Manganese(III) Acetate Initiated Oxidative Free Radical Reactions between 2-Amino-1,4-naphthoquinones and β-Dicarbonyl Compounds

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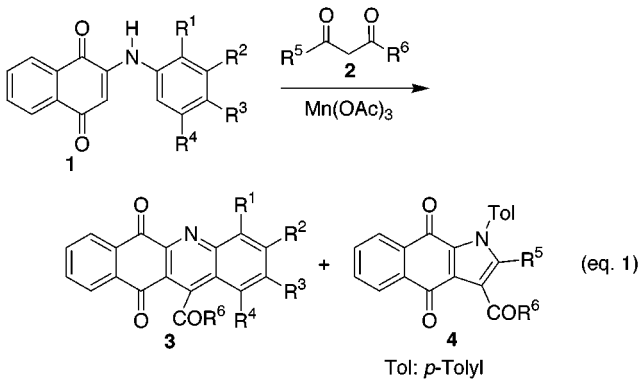
Free radical reactions have become increasingly important in organic synthesis in the last two decades.[1]Compounds containing the quinone group represent an important class of biologically active molecules that are widespread in nature.[2,3] Electrophilic radicals produced from the manganese(III) acetate oxidation of β-dicarbonyl compounds undergo efficient addition to a C−C double bond.[1d,e,4,5] These reactions can be performed intermolecularly and intramolecularly. The free radical reaction of 1,4-naphthoquinones has been reported.[5c−g,6] We found that oxidative free radical reactions of 2-amino-1,4-naphthoquinones with malonates and nitroacetate produced benzo[*b*]acridine-6,11-diones and benzo[*f*]indole-4,9-diones effectively.[5e,g] This report described our results on the reaction between 2-amino-1,4-naphthoquinones and β-dicarbonyl compounds via manganese(III) initiated oxidative free radical reactions.

We began our studies with the reaction shown in eq 1.



(eq. 1)

When 2-(*p*-toluidino)-1,4-naphthoquinone was treated with 2,4-pentanedione and manganese(III) acetate in acetic acid at room temperature, **3a** and **4a** were obtained in 77% and 18% yields, respectively (Table 1, entry a). A possible mechanism for this reaction is shown in Scheme 1. Initiation occurs with the manganese(III) acetate oxidation of 2,4-pentanedione to produce radical **5a** ($R^5 = R^6 =$ Me). This radical intermediate **5a** undergoes intermolecular addition to the quinone ring followed by oxidation to give **6**, which undergoes either condensation to produce **4a** (path a) or oxidation to generate radical **7** (path b). This radical **7** undergoes further intramolecular cyclization followed by aromatization to give **8**. 1,3-Diketone **8** undergoes retro Claisen condensation followed by oxidation to produce **3a**.[7] The results of this reaction with a variety of 1,3-diones are summarized in Table 1 (entries a−e). Acridine **3** is the major (or only) product except in entry e ($R^5 =$ Me, $R^6 =$ Ph), and the selectivity increases as the size of substituents on 1,3-diones increases. This is presumably due to the rate of condensation (path a) decreasing as the size of substituents increases. With $R^5 = R^6 =$ *t*-Bu, none of the desired product can be found (entry d). When 2-(*p*-toluidino)-1,4-naphthoquinone was treated with ethyl acetoacetate and manganese(III) acetate under similar conditions, **3f** [8] and **4f** were obtained in 45% and 7% yields, respectively (Table 1, entry f). **3f** and **4f** were formed presumably via a similar reaction route, shown in Scheme 1. On the basis of the results with 1,3-diones, we believed that the selectivity of this reaction could be increased by increasing the size of R^5. In agreement with this expectation, with ethyl butyryl acetate and ethyl benzoyl acetate, **3f** is the only product and no **4f** can be isolated. We also performed this reaction in DMSO with **1b**. In DMSO, the yield of **3g** is 53%, which is similar to that performed in acetic acid (Table 1, entry g); however, this reaction proceeds at a much slower reaction rate (80 °C, 39 h). The generalities of this reaction are also illustrated in Table 1 (entries f−l). In most cases, best results are obtained with ethyl butyryl acetate and **3** is the only product. With an electron-withdrawing group on the aniline ring, the yield is poor (entries k and l). These results can be rationalized so that the electron deficiency of radical intermediate **7** makes the rate of intramolecular cyclization to the aniline ring with an electron-withdrawing group much slower.

The oxidative free radical reaction between 2-(alkylamino)-1,4-naphthoquinone **10** and malonates has been studied in this laboratory.[5e] We have continued to study this manganese(III) acetate initiated free radical reaction with 2-(alkylamino)-1,4-naphthoquinone **10** and β-dicarbonyl compounds. When 2-(ethylamino)-1,4-naphthoquinone was treated with 2,4-pentanedione and manga-

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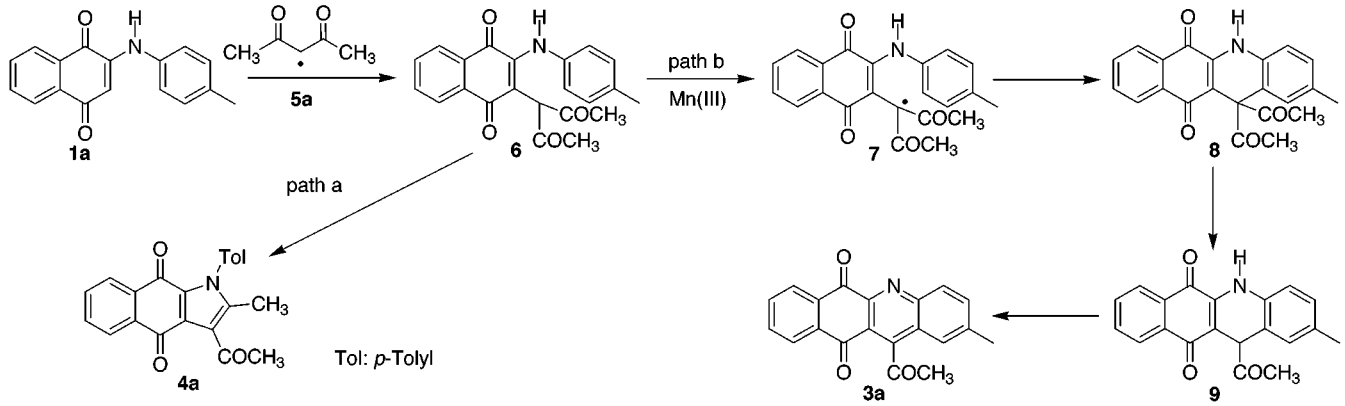
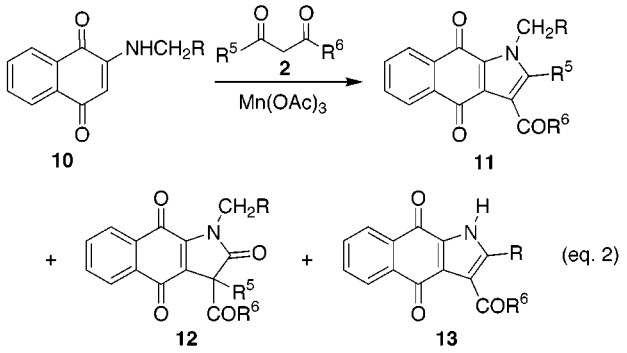
Table 1. Free Radical Reactions of 2-Anilino-1,4-naphthoquinone 1

entry	quinone	β-dicarbonyl compd	solvent	product (yield)	
a	**1a**: R^1 = H, R^2 = H, R^3 = Me, R^4 = H	**2a**: R^5 = Me, R^6 = Me	HOAc	**3a** (77%)	**4a** (18%)
b	**1a**: R^1 = H, R^2 = H, R^3 = Me, R^4 = H	**2b**: R^5 = Et, R^6 = Et	HOAc	**3b** (55%)	**4b** (11%)
c	**1a**: R^1 = H, R^2 = H, R^3 = Me, R^4 = H	**2c**: R^5 = *i*-Pr, R^6 = *i*-Pr	HOAc	**3c** (55%)	**4c** (0%)
d	**1a**: R^1 = H, R^2 = H, R^3 = Me, R^4 = H	**2d**: R^5 = *t*-Bu, R^6 = *t*-Bu	HOAc	**3d** (0%)	**4d** (0%)
e	**1a**: R^1 = H, R^2 = H, R^3 = Me, R^4 = H	**2e**: R^5 = Me, R^6 = Ph	HOAc	**3e** (0%)	**4e** (58%)
f	**1a**: R^1 = H, R^2 = H, R^3 = Me, R^4 = H	**2f**: R^5 = Me, R^6 = OEt	HOA	**3f** (45%)	**4f** (7%)
		2g: R^5 = Ph, R^6 = OEt	HOAc	**3f** (62%)	**4f** (0%)
		2h: R^5 = Pr, R^6 = OEt	HOAc	**3f** (54%)	**4f** (0%)
g	**1b**: R^1 = H, R^2 = Me, R^3 = H, R^4 = Me	**2g**: R^5 = Ph, R^6 = OEt	HOAc	**3g** (59%)	
			DMSO	**3g** (53%)	
		2h: R^5 = Pr, R^6 = OEt	HOAc	**3g** (68%)	
h	**1c**: R^1 = H, R^2 = H, R^3 = H, R^4 = H	**2g**: R^5 = Ph, R^6 = OEt	HOAc	**3h** (32%)	
		2h: R^5 = Pr, R^6 = OEt	HOAc	**3h** (49%)	
i	**1d**: R^1 = H, R^2 = H, R^3 = OMe, R^4 = H	**2g**: R^5 = Ph, R^6 = OEt	HOAc	**3i** (42%)	
		2h: R^5 = Pr, R^6 = OEt	HOAc	**3i** (63%)	
j	**1e**: R^1 = Me, R^2 = H, R^3 = OMe, R^4 = H	**2g**: R^5 = Ph, R^6 = OEt	HOAc	**3j** (28%)	
k	**1f**: R^1 = H, R^2 = H, R^3 = Cl, R^4 = H	**2g**: R^5 = Ph, R^6 = OEt	HOAc	**3k** (11%)	
		2h: R^5 = Pr, R^6 = OEt	HOAc	**3k** (35%)	
l	**1g**: R^1 = H, R^2 = H, R^3 = CO_2Et, R^4 = H	**2g**: R^5 = Ph, R^6 = OEt	HOAc	**3l** (0%)	
		2h: R^5 = Pr, R^6 = OEt	HOAc	**3l** (0%)	

Scheme 1



nese(III) acetate under similar conditions, **11a** was obtained in 65% yield (eq 2 and Table 2, entry a). It is



probable that **11a** was formed via a reaction route similar to path a shown in Scheme 1. The generalities of this reaction are shown in Table 2 (entries a−g). In most cases, the condensation reaction occurs on the less hindered carbonyl group of the 1,3-dione. This again is presumably due to the rate of condensation decreasing as the size of substituents increases.

The oxidative free radical reaction of 2-(alkylamino)-1,4-naphthoquinone **10** with ethyl acetoacetate in acetic acid gave **11** as the only product (Table 2, entries h and i). With other β-keto esters, this free radical reaction resulted in the formation of **11** and **12**[8] (Table 2, entries j−q). Treatment of 2-(*p*-methylbenzylamino)-1,4-naphthoquinone and ethyl isobutyryl acetate with manganese(III) acetate under similar conditions resulted in the formation of **12i** (44%) and **13a**[8] (23%) (Table 2, entry r). With ethyl benzoyl acetate in acetic acid, this reaction gave **13a** (30%) as the only product (Table 2, entry s). Benzo[*f*]indoles **11**−**13**[8] were formed presumably via the reaction routes shown in Scheme 2. Oxidation of the β-keto ester by manganese(III) acetate gives radical **5**. Addition of this radical intermediate to the quinone ring, followed by oxidation, gives **14**. When R^5 = Me, **14** undergoes condensation to produce **11** (path a). With larger R^5, **14** undergoes either condensation to generate **11** (path a) or oxidation to produce radical **15**. Radical **15** undergoes either cyclization (with R = H, Me, *i*-Pr) to give **16**, followed by alkyl group migration and oxidation to produce **12** (path b) or oxidation (with R = *p*-tolyl) by manganese(III) acetate to produce imine **18**. Imine **18** undergoes further intramolecular nucleophilic addition followed by retro Claisen condensation and oxidation to produce **13**. The ratios of **12**/**11** increase as the size of R (Table 2, entries l−n) or R^5 increases (Table 2, entries h, k, and p). This could account for the rate of condensation (path a) decreasing as the size of substituents on β-keto

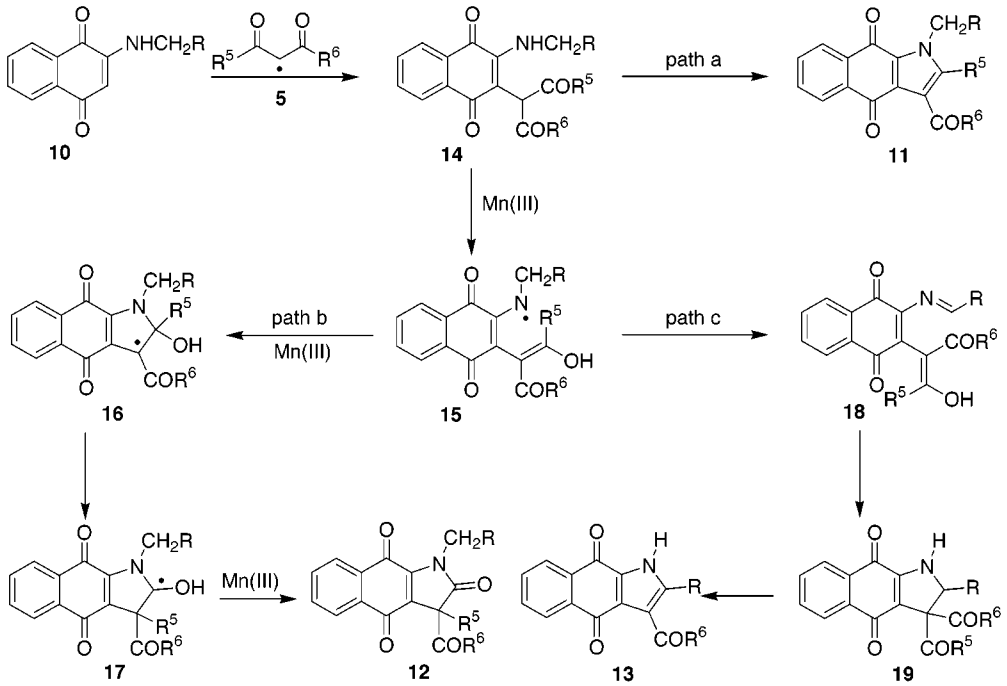
(8) Compounds **3**, **12**, and **13** have been formed from the manganese(III)-based oxidative free radical reactions of 2-amino-1,4-naphthoquinones with ethyl nitroacetate or α-alkyl malonates.[5e,g]

Table 2. Free Radical Reactions of 2-(Alkylamino)-1,4-naphthoquinone 10

entry	quinone	β-dicarbonyl compd	solvent	product (yield)	
a	**10a**: R = Me	**2a**: R^5 = Me, R^6 = Me	HOAc	**11a** (65%)	
b	**10a**: R = Me	**2b**: R^5 = Et, R^6 = Et	HOAc	**11b** (38%)	
c	**10a**: R = Me	**2d**: R^5 = *t*-Bu, R^6 = *t*-Bu	HOAc	**11c** (0%)	
d	**10a**: R = Me	**2e**: R^5 = Me, R^6 = Ph	HOAc	**11d** (87%)	
e	**10a**: R = Me	**2i**: R^5 = Me, R^6 = Bu	HOAc	**11e** (44%)[a]	
f	**10a**: R = Me	**2j**: R^5 = Me, R^6 = *i*-Bu	HOAc	**11g** (42%)	
g	**10a**: R = Me	**2k**: R^5 = Me, R^6 = *t*-Bu	HOAc	**11h** (71%)	
h	**10a**: R = Me	**2f**: R^5 = Me, R^6 = OEt	HOAc	**11i** (70%)	
i	**10b**: R = Pr	**2f**: R^5 = Me, R^6 = OEt	HOAc	**11j** (72%)	
j	**10c**: R = H	**2h**: R^5 = Pr, R^6 = OEt	HOAc	**11k** (54%)	**12a** (21%)
k	**10a**: R = Me	**2h**: R^5 = Pr, R^6 = OEt	HOAc	**11l** (35%)	**12b** (35%)
l	**10c**: R = H	**2l**: R^5 = $ClCH_2$, R^6 = OEt	HOAc	**11m** (23%)	**12c** (48%)
m	**10a**: R = Me	**2l**: R^5 = $ClCH_2$, R^6 = OEt	HOAc	**11n** (12%)	**12d** (59%)
n	**10d**: R = *i*-Pr	**2l**: R^5 = $ClCH_2$, R^6 = OEt	HOAc	**11o** (0%)	**12e** (76%)
o	**10a**: R = Me	**2m**: R^5 = CH_3OCH_2, R^6 = OMe	HOAc	**11p** (22%)	**12f** (57%)
p	**10a**: R = Me	**2n**: R^5 = *i*-Pr, R^6 = OMe	HOAc	**11q** (0%)	**12g** (75%)
q	**10a**: R = Me	**2o**: R^5 = *t*-Bu, R^6 = OEt	HOAc	**11r** (0%)	**12h** (0%)
r	**10e**: R = *p*-tolyl	**2p**: R^5 = *i*-Pr, R^6 = OEt	HOAc	**12i** (44%)	**13a** (23%)
s	**10e**: R = *p*-tolyl	**2g**: R^5 = Ph, R^6 = OEt	HOAc	**13a** (30%)	
			DMSO	**13a** (72%)	
t	**10a**: R = Me	**2g**: R^5 = Ph, R^6 = OEt	DMSO	**13b** (31%)	
u	**10f**: R = *p*-Cl-Ph	**2g**: R^5 = Ph, R^6 = OEt	DMSO	**13c** (79%)	
v	**10g**: R = 2-thienyl	**2g**: R^5 = Ph, R^6 = OEt	DMSO	**13d** (42%)	
w	**10h**: R = CO_2Me	**2g**: R^5 = Ph, R^6 = OEt	DMSO	**13e** (34%)	
x	**10b**: R = Pr	**2g**: R^5 = Ph, R^6 = OEt	DMSO	**13f** (27%)	
y	**10i**: R = *i*-Pr	**2g**: R^5 = Ph, R^6 = OEt	DMSO	**13g** (50%)	

[a] Another 5% of isomeric product **11f** was also obtained (R^5 = Bu, R^6 = Me).

Scheme 2



esters or amino groups increases and the oxidation of **14** to produce radical **15** occurred. The different reaction behavior of **15** can be ascribed to the liability of the benzylic group of **15a** (R = *p*-tolyl). The low yield of **13a** is probably due to the acidic liability of imine **18**. In DMSO, the reaction yield can be improved to 72% (Table 2, entry s). On the basis of the results shown above, we expected that the radical reaction of 2-(alkylamino)-1,4-naphthoquinone **10** and ethyl benzoyl acetate with manganese(III) acetate in DMSO would give **13** as the major (only) product. Indeed, when **10a** and ethyl benzoyl acetate were treated with manganese(III) acetate in DMSO, **13b** (31%) was obtained as the only product (Table 2, entry t). The scope of this reaction is illustrated in Table 2 (entries s−y). In all cases, **13** is the only product.

In conclusion, radical **5** can be generated from the oxidation of β-dicarbonyl compounds with manganese(III) acetate, and it undergoes efficient addition to the C−C double bond of 1,4-naphthoquinone derivatives. This free radical reaction provides a novel method for the synthesis of benzo[*b*]acridine-6,11-diones and benzo[*f*]-

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indole-4,9-diones from readily available 2-amino-1,4-naphthoquinones and β-dicarbonyl compounds.

Experimental Section

General Considerations. Melting points are uncorrected. The ^{1}H NMR and ^{13}C NMR spectra were recorded at 400 and 100 MHz in $CDCl_3$ and DMSO-d_6, respectively. Chemical shifts are reported in ppm relative to TMS as internal reference. Analytical thin-layer chromatography was performed with precoated silica gel 60 F-254 plates (0.25 mm thick) from EM Laboratories and visualized either by UV or by spraying with 5% phosphomolybdic acid in ethanol followed by heating. The reaction mixture was purified by column chromatography over EM Laboratories silica gel (70−230 mesh). The starting 1,4-naphthoquinones **1** and **10** were synthesized by literature procedures.[9] The spectral data of **3f**,**h**,**i**,**k** and **13a**,**b**,**f**,**g** have been reported.[5g]

Typical Experimental Procedure for the Reaction of 2-Amino-1,4-naphthoquinones. Method A. A solution of 151 mg (0.57 mmol) of 2-(*p*-toluidino)-1,4-naphthoquinone, 237 mg (2.37 mmol) of 2,4-pentanedione, and 768 mg (2.86 mmol) of manganese(III) acetate in 10 mL of acetic acid was stirred at room temperature for 24 h (the dark brown color of manganese(III) acetate disappeared), followed by the addition of 231 mg (2.31 mmol) of 2,4-pentanedione and 779 mg (2.91 mmol) of manganese(III) acetate. The reaction mixture was stirred for another 15 h and then diluted with 100 mL of ethyl acetate, washed with 50 mL of saturated aqueous sodium bisulfite, three 50 mL portions of water, and three 50 mL portions of aqueous saturated sodium bicarbonate, dried (Na_2SO_4), and concentrated in vacuo. The residue was chromatographed over 20 g of silica gel (eluted with 2:1 dichloromethane−hexane and then 50:1 dichloromethane−ethyl acetate) followed by recrystallization (hexanes−ethyl acetate) to give 35 mg (18%) of **4a** followed by 140 mg (77%) of **3a**.

Method B. A solution of 151 mg (0.57 mmol) of 2-(*p*-toluidino)-1,4-naphthoquinone, 369 mg (2.34 mmol) of ethyl butyryl acetate, and 768 mg (2.86 mmol) of manganese(III) acetate in 10 mL of acetic acid was stirred at room temperature for 24 h. After workup as described above, the residue was chromatographed over 20 g of silica gel (eluted with 70:1 dichloromethane−ethyl acetate) followed by recrystallization (hexanes−ethyl acetate) to give 107 mg (54%) of **3f**.

12-Acetyl-6,11-dihydro-6,11-dioxo-2-methylbenzo[*b*]acridine (3a) (Method A): yellow crystals; mp 290−291 °C; IR ($CHCl_3$) 3005, 1690 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.60 (s, 3H), 2.78 (s, 3H), 7.61 (s, 1H), 7.81 (dd, J = 8.7, 1.6 Hz, 1H), 7.84−7.93 (m, 2H), 8.28−8.36 (m, 1H), 8.40 (d, J = 8.7 Hz, 1H), 8.42−8.50 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 22.1, 31.6, 122.4, 124.4, 124.6, 127.6, 128.2, 131.7, 133.1, 133.9, 134.8, 135.0, 135.9, 141.6, 146.8, 148.8, 150.3, 181.0, 182.7, 203.3. Anal. Calcd for $C_{20}H_{13}NO_3$: N, 4.44; C, 76.18; H, 4.16. Found: N, 4.45; C, 76.11; H, 4.10.

3-Acetyl-4,9-dihydro-4,9-dioxo-2-methyl-1-(*p*-tolyl)-1*H*-benzo[*f*]indole (4a) (Method A): orange needles; mp 219−220 °C; IR ($CHCl_3$) 3010, 1665, 1595 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.19 (s, 3H), 2.49 (s, 3H), 2.79 (s, 3H), 7.15 (d, J = 7.9 Hz, 2H), 7.37 (d, J = 7.9 Hz, 2H), 7.64 (t, J = 7.5 Hz, 1H), 7.69 (t, J = 7.5 Hz, 1H), 8.00 (d, J = 7.5 Hz, 1H), 8.17 (d, J = 7.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 11.7, 21.3, 31.7, 122.5, 125.0, 126.2, 126.7, 130.2, 131.0, 133.0, 133.2, 133.3, 133.5, 134.2, 139.6, 142.8, 174.9, 180.9, 199.0. Anal. Calcd for $C_{22}H_{17}NO_3$: N, 4.08; C, 76.95; H, 4.99. Found: N, 4.09; C, 76.99; H, 4.97.

3-Acetyl-4,9-dihydro-4,9-dioxo-1-ethyl-2-methyl-1*H*-benzo[*f*]indole (11a) (Method B): yellow needles; 203−204 °C; IR ($CHCl_3$) 3005, 1660, 1595 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.42 (t, J = 7.1 Hz, 3H), 2.44 (s, 3H), 2.72 (s, 3H), 4.54 (q, J = 7.1 Hz, 2H), 7.67−7.73 (m, 2H), 8.10−8.19 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 10.5, 15.3, 31.6, 40.9, 122.9, 125.2, 126.2, 126.6, 129.4, 133.2, 133.3, 133.5, 140.9, 176.0, 180.7, 199.3. Anal. Calcd for $C_{17}H_{15}NO_3$: N, 4.98; C, 72.58; H, 5.37. Found: N, 4.83; C, 72.47; H, 5.40.

3-(Ethoxycarbonyl)-1-methyl-3-propyl-2,3,4,9-tetrahydro-2,4,9-trioxo-1*H*-benzo[*f*]indole (12a) (Method B): yellow powder; mp 102−103 °C; IR ($CHCl_3$) 2970, 1755, 1730, 1675, 1645 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.88 (t, J = 7.2 Hz, 3H), 0.98−1.13 (m, 2H), 1.19 (t, J = 7.1 Hz, 3H), 2.30−2.56 (m, 2H), 3.55 (s, 3H), 4.11−4.27 (m, 2H), 7.71−7.84 (m, 2H), 8.09 (dd, J = 7.4, 1.1 Hz, 1H), 8.12 (dd, J = 7.4, 1.1 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 13.9, 17.6, 29.0, 34.9, 60.7, 62.5, 126.3, 126.5, 131.7, 132.1, 133.2, 134.6, 147.1, 166.1, 175.1, 178.4. Anal. Calcd for $C_{19}H_{19}NO_5$: N, 4.30; C, 70.14; H, 5.89. Found: N, 4.32; C, 70.15; H, 5.91.

2-(*p*-Chlorophenyl)-4,9-dihydro-4,9-dioxo-3-(ethoxycarbonyl)-1*H*-benzo[*f*]indole (13c) (Method A in DMSO at 80 °C): yellow crystals; mp 248−249 °C; IR ($CHCl_3$) 3420, 3020, 1720, 1660, 1595 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.35 (t, J = 7.1 Hz, 3H), 4.41 (q, J = 7.1 Hz, 2H), 7.44 (d, J = 8.5 Hz, 2H), 7.62 (d, J = 8.5 Hz, 2H), 7.69 (td, J = 7.5, 1.1 Hz, 1H), 7.74 (td, J = 7.5, 1.1 Hz, 1H), 7.98 (dd, J = 7.5, 1.1 Hz, 1H), 8.19 (dd, J = 7.5, 1.1 Hz, 1H), 10.92 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 14.0, 61.8, 114.8, 126.3, 127.4, 128.0, 129.1, 129.5, 132.1, 132.5, 133.2, 134.1, 134.3, 136.0, 139.0, 164.5, 176.2, 179.2. Anal. Calcd for $C_{21}H_{14}ClNO_4$: N, 3.69; C, 66.41; H, 3.72. Found: N, 3.60; C, 66.20; H, 3.78.

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Supporting Information Available: Text giving characterization data for compounds **3b**,**c**,**g**,**j**, **4b**,**e**,**f**, **11b**−**p**, **12b**−**i**, and **13d**,**e**. This material is available free of charge via the Internet at http://pubs.acs.org.

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