A FACILE SYNTHESIS OF METHYL 5-AMINO-6-CHLORO-2*H*-1-BENZOPYRAN-8-CARBOXYLATE DERIVATIVES

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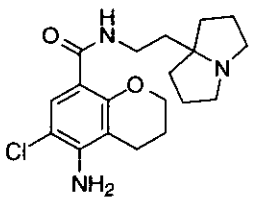
Abstract - Methyl 6-chloro-5-pivaloylamino-2*H*-1-benzopyran-8-carboxylate (**4d**) was prepared in good yield as a result of the thermal cylcization of methyl 5-chloro-4-pivaloylamino-2-propargyloxybenzoate (**3d**) using *N.N*-diethylaniline as a solvent.

In our previous paper, we reported the synthesis of 5-amino-*N*-[2-(1-azabicyclo[3.3.0]octan-5-yl)ethyl]-6-chloro-2*H*-1-benzopyran-8-carboxamide derivatives (**1**, **2**), which showed potent serotonin 5-HT_4 agonistic activity. However, a benzopyran derivative (**4b**), the key intermediate of **1** and **2**, was prepared only in low yields (25 - 30 %) *via* the Claisen rearrangement of the methyl 2-propargyloxybenzoate derivatives (**3b**) (Scheme 2). It is necessary to synthesize the methyl 2*H*-1-benzopyran-8-carboxylate derivatives (**4**) in good yields in order to develop the efficacious synthesis method of **1** and **2**. We examined the cyclization reactions of methyl 2-propargyloxybenzoates.



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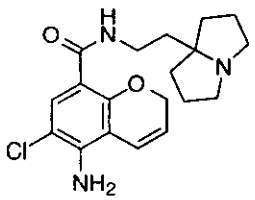

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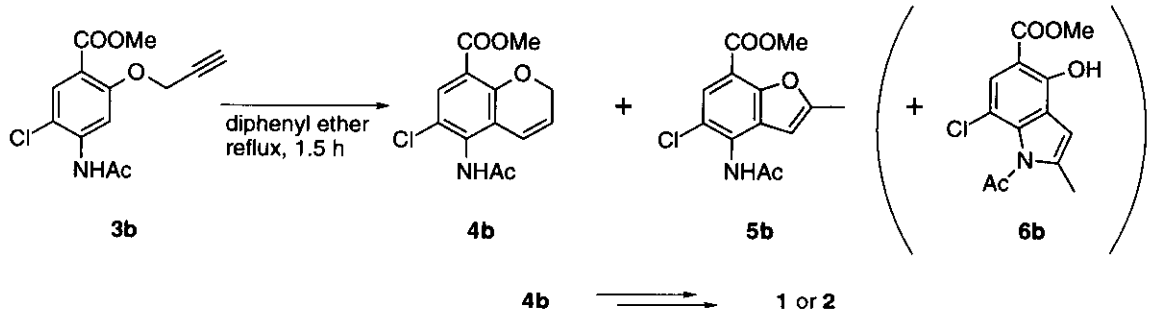
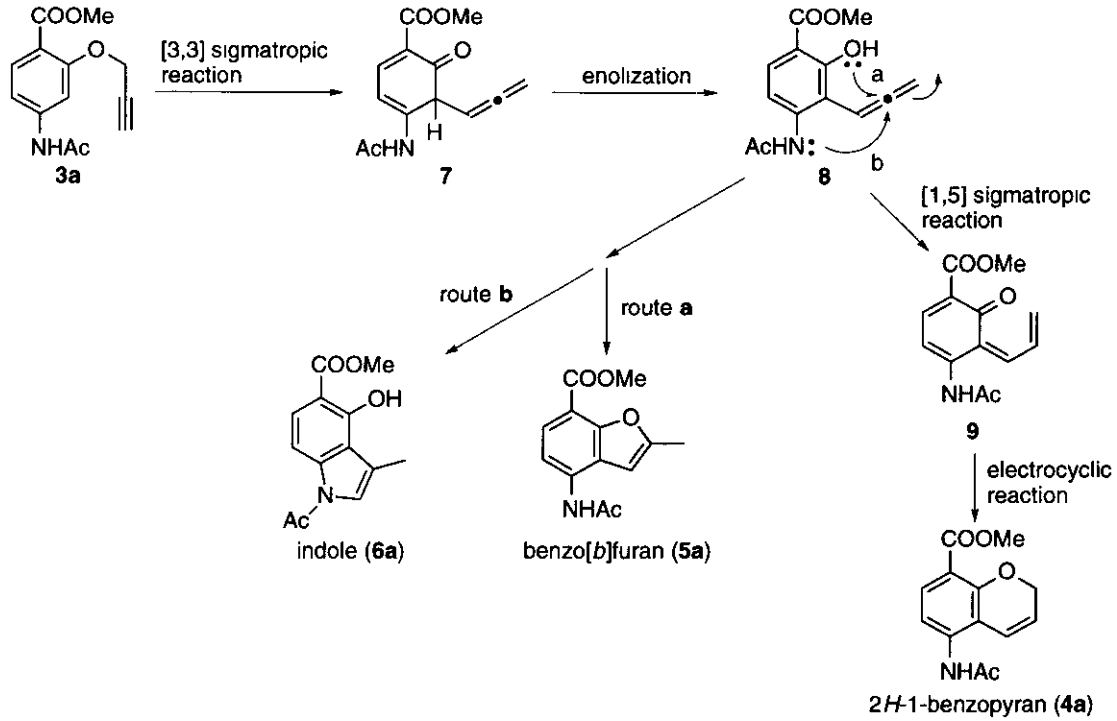
Scheme 1

This paper describes the thermal cyclization of methyl 2-propargyloxybenzoates to methyl 2*H*-1-benzopyran-8-carboxylates. The mechanism for foramtion of 2*H*-1-benzopyran and benzo[*b*]furan can be

proposed in Scheme 3.[2] A Claisen-like [3,3] sigmatropic rearrangement of a phenyl propargyl ether (**3a**) gives an allenylated cyclohexadienone (**7**), which aromatizes to form an *o*-allenylphenol (**8**). A [1,5] hydrogen shift of **8** followed by the electrocyclic reaction of **9** yields a 2*H*-1-benzopyran (**4a**). When the hydroxy group attacks at the allenic carbon *via* route **a**, a 2-methylbenzo[*b*]furan (**5a**) is formed. If the amide nitrogen combined with the allenic carbon *via* route **b**, an indole derivative (**6a**) would be produced.



Scheme 2

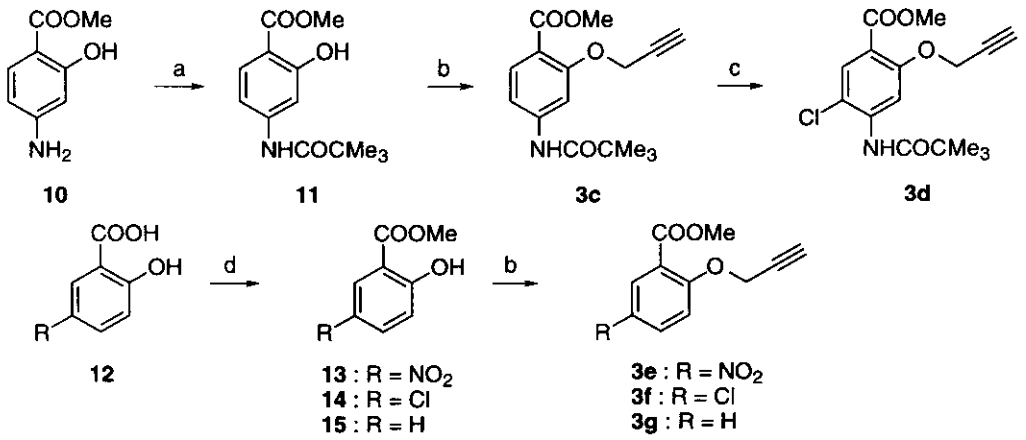


Scheme 3

It is reported that the cyclization process is influenced by the solvent or a property of the substituent at

the aryl group, and the product ratio of the 2*H*-1-benzopyran ring (**4**) or 2-methylbenzo[*b*]furan ring (**5**) depends on these factors.[3] However, the standardized condition has not been established, and we examined the reaction conditions for the thermal cyclization of some methyl 2-propargyloxybenzoates.

Methyl 4-acetylamino-2-propargyloxybenzoate (**3a**) and 5-chloro derivative (**3b**) were prepared by the method reported in our previous paper.[4] and other congeners (**3c–g**) were synthesized by the methods shown in Scheme 4. The cylcization reactions of **3a–g** were performed using diphenyl ether or *N,N*-diethylaniline as a solvent.



Reagents: a Me_3CCOCl, Et_3N ; b $BrCH_2C{\equiv}CH$, K_2CO_3 ; c NCS ; d MeOH, 97 % H_2SO_4 ; e *N*-carbethoxyphthalimide

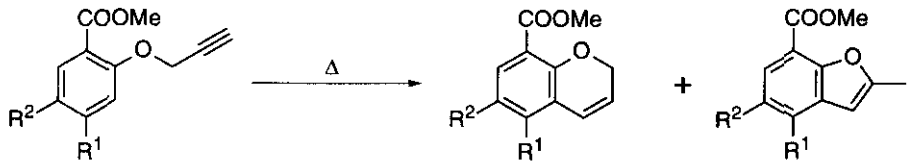
Scheme 4

The results are summarized in Table 1. *N,N*-Diethylaniline (method B) was a better solvent than diphenyl ether (method A) for the cyclization reaction of **3a–g**. Compounds (**3e–g**) without an acylamino group gave the cyclized products (**4**) and (**5**) in lower yields than other amides (**3c,d**). It is thought that the cyclization of **3e–g** was slow because the allene group turned to the opposite side as a result of steric hindrance with the hydroxyl group.

In the case of the *N*-acetyl derivatives (**3a,b**), the yield of both the 2*H*-1-benzopyran (**4**) and benzo[*b*]furan (**5**) derivatives is low. In our previous report,[4] the cyclization of **3a** in 1,2-dichlorobenzene (bp : 180 °C) gave methyl 4-acetylamino-2-methylbenzo[*b*]furan-7-carboxylate (**5a**) in 45% yield and methyl 1-acetyl-4-hydroxy-2-methylindol-5-carboxylate (**6a**) in 4% yield. But, the yield of methyl 5-acetylamino-2*H*-1-benzopyran-8-carboxylate (**4a**) was very low (< 8%). In this report, the cyclization of

3a and **3b** in diphenyl ether (bp : 259 °C) gave methyl 5-acetylamino-2*H*-1-benzopyran-8-carboxylate (**4a**) and methyl 5-acetylamino-6-chloro-2*H*-1-benzopyran-8-carboxylate (**4b**) in 13% and 27% yields. This implies that the high temparature is nesessary for the formation of 2*H*-1-benzopyran ring, and the decrease of yield is caused by the creation of indole derivatives together with benzo[*b*]furan and 2*H*-1-benzopyran derivatives because of the competition with cyclization at the *N*-atom (route **b**) (Scheme 3). On the other hand, in the case of the *N*-pivaloyl derivatives (**3c,d**), 2*H*-1-benzopyran (**4**) or benzo[*b*]furan (**5**) derivatives were obtained in good yield. It is conceived for the reason that the allene group turns to the hydroxy group side, and the cyclization between the allene and the *N*-atom is restricted because of the bulkiness of the *N*-pivaloyl group. Furthermore, it is possible to prepare 2*H*-1-benzopyran (**4**) or benzo[*b*]furan (**5**) derivatives separately by introducing a chlorine atom at the 5-position of *N*-pivaloyl derivatives. It is proved that the electron-attractiveness of chlorine atom at the 5-position controls the precedence [1,5] sigmatropic reaction and nucleophillic cyclization.

Table 1. Cyclization of Methyl 2-Propargyloxybenzoate Derivatives



3 **4** **5**

Compd.	R^1	R^2	Yield (%)[a] Method A[b]		Method B[c]	
			4	**5**	**4**	**5**
3a	NHAc	H	13	15	–[d]	–[d]
3b	NHAc	Cl	27	0	29	0
3c	$NHCOCMe_3$	H	15	49	6.5	68
3d	$NHCOCMe_3$	Cl	53	0	74	0
3e	H	NO^2	11	6	30	20
3f	H	Cl	–[d]	–[d]	42	10
3g	H	H	–[d]	–[d]	56	0

a) Isolated yield.

b) A mixture of a substrate and diphenyl ether [5.0 mL/g (substrate)] was refluxed for 2 h.

c) A mixture of a substrate and *N*,*N*-diethylaniline [5.0 mL/g (substrate)] was refluxed for 2 h.

d) Not tested.

In conclusion, methyl 6-chloro-5-pivaloylamino-2*H*-1-benzopyran-8-carboxylate (**4d**) was prepared in high yield as a result of thermal cyclization of methyl 5-chloro-4-pivaloylamino-2-propargyloxybenzoate (**3d**) using *N,N*-diethylaniline as a solvent.

EXPERIMENTAL SECTION

All melting points were determined using a Yanagimoto micromelting point apparatus and are uncorrected. IR spectra were recorded using a Perkin Elmer 1600. MS spectra were obtained on a JEOL JMS-SX 120A spectrometer. ^{1}H-NMR(270MHz) spectra were recorded using a JEOL JNM-GSX 270 in $CDCl_3$ or DMSO-d_6. Chemical shifts are expressed as δ values (ppm) with tetramethylsilane as an internal standard, and coupling constants (*J* values) are given in Hertz (Hz).

Methyl 2-Hydroxy-4-pivaroylaminobenzoate (11).

The solution of pivaloyl chloride (0.361 g, 2.99 mmol) in CH_2Cl_2 (3.0 mL) was added to a solution of methyl 4-amino-2-hydroxybenzoate (7) (0.500 g, 2.99 mmol) and triethylamine (0.00361 g, 3.29 mmol) in CH_2Cl_2 (7.0 mL) at 0-5 °C, and then stirred for 3 h at 20 °C. The reaction mixture was washed with saturated $NaHCO_3$ and then water, dried over Na_2SO_4, and thereafter, the solvent was concentrated *in vacuo*. The residue was purified by silica gel column chromatography ($CHCl_3$) to give 0.613 g (81.6%) of **11** as a powder. mp 141-142 °C. ^{1}H-NMR ($CDCl_3$) δ: 1.32 (9H, s, CH_3), 3.93 (3H, s, $COOCH_3$), 7.13 (1H, dd, *J*=2.5, 8.8 Hz, C5-H), 7.18 (1H, d, *J*=2.5 Hz, C3-H), 7.37 (1H, br s, NH), 7.78 (1H, d, *J*=8.8 Hz, C6-H), 10.8 (1H, s, OH). IR (KBr)cm^{-1}: 3303 (NH), 1683, 1661 (C=O). EI-MS *m/z* : 251 (M^+). *Anal.* Calcd for $C_{13}H_{17}NO_4$: C, 62.14; H, 6.82; N, 5.57. Found: C, 62.25; H, 6.68; N, 5.48.

Methyl 4-Pyvaroylamino-2-propargyloxybenzoate (3c).

A mixture of **11** (0.300 g, 1.20 mmol), propargyl bromide (0.156 g, 1.31 mmol), and potassium carbonate (0.181 g, 1.31 mmol) in *N,N*-dimethylformamide (5.0 mL) was stirred for 4 h at 70 °C. The reaction mixture was poured into ice-water (80 mL), and extracted with $CHCl_3$. The extract was washed with water, dried over Na_2SO_4, and thereafter, the solvent was concentrated *in vacuo*. The residue was purified by silica gel column chromatography (AcOEt : hexane = 1 : 2) to give 0.309 g (89.6%) of **3c** as a powder. mp 142-143 °C. ^{1}H-NMR ($CDCl_3$) δ: 1.33 (9H, s, CH_3), 2.54 (1H, t, *J*=2.4 Hz,CH), 3.87 (3H, s, $COOCH_3$), 4.81 (2H, d, *J*=2.4 Hz, CH_2), 6.94 (1H, dd, *J*=2.0, 8.3 Hz, C5-H), 7.42 (1H, br s, NH), 7.75 (1H, d, *J*=2.0 Hz, C3-H), 7.84 (1H, d, *J*=8.3 Hz, C6-H). IR (KBr)cm^{-1}: 3374 (NH), 1707, 1681 (C=O). EI-MS *m/z* : 289 (M^+). *Anal.* Calcd for $C_{16}H_{19}NO_4$: C, 66.42; H, 6.62; N, 4.84. Found: C, 66.35; H, 6.69;

N, 4.76.

Methyl 5-Chloro-4-pivaroylamino-2-propargyloxybenzoate (3d).

A mixture of **3c** (0.0700 g, 0.242 mmol) and *N*-chlorosuccinimide (0.0323 g, 0.242 mmol) in *N,N*-dimethylformamide (1.0 mL) was stirred for 5 h at 70 °C. The cooled reaction mixture was concentrated *in vacuo*. The residue was purified by silica gel column chromatography (AcOEt : hexane.= 1 : 3) to give 0.0620 g (79.1%) of **3d** as a powder. mp 89-90 °C. ^{1}H-NMR ($CDCl_3$) δ: 1.36 (9H, s, CH_3), 2.56 (1H, t, *J*=2.4 Hz,CH), 3.88 (3H, s, $COOCH_3$), 4.82 (2H, d, *J*=2.4 Hz, CH_2), 7.92 (1H, s, C3-H), 8.19 (1H, br s, NH), 8.48 (1H, s, C6-H). IR (KBr)cm^{-1}: 3419 (NH), 1727, 1686 (C=O). EI-MS *m/z* : 323 (M^+). *Anal.* Calcd for $C_{16}H_{18}NO_4Cl$: C, 59.35; H, 5.60; N, 4.33. Found: C, 59.32; H,5.75; N, 4.12.

Methyl 2-Hydroxy-5-nitrobenzoate (13).

A mixture of 2-hydroxy-5-nitrobenzoic acid (**12:R=NO_2**) (2.50 g, 13.7 mmol) and 97% H_2SO_4 (1.00g) in methanol (10 mL) was refluxed for 20 h. The cooled reaction mixture was poured into ice-water (40 mL). The resultant precipitate was collected by filtration to give 2.55 g (95.0%) of **13** as a powder. mp 109-110 °C. ^{1}H-NMR ($CDCl_3$) δ: 3.99 (3H, s, $COOCH_3$), 7.09 (1H, d, *J*=9.3 Hz, C3-H), 8.34 (1H, dd, *J*=2.9, 9.3 Hz, C4-H), 8.80 (1H, d, *J*=2.9 Hz, C6-H), 11.4 (1H, s, OH). IR (KBr)cm^{-1}: 1680 (C=O).[5]

Methyl 5-Nitro-2-propargyloxybenzoate (3e).

A mixture of **13** (5.00 g, 25.4 mmol), propargyl bromide (3.32 g, 27.9 mmol), and potassium carbonate (7.01 g, 50.8 mmol) in *N,N*-dimethylformamide (50 mL) was stirred for 2 h at 70 °C. The cooled reaction mixture was poured into ice-water (800 mL). The resultant precipitate was collected by filtration to give 5.54 g (93.0%) of **3e** as a powder. mp 90-91 °C. ^{1}H-NMR ($CDCl_3$) δ: 2.61 (1H, t, *J*=2.4 Hz, CH), 3.94 (3H, s, $COOCH_3$), 4.92 (2H, d, *J*=2.4 Hz, CH_2), 7.25 (1H, d, *J*=8.8 Hz, C4-H), 8.38 (1H, dd, *J*=2.9, 8.8 Hz, C4-H), 7.82 (1H, d, *J*=2.9 Hz, C6-H). IR (KBr)cm^{-1}: 1739 (C=O). EI-MS *m/z* : 235 (M^+). *Anal.* Calcd for $C_{11}H_9NO_5$: C, 56.17; H, 3.86; N, 5.96. Found: C, 56.32; H,3.91; N, 5.78.

Methyl 5-Chloro-2-propargyloxybenzoate (3f).

Methyl 2-hydroxy-5-chlorobenzoate (**14**) (5.00 g, 26.8 mmol) was converted to 5.54 g (98.7%) of **3f** in a similar procedure as employed in the synthesis of **3e** as a powder. mp 54-55 °C. ^{1}H-NMR ($CDCl_3$) δ: 2.54 (1H, t, *J*=2.4 Hz, CH), 3.90 (3H, s, $COOCH_3$), 4.78 (2H, d, *J*=2.4 Hz, CH_2), 7.10 (1H, d, *J*=8.8 Hz, C4-H), 7.43 (1H, dd, *J*=2.9, 8.8 Hz, C4-H), 7.79 (1H, d, *J*=2.9 Hz, C6-H). IR (KBr)cm^{-1}: 1726 (C=O). EI-MS *m/z* : 224 (M^+). *Anal.* Calcd for $C_{11}H_9O_3Cl$: C, 58.81; H, 4.04. Found: C, 58.92; H,3.92.

Methyl 2-Propargyloxybenzoate (3g).

A mixture of methyl 2-hydroxybenzoate (**15**) (2.50 g, 16.4 mmol), propargyl bromide (2.15 g, 18.1 mmol), and potassium carbonate (2.50 g, 18.1 mmol) in CH_3CN (10 mL) was refluxed for 24 h. After having filtered the insolubles, the filtrate was concentrated *in vacuo*. The residue was dissolved in $CHCl_3$, washed with water, dried over Na_2SO_4, and concentrated *in vacuo* to give 3.52 g (100 %) of **3g** as a syrup. ^{1}H-NMR ($CDCl_3$) δ: 2.52 (1H, t, J=2.4 Hz, CH), 3.89 (3H, s, $COOCH_3$), 4.80 (2H, d, J=2.4 Hz, CH_2), 7.05 (1H, m, C3-H), 7.13 (1H, d, *J*=8.3 Hz, C4-H), 7.48 (1H, m, C5-H), 7.82 (1H, dd, *J*=2.0, 4.8 Hz, C6-H).[6]

Cyclization method A

A mixture of a substrate and diphenyl ether [5.0 mL/g (substrate)] was refluxed for 2 h. The cooled reaction mixture was refined by silica gel column chromatography (AcOEt : hexane = 1 : 2) to give the methyl 2*H*-1-benzopyran-8-carboxylate derivative and the methyl 2-methylbenzo[*b*]furan-7- carboxylate derivative.

Cyclization method B

A mixture of a substrate and *N,N*-diethylaniline [5.0 mL/g (substrate)] was refluxed for 2 h. The cooled reaction mixture was dissolved in chloroform (30 mL), washed with water, 1N HCl, and then water, and thereafter, the solvent was concentrated *in vacuo*. The residue was refined by silica gel column chromatography (AcOEt : hexane = 1 : 2) to give the methyl 2*H*-1-benzopyran-8-carboxylate derivative and the methyl 2-methylbenzo[*b*]furan-7- carboxylate derivative.

Methyl 5-Pivaloylamino-2*H*-1-benzopyran-8-carboxylate (4c)

A syrup. ^{1}H-NMR ($CDCl_3$) δ: 1.34 (9H, s, CH_3), 3.86 (3H, s, $COOCH_3$), 4.82 (2H, dd, *J*=1.5, 3.9 Hz, CH_2), 5.95 (1H, dt, *J*=3.9, 9.8 Hz, CH), 6.37 (1H, dt, *J*=1.5, 9.8 Hz, CH), 7.38 (1H, s, NH), 7.40 (1H, d, *J*=9.8 Hz, C6-H), 7.68 (1H, d, *J*=9.8 Hz, C7-H). EI-MS *m/z* : 289 (M^+). *Anal.* Calcd for $C_{16}H_{19}NO_4$: C, 66.42; H, 6.62; N, 4.84. Found: C, 66.65; H,6.51; N, 4.87.

Methyl 2-Methyl-4-pivaloylaminobenzo[*b*]furan-7-carboxylate (5c)

A powder. mp 139-141 °C. ^{1}H-NMR ($CDCl_3$) δ: 1.37 (9H, s, CH_3), 2.52 (3H, s, CH_3), 3.97 (3H, s, $COOCH_3$), 6.34 (1H, d, J=0.98 Hz, CH), 7.63 (1H, s, NH), 7.84 (2H, s, C5,6-H). EI-MS *m/z* : 289 (M^+). *Anal.* Calcd for $C_{16}H_{19}NO_4$: C, 66.42; H, 6.62; N, 4.84. Found: C, 66.63; H,6.48; N, 4.85.

Methyl 6-Chloro-5-pivaloylamino-2*H*-1-benzopyran-8-carboxylate (4d)

A amorphous mass. ^{1}H-NMR ($CDCl_3$) δ: 1.38 (9H, s, CH_3), 3.88 (3H, s, $COOCH_3$), 4.90 (2H, dd, *J*=2.0, 3.9 Hz, CH_2), 5.91 (1H, dt, *J*=3.9, 9.8 Hz, CH), 6.21 (1H, dt, *J*=2.0, 9.8 Hz, CH), 7.35 (1H, s, NH), 7.73 (1H, s, *J*=9.8 Hz, C7-H). IR (KBr)cm^{-1}: 3376 (NH), 1718, 1678 (C=O). EI-MS *m/z* : 323 (M^+). *Anal.*

Calcd for $C_{16}H_{18}NO_4Cl$: C, 59.35; H, 5.60; N, 4.33. Found: C, 59.14; H,5.58; N, 4.52.

Methyl 6-Nitro-2*H*-1-benzopyran-8-carboxylate (4e)

A powder. mp 122-124 °C. ^{1}H-NMR ($CDCl_3$) δ: 3.86 (3H, s, $COOCH_3$), 5.13 (2H, dd, *J*=2.0, 3.4 Hz, CH_2), 5.95 (1H, dt, *J*=3.4, 9.8 Hz, CH), 6.21 (1H, dt, *J*=2.0, 9.8 Hz, CH), 7.92 (1H, d, *J*=2.4 Hz, C5-H), 7.73 (1H, d, *J*=2.4 Hz, C7-H). IR (KBr)cm^{-1}: 1706 (C=O), 1520 (NO). EI-MS *m/z* : 235 (M^+). *Anal.* Calcd for $C_{11}H_9NO_5$: C, 56.17; H, 3.86; N, 5.96. Found: C, 56.06; H, 3.79; N, 5.86.

Methyl 5-Nitro-2-methylbenzo[*b*]furan-7-carboxylate (5e)

A powder. mp 121-123 °C. ^{1}H-NMR ($CDCl_3$) δ: 2.59 (3H, s, CH_3), 4.04 (3H, s, $COOCH_3$), 6.60 (1H, s, C3-H), 8.55 (1H, d, *J*=2.5 Hz, C4-H), 8.77 (2H, d, *J*=2.5 Hz, C6-H). IR (KBr)cm^{-1}: 1714 (C=O), 1534 (NO). EI-MS *m/z* : 235 (M^+). *Anal.* Calcd for $C_{11}H_9NO_5$: C, 56.17; H, 3.86; N, 5.96. Found: C, 56.11; H, 3.71; N, 5.82.

Methyl 6-Chloro-2*H*-1-benzopyran-8-carboxylate (4f)

A amorphous mass. ^{1}H-NMR ($CDCl_3$) δ: 3.88 (3H, s, $COOCH_3$), 4.94 (2H, dd, *J*=2.0, 3.9 Hz, CH_2), 5.88 (1H, dt, *J*=3.9, 9.8 Hz, CH), 6.36 (1H, dt, *J*=2.0, 9.8 Hz, CH), 7.05 (1H, d, *J*=2.5 Hz, C5-H), 7.58 (1H, d, *J*=2.5 Hz, C7-H). IR (KBr)cm^{-1}: 1702 (C=O). EI-MS *m/z* : 224 (M^+). *Anal.* Calcd for $C_{11}H_9O_3Cl$: C, 58.81; H, 4.04. Found: C, 58.74; H, 3.99.

Methyl 5-Chloro-2-methylbenzo[*b*]furan-7-carboxylate (5f)

A powder. mp 68-70 °C. ^{1}H-NMR ($CDCl_3$) δ: 2.52 (3H, s, CH_3), 3.99 (3H, s, $COOCH_3$), 6.38 (1H, s, C3-H), 7.60 (1H, d, *J*=2.5 Hz, C4-H), 7.81 (2H, d, *J*=2.5 Hz, C6-H). IR (KBr)cm^{-1}: 1716 (C=O). EI-MS *m/z* : 224 (M^+). *Anal.* Calcd for $C_{11}H_9O_3Cl$: C, 58.81; H, 4.04. Found: C, 58.69; H, 3.15.

Methyl 2*H*-1-Benzopyran-8-carboxylate (4g)

A syrup. ^{1}H-NMR ($CDCl_3$) δ: 3.87 (3H, s, $COOCH_3$), 4.93 (2H, dd, *J*=1.9, 3.9 Hz, CH_2), 5.82 (1H, dt, *J*=3.9, 10.3 Hz, CH), 6.36 (1H, dt, *J*=1.9, 10.3 Hz, CH), 6.86 (1H, t, *J*=7.8 Hz, C6-H), 7.05 (1H, dd, *J*=1.5, 7.8 Hz, C5-H), 7.60 (1H, dd, *J*=1.5, 7.8 Hz, C7-H). IR (KBr)cm^{-1}: 1711 (C=O).[6]

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