Full Papers
doi.org/10.1002/ejoc.202100794

Chemistry Europe
European Chemical Societies Publishing

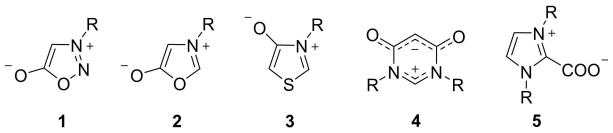
1,3-Thiazolium-4-aminides: Syntheses and Characterization of Fluorescent Mesoionic Compounds

Alena Therese Storm,[a] Mimoza Gjikaj,[b] Jan C. Namyslo,[a] Jörg Adams,[c] and Andreas Schmidt*[a]

A series of mesoionic 1,3-thiazolium-4-aminides was synthesized starting from thioamides and chloroacetonitrile *via* cyanomethylbenzimidothioates which were cyclized by benzoylchloride. Depending on the reaction conditions 4-amino-1,3-thiazolium salts and 4-*N*-benzamido-1,3-thiazolium salts were obtained (X-ray structure analysis). Substitution of the amino groups with benzoyl chloride gave a series of the title mesoionic compounds (X-ray structure analysis) which were examined spectroscopically. Negative solvatochromism was found and temperature-dependent as well as time-resolved fluorescence measurements were made. Long lifetimes of the excited states (30–50 ns) were detected. Calculated frontier orbital profiles gain insight into the characteristics of 1,3-thiazolium-4-aminides as conjugated mesomeric betaines.

Introduction

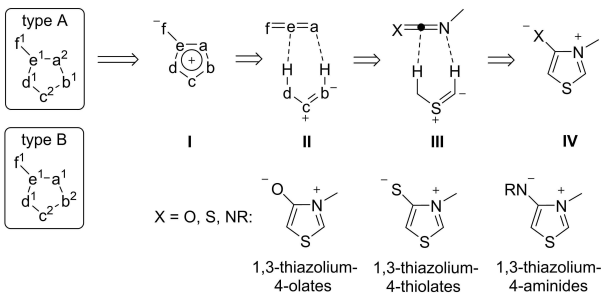
Mesomeric betaines are compounds which can exclusively be represented by dipolar canonical formulae in which the positive and negative charges are delocalized within a common π-electron system.[1] According to a recent classification, five distinct classes of mesomeric betaines can be distinguished, among those conjugated, cross-conjugated, and pseudo-cross-conjugated molecules.[2] Numerous applications of mesomeric betaines take advantage of the different types of conjugation. Thus, conjugated mesomeric betaines such as sydnones **1**,[3] münchnones **2**[4] and thioisomünchnones **3**[5,6] (Scheme 1) are versatile 1,3-dipoles in [2 + 3]-cycloadditions ("Huisgen reactions"[7]) and they have been exploited in numerous total syntheses of interesting target molecules such as natural products.[8] Cross-conjugated mesomeric betaines such as **4** are 1,4-dipoles and they are of interest as switchable molecules in materials chemistry,[9] whereas hetarenium-carboxylates like **5** are examples of pseudo-cross-conjugated mesomeric betaines which proved to be versatile precursors for the *in situ* generation of neutral N-heterocyclic carbenes by decarboxylation.[10] Interesting π-electron-rich anionic N-heterocyclic carbenes are available by deprotonation from the distinct



Scheme 1. Examples of mesomeric betaines including mesoionic compounds.

types of mesomeric betaines.[11] The intersection of the two classes of compounds was reviewed,[12] and CREF values (carbene relative energy of formation) were introduced to provide further impetus to research in this field.[13]

The term mesoionic compound historically[14] encompasses 5-membered representatives of the class of conjugated mesomeric betaines, and type A has to be distinguished from type B (Scheme 2).[15] Either type can be symbolized by general formula **I**, however, the two types differ in the origin of their 8 π-electrons as indicated by the superscripts of **a**–**f** which represent suitably substituted carbon, nitrogen, oxygen, and sulfur. The reasonable combination of **a**–**f** enables the design of 144 different structures of type A mesoionic compounds[15] and of 84 structures of type B which often exist as their ring-opened valence tautomers. Type A mesoionic compounds are derived



Scheme 2. Design of mesoionic compounds of type A. Thiazolium-4-olates, −4-thiolates, and the title −4-aminides as examples.

[a] *A. T. Storm, Dr. J. C. Namyslo, Prof. Dr. A. Schmidt*
Clausthal University of Technology, Institute of Organic Chemistry,
Leibnizstraße 6, 38678 Clausthal-Zellerfeld, Germany
E-mail: schmidt@ioc.tu-clausthal.de
[b] *Prof. Dr. M. Gjikaj*
Clausthal University of Technology, Institute of Institute of Inorganic and Analytical Chemistry,
Paul-Ernst-Straße 4, 38678 Clausthal-Zellerfeld, Germany
[c] *Prof. Dr. J. Adams*
Clausthal University of Technology, Institute of Physical Chemistry,
Arnold-Sommerfeld-Straße 4, D-38678 Clausthal-Zellerfeld, Germany

Supporting information for this article is available on the WWW under https://doi.org/10.1002/ejoc.202100794

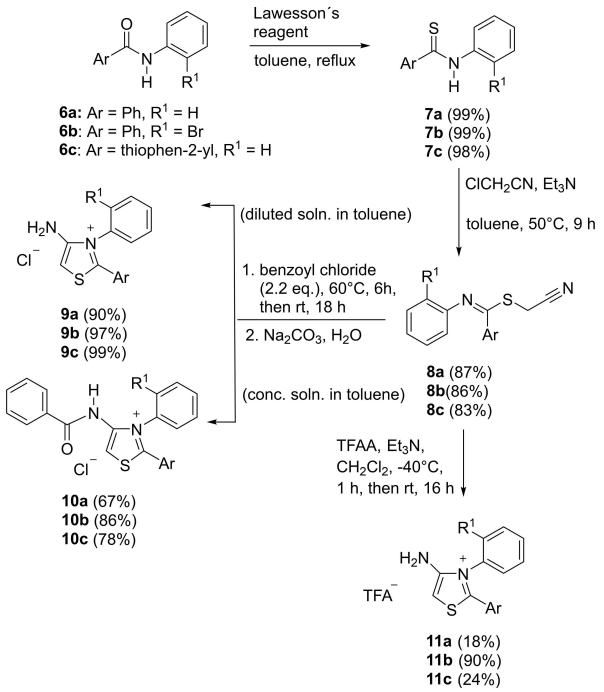
by union of heterocumulenes and 1,3-dipoles (**II**). Thus, the union of the thiocarbonyl ylide 1,3-dipole with isocyanates (**III**; X = O) give the aforementioned thioisomünchnones **3** (1,3-thiazolium-4-olates). 1,3-Thiazolium-4-thiolates (**IV**; X = S) have very scarcely been described in the literature[6,16] and the same is true for carbodiimides (**III**; X = NR) as partial structure of 1,3-thiazolium-4-aminides (**IV**; X = NR). The vast majority of the aforementioned combinations have not yet been prepared, characterized, and examined, so that numerous blank spaces on the map of mesomeric betaines remain to date. In view of the current interest in N-heterocyclic carbenes, new mesomeric betaines including mesoionic compounds could prove valuable in the future.

Concerning the title 1,3-thiazolium-4-aminides (1,3-thiazol-4-imines, anhydro-4-amino-1,3-thiazolium hydroxide, thioisomünchnone imines), few derivatives have been prepared,[17,18] used in cycloadditions,[19] photolyzed,[20] and calculated in terms of aromaticity.[21] In continuation of our interest in mesomeric betaines[22] and hetarenium salts,[23] we describe here reliable syntheses of 1,3-thiazolium-4-aminides and present results of calculations of frontier orbital calculations. We also performed UV/Vis and fluorescence measurements.

Results and Discussion

We started our investigation from the amides **6a–c** which were treated with Lawesson's reagent in toluene to give the corresponding thioamides **7a–c** in excellent yields by modification of literature procedures, respectively (Scheme 3). Thus, the yields were improved by changing the reaction time (**7a**[24]), the equivalents of Lawessons's reagent and the solvent (THF *vs.* toluene) (**7b**,[25] **7c**[26]). Reaction with chloroacetonitrile in toluene resulted in the formation of the cyanomethylbenzimidothioates **8a–c** in very good yields by adjusting the reaction parameters as summarized for the preparation of **8a** in Table 1. Thus, the yield increased by 36% in comparison to the literature.[17b]

Diluted solutions of benzoyl chloride in toluene at 60 °C, stirring for additional 18 hours and work-up with sodium carbonate in water converted **8a–c** into the thiazolium salts **9a–c** as yellow solids, respectively. Alternatively, the ring-closure of **8a** to **9a** can be accomplished with HCl in MeOH or isopropanol in lower yields.[17b] Conducting the reaction with less solvent converted **8a–c** into the *N*-benzoyl-substituted thiazolium salts **10a–c** in good yields as yellow to orange-colored solids. Trifluoroacetic anhydride (TFAA) resulted in the formation of the trifluoroacetates **11a–c**. Some thiazolium salts such as **9a** proved to be sensitive as they decomposed slowly on storage. In addition, the compounds **9a–c** and **10a–c** have a very limited solubility in organic solvents. On slow evaporation of a concentrated solution of **10a** in deuterated water, however, we were able to obtain single crystals suitable for an X-ray analysis (Figure 1). The molecule crystallized monoclinic [*P*21/c (no. 14)]. The phenyl rings attached to C2 and N3 are twisted from the plane of the 1,3-thiazolium, respectively. Dihedral angles of 67.11° [C2–N3–C21–C22; crystallographic numbering] and 43.39° [N3–C2–C15–C16] were determined. The C7=O8 bond was found to have a bond distance of 123.00 pm, and the adjacent bond lengths C7–N6 and N6–C4 were found to be



Scheme 3. Syntheses of 4-aminothiazolium salts.

Table 1. Optimization of the preparation of **8a**.

Entry	Eq. of $ClCH_2CN$	Eq. of Et_3N	V (toluene) [mL]	Yield
I	1.00	1.54	5	57%
II	1.20	1.54	5	69%
III	1.10	1.54	7	70%
IV	1.10	2.00	5	71%
V	1.10	1.00	5	73%
VI	1.10	1.54	5	87%

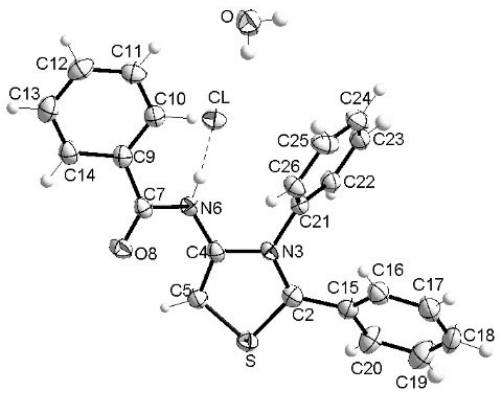


Figure 1. Molecular drawing of **10a** (displacement parameters are drawn at the 50% probability level). Selected bond lengths [pm] (crystallographic numbering): C7–C9: 149.59 pm, C4–C5: 134.95 pm, C5–S: 171.03 pm, S–C2: 169.87 pm, C2-N3: 133.66 pm, N3–C4: 139.30 pm, N3–C21: 146.76 pm, C2–C15: 146.93 pm.

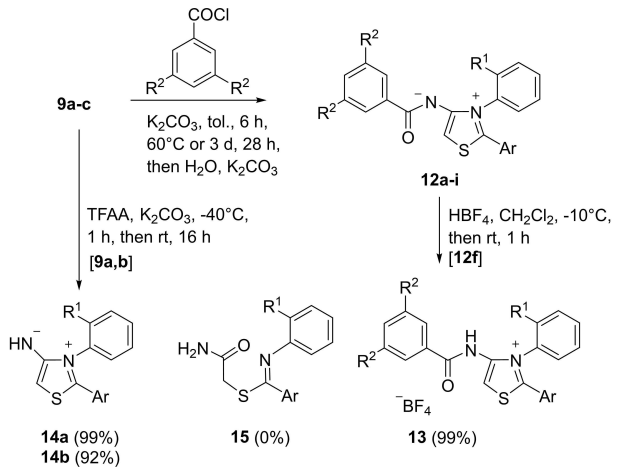
136.25 pm and 139.50 pm, respectively. The chloride anion forms a hydrogen bond to the proton of the exocyclic amide bond [232.16 pm].

Next, we optimized the reaction of 4-aminothiazolium salt **9a** with 3,5-dinitrobenzoyl chloride to give **12a** (Scheme 4 and Table 2). Equimolar amounts of potassium carbonate in toluene at 60 °C over a period of 6 h gave best yields (entry IX).

We applied the conditions of entry IX to react 3,5-dinitro-, 3,5-dichloro-, and 3,5-trifluoromethylbenzoyl chloride with the 4-aminothiazolium salts **9a**–**c** (Scheme 4 and Table 3). The phenyl derivatives **12a**–**f** were obtained in very good to excellent yields as yellow solids, respectively, whereas the thiophene-substituted thiazoles **12g**–**i** formed red oils. The aminides **12a**–**i** have a very limited solubility in organic solvents which made purification challenging. In addition, despite of long measurements not all carbon atoms could be detected in the ^{13}C NMR spectrum. By measuring two-dimensional spectra, the signals of these carbon atoms could be determined. For a spectroscopic comparison, we protonated aminide **12f** with HBF_4 in dichloromethane at −10 °C which gave the thiazolium salt **13** in quantitative yields as yellow solid, the purification of which proved to be difficult due to slow deprotonation and decomposition. No traces of the amides **15** as by-products were found. On protonation, the signal of 5-*H* shifted from 8.10 ppm to 8.20 ppm in DMSO-[D_6]. TFAA in the presence of K_2CO_3 converted the thiazolium salts **9a**, **b** into the *N*-unsubstituted thiazolium-4-aminides **14a,b** which were obtained as red oils in excellent yields, respectively.

A three-step one-pot synthesis of the *tert*-butyl substituted thioamide **16**, chloroacetonitrile, and 3,5-dinitrobenzoyl chloride (Scheme 5) gave aminide **17** in low yields, the syntheses of which was not possible according to the procedures shown in Scheme 4.

1,3-Thiazolium-4-aminides can be represented by several dipolar resonance forms, six of which (**A**–**F**) are shown in Scheme 6. These include thiocarbonyl ylides (**B**, **C**, **E**) associated with conjugated mesomeric betaines.[1] Correspondingly, common atoms for either charges in the canonical forms exist which are characteristic of this class of compounds.[1] In addition, a covalent structure **D** involving a tetravalent sulfur can be formulated which necessarily involves its 3d-orbitals. This form, however, is not believed to have a considerable contribution on the weighted average of all the canonical forms.[1][28] However, relatively short calculated [MP2/6-31G(d)] C_1–S–C_5 bond lengths of related 1,3-dithiolylium-4-olates (C2–S: 167.9 pm; C5–S: 166.7 pm) were interpreted as hints on some hypervalent character, and this was in agreement to diminished charge



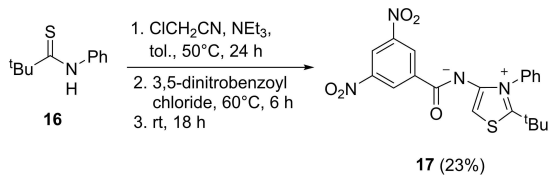
Scheme 4. Syntheses of thiazolium-4-aminides.

Table 2. Optimization of the synthesis of **12a**.

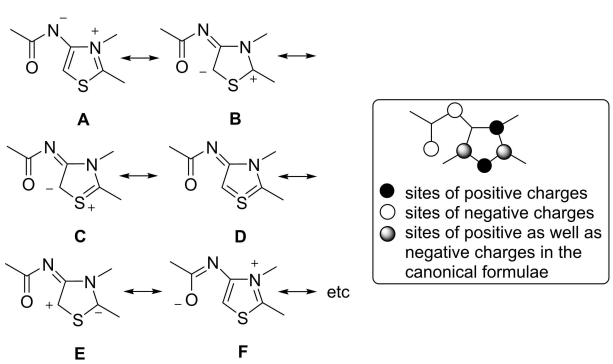
Entry	Eq. of K_2CO_3	Solvent	Conditions	Yield
I	1.5	toluene	60 °C, 6 h, rt, 18 h	12%
II	2.0	toluene	60 °C, 6 h, rt, 18 h	18%
III	1.0	acetone	reflux, 6 h, rt, 18 h	9%
IV	1.0	acetone	rt, 24 h	7%
V	1.0	toluene	60 °C, 6 h, rt, 18 h	35%
VI	1.0	toluene	60 °C, 8 h, rt, 16 h	46%
VII	1.0	toluene	60 °C, 16 h	56%
VIII	1.0	toluene	28 °C, 3 d	86%
IX	1.0	toluene	60 °C, 6 h	97%

Table 3. Substitution pattern and yields of thiazolium-4-aminides **12a**–**i**.

Compd.	Ar	R^1	R^2	Yield
12a	Ph	Br	NO_2	97%
12b	Ph	H	Cl	86%
12c	Ph	H	NO_2	97%
12d	Ph	H	CF_3	92%
12e	Ph	Br	Cl	94%
12f	Ph	Br	CF_3	90%
12g	thiophen-2-yl	H	Cl	22%
12h	thiophen-2-yl	H	NO_2	47%
12i	thiophen-2-yl	H	CF_3	14%



Scheme 5. One-pot-synthesis.



Scheme 6. Mesomerism and charge distribution according to the resonance forms.

separations between the heterocyclic ring and the exocyclic oxygen.[29]

We therefore grew single crystals to study bond lengths, bond angles and torsion angles in the solid state and also performed calculations to analyze frontier orbital profiles. Single crystals of 1,3-thiazolium-4-aminide **17** were obtained from a concentrated solution in DMSO-[D_6] over a period of some weeks (Figure 2). Compound **17** crystallized triclinic [*P* (no. 2)]. Similar to the thiazolium salt mentioned above, the phenyl ring attached to N3 is twisted from the plane of the thiazolium ring by −97.85° (C1–N3–C5–C17; crystallographic numbering). The bond length C2–O3 was measured to be 124.90 pm which is only slightly longer than the carbonyl group's bond of formaldehyde or formic acid (121 pm),[27] but considerably shorter than a C_{sp^2}–O single bond (134 pm).[27] Correspondingly, the bond C2–N2 (134.11 pm) is only slightly shortened in comparison to C_{sp^2}–N amide bonds (138 pm),[27] similar to the N2–C3 bond (135.04 pm). Concerning mesomeric structure **D**, the bond lengths C1–S and C11–S were found to be 169.78 pm and 171.01 pm, respectively, and they do not differ significantly from those of the thiazolium salt **10a**, so that **D** is seemingly not significant to the formulation of the structure of **17**. Taking the ^{13}C NMR chemical shift differences between the signals of C2 (156.7–173.8 ppm) and C5 (92.6–102.1 ppm) of the thiazolium into account, mesomeric structure **B** is relevant, and structure **E** can be neglected. Therefore, the exocyclic N and O atoms (Scheme 6) are not marked with gray circles, respectively, although they are formal sites of either charges.

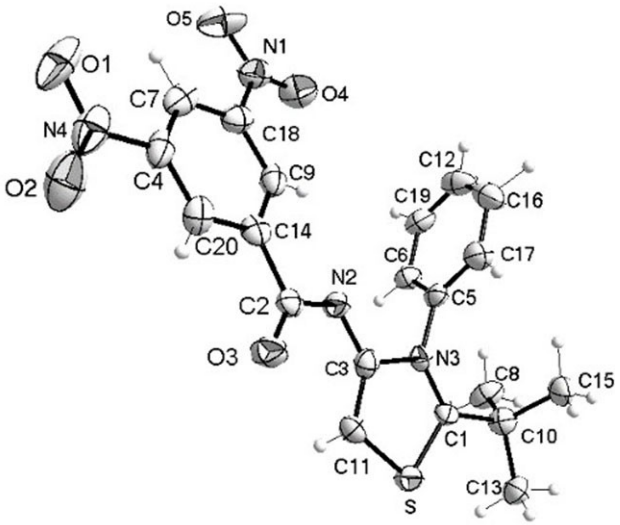


Figure 2. Molecular drawing of 1,3-thiazolium-4-aminide **17** (displacement parameters are drawn at the 30% probability level). Selected bond lengths [pm] (crystallographic numbering): C3–N3: 142.15 pm, N3–C1: 133.61 pm, C1–S: 169.78 pm, S–C11: 171.01 pm, C11–C3: 136.14 pm, N3–C5: 146.69 pm, C1–C10: 153.59 pm, C2–C14: 151.43 pm.

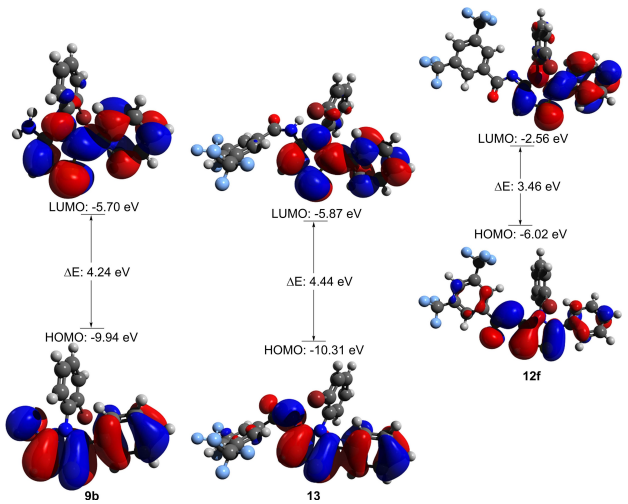


Figure 3. Frontier orbitals of **9b**, **13**, and **12f** as comparison.

To compare the frontier orbitals of the 4-amino-1,3-thiazolium salt with a 1,3-thiazolium-4-aminide and to see the effect of the benzoylation on the salt's orbitals, we calculated the molecular orbitals of the salts **9b** and **13** as well as of the mesoionic compound **12f** (PBE0-D3/def2-TZVP) (Figure 3). The highest occupied molecular orbital (HOMO) of the 4-amino-1,3-thiazolium salt **9b** is located in the central thiazolium ring and in the phenyl ring attached to C2, and the same is true for the lowest unoccupied molecular orbital (LUMO). Except for the development of a small atomic orbital coefficient on the oxygen atom, no fundamental changes of the frontier orbital profile is observable on benzoylation to form **13**. This is in accord with the fact, that the ^{15}N NMR resonance frequencies remain virtually unchanged on benzoylation. As expected, the energies decrease due to the electron-withdrawing properties by $\Delta E_{HOMO} = -0.37$ eV and $\Delta E_{LUMO} = -0.17$ eV. On betaine formation, however, the atomic orbital coefficient of the aminide increase considerably in the HOMO, whereas the trifluoromethyl-substituted phenyl ring as well as the phenyl ring attached to C2 are essentially electronically decoupled. In accordance with mesomeric structure **B** and the delocalization of the positive charge (*c.f.* Scheme 6), the phenyl ring attached to C2 possesses significant atomic orbital coefficients in the LUMO. As expected, the energies increase by $\Delta E_{HOMO} = +3.92$ eV and $\Delta E_{LUMO} = +3.14$ eV. Characteristic of conjugated mesomeric betaines, atomic orbital coefficients of HOMO and LUMO are localized in common parts of the π-electron system.

The betaines showed some interesting spectroscopic features such as solvatochromism and fluorescence. We examined the solvatochromism of **12h** as an example and chose *n*-hexane, toluene, ethyl acetate, dichloromethane, acetonitrile, ethanol, methanol and water as solvents. Figure 4 shows the normalized UV/Vis spectra in the range between 300 nm and 550 nm, since the range with the cut-off wavelengths of the used solvents for toluene start at 286 nm. Thereby, it was observed that, with the exception of *n*-hexane and dichloromethane, a significant hypochromic shift of more than 50 nm of the absorption maximum occurs when the polarity of the solvent is increased. In this case, it should also be mentioned that both *n*-hexane and dichloromethane display a shoulder in the range between 440 nm and 450 nm. The negative solvatochromism could also be observed for most of the aminides **12a–g**, **12i**, **14a–b** and **17**. However, these compounds do not

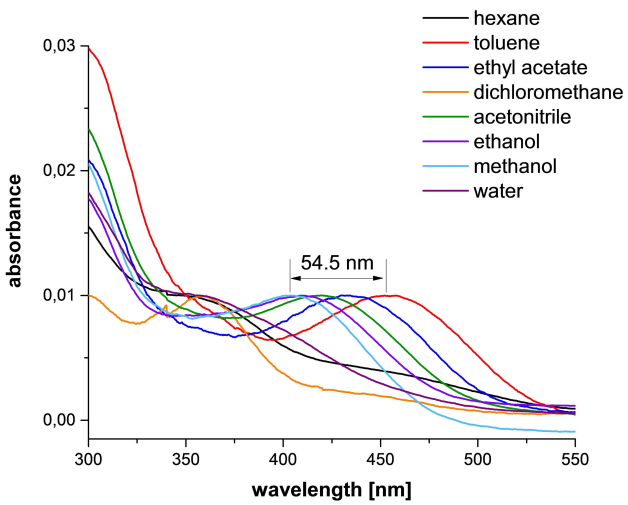


Figure 4. UV/Vis spectrum of thiazolium-4-aminide **12h** in solvents with different polarity.

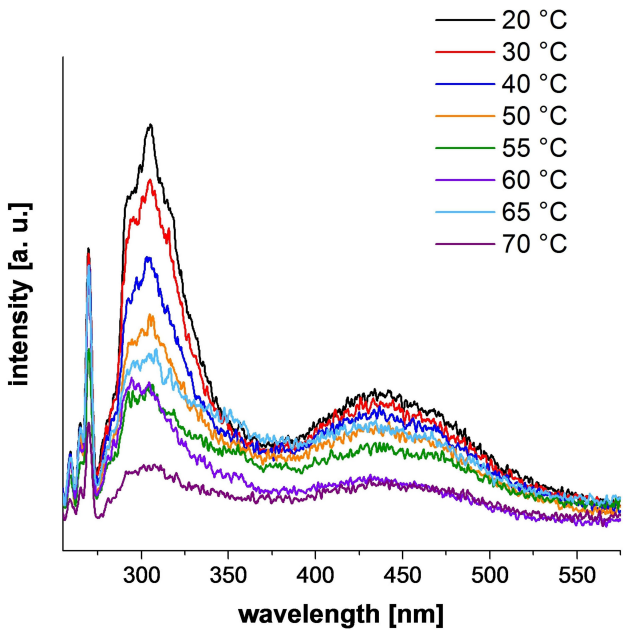


Figure 5. Fluorescence spectrum of **14b** at varying temperatures, absorbance 0.1 a. u., λ_{exc} 250 nm.

show in all cases bands as distinctive as **12h**. The maxima at largest wavelength sometimes are resolved as shoulders.

Furthermore, fluorescence spectra were measured because of the visible green fluorescence of thiazolium salts **9a** and **9b** in substance. The fluorescence spectra generally show similarities to the fluorescence spectra of excimer-forming molecules, *e.g.* to the phenomena observed with 9,10-dichloroanthracene,[30] as well as other 5-membered heterocycles.[31] However, the measurements suggest that at least no thiazolium excimers were formed during the experiments, because the fluorescence decay profile of the broad, non-structured fluorescence band (LWL) is not conform to the Birks scheme with exponential growth and decay term.[32] Neither ESIPT-reactions (excited state intramolecular proton transfer),[33,34] nor anion-π-interactions are possible in this case. In accordance with excimer forming molecules, higher temperatures lead to decreased intensities of the broad unstructured band of **14b** at approximately 450 nm. Figure 5 displays the temperature-depending fluorescence spectra of 1,3-thiazolium-4-aminide **14b** as an example. Two characteristic bands are visible, one with greater intensity at short wavelength (SWL) and another broad, unstructured band at long wavelength (LWL). For the temperature-dependent fluorescence measurements of **14b**, the ratio of I_{LWL} to I_{SWL} was plotted versus temperature. Although the outlier at 60 °C should be neglected, Figure 6 illustrates that I_{LWL}/I_{SWL} increases as a function of temperature. This phenomenon is reversible, as the original intensities reconstitute on cooling as depicted in Figure 6 (red data points). We measured the fluorescence spectra of the salts **9a**–**11c** and betaines **12a**–**i**, **14a**–**b** and **17** in MeCN, because dichloromethane caused quenching. It was also observed that the fluorescence was not quenched by oxygen.

In addition, Table 4 summarizes the adjusted excitation wavelengths λ_{exc} as obtained from UV/Vis measurements, and a classification of the strength of the broad, non-structured fluorescence band (LWL). The data show no differences between chlorides and trifluoroacetates, which is consistent to the assumption that no anion-π interactions exist.

Time-resolved fluorescence measurements were made to determine the lifetimes of the emission band at short wavelength (SWL) selected by an interference filter in the range of 263 nm to 330 nm. The one at long wavelength (LWL) was selected by a long pass filter (>404 nm). For this, dilute solutions were excited with a pulsed LED lamp with an excitation wavelength of 255 nm. All molecules classified as medium, strong or very strong in Table 4 were studied. The determination of lifetimes was carried out by fitting a

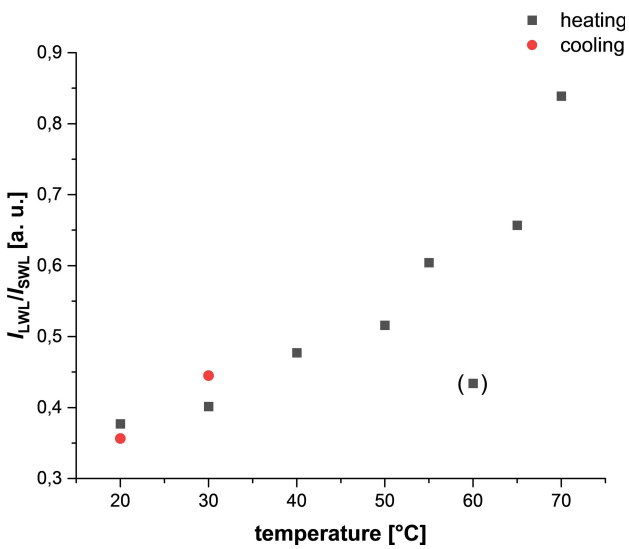


Figure 6. Ratio of the intensity of the unstructured (I_{LWL}) to the intensity of the structured band (I_{SWL}) of the fluorescence spectrum of **14b** against temperature.

Table 4. Results of fluorescence measurements.

Compd	λ_{exc}[a] [nm]	SWL [nm]	LWL [nm]
9a	234	305	479 (medium)
9b	235	304	465 (medium)
9c	270	328	494 (strong)
10b	263	304	427 (strong)
10c	355	397	472 (very strong)
11a	231	304	446 (medium)
11b	231	304	463 (medium)
11c	291	334	498 (strong)
12a	232	304	n. d. (almost none)
12b	236	306	332 (medium)
12c	230	305	n. d. (almost none)
12d	224	295	337 (medium)
12e	220	290	n. d. (none)
12f	231	305	333 (medium)
12g	288	323	487 (medium)
12h	305	347	534 (medium)
12i	225	294	480 (weak)
14a	231	303	450 (medium)
14b	250	305	442 (strong)
17	235	304	400 (almost none)

[a] Wavelength determined by UV/Vis spectroscopy is equal to λ_{exc}.

biexponential function with two lifetimes τ_1 and τ_2. The obtained results are presented in Table 5. No typical excimer-forming process could be observed in the time-resolved measurements. Therefore, the assignment of the broad unstructured band (LWL) to excimer-formation can be excluded. (Please note that although the relative amplitude A_2 of SWL of the long lifetime emission is only in range of 1%, its contribution to the total emitted fluorescence is considerable according to $I_2 = A_2 \cdot \tau_2$)

Conclusions

Hitherto only few examples of the mesoionic class of compounds of 1,3-thiazolium-4-aminides have been described. The synthesis starting from thioamides and chloroacetonitrile *via* cyanomethylbenzimidothioates and subsequent cyclization with benzoylchloride proved to be an efficient approach to the preparation of a series of 1,3-thiazolium-4-aminides by substitution of the free amino group. 1,3-Thiazolium-4-aminides are typical examples of mesoionic compounds as their charge distribution according to the rules of resonance identifies common atoms for either charge within the common π-electron system, and the atomic orbital coefficients of the highest occupied (HOMO) as well as lowest unoccupied molecular orbitals (LUMO) also share common atoms. Bond lengths, spectroscopic data, and the frontier orbital profile gain insight into the weighted average of canonical forms from which relevant structures can be chosen for suitable representations of these mesoionic compounds. The 1,3-thiazolium-4-aminides proved to be negatively solvatochromic. Some representatives of these mesoionic compounds are fluorescent in the solid state. Fluorescence measurements revealed that no excimers are formed.

Table 5. Results of time-resolved fluorescence measurements. All samples were measured with an excitation wavelength λ_{exc} of 255 nm; n. f. not fitted.

Compd	SWL τ_1 [ns]	SWL A_1 [%]	SWL τ_2 [ns]	SWL A_2 [%]	LWL τ_1 [ns]	LWL A_1 [%]	LWL τ_2 [ns]	LWL A_2 [%]
9a	1.2	99.2	31.3	0.8	1.1	62.7	8.9	37.3
9b	1.0	99.1	44.3	0.9	0.3	98.1	6.6	1.9
9c	1.1	89.5	52.9	10.5	1.3	87.1	7.6	12.9
10b	0.8	99.1	37.9	0.9	0.4	97.4	6.6	2.7
10c	1.0	98.9	43.4	1.1	0.9	92.7	8.0	7.3
11a	1.1	99.0	47.5	1.0	n. f.	n. f.	n. f.	n. f.
11b	0.7	99.4	51.2	0.6	1.4	86.2	8.4	13.8
11c	0.9	99.3	41.5	0.7	1.5	81.1	8.7	18.9
12b	1.0	99.2	44.3	0.8	1.2	88.9	8.2	11.1
12d	0.8	99.4	39.9	0.6	0.7	95.7	9.3	4.3
12f	0.7	99.3	33.8	0.7	1.3	89.7	11.1	10.3
12g	0.9	95.0	7.9	5.0	1.1	91.4	8.1	8.6
12h	0.7	98.5	12.0	1.5	1.5	89.4	13.4	10.6
14a	0.7	99.4	40.8	0.6	1.0	84.1	8.1	15.9
14b	1.0	99.0	43.3	1.0	1.2	89.0	7.0	11.0

Experimental Section

Flash-chromatography was performed on silica gel 60 (0.040–0.063 mm). Nuclear magnetic resonance (NMR) spectra were measured by means of a Bruker Avance 400 and a Bruker Avance III 600 MHz spectrometer. ^{1}H NMR spectra were recorded at 400 MHz or 600 MHz, respectively. ^{13}C NMR spectra were recorded at 100 MHz or 150 MHz, with the solvent peak or tetramethylsilane used as the internal reference. ^{15}N NMR measurements were performed at 61 MHz and nitromethane was used as external reference. ^{11}B NMR spectra were taken at 193 MHz and $BF_3 \cdot Et_2O$ was taken as the external reference. ^{19}F NMR spectra were measured at 377 MHz and Cl_3CF was taken as external reference. Multiplicities are described by the following abbreviations: s = singlet, bs = broad singlet, d = doublet, t = triplet, q = quartet, and m = multiplet. Peak assignments were described using the following abbreviations, *e.g.* 5-H/C-5: protons and carbons of the thiazolium ring; 2'-H/2'-C: protons and carbons of the phenyl and thiophene ring attached to C2 of the thiazolium ring; 2″-H/2″-C: phenyl ring attached to N3 of the thiazolium ring, respectively. H_i/C_i, H_o/C_o, H_m/C_m, and H_p/C_p correspond to the *ipso*, *ortho*, *meta* and *para*-positions of the benzoyl ring, respectively. Peak assignments base on *gs*-^{1}H,^{1}H-COSY, *gs*-^{1}H,^{13}C-HSQC, *gs*-^{1}H,^{13}C-HMBC, *gs*-^{1}H,^{15}N-HMBC, and NOESY experiments. IR spectra were recorded on a Bruker Vector 22 in the range of 400 to 4000 cm^{-1}. ATR-IR spectra were recorded on a Bruker Alpha in the range of 400 to 4000 cm^{-1}. The mass spectra (EIMS) were measured with a Varian 320 MS Triple Quad GC/MS/MS with a Varian 450-GC. The electrospray ionization mass spectra (HRESIMS) were measured with a Bruker Impact mass spectrometer. Melting points are uncorrected and were measured with a Stuart SMP3 melting apparatus. Yields are not optimized. Abbreviations: DCM = dichloromethane, EE = ethyl acetate; PE = petroleum ether.

Fluorescence measurements

The absorption spectra were recorded with a Jasco spectrophotometer V670 (bandwidth nm) and the static fluorescence spectra with a Jasco spectrophotometer FP-8500 (bandwidth nm). Set-up for the time-resolved fluorescence measurements consists of a time-correlated single-photon counting (TCSPC, 500 channels, 0.4 ns channel width, EG&G), a pulsed light source a flash LED (λ = 255 nm, 2 MHz pulse rate, 1.4 ns full width at half maximum,

Picoquant) and a photomultiplier tube from Hamamatsu for single photon detection. The fluorescence decay curves were fitted to a biexponential fit function using the Levenberg-Marquardt algorithm. The lamp shift and the background noise were also taken into account.

Calculations

DFT calculations were performed using ORCA 4.2.1[35] running on a MS Windows 10 Pro PC system with an AMD Ryzen Threadripper 3970X 32-Core and 128 GB RAM utilizing the appropriate message passing interface MS-MPI 10.0.12498.5. MMFF optimized structures were used as starting geometries for the geometry optimizations with the PBE0 density functional and the polarized triple-zeta basis set def2-TZVP. An additional D3 dispersion correction and the RIJCOSX approximation were used. Subsequent frequency calculations of all final structures evidenced the absence of imaginary frequencies and thus the presence of true minima on the potential energy surface.

X-Ray structure analyses

Suitable single crystals were selected under a polarization microscope and mounted in a glass capillary ($d = 0.3$ mm). The crystal structures were determined by X-ray diffraction analyses using graphite monochromated Mo-K_α radiation (0.71073 Å) [$T = 223(2)$ K], whereas the scattering intensities were collected with a single crystal diffractometer (STOE IPDS II). The crystal structures were solved by Direct Methods using SHELXS-97 and refined using alternating cycles of least squares refinements against F^2 (SHELXL-97). All non-H atoms were located in Difference Fourier maps and were refined with anisotropic displacement parameters. The H positions were determined by a final Difference Fourier Synthesis.[36]

For $C_{22}H_{19}ClN_2O_2S$ (10 a), $M = 410.90$ g mol^{-1}: $C_{22}H_{19}ClN_2O_2S$ crystallized in the monoclinic space group $P2_1/c$ (no. 14), lattice parameters $a = 11.869(4)$ Å, $b = 13.486(3)$ Å, $c = 13.107(4)$ Å, $\beta = 107.70(2)°$, 1998.7(10) Å^3, $Z = 4$, $d_{calc.} = 1.366$ g cm^{-3}, $F(000) = 856$ using 3792 independent reflections and 329 parameters. $R1 = 0.0533$, $wR2 = 0.1067$ [$I > 2\sigma(I)$], goodness of fit on $F^2 = 1.071$, residual electron density 0.292 and −0.274 e Å^{-3}.

For $C_{20}H_{18}N_4O_5S$ (17), $M = 426.44$ g mol^{-1}: $C_{20}H_{18}N_4O_5S$ crystallized in the triclinic space group $P1$ (no. 2), lattice parameters $a = 9.766(3)$ Å, $b = 10.085(3)$ Å, $c = 11.602(3)$ Å, $\alpha = 101.97(2)°$, $\beta = 96.32(2)°$, $\gamma = 113.93(2)°$, V = 997.3(5) Å^3, $Z = 2$, $d_{calc.} = 1.420$ g cm^{-3}, $F(000) = 444$ using 3726 independent reflections and 343 parameters. $R1 = 0.0870$, $wR2 = 0.1029$ [$I > 2\sigma(I)$], goodness of fit on $F^2 = 1.008$, residual electron density 0.274 and −0.243 e Å^{-3}.

***N*-Phenylbenzcarbothioamide 7 a**. Under an inert atmosphere, a suspension of benzanilide **6 a** (5.000 g, 25.40 mmol, 1.0 eq.) and Lawesson's reagent (6.150 g, 15.21 mmol, 0.6 eq.) in 200 mL of anhyd toluene was stirred for 2.5 h at reflux temperature. After removal of the solvent *in vacuo* the residue was chromatographed (PE:EE, 5.4:1). Yield: 5.375 g (25.20 mmol, 99 %) of a yellow-greenish solid, mp 164–166 °C.[37] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.29–7.32 (m, 1H), 7.44–7.51 (m, 5H), 7.77–7.86 (m, 4H), 9.02 (bs, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 123.8 (+, 2C), 126.8 (+, 2C), 127.1 (+, 1C), 128.8 (+, 2C), 129.2 (+, 2C), 131.4 (+, 1C), 139.2 (o, 1C), 143.4 (o, 1C), 198.6 (o, 1C) ppm. Data correspond to those reported.[37]

***N*-(2-Bromophenyl)benzcarbothioamide 7 b**. Under an inert atmosphere a suspension of *N*-(2-bromophenyl)benzamide **6 b** (1.569 g, 5.68 mmol, 1.0 eq.) and Lawesson's reagent (1.379 g, 3.41 mmol, 0.6 eq.) in 50 mL of anhydrous toluene was stirred at reflux over a period of 4 h. After distilling off the solvent, the residue was chromatographed (PE:EE, 2.7:1). The product was obtained as yellow-greenish solid. Yield: 1.648 g (5.64 mmol, 99 %), mp 82–84 °C.[25] ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.17 (t, $J_{H,H} = 7.9$ Hz, 1H), 7.40–7.54 (m, 4H), 7.67 (dd, $J_{H,H} = 7.9$, 1.4 Hz, 1H), 7.92 (bs, 2H), 8.63 (bs, 1H), 9.28 (bs, 1H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 117.9 (o, 1C), 125.8 (+, 1C), 127.2 (+, 2C), 127.9 (+, 1C), 128.1 (+, 1C), 128.8 (+, 2C), 131.6 (+, 1C), 132.9 (+, 1C), 137.0 (o, 1C), 142.9 (o, 1C), 198.4 (o, 1C) ppm. Data correspond to those reported in the literature.[25]

***N*-Phenylthiophene-2-carbothioamide 7 c**. Under an inert atmosphere a suspension of *N*-phenylthiophen-2-carboxamide **6 c** (1.850 g, 9.11 mmol, 1.0 eq.) and Lawesson's reagent (2.211 g, 5.47 mmol, 0.6 eq.) in 30 mL of anhydrous toluene was stirred at reflux temperature for 4 h. After removal of the solvent *in vacuo*, the crude product was chromatographed (PE:EE, 5:1). Yield: 1.950 g (8.90 mmol, 98 %), green solid, mp 93–95 °C.[38] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.09 (dd, $J_{H,H} = 5.1$, 4.0 Hz, 1H), 7.27–7.31 (m, 1H), 7.39-7.44 (m, 2H), 7.52 (bs, 1H), 7.54 (dd, $J_{H,H} = 5.1$, 1.0 Hz, 1H), 7.67 (d, $J_{H,H} = 7.8$ Hz, 2H), 8.98 (bs, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 124.4 (+, 2C), 124.8 (+, 1C), 127.2 (+, 1C), 128.1 (+, 1C), 129.2 (+, 2C), 133.2 (+, 1C), 138.6 (o, 1C), 148.1 (o, 1C), 188.0 (o, 1C) ppm. The data are in agreement with those reported in the literature.[38]

Cyanomethyl-*N*-phenylbenzcarboximidothioate 8 a. Under stirring, chloroacetonitrile (0.49 mL, 7.74 mmol, 1.1 eq.) and then Et_3N (1.50 mL, 10.82 mmol, 1.5 eq.) were added to a suspension of thiobenzanilide **7 a** (1.500 g, 7.03 mmol, 1.0 eq.) in 7.5 mL of toluene. After heating to 50 °C over a period of 9 h and distilling off the solvent, the residue was chromatographed (PE:EE, 2.4:1). The product was obtained as orange solid in 87 % yield (1.541 g, 6.11 mmol), mp. 68 °C.[17b] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.96 (bs, 2H), 6.74 (bs, 2H), 7.01 (bs, 1H), 7.16–7.34 (m, 7H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 16.3 (−, 1C), 116.6 (o, 1C), 121.3 (+, 2C), 124.1 (+, 1C), 128.2 (+, 2C), 128.7 (+, 2C), 128.9 (+, 2C), 130.5 (+, 1C), 134.4 (o, 1C), 148.8 (o, 1C), 162.4 (o, 1C) ppm. IR (ATR): ν = 3084, 3059, 3034, 3020, 2967, 2923, 2244, 1625, 1593, 1483, 1442, 1376, 1228, 1188, 1071, 1025, 998, 961, 909, 838, 760, 692, 587, 555, 512 cm^{-1}. EI-MS (DEP, 70 eV): *m/z* (%) = 252 [M]$^+$. HR-ESI-MS: calcd for $[C_{15}H_{12}N_2S + H]^+$: 253.0794. Found: 253.0784.

Cyanomethyl-*N*-(2-bromophenyl)benzcarboximidothioate 8 b. Under stirring, chloroacetonitrile (0.38 mL, 6.02 mmol, 1.1 eq.) and next Et_3N (1.17 mL, 8.43 mmol, 1.5 eq.) were added to a suspension of (*N*-bromophenyl)benzthioamide **7 b** (1.600 g, 5.48 mmol, 1.0 eq.) in 8 mL of toluene. The solvent was distilled off after a reaction time of 9 h at 50 °C. The crude reaction product was then chromatographed (PE:EE, 2.4:1). The product was obtained as orange oil, yield 86 % (1.555 g, 4.71 mmol). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 4.01 (bs, 2H), 6.53 (bs, 1H), 6.87 (t, $J_{H,H} = 7.6$ Hz, 1H) 7.05 (bs, 1H), 7.26–7.36 (m, 5H), 7.52 (d, $J_{H,H} = 7.6$ Hz, 1H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 16.6 (−, 1C), 115.9 (o, 1C), 116.4 (o, 1C), 121.5 (+, 1C), 125.2 (+, 1C), 127.8 (+, 2C), 127.9 (+, 1C), 128.8 (+, 2C), 130.9 (+, 1C), 132.9 (+, 1C), 134.2 (o, 1C), 147.7 (o, 1C), 164.6 (o, 1C) ppm. IR (ATR): ν = 3058, 3023, 2972, 2927, 2248, 1616, 1596, 1581, 1489, 1462, 1444, 1434, 1376, 1313, 1276, 1259, 1229, 1191, 1158, 1118, 1075, 1043, 1027, 1000, 954, 915, 857, 757, 729, 695, 662, 638, 612, 594, 562, 445, 423 cm^{-1}. EI-MS (DEP, 70 eV): *m/z* (%) = 330 [M]$^+$. HR-ESI-MS: calcd for $[C_{13}H_{11}BrN_2S + Na]^+$: 352.9719. Found: 352.9722.

Cyanomethyl-*N*-phenylthiophene-2-carboximidothioate 8 c

Under vigorous stirring, chloroacetonitrile (0.16 mL, 2.51 mmol, 1.1 eq.) and then Et_3N (0.49 mL, 3.52 mmol, 1.5 eq.) were added to a suspension of *N*-phenylthiophene-2-carbothioamide **7 c** (0.500 g, 2.28 mmol, 1.0 eq.) in 5 mL of toluene. After reacting for 9 h at

50 °C and removal of the solvent, the crude material was chromatographed (PE:EE, 2:1). Yield. 83% (487 mg; 1.89 mmol). The product was obtained as orange oil. ^{1}H NMR (600 MHz, $CDCl_3$): $\delta = 3.95$ (bs, 2H), 6.83 (d, $J_{H,H} = 6.1$ Hz, 2H), 6.94 (bs, 1H), 7.13 (t, $J_{H,H} = 7.3$ Hz, 1H), 7.31–7.39 (m, 4H, 6-H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): $\delta = 16.6$ (−, 1C), 116.4 (o, 1C), 120.2 (+, 2C), 124.4 (+, 1C), 126.9 (+, 1C), 129.5 (+, 2C), 131.3 (+, 1C), 131.4 (+, 1C), 134.1 (o, 1C), 149.7 (o, 1C), 154.0 (o, 1C) ppm. IR (ATR): $\nu = 3099$, 3075, 3060, 3027, 2970, 2926, 2246, 1607, 1589, 1530, 1507, 1482, 1445, 1413, 1375, 1349, 1238, 1215, 1182, 1134, 1067, 1048, 1025, 1001, 968, 937, 911, 882, 839, 795, 759, 716, 695, 642, 615, 586, 555, 498, 465 cm^{-1}. EI-MS (DEP, 70 eV): *m/z* (%) = 258 $[M]^+$. HR-ESI-MS: calcd for $[C_{13}H_{10}N_2S_2 + Na]^+$: 281.0178. Found: 281.0182.

General Procedure for the Preparation of 9a–11c

Method A) A suspension of 1.0 eq. of nitrile and 2.2 eq. or 10.0 eq. of benzoyl chloride in toluene was first heated over a period of 6 h at 60 °C and then stirred for 18 h at rt. After the solvent was distilled off *in vacuo*, the residue was resolved with DCM (30 mL), extracted with a solution of Na_2CO_3 in water (3×40 mL) and dried over $MgSO_4$. The crude product was finally chromatographed.

Method B) Under an atmosphere of nitrogen a suspension of 1.0 eq. of the nitrile and 2.0 eq. of Et_3N in anhyd. DCM was cooled to −40 °C and then 2.2 eq. of trifluoroacetanhydride (TFAA) was added. The mixture was stirred for 1 h at −40 °C and then allowed to warm to rt. Stirring was continued for additional 16 h. The crude product was chromatographed (DCM:EtOH, 30:1).

4-Amino-2,3-diphenyl-1,3-thiazolium chloride 9a. Method A). Cyanomethyl-*N*-phenylbenzcarboximidothioate (**8a**, 1.710 g, 6.78 mmol, 1.0 eq.) and benzoyl chloride (1.73 mL, 14.91 mmol, 2.2 eq.) in 17 mL of toluene were used. The crude product was chromatographed (PE:EE, 2.4:1, then EE:EtOH, 1:1), yield 1.758 g (6.09 mmol, 90%), yellow solid, mp. 154 °C.[17b] ^{1}H NMR (600 MHz, DMSO-d_6): δ = 6.51 (bs, 2H, NH_2), 6.92 (s, 1H, 5-H), 7.36–7.40 (m, 4H, 2′-H and 3′-H), 7.47–7.50 (m, 1H, 4′-H), 7.56–7.61 (m, 5H, 2″-H, 3″-H and 4″-H) ppm. ^{13}C NMR (150 MHz, DMSO-d_6): δ = 92.2 (+, 1C, 5-C), 126.4 (o, 1C, 1′-C), 128.0 (+, 2C, 2″-C or 3″-C), 129.0 (+, 2C, 2′-C or 3′-C), 129.4 (+, 2C, 2′-C or 3′-C), 130.2 (+, 2C, 2″-C or 3″-C), 131.2 (+, 1C, 4″-C), 131.9 (+, 1C, 4′-C), 133.9 (o, 1C, 1″-C), 151.8 (o, 1C, 4-C), 164.2 (o, 1C, 2-C) ppm. IR (ATR): ν = 3260, 3192, 3144, 3060, 2963, 2928, 1703, 1625, 1593, 1561, 1490, 1447, 1420, 1370, 1321, 1302, 1230, 1195, 1180, 1099, 1072, 1053, 1018, 957, 923, 891, 849, 756, 730, 690, 645, 570, 538, 477 cm^{-1}. EI-MS (DEP, 70 eV): *m/z* (%) = 253 $[M]^+$. HR-ESI-MS: calcd for $[C_{15}H_{13}N_2S]^+$: 253.0794. Found: 253.0794.

4-Amino-3-(2-bromophenyl)-2-phenyl-1,3-thiazolium chloride 9b. Method A). Cyanomethyl-*N*-(2-bromophenyl) benzcarboximidothioate (**8b**, 0.960 g, 2.90 mmol, 1.0 eq.) and benzoyl chloride (0.74 mL, 6.38 mmol, 2.2 eq.) in 10 mL of toluene were used. The crude product was chromatographed (PE:EE, 0.8:1, then EE:EtOH, 1:1). yield 1.035 g (2.82 mmol, 97%), yellow solid, mp. 160 °C (dec.). ^{1}H NMR (600 MHz, DMSO-d_6): δ = 6.72 (bs, 2H, NH_2), 6.92 (s, 1H, 5-H), 7.40–7.45 (m, 4H, 2′-H and 3′-H), 7.52–7.55 (m, 1H, 4′-H), 7.56–7.59 (m, 1H, 4″-H), 7.67 (td, $J_{H,H} = 11.6$, 1.3 Hz, 1H, 3″-H), 7.85 (dd, $J_{H,H} = 8.0$, 1.3 Hz, 1H, 5″-H), 7.99 (dd, $J_{H,H} = 8.0$, 1.6 Hz, 1H, 6″-H) ppm. ^{13}C NMR (150 MHz, DMSO-d_6): δ = 92.1 (+, 1C, 5-C), 120.9 (o, 1C, 2″-C), 125.8 (o, 1C, 1′-C), 129.2 (+, 2C, 2′-C), 129.2 (+, 2C, 3′-C), 129.8 (+, 1C, 3″-C), 131.0 (+, 1C, 6″-C), 132.4 (+, 1C, 4′-C), 132.7 (o, 1C, 1″-C), 133.6 (+, 1C, 4″-C), 134.1 (+, 1C, 5″-C), 151.6 (o, 1C, 4-C), 164.0 (o, 1C, 2-C) ppm. ^{15}N NMR (61 MHz, DMSO-d_6): δ = −320.8 (s, 1N, 6-N), −184.3 (s, 1N, 3-N) ppm. IR (ATR): ν = 3262, 3213, 3132, 3103, 3049, 1681, 1615, 1563, 1491, 1475, 1446, 1425, 1375, 1319, 1262, 1201, 1180, 1074, 1063, 1019, 891, 768, 755, 738, 715, 688, 658, 640, 618, 576, 509, 489, 440 cm^{-1}. HR-ESI-MS: calcd for $[C_{15}H_{12}BrN_2S]^+$: 330.9899. Found: 330.9904.

4-Amino-3-phenyl-2-(thiophen-2-yl)-1,3-thiazolium chloride 9c. Method A) Cyanomethyl-*N*-phenylthiophene-2-carboximidothioate (**8c**, 0.450 g, 1.74 mmol, 1.0 eq.) and benzoylchloride (0.45 mL, 3.84 mmol, 2.2 eq.) in 5 mL of toluene were used. The crude product was chromatographed (PE:EE, 0.8:1, then EE:EtOH, 1:1). Yield 0.508 g (1.73 mmol, 99%), yellow-orange solid, mp: 95–97 °C. ^{1}H NMR (600 MHz, DMSO-d_6): δ = 6.38 (bs, 2H, NH_2), 6.69 (s, 1H, 5-H), 7.16 (dd, $J_{H,H} = 5.0$, 3.9 Hz, 1H, 4′-H), 7.67 (dd, $J_{H,H} = 3.9$, 1.2 Hz, 1H, 5′-H), 7.70–7.74 (m, 4H, 2″-H and 3″-H), 7.76–7.79 (m, 1H, 4″-H), 7.92 (dd, $J_{H,H} = 5.0$, 1.2 Hz, 1H, 3′-H) ppm. ^{13}C NMR (150 MHz, DMSO-d_6): δ = 89.9 (+, 1C, 5-C), 127.5 (o, 1C, 1′-C), 128.5 (+, 1C, 4′-C), 128.5 (+, 2C, 2″-C), 131.1 (+, 2C, 3″-C), 132.4 (+, 1C, 4″-C), 133.4 (+, 1C, 5′-C), 133.4 (+, 1C, 3′-C), 135.0 (o, 1C, 1″-C), 151.2 (o, 1C, 4-C), 158.4 (o, 1C, 2-C) ppm. IR (ATR): ν = 3281, 3103, 3065, 2931, 1706, 1674, 1623, 1570, 1513, 1489, 1452, 1443, 1410, 1380, 1331, 1303, 1279, 1232, 1198, 1114, 1070, 1050, 1024, 1002, 915, 882, 856, 838, 761, 718, 694, 625, 578, 464 cm^{-1}. EI-MS (DEP, 70 eV): *m/z* (%) = 258 $[M-H]^+$. HR-ESI-MS: calcd for $[C_{13}H_{11}N_2S_2]^+$: 259.0358. Found: 259.0375.

4-Benzamido-2,3-diphenyl-1,3-thiazolium chloride 10a. Method A). Cyanomethyl-*N*-phenylbenzcarboximidothioate (**8a**, 0.430 g, 1.70 mmol, 1.0 eq.) and benzoyl chloride (0.44 mL, 3.75 mmol, 2.2 eq.) in 4 mL of toluene were used. The crude product was chromatographed (PE:EE, 0.8:1, then EE:EtOH, 1:1) yield 0.448 g (1.14 mmol, 67%), yellow solid. Mp. 154 °C (dec.). ^{1}H NMR (400 MHz, D_2O): δ = 6.83 (s, 1H, 5-H), 7.38-7.39 (m, 3H, H_{arom}), 7.48-7.54 (m, 7H, H_{arom}), 7.58-7.66 (m, 5H, H_{arom}) ppm. The limited solubility prevented us from measuring 2D NMR spectra, so that the assignment was done in analogy to other derivatives. ^{13}C NMR (100 MHz, D_2O): δ = 93.4 (+, 1C, 5-C), 125.9 (o, 1C, 1′-C), 127.6 (+, 4 C, C_m and 2″-C or 3″-C), 129.2 (+, 2C, C_o), 129.6 (+, 4C, 2′-C and 3′-C), 130.3 (o, 1C, C_i), 130.8 (+, 2C, 2″-C or 3″-C), 131.9 (+, 1C, 4″-C), 132.5 (+, 1C, 4′-C), 133.6 (+, 1C, C_p), 133.9 (o, 1C, 1″-C), 151.1 (o, 1C, 4-C), 166.0 (o, 1C, 2-C or C=O), 177.6 (o, 1C, 2-C or C=O) ppm.

4-Benzamido-3-(2-bromophenyl)-2-phenyl-1,3-thiazolium chloride 10b. Method A) Cyanomethyl-*N*-(2-bromophenyl) benzcarboximidothioate (**8b**, 0.500 g, 1.51 mmol, 1.0 eq.) and benzoyl chloride (1.75 mL, 15.10 mmol, 10.0 eq.) in 5 mL of toluene were used. The crude product was chromatographed (PE:EE, 0.8:1, then EE:EtOH, 1:1). Yield 0.609 g (1.29 mmol, 86%), yellow solid, mp: 173–175 °C. ^{1}H NMR (600 MHz, DMSO-d_6): δ = 6.68 (bs, 1H, NH), 6.89 (s, 1H, 5-H), 7.40–7.45 (m, 4H, 2′-H and 3′-H), 7.48–7.55 (m, 3H, 11-H and 4′-H), 7.57 (td, $J_{H,H} = 7.9$, 1.5 Hz, 1H, 6″-H), 7.60–7.63 (m, 1H, 12-H), 7.67 (td, $J_{H,H} = 7.9$, 1.3 Hz, 1H, 3″-H), 7.86 (dd, $J_{H,H} = 7.9$, 1.3 Hz, 1H, 5″-H), 7.93–7.95 (m, 2H, 10-H), 7.99 (dd, $J_{H,H} = 7.9$, 1.5 Hz, 1H, 4″-H) ppm. ^{13}C NMR (150 MHz, DMSO-d_6): δ = 92.0 (+, 1C, 5-C), 120.9 (o, 1C, 2″-C), 125.8 (o, 1C, 1′-C), 128.6 (+, 2C, C_m), 129.2 (+, 2C, 2′-C), 129.2 (+, 2C, 3′-C), 129.2 (+, 2C, C_o), 129.8 (+, 1C, 3″-C), 130.8 (o, 1C, C_i), 131.0 (+, 1C, 4″-C), 132.5 (+, 1C, 4′-C), 132.7 (o, 1C, 1″-C), 132.8 (+, 1C, C_p), 133.6 (+, 1C, 6″-C), 134.2 (+, 1C, 5″-C), 151.5 (o, 1C, 4-C), 164.1 (o, 1C, 2-C), 167.3 (o, 1C, C=O) ppm. ^{15}N NMR (61 MHz, DMSO-d_6): δ = −319.8 (s, 1N, 6-N), −184.2 (s, 1N, 3-N) ppm. IR (ATR): ν = 3263, 3212, 3133, 3102, 3049, 1682, 1615, 1562, 1510, 1491, 1474, 1446, 1425, 1376, 1320, 1260, 1222, 1201, 1179, 1157, 1126, 1099, 1071, 1022, 971, 955, 941, 922, 889, 848, 808, 768, 755, 738, 705, 688, 657, 640, 618, 575, 512, 486, 439 cm^{-1}. EI-MS (DEP, 20 eV): *m/z* (%) = 330 [cation-$C_7H_6O]^+$ (12), 258 (100). HR-ESI-MS: Calcd for $[C_{22}H_{16}BrN_2OS]^+$: 435.0161. Found: 435.0153.

4-Benzamido-3-phenyl-2-(thiophen-2-yl)-1,3-thiazolium chloride 10c. Method A) Cyanomethyl-*N*-phenylthiophene-2-carboximidothioate (**8c**, 0.240 g, 0.93 mmol, 1.0 eq.) and benzoylchloride (1.08 mL, 9.30 mmol, 10.0 eq.) in 3 mL of toluene were used. The crude product was chromatographed (PE:EE:EtOH, 0.8:1:0.1). Even

after recrystallization the product was not obtained in pure form. Yield of the crude product 0.290 g (0.73 mmol, 78%), orange solid, mp 147–149 °C. ^{1}H NMR (600 MHz, DMSO-d_6): δ = 6.39 (bs, 1H, NH_2), 6.70 (bs, 1H, 5-H), 7.16 (dd, $J_{H,H}$ = 5.0, 3.9 Hz, 1H, 4′-H), 7.48–7.51 (m, 2H, 2″-H), 7.60–7.63 (m, 1H, 5′-H), 7.64–7.72 (m, 6H, 11-H, 12-H, 3″-H and 4″-H), 7.92 (dd, $J_{H,H}$ = 5.0, 1.2 Hz, 3′-H), 7.93–7.95 (m, 2H, 10-H) ppm. ^{13}C NMR (150 MHz, DMSO-d_6): δ = 89.9 (+, 1C, 5-C), 127.4 (o, 1C, 1′-C), 128.3 (+, 1C, 4′-C), 128.4 (+, 2C, 2″-C), 128.6 (+, 2C, 11-C), 129.2 (+, 2C, 10-C), 130.2 (+, 2C, 3″-C), 130.8 (o, 1C, 9-C), 132.8 (+, 2C, 12-C und 4″-C), 133.3 (+, 1C, 5′-C), 133.4 (o, 1C, 1″-C), 135.0 (+, 1C, 3′-C), 151.2 (o, 1C, 4-C), 158.4 (o, 1C, 2-C), 167.3 (o, 1C, C=O) ppm. IR (ATR): ν = 3390, 3097, 3052, 3030, 3004, 2956, 2922, 2849, 2831, 2819, 2784, 2739, 1703, 1665, 1629, 1587, 1509, 1490, 1473, 1449, 1413, 1346, 1318, 1301, 1277, 1245, 1185, 1166, 1118, 1093, 1070, 1030, 1022, 1000, 935, 909, 874, 854, 839, 815, 802, 766, 694, 672, 628, 615, 595, 578, 561, 477, 458 cm^{-1}. EI-MS (DEP, 70 eV): *m/z* (%) = 363 $[M]^+$ (1), 186 (100). HR-ESI-MS: Calcd for $[C_{20}H_{15}N_2OS_2]^+$: 363.0620. Found: 363.0623.

4-Amino-2,3-diphenyl-1,3-thiazolium trifluoroacetate 11a. Method B). Cyanomethyl-*N*-phenylbenzcarboximidothioate (**8a**, 0.500 g, 1.98 mmol, 1.0 eq.), Et_3N (0.55 mL, 3.96 mmol, 2.0 eq.) and TFAA (0.61 mL, 4.63 mmol, 2.2 eq.) in 15 mL of anhyd DCM were used. Yield: 0.134 g (0.37 mmol, 18%), red solid. mp: 101–103 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.22–7.26 (m, 4H, 2′-H and 2″-H), 7.34–7.37 (m, 2H, 3′-H), 7.43–7.50 (m, 4H, 4′-H, 3″-H and 4″-H), 8.13 (s, 1H, 5-H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 101.1 (+, 1C, 5-C), 117.8 (o, q, $J_{C,F}$ = 286.8 Hz, 1C, anion), 127.1 (o, 1C, 1′-C), 128.1 (+, 2C, 2″-C), 129.2 (+, 2C, 2′-C), 129.4 (+, 2C, 3″-C), 129.6 (+, 2C, 3′-C), 130.4 (+, 1C, 4″-C), 132.3 (+, 1C, 4′-C), 136.1 (o, 1C, 1″-C), 156.9 (o, 1C, 4-C), 161.7 (o, 1C, 2-C), 162.6 (o, q, $J_{C,F}$ = 34.1 Hz, 1C, anion) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = −75.6 (s, 3F, anion) ppm. IR (ATR): ν = 3443, 3149, 3063, 2962, 2926, 1740, 1677, 1612, 1593, 1524, 1490, 1452, 1394, 1367, 1334, 1309, 1256, 1177, 1124, 1076, 1056, 1026, 1001, 900, 870, 802, 756, 736, 687, 615, 587, 560, 523, 498, 432, 409 cm^{-1}. EI-MS (DEP, 70 eV): *m/z* (%) = 375 (4), 366 $[M]^+$ (1), 105 (100). HR-ESI-MS: Calcd for $[C_{15}H_{13}N_2S]^+$: 253.0794. Found: 253.0793.

4-Amino-3-(2-bromophenyl)-2-phenyl-1,3-thiazolium trifluoroacetate 11b. Method B) Cyanomethyl-*N*-(2-bromophenyl) benzcarboximidothioate (**8b**, 0.420 g, 1.27 mmol, 1.0 eq.), Et_3N (0.35 mL, 2.54 mmol, 2.2 eq.) and TFAA (0.39 mL, 2.79 mmol, 2.2 eq.) in 15 mL of anhyd DCM were used. Yield: 0.508 g (1.14 mmol, 90%), yellow solid, mp. 95–97 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.31–7.33 (m, 2H, 2′-H), 7.34–7.40 (m, 4H, 3′-H, 4″-H and 6″-H), 7.45 (td, $J_{H,H}$ = 7.7, 1.4 Hz, 1H, 3″-H), 7.49–7.51 (m, 1H, 4′-H), 7.67 (dd, $J_{H,H}$ = 8.0, 1.4 Hz, 1H, 5″-H), 8.13 (s, 1H, 5-H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 101.3 (+, 1C, 5-C), 117.7 (o, q, $J_{C,F}$ = 286.8 Hz, 1C, anion), 121.9 (o, 1C, 2″-C), 126.6 (o, 1C, 1′-C), 128.6 (+, 1C, 3″-C), 129.1 (+, 2C, 2′-C), 129.6 (+, 2C, 3′-C), 130.1 (+, 1C, 4″-C or 6″-C), 132.0 (+, 1C, 4″-C or 6″-C), 132.7 (+, 1C, 4′-C), 133.8 (+, 1C, 5″-C), 135.8 (o, 1C, 1″-C), 156.4 (o, 1C, 4-C), 162.3 (o, 1C, 2-C), 162.6 (o, q, $J_{C,F}$ = 31.5 Hz, 1C, anion) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = −75.7 (s, 3F, anion) ppm. IR (ATR): ν = 3308, 3137, 3093, 3068, 3028, 1742, 1671, 1615, 1526, 1496, 1473, 1449, 1396, 1338, 1285, 1267, 1252, 1168, 1118, 1069, 1041, 1025, 1002, 965, 903, 866, 780, 756, 706, 686, 641, 616, 590, 568, 550, 527, 506, 489, 457, 441 cm^{-1}. HR-ESI-MS: Calcd for $[C_{15}H_{12}BrN_2S]^+$: 330.9899. Found: 330.9893.

4-Amino-3-phenyl-2-(thiophen-2-yl)-1,3-thiazolium trifluoroacetate 11c. Cyanomethyl-*N*-phenylthiophene-2-carboximidothioate (**8c**, 0.200 g, 0.78 mmol, 1.0 eq.), Et_3N (0.21 mL, 1.55 mmol, 2.0 eq.) and TFAA (0.24 mL, 1.71 mmol, 2.2 eq.) in 8 mL of anhyd DCM were used. Yield: 0.070 g (0.19 mmol, 24%), yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.18–7.20 (m, 1H, 4′-H), 7.45–7.46 (m, 2H, 2″-H), 7.64–7.66 (m, 2H, 3″-H), 7.74–7.78 (m, 3H, 3′-H, 5′-H and 4″-H), 8.48 (bs, 3H, 5-H and NH_2) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 91.9 (+, 1C, 5-C), 114.9 (o, q, $J_{C,F}$ = 287.2 Hz, 1C, anion), 126.2 (o, 1C, 1′-C), 127.7 (+, 2C, 2″-C), 129.5 (+, 1C, 4′-C), 131.2 (+, 2C, 3″-C), 133.0 (+, 1C, 3′-C or 5′-C), 133.5 (+, 1C, 4″-C), 136.6 (o, 1C, 1″-C), 138.6 (+, 1C, 3′-C or 5′-C), 157.7 (o, q, $J_{C,F}$ = 41.8 Hz, 1C, anion), 158.8 (o, 1C, 4-C), 164.9 (o, 1C, 2-C) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = −76.4 (s, 3F, anion) ppm. IR (ATR): ν = 3347, 3198, 3097, 2981, 2928, 1777, 1659, 1622, 1593, 1498, 1456, 1408, 1352, 1327, 1288, 1137, 1054, 1008, 942, 899, 859, 848, 801, 756, 721, 696, 662, 597, 579, 545, 517, 495, 434 cm^{-1}. EI-MS (DEP, 70 eV): *m/z* (%) = 259 $[M]^+$ (2), 111 (100). HR-ESI-MS: Calcd for $[C_{13}H_{11}N_2S_2]^+$: 259.0358. Found: 259.0362.

General Procedure for the Preparation of 12a–12i. A suspension of 1.0 eq. of thiazolium chloride, 1.0 eq. of K_2CO_3 and 2.2 eq. of the acyl chloride dissolved in toluene was heated for 6 h at 60 °C. After the solvent was distilled off *in vacuo*, the residue was resolved in DCM (40 mL), extracted three times (40 mL each) with K_2CO_3 in water and dried over $MgSO_4$. The crude product was purified by column chromatography.

3-(2-Bromophenyl)-*N*-(3,5-dinitrobenzoyl)-2-phenyl-1,3-thiazolium-4-aminide 12a. 4-Amino-3-(2-bromophenyl)-2-phenyl-1,3-thiazolium chloride (**9b**, 0.200 g, 0.54 mmol, 1.0 eq.), K_2CO_3 (0.075 g, 0.54 mmol, 1.0 eq.) and 3,5-dinitrobenzoylchloride (0.276 g, 1.20 mmol, 2.2 eq.) in 8 mL of toluene were used. The crude product was chromatographed (DCM:EtOH, 20:1) to give a yellow solid. Yield: 0.274 g (0.52 mmol, 97%), mp: 162–164 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.47-7.52 (m, 4H, 2′-H and 3′-H), 7.54-7.61 (m, 2H, 4′-H and 6″-H), 7.66 (td, $J_{H,H}$ = 6.8, 1.6 Hz, 1H, 3″-H), 7.86 (ddd, $J_{H,H}$ = 9.4, 6.8, 1.6 Hz, 2H, 4″-H and 5″-H), 8.17 (s, 1H, 5-H), 8.75 (t, $J_{H,H}$ = 2.3 Hz, 1H, H_p), 8.76 (d, $J_{H,H}$ = 2.3 Hz, 2H, H_o) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ = 100.2 (+, 1C, 5-C), 119.0 (+, 1C, C_p), 121.2 (o, 1C, 2″-C), 126.7 (o, 1C, 1′-C), 127.6 (+, 2C, C_o), 128.7 (+, 1C, 3″-C), 129.2 (+, 2C, 2′-C or 3′-C), 129.3 (+, 2C, 2′-C or 3′-C), 131.1 (+, 1C, 4″-C or 5″-C), 132.1 (+, 1C, 6″-C), 132.3 (+, 1C, 4′-C), 133.2 (+, 1C, 4″-C or 5″-C), 136.3 (o, 1C, 1″-C), 143.6 (o, 1C, C_i), 147.8 (o, 2C, C_m), 155.7 (o, 1C, 4-C), 162.2 (o, 1C, 2-C), 164.7 (o, 1C, C=O) ppm. ^{15}N NMR (61 MHz, DMSO-d_6): δ = −173.8 (s, 1N, 3-N), −16.6 (s, 2N, NO_2) ppm; N–C=O is not detectable. IR (ATR): ν = 3177, 3159, 3104, 3087, 1723, 1701, 1624, 1602, 1531, 1519, 1494, 1470, 1450, 1415, 1336, 1262, 1244, 1185, 1124, 1079, 1065, 1039, 1025, 997, 940, 924, 916, 905, 869, 838, 781, 764, 747, 720, 684, 659, 647, 640, 616, 587, 564, 532, 519, 509, 482, 447, 428, 418 cm^{-1}. EI-MS (DEP, 70 eV): *m/z* (%) = 524 $[M]^+$ (5), 105 (100). HR-ESI-MS: Calcd. for $[C_{22}H_{13}BrN_4O_5S + Na]^+$: 546.9682. Found: 546.9688.

***N*-(3,5-Dichlorobenzoyl)-2,3-diphenyl-1,3-thiazolium-4-aminide 12b**. 4-Amino-2,3-diphenyl-1,3-thiazolium chloride (**9a**, 0.500 g, 1.73 mmol, 1.0 eq.), K_2CO_3 (0.239 g, 1.73 mmol, 1.0 eq.) and 3,5-dichlorobenzoylchloride (0.54 mL, 3.81 mmol, 2.2 eq.) in 20 mL of toluene were used. The crude product was purified by column chromatography (DCM:EtOH, 20:1). Yield: 0.636 g (1.50 mmol, 86%), yellow solid, mp: 115–117 °C. ^{1}H NMR (600 MHz, DMSO-d_6): δ = 7.41–7.44 (m, 4H, 2′-H and 3′-H), 7.49–7.52 (m, 4H, 2″-H and 3″-H), 7.53–7.55 (m, 3H, H_p, 4′-H and 4″-H), 7.67 (d, $J_{H,H}$ = 2.0 Hz, 2H, H_o), 8.11 (s, 1H, 5-H) ppm. ^{13}C NMR (150 MHz, DMSO-d_6): δ = 99.0 (+, 1C, 5-C), 126.7 (+, 2C, C_o), 127.4 (o, 1C, 1′-C), 128.4 (+, 2C, 2″-C or 3″-C), 128.6 (+, 1C, C_p), 128.8 (+, 2C, 2″-C or 3″-C), 129.0 (+, 2C, 2′-C or 3′-C), 129.4 (+, 2C, 2′-C or 3′-C), 129.6 (+, 1C, 4″-C), 131.6 (+, 1C, 4′-C), 133.2 (o, 2C, C_m), 137.1 (o, 1C, 1″-C), 144.0 (o, 1C, 9-C), 156.1 (o, 1C, 4-C), 161.5 (o, 1C, 2-C), 166.1 (o, 1C, C=O) ppm. IR (ATR): ν = 3150, 3067, 2764, 1801, 1698, 1592, 1568, 1512, 1486, 1452, 1421, 1394, 1355, 1290, 1251, 1225, 1186, 1169, 1155, 1091, 1070, 1050, 1027, 999, 957, 931, 889, 870, 791, 772, 753, 733, 683, 662, 605, 587, 562, 519, 496, 480, 459 cm^{-1}. EI-MS (DEP, 70 eV): *m/z* (%) = 424 $[M]^+$ (18), 180 (100). HR-ESI-MS: Calcd. for $[C_{22}H_{14}Cl_2N_2OS + Na]^+$: 447.0096. Found: 447.0097.

***N*-(3,5-Dinitrobenzoyl)-2,3-diphenyl-1,3-thiazolium-4-aminide 12c**. 4-Amino-2,3-diphenyl-1,3-thiazolium chloride (**9a**, 0.200 g,

0.69 mmol, 1.0 eq.), K_2CO_3 (0.096 g, 0.69 mmol, 1.0 eq.) and 3,5-dinitrobenzoylchloride (0.351 g, 1.52 mmol, 2.2 eq.) in 8 mL of toluene were used. The crude product was purified by column chromatography (first PE:EE, 0.8:1, then EE:EtOH, 1:1). The product was obtained as yellow solid. Yield: 0.298 g (0.67 mmol, 97%). ^{1}H NMR (600 MHz, DMSO-d_6): δ = 7.46–7.49 (m, 2H, 2′-H or 3′-H), 7.53–7.55 (m, 5H, 2′-H, 2″-H and 4″-H or 2′-H, 3″-H and 4″-H or 3′-H, 2″-H and 4″-H or 3′-H, 3″-H and 4″-H), 7.58-7.60 (m, 1H, 4′-H), 7.62-7.64 (m, 2H, 2″-H or 3″-H), 8.59 (s, 1H, 5-H), 8.90 (d, $J_{H,H}$ = 2.3 Hz, 2H, H_o), 8.94 (t, $J_{H,H}$ = 2.3 Hz, 1H, H_p) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ = 100.1 (+, 1C, 5-C), 118.9 (+, 1C, C_p), 127.3 (o, 1C, 1′-C), 127.6 (+, 2C, C_o), 128.5 (+, 2C, 2″-C or 3″-C), 129.0 (+, 2C, 2′-C or 3′-C), 129.0 (+, 2C, 2″-C or 3″-C), 129.5 (+, 2C, 2′-C or 3′-C), 129.7 (+, 1C, 4′-C), 131.7 (+, 1C, 4″-C), 137.0 (o, 1C, 1″-C), 143.9 (o, 1C, C_i), 147.8 (o, 2C, C_m), 155.9 (o, 1C, 4-C), 162.2 (o, 1C, 2-C), 164.7 (o, 1C, C=O) ppm. IR (ATR): ν = 3090, 1729, 1684, 1629, 1582, 1542, 1494, 1457, 1342, 1285, 1244, 1168, 1142, 1076, 922, 760, 729, 720, 699, 671, 561Cm^{-1}. EI-MS (DEP, 70 eV): *m/z* (%) = 446 $[M]^+$ (10), 180 (100). HR-ESI-MS: calcd for $[C_{22}H_{14}N_4O_5S+H]^+$: 447.0758. Found: 447.0746. Calcd for $[C_{22}H_{14}N_4O_5S+Na]^+$: 469.0577. Found: 469.0565.

***N*-[3,5-Bis(trifluoromethyl)benzoyl]-2,3-diphenyl-1,3-thiazolium-4-aminide 12d**. 4-Amino-2,3-diphenyl-1,3-thiazolium chloride (**9a**, 0.500 g, 1.73 mmol, 1.0 eq.), K_2CO_3 (0.239 g, 1.73 mmol, 1.0 eq.) and 3,5-bis(trifluoromethyl)benzoylchloride (0.69 mL, 3.81 mmol, 2.2 eq.) in 20 mL of toluene were used. The crude product was chromatographed (DCM:EtOH, 20:1). Yield: 0.783 g (1.59 mmol, 92%), yellow solid, mp 136–138 °C (dec.). ^{1}H NMR (600 MHz, DMSO-d_6): δ = 7.41-7.47 (m, 4H, 2′-H and 3′-H), 7.49-7.55 (m, 6H, 4′-H, 2″-H, 3″-H and 4″-H), 8.03 (t, $J_{H,H}$ = 1.7 Hz, 1H, H_p), 8.13 (s, 1H, 5-H), 8.31 (d, $J_{H,H}$ = 1.7 Hz, 2H, H_o) ppm. ^{13}C NMR (150 MHz, DMSO-d_6): δ = 99.3 (+, 1C, 5-C), 122.6 (+, q, $J_{C,F}$ = 4.0 Hz, 1C, C_p), 123.4 (o, q, $J_{C,F}$ = 271.4 Hz, 2C, CF_3), 127.3 (o, 1C, 1′-C), 128.2 (+, q, $J_{C,F}$ = 5.5 Hz, 2C, C_o), 128.6 (+, 2C, 2″-C or 3″-C), 128.8 (+, 2C, 2″-C or 3″-C), 129.0 (+, 2C, 2′-C or 3′-C), 129.4 (+, 2C, 2′-C or 3′-C), 129.5 (+, 1C, 4″-C), 129.6 (o, q, $J_{C,F}$ = 32.6 Hz, 2C, C_m), 131.6 (+, 1C, 4′-C), 137.1 (o, 1C, 1″-C), 142.8 (o, 1C, C_i), 156.3 (o, 1C, 4-C), 161.8 (o, 1C, 2-C), 165.5 (o, 1C, C=O) ppm. IR (ATR): ν = 3174, 3077, 2925, 1623, 1572, 1518, 1486, 1448, 1417, 1323, 1281, 1237, 1162, 1116, 1050, 1028, 1004, 977, 949, 929, 899, 841, 791, 765, 751, 693, 679, 616, 591, 577, 557, 497, 469, 440, 412Cm^{-1}. EI-MS (DEP, 20 eV): *m/z* (%) = 492 $[M]^+$ (7), 105 (100). HR-ESI-MS: Calcd for $[C_{24}H_{14}F_6N_2OS+Na]^+$: 515.0623. Found: 515.0619.

3-(2-Bromophenyl)-*N*-(3,5-dichlorobenzoyl)-2-phenyl-1,3-thiazolium-4-aminide 12e. 4-Amino-3-(2-bromophenyl)-2-phenyl-1,3-thiazolium chloride (**9b**, 0.200 g, 0.54 mmol, 1.0 eq.), K_2CO_3 (0.075 g, 0.54 mmol, 1.0 eq.) and 3,5-dichlorobenzoylchloride (0.17 mL, 1.20 mmol, 2.2 eq.) in 8 mL of toluene were used. The crude product was chromatographed (DCM:EtOH, 20:1). The product was obtained as yellow solid, mp: 95–97 °C. Yield: 0.254 g (0.51 mmol, 94%). ^{1}H NMR (600 MHz, DMSO-d_6): δ = 7.44-7.49 (m, 4H, 2′-H and 3′-H), 7.51 (t, $J_{H,H}$ = 2.1 Hz, 1H, H_p), 7.52–7.55 (m, 2H, 4′-H and 4″-H), 7.60 (d, $J_{H,H}$ = 2.1 Hz, 2H, H_o), 7.63 (td, $J_{H,H}$ = 7.8, 1.3 Hz, 1H, 5″-H), 7.82 (dd, $J_{H,H}$ = 7.8, 1.6 Hz, 1H, 6″-H), 7.84–7.86 (m, 1H, 3″-H), 8.08 (s, 1H, 5-H) ppm. ^{13}C NMR (150 MHz, DMSO-d_6): δ = 99.1 (+, 1C, 5-C), 121.2 (o, 1C, 2″-C), 126.6 (+, 2C, C_o), 126.8 (o, 1C, 1′-C), 128.5 (+, 1C, C_p), 128.6 (+, 1C, 5″-C), 129.0 (+, 2C, 2′-C or 3′-C), 129.2 (+, 2C, 2′-C or 3′-C), 131.2 (+, 1C, 6″-C), 131.9 (+, 1C, 4″-C), 132.1 (+, 1C, 4′-C), 133.0 (+, 1C, 3″-C), 133.2 (o, 2C, C_m), 136.4 (o, 1C, 1″-C), 143.8 (o, 1C, C_i), 156.3 (o, 1C, 4-C), 161.4 (o, 1C, 2-C), 166.3 (o, 1C,C=O) ppm. IR (ATR): ν = 3155, 3084, 3070, 2957, 2923, 2852, 2653, 2549, 1691, 1590, 1567, 1550, 1523, 1471, 1445, 1404, 1345, 1278, 1238, 1163, 1118, 1093, 1068, 1041, 1024, 1000, 959, 908, 872, 804, 791, 769, 754, 709, 687, 659, 606, 566, 512, 498, 478, 457, 427 cm^{-1}. EI-MS (DEP, 20 eV): *m/z* (%) = 503 $[M+H]^+$ (7), 105 (100). HR-ESI-MS: Calcd. for $[C_{22}H_{13}BrCl_2N_2OS+Na]^+$: 524.9201. Found: 524.9197.

***N*-[3,5-Bis(trifluoromethyl)benzoyl]-3-(2-bromophenyl)-2-phenyl-1,3-thiazolium-4-aminide 12f**. 4-Amino-3-(2-bromophenyl)-2-phenyl-1,3-thiazolium chloride (**9b**, 0.200 g, 0.54 mmol, 1.0 eq.), K_2CO_3 (0.075 g, 0.54 mmol, 1.0 eq.) and 3,5-bis(trifluoromethyl) benzoylchloride (0.17 mL, 1.20 mmol, 2.2 eq.) in 8 mL of toluene were used. The crude product was chromatographed (DCM:EtOH, 20:1) to give a yellow solid, mp: 106–108 °C. ^{1}H NMR (600 MHz, DMSO-d_6): δ = 7.46–7.51 (m, 4H, 2′-H and 3′-H), 7.52–7.56 (m, 2H, 4′-H and 4″-H), 7.60–7.63 (m, 1H, 5″-H), 7.82–7.85 (m, 2H, 3″-H and 6″-H), 8.01 (bs, 1H, H_p), 8.10 (s, 1H, 5-H), 8.24 (bs, 2H, H_o) ppm. ^{13}C NMR (150 MHz, DMSO-d_6): δ = 99.5 (+, 1C, 5-C), 121.3 (o, 1C, 2″-C), 122.7 (+, q, $J_{C,F}$ = 3.3 Hz, 1C, C_p), 123.4 (o, q, $J_{C,F}$ = 272.9 Hz, 2C, CF_3), 126.7 (o, 1C, 1′-C), 128.2 (+, q, $J_{C,F}$ = 5.5 Hz, 2C, C_o), 128.6 (+, 3 C, 2′-C and 5″-C or 3′-C and 5″-C), 129.1 (+, 2C, 2′-C or 3′-C), 129.7 (o, q, $J_{C,F}$ = 32.6 Hz, 2C, C_m), 131.1 (+, 1C, 6″-C), 131.8 (+, 1C, 4″-C), 132.2 (+, 1C, 4′-C), 133.0 (+, 1C, 3″-C), 136.5 (o, 1C, 1″-C), 142.6 (o, 1C, C_i), 156.0 (o, 1C, 4-C), 161.8 (o, 1C, 2-C), 165.8 (o, 1C, C=O) ppm. IR (ATR): ν = 3095, 2786, 1710, 1622, 1587, 1519, 1473, 1451, 1436, 1360, 1345, 1274, 1173, 1127, 1026, 938, 913, 883, 845, 773, 756, 714, 698, 680, 543, 444 cm^{-1}. EI-MS (DEP, 20 eV): *m/z* (%) = 570 $[M]^+$ (6), 105 (100). HR-ESI-MS: Calcd. for $[C_{24}H_{13}BrF_6N_2OS+Na]^+$: 592.9728. Found: 592.9725.

***N*-(3,5-Dichlorobenzoyl)-3-phenyl-2-(thiophen-2-yl)-1,3-thiazolium-4-aminide 12g**. 4-Amino-3-phenyl-2-(thiophen-2-yl)-1,3-thiazolium chloride (**9c**, 0.200 g, 0.68 mmol, 1.0 eq.), K_2CO_3 (0.094 g, 0.68 mmol, 1.0 eq.) and 3,5-dichlorobenzoylchloride (0.21 mL, 1.50 mmol, 2.2 eq.) in 8 mL of toluene were used. The crude product was chromatographed (PE:EE:EtOH, 0.8:1:0.1). This and subsequent recrystallization were not sufficient to obtain the product in pure form. Yield of the crude product: 0.064 g (0.15 mmol, 22%), red solid, mp: 133–135 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.06 (t, $J_{H,H}$ = 4.2 Hz, 1H, 4′-H), 7.40–7.48 (m, 3H, 5′-H and 2″-H), 7.53–7.54 (m, 1H, 3′-H), 7.62–7.66 (m, 2H, 3″-H), 7.68–7.70 (m, 1H, 4″-H), 7.75 (bs, 1H, H_p), 7.89 (bs, 2H, H_o), 8.08 (bs, 1H, 5-H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 99.8 (+, 1C, 5-C), 126.2 (o, 1C, 1′-C), 127.4 (+, 1C, C_p), 128.4 (+, 2C, 2″-C), 128.5 (+, 3C, C_o and 4′-C), 130.3 (+, 2C, 3″-C), 131.4 (+, 1C, 4″-C), 132.4 (+, 1C, 5′-C), 133.4 (+, 1C, 3′-C), 134.3 (o, 2C, C_m), 135.2 (o, 1C, C_i), 136.0 (o, 1C, 1″-C), 154.6 (o, 1C, 4-C), 156.7 (o, 1C, 2-C), 165.6 (o, 1C, C=O) ppm. IR (ATR): ν = 3152, 3075, 3057, 2955, 2923, 2853, 1729, 1684, 1645, 1584, 1548, 1523, 1487, 1453, 1434, 1409, 1366, 1348, 1276, 1258, 1236, 1187, 1162, 1126, 1092, 1073, 1031, 1003, 963, 932, 906, 887, 859, 836, 795, 770, 723, 705, 690, 662, 603, 583, 558, 511, 481, 457, 426 cm^{-1}. EI-MS (DEP, 70 eV): *m/z* (%) = 430 $[M]^+$ (8), 186 (100). HR-ESI-MS: Calcd. for $[C_{20}H_{12}Cl_2N_2OS_2+H]^+$: 430.9841. Found: 430.9838.

***N*-(3,5-Dinitrobenzoyl)-3-phenyl-2-(thiophen-2-yl)-1,3-thiazolium-4-aminide 12h**. 4-Amino-3-phenyl-2-(thiophen-2-yl)-1,3-thiazolium chloride (**9c**, 0.200 g, 0.68 mmol, 1.0 eq.), K_2CO_3 (0.094 g, 0.68 mmol, 1.0 eq.) and 3,5-dinitrobenzoylchloride (0.345 g, 1.50 mmol, 2.2 eq.) in 8 mL of toluene were used. The crude product was chromatographed (PE:EE:EtOH, 0.8:1:0.1). This and recrystallization were not sufficient to obtain the product in pure form. Yield of the crude product: 0.144 g (0.32 mmol, 47%), red solid, mp: 152–154 °C. ^{1}H NMR (600 MHz, DMSO-d_6): δ = 7.19 (dd, $J_{H,H}$ = 5.0, 3.9 Hz, 1H, 4′-H), 7.62–7.64 (m, 2H, 2″-H), 7.70–7.76 (m, 4H, 5′-H, 3″-H and 4″-H), 7.93 (dd, $J_{H,H}$ = 5.0, 1.1 Hz, 1H, 3′-H), 8.03 (s, 1H, 5-H), 8.74 (t, $J_{H,H}$ = 2.2 Hz, 1H, H_p), 8.76 (d, $J_{H,H}$ = 2.2 Hz, 2H, H_o) ppm. ^{13}C NMR (150 MHz, DMSO-d_6): δ = 98.1 (+, 1C, 5-C), 119.0 (+, 1C, C_p), 127.5 (+, 2C, C_m), 128.2 (o, 1C, 1′-C), 128.4 (+, 1C, 4′-C), 128.6 (+, 2C, 2″-C), 129.8 (+, 2C, 3″-C), 130.8 (+, 1C, 4″-C), 133.1 (+, 1C, 5′-C), 134.6 (+, 1C, 3′-C), 136.8 (o, 2C, C_i and 1″-C), 147.7 (o, 2C, C_m), 155.7 (o, 1C, 4-C), 158.0 (o, 1C, 2-C), 164.0 (o, 1C, C=O) ppm. IR (ATR): ν = 3095, 2956, 2923, 2853, 1734, 1702, 1681, 1619, 1609, 1582, 1533, 1458, 1406, 1340, 1277, 1235, 1184, 1119, 1075, 1004, 959, 916, 892, 853, 819, 795, 765, 718, 693, 614, 585, 557, 526, 459,

442, 422Cm^{-1}. EI-MS (DEP, 70 eV): *m/z* (%) = 452 $[M]^+$ (25), 186 (100). HR-ESI-MS: Calcd for $[C_{20}H_{12}N_4O_5S_2+Na]^+$: 475.0141. Found: 475.0141.

***N*-[3,5-Bis(trifluoromethyl)benzoyl]-3-phenyl-2-(thiophen-2-yl)-1,3-thiazolium-4-aminide 12i**. 4-Amino-3-phenyl-2-(thiophen-2-yl)-1,3-thiazolium chloride (**9c**, 0.200 g, 0.68 mmol, 1.0 eq.), K_2CO_3 (0.094 g, 0.68 mmol, 1.0 eq.) and 3,5-bis(trifluoromethyl) benzoylchloride (0.27 mL, 1.50 mmol, 2.2 eq.) in 8 mL of toluene were used. The crude product was chromatographed (PE:EE:EtOH, 0.8:1:0.1). This and recrystallization were not sufficient to obtain the product in pure form. Yield of the crude product: 0.048 g (0.10 mmol, 14%), red solid, mp 92–94 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.06 (dd, $J_{H,H}$ = 4.8, 3.9 Hz, 1H, 4′-H), 7.25–7.27 (m, 1H, H_p), 7.40 (d, $J_{H,H}$ = 3.9 Hz, 1H, 5′-H), 7.51–7.54 (m, 3H, 3′-H and 2″-H), 7.59–7.62 (m, 2H, 3″-H), 7.64–7.66 (m, 1H, 4″-H), 7.92 (d, $J_{H,H}$ = 7.1 Hz, 2H, H_o), 8.07 (bs, 1H, 5-H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 102.1 (+, 1C, 5-C), 123.4 (o, q, $J_{C,F}$ = 282.8 Hz, 2C, CF_3), 127.9 (+, 1C, C_p), 128.5 (+, 1C, 4′-C), 128.6 (+, 2C, 2″-C), 128.7 (+, 2C, C_o), 128.8 (o, 1C, 1′-C), 129.6 (o, q, $J_{C,F}$ = 32.6 Hz, 2C, C_m), 130.2 (+, 2C, 3″-C), 131.4 (+, 1C, 4″-C), 132.5 (+, 1C, 5′-C), 133.8 (+, 1C, 3′-C), 136.0 (o, 1C, 1″-C), 136.1 (o, 1C, C_i), 154.4 (o, 1C, 4-C), 156.7 (o, 1C, 2-C), 171.4 (o, 1C, C=O) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = −63.3 (s, 6F, CF_3) ppm. IR (ATR): ν = 3190, 3086, 3072, 3032, 2955, 2924, 2854, 1724, 1678, 1630, 1587, 1547, 1505, 1486, 1450, 1410, 1359, 1337, 1276, 1172, 1127, 1073, 1027, 1008, 973, 932, 907, 890, 845, 795, 756, 723, 692, 616, 597, 577, 556, 486, 469, 438 cm^{-1}. EI-MS (DEP, 20 eV): *m/z* (%) = 498 $[M]^+$ (1), 186 (100). HR-ESI-MS: Calcd. for $[C_{20}H_{14}N_2OS_2+Na]^+$: 385.0440. Found: 385.0434.

4-[3,5-Bis(trifluoromethyl)benzamide]-3-(2-bromophenyl)-2-phenyl-1,3-thiazolium tetrafluoroborate 13. *N*-[3,5-Bis (trifluoromethyl)benzoyl]-3-(2-bromophenyl)-2-phenyl-1,3-thiazolium-4-aminide (**12f**, 0.100 g, 0.18 mmol, 1.0 eq.) in 10 mL anhyd DCM were cooled to −10 °C and treated with tetrafluoroboronic acid (54% in Et_2O, 0.02 mL, 0.18 mmol, 1.0 eq.). The solution was allowed to warm to rt and then stirred for 1 h at that temperature. The solvent was then removed, the resulting product was washed with DCM and Et_2O, respectively, and dried *in vacuo*. The product could not be obtained in pure form, as it decomposes on attempts of recrystallization or column chromatography. Yield of the crude product: 0.115 g (0.17 mmol, 99%), yellow solid, mp: 113–115 °C. ^{1}H NMR (600 MHz, DMSO-d_6): δ = 7.48–7.67 (m, 7H, 2′-H, 3′-H, 4′-H, 4″-H and 5″-H), 7.70–7.75 (m, 1H, 3″-H), 7.99 (d, $J_{H,H}$ = 8.0 Hz, 1H, 6″-H), 8.20 (bs, 1H, 5-H), 8.42 (bs, 1H, H_p), 8.44 (bs, 3H, NH and H_o) ppm. ^{13}C NMR (150 MHz, DMSO-d_6): δ = 120.5 (o, 1C, 2″-C), 123.0 (o, q, $J_{C,F}$ = 272.9 Hz, 2C, CF_3), 126.5 (+, q, $J_{C,F}$ = 3.3 Hz, 1C, C_m), 126.7 (o, 1C, 1′-C), 127.7 (+, 1C, 6″-C), 128.6 (+, 1C, 5-C), 128.6 (+, 2C, 2′-C or 3′-C), 129.3 (+, 2C, 2′-C or 3′-C), 129.6 (+, q, $J_{C,F}$ = 3.3 Hz, 2C, C_o), 129.9 (+, 1C, 5″-C), 130.9 (o, q, $J_{C,F}$ = 33.6 Hz, 2C, C_m), 131.0 (+, 1C, 4′-C), 132.9 (+, 1C, 4″-C), 133.6 (o and +, 2C, C_i and 3″-C), 136.6 (o, 1C, 1″-C), 164.6 (o, 1C, 4-C), 164.8 (o, 1C, C=O), 164.9 (o, 1C, 2-C) ppm. ^{13}C and ^{1}H NMR spectra correspond to **12f**, *i.e.* the deprotonated form. ^{11}B NMR (193 MHz, DMSO-d_6): δ = 0.0 (s, 1B, anion) ppm. IR (ATR): ν = 3366, 3202, 3098, 2787, 2686, 2618, 2524, 1704, 1622, 1588, 1523, 1471, 1438, 1358, 1274, 1169, 1127, 942, 912, 844, 798, 766, 721, 680, 546, 440 cm^{-1}. EI-MS (DEP, 70 eV): *m/z* (%) = 570 $[M]^+$ (12), 260 (100). HR-ESI-MS: Calcd. for $[C_{24}H_{14}BrF_6N_2OS]^+$: 570.9909. Found: 570.9913.

2,3-Diphenyl-1,3-thiazolium-4-aminide 14a. 4-Amino-2,3-diphenyl-1,3-thiazolium chloride (**9a**, 0.200 g, 0.69 mmol, 1.0 eq.) and K_2CO_3 (0.115 g, 0.83 mmol, 1.2 eq.) were cooled to −40 °C and then pre-cooled TFAA (4.00 mL, 28.40 mmol, 41.0 eq.) was added. The mixture was stirred for 1 h at −40 °C, then slowly warmed to rt and stirred for additional 16 h. The crude product was chromatographed (DCM:EtOH, 30:1). Yield: 0.175 g (0.69 mmol, 99%), orange oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 6.89 (bs, 1H, 5-H), 7.22-7.23 (m, 2H, 2′-H), 7.34-7.40 (m, 4H, 3′-H and 2″-H or 3′-H and 3″-H), 7.50-7.53 (m, 1H, 4′-H), 7.60-7.67 (m, 3H, 2″-H and 4″-H or 3″-H and 4″-H) ppm; NH not detectable due to H/D exchange. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 92.6 (+, 1C, 5-C), 125.6 (o, 1C, 1′-C), 127.3 (+, 2C, 2″-C or 3″-C), 129.2 (+, 2C, 2′-C), 129.9 (+, 2C, 3′-C), 131.5 (+, 2C, 2″-C or 3″-C), 132.5 (+, 1C, 4″-C), 133.2 (+, 1C, 4′-C), 134.3 (o, 1C, 1″-C), 151.7 (o, 1C, 4-C), 164.6 (o, 1C, 2-C) ppm. IR (ATR): ν = 3448, 3328, 3231, 3128, 3069, 1740, 1664, 1629, 1582, 1492, 1455, 1433, 1341, 1317, 1131, 1060, 1027, 1002, 913, 847, 795, 756, 722, 690, 598, 575, 546, 518, 492, 470, 435 cm^{-1}. EI-MS (DEP, 70 eV): *m/z* (%) = 252 $[M]^+$ (8), 180 (100). HR-ESI-MS: Calcd. for $[C_{15}H_{12}N_2S+H]^+$: 253.0794. Found: 253.0792.

3-(2-Bromophenyl)-2-phenyl-1,3-thiazolium-4-aminide 14b. A suspension of 4-amino-3-(2-bromophenyl)-2-phenyl-1,3-thiazolium chloride (**9b**, 0.200 g, 0.54 mmol, 1.0 eq.) and K_2CO_3 (0.090 g, 0.65 mmol, 1.2 eq.) was treated at −40 °C with TFAA (4.00 mL, 28.40 mmol, 52.2 eq.). After 1 h of stirring at that temperature, the mixture was allowed to warm to rt and stirred over 16 h. The resulting crude product was chromatographed (EE:EtOH, 1:1). Yield: 0.164 g (0.50 mmol, 92%), red oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.00 (bs, 1H, 5-H), 7.29–7.31 (m, 2H, 2′-H), 7.38–7.40 (m, 2H, 3′-H), 7.51–7.54 (m, 2H, 4′-H and 4″-H), 7.58–7.63 (m, 2H, 3″-H and 6″-H), 7.76–7.78 (m, 1H, 5″-H) ppm; NH not detectable due to H/D exchange. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 92.9 (+, 1C, 5-C), 121.4 (o, 1C, 2″-C), 125.5 (o, 1C, 1′-C), 129.1 (+, 2C, 2′-C), 129.8 (+, 2C, 3′-C), 130.0 (+, 1C, 6″-C), 130.4 (+, 1C, 3″-C), 132.6 (o, 1C, 1″-C), 133.3 (+, 1C, 4′-C), 134.1 (+, 1C, 4″-C), 135.1 (+, 1C, 5″-C), 151.5 (o, 1C, 4-C), 164.8 (o, 1C, 2-C) ppm. IR (ATR): ν = 3320, 3231, 3188, 3123, 3071, 1776, 1667, 1629, 1579, 1496, 1474, 1448, 1377, 1319, 1306, 1134, 1073, 1045, 1027, 1001, 969, 921, 887, 837, 798, 755, 718, 704, 688, 658, 637, 601, 577, 519, 489, 435 cm^{-1}. EI-MS (DEP, 70 eV): *m/z* (%) = 330 $[M]^+$ (10), 258 (100). HR-ESI-MS: Calcd. for $[C_{15}H_{11}BrN_2S+H]^+$: 330.9899. Found: 330.9910.

2-*tert*-Butyl-*N*-(3,5-dinitrobenzoyl)-3-phenyl-1,3-thiazolium-4-aminide 17. Under stirring, chloroacetonitrile (0.18 mL, 2.85 mmol, 1.1 eq.) and then Et_3N (0.55 mL, 3.98 mmol, 1.5 eq.) were added to a suspension of 2,2-dimethyl-*N*-phenylpropane-thioamide (**16**, 0.500 g, 2.59 mmol, 1.0 eq.) in 7 mL of toluene and stirred for 24 h at 50 °C. Then, 3,5-dinitrobenzoylchloride (1.312 g, 5.69 mmol, 2.2 eq.) was added and the mixture was stirred for 6 h at 60 °C and then for 18 h at rt. After the toluene was distilled off *in vacuo*, the residue was resolved in DCM (40 mL), extracted with Na_2CO_3 in water (3×40 mL) and dried over $MgSO_4$. The crude product was chromatographed (PE:EE, 2.4:1). Yield: 0.253 g (0.59 mmol, 23%), yellow solid, mp. 232 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.42 (s, 9H, 2′-H), 7.32-7.34 (m, 2H, 2″-H), 7.67-7.70 (m, 2H, 3″-H), 7.74-7.77 (m, 1H, 4″-H), 7.94 (s, 1H, 5-H), 8.85 (d, $J_{H,H}$ = 2.2 Hz, 2H, H_o), 8.89 (t, $J_{H,H}$ = 2.2 Hz, 1H, H_p) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 30.6 (+, 3C, 2′-C), 38.3 (o, 1C, 1′-C), 95.8 (+, 1C, 5-C), 119.0 (+, 1C, C_p), 128.7 (+, 2C, C_o), 128.8 (+, 2C, 2″-C), 129.5 (+, 2C, 3″-C), 130.9 (+, 1C, 4″-C), 138.0 (o, 1C, 1″-C), 144.5 (o, 1C, C_i), 148.1 (o, 2C, C_m), 159.2 (o, 1C, 4-C), 166.2 (o, 1C, C=O), 173.8 (o, 1C, 2-C) ppm. IR (ATR): ν = 3172, 3117, 3089, 3065, 1605, 1568, 1532, 1488, 1454, 1421, 1396, 1337, 1209, 1183, 1094, 1066, 927, 905, 894, 778, 770, 728, 700, 670, 650, 580, 458 cm^{-1}. EI-MS (DEP, 70 eV): *m/z* (%) = 426 $[M]^+$ (22), 104 (100). HR-ESI-MS: Calcd for $[C_{20}H_{18}N_4O_5S+H]^+$: 427.1071. Found: 427.1054. Calcd for $[C_{20}H_{18}N_4O_5S+Na]^+$: 449.0890. Found: 449.0873.

Deposition Numbers 2083310 (for $C_{22}H_{19}ClN_2O_2S$ (**10a**)) and 2083308 (for $C_{20}H_{18}N_4O_5S$ (**17**)) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.

Acknowledgments

Prof. Dr. Arnold Adam (Clausthal University of Technology, Institute of Anorganic and Analytical Chemistry) is gratefully acknowledged for helpful discussions about tetravalent sulfur compounds. Open Access funding enabled and organized by Projekt DEAL.

Conflict of Interest

The authors declare no conflict of interest.

Keywords: Betaines · Fluorescence · Heterocycles · Mesoionic compounds · Thiazole · Thiazolium

[1] W. D. Ollis, S. P. Stanforth, C. A. Ramsden, *Tetrahedron* **1985**, *41*, 2239–2329.
[2] a) C. A. Ramsden, *Tetrahedron* **2013**, *69*, 4146–4159.
[3] a) M. M. Popa, S. Shova, M. Hrubaru, L. Barbu, C. Draghici, F. Dumitrascu, D. E. Dumitrescu, *RSC Adv.* **2020**, *10*, 15656–15664; b) M. N. Kumbar, S. K. J. Shaikh, R. R. Kamble, P. K. Bayannavar, A. A. Kamble, R. K. Hunnur, *ACS Omega* **2019**, *4*, 4955–4962; c) V. Hladikova, J. Vana, J. Hanusek, *Beilstein J. Org. Chem.* **2018**, *14*, 1317–1348; d) S. Bernard, D. Audisio, M. Riomet, S. Bregant, A. Sallustrau, L. Plougastel, E. Decuypere, S. Gabillet, R. A. Kumar, J. Elyian, M. N. Trinh, O. Koniev, A. Wagner, S. Kolodych, F. Taran, *Angew. Chem.* **2017**, *129*, 15818–15822; *Angew. Chem. Int. Ed.* **2017**, *56*, 15612–15616; e) H. Liu, D. Audisio, L. Plougastel, E. Decuypere, D.-A. Buisson, O. Koniev, S. Kolodych, A. Wagner, M. Elhabiri, A. Krzyczmonik, S. Forsback, O. Solin, V. Gouverneur, F. Taran, *Angew. Chem.* **2016**, *128*, 12252–12256; *Angew. Chem. Int. Ed.* **2016**, *55*, 12073–12077; f) D. L. Browne, M. D. Helm, A. Plant, J. P. A. Harrity, *Angew. Chem.* **2007**, *119*, 8810–8812; *Angew. Chem. Int. Ed.* **2007**, *46*, 8656–8658.
[4] a) L. A. Aleksandrova, A. A. Fatykhov, A. R. Gataullina, E. A. Kantor, R. R. Gataullin, *Russ. J. Org. Chem.* **2018**, *54*, 1519–1530; b) Y. Durust, H. Karakus, B. M. Kariuki, D. W. Knight, *Synth. Commun.* **2018**, *48*, 2206–2220; c) G. M. Torres, J. S. Quesnel, D. Bijou, B. A. Arndtsen, *J. Am. Chem. Soc.* **2016**, *138*, 7315–7324; d) R. Huisgen, H. Gotthardt, H. O. Bayer, *Angew. Chem. Int. Ed. Engl.* **1964**, *3*, 135.
[5] a) H. Wamhoff, H. Höhmann, P. Sóhar, *Org. Lett.* **2000**, *2*, 581–584; b) J. Garcia de la Conception, M. Avalos, P. Cintas, J. L. Jimenez, E. M. Light, *Org. Biomol. Chem.* **2018**, *16*, 3438–3452; c) S. Muthusamy, C. Gangadurai, *Synthesis* **2016**, *48*, 2213–2225; d) M. H. Osterhout, W. R. Nadler, A. Padwa, *Synthesis* **1994**, *2*, 123–141; e) M. Baudy, A. Robert, G. Guimon, *Tetrahedron* **1982**, *38*, 214–252.
[6] D. Cantillo, M. Avalos, R. Babiano, P. Cintas, J. L. Jiménez, M. E. Light, J. C. Palacios, *J. Org. Chem.* **2009**, *74*, 7644–76506.
[7] a) F. de Moliner, N. Kielland, R. Lavilla, M. Vendrell, *Angew. Chem.* **2017**, *129*, 3812–3823; *Angew. Chem. Int. Ed.* **2017**, *56*, 3758–3769; b) F. Albota, M. D. Stanescu, *Rev. Roum. Chim.* **2017**, *62*, 711–734; c) D. L. Browne, J. P. Harrity, *Tetrahedron* **2010**, *66*, 553–568; d) *1,3-Dipolar Cycloaddition Chemistry*, Vol. 1 and 2, (Ed.: A. Padwa), Wiley, New York, 1984; e) *Synthetic Applications of 1,3-Dipolar Cycloaddition Chemistry Toward Heterocycles and Natural Products* (Eds.: A. Padwa, W. H. Pearson), Wiley, New York, 2002; f) R. Huisgen, in *1,3-Dipolar Cycloaddition Chemistry*, Vol. 1, (Ed.: A. Padwa), Wiley, New York, 1984, pp. 1–176.
[8] A. Padwa, L. S. Beall, T. M. Heidelbaugh, B. Liu, S. M. Sheehan, *J. Org. Chem.* **2000**, *65*, 2684–2695.
[9] a) A. Koch, U. Jonas, H. Ritter, H.-W. Spiess, *Tetrahedron* **2004**, *60*, 10011–10018; b) A. Theis, H. Ritter, *Macromol. Chem. Phys.* **2003**, *204*, 1297–1304; c) H. Tonami, H. Uyama, S. Kobayashi, B. Menges, S. Mittler, A. Theis, H. Ritter, *Macromol. Chem. Phys.* **2003**, *204*, 1079–1084.
[10] a) Z. Guan, S. Wiechmann, M. Drafz, E. Hübner, A. Schmidt, *Org. Biomol. Chem.* **2013**, *11*, 3558–3567; b) M. Fèvre, J. Pinaud, A. Leteneur, Y. Gnanou, J. Vignolle, D. Taton, K. Miqueu, J.-M. Sotiropoulos, *J. Am. Chem. Soc.* **2012**, *134*, 6776–6784; c) E. L. Kolychev, T. Bannenberg, M. Freytag, C. G. Daniliuc, P. G. Jones, M. Tamm, *Chem. Eur. J.* **2012**, *18*, 16938–16946; d) A. Schmidt, N. Münster, A. Dreger, *Angew. Chem.* **2010**, *122*, 2851–2854; *Angew. Chem. Int. Ed.* **2010**, *49*, 2790–2793; e) X. Sauvage, A. Demonceau, L. Delaude, *Adv. Synth. Catal.* **2009**, *351*, 2031–2038; f) A. Schmidt, A. Beutler, M. Albrecht, F. J. Ramírez, *Org. Biomol. Chem.* **2008**, *6*, 287–295; g) A. Schmidt, T. Habeck, *Lett. Org. Chem.* **2005**, *2*, 37–39; h) A. Schmidt, L. Merkel, W. Eisfeld, *Eur. J. Org. Chem.* **2005**, *10*, 2124–2130; i) D. Lavorato, J. K. Terlouw, T. K. Dargel, W. Koch, G. A. McGibbon, H. Schwarz, *J. Am. Chem. Soc.* **1996**, *118*, 11898–11904; j) A. R. Katritzky, H. M. Faid-Allah, *Synthesis* **1983**, *2*, 149–150; k) H. Quast, E. Schmitt, *Liebigs Ann. Chem.* **1970**, *732*, 43–63; l) R. Breslow, *J. Am. Chem. Soc.* **1958**, *80*, 3719–3726.
[11] a) S. Mummel, F. Lederle, E. Hübner, J. C. Namyslo, M. Nieger, A. Schmidt, *Angew. Chem.* **2021**, *133*, 19032 – 19037; *Angew. Chem. Int. Ed.* **2021**, *60*, 18882 – 18887; b) T. Freese, M. Nieger, J. C. Namyslo, A. Schmidt, *Tetrahedron Lett.* **2019**, *60*, 1272–1276; c) T. Freese, J. C. Namyslo, M. Nieger, A. Schmidt, *RSC Adv.* **2019**, *9*, 4781–4788; d) T. Freese, A.-L. Lücke, J. C. Namyslo, M. Nieger, A. Schmidt, *Eur. J. Org. Chem.* **2018**, *14*, 1646–1654; e) T. Freese, A.-L. Lücke, C. A. S. Schmidt, M. Polamo, M. Nieger, J. C. Namyslo, A. Schmidt, *Tetrahedron* **2017**, *73*, 5350–5357; f) V. César, V. Mallardo, A. Nano, G. Dahm, N. Lugan, G. Lavigne, S. Bellemin-Laponnaz, *Chem. Commun.* **2015**, *51*, 5271–5274; g) S. Wiechmann, T. Freese, M. H. H. Drafz, E. G. Hübner, J. C. Namyslo, M. Nieger, A. Schmidt, *Chem. Commun.* **2014**, *50*, 11822–11824; h) A. A. Danopoulos, K. Yu Monakhov, P. Braunstein, *Chem. Eur. J.* **2013**, *19*, 450–455; i) V. César, J.-C. Tourneux, N. Vujkovic, R. Brousses, N. Lugan, G. Lavigne, *Chem. Commun.* **2012**, *48*, 2349–2351; j) L. Benhamou, N. Vujkovic, V. César, H. Gornitzka, N. Lugan, G. Lavigne, *Organometallics* **2010**, *29*, 2616–2630; k) L. Benhamou, V. César, H. Gornitzka, N. Lugan, G. Lavigne, *Chem. Commun.* **2009**, *2009*, 4720–4722; l) A. T. Biju, K. Hirano, R. Fröhlich, F. Glorius, *Chem. Asian J.* **2009**, *4*, 1786–1789.
[12] A. Schmidt, S. Wiechmann, T. Freese, *ARKIVOC* **2013**, 424–469.
[13] a) C. A. Ramsden, W. P. Oziminski, *J. Org. Chem.* **2016**, *81*, 10295–10301; b) C. A. Ramsden, W. P. Oziminski, *J. Org. Chem.* **2017**, *82*, 12485–12491; c) W. P. Oziminski, C. A. Ramsden, *RSC Adv.* **2018**, *8*, 14833–14837.
[14] a) W. Baker, W. D. Ollis, V. D. Poole, *J. Chem. Soc.* **1949**, 307–314; b) W. Baker, W. D. Ollis, V. D. Poole, *J. Chem. Soc.* **1950**, 1542–1551.
[15] W. D. Ollis, C. A. Ramsden, *Adv. Heterocycl. Chem.* **1976**, *19*, 1–122.
[16] a) K. Takezawa, K. Nomura, E. Yoshii, K. Masuda, *Chem. Pharm. Bull.* **1984**, *32*, 4637–4640; b) M. Bssaibis, A. Robert, A. A. Souizi, *J. Chem. Soc. Perkin Trans. 1* **1994**, 1469–1472.
[17] a) M. Ohta, K. Yoshida, S. Sato, *Bull. Chem. Soc. Jpn.* **1966**, 39, 1269–1273; b) H. Chosho, K. Ichimura, M. Ohta, *Bull. Chem. Soc. Jpn.* **1964**, *37*, 1670–1673; c) K. Ichimura, M. Ohta, *Bull. Chem. Soc. Jpn.* **1965**, *38*, 707–709; d) W. Friedrichsen, M. König, *Synthesis* **1983**, 582–583.
[18] S. Sato, M. Ohta, *Bull. Chem. Soc. Jpn.* **1968**, *41*, 2801–2802 .
[19] K. T. Potts, S. Husain, S. Husain, *J. Chem. Soc. Chem. Commun.* **1970**, *20*, 1360–1361.
[20] A. Chinone, Y. Huseya, M. Ohta, *Bull. Chem. Soc. Jpn.* **1970**, *43*, 2650–2650 .
[21] Y. I. Nein, Y. Y. Morzherin, *Russ. Chem. Bull.* **2012**, *61*, 1111–1116.
[22] a) M. Liu, M. Nieger, E. Hübner, A. Schmidt, *Chem. Eur. J.* **2016**, *15*, 5416–5424; b) M. Liu, M. Nieger, A. Schmidt, *Chem. Commun.* **2015**, *51*, 477–479; c) A. Schmidt, A. Beutler, T. Habeck, T. Mordhorst, B. Snovydovych, *Synthesis* **2006**, *11*, 1882–1894; d) A. Schmidt, M. K. Kindermann, P. Vainiotalo, M. Nieger, *J. Org. Chem.* **1999**, *64*, 9499–9506.
[23] a) A. Schmidt, T. Mordhorst, *Synthesis* **2005**, *5*, 781–786; b) A. Schmidt, T. Mordhorst, T. Habeck, *Org. Lett.* **2002**, *4*, 1375–1377; c) A. Schmidt, M. K. Kindermann, *J. Org. Chem.* **1998**, *63*, 4636–4644.
[24] N. K. Downer-Riley, Y. A. Jackson, *Tetrahedron* **2008**, *64*, 7741–7744.
[25] G. Evindar, R. A. Batey, *J. Org. Chem.* **2006**, *71*, 1802–1808.
[26] M. V. Lunagariya, K. P. Thakor, B. N. Waghela, F. U. Vaidya, C. Pathak, M. N. Patel, *J. Biomol. Struct. Dyn.* **2018**, *36*, 14–31.
[27] F. H. Allen, O. Kennard, D. G. Watson, L. Brammer, A. G. Orpen, R. Taylor, *J. Chem. Soc. Perkin Trans. 2* **1987**, S1–S19.
[28] a) H. Gotthardt, F. Reiter, R. Gleiter, R. Bartetzko, *Chem. Ber.* **1979**, *112*, 260–265; b) R. Gleiter, R. Bartetzko, G. Brähler, H. Bock, *J. Org. Chem.* **1978**, *43*, 3893–3897; c) R. Bartetzko, R. Gleiter, *Angew. Chem.* **1978**, *90*, 481–482; *Angew. Chem. Int. Ed. Engl.* **1978**, *17*, 468–469; d) F. Gerson, G. Plattner, R. Bartetzko, R. Gleiter, *Helv. Chim. Acta* **1980**, *63*, 2144–2151; e) R. Gleiter, *Angew. Chem.* **1981**, *93*, 442–450; *Angew. Chem. Int. Ed. Engl.* **1981**, *20*, 444–452.
[29] J. Fabian, B. Andes Hess Jr., *Int. J. Quantum Chem.* **2002**, *90*, 1055–1063.
[30] F. J. Lederer, F. F. Graupner, B. Maerz, M. Braun, W. Zinth, *Chem. Phys.* **2014**, *428*, 82–89.
[31] J. B. Birks, *Rep. Prog. Phys.* **1975**, *38*, 903–974.

[32] G. Liu, *Macromolecules* **1992**, *25*, 5805–5815.
[33] M. A. Satam, R. K. Raut, A. B. Tathe, N. Sekar, *J. Fluoresc.* **2012**, *22*, 1237–1248.
[34] J. H. Huh, A. Pandith, C. S. Cho, H.-S. Kim, *Bull. Korean Chem. Soc.* **2018**, *39*, 1420–1431.
[35] a) F. Neese, *WIREs Comput. Mol. Sci.* **2012**, *2*, 73–78; b) F. Neese, Software Update: The ORCA Program System, Version 4.0. Wiley Interdiscip. *Rev. Comput. Mol. Sci.* **2018**, *8*, e1327.
[36] G. M. Sheldrick, SHELXS-97, Programs for Crystal Structure Determination, University of Göttingen, 1997.
[37] H. Xu, H. Deng, Z. Li, H. Xiang, X. Zhou, *Eur. J. Org. Chem.* **2013**, *31*, 7054–7057.
[38] B. V. Varun, A. Sood, K. R. Prabhu, *RSC Adv.* **2014**, *4*, 60798–60807.

Manuscript received: July 4, 2021
Revised manuscript received: August 12, 2021
Accepted manuscript online: August 16, 2021