SYNTHESES AND STRUCTURE STUDY ON 3,3aλ^4,4-TRITHIA-1-AZAPENTALENES AND THEIR 3-OXA ANALOGUES

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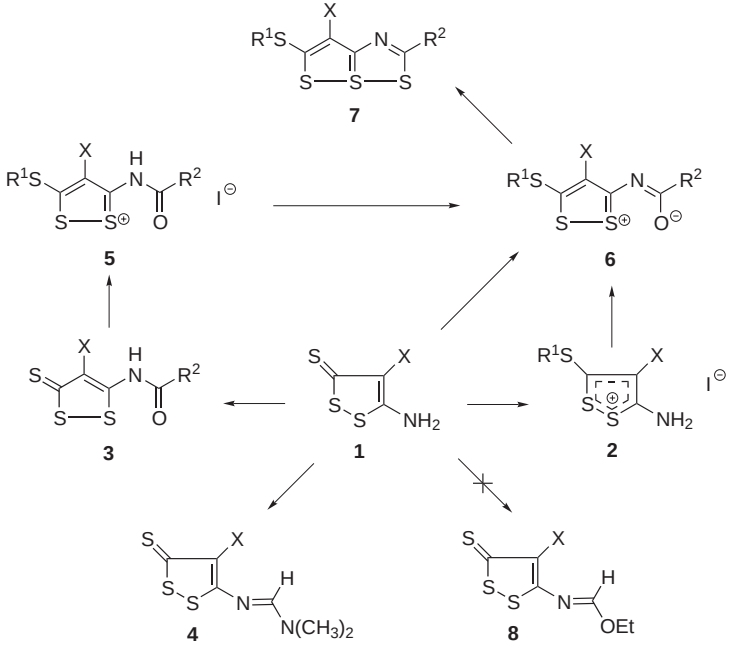
Reactions of nitrile, amide or ester of 5-amino-3-thioxo-3*H*-1,2-dithiole-4-carboxylic acid **1** with alkylation and acylation agents were studied. "Ionic" 1,2-dithiole amides **6** were formed in several ways. Treatment with phosphorus pentasulfide afforded the corresponding 3,3aλ^4,4-trithia-1-azapentalenes **7**. Structures of the synthesized heterocycles were studied using a combination of X-ray analysis, IR spectroscopy, and HF and DFT quantum-chemical calculations.

Keywords: Acylations; Alkylations; DFT calculation; Sulfur heterocycles; Trithiapentalenes; X-Ray diffraction; Disulfides; Cyclizations.

Syntheses of functional derivatives of 5-amino-3-thioxo-3*H*-1,2-dithiole-4-carboxylic acid (**1**; X = COOH) were originally described in 1963 [1]. Little attention[1,2] has been given to their reactivity in spite of their simple preparation from available compounds and the presence of easily convertible functional groups. This fact was probably caused by their poor solubility in polar aprotic solvents. Moreover, these compounds are also prone to undesirable transformations in basic medium[1,3]. In contrast, these derivatives have been utilized for example as lubricating oil additives[2] with anticorrosion and antiwear properties, herbicidal active compounds[4], or as sharpening ingredients for photographic materials[5]. The presence of disulfide function indicates the interesting possibility of participation in redox processes. This structural feature makes these compounds potential radical scavengers[6].

The mentioned spectrum of industrial application of 1,2-dithiole-3-thiones led us to the investigation of the reactivity of compounds **1** in

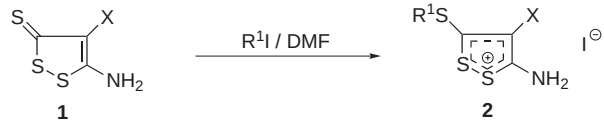
alkylation and acylation reactions, and to the structure and property analyses of reaction products (Scheme 1). Regioselectivity in the formation of compounds **2** and **3** has been reported[7]. Their other utilizations, which have been investigated in this work, are suggested in Scheme 1. Compounds **1** offer an interesting possibility to prepare systems with trithiazapentalene structural motif, as well as its oxa analogue. The present part of the work has been focused on preparation of compound **6** and its subsequent modification. The corresponding studies provided several intermediates as well as interesting information about the structure and properties of the obtained heterocyclic systems. Also compounds **6** offer potential applications like lubrication oil additives[6,8] (similarly to **1**) or electron transfer catalysts[9]. The second synthetic path leading to **6** was inferred from the widely used reaction of 1,2-enaminonitriles with triethyl orthoformate in acetic anhydride. The expected *N*-(ethoxymethylidene)amino derivative **8** offers a number of possible pathways leading to heteroannulated pyrimidines[10,11]. Unfortunately, these experiments have been rather unsuccessful.



SCHEME 1
Synthetic pathways to 1,2-dithiole derivatives

RESULTS AND DISCUSSION

The first part of the work was focused on the reactivity of compounds **1** towards the alkylation agents. We have found that their alkylation with alkyl iodides (R^1 = Me, Bn) proceeded only on the sulfur atom of the thioxo group under formation of salts **2** (Scheme 2). Predictably, bulky alkylation agents (*e.g.* isopropyl iodide, cyclohexyl iodide, *tert*-butyl iodide) generally failed to react.



SCHEME 2
Alkylation of dithioles **1**

The assumed structure of compounds **2** has been confirmed by X-ray structure analysis of **2a** (X = CN, R^1 = Me). Only in the case of compound **2a**, formation of a complex with solvent (DMF) was observed. The interaction is outlined in Fig. 1, structure **A**. For other structures, **2b** (X = COOEt, R^1 = Me) and **2c** (X = $CONH_2$, R^1 = Me), the presence of solvent has not been confirmed (IR spectra, see Experimental). We could assume stabilization by an intramolecular hydrogen bond between the amino group and the carbonyl oxygen (Fig. 1, structure **B**).

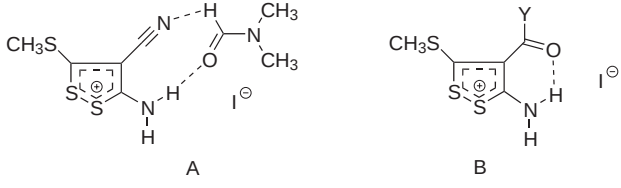
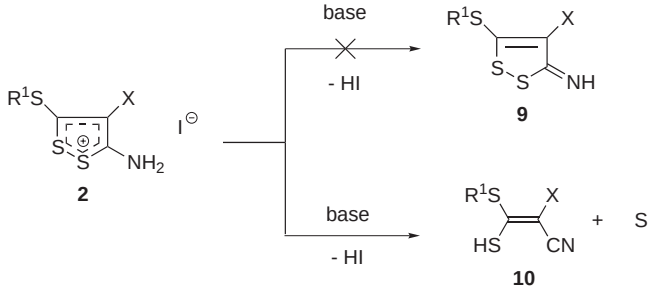


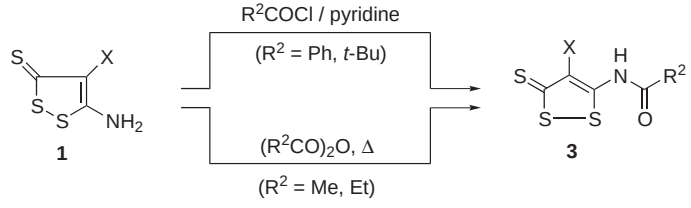
FIG. 1
A Structure of **2a** and its dimethylformamide complex; **B** intramolecular stabilization of salts **2b** and **2c** (Y = OEt, NH_2)

An attempt to liberate imines **9** from salts **2** in alkaline medium[3] provided corresponding 3-alkylsulfanyl-2-cyano-3-sulfanylpropenoic acid derivatives **10** and elemental sulfur (Scheme 3). This problem (instability in alkaline medium) was solved by protection of the amino group bonded to the 1,2-dithiole by acylation. Such modification prevented the ring opening and transformation to the cyano compound[1,3].



SCHEME 3
Transformation of salts **2** in alkaline medium

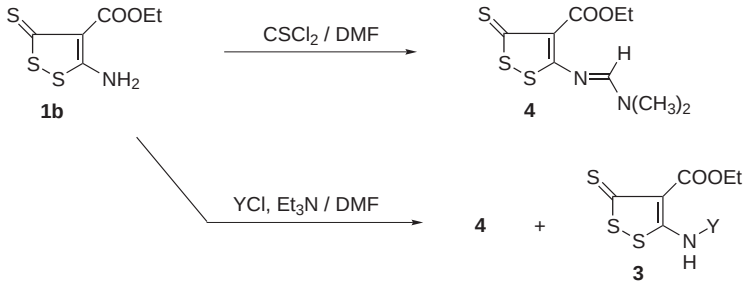
Refluxing compounds **1** in solution with acid anhydrides (R^2 = Me, Et) provided carbamoyl dithioles **3**. The same type of compounds was also obtained by reaction of **1** with corresponding acyl chloride (R^2 = Ph, *t*-Bu) in pyridine solution (Scheme 4).



SCHEME 4
Acylation of dithioles **1**

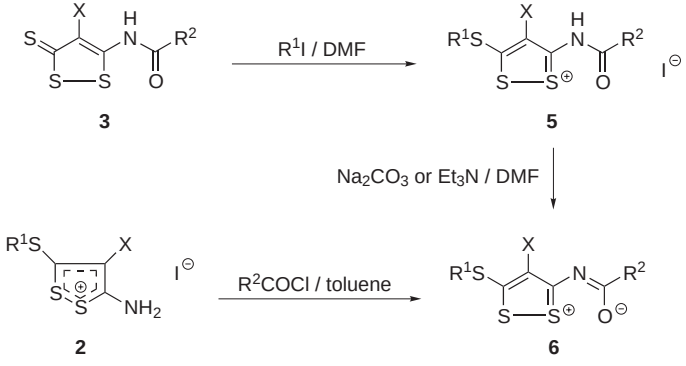
In contrast to previous assumption[12], the acylations of nitrile **1a** (X = CN), ester **1b** (X = COOEt) or amide **1c** (X = $CONH_2$) on the amino group proceeded easily. However, the isolation of the product from **1a** was complicate (see Experimental). Generally, the studied acylation has not been significantly influenced by the used acyl group (acetyl, propionyl, ethoxycarbonyl, benzoyl or 2,2-dimethylpropanoyl). With amide **1c**, a high excess of the acylation agent resulted in the double acylation of the amino group.

The benzoylation or ethoxycarbonylation of ester **1b** (in DMF in the presence of triethylamine or sodium hydrogencarbonate) led to the formation of amidine **4** together with amide **3**. The same amidine **4** (*cf.* ref.[13]) was also synthesized by reaction of **1b** with thiophosgene in DMF. Both reactions are presented in Scheme 5.



SCHEME 5
Formation of ethyl 5-{[(dimethylamino)methylidene]amino}-3-thioxo-3*H*-1,2-dithiole-4-carboxylate **4** (Y = Bz, COOEt)

Alkylation of amides **3** on the sulfur atom of the thioxo group yielded dithiolium salts **5**, previously considered as adducts[1]. These salts usually easily lose hydrogen halide to form imidates **6**. The conversion requires basification of the reaction mixture, for example with triethylamine or sodium carbonate (Scheme 6).

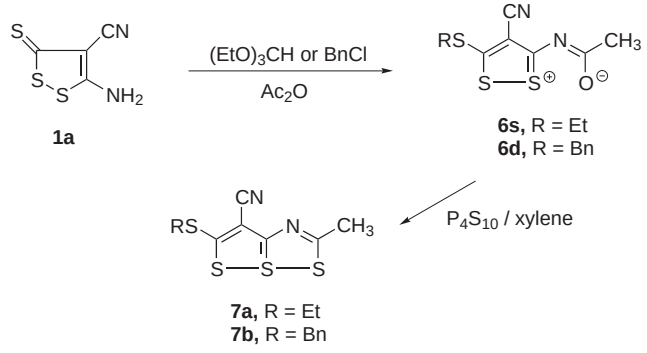


X = CN, COOEt, $CONH_2$; R^1 = Me, Bn; R^2 = Me, *t*-Bu, Ph

SCHEME 6
Alternative preparation of *N*-[4-X-3-(R^2-sulfanyl)-1,2-dithiol-1-ium-5-yl]-R^1-carboximidates **6**

The same type of products **6** have been obtained in the inverted order of reaction steps, *via* intermediate salt **2**. A small amount of imidate **6** (except X = CN) underwent dealkylation. In this case, amide **3** was isolated (Scheme 6). Nitrile **1a** showed a rather different reactivity. Reaction with triethyl orthoformate in the presence of acetic anhydride provided com-

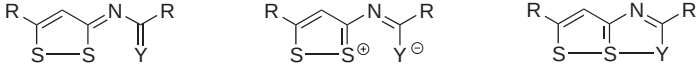
pound **6s** (R^1 = Et, R^2 = Me, X = CN) (Scheme 7). The ethylation with ethyl orthoformate is a rare reaction[14]. Analogous product **6d** has been synthesized using benzyl chloride.



SCHEME 7
Synthesis of 6-(alkylsulfanyl)-2-methyl-4λ⁴-[1,2]dithiolo[1,5-*b*][1,2,4]dithiazole-7-carbonitriles **7**

Amides **6d** and **6s** were then subjected to the reaction with phosphorus pentasulfide in refluxing xylene to provide trithiazapentalenes[15] **7a** and **7b** (Scheme 7). Replacement of P_4S_{10} by the Lawesson's reagent resulted in poor yields of the products.

The following part of the work is focused on structural studies of some of the above mentioned compounds with the oxadithiapentalene and trithiapentalene bicyclic systems. The FTIR and ^{13}C NMR data of compounds **6a** (X = CN, R^1 = Bn, R^2 = Me) and **7a** (X = CN, R^1 = Bn, R^2 = Me) indicated the presence of the non-typical carbonyl or thiocarbonyl functional group, respectively. The X-ray studies confirmed these compounds as 3,3aλ⁴,4-trithia-1-azapentalenes and their oxa analogues. The main problem was to establish whether these compounds are carbonyl (or thiocarbonyl) derivatives or rather oxadithiapentalene (or trithiapentalene) bicyclic systems (Scheme 8).



SCHEME 8
Possible structures of oxadithia/trithiapentalenes (Y = O, S)

The analysis of this problem has been performed using a combination of quantum chemistry and experimental structure analysis. The combined procedure enables a good insight into the distribution of electron density and binding relations in the studied molecules. The absence of a typical strong carbonyl absorption at 1660–1690 cm^{-1} has been observed for compound **6d**. IR spectroscopy indicated the increased saturation of C–O bond contrary to the normal carbonyl bond. Moreover, the S–S bond length in this compound is typical rather for a disulfide structure. The X-ray study of **6d** showed the following bond lengths: C–O 1.249 Å (tabulated for the carbonyl 1.33 Å)[16], S–S 2.127 Å (2.07 Å in disulfides)[16] and S···O 2.284 Å (1.58 Å is typical of sulfonates)[16]. From the results of theoretical calculations, namely from calculations on the B3LYP/6-31G* and on the B3LYP/6-311G** levels of theory, it is evident that the C10–O11 bond order is somewhat lower than two, and that the electron pair of this "double" bond is delocalized over the whole O11–C10–N9–C3–S2 atom sequence. Then, the carbonyl absorption is shifted to a lower wavenumber (from typical 1650 to 1567 cm^{-1}). The values of calculated partial charges (+0.286 for sulfur atom and –0.500 for oxygen atom) and bond order (0.366) support the existence of oxadithiapentalene structure with partially "ionic" S–O bond. Clearly, the polarity is certainly modified by the substitution in other positions of the pentalene system. Important results of the calculations together with comparative experimental data are summarized in Table I and Fig. 2.

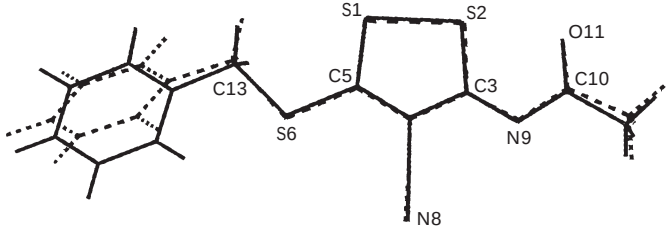


FIG. 2
Comparison of X-ray (solid) and theoretical B3LYP/6-31G* (dashed) structures of compound **6d**

Regarding the trithiapentalene systems, situation is somewhat different. The X-ray study of compound **7a** showed similar lengths of all C–S bonds (1.671, 1.755 and 1.712 Å). The distances between sulfur atoms are 2.185 and 2.522 Å, being similar to those in normal disulfides. The calculated bond orders (0.582 and 0.915), and partial charges (–0.105, 0.112 and –0.143) indicated the presence of covalent interaction between neighboring

sulfur atoms. The trithiapentalene system has the character of the bicyclic system rather that of the thiocarbonyl compound. The results of these calculations together with comparative experimental data are summarized in Table II and Fig. 3.

TABLE I
Calculated and experimental structural and electronic parameters of compound **6d**

Atom	Partial atomic charge, e		
	HF/6-31G*	B3LYP/6-31G*	B3LYP/6-31G**
S1	0.136	0.054	0.054
S2	0.268	0.285	0.286
O11	–0.572	–0.499	–0.500

Bond	Bond length, Å				Bond order
	X-ray	HF/6-31G*	B3LYP/6-31G*	B3LYP/6-31G**	
S1–S2	2.1270(11)	2.089	2.209	2.212	0.985
S2–O11	2.284(4)	2.548	2.203	2.224	0.366
O11–C10	1.249(4)	1.203	1.258	1.248	1.704
N9–C10	1.368(4)	1.389	1.360	1.362	1.358
N9–C3	1.319(4)	1.272	1.317	1.310	1.532
S1–C5	1.714(3)	1.734	1.725	1.725	1.131
S2–C3	1.760(3)	1.772	1.779	1.782	1.130
S6–C5	1.736(3)	1.751	1.751	1.750	1.220
S6–C13	1.832(3)	1.834	1.856	1.856	1.035

Frequency, cm^{-1}	Ref.[17]	Found	B3LYP/6-31G*	B3LYP/6-31G**
C=O	1630–1670	1567	1604	1613
C–NAc	1260–1310	1357	1368	1396
C–N (heterocycle)	1480–1660	1493	1492	1488
C–S	675–760	774	781	781

TABLE II
Calculated and experimental structural and electronic parameters of compound **7a**

Atom	Partial atomic charge, e		
	HF/6-31G*	B3LYP/6-31G*	B3LYP/6-31G**
S1	–0.177	–0.053	–0.053
S2	0.266	0.183	0.184
S11	0.114	0.266	0.032

Bond	Bond length, Å				Bond order
	X-ray	HF/6-31G*	B3LYP/6-31G*	B3LYP/6-31G**	
S1–S2	2.5221(17)	2.923	2.538	2.539	0.5815
S2–S11	2.1845(16)	2.083	2.274	2.273	0.9146
S11–C10	1.712(4)	1.743	1.732	1.732	1.3683
N9–C10	1.323(5)	1.267	1.306	1.306	1.5996
N9–C3	1.337(5)	1.370	1.351	1.351	1.3803
S1–C5	1.671(4)	1.648	1.691	1.691	1.3217
S2–C3	1.755(3)	1.762	1.779	1.779	1.2043
S6–C5	1.752(3)	1.754	1.759	1.759	1.1768
S6–C13	1.802(4)	1.822	1.848	1.847	1.0869

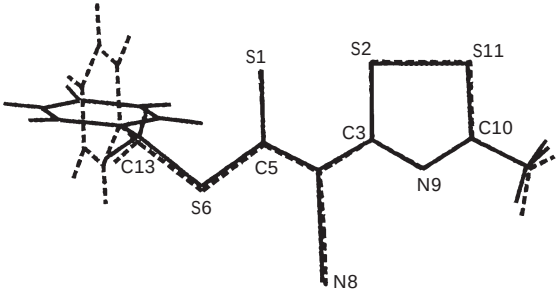


FIG. 3
Comparison of X-ray (solid) and theoretical B3LYP/6-31G* (dashed) structures of compound **7a**

CONCLUSIONS

In this paper, we have described several approaches to preparation of amides **6**. The general procedure involved successive or one-pot alkylation and acylation of 1,2-dithiole-3-thiones **1**. Intermediates **6** were converted into trithiapentalenes **7** by treatment with phosphorus pentasulfide.

Structures of compounds **6d** and **7a** were determined by X-ray structure analysis and used in a detailed structural study. Quantum mechanics calculation on HF/6-31G*, B3LYP/6-31G* and B3LYP/6-31G** levels together with X-ray structure data and spectral characteristics have been used for structure elucidation. Generally, the calculated structure and spectral data are in good agreement with experimental results. Both **6** and **7** are conjugate heterocyclic systems. In the case of **6**, a partly ionic S···O interaction has been observed. Thus, the interaction between the "carbonyl" oxygen atom and the close dithiole sulfur atom should be characterized by an "ionic" limiting structure or a polarized structure with partial charges.

On the other hand, trisulfur heterocycle **7** is a higher-covalent structure with more uniform distribution of electron density. Indeed, the S–S bond lengths do not respond equally to different substitution of individual rings. Contrary to the oxa analogues, the obtained results indicated the presence of heteropentalene bicyclic system.

EXPERIMENTAL

General

Unless otherwise noted, materials were obtained from commercial suppliers and were used without further purification. Dimethylformamide (DMF) and xylene were stored over 4 Å sieves. Pyridine was freshly distilled from BaO. Organic layers from aqueous extraction were dried over anhydrous Na_2SO_4 or $CaCl_2$ and concentrated *in vacuo*. Melting points, determined with a Kofler hot-stage apparatus, are uncorrected. All ^1H and ^{13}C NMR spectra were measured at 500 and 75.5 MHz, respectively (DRX 500 Avance Bruker). Chemical shifts are given in ppm (δ-scale) downfield from tetramethylsilane as internal reference. Coupling constants *J* are reported in Hz. FTIR spectra (in KBr; ν, cm^{-1}) were measured on a Genesis ATI Mattson spectrometer. Thin-layer chromatography was performed using commercial prepared silica gel plates (Silufol UV 254) and visualized with short-wavelength UV light (254 nm). Silica gel L 100/400 (Lachema, Brno) was used for column chromatography. Elemental analyses were carried out in Pliva-Lachema, Co., Brno, Czech Republic.

Calculation Methods

All theoretically studied molecules were optimized on the HF/6-31G*, B3LYP/6-31G* and B3LYP/6-311G** levels of theory using the Gaussian 94 quantum chemical program (Gaussian Inc., U.K.). The X-ray analysis provided the input geometries in all cases. Mulliken popu-

lation analysis was used to calculate partial charges. Mayer bond orders[18] were calculated on B3LYP/6-311G**/iii-iglo level by deMon v1.0 [19]. The vibration frequency analysis was performed for each levels of theory. The results of theoretical structure analysis have been confronted with experimentally obtained X-ray, FTIR and NMR data.

1,2-Dithiol-1-ium Iodides **2**. General Procedure

To a solution of **1** [1] (6.00 mmol) in DMF (10 ml) was added methyl iodide (0.75 ml, 12.05 mmol) or benzyl iodide (1.51 ml, 12.00 mmol). After standing at room temperature for 24 h, the precipitate was collected by filtration and washed with ethanol.

5-Amino-4-cyano-3-(methylsulfanyl)-1,2-dithiol-1-ium iodide (**2a**). Yield 1.25 g (66%), m.p. 195–196 °C (decomp.; DMF). IR: 3217 (m), 3060 (m), 2218 (w), 1610 (s), 1500 (s), 1443 (w), 1416 (w), 1346 (w), 1315 (w), 1016 (w). ^{1}H NMR (500 MHz, DMSO-d_6): 3.01 s, 3 H (CH_3); 5.85 s, br, 2 H (NH_2). ^{13}C NMR (500 MHz, DMSO-d_6): 16.5 (CH_3), 97.7 (C-4), 109.3 (CN), 180.5 (C-3), 188.8 (C-4). For $C_5H_5IN_2S_3$ (316.2) calculated: 18.99% C, 1.59% H, 8.86% N; found: 18.67% C, 1.58% H, 8.80% N.

5-Amino-4-(ethoxycarbonyl)-3-(methylsulfanyl)-1,2-dithiol-1-ium iodide (**2b**). Yield 1.66 g (76%), m.p. 172–173 °C (DMF). IR: 3284 (m), 3186 (w), 3070 (w), 3043 (w), 1682 (s), 1591 (s), 1471 (w), 1419 (w), 1367 (w), 1317 (w), 1261 (m), 1103 (w), 1020 (w). ^{1}H NMR (500 MHz, DMSO-d_6): 1.35 t, 3 H, J = 7.1 (C**H**$_3$CH$_2$); 2.89 s, 3 H (CH_3S); 4.41 q, 2 H, J = 7.1 (CH_2); 9.66 s, br, 1 H (NH_2); 10.65 s, br, 1 H (NH_2). ^{13}C NMR (500 MHz, DMSO-d_6): 13.6 (**C**H$_3$CH$_2$), 17.1 (CH_3S), 62.2 (CH_2), 113.8 (C-4), 160.7 (COO), 180.9 (C-3), 189.3 (C-5). For $C_7H_{10}INO_2S_3$ (363.3) calculated: 23.15% C, 2.77% H, 3.86% N; found: 22.89% C, 2.62% H, 3.58% N.

5-Amino-4-carbamoyl-3-(methylsulfanyl)-1,2-dithiol-1-ium iodide (**2c**). Yield 1.21 g (60%), m.p. 207–208 °C (DMF). IR: 3296 (w), 3249 (w), 3149 (w), 3062 (m), 1672 (s), 1587 (s), 1475 (w), 1441 (w), 1390 (m), 1282 (w), 1124 (w). ^{1}H NMR (500 MHz, DMSO-d_6): 2.85 s, 3 H (CH_3); 7.93 s, br, 2 H (NH_2). ^{13}C NMR (500 MHz, DMSO-d_6): 16.6 (CH_3), 123.1 (C-4), 161.2 (CO), 178.7, 179.5 (C-3, C-5). For $C_5H_7IN_2OS_3$ (334.2) calculated: 17.97% C, 2.11% H, 8.38% N; found: 18.06% C, 2.01% H, 8.31% N.

5-Amino-3-(benzylsulfanyl)-4-cyano-1,2-dithiol-1-ium iodide (**2d**). Yield 0.41 g (17%), m.p. 150 °C (subl.; DMF). IR: 3275 (m), 3221 (m), 3074 (m), 2222 (m), 1618 (s), 1493 (s), 1448 (w), 1431 (m), 1381 (w), 1342 (m), 1236 (w), 1066 (w). ^{1}H NMR (500 MHz, DMSO-d_6): 4.55 s, 2 H (CH_2); 7.20–7.37 m, 5 H (Ph); 9.48 s, br, 2 H (NH_2). ^{13}C NMR (500 MHz, DMSO-d_6): 37.7 (CH_2), 99.88 (C-4), 112.7 (CN), 126.7, 128.7, 129.0, 134.8 (Ph), 162.5 (C-3), 180.4 (C-5). For $C_{11}H_9IN_2S_3$ (392.3) calculated: 33.68% C, 2.31% H, 7.14% N; found: 33.37% C, 2.27% H, 7.19% N.

5-Amino-3-(benzylsulfanyl)-4-(ethoxycarbonyl)-1,2-dithiol-1-ium iodide (**2e**). Yield 1.53 g (58%), m.p. 176–177 °C (DMF). IR: 3303 (s), 2989 (s), 2891 (w), 1684 (s), 1593 (s), 1489 (w), 1468 (m), 1423 (s), 1383 (w), 1363 (s), 1329 (s), 1257 (s), 1097 (m), 1005 (m). ^{1}H NMR (500 MHz, DMSO-d_6): 1.31 t, 3 H, J = 7.1 (C**H**$_3$CH$_2$); 4.38 q, 2 H, J = 7.1 (CH$_3$C**H**$_2$); 4.73 s, 2 H (CH_2S); 7.18–7.53 m, 5 H (Ph); 9.72 s, br, 1 H (NH_2); 10.75 s, br, 1 H (NH_2). ^{13}C NMR (500 MHz, DMSO-d_6): 13.8 (**C**H$_3$CH$_2$), 37.8 (CH_2S), 63.0 (CH$_3$**C**H$_2$), 114.2 (C-4), 128.2, 128.8, 129.2, 133.6 (Ph), 160.7 (C-3), 180.9 (C-5), 186.9 (COO). For $C_{13}H_{14}INO_2S_3$ (439.3) calculated: 35.54% C, 3.21% H, 3.19% N; found: 35.58% C, 3.22% H, 3.13% N.

5-Amino-3-(benzylsulfanyl)-4-carbamoyl-1,2-dithiol-1-ium iodide (**2f**). Yield 1.38 g (56%), m.p. 169.5–170.5 °C (DMF). IR: 3294 (s), 3143 (m), 3062 (m), 1676 (s), 1658 (m), 1587 (s), 1479 (m), 1454 (s), 1390 (m), 1302 (w), 1238 (m), 1115 (w). ^{1}H NMR (500 MHz, DMSO-d_6):

4.68 s, 2 H (CH_2); 7.35–7.51 m, 5 H (Ph); 8.07 s, 1 H (NH_2); 10.33 s, br, 1 H (NH_2). ^{13}C NMR (500 MHz, DMSO-d_6): 37.6 (CH_2), 124.2 (C-4), 128.2, 128.7, 129.1, 134.3 (Ph), 161.1 (C-3), 176.0 (CO), 179.6 (C-5). For $C_{11}H_{11}IN_2OS_3$ (410.3) calculated: 32.20% C, 2.70% H, 6.83% N; found: 31.93% C, 2.57% H, 6.77% N.

Amides **3**. General Procedure

Method A

A solution of **1a** (0.3 g, 1.72 mmol) in dry pyridine (15 ml) was stirred with an acylating agent (**3a**: acetic anhydride (0.61 ml, 8.61 mmol); **3d**: benzoyl chloride (0.60 ml, 5.16 mmol); **3g**: 2,2-dimethylpropanoyl chloride (0.64 ml, 5.16 mmol)) at 0 °C for 30 min and at 50 °C for 3 h. The reaction mixture was poured on crushed ice (100 g) and extracted with dichloromethane (3 × 10 ml). Crude product was obtained by addition of dilute (1:3) hydrochloric acid.

N-(4-Cyano-3-thioxo-3H-1,2-dithiol-5-yl)acetamide (**3a**). Yield 0.11 g (30%), m.p. > 350 °C ($CHCl_3$). IR: 3240 (w), 3168 (w), 3016 (w), 2929 (w), 2218 (m), 1709 (s), 1527 (s), 1439 (w), 1367 (w), 1335 (m), 1225 (s), 1059 (m). ^{1}H NMR (500 MHz, DMSO-d_6): 2.35 s, 3 H (CH_3). ^{13}C NMR (500 MHz, DMSO-d_6): 22.7 (CH_3), 106.9 (C-4), 113.1 (CN), 173.2, 174.1 (CO, C-5), 206.5 (C-3). For $C_6H_4N_2OS_3$ (216.3) calculated: 33.32% C, 1.86% H, 12.95% N; found: 31.83% C, 2.57% H, 6.77% N.

N-(4-Cyano-3-thioxo-3H-1,2-dithiol-5-yl)benzamide (**3d**). Yield 0.13 g (27%), m.p. 220 °C (decomp.; $CHCl_3$). IR: 3212 (w), 3159 (w), 3020 (w), 2941 (w), 2228 (m), 1673 (s), 1536 (s), 1439 (w), 1328 (s), 1266 (s), 1093 (m), 1071 (w). ^{1}H NMR (500 MHz, DMSO-d_6): 7.49–7.59 m, 3 H (Ph); 8.15–8.17 m, 2 H (Ph). ^{13}C NMR (500 MHz, DMSO-d_6): 107.9 (C-4), 116.4 (CN), 128.5, 129.1, 132.3, 134.8 (Ph), 174.8 (CO), 181.8 (C-5), 203.0 (C-3). For $C_{11}H_6N_2OS_3$ (278.4) calculated: 47.46% C, 2.17% H, 10.06% N; found: 47.19% C, 2.02% H, 10.18% N.

N-(4-Cyano-3-thioxo-3H-1,2-dithiol-5-yl)-2,2-dimethylpropanamide (**3g**). Yield 0.35 g (79%), m.p. 197–198 °C ($CHCl_3$). IR: 3275 (m), 2986 (w), 2969 (w), 2936 (w), 2224 (m), 1685 (s), 1525 (s), 1435 (w), 1332 (s), 1262 (w), 1132 (s), 1060 (w). ^{1}H NMR (500 MHz, DMSO-d_6): 1.24 s, 9 H (CH_3); 10.09 s, br, 1 H (NH). ^{13}C NMR (500 MHz, $CDCl_3$): 27.1 (CH_3), 40.0 (Me_3C), 109.0 (C-4), 112.9 (CN), 170.0 (CO), 178.9 (C-5), 204.9 (C-3). For $C_9H_{10}N_2OS_3$ (258.4) calculated: 41.84% C, 3.90% H, 10.84% N; found: 41.66% C, 3.95% H, 10.99% N.

Method B

Appropriate acyl chloride (**3e**, **3f**: benzoyl chloride (4.80 mmol); **3h**, **3i**: 2,2-dimethylpropanoyl chloride (3.60 mmol)) was added dropwise to a solution of **1b** or **1c** (2.40 mmol) in dry pyridine (10 ml) at 0 °C. After stirring for 10 min, the solution was stirred at 55 °C for 6 h. Crushed ice (100 g) was added and the precipitate was filtered off and dried.

Ethyl 5-benzamido-3-thioxo-3H-1,2-dithiole-4-carboxylate (**3e**). Yield 0.56 g (72%), m.p. 190–191 °C ($CHCl_3$). IR: 3055 (w), 2983 (w), 1790 (w), 1653 (s), 1599 (w), 1522 (m), 1489 (m), 1396 (m), 1329 (m), 1263 (s), 1084 (w), 1038 (w). ^{1}H NMR (500 MHz, $CDCl_3$): 1.46 t, 3 H, J = 7.1 (CH_3); 4.48 q, 2 H, J = 7.1 (CH_2); 7.57–8.01 m, 5 H (Ph); 13.75 s, br, 1 H (NH). ^{13}C NMR (500 MHz, $CDCl_3$): 14.2 (CH_3), 62.7 (CH_2), 119.0 (C-4), 128.2, 129.6, 130.1, 134.5 (Ph), 166.6 (PhCO), 166.9 (COO), 175.3 (C-5), 208.1 (C-3). For $C_{13}H_{11}NO_3S_3$ (325.4) calculated: 47.98% C, 3.41% H, 4.30% N; found: 47.75% C, 3.21% H, 4.10% N.

5-Benzamido-3-thioxo-3H-1,2-dithiole-4-carboxamide (**3f**). Yield 0.25 g (35%), m.p. 200 °C (subl.; $CHCl_3$). IR: 3316 (w), 3232 (s), 2961 (w), 2921 (w), 2849 (w), 2774 (w), 1654 (s), 1594 (w), 1572 (m), 1504 (s), 1485 (s), 1411 (m), 1364 (w), 1308 (s), 1273 (m), 1230 (m), 1100 (w), 1064 (m), 1014 (m). ^{1}H NMR (500 MHz, DMSO-d_6): 7.65–7.99 m, 5 H (Ph); 8.58 s, br, 1 H (NH_2); 10.02 s, br, 1 H (NH_2). ^{13}C NMR (500 MHz, DMSO-d_6): 119.6 (C-4), 127.8, 129.5, 130.0, 134.3 (Ph), 166.4 (PhCO), 166.6 (C-5), 175.9 ($CONH_2$), 206.7 (C-3). For $C_{11}H_8N_2O_2S_3$ (296.4) calculated: 44.58% C, 2.72% H, 9.45% N; found: 44.72% C, 2.73% H, 9.19% N.

Ethyl 5-(2,2-dimethylpropanamido)-3-thioxo-3H-1,2-dithiole-4-carboxylate (**3h**). Yield 0.44 g (60%), m.p. 136–137 °C (cyclohexane). IR: 3062 (w), 2974 (m), 2932 (w), 2876 (w), 1662 (s), 1487 (s), 1395 (m), 1372 (m), 1333 (m), 1296 (m), 1278 (m), 1227 (s), 1128 (m), 1091 (w), 1033 (m). ^{1}H NMR (500 MHz, $CDCl_3$): 1.37 s, 9 H (($CH_3)_3$C); 1.43 t, 3 H, J = 7.1 (CH_3CH_2); 4.43 q, 2 H, J = 7.1 (CH_2); 13.08 s, 1 H (NH). ^{13}C NMR (500 MHz, $CDCl_3$): 14.1 (CH_3CH_2), 27.1 (($CH_3)_3$C), 40.0 ($(CH_3)_3$C), 62.6 (CH_2), 118.9 (C-4), 166.6 (COO), 175.2 (C-5), 179.7 ($(CH_3)_3$CCO), 208.1 (C-3). For $C_{11}H_{15}NO_3S_3$ (305.4) calculated: 43.26% C, 4.95% H, 4.59% N; found: 43.19% C, 5.02% H, 4.51% N.

5-(2,2-Dimethylpropanamido)-3-thioxo-3H-1,2-dithiole-4-carboxamide (**3i**). Yield 0.37 g (56%), m.p. 160 °C (subl.; DMF). IR: 3305 (w), 3247 (m), 2967 (w), 2930 (w), 2870 (w), 1665 (m), 1578 (m), 1487 (s), 1405 (m), 1299 (s), 1117 (m), 1028 (m), 1012 (m). ^{1}H NMR (500 MHz, DMSO-d_6): 1.27 s, 9 H (CH_3), 8.56 s, br, 1 H (NH_2); 9.98 s, br, 1 H (NH_2). ^{13}C (500 MHz, DMSO-d_6): 26.4 (CH_3), 119.4 (C-4), 166.5 (COO), 175.7 (C-5), 179.7 ($(CH_3)_3$CCO), 206.8 (C-3). For $C_9H_{12}N_2O_2S_3$ (276.4) calculated: 39.11% C, 4.38% H, 10.14% N; found: 39.43% C, 4.32% H, 9.77% N.

Ethyl 5-Acetamido-3-thioxo-3*H*-1,2-dithiole-4-carboxylate (**3b**)

A suspension of **1b** (1.00 g, 5.20 mmol) in acetic anhydride (25 ml, 263 mmol), was heated under reflux for 0.5 h. The residue after evaporation was crystallized to afford **3b** (2.15 g, 90%), m.p. 150–151 °C ($CHCl_3$). IR: 3024 (w), 2999 (w), 2937 (w), 1689 (m), 1657 (s), 1495 (s), 1400 (m), 1365 (m), 1329 (s), 1281 (s), 1254 (s), 1203 (m), 1113 (w), 1038 (m), 1011 (s). ^{1}H NMR (500 MHz, $CDCl_3$): 1.42 t, 3 H, J = 7.2 (CH_3CH_2); 2.39 s, 3 H (CH_3CO); 4.42 q, 2 H, J = 7.2 (CH_3CH_2); 12.68 s, br, 1 H (NH). ^{13}C NMR (500 MHz, $CDCl_3$): 14.1 (CH_3CH_2), 23.9 (CH_3CO), 62.6 (CH_2), 118.7 (C-4), 166.2 (COO), 170.5 (CH_3CO), 174.4 (C-5), 208.1 (C-3). For $C_8H_9NO_3S_3$ (263.3) calculated: 36.49% C, 3.44% H, 5.32% N; found: 36.27% C, 3.34% H, 5.38% N.

5-Acetamido-3-thioxo-3*H*-1,2-dithiole-4-carboxamide (**3c**)

A mixture of **1c** (1.00 g, 5.20 mmol) in acetic anhydride (25 ml, 263 mmol), was allowed to reflux for 15 min. After cooling the solution was added to crushed ice (100 g), the precipitate was collected by filtration and washed with water. The reaction gave 0.50 g (41%) of **3c** after crystallization ($CHCl_3$), m.p. 227–228 °C. IR: 3311 (w), 3236 (m), 1680 (m), 1655 (s), 1572 (m), 1491 (s), 1408 (m), 1298 (s), 1196 (m), 1024 (s). ^{1}H NMR (500 MHz, DMSO-d_6): 2.37 s, 3 H (CH_3); 8.37 s, br, 1 H (NH_2); 9.83 s, br, 1 H (NH_2). ^{13}C NMR (500 MHz, DMSO-d_6): 23.2 (CH_3), 119.4 (C-4), 165.8 ($CONH_2$), 171.5 (CH_3CO), 174.6 (C-5), 206.7 (C-3). For $C_6H_6N_2O_2S_3$ (234.3) calculated: 30.76% C, 2.58% H, 11.96% N; found: 30.57% C, 2.53% H, 11.69% N.

Ethyl 5-{[(Dimethylamino)methylidene]amino}-3-thioxo-3*H*-1,2-dithiole-4-carboxylate (**4**) and Ethyl 5-Benzamido-3-thioxo-3*H*-1,2-dithiole-4-carboxylate (**3e**)

To a solution of **1b** (2.00 g, 9.04 mmol) in DMF (40 ml, 517 mmol) was added anhydrous sodium carbonate (2.50 g, 23.6 mmol) and benzoyl chloride (1.05 ml, 9.05 mmol). The mixture was stirred for 6 h and, after filtration, evaporated under reduced pressure. A precipitate formed after diethyl ether addition to the reaction mixture was filtered off and products **3e** and **4** were separated and purified by chromatography (silica gel, $CHCl_3$).

Compound **4**: Yield 1.16 g (46%), m.p. 182–183 °C ($CHCl_3$). IR: 2978 (w), 2927 (w), 1722 (m), 1633 (s), 1508 (m), 1470 (w), 1377 (s), 1261 (w), 1228 (w), 1190 (w), 1120 (w), 1026 (w), 1003 (w). ^{1}H NMR (500 MHz, DMSO-d_6): 1.25 t, 3 H, J = 7.1 (CH_3CH_2); 3.05 s, 3 H (CH_3N); 3.23 s, 3 H (CH_3N); 4.21 q, 2 H, J = 7.1 (CH_2); 8.42 s, 1 H (CH). ^{13}C NMR (500 MHz, DMSO-d_6): 13.9 (CH_3CH_2), 35.2 (CH_3N), 40.9 (CH_3N), 60.7 (CH_2), 130.3 (C-4), 156.8 (CH), 163.8 (CO), 181.1 (C-5), 203.5 (C-3). For $C_9H_{12}N_2O_2S_3$ (276.4) calculated: 39.11% C, 4.38% H, 10.14% N; found: 39.11% C, 4.35% H, 10.17% N.

Compound **3e**: Yield 0.70 g (24%), m.p. 190–191 °C ($CHCl_3$); identical with that described above.

5-Acetamido-4-(ethoxycarbonyl)-3-(methylsulfanyl)-1,2-dithiol-1-ium Iodide (**5a**)

Methyl iodide (0.24 ml, 3.86 mmol) was added to a solution of **3b** (0.25 g, 0.95 mmol) in acetone (20 ml). The reaction mixture was allowed to stand at room temperature. The precipitate was crystallized from nitromethane (0.35 g, 91%), m.p. 157–158 °C. IR: 3165 (w), 2964 (w), 2931 (w), 2895 (w), 1680 (s), 1506 (s), 1387 (m), 1309 (w), 1250 (s), 1203 (w), 1114 (w), 1034 (w), 1011 (m). ^{1}H NMR (500 MHz, DMSO-d_6): 1.35 t, 3 H, J = 7.1 (CH_3CH_2); 2.43 s, 3 H (CH_3CO); 2.90 s, 3 H (CH_3S); 4.41 q, 2 H, J = 7.1 (CH_2); 4.97 s, br, 1 H (NH). ^{13}C NMR (500 MHz, DMSO-d_6): 13.9 (CH_3CH_2), 18.2 (CH_3CO), 23.5 (CH_3S), 62.7 (CH_2), 122.0 (C-4), 161.5 (CH_3CO), 176.4 (COO), 177.6 (C-5), 185.5 (C-3). For $C_9H_{12}INO_3S_3$ (405.3) calculated: 26.67% C, 2.98% H, 3.46% N; found: 26.82% C, 3.12% H, 3.57% N.

5-Acetamido-3-(benzylsulfanyl)-4-(ethoxycarbonyl)-1,2-dithiol-1-ium Iodide (**5b**)

Compound **3b** (3.00 g, 11.4 mmol) was treated with benzyl iodide (1.72 ml, 13.7 mmol) at room temperature for 6 h. The obtained precipitate was collected and washed with diethyl ether. Crystallization (from diethyl ether) gave 2.15 g (47%) of **5b**, m.p. 89–90 °C. IR: 3132 (w), 2976 (w), 2926 (w), 1689 (s), 1624 (w), 1493 (s), 1417 (w), 1375 (s), 1306 (w), 1236 (s), 1203 (m), 1032 (w), 1005 (m). ^{1}H NMR (500 MHz, DMSO-d_6): 1.43 t, 3 H, J = 7.1 (CH_3CH_2); 2.58 s, 3 H (CH_3CO); 4.54 q, 2 H, J = 7.1 (CH_2); 4.60 s, 2 H (CH_2S); 7.35–7.49 m, 5 H (Ph); 12.71 s, br, 1 H (NH). ^{13}C NMR (500 MHz, DMSO-d_6): 14.1 (CH_3CH_2), 24.0 (CH_3CO), 41.5 (CH_2S), 64.7 (CH_3CH_2), 119.8 (C-4), 129.0, 129.2, 129.8, 131.9 (Ph), 162.3, 162.5 (COO, CH_3CO), 171.6 (C-5), 188.1 (C-3). For $C_{15}H_{16}INO_3S_3$ (481.4) calculated: 37.43% C, 3.35% H, 2.91% N; found: 37.35% C, 3.29% H, 2.97% N.

Imidates **6**. General Procedure

Method A

The appropriate amide **3** was dissolved in DMF (10 ml) and an alkylation agent and a base were added. If Na_2CO_3 is used, it was added 24 h after an alkylation agent. After 12 h the mixture was poured into water (100 ml) and the precipitate was washed with water and dried.

N-[4-Cyano-3-(methylsulfanyl)-1,2-dithiol-1-ium-5-yl]acetimidate (**6a**). Compound **3a** (0.10 g, 0.46 mmol), methyl iodide (0.058 ml, 0.92 mmol) and triethylamine (0.130 ml, 0.92 mmol) gave 0.08 g (73%) of **6a**, m.p. 185 °C (subl.; $CHCl_3$). IR: 3013 (w), 2926 (w), 2855 (w), 2219 (w), 1563 (s), 1433 (m), 1359 (s), 1313 (s), 1266 (s), 1025 (m). ^{1}H NMR (500 MHz, $CDCl_3$): 2.50 s, 3 H (CH_3CO); 2.84 s, 3 H (CH_3S). ^{13}C NMR (500 MHz, $CDCl_3$): 17.7 (CH_3S), 24.5 (CH_3CO), 104.7 (C-4), 112.3 (CN), 182.2, 183.8, 184.6 (CO, C-3, C-5). For $C_7H_6N_2OS_3$ (230.3) calculated: 36.50% C, 2.63% H, 12.16% N; found: 36.40% C, 2.71% H, 12.03% N.

N-[4-Carbamoyl-3-(methylsulfanyl)-1,2-dithiol-1-ium-5-yl]acetimidate (**6c**). Compound **3c** (0.50 g, 2.13 mmol), methyl iodide (0.27 ml, 4.34 mmol) and triethylamine (0.60 ml, 4.30 mmol) gave 0.50 g (95%) of **6c**, m.p. 170 °C (subl.; $CHCl_3$). IR: 3293 (m), 3157 (w), 2968 (w), 2903 (w), 2786 (w), 1668 (s), 1574 (m), 1427 (s), 1362 (w), 1285 (s), 1240 (w), 1147 (w), 1014 (w). ^{1}H NMR (500 MHz, DMSO-d_6): 2.38 s, 3 H (CH_3CO); 2.69 s, 3 H (CH_3S); 7.81 s, br, 1 H (NH_2); 9.65 s, br, 1 H (NH_2). ^{13}C NMR (500 MHz, DMSO-d_6): 17.8 (CH_3S), 24.6 (CH_3CO), 123.1 (C-4), 163.2 ($CONH_2$), 180.1, 181.1, 185.5 (CH_3CO, C-3, C-5). For $C_7H_8N_2O_2S_3$ (248.3) calculated: 33.86% C, 3.25% H, 11.28% N; found: 33.52% C, 3.19% H, 11.40% N.

N-[3-(Benzylsulfanyl)-4-cyano-1,2-dithiol-1-ium-5-yl]acetimidate (**6d**). Compound **3a** (0.10 g, 0.46 mmol), benzyl bromide (0.082 ml, 0.69 mmol) and triethylamine (0.098 ml, 0.69 mmol) gave 0.06 g (44%) of **6d**. Its spectral characteristics are identical with those described above.

N-[3-(Benzylsulfanyl)-4-carbamoyl-1,2-dithiol-1-ium-5-yl]acetimidate (**6f**). Compound **3c** (0.50 g, 2.13 mmol), benzyl bromide (0.51 ml, 4.29 mmol) and triethylamine (0.60 ml, 4.30 mmol) gave 0.57 g (82%) of **6f**, m.p. 160 °C (subl.; $CHCl_3$). IR: 3254 (m), 3131 (w), 3027 (w), 2961 (w), 2923 (w), 1658 (s), 1573 (m), 1494 (w), 1422 (s), 1354 (m), 1299 (s), 1228 (w), 1013 (w). ^{1}H NMR (500 MHz, DMSO-d_6): 2.38 s, 3 H (CH_3); 4.46 s, 2 H (CH_2); 7.33–7.50 m, 5 H (Ph); 7.85 s, br, 1 H (NH_2); 9.65 s, br, 1 H (NH_2). ^{13}C NMR (500 MHz, DMSO-d_6): 24.8 (CH_3), 123.2 (C-4), 127.9, 128.8, 129.5, 134.9 (Ph), 163.4 (COO), 179.8 (CH_3CO), 181.3 (C-3), 183.3 (C-5). For $C_{13}H_{12}N_2O_2S_3$ (324.4) calculated: 48.13% C, 3.73% H, 8.63% N; found: 48.17% C, 3.77% H, 8.56% N.

N-[4-Cyano-3-(methylsulfanyl)-1,2-dithiol-1-ium-5-yl]benzimidate (**6g**). Compound **3d** (0.10 g, 0.36 mmol), methyl iodide (0.044 ml, 0.72 mmol) and triethylamine (0.100 ml, 0.72 mmol) gave 0.08 g (74%) of **6g**, m.p. 210 °C (subl.; $CHCl_3$). IR: 2990 (w), 2922 (w), 2222 (w), 1589 (w), 1537 (s), 1453 (m), 1424 (s), 1328 (s), 1278 (s), 1162 (w), 1112 (w), 1025 (w). ^{1}H NMR (500 MHz, $CDCl_3$): 2.86 s, 3 H (CH_3); 7.49–7.61 m, 3 H (Ph); 8.40–8.43 m, 2 H (Ph). ^{13}C NMR (500 MHz, $CDCl_3$): 17.7 (CH_3), 108.3 (C-4), 112.4 (CN), 128.8, 130.5, 132.9, 133.8 (Ph), 178.1 (CO), 182.4, 183.4 (C-3, C-5). For $C_{12}H_8N_2OS_3$ (292.4) calculated: 49.29% C, 2.76% H, 9.58% N; found: 49.44% C, 2.74% H, 9.53% N.

N-[4-(Ethoxycarbonyl)-3-(methylsulfanyl)-1,2-dithiol-1-ium-5-yl]benzimidate (**6h**). Compound **3e** (0.30 g, 0.92 mmol), methyl iodide (0.12 ml, 1.84 mmol) and anhydrous sodium carbon-

ate (0.60 g, 5.66 mmol) gave 0.23 g (74%) of **6h**, m.p. 104–105 °C (Et_2O). IR: 3062 (w), 2981 (w), 2905 (w), 2854 (w), 1676 (s), 1591 (w), 1549 (w), 1451 (s), 1424 (m), 1370 (m), 1335 (s), 1270 (s), 1214 (m), 1170 (w), 1112 (w), 1027 (m). ^{1}H NMR (500 MHz, $CDCl_3$): 1.53 t, 3 H, J = 7.1 (CH_3CH_2); 2.75 s, 3 H (CH_3CO); 4.54 q, 2 H, J = 7.1 (CH_2); 7.47–8.37 m, 5 H (Ph). ^{13}C NMR (500 MHz, $CDCl_3$): 14.6 (CH_3CH_2), 18.1 (CH_3CO), 62.2 (CH_2), 124.3 (C-4), 128.6, 130.1, 133.1, 134.2 (Ph), 163.5 (COO), 177.3 (CH_3CO), 180.9, 181.7 (C-3, C-5). For $C_{14}H_{13}NO_3S_3$ (339.4) calculated: 49.54% C, 3.86% H, 4.13% N; found: 49.17% C, 3.68% H, 4.12% N.

N-[4-Carbamoyl-3-(methylsulfanyl)-1,2-dithiol-1-ium-5-yl]benzimidate (**6i**). Compound **3f** (0.30 g, 1.01 mmol), methyl iodide (0.13 ml, 2.09 mmol) and triethylamine (0.29 ml, 2.08 mmol) gave 0.28 g (89%) of **6i**, m.p. 206 °C (decomp.; $CHCl_3$). IR: 3258 (m), 3128 (w), 3058 (w), 2971 (w), 2903 (w), 1660 (s), 1593 (w), 1548 (s), 1490 (w), 1425 (s), 1378 (w), 1318 (m), 1285 (s), 1172 (m), 1113 (w), 1067 (w), 1025 (w), 1003 (w). ^{1}H NMR (500 MHz, $CDCl_3$): 2.72 s, 3 H (CH_3); 5.94 s, br, 1 H (NH_2); 7.50–8.21 m, 5 H (Ph); 10.41 s, br, 1 H (NH_2). ^{13}C NMR (500 MHz, $CDCl_3$): 19.0 (CH_3), 123.4 (C-4), 128.9, 129.6, 133.2, 134.0 (Ph), 164.6 (COO), 176.3 (PhCO), 182.0 (C-5), 187.1 (C-3). For $C_{12}H_{10}N_2O_2S_3$ (310.4) calculated: 46.43% C, 3.25% H, 9.02% N; found: 46.12% C, 3.11% H, 9.09% N.

N-[3-(Benzylsulfanyl)-4-cyano-1,2-dithiol-1-ium-5-yl]benzimidate (**6j**). Compound **3d** (0.10 g, 0.36 mmol), benzyl bromide (0.064 ml, 0.54 mmol) and triethylamine (0.076 ml, 0.54 mmol) gave 0.08 g (60%) of **6j**, m.p. 186–187 °C ($CHCl_3$). IR: 3065 (w), 3028 (w), 2918 (w), 2223 (w), 1590 (m), 1548 (s), 1458 (m), 1429 (m), 1328 (s), 1277 (s), 1168 (m), 1112 (w), 1017 (w). ^{1}H NMR (500 MHz, DMSO-d_6): 4.78 s, 2 H (CH_2); 7.39–7.67 m, 8 H (Ph), 8.23–8.25 m, 2 H (Ph). ^{13}C NMR (500 MHz, DMSO-d_6): 104.6 (C-4), 112.3 (CN), 128.3, 128.8, 129.2, 129.4, 132.8, 133.4, 134.2 (Ph), 176.3 (PhCO), 181.9, 182.6 (C-3, C-5). For $C_{18}H_{12}N_2OS_3$ (368.5) calculated: 58.67% C, 3.28% H, 7.60% N; found: 58.44% C, 3.19% H, 7.40% N.

N-[3-(Benzylsulfanyl)-4-(ethoxycarbonyl)-1,2-dithiol-1-ium-5-yl]benzimidate (**6k**). Compound **3e** (0.50 g, 1.54 mmol), benzyl iodide (0.39 ml, 3.10 mmol) and anhydrous sodium carbonate (1.00 g, 9.43 mmol) gave 0.42 g (66%) of **6k**, m.p. 112–113 °C ($CHCl_3$). IR: 3061 (w), 3032 (w), 2983 (w), 2921 (w), 1681 (m), 1594 (w), 1547 (s), 1493 (w), 1451 (s), 1369 (m), 1337 (s), 1272 (s), 1216 (w), 1172 (w), 1112 (w), 1023 (m). ^{1}H NMR (500 MHz, $CDCl_3$): 1.51 t, 3 H, J = 7.2 (CH_3CH_2); 4.42 s, 2 H (CH_2S); 4.52 q, 2 H, J = 7.2 (CH_3CH_2); 7.34–8.37 m, 10 H (Ph). ^{13}C NMR (500 MHz, $CDCl_3$): 14.6 (CH_3CH_2), 40.0 (CH_2S), 62.2 (CH_3CH_2), 125.1 (C-4), 128.6, 129.2, 129.5, 130.2, 133.1, 134.0, 134.2 (Ph), 163.5 (COO), 177.3 (PhCO), 178.0 (C-5), 181.4 (C-3). For $C_{20}H_{17}NO_3S_3$ (415.5) calculated: 57.81% C, 4.12% H, 3.37% N; found: 57.72% C, 4.16% H, 3.45% N.

N-[3-(Benzylsulfanyl)-4-carbamoyl-1,2-dithiol-1-ium-5-yl]benzimidate (**6l**). Compound **3e** (0.30 g, 1.01 mmol), benzyl bromide (0.15 ml, 1.26 mmol) and triethylamine (0.18 ml, 1.29 mmol) gave 0.33 g (85%) of **6l**, m.p. 205 °C (subl.; $CHCl_3$). IR: 3450 (w), 3262 (m), 3137 (w), 3062 (w), 3027 (w), 2971 (m), 2926 (w), 2903 (w), 2867 (w), 1660 (s), 1569 (m), 1546 (m), 1495 (w), 1422 (s), 1390 (m), 1309 (s), 1181 (s), 1028 (w). ^{1}H NMR (CF_3COOD): 4.82 s, 2 H (CH_2); 7.46–8.09 m, 10 H (Ph). ^{13}C NMR (CF_3COOD): 44.5 (CH_2), 123.8 (C-4), 128.9, 130.7, 131.3, 131.9, 132.1, 132.2, 132.4, 138.8 (Ph), 167.7 (PhCO), 170.5 ($CONH_2$), 177.2 (C-5), 190.5 (C-3). For $C_{18}H_{14}N_2O_2S_3$ (386.5) calculated: 55.94% C, 3.65% H, 7.25% N; found: 55.87% C, 3.69% H, 7.14% N.

N-[4-Cyano-3-(methylsulfanyl)-1,2-dithiol-1-ium-5-yl]-2,2-dimethylpropanimidate (**6m**). Compound **3d** (0.10 g, 0.39 mmol), methyl iodide (0.048 ml, 0.77 mmol) and triethylamine (0.108 ml, 0.77 mmol) gave 0.04 g (36%) of **6m**, m.p. 160 °C (subl.; $CHCl_3$). IR: 2973 (m), 2927 (w), 2869 (w), 2220 (m), 1568 (m), 1545 (s), 1427 (s), 1385 (m), 1326 (s), 1286 (s),

1178 (s), 1030 (w). ^{1}H NMR (500 MHz, $CDCl_3$): 1.35 s, 9 H ($(CH_3)_3C$); 2.83 s, 3 H (CH_3S). ^{13}C NMR (500 MHz, $CDCl_3$): 17.6 (CH_3S), 27.7 ($(CH_3)_3C$), 40.4 ($(CH_3)_3C$), 104.9 (C-4), 112.4 (CN), 182.4, 183.2 (CO, C-5), 192.9 (C-3). For $C_{10}H_{12}N_2OS_3$ (272.4) calculated: 44.09% C, 4.44% H, 10.28% N; found: 43.82% C, 4.37% H, 10.19% N.

N-[4-(Ethoxycarbonyl)-3-(methylsulfanyl)-1,2-dithiol-1-ium-5-yl]-2,2-dimethylpropanimidate (**6n**). Compound **3h** (1.00 g, 3.27 mmol), methyl iodide (0.41 ml, 6.59 mmol) and triethylamine (0.92 ml, 6.60 mmol) gave 0.83 g (79%) of **6n**, m.p. 95 °C (subl.; $CHCl_3$). IR: 2959 (m), 2906 (w), 2867 (w), 1667 (s), 1567 (w), 1538 (m), 1478 (w), 1423 (m), 1405 (m), 1385 (m), 1339 (s), 1277 (m), 1197 (s), 1027 (m). ^{1}H NMR (500 MHz, $CDCl_3$): 1.33 s, 9 H ($(CH_3)_3C$); 1.44 t, 3 H, J = 7.1 (CH_3CH_2); 2.72 s, 3 H (CH_3S); 4.45 q, 2 H, J = 7.1 (CH_2). ^{13}C NMR (500 MHz, $CDCl_3$): 14.5 (CH_3CH_2), 18.0 (CH_3CO), 27.8 ($(CH_3)_3C$), 40.3 (Me_3C), 62.0 (CH_2), 124.1 (C-4), 137.8 (COO), 163.8 ($(CH_3)_3CCO$), 180.2, 181.4 (C-5, C-3). For $C_{12}H_{17}NO_3S_3$ (319.5) calculated: 45.12% C, 5.36% H, 4.38% N; found: 45.01% C, 5.11% H, 4.31% N.

N-[4-Carbamoyl-3-(methylsulfanyl)-1,2-dithiol-1-ium-5-yl]-2,2-dimethylpropanimidate (**6o**). Compound **3i** (0.40 g, 1.45 mmol), methyl iodide (0.18 ml, 2.89 mmol) and triethylamine (0.40 ml, 2.87 mmol) gave 0.31 g (74%) of **6o**, m.p. 145 °C (subl.; $CHCl_3$). IR: 3270 (m), 3138 (w), 2969 (m), 2908 (w), 2864 (w), 1659 (s), 1573 (m), 1547 (m), 1427 (s), 1388 (m), 1301 (s), 1174 (s), 1025 (w), 1003 (w). ^{1}H NMR (500 MHz, $CDCl_3$): 1.34 s, 9 H ($(CH_3)_3C$); 2.69 s, 3 H (CH_3S); 5.92 s, br, 1 H (NH_2); 10.36 s, br, 1 H (NH_2). ^{13}C NMR (500 MHz, $CDCl_3$): 18.9 (CH_3S), 28.0 ($(CH_3)_3C$), 40.2 (Me_3C), 122.9 (C-4), 164.7 ($CONH_2$), 181.8 ($(CH_3)_3CCO$), 186.7 (C-5), 190.2 (C-3). For $C_{10}H_{14}N_2O_2S_3$ (290.4) calculated: 41.36% C, 4.86% H, 9.65% N; found: 40.97% C, 4.95% H, 9.99% N.

N-[3-(Benzylsulfanyl)-4-cyano-1,2-dithiol-1-ium-5-yl]-2,2-dimethylpropanimidate (**6p**). Compound **3g** (0.10 g, 0.39 mmol), benzyl iodide (0.068 ml, 0.59 mmol) and triethylamine (0.080 g, 0.59 mmol) gave 0.03 g (22%) of **6p**, m.p. 146.5–147.5 °C ($CHCl_3$). IR: 3066 (w), 3041 (w), 2959 (m), 2925 (w), 2865 (w), 2219 (w), 1574 (m), 1547 (w), 1456 (s), 1433 (m), 1386 (w), 1324 (s), 1174 (s). ^{1}H NMR (500 MHz, $CDCl_3$): 1.35 s, 9 H ($(CH_3)_3C$); 4.50 s, 2 H (CH_2); 7.28–7.43 m, 5 H (Ph). ^{13}C NMR (500 MHz, $CDCl_3$): 27.7 ($(CH_3)_3C$), 39.8 (CH_2), 40.4 (Me_3C), 105.5 (C-4), 112.3 (CN), 129.0, 129.3, 133.3 (Ph), 181.0, 181.9 (CO, C-5), 192.8 (C-3). For $C_{16}H_{14}N_2OS_3$ (346.5) calculated: 55.46% C, 4.07% H, 8.08% N; found: 55.45% C, 4.00% H, 8.01% N.

N-[3-(Benzylsulfanyl)-4-(ethoxycarbonyl)-1,2-dithiol-1-ium-5-yl]-2,2-dimethylpropanimidate (**6q**). Compound **3h** (1.00 g, 3.27 mmol), benzyl iodide (0.49 ml, 3.90 mmol) and anhydrous sodium carbonate (1.00 g, 9.43 mmol) gave 0.97 g (75%) of **6q**, m.p. 75–76 °C (petroleum ether). IR: 3063 (w), 3032 (w), 2973 (m), 2957 (m), 2925 (w), 2905 (w), 2865 (w), 1683 (s), 1572 (m), 1547 (m), 1434 (s), 1385 (m), 1331 (s) 1286 (m), 1217 (m), 1173 (s), 1023 (m). ^{1}H NMR (500 MHz, $CDCl_3$): 1.32 s, 9 H ($(CH_3)_3C$)); 1.43 t, 3 H, J = 7.0 (CH_3CH_2); 4.39 s, 2 H (CH_2S); 4.43 q, 2 H, J = 7.0 (CH_3CH_2); 7.35–7.42 m, 5 H (Ph). ^{13}C NMR (500 MHz, $CDCl_3$): 14.5 (CH_3CH_2), 27.8 ($(CH_3)_3C$), 39.9 (Me_3C), 62.0 (CH_3CH_2), 125.0 (C-4), 128.6, 129.2, 129.4, 134.2 (Ph), 163.7 (COO), 176.9 ($(CH_3)_3CCO$), 181.1 (C-5), 191.8 (C-3). For $C_{18}H_{21}NO_3S_3$ (395.6) calculated: 54.66% C, 5.35% H, 3.54% N; found: 55.03% C, 5.31% H, 3.42% N.

N-[3-(Benzylsulfanyl)-4-carbamoyl-1,2-dithiol-1-ium-5-yl]-2,2-dimethylpropanimidate (**6r**). Compound **3i** (0.40 g, 1.45 mmol), methyl iodide (0.34 ml, 2.86 mmol) and triethylamine (0.40 ml, 2.87 mmol) gave 0.32 g (60%) of **6r**, m.p. 225 °C (subl.; $CHCl_3$). IR: 3439 (w), 3300 (m), 3163 (w), 3060 (w), 3029 (w), 2901 (w), 1661 (s), 1592 (w), 1542 (w), 1492 (w), 1447 (m), 1417 (s), 1381 (w), 1315 (s), 1288 (s), 1234 (w), 1171 (w), 1115 (w), 1069 (w), 1025 (w).

^{1}H NMR (CF_3COOD): 1.51 s, 9 H ($(CH_3)_3C$); 4.84 s, 2 H (CH_2); 7.50–7.53 m, 5 H (Ph). ^{13}C NMR (CF_3COOD): 27.7 ($(CH_3)_3C$), 42.1 (CH_2), 44.6 (Me_3C), 123.7 (C-4), 131.4, 131.9, 132.3, 132.4 (Ph), 167.8 ($CONH_2$), 177.1 ($(CH_3)_3CCO$), 184.3 (C-5), 190.6 (C-3). For $C_{16}H_{18}N_2O_2S_3$ (366.5) calculated: 52.43% C, 4.95% H, 7.64% N; found: 52.22% C, 4.84% H, 7.61% N.

Method B

A mixture of **2** (0.2 g), toluene (20 ml) and excess (5 equiv.) of acyl halide/anhydride (**6a**–**6f**: acetic anhydride; **6g**–**6l**: benzoyl chloride; **6m**–**6r**: 2,2-dimethylpropanoyl chloride) was refluxed for 5–24 h. After filtration, the solvent was removed *in vacuo*. The residue was dried and purified by column chromatography (silica gel, $CHCl_3$).

N-[4-Cyano-3-(methylsulfanyl)-1,2-dithiol-1-ium-5-yl]acetimidate (**6a**). Yield 0.11 g (76%).

N-[4-(Ethoxycarbonyl)-3-(methylsulfanyl)-1,2-dithiol-1-ium-5-yl]acetimidate (**6b**). Yield 0.07 g (50%) of **6b** and 0.03 g (18%) of **2b**.

N-[4-Carbamoyl-3-(methylsulfanyl)-1,2-dithiol-1-ium-5-yl]acetimidate (**6c**). Yield 0.020 g (13.9%) of **6c** and 0.004 g (2.9%) of **2c**.

N-[3-(Benzylsulfanyl)-4-cyano-1,2-dithiol-1-ium-5-yl]acetimidate (**6d**). Yield 0.06 g (32%).

N-[3-(Benzylsulfanyl)-4-(ethoxycarbonyl)-1,2-dithiol-1-ium-5-yl]acetimidate (**6e**). Yield 0.02 g (13%) of **6e** and 0.09 g (44%) of **2b**.

N-[3-(Benzylsulfanyl)-4-carbamoyl-1,2-dithiol-1-ium-5-yl]acetimidate (**6f**). Yield 0.031 g (22.0%) of **6f** and 0.014 g (7.3%) of **2b**.

N-[4-Cyano-3-(methylsulfanyl)-1,2-dithiol-1-ium-5-yl]benzimidate (**6g**). Yield 0.11 g (59%).

N-[4-(Ethoxycarbonyl)-3-(methylsulfanyl)-1,2-dithiol-1-ium-5-yl]benzimidate (**6h**). Yield 0.043 g (23.7%) of **6h** and 0.014 g (7.7%) of **2b**.

N-[4-Carbamoyl-3-(methylsulfanyl)-1,2-dithiol-1-ium-5-yl]benzimidate (**6i**). Yield 0.10 g (54%) of **6i** and 0.02 g (10%) of **2b**.

N-[3-(Benzylsulfanyl)-4-cyano-1,2-dithiol-1-ium-5-yl]benzimidate (**6j**). Yield 0.09 g (46%).

N-[3-(Benzylsulfanyl)-4-(ethoxycarbonyl)-1,2-dithiol-1-ium-5-yl]benzimidate (**6k**). Yield 0.015 g (10.0%) of **6k** and 0.092 g (48.7%) of **2b**.

N-[3-(Benzylsulfanyl)-4-carbamoyl-1,2-dithiol-1-ium-5-yl]benzimidate (**6l**). Yield 0.09 g (64%) of **6l** and 0.07 g (35%) of **2b**.

N-[4-Cyano-3-(methylsulfanyl)-1,2-dithiol-1-ium-5-yl]-2,2-dimethylpropanimidate (**6m**). Yield 0.11 g (79%).

N-[4-(Ethoxycarbonyl)-3-(methylsulfanyl)-1,2-dithiol-1-ium-5-yl]-2,2-dimethylpropanimidate (**6n**). Yield 0.06 g (39.6%) of **6n** and 0.011 g (7.8%) of **2b**.

N-[4-Carbamoyl-3-(methylsulfanyl)-1,2-dithiol-1-ium-5-yl]-2,2-dimethylpropanimidate (**6o**). Yield 0.11 g (80%) of **6o** and 0.03 g (20%) of **2b**.

N-[3-(Benzylsulfanyl)-4-cyano-1,2-dithiol-1-ium-5-yl]-2,2-dimethylpropanimidate (**6p**). Yield 0.05 g (28%).

N-[3-(Benzylsulfanyl)-4-(ethoxycarbonyl)-1,2-dithiol-1-ium-5-yl]-2,2-dimethylpropanimidate (**6q**). Yield 0.03 g (18%) of **6q** and 0.06 g (36%) of **2b**.

N-[3-(Benzylsulfanyl)-4-carbamoyl-1,2-dithiol-1-ium-5-yl]-2,2-dimethylpropanimidate (**6r**). Yield 0.06 g (48%) of **6r** and 0.07 g (38%) of **2b**.

Method C

A mixture of **5a** (2.00 g, 4.93 mmol) or **5b** (2.37 g, 4.93 mmol) and anhydrous sodium carbonate (1.30 g, 12.27 mmol) in DMF was stirred for 3 h. The suspension was filtered, the fil-

trate diluted with water (100 ml) and extracted with chloroform (3 × 25 ml). The organic layers were evaporated *in vacuo* and the residue crystallized from suitable solvents.

N-[4-(Ethoxycarbonyl)-3-(methylsulfanyl)-1,2-dithiol-1-ium-5-yl]acetimidate (**6b**). Yield 0.85 g (43%), m.p. 88–89 °C ($CHCl_3$). IR: 2980 (w), 2906 (w), 1684 (s), 1568 (m), 1439 (s), 1367 (m), 1327 (m), 1254 (s), 1014 (m). ^{1}H NMR (500 MHz, $CDCl_3$): 1.43 t, 3 H, *J* = 7.2 (CH_3CH_2); 2.45 s, 3 H (CH_3CO); 2.71 s, 3 H (CH_3S); 4.46 q, 2 H, *J* = 7.2 (CH_2). ^{13}C NMR (500 MHz, $CDCl_3$): 14.4 (CH_3CH_2), 18.0 (CH_3CO), 25.0 (CH_3S), 62.2 (CH_2), 124.4 (C-4), 163.1 (COO), 179.4 (CH_3CO), 181.7 (C-3), 183.7 (C-5). For $C_9H_{11}NO_3S_3$ (277.4) calculated: 38.97% C, 4.00% H, 5.05% N; found: 39.09% C, 4.00% H, 5.26% N.

N-[3-(Benzylsulfanyl)-4-(ethoxycarbonyl)-1,2-dithiol-1-ium-5-yl]acetimidate (**6e**). Yield 0.95 g (40%), m.p. 92–93 °C (Et_2O). IR: 3059 (w), 3028 (w), 2983 (w), 2920 (w), 2856 (w), 1674 (s), 1558 (m), 1423 (m), 1365 (s), 1315 (s), 1259 (s), 1198 (w), 1011 (m). ^{1}H NMR (500 MHz, $CDCl_3$): 1.40 t, 3 H, *J* = 7.1 (CH_3CH_2); 2.44 s, 3 H (CH_3CO); 4.38 s, 2 H (CH_2S); 4.44 q, 2 H, *J* = 7.1 (CH_3CH_2); 7.26–7.40 m, 5 H (Ph). ^{13}C NMR (500 MHz, $CDCl_3$): 14.3 (CH_3CH_2), 24.9 (CH_3CO), 40.0 (CH_2S), 62.3 (CH_3CH_2), 125.1 (C-4), 128.6, 129.2, 129.4, 134.0 (Ph), 163.1 (COO), 176.7 (CH_3CO), 181.1 (C-3), 183.5 (C-5). For $C_{15}H_{15}NO_3S_3$ (353.5) calculated: 50.97% C, 4.28% H, 3.96% N; found: 50.73% C, 4.20% H, 4.00% N.

N-[3-(Benzylsulfanyl)-4-cyano-1,2-dithiol-1-ium-5-yl]acetimidate (**6d**)

Compound **6d** was prepared from **1a** (4.00 g, 23.0 mmol), benzyl chloride (8.00 ml, 69.5 mmol), acetic acid (30 ml) and acetic anhydride (30 ml, 318 mmol) according to the procedure described for **6s** (with the exception of extraction with xylene). Yield 1.75 g (25%), m.p. 153–154 °C ($CHCl_3$). IR: 2213 (w), 1565 (s), 1429 (s), 1357 (m), 1311 (s), 1261 (s), 1234 (w), 1018 (m). ^{1}H NMR (500 MHz, $CDCl_3$): 2.42 s, 3 H (CH_3); 4.44 s, 2 H (CH_2); 7.31–7.37 m, 5 H (Ph). ^{13}C NMR (500 MHz, $CDCl_3$): 24.5 (CH_3), 39.8 (CH_2), 105.0 (C-4), 112.2 (CN), 129.1, 129.3, 133.1 (Ph), 181.6, 181.6, 184.2 (CO, C-3, C-5). For $C_{13}H_{10}N_2OS_3$ (306.4) calculated: 50.96% C, 3.29% H, 9.14% N; found: 51.01% C, 3.41% H, 9.03% N.

N-[4-Cyano-3-(ethylsulfanyl)-1,2-dithiol-1-ium-5-yl]acetimidate (**6s**)

A mixture of **1a** (2.00 g, 11.5 mmol), triethyl orthoformate (10 ml, 60.1 mmol) and acetic anhydride (50 ml, 530 mmol) was refluxed for 5 h. Excess volatiles were removed *in vacuo* and the resulting solid was extracted with toluene (3 × 50 ml). The residue obtained after evaporation of the solvent was washed with methanol and then crystallized (1.65 g, 59%), m.p. 135–136 °C ($CHCl_3$). IR: 2972 (w), 2929 (w), 2220 (w), 1566 (s), 1439 (m), 1362 (s), 1315 (s), 1257 (s), 1018 (m). ^{1}H NMR (500 MHz, $CDCl_3$): 1.56 t, 3 H, *J* = 7.1 (CH_3CH_2); 2.50 s, 3 H (CH_3S); 3.32 q, 2 H, *J* = 7.1 (CH_2). ^{13}C NMR (500 MHz, $CDCl_3$): 13.9 (CH_3CH_2), 24.6 (CH_3CO), 30.0 (CH_2), 105.0 (C-4), 112.3 (CN), 181.7, 182.0, 184.5 (CO, C-3, C-5). For $C_8H_8N_2OS_3$ (244.3) calculated: 39.32% C, 3.30% H, 11.46% N; found: 38.97% C, 2.97% H, 11.13% N.

6-(Alkylsulfanyl)-2-methyl-4λ^4-[1,2]dithiolo[1,5-*b*][1,2,4]dithiazole-7-carbonitrile (**7**). General Procedure

A solution of **6s** (0.50 g, 2.05 mmol) or **6d** (0.63 g, 2.06 mmol) and phosphorus pentasulfide (1.00 g, 2.25 mmol) in dry xylene (60 ml) was refluxed for 15 min. After cooling, the solu-

tion was washed with aqueous 1 M solution of sodium hydrogencarbonate (4 × 100 ml) and water (2 × 100 ml), dried and evaporated.

6-(Ethylsulfanyl)-2-methyl-4λ^4-[1,2]dithiolo[1,5-b][1,2,4]dithiazole-7-carbonitrile (**7a**). Yield 0.09 g (17%), m.p. 132–133 °C. IR: 2966 (w), 2924 (w), 2208 (w), 1407 (s), 1318 (s), 1231 (w), 1168 (w), 1004 (w). ^{1}H NMR (500 MHz, $CDCl_3$): 1.47 t, 3 H, *J* = 7.5 (CH_3CH_2); 2.90 s, 3 H (CH_3S); 3.28 q, 2 H, *J* = 7.5 (CH_2). ^{13}C NMR (500 MHz, $CDCl_3$): 13.2 (CH_3CH_2), 25.0 (CH_3S), 30.3 (CH_2), 107.6 (C-7), 115.0 (CN), 187.0 (C-4), 192.9 (C-2), 199.7 (C-6). For $C_8H_8N_2S_3$ (228.3) calculated: 36.90% C, 3.10% H, 10.76% N; found: 36.57% C, 3.02% H, 10.59% N.

6-(Benzylsulfanyl)-2-methyl-4λ^4-[1,2]dithiolo[1,5-b][1,2,4]dithiazole-7-carbonitrile (**7b**). Yield 0.08 g (12%), m.p. 168–169 °C. IR: 3065 (w), 3029 (w), 2923 (w), 2864 (w), 2208 (m), 1599 (w), 1494 (w), 1449 (w), 1406 (s), 1326 (s), 1268 (w), 1238 (m), 1170 (m), 1010 (m). ^{1}H NMR (500 MHz, $CDCl_3$): 2.90 s, 3 H (CH_3); 4.48 s, 2 H (CH_2); 7.31–7.43 m, 5 H (Ph). ^{13}C NMR (500 MHz, $CDCl_3$): 24.9 (CH_3), 40.5 (CH_2), 107.2 (C-7), 114.9 (CN), 128.3, 129.0, 129.5, 134.5 (Ph), 187.0 (C-4), 192.8 (C-2), 199.0 (C-6). For $C_{13}H_{10}N_2S_3$ (290.4) calculated: 48.42% C, 3.13% H, 8.69% N; found: 48.30% C, 3.08% H, 8.74% N.

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REFERENCES

1. Gewald K.: *J. Prakt. Chem.* **1966**, *31*, 214.
2. Brois S. J., Scattergood R., Czyzewski J. (Exxon Research and Engineering Co.): Brit. 1 575 202; *Chem. Abstr.* **1981**, *95*, P45828.
3. Gewald K.: *Chem. Ber.* **1968**, *101*, 383.
4. Hennig D., Heilmann D., Zeiger G., Kempter G.: *Wiss. Z. Paedagog. Hochsch. "Karl Liebknecht", Potsdam* **1977**, *21*, 47; *Chem. Abstr.* **1979**, *90*, 103787.
5. Sakamoto H., Kaneko Y. (Konica Co.): Japan 63 294 554; *Chem. Abstr.* **1990**, *113*, 68281.
6. Alekseeva G. N., Eltsov A. V., Kolesova M. B., Maksimova L. I., Rusanov A. M.: *Khim.-Farm. Zh.* **1972**, *6*, 23; *Chem. Abstr.* **1972**, *77*, 135153.
7. Čmelík R., Marek J., Pazdera P.: *Heterocycl. Commun.* **2002**, *8*, 55.
8. Rossi E., Fattori S. (SNAM Progetti S.p.A.): Ger. 2 242 637; *Chem. Abstr.* **1973**, *79*, 33408.
9. Bowyer J. R., Camilleri P., Stapleton A.: *FEBS Lett.* **1984**, *172*, 239.
10. Giudice M. R. D., Borini A., Mustazza C., Gatta F.: *J. Heterocycl. Chem.* **1994**, *31*, 1503.
11. Emam H. A., Hassan S. M., Al-Najjar A.-A. A.: *J. Chem. Res.* **1995**, 474.
12. Gewald K.: *Z. Chem.* **1963**, *3*, 26.
13. a) Sen A. K., Chattopadhyay G.: *Indian J. Chem., Sect. B: Org. Chem. Incl. Med. Chem.* **1979**, *18*, 307; b) Waring P.: *Aust. J. Chem.* **1988**, *41*, 667; c) Al-Shaar A. H. M., Chambers R. K., Gilmour D. W., Lythgoe D. J., McClenaghan I., Ramsden Ch. A.: *J. Chem. Soc., Perkin Trans. 1* **1992**, *21*, 2789.
14. Rutavicius A. I., Iokubaitite S. P.: *J. Org. Chem. USSR* **1984**, *20*, 2371; *Chem. Abstr.* **1984**, *100*, 191774.

15. a) Guillouzo G.: *Bull. Soc. Chim. Fr.* **1958**, 1316; b) Pfister-Guillouzo G., Lozac'h N.: *Bull. Soc. Chim. Fr.* **1963**, 153.
16. Allen F. H., Kennard O., Watson D. G., Brammar L., Watson A. G., Taylor R.: *J. Chem. Soc., Perkin Trans. 2* **1987**, S1.
17. Bellamy L. J.: *The Infra-Red Spectra of Complex Molecules*, p. 243. John Wiley & Sons, Inc., New York 1954.
18. Mayer I.: *Chem. Phys. Lett.* **1983**, *97*, 270.
19. Malkin V. G., Malkina I. L., Salahub D. R.: *deMon v1.0, A Gaussian Density Functional Program*. Université de Montreal, Montreal 1994.