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Synthesis of *N*- and *C*-azolyl-substituted pyrazolo[1,5-*a*]pyrimidines by recyclization of pyrimidinium salts

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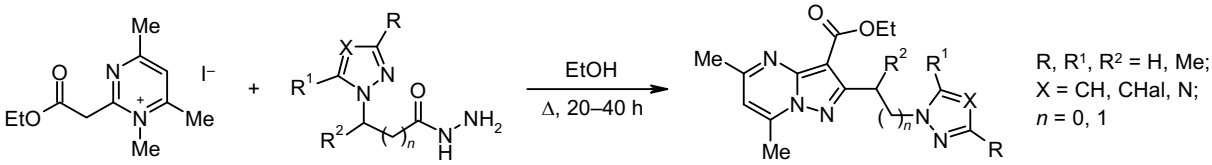


We studied the reaction of 2-(ethoxycarbonyl)methyl-1,4,6-trimethylpyrimidinium iodide with hydrazides of *N*-azolyl- and *C*-pyrazolyl-substituted carboxylic acids, which were synthesized by reacting the respective esters with hydrazine hydrate. This reaction was shown to result in recyclization and formation of ethyl 2-(pyrazolylalkyl)- and 2-(azolylalkyl)-5,7-dimethylpyrazolo[1,5-*a*]pyrimidine-3-carboxylates. Besides pyrazolopyrimidines, the separation of reaction mixture provided in some cases also another recyclization product, 2-hydroxy-5,7-dimethylpyrazolo[1,5-*a*]pyrimidine.

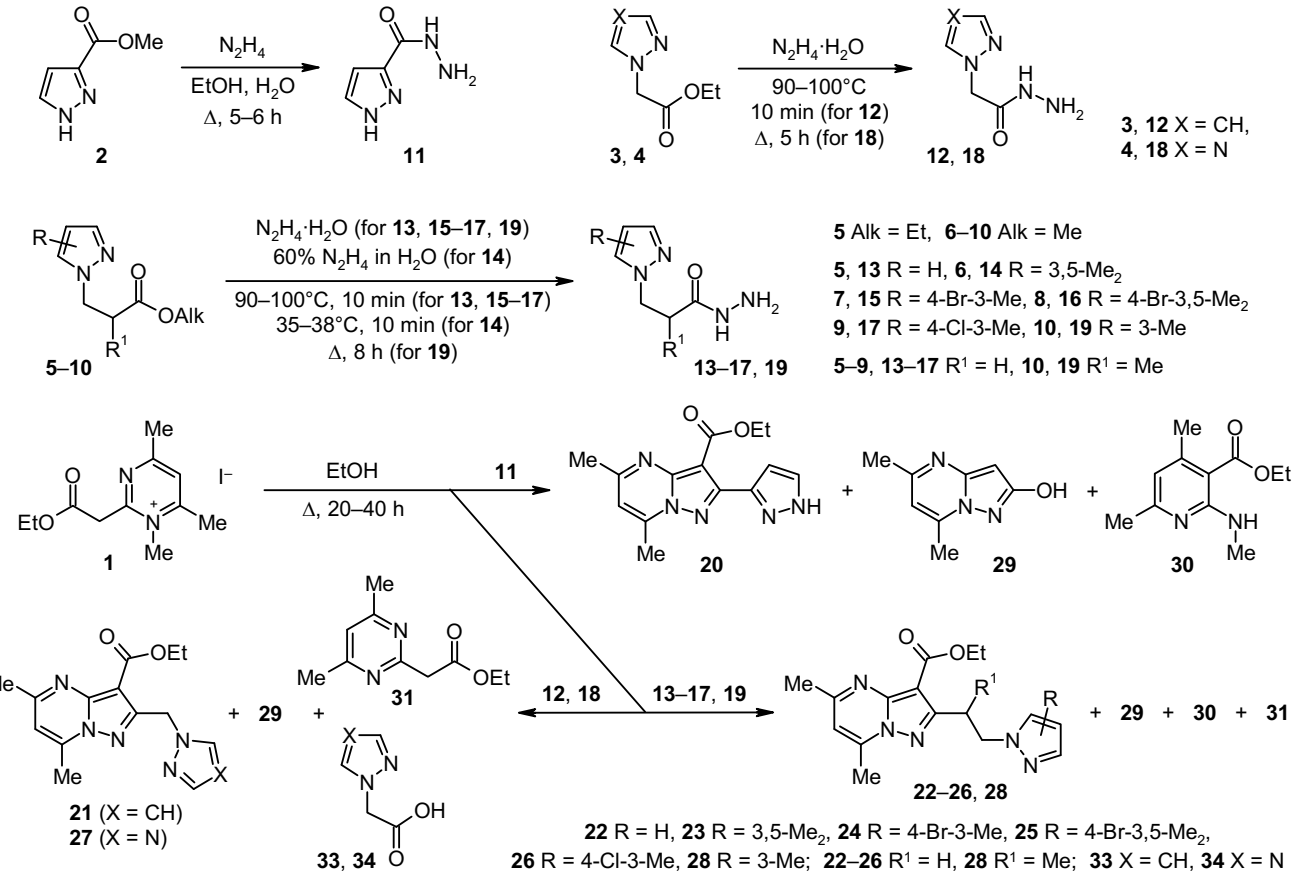
Keywords: hydrazide, pyrazole, pyrazolo[1,5-*a*]pyrimidine, pyrimidinium iodide, rearrangement.

Two synthetic strategies are currently known for the preparation of pyrazolo[1,5-*a*]pyrimidines, as well as other azolopyrimidines: starting either from the pyrimidine ring or from the five-membered ring, and constructing the other heterocycle.[1,2] Thus, syntheses of similar annulated systems from 5-aminopyrazoles and other α-aminoazoles have been described, where reactions with β-dicarbonyl compounds and their derivatives were used.[1,2] For example, synthesis of azolopyrimidines from a pyrimidine derivative was achieved by reacting 2-hydrazinopyrimidines with orthoformate and some other carboxylic acid derivatives.[3,4]

During an earlier study of recyclization reactions between pyrimidine derivatives and nitrogen-containing nucleophilic agents, we identified an unusual transformation of 2-(ethoxycarbonyl)methyl-1,4,6-trimethylpyrimidinium iodide (**1**) in the presence of certain acyl hydrazides, which unexpectedly provided pyrazolo[1,5-*a*]pyrimidine derivatives.[5] Recently we described such rearrangement in another short report.[6] This previously unknown transformation was performed in a single step by substituting the N(1)–CH_3 fragment in the starting salt with the terminal nitrogen atom of hydrazide group, with subsequent intramolecular cyclization, leading to the formation of pyrazole ring condensed with a pyrimidine ring.

In order to investigate the possibility of using this transformation for the synthesis of otherwise unavailable azolyl-substituted pyrazolopyrimidines, we performed the reaction of iodide **1** with hydrazides of azolyl-substituted carboxylic acids **11**–**19** (Scheme 1), which were prepared by reacting esters of pyrazole-3-carboxylic, (pyrazol-1-yl)-acetic, (1,2,4-triazol-1-yl)acetic, and (pyrazol-1-yl)propionic acids **2**–**10** with hydrazine hydrate. The subsequent heating of hydrazides **11**–**19** with iodide **1** in a sealed glass ampoule (at 2:1 stoichiometry) gave the 2-azolyl- and 2-(azolylalkyl)-substituted pyrazolo[1,5-*a*]pyrimidines **20**–**28**. We should

Scheme 1



note that, along with pyrazolopyrimidines **20**–**28**, another recyclization product, 2-hydroxy-5,7-dimethylpyrazolo-[1,5-*a*]pyrimidine (**29**), was isolated from the reaction mixtures in all cases. In some experiments, the starting salt **1** gave small amounts of enamine rearrangement product, ethyl 4,6-dimethyl-2-methylaminopyridine-3-carboxylate (**30**), and demethylation product, ethyl 4,6-dimethyl-pyrimidinyl-2-acetate (**31**), which were typically formed also in other nucleophilic recyclization reactions of pyrimidines by interaction of salt **1** with primary amines (Kost–Sagitullin enamine rearrangement and recyclization to 1,2,4-triazole derivatives).[7–10] In two cases, the formation of azolylcarboxylic acids **33**, **34** corresponding to the starting hydrazides was also noted. The reaction of salt **1** with hydrazide **14** also resulted in isolation of hydroiodide of the starting hydrazide.

The products of this recyclization were characterized by NMR spectroscopy (and X-ray structural analysis in the case of compound **26**), while the purity and individuality of the compounds were proved by TLC and elemental analysis.

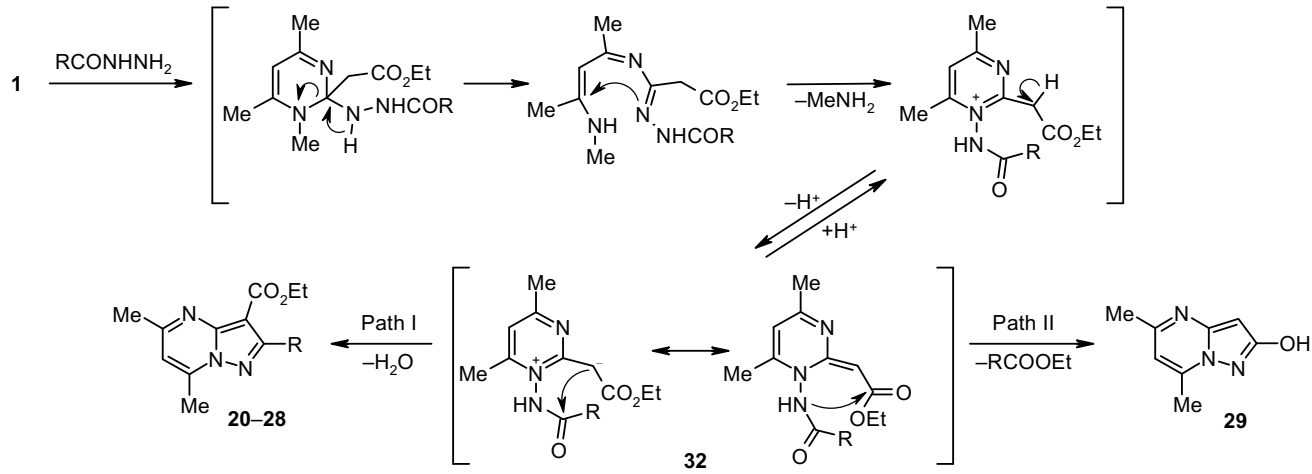
The ^{1}H NMR spectra of all synthesized pyrazolo[1,5-*a*]-pyrimidines **20**–**29** contained signals of ester and methyl group protons, as well as aromatic protons belonging to pyrimidine and pyrazole rings.

The ^{1}H NMR spectrum of pyrazolo[1,5-*a*]pyrimidine 2-pyrazolyl derivative **20** contained signals of ester group protons, doublets of two protons at the *ortho* positions of pyrazole ring at 6.91 ppm (br. d, J = 1.9 Hz, H-5') and 7.52 ppm (d, J = 1.9 Hz, H-4'), a quartet due to pyrimidine proton at 6.97 ppm (J = 0.8 Hz, H-6), as well as the signals of two methyl groups at 2.64 ppm (s, 5-CH_3) and 2.80 ppm (d, J = 0.8 Hz, 7-CH_3). The coupling constants between pyrimidine ring protons and one of the methyl groups allowed to unequivocally assign each methyl group signal. Similar coupling constants (J = 0.8–0.9 Hz) between the protons of pyrimidine ring and the 7-CH_3 methyl group were also observed in the ^{1}H NMR spectra of the other synthesized pyrazolo[1,5-*a*]pyrimidines **21**–**29**.

The rearrangements leading to pyrazolo[1,5-*a*]pyrimidine derivatives **20**–**29** can be apparently interpreted as involving an intermediate adduct, compound **32**, with a mechanism consisting of attack by terminal nitrogen atom of hydrazide at position 2 of the salt **1**, opening of pyrimidine ring at the the N(1)–C(2) bond, followed by a cyclization that includes hydrazine nitrogen atom into the pyrimidine ring. The last stage of recyclization, namely, the reaction of intermediate **32** leading to closure of five-membered ring, can occur in two different directions (I and II), leading to either compounds **20**–**28** or **29** (Scheme 2).

The ^{1}H NMR signal of methylene bridge between the two heterocycles in pyrazolo[1,5-*a*]pyrimidines **21** and **27** was observed at an unusually downfield location (5.72 and 5.79 ppm, respectively), apparently due to the high CH acidity of this fragment. The ethylene bridge protons between the rings in compounds **22**–**26** were observed as a

Scheme 2



pair of multiplets at stronger field, and the methylene group linked to pyrazole ring nitrogen atom gave a downfield signal (4.32–4.55 ppm) compared to the adjacent methylene group (3.43–3.60 ppm).

The reactions of iodide **1** with hydrazides **12** and **18** allowed us to isolate also *N*-azolylacetic acids **33** and **34**, corresponding to the starting hydrazides. The formation of these acids apparently could be explained by the elimination of azolylalkyl fragment during heterocyclization by route II and its reaction with water, eliminated by heterocyclization according to route I.

The molecular structure of compound **26** is presented in Figure 1 and features two planar cyclic fragments: pyrazole ring and bicyclic pyrazolo[1,5-*a*]pyrimidine. The maximum deviation of atoms from the respective least squares planes did not exceed 0.0042(2) Å in the pyrazole ring and 0.0284(3) Å in the pyrazolo[1,5-*a*]pyrimidine fragment. The three-dimensional molecular packing in the crystal featured an unusual C(8)–H(8)···O(13) hydrogen bond (the interatomic distances were the following: C–H 1.01(3) Å, H···O 2.46(3) Å, C···O 3.409(3) Å, while the C–H–O angle was 157(2)°). This hydrogen bond between pyrimidine H-5 proton of one molecule and carbonyl group oxygen of another molecule linked the molecules of this compound in an infinite chain in the [1 0 0] direction (Fig. 2).

Thus, we have used a large number of examples to demonstrate the general applicability of pyrimidine salt recyclization to polysubstituted 2-(azolylalkyl)pyrazolo-[1,5-*a*]pyrimidines that would be otherwise difficult to obtain. Such compounds may be of interest as novel bisheteroarylalkyl ligands for the synthesis of metal complexes.

Experimental

IR spectra were recorded in Nujol on a Specord UR-75 spectrometer. ^{1}H and ^{13}C NMR spectra were acquired on a Varian Mercury 300 spectrometer (300 and 75 MHz, respectively), the solvents were $CDCl_3$ (compound **23**) and 1:3 DMSO-d_6–CCl_4, (the rest of the compounds), internal standard was TMS. Mass spectra were recorded on an MK-1321 instrument with direct introduction of sample into the ion source, EI ionization (70 eV). Silufol UV-254 plates were used for TLC analysis of reaction mixtures and the obtained products, visualization with iodine vapor and Ehrlich's reagent. Column chromatography was performed with L 40/100 silica gel. The starting esters **2**,[11] **3**,[12] **5**,[12] **6**,[12] and **10**[13] were synthesized according to published procedures.

Ethyl (1*H*-1,2,4-triazol-1-yl)acetate (4). A mixture of 1,2,4-triazole (6.9 g, 0.1 mol), ethyl chloroacetate (24.5 g, 0.3 mol),

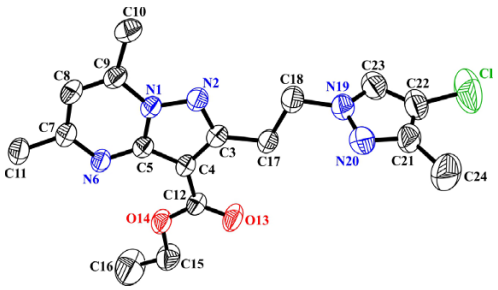


Figure 1. Molecular structure of compound **26** according to X-ray structural analysis with atoms represented by thermal vibration ellipsoids of 50% probability.

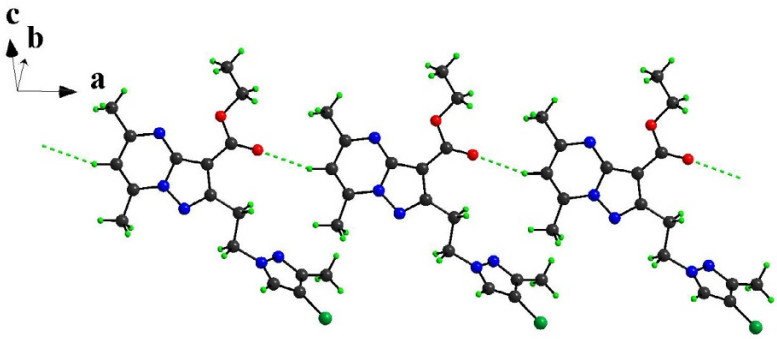


Figure 2. Infinite molecular chain in the structure of compound **26** along the [1 0 0] direction.

$Et_3BnN^+Cl^-$ (1.0 g, 5.2 mmol), K_2CO_3 (27.6 g, 0.2 mol), and Me_2CO (150 ml) was stirred for 4 h at 50–55°C. The reaction mixture was then cooled and filtered. Acetone was removed by evaporation, and the residue was distilled under vacuum. Yield 11.5 g (76%), colorless liquid, bp 123–130°C (3 mmHg) (oil,[14,15] bp 145–146°C[16]), n_D^{20} 1.4647. IR spectrum, ν, cm^{-1}: 1500 (ring), 1730 (C=O). ^1H NMR spectrum, δ, ppm (*J*, Hz): 1.30 (3H, t, *J* = 7.1, $OCH_2C\underline{H}_3$); 4.81 (2H, q, *J* = 7.1, $OC\underline{H}_2CH_3$); 4.94 (2H, s, NCH_2); 7.62 (1H, s, H-3); 8.25 (1H, s, H-5). Found, %: C 46.28; H 5.99; N 27.25. $C_6H_9N_3O_2$. Calculated, %: C 46.45; H 5.85; N 27.08.

Methyl 3-(4-bromo-3-methylpyrazol-1-yl)propionate (7). A mixture of methyl 3-(3-methyl-1*H*-pyrazol-1-yl)-propionate (26.8 g, 0.16 mol), AcONa (32.0 g, 0.40 mol), and H_2O (112 ml) was charged into a four-necked flask, stirred at room temperature, and treated by dropwise addition of a mixture of AcOH (19 ml) and Br_2 (10 ml, 31.2 g, 0.20 mol) at such rate that the reaction mixture temperature did not exceed 20–25°C. The reaction mixture was neutralized with aqueous Na_2CO_3, extracted with $CHCl_3$, and dried over $MgSO_4$. Chloroform was removed by evaporation and the residue was distilled under vacuum. Yield 24.1 g (61%), bp 127–128°C (3 mmHg), n_D^{20} 1.5082. IR spectrum, ν, cm^{-1}: 1520 (ring), 1710 (C=O). ^1H NMR spectrum, δ, ppm (*J*, Hz): 2.18 (3H, s, 3-CH_3); 2.82 (2H, t, *J* = 6.7, CHCO); 3.65 (3H, s, OCH_3); 4.26 (2H, t, *J* = 6.7, NCH_2); 7.56 (1H, s, H-5). Found, %: C 39.07; H 4.57; N 11.11. $C_8H_{11}BrN_2O_2$. Calculated, %: C 38.89; H 4.49; N 11.34.

Methyl 3-(4-bromo-3,5-dimethylpyrazol-1-yl)propionate (8). A mixture of methyl 3-(3,5-dimethyl-1*H*-pyrazol-1-yl)propionate (12.70 g, 70 mmol), AcONa (14.35 g, 175 mmol), and H_2O (49 ml) was charged into a four-necked flask, stirred at room temperature, and treated by dropwise addition of a mixture of AcOH (7 ml) and Br_2 (4.3 ml, 13.40 g, 84 mmol). Stirring was continued until complete fading of bromine color, then the reaction mixture was treated analogously to the procedure described for compound **7**. Yield 13.20 g (72%), colorless liquid, bp 117–119°C (1 mmHg), n_D^{20} 1.5098. IR spectrum, ν, cm^{-1}: 1540 (ring), 1720 (C=O). ^1H NMR spectrum, δ, ppm (*J*, Hz): 2.27 (3H, s, 5-CH_3); 2.73 (2H, t, *J* = 6.8, CH_2CO); 2.75 (3H, s, 3-CH_3); 3.60 (3H, s, OCH_3); 4.12 (2H, t, *J* = 6.8, NCH_2). Found, %: C 41.48; H 5.19; N 10.58. $C_9H_{13}BrN_2O_2$. Calculated, %: C 41.40; H 5.02; N 10.73.

Methyl 3-(4-chloro-3-methylpyrazol-1-yl)propionate (9). A mixture of methyl 3-(3-methylpyrazol-1-yl)propionate (33.6 g, 0.2 mol), AcOH (65 ml), and conc. HCl (27 ml) was charged into a two-necked flask with a reflux condenser and thermometer, then treated with 30% H_2O_2 (73 ml) in one portion. The reaction mixture was left overnight, diluted with H_2O, extracted with Et_2O, washed with aqueous Na_2CO_3, and dried over Na_2SO_4. Ether was removed at reduced pressure, the residue was distilled under vacuum, collecting the fraction with bp 105–120°C (3 mmHg). Yield 19.7 g (64%), yellowish liquid, n_D^{20} 1.4908. ^1H NMR spectrum, δ, ppm (*J*, Hz): 2.13 (3H, s, 3-CH_3); 2.81 (2H, t, *J* = 6.7, CH_2CO); 3.65 (3H, s, OCH_3); 4.24 (2H, t, *J* = 6.7, NCH_2); 7.55 (1H, s, H-5). Found, %: C 47.61; H 5.65; N 13.57. $C_8H_{11}ClN_2O_2$. Calculated, %: C 47.42; H 5.47; N 13.82.

Hydrazide of 1*H*-pyrazole-3-carboxylic acid (11). A solution of methyl 1*H*-pyrazole-3-carboxylate (**2**) (1.0 g, 8 mmol) in EtOH (10 ml) was treated with 60% aqueous hydrazine (1.5 g, 18 mmol), the mixture was heated for 5–6 h on a water bath. Ethanol and excess hydrazine were removed by evaporation, the residue was washed with hot hexane and Et_2O. Yield 1.0 g (99%), white crystals, mp 172–174°C (EtOH), R_f 0.1 (2:1 benzene–Me_2CO). ^1H NMR spectrum, δ, ppm (*J*, Hz): 4.22 (2H, br. s, NH_2); 6.66 (1H, d, *J* = 2.2, H-4); 7.52 (1H, d, *J* = 2.2, H-5); 9.03 (1H, br. s, $N\underline{H}NH_2$); 12.95 (1H, br. s, 1-NH). Found, %: C 37.89; H 4.83; N 44.51. $C_4H_6N_4O$. Calculated, %: C 38.09; H 4.80; N 44.42.

Synthesis of hydrazides 12, 13, 15–17 (General method). A mixture of $N_2H_4 \cdot H_2O$ (3.0 g, 0.06 mol) and ester **3**, **5**, **7**–**9** (0.02 mol) was stirred for 10 min at 90–100°C until complete dissolution. The obtained precipitate was filtered off after several minutes, washed on filter with a small amount of Et_2O, dried, and recrystallized from EtOH.

Hydrazide of (1*H*-pyrazol-1-yl)acetic acid (12). Yield 2.3 g (82%), white crystals, mp 110–112°C, R_f 0.2 (1:1 benzene–Me_2CO). ^1H NMR spectrum, δ, ppm (*J*, Hz): 4.23 (2H, br. s, NH_2); 4.70 (2H, s, NCH_2); 6.18 (1H, dd, *J* = 2.3, *J* = 1.8, H-4); 7.35 (1H, dd, *J* = 1.8, *J* = 0.7, H-3); 7.61 (1H, dd, *J* = 2.3, *J* = 0.7, H-5); 9.16 (1H, br. s, NH). Found, %: C 42.65; H 5.49; N 39.79. $C_5H_8N_4O$. Calculated, %: C 42.85; H 5.75; N 39.98.

Hydrazide of 3-(1*H*-pyrazol-1-yl)propionic acid (13). Yield 2.8 g (91%), white shiny crystals, mp 63–65°C, R_f 0.2 (1:1 benzene–Me_2CO). ^1H NMR spectrum, δ, ppm (*J*, Hz): 2.59 (2H, t, *J* = 6.9, CH_2CO); 3.97 (2H, br. s, NH_2); 4.34 (2H, t, *J* = 6.9, NCH_2); 6.11 (1H, dd, *J* = 2.3, *J* = 1.8, H-4); 7.31 (1H, dd, *J* = 1.8, *J* = 0.6, H-3); 7.49 (1H, dd, *J* = 2.3, *J* = 0.6, H-5); 8.95 (1H, br. s, NH). Found, %: C 46.89; H 6.64; N 36.55. $C_6H_{10}N_4O$. Calculated, %: C 46.74; H 6.54; N 36.34.

Hydrazide of 3-(4-bromo-3-methyl-1*H*-pyrazol-1-yl)-propionic acid (15). Yield 4.0 g (81%), white crystals, mp 120–122°C, R_f 0.4 (2:1 benzene–Me_2CO). ^1H NMR spectrum, δ, ppm (*J*, Hz): 2.13 (3H, s, CH_3); 2.56 (2H, t, *J* = 6.8, CH_2CO); 3.90 (2H, br. s, NH_2); 4.24 (2H, t, *J* = 6.8, NCH_2); 7.55 (1H, s, H-5); 8.97 (1H, br. s, NH). Found, %: C 34.28; H 4.21; N 22.45. $C_7H_{11}BrN_4O$. Calculated, %: C 34.03; H 4.49; N 22.67.

Hydrazide of 3-(4-bromo-3,5-dimethyl-1*H*-pyrazol-1-yl)-propionic acid (16). Yield 4.5 g (86%), white shiny crystals, mp 153–155°C, R_f 0.2 (1:1 benzene–Me_2CO). ^1H NMR spectrum, δ, ppm (*J*, Hz): 2.11 (3H, s, CH_3); 2.25 (3H, s, CH_3); 2.55 (2H, t, *J* = 6.9, CH_2CO); 3.92 (2H, br. s, NH_2); 4.17 (2H, t, *J* = 6.9, NCH_2); 8.95 (1H, br. s, NH). Found, %: C 36.58; H 5.15; N 21.57. $C_8H_{13}BrN_4O$. Calculated, %: C 36.80; H 5.02; N 21.46.

Hydrazide of 3-(4-chloro-3-methyl-1*H*-pyrazol-1-yl)-propionic acid (17). Yield 4.0 g (91%), yellow crystals, mp 105–107°C, R_f 0.3 (1:1 benzene–Me_2CO). ^1H NMR spectrum, δ, ppm (*J*, Hz): 2.13 (3H, s, CH_3); 2.55 (2H, t,

J = 6.8, CH_2CO); 4.22 (2H, t, J = 6.8, NCH_2); 5.19 (2H, br. s, NH_2); 7.53 (1H, s, H-5); 8.95 (1H, br. s, NH). Found, %: C 41.77; H 5.59; N 27.41. $C_7H_{11}ClN_4O$. Calculated, %: C 41.49; H 5.47; N 27.65.

Hydrazide of 3-(3,5-dimethyl-1*H*-pyrazol-1-yl)propionic acid (14). Methyl 3-(3,5-dimethyl-1*H*-pyrazol-1-yl)propionate (**6**) (10.0 g, 0.055 mol) was mixed at room temperature with 60% aqueous hydrazine (4 ml). The solution spontaneously heated up to 35–38°C, and the reaction product precipitated after 10 min. The mixture was cooled and the precipitate was filtered off, washed with hot hexane, and dried. Yield 9.7 g (97%), white shiny crystals, mp 125–127°C (EtOH), R_f 0.1 (1:1 benzene–Me_2CO). ^{1}H NMR spectrum, δ, ppm (J, Hz): 2.09 (3H, s, CH_3); 2.23 (3H, s, CH_3); 2.53 (2H, t, J = 7.1, CH_2CO); 3.79 (2H, br. s, NH_2); 4.10 (2H, t, J = 7.1, NCH_2); 5.62 (1H, s, H-4); 8.93 (1H, br. s, NH). Found, %: C 52.85; H 7.69; N 30.61. $C_8H_{14}N_4O$. Calculated, %: C 52.73; H 7.74; N 30.75.

Hydrazide of (1*H*-1,2,4-triazol-1-yl)acetic acid (18). A mixture of ethyl (1*H*-1,2,4-triazol-1-yl)acetate (**4**) (5 g, 0.03 mol) and $N_2H_4 \cdot H_2O$ (6 g, 0.12 mol) was refluxed for 5 h. The obtained precipitate was filtered off, washed on filter with a small amount of Et_2O and dried. Yield 3.96 g (94%), white crystals, mp 108–110°C (EtOH), R_f 0.1 (1:1 benzene–Me_2CO). ^{1}H NMR spectrum, δ, ppm (J, Hz): 4.27 (2H, br. s, NH_2); 4.80 (2H, s, NCH_2); 7.75 (1H, s, H-3); 8.34 (1H, s, H-5); 9.37 (1H, br. s, NH). Found, %: C 34.27; H 5.19; N 49.35. $C_4H_7N_5O$. Calculated, %: C 34.04; H 5.00; N 49.62.

Hydrazide of 2-methyl-3-(3-methyl-1*H*-pyrazol-1-yl)-propionic acid (19). A mixture of methyl 2-methyl-3-(3-methyl-1*H*-pyrazol-1-yl)propionate (**10**) (5.5 g, 0.03 mol) and $N_2H_4 \cdot H_2O$ (5.5 g, 0.11 mol) was refluxed for 8 h. The obtained precipitate was filtered off, washed on filter with a small amount of Et_2O, and dried. Yield 3.5 g (64%), white crystals, mp 78–80°C (EtOH), R_f 0.3 (1:1 benzene–Me_2CO). ^{1}H NMR spectrum, δ, ppm (J, Hz): 1.01 (3H, d, J= 6.9, $CHC\underline{H}_3$); 2.17 (3H, s, 3-CH_3); 2.74–2.87 (1H, m, $C\underline{H}CH_3$); 3.89 (1H, dd, J = 13.3, J = 7.0) and 4.18 (1H, dd, J = 13.3, J = 7.6, NCH_2); 3.90 (2H, br. s, NH_2); 5.85 (1H, d, J = 2.1, H-4); 7.28 (1H, d, J = 2.1, H-5); 8.93 (1H, br. s, NH). ^{13}C NMR spectrum, δ, ppm: 13.1; 15.0; 38.9; 53.6; 103.7; 130.0; 146.7; 172.5. Found, %: C 52.95; H 7.89; N 30.55. $C_8H_{14}N_4O$. Calculated, %: C 52.73; H 7.74; N 30.75.

Reaction of 2-(ethoxycarbonyl)methyl-1,4,6-trimethylpyrimidinium iodide (1) with hydrazide of 1*H*-pyrazole-3-carboxylic acid (11). A solution of iodide **1** (2.52 g, 7.5 mmol) in abs. EtOH (10 ml) was mixed with a solution of hydrazide **11** (1.89 g, 15.0 mmol) in abs. EtOH (8 ml). The reaction mixture was refluxed for 40 h, ethanol was evaporated, and the oily residue was treated with hot hexane. Hexane was evaporated, the residue was separated by silica gel column chromatography (2:1 benzene–Me_2CO), giving **ethyl 5,7-dimethyl-2-(1*H*-pyrazol-3-yl)-pyrazolo[1,5-*a*]pyrimidine-3-carboxylate (20)**, **2-hydroxypyrazolo[1,5-*a*]pyrimidine (29)**, and **ethyl 5,7-dimethyl-2-(dimethylamino)pyridine-3-carboxylate (30)**.

Compound 20. Yield 0.51 g (24%), white crystals, mp 171–173°C (hexane), R_f 0.5 (2:1 benzene–Me_2CO). ^{1}H NMR spectrum (1:3 DMSO-d_6–CCl_4), δ, ppm (J, Hz): 1.43 (3H, t, J = 7.1, $OCH_2C\underline{H}_3$); 2.64 (3H, s, 5-CH_3); 2.80 (3H, d, J = 0.8, 7-CH_3); 4.41 (2H, q, J = 7.1, $OC\underline{H}_2CH_3$); 6.91 (1H, br. d, J = 1.9, H-5'); 6.97 (1H, q, J = 0.8, H-6); 7.52 (1H, d, J = 1.9, H-4'); 13.25 (1H, br. s, NH). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (J, Hz): 1.52 (3H, t, J = 7.1, $OCH_2C\underline{H}_3$); 2.69 (3H, s, 5-CH_3); 2.82 (3H, d, J = 0.9, 7-CH_3); 4.54 (2H, q, J = 7.1, $OC\underline{H}_2CH_3$); 6.78 (1H, q, J = 0.9, H-6); 7.08 (1H, br. s, H-5'); 7.68 (1H, d, J = 1.5, H-4'). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 14.5; 17.2; 25.4; 61.5; 98.6; 105.6; 111.0; 136.0; 140.0; 146.1; 147.8; 149.2; 162.4; 165.4. Found, %: C 59.21; H 5.16; N 24.42. $C_{14}H_{15}N_5O_2$. Calculated, %: C 58.94; H 5.30; N 24.55.

Compound 29. Yield 0.28 g (23%), white crystals, mp 237–240°C (mp 239–240°C),[5] R_f 0.6 (1:1 benzene–Me_2CO).

Compound 30. Yield 0.3 g (19%), colorless crystals, mp 39–40°C (mp 39–40°C),[7,9,17] R_f 0.8 (2:1 benzene–Me_2CO, 2:1). Compounds **29** and **30** had the same ^{1}H and ^{13}C NMR spectra, as well as chromatographic retention times as the previously obtained samples.

Reaction of iodide 1 with hydrazide of (1*H*-pyrazol-1-yl)-acetic acid (12). A solution of iodide **1** (1.35 g, 4 mmol) in abs. EtOH (10 ml) was mixed with a solution of hydrazide **12** (1.12 g, 8 mmol) in abs. EtOH (15 ml). The reaction mixture was refluxed for 36 h, then ethanol was evaporated, and the oily residue was treated with hot hexane. Hexane was evaporated, the residue was separated by silica gel column chromatography (3:1 benzene–Me_2CO), giving **ethyl 5,7-dimethyl-2-(1*H*-pyrazol-1-yl-methyl)pyrazolo[1,5-*a*]pyrimidine-3-carboxylate (21)**, compound **29** (0.10 g, 15%), the product from demethylation of iodide **1**, **ethyl (5,7-dimethylpyrimidin-2-yl)acetate (31)**, as well as **(1*H*-pyrazol-1-yl)acetic acid (33)**.

Compound 21. Yield 0.50 g (44%), white crystals, mp 180–182°C (hexane), R_f 0.5 (2:1 benzene–Me_2CO). ^{1}H NMR spectrum, δ, ppm (J, Hz): 1.40 (3H, t, J = 7.2, $OCH_2C\underline{H}_3$); 2.62 (3H, s, CH_3); 2.73 (3H, d, J = 0.9, CH_3); 4.35 (2H, q, J = 7.2, $OC\underline{H}_2CH_3$); 5.72 (2H, s, CH_2N); 6.14 (1H, dd, J = 2.4, J = 1.8, H-4'); 6.94 (1H, q, J = 0.9, H-6); 7.30 (1H, dd, J = 1.8, J = 0.7, H-5'); 7.61 (1H, dd, J = 2.4, J = 0.7, H-3'). ^{13}C NMR spectrum, δ, ppm: 14.0; 16.3; 24.2; 48.3; 58.9; 98.8; 104.5; 110.3; 129.2; 137.8; 145.5; 147.6; 153.8; 161.3; 161.8. Found, %: C 59.95; H 5.39; N 23.64. $C_{15}H_{17}N_5O_2$. Calculated, %: C 60.19; H 5.72; N 23.40.

Compound 31. Yield 80 mg (10%), white crystals, mp 65–66°C (mp 65–66°C)[9], R_f 0.67 (1:1 benzene–Me_2CO).

Compound 33. Yield 80 mg (16%), white crystals, mp 175–176°C (mp 175–178°C)[18], R_f 0.35 (2:1 benzene–Me_2CO). The physicochemical and spectral characteristics of compounds **31**[9] and **33**[18] matched the literature.

Reaction of iodide 1 with 3-(1*H*-pyrazol-1-yl)propionic acid hydrazide (13). A solution of iodide **1** (1.68 g, 5 mmol) in abs. EtOH (10 ml) was mixed with a solution of hydrazide **13** (1.54 g, 10 mmol) in abs. EtOH (10 ml). The reaction mixture was refluxed for 36 h, then ethanol was evaporated, the oily residue was treated with hot hexane. Hexane was evaporated, the residue was separated by silica gel column chromatography (3:1 benzene–Me_2CO), giving **ethyl 5,7-dimethyl-2-[2-(1*H*-pyrazol-1-yl)ethyl]pyrazolo-**

[1,5-*a*]pyrimidine-3-carboxylate (22), compound **29** (150 mg, 18%), and compound **31** (70 mg, 7%).

Compound 22. Yield 0.6 g (38%), white crystals, mp 118–120°C (hexane), R_f 0.6 (2:1 benzene–Me_2CO). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.42 (3H, t, *J* = 7.1, $OCH_2C\underline{H}_3$); 2.62 (3H, s, CH_3); 2.72 (3H, d, *J* = 0.8, CH_3); 3.53–3.59 (2H, m, $C\underline{H}_2CH_2N$); 4.35 (2H, q, *J* = 7.1, $OC\underline{H}_2CH_3$); 4.49–4.55 (2H, m, $CH_2C\underline{H}_2N$); 6.11 (1H, dd, *J* = 2.3, *J* = 1.8, H-4'); 6.89 (1H, q, *J* = 0.8, H-6); 7.32 (1H, dd, *J* = 1.8, *J* = 0.6, H-5'); 7.48 (1H, dd, *J* = 2.3, *J* = 0.6, H-3'). ^{13}C NMR spectrum, δ, ppm: 14.1; 16.3; 24.2; 29.8; 49.7; 58.7; 98.8; 104.3; 109.7; 128.4; 138.0; 145.1; 147.8; 156.4; 160.8; 162.1. Found, %: C 61.59; H 6.30; N 22.61. $C_{16}H_{19}N_5O_2$. Calculated, %: C 61.33; H 6.11; N 22.35.

Reaction of iodide 1 with 3-(3,5-dimethyl-1*H*-pyrazol-1-yl)propionic acid hydrazide (14). A solution of iodide **1** (1.68 g, 5 mmol) and hydrazide **14** (1.82 g, 10 mmol) in abs. EtOH (20 ml) was refluxed for 20 h. After the reaction was complete, ethanol was evaporated, the oily residue was treated with hexane, resulting in crystallization. The crystals were filtered off and treated with Me_2CO (3 ml), the insoluble residue was filtered off and washed on filter with acetone, yielding hydroiodide of the unreacted 3-(3,5-dimethyl-1*H*-pyrazol-1-yl)propionic acid hydrazide (0.60 g, 67%), mp 170–171°C (neutralization of aqueous solution of the isolated salt with dilute KOH solution gave a precipitate of hydrazide **14**, mp 125–126°C; the 1:1 ratio of hydrazide : HI was established by titration). The filtrate was evaporated, the residue was separated by silica gel column chromatography (2:1 benzene–Me_2CO), giving **ethyl 5,7-dimethyl-2-[2-(3,5-dimethyl-1*H*-pyrazol-1-yl)-ethyl]pyrazolo[1,5-*a*]pyrimidine-3-carboxylate (23)**, compound **29** (0.29 g, 25%), compound **30** (0.07 g, 7%), and compound **31** (0.10 g, 10%).

Compound 23. Yield 0.44 g (26%), white crystals, mp 155–156°C (hexane), R_f 0.51 (1:1 benzene–Me_2CO). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.45 (3H, t, *J* = 7.1, $OCH_2C\underline{H}_3$); 2.19 (3H, s, 5'-CH_3); 2.25 (3H, s, 3'-CH_3); 2.65 (3H, s, 7-CH_3); 2.74 (3H, s, 5-CH_3); 3.58–3.64 (2H, m, $C\underline{H}_2CH_2N$); 4.40–4.47 (2H, m, $CH_2C\underline{H}_2N$); 4.44 (2H, q, *J* = 7.1, $OC\underline{H}_2CH_3$); 5.73 (1H, s, H-4'); 6.67 (1H, s, H-6). ^{13}C NMR spectrum, δ, ppm: 10.9; 12.2; 14.7; 17.3; 25.3; 29.6; 49.4; 60.3; 96.3; 105.1; 106.0; 110.2; 142.0; 145.9; 148.8; 156.4; 162.2; 163.3. Mass spectrum *m*/*z* (I_{rel}, %): 342 (20), 341 $[M]^+$ (100), 313 (39), 270 (9), 269 (45), 248 (11), 245 (10), 217 (10), 173 (28), 132 (21). Found, %: C 63.59; H 6.71; N 20.70. $C_{18}H_{23}N_5O_2$. Calculated, %: C 63.32; H 6.79; N 20.51.

Reaction of iodide 1 with 3-(4-bromo-3-methyl-1*H*-pyrazol-1-yl)propionic acid hydrazide (15). A solution of iodide **1** (1.68 g, 5 mmol) in abs. EtOH (10 ml) was mixed with a solution of hydrazide **15 (**2.47 g, 10 mmol) in abs. EtOH (15 ml). The reaction mixture was refluxed for 40 h, then ethanol was evaporated, the oily residue was treated with hot hexane. Hexane was evaporated, the residue was separated by silica gel column chromatography (3:1 benzene–Me_2CO), giving **ethyl 2-[2-(4-bromo-3-methyl-1*H*-pyrazol-1-yl)ethyl]-5,7-dimethylpyrazolo[1,5-*a*]pyrimidine-3-carboxylate (24)**, hydroxy derivative **29** (0.05 g, 6%), pyridine derivative **30** (0.10 g, 10%), and demethylation product **31** (0.05 g, 5%).

Compound 24. Yield 1.10 g (54%), white crystals, mp 128–130°C (hexane), R_f 0.5 (2:1 benzene–Me_2CO). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.42 (3H, t, *J* = 7.1, $OCH_2C\underline{H}_3$); 2.16 (3H, s, 3'-CH_3); 2.62 (3H, s, 5-CH_3); 2.72 (3H, d, *J* = 0.9, 7-CH_3); 3.50–3.56 (2H, m, $C\underline{H}_2CH_2N$); 4.35 (2H, q, *J* = 7.1, $OC\underline{H}_2CH_3$); 4.39–4.45 (2H, m, $CH_2C\underline{H}_2N$); 6.90 (1H, q, *J* = 0.9, H-6); 7.53 (1H, s, H-5'). ^{13}C NMR spectrum, δ, ppm: 11.2; 14.1; 16.3; 24.2; 29.5; 50.1; 58.7; 91.8; 98.8; 109.7; 129.2; 144.9; 145.4; 147.7; 156.2; 160.8; 162.1. Found, %: C 50.51; H 4.75; N 17.45. $C_{17}H_{20}BrN_5O_2$. Calculated, %: C 50.26; H 4.96; N 17.24.

Reaction of iodide 1 with 3-(4-bromo-3,5-dimethyl-1*H*-pyrazol-1-yl)propionic acid hydrazide (16). A solution of iodide **1** (1.68 g, 5 mmol) in abs. EtOH (10 ml) was mixed with a solution of hydrazide **16** (2.61 g, 10 mmol) in abs. EtOH (10 ml). The reaction mixture was heated for 40 h in a sealed ampoule at 90–100°C, then ethanol was evaporated, and the oily residue was treated with hot hexane. Hexane was evaporated, the residue was separated by silica gel column chromatography (3:1 benzene–Me_2CO), giving **ethyl 2-[2-(4-bromo-3,5-dimethyl-1*H*-pyrazol-1-yl)ethyl]-5,7-dimethylpyrazolo[1,5-*a*]pyrimidine-3-carboxylate (25)**, as well as compound **29** (0.10 g, 12%), pyridine derivative **30** (0.09 g, 9%), and demethylation product **31** (0.05 g, 4%).

Compound 25. Yield 1.05 g (50%), white crystals, mp 151–153°C (hexane), R_f 0.6 (2:1 benzene–Me_2CO). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.42 (3H, t, *J* = 7.1, $OCH_2C\underline{H}_3$); 2.12 (3H, s, 3'(5')-CH_3); 2.24 (3H, s, 5'(3')-CH_3); 2.62 (3H, s, 5-CH_3); 2.72 (3H, d, *J* = 0.9, 7-CH_3); 3.43–3.50 (2H, m, $C\underline{H}_2CH_2N$); 4.32–4.38 (2H, m, $CH_2C\underline{H}_2N$); 4.36 (2H, q, *J* = 7.1, $OC\underline{H}_2CH_3$); 6.90 (1H, q, *J* = 0.9, H-6). ^{13}C NMR spectrum, δ, ppm: 9.4; 11.7; 14.1; 16.3; 24.2; 29.3; 47.7; 58.8; 92.5; 98.9; 109.8; 135.9; 144.3; 145.0; 147.7; 156.3; 160.9; 162.2. Found, %: C 51.59; H 5.11; N 16.45. $C_{18}H_{22}BrN_5O_2$. Calculated, %: C 51.44; H 5.28; N 16.66.

Reaction of iodide 1 with 2-(4-chloro-3-methyl-1*H*-pyrazol-1-yl)propionic acid hydrazide (17). A solution of iodide **1** (1.68 g, 5 mmol) in abs. EtOH (10 ml) was mixed with a solution of hydrazide **17** (2.03 g, 10 mmol) in abs. EtOH (10 ml). The reaction mixture was refluxed for 36 h, then ethanol was evaporated, the oily residue was treated with hot hexane. Hexane was evaporated, the residue was separated by silica gel column chromatography (3:1 benzene–Me_2CO), giving **ethyl 2-[2-(4-chloro-3-methyl-1*H*-pyrazol-1-yl)ethyl]-5,7-dimethylpyrazolo[1,5-*a*]pyrimidine-3-carboxylate** (**26**), compound **29** (0.10 g, 12%), and demethylation product **31** (0.09 g, 9%).

Compound 26. Yield 0.75 g (42%), white crystals, mp 135–137°C (hexane), R_f 0.7 (2:1 benzene–Me_2CO). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.42 (3H, t, *J* = 7.1, $OCH_2C\underline{H}_3$); 2.15 (3H, s, 3'-CH_3); 2.62 (3H, s, 5-CH_3); 2.72 (3H, d, *J* = 0.8, 7-CH_3); 3.49–3.55 (2H, m, $C\underline{H}_2CH_2N$); 4.35 (2H, q, *J* = 7.1, $OC\underline{H}_2CH_3$); 4.38–4.43 (2H, m, $CH_2C\underline{H}_2N$); 6.90 (1H, q, *J* = 0.8, H-6); 7.51 (1H, s, H-5'). ^{13}C NMR spectrum, δ, ppm: 10.4; 14.1; 16.3; 24.2; 29.5;

50.1; 58.7; 98.8; 107.0; 109.7; 126.9; 143.7; 145.0; 147.7; 156.2; 160.8; 162.1. Found, %: C 56.19; H 5.41; N 19.55. $C_{17}H_{20}ClN_5O_2$. Calculated, %: C 56.43; H 5.57; N 19.36.

Reaction of iodide 1 with (1*H*-1,2,4-triazol-1-yl)acetic acid hydrazide (18). A solution of iodide **1** (0.84 g, 2.5 mmol) in abs. EtOH (10 ml) was mixed with a solution of hydrazide **18** (0.71 g, 5 mmol) in abs. EtOH (8 ml). The reaction mixture was refluxed for 40 h, then ethanol was evaporated, and the oily residue was treated with hot hexane. Hexane was evaporated, the residue was separated by silica gel column chromatography (2:1 benzene–Me_2CO), giving **ethyl 5,7-dimethyl-2-(1,2,4-triazol-1-yl-methyl)pyrazolo[1,5-*a*]pyrimidine-3-carboxylate (27)**, hydroxypyrazolo[1,5-*a*]pyrimidine **29** (0.03 g, 8%), demethylation product **31** (0.05 g, 10%), and **(1*H*-1,2,4-triazol-1-yl)-acetic acid (34)**.

Compound 27. Yield 0.23 g (31%), white crystals, mp 193–195°C (hexane), R_f 0.4 (1:1 benzene–Me_2CO). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.40 (3H, t, *J* = 7.1, $CH_2C\underline{H}_3$); 2.63 (3H, s, 5-CH_3); 2.73 (3H, d, *J* = 0.9, 7-CH_3); 4.36 (2H, q, *J* = 7.1, OCH_2); 5.79 (2H, s, CH_2); 6.97 (1H, q, *J* = 0.9, H-6); 7.72 (1H, s, H-3'); 8.34 (1H, s, H-5'). ^{13}C NMR spectrum, δ, ppm: 14.0; 16.2; 24.2; 46.2; 59.0; 98.8; 110.4; 143.7; 145.6; 147.6; 150.4; 152.8; 161.6; 161.9. Found, %: C 56.15; H 5.59; N 28.25. $C_{14}H_{16}N_6O_2$. Calculated, %: C 55.99; H 5.37; N 27.98.

Compound 34. Yield 40 mg (13%), white crystals, mp 196–199°C (mp 199–202°C)[15], R_f 0.2 (1:1 benzene–Me_2CO). The physicochemical and spectral characteristics of carboxylic acid **34** matched those of a sample obtained by the opposite route of synthesis (ethyl ester hydrolysis) according to a published procedure.[15]

Reaction of iodide 1 with 2-methyl-3-(3-methyl-1*H*-pyrazol-1-yl)propionic acid hydrazide (19). A solution of iodide **1** (1.00 g, 3 mmol) in abs. EtOH (10 ml) was mixed with a solution of hydrazide **19** (1.09 g, 6 mmol) in abs. EtOH (10 ml). The reaction mixture was refluxed for 40 h, then ethanol was evaporated, the oily residue was treated with hot hexane. Hexane was evaporated, the residue was separated by silica gel column chromatography (1:1 benzene–Me_2CO), giving **ethyl 5,7-dimethyl-2-[1-methyl-2-(3-methyl-1*H*-pyrazol-1-yl)-ethyl]pyrazolo[1,5-*a*]pyrimidine-3-carboxylate (28)**, hydroxypyrazolo[1,5-*a*]pyrimidine **29** (0.07 g, 14%), and demethylation product **31** (0.09 g, 16%).

Compound 28. Yield 0.35 g (34%), white crystals, mp 78–80°C (hexane), R_f 0.6 (2:1 benzene–Me_2CO). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.26 (3H, d, *J* = 6.2, $CHC\underline{H}_3$); 1.41 (3H, t, *J* = 7.1, $OCH_2C\underline{H}_3$); 2.18 (3H, s, 3'-CH_3); 2.61 (3H, s, 5-CH_3); 2.74 (3H, d, *J* = 0.9, 7-CH_3); 4.09–4.25 (2H, m, CH_2N); 4.34 (2H, q, *J* = 7.1, $OC\underline{H}_2CH_3$); 4.43–4.53 (1H, m, $C\underline{H}CH_3$); 5.84 (1H, d, *J* = 2.1, H-4'); 6.88 (1H, q, *J* = 0.9, H-6); 7.30 (1H, d, *J* = 2.1, H-5'). ^{13}C NMR spectrum, δ, ppm: 13.1; 14.1; 16.3; 17.0; 24.2; 33.9; 55.2; 58.7; 98.4; 103.8; 109.6; 129.6; 145.0; 146.5; 147.9; 160.7; 161.0; 162.1. Found, %: C 63.57; H 6.91; N 20.61. $C_{18}H_{23}N_5O_2$. Calculated, %: C 63.32; H 6.79; N 20.51.

X-ray structural analysis of compound 26 was performed at room temperature on an Enraf-Nonius CAD-4 automated diffractometer (graphite monochromator, MoKα radiation, ω-scanning). The parameters of monoclinic unit cell were determined and refined by 24 reflections with θ 13.1...14.2°. The correction for absorption was introduced by experimental azimuthal scan curves (T_{min} 0.56262, T_{max} 0.60134).[19] The structure was solved directly, hydrogen atom coordinates were partially determined by differential Fourier synthesis. The methyl group hydrogen atoms were calculated geometrically and refined by the "rider" model with the following constraints: C–H bond length 0.96 Å, $U_{iso}(H) = 1.5U_{eq}(C)$. The structure was refined by full matrix method of least squares in anisotropic approximation for non-hydrogen atoms and isotropically for hydrogen atoms. All structural calculations were performed with the SHELXTL software suite.[20]

The crystallographic data were deposited at the Cambridge Crystallographic Data Center (deposit CCDC 1005179).

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