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The reaction of methyl 2-(3-chloro-1,4-dioxo-1,4-dihydronaphthalen-2-yl)propenoate (**2a**) with primary amines gave 4-chloro-5-hydroxy-3-methoxycarbonyl-1*H*-benzo[*g*]indoles **5a-f** as major compounds and 3-methoxycarbonyl-4,9-dioxo-2,3,4,9-tetrahydro-1*H*-benzo[*f*]indoles **6a-d** as minor ones. Whereas the reaction of 3-(3-chloro-1,4-dioxo-1,4-dihydronaphthalen-2-yl)-3-buten-2-one (**2b**) with primary amines afforded the corresponding 1*H*-benzo[*g*]indoles **5g-i** as major products and 3-acetyl-4,9-dihydro-4,9-dioxo-1*H*-benzo[*f*]indoles **7g**, **h** as minor products.

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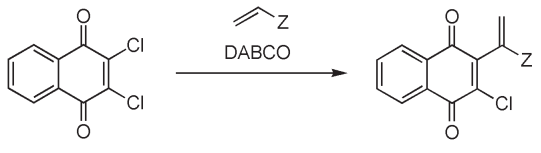
The chemistry of heterocyclic quinones is a subject of continuing interest [1] due to displaying diverse biological properties such as antitumor [2], antibiotic [3], antifungal [4] and agonist of the nerve growth factor receptor [5]. Synthetic approaches to the heterocyclic quinones developed so far, substitution of a halogen by an active methylene anion or enamine represents most of the reactions that leads directly to the formation of a carbon-carbon bond on the quinone core [6] and the remaining halogen could then be substituted by heteroatoms, and an intramolecular reaction could occur to give heterocyclic quinones [7].

We have recently reported [8] that the coupling of 2,3-dichloro-1,4-naphthoquinone (**1**) with methyl acrylate or methyl vinyl ketone in the presence of 1,4-diazabicyclo[2,2,2]octane (DABCO) provides α-vinylchloronaphthoquinones **2** as shown in Scheme I. In this paper, we report that α-vinylchloronaphthoquinones **2** are useful substrates in the synthesis of heterocyclic quinones such as 4-chloro-5-hydroxy-1*H*-benzo[*g*]indoles **5**, 3-methoxycarbonyl-4,9-dioxo-2,3,4,9-tetrahydro-1*H*-benzo[*f*]indoles **6** and 3-acetyl-4,9-dihydro-4,9-dioxo-1*H*-benzo[*f*]indoles **7**.

In general, 5-hydroxy-1*H*-benzo[*g*]indoles **5** can be prepared by the reaction of 1,4-naphthoquinone with aminocrotonates [9] using Nenitzescu indole synthetic method [10] and 4,9-dihydro-4,9-dioxo-1*H*-benzo[*f*]indoles **7** can be obtained from the reaction of 2-halo-3-(α-acetyl-α-ethoxycarbonylmethyl)-1,4-naphthoquinone with primary amines [7] or cerium salts mediated in the oxidative free radical reaction between 2-amino-1,4-naphthoquinone with β-dicarbonyl compounds [11].

Scheme I



1

2a Z = CO_2Me
2b Z = COMe

Treatment of methyl 2-(3-chloro-1,4-dioxo-1,4-dihydronaphthalen-2-yl)propenoate (**2a**) with primary amines such as methyl-, ethyl-, cyclopropyl- and benzylamine led to the formation of two products which were separated by column chromatography (Table). The first, major product was isolated as a solid and assigned as the 4-chloro-5-hydroxy-3-methoxycarbonyl-1*H*-benzo[*g*]indoles **5a-d** in 68-79% yields. The second product was isolated as a solid and was found to be the 3-methoxycarbonyl-4,9-dioxo-2,3,4,9-tetrahydro-1*H*-benzo[*f*]indoles **6a-d** in 6-14% yields. However, reaction of **2a** with ammonia and aniline yielded a single product **5e** (51%) and **5f** (75%), respectively [12]. Also, treatment of 3-(3-chloro-1,4-dioxo-1,4-dihydronaphthalen-2-yl)-3-buten-2-one (**2b**) with methyl- and ethylamine afforded the similar compounds, 3-acetyl-4-chloro-5-hydroxy-1*H*-benzo[*g*]indoles **5g** (82%) and **5h** (85%) as major products and 3-acetyl-4,9-dihydro-4,9-dioxo-1*H*-benzo[*f*]indoles **7g** (9%) and **7h** (8%) as minor ones. However, reaction of **2b** with ammonia produced **5i** as the sole product in a disappointing yield of 27%.

Table

1*H*-Benzoindoles **5**, **6**, and **7**

Reactant	Product (%)	Z	R
2a	**5a** (79), **6a** (13)	CO_2Me	Me
2a	**5b** (75), **6b** (14)	CO_2Me	Et
2a	**5c** (79), **6c** (6)	CO_2Me	*c*-Pr
2a	**5d** (68), **6d** (14)	CO_2Me	$PhCH_2$
2a	**5e** (51)	CO_2Me	H
2a	**5f** (75)	CO_2Me	Ph
2b	**5g** (82), **7g** (9)	COMe	Me
2b	**5h** (85), **7h** (8)	COMe	Et
2b	**5i** (27)	COMe	H

The structures **5**, **6** and **7** were established on the basis of spectroscopic data. For instance, in the ^{1}H nmr spectrum of **5a**, the signal from the C2 hydrogen atom appeared as a singlet at 8.04 ppm and the phenolic proton appeared as a singlet at 9.46 ppm and is exchangeable in deuterium

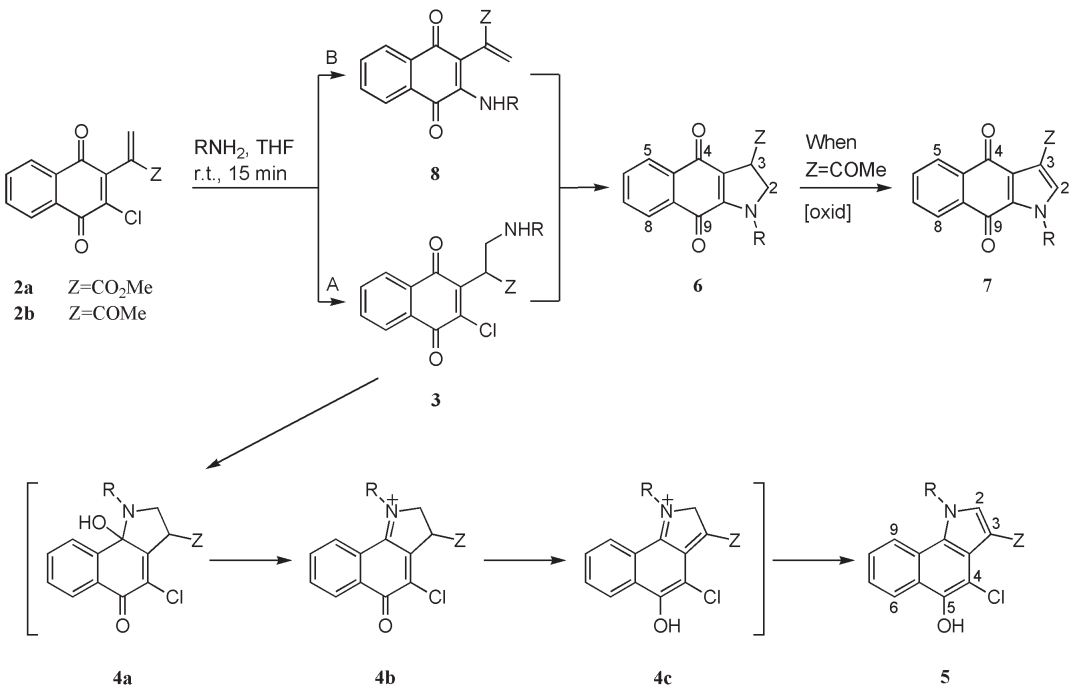
oxide. The signal corresponding to the two methyl hydrogen atoms appeared as two singlets at 3.78 (OCH_3) and 4.30 (NCH_3) ppm. The ^{13}C nmr showed one carbonyl carbon signal at 163.93 (ester) ppm, however, a *N*-methyl signal was not observed due to dimethyl sulfoxide-d_6 peaks. The infrared spectrum showed absorption bands in 3393 and 1705 cm^{-1} assignable for the phenolic OH bond and the ester carbonyl bond, respectively.

In the ^1H nmr spectrum of **6a**, the signals from the two C2 hydrogens appeared as two doublet of doublets at 3.79 (J = 12.2 and 7.3 Hz) and 4.11 ppm (J = 12.8 and 7.3 Hz), which arose as a result of coupling between the nonequivalent geminal hydrogen atoms and with the C3 hydrogen. The signal corresponding to the C3 hydrogen appears as a doublet of doublet at 3.97 ppm (J = 12.8 and 12.2 Hz), which arose from coupling with each of the C2 hydrogen atoms. The ^{13}C nmr showed three carbonyl carbon signals at 172.79, 176.52 and 180.45 ppm and its infrared spectrum showed absorption for carbonyl bands (1736 and 1668 cm^{-1}).

In the ^1H nmr spectrum of **7g**, the signal from the C2 hydrogen atom is observed as a singlet at 7.93 ppm and the signals corresponding to the two methyl peaks appeared as two singlets at 2.63 (CH_3) and 4.05 (NCH_3) ppm. The ^{13}C nmr revealed three carbonyl carbon absorptions at 176.88, 180.44 and 194.94 ppm and its infrared spectrum also showed absorption for carbonyl bands (1665 and 1647 cm^{-1}) [11].

These results suggest that the major compound **5** is formed by Michael reaction of the amine to the carbon-carbon double bond in **2** leading to the formation of intermediate **3**, followed by condensation of amino group to the quinone carbonyl group and then aromatization. The minor compound **6** is formed by a nucleophilic attack of the amino group in the intermediate **3** to the carbon bearing the chlorine by the addition-elimination mechanism (Path A), and further autooxidation of **6**, under the reaction condition, to spontaneously give **7**. Another possible explanation of the formation of minor compound **6** may involve a nucleophilic substitution of chlorine by the amine leading to intermediate **8**, followed by conjugate addition of the amino group to the carbon-carbon double bond (Path B), as illustrated in Scheme II. On the autooxidation process, the reason the ketones **6g**, **h** autooxidize more readily than the

Scheme II



5, 6, 7	Z	R	5, 6, 7	Z	R	5, 6, 7	Z	R
a	CO_2Me	Me	**d**	CO_2Me	$PhCH_2$	**g**	COMe	Me
b	CO_2Me	Et	**e**	CO_2Me	H	**h**	COMe	Et
c	CO_2Me	*c*-Pr	**f**	CO_2Me	Ph	**i**	COMe	H

esters **6a-d** is the former enolize more readily, to give intermediates susceptible to peroxide formation, and then eliminate hydrogen peroxide to give the indoles **7**.

In conclusion, the method is efficient for the preparation of 1*H*-benzo[*g*]indoles **5**, but not for compounds **6** or **7** using α-vinylchloronaphthoquinones **2** and primary amines.

EXPERIMENTAL

All reagents and solvents were reagent grade or were purified by standard methods before use. Silica gel 60 (70-230 mesh ASTM) used for column chromatography was supplied by E. Merck. Analytical thin layer chromatography (tlc) was carried out on Merck silica gel 60 F_{254} tlc plates. Melting points were taken using an Electrothermal melting point apparatus and are uncorrected. Microanalyses were obtained using a Carlo Erba EA 1180 element analyzer. Infrared spectra were recorded on a Nicolet Magna 550 FTIR spectrometer. The ^{1}H and ^{13}C NMR spectra were measured on a Gemini 300 spectrometer. All chemical shifts are reported in parts per million (δ) relative to tetramethylsilane and coupling constants (J) are expressed in Hertz.

The methyl 2-(3-chloro-1,4-dioxo-1,4-dihydronaphthalen-2-yl)propenoate (**2a**) and 3-(3-chloro-1,4-dioxo-1,4-dihydronaphthalen-2-yl)-3-buten-2-one (**2b**) were prepared following the literature procedure [8].

4-Chloro-5-hydroxy-3-methoxycarbonyl-1-methyl-1*H*-benzo[*g*]indole (**5a**) and 3-Methoxycarbonyl-1-methyl-4,9-dioxo-2,3,4,9-tetrahydro-1*H*-benzo[*f*]indole (**6a**).

To a stirred solution of **2a** (0.83 g, 3.0 mmoles) in tetrahydrofuran (15 ml) was added aqueous 40% methylamine (0.29 ml, 3.3 mmoles) at room temperature. After stirring at the same temperature for 15 minutes the solvent was evaporated *in vacuo*. The residue was chromatographed on silica gel eluting with hexane/ethyl acetate (5:1) to give 0.69 g (79%) of **5a** and 0.11 g (13%) of **6a** as solids.

For **5a**; mp 188.5-189.5 °C; ir (potassium bromide) 3393, 1705, 1634, 1617, 1586 cm^{-1}; ^{1}H nmr (dimethyl sulfoxide-d_6): δ 3.78 (s, 3 H, OCH_3), 4.30 (s, 3 H, NCH_3), 7.52-7.67 (m, 2 H, ArH), 8.04 (s, 1 H, C2H), 8.31 (d, 1 H, J = 8.5 Hz, ArH), 8.54 (d, 1 H, J = 8.5 Hz, ArH), 9.46 (s, 1 H, OH); ^{13}C nmr (dimethyl sulfoxide-d_6): δ 51.32, 107.03, 108.47, 120.90, 121.32, 122.08, 123.58, 124.22, 124.53, 126.29, 126.79, 136.56, 144.26, 163.93.

Anal. Calcd for $C_{15}H_{12}ClNO_3$: C, 62.19; H, 4.17; N, 4.83. Found: C, 61.93; H, 4.11; N, 4.60.

For **6a**; mp 140-142 °C; ir (potassium bromide) 1736, 1668, 1618, 1588, 1566 cm^{-1}; ^{1}H nmr (dimethyl sulfoxide-d_6): δ 3.28 (s, 3 H, NCH_3), 3.66 (s, 3 H, OCH_3), 3.79 (dd, 1 H, J = 12.2 and 7.3 Hz, C2H), 3.97 (dd, 1 H, J = 12.8 and 12.2 Hz, C3H), 4.11 (dd, 1 H, J = 12.8 and 7.3 Hz, C2H), 7.68-7.92 (m, 4 H, ArH); ^{13}C nmr (dimethyl sulfoxide-d_6): δ 30.44, 42.52, 51.96, 52.41, 115.62, 124.89, 126.02, 131.59, 131.85, 133.52, 134.95, 151.35, 172.79, 176.52, 180.45.

Anal. Calcd for $C_{15}H_{13}NO_4$: C, 66.41; H, 4.83; N, 5.16. Found: C, 66.12; H, 5.13; N, 4.79.

4-Chloro-1-ethyl-5-hydroxy-3-methoxycarbonyl-1*H*-benzo[*g*]indole (**5b**) and 1-Ethyl-3-methoxycarbonyl-4,9-dioxo-2,3,4,9-tetrahydro-1*H*-benzo[*f*]indole (**6b**).

Treatment of **2a** (0.83 g, 3.0 mmoles) with aqueous 70% ethylamine (0.18 ml, 3.3 mmoles) following a similar procedure to that described above provided 0.68 g (75%) of **5b** and 0.12 g (14%) of **6b** as solids.

For **5b**; mp 162.8-163.2 °C; ir (potassium bromide) 3406, 1703, 1586, 1527 cm^{-1}; ^{1}H nmr (dimethyl sulfoxide-d_6): δ 1.49 (t, 3 H, J = 7.0 Hz, CH_3), 3.82 (s, 3 H, OCH_3), 4.73 (q, 2 H, J = 7.0 Hz, NCH_2), 7.56-7.72 (m, 2 H, ArH), 8.08 (s, 1 H, C2H), 8.37 (d, 1 H, J = 8.0 Hz, ArH), 8.39 (d, 1 H, J = 8.0 Hz, ArH), 9.49 (s, 1 H, OH); ^{13}C nmr (dimethyl sulfoxide-d_6): δ 15.67, 45.24, 51.12, 107.29, 108.34, 121.11, 121.27, 123.49, 124.04, 124.28, 124.91, 126.89, 135.00, 144.12, 163.81.

Anal. Calcd for $C_{16}H_{14}ClNO_3$: C, 63.27; H, 4.65; N, 4.61. Found: C, 62.97; H, 4.76; N, 4.67.

For **6b**; mp 119-120 °C; ir (potassium bromide) 1716, 1674, 1622, 1589, 1556 cm^{-1}; ^{1}H nmr (dimethyl sulfoxide-d_6): δ 1.17 (t, 3 H, J = 7.0 Hz, CH_3), 3.68 (s, 3 H, OCH_3), 3.75 (q, 2 H, J = 7.0 Hz, NCH_2), 3.83 (dd, 1 H, J = 10.7 and 6.1 Hz, C2H), 4.05 (dd, 1 H, J = 12.8 and 10.7 Hz, C3H), 4.12 (dd, 1 H, J = 12.8 and 6.1 Hz, C2H), 7.66-7.91 (m, 4 H, ArH); ^{13}C nmr (dimethyl sulfoxide-d_6): δ 13.15, 42.00, 42.40, 52.17, 55.27, 115.90, 124.60, 125.79, 131.59, 131.74, 133.39, 134.66, 150.73, 172.85, 176.62, 180.30.

Anal. Calcd for $C_{16}H_{15}NO_4$: C, 67.36; H, 5.30; N, 4.91. Found: C, 67.03; H, 5.19; N, 4.60.

4-Chloro-1-cyclopropyl-5-hydroxy-3-methoxycarbonyl-1*H*-benzo[*g*]indole (**5c**) and 1-Cyclopropyl-3-methoxycarbonyl-4,9-dioxo-2,3,4,9-tetrahydro-1*H*-benzo[*f*]indole (**6c**).

Treatment of **2a** (0.83 g, 3.0 mmoles) with cyclopropylamine (0.23 ml, 3.3 mmoles) following a similar procedure to that described above provided 0.75 g (79%) of **5c** and 0.5 g (6%) of **6c** as solids.

For **5c**; mp 156.5-157.5 °C; ir (potassium bromide) 3373, 1711, 1585, 1520 cm^{-1}; ^{1}H nmr (dimethyl sulfoxide-d_6): δ 1.24-1.34 (m, 4 H, cyclopropyl), 3.80 (s, 3 H, OCH_3), 4.03-4.04 (s, 1 H, cyclopropyl), 7.55-7.68 (m, 2 H, ArH), 7.95 (s, 1 H, C2H), 8.35 (d, 1 H, J = 8.2 Hz, ArH), 9.03 (d, 1 H, J = 8.2 Hz, ArH), 9.51 (s, 1 H, OH); ^{13}C nmr (dimethyl sulfoxide-d_6): δ 9.26, 32.50, 51.16, 107.31, 108.13, 120.53, 121.80, 121.97, 123.22, 124.13, 124.44, 126.40, 126.83, 133.96, 144.15, 163.85.

Anal. Calcd for $C_{17}H_{14}ClNO_3$: C, 64.67; H, 4.47; N, 4.44. Found: C, 64.35; H, 4.46; N, 4.32.

For **6c**; mp 147.5-148.5 °C; ir (potassium bromide) 1726, 1674, 1626, 1586, 1563 cm^{-1}; ^{1}H nmr (dimethyl sulfoxide-d_6): δ 0.79-0.81 (m, 4 H, cyclopropyl), 3.09-3.17 (m, 1 H, cyclopropyl), 3.65 (s, 3 H, OCH_3), 3.75 (dd, 1 H, J = 11.0 and 7.0 Hz, C2H), 3.99 (dd, 1 H, J = 12.2 and 11.0 Hz, C3H), 4.08 (dd, 1 H, J = 12.2 and 7.0 Hz, C2H), 7.69-7.96 (m, 4 H, ArH); ^{13}C nmr (dimethyl sulfoxide-d_6): δ 7.21, 29.68, 30.31, 42.45, 52.56, 116.91, 125.77, 126.24, 132.44, 132.90, 133.17, 134.91, 152.57, 172.79, 177.32, 179.45.

Anal. Calcd for $C_{17}H_{15}NO_4$: C, 68.68; H, 5.09; N, 4.71. Found: C, 68.61; H, 4.98; N, 4.44.

1-Benzyl-4-chloro-5-hydroxy-3-methoxycarbonyl-1*H*-benzo[*g*]indole (**5d**) and 1-Benzyl-3-methoxycarbonyl-4,9-dioxo-2,3,4,9-tetrahydro-1*H*-benzo[*f*]indole (**6d**).

Treatment of **2a** (0.83 g, 3.0 mmoles) with benzylamine (0.36 ml, 3.3 mmoles) following a similar procedure to that described above provided 0.75 g (68%) of **5d** and 0.15 g (14%) of **6d** as solids.

For **5d**; mp 174-175 °C; ir (potassium bromide) 3378, 1719, 1672, 1614, 1586, 1529 cm^{-1}; ^1H nmr (dimethyl sulfoxide-d_6): δ 3.81 (s, 3 H, OCH_3), 5.99 (s, 2 H, NCH_2), 7.03-7.44 (m, 7 H, ArH), 8.17 (d, 1 H, J = 7.6 Hz, ArH), 8.24 (s, 1 H, C2H), 8.30 (d, 1 H, J = 7.3 Hz, ArH), 9.55 (s, 1 H, OH); ^{13}C nmr (dimethyl sulfoxide-d_6): δ 51.22, 53.28, 107.76, 108.26, 121.10, 121.27, 123.33, 124.06, 124.25, 125.35, 125.82, 126.41, 127.43, 128.90, 136.46, 137.27, 144.37, 163.83.

Anal. Calcd for $C_{21}H_{16}ClNO_3$: C, 68.95; H, 4.41; N, 3.83. Found: C, 68.71; H, 4.44; N, 3.78.

For **6d**; mp 118.5-119.5 °C; ir (potassium bromide) 1732, 1674, 1621, 1583, 1561 cm^{-1}; ^1H nmr (dimethyl sulfoxide-d_6): δ 3.62 (s, 3 H, OCH_3), 3.72 (dd, 1 H, J = 11.9 and 5.8 Hz, C2H), 3.94 (dd, 1 H, J = 12.5 and 11.9 Hz, C3H), 4.14 (dd, 1 H, J = 12.5 and 5.8 Hz, C2H), 4.96 and 5.04 (d, each 1 H, J = 15.6 Hz, NCH_2), 7.31-7.34 (m, 5 H, ArH), 7.70-7.92 (m, 4 H, ArH); ^{13}C nmr (dimethyl sulfoxide-d_6): δ 42.52, 50.46, 52.08, 52.63, 116.29, 124.60, 125.15, 127.18, 128.55, 131.77, 132.45, 133.38, 134.62, 135.25, 136.86, 150.77, 172.97, 177.30, 180.59.

Anal. Calcd for $C_{21}H_{17}NO_4$: C, 72.61; H, 4.93; N, 4.03. Found: C, 72.47; H, 5.03; N, 4.06.

4-Chloro-5-hydroxy-3-methoxycarbonyl-1*H*-benzo[*g*]indole (**5e**).

Treatment of **2a** (0.83 g, 3.0 mmoles) with aqueous 28% ammonium hydroxide (0.46 ml, 3.3 mmoles) following a similar procedure to that described above provided 0.42 g (51%) of **5e** as a solid; mp > 400 °C; ir (potassium bromide) 3508, 3490, 3416, 1696, 1629, 1592, 1524 cm^{-1}; ^1H nmr (dimethyl sulfoxide-d_6): δ 3.79 (s, 3 H, OCH_3), 7.49-7.64 (m, 2 H, ArH), 8.04 (s, 1 H, C2H), 8.22 (d, 1 H, J = 8.2 Hz, ArH), 8.38 (d, 1 H, J = 8.2 Hz, ArH), 9.34 (s, 1 H, OH), 12.79 (s, 1 H, NH); ^{13}C nmr (dimethyl sulfoxide-d_6): δ 51.21, 108.71, 109.10, 119.34, 121.04, 121.28, 123.41, 123.62, 124.89, 126.90, 127.32, 130.90, 144.18, 164.17.

Anal. Calcd for $C_{14}H_{10}ClNO_3$: C, 60.99; H, 3.66; N, 5.08. Found: C, 60.82; H, 3.51; N, 4.74.

4-Chloro-5-hydroxy-3-methoxycarbonyl-1-phenyl-1*H*-benzo[*g*]indole (**5f**).

Treatment of **2a** (0.83 g, 3.0 mmoles) with aniline (0.30 ml, 3.3 mmoles) following a similar procedure to that described above with the exception of reaction time (2 weeks) provided 0.79 g (75%) of **5f** as a solid; mp 207-208 °C; ir (potassium bromide) 3470, 1664, 1621, 1599, 1586, 1556 cm^{-1}; ^1H nmr (dimethyl sulfoxide-d_6) δ 3.61 (s, 3 H, OCH_3), 7.02-7.32 (m, 5 H, ArH), 7.95-8.16 (m, 5 H, C2H+ArH), 9.07 (s, 1 H, OH); ^{13}C nmr (dimethyl sulfoxide-d_6) δ 51.19, 95.87, 115.88, 122.85, 126.82, 129.68, 131.26, 131.78, 134.48, 134.86, 140.83, 141.11, 141.40, 144.27, 166.11, 177.68, 181.25.

Anal. Calcd for $C_{20}H_{14}ClNO_3$: C, 68.28; H, 4.01; N, 3.98. Found: C, 68.08; H, 3.82; N, 3.68.

3-Acetyl-4-chloro-5-hydroxy-1-methyl-1*H*-benzo[*g*]indole (**5g**) and 3-Acetyl-1-methyl-4,9-dihydro-4,9-dioxo-1*H*-benzo[*f*]indole (**7g**).

Treatment of **2b** (0.78 g, 3.0 mmoles) with aqueous 40% methylamine (0.29 ml, 3.3 mmoles) following a similar procedure to that described above provided 0.67 g (82%) of **5g** and 0.07 g (9%) of **7g** as solids.

For **5g**; mp > 400 °C; ir (potassium bromide) 3448, 1649, 1584, 1524 cm^{-1}; ^1H nmr (dimethyl sulfoxide-d_6): δ 2.52 (s, 3 H, CH_3), 4.31 (s, 3 H, NCH_3), 7.56-7.64 (m, 2 H, ArH), 8.23 (s, 1 H, C2H), 8.31 (d, 1 H, J = 8.2 Hz, ArH), 8.55 (d, 1 H, J = 8.2 Hz, ArH), 9.42 (s, 1 H, OH); ^{13}C nmr (dimethyl sulfoxide-d_6): δ 29.87, 108.90, 117.59, 119.40, 120.57, 121.27, 121.36, 121.84, 123.51, 124.17, 126.71, 137.62, 140.97, 144.22, 191.81.

Anal. Calcd for $C_{15}H_{12}ClNO_2$: C, 65.82; H, 4.42; N, 5.12. Found: C, 66.06; H, 4.49; N, 5.06.

For **7g**; mp 218-219 °C; ir (potassium bromide) 1665, 1647, 1590, 1527 cm^{-1}; ^1H nmr (dimethyl sulfoxide-d_6): δ 2.63 (s, 3 H, CH_3), 4.05 (s, 3 H, NCH_3), 7.83-7.87 (m, 2 H, ArH), 7.93 (s, 1 H, C2H), 8.05-8.10 (m, 2 H, ArH); ^{13}C nmr (dimethyl sulfoxide-d_6): δ 31.23, 37.91, 124.15, 124.59, 126.62, 127.20, 130.11, 132.30, 133.07, 134.25, 134.45, 137.17, 176.88, 180.44, 194.94.

Anal. Calcd for $C_{15}H_{11}NO_3$: C, 71.14; H, 4.38; N, 5.53. Found: C, 70.98; H, 4.34; N, 5.54.

3-Acetyl-4-chloro-1-ethyl-5-hydroxy-1*H*-benzo[*g*]indole (**5h**) and 3-Acetyl-1-ethyl-4,9-dihydro-4,9-dioxo-1*H*-benzo[*f*]indole (**7h**).

Treatment of **2b** (0.78 g, 3.0 mmoles) with aqueous 70% ethylamine (0.18 ml, 3.3 mmoles) following a similar procedure to that described above provided 0.73 g (85%) of **5h** and 0.06 g (8%) of **7h** as solids.

For **5h**; mp 155 °C (decomp.); ir (potassium bromide) 3421, 1649, 1586, 1523 cm^{-1}; ^1H nmr (dimethyl sulfoxide-d_6): δ 1.50 (t, 3 H, J = 7.0 Hz, CH_3), 2.54 (s, 3 H, CH_3), 4.70 (q, 2 H, J = 7.0 Hz, NCH_2), 7.54-7.70 (m, 2 H, ArH), 8.26 (s, 1 H, C2H), 8.35 (d, 1 H, J = 7.9 Hz, ArH), 8.41 (d, 1 H, J = 8.2 Hz, ArH), 9.43 (s, 1 H, OH); ^{13}C nmr (dimethyl sulfoxide-d_6): δ 15.70, 29.89, 45.38, 108.98, 117.95, 120.94, 121.16, 123.57, 124.14, 124.29, 125.47, 126.79, 136.14, 144.22, 191.80.

Anal. Calcd for $C_{16}H_{14}ClNO_2$: C, 66.79; H, 4.90; N, 4.87. Found: C, 66.52; H, 5.21; N, 4.60.

For **7h**; mp 156.5-157.5 °C; ir (potassium bromide) 1661, 1650, 1589, 1519 cm^{-1}; ^1H nmr (dimethyl sulfoxide-d_6): δ 1.39 (t, 3 H, J = 7.0 Hz, CH_3), 2.63 (s, 3 H, CH_3), 4.47 (q, 2 H, J = 7.0 Hz, NCH_2), 7.79-7.82 (m, 2 H, ArH), 7.97 (s, 1 H, C2H), 8.01-8.04 (m, 2 H, ArH); ^{13}C nmr (dimethyl sulfoxide-d_6): δ 15.83, 30.43, 44.47, 123.69, 124.14, 125.73, 126.32, 130.63, 132.29, 133.24, 133.46, 133.72, 134.91, 175.70, 179.64, 194.20.

Anal. Calcd for $C_{16}H_{13}NO_3$: C, 71.90; H, 4.90; N, 5.24. Found: C, 71.65; H, 4.74; N, 4.94.

3-Acetyl-4-chloro-5-hydroxy-1*H*-benzo[*g*]indole (**5i**).

Treatment of **2b** (0.78 g, 3.0 mmoles) with aqueous 28% ammonium hydroxide (0.46 ml, 3.3 mmoles) following a similar procedure to that described above provided 0.21 g (27%) of **5i** as a solid; mp > 400 °C; ir (potassium bromide) 3497, 3480, 3416, 1641, 1588 cm^{-1}; ^1H nmr (dimethyl sulfoxide-d_6): δ 2.55 (s, 3 H, CH_3), 7.49-7.65 (m, 2 H, ArH), 8.23 (d, 1 H, J = 8.2 Hz, ArH), 8.27 (d, 1 H, J = 3.4 Hz, C2H), 8.38 (d, 1 H, J = 7.9 Hz, ArH), 9.29 (br s, 1 H, NH); ^{13}C nmr (dimethyl sulfoxide-d_6): δ 29.44, 108.94, 118.72, 119.50, 120.77, 120.96, 123.01, 123.32, 124.48, 126.44, 127.43, 131.87, 143.84, 191.68.

Anal. Calcd for $C_{14}H_{10}ClNO_2$: C, 64.75; H, 3.88; N, 5.39. Found: C, 64.49; H, 4.08; N, 5.07.

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[12] A tiny amount of production of the minor product **6e** and **6f** was indicated by thin layer chromatography, however, isolation was unsuccessful.