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One-Step Synthesis of Naphthofurandione, Benzofurandione, and Phenalenofuranone Derivatives by the CAN-Mediated Cycloaddition

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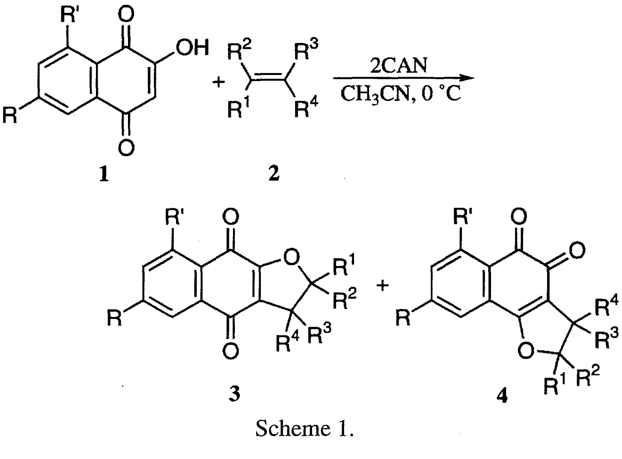
The 3+2-type cycloaddition reaction of 2-hydroxy-1,4-naphthoquinones with various alkenes or phenylacetylene was mediated by ammonium cerium(IV) nitrate (CAN) to give the corresponding naphtho[2,3-*b*]furan-4,9-dione and naphtho[1,2-*b*]furan-4,5-dione derivatives. The reaction of 2-hydroxy-1,4-benzoquinones with alkenes in the presence of CAN similarly proceeded to give benzofuran-4,7-dione and benzofuran-4,5-dione derivatives. 3-Hydroxy-1*H*-phenalen-1-one also underwent the CAN-mediated cycloaddition with alkenes or phenylacetylene to give the corresponding 7*H*-phenaleno[1,2-*b*]furan-7-one derivatives.

The synthesis of naphthofurandione and benzofurandione derivatives has recently attracted much attention, because a number of these compounds have been found in nature and some of them have proven to exhibit a wide range of biological activities.[1] Although many strategies have been used for the construction of naphthofurandione and benzofurandione skeletons,[2,3] most of approaches employ several steps to secure the target skeletons from readily available precursors.[2] In previous papers we reported on the photoinduced regioselective 3+2-type cycloaddition of 2-hydroxy-1,4-naphthoquinones and 2-hydroxy-1,4-benzoquinones[4] with various alkenes (or alkynes) leading to a one-pot formation of naphtho[2,3-*b*]furan-4,9-diones[2a] and benzofuran-4,7-diones,[2b] respectively. In this paper we wish to report that a similar type of cycloaddition can be mediated by ammonium cerium(IV) nitrate (CAN)[5] to give naphtho[2,3-*b*]furan-4,9-dione and benzofuran-4,7-dione derivatives along with the corresponding naphtho[1,2-*b*]furan-4,5-dione and benzofuran-4,5-dione derivatives.[6] We also found that this CAN-mediated reaction using 3-hydroxy-1*H*-phenalen-1-one as a related system of 2-hydroxy-1,4-naphthoquinone afforded 7*H*-phenaleno[1,2-*b*]furan-7-one derivatives.

Synthesis of Naphthofurandione and Benzofurandione Derivatives

We began our investigation by first examining the reaction between 2-hydroxy-1,4-naphthoquinones (**1a**) and 2,3-dimethyl-2-butene (**2a**). An acetonitrile solution of **1a** and 10 molar amounts of **2a** was treated with 2 molar amounts of CAN at 0 °C. After the usual work up, purification of the crude product by preparative TLC on silica gel afforded two pure products. The major and more mobile product (a lemon yellow solid) was identified as 2,2,3,3-tetramethyl-2,3-dihydronaphtho[2,3-*b*]furan-4,9-dione (**3a**) (61%) by a direct comparison with an authentic sample previously prepared by us.[1a] The minor and less mobile one (an orange solid) was identified as 2,2,3,3-tetramethyl-2,3-dihydronaphtho[1,2-*b*]furan-4,5-dione (**4a**) (10%) from its spectroscopic data, which characterize an orthoquinone structure.[7] The formation of each product was completely regioselective and no trace amounts of their corresponding regioisomers could be detected. Use of 2 molar amounts of CAN was essential for the satisfactory production of the products in the present reaction. Reactions between 2-hydroxy-1,4-naphthoquinones **1** and a range of alkenes **2** were then carried out under the same reaction conditions, and the corresponding naphthofurandiones **3** and **4** were obtained (Scheme 1). The results obtained are given in Table 1. The reactions with 2-methyl-2-butene (**2b**) and 2-ethyl-1-butene (**2c**) also gave the corresponding products in good yields (Entries 2 and 3, respectively). 1-Hexene (**2e**), on the other hand, gave the expected products only in a low yield (Entry 5). However, it is worth noting that no 3+2 cycloaddition products could be obtained by the photochemical reaction of **1a** with terminal alkenes.[1a] Styrenes were found to react more smoothly to give the expected adducts in higher yields and seem to favor the formation of the naphtho[1,2-*b*]furan-4,5-diones (Entries 6 and 7). The reaction of **1a** with ethyl vinyl ether (**2h**) was carried out in the presence of an equimolar amount of sodium hydrogencarbonate to afford the naphtho[2,3-*b*]furan-4,9-dione derivative **3h** as the sole



Scheme 1.

Table 1. Products from the CAN Mediated Reactions between the Naphthoquinones **1** and the Alkenes **2**

Entry	**1**		**2**		**3** (Yield/%)$^{a)}$		**4** (Yield/%)$^{a)}$	
1	**1a**	(R = R′ = H)	**2a**	($R^1 = R^2 = R^3 = R^4$ = Me)	**3a**	(61)	**4a**	(10)
2	**1a**		**2b**	($R^1 = R^2 = R^3$ = Me, R^4 = H)	**3b**	(70)	**4b**	(12)
3	**1a**		**2c**	($R^1 = R^2$ = Et, $R^3 = R^4$ = H)	**3c**	(72)	**4c**	(17)
4	**1a**		**2d**	[$R^1 = R^4$ = H, R^2–R^3 = $(CH_2)_3$]	**3d**	$(35)^{c)}$	**4d**	$(16)^{d)}$
5	**1a**		**2e**	(R^1 = *n*-Bu, $R^2 = R^3 = R^4$ = H)	**3e**	(12)	**4e**	(14)
6	**1a**		**2f**	(R^1 = Ph, R^2 = Me, $R^3 = R^4$ = H)	**3f**	(38)	**4f**	(48)
7	**1a**		**2g**	(R^1 = Ph, $R^2 = R^3 = R^4$ = H)	**3g**	(39)	**4g**	(33)
$8^{b)}$	**1a**		**2h**	(R^1 = OEt, $R^2 = R^3 = R^4$ = H)	**3h**	(34)	—	
9	**1a**		**2i**	(R^1 = OAc, $R^2 = R^3 = R^4$ = H)	**3i**	(12)	**4i**	(19)
10	**1a**		**2j**	(R^1 = CO_2Me, R^2 = Me, $R^3 = R^4$ = H)	**3j**	(12)	**4j**	(3)
11	**1b**	(R = OMe, R′ = H)	**2b**		**3k**	(47)	**4k**	(24)
12	**1b**		**2c**		**3l**	(48)	**4l**	(20)
13	**1c**	(R = H, R′ = OMe)	**2c**		**3m**	(58)	**4m**	(19)
14	**1c**		**2f**		**3n**	(39)	**4n**	(44)

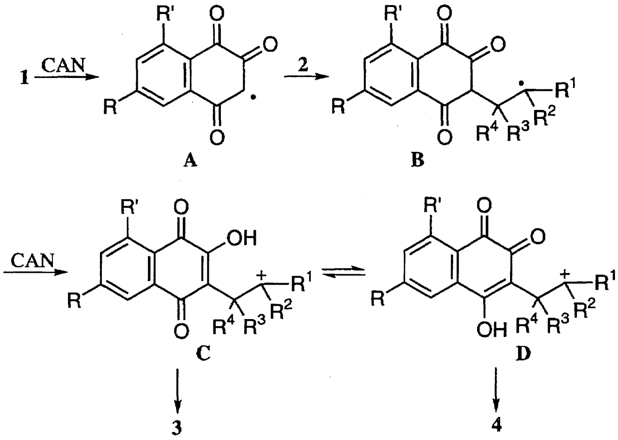
a) Yield of isolated product, purified by preparative TLC on SiO_2 (EtOAc–hexane). b) One molar amount of $NaHCO_3$ was used. c) *cis*-Fused (Ref. 1a). d) *cis*-Fused. The stereochemistry of this product was determined by a comparison of its ^1H NMR spectrum with that of **3d** (Ref. 1a).

isolated product (Entry 8). The corresponding naphtho[1,2-*b*]furan-4,5-dione derivative was not isolated, probably due to its instability under the reaction and/or work-up conditions. Vinyl acetate (**2i**) proved to be less effective; the yields of the corresponding adducts, **3i** and **4i**, were rather lower than those of the other products (Entry 9). Methyl methacrylate (**2j**) gave the corresponding products, **3j** and **4j** (Entry 10), although the yield was considerably low. Methyl acrylate and acrylonitrile, however, could not give any addition product under these conditions. When the reaction was carried out in MeOH instead of acetonitrile, the yield of the products was considerably decreased.

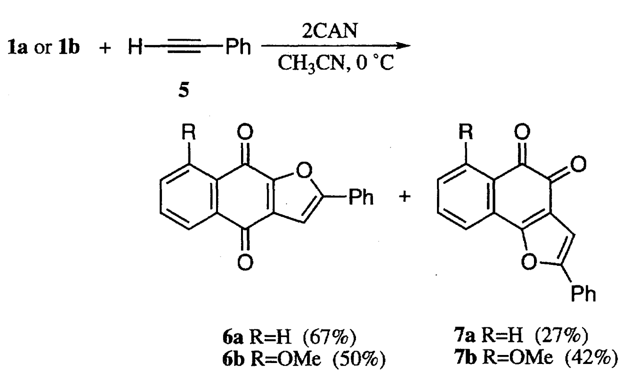
The foregoing results indicate that the pathway to the products of the present cycloaddition is analogous to that proposed previously for the dihydrofuran formation from 1,3-diketones and alkenes.[5] As shown in Scheme 2, the initial formation of a reactive radical intermediate **B** through **A** was followed by oxidation to give tautomeric carbenium ion intermediates, **C**, and **D**, which were trapped intramolecularly with the hydroxy groups of these intermediates to give rise to naphthofurandiones **3** and **4**, respectively. The good to high yields of the products from 2-methyl-2-butene (**2b**), 2-ethyl-1-butene (**2c**), and styrenes (**2f** and **2g**), and the low yields of those from 1-hexene (**2e**) and methyl methacrylate (**2j**) give support to this pathway. It can be assumed that the low yield of the product from vinyl acetate (**2i**) is due to loss of acetyl radical from the corresponding intermediate **B**.

The use of phenylacetylene instead of alkenes was equally effective in cycloaddition with the hydroxynaphthoquinones **1**. As shown in Scheme 3, the formation of products **6** and **7** was almost quantitative. The attempted cycloaddition of **1a** with other alkynes, such as diphenylacetylene or 1-hexyne, however, resulted in the formation of an intractable mixture in each case.

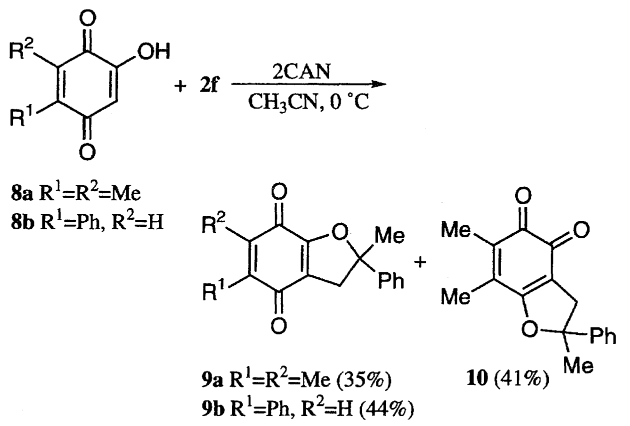
The reactions of 2-hydroxy-1,4-benzoquinones were also carried out in order to examine the scope of the present cycloaddition. When 2-hydroxy-5,6-dimethyl-1,4-benzoquinone (**8a**) was allowed to react with (1-methylvinyl)benzene (**2f**) in the presence of CAN under the above-mentioned conditions, benzofurandiones **9a** and **10** were obtained in good yield. 2-Hydroxy-5-phenyl-1,4-benzoquinone (**8b**) and **2f** gave the benzofuran-4,7-dione derivatives in moderate yield (Scheme 4). 2-Hydroxy-1,4-benzoquinone, which is too unstable to be isolated in a pure form,[8] has proven to be usable in the present reaction. When 1,2,4-benzenetriol (**11**)[8] was reacted with 2-methyl-2-butene (**2b**) or 2-ethyl-1-butene (**2c**) in the presence of 4 molar amounts of CAN at 0 °C, cycloaddition occurred via unstable 2-hydroxy-1,4-benzoquinone to afford the corresponding 2,3-dihydrobenzofuran-4,7-dione derivatives, **12a** or **12b** (Scheme 5).



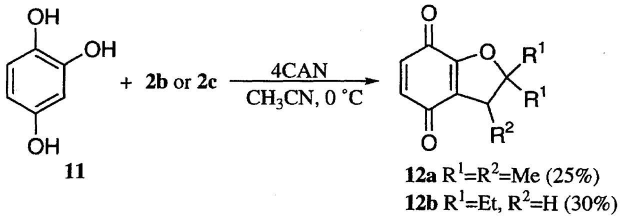
Scheme 2.



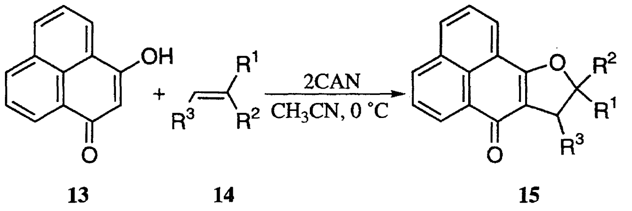
Scheme 3.



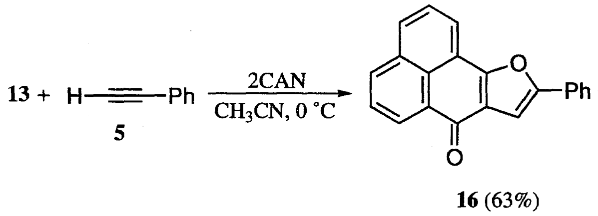
Scheme 4.



Scheme 5.



Scheme 6.



Scheme 7.

Synthesis of Phenalenofuranone Derivatives

Subsequently, we examined the possibility of utilizing the present CAN-mediated cycloaddition in preparing 7*H*-phenaleno[1,2-*b*]furan-7-one derivatives. Some compounds having structures based on this phenalenofuranone skeleton have been found in nature.[9] The only report on the synthesis of this class of molecules recorded by Frost and Morrison can be found in the literature.[10] Among several synthetic routes described in their report, the only successful general approach, which relies on the acid-catalyzed cyclization of 3-(1-naphthoyl)-4,5-dihydrofuran-2(3*H*)-ones, suffers from a tedious preparation of the starting materials. Therefore, it is important to develop a new general method for constructing this skeleton from readily available starting materials.

The preparation of 8,9-dihydro-7*H*-phenaleno[1,2-*b*]furan-7-ones **15** from 3-hydroxy-1*H*-phenalen-1-one (**13**) and a range of alkenes is outlined in Scheme 6. The cycloaddition reactions were carried out under conditions similar to those described above for the preparation of naphtho or benzofurandiones. The reactions proceeded smoothly to afford **15** with complete regioselectivity. The results are summarized in Table 2. The yields of the products were generally high, while vinyl acetate (**14h** = **2i**) gave a rather poor result (Entry 8), as observed in the preparation of naphthofurandiones. The spiro derivative **15c** was obtained with methylenecyclopentane (**14c**) (Entry 3). The reaction with *trans*-stilbene (**14g**) gave a separable mixture of stereoisomers **15g** (*trans* : *cis* = 82 : 18) (Entry 7). The stereochemistries of these products were determined on the basis of ^{1}H NMR spectral analyses. Thus, the *E* isomer exhibited absorption signals assignable to the 8- and 9-H at much higher fields than the *Z* isomer. The coupling constants between these protons were reasonable, taking the conformation of the fused dihydrofuran ring into consideration (see Experimental). The reaction of **13** with phenylacetylene (**5**) in the presence of CAN also proceeded to give the expected cycloaddition product, 9-phenyl-7*H*-phenaleno[1,2-*b*]furan-7-one (**16**), in a satisfactory yield, as shown in Scheme 7.

Table 2. CAN-Mediated Synthesis of 8,9-Dihydro-7*H*-phenaleno[1,2-*b*]furan-7-ones **15**

Entry	14		15 (Yield/%)[a]	
1	**14a**	(= **2b**; $R^1 = R^2 = R^3 = Me$)	**15a**	(68)
2	**14b**	(= **2c**; $R^1 = R^2 = Et$, $R^3 = H$)	**15b**	(82)
3	**14c**	[R^1–$R^2 = (CH_2)_4$, $R^3 = H$]	**15c**	(55)
4	**14d**	(= **2g**; $R^1 = Ph$, $R^2 = Me$, $R^3 = H$)	**15d**	(92)
5	**14e**	($R^1 = 4\text{-}MeC_6H_4$, $R^2 = R^3 = H$)	**15e**	(77)
6	**14f**	($R^1 = 4\text{-}ClC_6H_4$, $R^2 = R^3 = H$)	**15f**	(72)
7	**14g**	($R^1 = R^3 = Ph$, $R^2 = H$)	**15g**	(60)[b]
8	**14h**	(= **2i**; $R^1 = OAc$, $R^2 = R^3 = H$)	**15h**	(35)

a) Isolated yield by preparative TLC on silica gel or recrystallization. b) *trans* : *cis* = 82 : 18 (separable by preparative TLC on SiO_2).

In conclusion, the present CAN-mediated 3 + 2-type cycloaddition reactions can provide a one-step general method for preparing naphthofurandiones, benzofurandiones, and phenalenofuranones. The present method may found some value in organic synthesis because of simple manipulations as well as the ready availability of the starting materials.

Experimental

General Methods. The melting points were measured on a Laboratory Devices MEL-TEMP II melting apparatus and are uncorrected. IR spectra were determined for KBr disks, unless stated otherwise, with a Perkin–Elmer 1600 Series FT IR spectrometer. The ^{1}H NMR spectra were determined in $CDCl_3$ with either a JEOL JNX-PMX 60 NMR spectrometer operating at 60 MHz or a JEOL JNM-GX270 FT NMR spectrometer operating at 270 MHz. The chemical shifts were referenced relative to tetramethylsilane as an internal standard. Mass spectra were recorded with a JEOL AUTOMASS 20 spectrometer (Center for Cooperative Research and Development, this University). TLC was carried out on Merck Kieselgel 60 PF_{254}.

Materials. 2-Hydroxy-6-methoxy-1,4-naphthoquinone (**1b**),[11] 2-hydroxy-8-methoxy-1,4-naphthoquinone (**1c**),[12] 2-hydroxy-5,6-dimethyl-1,4-benzoquinone (**8a**),[13] 2-hydroxy-5-phenyl-1,4-benzoquinone (**8b**),[14] and 1,2,4-benzenetriol (**11**)[8] were prepared by the appropriate reported procedures. All other chemicals, including CAN (95%, Kanto Chemicals Co., Inc.), were commercially available and used without further purification, except that acetonitrile was dried over CaH_2 and distilled prior to use.

2,2,3,3-Tetramethyl-2,3-dihydronaphtho[2,3-*b*]furan-4,9-dione (3a) and 2,2,3,3-Tetramethyl-2,3-dihydronaphtho-[1,2-*b*]furan-4,5-dione (4a). General Synthetic Procedure. 2-Hydroxy-1,4-naphthoquinone (**1a**) (0.17 g, 1.0 mmol) and 2,3-dimethyl-2-butene (**2a**) (0.84 g, 10 mmol) were combined in acetonitrile (40 ml) and dissolved under stirring at room temperature. This solution was cooled to 0 °C and CAN (1.1 g, 2.0 mmol) was added in several portions to the yellow solution, which immediately turned into orange. The reaction was quenched after 20 min with a saturated aqueous NH_4Cl solution. After evaporation of the solvent and excess alkene, the crude product was extracted with Et_2O three times. The combined organic layers were washed successively with aqueous $NaHCO_3$ and brine, dried over anhydrous $MgSO_4$, and concentrated in vacuo. The crude product was purified by preparative TLC (SiO_2, 2 : 1 hexane–EtOAc) to afford the title compounds **3a** as a lemon yellow solid (0.16 g, 61%) and **4a** as an orange solid (26 mg, 10%). **3a**: Mp 101—102 °C (hexane–Et_2O) (lit,[1a]) mp 101—102 °C). **4a**: R_f 0.46 (1 : 2 EtOAc–hexane); an amorphous; IR (neat) 1701, 1640, and 1614 cm^{-1}; ^1H NMR (270 MHz) $\delta = 1.34$ (6H, s), 1.46 (6H, s), 7.5—7.65 (3H, m), and 8.05 (1H, d, $J = 7.6$ Hz); MS *m/z* (%) 256 (M^+; 84) and 241 (100). Found: C, 75.28; H, 6.01%. Calcd for $C_{16}H_{16}O_3$: C, 74.98; H, 6.29%.

The naphthofurandione (**3**,**4**,**6**, and **7**), benzofurandione (**9** and **10**), and phenalenofuranone derivatives (**15** and **16**) were prepared following the above-mentioned procedure, except for the reaction of **1a** with **2h**, yielding **3h**, which was carried out in the presence of $NaHCO_3$ (84 mg, 1.0 mmol).

2,2,3-Trimethyl-2,3-dihydronaphtho[2,3-*b*]furan-4,9-dione (3b): Mp 168—169 °C (hexane–Et_2O) (lit,[1a]) mp 168—169 °C).

2,2,3-Trimethyl-2,3-dihydronaphtho[1,2-*b*]furan-4,5-dione (4b): R_f 0.40 (1 : 2 EtOAc–hexane); mp 122—124 °C (hexane–CH_2Cl_2); IR 1697, 1646, 1633, and 1611 cm^{-1}; ^1H NMR (60 MHz) $\delta = 1.28$ (3H, d, $J = 7.2$ Hz), 1.43 (3H, s), 1.62 (3H, s), 3.22 (1H, q, $J = 7.2$ Hz), 7.45—7.7 (3H, m), and 7.95—8.15 (1H, m); MS *m/z* (%) 242 (M^+; 63) and 227 (100). Found: C, 74.30; H, 5.56%. Calcd for $C_{15}H_{14}O_3$: C, 74.36; H, 5.82%.

2,2-Diethyl-2,3-dihydronaphtho[2,3-*b*]furan-4,9-dione (3c): R_f 0.69 (1 : 2 EtOAc–hexane); mp 114—116 °C (hexane–CH_2Cl_2); IR 1682 and 1622 cm^{-1}; ^1H NMR (60 MHz) $\delta = 0.98$ (6H, t, $J = 7.2$ Hz), 1.86 (4H, q, $J = 7.2$ Hz), 2.96 (2H, s), 7.6—7.85 (2H, m), and 8.0—8.2 (2H, m); MS *m/z* (%) 256 (M^+; 54), 241 (67), and 227 (100). Found: C, 74.83; H, 6.30%. Calcd for $C_{16}H_{16}O_3$: C, 74.98; H, 6.29%.

2,2-Diethyl-2,3-dihydronaphtho[1,2-*b*]furan-4,5-dione (4c): R_f 0.44 (1 : 2 EtOAc–hexane); mp 139—140 °C (hexane–CH_2Cl_2); IR 1698, 1645, and 1612 cm^{-1}; ^1H NMR (60 MHz) $\delta = 0.93$ (6H, t, $J = 7.0$ Hz), 1.86 (4H, q, $J = 7.0$ Hz), 2.94 (2H, s), 7.55—7.75 (3H, m), and 8.0—8.25 (1H, m); MS *m/z* (%) 256 (M^+; 76) and 159 (100). Found: C, 74.69; H, 6.35%. Calcd for $C_{16}H_{16}O_3$: C, 74.98; H, 6.29%.

***cis*-2,3,3a,10b-Tetrahydro-1*H*-cyclopenta[*b*]naphtho[2,3-*d*]-furan-5,10-dione (3d):** Mp 133—134 °C (hexane–Et_2O) (lit,[1a]) mp 132—134 °C).

***cis*-7,8,9,9a-Tetrahydro-6b*H*-cyclopenta[*b*]naphtho[2,1-*d*]furan-5,6-dione (4d):** An amorphous; R_f 0.29 (1 : 2 EtOAc–hexane); IR (neat) 1698, 1642, and 1613 cm^{-1}; ^1H NMR (270 MHz) $\delta = 1.5$—1.9 (4H, m), 2.0—2.1 (1H, m), 2.2—2.3 (1H, m), 3.90 (1H, t, $J = 8.0$ Hz), 5.53 (1H, dd, $J = 8.0$ and 5.4 Hz), 7.55—7.65 (3H, m), and 8.07 (1H, d, $J = 7.6$ Hz); MS *m/z* (%) 240 (M^+; 55) and 212 (100). Found: C, 74.83; H, 5.16%. Calcd for $C_{15}H_{12}O_3$: C, 74.99; H, 5.03%.

2-Butyl-2,3-dihydronaphtho[2,3-*b*]furan-4,9-dione (3e): R_f 0.55 (1 : 3 EtOAc–hexane); mp 74—76 °C (hexane–CH_2Cl_2); IR 1682, 1650, and 1624 cm^{-1}; ^1H NMR (270 MHz) $\delta = 0.98$ (3H, t, $J = 7.3$ Hz), 1.35—1.6 (4H, m), 1.7—1.95 (2H, m), 2.85 (1H, dd, $J = 17.1$ and 8.3 Hz), 3.29 (1H, dd, $J = 17.1$ and 10.2 Hz), 5.0—5.1 (1H, m), 7.6—7.75 (2H, m), and 8.05—8.1 (2H, m); MS *m/z* (%) 256 (M^+; 47) and 213 (100). Found: C, 74.70; H, 6.58%. Calcd for $C_{16}H_{16}O_3$: C, 74.98; H, 6.29%.

2-Butyl-2,3-dihydronaphtho[1,2-*b*]furan-4,5-dione (4e): R_f 0.21 (1 : 3 EtOAc–hexane); mp 67—72 °C (hexane–CH_2Cl_2); IR 1698, 1648, and 1610 cm^{-1}; ^1H NMR (270 MHz) $\delta = 0.96$ (3H, t, $J = 7.3$ Hz), 1.4—1.6 (4H, m), 1.7—1.9 (2H, m), 2.79 (1H, dd, $J = 15.2$ and 7.6 Hz), 3.23 (1H, dd, $J = 15.2$ and 9.8 Hz), 5.0—5.1 (1H, m), 7.5—7.7 (3H, m), and 8.07 (1H, d, $J = 7.3$ Hz); MS *m/z* (%) 256 (M^+; 19), 172 (23), and 159 (100). Found: C, 75.26; H, 6.30%. Calcd for $C_{16}H_{16}O_3$: C, 74.98; H, 6.29%.

2-Methyl-2-phenyl-2,3-dihydronaphtho[2,3-*b*]furan-4,9-dione (3f): Mp 112—113.5 °C (hexane) (lit,[7]) mp 112—114 °C).

2-Methyl-2-phenyl-2,3-dihydronaphtho[1,2-*b*]furan-4,5-dione (4f): Mp 120—123 °C (hexane–Et_2O) (lit,[7]) mp 120—122 °C).

2-Phenyl-2,3-dihydronaphtho[2,3-*b*]furan-4,9-dione (3g): Mp 164—165 °C (hexane–Et_2O) (lit,[1a]) mp 163—165 °C).

2-Phenyl-2,3-dihydronaphtho[1,2-*b*]furan-4,5-dione (4g): Mp 162—164 °C (hexane) (lit,[7]) 162—164 °C).

2-Ethoxy-2,3-dihydronaphtho[2,3-*b*]furan-4,9-dione (3h): Mp 118—119 °C (hexane–Et_2O) (lit,[1a]) mp 119—120 °C).

2-Acetoxy-2,3-dihydronaphtho[2,3-*b*]furan-4,9-dione (3i): Mp 193—195 °C (hexane–Et_2O) (lit,[1a]) mp 193—195 °C).

2-Acetoxy-2,3-dihydronaphtho[1,2-*b*]furan-4,5-dione (4i): R_f 0.38 (1 : 1 EtOAc–hexane); mp 182—185 °C (hexane–CH_2Cl_2); IR 1753, 1695, 1651, and 1616 cm^{-1}; ^1H NMR (270 MHz) $\delta = 2.16$ (3H, s), 3.13 (1H, dd, $J = 17.0$ and 2.9 Hz), 3.41 (1H, dd, $J = 17.0$ and 7.6 Hz), 7.03 (1H, dd, $J = 7.6$ and 2.9 Hz), 7.55—7.7 (3H, m), and 8.11 (1H, dd, $J = 7.9$ and 1.5 Hz); MS *m/z* (%) 198 (M − AcOH; 76) and 170 (100). Found: C, 64.73; H, 3.97%. Calcd for $C_{14}H_{10}O_5$: C, 65.12; H, 3.90%.

Methyl 2-Methyl-4,9-dioxo-2,3,4,9-tetrahydronaphtho-[2,3-*b*]furan-2-carboxylate (3j): Mp 167—169 °C (hexane–Et_2O–CH_2Cl_2) (lit,[1a]) mp 167—169 °C).

Methyl 2-Methyl-4,5-dioxo-2,3,4,5-tetrahydronaphtho-[1,2-*b*]furan-2-carboxylate (4j): R_f 0.21 (1 : 2 EtOAc–hexane); mp 167 °C (hexane–CH_2Cl_2); IR 1757, 1702, 1652, and 1625 cm^{-1}; ^1H NMR (270 MHz) $\delta = 1.82$ (3H, s), 3.06 (1H, d, $J = 16.0$ Hz), 3.51 (1H, d, $J = 16.0$ Hz), 3.83 (3H, s), 7.55—7.75 (3H, m), and 8.10 (1H, dd, $J = 7.6$ and 1.5 Hz); MS *m/z* (%) 272 (M^+; 13), 244 (22), 212 (90), and 184 (100). Found: C, 66.40; H, 4.17%. Calcd for $C_{15}H_{12}O_5$: C, 66.17; H, 4.44%.

6-Methoxy-2,2,3-trimethyl-2,3-dihydronaphtho[2,3-*b*]furan-4,9-dione (3k): Mp 133—134 °C (hexane–CH_2Cl_2) (lit,[1a]) mp 133—134.5 °C).

8-Methoxy-2,2,3-trimethyl-2,3-dihydronaphtho[1,2-*b*]furan-4,5-dione (4k): R_f 0.29 (1 : 2 EtOAc–hexane); mp 178—179 °C (hexane–CH_2Cl_2); IR 1692, 1644, and 1618 cm^{-1}; ^1H NMR (60 MHz) $\delta = 1.28$ (3H, d, $J = 7.2$ Hz), 1.51 (6H, s), 3.22 (1H, q, $J = 7.2$ Hz), 3.94 (3H, s), 7.00 (1H, dd, $J = 8.4$ and 2.2 Hz), 7.02 (1H, d, $J = 2.2$ Hz), and 8.03 (1H, d, $J = 8.4$ Hz); MS *m/z* (%) 272 (M^+; 13), 244 (83), and 203 (100). Found: C, 70.35; H, 5.96%. Calcd for $C_{16}H_{16}O_4$: C, 70.58; H, 5.92%.

2,2-Diethyl-6-methoxy-2,3-dihydronaphtho[2,3-*b*]furan-4,9-

dione (3l): R_f 0.55 (1 : 2 EtOAc–hexane); mp 144—145 °C (hexane–CH_2Cl_2); IR 1672, 1644, and 1625 cm^{-1}; ^{1}H NMR (60 MHz) $\delta = 0.99$ (6H, t, $J = 7.2$ Hz), 1.86 (4H, q, $J = 7.2$ Hz), 2.95 (2H, s), 3.97 (3H, s), 7.08 (1H, dd, $J = 8.0$ and 2.6 Hz), 7.53 (1H, d, $J = 2.6$ Hz), and 8.03 (1H, d, $J = 8.0$ Hz); MS *m/z* (%) 286 (M^+; 44), 258 (45), and 189 (100). Found: C, 71.02; H, 6.39%. Calcd for $C_{17}H_{18}O_4$: C, 71.31; H, 6.34%.

2,2-Diethyl-8-methoxy-2,3-dihydronaphtho[1,2-*b*]furan-4,5-dione (4l): R_f 0.25 (1 : 2 EtOAc–hexane); mp 145—148 °C (hexane–CH_2Cl_2); IR 1684, 1649, and 1620 cm^{-1}; ^{1}H NMR (60 MHz) $\delta = 0.98$ (6H, t, $J = 7.2$ Hz), 1.80 (4H, q, $J = 7.2$ Hz), 2.90 (2H, s), 3.95 (3H, s), 6.97 (1H, dd, $J = 8.2$ and 2.6 Hz), 7.11 (1H, d, $J = 2.6$ Hz), and 8.04 (1H, d, $J = 8.2$ Hz); MS *m/z* (%) 286 (M^+; 86) and 257 (100). Found: C, 71.05; H, 6.04%. Calcd for $C_{17}H_{18}O_4$: C, 71.31; H, 6.34%.

2,2-Diethyl-8-methoxy-2,3-dihydronaphtho[2,3-*b*]furan-4,9-dione (3m): R_f 0.45 (1 : 2 THF–hexane); mp 89—90 °C (hexane–CH_2Cl_2); IR 1678 and 1643 cm^{-1}; ^{1}H NMR (270 MHz) $\delta = .97$ (6H, t, $J = 7.4$ Hz), 1.7—1.9 (4H, m), 2.93 (2H, s), 3.99 (3H, s), 7.23 (1H, d, $J = 8.5$ Hz), 7.63 (1H, dd, $J = 8.5$ and 7.4 Hz), and 7.74 (1H, dd, $J = 7.4$ and 1.1 Hz); MS *m/z* (%) 286 (M^+; 55), 257 (59), and 189 (100). Found: C, 71.31; H, 6.25%. Calcd for $C_{17}H_{18}O_4$: C, 71.31; H, 6.34%.

2,2-Diethyl-6-methoxy-2,3-dihydronaphtho[1,2-*b*]furan-4,5-dione (4m): R_f 0.15 (1 : 2 THF–hexane); mp 205—207 °C (hexane–CH_2Cl_2); IR 1683, 1646, and 1630 cm^{-1}; ^{1}H NMR (270 MHz) $\delta = 0.97$ (6H, t, $J = 7.4$ Hz), 1.84 (4H, q, $J = 7.4$ Hz), 2.88 (2H, s), 3.98 (3H, s), 7.16 (1H, d, $J = 8.4$ Hz), 7.30 (1H, dd, $J = 8.5$ and 7.4 Hz), and 7.59 (1H, dd, $J = 7.4$ and 1.1 Hz); MS *m/z* (%) 286 (M^+; 73) and 189 (100). Found: C, 71.25; H, 6.41%. Calcd for $C_{17}H_{18}O_4$: C, 71.31; H, 6.34%.

8-Methoxy-2-methyl-2-phenyl-2,3-dihydronaphtho[2,3-*b*]furan-4,9-dione (3n): R_f 0.58 (1 : 1 THF–hexane); mp 201—204 °C (hexane–CH_2Cl_2); IR 1673, 1644, and 1600 cm^{-1}; ^{1}H NMR (270 MHz) $\delta = 1.86$ (3H, s), 3.35 (1H, d, $J = 16.5$ Hz), 3.40 (1H, d, $J = 16.5$ Hz), 4.01 (3H, s), 7.2—7.5 (6H, m), 7.64 (1H, dd, $J = 8.4$, and 7.4 Hz), and 7.73 (1H, dd, $J = 7.4$ and 1.1 Hz); MS *m/z* (%) 320 (M^+; 100). Found: C, 74.72; H, 5.12%. Calcd for $C_{20}H_{16}O_4$: C, 74.99; H, 5.03%.

6-Methoxy-2-methyl-2-phenyl-2,3-dihydronaphtho[1,2-*b*]furan-4,5-dione (4n): R_f 0.33 (1 : 1 THF–hexane); mp 200—203 °C (hexane–CH_2Cl_2); IR 1682, 1651, and 1634 cm^{-1}; ^{1}H NMR (270 MHz) $\delta = 1.88$ (3H, s), 3.29 (1H, d, $J = 15.3$ Hz), 3.34 (1H, d, $J = 15.3$ Hz), 4.00 (3H, s), 7.20 (1H, d, $J = 8.4$ Hz, 7.3—7.45 (6H, m), and 7.63 (1H, dd, $J = 8.4$ and 7.4 Hz); MS *m/z* (%) 320 (M^+; 100). Found: C, 74.71; H, 5.16%. Calcd for $C_{20}H_{16}O_4$: C, 74.99; H, 5.03%.

2-Phenylnaphtho[2,3-*b*]furan-4,9-dione (6a): Mp 247—250 °C (hexane–CH_2Cl_2) (lit,[15]) mp 246.5—247.5 °C; lit,[1a]) mp 245—249 °C).

2-Phenylnaphtho[1,2-*b*]furan-4,5-dione (7a): R_f 0.18 (1 : 5 EtOAc–hexane); mp 217—219 °C (hexane–CH_2Cl_2); IR 1693, 1669, and 1656 cm^{-1}; ^{1}H NMR (270 MHz) $\delta = 7.06$ (1H, s), 7.25—7.5 (4H, m), 7.69 (1H, td, $J = 7.9$ and 1.5 Hz), 7.75—7.8 (3H, m), and 8.10 (1H, d, $J = 6.9$ Hz); MS *m/z* (%) 274 (M^+; 90), 246 (99), and 189 (100). Found: C, 78.55; H, 3.42%. Calcd for $C_{18}H_{20}O_3$: C, 78.83; H, 3.67%.

8-Methoxy-2-phenylnaphtho[2,3-*b*]furan-4,9-dione (6b): R_f 0.40 (1 : 2 THF–hexane); mp 217—220 °C (hexane–CH_2Cl_2); IR 1660 cm^{-1}; ^{1}H NMR (270 MHz) $\delta = 4.04$ (3H, s), 7.12 (1H, s), 7.34 (1H, d, $J = 8.4$ Hz), 7.4—7.5 (3H, m), 7.67 (1H, dd, $J = 8.4$ and 7.4 Hz), and 7.85—7.9 (3H, m); MS *m/z* (%) 304 (M^+; 68) and 105 (100). Found C, 74.98; H, 3.94%. Calcd for $C_{19}H_{12}O_4$: C, 74.99; H, 3.97%.

6-Methoxy-2-phenylnaphtho[1,2-*b*]furan-4,5-dione (7b): R_f 0.24 (1 : 2 THF–hexane); mp 187—191 °C (hexane–CH_2Cl_2); IR 1674 cm^{-1}; ^{1}H NMR (270 MHz) $\delta = 4.00$ (3H, s), 7.03 (1H, s), 7.06 (1H, d, $J = 7.4$ Hz), 7.3—7.5 (4H, m), 7.62 (1H, dd, $J = 8.4$ and 7.4 Hz), and 7.77 (2H, d, $J = 7.9$ Hz); MS *m/z* (%) 304 (M^+; 100). Found: C, 75.07; H, 3.96%. Calcd for $C_{19}H_{12}O_4$: C, 74.99; H, 3.97%.

2,5,6-Trimethyl-2-phenyl-2,3-dihydrobenzofuran-4,7-dione (9a): Mp 91—93 °C (Et_2O–hexane) (lit,[1b]) mp 91—92 °C).

2,6,7-Trimethyl-2-phenyl-2,3-dihydrobenzofuran-4,5-dione (10): An oil; R_f 0.35 (1 : 2 EtOAc–hexane); IR (neat) 1679, 1651, and 1632 cm^{-1}; ^{1}H NMR (270 MHz) $\delta = 1.79$ (3H, s), 1.90 (3H, s), 2.14 (3H, s), 3.13 (2H, s), and 7.1—7.4 (5H, m); MS *m/z* (%) 268 (M^+; 100). Found: C, 75.84; H, 5.95%. Calcd for $C_{17}H_{16}O_3$: C, 76.10; H, 6.01%.

2-Methyl-2,5-diphenyl-2,3-dihydrobenzofuran-4,7-dione (9b): Mp 86—87 °C (Et_2O–hexane) (lit,[1b]) 85—87 °C).

2,2,3-Trimethyl-2,3-Dihydrobenzofuran-4,7-dione (12a). A solution of 1,2,4-benzenetriol (**11**) (0.13 g, 1.0 mmol) and 2-methyl-2-butene (**2b**) (0.70 g, 10 mmol) in acetonitrile (40 ml) was treated with CAN (2.8 g, 4 mmol) at 0 °C for 35 min and worked up in a similar manner as described in General Synthetic Procedure to give **12** (48 mg, 25%) as a yellow oil: R_f 0.42 (1 : 3 EtOAc–hexane); IR (neat) 1674, 1640, and 1635 cm^{-1}; ^{1}H NMR (270 MHz) $\delta = 1.23$ (3H, d, $J = 6.9$ Hz), 1.43 (3H, s), 1.47 (3H, s), 3.15 (2H, q, $J = 6.9$ Hz), 6.54 (1H, d, $J = 10.6$ Hz), and 6.57 (1H, d, $J = 10.6$ Hz); MS *m/z* (%) 192 (M^+; 98) and 177 (100). Found: C, 68.99; H, 6.01%. Calcd for $C_{11}H_{12}O_3$: C, 68.73; H, 6.29%.

2,2-Diethyl-2,3-dihydrobenzofuran-4,7-dione (12b): An oil; R_f 0.43 (1 : 3 EtOAc–hexane); IR (neat) 1678, 1645, and 1627 cm^{-1}; ^{1}H NMR (60 MHz) $\delta = 0.96$ (6H, d, $J = 6.8$ Hz), 1.78 (4H, q, $J = 6.8$ Hz), 2.82 (2H, s), and 6.52 (2H, s); MS *m/z* (%) 206 (M^+; 30), 191 (43), and 177 (100). Found: C, 69.50; H, 6.65%. Calcd for $C_{12}H_{14}O_3$: C, 69.89; H, 6.84%.

8,9,9-Trimethyl-8,9-dihydro-7*H*-phenaleno[1,2-*b*]furan-7-one (15a): R_f 0.33 (1 : 3 EtOAc–hexane); mp 125—127 °C (hexane) (lit,[10]) mp 130—131 °C).

9,9-Diethyl-8,9-dihydro-7*H*-phenaleno[1,2-*b*]furan-7-one (15b): R_f 0.45 (1 : 2 EtOAc–hexane); mp 95—98 °C (hexane–CH_2Cl_2); IR 1646 and 1627 cm^{-1}; ^{1}H NMR (270 MHz) $\delta = 0.90$ (6H, t, $J = 7.3$ Hz), 1.77 (4H, q, $J = 7.3$ Hz), 2.92 (2H, s), 7.48 (1H, dd, $J = 8.3$ and 7.3 Hz), 7.59 (1H, t, $J = 7.6$ Hz), 7.9—8.2 (3H, m), and 8.51 (1H, d, $J = 7.3$ Hz); MS *m/z* (%) 278 (M^+; 21) and 249 (100). Found: C, 81.80; H, 6.38%. Calcd for $C_{19}H_{18}O_2$: C, 81.99; H, 6.52%.

Spiro[cyclopentane-1,9′(8′*H*)-7′*H*-phenaleno[1,2-*b*]furan]-7′-one (15c): R_f 0.20 (1 : 3 EtOAc–hexane); mp 155—158 °C (hexane–Et_2O); IR 1645 and 1626 cm^{-1}; ^{1}H NMR (270 MHz) $\delta = 1.6$—2.0 (6H, m), 2.2—2.3 (2H, m), 3.21 (2H, s), 7.58 (1H, t, $J = 7.4$ Hz), 7.71 (1H, t, $J = 7.4$ Hz), 8.0—8.15 (3H, m), and 8.61 (1H, dd, $J = 7.3$ and 1.1 Hz); MS *m/z* (%) 276 (M^+; 41) and 247 (100). Found: C, 82.64; H, 5.95%. Calcd for $C_{19}H_{16}O_2$: C, 82.58; H, 5.84%.

9-Methyl-9-phenyl-8,9-dihydro-7*H*-phenaleno[1,2-*b*]furan-7-one (15d): R_f 0.53 (1 : 2 THF–hexane); mp 97—100 °C (hexane–CH_2Cl_2); IR 1630 cm^{-1}; ^{1}H NMR (60 MHz) $\delta = 1.84$ (3H, s), 3.39 (2H, s), 7.2—7.75 (7H, m), 7.85—8.2 (3H, m), and 8.49 (1H, d, $J = 7.2$ Hz); MS *m/z* (%) 312 (M^+; 35) and 297 (100). Found: C, 84.78; H, 4.99%. Calcd for $C_{22}H_{16}O_2$: C, 84.59; H, 5.16%.

9-(4-Methylphenyl)-8,9-dihydro-7*H*-phenaleno[1,2-*b*]furan-7-one (15e): R_f 0.32 (1 : 3 EtOAc–hexane); mp 190—192 °C (hexane–CH_2Cl_2); IR 1643 and 1625 cm^{-1}; ^1H NMR (270 MHz) $\delta = 2.37$ (3H, s), 3.28 (1H, dd, $J = 15.3$ and 7.9 Hz), 3.68 (1H, dd, $J = 15.3$ and 10.6 Hz), 6.01 (1H, dd, $J = 10.6$ and 7.9 Hz), 7.22 (2H, d, $J = 7.9$ Hz), 7.34 (2H, d, $J = 7.9$ Hz), 7.60 (1H, dd, $J = 7.9$ and 7.4 Hz), 7.74 (1H, t, $J = 7.9$ Hz), 8.05—8.15 (3H, m), and 8.64 (1H, dd, $J = 7.4$ and 1.1 Hz); MS *m/z* (%) 312 (M^+; 100). Found: C, 84.74; H, 5.10%. Calcd for $C_{22}H_{16}O_2$: C, 84.59; H, 5.16%.

9-(4-Chlorophenyl)-8,9-dihydro-7*H*-phenaleno[1,2-*b*]furan-7-one (15f): R_f 0.38 (1 : 3 EtOAc–hexane); mp 165—166 °C (hexane–CH_2Cl_2); IR 1644 and 1627 cm^{-1}; ^1H NMR (270 MHz) $\delta = 3.23$ (1H, dd, $J = 15.7$ and 7.3 Hz), 3.70 (1H, dd, $J = 15.7$ and 10.5 Hz), 6.02 (1H, dd, $J = 10.5$ and 7.3 Hz), 7.38 (4H, s), 7.62 (1H, t, $J = 7.8$ Hz), 7.75 (1H, t, $J = 7.8$ Hz), 8.08 (2H, d, $J = 7.8$ Hz), 8.14 (1H, dd, $J = 7.8$ and 1.1 Hz), and 8.64 (1H, dd, $J = 7.8$ and 1.1 Hz); MS *m/z* (%) 332 (M^+; 100). Found: C, 76.05; H, 4.14%. Calcd for $C_{21}H_{13}ClO_2$: C, 75.79; H, 3.94%.

***trans*-8,9-Diphenyl-8,9-dihydro-7*H*-phenaleno[1,2-*b*]furan-7-one (*trans*-15g):** R_f 0.29 (1 : 3 EtOAc–hexane); mp 154—159 °C (hexane–CH_2Cl_2); IR 1630 cm^{-1}; ^1H NMR (270 MHz) $\delta = 4.72$ (1H, d, $J = 5.8$ Hz), 5.83 (1H, d, $J = 5.8$ Hz), 7.25—7.45 (10H, m), 7.68 (1H, t, $J = 7.9$ Hz), 7.73 (1H, t, $J = 7.9$ Hz), 8.12 (1H, dd, $J = 7.9$ and 1.1 Hz), 8.15 (1H, dd, $J = 7.9$ and 1.1 Hz), 8.22 (1H, dd, $J = 7.9$ and 1.1 Hz), and 8.56 (1H, dd, $J = 7.9$ and 1.1 Hz); MS *m/z* (%) 374 (M^+; 83) and 297 (100). Found: C, 86.42; H, 4.70%. Calcd for $C_{27}H_{18}O_2$: C, 86.60; H, 4.86%.

***cis*-8,9-Diphenyl-8,9-dihydro-7*H*-phenaleno[1,2-*b*]furan-7-one (*cis*-15g):** R_f 0.27 (1 : 3 EtOAc–hexane); mp 108—110 °C (hexane–CH_2Cl_2); IR 1637 and 1628 cm^{-1}; ^1H NMR (270 MHz), $\delta = 5.00$ (1H, d, $J = 9.5$ Hz), 6.31 (1H, d, $J = 9.5$ Hz), 6.85—7.3 (10H, m), 7.70 (1H, t, $J = 7.9$ Hz), 7.75 (1H, t, $J = 7.9$ Hz), 8.15 (1H, d, $J = 7.9$ Hz), 8.18 (1H, d, $J = 7.9$ Hz), 8.25 (1H, d, $J = 7.9$ Hz), and 8.59 (1H, d, $J = 7.9$ Hz); MS *m/z* (%) 374 (M^+; 85) and 297 (100). Found: C, 86.70; H, 4.91%. Calcd for $C_{27}H_{18}O_2$: C, 86.60; H, 4.86%.

9-Acetoxy-8,9-dihydro-7*H*-phenaleno[1,2-*b*]furan-7-one (15h): R_f 0.42 (1 : 1 EtOAc–hexane); mp 153—156 °C (hexane–CH_2Cl_2); IR 1758 and 1634 cm^{-1}; ^1H NMR (270 MHz) $\delta = 2.14$ (3H, s), 3.25 (1H, d, $J = 16.9$ Hz), 3.50 (1H, dd, $J = 16.9$ and 7.4 Hz), 7.07 (1H, d, $J = 7.4$ Hz), 7.6—7.8 (2H, m), 8.0—8.2 (3H, m), and 8.65 (1H, d, $J = 7.3$ Hz); MS *m/z* (%) 280 (M^+; 4.4) and 210 (100). Found: C, 72.64; H, 4.48%. Calcd for $C_{17}H_{12}O_4$: C, 72.85; H, 4.32%.

9-Phenyl-7*H*-phenaleno[1,2-*b*]furan-7-one (16): R_f 0.41 (1 : 3 EtOAc–hexane); mp 186—188 °C (hexane–Et_2O); IR 1645 cm^{-1}; ^1H NMR (270 MHz) $\delta = 7.20$ (1H, s), 7.34 (1H, t, $J = 7.3$ Hz), 7.44 (2H, t, $J = 7.3$ Hz), 7.59 (1H, dd, $J = 8.0$ and 7.3 Hz), 7.69 (1H, dd, $J = 8.0$ and 7.3 Hz), 7.79 (2H, d, $J = 7.3$ Hz), 7.93 (1H, d, $J = 8.0$ Hz), 8.09 (1H, d, $J = 8.0$ Hz), 8.14 (1H, d, $J = 7.3$ Hz), and 8.66 (1H, d, $J = 7.3$ Hz); MS *m/z* (%) 296 (M^+; 100). Found C, 84.83; H, 3.78%. Calcd for $C_{21}H_{12}O_2$: C, 85.12; H, 4.08%.

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