A Facile Synthesis of Annulated Thiatriazine Dioxides

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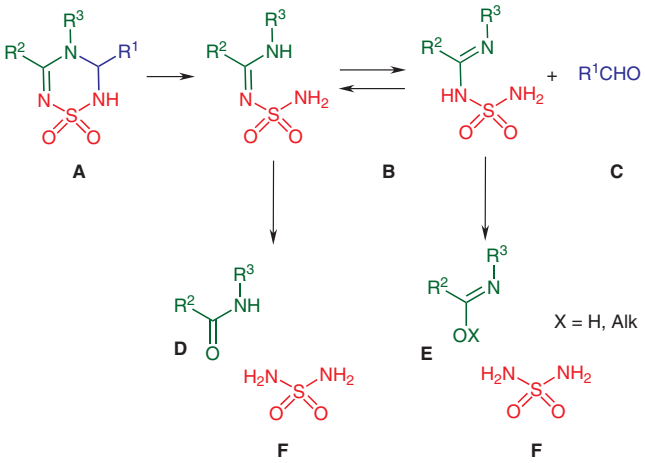
Abstract: The reactions of five-, six-, seven-, and eight-membered cyclic imido ethers with one equivalent of sulfamide lead to the corresponding sulfamoylamidines in 70–80% yields. Sulfamoylamidines undergo condensations with aliphatic and aromatic aldehydes as well as aliphatic ketones to give thiatriazine dioxides in 50–95% yields. The NMR spectroscopic studies reveal ring-chain tautomerism of some thiatriazine dioxides in solution. The ratio between the tautomers depends on the temperature, solvent polarity, and electronic properties of the substituents of the pendant aryl rings. Thiatriazine dioxides are readily alkylated and acylated at position 2.

Key words: imido ethers, sulfamide, sulfamoylamidines, thiatriazine dioxides, tautomerism

Some functionalized thiatriazine dioxides of type **A** (Scheme 1) are efficient anticholesteremic agents,[1] gastric secretion inhibitors,[2] herbicides,[3] and H2-antagonists.[4] These compounds are synthesized through the condensation of sulfonamides with formaldehyde and primary amines,[5] the reaction of 5-aminotetrazole with chlorosulfonyl isocyanate in the presence of a tertiary amine,[6] condensation of sulfonylamide with phthalaldehyde,[7] the rearrangement of thiatriazole dioxides,[8] and oxidation of thiatriazine oxides.[9] Thiatriazine dioxides are also synthesized starting from carboimidates.[10] These methods have technological drawbacks that hamper combinatorial synthesis of drug-like thiatriazine dioxides for systematic QASAR studies. Among these drawbacks are low multistep reaction procedures, long reaction times, low yields of target compounds, and the necessity to use highly reactive reagents such as chlorosulfonylamides, chlorosulfonyl isocyanate, and sodium amide.

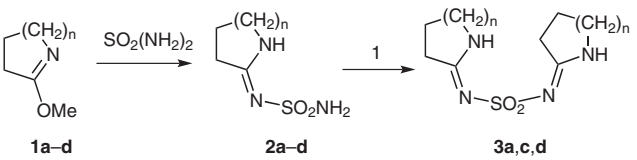
Retrosynthetic analysis revealed that molecules **A** (Scheme 1) contain three fragments that could be connected via two condensation reactions. Theoretically intermediate **B** could be synthesized through the reaction of amides **D** or imido ethers **E** with sulfamide **F**.

Herein we report a facile and versatile synthetic methodology for the annulation of the triazine dioxide ring to five-, six-, seven-, and eight-membered nitrogen-containing heterocycles.



Scheme 1 Retrosynthetic analysis of thiatriazine dioxides

Readily available cyclic imido ethers **1**[11] reacted with one equivalent of sulfamide in isopropyl alcohol (reflux, 3 h) to give sulfamoylamidines **2** in 70–95% yield after simple recrystallization from water (Scheme 2). Under similar conditions the corresponding cyclic lactams did not react with sulfamide, apparently due to their lower reactivity. The reaction of compounds **2** and **1** (*i*-PrOH, reflux, 10 h) afforded bisamidines **3** in 80–93% yield. Compounds **2** were also synthesized through the reaction of sulfamide with two equivalents of the corresponding imino ether **1**.



Scheme 2 Reaction of cyclic imido ethers with sulfamide

All attempts to synthesize compounds **2** from the corresponding cyclic amides and sulfamide failed (**D** + **F** in Scheme 1) most probably due to the lower reactivity of the amides compared to the imido ethers.

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Table 1 Yields of Thiatriazines **4–7**

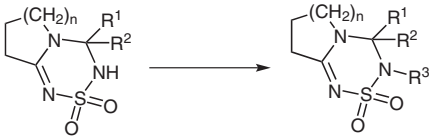
2 **4–7**

Product	n	R^1	R^2	Yield (%)
4a	1	H	H	74
4b	1	Me	H	61
4c	1	Ph	H	79
4d	1	3-MeC_6H_4	H	70
4e	1	4-ClC_6H_4	H	81
4f	1	4-$OHCC_6H_4$	H	79
4g	1	4-$O_2NC_6H_4$	H	94
4h	1	4-$Me_2NC_6H_4$	H	59
4i	1	4-$MeOC_6H_4$	H	56
4j	1	4-$HO_2CC_6H_4$	H	86
4k	1	4-HOC_6H_4	H	64
4l	1	Me	Me	84
4m	1	Et	Et	67
4n	1	4-FC_6H_4	H	74
5a	2	Ph	H	77
5b	2	4-ClC_6H_4	H	79
5c	2	4-$O_2NC_6H_4$	H	91
5d	2	4-$Me_2NC_6H_4$	H	51
5e	2	4-$MeOC_6H_4$	H	59
6a	3	H	H	61
6b	3	CH_2Cl	H	58
6c	3	2-pyridyl	H	71
6d	3	Ph	H	77
6e	3	4-ClC_6H_4	H	75
6f	3	4-$O_2NC_6H_4$	H	90
6g	3	4-$Me_2NC_6H_4$	H	49
6h	3	4-$MeOC_6H_4$	H	67
6i	3	2-MeC_6H_4	H	70
6j	3	4-FC_6H_4	H	71
7a	4	Ph	H	77
7b	4	4-ClC_6H_4	H	80
7c	4	4-$O_2NC_6H_4$	H	89
7d	4	4-$Me_2NC_6H_4$	H	61
7e	4	4-$MeOC_6H_4$	H	68

Compounds **2** readily reacted with aromatic and aliphatic aldehydes and ketones (*i*-PrOH, reflux, 6 h) to give thiatriazine dioxides **4–7** in 50–95% yield (Table 1). The reaction of acetals of aliphatic aldehydes also resulted in the corresponding thiatriazine sulfoxides in preparative yields. Compounds **4–7** crystallized from the reaction mixture and they were additionally purified by recrystallization from alcohols or acetonitrile.

Compounds **4** and **6** readily reacted with methyl iodide, bromoacetophenone, benzoyl chloride, and acetic anhydride (see the experimental section) to give derivatives **8** (Table 2) in 77–81% yield. Compounds **8** were purified by simple crystallization.

Table 2 Yields of Thiatriazine **8**[a]



4, 6 **8**

Product	n	R^1	R^2	R^3	Yield (%)
8a	1	4-MeC_6H_4	H	Me	78
8b	3	4-FC_6H_4	H	CH_2Bz	81
8c	1	Ph	H	Bz	71
8d	1	Ph	H	Ac	77

[a] For reagents and conditions, see the experimental section.

The composition and structure of compounds **2–8** were proved by LC-MS, elemental analysis, ^1H, ^{13}C, NOESY NMR spectroscopy, and single crystal X-ray crystallography.

Molecular structures of compounds **2a–d** are shown in Figure 1. The N2–C1 bond in **2a–d** is N1–C1 bond is shortened compared to the mean values for the Csp^2=N2 (1.313 Å)[12] and the Csp^2–N3 (1.339 Å) bonds respective-

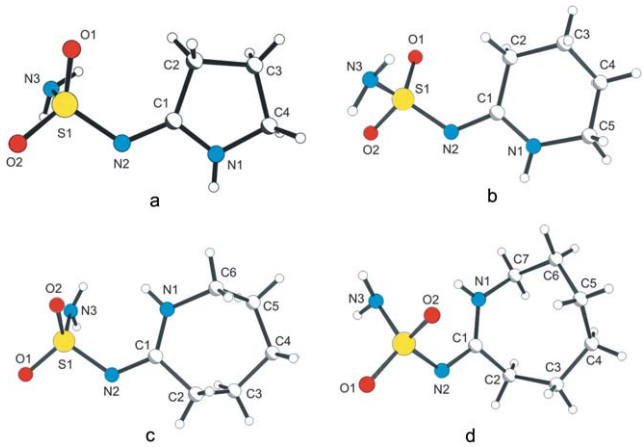
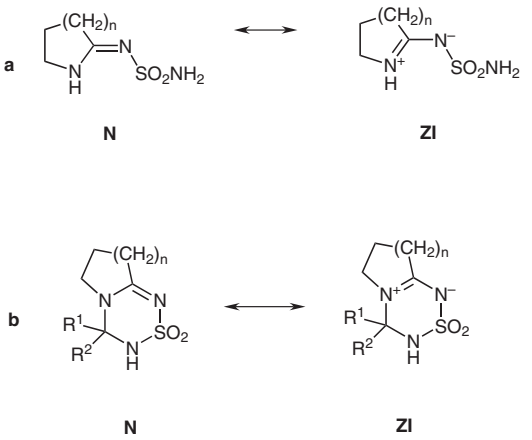


Figure 1 Molecular structures and numbering schemes of compounds (a) **2a**, (b) **2b**, (c) **2c**, and (d) **2d**

ly. Such a redistribution of the electron density allows considering the structure of **2a–d** as a superposition of neutral and zwitterionic resonance structures **N** and **ZI** (Scheme 3, top).



Scheme 3 Resonance structures of (a) **2a–d** and (b) **4l**, **5a**, **5b**, and **6i**

Molecular structures of compounds **4l**, **5a**, **5b**, and **6i** are shown in Figure 2. Analysis of the bond lengths within the fragment N1–C1–N2 revealed that these molecules can also be described as the superpositions of neutral and zwitterionic forms (Scheme 3, bottom).

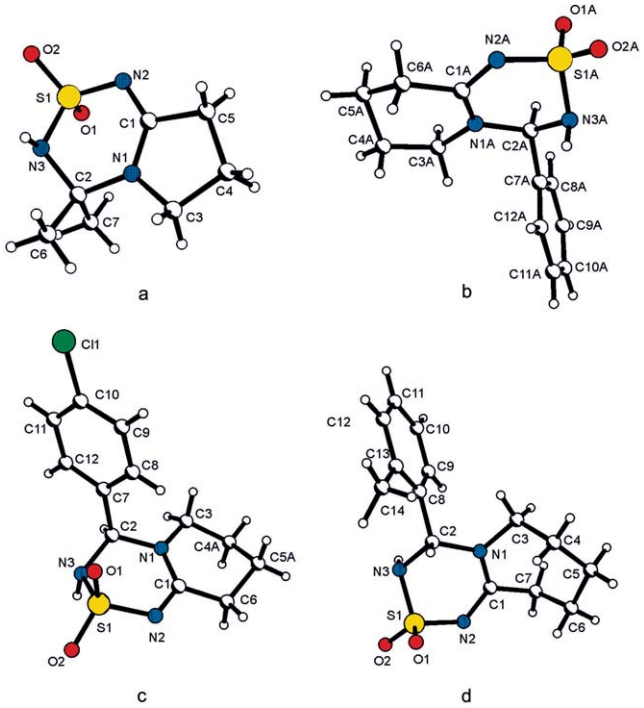


Figure 2 Molecular structures and numbering schemes of compound (a) **4l**, (b) **5a**, (c) **5b**, and (d) **6i**

The ^{1}H NMR spectra of compounds **4–7** bearing π-electron-donor functional groups in the *para*-position of the aryl ring measured in dimethyl sulfoxide-d_6 and deuterochloroform contain two sets of signals (Figure 3) whose ratio depends on the temperature, electronic effects of the substituents, and the size of the azaheterocycle. This can be explained by equilibrium between isomers **X** and **Y** which interconvert slowly on the NMR timescale. The NOESY experiments revealed that the NH and methine CH protons of form **Y** emerge as a broadened triplet and a sharp singlet, respectively. Form **Y** was further characterized by H7–H10, H7–H10′ NOESY correlations and the absence of NOE between H7 and H6 (Figure 3). In form **X** the methine proton H2 gives NOE to the NH proton H1 and two diastereotopic methylene protons H5 and H5′. No exchange cross peaks were observed between the signals of **X** and **Y** indicating that the equilibrium is slow on the human timescale. Variable temperature ^{1}H NMR measurements revealed considerable increase of [**Y**]/[**X**] in dimethyl sulfoxide-d_6 by three to four times upon raising the temperature from 303 K to 360 K. This indicates the higher entropy of open form **X** compared to cyclic form **Y**. Although nonlinearity of the ΔG vs. T plots prevented reliable estimation of ΔH and ΔS of the equilibrium it is possible to make conclusion that the transformation of **X** to **Y** is an endothermic, entropy-driven process.

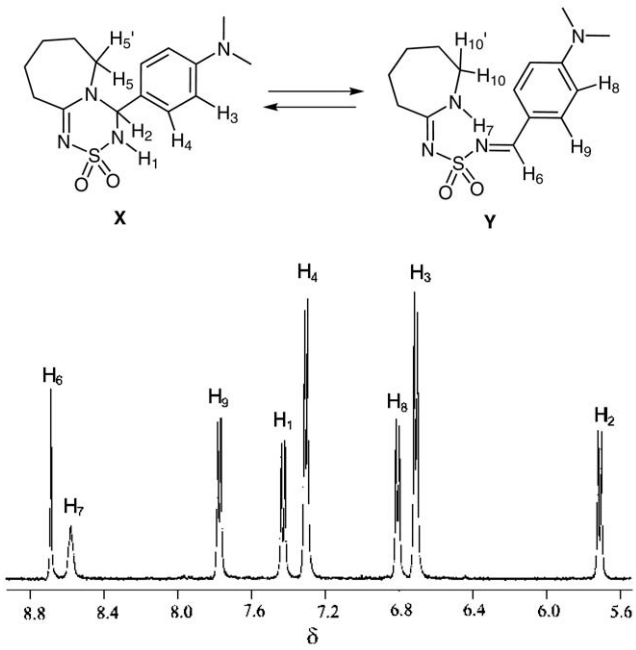


Figure 3 ^{1}H NMR spectra (298 K, 500 MHz) compound **6g** in DMSO-d_6. NOE: H1–H2, H2–H4, H2–H5, H2–H5′, H6–H9, H7–H10, H3–H4, H8–H9.

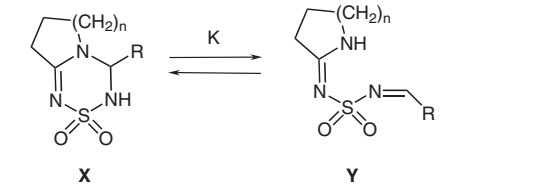
The data listed in Table 3 indicate that form **Y** is stabilized by π-electron-donor functional groups in the phenyl ring. In a simplistic way, this can be explained by stabilization of form **Y** through the resonance of neutral **N** and zwitterionic **ZI** structures. Apparently such π-electron-donor groups as OMe, and NMe_2 should stabilize the zwitterionic form favoring structure **Y**.

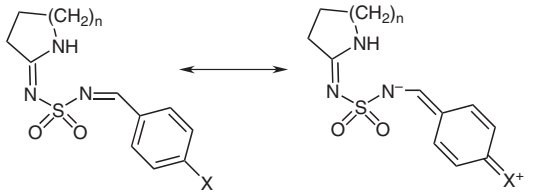
Form **Y** is more stable in the case of the larger azaheterocycles [$\Delta\Delta G$ (**5a–7a**) = 1.0 kcal/mol, $\Delta\Delta G$ (**4i–6h**) = 2.3

kcal/mol, $\Delta\Delta G$ (**4h–7e**) = $\Delta\Delta G$ (**5b–7b**) = 1.15 kcal/mol]. This can be explained by the larger entropy loss for larger azaheterocycles in the cyclization.

It should be noted that in dimethyl sulfoxide-d_6 the equilibrium constants are considerably lower than in deuterochloroform (see Table 3). Most probably this can be explained by stabilization of form **X** through hydrogen bonding between the sulfonamide fragment and molecules of dimethyl sulfoxide-d_6.

Table 3 Equilibrium Constants and ΔG Values for Equilibrium between **X** and **Y**





Compd	$CDCl_3$		DMSO-d_6	
	K	ΔG (kcal/mol)	K	ΔG (kcal/mol)
4c	<0.01	>2.7	<0.01	>2.7
4e	<0.01	>2.7	<0.01	>2.7
4h	0.75	0.17	0.09	1.42
4i	0.10	1.36	<0.01	>2.7
5a	0.15	1.12	<0.01	>2.7
5b	0.25	0.82	<0.01	>2.7
5d	15.70	–1.63	0.41	0.53
5e	0.90	0.06	0.03	2.07
6d	0.70	0.21	<0.01	>2.7
6e	0.85	0.10	<0.01	>2.7
6g	>100	<–2.7	3.76	–0.78
6h	4.60	–0.90	0.03	2.07
7a	0.90	0.06	<0.01	>2.7
7b	1.70	–0.31	<0.01	>2.7
7c	0.40	0.54	<0.01	>2.7
7d	>100	<–2.7	0.75	0.17
7e	5.25	–1.00	0.05	1.77

In conclusion the reaction of readily available sulfonamides **2** with various aromatic aliphatic aldehydes furnishes annulated drug-like thiatriazine dioxides **4–7** bearing various functional groups and, thus, can be used for systematic quantitative structure–activity relationships. There is no doubt that wide scope, high yield, and simple synthesis and purification protocol makes this synthetic approach applicable in combinatorial synthesis of functionalized thiatriazine dioxides. Compounds **4–7** bearing π-electron-donor functional groups in the pendant aromatic rings exist in dimethyl sulfoxide-d_6 and deuterochloroform as mixtures of cyclic and open tautomers that interconvert slowly on the NMR timescale. The position of this equilibrium depends on the *M*-effect of the functional group in the aromatic ring, temperature, polarity of solvent, and the size of the azaheterocycle. It is likely that this equilibrium may be used as a motif for rational design of covalent self-assembling systems.[13]

All commercially available starting materials were used without additional purification. All solvents were purified by standard methods. All procedures were carried out under an open atmosphere with no precautions taken to exclude ambient moisture. Melting points are uncorrected. ^{1}H NMR spectra were recorded on 400 MHz and 500 MHz spectrometers with TMS as internal standard. ^{13}C NMR (125 MHz) spectra and NMR experiments were recorded on a 500 MHz spectrometer with TMS as internal standard. LC/MS spectra were recorded using chromatography/mass spectrometric system that consists of HPLC unit equipped with diode-matrix and mass-selective detector. Ionization method is chemical ionization under atmospheric pressure (APCI). Ionization mode is simultaneous scanning of positive and negative ions in the mass range of 80–1000 *m/z*. According to HPLC-MS and ^{1}H NMR spectra data all the synthesized compounds have purity >95%.

Compounds 2a–d; General Procedure

A soln of freshly distilled imido ether **1** (0.3 mol) in *i*-PrOH (50 mL) was added dropwise to a stirred and refluxed soln of sulfamide (0.36 mol) in *i*-PrOH (300 mL). The mixture was stirred at reflux for 3 h. Upon cooling to r.t. a precipitate formed that was filtered off and washed with *i*-PrOH (2 × 20 mL). The crude product was recrystallized (H_2O) and dried.

***N*-(Pyrrolidin-2-ylidene)sulfamide (2a)**

White solid; yield: 78%; mp 200–201 °C.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 8.25 (s, 1 H, NH), 6.28 (s, 2 H, NH_2), 3.38–3.35 (m, 2 H, CH_2), 2.63 (s, 2 H, CH_2), 1.98–1.92 (m, 2 H, CH_2).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 170.9, 45.5, 31.6, 20.9.

MS (APCI): *m/z* = 164.0 $[M + H]^+$.

Anal. Calcd for $C_4H_9N_3O_2S$: C, 29.44; H, 5.56; N, 25.75; S, 19.65. Found: C, 29.27; H, 5.49; N, 25.82; S, 19.58.

***N*-(Piperidin-2-ylidene)sulfamide (2b)**

White solid; yield: 72%; mp 187–188 °C.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 8.10 (s, 1 H, NH), 6.30 (s, 2 H, NH_2), 3.33 (s, 2 H, CH_2), 2.44 (s, 2 H, CH_2), 1.65 (s, 4 H, CH_2).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 164.4, 42.0, 29.5, 21.6, 19.6.

MS (APCI): *m/z* = 178.0 $[M + H]^+$.

Anal. Calcd for $C_5H_{11}N_3O_2S$: C, 33.89; H, 6.26; N, 23.71; S, 18.09. Found: C, 33.78; H, 6.23; N, 23.74; S, 18.02.

***N*-(Azepan-2-ylidene)sulfamide (2c)**
White solid; yield: 74%; mp 147–148 °C.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 7.95 (s, 1 H, NH), 6.47 (s, 2 H, NH_2), 3.40–3.16 (m, 2 H, CH_2), 2.55–2.31 (m, 2 H, CH_2), 1.74–1.35 (m, 6 H, CH_2).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 170.3, 43.4, 35.3, 29.7, 29.1, 24.1.

MS (APCI): m/z = 192.0 $[M + H]^+$.

Anal. Calcd for $C_6H_{13}N_3O_2S$: C, 37.68; H, 6.85; N, 21.97; S, 16.77. Found: C, 37.73; H, 6.81; N, 21.95; S, 16.65.

***N*-(Azocan-2-ylidene]sulfamide (2d)**
White solid; yield: 81%; mp 158–159 °C.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 7.74 (s, 1 H, NH), 6.40 (s, 2 H, NH_2), 3.38 (s, 2 H, CH_2), 2.40 (s, 2 H, CH_2), 1.75–1.36 (m, 8 H, CH_2).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 168.3, 42.3, 32.0, 31.2, 29.2, 25.4, 24.0.

MS (APCI): m/z = 206.0 $[M + H]^+$.

Anal. Calcd for $C_7H_{15}N_3O_2S$: C, 40.96; H, 7.37; N, 20.47; S, 15.62. Found: C, 40.78; H, 7.33; N, 20.51; S, 15.54.

Compounds 3a,c,d; General Procedure
A soln of sulfamide (10 mmol) and imido ether **1** (40 mmol) in *i*-PrOH (30 mL) was stirred at reflux for 10 h. The mixture was cooled to r.t. and the precipitate was filtered off, washed with *i*-PrOH (2 × 2 mL) and H_2O and dried in vacuo to give **3** as a white solid. Analytical samples of compounds **3** were additionally purified by recrystallization (H_2O).

***N*,*N*′-Bis(pyrrolidin-2-ylidene)sulfamide (3a)**
White solid; yield: 93%, mp 248–249 °C.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 8.23 (s, 2 H, NH), 3.38–3.26 (m, 4 H, CH_2), 2.65–2.56 (m, 4 H, CH_2), 1.98–1.93 (m, 4 H, CH_2).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 170.9, 45.5, 31.6, 20.9.

MS (APCI): m/z = 231.0 $[M + H]^+$.

Anal. Calcd for $C_8H_{14}N_4O_2S$: C, 41.72; H, 6.13; N, 24.33; S, 13.92. Found: C, 41.63; H, 6.18; N, 24.20; S, 13.87.

***N*,*N*′-Bis(azepan-2-ylidene)sulfamide (3c)**
White solid; yield: 86%; mp 132–133 °C.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 8.14 (s, 2 H, NH), 3.37–3.31 (m, 4 H, CH_2), 2.55–2.47 (m, 4 H, CH_2), 1.73–1.40 (m, 12 H, CH_2).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 170.7, 43.6, 35.0, 29.8, 29.2, 24.2.

MS (APCI): m/z = 287.0 $[M + H]^+$.

Anal. Calcd for $C_{12}H_{22}N_4O_2S$: C, 50.33; H, 7.74; N, 19.56; S, 11.20. Found: C, 50.27; H, 7.63; N, 19.48; S, 11.24.

***N*,*N*′-Bis(azocan-2-ylidene)sulfamide (3d)**
White solid; yield: 80%; mp 179–180 °C.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 7.91 (s, 2 H, NH), 3.47–3.37 (m, 4 H, CH_2), 2.48–2.37 (m, 4 H, CH_2), 1.76–1.64 (m, 4 H, CH_2), 1.59–1.37 (m, 12 H, CH_2).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 169.4, 42.2, 31.9, 31.2, 29.4, 25.5, 24.4.

MS (APCI): m/z = 315.2 $[M + H]^+$.

Anal. Calcd for $C_{14}H_{26}N_4O_2S$: C, 53.47; H, 8.33; N, 17.82; S, 10.20. Found: C, 53.36; H, 8.27; N, 17.85; S, 10.17.

Compounds 4a and 6a; General Procedure
Paraformaldehyde (5.7 mmol) was added to a soln of sulfamoylamidine **2** (5.2 mmol) in *i*-PrOH (25 mL). The mixture was stirred at 50 °C for 16 h. The precipitate formed was filtered and the residue washed with H_2O (2 × 2 mL) and dried to give **4a** or **6a** as a white solid.

3,4,7,8-Tetrahydro-6*H*-pyrrolo[2,1-*c*][1,2,4,6]thiatriazine 2,2-Dioxide (4a)
White solid; yield: 74%; mp 178–179 °C (*i*-PrOH).

^{1}H NMR (500 MHz, DMSO-d_6): δ = 6.93 (t, ^3J = 8.5 Hz, 1 H, NH), 4.63 (d, ^3J = 8.5 Hz, 2 H, CH_2), 3.52 (t, ^3J = 7.0 Hz, 2 H, CH_2), 2.60 (t, ^3J = 7.5 Hz, 2 H, CH_2), 2.05–1.93 (m, 2 H, CH_2).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 167.9, 57.5, 50.9, 33.4, 19.0.

MS (APCI): m/z = 176.0 $[M + H]^+$.

Anal. Calcd for $C_5H_9N_3O_2S$: C, 34.28; H, 5.18; N, 23.98; S, 18.30. Found: C, 34.10; H, 5.12; N, 23.90; S, 18.22.

3,4,7,8,9,10-Hexahydro-6*H*-[1,2,4,6]thiatriazino[4,3-*a*]azepine 2,2-Dioxide (6a)
White solid; yield: 61%; mp 165–166 °C (*i*-PrOH).

^{1}H NMR (500 MHz, DMSO-d_6): δ = 7.18 (dd, ^3J = 9.0, 8.5 Hz, 1 H, NH), 4.64 (d, ^3J = 9.0 Hz, 2 H, CH_2), 3.51–3.89 (m, 2 H, CH_2), 2.46–2.38 (m, 2 H, CH_2), 1.75–1.50 (m, 8 H, CH_2).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 167.6, 62.3, 51.0, 37.4, 29.0, 27.3, 24.2.

MS (APCI): m/z = 204.0 $[M + H]^+$.

Anal. Calcd for $C_7H_{13}N_3O_2S$: C, 41.36; H, 6.45; N, 20.67; S, 15.78. Found: C, 41.22; H, 6.37; N, 20.50; S, 15.83.

4-Methyl-3,4,7,8-tetrahydro-6*H*-pyrrolo[2,1-*c*][1,2,4,6]thiatriazine 2,2-Dioxide (4b)
A soln of **2a** (1 g, 5.2 mmol) and acetaldehyde (0.44 mL, 7.8 mmol) in *i*-PrOH (30 mL) was refluxed for 4 h. The mixture was reduced to 20 mL and cooled to r.t. The crude product was recrystallized (MeCN) to give **4b** as a white solid; yield: 0.69 g (61%); mp 128–129 °C.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 6.97 (d, ^3J = 11.0 Hz, 1 H, NH), 4.92–5.01 (m, 1 H, CH), 3.61–3.51 (m, 2 H, CH_2), 2.65–2.56 (m, 2 H, CH_2), 1.98–1.87 (m, 2 H, CH_2), 1.43 (d, ^3J = 5.2 Hz, 3 H, CH_3).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 167.7, 64.7, 49.0, 33.4, 18.2, 18.0.

MS (APCI): m/z = 190.0 $[M + H]^+$.

Anal. Calcd for $C_6H_{11}N_3O_2S$: C, 38.08; H, 5.86; N, 22.21; S, 16.94. Found: C, 37.88; H, 5.82; N, 22.15; S, 16.87.

2*H*-1,2,4,6-Thiatriazine 1,1-Dioxides 4c–k, 5a–e, 6c–i, 7a–e; General Procedure
TsOH (10 mg) was added to a mixture of powdered **2** (6.1 mmol) and excess of the corresponding benzaldehyde (9.2 mmol) in *i*-PrOH (30 mL). The mixture was stirred at reflux for 8 h. Upon cooling a solid was formed, which was filtered off and washed with H_2O (3 × 5 mL) and *i*-PrOH (2 × 2 mL). The crude product was recrystallized.

4-Phenyl-3,4,7,8-tetrahydro-6*H*-pyrrolo[2,1-*c*][1,2,4,6]thiatriazine 2,2-Dioxide (4c)
White solid; yield: 79%; mp 192–193 °C (EtOH).

^{1}H NMR (500 MHz, DMSO-d_6): δ = 7.56–7.54 (m, 2 H, ArH), 7.44–7.42 (m, 3 H, ArH), 7.33 (d, ^3J = 13.5 Hz, 1 H, NH), 5.86 (d, ^3J = 13.5 Hz, 1 H, CH), 3.28–3.20 (m, 1 H, CH_2), 3.04–2.95 (m, 1 H, CH_2), 2.80–2.70 (m, 1 H, CH_2), 2.67–2.56 (m, 1 H, CH_2), 1.95–1.80 (m, 2 H, CH_2).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.58–7.42 (m, 5 H, ArH), 5.91 (d, ^3J = 12.0 Hz, 1 H, NH), 5.26 (d, ^3J = 11.5 Hz, 1 H, CH), 3.22–3.18 (m, 2 H, CH_2), 3.00–2.84 (m, 1 H, CH_2), 2.77–2.60 (m, 1 H, CH_2), 2.05–1.89 (m, 2 H, CH_2).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 168.5, 134.5, 130.0, 129.2, 128.5, 71.0, 50.4, 32.5, 18.0.

MS (APCI): m/z = 252.0 $[M + H]^+$.

Anal. Calcd for $C_{11}H_{13}N_3O_2S$: C, 52.57; H, 5.21; N, 16.72; S, 12.76. Found: C, 52.38; H, 5.25; N, 16.77; S, 12.69.

4-(3-Methylphenyl)-3,4,7,8-tetrahydro-6*H*-pyrrolo[2,1-*c*][1,2,4,6]thiatriazine 2,2-Dioxide (4d)
White solid; yield: 70%; mp 171–172 °C (EtOH).

^{1}H NMR (500 MHz, DMSO-d_6): δ = 7.44–7.20 (m, 5 H, ArH, NH), 5.82 (d, ^3J = 11.0 Hz, 1 H, CH), 3.30–3.20 (m, 1 H, CH_2), 3.09–2.99 (m, 1 H, CH_2), 2.83–2.71 (m, 1 H, CH_2), 2.72–2.57 (m, 1 H, CH_2), 2.34 (s, 3 H, CH_3), 1.99–1.83 (m, 2 H, CH_2).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 168.4, 138.5, 134.4, 130.6, 129.1, 129.0, 125.5, 71.0, 50.3, 33.7, 21.5, 18.2.

MS (APCI): m/z = 266.2 $[M + H]^+$.

Anal. Calcd for $C_{12}H_{15}N_3O_2S$: C, 54.32; H, 5.70; N, 15.84; S, 12.09. Found: C, 54.21; H, 5.65; N, 15.78; S, 12.14.

4-(4-Chlorophenyl)-3,4,7,8-tetrahydro-6*H*-pyrrolo[2,1-*c*][1,2,4,6]thiatriazine 2,2-Dioxide (4e)
White solid; yield: 81%; mp 210–211 °C (EtOH).

^{1}H NMR (500 MHz, DMSO-d_6): δ = 7.59–7.45 (m, 4 H, ArH), 7.39 (d, J = 8.0 Hz, 1 H, NH), 5.91 (d, J = 8.0 Hz, 1 H, CH), 3.30–3.23 (m, 1 H, CH_2), 3.11–3.03 (m, 1 H, CH_2), 2.80–2.70 (m, 1 H, CH_2), 2.68–2.59 (m, 1 H, CH_2), 1.97–1.84 (m, 2 H, CH_2).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 168.5, 134.5, 133.4, 130.3, 129.1, 70.1, 50.5, 33.7, 18.3.

MS (APCI): m/z = 286.0 $[M + H]^+$.

Anal. Calcd for $C_{11}H_{12}ClN_3O_2S$: C, 46.24; H, 4.23; Cl, 12.41; N, 14.71; S, 11.22. Found: C, 46.08; H, 4.27; Cl, 12.33; N, 14.60; S, 11.25.

4-(4-Nitrophenyl)-3,4,7,8-tetrahydro-6*H*-pyrrolo[2,1-*c*][1,2,4,6]thiatriazine 2,2-Dioxide (4g)
White solid; yield: 94%; mp 258–259 °C (EtOH).

^{1}H NMR (500 MHz, DMSO-d_6): δ = 8.25 (d, J = 8.8 Hz, 2 H, ArH), 7.75 (d, J = 8.4 Hz, 2 H, ArH), 7.60 (d, J = 8.8 Hz, 1 H, NH), 6.12 (d, J = 8.8 Hz, 1 H, CH), 3.43–3.32 (m, 1 H, CH_2), 3.29–3.16 (m, 1 H, CH_2), 2.87–2.63 (m, 2 H, CH_2), 2.09–1.88 (m, 2 H, CH_2).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 168.8, 148.3, 142.5, 129.6, 124.0, 69.7, 51.1, 33.0, 18.7.

MS (APCI): m/z = 297.0 $[M + H]^+$.

Anal. Calcd for $C_{11}H_{12}N_4O_4S$: C, 44.59; H, 4.08; N, 18.91; S, 10.82. Found: C, 44.70; H, 4.02; N, 18.80; S, 10.73.

4-[4-(Dimethylamino)phenyl]-3,4,7,8-tetrahydro-6*H*-pyrrolo[2,1-*c*][1,2,4,6]thiatriazine 2,2-Dioxide (4h)
Yellow solid; yield: 59%; mp 195–196 °C (MeCN).

^{1}H NMR (500 MHz, DMSO-d_6): δ = 7.36 (d, J = 6.8 Hz, 2 H, ArH), 7.12 (d, J = 9.2 Hz, 1 H, NH), 6.70 (d, J = 6.8 Hz, 2 H, ArH), 5.68 (d, J = 8.8 Hz, 1 H, CH), 3.21–3.14 (m, 1 H, CH_2), 3.00–2.93 (m, 1 H, CH_2), 2.90 [s, 6 H, $N(CH_3)_2$], 2.80–2.67 (m, 1 H, CH_2), 2.66–2.56 (m, 1 H, CH_2), 1.93–1.75 (m, 2 H, CH_2).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 168.6, 151.2, 129.3, 121.2, 111.9, 71.3, 50.1, 33.8, 21.4, 18.0.

MS (APCI): m/z = 295.2 $[M + H]^+$.

Anal. Calcd for $C_{13}H_{18}N_4O_2S$: C, 53.04; H, 6.16; N, 19.03; S, 10.89. Found: C, 52.94; H, 6.11; N, 18.98; S, 10.82.

4-(4-Methoxyphenyl)-3,4,7,8-tetrahydro-6*H*-pyrrolo[2,1-*c*][1,2,4,6]thiatriazine 2,2-Dioxide (4i)
White solid; yield: 56%; mp 200–201 °C (*i*-PrOH).

^{1}H NMR (500 MHz, DMSO-d_6): δ = 7.50 (d, J = 6.4 Hz, 2 H, ArH), 7.30 (d, J = 8.8 Hz, 1 H, NH), 6.97 (d, J = 6.4 Hz, 2 H, ArH), 5.79 (d, J = 8.8 Hz, 1 H, CH), 3.77 (s, 3 H, OCH_3), 3.24–3.16 (m, 1 H, CH_2), 3.00–2.92 (m, 1 H, CH_2), 2.77–2.68 (m, 1 H, CH_2), 2.66–2.56 (m, 1 H, CH_2), 1.94–1.77 (m, 2 H, CH_2).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.42 (d, J = 6.8 Hz, 2 H, ArH), 6.99 (d, J = 6.8 Hz, 2 H, ArH), 5.86 (d, J = 7.6 Hz, 1 H, NH), 4.96 (d, J = 8.8 Hz, 1 H, CH), 3.85 (s, 3 H, OCH_3), 3.19 (t, J = 7.1 Hz, 1 H, CH_2), 3.00–2.86 (m, 1 H, CH_2), 2.76–2.63 (m, 2 H, CH_2), 2.04–1.90 (m, 2 H, CH_2).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 168.3, 160.5, 129.9, 125.7, 114.5, 70.6, 55.7, 49.9, 33.7, 17.7.

MS (APCI): m/z = 282.2 $[M + H]^+$.

Anal. Calcd for $C_{12}H_{15}N_3O_3S$: C, 51.23; H, 5.37; N, 14.94; S, 11.40. Found: C, 51.27; H, 5.31; N, 14.86; S, 11.34.

4-(2,2-Dioxido-3,4,7,8-tetrahydro-6*H*-pyrrolo[2,1-*c*][1,2,4,6]thiatriazin-4-yl)benzoic Acid (4j)
White solid; yield: 86%; mp 257–258 °C.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 13.13 (s, 1 H, COOH), 7.98 (d, ^3J = 8.5 Hz, 2 H, ArH), 7.65 (d, ^3J = 8.0 Hz, 2 H, ArH), 7.48 (d, ^3J = 10.0 Hz, 1 H, NH), 6.00 (d, ^3J = 10.0 Hz, 1 H, CH), 3.35–3.27 (m, 1 H, CH_2), 3.19–3.09 (m, 1 H, CH_2), 2.85–2.74 (m, 1 H, CH_2), 2.73–2.61 (m, 1 H, CH_2), 2.02–1.89 (m, 2 H, CH_2).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 168.6, 167.3, 139.4, 132.1, 130.0, 128.6, 70.3, 50.7, 33.7, 18.4.

MS (APCI): m/z = 296.2 $[M + H]^+$.

Anal. Calcd for $C_{12}H_{13}N_3O_4S$: C, 48.80; H, 4.44; N, 14.23; S, 10.86. Found: C, 48.68; H, 4.38; N, 14.19; S, 10.82.

4-(2,2-Dioxido-3,4,7,8-tetrahydro-6*H*-pyrrolo[2,1-*c*][1,2,4,6]thiatriazin-4-yl)phenol (4k)
White solid; yield: 64%; mp 202–203 °C (*i*-PrOH).

^{1}H NMR (500 MHz, DMSO-d_6): δ = 9.73 (s, 1 H, OH), 7.38 (d, ^3J = 8.5 Hz, 2 H, ArH), 7.19 (d, ^3J = 11.0 Hz, 1 H, NH), 6.79 (d, ^3J = 8.5 Hz, 2 H, ArH), 5.74 (d, ^3J = 11.0 Hz, 1 H, CH), 3.25–3.15 (m, 1 H, CH_2), 3.03–2.93 (m, 1 H, CH_2), 2.78–2.68 (m, 1 H, CH_2), 2.67–2.56 (m, 1 H, CH_2), 1.97–1.79 (m, 2 H, CH_2).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 168.3, 158.8, 129.9, 124.7, 115.8, 70.8, 50.1, 33.7, 18.1.

MS (APCI): m/z = 268.2 $[M + H]^+$.

Anal. Calcd for $C_{11}H_{13}N_3O_3S$: C, 49.43; H, 4.90; N, 15.72; S, 12.00. Found: C, 49.25; H, 4.91; N, 15.68; S, 11.89.

4-(4-Methylphenyl)-3,4,7,8-tetrahydro-6*H*-pyrrolo[2,1-*c*][1,2,4,6]thiatriazine 2,2-Dioxide (4n)
White solid; yield: 74%; mp 164–165 °C (EtOH).

^{1}H NMR (500 MHz, DMSO-d_6): δ = 8.02 (d, ^3J = 10.5 Hz, 1 H, NH), 7.87 (d, ^3J = 9.0 Hz, 2 H, ArH), 7.57 (d, ^3J = 9.0 Hz, 2 H, ArH), 5.55 (d, ^3J = 10.5 Hz, 1 H, CH), 3.25–3.15 (m, 1 H, CH_2), 3.00–2.87 (m, 1 H, CH_2), 2.80–2.74 (m, 1 H, CH_2), 2.68–2.60 (m, 1 H, CH_2), 2.45 (s, 3 H, CH_3), 1.97–1.78 (m, 2 H, CH_2).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 167.6, 138.9, 134.9, 131.3, 129.8, 128.3, 125.0, 70.5, 51.6, 32.9, 20.6, 19.4.

MS (APCI): m/z = 266.2 $[M + H]^+$.

Anal. Calcd for $C_{12}H_{15}N_3O_2S$: C, 54.32; H, 5.70; N, 15.84; S, 12.09. Found: C, 54.39; H, 5.73; N, 15.76; S, 12.01.

4-Phenyl-3,4,6,7,8,9-hexahydropyrido[2,1-*c*][1,2,4,6]thiatriazine 2,2-Dioxide (5a)
White solid; yield: 77%; mp 178–179 °C (*i*-PrOH).

^{1}H NMR (500 MHz, DMSO-d_6): δ = 7.60 (d, *J* = 7.2 Hz, 1 H, NH), 7.47–7.33 (m, 5 H, ArH), 5.79 (d, *J* = 7.6 Hz, 1 H, CH), 3.11–3.02 (m, 1 H, CH_2), 2.94–2.81 (m, 1 H, CH_2), 2.60– 2.51 (m, 1 H, CH_2), 2.45–2.36 (m, 1 H, CH_2), 1.79–1.61 (m, 4 H, CH_2).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 162.8, 134.7, 133.8, 130.0, 128.8, 73.4, 48.0, 32.6, 22.4, 19.1.

MS (APCI): *m*/*z* = 266.0 $[M + H]^+$.

Anal. Calcd for $C_{12}H_{15}N_3O_2S$: C, 54.32; H, 5.70; N, 15.84; S, 12.09. Found: C, 54.21; H, 5.68; N, 15.79; S, 12.02.

4-(4-Chlorophenyl)-3,4,6,7,8,9-hexahydropyrido[2,1-*c*][1,2,4,6]thiatriazine 2,2-Dioxide (5b)
White solid; yield: 79%; mp 208–209 °C (EtOH).

^{1}H NMR (500 MHz, DMSO-d_6): δ = 7.68 (d, *J* = 8.8 Hz, 1 H, NH), 7.50–7.39 (m, 4 H, ArH), 5.82 (d, *J* = 8.8 Hz, 1 H, CH), 3.17–3.07 (m, 1 H, CH_2), 2.99–2.89 (m, 1 H, CH_2), 2.62–2.51 (m, 1 H, CH_2), 2.46–2.36 (m, 1 H, CH_2), 1.84–1.58 (m, 4 H, CH_2).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 163.1, 135.4, 129.3, 129.0, 128.2, 74.2, 47.9, 32.6, 22.7, 19.0.

MS (APCI): *m*/*z* = 300.2 $[M + H]^+$.

Anal. Calcd for $C_{12}H_{14}ClN_3O_2S$: C, 48.08; H, 4.71; Cl, 11.83; N, 14.02; S, 10.70. Found: C, 47.98; H, 4.67; N, 14.10; S, 10.63.

4-(4-Nitrophenyl)-3,4,6,7,8,9-hexahydropyrido[2,1-*c*][1,2,4,6]thiatriazine 2,2-Dioxide (5c)
White solid; yield: 91%; mp 229–230 °C.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 8.22 (d, *J* = 6.8 Hz, 2 H, ArH), 7.54 (d, *J* = 6.0 Hz, 1 H, NH), 7.63 (d, *J* = 6.8 Hz, 2 H, ArH), 5.98 (d, *J* = 6.4 Hz, 1 H, CH), 3.27–3.20 (m, 1 H, CH_2), 3.10–3.03 (m, 1 H, CH_2), 2.65–2.56 (m, 1 H, CH_2), 2.47–2.39 (m, 1 H, CH_2), 1.91–1.63 (m, 4 H, CH_2).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 162.4, 148.0, 143.6, 129.3, 123.8, 73.0, 48.6, 32.5, 22.3, 19.0.

MS (APCI): *m*/*z* = 311.0 $[M + H]^+$.

Anal. Calcd for $C_{12}H_{14}N_4O_4S$: C, 46.44; H, 4.55; N, 18.05; S, 10.33. Found: C, 46.50; H, 4.52; N, 17.96; S, 10.41.

4-[4-(Dimethylamino)phenyl]-3,4,6,7,8,9-hexahydropyrido[2,1-*c*][1,2,4,6]thiatriazine 2,2-Dioxide (5d)
Yellow solid; yield: 51%; mp 223–224 °C (MeCN).

^{1}H NMR (500 MHz, DMSO-d_6): δ = 7.74 (d, *J* = 7.2 Hz, 1 H, NH), 7.29 (d, *J* = 6.8 Hz, 2 H, ArH), 6.69 (d, *J* = 6.8 Hz, 2 H, ArH), 5.66 (d, *J* = 8.4 Hz, 1 H, CH), 3.15–3.05 (m, 1 H, CH_2), 2.90 [s, 6 H, $N(CH_3)_2$], 2.83–2.74 (m, 1 H, CH_2), 2.60–2.51 (m, 1 H, CH_2), 2.43–2.35 (m, 1 H, CH_2), 1.70–1.61 (m, 4 H, CH_2).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 163.1, 151.5, 133.7, 129.5, 112.1, 74.0, 46.9, 33.8, 23.3, 19.0.

MS (APCI): *m*/*z* = 309.0 $[M + H]^+$.

Anal. Calcd for $C_{14}H_{20}N_4O_2S$: C, 54.52; H, 6.54; N, 18.17; S, 10.40. Found: C, 54.32; H, 6.55; N, 18.20; S, 10.31.

4-(4-Methoxyphenyl)-3,4,6,7,8,9-hexahydropyrido[2,1-*c*][1,2,4,6]thiatriazine 2,2-Dioxide (5e)
White solid; yield: 59%; mp 162–163 °C (*i*-PrOH).

^{1}H NMR (500 MHz, DMSO-d_6): δ = 7.50 (d, *J* = 7.6 Hz, 1 H, NH), 7.39 (d, *J* = 6.4 Hz, 2 H, ArH), 6.94 (d, *J* = 6.8 Hz, 2 H, ArH), 5.74 (d, *J* = 7.6 Hz, 1 H, CH), 3.76 (s, 3 H, OCH_3), 3.07–2.96 (m, 1 H, CH_2), 2.88–2.77 (m, 1 H, CH_2), 2.57–2.47 (m, 1 H, CH_2), 2.44–2.35 (m, 1 H, CH_2), 1.75–1.62 (m, 4 H, CH_2).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 163.3, 160.0, 129.6, 127.5, 114.8, 74.1, 56.2, 47.7, 33.0, 22.8, 18.9.

MS (APCI): *m*/*z* = 196.0 $[M + H]^+$.

Anal. Calcd for $C_{13}H_{17}N_3O_3S$: C, 52.86; H, 5.80; N, 14.23; S, 10.86. Found: C, 52.71; H, 5.86; N, 14.31; S, 10.72.

4-Pyridin-3-yl-3,4,7,8,9,10-hexahydro-6*H*-[1,2,4,6]thiatriazino[4,3-*a*]azepine 2,2-Dioxide (6c)
White solid; yield: 71%; mp 173–174 °C (*i*-PrOH).

^{1}H NMR (500 MHz, DMSO-d_6): δ = 8.58–8.45 (m, 2 H, ArH), 7.83 (d, ^3J = 7.0 Hz, 1 H, ArH), 7.74 (d, ^3J = 7.0 Hz, 1 H, CH), 7.43–7.33 (m, 1 H, ArH), 6.00 (d, ^3J = 6.5 Hz, 1 H, NH), 3.71–3.58 (m, 1 H, CH_2), 3.22–3.10 (m, 1 H, CH_2), 2.94–2.80 (m, 1 H, CH_2), 2.42–2.31 (m, 1 H, CH_2), 1.92–1.72 (m, 2 H, CH_2), 1.66–1.42 (m, 4 H, CH_2).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 168.1, 149.8, 149.2, 135.7, 132.4, 123.6, 72.6, 51.1, 37.9, 28.9, 27.4, 24.4.

MS (APCI): *m*/*z* = 281.2 $[M + H]^+$.

Anal. Calcd for $C_{12}H_{16}N_4O_2S$: C, 51.41; H, 5.75; N, 19.98; S, 11.44. Found: C, 51.27; H, 5.69; N, 19.91; S, 11.42.

4-Phenyl-3,4,7,8,9,10-hexahydro-6*H*-[1,2,4,6]thiatriazino[4,3-*a*]azepine 2,2-Dioxide (6d)
White solid; yield: 77%; mp 174–175 °C (*i*-PrOH).

^{1}H NMR (500 MHz, DMSO-d_6): δ = 7.64 (d, *J* = 6.8 Hz, 1 H, NH), 7.44–7.31 (m, 5 H, ArH), 5.84 (d, *J* = 7.2 Hz, 1 H, CH), 3.51–3.43 (m, 1 H, CH_2), 3.19–3.10 (m, 1 H, CH_2), 2.79–2.70 (m, 1 H, CH_2), 2.46–2.37 (m, 1 H, CH_2), 1.87–1.38 (m, 6 H, CH_2).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 168.5, 135.9, 129.1, 128.7, 128.2, 74.5, 50.4, 38.0, 28.9, 27.0, 24.4.

MS (APCI): *m*/*z* = 280.0 $[M + H]^+$.

Anal. Calcd for $C_{13}H_{17}N_3O_2S$: C, 55.89; H, 6.13; N, 15.04; S, 11.48. Found: C, 55.80; H, 6.20; N, 14.89; S, 11.49.

4-(4-Chlorophenyl)-3,4,7,8,9,10-hexahydro-6*H*-[1,2,4,6]thiatriazino[4,3-*a*]azepine 2,2-Dioxide (6e)
White solid; yield: 75%; mp 183–184 °C (MeCN).

^{1}H NMR (500 MHz, DMSO-d_6): δ = 7.73 (d, *J* = 8.0 Hz, 1 H, NH), 7.48–7.33 (m, 4 H, ArH), 5.89 (d, *J* = 8.0 Hz, 1 H, CH), 3.65–3.48 (m, 1 H, CH_2), 3.20–3.06 (m, 1 H, CH_2), 2.87–2.73 (m, 1 H, CH_2), 2.45–2.29 (m, 1 H, CH_2), 1.90–1.36 (m, 6 H, CH_2).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 168.0, 135.8, 133.5, 130.0, 128.6, 73.7, 50.9, 37.9, 28.7, 27.4, 24.1.

MS (APCI): *m*/*z* = 314.0 $[M + H]^+$.

Anal. Calcd for $C_{13}H_{16}ClN_3O_2S$: C, 49.76; H, 5.14; N, 13.39; S, 10.22. Found: C, 49.58; H, 5.11; N, 13.42; S, 10.16.

4-(4-Nitrophenyl)-3,4,7,8,9,10-hexahydro-6*H*-[1,2,4,6]thiatriazino[4,3-*a*]azepine 2,2-Dioxide (6f)
White solid; yield: 90%; mp 239–240 °C.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 8.20 (d, *J* = 8.8 Hz, 2 H, ArH), 7.93 (d, *J* = 7.2 Hz, 1 H, NH), 7.60 (d, *J* = 8.8 Hz, 2 H, ArH), 6.10 (d, *J* = 7.2 Hz, 1 H, CH), 3.76–3.67 (m, 1 H, CH_2), 3.20–3.10 (m, 1 H, CH_2), 2.95–2.85 (m, 1 H, CH_2), 2.41–2.30 (m, 1 H, CH_2), 1.96–1.40 (m, 6 H, CH_2).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 168.0, 147.7, 144.6, 129.3, 123.5, 73.8, 51.1, 37.7, 29.0, 27.4, 24.1.

MS (APCI): m/z = 325.0 $[M + H]^+$.

Anal. Calcd for $C_{13}H_{16}N_4O_4S$: C, 48.14; H, 4.97; N, 17.27; S, 9.89. Found: C, 48.2; H, 5.01; N, 17.21; S, 9.84.

4-[4-(Dimethylamino)phenyl]-3,4,7,8,9,10-hexahydro-6*H*-[1,2,4,6]thiatriazino[4,3-*a*]azepine 2,2-Dioxide (6g)
Yellow solid; yield: 49%; mp 200–201 °C (MeCN).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.81 (s, 1 H, CH), 8.43 (br t, 1 H, NH), 7.77 (d, J = 6.8 Hz, 2 H, ArH), 6.67 (d, J = 6.8 Hz, 2 H, ArH), 3.45–3.34 (m, 2 H, CH_2), 3.09 [s, 6 H, $N(CH_3)_2$], 2.64–2.51 (m, 2 H, CH_2), 1.84–1.67 (m, 6 H, CH_2).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 166.9, 151.1, 133.2, 129.5, 112.0, 74.8, 43.9, 38.3, 30.0, 29.1, 24.2.

MS (APCI): m/z = 323.2 $[M + H]^+$.

Anal. Calcd for $C_{15}H_{22}N_4O_2S$: C, 55.88; H, 6.88; N, 17.38; S, 9.95. Found: C, 55.71; H, 6.82; N, 17.26; S, 9.90.

4-(4-Methoxyphenyl)-3,4,7,8,9,10-hexahydro-6*H*-[1,2,4,6]thiatriazino[4,3-*a*]azepine 2,2-Dioxide (6h)
White solid; yield: 67%; mp 162–163 °C (*i*-PrOH).

^{1}H NMR (500 MHz, DMSO-d_6): δ = 7.53 (d, J = 7.6 Hz, 1 H, NH), 7.36 (d, J = 6.4 Hz, 2 H, ArH), 6.92 (d, J = 6.8 Hz, 2 H, ArH), 5.78 (d, J = 7.2 Hz, 1 H, CH), 3.75 (s, 3 H, OCH_3), 3.42–3.32 (m, 1 H, CH_2), 3.20–3.09 (m, 1 H, CH_2), 2.74–2.62 (m, 1 H, CH_2), 2.50–2.40 (m, 1 H, CH_2), 1.81–1.33 (m, 6 H, CH_2).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 168.0, 160.0, 129.8, 127.4, 114.1, 74.3, 55.7, 49.9, 38.0, 28.8, 27.3, 24.7.

MS (APCI): m/z = 310.2 $[M + H]^+$.

Anal. Calcd for $C_{14}H_{19}N_3O_3S$: C, 54.35; H, 6.19; N, 13.58; S, 10.36. Found: C, 54.21; H, 6.11; N, 13.53; S, 10.32.

4-(2-Methylphenyl)-3,4,7,8,9,10-hexahydro-6*H*-[1,2,4,6]thiatriazino[4,3-*a*]azepine 2,2-Dioxide (6i)
White solid; yield: 70%; mp 192–193 °C (MeCN).

^{1}H NMR (500 MHz, DMSO-d_6): δ = 7.62 (d, ^3J = 8.0 Hz, 1 H, NH), 7.28–7.13 (m, 4 H, ArH), 5.88 (d, ^3J = 8.0 Hz, 1 H, CH), 3.57–3.47 (m, 1 H, CH_2), 3.16–3.06 (m, 1 H, CH_2), 2.92–2.80 (m, 1 H, CH_2), 2.45–2.38 (m, 1 H, CH_2), 2.36 (s, 3 H, CH_3), 1.94–1.75 (m, 2 H, CH_2), 1.68–1.45 (m, 4 H, CH_2).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 168.1, 136.8, 133.7, 131.0, 128.8, 127.4, 125.8, 72.3, 50.94, 38.0, 29.0, 27.5, 24.5, 19.1.

MS (APCI): m/z = 294.2 $[M + H]^+$.

Anal. Calcd for $C_{14}H_{19}N_3O_2S$: C, 57.31; H, 6.53; N, 14.32; S, 10.93. Found: C, 57.17; H, 6.46; N, 14.25; S, 10.88.

4-(4-Fluorophenyl)-3,4,7,8,9,10-hexahydro-6*H*-[1,2,4,6]thiatriazino[4,3-*a*]azepine 2,2-Dioxide (6j)
White solid; yield: 71%; mp 170–171 °C (EtOH).

^{1}H NMR (500 MHz, DMSO-d_6): δ = 7.67 (d, ^3J = 8.0 Hz, 1 H), 7.48–7.39 (m, 2 H), 7.19 (t, ^3J = 9.0 Hz, 2 H), 5.88 (d, ^3J = 8.5 Hz, 1 H), 3.56–3.44 (m, 1 H), 3.20–3.08 (m, 1 H), 2.82–2.71 (m, 1 H), 2.44–2.36 (m, 1 H), 1.86–1.66 (m, 2 H), 1.63–1.41 (m, 4 H).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 168.1, 161.6, 132.6, 130.4, 115.5, 73.8, 50.6, 28.9, 27.3, 24.4.

MS (ESI): m/z = 298.2 $[M + H]^+$.

Anal. Calcd for $C_{13}H_{16}FN_3O_2S$: C, 52.51; H, 5.42; N, 14.13; S, 10.78. Found: C, 52.37; H, 5.36; N, 14.08; S, 10.69.

4-Phenyl-3,4,6,7,8,9,10,11-octahydro[1,2,4,6]thiatriazino[4,3-*a*]azocine 2,2-Dioxide (7a)
White solid; yield: 77%; mp 154–155 °C (EtOH).

^{1}H NMR (500 MHz, DMSO-d_6): δ = 7.74 (d, J = 7.2 Hz, 1 H, NH), 7.50–7.33 (m, 5 H, ArH), 5.85 (d, J = 7.2 Hz, 1 H, CH), 3.90–3.79 (m, 1 H, CH_2), 2.99–2.87 (m, 1 H, CH_2), 2.85–2.70 (m, 1 H, CH_2), 2.32–2.21 (m, 1 H, CH_2), 1.97–1.21 (m, 8 H, CH_2).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 168.1, 135.8, 129.3, 128.9, 128.1, 72.2, 46.9, 35.2, 30.0, 28.7, 25.6, 23.6.

MS (APCI): m/z = 294.0 $[M + H]^+$.

Anal. Calcd for $C_{14}H_{19}N_3O_2S$: C, 57.31; H, 6.53; N, 14.32; S, 10.93. Found: C, 57.18; H, 6.48; N, 14.41; S, 10.86.

4-(4-Chlorophenyl)-3,4,6,7,8,9,10,11-octahydro[1,2,4,6]thiatriazino[4,3-*a*]azocine 2,2-Dioxide (7b)
White solid; yield: 80%; mp 205–206 °C (EtOH).

^{1}H NMR (500 MHz, DMSO-d_6): δ = 7.85 (d, J = 6.4 Hz, 1 H, NH), 7.43 (s, 4 H, ArH), 5.89 (d, J = 6.4 Hz, 1 H, CH), 3.88 (t, J = 10.8 Hz, 1 H, CH_2), 2.94 (d, J = 12.0 Hz, 1 H, CH_2), 2.82 (t, J = 9.6 Hz, 1 H, CH_2), 2.30–2.19 (m, 1 H, CH_2), 1.94–1.25 (m, 8 H, CH_2).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 167.5, 135.2, 133.7, 129.9, 128.7, 71.3, 47.5, 35.0, 29.9, 29.0, 25.4, 24.3.

MS (APCI): m/z = 328.0 $[M + H]^+$.

Anal. Calcd for $C_{14}H_{18}ClN_3O_2S$: C, 51.29; H, 5.53; Cl, 10.81; N, 12.82; S, 9.78. Found: C, 51.16; H, 5.49; Cl, 10.73; N, 12.73; S, 9.71.

4-(4-Nitrophenyl)-3,4,6,7,8,9,10,11-octahydro[1,2,4,6]thiatriazino[4,3-*a*]azocine 2,2-Dioxide (7c)
White solid; yield: 89%; mp 189–190 °C.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 8.21 (d, J = 6.8 Hz, 2 H, ArH), 8.08 (d, J = 6.0 Hz, 1 H, NH), 7.62 (d, J = 6.8 Hz, 2 H, ArH), 6.08 (d, J = 6.0 Hz, 1 H, CH), 3.98 (t, J = 10.8 Hz, 1 H, CH_2), 3.00 (d, J = 12.4 Hz, 1 H, CH_2), 2.90 (t, J = 10.0 Hz, 1 H, CH_2), 2.24 (d, J = 10.0 Hz, 1 H, CH_2), 1.96–1.34 (m, 8 H, CH_2).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 167.1, 148.0, 144.2, 128.8, 123.7, 70.8, 48.2, 34.9, 29.9, 29.1, 25.5, 24.5.

MS (APCI): m/z = 339.2 $[M + H]^+$.

Anal. Calcd for $C_{14}H_{18}N_4O_4S$: C, 49.69; H, 5.36; N, 16.56; S, 9.48. Found: C, 49.51; H, 5.32; N, 16.50; S, 9.35.

4-[4-(Dimethylamino)phenyl]-3,4,6,7,8,9,10,11-octahydro[1,2,4,6]thiatriazino[4,3-*a*]azocine 2,2-Dioxide (7d)
Yellow solid; yield: 61%; mp 214–215 °C (MeCN).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.82 (s, 1 H, CH), 8.20 (br t, 1 H, NH), 7.75 (d, J = 6.8 Hz, 2 H, ArH), 6.67 (d, J = 6.8 Hz, 2 H, ArH), 3.54–3.43 (m, 2 H, CH_2), 3.09 [s, 6 H, $N(CH_3)_2$], 2.50 (t, J = 5.2 Hz, 2 H, CH_2), 1.89–1.58 (m, 8 H, CH_2).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 168.6, 133.0, 129.2, 112.5, 112.0, 72.5, 42.3, 31.9, 29.2, 25.5, 24.4.

MS (APCI): m/z = 337.0 $[M + H]^+$.

Anal. Calcd for $C_{16}H_{24}N_4O_2S$: C, 57.12; H, 7.19; N, 16.65; S, 9.53. Found: C, 57.1; H, 7.15; N, 16.72; S, 9.48.

4-(4-Methoxyphenyl)-3,4,6,7,8,9,10,11-octahydro[1,2,4,6]thiatriazino[4,3-*a*]azocine 2,2-Dioxide (7e)
White solid; yield: 68%; mp 163–164 °C (MeCN).

^{1}H NMR (500 MHz, DMSO-d_6): δ = 7.62 (d, J = 7.6 Hz, 1 H, NH), 7.43 (d, J = 6.8 Hz, 2 H, ArH), 6.94 (d, J = 6.8 Hz, 2 H, ArH), 5.79 (d, J = 8.0 Hz, 1 H, CH), 3.76 (s, 3 H, OCH_3), 2.92 (d, J = 11.2 Hz, 1 H, CH_2), 2.74 (t, J = 8.8 Hz, 1 H, CH_2), 2.33–2.21 (m, 1 H, CH_2), 1.95–1.81 (m, 1 H, CH_2), 1.79–1.14 (m, 8 H, CH_2).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 168.0, 159.8, 129.2, 127.5, 114.3, 72.2, 55.8, 35.3, 30.4, 29.1, 26.0, 24.9.

MS (APCI): m/z = 324.0 $[M + H]^+$.

Anal. Calcd for $C_{15}H_{21}N_3O_3S$: C, 55.71; H, 6.54; N, 12.99; S, 9.91. Found: C, 55.53; H, 6.51; N, 12.87; S, 9.90.

4-(2,2-Dioxido-3,4,7,8-tetrahydro-6*H*-pyrrolo[2,1-*c*][1,2,4,6]thiatriazin-4-yl)benzaldehyde (4f)

Compound **2a** (1.5g, 9.2 mmol) was added in 0.1-g portions over 2 h to a stirred and refluxed soln of terephthalaldehyde (6.2 g, 46 mmol). The suspension was stirred under reflux for 2 h. The precipitate was filtered off and recrystallized (AcOH) to give a white solid; yield: 79%; mp 212–213 °C.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 10.04 (s, 1 H, COH), 9.95 (d, ^3J = 7.5 Hz, 2 H, ArH), 7.78 (d, ^3J = 7.5 Hz, 2 H, ArH), 7.30 (d, ^3J = 10.5 Hz, 1 H, NH), 5.96 (d, ^3J = 11.0 Hz, 1 H, CH), 3.42–3.27 (m, 1 H, CH_2), 3.20–3.07 (m, 1 H, CH_2), 2.89–2.75 (m, 1 H, CH_2), 2.75–2.63 (m, 1 H, CH_2), 2.11–1.92 (m, 2 H, CH_2).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 10.11 (s, 1 H, COH), 8.04 (d, ^3J = 7.5 Hz, 2 H, ArH), 7.72 (d, ^3J = 7.5 Hz, 2 H, ArH), 6.01 (br d, 1 H, NH), 5.15 (br d, 1 H, CH), 3.35–3.20 (m, 2 H, CH_2), 3.04–2.91 (m, 1 H, CH_2), 2.86–2.73 (m, 1 H, CH_2), 2.15–2.00 (m, 2 H, CH_2).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 193.3, 168.7, 141.2, 137.1, 130.1, 129.1, 70.3, 50.8, 33.7, 18.5.

MS (APCI): m/z = 280.2 $[M + H]^+$.

Anal. Calcd for $C_{12}H_{13}N_3O_3S$: C, 51.60; H, 4.69; N, 15.04; S, 11.48. Found: C, 51.48; H, 4.60; N, 14.98; S, 11.42.

4-(Chloromethyl)-3,4,7,8,9,10-hexahydro-6*H*-[1,2,4,6]thiatriazino[4,3-*a*]azepine 2,2-Dioxide (6b)

The mixture of chloroacetaldehyde (5.4 mmol) and a soln of **2c** (1 g, 5.2 mmol) in 0.1 M HCl (20 mL) was stirred at r.t. for 10 h. The cooled mixture (ice bath) was neutralized with Et_3N (0.35 mL) and extracted with CH_2Cl_2 (2 × 30 mL). The organic layer was washed with H_2O (2 × 30 mL) and dried (anhyd Na_2SO_4). The solvent was removed under reduced pressure and the white solid obtained was dried in vacuo; yield: 0.76 g (58%); mp 182–183 °C.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 7.65 (d, ^3J = 6.5 Hz, 1 H, NH), 4.85–4.70 (m, 1 H, CH_2), 4.07 (dd, ^2J = 12.0 Hz, ^3J = 10.5 Hz, 1 H, CH), 3.87–3.73 (m, 1 H, CH_2), 3.69–3.49 (m, 2 H, CH_2), 2.64–2.53 (m, 1 H, CH_2), 2.44–2.30 (m, 1 H, CH_2), 1.81–1.44 (m, 6 H, CH_2).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 167.0, 73.3, 51.2, 41.5, 37.8, 28.7, 27.9, 24.2.

MS (APCI): m/z = 252.2 $[M + H]^+$.

Anal. Calcd for $C_8H_{14}ClN_3O_2S$: C, 38.17; H, 5.61; Cl, 14.08; N, 16.69; S, 12.74. Found: C, 38.01; H, 5.57; Cl, 14.03; N, 16.67; S, 12.81.

Compounds 4l, 4m; General Procedure

TsOH (10 mg) was added to a soln of sulfamoylamidine **2** (6.1 mmol) in the corresponding ketone (30 mL) and the mixture was stirred at reflux for 24 h. The volume of the mixture was reduced to 10 mL, the precipitate was filtered off and washed with corresponding ketone (2 × 3 mL) and dried in vacuo.

4,4-Dimethyl-3,4,7,8-tetrahydro-6*H*-pyrrolo[2,1-*c*][1,2,4,6]thiatriazine 2,2-Dioxide (4l)

White solid; yield: 84%; mp 227–228 °C.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 7.02 (s, 1 H, NH), 3.60–3.51 (m, 2 H, CH_2), 2.64–2.53 (m, 2 H, CH_2), 1.94–1.84 (m, 2 H, CH_2), 1.48 (s, 6 H, CH_3).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 166.2, 71.7, 48.1, 33.7, 25.9, 17.7.

MS (APCI): m/z = 204.0 $[M + H]^+$.

Anal. Calcd for $C_7H_{13}N_3O_2S$: C, 41.36; H, 6.45; N, 20.67; S, 15.78. Found: C, 41.17; H, 6.38; N, 20.60; S, 15.71.

4,4-Diethyl-3,4,7,8-tetrahydro-6*H*-pyrrolo[2,1-*c*][1,2,4,6]thiatriazine 2,2-Dioxide (4m)

White solid; yield: 67%; mp 143–144 °C.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 6.84 (s, 1 H, NH), 3.58–3.48 (m, 2 H, CH_2), 2.66–2.56 (m, 2 H, CH_2), 2.01–1.74 (m, 6 H, CH_3), 0.92–0.82 (m, 6 H, CH_2).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 166.8, 77.2, 48.5, 33.6, 28.5, 18.2, 7.8.

MS (APCI): m/z = 232.0 $[M + H]^+$.

Anal. Calcd for $C_9H_{17}N_3O_2S$: C, 46.73; H, 7.41; N, 18.17; S, 13.86. Found: C, 46.60; H, 7.45; N, 18.13; S, 13.75.

Compounds 8a and 8b; General Procedure

MeI (for **8a**) or bromoacetophenone (for **8b**) (4.5 mmol) was added to a mixture of KOH (4.5 mmol) and a soln of the corresponding thiatriazine dioxide (3.77 mmol) in DMF (20 mL). The resulting mixture was stirred at 40 °C for 6 h. H_2O (100 mL) was added with stirring and the mixture was allowed to stand for several hours. The precipitate was filtered off, washed with H_2O (2 × 20 mL) and dried in vacuo.

3-Methyl-4-(4-methylphenyl)-3,4,7,8-tetrahydro-6*H*-pyrrolo[2,1-*c*][1,2,4,6]thiatriazine 2,2-Dioxide (8a)

White solid; yield: 78%; mp 155–156 °C (EtOH).

^{1}H NMR (500 MHz, DMSO-d_6): δ = 7.30 (d, ^3J = 8.0 Hz, 2 H, ArH), 7.24 (d, ^3J = 8.0 Hz, 2 H, ArH), 5.83 (s, 1 H, CH), 3.43–3.33 (m, 1 H, CH_2), 3.30–3.20 (m, 1 H, CH_2), 2.85–2.75 (m, 1 H, CH_2), 2.79–2.69 (m, 1 H, CH_2), 2.57 (s, 3 H, CH_3), 2.34 (s, 3 H, CH_3), 2.07–1.96 (m, 2 H, CH_2).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 168.1, 139.2, 131.8, 129.6, 128.4, 76.7, 51.7, 35.4, 33.5, 21.3, 18.1.

MS (APCI): m/z = 280.0 $[M + H]^+$.

Anal. Calcd for $C_{13}H_{17}N_3O_2S$: C, 55.89; H, 6.13; N, 15.04; S, 11.48. Found: C, 55.70; H, 6.05; N, 15.11; S, 11.47.

2-[4-(4-Fluorophenyl)-2,2-dioxido-7,8,9,10-tetrahydro-6*H*-[1,2,4,6]thiatriazino[4,3-*a*]azepin-3(4*H*)-yl]-1-phenylethanone (8b)

White solid; yield: 81%; mp 194–195 °C (AcOH).

^{1}H NMR (500 MHz, DMSO-d_6): δ = 8.09 (d, ^3J = 7.5 Hz, 2 H, ArH), 7.80–7.48 (m, 5 H, ArH), 7.31–7.13 (m, 2 H, ArH), 6.16 (s, 1 H, CH), 5.02 (d, ^2J = 18.5 Hz, 1 H, CH_2), 4.75 (d, ^2J = 18.5 Hz, 1 H, CH_2), 3.90–3.72 (m, 1 H, CH_2), 3.23–3.08 (m, 1 H, CH_2), 3.07–2.91 (m, 1 H, CH_2), 2.47–2.34 (m, 1 H, CH_2), 2.04–1.50 (m, 6 H, CH_2).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 194.6, 168.0, 163.4, 161.5, 135.4, 134.2, 133.5, 129.3, 128.5, 115.1, 79.5, 57.4, 52.5, 37.9, 29.3, 27.3, 24.5.

MS (APCI): m/z = 417.2 $[M + H]^+$.

Anal. Calcd for $C_{21}H_{22}FN_3O_3S$: C, 60.71; H, 5.34; N, 10.11; S, 7.72. Found: C, 60.53; H, 5.38; N, 10.08; S, 7.68.

3-Benzoyl-4-phenyl-3,4,7,8-tetrahydro-6*H*-pyrrolo[2,1-*c*][1,2,4,6]thiatriazine 2,2-Dioxide (8c)

BzCl (0.48 mL, 4.15 mmol) was added dropwise to a suspension of **4c** (1 g, 3.77 mmol) in anhyd pyridine (20 mL) at 0 °C with stirring. The mixture was warmed to r.t. and stirred for a further 6 h. H_2O (100mL) was added and the mixture was left to stand for 3 h. The precipitated formed was filtered off, washed with H_2O (2 × 5 mL) and recrystallized (AcOH) to give **8c** as a white solid; yield: 1 g (71%); mp 206–207 °C.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 7.72 (d, ^3J = 7.0 Hz, 2 H, ArH), 7.68–7.58 (m, 1 H, ArH), 7.57–7.33 (m, 7 H, ArH), 7.21 (s, 1 H, CH), 3.91–3.79 (m, 1 H, CH_2), 3.76–3.66 (m, 1 H, CH_2), 3.06–2.93 (m, 1 H, CH_2), 2.92–2.81 (m, 1 H, CH_2), 2.35–2.12 (m, 2 H, CH_2).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 171.1, 168.1, 135.7, 135.2, 133.3, 129.5, 129.3, 129.1, 128.7, 126.9, 69.6, 52.6, 33.3, 19.3.

MS (APCI): m/z = 356.2 $[M + H]^+$.

Anal. Calcd for $C_{18}H_{17}N_3O_3S$: C, 60.83; H, 4.82; N, 11.82; S, 9.02. Found: C, 60.72; H, 4.80; N, 11.85; S, 8.98.

3-Acetyl-4-phenyl-3,4,7,8-tetrahydro-6*H*-pyrrolo[2,1-*c*][1,2,4,6]thiatriazine 2,2-Dioxide (8d)

Anhyd Et_3N (0.56 mL, 4 mmol) was added to a soln of **4c** (1 g, 3.77 mmol) in Ac_2O (10 mL). The mixture was stirred at 80 °C for 4 h. Solvent was removed under reduced pressure and the residue was recrystallized (*i*-PrOH) to give **8d** as a brown solid; yield: 1 g (77%); mp 145–146 °C.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 7.46–7.32 (m, 5 H, ArH), 7.29 (s, 1 H, CH), 3.84–3.73 (m, 1 H, CH_2), 3.54–3.43 (m, 1 H, CH_2), 3.02–2.91 (m, 1 H, CH_2), 2.88–2.78 (m, 1 H, CH_2), 2.43 (s, 3 H, CH_2), 2.22–2.05 (m, 2 H, CH_2).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 169.0, 167.8, 135.5, 129.5, 129.0, 127.3, 68.1, 52.4, 33.3, 25.6, 19.2.

MS (APCI): m/z = 294.2 $[M + H]^+$.

Anal. Calcd for $C_{13}H_{15}N_3O_3S$: C, 53.23; H, 5.15; N, 14.32; S, 10.93. Found: C, 53.08; H, 5.11; N, 14.28; S, 10.97.

X-ray diffraction study. All crystallographic experiments were carried out on the «Xcalibur-3» diffractometer (graphite monochromated MoKα radiation, CCD detector, ω-scanning) at 273 K. The structures were solved by direct method using SHELXTL package.[14] Structures were refined within anisotropic approximation for non-hydrogen atoms. The restrictions on the bond lengths (Csp^3–Csp^3 1.54 Å, Csp^3–N 1.49 Å, Csp^3–NH 1.46 Å, C_{Ar}–C_{Ar} 1.38 Å) in the disordered fragment were applied in the refinement of structures **5a** and **5b**. The position of the hydrogen atoms were located from the electron density map and were calculated geometrically for the disordered fragments in **5a** and **5b** and were refined by 'riding' model with U_{iso} = 1.2 U_{eq} of non-hydrogen atom bonded with given hydrogen atom in **5a** and **5b**. The position of the hydrogen atoms in other structures were located from the electron density map and refined in isotropic approximation. The crystallographic data and experimental parameters are listed in Table 4.

Table 4 Crystallographic Data for Compounds **2a–d**, **4n**, **5a**,**b**, **6k**

Parameter	**2a**	**2b**	**2c**	**2d**	**4n**	**5a**	**5b**	**6k**
a (Å)	5.1160(1)	5.1992(9)	10.6994(2)	7.7446(2)	8.9699(4)	9.5150(4)	13.9509(4)	10.451(1)
b (Å)	10.1523(2)	14.811(2)	5.4982(1)	7.6854(2)	7.9729(4)	9.8652(5)	5.9620(2)	8.5089(7)
c (Å)	13.7515(4)	10.288(1)	14.8152(3)	8.4094(3)	13.0615(5)	14.7804(7)	16.3475(5)	16.829(1)
α (°)						72.166(4)		
β (°)	98.286(2)	97.45(1)	92.039(2)	105.893(3)	94.025(4)	89.852(4)	92.496(3)	108.020(8)
γ (°)						74.490(4)		
V (Å^3)	706.79(3)	785.6(2)	870.99(3)	481.40(2)	931.80(7)	1267.9(1)	1358.42(7)	1423.2(2)
F(000)	344	376	408	220	432	560	624	624
crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	triclinic	monoclinic	monoclinic
space group	*P*21/*c*	*P*21/*c*	*P*21/*c*	*P*21	*P*21/*c*	*P*-1	*P*21/*c*	*P*21/*n*
Z	4	4	4	2	4	4	4	4
μ (mm^{-1})	0.400	0.367	0.337	0.310	0.320	0.253	0.436	0.233
D_{calcd} (g/cm^3)	1.534	1.498	1.459	1.416	1.449	1.390	1.466	1.369
2 θ_{max} (°)	50	50	60	60	60	50	60	50
measured refln	4110	4789	8272	17049	8905	10124	14899	8158
independent refln	1231	2568	2531	4400	2712	4433	3962	2490
R_{int}	0.018	0.017	0.016	0.027	0.029	0.020	0.024	0.015
reflections with $F > 4\sigma(F)$	1009	2368	2041	2368	1783	2848	2471	2065
parameters	127	100	161	178	171	360	194	257
*R*1	0.027	0.071	0.028	0.022	0.041	0.047	0.041	0.029
*wR*2	0.071	0.191	0.080	0.052	0.109	0.128	0.107	0.082
S	0.964	1.069	0.953	0.989	0.898	0.970	0.886	1.085
CCDC number	730855	730856	730857	730858	730862	730859	730860	730861

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