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4-Functionally Substituted 3-Heterylpyrazoles: XIV.* *N*-Benzyl-*N*-[3-aryl(heteryl)-4-pyrazolylmethylene]amines and Their Derivatives

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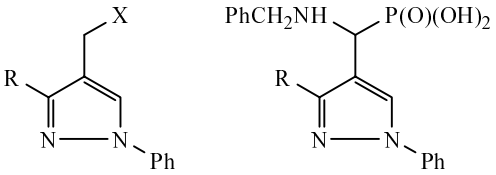
Abstract—Reduction with sodium tetrahydridoborate of Schiff bases derived from 3-aryl(heteryl)pyrazole-4-carbaldehydes and benzylamines gave *N*-benzyl-*N*-[3-aryl(heteryl)-4-pyrazolylmethylene]amines which were acylated with benzoyl chloride and succinic and maleic anhydrides to obtain the corresponding amides. Treatment of the title compounds with phenyl isothiocyanate afforded substituted thioureas.

We previously described [2–4] a series of new functionalized 3-aryl(heteryl)pyrazole derivatives in which functional substituent is linked to the C^4 atom of the pyrazole ring through a CH_2 or CH unit. The present communication reports on the synthesis and some general transformations of *N*-benzyl-*N*-(4-pyrazolyl)methanamines. Except for 3,5-diaminomethyl-1-phenylpyrazole [5], there are no published data on such compounds.

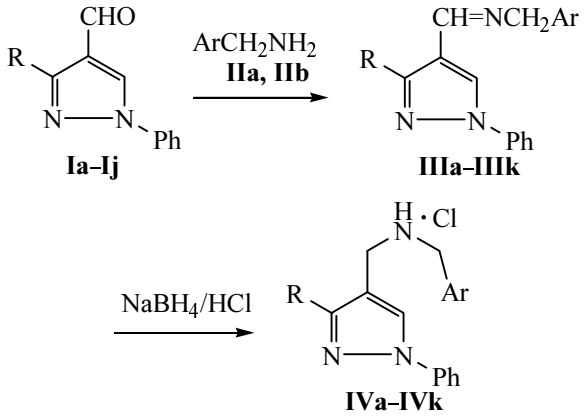


X = Cl, OH, CH, SCN, NCS.

As initial compounds we used pyrazole-4-carbaldehydes **Ia**–**Ij**; they were treated with benzylamines **IIa** and **IIb** according to the procedure developed by us previously [4]. Schiff bases **IIIa**–**IIIk** thus obtained were reduced with sodium tetrahydridoborate under mild conditions (Scheme 1). The reduction products, *N*-benzyl-*N*-[3-aryl(heteryl)-4-pyrazolylmethyl]amines, were undistillable viscous oily liquids. Their analytically pure samples were isolated as hydrochlorides **IVa**–**IVk**. Compounds **IVh** and **IVi** possessing a pyridine substituent in position *3* of the pyrazole ring were the corresponding dihydrochlorides.

Hydrochlorides **IVa**–**IVk** are colorless high-melting crystalline substances. Their structure was confirmed by

Scheme 1.



I, R = Ph (a), 4-BrC_6H_4 (**b**), 4-ClC_6H_4 (**c**), 4-FC_6H_4 (**d**), 4-MeC_6H_4 (**e**), 4-$MeOC_6H_4$ (**f**), 2-thienyl (**g**), 3-pyridyl (**h**), 4-pyridyl (**i**), 2-benzofuryl (**j**); **II**, Ar = Ph (**a**), 4-FC_6H_4 (**b**); **III**, **IV**, Ar = R = Ph (**a**); Ar = Ph, R = 4-BrC_6H_4 (**b**), 4-ClC_6H_4 (**c**), 4-FC_6H_4 (**d**), 4-MeC_6H_4 (**e**), 4-$MeOC_6H_4$ (**f**), 2-thienyl (**g**), 3-pyridyl (**h**), 4-pyridyl (**i**), 2-benzofuryl (**j**); Ar = 4-FC_6H_4, R = 4-$MeOC_6H_4$ (**k**).

the ^1H NMR spectra which contained singlets at δ 8.8–9.1 ppm typical of the 5-H proton in the pyrazole ring. As a rule, signals from the methylene protons overlap each other and appear as a broadened singlet or multiplet at δ 4.2–4.3 ppm. Exceptions are compounds **IVd**, **IVh**, and **IVj**; in their ^1H NMR spectra the singlet from the methylene group attached to the pyrazole ring is displaced slightly downfield relative to the signal from the benzyl methylene protons.

* For communication XIII, see [1].

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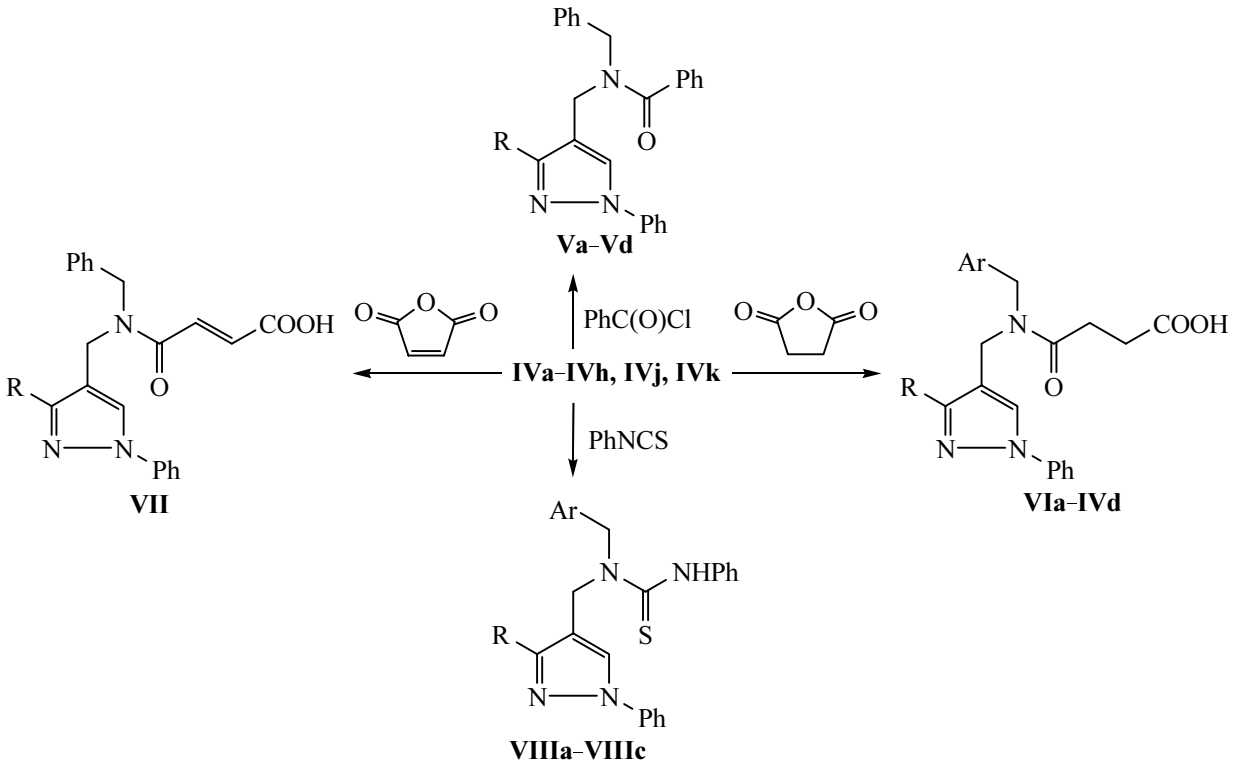
Scheme 2.



We examined the behavior of amine hydrochlorides **IVa**–**IVh**, **IVj**, and **IVk** in reactions with typical electrophiles such as benzoyl chloride, succinic and maleic anhydrides, and phenyl isothiocyanate. These reactions were complete in 3 h on heating in acetonitrile (in reactions with phenyl isothiocyanate, it is better to use ethanol as solvent) in the presence of an organic base. We thus obtained a series of new N,N-disubstituted benzamides **Va**–**Vd**, succinamic acids **VIa**–**VId**, maleamic acid **VII**, and thioureas **VIIIa**–**VIIIc** (Scheme 2).

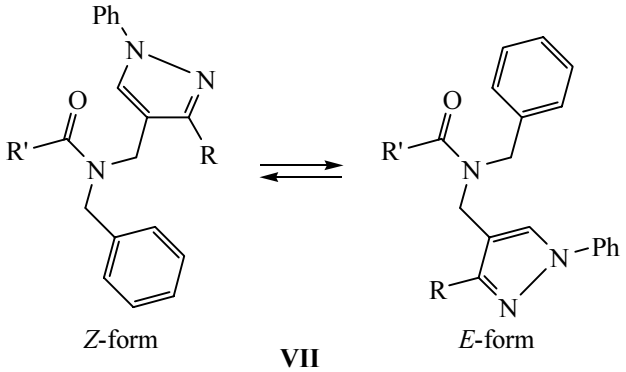
In the ^{1}H NMR spectra of amides **V**–**VII** in DMSO-d_6 we observed more complex signals from the methylene protons, 5-H, and α-CH= (**VII**). Protons of the methylene groups gave rise to a multiplet consisting of three overlapping signals, the intensity of one of these being approximately equal to the overall intensity of the two other signals. The 5-H proton appeared as two nearby singlets with approximately equal intensities, and the β-CH= proton in **VII** gave two doublets. This pattern is likely to result from the existence of compounds **V**–**VII** in DMSO-d_6 as mixtures of stereoisomers due to restricted rotation about the amide C–N bond [6] (Scheme 3); accurate assignment of signals to particular isomers requires an additional study.

Thioureas **VIIIa**–**VIIIc** are characterized by a higher barrier to rotation about the C–N bond, as compared to amides [7, 8]; therefore, they exist in DMSO-d_6 exclusively as the corresponding *E* isomers, in keeping with the presence in their ^{1}H NMR spectra of singlet signals from the above protons.

EXPERIMENTAL

The IR spectra were recorded on a UR-20 spectrometer from samples prepared as KBr pellets. The

Scheme 3.



R' = Ph, CH=CHCOOH, CH_2CH_2COOH.

^{1}H NMR spectra were measured on a Varian Gemini instrument (300 MHz) using DMSO-d_6 as solvent and TMS as internal reference.

Compounds **IIIa**–**IIIc** and **IIIg** were synthesized by the procedure reported in [4].

***N*-Benzyl-*N*-[3-aryl(heteryl)-1-phenyl-1*H*-pyrazol-4-ylmethylene]amines IIId–IIIf and IIIh–IIIk (*general procedure*).** Benzylamine **IIa** or **IIb**, 0.01 mol, and glacial acetic acid, 0.2 ml, were added to a solution of 0.01 mol of aldehyde **Id**–**If** or **Ih**–**Ij** in 20 ml of toluene, and the mixture was heated for 1 h in a flask equipped with a Dean–Stark trap. The mixture was cooled, the solvent was distilled off, the residue was treated with 3 ml of diethyl ether and 5 ml of hexane, and the precipitate was filtered off and recrystallized from ethanol.

Compound **IIId**. Yield 79%, mp 65–66°C. ^{1}H NMR spectrum, δ, ppm: 4.72 s (2H, CH_2), 7.23–7.97 m (14H, H_{arom}), 8.49 s (1H, 5-H), 8.94 s (1H, CH=). Found, %: C 77.53; H 4.98; N 11.69. $C_{23}H_{18}FN_3$. Calculated, %: C 77.74; H 5.07; N 11.83.

Compound **IIIe**. Yield 75%, mp 107–108°C. ^{1}H NMR spectrum, δ, ppm: 2.42 s (3H, CH_3), 4.72 s (2H, CH_2), 7.28–7.90 m (14H, H_{arom}), 8.46 s (1H, 5-H), 8.78 s (1H, CH=). Found, %: C 81.97; H 5.89; N 11.87. $C_{24}H_{21}N_3$. Calculated, %: C 82.05; H 5.98; N 11.96.

Compound **IIIf**. Yield 73%, mp 101–103°C. ^{1}H NMR spectrum, δ, ppm: 3.85 s (3H, CH_3O), 4.75 s (2H, CH_2), 7.05 d (2H, H_{arom}, J = 7.8 Hz), 7.26–7.50 m (8H, H_{arom}), 7.69 d (2H, H_{arom}, J = 7.8 Hz), 7.97 d (2H, H_{arom}, J = 7.7 Hz), 8.50 s (1H, 5-H), 8.88 s (1H, CH=). Found, %: C 78.69; H 5.60; N 11.28. $C_{24}H_{21}N_3O$. Calculated, %: C 78.47; H 5.72; N 11.44.

Compound **IIIh**. Yield 82%, mp 99–100°C. ^{1}H NMR spectrum, δ, ppm: 4.77 s (2H, CH_2), 7.31–7.95 m (10H, H_{arom}), 8.18 d (2H, H_{arom}, J = 7.6 Hz), 8.62 m (1H, H_{arom}), 8.90 s (1H, H_{arom}), 8.53 s (1H, 5-H), 8.97 s (1H, CH=). Found, %: C 77.81; H 5.19; N 16.39. $C_{22}H_{18}N_4$. Calculated, %: C 78.10; H 5.32; N 16.56.

Compound **IIIi**. Yield 76%, mp 92–93°C. ^{1}H NMR spectrum, δ, ppm: 4.79 s (2H, CH_2), 7.25–7.51 m (8H, H_{arom}), 7.83 d (1H, H_{arom}, J = 6.0 Hz), 7.94 d (2H, H_{arom}, J = 7.8 Hz), 8.64 d (1H, H_{arom}, J = 6.0 Hz), 8.59 s (1H, 5-H), 8.91 s (1H, CH=). Found, %: C 77.93; H 5.47; N 16.30. $C_{22}H_{18}N_4$. Calculated, %: C 78.10; H 5.32; N 16.56.

Compound **IIIj**. Yield 88%, mp 128–130°C. ^{1}H NMR spectrum, δ, ppm: 4.76 s (2H, CH_2), 7.03–7.94 m (15H, H_{arom}), 8.53 s (1H, 5-H), 8.96 s (1H, CH=). Found, %: C 79.31; H 4.86; N 11.33. $C_{25}H_{19}N_3O$. Calculated, %: C 79.57; H 5.04; N 11.14.

Compound **IIIk**. Yield 83%, mp 112–113°C. ^{1}H NMR spectrum, δ, ppm: 3.82 s (3H, CH_3O), 4.75 s (2H, CH_2), 7.03 d (2H, H_{arom}, J = 7.8 Hz), 7.30–7.49 m (7H, H_{arom}), 7.65 d (2H, H_{arom}, J = 7.8 Hz), 7.93 d (2H, H_{arom}, J = 7.7 Hz), 8.53 s (1H, 5-H), 8.83 s (1H, CH=). Found, %: C 74.56; H 5.02; N 10.70. $C_{24}H_{20}FN_3O$. Calculated, %: C 74.80; H 5.19; N 10.91.

***N*-Benzyl-*N*-[3-aryl(heteryl)-1-phenyl-1*H*-pyrazol-4-ylmethyl]amines IVa–IVk (*general procedure*).** A solution of 0.003 mol of Schiff base **IIIa**–**IIIk** in 40 ml of methanol was heated to 50–55°C, and a suspension of 1 g of sodium tetrahydridoborate in 50 ml of ethanol was added. The mixture was left to stand for 3 h at room temperature, diluted with 100 ml of water, and extracted with benzene (3 × 40 ml). The extract was dried over anhydrous sodium sulfate and saturated with dry hydrogen chloride, and the precipitate was filtered off and dried under reduced pressure.

Compound **IVa**. Yield 91%, mp 215–216°C. ^{1}H NMR spectrum, δ, ppm: 4.21 br.s (4H, CH_2), 7.39–7.83 m (15H, H_{arom}), 8.88 s (1H, 5-H), 9.78 br.s (2H, H_2N^+). Found, %: C 73.15; H 5.63; N 11.01. $C_{23}H_{22}ClN_3$. Calculated, %: C 73.50; H 5.85; N 11.18.

Compound **IVb**. Yield 93%, mp 228–229°C. ^{1}H NMR spectrum, δ, ppm: 4.22–4.24 m (4H, CH_2), 7.24–7.79 m (14H, H_{arom}), 8.88 s (1H, 5-H), 9.79 br.s (2H, H_2N^+). Found, %: C 60.39; H 4.47; N 9.03. $C_{23}H_{21}BrClN_3$. Calculated, %: C 60.72; H 4.62; N 9.24.

Compound **IVc**. Yield 91%, mp 210–211°C. ^{1}H NMR spectrum, δ, ppm: 4.23 br.s (4H, CH_2), 7.28–7.83 m (14H, H_{arom}), 8.90 s (1H, 5-H), 9.80 br.s (2H, H_2N^+). Found, %: C 67.69; H 5.21; N 10.03. $C_{23}H_{21}Cl_2N_3$. Calculated, %: C 67.32; H 5.12; N 10.24.

Compound **IVd**. Yield 86%, mp 212–214°C. ^{1}H NMR spectrum, δ, ppm: 4.21–4.24 m (4H, CH_2), 7.20–7.80 m (14H, H_{arom}), 8.80 s (1H, 5-H), 9.79 br.s (2H, H_2N^+). Found, %: C 69.90; H 5.15; N 10.48. $C_{23}H_{21}ClFN_3$. Calculated, %: C 70.14; H 5.33; N 10.67.

Compound **IVe**. Yield 78%, mp 219–221°C. ^{1}H NMR spectrum, δ, ppm: 2.36 s (3H, CH_3), 4.28–4.30 m (4H, CH_2), 7.26–7.52 m (10H, H_{arom}), 7.60 d (2H, H_{arom}, J = 7.8 Hz), 7.90 d (2H, H_{arom}, J = 7.9 Hz), 8.98 s (1H, 5-H), 9.84 br.s (2H, H_2N^+). Found, %: C 74.28; H 5.98; N 10.56. $C_{24}H_{24}ClN_3$. Calculated, %: C 73.94; H 6.16; N 10.78.

Compound **IVf**. Yield 77%, mp 217–218°C. ^{1}H NMR spectrum, δ, ppm: 3.72 s (3H, CH_3O), 4.29 br.s (4H, CH_2), 7.04 d (2H, H_{arom}, J = 7.9 Hz), 7.22–7.53 m (8H, H_{arom}), 7.66 d (2H, H_{arom}, J = 7.9 Hz), 7.94 d (2H, H_{arom}, J = 7.8 Hz), 8.96 s (1H, 5-H), 9.83 br.s (2H, H_2N^+). Found, %: C 70.73; H 5.70; N 10.08. $C_{24}H_{24}ClN_3O$. Calculated, %: C 71.02; H 5.92; N 10.36.

Compound **IVg**. Yield 81%, mp 187–189°C. ^{1}H NMR spectrum, δ, ppm: 4.27 br.s (4H, CH_2), 7.13–7.80 m (13H, H_{arom}), 8.82 s (1H, 5-H), 9.76 br.s (2H, H_2N^+). Found, %: C 66.31; H 5.16; N 10.83. $C_{21}H_{20}ClN_3S$. Calculated, %: C 66.05; H 5.24; N 11.07.

Compound **IVh**. Yield 73%, mp 208–209°C. ^{1}H NMR spectrum, δ, ppm: 4.24 br.s (4H, CH_2), 7.38–7.84 m (12H, H_{arom}), 8.23 d (1H, H_{arom}, J = 8.1 Hz), 8.72 s (1H, H_{arom}), 8.95 s (1H, 5-H), 9.84 br.s (2H, H_2N^+). Found, %: C 63.40; H 5.17; N 13.41. $C_{22}H_{22}Cl_2N_4$. Calculated, %: C 63.11; H 5.30; N 13.49.

Compound **IVi**. Yield 77%, mp 222–223°C. ^{1}H NMR spectrum, δ, ppm: 4.28 s (2H, CH_2), 4.40 s (2H, CH_2), 7.41–7.66 m (8H, H_{arom}), 7.89 d (2H, H_{arom}, J = 7.9 Hz), 8.35 d (2H, H_{arom}, J = 7.8 Hz), 8.97 d (2H, H_{arom}, J = 7.8 Hz), 9.10 s (1H, 5-H), 10.19 br.s (2H, H_2N^+). Found, %: C 63.43; H 5.45; N 13.30. $C_{22}H_{22}Cl_2N_4$. Calculated, %: C 63.11; H 5.30; N 13.49.

Compound **IVj**. Yield 85%, mp 228–230°C. ^{1}H NMR spectrum, δ, ppm: 4.32 s (2H, CH_2), 4.44 s (2H, CH_2), 7.29–7.69 m (13H, H_{arom}), 7.88 d (2H, H_{arom}, J = 7.8 Hz), 8.93 s (1H, 5-H), 9.88 br.s (2H, H_2N^+). Found, %: C 71.88; H 5.13; N 10.02. $C_{25}H_{22}ClN_3O$. Calculated, %: C 72.20; H 5.29; N 10.10.

Compound **IVk**. Yield 79%, mp 214–216°C. ^{1}H NMR spectrum, δ, ppm: 3.78 s (3H, CH_3O), 4.28 br.s (4H, CH_2), 7.08 d (2H, H_{arom}, J = 7.8 Hz), 7.29–7.51 m (7H, H_{arom}), 7.64 d (2H, H_{arom}, J = 7.8 Hz), 7.94 d (2H, H_{arom}, J = 7.8 Hz), 8.95 s (1H, 5-H), 9.90 br.s (2H, H_2N^+). Found, %: C 68.20; H 5.15; N 9.90. $C_{24}H_{23}ClFN_3O$. Calculated, %: C 68.00; H 5.47; N 9.91.

***N*-Benzyl-*N*-[3-aryl(heteryl)-1-phenyl-1*H*-pyrazol-4-ylmethyl]benzamides Va–Vd, *N*-benzyl-*N*-[3-aryl-1-phenyl-1*H*-pyrazol-4-ylmethyl]-succinamic acids VIa–VId, and *N*-benzyl-*N*-[3-(4-methoxyphenyl)-1-phenyl-1*H*-pyrazol-4-yl-methyl]maleamic acid (VII).** Benzoyl chloride, maleic anhydride, or succinic anhydride, 0.001mol, and triethylamine, 0.001 mol (with succinic or maleic anhydride) or 0.002 mol (with benzoyl chloride), were added to a suspension of 0.001 mol of hydrochloride **IVa**–**IVe**, **IVj**, or **IVk** in 10 ml of acetonitrile. The mixture was heated for 3 h under reflux, and 2 ml of water and 1 ml of ethanol were added to the hot mixture. The mixture was cooled, and the precipitate was filtered off, washed with water, dried, and recrystallized from ethanol (**Va**–**Vd**) or benzene (**VIa**–**VId**, **VII**).

Compound **Va**. Yield 75%, mp 115–116°C. IR spectrum: ν C=O 1715 cm^{-1}. ^{1}H NMR spectrum, δ, ppm: 4.38–4.58 m (4H, CH_2), 7.03–7.56 m (18H, H_{arom}), 7.92 d (2H, H_{arom}, J = 7.8 Hz), 8.31 s and 8.48 s (1H, 5-H). Found, %: C 80.97; H 5.51; N 9.33. $C_{30}H_{25}N_3O$. Calculated, %: C 81.26; H 5.64; N 9.48.

Compound **Vb**. Yield 70%, mp 130–131°C. IR spectrum: ν C=O 1710 cm^{-1}. ^{1}H NMR spectrum, δ, ppm: 4.36–4.60 m (4H, CH_2), 7.11–7.79 m (17H, H_{arom}), 7.88 d (2H, H_{arom}, J = 7.9 Hz), 8.35 s and 8.49 s (1H, 5-H). Found, %: C 75.16; H 4.91; N 8.58. $C_{30}H_{24}ClN_3O$. Calculated, %: C 75.39; H 5.03; N 8.79.

Compound **Vc**. Yield 76%, mp 122–123°C. IR spectrum: ν C=O 1710 cm^{-1}. ^{1}H NMR spectrum, δ, ppm: 2.34 s (3H, CH_3), 4.35–4.56 m (4H, CH_2), 7.07–7.51 m (17H, H_{arom}), 7.88 d (2H, H_{arom}, J = 7.8 Hz), 8.34 s and 8.51 s (1H, 5-H). Found, %: C 81.71; H 5.64; N 8.95. $C_{31}H_{27}N_3O$. Calculated, %: C 81.40; H 5.90; N 9.19.

Compound **Vd**. Yield 83%, mp 146–148°C. IR spectrum: ν C=O 1715 cm^{-1}. ^{1}H NMR spectrum, δ, ppm: 4.53–4.71 m (4H, CH_2), 6.99–7.62 m (18H, H_{arom}), 7.97 d (2H, H_{arom}, J = 7.9 Hz), 8.49 s and 8.61 s (1H, 5-H). Found, %: C 79.16; H 5.01; N 8.47. $C_{32}H_{25}N_3O_2$. Calculated, %: C 79.50; H 5.17; N 8.69.

Compound **VIa**. Yield 92%, mp 147–149°C. IR spectrum, ν, cm^{-1}: 1685, 1700 (C=O). ^{1}H NMR spectrum, δ, ppm: 2.41–2.71 m (4H, CH_2CH_2), 4.52–4.57 m (4H, CH_2), 7.10–7.83 m (15H, H_{arom}), 8.18 s and 8.36 s (1H, 5-H), 11.98 br.s (1H, COOH). Found, %: C 74.07; H 5.75; N 9.66. $C_{27}H_{25}N_3O_3$. Calculated, %: C 73.80; H 5.69; N 9.57.

Compound **VIb**. Yield 92%, mp 175–176°C. IR spectrum, ν, cm^{-1}: 1690, 1705 (C=O). ^{1}H NMR spectrum, δ, ppm: 2.45–2.74 m (4H, CH_2CH_2), 4.48–4.59 m (4H, CH_2), 7.07–7.83 m (14H, H_{arom}), 8.26 s and 8.37 s (1H, 5-H), 11.89 br.s (1H, COOH). Found, %: C 62.28; H 4.40; N 7.97. $C_{27}H_{24}BrN_3O_3$. Calculated, %: C 62.55; H 4.63; N 8.11.

Compound **VIc**. Yield 84%, mp 169–170°C. IR spectrum, ν, cm^{-1}: 1690, 1705 (C=O). ^{1}H NMR spectrum, δ, ppm: 2.38–2.74 m (4H, CH_2CH_2), 4.46–4.57 m (4H,

CH_2), 7.20–7.83 m (14H, H_{arom}), 8.27 s and 8.36 s (1H, 5-H), 12.01 br.s (1H, COOH). Found, %: C 70.66; H 5.17; N 8.95. $C_{27}H_{24}FN_3O_3$. Calculated, %: C 70.90; H 5.25; N 9.19.

Compound **VId**. Yield 88%, mp 165–166°C. IR spectrum, ν, cm^{-1}: 1680, 1700 (C=O). ^1H NMR spectrum, δ, ppm: 2.41–2.70 m (4H, CH_2CH_2), 3.81 s (3H, CH_3O), 4.48–4.54 m (4H, CH_2), 6.29–7.82 m (13H, H_{arom}), 8.15 s and 8.32 s (1H, 5-H), 11.98 br.s (1H, COOH). Found, %: C 69.35; H 5.19; N 8.40. $C_{28}H_{26}FN_3O_4$. Calculated, %: C 68.99; H 5.34; N 8.62.

Compound **VII**. Yield 80%, mp 155–156°C. IR spectrum, ν, cm^{-1}: 1695, 1705 (C=O). ^1H NMR spectrum, δ, ppm: 4.42–4.50 m (4H, CH_2), 5.98 d (J = 15.2 Hz), 6.06 d (1H, β-CH=, J = 15.2 Hz), 6.74 d (1H, α-CH=, J = 15.2 Hz), 6.91–7.45 m (11H, H_{arom}), 7.82 d (2H, H_{arom}, J = 8.0 Hz), 8.35 s and 8.38 s (1H, 5-H), 11.82 br.s (1H, COOH). Found, %: C 69.02; H 4.79; N 8.48. $C_{28}H_{24}FN_3O_4$. Calculated, %: C 69.28; H 4.95; N 8.66.

***N*-Benzyl-*N*-[3-aryl(heteryl)-1-phenyl-1*H*-pyrazol-4-ylmethyl)-*N*'-phenylthioureas VIIIa–VIIIc (*general procedure*).** To a solution of 0.001 mol of hydrochloride **IVf–IVh** in 10 ml of ethanol we added 0.001 mol (0.002 mol in the reaction with **IVh**) of triethylamine and 0.175 g (0.0013 mol) of phenyl isothiocyanate, and the mixture was heated for 1 h under reflux. The mixture was cooled, and the precipitate was filtered off, washed with water, dried, and recrystallized from acetic acid.

Compound **VIIIa**. Yield 70%, mp 154–157°C. IR spectrum: νNH 3355 cm^{-1}. ^1H NMR spectrum, δ, ppm: 3.81 s (3H, CH_3O), 5.02 s (2H, CH_2), 5.06 s (2H, CH_2), 6.96 d (2H, H_{arom}, J = 7.7 Hz), 7.18–7.49 m (13H, H_{arom}), 7.54 d (2H, H_{arom}, J = 7.7 Hz), 7.81 d (2H, H_{arom}, J = 7.6 Hz), 8.22 s (1H, 5-H, 9.36 s (1H, NH). Found, %: C 73.46; H 5.40; N 10.90. $C_{31}H_{28}N_4OS$. Calculated, %: C 73.81; H 5.55; N 11.11.

Compound **VIIIb**. Yield 68%, mp 131–133°C. IR spectrum: νNH 3360 cm^{-1}. ^1H NMR spectrum, δ, ppm: 5.09 s (2H, CH_2), 5.13 s (2H, CH_2), 7.09–7.53 m (16H, H_{arom}), 7.80 d (2H, H_{arom}, J = 7.6 Hz), 8.24 s (1H, 5-H), 9.42 s (1H, NH). Found, %: C 70.15; H 4.89; N 11.48. $C_{28}H_{24}N_4S_2$. Calculated, %: C 70.00; H 5.00; N 11.67.

Compound **VIIIc**. Yield 65%, mp 146–147°C. IR spectrum: νNH 3350 cm^{-1}. ^1H NMR spectrum, δ, ppm: 5.04 s (2H, CH_2), 5.13 s (2H, CH_2), 7.13–7.59 m (14H, H_{arom}), 7.84 d (2H, H_{arom}, J = 7.8 Hz), 8.01 d (1H, H_{arom}, J = 7.7 Hz), 8.55 d (1H, H_{arom}, J = 2.6 Hz), 8.84 s (1H, H_{arom}), 8.33 s (1H, 5-H), 9.38 s (1H, NH). Found, %: C 73.04; H 5.42; N 14.60. $C_{29}H_{25}N_5S$. Calculated, %: C 73.24; H 5.30; N 14.72.

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