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### NOVEL PREPARATION OF N'-ARYLTHIOCARBAMOYL-N,N-DIALKYLAMIDINES AND THEIR SYNTHETIC UTILITIES

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**Abstract:** Treatment of 5-(arylimino)-4-(dialkylamino)-5*H*-1,2,3-dithiazoles (2) with NaOH in aqueous EtOH at room temperature gave N'-arylthiocarbamoyl-N,N-dialkylamidines (3) in good to excellent yields. The reaction of 3 with sulfur monochloride, thiophosgene, thionyl chloride, sulfuryl chloride, N-phenylimidoyl dichloride, and phthaloyl chloride in CH<sub>2</sub>Cl<sub>2</sub> gave 2, 5-(arylimino)-4-(dialkylamino)- $\Delta^3$ -thiazoline-2-thiones (5), 5-(arylimino)-4-(dialkylamino)-5*H*-2, oxo-1, 2, 3-dithiazoles (6), 5-(arylimino)-4-(dialkylamino)-5*H*-2, 2-dioxo-1, 2, 3-dithiazoles (7), 5-(arylimino)-4-(dialkylamino)-2, 5-benzothiazocine-1, 6-diones (10) as major products, respectively. Copyright © 1996 Elsevier Science Ltd

Previously we reported synthesis of 5-(arylimino)-4-(dialkylamino)-5H-1,2,3-dithiazoles (2) from the reactions of 5-(arylimino)-4-chloro-5H-1,2,3-dithiazoles (1) with some dialkylamines in  $CH_2Cl_2$  at room



temperature.<sup>1</sup> Compound 1 is a kind of heteroaromatic compound having  $6\pi$  electrons but is susceptible to a nucleophilic attack, particularly at C-4, C-5, S-1 and S-2 positions. The reactivities of compound 1 to nucleophiles may be partly attributable to the presence of chlorine atom at C-4 because chlorine atom is readily expelled as a chloride ion during the reaction to generate a cyano functionality. Since an amino group is generally known to be a poorer leaving group than a chlorine atom, one might expect different reactivities from compound 2 compared with compound 1. We found that treatment of compound 2 with hydroxide base in aqueous EtOH solution gave N'-arylthiocarbamoyl-N,N-dialkylamidines (3) which reacted with various electrophiles to give new heterocyclic compounds. The results obtained are described herein.

## **RESULTS AND DISCUSSION**

*N'-Arylthiocarbamoyl-N,N-dialkylamidines* (3). Treatment of compound 2 with NaOH in aqueous EtOH at room temperature for a few hours afforded reddish *N'*-arylthiocarbamoyl-*N,N*-dialkylamidines (3) in good to excellent yields. Yields of 3 are summarized in Table 1.



Table 1. Yields of N'-Arylthiocarbamoyl-N, N-dialkylamidines (3)

Compound	Х	Y	R	Yield * (%)
3a	4-NO <sub>2</sub>	Н	Et	70
3b	4-NO <sub>2</sub>	н	<i>n</i> -Pr	99
3c	4-NO <sub>2</sub>	н	<i>n</i> -Bu	83
3d	4-NO <sub>2</sub>	н	Allyi	99
3e	4-NO <sub>2</sub>	2-Me	<i>n</i> -Pr	69
3f	4-Cl	н	<i>n</i> -Pr	77
3g	4-Br	н	<i>n</i> -Pr	82
3h	4-Me	Н	<i>n</i> -Pr	77
3i	4-MeO	н	<i>n</i> -Pr	76
3ј	4-MeO	н	<i>n</i> -Bu	79
3k	2-Cl	5-NO <sub>2</sub>	<i>n</i> -Pr	88
31	3-NO2	н	Et	68
3m	3-NO <sub>2</sub>	Н	<i>n-</i> Pr	79
3n	3-NO2	4-Cl	<i>n-</i> Pr	74
30	3-NO <sub>2</sub>	4-Cl	<i>n-</i> Bu	77

\* Isolated yield.

The formation of 3 from 2 in good to excellent yields is in contrast with that of N-arylcyanothioformami-

dines in low yields from 1 under the same conditions. Furthermore for the latter the separation of N-arylcyanothioformamides from the reaction mixtures is sometimes troublesome and tedious.<sup>2</sup>

The structures of 3 were determined on the basis of the spectroscopic and mass spectral data and elemental analyses. <sup>1</sup>H NMR spectra of compounds 3 show two singlets at 8.0-8.4 and 8.5-9.1 ppm assignable to imino and amino protons, respectively which are consistent with the results reported in the literature.<sup>3</sup> <sup>13</sup>C NMR spectrum of compound 3c shows six peaks at 122.51, 124.17, 139.63, 158.92, 164.15, and 175.95 ppm due to four aromatic carbons, a carbon atom bonded to sulfur atom, and an imino carbon atom in addition to eight peaks due to two butyl groups. Although the last two peaks, i.e. 175.95 and 164.15 ppm may be assignable to thione and imino carbons, respectively, in view of the literature values in which thione carbon atoms<sup>4</sup> and imino carbon atoms of amidines in CDCl<sub>3</sub> <sup>5</sup> absorb energy around 180 and 165 ppm, respectively, one cannot rule out the possibility of an equilibrium mixture of two tautomeric forms. IR spectra show a NH stretching absorption between 3192 and 3280 cm<sup>-1</sup> and a characteristic absorption of C=N double bond between 1642 and 1648 cm<sup>-1</sup>, which is in good agreement with the result observed from amidine derivatives.<sup>6</sup>

Although a variety of amidines have been reported,<sup>7</sup> amidines with N'-arylthiocarbamoyl group, to the best of our knowledge, have never appeared in the literature.

Of two geometrical isomers of 3, E-isomer having an imino N-H bond trans to C-NR<sub>2</sub> group is expected to be predominant in solution because of avoiding the steric overcrowding of the N-H and N-alkyl groups in view of the result obtained from N,N-dimethylbenzamidine.<sup>8</sup>

The formation of compounds 3 might be explained by a nucleophilic attack of hydroxide ion to S-2 to cleave a bond between S-1 and S-2 rather than S-2 and nitrogen atom, giving an intermediate 4 because of the presence of dialkylamino group at C-4 which is known as a poor leaving group. This is in contrast with the formations of dialkylamino disulfides<sup>1</sup> and dithiomethylenephosphoranes<sup>9</sup> from the reactions of 1 having a good leaving chlorine atom at C-4, with dialkylamines and stable phosphoranes, respectively. Rapid extrusion of SO, followed by protonation gives compounds 3 (Scheme 1).



Scheme 1

The synthetic potentialities of 3 are demonstrated in the reactions with various electrophiles as exemplified in Scheme 2.



Scheme 2

5-(Arylimino)-4-(dialkylamino)-5H-1,2,3-dithiazoles (2). Treatment of 3a (X = 4-NO<sub>2</sub>, Y = H, R = Et) with 1 molar equivalent of sulfur dichloride (SCl<sub>2</sub>) in the presence of pyridine (2 molar equiv) in CH<sub>2</sub>Cl<sub>2</sub> at room temperature gave 2a (X = 4-NO<sub>2</sub>, Y = H, R = Et) in 80 % yield. The reverse formation of 2a from 3a is exactly analogous to the formation of 1 by treatment of *N*-arylcyanothioformamides with SCl<sub>2</sub> under the same conditions. Similarly the reactions of 3 with 1 molar equivalent of sulfur monochloride (S<sub>2</sub>Cl<sub>2</sub>) under the same conditions gave 2. Yields of 2 obtained from the reaction of 3 with S<sub>2</sub>Cl<sub>2</sub> are summarized in Table 2.

5-(Arylimino)-4-(dialkylamino)- $\Delta^3$ -thiazoline-2-thiones (5). The reactions of 3 with 1 molar equivalent of thiophosgene (S=CCl<sub>2</sub>) in the presence of pyridine (2 molar equiv) in CH<sub>2</sub>Cl<sub>2</sub> at room temperature gave 5-(arylimino)-4-(dialkylamino)- $\Delta^3$ -thiazoline-2-thiones (5). Yields of 5 are summarized in Table 3.

All of the compounds 5 have never been reported. Cyclization of 3 by the reaction with thiophosgene is a new useful method for the synthesis of thiazoline-2-thiones, although some thiazoline-2-thiones have been prepared by the reaction of either ketones or aldehydes with sulfur in  $NH_3^{10}$  and the reaction of carbon disulfide with aziridine having appropriate substituents.<sup>11</sup>

Compound	x	Y	R	Yield * (%)
2a	4-NO2	Н	Et	80 <sup>6</sup>
2b	4-NO <sub>2</sub>	Н	<i>n</i> -Pr	72
2c	4-NO <sub>2</sub>	Н	<i>n-</i> Bu	65
2d	4-NO2	Н	Aliyi	50
2e	4-NO <sub>2</sub>	2-Me	<i>n</i> -Pr	81
2f	4-Cl	н	<i>n</i> -Pr	84
2g	4-Br	н	<i>n</i> -Pr	57
2h	4-Me	н	<i>n</i> -Pr	70
2i	4-MeO	н	<i>n</i> -Pr	44
2j	3-NO <sub>2</sub>	н	Et	77
2k	3-NO <sub>2</sub>	н	<i>n</i> -Pr	68

# Table 2. Yields of 5-(Arylimino)-4-(dialkylamino)-5H-1,2,3-dithiazoles (2)

<sup>a</sup> Isolated yield. <sup>b</sup> Yield from the reaction of 3a with SCl<sub>2</sub>.

# Table 3. Yields of 5-(Arylimino)-4-(dialkylamino)- $\Delta^3$ -thiazoline-2-thiones (5)

Compound	Х	Y	R	Yield * (%)
5a	4-NO2	н	Et	92
5b	4-NO <sub>2</sub>	н	<i>n</i> -Pr	82
5c	4-NO2	Н	<i>n</i> -Bu	97
5d	4-NO <sub>2</sub>	Н	Allyl	93
5e	4-Cl	Н	<i>n</i> -Pr	74
5f	3-NO <sub>2</sub>	Н	Et	95
5g	3-NO <sub>2</sub>	Н	<i>n</i> -Pr	71
5h	3-NO2	4-Cl	<i>n</i> -Pr	84

\* Isolated yield.

5-(Arylimino)-4-(dialkylamino)-5H-2-oxo-1,2,3-dithiazoles (6). The reaction of 3c with 1 molar equivalent of thionyl chloride (SOCl<sub>2</sub>) in the presence of pyridine (2 molar equiv) in CH<sub>2</sub>Cl<sub>2</sub> at room temperature gave 4-(di-n-butylamino)-5-(4-nitrophenylimino)-5H-2-oxo-1,2,3-dithiazole (6c) (X = 4-NO<sub>2</sub>, Y = H, R = n-Pr) in 42% yield along with the recovery of 3c in 55% yield, whereas 78% and 10% yields of the corresponding compounds were obtained by employing 2 molar equivalents of SOCl<sub>2</sub> under the same conditions. Therefore, 2 molar equivalents of SOCl<sub>2</sub> were used through the reactions. Yields of 6 are summarized in Table 4.

Compound	x	Y	R	Yield * (%)
6a	4-NO <sub>2</sub>	Н	Et	42 (44)
6b	4-NO <sub>2</sub>	Н	<i>n</i> -Pr	67 (61)
6c	4-NO <sub>2</sub>	Н	<i>n-</i> Bu	78 (62)
6d	4-NO <sub>2</sub>	н	Allyi	61
6e	4-Cl	Н	<i>n</i> -Pr	55 (56)
6f	4-Br	н	<i>n</i> -Pr	54
6g	4-Me	Н	<i>n</i> -Pr	24 (46)
6h	4-MeO	Н	<i>n</i> -Pr	21 (30)
6i	4-MeO	Н	<i>n</i> -Bu	(52)
6j	3-NO <sub>2</sub>	Н	Et	47 (45)
6k	3-NO <sub>2</sub>	н	<i>n</i> -Pr	55 (52)

### Table 4. Yields of 5-(Arylimino)-4-(dialkylamino)-5H-2-oxo-1,2,3-dithiazoles (6)

\* Isolated yield. Numbers in the parenthesis represent yields of 5 from the oxidation of selected 2 with m-CPBA (1 molar equiv).

The structures of compounds 6 were determined on the basis of the spectroscopic data and elemental analyses. IR spectra of 6 show a characteristic band of >S=O between 1130 and 1136 cm<sup>-1</sup>. <sup>1</sup>H NMR spectra of compounds 6 show two triplets assignable to two methylene groups bonded directly to nitrogen at C-4 at 3.8 and 3.6 ppm, respectively. Since only one triplet is observed from the corresponding methylene groups of compounds 2 and 5-(arylimino)-4-(dialkylamino)-5H-2,2-dioxo-1,2,3-dithiazoles (7) (vide infra), configuration of >S=O functionality in compounds 6 is considered to cause the dialkyl groups on nitrogen at C-4 to be magnetically nonequivalent.

Compounds 6 were also prepared by a direct oxidation of compounds 2 with 1 molar equivalent of m-CPBA in CH<sub>2</sub>Cl<sub>2</sub> at room temperature. The yields of 6 thus obtained are listed in the parenthesis in Table 4. Table 4 shows that the yields of 6 obtained from two independent routes (6a, 6b, 6c, 6e, 6j, 6k) are comparable for compounds 3 having an electron-withdrawing group at N'-aryl group, whereas better yields are obtained from a direct oxidation of 2 having electron-donating group at N'-aryl group (6g, 6h).

Compounds 6 are stable enough to be characterized by the spectroscopic method but decomposition occurs slowly to give quantitatively the corresponding precursors, compounds 3, at room temperature or in the refrigerator and in the descicator. This result presumably indicates that oxygen atom is attached to S-2 rather than S-1 of compounds 6 without oxygen transfer. It is noteworthy that treatment of compound 1 (X = Y = H) with *m*-CPBA (1 molar equiv) in CH<sub>2</sub>Cl<sub>2</sub> at room temperature for 17 h resulted in a bright yellow solution containing yellow solids which underwent decomposition to give a mixture of unknown compounds and white fume upon removal of the solvent in reduced pressure.

5-(Arylimino)-4-(dialkylamino)-5H-2, 2-dioxo-dithiazoles (7). The reaction of 3c with 1 molar equivalent of sulfuryl chloride (SO<sub>2</sub>Cl<sub>2</sub>) in the presence of pyridine (2 molar equiv) in CH<sub>2</sub>Cl<sub>2</sub> at room temperature for 3 days gave a complex mixture from which 4-(di-n-butylamino)-5-(4-nitrophenylimino)-5H-2,2-dioxo-1,2,3dithiazole (7a) (X = 4-NO<sub>2</sub>, Y = H, R = n-Bu) and unreacted starting material 3c were isolated in 14% and 43% yields, respectively. Both of the yields, 7a and 3c, decreased to 9% and 15%, respectively, when 2 molar equivalents of SO<sub>2</sub>Cl<sub>2</sub> was used under the same conditions. Similarly 7b (X = 3-NO<sub>2</sub>, Y = H, R = n-Pr) was obtained in 11% and 4% yields from the reactions of 3m with 1 and 1.5 molar equivalents of SO<sub>2</sub>Cl<sub>2</sub>, respectively.

As mentioned above two pairs of methylene protons bonded directly to nitrogen at C-4 of compounds 7 appears as a triplet, which is in contrast with two triplets observed by the corresponding protons of compounds 6.

5-(Arylimino)-4-(dialkylamino)-2-(phenylimino)- $\Delta^3$ -thiazolines (8). The reactions of 3 with Nphenylimidoyl dichloride (4 molar equiv) in CH<sub>2</sub>Cl<sub>2</sub> in the presence of pyridine (2 molar equiv) gave yellowish 5-(arylimino)-4-(dialkylamino)-2-(phenylimino)- $\Delta^3$ -thiazolines (8) as major products and reddish 1-aryl-4-(dialkylamino)-2-(phenylimino)-3-imidazoline-5-thiones (9) as minor products. Yields of 8 and 9 are summarized in Table 5.

The characteristic <sup>1</sup>H NMR spectra of compounds 8 shows two triplets exhibited by two pairs of methylene protons on nitrogen atom at 4.00 to 4.06 and 3.69 to 3.77 ppm in which the difference of chemical shift is 0.28 to 0.37 ppm, whereas those of compound 9 show the corresponding peaks at 4.25 to 4.35 and 3.61 to 3.81 ppm with the difference of chemical shift of 0.44 to 0.72 ppm. Differentiation between the structural isomers 8 and 9 simply based on <sup>1</sup>H NMR spectra was difficult. This difficulty was solved by comparison of <sup>13</sup>C NMR spectra of compound 8d with that of 9d. That is, compound 8d shows three singlets at 157, 159, and 162 ppm assigned to three imino carbons, C-2, C-4, and C-5.

Entry	х	Y	R	Yield <sup>a</sup> (%)
				8
a	4-NO2	н	<i>n</i> -Pr	93 <sup>b</sup>
b	4-NO <sub>2</sub>	н	<i>n</i> -Bu	91
с	4-NO <sub>2</sub>	2-Me	<i>n</i> -Pr	83 <sup>6</sup>
d	4-Cl	н	<i>n</i> -Pr	70

Η

Н

Н

Н

Н

Table 5. Yields of 5-(Arylimine	>)-4-(dialkylamino)-2-(phenylimino)-2	<sup>3</sup> -thiazolines (8) and 1-Aryl-4-
(dialkylami	no)-2-(phenylimino)-3-imidazoline-5-	thiones (9)

9

5

9 10

8

10

12

14

10

10

<sup>a</sup> Isolated yield. <sup>b</sup> The reactions were run at room temperature otherwise reflux temperature.

n-Pr

n-Pr

n-Pr

n-Bu

n-Pr

70

58

56

64<sup>b</sup>

70

The first two peaks might be due to C-2 and C-4. The peak appeared at 162 ppm is assigned to C-5 in view of  $^{13}$ C NMR spectrum of compound 9d exhibiting three singlets at 156, 160, and 183 ppm. The first two peaks are assigned to two imino carbons, C-2 and C-4 as in compound 8d. A singlet at 183 ppm, not observed from 7d, can be assignable to C-5, a thione carbon, which is consistent with the literature values.<sup>4</sup>



3-(Arylimino)-4-(dialkylamino)-2,5-benzothiazocine-1,6-diones (10). The synthetic potentiality of 3 for the formation of cyclic compounds other than five membered ring was demonstrated by the reaction with phthaloyl chloride in the presence of pyridine (2 molar equiv) in CH<sub>2</sub>Cl<sub>2</sub> at room temperature. From the reactions were obtained 3-(arylimino)-4-(dialkylamino)-2,5-benzothiazocine-1,6-diones (10) in good to moderate yields. Yields of 10 are summarized in Table 6.

e

f

g

h

i

4-Br

4-Me

4-MeO

4-MeO

3-NO<sub>2</sub>

Compound	X	Y	R	Yield *(%)
a	4-NO <sub>2</sub>	н	<i>n</i> -Pr	76
b	4-NO <sub>2</sub>	Н	<i>n</i> -Bu	80
c	4-NO <sub>2</sub>	2-Me	<i>n</i> -Pr	83
d	4-Cl	Н	<i>n</i> -Pr	78
e	4-Br	н	<i>n</i> -Pr	69
f	4-Me	Н	<i>n</i> -Pr	45
g	4-MeO	Н	<i>n</i> -Pr	46
h	4-MeO	Н	<i>n</i> -Bu	65
i	3-NO <sub>2</sub>	Н	<i>n</i> -Pr	71

Table 6. Yields of 3-(Arylimino)-4-(dialkylamino)-2,5-benzothiazocine-1,6-diones (10)

\* Isolated yield.

Eight membered cyclic compounds having a sulfur and a nitrogen atoms have been seldom reported: Sodium 3-dimethylaminopropane thiolate reacted with 1,3-dibromopropane in ethanol to give a bromide salt, which was converted to 1,5-thiazcane in 13% yield by treatment with lithiun aluminum hydride.<sup>12</sup> The reaction of 4-hydroxypent-2-enoic acid lactone with systeine gave 1,4-thiazocin-5-one in 50% yield.<sup>13</sup> Recently 1,3thiazocine derivatives was obtained from the reaction of cyclic secondary  $\alpha$ -amino acid with an excess formaldehyde and dimethyl acetylenedicarboxylate in one pot synthesis.<sup>14</sup> All of these reactions mentioned above lack the generality for the synthesis of either thiazocanes or thiazocines.

In conclusion, N'-arylthiocarbamoyl-N,N-dialkylamidines (3) prepared by the reaction of 5-(arylimino)-4-(dialkylamino)-5H-1,2,3-dithiazoles (2) with NaOH in aqueous EtOH at room temperature can be utilized as starting materials for the synthesis of various heterocyclic compounds such as 5-(arylimino)-4-(dialkylamino)- $\Delta^3$ -thiazoline-2-thiones (5), 5-(arylimino)-4-(dialkylamino)-5H-2-oxo-1,2,3-dithiazoles (6), 5-(arylimino)-4-(dialkylamino)-2-(phenylimino)- $\Delta^3$ -thiazolines (8) and 3-(arylimino)-4-(dialkylamino)-2,5-benzothiazocine-1,6diones (10). Further study on the synthetic potentiality of 3 is in progress.

## **EXPERIMENTAL**

5-(Arylimino)-4-(dialkylamino)-5H-1,2,3-dithiazoles<sup>1</sup> (2) and N-phenylimidoyl chloride<sup>15</sup> were prepared by the literature method. Sulfur monochloride, thiophosgene, thionyl chloride, sulfuryl chloride, and phthaloyl chloride were obtained from Aldrich Chemical Co. Inc.. Methylene chloride and pyridine and all other solvents were obtained from Duksan Pharm. Co. Ltd.. Thin layer chromatography was carried out on Merck Chromatogram Sheet (Kiesel gel 60  $F_{254}$ ). Chromatogram was visualized by a mineral U.V. lamp. Column chromatography was performed using silica gel (Merck, 70-230 or 230-400 mesh). <sup>1</sup>H NMR spectra were obtained with a Bruker AC-80 at 80 MHz, using tetramethylsilane as an internal standard. Infrared (IR) spectra were obtained using a Shimazu IR-470. Mass spectra (MS) were obtained by a VG 12-250 mass spectrometer at 70 eV. Melting points were determined on a Fisher-Johns melting point apparatus and are uncorrected.

*N*<sup>2</sup>-(4-Nitrophenyl)thiocarbamoyl-*N*,*N*-diethylamidine (3a): A mixture of 4-(diethylamino)-5-(4nitrophenylimino)-5*H*-1,2,3-dithiazole (2a) (372 mg, 1.20 mmol) and 5% aqueous NaOH (20 ml) in EtOH (50ml) was stirred for 40 min at room temperature. The bright reddish mixture was neutralized with diluted HCl (40%) using litmus paper to give yellow solution. After removal of EtOH, the residue was extracted with EtOAc (3 × 70 ml). The extract was dried over anhydrous MgSO<sub>4</sub>. Chromatography of the reaction mixture on silica gel column (70 - 230 mesh,  $3.5 \times 8$  cm) using a mixture of EtOAc and acetone (1:1) gave 3a (219 mg, 70%): mp 229-231 °C (from acetone + EtOAc); IR (KBr) 3224, 1643, 1603, 1041 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub> + DMSO-d<sub>6</sub>) δ 1.14-1.72 (m, 6H, 2CH<sub>3</sub>), 3.30-3.85 (m, 4H, 2NCH<sub>2</sub>), 7.31 (d, 2H, *J* = 9 Hz, ArH), 8.14 (d, 2H, *J* = 9 Hz, ArH), 8.23 (s, 1H, =NH), 8.70 (s, 1H, NH); MS (m/z) 280 (M<sup>+</sup>, 13.9), 265 (34.8), 180 (100), 134 (43.7), 122 (31.3), 99 (46.2). Anal. Calcd for C<sub>12</sub>H<sub>16</sub>N<sub>4</sub>O<sub>2</sub>S: C, 51.41; H, 5.75: N, 19.99; S, 11.44. Found: C, 51.34; H, 5.77; N, 20.01; S, 11.60.

*N'*-(4-Nitrophenyl)thiocarbamoyl-*N*,*N*-(di-*n*-propyl)amidine (3b): A mixture of 4-(di-*n*-propylamino)-5-(4-nitrophenylimino)-5*H*-1,2,3-dithiazole (2b) (1.22 g, 3.62 mmol) and 5% aqueous NaOH in EtOH was stirred for 2 h and worked up as with 3a. Chromatography of the reaction mixture on a silica gel column (230-400 mesh,  $3.5 \times 10$  cm) using a mixture of CH<sub>2</sub>Cl<sub>2</sub> and acetone (1:1) gave 3b (827 mg, 99%): mp 210-213 °C (from MeOH); IR (KBr) 3208, 1645, 1608, 1571, 1452, 1331, 1104, 1043 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub> + DMSO-d<sub>6</sub>) δ 0.65-1.02 (m, 6H, 2CH<sub>3</sub>), 1.40-2.00 (m, 4H, 2CH<sub>3</sub>), 3.15-3,65 (m, 4H, 2NCH<sub>2</sub>), 7.25 (d, 2H, *J* = 8 Hz, ArH), 8.08 (d, 2H, *J* = 8 Hz, ArH), 8.35 (s, 1H, =NH), 8.82 (s, 1H, NH); MS (m/z) 308 (M<sup>+</sup>, 3.8), 279 (32.8), 180 (100), 134 (35.0), 122 (26.0), 90 (31.0), 72 (87.2). Anal. Calcd for C<sub>14</sub>H<sub>20</sub>N<sub>4</sub>O<sub>2</sub>S: C, 54.53; H, 6.54; N, 18.17; S, 10.40. Found: C, 54.41; H, 6.57; N, 18.14; S, 10.60.

*N*'-(4-Nitrophenyl)thiocarbamoyl-*N*,*N*-(di-*n*-butyl)amidine (3c): A mixture of 4-(di-*n*-butylamino)-5-(4-nitrophenylimino)-5*H*-1,2,3-dithiazole (2c) (2.81 g, 7.67 mmol) and 5% aqueous NaOH in EtOH was stirred for 2 h and worked up as with 3a. Chromatography of the reaction mixture ( $5 \times 9.5$  cm) using a mixture of EtOAc and acetone (4:1) gave 3c (2.13 g, 83%): mp 209-210 °C (from CHCl<sub>3</sub> + acetone); IR (KBr) 3192, 1643, 1606, 1505, 1461, 1331, 1107, 1042 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub> + DMSO-d<sub>6</sub>)  $\delta$  0.85-1.06 (m, 6H, 2CH<sub>3</sub>), 1.13-1.85 (m, 4H, 2CH<sub>2</sub>), 3.20-3.75 (m, 4H, 2NCH<sub>2</sub>), 7.25 (d, 2H, J = 8 Hz, ArH), 8.08 (d, 2H, J = 8 Hz, ArH), 8.25 (s, 1H, =NH), 8.80 (s, 1H, NH); <sup>13</sup>C NMR (DMSO-d<sub>6</sub>)  $\delta$  13.60, 13.72, 19.13, 19.42, 27.62, 29.90, 46.62, 50.29, 122.51, 124.17, 139.63, 158.92, 164.15, 175.95; MS (m/z) 336 (M<sup>+</sup>, 5.8), 180 (82.5), 134 (37.0), 86 (100.0), 44 (50.6). Anal. Calcd for  $C_{16}H_{24}N_4O_2S$ : C, 57.11; H, 7.19; N, 16.65; S, 9.53. Found: C, 57.01; H, 7.21; N, 16.60; S, 9.75.

*N*'-(4-Nitrophenyl)thiocarbamoyl-*N*,*N*-(diallyl)amidine (3d): A mixture of 4-(di-2-propenylamino)-5-(4-nitrophenylimino)-5*H*-1,2,3-dithiazole (2d) (541 mg, 1.62 mmol) and 5% aqueous NaOH in EtOH was stirred for 3 h and worked up as with 3a. Chromatography of the reaction mixture on a silica gel column (230-400 mesh,  $2 \times 14$  cm) using a mixture of EtOAc and acetone (6:1) gave 3d (499 mg, 99%): mp 200-203 °C (from CHCl<sub>3</sub>); IR (KBr) 3216, 1642, 1594, 1562, 1410, 1325, 1102, 1042 cm<sup>-1</sup>; <sup>1</sup>H NMR (DMSO-d<sub>6</sub>)  $\delta$  3.92 (d, 2H, J = 4 Hz, NCH<sub>2</sub>), 4.22 (d, 2H, J = 4 Hz, NCH<sub>2</sub>), 5.21 (d, 2H, J = 5 Hz, =CH<sub>2</sub>), 5.40 (d, 2H, J = 5 Hz, =CH<sub>2</sub>), 5.60-6.20 (m, 2H, 2CH=), 7.25 (d, 2H, J = 8 Hz, ArH), 8.15 (d, 2H, J = 8 Hz, ArH), 8.40 (s, 1H, =NH), 9.10 (s, 1H, NH); MS (m/z) 304 (M<sup>+</sup>, 3.5), 180 (100), 134 (43.5), 90 (40.3), 82 (49.9), 70 (42.6), 68 (40.6), 41 (38.3). Anal. Calcd for C<sub>14</sub>H<sub>16</sub>N<sub>4</sub>O<sub>2</sub>S: C, 55.25; H, 5.30; N, 18.41; S, 10.53. Found: C, 55.12; H, 5.31; N, 18.41; S, 10.68.

*N*'-(2-Methyl-4-nitrophenyl)thiocarbamoyl-*N*,*N*-(di-*n*-propyl)amidine (3e): A mixture of 4-(di-*n*-propylamino)-5-(2-methyl-4-nitrophenylimino)-5*H*-1,2,3-dithiazole (2e) (540 mg, 1.53 mmol) and 5% aqueous NaOH in EtOH was stirred for 1.5 h and worked up as with 3a. Chromatography of the reaction mixture (3.0 × 9 cm) using a mixture of EtOAc and acetone (1:2) gave 3e (342 mg, 69%): mp 209-211 °C (from CHCl<sub>3</sub> + acetone); IR (KBr) 3232, 1645, 1606, 1558, 1328, 1085, 1037 cm<sup>-1</sup>; <sup>1</sup>H NMR (DMSO-d<sub>6</sub>) δ 0.72 (m, 6H, 2CH<sub>3</sub>), 1.40-1.89 (m, 4H, 2CH<sub>2</sub>), 2.12 (s, 3H, CH<sub>3</sub>), 3.26-3.63 (m, 4H, 2NCH<sub>2</sub>), 7.10 (d, 1H, *J* = 8 Hz, ArH), 7.89-7.99 (m, 2H, ArH), 8.32 (s, 1H, =NH), 8.74 (s, 1H, NH); MS (m/z) 322 (M<sup>+</sup>, 14.1), 293 (43.1), 288 (8.5). Anal. Calcd for C<sub>15</sub>H<sub>22</sub>N<sub>4</sub>O<sub>2</sub>S: C, 55.88; H, 6.88; N, 17.38; S, 9.95. Found: C, 55.77; H, 6.85; N, 17.30; S, 10.10.

N'-(4-Chlorophenyl)thiocarbamoyl-*N*,*N*-(di-*n*-propyl)amidine (3f): A mixture of 5-(4-chlorophenylimino)-4-(di-*n*-propylamino)-5*H*-1,2,3-dithiazole (2f) (1.30 g, 3.97 mmol) and 5% aqueous NaOH in EtOH was stirred for 2 h and worked up as with 3a. Chromatography of the reaction mixture (3 × 10 cm) using a mixture of CH<sub>2</sub>Cl<sub>2</sub> and acetone (3:1) gave 3f (912 mg, 77%): mp 200-203 °C (from CHCl<sub>3</sub> + acetone); IR (KBr) 3208, 1640, 1600, 1477, 1088, 1042 cm<sup>-1</sup>; <sup>1</sup>H NMR (DMSO-d<sub>6</sub>)  $\delta$  0.82-1.10 (m, 6H, 2CH<sub>3</sub>), 1.40-1.97 (m, 4H, 2CH<sub>2</sub>), 3.07-3.65 (m, 4H, 2NCH<sub>2</sub>), 7.00-7.35.(m, 4H, ArH), 8.20 (s, 1H, =NH), 8.65 (s, 1H, NH); MS (m/z) 299 (M<sup>+</sup> + 2, 3.0), 297 (M<sup>+</sup>, 7.4), 268 (55.9), 195 (53.6), 169 (80.1), 111 (100). Anal. Calcd for C<sub>14</sub>H<sub>20</sub>ClN<sub>3</sub>S: C, 56.46; H, 6.77; N, 14.11; S, 10.76. Found: C, 56.32; H, 6.79; N, 14.07; S, 10.91.

*N'*-(4-Bromophenyl)thiocarbamoyl-*N*,*N*-(di-*n*-propyl)amidine (3g): A mixture of 5-(4-bromophenylimino)-4-(di-*n*-propylamino)-5*H*-1,2,3-dithiazole (2g). (927 mg, 2.49 mmol) and 5% aqueous in EtOH was stirred for 1.5 h and worked up as with 3a. Chromatography of the reaction mixture ( $2.5 \times 9$  cm) using acetone gave 3g (702 mg, 82%): mp 205-207 °C (from CHCl<sub>3</sub> + acetone); IR (KBr) 3312, 3216, 1640, 1602, 1558, 1474, 1378, 1042 cm<sup>-1</sup>; <sup>1</sup>H NMR (DMSO-d<sub>6</sub>) δ 0.81-1.00 (m, 6H, 2CH<sub>3</sub>), 1.40-1.93 (m, 4H, 2CH<sub>2</sub>), 3.22-3.60 (m, 4H, 2NCH<sub>2</sub>), 7.20 (dd, 4H, J = 14, 8 Hz, ArH), 8.20 (s, 1H, =NH), 8.62 (s, 1H, NH); MS (m/z) 343 (M<sup>+</sup> + 2, 1.6), 341 (M<sup>+</sup>, 5.0), 314 (29.0), 312 (29.4), 241 (20.2), 239 (25.1), 215 (100), 197 (59.7), 157 (56.3), 155 (45.6). Anal. Calcd for C<sub>14</sub>H<sub>20</sub>BrN<sub>3</sub>S: C, 49.13; H, 5.89; N, 12.28; S, 9.37. Found: C, 49.04; H, 5.91; N, 12.20; S, 9.55

*N*'-(4-Methylphenyl)thiocarbamoyl-*N*,*N*-(di-*n*-propyl)amidine (3h): A mixture of 4-(di-*n*-propylamino)-5-(4-methylphenylimino)-5*H*-1,2,3-dithiazole (2h) (650 mg, 2.11 mmol) and 5% aqueous in EtOH was stirred for 2 h and worked up as with 3a. Chromatography of the reaction mixture ( $3.5 \times 9$  cm) using a mixture of EtOAc and acetone (1:2) gave 3h (452 mg, 77%): mp 242-243 °C (from CHCl<sub>3</sub> + acetone); IR (KBr) 3168, 1661, 1616, 1510, 1395 cm<sup>-1</sup>; <sup>1</sup>H NMR (DMSO-d<sub>6</sub>)  $\delta$  0.72-1.02 (m, 6H, 2CH<sub>3</sub>), 1.38-1.80 (m, 4H, 2CH<sub>2</sub>), 2.28 (s, 3H, CH<sub>3</sub>), 3.19-3.58 (m, 4H, 2NCH<sub>2</sub>), 7.41 (d, 2H, *J* = 8 Hz, ArH), 7.82 (d, 2H, *J* = 8 Hz, ArH), 9.41 (s, 1H, =NH), 9.66 (s, 1H, NH); MS (m/z) 277 (M<sup>+</sup>, 4.5), 248 (11.2), 206 (4.7), 171 (5.1), 150 (12.0). Anal. Calcd for C<sub>13</sub>H<sub>23</sub>N<sub>3</sub>S: C, 64.94; H, 8.36; N, 15.15; S, 11.56. Found: C, 64.82; H, 8.35; N, 15.10; S, 11.73.

*N*<sup>2</sup>-(4-Methoxyphenyl)thiocarbamoyl-*N*,*N*-(di-*n*-propyl)amidine (3i): A mixture of 4-(di-*n*-propylamino)-5-(4-methoxylphenylimino)-5*H*-1,2,3-dithiazole (2i) (754 mg, 2.33 mmol) and 5% aqueous NaOH in EtOH was stirred for 1.5 h and worked up as with 3a. Chromatography of the reaction mixture (3.0 × 11 cm) gave 3i (520 mg, 76%): mp 166-168 °C (from CHCl<sub>3</sub> + acetone); IR (KBr) 3184, 1658, 1610, 1507, 1254, 1034 cm<sup>-1</sup>; <sup>1</sup>H NMR (DMSO-d<sub>6</sub>) δ 0.80-0.98 (m, 6H, 2CH<sub>3</sub>), 1.44-1.82 (m, 4H, 2CH<sub>2</sub>), 3.41 (t, 4H, J = 7 Hz, 2NCH<sub>2</sub>), 3.76 (s, 3H, OCH<sub>3</sub>), 6.98 (d, 2H, J = 8 Hz, ArH), 7.73 (d, 2H, J = 8 Hz), 9.45 (m, 2H, =NH, NH); MS (m/z) 293 (M<sup>+</sup>, 20.0), 264 (100), 221 (6.0). Anal. Calcd for C<sub>15</sub>H<sub>23</sub>N<sub>3</sub>OS: C, 61.40; H, 7.90; N, 14.32; S, 10.93. Found: C, 61.27; H, 7.88; N, 14.30; S, 11.09.

*N*<sup>2</sup>-(4-Methoxyphenyl)thiocarbamoyl-*N*,*N*-(di-*n*-butyl)amidine (3j): A mixture of 4-(di-*n*-butylamino)-5-(4-methoxyphenylimino)-5*H*-1,2,3-dithiazole (1.13 g, 3.20 mmol) and 5% aqueous in EtOH was stirred for 2 h and worked up as with **3a**. Chromatography of the reaction mixture (3.5 × 13 cm) gave **3j** (812 mg, 79%): mp 164-166 °C (from CHCl<sub>3</sub> + acetone); IR (KBr) 3216, 1648, 1603, 1498, 1238, 1040 cm<sup>-1</sup>; <sup>1</sup>H NMR (DMSO-d<sub>6</sub>) δ 0.82-1.02 (m, 6H, 2CH<sub>3</sub>), 1.32-1.84 (m, 8H, 2CH<sub>2</sub>CH<sub>2</sub>), 3.43 (t, 4H, *J* = 7 Hz, 2NCH<sub>2</sub>), 3.77 (s, 3H, OCH<sub>3</sub>), 6.98 (d, 2H, *J* = 8 Hz, ArH), 7.73 (d, 2H, *J* = 8 Hz, ArH), 9.47 (m, 2H, =NH, NH); MS (m/z) 321 (M<sup>+</sup>, 23.4), 288 (13.1), 277 (100), 264 (8.3). Anal. Calcd for C<sub>17</sub>H<sub>27</sub>N<sub>3</sub>OS: C, 63.51; H, 8.46; N, 13.07; S, 9.97. Found: C, 63.40; H, 8.47; N, 13.00; S, 10.12.

*N'*-(2-Chloro-5-nitrophenyl)thiocarbamoyl-*N*,*N*-(di-*n*-propyl)amidine (3k): A mixture of 5-(2chloro-5-nitrophenylimino)-4-(di-*n*-propylamino)-5*H*-1,2,3-dithiazole (251 mg, 0.719 mmol) and 5% aqueous NaOH in EtOH was stirred for 1 h and worked up as with 3a. Chromatography of the reaction mixture (3.5 × 9 cm) gave 3k (202 mg, 88%): mp 163-164 °C (from CHCl<sub>3</sub>); IR (KBr) 3312, 3264, 1645, 1605, 1510, 1458, 1344, 1046 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub> + DMSO-d<sub>6</sub>)  $\delta$  0.84-1.11 (m, 6H, 2CH<sub>3</sub>), 1.53-2.01 (m, 4H, 2CH<sub>2</sub>), 3.39 (t, 2H, J = 8 Hz, NCH<sub>2</sub>), 3.69 (t, 2H, J = 8 Hz, NCH<sub>2</sub>), 7.52 (d, 1H, J = 6 Hz, ArH), 7.72 (dd, 1H, J = 6, 1 Hz, ArH), 8.09 (d, 1H, J = 1 Hz, ArH), 8.39 (s, 1H, =NH), 8.64 (s, 1H, NH); MS (m/z) 307 (M<sup>+</sup> – Cl, 2.8), 206 (55.1), 160 (100), 100 (68.2). Anal. Calcd for C<sub>14</sub>H<sub>19</sub>ClN<sub>4</sub>O<sub>2</sub>S: C, 49.05; H, 5.55; N, 16.34; S, 9.35. Found: C, 49.00; H, 5.58; N, 16.30; S, 9.51.

*N*'-(3-Nitrophenyl)thiocarbamoyl-*N*,*N*-diethylamidine (3l): A mixture of 4-(diethylamino)-5-(3nitrophenylimino)-5*H*-1,2,3-dithiazole (2j) (1.10 g, 3.53 mmol) and 5% aqueous NaOH in EtOH was stirred for 2 h and worked up as with 3a. Chromatography of the reaction mixture ( $3.5 \times 12$  cm) using a mixture of EtOAc and acetone (1:2) gave 3l (667 mg, 68%): mp 206-209 °C (from CHCl<sub>3</sub> + acetone); IR (KBr) 3208, 1648, 1602, 1550, 1507, 1346, 1035 cm<sup>-1</sup>; <sup>1</sup>H NMR (DMSO-d<sub>6</sub>)  $\delta$  1.05-1.38 (m, 6H, 2CH<sub>3</sub>), 3.13-3.80 (m, 4H, 2NCH<sub>2</sub>), 7.20-7.55 (m, 3H, ArH), 8.13 (s, 1H, ArH), 8.21 (s, 1H, =NH), 8.70 (s, 1H, NH); MS (m/z) 280 (M<sup>+</sup>, 9.5), 279 (47.5), 206 (100), 180 (70.4), 177 (86.8), 134 (67.7). Anal. Calcd for C<sub>12</sub>H<sub>16</sub>N<sub>4</sub>O<sub>2</sub>S: C, 51.41; H, 5.75; N, 19.99; S, 11.44. Found: C, 51.33; H, 5.78; N, 19.95; S, 11.59.

*N'*-(3-Nitrophenyl)thiocarbamoyl-*N*,*N*-(di-*n*-propyl)amidine (3m): A mixture of 4-(di-*n*-propylamino)-5-(3-nitrophenylimino)-5*H*-1,2,3-dithiazole (2k) (1.59 g, 4.71 mmol) and 5% aqueous NaOH in EtOH (40 ml) was stirred for 3 h and worked up as with 3a. Chromatography of the reaction mixture on a silica gel column (230-400 mesh,  $2.5 \times 7.5$  cm) gave 3m (1.14 g, 79%): mp 211-213 °C (from CHCl<sub>3</sub> + acetone); IR (KBr) 3312, 3216, 1642, 1608, 1515, 1467, 1347, 1038,1045 cm<sup>-1</sup>; <sup>1</sup>H NMR (DMSO-d<sub>6</sub>)  $\delta$  0.85-1.00 (m, 6H, 2CH<sub>3</sub>), 1.40-1.85 (m, 4H, 2CH<sub>2</sub>), 3.22-3.60 (m, 4H, 2NCH<sub>2</sub>), 7.25-7.85 (m, 3H, ArH), 8.10 (s, 1H, ArH), 8.30 (s, 1H, =NH), 8.80 (s, 1H, NH); MS (m/z) 308 (M<sup>+</sup>, 6.6), 279 (62.9), 180 (100), 134 (61.3). Anal. Calcd for C<sub>14</sub>H<sub>20</sub>N<sub>4</sub>O<sub>2</sub>S: C, 54.53;

H, 6.54; N, 18.17; S, 10.40. Found: C, 54.48; H, 6.57; N, 18.05; S, 10.45.

*N*'-(4-Chloro-3-nitrophenyl)thiocarbamoyl-*N*,*N*-(di-*n*-propyl)amidine (3n): A mixture of 5-(4chloro-3-nitrophenylimino)-4-(di-*n*-propylamino)-5*H*-1,2,3-dithiazole (368 mg, 0.987 mmol) and 5% aqueous NaOH in EtOH was stirred for 3 h and worked up as with 3a. Chromatography of the reaction mixture ( $3.5 \times 8$  cm) gave 3n (250 mg, 74%): mp 211-213 °C (from CHCl<sub>3</sub> + acetone); IR (KBr) 3424, 3224, 1640, 1606, 1562, 1520, 1466, 1346, 1046 cm<sup>-1</sup>; <sup>1</sup>H NMR (DMSO-d<sub>6</sub>)  $\delta$  0.61-1.03 (m, 6H, 2CH<sub>3</sub>), 1.40-1.90 (m, 4H, 2CH<sub>2</sub>), 3.17-3.60 (m, 4H, 2NCH<sub>2</sub>), 7.20-8.25 (m, 3H, ArH), 8.33 (s, 1H, =NH), 8.72 (s, 1H, NH); MS (m/z) 315 ((M<sup>+</sup> + 2) - Et, 2.2), 313 (M<sup>+</sup> - Et, 3.4), 214 (100), 168 (27.9), 156 (24.1), 133 (81.6). Anal. Calcd for C<sub>14</sub>H<sub>19</sub>ClN<sub>4</sub>O<sub>2</sub>S: C, 49.05; H, 5.55; N, 16.34; S, 9.35. Found: C, 48.94; H, 5.58; N, 16.30; S, 9.53.

*N'*-(4-Chloro-3-nitrophenyl)thiocarbamoyl-*N*,*N*-(di-*n*-butyl)amidine (30): A mixture of 5-(4-chloro-3-nitrophenylimino)-4-(di-*n*-butylamino)-5*H*-1,2,3-dithiazole. (655 mg, 1.64 mmol) and 5% aqueous NaOH in EtOH was stirred for 1.5 h and worked up as with 3a. Chromatography of the reaction mixture ( $2.5 \times 13$  cm) using a mixture of CH<sub>2</sub>Cl<sub>2</sub> and acetone (3:1) gave 3o (466 mg, 77%): mp 187-190 °C (from CHCl<sub>3</sub>); IR (KBr) 3427, 3220, 1645, 1610, 1561, 1466, 1346 cm<sup>-1</sup>; <sup>1</sup>H NMR (DMSO-d<sub>6</sub>)  $\delta$  0.92-1.76 (m, 10H, 2CH<sub>2</sub>CH<sub>3</sub>), 3.263.73 (m, 4H, 2NCH<sub>2</sub>), 7.45 (m, 2H, ArH), 7.98-8.12 (m, 3H, =NH, NH, ArH); MS (m/z) 370 (M<sup>+</sup> + 2, 3.4), 368 (M<sup>+</sup>, 8.7), 214 (100), 168 (23.7), 156 (30.2), 133 (72.6). Anal. Calcd for  $C_{16}H_{23}CIN_4O_2S$ : C, 52.10; H, 6.28; N, 15.19; S, 8.69. Found: C, 52.02; H, 6.30; N, 15.11; S, 8.83.

General Procedure for the Reactions of 3 with Sulfur monochloride ( $S_2Cl_2$ ). To a suspension of compound 3 (0.1-0.3 mmol) containing pyridine (0.2-0.7 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (40 ml) was added dropwisely  $S_2Cl_2$  (0.1-0.3 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (20 ml). The mixture was stirred for an appropriate time. During that time compound 3 was dissolved and the solution turned from yellow to red color. TLC (CH<sub>2</sub>Cl<sub>2</sub>: *n*-hexane = 1:1) of the reaction mixture showed two spots corresponding to compound 2 and an unknown having a smaller  $R_f$  value than compound 2. The unknown spot disappeared when the reaction was completed. The mixture was washed with water (2 × 20 ml), dried (MgSO<sub>4</sub>), and concentrated to give a residue, which was chromatographed on a silica gel column (70-230 mesh, 3.5 × 15 cm). Elution with petroleum ether (bp 30-60 °C) gave sulfur. Elution with a mixture of petroleum ether (bp 30-60 °C) and CH<sub>2</sub>Cl<sub>2</sub> (1:1) gave 2.

**Preparation of 2a**<sup>1</sup>: A mixture of **3a** (100 mg, 0.357 mmol), pyridine (99 mg, 1.25 mmol), and SCl<sub>2</sub> (54 mg, 0.524 mmol) in CH<sub>2</sub>Cl<sub>2</sub> was stirred for 20 min. Yield of **2a**: 89 mg (80%).

**Preparation of 2b**<sup>1</sup>: A mixture of **3b** (112 mg, 0.331 mmol), pyridine (58 mg, 0.733 mmol), and  $S_2Cl_2$  (46 mg, 0.341 mmol) in CH<sub>2</sub>Cl<sub>2</sub> was stirred for 100 min. Yield of **2b**: 81 mg (72%).

Preparation of  $2c^1$ : A mixture of 3c (85 mg, 0.253 mmol), pyridine (44 mg, 0.556 mmol), and  $S_2Cl_2$  (35 mg, 0.259 mmol) in CH<sub>2</sub>Cl<sub>2</sub> was stirred for 70 min. Yield of 2c: 60 mg (65%).

Preparation of  $2d^1$ : A mixture of 3d (22 mg, 0.0723 mmol), pyridine (12 mg, 0.152 mmol), and  $S_2Cl_2$  (8 mg, 0.0592 mmol) in CH<sub>2</sub>Cl<sub>2</sub> was stirred for 90 min. Yield of 2d: 12 mg (45%).

**Preparation of 2e**: A mixture of **3e** (82 mg, 0.284 mmol), pyridine (52 mg, 0.657 mmol), and S<sub>2</sub>Cl<sub>2</sub> (41 mg, 0.304 mmol) in CH<sub>2</sub>Cl<sub>2</sub> was stirred for 70 min. Yield of **2e**: 73 mg (81%); IR (neat) 2960, 1571, 1510, 1338, 1090, 806 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  0.87 (t, 6H, J = 7 Hz, 2CH<sub>3</sub>), 1.71 (sextet, 4H, J = 7 Hz, 2CH<sub>2</sub>), 2.25 (s, 3H, CH<sub>3</sub>), 3.80 (t, 4H, J = 7 Hz, 2NCH<sub>2</sub>), 7.02 (d, 1H, J = 10 Hz, ArH), 8.07-8.18 (m, 2H, ArH); MS (m/z) 352 (M<sup>+</sup>, 9.7), 323 (6.5), 276 (7.1), 249 (8.0). Anal. Calcd for C<sub>15</sub>H<sub>20</sub>N<sub>4</sub>O<sub>2</sub>S<sub>2</sub>: C, 51.11; H, 5.72; N, 15.90; S, 18.19. Found: C, 50.01; H, 5.70; N, 15.86; S, 18.31.

**Preparation of 2f**: A mixture of **3f** (370 mg, 1.24 mmol), pyridine (215 mg, 2.72 mmol), and S<sub>2</sub>Cl<sub>2</sub> (169 mg, 1.25 mmol) in CH<sub>2</sub>Cl<sub>2</sub> was stirred for 100 min. Yield of **2f**: 341 mg (76%); IR (neat) 2960, 1576, 1517, 1470, 1248, 1090 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  0.86 (t, 6H, J = 7 Hz, 2CH<sub>3</sub>), 1.80 (sextet, 4H, J = 7 Hz, 2CH<sub>2</sub>), 3.52 (t, 4H, J = 7 Hz, 2NCH<sub>2</sub>), 7.00 (d, 1H, J = 10 Hz, ArH), 7.33 (d, 2H, J = 8 Hz, ArH)); MS (m/z) 329 (M<sup>+</sup> + 2, 9.1), 327 (M<sup>+</sup>, 28.7), 298 (14.5), 252 (17.2). Anal. Calcd for C<sub>14</sub>H<sub>18</sub>ClN<sub>3</sub>S<sub>2</sub>: C, 51.28; H, 5.53; N, 12.82; S, 19.56. Found: C, 51.15; H, 5.49; N, 12.77; S, 19.74.

**Preparation of 2g^1:** A mixture of 3g (89 mg, 0.260 mmol), pyridine (44 mg, 0.556 mmol), and  $S_2Cl_2$  (35 mg, 0.259 mmol) in CH<sub>2</sub>Cl<sub>2</sub> was stirred for 60 min. Yield of 2g: 50 mg (52%).

**Preparation of 2h**<sup>1</sup>: A mixture of **3h** (64 mg, 0.231 mmol), pyridine (36 mg, 0.455 mmol), and  $S_2Cl_2$  (29 mg, 0.215 mmol) in CH<sub>2</sub>Cl<sub>2</sub> was stirred for 85 min. Yield of **2h**: 50 mg (71%).

**Preparation of 2i**<sup>1</sup>: A mixture of **3i** (79 mg, 0.269 mmol), pyridine (49 mg, 0.619 mmol), and  $S_2Cl_2$  (35 mg, 0.259 mmol) in CH<sub>2</sub>Cl<sub>2</sub> was stirred for 90 min. Yield of **2i**: 38 mg (44%).

**Preparation of 2** $j^1$ : A mixture of **31** (72 mg, 0.256 mmol), pyridine (49 mg, 0.619 mmol), and S<sub>2</sub>Cl<sub>2</sub> (37 mg, 0.274 mmol) in CH<sub>2</sub>Cl<sub>2</sub> was stirred for 130 min. Yield of **2**j: 61 mg (77%).

**Preparation of 2k^1:** A mixture of **3m** (64 mg, 0.208 mmol), pyridine (36 mg, 0.455 mmol), and  $S_2Cl_2$  (29 mg, 0.215 mmol) in CH<sub>2</sub>Cl<sub>2</sub> was stirred for 85 min. Yield of **2k**: 48 mg (68%).

**4-(Diethylamino)-5-(4-nitrophenylimino)-** $\Delta^3$ **-thiazoline-2-thione (5a)**: To a solution of **3a** (217 mg, 0.823 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (15 ml) containing pyridine (147 mg, 1.85 mmol) was dropwisely added thiophosgene (121 mg, 1.05 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 ml) for 30 min. The mixture was stirred for 21 h at room temperature. Chromatography of the residue on a silica gel column (70-230 mesh,  $2.5 \times 17$  cm) with CH<sub>2</sub>Cl<sub>2</sub> gave **5a** (232 mg, 92%): mp 194-195 °C (from *n*-hexane); IR (KBr) 1595, 1386, 1341, 1304, 1141 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  1.23-1.52 (m, 6H, 2CH<sub>3</sub>), 3.88 (q, 2H, J = 7 Hz, CH<sub>2</sub>), 4.38 (q, 2H, J = 7 Hz, CH<sub>2</sub>), 7.40 (d, 2H, J = 8 Hz, ArH), 8.33 (d, 2H, J = 8 Hz, ArH); MS (m/z) 322 (M<sup>+</sup>, 42.6), 307 (94.4), 261 (13.9), 143 (28.4), 113 (44.5). Anal. Calcd for C<sub>13</sub>H<sub>14</sub>N<sub>4</sub>O<sub>2</sub>S<sub>2</sub>: C, 48.43; H, 4.34; N, 17.38; S, 19.89. Found: C, 48.34; H, 4.36; N, 17.30; S, 20.09.

**4-(Di-***n***-propylamino)-(4-nitrophenylimino)-\Delta^3-thiazoline-2-thione (5b)**: To a solution of **3b** (166 mg, 0.540 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (15 ml) containing pyridine (88 mg, 1.11 mmol) was dropwisely added thiophosgene (75 mg, 0.656 mmol) in CH<sub>2</sub>Cl<sub>2</sub> for 25 min. The mixture was stirred for 20 h and worked up. Chromatography (3.5 × 10 cm) of the residue with a mixture of CH<sub>2</sub>Cl<sub>2</sub> and *n*-hexane (3 :1) gave **5b** (155 mg, 82%): mp 170-172 °C (from *n*-hexane); IR (KBr) 1594, 1515, 1387, 1342 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  0.85-1.11 (m, 6H, 2CH<sub>3</sub>), 1.57-2.00 (m, 4H, 2CH<sub>2</sub>), 3.76 (t, 2H, *J* = 8 Hz, NCH<sub>2</sub>), 4.20 (t, 2H, *J* = 8 Hz, NCH<sub>2</sub>), 7.40 (d, 2H, *J* = 9 Hz, ArH), 8.35 (d, 2H, *J* = 9 Hz, ArH); MS (m/z) 350 (M<sup>+</sup>, 16.0), 321 (100), 279 (27.5), 233 (9.3). Anal. Calcd for C<sub>15</sub>H<sub>18</sub>N<sub>4</sub>O<sub>2</sub>S<sub>2</sub>: C, 51.41; H, 5.18; N, 15.99; S, 18.30. Found: C, 51.31; H, 5.19; N, 16.00; S, 18.44.

4-(Di-*n*-butylamino)-5-(4-nitrophenylimino)- $\Delta^3$ -thiazoline-2-thione (5c): To a solution of 3c (195 mg, 0.581 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (15 ml) containing pyridine (147 mg, 1.85 mmol) was dropwisely added thiophosgene (106 mg, 0.918 mmol) in CH<sub>2</sub>Cl<sub>2</sub> for 25 min. The mixture was stirred for 20 h and worked up. Chromatography (2.5 × 7.5 cm) of the residue with a mixture of CH<sub>2</sub>Cl<sub>2</sub> and *n*-hexane (3 :1) gave 5c (213 mg, 97%): mp 123-125 °C (from *n*-hexane); IR (KBr) 1598, 1523, 1388, 1342, 1304 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  0.68-1.07 (m, 6H, 2CH<sub>3</sub>), 1.32-1.92 (m, 4H, 2CH<sub>2</sub>), 3.63 (t, 2H, *J* = 8 Hz, NCH<sub>2</sub>), 4.27 (t, 2H, *J* = 8 Hz, NCH<sub>2</sub>), 7.42 (dd, 2H, *J* = 9, 0.5 Hz, ArH), 8.37 (dd, 2H, *J* = 9, 0.5 Hz, ArH); MS (m/z) 378 (M<sup>+</sup>, 20.0), 321

(100), 335 (100), 279 (29.3), 233 (15.0). Anal. Calcd for C<sub>17</sub>H<sub>22</sub>N<sub>4</sub>O<sub>2</sub>S<sub>2</sub>: C, 53.94; H, 5.86; N, 14.80; S, 16.94. Found: C, 53.82; H, 5.84; N, 14.75; S, 17.05.

**4-(Di-2-propenylamino)-5-(4-nitrophenylimino)-** $\Delta^3$ **-thiazoline-2-thione (5d)**: To a solution of 3d (166 mg, 0.546 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (15 ml) containing pyridine (98 mg, 1.24 mmol) was dropwisely added thiophosgene (83 mg, 0.721 mmol) in CH<sub>2</sub>Cl<sub>2</sub> for 35 min. The mixture was stirred for 24 h and worked up. Chromatography (2.5 × 15 cm) of the residue with a mixture of CH<sub>2</sub>Cl<sub>2</sub> and *n*-hexane (3 :1) gave 5d (175 mg, 93%): mp 190-191 °C (from *n*-hexane and CH<sub>2</sub>Cl<sub>2</sub>); IR (KBr) 1582, 1517, 1384, 1342, 1283 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  4.42 (d, 2H, *J* = 4 Hz, NCH<sub>2</sub>), 5.01 (d, 2H, *J* = 4 Hz, NCH<sub>2</sub>), 5.24 (d, 2H, *J* = 3 Hz, =CH<sub>2</sub>), 5.40 (d, 2H, *J* = 3 Hz, =CH<sub>2</sub>), 5.71-6.23 (m, 2H, 2CH=), 7.44 (d, 2H, *J* = 8 Hz, ArH), 8.34 (d, 2H, *J* = 8 Hz, ArH); MS (m/z) 346 (M<sup>+</sup>, 12.2), 305 (49.1), 149 (100), 137 (41.1), 125 (56.6), 102 (59.1) 98 (37.8), 85 (68.8), 41 (34.9). Anal. Calcd for C<sub>13</sub>H<sub>14</sub>N<sub>4</sub>O<sub>2</sub>S<sub>2</sub>: C,52.01; H, 4.07; N, 16.17; S, 18.51. Found: C, 51.93; H, 4.10; N, 16.15; S, 18.66.

**5-(4-Chlorophenylimino)-4-(di-***n***-propylamino)-\Delta^3-thiazoline-2-thione (5e)**: To a solution of **3f** (218 mg, 0.731 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (15 ml) containing pyridine (127 mg, 1.61 mmol) was dropwisely added thiophosgene (98 mg, 0.852 mmol) in CH<sub>2</sub>Cl<sub>2</sub> for 30 min. The mixture was stirred for 32 h and worked up. Chromatography (3.5 × 13 cm) of the residue with a mixture of CH<sub>2</sub>Cl<sub>2</sub> and *n*-hexane (3 :1) gave **5e** (185 mg, 74%): mp 133-134 °C (from *n*-hexane); IR (KBr) 1592, 1483, 1382, 1299, 1267, 1277 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  0.82-1.02 (m, 6H, 2CH<sub>3</sub>), 1.60-2.00 (m, 4H, 2CH<sub>2</sub>), 3.76 (t, 2H, *J* = 8 Hz, NCH<sub>2</sub>), 4.20 (t, 2H, *J* = 8 Hz, NCH<sub>2</sub>), 7.11 (d, 2H, *J* = 8 Hz, ArH), 8.42 (d, 2H, *J* = 8 Hz, ArH); MS (m/z) 341 (M<sup>+</sup> + 2, 8.2), 339 (M<sup>+</sup>, 13.0), 310 (100), 268 (29.7). Anal. Calcd for C<sub>15</sub>H<sub>18</sub>ClN<sub>3</sub>S<sub>2</sub>:

C, 53.01; H, 5.34; N, 17.38; S, 19.89. Found: C, 52.84; H, 5.36; N, 17.35; S, 20.05.

4-(Diethylamino)-5-(3-nitrophenylimino)- $\Delta^3$ -thiazoline-2-thione (5f): To a solution of 3l (162 mg, 0.578 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (15 ml) containing pyridine (108 mg, 1.36 mmol) was dropwisely added thiophosgene (83 mg, 0.721 mmol) in CH<sub>2</sub>Cl<sub>2</sub> for 30 min. The mixture was stirred for 27 h and worked up. Chromatography (2.5 × 15 cm) of the residue with a mixture of CH<sub>2</sub>Cl<sub>2</sub> and *n*-hexane (3 :1) gave 5f (176 mg, 95%): mp 132-134 °C (from *n*-hexane); IR (KBr) 1594, 1520, 1389, 1347, 1306, 1142 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  0.98 (t, 6H, *J* = 6 Hz, 2CH<sub>3</sub>), 1.52-1.95 (m, 4H, 2CH<sub>2</sub>), 3.87 (t, 2H, *J* = 7 Hz, NCH<sub>2</sub>), 3.99 (t, 2H, *J* = 7 Hz, NCH<sub>2</sub>), 7.50-8.42 (m, 4H, ArH); MS (m/z) 322 (M<sup>+</sup>, 42.6), 307 (94.4), 261 (13.9), 143 (28.4), 113 (44.5). Anal. Calcd for C<sub>13</sub>H<sub>14</sub>N<sub>4</sub>O<sub>2</sub>S<sub>2</sub>: C, 48.43; H, 4.34; N, 17.38; S, 19.89. Found: C, 48.30; H, 4.35; N, 17.35; S, 20.05.

5-(3-Nitrophenylimino)-4-(di-*n*-propylamino)- $\Delta^3$ -thiazoline-2-thione (5g): To a solution of 3m (225 mg, 0.731 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (15 ml) containing pyridine (137 mg, 1.73 mmol) was dropwisely added thiophosgene (106 mg, 0.918 mmol) in CH<sub>2</sub>Cl<sub>2</sub> for 25 min. The mixture was stirred for 20 h and worked up. Chromatography (2.5 × 15 cm) of the residue with a mixture of CH<sub>2</sub>Cl<sub>2</sub> and *n*-hexane (3 :1) gave 5g (182 mg, 71%): mp 132-134 °C (from *n*-hexane); IR (KBr) 1598, 1525, 1390, 1346, 1301 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  0.98

(t, 6H, J = 6 Hz, 2CH<sub>3</sub>), 1.52-1.95 (m, 4H, 2CH<sub>2</sub>), 3.87 (t, 2H, J = 7 Hz, NCH<sub>2</sub>), 3.99 (t, 2H, J = 7 Hz, NCH<sub>2</sub>), 7.50-8.42 (m, 4H, ArH); MS (m/z) 350 (M<sup>+</sup>, 25.3), 321 (100), 279 (27.4), 233 (9.3). Anal. Calcd for C<sub>13</sub>H<sub>18</sub>N<sub>4</sub>O<sub>2</sub>S<sub>2</sub>: C, 51.41; H, 5.18; N, 15.99; S, 18.30. Found: C, 51.31; H, 5.19; N, 15.97; S, 18.44.

**5-(4-Chloro-3-nitrophenylimino)-4-(di-***n***-propylamino)-A^3-thiazoline-2-thione (5h)**: To a solution of **3n** (112 mg, 0.326 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (15 ml) containing pyridine (54 mg, 0.680 mmol) was dropwisely added thiophosgene (60 mg, 0.525 mmol) in CH<sub>2</sub>Cl<sub>2</sub> for 30 min. The mixture was stirred for 11 h and worked up. Chromatography (3.5 × 10 cm) of the residue with a mixture of CH<sub>2</sub>Cl<sub>2</sub> and *n*-hexane (3 :1) gave **5h** (102 mg, 81%): mp 150-152 °C (from *n*-hexane); IR (KBr) 1595, 1526, 1384, 1302 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  0.82-1.02 (m, 6H, 2CH<sub>3</sub>), 1.51-2.00 (m, 4H, 2CH<sub>2</sub>), 3.85 (t, 2H, *J* = 8 Hz, NCH<sub>2</sub>), 4.19 (t, 2H, *J* = 8 Hz, NCH<sub>2</sub>), 7.32-7.82 (m, 3H, ArH); MS (m/z) 384 (M<sup>+</sup>, 22.3), 357 (38.9), 355 (86.5), 313 (26.0). Anal. Calcd for C<sub>13</sub>H<sub>17</sub>ClN<sub>4</sub>O<sub>2</sub>S<sub>2</sub>: C, 46.81; H, 4.45; N, 14.56; S, 16.66. Found: C, 46.73; H, 4.48; N, 14.50; S, 16.82.

4-(Diethylamino)-5-(4-nitrophenylimino)-5H-2-oxo-1,2,3-dithiazole (6a): To a solution of 3a (73 mg, 0.260 mmol) and pyridine (49 mg, 0.618 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (20 ml) was dropwisely added thionyl chloride (83 mg, 0.699 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 ml) for 30 min. The mixture was stirred for 6 h at room temperature. After the solvent and thionyl chloride remained were removed in vacuo, chromatography (2.5 × 12 cm) of the residue on a silica gel column (70-230 mesh, 2.5 × 17 cm) using CH<sub>2</sub>Cl<sub>2</sub> gave 3a (29 mg, 40%) and 6a (36 mg, 42%); IR (neat) 2906, 1581, 1550, 1342, 1135, 911 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  1.20-1.46 (m, 6H, 2CH<sub>3</sub>), 3.75 (q, 2H, *J* = 7 Hz, NCH<sub>2</sub>), 4.05 (q, 2H, *J* = 7 Hz, NCH<sub>2</sub>), 7.17 (d, 2H, *J* = 8 Hz, ArH), 8.30 (d, 2H, *J* = 8 Hz, ArH). Anal. Calcd for C<sub>12</sub>H<sub>14</sub>N<sub>4</sub>O<sub>3</sub>S<sub>2</sub>: C, 44.16; H, 4.32; N, 17.17; S, 19.65. Found: C, 44.03; H, 4.32; N, 17.10; S, 19.79.

4-(Di-*n*-propylamino)-5-(4-nitrophenylimino)-5H-2-oxo-1,2,3-dithiazole (6b): To a solution of 3b (75 mg, 0.243 mmol) and pyridine (42 mg, 0.532 mmol) in CH<sub>2</sub>Cl<sub>2</sub> was dropwisely added thionyl chloride (73 mg, 0.617 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 ml) for 1 h. The mixture was stirred for 13 h and worked up as with 6a. Chromatography (2.5 × 12 cm) of the residue using CH<sub>2</sub>Cl<sub>2</sub> gave 6b (58 mg, 67%); IR (neat) 2960, 1581, 1554, 1437, 1339, 1138, 910 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  0.77-1.07 (m, 6H, 2CH<sub>3</sub>), 1.59-1.98 (m, 4H, 2CH<sub>2</sub>), 3.82 (t, 2H, J = 7 Hz, NCH<sub>2</sub>), 3.93 (t, 2H, J = 7 Hz, NCH<sub>2</sub>), 7.05 (d, 2H, J = 8 Hz, ArH), 8.29 (d, 2H, J = 8 Hz, ArH). Anal. Calcd for C<sub>14</sub>H<sub>18</sub>N<sub>4</sub>O<sub>3</sub>S<sub>2</sub>: C, 47.44; H, 5.12; N, 15.81; S, 18.09. Found: C, 47.33; H, 5.09; N, 15.75; S, 18.23.

4-(Di-*n*-butylamino)-5-(4-nitrophenylimino)-5H-2-oxo-1,2,3-dithiazole (6c): To a solution of 3c (110 mg, 0.327 mmol) and pyridine (54 mg, 0.680 mmol) in CH<sub>2</sub>Cl<sub>2</sub> was dropwisely added thionyl chloride (82 mg, 0.685 mmol) in CH<sub>2</sub>Cl<sub>2</sub> for 30 min. The mixture was stirred for 18 h and worked up as with 6a. Chromatography (2 × 13 cm) of the residue using CH<sub>2</sub>Cl<sub>2</sub> gave 3c (11 mg, 10%) and 6c (98 mg, 67%); IR (neat) 2928, 1550, 1333, 1133 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  0.80-1.02 (m, 6H, 2CH<sub>3</sub>), 1.18-1.91 (m, 8H, 2CH<sub>2</sub>CH<sub>2</sub>), 3.68 (t, 2H, J = 8 Hz, NCH<sub>2</sub>), 3.98 (t, 2H, J = 8 Hz, NCH<sub>2</sub>), 7.02 (d, 2H, J = 8 Hz, ArH), 8.29 (d,

2H, J = 8 Hz, ArH). Anal. Calcd for C<sub>16</sub>H<sub>22</sub>N<sub>4</sub>O<sub>3</sub>S<sub>2</sub>: C, 50.24; H, 5.80; N, 14.65; S, 17.55. Found: C, 50.11; H, 5.78; N, 14.60; S, 17.69.

**4-(Di-2-propenylamino)-5-(4-nitrophenylimino)-5H-2-oxo-1,2,3-dithiazole (6d)**: To a solution of 3d (77 mg, 0.253 mmol) and pyridine (39 mg, 0.495 mmol) in CH<sub>2</sub>Cl<sub>2</sub> was dropwisely added thionyl chloride (82 mg, 0.685 mmol) in CH<sub>2</sub>Cl<sub>2</sub> for 40 min. The mixture was stirred for 2 h and worked up as with 6a. Chromatography (2.5 × 13 cm) of the residue using CH<sub>2</sub>Cl<sub>2</sub> gave 6d (54 mg, 61%); IR (neat) 1547, 1509, 1339, 1136, 893 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  4.30 (d, 2H, J = 5 Hz, NCH<sub>2</sub>), 4.81 (d, 2H, J = 5 Hz, NCH<sub>2</sub>), 5.30-5.39 (m, 4H, 2=CH2), 5.67-6.13 (m, 2H, 2CH=), 7.04 (d, 2H, J = 8 Hz, ArH), 8.27 (d, 2H, J = 8 Hz, ArH). Anal. Calcd for C<sub>14</sub>H<sub>14</sub>N<sub>4</sub>O<sub>3</sub>S<sub>2</sub>: C, 47.80; H, 4.03; N, 15.99; S, 18.30. Found: C, 47.67; H, 4.01; N, 15.95; S, 18.45.

5-(4-Chlorophenylimino)-4-(di-*n*-propylamino)-5*H*-2-oxo-1,2,3-dithiazole (6e): To a solution of 3f (95 mg, 0.319 mmol) and pyridine (55 mg, 0.692 mmol) in CH<sub>2</sub>Cl<sub>2</sub> was dropwisely added thionyl chloride (95 mg, 0.795 mmol) in CH<sub>2</sub>Cl<sub>2</sub> for 1.5 h. The mixture was stirred for 12 h and worked up as with 6a. Chromatography (2.5 × 13 cm) of the residue using CH<sub>2</sub>Cl<sub>2</sub> gave 6e (60 mg, 55%); IR (neat) 1546, 1134, 1091, 909, 822 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  0.78-1.05 (m, 6H, 2CH<sub>3</sub>), 1.61-1.91 (m, 4H, 2CH<sub>2</sub>), 3.64 (t, 2H, *J* = 8 Hz, NCH<sub>2</sub>), 3.91 (t, 2H, *J* = 8 Hz, NCH<sub>2</sub>), 6.93 (d, 2H, *J* = 10 Hz, ArH), 7.37 (d, 2H, *J* = 10 Hz, ArH). Anal. Calcd for C<sub>14</sub>H<sub>18</sub>ClN<sub>3</sub>OS<sub>2</sub>: C, 48.90; H, 5.28; N, 12.22; S, 18.65. Found: C, 48.77; H, 5.27; N, 12.15; S, 18.85.

5-(4-Bromophenylimino)-4-(di-*n*-propylamino)-5H-2-oxo-1,2,3-dithiazole (6f): To a solution of 3g (91 mg, 0.266 mmol) and pyridine (46 mg, 0.581 mmol) in CH<sub>2</sub>Cl<sub>2</sub> was dropwisely added thionyl chloride (95 mg, 0.795 mmol) in CH<sub>2</sub>Cl<sub>2</sub> for 30 min. The mixture was stirred for 23 h and worked up as with 6a. Chromatography (2.5 × 15 cm) of the residue using CH<sub>2</sub>Cl<sub>2</sub> gave 6f (56 mg, 54%); IR (neat)) 1549, 1133, 907, 821 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  0.76-1.04 (m, 6H, 2CH<sub>3</sub>), 1.54-1.98 (m, 4H, 2CH<sub>2</sub>), 3.61 (t, 2H, J = 8 Hz, NCH<sub>2</sub>), 3.92 (t, 2H, J = 8 Hz, NCH<sub>2</sub>), 6.85 (d, 2H, J = 8 Hz, ArH), 7.52 (d, 2H, J = 8 Hz, ArH). Anal. Calcd for C<sub>14</sub>H<sub>18</sub>BrN<sub>3</sub>OS<sub>2</sub>: C, 43.30; H, 4.67; N, 10.82; S, 16.51. Found: C, 43.29; H, 4.64; N, 10.80; S, 16.64.

**4-(Di-***n***-propylamino)-5-(4-methylphenylimino)-5H-2-oxo-1,2,3-dithiazole (6g)**: To a solution of **3h** (89 mg, 0.290 mmol) and pyridine (50 mg, 0.631 mmol) in CH<sub>2</sub>Cl<sub>2</sub> was dropwisely added thionyl chloride (62 mg, 0.521 mmol) in CH<sub>2</sub>Cl<sub>2</sub> for 100 min. The mixture was stirred for 11 h and worked up as with **6a**. Chromatography (2.5 × 12 cm) of the residue using CH<sub>2</sub>Cl<sub>2</sub> gave **6g** (20 mg, 24%); IR (neat) 1550, 1134 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  0.76-1.05 (m, 6H, 2CH<sub>3</sub>), 1.75-1.94 (m, 4H, 2CH<sub>2</sub>), 2.34 (s, 3H, CH<sub>3</sub>), 3.62 (t, 2H, *J* = 7 Hz, NCH<sub>2</sub>), 3.94 (t, 2H, *J* = 7 Hz, NCH<sub>2</sub>), 6.91 (d, 2H, *J* = 8 Hz, ArH), 7.20 (d, 2H, *J* = 8 Hz, ArH). Anal. Calcd for C<sub>15</sub>H<sub>21</sub>N<sub>3</sub>OS<sub>2</sub>: C, 55.70; H, 6.54; N, 12.99; S, 19.83. Found: C, 55.61; H, 6.52; N, 12.90; S, 19.98.

4-(Di-n-propylamino)-5-(4-methoxyphenylimino)-5H-2-oxo-1,2,3-dithiazole (6h): To a solution of 3i (105 mg, 0.358 mmol) and pyridine (63 mg, 0.791 mmol) in CH<sub>2</sub>Cl<sub>2</sub> was dropwisely added thionyl chloride (114 mg, 0.962 mmol) in CH<sub>2</sub>Cl<sub>2</sub> for 1 h. The mixture was stirred for 26 h and worked up as with 6a. Chromatography (2 × 15 cm) of the residue using CH<sub>2</sub>Cl<sub>2</sub> gave 6h (26 mg, 21%); IR (neat) 1549, 1501, 1248, 1131 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  0.80-1.04 (m, 6H, 2CH<sub>3</sub>), 1.58-1.96 (m, 4H, 2CH<sub>2</sub>), 3.60 (t, 2H, J = 8 Hz, NCH<sub>2</sub>), 3.81 (s, 3H, OCH<sub>3</sub>), 3.94 (t, 2H, J = 8 Hz, NCH<sub>2</sub>), 6.98 (d, 2H, J = 3 Hz, ArH), 7.18 (d, 2H, J = 3 Hz, ArH). Anal. Calcd for C<sub>15</sub>H<sub>21</sub>N<sub>3</sub>O<sub>2</sub>S<sub>2</sub>: C, 53.07; H, 6.23; N, 12.38; S, 18.89. Found: C, 52.93; H, 6.20; N, 12.30; S, 19.05.

4-(Diethylamino)-5-(3-nitrophenylimino)-5H-2-oxo-1,2,3-dithiazole (6j): To a solution of 31 (91 mg, 0.350 mmol) and pyridine (61 mg, 0.767 mmol) in CH<sub>2</sub>Cl<sub>2</sub> was dropwisely added thionyl chloride (104 mg, 0.877 mmol) in CH<sub>2</sub>Cl<sub>2</sub> for 40 min. The mixture was stirred for 7 h and worked up as with 6a. Chromatography (2 × 14 cm) of the residue using a mixture of acetone and CH<sub>2</sub>Cl<sub>2</sub> (1:4) gave 6j (50 mg, 47%); IR (neat) 2960, 1581, 1550, 1342, 1135, 911 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  1.20-1.46 (m, 6H, 2CH<sub>3</sub>), 3.75 (q, 2H, J = 7 Hz, NCH<sub>2</sub>), 4.05 (q, 2H, J = 7 Hz, NCH<sub>2</sub>), 7.17 (d, 2H, J = 8 Hz, ArH), 8.30 (d, 2H, J = 8 Hz, ArH). Anal. Calcd for C<sub>12</sub>H<sub>14</sub>N<sub>4</sub>O<sub>3</sub>S<sub>2</sub>: C, 44.16; H, 4.32; N, 17.17; S, 19.65. Found: C, 44.04; H,4.30; N, 17.10; S, 19.81.

**4-(Di-***n***-propylamino)-5-(3-nitrophenylimino)-5H-2-oxo-1,2,3-dithiazole (6k)**: To a solution of **3m** (106 mg, 0.344 mmol) and pyridine (59 mg, 0.742 mmol) in CH<sub>2</sub>Cl<sub>2</sub> was dropwisely added thionyl chloride (122 mg, 1.03 mmol) in CH<sub>2</sub>Cl<sub>2</sub> for 30 min. The mixture was stirred for 2 h and worked up as with **6a**. Chromatography (2 × 15 cm) of the residue using CH<sub>2</sub>Cl<sub>2</sub> gave **6k** (67 mg, 55%); IR (neat) 1590, 1549, 1522, 1341, 1130, 685 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  0.79-1.07 (m, 6H, 2CH<sub>3</sub>), 1.64-2.01 (m, 4H, 2CH<sub>2</sub>), 3.82 (t, 2H, J = 7 Hz, NCH<sub>2</sub>), 3.96 (t, 2H, J = 7 Hz, NCH<sub>2</sub>), 7.23-8.15 (m, 4H, ArH Anal. Calcd for C<sub>14</sub>H<sub>18</sub>N<sub>4</sub>O<sub>3</sub>S<sub>2</sub>: C, 47.44; H, 5.12; N, 15.81; S, 18.09. Found: C, 47.32; H, 5.09; N, 15.80; S, 18.24.

General Procedure for the Reactions of 2 with *m*-Chloroperbenzoic acid (*m*-CPBA). To a solution of 2 (0.1-1 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (50 ml) was added *m*-CPBA (0.3-1 mmol, 50-60%). The mixture was stirred for an appropriate time at room temperature. After the solvent was evaporated in vacuo, the residue was chromatographed on a silica gel column (70-230 mesh,  $2 \times 16$  cm). Elution with *n*-hexane, followed by CH<sub>2</sub>Cl<sub>2</sub> gave 6.

**6a**: A mixture of 4-(diethylamino)-5-(4-nitrophenylimino)-5*H*-1,2,3-dithiazole (31 mg, 0.110 mmol) and *m*-CPBA (38 mg, 0.1 mmol) in CH<sub>2</sub>Cl<sub>2</sub> was stirred for 1 h. Chromatography of the residue gave **6a** (16 mg, 44%).

6b: A mixture of 2b (167 mg, 0.493 mmol) and *m*-CPBA (170 mg, 0.5 mmol) in  $CH_2Cl_2$  was stirred for 35 min. Chromatography of the residue gave 6b (106 mg, 61%).

6c: A mixture of 2c (394 mg, 1.08 mmol) and *m*-CPBA (370 mg, 1 mmol) in CH<sub>2</sub>Cl<sub>2</sub> was stirred for 40 min. Chromatography of the residue gave 6c (254 mg, 62%).

6e: A mixture of 2f (189 mg, 0.576 mmol) and *m*-CPBA (199 mg, 0.6 mmol) in  $CH_2Cl_2$  was stirred for 50 min. Chromatography of the residue gave 6e (111 mg, 56%).

**6g**: A mixture of **2h** (60 mg, 0.219 mmol) and *m*-CPBA (68 mg, 0.2 mmol) in  $CH_2Cl_2$  was stirred for 45 min. Chromatography of the residue gave **6g** (30 mg, 47%).

**6h**: A mixture of **2i** (48 mg, 0.148 mmol) and *m*-CPBA (51 mg, 0.15 mmol) in  $CH_2Cl_2$  was stirred for 70 min. Chromatography of the residue gave **6h** (15 mg, 30%).

6i: A mixture of 4-(di-*n*-butylamino)-5-(4-methoxyphenylimino)-5*H*-1,2,3-dithiazole (71 mg, 0.202 mmol) and *m*-CPBA (70 mg, 0.2 mmol) in CH<sub>2</sub>Cl<sub>2</sub> was stirred for 35 min. Chromatography of the residue gave 6i (39 mg, 52%); IR (neat) 1547, 1499, 1248, 1130 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  0.80 (m, 6H, 2CH<sub>3</sub>), 1.21-1.86 (m, 8H, 2CH<sub>2</sub>CH<sub>2</sub>), 3.62 (t, 2H, *J* = 7 Hz, NCH<sub>2</sub>), 3.81 (s, 3H, OCH<sub>3</sub>), 3.95 (t, 2H, *J* = 7 Hz, NCH<sub>2</sub>), 6.92 (d, 2H, *J* = 2 Hz ArH), 7.12 (d, 2H, *J* = 2 Hz ArH). Anal. Calcd for C<sub>17</sub>H<sub>25</sub>N<sub>3</sub>O<sub>2</sub>S<sub>2</sub>: C, 55.60; H, 6.86; N, 11.43; S, 17.45. Found: C, 55.48; H, 6.84; N, 11.37; S, 17.60.

6j: A mixture of 2j (68 mg, 0.242 mmol) and m-CPBA (83 mg, 0.25 mmol) in CH<sub>2</sub>Cl<sub>2</sub> was stirred for 50 min. Chromatography of the residue gave 6j (106 mg, 77%).

6k: A mixture of 2k (213 mg, 0.691 mmol) and m-CPBA (109 mg, 0.7 mmol) in CH<sub>2</sub>Cl<sub>2</sub> was stirred for 1
h. Chromatography of the residue gave 6k (117 mg, 68%).

**4-(Di-***n***-butylamino)-5-(4-nitrophenylimino)-5H-2,2-dioxo-1,2,3-dithiazole** (7a): To a solution of 3c (176 mg, 0.523 mmol) and pyridine (88 mg, 1.11 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (40 ml) was dropwisely added SO<sub>2</sub>Cl<sub>2</sub> (77 mg, 0.573 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (20 ml) for 1 h. The mixture was stirred for 3 days at room temperature. Chromatography of the residue on a silica gel column (70-230 mesh,  $2 \times 19$  cm) gave 7a (30 mg, 14%) and 3c (76 mg, 43%). 7a: IR (neat) 1571, 1507, 1330 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  0.80-1.71 (m, 14H, 2CH<sub>3</sub>), 3.65 (t, 4H, J = 6 Hz, 2NCH<sub>2</sub>), 7.13 (d, 2H, J = 10 Hz, ArH), 8.30 (d, 2H, J = 10 Hz ArH); MS (m/z) 399 (M<sup>+</sup> + 1, 2.0), 367 (67.1), 323 (51.3). Anal. Calcd for C<sub>16</sub>H<sub>22</sub>N<sub>4</sub>O<sub>4</sub>S<sub>2</sub>: C, 48.22; H, 5.56; N, 14.06; S, 16.09. Found: C, 48.10; H, 5.54; N, 14.02; S, 16.25.

4-(Di-*n*-propylamino)-5-(3-nitrophenylimino)-5H-2,2-dioxo-1,2,3-dithiazole (7b): To a solution of 3m (206 mg, 0.668 mmol) and pyridine (106 mg, 1.33 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (40 ml) was dropwisely added SO<sub>2</sub>Cl<sub>2</sub> (91 mg, 0.672 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (20 ml) for 40 min. The mixture was stirred for 23 h and worked up as with 7a. Chromatography of the residue gave 7b (26 mg, 11%) and 3m (95 mg, 46%). 7b: IR (neat) 1576, 1517, 1339 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  0.91 (t, 6H, J = 7 Hz, 2CH<sub>3</sub>), 1.69 (sextet, 4H, J = 6 Hz, 2CH<sub>2</sub>), 3.64 (t, 4H, J = 10 Hz, 2NCH<sub>2</sub>), 7.24-8.09 (m, 4H, ArH); MS (m/z) 371 (M<sup>+</sup> + 1, 18.3), 339 (100), 309 (51.1). Anal. Calcd for C<sub>14</sub>H<sub>18</sub>N<sub>4</sub>O<sub>4</sub>S<sub>2</sub>: C, 45.39; H, 4.90; N, 15.12; S, 17.31. Found: C, 45.27; H, 4.87; N, 15.06; S, 17.45.

4-(Di-*n*-propylamino)-5-(4-methoxyphenylimino)-5H-2,2-dioxo-1,2,3-dithiazole (7c): To a solution of 3i (191 mg, 0.651 mmol) and pyridine (108 mg, 1.36 mmol) in  $CH_2Cl_2$  (40 ml) was dropwisely added  $SO_2Cl_2$  (96 mg, 0.709 mmol) in  $CH_2Cl_2$  (20 ml) for 12 h. The mixture was stirred for 23 h and worked up as

with 7a. Chromatography of the residue gave 7c (23 mg, 10%) and 3i (85 mg, 45%). 7c: IR (neat) 1581, 1494, 1245, 1035 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  0.88 (t, 6H, J = 6 Hz, 2CH<sub>3</sub>), 1.88 (sextet, 4H, J = 7 Hz, 2CH<sub>2</sub>), 3.60 (t, 4H, J = 10 Hz, 2NCH<sub>2</sub>), 3.80 (s, 3H, OCH<sub>3</sub>), 7.01 (d, 2H, J = 7 Hz, ArH), 7.20 (d, 2H, J = 7 Hz, ArH); MS (m/z) 356 (M<sup>+</sup> + 1, 39.1), 324 (88.0), 294 (98.1). Anal. Calcd for C<sub>15</sub>H<sub>21</sub>N<sub>3</sub>O<sub>3</sub>S<sub>2</sub>: C, 50.68; H, 5.95; N, 11.82; S, 18.04. Found: C, 50.57; H, 5.94; N, 11.80; S, 18.15.

**4-(Di-***n***-propylamino)-5-(4-nitrophenylimino)-2-(phenylimino)-\Delta^3-thiazoline (8a)**: A mixture of **3b** (236 mg, 0.765 mmol), pyridine (147 mg, 1.85 mmol), and *N*-phenylimidoyl dichloride (528 mg, 3.03 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (40 ml) was refluxed for 5 h. Chromatography of the reaction mixture on a silica gel column (70-230 mesh,  $3 \times 20$  cm) using a mixture of *n*-hexane and CH<sub>2</sub>Cl<sub>2</sub> (1:1) gave 4-(di-*n*-propylamino)-1-(4-nitrophenyl)-2-(phenylimino)-3-imidazoline-5-thione (**9a**) (16 mg, 5%). Elution with CH<sub>2</sub>Cl<sub>2</sub> gave **8a** (292 mg, 93%); IR (neat) 1613, 1544, 1435, 1331 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  0.85-1.06 (m, 6H, 2CH<sub>3</sub>), 1.61-2.00 (m, 4H, 2CH<sub>2</sub>), 3.76 (t, 2H, *J* = 8 Hz, NCH<sub>2</sub>), 4.02 (t, 2H, *J* = 8 Hz, NCH<sub>2</sub>), 6.85-7.35 (m, 7H, ArH), 8.22 (d, 2H, *J* = 8 Hz, ArH); MS (m/z) 409 (M<sup>+</sup>, 8.9), 380 (33.8), 235 (11.5), 181 (10.4), 161 (16.7). Anal.Calcd for C<sub>21</sub>H<sub>23</sub>N<sub>5</sub>O<sub>2</sub>S: C, 61.57; H, 5.64; N, 17.07; S, 7.88. Found: C, 61.46; H, 5.61; N, 17.01; S, 7.99.

4-(Di-*n*-butylamino)-5-(4-nitrophenylimino)-2-(phenylimino)- $\Delta^3$ -thiazoline (8b): A mixture of 3c (225 mg, 0.669 mmol), pyridine (108 mg, 1.36 mmol), and *N*-phenylimidoyl dichloride (528 mg, 3.03 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (40 ml) was stirred for 3 days at room temperature. Chromatography of the reaction mixture using a mixture of *n*-hexane and CH<sub>2</sub>Cl<sub>2</sub> (1:1) gave 4-(di-*n*-butylamino)-1-(4-nitrophenyl)-2-(phenylimino)-3-imidazoline-5-thione (9b) (25 mg, 9%). Elution with CH<sub>2</sub>Cl<sub>2</sub> (40 ml) gave 8b (265 mg, 91%); IR (neat) 1613, 1546, 1437, 1338 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 0.80-1.04 (m, 6H, 2CH<sub>3</sub>), 1.26-1.73 (m, 8H, 2CH<sub>2</sub>CH<sub>2</sub>), 3.76 (t, 2H, *J* = 8 Hz, NCH<sub>2</sub>), 4.04 (t, 2H, *J* = 8 Hz, NCH<sub>2</sub>), 6.85-7.34 (m, 7H, ArH), 8.20 (d, 2H, *J* = 8 Hz, ArH); MS (m/z) 437 (M<sup>4</sup>, 28.5), 394 (36.4), 235 (14.7), 189 (10.0). Anal. Calcd for C<sub>23</sub>H<sub>27</sub>N<sub>5</sub>O<sub>2</sub>S: C, 63.13; H, 6.22; N, 16.01; S, 7.33. Found: C, 63.03; H, 6.21; N, 16.01; S, 7.43.

**4-(Di-***n***-propylamino)-5-(2-methyl-4-nitrophenylimino)-2-(phenylimino)-\Delta^3-thiazoline (8c)**: A mixture of **3e** (113 mg, 0.392 mmol), pyridine (78 mg, 0.989 mmol), and *N*-phenylimidoyl dichloride (277 mg, 1.59 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (40 ml) was refluxed for 6 h. Chromatography of the reaction mixture using a mixture of *n*hexane and CH<sub>2</sub>Cl<sub>2</sub> (1:1) gave 4-(di-*n*-propylamino)-1-(2-methyl-4-nitrophenyl)-2-(phenylimino)-3-imidazoline-5-thione (**9c**) (15 mg, 10%); IR (neat) 1558 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  0.82-1.01 (m, 6H, 2CH<sub>3</sub>), 1.62-1.94 (m, 4H, 2CH<sub>2</sub>), 2.21 (s, 3H, CH<sub>3</sub>), 3.81 (t, 2H, *J* = 8 Hz, NCH<sub>2</sub>), 4.25 (t, 2H, *J* = 8 Hz, NCH<sub>2</sub>), 6.85-7.51 (m, 6H, ArH), 8.16 (d, 2H, *J* = 8 Hz, ArH); MS (m/z) 423 (M<sup>+</sup>, 15.1), 380 (100), 350 (11.2). Anal. Calcd for C<sub>22</sub>H<sub>25</sub>N<sub>5</sub>O<sub>2</sub>S: C, 62.39; H, 5.95; N, 16.54; S, 7.57. Found: C, 62.25; H, 5.90; N, 16.47; S, 7.76. Elution with CH<sub>2</sub>Cl<sub>2</sub> gave 8c (136 mg, 89%) ; IR (neat) 1608, 1557, 1432, 1333, 1133, 1050 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ 0.81-1.02 (m, 6H, 2CH<sub>3</sub>), 1.64-1.99 (m, 4H, 2CH<sub>2</sub>), 2.19 (s, 3H, CH<sub>3</sub>), 3.76 (t, 2H, *J* = 8 Hz, NCH<sub>2</sub>), 4.04 (t, 2H, J = 8 Hz, NCH<sub>2</sub>), 6.78-7.33 (m, 6H, ArH), 8.03 (d, 2H, J = 8 Hz, ArH); MS (m/z) 423 (M<sup>+</sup>, 8.8), 394 (17.6), 163 (19.9), 161 (14.9). Anal. Calcd for C<sub>22</sub>H<sub>25</sub>N<sub>5</sub>O<sub>2</sub>S: C, 62.39; H, 5.95; N, 16.54; S, 7.57. Found: C, 62.39; H, 5.93; N, 16.49; S, 7.74.

**5-(4-Chlorophenylimino)-4-(di-***n***-propylamino)-2-(phenylimino)-Δ<sup>3</sup>-thiazoline (8d)**: A mixture of **3f** (95 mg, 0.319 mmol), pyridine (64 mg, 0.804 mmol), and *N*-phenylimidoyl dichloride (224 mg, 1.29 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (40 ml) was refluxed for 6 h. Chromatography of the reaction mixture using a mixture of *n*-hexane and CH<sub>2</sub>Cl<sub>2</sub> (1:1) gave 1-(4-chlorophenylimino)-4-(di-*n*-propylamino)-2-(phenylimino)-3-imidazoline-5-thione (**9d**) (10 mg, **8%**); IR (neat) 1590, 1558 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 0.80-1.00 (m, 6H, 2CH<sub>3</sub>), 1.58-1.92 (m, 4H, 2CH<sub>2</sub>), 3.60 (t, 2H, J = 8 Hz, NCH<sub>2</sub>), 4.28 (t, 2H, J = 8 Hz, NCH<sub>2</sub>), 7.03-7.53 (m, 9H, ArH); MS (m/z) 400 (M<sup>+</sup> + 2, 3.2), 398 (M<sup>+</sup>, 8.7), 385 (38.0), 383 (100), 368 (63.6), 326 (14.3). Anal. Calcd for C<sub>21</sub>H<sub>23</sub>ClN<sub>4</sub>S: C, 63.22; H, 5.81; N, 14.04; S, 8.04. Found: C,63.11; H, 5.80; N, 14.02; S, 8.17. Elution with CH<sub>2</sub>Cl<sub>2</sub> gave **8d** (89 mg, 70%) ; IR (neat) 1606, 1541, 1472, 1434, 1131, 1085, 1043 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 0.78-0.99 (m, 6H, 2CH<sub>3</sub>), 1.68-1.99 (m, 4H, 2CH<sub>2</sub>), 3.72 (t, 2H, J = 8 Hz, NCH<sub>2</sub>), 4.00 (t, 2H, J = 8 Hz, NCH<sub>2</sub>), 6.81-7.43 (m, 9H, ArH); MS (m/z) 400 (M<sup>+</sup> + 2, 23.1), 398 (M<sup>+</sup>, 100), 371 (82.2), 369 (86.1), 354 (34.1), 144 (48.0). Anal. Calcd for

C21H23CIN4S: C, 63.22; H, 5.81; N, 14.04; S, 8.04. Found: C, 63.09; H, 5.79; N, 14.01; S, 8.19.

**5-(4-Bromophenylimino)-4-(di-***n***-propylamino)-2-(phenylimino)-A^3-thiazoline (8e): A mixture of 3g** (115 mg, 0.336 mmol), pyridine (69 mg, 0.865 mmol), and *N*-phenylimidoyl dichloride (224 mg, 1.29 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (40 ml) was refluxed for 7 h. Chromatography of the reaction mixture using a mixture of *n*-hexane and CH<sub>2</sub>Cl<sub>2</sub> (1:1) gave 1-(4-bromophenyl)-4-(di-*n*-propylamino)-2-(phenylimino)-3-imidazoline-5-thione (9e) (15 mg, 10%); IR (neat) 1587, 1555 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  0.90-1.00 (m, 6H, 2CH<sub>3</sub>), 1.58-1.92 (m, 4H, 2CH<sub>2</sub>), 3.59 (t, 2H, *J* = 8 Hz, NCH<sub>2</sub>), 4.18 (t, 2H, *J* = 8 Hz, NCH<sub>2</sub>), 6.91-7.43 (m, 7H, ArH), 7.63 (d, 2H, *J* = 8 Hz, ArH); MS (m/z) 444 (M<sup>+</sup> + 2, 51.2), 442 (M<sup>+</sup>, 46.0), 415 (55.8), 413 (65.6), 195 (22.8), 144 (100). Anal. Calcd for C<sub>21</sub>H<sub>23</sub>BrN<sub>4</sub>S: C, 56.88; H, 5.23; N, 12.64; S, 7.23. Found: C, 56.76; H, 5.22; N, 12.60; S, 7.36. Elution with CH<sub>2</sub>Cl<sub>2</sub> gave **8e** (105 mg, 70%) ; IR (neat) 1606, 1541, 1470, 1434, 1366, 1050 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  0.90-1.00 (m, 6H, 2CH<sub>3</sub>), 1.58-1.98 (m, 4H, 2CH<sub>2</sub>), 3.69 (t, 2H, *J* = 8 Hz, NCH<sub>2</sub>), 3.98 (t, 2H, *J* = 8 Hz, NCH<sub>2</sub>) , 6.77-7.49 (m, 9H, ArH); MS (m/z) 444 (M<sup>+</sup> + 2, 81.5), 442 (M<sup>+</sup>, 68.2), 415 (88.9), 413(85.6), 184 (28.4), 182 (30.7), 144 (100). Anal. Calcd for C<sub>21</sub>H<sub>23</sub>BrN<sub>4</sub>S: C, 56.88; H, 5.23; N, 12.64; S, 7.23. Found: C, 56.76; H, 5.22; N, 12.60; S, 7.36.

4-(Di-*n*-propylamino)-5-(4-methylphenylimino)-2-(phenylimino)- $\Delta^3$ -thiazoline (8f): A mixture of 3h (108 mg, 0.389 mmol), pyridine (78 mg, 0.989 mmol), and *N*-phenylimidoyl dichloride (271 mg, 1.55 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (40 ml) was refluxed for 7 h. Chromatography of the reaction mixture using a mixture of *n*-hexane and CH<sub>2</sub>Cl<sub>2</sub> (1:1) gave 4-(di-*n*-propylamino)-2-(phenylimino)-1-(4-methylphenyl)-3-imidazoline-5-thione (9f) (18 mg, 12%); IR (neat) 1558 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  0.85-1.02 (m, 6H, 2CH<sub>3</sub>), 1.58-1.90 (m, 4H, 2CH<sub>2</sub>), 2.39

(s, 3H, CH<sub>3</sub>), 3.61 (t, 2H, J = 8 Hz, NCH<sub>2</sub>), 4.30 (t, 2H, J = 8 Hz, NCH<sub>2</sub>), 7.01-7.53 (m, 9H, ArH); MS (m/z) 378 (M<sup>+</sup>, 6.3), 335 (100), 305 (9.5). Anal. Calcd for C<sub>22</sub>H<sub>26</sub>N<sub>4</sub>S: C, 69.81; H, 6.92; N, 14.80; S, 8.47. Found: C, 69.71; H, 6.90; N, 14.75; S, 8.64. Elution with CH<sub>2</sub>Cl<sub>2</sub> gave 8f (85 mg, 58%) ; IR (neat) 1611, 1539, 1435, 1374, 1136, 1048 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  0.82-1.00 (m, 6H, 2CH<sub>3</sub>), 1.61-1.98 (m, 4H, 2CH<sub>2</sub>), 2.30 (s, 3H, CH<sub>3</sub>), 3.73 (t, 2H, J = 8 Hz, NCH<sub>2</sub>), 4.02 (t, 2H, J = 8 Hz, NCH<sub>2</sub>), 6.82-7.85 (m, 9H, ArH); MS (m/z) 378 (M<sup>+</sup>, 4.3), 349 (35.4), 175 (27.7), 150 (19.8), 144 (100). Anal. Calcd for C<sub>22</sub>H<sub>26</sub>N<sub>4</sub>S: C, 69.81; H, 6.92; N, 14.80; S, 8.47. Found: C, 69.72; H, 6.91; N, 14.75; S, 8.61.

**4-(Di-***n***-propylamino)-5-(4-methoxyphenylimino)-2-(phenylimino)-\Delta^3-thiazoline (8g)**: A mixture of **3i** (124 mg, 0.423 mmol), pyridine (83 mg, 1.05 mmol), and *N*-phenylimidoyl dichloride (290 mg, 1.67 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (40 ml) was refluxed for 5 h. Chromatography of the reaction mixture using a mixture of *n*-hexane and CH<sub>2</sub>Cl<sub>2</sub> (1:1) gave 4-(di-*n*-propylamino)-1-(4-methoxyphenyl)-2-(phenylimino)-3-imidazoline-5-thione (**9g**) (24 mg, 14%); IR (neat) 1555 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  0.82-1.02 (m, 6H, 2CH<sub>3</sub>), 1.64-2.01 (m, 4H, 2CH<sub>2</sub>), 3.58 (t, 2H, *J* = 8 Hz, NCH<sub>2</sub>), 3.80 (s, 3H, OCH<sub>3</sub>), 4.31 (t, 2H, *J* = 8 Hz, NCH<sub>2</sub>), 6.92-7.52 (m, 9H, ArH); MS (m/z) 394 (M<sup>+</sup>, 3.0), 365 (6.3), 191 (18.3), 111 (27.1). Anal. Calcd for C<sub>22</sub>H<sub>25</sub>N<sub>4</sub>OS: C, 67.15; H, 6.40; N, 14.23; S, 8.15. Found: C, 67.01; H, 6.37; N, 14.17; S, 8.30. Elution with CH<sub>2</sub>Cl<sub>2</sub> gave **8g** (94 mg, 56%); IR (neat) 1600, 1538, 1494, 1432, 1248, 1133, 1045, 1027 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  0.82-1.02 (m, 6H, 2CH<sub>3</sub>), 1.62-2.00 (m, 4H, 2CH<sub>2</sub>), 3.62 (t, 2H, *J* = 8 Hz, NCH<sub>2</sub>), 3.75 (s, 3H, OCH<sub>3</sub>), 3.98 (t, 2H, *J* = 8 Hz, NCH<sub>2</sub>), 6.79-7.45 (m, 9H, ArH); MS (m/z) 394 (M<sup>+</sup>, 7.5), 365 (10.6), 191 (13.7), 178 (16.0), 144 (100). Anal. Calcd for C<sub>22</sub>H<sub>26</sub>N<sub>4</sub>OS: C, 67.15; H, 6.40; N, 14.23; S, 8.15. Found: C, 67.15; H, 6.40; N, 14.23; S, 8.15. Found: C, 67.15; H, 6.40; N, 14.23; S, 8.15. Found: C, 67.15; H, 6.40; N, 14.21; S, 8.28.

**4-(Di-***n***-butylamino)-5-(4-methoxyphenylimino)-2-(phenylimino)-3-thiazoline (8h)**: A mixture of **3j** (134 mg, 0.417 mmol), pyridine (83 mg, 1.05 mmol), and *N*-phenylimidoyl dichloride (290 mg, 1.67 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (40 ml) was stirred for 3.5 days at room temperature. Chromatography of the reaction mixture using a mixture of *n*-hexane and CH<sub>2</sub>Cl<sub>2</sub> (1:1) gave 1-4-(di-*n*-butylamino)-1-(4-methoxyphenyl)-2-(phenylimino)-3-imidazoline-5-thione (**9h**) (17 mg, 10%); IR (neat) 1555 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  0.82-1.02 (m, 6H, 2CH<sub>3</sub>), 1.21-1.82 (m, 8H, 2CH<sub>2</sub>CH<sub>2</sub>), 3.63 (t, 2H, *J* = 8 Hz, NCH<sub>2</sub>), 3.82 (s, 3H, OCH<sub>3</sub>), 4.35 (t, 2H, *J* = 8 Hz, NCH<sub>2</sub>), 6.93-7.44 (m, 9H, ArH); MS (m/z) 422 (M<sup>+</sup>, 8.0), 399 (50.1), 367 (100). Anal. Calcd for C<sub>24</sub>H<sub>30</sub>N<sub>4</sub>OS: C, 68.21; H, 7.16; N, 13.26; S, 7.25. Found: C, 68.09; H, 7.15; N, 13.21; S, 7.35. Elution with CH<sub>2</sub>Cl<sub>2</sub> gave **8h** (113 mg, 64%) ; IR (neat) 1602, 1541, 1437, 1366, 1248, 1134, 1035 cm<sup>-1</sup>, <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  0.83-0.99 (m, 6H, 2CH<sub>3</sub>), 1.20-1.80 (m, 8H, 2CH<sub>2</sub>CH<sub>2</sub>), 3.69 (t, 2H, *J* = 8 Hz, NCH<sub>2</sub>), 3.75 (s, 3H, OCH<sub>3</sub>), 4.06 (t, 2H, *J* = 8 Hz, NCH<sub>2</sub>), 6.77-7.35 (m, 9H, ArH); MS (m/z) 422 (M<sup>+</sup>, 5.3), 379 (10.1), 191 (23.3), 144 (100). Anal. Calcd for C<sub>24</sub>H<sub>30</sub>N<sub>4</sub>OS: C, 68.21; H, 7.16; N, 13.26; S, 7.25. Found: C, 68.10; H, 7.14; N, 13.21; S, 7.37.

4-(Di-n-propylamino)-5-(3-nitrophenylimino)-2-(phenylimino)-△<sup>3</sup>-thiazoline (8i): A mixture of 3m (48 mg, 0.156 mmol), pyridine (30 mg, 0.383 mmol), and N-phenylimidoyl dichloride (108 mg, 0.621 mmol) in

CH<sub>2</sub>Cl<sub>2</sub> (40 ml) was stirred for 3.5 days at room temperature. Chromatography of the reaction mixture using a mixture of *n*-hexane and CH<sub>2</sub>Cl<sub>2</sub> (1:1) gave 4-(di-*n*-propylamino)-1-(3-nitrophenyl)-2-(phenylimino)-3-imidazoline-5-thione (9i) (15 mg, 10%). Elution with CH<sub>2</sub>Cl<sub>2</sub> gave 8i (105 mg, 70%); IR (neat) 1610, 1542, 1435, 1344, 1136, 1050 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  0.83-1.04 (m, 6H, 2CH<sub>3</sub>), 1.62-1.99 (m, 4H, 2CH<sub>2</sub>), 3.74 (t, 2H, J = 8 Hz, NCH<sub>2</sub>), 4.04 (t, 2H, J = 8 Hz, NCH<sub>2</sub>), 6.85-8.05 (m, 9H, ArH); MS (m/z) 409 (M<sup>+</sup>, 9.1), 380 (24.1), 235 (13.0), 181 (11.5), 161 (17.1). Anal. Calcd for C<sub>21</sub>H<sub>23</sub>N<sub>5</sub>O<sub>2</sub>S: C, 61.59; H, 5.66; N, 17.10; S, 7.83. Found: C, 61.46; H, 5.67; N, 17.05; S, 7.95.

**4-(Di-***n***-propylamino)-3-(4-nitrophenylimino)-benzothiazocine-1,6-dione (10a)**: To a solution of **3b** (85 mg, 0.276 mmol) and pyridine (49 mg, 0.618 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (30 ml) was dropwisely added phthaloyl chloride (56 mg, 0.278 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (20 ml) for 1h. The mixture was stirred for 29 h at room temperature. Chromatography of the reaction mixture on a silica gel column (70-230 mesh,  $3.5 \times 12$  cm) using CH<sub>2</sub>Cl<sub>2</sub> gave **10a** (92 mg, 76%); IR (neat) 1781, 1579, 1520, 1344, 1269, 1094, 907 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  0.89 (t, 6H, J = 7 Hz, 2CH<sub>3</sub>), 1.75 (sextet, 4H, J = 7 Hz, 2CH<sub>2</sub>), 3.90 (m, 4H, 2NCH<sub>2</sub>), 7.10 (d, 2H, J = 8 Hz, ArH), 7.34-7.78 (m, 4H, ArH), 8.13 (d, 2H, J = 8 Hz); MS (m/z) 439 (M<sup>+</sup> + 1, 22.0), 425 (6.1), 409 (7.0), 277 (11.1). Anal. Calcd for C<sub>22</sub>H<sub>22</sub>N<sub>4</sub>O<sub>4</sub>S: C, 60.26; H, 5.06; N, 12.78; S, 7.31. Found: C, 60.14; H, 5.05; N, 12.73; S, 7.43.

**4-(Di-***n***-butylamino)-3-(4-nitrophenylimino)-2,5-benzothiazocine-1,6-dione (10b)**: To a solution of **3c** (79 mg, 0.235 mmol) and pyridine (44 mg, 0.556 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (30 ml) was dropwisely added phthaloyl chloride (49 mg, 0.243 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (20 ml). The mixture was stirred for 27 h and worked up as with **10a**. Chromatography of the reaction mixture using CH<sub>2</sub>Cl<sub>2</sub> gave **10b** (87 mg, 80%); IR (neat) 1784, 1598, 1525, 1346, 1094, 906 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  0.90 (t, 6H, J = 7 Hz, 2CH<sub>3</sub>), 1.21-1.91 (m, 8H, 2CH<sub>2</sub>CH<sub>2</sub>), 3.90 (m, 4H, 2NCH<sub>2</sub>), 7.21 (d, 2H, J = 10 Hz, ArH), 7.38-7.78 (m, 4H, ArH), 8.13 (d, 2H, J = 10 Hz, ArH); MS (m/z) 467 (M<sup>+</sup> + 1, 37.0), 453 (20.1), 437 (11.2), 423 (10.5). Anal. Calcd for C<sub>24</sub>H<sub>26</sub>N<sub>4</sub>O<sub>4</sub>S: C, 61.78; H, 5.61; N, 12.01; S, 6.87. Found: C, 61.65; H, 5.58; N, 12.00; S, 6.99.

**4-(Di-***n***-propylamino)-3-(2-methyl-4-nitrophenylimino)-2,5-benzothiazocine-1,6-dione (10c**): To a solution of **3e** (117 mg, 0.406 mmol) and pyridine (73 mg, 0.927 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (30 ml) was dropwisely added phthaloyl chloride (85 mg, 0.416 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (20 ml). The mixture was stirred for 30 h and worked up as with **10a**. Chromatography of the reaction mixture using CH<sub>2</sub>Cl<sub>2</sub> gave **10c** (141 mg, 83%); IR (neat) 1781, 1598, 1520, 1264, 1094, 914 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  0.91 (t, 6H, J = 7 Hz, 2CH<sub>3</sub>), 1.79 (sextet, 4H, J = 7 Hz, 2CH<sub>2</sub>), 2.41 (s, 3H, OCH<sub>3</sub>), 3.92 (m, 4H, 2NCH<sub>2</sub>), 6.42-8.13 (m, 7H, ArH); MS (m/z) 424 (M<sup>+</sup> + 1, 39.1), 407 (22.5), 393 (21.9). Anal. Calcd for C<sub>23</sub>H<sub>24</sub>N<sub>4</sub>O<sub>4</sub>S: C, 61.05; H, 5.35; N, 12.38; S, 7.09. Found: C, 59.94; H, 5.34; N, 12.33; S, 7.23.

3-(4-Chlorophenylimino)-4-(di-*n*-propylamino)-2,5-benzothiazocine-1,6-dione (10d): To a solution of 3f (101 mg, 0.339 mmol) and pyridine (59 mg, 0.742 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (30 ml) was dropwisely added

phthaloyl chloride (71 mg, 0.347 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (20 ml). The mixture was stirred for 23 h and worked up as with 10a. Chromatography of the reaction mixture using CH<sub>2</sub>Cl<sub>2</sub> gave 10d (113 mg, 78%); IR (neat) 1778, 1597, 1408, 1269, 1093, 906 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  0.91 (t, 6H, J = 7 Hz, 2CH<sub>3</sub>), 1.75 (sextet, 4H, J = 7 Hz, 2CH<sub>2</sub>), 3.91 (m, 4H, 2NCH<sub>2</sub>), 6.85-7.76 (m, 8H, ArH); MS (m/z) 428 (M<sup>+</sup> + 1, 100). 398 (35.5), 368 (17.5). Anal. Calcd for C<sub>22</sub>H<sub>22</sub>ClN<sub>3</sub>O<sub>2</sub>S: C, 61.75; H, 5.18; N, 9.82; S, 7.49. Found: C, 61.64; H, 5.15; N, 9.81; S, 7.62.

**3-(4-Bromophenylimino)-4-(di-***n***-propylamino)-2,5-benzothiazocine-1,6-dione (10e)**: To a solution of **3g** (89 mg, 0.260 mmol) and pyridine (50 mg, 0.569 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (30 ml) was dropwisely added phthaloyl chloride (52 mg, 0.257 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (20 ml). The mixture was stirred for 22 h and worked up as with **10a**. Chromatography of the reaction mixture using CH<sub>2</sub>Cl<sub>2</sub> gave **10e** (85 mg, 69%); IR (neat) 1779, 1597, 1405, 1270, 1094, 909, 723 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  0.91 (t, 6H, J = 7 Hz, 2CH<sub>3</sub>), 1.78 (sextet, 4H, J = 7 Hz, 2CH<sub>2</sub>), 3.89 (m, 4H, 2NCH<sub>2</sub>), 6.84 (d, 2H, J = 8 Hz, ArH), 7.38 (d, 2H, J = 8 Hz), 7.58-7.78 (m, 4H, ArH); MS (m/z) 472 (M<sup>+</sup> + 1, 100), 442 (42.1), 430 (23.1), 412 (23.0). Anal. Calcd for C<sub>22</sub>H<sub>22</sub>BrN<sub>3</sub>O<sub>2</sub>S: C, 55.94; H, 4.69; N, 8.90; S, 6.79. Found: C, 55.82; H, 4.67; N, 8.85; S, 6.94.

**4-(Di-***n***-propylamino)-3-(4-methylphenylimino)-2,5-benzothiazocine-1,6-dione (10f)**: To a solution of **3h** (115 mg, 0.414 mmol) and pyridine (73 mg, 0.927 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (30 ml) was dropwisely added phthaloyl chloride (85 mg, 0.416 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (20 ml). The mixture was stirred for 23 h and worked up as with **10a**. Chromatography of the reaction mixture using CH<sub>2</sub>Cl<sub>2</sub> gave **10f** (76 mg, 45%); IR (neat) 1774, 1590, 1402, 1267, 1094, 907 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  0.90 (t, 6H, J = 7 Hz, 2CH<sub>3</sub>), 1.78 (sextet, 4H, J = 7 Hz, 2CH<sub>2</sub>), 2.21 (s, 3H, CH<sub>3</sub>), 3.92 (m, 4H, 2NCH<sub>2</sub>), 6.73 (d, 2H, J = 12 Hz, ArH), 6.90 (d, 2H, J = 12 Hz, ArH), 7.32-7.75 (m, 4H, ArH); MS (m/z) 408 (M<sup>+</sup> + 1, 100), 378 (36.2), 366 (21.0). Anal. Calcd for C<sub>23</sub>H<sub>25</sub>N<sub>3</sub>O<sub>2</sub>S: C, 67.79; H, 6.18; N, 10.31; S, 7.87. Found: C, 67.66; H, 6.16; N, 10.27; S, 8.02.

**4-(Di-***n***-propylamino)-3-(4-methoxyphenylimino)-2,5-benzothiazocine-1,6-dione** (10g): To a solution of **3i** (83 mg, 0.283 mmol) and pyridine (49 mg, 0.618 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (30 ml) was dropwisely added phthaloyl chloride (58 mg, 0.285 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (20 ml). The mixture was stirred for 28 h and worked up as with **10a**. Chromatography of the reaction mixture using CH<sub>2</sub>Cl<sub>2</sub> gave **10g** (55 mg, 46%); IR (neat) 1778, 1597, 1406, 1269, 1096, 904 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  0.91 (t, 6H, J = 7 Hz, 2CH<sub>3</sub>), 1.72 (sextet, 4H, J = 7 Hz, 2CH<sub>2</sub>), 3.67 (s, 3H, OCH<sub>3</sub>), 3.82 (m, 4H, 2NCH<sub>2</sub>), 6.72 (d, 2H, J = 12 Hz, ArH), 6.90 (d, 2H, J = 12 Hz), 7.30-7.72 (m, 4H, ArH); MS (m/z) 424 (M<sup>+</sup> + 1, 82.7), 394 (17.5), 382 (10.2). Anal. Calcd for C<sub>23</sub>H<sub>25</sub>N<sub>3</sub>O<sub>3</sub>S: C, 65.23; H, 5.95; N, 9.92; S, 7.57. Found: C, 65.12; H, 5.94; N, 9.90; S, 7.69.

4-(Di-*n*-butylamino)-3-(4-methoxyphenylimino)-2,5-benzothiazocine-1,6-dione (10h): To a solution of 3j (132 mg, 0.410 mmol) and pyridine (71 mg, 0.903 mmol) in  $CH_2Cl_2$  (30 ml) was dropwisely added phthaloyl chloride (85 mg, 0.416 mmol) in  $CH_2Cl_2$  (20 ml). The mixture was stirred for 23 h and worked up as with 10a. Chromatography of the reaction mixture using  $CH_2Cl_2$  gave 10h (121 mg, 65%); IR (neat) 1778,

1595, 1403, 1096, 906 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  0.92 (t, 6H, J = 7 Hz, 2CH<sub>3</sub>), 1.22-1.93 (m, 8H, 2CH<sub>2</sub>CH<sub>2</sub>), 3.67 (s, 3H, OCH<sub>3</sub>), 3.92 (m, 4H, 2NCH<sub>2</sub>), 6.73 (d, 2H, J = 12 Hz, ArH), 6.90 (d, 2H, J = 12 Hz, ArH), 7.32-7.75 (m, 4H, ArH); MS (m/z) 452 (M<sup>+</sup> + 1, 100), 422 (31.9), 408 (31.6), 396 (20.1). Anal. Calcd for C<sub>23</sub>H<sub>29</sub>N<sub>3</sub>O<sub>3</sub>S: C, 66.48; H, 6.47; N, 9.31; S, 7.10. Found: C, 66.35; H, 6.47; N, 9.28; S, 7.24.

**4-(Di-***n***-propylamino)-3-(3-nitrophenylimino)-2,5-benzothiazocine-1,6-dione (10i)**: To a solution of **3m** (61 mg, 0.198 mmol) and pyridine (34 mg, 0.433 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (30 ml) was dropwisely added phthaloyl chloride (41 mg, 0.201 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (20 ml). The mixture was stirred for 21 h and worked up as with **10a**. Chromatography of the reaction mixture using CH<sub>2</sub>Cl<sub>2</sub> gave **10i** (62 mg, 71%); IR (neat) 1781, 1597, 1525, 1395, 1347, 1275, 1256, 1094, 914 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  0.91 (t, 6H, J = 7 Hz, 2CH<sub>3</sub>), 1.78 (sextet, 4H, J = 7 Hz, 2CH<sub>2</sub>), 3.82 (m, 4H, 2NCH<sub>2</sub>), 7.39-8.19 (m, 8H, ArH); MS (m/z) 439 (M<sup>+</sup> + 1, 28.3), 425 (8.2), 409 (10.2). Anal. Calcd for C<sub>22</sub>H<sub>22</sub>N<sub>4</sub>O<sub>4</sub>S: C, 60.26; H, 5.06; N, 12.78; S, 7.31. Found: C, 60.15; H, 5.03; N, 12.70; S, 7.48.

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#### **REFERENCES AND NOTES**

- 1. Lee, H.; Kim, K.; Whang, D.; Kim, K. J. Org. Chem. 1994, 59, 6179.
- 2. Unpublished result.
- (a) Fuchigami, T.; Nonaka, T. Chem. Lett. 1979, 829. (b) Boyer, J. H.; Frints P. J. A. J. Org. Chem. 1970, 35, 2499. (c) Tamaru, Y.; Amine, Y.; Yashide, Z. J. Am. Chem. Soc. 1982, 104, 4108.
- (a) Assef, G.; Kister, J.; Metzger, J. Tetrahedron Lett. 1976, 37, 3313. (b) Sawhney, S. N.; Boykin, D. W. J. Org. Chem. 1979, 44, 1136.
- Häfelinger, G. in *The Chemistry of Amidines and Imidates*; Patai, S. Ed.; John Wiley and Sons, Inc.: New York, 1975; Chap. 1, pp. 73-74.
- 6. Ref. 5, pp. 43-57.
- Gautier, J. A.; Miocque, M.; Farnoux, C. C. in *The Chemistry of Amidines and Imidates*; Patai, S. Ed.; John Wiley and Sons, Inc.: New York, 1975; Chap. 7, pp. 283-348.
- 8. Lumbroso, H.; Pifferi, G. Bull. Soc. Chim. Fr. 1969, 3401.
- 9. Lee, H.-S.; Kim, K. Tetrahedron Lett. 1996, 869.
- 10. Asinger, F; Thiel, M. Angew. Chem. 1958, 70, 667.
- 11. Schaumann, E.; Grabley, S.; Seidel, K. D.; Karsch E. Tetrahedron Lett. 1977, 1351.
- 12. Leonard, N. J.; Yethon, A. E. Tetrahedron Lett. 1965, 4259.
- 13. Black, D. K. J. Chem. Soc. 1966, 1123.
- 14. Ardill, H.; Grigg, R.; Sridharan, V.; Malone, J. J. Chem. Soc., Chem. Commun. 1987, 1296.
- 15. (a) Murpy, D. B. J. Org. Chem. 1964, 29, 1613. (b) Dyson, G. M. J. Chem. Soc. 1940, 191.

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