

## Mn(III)-Based Oxidation of Methoxynaphthalenes with 3-Oxobutanamides

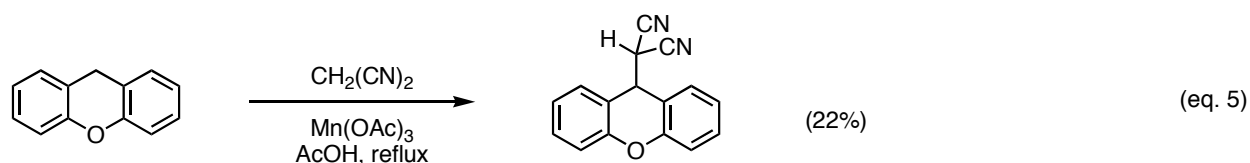
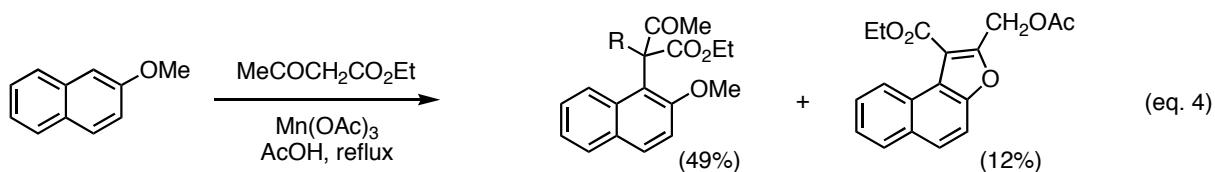
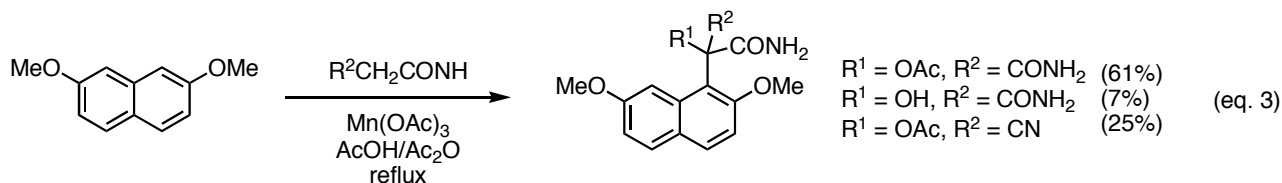
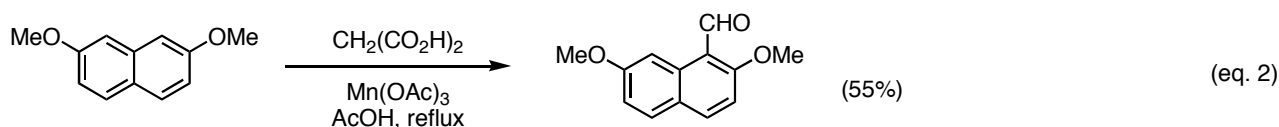
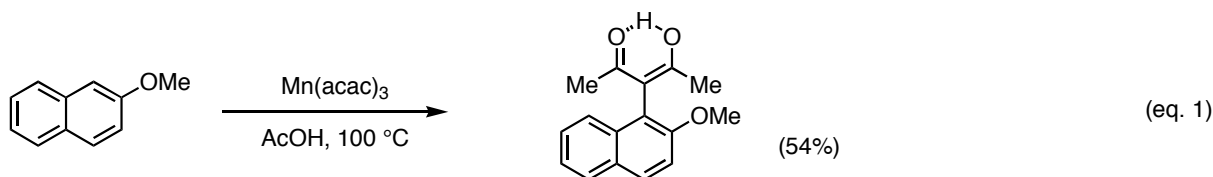
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**Abstract:** Oxidation of a mixture of 2,7-dimethoxynaphthalene and *N*-phenyl-3-oxobutanamide with manganese(III) acetate in acetic acid at reflux temperature gave direct 3-oxobutanamide-substituted naphthalene, naphtho[2,1-*b*]furan and lactam derivatives in moderate yields, respectively. The same procedure could be applied to a combination of other 2-methoxyl substituted naphthalenes with various 3-oxobutanamides, and the homologues were obtained in similar yields. The characterization of the reaction products, the examination of the optimum reaction conditions, and the mechanism for the formation of the products were discussed.

### Introduction

The reaction of aromatic compounds with active methylene species in the presence of manganese(III) acetate has been well-documented by us and other groups. Our group have reported that the oxidation of naphthalenes, anthracenes, and other aromatic substrates with tris(2,4-pentanedionato)manganese(III) (eq. 1),<sup>1</sup> and the reaction of the aromatic compounds with malonic acid (eq. 2),<sup>2</sup> malonamide (eq. 3),<sup>3</sup> ethyl 3-oxobutanoate (eq. 4),<sup>3</sup>  $\alpha$ -cyanoacetamide (eq. 3),<sup>3</sup> and malononitrile (eq. 5)<sup>4</sup> in the presence of manganese(III) acetate, gave direct active methylene-substituted arenes, formylated arenes, and substituted naphtho[2,1-*b*]furan derivatives.



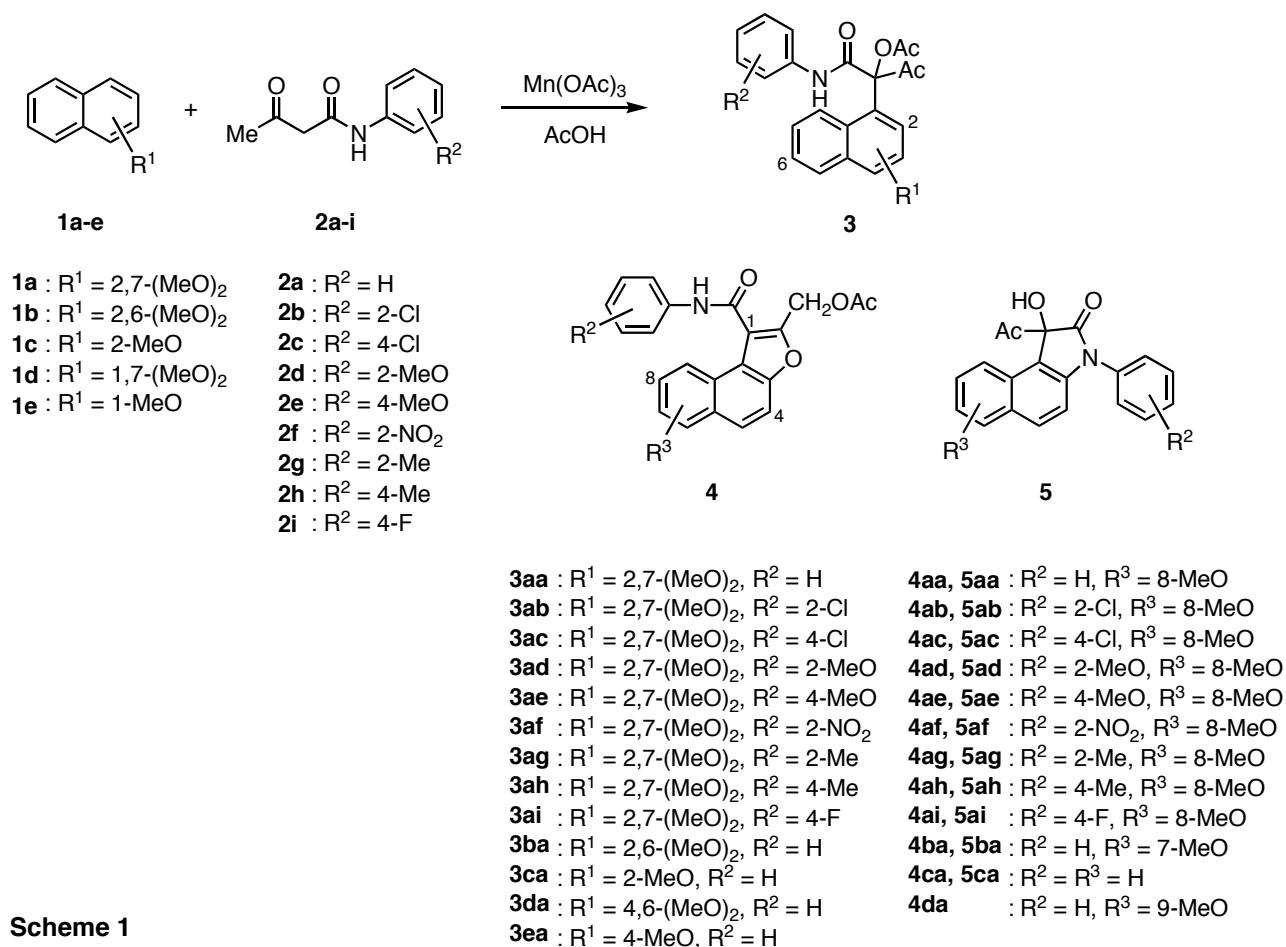
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Citterio et al. have also reported examples of the scope and limitations of aromatic malonylation reaction by manganese(III) acetate.<sup>5</sup> Most of the reactions mentioned above gave variety of products. Herein, we focused on the oxidation of a mixture of methoxynaphthalenes **1** and 3-oxobutanamides **2** with manganese(III) acetate, describing the optimization of the reaction conditions and the product distribution.

## Results and Discussion

2,7-Dimethoxynaphthalene (**1a**) was selected as an aromatic substrate in the reaction aimed at optimizing the reaction conditions since the obtained products could be readily separated and characterized. The reaction of **1a** with *N*-phenyl-3-oxobutanamide (**2a**) in the presence of manganese(III) acetate was examined in acetic acid under various reaction conditions (Scheme 1). As a result, direct 3-oxobutanamide-substituted naphthalene **3a**, naphtho[2,1-*b*]furan **4a** and lactam **5a** were obtained in the yields as shown in Table 1.<sup>6</sup>

When the reaction was carried out at 70 °C, the substitution product **3a** was preferentially formed (Entry 1). Although the reaction using high oxidant ratio in boiling acetic acid gave an intractable mixture, the addition products **4a** and **5a** were isolated along with **3a** (Entry 3). A similar reaction of **1a** with *N*-(2-chlorophenyl)- (**2b**), *N*-(4-chlorophenyl)- (**2c**), *N*-(2-methoxyphenyl)- (**2d**), *N*-(4-methoxyphenyl)- (**2e**), *N*-(2-nitrophenyl)- (**2f**), *N*-(2-methylphenyl)- (**2g**), *N*-(4-methylphenyl)- (**2h**), and *N*-(4-fluorophenyl)-3-oxobutanamide (**2i**) was conducted at 70 °C at the molar ratio of **1a**:**2b-i**:Mn(OAc)<sub>3</sub> = 1:1.2:6 to afford the substitution products **3ab-ai** and the addition products **4ab-ai** and **5ab-5ai**, respectively (Entries 4-11). The reaction using 2,6-dimethoxynaphthalene (**1b**), 2-methoxynaphthalene (**1c**), 1,7-dimethoxynaphthalene (**1d**), and 1-methoxynaphthalene (**1e**) instead of **1a** was also examined under similar reaction conditions, giving the corresponding **3**, **4**, and **5** in similar yields (Table 1, Entries 12-15).



Scheme 1

Table 1. Reaction of Methoxynaphthalenes **1a-e** with 3-Oxobutanamides **2a-i** in the Presence of Manganese(III) Acetate<sup>a</sup>

Entry	<b>1</b>	<b>2</b>	Molar ratio <sup>b</sup>	Reaction Temperature °C	Reaction Time min	Recovery %	Product (Yield/%)		
1	<b>1a</b>	<b>2a</b>	1:1.2:6	70	2	7	<b>3aa</b> (79)	<b>4aa</b> (5)	<b>5aa</b> (5)
2	<b>1a</b>	<b>2a</b>	1:1.3:6	reflux	2	4	<b>3aa</b> (63)	<b>4aa</b> (14)	<b>5aa</b> (8)
3	<b>1a</b>	<b>2a</b>	1:2:8	reflux	1	14	<b>3aa</b> (17)	<b>4aa</b> (25)	<b>5aa</b> (12)
4 <sup>c</sup>	<b>1a</b>	<b>2b</b>	1:1.2:6	70	2	9	<b>3ab</b> (76)	<b>4ab</b> (1)	<b>5ab</b> (11)
5	<b>1a</b>	<b>2c</b>	1:1.2:6	70	2	10	<b>3ac</b> (70)	<b>4ac</b> (4)	<b>5ac</b> (6)
6	<b>1a</b>	<b>2d</b>	1:1.2:6	70	2	9	<b>3ad</b> (59)	<b>4ad</b> (trace)	<b>5ad</b> (15)
7	<b>1a</b>	<b>2e</b>	1:1.2:6	70	2	37	<b>3ae</b> (30)	<b>4ae</b> (3)	<b>5ae</b> (trace)
8	<b>1a</b>	<b>2f</b>	1:1.2:6	70	2	5	<b>3af</b> (69)	<b>4af</b> (12)	<b>5af</b> (trace)
9	<b>1a</b>	<b>2g</b>	1:1.2:6	70	2	12	<b>3ag</b> (53)	<b>4ag</b> (19)	<b>5ag</b> (trace)
10	<b>1a</b>	<b>2h</b>	1:1.2:6	70	2	10	<b>3ah</b> (51)	<b>4ah</b> (8)	<b>5ah</b> (9)
11	<b>1a</b>	<b>2i</b>	1:1.2:6	70	2	14	<b>3ai</b> (60)	<b>4ai</b> (13)	<b>5ai</b> (15)
12	<b>1b</b>	<b>2a</b>	1:1.2:6	70	3	24	<b>3ba</b> (35)	<b>4ba</b> (9)	<b>5ba</b> (4)
13	<b>1c</b>	<b>2a</b>	1:1.2:6	70	2	14	<b>3ca</b> (35)	<b>4ca</b> (15)	<b>5ca</b> (12)
14	<b>1d</b>	<b>2a</b>	1:1.2:6	70	3	21	<b>3da</b> (28)	<b>4da</b> (9)	-
15	<b>1e</b>	<b>2a</b>	1:1.2:6	70	2	13	<b>3ea</b> (67)	-	-

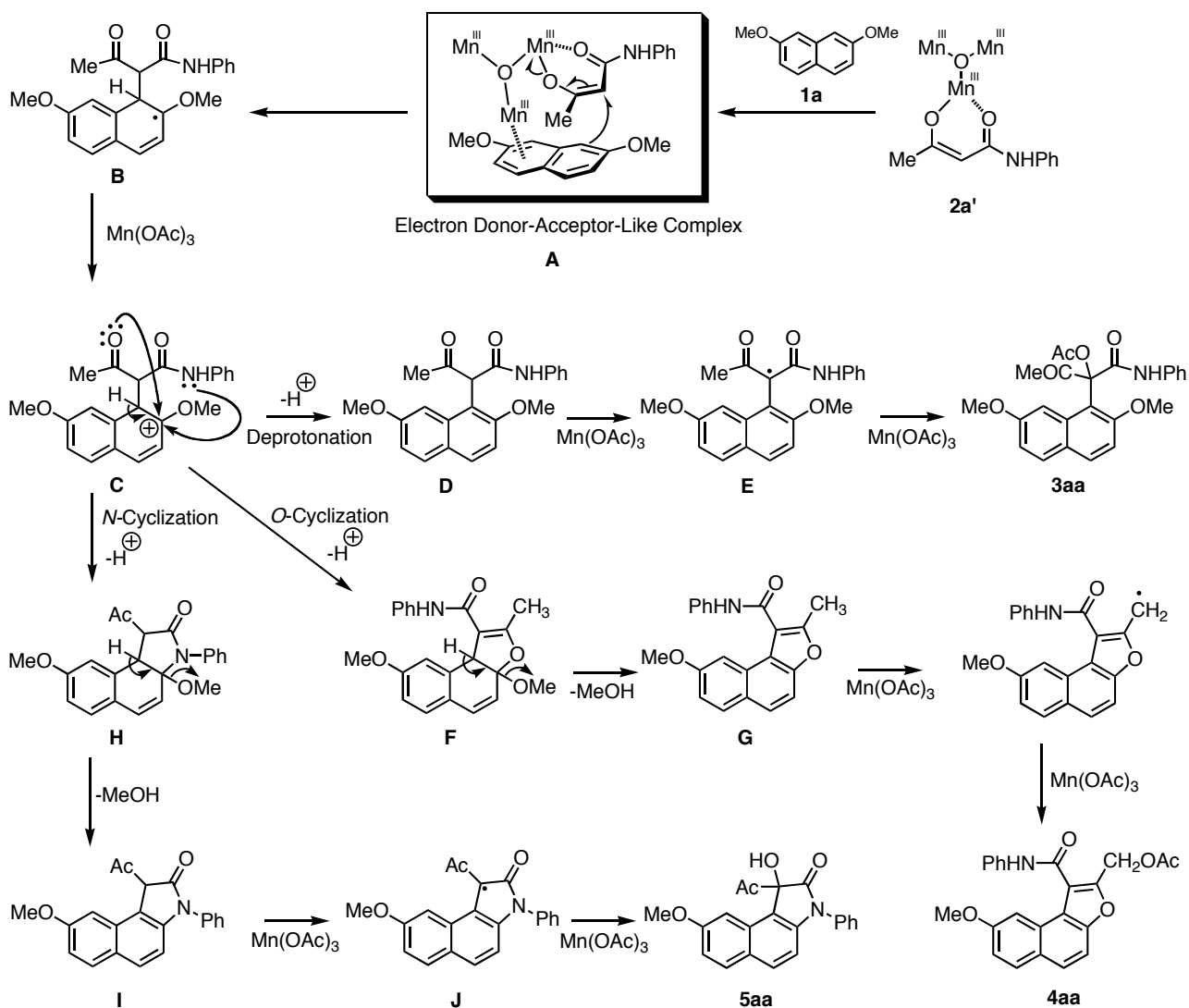
<sup>a</sup> The reaction was carried out in acetic acid (25 mL). <sup>b</sup> 1:2:Mn(OAc)<sub>3</sub>. <sup>c</sup> A mixture of 4 and 5 was obtained, and molar ratio was determined on the basis of NH and OH peak intensity.

The mechanism for the formation of three products **3**, **4**, and **5** would be explained as follows (Scheme 2). In analogy with the oxidative radical reaction pathway reported before,<sup>4,7</sup> manganese(III)-3-oxobutanamide enolate complex **2a'** was formed by the ligand-exchange reaction of manganese(III) acetate with 3-oxobutanamide at the first stage. The electron-deficient enolate complex **2a'** would interact with electron-rich methoxynaphthalene **1a** to afford an electron donor-acceptor-like complex **A**, followed by one-electron transfer to give radical **B**, which should be easily oxidized with manganese(III) to yield an intermediate cation **C**. It was expected that the aromatization process accompanied by deprotonation should be fast, giving a substitution product **D**. Since the product **D** has still an active methyne proton, the product **D** should be oxidized by an excess amount of manganese(III) acetate finally to give **3aa**. On the other hand, the intermediate cation **C** could be intramolecularly attacked by the acetyl oxygen or amide nitrogen. The *O*-cyclization followed by demethanol gave naphthofuran **G** which would be converted to acetoxymethylnaphthofuran **4aa** via benzyl-type oxidation. When the amide nitrogen would intramolecularly add the cation **C**, a benzoindolinone **I** would be produced and hydroxybenzoindolinone **5aa** would be eventually obtained by a similar oxidation.

The detailed discussion on the relationship among the conversion of substrate, the yield of products, and the utilization of Mn(III) is in progress. Furthermore, we expect that a new synthetic method of heterocyclic aromatic compounds would be developed by the present work.

## Experimental

Methoxynaphthalenes **1a-e** were prepared by the methylation of the corresponding naphthols with dimethyl sulfate in dry acetone in the presence of anhydrous potassium carbonate. The typical procedure for the reaction of methoxynaphthalenes **1** with 3-oxobutanamides **2** in the presence of manganese(III) acetate was as follows. To a heated solution of methoxynaphthalene **1** (1 mmol) and 3-oxobutanamide **2** (0.2 mmol) in acetic acid (18 mL), manganese (III) acetate was added.



Scheme 2

Followed, another portion of **2** (1 mmol) was added dropwise in acetic acid (7 mL) within 1-3 minutes (Table 1). The reaction mixture was cooled to room temperature, and then the solvent was removed in vacuo. The residue was triturated with a 2 M solution of HCl and followed by extraction with chloroform (20 mL  $\times$  3). The combined extracts was washed with saturated solution of sodium bicarbonate (20 mL  $\times$  2) and water (20 mL  $\times$  2), dried over  $\text{MgSO}_4$  and evaporated. The residue was separated by TLC (wakogel B-10) while dilute with chloroform. The products were purified by recrystallization with appropriate solvents. The characterization of the products were performed by spectroscopic method as well as elemental analysis.

## References

- 1) Nishino, H. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 1733-1739.
- 2) Nishino, H.; Tsunoda, K.; Kurosawa, K. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 545-550.
- 3) Tsunoda, K.; Yamane, M.; Nishino, H.; Kurosawa, K. *Bull. Chem. Soc. Jpn.* **1991**, *64*, 851-856.
- 4) Nishino, H.; Kamachi, H.; Baba, H.; Kurosawa, K. *J. Org. Chem.* **1992**, *57*, 3551-3557.
- 5) Citterio, A.; Santi, R.; Fiorani, T.; Strologo, S. *J. Org. Chem.* **1989**, *54*, 2703-2712.
- 6) Fujino, R.; Nishino, H. *Synthesis* **2005**, 731-740.
- 7) Nishino, H.; Nguyen, V.-H.; Yoshinaga, S.; Kurosawa, K. *J. Org. Chem.* **1996**, *61*, 8264-8271.

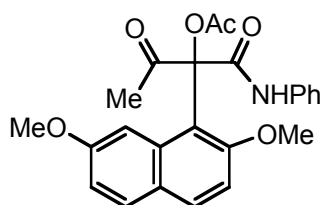
**(Supporting information)****Mn (III)-Based Oxidation of Methoxynaphthalenes with 3-Oxobutanamide**

Zhiqi Cong and Hiroshi Nishino

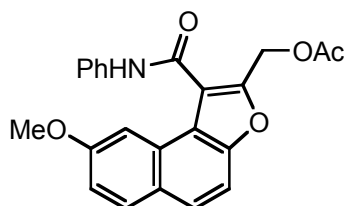
Department of Chemistry, Graduate School of Science and Technology, Kumamoto University  
Kurokami 2-39-1, Kumamoto 860-8555, Japan

**General Information**

The NMR spectra were recorded using a JNM EX300 FT NMR spectrometer at 300 MHz for  $^1\text{H}$  and at 75 MHz for  $^{13}\text{C}$ , with tetramethylsilane as the internal standard. The chemical shifts are given in  $\delta$  values (ppm). The IR spectra of neat samples were measured by the KBr disc method using a Shimadzu 8400 FT IR spectrophotometer and expressed in  $\text{cm}^{-1}$ . The EI MS spectra were recorded by a Shimadzu QP-5050A gas-chromatograph-mass spectrometer at the ionizing voltage of 70 eV. The elemental analyses were performed at the Analytical Center of Kumamoto University, Kumamoto, Japan. Manganese(II) acetate tetrahydrate was purchased from Wako Pure Chemical Ind., Ltd. Manganese(III) acetate dihydrate,  $\text{Mn}(\text{OAc})_3 \cdot 2\text{H}_2\text{O}$ , was prepared according to the method described in the literature.

***N*-phenyl-2-acetoxy-2-(2,7-dimethoxy-1-naphthyl)-3-oxobutanamide 3aa.**

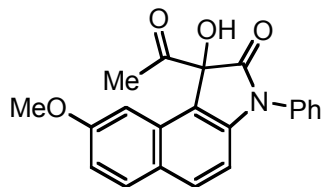
Colorless needles (from methanol); mp 161.5-162 °C;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.43 (1H, s), 7.78 (1H, d,  $J = 9.0$  Hz), 7.66-7.63 (2H, m), 7.47 (2H, d,  $J = 8.1$  Hz), 7.26 (2H, d,  $J = 8.7$  Hz), 7.08-7.04 (2H, m), 7.01 (1H, dd,  $J = 2.4, 9.0$  Hz), 3.87 (3H, s), 3.79 (3H, s), 2.35 (3H, s), 2.25 (3H, s);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  199.2, 168.3, 164.5, 158.1, 155.8, 137.4, 134.3, 132.2, 130.1, 128.9, 125.8, 124.5, 119.8, 116.7, 115.8, 110.9, 104.1, 89.6, 56.2, 55.0, 26.3, 21.1; IR  $\nu$  3427, 3389, 1768, 1730, 1701; MS (EI, 70 eV):  $m/z = 421$  [ $\text{M}^+$ ]; Anal. Calcd for  $\text{C}_{24}\text{H}_{23}\text{NO}_6$ : C, 68.40; H, 5.50; N, 3.32. Found: C, 68.20; H, 5.46; N, 3.25.

**(1-(phenylcarbamoyl)-8-methoxynaphtho[2,1-b]furan-2-yl)methyl acetate 4aa.**

Colorless needles (from ethanol); mp 177-177.5 °C;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  9.90 (1H, s),

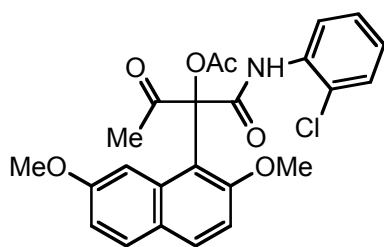
8.07 (1H, d,  $J = 2.7$  Hz), 7.88 (2H, d,  $J = 7.8$  Hz), 7.78 (1H, d,  $J = 9.0$  Hz), 7.70 (1H, d,  $J = 8.7$  Hz), 7.43 (1H, d,  $J = 8.7$  Hz), 7.40 (2H, t,  $J = 8.1$  Hz), 7.18 (1H, dt,  $J = 1.2, 7.5$  Hz), 7.12 (1H, dd,  $J = 2.7, 8.7$  Hz), 5.37 (2H, s), 3.87 (3H, s), 2.14 (3H, s);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  172.3, 162.4, 158.5, 152.9, 148.2, 138.6, 130.4, 129.1, 127.8, 125.4, 124.3, 119.7, 117.2, 109.0, 103.4, 58.9, 55.3, 20.8; IR  $\nu$  3309, 3018, 1732, 1670; MS (EI, 70 eV):  $m/z = 389$  [ $\text{M}^+$ ]; Anal. Calcd for  $\text{C}_{23}\text{H}_{19}\text{NO}_5$ : C, 70.94; H, 4.92; N, 3.60. Found: C, 70.79; H, 4.87; N, 3.60.

**1-acetyl-1-hydroxy-8-methoxy-3-phenyl-1H-benzo[e]indol-2(3H)-one 5aa.**



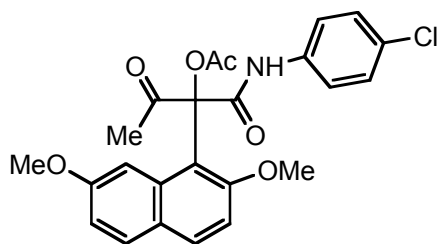
Colorless needles (from ethanol); mp 192-193 °C;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.54 (1H, s), 8.13 (1H, d,  $J = 2.4$  Hz), 8.07 (1H, d,  $J = 8.7$  Hz), 7.75 (1H, d,  $J = 9.0$  Hz), 7.58 (2H, d,  $J = 8.4$  Hz), 7.32 (2H, t,  $J = 8.1$  Hz), 7.23 (1H, d,  $J = 9.0$  Hz), 7.13 (1H, d,  $J = 8.7$  Hz), 7.12 (1H, d,  $J = 9.3$  Hz), 3.99 (3H, s), 1.92 (3H, s);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  197.5, 174.0, 163.4, 161.8, 161.6, 140.6, 137.0, 131.3, 130.2, 129.0, 124.8, 124.7, 119.9, 118.1, 110.5, 102.4, 89.8, 55.6, 22.6; IR  $\nu$  3317, 2970, 1695, 1629; MS (EI, 70 eV):  $m/z = 347$  [ $\text{M}^+$ ]; Anal. Calcd for  $\text{C}_{21}\text{H}_{17}\text{NO}_4$ : C, 72.61; H, 4.93; N, 4.03. Found: C, 72.47; H, 4.86; N, 3.97.

***N*-(*o*-chlorophenyl)-2-acetoxy-2-(2,7-dimethoxy-1-naphthyl)-3-oxobutanamide 3ab.**



Colorless needles (from methanol); mp 166-166.5 °C;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  9.09 (1H, s), 8.35 (1H, dd,  $J = 1.5, 8.1$  Hz), 8.02 (1H, d,  $J = 8.7$  Hz), 7.67 (1H, d,  $J = 9.3$  Hz), 7.61 (1H, s), 7.34 (1H, dd,  $J = 1.5, 8.1$  Hz), 7.21 (1H, d,  $J = 8.1$  Hz), 7.11 (1H, d,  $J = 9.0$  Hz), 7.05-6.99 (2H, m), 3.92 (3H, s), 3.81 (3H, s), 2.37 (3H, s), 2.30 (3H, s);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  198.0, 168.1, 164.8, 158.4, 155.5, 134.3, 134.0, 132.4, 132.3, 130.3, 129.0, 127.7, 125.7, 124.8, 122.8, 116.9, 115.7, 110.8, 103.8, 56.2, 55.1, 26.4, 21.1; IR  $\nu$  3373, 3346, 1759, 1730, 1707; Anal. Calcd for  $\text{C}_{24}\text{H}_{22}\text{ClNO}_6$ : C, 63.23; H, 4.86; N, 3.07. Found: C, 63.12; H, 4.81; N, 3.09.

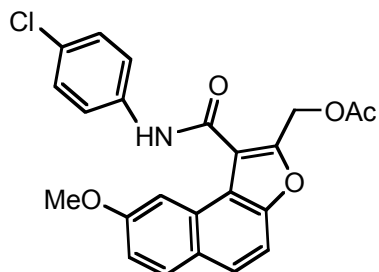
***N*-(*p*-chlorophenyl)-2-acetoxy-2-(2,7-dimethoxy-1-naphthyl)-3-oxobutanamide 3ac.**



Colorless microcrystals (from chloroform/ether); mp 198-199 °C;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.39 (1H, s), 7.69 (1H, d,  $J = 8.7$  Hz), 7.59 (1H, s), 7.56 (1H, d,  $J = 8.7$  Hz), 7.32 (2H, dd,  $J = 2.1,$

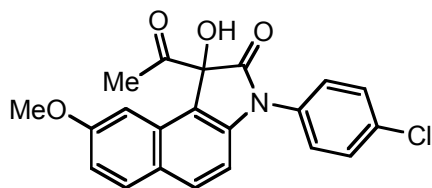
9.0 Hz), 7.13 (1H, d,  $J = 8.7$  Hz), 7.11 (1H, d,  $J = 8.7$  Hz), 6.97 (1H, d,  $J = 8.7$  Hz), 6.92 (1H, dd,  $J = 2.7, 8.7$  Hz), 3.77 (3H, s), 3.72 (3H, s), 2.23 (3H, s), 2.15 (3H, s);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  199.1, 168.4, 164.6, 158.3, 155.4, 135.9, 133.9, 132.3, 130.2, 129.3, 128.8, 125.6, 121.1, 116.7, 115.5, 110.7, 104.2, 89.2, 56.2, 55.0, 26.2, 21.0; IR  $\nu$  3361, 1761, 1722, 1693.

***N*-(*p*-chlorophenyl)-2-acetoxy-2-(2,7-dimethoxy-1-naphthyl)-3-oxobutanamide 4ac.**



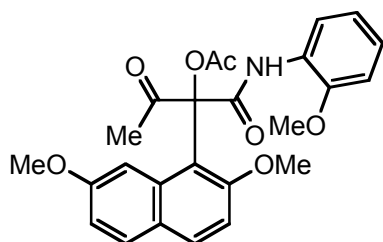
Colorless needles (from chloroform/ether); mp 190-191 °C;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  10.08 (1H, s), 8.06 (1H, d,  $J = 2.4$  Hz), 7.85 (2H, d,  $J = 8.7$  Hz), 7.79 (1H, d,  $J = 9.3$  Hz), 7.72 (1H, d,  $J = 8.7$  Hz), 7.44 (1H, d,  $J = 8.7$  Hz), 7.36 (2H, d,  $J = 8.7$  Hz), 7.13 (1H, dd,  $J = 2.7, 9.3$  Hz), 5.36 (2H, s), 3.89 (3H, s), 2.20 (3H, s);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  172.8, 162.1, 158.5, 153.4, 148.0, 137.1, 130.2, 129.4, 129.1, 127.8, 126.0, 120.9, 119.3, 119.0, 117.0, 109.1, 104.3, 58.9, 55.3, 20.9; IR  $\nu$  3240, 1740, 1647.

**1-acetyl-1-hydroxy-8-methoxy-3-(*p*-chlorophenyl)-1H-benzo[*e*]indol-2(3H)-one 5ac.**



Light yellow microcrystals (from ethanol); mp 244-247 °C;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.56 (1H, s), 8.12 (1H, d,  $J = 2.7$  Hz), 8.09 (1H, d,  $J = 8.7$  Hz), 7.76 (1H, d,  $J = 9.0$  Hz), 7.52-7.56 (2H, m), 7.22-7.30 (3H, m), 7.13 (1H, dd,  $J = 2.7, 8.7$  Hz), 3.99 (3H, s), 1.92 (3H, s);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  197.1, 174.0, 163.6, 161.8, 140.8, 135.6, 131.4, 130.3, 129.9, 129.1, 124.8, 121.2, 118.2, 110.5, 102.4, 89.6, 55.6, 22.7; IR  $\nu$  3333, 1705, 1674; Anal. Calcd for  $\text{C}_{21}\text{H}_{16}\text{NO}_4$ : C, 66.06; H, 4.22; N, 3.67. Found: C, 65.62; H, 4.14; N, 3.66.

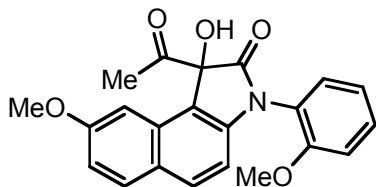
***N*-(*o*-methoxyphenyl)-2-acetoxy-2-(2,7-dimethoxy-1-naphthyl)-3-oxobutanamide 3ad.**



Colorless needles (from methanol); mp 177-177.5 °C;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  9.11 (1H, s), 8.30 (1H, dd,  $J = 1.5, 6.3$  Hz), 7.80 (1H, d,  $J = 8.4$  Hz), 7.65 (1H, dd,  $J = 1.5, 9.3$  Hz), 7.53 (1H, s), 7.10 (1H, dd,  $J = 1.5, 9.3$  Hz), 7.05 (1H, d,  $J = 7.8$  Hz), 7.01 (1H, t,  $J = 7.8$  Hz), 6.92 (1H, t,  $J = 7.8$

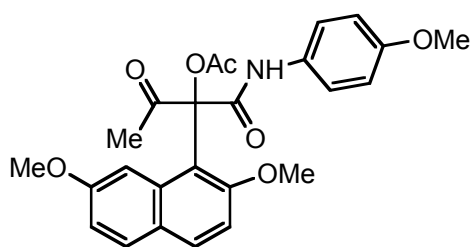
Hz), 6.85 (1H, d,  $J = 8.1$  Hz), 3.91 (3H, s), 3.84 (3H, s), 3.73 (3H, s), 2.39 (3H, s), 2.27 (3H, s);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  198.0, 167.9, 164.5, 158.3, 155.8, 148.1, 133.9, 132.1, 130.2, 127.1, 125.7, 124.2, 121.1, 119.7, 116.7, 116.6, 111.1, 110.1, 103.8, 90.4, 56.3, 55.9, 54.9, 26.7, 21.2; IR  $\nu$  3382, 1759, 1728, 1699; Anal. Calcd for  $\text{C}_{25}\text{H}_{25}\text{NO}_7$ : C, 66.51; H, 5.58; N, 3.10. Found: C, 66.15; H, 5.51; N, 3.04.

**1-acetyl-1-hydroxy-8-methoxy-3-(*o*-methoxyphenyl)-1H-benzo[*e*]indol-2(3H)-one 5ad.**



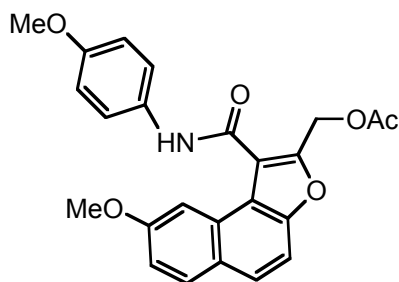
Colorless microcrystals (from ethanol); mp 147-148 °C;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  9.11 (1H, s), 8.36 (1H, dd,  $J = 1.5, 8.1$  Hz), 8.15 (1H, d,  $J = 2.7$  Hz), 8.07 (1H, d,  $J = 8.7$  Hz), 7.74 (1H, d,  $J = 8.7$  Hz), 7.23 (1H, s), 7.11 (1H, dd,  $J = 2.7, 8.7$  Hz), 7.04 (1H, dt,  $J = 1.5, 7.8$  Hz), 6.93 (1H, dt,  $J = 1.5, 7.8$  Hz), 6.85 (1H, dt,  $J = 1.2, 8.1$  Hz), 3.97 (3H, s), 3.89 (3H, s), 1.93 (3H, s);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  196.5, 173.8, 163.3, 161.6, 148.2, 140.2, 131.4, 130.1, 126.7, 124.7, 124.3, 121.1, 119.9, 118.0, 110.7, 110.4, 109.9, 102.4, 90.3, 55.9, 55.6, 22.0; IR  $\nu$  3415, 1716, 1679; Anal. Calcd for  $\text{C}_{22}\text{H}_{19}\text{NO}_5$ : C, 70.02; H, 5.07; N, 3.71. Found: C, 69.72; H, 5.06; N, 3.61.

***N*-(*p*-methoxyphenyl)-2-acetoxy-2-(2,7-dimethoxy-1-naphthyl)-3-oxobutanamide 3ae.**



Colorless microcrystals (from methanol); mp 162-162.5 °C;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.29 (1H, s), 7.81 (1H, d,  $J = 8.7$  Hz), 7.67 (1H, d,  $J = 9.0$  Hz), 7.60 (1H, s), 7.39 (2H, dd,  $J = 2.1, 9.0$  Hz), 7.10 (1H, d,  $J = 8.7$  Hz), 7.01 (1H, dd,  $J = 2.7, 8.7$  Hz), 6.82 (2H, dd,  $J = 2.1, 9.0$  Hz), 3.89 (3H, s), 3.79 (3H, s), 3.76 (3H, s), 2.36 (3H, s), 2.26 (3H, s);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  198.8, 168.3, 164.4, 158.3, 156.6, 155.7, 134.1, 132.2, 130.4, 130.2, 125.7, 121.6, 116.7, 116.3, 114.1, 111.0, 104.1, 89.8, 56.3, 55.4, 55.1, 26.5, 21.1; IR  $\nu$  3357, 1767, 1715, 1689; Anal. Calcd for  $\text{C}_{25}\text{H}_{25}\text{NO}_7$ : C, 66.51; H, 5.58; N, 3.10. Found: C, 66.34; H, 5.53; N, 3.09.

**(1-(*p*-methoxyphenylcarbamoyl)-8-methoxynaphtho[2,1-*b*]furan-2-yl)methyl acetate 4ae.**

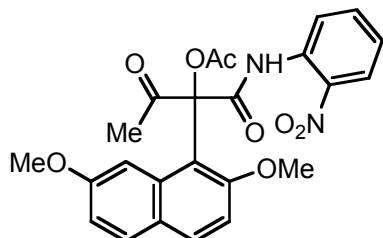


Light yellow microcrystals (from ethanol); mp 165-167 °C;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  9.77



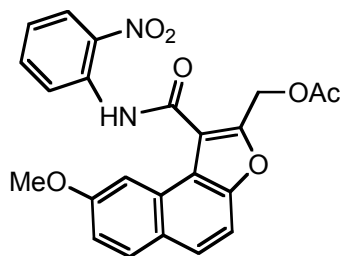
(1H, s), 8.12 (1H, s), 7.80 (2H, dd,  $J = 2.7, 9.3$  Hz), 7.73 (2H, dd,  $J = 2.7, 9.3$  Hz), 7.46 (1H, dd,  $J = 3.0, 8.7$  Hz), 7.14 (1H, dd,  $J = 2.7, 8.7$  Hz), 6.95 (1H, dd,  $J = 2.7, 8.7$  Hz), 6.94 (1H, dd,  $J = 3.0, 9.3$  Hz), 5.41 (2H, s), 3.90 (3H, s), 3.83 (3H, s), 2.20 (3H, s);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  172.8, 161.7, 158.5, 156.5, 153.6, 148.0, 131.8, 130.1, 129.4, 127.7, 126.1, 121.2, 119.7, 119.3, 117.1, 114.2, 109.2, 104.3, 58.9, 55.5, 55.4, 20.9; IR  $\nu$  3258, 1747, 1645; Anal. Calcd for  $\text{C}_{24}\text{H}_{21}\text{NO}_6$ : C, 68.73; H, 5.05; N, 3.34. Found: C, 68.65; H, 5.09; N, 3.41.

***N*-(*o*-nitrophenyl)-2-acetoxy-2-(2,7-dimethoxy-1-naphthyl)-3-oxobutanamide 3af.**



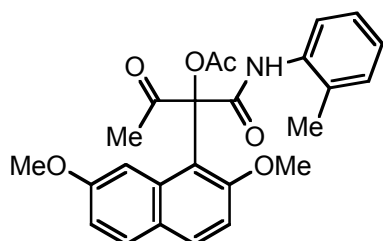
Yellow microcrystals (from methanol); mp 205.5-206.5 °C;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  11.25 (1H, s), 8.76 (1H, dd,  $J = 1.2, 8.4$  Hz), 8.18 (1H, dd,  $J = 1.5, 8.4$  Hz), 7.83 (1H, d,  $J = 9.0$  Hz), 7.68 (1H, d,  $J = 9.0$  Hz), 7.60 (1H, ddd,  $J = 1.8, 0.9, 1.5$  Hz), 7.54 (1H, s), 7.12-7.19 (2H, m), 7.01 (1H, dd,  $J = 2.7, 8.7$  Hz), 3.95 (3H, s), 3.80 (3H, s), 2.42 (3H, s), 2.37 (3H, s);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  197.1, 168.4, 166.0, 158.5, 155.6, 136.5, 135.9, 134.2, 133.9, 132.5, 130.4, 125.8, 125.6, 123.6, 122.1, 116.7, 114.9, 110.8, 103.7, 90.1, 56.1, 55.0, 26.5, 21.1; IR  $\nu$  3335, 1759, 1730, 1705; Anal. Calcd for  $\text{C}_{24}\text{H}_{22}\text{N}_2\text{O}_8$ : C, 61.80; H, 4.75; N, 6.01. Found: C, 61.65; H, 4.69; N, 6.00.

**(1-(*o*-nitrophenylcarbonyl)-8-methoxynaphtho[2,1-*b*]furan-2-yl)methyl acetate 4af.**



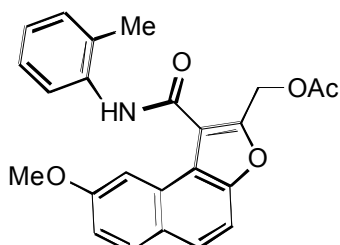
Yellow microcrystals (from ethanol); mp 198-199 °C;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  11.57 (1H, s), 8.85 (1H, d,  $J = 8.4$  Hz), 8.20 (1H, dd,  $J = 1.5, 8.4$  Hz), 8.13 (1H, s), 8.12 (1H, d,  $J = 8.7$  Hz), 7.76 (1H, d,  $J = 8.7$  Hz), 7.65 (1H, dt,  $J = 1.5, 8.7$  Hz), 7.37 (1H, d,  $J = 8.7$  Hz), 7.19 (1H, dt,  $J = 0.9, 8.4$  Hz), 7.12 (1H, dd,  $J = 2.1, 8.4$  Hz), 3.96 (3H, s), 1.96 (3H, s);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  194.5, 173.7, 164.9, 161.7, 140.5, 136.4, 136.1, 133.9, 131.3, 130.2, 125.8, 125.0, 123.9, 121.9, 118.3, 110.5, 102.3, 90.5, 55.6, 21.0; IR  $\nu$  3314, 1722, 1686; Anal. Calcd for  $\text{C}_{23}\text{H}_{18}\text{N}_2\text{O}_7$ : C, 63.59; H, 4.18; N, 6.45. Found: C, 63.91; H, 3.97; N, 6.68.

***N*-(*o*-methylphenyl)-2-acetoxy-2-(2,7-dimethoxy-1-naphthyl)-3-oxobutanamide 3ag.**



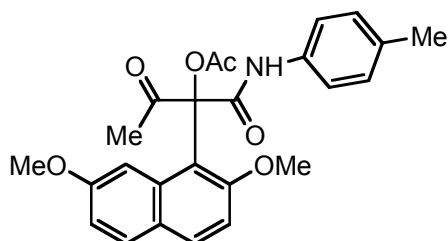
Colorless needles (from methanol); mp 160-161 °C;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.41 (1H, s), 7.92 (1H, d,  $J = 7.5$  Hz), 7.81 (2H, d,  $J = 8.7$  Hz), 7.67 (1H, d,  $J = 9.0$  Hz), 7.17-6.98 (5H, m), 3.91 (3H, s), 3.85 (3H, s), 2.35 (3H, s), 2.30 (3H, s), 2.14 (3H, s);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  199.7, 168.8, 164.2, 158.3, 155.0, 135.7, 134.2, 132.2, 130.3, 130.1, 127.8, 126.7, 125.8, 124.7, 121.6, 116.9, 116.1, 110.5, 104.6, 89.3, 56.0, 55.2, 26.2, 21.1, 17.3; IR  $\nu$  3358, 3161, 1759, 1725, 1695; Anal. Calcd for  $\text{C}_{25}\text{H}_{25}\text{NO}_6$ : C, 68.95; H, 5.79; N, 3.22. Found: C, 69.03; H, 5.59; N, 3.31.

**(1-(*o*-methylphenylcarbamoyl)-8-methoxynaphtho[2,1-b]furan-2-yl)methyl acetate 4ag.**



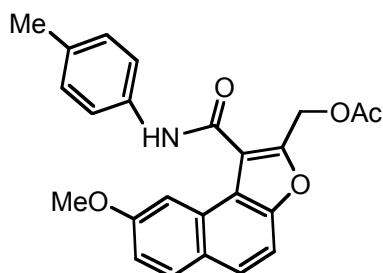
Colorless microcrystals (from ethanol); mp 207-209 °C;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  9.06 (1H, br, s), 8.05 (1H, d,  $J = 2.1$  Hz), 7.93 (1H, d,  $J = 7.8$  Hz), 7.83 (1H, d,  $J = 8.7$  Hz), 7.75 (1H, d,  $J = 9.0$  Hz), 7.49 (1H, d,  $J = 9.0$  Hz), 7.34-7.13 (4H, m), 5.47 (2H, s), 3.85 (3H, s), 2.39 (3H, s), 2.16 (3H, s);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  197.3, 174.1, 163.4, 161.6, 153.8, 140.7, 135.1, 131.3, 131.0, 130.6, 130.2, 127.6, 126.9, 125.3, 124.6, 121.5, 118.0, 110.5, 102.4, 90.0, 55.6, 22.6, 17.6; IR  $\nu$  3229, 1757, 1717; Anal. Calcd for  $\text{C}_{24}\text{H}_{21}\text{NO}_5$ : C, 71.45; H, 5.25; N, 3.47. Found: C, 71.21; H, 5.29; N, 3.62.

***N*-(*p*-methylphenyl)-2-acetoxy-2-(2,7-dimethoxy-1-naphthyl)-3-oxobutanamide 3ah.**



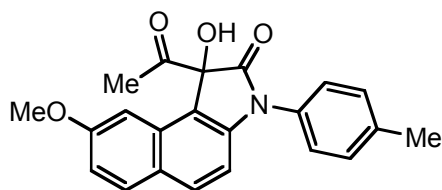
Colorless needles (from methanol); mp 169-170 °C;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.32 (1H, s), 7.80 (1H, d,  $J = 9.3$  Hz), 7.66 (1H, d,  $J = 9.0$  Hz), 7.60 (1H, d,  $J = 2.4$ ), 7.36 (2H, d,  $J = 8.4$  Hz), 7.09 (3H, d,  $J = 8.7$  Hz), 7.01 (1H, dd,  $J = 2.4, 9.0$  Hz), 3.90 (3H, s), 3.78 (3H, s), 2.36 (3H, s), 2.28 (3H, s), 2.26 (3H, s);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  199.3, 168.2, 164.3, 158.3, 155.8, 134.7, 134.3, 134.1, 132.2, 130.2, 129.5, 125.8, 119.9, 116.8, 116.3, 111.0, 104.1, 90.0, 56.4, 55.1, 26.5, 21.3, 20.8; IR  $\nu$  3396, 1771, 1715, 1695; Anal. Calcd for  $\text{C}_{25}\text{H}_{25}\text{NO}_6$ : C, 68.95; H, 5.79; N, 3.22. Found: C, 69.03; H, 5.65; N, 3.22.

**(1-(*p*-methylphenylcarbamoyl)-8-methoxynaphtho[2,1-b]furan-2-yl)methyl acetate 4ah.**



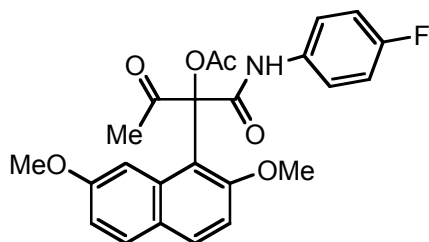
Colorless microcrystals (from ethanol); mp 197-199 °C;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.60 (1H, s), 8.15 (1H, d,  $J = 2.4$  Hz), 7.83 (1H, d,  $J = 8.7$ ), 7.72 (1H, d,  $J = 9.3$  Hz), 7.61 (2H, d,  $J = 8.7$  Hz), 7.45 (1H, d,  $J = 9.3$  Hz), 7.20 (2H, d,  $J = 8.1$  Hz), 7.14 (1H, dd,  $J = 2.4, 8.7$  Hz), 5.41 (2H, s), 3.90 (3H, s), 3.83 (3H, s), 2.20 (3H, s);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  172.9, 162.7, 158.5, 156.7, 153.3, 148.2, 134.5, 130.5, 129.7, 128.9, 127.2, 126.1, 121.2, 119.9, 119.3, 117.1, 114.2, 109.5, 104.0, 57.3, 55.3, 31.0, 21.0; IR  $\nu$  3420, 3215, 1716, 1683; Anal. Calcd for  $\text{C}_{24}\text{H}_{21}\text{NO}_5$ : C, 71.45; H, 5.25; N, 3.47. Found: C, 71.15; H, 5.31; N, 3.56.

**1-acetyl-1-hydroxy-8-methoxy-3-(*p*-methylphenyl)-1H-benzo[e]indol-2(3H)-one 5ah.**



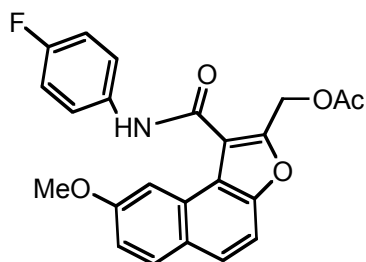
Colorless microcrystals (from ethanol); mp 215.5-218 °C;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.46 (1H, s), 8.13 (1H, d,  $J = 2.7$  Hz), 8.06 (1H, dd,  $J = 2.7, 8.7$  Hz), 7.73 (1H, dd,  $J = 2.7, 9.0$  Hz), 7.46 (1H, d,  $J = 8.4$  Hz), 7.45 (1H, d,  $J = 8.1$  Hz), 7.22 (1H, dd,  $J = 1.0, 8.7$  Hz), 7.10-7.14 (3H, m), 3.98 (3H, s), 2.30 (3H, s), 1.91 (3H, s);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  197.1, 173.9, 163.3, 161.7, 140.5, 134.5, 134.3, 131.3, 130.2, 129.5, 124.7, 119.9, 118.1, 110.6, 110.5, 102.4, 89.8, 55.6, 22.6, 20.9; IR  $\nu$  3344, 1701, 1672; Anal. Calcd for  $\text{C}_{22}\text{H}_{19}\text{NO}_4$ : C, 73.12; H, 5.30; N, 3.88. Found: C, 73.29; H, 5.22; N, 3.67.

***N*-(*p*-fluorophenyl)-2-acetoxy-2-(2,7-dimethoxy-1-naphthyl)-3-oxobutanamide 3ai.**



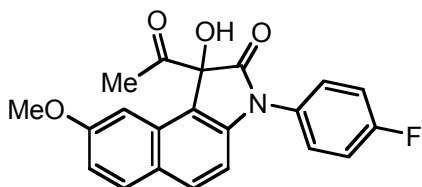
Colorless microcrystals (from methanol); mp 127-129 °C;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.44 (1H, s), 7.80 (1H, d,  $J = 8.7$  Hz), 7.67 (2H, d,  $J = 9.0$  Hz), 7.44 (1H, d,  $J = 8.7$  Hz), 7.43 (1H, d,  $J = 8.7$  Hz), 7.08 (1H, d,  $J = 9.3$  Hz), 7.02 (1H, dd,  $J = 2.4, 9.0$  Hz), 6.96 (2H, t,  $J = 8.7$  Hz), 3.89 (3H, s), 3.82 (3H, s), 2.34 (3H, s), 2.26 (3H, s);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  199.2, 168.4, 164.6, 161.0, 158.3, 157.8, 155.5, 134.0, 133.3, 132.3, 130.2, 125.7, 121.8, 121.7, 116.7, 115.7, 115.4, 110.8, 104.2, 89.3, 56.2, 55.1, 26.2, 21.1; IR  $\nu$  3381, 3309, 1757, 1718, 1684.

**(1-(*p*-fluorophenylcarbamoyl)-8-methoxynaphtho[2,1-*b*]furan-2-yl)methyl acetate 4ai.**



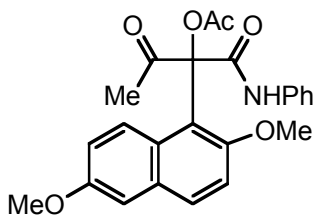
Colorless microcrystals (from ethanol); mp 148-150 °C;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  10.01 (1H, s), 8.15 (1H, d,  $J = 2.4$  Hz), 7.83 (1H, d,  $J = 8.7$ ), 7.72 (1H, d,  $J = 9.3$  Hz), 7.61 (2H, d,  $J = 8.7$  Hz), 7.45 (1H, d,  $J = 9.3$  Hz), 7.20 (2H, d,  $J = 8.1$  Hz), 7.14 (1H, dd,  $J = 2.4, 8.7$  Hz), 5.41 (2H, s), 3.90 (3H, s), 3.83 (3H, s), 2.20 (3H, s);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  172.3, 162.4, 158.5, 152.9, 148.2, 138.6, 130.4, 129.1, 127.8, 125.4, 124.3, 119.7, 117.2, 109.0, 103.4, 58.9, 55.3, 20.8; IR  $\nu$  3283, 1736, 1695.

**1-acetyl-1-hydroxy-8-methoxy-3-(*p*-fluorophenyl)-1H-benzo[e]indol-2(3H)-one 5ai.**



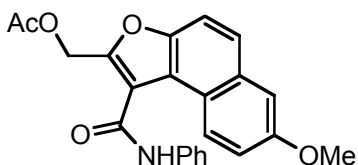
Colorless microcrystals (from ethanol); mp 177-177.5 °C;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.54 (1H, s), 8.12 (1H, d,  $J = 2.7$  Hz), 8.08 (1H, d,  $J = 9.3$  Hz), 7.75 (1H, d,  $J = 9.3$  Hz), 7.72-7.69 (1H, m), 7.57-7.52 (2H, m), 7.23 (1H, d,  $J = 9.3$  Hz), 7.13 (1H, dd,  $J = 2.7, 9.0$  Hz), 7.02 (1H, t,  $J = 9.0$  Hz), 3.99 (3H, s), 1.92 (3H, s);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  197.2, 173.7, 167.8, 163.5, 161.8, 140.7, 132.9, 131.3, 130.8, 128.8, 124.7, 121.8, 121.7, 118.2, 115.9, 115.5, 110.5, 102.4, 89.8, 55.6, 23.0; IR  $\nu$  3271, 1726, 1691.

***N*-phenyl-2-acetoxy-2-(2, 6-dimethoxy-1-naphthyl)-3-oxobutanamide 3ba.**



Colorless microcrystals (from methanol); mp 180-181 °C;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.50 (1H, s), 8.19 (1H, d,  $J = 9.6$  Hz), 7.76 (1H, d,  $J = 9.0$  Hz), 7.47 (2H, d,  $J = 8.4$  Hz), 7.47 (2H, t,  $J = 8.1$  Hz), 7.20 (1H, d,  $J = 9.0$  Hz), 7.47 (1H, dd,  $J = 2.7, 9.6$  Hz), 7.04-7.09 (2H, m), 3.83 (6H, s), 2.34 (3H, s), 2.22 (3H, s);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  198.8, 168.3, 164.6, 156.0, 153.4, 137.4, 131.7, 131.2, 128.8, 127.6, 124.5, 119.9, 119.4, 117.6, 114.3, 89.4, 56.5, 55.1, 26.3, 21.1; IR  $\nu$  3413, 1757, 1718. Anal. Calcd for  $\text{C}_{24}\text{H}_{23}\text{NO}_6$ : C, 68.40; H, 5.50; N, 3.32. Found: C, 68.07; H, 5.60; N, 3.24.

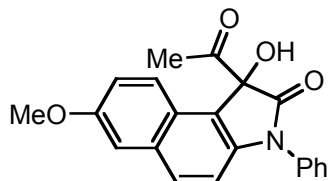
**(1-(phenylcarbamoyl)-7-methoxynaphtho[2, 1-b]furan-2-yl)methyl acetate 4ba.**



Colorless needles (from ethanol); mp 186-187 °C;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  9.92 (1H, s), 8.59 (1H, d,  $J = 8.7$  Hz), 7.87 (2H, d,  $J = 8.1$  Hz), 7.71 (1H, d,  $J = 8.7$  Hz), 7.58 (1H, d,  $J = 8.7$  Hz), 7.41 (2H, t,  $J = 8.1$  Hz), 7.12-7.22 (3H, m), 5.39 (2H, s), 3.91 (3H, s), 2.19 (3H, s);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  172.3, 162.1, 156.9, 152.1, 148.3, 139.7, 138.5, 132.5, 129.1, 126.9, 125.5, 124.6, 119.9, 118.7, 112.2, 107.9, 58.9, 55.4, 21.1; IR  $\nu$  3263, 3242, 1749, 1647; Anal. Calcd for  $\text{C}_{23}\text{H}_{19}\text{NO}_5$ : C,

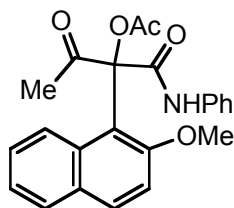
70.94; H, 4.92; N, 3.60. Found: C, 70.87; H, 4.84; N, 3.46.

**1-acetyl-1-hydroxy-7-methoxy-3-phenyl-1H-benzo[e]indol-2(3H)-one 5ba.**



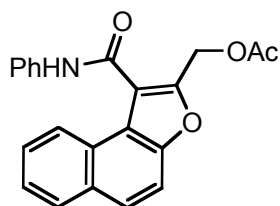
Colorless microcrystals (from ethanol); mp 177-177.5 °C;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.64 (1H, d,  $J = 8.7$  Hz), 8.56 (1H, s), 8.07 (1H, d,  $J = 9.0$  Hz), 7.58 (2H, d,  $J = 7.5$  Hz), 7.47-7.30 (3H, m), 7.21 (1H, d,  $J = 2.7$  Hz), 7.10-7.17 (2H, m), 4.00 (3H, s), 2.02 (3H, s);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  197.5, 173.3, 172.2, 163.4, 157.5, 139.7, 136.8, 131.0, 129.0, 124.8, 124.5, 121.9, 119.9, 114.1, 111.5, 107.9, 89.8, 55.4, 22.8; IR  $\nu$  3414, 3325, 1724, 1680;

**N-phenyl-2-acetoxy-2-(2-methoxy-1-naphthyl)-3-oxobutanamide 3ca.**



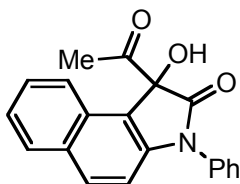
Colorless microcrystals (from methanol); mp 163-164.5 °C;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.46 (1H, s), 8.19 (1H, d,  $J = 8.4$  Hz), 7.90 (1H, d,  $J = 8.7$  Hz), 7.79 (1H, d,  $J = 8.1$  Hz), 7.42-7.51 (3H, m), 7.25-7.38 (4H, m), 7.08-7.13 (1H, m), 3.91 (3H, s), 2.35 (3H, s), 2.25 (3H, s);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  198.6, 168.2, 164.7, 155.2, 137.3, 132.7, 132.5, 130.4, 129.0, 128.9, 127.1, 124.9, 124.7, 124.0, 120.0, 117.4, 113.8, 89.8, 56.6, 26.4, 21.3; IR  $\nu$  3352, 1770, 1715, 1699; Anal. Calcd for  $\text{C}_{23}\text{H}_{21}\text{NO}_5$ : C, 70.58; H, 5.41; N, 3.58. Found: C, 70.66; H, 5.37; N, 3.68.

**(1-(phenylcarbamoyl)-naphtho[2, 1-b]furan-2-yl)methyl acetate 4ca.**



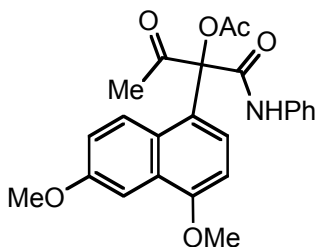
Colorless microcrystals (from ethanol); mp 192-194 °C;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  9.90 (1H, s), 8.65 (1H, d,  $J = 7.8$  Hz), 7.87-7.89 (3H, m), 7.79 (1H, d,  $J = 8.4$  Hz), 7.39-7.60 (5H, m), 7.16-7.23 (1H, m), 5.37 (2H, s), 2.18 (3H, s);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  182.8, 172.6, 164.7, 152.8, 138.2, 129.1, 128.0, 127.7, 127.0, 125.7, 125.1, 124.8, 124.6, 119.8, 111.7, 55.7, 20.9; IR  $\nu$  3273, 3190, 1750, 1651; Anal. Calcd for  $\text{C}_{22}\text{H}_{17}\text{NO}_4$ : C, 73.53; H, 4.77; N, 3.90. Found: C, 73.39; H, 4.67; N, 3.88.

**1-acetyl-1-hydroxy-3-phenyl-1H-benzo[e]indol-2(3H)-one 5ca.**



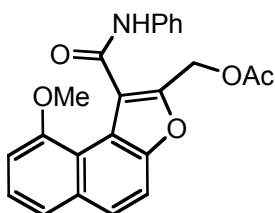
Colorless microcrystals (from ethanol); mp 192-193 °C;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.74 (1H, d,  $J = 7.5$  Hz), 8.59 (1H, s), 8.16 (1H, d,  $J = 8.7$  Hz), 7.87 (1H, d,  $J = 8.1$  Hz), 7.71 (1H, t,  $J = 8.1$  Hz), 7.59 (2H, d,  $J = 7.8$  Hz), 7.52 (1H, t,  $J = 7.2$  Hz), 7.41 (1H, dd,  $J = 1.8, 8.7$  Hz), 7.32 (2H, t,  $J = 7.5$  Hz), 7.12 (1H, t,  $J = 7.8$  Hz), 1.93 (3H, s);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  197.5, 173.8, 163.3, 141.0, 136.8, 130.3, 129.6, 129.1, 129.0, 128.7, 126.0, 124.8, 123.2, 120.0, 113.7, 111.3, 89.8, 22.8; IR  $\nu$  3407, 1705, 1684; Anal. Calcd for  $\text{C}_{20}\text{H}_{15}\text{NO}_3$ : C, 75.70; H, 4.76; N, 4.41. Found: C, 75.57; H, 4.72; N, 4.37.

**N-phenyl-2-acetoxy-2-(4,6-dimethoxy-1-naphthyl)-3-oxobutanamide 3da.**



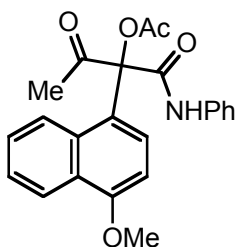
Colorless microcrystals (from methanol); mp 177-177.5 °C;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.79 (1H, br, s), 8.52 (1H, d,  $J = 9.6$  Hz), 7.61 (1H, d,  $J = 2.7$  Hz), 7.42 (2H, d,  $J = 7.5$  Hz), 7.30-7.23 (4H, m), 7.05 (1H, t,  $J = 7.2$  Hz), 6.73 (1H, d,  $J = 8.1$  Hz), 3.99 (3H, s), 3.92 (3H, s), 2.36 (3H, s), 2.32 (3H, s);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  203.5, 170.6, 164.4, 157.3, 155.9, 137.2, 128.8, 128.2, 127.5, 127.2, 124.5, 123.6, 121.2, 120.2, 119.5, 102.9, 101.1, 89.8, 55.5, 55.2, 26.9, 20.9; IR  $\nu$  3341, 1751, 1716, 1683;

**(1-(phenylcarbamoyl)-9-methoxynaphtho[2,1-b]furan-2-yl)methyl acetate 4da.**



Colorless needles (from ethanol); mp 177-177.5 °C;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.45 (1H, br, s), 7.82-7.74 (3H, m), 7.62 (1H, dd,  $J = 1.5, 9.0$  Hz), 7.51 (1H, d,  $J = 8.1$  Hz), 7.43-7.37 (3H, m), 7.15 (1H, dt,  $J = 1.5, 9.0$  Hz), 6.90 (1H, d,  $J = 7.8$  Hz), 5.33 (2H, s), 3.74 (3H, s), 2.12 (3H, s);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  171.2, 163.3, 155.2, 152.8, 148.4, 138.7, 132.3, 129.1, 127.1, 125.2, 124.1, 121.5, 119.3, 119.1, 117.4, 112.6, 105.8, 58.0, 54.8, 20.9; IR  $\nu$  3410, 1734, 1684;

**N-phenyl-2-acetoxy-2-(4-methoxy-1-naphthyl)-3-oxobutanamide 3ea.**



Colorless microcrystals (from methanol); mp 176-177 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 8.77 (1H, s), 8.55 (1H, d, *J* = 8.4 Hz), 8.33 (1H, dd, *J* = 1.2, 7.8 Hz), 7.58 (1H, t, *J* = 8.4 Hz), 7.52 (1H, d, *J* = 8.1 Hz), 7.41-7.48 (3H, m), 7.25 (1H, t, *J* = 7.8 Hz), 7.05 (1H, t, *J* = 8.1 Hz), 6.76 (1H, d, *J* = 8.4 Hz), 4.00 (3H, s), 2.37 (3H, s), 2.33 (3H, s); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 203.5, 170.6, 164.4, 157.0, 137.2, 132.1, 128.8, 127.4, 126.8, 126.4, 125.6, 124.6, 122.6, 121.1, 120.2, 102.4, 89.9, 55.6, 26.9, 21.0; IR *v* 3307, 1746, 1719, 1698; Anal. Calcd for C<sub>23</sub>H<sub>21</sub>NO<sub>5</sub>: C, 70.58; H, 5.41; N, 3.58. Found: C, 70.51; H, 5.39; N, 3.54.