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Synthesis of 2-thioxoimidazolines via reaction of 1-unsubstituted 3-aminoquinoline-2,4-diones with isothiocyanates

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ABSTRACT

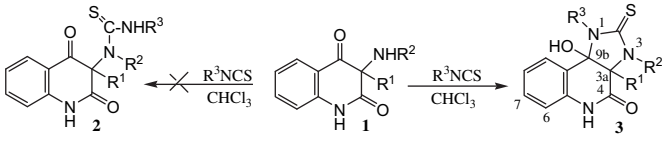
3-Alkyl/aryl-3-amino-1*H*,3*H*-quinoline-2,4-diones react with alkyl/aryl isothiocyanates to give 3a-alkyl/aryl-1,2,3,3a-tetrahydro-9b-hydroxy-2-thioxo-5*H*-imidazo[4,5-*c*]quinolin-4(9b*H*)-ones in high yields. These compounds rearrange in boiling acetic acid or concd hydrochloric acid to give novel 4-(2-aminophenyl)-1*H*-imidazole-2(3*H*)-thiones, 1,3-bis(2-(2,3-dihydro-2-thioxo-1*H*-imidazol-5-yl)phenyl)ureas and minor *N*-(2-(2,3-dihydro-2-thioxo-1*H*-imidazol-4-yl)phenyl)acetamides. In the presence of ethanol, the starting compounds rearrange in boiling acetic acid to give ethyl 2-(2,3-dihydro-2-thioxo-1*H*-imidazol-4-yl)phenylcarbamates. All compounds were characterized by their ^{1}H, ^{13}C, IR and MS spectra and some of them also by ^{15}N NMR data. The structures of two compounds were supported by single-crystal X-ray diffraction.

1. Introduction

In our laboratory, much attention has been paid to the reactivity of 3-amino, 3-hydroxy and 3-thiocyanato-1*H*,3*H*-quinoline-2,4-diones. Recently, the behaviour of the products of the reaction of 3-amino-1*H*,3*H*-quinoline-2,4-diones with isocyanic acid and isocyanates was investigated. In an acidic medium, these compounds are subject to molecular rearrangement, leading to novel heterocycles. A brief survey of these transformations was given in our last paper on this topic.[1]

The exceptional structural diversity of the products of the molecular rearrangement mentioned above gave us incentive to perform the analogous reaction of 3-amino-1*H*,3*H*-quinoline-2,4-diones with isothiocyanates and to examine how the products of this reaction would behave in an acidic environment. We anticipated the formation of new compounds containing a sulfur atom, which may be interesting, since many biologically active compounds contain a sulfur atom.[2,3]

The structure of the rearrangement products of the adducts of **1** with isocyanates is largely dependent on the character of the substituents at the 1, 3 and 1′ positions of the starting compounds **1**. Thus, according to this criterion, we divided the starting 3-amino-1*H*,3*H*-quinoline-2,4-diones into three different groups.[4] The first group contained compounds substituted at the 1-position with an alkyl or aryl groups and at the 3-position with an alkyl group. In our latest paper,[4] we demonstrated that compounds of this group afford—contrary to their reaction with isocyanates—a single cyclic addition product, which rearranges in an acidic environment to give three different types of spiro-imidazoline-4,3′-[3*H*]indole-2,2′(1*H*′)-diones, depending on the substituents at the 3 and 3a positions.



Key of substituents:

	a	b	c	d	e	f	g	h	i	j	k	l	m	n	o	p
R^1	Bu	Bu	Ph	Ph	Bu	Bu	Ph	Ph	Bu	Bu	Ph	Ph	Bu	Bu	Ph	Ph
R^2	H	H	H	H	Me	Me	Me	Me	Bu	Bu	Bu	Bu	Bz	Bz	Bz	Bz
R^3	Me	Ph	Me	Ph	Me	Ph	Me	Ph	Me	Ph	Me	Ph	Me	Ph	Me	Ph

Scheme 1.

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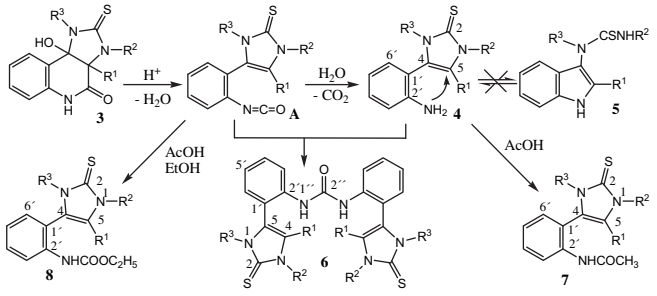
In this work, we demonstrate that the reaction of starting compounds **1** of the third group (compounds unsubstituted at the 1-position) also provides a single cyclic adduct, **3**, which rearranges in an acidic environment to give novel 4-(2-aminophenyl)-1*H*-imidazole-2(3*H*)-thiones (**4**), 1,3-bis(2-(2,3-dihydro-2-thioxo-1*H*-imidazol-5-yl)phenyl)ureas (**6**) and minor *N*-(2-(2,3-dihydro-2-thioxo-1*H*-imidazol-4-yl)phenyl)acetamides (**7**) (Scheme 1).

Table 1
Preparation of compounds **3** by the reaction of 3-aminoquinoline-2,4(1*H*,3*H*)-diones (**1**) with isothiocyanates

Entry	Educt	Substituents[a]			Product (yield, %)
		R^1	R^2	R^3	
1	**1a**	Bu	H	Me	**3a** (92)
2	**1a**	Bu	H	Ph	**3b** (80)
3	**1c**	Ph	H	Me	**3c** (85)
4	**1c**	Ph	H	Ph	**3d** (98)
5	**1e**	Bu	Me	Me	**3e** (82)
6	**1e**	Bu	Me	Ph	**3f** (97)
7	**1g**	Ph	Me	Me	**3g** (77)
8	**1g**	Ph	Me	Ph	**3h** (93)
9	**1i**	Bu	Bu	Me	**3i** (83)
10	**1i**	Bu	Bu	Ph	**3j** (96)
11	**1k**	Ph	Bu	Me	**3k** (74)
12	**1k**	Ph	Bu	Ph	**3l** (60)
13	**1m**	Bu	Bz	Me	**3m** (74)
14	**1m**	Bu	Bz	Ph	**3n** (96)
15	**1o**	Ph	Bz	Me	**3o** (76)
16	**1o**	Ph	Bz	Ph	**3p** (88)

[a] R^3 from isothiocyanate.



Scheme 2.

2. Results and discussion

Reactions of 3-amino-1*H*,3*H*-quinoline-2,4-diones **1** with isothiocyanates were performed by refluxing the reaction components in chloroform (Scheme 1).

Methylisothiocyanate and phenylisothiocyanate were chosen as model isothiocyanates. Starting aminoketones **1** were obtained from the corresponding 3-chloro derivatives, in accordance with the procedures described.[5]

As in the reaction of the 1-substituted compounds **1** with isothiocyanates,[4] only cyclic 1,2,3,3a-tetrahydro-9b-hydroxy-2-thioxo-5*H*-imidazo[4,5-*c*]quinolin-4(9b*H*)-ones **3** were isolated in good to very good yields (Scheme 1, Table 1). No single isomeric acyclic 3-thioureido-1*H*,3*H*-chinolin-2,4-dione **2** was isolated. The formation of tautomeric compounds bearing an SH group (theoretically possible in the case of **3a**–**d**) was not detected. Signals of the thioxo group of compounds **3** lie in the narrow region of 181.8–183.4 ppm of the ^{13}C NMR spectra, which is typical of the C=S group. The values of ^{1}J (^{15}N, ^{1}H)=90 and 98.8 Hz in the ^{15}N NMR spectrum of **3a** also exclude the presence of the C–SH group in this compound. The characteristic signals of C-3a in the ^{13}C NMR spectra of compounds **3** occur in the region of 68.1–78.3 ppm. For complete assignation of all signals in the ^{1}H and ^{13}C NMR spectra of compounds **3** to the corresponding atoms see Supplementary data.

We have found that 2-oxa-analogues[6] of compounds **3** rearrange to form two different types of products, through boiling in either acetic acid or concd hydrochloric acid.[7] Therefore, both of these reaction media were now used here also for the rearrangement of compounds **3** (Scheme 2).

The results are presented in Table 2. A comparison of the IR, NMR and MS spectra of the rearrangement products of **3** showed that three different types of products were formed. The first group of products consisted of 2-thioxoimidazolines **4**, which are single products of the rearrangement of **3** in concd hydrochloric acid (*Method B*), but also formed, to a lesser degree, in acetic acid (*Method A*).

In the IR spectra of compounds **4**, two absorption bands appear in the region of 3404–3476 and 3308–3378 cm^{-1}; these bands are characteristic of a primary amino group in *o*-substituted anilines.[8] In the ^{13}C NMR spectra (Table 3), the characteristic signals of the C=S group appeared in the region of 160.1–164.1 ppm; these signals are approximately 10 ppm downfield of the ^{13}C NMR spectra peaks of the respective 2-oxa-analogues.[7,9] In the case of

Table 2
Molecular rearrangement of compounds **3** in boiling AcOH (*Method A*), concd hydrochloric acid (*Method B*) and acetic acid/ethanol (9:1) (*Method C*)[a]

Entry	Educt	Method	Time (h)	Products (yield, %)	Entry	Educt	Method	Time (h)	Products (yield, %)
1	**3a**	*A*	2	**4a** (22), **6a** (29), **7a** (3)	19	**3i**	*B*	2.5	**4i** (56)
2	**3a**	*B*	2	**4a** (60)	20	**3j**	*A*	1.5	**4j** (5), **6j** (15)
3	**3b**	*A*	1.5	[b]	21	**3j**	*B*	1	**4j** (52)
4	**3b**	*B*	2	**4b** (49)	22	**3k**	*A*	1	**4k** (25), **6k** (26)
5	**3c**	*A*	1	**4c** (7), **6c** (33)	23	**3k**	*B*	1	**4k** (55)
6	**3c**	*B*	1	**4c** (69)	24	**3k**	*C*	1	**8k** (58)
7	**3c**	*C*	1	**8c** (74)	25	**3l**	*A*	1	**4l** (18), **6l** (40), **7l** (4)
8	**3d**	*A*	1.5	[b]	26	**3l**	*B*	1	**4l** (50)
9	**3d**	*B*	1	**4d** (50)	27	**3l**	*C*	1	**8l** (51)
10	**3e**	*A*	2	**4e** (6), **6e** (25)	28	**3m**	*A*	1.5	**4m** (12), **6m** (17)
11	**3e**	*B*	1.5	**4e** (43)	29	**3m**	*B*	0.5	**4m** (86)
12	**3f**	*A*	2.5	**4f** (28), **6f** (41), **7f** (6)	30	**3n**	*A*	2	**4n** (17), **6n** (20), **7n** (8)
13	**3f**	*B*	2.5	**4f** (76)	31	**3n**	*B*	2	**4n** (53)
14	**3g**	*A*	2	**4g** (41), **6g** (24), **7g** (10)	32	**3o**	*A*	1.5	**4o** (21), **6o** (45), **7o** (1)
15	**3g**	*B*	1	**4g** (76)	33	**3o**	*B*	1	**4o** (69)
16	**3h**	*A*	2.5	**4h** (2), **6h** (65), **7h** (4)	34	**3p**	*A*	2	**4p** (7), **6p** (37)
17	**3h**	*B*	1	**4h** (76)	35	**3p**	*B*	2	**4p** (71)
18	**3i**	*A*	2	**4i** (28), **6i** (23)					

[a] For key of substituents see Table 1 and Scheme 1.
[b] Inseparable mixtures of several compounds were obtained.

Table 3
^{1}H and ^{13}C chemical shifts (δ, ppm) of compounds **4a–p** in DMSO-d_6

Position	**4a**		**4b**		**4c**		**4d**		**4e**		**4f**		**4g**		**4h**	
	δ_H	δ_C	δ_H	δ_C	δ_H	δ_C	δ_H	δ_C	δ_H	δ_C	δ_H	δ_C	δ_H	δ_C	δ_H	δ_C
2 (C=S)	—	160.1	—	161.7	—	161.5	—	163.0	—	161.3	—	162.8	—	161.9	—	161.7
4	—	123.8	—	124.0	—	124.5	—	125.0	—	123.5	—	123.6	—	124.9	—	125.0
5	—	125.6	—	126.7	—	124.6	—	125.3	—	127.1	—	128.1	—	127.9	—	128.6
1′	—	111.9	—	112.0	—	112.2	—	112.1	—	111.6	—	111.7	—	111.8	—	111.4
2′	—	148.1	—	147.9	—	148.3	—	148.4	—	148.2	—	148.1	—	148.6	—	148.4
3′	6.77	114.9	6.58	114.5	6.83	115.0	6.58	114.5	6.64	114.8	6.51	114.4	6.71	114.7	6.44	114.2
4′	7.15	130.2	6.95	129.7	7.21	130.8	7.00	130.4	7.18	130.3	6.90	129.8	7.12	130.4	6.90	130.0
5′	6.62	115.9	6.38	115.4	6.63	116.3	6.40	115.5	6.80	115.8	6.33	115.2	6.52	115.7	6.31	115.0
6′	6.95	132.0	6.77	132.4	6.99	131.9	6.89	132.5	6.99	132.0	6.74	132.5	6.96	132.3	6.90	132.8
NH_2	5.00	—	5.07	—	5.22	—	5.26	—	5.07	—	5.07	—	5.23	—	5.25	—
1′ (R^1)	2.31	23.4	2.36	23.6	—	128.8	—	128.7	2.45	23.1	2.44	23.3	—	128.6	—	128.8
	2.23		2.27						2.38		2.35					
2′ (R^1)	1.48	30.3	1.54	30.0	7.40	125.5	7.47	125.7	1.42	30.3	1.43	29.9	7.38	129.9	[a]	129.9
3′ (R^1)	1.20	21.4	1.24	21.6	7.28	128.5	7.30	128.5	1.24	21.6	1.18	21.7	7.38	128.5	[a]	[b]
4′ (R^1)	0.79	13.6	0.82	13.6	7.21	127.2	7.21	128.1	0.79	13.5	0.74	13.5	7.38	128.6	[a]	[b]
1′ (R^2)	12.15	—	12.40	—	12.71	—	12.90	—	3.58	31.8	3.59	32.0	3.50	33.2	3.58	33.4
1′ (R^3)	3.19	31.2	—	137.0	3.23	31.1	—	136.7	3.26	32.1	—	137.2	3.22	32.1	—	137.2
2′ (R^3)	—	—	7.30	128.5	—	—	7.30	129.0	—	—	7.24	128.5	—	—	[a]	[b]
3′ (R^3)	—	—	7.30	128.1	—	—	7.30	128.2	—	—	7.24	128.2	—	—	[a]	[b]
4′ (R^3)	—	—	7.26	127.6	—	—	7.26	127.4	—	—	7.24	127.7	—	—	[a]	[b]

Position	**4i**		**4j**		**4k**		**4l**		**4m**		**4n**		**4o**		**4p**	
	δ_H	δ_C	δ_H	δ_C	δ_H	δ_C	δ_H	δ_C	δ_H	δ_C	δ_H	δ_C	δ_H	δ_C	δ_H	δ_C
2 (C=S)	—	160.8	—	162.3	—	161.2	—	162.7	—	162.2	—	163.9	—	162.6	—	164.1
4	—	123.8	—	123.8	—	125.2	—	125.1	—	124.3	—	124.2	—	125.6	—	125.6
5	—	126.7	—	127.5	—	127.6	—	128.4	—	127.0	—	128.1	—	127.8	—	128.5
1′	—	111.7	—	111.8	—	111.6	—	111.4	—	111.5	—	112.0	—	111.4	—	111.3
2′	—	148.1	—	147.9	—	148.5	—	148.2	—	148.2	—	147.4	—	148.5	—	148.2
3′	6.79	114.8	6.59	114.4	6.68	114.7	6.41	114.2	6.80	114.9	6.62	114.8	6.70	114.7	6.43	114.2
4′	7.18	130.3	6.96	129.8	7.09	130.3	6.86	129.9	7.17	130.4	6.99	130.0	7.11	130.4	6.87	130.0
5′	6.64	115.9	6.39	115.3	6.51	115.7	6.31	115.0	6.63	115.9	6.43	115.8	6.51	115.7	6.30	115.0
6′	6.99	132.0	6.80	132.4	6.97	132.5	6.93	132.9	7.00	132.0	6.86	132.5	6.99	132.5	6.96	132.9
NH_2	5.05	—	5.10	—	5.18	—	5.18	—	5.10	—	5.14	—	5.24	—	5.19	—
1′ (R^1)	2.47	23.0	2.50	23.2	—	128.8		128.8	2.34	23.2	2.42	23.5		128.4		128.6
	2.38		2.44						2.24		2.31					
2′ (R^1)	1.43	30.9	1.46	30.6	7.40	130.3	[a]	130.3	1.07	30.4	1.09	30.1	[c]	130.2	[d]	130.1
3′ (R^1)	1.22	21.4	1.24	21.7	7.40	128.4	[a]	[b]	1.02	21.4	1.02	21.6	[c]	128.2	[d]	[e]
4′ (R^1)	0.77	13.5	1.02	13.8	7.40	128.7	[a]	[b]	0.58	13.3	0.58	13.3	[c]	128.7	[d]	[e]
1′ (R^2)	4.02	44.4	4.10	44.6	4.09	44.6	4.15	44.8	5.54	47.7	5.70	47.9	5.49	48.2	5.63	48.4
					3.96		4.01		5.37		5.40		5.20		5.24	
2′ (R^2)	1.76	30.3	1.88	30.2	1.56	29.9	1.66	29.8	—	137.3	—	137.3	—	137.0	—	137.2
			1.79				1.62									
3′ (R^2)	1.43	19.6	1.46	19.7	1.16	19.3	1.20	19.3	7.34	126.7	[f]	126.9	7.10	127.0	[d]	127.0
4′ (R^2)	0.98	13.8	0.78	13.4	0.75	13.4	0.78	13.4	7.39	128.5	[f]	[g]	[c]	128.2	[d]	[e]
5′ (R^2)	—	—	—	—	—	—	—	—	7.31	127.2	[f]	[g]	[c]	127.0	[d]	[e]
1′ (R^3)	3.24	31.9	—	137.2	3.32	32.1	—	137.1	3.39	32.4	—	137.2	3.40	32.4	—	136.9
2′ (R^3)	—	—	7.30	128.4	—	—	[a]	[b]	—	—	[f]	[g]	—	—	[d]	[e]
3′ (R^3)	—	—	7.30	128.1	—	—	[a]	[b]	—	—	[f]	[g]	—	—	[d]	[e]
4′ (R^3)	—	—	7.30	127.7	—	—	[a]	[b]	—	—	[f]	[g]	—	—	[d]	[e]

[a] δ=7.30–7.53.
[b] δ=128.8, 128.6, 128.4, 128.2, 128.0.
[c] δ=7.08–7.28.
[d] δ=7.14–7.47.
[e] δ=128.6, 128.4, 128.3, 128.2.
[f] δ=7.30–7.41.
[g] δ=128.7, 128.6, 128.5, 128.3, 127.9.

compounds **4k** and **4l**, the structure was confirmed by single-crystal X-ray diffraction techniques (Figs. 1 and 2).

Both compounds crystallized in the triclinic space group *P*-1. Views of the molecular structures of both compounds (Figs. 1 and 2) show a perfectly planar arrangement of the five-membered core rings. Also, the substituting atoms reside in the same plane. The bond distances within these are shorter than standard single bond distances, and this is attributable to the conjugated character of the rings.[10] Moreover, the C1–S1 distances and the geometry of the respective groups are closest in character to a double bond.

The formation of compounds **4** can be smoothly elucidated from the hydrolysis of the isocyanate intermediate **A**, which arises via opening of the quinolone ring of **1** (Scheme 2).

The variety of molecular rearrangement products of **3** in acetic acid (*Method A*) is much more heterogeneous. In most cases, the main products are 1,3-bis(ureas) **6** (Table 2), which are structurally analogous to compounds isolated from the rearrangement of adducts of **1** with isocyanates.[7,9] Compounds **6** arise from the addition of compounds **4** to isocyanate intermediate **A** (Scheme 2). Unfortunately, the rearrangement of compounds **3b** and **3d** provides complicated mixtures of at least five compounds each. The presence of corresponding compounds **6b** and **6d** was proved by NMR. However, these compounds could not be separated.

APCI mass spectrometry allows for the identification of the molecular weights of compounds **6**. These mass spectra provide complementary ions in both polarity modes and are useful for the

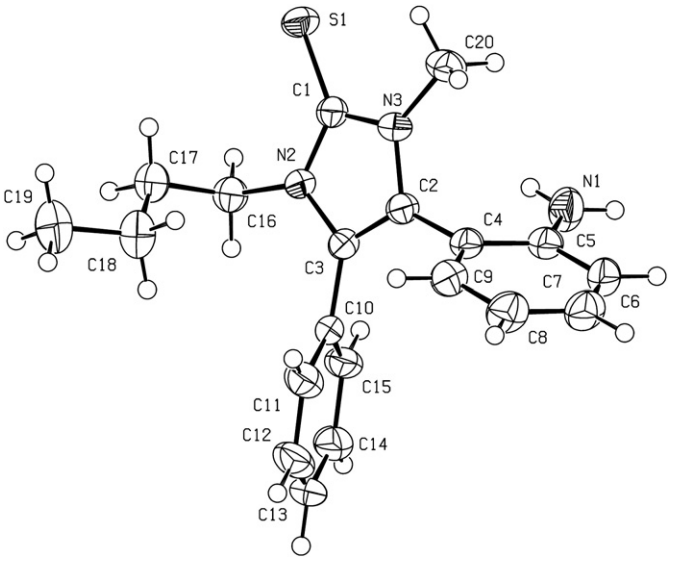


Figure 1. Molecular structure of compound **4k** with atom numbering scheme. (ORTEP 50% probability level), arbitrary spheres for hydrogen atoms.

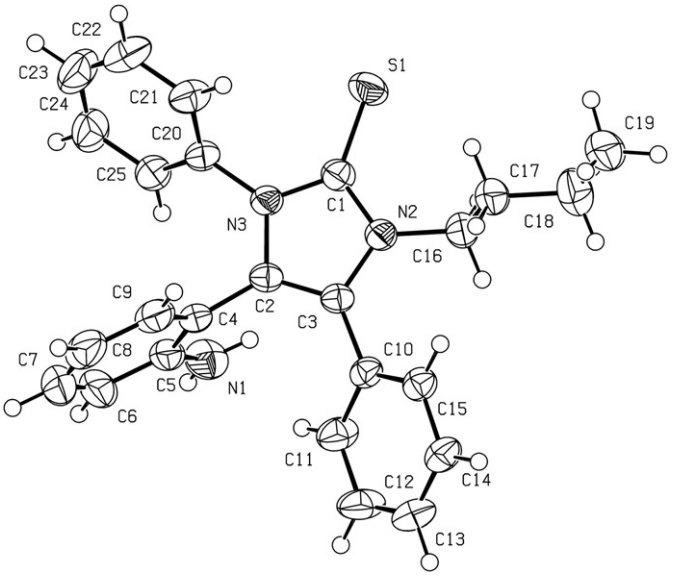


Figure 2. Molecular structure of compound **4l** with atom numbering scheme. (ORTEP 50% probability level), arbitrary spheres for hydrogen atoms.

determination and identification of alkyl/aryl substitution, such as the neutral losses of butene for butyl substitution. Another typical neutral loss is NCS fragment (or the appropriate alkyl/aryl-NCS). In the case of the compounds herein, the cleavage of the N–C bond in the –NH–CO–NH– group gave two series of ions labelled as $[F]^+$ and $[F+26]^+$ in the positive-ion spectra (also the $[F+26+N]^+$ ion was found), whereas the corresponding analogues in the negative-ion spectra are labelled as $[F-2H]^-$ and $[F+26-2H]^-$. These series were described in a previous paper.[7]

The NMR spectra of compounds **6** are very complex. The signals of the two components differ only slightly, both in the proton and carbon NMR spectra, and have a relative integral ratio near 1:1. This is a consequence of the co-occurrence of two *E*,*E-syn* and *E*,*E-anti* conformers, described earlier for their oxa-analogues.[7] Due to large number of atoms and the very strong overlap of appropriate pairs of signals in compounds **6**, complete assignment of all resonances was difficult and, in some cases, almost impossible. Therefore, characterization of only selected signals for compounds **6** is presented in Table 4.

Table 4
Selected ^{1}H and ^{13}C chemical shifts (δ, ppm) of compounds **6** in DMSO-d_6

Compound	δ_H (NHCONH)	δ_C (NHCONH)	δ_C (C=S)
6a	8.19, 8.17	152.90, 152.88	160.88, 161.80
6c	8.18, 8.06	152.51, 152.48	161.98, 161.95
6e	8.25, 8.18	152.82, 152.62	161.87, 161.85
6f	8.22, 8.09	152.06, 151.79	163.34. 163.06
6g	8.26, 8.06	152.34, 152.30	162.56, 161.48
6h	8.14, 8.10	151.36, 151.33	163.67, 161.62
6i	8.14, 8.10	152.80, 152.66	161.35, 161.28
6j	8.21, 8.05	152.08, 151.91	162.79, 162.55
6k	8.12, 8.02	152.24, 152.11	161.92, 161.88
6l	8.00, 7.96	151.28, 151.25	163.22, 163.04
6m	8.28, 8.18	152.63, 151.59	162.76. 162.58
6n	8.29, 8.11	151.99, 151.83	164.21, 164.03
6o	8.23, 8.08	152.20, 152.11	163.07, 163.04
6p	8.05, 7.97	151.33, 151.28	164.37, 164.31

To our surprise, we did not observe formation of the indole type compounds (**5**) during rearrangement of **3** in refluxing acetic acid. In the case of the molecular rearrangement of the oxa-analogues of compounds **3**, the oxa-analogues of compounds **5** were all isolated and their interconversion with the oxa-analogues of **4** was evident.[7,9] It is clear that the 2-thioxoimidazoline ring of compounds **4** is, in comparison with the imidazolone ring, much more resistant to nucleophilic attack of the amino group at the 5-position. The formation of minor compounds **7** is in agreement with this finding; the NMR spectra for compounds **7** are presented in Table 5. These compounds likely form from the acetylation of anilines **4** (Scheme 2). The alternative way to form these compounds is through the decomposition of the mixed anhydride of acetic and carbamoic acids, which can arise from the addition of acetic acid to isocyanate intermediate **A**. An analogous pathway is also possible for the formation of **6** from intermediate **A** and compound **4**.

For confirmation of the proposed isocyanate reaction mechanism for the rearrangement of compounds **3**, we carried out their rearrangements in acetic acid in the presence of ethanol (Table 2, *Method C*). The only isolated products of this reaction were carbamoic esters **8**, whose origin can be explained by alcoholysis of intermediate **A** or by alcoholysis of the mixed anhydride, formed from intermediate **A** and acetic acid. NMR spectra of compounds **8** are presented in Table 5. Compounds **7** and **8** have also been prepared by acylation of compounds **4**.

3. Conclusions

In conclusion, the described molecular rearrangement of compounds **3** is not merely interesting from a theoretical point of view but, owing to the simple reaction protocol, presents an easy pathway for the preparation of novel heterocyclic systems containing 2-thioxoimidazoline fragment. A number of 2-thioxoimidazolines and their derivatives exhibit significant biological activities[11,12] including inflammatory activity,[13] gentamycin nephrotoxicity,[14] dopamine β-hydroxylase inhibitory activity and anti-aggregating activity against collagen.[15] Therefore, it may be assumed that the compounds described in this paper should also display significant biological activity.

4. Experimental

4.1. General considerations

Melting points were determined on a Kofler block or Gallencamp apparatus. Elemental analyses (C, H, N) were performed with an EA 1108 Elemental Analyzer (Fisons Instrument). IR (KBr) spectra were recorded on a Mattson 3000 spectrophotometer. NMR spectra were recorded on a Bruker Avance spectrometer (500.13 MHz for ^{1}H, 125.76 MHz for ^{13}C, 50.68 MHz for ^{15}N) in

Table 5
^{1}H and ^{13}C chemical shifts (δ, ppm) of compounds **7** and **8** in DMSO-d_6

Position	**7a**		**7f**		**7g**		**7h**		**7l**		**7n**		**7o**		**8c**		**8k**		**8l**	
	δ_H	δ_C	δ_H	δ_C	δ_H	δ_C	δ_H	δ_C	δ_H	δ_C	δ_H	δ_C	δ_H	δ_C	δ_H	δ_C	δ_H	δ_C	δ_H	δ_C
2 (C=S)	—	160.4	—	163.1	—	162.4	—	163.5	—	163.1	—	163.9	—	163.0	—	161.6	—	161.5	—	162.7
4	—	122.9	—	122.5	—	123.9	—	123.8	—	124.0	—	123.4	—	124.9	—	123.8	—	124.5	—	124.3
5	—	125.8	—	128.4	—	128.0	—	128.2	—	128.4	—	128.0	—	127.5	—	124.8	—	127.7	—	[a]
1′	—	121.5	—	119.8	—	120.0	—	118.7	—	118.8	—	120.8	—	120.9	—	121.6	—	120.5	—	119.3
2′	—	137.8	—	137.8	—	137.9	—	137.7	—	137.6	—	137.6	—	137.8	—	138.3	—	138.1	—	137.8
3′	7.80	124.7	7.84	123.1	7.79	123.9	7.74	122.2	7.69	122.4	7.70	123.9	7.62	124.3	7.75	124.1	7.60	123.6	7.40	122.2
4′	7.45	129.4	7.24	129.0	7.38	129.0	7.15	129.7	7.14	[b]	7.23	129.1	7.37	129.7	7.52	130.3	7.35	129.7	7.14	129.1
5′	7.28	124.6	6.95	123.5	7.17	124.2	6.87	123.1	6.87	123.1	6.97	123.9	7.20	124.5	7.22	124.6	7.11	123.9	6.86	122.7
6′	7.32	132.0	7.00	132.3	7.30	132.3	7.05	132.5	7.08	132.5	6.97	132.3	7.41	132.4	7.34	132.2	7.27	132.5	7.14	132.5
1′ (R^1)	2.24	23.4	2.51	23.1	—	128.3	—	128.9	—	128.5	2.34	23.3	—	128.2	—	128.5	—	128.5	—	128.7
	2.14		2.41								2.24									
2′ (R^1)	1.48	29.9	1.49	29.6	7.30	129.7	[c]	129.7	[d]	130.0	1.14	29.9	[e]	129.7	7.25	125.7	7.37	130.4	[f]	130.6
3′ (R^1)	1.19	21.5	1.22	21.7	7.38	128.6	[c]	[g]	[d]	[b]	0.99	21.5	[e]	128.3	7.25	128.4	7.37	128.4	[f]	[a]
4′ (R^1)	0.78	13.5	0.77	13.4	7.38	128.7	[c]	[g]	[d]	[b]	0.55	13.2	[e]	128.4	7.25	128.0	7.37	128.8	[f]	[a]
1′ (R^2)	12.23	—	3.68	32.2	3.52	33.2	3.61	33.4	4.29	44.9	5.64	47.8	5.40	48.1	12.75	—	4.04	44.6	4.18	44.8
											5.53		5.31				3.94	—	3.97	—
2′ (R^2)	—	—	—	—	—	—	—	—	1.66	29.9	—	137.0	—	137.1	—	—	1.56	29.9	1.64	29.9
3′ (R^2)	—	—	—	—	—	—	—	—	1.23	19.3	[h]	126.7	[e]	126.7	—	—	1.17	19.2	1.20	19.3
4′ (R^2)	—	—	—	—	—	—	—	—	0.82	13.4	[h]	[g]	[e]	128.3	—	—	0.74	13.4	0.78	13.4
5′ (R^2)	—	—	—	—	—	—	—	—	—	—	[h]	127.2	[e]	127.1	—	—	—	—	—	—
1 (R^3)	3.21	31.6	—	137.1	3.34	32.8	—	137.0	—	136.9	—	137.2	3.44	33.1	3.23	31.6	3.31	32.5	—	137.0
2 (R^3)	—	—	7.28	128.6	—	—	[c]	[g]	[d]	[b]	[h]	[i]	—	—	—	—	—	—	[f]	[a]
3 (R^3)	—	—	7.28	128.2	—	—	[c]	[g]	[d]	[b]	[h]	[i]	—	—	—	—	—	—	[f]	[a]
4 (R^3)	—	—	7.28	127.8	—	—	[c]	[g]	[d]	[b]	[h]	[i]	—	—	—	—	—	—	[f]	[a]
NHCO	9.36	168.5	9.29	168.5	9.26	168.2	9.15	167.8	9.14	167.8	9.38	168.4	9.32	167.9	9.16	154.0	9.17	153.9	9.12	153.4
CO*CH*$_3$	2.01	23.5	2.07	23.8	1.92	23.6	1.90	23.8	1.94	23.9	2.01	23.6	1.90	23.4	—	—	—	—	—	—
CH$_2$CH$_3$	—	—	—	—	—	—	—	—	—	—	—	—	—	—	3.97	60.2	4.04	60.3	4.02	60.1
CH$_2$*CH*$_3$	—	—	—	—	—	—	—	—	—	—	—	—	—	—	1.12	14.5	1.26	14.6	1.28	14.7

[a] δ=129.0, 128.6, 128.4, 128.1, 127.9.
[b] δ=129.1, 128.9, 128.7, 128.6, 128.3, 128.0.
[c] δ=7.28–7.49.
[d] δ=7.28–7.45.
[e] δ=7.06–7.42.
[f] δ=7.28–7.45.
[g] δ=128.9, 128.8, 128.7, 128.6, 128.3, 128.1.
[h] δ=7.26–7.45.
[i] δ=128.9, 128.6, 128.3, 127.9.

DMSO-d_6. ^{1}H and ^{13}C chemical shifts are given on the δ scale (ppm) and are referenced to internal TMS. ^{15}N chemical shifts were referred to external neat nitromethane in co-axial capillary (δ=0.0). All 2D experiments (gradient-selected (gs)-COSY, gs-TOCSY, gs-HMQC, gs-HMBC) were performed using manufacturer's software. Proton spectra were assigned using gs-COSY and, when necessary, also TOCSY. Protonated carbons were assigned by gs-HMQC. Quaternary carbons were assigned by gs-HMBC. The positive- and negative-ion APCI mass spectra were measured on an ion trap analyser Agilent LC-MSD Trap XCT-Ultra (Agilent, Palo Alto, CA, USA) within the mass range m/z=50–500. Samples were dissolved in acetonitrile and analysed after direct injection (10 μL) at the flow rate of 400 μL/min acetonitrile. The ion source temperature was 350 °C, the APCI probe temperature was 350 °C, the flow rate and the pressure of nitrogen were 4 L/min and 45 psi, respectively. For MS/MS measurements, the isolation width of precursor ions was 4 m/z and the collision amplitude was 0.8 V. Column chromatography was carried out on silica gel (Merck, grade 60, 70–230 mesh) using chloroform and then successive mixtures of chloroform–ethanol (in ratios from 99:1 to 8:2, solvent system S1) or benzene and then successive mixtures of benzene–ethyl acetate (in ratios from 99:1 to 8:2, solvent system S2). Reactions as well as the course of separation and also the purity of substances were monitored by TLC (elution systems benzene–ethyl acetate, 4:1 (S3), chloroform–ethanol, 9:1 (S4) and/or 19:1 (S5), and chloroform–ethyl acetate, 7:3 (S6)) on Alugram® SIL G/UV$_{254}$ foils (Macherey–Nagel).

X-ray analysis. The X-ray data for colourless crystals of **4k** and **4l** (crystallized from a mixture of benzene and hexane) were obtained at 150(1) K using Oxford Cryostream low-temperature device on a Nonius KappaCCD diffractometer with Mo Kα radiation (λ=0.71073 Å), a graphite monochromator and the ϕ and χ scan mode. Data reductions were performed with DENZO-SMN.[16] The absorption was corrected by integration methods.[17] Structures were solved by direct methods (Sir92)[18] and refined by full matrix least-square based on F^2 (SHELXL97).[19] Hydrogen atoms were mostly localized on a difference Fourier map, however to ensure uniformity of treatment of crystal, all hydrogens were recalculated into idealized positions (riding model) and assigned temperature factors H_{iso}(H)=1.2 U_{eq} (pivot atom) or of 1.5 U_{eq} for the methyl moiety with C–H=0.96, 0.97, 0.86 and 0.93 Å for methyl, methylene, N–H and hydrogen atoms in aromatic ring.

Crystallographic data for ***4l***. $C_{25}H_{25}N_3S$, M=399.54, triclinic, P-1, a=9.0622(6), b=11.3578(8), c=11.8802(5), α=66.213(4), β=73.118(4), γ=85.825(5)°, Z=2, V=1069.30(11) Å^3, D_c=1.241 g cm^{-3}, μ=0.167 mm^{-1}, T_{min}=0.942, T_{max}=0.960; 21,596 reflections measured (θ_{max}=27.5°), 4897 independent (R_{int}=0.0925), 2582 with $I>2\sigma(I)$, 262 parameters, S=1.017, R1 (obs. data)=0.0586, wR2 (*all data*)=0.1077; max, min residual electron density=0.227, −0.317 e Å^{-3}.

Crystallographic data for ***4k***. $C_{20}H_{23}N_3S$, M=337.47, triclinic, P-1, a=8.1161(12), b=8.8611(14), c=13.7078(16), α=85.964(11), β=87.909(12), γ=68.305(13)°, Z=2, V=913.7(3) Å^3, D_c=1.227 g cm^{-3}, μ=0.183 mm^{-1}, T_{min}=0.926, T_{max}=0.969; 19,628 reflections measured (θ_{max}=27.5°), 4188 independent (R_{int}=0.0866), 2555 with $I>2\sigma(I)$, 217 parameters, S=1.096, R1 (obs. data)=0.0665, wR2 (*all data*)=0.1146; max, min residual electron density=0.268, −0.287 e Å^{-3}.

CCDC-734258 and 734259 for **4l** and **4k**, respectively, contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/data_request/cif.

4.2. Preparation of 3-amino-1*H*,3*H*-quinoline-2,4-diones (1)

Starting 3-substituted 3-amino-1*H*,3*H*-quinoline-2,4-diones (**1**) were prepared from corresponding 3-chloro derivatives according to the protocol described.[5]

4.3. General method for the preparation of 1,2,3,3a-tetrahydro-9b-hydroxy-2-thioxo-5*H*-imidazo[4,5-*c*]quinolin-4(9b*H*)-ones (3)

Phenylisothiocyanate (0.144 mL, 1.2 mmol) or methyl isothiocyanate (88 mg, 1.2 mmol) was added to the cooled (0 °C) and stirred solution of **1** (1 mmol) in chloroform (5 mL). In the case of **1c**, 1,4-dioxane was used as solvent. The reaction mixture was stirred overnight at room temperature and then heated to reflux for 1 h. After cooling and evaporating in vacuo to dryness, the residue was crystallized from appropriate solvent or column chromatographed. For NMR spectra of compounds **3** see Supplementary data.

*4.3.1. 3a-Butyl-9b-hydroxy-1-methyl-1,2,3,3a-tetrahydro-2-thioxo-5H-imidazo[4,5-c]quinolin-4(9bH)-one (**3a**).* Compound was prepared from **1a** in 92% yield. Colourless crystals, mp 200–209 °C (benzene), IR: 3333, 3210, 3067, 2958, 2921, 2861, 1675, 1598, 1492, 1437, 1404, 1365, 1331, 1283, 1227, 1161, 1123, 1105, 1053, 1044, 1004, 975, 761, 682, 625, 572, 515 cm^{-1}. Anal. Calcd (found) for $C_{15}H_{19}N_3O_2S$: C 58.99 (58.82); H 6.27 (6.38); N 13.76 (13.65). Positive-ion APCI-MS: m/z 306 $[M+H]^+$ (100%), 288 $[M+H-H_2S]^+$; positive-ion APCI-MS/MS of m/z 306: 233 $[M+H-CH_3NCS]^+$ (100%). Negative-ion APCI-MS: m/z 304 $[M-H]^-$ (100%), 286 $[M-H_2O]^-$; negative-ion APCI-MS/MS of m/z 304: 270 $[M-H-H_2S]^-$ (100%), 231 $[M-H-CH_3NCS]^-$.

*4.3.2. 3a-Butyl-9b-hydroxy-1-phenyl-1,2,3,3a-tetrahydro-2-thioxo-5H-imidazo[4,5-c]quinolin-4(9bH)-one (**3b**).* Compound was prepared from **1a** in 80% yield. Colourless crystals, mp 206–212 °C (ethyl acetate), IR: 3336, 3290, 3060, 2957, 2932, 2869, 1677, 1659, 1612, 1597, 1532, 1497, 1485, 1450, 1430, 1345, 1314, 1272, 1240, 1183, 1161, 1112, 955, 867, 760, 723, 700, 668, 618, 586, 526 cm^{-1}. Anal. Calcd (found) for $C_{20}H_{21}N_3O_2S$: C 65.37 (65.47); H 5.76 (5.92); N 11.44 (11.30). Positive-ion APCI-MS: m/z 368 $[M+H]^+$ (100%), 336 $[M+H-S]^+$; positive-ion APCI-MS/MS of m/z 368: 233 $[M+H-C_6H_5NCS]^+$ (100%). Negative-ion APCI-MS: m/z 366 $[M-H]^-$ (100%), 332 $[M-H-H_2S]^-$, 273 $[M+H-C_6H_5NH_2]^+$, 231 $[M-H-C_6H_5NCS]^-$; negative-ion APCI-MS/MS of m/z 366: 332 $[M-H-H_2S]^-$, 247 $[M-H-C_6H_5-NCO]^-$, 231 $[M-H-C_6H_5NCS]^-$ (100%).

*4.3.3. 9b-Hydroxy-1-methyl-3a-phenyl-1,2,3,3a-tetrahydro-2-thioxo-5H-imidazo[4,5-c]quinolin-4(9bH)-one (**3c**).* Compound was prepared from **1c** in 85% yield. Colourless crystals, mp 177–183 °C (ethyl acetate), IR: 3380, 3195, 3061, 2980, 2920, 1680, 1598, 1491, 1394, 1288, 1228, 1168, 1134, 1066, 1045, 976, 924, 894, 809, 759, 702, 654, 627, 588, 573 cm^{-1}. Anal. Calcd (found) for $C_{17}H_{15}N_3O_2S$: C 62.75 (62.59); H 4.65 (4.79); N 12.91 (12.88). Positive-ion APCI-MS: m/z 326 $[M+H]^+$ (68%), 308 $[M+H-H_2O]^+$, 294 $[M+H-S]^+$ (100%); positive-ion APCI-MS/MS of m/z 326: 253 $[M+H-CH_3NCS]^+$ (100%), 236 $[M+H-CH_3NHCSNH_2]^+$. Negative-ion APCI-MS: m/z 324 $[M-H]^-$ (100%), 306 $[M-H_2O]^-$; negative-ion APCI-MS/MS of m/z 324: 306 $[M-H_2O]^-$, 290 $[M-H_2S]^-$ (100%).

*4.3.4. 1,3a-Diphenyl-9b-hydroxy-1,2,3,3a-tetrahydro-2-thioxo-5H-imidazo[4,5-c]quinolin-4(9bH)-one (**3d**).* Compound was prepared from **1c** in 98% yield. Colourless crystals, mp 207–213 °C (ethyl acetate), IR: 3420, 3138, 3061, 2983, 2911, 1687, 1598, 1494, 1468, 1404, 1257, 1219, 1142, 1091, 1070, 1056, 949, 895, 809, 765, 753, 698, 657, 645, 596, 577, 529 cm^{-1}. Anal. Calcd (found) for $C_{22}H_{17}N_3O_2S$: C 68.20 (68.02); H 4.42 (4.52); N 10.85 (10.71). Positive-ion APCI-MS: m/z 388 $[M+H]^+$ (100%), 356 $[M+H-S]^+$, 253 $[M+H-C_6H_5NCS]^+$; positive-ion APCI-MS/MS of m/z 388: 253 $[M+H-C_6H_5NCS]^+$ (100%), 236 $[M+H-C_6H_5NHCSNH_2]^+$, 208 $[M+H-C_6H_5NHCSNH_2-CO]^+$. Negative-ion APCI-MS: m/z 386

$[M-H]^-$ (100%); negative-ion APCI-MS/MS of *m/z* 386: 352 $[M-H-H_2S]^-$, 267 $[M-H-C_6H_5-NCO]^-$, 251 $[M-H-C_6H_5NCS]^-$.

*4.3.5. 3a-Butyl-1,3-dimethyl-9b-hydroxy-1,2,3,3a-tetrahydro-2-thioxo-5H-imidazo[4,5-c]quinolin-4(9bH)-one (**3e**).* Compound was prepared from **1e** in 82% yield. Colourless crystals, mp 235–239 °C (ethyl acetate), IR: 3291, 3197, 3136, 3069, 2959, 2930, 2871, 1676, 1618, 1600, 1496, 1467, 1441, 1393, 1365, 1335, 1309, 1291, 1250, 1206, 1183, 1156, 1116, 1079, 1041, 1016, 1002, 969, 952, 909, 845, 759, 730, 693, 672, 648, 612, 566, 535, 510 cm^{-1}. Anal. Calcd (found) for $C_{16}H_{21}N_3O_2S$: C 60.16 (60.02); H 6.63 (6.78); N 13.16 (13.08). Positive-ion APCI-MS: *m/z* 320 $[M+H]^+$ (9%), 302 $[M+H-H_2O]^+$ (100%), 288 $[M+H-S]^+$; positive-ion APCI-MS/MS of *m/z* 320: 247 $[M+H-CH_3NCS]^+$ (100%), 229 $[M+H-CH_3NCS-H_2O]^+$, 201 $[M+H-CH_3NCS-H_2O-CO]^+$. Negative-ion APCI-MS: *m/z* 318 $[M-H]^-$ (100%), 289 $[M-H-CH_3N]^-$; negative-ion APCI-MS/MS of *m/z* 318: 274 $[M-H-C_3H_8]^-$, 245 $[M-H-CH_3NCS]^-$ (100%).

*4.3.6. 3a-Butyl-9b-hydroxy-3-methyl-1-phenyl-1,2,3,3a-tetrahydro-2-thioxo-5H-imidazo[4,5-c]quinolin-4(9bH)-one (**3f**).* Compound was prepared from **1e** in 97% yield. Colourless crystals, mp 258–263 °C (ethanol), IR: 3275, 3199, 3061, 2927, 2881, 1668, 1600, 1498, 1454, 1403, 1387, 1365, 1321, 1307, 1209, 1199, 1184, 1158, 1129, 1111, 1087, 1042, 1022, 1009, 987, 962, 945, 915, 838, 805, 756, 722, 698, 674, 645, 578, 523 cm^{-1}. Anal. Calcd (found) for $C_{21}H_{23}N_3O_2S$: C 66.12 (66.23); H 6.08 (6.23); N 11.01 (10.92). Positive-ion APCI-MS: *m/z* 382 $[M+H]^+$ (100%), 364 $[M+H-H_2O]^+$; positive-ion APCI-MS/MS of *m/z* 382: 263 $[M+H-C_6H_5-NCO]^+$, 247 $[M+H-C_6H_5NCS]^+$ (100%), 228 $[M+H-C_3H_8-C_6H_5-SH]^+$. Negative-ion APCI-MS: *m/z* 380 $[M-H]^-$ (100%); negative-ion APCI-MS/MS of *m/z* 380: 261 $[M-H-C_6H_5-NCO]^-$, 245 $[M-H-C_6H_5NCS]^-$ (100%).

*4.3.7. 1,3-Dimethyl-9b-hydroxy-3a-phenyl-1,2,3,3a-tetrahydro-2-thioxo-5H-imidazo[4,5-c]quinolin-4(9bH)-one (**3g**).* Compound was prepared from **1g** in 77% yield. Colourless crystals, mp 246–250 °C (benzene), IR: 3377, 3219, 3073, 2972, 2936, 1703, 1616, 1597, 1488, 1464, 1446, 1372, 1304, 1234, 1212, 1152, 1126, 1093, 1050, 1031, 1018, 974, 960, 945, 892, 872, 852, 743, 703, 659, 645, 613, 585, 562, 539 cm^{-1}. Anal. Calcd (found) for $C_{18}H_{17}N_3O_2S$: C 63.70 (63.57); H 5.05 (5.12); N 12.38 (12.21). Positive-ion APCI-MS: *m/z* 340 $[M+H]^+$ (47%), 322 $[M+H-H_2O]^+$ (100%), 308 $[M+H-S]^+$; positive-ion APCI-MS/MS of *m/z* 340: 267 $[M+H-CH_3NCS]^+$ (100%), 249 $[M+H-CH_3NCS-H_2O]^+$, 236, 221 $[M+H-C_6H_5-NCO]^+$. Negative-ion APCI-MS: *m/z* 338 $[M-H]^-$ (100%), 309 $[M-H-CH_3N]^-$; negative-ion APCI-MS/MS of *m/z* 338: 320 $[M-H-H_2O]^-$, 294, 265 $[M-H-CH_3NCS]^-$, 247 $[M-H-CH_3NCS-H_2O]^-$ (100%), 219 $[M-H-C_6H_5-NCO]^-$.

*4.3.8. 1,3a-Diphenyl-9b-hydroxy-3-methyl-1,2,3,3a-tetrahydro-2-thioxo-5H-imidazo[4,5-c]quinolin-4(9bH)-one (**3h**).* Compound was prepared from **1g** in 93% yield. Colourless crystals, mp 248–252 °C (benzene), IR: 3401, 3063, 3035, 2976, 2912, 1673, 1617, 1601, 1494, 1445, 1385, 1360, 1305, 1217, 1191, 1148, 1126, 1096, 1046, 1025, 1003, 976, 949, 912, 896, 836, 804, 748, 697, 682, 662, 584, 572, 529 cm^{-1}. Anal. Calcd (found) for $C_{23}H_{19}N_3O_2S$: C 68.81 (68.75); H 4.77 (4.90); N 10.47 (10.32). Positive-ion APCI-MS: *m/z* 402 $[M+H]^+$ (75%), 384 $[M+H-H_2O]^+$, 370 $[M+H-S]^+$ (100%); positive-ion APCI-MS/MS of *m/z* 402: 283 $[M+H-C_6H_5-NCO]^+$, 267 $[M+H-C_6H_5NCS]^+$ (100%), 249 $[M+H-C_6H_5NCS-H_2O]^+$, 236. Negative-ion APCI-MS: *m/z* 400 $[M-H]^-$ (100%), 265 $[M-H-C_6H_5NCS]^-$; negative-ion APCI-MS/MS of *m/z* 400: 382 $[M-H-H_2O]^-$, 281 $[M-H-C_6H_5-NCO]^-$, 265 $[M-H-C_6H_5NCS]^-$ (100%), 247 $[M-H-C_6H_5NCS-H_2O]^-$.

*4.3.9. 3,3a-Dibutyl-9b-hydroxy-1-methyl-1,2,3,3a-tetrahydro-2-thioxo-5H-imidazo[4,5-c]quinolin-4(9bH)-one (**3i**).* Compound was prepared from **1i** in 83% yield. Colourless crystals, mp 217–223 °C (ethyl acetate), IR: 3371, 3175, 3127, 2958, 2932, 2862, 1672, 1600, 1491, 1467, 1431, 1410, 1393, 1373, 1336, 1284, 1216, 1183, 1159, 1125, 1084, 1040, 1026, 1000, 973, 908, 856, 774, 758, 739, 690, 669, 650, 575, 528 cm^{-1}. Anal. Calcd (found) for $C_{19}H_{27}N_3O_2S$: C 63.13 (63.28); H 7.53 (7.42); N 11.62 (11.49). Positive-ion APCI-MS: *m/z* 362 $[M+H]^+$ (18%), 344 $[M+H-H_2O]^+$ (100%), 350 $[M+H-S]^+$; positive-ion APCI-MS/MS of *m/z* 362: 289 $[M+H-CH_3NCS]^+$ (100%). Negative-ion APCI-MS: *m/z* 360 $[M-H]^-$ (100%), 331 $[M-H-CH_3N]^-$; negative-ion APCI-MS/MS of *m/z* 360: 316 $[M-H-C_3H_8]^-$, 287 $[M-H-CH_3NCS]^-$ (100%), 241 $[M-H-CH_3NCS-H_2O-CO]^-$.

*4.3.10. 3,3a-Dibutyl-9b-hydroxy-1-phenyl-1,2,3,3a-tetrahydro-2-thioxo-5H-imidazo[4,5-c]quinolin-4(9bH)-one (**3j**).* Compound was prepared from **1i** in 96% yield. Colourless crystals, mp 234–238 °C (ethyl acetate), IR: 3330, 3062, 2958, 2932, 2861, 1665, 1600, 1497, 1466, 1459, 1444, 1414, 1387, 1379, 1336, 1286, 1226, 1187, 1155, 1125, 1043, 1021, 1002, 995, 913, 754, 747, 695, 672, 648, 579, 528 cm^{-1}. Anal. Calcd (found) for $C_{24}H_{29}N_3O_2S$: C 68.05 (67.89); H 6.90 (7.02); N 9.92 (9.78). Positive-ion APCI-MS: *m/z* 424 $[M+H]^+$, 406 $[M+H-H_2O]^+$ (100%), 392 $[M+H-S]^+$, 380 $[M+H-C_3H_8]^+$; positive-ion APCI-MS/MS of *m/z* 424: 305 $[M+H-C_6H_5-NCO]^+$, 289 $[M+H-C_6H_5NCS]^+$ (100%), 271 $[M+H-C_6H_5NCS-H_2O]^+$. Negative-ion APCI-MS: *m/z* 422 $[M-H]^-$ (100%), 393, 287 $[M-H-C_6H_5NCS]^-$.

*4.3.11. 3-Butyl-9b-hydroxy-1-methyl-3a-phenyl-1,2,3,3a-tetrahydro-2-thioxo-5H-imidazo[4,5-c]quinolin-4(9bH)-one (**3k**).* Compound was prepared from **1k** in 74% yield. Colourless crystals, mp 227–230 °C (benzene), IR: 3343, 3131, 3072, 2958, 2931, 2873, 1677, 1618, 1599, 1493, 1460, 1429, 1399, 1375, 1277, 1229, 1214, 1179, 1155, 1130, 1099, 1054, 1031, 973, 896, 858, 776, 754, 707, 678, 661, 558 cm^{-1}. Anal. Calcd (found) for $C_{21}H_{23}N_3O_2S$: C 66.12 (66.22); H 6.08 (6.22); N 11.01 (10.93). Positive-ion APCI-MS: *m/z* 382 $[M+H]^+$ (32%), 364 $[M+H-H_2O]^+$ (100%), 350 $[M+H-S]^+$, 338 $[M+H-C_3H_8]^+$; positive-ion APCI-MS/MS of *m/z* 382: 309 $[M+H-CH_3NCS]^+$ (100%), 291 $[M+H-C_6H_5CH_2]^+$, 263 $[M+H-C_6H_5-NCO]^+$. Negative-ion APCI-MS: *m/z* 380 $[M-H]^-$ (100%), 351 $[M-CH_3N]^-$; negative-ion APCI-MS/MS of *m/z* 380: 362 $[M-H-H_2O]^-$, 336 $[M-H-C_3H_8]^-$, 307 $[M-H-CH_3NCS]^-$, 289 $[M-H-C_6H_5CH_2]^-$, 261 $[M-H-C_6H_5-NCO]^-$ (100%), 247 $[M-H-C_4H_9NCS-H_2O]^-$.

*4.3.12. 3-Butyl-1,3a-diphenyl-9b-hydroxy-1,2,3,3a-tetrahydro-2-thioxo-5H-imidazo[4,5-c]quinolin-4(9bH)-one (**3l**).* Compound was prepared from **1k** in 60% yield. Colourless crystals, mp 251–254 °C (ethyl acetate), IR: 3372, 3129, 3069, 2959, 2932, 2871, 1673, 1600, 1494, 1457, 1397, 1368, 1285, 1224, 1145, 1132, 1100, 1055, 1046, 1027, 976, 951, 898, 836, 747, 695, 675, 581, 529 cm^{-1}. Anal. Calcd (found) for $C_{26}H_{25}N_3O_2S$: C 70.40 (70.27); H 5.68 (5.75); N 9.47 (9.39). Positive-ion APCI-MS: *m/z* 444 $[M+H]^+$ (100%), 309 $[M+H-C_6H_5NCS]^+$; positive-ion APCI-MS/MS of *m/z* 444: 325 $[M+H-C_6H_5-NCO]^+$, 309 $[M+H-C_6H_5NCS]^+$ (100%). Negative-ion APCI-MS: *m/z* 442 $[M-H]^-$ (100%), 307 $[M-H-C_6H_5NCS]^-$; negative-ion APCI-MS/MS of *m/z* 442: 424 $[M-H-H_2O]^-$, 398 $[M-H-CS]^-$, 323 $[M-H-C_6H_5-NCO]^-$, 307 $[M-H-C_6H_5NCS]^-$ (100%).

*4.3.13. 3-Benzyl-3a-butyl-9b-hydroxy-1-methyl-1,2,3,3a-tetrahydro-2-thioxo-5H-imidazo[4,5-c]quinolin-4(9bH)-one (**3m**).* Compound was prepared from **1m** in 74% yield. Colourless crystals, mp 216–224 °C (benzene), IR: 3305, 3203, 3162, 2955, 2930, 2859, 1691, 1615, 1601, 1494, 1453, 1415, 1395, 1352, 1334, 1293, 1284, 1246, 1176, 1153, 1128, 1107, 1070, 1049, 1001, 976, 942, 753, 714, 665, 632, 581, 563, 527 cm^{-1}. Anal. Calcd (found) for $C_{22}H_{25}N_3O_2S$: C 66.81 (66.70); H 6.37 (6.52); N 10.62 (10.49). Positive-ion APCI-MS: *m/z* 396 $[M+H]^+$ (19%), 378 $[M+H-H_2O]^+$ (100%), 364 $[M+H-S]^+$; positive-ion APCI-MS/MS of *m/z* 396: 365, 323 $[M+H-CH_3NCS]^+$ (100%), 303 $[M+H-C_6H_5NH_2]^+$, 277 $[M+H-C_6H_5-NCO]^+$, 272 $[M+H-C_6H_5CH_2-SH]^+$, 241,

215, 164. Negative-ion APCI-MS: *m/z* 394 $[M-H]^-$ (100%), 365 $[M-H-CH_3N]^-$; negative-ion APCI-MS/MS of *m/z* 394: 350 $[M-H-C_3H_8]^-$, 337 $[M-H-C_4H_9]^-$, 321 $[M-H-CH_3NCS]^-$ (100%), 303 $[M-H-C_6H_5CH_2]^-$, 275 $[M-H-C_6H_5-NCO]^-$.

*4.3.14. 3-Benzyl-3a-butyl-9b-hydroxy-1-phenyl-1,2,3,3a-tetrahydro-2-thioxo-5H-imidazo[4,5-c]quinolin-4(9bH)-one (**3n**).* Compound was prepared from **1m** in 96% yield. Colourless crystals, mp 219–222 °C (benzene), IR: 3354, 3185, 3130, 3065, 2959, 2928, 2870, 1666, 1600, 1496, 1445, 1409, 1385, 1368, 1320, 1293, 1243, 1181, 1156, 1125, 1085, 1074, 1037, 1023, 997, 951, 914, 753, 719, 698, 670, 648, 573, 528 cm^{-1}. Anal. Calcd (found) for $C_{27}H_{27}N_3O_2S$: C 70.87 (70.77); H 5.95 (6.12); N 9.18 (9.09). Positive-ion APCI-MS: *m/z* 458 $[M+H]^+$, 440 $[M+H-H_2O]^+$, 426 $[M+H-S]^+$, 414 $[M+H-C_3H_8]^+$ (100%); positive-ion APCI-MS/MS of *m/z* 458: 365 $[M+H-C_6H_5NH_2]^+$, 339 $[M+H-C_6H_5-NCO]^+$, 323 $[M+H-C_6H_5NCS]^+$ (100%). Negative-ion APCI-MS: *m/z* 456 $[M-H]^-$ (100%), 427, 321 $[M-H-C_6H_5NCS]^-$; negative-ion APCI-MS/MS of *m/z* 456: 337 $[M-H-C_6H_5-NCO]^-$, 321 $[M-H-C_6H_5NCS]^-$ (100%), 303 $[M-H-C_6H_5NCS-H_2O]^-$.

*4.3.15. 3-Benzyl-9b-hydroxy-1-methyl-3a-phenyl-1,2,3,3a-tetrahydro-2-thioxo-5H-imidazo[4,5-c]quinolin-4(9bH)-one (**3o**).* Compound was prepared from **1o** in 76% yield. Colourless crystals, mp 230–235 °C (ethyl acetate–hexane), IR: 3402, 3156, 3061, 2983, 2917, 1698, 1680, 1615, 1598, 1556, 1493, 1438, 1384, 1341, 1327, 1297, 1262, 1240, 1172, 1136, 1105, 1068, 1052, 1040, 1021, 993, 958, 895, 861, 761, 751, 724, 708, 666, 656, 633, 589, 564, 549 cm^{-1}. Anal. Calcd (found) for $C_{24}H_{21}N_3O_2S$: C 69.37 (69.23); H 5.09 (5.23); N 10.11 (9.97). Positive-ion APCI-MS: *m/z* 416 $[M+H]^+$, 398 $[M+H-H_2O]^+$ (100%), 384 $[M+H-S]^+$, 343 $[M+H-CH_3NCS]^+$; positive-ion APCI-MS/MS of *m/z* 416: 343 $[M+H-CH_3NCS]^+$ (100%), 325 $[M+H-C_6H_5CH_2]^+$, 297 $[M+H-C_6H_5-NCO]^+$, 236 $[M+H-C_6H_5CH_2NHCSNHCH_3]^+$. Negative-ion APCI-MS: *m/z* 414 $[M-H]^-$ (100%), 385 $[M-H-CH_3N]^-$; negative-ion APCI-MS/MS of *m/z* 414: 396 $[M-H-H_2O]^-$, 370, 341 $[M-H-CH_3NCS]^-$ (100%), 323 $[M-H-C_6H_5CH_2]^-$, 295 $[M-H-C_6H_5-NCO]^-$.

*4.3.16. 3-Benzyl-1,3a-diphenyl-9b-hydroxy-1,2,3,3a-tetrahydro-2-thioxo-5H-imidazo[4,5-c]quinolin-4(9bH)-one (**3p**).* Compound was prepared from **1o** in 88% yield. Colourless crystals, mp 257–263 °C (ethyl acetate), IR: 3350, 3061, 3028, 2984, 2905, 1674, 1615, 1597, 1493, 1451, 1434, 1367, 1340, 1301, 1268, 1235, 1170, 1152, 1138, 1103, 1089, 1071, 1050, 1024, 969, 945, 915, 896, 810, 766, 749, 720, 709, 694, 661, 640, 584, 560, 530, 516 cm^{-1}. Anal. Calcd (found) for $C_{29}H_{23}N_3O_2S$: C 72.93 (73.12); H 4.85 (4.91); N 8.80 (8.76). Positive-ion APCI-MS: *m/z* 478 $[M+H]^+$ (100%), 460 $[M+H-H_2O]^+$, 446 $[M+H-S]^+$; positive-ion APCI-MS/MS of *m/z* 478: 359 $[M+H-C_6H_5-NCO]^+$, 343 $[M+H-C_6H_5NCS]^+$ (100%). Negative-ion APCI-MS: *m/z* 476 $[M-H]^-$ (100%), 341 $[M-H-C_6H_5NCS]^-$; negative-ion APCI-MS/MS of *m/z* 476: 458 $[M-H-H_2O]^-$, 377, 341 $[M-H-C_6H_5NCS]^-$ (100%).

4.4. General methods for the molecular rearrangement of compounds 3

Method A. The solution of starting compound **3** (1 mmol) in acetic acid (8 mL) was heated to reflux for the time given in Table 2. The course of the reaction was monitored by TLC. After cooling, the reaction mixture was evaporated to dryness in vacuo and the residue was crystallized from appropriate solvent or separated by column chromatography on silica gel.

Method B. The solution of starting compound **3** (1 mmol) in concd hydrochloric acid (5 mL) was heated to reflux for the time given in Table 2. In same cases a small quantity of acetic acid was added to dissolution of starting compound. The course of the reaction was monitored by TLC. After cooling, the reaction mixture was evaporated to dryness in vacuo. The residue was dissolved in pyridine (3 mL) and solution was evaporated to dryness. The residue was washed with water and crystallized from appropriate solvent or separated by column chromatography on silica gel.

Method C. The reaction was carried out in the same manner as in *Method A*, however, a mixture of acetic acid and absolute ethanol (9:1) was used as the reaction medium.

*4.4.1. 4-(2-Aminophenyl)-5-butyl-3-methyl-1H-imidazole-2(3H)-thione (**4a**).* Compound was prepared from **3a** in respective yields 22% (*Method A*) or 60% (*Method B*). Colourless crystals, mp 211–212 °C (benzene), IR: 3404, 3321, 3079, 2953, 2928, 2871, 2740, 1628, 1571, 1506, 1457, 1391, 1307, 1239, 1156, 1135, 1034, 1012, 935, 855, 788, 743, 681, 635, 600, 534, 518 cm^{-1}. Anal. Calcd (found) for $C_{14}H_{19}N_3S$: C 64.33 (64.65); H 7.33 (7.45); N 16.08 (15.81). Positive-ion APCI-MS: *m/z* 262 $[M+H]^+$ (100%), 230 $[M+H-S]^+$; positive-ion APCI-MS/MS of *m/z* 262: 245 $[M+H-NH_3]^+$, 232, 219 $[M+H-C_3H_7]^+$, 206 $[M+H-C_4H_8]^+$, 172 $[M+H-C_4H_9-SH]^+$ (100%). Negative-ion APCI-MS: *m/z* 340 $[2\times(M-H)-H-2\times C_4H_9-SH-S]^-$, 260 $[M-H]^-$ (100%); negative-ion APCI-MS/MS of *m/z* 260: 245 $[M-H-CH_3]^-$, 226 $[M-H-H_2S]^-$, 211 $[M-H-H_2S-CH_3]^-$ (100%), 201 $[M-H-NHCS]^-$, 186 $[M-H-H_2O-C_4H_8]^-$, 170 $[M-H-H_2O-C_4H_9-SH]^-$.

*4.4.2. 4-(2-Aminophenyl)-5-butyl-3-phenyl-1H-imidazole-2(3H)-thione (**4b**).* Compound was prepared from **3b** in 49% yields (*Method B*). Yellow crystals, mp 258–265 °C (ethanol), IR: 3419, 3287, 3184, 3063, 2924, 2872, 2709, 1648, 1618, 1597, 1577, 1498, 1453, 1389, 1372, 1309, 1234, 1159, 1145, 1074, 1032, 934, 854, 839, 792, 770, 749, 699, 653, 624, 542, 515, 503 cm^{-1}. Anal. Calcd (found) for $C_{19}H_{21}N_3S$: C 70.55 (70.45); H 6.54 (6.65); N 12.99 (12.81). Positive-ion APCI-MS: *m/z* 324 $[M+H]^+$ (100%), 292 $[M+H-S]^+$; positive-ion APCI-MS/MS of *m/z* 324: 307 $[M+H-NH_3]^+$, 294 $[M+H-CH_2NH_2]^+$, 281 $[M+H-C_3H_7]^+$, 265 $[M+H-NHCS]^+$, 231 $[M+H-C_6H_5-NH_2]^+$, 189 $[M+H-C_6H_5NCS]^+$, 172 $[M+H-C_6H_5NHCS-NH_2]^+$, 130 $[M+H-C_6H_5NCS-NH_2-C_3H_7]^+$ (100%). Negative-ion APCI-MS: *m/z* 322 $[M-H]^-$ (100%); negative-ion APCI-MS/MS of *m/z* 322: 292 $[M-H-CH_2NH_2]^-$, 265 $[M-H-C_4H_9]^-$, 239 $[M-H-C_4H_9CN]^-$ (100%).

*4.4.3. 4-(2-Aminophenyl)-3-methyl-5-phenyl-1H-imidazole-2(3H)-thione (**4c**).* Compound was prepared from **3c** in yields 7% (*Method A*) or 69% yield (*Method B*). Colourless crystals, mp 310–315 °C (ethanol), IR: 3476, 3401, 3312, 3080, 2938, 2751, 1625, 1574, 1491, 1455, 1430, 1388, 1301, 1274, 1256, 1228, 1134, 1113, 1074, 1021, 962, 940, 918, 783, 770, 750, 697, 678, 614, 574, 546 cm^{-1}. Anal. Calcd (found) for $C_{16}H_{15}N_3S$: C 68.30 (68.15); H 5.37 (5.45); N 14.93 (14.80). Positive-ion APCI-MS: *m/z* 282 $[M+H]^+$ (100%); positive-ion APCI-MS/MS of *m/z* 282: 265 $[M+H-NH_3]^+$ (100%), 249 $[M+H-SH]^+$, 223 $[M+H-NHCS]^+$. Negative-ion APCI-MS: *m/z* 280 $[M-H]^-$ (100%); negative-ion APCI-MS/MS of *m/z* 280: 265 $[M-H-CH_3]^-$ (100%), 246 $[M-H-H_2S]^-$, 231 $[M-H-H_2S-CH_3]^-$.

*4.4.4. 4-(2-Aminophenyl)-3,5-diphenyl-1H-imidazole-2(3H)-thione (**4d**).* Compound was prepared from **3d** in 50% yield (*Method B*). Colourless crystals, mp 327–335 °C (DMF–methanol), IR: 3443, 3345, 3056, 2919, 2737, 1633, 1616, 1596, 1573, 1498, 1489, 1452, 1390, 1374, 1310, 1262, 1234, 1158, 1075, 1028, 1005, 967, 911, 788, 767, 759, 749, 725, 697, 637, 577, 552, 507 cm^{-1}. Anal. Calcd (found) for $C_{21}H_{17}N_3S$: C 73.44 (73.55); H 4.99 (5.15); N 12.23 (12.31). Positive-ion APCI-MS: *m/z* 344 $[M+H]^+$ (100%); positive-ion APCI-MS/MS of *m/z* 344: 327 $[M+H-NH_3]^+$, 224 $[M+H-C_6H_5CNH-NH_2]^+$, 209 $[M+H-C_6H_5NCS]^+$, 193 $[M+H-C_6H_5NCS-NH_2]^+$ (100%). Negative-ion APCI-MS: *m/z* 342 $[M-H]^-$ (100%); negative-ion APCI-MS/MS of *m/z* 342: 308 $[M-H-H_2S]^-$, 283 $[M-H-NHCS]^-$, 265

$[M-H-C_6H_5]^-$, 250 $[M-H-C_6H_5NH]^-$, 239 $[M-H-C_5H_5CN]^-$ (100%).

*4.4.5. 4-(2-Aminophenyl)-5-butyl-1,3-dimethyl-1H-imidazole-2(3H)-thione (**4e**).* Compound was prepared from **3e** in respective yields 6% (*Method A*) and 43% (*Method B*). Colourless crystals, mp 108–111 °C (cyclohexane), IR: 3406, 3314, 3202, 2958, 2928, 2859, 1624, 1573, 1494, 1454, 1391, 1310, 1260, 1214, 1177, 1127, 1094, 1017, 865, 755, 645, 514 cm^{-1}. Anal. Calcd (found) for $C_{15}H_{21}N_3S$: C 65.41 (65.53); H 7.69 (7.78); N 15.26 (15.11). Positive-ion APCI-MS: *m/z* 276 $[M+H]^+$ (100%); positive-ion APCI-MS/MS of *m/z* 276: 246 $[M+H-2\times CH_3]^+$, 233 $[M+H-C_3H_7]^+$, 219 $[M+H-C_4H_9]^+$, 206 $[M+H-CH_3-C_4H_7]^+$ (100%), 203 $[M+H-CH_3NCS]^+$, 172. Negative-ion APCI-MS: *m/z* 274 $[M-H]^-$ (100%); negative-ion APCI-MS/MS of *m/z* 575: 274 $[M-H]^-$ (100%); negative-ion APCI-MS/MS of *m/z* 274: 219 $[M-H-C_3H_7]^-$, 201 $[M-H-CH_3NCS]^-$, 186 $[M-H-C_3H_8-CS]^-$.

*4.4.6. 4-(2-Aminophenyl)-5-butyl-1-methyl-3-phenyl-1H-imidazole-2(3H)-thione (**4f**).* Compound was prepared from **3f** in 28% (*Method A*) and 76% yields (*Method B*). Yellowish crystals, mp 179–182 °C (benzene–hexane), IR: 3300, 3189, 2954, 2930, 2872, 1621, 1596, 1573, 1493, 1455, 1387, 1357, 1310, 1242, 1110, 1027, 791, 754, 743, 695, 648, 545 cm^{-1}. Anal. Calcd (found) for $C_{20}H_{23}N_3S$: C 71.18 (71.25); H 6.87 (6.95); N 12.45 (12.62). Positive-ion APCI-MS: *m/z* 338 $[M+H]^+$ (100%); positive-ion APCI-MS/MS of *m/z* 338: 295 $[M+H-C_3H_7]^+$, 281 $[M+H-C_4H_9]^+$, 265 $[M+H-CH_3NCS]^+$ (88%), 233, 206 $[M+H-C_4H_7-C_6H_5]^+$ (100%), 172 $[M+H-C_4H_7-C_6H_5-H_2S]^+$, 146, 130 $[M+H-C_3H_8-C_6H_5NCSNCH_3]^+$. Negative-ion APCI-MS: *m/z* 336 $[M-H]^-$ (100%); negative-ion APCI-MS/MS of *m/z* 336: 263 $[M-H-CH_3NCS]^-$ (100%).

*4.4.7. 4-(2-Aminophenyl)-1,3-dimethyl-5-phenyl-1H-imidazole-2(3H)-thione (**4g**).* Compound was prepared from **3g** in yields 41% (*Method A*) and 76% (*Method B*). Colourless crystals, mp 203–205 °C (benzene–hexane); IR: 3393, 3303, 3197, 3048, 2942, 1623, 1573, 1489, 1449, 1388, 1310, 1266, 1200, 1131, 1075, 1051, 1023, 1014, 946, 921, 856, 822, 767, 749, 726, 697, 678, 647, 526 cm^{-1}. Anal. Calcd (found) for $C_{17}H_{17}N_3S$: C 69.12 (69.03); H 5.80 (5.95); N 14.22 (14.08). Positive-ion APCI-MS: *m/z* 296 $[M+H]^+$ (100%), 264 $[M+H-S]^+$; positive-ion APCI-MS/MS of *m/z* 296: 279 $[M+H-NH_3]^+$, 265, 223 $[M+H-CH_3NCS]^+$ (100%), 208 $[M+H-CH_3NCS-CH_3]^+$, 193 $[M+H-CH_3NHCSNCH_3]^+$, 182. Negative-ion APCI-MS: *m/z* 294 $[M-H]^-$ (100%); negative-ion APCI-MS/MS of *m/z* 294: 221 $[M-H-CH_3NCS]^-$ (100%), 206 $[M-2H-CH_3NCS-CH_3]^-$.

*4.4.8. 4-(2-Aminophenyl)-3,5-diphenyl-1-methyl-1H-imidazole-2(3H)-thione (**4h**).* Compound was prepared from **3h** in respective yields 2% (*Method A*) or 76% (*Method B*). Colourless crystals, mp 297–301 °C (benzene), IR: 3371, 3331, 3203, 3052, 2924, 1619, 1596, 1575, 1498, 1453, 1424, 1383, 1355, 1308, 1235, 1155, 1108, 1023, 807, 790, 761, 747, 728, 705, 693, 659, 578, 544, 510 cm^{-1}. Anal. Calcd (found) for $C_{22}H_{19}N_3S$: C 73.92 (73.81); H 5.36 (5.51); N 11.75 (11.64). Positive-ion APCI-MS: *m/z* 358 $[M+H]^+$ (100%); positive-ion APCI-MS/MS of *m/z* 358: 285 $[M+H-CH_3NCS]^+$, 223 $[M+H-C_6H_5NCS]^+$, 208 $[M+H-C_6H_5NCSNH]^+$, 193 $[M+H-C_6H_5NCSNHCH_3]^+$ (100%); negative-ion APCI-MS: *m/z* 356 $[M-H]^-$ (100%).

*4.4.9. 4-(2-Aminophenyl)-1,5-dibutyl-3-methyl-1H-imidazole-2(3H)-thione (**4i**).* Compound was prepared from **3i** in respective yields 28% (*Method A*) or 56% (*Method B*). Colourless crystals, mp 106–109 °C (benzene–hexane), IR: 3353, 3301, 3235, 3205, 3069, 3031, 2955, 2929, 2858, 1633, 1596, 1569, 1493, 1459, 1442, 1408, 1391, 1357, 1312, 1287, 1263, 1204, 1174, 1157, 1139, 1127, 1085, 1043, 1018, 950, 931, 887, 849, 820, 750, 740, 681, 638, 613, 543 cm^{-1}. Anal. Calcd (found) for $C_{18}H_{27}N_3S$: C 68.09 (68.15); H 8.57 (8.76); N 13.23 (13.11). Positive-ion APCI-MS: *m/z* 318 $[M+H]^+$ (100%), 286 $[M+H-S]^+$; positive-ion APCI-MS/MS of *m/z* 318: 284 $[M+H-H_2S]^+$, 262 $[M+H-C_4H_8]^+$ (100%). Negative-ion APCI-MS: *m/z* 316 $[M-H]^-$ (100%); negative-ion APCI-MS/MS of *m/z* 316: 288, 259 $[M-H-C_4H_9]^-$, 201 $[M-H-C_4H_9NCS]^-$, 186 $[M-H-C_4H_9NCS-CH_3]^-$.

*4.4.10. 4-(2-Aminophenyl)-1,5-dibutyl-3-phenyl-1H-imidazole-2(3H)-thione (**4j**).* Compound was prepared from **3j** in respective yields 5% (*Method A*) and 52% (*Method B*). Colourless crystals, mp 155–156 °C (benzene–hexane), IR: 3310, 3181, 3046, 2954, 2928, 2868, 1616, 1599, 1574, 1499, 1465, 1454, 1432, 1404, 1394, 1378, 1356, 1312, 1292, 1265, 1158, 1121, 1173, 1127, 950, 778, 752, 736, 724, 692, 644, 547, 522 cm^{-1}. Anal. Calcd (found) for $C_{23}H_{29}N_3S$: C 72.78 (72.65); H 7.70 (7.86); N 11.07 (11.21). Positive-ion APCI-MS: *m/z* 380 $[M+H]^+$ (100%), 348 $[M+H-S]^+$; positive-ion APCI-MS/MS of *m/z* 380: 346 $[M+H-H_2S]^+$, 324 $[M+H-C_4H_8]^+$ (100%), 265 $[M+H-C_4H_9NCS]^+$, 245 $[M+H-C_6H_5NCS]^+$, 208 $[M+H-C_4H_9NCS-C_4H_9]^+$, 172.

*4.4.11. 4-(2-Aminophenyl)-1-butyl-3-methyl-5-phenyl-1H-imidazole-2(3H)-thione (**4k**).* Compound was prepared from **3k** in respective yields 25% (*Method A*) and 55% yield (*Method B*). Colourless crystals, mp 147–149 °C (benzene–hexane), IR: 3405, 3378, 3298, 3202, 3043, 2958, 2929, 2873, 2854, 1620, 1594, 1576, 1490, 1457, 1448, 1408, 1383, 1310, 1258, 1209, 1140, 1114, 1074, 1049, 1021, 934, 861, 814, 762, 748, 700, 641, 573, 535 cm^{-1}. Anal. Calcd (found) for $C_{20}H_{23}N_3S$: C 71.18 (71.02); H 6.87 (6.99); N 12.45 (12.61). Positive-ion APCI-MS: *m/z* 338 $[M+H]^+$ (100%), 306 $[M+H-S]^+$; positive-ion APCI-MS/MS of *m/z* 338: 304 $[M+H-H_2S]^+$, 282 $[M+H-C_4H_8]^+$ (100%), 265 $[M+H-CH_3NCS]^+$, 223 $[M+H-C_4H_9NCS]^+$, 193 $[M+H-C_4H_9NCS-CH_3]^+$. Negative-ion APCI-MS: *m/z* 336 $[M-H]^-$ (100%); negative-ion APCI-MS/MS of *m/z* 336: 263 $[M-H-CH_3NCS]^-$, 221 $[M-H-C_4H_9NCS]^-$ (100%), 206 $[M-H-C_4H_9NCS-CH_3]^-$.

*4.4.12. 4-(2-Aminophenyl)-3,5-diphenyl-1-butyl-1H-imidazole-2(3H)-thione (**4l**).* Compound was prepared from **3l** in respective yields 18% (*Method A*) and 50% (*Method B*). Colourless crystals, mp 147–149 °C (benzene–hexane), IR: 3407, 3279, 3183, 3056, 2961, 2929, 2871, 1618, 1596, 1575, 1557, 1494, 1454, 1401, 1370, 1306, 1291, 1264, 1239, 1156, 1133, 1076, 1025, 935, 851, 760, 748, 695, 661, 586, 542, 513 cm^{-1}. Anal. Calcd (found) for $C_{25}H_{25}N_3S$: C 75.15 (75.02); H 6.31 (6.45); N 10.52 (10.41). Positive-ion APCI-MS: *m/z* 400 $[M+H]^+$ (100%), 368 $[M+H-S]^+$; positive-ion APCI-MS/MS of *m/z* 400: 366 $[M+H-H_2S]^+$, 344 $[M+H-C_4H_8]^+$ (100%), 285 $[M+H-C_4H_9NCS]^+$. Negative-ion APCI-MS: *m/z* 398 $[M-H]^-$ (100%); negative-ion APCI-MS/MS of *m/z* 398: 342 $[M-H-C_4H_8]^-$ (100%), 283 $[M-H-C_4H_9NCS]^-$.

*4.4.13. 4-(2-Aminophenyl)-1-benzyl-5-butyl-3-methyl-1H-imidazole-2(3H)-thione (**4m**).* Compound was prepared from **3m** in respective yields 12% (*Method A*) and 86% (*Method B*). Colourless crystals, mp 132–133 °C (cyclohexane), IR: 3430, 3312, 3224, 3197, 2957, 2925, 2871, 1620, 1569, 1492, 1455, 1399, 1388, 1360, 1345, 1307, 1256, 1194, 1091, 1079, 1018, 963, 754, 738, 704, 530 cm^{-1}. Anal. Calcd (found) for $C_{21}H_{25}N_3S$: C 71.75 (71.69); H 7.17 (7.25); N 11.95 (11.79). Positive-ion APCI-MS: *m/z* 352 $[M+H]^+$ (100%); positive-ion APCI-MS/MS of *m/z* 352: 318 $[M+H-H_2S]^+$, 309 $[M+H-C_3H_7]^+$, 261 $[M+H-C_6H_5CH_2]^+$ (100%), 232 $[M+H-C_6H_5CH_2-CH_3N]^+$, 219, 201 $[M+H-NHCS-C_6H_5CH_3]^+$, 186 $[M+H-C_6H_5CH_2NCS-NH_3]^+$. Negative-ion APCI-MS: *m/z* 350 $[M-H]^-$ (100%); negative-ion APCI-MS/MS of *m/z* 350: 201 $[M-H-C_6H_5CH_2NCS]^-$ (100%), 186 $[M-H-C_6H_5CH_2NCS-CH_3]^-$, 170 $[M-H-C_6H_5CH_2NHCSNHCH_3]^-$.

*4.4.14. 4-(2-Aminophenyl)-1-benzyl-5-butyl-3-phenyl-1H-imidazole-2(3H)-thione (**4n**).* Compound was prepared from **3n** in respective

yields 17% (*Method A*) and 53% (*Method B*). Colourless crystals, mp 150–153 °C (benzene–hexane), IR: 3405, 3315, 3218, 3064, 3028, 2957, 2928, 2869, 1618, 1598, 1574, 1497, 1453, 1427, 1403, 1393, 1370, 1349, 1310, 1288, 1260, 1224, 1160, 1139, 1074, 1027, 957, 836, 751, 725, 700, 687, 649, 630, 589, 542, 525 cm^{-1}. Anal. Calcd (found) for $C_{26}H_{27}N_3S$: C 75.51 (75.40); H 6.58 (6.71); N 10.16 (10.27). Positive-ion APCI-MS: *m*/*z* 414 $[M+H]^+$ (100%), 382 $[M+H-S]^+$; positive-ion APCI-MS/MS of *m*/*z* 414: 323 $[M+H-C_6H_5CH_2]^+$ (100%), 294 $[M+H-C_6H_5-C_3H_7]^+$, 281, 263 $[M+H-C_6H_5NCS-NH_2]^+$. Negative-ion APCI-MS: *m*/*z* 412 $[M-H]^-$ (100%); negative-ion APCI-MS/MS of *m*/*z* 412: 321 $[M-H-C_6H_5CH_2]^-$ (100%), 292 $[M-H-C_6H_5-C_3H_7]^-$, 263 $[M-H-C_6H_5CH_2NCS]^-$.

*4.4.15. 4-(2-Aminophenyl)-1-benzyl-3-methyl-5-phenyl-1H-imidazole-2(3H)-thione (**4o**).* Compound was prepared from **3o** in respective yields 21% (*Method A*) or 69% (*Method B*). Colourless crystals, mp 180–182 °C (benzene–hexane), IR: 3393, 3308, 3209, 3060, 3031, 2940, 1621, 1573, 1588, 1446, 1436, 1402, 1383, 1357, 1309, 1260, 1206, 1158, 1108, 1075, 1048, 1022, 967, 923, 825, 765, 753, 699, 640, 591, 535 cm^{-1}. Anal. Calcd (found) for $C_{23}H_{21}N_3S$: C 74.36 (74.48); H 5.70 (5.81); N 11.31 (11.22). Positive-ion APCI-MS: *m*/*z* 372 $[M+H]^+$ (100%), 340 $[M+H-S]^+$; positive-ion APCI-MS/MS of *m*/*z* 372: 355 $[M+H-NH_3]^+$, 338 $[M+H-H_2S]^+$, 313 $[M+H-NHCS]^+$, 281 $[M+H-C_6H_5CH_2]^+$ (100%), 264 $[M+H-C_6H_5CH_2-NH_3]^+$, 221 $[M+H-C_6H_5NCS-NH_2]^+$. Negative-ion APCI-MS: *m*/*z* 370 $[M-H]^-$ (100%)+negative-ion APCI-MS/MS of *m*/*z* 370: 297 $[M-H-CH_3NCS]^-$, 279 $[M-H-C_6H_5CH_2]^-$, 221 $[M-H-C_6H_5CH_2NCS]^-$ (100%), 206 $[M-H-C_6H_5CH_2-CH_3NCS]^-$.

*4.4.16. 4-(2-Aminophenyl)-1-benzyl-3,5-diphenyl-1H-imidazole-2(3H)-thione (**4p**).* Compound was prepared from **3p** in respective yields 7% (*Method A*) or 71% (*Method B*). Colourless crystals, mp 211–214 °C (benzene–hexane), IR: 3443, 3327, 3059, 3032, 2917, 1614, 1575, 1556, 1538, 1495, 1453, 1428, 1401, 1368, 1308, 1266, 1177, 1158, 1103, 1076, 1028, 1002, 984, 959, 918, 850, 821, 789, 757, 728, 697, 657, 593, 576, 542, 512 cm^{-1}. Anal. Calcd (found) for $C_{28}H_{23}N_3S$: C 77.57 (77.41); H 5.35 (5.61); N 9.69 (9.51). Positive-ion APCI-MS: *m*/*z* 434 $[M+H]^+$ (100%), 402 $[M+H-S]^+$; positive-ion APCI-MS/MS of *m*/*z* 434: 417 $[M+H-NH_3]^+$, 400 $[M+H-H_2S]^+$, 375 $[M+H-NHCS]^+$, 356 $[M+H-C_6H_6]^+$, 343 $[M+H-C_6H_5CH_2]^+$ (100%), 283 $[M+H-C_6H_5NCS-NH_2]^+$. Negative-ion APCI-MS: *m*/*z* 432 $[M-H]^-$ (100%); negative-ion APCI-MS/MS of *m*/*z* 432: 341 $[M-H-C_6H_5CH_2]^-$ (100%).

*4.4.17. 1,3-Bis(2-(4-butyl-2,3-dihydro-1-methyl-2-thioxo-1H-imidazol-5-yl)phenyl)urea (**6a**).* Compound was prepared from **3a** in 29% yield (*Method A*). Colourless crystals, mp 140–148 °C (benzene–hexane), IR: 3275, 3170, 3106, 2956, 2930, 2871, 1709, 1579, 1525, 1501, 1449, 1388, 1290, 1248, 1192, 1135, 1035, 757, 612, 533 cm^{-1}. Anal. Calcd (found) for $C_{29}H_{36}N_6OS_2$: C 63.47 (63.29); H 6.61 (6.75); N 15.31 (15.43). Positive-ion APCI-MS: *m*/*z* 549 $[M+H]^+$ (100%), 517 $[M+H-S]^+$, 262 $[F]^+$ (100%); positive-ion APCI-MS/MS of *m*/*z* 549: 515 $[M+H-H_2S]^+$, 302 $[F+26+N]^+$ (100%), 288 $[F+26]^+$, 262 $[F]^+$. Negative-ion APCI-MS: *m*/*z* 547 $[M-H]^-$ (100%); negative-ion APCI-MS/MS of *m*/*z* 547: 286 $[F+26-2H]^-$ (100%).

*4.4.18. 1,3-Bis(2-(2,3-dihydro-1-methyl-4-phenyl-2-thioxo-1H-imidazol-5-yl)phenyl)urea (**6c**).* Compound was prepared from **3c** in 33% yield (*Method A*). Yellowish crystals, mp 305–316 °C (ethanol), IR: 3406, 3060, 2940, 2758, 1707, 1649, 1580, 1525, 1490, 1449, 1384, 1318, 1291, 1236, 1192, 1132, 1075, 1026, 962, 912, 787, 763, 694, 612, 562 cm^{-1}. Anal. Calcd (found) for $C_{33}H_{28}N_6OS_2$: C 67.32 (67.45); H 4.79 (4.85); N 14.27 (14.15). Positive-ion APCI-MS: *m*/*z* 589 $[M+H]^+$ (100%), 557 $[M+H-S]^+$, 452, 420, 380, 354, 321, 308 $[F+26]^+$, 282 $[F]^+$; positive-ion APCI-MS/MS of *m*/*z* 589: 322 $[F+26+N]^+$ (100%), 308 $[F+26]^+$, 296 $[F+N]^+$, 282 $[F]^+$. Negative-ion APCI-MS: *m*/*z* 587 $[M-H]^-$ (100%), 450, 442, 410, 352, 338, 322 $[F+26+N-2H]^-$, 306 $[F+26+2H]^-$, 280 $[F-2H]^-$; negative-ion APCI-MS/MS of *m*/*z* 587: 306 $[F+26+2H]^-$ (100%), 280 $[F-H]^-$.

*4.4.19. 1,3-Bis(2-(2,3-dihydro-1,3-dimethyl-4-butyl-2-thioxo-1H-imidazol-5-yl)phenyl)urea (**6e**).* Compound was prepared from **3e** in 25% yield (*Method A*). Colourless crystals, mp 213–217 °C (cyclohexane), IR: 3256, 2954, 2928, 2870, 1703, 1580, 1524, 1453, 1393, 1291, 1258, 1219, 1187, 1135, 1048, 1022, 950, 851, 781, 761, 668, 626, 517 cm^{-1}. Anal. Calcd (found) for $C_{31}H_{40}N_6OS_2$: C 64.55 (64.47); H 6.99 (7.06); N 14.57 (14.71). Positive-ion APCI-MS: *m*/*z* 577 $[M+H]^+$ (100%), 545 $[M+H-S]^+$; positive-ion APCI-MS/MS of *m*/*z* 577: 316 $[F+26+N]^+$ (100%), 302 $[F+26]^+$, 276 $[F]^+$, 259 $[F-NH_3]^+$. Negative-ion APCI-MS: *m*/*z* 575 $[M-H]^-$ (100%); negative-ion APCI-MS/MS of *m*/*z* 575: 274 $[F-2H]^-$ (100%).

*4.4.20. 1,3-Bis(2-(4-butyl-2,3-dihydro-3-methyl-1-phenyl-2-thioxo-1H-imidazol-5-yl)phenyl)urea (**6f**).* Compound was prepared from **3f** in 41% yield (*Method A*). Colourless crystals, mp 221–223 °C (cyclohexane), IR: 3318, 3065, 2956, 2929, 2861, 1706, 1598, 1580, 1518, 1501, 1449, 1391, 1363, 1287, 1256, 1190, 1111, 1073, 1028, 987, 831, 756, 694, 647, 537 cm^{-1}. Anal. Calcd (found) for $C_{41}H_{44}N_6OS_2$: C 70.25 (70.41); H 6.33 (6.41); N 11.99 (12.08). Positive-ion APCI-MS: *m*/*z* 701 $[M+H]^+$ (100%), 364 $[F+26]^+$; positive-ion APCI-MS/MS of *m*/*z* 701: 655 $[M+H-CSH_2]^+$, 378 $[F+26+N]^+$, 364 $[F+26]^+$ (100%), 338 $[F]^+$. Negative-ion APCI-MS: *m*/*z* 699 $[M-H]^-$ (100%); negative-ion APCI-MS/MS of *m*/*z* 699: 336 $[F-2H]^-$ (100%).

*4.4.21. 1,3-Bis(2-(2,3-dihydro-1,3-dimethyl-4-phenyl-2-thioxo-1H-imidazol-5-yl)phenyl)urea (**6g**).* Compound was prepared from **3g** in 24% yield (*Method A*). Colourless crystals, mp 298–301 °C (benzene), IR: 3440, 3262, 3058, 3030, 2926, 1710, 1604, 1578, 1521, 1451, 1390, 1288, 1262, 1228, 1179, 1142, 1075, 1047, 1023, 918, 856, 762, 699, 666, 645, 527 cm^{-1}. Anal. Calcd (found) for $C_{35}H_{32}N_6OS_2$: C 68.15 (68.23); H 5.23 (5.32); N 13.63 (13.58). Positive-ion APCI-MS: *m*/*z* 617 $[M+H]^+$ (100%); positive-ion APCI-MS/MS of *m*/*z* 617: 336 (100%) $[F+26+N]^+$, 322 $[F+26]^+$, 296 $[F]^+$. Negative-ion APCI-MS: *m*/*z* 615 $[M-H]^-$ (100%); negative-ion APCI-MS/MS of *m*/*z* 412: 294 (100%) $[F-2H]^-$, 221$[F-2H-CH_3NCS]^-$, 206.

*4.4.22. 1,3-Bis(2-(2,3-dihydro-1,4-diphenyl-3-methyl-2-thioxo-1H-imidazol-5-yl)phenyl)urea (**6h**).* Compound was prepared from **3h** in 65% yield (*Method A*). Colourless crystals, mp 310–317 °C (benzene–hexane), IR: 3415, 3338, 3061, 2923, 1705, 1598, 1579, 1524, 1498, 1448, 1385, 1359, 1291, 1247, 1190, 1113, 1077, 1023, 926, 821, 756, 737, 695, 663, 576, 547, 509 cm^{-1}. Anal. Calcd (found) for $C_{45}H_{36}N_6OS_2$: C 72.95 (72.80); H 4.90 (5.16); N 11.34 (11.22). Positive-ion APCI-MS: *m*/*z* 741 $[M+H]^+$ (100%), 384 $[F+26]^+$, 358 $[F]^+$; positive-ion APCI-MS/MS of *m*/*z* 741: 695, 398, 384 $[F+26]^+$ (100%), 358 $[F]^+$. Negative-ion APCI-MS: *m*/*z* 739 $[M-H]^-$ (100%), 409, 385, 371; negative-ion APCI-MS/MS of *m*/*z* 739: 356 $[F-2H]^-$ (100%).

*4.4.23. 1,3-Bis(2-(3,4-dibutyl-1-methyl-2-thioxo-2,3-dihydro-1H-imidazol-5-yl)phenyl)urea (**6i**).* Compound was prepared from **3i** in 23% yield (*Method A*). Colourless crystals, mp 183–188 °C (cyclohexane), IR: 3278, 3027, 3109, 3029, 2958, 2932, 2872, 1706, 1579, 1523, 1484, 1451, 1408, 1385, 1289, 1248, 1227, 1188, 1143, 1114, 1089, 1025, 950, 878, 765, 685, 628, 539 cm^{-1}. Anal. Calcd (found) for $C_{37}H_{52}N_6OS_2$: C 67.23 (67.45); H 7.93 (7.85); N 12.71 (12.58). Positive-ion APCI-MS: *m*/*z* 661.4 $[M+H]^+$ (100%); positive-ion APCI-MS/MS of *m*/*z* 661: 358 $[F+26+N]^+$ (100%), 344 $[F+26]^+$, 318 $[F]^+$. Negative-ion APCI-MS: *m*/*z* 659 $[M-H]^-$ (100%); negative-ion APCI-MS/MS of *m*/*z* 659: 316 $[F-2H]^-$ (100%).

*4.4.24. 1,3-Bis(2-(3,4-dibutyl-2,3-dihydro-1-phenyl-2-thioxo-1H-imidazol-5-yl)phenyl)urea (**6j**).* Compound was prepared from **3j**

(*Method A*) in 15% yield. Colourless crystals, mp 198–201 °C (cyclohexane), IR: 3457, 3309, 3068, 2958, 2931, 2871, 1706, 1638, 1598, 1580, 1523, 1500, 1449, 1405, 1372, 1286, 1247, 1222, 1187, 1132, 1112, 1075, 1027, 1004, 946, 836, 756, 694, 631, 541 cm^{-1}. Anal. Calcd (found) for $C_{47}H_{56}N_6OS_2$: C 71.90 (71.77); H 7.19 (7.26); N 10.70 (10.63). Positive-ion APCI-MS: *m/z* 785.4 $[M+H]^+$ (40%), 753 $[M+H-S]^+$, 406 $[F+26]^+$, 380 $[F]^+$ (100%); positive-ion APCI-MS/MS of *m/z* 785: 729 $[M+H-C_4H_8]^+$, 697 $[M+H-2\times C_3H_8]^+$, 462, 406 $[F+26]^+$ (100%), 380 $[F]^+$, 374 $[F+26-S]^+$, 350 $[F+26-C_4H_8]^+$. Negative-ion APCI-MS: *m/z* 783.5 $[M-H]^-$ (100%); negative-ion APCI-MS/MS of *m/z* 783: 378 $[F-2H]^-$ (100%).

*4.4.25. 1,3-Bis(2-(3-butyl-2,3-dihydro-1-methyl-4-phenyl-2-thioxo-1H-imidazol-5-yl)phenyl)urea (**6k**).* Compound was prepared from **3k** in 26% yield (*Method A*). Colourless crystals, mp 247–251 °C (ethyl acetate), IR: 3281, 3057, 2958, 2932, 2871, 1713, 1605, 1579, 1524, 1450, 1407, 1383, 1289, 1229, 1206, 1185, 1145, 1113, 1075, 1050, 1025, 858, 762, 702, 640, 562 cm^{-1}. Anal. Calcd (found) for $C_{41}H_{44}N_6OS_2$: C 70.25 (70.39); H 6.33 (6.51); N 11.99 (11.82). Positive-ion APCI-MS: *m/z* 701 $[M+H]^+$ (100%), 669 $[M+H-S]^+$; positive-ion APCI-MS/MS of *m/z* 701: 378 $[F+26+N]^+$ (100%), 364 $[F+26]^+$, 338 $[F]^+$, 330 $[F+26-H_2S]^+$, 322. Negative-ion APCI-MS: *m/z* 699 $[M-H]^-$ (100%); negative-ion APCI-MS/MS of *m/z* 699: 336 $[F-2H]^-$ (100%).

*4.4.26. 1,3-Bis(2-(1,4-diphenyl-3-butyl-2-thioxo-2,3-dihydro-1H-imidazol-5-yl)phenyl)urea (**6l**).* Compound was prepared from **3l** in 40% yield (*Method A*). Colourless crystals, mp 253–260 °C (benzene–hexane), IR: 3407, 3059, 2958, 2932, 2871, 1709, 1597, 1579, 1518, 1497, 1448, 1401, 1364, 1289, 1240, 1188, 1133, 1076, 1025, 945, 830, 755, 696, 656, 582 cm^{-1}. Anal. Calcd (found) for $C_{51}H_{48}N_6OS_2$: C 74.24 (74.15); H 5.86 (6.02); N 10.19 (10.06). Positive-ion APCI-MS: *m/z* 825 $[M+H]^+$ (100%), 793 $[M+H-S]^+$, 426 $[F+26]^+$, 400 $[F]^+$ (100%); positive-ion APCI-MS/MS of *m/z* 825: 791 $[M+H-H_2S]^+$, 770, 737 $[M+H-C_3H_8]^+$, 482 $[F+26+C_4H_8]^+$, 456, 426 $[F+26]^+$ (100%), 400 $[F]^+$. Negative-ion APCI-MS: *m/z* 823 $[M-H]^-$ (100%); negative-ion APCI-MS/MS of *m/z* 823: 398 $[F-2H]^-$ (100%).

*4.4.27. 1,3-Bis(2-(3-benzyl-4-butyl-2,3-dihydro-1-methyl-2-thioxo-1H-imidazol-5-yl)phenyl)urea (**6m**).* Compound was prepared from **3m** (*Method A*) in 17% yield. Colourless crystals, mp 144–150 °C (hexane), IR: 3459, 3292, 2955, 2929, 2869, 1708, 1579, 1519, 1453, 1402, 1391, 1357, 1289, 1193, 1091, 1026, 761, 731, 701 cm^{-1}. Anal. Calcd (found) for $C_{43}H_{48}N_6OS_2$: C 70.84 (70.81); H 6.64 (6.81); N 11.53 (11.50). Positive-ion APCI-MS: *m/z* 729 $[M+H]^+$ (75%), 697 $[M+H-S]^+$, 656 $[M+H-CH_3NCS]^+$, 432, 378 $[F+26]^+$, 352 $[F]^+$ (100%), 346 $[F+26-S]^+$, 320 $[F-S]^+$; positive-ion APCI-MS/MS of *m/z* 729: 638 $[M+H-C_6H_5CH_2]^+$, 605 $[M+H-C_6H_5CH_2-SH]^+$, 547 $[M+H-2\times C_6H_5CH_2]^+$, 428 $[M+H-NH_2CSNH_2]^+$, 392 $[F+26+N]^+$ (100%), 378 $[F+26]^+$, 352 $[F]^+$. Negative-ion APCI-MS: *m/z* 727 $[M-H]^-$ (100%), 365; negative-ion APCI-MS/MS of *m/z* 727: 350 $[F-2H]^-$ (100%).

*4.4.28. 1,3-Bis(2-(3-benzyl-4-butyl-2,3-dihydro-1-phenyl-2-thioxo-1H-imidazol-5-yl)phenyl)urea (**6n**).* Compound was prepared from **3n** (*Method A*) in 20% yield. Colourless crystals, mp 138–144 °C (benzene), IR: 3316, 3062, 3032, 2956, 2929, 2869, 1706, 1580, 1519, 1499, 1450, 1401, 1369, 1286, 1227, 1191, 1075, 1029, 959, 757, 701, 541 cm^{-1}. Anal. Calcd (found) for $C_{53}H_{52}N_6OS_2$: C 74.61 (74.65); H 6.14 (6.23); N 9.85 (9.72). Positive-ion APCI-MS: *m/z* 853 $[M+H]^+$ (11%), 440 $[F+26]^+$, 414 $[F]^+$ (100%), 408 $[F+26-S]^+$, 382 $[F-S]^+$; positive-ion APCI-MS/MS of *m/z* 853: 762 $[M+H-C_6H_5CH_2]^+$, 729 $[M+H-C_6H_5CH_2-SH]^+$, 671 $[M+H-2\times C_6H_5CH_2]^+$ (100%), 530, 440 $[F+26]^+$, 414 $[F]^+$, 349, 278 $[M+H-C_6H_5NCSH]^+$. Negative-ion APCI-MS: *m/z* 851 $[M-H]^-$ (100%), 427; negative-ion APCI-MS/MS of *m/z* 851: 412 $[F-2H]^-$, 412 $[F-2H-C_6H_5CH_2]^-$.

*4.4.29. 1,3-Bis(2-(3-benzyl-2,3-dihydro-1-methyl-4-phenyl-2-thioxo-1H-imidazol-5-yl)phenyl)urea (**6o**).* Compound was prepared from **3o** in 45% (*Method A*). Colourless crystals, mp 252–257 °C (benzene–hexane), IR: 3395, 3277, 3060, 3030, 2925, 2851, 1710, 1605, 1579, 1523, 1497, 1449, 1402, 1384, 1290, 1228, 1203, 1108, 1077, 1049, 1025, 968, 922, 859, 763, 738, 700, 640, 589, 549 cm^{-1}. Anal. Calcd (found) for $C_{47}H_{40}N_6OS_2$: C 73.41 (73.27); H 5.24 (5.39); N 10.93 (10.78). Positive-ion APCI-MS: *m/z* 769 $[M+H]^+$ (100%), 737 $[M+H-O]^+$, 398 $[F+26]^+$, 372 $[F]^+$, 340; positive-ion APCI-MS/MS of *m/z* 769: 678 $[M+H-C_6H_5CH_2]^+$, 645, 587 $[M+H-2\times C_6H_5CH_2]^+$, 474, 448, 412 $[F+26+N]^+$ (100%), 398 $[F+26]^+$, 372 $[F]^+$. Negative-ion APCI-MS: *m/z* 767 $[M-H]^-$ (100%), 412, 398, 385; negative-ion APCI-MS/MS of *m/z* 767: 370 $[F-H]^-$ (100%).

*4.4.30. 1,3-Bis(2-(2,3-dihydro-1,4-diphenyl-3-benzyl-2-thioxo-1H-imidazol-5-yl)phenyl)urea (**6p**).* Compound was prepared from **3p** in yield 37% (*Method A*). Colourless crystals, mp 262–265 °C (benzene–hexane), IR: 3409, 3359, 3060, 3032, 2925, 2853, 1711, 1597, 1580, 1519, 1496, 1449, 1397, 1366, 1287, 1264, 1231, 1187, 1077, 1027, 960, 921, 839, 791, 760, 699, 655, 595, 574, 548, 513 cm^{-1}. Anal. Calcd (found) for $C_{57}H_{44}N_6OS_2$: C 76.65 (76.47); H 4.97 (5.09); N 9.41 (9.30). Positive-ion APCI-MS: *m/z* 893 $[M+H]^+$ (86%), 861 $[M+H-S]^+$, 460 $[F+26]^+$ (68%), 434 $[F]^+$ (100%), 402; positive-ion APCI-MS/MS of *m/z* 893: 802 $[M+H-C_6H_5CH_2]^+$, 769, 711 $[M+H-2\times C_6H_5CH_2]^+$ (100%), 680, 460 $[F+26]^+$, 434 $[F]^+$, 368, 343. Negative-ion APCI-MS: *m/z* 891 $[M-H]^-$ (100%), 474, 447, 432 $[F-2H]^-$; negative-ion APCI-MS/MS of *m/z* 891: 432 $[F-2H]^-$ (100%), 341.

*4.4.31. N(2-(5-Butyl-2,3-dihydro-3-methyl-2-thioxo-1H-imidazol-4-yl)phenyl)acetamide (**7a**).* Compound was prepared from **3a** in yield 3% (*Method A*). Yellow crystals, mp 92–102 °C (hexane), IR: 3110, 2955, 2930, 2872, 1670, 1602, 1581, 1524, 1496, 1450, 1386, 1298, 1241, 1135, 1036, 1014, 929, 762, 680, 656, 601, 550, 531 cm^{-1}. Anal. Calcd (found) for $C_{16}H_{21}N_3OS$: C 63.33 (63.55); H 6.98 (7.25); N 13.85 (13.71). Positive-ion APCI-MS: *m/z* 304 $[M+H]^+$ (100%); positive-ion APCI-MS/MS of *m/z* 304: 262 $[M+H-NCO]^+$ (100%), 274. Negative-ion APCI-MS: *m/z* 302 $[M-H]^-$ (100%), 288; negative-ion APCI-MS/MS of *m/z* 302: 260 $[M-H-NCO]^-$ (100%).

*4.4.32. N(2-(5-Butyl-2,3-dihydro-1-methyl-3-phenyl-2-thioxo-1H-imidazol-4-yl)phenyl)acetamide (**7f**).* Compound was prepared from **3f** in 6% yield (*Method A*). Beige crystals, mp 180–187 °C (cyclohexane), IR: 3328, 3059, 2952, 2930, 2869, 1668, 1580, 1520, 1501, 1469, 1448, 1382, 1353, 1297, 1252, 1105, 1071, 767, 757, 695, 591, 536 cm^{-1}. Anal. Calcd (found) for $C_{22}H_{25}N_3OS$: C 69.62 (69.55); H 6.64 (6.85); N (11.07, 11.21). Positive-ion APCI-MS: *m/z* 380 $[M+H]^+$ (100%), 348 $[M+H-S]^+$; positive-ion APCI-MS/MS of *m/z* 380: 338 $[M+H-NCO]^+$ (100%). Negative-ion APCI-MS: *m/z* 378 $[M-H]^-$ (100%); negative-ion APCI-MS/MS of *m/z* 378: 360 $[M-H-H_2O]^-$, 336 $[M-H-NCO]^-$, 305 $[M-H-CH_3NCS]^-$ (100%), 263 $[M-H-C_4H_9NCS]^-$.

*4.4.33. N(2-(2,3-Dihydro-1,3-dimethyl-5-phenyl-2-thioxo-1H-imidazol-4-yl)phenyl)acetamide (**7g**).* Compound was prepared from **3g** in 10% yield (*Method A*). Colourless crystals, mp 248–249 °C (ethyl acetate–hexane), IR: 3362, 3050, 2983, 2946, 1686, 1605, 1581, 1521, 1474, 1445, 1387, 1301, 1243, 1206, 1185, 1139, 1073, 1049, 1027, 924, 859, 766, 747, 706, 673, 634, 583, 536 cm^{-1}. Anal. Calcd (found) for $C_{19}H_{19}N_3OS$: C 67.63 (67.75); H 5.86 (5.95); N 12.45 (12.62). Positive-ion APCI-MS: *m/z* 338 $[M+H]^+$ (100%); positive-ion APCI-MS/MS of *m/z* 338: 296 $[M+H-C_2H_2O]^+$ (100%). Negative-ion APCI-MS: *m/z* 336 $[M-H]^-$ (100%); negative-ion APCI-MS/MS of *m/z* 336: 318 $[M-H-H_2O]^-$, 294 $[M-H-C_2H_2O]^-$,

245 $[M-H-C_6H_5CH_2]^-$, 221 $[M-H-CH_3NCS-C_2H_2O]^-$ (100%), 206 $[M-H-CH_3NCS-C_2H_2O-CH_3]^-$.

*4.4.34. N(2-(2,3-Dihydro-3,5-diphenyl-1-methyl-2-thioxo-1H-imidazol-4-yl)phenyl)acetamide (**7h**).* Compound was prepared from **3h** in 4% yield (*Method A*). Colourless crystals, mp 252–257 °C (benzene–hexane), IR: 3356, 3257, 3051, 2923, 1693, 1678, 1660, 1598, 1579, 1524, 1499, 1449, 1382, 1357, 1298, 1257, 1158, 1113, 1075, 1023, 925, 820, 791, 758, 737, 696, 576, 550, 533 cm^{-1}. Anal. Calcd (found) for $C_{24}H_{21}N_3OS$: C 72.15 (69.98); H 5.30 (5.48); N 10.52 (10.43). Positive-ion APCI-MS: *m/z* 400 $[M+H]^+$ (100%); positive-ion APCI-MS/MS of *m/z* 400: 384 $[M+H-O]^+$, 358 $[M+H-NCO]^+$ (100%). Negative-ion APCI-MS: *m/z* 398 $[M-H]^-$ (100%); negative-ion APCI-MS/MS of *m/z* 398: 356 $[M-H-NCO]^-$, 325 $[M-H-CH_3NCS]^-$ (100%), 282 $[M-H-CH_3NCS-NHCO]^-$.

*4.4.35. N(2-(1-Butyl-2,3-dihydro-3,5-diphenyl-2-thioxo-1H-imidazol-4-yl)phenyl)acetamide (**7l**).* Compound was prepared from **3l** in 4% yield (*Method A*). Colourless crystals, mp 239–242 °C, IR: 3258, 3050, 2958, 2932, 2871, 1692, 1675, 1659, 1598, 1579, 1524, 1499, 1448, 1402, 1369, 1300, 1260, 1241, 1134, 1074, 1026, 948, 827, 789, 757, 695, 655, 581, 550, 535 cm^{-1}. Anal. Calcd (found) for $C_{27}H_{27}N_3OS$: C 73.44 (73.23); H 6.16 (6.24); N 9.52 (9.49). Positive-ion APCI-MS: *m/z* 442 $[M+H]^+$ (100%); positive-ion APCI-MS/MS of *m/z* 442: 400 $[M+H-C_2H_2O]^+$ (100%), 386 $[M+H-C_4H_8]^+$, 344 $[M+H-C_2H_2O-C_4H_8]^+$. Negative-ion APCI-MS: *m/z* 440 $[M-H]^-$ (100%); negative-ion APCI-MS/MS of *m/z* 440: 398 $[M-H-C_2H_2O]^-$ (100%), 384 $[M-H-C_4H_8]^-$, 375, 325 $[M-H-C_4H_9NCS]^-$.

*4.4.36. N(2-(1-Benzyl-5-butyl-2,3-dihydro-3-phenyl-2-thioxo-1H-imidazol-4-yl)phenyl)acetamide (**7n**).* Compound was prepared from **3n** (*Method A*) in 8% yield. Colourless crystals, mp 166–171 °C (ethyl acetate–hexane), IR: 3288, 2953, 2930, 2867, 1678, 1658, 1599, 1578, 1518, 1501, 1478, 1450, 1401, 1368, 1351, 1297, 1270, 1252, 1196, 1162, 1109, 1075, 1030, 964, 848, 758, 724, 700, 641, 604, 557, 536 cm^{-1}. Anal. Calcd (found) for $C_{28}H_{29}N_3OS$: C 73.81 (73.75); H 6.42 (6.53); N 9.22 (9.17). Positive-ion APCI-MS: *m/z* 456 $[M+H]^+$ (100%), 424 $[M+H-S]^+$; positive-ion APCI-MS/MS of *m/z* 456: 414 $[M+H-NCO]^+$, 365 $[M+H-C_6H_5CH_2]^+$, 336 $[M+H-C_6H_5CH_2-CH_3N]^+$, 323 $[M+H-C_6H_5CH_2-NCO]^+$, 294. Negative-ion APCI-MS: *m/z* 454 $[M-H]^-$ (100%); negative-ion APCI-MS/MS of *m/z* 454: 412 $[M-H-NCO]^-$, 321 $[M-H-C_6H_5CH_2-NCO]^-$, 305 $[M-H-C_6H_5CH_2NCS]^-$ (100%), 263 $[M-H-C_6H_5CH_2NCS-NCO]^-$.

*4.4.37. N(2-(1-Benzyl-2,3-dihydro-3-methyl-5-phenyl-2-thioxo-1H-imidazol-4-yl)phenyl)acetamide (**7o**).* Compound was prepared from **3o** in 1% yield (*Method A*). Colourless crystals, mp 96–105 °C (benzene–hexane), IR: 3415, 3330, 3060, 3031, 2946, 2930, 1691, 1605, 1581, 1521, 1496, 1477, 1447, 1402, 1383, 1299, 1249, 1209, 1158, 1110, 1076, 1025, 967, 923, 864, 765, 736, 701, 681, 642, 587, 553, 544 cm^{-1}. Anal. Calcd (found) for $C_{25}H_{23}N_3OS$: C 72.61 (72.73); H 5.61 (5.72); N 10.16 (10.23). Positive-ion APCI-MS: *m/z* 414 $[M+H]^+$ (100%); positive-ion APCI-MS/MS of *m/z* 414: 372 $[M+H-NCO]^+$ (100%), 323 $[M+H-C_6H_5CH_2]^+$. Negative-ion APCI-MS: *m/z* 412 $[M-H]^-$ (100%); negative-ion APCI-MS/MS of *m/z* 412: 321 $[M-H-C_6H_5CH_2]^-$ (100%), 278 $[M-H-C_6H_5CH_2NHCO]^-$.

*4.4.38. Ethyl 2-(2,3-dihydro-3-methyl-5-phenyl-2-thioxo-1H-imidazol-4-yl)phenylcarbamate (**8c**).* Compound was prepared from **3c** in 74% yield (*Method C*). Colourless crystals, mp 232–238 °C (ethyl acetate–hexane), IR: 3274, 3102, 2975, 2940, 1720, 1698, 1637, 1580, 1528, 1493, 1475, 1455, 1379, 1338, 1294, 1283, 1240, 1170, 1135, 1094, 1065, 1047, 1024, 963, 916, 881, 835, 787, 771, 744, 699, 679, 615, 559, 533 cm^{-1}. Anal. Calcd (found) for $C_{19}H_{19}N_3O_2S$: C 64.57 (64.65); H 5.42 (5.51); N 11.89 (11.76). Positive-ion APCI-MS: *m/z* 354 $[M+H]^+$ (100%), 322; positive-ion APCI-MS/MS of *m/z* 354: 326 $[M+H-CO]^+$, 308 $[M+H-H_2O-CO]^+$ (100%), 282. Negative-ion APCI-MS: *m/z* 352 $[M-H]^-$ (100%), 306 $[M-H-H_2O-CO]^-$; negative-ion APCI-MS/MS of *m/z* 352: 308 $[M-H-C_3H_8]^-$, 306 $[M-H-H_2O-CO]^-$ (100%).

*4.4.39. Ethyl 2-(1-butyl-2,3-dihydro-3-methyl-5-phenyl-2-thioxo-1H-imidazol-4-yl)phenylcarbamate (**8k**).* Compound was prepared from **3k** in 58% yield (*Method C*). Colourless crystals, mp 94–100 °C (hexane), IR: 3291, 2953, 2927, 2868, 1714, 1696, 1581, 1525, 1499, 1455, 1404, 1381, 1296, 1229, 1143, 1115, 1095, 1068, 1048, 1024, 947, 861, 844, 767, 728, 704, 638, 558, 504 cm^{-1}. Anal. Calcd (found) for $C_{23}H_{27}N_3O_2S$: C 67.45 (67.37); H 6.65 (6.81); N 10.26 (10.32). Positive-ion APCI-MS: *m/z* 410 $[M+H]^+$ (100%), 364 $[M+H-CO-H_2O]^+$, 338 $[M+H-COOC_2H_4]^+$; positive-ion APCI-MS/MS of *m/z* 410: 382 $[M+H-CO]^+$, 364 $[M+H-CO-H_2O]^+$ (100%), 338 $[M+H-COOC_2H_4]^+$. Negative-ion APCI-MS: *m/z* 408 $[M-H]^-$ (100%); negative-ion APCI-MS/MS of *m/z* 408: 362 $[M-H-CO-H_2O]^-$ (100%).

*4.4.40. [2-(1-Butyl-3,5-diphenyl-2-thioxo-2,3-dihydro-1H-imidazo-4-yl)-phenyl]-carbamic acid ethyl ester (**8l**).* Compound was prepared from **3l** in 24% yield (*Method A*). Colourless crystals, mp 151–153 °C (benzene–hexane), IR: 3346, 3061, 2960, 2932, 2872, 1733, 1698, 1585, 1518, 1497, 1450, 1401, 1362, 1300, 1224, 1208, 1171, 1134, 1096, 1059, 1026, 926, 838, 820, 785, 761, 751, 695, 655, 630, 581, 541, 521 cm^{-1}. Anal. Calcd (found) for $C_{28}H_{29}N_3O_2S$: C 71.31 (71.43); H 6.20 (6.33); N 8.91 (8.78). Positive-ion APCI-MS: *m/z* 472 $[M+H]^+$ (100%), 440 $[M+H-S]^+$, 426 $[M+H-H_2O-CO]^+$; positive-ion APCI-MS/MS of *m/z* 472: 444 $[M+H-CO]^+$, 438 $[M+H-H_2S]^+$, 426 $[M+H-H_2O-CO]^+$, 400, 370. Negative-ion APCI-MS: *m/z* 470 $[M-H]^-$ (100%); negative-ion APCI-MS/MS of *m/z* 470: 424 $[M-H-H_2O-CO]^-$ (100%), 398, 309 $[M-H-C_6H_5NCO-NCO]^-$.

4.5. General procedures for acylation of compounds 4

4.5.1. Acetylation. To the solution of compound **4** (0.2 mmol) in pyridine (1 mL), acetic anhydride (1 mL) was added at rt. After 24 h, the solution was evaporated to dryness and the residue was recrystallized. The following compounds, identical in all respects to those prepared from **3** by *Method A*, were obtained: **7g** (yield 63%), **7h** (yield 80%), **7l** (yield 83%) and **7n** (yield 72%).

4.5.2. Ethoxycarbonylation. To the solution of compound **4** (0.2 mmol) in pyridine (1 mL), ethyl chloroformate (0.3 mL, 0.315 mmol) was added at rt. After 4 h, the solution was evaporated to dryness and the residue was crystallized from benzene–hexane. The following compounds, identical in all respects to those prepared from **3** by *Method C*, were obtained: **8c** (yield 53%), **8l** (yield 58%).

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Supplementary data

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