Chemistry of Heterocyclic Compounds, Vol. 47, No. 5, August 2011 (Russian original Vol. 47, No. 5, May, 2011)

SYNTHESIS AND OXIDATIVE CYCLIZATION OF 3-AMINO-2-ARYLAZO-5-*tert*-CYCLOALKYLAMINOTHIOPHENES

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A series of 3-amino-4-arylazo-4,5-dihydrothiophenes has been synthesized by the reaction of arylhydrazonocyanothioacetamides (containing a tert-cycloalkylamino group) with α-halo ketones, 2-chloroacetonitrile, or 4-nitrobenzyl bromide. Their oxidation in the presence of metal acetates was investigated. It was shown that heating in pyridine with $Cu(OAc)_2$ leads to the formation of thieno-[3,4-d]-1,2,3-triazoliumolates.

Keywords: arylhydrazonothioacetamides, halocarbonyl compounds, thieno[3,4-*d*]-1,2,3-triazoliumolates, thiophenes, *tert*-cycloalkylamines, oxidation.

α-Halocarbonyl compounds, including such derivatives as α-chloroacetic acid and 2-halo ketones or phenacyl bromides, are widely used in organic synthesis for the preparation of different heterocyclic compounds [1–9]. We have previously shown that reaction of arylhydrazonothioacetamides with α-halo ketones gives 1,3-thiazoles or 4,5-dihydrothiophenes depending on the electronic effects and steric factors of the substituents on the nitrogen atom of the thioamide fragment and the nature of the substituent in the aromatic ring [6–9]. The aim of our work is to determine the area of applicability of this reaction in the synthesis of thiophenes and to study the chemical properties of the heterocyclic compounds obtained.

The reaction of the arylhydrazonothioacetamides **1a–h** (which contain a *tert*-cycloalkylamine substituent in the thioamide group) with the α-halo ketones **2a,c**, chloroacetonitrile **2b**, and 4-nitrobenzyl bromide **2d** was carried out by heating in the presence of strong bases.

As a result we obtained the series of 3-amino-2-arylazothiophenes **4a–m**, the mechanism of formation of which can be represented as a nucleophilic addition of the methylene group to the carbon atom of the cyano group in the initially formed intermediate **3**. The ^{1}H NMR spectra of the aminothiophenes **4a–m** show the presence of a signal for the NH_2 group as two broad, one-proton singlets or a two-proton singlet in the region 9.00–10.10 ppm together with signals for the proton-containing parts of the substituents R, R^1, and *tert*-cyclo-

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Dedicated to Academician V. N. Charushin on his 60th birthday.

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Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 5, pp. 684–691, May, 2011. Original article submitted February 28, 2011.

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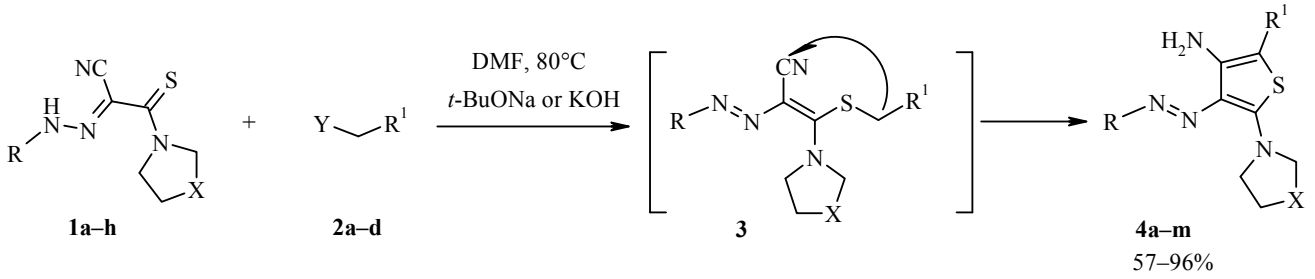
alkylamino groups. The IR spectra of the 3-aminothiophenes **4** show two absorption bands for the NH_2 group in the region 3260–3450 cm^{-1}. The absorption band corresponding to the C=O stretching vibration is shifted in the IR spectra of compounds **4a–c,e–g,i–l** to the region 1575–1600 cm^{-1} and this points to the formation of intramolecular hydrogen bonds in their molecules. With exchange of the acyl or benzoyl substituent R^1 in compounds **4a,c,e** for a cyano or a 4-nitrophenyl group the signals for the NH_2 group protons are shifted to high field in the ^1H NMR spectra of compounds **4d,h** by 2.6–2.0 and 0.6–1.2 ppm and this may be a consequence of weakening of the hydrogen bonding in which the group participates.

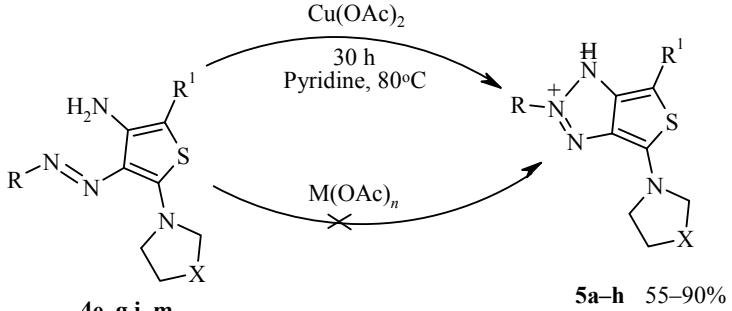


1a–h **2a–d** **3** **4a–m** 57–96%

1 a–c R = 4-$MeOC_6H_4$, **a** X = CH_2, **b** X = $(CH_2)_2$, **c** X = OCH_2, **d–h** R = Ph, **d** X = CH_2, **e** X = $(CH_2)_2$, **f** X = $(CH_2)_3$, **h** X = CH_2N–Ph; **2 a**, **b** Y = Cl, **a** R^1 = MeCO, **b** R^1 = CN; **c**, **d** Y = Br, **c** R^1 = 4-ClC_6H_4CO, **d** R^1 = 4-$NO_2C_6H_4CH_2$; **4 a–h** R = 4-$MeOC_6H_4$, **a–c** R^1 = COMe, **a** X = CH_2, **b** X = $(CH_2)_2$, **c** X = OCH_2, **d** R^1 = CN, X = CH_2, **e–g** R^1 = 4-ClC_6H_4CO, **e** X = CH_2, **f** X = $(CH_2)_2$, **g** X = OCH_2, **h** R^1 = 4-$NO_2C_6H_4$, X = OCH_2; **i–l** R = Ph, R^1 = 4-ClC_6H_4CO, **i** X = CH_2, **j** X = $(CH_2)_2$, **k** X = OCH_2, **l** X = $(CH_2)_3$, R = Ph, R^1 = 4-ClC_6H_4CO, **m** R = Ph, R^1 = 4-ClC_6H_4CO, X = Ph–NCH_2

We have found that the oxidation of the 3-amino-4-aryl-5-*tert*-cycloalkylaminothiophenes **4e–g,i–m** in pyridine in the presence of copper acetate with heating to 80ºC gives the 1*H*-thieno[3,4-*d*]-1,2,3-triazoliumolates **5a–h**, the structure of which was confirmed by spectroscopic methods and elemental analytical data.

The mass spectra of the bicyclic zwitterionic compounds **5a–h** show a molecular ion peak differing by 2 units from the molecular weight of the starting compounds. When compared with the thiophenes **4** the ^1H NMR spectra of the triazoliumolates **5a–h** have lost the NH_2 group signals and the signals for the protons in the *ortho*-position of the aromatic rings of the R substituent is shifted by 0.5 ppm to low field. The IR spectra of the thieno[3,4-*d*]-1,2,3-triazoliumolates **5a–h** show the absence of the corresponding amino group NH bond absorption band seen in the spectra of the starting thiophenes **4**. The stretching vibration band of the carbonyl CO bond is seen at 1575–1604 cm^{-1}.



4e–g,i–m **5a–h** 55–90%

M = Hg^{2+}, Ag^+ n = 1, 2

5 a–h R^1 = 4-ClC_6H_4CO, **a–c** R = 4-$MeOC_6H_4$, **a** X= CH_2, **b** X = $(CH_2)_2$, **c** X = OCH_2, **d–h** R = Ph, **d** X= CH_2, **e** X = $(CH_2)_2$, **f** X = OCH_2, **g** X = $(CH_2)_3$, **h** X = $PhNCH_2$

TABLE 1. Effect of the Ratio of Substrate to $Cu(OAc)_2$ on the Reaction Time and Yield of the Thieno[3,4-d]-1,2,3-triazolate **5f**

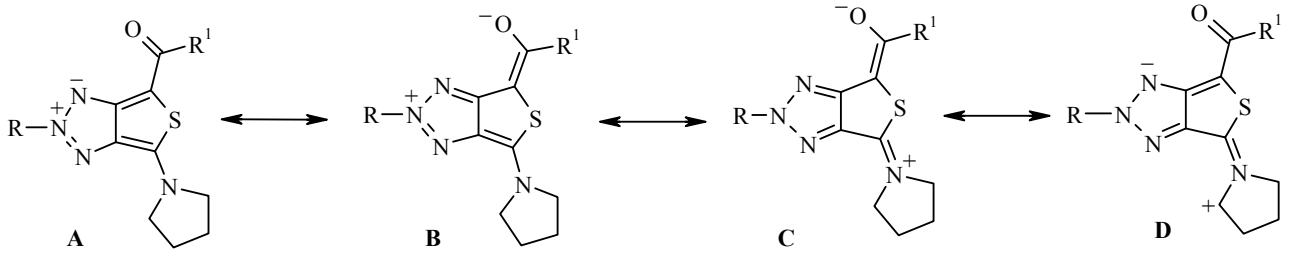
Experiment No.	**4g** : $Cu(OAc)_2$	Reaction time, h	Yield of **5f**, %
1	1 : 2	20	63
2	1 : 1	25	55
3	10 : 1	30	46

The UV spectra of the thieno[3,4-*d*]-1,2,3-triazoliumolates **5a–h** have three absorption maxima at 272–290, 360–370, and 482–540 nm. A marked bathochromic shift of the long wavelength maximum of 100 nm is observed when compared with the UV spectra of the starting 4-arylazo-5-*tert*-cycloalkylaminothiophenes **4**.

The use of different ratios of copper(II) acetate and arylhydrazonothiophene and also heating in the absence of $Cu(OAc)_2$ showed that the copper(II) salt acts as a catalyst in this reaction (Table 1).

Heating the arylazoaminothiophenes **4** in the presence of Hg(II) or silver(I) acetates did not lead to formation of novel products.

The use of the thiophenes **4d,h** (containing a cyano or 4-nitrophenyl group in position 5 of the thiophene ring) as the starting compounds in the oxidation involving $Cu(OAc)_2$ also did not yield novel compounds. This fact allows us to propose that the presence of a carbonyl group at position 2 of the heterocycle is an important feature in achieving the oxidative cyclization of the 3-amino-4-arylazothiophenes **4**. The activation mechanism for compounds **4e–g,i–m** may be connected to a catalytic effect of the C=O group *via* formation of a hydrogen bond with the amino group and also an increase in the stability of the bicyclic triazoliumolates **5a–h** through involvement of the carbonyl group at ring position 4 in the delocalization of negative charge.



The appearance of charges on the nitrogen and oxygen atoms is confirmed by the shift of signals in the ^{1}H NMR spectra, the bathochromic shift of the long wavelength maximum in the UV spectra, and also the shift of the absorption band for the carbonyl group in the IR spectra of the thieno[3,4-*d*]-1,2,3-triazoliumolates **5a–h**.

Given investigation demonstrated that the reaction of the 2-arylhydrazono-2-cyanothioacetamides **1** with α-halocarbonyl compounds and 4-nitrobenzyl bromide is a convenient method for the preparation of polyfunctional thiophenes. These can be used in the synthesis of novel condensed heterocyclic derivatives which include this cyclic fragment.

EXPERIMENTAL

IR spectra were taken on a Bruker Alpha Fourier Spectrometer (ATR, ZnSe). UV spectra were taken on a Perkin-Elmer Lambda 45 spectrometer using THF. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AVANCE II 400 instrument (400 and 100 MHz respectively) using DMSO-d_6 (compounds **4a–m**), pyridine-d_5 (compounds **5a,c,d,h**), or 1,4-dioxane-d_8 (compounds **5b,e–g**) with TMS as internal standard. Mass spectra were recorded on a Varian MAT 311A instrument with ionization energy 70 eV. Monitoring of the reaction course

and purity of the compounds prepared was performed by TLC on Sorbfil UV-254 plates in the systems ethyl acetate–hexane (1:1), chloroform–acetone (30:1), or chloroform–hexane–acetone (5:4:1).

The arylhydrazonocyanoacetamides were prepared by the previously reported method [10].

Reaction of the arylhydrazonothioacetamides 1a–h with the halocarbonyl compounds (2a–d). (General Method). Compound **2** (1 mmol) and *t*-BuOK (0.23 g, 2 mmol) were added to a solution of the arylhydrazonocyanothioacetamide **1** (1 mmol) in DMF (5 ml). The reaction product was held at 80ºC until the starting material had disappeared (TLC, poured into water, and the precipitate formed was filtered off and recrystallized from ethyl alcohol).

1-[3-Amino-4-(4-methoxyphenylazo)-5-(pyrrolidin-1-yl)thiophen-2-yl]ethanone (4a). Yield 47%; mp 238–239ºC. IR spectrum, ν, cm^{-1}: 1581 (CO), 2830, 2850, 2900, 2940, 2970 (C–H); 3350, 3400 (N–H). UV spectrum, λ_{max}, nm (log ε): 350 (6.86), 445 (6.38). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.09–2.12 (4H, m, $2CH_2$); 2.21 (3H, s, $COCH_3$); 3.79–3.85 (4H, m, $2CH_2$); 3.86 (3H, s, OCH_3); 6.94 and 7.55 (4H, AA'XX', *J* = 8.8, Ar); 8.76 (1H, br. s, NH); 9.01 (1H, br, s, NH). Mass spectrum, *m/z* (I_{rel}, %): 344 $[M]^+$ (29). Found, %: C 59.49; H 6.05; N 16.35; S 9.23. $C_{17}H_{20}N_4O_2S$. Calculated, %: C 59.28; H 5.85; N 16.27; S 9.31.

1-[3-Amino-4-(4-methoxyphenylazo)-5-piperidinothiophen-2-yl]ethanone (4b). Yield 55%; mp 236–237ºC. IR spectrum, ν, cm^{-1}: 1578 (CO), 2835, 2970 (C–H), 3355, 3440 (N–H). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.76–1.82 (6H, m, $3CH_2$); 2.09 (3H, s, $COCH_3$); 3.83 (3H, s, OCH_3); 3.85–3.90 (4H, m, $2CH_2$); 6.95 and 7.56 (4H, AA'XX', *J* = 9.2, Ar); 8.60 (1H, br. s, NH); 8.72 (1H, br. s, NH). Mass spectrum, *m/z* (I_{rel}, %): 358 $[M]^+$ (17). Found, %: C 60.19; H 6.28; N 15.48. $C_{18}H_{22}N_4O_2S$. Calculated, %: C 60.31; H 6.19; N 15.63.

1-[3-Amino-4-(4-methoxyphenylazo)-5-morpholinothiophen-2-yl]ethanone (4c). Yield 49%; mp 243–244ºC. IR spectrum, ν, cm^{-1}: 1596 (CO), 2850, 2975 (C–H), 3350, 3400 (N–H). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.12 (3H, s, $COCH_3$); 3.82–3.87 (4H, m, $2CH_2$); 3.84 (3H, s, OCH_3); 3.87–3.89 (4H, m, $2CH_2$); 7.58 and 7.97 (4H, AA'XX', *J* = 9.2, Ar); 8.57 (1H, s, NH); 8.63 (1H, s, NH). Mass spectrum, *m/z* (I_{rel}, %): 360 $[M]^+$ (22). Found, %: C 56.89; H 5.68; N 15.66. $C_{17}H_{20}N_4O_3S$. Calculated, %: C 56.65; H 5.59; N 15.54.

3-Amino-4-(4-methoxyphenylazo)-5-(pyrrolidin-1-yl)thiophene-2-carbonitrile (4d). Yield 60%; mp 240–241ºC. IR spectrum, ν, cm^{-1}: 2166 (C≡N), 2832, 2863, 2965, 2982 (C–H), 3300, 3370 (N–H). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.11–2.14 (4H, m, $2CH_2$); 3.75–3.78 (4H, m, $2CH_2$); 3.87 (3H, s, OCH_3); 6.77 (2H, br. s, NH_2); 6.95–7.00 (2H, m, Ar); 7.55–7.58 (2H, m, Ar). Mass spectrum, *m/z* (I_{rel}, %): 327 $[M]^+$ (18). Found, %: C 56.43; H 5.39; N 21.53. $C_{16}H_{17}N_5OS$. Calculated, %: C 58.70; H 5.23; N 21.39.

[3-Amino-4-(4-methoxyphenylazo)-5-(pyrrolidin-1-yl)thiophen-2-yl](4-chlorophenyl)methanone (4e). Yield 75%; mp 270–271ºC. IR spectrum, ν, cm^{-1}: 1600 (CO), 2830, 2850, 2900, 2940, 2960 (C–H), 3450 (NH). UV spectrum, λ_{max}, nm (log ε): 378 (6.68), 436 (6.48). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.03–2.14 (4H, m, $2CH_2$); 3.82 (3H, s, OCH_3); 4.63–4.82 (4H, m, $2CH_2$); 7.00 and 7.61 (4H, AA'XX', *J* = 8.8, Ar); 7.48 and 7.63 (4H, AA'XX', *J* = 8.3, Ar); 9.14 (1H, s, NH); 9.16 (1H, s, NH). Mass spectrum, *m/z* (I_{rel}, %): 440 $[M]^+$ (9). Found, %: C 60.25; H 5.14; N 12.43. $C_{22}H_{21}ClN_4O_2S$. Calculated, %: C 59.92; H 4.80; N 12.71.

[3-Amino-4-(4-methoxyphenylazo)-5-piperidinothiophen-2-yl](4-chlorophenyl)methanone (4f). Yield 51%; mp 202–203ºC. IR spectrum, ν, cm^{-1}: 1595 (CO), 2963 (C–H), 3320 (N–H). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.73–1.79 (6H, m, $3CH_2$); 3.84 (3H, s, OCH_3); 3.85–4.00 (4H, m, $2CH_2$); 6.97 and 7.59 (4H, AA'XX', *J* = 8.8, Ar); 7.43 and 7.60 (4H, AA'XX', *J* = 8.4, Ar); 9.14 (2H, br. s, NH_2). Mass spectrum, *m/z* (I_{rel}, %): 454 $[M]^+$ (8). Found, %: C 61.13; H 5.28; N 11.99. $C_{23}H_{23}ClN_4O_2S$. Calculated, %: C 60.72; H 5.10; N 12.31.

[3-Amino-4-(4-methoxyphenylazo)-5-(morpholinothiophen-2-yl](4-chlorophenyl)methanone (4g). Yield 63%; mp 204–205ºC. IR spectrum, ν, cm^{-1}: 1601 (CO), 2852, 2924, 2953 (C–H), 3433 (N–H). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 3.80–3.82 (4H, m, $2CH_2$); 3.85 (3H, s, OCH_3); 3.87–3.91 (4H, m, $2CH_2$); 6.98 and 7.60 (4H, AA'XX', *J* = 8.8, Ar); 7.44 and 7.62 (4H, AA'XX', *J* = 8.4, Ar); 9.07 (2H, br. s, NH_2). Mass spectrum, *m/z* (I_{rel}, %): 456 $[M]^+$ (18). Found, %: C 57.66; H 4.81; N 12.47. $C_{22}H_{21}ClN_4O_3S$. Calculated, %: C 57.83; H 4.63; N 12.26.

4-(4-Methoxyphenylazo)-5-morpholino-2-(4-nitrophenyl)thiophene-3-amine (4h). Yield 49%; mp 238–239ºC. IR spectrum, ν, cm^{-1}: 1585 (CO), 2840, 2969 (C–H), 3248, 3462 (N–H). ^{1}H NMR spectrum, δ, ppm

(*J*, Hz): 3.79 (3H, s, OCH_3); 3.80–3.92 (8H, m, $4CH_2$); 7.00 (2H, d, *J* = 8.8, Ar); 7.55–7.60 (4H, m, Ar); 8.12 (2H, br. s, NH_2); 8.19 (2H, d, *J* = 9.2, Ar). Mass spectrum, *m/z* (I_{rel}, %): 439 $[M]^+$ (22). Found, %: C 57.15; H 4.95; N 15.83. $C_{21}H_{21}N_5O_4S$. Calculated, %: C 57.39; H 4.82; N 15.94.

[3-Amino-5-(pyrrolidin-1-yl)-4-phenylazothiophen-2-yl](4-chlorophenyl)methanone (4i). Yield 65%; mp 225–226ºC. IR spectrum, ν, cm^{-1}: 1580 (CO), 2918, 2937, 2997 (C–H), 3430 (N–H). UV spectrum, λ_{max}, nm (log ε): 365 (6.24), 430 (5.83). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.11–1.18 (2H, m, CH_2); 1.20–1.28 (2H, m, CH_2); 2.05–2.13 (4H, m, $2CH_2$); 7.33 (1H, t, *J* = 7.2, Ph); 7.48–7.57 (4H, m, Ph); 7.64–7.70 (4H, m, Ar); 9.24 (1H, s, NH); 9.32 (1H, s, NH). Mass spectrum, *m/z* (I_{rel}, %): 410 $[M]^+$ (23). Found, %: C 61.60; H 4.80; N 13.75. $C_{21}H_{19}ClN_4OS$. Calculated, %: C 61.38; H 4.66; N 13.63.

[3-Amino-5-piperidino-4-phenylazothiophen-2-yl](4-chlorophenyl)methanone (4j). Yield 57%; mp 180–181ºC. IR spectrum, ν, cm^{-1}: 1579 (CO), 2854, 2943 (C–H); 3352 (N–H). UV spectrum, λ_{max}, nm (log ε): 366 (6.22), 445 (5.69). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.75–1.82 (6H, m, $3CH_2$); 3.94–3.97 (4H, m, $2CH_2$); 7.32 (1H, t, *J* = 7.2, Ar); 7.42–7.45 (4H, m, Ar); 7.60–7.62 (4H, m, Ar); 9.20 (2H, s, NH_2). Mass spectrum, *m/z* (I_{rel}, %): 424 $[M]^+$ (12). Found, %: C 61.92; H 5.50; N 13.26. $C_{22}H_{21}ClN_4OS$. Calculated, %: C 62.18; H 4.98; N 13.18.

[3-Amino-5-morpholino-4-phenylazothiophen-2-yl](4-chlorophenyl)methanone (4k). Yield 75%; mp 220–221ºC. IR spectrum, ν, cm^{-1}: 1580 (CO), 2856, 2922, 3029 (C–H); 3265, 3378 (N–H). UV spectrum, λ_{max}, nm (log ε): 360 (6.49), 450 (5.80). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 3.78–3.81 (4H, m, $2CH_2$); 3.92–3.95 (4H, m, $2CH_2$); 7.40 (1H, t, *J* = 7.2, Ar); 7.40–7.57 (4H, m, Ar); 7.65–7.70 (4H, m, Ar); 9.15 (2H, br. s, NH_2). Mass spectrum, *m/z* (I_{rel}, %): 426 $[M]^+$ (20). Found, %: C 59.22; H 4.61; N 13.20. $C_{21}H_{19}ClN_4O_2S$. Calculated, %: C 59.08; H 4.49; N 13.12.

[3-Amino-5-(azepan-1-yl)-4-phenylazothiophen-2-yl](4-chlorophenyl)methanone (4l). Yield 60%; mp 208–209ºC. IR spectrum, ν, cm^{-1}: 1575 (CO), 2924, 2939, 2941 (C–H), 3260 (N–H). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.55–1.67 (4H, m, $2CH_2$); 1.78–1.96 (4H, m, $2CH_2$); 3.94–3.96 (4H, m, $2CH_2$); 7.30 (1H, t, *J* = 7.4, Ar); 7.41–7.46 (4H, m, Ar); 7.55–7.63 (4H, m, Ar); 9.26 (1H, s, NH); 9.36 (1H, s, NH). Mass spectrum, *m/z* (I_{rel}, %): 438 $[M]^+$ (12). Found, %: C 63.19; H 5.41; N 12.88. $C_{23}H_{23}ClN_4OS$. Calculated, %: C 62.93; H 5.28; N 12.76.

[3-Amino-4-phenylazothiophen-2-yl-5-(4-phenylpiperazin-1-yl)](4-chlorophenyl)methanone (4m). Yield 68%; mp 213–214ºC. IR spectrum, ν, cm^{-1}: 1596 (CO), 2839, 2850 (C–H), 3430 (N–H). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 3.40–3.42 (4H, m, $2CH_2$); 4.11–4.13 (4H, m, $2CH_2$); 6.79 (1H, t, *J* = 7.6, Ar); 6.92 (2H, d, *J* = 7.2, Ar); 7.21 (2H, t, *J* = 7.2, Ar); 7.37 (1H, t, *J* = 7.2, Ar); 7.49–7.51 (4H, m, Ar); 7.62–7.67 (4H, m, Ar); 9.16 (2H, br. s, NH_2). Mass spectrum, *m/z* (I_{rel}, %): 501 $[M]^+$ (16). Found, %: C 64.38; H 4.95; N 13.88. $C_{27}H_{24}ClN_5OS$. Calculated, %: C 64.60; H 4.82; N 13.95.

Oxidation of 3-Amino-4-arylazo-5-*tert*-cycloalkylaminothiophenes 4. $Cu(OAc)_2$ (0.364 g, 2 mmol) was added to a solution of the 3-amino-4-arylazothiophene **4** (1 mmol) in pyridine and held with stirring at 80ºC for 20 h (TLC). The reaction product was poured onto ice and the precipitate formed was filtered off and washed with water.

[2-(4-Methoxyphenyl)-6-(pyrrolidin-1-yl)-4H-thieno[3,4-*d*]-1,2,3-triazol-2-ium-4-ylidene](4-chlorophenyl)methanolate (5a). Yield 90%; mp 266–267ºC. IR spectrum, ν, cm^{-1}: 1575 (CO), 2943 (C–H). UV spectrum, λ_{max}, nm (log ε): 275 (6.25), 348 (6.39), 478 (5.92). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.03–2.17 (4H, m, $2CH_2$); 4.63–4.82 (4H, m, $2CH_2$); 3.82 (3H, s, OCH_3); 6.99 and 8.04 (4H, AA'XX', *J* = 8.8, Ar); 7.45 and 8.15 (4H, AA'XX', *J* = 8.4, Ar). Mass spectrum, *m/z* (I_{rel}, %): 438 $[M]^+$ (100). Found, %: C 60.35; H 4.23; N 12.84. $C_{22}H_{19}ClN_4O_2S$. Calculated, %: C 60.20; H 4.36; N 12.76.

[2-(4-Methoxyphenyl)-6-piperidino-4H-thieno[3,4-*d*]-1,2,3-triazol-2-ium-4-ylidene](4-chlorophenyl)methanolate (5b). Yield 63%; mp 242–243ºC. IR spectrum, ν, cm^{-1}: 1575 (CO), 2860, 2943 (C–H). ^{1}H NMR Spectrum, δ, ppm (*J*, Hz): 1.90–2.02 (6H, m, $3CH_2$); 3.85 (3H, s, OCH_3); 3.87–3.94 (2H, m, CH_2); 4.15–4.22 (2H, m, CH_2); 7.05 and 8.05 (4H, AA'XX', *J* = 9.2, Ar); 7.40 and 8.10 (4H, AA'XX', *J* = 8.8, Ar). Mass

spectrum, *m/z* (I_{rel}, %): 452 $[M]^+$ (100). Found, %: C 60.73; H 4.56; N 12.25. $C_{23}H_{21}ClN_4O_2S$. Calculated, %: C 60.99; H 4.67; N 12.37.

[2-(4-Methoxyphenyl)-6-morpholino-4H-thieno[3,4-*d*]-1,2,3-triazol-2-ium-4-ylidene](4-chlorophenyl)methanolate (5c). Yield 56%; mp 260–261ºC. IR spectrum, ν, cm^{-1}: 1590 (CO), 2860, 2940 (C–H). ^1H NMR spectrum, δ, ppm (*J*, Hz): 3.87 (3H, s, OCH_3); 3.84–3.91 (4H, m, $2CH_2$); 3.92–3.99 (4H, m, $2CH_2$); 7.08 and 8.04 (4H, AA'XX', *J* = 9.2, Ar); 7.49 and 8.05 (4H, AA'XX', *J* = 8.4, Ar). Mass spectrum, *m/z* (I_{rel}, %): 454 $[M]^+$ (100). Found, %: C 58.22; H 4.32; N 12.53. $C_{22}H_{19}ClN_4O_3S$. Calculated, %: C 58.08; H 4.21; N 12.32.

[6-(Pyrrolidin-1-yl)-2-phenyl-4H-thieno[3,4-*d*]-1,2,3-triazol-2-ium-4-ylidene](4-chlorophenyl)methanolate (5d). Yield 94%; mp 220–221ºC. IR spectrum, ν, cm^{-1}: 1604 (CO). UV spectrum, λ_{max}, nm (log ε): 272 (6.44), 360 (6.14), 482 (6.07). ^1H NMR spectrum, δ, ppm (*J*, Hz): 1.82–1.93 (4H, m, $2CH_2$); 3.23–3.81 (4H, m, $2CH_2$); 7.21–7.58 (3H, m, Ar); 7.65 (2H, d, *J* = 8.4, Ar); 8.30 and 8.63 (4H, AA'XX', *J* = 8.0, Ar). Mass spectrum, *m/z* (I_{rel}, %): 408 $[M]^+$ (100). Found, %: C 61.53; H 4.02; N 13.81. $C_{21}H_{17}ClN_4OS$. Calculated, %: C 61.68; H 4.19; N 13.70.

[6-Piperidino-2-phenyl-4H-thieno[3,4-*d*]-1,2,3-triazol-2-ium-4-ylidene](4-chlorophenyl)methanolate (5e). Yield 52%; mp 198–199ºC. IR spectrum, ν, cm^{-1}: 1595 (CO), 2858, 2939 (C–H). UV spectrum, λ_{max}, nm (log ε): 272 (6.34), 370 (5.99), 523 (5.92). ^1H NMR spectrum, δ, ppm (*J*, Hz): 1.62–1.84 (6H, m, $3CH_2$); 3.57–3.71 (2H, m, CH_2); 3.96–3.99 (2H, m, CH_2); 7.45–7.60 (5H, m, Ar); 8.03 (1H, t, *J* = 8.8, Ar); 8.15–8.21 (3H, m, Ar). Mass spectrum, *m/z* (I_{rel}, %): 422 $[M]^+$ (100). Found, %: C 62.57; H 4.65; N 13.10. $C_{22}H_{19}ClN_4OS$. Calculated, %: C 62.48; H 4.53; N 13.25.

[(6-Morpholino)-2-phenyl-4H-thieno[3,4-*d*]-1,2,3-triazol-2-ium-4-ylidene](4-chlorophenyl)methanolate (5f). Yield 63%; mp 210–211ºC. IR spectrum, ν, cm^{-1}: 1589 (CO). UV spectrum, λ_{max}, nm (log ε): 280 (6.53), 360 (6.25), 540 (6.04). ^1H NMR spectrum, δ, ppm (*J*, Hz): 3.63–3.73 (2H, m, CH_2); 3.87–3.93 (6H, m, $3CH_2$); 7.43–7.58 (7H, m, Ar); 8.14 (2H, d, *J* = 8.4, Ar). Mass spectrum, *m/z* (I_{rel}, %): 424 $[M]^+$ (100). Found, %: C 59.15; H 4.12; N 13.34. $C_{21}H_{17}ClN_4O_2S$. Calculated, %: C 59.36; H 4.03; N 13.19.

[2-Phenyl-6-(4-phenylpiperazin-1-yl)-4H-thieno[3,4-*d*]-1,2,3-triazol-2-ium-4-ylidene](4-chlorophenyl)methanolate (5g). Yield 94%; mp 219–220ºC. IR spectrum, ν, cm^{-1}: 1589 (CO), 2854, 2943 (C–H). ^1H NMR spectrum, δ, ppm (*J*, Hz): 3.40–3.42 (2H, m, CH_2); 3.42–3.45 (2H, m, CH_2); 3.63–3.83 (2H, m, CH_2); 3.83–3.90 (2H, m, CH_2); 6.80–7.00 (4H, m, Ar); 7.20–7.28 (2H, m, Ar); 7.46–7.55 (6H, m, Ar); 8.17–8.22 (2H, m, Ar). Mass spectrum, *m/z* (I_{rel}, %): 499 $[M]^+$ (54). Found, %: C 64.87; H 4.75; N 14.15. $C_{27}H_{22}ClN_5OS$. Calculated, %: C 64.73; H 4.63; N 13.98.

[6-(Azepan-1-yl)-2-phenyl-4H-thieno[3,4-*d*]-1,2,3-triazol-2-ium-4-ylidene](4-chlorophenyl)methanolate (5h). Yield 53%; mp 230–231ºC. IR spectrum, ν, cm^{-1}: 1596 (CO), 2855, 2960 (C–H). ^1H NMR spectrum, δ, ppm (*J*, Hz): 1.47–1.49 (4H, m, $2CH_2$); 1.70–1.80 (4H, m, $2CH_2$); 3.42–3.60 (2H, m, CH_2); 4.09–4.22 (2H, m, CH_2); 7.46 (1H, t, *J* = 7.2, Ar); 7.53–7.60 (2H, m, Ar); 7.68 (2H, d, *J* = 8.4, Ar); 8.33 and 8.65 (4H, AA'XX', *J* = 8.0, Ar). Mass spectrum, *m/z* (I_{rel}, %): 436 $[M]^+$ (100). Found, %: C 63.35; H 4.73; N 13.02. $C_{23}H_{21}ClN_4OS$. Calculated, %: C 63.22; H 4.84; N 12.82.

This work was carried out with the financial support of the Russian Fund for Basic Research (RFFI 10-03-96084_p_урал-а).

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