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PAPER

Synthesis of imidazo[4,5-*e*]thiazolo[2,3-*c*]-1,2,4-triazine-2,8-diones via a rearrangement of imidazo[4,5-*e*]thiazolo[3,2-*b*]-1,2,4-triazine-2,7-diones in the reaction with isatins†

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An aldol condensation/skeletal rearrangement protocol for the synthesis of 1,3-dialkyl-7-(2-oxo-1,2-dihydro-3*H*-indol-3-ylidene)-1,3a,4,9a-tetrahydroimidazo[4,5-*e*]thiazolo[2,3-*c*]-1,2,4-triazine-2,8(3*H*,7*H*)-diones in good to high yields via one-pot reaction of 1,3-dialkyl-3,3a,9,9a-tetrahydroimidazo[4,5-*e*]thiazolo[3,2-*b*]-1,2,4-triazine-2,7(1*H*,6*H*)-diones and 1*H*-indole-2,3-diones (isatins) or through generation and rearrangement of 1,3-dialkyl-6-(2-oxo-1,2-dihydro-3*H*-indol-3-ylidene)-3,3a,9,9a-tetrahydroimidazo[4,5-*e*]thiazolo[3,2-*b*]-1,2,4-triazine-2,7(1*H*,6*H*)-diones has been developed.

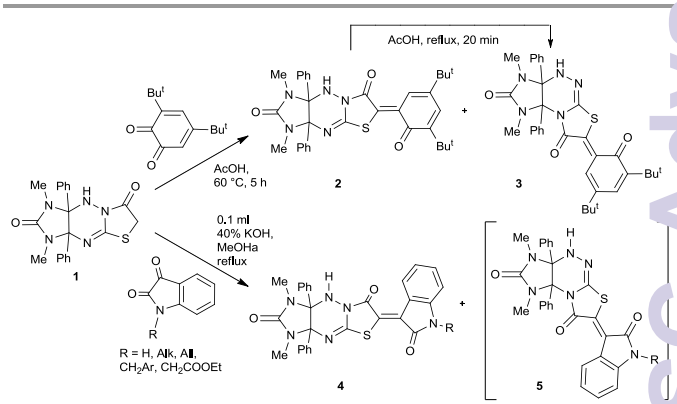
Introduction

Nitrogen- and sulfur-containing fused heterocycles have a broad range of biological activities and are attractive compounds in medicinal chemistry. Therefore, new strategies for the synthesis of such heterocyclic compounds and study of their practically valuable properties represent a challenging task for organic chemists.[1]

For instance, the synthesis of thiazolo[3,2-*b*]- or thiazolo[2,3-*c*]-1,2,4-triazines has attracted interest due to their antidepressant,[2] anti-HIV, anticancer,[3] antibacterial and antifungal activities.[4] The most common method reported in the literature for the synthesis of thiazolotriazines involves the reactions of triazinethiones with various α,β-bifunctional compounds, such as α-halogenoketones, α-halogenoaldehydes, α-halogenoacids, α,β-dihalogenoalkanes, chloroacetonitrile and others.[5] The mode of cyclization to thiazolo[3,2-*b*]-1,2,4-triazine or thiazolo[2,3-*c*]-1,2,4-triazine has been governed by the stability of the transition state, which is affected by the substituents in the triazine cycle and usually only one isomer is formed in each case.[5,6] On the one hand, unique regioselectivity is an advantage of the reactions of triazinethiones with α,β-bifunctional compounds. But, on the other hand, alternative methods for the synthesis of another isomer should be developed.[4a,7] Until now, the rearrangements of thiazolo[3,2-*b*]-1,2,4-triazine and thiazolo-[2,3-*c*]-1,2,4-triazine into each other have not been observed.

In general, the rearrangements and transformations of heterocycles in new heterocyclic structures are a nontrivial method for their preparation and have been rarely used for their target synthesis. Nevertheless, rearrangements and transformations are perspective approaches to the heterocycles that are inaccessible by other synthetic methods.[8]

5,7-Dialkyl-3-thioxoperhydroimidazo[4,5-*e*]-1,2,4-triazin-6-ones (thiones) react with halogenoacetic acids to give only imidazo[4,5-*e*]thiazolo[3,2-*b*]-1,2,4-triazine derivatives (see e.g. compound **1** in Scheme 1).[5e,6e] Recently, we have found that aldol condensation of compound **1** with 3,5-di-*tert*-butyl-1,2-benzoquinone in acetic acid led to two isomeric derivatives of imidazothiazolo[3,2-*b*]triazine **2** and imidazothiazolo[2,3-*c*]-triazine **3**, and the former was irreversibly converted into the latter upon reflux in acetic acid (Scheme 1).[9] In addition, we have studied the condensation of compound **1** with 1*H*-indole-2,3-dione (isatin) derivatives in acetic acid or in methanol in



Scheme 1 Background of This Work

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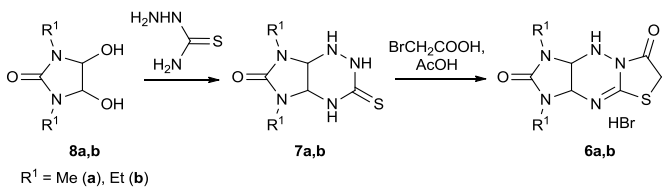
the presence of potassium hydroxide. In the latter case, in the ^{1}H NMR spectra of the reaction products **4**, the proton signals of the minor isomeric products **5** were also observed. One of the compounds **5** (R = allyl) was isolated and characterized (Scheme 1).[10] We have considered the rearrangement observed as potentially interesting for the preparation of new heterocyclic compounds. Taking into account the various biological activities of oxoindolinylidenethiazolidinones,[11] herein, we report a strategy for the synthesis of oxoindolinylidene derivatives of imidazo[4,5-*e*]thiazolo[2,3-*c*]-1,2,4-triazine via a rearrangement of corresponding readily available imidazo[4,5-*e*]thiazolo[3,2-*b*]-1,2,4-triazines.

Results and discussion

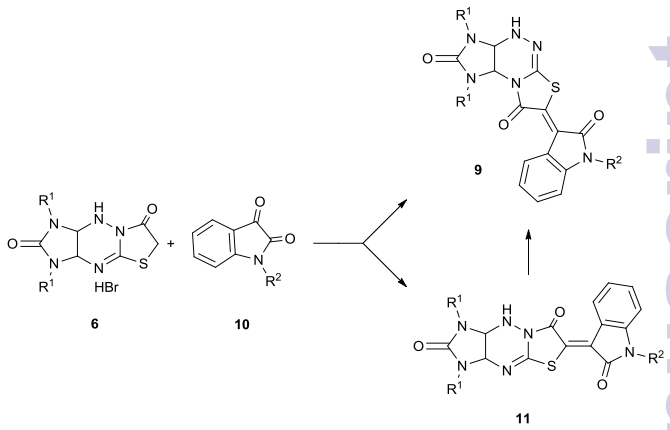
General method for the preparation of starting compounds **6a,b** from thioxoimidazotriazines **7a,b** and bromoacetic acid has been previously reported[5e] and is depicted in Scheme 2. Imidazotriazines **7a,b** were synthesized by cyclization of 4,5-dihydroxyimidazolidin-2-ones **8a,b** with thiosemicarbazide.[12]

We aimed on designing an aldol condensation/skeletal rearrangement protocol for the synthesis of oxoindolinylidene derivatives of imidazothiazolo[2,3-*c*]triazines **9** via one-pot reaction of imidazothiazolo[3,2-*b*]triazines **6** and isatins **10** or through generation and rearrangement of oxoindolinylidene derivatives **11** (Scheme 3).

We started by examining the reaction between 1,3-dimethyl derivative **6a** and isatin **10a** to optimize the reaction conditions, and the representative results are summarized in Table 1. The type of catalyst was examined using acetic acid or 40% aqueous potassium hydroxide. The reaction of compounds **6a** and **10a** led to product **11a** both in acetic acid and in methanol in the presence of KOH, but only in the presence of KOH the formation of isomeric derivative **9a** was observed (entries 1-4). Subsequently, we screened the amount of KOH (entries 3-6) and found that 1.07 equivalent of potassium hydroxide was enough to obtain compound **11a** in good yield (entry 3). To prepare isomeric product **9a** in high yield, 1.6 equivalent of potassium hydroxide was enough (entry 6). In the ^{1}H NMR spectrum of a filtrate concentrated to dryness after isolation of compound **9a**, the signals for the protons of decomposition products were observed when using 1.6 equivalent of KOH; so we have not increased the amount of catalyst any more. Further optimization was done by varying the reaction temperature, and it was found that refluxing in methanol gave the best result (entries 6, 7). Finally, it was established that the best yields of compounds **9a** and **11a**



Scheme 2 Synthesis of starting **6a,b**

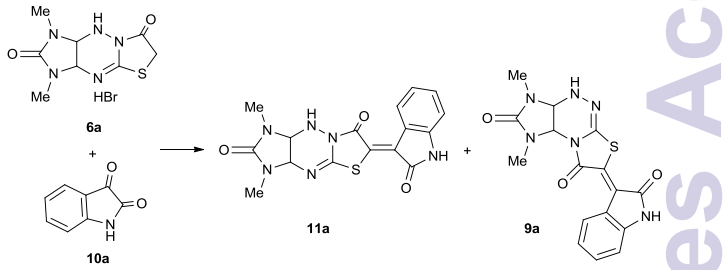


Scheme 3 Synthesis of **9** and **11**

were achieved for 120 and 30 min, respectively (entries 3,6,8-12).

With the optimized conditions in hand, we then investigated the substrate scope for this reaction. First, reactivity of different isatins **10** was studied in the condensation with compound **6a** under the optimal conditions for the synthesis of products **9** (Table 2). It was found that in addition to model substrate **10a**, various N-alkyl derivatives **10b-e** and N-phenylethyl isatin **10f** reacted efficiently with compound **6a** to afford the desired products **9a-f** in good to

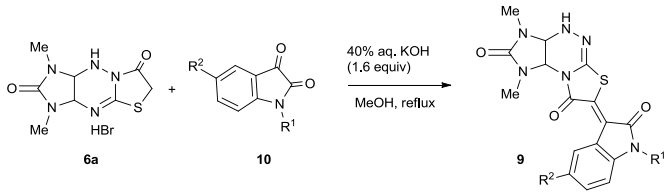
Table 1 Optimization of the Reaction Conditions[a]



entry	catalyst (equiv)	temp (°C)	time (min)	yield[b] of **11a** (%)	yield[b] of **9a** (%)
1	AcOH (as solvent)	reflux	120	17	0
2	AcOH (as solvent)	65	120	48	0
3	KOH (1.07)	reflux	120	57	0
4	KOH (1.24)	reflux	120	46	18
5	KOH (1.5)	reflux	120	0	51
6	KOH (1.6)	reflux	120	0	71
7	KOH (1.6)	40	120	0	28
8	KOH (1.07)	reflux	150	56	0
9	KOH (1.07)	reflux	90	26	0
10	KOH (1.6)	reflux	45	0	73
11	KOH (1.6)	reflux	30	0	74
12	KOH (1.6)	reflux	20	0	65

[a]Reaction conditions: heating the mixture of imidazo[4,5-*e*]thiazolo[3,2-*b*]-1,2,4-triazine **6a** (2.0 mmol), and isatin **10a** (2 mmol) either in acetic acid (15 ml) or in methanol (15 ml) with 40% aqueous KOH for 20-150 min. [b]Isolated yield.

Table 2 Synthesis of **9** via a reaction of **6a** with **10**[a]



entry	**10** R^1	R^2	product	yield[b] (%)
1	**10a** H	H	**9a**	74
2	**10b** Me	H	**9b**	66
3	**10c** Et	H	**9c**	80
4	**10d** Pr^i	H	**9d**	94
5	**10e** Bu	H	**9e**	87
6	**10f** $(CH_2)_2Ph$	H	**9f**	87
7	**10g** $CH_2CH=CH_2$	H	**9g**	80
8	**10h** $CH_2C\equiv CH$	H	**9h**	66
9	**10i** Me	Br	**9i**	92
10	**10j** CH(Me)COOMe	H	**9j**	71

[a]Reaction conditions: refluxing the mixture of imidazo[4,5-*e*]thiazolo[3,2-*b*]-1,2,4-triazine **6a** (2.0 mmol), isatins **10** (2 mmol), and 0.32 ml of 40% aqueous KOH (3.2 mmol) in methanol for 30 min. [b]Isolated yield.

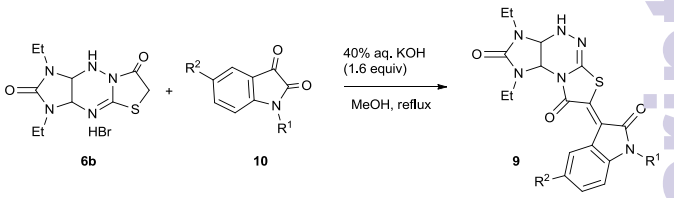
high yields (entries 1-6). N-Allyl and N-propargyl isatins **10g,h** were also applicable to this aldol condensation/skeletal rearrangement one-pot reaction, and the target products **9g,h** were obtained in 80 and 66% yield, respectively (entries 7, 8). Isatin **10i** bearing methyl substituent at the nitrogen atom and bromine atom at the 5-position was an effective substrate for this transformation, and the corresponding derivative **9i** was synthesized in 92% yield. The reaction of methyl ester of dioxoindolylpropanoic acid **10j** proceeded under the same conditions, affording the product with ester group **9j** in 71% yield. When ethyl ester of 2-(2,3-dioxo-1*H*-indol-1-yl)acetic acid **10k** was used in this reaction, no desired product was obtained. Due to the partial reesterification of ethyl ester, a mixture of methyl and ethyl esters of corresponding acid **9** was obtained (see Supplementary Information).

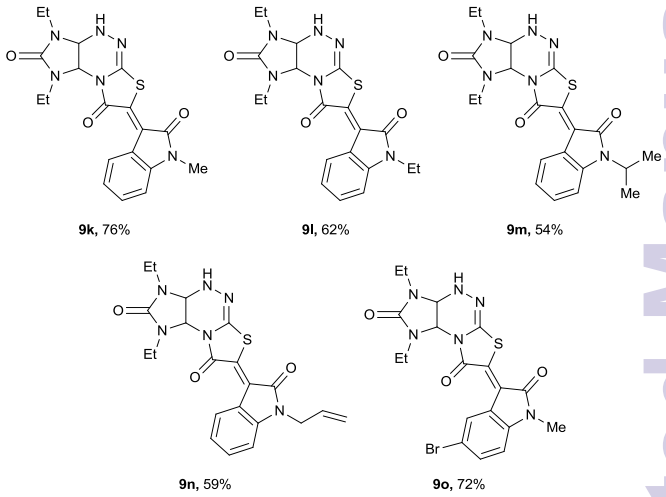
Next, 1,3-diethyl derivative **6b** was subjected to reaction with isatins **10** under the same conditions, and the results are shown in Table 3. Compound **6b** was a suitable substrate to react with isatins **10b-d,g,i**, giving the corresponding derivatives **9** bearing alkyl (**9k-m**), allyl (**9n**) substituents at the nitrogen atom and bromine atom at the 5-position of indole fragment (**9o**) in 54-76% yields.

Then various isatins **10** underwent condensation with compound **6a** under the optimal conditions for the synthesis of products **11**. It was found that unsubstituted isatin **10a** as well as isatins bearing either alkyl(arylalkyl) (**10b-d,f,m**) or functional substituent at the nitrogen atom (**10g,h,j-l,n,o**) and bromine atom at the 5-position (**10i**) could react with compound **6a** to produce the desired products **11a-n** in moderate to high yields (Table 4). The reaction was found to be tolerant to ethyl esters of dioxoindolylacetic or propanoic acids **10k,l** as well as ester of benzoic acid **10o** and generated the target products in good yields (entries 10,11,14).

1,3-Diethyl derivative **6b** was also studied in the reaction

Table 3 Synthesis of **9** via a reaction of **6b** with **10**[a]

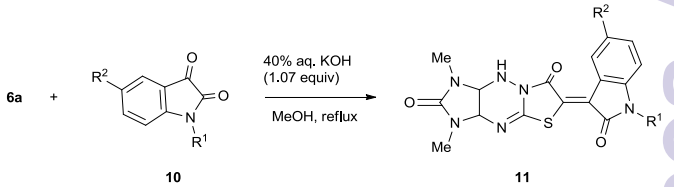




[a]Reaction conditions: refluxing the mixture of imidazo[4,5-*e*]thiazolo[3,2-*b*]-1,2,4-triazine **6b** (2.0 mmol), isatins **10** (2 mmol), and 0.32 ml of 40% aqueous KOH (3.2 mmol) in methanol for 30 min.

with isatins **10** under the same conditions, and the results are shown in Table 5. The desired N-unsubstituted (**11o**), N-alkyl

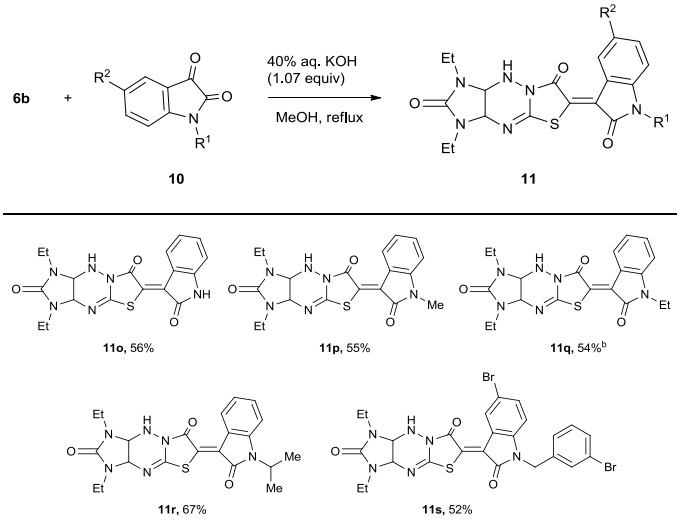
Table 4 Synthesis of **11** via a reaction of **6a** with **10**[a]



entry	**10** R^1	R^2	product	yield[b] (%)
1	**10a** H	H	**11a**	57
2	**10b** Me	H	**11b**	75
3	**10c** Et	H	**11c**	59[c]
4	**10d** Pr^i	H	**11d**	70
5	**10f** $(CH_2)_2Ph$	H	**11e**	82
6	**10g** $CH_2CH=CH_2$	H	**11f**	67
7	**10h** $CH_2C\equiv CH$	H	**11g**	67
8	**10i** Me	Br	**11h**	76
9	**10j** CH(Me)COOMe	H	**11i**	85
10	**10k** CH_2COOEt	H	**11j**	75
11	**10l** CH(Me)COOEt	H	**11k**	54
12	**10m** $CH_2C_6H_4Cl$-4	H	**11l**	55
13	**10n** CH_2OH	H	**11m**	69
14	**10o** CH_2OCOPh	H	**11n**	57

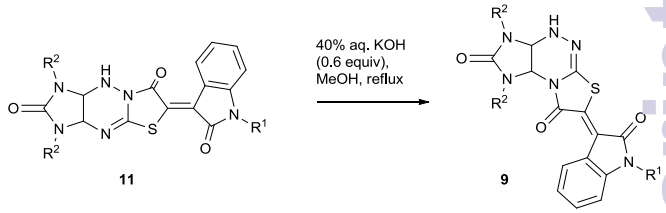
[a]Reaction conditions: refluxing the mixture of imidazo[4,5-*e*]thiazolo[3,2-*b*]-1,2,4-triazine **6a** (2.0 mmol), isatins **10** (2 mmol), and 0.215 ml of 40% aqueous KOH (2.14 mmol) in methanol for 2 h. [b]Isolated yield. [c]The reaction time was 2.5 h.

Table 5 Synthesis of **11** via a reaction of **6b** with **10**[a]



[a]Reaction conditions: refluxing the mixture of imidazo[4,5-*e*]thiazolo[3,2-*b*]-1,2,4-triazine **6b** (2.0 mmol), isatins **10** (2 mmol), and 0.215 ml of 40% aqueous KOH (2.14 mmol) in methanol for 2 h. [b]The reaction time was 2.5 h.

Table 6 Synthesis of **9** via a rearrangement of **11**[a]

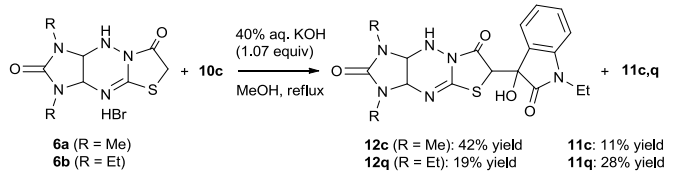


entry	**11** R^1	R^2	Product (R^1)[b]	Yield[c] (%)
1	**11a** H	Me	**9a**	89
2	**11b** Me	Me	**9b**	92
3	**11c** Et	Me	**9c**	91
4	**11d** Pr^i	Me	**9d**	93
5	**11e** $Ph(CH_2)_2$	Me	**9f**	94
6	**11f** $CH_2CH{=}CH_2$	Me	**9g**	89
7	**11h** CH(Me)COOMe	Me	**9j**	94
8	**11l** $CH_2C_6H_4Cl$-4	Me	**9p**	88
9	**11j** CH_2COOEt	Me	**9r** (CH_2COOMe)[b]	37
			9s (CH_2COOK)[b]	5
10	**11o** H	Et	**9q**	92
11	**11p** Me	Et	**9k**	91
12	**11r** Pr^i	Et	**9m**	90

[a]Reaction conditions: refluxing the mixture of imidazo[4,5-*e*]thiazolo[3,2-*b*]-1,2,4-triazine derivative **11** (2.0 mmol), and 0.12 ml of 40% aqueous KOH (1.2 mmol) in methanol for 20 min. [b]For the synthesis of **9r,s**, 0.20 ml of 40% aqueous KOH (2.4 mmol) was used. [c]Isolated yield.

(**11p-r**), and brominated at the 5-position of indole fragment N-arylalkyl (**11s**) products were synthesized in 52-67% yields. It was found that the condensation of compounds **6a,b** with 1-ethylisatin **10c** led to intermediates **12** along with the target compounds **11c,q** for 2 h (Scheme 4). Similar products were obtained by the reaction of thiazolidin-4-ones with isatins in ethanol with diethylamine as catalyst[13] or "on water" without catalyst.[14] To obtained the products **11c,q** in better yields, the interaction of compounds **6a,b** and **10c** was carried out for 2.5 h (Tables 4, 5).

Further, imidazothiazolo[3,2-*b*]triazine derivatives **11** underwent rearrangement into isomeric compounds **9** (Tables 6); 0.6 equivalent of KOH were used instead of neutralized hydrobromide, which was unavailable. All the studied compounds **11** were converted to isomers **9** in 88-94% yields. As 1,3-dimethylderivatives **11** (entries 1-9) could be employed to give the corresponding isomers **9**, the 1,3-diethylderivatives **11** (entries 10-12) could be used as well. N-Unsubstituted (**11a,o**), N-alkyl(arylalkyl)- (**11b-e,j,p,r**), N-allylsubstituted (**11f**) in indole fragment compounds underwent successfully rearrangement into target products **9**. When ethyl ester **11j** was used as substrate under the same conditions, however, the mixture of ethyl and methyl esters **9** was obtained again. Therefore, ethyl ester **11j** underwent rearrangement and reesterification with methanol using 1 equivalent of KOH.



Scheme 4 Synthesis of intermediates **12**

Partial hydrolysis of ethyl ester also took place. The yields of corresponding methyl ester **9r** and potassium salt of acid **9s** were 37 and 5%, respectively (entry 9).

All the compounds were characterized by IR, NMR and HRMS analytical methods. The signals were assigned using highly sensitive NOESY and HMBC methods. All reactions are diastereoselective and provide the products **9** and **11** as *Z*-isomers. ^{1}H NMR spectra of compounds **9a-s** and **11a-s** displayed a strong downfield shift of the indole H-4' proton signals (8.75-8.95 and 8.79-9.06 ppm, respectively), which is characteristic of proximity of the carbonyl group C(8)=O or C(7)=O. Besides, compounds **9j**, **11i** and **11k** with additional chiral carbon atom in indole moiety are obtained as a mixture of two diastereomers (1''*R**,3a*S**,9a*R**- and 1''*S**,3a*S**,9a*R**-isomers) and so some signals in the ^{1}H and ^{13}C NMR spectra of these products are double. The homogeneity of compounds **9b,d,e,n** and **11b,c** was confirmed by powder X-ray diffraction. Results of the analysis of the experimental powder diffraction patterns of the compounds **9b,d,e,n** and **11b,c** show that the investigated samples were single-phase.

Many successful cascade sequences initiated by Knoevenagel condensation[9,15] have been reported: Knoevenagel condensation/intramolecular aldol cyclization, Knoevenagel condensation/hetero-Diels-Alder reactions[17] and Knoevenagel condensation/Michael addition/cyclization reactions are among them.[18] A similar sequence that includes Knoevenagel condensation/skeletal rearrangement could be possible for the formation of imidazo[4,5-*e*]thiazolo[2,3-*c*]-1,2,4-triazine derivatives **9** from the starting **6a,b** and **10**. To get insight into the details of the reaction pathway, we

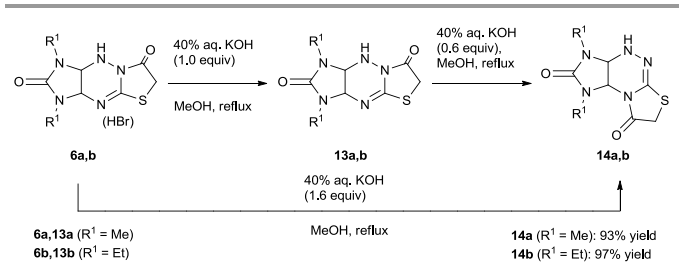
performed the rearrangement of imidazo[4,5-*e*]thiazolo[3,2-*b*]-1,2,4-triazine-2,7-diones (both hydrobromides **6a,b** and bases **13a,b**)[5e] into imidazo[4,5-*e*]thiazolo[2,3-*c*]-1,2,4-triazine-2,8-diones **14a,b** (Scheme 5). After heating compounds **13a,b** with 0.6 equivalent of KOH or hydrobromides **6a,b** with 1.6 equivalent of KOH for 45 to 60 min, the target isomers **14a,b** were prepared in high yields. The structures of **13a** and **14b** (the latter as its solvate with methanol) were unambiguously elucidated by X-ray diffraction (Figures 1, 2).

Meanwhile, one more controlled reaction was carried out to explore a plausible pathway for the formation of imidazo[4,5-*e*]thiazolo[2,3-*c*]-1,2,4-triazine derivatives **9**. When isatins **10** underwent condensation with imidazo[4,5-*e*]thiazolo[2,3-*c*]-1,2,4-triazine **14a** under reflux in methanol with 0.07 equiv. of 40% KOH, target compounds **9** were also formed (Scheme 6).

Based on the experimental results, at least two reaction pathways may be suggested. First, Knoevenagel type condensation of **13** (**6**) with isatins **10** may forego rearrangement of derivatives **11** formed into isomers **9**. Second, compounds **13** (**6**) can initially undergo rearrangement into isomers **14** followed by Knoevenagel type condensation of the latter with isatins **10**. Quantum chemical study of the reaction mechanism and investigation of biological activity of the products **9** and **11** are in progress.

Conclusions

We have developed an aldol condensation/skeletal rearrangement protocol for the synthesis of 7-ylideneimidazo[4,5-*e*]thiazolo[2,3-*c*]-1,2,4-triazine derivatives **9** in good to high yields via one-pot reaction of imidazo[4,5-*e*]thiazolo[3,2-*b*]-1,2,4-triazines **6a,b** and isatins **10** or through generation and rearrangement of 6-ylideneimidazo[4,5-*e*]thiazolo[3,2-*b*]-1,2,4-triazines **11**. Other sequence of the reactions including rearrangement of imidazo[4,5-*e*]thiazolo[3,2-*b*]-1,2,4-triazine-2,7-diones **6a,b** into imidazo[4,5-*e*]thiazolo[2,3-*c*]-1,2,4-triazine-2,8-diones **14** and Knoevenagel type condensation of the latter with isatins may be also used for two-step conversion into derivatives **9**.



Scheme 5 Synthesis of **14a,b**

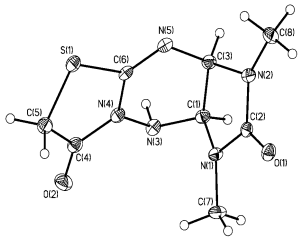


Fig. 1 General views of **13a** in representation of atoms via thermal ellipsoids (at 50% probability level).

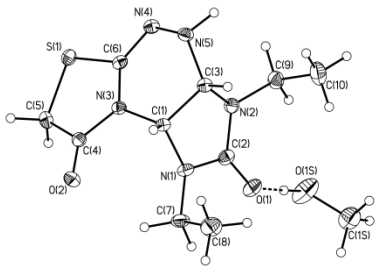


Fig. 2 General views of **14b** in representation of atoms via thermal ellipsoids (at 50% probability level).

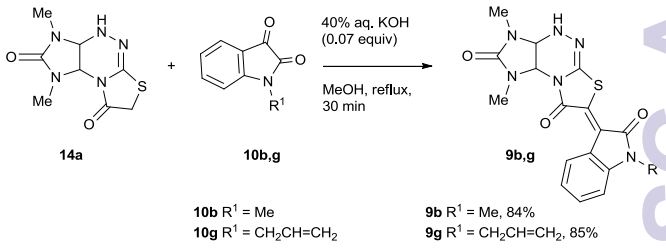
Experimental

General methods

All the reagents were purchased from Acros organics and used without further purification. Melting points were determined in open glass capillaries on a Gallenkamp (Sanyo) melting point apparatus. The ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker AM300 (300.13 MHz and 75.5 MHz, respectively) and Bruker AV600 (150.90 MHz (^{13}C)) spectrometers using DMSO-d_6 as solvent. Chemical shifts (δ) are given in ppm from TMS as internal standard. The NOESY and ^{1}H-^{13}C HMBC experiments were carried out on Bruker DRX500 spectrometer. Infrared (IR) spectra were recorded on a Bruker ALPHA instrument in KBr pellets. High resolution mass spectra (HRMS) were measured on a Bruker micrOTOF II instrument using electrospray ionization (ESI).

General procedure for the synthesis of compounds 9a-j

Procedure 1. To a stirred suspension of compound **6a** (644 mg, 2.0 mmol) and isatin **10a** (294 mg, 2.0 mmol) in refluxing methanol (15 mL), 0.32 ml of 40% aqueous KOH (3.2 mmol) was added. The resulting mixture was refluxed with stirring for 30 min. After cooling, the precipitate was filtered off and washed with water. The resulting solid product was purified by boiling in methanol (15 ml) or chloroform (15 ml) to give **9a** (548 mg, 74%).



Scheme 6 Reaction of **14a** with **10**

(*Z*)-1,3-Dimethyl-7-(2-oxo-1,2-dihydro-3*H*-indol-3-ylidene)-1,3a,4,9a-tetrahydroimidazo[4,5-*e*]thiazolo[2,3-*c*]-1,2,4-triazine-2,8(3*H*,7*H*)-dione (9a). Orange solid, mp 328-330 °C (decomp). Yield: 548 mg (74%); IR (KBr): ν_{max}/cm^{-1} 3268, 3210, 2924, 1711, 1691, 1646, 1614, 1463, 1402, 1333, 1317, 1241, 1193, 1087, 1020, 1003, 846, 827, 752; ^{1}H NMR (300 MHz, DMSO-d_6): δ (ppm) 2.67 (s, 3H), 2.93 (s, 3H), 4.82 (d, J = 5.7 Hz, 1H), 5.68 (d, J = 5.7 Hz, 1H), 6.95 (d, J = 7.7 Hz,1H), 7.06 (t, J = 7.7 Hz, 1H), 7.33 (t, J = 7.7 Hz, 1H), 8.03 (s, 1H), 8.76 (d, J = 7.9 Hz, 1H), 11.14 (s, 1H); ^{13}C NMR (75 MHz, DMSO-d_6): δ (ppm) 27.9, 31.3, 63.8, 65.7, 110.1, 120.3, 121.6, 123.0, 127.2, 130.8, 132.1, 136.9, 142.4, 159.0, 164.1, 168.5; HRMS (ESI-TOF) *m/z*: [M+H]$^+$ calcd for $C_{16}H_{14}N_6O_3S$ 371.0921, found 371.0925.

(*Z*)-1,3-Dimethyl-7-(1-methyl-2-oxo-1,2-dihydro-3*H*-indol-3-ylidene)-1,3a,4,9a-tetrahydroimidazo[4,5-*e*]thiazolo[2,3-*c*]-1,2,4-triazine-2,8(3*H*,7*H*)-dione (9b). Red solid, mp 290-291 °C (decomp). Yield: 510 mg (66%); IR (KBr): ν_{max}/cm^{-1} 3437, 3297, 2966, 2930, 1720, 1708, 1672, 1644, 1610, 1469, 1384, 1349, 1323, 1058, 1023, 802, 754; ^{1}H NMR (300 MHz, DMSO-d_6): δ (ppm) 2.67 (s, 3H), 2.93 (s, 3H), 3.26 (s, 3H), 4.83 (d, J = 5.4 Hz, 1H), 5.68 (d, J = 5.4 Hz, 1H), 7.09-7.14 (m, 2H), 7.42 (t, J = 7.5 Hz, 1H), 8.05 (s, 1H), 8.78 (d, J = 7.9 Hz, 1H); ^{13}C NMR (75 MHz, DMSO-d_6): δ (ppm) 26.4, 28.0, 31.5, 63.9, 65.9, 109.1, 119.7, 122.4, 127.1, 131.0, 131.8, 133.1, 136.8, 143.6, 159.1, 164.1, 167.1; HRMS (ESI-TOF) *m/z*: [M+H]$^+$ calcd for $C_{17}H_{16}N_6O_3S$ 385.1077, found 385.1079.

(*Z*)-7-(1-Ethyl-2-oxo-1,2-dihydro-3*H*-indol-3-ylidene)-1,3-dimethyl-1,3a,4,9a-tetrahydroimidazo[4,5-*e*]thiazolo[2,3-*c*]-1,2,4-triazine-2,8(3*H*,7*H*)-dione (9c). Orange solid, mp 282-284 °C (decomp). Yield: 640 mg (80%); IR (KBr): ν_{max}/cm^{-1} 3309, 2972, 1701, 1676, 1643, 1607, 1465, 1421, 1372, 1309, 1281, 1260, 1085, 784, 749; ^{1}H NMR (300 MHz, DMSO-d6): δ (ppm) 1.19 (t, J = 7.0 Hz, 3H), 2.67 (s, 3H), 2.93 (s, 3H), 3.80-3.87 (q, J = 7.0 Hz, 2H), 4.83 (d, J = 5.7 Hz, 1H), 5.68 (d, J = 5.7 Hz, 1H), 7.09-7.19 (m, 2H), 7.41 (t, J = 7.7 Hz, 1H), 8.05 (s, 1H), 8.80 (d, J = 7.7 Hz, 1H); ^{13}C NMR (151 MHz, DMSO-d_6): δ (ppm) 13.1, 28.4, 31.9, 35.0, 64.3, 66.3, 109.5, 120.2, 122.58, 122.61, 127.7, 131.3, 133.5, 137.2, 142.9, 159.5, 164.5, 167.2; HRMS (ESI-TOF) *m/z*: [M+H]$^+$ calcd for $C_{18}H_{18}N_6O_3S$ 399.1234, found 399.1231.

(*Z*)-1,3-Dimethyl-7-[1-(2-propyl)-2-oxo-1,2-dihydro-3*H*-indol-3-ylidene]-1,3a,4,9a-tetrahydroimidazo[4,5-*e*]thiazolo-[2,3-*c*]-1,2,4-triazine-2,8(3*H*,7*H*)-dione (9d). Orange solid, mp 298-299 °C (decomp). Yield: 773 mg (94%); IR (KBr) ν_{max}/cm-1 3433, 3279, 2971, 2925, 1727, 1680, 1647, 1606, 1465, 1339, 1315, 1246, 1197, 1023, 838, 754; ^{1}H NMR (300 MHz, DMSO-d_6): δ (ppm) 1.46 (d, J = 6.4 Hz, 6H), 2.67 (s, 3H), 2.92 (s, 3H), 4.56-4.65 (m, 1H), 4.83 (d, J = 4.9 Hz, 1H), 5.69 (d, J = 5.6 Hz, 1H), 7.11 (t, J = 7.5 Hz, 1H), 7.29 (d, J = 7.8 Hz, 1H), 7.40 (t, J = 7.4 Hz, 1H), 8.04 (s, 1H), 8.85 (d, J = 7.6 Hz, 1H); ^{13}C NMR (75 MHz, DMSO-d6): δ (ppm) 19.2, 27.9, 31.3, 44.1, 63.7, 65.7, 109.9, 119.9, 121.8, 122.3, 127.3, 130.7, 132.8, 136.8, 142.1, 159.0, 164.0, 166.7; HRMS (ESI-TOF) *m/z*: [M+H]$^+$ calcd for $C_{19}H_{20}N_6O_3S$ 413.1390, found 413.1392.

(*Z*)-7-(1-Buthyl-2-oxo-1,2-dihydro-3*H*-indol-3-ylidene)-1,3-dimethyl-1,3a,4,9a-tetrahydroimidazo[4,5-*e*]thiazolo[2,3-*c*]-1,2,4-triazine-2,8(3*H*,7*H*)-dione (9e). Orange solid, mp 258-260 °C (decomp). Yield: 741 mg (87%); IR (KBr): ν_{max}/cm^{-1} 3435, 3308, 2956, 2931, 1708, 1677, 1643, 1607, 1466, 1365, 1347, 1310, 1282, 1194, 1085, 784, 750; ^{1}H NMR (300 MHz, DMSO-d_6): δ (ppm) 0.89 (t, J = 7.2 Hz, 3H), 1.26-1.33 (m, 2H), 1.56-1.64 (m, 2H), 2.67 (s, 3H), 2.92 (s, 3H), 3.80 (t, J = 6.7 Hz, 2H), 4.82 (d, J = 5.6 Hz, 1H), 5.68 (d, J = 5.7 Hz, 1H), 7.09-7.18 (m, 2H), 7.41 (t, J = 7.6 Hz, 1H), 8.05 (s, 1H), 8.80 (d, J = 7.6 Hz, 1H); ^{13}C NMR (151 MHz, DMSO-d_6): δ (ppm) 13.6, 19.6, 28.0, 29.2, 31.5, 40.0, 63.9, 65.8, 109.2, 119.8, 122.0, 122.2, 127.3, 130.9, 133.2, 136.8, 142.8, 159.1, 164.1, 167.1; HRMS (ESI-TOF) *m/z*: [M+H]$^+$ calcd for $C_{20}H_{22}N_6O_3S$ 427.1547, found 427.1550.

(*Z*)-1,3-Dimethyl-7-(2-oxo-1-phenethyl-1,2-dihydro-3*H*-indol-3-ylidene)-1,3a,4,9a-tetrahydroimidazo[4,5-*e*]thiazolo-[2,3-*c*]-1,2,4-triazine-2,8(3*H*,7*H*)-dione (9f). Orange solid, mp 290-292 °C (decomp). Yield: 826 mg (87%); IR (KBr): ν_{max}/cm^{-1} 3269, 2922, 1718, 1684, 1646, 1607, 1467, 1384, 1365, 1336, 1318, 1248, 1177, 1024, 750; ^{1}H NMR (300 MHz, DMSO-d_6): δ (ppm) 2.67 (s, 3H), 2.92-2.95 (m, 5H), 4.03 (t, J = 7.3 Hz, 2H), 4.82 (d, J = 5.5 Hz, 1H), 5.67 (d, J = 5.9 Hz, 1H), 7.08-7.25 (m, 7H), 7.38 (t, J = 7.7 Hz, 1H), 8.05 (s, 1H), 8.80 (d, J = 7.8 Hz, 1H); ^{13}C NMR (75 MHz, DMSO-d_6): δ (ppm) 27.9, 31.4, 33.0, 41.2, 63.8, 65.8, 109.2, 119.6, 121.8, 122.1, 126.4, 127.1, 128.3, 128.8, 130.8, 133.0, 136.6, 138.1, 142.5, 159.0, 164.0, 166.9; HRMS (ESI-TOF) *m/z*: [M+H]$^+$ calcd for $C_{24}H_{22}N_6O_3S$ 475.1547, found 475.1540.

(*Z*)-7-(1-Allyl-2-oxo-1,2-dihydro-3*H*-indol-3-ylidene)-1,3-dimethyl-1,3a,4,9a-tetrahydroimidazo[4,5-*e*]thiazolo[2,3-*c*]-1,2,4-triazine-2,8(3*H*,7*H*)-dione (9g). Orange solid, mp 287-289 °C (decomp). Yield: 655 mg (80%); IR (KBr): ν_{max}/cm^{-1} 3306, 2981, 1702, 1680, 1640, 1607, 1465, 1380, 1363, 1349, 1192, 1090, 1023, 784, 752; ^{1}H NMR (300 MHz, DMSO-d_6): δ (ppm) 2.67 (s, 3H), 2.93 (s, 3H), 4.45 (br s, 2H), 4.83 (d, J = 5.1 Hz, 1H), 5.11-5.19 (m, 2H), 5.69 (d, J = 5.5 Hz, 1H), 5.84-5.93 (m, 1H), 7.07-7.17 (m, 2H), 7.41 (t, J = 7.7 Hz, 1H), 8.07 (s, 1H), 8.83 (d, J = 7.7 Hz, 1H); ^{13}C NMR (75 MHz, DMSO-d_6): δ (ppm) 27.9, 31.5, 41.9, 63.9, 65.8, 109.5, 117.1, 119.7, 122.3, 127.2, 127.5, 130.8, 130.9, 131.7, 136.7, 142.5, 159.1, 164.0, 166.9; HRMS (ESI-TOF) *m/z*: [M+H]$^+$ calcd for $C_{19}H_{18}N_6O_3S$ 411.1234, found 411.1237.

(*Z*)-1,3-Dimethyl-7-[2-oxo-1-(prop-2-yn-1-yl)-1,2-dihydro-3*H*-indol-3-ylidene]-1,3a,4,9a-tetrahydroimidazo[4,5-*e*]thiazolo[2,3-*c*]-1,2,4-triazine-2,8(3*H*,7*H*)-dione (9h). Orange solid, mp 303-305 °C (decomp). Yield: 539 mg (66%); IR (KBr): ν_{max}/cm^{-1} 3435, 3300, 2969, 2929, 2120, 1718, 1703, 1687, 1638, 1608, 1468, 1417, 1361, 1349, 1330, 1235, 1191, 1025, 808, 753; ^{1}H NMR (300 MHz, DMSO-d_6): δ (ppm) 2.69 (s, 3H), 2.95 (s, 3H), 3.23 (s, 1H), 4.69 (s, 2H), 4.85 (d, J = 5.7 Hz, 1H), 5.71 (d, J = 5.7 Hz, 1H), 7.16-7.22 (m, 2H), 7.47 (t, J = 7.7 Hz, 1H), 8.03 (s, 1H), 8.84 (d, J = 7.8 Hz, 1H); ^{13}C NMR (75 MHz, DMSO-d_6): δ (ppm) 27.9, 29.1, 31.4, 63.8, 65.8, 74.6, 77.7, 109.5, 119.8, 121.4, 122.7, 127.2, 130.7, 134.1, 136.3, 141.5, 159.0, 163.9, 166.4; HRMS (ESI-TOF) *m/z*: [M+H]$^+$ calcd for $C_{19}H_{16}N_6O_3S$ 409.1077, found 409.1073.

(*Z*)-7-(5-Bromo-1-methyl-2-oxo-1,2-dihydro-3*H*-indol-3-ylidene)-1,3-dimethyl-1,3a,4,9a-tetrahydroimidazo[4,5-*e*]-thiazolo[2,3-*c*]-1,2,4-triazine-2,8(3*H*,7*H*)-dione (9i). Dark-red solid, mp 269-271 °C (decomp). Yield: 850 mg (92%); IR (KBr):

ν_{max}/cm^{-1} 3435, 3282, 2930, 1690 (br.), 1639, 1606, 1479, 1465, 1366, 1333, 1273, 1191, 1140, 1083, 1059, 1025, 808, 755; ^{1}H NMR (300 MHz, DMSO-d_6): δ (ppm) 2.68 (s, 3H), 2.94 (s, 3H), 3.26 (s, 3H), 4.85 (d, J = 5.1 Hz, 1H), 5.70 (d, J = 5.6 Hz, 1H), 7.11 (d, J = 8.3 Hz, 1H), 7.60 (d, J = 8.3 Hz, 1H), 8.14 (s, 1H), 8.93 (s, 1H); ^{13}C NMR (75 MHz, DMSO-d_6): δ (ppm) 26.3, 27.8, 31.3, 63.7, 65.8, 110.7, 113.9, 120.5, 121.2, 129.0, 132.7, 135.0, 136.1, 142.4, 158.9, 163.8, 166.7; HRMS (ESI-TOF) *m/z*: [M+H]$^+$ calcd for $C_{17}H_{15}BrN_6O_3S$ 463.0182, found 463.0171.

(*R)-Methyl 2-((*Z*)-3-((3a*S**,9a*R**)-1,3-dimethyl-2,8-dioxo-1,2,3,3a,4,9a-hexahydroimidazo[4,5-*e*]thiazolo[2,3-*c*]-1,2,4-triazin-7(8*H*)-ylidene)-2-oxo-1,2-dihydro-3*H*-indol-1-yl)propanoate and (*S**)-Methyl 2-((*Z*)-3-((3a*S**,9a*R**)-1,3-dimethyl-2,8-dioxo-1,2,3,3a,4,9a-hexahydroimidazo[4,5-*e*]thiazolo[2,3-*c*]-1,2,4-triazin-7(8*H*)-ylidene)-2-oxo-1,2-dihydro-3*H*-indol-1-yl)-propanoate (9j).** Orange solid, mp 284-286 °C (decomp). Yield: 648 mg (71%); IR (KBr): ν_{max}/cm^{-1} 3278, 2952, 2923, 1738, 1723, 1699, 1685, 1644, 1608, 1467, 1394, 1377, 1318, 1231, 1196, 1087, 784, 755, 747; ^{1}H NMR (300 MHz, DMSO-d_6): δ (ppm) 1.58 (d, J = 7.0 Hz, 3H), 2.67 (s, 3H), 2.93 (s, 3H), 3.65 (s, 3H), 4.83 (d, J = 5.7 Hz, 1H), 5.32 (q, J = 7.0 Hz, 1H), 5.70 (d, J = 5.7 Hz, 1H), 7.10-7.18 (m, 2H), 7.41 (t, J = 7.6 Hz, 1H), 8.08 (s, 1H), 8.86 (d, J = 7.7 Hz, 1H); ^{13}C NMR (75 MHz, DMSO-d_6): δ (ppm) 14.2, 27.9, 31.3, 48.9, 52.5, 63.66, 63.73, 65.7, 109.2, 119.8, 121.3, 122.4, 127.3, 130.7, 134.0, 136.3, 141.5, 158.9, 163.8, 166.7, 170.0; HRMS (ESI-TOF) *m/z*: [M+H]$^+$ calcd for $C_{20}H_{20}N_6O_5S$ 457.1289, found 457.1280.

(*Z*)-1,3-Diethyl-7-(1-methyl-2-oxo-1,2-dihydro-3*H*-indol-3-ylidene)-1,3a,4,9a-tetrahydroimidazo[4,5-*e*]thiazolo[2,3-*c*]-1,2,4-triazine-2,8(3*H*,7*H*)-dione (9k). Orange solid, mp 265-267 °C (decomp). Yield: 626 mg (76%); IR (KBr): ν_{max}/cm^{-1} 3294, 2971, 2933, 1708, 1668, 1640, 1609, 1469, 1380, 1348, 1327, 1228, 1054, 753; ^{1}H NMR (300 MHz, DMSO-d_6): δ (ppm) 1.07 (t, J = 6.7 Hz, 3H), 1.15 (t, J = 6.6 Hz, 3H), 3.27-3.36 (m, 3H), 3.28 (s, 3H), 3.49-3.56 (m, 1H), 4.93 (d, J = 4.8 Hz, 1H), 5.77 (d, J = 5.5 Hz, 1H), 7.10-7.16 (m, 2H), 7.42 (t, J = 7.3 Hz, 1H), 7.91 (s, 1H), 8.78 (d, J = 7.7 Hz, 1H); ^{13}C NMR (75 MHz, DMSO-d_6): δ (ppm) 12.8, 13.1, 26.3, 34.9, 38.0, 61.7, 63.6, 109.0, 119.6, 122.2, 122.3, 126.9, 130.9, 132.8, 136.5, 143.5, 158.0, 164.0, 167.0; HRMS (ESI-TOF) *m/z*: [M+H]$^+$ calcd for $C_{19}H_{20}N_6O_3S$ 413.1390, found 413.1383.

(*Z*)-1,3-Diethyl-7-(1-ethyl-2-oxo-1,2-dihydro-3*H*-indol-3-ylidene)-1,3a,4,9a-tetrahydroimidazo[4,5-*e*]thiazolo[2,3-*c*]-1,2,4-triazine-2,8(3*H*,7*H*)-dione (9l). Orange solid, mp 255-256 °C (decomp). Yield: 529 mg (62%); IR (KBr): ν_{max}/cm^{-1} 3278, 2973, 2935, 1721, 1684, 1642, 1608, 1468, 1368, 1342, 1326, 1232, 1082, 1053, 752; ^{1}H NMR (300 MHz, DMSO-d_6): δ (ppm) 1.04 (t, J = 6.6 Hz, 3H), 1.13 (t, J = 6.7 Hz, 3H), 1.19 (t, J = 7.4 Hz, 3H), 3.06-3.10 (m, 1H), 3.27-3.34 (m, 2H), 3.48-3.54 (m, 1H), 3.82-3.86 (q, J = 7.4 Hz, 2H), 4.90 (d, J = 4.5 Hz, 1H), 5.76 (d, J = 5.6 Hz, 1H), 7.14 (t, J = 6.9 Hz, 1H), 7.18 (t, J = 7.2 Hz, 1H), 7.41 (t, J = 7.5 Hz, 1H), 8.04 (s, 1H), 8.79 (d, J = 7.5 Hz, 1H); ^{13}C NMR (151 MHz, DMSO-d_6): δ (ppm) 14.6, 14.7, 15.0, 36.4, 36.8, 39.9, 63.5, 65.5, 111.0, 121.6, 124.0, 124.1, 129.1, 132.8, 134.8, 138.4, 144.3, 159.9, 166.0, 168.6; HRMS (ESI-TOF) *m/z*: [M+Na]$^+$ calcd for $C_{20}H_{22}N_6O_3SNa$ 449.1366, found 449.1363.

(*Z*)-1,3-Diethyl-7-[1-(2-propyl)-2-oxo-1,2-dihydro-3*H*-indol-3-ylidene]-1,3a,4,9a-tetrahydroimidazo[4,5-*e*]thiazolo-[2,3-*c*]-1,2,4-triazine-2,8(3*H*,7*H*)-dione (9m). Orange solid, mp 257-259 °C (decomp). Yield: 476 mg (54%); IR (KBr): ν_{max}/cm^{-1} 3280, 2979, 2937, 1722, 1682, 1637, 1605, 1464, 1353, 1341, 1325, 1236, 1196, 1086, 1027, 753; ^{1}H NMR (300 MHz, DMSO-d_6): δ (ppm) 1.04 (t, J = 6.9 Hz, 3H), 1.12 (t, J = 6.9 Hz, 3H), 1.45 (d, J = 6.7 Hz, 6H), 3.03-3.10 (m, 1H), 3.24-3.31 (m, 2H), 3.46-3.53 (m, 1H), 4.56-4.62 (m, 1H), 4.90 (d, J = 5.1 Hz, 1H), 5.75 (d, J = 5.6 Hz, 1H), 7.12 (t, J = 7.5 Hz, 1H), 7.29 (d, J = 7.8 Hz, 1H), 7.40 (t, J = 7.5 Hz, 1H), 8.01 (s, 1H), 8.84 (d, J = 7.8 Hz, 1H); ^{13}C NMR (75 MHz, DMSO-d_6): δ (ppm) 12.7, 13.0, 19.2, 34.9, 38.0, 44.1, 61.6, 63.5, 109.9, 119.8, 121.9, 122.3, 127.2, 130.8, 132.7, 136.6, 142.1, 157.9, 164.0, 166.8; HRMS (ESI-TOF) *m/z*: [M+H]$^+$ calcd for $C_{21}H_{24}N_6O_3S$ 441.1703, found 441.1695.

(*Z*)-7-(1-Allyl-2-oxo-1,2-dihydro-3*H*-indol-3-ylidene)-1,3-diethyl-1,3a,4,9a-tetrahydroimidazo[4,5-*e*]thiazolo[2,3-*c*]-1,2,4-triazine-2,8(3*H*,7*H*)-dione (9n). Orange solid, mp 255-257 °C (decomp). Yield: 517 mg (59%); IR (KBr): ν_{max}/cm^{-1} 3426, 3280, 2969, 2932, 2919, 1721, 1686, 1640, 1610, 1468, 1362, 1344, 1325, 1229, 1191, 1088, 753; ^{1}H NMR (300 MHz, DMSO-d_6): δ (ppm) 1.04 (t, J = 6.9 Hz, 3H), 1.14 (t, J = 6.7 Hz, 3H), 3.04-3.11 (m, 1H), 3.25-3.32 (m, 2H), 3.47-3.54 (m, 1H), 4.45 (br.s, 2H), 4.91 (d, J = 5.5 Hz, 1H), 5.11-5.19 (m, 2H), 5.76 (d, J = 5.7 Hz, 1H), 5.83-5.91 (m, 1H), 7.06-7.17 (m, 2H), 7.40 (t, J = 7.7 Hz, 1H), 8.04 (s, 1H), 8.81 (d, J = 7.8 Hz, 1H); ^{13}C NMR (151 MHz, DMSO-d_6): δ (ppm) 13.3, 13.6, 35.4, 38.5, 42.4, 62.2, 64.1, 110.0, 117.6, 120.2, 122.4, 122.8, 127.6, 131.3, 132.2, 133.7, 136.9, 143.0, 158.5, 164.5, 167.3; HRMS (ESI-TOF) *m/z*: [M+H]$^+$ calcd for $C_{21}H_{22}N_6O_3S$ 439.1547, found 439.1541.

(*Z*)-7-(5-Bromo-1-methyl-2-oxo-1,2-dihydro-3*H*-indol-3-ylidene)-1,3-diethyl-1,3a,4,9a-tetrahydroimidazo[4,5-*e*]thiazolo[2,3-*c*]-1,2,4-triazine-2,8(3*H*,7*H*)-dione (9o). Red solid, mp 285-287 °C (decomp). Yield: 708 mg (72%); IR (KBr): ν_{max}/cm^{-1} 3300, 2972, 2933, 1723, 1687, 1634, 1604, 1464, 1415, 1366, 1333, 1224, 1187, 1081, 1049, 908, 814, 752; ^{1}H NMR (300 MHz, DMSO-d_6): δ (ppm) 1.07 (t, J = 6.9 Hz, 3H), 1.15 (t, J = 6.9 Hz, 3H), 3.07-3.14 (m, 1H), 3.27 (s, 3H), 3.27-3.37 (m, 2H), 3.50-3.57 (m, 1H), 4.95 (d, J = 4.8 Hz, 1H), 5.78 (d, J = 5.8 Hz, 1H), 7.10 (d, J = 8.2 Hz, 1H), 7.59 (d, J = 8.2 Hz, 1H), 7.99 (s, 1H), 8.95 (s, 1H); ^{13}C NMR (75 MHz, DMSO-d_6): δ (ppm) 12.8, 13.2, 26.5, 35.0, 38.2, 61.9, 63.9, 111.0, 114.0, 120.8, 121.4, 129.1, 132.9, 135.1, 136.1, 142.7, 158.0, 164.0, 166.8; HRMS (ESI-TOF) *m/z*: [M+H]$^+$ calcd for $C_{19}H_{19}BrN_6O_3S$ 491.0501, found 491.0498.

General procedure for the synthesis of compounds 11a-n

To a stirred suspension of compound **6a** (644 mg, 2.0 mmol) and isatin **10a** (294 mg, 2.0 mmol) in refluxing methanol (15 mL), 0.215 ml of 40% aqueous KOH (2.14 mmol) was added. The resulting mixture was refluxed with stirring for 2 h. After cooling, the precipitate was filtered off and washed with water. The resulting solid product was purified by boiling in methanol (15 ml) or chloroform (15 ml) to give **11a** (421 mg, 57%).

(*Z*)-1,3-Dimethyl-6-(2-oxo-1,2-dihydro-3*H*-indol-3-ylidene)-3,3a,9,9a-tetrahydroimidazo[4,5-*e*]thiazolo[3,2-*b*]-1,2,4-triazine-2,7(1*H*,6*H*)-dione (11a). Light brown solid, mp 224-226 °C (decomp). Yield: 421 mg (57%); IR (KBr): ν_{max}/cm^{-1} 3430, 3176, 3063, 2932, 1697, 1635, 1482, 1461, 1399, 1346, 1306, 1265, 1132, 1081, 1016, 789, 750; ^{1}H NMR (300 MHz, DMSO-d_6): δ (ppm) 2.61 (s, 3H), 2.79 (s, 3H), 4.80 (d, J = 5.9 Hz, 1H), 4.91 (d, J = 5.9 Hz, 1H), 6.95 (d, J = 7.6 Hz, 1H), 6.96 (s, 1H), 7.07 (t, J = 7.8 Hz, 1H), 7.37 (t, J = 7.7 Hz, 1H), 8.79 (d, J = 7.9 Hz, 1H), 11.18 (s, 1H); ^{13}C NMR (75 MHz, DMSO-d_6): δ (ppm) 26.9, 27.8, 65.1, 66.1, 110.3, 120.0, 121.9, 125.5, 127.6, 129.0, 131.8, 143.1, 150.2, 158.7, 160.5, 168.5; HRMS (ESI-TOF) *m/z*: [M+H]$^+$ calcd for $C_{16}H_{14}N_6O_3S$ 371.0921, found 371.0918.

(*Z*)-1,3-Dimethyl-6-(1-methyl-2-oxo-1,2-dihydro-3*H*-indol-3-ylidene)-3,3a,9,9a-tetrahydroimidazo[4,5-*e*]thiazolo[3,2-*b*]-1,2,4-triazine-2,7(1*H*,6*H*)-dione (11b). Orange solid, mp 297-299 °C (decomp). Yield: 579 mg (75%); IR (KBr): ν_{max}/cm^{-1} 3435, 3195, 3005, 2970, 2935, 1720, 1689, 1644, 1610, 1590, 1486, 1471, 1452, 1377, 1348, 1266, 1244, 1138, 1113, 1069, 1016, 878, 783, 744; ^{1}H NMR (300 MHz, DMSO-d_6): δ (ppm) 2.65 (s, 3H), 2.82 (s, 3H), 3.25 (s, 3H), 4.80 (d, J = 5.7 Hz, 1H), 4.92 (d, J = 5.7 Hz, 1H), 6.93 (s, 1H), 7.08-7.14 (m, 2H), 7.44 (t, J = 6.6 Hz, 1H), 8.81 (d, J = 7.8 Hz, 1H); ^{13}C NMR (75 MHz, DMSO-d_6): δ (ppm) 26.2, 26.9, 27.8, 65.1, 66.1, 109.1, 119.3, 122.4, 125.8, 127.3, 131.2, 131.7, 144.1, 150.0, 158.7, 160.3, 166.9; HRMS (ESI-TOF) *m/z*: [M+H]$^+$ calcd for $C_{17}H_{16}N_6O_3S$ 385.1077, found 385.1069.

(*Z*)-6-(1-Ethyl-2-oxo-1,2-dihydro-3*H*-indol-3-ylidene)-1,3-dimethyl-3,3a,9,9a-tetrahydroimidazo[4,5-*e*]thiazolo[3,2-*b*]-1,2,4-triazine-2,7(1*H*,6*H*)-dione (11c). The product was isolated via the general procedure but the reaction time was 2.5 h. Orange solid, mp 269-271 °C (decomp). Yield: 469 mg (59%); IR (KBr): ν_{max}/cm^{-1} 3433, 3218, 3002, 2917, 1723, 1688, 1639, 1607, 1466, 1376, 1349, 1248, 1120, 1071, 1015, 879, 745; ^{1}H NMR (300 MHz, DMSO-d_6): δ (ppm) 1.18 (t, J = 6.9 Hz, 3H), 2.61 (s, 3H), 2.80 (s, 3H), 3.78-3.85 (q, J = 6.9 Hz, 2H), 4.80 (dd, J = 2.2, 5.9 Hz, 1H), 4.92 (d, J = 5.9 Hz, 1H), 6.98 (d, J = 2.2 Hz, 1H), 7.10-7.20 (m, 2H), 7.45 (t, J = 7.7 Hz, 1H), 8.84 (d, J = 7.7 Hz, 1H); ^{13}C NMR (75 MHz, DMSO-d_6): δ (ppm) 12.6, 26.9, 27.8, 34.5, 65.2, 66.1, 109.1, 119.5, 122.3, 124.6, 127.6, 129.7, 131.7, 143.0, 150.0, 158.7, 160.4, 166.6; HRMS (ESI-TOF) *m/z*: [M+H]$^+$ calcd for $C_{18}H_{18}N_6O_3S$ 399.1234, found 399.1234.

(*Z*)-1,3-Dimethyl-6-[1-(2-propyl)-2-oxo-1,2-dihydro-3*H*-indol-3-ylidene]-3,3a,9,9a-tetrahydroimidazo[4,5-*e*]thiazolo-[3,2-*b*]-1,2,4-triazine-2,7(1*H*,6*H*)-dione (11d). Orange solid, mp 236-237 °C (decomp). Yield: 577 mg (70%); IR (KBr): ν_{max}/cm^{-1} 3431, 3271, 2974, 2937, 1726, 1702, 1681, 1638, 1605, 1461, 1364, 1313, 1135, 1259, 1079, 1009, 871, 787, 756; ^{1}H NMR (300 MHz, DMSO-d_6): δ (ppm) 1.44 (d, J = 6.6 Hz, 6H), 2.61 (s, 3H), 2.79 (s, 3H), 4.55-4.61 (m, 1H), 4.80 (d, J = 5.1 Hz, 1H), 4.91 (d, J = 5.7 Hz, 1H), 6.99 (s, 1H), 7.12 (t, J = 7.5 Hz, 1H), 7.28 (d, J = 7.9 Hz, 1H), 7.43 (t, J = 7.5 Hz, 1H), 8.88 (d, J = 7.8 Hz, 1H); ^{13}C NMR (75 MHz, DMSO-d_6): δ (ppm) 19.09, 19.13, 26.9, 27.8, 44.2, 65.1, 66.0, 110.1, 119.6, 122.0, 124.7, 127.7, 129.6, 131.6, 142.8, 150.1, 158.6, 160.4, 166.7; HRMS (ESI-TOF) *m/z*: [M+H]$^+$ calcd for $C_{19}H_{20}N_6O_3S$ 413.1390; found 413.1382.

(*Z*)-1,3-Dimethyl-6-(2-oxo-1-phenethyl-1,2-dihydro-3*H*-indol-3-ylidene)-3,3a,9,9a-tetrahydroimidazo[4,5-*e*]thiazolo-[3,2-*b*]-1,2,4-triazine-2,7(1*H*,6*H*)-dione (11e). Orange solid, mp 244-246 °C (decomp). Yield: 778 mg (82%); IR (KBr): ν_{max}/cm^{-1} 3435, 3239, 2948, 2930, 2897, 1738, 1682, 1626, 1607, 1466, 1349, 1250, 1126, 1012, 873, 778, 750; ^{1}H NMR (300 MHz, DMSO-d_6): δ (ppm) 2.62 (s, 3H), 2.80 (s, 3H), 2.92 (t, J = 7.3 Hz, 2H), 4.00 (t, J = 7.3 Hz, 2H), 4.80 (d, J = 5.9 Hz, 1H), 4.92 (d, J = 5.9 Hz, 1H), 6.96 (s, 1H), 7.08-7.28 (m, 7H), 7.41 (t, J = 7.7 Hz, 1H), 8.82 (d, J = 7.8 Hz, 1H); ^{13}C NMR (151 MHz, DMSO-d_6): δ (ppm) 27.0, 27.9, 33.0, 41.2, 65.2, 66.1, 109.4, 119.3, 122.4, 124.5, 126.5, 127.5, 128.4, 128.8, 129.8, 131.8, 138.1, 143.3, 150.0, 158.7, 160.4, 166.9; HRMS (ESI-TOF) *m/z*: [M+Na]$^+$ calcd for $C_{24}H_{22}N_6O_3SNa$ 497.1366, found 497.1359.

(*Z*)-6-(1-Allyl-2-oxo-1,2-dihydro-3*H*-indol-3-ylidene)-1,3-dimethyl-3,3a,9,9a-tetrahydroimidazo[4,5-*e*]thiazolo[3,2-*b*]-1,2,4-triazine-2,7(1*H*,6*H*)-dione (11f). Orange solid, mp 23[illegible]-240 °C (decomp). Yield: 549 mg (67%); IR (KBr): ν_{max}/cm^{-1} 3435, 3217, 2929, 1723, 1686, 1638, 1607, 1466, 1377, 1351, 1247, 1119, 1076, 1015, 876, 750; ^{1}H NMR (300 MHz, DMSO-d_6): δ (ppm) 2.63 (s, 3H), 2.81 (s, 3H), 4.40 (d, J = 3.8 Hz, 2H), 4.81 (d, J = 5.9 Hz, 1H), 4.93 (d, J = 5.9 Hz, 1H), 5.11-5.18 (m, 2H), 5.80-5.91 (m, 1H), 6.99 (s, 1H), 7.03-7.13 (m, 2H), 7.40 (t, J = 7.7 Hz, 1H), 8.82 (d, J = 7.8 Hz, 1H); ^{13}C NMR (75 MHz, DMSO-d_6): δ (ppm) 26.9, 27.8, 41.9, 65.2, 66.1, 109.6, 117.2, 119.4, 122.4, 124.3, 126.2, 127.5, 130.1, 131.6, 143.1, 149.9, 158.7, 160.3, 166.7; HRMS (ESI-TOF) *m/z*: [M+H]$^+$ calcd for $C_{19}H_{18}N_6O_3S$ 411.1234, found 411.1226.

(*Z*)-1,3-Dimethyl-6-[2-oxo-1-(prop-2-yn-1-yl)-1,2-dihydro-3*H*-indol-3-ylidene]-3,3a,9,9a-tetrahydroimidazo[4,5-*e*]thiazolo[3,2-*b*]-1,2,4-triazine-2,7(1*H*,6*H*)-dione (11g). Orange solid, mp 238-240 °C (decomp). Yield: 547 mg (67%); IR (KBr): ν_{max}/cm^{-1} 3436, 3222, 2928, 2126, 1690, 1635, 1608, 1466, 1362, 1245, 1125, 1081, 1014, 875, 750; ^{1}H NMR (300 MHz, DMSO-d_6): δ (ppm) 2.61 (s, 3H), 2.80 (s, 3H), 3.32 (s, 1H), 4.67 (br.s, 2H), 4.81 (d, J = 5.9 Hz, 1H), 4.93 (d, J = 5.9 Hz, 1H), 6.99 (br.s, 1H), 7.16-7.25 (m, 2H), 7.50 (t, J = 7.7 Hz, 1H), 8.87 (d, J = 7.8 Hz, 1H); ^{13}C NMR (75 MHz, DMSO-d_6): δ (ppm) 27.0, 27.9, 29.1, 65.2, 66.0, 74.7, 77.5, 109.6, 119.5, 122.8, 123.9, 127.5, 130.8, 131.6, 142.0, 149.8, 158.7, 160.2, 166.2; HRMS (ESI-TOF) *m/z*: [M+H]$^+$ calcd for $C_{19}H_{16}N_6O_3S$ 409.1077, found 409.1075.

(*Z*)-6-(5-Bromo-1-methyl-2-oxo-1,2-dihydro-3*H*-indol-3-ylidene)-1,3-dimethyl-3,3a,9,9a-tetrahydroimidazo[4,5-*e*]thiazolo[3,2-*b*]-1,2,4-triazine-2,7(1*H*,6*H*)-dione (11h). Light orange solid, mp 272-273 °C (decomp). Yield: 704 mg (76%); IR (KBr): ν_{max}/cm^{-1} 3178, 2931, 1729, 1688, 1645, 1607, 1466, 1366, 1320, 1267, 1144, 1126, 1078, 1063, 1016, 849, 798, 787; ^{1}H NMR (300 MHz, DMSO-d_6): δ (ppm) 2.63 (s, 3H), 2.81 (s, 3H), 3.22 (s, 3H), 4.82 (d, J = 5.7 Hz, 1H), 4.95 (d, J = 5.7 Hz, 1H), 7.05 (s, 1H), 7.08 (d, J = 8.3 Hz, 1H), 7.62 (d, J = 8.3 Hz, 1H), 8.96 (1H, s); ^{13}C NMR (75 MHz, DMSO-d_6): δ (ppm) 26.4, 26.9, 27.8, 65.2, 66.0, 110.9, 114.1, 120.9, 123.1, 129.4, 131.7, 133.6, 143.1, 149.6, 158.6, 160.2, 166.5; HRMS (ESI-TOF) *m/z*: [M+H]$^+$ calcd for $C_{17}H_{15}BrN_6O_3S$ 463.0182, found 463.0192.

(*R)-Methyl 2-((*Z*)-3-((3a*S**,9a*R**)-1,3-dimethyl-2,7-dioxo-1,2,3,3a,9,9a-hexahydroimidazo[4,5-*e*]thiazolo[3,2-*b*]-1,2,4-

triazin-6(7H)-ylidene)-2-oxo-1,2-dihydro-3*H*-indolyl-1-)propanoate and (*S)-Methyl 2-((*Z*)-3-((3a*S**,9a*R**)-1,3-dimethyl-2,7-dioxo-1,2,3,3a,9,9a-hexahydroimidazo[4,5-*e*]thiazolo[3,2-*b*]-1,2,4-triazin-6(7H)-ylidene)-2-oxo-1,2-dihydro-3*H*-indolyl-1-) propanoate (11i).** Light orange solid, mp 252-254 °C (decomp). Yield: 776 mg (85%); IR (KBr): ν_{max}/cm^{-1} 3231, 2954, 1751, 1737, 1722, 1696, 1640, 1607, 1463, 1370, 1264, 1252, 1075, 1015, 877, 745; ^{1}H NMR (300 MHz, DMSO-d_6): δ (ppm) 1.57 (d, *J* = 7.1 Hz, 3H), 2.61 (s, 3H), 2.79 (s, 3H), 3.64, 3.65 (both s, in total 3H), 4.81 (dd, *J* = 2.0, 5.8 Hz, 1H), 4.92 (d, *J* = 5.8 Hz, 1H), 5.27-5.34 (q, *J* = 7.1 Hz, 1H), 7.00 (br.s, 1H), 7.11-7.19 (m, 2H), 7.45 (t, *J* = 7.7 Hz, 1H), 8.90 (d, *J* = 7.9 Hz, 1H); ^{13}C NMR (75 MHz, DMSO-d_6): δ (ppm) 14.17, 14.21, 26.9, 27.8, 49.0, 52.5, 52.6, 65.2, 66.0, 109.5, 119.6, 122.6, 123.9, 127.8, 130.8, 131.7, 142.2, 149.7, 158.6, 160.2, 166.7, 170.0; HRMS (ESI-TOF) *m/z*: [M+H]$^+$ calcd for $C_{20}H_{20}N_6O_5S$ 457.1289, found 457.1281.

(*Z*)-Ethyl 2-(3-(1,3-dimethyl-2,7-dioxo-1,2,3,3a,9,9a-hexahydroimidazo[4,5-*e*]thiazolo[3,2-*b*]-1,2,4-triazin-6(7*H*)-ylidene)-2-oxo-1,2-dihydro-3*H*-indolyl-1-)acetate (11j). Orange solid, mp 275-276 °C (decomp). Yield: 685 mg (75%); IR (KBr): ν_{max}/cm^{-1} 3432, 3277, 2931, 1742, 1699, 1638, 1609, 1469, 1374, 1349, 1233, 1128, 1013, 876, 760; ^{1}H NMR (300 MHz, DMSO-d_6): δ (ppm) 1.20 (t, *J* = 7.0 Hz, 3H), 2.63 (s, 3H), 2.80 (s, 3H), 4.12-4.19 (q, *J* = 7.0 Hz, 2H), 4.69 (s, 2H), 4.81 (d, *J* = 5.8 Hz, 1H), 4.92 (d, *J* = 5.8 Hz, 1H), 6.98 (s, 1H), 7.12-7.17 (m, 2H), 7.42 (t, *J* = 7.6 Hz, 1H), 8.84 (d, *J* = 7.6 Hz, 1H); ^{13}C NMR (75 MHz, DMSO-d_6): δ (ppm) 14.0, 27.0, 27.8, 41.4, 61.4, 65.3, 66.1, 109.4, 119.4, 122.8, 123.9, 127.5, 130.7, 131.7, 143.0, 149.8, 158.7, 160.3, 167.2, 167.6; HRMS (ESI-TOF) *m/z*: [M+H]$^+$ calcd for $C_{20}H_{20}N_6O_5S$ 457.1289, found 457.1280.

(*R)-Ethyl 2-((*Z*)-3-((3a*S**,9a*R**)-1,3-dimethyl-2,7-dioxo-1,2,3,3a,9,9a-hexahydroimidazo[4,5-*e*]thiazolo[3,2-*b*]-1,2,4-triazin-6(7H)-ylidene)-2-oxo-1,2-dihydro-3H-indolyl-1-)propanoate and (*S**)-Ethyl 2-((*Z*)-3-((3a*S**,9a*R**)-1,3-dimethyl-2,7-dioxo-1,2,3,3a,9,9a-hexahydroimidazo[4,5-*e*]thiazolo[3,2-*b*]-1,2,4-triazin-6(7H)-ylidene)-2-oxo-1,2-dihydro-3H-indolyl-1-) propanoate (11k).** Orange solid, mp 250-252 °C (decomp). Yield: 508 mg (54%); IR (KBr): ν_{max}/cm^{-1} 3197, 2963, 2941, 1751, 1726, 1699, 1640, 1605, 1464, 1368, 1352, 1253, 1179, 1074, 1017, 874, 786, 744; ^{1}H NMR (300 MHz, DMSO-d_6): δ (ppm) 1.11 (t, *J* = 7.0 Hz, 3H), 1.57 (d, *J* = 6.3 Hz, 3H), 2.61 (s, 3H), 2.79 (s, 3H), 4.07-4.18 (m, 2H), 4.81 (dd, *J* = 2.2, 5.9 Hz, 1H), 4.92 (d, *J* = 5.9 Hz, 1H), 5.24-5.31 (q, *J* = 6.3 Hz, 1H), 6.99 (t, *J* = 2.9 Hz, 1H), 7.11-7.19 (m, 2H), 7.45 (t, *J* = 7.8 Hz, 1H), 8.89 (d, *J* = 7.8 Hz, 1H); ^{13}C NMR (75 MHz, DMSO-d_6): δ (ppm) 13.9, 14.17, 14.20, 26.9, 27.8, 49.1, 61.3, 65.2, 66.0, 109.5, 119.6, 122.6, 123.9, 127.7, 130.7, 131.6, 142.2, 149.76, 149.80, 158.6, 160.3, 166.7, 169.4; HRMS (ESI-TOF) *m/z*: [M+H]$^+$ calcd for $C_{21}H_{22}N_6O_5S$ 471.1445, found 471.1440.

(*Z*)-6-[1-(4-Chlorobenzyl)-2-oxo-1,2-dihydro-3*H*-indol-3-ylidene]-1,3-dimethyl-3,3a,9,9a-tetrahydroimidazo[4,5-*e*]-thiazolo[3,2-*b*]-1,2,4-triazine-2,7(1*H*,6*H*)-dione (11l). Orange solid, mp 245-247 °C (decomp). Yield: 545 mg (55%); IR (KBr): ν_{max}/cm^{-1} 3287, 2929, 1714, 1686, 1639, 1608, 1465, 1380, 1360, 1260, 1187, 1131, 1084, 1008, 756; ^{1}H NMR (300 MHz, DMSO-d_6): δ (ppm) 2.61 (s, 3H), 2.80 (s, 3H), 4.81 (dd, *J* = 2.0, 5.9 Hz, 1H), 4.93 (d, *J* = 5.9 Hz, 1H), 5.03 (s, 2H), 7.00 (d, *J* = 2.0 Hz, 1H), 7.05-7.16 (m, 2H), 7.32-7.41 (m, 5H), 8.86 (d, *J* = 7.9 Hz, 1H); ^{13}C NMR (75 MHz, DMSO-d_6): δ (ppm) 26.9, 27.8, 42.4, 65.2, 66.1, 109.6, 119.6, 122.7, 124.2, 127.6, 128.7, 129.1, 130.6, 131.6, 132.2, 134.9, 142.8, 149.9, 158.7, 160.3, 167.2; HRMS (ESI-TOF) *m/z*: [M+H]$^+$ calcd for $C_{23}H_{19}ClN_6O_3S$ 495.1001, found 495.0997.

(*Z*)-6-(1-Hydroxymethyl-2-oxo-1,2-dihydro-3*H*-indol-3-ylidene)-1,3-dimethyl-3,3a,9,9a-tetrahydroimidazo[4,5-*e*]thiazolo[3,2-*b*]-1,2,4-triazine-2,7(1*H*,6*H*)-dione (11m). Orange solid, mp 254-256 °C (decomp). Yield: 552 mg (69%); IR (KBr): ν_{max}/cm^{-1} 3369, 3246, 2963, 1706, 1687, 1638, 1607, 1464, 1365, 1262, 1138, 1062, 1038, 878, 751; ^{1}H NMR (300 MHz, DMSO-d_6): δ (ppm) 2.62 (s, 3H), 2.80 (s, 3H), 4.80 (dd, *J* = 2.2, 5.9 Hz, 1H), 4.92 (d, *J* = 5.9 Hz, 1H), 5.18 (d, *J* = 7.1 Hz, 2H), 6.44 (t, *J* = 7.1 Hz, 1H), 6.97 (d, *J* = 2.2 Hz, 1H), 7.16 (t, *J* = 7.7 Hz, 1H), 7.24 (d, *J* = 7.7 Hz, 1H), 7.47 (t, *J* = 7.7 Hz, 1H), 8.86 (d, *J* = 7.8 Hz, 1H); ^{13}C NMR (75 MHz, DMSO-d_6): δ (ppm) 26.9, 27.8, 62.8, 65.1, 66.1, 110.1, 119.4, 122.7, 124.5, 127.5, 130.1, 131.6, 142.8, 149.9, 158.7, 160.3, 166.8; HRMS (ESI-TOF) *m/z*: [M+Na]$^+$ calcd for $C_{17}H_{16}N_6O_4SNa$ 423.0846, found 423.0847.

(*Z*)-(3-(1,3-Dimethyl-2,7-dioxo-1,2,3,3a,9,9a-hexahydro-imidazo[4,5-*e*]thiazolo[3,2-*b*]-1,2,4-triazin-6(7*H*)-ylidene)-2-oxo-1,2-dihydro-3*H*-indolyl-1-)methyl benzoate (11n). Orange solid, mp 262-264 °C (decomp). Yield: 621 mg (57%); IR (KBr): ν_{max}/cm^{-1} 3261, 2965, 2912, 1714, 1694, 1637, 1609, 1468, 1365, 1263, 1132, 1080, 1063, 1009, 950, 878, 767; ^{1}H NMR (300 MHz, DMSO-d_6): δ (ppm) 2.62 (s, 3H), 2.80 (s, 3H), 4.82 (dd, *J* = 2.3, 5.9 Hz, 1H), 4.93 (d, *J* = 5.9 Hz, 1H), 6.10 (dd, *J* = 1.2, 13.7 Hz, 2H), 7.01 (d, *J* = 2.3 Hz, 1H), 7.22 (t, *J* = 7.6 Hz, 1H), 7.42 (d, *J* = 7.9 Hz, 1H), 7.48-7.53 (m, 3H), 7.66 (t, *J* = 7.4 Hz, 1H), 7.94 (d, *J* = 7.5 Hz, 2H), 8.91 (d, *J* = 7.9 Hz, 1H); ^{13}C NMR (75 MHz, DMSO-d_6): δ (ppm) 27.1, 28.0, 64.2, 65.4, 66.2, 110.1, 119.7, 123.5, 127.8, 128.8, 128.9, 129.0, 129.49, 129.54, 132.0, 134.0, 141.8, 149.8, 158.9, 160.4, 165.1, 167.3; HRMS (ESI-TOF) *m/z*: [M+H]$^+$ calcd for $C_{24}H_{20}N_6O_5S$ 505.1289, found 505.1290.

(Z)-1,3-Diethyl-6-(2-oxo-1,2-dihydro-3*H*-indol-3-ylidene)-3,3a,9,9a-tetrahydroimidazo[4,5-*e*]thiazolo[3,2-*b*]-1,2,4-triazine-2,7(1*H*,6*H*)-dione (11o). Red-orange solid, mp 285-287 °C (decomp). Yield: 446 mg (56%); IR (KBr): ν_{max}/cm^{-1} 3250, 2976, 2944, 1706, 1642, 1618, 1459, 1381, 1334, 1244, 1077, 752; ^{1}H NMR (300 MHz, DMSO-d_6): δ (ppm) 0.97 (t, *J* = 6.9 Hz, 3H), 1.15 (t, *J* = 7.1 Hz, 3H), 3.11-3.18 (m, 3H), 3.32-3.39 (m, 1H), 4.92-4.98 (m, 2H), 6.93-6.96 (m, 2H), 7.06 (t, *J* = 7.6 Hz, 1H), 7.37 (t, *J* = 7.6 Hz, 1H), 8.79 (d, *J* = 7.8 Hz, 1H), 11.18 (s, 1H); ^{13}C NMR (75 MHz, DMSO-d_6): δ (ppm) 12.8, 13.4, 34.4, 35.1, 63.1, 64.3, 110.3, 120.0, 121.9, 125.5, 127.6, 128.9, 131.8, 143.2, 150.2, 157.7, 160.5, 168.5; HRMS (ESI-TOF) *m/z*: [M+Na]$^+$ calcd for $C_{18}H_{18}N_6O_3SNa$ 421.1053, found 421.1052.

(*Z*)-1,3-Diethyl-6-(1-methyl-2-oxo-1,2-dihydro-3*H*-indol-3-ylidene)-3,3a,9,9a-tetrahydroimidazo[4,5-*e*]thiazolo[3,2-*b*]-1,2,4-triazine-2,7(1*H*,6*H*)-dione (11p). Orange solid, mp 240-241 °C (decomp). Yield: 453 mg (55%); IR (KBr): ν_{max}/cm^{-1} 3434, 3253, 2972, 2938, 1697, 1642, 1610, 1469, 1380, 1357, 1247, 1070, 877, 753; ^{1}H NMR (300 MHz, DMSO-d_6): δ (ppm) 0.97 (t, *J* = 6.9 Hz, 3H), 1.15 (t, *J* = 7.1 Hz, 3H), 3.12-3.18 (m, 3H), 3.33

(s, 3H), 3.33-3.40 (m, 1H), 4.96 (m, 2H), 6.93 (s, 1H), 7.09-7.15 (m, 2H), 7.44 (t, *J* = 7.7 Hz, 1H), 8.80 (d, *J* = 7.7 Hz, 1H); ^{13}C NMR (75 MHz, DMSO-d_6): δ (ppm) 12.8, 13.5, 26.3, 34.5, 35.1, 63.1, 64.3, 109.1, 119.3, 122.5, 124.7, 127.4, 129.6, 131.8, 144.2, 150.1, 157.8, 160.4, 166.9; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ calcd for $C_{19}H_{20}N_6O_3S$ 413.1390, found 413.1383.

(*Z*)-1,3-Diethyl-6-(1-ethyl-2-oxo-1,2-dihydro-3*H*-indol-3-ylidene)-3,3a,9,9a-tetrahydroimidazo[4,5-*e*]thiazolo[3,2-*b*]-1,2,4-triazine-2,7(1*H*,6*H*)-dione (11q). The product was isolated via the general procedure but the reaction time was 2.5 h. Orange solid, mp 257-259 °C (decomp). Yield: 461 mg (54%); IR (KBr): ν_{max}/cm^{-1} 3435, 3229, 2975, 2937, 1699, 1689, 1637, 1610, 1468, 1426, 1373, 1356, 1245, 1072, 874, 747; ^{1}H NMR (300 MHz, DMSO-d_6): δ (ppm) 0.97 (t, *J* = 7.0 Hz, 3H), 1.13-1.21 (m, 6H), 3.09-3.18 (m, 3H), 3.33-3.39 (m, 1H), 3.79-3.86 (q, *J* = 7.0 Hz, 2H), 4.96 (m, 2H), 6.96 (br s, 1H), 7.11 (t, *J* = 7.6 Hz, 1H), 7.20 (d, *J* = 7.9 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 1H), 8.84 (d, *J* = 7.8 Hz, 1H); ^{13}C NMR (75 MHz, DMSO-d_6): δ (ppm) 12.6, 12.8, 13.4, 34.4, 34.5, 35.1, 63.1, 64.3, 109.1, 119.5, 122.3, 124.6, 127.6, 129.7, 131.8, 143.1, 150.0, 157.7, 160.4, 166.6; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ calcd for $C_{20}H_{22}N_6O_3S$ 427.1547, found 427.1538.

(*Z*)-1,3-Diethyl-6-[1-(2-propyl)-2-oxo-1,2-dihydro-3*H*-indol-3-ylidene]-3,3a,9,9a-tetrahydroimidazo[4,5-*e*]thiazolo-[3,2-*b*]-1,2,4-triazine-2,7(1*H*,6*H*)-dione (11r). Orange solid, mp 257-259 °C (decomp). Yield: 590 mg (67%); IR (KBr): ν_{max}/cm^{-1} 3433, 3220, 2978, 2940, 1720, 1694, 1642, 1607, 1465, 1381, 1357, 1316, 1246, 1128, 1075, 1047, 871, 745; ^{1}H NMR (300 MHz, DMSO-d_6): δ (ppm) 0.99 (t, *J* = 7.0 Hz, 3H), 1.17 (t, *J* = 7.2 Hz, 3H), 1.46 (d, *J* = 6.9 Hz, 6H), 3.10-3.19 (m, 3H), 3.32-3.41 (m, 1H), 4.54-4.63 (m, 1H), 4.96 (m, 2H), 6.92 (br s, 1H), 7.12 (t, *J* = 7.7 Hz, 1H), 7.28 (d, *J* = 7.9 Hz, 1H), 7.44 (t, *J* = 7.7 Hz, 1H), 8.89 (d, *J* = 7.9 Hz, 1H); ^{13}C NMR (75 MHz, DMSO-d_6): δ (ppm) 12.9, 13.4, 19.1, 19.2, 34.4, 35.1, 44.2, 63.1, 64.4, 110.1, 119.6, 122.1, 124.9, 127.7, 129.6, 131.7, 142.8, 150.1, 157.7, 160.4, 166.7; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ calcd for $C_{21}H_{24}N_6O_3S$ 441.1703, found 441.1702.

(*Z*)-6-[5-Bromo-1-(3-bromobenzyl)-2-oxo-1,2-dihydro-3*H*-indol-3-ylidene]-1,3-diethyl-3,3a,9,9a-tetrahydroimidazo[4,5-*e*]thiazolo[3,2-*b*]-1,2,4-triazine-2,7(1*H*,6*H*)-dione (11s). Orange solid, mp 222-224 °C (decomp). Yield: 672 mg (52%); IR (KBr): ν_{max}/cm^{-1} 3435, 3200, 2972, 2933, 1719, 1691, 1643, 1606, 1462, 1430, 1375, 1352, 1244, 1082, 889, 772; ^{1}H NMR (300 MHz, DMSO-d_6): δ (ppm) 0.99 (t, *J* = 7.0 Hz, 3H), 1.17 (t, *J* = 7.1 Hz, 3H), 3.11-3.20 (m, 3H), 3.33-3.42 (m, 1H), 4.96-5.05 (m, 4H), 7.05-7.08 (m, 2H), 7.28-7.30 (m, 2H), 7.49 (m, 1H), 7.56 (s, 1H), 7.61 (d, *J* = 8.5 Hz, 1H), 9.06 (s, 1H); ^{13}C NMR (75 MHz, DMSO-d_6): δ (ppm) 12.7, 13.4, 34.5, 35.0, 42.5, 63.3, 64.2, 111.4, 114.5, 121.3, 121.9, 123.0, 126.2, 129.7, 129.9, 130.5, 130.8, 132.6, 133.6, 138.4, 141.8, 149.5, 157.6, 160.3, 166.8; HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ calcd for $C_{25}H_{22}Br_2N_6O_3SNa$ 666.9733, found 666.9730.

6-(1-Ethyl-3-hydroxy-2-oxo-1,2-dihydro-3*H*-indol-3-yl)-1,3-dimethyl-3,3a,9,9a-tetrahydroimidazo[4,5-*e*]thiazolo[3,2-*b*]-1,2,4-triazine-2,7(1*H*,6*H*)-dione (12c). The product was obtained via the general procedure for the preparation of compounds **11** from starting **6a** and **10c** for 2 h. Beige crystals, mp 257-259 °C (decomp). Yield: 350 mg (42%); IR (KBr): ν_{max}/cm^{-1} 3432, 3209, 2972, 2937, 2879, 1724, 1698, 1674, 1638, 1613, 1489, 1469, 1450, 1376, 1261, 1247, 1133, 1113, 1082, 1010, 789, 757; ^{1}H NMR (300 MHz, DMSO-d_6): δ (ppm) 1.16 (t, *J* = 7.0 Hz, 3H), 1.97 (s, 3H), 2.75 (s, 3H), 3.63-3.73 (m, 2H), 4.44 (d, *J* = 5.6 Hz, 1H), 4.64 (d, *J* = 5.6 Hz, 1H), 4.80 (s, 1H), 6.51 (s, 1H), 6.85 (t, *J* = 7.5 Hz, 1H), 6.94 (s, 1H), 7.00 (d, *J* = 7.9 Hz, 1H), 7.34 (t, *J* = 7.7 Hz, 1H), 7.44 (d, *J* = 7.3 Hz, 1H); ^{13}C NMR (75 MHz, DMSO-d_6): δ (ppm) 12.0, 26.6, 26.9, 34.2, 52.9, 64.9, 65.5, 74.2, 108.5, 122.2, 123.7, 126.4, 130.2, 142.8, 150.6, 158.2, 164.2, 174.0; HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ calcd for $C_{18}H_{20}N_6O_4SNa$ 439.1159, found 439.1152.

After isolation of **12c**, orange solid was precipitated from the filtrate for one day. Filtration and recrystallization from methanol gave 88 mg (11%) of compound **11c**.

1,3-Diethyl-6-(1-ethyl-3-hydroxy-2-oxo-1,2-dihydro-3*H*-indol-3-yl)-3,3a,9,9a-tetrahydroimidazo[4,5-*e*]thiazolo[3,2-*b*]-1,2,4-triazine-2,7(1*H*,6*H*)-dione (12q). The product was obtained via the general procedure for the preparation of compounds **11** from starting **6b** and **10c** for 2 h. Beige crystals, mp 223-225 °C (decomp). Yield: 169 mg (19%); IR (KBr): ν_{max}/cm^{-1} 3254, 2973, 2935, 2874, 1731, 1711, 1685, 1634, 1614, 1468, 1378, 1246, 1094, 1036, 775, 755; ^{1}H NMR (300 MHz, DMSO-d_6): δ (ppm) 0.48 (t, *J* = 6.9 Hz, 3H), 1.10-1.18 (m, 6H), 2.34-2.44 (m, 1H), 2.62-2.71 (m, 1H), 3.08-3.17 (m, 1H), 3.23-3.35 (m, 1H), 3.59-3.77 (m, 2H), 4.57 (d, *J* = 5.6 Hz, 1H), 4.71 (d, *J* = 5.6 Hz, 1H), 4.83 (s, 1H), 6.46 (s, 1H), 6.86 (t, *J* = 7.5 Hz, 1H), 6.92 (s, 1H), 6.99 (d, *J* = 7.8 Hz, 1H), 7.32 (t, *J* = 7.6 Hz, 1H), 7.47 (d, *J* = 7.3 Hz, 1H); ^{13}C NMR (75 MHz, DMSO-d_6): δ (ppm) 12.0, 13.4, 34.1, 34.3, 52.8, 62.5, 63.7, 74.0, 108.6, 122.1, 124.0, 126.5, 130.2, 142.9, 150.6, 157.3, 164.2, 174.0; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ calcd for $C_{20}H_{24}N_6O_4S$ 445.1653, found 445.1646.

After isolation of **12q**, orange solid was precipitated from the filtrate for one day. Filtration and recrystallization from methanol gave 239 mg (28%) of compound **11q**.

General procedure for the synthesis of compounds 9 via a rearrangement of compounds 11.

Procedure 2. To a stirred suspension of compound **11a** (741 mg, 2.0 mmol) in refluxing methanol (15 mL), 0.12 ml of 40% aqueous KOH (1.2 mmol) was added. The resulting mixture was refluxed with stirring for 20 min. After cooling, the precipitate was filtered off and washed with water to give **9a** (659 mg, 89%).

Compounds **9b-d,f,g,j,k,m,p** were obtained via the general procedure in 92% (707 mg), 91% (725 mg), 93% (767 mg), 94% (892 mg), 89% (731 mg), 94% (858 mg), 91% (751 mg), 90% (793 mg), 88% (871 mg), respectively.

Compound **9p** is too insoluble to record a good ^{13}C NMR spectrum.

(*Z*)-7-(1-(4-Chlorobenzyl)-2-oxo-1,2-dihydro-3*H*-indol-3-ylidene)-1,3-dimethyl-1,3a,4,9a-tetrahydroimidazo[4,5-*e*]thiazolo[2,3-*c*]-1,2,4-triazine-2,8(3*H*,7*H*)-dione (9p). Orange solid, mp 296-298 °C (decomp). Yield: 871 mg (88%); IR (KBr): ν_{max}/cm^{-1} 3308, 2946, 1701, 1676, 1643, 1608, 1465, 1383, 1364, 1308, 1279, 1091, 1014, 783, 752; ^{1}H NMR (300 MHz,

DMSO-d_6): δ (ppm) 2.67 (s, 3H), 2.93 (s, 3H), 4.84 (d, J = 4.7 Hz, 1H), 5.04 (br.s, 2H), 5.70 (d, J = 5.1 Hz, 1H), 7.05-7.15 (m, 2H), 7.32-7.40 (m, 5H), 8.07 (s, 1H), 8.82 (d, J = 7.7 Hz, 1H); HRMS (ESI-TOF) *m/z*: $[M+H]^+$ calcd for $C_{23}H_{19}ClN_6O_3S$ 495.1001, found 495.0996.

(*Z*)-1,3-Diethyl-7-(2-oxo-1,2-dihydro-3*H*-indol-3-ylidene)-1,3a,4,9a-tetrahydroimidazo[4,5-*e*]thiazolo[2,3-*c*]-1,2,4-triazine-2,8(3*H*,7*H*)-dione (9q). Orange solid, mp 325-327 °C (decomp). Yield: 733 mg (92%); IR (KBr): ν_{max}/cm^{-1} 3294, 3204, 3181, 2971, 1704, 1687, 1637, 1614, 1463, 1328, 1232, 1086, 1004, 778, 749; ^{1}H NMR (300 MHz, DMSO-d_6): δ (ppm) 1.04 (t, J = 6.7 Hz, 3H), 1.13 (t, J = 6.5 Hz, 3H), 3.04-3.13 (m, 1H), 3.31-3.54 (m, 3H), 4.90 (d, J = 5.3 Hz, 1H), 5.76 (d, J = 5.2 Hz, 1H), 6.96 (d, J = 7.8 Hz,1H), 7.07 (t, J = 7.6 Hz, 1H), 7.34 (t, J = 7.6 Hz, 1H), 7.99 (s, 1H), 8.75 (d, J = 7.7 Hz, 1H), 11.14 (s, 1H); ^{13}C NMR (75 MHz, DMSO-d_6): δ (ppm) 12.7, 13.0, 34.9, 37.9, 61.6, 63.6, 110.2, 120.3, 121.7, 123.1, 127.2, 129.0, 130.9, 136.7, 142.5, 158.0, 164.2, 168.5; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ calcd for $C_{18}H_{18}N_6O_3S$ 399.1234, found 399.1228.

Synthesis of compounds 9r,*s* via a rearrangement of 11j. To a stirred suspension of compound **11j** (913 mg, 2.0 mmol) in refluxing methanol (15 mL), 0.20 ml of 40% aqueous KOH (2.0 mmol) was added. The resulting mixture was refluxed with stirring for 20 min. After cooling, the precipitate was filtered off and washed with water to give **9r** (327 mg, 37%). After isolation of **9r**, orange solid was precipitated from the water-methanol filtrate for one day. Filtration and washing with methanol gave compound **9s** (47 mg, 5%).

(*Z*)-Methyl 2-(3-(1,3-dimethyl-2,8-dioxo-1,2,3,3a,4,9a-hexahydroimidazo[4,5-*e*]thiazolo[2,3-*c*]-1,2,4-triazin-7(8*H*)-ylidene)-2-oxo-1,2-dihydro-3*H*-indolyl-1-)acetate (9r). Orange solid, mp 275-277 °C (decomp). Yield: 327 mg (37%); IR (KBr): ν_{max}/cm^{-1} 3308, 3271, 2953, 2928, 1741, 1723, 1700, 1682, 1644, 1610, 1468, 1391, 1359, 1232, 1190, 1091, 1020, 783, 750; ^{1}H NMR (300 MHz, DMSO-d_6): δ (ppm) 2.67 (s, 3H), 2.93 (s, 3H), 3.70 (s, 3H), 4.74 (s, 2H), 4.83 (d, J = 5.3 Hz, 1H), 5.69 (d, J = 5.8 Hz, 1H), 7.14-7.18 (m, 2H), 7.40 (t, J = 7.7 Hz, 1H), 8.10 (s, 1H), 8.83 (d, J = 7.9 Hz, 1H); ^{13}C NMR (75 MHz, DMSO-d_6): δ (ppm) 27.9, 31.3, 41.2, 52.3, 63.7, 65.8, 109.2, 119.6, 121.3, 122.5, 127.1, 130.7, 134.0, 136.3, 142.3, 159.0, 163.9, 167.2, 168.2; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ calcd for $C_{19}H_{18}N_6O_5S$ 443.1132, found 443.1121.

Potassium (*Z*)-2-(3-(1,3-dimethyl-2,8-dioxo-1,2,3,3a,4,9a-hexahydroimidazo[4,5-*e*]thiazolo[2,3-*c*]-1,2,4-triazin-7(8*H*)-ylidene)-2-oxo-1,2-dihydro-3*H*-indolyl-1-)acetate (9s). Orange solid, mp 287-289 °C (decomp). Yield: 47 mg (5%); IR (KBr): ν_{max}/cm^{-1} 3432, 3271, 2928, 1719, 1684, 1676, 1645, 1609, 1468, 1397, 1381, 1361, 1340, 1235, 1194, 1087, 1037, 1021, 753; ^{1}H NMR (300 MHz, DMSO-d_6): δ (ppm) 2.66 (s, 3H), 2.92 (s, 3H), 3.97-4.05 (m, 2H), 4.80 (d, J = 4.5 Hz, 1H), 5.68 (d, J = 5.2 Hz, 1H), 6.88 (d, J = 7.5 Hz, 1H), 7.04 (t, J = 7.3 Hz, 1H), 7.33 (t, J = 7.3 Hz, 1H), 8.11 (s, 1H), 8.75 (d, J = 7.5 Hz, 1H); ^{13}C NMR (75 MHz, DMSO-d_6): δ (ppm) 27.8, 31.3, 44.5, 63.6, 65.6, 109.5, 119.4, 121.4, 122.9, 126.6, 130.5, 131.6, 136.7, 144.4, 158.9, 164.0, 166.7, 167.8; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ calcd for $C_{18}H_{16}N_6O_5S$ 429.0976, found 429.0963; $[M+K]^+$ calcd for $C_{18}H_{16}N_6O_5SK$ 467.0534, found 467.0524.

General procedure for the synthesis of compounds 14 via a rearrangement of compounds 6 (or 13).

To a stirred suspension of compound **6a** (644 mg, 2.0 mmol) or **13a** (483 mg, 2.0 mmol) in refluxing methanol (15 mL), 0.32 ml (3.2 mmol) or 0.12 ml (1.2 mmol), respectively, of 40% aqueous KOH was added. The resulting mixture was refluxed with stirring for 1 h. After cooling and filtration from cloudiness, the filtrate was left overnight. The separated precipitate was filtered off and washed with water to give **14a** (449 mg, 93%).

1,3-Dimethyl-1,3a,4,9a-tetrahydroimidazo[4,5-*e*]thiazolo-[2,3-*c*]-1,2,4-triazine-2,8(3*H*,7*H*)-dione (14a). Off-white crystals, mp 226-228 °C. Yield: 449 mg (93%); IR (KBr): ν_{max}/cm^{-1} 3318, 2935, 1710, 1638, 1474, 1448, 1379, 1313, 1290, 1012, 786; ^{1}H NMR (300 MHz, DMSO-d_6): δ (ppm) 2.60 (s, 3H), 2.8 (s, 3H), 3.96 (d, J = 16.7 Hz, 1H), 4.07 (d, J = 16.7 Hz, 1H), 4.70 (d, J = 6.2 Hz, 1H), 5.49 (d, J = 6.2 Hz, 1H), 7.47 (s, 1H); ^{13}C NMR (75 MHz, DMSO-d_6): δ (ppm) 27.6, 30.9, 31.3, 64.3, 66.0, 138.9, 158.9, 170.9; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ calcd for $C_8H_{11}N_5O_2S$ 242.0706, found 242.0704.

1,3-Diethyl-1,3a,4,9a-tetrahydroimidazo[4,5-*e*]thiazolo-[2,3-*c*]-1,2,4-triazine-2,8(3*H*,7*H*)-dione (14b). Off-white crystals, mp 171-173 °C. Yield: 522 mg (97%); IR (KBr): ν_{max}/cm^{-1} 3385, 3163, 2977, 1723, 1640, 1606, 1520, 1470, 1424, 1308, 1229, 1089, 836, 771; ^{1}H NMR (300 MHz, DMSO-d_6): δ (ppm) 0.98 (t, J = 7.0 Hz, 3H), 1.05 (t, J = 7.0 Hz, 3H), 2.98-3.24 (m, 3H), 3.34-3.45 (m, 1H), 3.95 (d, J = 16.7 Hz, 1H), 4.08 (d, J = 16.7 Hz, 1H), 4.75 (d, J = 5.0 Hz, 1H), 5.55 (d, J = 6.2 Hz, 1H), 7.44 (s, 1H); ^{13}C NMR (75 MHz, DMSO-d_6): δ (ppm) 12.7, 13.1, 31.3, 34.6, 37.4, 62.0, 63.7, 138.7, 157.9, 171.0; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ calcd for $C_{10}H_{15}N_5O_2S$ 270.1019, found 270.1018.

General procedure for the synthesis of compounds 9 via a condensation of starting 14 and 10.

To a stirred suspension of imidazo[4,5-*e*]thiazolo[2,3-*c*]-1,2,4-triazine **14a** (483 mg, 2.0 mmol) and isatin **10b** (322 mg, 2.0 mmol) in refluxing methanol (15 mL), 0.014 ml of 40% aqueous KOH (0.14 mmol) was added. The resulting mixture was refluxed with stirring for 30 min. After cooling, the precipitate was filtered off, washed with water and to give **9b** (646 mg, 84%).

Compound **9g** was obtained from starting **14a** and **10g** via the general procedure in 85% (698 mg) yield.

Crystallographic data

Crystals of **13a** ($C_8H_{11}N_5O_2S$, M = 241.28) are monoclinic, space group $P2_1/n$, at 100K: a = 6.8510(5), b = 7.7360(6), c = 19.3150(14) Å, β = 95.218(2)°, V = 1019.44(13) Å^3, Z = 4 (Z' = 1), d_{calc} = 1.572 gcm^{-3}, μ(MoKα) = 3.11 cm^{-1}, F(000) = 504. Crystals of **14b** ($C_{11}H_{19}N_5O_3S$, M = 301.37) are monoclinic, space group C2/c, at 100K: a = 26.710(4), b = 7.5095(10), c = 14.0757(19) Å

β = 96.942(2)°, V = 2802.6(7) Å^3, Z = 8 (Z' = 2), d_{calc} = 1.429 gcm^{-3}, μ(MoKα) = 2.47 cm^{-1}, F(000) = 1280. Intensities of 8078 and 10581 reflections were measured for **13a** and **14b** with a Bruker APEX2 CCD diffractometer [λ(MoKα) = 0.71072Å, ω-scans, 2θ<58°], and 2712 and 3653 independent reflections [R_{int} = 0.0334 and 0.0426], respectively, were used in further refinement. The structures were solved by direct method and refined by the full-matrix least-squares technique against F^2 in the anisotropic-isotropic approximation. The hydrogen atoms of NH groups and that of OH group of the solvent methanol molecule in **14b** were found in difference Fourier synthesis, the positions of other hydrogen atoms were calculated, and all of them were refined in the isotropic approximation within the riding model. For **13a**, the refinement converged to wR2 = 0.0975 and GOF = 1.005 for all the independent reflections (R1 = 0.0367 was calculated against F for 2192 observed reflections with I>2σ(I)). For **14b**, the refinement converged to wR2 = 0.1166 and GOF = 1.005 for all the independent reflections (R1 = 0.0381 was calculated against F for 3251 observed reflections with I>2σ(I)). All calculations were performed using SHELXTL PLUS 5.0.[19] CCDC 1045940 and 1045941 contain the supplementary crystallographic data for **13a** and **14b**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge, CB21EZ, UK; or deposit@ccdc.cam.ac.uk).

Powder diffraction data

High-quality experimental powder X-ray diffraction data for compounds **9b,d,e,n,11c,b** were obtained with a PANalytical EMPYREAN diffractometer (fine-focus sealed tube, Cu $Kα_1$ radiation (λ=1.5406 Å), Johanson's Hybrid Ge{111} monochromator for the primary beam, Bragg-Brentano geometry) using a position- sensitive detector PIXcel[1D]. The patterns were scanned in reflection mode, θ/2θ continuously scanned over the angular range 5° - 60° (2θ) with a step 0.013° (2θ) and counting time of 1000 s step^{-1}. Preferred orientation effects were reduced by grinding. Alignment and calibration were checked using Al_2O_3 (SRM676). Diffraction data were collected at room temperature (296K).

The extraction of peak position for indexing was performed with Pawley method. Patterns indexing were carried out by means of the program Ito or TREOR. Unit cell parameters were refined by least-squares fitting of Bragg's equation to the position of the diffraction lines. All calculations for the refinement of the diffraction patterns and refine the unit cell parameters were performed using complex programs available in PC software "High Score Plus" supplied by PANalytical EMPYREAN (Version: 3.0 t (3.0.5), Date 30-01-2012. Produced by: PANalytical B. V. Amelo, The Netherland).

The experimental powder XRD data and cell parameters obtained for compounds **9b,d,e,n,11c,b** are deposited at the PDF-base of International Centre for Diffraction Data (ICDD).

Results of the analysis of the experimental powder diffraction pattern of the compounds **9b,d,e,n,11c,b** show that the investigated samples were single-phase. Space group, unit cell parameters and characteristics of the investigated verification phases shown in Table 7. Figures giving powder diffraction patterns for the products are in Supplementary Information.

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Table 7 Space groups, unit cell parameters and characteristics of the investigated verification phases of compounds **9b,d,e,n,11c,b**

Compound	**9b**	**9d**	**9e**	**9n**	**11b**	**11c**
Sp. gr, Z	$P2_1/c$ 1, Z=4	P-1, Z=2	P-1, Z=4	P-1, Z=4	P-1, Z=4	$P2_1/m$, Z=4
a, (Å)	15.603(2)	4.492(8)	13.373(2)	7.638(1)	10.275(2)	7.164(1)
b, (Å)	26.769(5)	14.27(2)	11.724(2)	14.360(2)	25.970(4)	10.787(2)
c, (Å)	4.3094(8)	13.97(2)	14.623(2)	19.700(3)	6.864(1)	23.390(4)
α, (°)	90	82.465(9)	78.57(6)	93.656(5)	93.43(1)	90
β, (°)	93.281(3)	88.576(3)	94.779(2)	90.918(2)	105.308(3)	92.340(3)
γ, (°)	90	89.482(3)	80.003(3)	77.517(2)	89.194(3)	90
V(Å^3)	1796.92	887.64	2196.52	2105.59	1763.42	1806.02
Number of reflections	56	87	105	108	70	83
Snyder's FOM	24.7299	19.4289	9.0048	13.1699	10.7239	14.4113

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