Available online at www.sciencedirect.com
ScienceDirect
Tetrahedron
Tetrahedron 63 (2007) 11911–11919

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

Che-Ping Chuang* and An-I Tsai

Department of Chemistry, National Cheng Kung University, Tainan 70101, Taiwan, ROC

Received 15 August 2007; revised 8 September 2007; accepted 11 September 2007
Available online 14 September 2007

Abstract—The manganese(III) initiated oxidative free radical reactions of 2-amino-1,4-benzoquinone are described. The free radical reaction of 5,6-dimethyl-2-methylamino-1,4-benzoquinone (**1**) provides a novel method for the synthesis of indole-4,7-dione and indole-2,4,7-trione. High chemoselectivity was observed in different solvents. The regioselectivity of this reaction was also studied with 5-methyl-2-methylamino-1,4-benzoquinone (**19**). In most cases, indole-4,7-diones **20** and **21** were produced in high regioselectivity.

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, murayaquinones, 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 indoloquinone 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,5–8] Among these, manganese(III) acetate and cerium(IV) ammonium nitrate have been used most efficiently. Previously, we found that oxidative free radical reactions of 2-amino-1,4-naphthoquinones with malonate, nitroacetate, and carbonyl compounds produced 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 effectively.[6] This report describes our results on the manganese(III) acetate mediated oxidative free radical reaction between 2-amino-1,4-benzoquinones and carbonyl compounds.

2. Results and discussion

2.1. The oxidative free radical reaction of 5,6-dimethyl-2-methylamino-1,4-benzoquinone (1)

We began our studies of this manganese(III)-mediated free radical reaction with **1** and β-keto ester **2** (R^2=OR) (Eq. 1). When **1** was treated with ethyl acetoacetate (**2a**) and manganese(III) acetate in acetic acid at room temperature, **3a** was obtained as the only product in 77% yield (Table 1, entry 1). With other β-keto esters, in addition to the expected condensation product **3**, the rearrangement product **4** was also formed (Table 1, entries 2–5). Indoles **3** and **4** were formed presumably via the reaction routes presented in Scheme 1. Manganese(III) acetate oxidation of β-keto ester **2** produces radical **6**. This radical intermediate **6** undergoes intermolecular addition to the quinone ring followed by oxidation to generate **7**. When R^1=Me, **7** undergoes condensation reaction to produce **3** (path a). With larger R^1, **7** undergoes either condensation reaction to generate **3** (path a) or oxidation reaction to give radical **8** (path b). Radical **8** undergoes intramolecular cyclization followed by oxidation to produce **10**, which subsequently undergoes alkyl group (R^1) migration to produce **4**. The ratios of **4/3** increase as the size of R^1 increases. This can be attributed to the steric effect exerted by R^1 group—the condensation of **7** (path a) is retarded by the larger R^1 group and the oxidation of **7** to produce radical **8** occurred (path b). Since the cerium salt can enhance the rate of the condensation,[9] to improve the reaction yield of condensation product **3**, this oxidative free radical reaction between **1** and β-keto ester **2** was next investigated with Mn(III)–Ce(III) systems. Reaction of **1a** with methyl 4-methoxyacetoacetate (**2d**), manganese(III) acetate, and cerium(III) nitrate in acetic acid at room temperature gave **3d** and **4c** in 76 and 12% yields, respectively (Table 1, entry 7). Other examples are also shown in Table 1 (entries 6 and 8). The presence of cerium(III) nitrate appears to increase the **3/4** ratio, producing condensation product **3** as the major product. These results demonstrate that the condensation rate of **7** is enhanced by the addition of cerium salt.

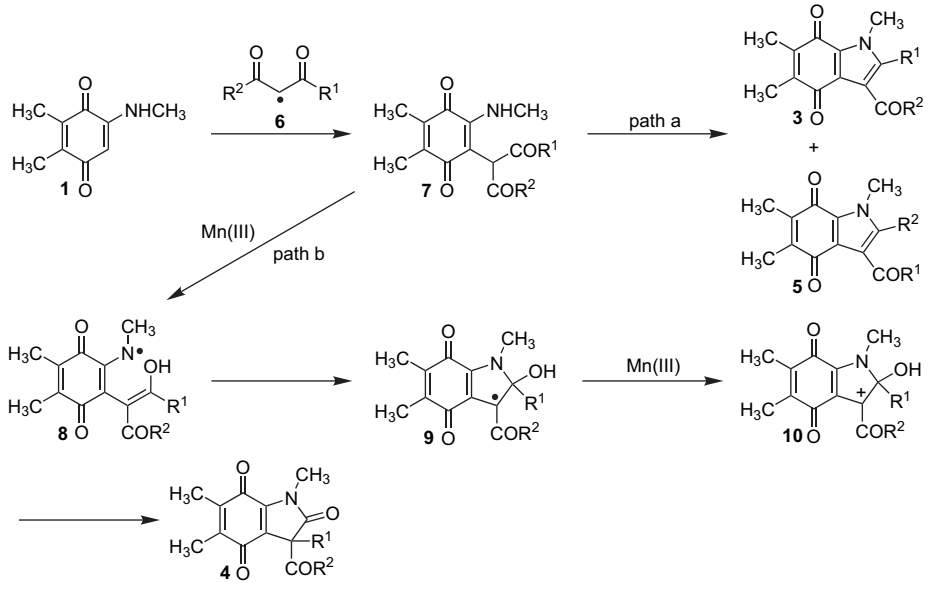
Keywords: Manganese(III) acetate; Free radical; 2-Amino-1,4-benzoquinones; Solvent effects; Regioselectivity.
* Corresponding author. Fax: +886 6 2740552; e-mail: cpchuang@mail.ncku.edu.tw

0040–4020/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2007.09.019

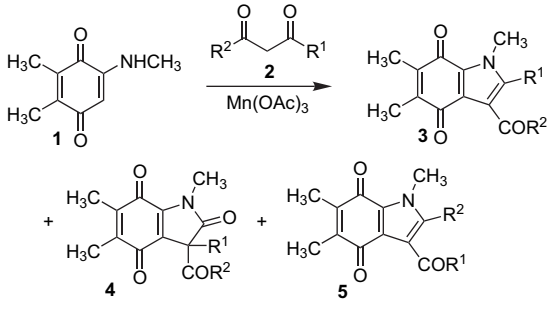
Table 1. Free radical reaction between **1** and β-dicarbonyl compounds

Entry	1,3-Dicarbonyl compounds	Solvent	Reaction time	Product (yield, %)	
1	**2a**: R^1=Me, R^2=OEt	HOAc	2 h	**3a** (77)	
2	**2b**: R^1=^{n}Pr, R^2=OEt	HOAc	4.5 h	**3b** (67)	**4a** (trace)
3	**2c**: R^1=^{i}Pr, R^2=OMe	HOAc	4.5 h	**3c** (32)	**4b** (32)
4	**2d**: R^1=$MeOCH_2$, R^2=OMe	HOAc	3.5 h	**3d** (27)	**4c** (63)
5	**2e**: R^1=$ClCH_2$, R^2=OEt	HOAc	2.5 h	**3e** (11)	**4d** (48)
6	**2c**: R^1=^{i}Pr, R^2=OMe	HOAc[a]	4.5 h	**3c** (67)	
7	**2d**: R^1=$MeOCH_2$, R^2=OMe	HOAc[a]	4 h	**3d** (76)	**4c** (12)
8	**2e**: R^1=$ClCH_2$, R^2=OEt	HOAc[a]	4 h	**3e** (56)	**4d** (12)
9	**2b**: R^1=^{n}Pr, R^2=OEt	HCO_2H	10 min	**3b** (60)	
10	**2c**: R^1=^{i}Pr, R^2=OMe	HCO_2H	10 min	**3c** (47)	
11	**2d**: R^1=$MeOCH_2$, R^2=OMe	HCO_2H	10 min	**3d** (28)	
12	**2e**: R^1=$ClCH_2$, R^2=OEt	HCO_2H	10 min	**3e** (32)	
13	**2d**: R^1=$MeOCH_2$, R^2=OMe	CF_3CH_2OH	30 min		**4c** (71)
14	**2d**: R^1=$MeOCH_2$, R^2=OMe	CH_3CN	30 min		**4c** (71)
15	**2d**: R^1=$MeOCH_2$, R^2=OMe	C_6H_6	30 min		**4c** (70)
16	**2d**: R^1=$MeOCH_2$, R^2=OMe	$CHCl_3$	30 min		**4c** (74)
17	**2b**: R^1=^{n}Pr, R^2=OEt	CF_3CH_2OH	30 min		**4a** (34)
18	**2c**: R^1=^{i}Pr, R^2=OMe	CF_3CH_2OH	30 min		**4b** (75)
19	**2e**: R^1=$ClCH_2$, R^2=OEt	$CHCl_3$	30 min		**4d** (66)
20	**2f**: R^1=Me, R^2=Me	HOAc	3.5 h	**3f** (78)	
21	**2g**: R^1=Et, R^2=Et	HOAc	4.5 h	**3g** (77)	
22	**2h**: R^1=Me, R^2=^{n}Bu	HOAc	4.5 h	**3h** (65)	**5a** (14)
23	**2i**: R^1=Me, R^2=^{i}Bu	HOAc	6 h	**3i** (70)	
24	**2j**: R^1=Me, R^2=^{t}Bu	HOAc	24 h	**3j** (67)	
25	**2k**: R^1=^{t}Bu, R^2=^{t}Bu	HOAc	24 h	**3k** (50)	
26	**2l**: R^1=Me, R^2=Ph	HOAc	3.5 h	**3l** (88)	

[a] The reaction was performed with additional 2 equiv of cerium(III) nitrate.



Scheme 1.



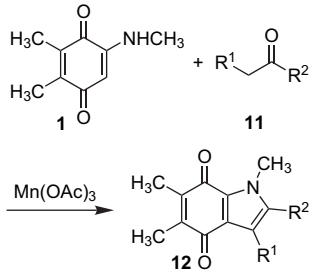
(1)

The solvent effects play an important role in the manganese(III) acetate mediated oxidative free radical reaction.[10] In an effort to study the effect of reaction medium on the chemoselectivity of the oxidative free radical reaction between **1** and β-keto ester **2** (R^2=OR), we next performed this reaction in various solvents. When a solution of **1** in formic acid was treated with ethyl butyrylacetate (**2b**) and manganese(III) acetate at 0 °C for 10 min, **3b** was obtained exclusively in 60% yield (Table 1, entry 9). Other β-keto ester **2** behaved similarly giving only the corresponding condensation product **3** (entries 10–12). These results

demonstrate that the higher acidity of formic acid enhances the condensation rate of **7** and path a is the only reaction route. This reaction was then performed in neutral solvents. Treatment of **1a** and **2d** with manganese(III) acetate in CF_3CH_2OH at 80 °C for 30 min resulted in the formation of **4c** (71%, entry 13). Reaction between **1** and **2d** was also performed in other neutral solvents (entries 14–16). The change of solvent to acetonitrile, benzene, and chloroform gave rearrangement product **4c** as the only product in 70–74% yields. This could account for the decrease in the rate of condensation (path a) as the acidity of reaction medium decreases and the oxidation of **7** to produce radical **8** (path b) becomes the major route. The generalities of this reaction were explored using a variety of β-keto esters and the results are also illustrated in Table 1 (entries 17–19). In all cases, rearrangement product **4** was produced in high selectivity.

Next, we investigated this manganese(III)-mediated reaction of **1** with 1,3-diones. Treatment of **1** with 2,4-pentanedione (**2f**) and manganese(III) acetate in acetic acid at room temperature led to the formation of **3f** in 78% yield (entry 20). The scope of this reaction is shown in Table 1 (entries 20–26). In contrast to the reaction between **1** and β-keto ester **2**, the condensation product **3** is the only product. Steric hindrance plays an important role in the final outcome of this reaction. In most cases, the condensation reaction occurs on the less hindered carbonyl group of the 1,3-diones (entries 22–26). With 1,3-dione **2h**, in addition to the expected product **3h** (65%), **5a** derived from the addition of amino group to the more hindered carbonyl group was also obtained as the minor product (14%, entry 22). The reaction yield decreases as the size of R^1 and R^2 increases. Again, this is presumably due to the decrease in the rate of condensation as the size of substituents increases.

We have continued to study this manganese(III)-mediated reaction with simple ketone **11** (Eq. 2). When **1** was treated with acetone (**11a**) (4 equiv) and manganese(III) acetate in acetic acid at 45 °C, **12a** was obtained in 20% yield (Table 2, entry 1). The reaction yield can be improved to 36% when 10 equiv of acetone (**11a**) was used (entry 2). The generalities of this reaction were examined with other simple ketones (entries 3 and 4). Indoles **12b** and **12c** were formed in 29 and 51% yields, respectively. These products were 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 **11** in neutral solvents would give **12** in a better result. Indeed, when **1** was reacted with acetone (**11a**) and manganese(III) acetate in acetonitrile at 60 °C for 16 h, **12a** was isolated in a better reaction yield (63%, entry 5) than that performed in acetic acid (36% yield, entry 2). This reaction can also be performed with acetone as solvent and **12a** was obtained in 72% yield (entry 6). The results of this reaction with a variety of simple ketones in neutral solvents are also summarized in Table 2 (entries 7–11). In all cases, indole **12** was obtained in a better reaction yield than those performed in acetic acid.



(2)

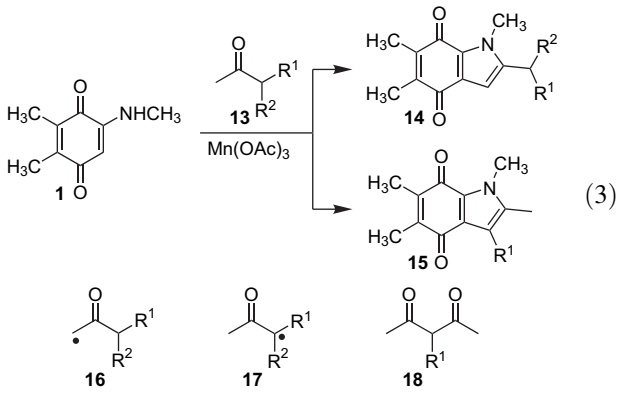
The regioselectivity of this free radical reaction was examined with unsymmetrical simple ketone **13** (Eq. 3). With butanone (**13a**: R^1=Me, R^2=H), **14a** and **15a** were obtained

Table 2. Free radical reaction between **1** and simple ketones

Entry	Carbonyl compounds	Solvent	Reaction time (h)	Product (yield, %)	
1	**11a**: R^1=H, R^2=Me	HOAc	39[a]	**12a** (20)	
2	**11a**: R^1=H, R^2=Me	HOAc	17[b]	**12a** (36)	
3	**11b**: R^1=H, R^2=Ph	HOAc	11[b]	**12b** (29)	
4	**11c**: R^1+R^2=$CH_2CH_2CH_2CH_2$	HOAc	5[b]	**12c** (51)	
5	**11a**: R^1=H, R^2=Me	CH_3CN	16[b]	**12a** (63)	
6	**11a**: R^1=H, R^2=Me		7[c]	**12a** (72)	
7	**11a**: R^1=H, R^2=Me	C_6H_6	13[b]	**12a** (67)	
8	**11a**: R^1=H, R^2=Me	$CHCl_3$	16[b]	**12a** (62)	
9	**11b**: R^1=H, R^2=Ph	CH_3CN	28[b]	**12b** (58)	
10	**11c**: R^1+R^2=$CH_2CH_2CH_2CH_2$	$CHCl_3$	3[b]	**12c** (76)	
11	**11d**: R^1=Ph, R^2=Ph	CH_3CN	6[b]	**12d** (73)	
12	**13a**: R^1=Me, R^2=H	$CHCl_3$	16[b]	**14a** (39)	**15a** (28)
13	**13b**: R^1=^{n}Bu, R^2=H	$CHCl_3$	16[b]	**14b** (42)	**15b** (29)
14	**13c**: R^1=^{i}Pr, R^2=H	$CHCl_3$	16[b]	**14c** (70)	**15c** (7)
15	**13d**: R^1=Me, R^2=Me	$CHCl_3$	16[b]	**14d** (55)	
16	**18a**: R^1=^{n}Bu	HOAc	16[d]		**15b** (55)
17	**18a**: R^1=^{n}Bu	CH_3CN	13[d]		**15b** (63)
18	**18b**: R^1=$CH_2CH_2CO_2Me$	HOAc	5[d]		**15d** (48)
19	**18b**: R^1=$CH_2CH_2CO_2Me$	CH_3CN	9[d]		**15d** (59)
20	**18c**: 2-Acetylcyclopentanone	CH_3CN	9[d]		**15e**[e] (56)

[a] The reaction was conducted with 4 equiv of acetone.
[b] The reaction was conducted with 10 equiv of corresponding simple ketone.
[c] The reaction was conducted with acetone as solvent.
[d] The reaction was conducted with 4 equiv of corresponding 1,3-dione.
[e] R^1=$CH_2CH_2CH_2CO_2H$.

in 39 and 28% yields, respectively (entry 12). These two products are derived from the intermolecular addition of radical **16a** and **17a**. As the size of R^1 and R^2 increases, the regioselectivity of this reaction increases and **14** becomes the major product (entries 12–15). 2-Alkyl-1,3-dione **18** can be used as the synthetic equivalent of radical intermediate **17** (R^2=H).[6g] For the selective formation of **15**, reaction between **1** and **18** was next investigated. Treatment of **1** and 1,3-dione **18a** (R^1=^{n}Bu) with manganese(III) acetate in acetic acid at room temperature gave **15b** as the only product in 55% yield (entry 16). The reaction yield can be improved to 63% when acetonitrile was used as solvent (entry 17). In contrast, with 2-heptanone (**13b**), **14b** and **15b** were obtained in 42 and 29% yields, respectively (entry 13). Other examples are also summarized in Table 2 (entries 18–20). In all cases, indole **15** was obtained as the only product.



(3)

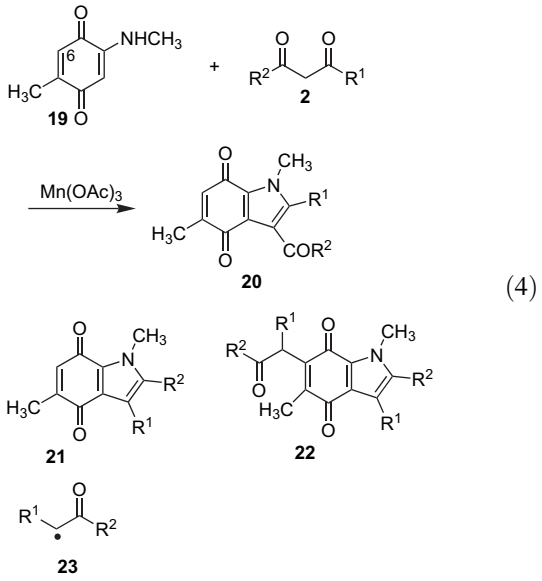
2.2. The regioselectivity of the oxidative free radical reaction between 5-methyl-2-methylamino-1,4-benzoquinone (19) and carbonyl compounds

We first tried the reaction between **19** and β-dicarbonyl compounds (Eq. 4). When **19** was treated with ethyl acetoacetate (**2a**) and manganese(III) acetate in acetic acid at room temperature for 7 h, **20a** was obtained exclusively in 61% yield and no product derived from the addition of radical **6a** to the C_6 of **19** can be found (Table 3, entry 1). This can be ascribed to the electron deficiency of radical intermediate **6a**, and this makes the rate of intermolecular addition to the C–C double bond bearing an electron-donating amino group much faster. Analogous results were obtained with other β-dicarbonyl compounds and the results are summarized in Table 3 (entries 2–6). In all cases, **20** was obtained as the only product in fair yield.

Table 3. The regioselectivity of the free radical reaction between **19** and carbonyl compounds

Entry	Carbonyl compounds	Reaction time (h)	Product (yield, %)	
1	**2a**: R^1=Me, R^2=OEt	7[a]	**20a** (61)	
2	**2b**: R^1=Pr, R^2=OEt	7[a]	**20b** (51)	
3	**2f**: R^1=Me, R^2=Me	7[a]	**20c** (53)	
4	**2i**: R^1=Me, R^2=^{t}Bu	24[a]	**20d** (47)	
5	**2j**: R^1=Me, R^2=^{t}Bu	35[a]	**20e** (33)	
6	**2l**: R^1=Me, R^2=Ph	7[a]	**20f** (61)	
7	**11a**: R^1=H, R^2=Me	13[b]	**21a** (38)	**22a** (25)
8	**11a**: R^1=H, R^2=Me	13[c]	**21a** (47)	**22a** (10)
9	**11e**: R^1=Me, R^2=Et	13[c]	**21b** (35)	**22b** (10)
10	**11b**: R^1=H, R^2=Ph	34[c]	**21c** (31)	
11	**11d**: R^1=Ph, R^2=Ph	7[c]	**21d** (75)	

[a] The reaction was performed with acetic acid as solvent.
[b] The reaction was performed with acetone as solvent.
[c] The reaction was performed with benzene as solvent.



(4)

We also examined the regioselectivity of this reaction with simple ketones. When **19** was treated with manganese(III) acetate in acetone (**11a**) at 60 °C for 13 h, in addition to expected product **21a** (38%), **22a** was also obtained in 25% yield (Table 3, entry 7). Indole **22a** was presumably derived from the further addition of radical **23a** to **21a**. In benzene, the **21a/22a** ratio rose to 4.7:1 (entry 8). The different behavior between **6a** and **23a** is presumably due to the less electron deficiency of radical intermediate **23a**, making the rate of intermolecular addition to C_6 of **19** much slower than that of **6a** and the addition of radical **23a** to **21a** occurred. Other examples are also shown in Table 3 (entries 9–11). For reasons that are not clear, as the size of simple ketone increases, the regioselectivity increases and **21** becomes the only product (entries 10 and 11).

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-benzoquinones. The free radical reaction of 2,5-dimethyl-2-methylamino-1,4-benzoquinone provides a novel method for the synthesis of indole-4,7-dione and indole-2,4,7-trione. With β-keto esters, by changing the solvent, the condensation product indole-4,7-dione and rearrangement product indole-2,4,7-trione can be generated in high chemoselectivity. With 1,3-diones, the condensation product is the only product. With simple ketones, the condensation product was produced and it gave better results in neutral solvents. Reaction of 5-methyl-2-methylamino-1,4-benzoquinone produced indole-4,9-dione derived from the intermolecular addition of radical intermediate to the C–C double bond with an electron-donating amino group in high regioselectivity.

3. Experimental

3.1. General

Melting points are uncorrected. Infrared spectra were taken with a Hitachi 260-30 spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AMX-400, AVANCE 500, or AVANCE 300 spectrometer. Chemical shifts are reported in parts per million relative to TMS as internal reference. Elemental analyses were performed with Heraeus CHN-Rapid Analyzer. Mass spectra were recorded with Finnigan MAT-95XL mass spectrometer. Analytical thin-layer chromatography was performed with precoated silica gel 60 F_{254} plates (0.25 mm thick) and visualized by UV. The reaction mixture was purified by column chromatography over silica gel (70–230 mesh). The starting 2-amino-1,4-benzoquinones **1** and **19** were synthesized according to literature procedure.[11]

3.2. Typical experimental procedure for the reaction in acidic solvent

A mixture of 5,6-dimethyl-2-methylamino-1,4-benzoquinone (**1**, 103 mg, 0.62 mmol), ethyl acetoacetate (**2a**, 323 mg, 2.48 mmol), and $Mn(OAc)_3$ (1.0 g, 3.73 mmol) in acetic acid (10 mL) was stirred at room temperature for 2 h. The reaction mixture was diluted with ethyl acetate (100 mL), washed with saturated aqueous sodium bisulfite (50 mL), water (3×50 mL), and saturated aqueous sodium bicarbonate (50 mL), and dried (Na_2SO_4). The solvent was evaporated under reduced pressure and the crude product was purified by column chromatography on silica gel (20 g) using dichloromethane–hexane (2:1) as eluent, followed by crystallization (ethyl acetate–hexane) to give **3a** (131 mg, 77%).

3.3. Typical experimental procedure for the reaction in neutral solvent

A mixture of 5,6-dimethyl-2-methylamino-1,4-benzoquinone (**1**, 120 mg, 0.73 mmol), methyl methoxyacetoacetate (**2d**, 477 mg, 3.27 mmol), and $Mn(OAc)_3$ (1.17 g, 4.37 mmol) in CF_3CH_2OH (10 mL) was heated at 80 °C for 30 min. After workup as described above, the residue was chromatographed over silica gel (20 g, eluted with 2:1 dichloromethane–hexane) followed by crystallization (ethyl acetate–hexane) to give **4c** (158 mg, 71%).

3.3.1. 3-Ethoxycarbonyl-1,2,5,6-tetramethyl-1*H*-indole-4,7-dione 3a. Orange crystals; mp 92–93 °C; IR ($CHCl_3$) 2990, 1705, 1645, 1620, 1465 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.40 (t, J=7.1 Hz, 3H, CH_3), 2.02 (s, 3H, CH_3), 2.04 (s, 3H, CH_3), 2.43 (s, 3H, CH_3), 3.90 (s, 3H, NCH_3), 4.38 (q, J=7.1 Hz, 2H, OCH_2); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 10.7 (q), 11.9 (q), 12.6 (q), 14.2 (q), 32.5 (q), 60.8 (t), 112.7 (s), 123.4 (s), 129.0 (s), 139.1 (s), 140.8 (s), 141.3 (s), 164.5 (s), 178.6 (s), 181.5 (s). Anal. Calcd for $C_{15}H_{17}NO_4$: C, 65.44; H, 6.22; N, 5.09. Found: C, 65.30; H, 6.26; N, 5.05.

3.3.2. 3-Ethoxycarbonyl-1,5,6-trimethyl-2-propyl-1*H*-indole-4,7-dione 3b. Yellow needles; mp 126–127 °C; IR ($CHCl_3$) 2975, 2930, 1700, 1625, 1300 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.99 (t, J=7.5 Hz, 3H, CH_3), 1.40 (t, J=7.2 Hz, 3H, CH_3), 1.61 (sextet, J=7.5 Hz, 2H, CH_2), 2.03 (s, 3H, CH_3), 2.05 (s, 3H, CH_3), 2.81 (t, J=7.5 Hz, 2H, CH_2), 3.92 (s, 3H, NCH_3), 4.38 (q, J=7.2 Hz, 2H, OCH_2); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 12.0 (q), 12.6 (q), 13.8 (q), 14.2 (q), 22.4 (t), 26.4 (t), 32.6 (q), 60.8 (t), 112.8 (s), 123.5 (s), 129.1 (s), 139.2 (s), 141.3 (s), 144.6 (s), 164.5 (s), 178.7 (s), 181.7 (s). Anal. Calcd for $C_{17}H_{21}NO_4$: C, 67.31; H, 6.98; N, 4.62. Found: C, 67.36; H, 6.96; N, 4.61.

3.3.3. 2-Isopropyl-3-methoxycarbonyl-1,5,6-trimethyl-1*H*-indole-4,7-dione 3c. Yellow crystals; mp 102–103 °C; IR ($CHCl_3$) 2975, 1730, 1645, 1280, 1230 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.33 (d, J=7.0 Hz, 6H, 2×CH_3), 2.02 (s, 6H, 2×CH_3), 3.19 (septet, J=7.0 Hz, 1H, CH), 3.93 (s, 3H, NCH_3), 3.98 (s, 3H, OCH_3); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 12.1 (q), 12.3 (q), 20.7 (2×q), 25.6 (d), 32.7 (q), 52.4 (q), 112.4 (s), 123.4 (s), 127.9 (s), 140.2 (s), 140.6 (s), 145.8 (s), 166.6 (s), 178.5 (s), 182.0 (s). Anal. Calcd for $C_{16}H_{19}NO_4$: C, 66.42; H, 6.62; N, 4.84. Found: C, 66.42; H, 6.63; N, 4.81.

3.3.4. 3-Methoxycarbonyl-2-methoxymethyl-1,5,6-trimethyl-1*H*-indole-4,7-dione 3d. Yellow needles; mp 142–143 °C; IR ($CHCl_3$) 2930, 1715, 1650, 1315, 1280 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.03 (s, 3H, CH_3), 2.05 (s, 3H, CH_3), 3.36 (s, 3H, OCH_3), 3.93 (s, 3H, NCH_3), 4.01 (s, 3H, OCH_3), 4.65 (s, 2H, OCH_2); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 11.9 (q), 12.6 (q), 33.1 (q), 52.0 (q), 57.9 (q), 62.5 (t), 114.5 (s), 122.7 (s), 130.1 (s), 138.5 (s), 139.5 (s), 141.8 (s), 164.5 (s), 178.9 (s), 181.3 (s). Anal. Calcd for $C_{15}H_{17}NO_5$: C, 61.85; H, 5.88; N, 4.81. Found: C, 61.65; H, 5.94; N, 4.72.

3.3.5. 2-Chloromethyl-3-ethoxycarbonyl-1,5,6-trimethyl-1*H*-indole-4,7-dione 3e. Yellow needles; mp 106–107 °C; IR ($CHCl_3$) 2990, 1705, 1650, 1620, 1510 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.43 (t, J=7.1 Hz, 3H, CH_3), 2.05 (s, 3H, CH_3), 2.07 (s, 3H, CH_3), 4.06 (s, 3H, NCH_3), 4.42 (q, J=7.1 Hz, 2H, OCH_2), 4.88 (s, 2H, $ClCH_2$); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 12.0 (q), 12.8 (q), 14.1 (q), 32.8 (q), 33.5 (t), 61.3 (t), 114.4 (s), 123.1 (s), 130.4 (s), 137.8 (s), 139.5 (s), 142.3 (s), 163.4 (s), 179.0 (s), 181.0 (s). Anal. Calcd for $C_{15}H_{16}ClNO_4$: C, 58.16; H, 5.21; N, 4.52. Found: C, 58.16; H, 5.27; N, 4.51.

3.3.6. 3-Acetyl-1,2,5,6-tetramethyl-1*H*-indole-4,7-dione 3f. Orange needles; mp 165–166 °C; IR ($CHCl_3$) 3010, 2955, 1645, 1505, 1435 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.04 (s, 3H, CH_3), 2.05 (s, 3H, CH_3), 2.37 (s, 3H, CH_3), 2.64 (s, 3H, CH_3), 3.91 (s, 3H, NCH_3); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 10.8 (q), 12.0 (q), 12.7 (q), 31.5 (q), 32.5 (q), 121.7 (s), 122.8 (s), 128.6 (s), 139.6 (s), 140.6 (s), 141.0 (s), 178.7 (s), 182.9 (s), 198.9 (s). Anal. Calcd for $C_{14}H_{15}NO_3$: C, 68.56; H, 6.16; N, 5.71. Found: C, 68.53; H, 6.20; N, 5.68.

3.3.7. 2-Ethyl-1,5,6-trimethyl-3-propanoyl-1*H*-indole-4,7-dione 3g. Yellow crystals; mp 118–119 °C; IR ($CHCl_3$) 2980, 1645, 1505, 1465, 1250 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.16 (t, J=7.5 Hz, 3H, CH_3), 1.19 (t, J=7.5 Hz, 3H, CH_3), 2.04 (s, 6H, 2×CH_3), 2.74 (q, J=7.5 Hz, 2H, CH_2), 3.02 (q, J=7.5 Hz, 2H, CH_2), 3.93

(s, 3H, NCH_3); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 8.5 (q), 11.9 (q), 12.5 (q), 13.5 (q), 17.8 (t), 32.2 (q), 36.4 (t), 121.1 (s), 122.7 (s), 128.4 (s), 139.7 (s), 140.8 (s), 145.1 (s), 178.5 (s), 182.9 (s), 202.4 (s). Anal. Calcd for $C_{16}H_{19}NO_3$: C, 70.31; H, 7.01; N, 5.12. Found: C, 70.42; H, 7.11; N, 5.11.

3.3.8. 1,2,5,6-Tetramethyl-3-pentanoyl-1*H*-indole-4,7-dione 3h. Yellow powders; mp 144–145 °C; IR ($CHCl_3$) 3010, 2960, 1645, 1510, 1465 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.91 (t, J=7.4 Hz, 3H, CH_3), 1.36 (sextet, J=7.4 Hz, 2H, CH_2), 1.63 (quintet, J=7.4 Hz, 2H, CH_2), 2.05 (s, 6H, 2×CH_3), 2.33 (s, 3H, CH_3), 3.02 (t, J=7.4 Hz, 2H, CH_2), 3.91 (s, 3H, NCH_3); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 10.6 (q), 12.0 (q), 12.7 (q), 14.0 (q), 22.4 (t), 26.8 (t), 32.5 (q), 43.1 (t), 121.9 (s), 122.6 (s), 128.5 (s), 139.7 (s), 139.9 (s), 140.9 (s), 178.7 (s), 182.9 (s), 202.4 (s). Anal. Calcd for $C_{17}H_{21}NO_3$: C, 71.06; H, 7.37; N, 4.87. Found: C, 71.05; H, 7.34; N, 4.78.

3.3.9. 1,2,5,6-Tetramethyl-3-(3-methylbutanoyl)-1*H*-indole-4,7-dione 3i. Yellow crystals; mp 120–121 °C; IR ($CHCl_3$) 2960, 1645, 1510, 1465, 1250 cm^{-1}; ^1H NMR (400 MHz, DMSO) δ 0.90 (d, J=6.8 Hz, 6H, 2×CH_3), 1.95 (s, 6H, 2×CH_3), 2.06 (nontet, J=6.8 Hz, 1H, CH), 2.32 (s, 3H, CH_3), 2.80 (d, J=6.8 Hz, 2H, CH_2), 3.85 (s, 3H, NCH_3); ^{13}C NMR (100.6 MHz, DMSO) δ 9.7 (q), 11.3 (q), 11.8 (q), 22.0 (2×q), 24.5 (d), 31.9 (q), 51.5 (t), 121.2 (s), 121.8 (s), 127.9 (s), 139.2 (s), 139.6 (s), 139.9 (s), 177.4 (s), 182.1 (s), 200.1 (s). Anal. Calcd for $C_{17}H_{21}NO_3$: C, 71.06; H, 7.37; N, 4.87. Found: C, 71.05; H, 7.42; N, 4.85.

3.3.10. 1,2,5,6-Tetramethyl-3-pivaloyl-1*H*-indole-4,7-dione 3j. Orange crystals; mp 168–169 °C; IR ($CHCl_3$) 2970, 1680, 1645, 1465, 1235 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.23 (s, 9H, 3×CH_3), 2.01 (s, 3H, CH_3), 2.02 (s, 3H, CH_3), 2.17 (s, 3H, CH_3), 3.88 (s, 3H, NCH_3); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 10.7 (q), 12.0 (q), 12.2 (q), 26.9 (3×q), 32.3 (q), 45.6 (s), 121.3 (s), 123.4 (s), 127.8 (s), 134.1 (s), 140.0 (s), 140.2 (s), 178.1 (s), 182.3 (s), 211.7 (s). Anal. Calcd for $C_{17}H_{21}NO_3$: C, 71.06; H, 7.37; N, 4.87. Found: C, 71.03; H, 7.38; N, 4.85.

3.3.11. 1,5,6-Trimethyl-2-(2-methylpropyl)-3-(pivaloyl)-1*H*-indole-4,7-dione 3k. Orange crystals; mp 167–168 °C; IR (KBr) 2955, 1645, 1505, 1455, 1240 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.92 (d, J=6.8 Hz, 6H, 2×CH_3), 1.24 (s, 9H, 3×CH_3), 1.91 (nontet, J=6.8 Hz, 1H, CH), 2.01 (s, 3H, CH_3), 2.03 (s, 3H, CH_3), 2.41 (d, J=6.8 Hz, 2H, CH_2), 3.90 (s, 3H, NCH_3); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 12.1 (q), 12.3 (q), 22.4 (2×q), 27.4 (3×q), 28.8 (d), 33.1 (q), 33.9 (t), 45.3 (s), 122.3 (s), 123.4 (s), 128.1 (s), 137.8 (s), 140.2 (s), 140.4 (s), 178.2 (s), 182.6 (s), 211.7 (s). Anal. Calcd for $C_{20}H_{27}NO_3$: C, 72.92; H, 8.26; N, 4.25. Found: C, 72.71; H, 8.25; N, 4.18.

3.3.12. 3-Benzoyl-1,2,5,6-tetramethyl-1*H*-indole-4,7-dione 3l. Orange crystals; mp 218–219 °C; IR ($CHCl_3$) 3010, 2955, 1645, 1615, 1585 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.91 (s, 3H, CH_3), 2.04 (s, 3H, CH_3), 2.29 (s, 3H, CH_3), 3.97 (s, 3H, NCH_3), 7.42 (t, J=7.6 Hz, 2H, ArH), 7.55 (t, J=7.6 Hz, 1H, ArH), 7.80–7.87 (m, 2H, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 10.5 (q), 12.1 (q), 12.4 (q), 32.5 (q), 120.0 (s), 124.0 (s), 128.3 (2×d), 129.3 (2×d), 133.0 (d), 138.4 (s), 139.2 (s), 140.0 (s), 140.7 (s), 178.6 (s), 181.9 (s), 193.1 (s). Anal. Calcd for $C_{19}H_{17}NO_3$: C, 74.25; H, 5.58; N, 4.56. Found: C, 74.26; H, 5.65; N, 4.55.

3.3.13. Ethyl 2,3,4,7-tetrahydro-1,5,6-trimethyl-2,4,7-trioxo-3-propyl-1*H*-indole-3-carboxylate 4a. Orange crystals; mp 99–100 °C; IR ($CHCl_3$) 2970, 1730, 1665, 1645, 1240 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.87 (t, J=7.1 Hz, 3H, CH_3), 0.94–1.06 (m, 2H, CH_2), 1.19 (t, J=7.1 Hz, 3H, CH_3), 2.05 (s, 6H, 2×CH_3), 2.20–2.40 (m, 2H, CH_2), 3.42 (s, 3H, NCH_3), 4.16 (q, J=7.1 Hz, 2H, OCH_2); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 11.9 (q), 12.3 (q), 13.87 (q), 13.92 (q), 17.5 (t), 28.7 (q), 34.7 (t), 60.6 (s), 62.3 (t), 123.0 (s), 138.3 (s), 141.4 (s), 145.1 (s), 166.3 (s), 175.1 (s), 180.6 (s), 180.8 (s). Anal. Calcd for $C_{17}H_{21}NO_5$: C, 63.94; H, 6.63; N, 4.39. Found: C, 63.92; H, 6.68; N, 4.44.

3.3.14. Methyl 2,3,4,7-tetrahydro-3-isopropyl-1,5,6-trimethyl-2,4,7-trioxo-1*H*-indole-3-carboxylate 4b. Orange crystals; mp 82–83 °C; IR ($CHCl_3$) 2960, 1755, 1730, 1645, 1235 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.95 (d, J=6.8 Hz, 3H, CH_3), 0.98 (d, J=6.8 Hz, 3H, CH_3), 2.06 (s, 6H, 2×CH_3), 2.95 (septet, J=6.8 Hz, 1H, CH), 3.43 (s, 3H, NCH_3), 3.70 (s, 3H, OCH_3); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 11.8 (q), 12.5 (q), 17.0 (q), 18.8 (q), 28.7 (q), 33.4 (d), 53.0 (q), 64.8 (s), 121.8 (s), 137.9 (s), 141.8 (s), 145.6 (s), 166.5 (s), 174.4 (s), 180.57 (s), 180.60 (s). Anal. Calcd for $C_{16}H_{19}NO_5$: C, 62.94; H, 6.27; N, 4.59. Found: C, 62.93; H, 6.28; N, 4.61.

3.3.15. Methyl 2,3,4,7-tetrahydro-3-methoxymethyl-1,5,6-trimethyl-2,4,7-trioxo-1*H*-indole-3-carboxylate 4c. Brick red crystals; mp 97–98 °C; IR ($CHCl_3$) 2960, 2925, 1760, 1730, 1645, 1605, 1265 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.06 (s, 6H, 2×CH_3), 3.25 (s, 3H, OCH_3), 3.43 (s, 3H, NCH_3), 3.70 (s, 3H, OCH_3), 4.12 (d, J=8.4 Hz, 1H, OCH), 4.21 (d, J=8.4 Hz, 1H, OCH); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 11.7 (q), 12.0 (q), 28.7 (q), 53.0 (q), 59.2 (q), 60.4 (s), 71.9 (t), 121.0 (s), 138.2 (s), 141.0 (s), 145.7 (s), 164.7 (s), 173.6 (s), 180.3 (s), 180.6 (s). Anal. Calcd for $C_{15}H_{17}NO_6$: C, 58.63; H, 5.58; N, 4.56. Found: C, 58.58; H, 5.60; N, 4.51.

3.3.16. Ethyl 3-chloromethyl-2,3,4,7-tetrahydro-1,5,6-trimethyl-2,4,7-trioxo-1*H*-indole-3-carboxylate 4d. Brick red crystals; mp 90–91 °C; IR ($CHCl_3$) 2990, 1730, 1665, 1625, 1265 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.22 (t, J=7.1 Hz, 3H, CH_3), 2.07 (s, 6H, 2×CH_3), 3.45 (s, 3H, NCH_3), 4.20 (q, J=7.1 Hz, 2H, OCH_2), 4.24 (d, J=10.9 Hz, 1H, ClCH), 4.29 (d, J=10.9 Hz, 1H, ClCH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 12.0 (q), 12.2 (q), 13.9 (q), 29.0 (q), 42.7 (t), 61.2 (s), 63.0 (t), 120.2 (s), 138.7 (s), 141.4 (s), 146.4 (s), 164.3 (s), 172.7 (s), 180.4 (s), 180.6 (s). Anal. Calcd for $C_{15}H_{16}ClNO_5$: C, 55.31; H, 4.95; N, 4.30. Found: C, 55.36; H, 5.08; N, 4.26.

3.3.17. 3-Acetyl-2-butyl-1,5,6-trimethyl-1*H*-indole-4,7-dione 5a. Yellow powders; mp 96–97 °C; IR ($CHCl_3$) 3010, 2960, 1645, 1505, 1465 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.94 (t, J=7.5 Hz, 3H, CH_3), 1.40 (sextet,

J=7.5 Hz, 2H, CH_2), 1.52 (quintet, J=7.5 Hz, 2H, CH_2), 2.048 (s, 3H, CH_3), 2.054 (s, 3H, CH_3), 2.63 (s, 3H, CH_3), 2.76 (t, J=7.5 Hz, 2H, CH_2), 3.92 (s, 3H, NCH_3); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 12.0 (q), 12.6 (q), 13.7 (q), 22.6 (t), 24.1 (t), 31.2 (t), 31.5 (q), 32.5 (q), 121.6 (s), 122.9 (s), 128.6 (s), 139.7 (s), 141.0 (s), 144.7 (s), 178.7 (s), 183.0 (s), 198.8 (s). Anal. Calcd for $C_{17}H_{21}NO_3$: C, 71.06; H, 7.37; N, 4.87. Found: C, 71.05; H, 7.36; N, 4.74.

3.3.18. 1,2,5,6-Tetramethyl-1*H*-indole-4,7-dione 12a. Orange needles; mp 120–121 °C; IR ($CHCl_3$) 2960, 1730, 1640, 1450, 1265 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.98 (s, 6H, 2×CH_3), 2.23 (s, 3H, CH_3), 3.82 (s, 3H, NCH_3), 6.25 (s, 1H, CH); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 11.9 (q), 12.0 (q), 12.2 (q), 32.1 (q), 106.1 (d), 125.8 (s), 129.0 (s), 137.9 (s), 139.8 (s), 140.3 (s), 177.8 (s), 183.2 (s). Anal. Calcd for $C_{12}H_{13}NO_2$: C, 70.92; H, 6.45; N, 6.89. Found: C, 70.95; H, 6.29; N, 6.80.

3.3.19. 1,5,6-Trimethyl-2-phenyl-1*H*-indole-4,7-dione 12b. Yellow crystals; mp 152–153 °C; IR ($CHCl_3$) 2960, 2925, 1730, 1645, 1265 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.03 (s, 6H, 2×CH_3), 3.89 (s, 3H, NCH_3), 6.55 (s, 1H, CH), 7.36–7.52 (m, 5H, ArH); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 12.1 (q), 12.2 (q), 34.1 (q), 107.3 (d), 125.9 (s), 128.6 (2×d), 128.7 (d), 129.1 (2×d), 129.7 (s), 130.4 (s), 140.2 (s), 140.7 (s), 142.1 (s), 178.1 (s), 182.9 (s). Anal. Calcd for $C_{17}H_{15}NO_2$: C, 76.96; H, 5.70; N, 5.28. Found: C, 76.92; H, 5.75; N, 5.26.

3.3.20. 2,3,5-Trimethyl-6,7,8,9-tetrahydro-5*H*-carbazole-1,4-dione 12c. Brick red needles; mp 126–127 °C; IR ($CHCl_3$) 2955, 2925, 1730, 1635, 1255 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.70–1.78 (m, 2H, CH_2), 1.81–1.89 (m, 2H, CH_2), 1.98 (s, 6H, 2×CH_3), 2.52 (t, J=6.0 Hz, 2H, CH_2), 2.74 (t, J=6.0 Hz, 2H, CH_2), 3.78 (s, 3H, NCH_3); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 12.0 (2×q), 21.5 (t), 22.2 (t), 22.3 (t), 22.5 (t), 31.8 (q), 120.2 (s), 122.5 (s), 127.9 (s), 137.6 (s), 139.7 (s), 140.2 (s), 177.6 (s), 184.2 (s). Anal. Calcd for $C_{15}H_{17}NO_2$: C, 74.05; H, 7.04; N, 5.76. Found: C, 73.95; H, 7.01; N, 5.77.

3.3.21. 1,5,6-Trimethyl-2,3-diphenyl-1*H*-indole-4,7-dione 12d. Brick red crystals; mp 204–205 °C; IR (KBr) 1645, 1505, 1455, 1285, 1225 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.03 (s, 3H, CH_3), 2.08 (s, 3H, CH_3), 3.86 (s, 3H, NCH_3), 7.13–7.18 (m, 2H, ArH), 7.18–7.22 (m, 5H, ArH), 7.31–7.36 (m, 3H, ArH); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 12.1 (q), 12.4 (q), 34.3 (q), 122.2 (s), 123.9 (s), 126.9 (d), 127.4 (2×d), 128.5 (2×d), 128.7 (d), 129.3 (s), 129.5 (s), 130.4 (2×d), 130.9 (2×d), 132.6 (s), 139.8 (s), 140.0 (s), 141.5 (s), 178.7 (s), 183.0 (s). Anal. Calcd for $C_{23}H_{19}NO_2$: C, 80.92; H, 5.61; N, 4.10. Found: C, 80.99; H, 5.63; N, 4.10.

3.3.22. 1,5,6-Trimethyl-2-pentyl-1*H*-indole-4,7-dione 14b. Brick red crystals; mp 68–69 °C; IR (KBr) 2935, 1635, 1455, 1370 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.92 (t, J=6.8 Hz, 3H, CH_3), 1.30–1.44 (m, 4H, 2×CH_2), 1.59–1.71 (m, 2H, CH_2), 2.03 (s, 6H, 2×CH_3), 2.56 (t, J=7.7 Hz, 2H, CH_2), 3.88 (s, 3H, NCH_3), 6.34 (s, 1H, CH); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 12.2 (q), 12.3 (q), 13.9 (q), 22.4 (t), 25.9 (t), 27.6 (t), 31.4 (t), 32.2 (q), 105.4 (d), 125.9 (s), 129.0 (s), 139.9 (s), 140.5 (s), 142.6 (s), 178.1 (s), 183.5 (s). Anal. Calcd for $C_{16}H_{21}NO_2$: C, 74.10; H, 8.16; N, 5.40. Found: C, 74.13; H, 8.19; N, 5.40.

3.3.23. 1,5,6-Trimethyl-2-(2-methylpropyl)-1*H*-indole-4,7-dione 14c. Brick red crystals; mp 105–106 °C; IR (KBr) 3110, 2955, 1635, 1445, 1360 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.97 (d, J=6.8 Hz, 6H, 2×CH_3), 1.92 (nontet, J=6.8 Hz, 1H, CH), 2.03 (s, 6H, 2×CH_3), 2.45 (d, J=6.8 Hz, 2H, CH_2), 3.88 (s, 3H, NCH_3), 6.33 (s, 1H, ArH); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 11.8 (q), 11.9 (q), 22.2 (2×q), 27.6 (d), 32.1 (q), 34.8 (t), 106.1 (d), 125.6 (s), 128.7 (s), 139.5 (s), 140.3 (s), 141.3 (s), 177.5 (s), 182.9 (s). Anal. Calcd for $C_{15}H_{19}NO_2$: C, 73.44; H, 7.81; N, 5.71. Found: C, 73.40; H, 7.90; N, 5.69.

3.3.24. 3-Isopropyl-1,5,6-trimethyl-1*H*-indole-4,7-dione 14d. Orange crystals; mp 137–138 °C; IR (KBr) 2960, 1635, 1495, 1365, 1240 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.27 (d, J=6.8 Hz, 6H, 2×CH_3), 2.03 (s, 6H, 2×CH_3), 2.93 (septet, J=6.8 Hz, 1H, CH), 3.91 (s, 3H, NCH_3), 6.38 (s, 1H, ArH); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 12.0 (q), 12.1 (q), 21.9 (2×q), 25.1 (q), 32.0 (d), 102.9 (d), 125.8 (s), 128.8 (s), 139.7 (s), 140.4 (s), 148.3 (s), 177.8 (s), 183.1 (s). Anal. Calcd for $C_{14}H_{17}NO_2$: C, 72.70; H, 7.41; N, 6.06. Found: C, 72.55; H, 7.48; N, 6.00.

3.3.25. 1,2,3,5,6-Pentamethyl-1*H*-indole-4,7-dione 15a. Brick red crystals; mp 179–180 °C; IR ($CHCl_3$) 2950, 1630, 1515, 1475 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.00 (s, 6H, 2×CH_3), 2.15 (s, 3H, CH_3), 2.25 (s, 3H, CH_3), 3.86 (s, 3H, NCH_3); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 9.3 (q), 10.0 (q), 12.1 (2×q), 32.4 (q), 118.2 (s), 123.4 (s), 128.0 (s), 135.5 (s), 140.1 (s), 140.2 (s), 177.7 (s), 184.6 (s). Anal. Calcd for $C_{13}H_{15}NO_2$: C, 71.87; H, 6.96; N, 6.45. Found: C, 71.75; H, 6.85; N, 6.43.

3.3.26. 3-Butyl-1,2,5,6-tetramethyl-1*H*-indole-4,7-dione 15b. Brick red crystals; mp 78–79 °C; IR (KBr) 2925, 1635, 1505, 1465, 1245 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.92 (t, J=7.2 Hz, 3H, CH_3), 1.35 (sextet, J=7.2 Hz, 2H, CH_2), 1.41–1.52 (m, 2H, CH_2), 2.01 (s, 6H, 2×CH_3), 2.17 (s, 3H, CH_3), 2.69 (t, J=7.2 Hz, 2H, CH_2), 3.87 (s, 3H, NCH_3); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 9.3 (q), 12.0 (q), 12.1 (q), 14.0 (q), 22.6 (t), 24.4 (t), 32.3 (q), 32.5 (t), 122.8 (s), 123.7 (s), 128.1 (s), 135.3 (s), 140.0 (s), 140.1 (s), 177.6 (s), 184.2 (s). Anal. Calcd for $C_{16}H_{21}NO_2$: C, 74.10; H, 8.16; N, 5.40. Found: C, 73.96; H, 8.19; N, 5.41.

3.3.27. 3-Isopropyl-1,2,5,6-tetramethyl-1*H*-indole-4,7-dione 15c. Brick red crystals; mp 93–94 °C; IR (KBr) 2920, 1635, 1455, 1250, 1025 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.29 (d, J=7.1 Hz, 6H, 2×CH_3), 2.01 (s, 3H, CH_3), 2.02 (s, 3H, CH_3), 2.24 (s, 3H, CH_3), 3.39 (septet, J=7.1 Hz, 1H, CH), 3.88 (s, 3H, NCH_3); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 10.4 (q), 12.0 (q), 12.5 (q), 21.1 (2×q), 25.1 (d), 32.3 (q), 122.5 (s), 128.7 (s), 129.4 (s), 134.2 (s), 139.5 (s), 140.5 (s), 178.0 (s), 183.9 (s). Anal. Calcd for $C_{15}H_{19}NO_2$: C, 73.44; H, 7.81; N, 5.71. Found: C, 73.27; H, 7.90; N, 5.59.

3.3.28. 3-(2-Methoxycarbonylethyl)-1,2,5,6-tetramethyl-1*H*-indole-4,7-dione 15d. Orange crystals; mp 114–

115 °C; IR ($CHCl_3$) 2955, 1730, 1635, 1465, 1250 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.00 (s, 6H, 2×CH_3), 2.21 (s, 3H, CH_3), 2.61 (t, J=7.3 Hz, 2H, CH_2), 2.95 (t, J=7.3 Hz, 2H, CH_2), 3.64 (s, 3H, OCH_3), 3.86 (s, 3H, NCH_3); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 9.9 (q), 12.2 (q), 12.3 (q), 20.0 (t), 32.2 (q), 33.4 (t), 55.1 (q), 120.8 (s), 122.7 (s), 128.4 (s), 135.7 (s), 140.0 (s), 140.2 (s), 173.7 (s), 177.7 (s), 184.0 (s). Anal. Calcd for $C_{16}H_{19}NO_4$: C, 66.42; H, 6.62; N, 4.84. Found: C, 66.56; H, 6.63; N, 4.81.

3.3.29. 4-(4,7-Dihydro-1,2,5,6-tetramethyl-4,7-dioxo-1*H*-indol-3-yl)-butyric acid 15e. Orange crystals; mp 160–161 °C; IR ($CHCl_3$) 3525 (br), 2925, 1710, 1635, 1250 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.86 (quintet, J=7.4 Hz, 2H, CH_2), 2.01 (s, 6H, 2×CH_3), 2.18 (s, 3H, CH_3), 2.37 (t, J=7.4 Hz, 2H, CH_2), 2.77 (t, J=7.4 Hz, 2H, CH_2), 3.87 (s, 3H, NCH_3); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 9.4 (q), 12.1 (q), 12.2 (q), 23.7 (t), 25.0 (t), 32.4 (q), 33.2 (t), 121.8 (s), 123.0 (s), 128.4 (s), 135.6 (s), 140.17 (s), 140.22 (s), 177.8 (s), 179.1 (s), 184.3 (s). Anal. Calcd for $C_{16}H_{19}NO_4$: C, 66.42; H, 6.62; N, 4.84. Found: C, 66.48; H, 6.62; N, 4.85.

3.3.30. 3-Ethoxycarbonyl-1,2,5-trimethyl-1*H*-indole-4,7-dione 20a. Yellow crystals; mp 113–114 °C; IR ($CHCl_3$) 2990, 1710, 1655, 1620, 1500 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.41 (t, J=7.1 Hz, 3H, CH_3), 2.07 (d, J=1.4 Hz, 3H, CH_3), 2.44 (s, 3H, CH_3), 3.91 (s, 3H, NCH_3), 4.39 (q, J=7.1 Hz, 2H, OCH_2), 6.36 (q, J=1.4 Hz, 1H, CH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 10.7 (q), 14.2 (q), 16.0 (q), 32.4 (q), 60.9 (t), 113.2 (s), 123.6 (s), 129.3 (s), 132.5 (d), 141.0 (s), 146.7 (s), 164.4 (s), 178.7 (s), 181.8 (s). Anal. Calcd for $C_{14}H_{15}NO_4$: C, 64.36; H, 5.79; N, 5.36. Found: C, 64.31; H, 5.77; N, 5.33.

3.3.31. 3-Ethoxycarbonyl-1,5-dimethyl-2-propyl-1*H*-indole-4,7-dione 20b. Yellow powders; mp 56–57 °C; IR ($CHCl_3$) 2970, 1660, 1645, 1615, 1460, 1265 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 0.99 (t, J=7.6 Hz, 3H, CH_3), 1.40 (t, J=7.1 Hz, 3H, CH_3), 1.62 (sextet, J=7.6 Hz, 2H, CH_2), 2.07 (d, J=1.5 Hz, 3H, CH_3), 2.81 (t, J=7.6 Hz, 2H, CH_2), 3.92 (s, 3H, NCH_3), 4.39 (q, J=7.1 Hz, 2H, CH_2), 6.36 (q, J=1.5 Hz, 1H, CH); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 13.8 (q), 14.2 (q), 15.9 (q), 22.4 (t), 26.4 (t), 32.4 (q), 60.9 (t), 113.3 (s), 123.7 (s), 129.3 (s), 132.6 (d), 144.8 (s), 146.7 (s), 164.4 (s), 178.7 (s), 181.9 (s). Anal. Calcd for $C_{16}H_{19}NO_4$: C, 66.42; H, 6.62; N, 4.84. Found: C, 66.32; H, 6.66; N, 4.81.

3.3.32. 3-Acetyl-1,2,5-trimethyl-1*H*-indole-4,7-dione 20c. Yellow powders; mp 190–191 °C; IR ($CHCl_3$) 3005, 2925, 1645, 1620, 1465, 1265 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 2.09 (d, J=1.3 Hz, 3H, CH_3), 2.38 (s, 3H, CH_3), 2.64 (s, 3H, CH_3), 3.91 (s, 3H, NCH_3), 6.39 (q, J=1.3 Hz, 1H, CH); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 10.7 (q), 16.0 (q), 31.5 (q), 32.3 (q), 122.1 (s), 122.9 (s), 128.8 (s), 132.9 (d), 140.7 (s), 146.3 (s), 178.7 (s), 183.2 (s), 198.7 (s). Anal. Calcd for $C_{13}H_{13}NO_3$: C, 67.52; H, 5.67; N, 6.06. Found: C, 67.43; H, 5.80; N, 5.82.

3.3.33. 1,2,5-Trimethyl-3-(3-methylbutanoyl)-1*H*-indole-4,7-dione 20d. Yellow crystals; mp 99–100 °C; IR ($CHCl_3$) 2960, 1645, 1620, 1460, 1265, 1235 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 0.94 (d, J=6.9 Hz, 6H, 2×CH_3), 2.08 (d, J=1.5 Hz, 3H, CH_3), 2.16 (nontet, J=6.9 Hz, 1H, CH), 2.34 (s, 3H, CH_3), 2.91 (d, J=6.9 Hz, 2H, CH_2), 3.90 (s, 3H, NCH_3), 6.37 (q, J=1.5 Hz, 1H, CH); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 10.5 (q), 15.9 (q), 22.6 (2×q), 25.5 (d), 32.3 (q), 52.3 (t), 122.56 (s), 122.65 (s), 128.6 (s), 132.9 (d), 139.9 (s), 146.2 (s), 178.6 (s), 183.0 (s), 201.9 (s). Anal. Calcd for $C_{16}H_{19}NO_3$: C, 70.31; H, 7.01; N, 5.12. Found: C, 70.25; H, 7.11; N, 5.13.

3.3.34. 1,2,5-Trimethyl-3-(pivaloyl)-1*H*-indole-4,7-dione 20e. Yellow crystals; mp 151–152 °C; IR ($CHCl_3$) 2970, 1645, 1615, 1465, 1270 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.24 (s, 9H, 3×CH_3), 2.03 (d, J=1.6 Hz, 3H, CH_3), 2.17 (s, 3H, CH_3), 3.88 (s, 3H, NCH_3), 6.35 (q, J=1.6 Hz, 1H, CH); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 10.8 (q), 15.6 (q), 27.0 (3×q), 32.3 (q), 45.7 (s), 122.0 (s), 123.6 (s), 128.2 (s), 133.6 (d), 134.3 (s), 145.5 (s), 178.3 (s), 182.7 (s), 211.7 (s). Anal. Calcd for $C_{16}H_{19}NO_3$: C, 70.31; H, 7.01; N, 5.12. Found: C, 70.17; H, 7.00; N, 5.10.

3.3.35. 3-Benzoyl-1,2,5-trimethyl-1*H*-indole-4,7-dione 20f. Yellow needles; mp 218–219 °C; IR ($CHCl_3$) 3010, 1645, 1615, 1465, 1325, 1275 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.94 (d, J=1.6 Hz, 3H, CH_3), 2.29 (s, 3H, CH_3), 3.96 (s, 3H, NCH_3), 6.38 (q, J=1.6 Hz, 1H, CH), 7.39–7.46 (m, 2H, ArH), 7.52–7.58 (m, 1H, ArH), 7.80–7.86 (m, 2H, ArH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 10.5 (q), 15.7 (q), 32.4 (q), 120.4 (s), 124.1 (s), 128.4 (2×d), 128.5 (s), 129.2 (2×d), 133.1 (d), 133.2 (d), 138.4 (s), 139.3 (s), 146.0 (s), 178.6 (s), 182.1 (s), 193.0 (s). Anal. Calcd for $C_{18}H_{15}NO_3$: C, 73.71; H, 5.15; N, 4.78. Found: C, 73.56; H, 5.17; N, 4.76.

3.3.36. 1,2,5-Trimethyl-1*H*-indole-4,7-dione 21a. Orange needles; mp 108–109 °C; IR (KBr) 2950, 1645, 1445, 1205, 1155 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.04 (d, J=1.6 Hz, 3H, CH_3), 2.27 (s, 3H, CH_3), 3.87 (s, 3H, NCH_3), 6.32 (q, J=1.6 Hz, 1H, CH), 6.34 (s, 1H, CH); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 11.9 (q), 15.5 (q), 32.0 (q), 106.5 (d), 126.0 (s), 129.1 (s), 133.7 (d), 138.2 (s), 145.1 (s), 177.8 (s), 183.4 (s). Anal. Calcd for $C_{11}H_{11}NO_2$: C, 69.83; H, 5.86; N, 7.40. Found: C, 69.74; H, 5.84; N, 7.36.

3.3.37. 2-Ethyl-1,3,5-trimethyl-1*H*-indole-4,7-dione 21b. Orange crystals; mp 91–92 °C; IR (KBr) 2970, 1640, 1470, 1230, 1175 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.14 (t, J=7.6 Hz, 3H, CH_3), 2.03 (d, J=1.5 Hz, 3H, CH_3), 2.28 (s, 3H, CH_3), 2.62 (q, J=7.6 Hz, 2H, CH_2), 3.90 (s, 3H, NCH_3), 6.31 (q, J=1.5 Hz, 1H, CH); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 9.8 (q), 13.3 (q), 15.5 (q), 16.8 (t), 32.1 (q), 118.3 (s), 123.6 (s), 128.1 (s), 133.8 (d), 141.2 (s), 145.4 (s), 177.8 (s), 184.9 (s). Anal. Calcd for $C_{13}H_{15}NO_2$: C, 71.87; H, 6.96; N, 6.45. Found: C, 71.71; H, 6.96; N, 6.43.

3.3.38. 1,5-Dimethyl-2-phenyl-1*H*-indole-4,7-dione 21c. Orange crystals; mp 124–125 °C; IR ($CHCl_3$) 3010, 2960, 1645, 1445, 1265 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.08 (d, J=1.5 Hz, 3H, CH_3), 3.91 (s, 3H, NCH_3), 6.40 (q, J=1.5 Hz, 1H, CH), 6.62 (s, 1H, CH), 7.36–7.52 (m, 5H, ArH); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 15.7 (q), 34.1 (q), 107.9 (d), 126.3 (s), 128.7 (2×d), 128.9 (d), 129.2

(2×d), 130.0 (s), 130.3 (s), 134.0 (d), 142.3 (s), 145.7 (s), 178.4 (s), 183.5 (s). Anal. Calcd for $C_{16}H_{13}NO_2$: C, 76.48; H, 5.21; N, 5.57. Found: C, 76.40; H, 5.29; N, 5.48.

3.3.39. 1,5-Dimethyl-2,3-diphenyl-1*H*-indole-4,7-dione 21d. Brick red crystals; mp 238–239 °C; IR (KBr) 1650, 1455, 1260, 1195 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.05 (d, J=1.5 Hz, 3H, CH_3), 3.86 (s, 3H, NCH_3), 6.45 (q, J=1.5 Hz, 1H, CH), 7.14–7.24 (m, 7H, ArH), 7.31–7.38 (m, 3H, ArH); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 15.8 (q), 34.1 (q), 122.3 (s), 124.4 (s), 127.0 (d), 127.5 (2×d), 128.5 (2×d), 128.8 (d), 129.3 (s), 129.4 (s), 130.4 (2×d), 130.9 (2×d), 132.4 (s), 133.3 (d), 139.9 (s), 146.8 (s), 178.7 (s), 183.2 (s). Anal. Calcd for $C_{22}H_{17}NO_2$: C, 80.71; H, 5.23; N, 4.28. Found: C, 80.57; H, 5.25; N, 4.22.

3.3.40. 1,2,5-Trimethyl-6-(2-oxo-propyl)-1*H*-indole-4,7-dione 22a. Orange crystals; mp 153–154 °C; IR (KBr) 2955, 1710, 1640, 1240, 1165 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.99 (s, 3H, CH_3), 2.267 (s, 3H, CH_3), 2.272 (s, 3H, CH_3), 3.67 (s, 2H, CH_2), 3.86 (s, 3H, NCH_3), 6.35 (s, 1H, CH); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 12.0 (q), 12.5 (q), 30.0 (q), 32.2 (q), 41.2 (t), 106.6 (d), 126.1 (s), 128.7 (s), 137.9 (s), 138.5 (s), 142.4 (s), 176.7 (s), 182.8 (s), 204.2 (s). Anal. Calcd for $C_{14}H_{15}NO_3$: C, 68.56; H, 6.16; N, 5.71. Found: C, 68.50; H, 6.14; N, 5.68.

3.3.41. 2-Ethyl-1,3,5-trimethyl-6-(1-methyl-2-oxo-butyl)-1*H*-indole-4,7-dione 22b. Brick red liquid; IR (KBr) 2970, 1715, 1630, 1460, 1245 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.04 (t, J=7.3 Hz, 3H, CH_3), 1.14 (t, J=7.6 Hz, 3H, CH_3), 1.32 (d, J=6.9 Hz, 3H, CH_3), 2.03 (s, 3H, CH_3), 2.28 (s, 3H, CH_3), 2.35 (q, J=7.3 Hz, 2H, CH_2), 2.62 (q, J=7.6 Hz, 2H, CH_2), 3.74 (q, J=6.9 Hz, 1H, CH), 3.89 (s, 3H, NCH_3); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 8.1 (q), 9.7 (q), 12.0 (q), 13.1 (q), 14.3 (q), 16.8 (t), 32.3 (q), 33.6 (t), 45.3 (d), 118.2 (s), 123.5 (s), 127.5 (s), 141.5 (s), 141.9 (s), 144.5 (s), 176.0 (s), 184.2 (s), 209.5 (s); HRMS calcd for $C_{18}H_{23}NO_3$: m/z 301.1678; found: m/z 301.1682.

Acknowledgements

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

References and notes

1. (a) Hart, D. J. *Science* **1984**, *223*, 883; (b) Neumann, W. P. *Synthesis* **1987**, 665; (c) Curran, D. P. *Synthesis* **1988**, 417 and 489; (d) Melikyan, G. G. *Synthesis* **1993**, 833; (e) Iqbal, J.; Bhatia, B.; Nayyar, N. K. *Chem. Rev.* **1994**, *94*, 519; (f) Snider, B. B. *Chem. Rev.* **1996**, *96*, 339.
2. (a) *The Chemistry of Functional Groups: The Chemistry of the Quinoid Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, NY, 1988; (b) Thomson, R. H. *Natural Occurring Quinones IV: Recent Advances*; Chapman and Hall: London, 1997.
3. (a) Shaw, K. J.; Luly, J. R.; Rapoport, H. *J. Org. Chem.* **1985**, *50*, 4515; (b) Murphy, W. S.; O'Sullivan, P. J. *Tetrahedron Lett.* **1992**, *33*, 531; (c) O'Sullivan, P. J.; Moreno, R.; Murphy, W. S. *Tetrahedron Lett.* **1992**, *33*, 535.
4. (a) Yogo, M.; Ito, C.; Furukawa, H. *Chem. Pharm. Bull.* **1991**, *39*, 328; (b) Bittner, S.; Krief, P.; Massil, T. *Synthesis* **1991**, 215; (c) Knölker, H.-J.; O'Sullivan, N. *Tetrahedron* **1994**, *50*, 10893; (d) Åkermark, B.; Oslob, J. D.; Heuschert, U. *Tetrahedron Lett.* **1995**, *36*, 1325; (e) Echavarran, A. M.; Tamayo, N.; De Frutos, O.; Garcia, A. *Tetrahedron* **1997**, *50*, 16835.
5. (a) Oumar-Mahamat, H.; Moustrou, C.; Surzur, J.-M.; Berstrand, M. P. *J. Org. Chem.* **1989**, *54*, 5684; (b) Snider, B. B.; Wan, B. Y. F.; Buckman, B. O.; Foxman, B. M. *J. Org. Chem.* **1991**, *56*, 5328; (c) Citterio, A.; Sebastiano, R.; Carvayal, M. C. *J. Org. Chem.* **1991**, *56*, 5335; (d) Citterio, A.; Sebastiano, R.; Nicolini, M. *Tetrahedron* **1993**, *49*, 7743.
6. (a) Chuang, C.-P.; Wang, S.-F. *Tetrahedron Lett.* **1994**, *35*, 4365; (b) Chuang, C.-P.; Wang, S.-F. *J. Chin. Chem. Soc.* **1997**, *44*, 271; (c) Chuang, C.-P.; Wang, S.-F. *Tetrahedron* **1998**, *54*, 10043; (d) Chuang, C.-P.; Wang, S.-F. *Heterocycles* **1999**, *50*, 489; (e) Chuang, C.-P.; Wu, Y.-L.; Jiang, M.-C. *Tetrahedron* **1999**, *55*, 11229; (f) Jiang, M.-C.; Chuang, C.-P. *J. Org. Chem.* **2000**, *65*, 5409; (g) Wu, Y.-L.; Chuang, C.-P.; Lin, P.-Y. *Tetrahedron* **2001**, *57*, 5543; (h) Tsai, A.-I.; Wu, Y.-L.; Chuang, C.-P. *Tetrahedron* **2001**, *57*, 7829; (i) Chuang, C.-P.; Wu, Y.-L. *Tetrahedron Lett.* **2001**, *42*, 1719; (j) Tseng, C.-C.; Wu, Y.-L.; Chuang, C.-P. *Tetrahedron* **2002**, *58*, 7625; (k) Tseng, C.-M.; Wu, Y.-L.; Chuang, C.-P. *Tetrahedron* **2004**, *60*, 12249; (l) Chen, H.-L.; Lin, C.-Y.; Cheng, Y.-C.; Tsai, A.-I.; Chuang, C.-P. *Synthesis* **2005**, 977; (m) Lin, C.-Y.; Cheng, Y.-C.; Tsai, A.-I.; Chuang, C.-P. *Org. Biomol. Chem.* **2006**, 1097.
7. (a) Liao, Y.-J.; Wu, Y.-L.; Chuang, C.-P. *Tetrahedron* **2003**, *59*, 3511; (b) Chuang, C.-P.; Wu, Y.-L. *Tetrahedron* **2004**, *60*, 1841; (c) Tsai, A.-I.; Lin, C.-H.; Chuang, C.-P. *Heterocycles* **2005**, 977; (d) Tsai, A.-I.; Chuang, C.-P. *Tetrahedron* **2006**, *62*, 2235.
8. (a) Jacobsen, N.; Torsell, K. *Acta Chem. Scand.* **1973**, *27*, 3211; (b) Brown, P. M.; Thomson, R. H. *J. Chem. Soc., Perkin Trans. 1* **1976**, 997; (c) Citterio, A.; Arnoldi, A.; Minisci, F. *J. Org. Chem.* **1979**, *44*, 2674; (d) Citterio, A.; Vismara, E.; Bernardi, R. *J. Chem. Res., Synop.* **1983**, 88; (e) Citterio, A.; Vismara, E.; Bernardi, R. *J. Chem. Res., Miniprint* **1983**, 876; (f) Williams, D. R.; Clark, M. P. *Tetrahedron Lett.* **1998**, *39*, 7629.
9. (a) Imamoto, T.; Sugiura, Y.; Takiyama, N. *Tetrahedron Lett.* **1984**, *25*, 4233; (b) Imamoto, T.; Takiyama, N.; Nakamura, K. *Tetrahedron Lett.* **1985**, *26*, 4763. Also see: Ref. 6j.
10. (a) Snider, B. B.; Merritt, J. E.; Dombroski, M. A.; Buckman, B. O. *J. Org. Chem.* **1991**, *56*, 5544; (b) Snider, B. B.; McCarthy, B. A. *J. Org. Chem.* **1993**, *58*, 6217; (c) Ishibashi, H.; Toyao, A.; Takeda, Y. *Synlett* **1999**, 1468. Also see: Ref. 6b–e,k.
11. (a) Kallmeyer, H.-J.; Tappe, C. *Arch. Pharmacol.* **1986**, *319*, 421; (b) Kallmeyer, H.-J.; Tappe, C. *Arch. Pharmacol.* **1986**, *41*, 29.