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# Synthesis of Novel 3-Acyloxy-1,3-dihydro-2*H*-indol-2-ones and Isomeric 4-Acyl-1,4-dihydro-3,1-benzoxazin-2-ones: Double Rearrangement of 3-Hydroxyquinoline-2,4(1*H*,3*H*)-diones

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**Abstract**—Substituted 3-hydroxyquinoline-2,4(1*H*,3*H*)-diones **3** were transformed into 3-acyloxy-1,3-dihydro-2*H*-indol-2-ones **4** and isomeric 4-acyl-1,4-dihydro-3,1-benzoxazin-2-ones **5**. The influence of the substituents and the reaction conditions on the course of the reaction was studied. In the proposed mechanism a double rearrangement takes place; α-ketol rearrangement of **3**, leading to α-hydroxy-β-diketone intermediate **8**, is followed by a rearrangement to the isomeric α-ketol-esters **4** and **5**. 

## Introduction

Recently, reactions of 3-hydroxyquinoline-2,4(1*H*,3*H*)-diones **3**, natural metabolites of some *Pseudomonas* species,[1] with ethyl (triphenylphosphoranylidene)acetate (Wittig reagent) have been described.[2] They proceed with high stereoselectivity to give *E*-4-ethoxycarbonylmethylene-3,4-dihydro-2-quinolones and to a small extent 3a-substituted furo[2,3-*c*]quinoline-2,4(3a*H*,5*H*)-diones. An independent synthesis of the latter by an intramolecular Wittig reaction has been described.[3] On the other hand, under the same reaction conditions, 5,8-disubstituted 3-benzyl-3-hydroxyquinoline-2,4(1*H*,3*H*)-diones **3** have been shown to react in a completely different manner yielding primarily products of indoline **4** and benzoxazine **5** structural type. Their formation was proposed to take place via a base catalysed molecular rearrangement of **3**, mediated by the Wittig reagent.[4]

In our present study we have tried to obtain additional information on the mechanism of this rearrangement. Substituted 3-hydroxyquinoline-2,4(1*H*,3*H*)-diones **3** were exposed to various organic bases. Additionally, we tried to find a combination of reaction conditions and/or substituents which would lead to the selective formation of **4** or **5**.

Despite possessing significant biological activity, only a few 3-acyloxy-1,3-dihydro-2*H*-indol-2-ones **4** are known. 3-Acetoxy-5-bromo-1,3-dihydro-2*H*-indol-2-one was found to have strong antihypoxic effects in mice subjected to hypobaric hypoxia, for example.[5] To the best of our knowledge, there is no example of a 4-acyl-1,4-dihydro-3,1-benzoxazin-2-one **5** described in the literature and only a few synthetic approaches to the parent 1,4-dihydro-3,1-benzoxazin-2-ones are documented.[6] However, there is a growing interest in their derivatives, triggered by their potent bio-activity such as the inhibition of HIV reverse transcriptase.[7]

## Results and Discussion

Starting materials (**3a**–**t**, Scheme 1, Table 1) were prepared by condensation of the corresponding anilines[8] **1a**–**t** with substituted diethyl malonates, followed by the oxidation[2,9] of 4-hydroxy-2(1*H*)-quinolones **2a**–**t** with peroxyacetic acid.

Rearrangement of **3a**–**t** was studied in refluxing xylene (in some cases cyclohexanol) solutions in the presence, as well as in the absence, of an organic base (Table 1). A catalytic amount, 0.2 molar equivalent, of 4-(dimethylamino)pyridine (DMAP), triphenylphosphane ($Ph_3P$), triphenylphosphane oxide ($Ph_3PO$) or *N*,*N*,*N*,*N*-tetramethylguanidine (TMG) was used as a base. Products were separated by column chromatography.

For the most direct comparison with previous results,[4] we first focused our attention on **3a**. By heating its xylene

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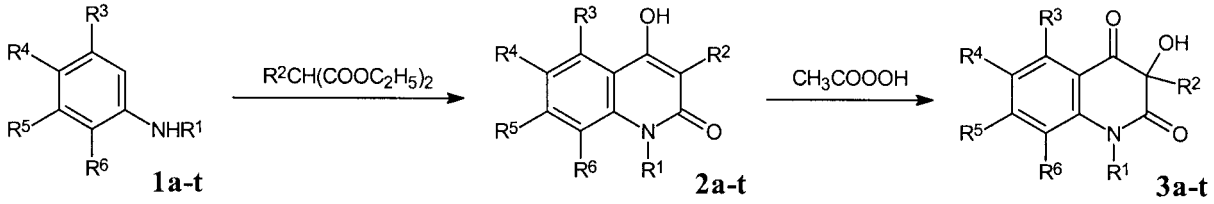



**Scheme 1.**

**Table 1.** Results of the rearrangement of compounds **3a**–**t**

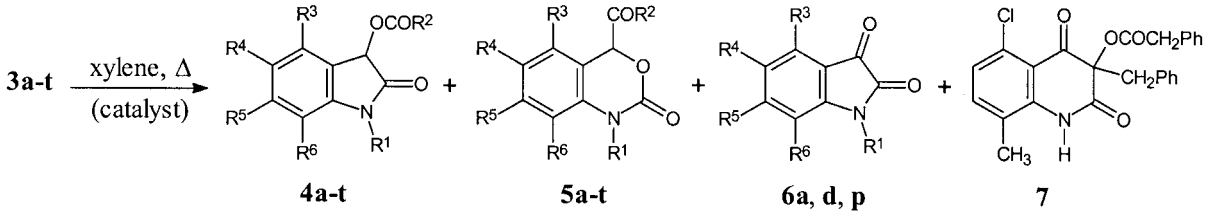
| 3 | $R^1$ | $R^2$ | $R^3$ | $R^4$ | $R^5$ | $R^6$ | Catalyst | Solvent | Time (h) | Isolated compounds (%) | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | | **4** | **5** | **6** | **3**[a] |
| **a** | H | $CH_2Ph$ | Cl | H | H | $CH_3$ | DMAP | Xylene | 5 | 39 | 8 | 5 | 9[b] |
| **b** | H | $C_4H_9$ | Cl | H | H | $CH_3$ | DMAP | Xylene | 3 | 31 | 0.3 | 2 | 33 |
| | | | | | | | None | Xylene | 3 | 8 | – | 1 | 76[c] |
| **c** | H | Ph | Cl | H | H | $CH_3$ | DMAP | Xylene | 2 | 21 | 27 | 3 | 10 |
| | | | | | | | None | Xylene | 2 | 15 | 4 | 4 | 60 |
| **d** | H | $CH_2Ph$ | $CH_3$ | H | H | $CH_3$ | DMAP | Xylene | 5 | 18 | – | 2 | 60 |
| **e** | H | $C_4H_9$ | $CH_3$ | H | H | $CH_3$ | DMAP | Xylene | 3 | 75 | – | 2 | 5 |
| | | | | | | | DMAP | *c*-$C_6H_{11}OH$ | 3 | 76 | – | 3 | 6 |
| | | | | | | | $Ph_3PO$ | Xylene | 3 | 81 | – | 1 | – |
| | | | | | | | $Ph_3P$ | *c*-$C_6H_{11}OH$ | 3 | 54 | – | – | 38 |
| | | | | | | | $Ph_3P$ | Xylene | 3 | 76 | – | – | 7 |
| | | | | | | | None | Xylene | 3 | 80 | – | – | 7 |
| **f** | H | Ph | $CH_3$ | H | H | $CH_3$ | DMAP | Xylene | 5 | 7 | 16 | 3 | 64 |
| | | | | | | | None | Xylene | 5 | 2 | 2 | 2 | 84 |
| **g** | H | $CH_2Ph$ | H | H | H | H | DMAP | Xylene | 12 | – | – | – | 81 |
| **h** | H | $C_4H_9$ | H | H | H | H | DMAP | Xylene | 5 | 8 | – | – | 70 |
| | | | | | | | $Ph_3P$ | Xylene | 6 | 9 | – | – | 73 |
| **i** | H | Ph | H | H | H | H | DMAP | Xylene | 12 | – | – | – | 75 |
| **j** | $CH_3$ | $C_4H_9$ | H | H | H | H | DMAP | Xylene | 10 | – | – | – | 82 |
| | | | | | | | $Ph_3P$ | Xylene | 9 | 9 | – | – | 83 |
| **k** | $CH_3$ | Ph | H | H | H | H | DMAP | Xylene | 4 | – | – | – | 85 |
| **l** | H | $C_4H_9$ | H | Cl | H | H | DMAP | Xylene | 4 | – | – | – | 88 |
| | | | | | | | DMAP | *c*-$C_6H_{11}OH$ | 6 | – | – | – | 91 |
| | | | | | | | $Ph_3P$ | Xylene | 6 | – | – | – | 98 |
| **m** | H | $C_4H_9$ | H | $CH_3$ | H | H | DMAP | Xylene | 6 | – | – | – | 96 |
| | | | | | | | $Ph_3P$ | Xylene | 6 | – | – | – | 94 |
| **n** | H | $C_4H_9$ | H | H | H | $CH_3$ | DMAP | Xylene | 6 | – | – | – | 89 |
| | | | | | | | $Ph_3P$ | Xylene | 9 | – | – | – | 94 |
| **o** | H | $CH_2Ph$ | H | H | Cl | $CH_3$ | DMAP | Xylene | 5 | 1 | – | – | 89 |
| | | | | | | | $Ph_3P$ | Xylene | 7 | – | – | – | 92 |
| **p** | H | $CH_2Ph$ | $CH_3$ | H | $CH_3$ | H | DMAP | Xylene | 8 | 14 | – | 2 | 48 |
| **r** | H | $C_4H_9$ | $CH_3$ | H | $CH_3$ | H | DMAP | Xylene | 7 | 19 | – | 1 | 46 |
| | | | | | | | $Ph_3P$ | Xylene | 7 | 51 | – | – | 34 |
| | | | | | | | None | Xylene | 7 | 38 | – | 1 | 51 |
| **s** | H | Ph | $CH_3$ | H | $CH_3$ | H | DMAP | Xylene | 9 | – | 4 | 1 | 83 |
| | | | | | | | TMG | Xylene | 6 | – | 8 | 3 | 69 |
| | | | | | | | $Ph_3P$ | Xylene | 9 | 1 | 13 | – | 80 |
| | | | | | | | $Ph_3P$ | *c*-$C_6H_{11}OH$ | 9 | 1 | 13 | – | 66 |
| **t** | $CH_3$ | $C_4H_9$ | $CH_3$ | H | $CH_3$ | H | $Ph_3P$ | Xylene | 12 | – | – | – | 84 |

[a] Recovered starting material.
[b] Compound **7** was also isolated in 9% yield.
[c] Compound **8b** was isolated in 5% yield.

solution under reflux in the presence of DMAP four products were formed: dioxindole **4a**, benzoxazinone **5a**, isatin **6a**, and ester **7** in 39, 8, 5, and 9% yield, respectively, accompanied by a small amount (9%) of unreacted starting material (Scheme 2, Table 1).

4-Chloro-7-methylisatin (**6a**) is formed by the hydrolysis and subsequent oxidation of **4a** with air moisture and oxygen, which is proved by an independent reaction (reflux of a xylene solution of **4a** in the presence of DMAP). The formation of ester **7** is rather unexpected since it was not formed by the reaction of **3a** in the presence of the Wittig reagent.[4] Moreover, it is known that the esterification of highly hindered tertiary alcohols (such as **3a**) with acids hardly proceeds in the presence of DMAP alone.[10] The transformation of **3a** to **7** could be explained by the involvement of ester **4a** in a transesterification reaction. The structure of **7** was confirmed by an independent synthesis from **3a** and phenylacetyl chloride.

We found that the conversion of starting compound **3**, mainly to dioxindole **4**, is significant when the substituent




**Scheme 2.**

$R^3$ is present in the molecule (Table 1). The yields are also affected by the substituent $R^6$; in the case of $R^6$=H they are distinctly lower. In contrast, benzoxazinone derivatives **5** arise as the main or even the only products when $R^2$ is a phenyl group (**3c**, **f**, **s**). It appeared that neither the nature of the catalyst nor the solvent significantly affected the course of the reaction. Surprisingly, the rearrangement also takes place in the absence of catalyst, though the yields are usually lower. Isatins **6** are formed to only a small extent and their structures are confirmed by comparison with independently prepared samples.[11]

Differentiation between isomeric **4** and **5** is achieved by comparison of their $^{13}$C NMR; the chemical shift assignment is based on our previous[4] work. Three characteristic resonances are found in the $^{13}$C NMR spectra for both isomeric compounds (Fig. 1). In isomer **4** carbons C-2, C-3, and ester carbonyl resonate in the range of $\delta$ 173–175, 69–71, 165–173 ppm, respectively, while isomer **5** can be recognised by the carbamate carbonyl (C-2), carbon C-4, and ketone group ($\delta$ 150–151, 76–79, and 192–200 ppm) resonances.

Infrared spectra of dioxindole esters **4** show characteristic absorption bands at 3200 $cm^{-1}$ (broad), 1720–1760 $cm^{-1}$ and 1610–1640 $cm^{-1}$ assigned to the amino, ester, and lactam group, respectively. However, the differentiation between isomeric **4** and **5** cannot be unequivocally achieved by their IR spectra alone, since the characteristic absorption bands of both isomeric heterocycles appear in nearly the same region.

Previously we demonstrated that by treating 5,8-disubstituted 3-benzyl-3-hydroxyquinoline-2,4(1*H*,3*H*)-diones **3** with the Wittig reagent, products of indoline and benzoxazine structural type are formed through a rearrangement of the quinoline framework. We proposed a mechanism in which the base-catalysed abstraction of NH proton is followed by ring-opening ring-closure via intermediately formed isocyanates (isocyanate mechanism). This was also in accord with the results obtained from the rearrangement of furo[2,3-*c*]quinoline-2,4(3a*H*,5*H*)-diones.[4]

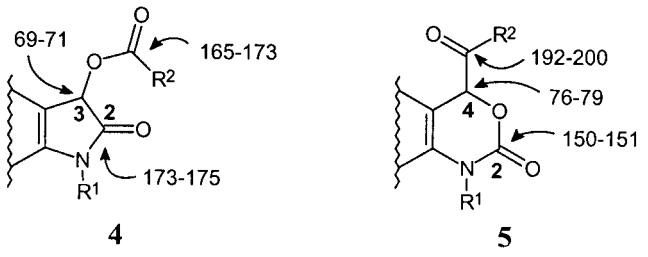


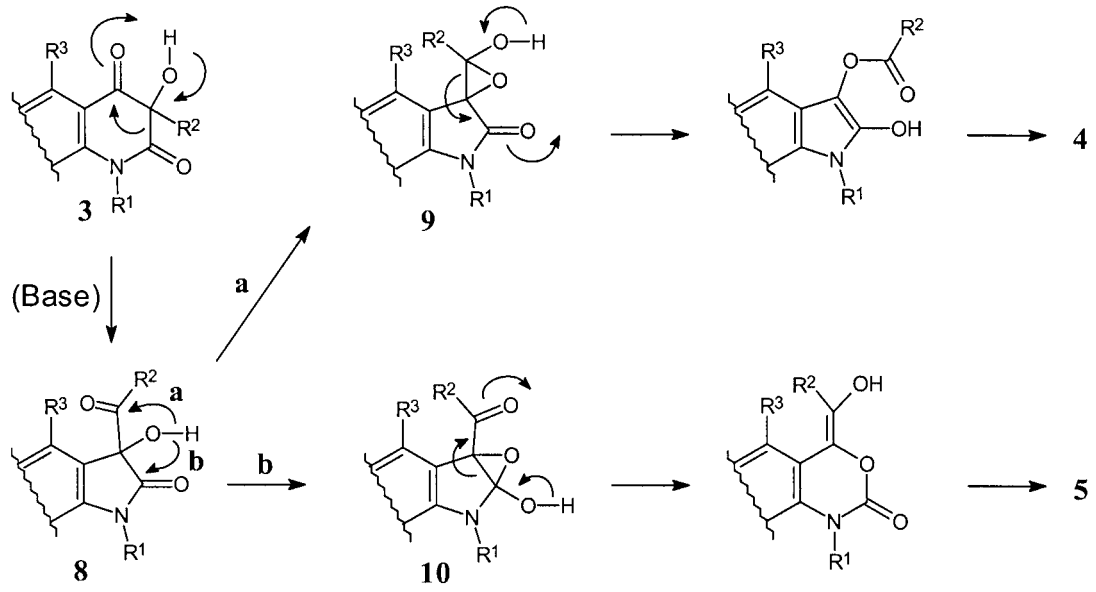

**Figure 1.** $^{13}$C NMR data for compounds **4** and **5**.

In order to establish this reaction pathway we decided to trap the isocyanate intermediates. Compounds **3e**, **l**, and **s** were subjected to the rearrangement conditions in cyclohexanol solution. We found that none of the expected cyclohexyl carbamates were formed; moreover, by comparison with results obtained in xylene solution, only marginal changes in product distribution were observed. As the abstraction of the NH proton is a key step in this mechanism, we decided to carry out the reaction with *N*-substituted derivatives **3**. Thus, xylene solutions of compounds **3j**, **k**, and **t** were heated in the presence of DMAP or $Ph_3P$. In the case of **3t** and **3k** no reaction was observed while **3j** rearranged, albeit in small yield, to dioxindole ester **4j** (Table 1). The formation of **4j** indicates that, at least in this particular case, the isocyanate mechanism is certainly not operating.

Based on the above experiments, it is obvious that the isocyanate mechanism no longer accounts for our current observations. Another mechanistic possibility, which cannot be ruled out, is shown in Scheme 3. First, 1,2-shift of carboxamide group in α-ketol type rearrangement[12] to intermediate **8** is proposed.[13] Indeed, small amounts (5%) of **8b** were isolated when xylene solution of **3b** was refluxed in the absence of base. Although it is known that the α-ketol rearrangement occurs by acid or base catalysis,[14] at least two examples of a thermally induced reaction have also been reported.[15] In our case, this can be explained by an intramolecular proton transfer.

For the base-catalysed α-ketol rearrangement it has been deduced that the migratory group acquires partial carbanionic character. So, electron-withdrawing groups $R^3$ would facilitate the reaction, while electron-donating groups would retard it. But in the case of **3a**–**t** it seems that just any group (e.g. Cl or Me) facilitates the rearrangement better than hydrogen. One could account for it by steric effects; a driving force for the formation of **8** could be ascribed to a release of the steric strain between neighbouring group $R^3$ and the carbonyl oxygen of the initial compound **3**. Still, the relatively small sizes of the methyl group and chlorine atom makes it less probable. We believe that this phenomenon can be best rationalised by the α-ketol rearrangement of **3** via a transition state with a diradicaloid character, which has been recently suggested by Sprecher.[16]

Except for the case of **3b**, intermediate **8** is too unstable to be isolated or even detected in the crude reaction mixture. It is further transformed to **5** and/or **4** most probably via an epoxide intermediate **10** and/or **9** (Scheme 3). Closely




**Scheme 3.**

related examples of α-hydroxy-β-diketone to α-ketol-ester rearrangement,[17] and vice versa,[18] recently described in the literature, have been accomplished under base catalysis; however, thermal reactions have been reported as well.[19]

The mechanism proposed in Scheme 3 also explains well an increase in the ratio **5**/**4** in the case of 3-phenyl derivatives of **3** ($R^2$=Ph), in which path **a** is suppressed due to lower reactivity of aromatic keto-group in the intermediate **8**. A more detailed analysis of the mechanism is beyond the scope of the present work and will be the subject of a forthcoming investigation.

## Experimental

Melting points were determined on a Kofler block or Gallenkamp apparatus. IR (KBr) spectra were recorded on a Perkin–Elmer 421 and Mattson 3000 spectrophotometers. NMR spectra were recorded on a Bruker DPX-300 spectrometer. Chemical shifts are given on the $\delta$ scale (ppm) and are referenced to internal TMS. MS spectra were obtained on a VG-Analytical AutospecQ instrument. Column chromatography was carried out on silica gel (Kavalier, Votice). Elemental analyses (C, H, N) were performed with a Perkin–Elmer 2400 CHN Analyzer.

**4-Hydroxy-2(1*H*)-quinolones (2a–t) and 3-hydroxyquinoline-2,4(1*H*,3*H*)-diones (3a–t)** were prepared according to the general procedure described in Ref. 4. For physical and spectroscopic data of compounds **2a**, **2d**, **3a**, and **3d**, see Ref. 4 and for **3g**–**k**, see Ref. 2.

**2b**: Colourless crystals, yield 41%, mp 164–167°C (ethanol), IR: 3490, 3185, 2975, 2945, 2880, 1630, 1586, 1478, 1402, 1378, 1340, 1228, 1212, 968, 853, 833, 676, 650 $cm^{-1}$. $\delta_H$ ($CDCl_3$): 0.95 (t, *J*=7.2 Hz, 3H, $CH_3$ of butyl), 1.37–1.50 (m, 2H, H-3 of butyl), 1.50–1.62 (m, 2H, H-2 of butyl), 2.43 (s, 3H, Ar-$CH_3$), 2.69 (t, *J*=7.5 Hz, 2H, H-1 of butyl), 7.08 (d, *J*=8.0 Hz, 1H, H-5), 7.20 (dd, *J*=8.0, 0.5 Hz, 1H, H-6), 8.49 (br s, 1H), 8.89 (br s, 1H). $\delta_C$ ($CDCl_3$): 14.03, 17.53, 22.92, 23.36, 30.23, 110.84, 115.61, 123.57, 123.80, 125.21, 130.77, 137.68, 157.20, 163.70. Anal. calcd (found) for $C_{14}H_{16}ClNO_2$: C 63.28 (63.29); H 6.07 (6.15); N 5.27 (5.32).

**2c**: Colourless crystals, yield 36%, mp 274–275°C (ethanol), IR: 3285, 3205, 3100, 3058, 1623, 1586, 1500, 1482, 1458, 1399, 1355, 1316, 1287, 1150, 972, 818, 778, 708, 648 $cm^{-1}$. $\delta_H$ ($CDCl_3$): 2.42 (s, 3H, Ar-$CH_3$), 7.15 (d, *J*=8.0 Hz, 1H, H-6), 7.27 (d, *J*=8.0 Hz, 1H, H-7), 7.47–7.54 (m, 5H, Ph), 8.67 (br s, 1H). $\delta_C$ (DMSO-$d_6$): 17.44, 112.67, 114.24, 122.66, 124.31, 127.18, 127.67, 127.95, 131.18, 131.45, 132.63, 138.59, 158.09, 161.80. EIMS, *m*/*z* (%): 287 ($M^+$, 40, $^{37}Cl$), 285 ($M^+$, 100, $^{35}Cl$), 170 (38, $^{35}Cl$), 168 (95, $^{37}Cl$), 140 (20), 118 (8), 104 (20), 89 (25), 77 (26), 69 (12), 63 (16), 57 (12). Anal. calcd (found) for $C_{16}H_{12}ClNO_2$: C 67.26 (67.63); H 4.23 (4.54); N 4.90 (5.29).

**2e**: Colourless crystals, yield 83%, mp 167–170°C (toluene), IR: 3409, 3276, 3028, 2956, 2931, 2869, 1707, 1672, 1626, 1620, 1570, 1479, 1444, 1267, 1207, 1161, 1082, 956, 848, 810, 787, 762 $cm^{-1}$. $\delta_H$ ($CDCl_3$): 0.96 (t, *J*=7.2 Hz, 3H, $CH_3$ of butyl), 1.38–1.50 (m, 2H, H-3 of butyl), 1.50–1.63 (m, 2H, H-2 of butyl), 2.37 (s, 3H, $C_{(8)}$-$CH_3$), 2.65 (t, *J*=7.6 Hz, 2H, H-1 of butyl), 2.76 (s, 3H, $C_{(5)}$-$CH_3$), 5.85 (br s, 1H, OH), 6.88 (d, *J*=7.5 Hz, 1H, H-5), 7.17 (d, *J*=7.5 Hz, 1H, H-6), 8.45 (br s, 1H, NH). $\delta_C$ (DMSO-$d_6$): 13.98, 17.28, 22.14, 22.47, 24.21, 30.35, 111.11, 114.29, 120.71, 124.38, 130.17, 133.25, 136.69, 159.94, 162.93. Anal. calcd (found) for $C_{15}H_{19}NO_2$: C 73.44 (73.39); H 7.81 (7.87); N 5.71 (5.99).

**2f**: Colourless crystals, yield 73%, mp 284–285°C (ethanol), IR: 3276, 3209, 3120, 2927, 2870, 1622, 1587, 1548, 1473, 1456, 1437, 1398, 1350, 1294, 1251, 1240, 1154, 1144, 812, 800, 771, 698 $cm^{-1}$. $\delta_H$ ($CDCl_3$): 2.40 (s, 3H, $C_{(8)}$-$CH_3$), 2.73 (s, 3H, $C_{(5)}$-$CH_3$), 6.24 (br s, 1H, OH), 6.91 (d, *J*=7.6 Hz, 1H, H-5), 7.23 (d, *J*=7.6 Hz, 1H,

H-6), 7.45–7.59 (m, 5H, Ph), 8.48 (br s, 1H, NH). $\delta_C$ (DMSO-$d_6$+$CDCl_3$): 17.42, 24.21, 112.33, 114.53, 120.73, 124.57, 127.11, 128.14, 130.92, 131.40, 133.01, 134.42, 137.57, 160.92, 162.25. EIMS, *m/z* (%): 265 ($M^+$, 100), 236 (6), 208 (6), 165 (5), 148 (72), 119 (28), 104 (13), 91 (18), 77 (20), 57 (14). Anal. calcd (found) for $C_{17}H_{15}NO_2$: C 76.96 (77.34); H 5.70 (5.71); N 5.28 (5.44).

**2l**: Colourless crystals, yield 61%, mp 193–194°C (ethyl acetate), IR: 3130, 2978, 2940, 1635, 1591, 1499, 1457, 1424, 1372, 1268, 1250, 1200, 1159, 1088, 901, 852, 822, 725, 701 $cm^{-1}$. $\delta_H$ ($CDCl_3$+DMSO-$d_6$): 0.93 (t, *J*=7.1 Hz, 3H, $CH_3$ of butyl), 1.34–1.58 (m, 4H, H-3 and H-2 of butyl), 2.68 (t, *J*=7.5 Hz, 2H, H-1 of butyl), 7.22 (d, *J*=8.7 Hz, 1H, H-8), 7.31 (dd, *J*=8.7, 2.3 Hz, 1H, H-7), 7.94 (d, *J*=2.3 Hz, 1H, H-5), 9.28 (br s, 1H, OH), 10.96 (br s, 1H, NH). $\delta_C$ (DMSO-$d_6$): 13.90, 22.18, 22.79, 30.21, 113.01, 116.63, 121.61, 124.95, 129.42, 135.94, 155.69, 163.23. Anal. calcd (found) for $C_{13}H_{14}ClNO_2$: C 62.03 (62.07); H 5.61 (5.63); N 5.56 (5.68).

**2m**: Colourless crystals, yield 78%, mp 192–194°C (ethanol), IR: 3132, 3051, 2964, 2873, 1643, 1618, 1591, 1558, 1448, 1431, 1381, 1288, 1275, 1267, 1223, 1195, 1165, 1064, 954, 858, 812, 723 $cm^{-1}$. $\delta_H$ (DMSO-$d_6$): 0.90 (t, *J*=7.0 Hz, 3H, $CH_3$ of butyl), 1.28–1.48 (m, 4H, H-2 and H-3 of butyl), 2.35 (s, 3H, Ar-$CH_3$), 2.50–2.60 (m, 2H, H-1 of butyl), 7.15 (d, *J*=8.3 Hz, 1H, ArH), 7.25 (dd, *J*=8.3, 1.5 Hz, 1H, ArH), 7.68 (br s, 1H, ArH), 9.87 (br s, 1H), 11.18 (br s, 1H). $\delta_C$ (DMSO-$d_6$): 13.95, 20.59, 22.21, 22.77, 30.39, 111.71, 114.63, 115.23, 121.97, 129.61, 130.65, 135.26, 156.60, 163.34. Anal. calcd (found) for $C_{14}H_{17}NO_2$: C 72.70 (72.44); H 7.41 (7.37); N 6.06 (5.83).

**2n**: Colourless crystals, yield 82%, mp 203–204°C (ethanol), IR: 3301, 2953, 2929, 2870, 1636, 1597, 1488, 1467, 1454, 1408, 1384, 1359, 1264, 1192, 1159, 1085, 1070, 904, 829, 801, 777, 746, 734, 709, 696 $cm^{-1}$. $\delta_H$ (DMSO-$d_6$): 0.91 (t, *J*=7.1 Hz, 3H, $CH_3$ of butyl), 1.28–1.50 (m, 4H, H-2 and H-3 of butyl), 2.42 (s, 3H, Ar-$CH_3$), 2.55–2.65 (m, 2H, H-1 of butyl), 7.06 (dd, $J_1$=$J_2$=7.6 Hz, 1H, ArH), 7.29 (d, *J*=7.6 Hz, 1H, ArH), 7.77 (d, *J*=7.6 Hz, 1H, ArH), 9.95 (br s, 1H), 10.45 (br s, 1H). $\delta_C$ (DMSO-$d_6$): 13.96, 17.23, 22.18, 22.73, 30.36, 111.39, 115.45, 120.42, 120.57, 122.83, 130.82, 135.61, 157.16, 163.76. Anal. calcd (found) for $C_{14}H_{17}NO_2$: C 72.70 (72.78); H 7.41 (7.66); N 6.06 (6.47).

**2o**: Colourless crystals, yield 32%, mp 270–271°C (acetic acid), IR: 3247, 3174, 3060, 2962, 2933, 1627, 1593, 1562, 1479, 1454, 1388, 1319, 1211, 1190, 1159, 1109, 1070, 995, 916, 820, 773, 735, 700, 648 $cm^{-1}$. $\delta_H$ (DMSO-$d_6$): 2.47 (s, 3H, $CH_3$), 3.96 (s, 2H, $CH_2$Ph), 7.09–7.16 (m, 1H, ArH), 7.19–7.29 (m, 5H, ArH), 7.80 (d, *J*=8.7 Hz, 1H, ArH), 10.50 (br s, 1H), 10.66 (br s, 1H). $\delta_C$ (DMSO−$d_6$): 13.77, 28.34, 110.40, 114.37, 120.68, 121.61, 121.67, 125.48, 127.91, 128.09, 134.84, 136.95, 140.46, 157.56, 163.81. Anal. calcd (found) for $C_{17}H_{14}ClNO_2$: C 68.12 (68.51); H 4.71 (4.67); N 4.67 (4.60).

**2p**: Colourless crystals, yield 82%, mp 196–199°C (acetic acid), IR: 3278, 3155, 3084, 3026, 2971, 2862, 1631, 1595, 1558, 1493, 1452, 1386, 1376, 1230, 1197, 1189, 1082, 885, 877, 854, 750, 698 $cm^{-1}$. $\delta_H$ (DMSO-$d_6$): 2.28 (s, 3H, $CH_3$), 2.69 (s, 3H, $CH_3$), 3.95 (s, 2H, $CH_2$Ph), 6.74 (br s, 1H, ArH), 6.92 (br s, 1H, ArH), 7.09–7.25 (m, 5H, Ph), 9.90 (br s, 1H), 11.20 (br s, 1H). $\delta_C$ (DMSO-$d_6$): 20.79, 23.81, 27.90, 109.28, 111.99, 113.14, 125.37, 126.20, 127.85, 128.03, 135.61, 138.91, 139.07, 140.61, 160.46, 162.91. Anal. calcd (found) for $C_{18}H_{17}NO_2$: C 77.40 (77.75); H 6.13 (6.20); N 5.01 (4.82).

**2r**: Colourless crystals, yield 48%, mp 200–206°C (ethanol), IR: 3267, 3139, 3066, 2962, 2863, 1630, 1593, 1548, 1493, 1477, 1386, 1375, 1357, 1281, 1250, 1221, 1186, 1169, 1090, 1062, 1034, 927, 889, 875, 841, 748, 723, 694, 665 $cm^{-1}$. $\delta_H$ (DMSO-$d_6$): 0.89 (t, *J*=6.8 Hz, 3H, $CH_3$ of butyl), 1.30–1.40 (m, 4H, H-2 and H-3 of butyl), 2.27 (s, 3H, Ar-$CH_3$), 2.50–2.60 (m, 2H, H-1 of butyl), 2.69 (s, 3H, Ar-$CH_3$), 6.70 (s, 1H, ArH), 6.90 (s, 1H, ArH), 9.53 (br s, 1H), 11.09 (br s, 1H). $\delta_C$ (DMSO-$d_6$): 13.97, 20.78, 22.20, 22.46, 23.83, 30.45, 110.47, 112.03, 113.05, 126.03, 135.31, 138.42, 138.75, 159.59, 162.91. Anal. calcd (found) for $C_{15}H_{19}NO_2$: C 73.44 (73.70); H 7.81 (8.04); N 5.71 (6.10).

**2s**: Colourless crystals, yield 40%, mp 334–336°C (acetic acid), IR: 3280, 3074, 2948, 1639, 1587, 1558, 1442, 1386, 1350, 1292, 1236, 1199, 1126, 1089, 887, 868, 833, 762, 692 $cm^{-1}$. $\delta_H$ (DMSO-$d_6$): 2.25 (s, 3H, Ar-$CH_3$), 2.66 (s, 3H, Ar-$CH_3$), 6.75 (br s, 1H, ArH), 6.93 (br s, 1H, ArH), 7.28–7.34 (m, 3H, Ph), 7.36–7.43 (m, 2H, Ph), 9.43 (br s, 1H), 11.24 (br s, 1H). Anal. calcd (found) for $C_{17}H_{15}NO_2$: C 76.96 (76.48); H 5.70 (5.55); N 5.28 (4.93).

**2t**: Colourless crystals, yield 81%, mp 188–189°C (ethanol), IR: 3172, 2950, 1620, 1602, 1581, 1562, 1494, 1465, 1447, 1380, 1357, 1324, 1298, 1271, 1197, 1151, 1042, 929, 832, 754, 133, 668 $cm^{-1}$. $\delta_H$ (DMSO-$d_6$): 0.89 (m, 3H, $CH_3$), 1.35 (m, 4H, $CH_2CH_2$), 2.37 (s, 3H, $CH_3$), 2.58 (m, 2H, $CH_2$), 2.73 (s, 3H, $CH_3$), 3.55 (s, 3H, $CH_3$), 6.83 (s, 1H, ArH), 7.11 (s, 1H, ArH), 9.54 (br s, 1H, OH). $\delta_C$ (DMSO-$d_6$): 13.95, 21.13, 22.18, 23.31, 24.50, 29.66, 30.37, 110.06, 112.65, 112.86, 126.53, 135.89, 138.90, 139.69, 158.43, 162.20. Anal. calcd (found) for $C_{16}H_{21}NO_2$: C 74.10 (73.78); H 8.16 (7.88); N 5.40 (5.17).

**3b**: Pale yellow crystals, yield 46%, mp 151–152°C (benzene–*c*-$C_6H_{12}$), IR: 3461, 3297, 2957, 2928, 2871, 1719, 1686, 1585, 1489, 1462, 1363, 1252, 1226, 1180, 1089, 1053, 956, 851, 806, 723 $cm^{-1}$. $\delta_H$ ($CDCl_3$): 0.84 (t, *J*=7.1 Hz, 3H, $CH_3$ of butyl), 1.19–1.32 (m, 4H, H-3 and H-2 of butyl), 1.80–2.02 (m, 2H, H-1 of butyl), 2.31 (s, 3H, Ar-$CH_3$), 3.94 (s, 1H, OH), 7.12 (d, *J*=8.2 Hz, 1H, H-6), 7.29 (dd, *J*=8.2, 0.6 Hz, 1H, H-7), 7.63 (s, 1H, NH). $\delta_C$ ($CDCl_3$): 13.74, 17.02, 22.45, 25.22, 39.76, 83.16, 117.11, 122.91, 126.04, 132.40, 136.62, 139.39, 171.68, 194.51. EIMS, *m/z* (%): 283 ($M^+$, 12, $^{37}Cl$), 281 ($M^+$, 36, $^{35}Cl$), 240 (11, $^{37}Cl$), 238 (33, $^{35}Cl$), 199 (45, $^{37}Cl$), 197 (100, $^{35}Cl$), 182 (3, $^{37}Cl$), 180 (10, $^{35}Cl$), 170 (3, $^{37}Cl$), 168 (10, $^{35}Cl$), 141 (7), 111 (7), 97 (15), 85 (26), 69 (35), 57 (54). Anal. calcd (found) for $C_{14}H_{16}ClNO_3$: C 59.68 (60.02); H 5.72 (5.92); N 4.97 (4.76).

**3c**: Pale yellow crystals, yield 67%, mp 182–185°C (methanol), IR: 3668, 3456, 3249, 3095, 2970, 2922,

2842, 1724, 1680, 1487, 1450, 1359, 1282, 1259, 1180, 1155, 1049, 1030, 981, 954, 845, 812, 783, 750, 700 $cm^{-1}$. $\delta_H$ ($CDCl_3$): 2.28 (s, 3H, Ar-$CH_3$), 4.45 (s, 1H, OH), 7.06 (d, $J$=8.2 Hz, 1H, H-6), 7.22 (d, $J$=8.2 Hz, H-7), 7.31–7.39 (m, 5H, Ph), 7.83 (br s, 1H, NH). $\delta_C$ (DMSO-$d_6$+$CDCl_3$): 17.35, 84.22, 118.50, 124.08, 124.80, 126.08, 128.72, 128.87, 130.17, 136.07, 137.48, 139.64, 170.41, 192.49. Anal. calcd (found) for $C_{16}H_{12}ClNO_3$: C 63.69 (63.97); H 4.01 (3.98); N 4.64 (4.80).

**3e**: Colourless crystals, yield 86%, mp 156–158°C (ethanol), IR: 3462, 3270, 2942, 2920, 2845, 1695, 1664, 1602, 1577, 1500, 1365, 1252, 1178, 1161, 1078, 1032, 963, 861, 810, 753, 718, 654 $cm^{-1}$. $\delta_H$ ($CDCl_3$): 0.83 (t, $J$=7.2 Hz, 3H, $CH_3$ of butyl), 1.19–1.31 (m, 4H, H-3 and H-2 of butyl), 1.75–1.98 (m, 2H, H-1 of butyl), 2.27 (s, 3H, $C_{(8)}$-$CH_3$), 2.56 (s, 3H, $C_{(5)}$-$CH_3$), 3.91 (s, 1H, OH), 6.90 (d, $J$=7.7 Hz, 1H, H-6), 7.26 (d, $J$=7.7 Hz, 1H, H-7), 7.45 (br s, 1H, NH). $\delta_C$ ($CDCl_3$): 13.78, 16.87, 20.88, 22.48, 25.28, 40.33, 82.90, 117.77, 121.39, 126.52, 136.25, 138.62, 139.61, 171.94, 197.43. EIMS, $m/z$ (%): 261 ($M^+$, 45), 218 (55), 205 (6), 177 (100), 176 (96), 148 (16), 137 (7), 119 (16), 104 (15), 91 (21), 77 (22), 69 (35), 57 (48). Anal. calcd (found) for $C_{15}H_{19}NO_3$: C 68.94 (70.09); H 7.33 (7.20); N 5.36 (4.99).

**3f**: Colourless crystals, yield 65%, mp 190–194°C (methanol), IR: 3562, 3525, 3487, 3448, 3238, 3085, 1712, 1670, 1614, 1579, 1502, 1450, 1388, 1367, 1284, 1180, 1157, 1142, 1080, 1028, 974, 850, 810, 787, 754, 700, 665 $cm^{-1}$. $\delta_H$ ($CDCl_3$): 2.28 (s, 3H, $C_{(8)}$-$CH_3$), 2.52 (s, 3H, $C_{(5)}$-$CH_3$), 4.49 (s, 1H, OH), 6.85 (d, $J$=7.7 Hz, 1H, H-6), 7.21 (d, $J$=7.7 Hz, 1H, H-7), 7.27–7.42 (m, 5H, Ph), 7.77 (br s, 1H, NH). $\delta_C$ ($CDCl_3$): 16.87, 20.96, 83.32, 118.49, 121.62, 125.73, 126.74, 129.10, 129.27, 136.47, 137.53, 138.19, 139.78, 170.35, 194.80. Anal. calcd (found) for $C_{17}H_{15}NO_3$: C 72.58 (72.43); H 5.37 (5.28); N 4.98 (5.15).

**3l**: Colourless crystals, yield 95%, mp 208–209°C (ethanol), IR: 3467, 3259, 2956, 2873, 1705, 1682, 1610, 1481, 1410, 1359, 1244, 1171, 1130, 1086, 1035, 902, 843, 723, 661 $cm^{-1}$. $\delta_H$ ($CDCl_3$): 0.84 (t, $J$=7.2 Hz, 3H, $CH_3$ of butyl), 1.19–1.48 (m, 4H, H-3 and H-2 of butyl), 1.77–2.00 (m, 2H, H-1 of butyl), 3.79 (br s, 1H, OH), 7.00 (d, $J$=8.4 Hz, 1H, H-8), 7.53 (dd, $J$=8.4, 2.4 Hz, 1H, H-7), 7.88 (d, $J$=2.4 Hz, 1H, H-5), 8.93 (br s, 1H, NH). $\delta_C$ (DMSO-$d_6$): 13.63, 21.90, 24.54, 81.67, 118.26, 120.17, 125.65, 126.36, 135.37, 140.21, 172.61, 194.96. Anal. calcd (found) for $C_{13}H_{14}ClNO_3$: C 58.32 (58.19); H 5.27 (5.26); N 5.23 (5.42).

**3m**: Colourless crystals, yield 74%, mp 174–177°C (ethyl acetate), IR: 3473, 3188, 3120, 3068, 2954, 2868, 1701, 1662, 1620, 1508, 1421, 1379, 1329, 1271, 1244, 1192, 1157, 1118, 1092, 1037, 960, 910, 839, 821, 706, 669 $cm^{-1}$. $\delta_H$ (DMSO-$d_6$+$CDCl_3$): 0.81 (t, $J$=7.0 Hz, 3H, $CH_3$ of butyl), 1.10–1.40 (m, 4H, H-3 and H-2 of butyl), 1.65–1.85 (m, 2H, H-1 of butyl), 2.32 (s, 3H, Ar-$CH_3$), 5.31 (br s, 1H, OH), 6.99 (d, $J$=8.2 Hz, 1H, H-8), 7.32 (d, $J$=8.2 Hz, 1H, H-7), 7.55 (s, 1H, H-5), 10.58 (br s, 1H, NH). $\delta_C$ (DMSO-$d_6$+$CDCl_3$): 13.74, 20.29, 22.25, 24.70, 39.90, 82.04, 116.27, 119.01, 126.57, 131.76, 136.43, 139.15, 173.02, 196.23. Anal. calcd (found) for $C_{14}H_{17}NO_3$: C 68.00 (67.78); H 6.93 (6.59); N 5.66 (6.03).

**3n**: Pale yellow crystals, yield 64%, mp 121–123°C (benzene–$c$-$C_6H_{12}$), IR: 1483, 3261, 3193, 3109, 2956, 2935, 2871, 1701, 1664, 1602, 1498, 1466, 1388, 1369, 1329, 1257, 1238, 1188, 1116, 1095, 1045, 899, 839, 793, 769, 754, 742, 719, 677 $cm^{-1}$. $\delta_H$ (DMSO-$d_6$): 0.76 (t, $J$=7.0 Hz, 3H, $CH_3$ of butyl), 1.10–1.40 (m, 4H, H-3 and H-2 of butyl), 1.60–1.80 (m, 2H, H-1 of butyl), 2.31 (s, 3H, Ar-$CH_3$), 5.63 (s, 1H, OH), 7.02 (dd, $J_1$=$J_2$=7.5 Hz, 1H, H-6), 7.42 (d, $J$=7.5 Hz, 1H, ArH), 7.58 (d, $J$=7.5 Hz, 1H, ArH), 9.90 (br s, 1H, NH). $\delta_C$ (DMSO-$d_6$): 13.65, 17.17, 21.87, 24.67, 39.26, 81.76, 119.48, 122.31, 124.44, 124.59, 137.02, 139.28, 173.15, 196.19. Anal. calcd (found) for $C_{14}H_{17}NO_3$: C 68.00 (68.27); H 6.93 (6.75); N 5.66 (5.62).

**3o**: Colourless crystals, yield 92%, mp 187–188°C (ethanol), IR: 3456, 3251, 3192, 3066, 2968, 2925, 2887, 1712, 1662, 1595, 1585, 1493, 1454, 1402, 1379, 1350, 1242, 1217, 1136, 1080, 1047, 1007, 914, 885, 829, 804, 785, 723, 712, 698, 681 $cm^{-1}$. $\delta_H$ (DMSO-$d_6$): 2.31 (s, 3H, $CH_3$), 3.32 (s, 2H, $CH_2$Ph), 5.90 (s, 1H, OH), 6.94–7.02 (m, 2H, Ph), 7.10–7.18 (m, 3H, Ph), 7.20 (d, $J$=8.4 Hz, 1H, ArH), 7.51 (d, $J$=8.4 Hz, 1H, ArH), 10.15 (br s, 1H, NH). $\delta_C$ (DMSO-$d_6$): 13.99, 45.87, 82.16, 118.79, 122.52, 123.20, 125.20, 126.70, 127.40, 130.05, 133.70, 140.36, 140.61, 172.44, 194.51. Anal. calcd (found) for $C_{17}H_{14}ClNO_3$: C 64.67 (65.05); H 4.47 (4.39); N 4.44 (4.73).

**3p**: Colourless crystals, yield 96%, mp 198–199°C (benzene), IR: 3479, 3201, 3157, 3041, 2974, 2947, 2918, 2846, 1703, 1668, 1616, 1577, 1523, 1496, 1458, 1427, 1402, 1386, 1286, 1240, 1205, 1161, 1126, 1037, 924, 848, 756, 746, 712, 675 $cm^{-1}$. $\delta_H$ ($CDCl_3$): 2.37 (s, 3H, Ar-$CH_3$), 2.44 (s, 3H, Ar-$CH_3$), 3.17 (d, $J$=13.5 Hz, 1H, $CH_2$Ph), 3.28 (d, $J$=13.5 Hz, 1H, $CH_2$Ph), 4.07 (s, 1H, OH), 6.74 (br s, 1H, ArH), 6.81 (br s, 1H, ArH), 7.01–7.10 (m, 2H, Ph), 7.18–7.25 (m, 3H, Ph), 9.88 (br s, 1H, NH). $\delta_C$ ($CDCl_3$): 20.86, 21.76, 47.32, 82.81, 115.40, 127.63, 128.20, 128.27, 130.14, 133.20, 140.82, 141.88, 146.81, 172.77, 195.37. Anal. calcd (found) for $C_{18}H_{17}NO_3$: C 73.20 (73.55); H 5.80 (5.80); N 4.74 (4.61).

**3r**: Colourless crystals, yield 79%, mp 158–162°C (benzene), IR: 3473, 3344, 3222, 3165, 3016, 2952, 2927, 2871, 1701, 1664, 1616, 1577, 1520, 1464, 1427, 1402, 1386, 1288, 1226, 1211, 1180, 1155, 1120, 1099, 1026, 966, 900, 845, 808, 744, 679 $cm^{-1}$. $\delta_H$ ($CDCl_3$): 0.82 (t, $J$=7.1 Hz, 3H, $CH_3$ of butyl), 1.15–1.30 (m, 3H), 1.35–1.54 (m, 1H), 1.75–2.02 (m, 2H, H-1 of butyl), 2.35 (s, 3H, Ar-$CH_3$), 2.57 (s, 3H, Ar-$CH_3$), 4.06 (s, 1H, OH), 6.77 (br s, 1H, ArH), 6.79 (br s, 1H, ArH), 9.72 (br s, 1H, NH). $\delta_C$ ($CDCl_3$): 13.79, 21.00, 21.73, 22.49, 25.21, 40.75, 82.54, 115.14, 115.19, 128.12, 140.98, 141.94, 146.65, 173.45, 196.71. Anal. calcd (found) for $C_{15}H_{19}NO_3$: C 68.94 (69.30); H 7.33 (7.13); N 5.36 (5.73).

**3s**: Colourless crystals, yield 79%, mp 224–231°C (ethyl acetate), IR: 3456, 3147, 3012, 2922, 1712, 1660, 1614, 1575, 1523, 1429, 1381, 1284, 1226, 1182, 1159, 1030, 881, 848, 745, 706, 696 $cm^{-1}$. $\delta_H$ (DMSO-$d_6$+$CDCl_3$):

2.26 (s, 3H, Ar-$CH_3$), 2.41 (s, 3H, Ar-$CH_3$), 6.07 (s, 1H, OH), 6.66 (br s, 1H, ArH), 6.75 (br s, 1H, ArH), 7.22–7.31 (m, 3H, Ph), 7.32–7.40 (m, 2H, Ph), 10.87 (br s, 1H, NH). $\delta_C$ (DMSO-$d_6$+$CDCl_3$): 20.99, 21.41, 83.05, 114.74, 115.95, 125.55, 126.86, 128.40, 128.46, 138.66, 140.72, 141.62, 145.20, 170.88, 194.59. Anal. calcd (found) for $C_{17}H_{15}NO_3$: C 72.58 (72.93); H 5.37 (5.51); N 4.98 (4.85).

**3t**: Colourless crystals, yield 85%, mp 70–74°C (benzene–*c*-$C_6H_{12}$), IR: 3485, 3429, 2956, 1703, 1660, 1607, 1570, 1494, 1461, 1342, 1297, 1153, 1075, 1029, 847 $cm^{-1}$. $\delta_H$ (DMSO-$d_6$): 0.74 (t, *J*=7.1 Hz, 3H, $CH_3$ of butyl), 0.95–1.36 (m, 4H, H-3 and H-2 of butyl), 1.64 (m, 2H, H-1 of butyl), 2.36 (s, 3H, Ar-$CH_3$), 2.45 (s, 3H, Ar-$CH_3$), 3.35 (s, 3H, N-$CH_3$), 5.50 (s, 1H, CH), 6.88 (s, 1H, ArH), 7.04 (s, 1H, ArH). $\delta_C$ (DMSO-$d_6$): 13.61, 20.71, 21.42, 21.84, 25.08, 30.13, 39.36, 82.51, 114.17, 117.20, 127.00, 139.67, 142.98, 144.60, 171.51, 196.61. Anal. calcd (found) for $C_{16}H_{21}NO_3$: C 69.79 (70.16); H 7.69 (8.00); N 5.09 (4.98).

### General procedure for the rearrangement of 3-hydroxyquinoline-2,4(1*H*,3*H*)-diones (3a–t)

A mixture of **3** (5 mmol) and the catalyst (1 mmol, Table 1) in xylene or cyclohexanol (15 mL) was refluxed for 2–12 h (Table 1). After cooling, the precipitated unreacted starting material **3** was filtered off with suction. Filtrate was evaporated and products **4**–**8** (Table 1) were separated by column chromatography, using benzene and then successive mixtures of benzene–ethyl acetate (in ratios from 99:1 to 8:2) as eluents. For yields see Table 1. For physical and spectroscopic data of compounds **4a** and **4d**, see Ref. 4.

**4-Chloro-7-methyl-2-oxo-1,3-dihydro-2*H*-indol-3-yl pentanoate (4b):** Pale yellow crystals, mp 108–113°C (*c*-$C_6H_{12}$), IR: 3165, 3100, 3043, 2982, 2960, 2885, 1756, 1731, 1628, 1605, 1488, 1434, 1290, 1248, 1219, 1119, 1098, 1026, 968, 812 $cm^{-1}$. $\delta_H$ ($CDCl_3$): 0.92 (t, *J*=7.3 Hz, 3H, $CH_3$ of butyl), 1.31–1.45 (m, 2H, H-3 of butyl), 1.62–1.73 (m, 2H, H-2 of butyl), 2.22 (s, 3H, Ar-$CH_3$), 2.47 (t, *J*=7.5 Hz, 2H, H-1 of butyl), 6.05 (s, 1H, H-3), 6.92 (d, *J*=8.4 Hz, 1H, H-5), 7.05 (d, *J*=8.4 Hz, 1H, H-6), 8.19 (br s, 1H, NH). $\delta_C$ ($CDCl_3$): 13.67, 15.86, 22.15, 26.95, 33.44, 69.70, 118.54, 121.67, 123.26, 128.62, 132.72, 141.83, 172.31, 174.50. Anal. calcd (found) for $C_{14}H_{16}ClNO_3$: C 59.68 (59.83); H 5.72 (5.87); N 4.97 (5.25).

**4c**: Pale yellow crystals, mp 221–222°C (ethyl acetate), IR: 3195, 3099, 2933, 1745, 1722, 1626, 1601, 1485, 1452, 1423, 1332, 1315, 1282, 1248, 1203, 1138, 1111, 1072, 802, 792, 762, 706 $cm^{-1}$. $\delta_H$ ($CDCl_3$): 2.24 (s, 3H, Ar-$CH_3$), 6.26 (s, 1H, H-3), 6.92 (d, *J*=8.3 Hz, 1H, H-5), 7.07 (d, *J*=8.3 Hz, 1H, H-6), 7.45 (m, 2H, *m*-Ph), 7.59 (m, 1H, *p*-Ph), 8.10 (m, 2H, *o*-Ph), 8.16 (br s, 1H, NH). $\delta_C$ (DMSO-$d_6$+$CDCl_3$): 16.10, 70.13, 118.75, 121.43, 122.34, 128.27, 128.43, 128.91, 129.89, 132.78, 133.45, 143.13, 165.02, 173.50. EIMS, *m*/*z* (%): 303 ($M^+$, 5, $^{37}Cl$), 301 ($M^+$, 17, $^{35}Cl$), 198 (5, $^{37}Cl$), 196 (16, $^{35}Cl$), 182 (5, $^{37}Cl$), 180 (15, $^{35}Cl$), 139 (5, $^{37}Cl$), 137 (16, $^{35}Cl$), 123 (14), 111 (18), 105 (100), 97 (34), 83 (38), 69 (62), 57 (52), 55 (45). Anal. calcd (found) for $C_{16}H_{12}ClNO_3$: C 63.69 (63.90); H 4.01 (3.96); N 4.64 (4.84).

**4e**: Pale yellow crystals, mp 107–110°C (*c*-$C_6H_{12}$), IR: 3165, 3093, 3039, 2954, 2933, 2871, 1749, 1724, 1633, 1604, 1508, 1454, 1425, 1348, 1284, 1242, 1163, 1089, 1053, 1039, 906, 806 $cm^{-1}$. $\delta_H$ ($CDCl_3$): 0.97 (t, *J*=7.3 Hz, 3H, $CH_3$ of butyl), 1.32–1.45 (m, 2H, H-3 of butyl), 1.61–1.72 (m, 2H, H-2 of butyl), 2.20 (s, 6H, 2×Ar-$CH_3$), 2.45 (t, *J*=7.4 Hz, 2H, H-1 of butyl), 6.08 (s, 1H, H-3), 6.76 (d, *J*=7.9 Hz, 1H, H-5), 7.00 (d, *J*=7.9 Hz, 1H, H-6), 7.88 (br s, 1H, NH). $\delta_C$ ($CDCl_3$): 13.67, 15.87, 17.63, 22.17, 27.00, 33.59, 70.10, 117.10, 122.31, 124.40, 131.47, 133.10, 140.42, 172.47, 174.91. EIMS, *m*/*z* (%): 261 ($M^+$, 12), 177 (100), 160 (29), 85 (15), 77 (16), 57 (45). Anal. calcd (found) for $C_{15}H_{19}NO_3$: C 68.94 (69.23); H 7.33 (7.61); N 5.36 (5.30).

**4f**: Pale violet crystals, mp 231–234°C (acetic acid), IR: 3182, 3099, 2935, 2852, 1743, 1718, 1635, 1604, 1508, 1450, 1421, 1334, 1315, 1288, 1248, 1111, 1070, 1043, 1026, 860, 806, 758, 731, 710, 667 $cm^{-1}$. $\delta_H$ ($CDCl_3$): 2.21 (s, 3H, Ar-$CH_3$), 2.22 (s, 3H, Ar-$CH_3$), 6.30 (s, 1H, H-3), 6.76 (d, *J*=7.9 Hz, 1H, H-5), 7.02 (d, *J*=7.9 Hz, 1H, H-6), 7.45 (m, 2H, *m*-Ph), 7.59 (m, 1H, *p*-Ph), 7.97 (br s, 1H, NH), 8.09 (m, 2H, *o*-Ph). $\delta_C$ (DMSO-$d_6$+$CDCl_3$): 15.98, 17.26, 70.80, 116.77, 122.20, 123.31, 128.64, 128.69, 129.42, 131.16, 132.22, 133.61, 141.45, 164.53, 173.68. EIMS, *m*/*z* (%): 281 ($M^+$, 35), 176 (82), 160 (24), 117 (7), 105 (100), 97 (8), 83 (7), 77 (24), 69 (6), 57 (7). Anal. calcd (found) for $C_{17}H_{15}NO_3$: C 72.58 (72.81); H 5.37 (4.99); N 4.98 (4.51).

**4h**: Colourless crystals, mp 72–74°C (*c*-$C_6H_{12}$), IR: 3220, 2960, 2933, 2873, 1737, 1695, 1620, 1599, 1469, 1388, 1361, 1346, 1327, 1292, 1261, 1230, 1197, 1165, 1153, 1105, 1036, 941, 906, 887, 841, 767, 744, 658 $cm^{-1}$. $\delta_H$ ($CDCl_3$): 0.92(t, *J*=7.3 Hz, 3H, $CH_3$ of butyl), 1.32–1.45 (m, 2H, H-3 of butyl), 1.62–1.73 (m, 2H, H-2 of butyl), 2.47 (dt, *J*=7.5, 0.8 Hz, 2H, H-1 of butyl), 5.95 (s, 1H, H-3), 6.86 (d, *J*=7.7 Hz, 1H, H-8), 7.04 (dd, *J*=7.7, 7.6 Hz, 1H, H-6), 7.31 (d, *J*=7.5 Hz, 1H, H-5), 7.71 (br s, 1H, NH). $\delta_C$ ($CDCl_3$): 13.67, 22.16, 26.93, 33.65, 70.12, 110.48, 123.08, 125.06, 125.71, 130.26, 141.71, 173.14, 174.81. EIMS, *m*/*z* (%): 233 ($M^+$, 22), 149 (100), 132 (42), 119 (24), 104 (20), 93 (25), 85 (30), 77 (26), 57 (53). Anal. calcd (found) for $C_{13}H_{15}NO_3$: C 66.94 (67.16); H 6.48 (6.55); N 6.00 (6.24).

**4j**: Pale yellow oil, IR: 3714, 2953, 2931, 2873, 1739, 1615, 1494, 1470, 1375, 1353, 1260, 1159, 1091, 1022, 753 $cm^{-1}$. $\delta_H$ ($CDCl_3$): 0.92 (t, *J*=7.3 Hz, 3H, $CH_3$ of butyl), 1.38 (m, 2H, H-3 of butyl), 1.67 (m, 2H, H-2 of butyl), 2.45 (m, 2H, H-1 of butyl), 3.22 (s, 3H, $CH_3$), 5.96 (s, 1H, H-3), 6.83 (d, *J*=7.5 Hz, 1H), 7.06 (dd, $J_1$=$J_2$=7.5 Hz, 1H), 7.30–7.40 (m, 2H). $\delta_C$ ($CDCl_3$): 13.68, 22.17, 26.38, 26.93, 33.68, 69.74, 108.48, 123.07, 124.63, 125.51, 130.27, 144.55, 172.36, 173.16. EIMS, *m*/*z* (%): 247 ($M^+$, 12), 163 (100), 146 (28), 111 (12), 97 (18), 91 (20), 85 (22), 77 (12), 71 (25), 57 (47). HR EIMS calcd for $C_{14}H_{17}NO_3$: 247.1208, found: 247.1201.

**4o**: Colourless crystals, mp 190–193°C (benzene), IR: 3487, 3402, 3180, 3145, 3064, 3031, 2923, 1761, 1724, 1622, 1601, 1495, 1454, 1336, 1282, 1234, 1219, 1185, 1074, 1069, 1022, 985, 879, 814, 798, 760, 733, 710, 692 $cm^{-1}$.

$\delta_H$ ($CDCl_3$): 2.26 (s, 3H, Ar-$CH_3$), 3.76 (m, 2H, Ph-$CH_2$), 5.89 (s, 1H, H-3), 6.95–7.05 (m, 2H), 7.24–7.38 (m, 5H), 8.39 (br s, 1H, NH). $\delta_C$ ($CDCl_3$): 13.85, 40.75, 70.78, 118.30, 122.66, 123.63, 123.72, 127.40, 128.70, 129.26, 133.09, 136.40, 141.43, 170.81, 174.17. EIMS, *m*/*z* (%): 317 ($M^+$, 4, $^{37}Cl$), 315 ($M^+$, 11, $^{35}Cl$), 199 (53, $^{37}Cl$), 197 (100, $^{35}Cl$), 182 (18, $^{37}Cl$), 180 (40, $^{35}Cl$), 152 (10), 91 (53). HR EIMS calcd for $C_{17}H_{14}{}^{35}ClNO_3$: 315.0662, found: 315.0671.

**4p**: Pale yellow crystals, mp 135–136°C (benzene–*c*-$C_6H_{12}$), IR: 3489, 3419, 3159, 3118, 3086, 3028, 2910, 2854, 1753, 1728, 1629, 1607, 1498, 1456, 1413, 1379, 1348, 1281, 1213, 1142, 1074, 1039, 1028, 953, 902, 841, 789, 760, 704, 621 $cm^{-1}$. $\delta_H$ (DMSO-$d_6$): 1.93 (s, 3H, Ar-$CH_3$), 2.22 (s, 3H, Ar-$CH_3$), 3.78 (s, 2H, $CH_2$Ph), 5.96 (s, 1H, H-3), 6.47 (s, 1H, ArH), 6.54 (s, 1H, ArH), 7.02–7.04 (m, 5H, Ph), 10.46 (br s, 1H, NH). $\delta_C$ (DMSO-$d_6$): 17.13, 21.11, 39.82, 70.11, 108.09, 119.69, 123.76, 126.90, 128.31, 129.22, 133.79, 134.80, 139.48, 142.95, 169.82, 173.29. EIMS, *m*/*z* (%): 295 ($M^+$, 15), 177 (100), 160 (54), 149 (11), 111 (15), 105 (26), 97 (24), 91 (51), 83 (27), 71 (34), 69 (35), 57 (49). HR EIMS calcd for $C_{18}H_{17}NO_3$: 295.1208, found: 295.1200.

**4r**: Colourless crystals, mp 96–102°C (*c*-$C_6H_{12}$), IR: 3193, 3130, 2931, 2869, 1736, 1693, 1628, 1606, 1464, 1373, 1342, 1271, 1140, 1165, 1140, 1109, 1076, 1035, 1005, 958, 895, 839, 733, 694, 615 $cm^{-1}$. $\delta_H$ (DMSO-$d_6$): 0.87 (t, *J*=7.3 Hz, 3H, $CH_3$ of butyl), 1.32 (m, 2H, H-3 of butyl), 1.54 (m, 2H, H-2 of butyl), 2.10 (s, 3H, Ar-$CH_3$), 2.24 (s, 3H, Ar-$CH_3$), 2.40 (t, *J*=7.3 Hz, 2H, H-1 of butyl), 5.96 (s, 1H, H-3), 6.48 (s, 1H, ArH), 6.58 (s, 1H, ArH), 10.45 (br s, 1H, NH). $\delta_C$ (DMSO-$d_6$): 13.45, 17.32, 21.14, 21.39, 26.54, 32.69, 69.61, 108.13, 119.92, 123.77, 134.68, 139.43, 142.98, 171.67, 173.48. EIMS, *m*/*z* (%): 261 ($M^+$, 16), 177 (100), 160 (35), 149 (20), 121 (15), 85 (21), 77 (16), 69 (21), 57 (40). Anal. calcd (found) for $C_{15}H_{19}NO_3$: C 68.94 (69.29); H 7.33 (7.56); N 5.36 (5.60).

**4s**: Pale yellow crystals, mp 189–193°C (acetic acid), IR: 3172, 3120, 2936, 1745, 1720, 1631, 1608, 1449, 1247, 1144, 1097, 1067, 840, 707 $cm^{-1}$. $\delta_H$ ($CDCl_3$): 2.20 (s, 3H, Ar-$CH_3$), 2.30 (s, 3H, Ar-$CH_3$), 6.27 (s, 1H), 6.58 (s, 1H), 6.66 (s, 1H), 7.44 (m, 2H, *m*-Ph), 7.58 (m, 1H, *p*-Ph), 8.09 (m, 3H, *o*-Ph, NH). $\delta_C$ ($CDCl_3$): 17.94, 21.68, 70.15, 108.80, 119.75, 125.31, 128.49, 128.97, 130.13, 133.53, 136.09, 140.74, 141.81, 165.38, 174.32. EIMS, *m*/*z* (%): 281 ($M^+$, 39), 176 (88), 160 (34), 147 (8), 117 (10), 105 (100), 91 (10), 77 (49), 57 (11). HR EIMS calcd for $C_{17}H_{15}NO_3$: 281.1052, found: 281.1059.

**5-Chloro-8-methyl-4-phenylacetyl-1,4-dihydro-2*H*-3,1-benzoxazin-2-one (5a):** Colourless crystals, mp 198–203°C (ethanol), IR: 3260, 3210, 3145, 1752, 1598, 1501, 1468, 1390, 1301, 1262, 1211, 1050, 971, 811, 766, 749, 718 $cm^{-1}$. $\delta_H$ (DMSO-$d_6$): 2.17 (s, 3H, Ar-$CH_3$), 3.85 and 4.01 (two d, *J*=16.8 Hz, 2H, $CH_2$Ph), 6.35 (s, 1H, H-4), 7.00–7.30 (m, 7H, Ph, Ar-H), 9.90 (s, 1H, NH). $\delta_C$ (DMSO-$d_6$): 16.26 ($C_{(8)}$-$CH_3$), 43.58 (Ar-$CH_2$), 79.03 (C-4), 114.39 (C-4a), 122.76 (C-8), 123.16 (C-6), 126.68 (C-4′), 127.75 (C-5), 128.13 (C-3′ and C-5′), 129.33 (C-2′ and C-6′), 132.61 (C-7), 133.12, 136.07, 150.45 (C-2), 200.02 ($CH_2C$=O). EIMS, *m*/*z* (%): 315 ($M^+$, 5), 196 (100), 168 (16), 140 (10), 119 (6), 91 (16). Anal. calcd (found) for $C_{17}H_{14}ClNO_3$: C 64.67 (64.51); H 4.47 (4.49); N 4.44 (4.32).

**5b**: Colourless crystals, mp 173–188°C (*c*-$C_6H_{12}$), IR: 3280, 2980, 2960, 2890, 1760, 1730, 1500, 1480, 1415, 1385, 1290, 1260, 1210, 1150, 1055, 1020, 965, 825, 800, 770, 750, 690, 660 $cm^{-1}$. $\delta_H$ ($CDCl_3$): 0.86 (t, *J*=7.3 Hz, 3H, $CH_3$ of butyl), 1.28 (m, 2H, H-3 of butyl), 1.55 (m, 2H, H-2 of butyl), 2.23 (s, 3H, $CH_3$), 2.61 (m, 2H, H-1 of butyl), 6.03 (s, 1H, CH), 7.04 (d, *J*=8.3 Hz, 1H, H-6), 7.10 (d, *J*=8.3 Hz, 1H, H-7), 7.48 (br s, 1H, NH). $\delta_C$ ($CDCl_3$): 13.70, 15.97, 22.10, 25.40, 38.01, 80.14, 114.40, 121.50, 123.91, 129.05, 132.32, 135.22, 151.11, 201.73. EIMS, *m*/*z* (%): 283 ($M^+$, 2, $^{37}Cl$), 281 ($M^+$, 6, $^{35}Cl$), 198 (38, $^{37}Cl$), 196 (77, $^{35}Cl$), 177 (17), 168 (11), 149 (6), 140 (7), 97 (11), 85 (84), 77 (20), 69 (43), 57 (100). HR EIMS calcd for $C_{14}H_{16}{}^{35}ClNO_3$: 281.0819, found: 281.0825.

**5c**: Colourless crystals, mp 188–189°C (ethyl acetate), IR: 3371, 3253, 3207, 3145, 3064, 2989, 2864, 1753, 1687, 1589, 1489, 1464, 1446, 1367, 1278, 1242, 1225, 1190, 1089, 1074, 1062, 991, 962, 951, 883, 862, 806, 756, 737, 725, 694 $cm^{-1}$. $\delta_H$ ($CDCl_3$): 2.23 (s, 3H, Ar-$CH_3$), 6.83 (s, 1H, H-4), 6.98 (d, *J*=8.2 Hz, 1H, H-6), 7.11 (d, *J*=8.2 Hz, 1H, H-7), 7.36 (br s, 1H, NH), 7.53 (m, 2H, *m*-Ph), 7.65 (m, 1H, *p*-Ph), 8.11 (m, 2H, *o*-Ph). $\delta_C$ ($CDCl_3$): 16.20, 76.87, 114.58, 121.65, 123.54, 128.84, 128.97, 129.62, 132.31, 134.07, 134.26, 135.25, 150.49, 192.34. EIMS, *m*/*z* (%): 303 ($M^+$, 8, $^{37}Cl$), 301 ($M^+$, 25, $^{35}Cl$), 277 (4, $^{37}Cl$), 275 (12, $^{35}Cl$), 273 (10), 264 (10), 198 (5, $^{37}Cl$), 196 (16, $^{35}Cl$), 137 (7), 105 (100), 95 (11), 77 (35), 69 (48), 57 (25). Anal. calcd (found) for $C_{16}H_{12}ClNO_3$: C 63.69 (63.91); H 4.01 (4.03); N 4.64 (4.34).

**5f**: Colourless crystals, mp 182–187°C (ethanol), IR: 3392, 3261, 3132, 2960, 2925, 2864, 1747, 1734, 1685, 1622, 1587, 1508, 1467, 1446, 1377, 1325, 1282, 1244, 1203, 1088, 1057, 968, 891, 868, 808, 758, 702, 654 $cm^{-1}$. $\delta_H$ ($CDCl_3$): 2.11 (s, 3H, Ar-$CH_3$), 2.21 (s, 3H, Ar-$CH_3$), 6.60 (s, 1H, H-4), 6.80 (d, *J*=7.8 Hz, 1H, Ar-H), 7.04 (br s, 1H, NH), 7.06 (d, *J*=7.8 Hz, 1H, Ar-H), 7.52 (m, 2H, *m*-Ph), 7.63 (m, 1H, *p*-Ph), 8.03 (m, 2H, *o*-Ph). $\delta_C$ ($CDCl_3$): 16.08, 18.49, 77.59, 115.02, 120.22, 124.93, 128.88, 129.31, 131.25, 132.57, 133.66, 133.96, 134.72, 150.77, 193.95. EIMS, *m*/*z* (%): 281 ($M^+$, 9), 176 (100), 148 (11), 105 (68), 77 (36), 57 (16). Anal. calcd (found) for $C_{17}H_{15}NO_3$: C 72.58 (72.80); H 5.37 (5.37); N 4.98 (5.22).

**5s**: Colourless crystals, mp 219–222°C (benzene–*c*-$C_6H_{12}$), IR: 3243, 3196, 3136, 2919, 1704, 1625, 1595, 1448, 1391, 1322, 1307, 1282, 1219, 1089, 975, 913, 844, 814, 753, 698, 637 $cm^{-1}$. $\delta_H$ (DMSO-$d_6$): 2.01 (s, 3H, Ar-$CH_3$), 2.20 (s, 3H, Ar-$CH_3$), 6.55 (br s, 1H, ArH), 6.62 (br s, 1H, ArH), 7.07 (s, 1H, H-4), 7.57 (m, 2H, *m*-Ph), 7.70 (m, 1H, *p*-Ph), 8.01 (m, 2H, *o*-Ph), 10.15 (br s, 1H, NH). $\delta_C$ (DMSO-$d_6$): 18.17, 20.68, 76.42, 112.22, 112.38, 125.07, 128.74, 128.97, 133.79, 134.62, 134.67, 136.34, 138.89, 150.05, 195.36. EIMS, *m*/*z* (%): 281 ($M^+$, 4), 176 (100), 149 (10), 120 (6), 105 (40), 77 (27), 57 (13). Anal. calcd (found) for $C_{17}H_{15}NO_3$: C 72.58 (72.92); H 5.37 (5.14); N 4.98 (4.53).

**4-Chloro-7-methyl-1*H*-indole-2,3-dione (6a):** Orange crystals, mp 281–286°C (acetic acid), Lit.[11] 273°C, IR: 3429, 3207, 3101, 3082, 3022, 1736, 1624, 1587, 1487, 1454, 1388, 1317, 1265, 1246, 1221, 1192, 1043, 983, 929, 879, 810, 706 $cm^{-1}$. $\delta_H$ (DMSO-$d_6$): 2.16 (s, 3H, Ar-$CH_3$), 6.97 (d, $J$=8.2 Hz, 1H, H-6), 7.39 (dd, $J$=8.2, 0.5 Hz, 1H, H-5), 11.22 (s, 1H, NH). $\delta_C$ (DMSO-$d_6$): 15.07, 114.29, 120.37, 123.25, 128.28, 139.90, 150.47, 159.13, 181.54. Anal. calcd (found) for $C_9H_6ClNO_2$: C 55.26 (55.27); H 3.09 (3.08); N 7.16 (7.21).

**6d**: Orange crystals, mp 274–276°C (benzene), Lit.[11] 267°C, IR: 3425, 3205, 3100, 1722, 1632, 1590, 1509, 1379, 1321, 1276, 1254, 1167, 962, 812, 715 $cm^{-1}$. $\delta_H$ (DMSO-$d_6$+$CDCl_3$): 2.19 (s, 3H, Ar-$CH_3$), 2.48 (s, 3H, Ar-$CH_3$), 6.72 (d, $J$=7.8 Hz, 1H, Ar-H), 7.18 (d, $J$=7.8 Hz, 1H, Ar-H), 10.76 (s, 1H, NH). $\delta_C$ (DMSO-$d_6$+$CDCl_3$): 15.31, 17.52, 115.77, 118.88, 124.92, 137.73, 139.21, 149.22, 160.08, 185.48. Anal. calcd (found) for $C_{10}H_9NO_2$: C 68.56 (68.75); H 5.18 (5.38); N 8.00 (7.98).

**6p**: Orange crystals, mp 246–249°C (ethanol), Lit.[20] 241–243°C, IR: 3430, 3204, 2922, 2871, 2360, 2332, 1755, 1727, 1715, 1627, 1603, 1459, 1376, 1331, 1272, 1146, 1073, 1036, 923, 853, 753, 683 $cm^{-1}$. $\delta_H$ (DMSO-$d_6$): 2.29 (s, 3H, Ar-$CH_3$), 2.39 (s, 3H, Ar-$CH_3$), 6.52, (s, 1H, ArH), 6.67 (s, 1H, ArH), 10.92 (br s, 1H, NH). $\delta_C$ (DMSO-$d_6$): 17.27, 21.97, 110.03, 113.66, 125.31, 139.50, 149.46, 151.07, 159.62, 183.93. Anal. calcd (found) for $C_{10}H_9NO_2$: C 68.56 (68.87); H 5.18 (5.32); N 8.00 (7.79).

**3-Benzyl-5-chloro-8-methyl-3-phenylacetoxyquinoline-2,4(1*H*,3*H*)-dione (7):** Colourless crystals, yield 9%, mp 169–171°C (ethyl acetate), IR: 3230, 3182, 3090, 3015, 2912, 1756, 1728, 1692, 1589, 1492, 1465, 1366, 1157, 1131, 1041, 989, 836, 743, 718 $cm^{-1}$. $\delta_H$ ($CDCl_3$): 2.07 (s, 3H, Ar-$CH_3$), 3.32 (s, 2H, $PhCH_2$), 3.85 (s, 2H, $PhCH_2$), 6.97 (d, $J$=8.1 Hz, 1H, H-6), 6.98–7.35 (m, 11 H, H-7, 2×Ph), 7.88 (br s, 1H, NH). $\delta_C$ ($CDCl_3$): 16.66, 29.70, 40.12, 42.91, 84.37, 117.43, 122.06, 125.92, 127.19, 127.80, 127.92, 128.54, 129.58, 130.20, 131.06, 132.92, 132.94, 136.24, 139.43, 167.91, 170.66, 188.30. EIMS, $m/z$ (%): 435 ($M^+$, 15, $^{37}Cl$), 433 ($M^+$, 45, $^{35}Cl$), 317 (4, $^{37}Cl$), 315 (12, $^{35}Cl$), 297 (56), 199 (6, $^{37}Cl$), 197 (18, $^{35}Cl$), 168 (7), 139 (10), 118 (12), 103 (9), 91 (100), 77 (12), 65 (24), 57 (7). Anal. calcd (found) for $C_{25}H_{20}ClNO_4$: C 69.20 (69.53); H 4.65 (4.92); N 3.23 (3.12).

**4-Chloro-3-hydroxy-7-methyl-3-valeryl-1,3-dihydro-2*H*-indol-2-one (8b):** Pale yellow crystals, yield 5%, mp 119–121°C (benzene), IR: 3427, 3166, 3098, 3037, 2958, 2945, 2875, 1747, 1729, 1713, 1624, 1601, 1481, 1424, 1406, 1371, 1288, 1218, 1167, 1122, 1066, 999, 862, 790, 747, 730, 604 $cm^{-1}$. $\delta_H$ ($CDCl_3$): 0.81 (t, $J$=7.3 Hz, 3H, $CH_3$ of butyl), 1.22 (m, 2H, H-3 of butyl), 1.58 (m, 2H, H-2 of butyl), 2.20–2.40 (m, 5H, Ar-$CH_3$, H-1 of butyl), 5.11 (s, 1H, OH), 6.94 (d, $J$=8.3 Hz, 1H, H-5), 7.11 (dd, $J$=8.3, 0.5 Hz, 1H, H-6), 9.39 (br s, 1H, NH). $\delta_C$ ($CDCl_3$): 13.62 (C-4 of butyl), 16.07 ($C_{(7)}$-$CH_3$), 21.91 (C-3 of butyl), 25.42 (C-2 of butyl), 35.78 (C-1 of butyl), 83.97 (C-3), 119.15 (C-7), 123.86 (C-3a), 124.14 (C-5), 128.71 (C-4), 133.46 (C-6), 142.26 (C-7a), 174.80 (C-2), 201.64 (Butyl-*C*O). EIMS, $m/z$ (%): 283 ($M^+$, 1, $^{37}Cl$), 281 ($M^+$, 4, $^{35}Cl$), 199 (30, $^{37}Cl$), 197 (76, $^{35}Cl$), 104 (8), 84 (86), 78 (36), 69 (37), 56 (100). Anal. calcd (found) for $C_{14}H_{16}ClNO_3$: C 59.68 (59.54); H 5.72 (5.66); N 4.97 (4.68).

**Independent synthesis of 3-benzyl-5-chloro-8-methyl-3-phenylacetoxyquinoline-2,4(1*H*,3*H*)-dione (7)**

To the solution of phenylacetic acid (136 mg, 1 mmol) in benzene (3 mL), 0.1 mL (98 mg, 1.23 mmol) of pyridine and 0.4 mL (655 mg, 5.5 mmol) of thionyl chloride were added. After 0.5 h standing at ambient temperature the solution was refluxed for 0.5 h and evaporated to dryness in vacuo. The residue was extracted with benzene (3 mL) and filtered. To the filtrate, the solution of **3a** (158 mg, 0.5 mmol) in benzene (5 mL) and pyridine (0.5 mL) was added. After 0.5 h standing, the reaction mixture was refluxed for 0.5 h, cooled and filtrated. The filtrate was washed with HCl (10%, 5 mL), water and sodium hydrogencarbonate (5%, 5 mL). After evaporation of organic layer the residue was column chromatographed using the solvent system as described above. Crude **7** (120 mg, 55%) was crystallised from ethanol to give 85 mg of product identical to compound which was isolated from rearrangement of **3a**.

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