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Synthesis of 2,3-Dihydro-4*H*-furo[3,2-c] chromen-4-ones and 2,3-Dihydronaphtho[2,3-b]furan-4,9-diones by the Radical Cyclizations of Hydroxyenones with Electron-Rich Alkenes using Manganese(III) Acetate

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Abstract: We have obtained dihydrofurans **3a**–**j** in the radical cyclization of 4-hydroxycoumarin **1a** and 2-hydroxy-1,4-naphtoquinone **1b** with electron rich alkenes **2a**–**i** by manganese(III) acetate. Methods **A** and **B**, which have different molar ratios were studied comparatively in these reactions, and we observed that method **B** (molar ratio 2:1:3) gave the best results. Treatment of 4-hydroxycoumarin **1a** and electron rich alkenes **2a**–**e** gave 2,3-dihydro-4*H*-furo[3,2-c]chromen-4-ones **3a**–**e** in 36–86% yields by the method **B**. Under the same conditions, the reactions of 2-hydroxy-1,4-naphtaquinone **1b** with conjugated alkenes **2b** and **2f**–**i** afforded 2,3-dihydronaphtho[2,3-b]furan-4,9-diones **3f**–**j** in an excellent yields.

Keywords: 2,3-dihydronaphtho[2,3-b]furan-4,9-dione, hydroxyenone 2,3-dihydro-4*H*-furo[3,2-c]chromen-4-one, manganese(III) acetate, oxidative addition, radical cyclization

In the past two decades, the synthetic opportunities offered by high-valent transition metal salt (Mn^{3+}, Ce^{4+}, Co^{3+}, Ag^{+}, etc.) oxidation of 1,3-

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dicarbonyl compounds in the presence of unsaturated systems have attracted attention.[1,2] Among these metal salts, manganese(III) acetate[3–10] and cerium(IV) ammonium nitrate (CAN)[11–13] have a prominent place and have been used efficiently in the synthesis of new organic molecules by forming a C-C bond.

We have reported the formation of dihydrofuran and furan derivatives as a result of oxidative cyclizations of 1,3-dicarbonyl compounds with alkenes and alkynes,[5,7] and the synthesis of 4,5-dihydrofuran and naphthalene derivatives included carboxamide because of the reaction of 1,3-dicarbonyls with α,β-unsaturated-amide[4]-mediated $Mn(OAc)_3$. Previously, we described the synthesis of 3-trifluoroacetyl-4,5-dihydrofurans and 3-[dihydrofuran-2(3H)-ylidene]-1,1,1-trifluoroacetones by the treatment of trifluoromethyl-1,3-dicarbonyl compounds with conjugated alkenes.[8] We have also reported oxidative cyclization of 3-oxopropanenitriles with alkenes, which gave 4,5-dihydrofuran-3-carbonitriles containing heterocycles.[9]

2,3-Dihydro-4*H*-furo[3,2-c]chromen-4-ones such as fercoprolone,[14] cyclobrachycoumarin,[15] and isoerlangefusciol[16] and 2,3-dihydronaphtho[2,3-b]furan-4,9-dione as dehydroiso-α-lapachone[17] showed selective activity toward DNA-repair-deficient yeast mutants widely distributed in nature. Moreover, it is well known that many compounds containing these skeleton structures show biological activities such as anticoagulant, insecticidal, anthelmintic, antifungal, and HIV protease inhibition activities.[18,19] Thus, obtaining these compounds with high yields and improving new synthetic methods are very important. Manganese (III) acetate (MAH), which is a very good radical oxidant and which can be easily synthesized, have not been used efficiently in the synthesis of these compounds.

Here, we have studied radical cyclization of various conjugated alkenes using manganese (III) acetate obtained by electrochemical methods[20] with 4-hydroxycoumarin **(1a)** and 2-hydroxy-1,4-naphthoquinone **(1b)** in detail. We have optimized reaction conditions such as temperature and different molar ratios of reagents. As a result, we have obtained 2,3-dihydro-4*H*-furo[3,2-c]chromen-4-ones (**3a–e**) and 2,3-dihydronaphtho[2,3-b]furan-4,9-diones (**3f–j**) in very good yields, and these compounds were characterized by spectroscopic techniques.

The radical cyclization of 4-hydroxycoumarin **(1a)** and 2-hydroxy-1,4-naphthoquinone **(1b)** with electron-rich alkenes (**2a–i**) were performed using methods **A** (1:1.5:2) and **B** (2:1:3) with different molar ratio [**1**:**2**:$Mn(OAc)_3$, respectively] under nitrogen at 100°C, in HOAc. All new compounds purified by column chromatography or preparative thin-layer chromatography (TLC) were characterized by infrared spectra (IR), ^1H and ^{13}C NMR, mass spectra (MS), and microanalysis, and the other products were characterized by ^1H NMR and MS.

The results of the reactions of **1a** with **2a–e** are given in Table 1. The oxidative cyclization of 4-hydroxycoumarin **(1a)** with 1-phenylpropene **(2a)** afforded 2,3-dihydro-4*H*-furo[3,2-c]chromen-4-one **(3a)** in 32% yield by

Table 1. Radical cyclization of 4-hydroxycoumarin **1a** with electron-rich alkenes **2a–e**

Entry	4-Hydroxycoumarin	Alkene	Dihydrofurocoumarin	Product and yield (%)	
				Method A[a]	Method B[b]
1		**2a**		**3a**, 32	50
2	**1a**	**2b**		**3b**, 65	81
3	**1a**	**2c**		**3c**, 71	86

4	**1a**	**2d**		**3d**, 23	36
5	**1a**	**2e**		**3e**, 45	54

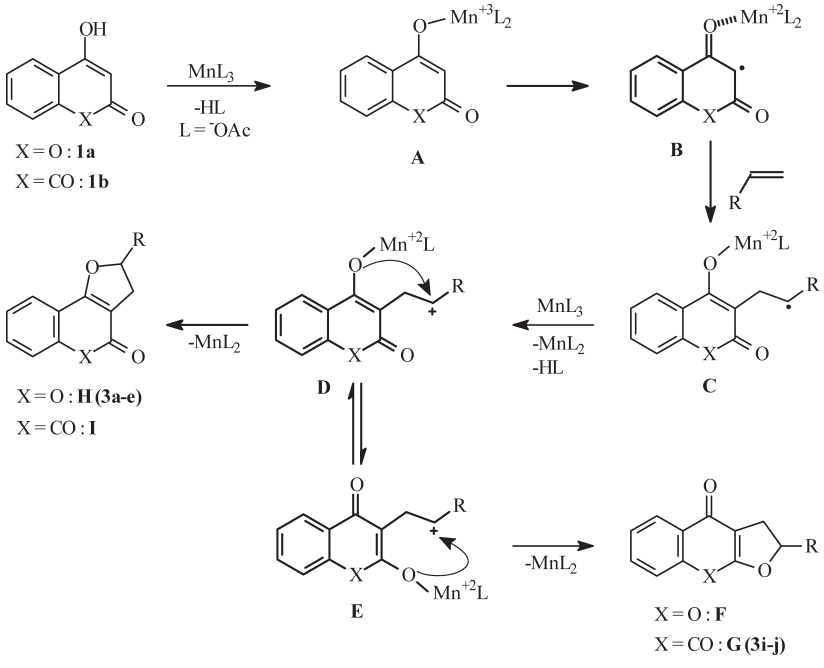
[a]Molar ratio is 1:1.5:2 [**1**:**2**:$Mn(OAc)_3$, respectively], and yield of product is based on **1a**.
[b]Molar ratio is 2:1:3 [**1**:**2**:$Mn(OAc)_3$, respectively], and yield of product is based on the alkene.

method A. On the other hand, we obtained this product in 50% yield by method B (in 30% yield by Ag^{+}/Celite[21]). The ^{1}H NMR spectra of **3a** show that the methyl and phenyl groups are in trans position because the coupling constants between H-2 and H-3 protons of this compound are $J_{trans} = 7.3$ Hz. It is reported that the coupling constants between these protons in same structures are $J_{cis} = 8-9$ Hz, in the literature.[22,23]

We got the best results in the reactions of **1a** with the other alkenes by manganese(III) acetate using method B. We obtained **3b** in 81% yield in the radical cylization of 2-phenyl-1-propene **1a** with **2b** by manganese(III) acetate. Product **3b** was obtained in lower yield (37%[21] and 46%[24] by Ag/Celite and 62%[12] and 70%[25] by CAN in the different reaction conditions).

The reaction of **1a** with 1,1-diphenyl substituted **(2c)** and 1,2-diphenyl substituted alkene **2d** gave 2,3-dihydro-4*H*-furo[3,2-c]chromen-4-ones **3c** (86%) and **3d** (36%) by method B. Treatment of **1a** with isopropenyl acetate **(2e)** gave 2-acetoxy-dihydrofurocoumarin derivative **3e** in 54% yield. Yet, this compound was obtained in 21% yield by CAN.[12]

The proposed reaction mechanism of **1a** and **1b** with alkenes is given in Scheme 1. According to this mechanism, $Mn(OAc)_3$ (MnL_3) and hydroxy-enone give manganese(III)–enolate complex **A**, and an α-carbon radical **B**



Scheme 1. Mechanism for the radical cyclizations of **1a** and **1b** with electron rich alkenes.

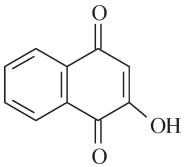
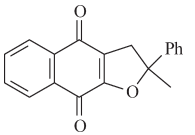
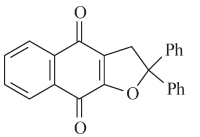
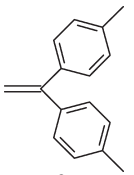
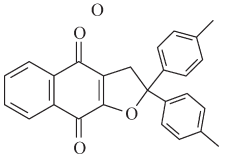
is formed on this structure while Mn^{+3} is reduced to Mn^{+2}. A radical intermediate product **C** is obtained in the addition of the α-carbon radical to alkene. This product is oxidized to carbocation **D** with equivalent of $Mn(OAc)_3$. The intramolecular cyclization of **D** can produce angular products **H** and **I**, and similarly the cyclization of **E** (the other enolic form of **D**) can lead to lineer products **F** and **G**. 2,3-Dihydro-4*H*-furo[3,2-c]chromen-4-one **H** and/or 2,3-dihydro-4*H*-furo[2,3-b]chromen-4-one **F** can occur in the reaction of **1a** with alkenes. These compounds were characterized according to the chemical shift values of carbonyl groups in their ^{13}C NMR spectra. The chemical shift values of the carbonyl groups were found at $\delta_{C=O}$ 160–161 ppm as lactone carbonyls, so that isolated compounds are 2,3-dihydro-4*H*-furo[3,2-c]chromen-4-one **H** (**3a–e**). 2,3-Dihydro-4*H*-furo [2,3-b]chromen-4-ones **F** were not obtained in the radical cyclization of **1a** with alkenes (**2a–e**). On the other hand, we obtained only 2,3-dihydronaphtho[2,3-b]furan-4,9-diones **G** (**3f–j**) in the treatment of 2-hydroxy-1, 4-naphthoquinone **(1b)** and alkenes, but 2,3-dihydronaphtho[1,2-b]furan-4,5-diones **I** were not formed. As it is described in the literature, the structures of **G** and **I** were determined on the basis of chemical shift values of carbonyl groups.[11] Linear products are lemon yellow, and angular products are orange.[26] Although angular products **3a–e** were obtained in the reactions of **1a** with alkenes, linear products **3f–j** were obtained in the treatments of **1b** with alkenes. This situation can be explained in that the intramoleculer cyclization of intermediate products **D** and **E** is carried out on the more stable enolic form of hydroxyenones **1a** and **1b**.

As a result of the reaction of 2-hydroxy-1,4-naphthoquinone **1b** with **2b** by CAN, it was occurred with both linear product 2-methyl-2-phenyl-2,3-dihydronaphtho[2,3-*b*]furan-4,9-dione (**3f**, 38%) and angular product 2-methyl-2-phenyl-2,3-dihydronaphtho[1,2-*b*]furan-4,5-dione (48%).[26] However, in this study we obtained only linear products regioselectively in the radical cyclization of **1b** with alkenes by manganese(III) acetate, and all results are given in Table 2. Product **3f** was obtained using methods **A** and **B** in 69 and 93% yields respectively in the treatment of **1b** and **2b**. The reactions of **1b** and alkenes of **1a** and alkenes gave better results using method B.

For instance, **3g** was formed in 95% yield in the treatment of **1b** and 1, 1-diphenylethylene **2f,** and 2,3-dihydronaphtho[1,2-b]furan-4,5-diones **3h** and **3i** were obtained in 98% yields in the reaction of **1b** and both **2g** and **2h**. Compound **3j** was obtained in 66% yield in the treatment of **1b** and 1-phenylcyclohexene **2i**, which are more sterically hindered than **2f–h**.

In conclusion, we comparatively studied methods **A** and **B** in different molar ratios in treatments of 4-hydroxycoumarin **1a** and 2-hydroxy-1,4-naphthoquinone **1b** with electron-rich alkenes by $Mn(OAc)_3$. As a result, 2,3-dihydro-4*H*-furo[3,2-c]chromen-4-ones **3a–e** and 2,3-dihydronaphtho [2,3-b]furan-4,9-diones **3f–j** were obtained in very good yields by method **B**.

Table 2. Radical cyclization of 2-hydroxy-1,4-naphthoquinone **1b** with conjugated alkenes

Entry	2-Hydroxy-1,4-naphtoquinone	Alkene	Dihydrofuronaphthoquinone	Yield (%) Method A[a]	Yield (%) Method B[b]
1	 **1b**	 **2b**		**3f**, 69	93
2	**1b**	 **2f**		**3 g**, 73	95
3	**1b**	 **2g**		**3 h**, 77	98

4	**1b**	**2h**		**3i**, 86	98
5	**1b**	**2i**		**3j**, 54	66

[a]Molar ratio is 1:1.5:2 [**1**:**2**:$Mn(OAc)_3$, respectively], and yield of product is based on **1b**.
[b]Molar ratio is 2:1:3 [**1**:**2**:$Mn(OAc)_3$, respectively], and yield of product is based on the alkene.

EXPERIMENTAL

Melting points were determined on a Gallencamp capillary melting-point apparatus. IR spectra (KBr disc) were obtained with a Matson 1000 IR in the 400–4000 cm^{-1} range with 4 cm^{-1} resolution. ^1H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on a Bruker Avance DPX-400 MHz and Varian Mercury-400 high-performance digital FT-NMR spectrophotometers. Mass spectra were measured on Shimadzu GC-17A/GC-MS-QP5000 (EIMS, 70 eV) spectrophotometers. Elemental analyses were performed on a Leco 932 CHNS-O instrument. TLC was performed on Merck aluminium-packed silica-gel plates. Purification of products was performed by column chromatography on silica gel (Merck silica gel 60, 40–63 μm) or preparative TLC on Merck silica gel ($PF_{254-366nm}$). All solvents and reagents were purchased from Merck.

General Procedure

Method A

A solution of manganese(III) acetate dihydrate (4 mmol, 1.10 g) in 20 mL in glacial acetic acid was heated under a nitrogen atmosphere at 80°C until it dissolved. After $Mn(OAc)_3$ dissolved completely, a solution of **1a–c** (2 mmol) and alkene (3 mmol) in 5 mL of acetic acid was added to this mixture and the temperature was warmed to 100°C. The reaction was complete when the dark brown color of the solution disappeared. Acetic acid was evaporated under reduced pressure. Water was added to the residue, and extraction was performed with $CHCl_3$ (3 × 20 mL). The combined organic extracts were neutralized with satd. $NaHCO_3$ solution, dried over anhydrous Na_2SO_4, and evaporated. Products were purified by column chromatography on silica gel or preparative TLC (20 × 20-cm plates, 2 mm thick) using n-hexane/EtOAc (1:1) as eluent.

Method B

The only difference with method A is that a 2:1:3 molar ratio [**1**:**2**:$Mn(OAc)_3$, respectively] was used.

Data

3-Methyl-2-phenyl-2,3-dihydro-4H-furo[3,2-c]chromen-4-one (3a). Colorless solid, mp 73–74°C (n-hexane–EtOAc), lit: 73°C;[21] δ_H (400 MHz, $CDCl_3$) 7.63 (1H, dd, $J = 6.3$, 1.5 Hz, ArH), 7.48 (1H, td, $J = 8.6$, 1.6 Hz, ArH), 7.35 (6H, m, ArH), 7.2 (1H, td, $J = 6.0$, 0.9 Hz, ArH), 5.54 (1H, d, $J = 7.3$ Hz, H-2), 3.49 (1H, m H-3), 1.47 (3H, d,

$J = 6.8$ Hz, Me); m/z (EI, 70 eV) 279 (MH^+, 17), 278 (M^+, 100), 263 (M^+ -CH_3, 44), 187 (M^+ -$PhCH_2$, 24), 158 (M^+ -$PhCOCH_2$, 54), 121 ($PhOCO^+$, 54), 91 ($PhCH_2^+$, 12), 77 ($C_6H_5^+$, 10), 65 ($C_5H_5^+$, 11).

2-Methyl-2-phenyl-2,3-dihydro-4H-furo[3,2-c]chromen-4-one (3b). Colorless solid, mp 114–116°C (n-hexane–EtOAc), lit: 105°C (Et_2O-hexane);[12] δ_H (400 MHz, $CDCl_3$) 7.71 (1H, dd, $J = 6.3$, 1.5 Hz, ArH), 7.5 (1H, td, $J = 8.65$, 1.59 Hz, ArH), 7.37–7.26 (7H, m, ArH), 3.35 (1H, d, $J = 15.4$ Hz, -CH_2), 3.26 (1H, d, $J = 15.1$ Hz, -CH_2), 1.83 (3 H, s, Me); m/z (EI, 70 eV) 279 (MH^+, 13), 278 (M^+, 55), 263 (M^+ -CH_3, 16), 184 (M^+ PhOH, 40), 158 (M^+ -CH_3COPh, 74), 121 ($C_7H_5O_2^+$, 100), 91 ($PhCH_2^+$, 36), 77 ($C_6H_5^+$, 56), 65 ($C_5H_5^+$, 46).

3-Ethyl-2,2-diphenyl-2,3-dihydro-4H-furo[3,2-c]chromen-4-one (3c). Colorless solid, mp 179–181°C (n-hexane–EtOAc), Found: C, 81.67; H, 5.31. $C_{25}H_{20}O_3$ requires C, 81.50; H, 5.47%. ν_{max} (KBr disc): 1729 (C═O), 1646 (C═C), 1201 (C-O-C), 995, 895, 756, cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.9 (1H, dd, $J = 6.3$, 1.5 Hz, H-9), 7.64 (2 H, dd, $J = 2.3$, 1.5 Hz), 7.59 (1H, m, H-6), 7.40–7.28 (10H, m, ArH), 4.02 (1H, t, $J = 6.65$ Hz, H-3), 1.65 (1H, m, -CH_2), 1.49 (1H, m, -CH_2), 0.75 (3H, t, $J = 7.4$ Hz, Me); δ_C (100 MHz, $CDCl_3$) 165.5 (C-9b), 161.4 (C = O, C-4), 144.5, 133.2 (C-7), 129.2, 128.7, 128.6, 127.6, 127.3, 124.7 (C-8), 123.5 (C-9), 117.6 (C-6), 113.5 (C-9a), 107.7 (C-3a), 100.9 (C-2), 49.6 (C-3), 24.8 (-CH_2), 11.5 (Me); m/z (EI, 70 eV) 369 (MH^+, 20), 368 (M^+, 78), 339 (M^+ -C_2H_5, 24), 325 (M^+ -CO_2, 51), 290 (M^+ -C_6H_5, 3), 277 (M^+ -$PhCH_2$, 7), 263 (M^+ -PhCO, 11), 206 (MH^+ -$C_9H_6O_3$, 18), 165 (Ph_2C^+, 100), 120 ($C_7H_5O_2^+$, 78), 105 ($PhCO^+$, 33), 91 ($PhCH_2^+$, 19), 77 ($C_6H_5^+$, 14), 65 ($C_5H_5^+$, 8).

2,3-Diphenyl-2-propyl-dihydro-4H-furo[3,2-c]chromen-4-one (3d). Pale yellow oil. Found: C, 81.79; H, 5.66. $C_{26}H_{22}O_3$ requires C, 81.65; H, 5.80%. ν_{max} (KBr disc, $CHCl_3$): 1729 (C═O), 1648 (C═C), 1606, 1030 (C-O-C), 970 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.71 (1H, dd, $J = 8.8$, 0.8 Hz, H-9), 7.63 (1H, td, $J = 8.0$, 1.6 Hz, ArH), 7.43–7.25 (10 H, m, ArH), 4.72 (1H, s, H-3), 1.57 (2 H, m, -CH_2), 1.38 (1H, m, -CH_2), 0.97 (1H, m, -CH_2), 0.69 (3 H, t, $J = 7.2$ Hz, Me); δ_C (100 MHz, $CDCl_3$) 166.2 (C-9b), 160.0 (C═O, C-4), 155.6 (C-5a), 144.8, 136.7, 132.9 (C-7), 129.1, 128.9, 128.2, 127.8, 124.4, 124.3 (C-8), 123.1 (C-9), 117.4 (C-6), 112.8 (C-9a), 105.0 (C-3a), 100.0 (C-2), 58.9 (C-3), 40.4 (-CH_2), 17.6 (-CH_2), 14.4 (Me); m/z (EI, 70 eV) 383 (MH^+, 15), 382 (M^+, 31), 339 (M^+ -C_3H_7, 19), 291 (M^+ -$PhCH_2^+$, 26), 288 (M^+ -$PhOH^+$, 18), 262 (M^+ -$PhOCO^+$, 15), 251 (M^+ -C_9H_7O, 33), 189 ($C_{11}H_9O_3^+$, 26), 131 ($C_9H_7O^+$, 46), 121 ($PhOCO^+$, 86), 105 ($PhCO^+$, 45), 91 ($PhCH_2$, 100), 77 ($C_6H_5^+$, 88), 65 ($C_5H_5^+$, 33), 43 ($C_3H_7^+$, 49).

2-Methyl-4-oxo-2,3-dihydro-4H-furo[3,2-c]chromen-2-yl acetate (3e). Colorless solid, mp 170–172°C (n-hexane–EtOAc), lit: 177–179°C

(Et_2O-DCM);[12] δ_H (400 MHz, $CDCl_3$) 7.6 (1H, dd, $J = 9.4$, 1.5 Hz, H-9), 7.5 (1H, td, $J = 8.7$, 1.6 Hz, H-8), 7.3 (1H, d, $J = 8.2$, H-7), 7.2 (1H, td, $J = 7.78$, 1.0 Hz, H-6), 3.45 (1H, d, $J = 16.8$ Hz, Ha-3), 3.1 (1H, d, $J = 16.8$, Hb-3), 2.03 (3 H, s, Me), 1.88 (3 H, s, Me); m/z (EI, 70 eV) 261 (MH^+, 2), 260 (M^+, 11), 219 (M^+ -CH_3CO, 22), 201 (M^+ -Ac, 13), 200 (M^+ -HOAc, 49), 176 (M^+ -$C_4H_6O_2$, 76), 121 ($C_7H_5O_2^+$, 23), 91 ($PhCH_2^+$, 7), 77 ($C_6H_5^+$, 10), 43 (CH_3CO^+, 100).

2-Methyl-2-phenyl-2,3-dihydronaphto[2,3-b]furan-4,9-dione (3f). A lemon-yellow solid, mp 166–168°C (n-hexane–EtOAc), lit: 112–113°C (hexane);[26] δ_H (400 MHz, $CDCl_3$) 8.13 (1H, dd, $J = 7.81$, 1.95 Hz, C-8), 8.07 (1H, dd, $J = 7.42$, 1.56 Hz, C-5), 7.71 (2H, m, ArH), 7.47 (2H, dt, $J = 7.43$, 1.56 Hz, ArH), 7.39 (2H, td, $J = 7.03$, 1.09 Hz, ArH), 7.31 (1H, tt, $J = 7.42$, 1.18 Hz, ArH), 3.48 (1H, d, $J = 17.2$ Hz, -CH_2), 3.38 (1H, d, $J = 17.2$ Hz, -CH_2), 1.88 (3 H, s, -Me).

2,2-Diphenyl-2,3-dihydronaphto[2,3-b]furan-4,9-dione (3g). A lemon-yellow solid, mp 194–196°C (n-hexane–EtOAc). Found: C, 81.90; H, 4.42. $C_{24}H_{16}O_3$ requires C, 81.80; H, 4.58%. ν_{max} (KBr disc): 1671 (C═O), 1641 (C═O), 1589, 1247 (C-O-C), 1197, 962, 700 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 8.13 (1H, dd, $J = 7.05$, 1.39 Hz, C-8), 8.07 (1H, dd, $J = 7.6$, 1.85 Hz, C-5), 7.73 (1H, td, $J = 7.43$, 1.64 Hz, ArH), 7.71 (4H, td, $J = 7.18$, 1.57 Hz, ArH), 7.48 (4H, dd, $J = 8.47$, 3.27 Hz, ArH), 7.38 (4H, td, $J = 8.2$, 1.39 Hz, ArH), 7.28 (2H, m, ArH), 3.96 (2H, s, H-3); δc (100 MHz, $CDCl_3$) 183.8 (C = O, C-4), 178.7 (C═O, C-9), 159.6 (C-9a), 144.4, 135.0, 133.9 (C-6), 133.8 (C-4a), 132.5 (C-7), 129.4 (C-8a), 129.2, 129.1, 129.0, 127.2, 126.8, 126.5 (C-5), 126.2 (C-8), 124.5 (C-3a), 97.0 (C-2), 41.9 (C-3); m/z (EI, 70 eV) 353 (MH^+, 1), 352 (M^+, 5), 324 (M^+ -CO, 22), 307 (MH^+ -CO_2, 17), 275 (M^+ -C_6H_5, 3), 247 (M^+ -PhCO, 5), 218 ($C_8H_6O_2^+$, 3), 165 (Ph_2C^+, 100), 105 ($PhCO^+$, 62), 91 ($PhCH_2^+$, 5), 77 ($C_6H_5^+$, 78), 65 ($C_5H_5^+$, 7).

2,2-Bis(4-methylphenyl)-2,3-dihydronaphto[2,3-b]furan-4,9dione (3h). A lemon-yellow solid, mp 163–165°C (n-hexane–EtOAc). Found: C, 81.81; H, 5.18. $C_{26}H_{20}O_3$ requires C, 82.08; H, 5.30%. ν_{max} (KBr disc): 1683 (C═O), 1629 (C═O), 1247 (C-O-C), 1197, 955, 812, 719 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 8.1 (2H, dd, $J = 10.92$, 1.76 Hz, ArH), 7.74–7.67 (2H, m, ArH), 7.35 (4H, td, $J = 8.28$, 1.80 Hz, ArH), 7.17 (4H, d, $J = 7.96$ Hz, ArH), 3.91 (2H, s, -CH_2), 2.35 (6H, s, Me); δc (100 MHz, $CDCl_3$) 182.5 (C═O, C-4), 177.9 (C = O, C-9), 158.9 (C-9a), 141.0, 138.2, 134.3 (C-6), 133.3 (C-7), 133.2 (C-4a), 132.0 (C-8a), 129.4, 126.5, 126.2 (C-5), 125.9 (C-8), 123.9 (C-3a), 96.8 (C-2), 41.7 (C-3), 21.2 (Me); m/z (EI, 70 eV) 381 (MH^+, 5), 380 (M^+, 21), 352 (M^+ -CO, 29), 337 (MH^+ -CO_2, 19), 289 (M^+ -$PhCH_2$, 7), 165 (Ph_2C^+, 24), 133 ($C_9H_4O_2^+$, 18), 105 ($PhCO^+$, 60), 91 ($PhCH_2^+$, 51), 77 ($C_6H_5^+$, 50), 65 ($C_5H_5^+$, 31).

2,2-Bis(4-fluorphenyl)-2,3-dihydronaphto[2,3-b]furan-4,9dione (3i). A lemon-yellow solid, mp 143–144°C (n-hexane–EtOAc). Found: C, 74.05; H, 3.58. $C_{24}H_{14}F_2O_3$ requires C, 74.22; H, 3.63%. ν_{max} (KBr disc): 1683 (C═O), 1643 (C═O), 1596, 1508, 1246 (C-O-C), 946, 839, 714, 571 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 8.04 (1H, dd, $J = 7.11$, 1.29 Hz, H-8), 7.99 (1H, dd, $J = 7.55$, 1.76 Hz, H-5), 7.66 (1H, td, $J = 7.32$, 1.55 Hz, ArH), 7.62 (1H, td, $J = 7.36$, 2.02 Hz, ArH), 7.35 (4H, dd, $J = 7.49$, 1.43 Hz, ArH), 6.98 (4H, td, $J = 7.2$, 1.85 Hz, ArH), 3.81 (2H, s, H-3); δc (100 MHz, $CDCl_3$) 183.2 (C = O, C-4), 178.6 (C═O, C-9), 164.7–162.2 (d, $^1J_{C\text{-}F} = 248.2$ Hz), 159.3 (C-9a), 140.0 (d, $^4J_{C\text{-}F} = 3.1$ Hz), 135.1 (C-6), 134.0 (C-7), 133.7 (C-4a), 132.4 (C-8a), 128.5 (d, $^3J_{C\text{-}F} = 8.3$ Hz), 127.2 (C-5), 126.9 (C-8), 124.2 (C-3a), 116.3 (d, $^2J_{C\text{-}F} = 21.0$ Hz), 96.6 (C-2), 42.1 (C-3); m/z (EI, 70 eV) 389 (MH^+, 2), 388 (M^+, 8), 360 (M^+ -CO, 29), 216 ($C_{14}H_{10}F_2^+$, 89), 201 ($C_{13}H_9F_2^+$, 100), 120 ($PhCOCH_3^+$, 8), 105 ($PhCO^+$, 78), 77 ($C_6H_5^+$, 26).

4a-Phenyl-1,2,3,4,4a,11b-hexahydro[b]naphtho[3,2-a]furan-6,11-dione (3j). A lemon-yellow solid, mp 132–134°C (n-hexane–EtOAc). Found C, 79.75; H, 5.64. $C_{22}H_{18}O_3$ requires C, 79.98; H, 5.49%. ν_{max} (KBr disc): 1677 (C═O), 1623 (C═O), 1592, 1201 (C-O-C), 947, 754, 719, 694 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 8.12 (1H, dd, $J = 7.06$, 2.18 Hz, H-6), 8.03 (1H, dd, $J = 6.77$, 1.83 Hz, H-7), 7.71 (1H, td, $J = 7.41$, 1.63 Hz, ArH), 7.68 (1H, td, $J = 7.13$, 2.06 Hz, ArH), 7.5 (2H, dd, $J = 7.49$, 1.43 Hz, ArH), 7.37 (2H, td, $J = 7.2$, 1.85 Hz, ArH), 7.29 (1H, m, ArH), 3.77 (1H, t, $J = 6.17$ Hz, H-6), 2.29 (1H, m), 2.02 (2H, m, $-CH_2$), 1.66 (4H, m, $-CH_2$); δc (100 MHz, $CDCl_3$) 183.5 (C═O, C-6), 179.4 (C═O, C-11), 160.1 (C-11a), 146.0, 134.9 (C-8), 134.0 (C-6a), 133.7 (C-9), 132.4 (C-10a), 129.3, 129.1, 128.5, 127.0 (C-7), 126.7 (C-10), 125.2 (C-5b), 95.5 (C-1a), 45.9 (C-5a), 34.6 ($-CH_2$), 25.7 ($-CH_2$), 19.1 ($-CH_2$), 18.9 ($-CH_2$); m/z (EI, 70 eV) 331 (MH^+, 7), 330 (M^+, 31), 302 (M^+ -CO, 13), 285 (M^+-CO_2, 13), 239 (M^+ -$PhCH_2$, 13), 226 (MH^+ -PhCO, 7), 188 ($C_{13}H_{16}O^+$, 23), 143 (M^+ -$C_{13}H_{16}O$, 45), 105 ($PhCO^+$, 57), 91 ($PhCH_2^+$, 60), 77 ($C_6H_5^+$, 100), 65 ($C_5H_5^+$, 21), 55 ($C_4H_7^+$, 31), 43 ($C_3H_7^+$, 17).

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