Formation of Triazinium-Imidothioate Zwitterions and Their Role as Key Intermediates for Novel S_N(ANRORC) Reaction Pathways[‡]

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Dedicated to Professor Dr. Dr. h. c. mult. Alan Roy Katritzky, FRS, on the occasion of his 75th birthday

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The formation of highly reactive zwitterionic triazinium-imidothioate intermediates **10** from bis(1,3,4-thiadiazolo)-1,3,5-triazinium halides is reported. These intermediates are the first structures to be isolated from the reaction pathway between bis(1,3,4-thiadiazolo)-1,3,5-triazinium halides **1** and benzylamines **2**. The reaction between **1** and **2** has a very complicated hypersurface and can yield unusual bis(1,2,4-triazolo)-1,3,5-triazinium halides **6**, [1,2,4]triazolo[1,3,4]thiadiazolo[1,3,5]triazinium halides **7** or highly substituted guanidines **5**. The formation of **6** and **7** can be understood in terms of an S_N(ANRORC) process. As could be demonstrated for the tricyclic cations **6**, these compounds, together with **7**, could be interesting in further synthetic applications. The salts **6** react with KOH/*t*BuOK to give novel aminals **16** in good to excellent yields. Most of the important steps in the course of the transformation of **1** into **5**, **6** and **7** are supported by B3LYP/6–311++G(d,p) calculations and the X-ray structures of **6a**, **7b**, **14b** and **16c**. From an electronic point of view, the more important reaction steps are governed by the conformation-controlling effect of negative hyperconjugation, accompanied by intramolecular proton-transfer reactions.

Introduction

The novel cationic 5/6/5-nitrogen-sulfur heterocycles **1**[1] (Scheme 1) are easily accessible and interesting for many synthetic applications, especially as precursors for a variety of unusual heterocyclic compounds. Both ring atoms C(3a) and C(4a) are sufficiently positively charged,[2] allowing the attack of a variety of suitable nucleophiles such as amines. We have shown that the addition of aliphatic (primary and secondary as well as heterocyclic) amines **2** to the 5/6/5 cations **1** results in several unexpected ring transformations, which then give rise to new oligo-substituted guanidines **5**.[3] It is noteworthy that the guanidine functionality is responsible for the biological activity in numerous natural compounds[4] and is used as a potential chiral auxiliary in asymmetric syntheses.[5] The development of reagents for their preparation is therefore becoming increasingly important.[6]

We have suggested that, after the attack of the amine at the C(4a) position and several proton shifts, this reaction pathway proceeds by cleavage of the S(5)−C(4a) bond of the thiadiazole moiety, which is then followed by nucleophilic attack by S(5) at the C(9) position. This step allows fission of the C(9)−N(10) bond in the triazinium ring, thus resulting in the formation of **5**, in which the former triazinium carbon C(9) is now part of a newly formed five-membered ring. On the basis of these mechanistic assumptions, we succeeded in synthesising new guanylating reagents − variants of **1**[1] − which allow convenient access to highly substituted guanidines **5** bearing up to three different heterocyclic moieties (cf. ref.[3a] and literature cited therein).

The presence of an excess of the 2-aminothiadiazole **3** on treatment of the salts **1** results in an interesting alternative transformation. In this case, unusual 1,1′-alkanediylbis(thiadiazols) **4** (heterocyclic "aminals") are formed.[1] This prompted us to focus our interest on mechanistic investigations aimed at better understanding of the intrinsic reaction steps. From these studies, we have now extended the synthetic potential of **1**, having observed surprising reaction

[‡] Bis(1,3,4-Thiadiazolo)-1,3,5-Triazinium Halides, 5. Part 4: Ref.[3c]

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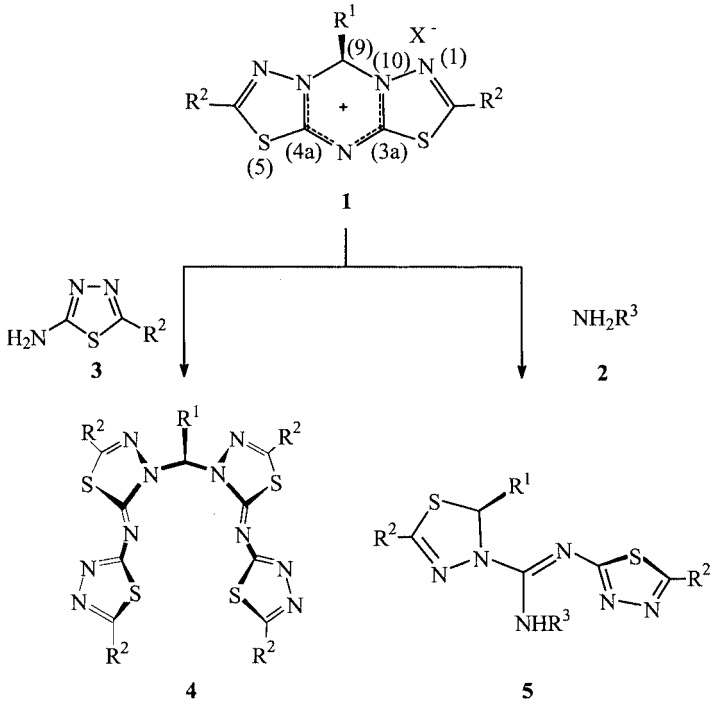


1, 2, 5, 6, 7, 10	R^1	R^2	R^3	1, 2, 5, 6, 7, 10, 14	R^1	R^2	R^3
a	4-MeC_6H_4	Me	Bzl	**h**	4-MeC_6H_4	Me	2-CH_2Py
b	4-MeC_6H_4	Me	2-MeOBzl	**i**	4-MeC_6H_4	Me	4-CH_2Py
c	4-MeC_6H_4	Me	2-ClBzl	**j**	2-HOC_6H_4	*t*Bu	2-CH_2CH_2Py
d	4-MeC_6H_4	Me	4-ClBzl	**k**	2-HOC_6H_4	*t*Bu	2-$CH_2CH_2C_4H_3S$
e	4-MeC_6H_4	Me	4-MeBzl	**l**	2-HOC_6H_4	*t*Bu	1-Bu
f	1-Naph	Me	Bzl	**m**	4-MeC_6H_4	Me	1-Bu
g	1-Bu	Me	Bzl				

Scheme 1

behaviour of the heterocyclic cations **1** towards several benzylamines. This study opens a novel, multistep pathway ending with the formation of bis(1,2,4-triazolo)-1,3,5-triazinium halides **6** or their "unsymmetrical" relatives **7** ([1,2,4]triazolo[1,3,4]thiadiazolo[1,3,5]triazinium halides, Scheme 2). As shown below, intermediate zwitterionic triazinium-imidothioate structures **10** (Schemes 3−5) play a dominant role in this reaction.

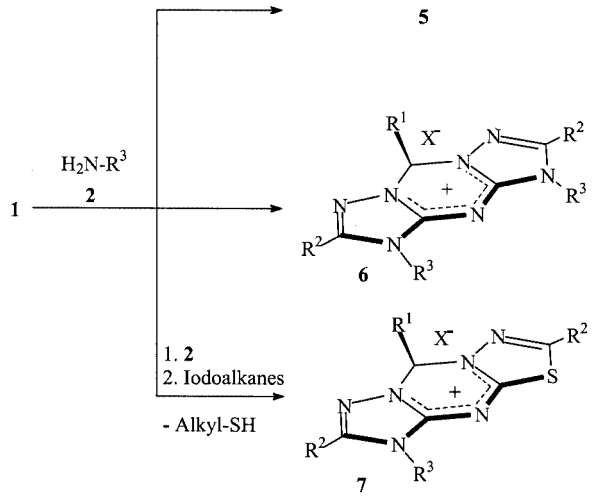
Results and Discussion

Compounds **1** were obtained from cyclisation reactions between 2-amino-5-alkyl-1,3,4-thiadiazoles **3**[7] and either *N*-(1-haloalkyl)pyridinium halides[8] or substituted *N*,*N*′-methylenebis(pyridinium) bromides, by use of a previously described procedure.[1]

Results of the Reactions between 1 and Benzylamines 2

Application of our standard procedure (pyridine, room temp.[3a,3b]) causes the salts **1** to react with two equivalents of primary and secondary amines to give the corresponding guanidines **5**. If the amine is a benzylamine **2** (R^3 = benzyl, substituted benzyl, pyridinylmethyl; Scheme 1), however, novel 5/6/5 cations **6** are also formed, in addition to the expected guanidines **5**. Both products are formed almost simultaneously. Analytically pure salts **6** can easily be separated from the **5/6** product mixtures either by column chromatography or by fractional crystallisation (cf. the Exp. Sect.).

The relative proportions of the two products can be controlled only to a minor extent by variation of the reaction conditions (i.e., excess of **2**, the reaction time or temperature). Use of one equivalent of **2a** instead of two, for ex-



Scheme 2

ample, reduced the yield of **5a** + **6a** by approximately half (ca. 61%, Table 1), the **5/6** product ratio remaining constant.

Table 1. Guanidines **5** and bis(triazolo)triazinium halides **6** from bis(thiadiazolo)triazinium halides **1a**, **1f**, **1g** and **1j** and benzylamines **2a**−**e**. Last three entries: treatment of **1a** and **1j** with primary aliphatic amines **2j**−**m** to give guanidines **5j**−**l** selectively

	Yield, % **5** + **6**	M.p., °C	Ratio, mol-% **5/6**[a]
5a	61	161	54:46
6a		238	
5b	78	146	87:13
6b		109	
5c	74	123	40:60
6c		187	
5d	67	137	42:58
6d		234	
5e	86	121	65:35
6e		225	
5f	64	130	50:50
6f		154	
5g	80	107[b]	50:50
6g		54[c]	
5h	33	161	38:62
6h		98[c]	
5i	61	155	53:47
6i		60[c]	
5j	72	184	100:0
5k	82	165	100:0
5l	72	159	100:0

[a] Determined by ^{1}H NMR analysis of the crude products. [b] BF_4^- salt. [c] Extremely hygroscopic.

Interestingly, exclusive formation of **5j**, **5k** and **5l** was observed with the use of **1j**[3b] (R^1 = 2-OHC_6H_4, R^2 = *t*Bu) and the ethyl hetarylamines **2j** and **2k** or 1-butylamine (**2l**) (Table 1), whereas the product **6h** is formed in significant amounts from the reaction between **1a** (R^1 = 4-MeC_6H_4, R^2 = Me) and the 2-(aminomethyl)pyridine (**2h**) (i.e., the methyl analogue of **2j**; ratio **5h/6h** = 38:62). No aminals **4** could be detected. We observed in all cases that the corresponding ammonium salt **2**·HBr was formed immediately upon combination of the reactants (analogously to the reaction between **1a** and piperidine or morpholine, in which piperidinium or morpholinium bromides are formed; cf.[3]).

What is the reason for the formation of structures **6** on replacement of the primary and secondary aliphatic amines by benzylamines **2a**−**g** and their hetaryl analogues **2h**−**i**? In order to find an explanation for these remarkable product changes caused by such a minor variation of the amine nucleophiles, we selected a model system (the reaction between the bromide **1a** and the benzylamine **2a** to give **5a** and **6a** in the ratio 54:46) for more sophisticated NMR studies (chloroform solution, 253 K). In addition, we calculated conceivable intermediates and reaction pathways for **1** and amines **2** at the B3LYP/6−311++G(d,p) level of theory. In order to keep the CPU time within acceptable limits, we used the modified 5/6/5 salt **1M** with R^1 = R^2 = CH_3 and methylamine **2M** as the nucleophilic reactant.[9]

Some Computational Details: Full geometry optimisations (i.e., without symmetry constraints) were carried out with the GAUSSIAN98 program package.[10] The final structures and relative energies were calculated by the hybrid Hartree−Fock-DFT approach [B3LYP/6−311++G(d,p)].[11] The DFT-calculated geometries were characterised as minima on the potential surface (PES) by calculation of the vibrational frequencies. Stationary points were rigorously characterised as minima or transition states according to the number of imaginary modes by application of a second-order derivative calculation (vibrational analysis).[12] Visualisation of the reactive mode in the transition structures was used to support the assignments of the pertaining minimum structures. Zero point energy (ZPE) corrections and thermal (ΔH) and entropic ($T\Delta S$) corrections were made both for activation barriers and for reaction energies simulating standard ambient temperature and pressure conditions.

The resulting model structures and corresponding reaction steps are depicted in Schemes 3 and 4. Total energies, zero point energies etc. are given in Table 2 (a and b), and relative Gibbs free energies (ΔG) are summarised in Table 3.

Schemes 3 and 4 summarise the pathways a and b as conceivable rearrangements, starting with the nucleophilic addition step of the amine **2M** to form **8Ma** (the index **M** stands for model compounds suitable for high level DFT calculations). The initial addition product is extremely unstable (DFT results) and tends to decompose back into the reactants. A proton shift transforms **8Ma** into the more stable N(4) tautomer **8Mb**, which we believe to be responsible for the reaction path leading to the aminals **4**.[3a] Because of the generally observed immediate formation of hydrobromide **2**·HBr, alternative reaction cascades are almost certainly only possible after the formation of deprotonated species such as the model conformers **9Ma** or **9Mb**. The DFT calculations show that **9Ma** has several interesting properties. This structure is the most stable confor-

Table 2. a) *E*: Calculated total energies (B3LYP/6−31++G(d,p); *G*: energies after thermal and entropic corrections at 298.5 K and 1 atm for the model compounds as depicted in Scheme 3 (formation of the guanidine **5M** from **1M** and **2M** via the zwitterion **10M**). b) *E*: Calculated total energies (B3LYP/6−31++G(d,p); *G*: energies after thermal and entropic corrections at 298.5 K and 1 atm for the model compounds as depicted in Scheme 4 (formation of the triazolo-thiadiazolo-triazinium system **7M** from the zwitterions **10M** under extrusion of H_2S). NPA charges of **6M** and **7M**

	E (a.u.)	ZPE (kcal·mol^{-1})	[NIMAG][a]	*G* (a.u.)
a)				
1M	−1380.952852	116.84	[0]	−1380.807963
2M	−95.8938894	40.03	[0]	−95.853039
8Ma	−1476.8278964	159.75	[0]	−1476.618419
8Mb	−1476.8416942	159.36	[0]	−1476.632122
9Ma	−1476.4527892	151.21	[0]	−1476.256394
9Mb	−1476.4449374	150.72	[0]	−1476.249983
TS-A	−1476.4394524	150.70	[1]	−1476.243750
10M	−1476.4587013	150.94	[0]	−1476.264657
TS-B	−1476.4197828	149.15	[1]	−1476.229678
5M	−1476.4694958	150.05	[0]	−1476.278090
b)				
10M	−1476.4587013	150.94	[0]	−1476.264657
11Ma	−1476.4389591	148.42	[0]	−1476.249398
TS-C	−1476.4038693	147.80	[1]	−1476.213579
13M	−1476.4487838	149.05	[0]	−1476.257130
11Mb	−1476.4522104	150.83	[0]	−1476.259389
TS-D	−1476.4231577	151.04	[1]	−1476.226560
12M	−1476.4286912	152.08	[0]	−1476.230370
7M[b]	−1077.4565507	144.51	[0]	−1077.269415
6M[b]	−773.9581026	172.05	[0]	−773.729501

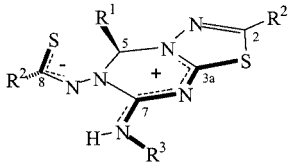
[a] Number of *Imag*inary Frequencies. [b] NPA Charges: **6M**: $q_{C3a} = q_{C4a} = +0.64$, $q_{N4} = -0.61$, $q_{N7} = -0.28$, $q_{N8} = -0.27$, $q_{C9} = +0.23$, $q_S = +0.45$; **7M**: $q_{C3a} = +0.31$, $q_{C4a} = +0.64$, $q_{N4} = -0.59$.

Table 3. Relative Gibbs free energies (Δ*G*), cf. Schemes 3 and 4

Separated reactants/compound	Δ*G* (kcal·mol^{-1})	Compound	Δ*G* (kcal·mol^{-1})
1M + **2M**	≡ 0.0	**10M**	≡ 0.0
8Ma	+26.7	**11Ma**	+9.6
8Mb	+18.1	***TS-C***	+32.1
9Ma	≡ 0.0	**13M**	+4.7
9Mb	+4.0	**11Mb**	+3.3
TS-A	+7.9	***TS-D***	+23.9
10M	−5.2	**12M**	+21.5
TS-B	+16.8		
5M	−13.6		

mation, the result of the rotation of the CH_3−NH moiety around the C(4a)−N(ex) bond. In this conformation, the interaction between the lone pair [$n_{(N)}$] at the exocyclic nitrogen N(ex) and the antibonding sigma orbital [$\sigma^*_{C(4a)-S(5)}$] is the most pronounced in comparison with alternative conformers such as **9Mb**. This negative hyperconjugation[13−16] results in an unusually long C(4a)−S(5) bond (193.6 pm) in **9Ma**. The fission of this bond via the transition structure ***TS-A*** needs only 7.9 kcal·mol^{-1} (cf. Table 2, ***TS-A***: C(4a)−S(5): 243.7 pm) and gives a zwitterionic structure **10M** [C(4a)−S(5): 382.6 pm]. This zwitterion is slightly more stable (ca. 5.2 kcal·mol^{-1}) than its precursor **9Ma** and is obviously the key intermediate determining the consecutive reactions steps. We finally succeeded in isolating and experimentally characterising several such zwitterions (**10a**, **10b**, **10k**−**m**) as yellow powders (cf. Figure 1 and the Exp. Sect.).

As an example, the zwitterion **10a** (R^1 = 4-MeC_6H_4, R^2 = Me, R^3 = benzyl) could be isolated from the reaction mixture of benzylamine (**2a**) and **1a** and proved to be stable in the solid state at room temperature for prolonged periods (over half a year). However, if compounds **10** are dissolved in $CHCl_3$, the resulting solutions are only stable up to 258 K. All ^{1}H and ^{13}C NMR spectroscopic data of these compounds are in agreement with a zwitterionic structure (Figure 1). 1D-TOCSY experiments show beyond a doubt that the NH signals (6.29−7.15 ppm) belong to a secondary amine proton with a neighbouring methylene group belonging to the benzyl or alkyl moiety. Moreover, the ^{13}C NMR signal of the imidothioate moiety appears at low field



Compd.	^{1}H NMR				
	2-CH_3	8-CH_3	5-CH	CH_2NH	NH
10a	2.50	2.36	8.35	4.58	6.94
10b	2.48	2.35	8.35	4.56	7.15
10k [c]	1.22 [a]	1.07 [a]	8.27	3.01	6.29
10l [c]	1.20 [a]	1.12 [a]	8.27	3.30	6.16
10m	2.46	2.25	8.28	3.28	6.70

Compd.	^{13}C NMR							
	2-CH_3	8-CH_3	C-2	C-3a	C-5	C-7	C-8	CH_2NH
10a	17.6	33.4	155.7	167.6	71.8	151.6	196.1	45.5
10b	16.9	32.8	154.7	166.8	71.0	150.8	194.7	45.7
10k [c]	30.5 [b]	29.0 [b]	168.4	167.7	70.1	149.9	204.3	47.0
10l [c]	30.5 [b]	29.0 [b]	168.5	168.1	70.2	151.4	204.1	47.0
10m	17.5	33.1	155.4	167.0	71.0	151.2	194.8	41.4

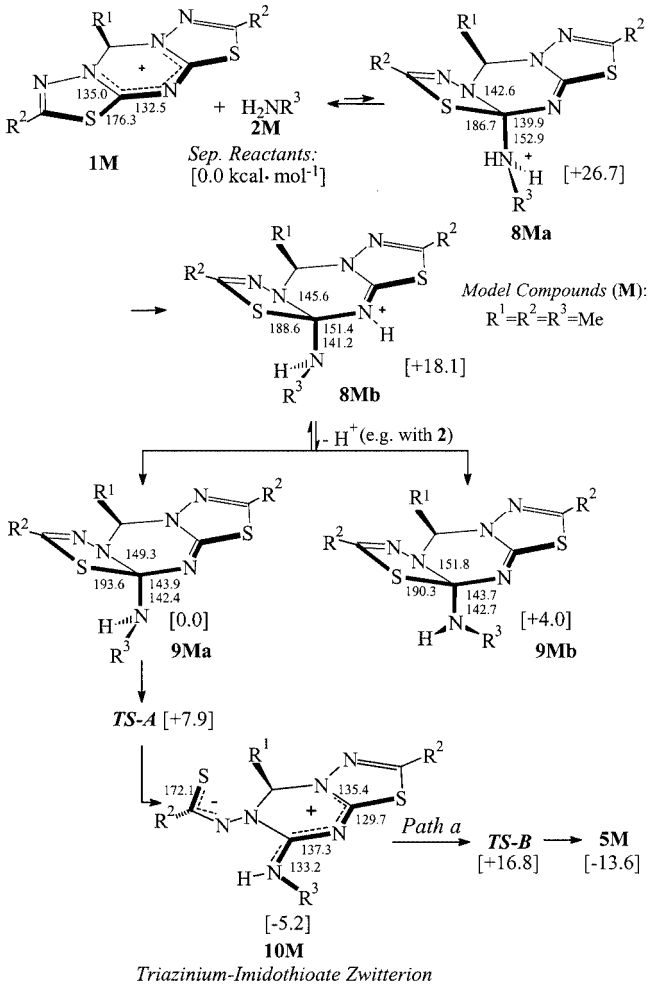
Figure 1. Isolated triazinium-imidothioate zwitterions **10a**, **10b**, **10k**, **10l** and **10m**: selected ^{1}H and ^{13}C NMR data (R^1, R^2, R^3: see Scheme 1)
[a] CH_3-*t*Bu. [b] CH_3-*t*Bu. [c] qC of *t*Bu = 36.2 at C2; 41.5 at C8

(194−204 ppm), due to its participation in an aza/thiaallyl anionic subunit (Scheme 3). Dipolar structures similar to **10** have been described as the results of addition reactions between 3-amino-2*H*-aziridines and 1,3,4-thiadiazol-2(3*H*)-ones.[17] The isolated intermediates **10** possess an interesting property: if they are heated to slightly above their melting points they are completely transformed into the corresponding guanidines **5** through an intramolecular S_N reaction. The melting points and the IR spectra of these rearrangement products and the genuine compounds **5**, prepared from **1** and **2**, are almost identical.

As a consequence of the charge separation in these zwitterionic species **10**, a wide variety of consecutive transformations appear to be plausible, especially inter- or intramolecular proton shifts as indicated in Scheme 4. The subsequent reactions steps are therefore determined by the properties of these zwitterions **10** (in the modelling procedure: **10M**).

Path a, Scheme 3:[3,13] The DFT calculations indicate that the negatively charged sulfur in **10M** is quite close to C(5) of the six-membered ring (Figure 1). Because of a delocalised positive charge, the ring-closure/ring-opening reaction through ***TS-B*** is easily feasible and needs 16.8 kcal·mol^{-1}. The guanidine **5M** is stabilised by 13.6 kcal·mol^{-1} relative to the most stable conformation **9Ma**.

Path b, Scheme 4**:** Proton shifts from the acidic iminium moiety HN^+ to the S^- or the former N(7) transform **10M** into the tautomers **11Ma** (SH) or **11Mb** (NH). Nothing is known about the energetic demands of these proton-transfer reactions. Under the experimental conditions used these reactions could be assisted by external effects (the presence of the hydrobromides, **2**·HBr, increasing acidity of that NH proton (depending on the properties of R^3) and also solvent

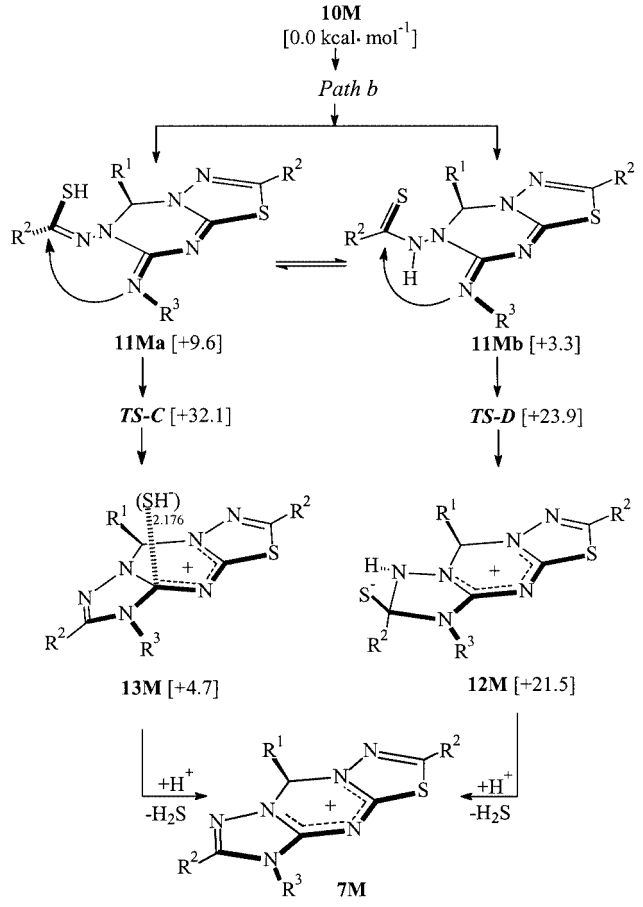


Scheme 3

effects). Our calculations indicate that the structures **11Ma** (+9.6 kcal·mol^{-1}) and **11Mb** (+3.3 kcal·mol^{-1}) appear to be accessible from the intermediate **10M** (relative energy set to 0.0 kcal·mol^{-1}) under the reaction conditions. Both structures allow nucleophilic attack of the NR^3 nitrogen at the C−(SH) or C=S carbon atom and, after extrusion of the HS^- anion, the formation of the new five-membered ring.

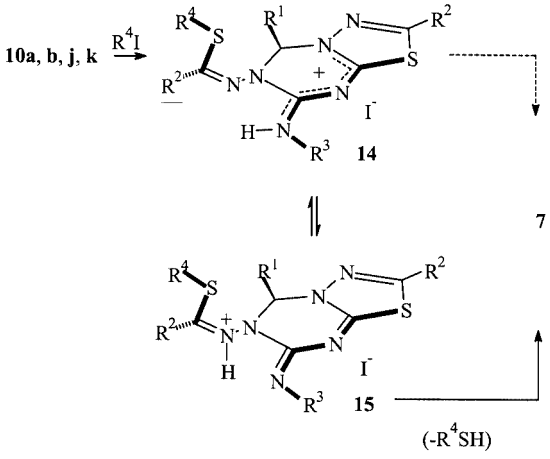
The DFT calculations indicate that both the back-reaction via **10M** as well as the novel ring-closure reaction to give **12M**, which has a barrier of 23.9 kcal·mol^{-1} that needs to be surmounted (***TS-D***), are possible. It could be that, supported by the ammonium bromide **2**·HBr, this reaction cascade is completed by the formation of **7M** via the intermediate formation of compounds such as **12M**, the protonation of the S^- position, and the elimination of hydrogen sulfide. An alternative reaction pathway via ***TS-C*** (+32.1 kcal·mol^{-1}) to give **13M** cannot be ruled out.

These steps i.e. **8Ma** → **10M** → **11Ma/11Mb** → **12M/13M** → **7M** can be repeated analogously with excess benzylamine at the C(3a) centre of **7M**, and so finally the products **6** are formed.



Scheme 4

Another experimentally convenient pathway for the formation of **7** starts with the formation of a cation similar to **14**, in which the SH substituent is replaced by S-Me or S-Et (Scheme 5).



R1; R2; R3: *cf.* Scheme 1

14	a	b	j	k
R4	Et	Et	Me	Me

Scheme 5

Examples of both compounds have synthesised almost quantitatively from **10** by treatment with alkyl iodides (0 °C, THF solution, Figure 2).

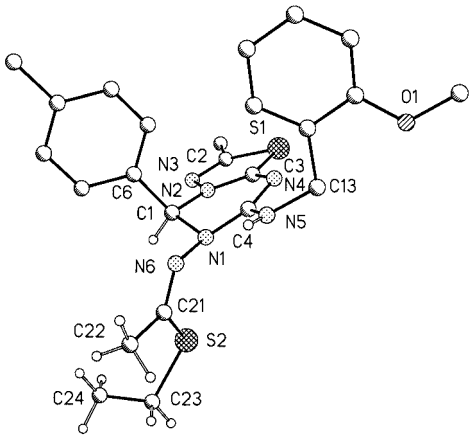


Figure 2. Crystal structure of **14b**; selected bond lengths [pm] and bond angles [deg]: N1−C1 149.4(8), N2−C1 147.5(8), N1−C4 138.1(8), N4−C4 135.3(8), N4−C3 131.8(8), N2−C3 134.5(8), N5−C4 131.5(8), N1−N6 145.5(7), N6−C21 129.6(9), N5−C13 146.8(8), S2−C21 176.3(7), S2−C23 183.8(8); N2−C1−N1 103.8(5), N1−C1−C6 113.6(5), N2−C1−C6 112.9(5), N4−C3−N2 126.1(6), N4−C4−N1 121.6(6)

At this point the nucleophilicity of the formerly negatively charged sulfur is significantly reduced and attack at C(5) (to give guanidines) becomes impossible. In **14**, the NHR^3 nitrogen appears not to be sufficiently nucleophilic for further ring-closure reactions. We suggest that this NH proton migrates to the (former) N(7) position to give **15**. After such a migration, pathway b again becomes feasible, since the imine nitrogen can now attack the $C\text{-}SR^4$ carbon. Extrusion of HSR^4 (or H_2S) gives the structures **7**, which have been isolated from these reactions in excellent yields. Interestingly, such reactions can be performed with structures **10**, the imine components of which stem from benzylamine (**14b**) or substituted ethylamines (**14c**, **14d**).

The thioalkyl compounds **14b−d** obtained were unequivocally identified by NMR spectroscopy. In contrast to **14c−d** (compounds with definite melting points), **14b** is not very stable at room temperature. In this case, the ring-closure reaction described above yields the salt **7b** after elimination of the corresponding alkyl sulfide. In the cases of **14c** or **14d**, the analogous reaction to give **7c** and **7d** requires heating of the reaction mixture (50−80 °C). All the NMR spectroscopic data are in agreement with the expected values for such cationic species. Some NMR properties of **14b** are listed here: the central C21 of the newly formed ethyl ethane-imidothioate moiety [N=C(Me)−S−Et, for the numbering cf. Figure 2] is shifted to lower field (δ = 184.4 ppm) than C2 of the 1,3,4-thiadiazole ring (δ = 157.6 ppm). This C atom in **14b** is slightly shifted to higher field than in the zwitterionic structures [e.g., **10b**; the C atom of the anionic N=C(Me)−S⁻ moiety: 194.7 ppm]. All cations of type **14** show broad iminium signals at 8.16−8.23 ppm in their ^1H NMR spectra, which could be characterised by COSY NMR experiments. In spite of the

instability of **14b**, we succeeded in preparing crystalline material (fractional crystallisation from chloroform/ethyl acetate) suitable for X-ray investigations (Figure 2). We conclude from the X-ray structure of **14b** that the subunit C2−N3−N2−C3−N4−C4−N1 and the exocyclic N5 form a conjugated system (with bond lengths between 129 and 138 ppm), which allows efficient delocalisation of the positive charge.

In order to detect some intermediate structures in the course of the interactions between cations **1** and amines **2** in the presence of alkyl iodides, we investigated and separated the product mixture after treatment of **1a** with **2b** and EtI at −10 °C in THF (vide supra). The composition of this mixture was determined by quantitative ^{1}H NMR investigations by using the signals of the hydrogens at the sp^3 carbon in the 1,3,5-triazinium rings as an indicator. The relative amounts of compounds **5b** (about 10%), **14b** (20%) and **7b** (55%) were determined.

The overall reaction between compounds **1** and amines **2** to give either **7** (iodides, bromides) or the sulfur-free products **6** can be described as a rearrangement in which the ring sulfur functions as a leaving group (ring-opening step) after the nucleophilic attack of a benzylamine nitrogen at the most electrophilic ring positions C(3a) or C(4a). The sulfur is replaced by the benzylamino group (ring-closure step). In contrast to guanidine formation[3] (Path a), the central dihydro-1,3,5-triazinium ring survives in the course of a Path b reaction, and so this reaction type can be classified as a novel example of a S_N(ANRORC) mechanism.[18] To the best of our knowledge, no analogous rearrangements have been described in the literature (cf.[3] and references cited therein). The only exception is the sulfur elimination in the course of the synthesis of 4-amino-1*H*-1,2,4-triazole derivatives on treatment of 1,3,4-thiadiazoles with hydrazine hydrate.[19]

Access to the two alternative pathways a and b is almost certainly governed by the NH-acidity of the nitrogen in the exocyclic iminium part of **10**. We assume that this acidity is slightly higher in the case of HN(+)-Bzl than in that of the HN(+)-butyl. The latter resembles the iminium moieties as they occur in the transformations to **5** with "standard" primary and secondary aliphatic amines such as piperidine or morpholine. In these cases, intermediates such as **11Ma** and **11Mb** could not be detected in the reaction mixture (NMR studies at 223 K). All these amines enter into Path a after the formation of the zwitterions **10**, which rapidly ends with the formation of guanidines. The slightly increased acidity of the corresponding benzyl iminium moiety in **10** obviously facilitates prototropy (to give **11Ma** or **11Mb**), which is not possible to the same extent in cases of standard aliphatic iminium functionalities.

Finally, the proton transfer from the iminium N atom to other acceptors in **10b** (R^3 = 2-MeOBzl) is presumably hindered by a hydrogen bond between the iminium nitrogen and oxygen. This could explain the low relative yield of **6b** from this synthesis (**5b**/**6b** = 87:13; cf. the standard situation: **5a**/**6a** = 54:46; Table 1).

Structural assignments of the new heterocyclic compounds **6a**−**6i**, the iodides or bromides **7** and of **14** are based on NMR spectroscopic data (in particular HMQC, HMBC, COSY, TOCSY and NOESY), mass spectra (CI), IR spectra, elemental analyses and, in some cases (**6a**, **14b** and **7b**), X-ray analyses. Like the sulfur-nitrogen compounds **1**,[1] the novel cations **6** should possess symmetrical structures, which is confirmed by the ^{13}C NMR spectra. Together with the sp^3-hybridised C(9) at δ = 69−77 ppm, there are only two additional ^{13}C signals (δ = 150 and 151 ppm) at almost constant fields characterising this new tricyclic bis(1,2,4-triazolo)triazinium structure. These peaks are shifted to significantly higher fields than the signals of the corresponding thiadiazole moiety in **1** (δ = 160 and 166 ppm). The same tendency is found for the MeC signals (δ = 12 ppm in **6**, δ = 17 ppm in **1**). As would be expected, the NMR signals of the two benzyl groups bound to the nitrogen atoms N(3) and N(5) of the newly formed 1,2,4-triazole rings collapse to give just one signal. Whereas the methylene protons of the racemic guanidine compounds **5** in the ^{1}H NMR spectra show the characteristic AB part of an ABX system in the range between δ = 4.5 and 4.8 ppm (2H), thus indicating their diastereotopicity and typical coupling properties with the adjacent NH proton, the diastereotopic benzylic methylene protons in **6** have only a double doublet, which is significantly shifted to lower fields at 5.2−5.4 ppm (4 H). This is caused by the electronic properties of the tricyclic cation. The HC(9) signals in **6** and **1** appear in the same range, around δ = 7.5 ppm. As with the naphthyl compound **1f**, a broad HC(9) signal also appears for **6f** at δ = 8.86 ppm, indicating the presence of

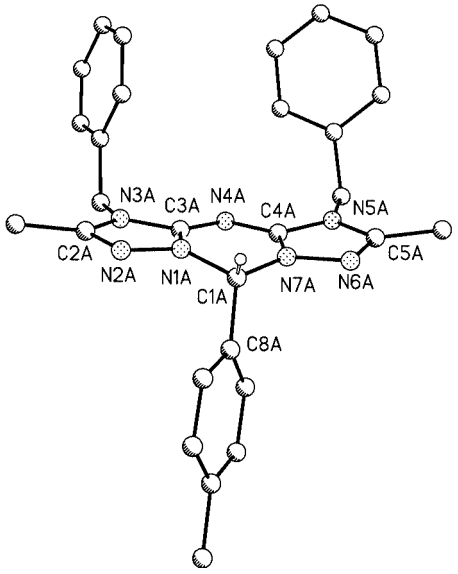


Figure 3. Crystal structure of **6a**; selected bond lengths [pm] and bond angles [deg]: N1A−C1A 147.8(7), N7A−C1A 147.0(7), C1A−C8A 150.8(8), N1A−C3A 135.3(7), N4A−C3A 131.4(7), N4A−C4A 135.7 (7), N7A−C4A 135.4(7), N3A−C15A 147.4(6), N5A−C22A 147.9(6), N3A−C3A 137.4(7), N5A−C4A 133.8(7); N7A−C1A−C8A 114.7(5), N7A−C1A−N1A 101.6(5), N1A−C1A−C8A 111.4(5), N4A−C3A−N1A 128.5(5), N5A−C4A−N4A 126.9(6), N7A−C4A−N4A 126.5(6), N7A−C1A−N1A 101.6(5), N1A−C1A−C8A 111.4(5)

a conformational equilibrium.[1] The other compounds **6** do not exhibit such broad signals for HC(9).

Calculations on the model cation **6** ($R^1 = R^2 = R^3 =$ Me) by the DFT method (at the same level as described above) give further insights into some properties of these interesting new compounds. We found an acceptable agreement with the X-ray structural data (Figure 3). The tricyclic system containing only N and C atoms is almost planar, with nearly identical C−N bond lengths in the three rings (130−138 pm, DFT: 130−139 pm) with the exception of the N(8)−C(9) and C(9)−N(10) bonds, which are significantly longer, as might be expected (147.4 pm, DFT: 147.0 pm). The bond angles at the C(9) atom (N1−C1−N7 = 101.6°; N1−C1−C8 = 111.4°; N7−C1−C8 = 114.7°) indicate that this C(9) is twisted out of the N(8)/C(4a)/N(4)/C(3a)/N(10) triazinium ring plane and therefore prefers a quasi half-chair conformation (recognisable from a side view of the ring plane, Figure 3). These properties are almost identical with those of the cations **1**.

The tricyclic compound **7b** has five ^{13}C signals in the expected range. There are some minor differences for the triazole, thiadiazole and triazinium C atoms. The shifts of the CH_3 group bound to the triazole ring (^1H: δ = 2.34 ppm; ^{13}C: δ = 11.8 ppm) differ slightly from the shifts of the thiadiazole CH_3 (δ = 2.56, 17.6 ppm). In the case of **7b**, we found acceptable agreement of the X-ray geometry with the DFT results (Figure 4). Obviously, the positive charge of the cation **7b** is delocalised similarly, as in the conjugated subunit of **6b**. Because of the structural similarity between **1** and the novel cations **6**, we expected comparable electronic properties, which should allow predictions for further synthetic use of these compounds. This assumption was supported by DFT calculations with inclusion of NPA analysis[20] to calculate the natural charges at the centres C(3a) and C(4a). In the case of model compound **6M** ($R^1 = R^2 = R^3 =$ Me) the charges q_{C3a} and q_{C4a} are +0.64 e. This should allow the attack of a suitable nucleophilic reagent. In view of these results, we checked the behaviour of some compounds **6** towards KOH/*t*BuOK in THF and succeeded in synthesising the new aminals **16a**, **16c**, **16d**, **16f** and **16h** in yields of up to 95% (Scheme 6).

Structural assignments of these 1,1′-alkanediylbis(4*H*-dihydro-1,2,4-triazols) **16** are based on IR spectra, NMR spectroscopic data, mass spectra (CI) and elemental analyses and were further supported by X-ray analysis (**16h**, Figure 5). These results have motivated us to design further reactions of the tricyclic compounds **6** with nitrogen, sulfur and carbon nucleophiles. These investigations are presently underway.

Conclusion

From this investigation we conclude that the reactivity patterns of cations such as **8** (**8Ma** and **8Mb**, Scheme 3) depend on the reaction conditions and the nature of R^3. Under basic conditions (with an excess of amines **2**), the predominant step is *deprotonation* of **8** with formation of **9**

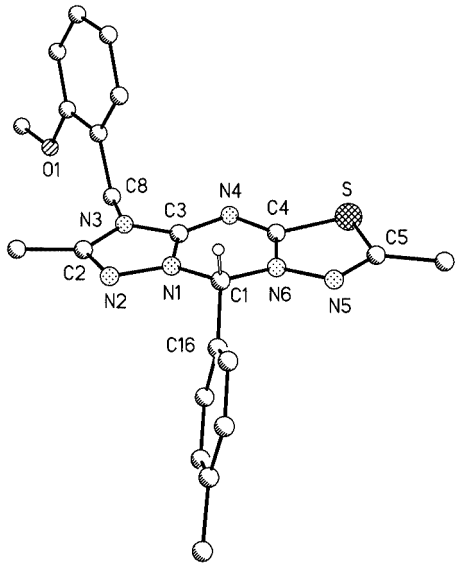
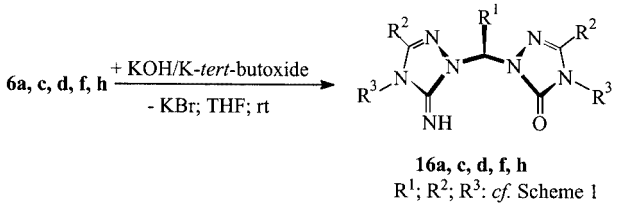


Figure 4. Crystal structure of **7b**; selected bond lengths [pm] and bond angles [deg]: N1−C1 145.8(5), N6−C1 147.9(5), N1−C1 133.7(5), N4−C3 133.9(5), N4−C4 131.8(5), N6−C4 135.1(5), C1−C16 150.3(5), N3−C8 146.7(5); N1−C1−N6 102.4(3), N6−C1−C16 113.9(3), N1−C1−C16 113.4(3), C4−N6−C1 124.7(3), N4−C4−N6 126.7(3), C4−N4−C3 110.6(3), N1−C3−N4 127.1(3), C3−N1−C1 125.4(3)



16a, c, d, f, h
R^1; R^2; R^3: *cf.* Scheme 1

Scheme 6

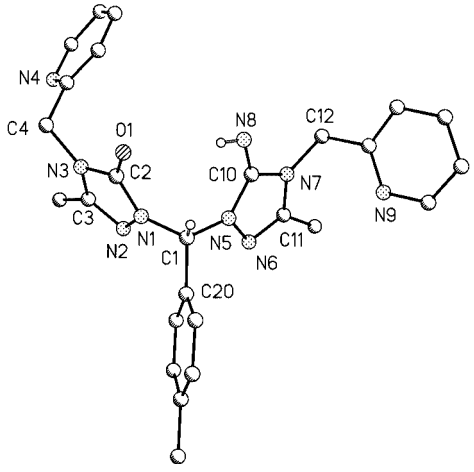


Figure 5. Crystal structure of **16h**; selected bond lengths [pm] and bond angles [deg]: C1−N1 145.6(3), N5−C1 144.7(3), C1−C20 151.7(3), N8−C10 126.2(3), O1−C2 124.3(3), N3−C4 146.7(3), N7−C12 145.5(3); N5−C1−N1 112.03(18), N1−C1−C20 113.26(19), N5−C1−C20 113.30(19), N8−C10−N7 125.0(2), O1−C2−N1 129.2(2), O1−C2−N3 127.4(2), N5−C10−N7 102.54(19)

(**9Ma** and **9Mb**), affording access to a reaction channel giving the zwitterions **10**. Their formation is controlled by the influence of negative hyperconjugation, here the $n_{N(ex.)}/\sigma^*_{C(4a)-S(5)}$ interaction. Interestingly, alternative reactions of **10** are the result of competition between nucleophilic attack by S^- at the C9 centre (Path a, to give guanidines) and proton shifts (Path b, Scheme 4; formation of **11Ma** or **11Mb**), allowing a novel type of nucleophilic ring-closure reaction with formation of **7** (model **7M**) and extrusion of H_2S. DFT calculations indicate that all of these steps are possible − all of the calculated activations barriers appear to be surmountable − and we believe that we have found a reasonable explanation for these alternative multistep reaction cascades. A more detailed theoretical study including the stereoelectronic effects in the uncharged (e.g. **9Ma**) *and* protonated cationic structures (such as **8Ma**, **8Mb** and further tautomers) is currently underway.

Experimental Section

General Remarks: All solvents were dried and distilled prior to use. Column chromatography: Fluka silica gel 60, 0.0036−0.2 mm (70−230 mesh ASTM). Melting points: Büchi B-549 or Lindstrom copper block apparatus. IR: Nicolet Avatar 320 (KBr) or Nicolet Impact 400 (ATR). NMR: Bruker DRX 400 and Bruker AVANCE 250; NMR spectra were recorded at 250/400 MHz and 62.5/100 MHz for proton and carbon, respectively. For ^1H and ^{13}C, [D_6]DMSO (H, δ = 2.49 ppm, C δ = 39.5 ppm) and $CDCl_3$ (H, δ = 7.24 ppm, C δ = 77.0 ppm) were used as solvents, and TMS was used as internal standard. MS: SSQ 710. Finnigan MAT. Elemental analyses (C, H, N, S): Leco CHNS-932; halogens were determined by the Schöninger method by potentiometric titration. Compounds **1a**, **1f**, **1g** and **1j** have been described in the literature.[1][3a] The amines and benzylamines **2a**−**2m** (VWR International; Merck) are commercially available and were purified by distillation. Nomenclature of new compounds: IUPAC Naming On I-Lab Via ACD/ChemSketch (www.acdlabs.com).

General Procedure for Reactions between the Tricyclic Compounds 1 and Benzylamines 2: The amine **2** (10 mmol) was added to a suspension of **1** (5 mmol) in pyridine (60 mL). The mixture was stirred at room temperature for 24 h. This procedure gave a clear solution with a slight red colouring, while the smell of hydrogen sulfide was observed. The pyridine solution was concentrated in vacuo (rotary evaporator), the crude product was extracted with *tert*-butyl methyl ether and the solid residue was washed with water. After filtration and drying in vacuo, the two main products **5** and **6** were isolated by fractional crystallisation or column chromatography on silica gel 60 (0.063−0.200 mm).

***N*-Benzyl-5-methyl-2-(4-methylphenyl)-*N′*-(5-methyl-1,3,4-thiadiazol-2-yl)-1,3,4-thiadiazole-3(2*H*)-carboximidamide (5a):** Yield 0.78 g, (37%), m.p. 161 °C. IR (ATR): $\tilde{\nu}$ = 1614 cm^{-1}, (C=N, exocyclic). ^1H NMR ($CDCl_3$): δ = 2.18 (s, 3 H, CH_3), 2.28 (s, 3 H, CH_3), 2.51 (s, 3 H, CH_3), 4.40−4.83 (ddd, 2 H, CH_2), 7.18 (s, 1 H, sp^3CH), 7.00−7.29 (m, 9 H, phenyl), 9.12 (br. s, 1 H, NH) ppm. ^{13}C NMR ($CDCl_3$): δ = 16.0, 16.6, 21.1, 48.9 (CH_2), 72.2 (sp^3C), 126.4, 127.1, 127.4, 129.2, 129.3, 138.1, 138.2, 138.8, 147.0, 151.9 ($C_{guanidine}$), 158.0, 174.1 ppm. MS (DCI/H_2O): *m*/*z* (%) = 423 (100) $[C_{21}H_{23}N_6S_2]^+$. $C_{21}H_{22}N_6S_2$ (422.56): calcd. C 59.69, H 5.25, N 19.89, S 15.17; found C 59.94, H 5.32, N 19.91, S 15.07.

***N*-(2-Methoxybenzyl)-5-methyl-2-(4-methylphenyl)-*N′*-(5-methyl-1,3,4-thiadiazol-2-yl)-1,3,4-thiadiazole-3(2*H*)-carboximidamide (5b):** Yield 1.77 g, (78%), m.p. 145−146 °C. IR (ATR): $\tilde{\nu}$ = 1606 cm^{-1}, C=N (exocyclic). ^1H NMR ($CDCl_3$): δ = 2.19 (s, 3 H, CH_3), 2.28 (s, 3 H, CH_3), 2.49 (s, 3 H, CH_3), 3.75 (s, 3 H, OCH_3), 4.58−4.75 (ddd, 2 H, CH_2), 6.81−7.23 (m, 8 H, phenyl), 7.21 (s, 1 H, sp^3CH), 8.98 (br. s, 1 H, NH) ppm. ^{13}C NMR ($CDCl_3$): δ = 16.0, 16.6, 21.1, 44.4 (CH_2), 55.2 (OCH_3), 72.1 (sp^3C), 110.3, 120.3, 122.8, 126.4, 128.6, 129.0, 129.1, 138.1, 138.2, 146.7, 152.1 ($C_{guanidine}$), 157.4, 157.8, 173.8 ppm. MS (DCI/H_2O): *m*/*z* (%) = 453 (100) $[C_{22}H_{25}N_6S_2]^+$. $C_{22}H_{24}N_6S_2$ (452.59): calcd. C 58.38, H 5.34, N 18.57, O 3.54, S 14.17; found C 58.52, H 5.65, N 18.24, S 13.88.

***N*-(2-Chlorobenzyl)-5-methyl-2-(4-methylphenyl)-*N′*-(5-methyl-1,3,4-thiadiazol-2-yl)-1,3,4-thiadiazole-3(2*H*)-carboximidamide (5c):** Yield 0.82 g, (36%), m.p. 123 °C. IR (KBr): $\tilde{\nu}$ = 1617 cm^{-1}, (C=N, exocyclic). ^1H NMR ($CDCl_3$): δ = 2.13 (s, 3 H, CH_3), 2.30 (s, 3 H, CH_3), 2.52 (s, 3 H, CH_3), 4.67−5.00 (ddd, 2 H, CH_2), 7.02−7.34 (m, 8 H, phenyl), 7.09 (s, 1 H, sp^3CH), 9.29 (br. s, 1 H, NH) ppm. ^{13}C NMR ($CDCl_3$): δ = 16.0, 16.5, 21.1, 46.6 (CH_2), 72.1 (sp^3C), 126.5, 126.9, 128.3, 129.0, 129.1, 129.3, 132.9, 136.6, 138.1, 138.2, 147.1, 151.8 ($C_{guanidine}$), 158.0, 174.2 ppm. MS (DCI/H_2O): *m*/*z* (%) = 457 (100) $[C_{21}H_{22}ClN_6S_2]^+$. $C_{21}H_{21}ClN_6S_2$ (457.01): calcd. C 55.19, H 4.63, Cl 7.76, N 18.39, S 14.03; found C 54.80, H 4.68, Cl 7.90, N 18.50, S 14.03.

***N*-(4-Chlorobenzyl)-5-methyl-2-(4-methylphenyl)-*N′*-(5-methyl-1,3,4-thiadiazol-2-yl)-1,3,4-thiadiazole-3(2*H*)-carboximidamide (5d):** Yield 0.64 g, (28%), m.p. 137 °C. IR (ATR) 1601 cm^{-1}, (C=N, exocyclic). ^1H NMR ($CDCl_3$): δ = 2.18 (s, 3 H, CH_3), 2.29 (s, 3 H, CH_3), 2.52 (s, 3 H, CH_3), 4.53−4.84 (ddd, 2 H, CH_2), 6.93−7.23 (2d, 8 H, phenyl), 7.18 (s, 1 H, sp^3CH), 9.28 (br. s, 1 H, NH) ppm. ^{13}C NMR ($CDCl_3$): δ = 16.0, 16.6, 21.2, 47.9 (CH_2), 72.0 (sp^3C), 126.5, 128.6, 128.8, 129.1, 132.8, 137.6, 137.9, 138.2, 147.2, 151.9 ($C_{guanidine}$), 158.1, 174.3 ppm. MS (DCI/H_2O): *m*/*z* (%) = 457 (100) $[C_{21}H_{22}ClN_6S_2]^+$. $C_{21}H_{21}ClN_6S_2$ (457.01): calcd. C 55.19, H 4.63, Cl 7.76, N 18.39, S 14.03; found C 55.17, H 4.75, Cl 7.59, N 18.27, S 14.07.

5-Methyl-*N*-(4-methylbenzyl)-2-(4-methylphenyl)-*N′*-(5-methyl-1,3,4-thiadiazol-2-yl)-1,3,4-thiadiazole-3(2*H*)-carboximidamide (5e): Yield 1.22 g, (56%), m.p. 121 °C. IR (KBr): $\tilde{\nu}$ = 1610 cm^{-1} (C=N, exocyclic). ^1H NMR ($CDCl_3$): δ = 2.19 (s, 3 H, CH_3), 2.29 (s, 3 H, CH_3), 2.32 (s, 3 H, CH_3), 2.51 (s, 3 H, CH_3), 4.57−4.75 (ddd, 2 H, CH_2), 7.01−7.11 (2d, 8 H, phenyl), 7.13 (s, 1 H, sp^3CH), 9.02 (br. s, 1 H, NH) ppm. ^{13}C NMR ($CDCl_3$): δ = 16.0, 16.6, 21.1, 23.4, 48.4 (CH_2), 72.0 (sp^3C), 125.0, 126.4, 127.5, 129.2, 135.2, 135.6, 136.7, 128.1, 146.9, 151.8 ($C_{guanidine}$), 158.0, 174.1 ppm. MS (DCI/H_2O): *m*/*z* (%) = 437 (100) $[C_{22}H_{25}N_6S_2]^+$. $C_{22}H_{24}N_6S_2$ (436.59): calcd. C 60.52, H 5.54, N 19.25, S 14.69; found C 60.87, H 5.78, N 19.17, S 14.70.

***N*-Benzyl-5-methyl-*N′*-(5-methyl-1,3,4-thiadiazol-2-yl)-2-(1-naphthyl)-1,3,4-thiadiazole-3(2*H*)-carboximidamide (5f):** Yield 0.80 g, (35%), m.p. 130 °C (diethyl ether). IR (KBr): $\tilde{\nu}$ = 1626 cm^{-1}, (C=N, exocyclic). ^1H NMR ($CDCl_3$): δ = 2.20 (s, 3 H, CH_3), 2.40 (s, 3 H, CH_3), 4.69−4.95 (ddd, 2 H, CH_2), 6.90−7.94 (m, 12 H, phenyl, naphthyl), 7.99 (s, 1 H, sp^3CH), 9.20 (br. s, 1 H, NH) ppm. ^{13}C NMR ($CDCl_3$): δ = 15.9, 16.7, 48.6 (CH_2), 68.9 (sp^3C), 122.7, 123.5, 125.6, 125.7, 126.3, 127.2, 127.6, 128.6, 128.7, 128.9, 129.3, 133.7, 136.3, 138.9, 148.2, 151.8 ($C_{guanidine}$), 158.2, 174.0 ppm. MS (DCI/H_2O): *m*/*z* (%) = 459 (100) $[C_{24}H_{23}N_6S_2]^+$. $C_{24}H_{22}N_6S_2$ (458.59): calcd. C 62.86, H 4.84, N 18.33, S 13.98; found C 62.46, H 5.11, N 18.22, S 13.64.

***N*-Benzyl-2-butyl-5-methyl-*N′*-(5-methyl-1,3,4-thiadiazol-2-yl)-1,3,4-thiadiazole-3(2*H*)-carboximidamide (5g):** Yield 0.76 g, (32%),

oil; HBF_4 salt: m.p. 107 °C. IR (film) 1608 cm^{-1}, (C=N, exocyclic). ^1H NMR ($CDCl_3$): δ = 0.86 (t, 3 H, CH_3), 1.18−1.30 (m, 4 H, CH_2CH_2), 2.13 (s, 3 H, CH_3), 2.30−2.40 (m, 2 H, CH_2), 2.56 (s, 3 H, CH_3), 4.57−4.74 (ddd, 2 H, CH_2), 6.23 (t, 1 H, sp^3CH), 7.21−7.33 (m, 5 H, phenyl) ppm. ^{13}C NMR ($CDCl_3$): δ = 13.8, 16.1, 16.8, 22.0, 26.6, 36.5, 48.8 (CH_2), 71.0 (sp^3C), 127.2, 127.4, 128.5, 138.8, 148.6, 152.1 ($C_{guanidine}$), 157.9, 174.3 ppm. MS (DCI/H_2O): *m/z* (%) = 389 (100) $[C_{18}H_{25}N_6S_2]^+$. $C_{18}H_{25}BF_4N_6S_2$ (476.36): calcd. C 45.39, H 5.29, B 2.27, F 15.95, N 17.64, S 13.46; found C 45.48, H 5.32, N 17.43, S 13.42.

5-Methyl-2-(4-methylphenyl)-*N*′-(5-methyl-1,3,4-thiadiazol-2-yl)-*N*-(pyridin-2-ylmethyl)-1,3,4-thiadiazole-3(2*H*)-carboximidamide (5h): Yield 0.42 g, (20%), m.p. 161 °C. IR (KBr): $\tilde{\nu}$ = 1619 cm^{-1}, (C=N, exocyclic). ^1H NMR ($CDCl_3$): δ = 2.21 (s, 3 H, CH_3), 2.19 (s, 3 H, CH_3), 2.52 (s, 3 H, CH_3), 4.83 (ddd, 2 H, CH_2), 7.03−7.24 (m, 7 H, phenyl, py, sp^3CH), 7.56 (t, 1 H, py), 8.52 (d, 1 H, py), 9.23 (br. s, 1 H, NH) ppm. ^{13}C NMR ($CDCl_3$): δ = 16.1, 16.6, 21.2, 49.8 (CH_2), 71.9 (sp^3C), 121.1, 121.9, 126.5, 129.2, 136.6, 138.2, 138.3, 147.3, 149.0, 151.9 ($C_{guanidine}$), 158.1, 158.2, 173.8 ppm. MS (DCI/H_2O): *m/z* (%) = 424 (100) $[C_{20}H_{21}N_7S_2]^+$. $C_{20}H_{20}N_7S_2$ (422.54): calcd. C 56.85, H 4.77, N 23.20, S 15.17; found C 57.05, H 5.21, N 23.44, S 15.00.

5-Methyl-2-(4-methylphenyl)-*N*′-(5-methyl-1,3,4-thiadiazol-2-yl)-*N*-(pyridin-4-ylmethyl)-1,3,4-thiadiazole-3(2*H*)-carboximidamide (5i): Yield 0.70 g, (33%), m.p. 155 °C. IR (KBr): $\tilde{\nu}$ = 1617 cm^{-1}, (C=N, exocyclic). ^1H NMR ([D$_6$]DMSO): δ = 2.21 (s, 3 H, CH_3), 2.25 (s, 3 H, CH_3), 2.44 (s, 3 H, CH_3), 4.51−4.66 (ddd, 2 H, CH_2), 6.98−7.08 (m, 7 H, phenyl, py, sp^3CH), 8.42 (d, 2 H, py), 8.78 (br. s, 1 H, NH) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 15.6, 16.2, 20.7, 45.6 (CH_2), 71.0 (sp^3C), 121.8, 125.6, 129.0, 137.8, 137.9, 148.0, 148.4, 149.4, 151.1 ($C_{guanidine}$), 157.6, 171.7 ppm. MS (DCI/H_2O): *m/z* (%) = 424 (100) $[C_{20}H_{21}N_7S_2]^+$. $C_{20}H_{20}N_7S_2$ (422.54): calcd. C 56.85, H 4.77, N 23.20, S 15.17; found C 56.72, H 5.12, N 23.22, S 14.96.

5-*tert*-Butyl-*N*′-(5-*tert*-butyl-1,3,4-thiadiazol-2-yl)-2-(2-hydroxyphenyl)-*N*-(2-pyridin-2-ylethyl)-1,3,4-thiadiazole-3(2*H*)-carboximidamide (5j): (Synthesised in 30 mL triethylamine, 5 mmol **1j** and 5 mmol **2j**). Yield 1.88 g, (72%), m.p. 184 °C, (ethyl acetate). IR (ATR): $\tilde{\nu}$ = 1518 cm^{-1}, (C=N, exocyclic). ^1H NMR ([D$_6$]DMSO): δ = 1.10 (s, 9 H, *t*Bu), 1.23 (s, 9 H, *t*Bu), 2.99 (t, 2 H, CH_2), 3.71 (m, 2 H, CH_2), 6.69 (t, 1 H, phenyl), 6.75 (d, 1 H, phenyl), 6.82 (d, 1 H, phenyl), 7.05 (t, 1 H, phenyl), 7.10 (s, 1 H, sp^3CH), 7.16−7.20 (m, 2 H, py), 7.63 (t, 1 H, py), 8.37 (br., 1 H, NH), 8.43 (d, 1 H, py), 9.91 (s, 1 H, OH) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 28.7 30.4, 35.7, 35.8, 37.5 (CH_2), 43.4 (CH_2), 65.9 (sp^3C), 115.4, 119.1, 121.6, 123.4, 124.7, 127.3, 129.1, 136.5, 149.0, 151.2 ($C_{guanidine}$), 153.1, 158.8, 161.6, 171.6, 172.0 ppm. MS (DCI/H_2O): *m/z* (%) = 524 (100) $[C_{26}H_{34}N_7OS_2]^+$. $C_{26}H_{33}N_7OS_2$ (523.7): calcd. C 59.63, H 6.35, N 18.72, O 3.05, S 12.24; found C 59.83, H 6.51, N 18.29, S 11.96.

5-*tert*-Butyl-*N*′-(5-*tert*-butyl-1,3,4-thiadiazol-2-yl)-2-(2-hydroxyphenyl)-*N*-(2-thien-2-ylethyl)-1,3,4-thiadiazole-3(2*H*)-carboximidamide (5k): (Synthesis cf. **5j**). Yield 2.17 g, (82%), m.p 165 °C, (ethyl acetate). IR (ATR): $\tilde{\nu}$ = 1517 cm^{-1}, (C=N, exocyclic). ^1H NMR ([D$_6$]DMSO): δ = 1.38 (s, 9 H, *t*Bu), 1.42 (s, 9 H, *t*Bu), 3.08 (t, 2 H, CH_2), 3.75−3.90 (m, 2 H, CH_2), 6.71 (d, 1 H, thienyl), 6.84 (t, 1 H, thienyl), 6.90−6.96 (m, 2 H, phenyl), 7.06 (d, 1 H, thienyl), 7.22 (t, 1 H, phenyl), 7.27 (s, 1 H, sp^3CH), 7.43 (d, 1 H, phenyl), 9.87 (br., 1 H, NH), 10.72 (br., 1 H, OH) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 29.1, 30.7, 31.1, 36.2, 36.6 (CH_2), 47.0 (CH_2), 65.6 (sp^3C), 118.7, 120.8, 123.8, 125.3, 126.4, 126.8, 129.1, 130.7, 140.5, 152.5 ($C_{guanidine}$), 154.5, 163.2, 172.5, 173.3 ppm. MS (DCI/H_2O): *m/z* (%) = 529 (100) $[C_{25}H_{33}N_6OS_3]^+$. $C_{25}H_{32}N_6OS_3$ (528.74): calcd. C 56.79, H 6.10, N 15.89, O 3.03, S 18.19; found C 57.19, H 6.47, N 15.84, S 18.17.

***N*-Butyl-5-*tert*-butyl-*N*′-(5-*tert*-butyl-1,3,4-thiadiazol-2-yl)-2-(2-hydroxyphenyl)-1,3,4-thiadiazole-3(2*H*)-carboximidamide (5l):** Yield 1.71 g, (72%), m.p. 159 °C. IR (ATR): $\tilde{\nu}$ = 1609 cm^{-1}, (C=N, exocyclic). ^1H NMR ([D$_6$]DMSO): δ = 0.89 (t, 3 H, CH_3), 1.21 (s, 9 H, *t*Bu), 1.23 (s, 9 H, *t*Bu), 1.31 (m, 2 H, CH_2), 3.50 (dd, 4 H, CH_2CH_2), 6.76 (t, 1 H, phenyl), 6.81 (d, 1 H, phenyl), 6.94 (d, 1 H, phenyl), 7.07 (t, 1 H, phenyl), 7.23 (s, 1 H, sp^3CH), 8.57 (br., 1 H, NH), 9.91 (br., 1 H, OH) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 13.9, 19.8, 29.0, 30.7, 32.2, 36.0, 36.1, 44.3, 66.3 (sp^3C), 115.7, 119.5, 125.1, 127.9, 129.4, 136.7, 150.0, 151.8 ($C_{guanidine}$), 153.5, 161.7, 171.6, 173.2 ppm. MS (DCI/H_2O): *m/z* (%) = 474 (100) $[C_{23}H_{35}N_6OS_2]^+$. $C_{23}H_{34}N_6OS_2$ (474.68): calcd. C 58.20, H 7.22, N 17.70, O 3.37, S 13.51; found C 58.60, H 7.47, N 17.69, S 13.28.

3,5-Dibenzyl-2,6-dimethyl-9-(4-methylphenyl)-3*H*,5*H*,9*H*-di[1,2,4]-triazolo[1,5-a:1′,5′-*d*][1,3,5]triazin-8-ium Bromide (6a): Yield 0.65 g (24%), m.p. 238 °C. ^1H NMR ($CDCl_3$): δ = 2.34 (s, 3 H, CH_3), 2.35 (s, 6 H, 2 × CH_3), 5.26−5.41 (dd, 4 H, 2 × CH_2), 7.25−7.39 (m, 14 H, phenyl), 7.47 (s, 1 H, sp^3CH) ppm. ^{13}C NMR ($CDCl_3$): δ = 11.9, 21.4, 47.3 (CH_2), 77.1 (sp^3C), 128.0, 128.1, 128.9, 129.3, 129.6, 130.1, 133.4, 141.8, 150.4, 150.8 ppm. MS (DCI/H_2O): *m/z* (%) = 462 (54) $[C_{28}H_{28}N_7]^+$. $C_{28}H_{28}BrN_7$ (542.48): calcd. C 61.99, H 5.20, Br 14.73, N 18.07; found C 61.52, H 5.32, Br 14.62, N 17.80.

3,5-Bis(2-methoxybenzyl)-2,6-dimethyl-9-(4-methylphenyl)-3*H*,5*H*,9*H*-di[1,2,4]triazolo[1,5-*a*:1′,5′-*d*][1,3,5]triazin-8-ium Bromide (6b): Yield 0.39 g (13%), m.p. 109 °C. ^1H NMR ($CDCl_3$): δ = 2.39 (s, 9 H, 3 × CH_3), 3.84 (s, 6 H, 2 × OCH_3), 5.22−5.37 (dd, 4 H, 2 × CH_2), 6.19−7.46 (m, 12 H, phenyl), 7.48 (s, 1 H, sp^3CH) ppm. ^{13}C NMR ($CDCl_3$): δ = 12.0, 21.8, 43.2 (CH_2), 55.8 (OCH_3), 77.3 (sp^3C), 111.1, 121.6, 128.5, 2 × 130.5, 130.9, 131.4, 142.0, 150.9, 151.3, 157.5 ppm. MS (DCI/H_2O): *m/z* (%) = 522 (8) $[C_{30}H_{32}N_7O_2]^+$. $C_{30}H_{32}BrN_7O_2$ (602.53): calcd. C 59.80, H 5.35, Br 13.26, N 16.27, O 5.31; found C 59.75, H 5.63, Br 12.55, N 15.86.

3,5-Bis(2-chlorobenzyl)-2,6-dimethyl-9-(4-methylphenyl)-3*H*,5*H*,9*H*-di[1,2,4]triazolo[1,5-*a*:1′,5′-*d*][1,3,5]triazin-8-ium Bromide (6c): Yield 1.16 g (38%), m.p. 127 °C. ^1H NMR ($CDCl_3$): δ = 2.24 (s, 6 H, 2 × CH_3), 2.35 (s, 3 H, CH_3), 5.37 (dd, 4 H, 2 × CH_2), 7.26−7.55 (m, 12 H, phenyl), 7.63 (s, 1 H, sp^3CH) ppm. ^{13}C NMR ($CDCl_3$): δ = 11.9, 21.4, 44.9 (CH_2), 77.3 (sp^3C), 127.8, 128.1, 129.0, 129.9, 130.1, 130.3, 130.4, 130.8, 132.9, 141.7, 150.2, 151.0 ppm. MS (DCI/H_2O): *m/z* (%) = 430 (10) $[C_{28}H_{26}Cl_2N_7]^+$. $C_{28}H_{26}BrCl_2N_7$ (611.37): calcd. C 55.01, H 4.29, Br 13.07, Cl 11.60, N 16.04; found C 54.85, H 4.46, Br 12.37, Cl 11.07, N 15.75.

3,5-Bis(4-chlorobenzyl)-2,6-dimethyl-9-(4-methylphenyl)-3*H*,5*H*,9*H*-di[1,2,4]triazolo[1,5-*a*:1′,5′-*d*][1,3,5]triazin-8-ium Bromide (6d): Yield 1.19 g (39%), m.p. 234 °C (dec.). ^1H NMR ($CDCl_3$): δ = 2.33 (s, 6 H, 2 × CH_3), 2.35 (s, 3 H, CH_3), 5.28 (dd, 4 H, 2 × CH_2), 7.24−7.36 (m, 12 H, phenyl), 7.51 (s, 1 H, sp^3CH) ppm. ^{13}C NMR ($CDCl_3$): δ = 11.8, 21.4, 46.5 (CH_2), 77.1 (sp^3C), 128.1, 129.4, 129.5, 129.6, 130.1, 131.8, 134.8, 141.8, 150.3, 150.8 ppm. MS (DCI/H_2O): *m/z* (%) = 530 (5) $[C_{28}H_{26}Cl_2N_7]^+$. $C_{28}H_{26}BrCl_2N_7$ (611.37): calcd. C 55.01, H 4.29, Br 13.07, Cl 11.60, N 16.04; found C 54.60, H 4.51, Br 12.92, Cl 11.52, N 15.66.

2,6-Dimethyl-3,5-bis(4-methylbenzyl)-9-(4-methylphenyl)-3*H*,5*H*,9*H*-di[1,2,4]triazolo[1,5-*a*:1′,5′-*d*][1,3,5]triazin-8-ium Bromide (6e): Yield 0.88 g (30%), m.p. 225 °C. ^1H NMR ($CDCl_3$): δ =

2.32 (s, 6 H, 2 × CH_3), 2.35 (s, 9 H, 3 × CH_3), 5.21−5.36 (dd, 4 H, 2 × CH_2), 7.13−7.35 (m, 12 H, phenyl), 7.45 (s, 1 H, sp^3CH) ppm. ^{13}C NMR ($CDCl_3$): δ = 11.9, 21.1, 21.4, 47.2 (CH_2), 77.1 (sp^3C), 128.0, 128.1, 129.7, 129.8, 129.9, 130.7, 138.8, 141.8, 150.4, 150.9 ppm. MS (DCI/H_2O): *m/z* (%) = 490 (46) $[C_{30}H_{32}N_7]^+$. $C_{30}H_{32}BrN_7 \cdot 1H_2O$ (588.55): calcd. C 61.22, H 5.82, Br 13.58, N 16.66, O 2.72; found C 61.36, H 6.11, Br 13.94, N 16.50.

9*H*-3,5-Dibenzyl-2,6-dimethyl-9-(1-naphthyl)-3*H*,5*H*,9*H*-di[1,2,4]triazolo[1,5-*a*:1′,5′-*d*][1,3,5]triazin-8-ium Bromide (6f): Yield 0.82 g (28%), m.p. 154 °C. ^1H NMR ($CDCl_3$): δ = 2.24 (s, 6 H, 2 × CH_3), 5.23−5.43 (dd, 4 H, 2 × CH_2), 7.00−7.99 (m, 17 H, phenyl, naphthyl), 8.86 (br. s, 1 H, sp^3CH) ppm. ^{13}C NMR ($CDCl_3$): δ = 11.7, 47.1(CH_2), 68.8 (sp^3C), 125.2, 125.5, 125.7, 126.4, 127.2, 127.5, 127.7, 128.5, 128.7, 129.2, 130.3, 132.4, 133.5, 134.1, 150.3, 150.8 ppm. MS (DCI/H_2O): *m/z* (%) = 498 (82) $[C_{31}H_{28}N_7]^+$. $C_{31}H_{28}BrN_7$ (578.51): calcd. C 64.36, H 4.88, Br 13.81, N 16.95; found C 63.89, H 5.24, Br 13.78, N 16.72.

3,5-Dibenzyl-9-(1-butyl)-2,6-dimethyl-3*H*,5*H*,9*H*-di[1,2,4]triazolo[1,5-*a*:1′,5′-*d*][1,3,5]triazin-8-ium Bromide (6g): Yield 1.22 g (48%), m.p. 54 °C (very hygroscopic). ^1H NMR ([D_6]DMSO): δ = 0.80 (t, 3 H, CH_3), 1.09−1.21 (m, 4 H, CH_2CH_2), 2.27 (m, 2 H, CH_2), 2.41 (s, 6 H, 2 × CH_3), 5.14−5.29 (dd, 4 H, 2 × CH_2), 6.64 (t, 1 H, sp^3CH), 7.28−7.42 (m, 10 H, phenyl) ppm. ^{13}C NMR ([D_6]DMSO): δ = 11.9, 13.7, 21.9, 24.1, 31.9, 47.1 (CH_2), 75.2 (sp^3C), 127.9, 128.8, 129.2, 133.6, 150.4, 151.2 ppm. MS (DCI/H_2O): *m/z* (%) = 428 (79) $[C_{25}H_{30}N_7]^+$. Elemental analyses gave different values and could not be reproduced; compound **6g** has significant hygroscopic properties.

2,6-Dimethyl-9-(4-methylphenyl)-3,5-bis(pyridin-2-ylmethyl)-3*H*,5*H*,9*H*-di[1,2,4]triazolo[1,5-a:1′,5′-*d*][1,3,5]triazin-8-ium Bromide (6h): Yield 0.87 g (32%), m.p. 98 °C (hygroscopic). ^1H NMR ([D_6]DMSO): δ = 2.32 (s, 6 H, 2 × CH_3), 2.35 (s, 3 H, CH_3), 5.33−5.39 (dd, 4 H, 2 × CH_2), 7.29−7.53 (m, 8 H, phenyl, py), 7.61 (s, 1 H, sp^3CH), 7.83 (t, 2 H, py), 8.47 (d, 2 H, py) ppm. ^{13}C NMR ([D_6]DMSO): δ = 10.9, 20.8, 46.8 (CH_2), 75.5 (sp^3C), 122.5, 123.4, 128.2, 129.6, 130.9, 137.3, 140.8, 149.4, 150.0, 150.9, 152.9 ppm. MS (DCI/H_2O): *m/z* (%) = 464 (10) $[C_{26}H_{26}N_9]^+$. $C_{26}H_{26}BrN_9$ (544.45): calcd. C 57.36, H 4.81, Br 14.68, N 23.15; found C 56.66, H 5.29, Br 12.93, N 22.91.

2,6-Dimethyl-9-(4-methylphenyl)-3,5-bis(pyridin-4-ylmethyl)-3*H*,5*H*,9*H*-di[1,2,4]triazolo[1,5-*a*:1′,5′-*d*][1,3,5]triazin-8-ium Bromide (6i): Yield 0.76 g (28%), m.p. 60 °C (hygroscopic). ^1H NMR ([D_6]DMSO): δ = 2.30 (s, 6 H, 2 × CH_3), 2.32 (s, 3 H, CH_3), 5.25 (s, 4 H, 2 × CH_2), 7.27 (d, 2 H, phenyl), 7.33 (d, 4 H, py), 7.45 (s, 1 H, sp^3CH), 7.49 (d, 2 H, phenyl), 8.47 (d, 4 H, py) ppm. ^{13}C NMR ([D_6]DMSO): δ = 10.6, 20.8, 44.8 (CH_2), 76.0 (sp^3C), 122.4, 128.7, 129.5, 130.5, 140.9, 142.7, 150.0, 150.1, 150.3 ppm. MS (FAB/dmba): *m/z* (%) = 465 (100) $[C_{26}H_{26}N_9]^+$. $C_{26}H_{26}BrN_9$ (544.45): calcd. C 57.36, H 4.81, Br 14.68, N 23.15; found C 56.14, H 5.38, Br 11.81, N 22.34.

General Preparation of Imidothioate Intermediates 10: A stirred suspension of **1** (5 mmol) in triethylamine (30 mL) was cooled to 0 °C. The amine **2** (5 mmol) was gradually added to this mixture. This causes a visible change in the consistency of the suspension. After stirring at 0 °C for 2 h the reaction mixture was poured into ice water (30 g). The solid precipitate was filtered off and then dried in vacuo at room temperature.

***N*-[7-(Benzylammonio)-5-(4-methylphenyl)-2-methyl[1,3,4]thiadiazolo[3,2-*a*][1,3,5]triazin-6(7*H*)-yl]ethanimidothioate (10a):** This compound was prepared from **1a** and **2a**; yield 1.50 g (71%), m.p. 120 °C. IR (KBr): ṽ = 3217 cm^{-1} (NH), 1603 cm^{-1} (C=N, exocyclic). ^1H NMR ($CDCl_3$, 253 K): δ = 1.16 (br., 9 H, triethylamine-CH_3), 2.30 (s, 3 H, CH_3), 2.36 (s, 3 H, CH_3), 2.50 (s, 3 H, CH_3), 2.79 (m, 6 H, triethylamine-CH_2), 4.58 (s, 2 H, CH_2), 6.94 (t, br., 1 H, NH), 7.13−7.33 (m, 9 H, phenyl), 8.35 (s, 1 H, sp^3CH) ppm. ^{13}C NMR ($CDCl_3$, 253 K): δ = 17.6 (thiadiazole-CH_3), 22.0 (phenyl-CH_3), 33.4 (ethanimidothioate-CH_3), 45.5 (benzyl-CH_2), 71.8 (sp^3C), 127.1, 128.0, 128.4, 129.4, 130.4, 132.7, 137.1, 141.2, 151.6, 155.7, 167.6, 196.1 (ethanimidothioate-C) ppm. 1D-TOCSY: $^1H \leftrightarrow {}^1H$ coupling (NH, 6.97; CH_2 4.59−4.71). According to ^1H NMR, the intermediate **10a** contained about 7% triethylamine, which could not be removed in vacuo at room temperature. Compound **10a** (10 mg, 0.024 mmol) was heated to its melting point in a glass tube. After solidification of the melt the resulting product was characterised as compound **5a** (by m.p., IR, NMR).

***N*-[7-(2-Methoxybenzylammonio)-5-(4-methylphenyl)-2-methyl-[1,3,4]thiadiazolo[3,2-*a*][1,3,5]triazin-6(7*H*)-yl]ethanimidothioate (10b):** This compound was prepared from **1a** and **2b**; yield 1.61 g (71%), m.p. 97 °C. IR (KBr): ṽ = 3217 cm^{-1} (NH), 1603 cm^{-1} (C=N, exocyclic). ^1H NMR ($CDCl_3$, 253 K): δ = 1.19 (br., 9 H, triethylamine-CH_3), 2.28 (s, 3 H, CH_3), 2.35 (s, 3 H, CH_3), 2.48 (s, 3 H, CH_3), 2.95 (m. 6 H, triethylamine-CH_2), 3.80 (s, 3 H, CH_3), 4.56 (s, 2 H, CH_2), 7.15 (t, br., 1 H, NH), 6.83−7.28 (m, 8 H, phenyl), 8.35 (s, 1 H, sp^3CH) ppm. ^{13}C NMR ($CDCl_3$, 253 K): δ = 16.9 (thiadiazole-CH_3), 21.3 (phenyl-CH_3), 32.8 (ethanimidothioate-CH_3), 45.7 (benzyl-CH_2), 55.1 (OCH_3), 71.8 (sp^3C), 110.1, 120.3, 124.3, 126.5, 129.0, 129.3, 129.7, 132.2, 141.0, 150.8, 154.7, 166.8, 194.7 (ethanimidothioate-C) ppm. 1D-TOCSY: $^1H \leftrightarrow {}^1H$ coupling (NH, 7.15; CH_2 4.56−4.66). According to ^1H NMR the intermediate **10b** contained about 23% triethylamine, which could not be removed in vacuo at room temperature. Compound **10b** (5 mg, 0.011 mmol) was heated to its melting point in a glass tube. After the melt had solidified, the resulting product was characterised as **5b** (by m.p., IR, NMR).

***N*-{2-*tert*-Butyl-5-(2-hydroxyphenyl)-7-[(thien-2-yl)ethylamino]-[1,3,4]thiadiazolo[3,2-*a*][1,3,5]triazin-6(7*H*)-yl}-2,2-dimethylpropanimidothioate (10k)·N(Et)$_3$:** This compound was prepared from **1j** and **2k**; yield 1.61 g (51%), m.p. 78 °C. IR (ATR): ṽ = 3348 cm^{-1}, NH; 1596 cm^{-1}, C=N (exocyclic). ^1H NMR ($CDCl_3$, 223 K): δ = 0.93 (br., 9 H, triethylamine-CH_3), 1.07 (s, 9 H, imidothioate-*t*Bu), 1.22 (s, 9 H, thiadiazole-*t*Bu), 1.25 (m, 2 H, CH_2), 2.53 (m, 6 H, triethylamine-CH_2), 3.01 (m, 2 H, CH_2), 6.29 (t, br., 1 H, NH), 6.53−7.12 (m, 7 H, phenyl, thienyl), 8.27 (s, 1 H, sp^3CH) ppm. ^{13}C NMR ($CDCl_3$, 223 K): δ = 11.6, 29.0, 30.5, 31.2, 36.2, 41.5, 45.3, 47.0, 70.1 (sp^3C), 116.8, 119.3, 119.6, 125.3, 127.2, 127.7, 131.6, 133.1, 138.4, 149.9, 156.3, 167.7, 168.4, 204.3 (imidothioate-C) ppm. $C_{25}H_{32}N_6OS_3 \cdot C_6H_{15}N$ (629.94): calcd. C 59.11, H 7.52, N 15.56, S 15.27; found C 59.89, H 8.02, N 16.35, S 15.77.

***N*-[2-*tert*-Butyl-5-(2-hydroxyphenyl)-7-(1-butylamino)-[1,3,4]-thiadiazolo[3,2-*a*][1,3,5]triazin-6(7*H*)-yl]-2,2-dimethylpropanimidothioate (10l)·N(Et)$_3$:** This compound was prepared from **1j** and **2l**; yield 2.48 g (86%), m.p. 73 °C. IR (ATR): ṽ = 3348 cm^{-1} (NH), 1598 cm^{-1} (C=N, exocyclic). ^1H NMR ($CDCl_3$, 223 K): δ = 0.83 (t, 3 H, 1-BuCH_3), 0.94 (br., 9 H, triethylamine-CH_3), 1.12 (s, 9 H, imidothioate-*t*Bu), 1.21 (s, 9 H, thiadiazole-*t*Bu), 1.25 (m, 2 H, 1-BuCH_2), 1.45 (m, 2 H, 1-BuCH_2), 2.56 (m, 6 H, triethylamine-CH_2), 3.30 (m, 2 H, 1-BuCH_2), 6.16 (t, broad, 1 H, NH), 6.51 (d, 1 H, phenyl), 6.63 (t, 1 H, phenyl), 7.10 (t, 1 H, phenyl), 7.14 (d, 1 H, phenyl), 8.27 (s, 1 H, sp^3CH) ppm. ^{13}C NMR ($CDCl_3$, 223 K): δ = 11.8, 13.8, 19.8, 29.0, 30.5, 31.2, 36.2, 36.2, 41.5, 47.0, 70.2 (sp^3C), 117.7, 120.8, 123.5, 126.8, 130.7, 151.4, 156.1, 168.1, 168.5, 204.1 (imidothioate-C) ppm. $C_{23}H_{34}N_6OS_2 \cdot C_6H_{15}N$ (575.87):

calcd. C 60.49, H 8.58, N 17.03, S 11.13; found C 60.60, H 8.53, N 17.35, S 11.33.

***N*-[7-(1-Butylamino)-5-(4-methylphenyl)-2-methyl[1,3,4]-thiadiazolo[3,2-*a*][1,3,5]triazin-6(7*H*)-yl]ethanimidothioate (10m):** This compound was prepared from **1a** and **2l**; yield 1.67 g (86%), m.p. 103−105 °C. IR (ATR): $\tilde{\nu}$ = 3350 cm^{-1} (NH), 1597 cm^{-1}, (C=N, exocyclic). ^1H NMR ($CDCl_3$, 223 K): δ = 0.83 (t, 3 H, 1-BuCH_3), 1.21 (m, 2 H, 1-BuCH_2), 1.41 (m, 2 H, 1-BuCH_2), 2.25 (s, 3 H, imidothioate-CH_3), 2.35 (s, 3 H, phenyl-CH_3), 2.46 (s, 3 H, thiadiazole-CH_3), 3.28 (m, 2 H, 1-BuCH_2), 6.70 (br., 1 H, NH), 7.11 (dd, 4 H, phenyl), 8.28 (s, 1 H, sp^3CH) ppm. ^{13}C NMR ($CDCl_3$, 223 K): δ = 14.1, 17.4 (thiadiazole-CH_3), 20.0, 21.7 (phenyl-CH_3), 31.8, 33.1 (ethanimidothioate-CH_3), 41.4, 71.0 (sp^3C), 126.6, 130.1, 132.2, 140.9, 151.2, 155.4, 167.0, 194.8 (ethanimidothioate-C) ppm. $C_{18}H_{24}N_6S_2$ (388.54): calcd. C 55.64, H 6.23, N 21.63, S 16.50; found C 55.16, H 6.37, N 21.72, S 16.42.

***N*-(6-{[1-(Ethylsulfanyl)ethylidene]amino}-2-methyl-5-(4-methylphenyl)-5,6-dihydro-7*H*-[1,3,4]thiadiazolo[3,2-*a*][1,3,5]triazin-7-ylidene)(2-methoxyphenyl)methaniminium Iodide (14b):** A solution of **2b** (0.69 g, 5.1 mmol) in THF (5 mL) was added at −10 °C to a stirred mixture of **1a** (0.99 g, 2.5 mmol) and THF (40 mL). The yellow mixture was kept at this temperature for 0.5 h, and a solution of iodoethane (0.39 g, 2.5 mmol) in THF (5 mL) was then added. After the mixture had stirred for 1 h at −10 to −5 °C, the solvent was evaporated in the cold and the resulting residue was washed with cold water and extracted with cold chloroform. The chloroform extracts were dried over $MgSO_4$ in a freezer and the solvents were again evaporated in the cold. According to ^1H NMR analysis at −5 °C, the residue (1.27 g) is essentially made up of the three products **5b** (10%), **14b** (20%) and **7b** (55%). Compound **14b** is thermally unstable and rearranges to **7b** even in the cold with elimination of ethanethiol, which can be observed in the ^1H NMR spectrum. Nevertheless, it was possible to obtain crystals of **14b** suitable for X-ray analysis by crystallisation from chloroform/ethyl acetate solution at −30 °C. **14b:** ^1H NMR ($CDCl_3$): δ = 1.32 (t, 3 H, ethyl-CH_3), 2.30 (s, 3 H, phenyl-CH_3), 2.51 (s, 3 H, ethanimidothioate-CH_3), 2.62 (s, 3 H, thiadiazole-CH_3), 3.15 (q, 2 H, ethyl-CH_2), 3.80 (s, 3 H, OCH_3), 4.76 (dd, 2 H, benzyl-CH_2), 6.77 (s, 1 H, sp^3CH), 6.80−7.34 (m, 8 H, phenyl), 7.36 (s, 1 H, NH) ppm. ^{13}C NMR ($CDCl_3$): δ = 14.0, 17.8, 21.3, 24.1 (ethanimidothioate-CH_3), 26.6, 41.8 (benzyl-C), 55.5, 73.9 (sp^3C), 110.3−157.1 (10 × phenyl-C), 151.4, 157.6 (C2), 167.8, 184.8 (ethanimidothioate-C) ppm.

***N*-(2-*tert*-Butyl-5-(2-hydroxyphenyl)-6-{[2,2-dimethyl-1-(methylsulfanyl)propylidene]amino}-5,6-dihydro-7*H*-[1,3,4]thiadiazolo-[3,2-*a*][1,3,5]triazin-7-ylidene)-2-(pyridin-2-yl)ethaniminium Iodide (14i):** This compound was prepared analogously to 1**4b**, from **1j**, **2j** and iodomethane, without chloroform extraction. The reaction mixture was allowed to warm to room temp. The precipitated **14i** was filtered off, washed with small amounts of diethyl ether and dried in vacuo. Yield 1.45 g (87%), m.p. 150 °C. IR (ATR): $\tilde{\nu}$ = 1610 cm^{-1}, (C=N, exocyclic). ^1H NMR ([D_6]DMSO): δ = 0.98 (s, 9 H, *t*Bu), 1.28 (s, 9 H, *t*Bu), 2.43 (s, 3 H, SCH_3), 3.09 (t, 2 H, CH_2), 3.85 (m, 2 H, CH_2), 6.82 (t, 1 H, phenyl), 6.85 (d, 1 H, phenyl), 7.17−7.29 (m, 5 H, sp^3CH, phenyl, py), 7.72 (t, 1 H, py), 8.23 (br., 1 H, NH), 8.46 (d, 1 H, py), 10.51 (s, 1 H, OH) ppm. ^{13}C NMR ([D_6]DMSO): δ = 16.8, 28.2, 29.5, 37.1, 37.3, 41.6, 43.1, 71.7 (sp^3C), 116.4, 119.2, 119.9, 122.3, 124.0, 130.9, 132.7, 137.3, 149.4, 152.2, 156.4, 158.7, 167.5, 170.1, 184.8 (propanimidothioate-C) ppm. MS (FAB, dmba): *m*/*z* (%) = 539 (3) $[C_{27}H_{36}N_7OS_2]^+$. $C_{27}H_{36}IN_7OS_2$ (665.65): calcd. C 48.72, H 5.45, I 19.06, N 14.73, O 2.39, S 9.63; found C 48.98, H 5.60, I 19.13, N 14.77, S 9.15.

***N*-(2-*tert*-Butyl)-5-(2-hydroxyphenyl)-6-{[2,2-dimethyl-1-(methylsulfanyl)propylidene]amino}-5,6-dihydro-7*H*-[1,3,4]thiadiazolo-[3,2-*a*][1,3,5]triazin-7-ylidene)-2-(thien-2-yl)ethaniminium Iodide (14k):** This compound was prepared analogously to **14b**, from **1j**, **2k** and iodomethane. Yield 1.56 g (93%), m.p. 158 °C. IR (ATR): $\tilde{\nu}$ = 1606 cm^{-1} (C=N, exocyclic). ^1H NMR ([D_6]DMSO): δ = 1.00 (s, 9 H, *t*Bu), 1.28 (s, 9 H, *t*Bu), 2.38 (s, 3 H, SCH_3), 3.09 (t, 2 H, CH_2), 3.65 (m, 2 H, CH_2), 6.82 (t, 1 H, phenyl), 6.83 (d, 1 H, phenyl), 6.93 (d, 1 H, thienyl), 6.95 (t, 1 H, thienyl), 7.18 (d, 1 H, phenyl), 7.21 (s, 1 H, sp^3CH), 7.28 (t, 1 H, phenyl), 7.36 (d, 1 H, thienyl), 8.16 (br., 1 H, NH), 10.45 (s, 1 H, OH) ppm. ^{13}C NMR ([D_6]DMSO): δ = 16.7 (SCH_3), 28.2, 29.6, 29.8, 37.1, 43.1, 43.3, 71.7 (sp^3C), 116.3, 119.2, 119.6, 124.8, 126.1, 127.5, 130.9, 132.7, 140.5, 152.2, 156.4, 167.6, 170.2, 184.9 (propanimidothioate-C) ppm. MS (FAB, dmba): *m*/*z* (%) = 543 (100) $[C_{26}H_{35}N_6OS_3]^+$. $C_{26}H_{35}IN_6OS_3$ (670.68): calcd. C 46.56, H 5.26, I 18.92, N 12.53, O 2.39, S 14.34; found C 46.95, H 5.37, I 19.22, N 12.69, S 14.33.

5-Benzyl-2,6-dimethyl-9-(4-methylphenyl)-5,9-dihydro-[1,3,4]-thiadiazolo[2,3-*d*][1,2,4]triazolo[1,5-*a*][1,3,5]triazin-8-ium Iodide (7a): A solution of **2a** (0.55 g, 5.1 mmol) in THF (5 mL) was added at −10 °C to a stirred mixture of **1a** (0.99 g, 2.5 mmol) and THF (40 mL). The yellow mixture was kept at this temperature for 0.5 h and a solution of iodoethane (0.38 g, 2.5 mmol) in THF (5 mL) was then added. The mixture was allowed to warm up gradually to room temperature (a strong smell of an alkyl sulfide was perceptible). After 5 h at room temperature and 1 h at 50 °C the precipitate − mainly phenylmethaniminium bromide − was filtered off. The THF filtrate was concentrated under reduced pressure, and the amorphous residue was washed with water and extracted with chloroform. The chloroform solution was dried ($MgSO_4$), concentrated and treated with *tert*-butyl methyl ether. The white precipitate was filtered off and dried in vacuo. Yield: 0.90 g (70%); m.p. 248 °C. ^1H NMR ($CDCl_3$): δ = 2.31 (s, 3 H, triazole-CH_3), 2.34 (s, 3 H, phenyl-CH_3), 2.55 (s, 3 H, thiadiazole-CH_3), 5.24−5.40 (dd, 2 H, benzyl-CH_2), 7.25−7.38 (m, 9 H, phenyl), 7.75 (s, 1 H, sp^3CH) ppm. ^{13}C NMR ($CDCl_3$): δ = 12.1 (triazole-CH_3), 17.5 (thiadiazole-CH_3), 21.4 (phenyl-CH_3), 47.8 (benzyl-C), 79.2(sp^3C), 128.0, 128.1, 129.0, 129.3, 130.0, 130.1, 132.6, 142.0, 148.3 (heterocyclic-C), 151.3 (heterocyclic-C), 157.0 (heterocyclic-C), 169.2 (heterocyclic-C) ppm. MS (DCI/H_2O): *m*/*z* (%) = 389 (100) $[C_{21}H_{21}N_6S]^+$. $C_{21}H_{21}IN_6S$ (516.40): calcd. C 48.84, H 4.40, I 24.57, N 16.27, S 6.21; found C 48.95, H 4.43, I 24.73, N 16.13, S 6.36.

5-(2-Methoxybenzyl)-2,6-dimethyl-9-(4-methylphenyl)-5,9-dihydro-[1,3,4]thiadiazolo[2,3-*d*][1,2,4]triazolo[1,5-*a*][1,3,5]triazin-8-ium Iodide (7b): Compound **1a** (0.99 g, 2.5 mmol) and the amine **2b** (0.70 g, 5.1 mmol) were treated as described for **7a** to give **7b**, which was recrystallised from chloroform/ethyl acetate. Yield 1.15 g (84%), m.p. 232−233 °C. ^1H NMR ($CDCl_3$): δ = 2.34 (s, 3 H, triazole-CH_3), 2.35 (s, 3 H, phenyl-CH_3), 2.56 (s, 3 H, thiadiazole-CH_3), 3.82 (s, 3 H, OCH_3), 5.17−5.33 (dd, 2 H, benzyl-CH_2), 6.87−7.42 (m, 8 H, phenyl), 7.76 (s, 1 H, sp^3CH) ppm. ^{13}C NMR ($CDCl_3$): δ = 11.8 (triazole-CH_3), 17.6 (thiadiazole-CH_3), 21.4 (phenyl-CH_3), 43.7 (benzyl-C), 55.5 (OCH_3), 79.0 (sp^3C), 110.7, 120.4, 2 × 128.0, 130.1, 130.3, 130.7, 130.8, 141.9, 148.4 (heterocyclic-C), 151.4 (heterocyclic-C), 2 × 157.0 (heterocyclic-C, phenyl-C−O), 168.9 (heterocyclic-C) ppm. MS (DCI/H_2O): *m*/*z* (%) = 419 (100) $[C_{22}H_{23}N_6OS]^+$. Perchlorate of **7b**: preparation from **7b** (100 mg) in 4.5 mL MeOH and $Zn(ClO_4)_2$ (35 mg); m.p. 260 °C. $C_{22}H_{23}ClN_6O_5S$ (518.97): calcd. C 50.92, H 4.47, Cl 6.83, N 16.19, O 15.41, S 6.18; found C 50.53, H 4.57, Cl 6.90, N 16.28, S 6.27.

2,6-Di-*tert*-butyl-5-(2-ethylpyridine)-9-(2-hydroxyphenyl)-5,9-dihydro[1,3,4]thiadiazolo[2,3-*d*][1,2,4]triazolo[1,5-*a*][1,3,5]triazin-8-ium Iodide (7c): A suspension of **14c** (1.33 g, 2 mmol) in pyridine (30 mL) was heated at reflux for 5 h (smell of a thiol compound is perceptible). The reaction mixture was concentrated to dryness and the solid residue was recrystallised from ethyl acetate. Yield 1.21 g (98%), m.p. 161 °C. ^{1}H NMR ([D$_6$]DMSO): δ = 1.21 (s, 9 H, *t*Bu), 1.32 (s, 9 H, *t*Bu), 3.32 (t, 2 H, CH$_2$), 4.59 (t, 2 H, CH$_2$), 6.88 (d, 1 H, phenyl), 6.96 (t, 1 H, phenyl), 7.31−7.41 (m, 3 H, phenyl), 7.66 (d, 1 H, py), 7.75 (t, 1 H, py), 7.86 (s, 1 H, sp^{3}CH), 10.40 (s, 1 H, OH) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 28.1, 29.5, 33.3, 36.3, 37.2, 44.9, 76.5 (sp^{3}C), 116.7, 119.5, 119.9, 122.7, 124.1, 131.7, 133.3, 137.4, 149.1, 149.7, 156.7, 156.8, 158.7, 168.6, 170.3 ppm. MS (FAB/dmba): *m*/*z* (%) = 490 (100) [C$_{26}$H$_{32}$N$_7$OS]$^+$. C$_{26}$H$_{32}$IN$_7$OS (617.55) × 0.5 ethyl acetate: calcd. C 50.83, H 5.48, I 19.18, N 14.82, O 4.84, S 4.85; found C 50.96, H 5.36, I 19.95, N 14.53, S 4.98.

2,6-Di-*tert*-butyl-9-(2-hydroxyphenyl)-5-(2-thien-2-ylethyl)-5,9-dihydro[1,3,4]thiadiazolo[2,3-*d*][1,2,4]triazolo[1,5-*a*][1,3,5]triazin-8-ium Iodide (7k): This compound was prepared analogously to **7c**, from **14k**. The product **7k** was recrystallised from MeCN. Yield 1.22 g (98%), m.p. 195 °C. ^{1}H NMR ([D$_6$]DMSO): δ = 1.22 (s, 9 H, *t*Bu), 1.28 (s, 9 H, *t*Bu), 3.37 (t, 2 H, CH$_2$), 4.39 (t, 2 H, CH$_2$), 6.82−6.98(m, 3 H, phenyl, thienyl), 7.21−7.43 (m, 3 H, phenyl, thienyl), 7.65 (d, 1 H, thienyl), 7.84 (s, 1 H, sp^{3}CH), 10.40 (s, 1 H, OH) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 28.1, 29.5, 33.3, 36.3, 37.2, 46.6, 76.6 (sp^{3}C), 116.6, 119.5, 119.8, 125.6, 127.1, 127.8, 131.8, 133.3, 138.2, 148.9, 156.8, 158.7, 168.6, 170.3 ppm. MS (FAB dmba): *m*/*z* (%) = 495 (100) [C$_{25}$H$_{31}$N$_6$OS$_2$]$^+$. C$_{25}$H$_{31}$IN$_6$OS$_2$ (622.58): calcd. C 48.23, H 5.02, I 20.38, N 13.50, O 2.57, S 10.30; found C 49.01, H 5.36, I 19.35, N 13.01, S 11.98.

General Procedure for the Reactions between Tricyclic Compounds 6 and KOH/*t*BuOK:[21] KOH (ground, 52 mg, 0.9 mmol) and *t*BuOK (106 mg, 0.9 mmol) were added to a suspension of **6** (0.9 mmol) in THF (30 mL). The mixture was stirred at room temperature for 3 h and filtered, and the filtrate was concentrated to dryness in vacuo. The oily residue was washed with water and extracted three times with CHCl$_3$. After drying over MgSO$_4$ and concentration in vacuo, the solid crude product was purified by extraction with petroleum ether (b.p. 40−70 °C).

4-Benzyl-2-{[4-benzyl-5-imino-3-methyl-4,5-dihydro-1*H*-1,2,4-triazol-1-yl](4-methylphenyl)methyl}-5-methyl-2,4-dihydro-3*H*-1,2,4-triazol-3-one (16a): Yield 0.31 g (71%), m.p. 152 °C. IR (KBr): $\tilde{\nu}$ = 3329 cm^{-1}, NH; 1708 cm^{-1}, C=O; 1633 cm^{-1}, C=N (exocyclic). ^{1}H NMR (CDCl$_3$): δ = 2.07 (s, 3 H, CH$_3$), 2.14 (s, 3 H, CH$_3$), 2.38 (s, 3 H, CH$_3$), 4.80−4.94 (dd, 4 H, 2 × CH$_2$), 7.20−7.39 (m, 16 H, phenyl, sp^{3}CH, NH) ppm. ^{13}C NMR (CDCl$_3$): δ = 12.2, 12.7, 21.5, 45.2, 45.3, 66.8 (sp^{3}C), 127.2, 127.4, 128.0, 128.5, 128.9, 129.1, 129.4, 129.5, 131.5, 135.9, 136.5, 138.8, 144.9, 145.2, 154.4, 154.9 ppm. MS (DCI/H$_2$O): *m*/*z* (%) = 480 (93) [C$_{28}$H$_{30}$N$_7$O]$^+$. C$_{28}$H$_{29}$N$_7$O (479.58): calcd. C 70.01, H 6.09, N 20.44, O 3.34; found C 70.01, H 6.37, N 19.89.

4-(2-Chlorobenzyl)-2-{[4-(2-chlorobenzyl)-5-imino-3-methyl-4,5-dihydro-1*H*-1,2,4-triazol-1-yl](4-methylphenyl)methyl}-5-methyl-2,4-dihydro-3*H*-1,2,4-triazol-3-one (16c): Yield 0.49 g (96%), m.p. 88 °C. IR (KBr): $\tilde{\nu}$ = 3324 cm^{-1}, NH; 1712 cm^{-1}, C=O; 1644 cm^{-1} (C=N, exocyclic). ^{1}H NMR (CDCl$_3$): δ = 2.05 (s, 3 H, CH$_3$), 2.13 (s, 3 H, CH$_3$), 2.36 (s, 3 H, CH$_3$), 4.98−4.99 (dd, 4 H, 2 × CH$_2$), 7.13−7.41 (m, 14 H, phenyl, sp^{3}CH, NH) ppm. ^{13}C NMR (CDCl$_3$): δ = 11.7, 12.3, 21.2, 44.4, 44.5, 66.6 (sp^{3}C), 127.6, 128.3, 2 × 128.8, 2 × 129.0, 2 × 129.2, 2 × 129.3, 130.7, 133.7, 133.9, 134.2, 134.4, 138.7, 144.5, 144.8, 153.6, 154.3 ppm. MS (DCI/H$_2$O): *m*/*z* (%) = 548 (8) [C$_{28}$H$_{28}$Cl$_2$N$_7$O]$^+$. C$_{28}$H$_{29}$N$_7$O·H$_2$O (566.48): calcd. C 59.37, H 5.16, Cl 12.52, N 17.31, O 5.65; found C 59.47, H 4.81, Cl 11.72, N 17.31.

4-(4-Chlorobenzyl)-2-{[4-(4-chlorobenzyl)-5-imino-3-methyl-4,5-dihydro-1*H*-1,2,4-triazol-1-yl](4-methylphenyl)methyl}-5-methyl-2,4-dihydro-3*H*-1,2,4-triazol-3-one (16d): Yield: 0.41 g (80%), m.p. 78 °C. IR (KBr): $\tilde{\nu}$ = 3324 cm^{-1}, NH; 1705 cm^{-1}, C=O; 1643 cm^{-1} (C=N, exocyclic). ^{1}H NMR (CDCl$_3$): δ = 2.06 (s, 3 H, CH$_3$), 2.12 (s, 3 H, CH$_3$), 2.35 (s, 3 H, CH$_3$), 4.80−4.83 (dd, 4 H, 2 × CH$_2$), 7.15−7.34 (m, 14 H, phenyl, sp^{3}CH, NH) ppm. ^{13}C NMR (CDCl$_3$): δ = 12.2, 12.7, 21.6, 44.6, 44.7, 66.9 (sp^{3}C), 128.0, 128.6, 129.2, 129.4, 129.6, 129.7, 131.2, 134.1, 134.4, 134.6, 135.0, 139.0, 144.8, 145.0, 154.2, 154.7 ppm. MS (DCI/H$_2$O): *m*/*z* (%) = 548 (9) [C$_{28}$H$_{28}$Cl$_2$N$_7$O]$^+$. C$_{28}$H$_{29}$N$_7$O·H$_2$O (566.48): calcd. C 59.37, H 5.16, Cl 12.52, N 17.31, O 5.65; found C 59.49, H 4.91, Cl 12.41, N 17.26.

4-Benzyl-2-{[4-benzyl-5-imino-3-methyl-4,5-dihydro-1*H*-1,2,4-triazol-1-yl](1-naphthyl)methyl}-5-methyl-2,4-dihydro-3*H*-1,2,4-triazol-3-one (16f): Yield: 0.36 g (72%), m.p. 97−98 °C. IR (KBr): $\tilde{\nu}$ = 3339 cm^{-1} (NH), 1709 (C=O), 1643 cm^{-1} (C=N, exocyclic). ^{1}H NMR (CDCl$_3$): δ = 2.01 (s, 3 H, CH$_3$), 2.12 (s, 3 H, CH$_3$), 4.80−4.92 (dd, 4 H, 2 × CH$_2$), 7.18−7.98 (m, 19 H, naphthyl, phenyl, sp^{3}CH, NH) ppm. ^{13}C NMR (CDCl$_3$): δ = 12.1, 12.7, 45.2, 45.3, 64.9 (sp^{3}C), 123.2, 125.5, 126.2, 126.9, 127.4, 127.6, 128.1, 128.5, 128.7, 129.2, 129.4, 130.1, 130.4, 130.7, 130.8, 134.2, 135.9, 136.2, 2 × 145.4, 154.1, 154.6 ppm. MS (DCI/H$_2$O): *m*/*z* (%) = 516 (11) [C$_{31}$H$_{30}$N$_7$O]$^+$. C$_{31}$H$_{29}$N$_7$O·1H$_2$O (553.63): calcd. C 69.77, H 5.86, N 18.37, O 6.00; found C 69.58, H 5.50, N 18.02.

2-{[5-Imino-3-methyl-4-(2-pyridinylmethyl)-4,5-dihydro-1*H*-1,2,4-triazol-1-yl](4-methylphenyl)methyl]-5-methyl}-4-(2-pyridinylmethyl)-2,4-dihydro-3*H*-1,2,4triazol-3-one (16h): Yield: 0.41 g (95%), m.p. 170−172 °C (recrystallised from ethyl acetate). IR (ATR) 3318 (NH), 1704 C=O, 1639 cm^{-1} (C=N, exocyclic). ^{1}H NMR ([D$_6$]DMSO): δ = 2.09 (s, 3 H, CH$_3$), 2.18 (s, 3 H, CH$_3$), 2.29 (s, 3 H, CH$_3$), 4.85−4.95 (dd, 4 H, 2 × CH$_2$), 7.11−7.29 (m, 10 H, phenyl, sp^{3}CH, NH), 7.56−7.60 (m, 2 H, py), 8.48 (d, 2 H, py) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 11.7, 12.2, 21.0, 46.6, 46.7, 66.2 (sp^{3}C), 121.5, 122.0, 122.6, 122.9, 127.6, 129.1, 131.0, 136.8, 137.1, 138.3, 144.9, 145.0, 149.3, 149.4, 153.7, 154.2, 155.0, 155.7 ppm. MS (DCI/H$_2$O): *m*/*z* (%) = 482 (60) [C$_{26}$H$_{28}$N$_9$O]$^+$. C$_{26}$H$_{27}$N$_9$O (481.55): calcd. C 64.85, H 5.65, N 26.18, O 3.32; found C 65.03, H 5.84, N 25.21.

Crystal Structure Determinations

The intensity data for the compounds were collected on a Nonius KappaCCD diffractometer, with graphite-monochromated Mo-K_α radiation. Data were corrected for Lorentz and polarisation effects, and for absorption effects for **6a** and **14b**.[22,23]

The structures were solved by direct methods (SHELXS [24]) and refined against F_0^2 by full-matrix, least-squares techniques (SHELXL-97[25]). For the iminium groups N5 of **14b** and for **16h** the hydrogen atoms were located by difference Fourier synthesis and refined isotropically. All other hydrogen atoms were included at calculated positions with fixed thermal parameters. All non-hydrogen atoms were refined anisotropically.[25] XP (SIEMENS Analytical X-ray Instruments, Inc.) was used for structure representations.

Crystal Data for 6a:[26] [C$_{28}$H$_{28}$N$_7$]$^+$ Br$^-$, *Mr* = 542.48 g·mol^{-1}, colourless prism, size 0.32 × 0.10 × 0.10 mm^3, monoclinic, space

group $P2_1/c$, a = 12.1459(5), b = 10.1806(4), c = 42.119(2) Å, β = 94.115(2)°, V = 5194.7(4) Å^3, T = −90 °C, Z = 8, $\rho_{calcd.}$ = 1.387 g·cm^{-3}, μ (Mo-K_α) = 16.13 cm^{-1}, semiempirical, transmin: 0.626, transmax: 0.855, F(000) = 2240, 16313 reflections in h(−15/4), k(−11/12), l(−53/54), measured in the range 1.88° ≤ Θ ≤ 27.49°, completeness Θ_{max} = 91.1%, 10873 independent reflections, R_{int} = 0.068, 4115 reflections with $F_0 > 4\sigma(F_o)$, 656 parameters, 0 restraints, $R1_{obsd.}$ = 0.078, $wR2_{obsd.}$ = 0.116, $R1_{all}$ = 0.240, $wR2_{all}$ = 0.159, GOOF = 0.949, largest difference peak and hole: 0.341/−0.360 e·Å^{-3}.

Crystal Data for 14b:[26] $[C_{24}H_{29}IN_6OS_2]^+$ I^-, Mr = 608.55 g·mol^{-1}, colourless prism, size 0.18 × 0.12 × 0.08 mm^3, monoclinic, space group $P2_1/c$, a = 9.4623(4), b = 13.2200(6), c = 22.4479(9) Å, β = 98.588(3)°, V = 2776.6(2) Å^3, T = −90 °C, Z = 4, $\rho_{calcd.}$ = 1.456 g·cm^{-3}, μ(Mo-K_α) = 13.31 cm^{-1}, semiempirical, transmin: 0.795, transm.$_{max}$ = 0.901, F(000) = 1232, 17094 reflections in h(−11/12), k(−15/17), l(−29/27), measured in the range 3.05° ≤ Θ ≤ 27.40°, completeness Θ_{max} = 99.3%, 6267 independent reflections, R_{int} = 0.091, 3959 reflections with $F_o > 4\sigma(F_o)$, 311 parameters, 0 restraints, $R1_{obsd.}$ = 0.113, $wR2_{obsd.}$ = 0.151, $R1_{all}$ = 0.194, $wR2_{all}$ = 0.172, GOOF = 1.163, largest difference peak and hole: 1.480/−0.714 e·Å^{-3}.

Crystal Data for 7b:[26] $[C_{22}H_{23}N_6OS]^+$ ClO_4^-, Mr = 518.97 g·mol^{-1}, colourless prism, size 0.20 × 0.18 × 0.12 mm^3, triclinic, space group $P\bar{1}$, a = 7.8676(3), b = 7.8957(5), c = 20.892(1) Å, α = 90.929(2), β = 100.661(3), γ = 108.207(3)°, V = 1207.7(1) Å^3, T = −90 °C, Z = 2, $\rho_{calcd.}$ = 1.427 g·cm^{-3}, μ(Mo-K_α) = 2.91 cm^{-1}, F(000) = 540, 7806 reflections in h(−10/8), k(−8/10), l(−27/26), measured in the range 3.21° ≤ Θ ≤ 27.50°, completeness Θ_{max} = 95.7%, 5303 independent reflections, R_{int} = 0.027, 3860 reflections with $F_o > 4\sigma(F_o)$, 316 parameters, 0 restraints, $R1_{obsd.}$ = 0.086, $wR2_{obsd.}$ = 0.207, $R1_{all}$ = 0.119, $wR2_{all}$ = 0.227, GOOF = 1.034, largest difference peak and hole: 1.156/−0.565 e·Å^{-3}.

Crystal Data for 16h:[26] $C_{26}H_{27}N_9O$, Mr = 481.57 g·mol^{-1}, colourless prism, size 0.20 × 0.18 × 0.12 mm^3, triclinic, space group $P\bar{1}$, a = 10.3487(6), b = 10.6149(8), c = 12.9281(9) Å, α = 74.003(4), β = 77.040(4), γ = 64.075(4)°, V = 1218.9(1) Å^3, T = −90 °C, Z = 2, $\rho_{calcd.}$ = 1.312 g·cm^{-3}, μ(Mo-K_α) = .86 cm^{-1}, F(000) = 508, 8063 reflections in h(−12/13), k(−13/13), l(−15/16), measured in the range 3.74° ≤ Θ ≤ 27.48°, completeness Θ_{max} = 96.9%, 5425 independent reflections, R_{int} = 0.031, 4193 reflections with $F_o > 4\sigma(F_o)$, 433 parameters, 0 restraints, $R1_{obsd.}$ = 0.093, $wR2_{obsd.}$ = 0.141, $R1_{all}$ = 0.130, $wR2_{all}$ = 0.153, GOOF = 1.177, largest difference peak and hole: 0.192/−0.296 e·Å^{-3}.

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