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SYNTHESIS OF UNUSUAL NAPHTHO[2,1-*b*]FURANS AND NOVEL 1*H*-BENZ[*e*]INDOLINONES *VIA* SELECTIVE INTRAMOLECULAR CYCLIZATION

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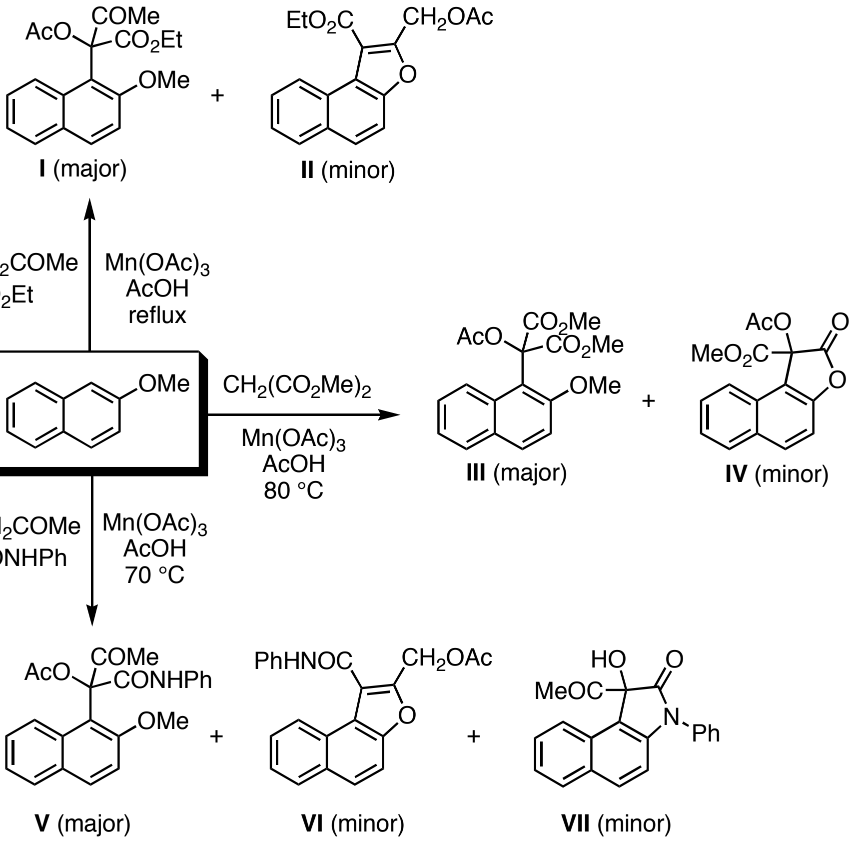
Abstract - The 2-(2-methoxy-1-naphthyl)-3-oxobutanamides were treated with concentrated hydrochloric acid in acetic acid at room temperature to exclusively give the unusual 5-chloronaphtho[2,1-*b*]furans in moderate to excellent yields. The same reaction was carried out in ethylene glycol at 80 °C to selectively produce the novel 1*H*-benz[*e*]indolinones in good yields. The characterization of the products and the reaction pathway of the selective intramolecular cyclization were discussed.

INTRODUCTION

The furan structure is found in numerous natural products.[1] Thus, we have a continuing interest in the synthesis of polyfunctionalized furans via the manganese(III)-based oxidative radical cyclization,[2] photo-induced transformations[3] and Lewis acid-catalyzed cyclization.[4] In recent years, we[5] and other groups[6] have developed various manganese(III)-mediated aromatic substitutions and additions using active methylene species, and we found that the reaction of methoxynaphthalenes with ethyl 3-oxobutanoate mainly gave the substituted product **I** together with a small amount of the naphtho[2,1-*b*]furan **II** (Scheme 1).[5c] Using dimethyl malonate also afforded a similar substituted product III and naphthofuranone **IV** (Scheme 1).[6a] Very recently, we reported that the oxidation of 2-methoxynaphthalene with manganese(III) acetate in the presence of *N*-phenyl-3-oxobutanamide gave the directly 3-oxobutanamide-substituted naphthalene **V** along with a small amount of the naphtho[2,1-*b*]furan **VI** and 1*H*-benz[*e*]indolinone **VII** as by-products (Scheme 1).[7] Since the naphtho[2,1-*b*]furan and benz[*e*]indolinone frameworks are found in a wide range of natural and synthetic products, which exhibit important biological and pharmacological activities,[8,9] a facile and convenient procedure for the synthesis of novel functionalized naphtho[2,1-*b*]furans and benz[*e*]indolinones is still necessary from the standpoint of its potential utility, though a significant effort has been directed toward the efficient synthesis of various naphtho[2,1-*b*]furans and benz[*e*]indolinones.[10,11] We now report the selective one-step route to the novel naphtho[2,1-*b*]furans and benz[*e*]indolinones by the intramolecular cyclization of 2-(2-methoxy-1-naphthyl)-3-oxobutanamides **1** such as **V**.

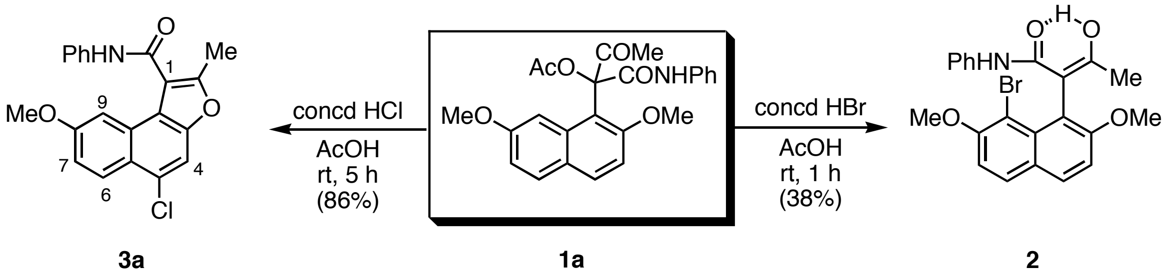
Scheme 1



RESULTS AND DISCUSSION

Synthesis of Naphtho[2,1-*b*]furan Derivatives 3. The 2-(2-methoxy-1-naphthyl)-3-oxobutanamides **1** were prepared by the manganese(III)-mediated oxidative aromatic substitution of the corresponding 2-methoxynaphthalenes with the *N*-aryl-3-oxobutanamides.[7] When 2-acetoxy-2-(2,7-dimethoxy-1-naphthyl)-*N*-phenyl-3-oxobutanamide (**1a**) was treated with acetic acid containing a small amount of concentrated hydrobromic acid at room temperature, one product **2** was isolated from the reaction mixture. The molecular ion peaks of **2** appeared at *m*/*z* 441 and 443 (relative intensity *ca.* 1:1) and the elemental analysis was identical to the molecular formula of $C_{22}H_{20}BrNO_4$. The ^1H NMR spectrum of **2** showed two peaks at $\delta = 3.99$ and 3.92 ppm, which were assigned to two methoxyl groups, and two AB spin systems ($\delta_A = 7.92$, $\delta_B = 7.18$ ppm, $J_{AB} = 9.0$ Hz and $\delta_{A'} = 7.83$, $\delta_{B'} = 7.29$ ppm, $J_{A'B'} = 9.0$ Hz, respectively) in the aromatic region. Other available information includes a peak at $\delta = 14.63$ ppm due to the intramolecular hydrogen-bonded hydroxyl group and a broad peak at $\delta = 6.69$ ppm assigned to a carbamoyl group which disappeared upon deuteration. These results indicated that the cyclization at the methoxyl group did not occur, but the bromine must be introduced at the *peri* position of the naphthalene ring (Scheme 2).

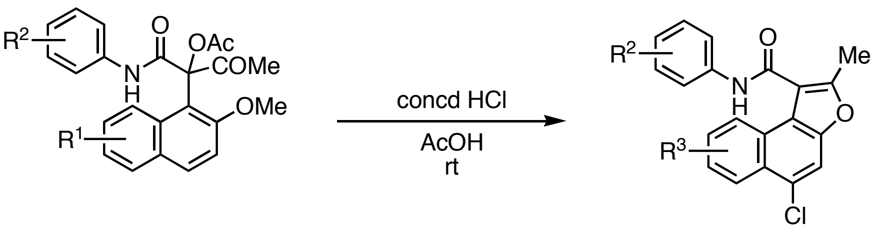
Scheme 2



Using concentrated hydrochloric acid in place of hydrobromic acid resulted in the expected product **3a** containing the naphtho[2,1-*b*]furan structure such as **VI** in Scheme 1 in a fairly good yield (Scheme 2). The molecular ion peaks of **3a** appeared at *m/z* 365 and 367 (relative intensity *ca.* 3:1) and the elemental analysis was identical with the molecular formula of $C_{21}H_{16}ClNO_3$. The product **3a** showed an α,β-unsaturated carbonyl absorption band at 1638 and 1624 cm^{-1} in the IR spectrum. In the ^{1}H NMR spectrum, the characteristic ABX pattern at $\delta_A = 8.20$ (1H, d, $J_{AB} = 9.0$ Hz), $\delta_B = 7.31$ (1H, dd, $J_{AB} = 9.0$, $J_{BX} = 2.7$ Hz), and $\delta_X = 7.82$ (1H, d, $J_{BX} = 2.7$ Hz) ppm was assigned to H-6, H-7, and a downfield shifted H-9, respectively. The most characteristic singlet aromatic proton appeared at $\delta = 7.95$ ppm due to H-4 adjacent to an electronegative substituent, such as a chlorine. A methoxyl and a methyl proton attached to an *sp*^{2} carbon appeared at $\delta = 3.68$ (3H, singlet) and $\delta = 2.62$ (3H, singlet) ppm, respectively. In the DEPT spectrum, seven peaks appeared in the aromatic region. This means that the chloro substituent should be introduced at the naphthalene ring. Accordingly, based on the above information, the structure of **3a** was determined to be 5-chloro-8-methoxy-2-methyl-1-phenylcarbamoylnaphtho[2,1-*b*]furan (Scheme 2). The reaction is in contrast to that using hydrobromic acid. Since the desired cyclization occurred in the presence of hydrochloric acid, the process was then applied to various 2-(2-methoxy-1-naphthyl)-3-oxobutanamides **1b**-**k**, which produced the corresponding 5-chloronaphtho[2,1-*b*]furans **3b**-**k** in moderate to excellent yields (Scheme 3 and Table 1, Entries 2-11).

Synthesis of 1*H*-Benz[*e*]indol-2(3*H*)-one Derivatives 4. Since the 1*H*-benz[*e*]indolinone **VII** was obtained by the manganese(III) oxidation of *N*-phenyl-3-oxobutanamide in the presence of 2-methoxynaphthalene (Scheme 1), we next examined the selective synthesis of the corresponding 1*H*-benz[*e*]indolinones using the (2-methoxynaphthyl)butanamides **1**. In order to selectively cyclize at the

Scheme 3



1a-k **3a-k**

Table 1. Cyclization of 2-(2-Methoxylnaphthyl)butanamides **1a-k** in Acetic Acid at Room Temperature[a]

Entry	Butanamide **1**			Time	Product **3**			
		R^1	R^2	h		R^2	R^3	Yield/%[b]
1	**1a**	7-MeO	H	5	**3a**	H	8-MeO	86
2	**1b**	7-MeO	2'-Cl	3	**3b**	2'-Cl	8-MeO	90
3	**1c**	7-MeO	4'-Cl	3	**3c**	4'-Cl	8-MeO	77
4	**1d**	7-MeO	2'-MeO	5	**3d**	2'-MeO	8-MeO	81
5	**1e**	7-MeO	4'-MeO	5	**3e**	4'-MeO	8-MeO	78
6	**1f**	7-MeO	2'-Me	9	**3f**	2'-Me	8-MeO	78
7	**1g**	7-MeO	4'-Me	7	**3g**	4'-Me	8-MeO	80
8	**1h**	7-MeO	2'-NO_2	9	**3h**	2'-NO_2	8-MeO	79
9	**1i**	7-MeO	4'-F	4	**3i**	4'-F	8-MeO	71
10	**1j**	6-MeO	H	4	**3j**	H	7-MeO	58
11	**1k**	H	H	7	**3k**	H	H	55

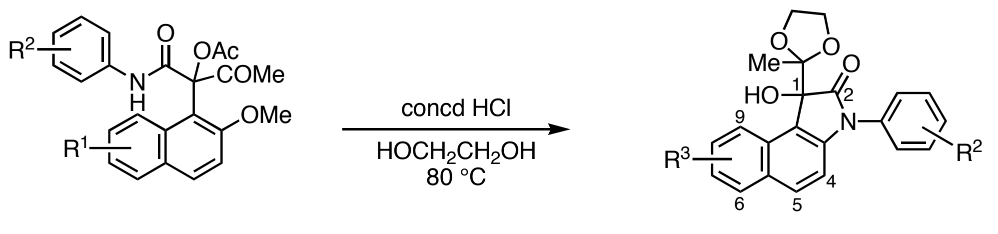
[a] The reaction of **1** (0.2 mmol) was carried out in the presence of concentrated hydrochloric acid (0.34 mL) in acetic acid (10 mL).

[b] Isolated yield based on **1** used.

nitrogen atom of the amide group, the protection of the acetyl carbonyl group was needed. Therefore, the reaction of **1a** was carried out in ethylene glycol in the presence of a small amount of concentrated hydrochloric acid. Fortunately, (2-metoxynaphthyl)butanamide **1a** underwent intramolecular cyclization at the nitrogen atom after the protection of the acetyl group to produce a hydroxylactam **4a** in good yield. The IR spectrum of **4a** exhibited absorption bands at 1693 cm^{-1} assigned to a typical lactam carbonyl group and at 3375 cm^{-1} due to a hydroxyl group. In the ^1H NMR spectrum of **4a**, characteristic AB and ABX splitting patterns appeared at $\delta_A = 7.69$ (1H, d) and $\delta_B = 7.01$ ppm (1H, d) with $J_{AB} = 9.0$ Hz, and at $\delta_A = 7.76$ (1H, d), $\delta_B = 6.95$ (1H, dd), and $\delta_X = 6.97$ ppm (1H, d) with $J_{AB} = 8.7$ and $J_{BX} = 2.7$ Hz, respectively, of the naphthalene ring protons along with a typical 1,3-dioxolane protective group at $\delta = 4.09$ (1H, m), $\delta = 3.85$ (2H, m), and $\delta = 3.54$ (1H, m), one methoxyl group at $\delta = 3.73$ (3H, s), a methyl group at $\delta = 1.78$ (3H, s), and a hydroxyl group at $\delta = 8.98$ ppm which disappeared upon deuteration. The

^{13}C NMR spectrum of **4a** also showed an amide carbonyl at $\delta = 166.9$, a quaternary carbon attached a hydroxyl group at $\delta = 85.8$, two methylenes of the 1,3-dioxolane at $\delta = 58.5$ and 57.1, a methoxyl group at $\delta = 55.1$, and a methyl group at $\delta = 21.9$ ppm. Therefore, the structure of **4a** was determined to be 1-hydroxy-8-methoxy-1-(2'-methyl-1',3'-dioxolan-2'-yl)-3-phenyl-1*H*-benz[*e*]indol-2(3*H*)-one (Scheme 4) and the combustion analysis was identical to the structural formula of $C_{23}H_{21}NO_5$. A similar reaction of other (2-metoxynaphthyl)butanamides **1b-h,j,k** was carried out and the corresponding benz[*e*]indolinone derivatives **4b-h,j,k** were obtained in 56-88% yields, respectively . Thsee results are listed in Table 2.

Scheme 4



1a-h,j,k **4a-h,j,k**

Table 2. Acid-Catalyzed Intramolecular Cyclization of the 2-(2-Methoxylnaphthyl)butanamides **1a-h,j,k** in Ethylene Glycol[a]

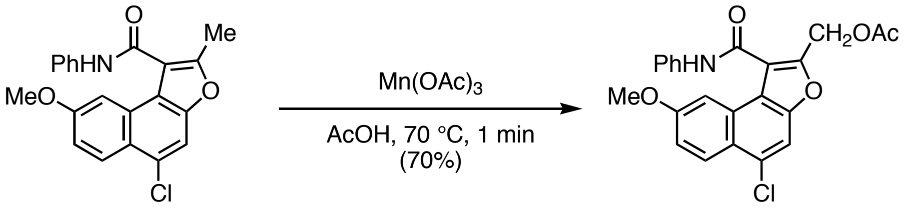
Entry	Butanamide **1**			Time	Product **4**			
		R^1	R^2	h		R^2	R^3	Yield%[b]
1	**1a**	7-MeO	H	1	**4a**	H	8-MeO	70
2	**1b**	7-MeO	2'-Cl	1.5	**4b**	2'-Cl	8-MeO	69
3	**1c**	7-MeO	4'-Cl	2.5	**4c**	4'-Cl	8-MeO	67
4	**1d**	7-MeO	2'-MeO	3.5	**4d**	2'-MeO	8-MeO	70
5	**1e**	7-MeO	4'-MeO	2	**4e**	4'-MeO	8-MeO	69
6	**1f**	7-MeO	2'-Me	1	**4f**	2'-Me	8-MeO	56
7	**1g**	7-MeO	4'-Me	1	**4g**	4'-Me	8-MeO	56
8	**1h**	7-MeO	2'-NO_2	3	**4h**	2'-NO_2	8-MeO	64
9	**1j**	6-MeO	H	1	**4j**	H	7-MeO	80
10	**1k**	H	H	1	**4k**	H	H	88

[a] The reaction of **1** (0.2 mmol) was carried out in the presence of concentrated hydrochloric acid (0.34 mL) in ethylene glycol (10 mL).

[b] Isolated yield based on **1** used.

Oxidation of 3a with Manganese(III) Acetate in Acetic Acid. In the manganese(III)-mediated oxidation of 2-methoxynaphthalene in the presence of *N*-phenyl-3-oxobutanamide, the reaction did not afford the 2-methylnaphtho[2,1-*b*]furan, but the 2-acetoxymethyl-substituted naphthofuran **VI** (Scheme 1).[5c,7] We were interested in the acetoxymethylation and examined the oxidation using the 5-chloro-2-methylnaphthofuran **3a** as a model compound in order to confirm the benzyl-type oxidation. The oxidation of naphthofuran **3a** with manganese(III) acetate was conducted in acetic acid to give the desired acetoxymethylnaphthofuran **5** in a 70% yield (Scheme 5). The ^{1}H NMR spectrum of **5** revealed a typical acetoxymethyl group instead of the methyl group. As a result, it was found that the methylnaphthofuran **3a** was subject to the benzyl-type oxidation as well as the oxidation of methylbenzenes.[12a-d]

Scheme 5



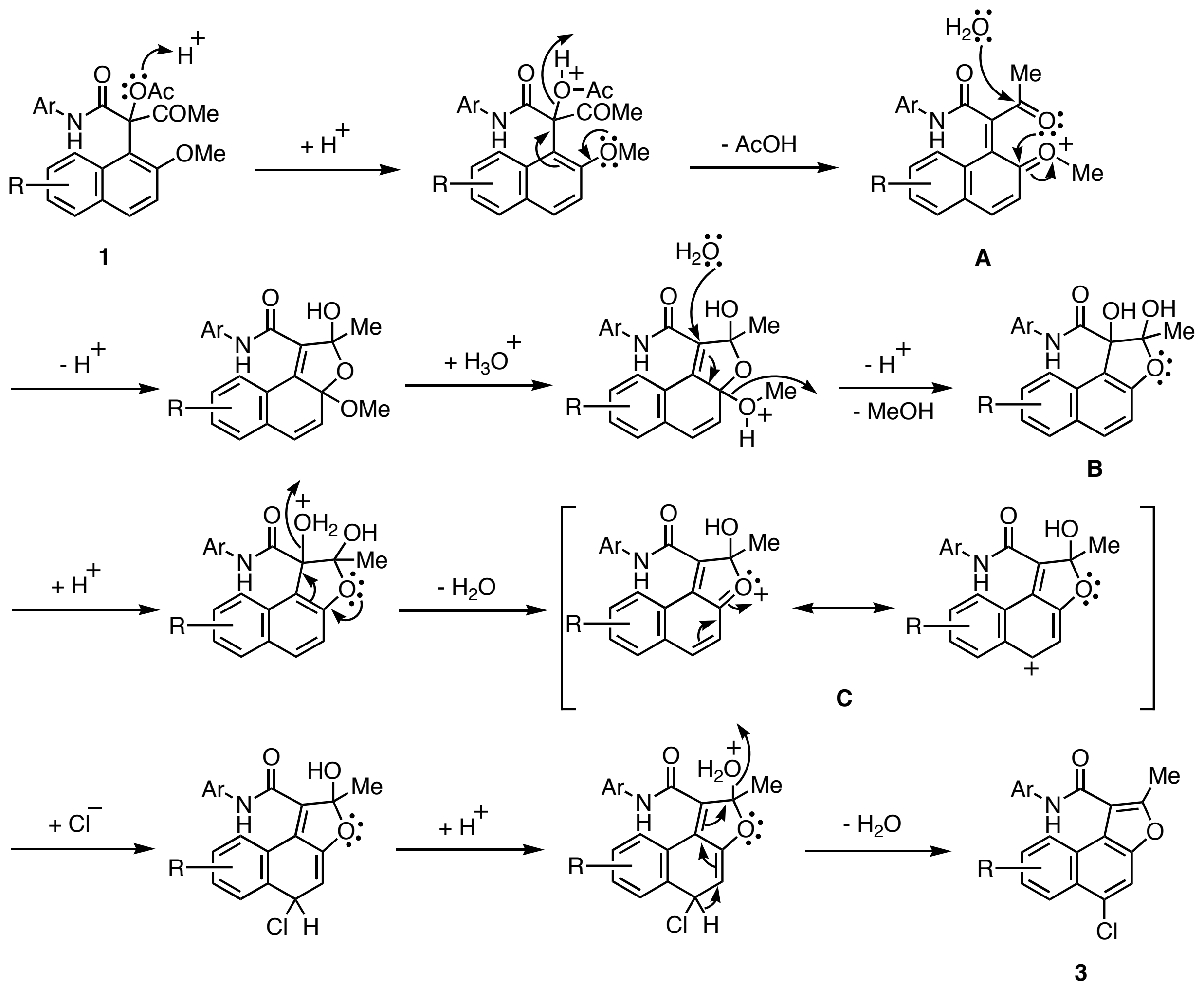
3a **5**

Proposed Mechanism for the Formation of 5-Chloronaphtho[2,1-*b*]furans 3 and Benz[*e*]indolinones 4.

The reaction with hydrochloric acid in acetic acid gave the unusual chloro-functionalized naphtho[2,1-*b*]furans **3**. To the best of our knowledge, there have been few related examples reported. Only two similar reactions were found for the cyclization of the naphthoquinones.[13] The reaction would start from the deacetoxylation to give the naphthoquinonemethide-type intermediate **A**, which might be cyclized and then demethanol to produce α-hydroxyhemiacetal intermediate **B** (Scheme 6). The intermediate **B** would be successively dehydrated to yield the corresponding cation **C**, which would be nucleophilically attacked by the chloride ion followed by aromatization *via* dehydration, and finally the 5-chloronaphtho[2,1-*b*]furans **3** would be produced. The proposed mechanism is illustrated in Scheme 6. It seemed that the formation of (bromonaphthyl)butanamide **2** in the reaction of **1a** with hydrobromic acid in Scheme 2 followed a very different reaction pathway. The bromine formed *in situ* might possibly electrophilically attack the most electronegative position of **1a**.

A similar mechanism for the formation of the 1*H*-benz[*e*]indolinones **4** was also proposed in Scheme 7. After protection with ethylene glycol, a similar deacetoxylation, as in the case of acetic acid, would occur to produce a similar naphthoquinonemethide-type intermediate **D** (Scheme 7). The intermediate **D** would cyclize at the amide nitrogen followed by demethanol, simultaneous aromatization, and then attack of water to finally furnish the corresponding 1*H*-benz[*e*]indolinones **4**. It is worth noting that the chlorine atom was not introduced into the benz[*e*]indolinone skeleton using ethylene glycol as the solvent. The reason for this is not clear at this moment, however, the indolinones **4**, which were the equivalents of the α-hydroxyhemiacetal intermediate **B** in Scheme 6, might be difficult to dehydrate and afford the corresponding cation because of the stability of the indolinones **4**.[14]

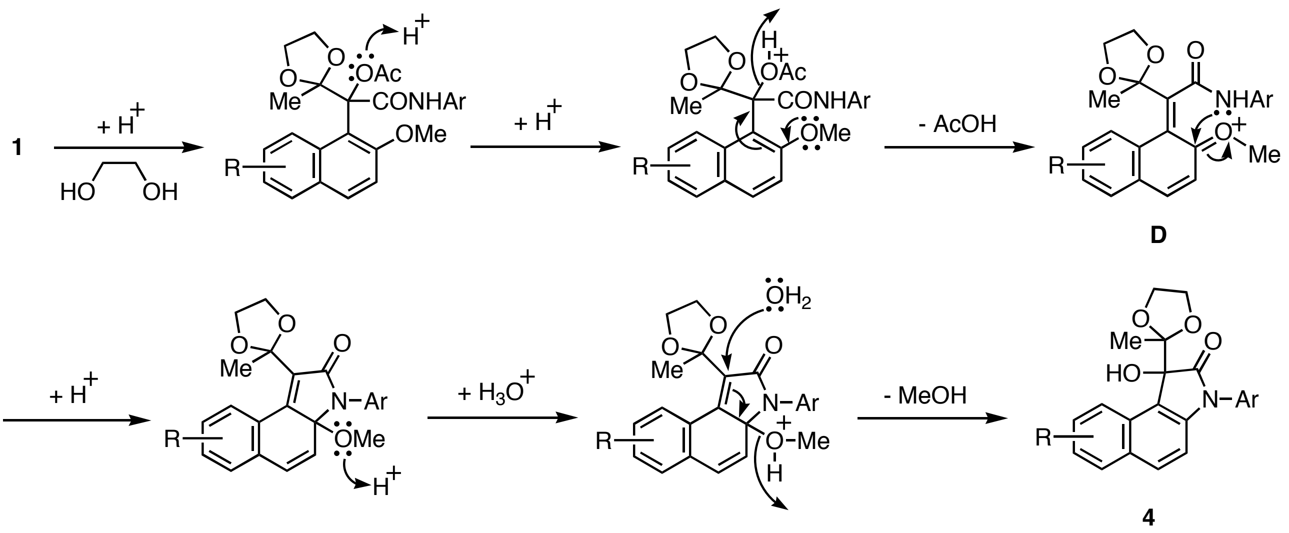
Scheme 6



CONCLUSION

We achieved the selective intramolecular cyclization of the 2-(2-methoxynaphthyl)butanamides **1**. When the reaction using concentrated hydrochloric acid was carried out in acetic acid at room temperature, the 5-chloro-substituted naphtho[2,1-*b*]furans **3** were exclusively produced in good to excellent yields. When the same reaction was conducted in ethylene glycol at 80 °C, the dioxolane-protected 1*H*-benz[*e*]indolinones **4** were selectively obtained in good yields. The unusual hydrochloric acid-mediated selective cyclization could be explained by the reaction pathway during the formation of the naphthoquinonmethide-type intermediate such as **A** and **D** in Schemes 6 and 7. The selective intramolecular cyclization would guarantee an efficient access to interesting functionalized heterocyclic compounds.

Scheme 7



EXPERIMENTAL

General Information. All of the NMR spectra were recorded by a JNM-AL300 FT-NMR spectrometer at 300 MHz for ^{1}H and at 75 MHz for ^{13}C, with tetramethylsilane as the internal standard. The chemical shifts are given in δ values (ppm) and the coupling constants in Hz. The IR spectra of the neat samples were measured by the KBr disc method using a Shimadzu FTIR-8400 spectrometer and expressed in cm^{-1}. The EI MS spectra were recorded by a Shimadzu GCMS-QP5050A with an ionizing voltage of 70 eV. The elemental analyses were performed at the Instrumental Analysis Center, Kumamoto University, Kumamoto, Japan.

The Reaction of (2-Methoxynaphthyl)butanamide 1a with Hydrobromic Acid. To a solution of naphthylbutanamide **1a** (0.2 mmol) in acetic acid (10 mL), a portion of the concentrated hydrobromic acid (47%, 0.28 mL) was slowly dropwise-added using a syringe. The mixture was stirred at rt for 1 h, and then water (50 mL) was added. The aqueous solution was extracted with $CHCl_3$ (30 × 3 mL). The combined extracts were successively washed with a saturated aqueous solution of $NaHCO_3$ (30 × 2 mL) and water (30 × 2 mL), then dried over anhydrous $MgSO_4$, and concentrated to dryness. The residue was separated by TLC (Wakogel B-10) while eluting with EtOAc-hexane (2:5, v/v) to give the 2-(8-bromo-2,7-dimethoxy-1-naphthyl)-*N*-phenyl-3-oxobutanamide (**2**) in a 38% yield.

2-(8-Bromo-2,7-dimethoxy-1-naphthyl)-*N*-phenyl-3-oxobutanamide (2): Colorless microcrystals (from Et_2O/hexane); mp 136-137 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 14.63 (1H, s, enol H), 7.92 (1H, d, J = 9.0 Hz, Naphthalene H), 7.83 (1H, d, J = 9.0 Hz, Naphthalene H), 7.29 (1H d, J = 9.0 Hz, Naphthalene H), 7.18 (1H, d, J = 9.0 Hz, Naphthalene H), 7.3-7.0 (5H, m, aromatic H), 6.69 (1H, br, s, NH), 3.99 (3H, s, OCH_3), 3.92 (3H, s, OCH_3), 1.49 (3H, s, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.8, 170.7, 158.4, 156.1, 137.5, 132.8, 132.2, 130.4, 128.7, 126.5, 124.1, 120.9, 115.4 111.4, 111.3, 105.4, 100.1, 57.0, 56.6, 19.7; IR ($CHCl_3$) 3404, 1636, 1612 cm^{-1}; MS *m/z* (rel intensity) 441 (M, 7), 443 (M, 7). *Anal.* Calcd for $C_{22}H_{20}BrNO_4$: C, 59.74; H, 4.56; N, 3.17. Found: C, 59.42; H, 4.51; N, 3.20.

The Reaction of (2-Methoxynaphthyl)butanamides 1a-k with Hydrochloric Acid. General Procedure for the Synthesis of the 5-Chloronaphtho[2,1-*b*]furans 3. To a solution of the butanamide **1** (0.2 mmol) in acetic acid (10 mL), a portion of the concentrated hydrochloric acid (36%, 0.34 mL) was slowly dropwise-added using a syringe. The reaction mixture was stirred at rt for 5 h and a precipitate was formed. Water (50 mL) was then added to the reaction mixture, and the produced precipitate was filtered and washed with water. The crude product was dried under vacuum and further purifed by recrystallization from the appropriate solvents.

5-Chloro-8-methoxy-2-methyl-1-phenylcarbamoylnaphtho[2,1-*b*]furan (3a): Colorless needles (from $CHCl_3$); mp 227-228 °C; ^1H NMR (300 MHz, DMSO-d_6) δ 10.71 (1H, s, NH), 8.20 (1H, d, $J = 9.0$ Hz, H-6), 7.95 (1H, s, H-4), 7.82 (1H, d, $J = 2.7$ Hz, H-9), 7.79 (2H, m, H-2', 6'), 7.39 (2H, m, H-3', 5'), 7.31 (1H, dd, $J = 9.0$, 2.7 Hz, H-7), 7.14 (1H, m, H-4'), 3.68 (3H, s, OCH_3), 2.62 (3H, s, CH_3); ^{13}C NMR (75 MHz, DMSO-d_6) δ 162.7, 158.3, 154.9, 150.0, 138.8, 128.9, 128.5, 127.6, 126.6, 124.1, 122.1, 119.7, 119.3, 117.4, 115.7, 110.4, 104.3, 54.9, 13.3; IR (KBr) 3180-3000, 1638, 1624 cm^{-1}; MS *m/z* (rel intensity) 365 (M, 81), 367 (M, 27). *Anal.* Calcd for $C_{21}H_{16}ClNO_3$: C, 68.95; H, 4.41; N, 3.83. Found: C, 68.70; H, 4.38; N, 3.89.

1-(2'-Chlorophenylcarbamoyl)-5-chloro-8-methoxy-2-methylnaphtho[2,1-*b*]furan (3b): Colorless needles (from EtOAc/hexane); mp 195-196 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 8.66 (1H, m, H-6'), 8.26 (1H, d, $J = 9.0$ Hz, H-6), 8.19 (1H, br, s, NH), 7.89 (1H, d, $J = 2.7$ Hz, H-9), 7.59 (1H, s, H-4), 7.44 (1H, m, H-3'), 7.38 (1H, m, H-5'), 7.21 (1H, dd, $J = 9.0$, 2.7 Hz, H-7), 7.13 (1H, m, H-4'), 3.79 (3H, s, OCH_3), 2.75 (3H, s, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.3, 158.7, 155.8, 151.0, 134.4, 129.6, 129.3, 128.8, 128.0, 127.1, 125.2, 123.0, 122.9, 121.4, 118.7, 117.7, 115.6, 110.0, 103.9, 55.3, 13.9; IR (KBr) 3223, 1647, 1622 cm^{-1}; MS *m/z* (rel intensity) 399 (M, 61), 401 (M, 20). *Anal.* Calcd for $C_{21}H_{15}Cl_2NO_3$: C, 63.02; H, 3.78; N, 3.50. Found: C, 62.83; H, 3.75; N, 3.42.

1-(4'-Chlorophenylcarbamoyl)-5-chloro-8-methoxy-2-methylnaphtho[2,1-*b*]furan (3c): Colorless needles (from $CHCl_3$); mp over 300 °C; ^1H NMR (300 MHz, DMSO-d_6) δ 10.85 (1H, s, NH), 8.22 (1H, d, $J = 9.0$ Hz, H-6), 7.98 (1H, s, H-4), 7.85 (2H, m, H-2',6'), 7.82 (1H, d, $J = 2.7$ Hz, H-9), 7.48 (2H, m, H-3',5'), 7.33 (1H, dd, $J = 9.0$, 2.7 Hz, H-7), 3.72 (3H, s, OCH_3), 2.64 (3H, s, CH_3); ^{13}C NMR (75 MHz, DMSO-d_6) δ 162.7, 158.3, 155.2, 149.9, 137.8, 128.9, 128.4, 127.7, 127.6, 126.6, 122.1, 121.3, 119.2, 117.4, 115.5, 110.4, 104.2, 55.0, 13.4; IR (KBr): 3254, 1645, 1624 cm^{-1}; MS: *m/z* (rel intensity) 400 (M+1, 34), 402 (M+1, 15). *Anal.* Calcd for $C_{21}H_{15}Cl_2NO_3$: C, 63.02; H, 3.78; N, 3.50. Found: C, 62.63; H, 3.72;

N, 3.40.

5-Chloro-1-(2’-methoxyphenylcarbamoyl)-8-methoxy-2-methylnaphtho[2,1-*b*]furan (3d): Colorless microcrystals (from CHCl$_3$/hexane); mp 176.5-177 °C; ^{1}H NMR (300 MHz, CDCl$_3$) δ 8.62 (1H, m, H-6$'$), 8.29 (1H, br, s, NH), 8.24 (1H, d, J = 9.3 Hz, H-6), 7.91 (1H, br. s, H-4), 7.57 (1H, br. s, H-9), 7.18 (1H, br. d, J = 9.3 Hz, H-7), 7.11 (1H, m, H-4$'$), 7.07 (1H, m, H-5$'$), 6.92 (1H, m, H-3$'$), 3.82 (3H, s, OCH$_3$), 3.75 (3H, s, OCH$_3$), 2.71 (3H, s, CH$_3$); ^{13}C NMR (75 MHz, CDCl$_3$) δ 162.8, 158.6, 155.3, 150.8, 148.0, 129.2, 128.9, 127.4, 127.0, 124.3, 122.9, 121.2, 119.9, 118.9, 117.6, 116.0, 110.0, 103.9, 55.6, 55.2, 13.6; IR (KBr) 3229, 1647, 1624 cm^{-1}; MS *m/z* (rel intensity) 395 (M, 89), 397 (M, 28). *Anal.* Calcd for C$_{22}$H$_{18}$ClNO$_4$: C, 66.75; H, 4.58; N, 3.54. Found: C, 66.77; H, 4.53; N, 3.63.

5-Chloro-1-(4’-methoxyphenylcarbamoyl)-8-methoxy-2-methylnaphtho[2,1-*b*]furan (3e): Colorless microcrystals (from CHCl$_3$); mp 269-270 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 10.56 (1H, s, NH), 8.20 (1H, d, J = 9.3 Hz, H-6), 7.95 (1H, s, H-4), 7.85 (1H, br. s, H-9), 7.70 (2H, m, H-2$'$,6$'$), 7.32 (1H, dd, J = 9.3, 2.7 Hz, H-7), 6.97 (2H, m, H-3$'$,5$'$), 3.75 (3H, s, OCH$_3$), 3.71 (3H, s, OCH$_3$), 2.62 (3H, s, CH$_3$); ^{13}C NMR (75 MHz, DMSO-d_6) δ 162.1, 158.3, 155.8, 154.7, 150.0, 132.0, 128.5, 127.6, 126.6, 122.1, 121.3, 119.4, 117.4, 115.8, 114.1, 110.4, 104.3, 55.3, 55.1, 13.4; IR (KBr) 3271, 1643, 1622 cm^{-1}; MS *m/z* (rel intensity) 396 (M+1, 87), 398 (M+1, 30). *Anal.* Calcd for C$_{22}$H$_{18}$ClNO$_4$: C, 66.75; H, 4.58; N, 3.54. Found: C, 66.65; H, 4.53; N, 3.51.

5-Chloro-8-methoxy-1-(2’-methylphenylcarbamoyl)-2-methylnaphtho[2,1-*b*]furan (3f): Colorless microcrystals (from EtOAc/hexane); mp 239-240 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 10.18 (1H, br. s, NH), 8.20 (1H, d, J = 9.3 Hz, H-6), 7.96 (1H, d, J = 2.7 Hz, H-9), 7.95 (1H, s, H-4), 7.54 (1H, m, H-6$'$), 7.33 (1H, dd, J = 9.3, 2.7 Hz, H-7), 7.31-7.20 (3H, m, arom H), 3.81 (3H, s, OCH$_3$), 2.72 (3H, s, CH$_3$), 2.33 (3H, s, CH$_3$); ^{13}C NMR (75 MHz, DMSO-d_6) δ 163.0, 158.3, 154.7, 150.0, 135.9, 133.1, 130.6, 128.6, 127.6, 126.6, 126.3, 126.0, 122.1, 119.6, 117.4, 115.5, 110.4, 104.5, 55.3, 18.3, 13.6; IR (KBr) 3258, 1643, 1624 cm^{-1}; MS *m/z* (rel intensity) 379 (M, 15), 381 (M, 8). *Anal.* Calcd for C$_{22}$H$_{18}$ClNO$_3$: C, 69.57; H, 4.78; N, 3.69. Found: C, 69.35; H, 4.71; N, 3.62.

5-Chloro-8-methoxy-1-(4’-methylphenylcarbamoyl)-2-methylnaphtho[2,1-*b*]furan (3g): Colorless needles (from CHCl$_3$/hexane); mp 248-249 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 10.61 (1H, s, NH), 8.20 (1H, d, J = 9.0 Hz, H-6), 7.96 (1H, s, H-4), 7.83 (1H, d, J = 2.4 Hz, H-9), 7.67 (2H, m, H-2’,6$'$), 7.31 (1H, dd, J = 9.0, 2.4 Hz, H-7), 7.19 (2H, m, H-3$'$, 5$'$), 3.70 (3H, s, OCH$_3$), 2.61 (3H, s, CH$_3$), 2.29 (3H, s, CH$_3$); ^{13}C NMR (75 MHz, DMSO-d_6) δ 162.4, 158.3, 154.8, 149.9, 136.3, 133.1, 129.3, 128.5, 127.6, 126.6, 122.1, 119.8, 119.4, 117.4, 115.8, 110.4, 104.3, 55.0, 20.6, 13.4; IR (KBr) 3254, 1639, 1624 cm^{-1}; MS *m/z* (rel intensity) 380 (M+1, 78), 381 (M+1, 24). *Anal.* Calcd for C$_{22}$H$_{18}$ClNO$_3$: C, 69.57; H, 4.78; N, 3.69. Found: C, 69.18; H, 4.75; N, 3.65.

5-Chloro-8-methoxy-2-methyl-1-(2’-nitrophenylcarbamoyl)naphtho[2,1-*b*]furan (3h): Yellow needles (from EtOAc/hexane); mp 239-240 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 11.12 (1H, s, NH), 8.22 (1H, d, J = 9.3 Hz, H-6), 8.04 (1H, m, H-3'), 7.99 (1H, s, H-4), 7.90 (1H, d, J = 2.7 Hz, H-9), 7.80 (1H, m, H-5'), 7.64 (1H, m, H-6'), 7.50 (1H, m, H-4'), 7.33 (1H, dd, J = 9.3, 2.7 Hz, H-7), 3.81 (3H, s, OCH$_3$), 2.75 (3H, s, CH$_3$); ^{13}C NMR (75 MHz, DMSO-d_6) δ 162.9, 158.4, 156.8, 150.2, 143.8, 134.1, 130.2, 128.6, 128.0, 126.5, 126.3, 126.0, 125.0, 122.2, 119.0, 117.6, 114.5, 110.3, 104.9, 55.4, 13.6; IR (KBr) 3233, 1647, 1625, 1526 cm^{-1}; MS m/z (rel intensity) 411 (M+1, 47), 413 (M+1, 29). *Anal.* Calcd for $C_{21}H_{15}ClN_2O_5$: C, 61.40; H, 3.68; N, 6.82. Found: C, 61.42; H, 4.03; N, 6.42.

5-Chloro-1-(4'-fluorophenylcarbamoyl)-8-methoxy-2-methylnaphtho[2,1-*b*]furan (3i): Colorless needles (from CHCl$_3$); mp 283-283.5 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 10.76 (1H, s, NH), 8.20 (1H, d, J = 9.3 Hz, H-6), 7.95 (1H, s, H-4), 7.82 (1H, d, J = 2.7 Hz, H-9), 7.80 (2H, m, H-2',6'), 7.31 (1H, dd, J = 9.3, 2.7 Hz, H-7), 7.25 (2H, m, H-3',5'), 3.70 (3H, s, OCH$_3$), 2.63 (3H, s, CH$_3$); ^{13}C NMR (75 MHz, DMSO-d_6) δ 162.5, 158.3, 155.0, 150.0, 135.2, 135.1, 128.4, 127.7, 126.6, 122.1, 121.6, 121.5, 119.3, 117.4, 115.7, 115.6, 115.4, 110.4, 104.3, 55.0, 20.6, 13.4; IR (KBr) 3250, 1643, 1622 cm^{-1}; MS m/z (rel intensity) 383 (M, 74), 385 (M, 12). *Anal.* Calcd for $C_{21}H_{15}ClFNO_3$: C, 65.72; H, 3.94; N, 3.65. Found: C, 65.54; H, 4.07; N, 3.53.

5-Chloro-7-methoxy-2-methyl-1-phenylcarbamoylnaphtho[2,1-*b*]furan (3j): Colorless needles (from CHCl$_3$); mp 275-276 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 10.63 (1H, s, NH), 8.28 (1H, d, J = 9.3 Hz, H-9), 8.07 (1H, s, H-4), 7.74 (2H, m, H-2',6'), 7.53 (1H, d, J = 2.4 Hz, H-6), 7.34 (2H, m , H-3',5'), 7.30 (1H, dd, J = 9.3, 2.4 Hz, H-8), 7.09 (1H, m, H-4'), 3.86 (3H, s, OCH$_3$), 2.57 (3H, s, CH$_3$); ^{13}C NMR (75 MHz, DMSO-d_6) δ 162.7, 157.4, 155.3, 148.3, 138.8, 128.9, 128.6, 126.2, 126.1, 124.1, 121.8, 120.3, 119.9, 119.2, 115.5, 113.2, 104.0, 55.3, 13.5; IR (KBr) 3246, 1647, 1625 cm^{-1}; MS m/z (rel intensity) 365 (M, 50), 367 (M, 16). *Anal.* Calcd for $C_{21}H_{16}ClNO_3$: C, 68.95; H, 4.41; N, 3.83. Found: C, 68.87; H, 4.36; N, 3.80.

5-Chloro-2-methyl-1-phenylcarbamoylnaphtho[2,1-*b*]furan (3k): Colorless microcrystals (from CHCl$_3$/hexane); mp 268-268.5 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 10.71 (1H, s, NH), 8.41 (1H, m, H-6), 8.31 (1H, m, H-9), 8.17 (1H, s, H-4), 7.80 (2H, m, H-2',6'), 7.68 (2H, m, H-7, 8), 7.40 (2H, m, H-3',5'), 7.16 (1H, m, H-4'), 2.64 (3H, s, CH$_3$); ^{13}C NMR (75 MHz, DMSO-d_6) δ 162.6, 155.3, 149.4, 138.8, 128.9, 127.6, 127.1, 127.0, 126.2, 124.8, 124.3, 124.1, 120.1, 119.9, 115.8, 113.0, 13.4; IR (KBr) 3290, 1647 cm^{-1}; MS m/z (rel intensity) 335 (M, 37), 337 (M, 12). *Anal.* Calcd for $C_{20}H_{14}ClNO_2$: C, 71.54; H, 4.20; N, 4.17. Found: C, 71.26; H, 4.25; N, 4.15.

General Procedure for the Synthesis of 1*H*-Benz[*e*]indolinones 4. To a solution of **1** (0.2 mmol) in ethylene glycol (10 mL), a portion of the concentrated hydrochloric acid (36%, 0.34 mL) was slowly dropwise-added using a syringe at rt. The mixture was then heated at 80 °C for 1 h with stirring. After cooling, water (50 mL) was added. The formed precipitates were filtered and dried under vacuum. The crude product was further purified by recrystallization from the appropriate solvents.

1-Hydroxy-8-methoxy-1-(2'-methyl-1',3'-dioxolan-2'-yl)-3-phenyl-1*H*-benz[*e*]indol-2(3*H*)-one (4a): Colorless microcrystals (from Et_2O/hexane); mp 167-168 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.98 (1H, s, OH), 7.76 (1H, d, *J* = 8.7 Hz, H-6), 7.69 (1H, d, *J* = 9.0 Hz, H-5), 7.64 (2H, m, H-2',6'), 7.34 (2H, m, H-3',5'), 7.14 (1H, m, H-4'), 7.01 (1H, d, *J* = 9.0 Hz, H-4), 6.97 (1H, d, *J* = 2.7 Hz, H-9), 6.95 (1H, dd, J = 8.7, 2.7 Hz, H-7), 4.09 (1H, m, H-CH), 3.85 (2H, m, CH_2), 3.73 (3H, s, OCH_3), 3.54 (1H, m, H-CH), 1.78 (3H, s, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.9, 159.2, 159.0, 137.0, 132.8, 132.0, 130.6, 129.1, 125.1, 124.7, 119.8, 115.8, 113.1 109.1, 108.7, 100.3, 85.8, 58.5, 57.1, 55.1, 21.9; IR (KBr) 3375, 1693 cm^{-1}; MS *m/z* (rel intensity) 392 (M+1, 19). *Anal.* Calcd for $C_{23}H_{21}NO_5$: C, 70.58; H, 5.41; N, 3.58. Found: C, 70.47; H, 5.47; N, 3.63.

3-(2'-Chlorophenyl)-1-hydroxy-8-methoxy-1-(2'-methyl-1',3'-dioxolan-2'-yl)-1*H*-benz[*e*]indol-2(3*H*)-one (4b): Colorless microcrystals (from Et_2O/hexane); mp 162-162.5 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.59 (1H, s, OH), 8.36 (1H, m, H-6'), 7.76 (1H, d, *J* = 9.0 Hz, H-5), 7.69 (1H, d, *J* = 9.0 Hz, H-6), 7.41 (1H, m, H-3'), 7.24 (1H, m, H-5'), 7.08 (1H, dd, *J* = 9.0 Hz, H-4), 7.04 (1H, d, *J* = 2.7 Hz, H-9), 6.99 (1H, m, H-4'), 6.95 (1H, dd, *J* = 9.0, 2.7 Hz, H-7), 4.03-4.08 (1H, m, H-CH), 3.84-3.88 (2H, m, CH_2), 3.76 (3H, s, OCH_3), 3.60-3.66 (1H, m, H-CH), 1.80 (3H, s, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.2, 159.3, 159.0, 133.8, 132.8, 131.9, 130.5, 129.1, 127.8, 125.2, 125.1, 123.4, 121.6, 116.1, 113.3 109.1, 108.6, 99.9, 86.1, 59.1, 57.4, 55.1, 21.5; IR (KBr) 3358, 1701 cm^{-1}. *Anal.* Calcd for $C_{23}H_{20}ClNO_5$: C, 64.87; H, 4.73; N, 3.29. Found: C, 64.82; H, 4.69; N, 3.27.

3-(4'-Chlorophenyl)-1-hydroxy-8-methoxy-1-(2'-methyl-1',3'-dioxolan-2'-yl)-1*H*-benz[*e*]indol-2(3*H*)-one (4c): Colorless needles (from $CHCl_3$); mp 224-224.5 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.99 (1H, s, OH), 7.77 (1H, d, *J* = 9.0 Hz, H-6), 7.71 (1H, d, *J* = 8.4 Hz, H-5), 7.60 (2H, m, H-2',6'), 7.31 (2H, m, H-3',5'), 6.95-7.09 (4H, m, aromatic H), 4.03-4.08 (1H, m, H-CH), 3.84-3.88 (2H, m, CH_2), 3.76 (3H, s, OCH_3), 3.60-3.66 (1H, m, H-CH), 1.80 (3H, s, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.1, 159.2, 159.0, 135.5, 132.9, 131.9, 130.6, 129.7, 129.1, 125.1, 121.0, 115.7, 112.9, 109.1, 108.7 100.3, 85.9, 58.5, 57.1, 55.1, 21.9; IR (KBr) 3387, 1693 cm^{-1}. *Anal.* Calcd for $C_{23}H_{20}ClNO_5$: C, 64.87; H, 4.73; N, 3.29. Found: C, 64.82; H, 4.69; N, 3.29.

1-Hydroxy-3-(2'-methoxyphenyl)-8-methoxy-1-(2'-methyl-1',3'-dioxolan-2'-yl)-1*H*-benz[*e*]indol-2(3*H*)-one (4d): Colorless microcrystals (from Et_2O/hexane); mp 150.5-151 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.52 (1H, s, OH), 8.36 (1H, m, H-6'), 7.76 (1H, d, *J* = 8.7 Hz, H-6), 7.69 (1H, d, *J* = 9.0 Hz, H-5), 6.90-7.10 (6H, m, aromatic H), 4.01-4.09 (1H, m, H-CH), 3.92 (3H, s, OCH_3), 3.81-3.90 (2H, m, CH_2), 3.73 (3H, s, OCH_3), 3.56-3.62 (1H, m, H-CH), 1.79 (3H, s, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.8, 159.2, 159.0, 148.5, 132.6, 132.0, 130.5, 126.7, 125.1, 124.4, 121.0, 120.0, 115.8, 113.7, 110.0, 109.2, 108.8, 100.4, 86.0, 58.9, 57.4, 55.8, 55.0, 21.7; IR (KBr) 3400, 3381, 1692 cm^{-1}. *Anal.* Calcd for

$C_{24}H_{23}NO_6$: C, 68.40; H, 5.50; N, 3.32. Found: C, 68.30; H, 5.48; N, 3.32.

1-Hydroxy-3-(4'-methoxyphenyl)-8-methoxy-1-(2'-methyl-1',3'-dioxolan-2'-yl)-1*H*-benz[*e*]indol-2(3*H*)-one (4e): Colorless microcrystals (from Et_2O/hexane); mp 154-154.5 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.87 (1H, s, OH), 7.76 (1H, d, J = 8.7 Hz, H-6), 7.70 (1H, d, J = 9.0 Hz, H-5), 7.55 (2H, m, H-2',6'), 7.00 (1H, d, J = 9.0 Hz, H-4), 6.95 (1H, d, J = 2.7 Hz, H-9), 6.90 (1H, dd, J = 8.7, 2.7 Hz, H-4), 6.87 (2H, m, H-3',5'), 3.95-4.04 (1H, m, H-CH), 3.83-3.89 (2H, m, CH_2), 3.78 (3H, s, OCH_3), 3.75 (3H, s, OCH_3), 3.51-3.58 (1H, m, H-CH), 1.78 (3H, s, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.6, 159.2, 158.9, 156.6, 132.7, 132.0, 130.6, 130.2, 125.1, 121.4, 115.8, 114.2, 113.2, 109.1, 108.8, 100.3, 85.8, 58.5, 57.1, 55.4, 55.1, 21.9; IR (KBr) 3406, 1687 cm^{-1}. *Anal.* Calcd for $C_{24}H_{23}NO_6$: C, 68.40; H, 5.50; N, 3.32. Found: C, 67.94; H, 5.48; N, 3.19.

1-Hydroxy-8-methoxy-3-(2'-methylphenyl)-1-(2'-methyl-1',3'-dioxolan-2'-yl)-1*H*-benz[*e*]indol-2(3*H*)-one (4f): Colorless microcrystals (from Et_2O/hexane); mp 154-155 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.85 (1H, s, OH), 7.95 (1H, m, H-6'), 7.77 (1H, d, J = 9.0 Hz, H-6), 7.71 (1H, d, J = 9.0 Hz, H-5), 7.20 (1H, d, J = 9.0 Hz, H-4), 7.06 (1H, d, J = 2.4 Hz, H-9), 7.20-7.02 (3H, m, aromatic H), 6.95 (1H, dd, J = 9.0, 2.4 Hz, H-7), 3.99-4.07 (1H, m, H-CH), 3.82-3.94 (2H, m, CH_2), 3.78 (3H, s, OCH_3), 3.55-3.62 (1H, m, H-CH), 2.35 (3H, s, CH_3), 1.81 (3H, s, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.8, 159.2, 159.0, 135.1, 132.8, 132.1, 130.6, 130.5, 128.4, 126.9, 125.3, 125.2, 122.1, 115.9, 113.3, 109.2, 108.8, 100.3, 86.2, 58.9, 57.3, 55.1, 21.8, 17.8; IR (KBr) 3406, 1701 cm^{-1}. *Anal.* Calcd for $C_{24}H_{23}NO_5$: C, 71.10; H, 5.72; N, 3.45. Found: C, 70.10; H, 5.75; N, 3.47.

1-Hydroxy-8-methoxy-1-(2'-methyl-1',3'-dioxolan-2'-yl)-3-(4'-methylphenyl)-1*H*-benz[*e*]indol-2(3*H*)-one (4g): Colorless microcrystals (from Et_2O/hexane); mp 172-173 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.91 (1H, s, OH), 7.76 (1H, d, J = 8.7 Hz, H-6), 7.69 (1H, d, J = 8.4 Hz, H-5), 7.52 (2H, m, H-2',6'), 7.14 (2H, m, H-3',5'), 7.01 (1H, d, J = 8.4 Hz, H-4), 6.99 (1H, d, J = 2.4 Hz, H-9), 6.90 (1H, dd, J = 8.7, 2.4 Hz, H-7), 3.96-4.04 (1H, m, H-CH), 3.83-3.93 (2H, m, CH_2), 3.74 (3H, s, OCH_3), 3.51-3.58 (1H, m, H-CH), 2.32 (3H, s, CH_3), 1.77 (3H, s, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.8, 159.2, 159.0, 134.5, 134.4, 132.8, 132.1, 130.6, 129.6, 125.2, 119.8, 115.9, 113.3, 109.1, 108.8, 100.3, 85.8, 58.6, 57.2, 55.1, 21.9, 20.9; IR (KBr) 3398, 1693 cm^{-1}. *Anal.* Calcd for $C_{24}H_{23}NO_5$: C, 71.10; H, 5.72; N, 3.45. Found: C, 70.15; H, 5.75; N, 3.47.

1-Hydroxy-8-methoxy-1-(2'-methyl-1',3'-dioxolan-2'-yl)-3-(2'-nitrophenyl)-1*H*-benz[*e*]indol-2(3*H*)-one (4h): Colorless microcrystals (from Et_2O/hexane); mp 152-153 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 11.87 (1H, s, OH), 8.77 (1H, m, H-3'), 8.25 (1H, d, J = 8.4 Hz, H-6'), 7.77 (1H, d, J = 8.7 Hz, H-6), 7.70 (1H, d, J = 8.7 Hz, H-5), 7.62 (1H, m, H-5'), 7.22 (1H, m, H-4'), 7.04 (1H, d, J = 2.4 Hz, H-9), 7.01 (1H, d, J = 8.7 Hz, H-4), 6.95 (1H, dd, J = 8.7, 2.4 Hz, H-7), 4.08-4.16 (1H, m, H-CH), 3.81-3.98 (2H, m, CH_2), 3.72 (3H, s, OCH_3), 3.63-3.69 (1H, m, H-CH), 1.79 (3H, s, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$)

δ 168.5, 159.3, 159.0, 136.9, 135.9, 133.6, 132.8, 131.9, 130.6, 125.8, 125.1, 123.9, 122.1, 116.0, 113.3, 109.2, 108.3, 99.9, 86.3, 59.3, 57.9, 55.0, 21.2; IR (KBr) 3315, 1705, 1530 cm^{-1}. *Anal.* Calcd for $C_{23}H_{20}N_2O_7$: C, 63.30; H, 4.62; N, 6.42. Found: C, 63.32; H, 4.64; N, 6.46.

1-Hydroxy-7-methoxy-1-(2'-methyl-1',3'-dioxolan-2'-yl)-3-phenyl-1*H*-benz[*e*]indol-2(3*H*)-one (4j): Colorless microcrystals (from Et_2O/hexane); mp 176-177 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.95 (1H, s, OH), 7.75 (1H, d, J = 9.0 Hz, H-9), 7.65 (1H, d, J = 9.0 Hz, H-5), 7.64 (2H, m, Ph), 7.34 (2H, m, Ph), 7.16 (1H, d, J = 2.4 Hz, H-6), 7.12 (1H, d, J = 9.0 Hz, H-4), 7.09 (1H, dd, J = 9.0, 2.4 Hz, H-8), 7.10 (1H, m, Ph), 3.84-4.01 (3H, m, H-CHCH$_2$), 3.89 (3H, s, OCH$_3$), 3.51-3.54 (1H, m, $\underline{H}$-CH), 1.77 (3H, s, CH$_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.9, 156.9, 156.1, 137.1, 131.6, 130.8, 129.1, 125.8, 124.7, 122.7, 120.5, 119.7, 114.3, 112.1, 108.5, 107.5, 86.1, 58.7, 57.3, 55.3, 21.7; IR (KBr) 3344, 1688 cm^{-1}. *Anal.* Calcd for $C_{23}H_{21}NO_5$: C, 70.58; H, 5.41; N, 3.58. Found: C, 70.58; H, 5.40; N, 3.58.

1-Hydroxy-1-(2'-methyl-1',3'-dioxolan-2'-yl)-3-phenyl-1*H*-benz[*e*]indol-2(3*H*)-one (4k): Colorless needles (from $CHCl_3$/hexane); mp 180-180.5 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.98 (1H, s, OH), 7.85 (1H, d, J = 9.0 Hz, H-5), 7.81-7.11 (10H, m, aromatic H), 3.91-4.03 (1H, m, $\underline{H}$-CH), 3.77-3.90 (2H, m, CH$_2$), 3.48-3.55 (1H, m, $\underline{H}$-CH), 1.79 (3H, s, CH$_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.8, 158.4, 137.1, 133.1, 130.6, 129.8, 129.1, 127.9, 124.9, 123.7, 121.3, 119.7, 114.0, 111.9, 108.8, 85.9, 58.6, 57.2, 21.7; IR (KBr) 3377, 1692 cm^{-1}. *Anal.* Calcd for $C_{22}H_{19}NO_4$: C, 73.12; H, 5.30; N, 3.88. Found: C, 73.18; H, 5.29; N, 3.86.

Oxidation of 3a with Manganese(III) Acetate in Acetic Acid. To a solution of **3a** (73 mg, 0.2 mmol) in AcOH (10 mL) containing acetic anhydride (1 mL) at 70 °C, manganese(III) acetate dihydrate (214mg, 0.8 mmol) was added. The reaction was stopped until the opaque dark-brown mixture changed to a clear reddish-brown solution (within 1 min). After cooling, the solvent was removed in vacuo and the residue was triturated with 2M hydrochloric acid (30 mL). The aqueous solution was extracted with $CHCl_3$ (30 × 3 mL), and the combined extract was successively washed with a saturated aqueous solution of $NaHCO_3$ (30 × 2 mL), water (30 × 2 mL), then dried over anhydrous $MgSO_4$. The solvent was evaporated under reduced pressure, and the crude product was purified by TLC to yield 2-acetoxymethyl-5-chloro-8-methoxy-1-phenylcarbamoylnaphtho[2,1-*b*]furan (**5**) (59 mg, 70%).

2-Acetoxymethyl-5-chloro-8-methoxy-1-phenylcarbamoylnaphtho[2,1-*b*]furan (5): Colorless needles (from MeOH), mp 188-189 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.99 (1H, s, NH), 8.25 (1H, d, J = 9.0 Hz, H-6), 8.14 (1H, s, H-4), 7.89 (2H, m, H-2',6'), 7.60 (1H, d, J = 2.7 Hz, H-9), 7.42 (2H, m, H-3',5'), 7.22 (1H, dd, J = 9.0, 2.7 Hz, H-7), 7.18 (1H, m, H-4'), 5.38 (2H, s, OCH$_2$), 3.91 (3H, s, OCH$_3$), 2.21 (3H, s, Ac); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.7, 161.7, 159.1, 152.3, 148.4, 138.4, 131.4, 129.7, 129.1, 127.0, 124.7, 123.1, 119.7, 119.5, 118.6, 117.9, 110.0, 104.7, 58.8, 55.5, 20.9; IR (KBr) 3288, 1736, 1645, 1622 cm^{-1}; MS m/z (rel intensity) 423 (M, 44), 425 (M, 15). *Anal.* Calcd for $C_{23}H_{18}ClNO_5$: C, 65.18; H, 4.28; N, 3.30. Found: C, 65.45; H, 4.35; N, 3.40.

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