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# Manganese(III) Acetate Initiated Oxidative Free Radical Reaction Between 1,4-Naphthoquinones And α-Alkylmalonates[1]

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***Abstract***: The manganese(III) initiated oxidative free radical reaction between 1,4-naphthoquinones and α-alkylmalonates is described. Benzo[a]anthraquinones, benzo[f]indole-4,9-diones and naphtho[2,3-b] furan-4,9-diones can be prepared effectively from readily available 1,4-naphthoquinones and α-alkylmalonates. 

## INTRODUCTION

Recently, there has been a growing interest in the application of free radical cyclization reactions to the formation of ring systems.[2] Compounds containing the quinone group represent an important class of biologically active molecules that are widespread in nature.[3,4] The manganese(III) - based oxidative free radical reactions have been studied by several groups.[2d,2e,5,6] These reactions can be performed intermolecularly and intramolecularly. The free radical addition of a carbon center radical to quinones has been reported.[1,6e,6f,7] This report described our results on the reactions between 1,4-naphthoquinones and α-alkylmalonates *via* manganese(III) initiated oxidative free radical reaction.

## RESULTS AND DISCUSSION

We began our studies with the reaction shown in equation 1. Thus, treatment of 1,4-naphthoquinone and dimethyl *p*-methylbenzylmalonate **2a** (2 eq) with manganese(III) acetate (5 eq) in acetic acid at 80 °C for 8 h gave **3a** in 51% yield. The generalities of this reaction are illustrated in Table 1 (Method A). A possible mechanism for this radical annulation reaction is shown in Scheme 1. Initiation occurs with the manganese(III) acetate oxidation of **2a** followed by intermolecular addition of malonyl radical **4** to produce radical intermediate **5**, which undergoes further intramolecular cyclization and oxidation to give **3a**.

It is known that 1,4-dihydroquinones can be oxidized to 1,4-quinones by a variety of oxidants.[8] We also studied the reaction shown in equation 1 by using 1,4-dihydroxynaphthalene as starting material. When 1,4-dihydroxynaphthalene and **2a** (2 eq) was treated with manganese(III) acetate (6 eq), **3a** was obtained in 58%

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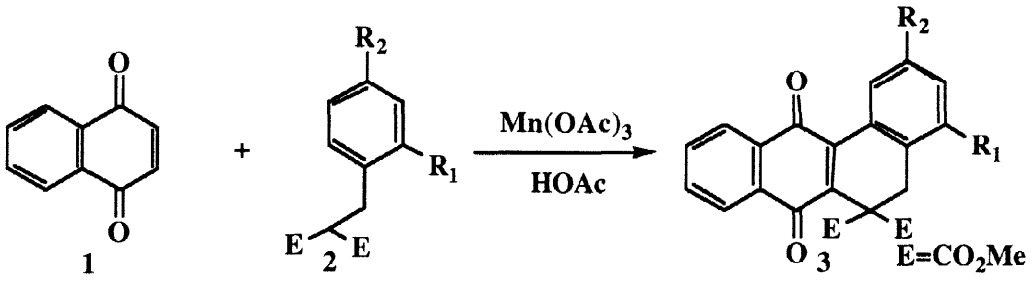


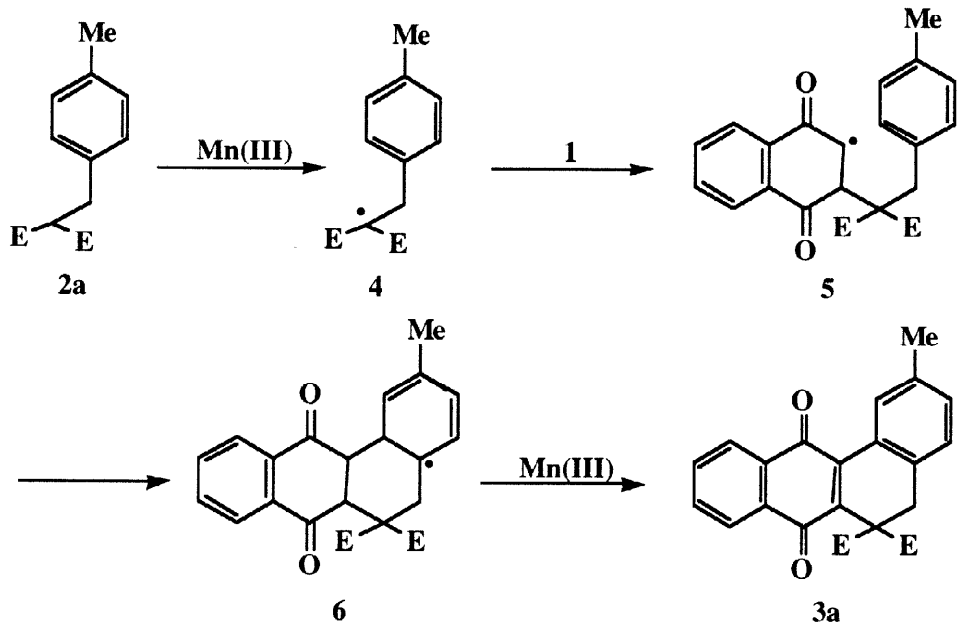

(1)

**Table 1.** The Free Radical Reaction Between 1,4-Naphthoquinone And Dimethyl α-Benzylmalonates **2**.

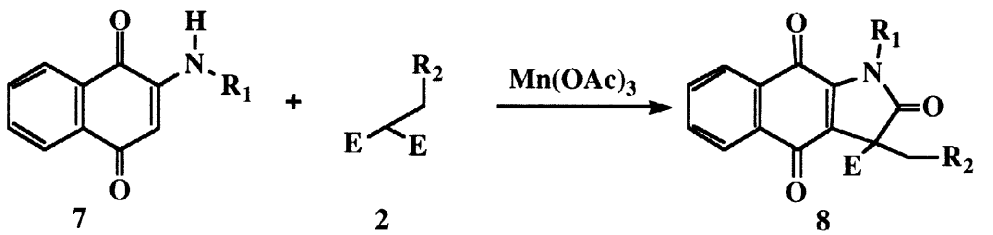
| Entry | Malonate | Method | Product | Yield |
|---|---|---|---|---|
| a | **2a:** $R_1$= H, $R_2$= $CH_3$ | A | **3a** | 51% |
| b | **2a:** $R_1$= H, $R_2$= $CH_3$ | B | **3a** | 58% |
| c | **2b:** $R_1$= H, $R_2$= H | A | **3b** | 59% |
| d | **2b:** $R_1$= H, $R_2$= H | B | **3b** | 51% |
| e | **2c:** $R_1$= H, $R_2$= $OCH_3$ | A | **3c** | 58% |
| f | **2c:** $R_1$= H, $R_2$= $OCH_3$ | B | **3c** | 54% |
| g | **2d:** $R_1$= H, $R_2$= Br | A | **3d** | 51% |
| h | **2d:** $R_1$= H, $R_2$= Br | B | **3d** | 40% |
| i | **2e:** $R_1$= $CH_3$, $R_2$= $CH_3$ | A | **3e** | 35% |
| j | **2e:** $R_1$= $CH_3$, $R_2$= $CH_3$ | B | **3e** | 32% |
| k | **2f:** $R_1$= $CH_3$, $R_2$= H | A | **3f** | 32% |

yield. Other examples are also shown in Table 1 (Method B), which are similar to those starting from 1,4-naphthoquinone.

We also studied this manganese(III) acetate initiated free radical reaction with 2-amino- and 2-hydroxynaphthoquinones. The reaction of **7a** and **2a** (2 eq) with manganese(III) acetate (5 eq) in acetic acid for 2 h gave **8a** in 19% yield (eq. 2). This is probably due to the liability of **7a** in acidic condition. We have recently shown that the use of DMSO and acetonitrile as solvents in similar reaction is advantageous for acid sensitive naphthoquinones.[6e,6f] We next performed this reaction in DMSO and acetonitrile. In DMSO, the yield of **8a** is increased significantly to 85%, however, it proceeds in a much slower reaction rate (16 h) than that performed in acetic acid. In acetonitrile, the yield of **8a** is 48% (24h). The proposed mechanism for the formation of **8a** is outlined in Scheme 2. The addition of malonyl radical **4** to quinone ring followed by oxidation gives **10**, which undergoes lactamization to produce **8a**. Examples for this reaction are shown in Table 2. The results demonstrate that the addition rate of malonyl radical **4** to amino substituted quinone ring is not only much faster than that to aromatic carbon carbon bond but also faster than that to olefinic carbon carbon bond. This can be ascribed to the electron density on quinone ring of **7** is increased by the electron donating effect of amino group, which increases the addition rate of electron deficient malonyl radical **4** to quinone ring of **7**.




Scheme 1

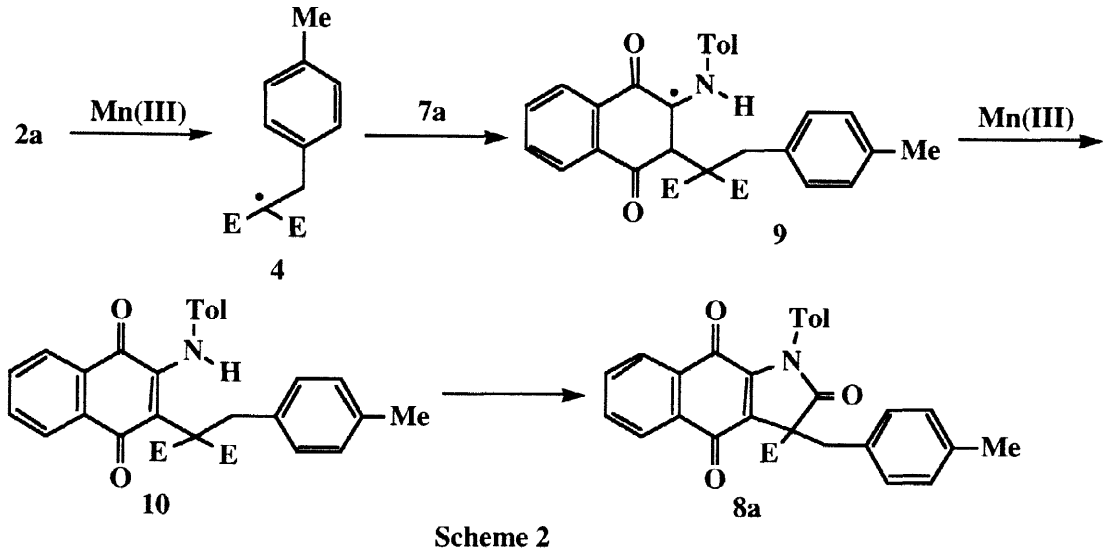



(2)

**Table 2.** The Free Radical Reaction Between 2-Amino-1,4-naphthoquinones **7** And α-Alkylmalonates **2**.

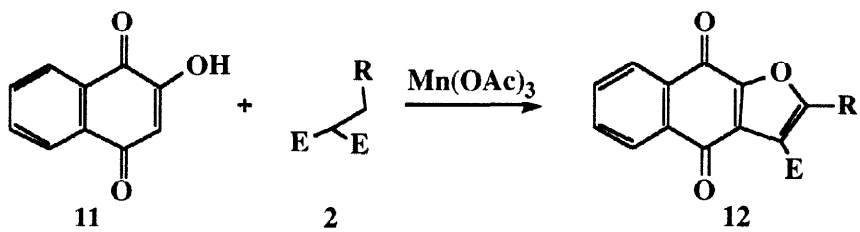
| Entry | Quinone | Malonate | Solvent | Product | Yield |
|---|---|---|---|---|---|
| a | **7a:** $R_1$= Ph | **2a:** $R_2$= *p*-Tol, E= $CO_2Me$ | HOAc | **8a** | 19% |
| b | **7a:** $R_1$= Ph | **2a:** $R_2$= *p*-Tol, E= $CO_2Me$ | $CH_3CN$ | **8a** | 48% |
| c | **7a:** $R_1$= Ph | **2a:** $R_2$= *p*-Tol, E= $CO_2Me$ | DMSO | **8a** | 85% |
| d | **7b:** $R_1$= Me | **2a:** $R_2$= *p*-Tol, E= $CO_2Me$ | DMSO | **8b** | 75% |
| e | **7b:** $R_1$= Me | **2g:** $R_2$= 3-Thienyl, E= $CO_2Me$ | DMSO | **8c** | 73% |
| f | **7b:** $R_1$= Me | **2h:** $R_2$= 2-Thienyl, E= $CO_2Me$ | DMSO | **8d** | 66% |
| g | **7b:** $R_1$= Me | **2I:** $R_2$= H, E= $CO_2Me$ | DMSO | **8e** | 76% |
| h | **7b:** $R_1$= Me | **2j:** $R_2$= $CH_2CH_2Cl$, E= $CO_2Et$ | DMSO | **8f** | 42% |
| | | | | **8g**[a] | 22% |
| i | **7b:** $R_1$= Me | **2k:** $R_2$= $CO_2Bu^n$, E= $CO_2Me$ | DMSO | **8h** | 49% |
| j | **7b:** $R_1$= Me | **2l:** $R_2$= $CH=C(Me)_2$, E= $CO_2Me$ | DMSO | **8i** | 47% |
| k | **7b:** $R_1$= Me | **2m:** $R_2$= $CH=CH_2$, E= $CO_2Me$ | DMSO | **8j** | 42% |

a. **8g:** $R_2$=$CH_2CH_2OAc$




Scheme 2

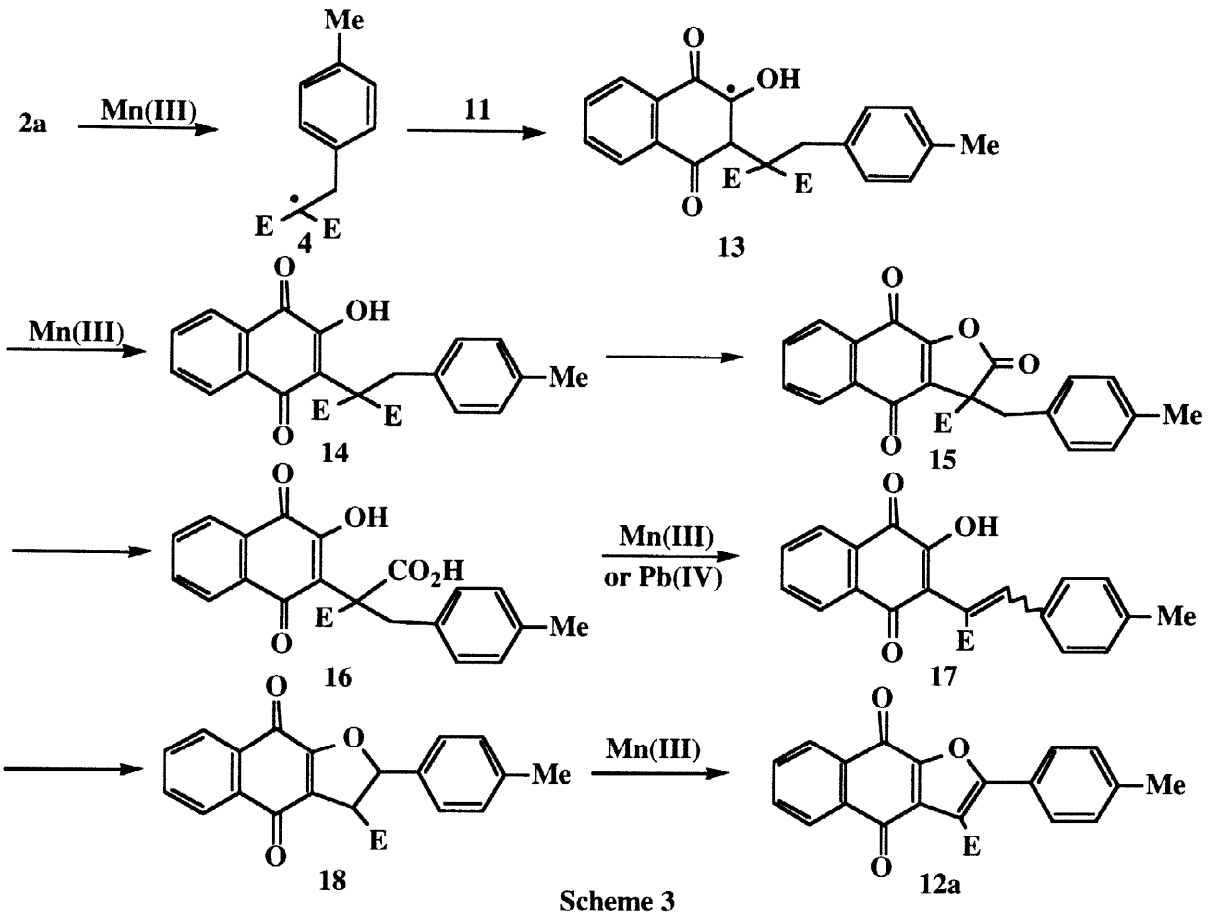
Treatment of 2-hydroxynaphthoquinone and **2a** (2 eq) with manganese(III) acetate (5 eq) in DMSO gave an unexpected product **12a** in 11% yield (eq. 3). There is no expected product **15** can be found. This free radical reaction presumably occurs *via* the mechanism shown in Scheme 3. **15** was formed analogously to **8a**. **15** undergoes further hydrolysis followed by decarboxylative elimination to give **17**, which is cyclized and then aromatized to give **12a**. It is well known that acid can undergo oxidative decarboxylation by lead tetraacetate.[9] To improve the reaction yield, we next performed this reaction by adding lead tetraacetate as cooxidant. The results are shown in Table 3. The reaction yield is improved by adding lead tetraacetate as cooxidant. With R=H, no desired product could be isolated (entry d). This can be rationalized by the lower acidity of methyl hydrogen than that of benzylic hydrogen.




(3)

**Table 3.** The Free Radical Reaction Between 2-Hydroxy-1,4-naphthoquinone And α-Alkylmalonates **2**.

| Entry | Malonate | Cooxidant | Product | Yield |
|---|---|---|---|---|
| a | **2a:** R= *p*-Tol | -- | **12a** | 11% |
| b | **2a:** R= *p*-Tol | $Pb(OAc)_4$ | **12a** | 23% |
| c | **2g:** R= 3-Thienyl | $Pb(OAc)_4$ | **12b** | 9% |
| d | **2l:** R= H | $Pb(OAc)_4$ | **12c** | 0% |




Scheme 3

In conclusion, this oxidative free radical reaction provides a novel method for the synthesis of benzo[a]anthraquinones, benzo[f]indole-4,9-diones and naphtho[2,3-b]furan-4,9-diones from readily available 1,4-naphthoquinones (or 1,4-dihydroxynaphthalene) and α–alkylmalonates.

## 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 123 mg (0.78 mmol) of naphthoquinone, 367 mg (1.56 mmol) of **2a** and 1.042 g (3.89 mmol) of manganese(III) acetate in 10 ml of acetic acid was heated in an 80°C oil bath for 8 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 concentrated in vacuo.

The residue was chromatographed over 20 g of silica gel (eluted with hexane-ethyl acetate, 7:1) followed by recrystallization (hexane-ethyl acetate) to give 156 mg (51%) of **3a**.

**2-Methyl-7,12-dioxo-7,12-dihydro-5*H*-benzo[a]anthracene-6,6-dicarboxylic acid dimethyl ester (3a)**: mp 206-207 °C; IR ($CHCl_3$) 3030, 2955, 1730, 1670, 1600, 1335, 1300, 1280, 1265, 1235 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 400 MHz) δ 2.39 (s, 3H, $CH_3$), 3.51 (s, 2H, $CH_2$), 3.74 (s, 6H, $OCH_3$), 7.20 (s, 2H, ArH), 7.73-7.81 (m, 2H, ArH), 7.84 (s, 1H, ArH), 8.10-8.15 (m, 1H, ArH), 8.15-8.21 (m, 1H, ArH); $^{13}C$ NMR ($CDCl_3$, 100.6 MHz) δ 21.4(q), 36.2(t), 53.2(q), 56.1(s), 126.57(d), 126.64(d), 127.8(s), 128.0(d), 131.0(d), 131.6(s), 131.9(d), 132.6(s), 133.8(d), 133.9(d), 137.0(s), 140.0(s), 140.6(s), 170.2(s), 182.5(s), 184.3(s); Anal. Calcd for $C_{23}H_{18}O_6$: C, 70.76; H, 4.65. Found: C, 70.69; H, 4.57.

**7,12-Dioxo-7,12-dihydro-5*H*-benzo[a]anthracene-6,6-dicarboxylic acid dimethyl ester (3b)**: mp 215-216 °C; IR ($CHCl_3$) 3025, 2955, 1740, 1670, 1600, 1335, 1305, 1280, 1230 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 400 MHz) δ 3.56 (s, 2H, $CH_2$), 3.74 (s, 6H, $OCH_3$), 7.31 (dd, J= 7.4, 1.4 Hz, 1H, ArH), 7.36 (td, J= 7.4, 1.4 Hz, 1H, ArH), 7.40 (td, J= 7.4, 1.4 Hz, 1H, ArH), 7.74 -7.82 (m, 2H, ArH), 8.04 (dd, J= 7.4, 1.4 Hz, 1H, ArH), 8.11-8.16 (m, 1H, ArH), 8.16-8.22 (m, 1H, ArH); $^{13}C$ NMR ($CDCl_3$, 100.6 MHz) δ 36.6(t), 53.3(q), 56.0(s), 126.6(d), 126.7(d), 127.4(d), 127.9(s), 128.2(d), 130.5(d), 131.1(d), 131.6(s), 132.6(s), 133.88(d), 133.90(d), 134.9(s), 140.1(s), 140.3(s), 170.2(s), 182.5(s), 184.2(s); Anal. Calcd for $C_{22}H_{16}O_6$: C, 70.21; H, 4.28. Found: C, 70.21; H, 4.27.

**2-Methoxy-7,12-dioxo-7,12-dihydro-5*H*-benzo[a]anthracene-6,6-dicarboxylic acid dimethyl ester (3c)**: mp 194-195 °C; IR ($CHCl_3$) 3010, 2955, 1740, 1665, 1600, 1350, 1295, 1280, 1240 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 400 MHz) δ 3.49 (s, 2H, $CH_2$), 3.74 (s, 6H, $OCH_3$), 3.85 (s, 3H, $OCH_3$), 6.94 (dd, J= 8.3, 2.6 Hz, 1H, ArH), 7.22 (d, J= 8.3 Hz, 1H, ArH), 7.65 (d, J= 2.6 Hz, 1H, ArH), 7.73-7.81 (m, 2H, ArH), 8.10-8.21 (m, 2H, ArH); $^{13}C$ NMR ($CDCl_3$, 100.6 MHz) δ 35.8(t), 53.2(q), 55.4(q), 56.2(s), 115.6(d), 117.1(d), 126.6(d), 126.7(d), 126.9(s), 128.7(s), 128.9(d), 131.5(s), 132.5(s), 133.86(d), 133.90(d), 140.1(s), 140.5(s), 158.6(s), 170.2(s), 182.5(s), 184.1(s); Anal. Calcd for $C_{23}H_{18}O_7$: C, 67.98; H, 4.46. Found: C, 67.94; H, 4.37.

**2-Bromo-7,12-dioxo-7,12-dihydro-5*H*-benzo[a]anthracene-6,6-dicarboxylic acid dimethyl ester (3d)**: mp 216-217 °C; IR ($CHCl_3$) 3010, 2955, 1740, 1670, 1600, 1300, 1270, 1230 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 400 MHz) δ 3.51 (s, 2H, $CH_2$), 3.76 (s, 6H, $OCH_3$), 7.20 (d, J= 8.1 Hz, 1H, ArH), 7.51 (dd, J= 8.1, 2.0 Hz, 1H, ArH), 7.75-7.83 (m, 2H, ArH), 8.10-8.16 (m, 1H, ArH), 8.16-8.22 (m, 1H, ArH), 8.25 (d, J= 2.0 Hz, 1H, ArH); $^{13}C$ NMR ($CDCl_3$, 100.6 MHz) δ 36.1(t), 53.4(q), 55.9(s), 121.2(s), 126.7(d), 126.8(d), 129.57(s), 129.60(d), 131.5(s), 132.3(s), 133.1(d), 133.7(s), 133.8(d), 134.06(d), 134.13(d), 138.8(s), 140.9(s), 169.8(s), 182.2(s), 183.6(s); Anal. Calcd for $C_{22}H_{15}BrO_6$: C, 57.99; H, 3.32. Found: C, 58.00; H, 3.25.

**2,4-Dimethyl-7,12-dioxo-7,12-dihydro-5*H*-benzo[a]anthracene-6,6-dicarboxylic acid dimethyl ester (3e)**: mp 199-200 °C; IR ($CHCl_3$) 3030, 2955, 1730, 1670, 1600, 1335, 1320, 1280, 1230

$cm^{-1}$; $^1H$ NMR ($CDCl_3$, 400 MHz) δ 2.35 (s, 3H, $CH_3$), 2.37 (s, 3H, $CH_3$), 3.48 (s, 2H, $CH_2$), 3.74 (s, 6H, $OCH_3$), 7.09 (s, 1H, ArH), 7.62 (s, 1H, ArH), 7.72-7.81 (m, 2H, ArH), 8.10-8.21 (m, 2H, ArH); $^{13}C$ NMR ($CDCl_3$, 100.6 MHz) δ 19.5(q), 21.3(q), 32.2(t), 53.3(q), 56.0(s), 126.5(d), 126.7(d), 127.8(s), 128.8(d), 130.5(s), 131.6(s), 132.7(s), 133.77(d), 133.81(d), 134.0(d), 135.4(s), 136.1(s), 139.6(s), 141.2(s), 170.4(s), 182.4(s), 184.4(s); Anal. Calcd for $C_{24}H_{20}O_6$: C, 71.28; H, 4.98. Found: C, 71.28; H, 4.91.

**4-Methyl-7,12-dioxo-7,12-dihydro-5*H*-benzo[a]anthracene-6,6-dicarboxylic acid dimethyl ester (3f)**: mp 212-213 °C; IR ($CHCl_3$) 3030, 2955, 1730, 1670, 1600, 1320, 1305, 1265 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 400 MHz) δ 2.41 (s, 3H, $CH_3$), 3.52 (s, 2H, $CH_2$), 3.74 (s, 6H, $OCH_3$), 7.24 (t, J= 7.2 Hz, 1H, ArH), 7.27 (dd, J= 7.2, 2.0 Hz, 1H, ArH), 7.73-7.81 (m, 2H, ArH), 7.82 (dd, J= 7.2, 2.0 Hz, 1H, ArH), 8.11-8.21 (m, 2H, ArH); $^{13}C$ NMR ($CDCl_3$, 100.6 MHz) δ 19.6(q), 32.5(t), 53.3(q), 55.9(s), 126.5(d), 126.6(d), 126.7(d), 127.8(s), 128.3(d), 131.6(s), 132.7(s), 133.1(d), 133.5(s), 133.79(d), 133.85(d), 135.6(s), 139.6(s), 141.0(s), 170.3(s), 182.4(s), 184.2(s); Anal. Calcd for $C_{23}H_{18}O_6$: C, 70.76; H, 4.65. Found: C, 70.75; H, 4.57.

**3-(4-Methylbenzyl)-1-*p*-tolyl-2,4,9-trioxo-2,3,4,9-tetrahydro-1*H*-benzo[f]indole-3-carboxylic acid methyl ester (8a)**: mp 162-163 °C; IR ($CHCl_3$) 3010, 2955, 1765, 1740, 1680, 1650, 1605, 1595, 1515, 1410, 1385, 1285, 1235 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 400 MHz) δ 2.25 (s, 3H, $CH_3$), 2.39 (s, 3H, $CH_3$), 3.74 and 3.82 (AB, J= 12.6 Hz, 2H, $CH_2$), 3.80 (s, 3H, $OCH_3$), 6.66 (bs, 2H, ArH), 6.92 (d, J= 8.8 Hz, 2H, ArH), 6.95 (d, J= 8.8 Hz, 2H, ArH), 7.20 (d, J= 8.4 Hz, 2H, ArH), 7.66 (td, J= 7.6, 1.2 Hz, 1H, ArH), 7.77 (td, J= 7.6, 1.2 Hz, 1H, ArH), 7.87 (dd, J= 7.6, 1.2 Hz, 1H, ArH), 8.16 (dd, J= 7.6, 1.2 Hz, 1H, ArH); $^{13}C$ NMR ($CDCl_3$, 100.6 MHz) δ 21.0(q), 21.3(q), 38.6(t), 53.6(q), 61.7(s), 126.1(s), 126.3(d), 126.5(d), 126.8(d), 128.9(d), 129.5(d), 129.7(d), 130.9(s), 131.1(s), 131.6(s), 131.8(s), 133.4(d), 134.4(d), 137.1(s), 139.0(s), 146.6(s), 166.4(s), 173.8(s), 176.4(s), 179.3(s); Anal. Calcd for $C_{29}H_{23}NO_5$: C, 74.83; H, 4.98; N, 3.01. Found: C, 74.73; H, 5.04; N, 2.90.

**1-Methyl-3-(4-methylbenzyl)-2,4,9-trioxo-2,3,4,9-tetrahydro-1*H*-benzo[f]indole-3-carboxylic acid methyl ester (8b)**: mp 130-131 °C; IR ($CHCl_3$) 3010, 2955, 1760, 1730, 1675, 1650, 1605, 1445, 1390, 1275, 1240 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 400 MHz) δ 2.18 (s, 3H, $CH_3$), 3.28 (s, 3H, $NCH_3$), 3.67 and 3.74 (AB, J= 13.3 Hz, 2H, $CH_2$), 3.75 (s, 3H, $OCH_3$), 6.83 (d, J= 8.2 Hz, 2H, ArH), 6.86 (d, J= 8.2 Hz, 2H, ArH), 7.70 (td, J= 7.6, 1.1 Hz, 1H, ArH), 7.78 (td, J= 7.6, 1.1 Hz, 1H, ArH), 8.00 (dd, J= 7.6, 1.1 Hz, 1H, ArH), 8.13 (dd, J= 7.6, 1.1 Hz, 1H, ArH); $^{13}C$ NMR ($CDCl_3$, 50.3 MHz) δ 20.8(q), 28.6(q), 38.4(t), 53.3(q), 61.5(s), 125.5(s), 126.1(d), 126.3(d), 128.7(d), 129.0(d), 130.8(s), 131.3(s), 131.8(s), 133.1(d), 134.5(d), 136.8(s), 146.7(s), 166.3(s), 174.5(s), 177.9(s), 178.8(s); Anal. Calcd for $C_{23}H_{19}NO_5$: C, 70.94; H, 4.92; N, 3.60. Found: C, 70.85; H, 4.99; N, 3.61.

**1-Methyl-3-(3-thienylmethyl)-2,4,9-trioxo-2,3,4,9-tetrahydro-1*H*-benzo[f]indole-3-carboxylic acid methyl ester (8c)**: mp 150-151 °C; IR ($CHCl_3$) 3015, 2955, 1760, 1730, 1675, 1650, 1605, 1445, 1385, 1280, 1240 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 400 MHz) δ 3.32 (s, 3H, $NCH_3$), 3.73 and 3.86 (AB, J= 14.3 Hz, 2H, $CH_2$), 3.75 (s, 3H, $OCH_3$), 6.66 (d, J= 4.8 Hz, 1H, ArH), 6.86 (d, J= 2.9 Hz, 1H, ArH), 7.04 (dd, J= 4.8, 2.9 Hz, 1H, ArH), 7.71 (t, J= 7.5 Hz, 1H, ArH), 7.79 (t, J= 7.5 Hz, 1H, ArH), 8.02 (d, J=

7.5 Hz, 1H, ArH), 8.12 (d, J= 7.5 Hz, 1H, ArH); $^{13}$C NMR ($CDCl_3$, 100.6 MHz) δ 28.8(q), 33.4(t), 53.5(q), 61.2(s), 123.3(d), 125.5(d), 125.6(s), 126.2(d), 126.5(d), 128.1(d), 131.5(s), 131.9(s), 133.3(d), 134.3(s), 134.6(d), 147.0(s), 166.2(s), 174.6(s), 177.9(s), 178.8(s); Anal. Calcd for $C_{20}H_{15}NO_5S$: C, 62.98; H, 3.96; N, 3.67. Found: C, 62.87; H, 4.04; N, 3.63.

**1-Methyl-3-(2-thienylmethyl)-2,4,9-trioxo-2,3,4,9-tetrahydro-1*H*-benzo[f]indole-3-carboxylic acid methyl ester (8d)**: mp 189-190 °C; IR ($CHCl_3$) 3015, 2955, 1760, 1730, 1675, 1650, 1605, 1445, 1390, 1280, 1265, 1240 cm$^{-1}$; $^1$H NMR ($CDCl_3$, 400 MHz) δ 3.35 (s, 3H, $NCH_3$), 3.75 (s, 3H, $OCH_3$), 3.94 and 4.04 (AB, J= 14.5 Hz, 2H, $CH_2$), 6.70 (dd, J= 3.3, 0.9 Hz, 1H, ArH), 6.75 (dd, J= 5.1, 3.3 Hz, 1H, ArH), 6.97 (dd, J= 5.1, 0.9 Hz, 1H, ArH), 7.71 (td, J= 7.5, 1.2 Hz, 1H, ArH), 7.78 (td, J= 7.5, 1.2 Hz, 1H, ArH), 8.03 (dd, J= 7.5, 1.2 Hz, 1H, ArH), 8.13 (dd, J= 7.5, 1.2 Hz, 1H, ArH); $^{13}$C NMR ($CDCl_3$, 50.3 MHz) δ 29.0(q), 33.0(t), 53.6(q), 61.4(s), 124.8(d), 125.4(s), 126.2(d), 126.5(d), 126.7(d), 127.2(d), 131.5(s), 132.0(s), 133.3(d), 134.6(d), 135.6(s), 147.4(s), 166.0(s), 174.3(s), 178.0(s), 178.8(s); Anal. Calcd for $C_{20}H_{15}NO_5S$: C, 62.98; H, 3.96; N, 3.67. Found: C, 62.97; H, 3.98; N, 3.63.

**1,3-Dimethyl-2,4,9-trioxo-2,3,4,9-tetrahydro-1*H*-benzo[f]indole-3-carboxylic acid methyl ester (8e)**: mp 125-126 °C; IR ($CHCl_3$) 3030, 2955, 1760, 1730, 1675, 1650, 1605, 1445, 1390, 1365, 1280, 1240 cm$^{-1}$; $^1$H NMR ($CDCl_3$, 400 MHz) δ 1.78 (s, 3H, $CH_3$), 3.56 (s, 3H, $NCH_3$), 3.72 (s, 3H, $OCH_3$), 7.74 (td, J= 7.4, 1.5 Hz, 1H, ArH), 7.78 (td, J= 7.4, 1.5 Hz, 1H, ArH), 8.08 (dm, J= 7.4 Hz, 1H, ArH), 8.12 (dm, J= 7.4 Hz, 1H, ArH); $^{13}$C NMR ($CDCl_3$, 50.3 MHz) δ 18.9(q), 29.1(q), 53.4(q), 55.3(s), 126.1(d), 126.5(d), 127.5(s), 131.5(s), 132.1(s), 133.2(d), 134.6(d), 146.2(s), 166.8(s), 175.5(s), 178.3(s), 178.4(s); Anal. Calcd for $C_{16}H_{13}NO_5$: C, 64.21; H, 4.38; N, 4.68. Found: C, 64.11; H, 4.40; N, 4.52.

**3-(3-Chloropropyl)-1-methyl-2,4,9-trioxo-2,3,4,9-tetrahydro-1*H*-benzo[f]indole-3-carboxylic acid ethyl ester (8f)**: mp 135-136 °C; IR ($CHCl_3$) 3030, 1755, 1730, 1675, 1650, 1600, 1445, 1390, 1275, 1240 cm$^{-1}$; $^1$H NMR ($CDCl_3$, 400 MHz) δ 1.19 (t, J= 7.1 Hz, 3H, $CH_3$), 1.51-1.66 (m, 2H, $CH_2$), 2.41-2.52 (m, 1H, CH), 2.52-2.63 (m, 1H, CH), 3.47 (t, J= 6.8 Hz, 2H, $CH_2$), 3.56 (s, 3H, $NCH_3$), 4.10-4.25 (m, 2H, $OCH_2$), 7.75 (td, J= 7.4, 1.2 Hz, 1H, ArH), 7.79 (td, J= 7.4, 1.2 Hz, 1H, ArH), 8.09 (dd, J= 7.4, 1.2 Hz, 1H, ArH), 8.13 (dd, J= 7.4, 1.2 Hz, 1H, ArH); $^{13}$C NMR ($CDCl_3$, 50.3 MHz) δ 13.8(q), 27.3(t), 29.0(q), 30.3(t), 43.9(t), 59.6(s), 62.5(t), 125.4(s), 126.1(d), 126.4(d), 131.5(s), 131.8(s), 133.3(d), 134.6(d), 147.2(s), 165.6(s), 174.4(s), 178.1(s), 178.2(s); Anal. Calcd for $C_{19}H_{18}ClNO_5$: C, 60.72; H, 4.83; N, 3.73. Found: C, 60.65; H, 4.84; N, 3.75.

**3-(3-Acetoxypropyl)-1-methyl-2,4,9-trioxo-2,3,4,9-tetrahydro-1*H*-benzo[f]indole-3-carboxylic acid ethyl ester (8g)**: mp 118-119 °C; IR ($CHCl_3$) 3030, 2985, 1755, 1730, 1675, 1650, 1600, 1445, 1390, 1370, 1275, 1240 cm$^{-1}$; $^1$H NMR ($CDCl_3$, 400 MHz) δ 1.19 (t, J= 7.1 Hz, 3H, $CH_3$), 1.34-1.50 (m, 2H, $CH_2$), 2.00 (s, 3H, $CH_3$), 2.38-2.60 (m, 2H, $CH_2$), 3.56 (s, 3H, $NCH_3$), 4.00 (t, J= 6.5 Hz, 2H, $OCH_2$), 4.12-4.25 (m, 2H, $OCH_2$), 7.72-7.82 (m, 2H, ArH), 8.08 (dm, J= 7.5 Hz, 1H, ArH), 8.13 (dm, J= 7.5 Hz, 1H, ArH); $^{13}$C NMR ($CDCl_3$, 50.3 MHz) δ 13.9(q), 20.8(q), 23.4(t), 29.1(q), 29.3(t), 60.0(s), 62.6(t), 63.5(t), 125.6(s), 126.2(d), 126.5(d), 131.6(s), 132.0(s), 133.3(d), 134.7(d), 147.3(s), 165.8(s),

170.9(s), 174.7(s), 178.26(s), 178.33(s); Anal. Calcd for $C_{21}H_{21}NO_7$: C, 63.15; H, 5.30; N, 3.51. Found: C, 62.94; H, 5.24; N, 3.56.

**3-Butoxycarbonylmethyl-1-methyl-2,4,9-trioxo-2,3,4,9-tetrahydro-1*H*-benzo[f]indole-3-carboxylic acid methyl ester (8h)**: mp 133-134 °C; IR ($CHCl_3$) 3030, 2960, 1760, 1730, 1680, 1645, 1605, 1450, 1385, 1250 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 400 MHz) δ 0.83 (t, J= 7.4 Hz, 3H, $CH_3$), 1.26 (hextet, J= 7.4 Hz, 2H, $CH_2$), 1.48 (tt, J= 7.4, 6.7 Hz, 2H, $CH_2$), 3.59 (s, 3H, $NCH_3$), 3.61 and 3.71 (AB, J= 17.7 Hz, 2H, $CH_2$), 3.71 (s, 3H, $OCH_3$), 3.90 (dt, J= 10.8, 6.7 Hz, 1H, OCH), 3.96 (dt, J= 10.8, 6.7 Hz, 1H, OCH), 7.73 (td, J= 7.4, 1.6 Hz, 1H, ArH), 7.77 (td, J= 7.4, 1.6 Hz, 1H, ArH), 8.06 (dm, J= 7.4 Hz, 1H, ArH), 8.12 (dm, J= 7.4 Hz, 1H, ArH); $^{13}C$ NMR ($CDCl_3$, 50.3 MHz) δ 13.4(q), 18.8(t), 29.2(q), 30.2(t), 37.1(t), 53.7(q), 56.6(s), 64.8(t), 124.5(s), 125.9(d), 126.5(d), 131.6(s), 132.0(s), 133.1(d), 134.4(d), 148.3(s), 165.5(s), 169.5(s), 174.3(s), 178.3(s), 178.6(s); Anal. Calcd for $C_{21}H_{21}NO_7$: C, 63.15; H, 5.30; N, 3.51. Found: C, 63.19; H, 5.34; N, 3.55.

**1-Methyl-3-(3-methyl-2-butenyl)-2,4,9-trioxo-2,3,4,9-tetrahydro-1*H*-benzo[f]indole-3-carboxylic acid methyl ester (8i)**: mp 150-151 °C; IR ($CHCl_3$) 3025, 2955, 1760, 1730, 1675, 1650, 1605, 1445, 1385, 1280, 1220 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 400 MHz) δ 1.53 (s, 3H, $CH_3$), 1.54 (s, 3H, $CH_3$), 3.13 (dd, J= 14.1, 7.7 Hz, 1H, CH), 3.20 (dd, J= 14.1, 7.7 Hz, 1H, CH), 3.52 (s, 3H, $NCH_3$), 3.71 (s, 3H, $OCH_3$), 4.72 (tm, J= 7.7 Hz, 1H, CH), 7.74 (td, J= 7.4, 1.4 Hz, 1H, ArH), 7.78 (td, J= 7.4, 1.4 Hz, 1H, ArH), 8.08 (dd, J= 7.4, 1.4 Hz, 1H, ArH), 8.12 (dd, J= 7.4, 1.4 Hz, 1H, ArH); $^{13}C$ NMR ($CDCl_3$, 50.3 MHz) δ 17.9(q), 25.7(q), 28.9(q), 31.7(t), 53.3(q), 60.0(s), 115.2(d), 125.8(s), 126.1(d), 126.4(d), 131.5(s), 132.0(s), 133.1(d), 134.5(d), 137.6(s), 147.0(s), 166.5(s), 174.6(s), 178.3(s), 178.4(s); Anal. Calcd for $C_{20}H_{19}NO_5$: C, 67.98; H, 5.42; N, 3.96. Found: C, 67.89; H, 5.42; N, 3.99.

**1-Methyl-3-(2-propenyl)-2,4,9-trioxo-2,3,4,9-tetrahydro-1*H*-benzo[f]indole-3-carboxylic acid methyl ester (8j)**: mp 166-167 °C; IR ($CHCl_3$) 3030, 2955, 1760, 1730, 1675, 1650, 1605, 1445, 1385, 1280, 1250 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 400 MHz) δ 3.12 (dd, J= 13.5, 7.3 Hz, 1H, CH), 3.25 (dd, J= 13.5, 7.7 Hz, 1H, CH), 3.53 (s, 3H, $NCH_3$), 3.72 (s, 3H, $OCH_3$), 4.97 (d, J= 10.0 Hz, 1H, =CH), 5.09 (d, J= 16.8 Hz, 1H, =CH), 5.35-5.48 (m, 1H, =CH), 7.74 (td, J= 7.4, 1.4 Hz, 1H, ArH), 7.79 (td, J= 7.4, 1.4 Hz, 1H, ArH), 8.09 (dd, J= 7.4, 1.4 Hz, 1H, ArH), 8.11 (dd, J= 7.4, 1.4 Hz, 1H, ArH); $^{13}C$ NMR ($CDCl_3$, 50.3 MHz) δ 29.0(q), 37.1(t), 53.5(q), 60.1(s), 120.6(t), 125.4(s), 126.2(d), 126.5(d), 130.2(d), 131.6(s), 132.0(s), 133.3(d), 134.6(d), 147.1(s), 166.3(s), 174.4(s), 178.3(s), 178.4(s); Anal. Calcd for $C_{18}H_{15}NO_5$: C, 66.46; H, 4.65; N, 4.31. Found: C, 66.36; H, 4.67; N, 4.32.

**2-*p*-Tolyl-4,9-dioxo-4,9-dihydro-naphtho[2,3-b]furan-3-carboxylic acid methyl ester (12a)**: mp 210-211 °C; IR ($CHCl_3$) 3030, 2955, 1730, 1675, 1595, 1550, 1500, 1445, 1370, 1330, 1230 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 400 MHz) δ 2.38 (s, 3H, $CH_3$), 4.01 (s, 3H, $OCH_3$), 7.26 (d, J= 8.2 Hz, 2H, ArH), 7.70-7.79 (m, 2H, ArH), 7.76 (d, J= 8.2 Hz, 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 21.5(q), 53.0(q), 111.9(s), 124.6(s), 126.7(d), 127.0(d), 127.3(d), 129.4(s), 129.6(d), 132.1(s), 133.1(s), 133.9(d), 141.6(s), 150.3(s), 158.5(s), 163.6(s), 173.0(s), 179.3(s); Anal. Calcd for $C_{21}H_{14}O_5$: C, 72.83; H, 4.07. Found: C, 72.73; H, 4.09.

**2-(3-Thienyl)-4,9-dioxo-4,9-dihydro-naphtho[2,3-b]furan-3-carboxylic acid methyl ester (12b)**: mp 207-208 °C; IR ($CHCl_3$) 3030, 2955, 1730, 1680, 1600, 1555, 1370, 1360, 1305, 1270, 1210, 1120 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 400 MHz) δ 4.04 (s, 3H, $OCH_3$), 7.44 (dd, J= 5.1, 3.0 Hz, 1H, ArH), 7.67 (dd, J= 5.1, 1.3 Hz, 1H, ArH), 7.74-7.87 (m, 2H, ArH), 8.15-8.26 (m, 3H, ArH); $^{13}C$ NMR ($CDCl_3$, 100.6 MHz) δ 52.9(q), 111.3(s), 126.4(d), 126.7(d), 127.2(d), 128.4(d), 128.5(s), 129.3(s), 132.1(s), 133.3(s), 133.9(d), 134.0(d), 150.2(s), 155.6(s), 163.3(s), 173.1(s), 179.2(s); Anal. Calcd for $C_{18}H_{10}O_5S$: C, 63.90; H, 2.98. Found: C, 63.78; H, 2.97.

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