HETEROCYCLES, Vol. 92, No. 6, 2016, pp. 1063 - 1074. © 2016 The Japan Institute of Heterocyclic Chemistry
Received, 29th February, 2016, Accepted, 4th April, 2016, Published online, 8th April, 2016
DOI: 10.3987/COM-16-13450

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

Kazuhiro Kobayashi,* Daiki Kado, and Kohei Nishikawa

Division of Applied Chemistry, Department of Chemistry and Biotechnology, Graduate School of Engineering, Tottori University, 4-101 Koyama-minami, Tottori 680-8552, Japan; E-mail: kkoba@chem.tottori-u.ac.jp

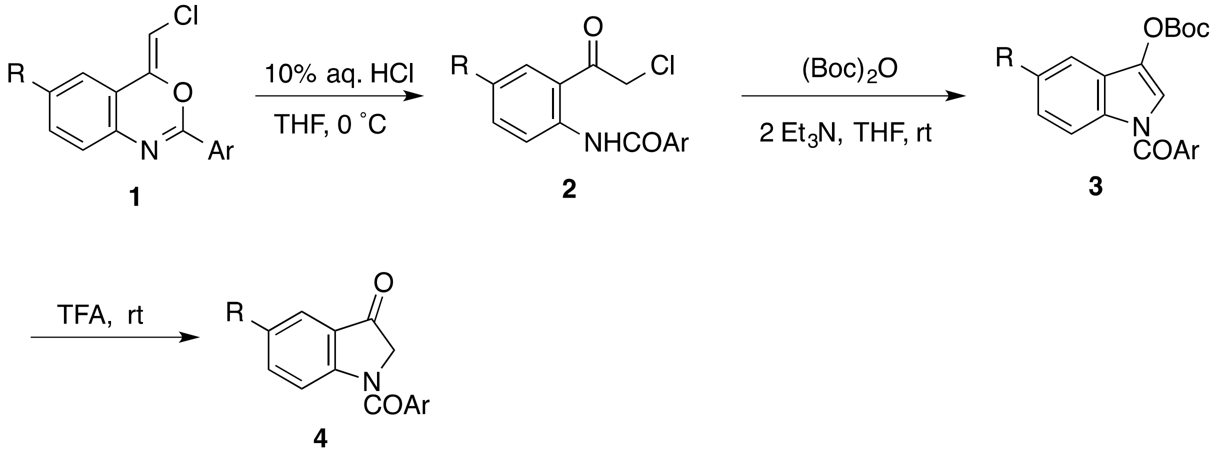
Abstract – 1-Aroyl-1,2-dihydro-3*H*-indol-3-ones can now be conveniently obtained from 2-aryl-4-(*Z*)-(chloromethylidene)-4*H*-3,1-benzoxazines using an easy operated three-step sequence under mild conditions. Thus, the starting materials are hydrolyzed with dilute hydrochloric acid at 0 ˚C to *N*-[2-(2-chloroacetyl)phenyl]benzamides, 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-3*H*-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.[1] An interesting natural product having this skeleton has been found in nature.[2] Accordingly, some practical methods for the preparation of this class of heterocycles have been developed.[3-6] Recently, Shu *et al*. demonstrated the use of gold-catalyzed intermolecular oxidation of *o*-ethynylanilines,[7] and more recently Gandy *et al*. reported a synthesis of 1-acetyl-1,2-dihydro-3*H*-indol-3-ones by the reaction of *N*-(2-cyanophenyl)glycine ethyl esters with acetic anhydride.[8] 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)-4*H*-3,1-benzoxazines (**1**).[9] As an extensive investigation of this study, we wish to describe here a convenient synthetic approach to 1,2-dihydro-3*H*-indol-3-one derivatives. We have found that 1-(het)aroyl-1,2-dihydro-3*H*-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

Table 1. Preparation of 1,2-dihydro-3*H*-indol-3-ones (**4**)

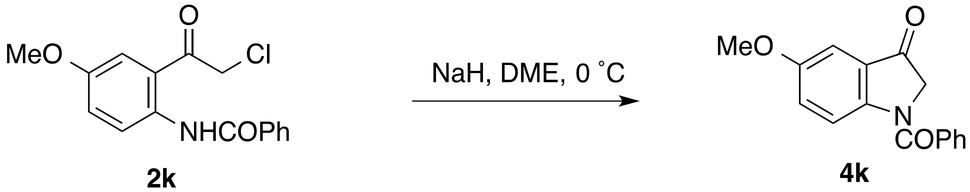
Entry	1	2	Yield/%[a]	4	Yield/%[a,b]
1	**1a** (R = H, Ar = Ph)	**2a**	94	**4a**	63
2	**1b** (R = H, Ar = *m*-Tol)	**2b**	98	**4b**	59
3	**1c** (R = H, Ar = *p*-Tol)	**2c**	97	**4c**	60
4	**1d** (R = H, Ar = 2-ClC_6H_4)	**2d**	91	**4d**	57
5	**1e** (R = H, Ar = 4-ClC_6H_4)	**2e**	93	**4e**	59
6	**1f** (R = H, Ar = 2,4-$Cl_2C_6H_4$)	**2f**	94	**4f**	75
7	**1g** (R = H, Ar = 3-$MeOC_6H_4$)	**2g**	90	**4g**	59
8	**1h** (R = H, Ar = thiophen-2-yl)	**2h**	98	**4h**	62
9	**1i** (R = H, Ar = pyridin-3-yl)	**2i**	56	**4i**	56
10	**1j** (R = Cl, Ar = 4-ClC_6H_4)	**2j**	72	**4j**	60
11	**1k** (R = OMe, Ar = Ph)	**2k**	83	**4k**	35[c]

[a] Yields of isolated products. [b] Overall yields from **2**. [c] This products 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*H*-indol-3-one by the reaction of *N*-[(2-chloroacetyl)phenyl]acetamide with sodium hydride in 1,2-dimethoxyethane (DME) at 0 ˚C in relatively good yield.[5] We first subjected substrate (**2a**) to these reaction conditions. Unfortunately, however, the reaction did proceed uncleanly to give the desired corresponding product 1-benzoyl-1,2-dihydro-3*H*-indol-3-one (**4a**) only in 15% yield. The reaction was then conducted using triethylamine in DMF at 0 ˚C; only 10% yield of **4a** was obtained. Subsequently, cyclization of **2a** with two equivalents of triethylamine in DMF at room temperature in the presence of an equivalent of di-*tert*-butyl dicarbonate was attempted. By using these conditions, compounds **2a** was converted into 1-benzoyl-1*H*-indol-3-yl 1,1-dimethylethyl carbonate (**3a**) in 69% yield. It is thought that the protection as 1,1-dimethylethyl carbonate depresses the self-condensation of the initially formed **4a**. This carbonate was converted into **4a** 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 **3a**. Thus, the crude reaction mixture containing **3a** was subjected to the deprotection without any purification after aqueous workup. The desired product **4a** was isolated in 63% overall yield from **2a** (Table 1, Entry 1). Other nine *N*-[2-(2-chloroacetyl)phenyl] amides (**2b**–**2j**) were similarly converted into the corresponding 1-(het)aroyl-1,2-dihdro-3*H*-indol-3-ones (**4b**–**4j**) in comparable yields (Entries 2-10).

It is notable that the treatment of *N*-[2-(2-chloroacetyl)phenyl]-4-methoxybenzamide (**2k**) with di-*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-(*tert*-butoxycarbonyloxy)-1*H*-indole derivative (**3k**) was observed in it as judged by TLC analyses on silica gel. However, when **2k** was treated with sodium hydride in 1,2-dimethoxyethane (DME) at 0 ˚C, 1-benzoyl-5-methoxy-1,2-dihydro-3*H*-indol-3-one (**4k**) was directly obtained albeit in relatively low yield (Scheme 2). This different reactivity of **2k** from the other *N*-[2-(2-chloroacetyl)phenyl] amides (**2a**–**2j**) is incomprehensible; we cannot provide any reasons for it.



Scheme 2

In conclusion, a convenient procedure for the synthesis of 1-(het)aroyl-1,2-dihydro-3*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 δ 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 $C_8H_6Cl_3N$ (M): 220.9566. Found: *m/z* 220.9574.

2-(2,2-Dichloroethenyl)-4-methoxybenzenamine. This compound was prepared from 5-methoxy-2-nitrobenzaldehyde[11] 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_2Cl_2/hexane 5:1); IR (neat) 3437, 3364, 3225, 1609 cm^{-1}; ^{1}H NMR δ 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 $C_9H_9Cl_2NO$ (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_2Cl_2); IR (KBr) 3198, 1639, 1601 cm^{-1}; ^{1}H NMR δ 2.46 (s, 3H), 6.90 (s, 1H), 7.22 (t, J = 7.4

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 $C_{16}H_{13}Cl_2NO$: 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)-4*H*-3,1-benzoxazine (1b): yield: 62%; a white solid; mp 105–107 ˚C (hexane/CH_2Cl_2); IR (KBr) 3114, 1638, 1611 cm^{-1}; ^{1}H 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); ^{13}C 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 $C_{16}H_{12}ClNO$ (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_2Cl_2); IR (KBr) 3309, 1641, 1612 cm^{-1}; ^{1}H 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 $C_{16}H_{13}Cl_2NO$ (M): 305.0374. Found: *m/z* 305.0376.

4-(*Z*)-(Chloromethylidene)-2-(4-methylphenyl)-4*H*-3,1-benzoxazine (1c): yield: 72%; a white solid; mp 97–99 ˚C (hexane/CH_2Cl_2); IR (KBr) 3121, 1639, 1613 cm^{-1}; ^{1}H 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); ^{13}C 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_2Cl_2); IR (KBr) 3210, 1644, 1615 cm^{-1}; ^{1}H 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). Anal. Calcd for $C_{15}H_{10}Cl_3NO$: 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_2Cl_2); IR (KBr) 3107, 1645, 1618 cm^{-1}; ^{1}H 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); ^{13}C 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 $C_{15}H_{10}Cl_2NO$ (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_2Cl_2); IR (KBr) 3267, 1655, 1616 cm^{-1}; ^{1}H 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). Anal. Calcd for $C_{15}H_{10}Cl_3NO$: 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/CH_2Cl_2); IR (KBr) 3104, 1644, 1613 cm^{-1}; ^{1}H 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); ^{13}C 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 $C_{15}H_9Cl_2NO$ (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/CH_2Cl_2); IR (KBr) 3173, 1654 cm^{-1}; ^{1}H 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 $C_{15}H_9Cl_4NO$: 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/CH_2Cl_2); IR (KBr) 3116, 1635, 1618 cm^{-1}; ^{1}H 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); ^{13}C 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 $C_{15}H_8Cl_3NO$: 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/CH_2Cl_2); IR (KBr) 3241, 1635, 1621 cm^{-1}; ^{1}H 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 $C_{16}H_{13}Cl_2NO_2$ (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/CH_2Cl_2); IR (KBr) 3108, 1637, 1615 cm^{-1}; ^{1}H 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); ^{13}C 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 $C_{16}H_{12}ClNO_2$: 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; *R_f* 0.36 (AcOEt/hexane 5:1); IR (neat) 3263, 1652 cm^{-1}; ^{1}H NMR δ 6.90 (s, 1H), 7.26 (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 $C_{14}H_{10}Cl_2N_2O$ (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/CH_2Cl_2); IR (KBr) 3087, 1640, 1616 cm^{-1}; ^{1}H NMR δ 5.99 (s, 1H), 7.24 (td, *J* = 6.9, 1.7 Hz, 1H), 7.27–7.43 (m, 4H), 8.48 (ddd, *J* = 8.0, 2.3, 1.7 Hz, 1H), 8.76 (d, *J* = 3.4 Hz, 1H), 9.45 (s, 1H); ^{13}C 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 $C_{14}H_9ClN_2O$: 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-dichloroethenyl)phenyl]benzamide: yield: 74%; a white solid; mp 153–154 ˚C (hexane/CH_2Cl_2); IR (KBr) 3271, 1652 cm^{-1}; ^{1}H NMR δ 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 $C_{15}H_9Cl_4NO$: 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_4Cl to the reaction mixture in 85% yield; a white solid; mp 223–225 ˚C (THF); IR (KBr) 3119, 1645, 1617 cm^{-1}. This compound was of quite insolubility in most organic solvents. HR-MS (EI). Calcd for $C_{15}H_8Cl_3NO$ (M): 322.9671. Found: *m/z* 322.9687.

***N*-[2-(2,2-Dichloroethenyl)phenyl-4-methoxy]benzamide:** yield: 86%; a white solid; mp 131–133 ˚C (hexane/ CH_2Cl_2); IR (KBr) 3335, 1645, 1616 cm^{-1}; ^{1}H NMR δ 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 $C_{16}H_{13}Cl_2NO_2$ (M): 321.0323. Found: *m/z* 321.0318.

4-(Chloromethylidene)-6-methoxy-2-phenyl-3,1-benzoxazine (1k): yield: 99%; a white solid; mp 92–94 ˚C (hexane/ CH_2Cl_2); IR (KBr) 3110, 1642, 1613 cm^{-1}; ^{1}H NMR δ 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); ^{13}C NMR δ 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 $C_{16}H_{12}ClNO_2$: 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 $NaHCO_3$ (30 mL) was added and the mixture was extracted with AcOEt (3 × 25 mL). The combined extracts were washed with brine (30 mL), dried (Na_2SO_4), and concentrated by evaporation. The residual solid was recrystallized from hexane/CH_2Cl_2 to give **2a** (1.1 g, 94%); a white solid; mp 136–138 ˚C; IR (KBr) 3240, 1674, 1661, 1611 cm^{-1}; ^{1}H NMR δ 4.85 (s, 2H), 7.20 (ddd, *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 $C_{15}H_{12}ClNO_2$: 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/CH_2Cl_2); 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 $C_{16}H_{14}ClNO_2$ (M): 287.0713. Found: *m/z* 287.0724.

***N*-[2-(2-Chloroacetyl)phenyl]-4-methylbenzamide (2c):** a white solid; mp 136–138 ˚C (hexane/CH_2Cl_2); 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, 7.4 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 $C_{16}H_{14}ClNO_2$: 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/CH_2Cl_2); IR (KBr) 3238, 1689, 1664 cm^{-1}; ^1H NMR δ 4.81 (s, 2H), 7.22 (ddd, *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 (ddd, *J* = 8.6, 7.4, 1.7 Hz, 1H), 7.87 (dd, *J* = 8.0, 1.1 Hz, 1H), 8.98 (d, *J* = 8.6 Hz, 1H), 11.81 (br s, 1H). HR-MS (EI). Calcd for $C_{15}H_{11}Cl_2NO_2$ (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/CH_2Cl_2); IR (KBr) 3242, 1671, 1663, 1610 cm^{-1}; ^1H NMR δ 4.85 (s, 2H), 7.20 (ddd, *J* = 8.0, 7.4, 1.1 Hz, 1H), 7.50 (d, *J* = 8.6 Hz, 2H), 7.68 (ddd, *J* = 8.0, 7.4, 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 $C_{15}H_{11}Cl_2NO_2$: 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/CH_2Cl_2); IR (KBr) 3240, 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 $C_{15}H_{10}Cl_3NO_2$ (M): 340.9777. Found: *m/z* 340.9769.

***N*-[2-(2-Chloroacetyl)phenyl]-3-methoxybenzamide (2g):** a white solid; mp 154–156 ˚C (hexane/CH_2Cl_2); 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 (ddd, *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 $C_{16}H_{14}ClNO_3$: 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/CH_2Cl_2); 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}; ^{1}H NMR δ 4.84 (s, 2H), 7.24 (ddd, 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), 7.92 (dd, J = 8.0, 1.1 Hz, 1H), 8.34 (ddd, J = 8.0, 2.3, 1.7 Hz, 1H), 8.82 (dd, J = 4.6, 1.7 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}; ^{1}H 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), 8.99 (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}; ^{1}H 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-3*H*-indol-3-ones (4). 1-Benzoyl-1,2-dihydro-3*H*-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 Et_3N (0.16 g, 1.6 mmol). After stirring overnight at the same temperature, saturated aqueous $NaHCO_3$ (15 mL) was added and the mixture was extracted with AcOEt (3 × 10 mL). The combined extracts were washed with H_2O (3 × 10 mL) and brine (10 mL), dried (Na_2SO_4), 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 CH_2Cl_2 (15 mL) and anhydrous K_2CO_3 (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 SiO_2 (AcOEt/hexane 1:3) to afford **4a** (0.12 g, 63 %); a pale-yellow solid; mp 122–124 ˚C (hexane/CH_2Cl_2) (lit.,[3] 124–125 ˚C). The spectral data (IR and ^{1}H NMR) for this product were identical to those reported previously.[3]

1-Benzoyl-1*H*-indol-3-yl 1,1-Dimethylethyl Carbonate (3a). This compound could be isolated by column chromatography on SiO_2 (CH_2Cl_2/hexane 1:5). A pale-yellow solid; mp 116–118 ˚C (hexane/CH_2Cl_2); IR (KBr) 1763, 1688, 1602 cm^{-1}; ^{1}H 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); ^{13}C 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 $C_{20}H_{20}NO_4$ (M+H): 338.1392. Found: *m/z* 338.1389.

1-(3-Methylbenzoyl)-1,2-dihydro-3*H*-indol-3-one (4b): a pale-yellow solid; mp 76–77 ˚C (hexane/CH_2Cl_2); IR (KBr) 1721, 1667 cm^{-1}; ^1H NMR δ 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}C NMR δ 21.35, 57.83, 118.67, 123.78, 124.02, 124.48, 125.32, 127.60, 128.69, 131.79, 135.69, 136.98, 138.84, 153.79, 168.88, 195.26. HR-MS (EI). Calcd for $C_{16}H_{13}NO_2$ (M): 251.0946. Found: *m/z* 251.0954. Anal. Calcd for $C_{16}H_{13}NO_2$: 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*H*-indol-3-one (4c): a pale-yellow solid; mp 133–135 ˚C (hexane/CH_2Cl_2); IR (KBr) 1718, 1663, 1607 cm^{-1}; ^1H NMR δ 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}C NMR δ 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 $C_{16}H_{13}NO_2$ (M): 251.0946. Found: *m/z* 251.0939. Anal. Calcd for $C_{16}H_{13}NO_2$: 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*H*-indol-3-one (4d): a white solid; mp 140–142 ˚C (hexane/CH_2Cl_2); IR (KBr) 1718, 1662 cm^{-1}; ^1H NMR δ 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}C NMR δ 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 $C_{15}H_{10}ClNO_2$ (M): 271.0400. Found: *m/z* 271.0412. Anal. Calcd for $C_{15}H_{10}ClNO_2$: 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*H*-indol-3-one (4e): a white solid; mp 111–114 ˚C (hexane/CH_2Cl_2); IR (KBr) 1717, 1646 cm^{-1}; ^1H NMR δ 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}C NMR δ 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 $C_{15}H_{10}ClNO_2$ (M): 271.0400. Found: *m/z* 271.0404. Anal. Calcd for $C_{15}H_{10}ClNO_2$: 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*H*-indol-3-one (4f): a pale-yellow solid; mp 178–180 ˚C (hexane/CH_2Cl_2); IR (KBr) 1724, 1659 cm^{-1}; ^1H NMR δ 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}C NMR δ 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 $C_{15}H_9Cl_2NO_2$ (M): 305.0010. Found: *m/z* 305.0021. Anal. Calcd for $C_{15}H_9Cl_2NO_2$: 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-3*H*-indol-3-one (4g): a pale-yellow oil: *Rf* 0.38 (AcOEt/hexane 1:2); IR (neat) 1722, 1666, 1602 cm^{-1}; ^{1}H 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); ^{13}C 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, 159.75, 168.37, 195.07. HR-MS (DART). Calcd for $C_{16}H_{14}NO_3$ (M+H): 268.0973. Found: *m/z* 268.0961. Anal. Calcd for $C_{16}H_{13}NO_3$: 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-3*H*-indol-3-one (4h): a white solid; mp 116–118 ˚C (hexane/CH_2Cl_2); IR (KBr) 1724, 1623, 1604 cm^{-1}; ^{1}H 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); ^{13}C 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 $C_{13}H_{10}NO_2S$ (M+H): 244.0432. Found: *m/z* 244.0420. Anal. Calcd for $C_{13}H_9NO_2S$: 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-3*H*-indol-3-one (4i): a beige solid; mp 132 ˚C (decomp) (hexane/CH_2Cl_2); IR (KBr) 1722, 1674, 1602 cm^{-1}; ^{1}H 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); ^{13}C 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 $C_{14}H_{10}N_2O_2$ (M): 238.0742. Found: *m/z* 238.0748. Anal. Calcd for $C_{14}H_{10}N_2O_2$: 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-3*H*-indol-3-one (4j): a white solid; mp 132–134 ˚C (hexane/CH_2Cl_2); IR (KBr) 1726, 1668 cm^{-1}; ^{1}H 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); ^{13}C 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 $C_{15}H_9Cl_2NO_2$ (M): 305.0010. Found: *m/z* 305.0017. Anal. Calcd for $C_{15}H_9Cl_2NO_2$: 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-3*H*-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 NH_4Cl (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 (Na_2SO_4), and concentrated by evaporation. The residue was purified by column chromatography on SiO_2 (AcOEt/hexane 1:3) to afford **4k** (31 mg, 35%); a pale-yellow solid; mp 167–169 ˚C (hexane/CH_2Cl_2); IR (KBr) 1718, 1650 cm^{-1}; ^{1}H 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); ^{13}C NMR δ

55.77, 104.42, 119.90, 125.88, 126.22, 127.05, 128.79, 130.93, 135.80, 148.55, 156.84 (2 overlapped Cs), 168.10, 194.94. 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.

ACKNOWLEDGEMENTS

We thank Mrs. Miyuki Tanmatsu of our university for her assistance in obtaining mass spectra and elemental analytical data.

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