A Novel *bis*-Lactonisation of Naphtho- and Phenanthro-1,2-Dioxines with Malonate Nucleophiles

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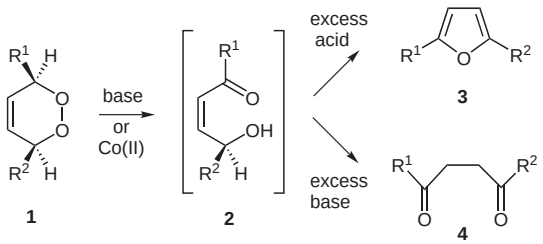
Abstract: Malonate nucleophiles add in a conjugate fashion to substituted naphtho- and phenanthro-1,2-dioxines to furnish functionalised *bis*-lactones in high yield and with high de. The basicity of the malonate nucleophile is sufficiently mild to rearrange the 1,2-dioxines to yield the transient *cis*-γ-hydroxy enone species with no further Kornblum–DeLaMare rearrangement. The *cis*-γ-hydroxy enones readily undergo conjugate addition by malonate nucleophiles in a highly diastereoselective fashion. An intramolecular domino cyclisation then ensues yielding the observed *bis*-lactones. The relative configuration of the *bis*-lactone series was established by 1- and 2-D ^{1}H, ^{13}C NMR techniques and further confirmed by single crystal X-ray analysis.

Key words: *bis*-lactones, peroxides, *cis*-γ-Hydroxy enones, domino reactions, michael additions

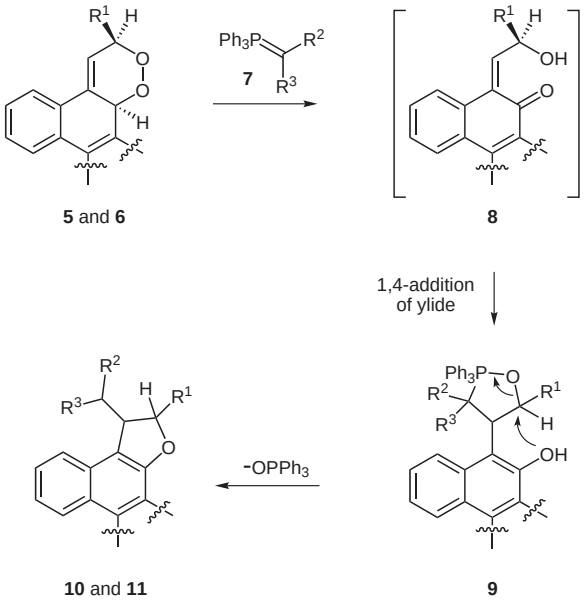
The reported base-catalysed rearrangement[1] of 1,2-dioxines **1**, to afford their isomeric *cis*-γ-hydroxy enones **2**, has been a difficult transformation to control due to the inherent instability of the enones. They readily undergo dehydration to generate furans **3** in the presence of acid[2] or readily undergo a Kornblum–DeLaMare rearrangement to furnish 1,4-diketones **4**, under excessively basic conditions (Scheme 1).[2,3]



Scheme 1

In this connection, our group has been interested in the use of 1,2-dioxines as masked *cis*-γ-hydroxy enones and the transformation of these enones into biologically interesting species. This research has subsequently shown that 1,2-dioxines can be transformed into the reactive *cis*-γ-hydroxy enone moiety under mildly basic conditions[1b,4] or with the use of Co(II)[5] mediated homolytic ring cleavage, without significant decomposition of the transient enones.

Furthermore, these *cis*-γ-hydroxy enones have been efficiently transformed into a range of biologically important substrates by the addition of stabilised nucleophiles.[1b,4] Naphtho- and phenanthro-1,2-dioxines **5** and **6** have previously been shown to rearrange to their isomeric *cis*-γ-hydroxy enones **8**, in the presence of mildly basic stabilised ylides **7**.[6,7] These *cis*-γ-hydroxy enones have then undergone 1,4-conjugate addition by **7** followed by concomitant expulsion of triphenylphosphine oxide from the intermediate **9** to generate 1,2-dihydronaphthyl- **10**[6] and 1,2-dihydrophenanthrylfurans **11**[7] in good to excellent yields (Scheme 2).



Scheme 2

In this study we wished to further extend the methodology by the addition of highly stabilised malonate nucleophiles. Consequently, not only would the basic nature of the malonate induce ring-opening of the parent 1,2-dioxines to their isomeric *cis*-γ-hydroxy enones as seen with stabilised ylides, conjugate addition by the malonate to **8** followed by a double cyclisation via structure **12** could occur to yield the novel *bis*-lactone series **13** (Scheme 3). Herein we report a novel diastereoselective route to highly substituted *cis*-fused *bis*-lactones from a range of substituted naphtho- and phenanthro-1,2-dioxines and malonate.

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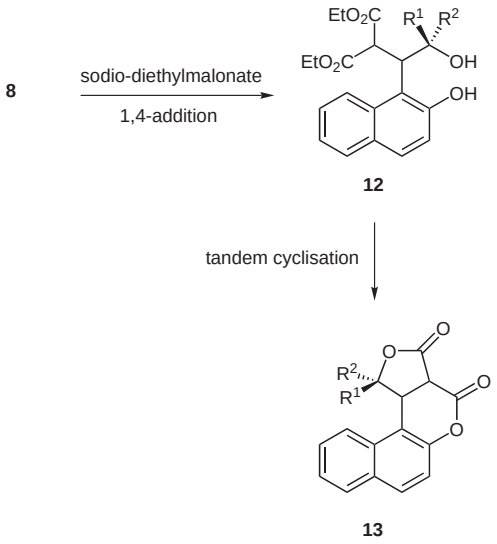
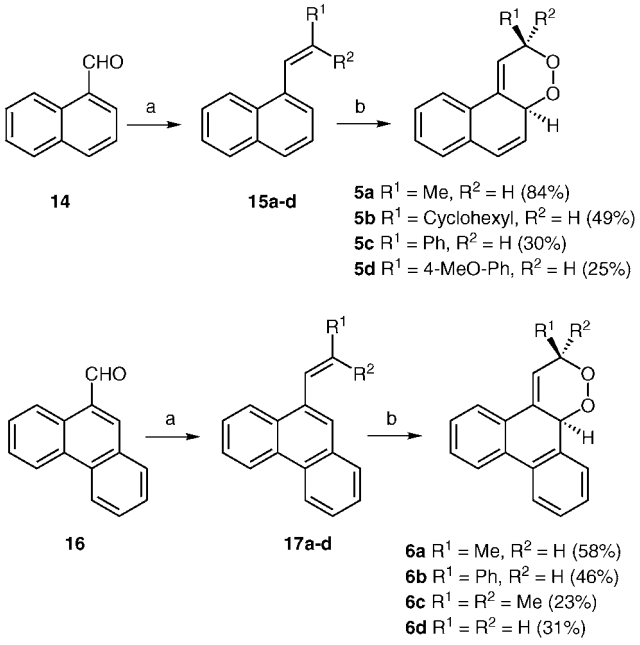


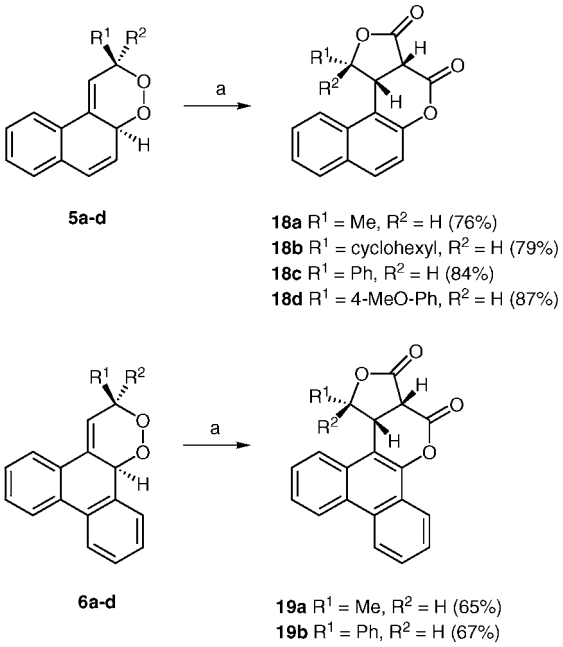
Scheme 3

The 1,2-dioxines chosen for this study are depicted in Scheme 4. Wittig olefination of aldehydes **14** and **16** with various ylides furnished the olefins **15** and **17** respectively, in excellent yields. The olefins were then photolysed[1a,6,8,9] in the presence of the photosensitiser, rose bengal *bis*(triethylammonium) salt and oxygen, consequently affording the naphtho-1,2-dioxines **5a**–**d**,[6,8a] and phenanthro-1,2-dioxines **6a**–**d**,[8b] respectively. 1,2-Dioxines **5b** and **5d** have not been previously reported and were fully characterized and the relative configuration assigned by 1- and 2-D ^{1}H NMR and ^{13}C NMR spectroscopy.



Scheme 4 (a) $Ph_3P{=}CR^1R^2$, CH_2Cl_2; (b) $^1O_2$, hυ, rose Bengal, CH_2Cl_2

The naphtho-1,2-dioxines **5a**–**d** were each treated with sodio-diethyl malonate to yield the novel *bis*-lactones **18a**–**d** in good yields of 76–87% and with excellent de (>98% by ^{1}H NMR). The phenanthro-1,2-dioxines **6a**–**d**, were similarly treated with sodio-diethyl malonate to furnish *bis*-lactones **19a** and **19b** in comparable yields and de (Scheme 5). However, the *gem*-dimethylphenanthro-1,2-dioxine **6c**, and parent phenanthro-1,2-dioxine **6d** failed to yield the desired *bis*-lactones. While an explanation for the failure of **6c** to yield the *bis*-lactone does not readily present itself, it must be noted that the parent phenanthro-1,2-dioxine **6d** undergoes facile polymerisation at ambient temperature.[7,8b]



Scheme 5 (a) Diethyl malonate, NaOEt, THF, 16 h, r.t.

The relative configuration of the series **18** and **19,** was determined via 1-D and 2-D ^{1}H and ^{13}C NMR techniques. Of note, was the ROESY correlations observed for H_a/H_b and H_b/H_c (Figure 1). This ROESY correlation was observed for all the *bis*-lactones and supported the proposed configuration of the fused ring system; namely a *cis*-fused ring system and H_b/H_c being *syn*. Further confirmation of the configuration was via single crystal X-ray analysis of **18a** (Figure 2) and **18d**.[10]

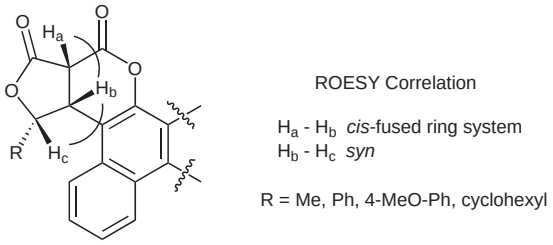


Figure 1 ROESY Correlations for the *bis*-lactone series **18** and **19**.

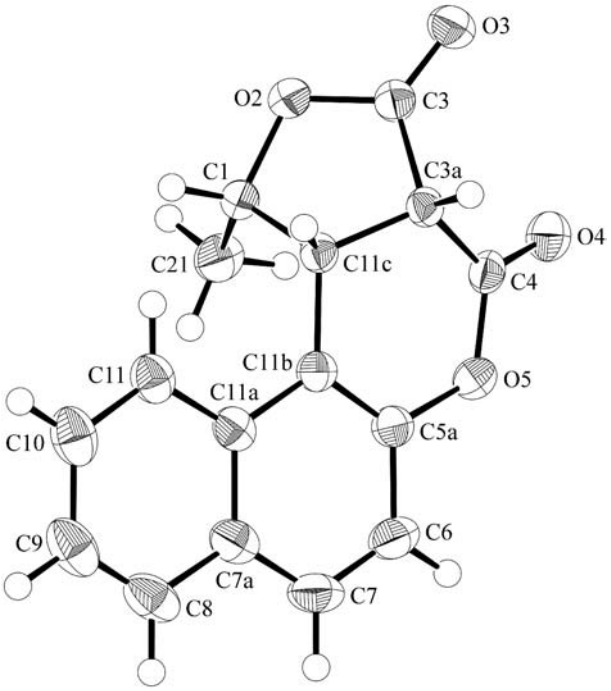
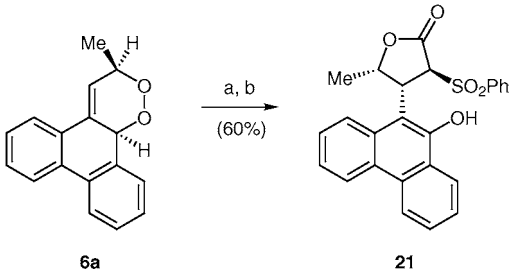


Figure 2 Molecular structure of **18a**.

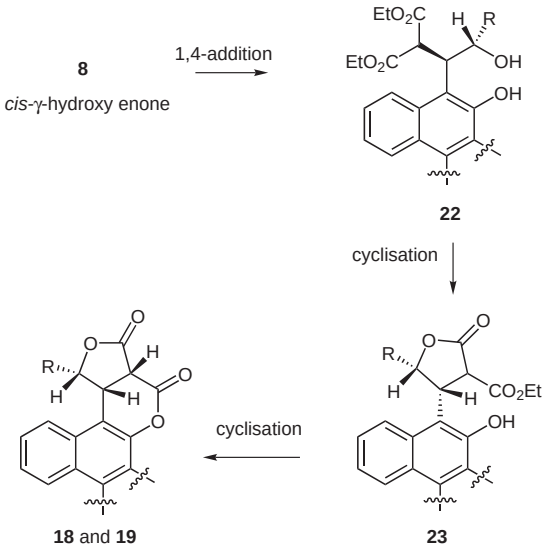
The mechanism of the double cyclisation deserves further discussion. While the formation of the 5-membered lactone ring is thermodynamically more favourable, the cyclisation to yield the 6-membered lactone would involve the participation of the more nucleophilic phenolic hydroxyl. To investigate which ring formed first, 1,2-dioxine **6a** was treated with the enolate of the sulfonyl ester nucleophile **20**. This stabilised nucleophile was chosen since only one cyclisation could occur and hence this may elucidate some insights into which ring is formed first and/or which ring is more thermodynamically favoured. Exposure of 1,2-dioxine **6a** to **20**, furnished the *mono*-lactone **21** in a good yield of 60% (Scheme 6), showing that the 5-membered lactone was formed first.



6a **21**

Scheme 6 (a) **20**, NaOMe, THF; (b) 1 M HCl

We therefore propose the following mechanism for the generation of the *bis*-fused lactones (Scheme 7). The malonate anion induces ring opening of the 1,2-dioxines to initially generate the isomeric *cis*-γ-hydroxy enones. The intermediate *cis*-γ-hydroxy enones **8** then readily undergo *syn*-1,4-conjugate addition by the ester nucleophile to generate intermediate **22**. The first cyclisation is by the γ-hydroxyl to generate the thermodynamically stable *mono*-γ-lactone **23**. This species then undergoes further lactonisation via the phenolic hydroxyl to furnish the observed *bis* fused *cis*-γ,δ-lactones **18** and **19**.



Scheme 7

In conclusion, the methodology described here provides a novel one-pot route to *bis*-fused lactones of types **18** and **19** in good overall yields and further expands the synthetic utility of the under-utilised *cis*-γ-hydroxy enone functionality. The use of the 1,2-dioxine moiety as a masking group for the sensitive *cis*-γ-hydroxy enones is a topic of interest within our group and further synthetic uses are currently being pursed and will be reported on in due course.

^{1}H and ^{13}C NMR was performed using a Varian Gemini-200, Bruker ACP-300 or a Varian Innova-600 spectrometer operating at 200 MHz, 300 MHz and 600 MHz respectively for ^{1}H and 50 MHz, 75 MHz and 150 MHz for ^{13}C in $CDCl_3$. ^{1}H NMR were referenced to internal trimethylsilane (δ 0.00). ^{13}C NMR were referenced to $CDCl_3$ (δ 77.0). Multiplicities are assigned as s: singlet, d: doublet, t: triplet, q: quartet, p: pentet, and br: broad denotes broadened signals. Infrared Spectra were recorded using a Perkin Elmer spectrum BX FT-IR system as either nujol mulls or in the neat form as denoted. Melting points were detemined on a Reichert hot stage apparatus and are uncorrected. Mass spectra were acquired using a VG ZAB 2HF spectrometer and HRMS were performed by the Organic Mass Spectrometry Facility, Central Science Laboratory, University of Tasmania. Microanalysis were performed at the University of Otago. Thin layer chromatography were performed using Merck silica gel 60 F_{254} aluminium backed silica sheets. Flash chromatography were performed using Merck silica gel 60 (230–400 mesh). All reagents were of analytical grade and purchased from Aldrich and used without further purification. THF was distilled from sodium/benzophenone ketyl and CH_2Cl_2 was distilled from P_2O_5 prior to use.

Synthesis of Substituted 1,2-Dioxines 5a–d and 6a–d; General Procedure

All 1,2-dioxines were prepared by the Rose Bengal, *bis*(triethylammonium) salt sensitised [4π + 2π] cycloaddition of singlet oxygen

and to the corresponding substituted vinylic naphthalenes **15a**–**d**, and phenanthrolenes **17a**–**d**, detailed in previous work.[6,8] All yields reported were based upon recovered starting materials. 1,2-Dioxines **5a**,[8a] **5c**,[8a] and **6a**–**d**,[8b] have been previously reported, however, the following have not been characterised.

2-Cyclohexyl-2,4a-dihydronaphtho[2,1-*c*][1,2]dioxine (5b)
Yield 49%; R_f 0.35 (25% CH_2Cl_2–hexanes).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 0.83–0.89 (m, 1 H), 1.00–1.38 (m, 5 H), 1.67 (br d, *J* = 12.4 Hz, 1 H), 1.70–1.72 (m, 2 H), 1.90–1.98 (m, 1 H), 2.11 (br d, *J* = 12.9 Hz, 1 H), 4.12 (ddd, *J* = 3.0, 3.0, 7.7 Hz, 1 H), 5.76 (ddd, *J* = 0.8, 2.3, 9.9 Hz, 1 H), 5.86 (dddd, *J* = 2.3, 3.0, 3.0, 4.0 Hz, 1 H), 6.14 (ddd, *J* = 0.8, 3.0, 4.0 Hz, 1 H), 6.40–6.42 (m, 1 H), 7.02 (dd, *J* = 1.9, 7.2 Hz, 1 H), 7.18–7.22 (m, 2 H), 7.41 (dd, *J* = 2.1, 6.6 Hz, 1 H).

^{13}C NMR ($CDCl_3$, 300MHz): δ = 25.8, 25.9, 26.3, 29.3, 29.7, 42.7, 78.7, 84.9, 121.0, 123.7, 123.8, 127.2, 128.3, 128.6, 129.0, 131.3, 131.9, 134.8.

MS: *m*/*z* (%) = 268 (M^+, 50), 171 (97), 157 (91), 128 (35), 83 (100).

HRMS: *m*/*z* calcd for $C_{18}H_{20}O_2$, 268.1463; found, 268.1464.

2-(4-Methoxyphenyl)-2,4a-dihydronaphtho[2,1-*c*][1,2]dioxine (5d)
Yield 25%, mp 136–138 °C; R_f 0.43 (50% CH_2Cl_2–hexanes).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 3.79 (s, 3 H), 5.49 (dd, *J* = 2.7 Hz, 1 H), 5.80 (dd, *J* = 1.8, 10.2 Hz, 1 H), 6.00 (dddd, *J* = 1.8, 2.7, 2.7, 3.0 Hz, 1 H), 6.16 (dd, *J* = 2.7, 2.7 Hz, 1 H), 6.46 (dd, *J* = 3.0, 10.2 Hz, 1 H), 6.88–6.90 (m, 2 H), 7.07 (dd, *J* = 1.2, 7.8 Hz, 1 H), 7.20–7.28 (m, 2 H), 7.40–7.43 (m, 2 H), 7.47 (d, *J* = 7.8 Hz, 1 H).

^{13}C NMR ($CDCl_3$, 300MHz): δ 55.3, 79.0, 81.3, 113.8, 120.2, 124.0, 124.1, 127.4, 128.5, 128.9, 129.1, 130.1, 131.2, 131.7, 132.2, 135.7, 159.8.

MS: *m*/*z* (%) = (M^+, 274), 259 (48), 231 (18), 202 (14), 135 (100).

HRMS: *m*/*z* calcd for $C_{19}H_{17}O_3$ [M + H]$^+$, 293.1178; found, 293.1161.

***bis*-Lactonisation of Naphtho- and Phenanthro-1,2-Dioxines 5 and 6; General Procedure**
To a solution of sodio-diethyl malonate, prepared from NaOEt (0.5 M, 2.2 mL) and diethyl malonate (0.17 g, 1.1 mmol), in anhyd THF (4 mL) was added a solution of the 1,2-dioxine, **5** or **6** (1 mmol) in anhyd THF (1 mL) and the reaction left to stir for 16 h under N_2. After this period the reaction was quenched by the addition of 1M HCl (2 mL) and the mixture partitioned between CH_2Cl_2 (50 mL) and 1M HCl (50 mL). The aqueous layer was then extracted with CH_2Cl_2 (3 × 50 mL) and the organic layers dried ($MgSO_4$), filtered and the solvent removed under reduced pressure. Each *bis*-lactone was purified by crystallisation from CH_2Cl_2–hexanes or acetone–hexanes. By this method the following *bis*-lactones were obtained.

1-Methyl-1,3a,4,11c-tetrahydro-3*H*-benzo[*f*]furo[3,4-*c*]chromen-3,4-dione (18a)
Yield: 76%; mp 234–236 °C (acetone–hexanes).

IR (nujol): 1788, 1749, 1625, 1515, 1337, 1269, 1214, 1168 cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 0.91 (d, *J* = 6.6 Hz, 3 H), 3.84 (d, *J* = 10.8 Hz, 1 H), 4.65 (dd, *J* = 7.8, 10.8 Hz, 1 H), 5.30 (dt, *J* = 6.6, 7.8 Hz, 1 H), 7.22 (d, *J* = 9.0 Hz, 1 H), 7.50–7.47 (m, 1 H), 7.60–7.57 (m, 1 H), 7.74 (d, *J* = 9.0 Hz, 1 H), 7.82 (d, *J* = 9.0 Hz, 1 H), 7.86–7.84 (m, 1 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 17.2, 37.9, 41.9, 78.6, 110.8, 117.5, 122.0, 126.0, 128.4, 129.3, 130.9, 131.0, 131.1, 149.5, 159.8, 168.6.

MS: *m*/*z* (%) = 268 (M^+, 18), 196 (68), 168 (49), 139 (35), 97 (30), 81 (36), 69 (95), 43 (100).

HRMS: *m*/*z* calcd for $C_{16}H_{12}O_4$, 268.0736; found, 268.0732.

Crystal data for 18a
$C_{16}H_{12}O_4$, *M* = 268.3, *T* = 223(2) K, monoclinic, $P2_1/c$, *a* = 9.9053(10), *b* = 18.0747(17), *c* = 7.1622(7) Å, b = 99.262(2)°, *V* = 1265.6(2) Å^3, *Z* = 4, D_x = 1.408, *F*(000) = 560, m = 0.102 mm^{-1}, no. of unique data (Bruker AXS SMART CCD using Mo Ka radiation so that q_{max} = 30.0°) = 3662, no. of parameters = 181, *R* (all data) = 0.077, *wR* (all data) = 0.128, r = 0.34 e Å^{-3}. CCDC deposition number = 190919. Selected bond distances [A] and angles [o]: C1–O2 1.4644(16), C3–O2 1.3453(16), C3–O3 1.1987(16), C4–O4 1.1949(16), C4–O5 1.3547(16), C5a–O5 1.4011(16), C1–O2–C3 111.55(10), C3–C3a–C4 110.18(10) and C4–O5–O5a 122.41(10).

1-Cyclohexyl-1,3a,4,11c-tetrahydro-3*H*-benzo[*f*]furo[3,4-*c*]-chromen-3,4-dione (18b)
Yield: 79%, mp 257–259 °C (CH_2Cl_2–hexanes).

IR (nujol): 1786, 1748, 1625, 1338, 1271, 1215, 1165 cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 0.70–0.92 (m, 7 H), 1.12–1.18 (m, 1 H), 1.27–1.30 (m, 1 H), 1.35–1.38 (m, 1 H), 1.50–1.54 (m, 1 H), 3.80 (d, *J* = 11.4 Hz, 1 H), 4.68 (dd, *J* = 9.0, 11.4 Hz, 1 H), 4.92 (dd, *J* = 6.6, 9.0 Hz, 1 H), 7.21 (d, *J* = 9.0 Hz, 1 H), 7.50–7.47 (m, 1 H), 7.61–7.58 (m, 1 H), 7.72 (d, *J* = 9.0 Hz, 1 H), 7.82 (d, *J* = 9.0 Hz, 1 H), 7.85–7.83 (m, 1 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 25.2, 25.4, 25.5, 26.8, 30.2, 37.4, 39.4, 42.3, 86.1, 110.0, 117.4, 122.4, 125.9, 128.5, 129.3, 130.9, 131.1, 131.5, 149.3, 159.7, 168.8.

MS: *m*/*z* (%) = 336 (M^+, 10), 197 (15), 196 (100), 168 (25), 139 (12).

Anal. Calcd for $C_{21}H_{20}O_4$: C, 74.98; H, 5.99. Found: C, 74.83; H, 5.92%.

1-Phenyl-1,3a,4,11c-tetrahydro-3*H*-benzo[*f*]furo[3,4-*c*]chromen-3,4-dione (18c)
Yield: 84%; mp 209–211 °C (CH_2Cl_2–hexanes).

IR (nujol): 1786, 1750, 1715, 1221, 1162 cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 3.83 (d, *J* = 10.2 Hz, 1 H), 4.87 (dd, *J* = 7.8, 10.2 Hz, 1 H), 6.16 (d, *J* = 7.8 Hz, 1 H), 6.54–6.55 (m, 2 H), 6.83 (d, *J* = 9.0 Hz, 1 H), 6.88–6.91 (m, 2 H), 7.00–7.03 (m, 1 H), 7.50–7.53 (m, 1 H), 7.65 (d, *J* = 9.0 Hz, 1 H), 7.68–7.71 (m, 1 H), 7.82 (d, *J* = 8.4 Hz, 1 H), 7.99 (d, *J* = 8.4 Hz, 1 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 39.7, 41.6, 82.0, 109.4, 117.0, 122.1, 124.7, 125.8, 126.1, 128.2, 128.5, 128.8, 129.4, 130.8, 150.8, 157.7, 168.6 (two aromatic signals masked).

MS: *m*/*z* (%) = 330 (M^+, 35), 286 (15), 262 (18), 244 (19), 221 (25), 196 (35), 105 (30), 43 (100).

HRMS: *m*/*z* calcd for $C_{21}H_{14}O_4$, 330.0892; found, 330.0892.

1-(4-Methoxyphenyl)-1,3a,4,11c-tetrahydro-3*H*-benzo[*f*]furo-[3,4-*c*]chromen-3,4-dione (18d)
Yield: 87%; mp 229–231 °C (acetone–hexanes).

IR (nujol): 1787, 1748, 1621, 1516, 1263, 1156 cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 3.58 (s, 3 H), 3.81 (d, *J* = 10.2 Hz, 1 H), 4.82 (dd, *J* = 7.8, 10.2 Hz, 1 H), 6.12 (d, *J* = 7.8 Hz, 1 H), 6.40–6.46 (m, 4 H), 6.85 (d, *J* = 9.0 Hz, 1 H), 7.50–7.53 (m, 1 H), 7.66 (d, *J* = 9.0 Hz, 1 H), 7.67–7.70 (m, 1 H), 7.82 (d, *J* = 8.4 Hz, 1 H), 7.98 (d, *J* = 8.4 Hz, 1 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 39.8, 41.6, 55.1, 81.9, 109.4, 113.6, 117.1, 122.1, 125.8, 125.9, 126.0, 128.4, 129.4, 130.8, 130.9, 145.2, 158.5, 169.5 (two aromatic signals masked).

MS: *m*/*z* (%) = 360 (M^+, 20), 274 (15), 197 (20), 196 (100), 168 (35), 135 (34), 97 (32), 57 (67).

HRMS: *m*/*z* calcd for $C_{22}H_{16}O_5$, 360.0998; found, 360.1001.

13-Methyl-10a,11,13,13a-tetrahydro-10*H*-dibenzo[*f*,*h*]furo[3,4-*c*]chromen-10,11-dione (19a)

Yield: 65%; mp 270–273 °C (acetone–hexanes).

IR (nujol): 1789, 1748, 1496, 1322, 1172, 1159 cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.04 (d, *J* = 6.6 Hz, 3 H), 3.97 (d, *J* = 10.2 Hz, 1 H), 4.72 (dd, *J* = 8.4, 10.2 Hz, 1 H), 5.41 (dq, *J* = 6.6, 8.4 Hz, 1 H), 7.68–7.73 (m, 3 H), 7.76–7.78 (m, 1 H), 7.79–7.84 (m, 1 H), 8.40–8.42 (m, 1 H), 8.70–8.74 (m, 2 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 17.3, 38.3, 42.1, 78.7, 106.9, 122.4, 122.7, 122.8, 123.2, 123.7, 126.7, 127.7, 128.3, 128.4, 128.6, 128.9, 131.3, 145.8, 159.6, 168.6.

MS: *m*/*z* (%) = 318 (M^+, 48), 246 (100), 218 (78), 189 (55), 69 (71), 43 (58).

Anal. Calcd for $C_{20}H_{14}O_4$: C, 75.46; H, 4.43. Found: C, 75.60; H, 4.51.

13-Phenyl-10a,11,13,13a-tetrahydro-10*H*-dibenzo[*f*,*h*]furo[3,4-*c*]chromen-10,11-dione (19b)

Yield: 67%, mp 280–284 °C (CH_2Cl_2–hexanes).

IR (nujol): 1808, 1790, 1748, 1608, 1189, 1156 cm^{-1}.

^{1}H NMR (600 MHz, DMSO-d_6): δ = 4.63 (d, *J* = 10.8 Hz, 1 H), 5.23 (dd, *J* = 8.4, 10.8 Hz, 1 H), 6.53 (d, *J* = 8.4 Hz, 1 H), 6.57–6.59 (m, 2 H), 6.89–6.95 (m, 3 H), 7.59–7.61 (m, 1 H), 7.68–7.75 (m, 2 H), 7.82–7.85 (m, 1 H), 7.87–7.89 (m, 1 H), 8.41 (d, *J* = 7.8 Hz, 1 H), 8.79 (d, *J* = 8.4 Hz, 1 H), 8.83 (d, *J* = 7.8 Hz, 1 H).

^{13}C NMR (150 MHz, DMSO-d_6): δ 38.6, 41.3, 81.5, 108.2, 121.1, 122.2, 123.1, 123.6, 124.4, 126.5, 127.7, 127.5, 127.9, 128.1, 128.3, 128.3, 129.2, 130.9, 135.2, 144.4, 160.3, 170.2 (one aromatic carbon masked).

MS: *m*/*z* (%) = 380 (M^+, 18), 246 (100), 218 (80), 189 (61), 149 (15), 105 (25), 57 (52), 43 (58).

HRMS: *m*/*z* calcd for of $C_{25}H_{16}O_4$, 380.1049; found, 380.1049.

Preparation of 5-Methyl-4-(9-phenanthryl)-3-(phenylsulfonyl)-tetrahydro-2-furanone (21)

To a solution of sodio-methyl phenylsulfonyl acetate, prepared from NaOMe (0.5 M, 2.2 mL) and methyl phenylsulfonyl acetate **20** (0.236 g, 1.1 mmol), in anhyd THF (4 mL) was added a solution of the 1,2-dioxine, **6a** (0.256 g, 1.0 mmol) in anhyd THF (2 mL) and the reaction left to stir for 16 h under N_2. After this period the reaction was quenched by the addition of 1 M HCl (2 mL) and the mixture partitioned between CH_2Cl_2 (50 mL) and 1 M HCl (50 mL). The aqueous layer was then extracted further with CH_2Cl_2 (3 × 50 mL) and the organic layers dried ($MgSO_4$), filtered and the solvent removed under reduced pressure. The title compound was purified by recrystallisation from acetone–hexanes, to yield pale pink crystals.

Yield: 60%; mp 263–266 °C.

IR (nujol): 3434, 1758, 1600, 1502, 1448, 1308, 1211, 1147 cm^{-1}.

^{1}H NMR (300 MHz, DMSO-d_6): δ = 0.97 (d, *J* = 6.6 Hz, 3 H), 4.96 (d, J = 2.4 Hz, 1 H), 5.16 (dd, *J* = 2.4, 8.1 Hz, 1 H), 5.28 (dq, *J* = 6.6, 8.1 Hz, 1 H), 7.50–7.75 (m, 7 H), 7.95–7.99 (m, 2 H), 8.05–8.08 (m, 1 H), 8.27–8.29 (m, 1 H), 8.77–8.83 (m, 2 H), 10.20 (br s, 1 H).

^{13}C NMR (75 MHz, DMSO-d_6): δ 16.5, 71.9, 78.3, 83.5, 113.7, 122.4, 123.0, 123.3, 124.2, 125.8, 126.1, 127.5, 129.0, 129.4, 130.7, 131.7, 134.6, 136.9, 149.7, 168.4 (three aromatic signals masked).

MS: *m*/*z* (%) = 432 (M^+, 10), 415 (10), 388 (30), 319 (38), 291 (42), 218 (78), 105 (74), 47 (100).

HRMS: *m*/*z* calcd for of $C_{25}H_{20}O_5S$, 432.1048; found, 432.1024.

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