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DIRECTED SYNTHESIS OF SEMICARBAZONES, THIOSEMICARBAZONES, AND GUANYLHYDRAZONES OF 1-VINYLPYRROLE-2-CARBALDEHYDES*

A. I. Mikhaleva[1], A. V. Ivanov[1], A. M. Vasil'tsov[1], I. A. Ushakov[1], Jin Shi Ma[2], and Gwokyang Yang[2]

Previously unknown 1-vinylpyrrole semicarbazones, thiosemicarbazones, and guanylhydrazones have been obtained in 68.0-90.5% yield by the reaction of 1-vinylpyrrole-2-carbaldehydes with semicarbazide, thiosemicarbazide, and aminoguanidine.

Keywords: 1-vinylpyrrole-2-carbaldehydes, guanylhydrazones, semicarbazones, thiosemicarbazones.

Semicarbazones, thiosemicarbazones, guanylhydrazones, and metal complexes based on them display antitubercular, antibacterial, antimalarial, antiviral, antitumor, anticonvulsive, and other forms of biological activity [1-12]. Thiosemicarbazones of heterocyclic aldehydes and ketones containing the chemically reactive chromophore =NNH(C=S)- are model compounds for sulfur-containing analogs of purine and pyrimidine bases, consequently study of their coordination with metal cations raises considerable interest [13]. On interacting thiosemicarbazones of pyrrole-2-carbaldehyde and 2-acetylpyrrole with halides of Zn(II), Cd(II), and Hg(II), complexes are formed in which the metal atom is tetracoordinated, but the ligand is neutral and S-monodentate [6]. However, after deprotonation of the hydrazine fragment $N_{(2)}H$ isomerization of the ligand into a *Z*-form and bonding of the metal in the $N_{(3)}$,S chelate form usually occurs [11].

1-Vinylpyrrole-2-carbaldehyde, having become available recently [14], is a convenient constructional block for fine organic synthesis [15].

In a continuation of the study of their chemical properties, and with the aim of obtaining promising pharmacological preparations based on 1-vinylpyrroles [16], the corresponding semicarbazones **2a-c**, thiosemicarbazones **3a-c**, and guanylhydrazones **4a-c** have been synthesized from 1-vinylpyrrole-2-carbaldehydes **1a-c** in the present work.

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[1]A. E. Favorsky Irkutsk Institute of Chemistry, Siberian Branch of the Russian Academy of Sciences, Irkutsk 664033; e-mail: mikh@irioch.irk.ru. [2]CAS Key Laboratory of Photochemistry, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, China; e-mail: jsma@iccas.ac.cn. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 9, pp. 1384-1390, September, 2008. Original article submitted April 29, 2008.

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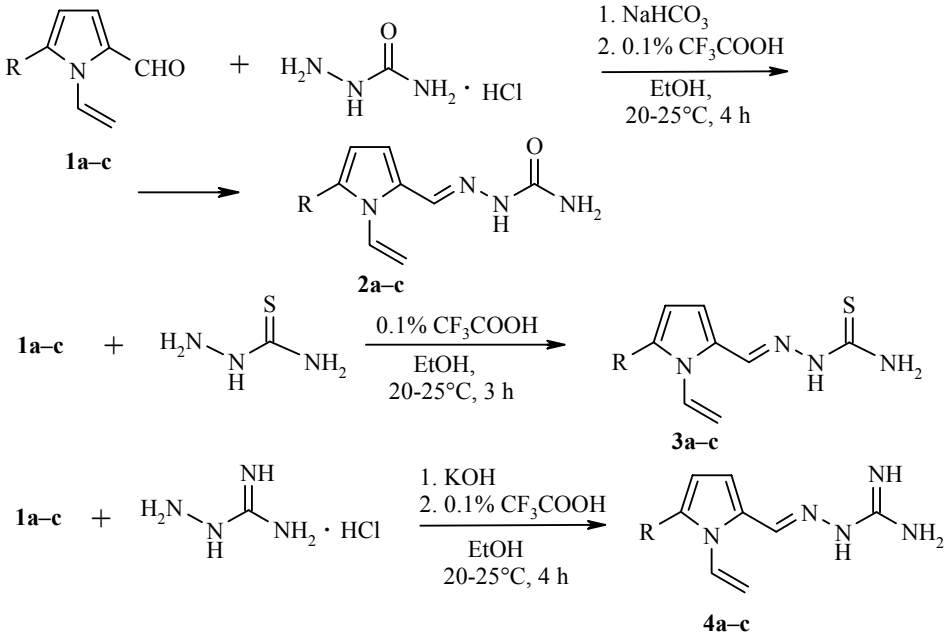
Usually the condensation of amidohydrazines with aldehydes (including pyrrole-2-carbaldehyde [13]) is carried out in aqueous or absolute ethanol, occasionally in the presence of acetic acid, on heating and without it [16-18], and in the case of guanylhydrazones on boiling (1-12 h) with the addition of conc. HCl [5, 9]. However stirring an alcohol solution of a mixture of aldehyde **1b** and thiosemicarbazide (20-25°C, 24 h) did not lead to the formation of thiosemicarbazone **3b**. On boiling the same mixture in ethanol for 5 h the yield of product **3b** was only 7%. This is a fairly unexpected result. According to the correlation of Hettler [19], the reaction rate constants for oximation are always less than the reaction rate constants for the formation of the corresponding semicarbazones, thiosemicarbazones, and guanylhydrazones. In the case of aldehydes **1** oximation proceeds practically quantitatively (95-99%) even without additional heating (ethanol, 20-25°C, 3 h). Evidently this is a result of the lower steric hindrance caused by the vinyl group in the case of hydroxylamine in comparison with the more bulky amidohydrazines. It is known for example that semicarbazones are readily decomposed on adding mineral acids [18]. In spite of that we found that azomethines **2-4** are formed in high yield (68.0-90.5%) from carbaldehydes **1** and semicarbazide, thiosemicarbazide, and aminoguanidine, respectively, on stirring the reactants in ethanol (20-25°C, 3 h) after adding ~0.1% trifluoroacetic acid as catalyst.



1–4 a R = H, **b** R = Ph, **c** R = 2-naphthyl

The hydrochlorides of semicarbazide and aminoguanidine were first converted into bases by stirring for 1 h at room temperature with an equimolar quantity of $NaHCO_3$ in the first case or KOH in the second (with $NaHCO_3$ insoluble aminoguanidine carbonate is formed). The consumption of aldehyde **1** was checked by GLC. The synthesized compounds **2-4** were fine, colored crystals with high melting points, readily soluble in DMSO and acetone, and moderately soluble in chloroform and diethyl ether.

Advantages of the developed method in comparison with known include the mild reaction conditions and the simplicity of carrying it out, which enables avoidance of conversions at the vinyl group sensitive to acidic reagents in 1-vinylpyrroles [16] (especially in the case of guanylcarbazones).

In the ^1H and ^{13}C NMR spectra of compounds **2-4** there was no doubling, which affords the conclusion that they exist in solution as one isomer. Characteristic signals in the ^1H NMR spectra are the singlet for the azomethine proton, signals of the pyrrole ring protons, and of the N-vinyl substituent. Assignment of the signals was carried out using COSY, NOESY, HSQC, and HMBC two-dimensional homo- and heteronuclear experiments. On

the basis of characteristic values for the chemical shifts of the azomethine proton (7.85-8.24 ppm) and the direct $^{1}H–^{13}C$ coupling constant (164-168 Hz) in the azomethine fragment [20, 21], it was established that all compounds **2-4** are *E*-isomers.

In the IR spectra of the synthesized compounds characteristic absorption bands were observed for the vinyl ($\nu_{C=C}$ 1639±5 cm^{-1}) and azomethine ($\nu_{C=N}$ 1614±15 cm^{-1}) functional groups [15, 22]. For the amide functions $C(=X)NH_2$ stretching vibrational bands at 1693±6 (X = O), 1591±11 (X = S), and 1657±13 cm^{-1} (X = NH) were characteristic.

A general efficient method has therefore been developed for the synthesis of previously unknown semicarbazones, thiosemicarbazones, and guanylhydrazones of 1-vinylpyrrole-2-carbaldehydes, which are promising as pyrrole ligands, biologically active compounds, and constructional blocks.

EXPERIMENTAL

The IR spectra were obtained on a Bruker IFS 25 instrument in KBr disks (compounds **2-4**) and in a thin film (compound **1c**). The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DPX 400 (400 and 100 MHz respectively) in $CDCl_3$ (compound **1c**) and DMSO-d_6 (compounds **2-4**), internal standard was HMDS. The initial aldehydes **1a-c** were synthesized according to the known method of [14]. A check on the progress of reactions (by the decrease of aldehyde **1**) was effected by GLC on an Agilent 6890N instrument (internal standard was *n*-hexanol). Compound **1c** was synthesized for the first time.

5-(2-Naphthyl)-1-vinylpyrrole-2-carbaldehyde (1c). Yield was 72.0%, viscous liquid of a raspberry color. IR spectrum, ν, cm^{-1}: 3295, 3120, 3055, 2957, 2923, 2834, 2805, 2780, 2725, 1664, 1601, 1536, 1489, 1451, 1424, 1361, 1320, 1292, 1271, 1249, 1219, 1133, 1094, 1038, 957, 898, 861, 839, 821, 785, 767, 750, 696, 679, 668, 630, 517, 478. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 9.69 (1H, s, CHO); 7.97 (1H, s, H arom); 7.88 (3H, m, H arom); 7.54 (3H, m, H arom); 7.52 (1H, dd, $^{3}J_{B,X}$ = 15.7, $^{3}J_{AX}$ = 8.6, H_X); 7.14 (1H, d, *J* = 4, H-3); 6.51 (1H, d, *J* = 4.1, H-4); 5.12 (1H, d, $^{3}J_{A,X}$ = 8.6, H_A); 4.92 (1H, d, $^{3}J_{B,X}$ = 15.7, H_B). ^{13}C NMR spectrum, δ, ppm: 179.51 (COH); 142.33 (C-5); 133.55 (C-2); 133.22 (C arom); 132.99 (C arom); 131.38 (C_α); 129.07-126.72 (8C, C arom); 124.56 (C-3); 113.15 (C-4); 112.70 (C_β). Found, %: C 83.05; H 5.83; N 5.12. $C_{17}H_{13}NO$. M 247.30. Calculated, %: C 82.57; H 5.30; N 5.66.

Interaction of N-Vinylpyrrolecarbaldehydes 1 with Semicarbazide. Semicarbazide hydrochloride (1.4 g, 12 mmol) and $NaHCO_3$ (1.0 g, 12 mmol) were added to a solution of aldehyde **1** (10 mmol) in ethanol (25 ml). The mixture was stirred for 1 h, then CF_3COOH (~25 mg, ~0.1%)) was added and the mixture stirred a further 3 h. The precipitated solid product **2** was filtered off on a Schott funnel, washed with water, with ethanol, dried in vacuum, and product **2** was obtained as colored crystals.

2-[(1-Vinylpyrrol-2-yl)methylidene]hydrazinecarboxamide (2a). Yield 1.27 g (71.5%), light-yellow crystals; mp 197-199°C (decomp.). IR spectrum, ν, cm^{-1}: 3471, 3302, 3194, 3141, 3060, 2999, 2926, 2855, 1687, 1643, 1603, 1536, 1510, 1461, 1433, 1320, 1283, 1232, 1180, 1138, 1079, 970, 939, 884, 876, 804, 758, 723, 702, 648, 635, 574, 495, 420. ^{1}H NMR spectrum, δ, ppm (*J*, Hz); 9.97 (1H, br. s, NH); 7.73 (1H, dd, $^{3}J_{B,X}$ = 15.6, $^{3}J_{A,X}$ = 8.8, H_X); 7.85 (1H, s, N=CH); 7.40 (1H, m, H-5); 6.48 (1H, m, H-3); 6.26 (2H, br. s, NH_2); 6.22 (1H, m, H-4); 5.31 (1H, d, $^{3}J_{B,X}$ = 15.6, H_B); 4.80 (1H, d, $^{3}J_{A,X}$ = 8.8, H_A). ^{13}C NMR spectrum, δ, ppm: 156.71 (C=O); 133.31 (N=CH); 132.43 (C_α); 127.15 (C-2); 121.41 C-5); 114.95 (C-3); 110.74 (C-4); 100.34 (C_β). Found, %: C 53.99; H 5.90; N 30.91. $C_8H_{10}N_4O$. M 178.19. Calculated, %: C 53.92; H 5.66; N 31.44.

2-[(5-Phenyl-1-vinylpyrrol-2-yl)methylidene]hydrazinecarboxamide (2b). Yield 1.73 g (68.0%), light-yellow crystals; mp 221-223°C (decomp.). IR spectrum, ν, cm^{-1}: 3473, 3341, 3273, 3211, 3149, 3065, 3038, 2989, 2927, 1686, 1636, 1578, 1550, 1488, 1460, 1414, 1368, 1319, 1286, 1234, 1200, 1139, 1098, 1074, 1027, 1001, 965, 934, 919, 818, 782, 761, 735, 699, 656, 643, 597, 559, 480, 449. ^{1}H NMR spectrum, δ,

ppm (*J*, Hz): 10.07 (1H, br. s, NH); 7.90 (1H, s, N=CH); 7.39 (4H, m, $H_{o,m}$); 7.29 (1H, m, H_p); 7.14 (1H, dd, $^3J_{B,X}$ = 15.6, $^3J_{A,X}$ = 8.4, H_X); 6.73 (1H, d, *J* = 3.7, H-3); 6.35 (1H, d, *J* = 3.7, H-4); 6.30 (2H, br. s, NH_2); 5.23 (1H, d, $^3J_{A,X}$ = 8.4, H_A); 4.87 (1H, d, $^3J_{B,X}$ = 15.6, H_B. ^{13}C NMR spectrum, δ, ppm: 157.19 (C=O); 136.18 (C-5); 133.18 (N=CH); 132.39 (C_α); 132.26 (C_i); 130.07 (C-2); 128.83 (C_m); 128.67 (C_o); 127.49 (C_p); 113.36 (C_β); 112.05 (C-3); 111.54 (C-4). Found, %: C 65.94; H 5.54; N 22.24. $C_{14}H_{14}N_4O$. M 254.29. Calculated, %: C 66.13; H 5.55; N 22.03.

2-[(5-(2-Naphthyl)-1-vinylpyrrol-2-yl)methylidene]hydrazinecarboxamide (2c). Yield was 2.31 g 76.0%), light-pink crystals; mp 234-236°C (decomp.). IR spectrum, ν, cm^{-1}: 3473, 3352, 3277, 3216, 3153, 3050, 2930, 1699, 1638, 1625, 1593, 1548, 1503, 1440, 1412, 1387, 1341, 1309, 1287, 1249, 1221, 1195, 1139, 1128, 1087, 1014, 973, 922, 895, 860, 819, 780, 765, 748, 600, 553, 491, 475, 454. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 10.07 (1H, br. s, NH); 7.97 (1H, s, H arom); 7.96 (1H, s, N=CH); 7.90 (2H, m, H arom); 7.53 (4H, m, H arom); 7.28 (1H, dd, $^3J_{B,X}$ = 15.7, $^3J_{A,X}$ = 8.3, H_X); 6.80 (1H, d, *J* = 3.8, H-3); 6.50 (1H, d, *J* = 3.8, H-4); 6,36 (2H, br. s, NH_2); 5.26 (1H, d, $^3J_{A,X}$ = 8.3, H_A); 4.92 (1H, d, $^3J_{B,X}$ = 15.7, H_B). ^{13}C NMR spectrum, δ, ppm: 156.69 (C=O); 135.70 (C-5); 132.89 (C arom); 132.45 (N=CH); 132.19 (C_α); 131.80, 129.68, 127,87-126.13 (9C, C arom); 130.19 (C-2); 113.03 (C_β); 111.82 (C-3); 111.75 (C-4). Found, %: C 71.76; H 5.69; N 18.13. $C_{18}H_{16}N_4O$. M 304.35. Calculated, %: C 71.04; H 5.30; N 18.41.

Interaction of N-Vinylpyrrolecarbaldehydes 1 with Thiosemicarbazide. Thiosemicarbazide (1.1 g, 12 mmol) and CF_3COOH (~25 mg, ~0.1%) were added to a solution of aldehyde **1** (10 mmol) in ethanol (25 ml), and the mixture was stirred for 3 h. The precipitated solid product **3** was separated and treated as described for product **2**.

2-[(1-Vinylpyrrol-2-yl)methylidene]hydrazinecarbothioamide (3a). Yield was 1.38 g (71.0%), light-yellow crystals; mp 203-205°C (decomp.). IR spectrum, ν, cm^{-1}: 3406, 3247, 3156, 3041, 2984, 2814, 1639, 1617, 1602, 1545, 1520, 1471, 1455, 1430, 1360, 1324, 1280, 1229, 1102, 1079, 1059, 966, 938, 872, 846, 790, 737, 727, 680, 645, 619, 589, 568, 535, 500, 442, 406. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 11.14 (1H, br. s, NH); 8.08 (1H, br. s, NH_2); 8.06 (1H, s, N=CH); 7.75 (1H, dd, $^3J_{B,X}$ = 15.7, $^3J_{A,X}$ = 8.8, H_X); 7.50 (1H, br. s, NH_2); 7.47 (1H, m, H-5); 6.61 (1H, m, H-3); 6.26 (1H, m, H-4); 5.35 (1H, d, $^3J_{B,X}$ = 15.7, H_B); 4.83 (1H, d, $^3J_{A,X}$ = 8.8, H_A). ^{13}C NMR spectrum, δ, ppm: 177.13 (C=S); 136.17 (N=CH); 132.47 (C_α); 126.48 (C-2); 122.60 (C-5); 116.89 (C-3); 111.11 (C-4); 100.96 (C_β). Found, %: C 50.08; H 5.38; N 28.26; S 16.44. $C_8H_{10}N_4S$. M 194.25. Calculated, %: C 49.47; H 5.19; N 28.84; S 16.50.

2-[(5-Phenyl-1-vinylpyrrol-2-yl)methylidene]hydrazinecarbothioamide (3b). Yield was 1.93 g (71.5%), finely crystalline, yellow powder; mp 206-208°C. IR spectrum, ν, cm^{-1}: 3425, 3386, 3242, 3032, 2991, 1644, 1589, 1550, 1503, 1464, 1448, 1415, 1393, 1341, 1325, 1299, 1238, 1116, 1076, 1056, 966, 919, 851, 804, 780, 762, 700, 669, 620, 519, 441. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 11.24 (1H, br. s, NH); 8.12 (1H, s, N=CH); 8.01 (1H, br. s, NH_2); 7.59 (1H, br. s, NH_2); 7.40 (4H, m, H_o, H_m); 7.29 (1H, m, H_p); 7.12 (1H, dd, $^3J_{B,X}$ = 15.7, $^3J_{A,X}$ = 8.4, H_X); 6.87 (1H, d, *J* = 3.9, H-3); 6.37 (1H, d, *J* = 3.9, H-4); 5.26 (1H, d, $^3J_{A,X}$ = 8.4, H_A); 4.92 (1H, d, $^3J_{B,X}$ = 15.7, H_B). ^{13}C NMR spectrum, δ, ppm: 177.22 (C=S); 137.16 (C-5); 135.92 (N=CH); 132.12 (C_α); 132.07 (C_i); 129.41 (C-2); 128.81 (C_m); 128.66 (C_o); 127.64 (C_p); 113.77 (C_β); 113.44 (C-3); 111.75 (C-4). Found, %: C 61.66; H 5.53; N 21.01; S 11.80. $C_{14}H_{14}N_4S$. M 270.35. Calculated, %: C 62.20; H 5.22; N 20.72; S 11.86.

2-[(5-(2-Naphthyl)-1-vinylpyrrol-2-yl)methylidene]hydrazinecarbothioamide (3c). Yield was 2.90 g (90.5%), yellow crystals; mp 238-240°C. IR spectrum, ν, cm^{-1}: 3523, 3454, 3373, 3258, 3161, 3123, 3048, 2986, 2814, 1635, 1607, 1581, 1553, 1506, 1472, 1450, 1412, 1385, 1362, 1344, 1322, 1292, 1250, 1224, 1135, 1112, 1091, 1060, 1015, 922, 856, 821, 803, 785, 752, 669, 645, 479, 447. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 11.31 (1H, br. s, NH); 8.20 (1H, s, N=CH); 8.15 (1H, br. s, NH_2); 7.98 (1H, s, H arom); 7.91 (2H, m, H arom); 7.66 (1H, br. s, NH_2); 7.52 (4H, m, H arom); 7.28 (1H, dd, $^3J_{B,X}$ = 15.7, $^3J_{A,X}$ = 8.3, H_X); 6.96 (1H, d, *J* = 3.9, H-3); 6.54 (1H, d, *J* = 3.9, H-4); 5.30 (1H, d, $^3J_{A,X}$ = 8.3, H_A); 4.98 (1H, d, $^3J_{B,X}$ = 15.7, H_B). ^{13}C NMR spectrum, δ, ppm: 177.09 (C=S); 136.67 (C-5); 135.32 (N=CH); 132.85 (C arom); 132.03 (C_α); 131.87, 129.43-126.24 (9C, C arom); 129.55 (C-2); 113.53 (C_β); 113.22 (C-3); 111.99 (C-4). Found, %: C 67.45; H 5.24; N 17.47; S 9.84. $C_{18}H_{16}N_4S$. M 320.41. Calculated, %: C 67.48; H 5.03; N 17.49; S 10.01.

Interaction of N-Vinylpyrrolecarbaldehydes 1 with Aminoguanidine. Aminoguanidine hydrochloride (1.3 g, 12 mmol) and KOH·0.5H_2O (0.78 g, 12 mmol) were added to a solution of aldehyde **1** (10 mmol) in ethanol (25 ml). The mixture was stirred for 1 h, then CF_3COOH (~25 mg, ~0.1%) was added, and stirring was continued for a further 3 h. The precipitated solid product **4** was isolated and treated as for product **2**.

2-[(1-Vinylpyrrol-2-yl)methylidene]hydrazinecarboximidamide (4a). Yield was 1.22 g (69.0%), orange crystals; mp 186-188°C (decomp.). IR spectrum, ν, cm^{-1}: 3454, 3359, 3099, 2964, 2848, 1644, 1619, 1595, 1539, 1444, 1428, 1362, 1332, 1312, 1278, 1222, 1182, 1155, 1078, 970, 934, 864, 801, 793, 725, 702, 690, 590, 524, 418. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 8.01 (1H, s, N=CH); 7.92 (1H, dd, $^3J_{B,X}$ = 15.7, $^3J_{A,X}$ = 8.8, H_X); 7.32 (1H, m, H-5); 6.36 (1H, m, H-3); 6.18 (1H, m, H-4); 5.67 (2H. br. s, NH); 5.46 (2H, br. s, NH_2); 5.26 (1H, d, $^3J_{B,X}$ = 15.7, H_B); 4.72 (1H, d, $^3J_{A,X}$ = 8.8, H_A). ^{13}C NMR spectrum, δ, ppm: 159.59 (C=NH); 137.21 (N=CH); 132.98 (C_α); 129.48 (C-2); 119.86 (C-5); 113.31 (C-3); 110.56 (C-4); 98.81 (C_β). Found, %: C 55.30; H 5.86; N 38.84. $C_8H_{11}N_5$. M 177.21. Calculated, %: C 54.22; H 6.26; N 39.52.

2-[(5-Phenyl-1-vinylpyrrol-2-yl)methylidene]hydrazinecarboximidamide (4b). Yield was 2.05 g (80.8%), light-orange crystals; mp 192-194°C. IR spectrum, ν, cm^{-1}: 3484, 3373, 3318, 3161, 3108, 1662, 1638, 1598, 1550, 1529, 1467, 1447, 1416, 1401, 1367, 1328, 1285, 1230, 1200, 1160, 1075, 1029, 1008, 970, 933, 901, 817, 777, 757, 733, 701, 657, 615, 523, 494, 462. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 8.02 (1H, s, N=CH); 7.40 (4H, m, H_o, H_m,); 7.30 (1H, dd, $^3J_{B,X}$ = 15.7, $^3J_{A,X}$ = 8.3, H_X); 7.27 (1H, m, H_p); 6.59 (1H, d, *J* = 3.9, H-3); 6.30 (1H, d, *J* = 3.9, H-4); 5.73 (2H, br. s, NH); 5.39 (2H, br. s, NH_2); 5.13 (1H, d, $^3J_{A,X}$ = 8.3, H_A); 4.76 (1H, d, $^3J_{B,X}$ = 15.7, H_B). ^{13}C NMR spectrum, δ, ppm: 159.60 (C=NH); 136.32 (N=CH); 134.77 (C-5); 132.63 (C_i); 132.56 (C_α); 132.17 (C-2); 128.32 (C_m); 128.25 (C_o); 126.68 (C_p); 111.33 (C-4); 111.27 (C_β); 110.66 (C-3). Found, %: C 66.09; H 6.23; N 28.00. $C_{14}H_{15}N_5$. M 253.31. Calculated, %: C 66.38; H 5.97; N 27.65.

2-[(5-(2-Naphthyl)-1-vinylpyrrol-2-yl)methylidene]hydrazinecarboximidamide (4c). Yield was 2.61 g (86.0%), light-pink crystals; mp 210-212°C. IR spectrum, ν, cm^{-1}: 3400, 3332, 3236, 3163, 3052, 2991, 2895, 2834, 1670, 1639, 1624, 1548, 1506, 1468, 1447, 1411, 1384, 1341, 1323, 1291, 1252, 1224, 1208, 1194, 1155, 1131, 1079, 1022, 959, 939, 899, 862, 823, 782, 754, 743, 726, 671, 625, 478, 448. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 11.98 (2H, br. s, NH); 8.24 (1H, s, N=CH); 7.99 (1H, s, H arom); 7.92 (2H, m, H arom); 7.68 (2H, br. s, NH_2); 7.54 (4H, m, H arom); 7.32 (1H, dd, $^3J_{B,X}$ = 15.2, $^3J_{A,X}$ = 8.3, H_X); 7.02 (1H, d, *J* = 3.9, H-3); 6.57 (1H, d, *J* = 3.9, H-4); 5.33 (1H, d, $^3J_{A,X}$ = 8.3, H_A); 5.01 (1H, d, $^3J_{B,X}$ = 15.2, H_B). ^{13}C NMR spectrum, δ, ppm: 154.99 (C=NH); 139.25 (N=CH); 137.10 (C-5); 132.84 (C arom); 132.02 (C_α); 131.95, 129.28, 127.95-126.34 (9C, C arom); 128.81 (C-2); 113.99 (C_β); 113.99 (C-3); 112.05 (C-4). Found, %: C 71.30; H 5.88; N 22.82. $C_{18}H_{17}N_5$. M 303.37. Calculated, %: C 71.27; H 5.65; N 23.09.

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