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Tetrahedron
Tetrahedron 60 (2004) 12249–12260

# Solvent effects on the oxidative free radical reactions of 2-amino-1,4-naphthoquinones

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Received 18 August 2004; accepted 5 October 2004

Available online 28 October 2004

**Abstract**—Solvent effects on the manganese (III) initiated oxidative free radical reactions of 2-amino-1,4-naphthoquinones are described. This free radical reaction provides a novel method for the synthesis of benzo[*f*]indole-4,9-diones, benzo[*f*]indole-2,4,9-triones, benzo[*b*]carbazole-6,11-diones and benzo[*b*]acridine-6,11-diones. High chemoselectivity was observed in different solvents.


## 1. Introduction

Carbon–carbon bond forming reactions mediated by radical have received considerable attention in organic synthesis during the last two decades.[1] Naturally occurring quinones such as mitosenes, kinamycins, murrayaquinones, etc. represent an important class of biologically significant natural products.[2] A common building block to these compounds is the indoloquinone unit. The development of new synthetic methodologies for the synthesis of indolequinone ring system is therefore important.[3,4] The oxidative free radical reaction mediated by metal salts has been developed into a versatile protocol for the formation of highly functionalized products from simple precursors.[1d–f,5–7] Among these, manganese (III) acetate and cerium (IV) ammonium nitrate have been used most efficiently. The solvent effects play an important role in this oxidative free radical reaction.[8] The free radical reaction of 1,4-naphthoquinones has been reported.[6c–j,9] In this report, we wish to describe the solvent effects on the oxidative free radical reaction between 2-amino-1,4-naphthoquinones and carbonyl compounds.

## 2. Results and discussion

### 2.1. The oxidative free radical reactions of 2-(alkylamino)-1,4-naphthoquinones

We reported previously that the manganese (III) acetate mediated reaction between 2-(alkylamino)-1,4-naphthoquinones **1** and β-keto ester **2** ($R^2$=OR) in acetic acid gave **3** and **4** (Eq. 1).[6h] The product distributions are highly dependent on the substituents of β-keto ester **2**. Indoles **3** and **4** were formed presumably via the reaction route outlined in Scheme 1. Initiation occurs with the manganese (III) acetate oxidation of **2** to produce radical **5**. This radical intermediate **5** undergoes intermolecular addition to the quinone ring followed by oxidation to give **6**, which undergoes either condensation to generate **3** (path a) or oxidation to produce radical **7** (path b). Radical **7** undergoes intramolecular cyclization followed by oxidation to produce **9**, which subsequently undergoes alkyl group ($R^1$) migration to produce **4**. On the contrary, when **1** and **2** were treated with cerium (IV) sulfate in methanol, indole **3** was obtained as the only product.[6j] This different reaction behavior of intermediate **6** can be ascribed to the presence of cerium salt, which acts as a Lewis acid and the condensation rate of **6** was enhanced.[10] Based on these results, we believe that the acidity of the reaction medium would affect the production distributions of this reaction. To test this hypothesis, this oxidative free radical reaction was performed in various solvents. When a solution of 2-(methylamino)-1,4-naphthoquinone (**1a**) in formic acid was treated with ethyl butyrylacetate (**2a**) and manganese (III) acetate at 0 °C for 30 min, **3a** was obtained exclusively in 85% yield (Table 1, entry 1). Other β-keto ester **2** behaved similarly giving only the corresponding condensation product **3** (entries 2–5). It is well known that Brønsted acid can also catalyze the condensation reaction of carbonyl compounds. These results demonstrate that the higher acidity of formic acid enhances the condensation rate of **6** and path a is the only reaction route. We next performed this reaction in less acidic or neutral solvents. Treatment of **1a** and **2a** with manganese (III) acetate in $CF_3CH_2OH$ at 80 °C for 16 h resulted in the formation of **3a** (12%) and **4a** (63%). Results of this reaction between **1a** and **2a** in different solvents are summarized in

*Keywords*: Manganese (III) acetate; Free radical; 2-Amino-1,4-naphthoquinones; Solvent effects.
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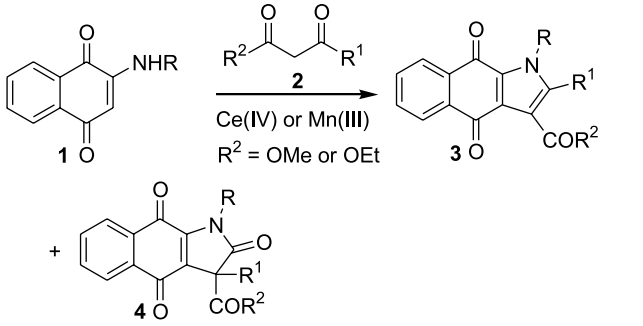
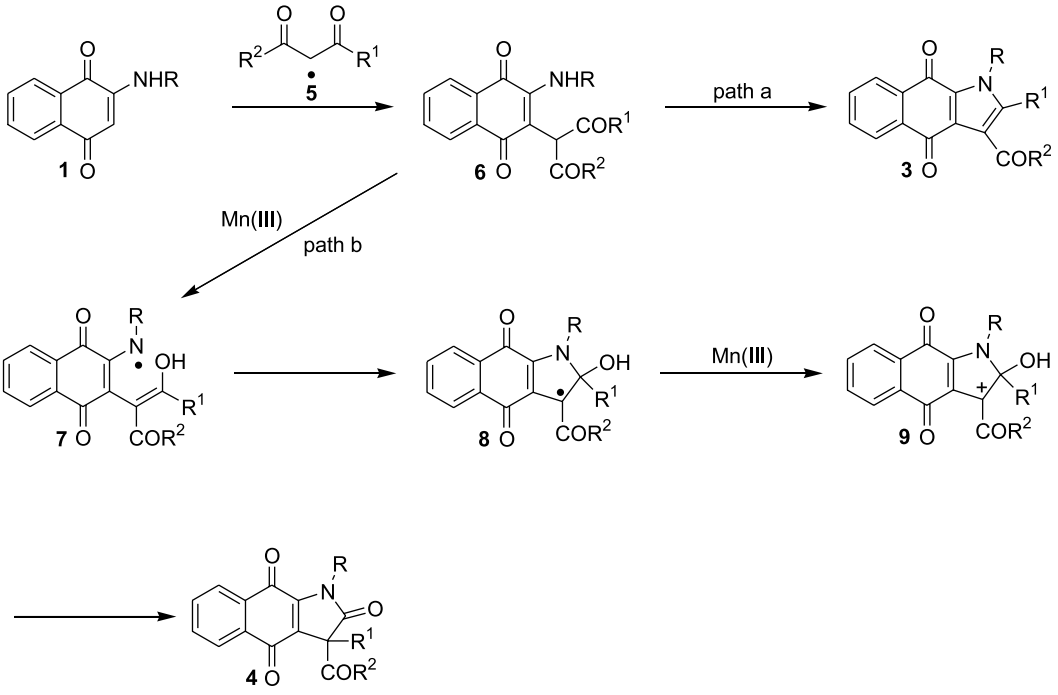
doi:10.1016/j.tet.2004.10.029

Table 1 (entries 7–10). In all cases, it gave higher **4a/3a** ratio than those performed in acetic acid (entry 6). This could account for the rate of condensation (path a) decreasing as the acidity of reaction medium decreases and the oxidation of **6** to produce radical **7** became the major route (path b). The scope of this reaction was explored using a variety of β-keto esters and the results are also illustrated in Table 1 (entries 11–14). In all cases, **4** is the major product.




(1)

Manganese (III) acetate mediated free radical reaction between 2-(alkylamino)-1,4-naphthoquinone **1** and simple ketone **10** in acetic acid produced **11** as the only product (Eq. 2).[6i] Indole **11** was formed presumably via a similar reaction route as shown in Scheme 1 (path a). Due to the instability of **1** in acidic medium, we expected that the radical reaction between **1** and **10** in neutral solvents would give **11** in better result. Indeed, when **1a** and acetone (**10a**) were reacted with manganese (III) acetate in acetonitrile at 80 °C for 39 h, **11a** was isolated in a better reaction yield (85%, Table 2, entry 1) than that performed in acetic acid (73%). The results of this reaction with a variety of simple ketones in different solvents are summarized in Table 2 (entries 1–11). In all cases, indole **11** was obtained in a better reaction yield than those performed in acetic acid. This reaction can also be performed with corresponding ketones as solvent and **11** was obtained in a similar (better) result. The regioselectivity of this reaction was also studied. With butanone (**10e**: $R^1$=H, $R^2$=Me), **11e** and **12a** were obtained in 37 and 57% yields, respectively (entry 12). These two products are derived from




**Scheme 1.**

**Table 1.** Free radical reactions between 2-(methylamino)-1,4-naphthoquinone (**1a**) and β-keto esters

| Entry | β-Keto ester | Solvent time | Reaction | Product (yield (%)) | |
|---|---|---|---|---|---|
| 1 | **2a**: $R^1$=*n*-Pr, $R^2$=OEt | $HCO_2H$ | 30 min | **3a** (85) | |
| 2 | **2b**: $R^1$=*i*-Pr, $R^2$=OMe | $HCO_2H$ | 30 min | **3b** (75) | |
| 3 | **2c**: $R^1$=Et, $R^2$=OMe | $HCO_2H$ | 30 min | **3c** (76) | |
| 4 | **2d**: $R^1$=$ClCH_2$, $R^2$=OEt | $HCO_2H$ | 30 min | **3d** (66) | |
| 5 | **2e**: $R^1$=$MeOCH_2$, $R^2$=OMe | $HCO_2H$ | 30 min | **3e** (63) | |
| 6 | **2a**: $R^1$=*n*-Pr, $R^2$=OEt | HOAc | 16 h | **3a** (54) | **4a** (21)[a] |
| 7 | **2a**: $R^1$=*n*-Pr, $R^2$=OEt | $CF_3CH_2OH$ | 16 h | **3a** (12) | **4a** (63) |
| 8 | **2a**: $R^1$=*n*-Pr, $R^2$=OEt | $CH_3CN$ | 16 h | **3a** (13) | **4a** (48) |
| 9 | **2a**: $R^1$=*n*-Pr, $R^2$=OEt | $C_6H_6$ | 16 h | **3a** (8) | **4a** (56) |
| 10 | **2a**: $R^1$=*n*-Pr, $R^2$=OEt | $CHCl_3$ | 16 h | **3a** (8) | **4a** (52) |
| 11 | **2b**: $R^1$=*i*-Pr, $R^2$=OMe | $CF_3CH_2OH$ | 16 h | **3b** (8) | **4b** (79) |
| 12 | **2c**: $R^1$=Et, $R^2$=OMe | $CF_3CH_2OH$ | 16 h | **3c** (11) | **4c** (62) |
| 13 | **2d**: $R^1$=$ClCH_2$, $R^2$=OEt | $CF_3CH_2OH$ | 16 h | **3d** (6) | **4d** (72) |
| 14 | **2e**: $R^1$=$MeOCH_2$, $R^2$=OMe | $CF_3CH_2OH$ | 16 h | | **4e** (73) |

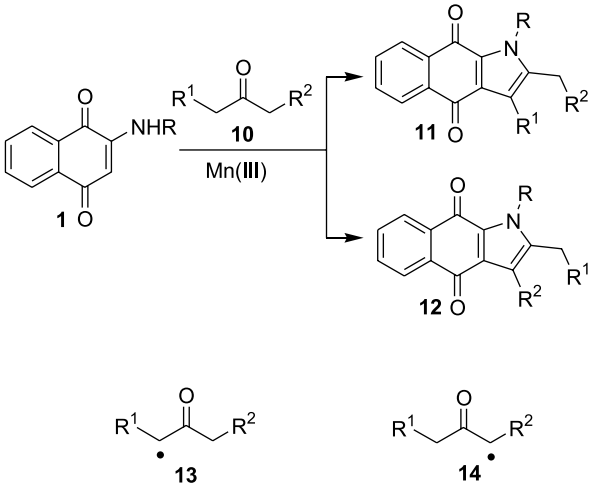
[a] The result has been reported previously.[6h]

**Table 2.** Free radical reactions between 2-(methylamino)-1,4-naphthoquinone (**1a**) and simple ketones

| Entry | Ketone | Solvent | Reaction time | Product (yield (%)) | |
|---|---|---|---|---|---|
| 1 | **10a**: $R^1$=H, $R^2$=H | $CH_3CN$ | 39 h | **11a** (85) | |
| 2 | **10a**: $R^1$=H, $R^2$=H | $C_6H_6$ | 42 h | **11a** (86) | |
| 3 | **10a**: $R^1$=H, $R^2$=H | $CHCl_3$ | 16 h | **11a** (80) | |
| 4 | **10a**: $R^1$=H, $R^2$=H | $HCO_2H$ | 30 min | **11a** (0) | |
| 5 | **10a**: $R^1$=H, $R^2$=H | | 16 h | **11a** (90)[a] | |
| 6 | **10b**: $R^1$=Me, $R^2$=Me | $CH_3CN$ | 41 h | **11b** (72) | |
| 7 | **10b**: $R^1$=Me, $R^2$=Me | | 16 h | **11b** (91)[a] | |
| 8 | **10c**: $R^1$ + $R^2$=$CH_2CH_2CH_2$ | $CH_3CN$ | 16 h | **11c** (90) | |
| 9 | **10c**: $R^1$ + $R^2$=$CH_2CH_2CH_2$ | | 24 h | **11c** (87)[a] | |
| 10 | **10d**: $R^1$ + $R^2$=$CH_2CH_2$ | $CH_3CN$ | 22 h | **11d** (38) | |
| 11 | **10d**: $R^1$ + $R^2$=$CH_2CH_2$ | | 26 h | **11d** (38)[a] | |
| 12 | **10e**: $R^1$=H, $R^2$=Me | $CH_3CN$ | 21 h | **11e** (37) | **12a** (57) |
| 13 | **10f**: $R^1$=H, $R^2$=*i*-Pr | $CH_3CN$ | 41 h | **11f** (70) | **12b** (17) |

[a] The reaction was performed in corresponding ketone.

the intermolecular addition of radical **13a** and **14a**. The regioselectivity increases as the size of $R^2$ increases (entry 13).




(2)

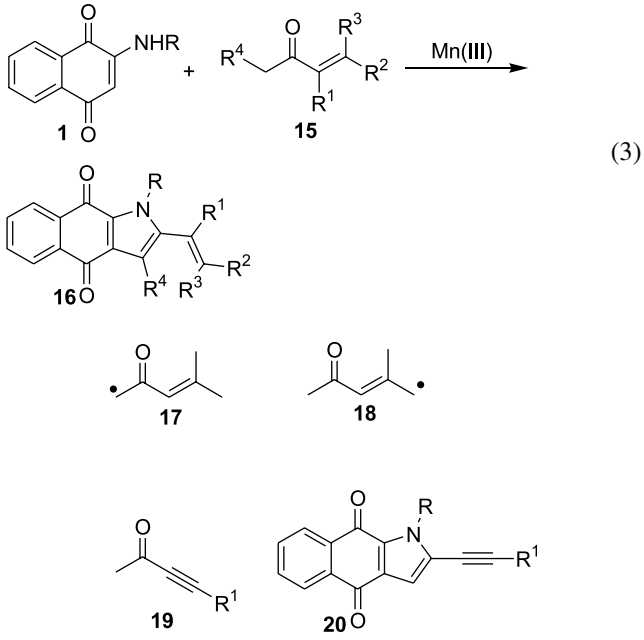
Unsaturated α′-keto radical can be generated regioselectively from the manganese (III) oxidation of α,β-unsaturated ketones.[7] We next studied the free radical reaction of 2-(alkylamino)-1,4-naphthoquinone **1** with α,β-unsaturated ketone **15** (Eq. 3). Treatment of 2-(methylamino)-1,4-naphthoquinone (**1a**) with *trans*-4-phenyl-3-buten-2-one (**15a**) (4 equiv) and manganese (III) acetate (5 equiv) in acetonitrile at 80 °C for 43 h gave indole **16a** in 31% yield (Table 3, entry 1). Using 10 equiv of **15a**, the desired indole **16a** was afforded in 58% yield (entry 2). We also performed this reaction in various solvents. In benzene, the yield of **16a** is 52% (35 h, 80 °C). In $CF_3CH_2OH$, the reaction rate is much slower. After heated at 80 °C for 86 h, the yield of **16a** is 35% based on 71% conversion of **1a**. In acetic acid, it proceeded in a much faster reaction rate (26 h, 45 °C), however, **16a** was obtained in a much poor yield (13%) and an uncharacterized product was also obtained. The results are summarized in Table 3 (entries 1–5). Best yields are obtained in acetonitrile. Indole **16a** was generated via a similar reaction route as shown in Scheme 1 (path a). The scope of this oxidative annulation process with other 4-aryl-3-buten-2-one **15** are also illustrated in Table 3 (entries 6–10). To study the steric effect on the reactivity of enone **15**, we also examined this reaction with **15f** and **15g**. On the reaction of **15f** with **1a**, indole **16f** was produced though in a slower reaction rate. After heated for 71 h, **16f** was obtained in 65% yield (entry 11). With **15g**, indole **16g** was also produced effectively via this oxidative annulation process (entry 12). These observations demonstrate that the bulkiness of substituent $R^4$ has little effect on this reaction. In order to test the regioselectivity of this reaction, butenone **15i** was allowed to react with **1a** and **16i** was obtained as the only product (entry 14). This

**Table 3.** Free radical reactions of 2-(methylamino)-1,4-naphthoquinone (**1a**) and α,β-unsaturated ketones

| Entry | α,β-Unsaturated ketone | Solvent | Reaction time (h) | Product (yield(%)) |
|---|---|---|---|---|
| 1 | **15a**: $R^1$=H, $R^2$=$C_6H_5$, $R^3$=H, $R^4$=H | $CH_3CN$ | 43 | **16a** (31)[a] |
| 2 | **15a**: $R^1$=H, $R^2$=$C_6H_5$, $R^3$=H, $R^4$=H | $CH_3CN$ | 41 | **16a** (58) |
| 3 | **15a**: $R^1$=H, $R^2$=$C_6H_5$, $R^3$=H, $R^4$=H | $C_6H_6$ | 35 | **16a** (52) |
| 4 | **15a**: $R^1$=H, $R^2$=$C_6H_5$, $R^3$=H, $R^4$=H | HOAc | 26 | **16a** (13) |
| 5 | **15a**: $R^1$=H, $R^2$=$C_6H_5$, $R^3$=H, $R^4$=H | $CF_3CH_2OH$ | 86 | **16a** (35)[b] |
| 6 | **15b**: $R^1$=H, $R^2$=4-Cl($C_6H_4$), $R^3$=H, $R^4$=H | $CH_3CN$ | 45 | **16b** (63) |
| 7 | **15b**: $R^1$=H, $R^2$=4-Cl($C_6H_4$), $R^3$=H, $R^4$=H | $C_6H_6$ | 24 | **16b** (39) |
| 8 | **15c**: $R^1$=H, $R^2$=4-$MeO_2C$($C_6H_4$), $R^3$=H, $R^4$=H | $CH_3CN$ | 46 | **16c** (64) |
| 9 | **15d**: $R^1$=H, $R^2$=4-MeO($C_6H_4$), $R^3$=H, $R^4$=H | $CH_3CN$ | 66 | **16d** (37) |
| 10 | **15e**: $R^1$=H, $R^2$=2-thienyl, $R^3$=H, $R^4$=H | $CH_3CN$ | 45 | **16e** (59) |
| 11 | **15f**: $R^1$=H, $R^2$=$C_6H_5$, $R^3$=H, $R^4$=Me | $CH_3CN$ | 71 | **16f** (65) |
| 12 | **15g**: $R^1$=H, $R^2$=$C_6H_5$, $R^3$=H, $R^4$=*i*-Pr | $CH_3CN$ | 64 | **16g** (68) |
| 13 | **15h**: $R^1$=H, $R^2$=$CO_2$Me, $R^3$=H, $R^4$=H | $CH_3CN$ | 17 | **16h** (59) |
| 14 | **15i**: $R^1$=H, $R^2$=Me, $R^3$=Me, $R^4$=H | $CH_3CN$ | 28 | **16i** (50) |
| 15 | **15j**: $R^1$=Me, $R^2$=Me, $R^3$=H, $R^4$=H | $CH_3CN$ | 68 | **16j** (41) |
| 16 | **15k**: $R^1$+$R^2$=$CH_2CH_2CH_2CH_2$, $R^3$=H, $R^4$=H | $CH_3CN$ | 45 | **16k** (32) |
| 17 | **19a**: $R^1$=Ph | $CH_3CN$ | 40 | **20a** (76) |
| 18 | **19b**: $R^1$=Et | $CH_3CN$ | 17 | **20b** (66) |

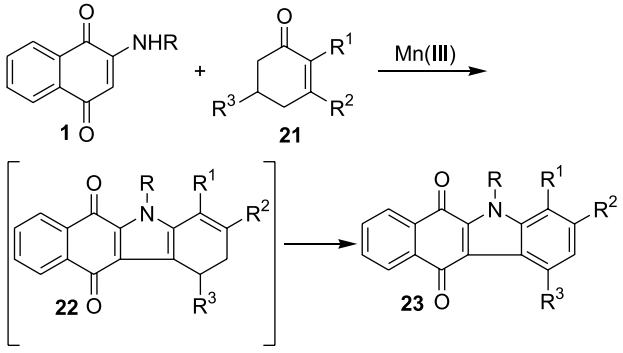
[a] The reaction was conducted with 4 equiv of **15a**.
[b] Based on 71% conversion of **1a**.

product **16i** was formed via the intermolecular addition of an $\alpha'$-keto radical **17** to the quinone ring. No product derived from the addition of a $\gamma$-keto radical **18** to the quinone ring can be detected. Similarly, reaction of enones **15j** and **15k** with manganese (III) acetate gave annulation products **16j** and **16k**, respectively via the addition of a similar $\alpha'$-keto radical (entries 15 and 16). Notably, butynone **19** behaved similarly, giving the corresponding annulation product **20** effectively (entries 17 and 18).




(3)

We also investigated this manganese (III) mediated radical reaction with 2-cyclohexenone **21** (Eq. 4). Reaction of 2-(methylamino)-1,4-naphthoquinone (**1a**) with 3-ethoxy-2-cyclohexenone (**21a**) and manganese (III) acetate in acetonitrile at 80 °C for 36 h provides **23a** in 66% yield (Table 4, entry 1). Carbazole **23a** was produced presumably from the dehydrogenation of **22a** ($R^1$=H, $R^2$=OEt, $R^3$=H), which was formed via a similar reaction route outlined in Scheme 1 (path a). With other 3-ethoxy-2-cyclohexenone **21**, the corresponding carbazole **23** was afforded effectively under identical conditions (entries 3–6). As shown in Table 4, benzene proved superior to acetonitrile as a reaction solvent. With 3-methyl-2-cyclohexenone (**21d**), in contrast to **22a**, the dehydrogenation of **22f** ($R^1$=H, $R^2$=Me, $R^3$=H) proceeded in a much slower reaction rate. After heating in benzene for 16 h, carbazoles **22f** and **23f** were obtained in 45 and 43% yields, respectively (entry 7). The different behavior between **22a** and **22f** suggests that the strong electron donating ethoxy group enhances the dehydrogenation rate of **22a**. Since the separation of **22f** and **23f** was problematic, the reaction mixture of **22f** and **23f** was heated further for another 99 h with another 2 equiv of manganese (III) acetate and **23f** was afforded in 66% yield (entry 8). The reaction yield of **23f** can be improved significantly to 79% by heating the crude product mixture of **22f** and **23f** directly with DDQ for 1 h (entry 9). Other 3-substituted cyclohexenones (**21e**, **21f**) behaved similarly, giving the corresponding product mixture of **22** and **23**, and again this crude product mixture could be converted to **23** effectively by heating further with DDQ (entries 10 and 11). With 3-unsubstituted 2-cyclohexenone **21**, carbazole **23** was formed in poor yield and no **22** could be detected (entries 12–15). When cyclohexenones **24** and **26**, bearing geminal dimethyl group, were allowed to react with **1**, dihydrocarbazoles **25** and **27** were obtained (entries 16 and 17).

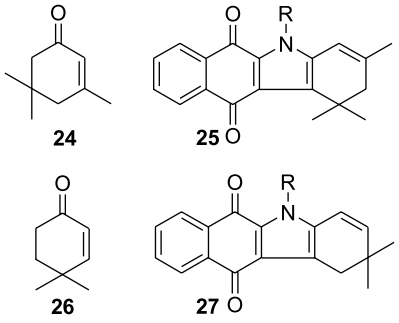



(4)

**Table 4.** Free radical reactions of 2-(alkylamino)-1,4-naphthoquinone **1** and 2-cyclohexenones

| Entry | Quinone | 2-Cyclohexenone | Solvent | Reaction time (h) | Product (yield(%)) | |
|---|---|---|---|---|---|---|
| 1 | **1a**: R=Me | **21a**: $R^1$=H, $R^2$=OEt, $R^3$=H | $CH_3CN$ | 36 | **23a** (66) | |
| 2 | **1b**: R=Et | **21a**: $R^1$=H, $R^2$=OEt, $R^3$=H | $C_6H_6$ | 26 | **23b** (87) | |
| 3 | **1a**: R=Me | **21b**: $R^1$=H, $R^2$=OEt, $R^3$=Me | $CH_3CN$ | 43 | **23c** (47) | |
| 4 | **1b**: R=Et | **21b**: $R^1$=H, $R^2$=OEt, $R^3$=Me | $C_6H_6$ | 24 | **23d** (62) | |
| 5 | **1a**: R=Me | **21c**: $R^1$=H, $R^2$=OEt, $R^3$=Ph | $CH_3CN$ | 49 | **23e** (66) | |
| 6 | **1a**: R=Me | **21c**: $R^1$=H, $R^2$=OEt, $R^3$=Ph | $C_6H_6$ | 39 | **23e** (72) | |
| 7 | **1b**: R=Et | **21d**: $R^1$=H, $R^2$=Me, $R^3$=H | $C_6H_6$ | 16 | **22f** (45) | **23f** (43) |
| 8 | **1b**: R=Et | **21d**: $R^1$=H, $R^2$=Me, $R^3$=H | $C_6H_6$ | 16 | **23f** (66)[a] | |
| 9 | **1b**: R=Et | **21d**: $R^1$=H, $R^2$=Me, $R^3$=H | $C_6H_6$ | 16 | **23f** (79)[b] | |
| 10 | **1a**: R=Me | **21e**: $R^1$=H, $R^2$=Me, $R^3$=Me | $C_6H_6$ | 19 | **23g** (70)[b] | |
| 11 | **1a**: R=Me | **21f**: $R^1$=Cl, $R^2$=Me, $R^3$=H | $C_6H_6$ | 72 | **23h** (56)[b] | |
| 12 | **1a**: R=Me | **21g**: $R^1$=H, $R^2$=H, $R^3$=H | $CH_3CN$ | 53 | **23i** (19) | |
| 13 | **1b**: R=Et | **21g**: $R^1$=H, $R^2$=H, $R^3$=H | $C_6H_6$ | 39 | **23j** (0) | |
| 14 | **1a**: R=Me | **21h**: $R^1$=Cl, $R^2$=H, $R^3$=H | $CH_3CN$ | 68 | **23k** (20) | |
| 15 | **1a**: R=Me | **21h**: $R^1$=Cl, $R^2$=H, $R^3$=H | $C_6H_6$ | 34 | **23k** (23) | |
| 16 | **1a**: R=Me | **24** | $C_6H_6$ | 23 | **25** (76) | |
| 17 | **1b**: R=Et | **26** | $C_6H_6$ | 17 | **27** (57) | |

[a] The reaction mixture was reacted further with another 2 equiv of $Mn(OAc)_3$ for 99 h.
[b] The crude product was heated further with 1 equiv of DDQ for 1 h.

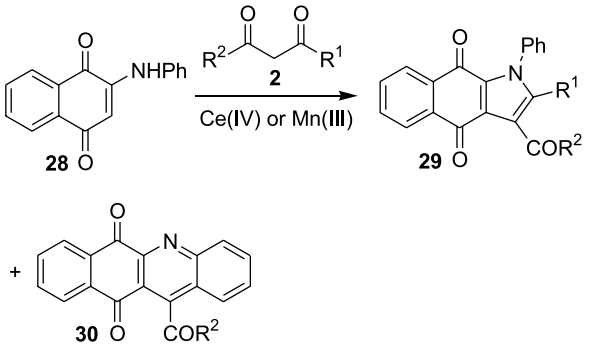



## 2.2. The oxidative free radical reactions of 2-(anilino)-1,4-naphthoquinones

Manganese (III) mediated free radical reaction between 2-(anilino)-1,4-naphthoquinone (**28**) and β-dicarbonyl compound **2** in acetic acid produced **29** and **30** (Eq. 5).[6h] In all cases, acridine **30** is the major product. A possible mechanism for this reaction is shown in Scheme 2. Oxidation of the β-dicarbonyl compound **2** by manganese (III) acetate oxidation produces radical **5**. This radical intermediate **5** undergoes intermolecular addition to the quinone ring followed by oxidation to give **31**, which undergoes either condensation to produce **29** (path a) or oxidation to generate radical **32** (path b). This radical **32** undergoes further intramolecular cyclization followed by aromatization to give **33**. Quinone **33** undergoes retro Claisen condensation followed by aromatization to produce **30**. On the contrary, in the reaction between **28** and **2** mediated by cerium (IV) sulfate, indole **29** was obtained as the only product.[6j] This is presumably due to the Lewis acidity of cerium salt, which enhances the condensation rate of **31** (path a). Based on these results, we expected that the chemoselectivity of this reaction would be affected by the acidity of the solvent. In agreement with this expectation, when 2-(anilino)-1,4-naphthoquinone (**28**) was reacted with ethyl butyrylacetate (**2a**) and manganese (III) acetate in 80% aqueous formic acid at 0 °C, **29a** was obtained as the only product in 66% yield and no trace of **30a** could be isolated (Table 5, entry 1). This can be ascribed to the higher acidity of formic acid, which promotes the condensation of **31**. These reaction conditions were then applied to other β-dicarbonyl compounds and the corresponding **29** was isolated as the only product. Steric hindrance plays an important role in the final outcome of this reaction. In most cases, the reaction yield decreases as the size of $R^1$ and $R^2$ increases (entries 1–6) and the condensation reaction occurs only on the less hindered carbonyl group of the 1,3-diones (entries 7–9). We next studied this reaction in less acidic or neutral solvents. Treatment of **28** with **2a** and manganese (III) acetate in $CF_3CH_2OH$ at 80 °C resulted in the formation of **30a** (64%) and no trace of **29a** could be found (entry 10). This again is presumably due to the rate of condensation (path a) decreases as the acidity of reaction medium decreases and the oxidation of **31** (→**32**) occurred (path b). In attempt to investigate the range of solvents compatible with this reaction, this manganese (III) mediated reaction between **28** and **2a** was performed in various solvents. As shown in Table 5 (entry 10–13), it gave best results in $CF_3CH_2OH$. This investigation was extended to a number of other β-dicarbonyl compounds and the results are also summarized in Table 5 (entries 14–17). It shows the same selectivity, in all cases, acridine **30** was obtained as the only product.

**Table 5.** Free radical reactions between 2-(anilino)-1,4-naphthoquinone (**28**) and β-dicarbonyl compounds

| Entry | β-Dicarbonyl compound | Solvent | Reaction time | Product (yield(%)) |
|---|---|---|---|---|
| 1 | **2a**: $R^1$=*n*-Pr, $R^2$=OEt | $HCO_2H$ | 30 min | **29a** (66) |
| 2 | **2b**: $R^1$=*i*-Pr, $R^2$=Ome | $HCO_2H$ | 3.5 h | **29b** (15) |
| 3 | **2f**: $R^1$=Me, $R^2$=OEt | $HCO_2H$ | 30 min | **29c** (71) |
| 4 | **2g**: $R^1$=Me, $R^2$=Me | $HCO_2H$ | 30 min | **29d** (76) |
| 5 | **2h**: $R^1$=Et, $R^2$=Et | $HCO_2H$ | 30 min | **29e** (77) |
| 6 | **2i**: $R^1$=*i*-Pr, $R^2$=*i*-Pr | $HCO_2H$ | 5 h | **29f** (0) |
| 7 | **2j**: $R^1$=Me, $R^2$=Ph | $HCO_2H$ | 30 min | **29g** (68) |
| 8 | **2k**: $R^1$=Me, $R^2$=*i*-Bu | $HCO_2H$ | 1 h | **29h** (50) |
| 9 | **2l**: $R^1$=Me, $R^2$=*t*-Bu | $HCO_2H$ | 3.5 h | **29i** (17) |
| 10 | **2a**: $R^1$=*n*-Pr, $R^2$=OEt | $CF_3CH_2OH$ | 48 h | **30a** (64) |
| 11 | **2a**: $R^1$=*n*-Pr, $R^2$=OEt | $CH_3CN$ | 42 h | **30a** (46) |
| 12 | **2a**: $R^1$=*n*-Pr, $R^2$=OEt | $C_6H_6$ | 47 h | **30a** (48) |
| 13 | **2a**: $R^1$=*n*-Pr, $R^2$=OEt | $CHCl_3$ | 42 h | **30a** (46) |
| 14 | **2f**: $R^1$=Me, $R^2$=OEt | $CF_3CH_2OH$ | 39 h | **30a** (66) |
| 15 | **2g**: $R^1$=Me, $R^2$=Me | $CF_3CH_2OH$ | 23 h | **30b** (69) |
| 16 | **2h**: $R^1$=Et, $R^2$=Et | $CF_3CH_2OH$ | 23 h | **30c** (56) |
| 17 | **2i**: $R^1$=*i*-Pr, $R^2$=*i*-Pr | $CF_3CH_2OH$ | 23 h | **30d** (57) |

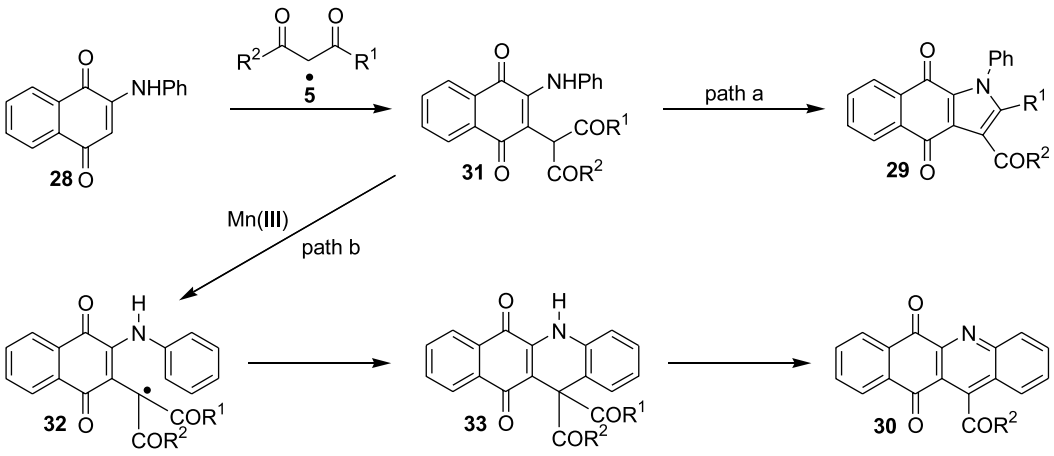



(5)

In conclusion, carbon radical can be generated from the manganese (III) acetate oxidation of carbonyl compounds and it undergoes efficient addition to the C–C double bond of 2-amino-1,4-naphthoquinones. This free radical reaction provides a novel method for the synthesis of benzo[*f*]indole-4,9-diones, benzo[*f*]indole-2,4,9-triones, benzo[*b*]carbazole-6,11-diones and benzo[*b*]acridine-6,11-diones. With β-dicarbonyl compounds, by changing the solvent, these products can be generated in high chemoselectivities. With simple ketones and α,β-unsaturated ketones, these reactions gave better results in neutral solvents.

## 3. Experimental

Melting points are uncorrected. Infrared spectra were taken with a Hitachi 260-30 spectrometer. $^1H$ and $^{13}C$ NMR spectra were recorded on a Bruker AMX-400 or AVANCE 300 spectrometer. Chemical shifts are reported in ppm relative to TMS as internal reference. Elemental analyses were performed with Heraeus CHN-Rapid Analyzer. Analytical thin-layer chromatography was performed with precoated silica gel 60 F-254 plates (0.25 mm thick) from EM Laboratories and visualized by UV. The reaction mixture was purified by column chromatography over EM




**Scheme 2.**

Laboratories silica gel (70–230 mesh). The starting 2-amino-1,4-naphthoquinone **1**,[11] **28**,[4c] enones **21b**,[12a] **21c**,[12a] **21f**[12b] and **21h**[12b] were synthesized according to literature procedure. The spectra data of **3a**,[6j] **3b**,[6j] **3d**,[6h] **3e**,[6j] **4a**,[6h] **4d**,[6h] **11b–f**,[6i] **12a**,[6i] **12b**,[6i] **29a**,[6j] **29c**,[6j] **29d**,[6j] **29g**[6j] and **30a**[6h] have been reported.

### 3.1. Typical experimental procedure for the reaction between 2-(methylamino)-1,4-naphthoquinone (1a) and β-keto esters in formic acid

A mixture of 152 mg (0.81 mmol) of 2-(methylamino)-1,4-naphthoquinone (**1a**), 508 mg (3.22 mmol) of ethyl butyrylacetate (**2a**) and 1.29 g (4.81 mmol) of $Mn(OAc)_3$ in 10 mL of formic acid was stirred at 0 °C for 30 min. 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, 50 mL of saturated aqueous sodium bicarbonate, dried ($Na_2SO_4$), The solvent was evaporated under reduced pressure and the crude product was purified by column chromatography on silica (20 g) using dichloromethane–hexane (2:1) as eluent, followed by crystallization (ethyl acetate–hexane) to give 224 mg (85%) of **3a**.

### 3.2. Typical experimental procedure for the reaction between 2-(methylamino)-1,4-naphthoquinone (1a) and β-keto esters in less acidic or neutral solvent

A mixture of 150 mg (0.80 mmol) of 2-(methylamino)-1,4-naphthoquinone (**1a**), 520 mg (3.29 mmol) of ethyl butyrylacetate (**2a**) and 1.29 g (4.81 mmol) of $Mn(OAc)_3$ in 10 mL of $CF_3CH_2OH$ was heated at 80 °C for 16 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, dried ($Na_2SO_4$), and concentrated in vacuo. The residue was chromatographed over 20 g of silica gel (eluted with 1:15 ethyl acetate–hexane and then 1:12 ethyl acetate–hexane) followed by crystallization (ethyl acetate–hexane) to give 174 mg (63%) of **4a** and 32 mg (12%) of **3a**.

**3.2.1. 2-Ethyl-4,9-dihydro-3-(methoxycarbonyl)-1-methyl-4,9-dioxo-1*H*-benzo[*f*]indole 3c.** Yellow needles; mp 119–120 °C; IR ($CHCl_3$) 1715, 1660, 1600, 1505, 1275 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 1.26 (t, $J$=7.6 Hz, 3H, $CH_3$), 2.89 (q, $J$=7.6 Hz, 2H, $CH_2$), 3.96 (s, 3H, $OCH_3$), 4.07 (s, 3H, $NCH_3$), 7.63–7.70 (m, 2H, ArH), 8.08–8.17 (m, 2H, ArH); $^{13}C$ NMR (100.6 MHz, $CDCl_3$) $\delta$ 13.3 (q), 18.2 (t), 32.8 (q), 52.1 (q), 112.8 (s), 125.6 (s), 126.1 (d), 126.7 (d), 130.5 (s), 132.9 (d), 133.1 (s), 133.3 (d), 133.8 (s), 147.5 (s), 165.0 (s), 176.4 (s), 179.5 (s). Anal. Calcd for $C_{17}H_{15}NO_4$: C, 68.68; H, 5.09; N, 4.71. Found: C, 68.64; H, 5.15; N, 4.71.

**3.2.2. 2,3,4,9-Tetrahydro-3-isopropyl-3-(methoxycarbonyl)-1-methyl-2,4,9-trioxo-1*H*-benzo[*f*]indole 4b.** Orange crystals; mp 153–154 °C; IR ($CHCl_3$) 2975, 1760, 1675, 1595, 1275, 1240 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 1.02 (d, $J$=6.9 Hz, 3H, $CH_3$), 1.03 (d, $J$=6.9 Hz, 3H, $CH_3$), 3.06 (septet, $J$=6.9 Hz, 1H, CH), 3.55 (s, 3H, $NCH_3$), 3.71 (s, 3H, $OCH_3$), 7.73 (td, $J$=7.3, 1.4 Hz, 1H, ArH), 7.78 (td, $J$=7.3, 1.4 Hz, 1H, ArH), 8.09 (dd, $J$=7.3, 1.4 Hz, 1H, ArH), 8.11 (dd, $J$=7.3, 1.4 Hz, 1H, ArH); $^{13}C$ NMR (100.6 MHz, $CDCl_3$) $\delta$ 17.0 (q), 18.8 (q), 28.9 (q), 33.6 (d), 53.1 (q), 64.9 (s), 125.2 (s), 126.3 (d), 126.5 (d), 131.5 (s), 132.3 (s), 133.1 (d), 134.6 (d), 147.6 (s), 166.4 (s), 174.4 (s), 178.3 (s), 178.5 (s). Anal. Calcd for $C_{18}H_{17}NO_5$: C, 66.05; H, 5.23; N, 4.28. Found: C, 65.99; H, 5.26; N, 4.29.

**3.2.3. 3-Ethyl-2,3,4,9-tetrahydro-3-(methoxycarbonyl)-1-methyl-2,4,9-trioxo-1*H*-benzo[*f*]indole 4c.** Yellow crystals; mp 155–156 °C; IR ($CHCl_3$) 1760, 1675, 1600, 1240, 1390 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 0.74 (t, $J$=7.5 Hz, 3H, $CH_3$), 2.40–2.58 (m, 2H, $CH_2$), 3.56 (s, 3H, $NCH_3$), 3.71 (s, 3H, $OCH_3$), 7.74 (td, $J$=7.4, 1.6 Hz, 1H, ArH), 7.79 (td, $J$=7.4, 1.6 Hz, 1H, ArH), 8.09 (dd, $J$=7.4, 1.6 Hz, 1H, ArH), 8.13 (dd, $J$=7.4, 1.6 Hz, 1H, ArH); $^{13}C$ NMR (100.6 MHz, $CDCl_3$) $\delta$ 8.3 (q), 26.3 (t), 29.0 (q), 53.3 (q), 61.0 (s), 125.6 (s), 126.3 (d), 126.5 (d), 131.7 (s), 132.1 (s), 133.2 (d), 134.6 (d), 147.4 (s), 166.7 (s), 174.8 (s), 178.3 (s), 178.4 (s). Anal. Calcd for $C_{17}H_{15}NO_5$: C, 65.17; H, 4.83; N, 4.47. Found: C, 65.10; H, 4.85; N, 4.42.

**3.2.4. 2,3,4,9-Tetrahydro-3-(methoxycarbonyl)-3-(methoxymethyl)-1-methyl-2,4,9-trioxo-1*H*-benzo[*f*]indole 4e.** Yellow crystals; mp 207–208 °C; IR ($CHCl_3$) 3015, 1760, 1730, 1650, 1240 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$ 3.25 (s, 3H, $OCH_3$), 3.55 (s, 3H, $NCH_3$), 3.72 (s, 3H, $OCH_3$), 4.21 (d, $J$=8.6 Hz, 1H, OCH), 4.33 (d, $J$=8.6 Hz, 1H,

OCH), 7.70–7.82 (m, 2H, ArH), 8.05–8.15 (m, 2H, ArH); $^{13}$C NMR (75.5 MHz, $CDCl_3$) $\delta$ 29.2 (q), 53.4 (q), 59.4 (q), 60.8 (s), 72.3 (t), 124.5 (s), 126.1 (d), 126.5 (d), 131.8 (s), 132.2 (s), 133.2 (d), 134.5 (d), 147.9 (s), 164.8 (s), 173.8 (s), 178.4 (s), 178.6 (s). Anal. Calcd for $C_{17}H_{15}NO_6$: C, 62.00; H, 4.59; N, 4.25. Found: C, 62.29; H, 4.63; N, 4.20.

### 3.3. Typical experimental procedure for the reaction between 2-(methylamino)-1,4-naphthoquinone (1a) and simple ketones

A mixture of 118 mg (0.63 mmol) of 2-(methylamino)-1,4-naphthoquinone (**1a**), 375 mg (6.47 mmol) of acetone (**10a**) and 1.03 g (3.84 mmol) of $Mn(OAc)_3$ in 10 mL of $CH_3CN$ was heated at 80 °C for 16 h, followed by the addition of 1.04 g (3.88 mmol) of $Mn(OAc)_3$. The reaction mixture heated for another 23 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, dried ($Na_2SO_4$), The solvent was evaporated under reduced pressure and the crude product was purified by column chromatography on silica (20 g) using dichloromethane–hexane (1:1) as eluent, followed by crystallization (ethyl acetate–hexane) to give 121 mg (85%) of **11a**.

**3.3.1. 4,9-Dihydro-1,2-dimethyl-4,9-dioxo-1*H*-benzo[*f*]indole 11a.** Yellow crystals; mp 236–237 °C; IR ($CHCl_3$) 1650, 1600, 1500, 1485, 1250 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 2.32 (s, 3H, $ArCH_3$), 4.00 (s, 3H, $NCH_3$), 6.52 (s, 1H, ArH), 7.60–7.70 (m, 2H, ArH), 8.09–8.17 (m, 2H, ArH); $^{13}$C NMR (100.6 MHz, $CDCl_3$) $\delta$ 12.2 (q), 32.6 (q), 107.2 (d), 126.28 (d), 126.32 (d), 128.2 (s), 130.6 (s), 132.7 (d), 132.9 (d), 133.5 (s), 134.2 (s), 139.9 (s), 175.6 (s), 181.1 (s). Anal. Calcd for $C_{14}H_{11}NO_2$: C, 74.65; H, 4.92; N, 6.22. Found: C, 74.64; H, 4.94; N, 6.25.

### 3.4. Typical experimental procedure for the reaction between 2-(methylamino)-1,4-naphthoquinone (1a) and α,β-unsaturated ketones

A mixture of 101 mg (0.54 mmol) of 2-(methylamino)-1,4-naphthoquinone (**1a**), 782 mg (5.35 mmol) of *trans*-4-phenyl-3-buten-2-one (**15a**) and 717 mg (2.67 mmol) of $Mn(OAc)_3$ in 10 mL of $CH_3CN$ was heated at 80 °C for 24 h, followed by the addition of 287 mg (1.07 mmol) of $Mn(OAc)_3$. The reaction mixture heated for another 17 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, dried ($Na_2SO_4$), and concentrated in vacuo. The residue was chromatographed over 20 g of silica gel (eluted with 2:1 dichloromethane–hexane) followed by crystallization (ethyl acetate–hexane) to give 97 mg (58%) of **16a**.

### 3.5. Typical experimental procedure for the reaction between 2-(methylamino)-1,4-naphthoquinone (1a) and α,β-unsaturated ketones followed by DDQ oxidation

A mixture of 120 mg (0.60 mmol) of 2-(ethylamino)-1,4-naphthoquinone (**1b**), 658 mg (5.98 mmol) of 3-methyl-2-cyclohexenone (**21d**) and 801 mg (2.99 mmol) of manganese (III) acetate in 10 mL of benzene was heated at 80 °C for 16 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, dried ($Na_2SO_4$). The solvent was evaporated under reduced pressure and the crude product mixture of **22f** and **23f** was then heated at 80 °C with DDQ (136 mg, 0.60 mmol) in 10 mL of benzene for another 1 h. The reaction mixture was diluted with 100 mL of ethyl acetate, washed with three 50 mL portions of water and dried ($Na_2SO_4$). The solvent was evaporated under reduced pressure and the crude product was purified by column chromatography on silica (20 g) using dichloromethane–hexane (2:1) as eluent, followed by crystallization (ethyl acetate–hexane) to give **23f** (135 mg, 79%).

**3.5.1. 4,9-Dihydro-1-methyl-(*E*)-4,9-dioxo-2-styryl-1*H*-benzo[*f*]indole 16a.** Red needles; mp 205–206 °C; IR ($CHCl_3$) 3010, 2955, 1645, 1595, 1470 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 4.11 (s, 3H, $NCH_3$), 6.90 (d, $J$= 16.1 Hz, 1H, =CH), 6.97 (s, 1H, ArH), 7.14 (d, $J$=16.1 Hz, 1H, =CH), 7.28–7.35 (m, 1H, ArH), 7.35–7.42 (m, 2H, ArH), 7.45–7.54 (m, 2H, ArH), 7.54–7.68 (m, 2H, ArH), 8.06–8.17(m, 2H, ArH); $^{13}$C NMR (75.4 MHz, $CDCl_3$) $\delta$ 32.7 (q), 105.4 (d), 114.1 (d), 126.3 (2×d), 126.8 (2×d), 128.6 (s), 128.7 (d), 128.9 (2×d), 130.8 (s), 132.7 (d), 133.1 (d), 133.4 (s), 134.1 (d), 134.5 (s), 136.1 (s), 141.1 (s), 175.5 (s), 180.8 (s). Anal. Calcd for $C_{21}H_{15}NO_2$: C, 80.49; H, 4.82; N, 4.47. Found: C, 80.28; H, 4.83; N, 4.49.

**3.5.2. (*E*)-2-[2-(4-Chlorophenyl)vinyl]-4,9-dihydro-1-methyl-4,9-dioxo-1*H*-benzo[*f*]indole 16b.** Red crystals; mp 264–265 °C; IR ($CHCl_3$) 2930, 1730, 1650, 1595, 1495 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 4.19 (s, 3H, $NCH_3$), 6.96 (d, $J$=16.1 Hz, 1H, =CH), 7.05 (s, 1H, ArH), 7.16 (d, $J$=16.1 Hz, 1H, =CH), 7.36 (d, $J$=8.5 Hz, 2H, ArH), 7.45 (d, $J$=8.5 Hz, 2H, ArH), 7.63–7.72 (m, 2H, ArH), 8.12–8.20 (m, 2H, ArH); $^{13}$C NMR (75.4 MHz, $CDCl_3$) $\delta$ 32.8 (q), 105.6 (d), 114.8 (d), 126.5 (2×d), 127.9 (2×d), 128.7 (s), 129.1 (2×d), 131.0 (s), 132.8 (d), 132.9 (d), 133.2 (d), 133.5 (s), 134.47 (s), 134.54 (s), 134.6 (s), 140.8 (s), 175.7 (s), 181.0 (s). Anal. Calcd for $C_{21}H_{14}ClNO_2$: C, 72.52; H, 4.06; N, 4.03. Found: C, 72.30; H, 4.14; N, 3.98.

**3.5.3. 4,9-Dihydro-(*E*)-2-[2-(4-methoxycarbonylphenyl)-vinyl]-1-methyl-4,9-dioxo-1*H*-benzo[*f*]indole 16c.** Orange needles; mp 208–209 °C; IR ($CHCl_3$) 1720, 1670, 1645, 1410, 1285 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 3.94 (s, 3H, $OCH_3$), 4.20 (s, 3H, $NCH_3$), 7.089 (d, $J$=16.1 Hz, 1H, =CH), 7.093 (s, 1H, ArH), 7.23 (d, $J$=16.1 Hz, 1H, =CH), 7.57 (d, $J$=8.3 Hz, 2H, ArH), 7.62–7.73 (m, 2H, ArH), 8.05 (d, $J$=8.3 Hz, 2H, ArH), 8.14–8.20 (m, 2H, ArH); $^{13}$C NMR (75.4 MHz, $CDCl_3$) $\delta$ 32.8 (q), 52.2 (q), 106.0 (d), 116.6 (d), 126.5 (2×d), 126.6 (2×d), 128.7 (s), 129.9 (s), 130.1(s), 130.17 (2×d), 131.2 (s), 132.7 (d), 133.0 (d), 133.2 (d), 133.4 (s), 134.5 (s), 140.4 (s), 166.6 (s), 175.8 (s), 180.9 (s). Anal. Calcd for $C_{23}H_{17}NO_4$: C, 74.38; H, 4.61; N, 3.77. Found: C, 74.18; H, 4.64; N, 3.70.

**3.5.4. 4,9-Dihydro-(*E*)-2-[2-(4-methoxyphenyl)vinyl]-1-methyl-4,9-dioxo-1*H*-benzo[*f*]indole 16d.** Red needles; mp 207–208 °C; IR ($CHCl_3$) 3010, 2960, 1645, 1510, 1465 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 3.85 (s, 3H, $OCH_3$), 4.16 (s, 3H, $NCH_3$), 6.83 (d, $J$=16.0 Hz, 1H,

=CH), 6.92 (d, $J$=8.7 Hz, 2H, ArH), 7.00 (s, 1H, ArH), 7.16 (d, $J$=16.0 Hz, 1H, =CH), 7.46 (d, $J$=8.7 Hz, 2H, ArH), 7.61–7.70 (m, 2H, ArH), 8.12–8.16 (m, 2H, ArH); $^{13}$C NMR (75.4 MHz, $CDCl_3$) $\delta$ 32.7 (q), 55.4 (q), 105.0 (d), 112.0 (d), 114.3 (2×d), 126.4 (2×d), 128.2 (2×d), 128.8 (s), 128.9 (s), 130.6 (s), 132.7 (d), 133.1 (d), 133.5 (s), 133.9 (d), 134.6 (s), 141.7 (s), 160.2 (s), 175.4 (s), 181.1 (s). Anal. Calcd for $C_{22}H_{17}NO_3$: C, 76.95; H, 4.99; N, 4.08. Found: C, 76.67; H, 5.04; N, 4.02.

**3.5.5. 4,9-Dihydro-1-methyl-4,9-dioxo-(*E*)-2-(2-thieylvinyl)-1*H*-benzo[*f*]indole 16e.** Red needles; mp 215–216 °C; IR ($CHCl_3$) 3015, 2955, 1645, 1595, 1410 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 4.14 (s, 3H, $NCH_3$), 6.74 (d, $J$=15.9 Hz, 1H, =CH), 6.98 (s, 1H, ArH), 7.04 (dd, $J$=4.6, 3.6 Hz, 1H, ArH), 7.14 (d, $J$=3.6 Hz, 1H, ArH), 7.28 (d, $J$=4.6 Hz, 1H, ArH), 7.30 (d, $J$=15.9 Hz, 1H, =CH), 7.60–7.69 (m, 2H, ArH), 8.10–8.16 (m, 2H, ArH); $^{13}$C NMR (75.4 MHz, $CDCl_3$) $\delta$ 32.7 (q), 105.3 (d), 113.5 (d), 125.9 (d), 126.4 (2×d), 127.0 (d), 128.0 (2×d), 128.7 (s), 130.8 (s), 132.8 (d), 133.1 (d), 133.4 (s), 134.6 (s), 140.8 (s), 141.6 (s), 175.5 (s), 180.9 (s). Anal. Calcd for $C_{19}H_{13}NO_2S$: C, 71.45; H, 4.10; N, 4.39. Found: C, 71.41; H, 4.11; N, 4.44.

**3.5.6. 4,9-Dihydro-1,3-dimethyl-4,9-dioxo-(*E*)-2-styryl-1*H*-benzo[*f*]indole 16f.** Red crystals; mp 218–219 °C; IR ($CHCl_3$) 3015, 2950, 1645, 1595, 1495, 1465 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 2.60 (s, 3H, $ArCH_3$), 4.14 (s, 3H, $NCH_3$), 6.93 (d, $J$=16.5 Hz, 1H, =CH), 6.99 (d, $J$=16.5 Hz, 1H, =CH), 7.30–7.37 (m, 1H, ArH), 7.37–7.44 (m, 2H, ArH), 7.49–7.53 (m, 2H, ArH), 7.60–7.68 (m, 2H, ArH), 8.10–8.17 (m, 2H, ArH); $^{13}$C NMR (75.4 MHz, $CDCl_3$) $\delta$ 11.7 (q), 33.5 (q), 115.1 (d), 121.4 (s), 125.7 (s), 126.1 (d), 126.2 (d), 126.6 (2×d), 128.7 (d), 128.9 (2×d), 130.0 (s), 132.76 (d), 132.82 (d), 134.0 (s), 134.3 (s), 135.7 (d), 136.5 (s), 138.1 (s), 175.7 (s), 182.2 (s). Anal. Calcd for $C_{22}H_{17}NO_2$: C, 80.71; H, 5.23; N, 4.28. Found: C, 80.68; H, 5.24; N, 4.29.

**3.5.7. 4,9-Dihydro-3-isopropyl-1-methyl-4,9-dioxo-(*E*)-2-styryl-1*H*-benzo[*f*]indole 16g.** Red needles; mp 165–166 °C; IR ($CHCl_3$) 3010, 1590, 1460, 1410, 1360 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$1.43 (d, $J$=7.1 Hz, 6H, 2×$CH_3$), 3.54 (septet, $J$=7.1 Hz, 1H, CH), 4.11 (s, 3H, $NCH_3$), 6.82 (d, $J$=17.7 Hz, 1H, =CH), 6.96 (d, $J$=17.7 Hz, 1H, =CH), 7.32–7.38 (m, 1H, ArH), 7.39–7.45 (m, 2H, ArH), 7.52–7.56 (m, 2H, ArH), 7.64–7.68 (m, 2H, ArH), 8.12–8.20 (m, 2H, ArH); $^{13}$C NMR (75.4 MHz, $CDCl_3$) $\delta$ 21.1 (2×q), 25.9 (d), 34.3 (q), 115.9 (d), 125.1 (s), 125.9 (d), 126.6 (d), 126.7 (2×d), 128.8 (d), 128.9 (2×d), 131.4 (s), 132.3 (s), 132.7 (d), 132.9 (d), 133.8 (s), 134.3 (s), 136.1 (s), 137.3 (d), 137.6 (s), 176.2 (s), 181.1 (s). Anal. Calcd for $C_{24}H_{21}NO_2$: C, 81.10; H, 5.96; N, 3.94. Found: C, 81.14; H, 6.00; N, 3.91.

**3.5.8. 4,9-Dihydro-(*E*)-2-[2-(methoxycarbonyl)vinyl]-1-methyl-4,9-dioxo-1*H*-benzo[*f*]indole 16h.** Yellow crystals; mp 248–249 °C; IR ($CHCl_3$) 3015, 2955, 1730, 1655, 1440 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 3.84 (s, 3H, $OCH_3$), 4.19 (s, 3H, $NCH_3$), 6.51 (d, $J$=15.8 Hz, 1H, =CH), 7.16 (s, 1H, ArH), 7.65 (d, $J$=15.8 Hz, 1H, =CH), 7.68–7.73 (m, 2H, ArH), 8.12–8.20 (m, 2H, ArH); $^{13}$C NMR (75.4 MHz, $CDCl_3$) $\delta$ 32.9 (q), 52.0 (q), 108.5 (d), 121.4 (d), 126.64 (d),126.66 (d), 128.3 (s), 130.0 (d), 132.4 (s), 133.32 (d), 133.36 (d), 133.40 (s), 134.3 (s), 137.4 (s), 166.6 (s), 176.3 (s), 180.5 (s). Anal. Calcd for $C_{17}H_{13}NO_4$: C, 69.15; H, 4.44; N, 4.74. Found: C, 69.01; H, 4.51; N, 4.72.

**3.5.9. 4,9-Dihydro-1-methyl-2-(2-methyl-1-propenyl)-4,9-dioxo-1*H*-benzo[*f*]indole 16i.** Orange needles; mp 159–160 °C; IR ($CHCl_3$) 3010, 2925, 1650, 1595, 1470 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 1.94 (s, 3H, $CH_3$), 2.00 (s, 3H, $CH_3$), 3.99 (s, 3H, $NCH_3$), 6.01 (s, 1H, =CH), 6.66 (s, 1H, ArH), 7.60–7.68 (m, 2H, ArH), 8.09–8.15 (m, 2H, ArH); $^{13}$C NMR (75.4 MHz, $CDCl_3$) $\delta$ 20.4 (q), 27.1 (q), 32.8 (q), 108.0 (d), 112.4 (d), 126.2 (2×d), 128.1 (s), 129.7 (s), 132.6 (d), 132.9 (d), 133.5 (s), 134.4 (s), 140.3 (s), 143.2 (s), 175.6 (s), 181.1 (s). Anal. Calcd for $C_{17}H_{15}NO_2$: C, 76.96; H, 5.70; N, 5.28. Found: C, 76.93; H, 5.80; N, 5.28.

**3.5.10. 4,9-Dihydro-1-methyl-(*E*)-2-(1-methyl-1-propenyl)-4,9-dioxo-1*H*-benzo[*f*]indole 16j.** Orange needles; mp 101–102 °C; IR ($CHCl_3$) 3010, 1655, 1595, 1475, 1445 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 1.85 (d, $J$=6.5 Hz, 3H, $CH_3$), 1.98 (d, $J$=1.3 Hz, 3H, $CH_3$), 3.99 (s, 3H, $NCH_3$), 5.78 (qq, $J$=6.5, 1.3 Hz, 1H, =CH), 6.58 (s, 1H, ArH), 7.61–7.70 (m, 2H, ArH), 8.10–8.18 (m, 2H, ArH); $^{13}$C NMR (75.4 MHz, $CDCl_3$) $\delta$ 14.2 (q), 16.9 (q), 34.5 (q), 106.7 (d), 126.0 (s), 126.30 (d), 126.34 (d), 128.2 (s), 130.1 (d), 130.7 (s), 132.7 (d), 133.0 (d), 133.6 (s), 134.4 (s), 147.2 (s), 175.9 (s), 181.2 (s). Anal. Calcd for $C_{17}H_{15}NO_2$: C, 76.96; H, 5.70; N, 5.28. Found: C, 76.94; H, 5.77; N, 5.30.

**3.5.11. 2-(1-Cyclohexenyl)-4,9-dihydro-1-methyl-4,9-dioxo-1*H*-benzo[*f*]indole 16k.** Yellow needles; mp 155–156 °C; IR ($CHCl_3$) 3010, 2940, 1650, 1455, 1340 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 1.67–1.74 (m, 2H, $CH_2$), 1.74–1.83 (m, 2H, $CH_2$), 2.22–2.31 (m, 4H, $CH_2$), 4.00 (s, 3H, $NCH_3$), 5.96 (s, 1H, =CH), 6.58 (s, 1H, ArH), 7.61–7.67 (m, 2H, ArH), 8.09–8.15 (m, 2H, ArH); $^{13}$C NMR (75.4 MHz, $CDCl_3$) $\delta$ 21.6 (t), 22.5 (t), 25.5 (t), 29.0 (t), 34.5 (q), 106.5 (d), 126.2 (2×d), 128.06 (s), 128.09 (s), 130.7 (s), 131.9 (d), 132.6 (d), 132.9 (d), 133.5 (s), 134.3 (s), 145.8 (s), 175.7 (s), 181.1 (s). Anal. Calcd for $C_{19}H_{17}NO_2$: C, 78.33; H, 5.88; N, 4.81. Found: C, 78.29; H, 5.90; N, 4.82.

**3.5.12. 4,9-Dihydro-1-methyl-4,9-dioxo-2-(phenylethynyl)-1*H*-benzo[*f*]indole 20a.** Orange needles; mp 193–194 °C; IR ($CHCl_3$) 3010, 1660, 1595, 1480, 1465 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 4.15 (s, 3H, $NCH_3$), 6.97 (s, 1H, ArH), 7.36–7.41 (m, 3H, ArH), 7.52–7.57 (m, 2H, ArH), 7.63–7.68 (m, 2H, ArH), 8.09–8.18 (m, 2H, ArH); $^{13}$C NMR (75.4 MHz, $CDCl_3$) $\delta$ 34.3 (q), 78.5 (s), 97.9 (s), 112.8 (d), 121.6 (s), 125.2 (s), 126.4 (d), 126.6 (d), 127.8 (s), 128.5 (2×d), 129.3 (d), 131.0 (s), 131.6 (2×d), 133.1 (2×d), 133.5 (s), 134.0 (s), 175.6 (s), 180.3 (s). Anal. Calcd for $C_{21}H_{13}NO_2$: C, 81.01; H, 4.21; N, 4.50. Found: C, 80.94; H, 4.27; N, 4.50.

**3.5.13. 2-(Butyn-1-yl)-4,9-dihydro-1-methyl-4,9-dioxo-1*H*-benzo[*f*]indole 20b.** Yellow needles; mp 192–193 °C; IR ($CHCl_3$) 3010, 2990, 1660, 1595, 1465 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 1.28 (t, $J$=7.5 Hz, 3H, $CH_3$), 2.51 (q, $J$=7.5 Hz, 2H, $CH_2$), 4.05 (d, $J$=1.9 Hz, 3H, $NCH_3$), 6.80 (d, $J$=1.9 Hz,1H, ArH), 7.61–7.68 (m, 2H, ArH),

8.07–8.16 (m, 2H, ArH); $^{13}$C NMR (75.4 MHz, $CDCl_3$) $\delta$ 13.3 (t), 13.5 (q), 34.1 (q), 69.5 (s), 101.1 (s), 111.9 (d), 126.0 (s), 126.4 (d), 126.5 (d), 127.6 (s), 130.4 (s), 132.95 (d), 133.02 (d), 133.6 (s), 134.0 (s), 175.5 (s), 180.4 (s). Anal. Calcd for $C_{17}H_{13}NO_2$: C, 77.55; H, 4.98; N, 5.32. Found: C, 77.22; H, 5.09; N, 5.30.

**3.5.14. 5-Ethyl-1,2,6,11-tetrahydro-3-methyl-6,11-dioxo-5*H*-benzo[*b*]carbazole 22f.** Red crystals; mp 195–196 °C; IR($CHCl_3$) 2985, 2930, 1635, 1595, 1575, 1475 cm$^{-1}$; $^1$H NMR(400 MHz, $CDCl_3$) $\delta$ 1.40 (t, $J$=7.2 Hz, 3H, $CH_3$), 1.97 (s, 3H, $CH_3$), 2.39 (t, $J$=8.7 Hz, 2H, $CH_2$), 3.08 (t, $J$=8.7 Hz, 2H, $CH_2$), 4.46 (q, $J$=7.2 Hz, 2H, $NCH_2$), 6.15 (s, 1H, =CH), 7.56–7.66 (m, 2H, ArH), 8.06–8.13 (m, 2H, ArH); $^{13}$C NMR (75.4 MHz, $CDCl_3$) $\delta$ 15.9 (q), 20.1 (t), 24.3 (q), 29.5 (t), 40.2 (t), 110.2 (d), 118.7 (s), 124.6 (s), 125.9 (2×d), 128.1 (s), 132.1 (d), 132.8 (d), 133.9 (s), 134.9 (s), 138.5 (s), 143.7 (s), 174.0 (s), 182.4 (s). Anal. Calcd for $C_{19}H_{17}NO_2$: C, 78.33; H, 5.88; N, 4.81. Found: C, 78.32; H, 5.89; N, 4.84.

**3.5.15. 3-Ethoxy-6,11-dihydro-5-methyl-6,11-dioxo-5*H*-benzo[*b*]carbazole 23a.** Orange needles; mp 233–234 °C; IR ($CHCl_3$) 2990, 1655, 1625, 1595, 1480 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 1.48 (t, $J$=7.0 Hz, 3H, $CH_3$), 4.11 (q, $J$=7.0 Hz, 2H, $OCH_2$), 4.18 (s, 3H, $NCH_3$), 6.75 (d, $J$=2.1 Hz, 1H, ArH), 7.01 (dd, $J$=8.9, 2.1 Hz, 1H, ArH), 7.62–7.72 (m, 2H, ArH), 8.10–8.20 (m, 2H, ArH), 8.27 (d, $J$=8.9 Hz, 1H, ArH); $^{13}$C NMR (75.4 MHz, $CDCl_3$) $\delta$ 14.8 (q), 31.9 (q), 63.9 (t), 93.2 (d), 116.0 (d), 118.0 (s), 119.3 (s), 124.6 (d), 126.1 (d), 126.3 (d), 132.7 (d), 133.4 (d), 133.7 (s), 134.0 (s), 134.5(s), 141.5 (s), 159.6 (s), 178.4 (s), 181.3 (s). Anal. Calcd for $C_{19}H_{15}NO_3$: C, 74.74; H, 4.95; N, 4.59. Found: C, 74.77; H, 4.91; N, 4.57.

**3.5.16. 3-Ethoxy-5-ethyl-6,11-dihydro-6,11-dioxo-5*H*-benzo[*b*]carbazole 23b.** Orange needles; mp 190–191 °C; IR ($CHCl_3$) 2990, 1655, 1625, 1505, 1475 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 1.43 (t, $J$=7.2 Hz, 3H, $CH_3$), 1.44 (t, $J$=7.0 Hz, 3H, $CH_3$), 4.03 (q, $J$=7.0 Hz, 2H, $OCH_2$), 4.60 (q, $J$=7.2 Hz, 2H, $NCH_2$), 6.66 (d, $J$=2.1 Hz, 1H, ArH), 6.92 (dd, $J$=8.8, 2.1 Hz, 1H, ArH), 7.60 (td, $J$=7.2, 1.7 Hz, 1H, ArH), 7.64 (td, $J$=7.2, 1.7 Hz, 1H, ArH), 8.05 (dd, $J$=7.2, 1.7 Hz, 1H, ArH), 8.10 (dd, $J$=7.2, 1.7 Hz, 1H, ArH), 8.19 (d, $J$=8.8 Hz, 1H, ArH); $^{13}$C NMR (75.4 MHz, $CDCl_3$) $\delta$ 14.7 (q), 14.9 (q), 40.1 (t), 63.7 (t), 93.1 (d), 115.6 (d), 118.0 (s), 119.2 (s), 124.5 (d), 125.9 (d), 126.1 (d), 132.6 (d), 133.2 (d), 133.6 (s), 133.7 (s), 133.8 (s), 140.3 (s), 159.3 (s), 177.8 (s), 181.2 (s). Anal. Calcd for $C_{20}H_{17}NO_3$: C, 75.22; H, 5.37; N, 4.39. Found: C, 75.19; H, 5.42; N, 4.37.

**3.5.17. 3-Ethoxy-6,11-dihydro-1,5-dimethyl-6,11-dioxo-5*H*-benzo[*b*]carbazole 23c.** Red needles; mp 227–228 °C; IR ($CHCl_3$) 2925, 1655, 1615, 1595, 1495 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 1.47 (t, $J$=6.9 Hz, 3H, $CH_3$), 2.94 (s, 3H, $ArCH_3$), 4.08 (q, $J$=6.9 Hz, 2H, $OCH_2$), 4.16 (s, 3H, $NCH_3$), 6.53 (s, 1H, ArH), 6.75 (s, 1H, ArH), 7.59–7.69 (m, 2H, ArH), 8.04–8.17 (m, 2H, ArH); $^{13}$C NMR (75.4 MHz, $CDCl_3$) $\delta$ 14.8 (q), 23.7 (q), 32.1 (q), 63.7 (t), 90.3 (d), 117.2 (d), 118.0 (s), 120.7 (s), 125.7 (d), 126.5 (d), 132.4 (d), 133.0 (s), 133.4 (d), 134.4 (s), 134.9 (s), 136.8 (s), 142.3 (s), 159.2 (s), 178.7 (s), 180.1 (s). Anal. Calcd for $C_{20}H_{17}NO_3$: C, 75.22; H, 5.37; N, 4.39. Found: C, 75.07; H, 5.39; N, 4.40.

**3.5.18. 3-Ethoxy-5-ethyl-6,11-dihydro-1-methyl-6,11-dioxo-5*H*-benzo[*b*]carbazole 23d.** Red crystals; mp 168–169 °C; IR ($CHCl_3$) 2985, 2930, 1655, 1615, 1595, 1495 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 1.45 (t, $J$=7.2 Hz, 3H, $CH_3$), 1.47 (t, $J$=7.0 Hz, 3H, $CH_3$), 2.95 (s, 3H, $ArCH_3$), 4.09 (q, $J$=7.0 Hz, 2H, $OCH_2$), 4.70 (q, $J$=7.2 Hz, 2H, $NCH_2$), 6.58 (d, $J$=2.0 Hz, 1H, ArH), 6.74–6.80 (m, 1H, ArH), 7.63 (td, $J$=7.3, 1.6 Hz, 1H, ArH), 7.67 (td, $J$=7.3, 1.6 Hz, 1H, ArH), 8.09 (dd, $J$=7.3, 1.6 Hz, 1H, ArH), 8.15 (dd, $J$=7.3, 1.6 Hz, 1H, ArH); $^{13}$C NMR (75.4 MHz, $CDCl_3$) $\delta$ 14.7 (q), 14.8 (q), 23.7 (q), 40.2 (t), 63.7 (t), 90.3 (d), 117.0 (d), 118.3 (s), 120.9 (s), 125.7 (d), 126.5 (d), 132.4 (d), 133.0 (s), 133.4 (d), 134.36 (s), 134.38 (s), 136.9 (s), 141.2 (s), 159.2 (s), 178.3 (s), 180.2 (s). Anal. Calcd for $C_{21}H_{19}NO_3$: C, 75.66; H, 5.74; N, 4.20. Found: C, 75.45; H, 5.77; N, 4.15.

**3.5.19. 3-Ethoxy-6,11-dihydro-5-methyl-6,11-dioxo-1-phenyl-5*H*-benzo[*b*]carbazole 23e.** Red crystals; mp 246–247 °C; IR ($CHCl_3$) 3010, 1655, 1615, 1495, 1480 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 1.46 (t, $J$=7.0 Hz, 3H, $CH_3$), 4.12 (q, $J$=7.0 Hz, 2H, $OCH_2$), 4.24 (s, 3H, $NCH_3$), 6.77 (d, $J$=2.0 Hz, 1H, ArH), 6.93 (d, $J$=2.0 Hz, 1H, ArH), 7.35–7.40 (m, 2H, ArH), 7.43–7.48 (m, 3H, ArH), 7.57–7.62 (m, 2H, ArH), 7.95–7.99 (m, 1H, ArH), 8.06–8.11 (m, 1H, ArH); $^{13}$C NMR (75.4 MHz, $CDCl_3$) $\delta$ 14.8 (q), 32.2 (q), 64.0 (t), 92.3 (d), 116.2 (s), 117.6 (d), 120.2 (s), 125.7 (d), 126.7 (d), 127.2 (d), 127.4 (2×d), 128.8 (2×d), 132.2 (d), 132.9 (s), 133.4 (d), 134.5 (s), 135.5 (s), 140.3 (s), 142.1 (s), 142.4 (s), 158.8 (s), 178.8 (s), 178.9 (s). Anal. Calcd for $C_{25}H_{19}NO_3$: C, 78.72; H, 5.02; N, 3.67. Found: C, 78.71; H, 5.11; N, 3.60.

**3.5.20. 5-Ethyl-6,11-dihydro-3-methyl-6,11-dioxo-5*H*-benzo[*b*]carbazole 23f.** Orange crystals; mp 223–224 °C; IR ($CHCl_3$) 2930, 1655, 1625, 1595, 1475 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 1.48 (t, $J$=7.1 Hz, 3H, $CH_3$), 2.50 (s, 3H, $ArCH_3$), 4.72 (q, $J$=7.1 Hz, 2H, $NCH_2$), 7.20 (d, $J$=8.1 Hz, 1H, ArH), 7.21 (s, 1H, ArH), 7.63–7.72 (m, 2H, ArH), 8.13 (d, $J$=7.2 Hz, 1H, ArH), 8.18 (d, $J$=7.2 Hz, 1H, ArH), 8.29 (d, $J$=8.1 Hz, 1H, ArH); $^{13}$C NMR (75.4 MHz, $CDCl_3$) $\delta$ 15.2 (q), 22.3 (q), 40.1 (t), 110.4 (d), 119.1(s), 122.0 (s), 123.5 (d), 126.2 (d), 126.3 (d), 126.6 (d), 132.7 (d), 133.6 (d), 133.7 (s), 134.12 (s), 134.13 (s), 137.8 (s), 139.5 (s), 178.7 (s), 181.2 (s). Anal. Calcd for $C_{19}H_{15}NO_2$: C, 78.87; H, 5.23; N, 4.84. Found: C, 78.86; H, 5.25; N, 4.84.

**3.5.21. 6,11-Dihydro-1,3,5-trimethyl-6,11-dioxo-5*H*-benzo[*b*]carbazole 23g.** Orange needles; mp 247–248 °C; IR ($CHCl_3$) 3010, 1655, 1620, 1595, 1495, 1480 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 2.43 (s, 3H, $ArCH_3$), 2.96 (s, 3H, $ArCH_3$), 4.18 (s, 3H, $NCH_3$), 6.94 (s, 1H, ArH), 7.00 (s, 1H, ArH), 7.60–7.73 (m, 2H, ArH), 8.10 (d, $J$=7.3 Hz, 1H, ArH), 8.17 (d, $J$=7.3 Hz, 1H, ArH); $^{13}$C NMR (75.4 MHz, $CDCl_3$) $\delta$ 21.9 (q), 23.5 (q), 32.1 (q), 107.8 (d), 120.3 (s), 121.6 (s), 125.7 (d), 126.6 (d), 128.2 (d), 132.4 (d), 133.0 (s), 133.6 (d), 134.5 (s), 135.1 (s), 135.3 (s), 137.8 (s), 141.3 (s), 179.3 (s), 180.0 (s). Anal. Calcd for $C_{19}H_{15}NO_2$: C, 78.87; H, 5.23; N, 4.84. Found: C, 78.92; H, 5.28; N, 4.87.

**3.5.22. 4-Chloro-6,11-dihydro-3,5-dimethyl-6,11-dioxo-5*H*-benzo[*b*]carbazole 23h.** Orange needles; mp 269–270 °C; IR ($CHCl_3$) 3065, 2915, 1660, 1520, 1465, 1250 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 2.52 (s, 3H, $ArCH_3$), 4.70 (s, 3H, $NCH_3$), 7.25 (d, $J$=8.2 Hz, 1H, ArH), 7.65–7.79 (m, 2H, ArH), 8.12–8.25 (m, 2H, ArH), 8.31 (d, $J$=8.2 Hz, 1H, ArH); $^{13}C$ NMR (75.4 MHz, $CDCl_3$) $\delta$ 20.7 (q), 35.5 (q), 118.2 (s), 118.9 (s), 121.7 (d), 125.1 (s), 126.1 (d), 126.7 (d), 127.8 (d), 131.7 (s), 133.0 (d), 133.7 (d+s), 135.5 (s), 136.1 (s), 136.5 (s), 179.0 (s), 181.1 (s). Anal. Calcd for $C_{18}H_{12}ClNO_2$: C, 69.80; H, 3.90; N, 4.52. Found: C, 69.67; H, 3.97; N, 4.52.

**3.5.23. 6,11-Dihydro-5-methyl-6,11-dioxo-5*H*-benzo[*b*]-carbazole 23i.** Yellow needles; mp 213–214 °C; IR ($CHCl_3$) 3015, 2925, 1660, 1595, 1480 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 4.19 (s, 3H, $NCH_3$), 7.30–7.45 (m, 3H, ArH), 7.64 (td, $J$=7.4, 1.5 Hz, 1H, ArH), 7.69 (td, $J$=7.4, 1.5 Hz, 1H, ArH), 8.10 (dd, $J$=7.4, 1.5 Hz, 1H, ArH), 8.16 (dd, $J$=7.4, 1.5 Hz, 1H, ArH), 8.38 (d, $J$=8.0 Hz, 1H, ArH); $^{13}C$ NMR (75.4 MHz, $CDCl_3$) $\delta$ 31.9 (q), 110.7 (d), 118.6 (s), 123.7 (d), 123.8 (s), 124.4 (d), 126.1 (d), 126.3 (d), 127.1 (d), 132.7 (d), 133.4 (s), 133.6 (d), 134.0 (s), 135.0 (s), 139.8 (s), 179.0 (s), 180.9 (s). Anal. Calcd for $C_{17}H_{11}NO_2$: C, 78.15; H, 4.24; N, 5.36. Found: C, 78.16; H, 4.25; N, 5.36.

**3.5.24. 4-Chloro-6,11-dihydro-5-methyl-6,11-dioxo-5*H*-benzo[*b*]carbazole 23k.** Yellow needles; mp 225–226 °C; IR ($CHCl_3$) 3015, 2925, 1665, 1600, 1470 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 4.62 (s, 3H, $NCH_3$), 7.21 (t, $J$=7.8 Hz, 1H, ArH), 7.34 (d, $J$=7.8 Hz, 1H, ArH), 7.63–7.74 (m, 2H, ArH), 8.07–8.18 (m, 2H, ArH), 8.37 (d, $J$=7.8 Hz, 1H, ArH); $^{13}C$ NMR (75.4 MHz, $CDCl_3$) $\delta$ 35.1 (q), 118.5 (s), 118.7 (s), 122.5 (d), 124.8 (d), 126.1 (d), 126.6 (d), 126.8 (s), 129.0 (d), 132.9 (d), 133.5 (s), 133.6 (s), 133.8 (d), 135.2 (s), 135.7 (s), 178.9 (s), 180.7 (s). Anal. Calcd for $C_{17}H_{10}ClNO_2$: C, 69.05; H, 3.41; N, 4.74. Found: C, 68.82; H, 3.37; N, 4.71.

**3.5.25. 1,2,6,11-Tetrahydro-1,1,3,5-tetramethyl-6,11-dioxo-5*H*-benzo[*b*]carbazole 25.** Red needles; mp 152–153 °C; IR ($CHCl_3$) 3010, 2915, 1640, 1590, 1410 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 1.44 (s, 6H, 2×$CH_3$), 1.98 (s, 3H, $CH_3$), 2.28 (s, 2H, $CH_2$), 4.03 (s, 3H, $NCH_3$), 6.19 (s, 1H, =CH), 7.59–7.64 (m, 2H, ArH), 8.07–8.13 (m, 2H, ArH); $^{13}C$ NMR (75.4 MHz, $CDCl_3$) $\delta$ 24.2 (q), 27.7 (2×q), 32.5 (q), 33.1 (s), 47.5 (t), 109.4 (d), 124.7 (s), 125.6 (d), 126.4 (d), 127.6 (s), 130.0 (s), 132.4 (d), 132.6 (d), 134.1 (s), 134.2 (s), 138.7 (s), 142.6 (s), 175.1 (s), 181.3 (s). Anal. Calcd for $C_{20}H_{19}NO_2$: C, 78.66; H, 6.27; N, 4.59. Found: C, 78.70; H, 6.27; N, 4.62.

**3.5.26. 5-Ethyl-1,2,6,11-tetrahydro-2,2-dimethyl-6,11-dioxo-5*H*-benzo[*b*]carbazole 27.** Orange crystals; mp 142–143 °C; IR ($CHCl_3$) 2970, 2930, 1640, 1595, 1480 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 1.14 (s, 6H, 2×$CH_3$), 1.42 (t, $J$=7.2 Hz, 3H, $CH_3$), 3.01 (s, 2H, $CH_2$), 4.52 (q, $J$=7.2 Hz, 2H, $NCH_2$), 5.94 (d, $J$=10.0 Hz, 1H, =CH), 6.32 (d, $J$=10.0 Hz, 1H, =CH), 7.60–7.70 (m, 2H, ArH), 8.09–8.17 (m, 2H, ArH); $^{13}C$ NMR (75.4 MHz, $CDCl_3$) $\delta$ 16.1 (q), 28.5 (q), 28.6 (q), 33.6 (s), 34.9 (t), 40.5 (t), 112.3 (d), 120.0 (s), 125.3 (s), 126.1 (2×d), 128.8 (s), 132.4 (d), 132.9 (d), 133.8 (s), 134.8 (s), 136.5 (s), 144.0 (d), 174.6 (s), 182.4 (s). Anal. Calcd for $C_{20}H_{19}NO_2$: C, 78.66; H, 6.27; N, 4.59. Found: C, 78.25; H, 6.28; N, 4.55.

### 3.6. Typical experimental procedure for the reaction between 2-(anilino)-1,4-naphthoquinone (28) and β-dicarbonyl compounds in formic acid

A mixture of 151 mg (0.61 mmol) of 2-(anilino)-1,4-naphthoquinone (**28**), 383 mg (2.42 mmol) of ethyl butyrylacetate (**2a**) and 646 mg (2.41 mmol) of $Mn(OAc)_3$ in 10 mL of 80% aqueous formic acid was stirred at 0 °C for 30 min. 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, 50 mL of saturated aqueous 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) followed by crystallization (ethyl acetate–hexane) to give 155 mg (66%) of **29a**.

**3.6.1. 4,9-Dihydro-2-isopropyl-3-(methoxycarbonyl)-4,9-dioxo-1-phenyl-1*H*-benzo[*f*]indole 29b.** Yellow powders; mp 210–211 °C; IR ($CHCl_3$) 1730, 1665, 1595, 1290, 1240 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 1.24 (d, $J$=7.1 Hz, 6H, 2×$CH_3$), 2.81 (septet, $J$=7.1 Hz, 1H, CH), 4.03 (s, 3H, $OCH_3$), 7.28–7.34 (m, 2H, ArH), 7.55–7.60 (m, 3H, ArH), 7.62 (td, $J$=7.2, 1.6 Hz, 1H, ArH), 7.66 (td, $J$=7.2, 1.6 Hz, 1H, ArH), 7.94–7.99 (m, 1H, ArH), 8.13 (dd, $J$=7.2, 1.6 Hz, 1H, ArH); $^{13}C$ NMR (100.6 MHz, $CDCl_3$) $\delta$ 21.4 (2×q), 26.1 (d), 52.7 (q), 113.2 (s), 125.9 (s), 126.3 (d), 126.5 (d), 127.5 (2×d), 129.5 (2×d), 129.7 (d), 130.0 (s), 133.2 (2×d), 133.3 (s), 133.4 (s), 136.8 (s), 148.4 (s), 166.4 (s), 174.6 (s), 180.1 (s). Anal. Calcd for $C_{23}H_{19}NO_4$: C, 73.98; H, 5.13; N, 3.75. Found: C, 74.04; H, 5.18; N, 3.74.

**3.6.2. 2-Ethyl-4,9-dihydro-4,9-dioxo-1-phenyl-3-propionyl-1*H*-benzo[*f*]indole 29e.** Yellow powders; mp 120–121 °C; IR ($CHCl_3$) 1660, 1600, 1495, 1465, 1270 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 1.02 (t, $J$=7.5 Hz, 3H, $CH_3$), 1.26 (t, $J$=7.3 Hz, 3H, $CH_3$), 2.56 (q, $J$=7.5 Hz, 2H, $CH_2$), 3.16 (q, $J$=7.3 Hz, 2H, $CH_2$), 7.25–7.35 (m, 2H, ArH), 7.54–7.61 (m, 3H, ArH), 7.64 (td, $J$=7.6, 1.4 Hz, 1H, ArH), 7.68 (td, $J$=7.6, 1.4 Hz, 1H, ArH), 7.98 (dd, $J$=7.6, 1.4 Hz, 1H, ArH), 8.16 (dd, $J$=7.6, 1.4 Hz, 1H, ArH); $^{13}C$ NMR (100.6 MHz, $CDCl_3$) $\delta$ 8.6 (q), 14.4 (q), 18.3 (t), 37.0 (t), 122.2 (s), 125.2 (s), 126.2 (d), 126.7 (d), 127.3 (2×d), 129.5 (2×d), 129.6 (d), 130.8 (s), 133.2 (s), 133.3 (2×d), 133.5 (s), 136.8 (s), 147.2 (s), 174.9 (s), 181.0 (s), 202.8 (s). Anal. Calcd for $C_{23}H_{19}NO_3$: C, 77.29; H, 5.36; N, 3.92. Found: C, 77.02; H, 5.35; N, 3.97.

**3.6.3. 4,9-Dihydro-3-isovaleryl-2-methyl-4,9-dioxo-1-phenyl-1*H*-benzo[*f*]indole 29h.** Pale yellow powders; mp 151–152 °C; IR ($CHCl_3$) 2960, 1660, 1595, 1500, 1285 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 1.01 (d, $J$=6.8 Hz, 6H, 2×$CH_3$), 2.16 (s, 3H, $ArCH_3$), 2.27 (septet, $J$=6.8 Hz, 1H, CH), 3.08 (d, $J$=6.8 Hz, 2H, $CH_2$), 7.27–7.32 (m, 2H, ArH), 7.55–7.60 (m, 3H, ArH), 7.64 (td, $J$=7.4, 1.5 Hz, 1H, ArH), 7.69 (td, $J$=7.4, 1.5 Hz, 1H, ArH), 7.99 (dd, $J$=7.4, 1.5 Hz, 1H, ArH), 8.18 (dd, $J$=7.4, 1.5 Hz, 1H, ArH); $^{13}C$ NMR (100.6 MHz, $CDCl_3$) $\delta$ 11.6 (q), 22.7

(2×q), 25.4 (d), 52.5 (t), 123.1 (s), 125.0 (s), 126.2 (d), 126.8 (d), 127.1 (2×d), 129.6 (3×d), 130.9 (s), 133.1 (s), 133.27 (d), 133.31 (d), 133.5 (s), 136.9 (s), 141.8 (s), 174.9 (s), 180.8 (s), 202.2 (s). Anal. Calcd for $C_{24}H_{21}NO_3$: C, 77.61; H, 5.70; N, 3.77. Found: C, 77.56; H, 5.77; N, 3.73.

**3.6.4. 4,9-Dihydro-2-methyl-4,9-dioxo-1-phenyl-3-pivaloyl-1*H*-benzo[*f*]indole 29i.** Yellow powders; mp 155–156 °C; IR ($CHCl_3$) 1660, 1595, 1505, 1430, 1280 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 1.34 (s, 9H, 3×$CH_3$), 2.03 (s, 3H, Ar$CH_3$), 7.29–7.33 (m, 2H, ArH), 7.54–7.60 (m, 3H, ArH), 7.63 (td, $J$=7.4, 2.0 Hz, 1H, ArH), 7.66 (td, $J$=7.4, 2.0 Hz, 1H, ArH), 7.98–8.19 (m, 1H, ArH), 8.14–8.56 (m, 1H, ArH); $^{13}C$ NMR (100.6 MHz, $CDCl_3$) $\delta$ 11.6 (q), 27.1 (3×q), 45.9 (s), 122.4 (s), 126.2 (s), 126.4 (d), 126.5 (d), 127.2 (2×d), 129.5 (3×d), 130.4 (s), 133.1 (d), 133.3 (d), 133.6 (s), 136.3 (s), 136.9 (s), 174.6 (s), 180.6 (s), 211.6 (s). Anal. Calcd for $C_{24}H_{21}NO_3$: C, 77.61; H, 5.70; N, 3.77. Found: C, 77.62; H, 5.69; N, 3.77.

### 3.7. Typical experimental procedure for the reaction between 2-(anilino)-1,4-naphthoquinone (28) and β-dicarbonyl compounds in less acidic or neutral solvent

A mixture of 151 mg (0.61 mmol) of 2-(anilino)-1,4-naphthoquinone (**28**), 390 mg (2.47 mmol) of ethyl butyrylacetate (**2a**) and 969 g (3.61 mmol) of $Mn(OAc)_3$ in 10 mL of $CF_3CH_2OH$ was heated at 80 °C for 24 h, followed by the addition of 971 mg (3.62 mmol) of $Mn(OAc)_3$. The reaction mixture was heated for another 24 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, dried ($Na_2SO_4$), and concentrated in vacuo. The residue was chromatographed over 20 g of silica gel (eluted with dichloromethane) followed by crystallization (chloroform–hexane) to give 129 mg (64%) of **30a**.

**3.7.1. 12-Acetyl-6,11-dihydro-6,11-dioxo-benzo[*b*]acridine 30b.** Pale yellow powders; mp 314–315 °C; IR ($CHCl_3$) 1690, 1600, 1335, 1310, 1255 $cm^{-1}$; $^1H$ NMR (400 MHz, $CF_3COOD$) $\delta$ 3.06 (s, 3H, $CH_3$), 8.11–8.22 (m, 2H, ArH), 8.30–8.41 (m, 2H, ArH), 8.53–8.64 (m, 3H, ArH), 8.88 (d, $J$=8.7 Hz, 1H, ArH); $^{13}C$ NMR (100.6 MHz, $CF_3COOD$) $\delta$ 30.9 (q), 123.0 (s), 123.1 (d), 127.8 (d), 127.9 (s), 129.5 (d), 129.6 (d), 131.8 (s), 133.0 (s), 135.0 (d), 137.4 (d), 138.8 (d), 140.4 (s), 141.4 (d), 141.6 (s), 159.9 (s), 176.2 (s), 179.5 (s), 205.6 (s). Anal. Calcd for $C_{19}H_{11}NO_3$: C, 75.74; H, 3.68; N, 4.65. Found: C, 75.52; H, 3.68; N, 4.67.

**3.7.2. 6,11-Dihydro-6,11-dioxo-12-propionyl-benzo[*b*]-acridine 30c.** Pale yellow powders; mp 218–219 °C; IR ($CHCl_3$) 1690, 1595, 1550, 1335, 1260 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 1.49 (t, $J$=7.1 Hz, 3H, $CH_3$), 2.67–2.83 (m, 1H, $CH_2$), 3.06–3.23 (m, 1H, $CH_2$), 7.76–7.96 (m, 4H, ArH), 7.97–8.04 (m, 1H, ArH), 8.29–8.35 (m, 1H, ArH), 8.47–8.51 (m, 1H, ArH), 8.54 (d, $J$=8.8 Hz, 1H, ArH); $^{13}C$ NMR (100.6 MHz, $CDCl_3$) $\delta$ 7.8 (q), 37.6 (t), 122.7 (s), 125.0 (s), 126.0 (d), 127.8 (d), 128.3 (d), 130.7 (d), 132.1 (d), 133.2 (s), 133.5 (d), 134.0 (s), 134.9 (d), 135.1 (d), 147.7 (s), 150.1 (s), 151.6 (s), 181.2 (s), 182.6 (s), 206.0 (s). Anal. Calcd for $C_{20}H_{13}NO_3$: C, 76.18; H, 4.16; N, 4.44. Found: C, 76.23; H, 4.12; N, 4.42.

**3.7.3. 6,11-Dihydro-12-isobutyryl-6,11-dioxo-benzo[*b*]-acridine 30d.** Pale yellow powders; mp 229–230 °C; IR ($CHCl_3$) 1690, 1600, 1335, 1255, 1105 $cm^{-1}$; $^1H$ NMR (400 MHz, $C_2D_2Cl_4$) $\delta$ 1.12 (d, $J$=6.9 Hz, 3H, $CH_3$), 1.35 (d, $J$=6.9 Hz, 3H, $CH_3$), 3.00 (septet, $J$=6.9 Hz, 1H, CH), 7.71–7.88 (m, 4H, ArH), 7.96 (t, $J$=7.5 Hz, 1H, ArH), 8.24–8.29 (m, 1H, ArH), 8.34–8.40 (m, 1H, ArH), 8.43 (d, $J$=8.5 Hz, 1H, ArH); $^{13}C$ NMR (100.6 MHz, $C_2D_2Cl_4$) $\delta$ 18.1 (q), 19.0 (q), 42.4 (d), 123.5 (s), 125.5 (s), 127.0 (d), 127.9 (d), 128.3 (d), 130.8 (d), 131.9 (d), 133.2 (s), 133.9 (d), 135.2 (d), 135.4 (d), 147.7 (s), 149.9 (s), 151.3 (s), 181.4 (s), 182.8 (s), 209.4 (s). Anal. Calcd for $C_{21}H_{15}NO_3$: C, 76.58; H, 4.59; N, 4.25. Found: C, 76.49; H, 4.63; N, 4.11.

## Acknowledgements

We are grateful to the National Science Council of the ROC for financial support (Grant No. NSC-92-2113-M-006-008).

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