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Ceric Ammonium Nitrate (CAN)-Mediated Oxidative Cycloaddition of 1,3-Dicarbonyls to Conjugated Compounds. Efficient Synthesis of Dihydrofurans, Dihydrofurocoumarins, Dihydrofuroquinolinones, Dihydrofurophenalenones, and Furonaphthoquinone Natural Products

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Abstract—Ceric ammonium nitrate-mediated oxidative cycloaddition of 1,3-dicarbonyls to conjugated compounds afforded substituted dihydrofurans, dihydrofurocoumarins, dihydrofuroquinolinones, and dihydrofurophenalenones in moderate yields. This new synthetic method has been applied to the synthesis of furonaphthoquinone natural products.

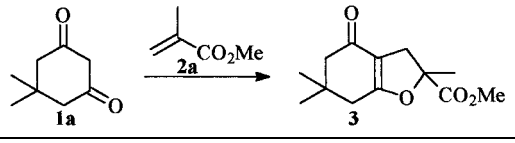
The oxidative addition of carbon-centered radicals to alkenes mediated by metal salts (Mn^{III}, Ce^{IV}, Co^{II}, and V^{V}) has received considerable attention over the last decade in organic synthesis for construction of carbon–carbon bonds.[1] Among these, manganese(III) acetate and ceric(IV) ammonium nitrate (CAN) have been used most efficiently. Recently CAN-mediated oxidative cycloaddition of 1,3-dicarbonyl compounds to alkenes,[2] vinyl acetates,[3] enol silyl ethers,[4] and enol ethers[5] has been studied extensively. Although these reactions have aroused great interest in reactions for the carbon–carbon formation, there is little information available on the CAN-mediated oxidative cycloaddition to conjugated compounds as a radical acceptor. We describe here our detailed results on the CAN-mediated cycloaddition of cyclic and acyclic 1,3-dicarbonyl compounds to a variety of conjugated compounds.

In order to check the reactivity of conjugated compounds, reaction of dimedone **1a** with methyl methacrylate **2a** was first attempted utilizing several oxidizing agents. When **1a** was treated with **2a** in the presence of $Mn(OAc)_3{\cdot}2H_2O$ in acetic acid, no adduct was obtained (Table 1). However, Ag_2CO_3/Celite gave the dihydrofuran **3** in low yield (8%), whereas CAN(IV) provided **3** in a good yield (88%). We found that CAN(IV) was the much superior reagent for this oxidative cycloaddition than $Mn(OAc)_3{\cdot}2H_2O$ and Ag_2CO_3/Celite.

The reactions were typically carried out at 0°C starting from 1,3-dicarbonyl compounds with conjugated compounds (5-fold excess) in the presence of 2.2 equiv. of CAN and excess amounts of $NaHCO_3$ in acetonitrile.

Reactions of 1,3-dicarbonyl compounds to acyclic α,β-unsaturated esters were first examined. When ethyl acetoacetate **1b** was treated with **2a**, cycloadduct **4** was obtained in 66% yield (Table 2, entry 1). The assignment of **4** is confirmed by ^1H NMR analysis of the expected chemical shifts and geminal coupling constants associated with the methylene group of the dihydrofuran ring. Similarly, reaction of 1,3-cyclopentanedione (**1c**) with **2a** afforded the fused dihydrofuran **5** in 50% yield (entry 2). Reaction of 4-hydroxycoumarin **1e** and 4-hydroxy-2-quinolone **1f** with **2a** gave the biologically interesting dihydrofurocoumarin **7** and dihydrofuroquinolinone **8** in 35 and 30% yields, respectively, without any formation of regioisomers (Table 2, entries 4 and 5). Compounds **7** and **8** have been clearly

Table 1. Effect of oxidants in the reaction of dimedone and methyl methacrylate



Oxidant	Solvent	Temperature	Time (h)	Yield (%)
$Mn(OAc)_3{\cdot}2H_2O$	AcOH	80°C	3	0
Ag_2CO_3/Celite	CH_3CN	Reflux	3	8
$Ce(NH_4)_2(NO_3)_6$	CH_3CN	0°C	3	88

Keywords: ceric ammonium nitrate; furonaphthoquinone; cycloaddition.
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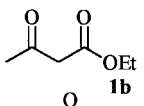
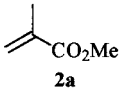
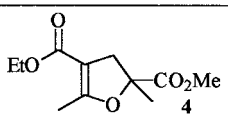
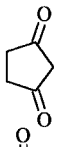
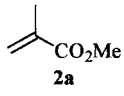
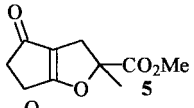
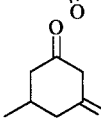
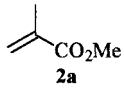
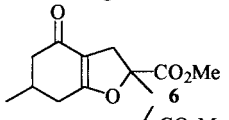
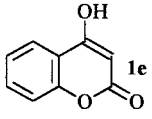
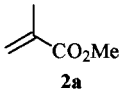
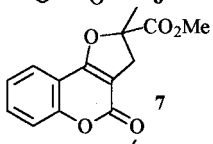
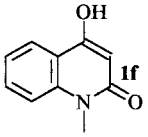
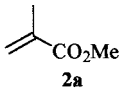
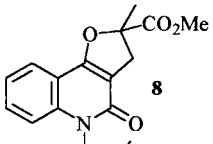
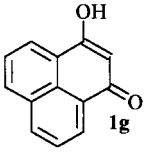
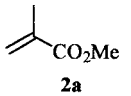
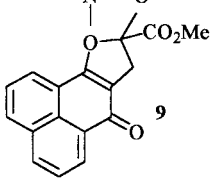
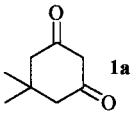
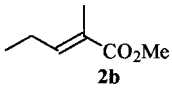
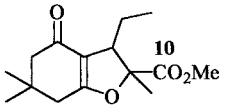
Table 2. Reaction of 1,3-dicarbonyl compounds with acyclic α,β-unsaturated esters

entry	1,3-dicarbonyl compound	α,β-unsaturated ester	dihydrofuran	yield (%)
1	 **1b**	 **2a**	 **4**	66
2	 **1c**	 **2a**	 **5**	50
3	 **1d**	 **2a**	 **6**	79
4	 **1e**	 **2a**	 **7**	35
5	 **1f**	 **2a**	 **8**	30
6	 **1g**	 **2a**	 **9**	71
7	 **1a**	 **2b**	 **10**	49

shown to be angular by their spectral analysis and by comparison with reported data in the literature.[6,7] These dihydrofurocoumarin[8] and dihydrofuroquinolinone derivatives[9] have been widely found in nature and reported to have various biological activities such as anticoagulant, insecticidal, anthelmintic, hypnotic, antifungal, anthidiuretic, and antiarrhythmic.[10,11]

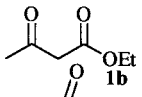
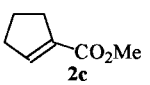
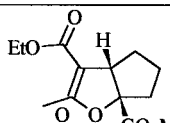
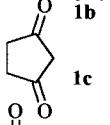
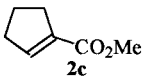
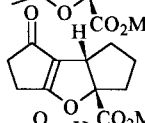
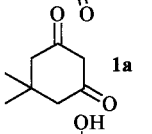
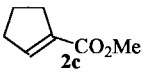
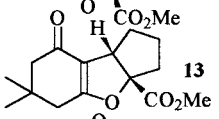
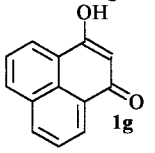
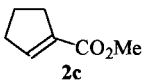
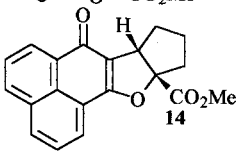
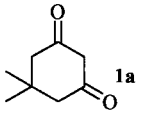
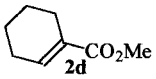
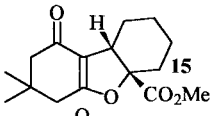
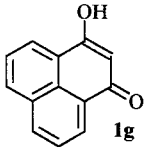
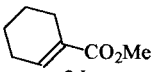
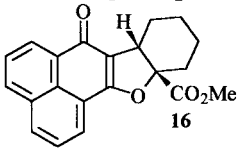
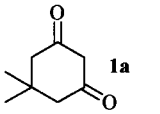
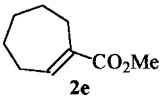
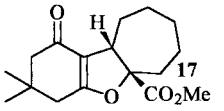
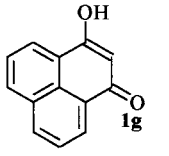
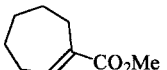
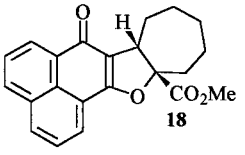
Treatment of **1g** with **2a** gave expected dihydrofurophenalenone **9** in 71% yield (Table 2, entry 6). These derivatives were also reported to have various biological activities such as antibiotics, antimicrobial, antifungal, and phytoalexin.[12] On the other hand, when **1a** of entry 7 was treated with **2b**, cycloadduct **10** was produced in 49% yield. Importantly, our result is in clear contrast of the regiochemistry to that of Roy who recently reported that the reaction of dimedone to a cinnamic ester, an α,β-unsaturated ester, afforded a dihydrofuran adduct which should not be attributed to a Michael type addition but to the radical addition of the styrene moiety of the cinnamic ester.[13]

In order to extend the utility of these oxidative cycloadditions, additional reactions were investigated with cyclic α,β-unsaturated esters. Treatment of **1b** with **2c** gave the fused dihydrofuran **11** in 43% yield (Table 3, entry 1). The stereochemistry of **11** is assigned as *cis* by spectral analysis and by the analogy with the earlier reported data.[13] With 1,3-cyclopentanedione (**1c**), tricyclic adduct **12** was obtained in 31% yield (Table 3, entry 2). Similarly, when **1a** and **1g** of entries 3 and 4 were treated with **2c**, the adducts **13** and **14** were obtained in 81 and 63% yields, respectively. On the other hand, reaction of **1a** and **1g** of entries 5 and 6 to cyclic ester **2d** with the six membered ring produced cycloadducts **15** and **16** in 70 and 52% yields, while that of **1a** and **1g** of entries 7 and 8 to cyclic ester **2e** with a seven membered ring afforded **17** and **18** in 67 and 59% yields, respectively. These CAN-mediated oxidative reactions provide a rapid route to the preparation of a variety of polycycles and heterocycles.

Next, reactions of 1,3-dicarbonyl compounds with conjugated enones were investigated to afford other types of heterocycles. The starting enones, **2f** and **2g**, were prepared by Amri method in 58 and 65% yields, respectively.[14] With acyclic enone **2f** and **2g**, dihydrofurans **19**–**21** were obtained in 31–47% yields (Table 4, entries 1–3). Similarly, reaction of **1a** with cyclic enones **2h** and **2i** afforded fused tricyclic adducts **22** and **23** in 32 and 30% yields, respectively (Table 4, entries 4 and 5). Although the adducts were formed in low yield, no by-products were found other than the starting material.

Finally, reactions with conjugated dienes were investigated. It has been reported by Ruzziconi that reaction of acyclic 1,3-dicarbonyl compounds with 1,3-butadiene provides products as a 1:1 mixture of 1,2- and 1,4-nitroxy adduct.[15] This synthetic method has been strongly limited by the lack of regioselectivity, by the low stability of the 1,2-adduct,

Table 3. Reaction of 1,3-dicarbonyl compounds with cyclic α,β-unsaturated esters

entry	1,3-dicarbonyl compound	α,β-unsaturated ester	dihydrofuran	yield (%)
1	 **1b**	 **2c**	 **11**	43
2	 **1c**	 **2c**	 **12**	31
3	 **1a**	 **2c**	 **13**	81
4	 **1g**	 **2c**	 **14**	63
5	 **1a**	 **2d**	 **15**	70
6	 **1g**	 **2d**	 **16**	52
7	 **1a**	 **2e**	 **17**	67
8	 **1g**	 **2e**	 **18**	59

and mostly by the difficulties met with the conversion of the allylic nitroxy group.[16]

Treatment of dimedone **1a** with 2,3-dimethyl-1,3-butadiene (**2j**) gave dihydrofuran **24** in 77% yield, without isolation of expected nitroxy adducts (Table 5, entry 1). The structure of **24** was easily established by the chemical shifts of the methylene and methyl groups of the dihydrofuran ring, and by the isopropenyl group. Similarly, reactions of **1h** and **1g** with **2j** afforded the expected adducts, **25** and **26**, as single compounds, respectively (entries 2 and 3). However, reaction of **1i** with **2j** resulted in dihydrofuronaphthoquinones **27** (50%) and **28** (40%) as a mixture of linear and angular regioisomers (entry 4). The mixture was easily separated by column chromatography and the two isomers were assigned by their spectroscopic data and by comparison with reported data in the literature.[17] The proton NMR spectra showed absorption at δ 1.66 as a singlet for the methyl group in the isopropenyl moeity of **27** and δ 1.68 of **28**. The clear assignments come from the IR carbonyl absorptions at 1680 and 1644 cm^{-1} for the carbonyl groups in **27** and at 1698 and 1647 cm^{-1} in **28**. Similarly, with isoprene **2k**, two regioisomers, **29** and **30**, were also obtained in 31 and 40% yields, respectively (entry 5). Reaction of **1f** with **2l** gave product **31** in 46% yield, and while treatment of **1f** with myrcene **2m** afforded **32** in 58% yield (Table 5, entries 6 and 7). Importantly, these reactions are very surprising in comparison to reported results by Ruzziconi.[15] This new synthetic method is also expected to provide a rapid route toward the synthesis of naturally occurring furocoumarins, furoquinolinone alkaloids, dihydrofurophenalenones, and furonaphthoquinones.

Although the exact mechanism of the reaction is still not clear, it is best described as shown in Scheme 1. The dimedone **1a** was first oxidized by CAN(IV) to generate the α-oxoalkyl radical **33**, which then attacks the methylmethacrylate **2a** to give the another carbon radical **34**. The adduct **34** now undergoes fast oxidation by CAN(IV) to a carbocation **35**. Cyclization of **35** furnishes intermediate **36**, which finally undergoes elimination to give the dihydrofuran **3**.

As an application of this methodology, the total synthesis of the furonaphthoquinone natural products **37** and **38** were examined. They are isolated from the *Tabebuia cassinoides* and they are reported to have significant biological properties such as antileukemic activity and in vitro cytotoxicity against KB, K562, and P388 cells.[18,19] These furonaphthoquinone derivatives have been also used in traditional

Table 4. Reaction of 1,3-dicarbonyl compounds with α,β-unsaturated enones

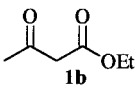
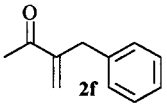
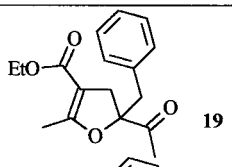
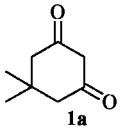
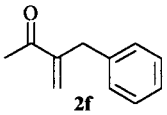
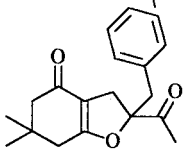
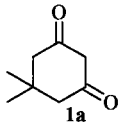
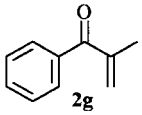
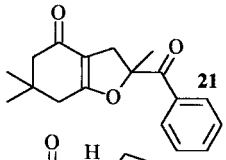
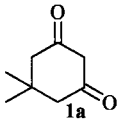
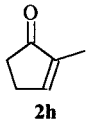
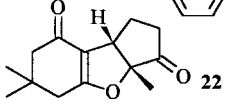
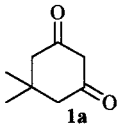
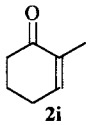
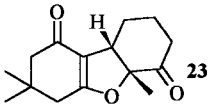
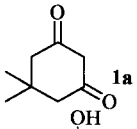
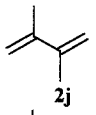
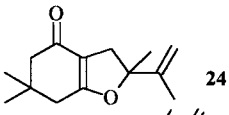
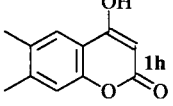
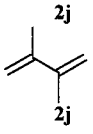
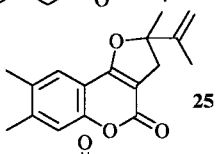
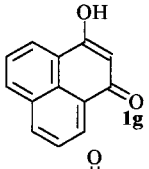
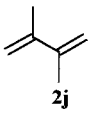
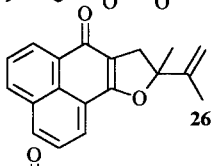
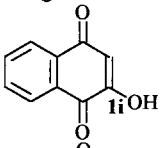
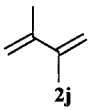
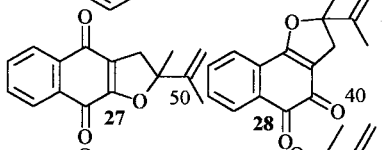
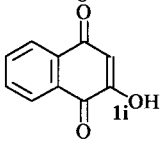
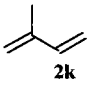
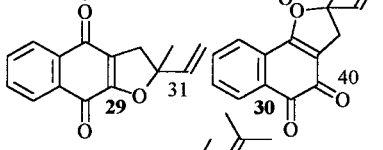
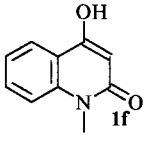
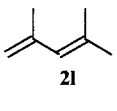
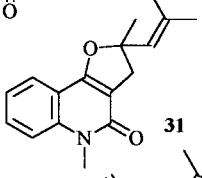
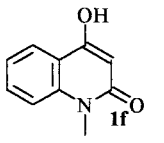
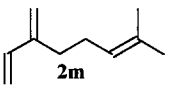
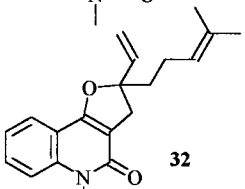
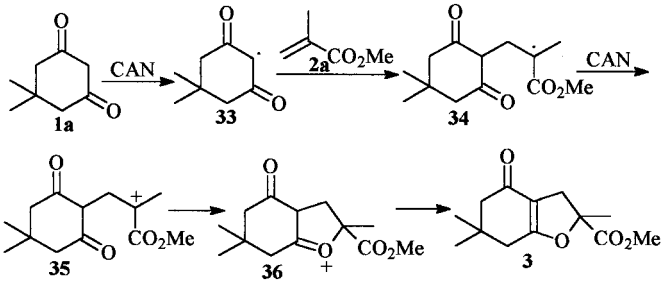
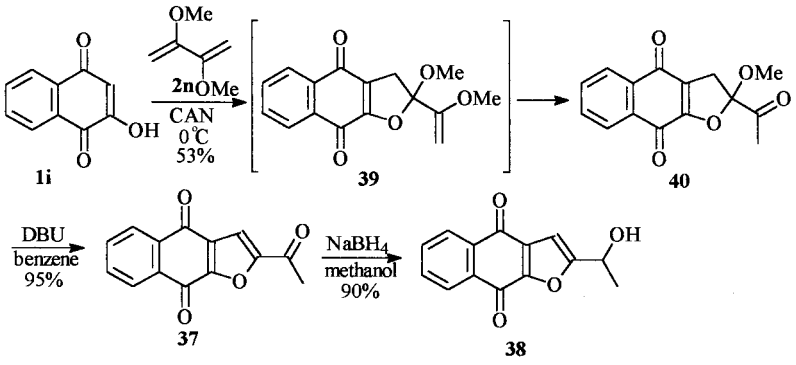
entry	1,3-dicarbonyl compound	α,β-unsaturated enone	dihydrofuran	yield (%)
1	 **1b**	 **2f**	 **19**	31
2	 **1a**	 **2f**	 **20**	47
3	 **1a**	 **2g**	 **21**	45
4	 **1a**	 **2h**	 **22**	32
5	 **1a**	 **2i**	 **23**	30

Table 5. Reaction of 1,3-dicarbonyl compounds with 1,3-butadienes

entry	1,3-dicarbonyl compound	1,3-butadiene	dihydrofuran	yield (%)
1	 **1a**	 **2j**	 **24**	77
2	 **1h**	 **2j**	 **25**	40
3	 **1g**	 **2j**	 **26**	66
4	 **1i**	 **2j**	 **27** 50 **28** 40	
5	 **1i**	 **2k**	 **29** 31 **30** 40	
6	 **1f**	 **2l**	 **31**	46
7	 **1f**	 **2m**	 **32**	58

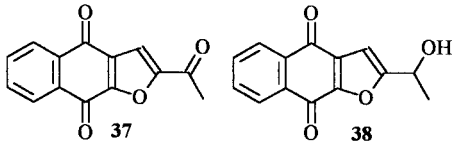


Scheme 1.



Scheme 2.

medicine as Pau d'Arco, Ipé Roxo, Lapacho, and Taheebo for many years in North and South America as anticancer, antifungal, antibacterial, and antiinflammatory drugs.[20]



Treatment of **1i** with 2,3-dimethoxy-1,3-butadiene (**2n**) (2-fold excess) in the presence of 3.0 equiv. of CAN in acetonitrile at 0°C for 5 h afforded the dihydrofuronaphthoquinone **40** in 53% yield (Scheme 2). The formation of **40** was confirmed by the analysis of the expected chemical shifts associated with the methylene group of the dihydrofuran ring and the methyl group of the acetyl moiety as a singlet at δ 2.39. The product **40** probably results from CAN-mediated oxidative cycloaddition and followed by the methyl group cleavage of intermediate **39**. The conversion of compound **40** to natural products was begun by elimination under basic condition. Reaction of **40** with DBU in benzene at room temperature for 5 h results in furonaphthoquinone **37** in 95% yield. The spectroscopic properties of our synthetic material **37** agreed well with those reported in the literature.[21] Next, the synthesis of furonaphthoquinone **38** was easily achieved by reduction of **37** with sodium borohydride in methanol in 90% yield. This synthetic material also exhibited spectroscopic properties consistent with the literature.[21]

In conclusion, CAN-mediated oxidative cycloaddition of 1,3-dicarbonyls to conjugated compounds such as α,β-unsaturated esters, enones, and 1,3-butadienes is described. The method provides a simple and efficient synthesis of substituted dihydrofurans, dihydrofurocoumarins, dihydrofuroquinolinones, and dihydrofurophenalenones. This new method has been also applied to the synthesis of furonaphthoquinone natural products.

Experimental

All experiments were carried out under a nitrogen atmosphere. Merck precoated silica gel plates (Art. 5554) with a fluorescent indicator were used for analytical TLC. Flash column chromatography was performed using silica gel 9385 (Merck). Melting points were determined with microcover glasses on a Fisher-Johns apparatus and are uncorrected. Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded on a Bruker Model ARX (300 MHz) spectrometer. IR spectra were recorded on a JASCO FTIR 5300 spectrophotometer. High resolution mass (HRMS) spectra were obtained on JEOL JMS-700 spectrometer at Korea Basic Science Institute.

General procedure

To a solution of 1,3-dicarbonyl compound (1.0 mmol) and conjugated compound (5.0 mmol) in acetonitrile (20 mL) was added CAN (1.206 g, 2.2 mmol) and $NaHCO_3$ (420 mg, 5.0 mmol) at 0°C. The reaction mixture was stirred for 3 h at 0°C. The mixture was diluted with water and extracted with ethyl acetate (3×100 mL). The combined organic extracts were washed with brine, dried ($MgSO_4$), and evaporated under reduced pressure to give the residue. The residue was purified by flash column chromatography on sillica gel to give product.

Methyl 2,6,6-trimethyl-4-oxo-2,3,4,5,6,7-hexahydro-1-benzofuran-2-carboxylate (3). Reaction of 5,5-dimethyl-1,3-cyclohexanedione (**1a**) (140 mg, 1 mmol) with methyl methacrylate **2a** (500 mg, 5 mmol) in acetonitrile (20 mL) afforded **3** (210 mg, 88%) as a liquid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.79 (3H, s), 3.18 (1H, d, J=14.9 Hz), 2.76 (1H, d, J=14.9 Hz), 2.47 (2H, m), 2.24 (2H, s), 1.66 (3H, s), 1.11 (6H, s); IR (neat) 2959, 1745, 1643, 1452, 1407, 1352, 1263, 1167, 1122, 1030, 985, 885, 790 cm^{-1}; HRMS m/z(M^+) calcd for $C_{13}H_{18}O_4$, 238.1205. Found 238.1206.

4-Ethyl-2-methyl-2,5-dimethyl-2,3-dihydro-2,4-furandicarboxylate (4). Reaction of ethyl acetoacetate (**1b**) (130 mg, 1 mmol) with methyl methacrylate **2a** (500 mg, 5 mmol) in acetonitrile (20 mL) afforded **4** (151 mg, 66%) as a liquid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.16 (2H, q, J=7.1 Hz), 3.79 (3H, s), 3.25 (1H, d, J=15.0 Hz), 2.81 (1H, d, J=15.0 Hz), 2.24 (3H, s), 1.61 (3H, s), 1.28 (3H, t, J=7.1 Hz); IR (neat) 2984, 1746, 1703, 1655, 1447, 1383, 1335, 1289, 1246, 1204, 1173, 1125, 1065, 980, 835, 812, 764 cm^{-1}; HRMS m/z(M^+) calcd for $C_{11}H_{16}O_5$, 228.0998. Found 228.0998.

Methyl 2-methyl-4-oxo-3,4,5,6-tetrahydro-2*H*-cyclopenta[*b*]furan-2-carboxylate (5). Reaction of 1,3-cyclopentanedione (**1c**) (96 mg, 1 mmol) with methyl methacrylate **2a** (500 mg, 5 mmol) in acetonitrile (20 mL) afforded **5** (98 mg, 50%) as a liquid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.82 (3H, s), 3.12 (1H, d, J=14.6 Hz), 2.81 (2H, t, J=4.5 Hz), 2.71–2.63 (3H, m), 1.74 (3H, s); IR (neat) 2955, 1744, 1694, 1640, 1443, 1395, 1254, 1111, 1017, 984, 793, 752 cm^{-1}; HRMS m/z(M^+) calcd for $C_{10}H_{12}O_4$, 196.0735. Found 196.0735.

Methyl 2,6-dimethyl-4-oxo-2,3,4,5,6,7-hexahydro-1-benzofuran-2-carboxylate (6). Reaction of 5-methyl-1,3-cyclohexanedione (**1d**) (126 mg, 1 mmol) with methyl methacrylate **2a** (500 mg, 5 mmol) in acetonitrile (20 mL) afforded **6** (177 mg, 79%) as a liquid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.79 (3H, s), 3.17 (1H, d, J=15.0 Hz), 2.74 (1H, d, J=15.0 Hz), 2.52–2.02 (5H, m), 1.66 and 1.64 (3H, s), 1.12 (3H, d, J=6.2 Hz); IR (neat) 2957, 1746, 1642, 1454, 1402, 1300, 1260, 1205, 1038, 986, 910, 885, 860, 799 cm^{-1}; HRMS m/z(M^+) calcd for $C_{12}H_{16}O_4$, 224.1049. Found 224.1050.

Methyl 2-methyl-4-oxo-2,3-dihydro-4*H*-furo[3,2-*c*]chromene-2-carboxylate (7). Reaction of 4-hydroxycoumarin **1e** (162 mg, 1 mmol) with methyl methacrylate **2a** (500 mg, 5 mmol) in acetonitrile (20 mL) afforded **7** (91 mg, 35%) as a solid: mp 128°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.70 (1H, dd, J=7.8, 1.3 Hz), 7.56 (1H, t, J=8.5 Hz), 7.36 (1H, d, J=8.5 Hz), 7.28 (1H, t, J=7.6 Hz), 3.81 (3H, s), 3.55 (1H, d, J=15.7 Hz), 3.08 (1H, d, J=15.7 Hz), 1.80 (3H, s); IR (KBr) 2955, 2868, 1723, 1655, 1609, 1570, 1501, 1460, 1414, 1292, 1208, 1100, 1032, 968, 895, 770 cm^{-1}; HRMS m/z(M^+) calcd for $C_{14}H_{12}O_5$, 260.0685. Found 260.0684.

Methyl 2,5-dimethyl-4-oxo-2,3,4,5-tetrahydrofuro[3,2-*c*]-quinoline-2-carboxylate (8). Reaction of 4-hydroxy-1-methyl-2(1*H*)-quinolone **1f** (175 mg, 1 mmol) with methyl methacrylate **2a** (500 mg, 5 mmol) in acetonitrile (20 mL) afforded **8** (82 mg, 30%) as a solid: mp 119–120°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.81 (1H, dd, J=7.9, 1.3 Hz), 7.57 (1H, m), 7.36 (1H, d, J=8.6 Hz), 7.24 (1H, m), 3.78 (3H, s), 3.68 (3H, s), 3.59 (1H, d, J=15.9 Hz), 3.14 (1H, d, J=15.9 Hz), 1.77 (3H, s); IR (KBr) 2919, 1748, 1669, 1601, 1572, 1508, 1460, 1426, 1379, 1354, 1290, 1254, 1200, 1152, 1080, 965, 908, 804, 754 cm^{-1}; HRMS m/z(M^+) calcd for $C_{15}H_{15}NO_4$, 273.1002. Found 273.1005.

Methyl 2-methyl-4-oxo-2,3-dihydro-4*H*-furo[3,2-*c*]phenalene-2-carboxylate (9). Reaction of 4-hydroxy-1*H*-phenalen-1-one **1g** (196 mg, 1 mmol) with methyl methacrylate **2a** (500 mg, 5 mmol) in acetonitrile (20 mL) afforded **9** (209 mg, 71%) as a solid: mp 148–150°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.60 (1H, d, J=7.3 Hz), 8.13–8.10 (2H, m), 8.06 (1H, d, J=8.4 Hz), 7.72 (1H, t, J=7.9 Hz), 7.61 (1H, t, J=7.9 Hz), 3.80 (3H, s), 3.60 (1H, d, J=15.9 Hz), 3.15 (1H, d, J=15.9 Hz), 1.81 (3H, s); IR (KBr) 3057, 2992, 1755, 1649, 1589, 1572, 1510, 1454, 1422, 1379, 1321, 1290, 1262, 1229, 1206, 1121, 1098, 1020, 876, 843, 775 cm^{-1}; HRMS m/z(M^+) calcd for $C_{18}H_{14}O_4$, 294.0892. Found 294.0894.

Methyl 3-ethyl-2,6,6-trimethyl-4-oxo-2,3,4,5,6,7-hexahydro-1-benzofuran-2-carboxylate (10). Reaction of 5,5-dimethyl-1,3-cyclohexanedione (**1a**) (140 mg, 1 mmol) with methyl *trans*-2-methyl-2-pentanoate (**2b**) (641 mg, 5 mmol) in acetonitrile (20 mL) afforded **10** (131 mg, 49%) as a liquid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.72 (3H, s), 3.20 (1H, t, J=6.1 Hz), 2.32 (2H, m), 2.19 (2H, s), 1.65 (2H, m), 1.60 (3H, s), 1.08 (6H, s), 0.93 (3H, t, J=7.4 Hz); IR (neat) 2961, 2878, 1744, 1644, 1454, 1397, 1221, 1146, 1121, 1032, 982, 918, 887 cm^{-1}; HRMS m/z(M^+) calcd for $C_{15}H_{22}O_4$, 266.1519. Found 266.1522.

3-Ethyl 6a-methyl 2-methyl-4,5,6,6a-tetrahydro-3a*H*-cyclopenta[*b*]furan-3,6a-dicarboxylate (11). Reaction of ethyl acetoacetate **1b** (130 mg, 1 mmol) with methyl 1-cyclopentene-1-carboxylate **2c** (631 mg, 5 mmol) in acetonitrile (20 mL) afforded **11** (110 mg, 43%) as a liquid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.16 (2H, m), 3.75 (3H, s), 3.71 (1H, m), 2.22 (3H, s), 2.12 (2H, m), 1.91–1.75 (3H, m), 1.62 (1H, m), 1.25 (3H, t, J=7.1 Hz); IR (neat) 2959, 2874, 1742, 1701, 1649, 1439, 1381, 1341, 1287, 1250, 1209, 1132, 1074, 978, 932, 853, 772 cm^{-1}; HRMS m/z(M^+) calcd for $C_{13}H_{18}O_5$, 254.1149. Found 254.1147.

Methyl 7-oxo-1,2,3,3a,5,6,7,7b-octahydrodicyclopenta[*b*,*d*]furan-3a-carboxylate (12). Reaction of 1,3-cyclopentanedione (**1c**) (96 mg, 1 mmol) with methyl 1-cyclopentene-1-carboxylate **2c** (631 mg, 5 mmol) in acetonitrile (20 mL) afforded **12** (69 mg, 31%) as a liquid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.79 (3H, s), 3.64 (1H, m), 2.77 (2H, t, J=4.2 Hz), 2.60 (2H, m), 2.18 (2H, m), 1.92–1.82 (3H, m), 1.67 (1H, m); IR (neat) 2957, 1746, 1694, 1642, 1439, 1395, 1289, 1209, 1157, 1084, 1036, 970, 928, 856, 787 cm^{-1}; HRMS m/z(M^+) calcd for $C_{12}H_{14}O_4$, 222.0892. Found 222.0892.

Methyl 6,6-dimethyl-8-oxo-2,3,3a,5,6,7,8,8b-octahydro-1*H*-benzo[*b*]cyclopenta[*d*]furan-3a-carboxylate (13). Reaction of 5,5-dimethyl-1,3-cyclohexanedione (**1a**) (140 mg, 1 mmol) with methyl 1-cyclopentene-1-carboxylate **2c**

(631 mg, 5 mmol) in acetonitrile (20 mL) afforded **13** (214 mg, 81%) as a liquid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.76 (3H, s), 3.70 (1H, m), 2.41–2.17 (4H, m), 2.13 (2H, m), 1.94–1.78 (3H, m), 1.52 (1H, m), 1.09 (3H, s), 1.06 (3H, s); IR (neat) 2959, 2872, 1746, 1644, 1437, 1402, 1285, 1211, 1163, 1098, 1044, 978, 930, 814, 785, 754 cm^{-1}; HRMS *m*/*z* (M^+) calcd for $C_{15}H_{20}O_4$, 264.1362. Found 264.1364.

Methyl 7-oxo-8,9,10,10a-tetrahydro-7*H*,7b*H*-cyclopenta-[*b*]phenaleno[2,1-*d*]furan-10a-carboxylate (14). Reaction of 4-hydroxy-1*H*-phenalen-1-one **1g** (196 mg, 1 mmol) with methyl 1-cyclopentene-1-carboxylate **2c** (631 mg, 5 mmol) in acetonitrile (20 mL) afforded **14** (202 mg, 63%) as a solid: mp 107–108°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.55 (1H, d, *J*=7.4 Hz), 8.10–8.05 (2H, m), 8.02 (1H, d, *J*=8.0 Hz), 7.67 (1H, t, *J*=7.4 Hz), 7.57 (1H, t, *J*=7.9 Hz), 4.12 (1H, dd, *J*=7.9, 2.1 Hz), 3.78 (3H, s), 2.32 (2H, m), 2.10 (2H, m), 1.89 (1H, m), 1.68 (1H, m); IR (KBr) 2957, 2870, 1742, 1632, 1589, 1508, 1435, 1420, 1381, 1321, 1285, 1206, 1165, 1144, 1084, 1034, 889, 845, 781, 733 cm^{-1}; HRMS *m*/*z*(M^+) calcd for $C_{20}H_{16}O_4$, 320.1049. Found 320.1051.

Methyl 7,7-dimethyl-9-oxo-1,3,4,4a,6,7,8,9,9b-decahydro-dibenzo[*b*,*d*]furan-4a-carboxylate (15). Reaction of 5,5-dimethyl-1,3-cyclohexanedione (**1a**) (140 mg, 1 mmol) with methyl 1-cyclohexene-1-carboxylate **2d** (701 mg, 5 mmol) in acetonitrile (20 mL) afforded **15** (195 mg, 70%) as a liquid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.73 (3H, s), 3.36 (1H, t, *J*=5.9 Hz), 2.44–2.18 (4H, m), 1.94 (2H, m), 1.68–1.52 (3H, m), 1.50–1.41 (3H, m), 1.08 (6H, s); IR (neat) 2955, 2870, 1742, 1642, 1435, 1400, 1350, 1242, 1192, 1140, 1073, 988, 965, 926, 793, 648 cm^{-1}; HRMS *m*/*z*(M^+) calcd for $C_{16}H_{22}O_4$, 278.1519. Found 278.1515.

Methyl 7-oxo-7b,8,9,10,11,11a-hexahydro-7*H*-benzo[*b*]-phenaleno[2,1-*d*]furan-11a-carboxylate (16). Reaction of 4-hydroxy-1*H*-phenalen-1-one **1g** (196 mg, 1 mmol) with methyl 1-cyclohexene-1-carboxylate **2d** (701 mg, 5 mmol) in acetonitrile (20 mL) afforded **16** (174 mg, 52%) as a solid: mp 113–115°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.56 (1H, d, *J*=7.2 Hz), 8.14 (1H, d, *J*=7.2 Hz), 8.09 (1H, d, *J*=8.2 Hz), 8.04 (1H, d, *J*=8.2 Hz), 7.69 (1H, t, *J*=8.0 Hz), 7.60 (1H, t, *J*=8.0 Hz), 3.81 (1H, t, *J*=6.3 Hz), 3.73 (3H, s), 2.14 (2H, m), 1.88–1.63 (3H, m), 1.60–1.44 (3H, m); IR (KBr) 2949, 2866, 1740, 1632, 1586, 1510, 1435, 1379, 1306, 1229, 1165, 1123, 1015, 878, 845, 783 cm^{-1}; HRMS *m*/*z*(M^+) calcd for $C_{21}H_{18}O_4$, 334.1205. Found 334.1208.

Methyl 3,3-dimethyl-1-oxo-2,3,4,5a,6,7,8,9,10,10a-deca-hydro-1*H*-benzo[*b*]cyclohepta[*d*]furan-5a-carboxylate (17). Reaction of 5,5-dimethyl-1,3-cyclohexanedione (**1a**) (140 mg, 1 mmol) with methyl 1-cycloheptene-1-carboxyl-ate **2e** (771 mg, 5 mmol) in acetonitrile (20 mL) afforded **17** (196 mg, 67%) as a liquid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.73 (3H, s), 3.59 (1H, m), 2.35 (2H, m), 2.19 (2H, s), 2.04 (2H, m), 1.76 (1H, m), 1.60–1.52 (5H, m), 1.35 (2H, m), 1.09 (6H, s); IR (neat) 2930, 2857, 1740, 1644, 1453, 1399, 1350, 1258, 1223, 1148, 1101, 1044, 1003, 897, 814, 779, 644 cm^{-1}; HRMS *m*/*z*(M^+) calcd for $C_{17}H_{24}O_4$, 292.1675. Found 292.1676.

Methyl 7-oxo-8,9,10,11,12,12a-hexahydro-7*H*,7b*H*-cyclo-hepta[*b*]phenaleno[2,1-*d*]furan-12a-carboxylate (18). Reaction of 4-hydroxy-1*H*-phenalen-1-one **1g** (196 mg, 1 mmol) with methyl 1-cycloheptene-1-carboxylate **2e** (771 mg, 5 mmol) in acetonitrile (20 mL) afforded **18** (206 mg, 59%) as a solid: mp 139–141°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.56 (1H, dd, *J*=7.2, 1.0 Hz), 8.13 (1H, dd, *J*=7.2, 1.0 Hz), 8.08 (1H, dd, *J*=8.2, 1.0 Hz), 8.03 (1H, d, *J*=8.2 Hz), 7.68 (1H, t, *J*=7.6 Hz), 7.59 (1H, t, *J*=7.6 Hz), 4.04 (1H, dd, *J*=6.6, 3.2 Hz), 3.74 (3H, s), 2.29 (2H, m), 1.98 (2H, m), 1.65–1.59 (4H, m), 1.38 (2H, m); IR (KBr) 2926, 2853,1740, 1632, 1591, 1510, 1435, 1420, 1379, 1321, 1254, 1217, 1171, 1096, 1034, 986, 889, 870, 785 cm^{-1}; HRMS *m*/*z*(M^+) calcd for $C_{22}H_{20}O_4$, 348.1362. Found 348.1364.

Ethyl 5-acetyl-5-benzyl-2-methyl-4,5-dihydro-3-furan-carboxylate (19). Reaction of ethyl acetoacetate **1b** (130 mg, 1 mmol) with 3-benzyl-3-buten-2-one (**2f**) (801 mg, 5 mmol) in acetonitrile (20 mL) afforded **19** (89 mg, 31%) as a liquid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.28–7.14 (5H, m), 4.10 (2H, q, *J*=7.2 Hz), 3.14 (1H, d, *J*=14.0 Hz), 3.03 (1H, m), 2.99 (1H, d, *J*=14.0 Hz), 2.83 (1H, m), 2.21 (3H, s), 2.01 (3H, s), 1.20 (3H, t, *J*=7.7 Hz); IR (neat) 3088, 2982, 1713, 1645, 1605, 1495, 1454, 1383, 1236, 1098, 1024, 972, 916, 835, 810 cm^{-1}; HRMS *m*/*z*(M^+) calcd for $C_{17}H_{20}O_4$, 288.1362. Found 288.1365.

2-Acetyl-2-benzyl-6,6-dimethyl-2,3,4,5,6,7-hexahydro-benzo[*b*]furan-4-one (20). Reaction of 5,5-dimethyl-1,3-cyclohexanedione (**1a**) (140 mg, 1 mmol) with 3-benzyl-3-buten-2-one (**2f**) (801 mg, 5 mmol) in acetonitrile (20 mL) afforded **20** (140 mg, 47%) as a liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.30–7.15 (5H, m), 3.18 (1H, d, *J*=14.1 Hz), 2.98 (1H, d, *J*=14.1 Hz), 2.95 (1H, d, *J*=15.3 Hz), 2.81 (1H, d, *J*=15.3 Hz), 2.34–1.99 (4H, m), 2.11 (3H, s), 1.04 (3H, s), 0.86 (3H, s); IR (neat) 3063, 3032, 2959, 2872, 1721, 1644, 1454, 1400, 1356, 1235, 1169, 1144, 1092, 993, 914, 887, 862 cm^{-1}; HRMS *m*/*z*(M^+) calcd for $C_{19}H_{22}O_3$, 298.1570. Found 298.1572.

2-Benzoyl-2,6,6,-trimethyl-2,3,4,5,6,7-hexahydrobenzo-[*b*]furan-4-one (21). Reaction of 5,5-dimethyl-1,3-cyclo-hexanedione (**1a**) (140 mg, 1 mmol) with 2-methyl-1-phenyl-2-propen-1-one (**2g**) (731 mg, 5 mmol) in aceto-nitrile (20 mL) afforded **21** (128 mg, 45%) as a liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.96–7.91 (2H, m), 7.55–7.25 (3H, m), 3.44 (1H, d, *J*=15.0 Hz), 2.82 (1H, d, *J*=15.0 Hz), 2.33–2.22 (4H, m), 1.73(3H, s), 1.11 (3H, s), 1.06 (3H, s); IR (neat) 3065, 2961, 2872, 1684, 1645, 1451, 1402, 1372, 1235, 1146, 1071, 1030, 980, 914, 837, 795, 766 cm^{-1}; HRMS *m*/*z* (M^+) calcd for $C_{18}H_{20}O_3$, 284.1413. Found 284.1412.

3a,6,6-Trimethyl-2,3,3a,5,6,7,8,8b-octahydro-1*H*-benzo-[*b*]cyclopenta[*d*]furan-3,8-dione (22). Reaction of 5,5-dimethyl-1,3-cyclohexanedione (**1a**) (140 mg, 1 mmol) with 2-methyl-2-cyclopenten-1-one (**2h**) (481 mg, 5 mmol) in acetonitrile (20 mL) afforded **22** (75 mg, 32%) as a solid: mp 135–137°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.56 (1H, dd, *J*=7.4, 1.4 Hz), 2.37–2.23 (5H, m), 2.21 (2H, s), 2.00 (1H, m), 1.45 (3H, s), 1.08 (3H, s), 1.06 (3H, s); IR (KBr) 2965, 2903, 1746, 1661, 1466, 1404, 1345, 1292, 1235, 1167, 1140, 1063, 1026, 918, 891, 862, 779, 735 cm^{-1}; HRMS *m*/*z* (M^+) calcd for $C_{14}H_{18}O_3$, 234.1256. Found 234.1258.

3,3,5a-Trimethyl-1,2,3,4,5a,6,7,8,9,9a-decahydrodibenzo-[*b*,*d*]furan-1,6-dione (23). Reaction of 5,5-dimethyl-1,3-cyclohexanedione (**1a**) (140 mg, 1 mmol) with 2-methyl-2-cyclohexen-1-one (**2i**) (551 mg, 5 mmol) in acetonitrile (20 mL) afforded **23** (74 mg, 30%) as a liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.32 (1H, m), 2.58–2.25 (4H, m), 2.21 (2H, s). 1.90–1.82 (4H, m), 1.48 (3H, s), 1.09 (6H, s); IR (neat) 2955, 2876, 1723, 1636, 1466, 1400, 1345, 1306, 1258, 1235, 1150, 1100, 1030, 1017, 995, 912, 885, 843, 775 cm^{-1}; HRMS *m*/*z*(M^+) calcd for $C_{15}H_{20}O_3$, 248.1413. Found 248.1412.

2-Isopropenyl-2,6,6-trimethyl-3,5,6,7-tetrahydro-2*H*-benzofuran-4-one (24). Reaction of 5,5-dimethyl-1,3-cyclohexanedione (**1a**) (140 mg, 1 mmol) with 2,3-dimethyl-1,3-butadiene (**2j**) (411 mg, 5 mmol) in acetonitrile (20 mL) afforded **24** (170 mg, 77%) as a liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.96 (1H, s), 4.82 (1H, s), 2.83 (1H, d, *J*=16.1 Hz), 2.61 (1H, d, *J*=16.1 Hz), 2.28 (2H, s), 2.02 (2H, s), 1.75 (3H, s), 1.49 (3H, s), 1.10 (3H, s), 1.07 (3H, s); IR (neat) 2959, 1636, 1520, 1402, 1354, 1242, 1167, 1144, 1121, 1098, 1028, 910, 847, 760 cm^{-1}; HRMS *m*/*z*(M^+) calcd for $C_{14}H_{20}O_2$, 220.1464. Found 220.1461.

2-Isopropenyl-2,7,8-trimethyl-2,3-dihydro-furo[3,2-*c*]-chromen-4-one (25). Reaction of 4-hydroxy-6,7-dimethylcoumarin (**1h**) (190 mg, 1 mmol) with 2,3-dimethyl-1,3-butadiene (**2j**) (411 mg, 5 mmol) in acetonitrile (20 mL) afforded **25** (108 mg, 40%) as a liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.91 (1H, s), 7.16 (1H, s), 5.09 (1H, s), 4.90 (1H, s), 3.19 (1H, d, *J*=14.2 Hz), 2.97 (1H, d, *J*=14.2 Hz), 2.34 (3H, s); IR (neat) 2976, 1620, 1555, 1462, 1377, 1348, 1262, 1190, 1146, 1107, 1053, 905, 860, 775 cm^{-1}; HRMS *m*/*z*(M^+) calcd for $C_{17}H_{18}O_3$, 270.1256. Found 270.1252.

9-Isopropenyl-9-methyl-8,9-dihydro-phenaleno[1,2-*b*]-furan-7-one (26). Reaction of 4-hydroxy-1*H*-phenalen-1-one (**1g**) (196 mg, 1 mmol) with 2,3-dimethyl-1,3-butadiene (**2j**) (247 mg, 3 mmol) in acetonitrile (20 mL) afforded **26** (182 mg, 66%) as a liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.06 (1H, d, *J*=7.2 Hz), 8.11–8.03 (3H, m), 7.71 (1H, t, *J*=7.8 Hz), 7.60 (1H, t, *J*=7.8 Hz), 5.13 (1H, s), 4.90 (1H, s), 3.25 (1H, d, *J*=15.4 Hz), 3.04 (1H, d, *J*=15.4 Hz), 1.86 (3H, s), 1.67 (3H, s); IR (neat) 2976, 1630, 1584, 1510, 1422, 1381, 1327, 1263, 1236, 1101, 1065, 1024, 901, 870, 845, 779 cm^{-1}; HRMS *m*/*z*(M^+) calcd for $C_{19}H_{16}O_2$, 276.1151. Found 276.1153.

2-Isopropenyl-2-methyl-2,3-dihydro-naphtho[2,3-*b*]furan-4,9-dione (27) and 2-isopropenyl-2-methyl-2,3-dihydro-naphtho[1,2-*b*]furan-4,5-dione (28). Reaction of 4-hydroxy-1,4-naphthoquinone **1i** (174 mg, 1 mmol) with 2,3-dimethyl-1,3-butadiene (**2j**) (411 mg, 5 mmol) in acetonitrile (20 mL) afforded **27** (127 mg, 50%) and **28** (102 mg, 40%) as a mixture. **27**: mp 134–135°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.08 (2H, m), 7.70 (2H, m), 5.12 (1H, s), 4.92 (1H, s), 3.23 (1H, d, *J*=17.1 Hz), 3.00 (1H, d, *J*=17.1 Hz), 1.85 (3H, s), 1.66 (3H, s); IR (KBr) 2984, 1680, 1644, 1624, 1591, 1572, 1439, 1395, 1370, 1314, 1256, 1206, 1155, 1107, 1046, 957, 910, 837, 756 cm^{-1}; HRMS *m*/*z*(M^+) calcd for $C_{16}H_{14}O_3$, 254.0943. Found 254.0943. **28**: mp 146–147°C: ^{1}H NMR δ 8.10 (1H, d, *J*=7.0 Hz), 7.72–7.56 (3H, m), 5.11(1H, s), 4.95 (1H, s), 3.17 (1H, d, *J*=15.4 Hz), 2.96 (1H, d, *J*=15.4 Hz), 1.85 (3H, s), 1.68 (3H, s); IR (KBr) 3071, 1698, 1647, 1618, 1589, 1572, 1491, 1451, 1410, 1360, 1279, 1256, 1215, 1154, 1107, 1067, 982, 914, 880, 851, 816, 760 cm^{-1}; HRMS *m*/*z*(M^+) calcd for $C_{16}H_{14}O_3$, 254.0943. Found 254.0942.

2-Methyl-2-vinyl-2,3-dihydro-naphtho[2,3-*b*]furan-4,9-dione (29) and 2-methyl-2-vinyl-2,3-dihydro-naphtho[1,2-*b*]furan-4,5-dione (30). Reaction of 4-hydroxy-1,4-naphthoquinone **1i** (174 mg, 1 mmol) with isoprene **2k** (341 mg, 5 mmol) in acetonitrile (20 mL) afforded **29** (75 mg, 31%) and **30** (96 mg, 40%) as a mixture. **29**: mp 148–149°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.08 (2H, m), 7.70 (2H, m), 6.07 (1H, dd, *J*=17.3, 10.9 Hz), 5.65 (1H, d, *J*=17.3 Hz), 5.21 (1H, d, *J*=10.9 Hz), 3.22 (1H, d, *J*=17.0 Hz), 3.03 (1H, d, *J*=17.0 Hz), 1.67 (3H, s); IR(KBr) 3071, 2975, 1682, 1644, 1622, 1593, 1447, 1391, 1370, 1254, 1206, 1157, 1051, 955, 793, 754 cm^{-1}; HRMS *m*/*z*(M^+) calcd for $C_{15}H_{12}O_3$, 240.0787. Found 240.0783. 30: mp 149–151°C; ^{1}H NMR δ 8.12 (1H, d, *J*=7.6 Hz), 7.73–7.61 (3H, m), 6.11 (1H, dd, *J*=17.3, 10.7 Hz), 5.38 (1H, d, *J*=17.3 Hz), 5.26 (1H, d, *J*=10.7 Hz), 3.17 (1H, d, *J*=15.4 Hz), 3.01 (1H, d, *J*=15.4 Hz), 1.71 (3H, s); IR (KBr) 3086, 2976, 1694, 1644, 1613, 1570, 1487, 1447, 1404, 1381, 1350, 1252, 1217, 1159, 1073, 1020, 1001, 930, 891, 847, 768 cm^{-1}; HRMS *m*/*z*(M^+) calcd for $C_{15}H_{12}O_3$, 240.0787. Found 240.0789.

2,5-Dimethyl-2-(2-methyl-propenyl)-3,5-dihydro-2*H*-furo[3,2-*c*]quinolin-4-one (31). Reaction of 4-hydroxy-1-methyl-2(1*H*)-quinolone **1f** (175 mg, 1 mmol) with 2,4-dimethyl-1,3-pentadiene (**2l**) (481 mg, 5 mmol) in acetonitrile (20 mL) afforded **31** (124 mg, 46%) as a liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.76 (1H, d, *J*=7.4 Hz), 7.55 (1H, t, *J*=8.0 Hz), 7.35 (1H, d, *J*=8.0 Hz), 7.21 (1H, t, *J*=7.4 Hz), 5.58 (1H, s), 3.69 (3H, s), 3.27 (1H, d, *J*=15.3 Hz), 3.14 (1H, d, *J*=15.3 Hz), 1.75 (3H, s), 1.72 (3H, s), 1.57 (3H, s); IR (neat) 2973, 1659, 1597, 1570, 1508, 1460, 1422, 1356, 1290, 1165, 1103, 1053, 864, 756 cm^{-1}; HRMS *m*/*z*(M^+) calcd for $C_{17}H_{19}O_2N$, 269.1417. Found 269.1418.

5-Methyl-2-(4-methyl-pent-3-enyl)-2-vinyl-3,5-dihydro-2*H*-furo[3,2-*c*]quinolin-4-one (32). Reaction of 4-hydroxy-1-methyl-2(1*H*)-quinolone **1f** (175 mg, 1 mmol) with myrcene **2m** (681 mg, 5 mmol) in acetonitrile (20 mL) afforded **32** (180 mg, 58%) as a liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.83 (1H, d, *J*=7.9 Hz), 7.59 (1H, t, *J*=8.5 Hz), 7.38 (1H, d, *J*=8.5 Hz), 7.25 (1H, m), 6.01 (1H, dd, *J*=17.2, 10.8 Hz), 5.34 (1H, d, *J*=17.2 Hz), 5.18 (1H, d, *J*=10.8 Hz), 5.16 (1H, m), 3.71 (3H, s), 3.17 (2H, s), 2.14–1.91 (4H, m), 1.68 (3H, s), 1.60 (3H, s); IR (neat) 2930, 1659, 1597, 1549, 1508, 1462, 1424, 1360, 1290, 1161, 1096, 1040, 1003, 903, 756 cm^{-1}; HRMS *m*/*z*(M^+) calcd for $C_{20}H_{23}NO_2$, 309.1730. Found 309.1732.

2-Acetyl-2-methoxy-2,3-dihydro-naphtho[2,3-*b*]furan-4,9-dione (40). To a solution of 2-hydroxy-1,4-naphthoquinone **1i** (1.741 g, 0.01 mol) and 2,3-dimethoxy-1,3-butadiene (**2n**) (2.282 g, 0.02 mol) in acetonitrile (100 mL) was added CAN (16.447 g, 0.03 mol) at 0°C and the reaction mixture was stirred under nitrogen for 5 h. The mixture

was diluted with water and extracted with ethyl acetate (3×100 mL). The combined organic extracts were washed with brine, dried ($MgSO_4$), and evaporated under reduced pressure to give the residue. The residue was purified by flash column chromatography on sillica gel (*n*-hexane/ethyl acetate=5:1) to give **40** (1.443 g, 53%) as a solid: mp 146°; ^{1}H NMR($CDCl_3$) δ 8.08 (2H, m), 7.71 (2H, m), 3.69 (1H, d, J=19.1 Hz), 3.44 (3H, s), 3.13 (1H, d, J=19.1 Hz), 2.40 (3H, s); IR (KBr) 2946, 1738, 1682, 1653, 1634, 1593, 1429, 1389, 1360, 1248, 1204, 1173, 1090, 953, 855, 793, 745, 720 cm^{-1}; HRMS *m/z* (M^+−OMe) calcd for $C_{14}H_9O_4$, 240.0422. Found 240.0423.

2-Acetyl-naphtho[2,3-*b*]furan-4,9-dione (37). To a solution of **40** (1.400 g, 5.1 mmol) in benzene (60 mL) was added DBU (1.553 g, 10.2 mmol). The reaction mixture was stirred at room temperature for 5 h. The reaction mixture was quenched with aqueous ammonium chloride and extracted with ethyl acetate (3×40 mL). The combined organic extracts were washed with brine, dried ($MgSO_4$), and evaporated under reduced pressure to give the residue. The residue was purified by flash column chromatography on sillica gel (*n*-hexane/ethylacetate=4:1) to give **37** (1.164 g, 95%) as a solid: mp 222° (lit.[21] mp 222–224°); ^{1}H NMR($CDCl_3$) δ 8.23 (2H, m), 7.79 (2H, m), 7.59 (1H, s), 2.65 (3H, s); IR (KBr) 3113, 1699, 1676, 1580, 1439, 1358, 1285, 1262, 1225, 1198, 1167, 1096, 976, 959, 934, 874, 793, 718 cm^{-1}.

2-(1-Hydroxy-ethyl)-naphtho[2,3-*b*]furan-4,9-dione (38). To a solution of **37** (1.150 g, 4.8 mmol) in methanol (60 mL) was added sodium borohydride (0.567 g, 15.0 mmol) at 0°C. The reaction mixture was stirred at room temperature for 2 h. The mixture was acidified with 10% hydrochloric acid, evaporated to remove methanol under reduced pressure, and extracted with ethyl acetate (3×40 mL). The combined organic extracts were washed with brine, dried ($MgSO_4$), and evaporated to give the residue. The residue was purified by flash column chromatography on sillica gel (*n*-hexane/ethylacetate=4:1) to give **38** (1.044 g, 90%) as a solid: mp 143° (lit.[21] mp 139–140°); ^{1}H NMR($CDCl_3$) δ 8.18 (2H, m), 7.73 (2H, m), 6.84 (1H, s), 5.03 (1H, q, J=6.4 Hz), 1.64 (3H, d, J=6.4 Hz); IR (KBr) 3422, 2926, 1678, 1591, 1535, 1458, 1368, 1329, 1262, 1221, 1084, 961, 802, 714 cm^{-1}.

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