

## Metathesis of azomethine imines in the reaction of 6-aryl-1,5-diazabicyclo-[3.1.0]hexanes with carbonyl compounds

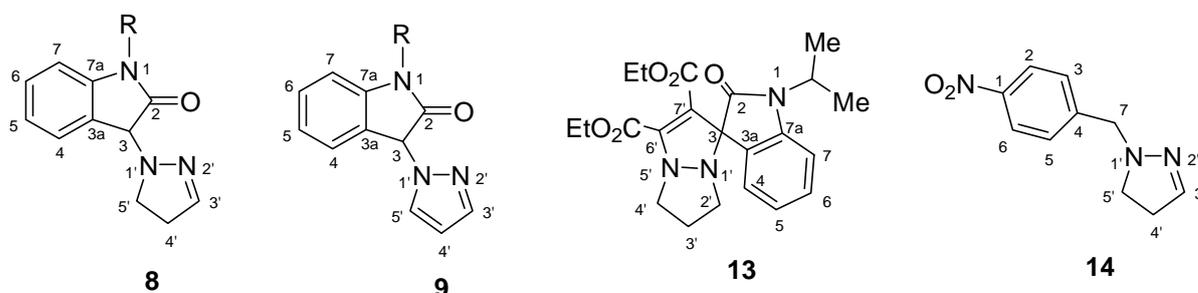
Vera Yu. Petukhova, Mikhail I. Pleshchev, Leonid L. Fershtat, Vladimir V. Kuznetsov, Vadim V. Kachala and Nina N. Makhova\*

Elemental analysis was performed by the CHN Analyzer Perkin-Elmer 2400. All new compounds gave satisfactory elemental analyses. The IR spectra were measured using a SPECORD-M82 spectrometer. The NMR spectra of all compounds were recorded using a Bruker AM-300 spectrometer at 300 MHz for  $^1\text{H}$  and 75.47 MHz for  $^{13}\text{C}$  spectra as well as Bruker AV-600 instrument with the frequencies 600.13, 150.90 and 60.81 MHz for  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{15}\text{N}$ , respectively, in  $\text{CDCl}_3$ . The chemical shifts of the signals of  $\text{CDCl}_3$  residual proton (7.27 ppm) and carbon (77.0 ppm) were used as the internal standard. The  $^{15}\text{N}$  spectra were measured with  $\text{CH}_3\text{NO}_2$  ( $\delta_{15\text{N}} = 0.0$  ppm) as the external standard. All 2D-spectra were recorded using standard Bruker methods with Z-gradient. The spectra were measured at 30 °C. Mass spectra were measured with a Finigan MAT INCOS-50 instrument. Analytical thin-layer chromatography (TLC) was conducted on silica gel plates (Silufol UV-254). New compounds were purified by column chromatography on Silica gel, 0.060-0200 mm, 60 A (ACROS). Compound **2b** was prepared by analogy with reported method.<sup>1</sup>

*6-(4-Ethoxyphenyl)-1,5-diazabicyclo[3.1.0]hexane 2b*. Yield 62%;  $R_f$  0.45 ( $\text{CHCl}_3$  washed with saturated  $\text{NH}_3$ ); mp 108-109 °C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 200 MHz)  $\delta$ : 1.40 (t, 3H,  $\text{CH}_3$ ,  $^3J$  6.7 Hz); 1.92 (m, 2H,  $\text{NCH}_2\text{CH}_2$ ); 3.05 (s, 1H, NCHN); 3.15, 3.60 (both m, 4H,  $\text{N}(\text{CH}_2)_2$ ); 4.02 (q, 2H,  $\text{CH}_3\text{CH}_2\text{O}$ ,  $^3J$  6.7 Hz); 6.82, 7.25 (both d, 4H, CH in Ar,  $^3J$  10.0 Hz).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 14.90 ( $\text{CH}_3$ ), 21.84 ( $\text{NCH}_2\text{CH}_2$ ), 52.24 ( $\text{NCH}_2$ ); 56.48 (NCHN); 63.45 ( $\text{CH}_3\text{CH}_2\text{O}$ ), 114.42, 125.44, 128.96, 159.35 (Ar). IR ( $\nu/\text{cm}^{-1}$ ): 812, 864, 876, 924, 956, 972, 1012, 1048, 1096, 1116, 1176, 1248, 1312, 1344, 1400, 1444, 1456, 1480, 1520, 1588, 1616, 1644, 2880, 2948, 2976. MS,  $m/z$  203 (M – H).

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<sup>1</sup> V. V. Kuznetsov, S. A. Kutepov, N. N. Makhova, K. A. Lyssenko and D. E. Dmitriev, *Izv. Akad. Nauk, Ser. Khim.*, 2003, 638 (*Russ. Chem. Bull., Int. Ed.*, 2003, **52**, 665).



*3-(4,5-Dihydro-1H-pyrazol-1-yl)-1-methylindolin-2-one* **8a**.  $R_f$  0.30 (ethyl acetate : light petroleum, 3:1); nondistilled oil.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 600 MHz)  $\delta$ : 2.71 (m, 2H,  $\text{H}_2(4')$ ,  $^3J$  1.7 Hz,  $^3J$  10.2 Hz); 3.19 (m, 2H,  $\text{H}_2(5')$ ); 3.20 (s, 3H, Me); 5.06 (s, 1H, H(3)); 6.83 (d, H(7),  $^3J$  7.8 Hz); 6.87 (t, 1H, H(3'),  $^3J$  1.7 Hz); 7.31 (t, 1H, H(6),  $^3J$  7.8 Hz), 7.41 (d, 1H, H(4),  $^3J$  7.5 Hz).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 600 MHz)  $\delta$ : 26.03 (Me); 34.19 (C(4')); 48.05 (C(5')); 63.64 (C(3)); 108.18 (C(7)); 122.71 (C(5)); 125.07 (C(3a)); 125.45 (C(4)); 129.21 (C(6)); 144.24 (C(7a)); 144.63 (C(3')); 173.99 (C(2)).  $^{15}\text{N}$  NMR ( $\text{CDCl}_3$ , 600 MHz)  $\delta$ : -22.3 (N(2')); -232.5 (N(1')); -239.2 (N(1)). Significant NOESY H-H correlations: Me-H(7); H(3)-H(4, 5'); H(5')-H(3); HMBC C-H, N-H correlations: N(1)-H(Me); C(2)-H(3, Me); C(3)-H(4, 5'); C(3a)-H(3, 4, 5, 7), C(4)-H(5, 6); C(5)-H(4, 7); C(6)-H(4); C(7)-H(5); C(7a)-H(Me, 3, 4, 6); N(1')-H(3', 4', 5'); N(2')-H(3, 3', 4'); C(3')-H(4', 5'); C(4')-H(5'), C(5')-H(3', 4'). Found (%): C, 66.90; H, 6.11; N, 19.48. Calc. for  $\text{C}_{12}\text{H}_{13}\text{N}_3\text{O}$  (%): C, 66.96; H, 6.09; N, 19.52.

*3-(4,5-Dihydro-1H-pyrazol-1-yl)-1-isopropylindolin-2-one* **8b**.  $R_f$  0.31 (ethyl acetate : petroleum ether 3:1); nondistilled oil,  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$ : 1.48 (d, 6H,  $(\text{CH}_3)_2\text{CH}$ ,  $^3J$  7.3 Hz); 2.70 (m, 2H,  $\text{H}_2(4')$ ,  $^3J$  10.1 Hz); 3.11 (m, 2H,  $\text{H}_2(5')$ ,  $^3J$  10.1 Hz); 4.64 (m,  $(\text{CH}_3)_2\text{CH}$ ,  $^3J$  7.3 Hz); 5.05 (s, 1H, H(3)); 6.86 (br s, 1H, H(7)); 7.01 (m, 2H, H(3', 5)); 7.28 (m, 1H, H(6)), 7.41 (d, 1H, H(4),  $^3J$  7.3 Hz).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$ : 19.30, 19.38 ( $(\text{CH}_3)_2\text{CH}$ ); 34.20 (C(4')); 43.79( $\text{CH}_3)_2\text{CH}$ ); 47.58 (C(5')); 63.57 (C(3)); 109.85 (C(7)); 122.16 (C(5)); 125.55 (C(3a)); 125.87 (C(4)); 128.94 (C(6)); 143.07 (C(7a)); 144.23 (C(3')); 173.68 (C(2)). Found (%): C, 69.08; H, 7.01; N, 17.23. Calc. for  $\text{C}_{14}\text{H}_{17}\text{N}_3\text{O}$  (%): C, 69.11; H, 7.04; N, 17.27.

*3-(4,5-Dihydro-1H-pyrazol-1-yl)indolin-2-one* **8c**.  $R_f$  0.25 (ethyl acetate : light petroleum, 3:1); nondistilled oil,  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$ : 2.73 (m, 2H,  $\text{H}_2(4')$ ,  $^3J$  9.6 Hz); 3.20 (m, 2H,  $\text{H}_2(5')$ ,  $^3J$  9.6 Hz); 5.13 (s, 1H, H(3)); 6.89 (m, 1H, H(7)); 7.03 (m, 2H, H(3', 5)); 7.30 (m, 1H, H(6)), 7.85 (d, 1H, H(4),  $^3J$  8.9 Hz), 9.90 (br s, 1H, NH).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$ : 33.49 (C(4')); 49.17 (C(5')); 67.19 (C(3)); 109.35 (C(7)); 121.76 (C(5)); 125.82 (C(3a)); 125.93

(C(4)); 129.80 (C(6)); 143.42 (C(7a)); 146.31 (C(3')); 171.36 (C(2)). Found (%): C, 65.59; H, 5.56; N, 20.95. Calc. for C<sub>11</sub>H<sub>11</sub>N<sub>3</sub>O (%): C, 65.66; H, 5.51; N, 20.88.

*1-Methyl-3-(1H-pyrazol-1-yl)indolin-2-one 9a*. R<sub>f</sub> 0.55 (ethyl acetate : light petroleum, 3:1); mp 138-140 °C (decomp.). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz) δ: 3.27 (s, 3H, Me), 5.79 (s, 1H, H(3)); 6.35 (t, 1H, H(4'), <sup>3</sup>J 1.5 Hz, <sup>3</sup>J 2.3 Hz); 6.92 (d, H(7), <sup>3</sup>J 7.8 Hz); 7.11 (t, 1H, H(5), <sup>3</sup>J 7.4 Hz, <sup>3</sup>J 7.8 Hz); 7.25 (d, 1H, H(4), <sup>3</sup>J 7.4 Hz), 7.39 (t, 1H, H(6), <sup>3</sup>J 7.8 Hz); 7.55 (d, 1H, H(5), <sup>3</sup>J 2.3 Hz); 7.60 (d, 1H, H(3), <sup>3</sup>J 1.5 Hz). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 600 MHz) δ: 26.03 (Me); 62.48 (C(3)); 106.88 (C(4')); 108.78 (C(7)); 123.29 (C(5)); 124.35 (C(3a)); 124.98 (C(4)); 129.63 (C(5')); 130.24 (C(6)); 140.88 (C(3')); 144.00 (C(7a)); 171.31 (C(2)). <sup>15</sup>N NMR (CDCl<sub>3</sub>, 600 MHz) δ: -67.8 (N(2')); -167.2 (N(1')); -241.4 (N(1)). IR (ν/cm<sup>-1</sup>): 644, 688, 716, 756, 776, 820, 840, 972, 1060, 1088, 1120, 1176, 1212, 1244, 1272, 1300, 1316, 1396, 1492, 1512, 1624, 1732, 2856, 2924, 3100. Significant NOESY H-H correlations: Me-H(7); H(3)-H(4, 5'); H(5')-H(3), HMBC C-H, N-H correlations: N(1)-H(Me, 7); C(2)-H(3, Me); C(3)-H(4); C(3a)-H(3, 5, 7), C(4)-H(5, 6); C(5)-H(4, 7); C(6)-H(4); C(7)-H(5); C(7a)-H(Me, 3, 4, 6); N(1')-H(3, 3', 4', 5'); N(2')-H(3, 3', 4'); C(3')-H(4', 5'); C(4')-H(3, 5'), C(5')-H(3', 4'). MS (EI, 70 eV), *m/z* (I, %): 213 [M]<sup>+</sup> (57), 212 [M - H]<sup>+</sup> (100), 185 [M - CO]<sup>+</sup> (21), 158 [M - N(Me)CO]<sup>+</sup> (12), 146 [M - pyrazole ring]<sup>+</sup> (25). Found (%): C, 67.52; H 5.29; N 19.53. Calc. for C<sub>12</sub>H<sub>11</sub>N<sub>3</sub>O (%): C, 67.59; H, 5.20; N, 19.71.

*1-Isopropyl-3-(1H-pyrazol-1-yl)indolin-2-one 9b*. R<sub>f</sub> 0.87 (ethyl acetate : light petroleum, 3:1), nondistilled oil, <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) δ: 1.53 (d, 6H, (CH<sub>3</sub>)<sub>2</sub>CH, <sup>3</sup>J 7.3 Hz), 4.64 (m, 1H, (CH<sub>3</sub>)<sub>2</sub>CH), <sup>3</sup>J 6.6 Hz); 5.75 (s, 1H, H(3)); 6.34 (br s, 1H, H(4')); 7.06 and 7.09 (both br s, 2H, H(5, 7)); 7.27 (d, 1H, H(4), <sup>3</sup>J 5.1 Hz); 7.35 (m, 1H, H(6)); 7.49 (br s, 1H, H(5')); 7.60 (br s, 1H, H(3')). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 300 MHz) δ: 19.35, 19.39 (CH<sub>3</sub>)<sub>2</sub>CH); 44.57 (CH<sub>3</sub>)<sub>2</sub>CH); 62.65 (C(3)); 106.42 (C(4')); 110.38 (C(7)); 122.79 (C(5)); 124.92 (C(3a)); 125.33 (C(4)); 129.36 (C(5')); 129.98 (C(6)); 140.79 (C(3')); 142.83 (C(7a)); 171.08 (C(2)). IR (ν/cm<sup>-1</sup>): 612, 640, 688, 720, 756, 884, 916, 968, 1028, 1048, 1096, 1132, 1160, 1196, 1228, 1296, 1316, 1352, 1396, 1468, 1484, 1516, 1608, 1720, 2936, 2976. MS (EI, 70 eV), *m/z* (I, %): 241 [M]<sup>+</sup> (22), 198 [M - *i*-Pr]<sup>+</sup> (32), 171 [M - *i*-Pr - CO]<sup>+</sup> (12), 158 [M - N(*i*-Pr)CO]<sup>+</sup> (23), 43 [*i*-Pr]<sup>+</sup> (100). Found (%): C, 69.73; H, 6.18; N, 17.50. Calc. for C<sub>14</sub>H<sub>15</sub>N<sub>3</sub>O (%): C, 69.69; H, 6.27; N, 17.41.

*3-(1H-Pyrazol-1-yl)indolin-2-one 9c*. R<sub>f</sub> 0.71 (ethyl acetate : light petroleum, 3:1); mp 145-151 °C (decomp.). <sup>1</sup>H NMR (CD<sub>3</sub>CN, 300 MHz) δ: 5.85 (s, 1H, H(3)); 6.34 (s, 1H, H(4')); 6.98 (m, 2H, H(5, 7)); 7.09 (d, 1H, H(4), <sup>3</sup>J 7.3 Hz); 7.31 (t, 1H, H(6), <sup>3</sup>J 7.3 Hz); 7.51 (s, 1H, H(5')); 7.73

(s, 1H, H(3')); 8.64 (br s, 1H, NH). <sup>13</sup>C NMR (CD<sub>3</sub>)<sub>2</sub>CO, 300 MHz) δ: 62.60 (C(3)); 105.46 (C(4')); 110.07 (C(7)); 122.15 (C(5)); 123.05 (C(3a)); 124.83 (C(4)); 129.66 (C(5')); 130.40 (C(6)); 138.35 (C(3')); 139.96 (C(7a)); 1720.67 (C(2)). IR (ν/cm<sup>-1</sup>): 612, 632, 684, 748, 804, 884, 976, 1016, 1092, 1192, 1224, 1260, 1324, 1400, 1472, 1516, 1620, 1736. MS (EI, 70 eV), *m/z* (I, %): 199 [M]<sup>+</sup> (25), 171 [M – CO]<sup>+</sup> (19), 132 [M – pyrazole ring]<sup>+</sup> (18). Found (%): C, 66.39; H, 4.51; N, 21.17. Calc. for C<sub>11</sub>H<sub>9</sub>N<sub>3</sub>O (%): C, 66.32; H, 4.55; N, 21.09.

*Diethyl 1-isopropyl-2-oxo-6',7'-dihydro-5'H-spiro[indoline-3,1'-pyrazolo[1,2-a]pyrazole]-2',3'-dicarboxylate* **13**. A catalytic amount (0.20 mmol) of BF<sub>3</sub>·Et<sub>2</sub>O and 1 mmol of 1-isopropyl-1*H*-indole-2,3-dione **6b** was added to a mixture of 1 mmol of 6-(4-methoxyphenyl)-1,5-diazabicyclo[3.1.0]hexane **2a** and 1.5 ml of the ionic liquid ([bmim][BF<sub>4</sub>]) and stirred this mass for 2 days at 20 °C. Then diethyl but-2-ynedioate (0.19 g, 1.1 mmol) was added dropwise and the reaction mass was additionally stirred for 2 days at this temperature. The equal amount of H<sub>2</sub>O was added and the obtained product was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3×5 ml). Organic layer was washed with 5 ml of 5% aqueous solution of NaHCO<sub>3</sub>, dried with Na<sub>2</sub>SO<sub>4</sub>, the solvent was evaporated *in vacuo* and final product was isolated by column chromatography on SiO<sub>2</sub> (ethyl acetate : light petroleum, 1:2). Yield 23%. <sup>1</sup>H NMR (CD<sub>3</sub>CN, 600 MHz) δ: 0.89, 1.32 (both t, 6H, CH<sub>3</sub>CH<sub>2</sub>, <sup>3</sup>*J* 7.3 Hz); 1.44 (d, 6H, CH(CH<sub>3</sub>)<sub>2</sub>, <sup>3</sup>*J* 7.2 Hz); 2.07, 2.13 (both m, 2H, H<sub>2</sub>(3')); 2.85 (m, 1H, H(2')); 3.20 (q, 1H, H(2'), <sup>3</sup>*J* 7.7 Hz); 3.33, 3.37 (both m, 2H, H<sub>2</sub>(4')); 3.81, 3.89 (both m, 2H, CH<sub>3</sub>CH<sub>2</sub> (7')); 4.33 (q, 2H, CH<sub>3</sub>CH<sub>2</sub> (6'), <sup>3</sup>*J* 7.3 Hz), 4.53 (m, 1H, CH(CH<sub>3</sub>)<sub>2</sub>, <sup>3</sup>*J* 7.2 Hz); 6.89 (d, 1H, H(7), <sup>3</sup>*J* 7.8 Hz); 6.93 (t, 1H, H(5), <sup>3</sup>*J* 7.6 Hz); 7.18 (t, 1H, H(6), <sup>3</sup>*J* 7.8 Hz), 7.29 (d, 1H, H(4), <sup>3</sup>*J* 7.5 Hz). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 150.90 MHz) δ: 13.92, 14.00 (CH<sub>3</sub>CH<sub>2</sub>); 19.07, 19.27 (CH(CH<sub>3</sub>)<sub>2</sub>); 26.24 (C(3')); 44.22 (CH(CH<sub>3</sub>)<sub>2</sub>); 46.09 (C(4')); 47.84 (C(2')); 59.73 (CH<sub>3</sub>CH<sub>2</sub> (7')); 69.45 (CH<sub>3</sub>CH<sub>2</sub> (6')); 72.90 (C(3)); 105.21 (C(7')); 109.71 (C(7)), 122.33 (C(5)); 124.94 (C(4)); 129.30 (C(6)); 129.51 (C(3a), 142.28 (C(7a)); 161.87 (C(7)CO<sub>2</sub>Et), 162.05 (C(6)CO<sub>2</sub>Et), 172.42 (C(2)). <sup>15</sup>N NMR (CDCl<sub>3</sub>, 60.81 MHz) δ: -221.3 (N(1)); -225.7 (N(5')); -234.8 (N(1')). Significant NOESY H-H correlations: H(7) – CH, CH<sub>3</sub> (*i*-Pr); H(4) – H<sub>2</sub>(2'). HMBC C-H, N-H correlations: N(1)-CH<sub>3</sub>(*i*-Pr); C(2)-CH(*i*-Pr); C(3)-H(4, 2'); C(3a)-H(4, 5, 7), C(4)-H(5, 6); C(5)-H(4, 6, 7); C(6)-H(4, 5, 7); C(7)-H(5, 6); C(7a)-H(4, 6, 7); N(1')-H(2', 4'), C(2') – H(3', 4'); C(3') – H(2', 4'); C(4') – H(2', 3'); N(5') – H(4', 2', 3'); C(6') – H(4'). MS (EI, 70 eV), *m/z* (I, %): 413 [M]<sup>+</sup> (2.5), 370 [M – *i*-Pr]<sup>+</sup> (38), 340 [M – CO<sub>2</sub>Et]<sup>+</sup> (4), 312 [M – CO<sub>2</sub>Et – CO]<sup>+</sup> (8), 270 [M – CO<sub>2</sub>Et – CO – *i*-Pr]<sup>+</sup> (9), 43 [*i*-Pr]<sup>+</sup> (100). Found (%): C, 67.20; H, 7.01; N, 10.15. Calc. for C<sub>23</sub>H<sub>29</sub>N<sub>3</sub>O<sub>4</sub> (%): C, 67.13; H, 7.10; N, 10.21.

*1-(4-Nitrobenzyl)-4,5-dihydro-1H-pyrazole* **14**.  $R_f$  0.34 (ethyl acetate : light petroleum, 1:1);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 200 MHz)  $\delta$ : 2.69 (m, 2H,  $\text{H}_2(4')$ ); 2.97 (m, 2H,  $\text{H}_2(5')$ ); 4.25 (s, 2H,  $\text{H}_2(7)$ ); 6.84 (s, 1H,  $\text{H}(3')$ ); 7.56 (d, 2H,  $\text{H}(3, 5)$ ,  $^3J = 8.1$  Hz); 8.19 (d, 2H,  $\text{H}(2, 6)$ ,  $^3J = 8.1$  Hz).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 50 MHz)  $\delta$ : 34.35 ( $\text{C}(4')$ ); 52.52 ( $\text{C}(5')$ ); 59.79 ( $\text{C}(7)$ ); 123.61 ( $\text{C}(3, 5)$ ); 129.49 ( $\text{C}(2, 6)$ ); 144.19 ( $\text{C}(3')$ ); 144.36 ( $\text{C}(4)$ ); 145.24 ( $\text{C}(1)$ ).  $^{14}\text{N}$  NMR ( $\text{CDCl}_3$ , 21.69 MHz)  $\delta$ : -12.30 ( $\text{NO}_2$ ). Found (%): C, 58.79; H, 5.23; N, 20.37. Calc. for  $\text{C}_{10}\text{H}_{11}\text{N}_3\text{O}_2$  (%): C, 58.53; H, 5.40; N, 20.48.