MANGANESE(III) ACETATE INITIATED OXIDATIVE FREE RADICAL REACTION BETWEEN 2-ARYLOXY-1,4-NAPHTHOQUINONES AND DIALKYL MALONATES

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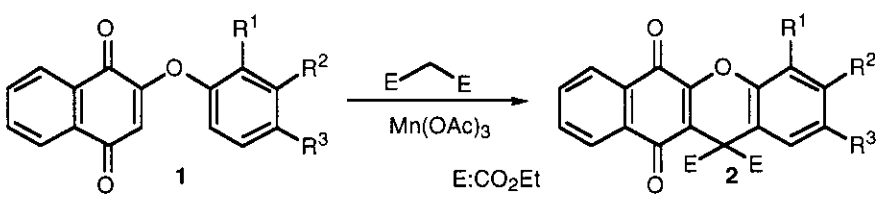
Abstract - A free radical reaction between 2-aryloxy-1,4-naphthoquinones and dialkly malonates initiated by manganese(III) acetate is described. This reaction provides a new method for the synthesis of 6,11-dihydro-6,11-dioxo-benzo[*b*]xanthenes. With *meta* substituent on aryloxy ring, this reaction shows unusual high regioselectivity.

The carbon-centered radicals initiated reaction is currently being used in organic synthesis as a valuable method for C-C bond formation.[1] Electrophilic radicals produced from the manganese(III) acetate oxidation of β-dicarbonyl compounds undergo efficient addition to a C-C double bond.[2,3] The free radical addition of a carbon center radical to quinones has been reported.[4,5,6] Benzoxanthentrione ring systems have been found in naturally occurring products (e.g. Bikaverin and Norbikaverin)[7] and synthetic approach to such systems has been reported.[8] 2-Aryloxy-1,4-naphthoquinones are readily available from 2-bromo-1,4-naphthoquinone and phenols.[9] We report here a new method for the synthesis of benzo[*b*]xanthene (**2**) from 2-aryloxy-1,4-naphthoquinones and dialkyl malonate *via* manganese(III) initiated oxidative free radical reaction.

We began our studies with the reaction shown in Scheme 1. Treatment of **1a** with diethyl malonate and manganese(III) acetate in DMSO at 80 °C for 9 h gave **2a** in 70% yield. This reaction proceeds faster, however, poorer reaction yield than that of 2-phenylthio-1,4-naphthoquinones in similar. This can be rationalized by the higher electron donating effect of phenoxy group. This makes the quinone ring more electron rich and increases the rate of addition of electron poor malonyl radical onto quinone ring. This poorer reaction yield probably due to the liability of phenoxy group in this oxidative condition. We also performed this reaction with **1a** in acetonitrile, it proceeds at a much slower reaction rate (48 h), however,



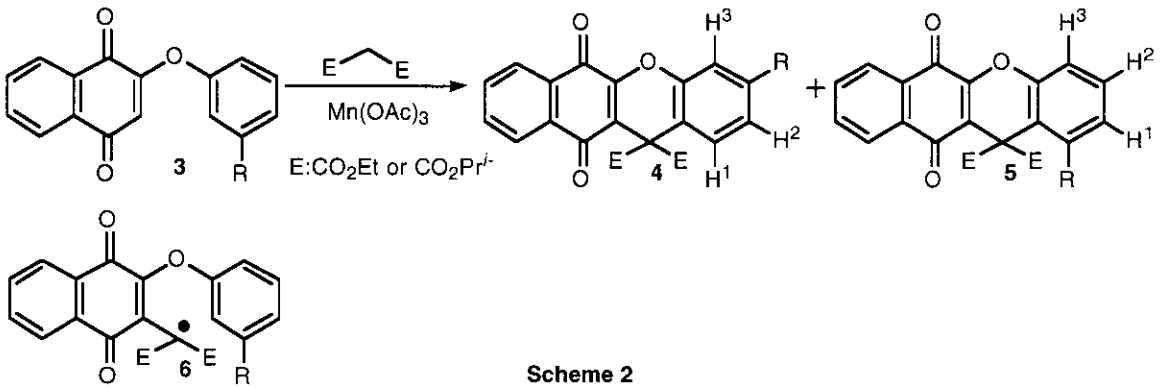
Scheme 1

Table 1: The Free Radical Reaction between 2-Aryloxy-1,4-naphthoquinones (**1**) and Diethyl Malonate

Entry		Substrate			Solvent	Product
		R^1	R^2	R^3		(Yield, %)
a	**1a**	H	H	H	DMSO acetonitrile	**2a**(70) **2a**(83)
b	**1b**	Me	Me	H	DMSO acetonitrile	**2b**(50) **2b**(73)
c	**1c**	Br	H	H	DMSO acetonitrile	**2c**(48) **2c**(73)
d	**1d**	H	H	Me	DMSO acetonitrile	**2d**(65) **2d**(55)
e	**1e**	H	H	Cl	DMSO acetonitrile	**2e**(57) **2e**(42)
f	**1f**	H	H	Br	DMSO acetonitrile	**2f**(51) **2f**(36)
g	**1g**	H	H	CN	DMSO acetonitrile	**2g**(41) **2g**(34)
h	**1h**	H	H	COMe	DMSO acetonitrile	**2h**(33) **2h**(26)
i	**1i**	H	H	CO_2Me	DMSO acetonitrile	**2i**(65) **2i**(61)

2a was obtained in better yield (83%). The generalities for this reaction by using DMSO and acetonitrile as solvents are shown in Table 1. In most cases except with *para* substituent on aryloxy ring, better results were obtained in acetonitrile. This free radical reaction presumably occurs *via* the addition of malonyl radical generated from the oxidation of malonate by manganese(III) acetate to quinone ring and aryloxy ring consecutively. With *meta* substituent on aryloxy ring, the regioselectivity of this reaction was also examined. Presumably, two possible products (**4**) and (**5**) could be obtained (Scheme 2). When **3a** was treated with diethyl malonate and manganese(III) acetate in DMSO surprisingly only **4a** was isolated in 76% yield and no trace of **5a** could be found. The structure of **4a** was determined by the ^{1}H NMR analysis. The ^{1}H NMR spectrum clearly shows three signals at δ 7.06 (br d, *J*=8.1 Hz), δ 7.20 (br s) and δ 7.54 (d, *J*=8.1 Hz) corresponding to the aromatic protons on benzopyran ring. Other examples are summarized in Table 2. Better yields were also obtained in acetonitrile. The NMR spectral data for protons on benzopyran ring are listed in Table 3. In most cases, only one product was obtained. With R=Cl, this reaction is less regioselective, and the minor isomer (**5**) was also obtained (Table 2, Entries h and i). It gives higher regioselectivity by using DMSO as solvent and/or using diisopropyl malonate. This high

regioselectivity can be ascribed to the steric effect between tertiary malonyl radical (**6**) and substituent R. Similiar results have been reported by this laboratory.[6,10]



Scheme 2

Table 2: The Regioselective Free Radical Reaction between 2-Aryloxy-1,4-naphthoquinones (**3**) and Malonates

Entry		Substrate R	Malonate E	Solvent	Product (Yield, %)	
a	**3a**	Me	CO_2Et	DMSO acetonitrile	**4a**(76) **4a**(72)	
b	**3b**	Et	CO_2Et	DMSO acetonitrile	**4b**(68) **4b**(72)	
c	**3c**	CO_2Me	CO_2Et	DMSO acetonitrile	**4c**(61) **4c**(81)	
d	**3d**	COMe	CO_2Et	DMSO acetonitrile	**4d**(30) **4d**(46)	
e	**3e**	NO_2	CO_2Et	DMSO acetonitrile	**4e**(35) **4e**(77)	
f	**3f**	Br	CO_2Et	DMSO	**4f**(60)	
g	**3f**	Br	CO_2Pr^i	DMSO	**4g**(35)	
h	**3g**	Cl	CO_2Et	DMSO acetonitrile	**4h**(45) **4h**(58)	**5a**(0.8) **5a**(14)
i	**3g**	Cl	CO_2Pr^i	DMSO acetonitrile	**4i**(38) **4i**(59)	 **5b**(11)

In conclusion, the malonyl radical produced by the manganese(III) acetate oxidation undergoes intermolecular addition followed by intramolecular cyclization effectively with 2-aryloxy-1,4-

dihydro-6,11-dioxobenzo[*b*]xanthenes. With *meta* substituent on aryloxy ring, this reaction shows unusual high regioselectivity.

Table 3: The ^{1}H NMR Spectral Data for 1,4-Naphthoquinones (**4**)

Entry	Substrate	H^1	H^2	H^3
a	**4a**	7.54(d, *J*=8.1 Hz)	7.06(br d, *J*=8.1 Hz)	7.19(br s)
b	**4b**	7.56(d, *J*=8.1 Hz)	7.08(dd, *J*=8.1,1.1 Hz)	7.22(br s)
c	**4c**	7.75(d, *J*=8.2 Hz)	7.91(dd, *J*=8.2,1.5 Hz)	8.05(d, *J*=1.5 Hz)
d	**4d**	7.74-7.87(m)	7.77(br d, *J*=8.2 Hz)	7.96(br s)
e	**4e**	7.88(d, *J*=8.7 Hz)	8.11(dd, *J*=8.7,2.3 Hz)	8.24(d, *J*=2.3 Hz)
f	**4f**	7.54(d, *J*=8.5 Hz)	7.38(dd, *J*=8.5,1.9 Hz)	7.56(d, *J*=1.9 Hz)
g	**4g**	7.52(d, *J*=8.5 Hz)	7.37(dd, *J*=8.5,1.8 Hz)	7.55(d, *J*=1.8 Hz)
h	**4h**	7.61(d, *J*=8.5 Hz)	7.23(dd, *J*=8.5,1.9 Hz)	7.40(d, *J*=1.9 Hz)
i	**4i**	7.58(d, *J*=8.4Hz)	7.22(br d, *J*=8.4 Hz)	7.39(br s)

EXPERIMENTAL

Melting points are uncorrected. NMR spectra were recorded on Bruker AC-200 or Bruker AMX-400 spectrometer. Elemental analyses were performed with a Heraeus CHN-Rapid Analyzer. All reactions were carried out under a nitrogen atmosphere. Analytical thin layer chromatography was performed by precoated silica gel 60 F-254 plates (0.25 mm thick) of EM Laboratories and visualized either by UV or by spraying with 5% phosphomolybdic acid in ethanol following by heating. The reaction mixture was purified by column chromatography over EM Laboratories silica gel (230-400 Mesh).

Typical experimental procedure: A solution of 158 mg (0.63 mmol) of **1a**, 410 mg (2.56 mmol) of diethyl malonate and 1.02 g (3.80 mmol) of manganese(III) acetate in 10 mL of DMSO was heated in an 80 °C oil bath for 9 h. The reaction mixture was diluted with 100 mL of ethyl acetate, washed with 50 mL of saturated aqueous sodium bisulfite, three 25-mL portions of water, dried (Na_2SO_4) and the extract was concentrated in vacuo. The residue was chromatographed over 20 g of silica gel (eluted with dichloromethane-hexane, 2:1) followed by recrystallization (chloroform-hexane) to give 179 mg (70%) of **2a** .

12,12-Diethoxycarbonyl-6,11-dihydro-6,11-dioxobenzo[*b*]xanthene (2a): mp 174-175 °C; IR ($CHCl_3$) 3025, 2990, 1745, 1685, 1665, 1600, 1490, 1360, 1295, 1235 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.19 (t, *J*= 7.1 Hz, 6H, CH_3), 4.11-4.27 (m, 4H, OCH_2), 7.22-7.27 (m, 1H, ArH), 7.35-7.43 (m, 2H, ArH), 7.67 (dd, *J*= 7.9, 1.1 Hz, 1H, ArH), 7.74-7.82 (m, 2H, ArH), 8.13-8.17 (m, 1H, ArH), 8.18-8.24 (m, 1H, ArH); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 13.8(q), 53.3(s), 62.6(t), 117.6(s), 117.7(d),

118.8(s), 125.6(d), 126.6(d), 126.7(d), 129.0(d), 130.1(d), 130.6(s), 131.6(s), 133.7(d), 134.6(d), 147.8(s), 150.0(s), 167.5(s), 178.1(s), 182.7(s); Anal. Calcd for $C_{23}H_{18}O_7$: C, 67.98; H, 4.46. Found: C, 67.98; H, 4.42.

12,12-Diethoxycarbonyl-6,11-dihydro-3,4-dimethyl-6,11-dioxobenzo[*b*]xanthene (2b): mp 178-179 °C; IR ($CHCl_3$) 2990, 2935, 1740, 1660, 1600, 1360, 1250, 1040 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.19 (t, *J*= 7.1 Hz, 6H, CH_3), 2.32 (s, 3H, CH_3), 2.41 (s, 3H, CH_3), 4.13-4.27 (m, 4H, OCH_2), 7.05 (d, *J*= 8.1 Hz, 1H, ArH), 7.37 (d, *J*= 8.1 Hz, 1H, ArH), 7.72-7.82 (m, 2H, ArH), 8.11-8.22 (m, 2H, ArH); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 11.9(q), 13.8(q), 19.8(q), 53.6(s), 62.5(t), 114.9(s), 118.6(s), 125.5(d), 125.8(s), 126.5(d), 126.7(d), 126.8(d), 130.8(s), 131.7(s), 133.6(d), 134.5(d), 139.2(s), 145.8(s), 150.2(s), 167.8(s), 178.3(s), 182.8(s); Anal. Calcd for $C_{25}H_{22}O_7$: C, 69.12; H, 5.10. Found: C, 69.12; H, 5.05.

4-Bromo-12,12-diethoxycarbonyl-6,11-dihydro-6,11-dioxobenzo[*b*]xanthene (2c): mp 186-187 °C; IR ($CHCl_3$) 3010, 2990, 1745, 1690, 1665, 1450, 1355, 1280, 1240 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.17 (t, *J*= 7.1 Hz, 6H, CH_3), 4.13-4.27 (m, 4H, OCH_2), 7.11 (t, *J*= 7.9 Hz, 1H, ArH), 7.60 (dd, *J*= 7.9, 1.2 Hz, 1H, ArH), 7.63 (dd, *J*= 7.9, 1.2 Hz, 1H, ArH), 7.74-7.82 (m, 2H, ArH), 8.10-8.17 (m, 1H, ArH), 8.17-8.23 (m, 1H, ArH); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 13.8(q), 53.6(s), 62.8(t), 112.0(s), 119.4(s), 126.1(d), 126.67(d), 126.74(d), 128.2(d), 130.6(s), 131.5(s), 133.9(d), 134.0(d), 134.6(d), 144.8(s), 149.7(s), 167.1(s), 177.4(s), 182.5(s); Anal. Calcd for $C_{23}H_{17}O_7Br$: C, 56.93; H, 3.53. Found: C, 56.82; H, 3.54.

12,12-Diethoxycarbonyl-6,11-dihydro-6,11-dioxo-2-methylbenzo[*b*]xanthene (2d): mp 177-178 °C; IR ($CHCl_3$) 3010, 2990, 1745, 1685, 1660, 1600, 1500, 1360, 1290, 1250 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.19 (t, *J*= 7.1 Hz, 6H, CH_3), 2.37 (s, 3H, CH_3), 4.14-4.30 (m, 4H, OCH_2), 7.20 (dd, *J*= 8.4, 1.7 Hz, 1H, ArH), 7.26 (d, *J*= 8.4 Hz, 1H, ArH), 7.48 (d, *J*= 1.7 Hz, 1H, ArH), 7.77 (td, *J*= 7.2, 1.9 Hz, 1H, ArH), 7.80 (td, *J*= 7.2, 1.9 Hz, 1H, ArH), 8.12-8.17 (m, 1H, ArH), 8.17-8.23 (m, 1H, ArH); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 13.8(q), 20.9(q), 53.2(s), 62.5(t), 117.1(s), 117.5(d), 118.7(s), 126.6(d), 126.7(d), 128.9(d), 130.7(s), 130.9(d), 131.6(s), 133.7(d), 134.6(d), 135.6(s), 145.7(s), 150.0(s), 167.5(s), 178.3(s), 182.8(s); Anal. Calcd for $C_{24}H_{20}O_7$: C, 68.57; H, 4.79. Found: C, 68.46; H, 4.84.

2-Chloro-12,12-diethoxycarbonyl-6,11-dihydro-6,11-dioxobenzo[*b*]xanthene (2e): mp 207-208 °C; IR ($CHCl_3$) 3030, 2990, 1745, 1690, 1665, 1650, 1480, 1355, 1280 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.21 (t, *J*= 7.1 Hz, 6H, CH_3), 4.16-4.31 (m, 4H, OCH_2), 7.32 (d, *J*= 8.8 Hz, 1H, ArH), 7.37 (dd, *J*= 8.8, 2.3 Hz, 1H, ArH), 7.66 (d, *J*= 2.3 Hz, 1H, ArH), 7.75-7.84 (m, 2H, ArH), 8.12-8.18 (m, 1H, ArH), 8.18-8.24 (m, 1H, ArH); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 13.8(q), 53.3(s), 62.9(t), 118.5(s), 119.1(d), 126.7(d), 126.8(d), 128.8(d), 130.4(d), 130.6(s), 130.9(s), 131.5(s), 133.9(d), 134.7(d), 146.4(s), 149.7(s), 167.0(s), 177.9(s), 182.5(s); Anal. Calcd for $C_{23}H_{17}O_7Cl$: C, 62.67; H, 3.89. Found: C, 62.45; H, 3.94.

2-Bromo-12,12-diethoxycarbonyl-6,11-dihydro-6,11-dioxobenzo[*b*]xanthene (2f): mp 189-190 °C; IR ($CHCl_3$) 3030, 2990, 1740, 1685, 1665, 1600, 1480, 1355, 1280, 1230, 1050 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.22 (t, *J*= 7.1 Hz, 6H, CH_3), 4.17-4.32 (m, 4H, OCH_2), 7.26 (d, *J*= 8.8 Hz, 1H, ArH), 7.51 (dd, *J*= 8.8, 2.3 Hz, 1H, ArH), 7.75-7.87 (m, 3H, ArH), 8.11-8.24 (m, 2H, ArH);

^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 13.7(q), 53.2(s), 62.9(t), 118.3(s), 118.6(s), 119.4(d), 126.7(d), 126.8(d), 130.5(s), 131.5(s), 131.7(d), 133.3(d), 133.9(d), 134.7(d), 146.9(s), 149.6(s), 167.0(s), 177.8(s), 182.5(s); Anal. Calcd for $C_{23}H_{17}O_7Br$: C, 56.93; H, 3.53. Found: C, 56.85; H, 3.57.

2-Cyano-12,12-diethoxycarbonyl-6,11-dihydro-6,11-dioxobenzo[*b*]xanthene (2g): mp 243-244 °C; IR ($CHCl_3$) 3025, 2990, 2230, 1740, 1690, 1665, 1600, 1490, 1350, 1250, 1040 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.24 (t, *J*= 7.1 Hz, 6H, CH_3), 4.20-4.33 (m, 4H, OCH_2), 7.48 (d, *J*= 8.6 Hz, 1H, ArH), 7.70 (dd, *J*= 8.6, 1.6 Hz, 1H, ArH), 7.78-7.88 (m, 2H, ArH), 8.00 (d, *J*= 1.6 Hz, 1H, ArH), 8.13-8.27 (m, 2H, ArH); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 13.8(q), 53.1(s), 63.2(t), 109.6(s), 117.6(s), 119.0(d), 119.3(s), 126.8(d), 126.9(d), 130.4(s), 131.4(s), 133.7(d), 133.9(d), 134.1(d), 134.9(d), 149.2(s), 150.5(s), 166.7(s), 177.4(s), 182.2(s); Anal. Calcd for $C_{24}H_{17}NO_7$: C, 66.82; H, 3.97; N, 3.25. Found: C, 66.79; H, 4.03; N, 3.11.

2-Acetyl-12,12-diethoxycarbonyl-6,11-dihydro-6,11-dioxobenzo[*b*]xanthene (2h): mp 212-213 °C; IR ($CHCl_3$) 3010, 2990, 1740, 1690, 1665, 1580, 1495, 1355, 1265, 1050, 1000 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.22 (t, *J*= 7.1 Hz, 6H, CH_3), 2.62 (s, 3H, CH_3), 4.18-4.32 (m, 4H, OCH_2), 7.45 (d, *J*= 8.7 Hz, 1H, ArH), 7.77-7.85 (m, 2H, ArH), 8.03 (dd, *J*= 8.7, 2.0 Hz, 1H, ArH), 8.14-8.20 (m, 1H, ArH), 8.20-8.25 (m, 1H, ArH), 8.28 (d, *J*= 2.0 Hz, 1H, ArH); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 13.8(q), 26.5(q), 53.3(s), 62.9(t), 118.0(s), 118.1(d), 118.9(s), 126.7(d), 126.8(d), 130.10(d), 130.12(d), 130.5(s), 131.5(s), 133.9(d), 134.5(s), 134.7(d), 149.5(s), 150.8(s), 167.1(s), 177.7(s), 182.5(s), 195.9(s); Anal. Calcd for $C_{25}H_{20}O_8$: C, 66.96; H, 4.50. Found: C, 66.95; H, 4.43.

12,12-Diethoxycarbonyl-6,11-dihydro-6,11-dioxo-2-methoxycarbonylbenzo[*b*]xanthene (2i): mp 197-198 °C; IR ($CHCl_3$) 3030, 2990, 1725, 1690, 1665, 1590, 1355, 1300, 1275, 1240 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.21 (t, *J*= 7.1 Hz, 6H, CH_3), 3.93 (s, 3H, OCH_3), 4.17-4.31 (m, 4H, OCH_2), 7.42 (d, *J*= 8.6 Hz, 1H, ArH), 7.75-7.84 (m, 2H, ArH), 8.08 (dd, *J*= 8.6, 1.9 Hz, 1H, ArH), 8.13-8.19 (m, 1H, ArH), 8.19-8.25 (m, 1H, ArH), 8.36 (d, *J*= 1.9 Hz, 1H, ArH); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 13.7(q), 52.2(q), 53.3(s), 62.8(t), 117.8(d), 117.9(s), 118.9(s), 126.6(d), 126.7(d), 127.6(s), 130.4(s), 131.1(d), 131.41(s), 131.44(d), 133.9(d), 134.7(d), 149.5(s), 150.7(s), 165.5(s), 167.1(s), 177.6(s), 182.4(s); Anal. Calcd for $C_{25}H_{20}O_9$: C, 64.65; H, 4.34. Found: C, 64.67; H, 4.29.

12,12-Diethoxycarbonyl-6,11-dihydro-6,11-dioxo-3-methylbenzo[*b*]xanthene (4a): mp 195-196 °C; IR ($CHCl_3$) 3030, 2985, 1745, 1685, 1660, 1595, 1505, 1355, 1300, 1205, 1050 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.18 (t, *J*= 7.1 Hz, 6H, CH_3), 2.38 (s, 3H, CH_3), 4.14-4.27 (m, 4H, OCH_2), 7.06 (br d, *J*= 8.1 Hz, 1H, ArH), 7.19 (br s, 1H, ArH), 7.54 (d, *J*= 8.1 Hz, 1H, ArH), 7.72-7.82 (m, 2H, ArH), 8.11-8.17 (m, 1H, ArH), 8.17-8.23 (m, 1H, ArH); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 13.8(q), 21.1(q), 53.1(s), 62.5(t), 114.6(s), 118.0(d), 118.9(s), 126.6(d), 126.7(d), 128.6(d), 130.7(s), 131.6(s), 133.7(d), 134.6(d), 140.7(s), 147.6(s), 150.1(s), 167.6(s), 178.2(s), 182.8(s); Anal. Calcd for $C_{24}H_{20}O_7$: C, 68.57; H, 4.79. Found: C, 68.35; H, 4.89.

12,12-Diethoxycarbonyl-6,11-dihydro-6,11-dioxo-3-ethylbenzo[*b*]xanthene (4b): mp 144-145 °C; IR ($CHCl_3$) 2975, 1740, 1660, 1600, 1355, 1300, 1250, 1040 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.19 (t, *J*= 7.1 Hz, 6H, CH_3), 1.26 (t, *J*= 7.6 Hz, 3H, CH_3), 2.69 (q, *J*= 7.6 Hz, 2H, CH_2), 4.13-4.28 (m, 4H, OCH_2), 7.08 (dd, *J*= 8.1, 1.1 Hz, 1H, ArH), 7.22 (br s, 1H, ArH), 7.56 (d, *J*= 8.1 Hz, 1H, ArH), 7.72-7.84 (m, 2H, ArH), 8.10-8.18 (m, 1H, ArH), 8.18-8.26 (m, 1H, ArH); ^{13}C NMR ($CDCl_3$,

50.3 MHz) δ 13.8(q), 14.8(q), 28.3(t), 53.1(s), 62.5(t), 114.7(s), 116.7(d), 118.9(s), 125.6(d), 126.6(d), 126.7(d), 128.6(d), 130.6(s), 131.6(s), 133.7(d), 134.5(d), 146.8(s), 147.7(s), 150.1(s), 167.6(s), 178.2(s), 182.8(s); Anal. Calcd for $C_{25}H_{22}O_7$: C, 69.12; H, 5.10. Found: C, 69.14; H, 5.05.

12,12-Diethoxycarbonyl-6,11-dihydro-6,11-dioxo-3-methoxycarbonylbenzo[*b*]xanthene (4c): mp 207-208 °C; IR ($CHCl_3$) 3030, 2990, 1730, 1690, 1665, 1575, 1440, 1355, 1300, 1265, 1180, 1095 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.20 (t, *J*= 7.1 Hz, 6H, CH_3), 3.95 (s, 3H, OCH_3), 4.17-4.30 (m, 4H, OCH_2), 7.75 (d, *J*= 8.2 Hz, 1H, ArH), 7.75-7.84 (m, 2H, ArH), 7.91 (dd, *J*= 8.2, 1.5 Hz, 1H, ArH), 8.05 (d, *J*= 1.5 Hz, 1H, ArH), 8.13-8.24 (m, 2H, ArH); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 13.7(q), 52.5(q), 53.5(s), 62.8(t), 118.5(s), 119.0(d), 122.1(s), 126.2(d), 126.65(d), 126.72(d), 129.3(d), 130.5(s), 131.4(s), 132.1(s), 133.9(d), 134.6(d), 147.7(s), 149.8(s), 165.4(s), 167.0(s), 177.7(s), 182.5(s); Anal. Calcd for $C_{25}H_{20}O_9$: C, 64.65; H, 4.34. Found: C, 64.67; H, 4.33.

3-Acetyl-12,12-diethoxycarbonyl-6,11-dihydro-6,11-dioxobenzo[*b*]xanthene (4d): mp 209-210 °C; IR ($CHCl_3$) 3015, 2990, 1740, 1690, 1665, 1570, 1415, 1355, 1290, 1260, 1210 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.20 (t, *J*= 7.0 Hz, 6H, CH_3), 2.63 (s, 3H, CH_3), 4.17-4.32 (m, 4H, OCH_2), 7.77 (br d, *J*= 8.2 Hz, 1H, ArH), 7.74-7.87 (m, 3H, ArH), 7.96 (br s, 1H, ArH), 8.13-8.19 (m, 1H, ArH), 8.19-8.26 (m, 1H, ArH); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 13.7(q), 26.6(q), 53.5(s), 62.8(t), 117.8(d), 118.6(s), 122.1(s), 124.7(d), 126.66(d), 126.72(d), 129.5(d), 130.5(s), 131.4(s), 133.9(d), 134.7(d), 138.6(s), 147.9(s), 149.8(s), 166.9(s), 177.7(s), 182.5(s), 196.2(s); Anal. Calcd for $C_{25}H_{20}O_8$: C, 66.96; H, 4.50. Found: C, 66.94; H, 4.51.

12,12-Diethoxycarbonyl-6,11-dihydro-6,11-dioxo-3-nitrobenzo[*b*]xanthene (4e): mp 209-210 °C; IR ($CHCl_3$) 3030, 2990, 1745, 1690, 1600, 1530, 1350, 1300, 1235, 1040 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.23 (t, *J*= 7.1 Hz, 6H, CH_3), 4.20-4.33 (m, 4H, OCH_2), 7.79-7.93 (m, 2H, ArH), 7.88 (d, *J*= 8.7 Hz, 1H, ArH), 8.11 (dd, *J*= 8.7, 2.3 Hz, 1H, ArH), 8.15-8.29 (m, 2H, ArH), 8.24 (d, *J*= 2.3 Hz, 1H, ArH); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 13.7(q), 53.6(s), 63.1(t), 113.3(d), 118.5(s), 119.8(d), 124.2(s), 126.7(d), 126.8(d), 130.4(s), 130.5(d), 131.3(s), 134.0(d), 134.8(d), 148.0(s), 148.6(s), 149.4(s), 166.4(s), 177.2(s), 182.2(s); Anal. Calcd for $C_{23}H_{17}NO_9$: C, 61.20; H, 3.80; N, 3.10. Found: C, 61.22; H, 3.87; N, 3.07.

3-Bromo-12,12-diethoxycarbonyl-6,11-dihydro-6,11-dioxobenzo[*b*]xanthene (4f): mp 195-196 °C; IR ($CHCl_3$) 3030, 2990, 1745, 1685, 1600, 1485, 1350, 1295, 1230, 1040 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.19 (t, *J*= 7.1 Hz, 6H, CH_3), 4.15-4.28 (m, 4H, OCH_2), 7.38 (dd, *J*= 8.5, 1.9 Hz, 1H, ArH), 7.54 (d, *J*= 8.5 Hz, 1H, ArH), 7.56 (d, *J*= 1.9 Hz, 1H, ArH), 7.75-7.84 (m, 2H, ArH), 8.11-8.18 (m, 1H, ArH), 8.18-8.24 (m, 1H, ArH); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 13.8(q), 53.1(s), 62.8(t), 116.8(s), 118.8(s), 120.9(d), 123.4(s), 126.7(d), 126.8(d), 128.9(d), 130.3(d), 130.6(s), 131.5(s), 133.9(d), 134.7(d), 148.2(s), 149.6(s), 167.1(s), 177.7(s), 182.6(s); Anal. Calcd for $C_{23}H_{17}O_7Br$: C, 56.93; H, 3.53. Found: C, 56.87; H, 3.62.

3-Bromo-6,11-dihydro-12,12-diisopropoxycarbonyl-6,11-dioxobenzo[*b*]xanthene (4g): mp 187-188 °C; IR ($CHCl_3$) 3030, 2990, 1735, 1665, 1600, 1480, 1355, 1230, 1100 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.17 (d, *J*= 6.2 Hz, 6H, CH_3), 1.21 (d, *J*= 6.2 Hz, 6H, CH_3), 5.07 (septet, *J*= 6.2 Hz, 2H, OCH), 7.37 (dd, *J*= 8.5, 1.8 Hz, 1H, ArH), 7.52 (d, *J*= 8.5 Hz, 1H, ArH), 7.55 (d, *J*= 1.8 Hz, 1H, ArH), 7.73-7.84 (m, 2H, ArH), 8.11-8.24 (m, 2H, ArH); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 21.3(q),

53.5(s), 70.7(t), 117.1(s), 119.1(s), 120.8(d), 123.2(s), 126.6(d), 126.7(d), 128.6(d), 130.3(d), 130.6(s), 131.6(s), 133.8(d), 134.7(d), 148.2(s), 149.6(s), 166.7(s), 177.8(s), 182.4(s); Anal. Calcd for $C_{25}H_{21}O_7Br$: C, 58.49; H, 4.12. Found: C, 58.47; H, 4.15.

3-Chloro-12,12-diethoxycarbonyl-6,11-dihydro-6,11-dioxobenzo[*b*]xanthene (4h): mp 203-204 °C; IR ($CHCl_3$) 3025, 2985, 1745, 1685, 1600, 1485, 1225, 1215, 1050, 1000 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.20 (t, J= 7.1 Hz, 6H, CH_3), 4.15-4.28 (m, 4H, OCH_2), 7.23 (dd, J= 8.5, 1.9 Hz, 1H, ArH), 7.40 (d, J= 1.9 Hz, 1H, ArH), 7.61 (d, J= 8.5 Hz, 1H, ArH), 7.76-7.84 (m, 2H, ArH), 8.11-8.18 (m, 1H, ArH), 8.18-8.24 (m, 1H, ArH); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 13.7(q), 53.1(s), 62.8(t), 116.3(s), 118.0(d), 118.9(s), 126.0(d), 126.67(d), 126.74(d), 130.1(d), 130.6(s), 131.5(s), 133.9(d), 134.7(d), 135.7(s), 148.1(s), 149.6(s), 167.1(s), 177.7(s), 182.5(s); Anal. Calcd for $C_{23}H_{17}O_7Cl$: C, 62.67; H, 3.89. Found: C, 62.39; H, 3.98.

3-Chloro-6,11-dihydro-12,12-diisopropoxycarbonyl-6,11-dioxobenzo[*b*]xanthene (4i): mp 177-178 °C; IR ($CHCl_3$) 2990, 1730, 1685, 1665, 1575, 1485, 1350, 1230, 1100 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.17 (d, *J*= 6.2 Hz, 6H, CH_3), 1.21 (d, *J*= 6.2 Hz, 6H, CH_3), 5.07 (septet, *J*= 6.2 Hz, 2H, OCH), 7.22 (br d, *J*= 8.4 Hz, 1H, ArH), 7.39 (br s, 1H, ArH), 7.58 (d, *J*= 8.4 Hz, 1H, ArH), 7.73-7.83 (m, 2H, ArH), 8.12-8.23 (m, 2H, ArH); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 21.3(q), 53.3(s), 70.6(d), 116.5(s), 117.8(d), 119.0(s), 125.7(d), 126.55(d), 126.61(d), 130.0(d), 130.5(s), 131.5(s), 133.7(d), 134.6(d), 135.4(s), 148.1(s), 149.5(s), 166.7(s), 177.7(s), 182.3(s); Anal. Calcd for $C_{25}H_{21}O_7Cl$: C, 64.04; H, 4.51. Found: C, 63.96; H, 4.54.

1-Chloro-12,12-diethoxycarbonyl-6,11-dihydro-6,11-dioxobenzo[*b*]xanthene (5a): mp 179-180 °C; IR ($CHCl_3$) 3030, 2985, 1745, 1685, 1640, 1600, 1450, 1290, 1245, 1205, 1040, 995 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.30 (t, *J*= 7.1 Hz, 6H, CH_3), 4.22-4.40 (m, 4H, OCH_2), 7.34 (s, 3H, ArH), 7.73-7.82 (m, 2H, ArH), 8.14-8.20 (m, 2H, ArH); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 13.7(q), 54.7(s), 62.9(t), 116.7(d), 118.1(s), 119.1(s), 126.4(d), 127.1(d), 128.6(d), 130.0(d), 130.2(s), 132.0(s), 133.7(d), 134.8(d), 135.5(s), 149.8(s), 149.9(s), 167.7(s), 177.6(s), 182.1(s); Anal. Calcd for $C_{23}H_{17}O_7Cl$: C, 62.67; H, 3.89. Found: C, 62.58; H, 3.93.

1-Chloro-6,11-dihydro-12,12-diisopropoxycarbonyl-6,11-dioxobenzo[*b*]xanthene (5b): mp 186-187 °C; IR ($CHCl_3$) 3020, 2985, 1730, 1685, 1640, 1595, 1450, 1290, 1245, 1210, 1105, 1000 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.24 (d, *J*= 6.2 Hz, 6H, CH_3), 1.33 (d, *J*= 6.2 Hz, 6H, CH_3), 5.13 (septet, *J*= 6.2 Hz, 2H, OCH), 7.32 (s, 3H, ArH), 7.72-7.82 (m, 2H, ArH), 8.14-8.20 (m, 2H, ArH); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 21.2(q), 21.3(q), 55.2(s), 70.9(d), 116.7(d), 118.2(s), 119.4(s), 126.4(d), 127.0(d), 128.5(d), 129.9(d), 130.2(s), 132.1(s), 133.6(d), 134.7(d), 135.5(s), 149.7(s), 149.8(s), 167.2(s), 177.8(s), 182.0(s); Anal. Calcd for $C_{25}H_{21}O_7Cl$: C, 64.04; H, 4.51. Found: C, 64.07; H, 4.51.

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