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Metal Salt Mediated Radical Reactions of 2-Substituted-1,4-Naphthoquinones

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The silver(II)- and manganese(III)-mediated radical reactions of 2-substituted-1,4-naphthoquinones are described. Acyl radicals generated by the oxidative decarboxylation of α-keto acids with silver(I) nitrate and persulfate undergo efficient radical addition to the C=C bond of 2-(1-hydroxyalkyl)-1,4-naphthoquinones and 2-(1-amidoalkyl)-1,4-naphthoquinones. This reaction provides an effective method for the synthesis of naphtho[2,3-*c*]furan-4,9-diones and benzo[*f*]isoindole-4,9-diones. In the presence of O_2, manganese(III) acetate oxidation of β-keto esters also generates acyl radicals, which then undergo radical addition to 2-(1-amidoalkyl)-1,4-naphthoquinones, and subsequently, benzo[*f*]isoindole-4,9-diones are produced.

Introduction

There has been a growing interest in the application of free radical reactions and many new methods proceeding through radical reactions designed for organic synthesis have been developed.[1,2] The addition of carbon-centered radicals produced by metal salt oxidation of 1,3-dicarbonyl compounds to alkenes has received considerable attention in organic synthesis for the construction of carbon–carbon bonds. Among these, manganese(III) acetate and cerium(IV) ammonium nitrate have been used most efficiently.[2–5] Carbon radicals can be produced effectively by silver ion catalyzed oxidative decarboxylation of carboxylic acids with persulfate,[6] and they undergo homolytic alkylation with heteroaromatics[7] and 1,4-quinones.[8] Compounds containing the quinone group are an important class of biologically active molecules that are widespread in nature.[9,10]

Previously, we found that the manganese(III) acetate mediated oxidative free radical reaction of 2-benzoyl-(3-ethoxycarbonylmethyl)-1,4-naphthoquinones, in addition to the expected 6-hydroxy-naphthacene-5,12-diones, produced the novel naphtho[2,3-*c*]furan-4,9-diones as the major products.[5g] These naphtho[2,3-*c*]furan-4,9-diones can also be generated directly from the intermolecular oxidative free radical reaction of 2-benzoyl-1,4-naphthoquinones with 1,3-dicarbonyl compounds.[5h] Naphtho[2,3-*c*]furan-4,9-diones form the largest subset of natural products containing a *c*-fused furan ring.[10] Methods for their synthesis have been reviewed.[9c] The corresponding isofuran derivatives have served as quinodimethane synthetic analogues in Diels–Alder reactions and are widely used in the preparation of complex molecules.[12] The benzo[*f*]isoindole-4,9-dione skeleton has also attracted considerable attention in the literature and several pathways have been developed for its synthesis.[13] Acyl radicals were produced by the oxidative decarboxylation of α-keto acids with silver(I) ion and persulfate, and they were then utilized for the acylation of 1,4-quinones.[14] As part of our study on the development of new routes to heterocyclic systems proceeding through metal salt mediated radical reactions,[5,11] we now report a new method for the synthesis of naphtho[*c*]furan-4,9-dione and benzo[*f*]isoindole-4,9-dione derivatives from 2-substituted-1,4-naphthoquinones.

Results and Discussion

We began our studies of the silver(I)-catalyzed reaction with 2-(1-hydroxyalkyl)-1,4-naphthoquinones **1** and α-keto acids **2** (Scheme 1). When 2-(1-hydroxybenzyl)-1,4-naphthoquinone (**1a**, R^1 = Ph) was treated with 2-oxopropionic acid (**2a**, R^2 = Me), silver(I) nitrate and potassium persulfate in acetonitrile/H_2O at 70 °C, naphtho[*c*]furan-4,9-dione **3a** was obtained in 57% yield (Table 1, Entry 1). The structure of **3a** is clearly assigned by ^{1}H NMR and ^{13}C NMR spectroscopy. Although the mechanistic details of this reaction are unclear, **3a** may be formed by the reaction route presented in Scheme 2. Silver(II)-mediated decarboxylation of **6a** produces acyl radical **4a**. Intermolecular addition of acyl radical intermediate **4a** to the quinone ring followed by oxidation produces **5a**. Acylation product **5a** is then converted into **3a** by an intramolecular condensation reaction. The generalities of this reaction were examined with other α-keto acids **2**, and the results are summarized in Table 1 (Entries 1–5). In all cases, **1a** was converted into the corresponding isofuran products **3** effectively. We also applied $Ag^I/S_2O_8^{-2}$ reaction conditions to 2-(1-hydroxyethyl)-1,4-

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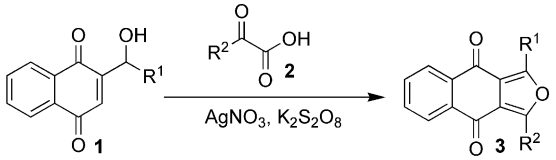
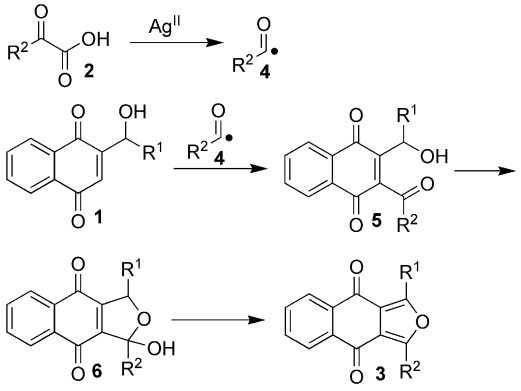
naphthoquinone (**1b**, R^1 = Me). The reaction worked well and isofurans **3f**–**h** were formed in 74–56% yield (Table 1, Entries 6–8). This reaction provides an efficient method for the formation of naphtho[2,3-*c*]furan-4,9-diones.



Scheme 1. Reaction between 2-(1-hydroxyalkyl)-1,4-naphthoquinones **1** and α-keto acids **2**.

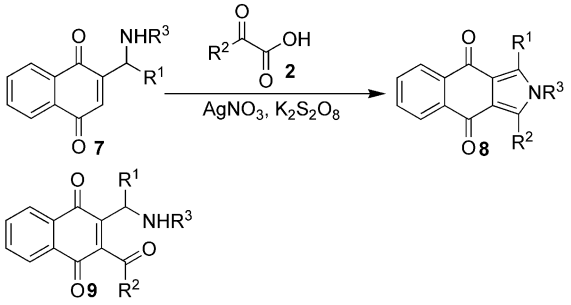
Table 1. Reaction between 2-(1-hydroxyalkyl)-1,4-naphthoquinones **1** and α-keto acids **2**.

Entry	Quinone	Acid	Product (% yield)
1	**1a**: R^1 = Ph	**2a**: R^2 = Me	**3a** (57)
2	**1a**: R^1 = Ph	**2b**: R^2 = Et	**3b** (54)
3	**1a**: R^1 = Ph	**2c**: R^2 = Pr	**3c** (54)
4	**1a**: R^1 = Ph	**2d**: R^2 = *i*Bu	**3d** (54)
5	**1a**: R^1 = Ph	**2e**: R^2 = Ph	**3e** (75)
6	**1b**: R^1 = Me	**2a**: R^2 = Me	**3f** (61)
7	**1b**: R^1 = Me	**2b**: R^2 = Et	**3g** (56)
8	**1b**: R^1 = Me	**2e**: R^2 = Ph	**3a** (74)



Scheme 2. Probable mechanism for the reaction between **1** and **2**.

In view of the good results on the formation of naphtho[2,3-*c*]furan-4,9-diones **3**, we reasoned that it might be possible to produce benzo[*f*]isoindole-4,9-diones **8** through the condensation reaction of **9**, which was formed by the acyl radical addition of 2-(1-amidoalkyl)-1,4-naphthoquinones **7**. We next investigated the silver(II)-mediated reaction between 2-(1-amidoalkyl)-1,4-naphthoquinones **11** and α-keto acids **2** for the synthesis of benzo[*f*]isoindole-4,9-diones **8** (Scheme 3). Treatment of 2-[*N*-acetyl-(1-aminobenzyl)]-1,4-naphthoquinone (**7a**, R^1 = Ph, R^3 = Ac) with 2-oxopropionic acid (**2a**, R^2 = Me), silver(I) nitrate, and potassium persulfate in acetonitrile/H_2O at 70 °C generated benzo[*f*]isoindole-4,9-dione **8a** in 64% yield (Table 2, Entry 1). The structure of **8a** was revealed by ^1H and ^{13}C NMR spectroscopy. The results of the reaction between [*N*-acetyl-(1-aminobenzyl)]-1,4-naphthoquinone (**7a**) and other α-keto acids **2** are also summarized in Table 2 (Entries 2–5). In all cases, **7a** was converted into the corresponding isoindole products **8** effectively. The reaction yield decreased as the size of the substituent (R^2) increased. This can be attributed to the steric effect exerted by the R^2 group – the condensation rate of **9** is retarded by the larger R^2 group. This reaction provides a straightforward method for the synthesis of benzo[*f*]isoindole-4,9-diones **8**. Other N-protecting groups were also employed to examine the scope of this reaction. As shown in Table 2 (Entries 6–13), isoindoles **8** were obtained in moderate to good yields. With R^3 = CO_2Et, isoindoles **8** were obtained with best results. This is presumably due to the higher nucleophilicity of the ethoxycarbonylamino group.



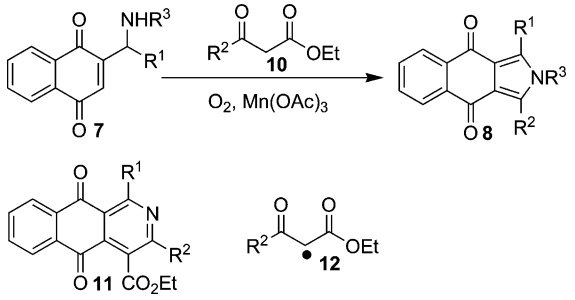
Scheme 3. Reaction between 2-(1-amidoalkyl)-1,4-naphthoquinones **7** and α-keto acids **2**.

Table 2. Reaction between 2-(1-amidoalkyl)-1,4-naphthoquinones **7** and α-keto acids **2**.

Entry	Quinone	Acid	Product (% yield)
1	**7a**: R^1 = Ph, R^3 = Ac	**2a**: R^2 = Me	**8a** (64)
2	**7a**: R^1 = Ph, R^3 = Ac	**2b**: R^2 = Et	**8b** (59)
3	**7a**: R^1 = Ph, R^3 = Ac	**2c**: R^2 = Pr	**8c** (43)
4	**7a**: R^1 = Ph, R^3 = Ac	**2d**: R^2 = *i*Bu	**8d** (30)
5	**7a**: R^1 = Ph, R^3 = Ac	**2e**: R^2 = Ph	**8e** (13)
6	**7b**: R^1 = Ph, R^3 = Bz	**2a**: R^2 = Me	**8f** (73)
7	**7b**: R^1 = Ph, R^3 = Bz	**2b**: R^2 = Et	**8g** (65)
8	**7b**: R^1 = Ph, R^3 = Bz	**2c**: R^2 = Pr	**8h** (47)
9	**7c**: R^1 = Ph, R^3 = CO_2Et	**2a**: R^2 = Me	**8i** (84)
10	**7c**: R^1 = Ph, R^3 = CO_2Et	**2b**: R^2 = Et	**8j** (84)
11	**7c**: R^1 = Ph, R^3 = CO_2Et	**2c**: R^2 = Pr	**8k** (60)
12	**7c**: R^1 = Ph, R^3 = CO_2Et	**2d**: R^2 = *i*Bu	**8l** (55)
13	**7c**: R^1 = Ph, R^3 = CO_2Et	**2e**: R^2 = Ph	**8m** (33)

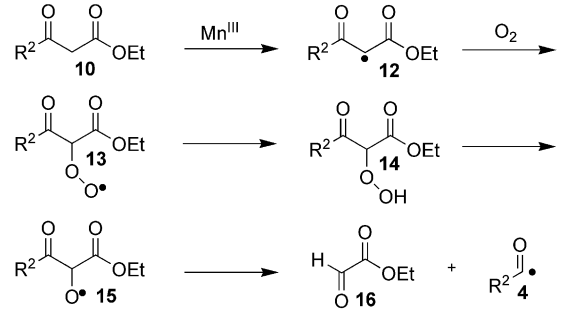
Previously, we found that oxidative free radical reactions of 2-alkylamino-1,4-naphthoquinones with β-keto esters produced benzo[*f*]indole-4,9-diones and benzo[*f*]indole-2,4,9-triones.[5a,5f] In acidic solvent, the condensation products − benzo[*f*]indole-4,9-diones − are the major product. Naturally occurring 2-azaanthraquinones are of special interest due to their important physiological properties.[9b,10b,15] We believe that radical reaction between 2-(1-amidoalkyl)-1,4-naphthoquinones **7** and β-keto esters **10** would generate 2-azaanthraquinones **11** through intermolecular addition of radical **12** to the quinone ring followed by an intramolecular condensation reaction. We have continued to examine the manganese(III)-mediated oxidative free radical reaction between 2-(1-amidoalkyl)-1,4-naphthoquinones **7** and β-keto esters **10** (Scheme 4). When [*N*-benzoyl-(1-aminobenzyl)-1,4-naphthoquinone] (**7b**, R^1 =

Ph, R^3 = Bz) was treated with ethyl acetoacetate (**10a**, R^2 = Me) and manganese(III) acetate in acetic acid at 80 °C for 14 h, desired product **11a** was not found, and instead, benzo[*f*]isoindole-4,9-dione **8f** was obtained in 34% yield (Table 3, Entry 1).



Scheme 4. Reaction between 2-(1-amidoalkyl)-1,4-naphthoquinones **7** and β-keto esters **10**.

Isoindole product **8f** was formed by a similar acyl radical addition mechanism shown in Scheme 2, and acyl radical **4a** was presumably formed by the reaction mechanism outlined in Scheme 5. Manganese(III) acetate oxidation of **10a** produces radical **12a**. This radical intermediate **12a** undergoes oxygen trapping to give hydroperoxide **14a**.[16] Thermal fragmentation of **14a** produces acyl radical **4a**.[17] This unusual acyl radical formation can be attributed to the steric effect exerted by the 1-amidobenzyl group; the addition of radical **12a** to the quinone ring of **7** is retarded by this large 1-amidobenzyl group, and the formation of acyl radical **4a** by the oxygen trapping of radical **12a** becomes the major route. Although the expected reaction did not occur, the formation of **8a** prompted us to examine the applicability of this reaction. With the reasonable assumption that oxygen takes part in the reaction leading to the formation of acyl radical **4a**, the reaction between **7b** and **10a** was repeated under an atmosphere of oxygen. In this case, the yield of **8f** increased to 60% and the reaction time was shorten to 30 min (Table 3, Entry 2). Other β-keto esters **10** were also subjected to the manganese(III) acetate reaction with **7b** under oxygenated conditions. As shown in Table 3, isoindole products **8** were obtained effectively, and the reaction yields of **8** decreased as the size of the R^2 group increased (Table 3, Entries 2–4). Other N-protecting groups were also employed to examine the scope of this reaction.



Scheme 5. Probable mechanism for the formation of acyl radical **4**.

In all cases, isoindole products **8** were obtained with moderate yields (Table 3, Entries 5–10).

Table 3. Reaction between 2-(1-amidoalkyl)-1,4-naphthoquinones **7** and β-keto esters **10**.

Entry	Quinone	β-Keto ester	Product (% yield)
1[a]	**7b**: R^1 = Ph, R^3 = Bz	**10a**: R^2 = Me	**8f** (34)
2[b]	**7b**: R^1 = Ph, R^3 = Bz	**10a**: R^2 = Me	**8f** (60)
3[b]	**7b**: R^1 = Ph, R^3 = Bz	**10b**: R^2 = Et	**8g** (37)
4[b]	**7b**: R^1 = Ph, R^3 = Bz	**10c**: R^2 = Pr	**8h** (39)
5[b]	**7c**: R^1 = Ph, R^3 = CO_2Et	**10a**: R^2 = Me	**8i** (56)
6[b]	**7c**: R^1 = Ph, R^3 = CO_2Et	**10b**: R^2 = Et	**8j** (43)
7[b]	**7c**: R^1 = Ph, R^3 = CO_2Et	**10c**: R^2 = Pr	**8k** (41)
8[b]	**7a**: R^1 = Ph, R^3 = Ac	**10a**: R^2 = Me	**8a** (50)
9[b]	**7a**: R^1 = Ph, R^3 = Ac	**10b**: R^2 = Et	**8b** (34)
10[b]	**7a**: R^1 = Ph, R^3 = Ac	**10c**: R^2 = Pr	**8c** (29)

[a] The reaction was performed under an atmosphere of N_2 for 14 h. [b] The reaction was performed under an atmosphere of O_2 for 30 min.

Conclusions

The silver-catalyzed decarboxylation of α-keto acids by persulfate leads to acyl radicals, which can undergo efficient radical addition to the C=C bond of 2-(1-hydroxyalkyl)-1,4-naphthoquinones and 2-(1-amidoalkyl)-1,4-naphthoquinones. This reaction provides an effective method for the synthesis of naphtho[*c*]furan-4,7-diones and benzo[*f*]isoindole-4,9-diones. In the presence of O_2, manganese(III) acetate oxidation of β-keto esters can also generate acyl radicals from hydroperoxide, which then undergo a similar radical addition reaction to 2-(1-amidoalkyl)-1,4-naphthoquinones; subsequently, benzo[*f*]isoindole-4,9-diones are produced.

Experimental Section

General Considerations: Melting points were measured with a Büchi melting point apparatus B-540. Infrared spectra were recorded with a Hitachi 260–30 spectrometer. ^1H and ^{13}C NMR spectra were recorded with a Bruker Avance-300 or AMX-400 spectrometer. Chemical shifts are reported in ppm relative to TMS as internal reference. The multiplicity of the ^{13}C NMR signals was determined by DEPT 135 experiments. Elemental analyses were performed with a Heraeus CHN-Rapid Analyzer. Mass spectra were recorded with a Jeol JMS-SX 102A mass spectrometer. 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 Laboratories silica gel (70–230 mesh).

Typical Procedure for the Silver(II)-Catalyzed Reaction between 2-(1-Hydroxyalkyl)-1,4-naphthoquinones and α-Keto Acids: A mixture of 2-(1-hydroxybenzyl)-1,4-naphthoquinone (**1a**; 131 mg, 0.50 mmol), 2-oxopropionic acid (**2a**; 133 mg, 1.51 mmol), silver(I) nitrate (34 mg, 0.20 mmol), and potassium persulfate (484 mg, 1.79 mmol) in acetonitrile (2 mL) and H_2O (6 mL) was heated at 70 °C for 3 h. The reaction mixture was diluted with ethyl acetate (100 mL), washed with water (3 × 50 mL), dried (Na_2SO_4), and concentrated in vacuo. The crude product was purified by column

chromatography over silica gel (20 g; ethyl acetate/hexane, 1:15) followed by recrystallization (ethyl acetate/hexane) to give **3a** (82 mg, 57%).

1-Methyl-3-phenylnaphtho[2,3-*c*]furan-4,9-dione (3a): Yellow needles; yield 82 mg, 57%; m.p. 122–123 °C (ethyl acetate/hexane). IR (KBr): $\tilde{\nu}$ = 3070, 1675, 1590, 1400, 1250 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.85 (s, 3 H, CH_3), 7.45–7.56 (m, 3 H, ArH), 7.73–7.81 (m, 2 H, ArH), 8.25–8.31 (m, 1 H, ArH), 8.32–8.37 (m, 1 H, ArH), 8.44–8.51 (m, 2 H, ArH) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 13.5 (q), 116.7 (s), 118.6 (s), 126.3 (d), 127.32 (2 d), 127.35 (d), 128.1 (s), 128.2 (2 d), 130.5 (d), 133.1 (d), 133.4 (d), 134.7 (s), 136.0 (s), 155.2 (s), 157.8 (s), 178.6 (s), 180.2 (s) ppm. $C_{19}H_{12}O_3$ (288.08): calcd. C 79.16, H 4.20; found C 78.82, H 4.18.

1-Ethyl-3-phenylnaphtho[2,3-*c*]furan-4,9-dione (3b): Yellow crystals; yield 80 mg, 54%; m.p. 122–123 °C (ethyl acetate/hexane). IR (KBr): $\tilde{\nu}$ = 2975, 1670, 1590, 1490, 1245 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.42 (t, J = 7.6 Hz, 3 H, CH_3), 3.29 (q, J = 7.6 Hz, 2 H, CH_2), 7.46–7.57 (m, 3 H, ArH), 7.72–7.81 (m, 2 H, ArH), 8.26–8.31 (m, 1 H, ArH), 8.32–8.38 (m, 1 H, ArH), 8.44–8.50 (m, 2 H, ArH) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 11.5 (q), 21.3 (t), 116.9 (s), 117.9 (s), 126.5 (d), 127.49 (d), 127.54 (2 d), 128.36 (2 d), 128.41 (s), 130.6 (d), 133.3 (d), 133.5 (d), 135.0 (s), 136.2 (s), 155.4 (s), 162.9 (s), 179.1 (s), 180.5 (s) ppm. $C_{20}H_{14}O_3$ (302.09): calcd. C 79.46, H 4.67; found C 79.47, H 4.66.

1-Phenyl-3-propylnaphtho[2,3-*c*]furan-4,9-dione 3c: Yellow needles; yield 85 mg, 54%; m.p. 151–152 °C (ethyl acetate/hexane). IR (KBr): $\tilde{\nu}$ = 2960, 1670, 1275, 1245, 925 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.07 (t, J = 7.4 Hz, 3 H, CH_3), 1.89 (sext., J = 7.4 Hz, 2 H, CH_2), 3.25 (t, J = 7.4 Hz, 2 H, CH_2), 7.46–7.57 (m, 3 H, ArH), 7.73–7.81 (m, 2 H, ArH), 8.26–8.32 (m, 1 H, ArH), 8.32–8.39 (m, 1 H, ArH), 8.44–8.51 (m, 2 H, ArH) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 13.8 (q), 21.1 (t), 29.6 (t), 117.0 (s), 118.6 (s), 126.7 (d), 127.63 (d), 127.72 (2 d), 128.50 (2 d), 128.55 (s), 130.7 (d), 133.5 (d), 133.7 (d), 135.2 (s), 136.4 (s), 155.7 (s), 162.2 (s), 179.4 (s), 180.7 (s) ppm. $C_{21}H_{16}O_3$ (316.11): calcd. C 79.73, H 5.10; found C 79.63, H 4.98.

1-Isobutyl-3-phenylnaphtho[2,3-*c*]furan-4,9-dione (3d): Yellow crystals; yield 89 mg, 54%; m.p. 117–118 °C (ethyl acetate/hexane). IR (KBr): $\tilde{\nu}$ = 2950, 1670, 1280, 1245, 720 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.06 (d, J = 6.8 Hz, 6 H, 2 CH_3), 2.27 (nont., J = 6.8 Hz, 1 H, CH), 3.15 (d, J = 6.8 Hz, 2 H, CH_2), 7.43–7.59 (m, 3 H, ArH), 7.70–7.81 (m, 2 H, ArH), 8.22–8.31 (m, 1 H, ArH), 8.31–8.39 (m, 1 H, ArH), 8.47 (d, J = 7.2 Hz, 2 H, ArH) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 22.5 (2 q), 28.3 (d), 36.3 (t), 117.0 (s), 119.2 (s), 126.7 (d), 127.6 (d), 127.7 (2 d), 128.50 (2 d), 128.54 (s), 130.7 (d), 133.5 (d), 133.7 (d), 135.3 (s), 136.4 (s), 155.8 (s), 161.7 (s), 179.4 (s), 180.7 (s) ppm. MS (EI, 70 eV): m/z (%) = 330 $[M]^+$, 315 (27), 287 (100), 259 (2), 231 (2). HRMS: calcd. for $C_{22}H_{18}O_3$ 330.1256; found 330.1253.

1,3-Diphenylnaphtho[2,3-*c*]furan-4,9-dione (3e): Yellow needles; yield 131 mg, 75%; m.p. 229–230 °C (ethyl acetate/hexane). IR (KBr): $\tilde{\nu}$ = 1670, 1490, 1270, 905, 715 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.47–7.58 (m, 6 H, ArH), 7.72–7.79 (m, 2 H, ArH), 8.28–8.35 (m, 2 H, ArH), 8.42–8.53 (m, 4 H, ArH) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 118.7 (2 s), 127.3 (2 d), 128.3 (4 d), 128.4 (2 s), 128.5 (4 d), 131.0 (2 d), 133.7 (2 d), 135.6 (2 s), 156.2 (2 s), 179.6 (2 s) ppm. $C_{24}H_{14}O_3$ (350.09): calcd. C 82.27, H 4.03; found C 82.23, H 4.02.

1,3-Dimethylnaphtho[2,3-*c*]furan-4,9-dione (3f): White crystals; yield 89 mg, 61%; m.p. 175–176 °C (ethyl acetate/hexane). IR (KBr): $\tilde{\nu}$ = 1670, 1605, 1415, 1385, 1245 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.72 (s, 6 H, 2 CH_3), 7.72–7.78 (m, 2 H, ArH), 8.25–8.31 (m, 2 H, ArH) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 13.4 (2 q), 117.1 (2 s), 126.8 (2 d), 133.3 (2 d), 135.7 (2 s), 156.9 (2 s), 180.0 (2 s) ppm. $C_{14}H_{10}O_3$ (226.06): calcd. C 74.33, H 4.46; found C 74.25, H 4.44.

1-Ethyl-3-methylnaphtho[2,3-*c*]furan-4,9-dione (3g): Light-yellow powder; yield 87 mg, 56%; m.p. 111–112 °C (ethyl acetate/hexane). IR (KBr): $\tilde{\nu}$ = 2980, 1670, 1595, 1415, 1245 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.34 (t, J = 7.6 Hz, 3 H, CH_3), 2.73 (s, 3 H, CH_3), 3.15 (q, J = 7.6 Hz, 2 H, CH_2), 7.71–7.78 (m, 2 H, ArH), 8.24–8.31 (m, 2 H, ArH) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 11.6 (q), 13.5 (q), 21.0 (t), 116.3 (s), 117.1 (s), 126.78 (d), 126.82 (d), 133.23 (d), 133.25 (d), 135.7 (s), 135.8 (s), 156.9 (s), 162.0 (s), 180.1 (s), 180.2 (s) ppm. $C_{15}H_{12}O_3$ (240.08): calcd. C 74.99, H 5.03; found C 74.97, H 5.02.

Typical Procedure for the Synthesis of Benzo[*f*]isoindole-4,9-diones 12 by the Silver(II)-Catalyzed Reaction between 2-(1-Amidoalkyl)-1,4-naphthoquinones and α-Keto Acids (Method A): A mixture of 2-[*N*-acetyl-1-(aminobenzyl)]-1,4-naphthoquinone (**7a**; 127 mg, 0.42 mmol), 2-oxopropionic acid (**2a**; 111 mg, 1.25 mmol), silver(I) nitrate (29 mg, 0.17 mmol), and potassium persulfate (408 mg, 1.51 mmol) in acetonitrile (10 mL) and H_2O (5 mL) was heated at 70 °C for 3 h. The reaction mixture was diluted with ethyl acetate (100 mL), washed with water (3 × 50 mL), dried (Na_2SO_4), and concentrated in vacuo. The crude product was purified by column chromatography over silica gel (20 g; dichloromethane/hexane, 2:1) followed by recrystallization (chloroform/hexane) to give **8a** (88 mg, 64%).

Typical Procedure for the Synthesis of Benzo[*f*]isoindole-4,9-Diones 12 by the Manganese(III)-Mediated reaction between 2-(1-Amidoalkyl)-1,4-Naphthoquinones and β-Keto Esters (Method B): A mixture of 2-[*N*-benzoyl-1-(aminobenzyl)]-1,4-naphthoquinone (**7b**; 121 mg, 0.33 mmol), ethyl acetoacetate (**10a**; 871 mg, 6.7 mmol), and manganese(III) acetate (881 mg, 3.28 mmol) in acetic acid (10 mL) was heated at 70 °C under an atmosphere of O_2 (1 atm) for 30 min. The reaction mixture was diluted with ethyl acetate (100 mL), washed with saturated aqueous sodium bisulfite (50 mL), water (3 × 50 mL), and aqueous saturated sodium hydrogen carbonate (3 × 50 mL), dried (Na_2SO_4), and concentrated in vacuo. The crude product was purified by column chromatography over silica gel (20 g; dichloromethane/hexane, 2:1) followed by recrystallization (chloroform/hexane) to give **8f** (78 mg, 60%).

2-Acetyl-1-methyl-3-phenylbenzo[*f*]isoindole-4,9-dione (8a): Yellow crystals; yield 88 mg, 64% (method A), 55 mg, 50% (method B); m.p. 184–185 °C (chloroform/hexane). IR (KBr): $\tilde{\nu}$ = 1740, 1670, 1540, 1215, 1165 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.00 (s, 3 H, CH_3), 2.86 (s, 3 H, CH_3), 7.50–7.59 (m, 3 H, ArH), 7.59–7.61 (m, 2 H, ArH), 7.69 (td, J = 7.5, 1.6 Hz, 1 H, ArH), 7.72 (td, J = 7.5, 1.6 Hz, 1 H, ArH), 8.17 (dd, J = 7.5, 1.6 Hz, 1 H, ArH), 8.28 (dd, J = 7.5, 1.6 Hz, 1 H, ArH) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 12.6 (q), 28.2 (q), 118.5 (s), 118.6 (s), 126.66 (d), 126.68 (d), 128.6 (2 d), 129.85 (d), 129.88 (2 d), 130.2 (s), 133.07 (d), 133.11 (d), 135.74 (s), 135.76 (s), 135.82 (s), 138.0 (s), 173.1 (s), 179.9 (s), 181.3 (s) ppm. $C_{21}H_{15}NO_3$ (329.11): calcd. C 76.58, H 4.59, N 4.25; found C 76.68, H 4.62, N 4.25.

2-Acetyl-1-ethyl-3-phenylbenzo[*f*]isoindole-4,9-dione (8b): Yellow crystals; yield 133 mg, 59% (method A), 42 mg, 34% (method B); m.p. 146–147 °C (chloroform/hexane). IR (KBr): $\tilde{\nu}$ = 1745, 1665, 1540, 1240, 1210 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.33 (t, J = 7.4 Hz, 3 H, CH_3), 2.01 (s, 3 H, CH_3), 3.31 (q, J = 7.4 Hz, 2 H, CH_2), 7.50–7.55 (m, 3 H, ArH), 7.56–7.62 (m, 2 H, ArH), 7.69 (td, J = 7.4, 1.6 Hz, 1 H, ArH), 7.72 (td, J = 7.4, 1.6 Hz, 1 H,

ArH), 8.18 (dd, J = 7.4, 1.6 Hz, 1 H, ArH), 8.28 (dd, J = 7.4, 1.6 Hz, 1 H, ArH) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 13.8 (q), 19.4 (t), 28.3 (q), 117.8 (s), 118.5 (s), 126.59 (d), 126.65 (d), 128.6 (2 d), 129.80 (d), 129.84 (2 d), 130.1 (s), 133.0 (d), 133.05 (d), 135.4 (s), 135.7 (s), 135.8 (s), 143.9 (s), 173.2 (s), 179.9 (s), 180.9 (s) ppm. $C_{22}H_{17}NO_3$ (343.12): calcd. C 76.95, H 4.99, N 4.08; found C 76.92, H 4.98, N 4.03.

2-Acetyl-1-phenyl-3-propylbenzo[*f*]isoindole-4,9-dione (8c): Yellow crystals; yield 100 mg, 43% (method A), 38 mg, 29% (method B); m.p. 129–130 °C (chloroform/hexane). IR (KBr): $\tilde{\nu}$ = 1745, 1660, 1540, 1230, 1215 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.06 (t, J = 7.5 Hz, 3 H, CH_3), 1.73 (sext., J = 7.5 Hz, 2 H, CH_2), 2.00 (s, 3 H, CH_3), 3.23–3.31 (m, 2 H, CH_2), 7.46–7.56 (m, 3 H, ArH), 7.56–7.63 (m, 2 H, ArH), 7.69 (td, J = 7.4, 1.6 Hz, 1 H, ArH), 7.72 (td, J = 7.4, 1.6 Hz, 1 H, ArH), 8.18 (dd, J = 7.4, 1.6 Hz, 1 H, ArH), 8.27 (dd, J = 7.4, 1.6 Hz, 1 H, ArH) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 14.0 (q), 23.0 (t), 27.6 (t), 28.4 (q), 118.3 (s), 118.5 (s), 126.66 (d), 126.73 (d), 128.6 (2 d), 129.86 (d), 129.91 (2 d), 130.2 (s), 133.05 (d), 133.13 (d), 135.6 (s), 135.8 (s), 135.9 (s), 142.6 (s), 173.3 (s), 180.0 (s), 181.0 (s) ppm. $C_{23}H_{19}NO_3$ (357.14): calcd. C 77.29, H 5.36, N 3.92; found C 77.17, H 5.32, N 3.85.

2-Acetyl-1-isobutyl-3-phenylbenzo[*f*]isoindole-4,9-dione (8d): Yellow crystals; yield 76 mg, 30% (method A); m.p. 157–158 °C (chloroform/hexane). IR (KBr): $\tilde{\nu}$ = 1750, 1660, 1540, 1230, 1215 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.00 (d, J = 6.9 Hz, 6 H, 2 CH_3), 1.99 (s, 3 H, CH_3), 2.01 (nont., J = 6.9 Hz, 1 H, CH), 3.26 (d, J = 6.9 Hz, 2 H, CH_2), 7.47–7.56 (m, 3 H, ArH), 7.56–7.65 (m, 2 H, ArH), 7.68 (td, J = 7.4, 1.6 Hz, 1 H, ArH), 7.72 (td, J = 7.4, 1.6 Hz, 1 H, ArH), 8.18 (dd, J = 7.4, 1.6 Hz, 1 H, ArH), 8.27 (dd, J = 7.4, 1.6 Hz, 1 H, ArH) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 22.3 (2 q), 28.6 (q), 29.8 (d), 33.7 (t), 118.6 (s), 118.9 (s), 126.8 (2 d), 128.7 (3 d), 129.9 (d), 130.0 (d), 130.2 (s), 133.10 (d), 133.18 (s + d), 135.87 (s), 135.91 (s), 141.9 (s), 173.6 (s), 180.1 (s), 181.1 (s) ppm. $C_{24}H_{21}NO_3$ (371.15): calcd. C 77.61, H 5.70, N 3.77; found C 77.58, H 5.75, N 3.70.

1-Acetyl-1,3-diphenylbenzo[*f*]isoindole-4,9-dione (8e): Yellow crystals; yield 35 mg, 13% (method A); m.p. 203–204 °C (chloroform/hexane). IR (KBr): $\tilde{\nu}$ = 1745, 1665, 1480, 1215, 990 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.99 (s, 3 H, CH_3), 7.45–7.54 (m, 6 H, ArH), 7.54–7.62 (m, 4 H, ArH), 7.65–7.73 (m, 2 H, ArH), 8.15–8.22 (m, 2 H, ArH) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 28.9 (q), 118.9 (2 s), 126.8 (2 d), 128.5 (4 d), 129.6 (2 s), 129.8 (2 d), 130.1 (4 d), 133.3 (2 d), 135.8 (2 s), 137.0 (2 s), 172.6 (s), 180.2 (2 s) ppm. MS (EI, 70 eV): m/z (%) = 391 $[M]^+$, 366 (14), 349 (100), 320 (2), 291 (4), 265 (3). HRMS: calcd. for $C_{26}H_{17}NO_3$ 391.1208; found 391.1204.

2-Benzoyl-1-methyl-3-phenylbenzo[*f*]isoindole-4,9-dione (8f): Yellow crystals; yield 156 mg, 73% (method A), 78 mg, 60% (method B); m.p. 204–205 °C (chloroform/hexane). IR (KBr): $\tilde{\nu}$ = 1715, 1665, 1485, 1240, 1050 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.76 (s, 3 H, CH_3), 7.19–7.26 (m, 3 H, ArH), 7.32 (t, J = 7.9 Hz, 2 H, ArH), 7.42–7.48 (m, 2 H, ArH), 7.48–7.56 (m, 3 H, ArH), 7.68–7.77 (m, 2 H, ArH), 8.20–8.24 (m, 1 H, ArH), 8.28–8.34 (m, 1 H, ArH) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 12.2 (q), 117.7 (s), 118.6 (s), 126.6 (d), 126.8 (d), 127.9 (2 d), 128.8 (2 d), 129.2 (d), 129.4 (s), 130.0 (2 d), 130.4 (2 d), 132.5 (s), 133.08 (d), 133.13 (d), 134.9 (d), 135.7 (s), 136.1 (s), 137.5 (s), 137.7 (s), 170.1 (s), 180.0 (s), 181.5 (s) ppm. $C_{26}H_{17}NO_3$ (391.12): calcd. C 79.78, H 4.38, N 3.58; found C 79.76, H 4.35, N 3.52.

2-Benzoyl-1-ethyl-3-phenylbenzo[*f*]isoindole-4,9-dione (8g): Yellow crystals; yield 73 mg, 65% (method A), 49 mg, 37% (method B); m.p. 151–152 °C (chloroform/hexane). IR (KBr): $\tilde{\nu}$ = 1710, 1670, 1545, 1255, 1000 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.27 (t, J = 7.4 Hz, 3 H, CH_3), 3.24 (q, J = 7.4 Hz, 2 H, CH_2), 7.17–7.25 (m, 3 H, ArH), 7.29 (t, J = 7.9 Hz, 2 H, ArH), 7.39–7.46 (m, 2 H, ArH), 7.46–7.52 (m, 3 H, ArH), 7.71 (td, J = 7.3, 1.7 Hz, 1 H, ArH), 7.74 (td, J = 7.3, 1.7 Hz, 1 H, ArH), 8.22 (dd, J = 7.3, 1.7 Hz, 1 H, ArH), 8.31 (dd, J = 7.3, 1.7 Hz, 1 H, ArH) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 13.9 (q), 19.4 (t), 117.7 (s), 117.9 (s), 126.7 (d), 126.9 (d), 127.9 (2 d), 128.7 (2 d), 129.2 (d), 129.5 (s), 130.1 (2 d), 130.4 (2 d), 132.6 (s), 133.1 (2 d), 134.9 (d), 135.8 (s), 136.1 (s), 137.3 (s), 144.1 (s), 170.3 (s), 180.2 (s), 181.3 (s) ppm. $C_{27}H_{19}NO_3$ (405.14): calcd. C 79.98, H 4.72, N 3.45; found C 79.95, H 4.74, N 3.36.

2-Benzoyl-3-phenyl-1-propylbenzo[*f*]isoindole-4,9-dione (8h): Yellow crystals; yield 107 mg, 47% (method A), 54 mg, 39% (method B); m.p. 119–120 °C (chloroform/hexane). IR (KBr): $\tilde{\nu}$ = 1710, 1660, 1545, 1240, 1000 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.99 (t, J = 7.5 Hz, 3 H, CH_3), 1.68 (sext., J = 7.5 Hz, 2 H, CH_2), 3.21 (t, J = 7.5 Hz, 2 H, CH_2), 7.15–7.25 (m, 3 H, ArH), 7.29 (t, J = 7.9 Hz, 2 H, ArH), 7.38–7.56 (m, 5 H, ArH), 7.70 (td, J = 7.3, 1.5 Hz, 1 H, ArH), 7.74 (td, J = 7.3, 1.5 Hz, 1 H, ArH), 8.22 (dd, J = 7.3, 1.5 Hz, 1 H, ArH), 8.30 (dd, J = 7.3, 1.5 Hz, 1 H, ArH) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 13.9 (q), 23.0 (t), 27.6 (t), 117.6 (s), 118.3 (s), 126.6 (d), 126.8 (d), 127.9 (2 d), 128.7 (2 d), 129.2 (d), 129.5 (s), 130.1 (2 d), 130.3 (2 d), 132.6 (s), 133.1 (2 d), 134.8 (d), 135.8 (s), 136.0 (s), 137.4 (s), 142.8 (s), 170.3 (s), 180.1 (s), 181.2 (s) ppm. $C_{28}H_{21}NO_3$ (419.15): calcd. C 80.17, H 5.05, N 3.34; found C 80.18, H 5.02, N 3.31.

2-Ethoxycarbonyl-1-methyl-3-phenylbenzo[*f*]isoindole-4,9-dione (8i): Yellow crystals; yield 118 mg, 84% (method A), 74 mg, 56% (method B); m.p. 221–222 °C (chloroform/hexane). IR (KBr): $\tilde{\nu}$ = 1765, 1670, 1560, 1240, 1015 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.90 (t, J = 7.1 Hz, 3 H, CH_3), 2.93 (s, 3 H, CH_3), 4.13 (q, J = 7.1 Hz, 2 H, OCH_2), 7.47 (s, 5 H, ArH), 7.67 (td, J = 7.4, 1.5 Hz, 1 H, ArH), 7.70 (td, J = 7.4, 1.5 Hz, 1 H, ArH), 8.15 (dd, J = 7.4, 1.5 Hz, 1 H, ArH), 8.27 (dd, J = 7.4, 1.5 Hz, ArH) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 12.8 (q), 13.1 (q), 64.9 (t), 118.7 (s), 118.9 (s), 126.75 (d), 126.84 (d), 128.0 (2 d), 129.0 (d), 129.3 (2 d), 131.1 (s), 133.2 (2 d), 135.8 (s), 135.9 (s), 137.3 (s), 138.7 (s), 150.6 (s), 179.9 (s), 181.4 (s) ppm. $C_{22}H_{17}NO_4$ (359.11): calcd. C 73.53, H 4.77, N 3.90; found C 73.31, H 4.75, N 3.84.

2-Ethoxycarbonyl-1-ethyl-3-phenylbenzo[*f*]isoindole-4,9-dione (8j): Yellow crystals; yield 117 mg, 84% (method A), 58 mg, 43% (method B); m.p. 126–127 °C (chloroform/hexane). IR (KBr): $\tilde{\nu}$ = 1765, 1665, 1540, 1250, 1230 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.92 (t, J = 7.1 Hz, 3 H, CH_3), 1.35 (t, J = 7.4 Hz, 3 H, CH_3), 3.40 (q, J = 7.4 Hz, 2 H, CH_2), 4.14 (q, J = 7.1 Hz, 2 H, OCH_2), 7.43–7.55 (m, 5 H, ArH), 7.68 (td, J = 7.3, 1.5 Hz, 1 H, ArH), 7.72 (td, J = 7.3, 1.5 Hz, 1 H, ArH), 8.17 (dd, J = 7.3, 1.5 Hz, 1 H, ArH), 8.28 (dd, J = 7.3, 1.5 Hz, 1 H, ArH) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 13.1 (q), 13.7 (q), 19.7 (t), 65.1 (t), 118.0 (s), 118.8 (s), 126.8 (d), 126.9 (d), 128.0 (2 d), 129.1 (d), 129.4 (2 d), 130.9 (s), 133.2 (2 d), 135.9 (s), 136.0 (s), 137.2 (s), 144.4 (s), 150.6 (s), 180.0 (s), 181.2 (s) ppm. $C_{23}H_{19}NO_4$ (373.13): calcd. C 73.98, H 5.13, N 3.75; found C 73.87, H 5.13, N 3.69.

2-Ethoxycarbonyl-1-phenyl-3-propylbenzo[*f*]isoindole-4,9-dione (8k): Yellow crystals; yield 92 mg, 60% (method A), 59 mg, 41% (method B); m.p. 143–144 °C (chloroform/hexane). IR (KBr): $\tilde{\nu}$ = 1770, 1665, 1540, 1230, 990 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.91 (t, J = 7.1 Hz, 3 H, CH_3), 1.07 (t, J = 7.5 Hz, 3 H, CH_3), 1.76 (sext., J = 7.5 Hz, 2 H, CH_2), 3.36 (t, J = 7.5 Hz, 2 H, CH_2), 4.12 (q, J = 7.1 Hz, 2 H, OCH_2), 7.42–7.54 (m, 5 H, ArH), 7.68 (td, J = 7.4, 1.6 Hz, 1 H, ArH), 7.72 (td, J = 7.4, 1.6 Hz, 1 H,

ArH), 8.17 (dd, J = 7.4, 1.6 Hz, 1 H, ArH), 8.27 (dd, J = 7.4, 1.6 Hz, 1 H, ArH) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 13.1 (q), 14.0 (q), 22.9 (t), 27.8 (t), 65.0 (t), 118.4 (s), 118.7 (s), 126.7 (d), 126.9 (d), 128.0 (2 d), 129.1 (d), 129.3 (2 d), 130.9 (s), 133.13 (d), 133.16 (d), 135.85 (s), 135.92 (s), 137.2 (s), 143.0 (s), 150.7 (s), 180.0 (s), 181.1 (s) ppm. $C_{24}H_{21}NO_4$ (387.15): calcd. C 74.40, H 5.46, N 3.62; found C 74.41, H 5.47, N 3.54.

2-Ethoxycarbonyl-1-isobutyl-3-phenylbenzo[*f*]isoindole-4,9-dione (8l): Yellow powders; yield 89 mg, 55% (method A); m.p. 89–90 °C (chloroform/hexane). IR (KBr): $\tilde{\nu}$ = 1765, 1665, 1545, 1240, 990 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.90 (t, J = 7.2 Hz, 3 H, CH_3), 1.01 (d, J = 6.9 Hz, 6 H, 2 CH_3), 2.06 (nont., J = 6.9 Hz, 1 H, CH), 3.34 (d, J = 6.9 Hz, 2 H, CH_2), 4.10 (q, J = 7.2 Hz, 2 H, OCH_2), 7.43–7.53 (m, 5 H, ArH), 7.68 (td, J = 7.5, 1.7 Hz, 1 H, ArH), 7.71 (td, J = 7.5, 1.7 Hz, 1 H, ArH), 8.17 (dd, J = 7.5, 1.7 Hz, 1 H, ArH), 8.27 (dd, J = 7.5, 1.7 Hz, 1 H, ArH) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 13.1 (q), 22.3 (2 q), 29.7 (d), 33.9 (t), 65.0 (t), 118.7 (s), 119.0 (s), 126.81 (d), 126.87 (d), 128.0 (2 d), 129.1 (d), 129.4 (2 d), 131.0 (s), 133.15 (d), 133.2 (d), 135.92 (s), 135.94 (s), 137.5 (s), 142.3 (s), 150.9 (s), 180.1 (s), 181.1 (s) ppm. $C_{25}H_{23}NO_4$ (401.16): calcd. C 74.79, H 5.77, N 3.49; found C 74.76, H 5.67, N 3.48.

2-Ethoxycarbonyl-1,3-diphenylbenzo[*f*]isoindole-4,9-dione (8m): Yellow crystals; yield 54 mg, 33% (method A); m.p. 146–147 °C (chloroform/hexane). IR (KBr): $\tilde{\nu}$ = 1775, 1670, 1240, 1225, 990 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.79 (t, J = 7.2 Hz, 3 H, CH_3), 3.97 (q, J = 7.2 Hz, 2 H, OCH_2), 7.46–7.54 (m, 6 H, ArH), 7.54–7.62 (m, 4 H, ArH), 7.66–7.73 (m, 2 H, ArH), 8.16–8.22 (m, 2 H, ArH) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 12.9 (q), 65.3 (t), 118.9 (2 s), 126.9 (2 d), 128.1 (4 d), 129.5 (2 d), 129.7 (4 d), 129.8 (2 s), 133.3 (2 d), 135.8 (2 s), 137.9 (2 s), 150.3 (s), 180.1 (2 s) ppm. $C_{27}H_{19}NO_4$ (421.13): calcd. C 76.95, H 4.54, N 3.32; found C 76.68, H 4.59, N 3.28.

Supporting Information (see footnote on the first page of this article): Experimental details for the preparation of 2-substituted-1,4-naphthoquinones **1** and **7**; ^{1}H and ^{13}C NMR spectroscopic data for naphtho[2,3-*c*]furan-4,9-diones **4** and benzo[*f*]isoindole-4,9-diones **8**.

Acknowledgments

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[1] a) W. P. Neumann, *Synthesis* **1987**, 665–682; b) D. P. Curran, *Synthesis* **1988**, 417–439: D. P. Curran, *Synthesis* **1988**, 489–513; c) B. Giese, B. Kopping, T. Gobel, J. Dickhaut, G. Thoma, K. J. Kulicke, F. Trach in *Organic Reactions*, Wiley, New York, **1996**, vol. 48, ch. 2, pp. 301–855; d) W. R. Bowman, C. F. Bridge, P. Brookes, *J. Chem. Soc. Perkin Trans. 1* **2000**, 1–14; e) W. Zheng, *Tetrahedron* **2001**, *57*, 7237–7262.

[2] a) G. G. Melikyan, *Synthesis* **1993**, 833–850; b) J. Iqbal, B. Bhatia, N. K. Nayyar, *Chem. Rev.* **1994**, *94*, 519–564; c) B. B. Snider, *Chem. Rev.* **1996**, *96*, 339–363; d) V. Nair, S. B. Panicker, L. G. Nair, T. G. George, A. Augustine, *Synlett* **2003**, 156–165; e) V. Nair, L. Balagopal, R. Rajan, J. Mathew, *Acc. Chem. Res.* **2004**, *37*, 21–30.

[3] a) H. Oumar-Mahamat, C. Moustrou, J.-M. Surzur, M. P. Berstrand, *J. Org. Chem.* **1989**, *54*, 5684–5688; b) B. B. Snider, B. Y. F. Wan, B. O. Buckman, B. M. Foxman, *J. Org. Chem.* **1991**, *56*, 328–334.

[4] a) A. Citterio, R. Sebastiano, A. Marion, *J. Org. Chem.* **1991**, *56*, 5328–5335; b) A. Citterio, R. Sebastiano, M. Nicolini, *Tetrahedron* **1993**, *49*, 7743–7760; c) Y.-L. Wu, C.-P. Chuang, P.-Y. Lin, *Tetrahedron* **2000**, *56*, 6209–6217; d) Y.-J. Liao, Y.-L. Wu, C.-P. Chuang, *Tetrahedron* **2003**, *59*, 3511–3520.

[5] a) M.-C. Jiang, C.-P. Chuang, *J. Org. Chem.* **2000**, *65*, 5409–5412; b) Y.-L. Wu, C.-P. Chuang, *Tetrahedron Lett.* **2001**, *42*, 1717–1719; c) Y.-L. Wu, C.-P. Chuang, P.-Y. Lin, *Tetrahedron* **2001**, *57*, 5543–5549; d) A.-I. Tsai, Y.-L. Wu, C.-P. Chuang, *Tetrahedron* **2001**, *57*, 7829–7837; e) C.-C. Tseng, Y.-L. Wu, C.-P. Chuang, *Tetrahedron* **2002**, *58*, 7625–7633; f) C.-M. Tseng, Y.-L. Wu, C.-P. Chuang, *Tetrahedron* **2004**, *60*, 12249–12260; g) H.-L. Chen, C.-Y. Lin, Y.-C. Cheng, A.-I. Tsai, C.-P. Chuang, *Synthesis* **2005**, 977–985; h) C.-Y. Lin, Y.-C. Cheng, A.-I. Tsai, C.-P. Chuang, *Org. Biomol. Chem.* **2006**, *4*, 1097–1103.

[6] J. M. Anderson, J. K. Kochi, *J. Am. Chem. Soc.* **1970**, *92*, 1651–1659.

[7] a) N. Kanomata, H. Nagahara, M. Tada, *J. Heterocycl. Chem.* **1992**, *29*, 1567–1571; b) R. Jain, L. A. Cohen, N. A. El-Kadi, M. M. King, *Tetrahedron* **1997**, *53*, 2365–2370; c) K. B. Hansen, S. A. Springfield, R. Desmond, P. N. Devine, E. J. J. Grabowski, P. J. Reider, *Tetrahedron Lett.* **2001**, *42*, 7353–7355.

[8] a) N. Jacobsen, K. Torsell, *Acta Chem. Scand.* **1973**, *27*, 3211–3216; b) P. M. Brown, R. H. Thomson, *J. Chem. Soc. Perkin Trans. 1* **1976**, 997–1000; c) B. Kesteleyn, N. De Kimpe, L. Van Puyvelde, *J. Org. Chem.* **1999**, *64*, 1173–1179; d) G. A. Kraus, P. K. Choudhury, *Tetrahedron Lett.* **2001**, *42*, 6649–6650.

[9] a) R. H. Thomson, *Natural Occurring Quinones IV: Recent Advances*, Chapman and Hall, London, **1997**; b) A. P. Krapcho, D. J. Waterhouse, *Heterocycles* **1999**, *51*, 737–750; c) M. J. Piggott, *Tetrahedron* **2005**, *61*, 9929–9954.

[10] a) T. Hanumaiah, G. S. R. Rao, C. P. Rao, K. V. J. Rao, H. J. Cowe, P. J. Cox, R. A. Howie, D. S. Marshall, R. H. Thomson, *Tetrahedron* **1985**, *41*, 635–642; b) A. Miljkovic, P. G. Mantle, D. J. Williams, B. Rassing, *J. Nat. Prod.* **2001**, *64*, 1251–1253; c) Y. Yamamoto, Y. Kinoshita, G. R. Thor, M. Hasumi, K. Kinoshita, K. Koyama, K. Takahashi, I. Yoshimura, *Phytochemistry* **2002**, *60*, 741–745; d) R. D. Stipanovic, J. Zhang, B. D. Bruton, M. H. Wheeler, *J. Agric. Food Chem.* **2004**, *52*, 4109–4112.

[11] a) Y.-L. Wu, C.-P. Chuang, *Tetrahedron* **2004**, *60*, 1841–1847; b) A.-I. Tsai, C.-P. Chuang, *Tetrahedron* **2006**, *62*, 2235–2239.

[12] a) W. C. Christopfel, L. L. Miller, *Tetrahedron* **1987**, *43*, 3681–3688; b) P. Magnus, S. A. Eisenbeis, N. A. Magnus, *J. Chem. Soc., Chem. Commun.* **1994**, 1545–1546; c) A. R. Wartini, H. A. Staab, F. A. Neugebauer, *Eur. J. Org. Chem.* **1998**, 1161–1170; d) X.-P. Yang, D.-M. Du, Q. Li, T. C. W. Mak, H. N. C. Wong, *J. Chem. Commun.* **1999**, 1607–1608; e) H. S. Sutherland, F. E. S. Souza, R. G. A. Rodrigo, *J. Org. Chem.* **2001**, *66*, 3639–3641; f) S. Chakrabarti, M. Liu, D. H. Waldeck, A. M. Oliver, M. N. Paddon-Row, *J. Am. Chem. Soc.* **2007**, *129*, 3247–3256.

[13] a) D. V. Nightinggale, J. A. Gallagher, *J. Org. Chem.* **1959**, *24*, 501–504; b) J. A. Myers, L. D. Moore Jr., W. L. Whitter, S. L. Council, R. M. Waldo, J. L. Lanier, B. U. Omoji, *J. Org. Chem.* **1980**, *45*, 1202–1206; c) M. Schubert-Zsilavecz, W. Likussar, D. Gusterhuber, A. Michelitsch, *Monatsh. Chem.* **1991**, *122*, 383–387; d) R. Di Santo, R. Costi, S. Massa, M. Artico, *Synth. Commun.* **1996**, *26*, 1839–1847; e) M. Chakraborty, D. B. McConville, G. F. Koser, C. A. Tessier, T. Saito, P. L. Rinaldi, W. J. Youngs, *J. Org. Chem.* **1997**, *62*, 8193–8197; f) M. S. Shvartsberg, I. D. Ivanchikova, N. I. Lebedeva, *Tetrahedron Lett.* **2000**, *41*, 5757–5760.

[14] a) F. Fontana, F. Minisci, M. C. N. Barbosa, E. Vismara, *J. Org. Chem.* **1991**, *56*, 2866–2869; b) C. J. Rao, W. C. Agota, *Tetrahedron Lett.* **1992**, *33*, 4133–4136; c) N. Sato, H. Kadota, *J. Heterocycl. Chem.* **1992**, *29*, 1685–1688; d) G. A. Kraus, A. Melekhov, *Tetrahedron Lett.* **1998**, *39*, 3957–3960; e) M. K.-H. Doll, *J. Org. Chem.* **1999**, *64*, 1372–1374.

[15] a) B. S. Davidson, *Tetrahedron Lett.* **1992**, *33*, 3721–3724; b) Y. Moriyasu, H. Miyagawa, N. Hamada, H. Miyawaki, T. Ueno, *Phytochemistry* **2001**, *58*, 239–241.
[16] Similar oxygen trapping of α,α-dicarbonyl radicals has been reported: a) T. Ohshima, M. Sodeoka, M. Shibasaki, *Tetrahedron Lett.* **1993**, *34*, 8509–8512; b) V. Nair, L. G. Nair, J. Mathew, *Tetrahedron Lett.* **1998**, *39*, 2801–2804; c) V. Nair, V. Sheeba, *J. Org. Chem.* **1999**, *64*, 6898–6900; d) J.-H. Ye, J. Xue, K.-Q. Ling, J.-H. Xu, *Tetrahedron Lett.* **1999**, *40*, 1365–1368.
[17] For similar cleavage reactions of α-oxycarbonyl radicals, see: a) A. L. Nussbaum, E. P. Yuan, C. H. Robinson, A. Mitchell, E. P. Oliveto, J. M. Beaton, D. H. R. Barton, *J. Org. Chem.* **1962**, *27*, 20–23; b) J. A. Murphy, C. W. Patterson, N. F. Wooster, *Tetrahedron Lett.* **1988**, *29*, 955–958.

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