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SYNTHESIS AND SOME PROPERTIES OF 3-ETHYL-2-THIOXO-2,3-DIHYDRO-1H-SPIRO[BENZO[h]QUINAZOLINE-5,1'-CYCLOHEPTANE]-4(6H)-ONE

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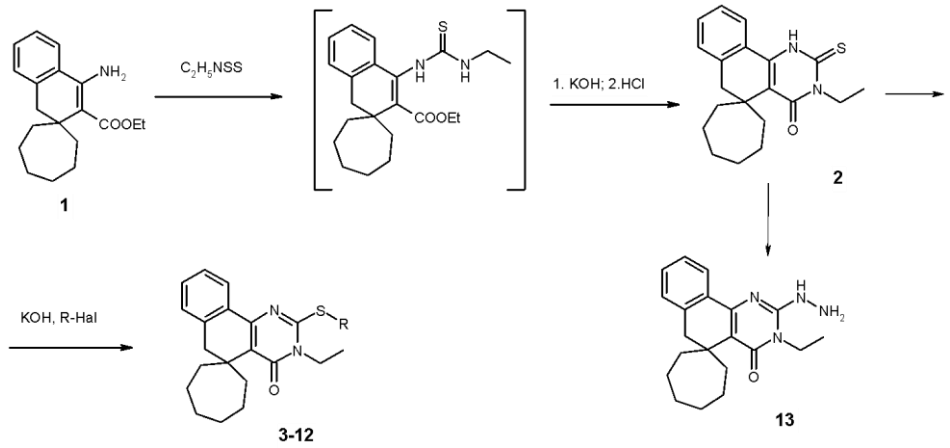
Based on 4'-amino-1'H-spiro[cycloheptane-1,2'-naphthalene]-3'-carboxylate, a synthesis method was developed for 3-ethyl-2-thioxo-2,3-dihydro-1H-spiro[benzo[h]quinazoline-5,1'-cycloheptane]-4(6H)-one, which was converted into 2-sulfanyl-substituted 3-ethyl-3H-spiro[benzo[h]quinazoline-5,1'-cycloheptane]-4(6H)-ones and 3-ethyl-2-hydrazinyl-3H-spiro[benzo[h]quinazoline-5,1'-cycloheptane]-4(6H)-one. By transformations of the latter, 3-ethyl-2-[2-(propan-2-ylidene)hydrazinyl]-3H-spiro[benzo[h]quinazoline-5,1'-cycloheptane]-4(6H)-one, N'-(3-ethyl-4-oxo-4,6-dihydro-3H-spiro[benzo[h]quinazoline-5,1'-cycloheptane]-2-yl) benzohydrazide, N-[2-(3-ethyl-4-oxo-4,6-dihydro-3H-spiro[benzo[h]quinazoline-5,1'-cycloheptane]-2-yl]hydrazinecarbonothioyl)benzamide, 3-ethyl-3H-spiro[benzo[h]quinazoline-5,1'-cycloheptane]-4(6H)-one, 4-ethyl-4H-spiro[benzo[h][1,2,4]triazolo[4,3-a]quinazoline-6,1'-cycloheptane]-5(7H)-one, 4-ethyl-1-mercapto-4H-spiro[benzo[h]-[1,2,4]triazolo[4,3-a]quinazoline-6,1'-cycloheptane]-5(7H)-one and 1-sulfanylsubstituted 4-ethyl-4H-spiro-[benzo[h][1,2,4]triazolo[4,3-a]quinazoline-6,1'-cycloheptane]-5(7H)-ones were synthesized.

References 17.

The work carried out during the recent years in the field of benzo[h]quinazoline series shows that the compounds of this heterocyclic series have valuable biological properties [1-13], which indicates the topicality of such studies. Benzo[h]quinazolines spiro-condensed in the fifth position with a cycloheptane cycle are still poorly studied and there are only a few reports available in the literature [14–17]. This report presents data on the synthesis of derivatives of 3-ethyl-spiro[benzo[h]quinazoline-5,1'-cycloheptane].

By reacting the ethyl 4'-amino-1'H-spiro[cycloheptane-1,2'-naphthalene]-3'-carboxylate (aminoester) (**1**) [17] with ethylisothiocyanate corresponding thioureido derivative was obtained, which, without isolation from the reaction medium, was subjected to cyclization, leading to the synthesis of ethyl 3-ethyl-

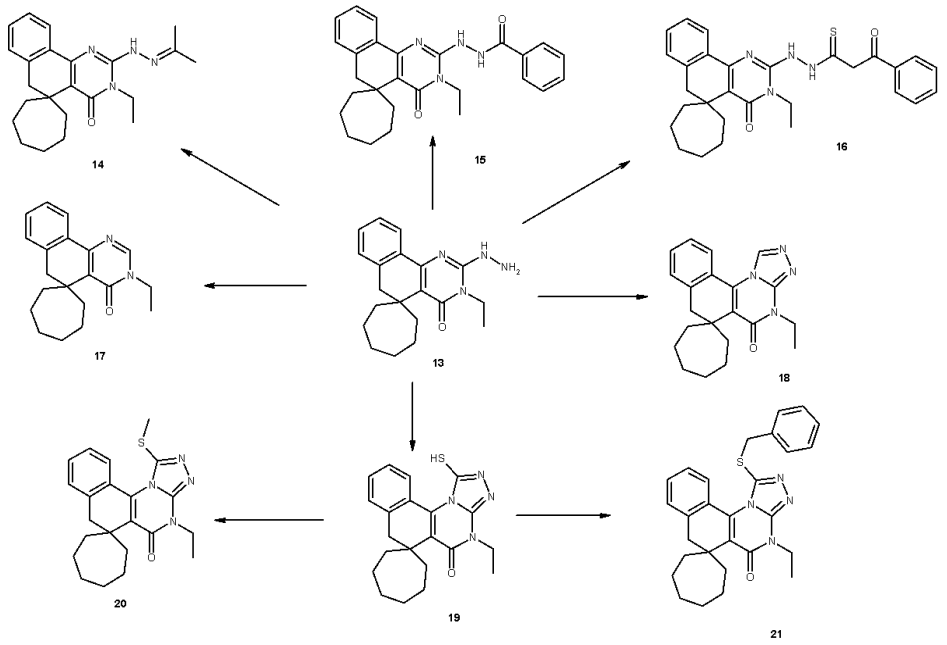
2-thioxo-2,3-dihydro-1H-spiro[benzo[h]quinazoline-5,1'-cycloheptane]-4(6H)-one (**2**). The latter in the presence of potassium hydroxide was reacted with halides of various structures, as a result of which 2-sulfanyl-substituted 3-ethyl-3H-spiro[benzo[h]quinazoline-5,1'-cycloheptane]-4(6H)-ones (**3-12**) were obtained. By condensation of 2-thioxobenzo[h]quinazoline **2** with hydrazine hydrate, 3-ethyl-2-hydrazinyl-3H-spiro[benzo[h]quinazoline-5,1'-cycloheptane]-4(6H)-one (**13**) was synthesized according to the Scheme:



R=CH_3 (**3**), C_2H_5 (**4**), C_3H_7 (**5**), i-C_3H_7 (**6**), $CH_2CH{=}CH_2$ (**7**), C_4H_9 (**8**), CH_2COOEt (**9**), $CH_2C_6H_5$ (**10**), 4-$ClC_6H_4CH_2$(**11**), 4-$CH_3C_6H_4CH_2$(**12**)

Some transformations of 3-ethyl-2-hydrazinyl-3H-spiro[benzo[h]quinazoline-5,1'-cycloheptane]-4(6H)-one (**13**) have been studied, in particular, its interaction with acetone, benzoyl chloride and benzoylisothiocyanate, resulting in 3-ethyl-2-[2-(propan-2-ylidene)hydrazinyl]-3H-spiro[benzo[h]-quinazoline-5,1'-cycloheptane]-4(6H)-one (14), N'-(3-ethyl-4-oxo-4,6-dihydro-3H-spiro [benzo[h]-quinazoline-5,1'-cycloheptane]-2-yl)benzohydrazide (**15**) and N-[2-(3-ethyl-4-oxo-4,6-dihydro-3H-spiro[benzo[h]quinazoline-5,1'-cycloheptane]-2-yl)hydrazinecarbonothioyl]benzamide (**16**) respecti-vely. It is shown that the specified hydrazinobenzo[h]quinazoline in the presence of a base undergoes dehydrazination to afford 3-ethyl-3H-spiro[benzo[h]quinazoline-5,1'-cycloheptane]-4(6H)-one (**17**).

By condensation of 2-hydrazinobenzo[h]quinazoline and ethyl ether of orthoformic acid and carbon disulfide, 4-ethyl-4H spiro[benzo[h][1,2,4] triazolo[4,3-a]quinazoline-6,1'-cycloheptane]-5(7H)-one (**18**) and 4-ethyl-1-mercapto-4H-spiro[benzo[h][1,2,4]triazolo[4,3-a]quinazoline-6,1'-cycloheptane]-5(7H)-one (**19**) were obtained respectively. The latter, in the presence of KOH, was put into interaction with methyl iodide and benzylchloride, which led to the production of the corresponding 1-sulfanylsubstituted 4-ethyl-4H-spiro[benzo[h][1,2,4]triazolo[4,3-a]quinazoline-6,1'-cycloheptane]-5(7H)-ones (**20, 21**) according to the Scheme:



Experimental part

The IR spectra were recorded on a Thermo "Nicolet Nexus FTIR" spectrometer from samples dispersed in mineral oil. The ^{1}H and ^{13}C NMR spectra were recorded on a Varian "Mercury-300VX" instrument from solutions in DMSO-d_6-CCl_4 (1:3); the chemical shifts were measured relative to tetramethylsilane or hexamethyldisiloxane as internal standard. Silufol plates were used for analytical TLC; spots were visualized by treatment with iodine vapor.

3-Ethyl-2-thioxo-2,3-dihydro-1H-spiro[benzo[h]quinazoline-5,1'-cycloheptane]-4(6H)-one (2). The reaction mixture of 29.9 *g* (0.1 *mol*) of ethyl 4'-amino-1'H-spiro[cycloheptane-1,2'-naphthalene]-3'-carboxylate (**1**), 8.7 *g* (0.1 *mol*) of ethyl isothiocyanate and 15 *ml* of ethanol was refluxed for 20 *hrs*, then a solution of 11.2 *g* (0.2 *mol*) of KOH in 70 *ml* of H_2O was added and the mixture was boiled for additional 3 *hrs*. After cooling, the mixture was acidified with a solution of 10% hydrochloric acid. The precipitated crystals were filtered, washed with water, and recrystallized from ethanol. Yield 22.7 *g* (67%) of **2,** mp 212-213°C, R_f 0.78 (ethyl acetate-heptane, 1:1). IR spectrum, ν, cm^{-1}: 1616 (C=C arom); 1676 (C=O); 3221 (NH). ^{1}H NMR spectrum (300 MHz, DMSO-d_6-CCl_4 1/3), δ, ppm: 1.26-1.36 (m, 2H, CH_2 cycloheptane), 1.29 (t, 3H, J=7.0, N-CH_2-$\underline{CH_3}$), 1.43-1.70 (m, 6H, 3×CH_2 cycloheptane), 1.71-1.85 (m, 2H, CH_2 cycloheptane), 2.17-2.28 (m, 2H, CH_2 cycloheptane), 2.85 (s, 2H, C6H_2), 4.42 (q, 2H, J=7.0, N-$\underline{CH_2}$-CH_3), 7.18-7.39 (m, 3H, 3×CH Ar),7.88-7.93 (m, 1H, CH Ar), 11.94 (s, 1H, NH). ^{13}C NMR spectrum (75 MHz, DMSO-d_6-CCl_4 1/3), δ, ppm: 11.41 (N-CH_2-$\underline{CH_3}$), 23.86 (2×CH_2 cycloheptane), 29.50 (2×CH_2

cycloheptane), 35.33 (2×CH_2 cycloheptane), 39.28 (C*5*), 40.28 (N-$\underline{CH_2}$-CH_3), 40.89 (C*6*H_2), 119.51 (C*4*$_a$), 124.58 (CH Ar), 125.35 (C Ar), 126.03 (CH Ar), 127.59 (CH Ar), 130.36 (CH Ar), 136.44 (C Ar), 142.38 (C*10*$_b$), 158.70 (C*4*), 174.88 (C*2*). Found, %: C 70.38; H 7.25; N 8.08; S 9.54. $C_{20}H_{24}N_2OS$. Calculated, %: C 70.55; H 7.10; N 8.23; S 9.42.

2-Alkylthio-ethyl-3H-spiro[benzo[h]quinazoline-5,1'-cycloheptane]-4(6H)-ones (3-12) (General method). A mixture of 1.7 *g* (5 *mmol*) of **3**, 0.4 *g* (7 *mmol*) of KOH and 30 *ml* of absolute ethanol was placed into a round-bottom flask and boiled for 30 *min*. Then 7 *mmol* of halogenide was added and boiling continued for 12 *hrs*. The reaction mixture was cooled and 20 *ml* of water was added. The precipitate was filtered off and recrystallized from ethanol.

3-Ethyl-2-(methylthio)-3H-spiro[benzo[h]quinazoline-5,1'-cycloheptane]-4(6H)-one (**3**). Yield 1.7 *g* (96%) of **3,** mp 163-164°C, R_f 0.76 (ethyl acetate-benzene, 1:10). IR spectrum, ν, cm^{-1}: 1600 (C=C arom); 1644 (C=O).^{1}H NMR spectrum (300 MHz, DMSO-d_6-CCl_4 1/3), δ, ppm: 1.33-1.43 (m, 2H, CH_2 cycloheptane), 1.34 (t, 3H, J=7.0, N-CH_2-$\underline{CH_3}$), 1.46-1.70 (m, 6H, 3×CH_2 cycloheptane), 1.72-1.86 (m, 2H, CH_2 cycloheptane), 2.24-2.35 (m, 2H, CH_2 cycloheptane), 2.68 (s, 3H, S-CH_3), 2.87 (s, 2H, C*6*H_2), 4.04 (q, 2H, J=7.0, N-$\underline{CH_2}$-CH_3), 7.11-7.17 (m, 1H, CH Ar), 7.20-7.32 (m, 2H, 2×CH Ar), 8.00-8.06 (m, 1H, CH Ar). ^{13}C NMR spectrum (75 MHz, DMSO-d_6-CCl_4 1/3), δ, ppm: 12.41 (N-CH_2-$\underline{CH_3}$), 14.09 (S-CH_3), 23.87 (2×CH_2 cycloheptane), 29.63 (2×CH_2 cycloheptane), 35.67 (2×CH_2 cycloheptane), 38.88 (N-$\underline{CH_2}$-CH_3), 39.57 (C*5*), 40.10 (C*6*H_2), 122.89 (C*4*$_a$), 124.63 (CH Ar), 125.86 (CH Ar), 127.15 (CH Ar), 129.41 (CH Ar), 132.06 (C Ar), 136.23 (C Ar), 150.56 (C*10*$_b$), 157.82 (C*2*), 159.76 (C*4*). Found, %: C 70.98; H 7.25; N 7.78; S 9.21. $C_{21}H_{26}N_2OS$. Calculated, %: C 71.15; H 7.39; N 7.90; S 9.04.

3-Ethyl-2-(ethylthio)-3H-spiro[benzo[h]quinazoline-5,1'-cycloheptane]-4(6H)-one (**4**). Yield 1.7 *g* (92%) of **4,** mp 130-131°C, R_f 0.73 (ethyl acetate-benzene, 1:10). IR spectrum, ν, cm^{-1}: 1605 (C=C arom); 1652 (C=O); 1742 (C=O). ^{1}H NMR spectrum (300 MHz, DMSO-d_6-CCl_4 1/3), δ, ppm: 1.32-1.43 (m, 2H, CH_2 cycloheptane), 1.33 (t, 3H, J=7.0, N-CH_2-$\underline{CH_3}$), 1.45-1.70 (m, 6H, 3×CH_2 cycloheptane), 1.49 (t, 3H, J=7.3, S-CH_2-$\underline{CH_3}$), 1.72-1.86 (m, 2H, CH_2 cycloheptane), 2.24-2.35 (m, 2H, CH_2 cycloheptane), 2.87 (s, 2H, C*6*H_2), 3.30 (q, 2H, J=7.3, S-$\underline{CH_2}$-CH_3), 4.03 (q, 2H, J=7.0, N-$\underline{CH_2}$-CH_3), 7.12-7.17 (m, 1H, CH Ar), 7.20-7.32 (m, 2H, 2×CH Ar), 7.95-8.00 (m, 1H, CH Ar). ^{13}C NMR spectrum (75 MHz, DMSO-d_6-CCl_4 1/3), δ, ppm: 12.41 (N-CH_2-$\underline{CH_3}$), 13.75 (S-CH_2-$\underline{CH_3}$), 23.88 (2×CH_2 cycloheptane), 25.52 (S-$\underline{CH_2}$-CH_3), 29.64 (2×CH_2 cycloheptane), 35.69 (2×CH_2 cycloheptane), 38.82 (N-$\underline{CH_2}$-CH_3), 39.59 (C*5*), 40.14 (C*6*H_2), 122.95 (C*4*$_a$), 124.45 (CH Ar), 125.90 (CH Ar), 127.18 (CH Ar), 129.30 (CH Ar), 132.10 (C Ar), 136.27 (C Ar), 150.61(C*10*$_b$), 157.39 (C*2*), 159.82 (C*4*). Found, %: C 71.62; H 7.78; N 7.52; S 8.84. $C_{22}H_{28}N_2OS$. Calculated, %: C 71.70; H 7.66; N 7.60; S 8.70.

3-Ethyl-2-(propylthio)-3H-spiro[benzo[h]quinazoline-5,1'-cycloheptane]-4(6H)-one (**5**). Yield 1.24 *g* (65%) of **5,** mp 70-72°C, R_f 0.67 (ethyl acetate-benzene, 1:10). IR spectrum, ν, cm^{-1}: 1600 (C=C arom); 1663 (C=O). ^{1}H NMR spectrum (300 MHz, DMSO-d_6-CCl_4 1/3), δ, ppm: 1.11 (t, 3H, J=7.3, S-CH_2-CH_2-$\underline{CH_3}$), 1.32-1.43 (m, 2H, CH_2 cycloheptane), 1.33 (t, 3H, J=7.0, N-CH_2-$\underline{CH_3}$), 1.46-1.70 (m, 6H, 3×CH_2 cycloheptane), 1.71-1.93 (m, 4H, CH_2 cycloheptane, S-CH_2-$\underline{CH_2}$-CH_3), 2.23-2.35 (m, 2H, CH_2 cycloheptane), 2.87 (s, 2H, C*6*H_2), 3.27 (t, 2H, J=7.1, S-$\underline{CH_2}$-CH_2-CH_3), 4.04 (q, 2H, J=7.0, N-$\underline{CH_2}$-CH_3), 7.11-7.17 (m, 1H, CH Ar), 7.20-7.32 (m, 2H, 2×CH Ar), 7.94-7.99 (m, 1H, CH Ar). ^{13}C NMR spectrum (75 MHz, DMSO-d_6-CCl_4 1/3), δ, ppm: 12.43 (N-CH_2-$\underline{CH_3}$), 12.97 (S-CH_2-CH_2-$\underline{CH_3}$), 21.74 (S-CH_2-$\underline{CH_2}$-CH_3), 23.87 (2×CH_2 cycloheptane), 29.63 (2×CH_2 cycloheptane), 33.02 (S-$\underline{CH_2}$-CH_2-CH_3), 35.67 (2×CH_2 cycloheptane), 38.84 (N-$\underline{CH_2}$-CH_3), 39.58 (C*5*), 40.13 (C*6*H_2), 122.91 (C4_a), 124.39 (CH Ar), 125.90 (CH Ar), 127.21 (CH Ar), 129.30 (CH Ar), 132.08 (C Ar), 136.27 (C Ar), 150.57 (C10_b), 157.49 (C*2*), 159.84 (C*4*). Found, %: C 72.36; H 7.75; N 7.18; S 8.54. $C_{23}H_{30}N_2OS$. Calculated, %: C 72.21; H 7.90; N 7.32; S 8.38.

3-Ethyl-2-(isopropylthio)-3H-spiro[benzo[h]quinazoline-5,1'-cycloheptane]-4(6H)-one (**6**). Yield 1.19 *g* (62%) of **6,** mp 108-110°C, R_f 0.75 (ethyl acetate-benzene, 1:10). IR spectrum, ν, cm^{-1}: 1603 (C=C arom); 1659 (C=O). ^{1}H NMR spectrum (300 MHz, DMSO-d_6-CCl_4 1/3), δ, ppm: 1.32 (t, 3H, J=7.0, N-CH_2-$\underline{CH_3}$), 1.33-1.43 (m, 2H, CH_2 cycloheptane), 1.47-1.69 (m, 6H, 3×CH_2 cycloheptane), 1.52 (d, 6H, J=6.8, S-CH-($\underline{CH_3}$)$_2$), 1.71-1.86 (m, 2H, CH_2 cycloheptane), 2.23-2.35 (m, 2H, CH_2 cycloheptane), 2.88 (s, 2H, C*6*H_2), 4.00 (q, 2H, J=7.0, N-$\underline{CH_2}$-CH_3), 4.13 (sp, 1H, J=6.8, S-$\underline{CH}$-(CH_3)$_2$), 7.12-7.17 (m, 1H, CH Ar), 7.20-7.32 (m, 2H, 2×CH Ar), 7.92-7.98 (m, 1H, CH Ar). ^{13}C NMR spectrum (75 MHz, DMSO-d_6-CCl_4 1/3), δ, ppm: 12.41 (N-CH_2-$\underline{CH_3}$), 22.27 (S-CH-($\underline{CH_3}$)$_2$), 23.88 (2×CH_2 cycloheptane), 29.65 (2×CH_2 cycloheptane), 35.70 (2×CH_2 cycloheptane), 36.83 (S-$\underline{CH}$-(CH_3)$_2$), 38.80 (N-$\underline{CH_2}$-CH_3), 39.59 (C*5*), 40.16 (C*6*H_2), 122.93 (C4_a), 124.40 (CH Ar), 125.94 (CH Ar), 127.22 (CH Ar), 129.40 (CH Ar), 132.12 (C Ar), 136.29 (C Ar), 150.69 (C10_b), 157.49 (C*2*), 159.80 (C*4*). Found, %: C 72.40; H 7.84; N 7.20; S 8.48. $C_{23}H_{30}N_2OS$. Calculated, %: C 72.21; H 7.90; N 7.32; S 8.38.

2-(Allylthio)-3-ethyl-3H-spiro[benzo[h]quinazoline-5,1'-cycloheptane]-4(6H)-one (**7**). Yield 1.8 *g* (94%) of **7,** mp 104-106°C, R_f 0.74 (ethyl acetate-benzene, 1:10). IR spectrum, ν, cm^{-1}: 1615 (C=C arom); 1661 (C=O). ^{1}H NMR spectrum (300 MHz, DMSO-d_6-CCl_4 1/3), δ, ppm: 1.32-1.43 (m, 2H, CH_2 cycloheptane), 1.34 (t, 3H, J=7.0, N-CH_2-$\underline{CH_3}$), 1.46-1.70 (m, 6H, 3×CH_2 cycloheptane), 1.72-1.86 (m, 2H, CH_2 cycloheptane), 2.24-2.35 (m, 2H, CH_2 cycloheptane), 2.87 (s, 2H, C*6*H_2), 3.97 (dt, 2H, J=6.9, 1.2, S-$\underline{CH_2}$-CH=CH_2), 4.04 (q, 2H, J=7.0, N-$\underline{CH_2}$-CH_3), 5.18 (dq, 1H, J=10.1, 1.2, S-CH_2-CH=$\underline{CH_2}$), 5.37 (dq, 1H, J=17.0, 1.2, S-CH_2-CH=$\underline{CH_2}$), 6.02 (ddt, 1H, J=17.0, 10.1, 6.9, S-CH_2-$\underline{CH}$=CH_2), 7.12-7.17 (m, 1H, CH Ar), 7.21-7.32 (m, 2H, 2×CH Ar), 7.96-

8.01 (m, 1H, CH Ar). ^{13}C NMR spectrum (75 MHz, DMSO-d_6-CCl_4 1/3), δ, ppm: 12.45 (N-CH_2-$\underline{CH_3}$), 23.87 (2×CH_2 cycloheptane), 29.63 (2×CH_2 cycloheptane), 33.82 (S-$\underline{CH_2}$-CH_2-CH_3), 35.65 (2×CH_2 cycloheptane), 38.93 (N-$\underline{CH_2}$-CH_3), 39.60 (C*5*), 40.09 (C*6*H_2), 118.11 (CH_2-CH=$\underline{CH_2}$), 123.08 (C4_a), 124.50 (CH Ar), 125.93 (CH Ar), 127.20 (CH Ar), 129.45 (CH Ar), 131.98 (C Ar), 132.26 (S-CH_2-$\underline{CH}$=CH_2), 136.26 (C Ar), 150.59 (C10_b), 156.88 (C*2*), 159.76 (C*4*). Found, %: C 72.66; H 7.55; N 7.48; S 8.24. $C_{23}H_{28}N_2OS$. Calculated, %: C 72.59; H 7.42; N 7.36; S 8.43.

2-(Butylthio)-3-ethyl-3H-spiro[benzo[h]quinazoline-5,1'-cycloheptane]-4(6H)-one (**8**). Yield 1.45 *g* (73%) of **8,** mp 83-85°C, R_f 0.75 (ethyl acetate-benzene, 1:10). IR spectrum, ν, cm^{-1}: 1604 (C=C arom); 1661 (C=O). ^{1}H NMR spectrum (300 MHz, DMSO-d_6-CCl_4 1/3), δ, ppm: 1.00 (t, 3H, J=7.3, S-CH_2-CH_2-CH_2-$\underline{CH_3}$), 1.32-1.43 (m, 2H, CH_2 cycloheptane), 1.33 (t, 3H, J=7.0, N-CH_2-$\underline{CH_3}$), 1.45-1.69 (m, 8H, 3×CH_2 cycloheptane, S-CH_2-CH_2-$\underline{CH_2}$-CH_3), 1.72-1.86 (m, 4H, CH_2 cycloheptane, S-CH_2-$\underline{CH_2}$-CH_2-CH_3), 2.23-2.35 (m, 2H, CH_2 cycloheptane), 2.87 (s, 2H, C*6*H_2), 3.29 (t, 2H, J=7.1, S-$\underline{CH_2}$-CH_2-CH_2-CH_3), 4.03 (q, 2H, J=7.0, N-$\underline{CH_2}$-CH_3), 7.11-7.17 (m, 1H, CH Ar), 7.20-7.32 (m, 2H, 2×CH Ar), 7.94-7.99 (m, 1H, CH Ar). ^{13}C NMR spectrum (75 MHz, DMSO-d_6-CCl_4 1/3), δ, ppm: 12.43 (N-CH_2-$\underline{CH_3}$), 13.15 (S-CH_2-CH_2-CH_2-$\underline{CH_3}$), 21.41 (S-CH_2-CH_2-$\underline{CH_2}$-CH_3), 23.87 (2×CH_2 cycloheptane), 29.63 (2×CH_2 cycloheptane), 30.38 (S-CH_2-$\underline{CH_2}$-CH_2-CH_3), 30.81 (S-$\underline{CH_2}$-CH_2-CH_2-CH_3), 35.67 (2×CH_2 cycloheptane), 38.82 (N-$\underline{CH_2}$-CH_3), 39.60 (C*5*), 40.12 (C*6*H_2), 122.90 (C4_a), 124.40 (CH Ar), 125.86 (CH Ar), 127.21 (CH Ar), 129.39 (CH Ar), 132.09 (C Ar), 136.28 (C Ar), 150.58 (C10_b), 157.50 (C*2*), 159.84 (C*4*). Found, %: C 72.54; H 8.32; N 7.16; S 7.94. $C_{24}H_{32}N_2OS$. Calculated, %: C 72.68; H 8.13; N 7.06; S 8.09.

Ethyl 2-((3-ethyl-4-oxo-4,6-dihydro-3H-spiro[benzo[h]quinazoline-5,1'-cycloheptane]-2-yl)thio)acetate (**9**). Yield 1.4 *g* (66%) of **9,** mp 104-105°C, R_f 0.75 (ethyl acetate-benzene, 1:10). IR spectrum, ν, cm^{-1}: 1604 (C=C arom); 1657 (C=O): 1747 (C=O ester). ^{1}H NMR spectrum (300 MHz, DMSO-d_6-CCl_4 1/3), δ, ppm: 1.26 (t, 3H, J=7.1, O-CH_2-$\underline{CH_3}$), 1.32-1.43 (m, 2H, CH_2 cycloheptane), 1.38 (t, 3H, J=7.0, N-CH_2-$\underline{CH_3}$), 1.45-1.69 (m, 6H, 3×CH_2 cycloheptane), 1.71-1.85 (m, 2H, CH_2 cycloheptane), 2.23-2.34 (m, 2H, CH_2 cycloheptane), 2.87 (s, 2H, C*6*H_2), 4.03 (s, 2H, S-CH_2), 4.07 (q, 2H, J=7.0, N-$\underline{CH_2}$-CH_3), 4.14 (q, 2H, J=7.1, O-$\underline{CH_2}$-CH_3), 7.11-7.16 (m, 1H, CH Ar), 7.20-7.32 (m, 2H, 2×CH Ar), 7.94-7.99 (m, 1H, CH Ar). ^{13}C NMR spectrum (75 MHz, DMSO-d_6-CCl_4 1/3), δ, ppm, 12.46 (N-CH_2-$\underline{CH_3}$), 13.64 (O-CH_2-$\underline{CH_3}$), 23.88 (2×CH_2 cycloheptane), 29.64 (2×CH_2 cycloheptane), 33.38 (S-CH_2), 35.64 (2×CH_2 cycloheptane), 39.22 (N-$\underline{CH_2}$-CH_3), 39.61 (C*5*), 40.05 (C*6*H_2), 60.68 (O-$\underline{CH_2}$-CH_3), 123.27 (C4_a), 124.76 (CH Ar), 125.82 (CH Ar), 127.15 (CH Ar), 129.51 (CH Ar), 131.78 (C Ar), 36.25 (C Ar), 150.67(C10_b), 156.50 (C*2*), 159.63 (C*4*), 167.08 ($\underline{C(O)}$-O-CH_2-CH_3). Found, %: C 67.69; H 6.95; N 6.48; S 7.67. $C_{24}H_{30}N_2O_3S$. Calculated, %: C 67.58; H 7.09; N 6.57; S 7.52.

2-(Benzylthio)-3-ethyl-3H-spiro[benzo[h]quinazoline-5,1'-cycloheptane]-4(6H)-one (**10**). Yield 1.9 *g* (90%) of **10,** mp 123-125°C, R_f 0.76 (ethyl acetate-benzene, 1:10). IR spectrum, ν, cm^{-1}: 1604 (C=C arom); 1648 (C=O). ^{1}H NMR spectrum (300 MHz, DMSO-d_6-CCl_4 1/3), δ, ppm: 1.33 (t, 3H, J=7.0, N-CH_2-$\underline{CH_3}$), 1.35-1.44 (m, 2H, CH_2 cycloheptane), 1.46-1.70 (m, 6H, 3×CH_2 cyclo-heptane), 1.72-1.87 (m, 2H, CH_2 cycloheptane), 2.24-2.36 (m, 2H, CH_2 cycloheptane), 2.88 (s, 2H, C_6H_2), 4.03 (q, 2H, J=7.0, N-$\underline{CH_2}$-CH_3), 4.57 (s, 2H, S-$\underline{CH_2}$-Ph), 7.13-7.18 (m, 1H, CH Ar), 7.20-7.34 (m, 5H, 5×CH Ar), 7.39-7.45 (m, 2H, 2×CH Ar), 8.00-8.05 (m, 1H, CH Ar). ^{13}C NMR spectrum (75 MHz, DMSO-d_6-CCl_4 1/3), δ, ppm: 12.48 (N-CH_2-$\underline{CH_3}$), 23.88 (2×CH_2 cycloheptane), 29.63 (2×CH_2 cycloheptane), 35.58 (S-$\underline{CH_2}$-Ph), 35.65 (2×CH_2 cycloheptane), 38.94 (N-$\underline{CH_2}$-CH_3), 39.64 (C*5*), 40.10 (C*6*H_2), 123.20 (C4_a), 124.64 (CH Ar), 125.94 (CH Ar), 126.94 (CH Ar), 127.22 (CH Ar), 128.00 (2×CH Ar), 128.56 (2×CH Ar), 129.47 (CH Ar), 131.98 (C Ar), 135.58 (C Ar), 136.27 (C Ar), 150.62 (C10_b), 157.25 (C*2*), 159.74 (C*4*). Found, %: C 75.48; H 7.15; N 6.68; S 7.64. $C_{27}H_{30}N_2OS$. Calculated, %: C 75.31; H 7.02; N 6.51; S 7.45.

2-(4-Chlorobenzylthio)-3-ethyl-3H-spiro[benzo[h]quinazoline-5,1'-cycloheptane]-4(6H)-one (**11**). Yield 1.93 *g* (83%) of **11,** mp 148-149°C, R_f 0.75 (ethyl acetate-benzene, 1:10). IR spectrum, ν, cm^{-1}: 1600 (C=C arom); 1673 (C=O). ^{1}H NMR spectrum (300 MHz, DMSO-d_6-CCl_4 1/3), δ, ppm: 1.32 (t, 3H, J=7.0, N-CH_2-$\underline{CH_3}$), 1.34-1.43 (m, 2H, CH_2 cycloheptane), 1.46-1.70 (m, 6H, 3×CH_2 cycloheptane), 1.71-1.87 (m, 2H, CH_2 cycloheptane), 2.23-2.35 (m, 2H, CH_2 cycloheptane), 2.89 (s, 2H, C*6*H_2), 4.02 (q, 2H, J=7.0, N-$\underline{CH_2}$-CH_3), 4.56 (s, 2H, S-$\underline{CH_2}$-Ph), 7.13-7.19 (m, 1H, CH Ar), 7.21-7.33 (m, 4H, 4×CH Ar), 7.39-7.5 (m, 2H, 2×CH Ar), 7.97-8.02 (m, 1H, CH Ar). ^{13}C NMR spectrum (75 MHz, DMSO-d_6-CCl_4 1/3), δ, ppm: 12.48 (N-CH_2-$\underline{CH_3}$), 23.87 (2×CH_2 cycloheptane), 29.62 (2×CH_2 cycloheptane), 34.57 (S-$\underline{CH_2}$-Ph), 35.62 (2×CH_2 cycloheptane), 39.00 (N-$\underline{CH_2}$-CH_3), 39.65 (C*5*), 40.07 (C*6*H_2), 123.30 (C4_a), 124.56 (CH Ar), 125.98 (CH Ar), 127.29 (CH Ar), 128.07 (2×CH Ar), 129.54 (CH Ar), 130.09 (2×CH Ar), 131.9 (C Ar), 132.43 (C Ar), 134.83 (C Ar), 136.30 (C Ar), 150.60 (C10_b), 156.92 (C*2*), 159.71 (C*4*). Found, %: C 73.88; H 6.16; N 6.17; S 6.65. $C_{27}H_{29}ClN_2OS$. Calculated, %: C 69.73; H 6.29; N 6.02; S 6.89.

3-Ethyl-2-((4-methylbenzyl)thio)-3H-spiro[benzo[h]quinazoline-5,1'-cycloheptane]-4(6H)-one (**12**). Yield 1.90 *g* (85%) of **12,** mp 172-174°C, R_f 0.74 (ethyl acetate-benzene, 1:10). IR spectrum, ν, cm^{-1}: 1603 (C=C arom); 1659 (C=O). ^{1}H NMR spectrum (300 MHz, DMSO-d_6-CCl_4 1/3), δ, ppm: 1.32 (t, 3H, J=7.0, N-CH_2-$\underline{CH_3}$), 1.34-1.43 (m, 2H, CH_2 cycloheptane), 1.46-1.70 (m, 6H, 3×CH_2 cycloheptane), 1.71-1.87 (m, 2H, CH_2 cycloheptane), 2.23-2.35 (m, 2H, CH_2 cycloheptane), 2.33 (s, 3H, $\underline{CH_3}$-Ph), 2.89 (s, 2H, C_6H_2), 4.02 (q, 2H, J=7.0, N-$\underline{CH_2}$-CH_3), 4.52 (s, 2H, S-$\underline{CH_2}$-Ph), 7.05-7.33 (m, 7H, 7×CH Ar), 8.01-8.06 (m, 1H, CH Ar). ^{13}C NMR spectrum (75 MHz, DMSO-d_6-CCl_4 1/3), δ, ppm: 12.48 (N-CH_2-$\underline{CH_3}$), 20.55 ($\underline{CH_3}$-Ph), 23.90 (2×CH_2 cycloheptane), 29.65

(2×CH_2 cycloheptane), 35.43 (S-$\underline{CH_2}$-Ph), 35.67 (2×CH_2 cycloheptane), 38.95 (N-$\underline{CH_2}$-CH_3), 39.65 (C*5*), 40.12 (C*6*H_2), 123.16 (C4_a), 124.67 (CH Ar), 125.94 (CH Ar), 127.23 (CH Ar), 128.51 (2×CH Ar), 128.67 (2×CH Ar), 129.48 (CH Ar), 132.01 (C Ar), 132.39 (C Ar), 136.24 (C Ar), 136.28 (C Ar), 50.63 (C10_b), 157.38 (C*2*), 159.76 (C*4*). Found, %: C 75.49; H 7.08; N 6.48; S 7.09. $C_{28}H_{32}N_2OS$. Calculated, %: C 75.64; H 7.25; N 6.30; S 7.21.

3-Ethyl-2-hydrazinyl-3H-spiro[benzo[h]quinazoline-5,1'-cycloheptane]-4(6H)-one (**13**). The mixture of 25.0 *g* (0.073 *mol)* of 2-thioxoquinazoline **2** and 125 *ml* of hydrazine hydrate was boiled for 3 *hrs* in a reaction flask with a backflow condenser. Then 120 *ml* of water was added, the precipitate was filtered, washed with water and recrystallized from butanol. Yield 15.8 *g* (64%) of **13,** mp 207-209°C, R_f 0.73 (methanol-benzene, 1:10). IR spectrum, ν, cm^{-1}: 1604 (C=C arom); 1656 (C=O); 3150-3290 ($NHNH_2$). ^{1}H NMR spectrum (300 MHz, DMSO-d_6-CCl_4 1/3), δ, ppm: 1.20 (t, 3H, J=7.0, N-CH_2-$\underline{CH_3}$), 1.28-1.39 (m, 2H, CH_2 cycloheptane), 1.43-1.69 (m, 6H, 3×CH_2 cycloheptane), 1.70-1.85 (m, 2H, CH_2 cycloheptane), 2.23-2.35 (m, 2H, CH_2 cycloheptane), 2.82 (s, 2H, C*6*H_2), 3.93 (q, 2H, J=7.0, N-$\underline{CH_2}$-CH_3), 4.17 (s, 2H, NH_2), 7.07-7.14 (m, 1H, CH Ar), 7.17-7.27 (m, 2H, 2×CH Ar), 8.05-8.12 (m, 1H, CH Ar), 8.16 (s, 1H, NH). ^{13}C NMR spectrum (75 MHz, DMSO-d_6-CCl_4 1/3), δ, ppm: 12.30 (N-CH_2-$\underline{CH_3}$), 24.00 (2×CH_2 cycloheptane), 29.73 (2×CH_2 cycloheptane), 34.39 (N-$\underline{CH_2}$-CH_3), 36.23 (2×CH_2 cycloheptane), 39.32 (C*5*), 40.67 (C*6*H_2), 117.32 (C4_a), 124.76 (CH Ar), 125.55 (CH Ar), 126.89 (CH Ar), 128.77 (CH Ar), 132.96 (C Ar), 136.45 (C Ar), 151.23 (C10_b), 153.47 (C*2*), 160.42 (C*4*). Found, %: C 73.17; H 8.18; N 14.66. $C_{23}H_{30}N_4O$. Calculated, %: C 72.98; H 7.99; N 14.80.

3-Ethyl-2-(2-(propan-2-ylidene)hydrazinyl)-3H-spiro[benzo[h]quinazoline-5,1'-cyclo-heptane]-4(6H)-one (**14**). The mixture of 2.0 *g* (0.006 *mol*) of 3-ethyl-2-hydrazinyl-3H-spiro-[benzo[h]quinazoline-5,1'-cycloheptane]-4(6H)-one (**13**), 3 *ml* of acetone and 25 *ml* of ethanol was boiled for 5 *hrs* in a reaction flask with a backflow condenser. After the solvent distillation, the precipitate was recrystallized from ethanol. Yield 1.3 *g* (57%) of **14,** mp 169-171 °C, R_f 0.78 (ethyl acetate-benzene, 1:1). IR spectrum, ν, cm^{-1}: 1604 (C=C arom); 1642 (C=N); 1663 (C=O); 3318 (NH). ^{1}H NMR spectrum (300 MHz, DMSO-d_6-CCl_4 1/3), δ, ppm: 1.23 (t, 3H, J=7.0, N-CH_2-$\underline{CH_3}$), 1.27-1.39 (m, 2H, CH_2 cycloheptane), 1.42-1.70 (m, 6H, 3×CH_2 cycloheptane), 1.71-1.85 (m, 2H, CH_2 cycloheptane), 2.05 (s, 6H, N=C($\underline{CH_3}$)$_2$), 2.21-2.33 (m, 2H, CH_2 cycloheptane), 2.85 (s, 2H, C*6*H_2), 4.00 (q, 2H, J=7.0, N-$\underline{CH_2}$-CH_3), 7.23-7.29 (m, 1H, CH Ar), 7.33-7.43 (m, 3H, 3×CH Ar), 9.37 (s, 1H, NH). ^{13}C NMR spectrum (75 MHz, DMSO-d_6-CCl_4 1/3), δ, ppm: 11.73 (N-CH_2-$\underline{CH_3}$), 17.38 (N=C($\underline{CH_3}$)$_2$), 23.93 (2×CH_2 cycloheptane), 24.72 (N=C($\underline{CH_3}$)$_2$), 29.60 (2×CH_2 cycloheptane), 34.53 (N-$\underline{CH_2}$-CH_3), 36.18 (2×CH_2 cycloheptane), 38.82 (C*5*), 40.61 (C*6*H_2), 113.41 (C4_a), 120.39 (CH Ar), 126.41 (C Ar), 126.46 (CH Ar), 128.23 (CH Ar), 130.13 (CH Ar), 136.80 (C Ar), 138.94 (C10_b), 147.60 (N=$\underline{C}$(CH_3)$_2$), 157.69 (C*2*),

160.04 (C*4*). Found, %: C 73.17; H 7.81; N 14.78. $C_{23}H_{30}N_4O$. Calculated, %: C 72.98; H 7.99; N 14.80.

N'-(3-ethyl-4-oxo-4,6-dihydro-3H-spiro[benzo[h]quinazoline-5,1'-cycloheptane]-2-yl)- benzohydrazide (**15**). The mixture of 2.0 *g* (0.006 *mol*) of 3-ethyl-2-hydrazinyl-3H-spiro-[benzo[h]quinazoline-5,1'-cycloheptane]-4(6H)-one (**13**), 1.4 *g* (0.01 *mol*) of benzoil chloride and 25 *ml* of benzene was boiled for 10 *hrs* in a reaction flask with a backflow condenser. After the solvent distillation, the precipitate was recrystallized from butanol. Yield 2.1 *g* (49%) of **15,** mp 190-191°C, R_f 0.55 (ethyl acetate-benzene, 1:1). IR spectrum, ν, cm^{-1}: 1600 (C=C arom); 1625 (C=N); 1640 (C=O); 16773 (C=Oamid); 3150-3250 (NH). ^{1}H NMR spectrum (300 MHz, DMSO-d_6-CCl_4 1/3), δ, ppm: 1.30-1.41 (m, 2H, CH_2 cycloheptane), 1.34 (t, 3H, J=7.0, N-CH_2-$\underline{CH_3}$), 1.44-1.70 (m, 6H, 3×CH_2 cycloheptane), 1.71-1.86 (m, 2H, CH_2 cycloheptane), 2.26-2.38 (m, 2H, CH_2 cycloheptane), 2.82 (s, 2H, C*6*H_2), 4.11 (q, 2H, J=7.0, N-$\underline{CH_2}$-CH_3), 7.02-7.11 (m, 2H, 2×CH Ar), 7.15-7.22 (m, 1H, CH Ar), 7.45-7.57 (m, 3H, 3×CH Ar), 7.78-7.83 (m, 1H, CH Ar), 7.97-8.03 (m, 2H, 2×CH Ar), 9.02 (s, 1H, NH), 10.25 (s, 1H, NH). ^{13}C NMR spectrum (75 MHz, DMSO-d_6-CCl_4 1/3), δ, ppm: 12.64 (N-CH_2-$\underline{CH_3}$), 24.04 (2×CH_2 cycloheptane), 29.78 (2×CH_2 cycloheptane), 35.16 (N-$\underline{CH_2}$-CH_3), 36.20 (2×CH_2 cycloheptane), 39.48 (C*5*), 40.63 (C*6*H_2), 118.58 (C4_a), 124.80 (CH Ar), 125.67 (CH Ar), 126.97 (CH Ar), 127.37 (2×CH Ar), 127.82 (2×CH Ar), 128.93 (CH Ar), 130.94 (CH Ar), 132.85 (C Ar), 133.05 (C Ar), 136.46 (C Ar), 151.58 (C10_b), 152.05 (C*2*), 160.42 (C*4*), 166.44 (C(O)-NH). Found, %: C 73.41; H 6.72; N 12.48. $C_{27}H_{30}N_4O_2$. Calculated, %: C 73.28; H 6.83; N 12.66.

N-(2-(3-ethyl-4-oxo-4,6-dihydro-3H-spiro[benzo[h]quinazoline-5,1'-cycloheptane]-2-yl)-hydrazinecarbonothioyl)benzamide (**16**). The mixture of 3.3 *g* (0.01 *mol)* of 3-ethyl-2-hydrazinyl-3H-spiro[benzo[h]quinazoline-5,1'-cycloheptane]-4(6H)-one (**13**), 1.63 *g* (0.01 *mol*) of benzoylisothiocyanate and 30 *ml* of ethanol was boiled for 10 *hrs* with a backflow condenser. Then it was cooled and 10 *ml* of water was added. The precipitate was filtered, washed with 70% ethanol. Yield 3.20 *g* (64%) of **16,** mp 215-217°C, R_f 0.45 (ethyl acetate-benzene, 1:1). IR spectrum, ν, cm^{-1}: 1603 (C=C arom); 1662 (C=O); 3214 (NH). ^{1}H NMR spectrum (300 MHz, DMSO-d_6-CCl_4 1/3), δ, ppm: 1.30-1.86 (m, 10H, 5×CH_2 cycloheptane), 1.42 (t, 3H, J=7.0, N-CH_2-$\underline{CH_3}$), 2.24-2.36 (m, 2H, CH_2 cycloheptane), 2.86 (s, 2H, C*6*H_2), 4.10 (q, 2H, J=7.0, N-$\underline{CH_2}$-CH_3), 7.08-7.14 (m, 1H, CH Ar), 7.21-7.28 (m, 2H, 2×CH Ar), 7.46-7.54 (m, 2H, 2×CH Ar), 7.57-7.64 (m, 1H, CH Ar), 8.09-8.15 (m, 2H, 2×CH Ar), 8.17-8.24 (m, 1H, CH Ar), 9.53 (s, 1H, NH), 11.56 (s, 1H, NH), 13.24 (br.s, 1H, NH). ^{13}C NMR spectrum (75 MHz, DMSO-d_6-CCl_4 1/3), δ, ppm: 12.33 (N-CH_2-$\underline{CH_3}$), 23.99 (2×CH_2 cycloheptane), 29.75 (2×CH_2 cycloheptane), 35.33 (N-$\underline{CH_2}$-CH_3), 36.09 (2×CH_2 cycloheptane), 39.48 (C*5*), 40.51 (C*6*H_2), 119.65 (C4_a), 125.28 (CH Ar), 126.01 (CH Ar), 126.86 (CH Ar), 127.72 (2×CH Ar), 128.53 (2×CH Ar), 129.19 (CH Ar), 131.65 (C Ar), 132.23 (CH Ar), 132.29 (C Ar), 136.30 (C Ar),

148.89 (C*10*$_b$), 151.20 (C*2*), 159.96 (C*4*), 167.45 (C(O)-NH), 175.60 (C=S). Found, %: C 66.88; H 6.40; N 14.12; S 6.58. $C_{28}H_{31}N_5O_2S$. Calculated, %: C 67.04; H 6.23; N 13.96; S 6.39.

3-Ethyl-3H-spiro[benzo[h]quinazoline-5,1'-cycloheptane]-4(6H)-one (**17**). The mixture of 2.0 *g* (0.006 *mol*) of 3-ethyl-2-hydrazinyl-3H-spiro[benzo[h]quinazoline-5,1'-cycloheptane]-4(6H)-one (**13**), 0.56 *g* (0.001 *mol*) of KOH and 25 *ml* of 90 % ethanol was boiled for 10 *hrs* in a reaction flask with a backflow condenser. After the solvent distillation, the precipitate was recrystallized from ethanol. Yield 1.2 *g* (65%) of **17,** mp 140-142 ^{o}C, R_f 0.63 (ethyl acetate-benzene, 1:1). IR spectrum, ν, cm^{-1}: 1599 (C=C arom); 1625 (C-N); 1668 (C=O). ^{1}H NMR spectrum (300 MHz, DMSO-d_6-CCl_4 1/3), δ, ppm: 1.33-1.44 (m, 2H, CH_2 cycloheptane), 1.37 (t, 3H, J=7.0, N-CH_2-$\underline{CH_3}$), 1.46-1.72 (m, 6H, 3×CH_2 cycloheptane), 1.73-1.88 (m, 2H, CH_2 cycloheptane), 2.26-2.38 (m, 2H, CH_2 cycloheptane), 2.88 (s, 2H, C*6*H_2), 3.95 (q, 2H, J=7.0, N-$\underline{CH_2}$-CH_3), 7.11-7.18 (m, 1H, CH Ar), 7.20-7.31 (m, 2H, 2×CH Ar), 7.98-8.04 (m, 1H, CH Ar), 8.16 (s, 1H, C*2*H).^{13}C NMR spectrum (75 MHz, DMSO-d_6-CCl_4 1/3), δ, ppm: 14.37 (N-CH_2-$\underline{CH_3}$), 23.90 (2×CH_2 cycloheptane), 29.63 (2×CH_2 cycloheptane), 35.47 (2×CH_2 cycloheptane), 39.91 (C*5*), 40.03 (N-$\underline{CH_2}$-CH_3), 41.13 (C*6*H_2), 124.91 (CH Ar), 125.90 (CH Ar), 127.04 (CH Ar), 127.81 (C*4*$_a$), 129.33 (CH Ar), 132.06 (C Ar), 135.90 (C Ar), 148.40 (C*2*H), 152.22 (C*10*$_b$), 159.22 (C*4*). Found, %: C 77.93; H 7.796; N 77.71. $C_{20}H_{24}N_2O$. Calculated, %: C 77.89; H 7.84;

4-Ethyl-4H-spiro[benzo[h][1,2,4]triazolo[4,3-a]quinazoline-6,1'-cycloheptane]-5(7H)-one (**18**). The mixture of 2.20 *g* (0.0065 *mol*) of 3-ethyl-2-hydrazinyl-3H-spiro[benzo[h]quinazoline-5,1'-cycloheptane]-4(6H)-one (**13**) and 15 *ml* of ethylorthoformate was boiled for 15 *hrs* with a backflow condenser. After distillation of the excess of ethylorthoformate, the precipitate was recrystallized from absolute ethanol. Yield 1.0 *g* (44%) of **18,** mp 178-179^{o}C, R_f 0.40 (ethyl acetate-benzene, 1:1). IR spectrum, ν, cm^{-1}: 1590 (C=C arom); 1617 C=N); 1669 (C=O). ^{1}H NMR spectrum (300 MHz, DMSO-d_6-CCl_4 1/3), δ, ppm: 1.24-1.33 (m, 2H, CH_2 cycloheptane), 1.40 (t, 3H, J=7.0, N-CH_2-$\underline{CH_3}$), 1.45-1.72 (m, 6H, 3×CH_2 cycloheptane), 1.73-1.88 (m, 2H, CH_2 cycloheptane), 2.23-2.35 (m, 2H, CH_2 cycloheptane), 2.92 (s, 2H, C*7*H_2), 4.25 (q, 2H, J=7.0, N-$\underline{CH_2}$-CH_3), 7.32-7.50 (m, 3H, 3×CH Ar), 7.81-7.87 (m, 1H, CH Ar), 8.98 (s, 1H, C*1*H). ^{13}C NMR spectrum (75 MHz, DMSO-d_6-CCl_4 1/3), δ, ppm: 12.06 (N-CH_2-$\underline{CH_3}$), 24.03 (2×CH_2 cycloheptane), 29.32 (2×CH_2 cycloheptane), 34.54 (2×CH_2 cycloheptane), 37.44 (C*7*H_2), 40.29 (N-$\underline{CH_2}$-CH_3), 40.50 (C*6*), 124.29 (CH Ar), 124.33 (C*5*$_a$), 125.28 (C Ar), 126.75 (CH Ar), 128.25 (CH Ar), 130.62 (CH Ar), 135.10 (C*1*H), 136.07 (C Ar), 136.71 (C*11*$_b$), 147.86 (C*3a*), 157.22 (C*5*). Found, %: C 72.56; H 7.12; N 16.26 $C_{21}H_{24}N_4O$. Calculated, %: C 72.39; H 6.94; N 16.08.

4-Ethyl-1-mercapto-4H-spiro[benzo[h][1,2,4]triazolo[4,3-a]quinazoline-6,1'-cycloheptane]-5(7H)-one (**19**). The mixture of 2.2 *g* (0.0065 *mol*) of 3-

ethyl-2-hydrazinyl-3H-spiro[benzo[h]-quinazoline-5,1'-cycloheptane]-4(6H)-one (**13**), 15 *ml* of carbon disulfide and 15 *ml* of pyridine was boiled for 20 *hrs* with a backflow condenser. Then the mixture was cooled and acidified by chlorhydric acid up to pH=3.0-3.5. The precipitate was filtered and recrystallized from butanol. Yield 1.80 *g* (75%) of **19,** mp 240-241°C, R_f 0.60 (ethyl acetate-benzene, 1:1). IR spectrum, ν, cm^{-1}: 1585 (C=C arom); 1632 (C=N); 1672 (C=O). ^{1}H NMR spectrum (300 MHz, DMSO-d_6-CCl_4 1/3), δ, ppm: 0.80-2.20 (br.m, 11H, 11×CH cycloheptane), 1.35 (t, 3H, J=7.0, N-CH_2-$\underline{CH_3}$), 2.56-3.10 (br.m, 3H, CH cycloheptane, C*7*H_2), 4.08 (q, 2H, J=7.0, N-$\underline{CH_2}$-CH_3), 7.14-7.22 (m, 2H, 2×CH Ar), 7.28-7.35 (m, 1H, CH Ar), 7.52-7.57 (m, 1H, CH Ar), 13.79 (s, 1H, SH). ^{13}C NMR spectrum (75 MHz, DMSO-d_6-CCl_4 1/3), δ, ppm: 11.78 (N-CH_2-$\underline{CH_3}$), 24.01 (2×CH_2 cycloheptane), 28.93 (2×CH_2 cycloheptane), 29.23 (2×CH_2 cycloheptane), 36.99 (C*7*H_2), 40.15 (N-$\underline{CH_2}$-CH_3), 41.30 (C*6*), 123.64 (CH Ar), 123.99 (C5_a), 126.45 (CH Ar), 129.08 (C Ar), 129.28 (CH Ar), 129.71 (CH Ar), 134.79 (C*1*), 138.96 (C Ar), 145.48 (C11_b), 156.69 (C*3a*), 162.34 (C*5*). Found, %: C 66.12; H 6.45; N 14.78; S 8.60. $C_{21}H_{24}N_4OS$. Calculated, %: C 66.29; H 6.36; N 14.72; S, 8.43.

4-Ethyl-1-(methylthio)-4H-spiro[benzo[h]imidazo[1,2-a]quinazoline-6,1'-cycloheptane]-5(7H)-one (**20**). In a round bottom flask with a backflow condenser a mixture of 3.4 *g* (0.01 *mol*) of 4-ethyl-1-mercapto-4H-spiro[benzo[h][1,2,4]triazolo[4,3-a]quinazoline-6,1'-cycloheptane]-5(7H)-one (**19**), 0.56 *g* (0.01 *mol*) of KOH, 30 *ml* of absolute ethanol was placed and boiled for 30 *min*. Then 1.41 *g* (0.01 *mol*) of methyl iodide was added and boiling continued for another 10 *hrs*. The reaction mixture was cooled and 20 *ml* of water was added. The precipitate was filtered and recrystallized from ethanol. Yield 3.1 *g* (79%) of **20,** mp 203-205°C, R_f 0.54 (ethyl acetate-benzene, 1:1). IR spectrum, ν, cm^{-1}: 1614 (C=C arom); 1660 (C=O). ^{1}H NMR spectrum (300 MHz, DMSO-d_6-CCl_4 1/3), δ, ppm: 0.80-2.20 (br.m, 11H, 11×CH cycloheptane), 1.39 (t, 3H, J=7.0, N-CH_2-$\underline{CH_3}$), 2.61 (s, 3H, S-CH_3), 2.56-3.10 (br.m, 3H, CH cycloheptane, C*7*H_2), 4.21 (br.q, 2H, J=7.0, N-$\underline{CH_2}$-CH_3), 7.28-7.46 (m, 4H, 4×CH Ar). ^{13}C NMR spectrum (75 MHz, DMSO-d_6-CCl_4 1/3), δ, ppm: 12.01 (N-CH_2-$\underline{CH_3}$), 16.62 (S-CH_3), 23.95 (2×CH_2 cycloheptane), 28.67 (2×CH_2 cycloheptane), 29.33 (2×CH_2 cycloheptane), 37.35 (C*7*H_2), 40.12 (N-$\underline{CH_2}$-CH_3), 41.37 (C*6*), 124.92 (C5_a), 125.21 (CH Ar), 125.28 (CH Ar), 126.70 (C Ar), 127.61 (CH Ar), 130.54 (CH Ar), 135.64 (C*1*), 136.93 (C Ar), 143.63 (C11_b), 149.53 (C*3a*), 156.79 (C*5*). Found, %: C 70.02; H 6.75; N 10.85; S 8.30. $C_{23}H_{27}N_3OS$. Calculated, %: C 70.19; H 6.92; N 10.68; S 8.15.

1-(Benzylthio)-4-ethyl-4H-spiro[benzo[h][1,2,4]triazolo[4,3-a]quinazoline-6,1'-cycloheptane]-5(7H)-one (21). Similarly, from 3.4 *g* (0.01 *mol*) of 4-ethyl-1-mercapto-4H-spiro[benzo[h]-[1,2,4]triazolo[4,3-a]quinazoline-6,1'-cycloheptane]-5(7H)-one (**19**), 0.56 *g* (0.01 *mol*) of KOH and 1.27 *g* (0.01 *mol*) of benzyl chloride, 3.7 *g* (78%) of **21** was obtained**,** mp 135-137 °C, R_f 0.67 (ethyl acetate-benzene, 1:1). IR spectrum, ν, cm^{-1}: 1616 (C=C arom); 1654

(C=O). ^{1}H NMR spectrum (300 MHz, DMSO-d_6-CCl_4 1/3), δ, ppm: 0.80-2.20 (br.m, 11H, 11×CH cycloheptane), 1.39 (t, 3H, J=7.0, N-CH_2-$\underline{CH_3}$), 2.56-3.10 (br.m, 3H, CH cycloheptane, C7H_2), 4.21 (br.q, 2H, J=7.0, N-$\underline{CH_2}$-CH_3), 4.24-4.33 (br.s, 2H, CH_2-Ph), 7.12-7.43 (m, 9H, 9×CH Ar). ^{13}C NMR spectrum (75 MHz, DMSO-d_6-CCl_4 1/3), δ, ppm: 11.97 (N-CH_2-$\underline{CH_3}$), 23.96 (2×CH_2 cycloheptane), 28.74 (2×CH_2 cycloheptane), 29.23 (2×CH_2 cycloheptane), 29.86 (CH_2-Ph), 37.30 (C7H_2), 39.90 (N-$\underline{CH_2}$-CH_3), 41.17 (C6), 125.02 (C5$_a$), 125.18 (CH Ar), 125.23 (CH Ar), 126.69 (C Ar), 126.95 (CH Ar), 127.59 (CH Ar), 127.82 (2×CH Ar), 128.52 (2×CH Ar), 130.50 (CH Ar), 135.50 (C1), 135.84 (C Ar), 136.90 (C Ar), 142.29 (C11$_b$), 149.40 (C3a), 156.72 (C5). Found, %: C 71.63; H 6.35; N 11.78; S 6.94. $C_{28}H_{30}N_4OS$. Calculated, %: C 71.46; H 6.43; N 11.90; S 6.81.

3-ԷԹԻԼ-2-ԹԻՕՔՍՈ-2,3-ԴԻՀԻԴՐՈՍՊԻՐՈ [ԲԵՆԶՕ[h]ԽԻՆԱԶՈԼԻՆ-5,1'-ՑԻԿԼՈՀԵՊՏԱՆ]-4(6H)-ՈՆԻ ՍԻՆԹԵԶԸ ԵՎ ՈՐՈՇ ՀԱՏԿՈՒԹՅՈՒՆՆԵՐԸ

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Էթիլ 4'-ամինո-'H-սպիրո[ցիկլոհեպտան-1,2'-նավթալին]-3'-կարբօքսիլատի և էթիլ-իզոթիոցիանատի փոխազդեցությունից ստացված թիոուրեիդոածանցյալն, առանց ռեակցիոն միջավայրից անջատելու, ենթարկվել է ցիկլման, ինչը բերել է 3-էթիլ-2-թիօքսո-2,3-դիհիդրոսպիրո[բենզո[h]խինազոլին-5,1'-ցիկլոհեպտան]-4(6H)-ոնի ստացմանը: Վերջինս հիմքի ներկայությամբ կոնդենսվել է հալոգենիդների հետ, որի արդյունքում ստացվել են 2-սուլֆանիլտեղակալված 3-էթիլ-3H-սպիրո[բենզո[h]խինազոլին-5,1'-ցիկլոհեպտան]-4(6H)-ոններ: Վերոհիշյալ 2-թիօքսոբենզո[h]խինազոլինից անցում է կատարվել 3-էթիլ-2-հիդրազինիլ-3H-սպիրո[բենզո[h]խինազոլին-5,1'-ցիկլոհեպտան]-4(6H)-ոնի: Վերջինս փոխազդեցության մեջ է դրվել ացետոնի, բենզոիլքլորիդի և բենզոիլիզոթիոցիանատի հետ, որի արդյունքում ստացվել են համապատասխանաբար 3-էթիլ-2-[2-(պրոպան-2-իլիդեն)հիդ–րազինիլ]-3H-սպիրո[բենզո[h]խինազոլին-5,1'-ցիկլո-հեպտան]-4(6H)-ոն, N'-(3-էթիլ-4-օքսո-4,6-դիհիդրո-3H-սպիրո[բենզո[h]խինազոլին-5,1'-ցիկլոհեպտան]-2-իլ)բենզոհիդրազիդ և N-[2-(3-էթիլ-4-օքսո-4,6-դիհիդրո-3H-սպիրո[բենզո[h]խինազոլին-5,1'-ցիկլոհեպտան]-2-իլ)հիդրազինոկարբոնոթիոիլ]բենզամիդ Ցույց է տրվել, որ նշված հիդրազինոբենզո[h]խինազոլինը հիմքի ներկայությամբ ենթարկվում է դեհիդրազինացման, առաջացնելով 3-էթիլ-3H-սպիրո[բենզո[h]խինազոլին-5,1'-ցիկլոհեպտան]-4(6H)-ոն: Հիդրազինոբենզո[h]խինազոլինի և օրթոմրջնաթթվի էթիլ էսթերի կամ ծծմբաածխածնի կոնդենսման արդյունքում սինթեզվել են համապատասխանաբար 4-էթիլ-4H-սպիրո[բենզո[h][1,2,4]տրիազոլո[4,3-a]խինազոլին-6,1'-ցիկլո-հեպտան]-5(7H)-ոն և 1-մերկապտո-4-էթիլ-4H-սպիրո[բենզո[h][1,2,4]տրիազոլո[4,3-a]խինազոլին-6,1'-ցիկլոհեպտան]-5(7H)-ոն: Վերջինից անցում է կատարվել 1-մեթիլթիո- և 1-բենզիլթիո-4-էթիլ-4H-սպիրո[բենզո[h][1,2,4]տրիազոլո[4,3-a]խինազոլին-6,1'-ցիկլոհեպտան]-5(7H)-ոնների:

СИНТЕЗ И НЕКОТОРЫЕ СВОЙСТВА 3-ЭТИЛ-2-ТИОКСО-2,3-ДИГИДРОСПИРО [БЕНЗО[h]ХИНАЗОЛИН-5,1'-ЦИКЛОГЕПТАН]-4(6H)-ОНА

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Тиоуреидопроизводное, полученное взаимодействием этил 4'-амино-'H-спиро[циклогептан-1,2'-нафталин]-3'-карбоксилата и этилизотиоцианата без выделения из реакционной среды, подвергнуто циклизации, приведшей к 3-этил-2-тиоксо-2,3-дигидроспиро[бензо[h]хиназолин-5,1'-циклопентан]-4(6H)-онам. Последний в присутствии оснований конденсирован с галогенидами, в результате чего получены 2-сульфанилзамещенные 3-этил-3H-спиро[бензо[h]хиназолин-5,1'-циклопентан]-4(6H)-оны. От вышеуказанного 2-тиоксобензо[h]хиназолина совершен переход к 3-этил-2-гидразинил-3H-спиро[бензо[h]хиназолин-5,1'-циклогептан]-4(6H)-ону. Последний поставлен во взаимодействие с ацетоном, бензоилхлоридом и бензоилизотиоцианатом, в результате чего получены соответственно 3-этил-2-[2-(пропан-2-илиден)гидразинил]-3H-спиро[бензо[h]хиназолин-5,1'-циклопентан]-4(6H)-он, N'-(3-этил-4-оксо-4,6-дигидро-3H-спиро[бензо[h]хиназолин-5,1'-циклопентан]-2-ил)бензгидразид и N-[2-(3-этил-4-оксо-4,6-дигидро-3H-спиро[бензо[h]хиназолин-5,1'-циклогептан]-2-ил)гидразинокарбонотиоил]бензамид. Показано, что указанный гидразинобензо[h]хиназолин в присутствии основания подвергается дегидразинированию, образуя 3-этил-3H-спиро[бензо[h]хиназолин-5,1'-циклогептан]-4(6H)-он. Конденсацией 2-гидразинобензо[h]хиназолина и этилового эфира ортомуравьиной кислоты или сероуглерода синтезированы соответственно 4-этил-4H-спиро[бензо[h][1,2,4]триазоло[4,3-a]хиназолин-6,1'-циклогептан]-5(7H)-он и 1-меркапто-4-этил-4H-спиро[бензо[h][1,2,4]триазоло[4,3-a]хиназолин-6,1'-циклогептан]-5(7H)-он. От последнего совершен переход к 1-метилтио- и 1-бензилтио-4-этил-4H-спиро[бензо[h][1,2,4]триазоло[4,3-a]хиназолин-6,1'-циклогептан]-5(7H)-онам.

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