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Synthesis of Dihydrobenzofuran Derivatives from Substituted *p*-Benzoquinones

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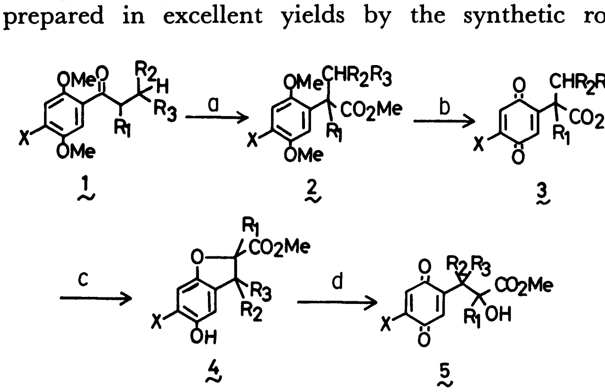
A series of *p*-benzoquinones having an ester functional group in the α position of alkyl side chains was prepared. Irradiation of these quinones, except for methyl 3-methyl-2-(4-methyl-3,6-dioxo-1,4-cyclohexadienyl)-butyrate (**3e**), rapidly gave methyl 3-substituted 2,3-dihydro-5-hydroxybenzofuran-2-carboxylate in fairly good yields, and it was found that rearrangement of the side chain occurred concomitantly. Photolysis of quinone **3e** afforded methyl 2-(2,5-dihydroxy-4-methylphenyl)-3-methyl-3-butenoate as the major product. An intermediate was postulated to account for the isolated photoproduct.

2,3-Dihydrobenzofurans are of interest as a potential synthetic intermediate of a variety of medicinally important natural products[1] in addition to their own pharmacological activity.

In this report, syntheses of a variety of methyl 2,3-dihydro-5-hydroxybenzofuran-2-carboxylate derivatives by way of photochemical reactions are described. One of the possible approaches to the synthesis of this system is photocyclization of substituted *p*-quinones.[2,3] The present author has developed a simple general route to the dihydrobenzofuran derivatives starting from alkyl substituted *p*-benzoquinones. The alkyl group has a methoxycarbonyl grouping in its α position.[4] It is anticipated that the β-hydrogen atom of the alkyl side chain will occupy a favorable position for the γ-hydrogen abstraction by a photoexcited quinonoid carbonyl group, because of the dipole-dipole repulsion between quinonoid carbonyl and methoxycarbonyl groups. The most interesting aspect of the present results is that the photochemical reaction of these quinones occurs with rearrangement to give methyl 3-substituted, 2,3-dihydro-5-hydroxybenzofuran-2-carboxylates.

Results and Discussion

Preparation of Quinones. All quinones **3a**—**n** were prepared in excellent yields by the synthetic route shown in Scheme 1. That is, oxythallation of the ketone **1** with thallium(III) nitrate (TTN)[5] and trimethyl orthoformate (TMOF) in methanol followed by oxidation of the ester **2** with ceric ammonium nitrate (CAN)[6a] in 70% aqueous acetonitrile to give the quinone **3**.



(a) $Tl(NO_3)_3 \cdot 3H_2O$, $CH(OCH_3)_3$, MeOH; (b) CAN/aq CH_3CN; (c) hν, benzene; (d) CAN/aq CH_3CN
R_1=H, Me
R_2=H, Me, Et, *n*-Pr, CO_2Me, $(CH_2)_2CO_2Me$, $(CH_2)_3$-NPht,* $(CH_2)_3NHCOCF_3$, $CH_2OCO_2C_6H_5$
R_3=H, Me
X=H, Me, Br, OMe
* NPht=phthalimido

Scheme 1.

Irradiation of Quinones. On irradiation of a solution of the quinone **3** (2 mmol) in dry benzene with a high pressure Hg lamp (300 W) after bubbling nitrogen, the quinone solution rapidly turned from yellow to colorless. The photochemical reaction was complete within several hours (0.5—5 h) at 0—10 °C and gave methyl 3-substituted 2,3-dihydro-5-hydroxybenzofuran-2-carboxylate **4** in relatively good yields after purification by column chromatography. The results of photolyses of the quinones **3a**—**n** are summarized in Table 1.

The structures of the irradiation products **4a**—**n** were established by their IR, ^{1}H NMR data, and chemical reactions. In particular, the structure of **4a** was confirmed as follows. The ^{1}H NMR spectrum of **4a** consisted of a characteristic AB pattern due to geminal protons at C-3 (J_{AB}=15 Hz),[7] indicating the presence of a C-2 methoxycarbonyl-substituted 2,3-dihydrobenzofuran ring (C-2 methoxycarbonyl, IR: 1740 cm^{-1}, CO). Such an ABX pattern of C-2 substituted 2,3-dihydrobenzofuran was similar to that of ethyl 2,3-

TABLE 1. FORMATION OF PHOTOREARRANGED DIHYDROBENZOFURAN **4** FROM QUINONE **3**

Quinone	X	R_1	R_2	R_3	Product	Yield/%[a]
3a	Me	H	H	H	**4a**	41
3b	Me	H	Me	H	**4b**	65
3c	Me	Me	H	H	**4c**	45
3d	Me	H	Et	H	**4d**	68
3e	Me	H	Me	Me	**4e**[b]	40
3f	Me	H	*n*-Pr	H	**4f**	60
3g	Me	H	CO_2Me	H	**4g**	56
3h	Me	H	$(CH_2)_2CO_2Me$	H	**4h**	51
3i	Me	H	$(CH_2)_3NPht$	H	**4i**	75
3j	Me	H	$(CH_2)_3NHCOCF_3$	H	**4j**	69
3k	Me	H	$CH_2OCO_2C_6H_5$	H	**4k**	39
3l	H	H	Me	H	**4l**	60
3m	Br	H	Me	H	**4m**	31
3n	OMe	H	Me	H	**4n**	42

a) Reported yield are for isolated, purified products. b) No dihydrobenzofuran deriv was isolated. Product was methyl 2-(2,5-dihydroxy-4-methylphenyl)-3-methyl-3-butenoate.

dihydro-5-hydroxybenzofuran-2-carboxylate.[8)]

For the photoproduct **4c**, the ^{1}H NMR spectrum showed a coupling ($J_{AB}=15$ Hz),[7)] which suggested that the substitution pattern was similar to that of **4a**. Furthermore, the structures of **4a** and **4c** were also supported by oxidation with ceric ammonium nitrate[6b)] to the corresponding quinones **5a** and **5c**. ^{1}H NMR spectra of **5a** and **5c** showed the presence of methylene protons directly attaching to the quinone ring. The methylene protons were long-range coupled with the quinone ring proton ($J=1.2$ Hz).[9)]

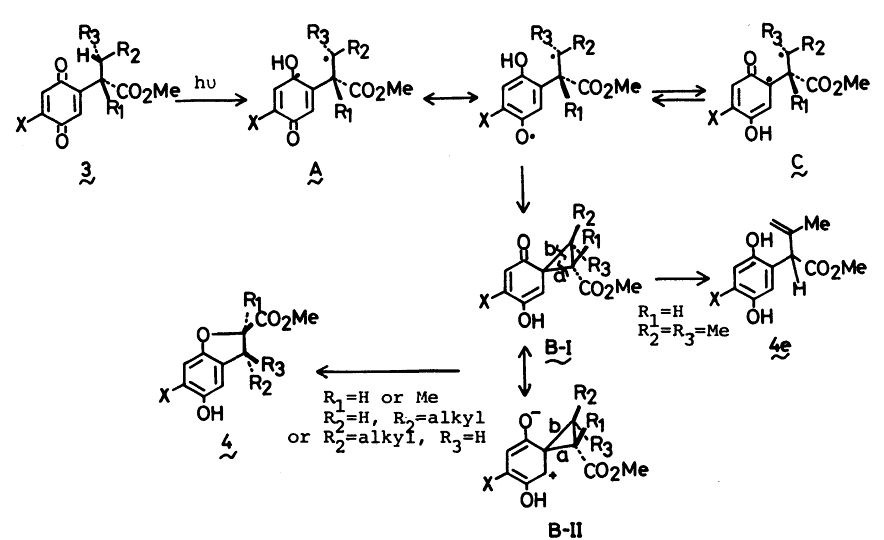
The photoproduct **4g** was compatible with the structure of dimethyl 2,3-dihydro-5-hydroxy-6-methylbenzofuran-2,3-dicarboxylate on the basis of the spectral data outlined below. Its IR spectrum showed three characteristic bands at 3340 (phenolic OH), 1735 (ester CO), and 1695 cm^{-1} (ester CO). Its ^{1}H NMR spectrum showed two doublets at δ 4.41 ($J=6$ Hz) and δ 5.56 ($J=6$ Hz) due to the protons C_3–H and C_2–H, respectively, and a broad singlet at δ 5.32 due to the phenolic hydroxyl proton.

Irradiation of the quinones **3b**, **3d**, **3f**, **3l**, **3m**, and **3n** afforded predominantly the corresponding dihydrobenzofurans **4b**, **4d**, **4f**, **4l**, **4m**, and **4n**, respectively, and a small amount of isomers. The major photoproducts in the reactions wer eisolated by chromatoggraphy and/or fractional crystallization. The minor products were detected by ^{1}H NMR and GC, but not isolated. The ^{1}H NMR spectra of the above six major products showed similar chemical shifts and coupling constants for the proton signals at C-3 and C-2 on the dihydrobenzofuran ring as shown in Table 2. The regiochemistry for the substituents around C-2 and C-3 of these photoproducts cannot be determined directly by comparison with the chemical shifts of C-2 and C-3 protons of other products, *i.e.*, **4a**, **4c**, and **4g** as was already described. In general, chemical shifts of C-2 and C-3 protons on 2,3-disubstituted 2,3-dihydrobenzofurans are variable according to the substituent groups and stereospecific environment.[10)] Therefore, **4b**, **4d**, and **4f** were converted by oxidation with CAN to quinones **5b**, **5d**, and **5f**, respectively. The structures of these three quinones were assigned on the basis of the spectroscopic data. For example, quinone **5f** showed three characteristic bands at 3470 (OH), 1720 (ester CO), and 1650 cm^{-1} (quinone CO) in its IR spectrum. Its ^{1}H NMR spectrum consisted of the signals at δ 1.64 (m, 4H), at δ 2.87 (d, $J=7$ Hz, 1H), at δ 3.31 (m, 1H), and at δ 4.31 (dd, $J=3.5$ Hz, and 7 Hz, 1H). On adding D_2O the signal at δ 2.87 disappeared and the double doublets signal at δ 4.31 was simplified to a doublet ($J=3.5$ Hz). Irradiation of the methylene proton at δ 1.64 changed the signal at δ 3.31 to a sharp doublet ($J=3.5$ Hz), and the signal at δ 4.31 coupled with the methine proton (δ 3.31) to a triplet ($J=7$ Hz) and the hydroxyl proton signal at δ 2.87 to a singlet. These results suggested that the quinone **5f** included the partial structure $-CH_2\overset{|}{C}HCH(OH)CO-$ in the side chains. Further support for the structure **5f** was provided by the reduction of the quinone **5f** with sodium dithionite followed by acetylation of the obtained hydroquinone with acetic anhydride–pyridine to the corresponding triacetate **7**. However, the methine proton signal adjacent to the acetoxyl group showed a downfield shift at δ 5.18 (d, $J=5$ Hz) due to a deshielding effect of the acetoxyl carbonyl. The above results indicated that these original photoproducts **4b**, **4d**, **4f**, **4l**, **4m**, and **4n** contain an ester group at C-2 position and other substituent group (R_2 and R_3) at C-3 position, respectively.

Irradiation of other substituted quinones **3h**, **3i**, **3j**, and **3k** also gave corresponding photocyclization products **4h**, **4i**, **4j**, and **4k**.

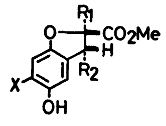
The ^{1}H NMR spectrum of photoproduct **4k** showed the presence of a methine proton signal at δ 5.02 (d, $J=5.1$ Hz), probably at C-2 position. This lower field shift can be explained in terms of the deshielding effect of the carbonate carbonyl group.

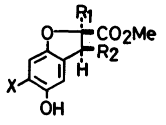
The structures of the major and the minor components were correlated with each other by their chemical reactions and by comparing their ^{1}H NMR spectra. Acetylation of crude photoproducts **4b**, **4d**, **4f**, and

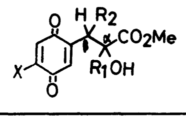


Scheme 2.

Table 2. ^{1}H NMR spectra of dihydrobenzofurans **4** and quinones **5**







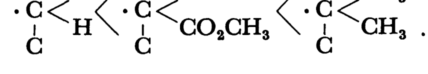
			Dihydrobenzofuran **4**					Quinone **5**		
			trans-Isomer			*cis*-Isomer				
X	R_1	R_2	C_2-H	C_3-H	R_2=Me	C_2-H	R_2=Me	C_α-H	C_β-H	OH
a	Me H	H	5.12(dd) J=7 Hz J=10 Hz	3.14 ≀ (m) 3.62 A	—	—	—	4.13(dd) J=5 Hz J=8.5 Hz	D	B
b	Me H	Me	4.63(d) J=7 Hz	3.40 ≀ (m) 3.68	1.40(d) J=7 Hz	5.15(d) J=9 Hz	1.16(d)	4.30(bm)	3.46(dq) J=4 Hz J=7 Hz	3.00(bs)
c	Me Me	H	—	3.00(d) J=15 Hz 3.50 J=15 Hz	—	—	—	—	2.70(d) J=13.5 Hz 2.97(d) J=13.5 Hz	3.34(s)
d	Me H	Et	4.74(d) J=5 Hz	3.42(m)	—	5.14(d) J=8.5 Hz	—	4.36 J=3.5 Hz J=7.6 Hz	3.23(dt) J=3.5 Hz J=7 Hz	2.98(d) J=7.6 Hz
f	Me H	*n*-Pr	4.76(d) J=5 Hz	3.46(m)	—	5.12(d) J=8.5 Hz	—	4.31(dd) J=3.5 Hz J=7 Hz	3.31(m) J=3.5 Hz J=7 Hz	2.87(d) J=7 Hz
g	Me H	CO_2Me	5.56(d) J=6 Hz	4.41(d) J=6 Hz	—	C	—	4.86(d) J=4.2 Hz	4.32(d) J=4.2 Hz	3.75(bs)
h	Me H	$(CH_2)_2CO_2Me$	4.77(d) J=6 Hz	3.44–	—	C	—	4.35(bs)	3.38(m)	3.07(bd) J=8 Hz
i	Me H	$(CH_2)_3NPht$	4.76(d) J=5 Hz	B	—	C	—			
j	Me H	$(CH_2)_3NHCOCF_3$	4.71(d) J=5 Hz	B	—	5.15(d) J=9 Hz	—			
k	Me H	$CH_2OCO_2C_6H_5$	5.02(d) J=5.1 Hz	3.90(m)	—	C	—			
l	H H	Me	4.64(d) J=7 Hz	3.53(m)	1.38(d) J=7 Hz	5.16(d) J=9 Hz	1.13(d) J=7 Hz			
m	Br H	Me	4.65(d) J=7 Hz	3.53(m)	1.40(d) J=7 Hz	5.15(d) J=9 Hz	1.16(d) J=7 Hz			
n	OMe H	Me	4.66(d) J=7 Hz	3.56(m)	1.41(d) J=7 Hz	5.17(d) J=8.5 Hz	1.15(d) J=7 Hz			

a) The *cis*-isomer, which was a minor component of the mixture of products, was detectable only by the ^{1}H NMR spectrum. (A) AB type: J=15 Hz, (B) Chemical shifts were not determined because of overlapping of the signal with those of other protons. (C) Not detected. (D) δ 2.69(dd), J=8.5 and 15 Hz, 1H), δ 2.98 (dd, J=5 and 15 Hz, 1H).

4i containing minor components with acetic anhydride in pyridine solution gave only the single monoacetate **6b**, **6d**, **6f**, and **6i**, respectively. The minor components are therefore presumed to be the stereoisomers of the thermodynamically stable major products. In the ^{1}H NMR spectra, the coupling constants due to C-2 and C-3 protons of 2,3-disubstituted 2,3-dihydrobenzofuran are $J_{cis}>J_{trans}$[11] as predicted by the Karplus equation.[12] The most striking differences between the ^{1}H NMR spectra of the *cis* and *trans* isomers of 2,3-disubstituted 2,3-dihydrobenzofuran, other than the values of $J_{2,3}$ are the different values for the chemical shift of the C-2 proton. The ^{1}H NMR signal of the C-2 proton of the *trans* isomers is located upfield at about δ 0.3 compared to the corresponding proton of the *cis* isomers. The major product **4** (δ 4.63—4.77, J=5—7 Hz) is concluded to be *trans*, and the minor to be *cis* (δ 5.14—5.17, J=8.5—9 Hz) as shown in Table 2.

On the other hand, the photolysis of quinone **3e** did not afford a dihydrobenzofuran derivative, but methyl 2-(2,5-dihydroxy-4-methylphenyl)-3-methyl-3-butenoate **4e** as the major product.

The proposed mechanism of these photochemical reactions is given in Scheme 2. γ-Hydrogen abstraction by photoexcited carbonyl of the quinone **3** forms the biradical intermediate **A**[13] and subsequently yields the spirocyclopropyl ketone **B-1**[3] and/or spirocyclopropyl zwitter-ion intermediate **B-2**;[3] then the cyclopropane ring opens to afford the observed product **4**. However it is difficult to anticipate a ring-opened zwitter-ion intermediate,[14] because the three-membered ring may cleave to give a positive charge at the α position to the methoxycarbonyl group. From the present results preferential cleavage of bond **a** can be recognized **B-1** to give phenyl migrated products **4** with exception of only one case **3e** ($R_2=R_3=Me$). In the latter case cleavage of bond **b** may be the preferential course to give **4e**, in which no phenyl migration occurs. Thus, among the alkyl substituted *p*-benzoquinones examined, the trend of phenyl migration initiated by photochemical γ-hydrogen abstraction reaction may be explained in terms of the stability of the radical intermediates involved. The present results indicate the stability of the radical to be



$$\underset{\underset{\textstyle C}{|}}{\cdot C}\Big<{}^{H}_{H} \;\Big<\; \underset{\underset{\textstyle C}{|}}{\cdot C}\Big<{}^{H}_{CO_2CH_3} \;\Big<\; \underset{\underset{\textstyle C}{|}}{\cdot C}\Big<{}^{CH_3}_{CH_3}\ .$$

Of course, this trend should be applied under the very limited conditions, for a contribution of a dipolar intermediate, such as **B-2**, could not be excluded in the present reactions.

Experimental

Melting points and boiling points were uncorrected. Bulb to bulb distillations were carried out on a Kugelrohr-type apparatus. IR spectra were measured on a JASCO IRA-1 spectrophotometer. ^{1}H NMR spectra were measured on a JEOL PS-100 instrument with tetramethylsilane as an internal standard and the chemical shifts are reported in δ values. Mass spectra were obtained with a Hitachi M-52 mass spectrometers (20 eV). Elemental analyses were performed by the Kyoto University Microanalytical Laboratories. Column chromatography was performed using Wako reagent grade silica gel (200 mesh). The irradiation was carried out in a Pyrex vessel at 0—10 °C, using an Eikosha 300-W high pressure Hg lamp.

Materials. 3-(Methoxycarbonyl)propionyl chloride[15] and 5-(methoxycarbonyl)pentanoyl chloride[16] were prepared from the corresponding methyl hydrogen succinate and methyl hydrogen adipate, respectively. 6-Phthalimidohexanoyl chloride[17] and 6-(trifluoroacetamido)hexanoyl chloride[18] were prepared from 6-aminohexanoic acid. Other acid chlorides were commercially available.

Preparation of Starting Materials. All of the compounds **1a**—**n**, except for **1k**, were prepared by the Friedel-Crafts acylation according to the previous reported methods.[5a]

Physical Properties of the Starting Materials. *2'5,'-Dimethoxy-4'-methylpropiophenone* **1a**: 96%; mp 78 °C,[5a] (lit,[19] mp76—77 °C).

2',5'-Dimethoxy-4'-methylbutyrophenone **1b**: 96%; bp 129—130 °C at 3 Torr (1 Torr=133.322 Pa); mp 46—46.5 °C (hexane–ether); IR (KBr): 1660 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ: 0.93 (t, 3H), 1.67 (m, 2H), 2.23 (s, 3H), 2.92 (t, 2H), 3.80 (s, 3H), 3.84 (s, 3H), 6.74 (s, 1H), and 7.20 (s, 1H); Found: C, 69.99; H, 8.21%. Calcd for $C_{13}H_{18}O_3$: C, 70.24; H, 8.16%.

2',5'-Dimethoxy-2,4'-dimethylpropiophenone **1c**: 99%; bp 125—127 °C at 3 Torr; mp 38—39 °C (petroleum ether); IR (neat): 1675 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ: 1.14 (d, 6H), 2.25 (s, 3H), 3.57 (m, 1H), 3.82 (s, 3H), 3.86 (s, 3H), 6.78 (s, 1H), and 7.14 (s, 1H); Found: C, 69.96; H, 8.20%. Calcd for $C_{13}H_{18}O_3$: C, 70.24; H, 8.16%.

2',5'-Dimethoxy-4'-methylvalerophenone **1d**: 95%; bp 140—143 °C at 3 Torr; mp 33.5—34 °C (petroleum ether); IR (KBr): 1670 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ: 1.92 (t, 3H,) 1.20—1.90 (m, 4H), 2.25 (s, 3H), 2.97 (t, 2H), 3.80 (s, 3H), 3.85 (s, 3H), 6.77 (s, 1H), and 7.21 (s, (1H); Found: C, 71.21; H, 8.75%. Calcd for $C_{14}H_{20}O_3$: C, 71.16; H, 8.53%.

2',5'-Dimethoxy-3,4'-dimethylbutyrophenone **1e**: 88%; bp 140—143 °C at 3 Torr; mp 48—48.5 °C (petroleum ether); IR (KBr): 1600 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ: 0.97 (d, 6H), 2.08—2.41 (m, 1H), 2.26 (s, 3H), 2.84 (d, 2H), 3.81 (s, 3H), 3.85 (s, 3H), 6.76 (s, 1H), and 7.19 (s, 1H); Found: C, 71.42; H, 8.69%. Calcd for $C_{14}H_{20}O_3$: C, 71.16; H, 8.53%.

2',5'-Dimethoxy-4'-methylhexanophenone **1f**: 85%; bp 183 °C at 3 Torr; IR (neat): 1665 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ: 0.90 (t, 3H), 1.22—1.82 (m, 6H), 2.26 (s, 3H), 2.98 (t, 2H), 3.84 (s, 3H), 3.88 (s, 3H), 6.81 (s, 1H), and 7.27 (s, 1H); Found: C, 72.25; H, 8.87%. Calcd for $C_{15}H_{22}O_3$: C, 71.97; H, 8.86%.

Methyl 3-(2,5-Dimethoxy-4-methylbenzoyl)propionate **1g**: 90%; mp 89—90 °C (petroleum ether–dichloromethane); IR (KBr): 1735 and 1660 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ: 2.26 (s, 3H), 2.69 (t, 2H), 3.32 (t, 2H), 3.70 (s, 3H), 3.81 (s, 3H), 3.88 (s, 3H), 6.77 (s, 1H), and 7.30 (s, 1H); Found: C, 63.33; H, 6.86%. Calcd for $C_{14}H_{18}O_3$: C, 63.14; H, 6.81%.

Methyl 5-(2,5-Dimethoxy-4-methylbenzoyl)pentanoate **1h**: 73%; mp 80—81 °C (petroleum ether–dichloromethane); IR (KBr): 1730 and 1660 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ: 1.64—1.86 (m, 4H), 2.26 (s, 3H), 2.36 (m, 2H), 3.00 (m, 2H), 3.67 (s, 3H), 3.82 (s, 3H), 3.87 (s, 3H), 6.78 (s, 1H), and 7.23 (s, 1H); Found: C, 65.33; H, 7.58%. Calcd for $C_{16}H_{22}O_5$: C, 65.29; H, 7.53%.

2',5'-Dimethoxy-4'-methyl-6-(phthalimido)hexanophenone **1i**: 71%; mp 156—157 °C (methanol–dichloromethane); IR (KBr): 1775, 1715, and 1660 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ: 1.31—1.87 (m, 6H), 2.25 (s, 3H), 2.97 (t, 2H), 3.69 (t, 2H), 3.81 (s, 3H), 3.86 (s, 3H), 6.75 (s, 1H), 7.21 (s, 1H), and 7.63—7.77 (m, 4H); Found: C, 69.92; H, 6.39, N, 3.54%. Calcd for $C_{23}H_{25}O_5N$: C, 69.85; H, 6.37; N, 3.54%.

2',5'-Dimethoxy-4'-methyl-6-(trifluoroacetamido)hexanophenone **1j**: 56%; mp 87.5—89 °C (petroleum ether–dichloromethane); IR (KBr): 3300, 1730, and 1640 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.20—1.84 (m, 6H), 2.25 (s, 3H), 3.00 (t, 2H), 3.39(q, 2H), 3.82 (s, 3H), 3.86 (s, 3H), 6.80 (s, 1H), 6.90 (bs, 1H), and 7.24 (s, 1H); Found: C, 56.43; H, 6.12; N, 4.00%. Calcd for $C_{17}H_{22}O_4NF_3$: C, 56.50; H, 6.14; N, 3.88%.

2',5'-Dimethoxy-4'-methyl-4-(phenoxycarbonyloxy)butyrophenone **1k**: was prepared from **1g** in the following three steps. Reduction of the **1g** with excess lithium aluminum hydride in THF followed by reaction of the obtained 1-(2,5-dimethoxy-4-methylphenyl)-1,4-butanediol (1 mol equiv.) in dichloromethane with phenyl chloroformate (1.2 mol equiv.) in the presence of pyridine at 0 °C afforded 1-(2,5-dimethoxy-4-methylphenyl)-4-(phenoxycarbonyloxy)-1-butanol, which on oxidation with excess Cr–Pyr complex in dichloromethane yield **1k**, total yield: 30%; IR (neat): 1760 and 1660 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ: 2.00—2.36 (m, 2H), 2.21 (s, 3H), 3.12 (t, J=7 Hz, 2H), 3.81 (s, 3H), 3.87 (s, 3H), 4.31 (d, J=6.5 Hz, 2H), 6.78 (s, 1H), and 7.12—7.46 (m, 6H); Found: C, 66.81; H, 6.30%. Calcd for $C_{20}H_{22}O_6$: C, 67.02; H, 6.19%.

2',5'-Dimethoxybutyrophenone **1l**: 90%; bp 121—123 °C at 3 Torr, (lit,[20] bp 172—175 °C at 25 Torr).

2',4',5'-Trimethoxybutyrophenone **1n**: 88%; mp 79 °C (petroleum ether–dichloromethane), (lit,[21,22] mp 77 °C, 78.5—80 °C).

The following esters **2a**—**n**, except for **2m**, were prepared according to the reported methods.[5]

Methyl 2-(2,5-Dimethoxy-4-methylphenyl)propionate **2a**: was prepared from **1a** with $Tl(NO_3)_3$–TMOF–MeOH as described previously[5a)] (90%): bp 162—165 °C at 4 Torr (bulb to bulb).

Methyl 2-(2,5-Dimethoxy-4-methylphenyl)butyrate ***2b***: was prepared from **1b** with $Tl(NO_3)_3$–TMOF–MeOH following by the general procedure (96%): bp 150—152 °C at 3 Torr (bulb to bulb); IR (neat): 1735 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ: 0.87 (t, 3H), 1.56—2.20 (m, 2H), 2.20 (s, 3H), 3.64 (s, 3H), 3.77 (s, 6H), 3.90 (t, 1H), 6.68 (s, 1H), and 6.74 (s, 1H); Found: C, 66.49; H, 8.17%. Calcd for $C_{14}H_{20}O_4$: C, 66.64; H, 7.99%.

Methyl 2-Methyl-2-(2,5-dimethoxy-4-methylphenyl)propionate ***2c***: was prepared from **1c** with $Tl(NO_3)_3$–TMOF–MeOH following by the same general procedure (95%): bp 154—156 °C at 4 Torr (bulb to bulb); IR (neat): 1740 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ: 1.49 (s, 6H), 2.18 (s, 3H), 3.60 (s, 3H), 3.68 (s, 3H), 3.78 (s, 3H), 6.63 (s, 1H), and 6.74 (s, 1H); Found: C, 66.50; H, 8.27%. Calcd for $C_{14}H_{20}O_4$: C, 66.64; H, 7.99%.

Methyl 2-(2,5-Dimethoxy-4-methoxy-4-methylphenyl)pentanoate ***2d***: was prepared from **1d** with $Tl(NO_3)_3$–TMOF–MeOH following by the general reaction procedure (98%): bp 158—159 °C at 3 Torr (bulb to bulb); IR (neat): 1730 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ: 0.90 (t, 3H), 1.09—2.10 (m,4H), 2.19 (s, 3H), 3.63 (s, 3H), 3.77 (s, 3H), 4.00 (t, 1H), 6.67 (s, 1H), and 6.76 (s, 1H); Found: C, 67.79; H, 8.49%. Calcd for $C_{15}H_{22}O_4$: C, 67.64; H, 8.33%.

Methyl 2-(2,5-Dimethoxy-4-methylphenyl)-3-methylbutyrate ***2e***: was prepared from **1e** with $Tl(NO_3)_3$–TMOF–MeOH following by the usual manner (81%): bp 133—135 °C at 3 Torr (bulb to bulb); mp 78—79 °C (petroleum ether); IR (KBr): 1735 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ: 0.71 (d, 3H), 1.03 (d, 3H), 2.00—2.26 (m, 1H), 2.20 (s, 3H), 3.65 (s, 3H), 3.79 (s, 6H), 3.84 (d, 1H), 6.71 (s, 1H), and 6.91 (s, 1H); Found: C, 67.69; H, 8.41%. Calcd for $C_{15}H_{22}O_4$: C, 67.64; H, 8.33%.

Methyl 2-(2,5-Dimethoxy-4-methylphenyl)hexanoate ***2f***: was prepared from **1f** with $Tl(NO_3)_3$–TMOF–MeOH following by the general method (90%): bp 135—140 °C at 0.1 Torr (bulb to bulb); IR (neat): 1735 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ: 0.86 (t, 3H), 1.00—2.19 (m, 6H), 2.19 (s, 3H), 3.64 (s, 3H), 3.78 (s, 6H), 3.98 (t, 1H), 6.68 (s, 1H), and 6.75 (s, 1H); Found: C, 68.30; H, 8.77%. Calcd for $C_{16}H_{24}O_4$: C, 68.54; H, 8.63%.

Dimethyl 2-(2,5-Dimethoxy-4-methylphenyl)succinate ***2g***: was prepared from **1g** with $Tl(NO_3)_3$–TMOF–MeOH following by the general procedure (95%): mp 93—94 °C (petroleum ether–dichloromethane); IR (KBr): 1735 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ: 2.18 (s, 3H), 2.54 (dd, 1H), 3.14 (dd, 1H), 3.65 (s, 6H), 3.75 (s, 6H), 4.35 (dd, 1H), 6.62 (s, 1H), and 6.67 (s, 1H); Found: C, 60.57; H, 6.86%. Calcd for $C_{15}H_{20}O_6$: C, 60.80; H, 6.80%.

Dimethyl 2-(2,5-Dimethoxy-4-methylphenyl)hexanedioate ***2h***: was prepared from **1h** with $Tl(NO_3)_3$–TMOF–MeOH by the same method (99%): bp 129—131 °C at 0.06 Torr (bulb to bulb); IR (neat): 1735 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ: 1.40—2.20 (m, 4H), 2.22 (s, 3H), 2.34 (t, 2H), 3.66 (s, 6H), 3.80 (s, 6H), 4.02 (t, 1H), 6.72 (s, 1H), and 6.75 (s, 1H); Found: C, 62.68; H, 7.40%. Calcd for $C_{17}H_{24}O_6$: C, 62.95; H, 7.46%.

Methyl 2-(2,5-Dimethoxy-4-methylphenyl)-6-(phthalimido)hexanoate ***2i***: was prepared from **1i** with $Tl(NO_3)_3$–TMOF–MeOH by the usual method (84%): mp 96—97.5 °C (methanol); IR (KBr): 1775, 1720, and 1710 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ: 1.16—1.84 (m, 6H), 2.14 (s, 3H), 3.60 (s, 3H), 3.60 (m, 2H), 3.73 (s, 6H), 3.95 (t, 1H), 6.62 (s, 1H), 6.68 (s, 1H), and 7.58—7.84 (m, 4H); Found: C, 67.70; H, 6.39; N, 3.28%. Calcd for $C_{24}H_{27}O_6N$: C, 67.75; H, 6.40; N, 3.29%.

Methyl 2-(2,5-Dimethoxy-4-methylphenyl)-6-(trifluoroacetamido)-hexanoate ***2j***: was prepared from **1j** with $Tl(NO_3)_3$–TMOF–MeOH following by the general procedure (93%): mp 86.5—88 °C (petroleum ether–ether); IR (KBr): 3340, 1725, and 1710 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ: 1.20—2.20 (m, 6H), 2.20 (s, 3H), 3.34 (q, 2H), 3.66 (s, 3H), 3.79 (s, 6H), 6.56 (bs, 1H), and 6.71 (s, 2H); Found: C, 55.27; H, 6.30; N, 3.52%. Calcd for $C_{18}H_{24}O_5NF_3$: C, 55.24; H, 6.18; N, 3.58%.

Methyl 2-(2,5-Dimethoxy-4-methylphenyl)-4-(phenoxycarbonyloxy)butyrate ***2k***: was prepared from **1k** with $Tl(NO_3)_3$–TMOF–MeOH following by the same procedure (70%): IR (neat): 1760 and 1735 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ: 1.92—2.71 (m, 2H), 2.21 (s, 3H), 3.67 (s, 3H), 3.77 (s, 6H), 4.07—4.33 (m, 3H), 6.73 (s, 2H), and 7.13—7.42 (m, 5H); Found: C, 65.13; H, 6.25%. Calcd for $C_{21}H_{24}O_7$: C, 64.93; H, 6.23%.

Methyl 2-(2,5-Dimethoxyphenyl)butyrate ***2l***: was prepared from **1l** with $Tl(NO_3)_3$–TMOF–MeOH following by the general procedure (91%): bp 120—121 °C at 3 Torr (bulb to bulb); IR (neat): 1730 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ: 0.88 (t, 3H), 1.57—2.19 (m, 2H), 3.64 (s, 3H), 3.75 (s, 3H), 3.77 (s, 3H), 3.89 (t, 1H), and 6.77—6.83 (m, 3H); Found: C, 65.81; H, 7.80%. Calcd for $C_{13}H_{18}O_4$: C, 65.53; H, 7.61%.

Methyl 2-(4-Bromo-2,5-dimethoxyphenyl)butyrate ***2m***: was prepared from **2l** with bromine in chloroform (96%): bp 136—140 °C at 0.05 Torr (bulb to bulb); IR (neat): 1730 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ: 0.88 (t, 3H), 1.56—2.18 (m, 2H), 3.66 (s, 3H), 3.84 (s, 3H), 3.89 (s, 3H), 3.89 (m, 1H), 6.86 (s, 1H), and 7.04 (s, 1H); Found: C, 49.24; H, 5.52; Br, 25.18%. Calcd for $C_{13}H_{17}O_4Br$: C, 49.22; H, 5.40; Br, 25.20%.

Methyl 2-(2,4,5-Trimethoxyphenyl)butyrate ***2n***: was prepared from **1n** with $Tl(NO_3)_3$–TMOF–MeOH following by the general method (60%): mp 60—62 °C (petroleum ether); IR (KBr): 1735 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ: 0.87 (t, 3H), 1.60—2.12 (m, 2H), 3.64 (s, 3H), 3.80 (s, 3H), 3.82 (s, 3H), 3.88 (s, 3H and m, 1H), 6.49 (s, 1H), and 6.80 (s, 1H); Found: C, 62.91; H, 7.60%. Calcd for $C_{14}H_{20}O_5$: C, 62.67; H, 7.51%.

Preparation of Quinones 3. Quinones **3a**—**n** were prepared from the corresponding **2a**—**n** with ceric ammonium nitrate (CAN) in aq acetonitrile by the method of Jacob *et al.*[6a)]

Methyl 2-(4-Methyl-3,6-dioxo-1,4-cyclohexadienyl)propionate ***3a***: (CAN oxidation of **2a**): 88%; mp 59—60 °C.[5a)]

Methyl 2-(4-Methyl-3,6-dioxo-1,4-cyclohexadienyl)butyrate ***3b***: (CAN oxidation of **2b**): 98%; bp 130—131 °C at 3 Torr (bulb to bulb); IR (neat): 1735 and 1655 cm^{-1}: ^{1}H NMR ($CDCl_3$) δ: 0.92 (t, J=7 Hz, 3H), 1.60—2.00 (m, 2H), 2.04 (d, J=1.6 Hz, 3H), 3.70 (s, 3H), 3.70—3.98 (m, 1H), 6.64 (q, J=1.6 Hz, 1H), and 6.70 (s, 1H); Found: C, 64.98; H, 6.60%. Calcd for $C_{12}H_{14}O_4$: C, 64.85; H, 6.35%.

Methyl 2-Methyl-2-(4-methyl-3,6-dioxo-1,4-cyclohexadienyl)propinate ***3c***: (CAN oxidation of **2c**): 95%; mp 111—112 °C (petroleum ether); IR (KBr): 1740 and 1650 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ: 1.42 (s, 6H), 2.03 (d, J=1.6 Hz, 3H), 3.62 (s, 3H), 6.56 (q, J=1.6 Hz, 1H), and 6.59 (s, 1H); Found: C, 64.56; H, 6.35%. Calcd for $C_{12}H_{14}O_4$: C, 64.85; H, 6.35%.

Methyl 2-(4-Methyl-3,6-dioxo-1,4-cyclohexadienyl)pentanoate ***3d***: (CAN oxidation of **2d**): 96%; bp 143—145 °C at 3 Torr (bulb to bulb); IR (neat): 1735 and 1655 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ: 0.92 (t, J=7 Hz, 3H), 1.15—2.04 (m, 4H), 2.04 (d, J=1.6 Hz, 3H), 3.68 (s, 3H), 3.90 (t, J=7 Hz, 1H), 6.62 (q, J=1.6 Hz, 1H), and 6.69 (s, 1H); Found: C, 66.05; H, 6.89%. Calcd for $C_{13}H_{16}O_4$: C, 66.08; H, 6.83%.

Methyl 3-Methyl-2-(4-methyl-3,6-dioxo-1,4-cyclohexadienyl)-butyrate ***3e***: (CAN oxidation of **2e**): 96%; bp 140—143 °C at 3 Torr (bulb to bulb); IR (neat): 1735 and 1655 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ: 0.83 (d, J=7 Hz, 3H), 0.99 (d, J=7 Hz, 3H), 2.03 (d, J=1.6 Hz, 3H), 1.91—2.38 (m, 1H), 3.65 (s, 1H), 3.74 (t, J=7 Hz, 1H), 6.60 (q, J=1.6 Hz, 1H), and 6.84 (s, 1H); Found: C, 66.04; H, 6.96%. Calcd for $C_{13}H_{16}O_4$: C, 66.08; H, 6.83%.

Methyl 2-(4-Methyl-3,6-dioxo-1,4-cyclohexadienyl)hexanoate ***3f***: (CAN oxidation of **2f**): 90%; IR (neat): 1735 and 1655 cm^{-1};

^{1}H NMR (CDCl$_3$) δ: 0.88 (t, J=7 Hz, 3H), 1.00—2.04 (m, 6H), 3.68 (s, 3H), 3.82 (t, J=7 Hz, 1H), 6.60 (q, J=1.6 Hz, 1H), and 6.68 (s, 1H); Found: C, 66.95; H, 7.38%. Calcd for $C_{14}H_{18}O_4$: C, 67.18; H, 7.25%.

Dimethyl 2-(4-Methyl-3,6-dioxo-1,4-cyclohexadienyl)succinate ***3g***: (CAN oxidation of **2g**): 80%; mp 85—86 °C (methanol–petroleum ether); IR (KBr): 1735 and 1640 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ: 2.06 (d, J=1.6 Hz, 3H), 2.61 (dd, J=6 and 17 Hz, 1H), 3.06 (dd, J=6 and 17 Hz, 1H), 3.66 (s, 3H), 3.68 (s, 3H), 4.12 (t, J=7 Hz, 1H), and 6.63 (m, 2H); Found: C, 58.57; H, 5.36%. Calcd for $C_{13}H_{14}O_6$: C, 58.64; H, 5.30%.

Dimethyl 2-(4-Methyl-3,6-dioxo-1,4-cyclohexadioenyl)hexanediate ***3h***: (CAN oxidation of **2h**): 88%; bp 169—172 °C at 0.03 Torr (bulb to bulb); IR (neat): 1735 and 1655 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ: 1.36—2.05 (m, 4H), 2.05 (d, J=1.6 Hz, 3H), 2.33 (t, J=7.5 Hz, 2H), 3.64 (s, 3H), 3.67 (s, 3H and m, 1H), 6.60 (q, J=1.6 Hz, 1H), and 6.64 (s, 1H); Found: C, 61.18; H, 6.30%. Calcd for $C_{15}H_{18}O_6$: C, 61.21; H, 6.17%.

Methyl 2-(4-Methyl-3,6-dioxo-1,4-cyclohexadienyl)-6-(phthalimido)hexanoate ***3i***: (CAN oxidation of **2i**): 88%; IR (neat): 1775, 1735, 1710, and 1655 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ: 1.18—1.88 (m, 6H), 2.03 (d, J=1.6 Hz, 3H), 3.61 (s, 3H), 3.56—3.7 (m, 2H), 3.87 (m, 1H), 6.58 (q, J=1.6 Hz, 1H), 6.64 (d, J=1.2 Hz, 1H), and 7.60—7.82 (m, 4H); Found: C, 66.77; H, 5.42; N, 3.58%. Calcd for $C_{22}H_{21}O_6N$: C, 66.82; H, 5.35; N, 3.54%.

Methyl 2-(4-Methyl-3,6-dioxo-1,4-cyclohexadienyl)-6-(trifluoroacetamido)hexanoate ***3j***: (CAN oxidation of **2j**): 80%; IR (neat): 3320, 1710, and 1650 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ: 1.00—2.00 (m, 6H), 2.04 (d, J=1.6 Hz, 3H), 3.35 (q, J=7 Hz, 2H), 3.68 (s, 3H), 3.76 (m, 1H), 6.63 (q, J=1.6 Hz, 1H), 6.67 (s, 1H), and 6.68 (bs, 1H); Found: C, 52.87; H, 5.13; N, 3.84%. Calcd for $C_{16}H_{18}O_5NF_3$: C, 53.18; H, 5.02; N, 3.88%.

Methyl 2-(4-Methyl-3,6-dioxo-1,4-cyclohexadienyl)-4-(phenoxycarbonyloxy)butyrate ***3k***: (CAN oxidation of **2k**): 71%; IR (neat): 1750 and 1655 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ: 2.05 (d, J=1.6 Hz, 3H), 2.05—2.59 (m, 2H), 3.72 (s, 3H), 3.88 (t, J=7.5 Hz, 1H), 4.28 (t, J=6.5 Hz, 2H), 6.63 (q, J=1.6 Hz, 1H), 6.71 (s, 1H), and 7.11—7.46 (m, 5H); Found: C, 63.29; H, 5.19%. Calcd for $C_{19}H_{18}O_7$: C, 63.68; H, 5.06%.

Methyl 2-(3,6-Dioxo-1,4-cyclohexadienyl)butyrate ***3l***: (CAN oxidation of **2l**): 54%; bp 131—134 °C at 3 Torr (bulb to bulb); IR (neat): 1730 and 1655 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ: 0.95 (t, J=7 Hz, 3H), 1.56—2.13 (m, 2H), 3.68 (s, 3H and m, 1H), 6.69 (m, 1H), and 6.75 (s, 2H); Found: C, 63.17; H, 6.06%. Calcd for $C_{11}H_{12}O_4$: C, 63.45; H, 5.81%.

Methyl 2-(4-Bromo-3,6-dioxo-1,4-cyclohexadienyl)butyrate ***3m***: (CAN oxidation of **2m**): 68%; bp 140—145 °C at 0.05 Torr (bulb to bulb); IR (neat): 1735 and 1660 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ: 0.95 (t, J=7 Hz, 3H), 1.56—2.15 (m, 2H), 3.62 (t, J=7.5 Hz, 1H), 3.68 (s, 3H), 6.88 (s, 1H), and 7.27 (s, 1H); Found: C, 45.81; H, 3.87; Br, 28.07%. Calcd for $C_{11}H_{11}O_4Br$: C, 46.06; H, 3.86; Br, 27.83%.

Methyl 2-(4-Methoxy-3,6-dioxo-1,4-cyclohexadienyl)butyrate ***3n***: (CAN oxidation of **2n**): 60%; mp 70—72 °C (petroleum ether); IR (KBr): 1740 and 1665 cm^{-1} ^{1}H NMR (CDCl$_3$) δ: 0.94 (t, J=7 Hz, 3H), 1.55—2.13 (m, 2H), 3.69 (s, 3H and m, 1H), 3.83 (s, 3H), 5.95 (s, 1H), and 6.64 (s, 1H); Found: C, 60.29; H, 5.99%. Calcd for $C_{12}H_{14}O_5$: C, 60.50; H, 5.92%.

Irradiation of Quinones **3**. *Irradiation of* ***3a***: A solution of **3a** (416 mg, 2 mmol) in dry benzene (200 ml) was purged with nitrogen for 20 min and irradiated for 1 h. Evaporation of the solvent and column chromatography of the residue on silica gel with 10% ether–benzene as eluant gave methyl 2,3-dihydro-5-hydroxy-6-methylbenzofuran-2-carboxylate **4a** (171 mg, 41%); mp 153—154 °C (dichloromethane–petroleum ether); IR (KBr): 3420 and 1740 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ: 2.20 (s, 3H), 3.26 (dd, J=7 and 15 Hz, 1H), 3.51 (dd, J=10 and 15 Hz, 1H), 3.80 (s, 3H), 4.50 (s, 1H), 5.12 (dd, J=7 and 10 Hz, 1H), 6.60 (s, 1H), and 6.74 (s, 1H); MS, *m/e* (rel intensity), 208 (M$^+$, 65), 176 (42), 149 (100); Found: C, 63.18; H, 5.89%. Calcd for $C_{11}H_{12}O_4$: C, 63.45; H, 5.81%.

Irradiation of ***3b***: A solution of **3b** (444 mg, 2 mmol) in dry benzene (200 ml) was purged with nitrogen for 20 min and irradiated for 1 h. After evaporation of the solvent, the residue was purified by chromatography on silica gel with 10% ether–benzene to give methyl 2,3-dihydro-5-hydroxy-3,6-dimethylbenzofuran-2-carboxylate **4b** (289 mg, 65%): mp 99—101 °C (dichloromethane–petroleum ether); IR (KBr): 3440 and 1745 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ: 1,40 (d, J=7 Hz, 3H), 2.18 (s, 3H), 3.40—3.68 (m, 1H), 3.79 (s, 3H), 4.63 (d, J=7 Hz, 1H), 4.71 (bs, 1H), 6.56 (s, 1H), and 6.63 (s, 1H); MS, *m/e* (rel intensity), 222 (M$^+$, 100). 191 (17), 190 (17), 163 (68), 162 (91); Found: C, 64.85; H, 6.34%. Calcd for $C_{12}H_{14}O_4$: C, 64.85; H, 6.35%.

Irradiation of ***3c***: A solution of **3c** (222 mg, 1 mmol) in dry benzene (100 ml) was purged with nitrogen for 20 min and irradiated for 1 h. The solvent was evaporated, and the residue was chromatographed on silica gel with 10% ether–benzene to give methyl 2,3-dihydro-5-hydroxy-2,6-dimethylbenzofuran-2-carboxylate **4c** (100 mg, 45%): bp 170—180 °C at 0.01 Torr (bulb to bulb); IR (neat): 3420 and 1735 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ: 1.64 (s, 3H), 2.16 (s, 3H), 3.00 (d, J=15 Hz, 1H), 3.50 (d, J=15 Hz, 1H), 3.75 (s, 3H), and 6.56 (s, 2H); MS, *m/e*, 222 (M$^+$); Found: C, 68.69; H, 6.21%. Calcd for $C_{12}H_{14}O_4$: C, 68.85; H, 6.35%.

Irradiation of ***3d***: A solution of **3d** (473 mg, 2 mmol) in dry benzene (200 ml) was purged with nitrogen for 15 min and irradiated for 1 h. After evaporation of the solvent, the residue was chromatographed on silica gel with 10% ether–benzene to give methyl 3-ethyl-2,3-dihydro-5-hydroxy-6-methylbenzofuran-2-carboxylate **4d** (322 mg, 68%): mp 101—102 °C (dichloromethane–petroleum ether); IR (KBr): 3440 and 1740 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ: 1.00 (t, J=7 Hz, 3H), 1.40—2.00 (m, 2H), 2.19 (s, 3H), 3.42 (m, 1H), 3.76 (s, 3H), 4.51 (s, 1H), 4.74 (d, J=5 Hz, 1H), 6.58 (s, 1H), and 6.63 (s, 1H); MS, *m/e* (rel intensity), 236 (M$^+$, 100), 205 (31), 204 (55); Found: C, 66.36; H, 7.07%. Calcd for $C_{13}H_{16}O_4$: C, 66.08; H, 6.83%.

Irradiation of ***3e***: A solution of **3e** (473 mg, 2 mmol) in dry benzene (200 ml) was purged with nitrogen for 20 min and irradiated for 1 h. The solvent was removed, and the crude oil was chromatographed on silica gel with 20% ether–benzene to give methyl 4-methyl-2-(2,5-dihydroxy-4-methylphenyl)-3-butenoate **4e** (189 mg, 40%): mp 130—131 °C (dichloromethane–petroleum ether); IR (KBr): 3400, 3340, 1715, and 900 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ: 1.78 (s, 3H), 2.15 (s, 3H), 3.77 (s, 1H), 4.38 (bs, 1H), 4.84 (s, 1H), 5.02 (bs, 1H), 6.60 (s, 1H), and 6.64 (s, 1H); MS, *m/e* (rel intensity), 236 (M$^+$, 3), 204 (57), 175 (100).

Irradiation of ***3f***: A solution of **3f** (500 mg, 2 mmol) in dry benzene (200 ml) was purged with nitrogen for 10 min and irradiated for 1 h. Removal of the solvent left a dark oil which was subjected to column chromatography on silica gel with 10% ether–benzene. The only component isolated was methyl 2,3-dihydro-5-hydroxy-6-methyl-3-propylbenzofuran-2-carboxylate **4f** (300 mg, 60%): IR (neat): 3440 and 1745 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ: 0.94 (t, J=7 Hz, 3H), 1.20—1.82 (m, 4H), 2.18 (s,1H), 3.46 (m, 1H), 3.77 (s, 3H), 4.54 (bs, 1H), 4.76 (d, J=5 Hz, 1H), 6.57 (s, 1H), and 6.63 (s, 1H); Found: C, 67.14; H, 7.50%. Calcd for $C_{14}H_{18}O_4$: C, 67.18; H, 7.25%.

Irradiation of ***3g***: A solution of **3f** (532 mg, 2 mmol) in dry benzene (200 ml) was purged with nitrogen for 20 min and irradiated for 2 h. The solvent was removed, and the residue was subjected to column chromatography on silica gel with 10% ether–chloroform. The product isolated was dimethyl 2,3-dihydro-5-hydroxy-6-methylbenzofuran-2,3-dicarboxylate **4g** (299 mg, 56%): 180—181 °C (dichloromethane–petroleum ether); IR (KBr): 3340, 1735, and 1695 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ: 2.17 (s, 3H), 3.77 (s, 3H), 3.80 (s, 3H), 4.41 (d, J=6 Hz, 1H), 5.32 (bs, 1H), 5.56 (d, J=6 Hz, 1H), 6.65 (s, 1H), and 6.78 (s, 1H); MS, *m/e* (rel intensity), 266 (M$^+$, 8), 264 (100); Found: C, 58.35; H, 5.24%. Calcd for $C_{13}H_{14}O_6$: C, 58.64; H, 5.30%.

Irradiation of 3h: A solution of **3h** (589 mg, 2 mmol) in dry benzene (300 ml) was purged with nitrogen for 10 min and irradiated for 1 h. The solution was concentrated, and the crude residue was purified by column chromatography on silica gel with 10% ether-chloroform to give methyl 2,3-dihydro-5-hydroxy-3-[2-(methoxycarbonyl)ethyl]-6-methylbenzofuran-2-carboxylate **4h** (300 mg, 51%): mp 136—137 °C (dichloromethane–petroleum ether); IR (KBr): 3480, 1750, and 1730 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ: 2.02 (m, 2H), 2.20 (s, 3H), 2.46 (t, J=7 Hz, 2H), 3.44—3.69 (m, 1H), 3.69 (s, 3H), 3.78 (s, 3H), 4.77 (d, J=6 Hz, 1H), 4.88 (s, 1H), 6.60 (s, 1H), and 6.67 (s, 1H); MS, *m/e* (rel intensity), 294 (M$^+$, 26), 174 (100); Found: C, 60.93; H, 6.13%. Calcd for $C_{15}H_{18}O_6$: C, 61.21; H, 6.17%.

Irradiation of 3i: A solution of **3i** (791 mg, 2 mmol) in dry benzene (300 ml) was purged with nitrogen for 15 min and irradiated for 1 h. The solvent was removed, and the residue was chromatographed on silica gel with 10% ether–chloroform to give methyl 2,3-dihydro-5-hydroxy-6-methyl-3-[3-(phthalimido)propyl]benzofuran-2-carboxylate **4i** (593 mg, 75%): mp 180—181 °C (dichloromethane–petroleum ether); IR (KBr): 3480, 1775, 1745, and 1705 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ: 1.40—2.00 (m, 4H), 2.17 (s, 3H), 3.30—4.00 (m, 3H), 3.76 (s, 3H), 4.76 (d, J=5 Hz, 1H), 5.56 (bs, 1H), 6.63 (s, 2H), and 7.60—7.90 (m, 4H); MS, *m/e* (rel intensity), 395 (M$^+$, 61), 203 (100); Found: C, 66.50; H, 5.40; N, 3.56%. Calcd for $C_{22}H_{21}O_6N$: C, 66.82; H, 5.35; N, 3.54%.

Irradiation of 3j: A solution of **3j** (723 mg, 2 mmol) in dry benzene (300 ml) was purged with nitrogen for 10 min and irradiated for 1 h. Removal of the solvent left a crude oil which was purified by column chromatography on silica gel using 10% ether–chloroform. The only component isolated was identified as methyl 2,3-dihydro-5-hydroxy-6-methyl-3-[3-(trifluoroacetamido)propyl]benzofuran-2-carboxylate **4j** (499 mg, 69%): IR (neat): 3300 and 1740—1700 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ: 1.69 (m, 4H), 2.17 (s, 3H), 3.38 (m, 3H), 3.77 (s, 3H), 4.71 (d, J=5 Hz, 1H), 6.57 (s, 1H), 6.63 (s, 1H), and 6.95 (bs, 1H); MS, *m/e*, 361 (M$^+$); Found: C, 52.80; H, 5.16; N, 3.82%. Calcd for $C_{16}H_{18}O_5NF_3$: C, 53.18; H, 5.02; N, 3.88%.

Irradiation of 3k: A solution of **3k** (300 mg, 0.83 mmol) in dry benzene (150 ml) was purged with nitrogen for 5 min and irradiated for 1 h. The solution was concentrated. The residue was chromatographed on silica gel with 10% ether–chloroform to give methyl 2,3-dihydro-5-hydroxy-6-methyl-3-(phenoxycarbonyloxymethyl) benzofuran-2-carboxylate **4k** (117 mg, 39%): IR (neat): 3440 and 1750 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ: 2.17 (s, 3H), 3.79 (s, 3H), 3.90 (m, 1H), 4.35 (m, 2H), 5.02 (d, J=5.1 Hz, 1H), 5.55 (bs, 1H), 6.61 (s, 1H), 6.67 (s, 1H), and 7.08—7.43 (m, 5H); Found: C, 63.50; H, 5.20%. Calcd for $C_{19}H_{18}O_7$: C, 63.68; H, 5.06%.

Irradation of 3l: A solution of **3l** (416 mg, 2 mmol) in dry benzene (200 ml) was purged with nitrogen for 20 min and irradiated for 1 h. Removal of the solvent left an oil which was subjected to chromatography on silica gel with 10% ether–benzene. The product obtained was methyl 2,3-dihydro-5-hydroxy-3-methylbenzofuran-2-carboxylate **4l** (250 mg, 60%): IR (neat): 3400 and 1735 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ: 1.38 (d, J=7 Hz, 3H), 3.53 (m, 1H), 3.79 (s, 3H), 4.64 (d, J=7 Hz, 1H), and 6.60 (s, 3H and bs, 1H); Found: C, 63.19; H, 5.81%. Calcd for $C_{11}H_{12}O_4$: C, 63.45; H, 5.81%.

Irradiation of 3m: A solution of **3m** (574 mg, 2 mmol) in dry benzene (200 ml) was purged with nitrogen for 20 min and irradiated for 1 h. Evaporation of the solvent gave a dark oil. The oil was chromatographed on silica gel to give methyl 6-bromo-2,3-dihydro-5-hydroxy-3-methylbenzofuran-2-carboxylate **4m** (178 mg, 31%): IR (neat): 3420 and 1735 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ: 1.41 (d, J=7 Hz, 3H), 3.53 (m, 1H), 3.78 (s, 3H), 4.65 (d, J=7 Hz, 1H), 6.74 (s, 1H), and 6.90 (s, 1H); MS, *m/e* (rel intensity), 287 (M$^+$, 67); Found: C, 45.79; H, 3.95%. Calcd for $C_{11}H_{11}O_4Br$: C, 46.01; H, 3.86%.

Irradiation of 3n: A solution of **3n** (476 mg, 2 mmol) in dry benzene (200 ml) was purged with nitrogen for 10 min and irradiated for 1 h. Evaporation of the solvent and chromatographic separation of the crude oil by column chromatography on silica gel with 20% ether–benzene gave two compounds: The first fractions gave methyl 5-hydroxy-6-methoxy-3-methylbenzofuran-2-carboxylate (76 mg, 16%): mp 179—180 °C (dichloromethane–petroleum ether); IR (KBr): 3510 and 1720 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ: 2.51 (s, 3H), 3.94 (s, 6H), 5.58 (s, 1H), 6.98 (s, 1H), and 7.04 (s, 1H), Found: C, 60.72; H, 5.24%. Calcd for $C_{12}H_{12}O_5$: C, 61.01; H, 5.12%. The second fractions gave methyl 2,3-dihydro-5-hydroxy-6-methoxy-3-methylbenzofuran-2-carboxylate **4n** (200 mg,42%): IR (neat): 3500 and 1735 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ: 1.41 (d, J=7 Hz, 3H), 3.56 (m, 1H), 3.80 (s, 3H), 3.83 (s, 3H), 4.66 (d, J=7 Hz, 1H), 5.32 (s, 1H), 6.49 (s, 1H), and 6.68 (s, 1H); Found: C, 60.25; H, 5.87%. Calcd for $C_{12}H_{14}O_5$: C, 60.50; H, 5.92%.

Preparation of Quinones 5 by Oxidative Cleavage$^{6b)}$ *of Photoproducts 4. Methyl 2-Hydroxy-3-(4-methyl-3,6-dioxo-1,4-cyclohexadienyl)propionate 5a*: A solution of **4a** (208 mg, 1 mmol) in 70% aq cetonitrile (5 ml) was treated with ceric ammonium nitrate 1.21 g, 2.2 mmol) in water (3 ml). The mixture was stirred at 0 °C for 30 min, poured into water (100 ml), and extracted with chloroform(2 × 20 ml). The extract was washed with water, dried, and evaporated to give **5a** (174 mg, 78%): IR (neat): 3500, 1735, and 1650 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ: 2.03 (d, J=1.6 Hz, 3H), 2.69 (dd, J=8.5 and 15 Hz, 1H), 2.98 (dd, J=5 and 15 Hz, 1H), 3.81 (s, 3H), 4.18 (dd, J=5 and 8.5 Hz, 1H), 6.61 (q, J=1.6 Hz, 1H), and 6.71 (s, 1H); MS, *m/e* (rel intensity), 224 (M$^+$, 6), 206 (12), 164 (86), 136 (100); Found: C, 58.79; H, 5.50%. Calcd for $C_{11}H_{12}O_5$: C, 58.92; H, 5.40%.

Methyl 2-Hydroxy-3-(4-methyl-3,6-dioxo-1,4-cyclohexadienyl)-butyrate 5b: A solution of **4b** in aq acetonitrile was treated with CAN by the general procedure to give **5b** (80%): mp 104.5—105.5 °C (dichloromethane–petroleum ether); IR (KBr): 3480, 1725, and 1650 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ: 1.28 (d, J=7 Hz, 3H), 2.04 (d, J=1.6 Hz, 3H), 3.00 (bs, 1H), 3.46 (dq, J=7 and 4 Hz, 1H), 3.76 (s, 3H), 4.30 (bs, 1H), 6.60 (q, J=1.6 Hz, 1H), and 6.71 (s, 1H); Found: C, 60.54; H, 6.12%. Calcd for $C_{12}H_{14}O_5$: C, 60.50; H, 5.92%.

Methyl 2-Hydroxy-2-methyl-3-(4-methyl-3,6-dioxo-1,4-cyclohexadienyl)propionate 5c: A solution of **4c** in aq acetonitrile was treated with CAN by the same method to give **5c** (67%): mp 78 °C (petroleum ether); IR (KBr): 3480, 1720, and 1655 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ: 1.47 (s, 3H), 2.04 (d, J=1.6 Hz, 3H), 2.70 (d, J=13.5 Hz, 1H), 2.97 (d, J=13.5 Hz, 1H), 3.34 (s, 1H), 3.78 (s, 3H), 6.59 (q, J=1.6 Hz, 1H), and 6.70 (s, 1H); Found: C, 60.74; H. 5.98%. Calcd for $C_{12}H_{14}O_5$: C, 60.50; H, 5.92%.

Methyl 2-Hydroxy-3-(4-methyl-3,6-dioxo-1,4-cyclohexadienyl)-

pentanoate **5d**: A solution of **4d** in aq acetonitrile was treated with CAN by the usual method to give **5d** (97%): mp 97—98 °C (petroleum ether); IR (KBr): 3420, 1720, and 1650 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ: 0.94 (t, J=7.5 Hz, 3H), 1.57—1.94 (m, 2H), 2.04 (d, J=1.6 Hz, 3H), 2.98 (d, J=7.6 Hz, 1H), 3.27 (dt, J=3.5 and 7 Hz, 1H), 3.74 (s, 3H), 4.36 (dd, J=3.5 and 7.6 Hz, 1H), 6.58 (q, J=1.6 Hz, 1H), and 6.71 (s, 1H); Found: C, 61.64; H, 6.38%. Calcd for $C_{13}H_{16}O_5$: C, 61.89; H, 6.39%.

Methyl 2-Hydroxy-3-(4-methyl-3,6-dioxo-1,4-cyclohexadienyl)-hexanoates **5f**: A solution of **4f** in aq acetonitrile was treated with CAN by the usual manner to give **5f** (80%): mp 75—76 °C; IR (KBr): 3470, 1720, 1650, and 1645 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ: 0.90 (t, J=7 Hz, 3H), 1.31 (m, 2H), 1.64 (m, 2H), 2.02 (d, J=1.6 Hz, 3H), 2.87 (d, J=7 Hz, 1H), 3.31 (m, 1H), 3.92 (s, 3H), 4.31 (dd, J=3.5 and 7 Hz, 1H), 6.55 (q, J=1.6 Hz, 1H), and 6.68 (s, 1H); Found: C, 62.87; H, 6.73%. Calcd for $C_{14}H_{18}O_5$: C, 63.14; H, 6.81%.

Dimethyl 2-Hydroxy-3-(4-methyl-3,6-dioxo-1,4-cyclohexadienyl)-succinate **5g**: A solution of **4g** in aq acetonitrile was treated with CAN by the general procedure to give **5g** (50%): IR (neat): 3470, 1735, and 1650 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ: 2.03 (d, J=1.6 Hz, 3H), 3.75 (s, 6H and 1H), 4.32 (d, J=4.2 Hz, 1H), 4.86 (d, J=4.2 Hz, 1H), 6.62 (q, J=1.6 Hz, 1H), and 6.87 (s, 1H); Found: C, 55.03; H, 5.23%. Calcd for $C_{13}H_{14}O_7$: C, 55.32; H, 5.00%.

Dimethyl 2-Hydroxy-3-(4-methyl-3,6-dioxo-1,4-cyclohexadienyl)-hexanedioate **5h**: A solution of **4h** in aq acetonitrile was treated with CAN according to the general method to give **5h** (98%): IR (neat): 3460, 1730, and 1650 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ: 2.04 (d, J=1.6 Hz, 3H), 2.00—2.42 (m, 4H), 3.07 (bd, J=8 Hz, 1H), 3.38 (m, 1H), 3.68 (s, 3H), 3.37 (s, 3H), 4.35 (bs, 1H), 6.59 (q, J=1.6 Hz, 1H), and 6.74 (s, 1H); Found: C, 58.30; H, 6.01%. Calcd for $C_{15}H_{18}O_7$: C, 58.06; H, 5.85%.

Acetylation of Photoproducts **4b**, **4d**, **4f**, *and* **4i**. *Methyl 5-Acetoxy-2,3-dihydro-3,6-dimethylbenzofuran-2-carboxylate* **6b**: The compound **4b** (111 mg, 0.5 mmol) was acetylated with acetic anhydride (5 ml) in the presence of pyridine (1 ml) to give **6b** (80%): mp 86—87 °C (petroleum ether); IR (KBr): 1750 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ: 1.45 (d, J=7 Hz, 3H), 2.13 (s, 3H), 2.30 (s, 3H), 3.64 (m, 1H), 3.83 (s, 3H), 4.73 (d, J=7.2 Hz, 1H), 6.75 (s, 1H), and 6.78 (s, 1H). Found: C, 63.50; H, 6.04%. Calcd for $C_{14}H_{16}O_5$: C, 63.62; H, 6.10%.

Methyl 5-Acetoxy-3-ethyl-2,3-dihydro-6-methylbenzofuran-2-carboxylate **6d**: Acetylation of **4d** as described above gave **6d** (85%): mp 98—98.5 °C (dichloromethane–petroleum ether); IR (KBr): 1760 and 1745 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ: 1.01 (t, J=7.5 Hz, 3H), 1.78 (m, 2H), 2.13 (s, 3H), 2.31 (s, 3H), 3.50 (dt, J=5.5 and 7 Hz, 1H), 3.80 (s, 3H), 4.84 (d, J=5.5 Hz, 1H), 6.77 (s, 1H), and 6.82 (s, 1H); Found: C, 64.79; H, 6.49%. Calcd for $C_{15}H_{18}O_5$: C, 64.73; H, 6.52%.

Methyl 5-Acetoxy-2,3-dihydro-6-methyl-3-propylbenzofuran-2-carboxylate **6f**: The compound **4f** was treated with acetic anhydride–pyridine to give **6f** (82%): IR (neat): 1760 and 1735 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ: 0.96 (t, J=7 Hz, 3H), 1.06—1.84 (m, 4H), 2.08 (s, 3H), 2.21 (s, 3H), 3.46 (m, 1H), 3.72 (s, 3H), 4.67 (d, J=5 Hz, 1H), 6.59 (s, 1H), and 6.65 (s, 1H); MS, *m/e* (rel intensity), 292 (M$^+$, 4), 250 (100). Found: C, 65.59; H, 6.97%. Calcd for $C_{16}H_{20}O_5$: C, 65.74; H, 6.90%.

Methyl 5-Acetoxy-2,3-dihydro-6-methyl-3-[3-(phthalimido)-propyl]benzofuran-2-carboxylate **6i**: The title compound was prepared from **4i** by acetylation with acetic anhydride in pyridine (77%): mp 128—129 °C (methanol); IR (KBr): 1760 and 1710 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ: 1.40—2.00 (m, 4H), 2.10 (s, 3H), 2.28 (s, 3H), 3.47—4.00 (m, 3H), 3.76 (s, 3H), 4.81 (d, J=5 Hz, 1H), 6.72 (s, 1H), 6.80 (s, 1H), and 6.80 (s, 1H), and 7.60—7.90 (m, 4H); Found: C, 65.62; H, 5.24; N, 3.11%. Calcd for $C_{24}H_{23}O_7N$: C, 65.89; H, 5.30; N, 3.20%.

Methyl 2-Acetoxy-3-(2,5-diacetoxy-4-methylphenyl)hexanoate **7**: A solution of **5f** (133 mg, 0.5 mmol) in ether (50 ml) was reduced with excess aq sodium dithionite to give methyl 2-hydroxy-3-(2,5-dihydroxy-4-methylphenyl)hexanoate, which was acetylated with acetic anhydride (2 ml) in the presence of pyridine (0.1 ml) to afford **7** (118 mg, 60%): IR (neat): 1760 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ: 0.86 (t, J=7 Hz, 3H), 1.27 (m, 2H), 1.64 (m, 2H), 2.10 (s, 3H), 2.16 (s, 3H), 2.33 (s, 6H), 3.46 (m, 1H), 3.65 (s, 3H), 5.18 (d, J=5 Hz, 1H), 6.96 (s, 1H), and 7.09 (s, 1H); MS, *m/e* (rel intensity), 394 (M$^+$, 1), 352 (38), and 310 (100); Found: C, 60.66; H, 6.87%. Calcd for $C_{20}H_{26}O_8$: C, 60.90; H, 6.64%.

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