Photochromic dihetarylethenes

7.* Synthesis of bis(thienylazoles), photochromic analogs of diarylethenes**

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Procedures for the synthesis of 4,5-bis[2,5-dimethyl(3-thienyl)]-1,3-azoles based on 1,2-bis[2,5-dimethyl(3-thienyl)]-2-hydroxyethan-1-one, 2-chloro-1,2-bis[2,5-dimethyl(3-thienyl)]ethan-1-one, and 1,2-bis[2,5-dimethyl(3-thienyl)]ethane-1,2-dione were developed. Dithienylethenic compounds in which the thienyl rings are linked through the azole rings exhibit photochromic properties.

Key words: 1,2-dithienylethenes, 1,3-azoles, α-diketone, α-hydroxyketone, α-chloroketone, photochromes.

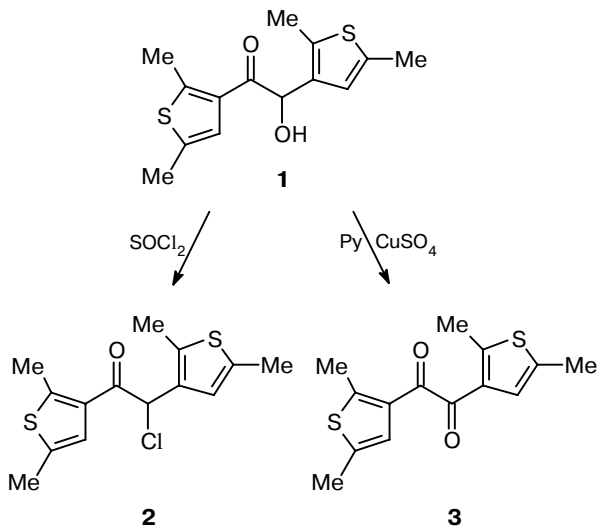
The chemistry of thermally irreversible photochromic dihetarylethenes is being developed intensively.[2—4] In most of such photochromes, the ethene fragments of perfluorocyclopentene, maleic anhydride, or maleimide serve as bridges.[1—4] It should be emphasized that only hexafluorocyclopentene photochromes were synthesized in rather high yields. The yields of products based on maleic anhydride or maleimide were no higher than 5%.

As part of continuing studies aimed at searching for new readily accessible photochromes, we developed procedures for the synthesis of dihetarylethenes in which the thienyl rings are linked through the 1,3-azole rings starting from 1,2-bis[2,5-dimethyl(3-thienyl)]-2-hydroxyethan-1-one (**1**), 2-chloro-1,2-bis[2,5-dimethyl(3-thienyl)]ethan-1-one (**2**), and 1,2-bis[2,5-dimethyl(3-thienyl)]ethane-1,2-dione (**3**).

One of the widely accepted approaches to the construction of 1,3-azoles containing substituents at positions 4 and 5 of the ring is based on the use of 1,2-bifunctional starting compounds, such as α-diketones, α-hydroxyketones (acyloins), and α-chloroketones.[5—7] Previously, we have described the synthesis of the key substrate, *viz.*, acyloin **1**.[8] α-Haloketone **2** and α-diketone **3** were synthesized starting from **1** (Scheme 1).

Treatment of acyloin **1** with thionyl chloride afforded unstable chloroketone **2**, which was used without additional purification. Oxidation of compound **1** in pyridine in the presence of copper sulfate gave rise to diketone **3** in quantitative yield.

Scheme 1



Substituted 4,5-bis[2,5-dimethyl(3-thienyl)]oxazoles **5** were prepared from acyloin **1** according to a procedure reported previously[5] (Scheme 2).

Intermediates **4**, which were obtained by the reactions of acyloin **1** with the corresponding benzoyl chlorides in pyridine, were introduced into the subsequent reactions without additional purification. Cyclization giving rise to the desired final products **5** was performed under the action of ammonium acetate on benzoates **4** in acetic acid.

* For Part 6, see Ref. 1.

** Dedicated to the memory of Professor Ya. L. Gol'dfarb on the occassion of his 100th birthday.

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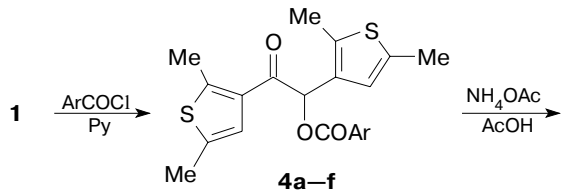
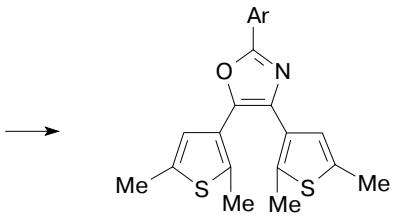
Scheme 2

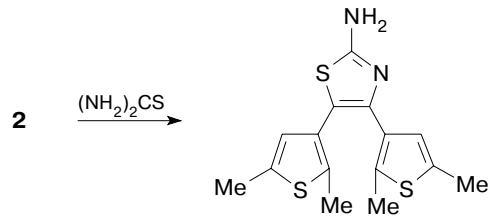




Ar = Ph (**a**); 4-MeC_6H_4 (**b**); 4-$NO_2C_6H_4$ (**c**); 4-ClC_6H_4 (**d**); 3,5-$(NO_2)_2C_6H_3$ (**e**); 4-$MeOC_6H_4$ (**f**)

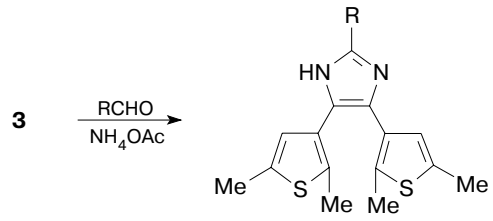
2-Amino-1,3-thiazole **6** was prepared by heating of α-chloroketone **2** with an excess of thiourea in aqueous ethanol[6] (Scheme 3).

Scheme 3



The reactions of diketone **3** with aldehydes in the presence of ammonium acetate in acetic acid performed according to a procedure reported previously[7] afforded various substituted 4,5-bis[2,5-dimethyl(3-thienyl)]imidazoles **7** (Scheme 4).

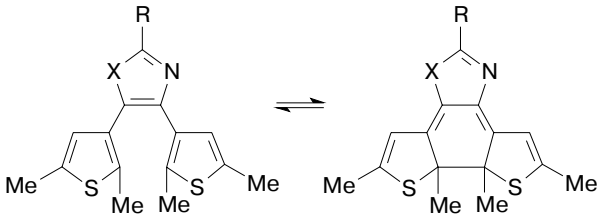
Scheme 4



7: R = Ph (**a**); 3,4,5-$(MeO)_3C_6H_2$ (**b**); 4-BrC_6H_4 (**c**); 4-MeC_6H_4 (**d**); 2-HOC_6H_4 (**e**); 4-$NO_2C_6H_4$ (**f**); 2-ClC_6H_4 (**g**); 2,4-$Cl_2C_6H_3$ (**h**); 2,5-$(MeO)_2C_6H_3$ (**i**); 4-ClC_6H_4 (**k**); *n*-C_6H_{13} (**l**); 3-pyridyl (**m**)

The photochemical characteristics of compounds **5—7** were examined in acetonitrile solutions. Most of these compounds (**5a**, **5b**, **5d**, **5f**, **6**, **7a—e**, **7g**, and **7i—m**) exhibit photochromic properties (Scheme 5). In our opinion, this fact indicates that the further synthesis of dihetarylethenes containing heterocyclic bridges is worthwhile.

Scheme 5



Mono- and dinitro-substituted oxazoles (**5c,e**) and dichloro- and nitro-substituted imidazoles (**7f,h**) do not exhibit photochromic properties and are resistant to UV irradiation even upon prolonged exposure. It is worthy of note that compounds containing electron-withdrawing groups in the aromatic ring do not possess the photochromic properties. Apparently, the presence of electron-withdrawing substituents leads to a decrease in the electron density at the carbon atoms at positions 2 and 2′ of the thiophene rings, thus hindering photocyclization.

The characteristic spectrum of photochrome **5a** is shown in Fig. 1.

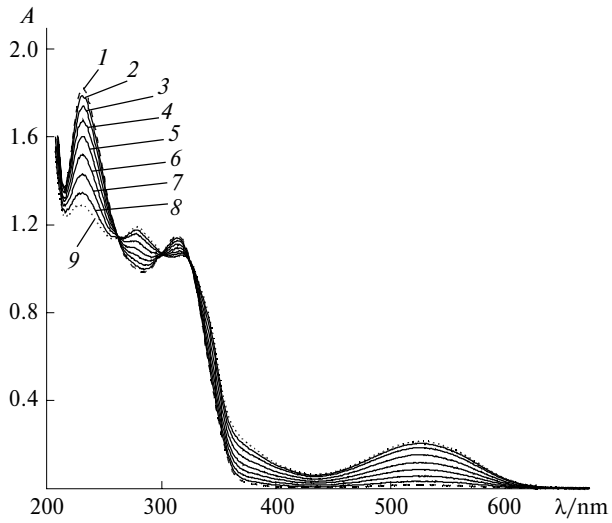


Fig. 1. Changes in the absorption spectrum of 4,5-bis[2,5-dimethyl(3-thienyl)]-2-phenyloxazole (**5a**) in a solution in acetonitrile before irradiation (open form) (*1*) and after irradiation with light at λ = 313 nm; the time of exposure: 40 s (*2*), 100 s (*3*), 3 min (*4*), 5 min (*5*), 8 min (*6*), 12 min (*7*), 17 min (*8*), and 22 min (*9*, the photostationary state (the maximum content of the cyclic form)).

Table 1. The long-wavelength absorption bands of compounds **5—7**

Compound	λ_{max}/nm	
	Open form (**A**)	Cyclic form (**B**)
5a	314	525
5b	313	523
5c	379	—
5d	320	530
5e	362	—
5f	312	513
6	308	485
7a	304	568
7b	308	516
7c	317	570
7d	304	558
7e	321	544
7f	395	—
7g	296	554
7h	317	—
7i	330	575
7k	315	570
7l	229	533
7m	315	566

The long-wavelength absorption bands of the open forms (Table 1) of 2-aryl-substituted dithienylazoles synthesized in this study are observed in the region of 304—330 nm, except for nitro derivatives **5c,e** and **7f**, whose spectra have analogous absorption bands in the region of 362—395 nm. In addition, the absorption spectra of the open forms of all 2-aryl-substituted dithienylazoles, except for those of hydroxy and methoxy derivatives, have a band at 230—236 nm. The maxima of the first absorption bands of the cyclic forms of photochromic oxazoles **5** and imidazoles **7** are observed at 513—575 nm and the corresponding band of thioazole **6** is observed at 485 nm. The long-wavelength absorption bands of the cyclic and open forms of photochromic imidazoles **7a,d,k** are shifted bathochromically (by ~40 nm) and hypsochromically (by 5—10 nm), respectively, compared to the analogously substituted photochromic oxazoles **5a,b,d**. In the case of the open forms of nonphotochromic imidazole **7f** and oxazole **5c**, this band is shifted batochromically by 16 nm.

The cyclic forms of all photochromes synthesized are thermally unstable. For oxazoles **5** and thiazole **6**, the decay periods are about several hours. For imidazoles **7**, these periods are no longer than 3 min. It should be noted that all these compounds exhibit low fatigue resistance and the optical densities of the cyclic forms are regained by no more than 80% after three- to fivefold photochromic conversions. Apparently, an increase in the fatigue resistance can be achieved either by additional introduction of the methyl groups at positions 4 and 4′ of the 2,5-dimethylthienyl rings[2] or by replacement of the methyl groups at positions 5 and 5′ by the fused benzoazole fragments.[1]

Experimental

The ^{1}H NMR spectra were recorded on Bruker AM-300 (300.13 MHz) and Bruker WM-250 (250.13 MHz) instruments in DMSO-d_6 and $CDCl_3$. The melting points were measured on a Boetius heating table and were not corrected. The course of the reactions and the purities of the products were monitored by TLC on Silufol UV-254 plates using an AcOEt—hexane mixture as the eluent. The samples were irradiated with a DRSh-500 mercury lamp using light filters to separate lines with wavelengths of 313, 546, and 578 nm. The intensity of irradiation of the mercury lamp was determined with the use of an F4 photodetector calibrated against a ferrioxalate actinometer[9] for λ = 313 nm and against an actinometer based on Reinecke salt[10] for λ = 546 and 578 nm. The absorption spectra were recorded on a Shimadzu UV-2101PC spectrophotometer. All reagents and solvents (Aldrich) were used without additional purification.

1,2-Bis[2,5-dimethyl(3-thienyl)]-2-hydroxyethan-1-one (1) was prepared according to a known procedure.[8]

2-Chloro-1,2-bis[2,5-dimethyl(3-thienyl)]ethan-1-one (2). A solution of acyloin **1** (0.28 g, 1 mmol) in $SOCl_2$ (1 mL) was stirred at ~20 °C for 2 h. Then $SOCl_2$ was distilled off *in vacuo* and the product was extracted with hexane. After evaporation of hexane, chloroketone **2** was obtained in a yield of 0.284 g (95%). ^{1}H NMR ($CDCl_3$), δ: 2.35 (s, 3 H, CH_3); 2.37 (s, 3 H, CH_3); 2.47 (s, 3 H, CH_3); 2.70 (s, 3 H, CH_3); 6.00 (s, 1 H, CH); 6.65 (s, 1 H, CH); 6.80 (s, 1 H, CH).

1,2-Bis[2,5-dimethyl(3-thienyl)]ethane-1,2-dione (3). A solution of acyloin **1** (3.41 g, 0.012 mol) in Py (10 mL) was added to a solution of $CuSO_4 \cdot 5H_2O$ (26 g, 0.104 mol) in Py (26 mL) and water (20 mL). The mixture was stirred with heating on a water bath at 70—80 °C for 2 h. The product was extracted with ether (3 × 15 mL). The extract was washed successively with a 10% HCl solution and water and dried with $MgSO_4$. The solvent was concentrated *in vacuo* and the residue was crystallized from AcOH. Diketone **3** was obtained in a yield of 3.14 g (93%), m.p. 64—65 °C (*cf.* lit. data:[11] m.p. 64.5—65.5 °C).

Synthesis of 2-aryl-4,5-bis[2,5-dimethyl(3-thienyl)]-1,3-oxazoles (5) (general procedure). A solution of acyloin **1** (0.560 g, 2 mmol) in Py (3 mL) was added with stirring to a solution of the corresponding aromatic carboxylic acid chloride (2.2 mmol) in Py (3 mL). The mixture was kept at ~20 °C for 12 h, poured into water (20—30 mL), and extracted with ether (3 × 10 mL). The extract was washed successively with water, a 10% HCl solution, and water and dried with $MgSO_4$. The solvent was evaporated and a solution of NH_4OAc (1 g, 13 mmol) in AcOH (5—10 mL) was added to the residue. The mixture was refluxed for 3 h and cooled. Then water (20—30 mL) was added, the precipitate that formed was filtered off, and the product was crystallized from 95% EtOH. The characteristics of 1,3-oxazoles **5a—f** are given in Table 2.

2-Amino-4,5-bis[2,5-dimethyl(3-thienyl)]-1,3-thiazole (6). A mixture of a solution of chloroketone **2** (0.30 g, 1 mmol) and thiourea (0.25 g, 3.3 mmol) in 95% EtOH (2 mL) and water (2 mL) was refluxed for 3 h. Then the solution was cooled and poured into a 10% KOH solution (10 mL). The precipitate that formed was filtered off and the product was crystallized from aqueous EtOH. Aminothiazole **6** was obtained in a yield of 0.558 g (87%), m.p. 173—175 °C. Found (%): C, 56.08; H, 5.09; N, 8.49; S, 30.22. $C_{15}H_{16}N_2S_3$. Calculated (%): C, 56.21; H, 5.03; N, 8.74; S, 30.01. ^{1}H NMR (DMSO-d_6), δ: 1.80 (s, 3 H, CH_3); 2.05 (s, 3 H, CH_3); 2.30 (s, 3 H, CH_3); 2.33 (s, 3 H, CH_3); 6.45 (s, 2 H, 2 CH); 6.95 (s, 2 H, NH_2).

Table 2. Characteristics of 1,3-oxazoles **5a—f**

Compound	M.p./°C	Molecular formula	Found / Calculated (%)				^{1}H NMR (DMSO-d_6, δ, *J*/Hz)	Yield (%)
			C	H	N	S		
5a[a]	97—99	$C_{21}H_{19}NOS_2$	69.22 69.01	5.20 5.24	3.75 3.83	17.25 17.54	2.22 (s, 3 H, CH_3); 2.32 (s, 3 H, CH_3); 2.41 (s, 3 H, CH_3); 2.43 (s, 3 H, CH_3); 6.68 (s, 1 H, CH); 6.75 (s, 1 H, CH); 7.68 (m, 3 H, 3 CH_{Ar}); 8.12 (m, 2 H, 2 CH_{Ar})[b]	19
5b	103—105	$C_{22}H_{21}NOS_2$	69.38 69.62	5.50 5.58	3.33 3.69	16.75 16.90	2.15 (s, 3 H, CH_3); 2.22 (s, 3 H, CH_3); 2.38 (s, 9 H, 3 CH_3); 6.78 (s, 1 H, CH); 6.82 (s, 1 H, CH); 7.35 (d, 2 H, 2 CH_{Ar}, *J* = 7.7); 7.90 (d, 1 H, CH_{Ar}, *J* = 7.7)	26
5c	141—143	$C_{21}H_{18}N_2O_3S_2$	61.62 61.44	4.50 4.42	6.67 6.82	15.37 15.62	2.18 (s, 3 H, CH_3); 2.25 (s, 3 H, CH_3); 2.38 (s, 3 H, CH_3); 2.40 (s, 3 H, CH_3); 6.73 (s, 1 H, CH); 6.77 (s, 1 H, CH); 8.25 (d, 2 H, 2 CH_{Ar}, *J* = 8.5); 8.40 (d, 2 H, 2 CH_{Ar}, *J* = 8.5)	16
5d[c]	105—107	$C_{21}H_{18}ClNOS_2$	63.25 63.06	4.47 4.54	3.31 3.50	16.42 16.03	2.18 (s, 3 H, CH_3); 2.25 (s, 3 H, CH_3); 2.35 (s, 3 H, CH_3); 2.40 (s, 3 H, CH_3); 6.71 (s, 1 H, CH); 6.75 (s, 1 H, CH); 7.63 (d, 2 H, 2 CH_{Ar}, *J* = 7.7); 8.05 (d, 2 H, 2 CH_{Ar}, *J* = 7.7)	15
5e[d]	205—207	$C_{21}H_{17}N_3O_5S_2$	55.65 55.37	3.68 3.76	9.18 9.22	14.25 14.08		9
5f	119—120	$C_{22}H_{21}NO_2S_2$	66.76 66.81	5.31 5.35	3.17 3.54	16.09 16.21	2.15 (s, 3 H, CH_3); 2.21 (s, 3 H, CH_3); 2.35 (s, 3 H, CH_3); 2.38 (s, 3 H, CH_3); 3.82 (s, 3 H, OCH_3); 6.72 (s, 2 H, 2 CH); 7.10 (d, 2 H, 2 CH_{Ar}, *J* = 7.7); 7.95 (d, 2 H, 2 CH_{Ar}, *J* = 7.7)	34

[a] MS, *m/z*: 365 [M^+].
[b] In $CDCl_3$.
[c] Found (%): Cl, 8.99. Calculated (%): Cl, 8.86.
[d] MS, *m/z*: 454 [M^+].

Synthesis of 2-substituted 4,5-bis[2,5-dimethyl(3-thienyl)]-1*H*-imidazoles (7) (general procedure). A mixture of diketone **3** (0.278 g, 1 mmol), the corresponding aldehyde (1.25 mmol), and NH_4OAc (0.5 g, 7 mmol) in AcOH (3 mL) was refluxed for 3 h. Then the solution was cooled and poured into water. The residue was filtered off and the product was crystallized from 95% EtOH. The characteristics of imidazoles **7** are given in Table 3.

Table 3. Characteristics of imidazoles **7a—m**

Compound	M.p./°C	Molecular formula	Found / Calculated (%)				^{1}H NMR (DMSO-d_6, δ, *J*/Hz)	Yield (%)
			C	H	N	S		
7a	226—228	$C_{21}H_{20}N_2S_2$	69.31 69.19	5.49 5.53	7.99 7.68	17.36 17.59	2.02 (s, 3 H, CH_3); 2.18 (s, 3 H, CH_3); 2.32 (s, 3 H, CH_3); 2.41 (s, 3 H, CH_3); 6.60 (s, 1 H, CH); 6.75 (s, 1 H, CH); 7.40 (m, 3 H, 3 CH_{Ar}); 8.05 (d, 2 H, 2 CH_{Ar}, *J* = 7.4); 12.50 (s, 1 H, NH)	89
7b	274—276	$C_{24}H_{26}N_2O_3S_2$	63.25 63.41	5.81 5.76	6.52 6.16	14.39 14.11	1.80 (s, 3 H, CH_3); 1.82 (s, 3 H, CH_3); 2.05 (s, 3 H, CH_3); 2.37 (s, 3 H, CH_3); 3.70 (s, 3 H, OCH_3); 3.86 (s, 6 H, 2 OCH_3); 6.68 (s, 2 H, 2 CH); 7.35 (s, 2 H, 2 CH_{Ar})	91
7c[a]	254—256	$C_{21}H_{19}BrN_2S_2$	56.80 56.88	4.28 4.32	6.53 6.32	14.61 14.46	1.95 (s, 3 H, CH_3); 2.15 (s, 3 H, CH_3); 2.33 (s, 3 H, CH_3); 2.42 (s, 3 H, CH_3); 6.57 (s, 1 H, CH); 6.75 (s, 1 H, CH); 7.65 (d, 2 H, 2 CH_{Ar}, *J* = 7.4); 7.96 (d, 2 H, 2 CH_{Ar}, *J* = 7.4); 12.60 (s, 1 H, NH)	96

(*to be continued*)

Table 3 (*continued*)

Compound	M.p./°C	Molecular formula	Found / Calculated (%) C	H	N	S	^{1}H NMR (DMSO-d_6, δ, *J*/Hz)	Yield (%)
7d	240—242	$C_{22}H_{22}N_2S_2$	69.95 69.80	5.89 5.86	7.25 7.40	16.88 16.94	1.98 (s, 3 H, CH_3); 2.12 (s, 3 H, CH_3); 2.33 (s, 3 H, CH_3); 2.35 (s, 3 H, CH_3); 2.42 (s, 3 H, CH_3); 6.60 (s, 1 H, CH); 6.75 (s, 1 H, CH); 7.25 (d, 2 H, 2 CH_{Ar}, *J* = 7.2); 7.92 (d, 2 H, 2 CH_{Ar}, *J* = 7.2); 12.40 (s, 1 H, NH)	98
7e	174—176	$C_{21}H_{20}N_2OS_2$	66.51 66.28	5.35 5.30	7.22 7.36	16.77 16.85	2.05 (s, 3 H, CH_3); 2.18 (s, 3 H, CH_3); 2.33 (s, 3 H, CH_3); 2.42 (s, 3 H, CH_3); 6.58 (s, 1 H, CH); 6.80 (s, 1 H, CH); 6.95 (m, 2 H, 2 CH_{Ar}); 7.25 (m, 1 H, CH_{Ar}); 7.95 (m, 1 H, CH_{Ar}); 12.85 (s, 1 H, OH); 13.00 (s, 1 H, NH)	83
7f	233—235	$C_{21}H_{19}N_3O_2S_2$	61.72 61.59	4.75 4.68	10.14 10.26	15.54 15.66	2.00 (s, 3 H, CH_3); 2.18 (s, 3 H, CH_3); 2.32 (s, 3 H, CH_3); 2.43 (s, 3 H, CH_3); 6.58 (s, 1 H, CH); 6.78 (s, 1 H, CH); 8.30 (m, 4 H, 4 CH_{Ar}); 12.95 (s, 1 H, NH)	60
7g[b]	221—223	$C_{21}H_{19}ClN_2S_2$	63.43 63.22	4.76 4.80	6.95 7.02	16.35 16.07	2.05 (s, 3 H, CH_3); 2.22 (s, 3 H, CH_3); 2.34 (s, 3 H, CH_3); 2.40 (s, 3 H, CH_3); 6.55 (s, 1 H, CH); 6.70 (s, 1 H, CH); 7.43 (m, 2 H, 2 CH_{Ar}); 7.57 (m, 1 H, CH_{Ar}); 7.80 (m, 1 H, CH_{Ar}); 12.32 (s, 1 H, NH)	75
7h[c]	188—190	$C_{21}H_{18}Cl_2N_2S_2$	58.49 58.20	4.25 4.19	6.59 6.46	14.76 14.80	2.05 (s, 3 H, CH_3); 2.22 (s, 3 H, CH_3); 2.32 (s, 3 H, CH_3); 2.40 (s, 3 H, CH_3); 6.54 (s, 1 H, CH); 6.69 (s, 1 H, CH); 7.54 (d, 1 H, CH_{Ar}, *J* = 7.7); 7.74 (s, 1 H, CH_{Ar}); 7.83 (d, 1 H, CH_{Ar}, *J* = 7.7); 12.40 (s, 1 H, NH)	83
7i	163—165	$C_{23}H_{24}N_2O_2S_2$	65.21 65.06	5.64 5.70	6.51 6.60	14.95 15.10	2.05 (s, 3 H, CH_3); 2.18 (s, 3 H, CH_3); 2.32 (s, 3 H, CH_3); 2.40 (s, 3 H, CH_3); 3.78 (s, 3 H, OCH_3); 3.88 (s, 3 H, OCH_3); 6.55 (s, 1 H, CH); 6.68 (s, 1 H, CH); 6.94 (m, 1 H, CH_{Ar}); 7.08 (d, 1 H, CH_{Ar}, *J* = 8.8); 7.62 (m, 1 H, CH_{Ar}); 11.58 (s, 1 H, NH)	71
7k[d]	254—255	$C_{21}H_{19}ClN_2S_2$	63.41 63.22	4.71 4.80	7.31 7.02	15.89 16.07	2.00 (s, 3 H, CH_3); 2.17 (s, 3 H, CH_3); 2.22 (s, 3 H, CH_3); 2.42 (s, 3 H, CH_3); 6.58 (s, 1 H, CH); 6.74 (s, 1 H, CH); 7.52 (d, 2 H, 2 CH_{Ar}, *J* = 8.4); 8.05 (d, 2 H, 2 CH_{Ar}, *J* = 8.4); 12.55 (s, 1 H, NH)	52
7l	243—245	$C_{21}H_{26}N_2S_2$	68.27 68.06	6.98 7.07	7.19 7.56	17.08 17.30	1.30 (m, 3 H, 3 CH); 1.57 (m, 2 H, 2 CH); 1.68 (m, 1 H, CH); 1.78 (m, 2 H, 2 CH); 1.95 (m, 2 H, 2 CH); 2.00 (s, 3 H, CH_3); 2.05 (s, 3 H, CH_3); 2.31 (s, 3 H, CH_3); 2.33 (s, 3 H, CH_3); 2.65 (m, 1 H, CH); 6.55 (s, 2 H, 2 CH); 11.65 (s, 1 H, NH)	54
7m	231—233	$C_{20}H_{19}N_3S_2$	65.66 65.72	5.31 5.24	11.19 11.50	17.23 17.54	1.98 (s, 3 H, CH_3); 2.12 (s, 3 H, CH_3); 2.32 (s, 3 H, CH_3); 2.41 (s, 3 H, CH_3); 6.58 (s, 1 H, CH); 6.75 (s, 1 H, CH); 7.45 (m, 1 H, CH_{Ar}); 8.33 (m, 1 H, CH_{Ar}); 8.53 (m, 1 H, CH_{Ar}); 9.18 (s, 1 H, CH_{Ar}); 12.73 (s, 1 H, NH)	97

[a] Found (%): Br, 18.24. Calculated (%): Br, 18.02.
[b] Found (%): Cl, 8.92. Calculated (%): Cl, 8.89.
[c] Found (%): Cl, 16.54. Calculated (%): Cl, 16.36.
[d] Found (%): Cl, 8.75. Calculated (%): Cl, 8.89.

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