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Oxidative free radical reactions between 2-amino-1,4-naphthoquinones and carbonyl compounds

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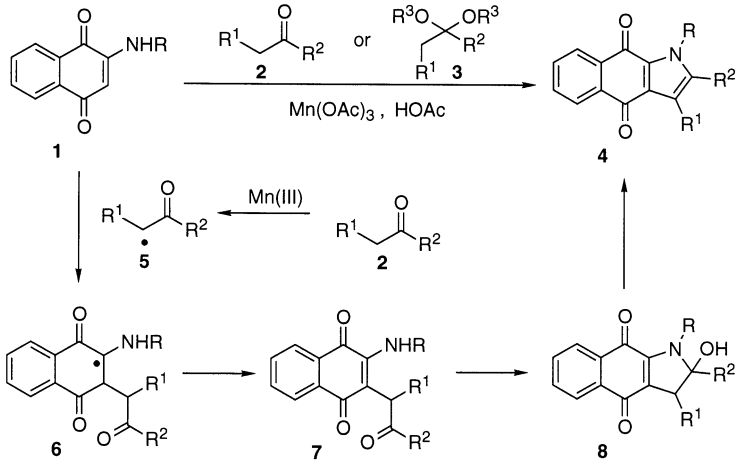
Abstract—The manganese(III) initiated oxidative free radical reaction provides a novel method for the synthesis of benzo[*f*]indole-4,9-diones from 2-amino-1,4-naphthoquinones and carbonyl compounds. The regioselectivity of this reaction was also studied with unsymmetrical ketones from which both isomeric indoles **10** and **11** were formed. With α-halo, α-phenoxy and α-methanesulfonyl ketones, in most cases, this reaction gave high regioselectivity. With 2-alkyl substituted-1,3-dione **14**, indole **11** was obtained as the only product.

1. Introduction

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–f,4,5] These reactions can be performed intermolecularly and intramolecularly. The free radical reaction of 1,4-naphthoquinones has been reported.[5c–f,6] We found that oxidative free radical reactions of 2-amino-1,4-naphthoquinones with malonates, nitroacetate and β-dicarbonyl compounds produced benzo[*b*]acridine-6,11-diones and benzo[*f*]indole-4,9-diones effectively.[5e–f] This report described our result on the reaction between 2-amino-1,4-naphthoquinones and carbonyl compounds via manganese(III) initiated oxidative free radical reactions.

2. Results and discussion

We began our studies with the reaction shown in Scheme 1. When 2-ethylamino-1,4-naphthoquinone was treated with acetone and manganese(III) acetate in acetic acid at 45°C,



Scheme 1.

Keywords: manganese(III) acetate; oxidative; free radical; 2-amino-1,4-naphthoquinone; carbonyl compounds.
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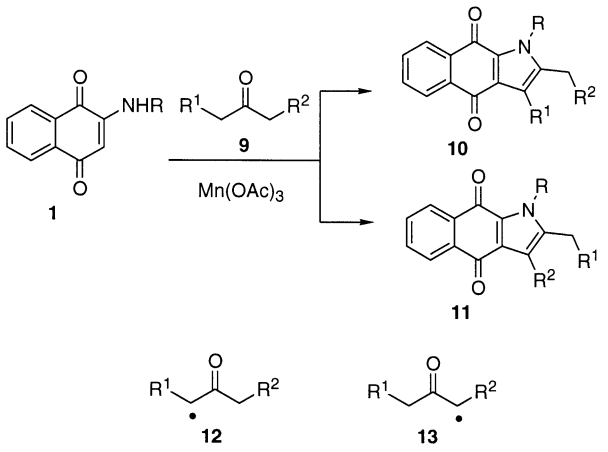
Table 1. The free radical reactions of 2-amino-1,4-naphthoquinone **1**

Entry	Quinone	Carbonyl compound	Product (yield)
a	**1a**: R=Et	**2a**: R^1=H, R^2=Me	**4a** (73%)
b	**1b**: R=Me	**2b**: R^1=Me, R^2=Et	**4b** (45%)
c	**1b**: R=Me	**2c**: R^1, R^2=$CH_2CH_2CH_2$	**4c** (61%)
d	**1b**: R=Me	**2d**: R^1, R^2=$CH_2CH_2CH_2CH_2$	**4d** (73%)
e	**1b**: R=Me	**2e**: R^1=H, R^2=Ph	**4e** (53%)
f	**1b**: R=Me	**2f**: R^1=Me, R^2=Ph	**4f** (22%)
g	**1b**: R=Me	**2g**: R^1=Me, R^2=H	**4g** (86%)
h	**1b**: R=Me	**2h**: R^1=Ph, R^2=H	**4h** (41%)
i	**1b**: R=Me	**2h**: R^1=Ph, R^2=H	**4h** (50%)[a]
j	**1b**: R=Me	**2i**: R^1=H, R^2=H	**4i** (85%)[b]
k	**1b**: R=Me	**2j**: R^1=H, R^2=CO_2Et	**4j** (56%)

[a] This reaction was performed with corresponding dimethyl acetal.
[b] This reaction was performed with corresponding diethyl acetal.

4a was obtained in 73% yield (Table 1, entry a). A possible mechanism for this reaction is shown in Scheme 1. Initiation occurs with the manganese(III) acetate oxidation of acetone to produce radical **5a** (R^1=H, R^2=Me). This radical intermediate **5a** undergoes intermolecular addition to the quinone ring followed by oxidation to give **7a**, which undergoes condensation to produce **4a**. The generalities of this reaction are shown in Table 1. Indole **4** can be synthesized effectively from simple ketones and aldehydes. Since dialkyl acetals could be hydrolyzed in aqueous acetic acid, we also performed this reaction with acetals and indole **4** was produced effectively (entries i, j). We also studied the regioselectivity of this reaction (Eq. (1)). With butanone (R^1=H, R^2=Me), **10a** and **11a** were obtained in 32 and 41% yields, respectively (Table 2, entry a). These two products are derived from the intermolecular addition of radical **12a** and **13a** (R^1=H, R^2=Me). The regioselectivity increases as the size of R^2 increases (entry b). Due to the strong radical stabilizing effect of carbonyl groups, the oxidative free radical reaction between 2-amino-1,4-naphthoquinone and β-dicarbonyl compounds occurs via the intermolecular addition of radical **13** (R^2=RC═O).[5f] It is known that halogeno, phenoxy and methanesulfonyl groups have small radical stabilizing effect.[7] We next studied the regioselectivity of this reaction with α-halo, α-phenoxy, α-methanesulfonyl ketones. With α-halo ketones, indole **11** was generated as the major product (entries c, d) via the intermolecular addition of radical **13** (R^2=Cl, Br). This can be ascribed to the radical stabilizing effect of small halogeno groups. With α-phenoxy and α-methanesulfonyl ketones, indole **10** was produced as the major product (entries e–h) via the intermolecular addition of radical **12** (R^2=PhO, Ms). This is presumably due to the steric effect of large phenoxy and methanesulfonyl groups and the regioselectivity decreases as the size of R^1 increases (entries g).



(1)

Benzo[*f*]indole-4,9-diones can be formed from the reaction of 2-amino-1,4-naphthoquinone and 1,3-diones.[5f] We continue this radical reaction with 2-alkyl substituted-1,3-diones **14**. Treatment of 2-methylamino-1,4-naphthoquinone and 1,3-dione **14a** with manganese(III) acetate at room temperature gave **11a** as the only product in 78% yield (Table 3, entry a). On the contrary, with butanone, **10a** and **11a** were obtained (Table 2, entry a). The generalities of this reaction are shown in Table 3. In all cases, indole **11** was obtained as the only product. 1,3-Dione **14** can be used as the synthetic equivalent of radical intermediate **13**. Indole **11a** was formed presumably via the reaction route outlined in Scheme 2. Oxidation of dione **14a** by manganese(III) acetate produces radical **15a**. This radical intermediate **15a** undergoes intermolecular addition to the quinone ring followed by oxidation to give **16a**. Quinone **16a** undergoes either addition reaction to give **17a**, followed by deacetylation and dehydration to produce **11a** (path a) or deacetylation followed by condensation to produce **11a** (path b).[8] Based on the production of **11k** (not **4c**), path a is the most likely reaction route for the formation of **11** (Table 3, entry f).

Table 2. The regioselectivity of the free radical reactions of 2-amino-1,4-naphthoquinone **1**

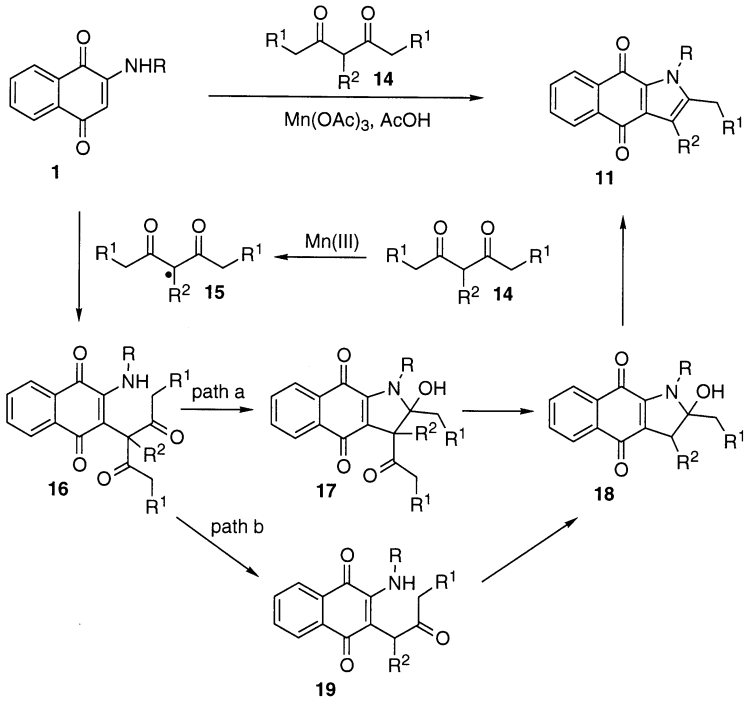
Entry	Quinone	Carbonyl compound	Product (yield)
a	**1b**: R=Me	**9a**: R^1=H, R^2=Me	**10a** (32%) **11a** (41%)
b	**1b**: R=Me	**9b**: R^1=H, R^2=*i*-Pr	**10b** (44%) **11b** (5%)
c	**1b**: R=Me	**9c**: R^1=H, R^2=Cl	**10c** (7%) **11c** (43%)[a]
d	**1b**: R=Me	**9d**: R^1=*i*-Pr, R^2=Br	**10d** (0%) **11d** (28%)[a,b]
e	**1b**: R=Me	**9e**: R^1=H, R^2=OPh	**10e** (53%) **11c** (4%)[a]
f	**1b**: R=Me	**9f**: R^1=Pentyl, R^2=OPh	**10f** (48%) **11e** (0%)
g	**1b**: R=Me	**9g**: R^1=*i*-Pr, R^2=OPh	**10g** (9%) **11d** (13%)[a]
h	**1c**: R=Octyl	**9h**: R^1=H, R^2=Ms	**10h** (31%) **11f** (6%)

[a] R^2=OAc.
[b] 2-Bromo-3-methylamino-1,4-naphthoquinone was also obtained in 26% yield.

Table 3. The free radical reactions between 2-amino-1,4-naphthoquinone **1** and 2-alkyl substituted-1,3-dione **15**

Entry	Quinone	1,3-Diones	Product (yield)
a	**1b**: R=Me	**14a**: R^1=H, R^2=Me	**11a** (78%)
b	**1b**: R=Me	**14b**: R^1=H, R^2=Bu	**11g** (48%)
c	**1d**: R=H	**14b**: R^1=H, R^2=Bu	**11h** (71%)
d	**1b**: R=Me	**14c**: R^1=H, R^2=$CH_2CH_2CO_2Me$	**11i** (70%)
e	**1d**: R=H	**14c**: R^1=H, R^2=$CH_2CH_2CO_2Me$	**11j** (76%)
f	**1b**: R=Me	**14d**: 2-acetylcyclopentanone	**11k** (79%)[a]

[a] R^1=H, R^2=$CH_2CH_2CH_2CO_2H$.



Scheme 2.

3. Conclusion

Carbon radicals generated from the oxidation of carbonyl compounds with manganese(III) acetate undergoes efficient addition to the C–C double bond of 2-amino-1,4-naphthoquinone. This free radical reaction provides a novel method for the synthesis of benzo[*f*]indole-4,9-diones from readily available 2-amino-1,4-naphthoquinones and carbonyl compounds.

4. Experimental

4.1. General

Melting points are uncorrected. The ^{1}H NMR and ^{13}C NMR spectra were recorded at 400 and 100.6 MHz in $CDCl_3$ or DMSO-d_6, respectively. Chemical shifts are reported in ppm relative to TMS as internal reference. Analytical thin layer chromatography was performed by precoated silica gel 60 F-254 plates (0.25 mm thick) of EM Laboratories and visualized by uv. The reaction mixture was purified by column chromatography over EM Laboratories silica gel (70–230 mesh). The spectral data of 2-bromo-3-methyl-1,4-naphthoquinone have been reported.[9] The starting 1,4-naphthoquinone **1** was synthesized by literature procedure.[10]

4.2. Typical experimental procedure for the reaction of 2-amino-1,4-naphthoquinones with simple aldehydes and ketones

A solution of 101 mg (0.50 mmol) of 2-ethylamino-1,4-naphthoquinone, 119 mg (2.05 mmol) of acetone and 668 mg (2.49 mmol) of manganese(III) acetate in 10 ml of acetic acid was stirred at 45°C for 24 h. The reaction mixture was diluted with 100 ml of ethyl acetate, washed with 50 ml of saturated aqueous sodium bisulfite, three 50 ml portions of water, 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 dichloromethane–hexane, 1:1) followed by recrystallization (hexane–ethyl acetate) to give 88 mg (73%) of **4a**.

4.3. Typical experimental procedure for the reaction of 2-amino-1,4-naphthoquinones with 2-alkly substituted-1,3-diones

A solution of 150 mg (0.80 mmol) of 2-methylamino-1,4-naphthoquinone, 366 mg (3.21 mmol) of 3-methyl-2,4-pentanedione and 1.08 g (4.01 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 371 mg (3.25 mmol) of 3-methyl-2,4-pentanedione and 1.07 g (3.99 mmol) of manganese(III) acetate. The reaction mixture was stirred for another 15 h. After work up as described above, the residue was chromatographed over 20 g of silica gel (eluted with dichloromethane–hexane, 1:1) followed by recrystallization (hexane–ethyl acetate) to give 150 mg (78%) of **11a**.

4.3.1. 1-Ethyl-2-methyl-4,9-dihydro-4,9-dioxo-1*H*-benzo-[*f*]indole 4a. Yellow crystals; mp 164–165°C; IR ($CHCl_3$) 2960, 1730, 1650, 1595, 1495 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.41 (t, J=7.1 Hz, 3H, CH_3), 2.35 (s, 3H, CH_3), 4.46 (q, J=7.1 Hz, 2H, NCH_2), 6.52 (s, 1H, CH), 7.60–7.69 (m, 2H, ArH), 8.09–8.17 (m, 2H, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 12.0(q), 15.6(q), 40.7(t), 107.5(d), 126.3(d), 128.3(s), 129.9(s), 132.7(d), 132.9(d), 133.4(s), 134.2(s), 139.0(s), 175.1(s), 181.1(s); Anal. calcd for

$C_{15}H_{13}NO_2$: C, 75.30; H, 5.48; N, 5.85. Found: C, 75.35; H, 5.50; N, 5.89.

4.3.2. 2-Ethyl-1,3-dimethyl-4,9-dihydro-4,9-dioxo-1*H*-benzo[*f*]indole 4b. Yellow crystals; mp 176–177°C; IR ($CHCl_3$) 2980, 1660, 1595, 1490, 1410 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.18 (t, J=7.6 Hz, 3H, CH_3), 2.38 (s, 3H, CH_3), 2.66 (q, J=7.6 Hz, 2H, CH_2), 4.03 (s, 3H, NCH_3), 7.59–7.68 (m, 2H, ArH), 8.08–8.17 (m, 2H, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 10.0(q), 13.2(q), 17.0(t), 32.7(q), 118.7(s), 125.5(s), 126.0(d), 126.03(d), 129.5 (s), 132.5(d), 132.7(d), 134.0(s), 134.3(s), 142.9(s), 175.4(s), 182.3(s); Anal. calcd for $C_{16}H_{15}NO_2$: C, 75.87; H, 5.97; N, 5.53. Found: C, 75.88; H, 6.04; N, 5.59.

4.3.3. 10-Methyl-1,2,3,4,9,10-hexahydro-4,9-dioxo-10-aza-pentaleno[1,2-*b*]naphthalene 4c. Orange needles; mp 205–206°C; IR ($CHCl_3$) 2955, 1645, 1595, 1480, 1465 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.46 (quintet, J=7.1 Hz, 2H, CH_2), 2.64 (t, J=7.1 Hz, 2H, CH_2), 2.84 (t, J=7.1 Hz, 2H, CH_2), 3.88 (s, 3H, NCH_3), 7.57–7.69 (m, 2H, ArH), 8.04–8.15 (m, 2H, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 23.8(t), 25.1(t), 28.4(t), 34.6(q), 123.1(s), 126.0(d), 126.1(d), 128.3(s), 132.4(d), 132.7(d), 133.4(s), 134.3(s), 150.6(s), 175.0(s), 181.4(s); Anal. calcd for $C_{16}H_{13}NO_2$: C, 76.58; H, 5.21; N, 5.57. Found: C, 76.47; H, 5.18; N, 5.57.

4.3.4. 1-Methyl-2,3,4,5,6,11-hexahydro-6,11-dioxo-1*H*-benzo[*b*]carbazole 4d. Yellow needles; mp 183–184°C; IR ($CHCl_3$) 2945, 1645, 1595, 1490, 1470 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.74–1.83 (m, 2H),1.83–1.93 (m, 2H), 2.57 (t, J=5.8 Hz, 2H, CH_2), 2.87 (t, J=5.8 Hz, 2H, CH_2), 3.92 (s, 3H, NCH_3), 7.59–7.68 (m, 2H, ArH), 8.06–8.16 (m, 2H, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 21.8(t), 22.2(t), 22.6(t), 32.3(q), 121.3(s), 124.7(s), 126.0(d), 129.5(s), 132.5 (d), 132.7(d), 133.8(s), 134.3(s), 139.7(s), 175.5(s), 182.0(s); Anal. calcd for $C_{17}H_{15}NO_2$: C, 75.87; H, 5.97; N, 5.37. Found: C, 75.84; H, 5.88; N, 5.42.

4.3.5. 1-Methyl-2-phenyl-4,9-dihydro-4,9-dioxo-1*H*-benzo[*f*]indole 4e. Red powders; mp 153–154°C; IR ($CHCl_3$) 3010, 1660, 1595, 1480, 1465 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.06 (s, 3H, NCH_3), 6.81 (s, 1H, CH), 7.42–7.55 (m, 5H, ArH), 7.64–7.74 (m, 2H, ArH), 8.14–8.22 (m, 2H, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 34.7(q), 108.3(d), 126.4(d), 126.5(d), 128.3(s), 128.8(d), 129.1(d), 129.3(d), 130.3(s), 131.4(s), 133.0(d), 133.1(d), 133.6(s), 134.3(s), 143.9(s), 176.2(s), 181.1(s); Anal. calcd for $C_{19}H_{13}NO_2$: C,79.34; H, 4.56; N, 4.87. Found: C, 79.40; H, 4.50; N, 4.83.

4.3.6. 1,3-Dimethyl-2-phenyl-4,9-dihydro-4,9-dioxo-1*H*-benzo[*f*]indole 4f. Orange crystals; mp 149–150°C; IR ($CHCl_3$) 3010, 2925, 1650, 1495, 1460 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.33 (s, 3H, CH_3), 3.90 (s, 3H, NCH_3), 7.30–7.39 (m, 2H, ArH), 7.44–7.57 (m, 3H, ArH), 7.61–7.70 (m, 2H, ArH), 8.09–8.19 (m, 2H, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 10.8(q), 34.4(q), 120.4(s), 125.4(s), 126.06(d), 126.13(d), 128.7(d), 129.0(d), 129.4(s), 130.1(s), 130.4(d), 132.7(d), 134.0(s), 134.2(s), 141.4(s), 175.9(s), 182.1(s); Anal. calcd for $C_{20}H_{15}NO_2$: C, 79.72; H, 5.02; N, 4.65. Found: C, 79.80; H, 5.03; N, 4.71.

4.3.7. 1,3-Dimethyl-4,9-dihydro-4,9-dioxo-1*H*-benzo[*f*]-indole 4g. Yellow needles; mp 203–204°C; IR ($CHCl_3$) 3010, 1655, 1595, 1460, 1400 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.37 (s, 3H, CH_3), 4.00 (s, 3H, NCH_3), 6.64 (s, 1H, CH), 7.60–7.69 (m, 2H, ArH), 8.06–8.16 (m, 2H, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 11.1(q), 36.4(q), 121.8(s), 125.7(s), 126.0(d), 126.2(d), 130.7(d), 132.6(d), 132.8(d), 133.9(s), 134.2(s), 176.0(s), 181.8(s); Anal. calcd for $C_{14}H_{11}NO_2$: C, 74.65; H, 4.92; N, 6.22. Found: C, 74.79; H, 4.95; N, 6.32.

4.3.8. 1-Methyl-3-phenyl-4,9-dihydro-4,9-dioxo-1*H*-benzo-[*f*]indole 4h. Orange needles; mp 156–157°C; IR ($CHCl_3$) 3010, 2925, 1740, 1635, 1595 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.11 (s, 3H, NCH_3), 6.96 (s, 1H, CH), 7.31–7.45 (m, 3H, ArH), 7.61–7.72 (m, 4H, ArH), 8.10–8.18 (m, 2H, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 37.1(q), 123.7(s), 126.0(d), 126.5(s), 126.7(d), 127.7(d), 128.1(d), 128.9(d), 130.7(d), 131.6(s), 132.5(s), 132.8(d), 133.2(d), 133.4(s), 134.6(s), 176.7(s), 180.6(s); Anal. calcd for $C_{19}H_{13}NO_2$: C, 79.43; H, 4.56; N, 4.87. Found: C, 79.47; H, 4.62; N, 4.88.

4.3.9. 1-Methyl-4,9-dihydro-4,9-dioxo-1*H*-benzo[*f*]indole 4i. Yellow needles; mp 191–192°C; IR ($CHCl_3$) 3010, 1660, 1595, 1510, 1400 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.08 (s, 3H, NCH_3), 6.72 (d, J=2.6 Hz, 1H, CH), 6.90 (d, J=2.6 Hz, 1H, CH), 7.61–7.71 (m, 2H, ArH), 8.09–8.19 (m, 2H, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 36.7(q), 107.7(d), 126.3(d), 126.5(d), 128.7(s), 130.8(s), 131.6(d), 132.97(d), 133.02(d), 133.9(s), 176.3(s), 180.8(s); Anal. calcd for $C_{13}H_9NO_2$: C,73.92; H, 4.29; N, 6.63. Found: C, 73.95; H, 4.33; N, 6.63.

4.3.10. 2-Ethoxycarbonyl-1-methyl-4,9-dihydro-4,9-dioxo-1*H*-benzo[*f*]indole 4j. Yellow needles; mp 161–162°C; IR ($CHCl_3$) 2990, 1725, 1660, 1525, 1490 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.41 (t, J=7.1 Hz, 3H, CH_3), 4.37 (q, J=7.1 Hz, 2H, OCH_2), 4.42 (s, 3H, NCH_3), 7.42 (s, 1H, CH), 7.66–7.73 (m, 2H, ArH), 8.12–8.20 (m, 2H, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 14.1(q), 35.0(q), 61.2(t), 114.8(d), 126.55(d), 126.62(s), 126.7(d), 130.0(s), 133.2(d), 133.3(s), 133.4(d), 134.0(s), 160.3(s), 176.9(s), 180.0(s); Anal. calcd for $C_{16}H_{13}NO_4$: C, 67.84; H, 4.63; N, 4.95. Found: C, 67.81; H, 4.72; N, 4.96.

4.3.11. 2-Ethyl-1-methyl-4,9-dihydro-4,9-dioxo-1*H*-benzo-[*f*]indole 10a. Yellow powders; mp 223–224°C; IR ($CHCl_3$) 2925, 1720, 1650, 1595, 1495, 1475 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.33 (t, J=7.5 Hz, 3H, CH_3), 2.63 (q, J=7.5 Hz, 2H, CH_2), 3.99 (s, 3H, NCH_3), 6.54 (s, 1H, CH), 7.59–7.71 (m, 2H, ArH), 8.07–8.18 (m, 2H, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 11.9(q), 19.5(t), 32.5(q), 105.4(d), 126.26(d), 126.29(d), 128.1(s), 130.6(s), 132.7 (d), 132.9(d), 133.5(s), 134.2(s), 145.7(s), 175.7(s), 181.1(s); Anal. calcd for $C_{15}H_{13}NO_2$: C, 75.30; H, 5.48; N, 5.85. Found: C, 75.35; H, 5.49; N, 5.73.

4.3.12. 2-Isobutyl-1-methyl-4,9-dihydro-4,9-dioxo-1*H*-benzo[*f*]indole 10b. Yellow needles; mp 118–119°C; IR ($CHCl_3$) 2960, 1650, 1595, 1495, 1475 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.01 (t, J=6.8 Hz, 6H, CH_3), 1.98 (nontet, J=6.8 Hz, 1H, CH), 2.51 (d, J=6.8 Hz, 2H, CH_2),

4.01 (s, 3H, NCH_3), 6.53 (s, 1H, CH), 7.60–7.66 (m, 2H, ArH), 8.10–8.17 (m, 2H, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 22.5(q), 27.9(d), 32.8(q), 35.2(t), 107.3(d), 126.3(d), 128.1(s), 130.5(s), 132.7(d), 132.9(d), 133.5(s), 134.3(s), 143.5(s), 175.6(s), 181.2(s); Anal. calcd for $C_{17}H_{17}NO_2$: C, 76.38; H, 6.41; N, 5.24. Found: C, 76.32; H, 6.46; N, 5.26.

4.3.13. 2-Chloromethyl-1-methyl-4,9-dihydro-4,9-dioxo-1*H*-benzo[*f*]indole 10c. Yellow powders; mp 193–194°C; IR ($CHCl_3$) 2925, 1660, 1585, 1495, 1475 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.15 (s, 3H, NCH_3), 4.66 (s, 2H, $ClCH_2$), 6.79 (s, 1H, CH), 7.65–7.72 (m, 2H, ArH), 8.11–8.19 (m, 2H, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 33.0(q), 36.1(t), 109.3(d), 126.6(d), 127.6(s), 132.2(s), 133.2(d), 133.3(d), 133.5(s), 134.0(s), 137.2(s), 176.5(s), 180.5(s); Anal. calcd for $C_{14}H_{10}ClNO_2$: C, 64.75; H, 3.88; N, 5.39. Found: C, 64.88; H, 3.90; N, 5.38.

4.3.14. 1-Methyl-2-phenoxymethyl-4,9-dihydro-4,9-dioxo-1*H*-benzo[*f*]indole 10e. Yellow powders; mp 176–177°C; IR ($CHCl_3$) 3010, 1660, 1595, 1495, 1445 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.13 (s, 3H, NCH_3), 5.07 (s, 2H, OCH_2), 6.82 (s, 1H, CH), 6.94–7.06 (m, 3H, ArH), 7.27–7.37 (m, 2H, ArH), 7.62–7.71 (m, 2H, ArH), 8.09–8.19 (m, 2H, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 33.4(q), 61.4(t), 109.5(d), 114.8(d), 121.9(d), 126.48(d), 126.52(d), 127.6(s), 129.7(d), 133.08 (d), 133.13(s), 133.6(s), 134.1(s), 137.3(s), 157.8(s), 176.5(s), 180.7(s); Anal. calcd for $C_{20}H_{15}NO_3$: C, 75.70; H, 4.76; N, 4.41. Found: C, 75.71; H, 4.84; N, 4.46.

4.3.15. 1-Methyl-3-pentyl-2-phenoxymethyl-4,9-dihydro-4,9-dioxo-1*H*-benzo[*f*]indole 10f. Yellow needles; mp 89–90°C; IR ($CHCl_3$) 2925, 1655, 1595, 1495, 1475 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.87 (t, J=7.2 Hz, 3H, CH_3), 1.29–1.40 (m, 4H), 1.53–1.64 (m, 2H), 2.89 (t, J=7.2 Hz, 2H, CH_2), 4.13 (s, 3H, NCH_3), 5.01 (s, 2H, OCH_2), 7.01 (d, J=7.8 Hz, 2H, ArH), 7.04 (t, J=7.8 Hz, 1H, ArH), 7.34 (d, J=7.8 Hz, 1H, ArH), 7.36 (d, J=7.8 Hz, 1H, ArH), 7.62–7.72 (m, 2H, ArH), 8.10–8.23 (m, 2H, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 14.1(q), 22.6(t), 24.7(t), 30.7(t), 31.7(t), 33.4(q), 58.6(t), 114.9(d), 121.8 (d), 124.5(s), 126.25(d), 126.33(d), 127.6(s), 129.7(d), 131.4(s), 132.8 (d), 133.1(d), 134.0(s), 134.1(s), 134.3(s), 158.1(s), 176.6(s), 181.6(s); Anal. calcd for $C_{25}H_{25}NO_3$: C, 77.49; H, 6.50; N, 3.61. Found: C, 77.50; H, 6.50; N, 3.66.

4.3.16. 3-Isopropyl-1-methyl-2-phenoxymethyl-4,9-dihydro-4,9-dioxo-1*H*-benzo[*f*]indole 10g. Yellow crystals; mp 176–177°C; IR ($CHCl_3$) 2925, 1655, 1595, 1490, 1480 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.39 (t, J=7.0 Hz, 6H, CH_3), 3.58 (septet, J=7.0 Hz, 1H, CH), 4.13 (s, 3H, NCH_3), 5.09 (s, 2H, OCH_2), 7.01 (d, J=7.7 Hz, 2H, ArH), 7.04 (t, J=7.7 Hz, 1H, ArH), 7.34 (t, J=7.7 Hz, 1H, ArH), 7.36 (t, J=7.7 Hz, 1H, ArH), 7.61–7.72 (m, 2H, ArH), 8.09–8.22 (m, 2H, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 21.7(q), 25.5(d), 33.2(q), 59.2(t), 115.0(d), 121.9(d), 124.2(s), 126.1(d), 126.6(d), 129.7(d), 131.9(s), 132.7(d), 133.2(d), 133.4(s), 133.5(s), 133.6(s), 134.3(s), 158.1(s), 176.8(s), 181.2(s); Anal. calcd for $C_{23}H_{21}NO_3$: C, 76.86; H, 5.89; N, 3.92. Found: C, 76.91; H, 5.88; N, 3.99.

4.3.17. 2-Methanesulfonylmethyl-1-octyl-4,9-dihydro-4,9-dioxo-1*H*-benzo[*f*]indole 10h. Yellow needles; mp 146–147°C; IR ($CHCl_3$) 2925, 1660, 1595, 1490, 1470 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.87 (t, J=7.3 Hz, 3H, CH_3), 1.19–1.47 (m, 10H), 1.77 (quintet, J=7.3 Hz, 2H, CH_2), 2.98 (s, 3H, SO_2CH_3), 4.43 (s, 2H, SO_2CH_2), 4.62 (t, J=7.3 Hz, 2H, NCH_2), 6.68 (s, 1H, CH), 7.65–7.74 (m, 2H, ArH), 8.10–8.20 (m, 2H, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 14.0(q), 22.6(t), 26.7(t), 29.1(t), 29.2(t), 31.0(t), 31.7(t), 39.4(q), 46.4(t), 52.3(t), 110.9(d), 126.5(d), 126.7(d), 128.1(s), 128.9(s), 131.9(s), 133.2(d), 133.26(d), 133.33(s), 133.9(s), 175.7(s), 180.5(s); Anal. calcd for $C_{22}H_{27}NO_4S$: C, 65.81; H, 6.78; N, 3.49. Found: C, 65.86; H, 6.79; N, 3.48.

4.3.18. 1,2,3-Trimethyl-4,9-dihydro-4,9-dioxo-1*H*-benzo-[*f*]indole 11a. Orange powders; mp 222–223°C; IR ($CHCl_3$) 3010, 1645, 1595, 1495, 1465 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.09 (s, 3H, CH_3), 2.25 (s, 3H, CH_3), 3.88 (s, 3H, NCH_3), 7.52–7.69 (m, 2H, ArH), 7.98–8.11 (m, 2H, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 9.3(q), 10.1(q), 32.6(q), 119.0(s), 125.1(s), 125.9(d), 129.2(s), 132.4(d), 132.5 (d), 133.8(s), 134.1(s), 137.4(s), 174.9(s),181.9(s); Anal. calcd for $C_{15}H_{13}NO_2$: C, 75.30; H, 5.48; N, 5.85. Found: C, 75.27; H, 5.55; N, 5.79.

4.3.19. 3-Isopropyl-1,2-dimethyl-4,9-dihydro-4,9-dioxo-1*H*-benzo[*f*]indole 11b. Yellow needles; mp 122–123°C; IR ($CHCl_3$) 2925, 1645, 1595, 1490, 1455 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.36 (t, J=7.1 Hz, 6H, CH_3), 2.32 (s, 3H, CH_3), 3.59 (septet, J=7.1 Hz, 1H, CH), 4.03 (s, 3H, NCH_3), 7.58–7.68 (m, 2H, ArH), 8.06–8.17 (m, 2H, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 10.7(q), 21.2(q), 25.1(q), 29.7(d), 32.8(q), 124.6(s), 125.9(d), 126.4(d), 130.15(s), 130.23(s), 132.55(d), 132.65(d), 133.9(s), 134.2(s), 136.4(s), 175.7(s), 181.6(s); Anal. calcd for $C_{17}H_{17}NO_2$: C, 76.38; H, 6.41; N, 5.24. Found: C, 76.51; H, 6.45; N, 5.24.

4.3.20. 3-Acetoxy-1,2-dimethyl-4,9-dihydro-4,9-dioxo-1*H*-benzo[*f*]indole 11c. Yellow needles; mp 227–228°C; IR ($CHCl_3$) 3010, 1775, 1655, 1595, 1465 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.19 (s, 3H, CH_3), 2.42 (s, 3H, CH_3), 4.01(s, 3H, NCH_3), 7.61–7.69 (m, 2H, ArH), 8.05–8.14 (m, 2H, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 8.3(q), 20.6(q), 32.9(q), 118.2(s), 126.1(d), 126.4(d), 126.9(s), 130.5(s), 132.3(s), 132.9(d), 133.1(d), 133.5(s), 134.0(s), 169.1(s), 175.6(s), 179.9(s); Anal. calcd for $C_{16}H_{13}NO_4$: C, 67.84; H, 4.63; N, 4.94. Found: C, 67.86; H, 4.61; N, 5.03.

4.3.21. 3-Acetoxy-2-isobutyl-1-methyl-4,9-dihydro-4,9-dioxo-1*H*-benzo[*f*]indole 11d. Orange powders; mp 165–166°C; IR ($CHCl_3$) 2960, 1780, 1655, 1595, 1460 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.98 (t, J=6.8 Hz, 6H, CH_3), 1.84–1.98 (m, 1H, CH), 2.41 (s, 3H, CH_3), 2.48 (d, J=7.3 Hz, 2H, CH_2), 4.02 (s, 3H, NCH_3), 7.61–7.69 (m, 2H, ArH), 8.04–8.11 (m, 1H, ArH), 8.11–8.16 (m, 1H, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 20.6(q), 22.4(q), 28.3(d), 31.7(t), 33.2(q), 118.1(s), 126.1(d), 126.4(d), 127.0 (s), 132.9(d), 133.0(d), 133.5(s), 133.7(s), 134.1(s), 169.0(s), 175.6 (s), 179.9(s); Anal. calcd for $C_{19}H_{19}NO_4$: C, 70.14; H, 5.89; N, 4.30. Found: C, 70.12; H, 5.93; N, 4.30.

4.3.22. 3-Methanesulfonyl-2-methyl-1-octyl-4,9-dihydro-4,9-dioxo-1*H*-benzo[*f*]indole 11f. Yellow needles; mp 147–148°C; IR ($CHCl_3$) 2925, 2855, 1660, 1595, 1425 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.89 (t, J=7.3 Hz, 3H, CH_3), 1.17–1.50 (m, 10H), 1.75 (quintet, J=7.3 Hz, 2H, CH_2), 2.70 (s, 3H, CH_3), 3.50 (s, 3H, SO_2CH_3), 4.50 (t, J=7.3 Hz, 2H, NCH_2), 7.67–7.77 (m, 2H, ArH), 8.09–8.21 (m, 2H, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 10.6(q), 14.0(q), 22.6(t), 26.7(t), 29.1(t), 30.3(t), 31.7(t), 44.4(q), 46.0(t), 124.8(s), 126.4(d), 127.0(d), 130.8(s), 132.7(s), 133.2(s), 133.5(d), 133.7(d), 142.7(s), 176.1(s), 179.4(s); Anal. calcd for $C_{22}H_{27}NO_4S$: C, 65.81; H, 6.78; N, 3.49; S, 7.98. Found: C, 65.87; H, 6.77; N, 3.47; S, 7.99.

4.3.23. 3-Butyl-1,2-dimethyl-4,9-dihydro-4,9-dioxo-1*H*-benzo[*f*]indole 11g. Orange crystals; mp 142–143°C; IR ($CHCl_3$) 2955, 2925, 1645, 1595, 1465 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.94 (t, J=7.4 Hz, 3H, CH_3), 1.38 (sextet, J=7.4 Hz, 2H, CH_2), 1.52 (quintet, J=7.4 Hz, 2H, CH_2), 2.20 (s, 3H, CH_3), 2.77 (t, J=7.4 Hz, 2H, CH_2), 3.98 (s, 3H, NCH_3), 7.59–7.66 (m, 2H, ArH), 8.06–8.13 (m, 2H, ArH); 13C NMR (100.6 MHz, $CDCl_3$) δ 9.5(q), 14.0(q), 22.6(t), 24.5(t), 32.6(t), 32.7(q), 124.5(s), 124.8(s), 125.9(d), 126.0(d), 129.6(s), 132.5(d), 132.6(d), 133.9(s), 134.1(s), 137.3(s), 175.2(s), 181.8(s); Anal. calcd for $C_{18}H_{19}NO_2$: C, 76.84; H, 6.81; N, 4.98. Found: C, 76.76; H, 6.81; N, 4.97.

4.3.24. 3-Butyl-2-methyl-4,9-dihydro-4,9-dioxo-1*H*-benzo-[*f*]indole 11h. Yellow needles; mp 222–223°C; IR ($CHCl_3$) 3220, 2960, 1645, 1595, 1465 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.94 (t, J=7.4 Hz, 3H, CH_3), 1.40 (sextet, J=7.4 Hz, 2H, CH_2), 1.58 (quintet, J=7.4 Hz, 2H, CH_2), 2.40 (s, 3H, CH_3), 2.79 (t, J=7.4 Hz, 2H, CH_2), 7.61–7.71 (m, 2H, ArH), 8.07–8.18 (m, 2H, ArH), 10.7 (s, 1H, NH); 13C NMR (100.6 MHz, $CDCl_3$) δ 11.3(q), 14.0(q), 22.6(t), 24.4(t), 32.5(t), 125.3(s), 125.7(s), 125.9(d), 126.7(d), 130.6(s), 132.7(d), 133.1(d), 133.5(s), 134.7(s), 136.0(s), 174.9(s), 181.9(s); Anal. calcd for $C_{17}H_{17}NO_2$: C, 76.38; H, 6.41; N, 5.24. Found: C, 76.35; H, 6.40; N, 5.23.

4.3.25. 3-(2-Methoxycarbonylethyl)-1,2-dimethyl-4,9-dihydro-4,9-dioxo-1*H*-benzo[*f*]indole 11i. Orange needles; mp 161–162°C; IR ($CHCl_3$) 3010, 2955, 1730, 1645, 1595, 1465 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.27 (s, 3H, CH_3), 2.69 (t, J=7.3 Hz, 2H, CH_2), 3.08 (t, J=7.3 Hz, 2H, CH_2), 3.64 (s, 3H, OCH_3), 4.00 (s, 3H, NCH_3), 7.58–7.67 (m, 2H, ArH), 8.06–8.15 (m, 2H, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 9.6(q), 20.4(t), 32.8(q), 33.9(t), 51.5(q), 121.8(s), 124.9(s), 126.1(d), 130.0(s), 132.7(d), 132.8(d), 133.8(s), 134.1(s), 137.8(s), 173.8(s), 175.4(s), 181.8(s); Anal. calcd for $C_{18}H_{17}NO_4$: C, 69.44; H, 5.50; N, 4.50. Found: C, 69.41; H, 5.53; N, 4.55.

4.3.26. 3-(2-Methoxycarbonylethyl)-2-methyl-4,9-dihydro-4,9-dioxo-1*H*-benzo[*f*]indole 11j. Orange crystals; mp 251–252°C; IR ($CHCl_3$) 3215, 2950, 1730, 1645, 1595 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.43 (s, 3H, CH_3), 2.75 (t, J=6.9 Hz, 2H, CH_2), 3.06 (t, J=6.9 Hz, 2H, CH_2), 3.65 (s, 3H, OCH_3), 7.61–7.73 (m, 2H, ArH), 8.06–8.19 (m, 2H, ArH), 10.23 (s, 1H, NH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 11.3(q), 20.2(t), 33.8(t), 51.5(q), 122.3(s), 125.6(s), 126.0(d), 126.7(d), 131.0(s), 132.9(d), 133.2(d), 133.3(s), 134.4(s), 135.8(s), 173.8(s), 174.9(s), 181.8(s); Anal. calcd for $C_{17}H_{15}NO_4$: C, 68.68; H, 5.09; N, 4.71. Found: C, 68.69; H, 5.14; N, 4.71.

4.3.27. 4-(1,2-Dimethyl-4,9-Dihydro-4,9-dioxo-1*H*-benzo-[*f*]indol-3-yl)butyric acid 11k. Orange crystals; mp 220–221°C; IR ($CHCl_3$) 2925, 1705, 1645, 1595, 1495 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.93 (quintet, J=7.4 Hz, 2H, CH_2), 2.25 (s, 3H, CH_3), 2.43 (t, J=7.4 Hz, 2H, CH_2), 2.90 (t, J=7.4 Hz, 2H, CH_2), 4.02 (s, 3H, NCH_3), 7.60–7.67 (m, 2H, ArH), 8.05–8.15 (m, 2H, ArH); ^{13}C NMR (100.6 MHz, DMSO) δ 9.3(q), 23.5(t), 25.4(t), 32.7(q), 33.4(t), 122.4(s), 124.3(s), 125.8(d), 125.9(d), 129.0(s), 133.1(d), 133.3(d), 133.4(s), 133.8(s), 138.9(s), 174.2(s), 174.7(s), 180.9(s); Anal. calcd for $C_{18}H_{17}NO_4$: C, 69.44; H, 5.50; N, 4.50. Found: C, 69.59; H, 5.51; N, 4.50.

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