TRANSFORMATION OF 1,2-DITHIOLE-3-THIONES INTO 1,6,6aλ^4-TRITHIAPENTALENES via REACTION WITH BROMOETHANONES

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We report the reactions of derivatives of 5-amino-3-thioxo-3*H*-1,2-dithiole-4-carboxylic acid **1** with bromoethanones and acylation agents. Two different routes were used to obtain the products, 3-(acylmethylidene)-3*H*-1,2-dithioles **4**. These compounds were synthesized by acylation of compounds **1** on the amino group, followed by the reaction with bromoethanones and excess of triethylamine. Another method was based on the inverted order of the mentioned reaction steps and in absence of a base. The treatment of **4** with thionyl chloride gave new unsaturated fused lactones **13** whereas thionation led to desired 1,6,6aλ^4-trithiapentalenes **5**. The structures of products and the reaction mechanisms are discussed.

Keywords: 1,2-Dithiole-3-thiones; Sulfur heterocycles; Trithiapentalenes; Rearrangements; X-ray diffraction; Reaction mechanism; Heterocyclizations.

The sulfur aromatic heterocycles may display physico-chemical properties with relevance in catalysis, in particular those relating to design of supramolecular ligands. Heterocyclic building blocks on the basis of 1,6,6aλ^4-trithiapentalenes represent an interesting approach to modify complexation properties of macrocyclic switchable ionophores[1]. This type of compounds is generally obtained from 1,2-dithioles or 1,2-dithiolium salts. A large number of other methods have also been reported[2]. There are several synthetic pathways to 1,6,6aλ^4-trithiapentalenes: cycloadditions of 1,2-dithiole-3-thiones to alkynes[3] and benzylidene-1,2-dithioles to isothiocyanates[4], nucleophilic substitution of the alkylsulfanyl, 2-(alkylsulfanyl)-vinyl, 2-(dialkylamino)vinyl groups or the hydrogen at carbon atoms C-3 or C-5 of 1,2-dithiolium moiety with dithiocarboxylic acids[5] or sulfides[6]. An easy and widely used route is based on the thionation of 1-oxa-6,6aλ^4-dithiapentalene with phosphorus pentasulfide[7].

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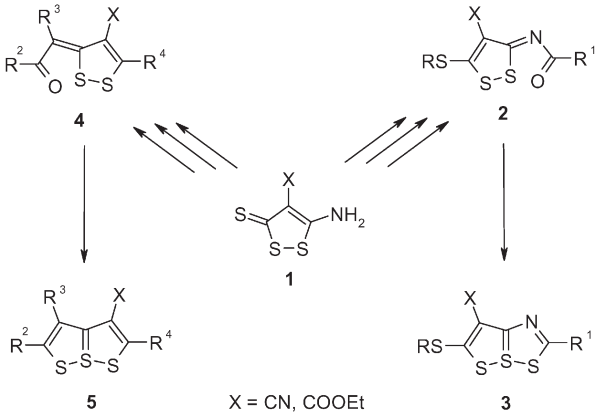
RESULTS AND DISCUSSION

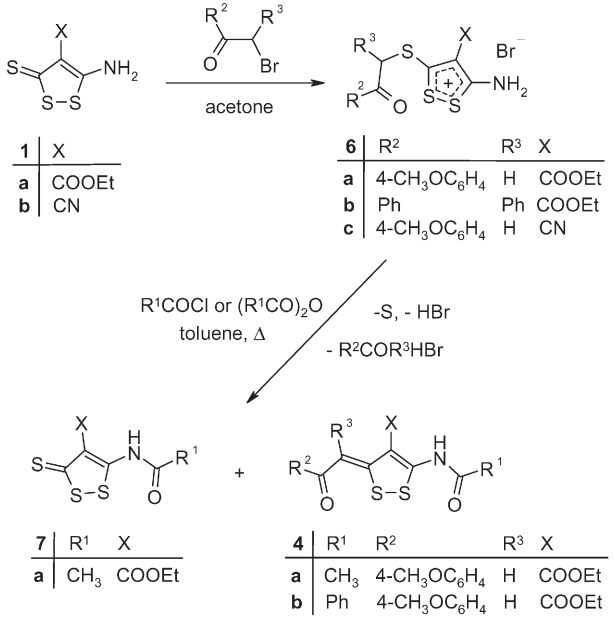
This work was focused on the study of the reactivity of ethyl ester and nitrile derived from 5-amino-3-thioxo-3*H*-1,2-dithiole-4-carboxylic acid (**1**; X = COOH). In earlier paper[8] the preparations of corresponding *N*-(1,2-dithiole-3-ylidene)amides **2** and subsequently 3,3aλ^4,4-trithia-1-azapentalenes **3** have been described (Scheme 1). While the previous approach started with the new ring formation by modification of the present amino group, in this case the heterocyclic system was expanded over the thioxo side of compounds **1**. These syntheses were based on alkylation of the 1,2-dithiole-3-thione part of **1** with substituted phenacyl halides, followed by basic or thermally induced transformation leading to intermediates **4**. The final step of the procedure included oxygen–sulfur exchange taking place at the oxo group of **4** and resulted in 1,6,6aλ^4-trithiapentalenes **5** (Scheme 1).



SCHEME 1
Synthetic pathways to 3,3aλ^4,4-trithia-1-azapentalenes and 1,6,6aλ^4-trithiapentalenes

Two sets of experiments have been carried out to achieve the synthetic aims. In the first experiments, thiones **1** were treated with bromoethanones, namely with 2-bromo-1,2-diphenylethan-1-one, 2-bromo-1-(4-methoxyphenyl)ethan-1-one, in acetone. The obtained precipitates, which were isolated in moderate yield (27–47%), were identified as bromide salts **6**. The subsequent reaction of **6** with acylation agents (such as acetic anhydride and benzoyl chloride) in refluxing toluene provided compounds **4**. The products were accompanied by small quantities of by-products, amides **7** (Scheme 2). An explanation, in which the formation of **7** was ascribed to degradation of the main products **4**, has not been supported by additional

experiments. In contrast to the reported stability of *S*-phenacyl type salts **6** in warm solvents[9], the side reaction was considered to consist of dealkylation and acylation. The mechanism suggested for the pathway leading to compounds **4** is presented below (Scheme 5).



1	X
a	COOEt
b	CN

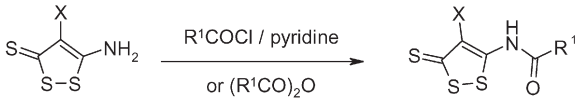
6	R^2	R^3	X
a	4-$CH_3OC_6H_4$	H	COOEt
b	Ph	Ph	COOEt
c	4-$CH_3OC_6H_4$	H	CN

7	R^1	X
a	CH_3	COOEt

4	R^1	R^2	R^3	X
a	CH_3	4-$CH_3OC_6H_4$	H	COOEt
b	Ph	4-$CH_3OC_6H_4$	H	COOEt

SCHEME 2
Formation of amides **4** and **7**

Another starting material, *N*-acyl derivatives **7**, by-products of the transformation of salts **6** into amide **4**, were more easily obtained by acylation of compounds **1** with acetic anhydride or acyl halides in pyridine[8] (Scheme 3).

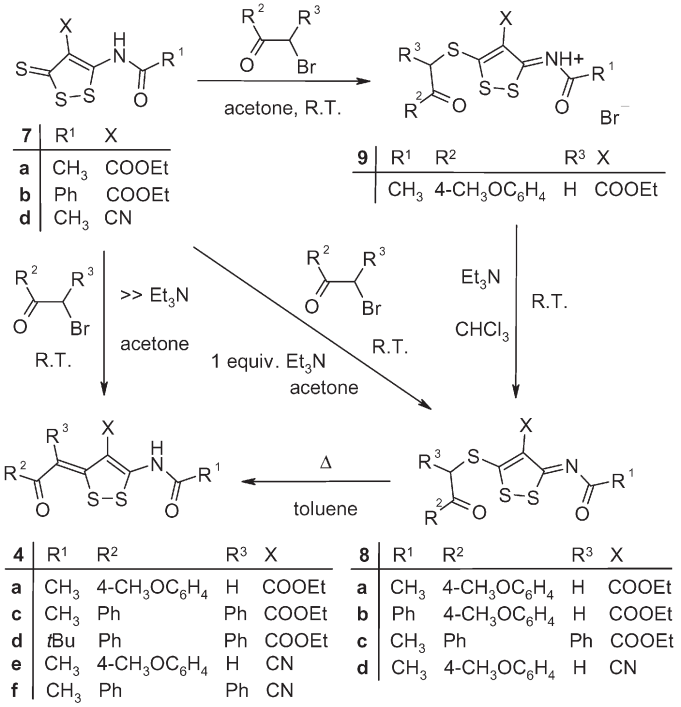


1	X
a	COOEt
b	CN

7	R^1	X
a	CH_3	COOEt
b	Ph	COOEt
c	*t*Bu	COOEt
d	CH_3	CN

SCHEME 3
Acylation of dithioles **1**

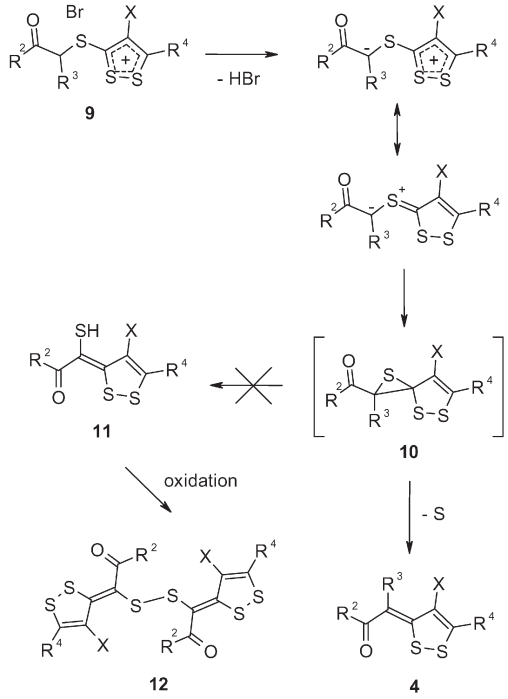
When the amides **7** were allowed to react with bromoethanones, three products **4**, **8**, and **9** were isolated. The amount of added triethylamine played crucial role (Scheme 4). Formation of salt **9** was observed in the absence of a base. If the reaction was performed with one equivalent of the base, compound **8** was formed. (Compound **9** was converted into **8** in alkaline solution.) On the other hand, the treatment with high excess of triethylamine (4 equivalents) gave solely amide **4**. Moreover, heating of alkylsulfanyl dithiole **8d** in toluene at 110 °C for 1 h was sufficient to afford only the expected methylidenedithiole **4e** (Scheme 4).



SCHEME 4
Alternative preparations of 4-X-5-(R^1-amido)-3-(2-oxo-2-R^2-1-R^3-ethylidene)-3*H*-1,2-dithioles **4**

We considered the explanation suggested by Varache-Lembege et al.[10] proposed for the rearrangement of the 5-aryl-3-(phenacylsulfanyl)-1,2-dithiolium salts, as adequate also for the formation of compounds **4**. The mechanism illustrated in Scheme 5, involved the isomerization of thiocarbonylylide into unstable intermediary thiirane **10**, followed by ring opening and release of sulfur atom. We have not observed rearrangement

of thiirane **10** to give enethiol **11** whose air oxidation led to disulfide **12**. The influence of R^2 and R^4 substituents on the nature and proportion of both possible products has not been explained yet[10]. We hypothesized that compound **4** was preferred to **11** due to better conjugation (i.e. higher stability), which was associated with the $O=C(R^2)–CH=C–C(X)=C–R^4$ system planarity as well as with lower steric interactions between hydrogen atom in the position of R^3 and X group than between SH and X groups.



SCHEME 5
Mechanism of formation of amides **4** [10]

The bonding in compounds **4** was inferred by physico-chemical methods. In the electrospray ionization mass spectrum, two peaks in positive ion mode corresponding to $[M + Na]^+$ and $[M + H]^+$ and one peak in negative ion mode $[M – H]^–$ dominated over the others, which were of very low intensity. ^{1}H NMR spectra of compounds **4a**, **4b**, **4e** revealed a singlet at about δ 8.25 ppm for the vinyl proton while spectra of compounds **4c**, **4d**, **4f** showed no signal in the δ 6.0–7.0 ppm range. The possible structures of compounds **4** outlined in Fig. 1 were in agreement with the NMR and MS data, the others were excluded. The structure of prepared compounds was

confirmed by X-ray analysis of **4c** (Fig. 2). The C3–C4, C4–C5, C5–C15, C15–C16 and C16–O17 bond lengths (see Table I) were very similar to those in conjugated unsaturated ketones[11]. The S1···O17 distance was found to be 2.362 Å. IR spectrum showed only two (one) (for X = COOEt (CN)) absorptions between 1710 and 1650 cm^{-1} for the C=O stretchings. Those indicated a dipolar structure with the presence of enol (enolate) portion in the ketone carbonyl of **4** (refs[2,12]). On the basis of spectroscopic measurements the contribution of **B** and **C** structures (Fig. 1) in these compound types were assessed.

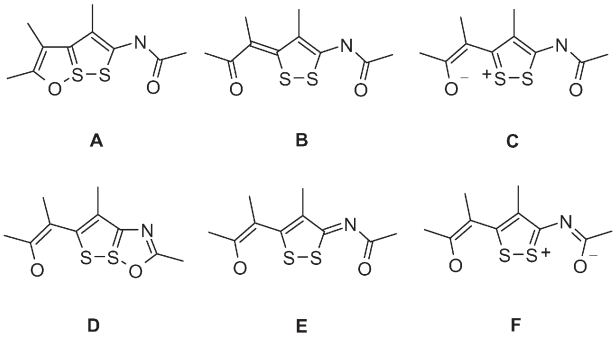


FIG. 1
Possible structures of 3-oxa-3aλ^4,4-dithia-1-azapentalenes/1-oxa-6,6aλ^4-dithiapentalenes **4** and **15**

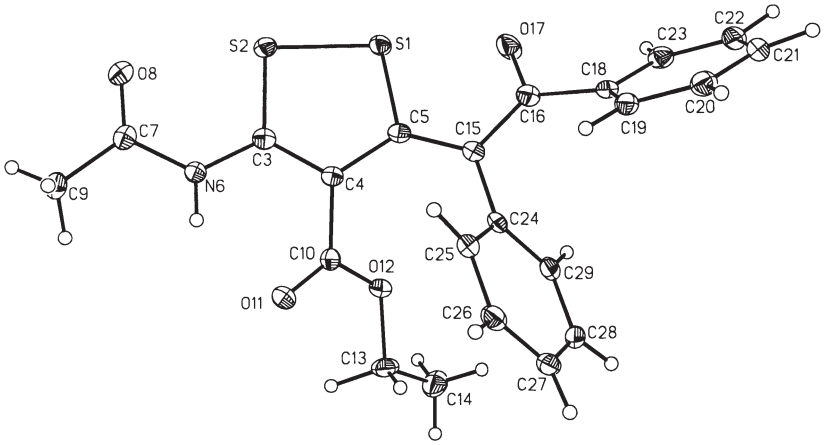
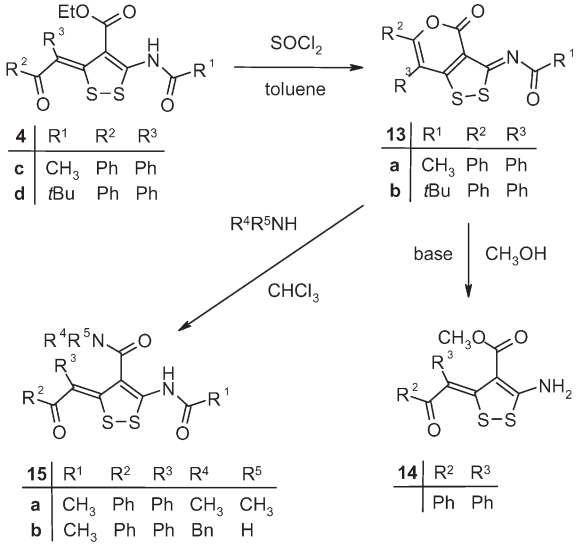


FIG. 2
X-ray structure of ethyl 5-acetamido-3-(2-oxo-1,2-diphenylethylidene)-3*H*-1,2-dithiole-4-carboxylate (**4c**)

In the second part of our work, we dealt with the synthesis of compounds **5** with a trithiapentalene structure. The first method was based on double nucleophilic substitution occurring on enolized carbonyl group of **4**. In the two step synthesis, starting amide **4** (X = COOEt) was treated with thionyl chloride in toluene and then with sodium sulfide in methanol. It has been shown, however, that addition of thionyl chloride induced the formation of bicyclic lactone **13**. The ^{1}H NMR spectra of **13** showed some resemblance to those of **4**. The only notable difference was the absence of a triplet centered at δ 1.05 ppm and a quartet at 3.35 ppm indicating that **13** did not contain an ethyl group. The structure of compounds **13** was deduced from IR spectra, which contained a lactone signal at 1730 cm^{-1} and an amide band at 1690 cm^{-1}.

The deacylation on the nitrogen atom and methanolysis of the pyranone ring of **13** occurred due to the ability of sulfide anion to act as a base. The mentioned transformations gave rise of methyl ester **14** (Scheme 6). The strong absorption in the region 1600–1750 cm^{-1} of IR spectrum of **14** indicated either conjugation of the ketone carbonyl with another double bond or a close interaction between carbonyl oxygen atom and sulfur atom of the dithiole ring. We have preferred the former idea according to the conclusion for an analogous moiety included in structure of **4**.



4	R^1	R^2	R^3
c	CH_3	Ph	Ph
d	*t*Bu	Ph	Ph

13	R^1	R^2	R^3
a	CH_3	Ph	Ph
b	*t*Bu	Ph	Ph

15	R^1	R^2	R^3	R^4	R^5
a	CH_3	Ph	Ph	CH_3	CH_3
b	CH_3	Ph	Ph	Bn	H

14	R^2	R^3
	Ph	Ph

SCHEME 6
Transformation of esters **4c** and **4d**

The structure of compound **13** was further confirmed by analyzing products of its aminolysis with dimethylamine or benzylamine **15** by X-ray diffraction of **15a** (Fig. 3). The bond lengths and angles (Table I) in **15a** were almost identical with the corresponding parameters in the molecule of **4c**. Therefore, both the molecular structures are similar.

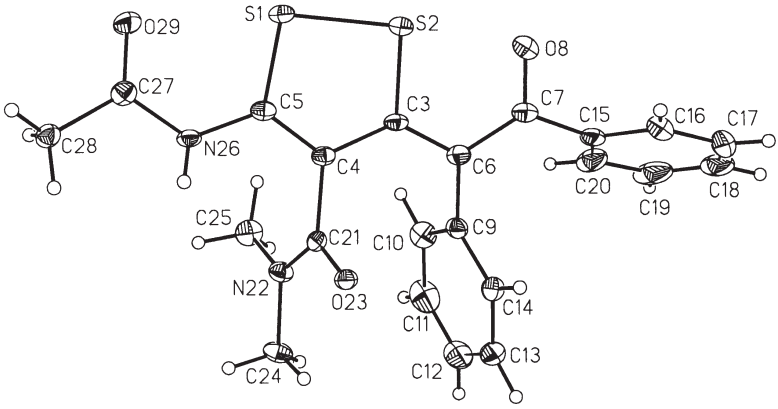
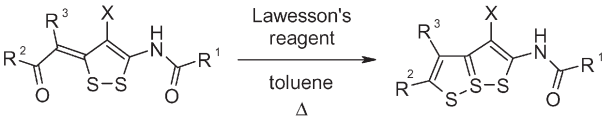


FIG. 3
X-ray structure of 5-acetamido-*N*,*N*-dimethyl-3-(2-oxo-1,2-diphenylethylidene)-3*H*-1,2-dithiole-4-carboxamide (**15a**)

Thionation of ester **4a** with Lawesson's reagent furnished a simpler route to trithiapentalene **5** (Scheme 7). The regioselectivity of the reaction proceeding on the ketone carbonyl was supported by ^{1}H NMR spectra of **5** and **4a**, which showed the resonances of vinyl protons at δ 8.18 and 8.96 ppm and neighboring aromatic protons at δ 7.95 and 7.79 ppm. Regarding the bicyclic constitution of **5**, it is now well established that 1,6,6aλ^4-trithiapentalene can be considered as a naphtalene-like ten-π-electron system[13].



4	R^1	R^2	R^3	X
a	CH_3	4-$CH_3OC_6H_4$	H	COOEt

5	R^1	R^2	R^3	X
	CH_3	4-$CH_3OC_6H_4$	H	COOEt

SCHEME 7
Synthesis of ethyl 2-acetamido-5-(4-methoxyphenyl)-7λ^4-[1,2]dithiolo[1,5-*b*][1,2]dithiole-3-carboxylate (**5**)

TABLE I
X-ray structural data of compounds **4c** and **15a**. Comparison of corresponding bond lengths and angles

4c		**15a**		**4c**		**15a**	
Bond	Bond length, Å	Bond	Bond length, Å	Angle	Bond angle, °	Angle	Bond angle, °
S1–S2	2.1042(7)	S2–S1	2.1140(8)	S1–C5–C15	118.76(15)	S2–C3–C6	118.73(16)
S1–C5	1.756(2)	S2–C3	1.756(2)	S2–C3–N6	119.34(15)	S1–C5–N26	119.87(16)
S2–C3	1.721(2)	S1–C5	1.728(2)	C3–C4–C5	117.54(18)	C5–C4–C3	117.93(19)
C3–C4	1.383(3)	C5–C4	1.374(3)	C3–N6–C7	124.72(18)	C5–N26–C27	124.32(19)
C3–N6	1.372(3)	C5–N26	1.389(3)	C5–C15–C16	115.76(18)	C3–C6–C7	116.2(2)
C4–C5	1.442(3)	C4–C3	1.440(3)	N6–C7–O8	120.89(19)	N26–C27–O29	121.9(2)
C5–C15	1.391(3)	C3–C6	1.394(3)	C15–C16–O17	119.45(18)	C6–C7–O8	119.2(2)
N6–C7	1.385(3)	N26–C27	1.376(3)				
C7–O8	1.215(3)	C27–O29	1.220(3)				
C15–C16	1.443(3)	C6–C7	1.431(3)				
C16–O17	1.246(3)	C7–O8	1.268(3)				

In comparison with sulfur pentasulfide, the O,S-interchange reaction with Lawesson's reagent was more selective[14], but the product isolation was successful only in the mentioned case of thionation of **4a**.

CONCLUSION

We have demonstrated the synthesis of compound **5** involving the 1,6,6aλ^4-trithiapentalene structural motif. 1,2-Dithiole-3-thiones **1** were converted into 3-(2-acylalkan-1-ylidene)-1,2-dithiole **4** by successive treatment with acylation and phenacylation agents. The route for the formation of these compounds from the 3-(acylamino)-1,2-dithiole precursors **7** is suggested. Thionation of oxo derivative **4** with Lawesson's reagent afforded the desired trithiapentalene **5**. The X-ray structure analysis and spectroscopic measurements supported the assumption that compounds **4** were monocyclic carbonyl derivatives rather than oxadithia(aza)pentalene bicyclic system.

EXPERIMENTAL

General

Unless otherwise stated, chemicals were obtained from commercial suppliers and were used without further purification. Dimethylformamide was distilled and stored over 4Å sieves. Acetone and chloroform were dried over anhydrous calcium chloride, pyridine and triethylamine over potassium hydroxide, toluene over phosphorus pentoxide, and distilled before use.

Melting points were determined on a Kofler hot-stage apparatus and are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on a DRX 300 Avance instrument (Bruker Biospin). Chemical shifts (δ) are given in ppm downfield from tetramethylsilane as an internal reference. Coupling constants *J* are reported in Hz. FTIR spectra (in KBr pellets; ν in cm^{-1}) were taken on a Genesis Mattson spectrometer. Mass spectra were obtained with an Esquire LC ion-trap mass spectrometer (Bruker Daltonics) equipped with an ESI source. The MS samples were dissolved in acetonitrile at concentrations of 10 μM. Analytical thin-layer chromatography was conducted on Merck silica gel 60 F254 precoated aluminium plates and visualized with short-wavelength UV light (254 nm). Column chromatography was carried out with silica gel Fluka 60 (220–440 mesh). Elemental analyses were carried out in Pliva–Lachema Co., Brno (Czech Republic). All X-ray intensity data were collected at 120 K on a KUMA KM4 four-circle diffractometer with MoKα radiation (λ = 0.71073 Å). The structures were solved by direct methods (program: SHELXS97) and refined by weighted full-matrix least-square treatment (SHELXL97). All non-hydrogen atoms were refined anisotropically, hydrogens were localized from the difference of Fourier map and refined isotropically.

Ethyl 5-amino-3-thioxo-3*H*-1,2-dithiole-4-carboxylate (**1a**), 5-amino-3-thioxo-3*H*-1,2-dithiole-4-carbonitrile (**1b**), ethyl 5-acetamido-3-thioxo-3*H*-1,2-dithiole-4-carboxylate (**7a**), ethyl 5-benzamido-3-thioxo-3*H*-1,2-dithiole-4-carboxylate (**7b**), ethyl 5-(2,2-dimethylpropan-

amido)-3-thioxo-3*H*-1,2-dithiole-4-carboxylate (**7c**), *N*-(4-cyano-3-thioxo-3*H*-1,2-dithiol-5-yl)-acetamide (**7d**) were obtained according to the previously described procedure[8].

Preparation of Esters **4**. General Procedures

Method A

A mixture of **6a** (0.15 g, 0.33 mmol), toluene (80 ml) and excess (7 equiv.) of acylation agent (**4a**: acetic anhydride; **4b**: benzoyl chloride) was refluxed for 4 h. Excess volatiles were removed in vacuo. The residue obtained after evaporation was purified by column chromatography (silica gel, dichloromethane–ethyl acetate 30:1).

Ethyl 5-acetamido-3-[2-(4-methoxyphenyl)-2-oxoethylidene]-3H-1,2-dithiole-4-carboxylate (**4a**). This reaction yielded 0.034 g (39%) of **7a**: m.p. 87–88 °C (dichloromethane) and 0.055 g (44%) of **4a**: m.p. 230 °C (subl.; dichloromethane). IR: 2983 (w), 2962 (w), 2846 (w), 1695 (w), 1657 (w), 1603 (w), 1543 (m), 1460 (m), 1444 (s), 1402 (m), 1365 (w), 1327 (w), 1255 (s), 1227 (w), 1213 (w), 1173 (w), 1029 (w). ^{1}H NMR (300 MHz, $CDCl_3$): 1.77 t, 3 H, *J* = 7.1 (C**H**$_3$CH$_2$); 2.34 s, 2 H (CH_3CO); 3.88 s, 3 H (CH_3O); 4.52 q, 2 H, *J* = 7.1 (CH_2); 6.97 d, 2 H, *J* = 8.8 (phenylene); 7.95 d, 2 H, *J* = 8.8 (phenylene); 8.18 s, 1 H (COCH); 12.74 s, br, 1 H (NH). ^{13}C NMR (300 MHz, $CDCl_3$): 14.5 (CH_3CH_2), 24.2 (CH_3CO), 55.6 (CH_3O), 62.4 (CH_2), 106.8 (COCH), 108.8 (C-4), 114.1 (phenylene), 129.6 (phenylene), 130.4 (phenylene), 162.6, 165.3, 166.7, 167.4, 169.0, 184.4 (COCH). For $C_{17}H_{17}NO_5S_2$ (379.5) calculated: 53.81% C, 4.52% H, 3.69% N; found: 53.31% C, 4.50% H, 3.65% N.

Ethyl 5-benzamido-3-[2-(4-methoxyphenyl)-2-oxoethylidene]-3H-1,2-dithiole-4-carboxylate (**4b**). This reaction yielded 0.120 g (82%) of **4b**: m.p. 223–224 °C (CH_2Cl_2). IR: 3072 (w), 2997 (w), 2981 (w), 2941 (w), 2841 (w), 1676 (w), 1655 (w), 1603 (m), 1585 (w), 1545 (m), 1439 (s), 1400 (m), 1333 (w), 1259 (s), 1225 (m), 1171 (m), 1030 (w). ^{1}H NMR (300 MHz, $CDCl_3$): 1.61 t, 3 H, *J* = 7.1 (C**H**$_3$CH$_2$); 3.85 s, 3 H (CH_3O); 4.57 q, 2 H, *J* = 7.1 (CH_2); 6.95 d, 2 H, *J* = 8.8 (phenylene); 7.55–7.66 m, 3 H (Ph); 7.95 d, 2 H, *J* = 8.8 (phenylene); 8.03 m, 2 H (Ph); 8.20 s, 1 H (COCH); 13.77 s, br, 1 H (NH). ^{13}C NMR (300 MHz, $CDCl_3$): 14.6 (CH_3CH_2), 55.6 (CH_3O), 62.6 (CH_2), 106.8 (COCH), 109.2 (C-4), 114.1 (phenylene), 128.1, 129.4 (Ph), 129.6 (phenylene), 130.4, 131.4, 133.9, 162.6, 165.2, 165.3, 167.1, 168.1, 184.3 (COCH). For $C_{22}H_{19}NO_5S_2$ (441.5) calculated: 59.85% C, 4.34% H, 3.17% N; found: 59.80% C, 4.24% H, 3.18% N.

Method B

An appropriate amide **7** was dissolved in acetone (10 ml) and an α-bromoethanone compound and triethylamine were added. The mixture was stirred for 24 h. The residue after evaporation was crystallized and purified by chromatography (silica gel, dichloromethane).

Ethyl 5-acetamido-3-[2-(4-methoxyphenyl)-2-oxoethylidene]-3H-1,2-dithiole-4-carboxylate (**4a**). Compound **7a** (0.10 g, 0.38 mmol), 2-bromo-1-(4-methoxyphenyl)ethan-1-one (0.13 g, 0.57 mmol) and triethylamine (0.53 ml, 3.80 mmol) gave 0.039 g (27%) of **4a:** m.p. 230 °C (subl.; CH_2Cl_2); identical with described above.

Ethyl 5-acetamido-3-(2-oxo-1,2-diphenylethylidene)-3H-1,2-dithiole-4-carboxylate (**4c**). Compound **7a** (0.10 g, 0.38 mmol), 2-bromo-1,2-diphenylethan-1-one (0.17 g, 0.57 mmol) and triethylamine (0.21 ml, 1.52 mmol) gave 0.115 g (71%) of **4c**: m.p. 195 °C (CH_2Cl_2). IR: 3278 (w), 3058 (w), 2996 (w), 2932 (w), 2900 (w), 1702 (w), 1669 (s), 1547 (m), 1520 (s), 1444 (m), 1394 (m), 1375 (m), 1334 (s), 1305 (s), 1272 (m), 1235 (s), 1209 (m), 1177 (w).

^{1}H NMR (300 MHz, $CDCl_3$): 1.09 t, 3 H, J = 7.1 (C**H**$_3$CH$_2$); 2.39 s, 2 H (CH_3CO); 3.37 q, 2 H, J = 7.1 (CH_2); 7.15–7.37 m, 10 H (Ph); 10.98 s, br, 1 H (NH). ^{13}C NMR (300 MHz, $CDCl_3$): 13.9 (**C**H$_3$CH$_2$), 24.1 (**C**H$_3$CO), 61.7 (CH_2), 112.6 (C-4), 123.9, 127.1, 127.7, 128.7, 129.4, 129.9, 130.7 (Ph), 138.4, 139.8, 161.3, 166.1, 166.5, 168.4, 187.3 (Ph**C**OC). For $C_{22}H_{19}NO_4S_2$ (425.5) calculated: 62.10% C, 4.50% H, 3.29% N; found: 62.14% C, 4.45% H, 3.20% N. Crystallographic data for **4c**: $C_{22}H_{19}NO_4S_2$, M = 425.50, triclinic crystal system, space group P-1, a = 7.5443(8) Å, b = 9.3569(10) Å, c = 14.1196(15) Å, α = 96.982(9)°, β = 100.261(9)°, γ = 96.593(9)°, V = 963.96(18) Å^3, Z = 2, D_{calc} = 1.466 Mg m^{-3}. Number of collected/independent reflections was 5161/3288; R_{int} = 0.0440. The final R indices [$I > 2\sigma(I)$]: $R1$ = 0.0336, $wR2$ = 0.1034, the largest different peak and hole were 0.266 and –0.419 e Å^{-3}. CCDC 284866 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

Ethyl 3-(2-oxo-1,2-diphenylethylidene)-5-(2,2-dimethylpropanamido)-3H-1,2-dithiole-4-carboxylate (**4d**). Compound **7c** (0.30 g, 0.98 mmol), 2-bromo-1,2-diphenylethan-1-one (0.40 g, 1.47 mmol) and triethylamine (0.55 ml, 3.93 mmol) gave 0.113 g (25%) of **4d**: m.p. 161–162 °C (CH_2Cl_2). IR: 2967 (w), 2934 (w), 2901 (w), 2868 (w), 1698 (w), 1664 (s), 1540 (s), 1447 (w), 1389 (m), 1370 (m), 1341 (s), 1306 (m), 1273 (m), 1233 (m), 1184 (w), 1130 (m), 1095 (w), 1022 (m). ^{1}H NMR (300 MHz, $CDCl_3$): 1.04 t, 3 H, J = 7.0 (C**H**$_3$CH$_2$); 1.42 s, 9 H ((CH$_3$)$_3$C); 3.35 q, 2 H, J = 7.0 (CH_2); 7.14–7.34 m, 10 H (Ph); 11.38 s, br, 1 H (NH). ^{13}C NMR (300 MHz, $CDCl_3$): 14.0 (**C**H$_3$CH$_2$), 27.3 ((**C**H$_3$)$_3$C), 40.3 ((CH$_3$)$_3$**C**), 61.7 (CH_2), 112.6 (C-4), 123.7, 127.0, 127.6, 128.7, 129.3, 129.8, 130.7 (Ph), 138.5, 140.0, 162.0, 166.0, 166.7, 177.4, 187.4 (Ph**C**OC). For $C_{25}H_{25}NO_4S_2$ (467.6) calculated: 64.22% C, 5.39% H, 3.00% N; found: 64.10% C, 5.30% H, 2.89% N.

N-{4-Cyano-3-[2-(4-methoxyphenyl)-2-oxoethylidene]-3H-1,2-dithiol-5-yl}acetamide (**4e**). Compound **7d** (0.10 g, 0.46 mmol), 2-bromo-1-(4-methoxyphenyl)ethan-1-one (0.16 g, 0.69 mmol) and triethylamine (0.26 ml, 1.84 mmol) gave 0.036 g (24%) of **4e**: m.p. 230 °C (decomp.; CH_2Cl_2). IR: 3267 (w), 3222 (w), 3060 (w), 2958 (w), 2935 (w), 2837 (w), 2222 (m), 1711 (m), 1666 (w), 1599 (s), 1549 (m), 1510 (w), 1439 (s), 1363 (m), 1313 (m), 1255 (s), 1228 (m), 1174 (s), 1117 (w), 1026 (m). ^{1}H NMR (300 MHz, DMSO-d_6): 2.30 s, 3 H (C**H**$_3$CO); 3.83 s, 3 H (CH_3O); 7.05 d, 2 H, J = 8.7 (phenylene); 7.28 s, 1 H (COCH); 7.93 d, 2 H, J = 8.7 (phenylene). ^{13}C NMR (300 MHz, DMSO-d_6): 22.7 (**C**H$_3$CO), 55.4 (CH_3O), 102.5 (C-4), 113.1 (phenylene), 114.1 (phenylene), 129.0 (phenylene), 129.4 (CH-phenylene), 162.4, 164.0, 165.2, 171.1, 183.1 (**C**OCH). For $C_{15}H_{12}N_2O_3S_2$ (332.4) calculated: 54.20% C, 3.64% H, 8.43% N; found: 54.42% C, 3.54% H, 8.40% N.

N-[4-Cyano-3-(2-oxo-1,2-diphenylethylidene)-3H-1,2-dithiol-5-yl]acetamide (**4f**). Compound **7d** (0.10 g, 0.46 mmol), 2-bromo-1,2-diphenylethan-1-one (0.19 g, 0.69 mmol) and triethylamine (0.26 ml, 1.84 mmol) gave 0.012 g (7%) of **4f**: m.p. 237–238 °C (ethyl acetate). IR: 3263 (w), 3060 (w), 3028 (w), 2935 (w), 2212 (w), 1684 (m), 1533 (s), 1444 (m), 1385 (w), 1352 (s), 1327 (m), 1308 (m), 1228 (m), 1180 (w), 1074 (w), 1028 (w). ^{1}H NMR (300 MHz, DMSO-d_6): 2.27 s, 3 H (CH_3); 7.16–7.32 m, 10 H (Ph). ^{13}C NMR (300 MHz, DMSO-d_6): 23.0 (CH_3), 92.8 (C-4), 111.6 (CN), 120.8, 127.6, 128.2 (Ph), 128.3 (**C**OCH), 129.7, 132.5 (Ph), 136.1, 137.8, 163.4, 168.0, 171.0, 185.3 (**C**OCH). For $C_{20}H_{14}N_2O_2S_2$ (378.5) calculated: 63.47% C, 3.73% H, 7.40% N; found: 63.36% C, 3.60% H, 7.45% N.

Alternative preparation of N-{4-cyano-3-[2-(4-methoxyphenyl)-2-oxoethylidene]-3H-1,2-dithiol-5-yl}acetamide (**4e**). A mixture of **8d** (0.10 g, 0.27 mmol) and toluene (50 ml) was refluxed

(for 24 h) until the starting material could be detected (TLC). The solvent was removed in vacuo. The residue was dried and purified by column chromatography (silica gel, CH_2Cl_2–ethyl acetate 5:1). Compound **4e** was obtained in a yield of 0.041 g (46%): m.p. 235 °C (decomp.; CH_2Cl_2); identical with that described above.

Ethyl 2-acetamido-5-(4-methoxyphenyl)-7λ^4-[1,2]dithiolo[1,5-b][1,2]dithiole-3-carboxylate (**5**). Ester **4a** (0.10 g, 0.26 mmol) was added to a solution of Lawesson's reagent (0.33 g, 0.78 mmol) in benzene (20 ml). The resulting solution was stirred under reflux for 3 h. The solvent was removed on a rotatory evaporator and the resulting solid was purified by chromatography (silica gel, CH_2Cl_2–ethyl acetate 20:1) to give **5** (0.016 g; 16%): m.p. 180–181 °C (CH_2Cl_2). IR: 2924 (w), 2839 (w), 1703 (w), 1653 (m), 1601 (m), 1523 (w), 1456 (s), 1367 (w), 1327 (w), 1259 (s), 1230 (w), 1176 (m), 1028 (w). ^{1}H NMR (300 MHz, DMSO-d_6): 1.55 t, 3 H, J = 7.1 (C**H**$_3$CH$_2$); 2.32 s, 2 H (CH_3CO); 3.88 s, 3 H (CH_3O); 4.54 q, 2 H, J = 7.1 (CH_2); 6.95 d, 2 H, J = 8.8 (phenylene); 7.79 d, 2 H, J = 8.8 (phenylene); 8.96 s, 1 H (CH); 12.28 s, br, 1 H (NH). ^{13}C NMR (300 MHz, DMSO-d_6): 14.6 (**C**H$_3$CH$_2$), 25.2 (**C**H$_3$CO), 55.7 (CH_3O), 62.5 (CH_2), 114.5 (phenylene), 115.3, 124.9 (CSCHCS), 129.3 (phenylene), 132.4 (Ph), 162.0, 167.1, 168.3, 172.0, 178.6, 181.9. For $C_{17}H_{17}NO_4S_3$ (395.5) calculated: 51.63% C, 4.33% H, 3.54% N; found: 51.64% C, 4.39% H, 3.72% N.

Preparation of 1,2-Dithiol-1-ium Bromides **6**. General Procedure

The corresponding α-bromoethanone (3.00 mmol) was added to a solution of **1** (2.00 mmol) in acetone (50 ml). After stirring at room temperature for 24 h, the precipitate was collected by filtration, and washed with acetone.

5-Amino-4-(ethoxycarbonyl)-3-{[2-(4-methoxyphenyl)-2-oxoethyl]sulfanyl}-1,2-dithiol-1-ium bromide (**6a**). This compound was obtained in a yield of 0.32 g (36%): m.p. 185–186 °C (acetone). IR: 3302 (w), 3280 (w), 3026 (w), 2999 (w), 2980 (w), 2868 (w), 2845 (w), 1691 (m), 1662 (w), 1597 (s), 1512 (w), 1427 (w), 1373 (m), 1338 (s), 1271 (s), 1207 (w), 1173 (m), 1011 (w). ^{1}H NMR (300 MHz, DMSO-d_6): 1.30 t, 3 H, J = 7.1 (C**H**$_3$CH$_2$); 3.87 s, 3 H (CH_3O); 4.30 q, 2 H, J = 7.1 (CH_3C**H**$_2$); 7.12 d, 2 H, J = 8.8 (phenylene); 8.04 d, 2 H, J = 8.8 (phenylene). ^{13}C NMR (300 MHz, DMSO-d_6): 13.8 (**C**H$_3$CH$_2$), 55.5 (CH_3O), 61.4 (CH_3**C**H$_2$), 88.9 (C-4), 114.7 (phenylene), 126.7, 131.7 (phenylene), 162.6, 164.7, 166.7, 169.7, 180.6, 187.0, 194.7 (**C**OCH$_2$). For $C_{15}H_{16}BrNO_4S_3$ (450.4) calculated: 40.00% C, 3.58% H, 3.11% N; found: 39.61% C, 3.72% H, 3.00% N.

5-Amino-4-(ethoxycarbonyl)-3-[(2-oxo-1,2-diphenylethyl)sulfanyl]-1,2-dithiol-1-ium bromide (**6b**). This compound was obtained in a yield of 0.27 g (27%): m.p. 180–181 °C (acetone). IR: 3295 (m), 2978 (w), 2936 (w), 2850 (w), 1693 (s), 1678 (s), 1599 (s), 1468 (w), 1449 (m), 1419 (m), 1367 (m), 1335 (s), 1267 (s), 1189 (w), 1119 (w), 1106 (w), 1006 (m). ^{1}H NMR (300 MHz, DMSO-d_6): 1.27 t, 3 H, J = 7.1 (C**H**$_3$CH$_2$); 4.29 q, 2 H, J = 7.1 (CH_3C**H**$_2$); 6.86–8.13 m, 10 H (Ph). ^{13}C NMR (300 MHz, DMSO-d_6): 13.9 (CH_3), 61.5 (CH_2), 126.5, 127.4, 129.1, 129.5, 129.6, 130.5, 132.3, 135.6, 152.5, 160.9, 168.8, 172.1, 194.9 (**C**OCH). For $C_{20}H_{18}BrNO_3S_3$ (496.5) calculated: 48.39% C, 3.65% H, 2.82% N; found: 48.03% C, 3.53% H, 2.80% N.

5-Amino-4-cyano-3-{[2-(4-methoxyphenyl)-2-oxoethyl]sulfanyl}-1,2-dithiol-1-ium bromide (**6c**). This compound was obtained in a yield of 0.38 g (47%): m.p. 221–222 °C (acetone). IR: 3240 (w), 2978 (w), 2866 (w), 2843 (w), 2220 (w), 1662 (m), 1601 (s), 1574 (w), 1512 (m), 1444 (w), 1421 (w), 1329 (m), 1263 (m), 1207 (m), 1169 (s), 1009 (w). ^{1}H NMR (300 MHz,

DMSO-d_6): 3.88 s, 3 H (CH_3); 5.46 s, 2 H (CH_2); 7.12 d, 2 H, *J* = 8.8 (phenylene); 8.06 d, 2 H, *J* = 8.8 (phenylene). For $C_{13}H_{11}BrN_2O_2S_3$ (403.3) calculated: 38.71% C, 2.75% H, 6.95% N; found: 38.39% C, 2.68% H, 6.97% N.

Preparation of 3-(Acylimino)-1,2-dithioles **8**. General Procedure

A mixture of appropriate amide **7**, α-bromoethanone, triethylamine and acetone (10–25 ml) was stirred for 24 h. The resulting precipitate was collected and purified by column chromatography (silica gel, CH_2Cl_2).

Ethyl 3-(acetylimino)-5-{[2-(4-methoxyphenyl)-2-oxoethyl]sulfanyl}-3H-1,2-dithiole-4-carboxylate (**8a**). Compound **7a** (0.10 g, 0.38 mmol), 2-bromo-1-(4-methoxyphenyl)ethan-1-one (0.17 g, 0.76 mmol) and triethylamine (0.05 ml, 0.38 mmol) gave 0.092 g (59%) of **8a**: m.p. 142–143 °C (CH_2Cl_2). IR: 2980 (w), 2945 (w), 2899 (w), 2850 (w), 1720 (s), 1672 (m), 1601 (m), 1574 (m), 1510 (w), 1423 (m), 1358 (m), 1259 (s), 1182 (s), 1020 (s), 1009 (w). ^{1}H NMR (300 MHz, $CDCl_3$): 1.45 t, 3 H, *J* = 7.1 (C**H**$_3$CH$_2$); 2.46 s, 2 H (CH_3CO); 3.91 s, 3 H (CH_3O); 4.49 q, 2 H, *J* = 7.1 (CH_3C**H**$_2$); 4.69 s, 2 H ($COCH_2$); 6.99 d, 2 H, *J* = 8.7 (phenylene); 7.98 d, 2 H, *J* = 8.7 (phenylene). ^{13}C NMR (300 MHz, $CDCl_3$): 14.4 (**C**H$_3$CH$_2$), 24.9 (**C**H$_3$CO), 43.1 (CO**C**H$_2$), 55.8 (CH_3O), 62.4 (CH_3**C**H$_2$), 114.5 (phenylene), 128.0, 131.1 (phenylene), 130.4 (phenylene), 162.9, 164.7, 175.6, 183.8, 184.9, 189.8 (**C**OCH$_2$). For $C_{17}H_{17}NO_5S_3$ (411.5) calculated: 49.62% C, 4.16% H, 3.40% N; found: 49.21% C, 4.20% H, 3.36% N.

Ethyl 3-(benzoylimino)-5-{[2-(4-methoxyphenyl)-2-oxoethyl]sulfanyl}-3H-1,2-dithiole-4-carboxylate (**8b**). Compound **7b** (0.10 g, 0.31 mmol), 2-bromo-1-(4-methoxyphenyl)ethanone (0.14 g, 0.62 mmol) and triethylamine (0.09 ml, 0.62 mmol) gave 0.045 g (31%) of **8b**: m.p. 182–183 °C (CH_2Cl_2). IR: 3016 (w), 2983 (w), 2941 (w), 2891 (w), 2848 (w), 1712 (s), 1676 (m), 1601 (m), 1539 (m), 1452 (w), 1421 (m), 1329 (s), 1279 (s), 1182 (s), 1113 (w), 1020 (w). ^{1}H NMR (300 MHz, DMSO-d_6): 1.42 t, 3 H, *J* = 7.1 (C**H**$_3$CH$_2$); 3.87 s, 3 H (CH_3O); 4.46 q, 2 H, *J* = 7.1 (CH_3C**H**$_2$); 5.24 s, 2 H ($COCH_2$); 7.11 d, 2 H, *J* = 8.8 (phenylene); 7.53–7.65 m, 3 H (Ph); 8.06 d, 2 H, *J* = 8.8 (phenylene); 8.22 m, 2 H (Ph). ^{13}C NMR (300 MHz, DMSO-d_6): 14.3 (**C**H$_3$CH$_2$), 42.7 (CO**C**H$_2$), 55.8 (CH_3O), 61.8 (CH_3**C**H$_2$), 114.2 (phenylene), 125.6, 127.8, 128.8, 129.4, 131.1 (phenylene), 133.1, 133.7, 162.8, 164.0, 176.0, 176.9, 180.8, 190.6 (**C**OCH$_2$). For $C_{22}H_{19}NO_5S_3$ (473.6) calculated: 55.80% C, 4.04% H, 2.96% N; found: 55.63% C, 4.07% H, 2.89% N.

Ethyl 3-(acetylimino)-5-[(2-oxo-1,2-diphenylethyl)sulfanyl]-3H-1,2-dithiole-4-carboxylate (**8c**). Compound **7a** (0.25 g, 0.95 mmol), 2-bromo-1,2-diphenylethan-1-one (0.39 g, 1.43 mmol) and triethylamine (0.13 ml, 0.95 mmol) gave 0.288 g (66%) of **8c**: m.p. 158–159 °C (CH_2Cl_2). IR: 3060 (w), 2980 (w), 2931 (w), 1728 (m), 1680 (m), 1566 (w), 1425 (w), 1365 (m), 1323 (m), 1269 (s), 1200 (w), 1012 (m). ^{1}H NMR (300 MHz, $CDCl_3$): 1.41 t, 3 H, *J* = 7.1 (C**H**$_3$CH$_2$); 2.44 s, 3 H (CH_3CO); 4.46 q, 2 H, *J* = 7.1 (CH_3C**H**$_2$); 6.39 s, 1 H (COCH); 7.27–8.01 m, 10 H (Ph). ^{13}C NMR (300 MHz, $CDCl_3$): 14.3 (**C**H$_3$CH$_2$), 24.9 (**C**H$_3$CO), 61.0 (CO**C**H), 62.5 (CH_3**C**H$_2$), 116.1 (C-4), 127.5, 129.2, 129.3, 129.5, 129.7, 129.9, 133.8, 134.8, 163.1, 173.3, 181.2, 183.8, 192.8 (**C**OCH). For $C_{22}H_{19}NO_4S_3$ (457.6) calculated: 57.75% C, 4.19% H, 3.06% N; found: 57.49% C, 4.29% H, 3.10% N.

N-(4-Cyano-5-{[2-(4-methoxyphenyl)-2-oxoethyl]sulfanyl}-3H-1,2-dithiol-3-ylidene)acetamide (**8d**). A mixture of **7d** (0.20 g, 0.92 mmol), 2-bromo-1-(4-methoxyphenyl)ethan-1-one (0.21 g, 0.92 mmol), triethylamine (0.13 ml, 0.92 mmol) and dimethylformamide (5 ml) was stirred for 12 h. The mixture was diluted with water and ice. The resulting precipitate was worked up according to the general procedure described for **8**. Compound **8d** was obtained in a yield

of 0.118 g (70%): m.p. 186–187 °C (CH_2Cl_2). IR: 3010 (w), 2974 (w), 2908 (w), 2845 (w), 2216 (w), 1670 (m), 1601 (s), 1574 (m), 1512 (w), 1444 (m), 1363 (m), 1317(s), 1267 (s), 1215 (m), 1186 (m), 1026 (m). ^{1}H NMR (300 MHz, $CDCl_3$): 2.39 s, 3 H (CH_3CO); 3.88 s, 3 H (CH_3O); 5.37 s, 1 H ($COCH_2$); 7.12 d, 2 H, *J* = 8.6 (phenylene); 8.07 d, 2 H, *J* = 8.6 (phenylene). ^{13}C NMR (300 MHz, $CDCl_3$): 24.3 (CH_3CO), 24.9 (CH_2), 55.7 (CH_3O), 112.4 (C-4), 114.2 (phenylene), 127.5, 131.1 (phenylene), 164.1, 181.3, 182.8, 183.4, 189.9 ($COCH_2$). For $C_{15}H_{12}N_2O_3S_3$ (364.5) calculated: 49.43% C, 3.32% H, 7.69% N; found: 49.45% C, 3.30% H, 7.61% N.

Alternative preparation of ethyl 3-(acetylimino)-5-{[2-(4-methoxyphenyl)-2-oxoethyl]sulfanyl}-3H-1,2-dithiole-4-carboxylate (**8a**). The suspension of **9** (0.10 g, 0.20 mmol) in chloroform was treated with triethylamine (0.06 ml, 0.40 mmol). The initially heterogenous mixture became homogenous. After stirring at room temperature for 12 h, the reaction mixture was evaporated. The crude product was recrystallized from dichloromethane to afford **8a** (0.041 g, 50%): m.p. 142–143 °C (CH_2Cl_2); identical with described above.

5-Acetamido-4-(ethoxycarbonyl)-3-{[2-(4-methoxyphenyl)-2-oxoethyl]sulfanyl}-1,2-dithiol-1-ium bromide (**9**). The amide **7a** (0.10 g, 0.38 mmol) was dissolved in acetone (10 ml) and 2-bromo-1-(4-methoxyphenyl)ethan-1-one (0.13 g, 0.57 mmol) was added. A precipitate appeared within ca. 10 min. After stirring overnight the product was collected and washed with acetone. Compound **9** was obtained in a yield of 0.160 g (68%): m.p. 159–160 °C (acetone). IR: 3399 (m), 3299 (w), 3146 (w), 2986 (w), 2933 (w), 2906 (w), 1688 (s), 1676 (s), 1596 (m), 1501 (m), 1381 (s), 1365 (w), 1312 m, 1264 (s), 1247 (s), 1205 (m), 1172 (s), 1006 (m). ^{1}H NMR (300 MHz, DMSO-d_6): 1.36 t, 3 H, *J* = 7.1 (CH_3CH_2); 2.38 s, 2 H (CH_3CO); 3.88 s, 3 H (CH_3O); 4.42 q, 2 H, *J* = 7.1 (CH_3CH_2); 5.24 s, 2 H ($COCH_2$); 7.11 d, 2 H, *J* = 8.9 (phenylene); 8.05 d, 2 H, *J* = 8.9 (phenylene). ^{13}C NMR (300 MHz, DMSO-d_6): 13.8 (CH_3CH_2), 23.9 (CH_3CO), 43.1 (CH_3O), 55.6 ($COCH_2$), 62.2 (CH_3CH_2), 114.1 (phenylene), 127.6, 130.9 (phenylene), 161.9, 163.9, 178.1, 180.0, 190.2. For $C_{17}H_{18}BrNO_5S_3$ (492.4) calculated: 41.47% C, 3.68% H, 2.84% N; found: 41.37% C, 3.72% H, 2.73% N.

Preparation of Lactones **13**. General Procedure

To a stirred solution of ester **4c** (0.10 g, 0.24 mmol) or **4d** (0.11 g, 0.24 mmol) in toluene (10 ml), excess of thionyl chloride (0.35 ml, 4.80 mmol) was added dropwise during 10 min. After 6 h, the precipitated product was collected and washed with toluene.

N-[4-Oxo-6,7-diphenyl-3H,4H-[1,2]dithiolo[4,3-c]pyran-3-ylidene]acetamide (**13a**). This compound was obtained in a yield of 0.065 g (71%): m.p. 191–192 °C (toluene). IR: 3063 (w), 1733 (s), 1694 (s), 1586 (w), 1563 (m), 1480 (s), 1400 (m), 1367 (w), 1211 (m), 1127 (w), 1070 (w). ^{1}H NMR (300 MHz, $CDCl_3$): 2.68 s, 3 H (CH_3); 7.27–7.72 m, 10 H (Ph). ^{13}C NMR (300 MHz, $CDCl_3$): 27.0 (CH_3), 115.6 (C-4), 116.2 (C-5), 128.6, 130.0, 130.1, 130.7, 130.8, 131.4, 133.3 (Ph), 154.4, 157.4, 176.4, 181.4, 184.7. For $C_{20}H_{13}NO_3S_2$ (379.5) calculated: 63.31% C, 3.45% H, 3.69% N; found: 63.57% C, 3.51% H, 3.76% N.

2,2-Dimethyl-N-[4-oxo-6,7-diphenyl-3H,4H-[1,2]dithiolo[4,3-c]pyran-3-ylidene]propanamide (**13b**). This compound was obtained in a yield of 0.095 g (94%): m.p. 187–188 °C (toluene). IR: 3071 (w), 2963 (w), 2876 (w), 1726 (m), 1687 (w), 1565 (w), 1486 (s), 1401 (w), 1270 (w), 1205 (w), 1142 (m), 1069 (w). ^{1}H NMR (300 MHz, DMSO-d_6): 1.31 s, 9 H (CH_3); 7.33–7.48 m, 10 H (Ph). ^{13}C NMR (300 MHz, DMSO-d_6): 27.3 ((CH_3)$_3$C), 44.5 ((CH_3)$_3$C), 115.7 (C-4), 119.8 (C-5), 128.4, 128.9, 129.3, 129.5, 130.4, 131.0, 131.7, 132.9 (Ph), 153.3, 156.6, 175.8, 180.4,

191.3. For $C_{23}H_{19}NO_3S_2$ (421.5) calculated: 65.53% C, 4.54% H, 3.32% N; found: 65.95% C, 4.36% H, 3.32% N.

Methyl 5-amino-3-(2-oxo-1,2-diphenylethylidene)-3H-1,2-dithiole-4-carboxylate (**14**). An excess of sodium sulfide nonahydrate (0.08 g, 0.33 mmol) was added at room temperature to a suspension of **13a** or **13b** (0.13 mmol) in methanol (10 ml). The mixture was stirred for 24 h. It was then evaporated and further purified by chromatography (silica gel, CH_2Cl_2). This compound was obtained in a yield of 0.015 g (31%) or 0.036 g (66%), respectively: m.p. 180 °C (decomp.; CH_2Cl_2). IR: 3414 (w), 3299 (m), 3173 (w), 3056 (w), 2991 (w), 2940 (w), 1669 (s), 1594 (s), 1514 (m), 1438 (m), 1378 (s), 1335 (s), 1307 (w), 1246 (w), 1113 (w). ^{1}H NMR (300 MHz, $CDCl_3$): 2.88 s, 3 H (CH_3); 6.72 s, br, 2 H (NH_2); 7.06–7.28 m, 10 H (Ph). ^{13}C NMR (300 MHz, $CDCl_3$): 51.3 (CH_3), 106.8 (C-4), 121.3, 126.8, 127.8, 128.8, 129.3, 129.8, 137.2, 139.3 (Ph), 166.2, 173.1, 174.1, 184.3 (PhCO). ESI-MS (positive ion mode): 413.2 (M + 2 Na – H), 391.8 (M + Na), 369.8 (M + H); (negative ion mode): 467.7 (M – H). For $C_{19}H_{15}NO_3S_2$ (369.5) calculated: 61.77% C, 4.09% H, 3.79% N; found: 61.96% C, 3.92% H, 3.78% N.

Aminolysis of Lactone **13a**. General Procedure

Lactone **13a** (0.1 g, 0.26 mmol) in chloroform (15 ml) was treated at room temperature with an appropriate amine (**15a**: dimethylamine (33% in ethanol); **15b**: benzylamine (0.62 mmol)) and stirred for 3 h. The mixture was concentrated in vacuo and the residue was recrystallized from CH_2Cl_2.

5-Acetamido-N,N-dimethyl-3-(2-oxo-1,2-diphenylethylidene)-3H-1,2-dithiole-4-carboxamide (**15a**). This compound was obtained in a yield of 0.089 g (81%): m.p. 166–167 °C (CH_2Cl_2). IR: 3020 (w), 2778 (w), 1700 (s), 1616 (s), 1546 (m), 1442 (w), 1337 (s), 1304 (w), 1270 (m), 1235 (w), 1139 (w), 1021 (m). ^{1}H NMR (300 MHz, DMSO-d_6): 2.10 s, 3 H (CH_3CO); 2.23 s, 3 H (CH_3N); 2.56 s, 3 H (CH_3N); 6.99–7.21 m, 10 H (Ph). ^{13}C NMR (300 MHz, DMSO-d_6): 23.1 (CH_3CO), 33.7 (CH_3N), 37.2 (CH_3N), 118.7 (C-4), 120.0 (PhCOCPh), 126.9, 127.1, 127.3, 127.5, 128.1, 128.8, 131.1, 131.8, 132.9, 135.9, 138.8 (Ph), 155.9, 162.6, 164.0, 170.1, 184.9 (PhCOCPh). ESI-MS (positive ion mode): 446.9 (M + Na); (negative ion mode): 422.8 (M – H). For $C_{22}H_{20}N_2O_3S_2$ (424.5) calculated: 62.24% C, 4.75% H, 6.60% N; found: 62.49% C, 4.61% H, 6.50% N. Crystallographic data for **15a**: $C_{44}H_{40}N_4O_6S_4$, M = 849.04, monoclinic crystal system, space group P-1, a = 12.2866(8) Å, b = 29.640(2) Å, c = 22.4405(12) Å, α = 90°, β = 94.665(4)°, γ = 90°, V = 8145.2(9) Å^3, Z = 8, D_{calc} = 1.385 Mg m^{-3}. Number of collected/independent reflections was 25834/7161; R_{int} = 0.0522. The final R indices [$I > 2\sigma(I)$]: $R1$ = 0.0421, $wR2$ = 0.0978, the largest different peak and hole were 0.422 and –0.273 e Å^{-3}. CCDC 284865 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

5-(Acetylimino)-N-benzyl-3-(2-oxo-1,2-diphenylethyl)-3H-1,2-dithiole-4-carboxamide (**15b**). This compound was obtained in a yield of 0.076 g (60%): m.p. 165–166 °C ($CHCl_3$). IR: 3052 (w), 3001 (w), 2926 (w), 2874 (w), 1703 (m), 1627 (m), 1537 (s), 1513 (s), 1382 (w), 1340 (s), 1305 (m), 1272 (m), 1245 (w), 1216 (m), 1181 (w). ^{1}H NMR (300 MHz, DMSO-d_6): 2.20 s, 3 H (CH_3); 3.37 s, 2 H (CH_2); 7.01–7.47 m, 15 H (Ph). ^{13}C NMR (300 MHz, DMSO-d_6): 23.4 (CH_3), 42.4 (CH_2), 118.8 (C-4), 121.2 (PhCOCPh), 126.9, 127.2, 127.5, 127.7, 128.2, 128.4, 128.8, 128.9, 129.2, 131.7, 132.5, 137.6, 137.9, 138.8 (Ph), 157.7, 163.0, 165.3, 169.5, 185.2

(PhCOCPh). ESI-MS (positive ion mode): 509.1 (M + Na), 486.9 (M + H); (negative ion mode): 484.9 (M – H). For $C_{27}H_{22}N_2O_3S_2$ (486.6) calculated: 66.64% C, 4.56% H, 5.76% N; found: 66.52% C, 4.70% H, 5.93% N.

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