

# Thermal reaction of 3aH,5H-thiazolo[5,4-c]quinoline-2,4-diones – an easy pathway to 4-amino-1H-quinolin-2-ones and novel 6H-thiazolo[3,4-c]quinazoline-3,5-diones

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## Abstract

S-(3-Alkyl/aryl-2,4-dioxo-1,2,3,4-tetrahydroquinolin-3-yl)thiocarbamates **3** were thermally reacted to form 4-hydroxy-1H-quinolin-2-ones **1**. Under the same reaction conditions, 3a-alkyl/aryl-[1,3]thiazolo[5,4-c]quinoline-2,4(3aH,5H)-diones **4** reacted to yield one of two different types of products, depending on the nature of substituent at the 5 position. Substitution with an alkyl or aryl group produced 4-amino-3-alkyl/aryl-1H-quinolin-2-ones **5**, whereas the N-5 unsubstituted analogues rearranged to form novel 6H-thiazolo[3,4-c]quinazoline-3,5-diones **6** in high yields. The reaction mechanisms for the above transformations are discussed. All new products were characterized by NMR, MS and IR spectra. The structure of 1-butyl-9-methyl-6H-thiazolo[3,4-c]quinazoline-3,5-dione **6b** was confirmed by single-crystal X-ray diffraction analysis.

**Keywords:** 4-Aminoquinolones, 4-hydroxyquinolones, molecular rearrangement, organic thiocyanates, reaction mechanism

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## Introduction

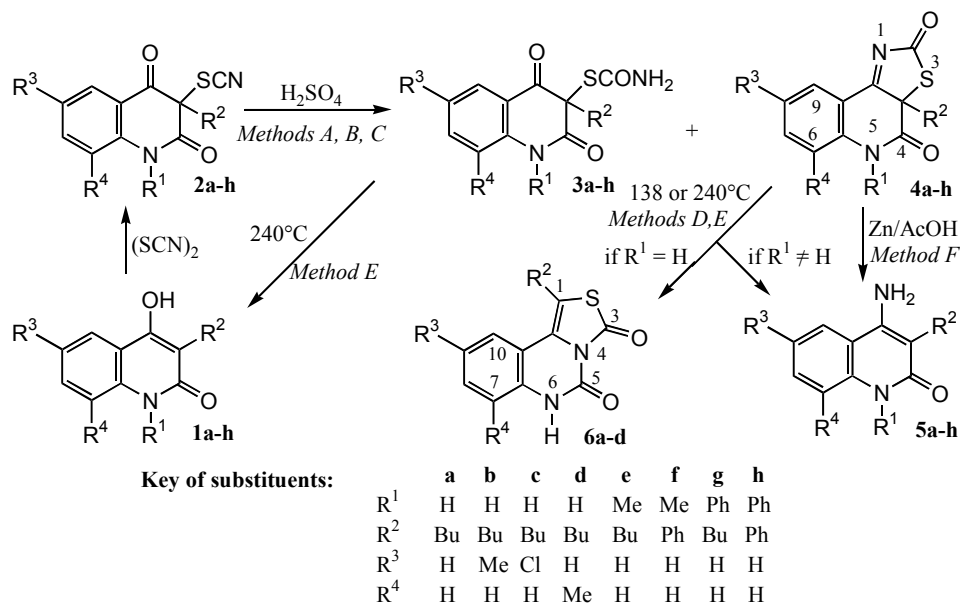
As part of our continued interest in quinolinone chemistry, we have recently reported a synthetic route to forming novel 3-thiocyanato-1H,3H-quinoline-2,4-diones **2** by the reaction of 4-hydroxy-1H-quinolin-2-ones **1** with thiocyanogen.<sup>1</sup> While compounds of type **2** are relatively stable in the crystalline state, they are highly reactive in solution toward a variety of nucleophiles. Examples of electrophilic thiocyanato group transfer to other nucleophiles have been demonstrated.<sup>2</sup> In wet polar solvents, compounds **2** rapidly hydrolyze back to the starting

compounds **1**. However, if the hydrolysis of thiocyanates of type **2** is conducted in concentrated sulfuric acid, S-(2,4-dioxo-1,2,3,4-tetrahydroquinolin-3-yl)thiocarbamates **3** are obtained, which can further cyclodehydrate to [1,3]thiazolo[5,4-*c*]quinoline-2,4(3*aH*,5*H*)-diones **4** (Scheme 1).<sup>3</sup> Similarly to thiocyanates **2**, thiocarbamates **3** were also found to be unstable and, in the presence of water, to rapidly revert to 4-hydroxyquinolones **1**. Examination of thiocarbamates **3** and thiazoloquinolones **4** revealed that these compounds melt in a relatively wide temperature range, despite being chromatographically pure. This indicated their thermal instability.

Herein, we report the thermal reaction of thiocarbamates **3** and N-5 substituted thiazoloquinolones **4** to produce 4-hydroxy-1*H*-quinolin-2-ones **1** or 4-amino-1*H*-quinolin-2-ones **5**. However, N-5 unsubstituted analogues of **4** behave differently, undergoing molecular rearrangement to afford 6*H*-thiazolo[3,4-*c*]quinazoline-3,5-diones **6** in high yields.

## Results and Discussion

The starting materials, thiocarbamates **3** and thiazoloquinolones **4**, were prepared by tandem hydration/cyclodehydration of thiocyanates **2** according to the general procedure described previously (Scheme 1).<sup>3</sup>



**Scheme 1.** Preparation and transformation of thiocarbamates **3** and thiazoloquinolones **4**.

We conducted semi-micro experiments to screen for the optimal temperature at which to perform the transformations of compounds **3** and **4**. The compounds were heated neat in a melting point apparatus, and the resulting material was analyzed by TLC. Most of the compounds underwent relatively clean conversions in the range of approximately 150–250 °C,

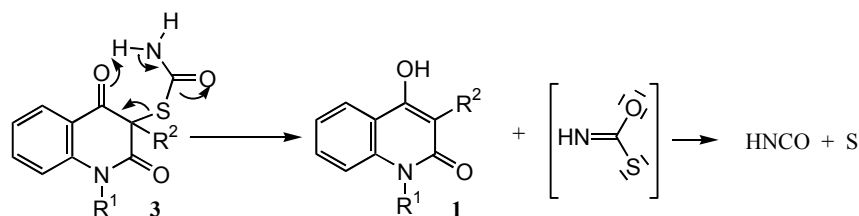
whereas at higher temperatures, decomposition to complex mixtures of products occurred. Based on this information, we decided to run the thermal reactions on a preparative scale in refluxing *p*-xylene (138 °C) or cyclohexylbenzene (240 °C).

Thermal reactions of thiocarbamates **3** were conducted in boiling cyclohexylbenzene (*Method E*). As indicated in Table 1, the starting material was consumed within 5-30 min. We expected thiocarbamates **3** to undergo thermal cyclodehydration and subsequent rearrangement to new heterocycles, similarly to our previous experiences with analogous 3-ureido-1*H*,3*H*-quinoline-2,4-diones, which formed novel heterocycles of imidazoquinoline or indolin-2-one structures.<sup>4,6</sup> Instead, 4-hydroxy-2*H*-quinolin-2-ones **1** (Scheme 1, Table 1) were isolated, the formation of which could be explained by S-C bond cleavage, as shown in Scheme 2. We were unable to detect the HNCOS fragment, but since elemental sulfur was isolated as a by-product from the reaction of **3e**, its decomposition to sulfur and isocyanic acid may be inferred. As the transformation of thiocarbamates **3** to 4-hydroxy-2*H*-quinolin-2-ones **1** is of no interest from the synthetic point of view, further work focused on thiazoloquinolinediones **4**.

**Table 1.** Thermal reactions of compounds **3** and **4** (*Methods D and E*)

Entry	Starting compound	Substituents				Method	Reaction time (min)	Product (yield %)
		R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	R <sup>4</sup>			
1	<b>3a</b>	H	Bu	H	H	E	30	<b>1a</b> (72)
2	<b>3b</b>	H	Bu	Me	H	E	15	<b>1b</b> (36)
3	<b>3c</b>	H	Bu	Cl	H	E	30	<b>1c</b> (86)
4	<b>3d</b>	H	Bu	H	Me	E	30	<b>1d</b> (74)
5	<b>3e</b>	Me	Bu	H	H	E	15	<b>1e</b> (56) <sup>a</sup>
6	<b>3f</b>	Me	Ph	H	H	E	5	<b>1f</b> (83)
7	<b>3g</b>	Ph	Bu	H	H	E	5	<b>1g</b> (89)
8	<b>3h</b>	Ph	Ph	H	H	E	30	<b>1h</b> (55)
9	<b>4a</b>	H	Bu	H	H	D	540	<b>6a</b> (82)
10						E	10	<b>6a</b> (73)
11	<b>4b</b>	H	Bu	Me	H	E	10	<b>6b</b> (71)
12	<b>4c</b>	H	Bu	Cl	H	E	30	<b>6c</b> (70)
13	<b>4d</b>	H	Bu	H	Me	D	480	<b>6d</b> (40)
14						E	30	<b>6d</b> (86)
15	<b>4e</b>	Me	Bu	H	H	E	40	<b>5e</b> (49) <sup>a</sup>
16	<b>4f</b>	Me	Ph	H	H	F	30	<b>5f</b> (50), <b>7f</b> (29)
17	<b>4g</b>	Ph	Bu	H	H	D	210	<b>5g</b> (2)
18						E	90	<b>5g</b> (62)
19	<b>4h</b>	Ph	Ph	H	H	E	45	<b>5h</b> (59)

<sup>a</sup> Elemental sulfur (27% in Entry 5 and 51% in Entry 15) was also isolated.



**Scheme 2.** Thermal degradation of thiocarbamates **3** to 4-hydroxy-2-quinolinones **1**.

Initial thermal experiments with compounds **4** were conducted in boiling *p*-xylene (*Method D*, Table 1, Entries 9, 13, and 17). Because the reaction times were very long and the yields of products were low, we changed the solvent to boiling cyclohexylbenzene (*Method E*). The thermal reaction of compounds **4** yielded one of two different types of products, depending on the nature of N-5 substituents. In those examples where N-5 substituents were alkyl or aryl groups (**4e-h**), the reaction products were 4-amino-1*H*-quinolin-2-ones **5** (Scheme 1, Table 1). Proton and carbon NMR spectra of **5** were similar to those of the corresponding 4-hydroxy-2-quinolinones **1**, with the amino group resonance appearing at approximately  $\delta$  6 ppm. In the electron-impact mass spectra of 3*a*-butyl derivatives **5** ( $R^2 = \text{Bu}$ ), the base peaks corresponded to  $m/z$   $[M - 42]^+$ , and the other peaks of subsequent intensities corresponded to  $m/z$   $[M - 15]^+$ ,  $[M - 43]^+$ , and  $[M - 71]^+$ . The base peaks for 3*a*-phenyl-substituted compounds **5** corresponded to  $m/z$  of the  $[M - 1]^+$  ion.

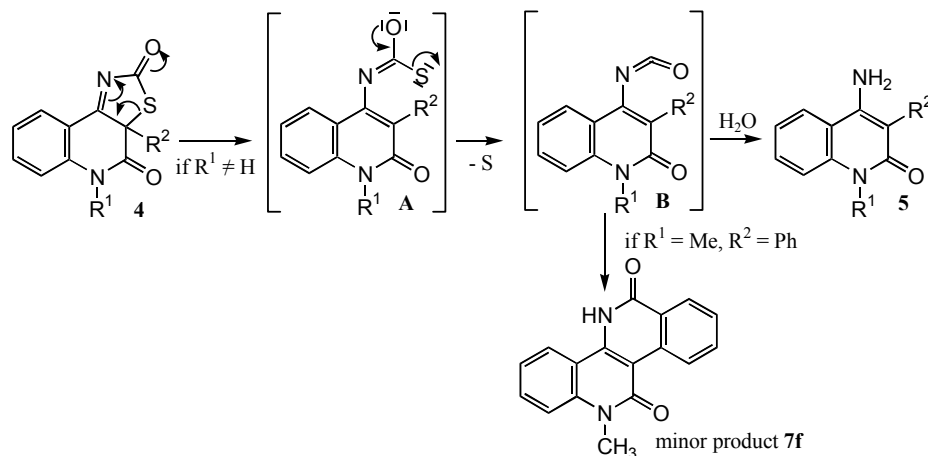
We found that 4-amino-2*H*-quinolin-2-ones **5** could alternatively be prepared from thiazoloquinolinediones **4** via reduction with zinc in acetic acid (Table 2, Scheme 1, *Method F*), and both procedures described herein represent new pathways to access compounds of type **5**.

**Table 2.** Reduction of thiazoloquinolinediones **4** to 4-amino-1*H*-quinolin-2-ones **5** with zinc in acetic acid (*Method F*)

Entry	Starting compound	Substituents				Reaction time (min)	Product (yield %)
		R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	R <sup>4</sup>		
1	<b>4a</b>	H	Bu	H	H	10	<b>5a</b> (31)
2	<b>4b</b>	H	Bu	Me	H	30	<b>5b</b> (53)
3	<b>4c</b>	H	Bu	Cl	H	10	<b>5c</b> (35)
4	<b>4d</b>	H	Bu	H	Me	30	<b>5d</b> (38)
8	<b>4e</b>	Me	Bu	H	H	30	<b>5e</b> (37)
9	<b>4f</b>	Me	Ph	H	H	10	<b>5f</b> (49)
10	<b>4g</b>	Ph	Bu	H	H	10	<b>5g</b> (70)
11	<b>4h</b>	Ph	Ph	H	H	10	<b>5h</b> (54)

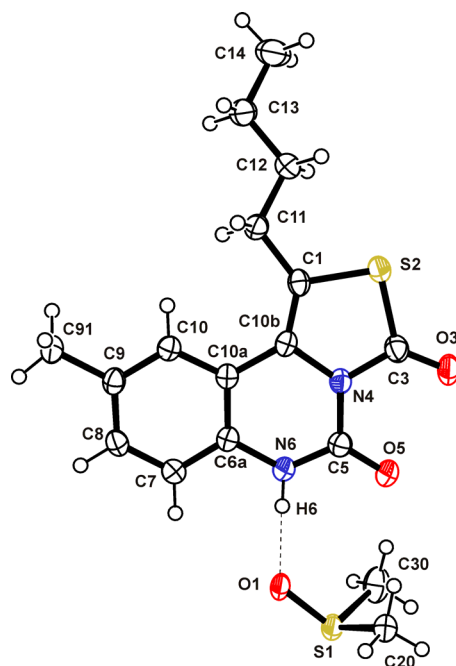
A proposed reaction mechanism that could account for the formation of **5e-h** from **4e-h** is

depicted in Scheme 3. We believe that the C-S bond initially splits in a manner analogous to the decomposition of thiocarbamates **3**, as described earlier. Elimination of a sulfur atom from the intermediate **A** leads to the isocyanate **B**, which, in turn, transforms to **5** during the isolation workup. This mechanism is supported by the fact that elemental sulfur was isolated as a reaction by-product from the thermal transformation of **4e**. The proposed mechanism is at least partly supported by the isolation of side-product **7f** from the thermal reaction of **4f** (Table 1, Entry 16). Its formation can be rationalized by an intramolecular acylation of the phenyl ring in intermediate **B**.



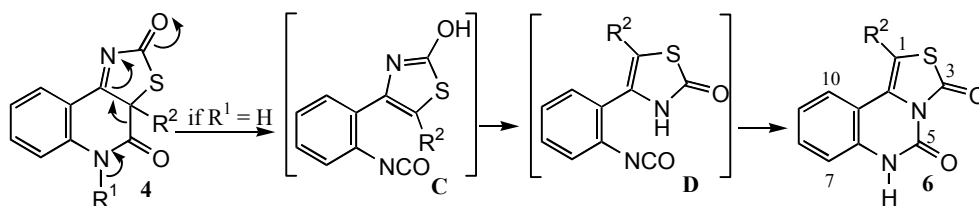
**Scheme 3.** Proposed reaction mechanism for the thermal rearrangement of **4** to **5**.

Interestingly, the N-5 unsubstituted thiazoloquinolinediones **4a-d** behave differently and do not lead to 4-aminoquinolinones **5**. The <sup>13</sup>C NMR spectra of the thermal reaction products show no signals in the region of 77-78 ppm, which corresponds to the region of the sp<sup>3</sup> hybridized carbon atom C-3a in compounds **4**. In fact, both the <sup>1</sup>H and <sup>13</sup>C NMR spectra of these products were very similar to those of 2,6-dihydro-imidazo[1,5-*c*]quinazoline-3,5-diones<sup>4</sup> strongly indicating that the products were thiazolo[3,4-*c*]quinazoline-3,5-diones **6**. In mass spectra, compounds **6** bearing a butyl group at position 3 exhibited base peaks at *m/z* values corresponding to [M - 43]<sup>+</sup>, and other significant peaks correspond to the ions [M - 42]<sup>+</sup> and [M - 71]<sup>+</sup>. In the case of **6b**, the structure was confirmed by single-crystal X-ray diffraction (Figure 1). Crystals of **6b** · DMSO-*d*<sub>6</sub> were grown by slow evaporation of the solution of **6b** in DMSO-*d*<sub>6</sub> in a stream of nitrogen at 23 °C. A short N6 - H6 ... O1 contact of 2.778(3) Å between the DMSO-*d*<sub>6</sub> oxygen and the H-6 of the heterocycle was observed in the crystal structure.



**Figure 1.** ORTEP view of **6b** · DMSO-*d*<sub>6</sub> from the X-ray crystal structure (thermal ellipsoids are at 50% probability).

The proposed reaction mechanism for the rearrangement of the N-5 unsubstituted thiazoloquinolinediones **4a-d** ( $R^1 = H$ ) is shown in Scheme 4. The initial ring opening of the quinolinone skeleton to the isocyanate intermediate **C** is followed by tautomerization to **D** and ring closure to the corresponding quinazolinone **6**. Similar isocyanate intermediates have been recently proposed in molecular rearrangements of structurally related 3-aminoquinoline-2,4-dione derivatives,<sup>4</sup> pyrrolo[2,3-*c*]quinoline-2,4(3*aH*,5*H*)-diones,<sup>7</sup> and furo[2,3-*c*]quinoline-2,4(3*aH*,5*H*)-diones.<sup>8,9</sup> To the best of our knowledge, no compounds of type **6** have been heretofore described in the literature.



**Scheme 4.** Proposed reaction mechanism for the rearrangement of **4** to **6**.

## Conclusions

In conclusion, the thermally induced transformation of 3*aH*,5*H*-thiazolo[5,4-*c*]quinoline-2,4-diones **4** is interesting from both a mechanistic and a preparative point of view, as it represents an alternative pathway for the preparation of 4-amino-2*H*-quinolin-2-ones **5**. Only a small number of 4-amino-3-alkyl/aryl-1*H*-quinolin-2-ones **5** have been described so far. They were prepared starting from 4-hydroxy-2-quinolones,<sup>10-12</sup> 4-halogeno-2-quinolones,<sup>11, 13-14</sup> 2-aminobenzonitriles,<sup>15-19</sup> and 2-bromobenzonitrile.<sup>20</sup> Compounds **5** have been employed in the synthesis of indolo[3,2-*c*]quinolin-6-ones and dibenzonaphthyridine-6,11-diones.<sup>21</sup> To date, few 4-aminoquinolin-2-ones have been tested for biological activity. 7-Chloro-3-phenyl-substituted compounds **5** and their *N*-alkyl and *N*-acyl derivatives exhibited *in vivo* anticonvulsant activity in the DBA/2 strain of mouse<sup>18</sup> and *in vitro* antagonist activity at the glycine site of the N-methyl-D-aspartate receptor.<sup>17</sup>

We believe that the most significant contribution of the present work is the synthesis of novel thiazolo[3,4-*c*]quinazoline-3,5-diones **6**. Due to the fact that a high number biologically active compounds contain a sulfur atom<sup>22,23</sup> and biological activity of isomeric [3,2-*a*], [3,4-*a*], [2,3-*b*], [4,3-*b*], [4,5-*d*], [5,4-*f*], and [4,5-*h*] thiazoloquinazolines is frequently described in the literature, novel compounds of type **6** may also be of interest in screening studies of biological activity.

## Experimental Section

**General Procedures.** Melting points were determined on a Kofler block or Gallencamp apparatus. IR (KBr) spectra were recorded on a Mattson 3000 Spectrometer. NMR spectra were recorded on a Bruker DPX-300 spectrometer in the respective solvents. Chemical shifts are given on the  $\delta$  scale (ppm) and are referred to internal TMS. Mass spectra were obtained on a VG-Analytical AutospecQ instrument. Column chromatography was carried out on silica gel (Merck, grade 60, 70-230 mesh) using benzene and then successive mixtures of benzene-ethyl acetate (from the ratios of 99:1 to 8:2) as eluent. The course of reaction and also the purity of substances were monitored by TLC (elution systems benzene-ethyl acetate 4:1, and chloroform-ethanol 9:1 and/or 19:1) on Alugram<sup>®</sup> SIL G/UV<sub>254</sub> foils (Macherey-Nagel). Elemental analyses (CHN) were performed with EA 1108 Elemental Analyzer (Fisons Instrument).

**3-Thiocyanato-1*H*,3*H*-quinoline-2,4-diones (2*a-h*)** were prepared from 4-hydroxy-quinoline-2(1*H*)-ones (**1*a-h***) by general procedure described in the literature.<sup>1</sup>

**S-(3-Butyl-6-methyl-2,4-dioxo-1,2,3,4-tetrahydroquinolin-3-yl)thiocarbamate (3*b*) and 3-butyl-8-methyl-[1,3]thiazolo[5,4-*c*]quinoline-2,4(3*aH*,5*H*)-dione (4*b*)** were prepared from 3-butyl-3-thiocyanato-1*H*,3*H*-quinoline-2,4-dione (**2*b***) according to the general procedure described in literature<sup>3</sup> using *conc.* sulphuric acid (*Method A*), a mixture of *conc.* sulphuric acid and acetic acid (9:1, v/v) (*Method B*), and a mixture of *conc.* sulphuric acid and acetic acid (9:1,

v/v) and P<sub>2</sub>O<sub>5</sub> (0.6 g/mmol of **2b**) (*Method C*).

**S-(3-Butyl-6-methyl-2,4-dioxo-1,2,3,4-tetrahydroquinolin-3-yl) thiocarbamate (3b)**. This compound was prepared (besides **4b**) from **2b** in respective yields 42% (*Method A*), 44% (*Method B*), and 14% (*Method C*). Colourless crystals, mp 165-172°C (tetrahydrofuran-cyclohexane). IR: 3448, 3238, 3161, 2955, 2928, 2870, 1692, 1663, 1619, 1601, 1507, 1410, 1320, 1254, 1224, 826, 683, 669, 622, 538 cm<sup>-1</sup>. <sup>1</sup>H NMR: (DMSO-*d*<sub>6</sub>) δ 0.73 (t, *J* = 6.7 Hz, 3H, H-4'), 1.00-1.25 (m, 4H, H-2' and H-3'), 1.74-1.85 (m, 2H, H-1'), 2.29 (s, 3H, Ar-CH<sub>3</sub>), 7.01 (d, *J* = 8.2 Hz, 1H, H-8), 7.41 (dd, *J* = 8.2 a 1.4 Hz, 1H, H-7), 7.56 (s, 1H, H-5), 10.87 (s, 1H, NH). <sup>13</sup>C NMR: (DMSO-*d*<sub>6</sub>) δ 13.39, 19.99, 21.90, 25.94, 35.89, 65.19, 116.17, 118.72, 126.20, 131.25, 136.54, 139.22, 166.15, 170.79, 193.59 ppm. EIMS *m/z* (%): 306 (M<sup>+</sup>, 4), 263 (9), 230 (7), 220 (42), 207 (100), 202 (10), 198 (36), 176 (11), 162 (13), 134 (27), 104 (12), 77 (9). Anal. Calcd for C<sub>15</sub>H<sub>18</sub>N<sub>2</sub>O<sub>3</sub>S: C, 58.80; H, 5.92; N, 9.14. Found: C, 58.69; H, 6.01; N, 9.02.

**3a-Butyl-8-methyl[1,3]thiazolo[5,4-*c*]quinoline-2,4-(3a*H*,5*H*)-dione (4b)**. This compound was prepared (besides **3g**) from **2g** in respective yields 21% (*Method A*), 38% (*Method B*), and 33% (*Method C*). Yellow crystals, mp 96-100°C (benzene-hexane). IR: 3311, 3280, 3031, 2964, 2942, 2860, 1708, 1619, 1571, 1494, 1413, 1321, 1292, 1234, 1150, 1118, 1090, 1036, 1019, 958, 887, 832, 783, 721, 684, 658, 630, 598, 583, 538 cm<sup>-1</sup>. <sup>1</sup>H NMR: (DMSO-*d*<sub>6</sub>) δ 0.77 (t, *J* = 7.0 Hz, 3H, H-4'), 1.10-1.24 and 1.31-1.37 (two m, 3H and 1H, H-2' and H-3'), 1.80-1.92 and 2.08-2.20 (two m, 1H and 1H, H-1'), 2.34 (s, 3H, Ar-CH<sub>3</sub>), 7.10 (d, *J* = 8.3 Hz, 1H, H-6), 7.53 (dd, *J* = 8.3 a 1.8 Hz, 1H, H-7), 7.75 (d, *J* = 1.8 Hz, 1H, H-9), 11.15 (s, 1H, NH). <sup>13</sup>C NMR: (DMSO-*d*<sub>6</sub>) δ 13.48, 19.94, 21.30, 27.11, 41.88, 77.47, 114.77, 116.82, 127.46, 132.90, 137.79, 138.64, 167.05, 185.03, 192.23 ppm. EIMS *m/z* (%): 288 (M<sup>+</sup>, 79), 255 (7), 245 (94), 232 (26), 217 (63), 203 (8), 185 (16), 157 (7), 131 (9), 89 (9), 78 (100). HR-MS: for C<sub>15</sub>H<sub>17</sub>N<sub>2</sub>O<sub>2</sub>S [M+H]<sup>+</sup> calculated 289.1011, found 289.1019.

**General procedure for the thermal conversions of S-(2,4-dioxo-1,2,3,4-tetrahydroquinolin-3-yl) thiocarbamates (3) and [1,3]thiazolo[5,4-*c*]quinoline-2,4-(3a*H*,5*H*)-diones (4)**. A solution of appropriate starting compound **3** or **4** (0.8 mmol) in *p*-xylene (*Method D*) or cyclohexylbenzene (*Method E*) (3 mL) was refluxed for the time given in Table 2 and the course of the reaction was monitored by TLC. After disappearing of starting compound, the reaction mixture was cooled; the precipitated crude product was filtered off with suction and recrystallized from appropriate solvent. The solution after filtration of crude product was applied to a chromatographic column and separated. The structure of all isolated products **1** was confirmed by comparison of their IR spectra with those of authentic samples. The structure of all isolated products **5** was confirmed by comparison of their IR spectra with those of compounds prepared according to paragraph 3.4. (*Method F*). In the case of **4e**, the residue after evaporation of chloroform was crystallized from acetone and 57 mg (51%) of elemental sulfur was obtained (Table 1, Entry 15).

**4-Amino-3-butyl-1-methyl-1*H*-quinolin-2-one (5e)**. This compound was prepared from **4e** in 49% yield. Colourless crystals, mp 108-112 °C (benzene-hexane), Lit.,<sup>24</sup> mp 105-106°C. IR: 3418, 3360, 3257, 2954, 2924, 2865, 1646, 1621, 1598, 1563, 1510, 1459, 1420, 1375, 1345,



1299, 1283, 1231, 1173, 1130, 1094, 1049, 1009, 929, 761, 751, 673, 633, 548, 531  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{DMSO-}d_6$ )  $\delta$  0.90 (t,  $J = 6.7$  Hz, 3H, H-4'), 1.30-1.45 (m, 4H, H-3' and H-2'), 2.50-2.59 (m, 2H, H-1'), 3.55 (s, 3H, N- $\text{CH}_3$ ), 6.10 (s, 2H,  $\text{NH}_2$ ), 7.18 (t,  $J = 7.5$  Hz, 1H, H-6), 7.37 (d,  $J = 8.3$  Hz, 1H, H-8), 7.62 (t,  $J = 7.5$  Hz, 1H, H-7), 8.02 (d,  $J = 7.8$  Hz, 1H, H-5);  $^{13}\text{C}$  NMR ( $\text{DMSO-}d_6$ )  $\delta$  14.09 (C-4'), 22.28 (C-3'), 24.35 (C-2'), 28.74 (N- $\text{CH}_3$ ), 29.64 (C-1'), 104.71, 114.17, 114.70, 120.39, 122.82, 129.50, 138.49, 146.70, 161.77 (C=O). EIMS,  $m/z$  (%): 230 ( $\text{M}^+$ , 46), 215 (19), 201 (67), 188 (100), 187 (85), 173 (6), 159 (21), 144 (11), 133 (6), 130 (12), 117 (12), 106 (6), 103 (9), 91 (8), 77 (16). Anal. Calcd for  $\text{C}_{14}\text{H}_{18}\text{N}_2\text{O}$ : C, 73.01; H, 7.88; N, 12.16. Found: C, 72.75; H, 8.14; N, 12.02.

**4-Amino-1-methyl-3-phenyl-1H-quinolin-2-one (5f)**. This compound was prepared from **4f** in 50% yield. Colourless crystals, mp 212-215°C (benzene), Lit.,<sup>10,11</sup> mp 276°C. IR: 3428, 3316, 3193, 3076, 3053, 3025, 2938, 2891, 1644, 1619, 1599, 1574, 1507, 1443, 1421, 1333, 1247, 1110, 1059, 956, 787, 760, 748, 702, 678, 647, 551, 514  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  3.70 (s, 3H, N- $\text{CH}_3$ ), 4.56 (s, 2H,  $\text{NH}_2$ ), 7.21 (t,  $J = 7.8$  Hz, 1H, H-6), 7.25-7.45 (m, 6H, H-8 and five Ph-H), 7.57 (dt,  $J = 7.8$  and 1.1 Hz, 1H, H-7), 7.64 (dd,  $J = 8.0$  and 1.1 Hz, 1H, H-5);  $^1\text{H}$  NMR ( $\text{DMSO-}d_6$ )  $\delta$  3.56 (s, 3H, N- $\text{CH}_3$ ), 5.81 (s, 2H,  $\text{NH}_2$ ), 7.20-7.37 (m, 4H, *o*- and *p*-Ph, and H-8), 7.40-7.49 (m, 3H, *m*-Ph and H-6), 7.61 (t,  $J = 7.3$  Hz, 1H, H-7), 8.09 (d,  $J = 8.0$  Hz, 1H, H-5);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ) 29.32, 108.98, 114.57, 114.78, 121.21, 122.21, 127.49, 128.27, 128.91, 130.72, 134.74, 139.56, 146.61, 162.10;  $^{13}\text{C}$  NMR ( $\text{DMSO-}d_6$ ): 28.76 (N- $\text{CH}_3$ ), 105.95, 114.39, 114.45, 120.69, 123.50, 126.67, 128.38, 130.50, 130.90, 135.50, 139.15, 147.30, 160.86 (C=O). EIMS,  $m/z$  (%): 250 ( $\text{M}^+$ , 81), 249 ( $[\text{M}-1]^+$ , 100), 234 (15), 219 (4), 206 (9), 125 (4), 118 (7), 103 (5), 89 (4), 77 (11). Anal. Calcd for  $\text{C}_{16}\text{H}_{14}\text{N}_2\text{O}$ : C, 76.38; H, 5.64; N, 11.19. Found: C, 76.60; H, 5.76; N, 11.45.

**4-Amino-3-butyl-1-phenyl-1H-quinolin-2-one (5g)**. This compound was prepared from **4g** in 62% yield. Colourless crystals, mp 263-268°C (ethyl acetate). IR: 3468, 3337, 3240, 2949, 2927, 2859, 1651, 1600, 1574, 1557, 1503, 1443, 1418, 1362, 1328, 1235, 1114, 763, 701, 673, 662, 588, 553  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{DMSO-}d_6$ )  $\delta$  0.90 (t,  $J = 6.8$  Hz, 3H, H-4'), 1.30-1.50 (m, 4H, H-3' and H-2'), 2.48-2.60 (m, 2H, H-1'), 6.28 (s, 2H,  $\text{NH}_2$ ), 6.43 (d,  $J = 8.4$  Hz, 1H, H-8), 7.11-7.61 (m, 7H, H-6, H-7, and five Ph-H), 8.05 (d,  $J = 7.8$  Hz, 1H, H-5);  $^{13}\text{C}$  NMR ( $\text{DMSO-}d_6$ )  $\delta$  14.04 (C-4'), 22.30 (C-3'), 24.02 (C-2'), 29.59 (C-1'), 104.43, 114.45, 115.06, 120.66, 122.79, 127.88, 129.09, 129.51, 129.57, 138.87, 139.43, 147.38, 161.82 (C=O); EIMS,  $m/z$  (%): 292 ( $\text{M}^+$ , 23), 277 (24), 266 (61), 250 (100), 249 (76), 235 (6), 221 (11), 219 (12), 204 (11), 195 (7), 167 (6), 124 (6), 116 (5), 97 (6), 83 (7), 77 (14), 69 (10), 57 (12). Anal. Calcd for  $\text{C}_{19}\text{H}_{20}\text{N}_2\text{O}$ : C, 78.05; H, 6.89; N, 9.58. Found: C, 77.85; H, 7.08; N, 9.29.

**4-Amino-1,3-diphenyl-1H-quinolin-2-one (5h)**. This compound was prepared from **4h** in 59% yield. Colourless crystals, mp 336-340°C (ethanol), Lit.,<sup>11</sup> mp 260 °C. IR: 3452, 3330, 3237, 3217, 3069, 1643, 1600, 1581, 1554, 1504, 1489, 1444, 1425, 1354, 1317, 1283, 1235, 1171, 1152, 1069, 1015, 955, 757, 700, 660, 516  $\text{cm}^{-1}$ . Anal. calcd (found) for  $\text{C}_{21}\text{H}_{16}\text{N}_2\text{O}$ : C 80.75 (80.59); H 5.16 (4.93); N 8.97 (8.77).  $^1\text{H}$  NMR ( $\text{DMSO-}d_6$ )  $\delta$  6.01 (s, 2H,  $\text{NH}_2$ ), 6.48 (d,  $J = 8.5$  Hz, 1H, H-8), 7.15-7.62 (m, 12 H, H-6, H-7 and ten Ph-H), 8.13 (d,  $J = 8.0$  Hz, 1H, H-5);  $^{13}\text{C}$

NMR (DMSO- $d_6$ )  $\delta$  105.57, 114.17, 115.27, 120.95, 123.49, 126.72, 128.02, 128.33, 129.49, 129.62, 130.10, 130.97, 134.99, 138.53, 140.10, 147.99, 160.82 (C=O); EIMS,  $m/z$  (%): 312 ( $M^+$ , 67), 311 ([ $M-1$ ] $^+$ , 100), 109 (6), 97 (9), 85 (7), 77 (10), 69 (16), 57 (17). Anal. Calcd for  $C_{21}H_{16}N_2O$ : C, 80.75; H, 5.16; N, 8.97. Found: C, 80.59; H, 4.93; N, 8.77.

**1-Butyl-6H-thiazolo[3,4-c]quinazoline-3,5-dione (6a).** This compound was prepared from **4a** in yields 82% (*Method D*) and 73% (*Method E*). Yellowish crystals, mp 197-202 °C (benzene). IR: 3207, 3146, 3094, 2956, 2929, 2868, 1739, 1598, 1488, 1466, 1437, 1371, 1311, 1250, 1223, 1145, 1119, 743, 667, 645, 608  $cm^{-1}$ .  $^1H$  NMR (DMSO- $d_6$ ):  $\delta$  0.93 (t,  $J = 7.2$  Hz, 1H, H-4'), 1.38-1.50 (m, 2H, H-3'), 1.52-1.65 (m, 2H, H-2'), 2.85 (t,  $J = 7.6$  Hz, 1H, H-1'), 7.01 (d,  $J = 8.0$  Hz, 1H, H-7), 7.11 (t,  $J = 7.7$  Hz, 1H, H-9), 7.31 (t,  $J = 7.6$  Hz, 1H, H-8), 7.65 (d,  $J = 8.0$  Hz, 1H, H-10), 10.85 (s, 1H, NH).  $^{13}C$  NMR (DMSO- $d_6$ ):  $\delta$  13.58 (C-4'), 21.76, 27.54, 30.75, 112.19, 114.05, 115.00, 122.93, 123.33, 124.61, 129.36, 134.81, 144.69 (C-5), 166.29 (C-3) ppm. EIMS,  $m/z$  (%): 274 ( $M^+$ , 85), 232 (21), 231 (100), 213 (12), 203 (80), 185 (6), 175 (13), 171 (15), 160 (6), 145 (15), 129 (7), 116 (15), 102 (20), 90 (10), 77 (6), 57 (8). Anal. Calcd for  $C_{14}H_{14}N_2O_2S$ : C, 61.29; H, 5.14; N, 10.21; S, 11.69. Found: C, 61.53; H, 5.23; N, 10.11; S, 11.37.

**1-Butyl-9-methyl-6H-thiazolo[3,4-c]quinazoline-3,5-dione (6b).** This compound was prepared from **4b** in yield 71% (*Method E*). Colourless crystals, mp 245-246°C (ethyl acetate-hexane). IR: 3267, 2957, 2927, 2869, 1754, 1668, 1504, 1339, 1320, 1288, 1244, 1222, 1142, 828, 757, 600, 501  $cm^{-1}$ .  $^1H$  NMR (DMSO- $d_6$ ):  $\delta$  0.95 (t,  $J = 7.3$  Hz, 3H, H-4'), 1.36-1.53 (m, 2H, H-3'), 1.53-1.69 (m, 2H, H-2'), 2.30 (s, 3H, Ar- $CH_3$ ), 2.90 (t,  $J = 7.6$  Hz, 1H, H-1'), 6.93 (d,  $J = 8.2$  Hz, 1H, H-7), 7.15 (t,  $J = 8.2$  Hz, 1H, H-8), 7.46 (s, 1H, H-10), 10.79 (s, 1H, NH).  $^{13}C$  NMR (DMSO- $d_6$ ):  $\delta$  13.52 (C-4'), 20.58, 21.67, 27.39, 30.62, 111.98, 113.91, 114.93, 123.39, 124.59, 130.13, 131.91, 132.51, 144.68 (C-5), 166.33 (C-3) ppm. EIMS,  $m/z$  (%): 288 ( $M^+$ , 84), 246 (17), 245 (100), 227 (7), 217 (66), 189 (11), 185 (15), 157 (6), 131 (8), 116 (6), 89 (8), 77 (6). Anal. Calcd for  $C_{15}H_{16}N_2O_2S$ : C, 62.48; H, 5.59; N, 9.71. Found: C, 62.56; H, 5.65; N, 9.70.

**1-Butyl-9-chloro-6H-thiazolo[3,4-c]quinazoline-3,5-dione (6c).** This compound was prepared from **4c** in yield 70% (*Method E*). Colourless crystals, mp 253-255°C (ethanol). IR: 3211, 2959, 2929, 2871, 1756, 1681, 1671, 1612, 1487, 1332, 1318, 1284, 1249, 1224, 1144, 1127, 829, 749, 608, 586, 535  $cm^{-1}$ .  $^1H$  NMR (DMSO- $d_6$ ):  $\delta$  0.95 (t,  $J = 7.2$  Hz, 3H, H-4'), 1.38-1.50 (m, 2H, H-3'), 1.55-1.64 (m, 2H, H-2'), 2.85 (t,  $J = 7.5$  Hz, 1H, H-1'), 7.01 (d,  $J = 8.5$  Hz, 1H, H-7), 7.37 (t,  $J = 8.5$  Hz, 1H, H-8), 7.54 (s, 1H, H-10), 10.98 (s, 1H, NH).  $^{13}C$  NMR (DMSO- $d_6$ ):  $\delta$  13.50 (C-4'), 21.72, 27.29, 30.42, 113.99, 115.53, 116.73, 122.27, 123.80, 126.62, 129.16, 133.87, 144.45 (C-5), 166.03 (C-3) ppm. EIMS,  $m/z$  (%): 308 ( $M^+$ , 88), 267 (45), 266 (15), 265 (100), 247 (10), 237 (77), 230 (19), 209 (16), 205 (12), 197 (9), 151 (9), 136 (7), 124 (7), 100 (6), 83 (7), 69 (12), 57 (14). Anal. Calcd for  $C_{14}H_{13}ClN_2O_2S$ : C, 54.46; H, 4.24; N, 9.07; S, 10.38. Found: C, 54.26; H, 4.32; N, 8.85; S, 10.12.

**1-Butyl-7-methyl-6H-thiazolo[3,4-c]quinazoline-3,5-dione (6d).** This compound was prepared from **4d** in yields 40% (*Method D*) and 86% (*Method E*). Colourless crystals, mp 215-218°C (ethyl acetate). IR: 3247, 3218, 3150, 2953, 2928, 2869, 1743, 1671, 1596, 1574, 1469, 1366,

1307, 1266, 1254, 1218, 1138, 1097, 933, 773, 728, 623, 589  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (DMSO- $d_6$ ):  $\delta$  0.92 (t,  $J = 7.2$  Hz, 3H, H-4'), 1.36-1.48 (m, 2H, H-3'), 1.54-1.64 (m, 2H, H-2'), 2.27 (s, 3H, Ar-CH<sub>3</sub>), 2.84 (t,  $J = 7.6$  Hz, 1H, H-1'), 7.02 (d,  $J = 7.7$  Hz, 1H, H-9), 7.16 (t,  $J = 7.7$  Hz, 1H, H-8), 7.49 (s, 1H, H-10), 9.88 (s, 1H, NH).  $^{13}\text{C}$  NMR (DMSO- $d_6$ ):  $\delta$  13.58 (C-4'), 17.58, 21.76, 27.68, 30.79, 112.09, 114.21, 122.50, 122.71, 123.34, 123.66, 130.93, 132.93, 144.98 (C-5), 166.30 (C-3) ppm. EIMS,  $m/z$  (%): 288 ( $\text{M}^+$ , 85), 246 (23), 245 (100), 227 (9), 217 (80), 189 (12), 185 (17), 159 (9), 131 (12), 116 (13), 89 (12), 69 (12), 57 (16). Anal. Calcd for C<sub>15</sub>H<sub>16</sub>N<sub>2</sub>O<sub>2</sub>S: C, 62.48; H, 5.59; N, 9.71; S, 11.12. Found: C, 62.22; H, 5.73; N, 9.58; S, 10.85.

**12-Methyl-5H,12H-dibenzo[*c,h*][1,6]naphthyridine-6,11-dione (7f).** This compound was obtained as minor product from **4f** (besides **5f**) in 29% yield (*Method E*). Colourless crystals, mp >350°C (butanol). IR: 3117, 3032, 1679, 1631, 1590, 1569, 1472, 1455, 1349, 1316, 1032, 971, 821, 790, 763, 716, 680, 626, 579  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (DMSO- $d_6$ ):  $\delta$  3.76 (s, 3H, H-4'), 7.37 (t,  $J = 7.9$  Hz, 1H), 7.60-7.68 (m, 2H), 7.74 (t,  $J = 7.6$  Hz, 1H), 7.86 (t,  $J = 7.2$  Hz, 1H), 8.37 (d,  $J = 6.8$  Hz, 1H), 8.73 (d,  $J = 8.0$  Hz, 1H), 9.80 (d,  $J = 8.4$  Hz, 1H), 11.95 (br s, 1H, NH). EIMS  $m/z$  (%): 276 ( $\text{M}^+$ , 100), 247 (24), 232 (5), 219 (8), 190 (5), 138 (8), 83 (5), 69 (7), 57 (10). Anal. Calcd for C<sub>17</sub>H<sub>12</sub>N<sub>2</sub>O<sub>2</sub>: C, 73.90; H, 4.38; N, 10.14. Found: C, 73.69; H, 4.51; N, 9.95.

**General procedure for the reduction of [1,3]thiazolo[5,4-*c*]quinoline-2,4-(3*aH*,5*H*)-diones (4) to 4-amino-1*H*-quinolin-2-ones (5) (Method F).** To the stirred and heated (50°C) solution of **4** (3.5 mmol) in glacial acetic acid (50 mL), powdered zinc (980 mg, 15 mmol) was added in small portions during 10 min. The reaction mixture was stirred for 10 min and filtered. The filtrate was evaporated to dryness *in vacuo* and the residue was extracted with chloroform (2 x 20 mL). The chloroform layer was washed with a solution (5%) of potassium carbonate. After drying and evaporation, the residue was purified by column chromatography and the corresponding 4-amino-1*H*-quinolin-2-one was crystallized from appropriate solvent.

**4-Amino-3-butyl-1*H*-quinolin-2-one (5a).** This compound was prepared from **4a** in 31% yield. Colourless crystals, mp 163-167°C (ethyl acetate). IR: 3486, 3473, 3331, 3230, 3137, 3100, 2955, 2927, 2869, 1632, 1612, 1595, 1554, 1505, 1409, 1368, 1280, 1222, 1172, 872, 759, 713, 674, 630, 546, 510  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (DMSO- $d_6$ )  $\delta$  0.90 (t,  $J = 6.2$  Hz, 3H, H-4'), 1.30-1.45 (m, 4H, H-3' and H-2'), 2.51 (s, 2H, H-1'), 6.08 (s, 2H, NH<sub>2</sub>), 7.06 (t,  $J = 7.5$  Hz, 1H, H-6), 7.19 (d,  $J = 8.0$  Hz, 1H, H-8), 7.37 (t,  $J = 7.5$  Hz, 1H, H-7), 7.91 (d,  $J = 8.1$  Hz, 1H, H-5), 10.79 (s, 1H, NH);  $^{13}\text{C}$  NMR (DMSO- $d_6$ )  $\delta$  14.07 (C-4'), 22.27 (C-3'), 23.40 (C-21'), 29.62 (C-1'), 104.74, 113.77, 114.87, 120.10, 122.37, 128.93, 137.59, 147.71, 162.54 (C=O); EIMS,  $m/z$  (%): 216 ( $\text{M}^+$ , 35), 201 (21), 187 (50), 174 (100), 173 (87), 169 (8), 156 (16), 145 (26), 128 (12), 117 (10), 91 (8), 77 (15), 65 (7), 55 (7). Anal. Calcd for C<sub>13</sub>H<sub>16</sub>N<sub>2</sub>O: C, 72.19; H, 7.46; N, 12.95. Found: C, 71.91; H, 7.32; N, 12.74.

**4-Amino-3-butyl-6-methyl-1*H*-quinolin-2-one (5b).** This compound was prepared from **4b** in 53% yield. Colourless crystals, mp 203-205°C (benzene). IR: 3486, 3349, 3227, 2962, 2926, 2855, 1642, 1621, 1588, 1549, 1514, 1429, 1396, 1334, 1287, 1227, 1213, 812, 685, 664, 556, 475  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (DMSO- $d_6$ )  $\delta$  0.89 (t,  $J = 6.1$  Hz, 3H, H-4'), 1.36 (m, 4H, H-3' and H-2'), 2.34 (s, 3H, Ar-CH<sub>3</sub>), 2.47 (s, 2H, H-1'), 6.03 (s, 2H, NH<sub>2</sub>), 7.09 (d,  $J = 8.2$  Hz, 1H, H-8), 7.20

(d,  $J = 8.2$  Hz, 1H, H-7), 7.74 (s, 1H, H-5), 10.77 (s, 1H, NH);  $^{13}\text{C}$  NMR (DMSO- $d_6$ )  $\delta$  14.12 (C-4'), 20.65 (Ar-CH<sub>3</sub>), 22.31 (C-3'), 23.47 (C-2'), 29.69 (C-1'), 104.74, 113.67, 114.91, 122.08, 129.05, 130.14, 135.54, 147.70, 162.53 (C=O); EIMS,  $m/z$  (%): 230 ( $\text{M}^+$ , 26), 215 (14), 201 (39), 188 (100), 187 (87), 159 (16), 97 (8), 83 (9), 69 (18), 60 (30). Anal. Calcd for C<sub>14</sub>H<sub>18</sub>N<sub>2</sub>O: C, 73.01; H, 7.88; N, 12.16. Found: C, 72.82; H, 7.65; N, 12.01.

**4-Amino-3-butyl-6-chloro-1H-quinolin-2-one (5c).** This compound was prepared from **4c** in 35% yield. Colourless crystals, mp 235-238°C (ethanol). IR: 3357, 3243, 2954, 2929, 2868, 1629, 1588, 1499, 1437, 1380, 1174, 1049, 905, 817, 784, 637, 522 cm<sup>-1</sup>.  $^1\text{H}$  NMR (DMSO- $d_6$ )  $\delta$  0.89 (t,  $J = 6.1$  Hz, 3H, H-4'), 1.36 (m, 4H, H-3' and H-2'), 2.48 (s, 2H, H-1'), 6.17 (s, 2H, NH<sub>2</sub>), 7.20 (d,  $J = 8.5$  Hz, 1H, H-8), 7.41 (d,  $J = 8.5$  Hz, 1H, H-7), 8.06 (s, 1H, H-5), 10.94 (s, 1H, NH);  $^{13}\text{C}$  NMR (DMSO- $d_6$ )  $\delta$  14.05 (C-4'), 22.26 (C-3'), 23.46 (C-2'), 29.49 (C-1'), 105.73, 115.06, 116.70, 121.89, 124.48, 128.87, 136.35, 146.87, 162.37 (C=O); EIMS,  $m/z$  (%): 250 ( $\text{M}^+$ , 24), 235 (17), 221 (41), 208 (100), 207 (77), 190 (9), 179 (15), 97 (10), 83 (12), 69 (16), 57 (22). Anal. Calcd for C<sub>13</sub>H<sub>15</sub>ClN<sub>2</sub>O: C, 62.28; H, 6.03; N, 11.17. Found: C, 62.02; H, 6.06; N, 10.90.

**4-Amino-3-butyl-8-methyl-1H-quinolin-2-one (5d).** This compound was prepared from **4d** in 38% yield. Colourless crystals, mp 163-166°C (benzene). IR: 3457, 3318, 3272, 3206, 2954, 2932, 2870, 1648, 1619, 1593, 1567, 1495, 1407, 1366, 1215, 1153, 773, 740, 634, 616, 578, 525 cm<sup>-1</sup>.  $^1\text{H}$  NMR (DMSO- $d_6$ )  $\delta$  0.91 (t,  $J = 6.1$  Hz, 3H, H-4'), 1.30-1.47 (m, 4H, H-3' and H-2'), 2.40 (s, 3H, Ar-CH<sub>3</sub>), 2.51 (s, 2H, H-1'), 6.11 (s, 2H, NH<sub>2</sub>), 7.00 (t,  $J = 7.2$  Hz, 1H, H-6), 7.25 (d,  $J = 6.7$  Hz, 1H, H-7), 7.80 (d,  $J = 7.7$  Hz, 1H, H-5), 10.01 (s, 1H, NH);  $^{13}\text{C}$  NMR (DMSO- $d_6$ )  $\delta$  14.09 (C-4'), 17.30 (Ar-CH<sub>3</sub>), 22.25 (C-3'), 23.42 (C-2'), 29.63 (C-1'), 104.48, 113.79, 119.94, 120.38, 122.84, 130.32, 135.91, 148.26, 162.81 (C=O); EIMS,  $m/z$  (%): 230 ( $\text{M}^+$ , 35), 215 (21), 201 (50), 188 (100), 187 (84), 170 (10), 159 (20), 77 (7), 69 (10), 57 (11). Anal. Calcd for C<sub>14</sub>H<sub>18</sub>N<sub>2</sub>O: C, 73.01; H, 7.88; N, 12.16. Found: C, 72.86; H, 7.80; N, 11.91.

**4-Amino-3-butyl-1-methyl-1H-quinolin-2-one (5e).** This compound, identical in all respects to that prepared by *Method E*, was obtained from **4e** in 37% yield.

**4-Amino-1-methyl-3-phenyl-1H-quinolin-2-one (5f).** This compound, identical in all respects to that prepared by *Method E*, was obtained from **4f** in 49% yield.

**4-Amino-3-butyl-1-phenyl-1H-quinolin-2-one (5g).** This compound, identical in all respects to that prepared by *Method E*, was obtained from **4g** in 70% yield.

**Amino-1,3-diphenyl-1H-quinolin-2-one (5h).** This compound, identical in all respects to that prepared by *Method E*, was obtained from **4h** in 54% yield.

**X-Ray structure determination of 6b · DMSO- $d_6$ .** Crystal data: C<sub>15</sub>H<sub>16</sub>N<sub>2</sub>O<sub>2</sub>S · (CD<sub>3</sub>)<sub>2</sub>SO,  $M = 372.52$ , triclinic, space group P-1,  $a = 12.2374(3)$  Å,  $b = 12.6977(2)$  Å,  $c = 13.3244(3)$  Å,  $\alpha = 101.3998(9)^\circ$ ,  $\beta = 109.1986(10)^\circ$ ,  $\gamma = 103.0765(8)^\circ$ ,  $V = 1819.39(7)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 1.360$  g cm<sup>-3</sup>,  $\mu = 0.310$  mm<sup>-1</sup>. A colourless block of compound **6b · DMSO- $d_6$**  with dimensions of 0.30 × 0.13 × 0.10 was greased on a glass thread. Diffraction data were collected on a Nonius Kappa CCD diffractometer with area detector at 150 K. A Cryostream Cooler (Oxford Cryosystems) was used for cooling the sample. A graphite monochromated MoK $\alpha$  radiation ( $\lambda = 0.71073$  Å)

was employed. A total of 13334 reflections were measured, 8168 were independent, and 6019 [ $I > 2\sigma(I)$ ] were considered observed. The structure was solved by direct methods using SIR-92<sup>25</sup> and refined by a full-matrix least-squares procedure based on  $F^2$  using SHELXL-97.<sup>26</sup> All the non-hydrogen atoms were refined anisotropically. N-H hydrogen atoms were visible in last stages of the refinement and were refined freely, while the C-H hydrogen atoms were included in the model at geometrically calculated positions and refined using a riding model. Final R indices [ $I > 2\sigma(I)$ ] R1 = 0.0480, wR2 = 0.1033, and (all data) R1 = 0.0764, wR2 = 0.1177 was found.

## Supporting Information Available

X-Ray crystallographic data (CIF files) for the structure of **6b** · **DMSO- $d_6$**  have been deposited with the Cambridge Crystallographic Data Centre with quotation number CCDC 687682 and are available free of charge on request to the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

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