SYNTHESIS OF 1,4-DIHYDRO-2H-3,1-BENZOXAZIN-2-ONES BY HYDRIODIC ACID MEDIATED CYCLIZATION OF t-BUTYL 2-VINYLPHENYLCARBAMATES

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Abstract - A two-step facile synthesis of 4,4-disubstituted 1,4-dihydro-2H-3,1-benzoxazin-2-ones starting from α-substituted 2-aminostyrenes is described. The method involves the hydriodic acid mediated cyclization of t-butyl 2-vinylphenylcarbamate derivatives, which could be easily prepared by N-t-butoxycarbonylation of α-substituted 2-aminostyrene derivatives, under mild conditions.

1,4-Dihydro-2H-3,1-benzoxazin-2-one derivatives have attracted considerable attention, mainly because some of these derivatives reveal significant biological activity.1 However, few general methods for synthesizing this class of molecules conveniently have been reported so far. Most of these compounds have been prepared by treatment of the corresponding 2-aminobenzyl alcohol derivatives with deadly poisonous phosgene.2 We became interested in developing a convenient method for the general preparation of 1,4-dihydro-2H-3,1-benzoxazin-2-one derivatives. In a previous paper,3 we demonstrated a new and convenient method for synthesizing 4,4-disubstituted 1,4-dihydro-2H-3,1-benzoxazin-2-one derivatives based on iodocyclization of t-butyl 2-vinylphenylcarbamate derivatives in acetonitrile, affording 4-iodomethyl-1,4-dihydro-2H-3,1-benzoxazin-2-one derivatives, the iodomethyl substituent of which could be reduced with tributyltin hydride in benzene to the methyl substituent. Herein, we wish to report that a more convenient method for the preparation of 1,4-dihydro-2H-3,1-benzoxazin-2-one derivatives has been developed. Thus, we found that 4,4-disubstituted 1,4-dihydro-2H-3,1-benzoxazin-2-one derivatives (2) could be prepared by simply treating t-butyl 2-vinylcarbamate derivatives (1) with concentrated hydriodic acid in acetonitrile under mild conditions (at 0 °C or room temperature).

t-Butyl 2-vinylphenylcarbamate derivatives (1) were readily prepared by the N-t-butoxycarbonylation of the respective 2-vinylaniline derivatives with di-t-butyl dicarbonate in the presence of sodium hydride in 1,4-dioxane–water under the conditions reported by Misawa et al.4 As shown in Scheme 1, the reactions for transforming the carbamates (1) into 4,4-disubstituted 1,4-dihydro-2H-3,1-benzoxazin-
2-one derivatives (2) were carried out in acetonitrile using an equimolar amount of concentrated hydriodic acid at the temperature indicated in Table 1. It shows that the reactions using most of the carbamates (1) proceeded smoothly at 0 °C to give (after the usual workup and the subsequent purification by recrystallization or preparative TLC on silica gel) the corresponding dihydrobenzoxazinone derivatives (2) in fair to good yields. It is worthwhile to mention that the reaction using t-butyl 4,5-dimethoxy-3-(1-methylethenyl)phenylcarbamate (1h) proceeded very quickly to give the corresponding desired product (2h) in satisfactory isolated yield (Entry 8). Although the reactions of t-butyl 2-vinylcarbamates carrying a methyl group at the β-position (R² = Me; 1i and 1j) with hydriodic acid required somewhat prolonged reaction times, the desired products (2i) and (2j), respectively, were obtained in fair yields (Entries 9 and 10). On the other hand, the reactions using t-butyl [2-(1-phenylethenyl)phenyl]carbamates (1b) and t-butyl 4-chloro-[2-(1-phenylethenyl)phenyl]carbamate (1f) as substrates proceeded very sluggishly even at room temperature to give somewhat lower yields of the corresponding desired products (2b) and (2f), respectively (Entries 2 and 6); a considerable amount of the starting carbamate was recovered in each case. Unfortunately, however, we are unable to explain the reason for this.

![Scheme 1](image)

**Table 1. Preparation of 1,4-Dihydro-2H-3,1-benzoxazin-2-one Derivatives (2)**

<table>
<thead>
<tr>
<th>Entry</th>
<th>1</th>
<th>Temp</th>
<th>Time</th>
<th>2 (Yield/%)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1a (R¹ = R² = R³ = H, R⁴ = Me)</td>
<td>0 °C</td>
<td>2 h</td>
<td>2a (56)</td>
</tr>
<tr>
<td>2</td>
<td>1b (R¹ = R² = R³ = H, R⁴ = Ph)</td>
<td>rt</td>
<td>1 d</td>
<td>2b (45; 64b)</td>
</tr>
<tr>
<td>3</td>
<td>1c (R¹ = R² = R³ = H, R⁴ = 4-ClC₆H₄)</td>
<td>0 °C</td>
<td>4 h</td>
<td>2c (66)</td>
</tr>
<tr>
<td>4</td>
<td>1d (R¹ = R² = R³ = H, R⁴ = 4-MeOC₆H₄)</td>
<td>0 °C</td>
<td>1 h</td>
<td>2d (75)</td>
</tr>
<tr>
<td>5</td>
<td>1e (R¹ = R² = H, R³ = F, R⁴ = Me)</td>
<td>0 °C</td>
<td>4 h</td>
<td>2e (90)</td>
</tr>
<tr>
<td>6</td>
<td>1f (R¹ = Cl, R² = R³ = H, R⁴ = Ph)</td>
<td>rt</td>
<td>40 h</td>
<td>2f (44; 59b)</td>
</tr>
<tr>
<td>7</td>
<td>1g (R¹ = OMe, R² = R³ = H, R⁴ = Ph)</td>
<td>0 °C</td>
<td>8 h</td>
<td>2g (53)</td>
</tr>
<tr>
<td>8</td>
<td>1h (R¹ = R² = OMe, R³ = Me, R⁴ = H)</td>
<td>0 °C</td>
<td>5 min</td>
<td>2h (76)</td>
</tr>
<tr>
<td>9</td>
<td>1i (R¹ = R² = OMe, R³ = Et, R⁴ = Me)</td>
<td>0 °C</td>
<td>6 h</td>
<td>2i (75)</td>
</tr>
<tr>
<td>10</td>
<td>1j (R¹ = R² = OMe, R³ = Ph, R⁴ = Me)</td>
<td>0 °C</td>
<td>8 h</td>
<td>2j (63)</td>
</tr>
</tbody>
</table>

*Isolated yields. bYields based on consumed starting materials.

The use of an equimolar amount of hydriodic acid is essential for the satisfactory production of the desired products. The use of a catalytic amount of hydriodic acid resulted in the recovery of considerable amounts of the starting materials. The necessity of an equimolar amount of hydriodic acid...
may be explained by the mechanism depicted in Scheme 1. Thus, protonation of the vinyl moiety of the starting (1) generates the benzyl cation intermediate (3). Then, the carbonyl oxygen attacks on this cation center to give the more stabilized cationic intermediate (4). Elimination of $t$-butyl group as $t$-butyl iodide gives 2.

In conclusion, we have demonstrated that 4,4-disubstituted 1,4-dihydro-$2H$-3,1-benoxazin-2-ones could be obtained by the hydriodic acid mediated cyclization of $t$-butyl (2-vinylphenyl)carbamate derivatives. In view of the ready availability of the starting materials as well as the ease of operations, the present procedure offers a convenient synthetic method for this class of heterocycles. Studies toward the synthesis of related heterocycles by utilizing the hydriodic acid mediated cyclization of appropriately ortho-substituted styrene derivatives are currently under way in our laboratory.

**EXPERIMENTAL**

The melting points were determined on a Laboratory Devices MEL-TEMP II melting-point apparatus and are uncorrected. The IR spectra were recorded on a Shimadzu FTIR-8300 spectrometer. The $^1$H NMR spectra were determined in CDCl$_3$ using SiMe$_4$ as an internal reference with a JEOL ECP500 FT NMR spectrometer operating at 500 MHz or a JEOL LA400 FT NMR spectrometer operating at 400 MHz. The $^{13}$C NMR spectrum was determined in CDCl$_3$ using TMS as an internal reference with a JEOL ECP500 FT NMR spectrometer operating at 125 MHz. Low-resolution MS spectra (EI, 70 eV) were measured by a JEOL JMS-AX505 HA spectrometer. Thin-layer chromatography (TLC) was carried out on Merck Kieselgel 60 PF$_{254}$. Column chromatography was performed using Merck Kieselgel 60 (0.063–0.200 mm). All of the solvents used were dried over appropriate drying agents and distilled under argon prior to use.

**Starting Materials.** 2-[1-(4-Chlorophenyl)ethenyl]benzenamine,$^5$ 2-[1-(4-methoxyphenyl)ethenyl]benzenamine,$^6$ 4-chloro-2-(1-phenylethenyl)benzenamine,$^7$ 1-(2-amino-4,5-dimethoxyphenyl)-1-propanone,$^8$ and $t$-butyl 2-vinylphenylcarbamates (1a), (1b), (1e), (1g), and (1h)$^3$ were prepared according to the previously reported appropriate procedures. All other chemicals used in this study were commercially available.
t-Butyl 2-[(4-Chlorophenyl)ethenyl]phenylcarbamate (1c). This compound was prepared by treatment of 2-[1-(4-chlorophenyl)ethenyl]benzamine with di-t-butyl dicarbonate in 20% aqueous NaOH–1,4-dioxane (1:1) at 50 °C for 68 h in 64% yield; a pale-yellow oil; R\textsubscript{f} 0.54 (1:5 Et\textsubscript{2}O–hexane); IR (neat) 3426, 1732 cm\textsuperscript{-1}; \textsuperscript{1}H NMR (500 MHz) δ 1.39 (9H, s), 5.36 (1H, d, J = 0.9 Hz), 5.88 (1H, d, J = 0.9 Hz), 6.32 (1H, br s), 7.08 (1H, ddd, J = 7.8, 7.3, 0.9 Hz), 7.16 (1H, ddd, J = 7.8, 1.8 Hz), 7.24 (2H, d, J = 8.7 Hz), 7.28 (2H, d, J = 8.7 Hz), 7.35 (1H, ddd, J = 8.2, 7.3, 1.8 Hz), 7.97 (1H, d, J = 8.2 Hz). Anal. Calcd for C\textsubscript{19}H\textsubscript{20}ClNO\textsubscript{2}: C, 69.19; H, 6.11; N, 4.25. Found: C, 69.06; H, 6.24; N, 4.45.

t-Butyl 2-[(4-Methoxyphenyl)ethenyl]phenylcarbamate (1d). This compound was prepared by treatment of 2-[1-(4-methoxyphenyl)ethenyl]benzamine with di-t-butyl dicarbonate in 20% aqueous NaOH–1,4-dioxane (1:1) at 50 °C for 24 h in 76% yield; a yellow oil; \( R_f 0.48 \) (1:10 Et\textsubscript{2}O–hexane); IR (neat) 3418, 1732, 1607 cm\textsuperscript{-1}; \textsuperscript{1}H NMR (400 MHz) δ 1.39 (9H, s), 3.80 (3H, s), 5.22 (1H, d, J = 1.4 Hz), 5.79 (1H, d, J = 1.4 Hz), 6.47 (1H, br s), 6.83 (2H, d, J = 8.7 Hz), 7.05 (1H, ddd, J = 7.7, 7.3, 1.5 Hz), 7.16 (1H, ddd, J = 7.7, 1.5 Hz), 7.24 (2H, d, J = 8.7 Hz), 7.32 (1H, ddd, J = 7.7, 7.3, 1.5 Hz), 8.01 (1H, d, J = 7.7 Hz). Anal. Calcd for C\textsubscript{20}H\textsubscript{23}NO\textsubscript{2}: C, 73.82; H, 7.12; N, 4.30. Found: C, 73.68; H, 7.25; N, 4.05.

t-Butyl 4-Chloro-2-[(1-phenylethenyl)phenyl]carbamate (1f). This compound was prepared by treatment of 4-chloro-2-[(1-phenylethenyl)benzamine with di-t-butyl dicarbonate in 20% aqueous NaOH–1,4-dioxane (1:1) at 50 °C for 5 d in 54% yield; a pale-yellow oil; \( R_f 0.55 \) (1:20 AcOEt–hexane); IR (neat) 3423, 1732 cm\textsuperscript{-1}; \textsuperscript{1}H NMR (400 MHz) δ 1.37 (9H, s), 5.35 (1H, s), 5.91 (1H, s), 6.37 (1H, br s), 7.17 (1H, d, J = 2.6 Hz), 7.28–7.33 (6H, m), 7.98 (1H, d, J = 8.7 Hz). Anal. Calcd for C\textsubscript{19}H\textsubscript{20}ClNO\textsubscript{2}: C, 69.19; H, 6.11; N, 4.25. Found: C, 69.06; H, 6.40; N, 4.19.

3-(2-Amino-4,5-dimethoxyphenyl)pentan-3-ol. This compound was prepared by the reaction of methyl 2-amino-4,5-dimethoxybenzoate with EtMgBr in Et\textsubscript{2}O at 0 °C in 67% yield; a white solid; mp 94–96 °C (hexane); IR (KBr) 3487, 3452, 3433, 3363, 3344, 1618 cm\textsuperscript{-1}; \textsuperscript{1}H NMR (500 MHz) δ 0.86 (6H, t, J = 7.3 Hz), 1.59 (1H, br), 1.84–1.99 (4H, m), 3.79 (3H, s), 3.82 (3H, s), 4.02 (2H, br), 6.23 (1H, s), 6.56 (1H, s). Anal. Calcd for C\textsubscript{13}H\textsubscript{23}NO\textsubscript{2}: C, 65.25; H, 8.84; N, 5.85. Found: C, 65.23; H, 8.75, N, 5.63.

2-(1-Ethyl-1-propenyl)-4,5-dimethoxybenzene. This compound was prepared by thermal dehydration of 3-(2-amino-4,5-dimethoxyphenyl)pentan-3-ol (150 °C, neat, 1 h) in 60% yield; a mixture of stereoisomers (\( E:Z = ca. 4:6 \)); a colorless oil; \( R_f 0.50 \) (1:3 THF–hexane); IR (neat) 3445, 3364, 1614 cm\textsuperscript{-1}; \textsuperscript{1}H NMR (500 MHz) δ 0.94 (1.8H, t, J = 7.3 Hz), 0.98 (1.2H, t, J = 7.3 Hz), 1.48 (1.2H, d, J = 6.9 Hz), 1.78 (1.8H, d, J = 6.9 Hz), 2.26 (0.8 H, q, J = 7.3 Hz), 2.38 (1.2H, q, J = 7.3 Hz), 3.47 (2H, br), 3.79 (1.8H, s), 3.80 (1.2H, s), 3.83 (1.8H, s), 3.84 (1.2H, s), 5.46 (0.6H, q, J = 6.9 Hz), 5.63 (0.4H, q, J = 6.9 Hz), 6.31 (0.6H, s), 6.33 (0.4H, s), 6.47 (0.4H, s), 6.52 (0.6H, s). Anal. Calcd for C\textsubscript{13}H\textsubscript{19}NO\textsubscript{2}: C, 70.56; H, 8.65; N, 6.33. Found: C, 70.54; H, 8.94, N, 6.25.

t-Butyl 2-(1-Ethyl-1-propenyl)-4,5-dimethoxyphenylcarbamate (1i). This compound was prepared by treatment of 2-(1-ethyl-1-propenyl)-4,5-dimethoxybenzamine with di-t-butyl dicarbonate in 20%
aqueous NaOH–1,4-dioxane (1:1) at 50 °C for 1 h in 87% yield; a mixture of stereoisomers (E:Z = ca. 2:8); a pale-yellow oil; \( R_f \) 0.70 (1:3 THF–hexane); IR (neat) 3421, 3350, 1728, 1612 cm\(^{-1}\); \(^1\)H NMR (500 MHz) \( \delta \) 0.91 (2.4H, t, \( J = 7.3 \) Hz), 0.97 (0.6H, t, \( J = 7.3 \) Hz), 1.44 (0.6H, d, \( J = 6.9 \) Hz), 1.51 (9H, s), 1.81 (2.4H, d, \( J = 6.9 \) Hz), 2.26 (0.4H, q, \( J = 6.9 \) Hz), 2.35 (1.6H, q, \( J = 6.9 \) Hz), 3.827 (2.4H, s), 3.833 (0.6H, s), 3.91 (2.4H, s), 3.92 (0.6H, s), 5.43 (0.8H, q, \( J = 6.9 \) Hz), 5.72 (0.2H, q, \( J = 6.9 \) Hz), 6.40 (0.2H, br s), 6.50 (0.4H, s), 6.54 (1.6H, s), 7.65 (0.8H, br s). Anal. Calcd for C\(_{18}\)H\(_{27}\)NO\(_4\): C, 67.26; H, 8.47; N, 4.36. Found: C, 67.00; H, 8.44, N, 4.33.

1-(2-Amino-4,5-dimethoxyphenyl)-1-phenyl-1-propanol. This compound was prepared by the reaction of 1-(2-amino-4,5-dimethoxyphenyl)-1-propanone\(^a\) with PhMgBr in Et\(_2\)O at 0 °C in 99 % yield; a brown solid; mp 115–117 °C (hexane–CH\(_2\)Cl\(_2\)); IR (KBr) 3436, 3418, 3352, 1614 cm\(^{-1}\); \(^1\)H NMR (500 MHz) \( \delta \) 0.91 (3H, t, \( J = 7.3 \) Hz), 1.43 (1H, s), 2.08–2.15 (1H, m), 2.25–2.32 (1H, m), 3.45 (2H, br), 3.81 (3H, s), 3.88 (3H, s), 6.23 (1H, s), 7.02 (1H, s), 7.22 (1H, tt, \( J = 7.3, 1.4 \) Hz), 7.29 (2H, dd, \( J = 7.8, 7.3 \) Hz), 7.36 (2H, dd, \( J = 7.8, 1.4 \) Hz). Anal. Calcd for C\(_{17}\)H\(_{21}\)NO\(_3\): C, 71.06; H, 7.37; N, 4.87. Found: C, 70.97; H, 7.52, N, 4.82.

4,5-Dimethoxy-2-(1-phenyl-1-propenyl)benzamidine. This compound was prepared by thermal dehydration of 1-(2-amino-4,5-dimethoxyphenyl)-1-phenyl-1-propanol (145 °C, neat, 10 min) in 58% yield; a mixture of stereoisomers (E:Z = ca. 7:3); \( R_f \) 0.36 (1:3 THF–hexane); IR (neat) 3445, 3366, 1614 cm\(^{-1}\); \(^1\)H NMR (500 MHz) \( \delta \) 1.72 (0.9H, d, \( J = 6.9 \) Hz), 1.89 (2.1H, d, \( J = 6.9 \) Hz), 3.36 (2H, br s), 3.77 (0.9H, s), 3.80 (2.1H, s), 3.82 (2.1H, s), 3.87 (0.9H, s), 5.92 (0.7H, q, \( J = 6.9 \) Hz), 6.23 (0.7H, s), 6.35 (0.3H, q, \( J = 6.9 \) Hz), 6.37 (0.3H, s), 6.51 (0.3H, s), 6.64 (0.7H, s), 7.25–7.28 (3H, m), 7.34 (2H, dd, \( J = 7.8, 7.3 \) Hz). Anal. Calcd for C\(_{17}\)H\(_{19}\)NO\(_3\): C, 75.81; H, 7.11; N, 5.20. Found: C, 75.74; H, 7.13; N, 5.34.

t-Butyl 4,5-Dimethoxy-2-(1-ethyl-1-propenyl)phenylcarbamate (1j). This compound was prepared by treatment of 4,5-dimethoxy-2-(1-phenyl-1-propenyl)benzamidine with di-t-butyl dicarbonate in 20% aqueous NaOH–1,4-dioxane (1:1) at 50 °C for 2 h in 63% yield; a mixture of stereoisomers (E:Z = ca. 9:1); \( R_f \) 0.50 (2:9 THF–hexane); IR (neat) 3419, 3356, 1732, 1610 cm\(^{-1}\); \(^1\)H NMR (500 MHz) \( \delta \) 1.38 (8.1H, s), 1.43 (0.9H, s), 1.67 (0.3H, d, \( J = 6.9 \) Hz), 1.94 (2.7H, d, \( J = 6.9 \) Hz), 3.78 (0.3H, s), 3.83 (2.7H, s), 3.90 (2.7H, s), 3.96 (0.3H, s), 5.90 (0.9H, q, \( J = 6.9 \) Hz), 6.28 (0.9H, s), 6.35 (0.1H, s), 6.43 (0.1H, q, \( J = 6.9 \) Hz), 6.51 (0.1H, s), 6.69 (0.9H, s), 7.20–7.27 (3H, m), 7.34 (2H, t, \( J = 7.3 \) Hz), 7.51 (0.9H, br s), 7.78 (0.1H, br s). Anal. Calcd for C\(_{22}\)H\(_{25}\)NO\(_4\): C, 71.52; H, 7.37; N, 3.79. Found: C, 71.31; H, 7.40; N, 3.49.

**General Procedure for the Preparation of Benzoxazinone Derivatives (2).** To a stirred solution of 1 (1.0 mmol) in MeCN (4 mL) at 0 °C was added concentrated hydriodic acid (0.22 g, 1.0 mmol); stirring was continued at the reaction temperature indicated in Table 1. The reaction was monitored by TLC on silica gel (1:3 THF–hexane). After the time indicated in Table 1, saturated aqueous NaHCO\(_3\) (10 mL) was added. MeCN was removed by evaporation, and the organic materials were extracted with Et\(_2\)O.
three times (10 mL each). The combined extracts were washed with brine, dried over anhydrous Na₂SO₄, and evaporated. The residue was purified by recrystallization or preparative TLC on silica gel to give 2.

4,4-Dimethyl-1,4-dihydro-2H-3,1-benzoxazin-2-one (2a): This compound was isolated by preparative TLC on silica gel (1:2 THF–hexane); a white solid; mp 112–114 ºC (hexane–Et₂O) (lit., 3 111–113 ºC; lit., 9 115–116 ºC). The spectral data for this compound were identical to those reported previously. 3

4-Methyl-4-phenyl-1,4-dihydro-2H-3,1-benzoxazin-2-one (2b): This compound was isolated by recrystallization; a white solid; mp 219–221 ºC (THF) (lit., 3 219–221 ºC). The spectral data for this compound were identical to those reported previously. 3

4-(4-Chlorophenyl)-4-methyl-1,4-dihydro-2H-3,1-benzoxazin-2-one (2c): This compound was isolated by recrystallization; a white solid; mp 169–170 ºC (hexane–CH₂Cl₂); IR (KBr) 3235, 1716 cm⁻¹; 1H NMR (500 MHz) δ 2.03 (3H, s), 6.85 (1H, d, J = 7.8 Hz), 7.16 (1H, ddd, J = 7.8, 7.3, 0.9 Hz), 7.22 (2H, d, J = 8.7 Hz), 7.25–7.28 (3H, m), 7.33 (1H, ddd, J = 7.8, 7.3, 1.4 Hz), 8.21 (1H, br s); MS m/z 273 (M⁺, 46), 228 (100). Anal. Calcd for C₁₇H₁₄ClNO₂: C; 65.82; H, 4.42; N, 5.12. Found: C, 65.73; H, 4.42; N, 5.01.

4-(4-Methoxyphenyl)-4-methyl-1,4-dihydro-2H-3,1-benzoxazin-2-one (2d): This compound was isolated by recrystallization; a pale-yellow solid; mp 169–170 ºC (hexane–CH₂Cl₂); IR (KBr) 3248, 1716 cm⁻¹; 1H NMR (400 MHz) δ 2.02 (3H, s), 3.77 (3H, s), 6.81 (2H, d, J = 8.8 Hz), 6.83 (1H, d, J = 7.7 Hz), 7.12 (1H, ddd, J = 7.7, 7.3 Hz), 7.19 (2H, d, J = 8.8 Hz), 7.23 (1H, d, J = 7.7 Hz), 7.30 (1H, ddd, J = 7.7, 7.3, 1.5 Hz), 8.09 (1H, br s); MS m/z 269 (M⁺, 21), 224 (65), 210 (100). Anal. Calcd for C₁₇H₁₃NO₃: C; 71.36; H, 5.61; N, 5.20. Found: C, 71.16; H, 5.50; N, 5.56.

7-Fluoro-4,4-dimethyl-1,4-dihydro-2H-3,1-benzoxazin-2-one (2e): This compound was isolated by recrystallization; a white solid; mp 140–142 ºC (hexane–Et₂O) (lit., 3 140–142 ºC). The spectral data for this compound were identical to those reported previously. 3

6-Chloro-4-methyl-4-phenyl-1,4-dihydro-2H-3,1-benzoxazin-2-one (2f): This compound was isolated by preparative TLC on silica gel (1:3 AcOEt–hexane); a pale-yellow solid; mp 222–224 ºC (hexane–CHCl₃); IR (KBr) 3198, 1714 cm⁻¹; 1H NMR (400 MHz) δ 2.02 (3H, s), 6.80 (1H, J = 8.4 Hz), 7.17–7.36 (7H, m), 8.44 (1H, br s); MS m/z 273 (M⁺, 44), 228 (100). Anal. Calcd for C₁₅H₁₂ClNO₂: C, 65.82; H, 4.42; N, 5.12. Found: C, 65.52; H, 4.43; N, 5.03.

6-Methoxy-4-methyl-4-phenyl-1,4-dihydro-2H-3,1-benzoxazin-2-one (2g): This compound was isolated by recrystallization; a white solid; mp 164–166 ºC (hexane–CHCl₃) (lit., 3 164–166 ºC). The spectral data for this compound were identical to those reported previously. 3

6,7-Dimethoxy-4,4-dimethyl-1,4-dihydro-2H-3,1-benzoxazin-2-one (2h): This compound was isolated by recrystallization; a white solid; mp 136–138 ºC (hexane–CHCl₃) (lit., 3 136–138 ºC). The spectral data for this compound were identical to those reported previously. 3
4,4-Diethyl-6,7-dimethoxy-1,4-dihydro-2H-3,1-benzoxazin-2-one (2i): This compound was isolated by recrystallization; a white solid; mp 175–177 °C (hexane–CHCl₃); IR (KBr) 3217, 1712, 1611 cm⁻¹; ¹H NMR (500 MHz) δ 0.90 (6H, t, J = 7.3 Hz), 1.88–2.06 (4H, m), 3.85 (3H, s), 3.87 (3H, s), 6.35 (1H, s), 6.47 (1H, s), 8.65 (1H, s); ¹³C NMR δ 7.90, 33.35, 56.15, 56.70, 89.76, 98.81, 108.18, 112.76, 129.05, 145.17, 149.55, 153.32; MS m/z 265 (M⁺, 19), 236 (100). Anal. Calcd for C₁₄H₁₉NO₄: C, 63.38; H, 7.22; N, 5.28%. Found: C, 63.19; H, 7.13; N, 5.13%.

4-Ethyl-6,7-dimethoxy-4-phenyl-1,4-dihydro-2H-3,1-benzoxazin-2-one (2j): This compound was isolated by recrystallization; a white solid; mp 197–199 °C (hexane–CH₂Cl₂); IR (KBr) 3215, 1720, 1626, 1612 cm⁻¹; ¹H NMR (500 MHz) δ 1.06 (3H, t, J = 7.3 Hz), 2.25–2.37 (2H, m), 3.88 (3H, s), 3.89 (3H, s), 6.37 (1H, s), 6.77 (1H, s), 7.28–7.30 (5H, m), 8.20 (1H, br s); MS m/z 313 (M⁺, 37), 284 (100). Anal. Calcd for C₁₈H₁₉NO₄: C, 68.99; H, 6.11; N, 4.47. Found: C, 68.96; H, 6.35; N, 4.38.

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REFERENCES AND NOTES