).

3) Copies of ¹H and ¹³C NMR spectra of compounds



































































































