SYNTHESIS OF 1-AROYL-1,2-DIHYDRO-3H-INDOL-3-ONES VIA CYCLIZATION OF N-[2-(2-CHLOROACETYL)PHENYL]BENZAMIDES WITH TRIETHYLAMINE IN THE PRESENCE OF DI-tert-BUTYL DICARBONATE

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Abstract – 1-Aroyl-1,2-dihydro-3H-indol-3-ones can now be conveniently obtained from 2-aryl-4-(Z)-(chloromethylidene)-4H-3,1-benzoxazines using an easy operated three-step sequence under mild conditions. Thus, the starting materials are hydrolyzed with dilute hydrochloric acid at 0 °C to N-[2-(2-chloroacetyl)phenyl]benzamides, of which treatment with triethylamine in the presence of di-tert-butyl dicarbonate at room temperature, followed by deprotection with trifluoroacetic acid at room temperature, provides the desired products.

INTRODUCTION

1,2-Dihydro-3H-indol-3-one derivatives are an important class of heterocycles. Some of these derivatives have been utilized in the synthesis of a number of more structurally complex and/or biologically important compounds. An interesting natural product having this skeleton has been found in nature. Accordingly, some practical methods for the preparation of this class of heterocycles have been developed. Recently, Shu et al. demonstrated the use of gold-catalyzed intermolecular oxidation of o-ethynylanilines, and more recently Gandy et al. reported a synthesis of 1-acetyl-1,2-dihydro-3H-indol-3-ones by the reaction of N-(2-cyanophenyl)glycine ethyl esters with acetic anhydride. On the other hand, we previously reported that N-(2,2-dichloroethenyl)(het)arenecarboxamides underwent intramolecular cyclization on treatment with sodium hydride to afford 2-(het)aryl-4-(Z)-(chloromethylidene)-4H-3,1-benzoxazines (I). As an extensive investigation of this study, we wish to describe here a convenient synthetic approach to 1,2-dihydro-3H-indol-3-one derivatives. We have found
that 1-(het)aryl-1,2-dihydro-3H-indol-3-ones (4) can be formed by cyclization of \(N\)-[2-(2-chloroacetyl)phenyl](het)arenecarboxamides (2), which can be readily obtained by acid hydrolysis of 1.

**RESULTS AND DISCUSSION**

Our synthesis of 4 from 1 was carried out according to the sequence illustrated in Scheme 1. The first step in the present procedure was hydrolysis of 1, which were easily prepared from 2-(2,2-dichloroethenyl)benzenamines according to the procedure reported previously by us.\(^9\) These amines were easily accessible from readily available starting materials, 2-nitrobenzaldehydes, by the established procedure.\(^10\) Hydrolysis of 1 with 10% aqueous hydrochloric acid in THF proceeded smoothly and cleanly at 0 °C to give 2 in generally good yields as compiled in Table 1, while the yield of the pyridine-3-carboxamide derivative (2i) was moderate (Entry 9).

![Scheme 1](image)

<table>
<thead>
<tr>
<th>Entry</th>
<th>1</th>
<th>2</th>
<th>Yield/%(^a)</th>
<th>4</th>
<th>Yield/%(^a,b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1a (R = H, Ar = Ph)</td>
<td>2a</td>
<td>94</td>
<td>4a</td>
<td>63</td>
</tr>
<tr>
<td>2</td>
<td>1b (R = H, Ar = m-Tol)</td>
<td>2b</td>
<td>98</td>
<td>4b</td>
<td>59</td>
</tr>
<tr>
<td>3</td>
<td>1c (R = H, Ar = p-Tol)</td>
<td>2c</td>
<td>97</td>
<td>4c</td>
<td>60</td>
</tr>
<tr>
<td>4</td>
<td>1d (R = H, Ar = 2-ClC(_6)H(_4))</td>
<td>2d</td>
<td>91</td>
<td>4d</td>
<td>57</td>
</tr>
<tr>
<td>5</td>
<td>1e (R = H, Ar = 4-ClC(_6)H(_4))</td>
<td>2e</td>
<td>93</td>
<td>4e</td>
<td>59</td>
</tr>
<tr>
<td>6</td>
<td>1f (R = H, Ar = 2,4-Cl(_2)C(_6)H(_4))</td>
<td>2f</td>
<td>94</td>
<td>4f</td>
<td>75</td>
</tr>
<tr>
<td>7</td>
<td>1g (R = H, Ar = 3-MeOC(_6)H(_4))</td>
<td>2g</td>
<td>90</td>
<td>4g</td>
<td>59</td>
</tr>
<tr>
<td>8</td>
<td>1h (R = H, Ar = thiophen-2-yl)</td>
<td>2h</td>
<td>98</td>
<td>4h</td>
<td>62</td>
</tr>
<tr>
<td>9</td>
<td>1i (R = H, Ar = pyridin-3-yl)</td>
<td>2i</td>
<td>56</td>
<td>4i</td>
<td>56</td>
</tr>
<tr>
<td>10</td>
<td>1j (R = Cl, Ar = 4-ClC(_6)H(_4))</td>
<td>2j</td>
<td>72</td>
<td>4j</td>
<td>60</td>
</tr>
<tr>
<td>11</td>
<td>1k (R = OMe, Ar = Ph)</td>
<td>2k</td>
<td>83</td>
<td>4k</td>
<td>35(^c)</td>
</tr>
</tbody>
</table>

\(^a\) Yields of isolated products. \(^b\) Overall yields from 2. \(^c\) This product was obtained directly from 2k on treatment with NaH in DME at 0 °C.
The second part of the sequence was cyclization of 2. In 1979, Sugasawa et al. reported the synthesis of 1-acetyl-1,2-dihydro-3\textit{H}-indol-3-one by the reaction of \textit{N}-[(2-chloroacetyl)phenyl]acetamide with sodium hydride in 1,2-dimethoxylethane (DME) at 0 °C in relatively good yield.\textsuperscript{5} We first subjected substrate (2\textsuperscript{a}) to these reaction conditions. Unfortunately, however, the reaction did proceed uncleanly to give the desired corresponding product 1-benzoyl-1,2-dihydro-3\textit{H}-indol-3-one (4\textsuperscript{a}) only in 15% yield. The reaction was then conducted using triethylamine in DMF at 0 °C; only 10% yield of 4\textsuperscript{a} was obtained. Subsequently, cyclization of 2\textsuperscript{a} with two equivalents of triethylamine in DMF at room temperature in the presence of an equivalent of di-\textit{tert}-butyl dicarbonate was attempted. By using these conditions, compounds 2\textsuperscript{a} was converted into 1-benzoyl-\textit{1H}-indol-3-yl 1,1-dimethylethyl carbonate (3\textsuperscript{a}) in 69% yield. It is thought that the protection as 1,1-dimethylethyl carbonate depresses the self-condensation of the initially formed 4\textsuperscript{a}. This carbonate was converted into 4\textsuperscript{a} in an almost quantitative yield through deprotection with trifluoroacetic acid (TFA) at room temperature.

In order to make this methodology more practical, the two steps were carried out without isolation of 3\textsuperscript{a}. Thus, the crude reaction mixture containing 3\textsuperscript{a} was subjected to the deprotection without any purification after aqueous workup. The desired product 4\textsuperscript{a} was isolated in 63% overall yield from 2\textsuperscript{a} (Table 1, Entry 1). Other nine \textit{N}-[2-(2-chloroacetyl)phenyl] amides (2\textsuperscript{b}–2\textsuperscript{j}) were similarly converted into the corresponding 1-(het)aroyle-1,2-dihydro-3\textit{H}-indol-3-ones (4\textsuperscript{b}–4\textsuperscript{j}) in comparable yields (Entries 2-10).

It is notable that the treatment of \textit{N}-[2-(2-chloroacetyl)phenyl]-4-methoxybenzamide (2\textsuperscript{k}) with di-\textit{tert}-butyl dicarbonate under the above-mentioned cyclization conditions resulted in the formation of a considerably intractable mixture of products and that only a trace amount of the corresponding 3-((\textit{tert}-butoxycarbonyloxy))-1\textit{H}-indole derivative (3\textsuperscript{k}) was observed in it as judged by TLC analyses on silica gel. However, when 2\textsuperscript{k} was treated with sodium hydride in 1,2-dimethoxylethane (DME) at 0 °C, 1-benzoyl-5-methoxy-1,2-dihydro-3\textit{H}-indol-3-one (4\textsuperscript{k}) was directly obtained albeit in relatively low yield (Scheme 2). This different reactivity of 2\textsuperscript{k} from the other \textit{N}-[2-(2-chloroacetyl)phenyl] amides (2\textsuperscript{a}–2\textsuperscript{j}) is incomprehensible; we cannot provide any reasons for it.

![Scheme 2](image_url)

In conclusion, a convenient procedure for the synthesis of 1-(het)aroyle-1,2-dihydro-3\textit{H}-indol-3-ones has been developed. As the procedure is experimentally very simple and the reactions can be run under mild reaction conditions, it is of value in organic synthesis. Further elaboration of the aforementioned
N-[(2-chloroacetyl)phenyl](het)arenecarboxamides to functionalized heterocycles, hard to prepare by previous methods, is under way.

EXPERIMENTAL

All melting points were obtained on a Laboratory Devices MEL-TEMP II melting apparatus and are uncorrected. IR spectra were recorded with a Perkin–Elmer Spectrum 65 FTIR spectrophotometer. \(^{1}\)H NMR and \(^{13}\)C NMR spectra were recorded in CDCl\(_3\) using TMS as an internal reference with a JEOL ECP500 FT NMR spectrometer operating at 500 and 125 MHz, respectively. High-resolution MS spectra were measured by a Thermo Scientific Exactive spectrometer (DART or ESI, positive) or a JEOL JMS-T100GCV (EI, TOF; 70eV) spectrometer. Elemental analyses were performed with an Elementar Vario EL II instrument. TLC was carried out on Merck Kieselgel 60 PF\(_{254}\). Column chromatography was performed using WAKO GEL C-200E. All of the organic solvents used in this study were dried over appropriate drying agents and distilled prior to use.

Starting Materials. 2-(2,2-Dichloroethenyl)benzenamine\(^{10}\) and 5-methoxy-2-nitrobenzaldehyde\(^{11}\) were prepared according to the reported procedure. All other chemicals used in this study were commercially available.

4-Chloro-2-(2,2-dichloroethenyl)benzenamine. This compound was prepared from 5-chloro-2-nitrobenzaldehyde by the same procedure for the preparation of 2-(2,2-dichloroethenyl)benzenamine from 2-nitrobenzaldehyde.\(^{10}\) Yield: 69%; a yellow oil: \(R_f\) 0.42 (AcOEt/hexane 1:5); IR (neat) 3474, 3391, 1623 cm\(^{-1}\); \(^{1}\)H NMR \(\delta\) 3.70 (br s, 2H), 6.64 (d, \(J = 8.6\) Hz, 1H), 6.68 (s, 1H), 7.09 (dd, \(J = 8.6, 2.3\) Hz, 1H), 7.31 (d, \(J = 2.3\) Hz, 1H). HR-MS (EI). Calcd for C\(_8\)H\(_6\)Cl\(_3\)N (M): 220.9566. Found: \(m/z\) 220.9574.

2-(2,2-Dichloroethenyl)-4-methoxybenzenamine. This compound was prepared from 5-methoxy-2-nitrobenzaldehyde by the same procedure for the preparation of 2-(2,2-dichloroethenyl)benzenamine from 2-nitrobenzaldehyde.\(^{10}\) Yield: 60%; a yellow oil: \(R_f\) 0.30 (CH\(_2\)Cl\(_2\)/hexane 5:1); IR (neat) 3437, 3391, 1623 cm\(^{-1}\); \(^{1}\)H NMR \(\delta\) 3.45 (br s, 2H), 3.76 (s, 3H), 6.67 (d, \(J = 8.6\) Hz, 1H), 6.76 (dd, \(J = 9.2, 2.9\) Hz, 1H), 6.78 (s, 1H), 6.95 (d, \(J = 2.9\) Hz, 1H). HR-MS (EI). Calcd for C\(_9\)H\(_9\)Cl\(_2\)NO (M): 217.0061. Found: \(m/z\) 217.0053.

2-Aryl-4-(Z)-(chloromethylidene)-4\(H\)-3,1-benzoxazines (1). These compounds were prepared from the respective 2-(2,2-dichloroethenyl)benzenamines and (het)aroyl chlorides, via N-[2-(2,2-dichloroethenyl)phenyl](het)arenecarboxamides, according to the reported procedure.\(^{9}\) The physical, spectral, and analytical data for new compounds follow.

N-[2-(2,2-Dichloroethenyl)phenyl]-3-methylbenzamide: yield 82%; a white solid; mp 86–88 °C (hexane/CH\(_2\)Cl\(_2\)); IR (KBr) 3198, 1639, 1601 cm\(^{-1}\); \(^{1}\)H NMR \(\delta\) 2.46 (s, 3H), 6.90 (s, 1H), 7.22 (t, \(J = 7.4\) Hz, 1H), 7.30 (d, \(J = 2.3\) Hz, 1H), 7.35 (d, \(J = 2.3\) Hz, 1H), 7.60 (s, 1H), 7.67 (d, \(J = 2.3\) Hz, 1H), 7.70 (d, \(J = 8.6\) Hz, 1H), 7.80 (s, 1H), 7.85 (d, \(J = 8.6\) Hz, 1H), 7.90 (t, \(J = 7.4\) Hz, 1H), 7.95 (s, 1H), 8.00 (d, \(J = 2.3\) Hz, 1H). HR-MS (EI). Calcd for C\(_{18}\)H\(_{14}\)Cl\(_2\)N (M): 315.8304. Found: \(m/z\) 315.8315.
Hz, 1H), 7.40–7.45 (m, 5H), 7.65 (d, J = 6.3 Hz, 1H), 7.71 (s, 1H), 8.08 (d, J = 8.0 Hz, 1H). Anal. Calcd for C_{16}H_{13}Cl_{2}NO: C, 62.76; H, 4.28; N, 4.57. Found: C, 62.74; H, 4.46; N, 4.51.

4-(Z)-(Chloromethylidene)-2-(3-methylphenyl)-4H-3,1-benzoxazine (1b): yield: 62%; a white solid; mp 105–107 °C (hexane/CH_{2}Cl_{2}); IR (KBr) 3114, 1638, 1611 cm⁻¹; ¹H NMR δ 2.44 (s, 3H), 5.96 (s, 1H), 7.20 (td, J = 8.0, 2.3 Hz, 1H), 7.35–7.39 (m, 5H), 8.05 (d, J = 8.0 Hz, 1H), 8.06 (s, 1H); ¹³C NMR δ 21.43, 92.44, 119.41, 121.12, 125.19, 126.87, 127.68, 128.36, 128.47, 130.78, 130.91, 132.85, 138.17, 138.26, 146.22, 154.22. HR-MS (EI). Calcd for C_{16}H_{12}Cl_{2}NO (M): 269.0607. Found: m/z 269.0617.

N-[2-(2,2-Dichloroethenyl)phenyl]-4-methylbenzamide: yield: 83%; a white solid; mp 142–144 °C (hexane/CH_{2}Cl_{2}); IR (KBr) 3309, 1641, 1612 cm⁻¹; ¹H NMR δ 2.45 (s, 3H), 6.89 (s, 1H), 7.22 (dd, J = 8.0, 7.4 Hz, 1H), 7.32 (d, J = 8.0 Hz, 2H), 7.41 (dt, J = 8.0, 7.4 Hz, 1H), 7.44 (d, J = 8.0 Hz, 1H), 7.71 (br s, 1H), 7.78 (d, J = 8.0 Hz, 2H), 8.09 (d, J = 8.0 Hz, 1H). HR-MS (EI). Calcd for C_{16}H_{13}Cl_{2}NO (M): 305.0374. Found: m/z 305.0376.

4-(Z)-(Chloromethylidene)-2-(4-methylphenyl)-4H-3,1-benzoxazine (1c): yield: 72%; a white solid; mp 97–99 °C (hexane/CH_{2}Cl_{2}); IR (KBr) 3121, 1639, 1613 cm⁻¹; ¹H NMR δ 2.42 (s, 3H), 5.94 (s, 1H), 7.19 (ddd, J = 8.0, 7.4, 1.7 Hz, 1H), 7.28 (d, J = 8.6 Hz, 2H), 7.33–7.36 (m, 3H), 8.14 (d, J = 8.6 Hz, 2H); ¹³C NMR δ 21.66, 92.33, 119.34, 121.11, 126.78, 127.52, 127.98, 128.09, 129.19, 130.89, 138.36, 142.58, 146.24, 154.17. Anal. Calcd for C_{16}H_{12}ClNO: C, 71.25; H, 4.48; N, 5.19. Found: C, 70.99; H, 4.52; N, 5.13.

2-Chloro-N-[2-(2,2-dichloroethenyl)phenyl]benzamide: yield: 89%; a white solid; mp 90–93 °C (hexane/CH_{2}Cl_{2}); IR (KBr) 3210, 1644, 1615 cm⁻¹; ¹H NMR δ 6.95 (s, 1H), 7.25 (t, J = 7.4 Hz, 1H), 7.41–7.50 (m, 5H), 7.87 (dd, J = 7.4, 1.7 Hz, 1H), 7.94 (br, 1H), 8.13 (d, J = 8.6 Hz, 1H). Ana. Calcd for C_{15}H_{10}Cl_{3}NO: C, 55.16; H, 3.09; N, 4.29. Found: C, 55.13; H, 3.21; N, 4.07.

4-(Chloromethylidene)-2-(2-chlorophenyl)-3,1-benzoxazine (1d): yield: 67%; a white solid; mp 93–95 °C (hexane/CH_{2}Cl_{2}); IR (KBr) 3107, 1645, 1618 cm⁻¹; ¹H NMR δ 5.98 (s, 1H), 7.26 (t, J = 7.6 Hz, 1H), 7.36–7.44 (m, 5H), 7.50 (d, J = 8.0 Hz, 1H), 7.89 (d, J = 7.4 Hz, 1H); ¹³C NMR δ 92.88, 119.31, 121.11, 126.74, 127.07, 128.46, 130.84, 130.94, 130.99, 131.21, 131.87, 133.41, 137.61, 146.17, 153.89. HR-MS (DART). Calcd for C_{15}H_{10}Cl_{2}NO (M+H): 290.0134. Found: m/z 290.0132.

4-Chloro-N-[2-(2,2-dichloroethenyl)phenyl]benzamide: yield: 89%; a white solid; mp 143–145 °C (hexane/CH_{2}Cl_{2}); IR (KBr) 3267, 1655, 1616 cm⁻¹; ¹H NMR δ 6.88 (s, 1H), 7.24 (dd, J = 8.0, 7.4 Hz, 1H), 7.42 (dd, J = 8.0, 7.4 Hz, 1H), 7.44 (d, J = 8.0 Hz, 1H), 7.50 (d, J = 8.6 Hz, 2H), 7.68 (br s, 1H), 7.82 (d, J = 8.6 Hz, 2H), 8.04 (d, J = 8.0 Hz, 1H). Ana. Calcd for C_{15}H_{10}Cl_{3}NO: C, 55.16; H, 3.09; N, 4.29. Found: C, 55.14; H, 3.38; N, 4.07.
4-(Chloromethylidene)-2-(4-chlorophenyl)-3,1-benzoxazine (1e): yield: 64%; a yellow solid; mp 162–165 °C (hexane/CH₂Cl₂); IR (KBr) 3104, 1644, 1613 cm⁻¹; ¹H NMR δ 5.97 (s, 1H), 7.24 (ddd, J = 8.6, 8.0, 1.7 Hz, 1H), 7.35–7.41 (m, 3H), 7.46 (d, J = 9.2 Hz, 2H), 8.19 (d, J = 9.2 Hz, 2H); ¹³C NMR δ 92.73, 119.30, 121.14, 126.91, 127.94, 128.74, 129.26, 129.30, 131.00, 137.91, 138.22, 146.01, 153.03. HR-MS (EI). Calcd for C₁₅H₉Cl₂NO (M): 289.0061. Found: m/z 289.0061.

2,4-Dichloro-N-[2-(2,2-dichloroethenyl)phenyl]benzamide: yield: 89%; a white solid; mp 127–129 °C (hexane/CH₂Cl₂); IR (KBr) 3173, 1654 cm⁻¹; ¹H NMR δ 6.92 (s, 1H), 7.25 (dd, J = 8.0, 7.4 Hz, 1H), 7.40–7.47 (m, 3H), 7.51 (d, J = 1.7 Hz, 1H), 7.84 (d, J = 8.0 Hz, 1H), 7.95 (br s, 1H), 8.10 (d, J = 8.0 Hz, 1H). Anal. Calcd for C₁₅H₉Cl₄NO: C, 49.90; H, 2.51; N, 3.88. Found: C, 49.90; H, 2.84; N, 3.81.

4-(Chloromethylidene)-2-(2,4-dichlorophenyl)-3,1-benzoxazine (1f): yield: 64%; a white solid; mp 154–156 °C (hexane/CH₂Cl₂); IR (KBr) 3116, 1635, 1618 cm⁻¹; ¹H NMR δ 5.97 (s, 1H), 7.26 (ddd, J = 8.0, 7.4, 1.7 Hz, 1H), 7.34–7.40 (m, 4H), 7.52 (d, J = 1.7 Hz, 1H), 7.87 (d, J = 8.6 Hz, 1H); ¹³C NMR δ 93.07, 119.32, 121.14, 127.13 (two overlapped Cs), 128.62, 129.19, 130.91, 131.04, 132.17, 134.47, 137.45, 137.49, 146.10, 152.93. Anal. Calcd for C₁₅H₈Cl₃NO: C, 55.51; H, 2.48; N, 4.32. Found: C, 55.31; H, 2.74; N, 4.26.

N-[2-(2,2-Dichloroethenyl)phenyl]-3-methoxybenzamide: yield: 94%; a white solid; mp 112–114 °C (hexane/CH₂Cl₂); IR (KBr) 3241, 1635, 1621 cm⁻¹; ¹H NMR δ 3.90 (s, 3H), 6.90 (s, 1H), 7.11–7.14 (m, 1H), 7.23 (td, J = 7.4, 1.1 Hz, 1H), 7.39–7.47 (m, 5H), 7.74 (br, 1H), 8.10 (d, J = 8.0 Hz, 1H). HR-MS (EI). Calcd for C₁₆H₁₃Cl₂NO₂ (M): 321.0323. Found: m/z 321.0318.

4-(Chloromethylidene)-2-(3-methoxyphenyl)-3,1-benzoxazine (1g): yield: 85%; a pale-yellow solid; mp 108–110 °C (hexane/CH₂Cl₂); IR (KBr) 3108, 1637, 1615 cm⁻¹; ¹H NMR δ 3.91 (s, 3H), 5.95 (s, 1H), 7.09 (dd, J = 8.0, 1.7 Hz, 1H), 7.19–7.22 (m, 1H), 7.34–7.40 (m, 4H), 7.79 (d, J = 1.1 Hz, 1H), 7.85 (dd, J = 8.0, 1.1 Hz, 1H); ¹³C NMR δ 55.37, 92.50, 112.36, 118.51, 119.37, 119.37, 120.49, 121.11, 126.90, 127.79, 129.46, 130.92, 132.14, 138.10, 146.12, 153.78, 159.53. Anal. Calcd for C₁₆H₁₂ClNO₂: C, 67.26; H, 4.23; N, 4.90. Found: C, 67.32; H, 4.09; N, 4.66.

N-[2-(2,2-Dichloroethenyl)phenyl]pyridine-3-carboxamide: yield: 87%; a yellow oil; Rₛ 0.36 (AcOEt/hexane 5:1); IR (neat) 3263, 1652 cm⁻¹; ¹H NMR δ 6.90 (s, 1H), 7.09 (dd, J = 8.0, 1.7 Hz, 1H), 7.19–7.22 (m, 1H), 7.34–7.40 (m, 4H), 7.79 (d, J = 1.1 Hz, 1H); ¹³C NMR δ 55.37, 92.50, 112.36, 118.51, 119.37, 120.49, 121.11, 126.90, 127.79, 129.46, 130.92, 132.14, 138.10, 146.12, 153.78, 159.53. Anal. Calcd for C₁₆H₁₄Cl₂N₂O: C, 67.26; H, 4.23; N, 4.90. Found: C, 67.32; H, 4.09; N, 4.66.

N-[2-(2,2-Dichloroethenyl)phenyl]pyridine-3-carboxamide: yield: 87%; a yellow oil; Rₛ 0.36 (AcOEt/hexane 5:1); IR (neat) 3263, 1652 cm⁻¹; ¹H NMR δ 6.90 (s, 1H), 7.24 (t, J = 7.4 Hz, 1H), 7.41–7.50 (m, 3H), 7.78 (br s, 1H), 8.04 (d, J = 7.4 Hz, 1H), 8.22 (d, J = 8.0 Hz, 1H), 8.81 (dd, J = 4.6, 1.1 Hz, 1H), 9.10 (s, 1H). HR-MS (EI). Calcd for C₁₄H₁₀Cl₂N₂O (M): 292.0170. Found: m/z 292.0160.

4-(Chloromethylidene)-2-(pyridin-3-yl)-3,1-benzoxazine (1i): yield: 56%; a white solid; mp 104–106 °C (hexane/CH₂Cl₂); IR (KBr) 3087, 1640, 1616 cm⁻¹; ¹H NMR δ 5.99 (s, 1H), 7.24 (td, J = 6.9, 1.7 Hz, 1H), 7.27–7.43 (m, 4H), 8.48 (dd, J = 8.0, 2.3, 1.7 Hz, 1H), 8.76 (d, J = 3.4 Hz, 1H), 9.45 (s, 1H); ¹³C NMR δ 93.19, 119.50, 121.91, 123.21, 126.90, 127.09, 128.30, 131.06, 135.17, 137.61, 145.84, 149.43,
152.22, 152.39. Anal. Calcd for C\textsubscript{14}H\textsubscript{9}ClN\textsubscript{2}O: C, 65.51; H, 3.53; N, 10.91. Found: C, 65.45; H, 3.46; N, 10.83.

4-Chloro-N-[4-chloro-2-(2,2-dichloroethyl)phenyl]benzamide: yield: 74%; a white solid; mp 153–154 °C (hexane/CH\textsubscript{2}Cl\textsubscript{2}); IR (KBr) 3271, 1652 cm\textsuperscript{-1}; \textsuperscript{1}H NMR \(\delta\) 6.82 (s, 1H), 7.38 (dd, \(J = 8.6, 2.3\) Hz, 1H), 7.43 (d, \(J = 2.3\) Hz, 1H), 7.50 (d, \(J = 8.6\) Hz, 2H), 7.63 (br s, 1H), 7.80 (d, \(J = 8.6\) Hz, 2H), 8.03 (d, \(J = 8.6\) Hz, 1H). Anal. Calcd for C\textsubscript{15}H\textsubscript{9}Cl\textsubscript{4}NO: C, 49.90; H, 2.51; N, 3.88. Found: C, 49.67; H, 2.76; N, 3.79.

6-Chloro-4-(chloromethylidene)-2-(4-chlorophenyl)-3,1-benzoxazine (1j). This compound was isolated by filtration and washing with water after addition of saturated aqueous NH\textsubscript{4}Cl to the reaction mixture in 85% yield; a white solid; mp 223–225 °C (THF); IR (KBr) 3119, 1645, 1617 cm\textsuperscript{-1}. This compound was of quite insolubility in most organic solvents. HR-MS (EI). Calcd for C\textsubscript{15}H\textsubscript{8}Cl\textsubscript{3}NO (M): 322.9671. Found: \textit{m}/\textit{z} 322.9687.

N-[2-(2,2-Dichloroethyl)phenyl-4-methoxy]benzamide: yield: 86%; a white solid; mp 131–133 °C (hexane/CH\textsubscript{2}Cl\textsubscript{2}); IR (KBr) 3335, 1645, 1616 cm\textsuperscript{-1}; \textsuperscript{1}H NMR \(\delta\) 3.83 (s, 3H), 6.88 (s, 1H), 6.95 (dd, \(J = 8.6, 2.9\) Hz, 1H), 7.04 (d, \(J = 2.9\) Hz, 1H), 7.51 (t, \(J = 7.4\) Hz, 2H), 7.58 (t, \(J = 7.4\) Hz, 1H), 7.59 (br s, 1H), 7.80 (d, \(J = 8.6\) Hz, 1H), 7.87 (d, \(J = 7.4\) Hz, 2H). HR-MS (EI). Calcd for C\textsubscript{16}H\textsubscript{13}Cl\textsubscript{2}NO\textsubscript{2} (M): 321.0323. Found: \textit{m}/\textit{z} 321.0318.

4-(Chloromethylidene)-6-methoxy-2-phenyl-3,1-benzoxazine (1k): yield: 99%; a white solid; mp 92–94 °C (hexane/CH\textsubscript{2}Cl\textsubscript{2}); IR (KBr) 3110, 1642, 1613 cm\textsuperscript{-1}; \textsuperscript{1}H NMR \(\delta\) 3.83 (s, 3H), 5.93 (s, 1H), 6.82 (d, \(J = 2.9\) Hz, 1H), 6.94 (dd, \(J = 8.6, 2.9\) Hz, 1H), 7.32 (d, \(J = 8.6\) Hz, 1H), 7.46–7.52 (m, 3H), 8.23 (dd, \(J = 7.4, 1.7\) Hz, 2H); \textsuperscript{13}C NMR \(\delta\) 55.59, 92.44, 105.30, 117.22, 120.11, 127.68, 128.31, 128.41, 131.03, 131.60, 131.99, 146.20, 152.26, 158.93. Anal. Calcd for C\textsubscript{16}H\textsubscript{12}ClNO\textsubscript{2}: C, 67.26; H, 4.23; N, 4.90. Found: C, 66.99; H, 4.29; N, 4.83.

Typical Procedure for the Preparation of N-[2-(2-Chloroacetyl)phenyl]benzamides (2). N-[2-(2-Chloroacetyl)phenyl]benzamide (2a). A solution of 1a (1.1 g, 4.4 mmol) in THF (12 mL) containing 10% aqueous HCl (1.5 mL) was stirred at rt for 5.5 h. Saturated aqueous NaHCO\textsubscript{3} (30 mL) was added and the mixture was extracted with AcOEt (3 \times 25 mL). The combined extracts were washed with brine (30 mL), dried (Na\textsubscript{2}SO\textsubscript{4}), and concentrated by evaporation. The residual solid was recrystallized from hexane/CH\textsubscript{2}Cl\textsubscript{2} to give 2a (1.1 g, 94%); a white solid; mp 136–138 °C; IR (KBr) 3240, 1674, 1661, 1611 cm\textsuperscript{-1}; \textsuperscript{1}H NMR \(\delta\) 4.85 (s, 2H), 7.20 (dd, \(J = 8.0, 7.4, 1.1\) Hz, 1H), 7.53–7.59 (m, 3H), 7.69 (ddd, \(J = 8.5, 7.4, 1.1\) Hz, 1H), 7.90 (dd, \(J = 8.0, 1.1\) Hz, 1H), 8.07 (dd, \(J = 8.0, 1.1\) Hz, 2H), 9.03 (d, \(J = 8.5\) Hz, 1H), 12.33 (s, 1H). Anal. Calcd for C\textsubscript{15}H\textsubscript{12}ClNO\textsubscript{2}: C, 65.82; H, 4.42; N, 5.12. Found: C, 65.70; H, 4.64; N, 4.96.
**N-[2-(2-Chloroacetyl)phenyl]-3-methylbenzamide (2b):** a pale-yellow solid; mp 138–140 °C (hexane/CH₂Cl₂); IR (KBr) 3238, 1671, 1657, 1605 cm⁻¹; ¹H NMR δ 2.47 (s, 3H), 4.82 (s, 2H), 7.19 (dd, J = 8.0, 7.4 Hz, 1H), 7.39 (t, J = 7.4 Hz, 1H), 7.42 (t, J = 7.4 Hz, 1H), 7.68 (t, J = 8.0 Hz, 1H), 7.85–7.90 (m, 3H), 9.02 (d, J = 8.6 Hz, 1H), 12.26 (br s, 1H). HR-MS (EI). Calcd for C₁₆H₁₄ClNO₂ (M): 287.0713. Found: m/z 287.0724.

**N-[2-(2-Chloroacetyl)phenyl]-4-methylbenzamide (2c):** a white solid; mp 136–138 °C (hexane/CH₂Cl₂); IR (KBr) 3275, 1673, 1660, 1612 cm⁻¹; ¹H NMR δ 2.44 (s, 3H), 4.83 (s, 2H), 7.18 (dd, J = 8.0, 7.4 Hz, 1H), 7.33 (d, J = 8.0 Hz, 2H), 7.67 (dd, J = 8.0, 1.1 Hz, 1H), 7.89 (dd, J = 8.0, 1.1 Hz, 1H), 7.99 (d, J = 8.0 Hz, 2H), 9.03 (d, J = 8.0 Hz, 1H), 12.28 (br s, 1H). Anal. Calcd for C₁₆H₁₄ClNO₂: C, 66.79; H, 4.90; N, 4.87. Found: C, 66.93; H, 5.30; N, 4.56.

**2-Chloro-N-[2-(2-chloroacetyl)phenyl]benzamide (2d):** a pale-yellow solid; mp 102–105 °C (hexane/CH₂Cl₂); IR (KBr) 3238, 1689, 1664 cm⁻¹; ¹H NMR δ 4.81 (s, 2H), 7.22 (dd, J = 8.0, 7.4, 1.1 Hz, 1H), 7.38 (td, J = 7.4, 1.1 Hz, 1H), 7.43 (td, J = 7.4, 1.7 Hz, 1H), 7.48 (dd, J = 8.0, 1.1 Hz, 1H), 7.65 (dd, J = 7.4, 1.7 Hz, 1H), 7.69 (dd, J = 8.0, 7.4 Hz, 1H), 7.87 (dd, J = 8.0, 1.1 Hz, 1H), 8.98 (d, J = 8.0 Hz, 1H), 11.81 (br s, 1H). HR-MS (EI). Calcd for C₁₅H₁₁Cl₂NO₂ (M): 307.0167. Found: m/z 307.0170.

**4-Chloro-N-[2-(2-chloroacetyl)phenyl]benzamide (2e):** a pale-yellow solid; mp 135–138 °C (hexane/CH₂Cl₂); IR (KBr) 3242, 1671, 1663, 1610 cm⁻¹; ¹H NMR δ 4.85 (s, 2H), 7.20 (dd, J = 8.0, 7.4, 1.1 Hz, 1H), 7.50 (d, J = 8.6 Hz, 2H), 7.68 (dd, J = 8.0, 1.1 Hz, 1H), 7.89 (dd, J = 8.0, 1.1 Hz, 1H), 8.01 (d, J = 8.6 Hz, 2H), 8.99 (d, J = 8.0 Hz, 1H), 12.34 (s, 1H). Anal. Calcd for C₁₅H₁₁Cl₂NO₂: C, 58.47; H, 3.60; N, 4.55. Found: C, 58.31; H, 3.64; N, 4.22.

**2,4-Dichloro-N-[2-(2-chloroacetyl)phenyl]benzamide (2f):** a white solid; mp 150–152 °C (hexane/CH₂Cl₂); IR (KBr) 3242, 1687, 1666, 1607 cm⁻¹; ¹H NMR δ 4.79 (s, 2H), 7.23 (dd, J = 8.0, 7.4 Hz, 1H), 7.37 (dd, J = 8.6, 1.1 Hz, 1H), 7.51 (d, J = 1.1 Hz, 1H), 7.61 (d, J = 8.0 Hz, 1H), 7.70 (dd, J = 8.0, 7.4 Hz, 1H), 7.88 (d, J = 8.0 Hz, 1H), 8.94 (d, J = 8.6 Hz, 1H), 11.8 (br s, 1H). HR-MS (EI). Calcd for C₁₅H₁₀Cl₃NO₂ (M): 340.9777. Found: m/z 340.9769.

**N-[2-(2-Chloroacetyl)phenyl]-3-methoxybenzamide (2g):** a white solid; mp 154–156 °C (hexane/CH₂Cl₂); IR (KBr) 3270, 1673, 1662, 1605 cm⁻¹; ¹H NMR δ 3.90 (s, 3H), 4.83 (s, 2H), 7.12 (dd, J = 8.0, 2.9 Hz, 1H), 7.18 (dd, J = 8.0, 7.6, 1.1 Hz, 1H), 7.44 (dd, J = 8.0, 7.4 Hz, 1H), 7.60 (d, J = 2.3 Hz, 1H), 7.63 (d, J = 7.4 Hz, 1H), 7.69 (td, J = 7.4, 1.1 Hz, 1H), 7.88 (d, J = 7.4 Hz, 1H), 8.90 (d, J = 8.0 Hz, 1H), 12.31 (s, 1H). Anal. Calcd for C₁₆H₁₄ClNO₃: C, 63.27; H, 4.65; N, 4.61. Found: C, 63.32; H, 4.42; N, 4.45.

**N-[2-(2-Chloroacetyl)phenyl]thiophene-2-carboxamide (2h):** a white solid; mp 124–126 °C (hexane/CH₂Cl₂); IR (KBr) 3235, 1655, 1608 cm⁻¹; ¹H NMR δ 4.85 (s, 2H), 7.15–7.18 (m, 2H), 7.60 (dd,
J = 4.6, 1.1 Hz, 1H), 7.65 (td, J = 7.4, 1.1 Hz, 1H), 7.85–7.88 (m, 2H), 8.91 (dd, J = 7.4, 1.1 Hz, 1H), 12.34 (br s, 1H). HR-MS (DART). Calcd for C_{13}H_{11}ClNO_2S (M+H): 280.0199. Found: m/z 280.0193.

N-[2-(2-Chloroacetyl)phenyl]pyridine-3-carboxamide (2i): a white solid; mp 145 °C (decomp.) (hexane/CH_2Cl_2); IR (KBr) 3239, 1698, 1663, 1611 cm–1; ¹H NMR δ 4.84 (s, 2H), 7.24 (dd, J = 8.0, 7.4, 1.1 Hz, 1H), 7.49 (dd, J = 8.6, 4.6 Hz, 1H), 7.71 (ddd, J = 8.0, 7.4, 1.1 Hz, 1H), 9.00 (d, J = 8.6 Hz, 1H), 9.32 (d, J = 2.3 Hz, 1H), 12.43 (br s, 1H). Anal. Calcd for C_{14}H_{11}ClN_2O_2: C, 61.21; H, 4.04; N, 10.20. Found: C, 60.96; H, 4.02; N, 10.11.

4-Chloro-N-[4-chloro-2-(2-chloroacetyl)phenyl]benzamide (2j): colorless needles; mp 166–168 °C (hexane/CH_2Cl_2); IR (KBr) 3245, 1669, 1605 cm–1; ¹H NMR δ 4.80 (s, 2H), 7.51 (d, J = 8.6 Hz, 2H), 7.64 (dd, J = 9.2, 2.9 Hz, 1H), 7.85 (d, J = 2.9 Hz, 1H), 7.99 (d, J = 8.6 Hz, 2H), 9.00 (d, J = 9.2 Hz, 1H), 12.22 (br s, 1H). Anal. Calcd for C_{15}H_{10}Cl_3NO_2: C, 52.59; H, 2.94; N, 4.09. Found: C, 52.44; H, 3.07; N, 3.87.

N-[2-(2-Chloroacetyl)-4-methoxyphenyl]benzamide (2k): a white solid; mp 148–150 °C (hexane/CH_2Cl_2); IR (KBr) 3289, 1662, 1617, 1601 cm–1; ¹H NMR δ 3.88 (s, 3H), 4.80 (s, 2H), 7.25–7.28 (m, 2H), 7.35 (d, J = 2.9 Hz, 1H), 7.51–7.58 (m, 3H), 8.05 (d, J = 9.2 Hz, 2H), 12.00 (br s, 1H). Anal. Calcd for C_{16}H_{14}ClNO_3: C, 63.27; H, 4.65; N, 4.61. Found: C, 63.26; H, 4.66; N, 4.50.

Typical Procedure for the Preparation of 1-Aroyl-1,2-dihydro-3H-indol-3-ones (4). 1-Benzoyl-1,2-dihydro-3H-indol-3-one (4a).³ To a stirred solution of 2a (0.22 g, 0.80 mmol) in DMF (3 mL) containing (Boc)_2O (0.17 g, 0.8 mmol) at rt was added Et₃N (0.16 g, 1.6 mmol). After stirring overnight at the same temperature, saturated aqueous NaHCO₃ (15 mL) was added and the mixture was extracted with AcOEt (3 × 10 mL). The combined extracts were washed with H₂O (3 × 10 mL) and brine (10 mL), dried (Na₂SO₄), and concentrated by evaporation to give a residue containing 3a. To this residue was added TFA (0.5 mL) at rt and the solution was stirred for 1 h. The solution was diluted with anhydrous CH₂Cl₂ (15 mL) and anhydrous K₂CO₃ (1 g) was added. After stirring for 30 min, the solid materials were filtered off under reduced pressure and the filtrate was concentrated by evaporation. The residue was purified by column chromatography on SiO₂ (AcOEt/hexane 1:3) to afford 4a (0.12 g, 63 %); a pale-yellow solid; mp 122–124 °C (hexane/CH₂Cl₂) (lit.,³ 124–125 °C). The spectral data (IR and ¹H NMR) for this product were identical to those reported previously.³

1-Benzoyl-1H-indol-3-yl 1,1-Dimethylethyl Carbonate (3a). This compound could be isolated by column chromatography on SiO₂ (CH₂Cl₂/hexane 1:5). A pale-yellow solid; mp 116–118 °C (hexane/CH₂Cl₂); IR (KBr) 1763, 1688, 1602 cm⁻¹; ¹H NMR δ 1.57 (s, 9H), 7.35 (ddd, J = 8.0, 7.4, 1.1 Hz, 1H), 7.42 (td, J = 7.4, 1.1 Hz, 1H), 7.49 (s, 1H), 7.53 (t, J = 7.4 Hz, 2H), 7.55–7.62 (m, 2H), 7.75 (dd, J = 7.4, 1.1 Hz, 2H), 8.41 (d, J = 8.0 Hz, 1H); ¹³C NMR δ 27.62, 84.13, 115.12, 116.52, 117.76, 123.95,
124.00, 125.94, 128.65, 129.10, 131.93, 133.59, 134.26, 134.85, 150.50, 168.58. HR-MS (ESI). Calcd for \( \text{C}_{20}\text{H}_{20}\text{NO}_4 (\text{M}+\text{H}) \): 338.1392. Found: \( m/z \) 338.1389.

1-(3-Methylbenzoyl)-1,2-dihydro-3\( ^{\text{H}} \)-indol-3-one (4b): a pale-yellow solid; \( \text{mp} \) 76–77 °C (hexane/\( \text{CH}_2\text{Cl}_2 \)); IR (KBr) 1721, 1667 \( \text{cm}^{-1} \); \( ^{1}\text{H} \) NMR \( \delta \) 2.32 (s, 3H), 4.18 (s, 2H), 7.14 (t, \( J = 7.4 \) Hz, 1H), 7.23–7.29 (m, 4H), 7.56 (br t, \( J = 7.4 \) Hz, 1H), 7.67 (d, \( J = 7.4 \) Hz, 1H), 8.15 (br, 1H); \( ^{13}\text{C} \) NMR \( \delta \) 21.35, 57.83, 118.67, 123.78, 124.02, 124.48, 125.32, 127.60, 131.79, 135.69, 136.98, 138.84, 153.79, 168.88, 195.26. HR-MS (EI). Calcd for \( \text{C}_{16}\text{H}_{13}\text{NO}_2 (\text{M}) \): 251.0946. Found: \( m/z \) 251.0954. Anal. Calcd for \( \text{C}_{16}\text{H}_{13}\text{NO}_2 \): C, 76.48; H, 5.21; N, 5.57. Found: C, 76.77; H, 5.40; N, 5.70.

1-(4-Methylbenzoyl)-1,2-dihydro-3\( ^{\text{H}} \)-indol-3-one (4c): a pale-yellow solid; \( \text{mp} \) 133–135 °C (hexane/\( \text{CH}_2\text{Cl}_2 \)); IR (KBr) 1718, 1663, 1607 \( \text{cm}^{-1} \); \( ^{1}\text{H} \) NMR \( \delta \) 2.44 (s, 3H), 4.29 (s, 2H), 7.24 (t, \( J = 7.4 \) Hz, 1H), 7.29 (d, \( J = 8.0 \) Hz, 2H), 7.48 (d, \( J = 8.0 \) Hz, 2H), 7.65 (t, \( J = 7.4 \) Hz, 1H), 7.77 (d, \( J = 7.4 \) Hz, 1H), 8.22 (br, 1H); \( ^{13}\text{C} \) NMR \( \delta \) 21.52, 57.89, 118.71, 123.76, 124.39, 125.33, 127.27, 129.43, 132.84, 136.91, 141.60, 153.95, 168.82, 195.28. HR-MS (EI). Calcd for \( \text{C}_{16}\text{H}_{13}\text{NO}_2 (\text{M}) \): 251.0946. Found: \( m/z \) 251.0939. Anal. Calcd for \( \text{C}_{16}\text{H}_{13}\text{NO}_2 \): C, 76.48; H, 5.21; N, 5.57. Found: C, 76.24; H, 5.15; N, 5.48.

1-(2-Chlorobenzoyl)-1,2-dihydro-3\( ^{\text{H}} \)-indol-3-one (4d): a white solid; \( \text{mp} \) 140–142 °C (hexane/\( \text{CH}_2\text{Cl}_2 \)); IR (KBr) 1718, 1662 \( \text{cm}^{-1} \); \( ^{1}\text{H} \) NMR \( \delta \) 4.07 (br s, 2H), 7.32 (t, \( J = 7.4 \) Hz, 1H), 7.40–7.53 (m, 4H), 7.74–7.80 (m, 2H), 8.71 (d, \( J = 8.6 \) Hz, 1H); \( ^{13}\text{C} \) NMR \( \delta \) 56.35, 118.88, 123.79, 125.07, 125.32, 127.45, 127.59, 129.71, 130.03, 131.27, 135.75, 137.31, 152.96, 165.47, 194.54. HR-MS (EI). Calcd for \( \text{C}_{15}\text{H}_{10}\text{ClNO}_2 (\text{M}) \): 271.0400. Found: \( m/z \) 271.0412. Anal. Calcd for \( \text{C}_{15}\text{H}_{10}\text{ClNO}_2 \): C, 66.31; H, 3.71; N, 5.16. Found: C, 66.24; H, 3.66; N, 5.13.

1-(4-Chlorobenzoyl)-1,2-dihydro-3\( ^{\text{H}} \)-indol-3-one (4e): a white solid; \( \text{mp} \) 111–114 °C (hexane/\( \text{CH}_2\text{Cl}_2 \)); IR (KBr) 1717, 1646 \( \text{cm}^{-1} \); \( ^{1}\text{H} \) NMR \( \delta \) 4.27 (s, 2H), 7.27 (dd, \( J = 8.0, 7.4 \) Hz, 1H), 7.49 (d, \( J = 8.6 \) Hz, 2H), 7.54 (d, \( J = 8.6 \) Hz, 2H), 7.68 (t, \( J = 7.4 \) Hz, 1H), 7.78 (d, \( J = 8.0 \) Hz, 1H), 8.28 (br, 1H); \( ^{13}\text{C} \) NMR \( \delta \) 57.65, 118.40, 123.85, 124.75, 125.32, 128.64, 129.17, 133.97, 137.02, 137.35, 153.51, 167.50, 194.73. HR-MS (EI). Calcd for \( \text{C}_{15}\text{H}_{10}\text{ClNO}_2 (\text{M}) \): 271.0400. Found: \( m/z \) 271.0404. Anal. Calcd for \( \text{C}_{15}\text{H}_{10}\text{ClNO}_2 \): C, 66.31; H, 3.71; N, 5.16. Found: C, 66.11; H, 3.79; N, 5.00.

1-(2,4-Dichlorobenzoyl)-1,2-dihydro-3\( ^{\text{H}} \)-indol-3-one (4f): a pale-yellow solid; \( \text{mp} \) 178–180 °C (hexane/\( \text{CH}_2\text{Cl}_2 \)); IR (KBr) 1724, 1659 \( \text{cm}^{-1} \); \( ^{1}\text{H} \) NMR \( \delta \) 4.06 (s, 2H), 7.33 (t, \( J = 7.4 \) Hz, 1H), 7.36–7.42 (m, 3H), 7.74–7.80 (m, 2H), 8.68 (d, \( J = 8.0 \) Hz, 1H); \( ^{13}\text{C} \) NMR \( \delta \) 56.23, 118.93, 120.37, 120.92, 123.87, 125.30, 128.09, 128.49, 130.05, 134.25, 136.82, 137.36, 152.86, 164.54, 194.14. HR-MS (EI). Calcd for \( \text{C}_{15}\text{H}_{9}\text{Cl}_2\text{NO}_2 (\text{M}) \): 305.0010. Found: \( m/z \) 305.0021. Anal. Calcd for \( \text{C}_{15}\text{H}_{9}\text{Cl}_2\text{NO}_2 \): C, 58.85; H, 2.96; N, 4.58. Found: C, 58.62; H, 3.09; N, 4.55.
1-(3-Methoxybenzoyl)-1,2-dihydro-3H-indol-3-one (4g): a pale-yellow oil; Rf 0.38 (AcOEt/hexane 1:2); IR (neat) 1722, 1666, 1602 cm⁻¹; ¹H NMR δ 3.85 (s, 3H), 4.29 (s, 2H), 7.06–7.09 (m, 2H), 7.13 (dd, J = 7.4, 1.1 Hz, 1H), 7.26 (t, J = 7.4 Hz, 1H), 7.41 (t, J = 8.0 Hz, 1H), 7.67 (br, 1H), 7.78 (d, J = 7.4 Hz, 1H), 8.30 (br, 1H); ¹³C NMR δ 55.41, 60.37, 112.28, 116.86, 118.72, 118.99, 123.77, 124.56, 125.35, 130.01, 136.91, 136.97, 153.63, 156.97, 159.75, 168.37, 195.07. HR-MS (DART). Calcd for C₁₆H₁₄NO₃ (M+H): 268.0973. Found: m/z 268.0961. Anal. Calcd for C₁₆H₁₃NO₃: C, 71.90; H, 4.90; N, 5.24. Found: C, 71.87; H, 5.07; N, 5.14.

1-(Thiophen-2-ylcarbonyl)-1,2-dihydro-3H-indol-3-one (4h): a white solid; mp 116–118 °C (hexane/CH₂Cl₂); IR (KBr) 1724, 1623, 1604 cm–¹; ¹H NMR δ 4.63 (s, 2H), 7.18 (dd, J = 4.6, 4.0 Hz, 1H), 7.27 (dd, J = 8.0, 6.9 Hz, 1H), 7.64 (d, J = 4.6 Hz, 1H), 7.69–7.72 (m, 2H), 7.79 (d, J = 7.4 Hz, 1H), 8.58 (d, J = 8.6 Hz, 1H); ¹³C NMR δ 57.42, 119.46, 123.71, 124.74, 124.92, 127.76, 131.34, 131.76, 137.26, 137.65, 154.34, 160.83, 195.02. HR-MS (DART). Calcd for C₁₃H₁₀NO₂S (M+H): 244.0432. Found: m/z 244.0420. Anal. Calcd for C₁₃H₉NO₂S: C, 64.18; H, 3.73; N, 5.76. Found: C, 63.92; H, 3.67; N, 5.55.

1-(Pyridin-3-ylcarbonyl)-1,2-dihydro-3H-indol-3-one (4i): a beige solid; mp 132 °C (decomp) (hexane/CH₂Cl₂); IR (KBr) 1722, 1674, 1602 cm–¹; ¹H NMR δ 4.31 (s, 2H), 7.34 (t, J = 7.4 Hz, 1H), 7.74–7.82 (m, 3H), 8.27 (d, J = 7.4 Hz, 1H), 8.89 (br s, 1H), 9.05 (br s, 1H), 9.25 (br, 1H); ¹³C NMR δ 57.29, 118.81, 124.11, 125.42, 125.51, 125.65, 133.50, 137.33, 138.88, 144.69, 147.95, 152.92, 164.01, 193.72. HR-MS (EI). Calcd for C₁₄H₁₀N₂O₂ (M): 238.0742. Found: m/z 238.0748. Anal. Calcd for C₁₄H₁₀N₂O₂: C, 70.58; H, 4.23; N, 11.76. Found: C, 70.58; H, 4.36; N, 11.71.

5-Chloro-1-(4-chlorobenzoyl)-1,2-dihydro-3H-indol-3-one (4j): a white solid; mp 132–134 °C (hexane/CH₂Cl₂); IR (KBr) 1726, 1668 cm⁻¹; ¹H NMR δ 4.29 (s, 2H), 7.49 (d, J = 8.6 Hz, 2H), 7.53 (d, J = 8.6 Hz, 2H), 7.63 (dd, J = 7.4, 1.7 Hz, 1H), 7.73 (d, J = 1.7 Hz, 1H), 8.25 (br, 1H); ¹³C NMR δ 58.05, 120.06, 123.38, 126.61, 128.66, 129.27, 130.60, 133.59, 136.82, 137.66, 151.98, 167.45, 193.38. HR-MS (EI). Calcd for C₁₅H₉Cl₂NO₂ (M): 305.0010. Found: m/z 305.0017. Anal. Calcd for C₁₅H₉Cl₂NO₂: C, 58.85; H, 2.96; N, 4.58. Found: C, 58.81; H, 3.01; N, 4.29.

1-Benzoyl-5-methoxy-1,2-dihydro-3H-indol-3-one (4k). To a stirred suspension of NaH (60% in mineral oil; 14 mg, 0.36 mmol) in DME (5 mL) at 0 °C was added a solution of 2k (0.10 g, 0.33 mmol) in DME (3 mL) dropwise. After 5 min, saturated aqueous NH₄Cl (20 mL) was added and the mixture was extracted with AcOEt (3 × 10 mL). The combined extracts were washed with water (3 × 15 mL) and brine (15 mL), dried (Na₂SO₄), and concentrated by evaporation. The residue was purified by column chromatography on SiO₂ (AcOEt/hexane 1:3) to afford 4k (31 mg, 35%); a pale-yellow solid; mp 167–169 °C (hexane/CH₂Cl₂); IR (KBr) 1718, 1650 cm⁻¹; ¹H NMR δ 3.85 (s, 3H), 4.28 (s, 2H), 7.17 (d, J = 2.3 Hz, 1H), 7.27 (br, 1H), 7.47–7.53 (m, 3H), 7.56 (dd, J = 8.0, 1.1 Hz, 2H), 8.30 (br, 1H); ¹³C NMR δ...
HR-MS (EI). Calcd for C_{16}H_{13}NO_{3} (M): 267.0895. Found: m/z 267.0885. Anal. Calcd for C_{16}H_{13}NO_{3}: C, 71.90; H, 4.90; N, 5.24. Found: C, 71.73; H, 4.84; N, 5.18.

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REFERENCES


