SUPPLEMENTARY INFORMATION

SYNTHESIS OF NEW PYRAZOLO[1,5-*a*]QUINAZOLINE DERIVATES

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I. General information

IR spectra were recorded with a Bruker Tensor 27 FT-IR spectrophotometer. ^1H NMR and ^{13}C spectra were recorded in DMSO- d_6 or in pyridine- d_5 using TMS as an internal reference with a Bruker Avance III. spectrometer operating at 500 MHz and 125 MHz respectively (^1H -, DEPTQ-, HSQC-, HMBC-, NOE-NMR). High-resolution MS spectra were measured by Agilent 6230 TOF LC/MS spectrometer. All dry solvents were purchased from commercial sources (Aldrich, Merck, Reanal).

II. General procedures for the isolated products

Preparation of 2-hydrazino-benzoic acids

General procedure: The corresponding anthranilic acid (1 mmol) or their esters (1 mmol) were suspended in hydrochloric acid (6M, 2.4 ml) and cooled to $-5\text{ }^\circ\text{C}$. Sodium nitrit (1.1 mmol) was dissolved in water (0.4 ml) and added dropwise. The reaction mixture was stirred for 1h at $-5\text{ }^\circ\text{C}$ and then $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ was added (0.451 g, 2 mmol dissolved in 0.6 ml of 6M aqueous HCl). The product was precipitated and filtered, washed with water and dried *in vacuo*. All product was used without any further purification.

2-Hydrazino-3-methyl-benzoic acid (1b): 0.20 g (100 %); light brown powder; ^1H -NMR (400 MHz, DMSO- d_6): 9.96 (brs, 4H, COOH, NH_2), 8.54 (brs, 2H, NH), 7.82 (d, 1H, $J = 6.0\text{ Hz}$, Ar-6'H), 7.50 (d, 1H, $J = 6.0\text{ Hz}$, Ar-4'H), 7.24 (t, 1H, $J = 6.2\text{ Hz}$, Ar-5'H), 2.40 (s, 3H, CH_3).

2-Hydrazino-5-methyl-benzoic acid (1c): 0.20 g (100 %); light brown powder; ¹H-NMR (400 MHz, DMSO-d₆): 10.02 (brs, 4H, COOH, NH, NH₂), 7.69 (d, 1H, *J* = 1.6 Hz, Ar-6'H), 7.37 (dd, 1H, *J*₁ = 2.0 Hz *J*₂ = 8.5 Hz, Ar-4'H), 7.04 (d, 1H, *J* = 8.5 Hz, Ar-3'H), 2.24 (s, 3H, CH₃).

2-Hydrazino-4-methyl-benzoic acid (1d): 0.18 g (90 %); light brown powder; ¹H-NMR (400 MHz, DMSO-d₆): 10.52 (brs, 3H, COOH, NH₂), 9.07 (brs, 1H, NH), 7.77 (d, 1H, *J* = 8.0 Hz, Ar-6'H), 6.97 (s, 1H, Ar-6'H), 6.76 (d, 1H, *J* = 8.0 Hz, Ar-5'H), 2.32 (s, 3H, CH₃).

Methyl, 2-hydrazino-6-methyl-benzoic acid (1e): 0.19 g (88 %); light brown powder; ¹H-NMR (400 MHz, DMSO-d₆): 10.18 (brs, 3H, NH₂), 8.03 (brs, 1H, NH), 7.37 (t, 1H, *J* = 8.0 Hz, Ar-4'H), 6.96-6.89 (m, 2H, Ar-3'H, Ar-5'H), 3.87 (s, 3H, COO CH₃), 2.30 (s, 3H, CH₃).

Methyl, 2-hydrazino-5-methoxy-benzoate (1f): 0.15 g (64 %); light brown powder; ¹H-NMR (400 MHz, DMSO-d₆): 9.96 (s, 3H, NH₂), 8.56 (s, 1H, NH), 7.40 (d, 1H, *J* = 3.2 Hz, Ar-6'H), 7.29 (dd, 1H, *J*₁ = 2.8 Hz *J*₂ = 9.2 Hz, Ar-4'H), 7.11 (d, 1H, *J* = 8.8 Hz, Ar-3'H), 3.86 (s, 3H, COOCH₃), 3.75 (s, 3H, O CH₃).

Methyl, 2-hydrazino-6-bromo-benzoate (1g): 0.21 g (73 %); light brown powder; ¹H-NMR (400 MHz, DMSO-d₆): 9.99 (brs, 3H, NH₂), 8.14 (brs, 1H, NH), 7.39 (t, 1H, *J* = 8.0 Hz, Ar-4'H), 7.28 (d, 1H, *J* = 8.0 Hz, Ar-5'H), 7.06 (d, 1H, *J* = 8.4 Hz, Ar-3'H), 3.86 (s, 3H, COOCH₃).

Reaction of hydrazines with α -oxo-cyanides

General procedure: The corresponding 2-hydrazino-benzoic acid or methyl, 2-hydrazino-benzoate (1.1 mmol) and the α -oxo-cyano compound (1 mmol) was suspended in dry ethanol (5.5 ml) and refluxed for 3 hours. After cooling the product was precipitated and filtered off, dried *in vacuo* to yield the title products.

6,7-Dihydro-5H,9H-thieno[3',4'.3,4]pyrazolo[1,5-a]quinazoline-5-one (4a): 0.180g (74 %); white powder; $^1\text{H-NMR}$ (500 MHz, DMSO- d_6): 12.28 (s, 1H, NH), 8.11 (d, 1H, $J = 7.5$ Hz, Ar-4'H), 7.97 (d, 1H, $J = 8.0$ Hz, Ar-1'H), 7.84 (t, 1H, $J = 8.4$ Hz, Ar-2'H), 7.45 (t, 1H, $J = 7.5$ Hz, Ar-3'H), 4.02 (s, 2H, H-9), 3.83 (s, 2H, H-7); $^{13}\text{C-NMR}$ (125 MHz, DMSO- d_6): 161.3 (q), 158.8 (q), 138.5 (q), 135.6 (CH), 132.7 (q), 128.6 (CH), 125.5 (CH), 116.2 (q), 114.6 (CH), 104.7 (q), 28.9 (CH_2), 26.8 (CH_2); IR (KBr, cm^{-1}): 2820, 1667. HRMS m/z calcd for $\text{C}_{12}\text{H}_9\text{N}_3\text{OS}$ ($\text{M}+\text{H}$) $^+$ 244.0546, found 244.0541;

1-Methyl-6,7-dihydro-5H,9H-thieno[3',4'.3,4]pyrazolo[1,5-a]quinazoline-5-one (4b): 0.023 g (9 %) white powder; $^1\text{H-NMR}$ (500 MHz, DMSO- d_6): 12.37 (s, 1H, NH), 8.05 (d, 1H, $J = 7.5$ Hz, Ar-4'H), 7.68 (d, 1H, $J = 7.5$ Hz, Ar-2'H), 7.36 (t, 1H, $J = 7.5$ Hz, Ar-3'H), 4.04 (s, 2H, 9-H), 3.87 (s, 2H, 7-H), 2.85 (s, 3H, CH_3); $^{13}\text{C-NMR}$ (125 MHz, DMSO- d_6): 160.4 (q), 159.0 (q), 138.7 (CH), 137.2 (q), 133.1 (q), 126.9 (q), 126.8 (CH), 125.1 (CH), 117.5 (q), 104.0 (q), 29.2 (CH_2), 27.0 (CH_2), 23.4 (CH_3); IR (KBr, cm^{-1}): 1682. HRMS m/z calcd for $\text{C}_{13}\text{H}_{11}\text{N}_3\text{OS}$ ($\text{M}+\text{H}$) $^+$ 258.0703, found 258.0695;

3-Methyl-6,7-dihydro-5*H*,9*H*-thieno[3',4'.3,4]pyrazolo[1,5-*a*]quinazoline-5-one (4c): 0.11 g (43 %); white powder; ¹H-NMR (500 MHz, DMSO-*d*₆): 12.20 (s, 1H, NH), 7.91 (br d, 1H, Ar-4'H), 7.88 (d, 1H, *J*= 8.4 Hz, Ar-1'H), 7.67 (dd, 1H, *J*₁= 1.6 Hz *J*₂= 8.4 Hz, Ar-2'H), 4.01 (s, 2H, 9-H), 3.83 (s, 2H, 7-H), 2.42 (s, 3H, CH₃); ¹³C-NMR (125 MHz, DMSO-*d*₆): 160.9 (q), 158.8 (q), 136.5 (q), 136.4 (CH), 135.0 (q), 132.4 (q), 128.2 (CH), 116.0 (q), 114.5 (CH), 104.6 (q), 28.9 (CH₂), 26.8 (CH₂), 21.0 (CH₃); IR (KBr, cm⁻¹): 2824, 1681, 1514. HRMS *m/z* calcd for C₁₃H₁₁N₃OS (M+H)⁺ 258.0703, found 258.0696;

2-Methyl-6,7-dihydro-5*H*,9*H*-thieno[3',4'.3,4]pyrazolo[1,5-*a*]quinazoline-5-one (4d): 0.13 g (49 %); white powder; ¹H-NMR (500 MHz, DMSO-*d*₆): 12.21 (s, 1H, NH), 7.99 (d, 1H, *J*= 8.0 Hz, Ar-4'H), 7.82 (s, 1H, Ar-1'H), 7.28 (d, 1H, *J*= 8.0 Hz, Ar-3'H), 4.01 (s, 2H, 9-H), 3.84 (s, 2H, 7-H), 2.50 (s, 3H, CH₃); ¹³C-NMR (125 MHz, DMSO-*d*₆): 161.2 (q), 158.8 (q), 146.5 (q), 138.4 (q), 132.9 (q), 128.6 (CH), 126.7 (CH), 114.5 (CH), 113.8 (q), 104.6 (q), 28.9 (CH₂), 26.8 (CH₂), 22.1 (CH₃); IR (KBr, cm⁻¹): 2804, 1676. HRMS *m/z* calcd for C₁₃H₁₁N₃OS (M+H)⁺ 258.0703, found 258.0696;

4-Methyl-6,7-dihydro-5*H*,9*H*-thieno[3',4'.3,4]pyrazolo[1,5-*a*]quinazoline-5-one (4e): 0.039 g (15 %); white powder; ¹H-NMR (500 MHz, DMSO-*d*₆): 12.08 (s, 1H, NH), 7.90 (d, 1H, *J*= 8.0 Hz, Ar-1'H), 7.68 (t, 1H, *J*= 7.8 Hz, Ar-2'H), 7.23 (d, 1H, *J*= 7.5 Hz, Ar-3'H), 4.01 (s, 2H, H-9), 3.83 (s, 2H, H-7), 2.76 (s, 3H, CH₃); ¹³C-NMR (125 MHz, DMSO-*d*₆): 161.3 (q), 159.8 (q), 142.7 (q), 139.7 (q), 134.6 (CH), 132.5 (q), 128.6 (CH), 114.1 (q), 112.9 (CH), 103.9 (q), 28.9

(CH₂), 26.8 (CH₂), 23.1 (CH₃); IR (KBr, cm⁻¹): 2818, 1673. HRMS *m/z* calcd for C₁₃H₁₁N₃OS (M+H)⁺ 258.0703, found 258.0696;

3-Methoxy-6,7-dihydro-5*H*,9*H*-thieno[3',4'.3,4]pyrazolo[1,5-*a*]quinazoline-5-one (4f): 0.15 g (56 %); white powder; ¹H-NMR (500 MHz, DMSO-*d*₆): 12.30 (s, 1H, NH), 7.92 (d, 1H, *J*= 9.0 Hz, Ar-1'H), 7.53 (d, 1H, *J*= 3.0 Hz, Ar-4'H), 7.45 (dd, 1H, *J*₁= 3.0 Hz *J*₂= 9.0 Hz, Ar-2'H), 4.00 (brs, 2H, 9-H), 3.86 (s, 3H, OCH₃), 3.83 (brs, 2H, H-7); ¹³C-NMR (125 MHz, DMSO-*d*₆): 160.4 (q), 158.6 (q), 156.9 (q), 132.8 (q), 131.9 (q), 123.7 (CH), 117.1 (q), 116.4 (CH), 110.0 (CH), 104.4 (q), 56.1 (CH₃), 28.9 (CH₂), 26.7 (CH₂); IR (KBr, cm⁻¹): 3366, 2774, 1650, 1504; HRMS *m/z* calcd for C₁₃H₁₁N₃O₂S (M+H)⁺ 274.0652, found 274.0648;

4-Bromo-6,7-dihydro-5*H*,9*H*-thieno[3',4'.3,4]pyrazolo[1,5-*a*]quinazoline-5-one (4g): 0.029 g (9 %); white powder; ¹H-NMR (500 MHz, DMSO-*d*₆): 12.29 (s, 1H, NH), 8.05 (dd, 1H, *J*₁= 1.5 Hz *J*₂= 8.0 Hz, Ar-1'H), 7.69 (dd, 1H, *J*₁= 1.5 Hz *J*₂= 8.0 Hz, Ar-3'H), 7.66 (t, 1H, *J*= 7.8 Hz, Ar-2'H), 4.01 (s, 1H, H-9), 3.82 (s, 2H, H-7); ¹³C-NMR (125 MHz, DMSO-*d*₆): 161.8 (q), 157.2 (q), 140.7 (q), 135.6 (CH), 132.5 (q), 132.2 (CH), 123.3 (q), 114.8 (CH), 113.6 (q), 104.3 (q), 28.8 (CH₂), 26.7 (CH₂); IR (KBr, cm⁻¹): 2815, 1673. HRMS *m/z* calcd for C₁₂H₈BrN₃OS (M+H)⁺ 321.9651, found 321.9657;

6,7,8,9-Tetrahydro-5*H*-cyclopenta[3,4]pyrazolo[1,5-*a*]quinazoline-5-one (10a): 0.12 g (54 %); white powder; ¹H-NMR (500 MHz, DMSO-*d*₆): 12.09 (s, 1H, NH), 8.08 (d, 1H, *J*= 7.7 Hz, Ar-4'H), 7.97 (d, 1H, *J*= 8.0 Hz, Ar-1'H), 7.81 (t, 1H, *J*= 7.7 Hz, Ar-2'H), 7.39 (t, 1H, *J*= 7.5

Hz, Ar-3'H), 2.70 (t, 2H, J = 7.5 Hz, H-9), 2.61 (t, 2H, J = 7.0 Hz, H-7), 2.37 (m, 2H, H-8); ^{13}C -NMR (125 MHz, DMSO- d_6): 164.9 (q), 159.0 (q), 138.9 (q), 135.4 (CH), 132.6 (q), 128.6 (CH), 124.6 (CH), 114.4 (CH), 106.7 (q), 29.8 (CH $_2$), 25.0 (CH $_2$), 22.7 (CH $_2$); IR (KBr, cm^{-1}): 1668, 1485, 1381. HRMS m/z calcd for $\text{C}_{13}\text{H}_{11}\text{N}_3\text{O}$ ($\text{M}+\text{H}$) $^+$ 226.0982, found 226.0970;

3-Methyl-6,7,8,9-tetrahydro-5H-cyclopenta[3,4]pyrazolo[1,5-a]quinazoline-5-one (10b):

0.11 g (44 %); white powder; ^1H -NMR (500 MHz, DMSO- d_6): 12.00 (s, 1H, NH), 7.88 (d, 1H, J = 1.6 Hz, Ar-4'H), 7.86 (d, 1H, J = 8.2 Hz, Ar-1'H), 7.62 (dd, 1H, J_1 = 8.2 Hz, J_2 = 1.6 Hz, Ar-2'H), 2.69 (t, 2H, J = 7.4 Hz, H-9), 2.61 (t, 2H, J = 7.0 Hz, H-7), 2.40 (s, 3H), 2.36 (m, 2H, H-8); ^{13}C -NMR (125 MHz, DMSO- d_6): 164.4 (q), 159.0 (q), 136.9 (q), 136.3 (CH), 134.0 (q), 132.3 (q), 128.2 (CH), 115.5 (q), 114.4 (CH), 106.5 (q), 29.7 (CH $_2$), 25.0 (CH $_2$), 22.7 (CH $_2$), 20.9 (CH $_3$); IR (KBr, cm^{-1}): 2812, 1665, 1514. HRMS m/z calcd for $\text{C}_{14}\text{H}_{13}\text{N}_3\text{O}$ ($\text{M}+\text{H}$) $^+$ 240.1139, found 240.1123;

3-Methoxy-6,7,8,9-tetrahydro-5H-cyclopenta[3,4]pyrazolo[1,5-a]quinazoline-5-one (10c):

0.077 g (30 %); white powder; ^1H -NMR (500 MHz, DMSO- d_6): 12.11 (s, 1H, NH), 7.91 (d, 1H, J = 9.0 Hz, Ar-1'H), 7.51 (d, 1H, J = 3.0 Hz, Ar-4'H), 7.42 (dd, 1H, J_1 = 3.0 Hz, J_2 = 9.0 Hz, Ar-2'H), 3.85 (s, 3H, OCH $_3$), 2.69 (t, 2H, J = 7.3 Hz, H-9), 2.60 (t, 2H, J = 7.0 Hz, H-9), 2.36 (m, 2H, H-8); ^{13}C -NMR (125 MHz, DMSO- d_6): 164.0 (q), 159.8 (q), 156.4 (q), 133.3 (q), 131.8 (q), 123.7 (CH), 116.6 (q), 116.2 (CH), 110.0 (CH), 106.3 (q), 56.1 (CH $_3$), 29.8 (CH $_2$), 25.0 (CH $_2$), 22.8 (CH $_2$). IR (KBr, cm^{-1}): 3484, 2958, 1650, 1510. HRMS m/z calcd for $\text{C}_{14}\text{H}_{13}\text{N}_3\text{O}_2$ ($\text{M}+\text{H}$) $^+$ 256.1088, found 256.1077;

4-Bromo-6,7,8,9-tetrahydro-5H-cyclopenta[3,4]pyrazolo[1,5-a]quinazoline-5-one (10d):

0.0243 g (8 %); white powder; ^1H -NMR (500 MHz, DMSO- d_6): 12.09 (s, 1H, NH), 8.04 (m, 1H, Ar-3'H), 7.61 (m, 1H, Ar-1'H), 7.61 (m, 1H, Ar-2'H), 2.69 (t, 2H, J = 7.3 Hz, H-9), 2.59 (t, 2H, J = 7.3 Hz, H-7), 2.36 (quint., 2H, H-8); ^{13}C -NMR (125 MHz, DMSO- d_6): 165.5 (q), 157.4 (q), 141.1 (q); 135.5 (CH), 132.3 (q), 131.4 (CH), 123.2 (q), 114.7 (CH), 113.0 (q), 106.3 (q), 29.7 (CH₂), 25.0 (CH₂), 22.7 (CH₂); IR (KBr, cm^{-1}): 1657, 1594. HRMS m/z calcd for C₁₃H₁₀BrN₃O (M+H)⁺ 340.0087, found 340.0076;

7,8,9,10-Tetrahydroindazolo[2,3-a]quinazoline-5(6H)-one (10e): 0.132 g (55 %); white

powder; ^1H -NMR (500 MHz, DMSO- d_6): 12.10 (s, 1H, NH), 8.10 (d, 1H, J = 8.0 Hz, Ar-4'H), 7.97 (d, 1H, J = 8.0 Hz, Ar-1'H), 7.81 (t, 1H, J = 7.8 Hz, Ar-2'H), 7.40 (t, 1H, J = 7.8 Hz, Ar-3'H), 2.65 (t, 2H, J = 6.2 Hz, H-10), 2.48 (t, 2H, J = 6.0 Hz, H-7), 1.77 (m, 2H, H-9), 1.70 (m, 2H, H-8); ^{13}C -NMR (125 MHz, DMSO- d_6): 159.2 (q), 152.3 (q), 138.1 (q), 135.4 (CH), 134.9 (q), 128.6 (CH), 124.9 (CH), 116.1 (q), 114.4 (CH), 98.1 (q), 23.9 (CH₂), 23.1 (CH₂), 23.0 (CH₂), 19.5 (CH₂); IR (KBr, cm^{-1}): 2940, 1661; HRMS m/z calcd for C₁₄H₁₃N₃O (M+H)⁺ 240.1139, found 240.1121;

3-Methyl-7,8,9,10-tetrahydroindazolo[2,3-a]quinazoline-5(6H)-one (10f): 0.119 g (47 %);

white powder; ^1H -NMR (500 MHz, DMSO- d_6): 12.04 (s, 1H, NH), 7.88-7.85 (m, 2H, Ar-4'H, Ar-1'H), 7.61 (dd, 1H, J_1 = 1.9 Hz J_2 = 8.4 Hz, Ar-2'H), 2.63 (t, 2H, J = 6.1 Hz, 10-H), 2.47 (t, 2H, J = 5.9 Hz, 7-H), 2.40 (s, 3H, CH₃), 1.75 (m, 2H, H-9), 1.69 (m, 2H, H-8); ^{13}C -NMR (125

MHz, DMSO- d_6): 159.2 (q), 151.8 (q), 136.3 (CH), 134.6 (q), 134.2 (q), 128.2 (CH), 115.9 (q), 114.4 (CH), 97.9 (q), 23.9 (CH₂), 23.2 (CH₂), 23.0 (CH₂), 21.0 (CH₃), 19.5 (CH₂); IR (KBr, cm⁻¹): 2829, 1673, 1514; HRMS m/z calcd for C₁₅H₁₅N₃O (M+H)⁺ 254.1295, found 254.1281;

3-Methoxy-7,8,9,10-tetrahydroindazolo[2,3-*a*]quinazoline-5(6*H*)-one (10g): 0.14 g (52 %); white powder; ¹H-NMR (500 MHz, DMSO- d_6): 12.15 (s, 1H, NH), 7.91 (d, 1H, J = 9.0 Hz, Ar-1'H), 7.53 (d, 1H, J = 3.0 Hz, Ar-4'H), 7.42 (dd, 1H, J_1 = 3.0 Hz J_2 = 9.0 Hz, Ar-2'H), 3.85 (s, 3H, OCH₃), 2.64 (t, 2H, J = 6.2 Hz, H-10), 2.47 (t, 2H, J = 6.2 Hz, H-7), 1.76 (m, 2H, H-9), 1.69 (m, 2H, H-8); ¹³C-NMR (125 MHz, DMSO- d_6): 159.0 (q), 156.5 (q), 151.4 (q), 134.1 (q), 132.6 (q), 123.6 (CH), 117.0 (q), 116.2 (CH), 110.1 (CH), 97.8 (q), 56.1 (CH₃), 23.8 (CH₂), 23.2 (CH₂), 23.0 (CH₂), 19.5 (CH₂); IR (KBr, cm⁻¹): 2833, 1665, 1511. HRMS m/z calcd for C₁₅H₁₅N₃O₂ (M+H)⁺ 270.1244, found 270.1229;

4-Bromo-7,8,9,10-tetrahydroindazolo[2,3-*a*]quinazoline-5(6*H*)-one (10h) 0.0095 g (3 %); white powder; ¹H-NMR (500 MHz, DMSO- d_6): 12.13 (s, 1H, NH), 8.04 (dm, 1H, J_1 = 7.0 Hz, Ar-3'H), 7.64 (d, 1H, J = 5.5 Hz, Ar-1'H), 7.62 (t, 1H, J_1 = 5.5 Hz, J_2 = 7.0 Hz, Ar-2'H), 2.64 (t, 2H, J = 6.0 Hz, H-10), 2.47 (t, 2H, J = 6.0 Hz, H-7), 1.75 (m, 2H, H-8), 1.69 (m, 2H, H-9); ¹³C-NMR (125 MHz, DMSO- d_6): 157.5 (q), 152.9 (q), 140.3 (q), 135.5 (CH), 134.6 (q), 131.6 (CH), 123.2 (q), 114.6 (CH), 113.4 (q), 97.7 (q), 23.9 (CH₂), 23.1 (CH₂), 22.9 (CH₂), 19.5 (CH₂); IR (KBr, cm⁻¹): 2934, 1667, 1596; HRMS m/z calcd for C₁₄H₁₂BrN₃O (M+H)⁺ 318.0244, found 318.0241;

Lactam reduction

General procedure: The corresponding indazolo[2,3-*a*]kinazolin-5(6*H*)-on or pyrazolo[1,5-*a*]quinazoline-5-one (1 mmol) was dissolved in dry tetrahydrofuran (30 ml) and at -5 °C under nitrogen atmosphere BH₃.THF solution (1M, 7 ml) was added dropwise. The mixture was stirred at room temperature for 4 hours, then aqueous hydrochloric acid solution (6 M, until no more gas evolved) was added. The pH was adjusted to 13 with 2M sodium hydroxide solution, then it was extracted with dichloromethane (2 x 200 ml), dried over sodium sulfate, evaporated. The crude product was purified by column chromatography over silica (eluent: heptane – ethyl acetate 3:1) to yield the product.

6,7-Dihydro-5*H*,9*H*-thieno[3',4'.3,4]pyrazolo[1,5-*a*]quinazoline (5a): 0.117 g (51 %); white powder; ¹H-NMR (500 MHz, DMSO-*d*₆): 7.45 (dm, 1H, *J*= 8.0 Hz, Ar-1'H), 7.29 (m, 1H, Ar-2'H), 7.23 (dm, 1H, *J*= 7.3 Hz, Ar-4'H), 7.09 (m, 1H, Ar-3'H), 6.75 (brs, 1H, NH), 4.34 (brs, 2H, H-5), 3.85 (brt, 2H, H-9), 3.68 (brt, 2H, H-7); ¹³C-NMR (125 MHz, DMSO-*d*₆): 160.3 (q), 140.8 (q), 135.9 (q), 128.7 (CH), 126.8 (CH), 124.6 (CH), 121.5 (q), 113.7 (CH), 102.5 (q), 42.8 (CH₂), 28.9 (CH₂), 26.7 (CH₂). IR (KBr, cm⁻¹): 3280, 2916. HRMS *m/z* calcd for C₁₂H₁₁N₃S (M+H)⁺ 230.0754, found 230.0741;

3-Methyl-6,7-dihydro-5*H*,9*H*-thieno[3',4'.3,4]pyrazolo[1,5-*a*]quinazoline (5c): 0.23 g (95 %); white powder; ¹H-NMR (500 MHz, DMSO-*d*₆): 7.33 (d, 1H, *J*= 8.0 Hz, Ar-1'H), 7.09 (brd, 1H, Ar-2'H), 7.04 (brs, 1H, Ar-4'H), 6.69 (brs, 1H, NH), 4.29 (s, 2H, 5-H), 3.83 (s, 2H, 9-H), 3.67 (s, 2H, 7-H), 2.26 (s, 3H, CH₃). ¹³C-NMR (125 MHz, DMSO-*d*₆): 159.8 (q), 140.5 (q),

133.7 (q), 133.7 (q), 129.0 (CH), 127.2 (CH), 121.4 (q), 113.6 (CH), 102.4 (q), 28.9 (CH₂), 26.7 (CH₂), 21.0 (CH₃). IR (KBr, cm⁻¹): 3292, 2824, 1618. HRMS *m/z* calcd for C₁₃H₁₃N₃S (M+H)⁺ 244.0910, found 244.0919;

3-Methoxy-6,7-dihydro-5*H*,9*H*-thieno[3',4'.3,4]pyrazolo[1,5-*a*]quinazoline (5f): 0.22 g (85 %); white powder; ¹H-NMR (500 MHz, DMSO-*d*₆): 7.38 (m, 1H, Ar-1'H), 6.87 (m, 1H, Ar-2'H), 6.86 (m, 1H, Ar-4'H), 4.30 (brd, 2H, 5-H), 3.83 (s, 2H, 9-H), 3.74 (s, 3H, OCH₃), 3.67 (s, 2H, 7-H); ¹³C-NMR (125 MHz, DMSO-*d*₆): 159.3 (q), 156.5 (q), 140.1 (q), 129.7 (q), 123.0 (q), 114.8 (CH), 113.7 (CH), 112.4 (CH), 102.5 (q), 55.8 (CH₃), 43.0 (CH₂), 28.9 (CH₂), 26.8 (CH₂); IR (KBr, cm⁻¹): 3245, 2987, 1632, 1246. HRMS *m/z* calcd for C₁₃H₁₃N₃OS (M+H)⁺ 260.0859, found 260.0852;

6,7,8,9-Tetrahydro-5*H*-cyclopenta[3,4]pyrazolo[1,5-*a*]quinazoline (11a): 0.184 g (87 %); white powder; ¹H-NMR (500 MHz, DMSO-*d*₆): 7.43 (d, 1H, *J* = 8.0 Hz, Ar-1'H), 7.26 (m, 1H, Ar-2'H), 7.21 (d, 1H, *J* = 7.3 Hz, Ar-4'H), 7.03 (m, 1H, Ar-3'H), 6.49 (brt, 1H, N-6'H), 4.27 (d, 2H, *J* = 1.4 Hz, 5-H), 2.53 (t, 2H, *J* = 7.4 Hz, 9-H), 2.45 (t, 2H, *J* = 7.0 Hz, 7-H), 2.28 (m, 2H, 8-H). ¹³C-NMR (125 MHz, DMSO-*d*₆): 163.8 (q), 140.7 (q), 136.5 (q), 128.5 (CH), 126.7 (CH), 123.8 (CH), 121.5 (q), 113.6 (CH), 104.4 (q), 43.2 (CH₂), 29.8 (CH₂), 24.9 (CH₂), 22.5 (CH₂); IR (KBr, cm⁻¹): 3330, 2855; HRMS *m/z* calcd for C₁₃H₁₃N₃ (M+H)⁺ 212.1189, found 212.1181;

3-Methyl-6,7,8,9-tetrahydro-5*H*-cyclopenta[3,4]pyrazolo[1,5-*a*]quinazoline (11b): 0.196 g (87 %); white powder; ¹H-NMR (500 MHz, DMSO-*d*₆): 7.32 (d, 1H, *J* = 8.5 Hz, Ar-1'H), 7.06

(brd, 1H, Ar-2'H), 7.02 (brs, 1H, Ar-4'H), 6.43 (brt, 1H, NH), 4.23 (brs, 2H, 5-H), 2.52 (t, 2H, $J = 8.0$ Hz, H-9), 2.44 (t, 2H, $J = 7.0$ Hz, H-7), 2.27 (m, 2H, H-8), 2.25 (s, 3H, CH₃). ¹³C-NMR (125 MHz, DMSO-d₆): 163.3 (q), 140.4 (q), 134.3 (q), 132.7 (q), 128.9 (CH), 127.1 (CH), 121.5 (Cq), 113.5 (CH), 104.3 (q), 29.8 (CH₂), 24.9 (CH₂), 22.5 (CH₂), 20.9 (CH₃). IR (KBr, cm⁻¹): 3235, 2923, 1631. HRMS m/z calcd for C₁₄H₁₅N₃ (M+H)⁺ 226.1346, found 226.1352;

3-Methoxy-6,7,8,9-tetrahydro-5H-cyclopenta[3,4]pyrazolo[1,5-*a*]quinazoline (11c): 0.138 g (57 %); white powder; ¹H-NMR (500 MHz, DMSO-d₆): 7.36 (m, 1H, Ar-1'H), 6.84 (m, 1H, Ar-2'H), 6.84 (m, 1H, Ar-4'H), 6.39 (s, 1H, NH), 4.24 (s, 2H, 5-H), 3.73 (s, 3H, OCH₃), 2.52 (t, 2H, 9-H), 2.44 (t, 2H, 7-H), 2.27 (m, 2H, 8-H). ¹³C-NMR (125 MHz, DMSO-d₆): 162.7 (q), 156.0 (q), 140.0 (q), 130.4 (q), 123.0 (q), 114.6 (CH), 113.5 (CH), 112.3 (CH), 104.3 (q), 43.4 (CH₂), 29.8 (CH₂), 24.9 (CH₂), 22.5 (CH₂). IR (KBr, cm⁻¹): 3231, 2920, 1629. HRMS m/z calcd for C₁₄H₁₅N₃O (M+H)⁺ 242.1295, found 242.1299;

5,6,7,8,9,10-Hexahydroindazolo[2,3-*a*]quinazoline (11e): 0.059 g (26 %); white powder; ¹H-NMR (500 MHz, DMSO-d₆): 7.44 (d, 1H, $J = 7.6$ Hz, Ar-1'H), 7.26 (t, 1H, $J = 7.8$ Hz, Ar-2'H), 7.22 (d, 1H, $J = 7.6$ Hz, Ar-4'H), 7.04 (tm, 1H, $J = 7.4$ Hz, Ar-3'H), 6.32 (brt, 1H, NH), 4.29 (d, 2H, $J = 1.6$ Hz, 5-H), 2.5 (brt, 2H, 10-H), 2.30 (t, 2H, $J = 6.0$ Hz, 7-H), 1.69 (m, 2H, 9-H), 1.66 (m, 2H, 8-H). ¹³C-NMR* (125 MHz, DMSO-d₆): 151.2 (q), 142.8 (q), 135.4 (q), 128.5 (CH), 126.6 (CH), 124.0 (CH), 121.7 (q), 113.4 (CH), 96.0 (q), 43.1 (CH₂), 23.9 (CH₂), 23.3 (CH₂), 23.3 (CH₂), 19.5 (CH₂). IR (KBr, cm⁻¹): 3192, 2926. HRMS m/z calcd for C₁₄H₁₅N₃ (M+H)⁺ 226.1346, found 226.1336;

(*¹³C- NMR was not performed directly, the chemical shifts was based on the HSQC.)

3-Methyl-5,6,7,8,9,10-hexahydroindazolo[2,3-*a*]quinazoline (11f) : 0.105 g (44 %); white powder; ¹H-NMR (500 MHz, DMSO-*d*₆): 7.32 (d, 1H, *J*= 8.0 Hz, Ar-1'H), 7.06 (brd, 1H, Ar-2'H), 7.03 (brs, 1H, Ar-4'H), 6.29 (brs, 1H, NH), 4.24 (brs, 2H, 5-H), 2.48 (t, 2H, *J*= 6.3 Hz, H-10), 2.28 (t, 2H, *J*= 6.1 Hz, H-7), 2.25 (s, 3H, CH₃), 1.69 (m, 2H, H-8), 1.64 (m, 2H, H-9); ¹³C-NMR (125 MHz, DMSO-*d*₆): 150.7 (q), 142.6 (q), 133.5 (q), 132.9 (q), 128.9 (CH), 127.2 (CH), 121.9 (q), 113.4 (CH), 96.0 (q), 43.2 (CH₂), 24.1 (CH₂), 23.5 (CH₂), 23.4 (CH₂), 20.9 (CH₃), 19.7 (CH₂). IR (KBr, cm⁻¹): 3187, 2920, 1617. HRMS *m/z* calcd for C₁₅H₁₇N₃ (M+H)⁺ 240.1502, found 240.1489;

III. ¹H and ¹³C Spectras of the isolated products

DMSO, 400 MHz

DMSO, 500 MHz

DMSO, 125 MHz