A Simple Synthesis of 1-Acyl-3-aryl-3*H*-pyrrolo[2′,3′:4,5]pyrimido[6,1-*b*]benzothiazol-6-ium-2-olates: Betainic Derivatives of a Novel Heterocyclic System

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Abstract: The title compounds were obtained by acylation of 5-amino-1-aryl-4-(2-benzothiazolyl)-2,3-dihydro-2-pyrrolones with 3-fold excess of acid chlorides. Starting pyrrolones were prepared in high yields by alkylation of 2-benzothiazoleacetonitrile with chloroacetic acid anilides. An X-ray crystallographic study of 1-benzoyl-3,5-diphenyl-3*H*-pyrrolo[2′,3′:4,5]pyrimido[6,1-*b*]benzothiazole-6-ium-2-olate was carried out to confirm the structure of title compounds unambiguously. The charge distribution in the obtained betaines was discussed.

Key words: acylations, alkylations, 5-amino-2-pyrrolones, heterocycles, pyrrolo[2′,3′:4,5]pyrimido[6,1-*b*]benzothiazoles

The different methods for the preparation of various 4-heteroaryl substituted 5-amino-3-pyrrolones have been elaborated in our laboratory.[1,2] In particular, the 5-amino-4-(2-benzothiazolyl)-2,3-dihydro-3-pyrrolones **1** (X = O, Y = H_2) (Figure 1) were synthesized.[2d–f,2h] Further investigation of their chemistry revealed a low reactivity of both the amino and the carbonyl groups. Thus, aminopyrrolones **1** were found not to give typical amine derivatives under treatment with acid chlorides and isocyanates[2h] and not to form hydrazones at the carbonyl moiety.[2f] This behavior was explained by strong vinylogous amide conjugation between amino and carbonyl groups of aminopyrrolones **1**. Recently the conjugation has been confirmed by an X-ray crystallographic study, which established the considerable deviations of the appropriate bonds length in the β-enaminoketone moiety from their standard values.[2h] The same conjugation was noted for related derivatives by other researchers,[3] also on the basis of crystallographic investigations. Continuing our research in this field, we were interested in the preparation of hitherto unknown derivatives with isomeric oxomethylene moiety topology, namely 5-amino-2-pyrrolones **2** (X = H_2, Y = O) (Figure 1), and in the comparison of their properties with those of compounds **1**. Since the above-mentioned conjugation cannot be realized in the structure **2**, the desired 2-pyrrolone derivatives are assumed to be more reactive. Herein, the synthesis of compounds of type **2** as well as the results of the study of their acylation is reported.

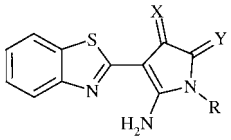
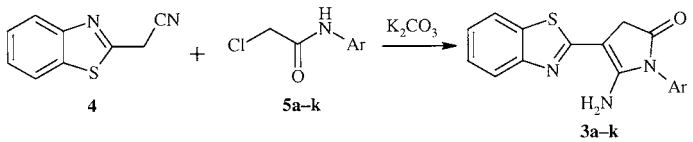


Figure 1 The structures of compounds **1**: X = O, Y = H_2; and **2**: X = H_2, Y = O

A literature search revealed a synthetic approach to the 5-amino-2-pyrrolones via alkylation of malononitrile or ethyl cyanoacetate with chloroacetic acid anilides,[4] and was successfully applied to the synthesis of target derivatives. Thus, 5-amino-1-aryl-4-(2-benzothiazolyl)-2,3-dihydro-2-pyrrolones **3** were obtained in high yields by alkylation of benzothiazoleacetonitrile **4** with chloroacetic acid anilides **5** in the presence of K_2CO_3 (Scheme 1). The possible alkylation of the nitrogen atom of the benzothiazole moiety[5] was not observed. Moreover, this method turned out to be very convenient and the isolation procedure was simple, allowing it to be used for large scale preparation



4 **5a–k** **3a–k**

Scheme 1 **3**, **5**: Ar = **a**: Ph, **b**: 4-(*i*-Pr)C_6H_4, **c**: 1-naphthyl, **d**: 3-MeOC_6H_4, **e)** 5-Cl,2-MeOC_6H_3, **f**: 2,4-$Me_2C_6H_3$, **g**: 2,4-$F_2C_6H_3$, **h**: 4-EtOC_6H_4, **i)** 4-$NO_2C_6H_4$, **j**: 2-BrC_6H_4, **k**: 4-(*t*-Bu)C_6H_4

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(ca. 0.5 mol) without modification. Since certain 5-amino-2-pyrrolone derivatives were reported to posses antimicrobial[4d,f] and radioprotective[4e] activities the compounds **3** can be also interesting from the biological viewpoint.

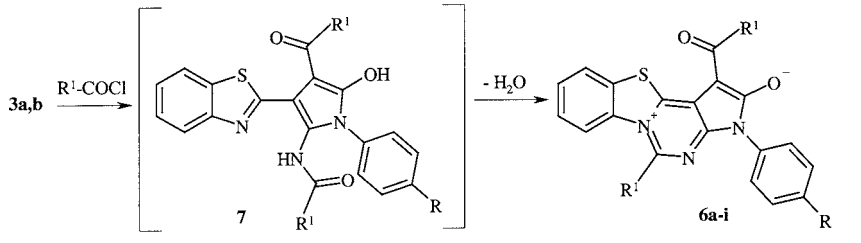
The structure of pyrrolones **3** was assigned on the basis of analytical and spectral data. Their IR spectra revealed a strong absorption band at 1715–1735 cm^{-1}, which is a typical value for carbonyl vibration of 5-membered lactams.[6] Absorption of the primary amino group was also present at 3150–3330 cm^{-1}, while there was no absorption of nitrile. ^1H NMR spectra of compounds **3** recorded in DMSO-d_6 solution exhibited a two-proton singlet of the methylene group at 3.4 ppm and a set of signals from benzothiazole moiety (two doublets at 7.8 and 7.6, and two triplets at 7.3 and 7.1 ppm). The signal from amino group protons was observed at 7.3–7.8 ppm region as a two proton D_2O-exchangeable singlet. The protons of aryl group exhibited their signals at expected δ values. Therefore, according to the spectral data compounds **3** exist as amino-oxo tautomers at least in DMSO-d_6 solution. It is noteworthy that the methylene group of the 1-naphthyl substituted derivative **3c** appears in its ^1H NMR spectrum as two one-proton doublets at 3.55 and 3.70 ppm with the coupling constant J = 21.5 Hz. It is explained in terms of hindered rotation of the naphthyl group around C–N bond due to substituents at second and fifth positions of the pyrroline ring. Hence, the molecule of **3c** acquires an axial chirality and the methylene protons become diastereotopic, as a result their signal transforms from a singlet into two doublets with geminal spin-spin coupling.

It should be noted that in contrast to compounds **3** the amino group signals of the 3-pyrrolones **1** was observed in ^1H NMR spectra as two separate one-proton singlets in the range of 8.0–9.0 ppm.[2d–h] It could be explained by either intramolecular hydrogen bond between amino group proton and the nitrogen of the neighboring benzothiazolyl substituent or the restricted C–N bond rotation due to amide-like conjugation with the carbonyl. The fragment consisting of vicinal amino group and benzothiazole moiety is retained in the structure of 2-pyrrolones **3**, but the signal of the amino group protons is observed as two-proton singlet. That allows us to state that magnetically non-equivalence protons of the amino group in the 3-pyrrolones **1** is caused by the amide-like restricted C–N bond rotation.

Further investigation was directed towards the study of acylation of 5-amino-2-pyrrolones **3a**,**b** with acid chlorides. In contrast to their isomers **1**, compounds **3a**,**b**, were found to react readily with acid chlorides yielding the products containing two acyl residues. The betainic structure of 1-acyl-3-aryl-3*H*-pyrrolo[2′,3′:4,5]pyrimido[6,1-*b*]benzothiazol-6-ium-2-olates **6** was assigned to them (Scheme 2). It can be represented as a superposition of the four canonic structures **A**–**D** (Scheme 3) with positive charge distributed between nitrogen atoms at third and sixth positions and the negative one delocalized at the β-diketone moiety. Betaines **6** were the sole obtained products when the reaction was performed in various molar ratio of the reagents. However, the highest yields of compounds **6** (~70%) were achieved using 3-fold excess of the acid chloride. The additional equivalent of the acid chloride is supposed to act as a dehydrating agent for bis-acylated intermediates **7** (Scheme 2).

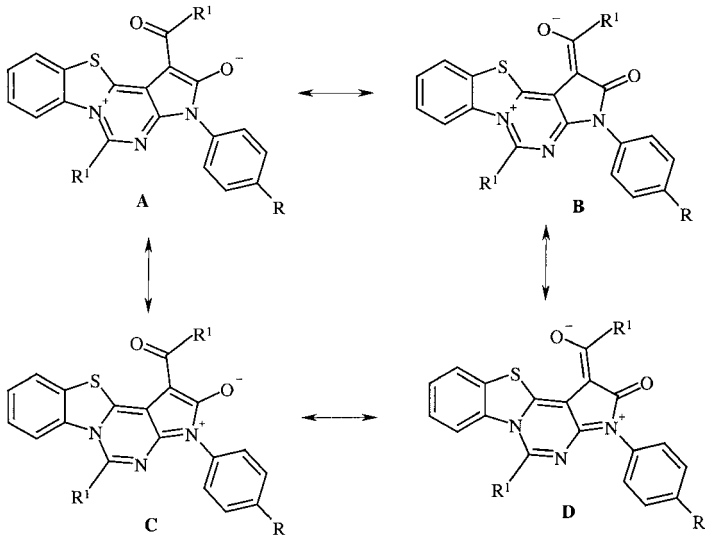
The structure of compounds **6** was initially deduced from the spectral data. First of all, the significant difference in the spectra of 5-methyl compounds **6c**,**e** and 5-aryl derivatives **6a**,**b**,**d**,**f**–**i** should be mentioned. Thus, ^1H NMR spectra of compounds **6c**,**e** showed 1 H doublet at 8.4–8.5 ppm and 3 H singlet at 3.2–3.3 ppm, which are in too low field as for an ordinary aryl proton and C-methyl group respectively. These signals were assigned to the 7-H and 5-CH_3, the deshielding of these protons can be explained by the influence of ring current of pyrimidine nuclei at 7-H and of benzene moiety at 5-CH_3. Moreover, a NOESY experiment carried out for compound **6c** revealed the positive NOE between the above-mentioned signals, thus confirming pyrimidine ring closure. The signals of the other protons of the former benzothiazolyl moiety are shifted downfield to 0.3–0.4 ppm pointing at some cationic character of the nitrogen atom.

On the other hand, the ^1H NMR spectra of 5-aryl derivatives **6a**,**b**,**d**,**f**–**i** exhibited an opposite effect. An unusually high-field 1 H doublet at 6.4–6.7 ppm was observed there-



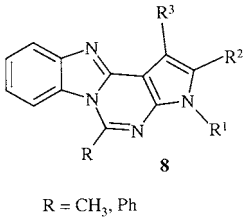
6	a	b	c	d	e	f	g	h	i
R	H	H	H	i-Pr	i-Pr	i-Pr	i-Pr	i-Pr	i-Pr
R^1	Ph	4-MeC_6H_4	Me	4-MeC_6H_4	Me	2-ClC_6H_4	2-furyl	4-$MeOC_6H_4$	4-(t-Bu)-C_6H_4

Scheme 2



Scheme 3

in. It also was assigned to the 7-H. Its strong shielding is caused by the ring current of 5-aryl group. The latter is approximately perpendicular to the tetracycle's plane, therefore 7-H turned out to be located almost above the center of aryl substituent. At the same time the signals of the other protons of the benzothiazolyl moiety remained shifted downfield as in 5-methyl derivatives **6c**,**e**. The above given spectral data are similar to those reported for 5-methyl and 5-aryl derivatives of pyrrolo[2′,3′:4,5]pyrimido[6,1-*a*]benzimidazole system **8** (Figure 2).[1c,2f] The latter is a good model for the system under investigation and the resemblance of their spectra confirms the assigned structure **6**. Moreover, the ^{13}C NMR spectra recorded for 5-methyl and 5-aryl derivatives **6e** and **6d** together with COSY, HSQC and HMBC experiments performed to facilitate the signals assignment, were in good agreement with the structure **6**. Finally, mass spectra of **6e** and **6d** established expected $M^{\cdot+}$ values 415 and 576, respectively.

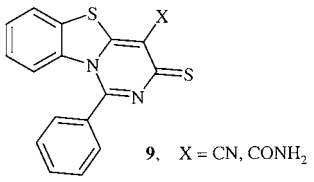


R = CH_3, Ph

Figure 2 The structure of comound **8**

To the best of our knowledge compounds **6** are the representatives of a hitherto unknown heterocyclic system – pyrrolo[2′,3′:4,5]pyrimido[6,1-*b*]benzothiazole. The preparation of their analogues – benzothiazolo[3,2-*c*]quinazoline derivatives, where pyrrole ring is replaced by a benzene one, was reported starting from 2-(2-aminophenyl)benzothiazole or -benzothiazoline.[7] Certain similarities of the approaches to the pyrimidine ring closure in both cases can be pointed out, though only uncharged derivatives of partially hydrogenated benzothiazolo[3,2-*c*]quinazoline system were described previously.[7] It is noteworthy that some pyrimido[6,1-*b*]benzothiazoles, which moiety is included into the skeleton of **6**, were reported to exhibit antiallergic,[8a,b] anti-inflammatory[8a,b] and plant protective[8c] properties.

About 15 years ago Elgemeie and co-workers[9] described the synthesis of 1-phenylpyrimido[6,1-*b*]benzothiazole-3-thiones **9** (Figure 3) by treatment of 2-benzothiazole acetic acid derivatives with benzoyl isothiocyanate. The structure of **9** contains a moiety of phenyl substituted pyrimido[6,1-*b*]benzothiazole similar to that found in 5-aryl substituted derivatives **6a**,**b**,**d**,**f**–**i**. Consequently, the high-field doublet described above for compounds **6a**,**b**,**d**,**f**–**i** should be present in ^1H NMR spectra of **9**. However, there was nothing upfield from 7.2 ppm in the spectra of compounds **9** reported.[9] Moreover the signals separated from the other ones at high-field side were not described in the spectra of derivatives **9**. Hence a wrong structure had been assigned anyway. Our assignment of structure **6** seems to be clearer as only IR and ^1H NMR spectra were used by Elgemeie and co-workers to confirm their structure. Nevertheless, to exclude any doubt and to obtain the information about bond length, allowing to consider the charges distribution in the betaines **6**, the X-ray crystallographic study of 1-benzoyl-3,5-diphenyl-3*H*-pyrrolo[2′,3′:4,5]pyrimido[6,1-*b*]benzothiazole **6a** was carried out. It proved the structure **6** to be true (Figure 4), therefore Elgemeie's structure **9** should be revised.



9, X = CN, $CONH_2$

Figure 3 The structure of compound **9**

The crystals of **6a** suitable for X-ray analysis were obtained as a 1:1 solvate with DMF molecule. The above given assumption about mutual arrangement of 7-H and 5-aryl substituent in compounds **6a**,**b**,**d**,**f**–**i** deduced from their ^{1}H NMR spectra is confirmed by X-ray data. Thus, the phenyl substituent C(20)–C(25) is turned out from pyrrolopyrimidine plane at an angle 66.2°. Such conformation results in intramolecular CH–π bonding with following parameters: C(5)–H(5)–X, H(5)–X distance is 2.57 Å, C(5)–H(5)–X angle is 142°, where X represents the center of the phenyl ring C(20)–C(25).

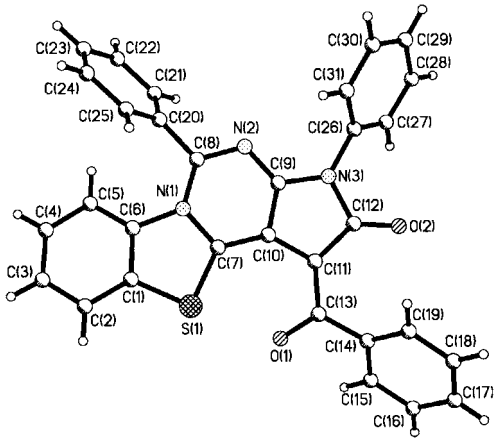


Figure 4 X-ray molecular structure of compound **6a** with the atom numbering used in the crystallographic analysis

Analysis of the bonds length in the β-diketone moiety allows to suggest more contribution from canonic structures B and D (Scheme 3) than of A and C in the molecule of **6a**. So, the bond C(13)–O(1) [1.241(5) Å] is considerably longer than C(12)–O(2) [1.218(5) Å] and the bond C(11)–C(12) [1.446(6) Å] is also longer than C(11)–C(13) [1.434(6) Å]. Therefore the negative charge is located predominantly at O(1). Probably, it is due to its additional stabilization by donating interaction O(1)→ S(1) [the distance is 2.66 Å whereas van der Waals radii sum is 3.09 Å,[10] the angle O(1)–S(1)–C(1) is 162.3°].

The positive charge in compound **6a** is effectively delocalized at the chain N(1)–C(8)–N(2)–C(9)–N(3) and is distributed between N(1) and N(3) approximately equally. This is confirmed by the close values of N(1)–C(8) and N(3)–C(9) bond lengths [1.371(5) Å and 1.366(5) Å, respectively]. The bonds N(2)–C(8) and N(2)–C(9) are also almost equal [1.327(5) Å and 1.330(5) Å, respectively]. So in the solid state, the molecule **6a** is represented by superposition of canonic structures B and D with insignificant contributions from A and C.

However, ^{13}C NMR data allow us to suggest that the negative charge distribution in **6** in their solutions is different. Thus, ^{13}C NMR spectra of compounds **6d** and **6e** show the presence of the lowest-field signal at 184.0 and 188.2 ppm respectively, assigned to carbon of oxo group of the acyl substituent at first position based on long-range C-H correlation data. For **6d** this signal gave correlation with two-proton doublet at 7.76 ppm from 2′,6′-H of *p*-toluoyl moiety, while for derivative **6e** corresponding correlation with the three-proton singlet of methyl at 2.33 ppm was observed. These values of ^{13}C NMR shifts indicate their carbonyl character, hence the negative charge should be placed at the oxygen at second position. Therefore, according to the spectral data in DMSO-d_6 solution canonic structures A and C seem to be more preferable than B and D in contrast to the solid state.

In summary, a convenient method for 5-amino-4-(2-benzothiazolyl)-2,3-dihydro-2-pyrrolones **3** preparation has been worked out. Their acylation with acid chlorides has been shown to lead to the derivatives of a novel heterocyclic system namely 1-acyl-3-aryl-3*H*-pyrrolo-[2′,3′:4,5]pyrimido[6,1-*b*]benzothiazol-6-ium-2-olates **6**. The charge distribution in betaines **6** in solid state and in their solution in DMSO has been discussed. The comparison of the reactivity of compounds **3** with those of isomeric 3-pyrrolones **1** confirmed the amide-type conjugation in **1** to be the cause of their low reactivity.

2-Benzothiazoleacetonitrile (**4**) was prepared as reported.[11] Chloroacetic acid anilides **5a**–**k** were obtained according to described procedures.[12] Acid chlorides were commercially available or prepared from corresponding commercially available acids via standard methods. All mps were determined in capillary tubes in a Thiele apparatus and are uncorrected. IR spectra were obtained for KBr tablets on a Pye Unicam SP 3-300 apparatus. ^{1}H NMR spectra were recorded on a Varian VXR-300 (300 MHz) spectrometer in DMSO-d_6 solution. Chemical shifts (δ) are given in ppm downfield from internal standard ($SiMe_4$). *J* values are in Hz. Besides the standard abbreviations, dist for distorted and Bth for benzothiazolyl were used. ^{13}C NMR and 2D NMR experiments were performed on a Bruker Avance 500 (500 MHz for ^{1}H, 125 MHz for ^{13}C) spectrometer. Mass spectra were determined on a Varian 212 instrument at 70 eV. The purity of all compounds prepared was checked by ^{1}H NMR.

5-Amino-1-aryl-4-(2-benzothiazolyl)-2,3-dihydro-2-pyrrolones 3a–k; General Procedure

Powdered K_2CO_3 (0.485 g, 3.5 mmol) was added to a solution of 2-benzothiazoleacetonitrile (**4**; 0.522 g, 3 mmol) and 2-chloroacetanilide **5** (3 mmol) in absolute EtOH (4 mL) and the resulting mixture was refluxed for 1 h. After cooling, the precipitate formed was filtered, thoroughly washed with H_2O and dried to yield pure compounds **3a**–**k** (~60%). An additional portion (20–30%) can be obtained by pouring the filtrate into H_2O, filtration of the precipitated solid and recrystallization from appropriate solvent.

5-Amino-4-(2-benzothiazolyl)-2,3-dihydro-1-phenyl-2-pyrrolone (3a)

Mp 225 °C (1,4-dioxane); yield: 0.75 g (81%).

IR: 3420, 3050 (NH), 1720 (C=O), 1630, 1500, 1490, 1380, 1295, 1255, 740, 685 cm^{-1}.

^{1}H NMR: δ = 3.44 (s, 2 H, CH_2), 7.11 (t, 1 H, *J* = 7.8 Hz, 5-H_{Bth}), 7.31 (t, 1 H, *J* = 7.8 Hz, 6-H_{Bth}), 7.35 (d, 2 H, *J* = 7.2 Hz, 2,6-H_{Ar}), 7.40 (br s, 2 H, NH_2), 7.49 (t, 1 H, *J* = 7.8 Hz, 4-H_{Ar}), 7.56 (m, 2 H, 3,5-H_{Ar}), 7.63 (d, 1 H, *J* = 7.8 Hz, 7-H_{Bth}), 7.78 (d, 1 H, *J* = 7.8 Hz, 4-H_{Bth}).

^{13}C NMR: δ = 32.62 (CH_2), 77.06 (4-C), 118.95 (6-C_{Bth}), 120.72 (7-C_{Bth}), 120.77 (4-C_{Ar}), 121.38 (5-C_{Bth}), 125.05 (3,5-C_{Ar}), 125.79 (4-C_{Bth}), 129.63 (7a-C_{Bth}), 134.44 (2,6-C_{Ar}), 145.39 (1-C_{Ar}), 151.00 (3a-C_{Bth}), 153.54 (2-C_{Bth}), 164.16 (5-C), 174.11 (C=O).

Anal. Calcd for $C_{17}H_{13}N_3OS$: C, 66.43; H, 4.26; N, 13.67; S, 10.43. Found: C, 66.25; H, 4.31; N, 13.55; S, 10.42.

5-Amino-4-(2-benzothiazolyl)-2,3-dihydro-1-[4-(isopropyl)phenyl]-2-pyrrolone (3b)
Mp 231 °C (EtOH); yield: 0.94 g (90%).

IR: 3430, 3150 (NH), 2950 (CH), 1715 (C=O), 1620, 1485, 1280, 1195, 1150, 745 cm^{-1}.

^1H NMR: δ = 1.27 (d, 6 H, *J* = 6.9 Hz, 2 CH_3), 2.98 [m, 1 H, $CH(CH_3)_2$], 3.42 (s, 2 H, CH_2), 7.10 (t, 1 H, *J* = 7.8 Hz, 5-H_{Bth}), 7.20–7.35 (m, 5 H, 6-H_{Bth}, 2 H_{Ar}, NH_2), 7.40 (d, 2 H_{Ar}, *J* = 8.4 Hz), 7.62 (d, 1 H, *J* = 7.8 Hz, 7-H_{Bth}), 7.77 (d, 1 H, *J* = 7.8 Hz, 4-H_{Bth}).

^{13}C NMR: δ = 23.28 (2 CH_3), 32.83 (CH_2), 34.68 (*C*HMe_2), 76.99 (4-C), 118.81 (6-C_{Bth}), 120.84 (7-C_{Bth}), 121.40 (5-C_{Bth}), 125.48 (4-C_{Bth}), 127.05 (2,6-C_{Ar}), 127.30 (3,5-C_{Ar}), 129.68 (7a-C_{Bth}), 131.00 (4-C_{Ar}), 148.65 (1-C_{Ar}), 150.86 (3a-C_{Bth}), 154.10 (2-C_{Bth}), 164.17 (5-C), 173.02 (C=O).

Anal. Calcd for $C_{20}H_{19}N_3OS$: C, 68.74; H, 5.48; N, 12.02; S, 9.18. Found: C, 68.65; H, 5.31; N, 12.05; S, 9.22.

5-Amino-4-(2-benzothiazolyl)-2,3-dihydro-1-(1-naphthyl)-2-pyrrolone (3c)
Mp 240 °C (1,4-dioxane); yield: 0.97 g (91%).

IR: 3430, 3150 (NH), 2950 (CH), 1715 (C=O), 1630, 1490, 1195, 765 cm^{-1}.

^1H NMR: δ = 3.55 (d, 1 H, *J* = 21.5 Hz, 3-H), 3.69 (d, 1 H, *J* = 21.5 Hz, 3-H), 7.13 (t, 1 H, *J* = 7.8 Hz, 5-H_{Bth}), 7.3–7.4 (m, 3 H, 6-H_{Bth}, NH_2), 7.5–7.7 (m, 6 H, 7-H_{Bth} and 5 H_{Ar}), 7.82 (d, 1 H, *J* = 7.8 Hz, 4-H_{Bth}), 8.1 (m, 2 H_{Ar}).

^{13}C NMR: δ = 31.09 (CH_2), 76.32 (4-C), 111.46 (4-C_{Ar}), 119.56 (6-C_{Bth}), 120.00 (7-C_{Bth}), 120.16 (7-C_{Ar}), 121.23 (5-C_{Ar}), 121.48 (6-C_{Ar}), 122.43 (5-C_{Bth}), 124.21 (4-C_{Bth}), 125.92 (3-C_{Ar}), 128.47 (8-C_{Ar}), 128.56 (4a-C_{Ar}), 130.59 (7a-C_{Bth}), 134.48 (2-C_{Ar}), 138.08 (8a-C_{Ar}), 142.66 (1-C_{Ar}), 150.15 (3a-C_{Bth}), 155.26 (2-C_{Bth}), 164.99 (5-C), 173.55 (C=O).

Anal. Calcd for $C_{21}H_{15}N_3OS$: C, 70.57; H, 4.23; N, 11.76; S, 8.97. Found: C, 70.55; H, 4.31; N, 11.65; S, 8.92.

5-Amino-4-(2-benzothiazolyl)-2,3-dihydro-1-(3-methoxyphenyl)-2-pyrrolone (3d)
Mp 250 °C (1,4-dioxane); yield: 0.77 g (76%).

^1H NMR: δ = 3.43 (s, 2 H, CH_2), 3.81 (s, 3 H, OCH_3), 6.91 (m, 2 H, 2,4-H_{Ar}), 7.03 (d, 1 H, *J* = 7.8 Hz, 6-H_{Ar}), 7.10 (t, 1 H, *J* = 7.8 Hz, 5-H_{Bth}), 7.30 (t, 1 H, *J* = 7.8 Hz, 6-H_{Bth}), 7.4–7.5 (m, 3 H, 5-H_{Ar}, NH_2), 7.63 (d, 1 H, *J* = 7.8 Hz, 7-H_{Bth}), 7.78 (1 H, d, *J* = 7.8 Hz, 4-H_{Bth}).

^{13}C NMR: δ = 33.16 (CH_2), 56.90 (OCH_3), 77.61 (4-C), 105.53 (4-C_{Ar}), 117.71 (2-C_{Ar}), 118.16 (6-C_{Bth}), 120.33 (7-C_{Bth}), 120.87 (5-C_{Bth}), 122.11 (6-C_{Ar}), 126.46 (4-C_{Bth}), 127.31 (5-C_{Ar}), 129.59 (7a-C_{Bth}), 148.42 (1-C_{Ar}), 150.38 (3a-C_{Bth}), 154.75 (2-C_{Bth}), 157.79 (3-C_{Ar}), 163.49 (5-C), 175.18 (C=O).

Anal. Calcd for $C_{18}H_{15}N_3O_2S$: C, 64.08; H, 4.48; N, 12.45; S, 9.50. Found: C, 64.05; H, 4.32; N, 12.65; S, 9.62.

5-Amino-4-(2-benzothiazolyl)-1-(5-chloro-2-methoxyphenyl)-2,3-dihydro-2-pyrrolone (3e)
Mp 221 °C (1,4-dioxane); yield: 0.83 g (75%).

^1H NMR: δ = 3.43 (s, 2 H, CH_2), 3.82 (s, 3 H, OCH_3), 7.11 (t, 1 H, *J* = 7.5 Hz, 5-H_{Bth}), 7.23 (d, 1 H, *J* = 9.0 Hz, 3-H_{Ar}), 7.31 (t, 1 H, *J* = 7.5 Hz, 6-H_{Bth}), 7.38 (d, 1 H, *J* = 1.5 Hz, 6-H_{Ar}), 7.42 (br s, 2 H, NH_2), 7.52 (dd, 1 H, ^3J = 9.0, ^4J = 1.5 Hz, 4-H_{Ar}), 7.63 (d, 1 H, *J* = 7.5 Hz, 7-H_{Bth}), 7.78 (d, 1 H, *J* = 7.5 Hz, 4-H_{Bth}).

^{13}C NMR: δ = 32.09 (CH_2), 55.26 (OCH_3), 76.47 (4-C), 112.97 (3-C_{Ar}), 117.99 (4-C_{Ar}), 119.64 (6-C_{Bth}), 120.84 (7-C_{Bth}), 121.12 (5-C_{Bth}), 123.77 (5-C_{Ar}), 124.71 (4-C_{Bth}), 129.41 (7a-C_{Bth}), 131.52 (6-C_{Ar}), 134.29 (1-C_{Ar}), 150.24 (3a-C_{Bth}), 155.84 (2-C_{Bth}), 164.30 (5-C), 164.32 (2-C_{Ar}), 172.99 (C=O).

Anal. Calcd for $C_{18}H_{14}ClN_3O_2S$: C, 58.14; H, 3.79; Cl, 9.53; N, 11.30; S, 8.62. Found C, 58.15; H, 3.71; Cl, 9.47; N, 11.25; S, 8.82.

5-Amino-4-(2-benzothiazolyl)-1-(2,4-dimethylphenyl)-2,3-dihydro-2-pyrrolone (3f)
Mp 211 °C (1,4-dioxane); yield: 0.71 g (71%).

^1H NMR: δ = 2.13 (s, 3 H, CH_3), 2.37 (s, 3 H, CH_3), 3.44 (s, 2 H, CH_2), 7.05–7.18 (m, 3 H, 5-H_{Bth}, 5,6-H_{Ar}), 7.22 (s, 1 H, 3-H_{Ar}), 7.30 (m, 3 H, 6-H_{Bth}, NH_2), 7.61 (d, 1 H, *J* = 7.8 Hz, 7-H_{Bth}), 7.78 (d, 1 H, *J* = 7.8 Hz, 4-H_{Bth}).

^{13}C NMR: δ = 17.72 (CH_3), 20.65 (CH_3), 30.95 (CH_2), 77.22 (4-C), 118.81 (6-C_{Bth}), 120.19 (7-C_{Bth}), 120.34 (5-C_{Ar}), 120.59 (5-C_{Bth}), 125.48 (4-C_{Bth}), 125.63 (4-C_{Ar}), 128.34 (7a-C_{Bth}), 128.80 (3-C_{Ar}), 130.50 (6-C_{Ar}), 134.81 (2-C_{Ar}), 144.68 (1-C_{Ar}), 150.86 (3a-C_{Bth}), 154.26 (2-C_{Bth}), 166.24 (5-C), 173.58 (C=O).

Anal. Calcd for $C_{19}H_{17}N_3OS$: C, 68.04; H, 5.11; N, 12.53; S, 9.56. Found: C, 68.15; H, 5.21; N, 12.45; S, 9.62.

5-Amino-4-(2-benzothiazolyl)-1-(2,4-difluorophenyl)-2,3-dihydro-2-pyrrolone (3g)
Mp 247 °C (1,4-dioxane); yield: 0.84 g (82%).

^1H NMR: δ = 3.44 (s, 2 H, CH_2), 7.11 (t, 1 H, *J* = 7.5 Hz, 5-H_{Bth}), 7.22 (m, 1 H_{Ar}), 7.31 (t, 1 H, *J* = 7.5 Hz, 6-H_{Bth}), 7.41 (m, 1 H_{Ar}), 7.45–7.60 (m, 3 H, NH_2, 1 H_{Ar}), 7.65 (d, 1 H, *J* = 7.5 Hz, 7-H_{Bth}), 7.78 (d, 1 H, *J* = 7.5 Hz, 4-H_{Bth}).

^{13}C NMR: δ = 32.83 (CH_2), 76.06 (4-C), 108.12 (t, J_{CF} = 28.4 Hz, 3-C_{Ar}), 118.64 (6-C_{Bth}), 120.84 (7-C_{Bth}), 122.39 (5-C_{Bth}), 125.11 (4-C_{Bth}), 126.09 (dd, J_{CF} = 28.0, J_{CF} = 2.8 Hz, 5-C_{Ar}), 130.35 (dd, J_{CF} = 28.0, J_{CF} = 2.8 Hz, 1-C_{Ar}), 131.06 (7a-C_{Bth}), 145.73 (t, J_{CF} = 7.2 Hz, 6-C_{Ar}), 151.49 (3a-C_{Bth}), 151.66 (dd, J_{CF} = 260.0, J_{CF} = 7.2 Hz, 4-C_{Ar}), 154.10 (2-C_{Bth}), 158.53 (d, J_{CF} = 2.4 Hz, 5-C), 170.66 (d, J_{CF} = 2.4 Hz, C=O), 172.40 (dd, J_{CF} = 260.0 Hz, J_{CF} = 7.2, 2-C_{Ar}).

Anal. Calcd for $C_{17}H_{11}F_2N_3OS$: C, 59.47; H, 3.23; N, 12.24; S, 9.34. Found: C, 59.35; H, 3.21; N, 12.33; S, 9.27.

5-Amino-4-(2-benzothiazolyl)-1-(4-ethoxyphenyl)-2,3-dihydro-2-pyrrolone (3h)
Mp 210 °C (EtOH); yield: 0.88 g (84%).

^1H NMR: δ = 1.39 (t, 3 H, *J* = 7.1 Hz, CH_2CH_3), 3.40 (s, 2 H, CH_2), 4.07 (q, 2 H, *J* = 7.1 Hz, CH_2CH_3), 7.04 (d, 2 H, *J* = 8.7 Hz, 3,5-H_{Ar}), 7.09 (t, 1 H, *J* = 7.8 Hz, 5-H_{Bth}), 7.23 (d, 2 H, *J* = 8.7 Hz, 2,6-H_{Ar}), 7.27–7.35 (m, 3 H, 6-H_{Bth}, NH_2), 7.63 (d, 1 H, *J* = 7.8 Hz, 7-H_{Bth}), 7.80 (d, 1 H, *J* = 7.8 Hz, 4-H_{Bth}).

^{13}C NMR: δ = 14.69 (CH_3), 32.56 (CH_2), 63.63 (OCH_2), 77.39 (4-C), 110.99 (3,5-C_{Ar}), 118.81 (6-C_{Bth}), 119.86 (7-C_{Bth}), 121.58 (5-C_{Bth}), 125.13 (4-C_{Bth}), 128.04 (2,6-C_{Ar}), 128.22 (7a-C_{Bth}), 139.92 (1-C_{Ar}), 148.67 (4-C_{Ar}), 150.19 (3a-C_{Bth}), 153.94 (2-C_{Bth}), 166.19 (5-C), 172.67 (2-C=O).

Anal. Calcd for $C_{19}H_{17}N_3O_2S$: C, 64.94; H, 4.88; N, 11.96; S, 9.12. Found: C, 64.85; H, 4.67; N, 12.03; S, 9.21.

5-Amino-4-(2-benzothiazolyl)-2,3-dihydro-1-(4-nitrophenyl)-2-pyrrolone (3i)
Mp 252 °C (1,4-dioxane); yield: 0.87 g (83%).

IR: 3200, 3150 (NH), 1730 (C=O), 1635, 1490, 1330, 1155, 850, 765, 750 cm^{-1}.

^{1}H NMR: δ = 3.49 (s, 2 H, CH_2), 7.14 (t, 1 H, *J* = 7.8 Hz, 5-H_{Bth}), 7.33 (t, 1 H, *J* = 7.8 Hz, 6-H_{Bth}), 7.59 (br s, 2 H, NH_2), 7.67 (m, 3 H, 7-H_{Bth}, 2,6-H_{Ar}), 7.80 (d, 1 H, *J* = 7.8 Hz, 4-H_{Bth}), 8.38 (d, 1 H, *J* = 9.0 Hz, 3,5-H_{Ar}).

^{13}C NMR: δ = 31.69 (CH_2), 76.05 (4-C), 118.49 (6-C_{Bth}), 120.94 (7-C_{Bth}), 121.40 (5-C_{Bth}), 123.19 (3,5-C_{Ar}), 126.33 (4-C_{Bth}), 128.42 (7a-C_{Bth}), 129.59 (2,6-C_{Ar}), 135.09 (4-C_{Ar}), 150.86 (3a-C_{Bth}), 154.72 (2-C_{Bth}), 154.99 (1-C_{Ar}), 164.09 (5-C), 175.21 (C=O).

Anal. Calcd for $C_{17}H_{14}N_4O_3S$: C, 57.62; H, 3.98; N, 15.81; S, 9.05. Found: C, 57.85; H, 3.97; N, 15.73; S, 9.01.

5-Amino-4-(2-benzothiazolyl)-1-(2-bromophenyl)-2,3-dihydro-2-pyrrolone (3j)

Mp 207 °C (*n*-BuOH); yield: 1.00 g (87%).

IR: 3250, 3150 (NH), 1715 (C=O), 1625, 1500, 1470, 1435, 1280, 1200, 1150, 740, 705 cm^{-1}.

^{1}H NMR: δ = 3.47 (s, 2 H, CH_2), 7.14 (t, 1 H, *J* = 7.5 Hz, 5-H_{Bth}), 7.30 (t, 1 H, *J* = 7.5 Hz, 6-H_{Bth}), 7.42 (br s, 2 H, NH_2), 7.47 (m, 2 H, 6,4-H_{Ar}), 7.57 (t, 1 H, *J* = 7.2 Hz, 5-H_{Ar}), 7.63 (d, 1 H, *J* = 7.5 Hz, 7-H_{Bth}), 7.80 (m, 2 H, 3-H_{Ar}, 4-H_{Bth}).

^{13}C NMR: δ = 33.24 (CH_2), 76.28 (4-C), 117.43 (6-C_{Bth}), 120.18 (4-C_{Ar}), 120.41 (7-C_{Bth}), 121.40 (5-C_{Bth}), 126.04 (4-C_{Bth}), 130.28 (7a-C_{Bth}), 130.94 (5-C_{Ar}), 135.72 (2-C_{Ar}), 137.45 (3-C_{Ar}), 143.83 (6-C_{Ar}), 145.61 (1-C_{Ar}), 150.86 (3a-C_{Bth}), 154.38 (2-C_{Bth}), 163.64 (5-C), 173.19 (C=O).

Anal. Calcd for $C_{17}H_{12}BrN_3OS$: C, 52.86; H, 3.13; Br, 20.69; N, 10.88; S, 8.30. Found: C, 52.85; H, 3.17; Br, 20.63; N, 10.73; S, 8.37.

5-Amino-4-(2-benzothiazolyl)-1-[4-(*tert*-butyl)phenyl]-2,3-dihydro-2-pyrrolone (3k)

Mp 258 °C (*n*-BuOH); yield: 0.85 g (78%).

^{1}H NMR: δ = 1.35 (s, 9 H, *t*-C_4H_9), 3.42 (s, 2 H, CH_2), 7.10 (t, 1 H, *J* = 7.8 Hz, 5-H_{Bth}), 7.20–7.40 (m, 5 H, 6-H_{Bth}, 2,6-H_{Ar}, NH_2), 7.55 (d, 2 H, *J* = 8.7 Hz, 3,5-H_{Ar}), 7.63 (d, 1 H, *J* = 7.8 Hz, 7-H_{Bth}), 7.78 (d, 1 H, *J* = 7.8 Hz, 4-H_{Bth}).

^{13}C NMR: δ = 31.42 (CH_3), 31.55 (CH_2), 34.15 (*C*Me_3), 76.28 (4-C), 117.34 (6-C_{Bth}), 120.84 (7-C_{Bth}), 121.76 (5-C_{Bth}), 123.84 (3,5-C_{Ar}), 125.18 (4-C_{Bth}), 127.40 (2,6-C_{Ar}), 129.02 (7a-C_{Bth}), 142.60 (4-C_{Ar}), 145.78 (1-C_{Ar}), 149.73 (3a-C_{Bth}), 154.46 (2-C_{Bth}), 164.17 (5-C), 172.73 (C=O).

Anal. Calcd for $C_{21}H_{21}N_3OS$: C, 69.39; H, 5.82; N, 11.56; S, 8.82. Found: C, 69.35; H, 5.87; N, 11.73; S, 8.97.

1-Aroyl-3,5-diaryl-3*H*-pyrrolo[2′,3′:4,5]pyrimido[6,1-*b*]benzothiazol-6-ium-2-olates 6a,b,d,f–i; General Procedure

Method A: The appropriate acid chloride (10 mmol) was added to a solution of aminopyrrolone **3a** or **3b** (3 mmol) and Et_3N (1.24 mL, 9 mmol) in anhyd 1,4-dioxane (7 mL) and the resulting mixture was heated on a water-bath for 2 h. On cooling, the solid containing triethylamine hydrochloride and the desired compound precipitated. It was thoroughly washed with large amount of H_2O to give 20–30% of pure **6**. 1,4-Dioxane mother liquor was evaporated in vacuo to dryness and the residue was treated with H_2O, collected by suction and recrystallized from appropriate solvent to yield an additional portion of **6**.

Method B: The appropriate acid chloride (10 mmol) was added to a solution of aminopyrrolone **3a** or **3b** (3 mmol) in anhyd pyridine (5 mL) and the resulting mixture was heated at 100 °C for 2 h. After cooling the solvent was removed in vacuo and the residue was treated with H_2O, filtered and recrystallized from appropriate solvent to yield compounds **6**.

1-Benzoyl-3,5-diphenyl-3*H*-pyrrolo[2′,3′:4,5]pyrimido[6,1-*b*]-benzothiazol-6-ium-2-olate (6a)

Mp 275 °C (1,4-dioxane); yield: 58% (Method A); 63% (Method B).

IR: 3025 (CH), 1675, 1570, 1550, 1515, 1490, 1445, 1405, 1225, 1175, 835, 745, 690 cm^{-1}.

^{1}H NMR: δ = 6.60 (d, 1 H, *J* = 8.7 Hz, 7-H), 7.19 (t, 1 H, *J* = 8.7 Hz, 8-H), 7.35–7.73 [m, 14 H, 5-R^1, 3-C_6H_5, 3,4,5-H (COR^1), 9-H], 7.78 [d, 2 H, *J* = 7.2 Hz, 2,6-H (COR^1)], 8.16 (d, 1 H, *J* = 9.0 Hz, 10-H).

^{13}C NMR: δ = 98.87 (1-C), 112.66 [4-C (5-R^1)], 113.29 (11b-C), 121.72 (7-C), 126.27 (9-C), 127.15 [4-C (C_6H_4R)], 129.37 (10a-C), 129.61 [2,6-C (C_6H_4R)], 130.51 (8-C), 131.02 [2,6-C (COR^1)], 131.19 (6a-C), 131.64 [1-C (COR^1)], 131.81 [3,5-C (COR^1)], 132.39 [3,5-C (5-R^1)], 132.41 [3,5-C (C_6H_4R)], 133.27 (10-C), 135.19 [2,6-C (5-R^1)], 137.50 [4-C (COR^1)], 145.87 (N^3-C), 153.69 (2-C), 155.38 (11a-C), 158.80 (3a-C), 164.02 [1-C (5-R^1)], 174.20 (5-C), 184.22 (1-C=O).

Anal. Calcd for $C_{31}H_{19}N_3O_2S$: C, 74.83; H, 3.85; N, 8.44; S, 6.44: Found C, 74.95; H, 4.00; N, 8.53; S, 6.37.

1-(4-Methylbenzoyl)-5-(4-methylphenyl)-3-phenyl-3*H*-pyrrolo[2′,3′:4,5]pyrimido[6,1-*b*]benzothiazol-6-ium-2-olate (6b)

Mp >300 °C (1,4-dioxane); yield: 45% (Method A), 65% (Method B).

IR: 1670, 1510, 1445, 1410, 1225, 840, 820, 755 cm^{-1}.

^{1}H NMR: δ = 2.39 (s, 3 H, CH_3), 2.47 (s, 3 H, CH_3), 6.71 (d, 1 H, *J* = 8.7 Hz, 7-H), 7.16–7.24 [m, 3 H, 8-H, 3,5-H (5-R^1)], 7.35–7.54 (m, 8 H, 3,5-H (COR^1), 3-C_6H_5, 9-H), 7.59 [d, 2 H, *J* = 7.5 Hz, 2,6-H (5-R^1)], 7.71 [d, 2 H, *J* = 8.1, 2,6-H (COR^1)], 8.16 (d, 1 H, *J* = 8.7, 10-H).

^{13}C NMR: δ = 21.28 (CH_3), 21.38 (CH_3), 99.17 (1-C), 113.29 (11b-C), 120.54 (4-C (5-R^1)), 122.37 (7-C), 125.84 (9-C), 127.15 [4-C (C_6H_4R)], 128.49 (10a-C), 129.61 [2,6-C (C_6H_4R)], 130.92 [2,6-C (COR^1)], 131.05 [3,5-C (5-R^1)], 131.16 (8-C), 131.19 (6a-C), 131.59 [1-C (COR^1)], 132.83 [2,6-C (5-R^1)], 133.24 [3,5-C (COR^1)], 132.41 [3,5-C (C_6H_4R)], 133.44 (10-C), 150.21 [4-C (COR^1)], 152.67 (2-C), 155.73 (11a-C), 158.74 (3a-C), 164.78 [1-C (5-R^1)], 172.87 (N^3-C), 174.44 (5-C), 182.81 (1-C=O).

Anal. Calcd for $C_{33}H_{23}N_3O_2S$: C, 75.41; H, 4.41; N, 7.99; S, 6.10. Found: C, 75.35; H, 4.33; N, 8.03; S, 6.07.

1-(4-Methylbenzoyl)-5-(4-methylphenyl)-3-[4-(isopropyl)phenyl]-3*H*-pyrrolo[2′,3′:4,5]pyrimido[6,1-*b*]benzothiazol-6-ium-2-olate (6d)

Mp >300 °C (1,4-dioxane); yield 49% (Method A), 65% (Method B).

IR: 2950, 1665, 1510, 1450, 1415, 1395, 1225, 1180, 1060, 1015, 1000, 925, 840, 825, 755 cm^{-1}.

^{1}H NMR: δ = 1.24 [d, 6 H, *J* = 6.9 Hz, CH(CH_3)$_2$], 2.37 (s, 3 H, CH_3), 2.46 (s, 3 H, CH_3), 2.95 [m, 1 H, C*H*(CH_3)$_2$], 6.67 (d, 1 H, *J* = 8.4 Hz, 7-H), 7.19 [d, 2 H, *J* = 7.8 Hz, 3,5-H (5-R^1)], 7.24 (t, 1 H, *J* = 8.4 Hz, 8-H), 7.35 [d, 2 H, *J* = 7.8 Hz, 3,5-H (COR^1)], 7.44 (dist s, 4 H, 3-C_6H_4R), 7.54 (t, 1 H, *J* = 8.4 Hz, 8-H), 7.62 [d, 2 H, *J* = 7.8 Hz, 2,6-H (5-R^1)], 7.74 [d, 2 H, *J* = 7.8 Hz, 2,6-H (COR^1)], 8.15 (d, 1 H, *J* = 8.4 Hz, 10-H).

^{13}C NMR: δ = 22.65 (CH_3), 22.93 (CH_3), 24.86 [CH(*C*H_3)$_2$], 36.70 [*C*H(CH_3)$_2$], 98.94 (1-C), 113.78 (11b-C), 120.54 [4-C (5-R^1)], 122.19 (7-C), 125.84 (9-C), 129.50 [2,6-C (C_6H_4R)], 129.74 (10a-C), 130.77 (8-C), 130.92 [2,6-C (COR^1)], 131.05 [3,5-C (5-R^1)], 131.19 (6a-C), 131.59 [1-C (COR^1)], 132.83 [2,6-C (5-R^1)], 133.09 (10-C), 133.24 [3,5-C (COR^1)], 133.35 [3,5-C (C_6H_4R)], 137.90 [4-C (C_6H_4R)], 148.80 (N^3-C), 150.21 [4-C (COR^1)], 153.57 (2-C),

156.15 (11a-C), 159.42 (3a-C), 164.70 [1-C (5-R^1)], 174.44 (5-C), 183.96 (1-C=O).

MS: *m*/*z* = 576(M^{+}), 524, 450, 407, 379, 303, 277, 249, 186, 136, 119, 91, 78, 44, 28.

1-(2-Chlorobenzoyl)-5-(2-chlorophenyl)-3-[4-(isopropyl)phenyl]-3*H*-pyrrolo[2′,3′:4,5] pyrimido[6,1-*b*]benzothiazol-6-ium-2-olate (6f)

Mp >300 °C (EtOH); yield: 68% (Method B).

^{1}H NMR: δ = 1.20 [d, 6 H, *J* = 6.9 Hz, CH(C*H*$_3$)$_2$], 2.91 [m, 1 H, C*H*(CH$_3$)$_2$], 6.47 (d, 1 H, *J* = 9.0 Hz, 7-H), 7.30–7.45 [m, 9 H, 3,4,5-H (5-R^1), 3,5-H (C$_6$H$_4$R), 3,4,5-H (COR^1), 8-H], 7.60–7.75 [m, 2 H, 6-H (5-R^1), 9-H] 7.80 [d, 2 H, *J* = 3.3 Hz, 2,6-H (C$_6$H$_4$R)], 7.86 [d, 1 H, *J* = 6.6 Hz, 6-H (COR^1)], 8.32 (d, 1 H, *J* = 8.1 Hz, 10-H).

^{13}C NMR: δ = 23.03 (CH$_3$), 33.70 (*C*HMe$_2$), 98.43 (1-C), 109.95 [4-C (5-R^1)], 114.27 (11b-C), 119.47 [1-C (5-R^1)], 122.35 (7-C), 125.34 (9-C), 128.76 (10a-C), 129.50 [2,6-C (C$_6$H$_4$R)], 129.99 [5-C (5-R^1)], 130.19 (8-C), 130.95 [1-C (COR^1)], 131.84 (6a-C), 132.01 [6-C (COR^1)], 132.07 [5-C (COR^1)], 133.14 [3-C (5-R^1)], 133.35 [3,5-C (C$_6$H$_4$R)], 133.82 [3-C (COR^1)], 134.08 (10-C), 137.90 [4-C (C$_6$H$_4$R)], 138.47 [4-C (COR^1)], 139.51 [2-C (5-R^1)], 140.20 [2-C (COR^1)], 141.09 [6-C (5-R^1)], 148.80 (N^3-C), 153.07 (2-C), 156.15 (11a-C), 159.57 (3a-C), 173.96 (5-C), 185.47 (1-C=O).

Anal. Calcd for $C_{34}H_{23}Cl_2N_3O_2S$: C, 67.11; H, 3.81; N, 6.90; S, 5.27. Found: C, 67.15; H, 3.66; N, 6.74; S, 5.31.

1-(2-Furoyl)-5-(2-furyl)-3-[4-(isopropyl)phenyl]-3*H*-pyrrolo-[2′,3′:4,5]pyrimido[6,1-*b*]benzothiazol-6-ium-2-olate (6g)

Mp >300 °C (1,4-dioxane); yield: 72% (Method B).

IR: 2950, 1660, 1505, 1455, 1410, 1230, 1010, 885, 750 cm^{-1}.

^{1}H NMR: δ = 1.28 [d, 6 H, *J* = 6.9 Hz, CH(C*H*$_3$)$_2$], 2.99 [m, 1 H, C*H*(CH$_3$)$_2$], 6.37 (d, 1 H, *J* = 9.0 Hz, 7-H), 6.63 [dist s, 1 H, 5-H (5-R^1)], 6.88 [dist s, 1 H, 4-H (5-R^1)], 7.19 (d, 1 H, *J* = 2.4 Hz, 3-H (5-R^1)], 7.40–7.55 (m, 5 H, 8-H, C$_6$H$_4$R), 7.63 (t, 1 H, *J* = 9.0 Hz, 9-H), 7.86 [dist s, 1 H, 5-H (COR^1)], 8.03 [dist s, 1 H, 4-H (COR^1)], 8.15 [d, 1 H, *J* = 3.0 Hz, 3-H (COR^1)], 8.21 (d, 1 H, *J* = 9.0 Hz, 10-H).

^{13}C NMR: δ = 23.58 (CH$_3$), 33.09 (*C*HMe$_2$), 98.38 (1-C), 110.03 [4-C (5-R^1)], 111.36 [4-C (COR^1)], 113.74 (11b-C), 114.28 [3-C (5-R^1)], 121.57 (7-C), 126.18 (9-C), 129.40 [2,6-C (C$_6$H$_4$R)], 129.74 (10a-C), 130.38 (8-C), 131.27 (6a-C), 131.31 [3-C (COR^1)], 132.58 [3,5-C (C$_6$H$_4$R)], 132.83 (10-C), 137.90 [4-C (C$_6$H$_4$R)], 143.96 [2-C (COR^1)], 144.45 [5-C (COR^1)], 148.24 [5-C (5-R^1)], 151.43 (N^3-C), 154.19 (2-C), 156.74 (11a-C), 158.90 (3a-C), 159.21 (5-C), 160.47 [2-C (5-R^1)], 183.28 (1-C=O).

Anal. Calcd for $C_{30}H_{21}N_3O_4S$: C, 69.35; H, 4.07; N, 8.09; S, 6.17. Found: C, 69.26, H, 4.07; N, 8.09; S, 6.11.

1-(4-Methoxybenzoyl)-5-(4-methoxyphenyl)-3-[4-(isopropyl)-phenyl]-3*H*-pyrrolo[2′,3′:4,5]pyrimido[6,1-*b*]benzothiazol-6-ium-2-olate (6h)

Mp 286 °C (EtOH); yield: 69% (Method B),

^{1}H NMR: δ = 1.23 [d, 6 H, *J* = 6.9 Hz, CH(C*H*$_3$)$_2$], 2.95 [m, 1 H, C*H*(CH$_3$)$_2$], 3.82 (s, 3 H, OCH$_3$), 3.87 (s, 3 H, OCH$_3$), 6.69 (d, 1 H, *J* = 8.7 Hz, 7-H), 6.93 [d, 2 H, *J* = 9.0 Hz, 3,5-H (5-R^1)], 7.17 [d, 2 H, *J* = 8.7 Hz, 3,5-H (COR^1)], 7.28 (t, 1 H, *J* = 8.7 Hz, 8-H], 7.37 [d, 2 H, *J* = 8.4 Hz, 3,5-H (C$_6$H$_4$R)], 7.45 [d, 2 H, *J* = 8.4 Hz, 2,6-H (C$_6$H$_4$R)], 7.55 (t, 1 H, *J* = 8.7 Hz, 9-H), 7.65 [d, 2 H, *J* = 9.0 Hz, 2,6-H (5-R^1)], 7.85 [d, 2 H, *J* = 8.7 Hz, 2,6-H (COR^1)], 8.18 (d, 1 H, *J* = 8.7 Hz, 10-H).

^{13}C NMR: δ = 24.58 (CH$_3$), 32.85 (*C*HMe$_2$), 55.02 (OCH$_3$), 55.22 (OCH$_3$), 99.61 (1-C), 113.85 (11b-C), 117.30 [3,5-C (5-R^1)], 117.71 [3,5-C (COR^1)], 122.19 (7-C), 124.73 (9-C), 129.16 (10a-C), 129.45 [1-C (COR^1)]), 129.50 [2,6-C (C$_6$H$_4$R)], 131.29 (8-C), 131.89 (6a-C), 132.71 (10-C), 133.35 [3,5-C (C$_6$H$_4$R)], 134.60 [2,6-C (COR^1)], 137.90 [4-C (C$_6$H$_4$R)], 138.18 [2,6-C (5-R^1)], 142.79 [4-C (5-R^1)], 148.80 (N^3-C), 153.44 (2-C), 156.15 (11a-C), 159.41 (3a-C), 160.24 [1-C (5-R^1)], 170.15 [4-C (COR^1)], 174.72 (5-C), 183.34 (1-C=O).

Anal. Calcd for $C_{36}H_{29}N_3O_4S$: C, 72.10; H, 4.87; N, 7.01; S, 5.35. Found: C, 71.97; H, 4.91; N, 7.03; S, 5.31.

1-[4-(*tert*-Butyl)benzoyl]-5-[4-(*tert*-butyl)phenyl]-3-[4-(isopropyl)phenyl]-3*H*-pyrrolo[2′,3′:4,5] pyrimido[6,1-*b*]benzothiazol-6-ium-2-olate (6i)

Mp >300 °C (EtOH); yield: 75% (Method B).

^{1}H NMR: δ = 1.27 [d, 6 H, *J* = 7.2 Hz, CH(C*H*$_3$)$_2$], 1.35 (s, 9 H, *t*-C$_4$H$_9$), 1.39 [s, 9 H, *t*-C$_4$H$_9$), 2.96 [m, 1 H, C*H*(CH$_3$)$_2$], 6.62 (d, 1 H, *J* = 8.7, 7-H), 7.17 (t, 1 H, *J* = 8.7, 8-H), 7.30–7.45 [m, 6 H, 5-R^1, 3,5-H (COR^1)], 7.54 (t, 1 H, *J* = 8.7 Hz, 9-H), 7.61 (dist s, 4 H, C$_6$H$_4$R), 7.74 [d, 2 H, *J* = 8.1 Hz, 2,6-H (COR^1)], 8.16 (d, 1 H, *J* = 8.7 Hz, 10-H).

^{13}C NMR: δ = 23.05 [CH(*C*H$_3$)$_2$], 30.10 [C(*C*H$_3$)$_3$], 30.15 [C(*C*H$_3$)$_3$], 33.41 (*C*HMe$_2$), 33.57 (*C*Me$_3$), 34.20 (*C*Me$_3$), 98.72 (1-C), 113.78 (11b-C), 121.94 (7-C), 125.08 (9-C), 127.56 [3,5-C (5-R^1)], 129.05 [2,6-C (C$_6$H$_4$R], 129.41 [3,5-C (COR^1)], 130.00 (10a-C), 130.29 (8-C), 130.98 [2,6-C (COR^1)], 131.10 [1-C (COR^1)], 131.19 (6a-C), 132.46 (10-C), 132.58 [4-C (5-R^1)], 132.89 [2,6-C (5-R^1)], 134.29 [3,5-C (C$_6$H$_4$R)], 138.18 [4-C (C$_6$H$_4$R)], 147.59 (N^3-C), 153.82 (2-C), 157.19 (11a-C), 159.67 (3a-C), 163.28 [4-C (COR^1)], 164.20 [1-C (5-R^1)], 173.51 (5-C), 184.22 (1-C=O).

Anal. Calcd for $C_{42}H_{41}N_3O_2S$: C, 77.39; H, 6.34; N, 6.45; S, 4.92. Found: C, 77.47; H, 6.27; N, 6.33; S, 4.81.

1-Acetyl-3-aryl-5-methyl-3*H*-pyrrolo[2′,3′:4,5]pyrimido[6,1-*b*]benzothiazol-6-ium-2-olates 6c,e; General Procedure

A solution of aminopyrrolone **3a** or **3b** (5 mmol) in Ac$_2$O (6 mL) was refluxed for 3 h. After cooling, the precipitate formed was filtered, washed with H$_2$O and dried to give pure compounds **6c** or **6e**. These derivatives also could be obtained using AcCl according to the Methods A or B described above in approximately equal yields**.**

1-Acetyl-5-methyl-3-phenyl-3*H*-pyrrolo[2′,3′:4,5]pyrimido[6,1-*b*]benzothiazol-6-ium-2-olate (6c)

Mp >300 °C (DMF); yield: 71%.

^{1}H NMR: δ = 2.36 (s, 3 H, COCH$_3$), 3.10 (s, 3 H, 5-CH$_3$), 7.40–7.80 (m, 7 H, C$_6$H$_5$, 8-H, 9-H), 8.16 (d, 1 H, *J* = 8.0 Hz, 10-H), 8.48 (d, 1 H, *J* = 8.0 Hz, 7-H).

^{13}C NMR: δ = 25.37 (5-CH$_3$), 27.16 (CO*C*H$_3$), 90.22 (1-C), 112.84 (11b-C), 119.33 (7-C), 121.58 (9-C), 124.62 [4-C (C$_6$H$_4$R)], 125.45 [2′,6′-C (C$_6$H$_4$R)], 125.02 [3′,5′-C (C$_6$H$_4$)], 125.80 (8-C), 127.39 (10-C), 127.15 (10a-C), 130.42 (6a-C), 138.46 (N^3-C), 143.23 (2-C), 146.05 (3a-C), 149.57 (5-C), 163.80 (11a-C), 189.61 (1-C=O).

Anal. Calcd for $C_{21}H_{15}N_3O_2S$: C, 67.54; H, 4.05; N, 11.25; S, 8.59. Found: C, 67.47; H, 4.07; N, 11.33; S, 8.61.

1-Acetyl-5-methyl-3-[4-(isopropyl)phenyl]-3*H*-pyrrolo-[2′,3′:4,5]pyrimido[6,1-*b*]benzothiazol-6-ium-2-olate (6e)

Mp >300 °C (DMF); yield: 77%.

IR: 2950, 1660, 1550, 1510, 1470, 1440, 1245, 1190, 1020, 1000, 890, 795, 750 cm^{-1}.

^{1}H NMR: δ = 1.29 [d, 6 H, *J* = 6.9 Hz, CH(C*H*$_3$)$_2$], 2.32 (s, 3 H, COCH$_3$), 3.00 [m, 1 H, *J* = 6.9 Hz, C*H*(CH$_3$)$_2$], 3.20 (s, 3 H, 5-CH$_3$), 7.42 (dist s, 4 H$_{Ar}$, *i*-PrC$_6$*H*$_4$), 7.50–7.70 (m, 2 H, 8-H, 9-H), 8.12 (d, 1 H, *J* = 8.1 Hz, 10-H), 8.44 (d, 1 H, *J* = 8.1 Hz, 7-H).

^{13}C NMR: δ = 22.65 [CH(CH_3)$_2$], 25.76 (5-CH_3), 26.18 (COCH_3), 32.01 [CH(CH$_3$)$_2$], 90.11 (1-C), 112.35 (11b-C), 118.59 (7-C), 122.30 (9-C), 125.33 [2′,6′-C (C_6H_4R)], 125.67 (8-C), 125.99 [3′,5′-C (C_6H_4R)], 127.00 (10-C), 128.38 (10a-C), 130.14 (6a-C), 135.37 [4-C (C_6H_4R)], 141.38 (N^3-C), 143.40 (2-C), 146.67 (3a-C), 148.90 (5-C), 163.35 (11a-C), 188.24 (1-C=O).

MS: *m*/*z* = 415($M^{\cdot+}$), 400, 372, 357, 303, 186, 159, 104, 44.

X-Ray Crystal Structure Determination of Compound 6a

Single crystals were obtained from DMF. Intensity data were collected with a Siemens P3/PC difractometer using 2θ/θ scan, $2\theta_{max}$ = 50°, MoKα radiation. Crystal data: $C_{31}H_{19}N_3O_2S{\cdot}C_3H_7NO$, M_r = 570.68, triclinic, a = 10.087(6), b = 12.437(6), c = 13.319(7) Å, α = 114.03(4)°, β = 90.37(4)°, γ = 112.73(4)°, V = 1380(1) Å^3, T = 293 K, space group P1, Z = 2, μ(MoKα) = 0.162 mm^{-1}. 4728 reflections were measured, 4449 were unique, R_{int} = 0.0117. The structure was solved by direct method with the SHELX97 program package.[13] The positions of hydrogen atoms were located by Fourier difference synthesis and refined by riding model with $U_{iso} = nU_{eq}$ of non-hydrogen atom bonded with hydrogen atom given (n = 1.5 for hydrogen atoms of methyl groups and n = 1.2 for the rest of hydrogen). The structure was refined by full-matrix, least-squares methods, using 4449 reflections (R_1 = 0.0058 at 1766 reflections with F>4σ(F), S = 0.784) and anisotropic thermal parameters for all non-hydrogen atoms. The final wR(F^2) value was 0.120.

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