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Synthesis of 2-Aryl-4-(R-sulfanylmethyl)-3-methyl-6,7-dihydro-2*H*-pyrazolo[3,4-*d*]pyridazin-7-ones

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Abstract—Bromination of ethyl 1-aryl-4-acetyl-5-methyl-1*H*-pyrazole-3-carboxylates gave ethyl 1-aryl-4-(bromoacetyl)-5-methyl-1*H*-pyrazol-3-carboxylates which were used to alkylate benzenethiol and heterocyclic thiones at the sulfur atom. Reactions of the resulting S-alkylation products with hydrazine or methylhydrazine involved closure of pyridazine ring to afford 2-aryl-3-methyl-4-[phenyl(or hetaryl)sulfanylmethyl]-6,7-dihydro-2*H*-pyrazolo[3,4-*d*]pyridazin-7-ones.

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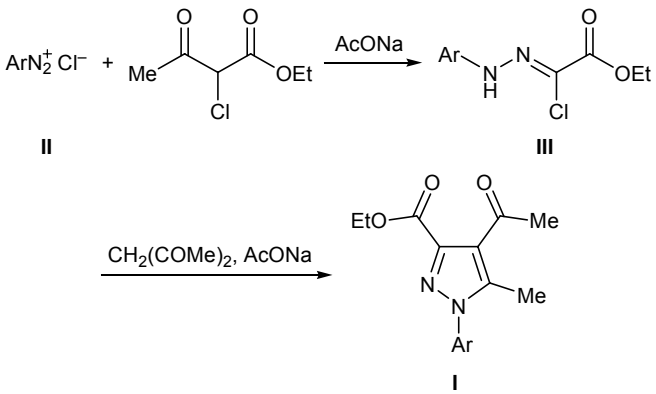
1-Arylpyrazoles having functional substituents at positions *3* and *4* attract interest as reagents for the synthesis of more complex heterocyclic assemblies, including fused heterocyclic systems [1–3], and design of new pharmacologically active agents [4–6], as well as electroluminescent materials [7]. We previously reported on effective procedure for the synthesis of ethyl 1-aryl-4-acetyl-5-methyl-1*H*-pyrazole-3-carboxylates **I** by reaction of arenediazonium salts **II** with ethyl 2-chloroacetoacetate (Japp–Klingemann reaction), followed by condensation of hydrazones **III** thus formed with acetylacetone (Scheme 1). It was also reported that compounds **I** react with hydrazine and its derivatives to give products in which pyridazine ring is fused at the *c* side of the pyrazole ring [2].

In the present article we report on the synthesis of previously unknown pyrazole derivatives, 2-aryl-4-(R-sulfanylmethyl)-3-methyl-6,7-dihydro-2*H*-pyrazolo[3,4-*d*]pyridazin-7-ones. For this purpose, in the first step pyrazoles **Ia**–**Ie** were subjected to bromination of at the acetyl fragment on C^4. The optimal bromination procedure was treatment of solutions of **Ia**–**Ie** in acetic acid with bromine in the presence of a catalytic amount of sulfuric acid. We thus obtained ethyl 1-aryl-4-(bromoacetyl)-5-methyl-1*H*-pyrazole-3-carboxylates **IVa**–**IVe** (Scheme 2).

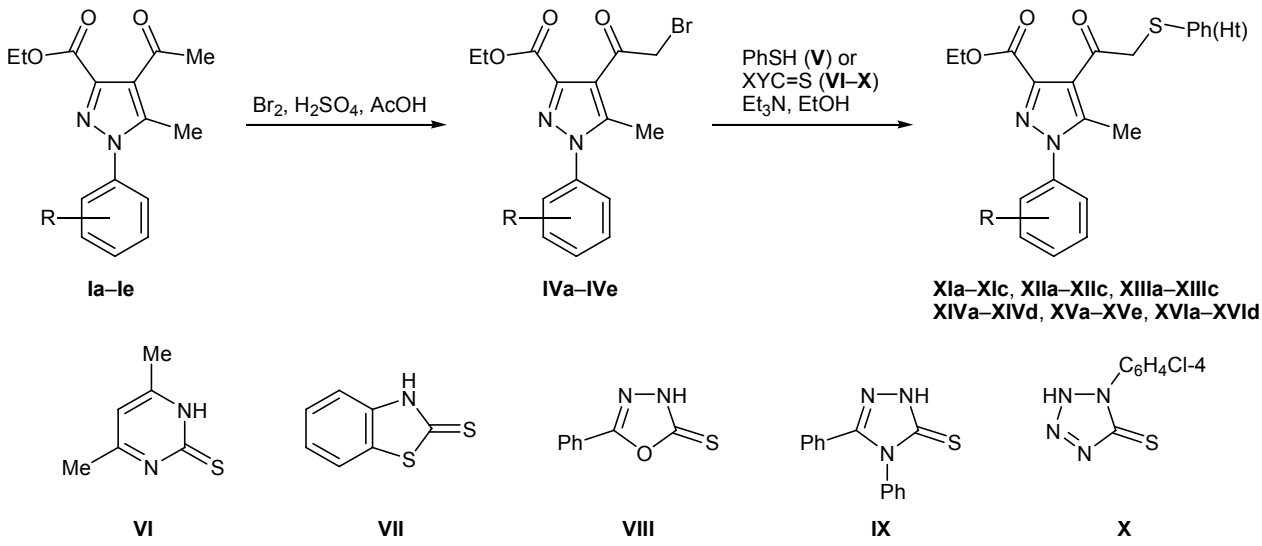
Scheme 1.



α-Halo ketones are convenient reagents for the alkylation of various nucleophiles [8]. Such transformations of bromo ketones **IV** could give rise to many polyfunctional 1-arylpyrazole derivatives. We used compounds **IVa**–**IVe** to perform S-alkylation of benzenethiol (**V**) and various heterocyclic thiones **VI**–**X**. The reactions were carried out by heating the reactants in ethanol in the presence of triethylamine. As a result, the corresponding 4-[phenyl(hetaryl)sulfanylacetyl]-pyrazoles **XI**–**XVI** were isolated (Scheme 2). Ethyl 1-aryl-5-methyl-4-(R-sulfanylacetyl)-1*H*-pyrazole-3-carboxylates **XI**–**XVI** are polyfunctionalized compounds and are therefore convenient building blocks for the design of fused heterocyclic systems. By reaction of compounds **XI**–**XVI** with hydrazine or methylhydrazine we obtained previously unknown pyrazolo-[3,4-*d*]pyridazin-7-ones **XVII**–**XXVII** (Scheme 3).

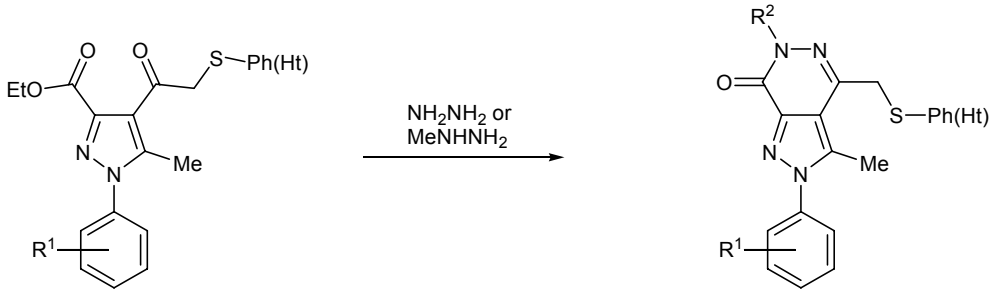
To conclude, we have developed an efficient procedure for the synthesis of functionally substituted 2-aryl-6,7-dihydro-2*H*-pyrazolo[3,4-*d*]pyridazin-7-ones.

Scheme 2.



I, **IV**, R = 2-Cl (**a**), 3-Cl (**b**), 4-Cl (**c**), 2,4-Cl_2 (**d**), 2,5-Cl_2 (**e**); **XI**, Ph, R = 3-Cl (**a**), 4-Cl (**b**), 2,5-Cl_2 (**c**); **XII**, Ht = 4,6-dimethylpyrimidin-2-yl, R = 2-Cl (**a**), 4-Cl (**b**), 2,5-Cl_2 (**c**); **XIII**, Ht = 1,3-benzothiazol-2-yl, R = 4-Cl (**a**), 2,4-Cl_2 (**b**), 2,5-Cl_2 (**c**); **XIV**, Ht = 5-phenyl-1,3,4-oxadiazol-2-yl, R = 3-Cl (**a**), 4-Cl (**b**), 2,4-Cl_2 (**c**), 2,5-Cl_2 (**d**); **XV**, Ht = 4,5-diphenyl-4*H*-1,2,4-triazol-3-yl, R = 2-Cl (**a**), 3-Cl (**b**), 4-Cl (**c**), 2,4-Cl_2 (**d**), 2,5-Cl_2 (**e**); **XVI**, Ht = 1-(4-chlorophenyl)-1*H*-tetrazol-5-yl, R = 2-Cl (**a**), 4-Cl (**b**), 2,4-Cl_2 (**c**), 2,5-Cl_2 (**d**).

Scheme 3.



XVII, Ph, R = 2-Cl (**a**), 4-Cl (**b**), 2,5-Cl_2 (**c**); **XVIII**, Ht = 4,6-dimethylpyrimidin-2-yl, R = 2-Cl (**a**), 4-Cl (**b**), 2,5-Cl_2 (**c**); **XIX**, Ht = 1,3-benzothiazol-2-yl, R = 2,4-Cl_2 (**a**), 2,5-Cl_2 (**b**); **XX**, Ht = 5-phenyl-1,3,4-oxadiazol-2-yl, R = 3-Cl (**a**), 4-Cl (**b**), 2,4-Cl_2 (**c**), 2,5-Cl_2 (**d**); **XXI**, Ht = 4,5-diphenyl-4*H*-1,2,4-triazol-3-yl, R = 2-Cl (**a**), 3-Cl (**b**), 4-Cl (**c**), 2,4-Cl_2 (**d**), 2,5-Cl_2 (**e**); **XXII**, Ht = 1-(4-chlorophenyl)-1*H*-tetrazol-5-yl, R = 2-Cl (**a**), 2,4-Cl_2 (**b**), 2,5-Cl_2 (**c**); **XXIII**, Ph, R^1 = 2,5-Cl_2, R^2 = Me; **XXIV**, Ht = 4,6-dimethylpyrimidin-2-yl, R^1 = 2-Cl (**a**), 4-Cl (**b**), R^2 = Me; **XXV**, Ht = 1,3-benzothiazol-2-yl, R^1 = 4-Cl, R^2 = Me; **XXVI**, Ht = 4,5-diphenyl-4*H*-1,2,4-triazol-3-yl, R^1 = 2,4-Cl_2 (**a**), 2,5-Cl_2 (**b**), R^2 = Me; **XXVII**, Ht = 1-(4-chlorophenyl)-1*H*-tetrazol-5-yl, R^1 = 4-Cl (**a**), 2,4-Cl_2 (**b**), R^2 = Me.

EXPERIMENTAL

The ^{1}H NMR spectra were recorded on Varian Mercury spectrometers operating at 200 and 400 MHz; the chemical shifts were measured relative to tetramethylsilane as internal reference.

Ethyl 1-aryl-4-acetyl-5-methyl-1*H*-pyrazol-3-carboxylates **Ia**–**Ic** and the procedure for their synthesis were reported previously [2]. Compounds **Id** and **Ie** were synthesized in a similar way.

Ethyl 4-acetyl-1-(2,4-dichlorophenyl)-5-methyl-1*H*-pyrazole-3-carboxylate (Id). Yield 89%, mp 92°C. ^{1}H NMR spectrum (200 MHz, $CDCl_3$), δ, ppm: 1.42 t (3H, CH_3, J = 7.2 Hz), 2.29 s (3H, CH_3), 2.61 s (3H, CH_3), 4.46 q (2H, CH_2O, J = 7.2 Hz), 7.35 d (1H, H_{arom}, ^3J = 8.6 Hz), 7.43 d.d (1H, H_{arom}, ^3J = 8.6, ^4J =

2.0 Hz), 7.35 d (1H, H_{arom}, ^4J = 2.0 Hz). Found, %: C 52.62; H 4.03; N 8.27. $C_{15}H_{14}Cl_2N_2O_3$. Calculated, %: C 52.80; H 4.14; N 8.21.

Ethyl 4-acetyl-1-(2,5-dichlorophenyl)-5-methyl-1*H*-pyrazole-3-carboxylate (Ie). Yield 85%, mp 110°C. ^{1}H NMR spectrum (200 Hz, $CDCl_3$), δ, ppm: 1.43 t (3H, CH_3, J = 7.2 Hz), 2.31 s (3H, CH_3), 2.62 s (3H, CH_3), 4.46 q (2H, CH_2O, J = 7.2 Hz), 7.43–7.53 m (3H, H_{arom}). Found, %: C 52.73; H 4.26; N 8.05. $C_{15}H_{14}Cl_2N_2O_3$. Calculated, %: C 52.80; H 4.14; N 8.21.

Ethyl 1-aryl-4-(bromoacetyl)-5-methyl-1*H*-pyrazole-3-carboxylates IVa–IVe (*general procedure*). Concentrated sulfuric acid, 2–3 drops, was added to a solution of 30 mmol **of** acetylpyrazole **Ia–Ie** in 80 ml of glacial acetic acid, a solution of 1.55 ml (30 mmol) of bromine in 20 ml of glacial acetic acid was slowly added dropwise, and the mixture was stirred for 7 h and poured into 500 ml of water. The precipitate was filtered off, dried, and recrystallized from ethanol.

Ethyl 4-(bromoacetyl)-1-(2-chlorophenyl)-5-methyl-1*H*-pyrazole-3-carboxylate (IVa). Yield 81%, mp 59°C. ^{1}H NMR spectrum (400 Hz, DMSO-d_6), δ, ppm: 1.38 t (3H, CH_3, J = 7.2 Hz), 2.24 s (3H, CH_3), 4.37 q (2H, CH_2O, J = 7.2 Hz), 4.63 s (2H, CH_2Br), 7.55–7.72 m (4H, H_{arom}). Found, %: C 46.47; H 3.60; N 7.32. $C_{15}H_{14}BrClN_2O_3$. Calculated, %: C 46.72; H 3.66; N 7.26.

Ethyl 4-(bromoacetyl)-1-(3-chlorophenyl)-5-methyl-1*H*-pyrazole-3-carboxylate (IVb). Yield 93%, mp 104°C. ^{1}H NMR spectrum (400Hz, DMSO-d_6), δ, ppm: 1.39 t (3H, CH_3, J = 7.2 Hz), 2.43 s (3H, CH_3), 4.38 q (2H, CH_2O, J = 7.2 Hz), 4.60 s (2H, CH_2Br), 7.53–7.69 m (4H, H_{arom}). Found, %: C 46.80; H 3.78; N 7.07. $C_{15}H_{14}BrClN_2O_3$. Calculated, %: C 46.72; H 3.66; N 7.26.

Ethyl 4-(bromoacetyl)-1-(4-chlorophenyl)-5-methyl-1*H*-pyrazole-3-carboxylate (IVc). Yield 95%, mp 138°C. ^{1}H NMR spectrum (400 Hz, DMSO-d_6), δ, ppm: 1.38 t (3H, CH_3, J = 7.2 Hz), 2.41 s (3H, CH_3), 4.38 q (2H, CH_2O, J = 7.2 Hz), 4.60 s (2H, CH_2Br), 7.60 s (4H, H_{arom}). Found, %: C 46.33; H 3.72; N 7.34. $C_{15}H_{14}BrClN_2O_3$. Calculated, %: C 46.72; H 3.66; N 7.26.

Ethyl 4-(bromoacetyl)-1-(2,4-dichlorophenyl)-5-methyl-1*H*-pyrazole-3-carboxylate (IVd). Yield 77%, mp 77°C. ^{1}H NMR spectrum (200 Hz, $CDCl_3$), δ, ppm: 1.43 t (3H, CH_3, J = 7.2 Hz), 2.22 s (3H, CH_3), 4.40 s (2H, CH_2Br), 4.45 q (2H, CH_2O, J = 7.2 Hz), 7.12–7.48 m (3H, H_{arom}). Found, %: C 42.72; H 3.24; N 6.54. $C_{15}H_{13}BrCl_2N_2O_3$. Calculated, %: C 42.89; H 3.12; N 6.67.

Ethyl 4-(bromoacetyl)-1-(2,5-dichlorophenyl)-5-methyl-1*H*-pyrazole-3-carboxylate (IVe). Yield 78%, mp 99°C. ^{1}H NMR spectrum (200 Hz, $CDCl_3$), δ, ppm: 1.44 t (3H, CH_3, J = 7.2 Hz), 2.32 s (3H, CH_3), 4.48 q (2H, CH_2O, J = 7.2 Hz), 4.61 s (2H, CH_2Br), 7.48–7.52 m (3H, H_{arom}). Found, %: C 42.96; H 3.19; N 6.45. $C_{15}H_{13}BrCl_2N_2O_3$. Calculated, %: C 42.89; H 3.12; N 6.67.

S-Alkylation of benzenethiol (V) and heterocyclic thiones V–X with 4-(bromoacetyl)pyrazoles IVa–IVe (*general procedure*). Triethylamine, 1.16 ml (8.25 mmol), was added to a solution of 7.5 mmol of compound **V–X** in 5 ml of ethanol, the mixture was stirred for 0.5 h, a solution of 7.5 mmol of bromoacetylpyrazole **IVa–IVe** in 30 ml of ethanol was added, and the mixture was heated for 3 h under reflux. After cooling, the mixture was diluted with 40 ml of water, and the precipitate was filtered off, dried, and recrystallized from ethanol.

Ethyl 1-(3-chlorophenyl)-5-methyl-4-(2-phenylsulfanyl-1-oxoethyl)-1*H*-pyrazole-3-carboxylate (XIa). Yield 78%, oily substance. ^{1}H NMR spectrum (200 Hz, DMSO-d_6), δ, ppm: 1.42 t (3H, CH_3, J = 7.2 Hz), 2.29 s (3H, CH_3), 4.45 q (2H, CH_2O, J = 7.2 Hz), 4.55 s (2H, CH_2S), 7.25–7.49 m (5H, H_{arom}), 7.53–7.64 m (4H, H_{arom}). Found, %: C 60.54; H 4.69; N 6.57. $C_{21}H_{19}ClN_2O_3S$. Calculated, %: C 60.79; H 4.62; N 6.75.

Ethyl 1-(4-chlorophenyl)-5-methyl-4-(2-phenylsulfanyl-1-oxoethyl)-1*H*-pyrazole-3-carboxylate (XIb). Yield 86%, oily substance. ^{1}H NMR spectrum (200 MHz, DMSO-d_6), δ, ppm: 1.43 t (3H, CH_3, J = 7.2 Hz), 2.31 s (3H, CH_3), 4.47 q (2H, CH_2O, J = 7.2 Hz), 4.58 s (2H, CH_2S), 7.35 t (1H, Ph, J = 7.6 Hz), 7.43 t (2H, Ph, J = 7.6 Hz), 7.48 d (2H, Ph, J = 7.6 Hz), 7.60 d (2H, C_6H_4, J = 8.0 Hz), 7.65 d (2H, C_6H_4, J = 8.0 Hz). Found, %: C 60.61; H 4.47; N 6.69. $C_{21}H_{19}ClN_2O_3S$. Calculated, %: C 60.79; H 4.62; N 6.75.

Ethyl 1-(2,5-dichlorophenyl)-5-methyl-4-(2-phenylsulfanyl-1-oxoethyl)-1*H*-pyrazole-3-carboxylate (XIc). Yield 75%, mp 97°C. ^{1}H NMR spectrum (200 MHz, $CDCl_3$), δ, ppm: 1.43 t (3H, C**H**$_3$CH$_2$, J = 7.2 Hz), 2.30 s (3H, CH_3), 4.47 q (2H, CH_2O, J = 7.2 Hz), 4.60 s (2H, CH_2S), 7.35–7.49 m (6H, H_{arom}), 7.57–7.63 m (2H, H_{arom}). Found, %: C 56.08; H 4.27; N 6.09. $C_{21}H_{18}Cl_2N_2O_3S$. Calculated, %: C 56.13; H 4.04; N 6.23.

Ethyl 1-(2-chlorophenyl)-4-[2-(4,6-dimethylpyrimidin-2-ylsulfanyl)-1-oxoethyl]-5-methyl-1*H*-pyrazole-3-carboxylate (XIIa). Yield 67%, mp 48°C. ^{1}H NMR spectrum (400 Hz, DMSO-d_6), δ, ppm: 1.37 t (3H, C**H**$_3$CH$_2$, J = 7.2 Hz), 2.29 s (6H, CH$_3$), 2.31 s (3H, CH$_3$), 4.35 s (2H, CH$_2$S), 4.37 q (2H, CH$_2$O, J = 7.2 Hz), 6.83 s (1H, 5′-H), 7.55–7.71 m (4H, H$_{arom}$). Found, %: C 56.55; H 4.49; N 12.52. $C_{21}H_{21}ClN_4O_3S$. Calculated, %: C 56.69; H 4.76; N 12.59.

Ethyl 1-(4-chlorophenyl)-4-[2-(4,6-dimethylpyrimidin-2-ylsulfanyl)-1-oxoethyl]-5-methyl-1*H*-pyrazole-3-carboxylate (XIIb). Yield 82%, mp 74°C. ^{1}H NMR spectrum (400 Hz, DMSO-d_6), δ, ppm: 1.39 t (3H, C**H**$_3$CH$_2$, J = 7.2 Hz), 2.28 s (6H, CH$_3$), 2.33 s (3H, CH$_3$), 4.36 s (2H, CH$_2$S), 4.37 q (2H, CH$_2$O, J = 7.2 Hz), 6.83 s (1H, 5′-H), 7.56 br.s (4H, H$_{arom}$). Found, %: C 56.52; H 4.85; N 12.70. $C_{21}H_{21}ClN_4O_3S$. Calculated, %: C 56.69; H 4.76; N 12.59.

Ethyl 1-(2,5-dichlorophenyl)-4-[2-(4,6-dimethylpyrimidin-2-ylsulfanyl)-1-oxoethyl]-5-methyl-1*H*-pyrazole-3-carboxylate (XIIc). Yield 75%, oily substance. ^{1}H NMR spectrum (400 Hz, DMSO-d_6), δ, ppm: 1.39 t (3H, C**H**$_3$CH$_2$, J = 7.2 Hz), 2.32 s (6H, CH$_3$), 2.34 s (3H, CH$_3$), 4.35 s (2H, CH$_2$S), 4.38 q (2H, CH$_2$O, J = 7.2 Hz), 6.87 s (1H, 5′-H), 7.67–7.90 m (3H, H$_{arom}$). Found, %: C 52.74; H 4.30; N 11.53. $C_{21}H_{20}Cl_2N_4O_3S$. Calculated, %: C 52.61; H 4.21; N 11.69.

Ethyl 4-[2-(1,3-benzothiazol-2-ylsulfanyl)-1-oxoethyl]-1-(4-chlorophenyl)-5-methyl-1*H*-pyrazole-3-carboxylate (XIIIa). Yield 73%, mp 69°C. ^{1}H NMR spectrum (200 Hz, CDCl$_3$), δ, ppm: 1.45 t (3H, C**H**$_3$CH$_2$, J = 7.2 Hz), 2.32 s (3H, CH$_3$), 4.49 q (2H, CH$_2$O, J = 7.2 Hz), 4.76 s (2H, CH$_2$S), 7.18–7.58 m (6H, H$_{arom}$), 7.64–7.85 m (2H, H$_{arom}$). Found, %: C 55.74; H 3.76; N 8.98. $C_{22}H_{18}ClN_3O_3S_2$. Calculated, %: C 55.98; H 3.84; N 8.90.

Ethyl 4-[2-(1,3-benzothiazol-2-ylsulfanyl)-1-oxoethyl]-1-(2,4-dichlorophenyl)-5-methyl-1*H*-pyrazole-3-carboxylate (XIIIb). Yield 82%, mp 83°C. ^{1}H NMR spectrum (200 Hz, CDCl$_3$), δ, ppm: 1.46 t (3H, C**H**$_3$CH$_2$, J = 7.2 Hz), 2.16 s (3H, CH$_3$), 4.50 q (2H, CH$_2$O, J = 7.2 Hz), 4.74 s (2H, CH$_2$S), 7.22–7.56 m (5H, H$_{arom}$), 7.69–7.81 m (2H, H$_{arom}$). Found, %: C 52.02; H 3.27; N 8.54. $C_{22}H_{17}Cl_2N_3O_3S_2$. Calculated, %: C 52.18; H 3.38; N 8.30.

Ethyl 4-[2-(1,3-benzothiazol-2-ylsulfanyl)-1-oxoethyl]-1-(2,5-dichlorophenyl)-5-methyl-1*H*-pyrazole-3-carboxylate (XIIIc). Yield 90%, mp 104°C. ^{1}H NMR spectrum (200 Hz, CDCl$_3$), δ, ppm: 1.46 t (3H, C**H**$_3$CH$_2$, J = 7.2 Hz), 2.18 s (3H, CH$_3$), 4.50 q (2H, CH$_2$O, J = 7.2 Hz), 4.75 s (2H, CH$_2$S), 7.21–7.44 m (5H, H$_{arom}$), 7.69–7.79 m (2H, H$_{arom}$). Found, %: C 52.34; H 3.25; N 8.34. $C_{22}H_{17}Cl_2N_3O_3S_2$. Calculated, %: C 52.18; H 3.38; N 8.30.

Ethyl 1-(3-chlorophenyl)-5-methyl-4-[1-oxo-2-(5-phenyl-1,3,4-oxadiazol-2-ylsulfanyl)ethyl]-1*H*-pyrazole-3-carboxylate (XIVa). Yield 83%, mp 103°C. ^{1}H NMR spectrum (200 Hz, CDCl$_3$), δ, ppm: 1.45 t (3H, C**H**$_3$CH$_2$, J = 7.2 Hz), 2.33 s (3H, CH$_3$), 4.49 q (2H, CH$_2$O, J = 7.2 Hz), 4.82 s (2H, CH$_2$S), 7.29–7.58 m (7H, H$_{arom}$), 7.94–8.06 m (2H, H$_{arom}$). Found, %: C 57.11; H 3.85; N 11.54. $C_{23}H_{19}ClN_4O_4S$. Calculated, %: C 57.20; H 3.97; N 11.60.

Ethyl 1-(4-chlorophenyl)-5-methyl-4-[1-oxo-2-(5-phenyl-1,3,4-oxadiazol-2-ylsulfanyl)ethyl]-1*H*-pyrazole-3-carboxylate (XIVb). Yield 88%, mp 127°C. ^{1}H NMR spectrum (200 Hz, CDCl$_3$), δ, ppm: 1.42 t (3H, C**H**$_3$CH$_2$, J = 7.2 Hz), 2.31 s (3H, CH$_3$), 4.45 q (2H, CH$_2$O, J = 7.2 Hz), 4.80 s (2H, CH$_2$S), 7.45–7.71 m (7H, H$_{arom}$), 7.86–7.91 m (2H, H$_{arom}$). Found, %: C 57.45; H 3.98; N 11.63. $C_{23}H_{19}ClN_4O_4S$. Calculated, %: C 57.20; H 3.97; N 11.60.

Ethyl 1-(2,4-dichlorophenyl)-5-methyl-4-[1-oxo-2-(5-phenyl-1,3,4-oxadiazol-2-ylsulfanyl)ethyl]-1*H*-pyrazole-3-carboxylate (XIVc). Yield 83%, mp 121°C. ^{1}H NMR spectrum (200 Hz, CDCl$_3$), δ, ppm: 1.44 t (3H, C**H**$_3$CH$_2$, J = 7.2 Hz), 2.27 s (3H, CH$_3$), 4.48 q (2H, CH$_2$O, J = 7.2 Hz), 4.83 s (2H, CH$_2$S), 7.33–7.59 m (6H, H$_{arom}$), 7.95–8.06 m (2H, H$_{arom}$). Found, %: C 53.32; H 3.48; N 10.79. $C_{23}H_{18}Cl_2N_4O_4S$. Calculated, %: C 53.39; H 3.51; N 10.83.

Ethyl 1-(2,5-dichlorophenyl)-5-methyl-4-[1-oxo-2-(5-phenyl-1,3,4-oxadiazol-2-ylsulfanyl)ethyl]-1*H*-pyrazole-3-carboxylate (XIVd). Yield 72%, mp 139°C. ^{1}H NMR spectrum (200 Hz, CDCl$_3$), δ, ppm: 1.45 t (3H, C**H**$_3$CH$_2$, J = 7.2 Hz), 2.29 s (3H, CH$_3$), 4.49 q (2H, CH$_2$O, J = 7.2 Hz), 4.83 s (2H, CH$_2$S), 7.42–7.58 m (6H, H$_{arom}$), 7.94–8.03 m (2H, H$_{arom}$). Found, %: C 53.45; H 3.63; N 10.70. $C_{23}H_{18}Cl_2N_4O_4S$. Calculated, %: C 53.39; H 3.51; N 10.83.

Ethyl 1-(2-chlorophenyl)-4-[2-(4,5-diphenyl-4*H*-1,2,4-triazol-3-ylsulfanyl)-1-oxoethyl]-5-methyl-1*H*-pyrazole-3-carboxylate (XVa). Yield 60%, mp 188°C. ^{1}H NMR spectrum (400 Hz, DMSO-d_6), δ, ppm: 1.36 t (3H, C**H**$_3$CH$_2$, J = 7.2 Hz), 2.22 s (3H, CH$_3$), 4.36 q (2H, CH$_2$O, J = 7.2 Hz), 4.58 s (2H, CH$_2$S), 7.27–7.38 m (7H, H$_{arom}$), 7.54–7.69 m (7H, H$_{arom}$). Found,

%: C 62.49; H 4.15; N 12.67. $C_{29}H_{24}ClN_5O_3S$. Calculated, %: C 62.42; H 4.33; N 12.55.

Ethyl 1-(3-chlorophenyl)-4-[2-(4,5-diphenyl-4*H*-1,2,4-triazol-3-ylsulfanyl)-1-oxoethyl]-5-methyl-1*H*-pyrazole-3-carboxylate (XVb). Yield 63%, mp 163°C. ^{1}H NMR spectrum (200 Hz, DMSO-d_6), δ, ppm: 1.29 t (3H, C**H**$_3$CH$_2$, J = 7.0 Hz), 2.39 s (3H, CH$_3$), 4.35 q (2H, CH$_2$O, J = 7.0 Hz), 4.66 s (2H, CH$_2$S), 7.27–7.44 m (7H, H$_{arom}$), 7.50–7.76 m (7H, H$_{arom}$). Found, %: C 62.49; H 4.35; N 12.49. $C_{29}H_{24}ClN_5O_3S$. Calculated, %: C 62.42; H 4.33; N 12.55.

Ethyl 1-(4-chlorophenyl)-4-[2-(4,5-diphenyl-4*H*-1,2,4-triazol-3-ylsulfanyl)-1-oxoethyl]-5-methyl-1*H*-pyrazole-3-carboxylate (XVc). Yield 67%, mp 175–176°C. ^{1}H NMR spectrum (400 Hz, DMSO-d_6), δ, ppm: 1.36 t (3H, C**H**$_3$CH$_2$, J = 7.2 Hz), 2.41 s (3H, CH$_3$), 4.37 q (2H, CH$_2$O, J = 7.2 Hz), 4.59 s (2H, CH$_2$S), 7.26–7.36 m (7H, H$_{arom}$), 7.53–7.60 m (7H, H$_{arom}$). Found, %: C 62.26; H 4.30; N 12.43. $C_{29}H_{24}ClN_5O_3S$. Calculated, %: C 62.42; H 4.33; N 12.55.

Ethyl 1-(2,4-dichlorophenyl)-4-[2-(4,5-diphenyl-4*H*-1,2,4-triazol-3-ylsulfanyl)-1-oxoethyl]-5-methyl-1*H*-pyrazole-3-carboxylate (XVd). Yield 63%, mp 216°C. ^{1}H NMR spectrum (200 Hz, DMSO-d_6), δ, ppm: 1.28 t (3H, C**H**$_3$CH$_2$, J = 7.2 Hz), 2.20 s (3H, CH$_3$), 4.33 q (2H, CH$_2$O, J = 7.2 Hz), 4.64 s (2H, CH$_2$S), 7.23–7.62 m (10H, H$_{arom}$), 7.65–7.77 m (2H, H$_{arom}$), 8.00 d (1H, H$_{arom}$, J = 1.4 Hz). Found, %: C 58.69; H 3.78; N 11.97. $C_{29}H_{23}Cl_2N_5O_3S$. Calculated, %: C 58.79; H 3.91; N 11.82.

Ethyl 1-(2,5-dichlorophenyl)-4-[2-(4,5-diphenyl-4*H*-1,2,4-triazol-3-ylsulfanyl)-1-oxoethyl]-5-methyl-1*H*-pyrazole-3-carboxylate (XVe). Yield 68%, mp 191°C. ^{1}H NMR spectrum (200 Hz, DMSO-d_6), δ, ppm: 1.28 t (3H, C**H**$_3$CH$_2$, J = 7.2 Hz), 2.22 s (3H, CH$_3$), 4.33 q (2H, CH$_2$O, J = 7.2 Hz), 4.63 s (2H, CH$_2$S), 7.16–7.93 m (13H, H$_{arom}$). Found, %: C 58.57; H 3.80; N 11.74. $C_{29}H_{23}Cl_2N_5O_3S$. Calculated, %: C 58.79; H 3.91; N 11.82.

Ethyl 1-(2-chlorophenyl)-4-{2-[1-(4-chlorophenyl)-1*H*-tetrazol-5-ylsulfanyl]-1-oxoethyl}-5-methyl-1*H*-pyrazole-3-carboxylate (XVIa). Yield 73%, mp 124°C. ^{1}H NMR spectrum (200 Hz, $CDCl_3$), δ, ppm: 1.43 t (3H, C**H**$_3$CH$_2$, J = 7.2 Hz), 2.27 s (3H, CH$_3$), 4.48 q (2H, CH$_2$O, J = 7.2 Hz), 4.96 s (2H, CH$_2$S), 7.40–7.63 m (8H, H$_{arom}$). Found, %: C 51.14; H 3.73; N 16.17. $C_{22}H_{18}Cl_2N_6O_3S$. Calculated, %: C 51.07; H 3.51; N 16.24.

Ethyl 5-methyl-1-(4-chlorophenyl)-4-{2-[1-(4-chlorophenyl)-1*H*-tetrazol-5-ylsulfanyl]-1-oxoethyl}-1*H*-pyrazole-3-carboxylate (XVIb). Yield 76%, mp 108°C. ^{1}H NMR spectrum (200 Hz, DMSO-d_6), δ, ppm: 1.31 t (3H, C**H**$_3$CH$_2$, J = 7.2 Hz), 2.37 s (3H, CH$_3$), 4.36 q (2H, CH$_2$O, J = 7.2 Hz), 4.94 s (2H, CH$_2$S), 7.45–7.83 m (8H, H$_{arom}$). Found, %: C 50.80; H 3.44; N 16.35. $C_{22}H_{18}Cl_2N_6O_3S$. Calculated, %: C 51.07; H 3.51; N 16.24.

Ethyl 4-{2-[1-(4-chlorophenyl)-1*H*-tetrazol-5-ylsulfanyl]-1-oxoethyl}-1-(2,4-dichlorophenyl)-5-methyl-1*H*-pyrazole-3-carboxylate (XVIc). Yield 67%, mp 158°C. ^{1}H NMR spectrum (200 Hz, DMSO-d_6), δ, ppm: 1.30 t (3H, C**H**$_3$CH$_2$, J = 7.0 Hz), 2.21 s (3H, CH$_3$), 4.35 q (2H, CH$_2$O, J = 7.0 Hz), 4.93 s (2H, CH$_2$S), 7.66–7.83 m (6H, H$_{arom}$), 8.02 d (1H, H$_{arom}$, ^4J = 2.0 Hz). Found, %: C 47.79; H 3.23; N 15.45. $C_{22}H_{17}Cl_3N_6O_3S$. Calculated, %: C 47.88; H 3.11; N 15.23.

Ethyl 4-{2-[1-(4-chlorophenyl)-1*H*-tetrazol-5-ylsulfanyl]-1-oxoethyl}-1-(2,5-dichlorophenyl)-5-methyl-1*H*-pyrazole-3-carboxylate (XVId). Yield 78%, mp 117°C. ^{1}H NMR spectrum (200 Hz, DMSO-d_6), δ, ppm: 1.30 t (3H, C**H**$_3$CH$_2$, J = 7.0 Hz), 2.23 s (3H, CH$_3$), 4.36 q (2H, CH$_2$O, J = 7.0 Hz), 4.93 s (2H, CH$_2$S), 7.56–7.87 m (6H, H$_{arom}$), 7.95 d (1H, H$_{arom}$, ^4J = 1.8 Hz). Found, %: C 47.71; H 3.02; N 15.10. $C_{22}H_{17}Cl_3N_6O_3S$. Calculated, %: C 47.88; H 3.11; N 15.23.

Pyrazolo[3,4-*d*]pyridazin-7-ones XVII–XXVII (*general procedure*). A mixture of 0.01 mol of pyrazole **XI–XVI** dissolved in 20 ml of ethanol and 1.46 ml (0.03 mol) of hydrazine hydrate or 0.80 ml (0.015 mol) of methylhydrazine was heated for 5 h under reflux. The mixture was cooled, and the precipitate was filtered off, dried, and recrystallized from dimethylformamide.

2-(3-Chlorophenyl)-3-methyl-4-(phenylsulfanylmethyl)-6,7-dihydro-2*H*-pyrazolo[3,4-*d*]pyridazin-7-one (XVIIa). Yield 66%, mp 202°C. ^{1}H NMR spectrum (200 Hz, DMSO-d_6), δ, ppm: 2.69 s (3H, CH$_3$), 4.42 s (2H, CH$_2$S), 7.18–7.47 m (5H, H$_{arom}$), 7.64–7.76 m (3H, H$_{arom}$), 7.84 d (1H, H$_{arom}$, ^4J = 1.2 Hz), 12.22 s (1H, NH). Found, %: C 59.51; H 3.82; N 14.74. $C_{19}H_{15}ClN_4OS$. Calculated, %: C 59.60; H 3.95; N 14.63.

2-(4-Chlorophenyl)-3-methyl-4-(phenylsulfanylmethyl)-6,7-dihydro-2*H*-pyrazolo[3,4-*d*]pyridazin-7-one (XVIIb). Yield 70%, mp 277°C. ^{1}H NMR spec-

trum (400 Hz, DMSO-d_6), δ, ppm: 2.70 s (3H, CH_3), 4.32 s (2H, CH_2S), 7.20 t (1H, Ph, J = 7.6 Hz), 7.29 t (2H, Ph, J = 7.6 Hz), 7.38 d (2H, Ph, J = 7.6 Hz), 7.62 d (2H, C_6H_4, J = 8.4 Hz), 7.66 d (2H, C_6H_4, J = 8.4 Hz), 12.05 s (1H, NH). Found, %: C 59.78; H 3.90; N 14.71. $C_{19}H_{15}ClN_4OS$. Calculated, %: C 59.60; H 3.95; N 14.63.

2-(2,5-Dichlorophenyl)-3-methyl-4-(phenylsulfanylmethyl)-6,7-dihydro-2*H*-pyrazolo[3,4-*d*]pyridazin-7-one (XVIIc). Yield 70%, mp 249°C. ^{1}H NMR spectrum (200 Hz, DMSO-d_6), δ, ppm: 2.53 s (3H, CH_3), 4.44 s (2H, CH_2S), 7.17–7.46 m (5H, H_{arom}), 7.77–7.92 m (2H, H_{arom}), 8.03 br.s (1H, H_{arom}), 12.24 s (1H, NH). Found, %: C 54.96; H 3.47; N 13.38. $C_{19}H_{14}Cl_2N_4OS$. Calculated, %: C 54.68; H 3.38; N 13.43.

2-(2-Chlorophenyl)-4-(4,6-dimethylpymiridin-2-ylsulfanylmethyl)-3-methyl-6,7-dihydro-2*H*-pyrazolo[3,4-*d*]pyridazin-7-one (XVIIIa). Yield 55%, mp 246–247°C. ^{1}H NMR spectrum (400 Hz, DMSO-d_6), δ, ppm: 2.38 s (6H, CH_3), 2.47 s (3H, CH_3), 4.61 s (2H, CH_2S), 6.90 s (1H, 5′-H), 7.59–7.76 m (4H, H_{arom}), 12.23 s (1H, NH). Found, %: C 55.19; H 4.01; N 20.18. $C_{19}H_{17}ClN_6OS$. Calculated, %: C 55.27; H 4.15; N 20.35.

2-(4-Chlorophenyl)-4-(4,6-dimethylpymiridin-2-ylsulfanylmethyl)-3-methyl-6,7-dihydro-2*H*-pyrazolo[3,4-*d*]pyridazin-7-one (XVIIIb). Yield 60%, mp 279°C. ^{1}H NMR spectrum (400 Hz, DMSO-d_6), δ, ppm: 2.39 s (6H, CH_3), 2.65 s (3H, CH_3), 4.60 s (2H, CH_2S), 6.90 s (1H, 5′-H), 7.61 d (2H, H_{arom}, J = 8.8 Hz), 7.65 d (2H, H_{arom}, J = 8.8 Hz), 12.17 s (1H, NH). Found, %: C 55.55; H 4.03; N 20.48. $C_{19}H_{17}ClN_6OS$. Calculated, %: C 55.27; H 4.15; N 20.35.

2-(2,5-Dichlorophenyl)-4-(4,6-dimethylpyrimidin-2-ylsulfanylmethyl)-3-methyl-6,7-dihydro-2*H*-pyrazolo[3,4-*d*]pyridazin-7-one (XVIIIc). Yield 67%, mp 245°C. ^{1}H NMR spectrum (200 Hz, DMSO-d_6), δ, ppm: 2.36 s (6H, CH_3), 2.55 s (3H, CH_3), 4.68 s (2H, CH_2S), 7.01 s (1H, 5′-H), 7.77–7.90 m (2H, H_{arom}), 8.00 d (1H, H_{arom}, ^4J = 2.0 Hz), 12.36 s (1H, NH). Found, %: C 51.19; H 3.56; N 18.50. $C_{19}H_{16}Cl_2N_6OS$. Calculated, %: C 51.01; H 3.61; N 18.79.

4-(1,3-Benzothiazol-2-ylsulfanylmethyl)-2-(2,4-dichlorophenyl)-3-methyl-6,7-dihydro-2*H*-pyrazolo[3,4-*d*]pyridazin-7-one (XIXa). Yield 63%, mp 206°C. ^{1}H NMR spectrum (200 MHz, DMSO-d_6), δ, ppm: 2.48 s (3H, CH_3), 4.93 s (2H, CH_2S), 7.29–7.52 m (2H, H_{arom}), 7.69–7.90 m (3H, H_{arom}), 7.99–8.03 m (2H, H_{arom}), 12.40 s (1H, NH). Found, %: C 50.48; H 2.63; N 14.89. $C_{20}H_{13}Cl_2N_5OS_2$. Calculated, %: C 50.64; H 2.76; N 14.76.

4-(1,3-Benzothiazol-2-ylsulfanylmethyl)-2-(2,5-dichlorophenyl)-3-methyl-6,7-dihydro-2*H*-pyrazolo[3,4-*d*]pyridazin-7-one (XIXb). Yield 70%, mp 291°C. ^{1}H NMR spectrum (200 MHz, DMSO-d_6), δ, ppm: 2.56 s (3H, CH_3), 4.95 s (2H, CH_2S), 7.33–7.54 m (2H, H_{arom}), 7.78–7.93 m (3H, H_{arom}), 8.04 d (2H, H_{arom}, J = 8.4 Hz), 12.43 s (1H, NH). Found, %: C 50.89; H 2.70; N 14.54. $C_{20}H_{13}Cl_2N_5OS_2$. Calculated, %: C 50.64; H 2.76; N 14.76.

2-(3-Chlorophenyl)-3-methyl-4-(5-phenyl-1,3,4-oxadiazol-2-ylsulfanylmethyl)-6,7-dihydro-2*H*-pyrazolo[3,4-*d*]pyridazin-7-one (XXa). Yield 63%, mp 254°C. ^{1}H NMR spectrum (200 Hz, DMSO-d_6), δ, ppm: 2.72 s (3H, CH_3), 4.89 s (2H, CH_2S), 7.54–7.76 m (5H, H_{arom}), 7.83 br.s (1H, H_{arom}), 7.93–8.05 m (3H, H_{arom}), 12.40 s (1H, NH). Found, %: C 55.83; H 3.20; N 18.79. $C_{21}H_{15}ClN_6O_2S$. Calculated, %: C 55.94; H 3.35; N 18.64.

2-(4-Chlorophenyl)-3-methyl-4-(5-phenyl-1,3,4-oxadiazol-2-ylsulfanylmethyl)-6,7-dihydro-2*H*-pyrazolo[3,4-*d*]pyridazin-7-one (XXb). Yield 68%, mp 245–246°C. ^{1}H NMR spectrum (400 Hz, DMSO-d_6), δ, ppm: 2.74 s (3H, CH_3), 4.83 s (2H, CH_2S), 7.55–7.70 m (7H, H_{arom}), 7.96–8.01 m (2H, H_{arom}), 12.23 s (1H, NH). Found, %: C 56.19; H 3.19; N 18.72. $C_{21}H_{15}ClN_6O_2S$. Calculated, %: C 55.94; H 3.35; N 18.64.

2-(2,4-Dichlorophenyl)-3-methyl-4-(5-phenyl-1,3,4-oxadiazol-2-ylsulfanylmethyl)-6,7-dihydro-2*H*-pyrazolo[3,4-*d*]pyridazin-7-one (XXc). Yield 72%, mp 236°C. ^{1}H NMR spectrum (200 MHz, DMSO-d_6), δ, ppm: 2.55 s (3H, CH_3), 4.90 s (2H, CH_2S), 7.54–7.86 m (5H, H_{arom}), 7.93–8.03 m (2H, H_{arom}), 8.06 d (1H, H_{arom}, ^4J = 2.0 Hz), 12.42 s (1H, NH). Found, %: C 51.86; H 3.06; N 17.49. $C_{21}H_{14}Cl_2N_6O_2S$. Calculated, %: C 51.97; H 2.91; N 17.32.

2-(2,5-Dichlorophenyl)-3-methyl-4-(5-phenyl-1,3,4-oxadiazol-2-ylsulfanylmethyl)-6,7-dihydro-2*H*-pyrazolo[3,4-*d*]pyridazin-7-one (XXd). Yield 73%, mp 281°C. ^{1}H NMR spectrum (200 MHz, DMSO-d_6), δ, ppm: 2.56 s (3H, CH_3), 4.90 s (2H, CH_2S), 7.55–7.70 m (3H, H_{arom}), 7.78–7.93 m (2H, H_{arom}), 7.96–8.04 m (3H, H_{arom}), 12.43 s (1H, NH). Found, %: C 52.19; H 2.95; N 17.14. $C_{21}H_{14}Cl_2N_6O_2S$. Calculated, %: C 51.97; H 2.91; N 17.32.

2-(2-Chlorophenyl)-4-(4,5-diphenyl-4*H*-1,2,4-triazol-3-ylsulfanylmethyl)-3-methyl-6,7-dihydro-2*H*-pyrazolo[3,4-*d*]pyridazin-7-one (XXIa). Yield 63%, mp 298°C. ^{1}H NMR spectrum (200 Hz, DMSO-d_6), δ, ppm: 2.42 s (3H, CH_3), 4.55 s (2H, CH_2S), 7.28–7.97 m (14H, H_{arom}), 12.28 s (1H, NH). Found, %: C 61.47; H 3.75; N 18.89. $C_{27}H_{20}ClN_7OS$. Calculated, %: C 61.65; H 3.83; N 18.64.

2-(3-Chlorophenyl)-4-(4,5-diphenyl-4*H*-1,2,4-triazol-3-ylsulfanylmethyl)-3-methyl-6,7-dihydro-2*H*-pyrazolo[3,4-*d*]pyridazin-7-one (XXIb). Yield 83%, mp 256°C. ^{1}H NMR spectrum (200 Hz, DMSO-d_6), δ, ppm: 2.60 s (3H, CH_3), 4.53 s (2H, CH_2S), 7.27–7.52 m (10H, H_{arom}), 7.58–7.80 m (4H, H_{arom}), 12.26 s (1H, NH). Found, %: C 61.54; H 3.61; N 18.50. $C_{27}H_{20}ClN_7OS$. Calculated, %: C 61.65; H 3.83; N 18.64.

2-(4-Chlorophenyl)-4-(4,5-diphenyl-4*H*-1,2,4-triazol-3-ylsulfanylmethyl)-3-methyl-6,7-dihydro-2*H*-pyrazolo[3,4-*d*]pyridazin-7-one (XXIc). Yield 74%, mp > 300°C. ^{1}H NMR spectrum (400 Hz, DMSO-d_6), δ, ppm: 2.63 s (3H, CH_3), 4.52 s (2H, CH_2S), 7.20–7.47 m (10H, H_{arom}), 7.63 br.s (4H, H_{arom}), 12.13 s (1H, NH). Found, %: C 61.81; H 3.70; N 18.75. $C_{27}H_{20}ClN_7OS$. Calculated, %: C 61.65; H 3.83; N 18.64.

2-(2,4-Dichlorophenyl)-4-(4,5-diphenyl-4*H*-1,2,4-triazol-3-ylsulfanylmethyl)-3-methyl-6,7-dihydro-2*H*-pyrazolo[3,4-*d*]pyridazin-7-one (XXId). Yield 85%, mp 293°C. ^{1}H NMR spectrum (200 MHz, DMSO-d_6), δ, ppm: 2.44 s (3H, CH_3), 4.55 s (2H, CH_2S), 7.28–7.64 m (10H, H_{arom}), 7.75 br.s (2H, H_{arom}), 8.05 br.s (1H, H_{arom}), 12.30 s (1H, NH). Found, %: C 57.65; H 3.35; N 17.25. $C_{27}H_{19}Cl_2N_7OS$. Calculated, %: C 57.86; H 3.42; N 17.49.

2-(2,5-Dichlorophenyl)-4-(4,5-diphenyl-4*H*-1,2,4-triazol-3-ylsulfanylmethyl)-3-methyl-6,7-dihydro-2*H*-pyrazolo[3,4-*d*]pyridazin-7-one (XXIe). Yield 59%, mp 295°C. ^{1}H NMR spectrum (200 Hz, DMSO-d_6), δ, ppm: 2.47 s (3H, CH_3), 4.57 s (2H, CH_2S), 7.37 br.s (6H, H_{arom}), 7.46–7.57 m (3H, H_{arom}), 7.76–7.98 m (4H, H_{arom}), 12.32 s (1H, NH). Found, %: C 57.69; H 3.30; N 17.63. $C_{27}H_{19}Cl_2N_7OS$. Calculated, %: C 57.86; H 3.42; N 17.49.

2-(2-Chlorophenyl)-4-[1-(4-chlorophenyl)-1*H*-tetrazol-5-ylsulfanylmethyl]-3-methyl-6,7-dihydro-2*H*-pyrazolo[3,4-*d*]pyridazin-7-one (XXIIa). Yield 69%, mp 236°C. ^{1}H NMR spectrum (200 Hz, DMSO-d_6), δ, ppm: 2.48 s (3H, CH_3), 4.85 s (2H, CH_2S), 7.60–7.88 m (8H, H_{arom}), 12.35 s (1H, NH). Found, %: C 49.66; H 2.79; N 22.84. $C_{20}H_{14}Cl_2N_8OS$. Calculated, %: C 49.49; H 2.91; N 23.09.

4-[1-(4-Chlorophenyl)-1*H*-tetrazol-5-ylsulfanylmethyl]-2-(2,4-dichlorophenyl)-3-methyl-6,7-dihydro-2*H*-pyrazolo[3,4-*d*]pyridazin-7-one (XXIIb). Yield 79%, mp 243°C. ^{1}H NMR spectrum (200 Hz, DMSO-d_6), δ, ppm: 2.49 s (3H, CH_3), 4.83 s (2H, CH_2S), 7.68–7.76 m (6H, H_{arom}), 8.06 d (1H, H_{arom}, ^4J = 2.0 Hz), 12.35 s (1H, NH). Found, %: C 46.06; H 2.40; N 21.33. $C_{20}H_{13}Cl_3N_8OS$. Calculated, %: C 46.21; H 2.52; N 21.56.

4-[1-(4-Chlorophenyl)-1*H*-tetrazol-5-ylsulfanylmethyl]-2-(2,5-dichlorophenyl)-3-methyl-6,7-dihydro-2*H*-pyrazolo[3,4-*d*]pyridazin-7-one (XXIIc). Yield 62%, decomposition point 247°C. ^{1}H NMR spectrum (200 Hz, DMSO-d_6), δ, ppm: 2.50 s (3H, CH_3), 4.83 s (2H, CH_2), 7.67–7.98 m (7H, H_{arom}), 12.36 s (1H, NH). Found, %: C 46.10; H 2.38; N 21.70. $C_{20}H_{13}Cl_3N_8OS$. Calculated, %: C 46.21; H 2.52; N 21.56.

2-(2,5-Dichlorophenyl)-3,6-dimethyl-4-(phenylsulfanylmethyl)-6,7-dihydro-2*H*-pyrazolo[3,4-*d*]-pyridazin-7-one (XXIII). Yield 60%, mp 198°C. ^{1}H NMR spectrum (200Hz, DMSO-d_6), δ, ppm: 2.49 s (3H, CH_3), 3.53 s (3H, CH_3N), 4.40 s (2H, CH_2S), 7.20–7.48 m (5H, H_{arom}), 7.72–8.05 m (3H, H_{arom}). Found, %: C 55.54; H 3.63; N 13.14. $C_{20}H_{16}Cl_2N_4OS$. Calculated, %: C 55.69; H 3.74; N 12.99.

2-(2-Chlorophenyl)-4-(4,6-dimethylpyrimidin-2-ylsulfanylmethyl)-3,6-dimethyl-6,7-dihydro-2*H*-pyrazolo[3,4-*d*]pyridazin-7-one (XXIVa). Yield 43%, mp 160°C. ^{1}H NMR spectrum (400 Hz, DMSO-d_6), δ, ppm: 2.39 s (6H, CH_3), 2.47 s (3H, CH_3), 3.70 s (3H, CH_3N), 4.60 s (2H, CH_2S), 6.91 s (1H, 5′-H), 7.58–7.74 m (4H, H_{arom}). Found, %: C 56.19; H 4.36; N 19.84. $C_{20}H_{19}ClN_6OS$. Calculated, %: C 56.27; H 4.49; N 19.69.

2-(4-Chlorophenyl)-4-(4,6-dimethylpyrimidin-2-ylsulfanylmethyl)-3,6-dimethyl-6,7-dihydro-2*H*-pyrazolo[3,4-*d*]pyridazin-7-one (XXIVb). Yield 58%, mp 195°C. ^{1}H NMR spectrum (400 MHz, DMSO-d_6), δ, ppm: 2.39 s (6H, CH_3), 2.64 s (3H, CH_3), 3.69 s (3H, CH_3N), 4.57 s (2H, CH_2S), 6.90 s (1H, 5′-H), 7.60 d (2H, H_{arom}, J = 8.8 Hz), 7.64 d (2H, H_{arom}, J = 8.8 Hz). Found, %: C 56.01; H 4.56; N 19.53. $C_{20}H_{19}ClN_6OS$. Calculated, %: C 56.27; H 4.49; N 19.69.

4-(1,3-Benzothiazol-2-ylsulfanylmethyl)-2-(4-chlorophenyl)-3,6-dimethyl-6,7-dihydro-2*H*-pyrazolo[3,4-*d*]pyridazin-7-one (XXV). Yield 66%,

mp 229°C. ^{1}H NMR spectrum (200 Hz, DMSO-d_6), δ, ppm: 2.68 s (3H, CH_3), 3.64 s (3H, CH_3N), 4.92 s (2H, CH_2S), 7.32–7.88 m (8H, H_{arom}). Found, %: C 55.63; H 3.51; N 15.48. $C_{21}H_{16}ClN_5OS_2$. Calculated, %: C 55.56; H 3.55; N 15.43.

2-(2,4-Dichlorophenyl)-4-(4,5-diphenyl-4*H*-1,2,4-triazol-3-ylsulfanylmethyl)-3,6-dimethyl-6,7-dihydro-2*H*-pyrazolo[3,4-*d*]pyridazin-7-one (XXVIa). Yield 55%, mp 154–155°C. ^{1}H NMR spectrum (200 MHz, DMSO-d_6), δ, ppm: 2.44 s (3H, CH_3), 3.56 s (3H, CH_3N), 4.47 s (2H, CH_2S), 7.08–7.58 m (10H, H_{arom}), 7.75 br.s (2H, H_{arom}), 8.06 br.s (1H, H_{arom}). Found, %: C 58.46; H 3.81; N 16.80. $C_{28}H_{21}Cl_2N_7OS$. Calculated, %: C 58.54; H 3.68; N 17.07.

2-(2,5-Dichlorophenyl)-4-(4,5-diphenyl-4*H*-1,2,4-triazol-3-ylsulfanylmethyl)-3,6-dimethyl-6,7-dihydro-2*H*-pyrazolo[3,4-*d*]pyridazin-7-one (XXVIb). Yield 60%, mp 196°C. ^{1}H NMR spectrum (200 MHz, DMSO-d_6), δ, ppm: 2.47 s (3H, CH_3), 3.57 s (3H, CH_3N), 4.49 s (2H, CH_2S), 7.28–7.56 m (10H, H_{arom}), 7.77–7.98 m (3H, H_{arom}). Found, %: C 58.38; H 3.50; N 17.19. $C_{28}H_{21}Cl_2N_7OS$. Calculated, %: C 58.54; H 3.68; N 17.07.

2-(4-Chlorophenyl)-4-[1-(4-chlorophenyl)-1*H*-tetrazol-5-ylsulfanylmethyl]-3,6-dimethyl-6,7-dihydro-2*H*-pyrazolo[3,4-*d*]pyridazin-7-one (XXVIIa). Yield 65%, mp 194°C. ^{1}H NMR spectrum (200 Hz, DMSO-d_6), δ, ppm: 2.64 s (3H, CH_3), 3.55 s (3H, CH_3N), 4.73 s (2H, CH_2S), 7.42–7.79 m (8H, H_{arom}). Found, %: C 50.68; H 3.17; N 22.28. $C_{21}H_{16}Cl_2N_8OS$. Calculated, %: C 50.51; H 3.23; N 22.44.

4-[1-(4-Chlorophenyl)-1*H*-tetrazol-5-ylsulfanylmethyl]-2-(2,4-dichlorophenyl)-3,6-dimethyl-6,7-dihydro-2*H*-pyrazolo[3,4-*d*]pyridazin-7-one (XXVIIb). Yield 69%, mp 229°C. ^{1}H NMR spectrum (200 Hz, DMSO-d_6), δ, ppm: 2.54 s (3H, CH_3), 3.56 s (3H, CH_3N), 4.77 s (2H, CH_2S), 7.65–7.78 m (6H, H_{arom}), 8.06 br.s (1H, H_{arom}). Found, %: C 47.38; H 2.69; N 21.16. $C_{21}H_{15}Cl_3N_8OS$. Calculated, %: C 47.25; H 2.83; N 20.99.

REFERENCES

1. Matiichuk, V.S., Potopnyk, M.A., and Obushak, N.D., *Russ. J. Org. Chem*., 2009, vol. 45, p. 712.
2. Matiichuk, V.S., Potopnyk, M.A., and Obushak, N.D., *Russ. J. Org. Chem*., 2008, vol. 44, p. 1352.
3. Al-Zaydi, K.M. and Hafez, E.A.A., *J. Chem. Res., Miniprint*, 1999, p. 1621.
4. Carpino, P.A. and Dow, R.L., WO Patent no. 111849, 2006.
5. Carpino, P.A. and Sakya, S.M., WO Patent no. 61504, 2005.
6. Bildirici, I., Şener, A., Atalan, E., Battal, A., and Genz, H., *Med. Chem. Res*.,, 2009, vol. 18, p. 327.
7. Chang, E.-M., Lin, C.-J., Wong, F.F, and Yeh, M.-Y., *Heterocycles*, 2006, vol. 68, p. 733.
8. Erian, A.W., Sherif, M.S., and Gaber, H.M., *Molecules*, 2003, vol. 8, p. 793.