ՀԱՅԱՍՏԱՆԻ ՀԱՆՐԱՊԵՏՈՒԹՅԱՆ ԳԻՏՈՒԹՅՈՒՆՆԵՐԻ
ԱԶԳԱՅԻՆ ԱԿԱԴԵՄԻԱ
НАЦИОНАЛЬНАЯ АКАДЕМИЯ НАУК РЕСПУБЛИКИ АРМЕНИЯ
NATIONAL ACADEMY OF SCIENCES OF THE REPUBLIC OF ARMENIA

Հայաստանի քիմիական հանդես
Химический журнал Армении **73, №4, 2020** Chemical Journal of Armenia

SYNTHESIS OF NEW DERIVATIVES OF 3-ALLYL-SPIRO[BENZO[h]QUINAZOLINE-5,1'-CYCLOHEPTANE]

A. S. AYVAZYAN

The Scientific Technological Center of Organic and Pharmaceutical Chemistry NAS RA
26, Azatutyan Str., Yerevan, 0014, Armenia
Phone: +374 10 288 443 E-mail: ani.ayvazyan17@mail.ru

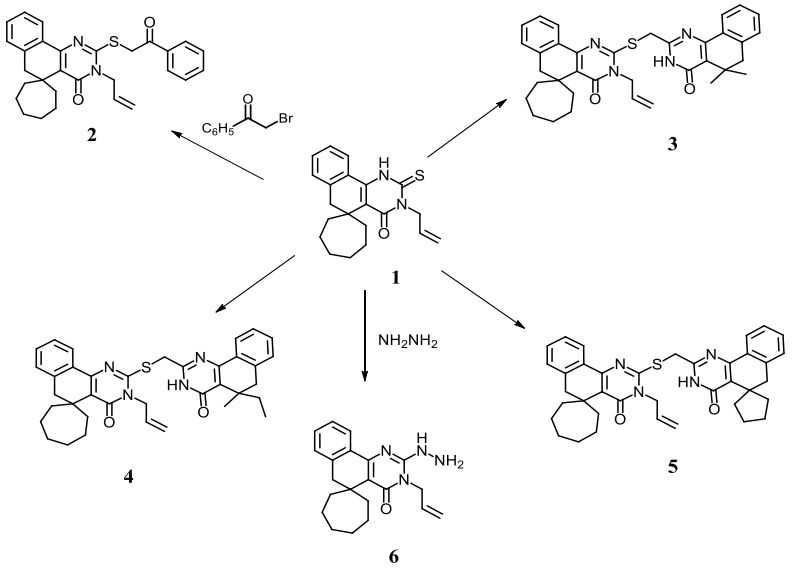
As a result of condensation of 3-allyl-2-thioxo-2,3-dihydro-*1H*-spiro[benzo[h]quinazoline-5,1'-cycloheptan]-4(*6H*)-one with 2-bromo-1-phenylethanone and 2-thioxobenzo[h]quinazolines of various structures, 2-methylthio derivatives of spiro[benzo[h]quinazoline-5,1'-cycloheptane] were synthesized. By the transformations of 3-allyl-2-hydrazinyl-*3H*-spiro[benzo[h]quinazoline-5,1'-cycloheptan]-4(*6H*)-one, benzhydrazide, hydrazino-carbonothioylbenzamide, arylidenhydrazides, 4-allyl-*4H*-spiro[benzo[h[1,2,4]triazolo[4,3-a]quinazoline-6,1'-cycloheptan]-5(*7H*)-one and 4-allyl-1-mercapto-*4H*-spiro[benzo[h][1,2,4]triazolo[4,3-a]quinazoline-6,1'-cyclo-heptan]-5(*7H*)-one were synthesized. The latter by alkylation with various halides was converted into 1-alkylthio derivatives.

References 25.

The number of publications in the field of benzo[h]quinazoline derivatives synthesis has grown significantly in recent years [1-16]. However, there are limited number of publications on benzo[h]quinazolines of spirocyclic structure, containing a cyclohexane spirocyclic fragment [17-21]. This report describes the synthesis of new derivatives of 3-allyl-spiro[benzo[h]quinazoline-5,1'-cycloheptane]. We studied the reaction of 3-allyl-2-thioxo-2,3-dihydro-*1H*-spiro[benzo[h]quinazoline-5,1'-cycloheptan]-4(*6H*)-one (**1**) [22] with halogens of various structures, in the presence of KOH. Using 2-bromo-1-phenylethanone, as a halide, 3-allyl-2-((2-oxo-2-phenylethyl)thio)-*3H*-spiro[benzo[h]quinazoline-5,1'-cycloheptan]-4(*6H*)-one (**2**) was synthesized. By condensation of **1** with 2-chloromethyl-5,5-dimethyl-5,6-dihydrobenzo[h]quinazoline-4(*3H*)-one [23], 2-chloromethyl-5-ethyl-5-methyl-5,6-dihydrobenzo[h] quinazoline-4(*3H*)-one [24] and 2-chloromethyl-*3H*-spiro[benzo[h]quinazoline-5,1'-cyclopentan]-4(*6H*)-one [25], were synthesized 2-{[(3-allyl-4-oxo-4,6-dihydro-*3H*-spiro[benzo[h]-quinazoline-5,1'-cycloheptan]-2-yl)thio]methyl}-5,5-dimethyl-5,6-dihydrobenzo[h]quinazoline-4(*3H*)-one (**3**), 2-{[(3-allyl-4-oxo-4,6-dihydro-

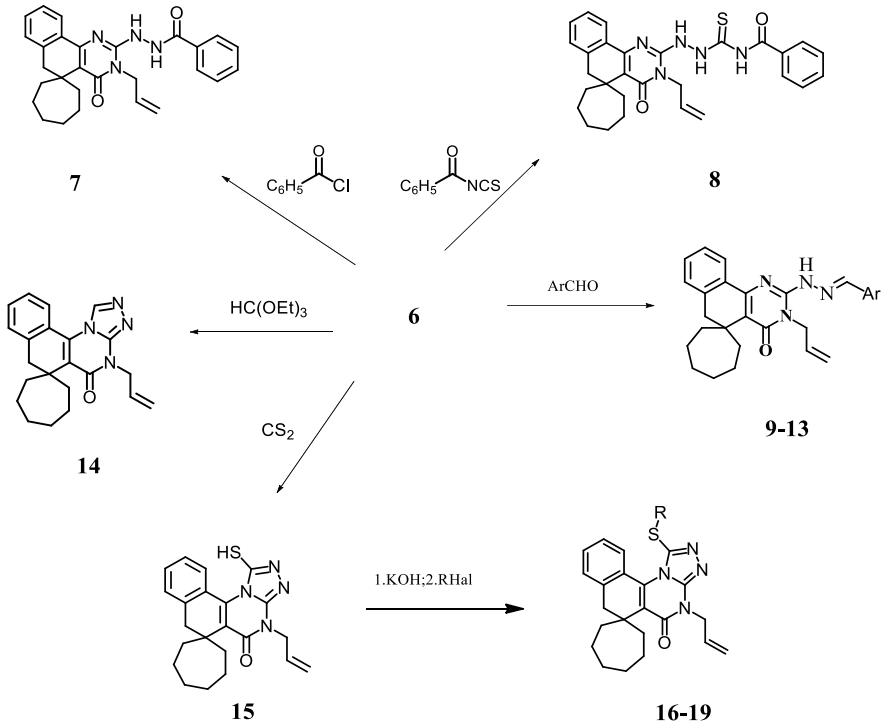
3H-spiro[benzo[h]quinazoline-5,1'-cycloheptan]-2-yl)thio]methyl}-5-ethyl-5-methyl-5,6-dihydrobenzo[h]quinazoline-4(3H)-one (**4**) and 3-allyl-2-{[(4-oxo-4,6-dihydro-*3H*-spiro [benzo[h]quinazoline-5,1'-cyclopentan]-2-yl)methyl]thio}-*3H*-spiro[benzo[h]quinazoline-5,1'-cyclo-pentan]-4(*6H*)-one (**5**), respectively (Scheme 1).

Scheme 1



By transformations of 3-allyl-2-hydrazinyl-*3H*-spiro[benzo[h]quinazoline-5,1'-cycloheptan]-4(*6H*)-one (**6**) [22], N'-(3-allyl-4-oxo-4,6-dihydro-*3H*-spiro[benzo[h]quinazoline-5,1'-cycloheptan]-2-yl)benzohydrazide (**7**), N-(2-(3-allyl-4-oxo-4,6-dihydro-*3H*-spiro[benzo[h]quinazoline-5,1'-cycloheptan]-2-yl)hydrazinecarbonothioyl)benzamide (**8**) and **9-13** arylidenhydrazines were synthesized. The hydrazinoderivative **6** was reacted with ethylorthoformate and carbon disulfide, resulting in 4-allyl-*4H*-spiro[benzo[h][1,2,4]triazolo[4,3-a]quinazoline-6,1'-cycloheptan]-5(*7H*)-one (**14**) and 4-allyl-1-mercapto-*4H*-spiro[benzo[h][1,2,4]triazolo[4,3-a]quinazoline-6,1'-cycloheptan]-5(*7H*)-one (**15**), respectively. The latter by alkylation with halides of various structures is converted to 4-allyl-1-(alkylthio)-*4H*-spiro[benzo[h][1,2,4]triazolo[4,3-a]quinazoline-6,1'-cycloheptan]-5(*7H*)-one (**16-19**) according to Scheme 2.

Scheme 2



R=CH_3 (**16**), C_2H_5 (**17**), $CH_2CH{=}CH_2$, (**18**), $CH_2C_6H_5$ (**19**)

Experimental part

The IR spectra were recorded on a Thermo Nicolet Nexus FT-IR spectrometer from samples dispersed in mineral oil. The ^1H 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-Allyl-2-((2-oxo-2-phenylethyl)thio)-*3H*-spiro[benzo[h]quinazoline-5,1'-cycloheptan]-4(*6H*)-one (2). The reaction mixture of 1.76 *g* (5 *mmol*) of 3-allyl-2-thioxo-2,3-dihydro-*1H*-spiro[benzo[h]quinazoline-5,1'-cycloheptan]-4(*6H*)-one (**1**), 1.0 *g* (5 *mmol*) of 2-bromo-1-phenylethanone and 30 *ml* of absolute acetone was placed into a single-necked round-bottom flask and boiled for 10 *hrs*. Then reaction mixture was cooled and 10 *ml* water was added. The precipitate was filtered off and recrystallized from acetone. Yield 1.10 *g* (47%) of **2**, mp 159-161ºC, R_f 0.67 (ethylacetate-benzene, 1:5). IR spectrum, *v*, cm^{-1}: 1594 (C=C arom); 1663 (C=O); 1697 (C=O). ^1H NMR spectrum (300 MHz, DMSO-d6/CCl_4 1/3), δ, ppm: 1.29-1.41 (m, 2H, cycloheptane), 1.45-1.70 (m, 6H, cycloheptane), 1.71-1.85 (m, 2H,

cycloheptane), 2.21-2.33 (m, 2H, cycloheptane), 2.83 (s, 2H, C*6*H_2), 4.70 (dt, 2H, J=7.0, 1.2, $\underline{CH_2}$-CH=CH_2), 4.83 (s, 2H, S-CH_2), 5.28 (dq, 1H, J=10.1, 1.2, CH_2-CH=$\underline{CH_2}$), 5.33 (dq, 1H, J=17.0, 1.2, CH_2-CH=$\underline{CH_2}$), 5.96 (ddt, 1H, J=17.0, 10.1, 7.0, CH_2-$\underline{CH}$=CH_2), 6.78-6.85 (m, 1H, Ar), 7.05-7.10 (m, 1H, Ar), 7.11-7.20 (m, 1H, Ar), 7.44-7.49 (m, 1H, Ar), 7.50-7.57 (m, 2H, Ar), 7.61-7.68 (m, 1H, Ar), 8.05-8.10 (m, 2H, Ar). ^{13}C NMR spectrum (75 MHz, DMSO-d6/CCl_4 1/3), δ, ppm: 23.8 (2×CH_2 cycloheptane), 29.6 (2×CH_2 cycloheptane), 35.6 (2×CH_2 cycloheptane), 38.8 (C*5*), 39.6 (C*6*H_2), 39.9 ($\underline{CH_2}$-CH=CH_2), 45.9 (S-CH_2), 118.1 (CH_2-CH=$\underline{CH_2}$), 123.0 (C4_a), 124.7 (CH Ar), 125.7 (CH Ar), 127.0 (CH Ar), 128.0 (2×CH Ar), 128. (2×CH Ar), 129.3 (CH Ar), 130.5 (CH Ar), 131.5 (C Ar), 132.7 (CH_2-$\underline{CH}$=CH_2), 135.7 (C Ar), 136.1 (C Ar), 150.7 (C10_b), 157.3 (C*2*), 159.6 (C*4*), 191.2 ($\underline{C}$(O)-Ph). Found, %: C 74.11; H 6.59; N 5.83; S 6.74. $C_{29}H_{30}N_2O_2S$. Calculated, %: C 74.01; H 6.43; N 5.95; S 6.81.

2-{[(3-Allyl-4-oxo-4,6-dihydro-*3H*-spiro[benzo[h]quinazoline-5,1'-cycloheptan]-2-yl)thio]-methyl}-5,5-dimethyl-5,6-dihydrobenzo[h]quinazoline-4(*3H*)-one (3). A mixture of 1.76 *g* (5 *mmol*) of 3-allyl-2-thioxo-2,3-dihydro-*1H*-spiro[benzo[h]quinazoline-5,1'-cycloheptan]-4(*6H*)-one (**1**), 0.3 *g* (9 *mmol*) of KOH and 30 *ml* of absolute ethanol was placed into a round-bottom flask and boiled for 30 *min*. Then 1.37 *g* (5 *mmol*) of 2-chloromethyl-5,5-dimethyl-5,6-dihydrobenzo[h]quinazolin-4(*3H*)-one was added and boiling continued for 12 *hrs*. The reaction mixture was cooled, and 10 *ml* of water was added. The precipitate was filtered off and recrystallized from butanol. Yield 2.8 *g* (95%) of **3**, mp 242-244 °C, R_f 0.70 (ethyl acetate-benzene, 1:2). IR spectrum, *v*, cm^{-1}: 1604 (C=C arom); 1653 (C=O); 1672 (C=O); 3150 (NH). ^{1}H NMR spectrum (300 MHz, DMSO-d6/CCl_4 1/3), δ, ppm: 1.31-1.43 (m, 2H, cycloheptane), 1.34 (s, 6H,C($\underline{CH_3}$)$_2$), 1.44-1.69 (m, 6H, cycloheptane), 1.70-1.84 (m, 2H, cycloheptane), 2.22-2.34 (m, 2H, cycloheptane), 2.72 (s, 2H, [C6]H_2), 2.87 (s, 2H, C6H_2), 4.50 (s, 2H, S-CH_2), 4.69 (dt, 2H, J=7.0, 1.2, $\underline{CH_2}$-CH=CH_2), 5.27 (dq, 1H, J=10.1, 1.2, CH_2-CH=$\underline{CH_2}$), 5.32 (dq, 1H, J=17.0, 1.2, CH_2-CH=$\underline{CH_2}$), 5.94 (ddt, 1H, J=17.0, 10.1, 7.0, CH_2-$\underline{CH}$=CH_2), 7.07-7.15 (m, 2H, Ar), 7.16-7.31 (m, 4H, Ar), 8.04-8.09 (m, 1H, Ar), 8.13-8.18 (m, 1H, Ar), 12.41 (s, 1H, NH). ^{13}C NMR spectrum (75 MHz, DMSO-d6/CCl_4 1/3), δ, ppm: 23.9 (2×CH_2 cycloheptane), 25.4 (C($\underline{CH_3}$)$_2$), 29.6 (2×CH_2 cycloheptane), 32.8 ([C5]), 34.1 ([C6]H_2), 35.6 (2×CH_2 cycloheptane), 39.7 (C5), 40.1 (C6H_2), 44.0 ($\underline{CH_2}$-CH=CH_2), 45.7 (S-CH_2), 118.1 (CH_2-CH=$\underline{CH_2}$), 123.2 (C4_a), 124.37 ([C4_a]), 125. (2×CH Ar), 125.9 (CH Ar), 126.2 (CH Ar), 127.0 (C Ar),127.0 (CH Ar), 129.3 (CH Ar), 129.5 (CH Ar), 130.6 (CH Ar), 131.8 (C Ar), 131.9 (CH_2-$\underline{CH}$=CH_2), 136.0 (C Ar), 136.2 (C Ar), 151.0 (C10_b), 152.8 ([C10_b]), 154.3 ([C2]), 157.3 (C2), 159.7 (C4), 161.3 ([C4]). Found, %: C 73.38; H 6.59; N 9.56. S 5.33. $C_{36}H_{38}N_4O_2S$. Calculated, %: C 73.19; H 6.48; N 9.48; S 5.43.

2-{[(3-Allyl-4-oxo-4,6-dihydro-*3H*-spiro[benzo[h]quinazoline-5,1'-cycloheptan]-2-yl)thio]-methyl}-5-ethyl-5-methyl-5,6-dihydrobenzo[h]quinazoline-4(*3H*)-one (4). Similarly, from 1.76 *g* (5 *mmol*) of 3-allyl-2-thioxo-2,3-dihydro-*1H*-spiro[benzo[h]quinazoline-5,1'-cycloheptan]-4(*6H*)-one (**1**), 0.3 *g* (9 *mmol*) of KOH and 1.44 *g* (5 *mmol*) of 2-chloromethyl-5-ethyl-5-methyl-5,6-dihydro-benzo[h]-quinazoline-4(*3H*)-one, 2.8 *g* (93%) of **4** was obtained: mp 244-246ºC, R_f 0.73 (ethyl acetate-benzene, 1:2). IR spectrum, *v*, cm^{-1}: 1604 (C=C arom); 1651 (C=O); 1670 (C=O); 3150 (NH). ^{1}H NMR spectrum (300 MHz, DMSO-d6/CCl_4 1/3), δ, ppm: 0.77 (t, 3H, J=7.4, CH_2-$\underline{CH_3}$), 1.31-1.43 (m, 2H, cycloheptane), 1.32 (s, 3H, CH_3), 1.44-1.69 (m, 7H, 6×CH cycloheptane, 1×CH $\underline{CH_2}$-CH_3), 1.70-1.84 (m, 2H, cycloheptane), 2.00 (dq, 1H, J=14.8, 7.4, $\underline{CH_2}$-CH_3), 2.21-2.34 (m, 2H, cycloheptane), 2.58 (d, 1H, J=15.7, [C*6*]H_2), 2.87 (s, 2H, C*6*H_2), 2.90 (d, 1H, J=15.7, [C*6*]H_2), 4.48 (d, 1H, J=15.0, S-CH_2), 4.54 (d, 1H, J=15.0, S-CH_2), 4.69 (dt, 2H, J=7.0, 1.2, $\underline{CH_2}$-CH=CH_2), 5.27 (dq, 1H, J=10.1, 1.2, CH_2-CH=$\underline{CH_2}$), 5.32 (dq, 1H, J=17.0, 1.2, CH_2-CH=$\underline{CH_2}$), 5.94 (ddt, 1H, J=17.0, 10.1, 7.0, CH_2-$\underline{CH}$=CH_2), 7.06-7.31 (m, 6H, Ar), 8.05-8.10 (m, 1H, Ar), 8.11-8.16 (m, 1H, Ar), 12.40 (s, 1H, NH). ^{13}C NMR spectrum (75 MHz, DMSO-d6/CCl_4 1/3), δ, ppm: 19.0 (CH_2-$\underline{CH_3}$), 23.9 (2×CH_2 cycloheptane), 24.0 (CH_3), 29.6 (2×CH_2 cycloheptane), 30.0 ($\underline{CH_2}$-CH_3), 34.1 ([C6]H_2), 35.6 (CH_2 cycloheptane), 35.7 (CH_2 cycloheptane), 36.3 ([C5]), 39.6 (C5), 39.9 (C6H_2), 40.1 ($\underline{CH_2}$-CH=CH_2), 45.7 (S-CH_2), 118.0 (CH_2-CH=$\underline{CH_2}$), 123.2 ($C4_a$), 123.5 ([$C4_a$]), 125.4. (CH Ar), 125.4 (CH Ar), 125.7 (CH Ar), 126.1 (CH Ar), 127.0 (CH Ar), 127.0 (C Ar), 129.4 (CH Ar), 129.5 (CH Ar), 130.6 (CH Ar), 131.8 (C Ar), 131.8 (CH_2-$\underline{CH}$=CH_2), 136.1 (C Ar), 136.3 (C Ar), 150.9 ($C10_b$), 153.6 ([$C10_b$]), 154.3 ([C2]), 157.3 (C2), 159.7 (C4), 161.4 ([C4]). Found, %: C 73.66; H 6.62; N 9.43. S 5.19. $C_{37}H_{40}N_4O_2S$. Calculated, %: C 73.48; H 6.67; N 9.26; S 5.30.

3-Allyl-2-{[(4-oxo-4,6-dihydro-*3H*-spiro[benzo[h]quinazoline-5,1'-cyclopentan]-2-yl)methyl]-thio}-3H-spiro[benzo[h]quinazoline-5,1'-cyclopentan]-4(*6H*)-one (5). Similarly, from 1.76 *g* (5 *mmol*) of 3-allyl-2-thioxo-2,3-dihydro-*1H*-spiro[benzo[h]quinazoline-5,1'-cycloheptan]-4(*6H*)-one (**1**), 0.3 *g* (9 *mmol*) of KOH and 1.5 *g* (5 *mmol*) of 2-chloromethyl-*3H*-spiro[benzo[h]quinazoline-5,1'-cyclopentan]-4(*6H*)-one, 1.9 *g* (62%) of **4** was obtained: mp 243-246ºC, R_f 0.73 (ethyl acetate-benzene, 1:2). IR spectrum, *v*, cm^{-1}: 1604 (C=C arom); 1661 (C=O); 1675 (C=O); 3180 (NH). ^{1}H NMR spectrum (300 MHz, DMSO-d6/CCl_4 1/3), δ, ppm: 1.30-1.94 (m, 16H, 10×CH cycloheptane, 6×CH cyclopentane), 2.21-2.35 (m, 4H, 2×CH cycloheptane, 2×CH cyclopentane), 2.76 (s, 2H, [C*6*]H_2), 2.87 (s, 2H, C*6*H_2), 4.51 (s, 2H, S-CH_2), 4.68 (dt, 2H, J=7.0, 1.2, $\underline{CH_2}$-CH=CH_2), 5.27 (dq, 1H, J=10.1, 1.2, CH_2-CH=$\underline{CH_2}$), 5.31 (dq, 1H, J=17.0, 1.2, CH_2-CH=$\underline{CH_2}$), 5.94 (ddt, 1H, J=17.0, 10.1, 7.0, CH_2-$\underline{CH}$=CH_2),

7.05-7.31 (m, 6H, Ar), 8.04-8.10 (m, 1H, Ar), 8.14-8.20 (m, 1H, Ar), 12.43 (s, 1H, NH). ^{13}C NMR spectrum (75 MHz, DMSO-d6/CCl_4 1/3), δ, ppm: 23.9 (2×CH_2 cycloheptane), 25.1 (2×CH_2 cyclopentane), 29.6 (2×CH_2 cycloheptane), 34.1 ([C*6*]H_2), 35.1 (2×CH_2 cyclopentane), 35.6 (2×CH_2 cycloheptane), 39.7 (C*5*), 40.1 (C*6*H_2), 41.6 ($\underline{CH_2}$-CH=CH_2), 43.1 ([C*5*]), 45.7 (S-CH_2), 118.1 (CH_2-CH=$\underline{CH_2}$), 123.2 (C*4*$_a$), 124.8 ([C*4*$_a$]), 125.4 (CH Ar), 125.5 (CH Ar), 125. (CH Ar), 126.2 (CH Ar), 127.0 (C Ar), 129.2 (CH Ar), 129.5 (CH Ar), 130.6 (CH Ar), 131.9 (C Ar), 132.3 (CH_2-$\underline{CH}$=CH_2), 136.1 (C Ar), 136.2 (C Ar), 151.0 (C*10*$_b$), 153.1 ([C*10*$_b$]), 154.0 ([C*2*]), 157.3 (C*2*), 159.7 (C*4*), 161.1 ([C*4*]). Found, %: C 74.16; H 6.69; N 9.22; S 5.35. $C_{38}H_{40}N_4O_2S$. Calculated, %: C 73.99; H 6.54; N 9.08; S 5.20.

N'-(3-Allyl-4-oxo-4,6-dihydro-*3H*-spiro[benzo[h]quinazoline-5,1'-cycloheptan]-2-yl)benzo-hydrazide (7). The mixture of 2.1 *g* (6 *mmol)* of 3-allyl-2-hydrazinyl-*3H*-spiro[benzo[h]quinazoline-5,1'-cycloheptan]-4(*6H*)-one (**6**), 1.12 *g* (8 *mmol*) of benzoyl chloride and 25 *ml* of benzene was boiled for 10 *hrs* in a reaction flask with a backflow condenser. After solvent distillation, the precipitate was recrystallized from ethanol. Yield 2.5 *g* (92%) of **7,** mp 178-179ºC, R_f 0.45 (ethylacetate-benzene, 3:1). IR spectrum, *v, cm*$^{-1}$: 1600 (C=C arom); 1645 (C=O); 1686 (C=O); 3347 (NH). ^{1}H NMR spectrum (300 MHz, DMSO-d6/CCl_4 1/3), δ, ppm: 1.31-1.44 (m, 2H, CH_2 cycloheptane), 1.46-1.87 (m, 8H, 4×CH_2 cycloheptane), 2.25-2.37 (m, 2H, CH_2 cycloheptane), 2.84(s, 2H, C*6*H_2), 4.73 (dt, 2H, J=5.4, 1.5, $\underline{CH_2}$-CH=CH_2), 5.22 (dq, 1H, J=10.3, 1.5, CH_2-CH=$\underline{CH_2}$), 5.33 (dq, 1H, J=17.3, 1.5, CH_2-CH=$\underline{CH_2}$), 5.96 (ddt, 1H, J=17.3, 10.3, 5.4, CH_2-$\underline{CH}$=CH_2), 7.03-7.11 (m, 2H, 2×CH Ar), 7.15-7.23 (m, 1H, CH Ar), 7.44-7.59 (m, 3H, 3×CH Ar), 7.79-7.85 (m, 1H, CH Ar), 7.96-8.03 (m, 2H, 2×CH Ar), 8.86 (s, 1H, NH), 10.27 (s, 1H, NH). ^{1}H NMR spectrum (300 MHz, DMSO-d6/CCl_4 1/3), δ, ppm: 23.9 (2×CH_2 cycloheptane), 29.7 (2×CH_2 cycloheptane), 36.1 (2×CH_2 cycloheptane), 39.4 (C*5*), 40.48 (C*6*H_2),41.7 ($\underline{CH_2}$-CH=CH_2), 116.8 (CH Ar), 118.4 (CH_2-CH=$\underline{CH_2}$), 124.8 (C*4*$_a$), 125.6 (CH Ar), 126.9 (CH Ar), 127.3 (2×CH Ar), 127.7 (2×CH Ar), 128.9 (CH Ar), 130.9 (CH Ar), 131.4 (CH_2-$\underline{CH}$=CH_2), 132.7 (C Ar), 132.9 (C Ar), 136.4 (C Ar), 151.7 (C*10*$_b$), 152.0 (C*2*), 160.3 (C*4*), 166.2 (C=O). Found, %: C 74.11; H 6.59; N 12.53. $C_{28}H_{30}N_4O_2$. Calculated, %: C 73.98; H 6.65; N 12.33.

N-[2-(3-Allyl-4-oxo-4,6-dihydro-*3H*-spiro[benzo[h]quinazoline-5,1'-cycloheptan]-2-yl)-hydrazinecarbonothioyl]benzamide (8). The mixture of 2.1 *g* (6 *mmol)* of 3-allyl-2-hydrazinyl-*3H*-spiro[benzo[h]quinazoline-5,1'-cycloheptan]-4(*6H*)-one (**6**), 1.14 *g* (7 *mmol*) of benzoylisothiocyanate and 30 *ml* of methanol was boiled for 5 *hrs* with a backflow condenser. The precipitate was filtered, washed with 70% ethanol and recrystallized from butanol. Yield 1.0 *g* (58%) of **8,** mp 209-210ºC, R_f 0.62 (ethyl acetate-benzene-hexane, 1:7:1). IR spectrum, *v, cm*$^{-1}$: 1600 (C=C arom); 1650 (C=O); 1669 (C=O); 3187 (NH). ^{1}H NMR spectrum (300 MHz, DMSO-

d6/CCl_4 1/3), δ, ppm: 1.30-1.42 (m, 2H, cycloheptane), 1.44-1.71 (m, 6H, cycloheptane), 1.72-1.86 (m, 2H, cycloheptane), 2.22-2.34 (m, 2H, cycloheptane), 2.88 (s, 2H, C*6*H_2), 4.72 (dt, 2H, J=7.0, 1.2, $\underline{CH_2}$-CH=CH_2), 5.39 (dq, 1H, J=10.1, 1.2, CH_2-CH=$\underline{CH_2}$), 5.51 (dq, 1H, J=17.0, 1.2, CH_2-CH=$\underline{CH_2}$), 5.97 (ddt, 1H, J=17.0, 10.1, 7.0, CH_2-$\underline{CH}$=CH_2), 7.10-7.17 (m, 1H, Ar), 7.24-7.34 (m, 2H, Ar), 7.45-7.54 (m, 2H, Ar), 7.56-7.64 (m, 1H, Ar), 8.08-8.14 (m, 2H, Ar), 8.25-8.31 (m, 1H, Ar), 9.31 (s, 1H, NH), 11.63 (s, 1H, NH), 13.64 (brs, 1H, NH). ^{13}C NMR spectrum (75 MHz, DMSO-d6/CCl_4 1/3), δ, ppm: 24.0 (2×CH_2 cycloheptane), 29.7 (2×CH_2 cycloheptane), 36.1 (2×CH_2 cycloheptane), 39.5 (C*5*), 40.4 (C*6*H_2), 42.5 ($\underline{CH_2}$-CH=CH_2), 118.8 (CH_2-CH=$\underline{CH_2}$), 119.7 (C*4$_a$*), 125.38 (CH Ar), 126.1 (CH Ar), 126.9 (CH Ar), 127.7 (2×CH Ar), 128.5 (2×CH Ar), 129.4 (CH Ar), 130.5 (CH Ar), 131.6 (C Ar), 132.0 (C Ar), 132.3 (CH_2-$\underline{CH}$=CH_2), 136.3 (C Ar), 148.4 (C*10$_b$*), 151.4 (C*2*), 159.7 (C*4*), 167.6 (C(O)-Ph), 172.8 (C=S) . Found, %: C 67.98; H 6.24; N 13.53. S 6.24.$C_{29}H_{31}N_5O_2S$. Calculated, %: C 67.81; H 6.08; N 13.63; S 6.24.

Synthesis of 2-(arylidenehydrazinyl)-3-allyl-*3H*-spiro[benzo[h]quinazoline-5,1'-cycloheptan]-4(*6H*)-ones (9-13). (General method). The mixture of 2.8 *g* (8 *mmol*) of 3-allyl-2-hydrazinyl-3H-spiro-[benzo[h]quinazoline-5,1'-cycloheptan]-4(6H)-one **(6**), 8 *mmol* of aromatic aldehyde and 30 *ml* of benzene was boiled under reflux for 10 *hrs*. It was cooled and 30 *ml* of hexane was added to the reaction mixture. The precipitate was filtered, washed with hexane and dried on air.

3-Allyl-2-(2-(4-methoxybenzylidene)hydrazinyl)-*3H*-spiro[benzo[h]quinazoline-5,1'-cycloheptan]-4(*6H*)-one (Ar=4-$CH_3OC_6H_4$) **(9).** Yield 3.0 *g* (80%) of **9,** mp 184-185^{o}C, R_f 0.75 (ethyl acetate-benzene, 1:5). IR spectrum, *v*, cm^{-1}: 1593 (C=C arom); 1615 (C=N); 1668 (C=O); 3367 (NH). ^{1}H NMR spectrum (300 MHz, DMSO-d6/CCl_4 1/3), δ, ppm: 1.30-1.42 (m, 2H, cycloheptane), 1.44-1.71 (m, 6H, cycloheptane), 1.72-1.86 (m, 2H, cycloheptane), 2.22-2.34 (m, 2H, cycloheptane), 2.89 (s, 2H, C*6*H_2), 3.84 (s, 3H, O-CH_3), 4.60 (dt, 2H, J=7.0, 1.2, $\underline{CH_2}$-CH=CH_2), 5.14 (dq, 1H, J=10.1, 1.2, CH_2-CH=$\underline{CH_2}$), 5.27 (dq, 1H, J=17.0, 1.2, CH_2-CH=$\underline{CH_2}$), 5.93 (ddt, 1H, J=17.0, 10.1, 7.0, CH_2-$\underline{CH}$=CH_2), 6.90-6.96 (m, 2H, Ar), 7.24-7.31 (m, 1H, Ar), 7.38-7.48 (m, 2H, Ar), 7.52-7.59 (m, 1H, Ar), 7.64-7.71 (m, 2H, Ar), 8.27 (s, 1H, N=CH), 9.59 (s, 1H, NH). ^{13}C NMR spectrum (75 MHz, DMSO-d6/CCl_4 1/3), δ, ppm: 23.9 (2×CH_2 cycloheptane), 29.5 (2×CH_2 cycloheptane), 36.1 (2×CH_2 cycloheptane), 38.9 (C5), 40.5 (C6H_2), 41.5 ($\underline{CH_2}$-CH=CH_2), 54.6 (OCH_3), 113.6 (2×CH Ar), 113.8 (C4$_a$), 116.8 (CH_2-CH=$\underline{CH_2}$), 20.9 (CH Ar), 126.3 (C Ar), 126.6 (CH Ar), 127.4 (C Ar), 128.2 (CH Ar), 128.2 (2×CH Ar), 130.3 (CH Ar), 132.1 (CH_2-$\underline{CH}$=CH_2), 136.8 (C Ar), 139.4 (C10$_b$), 149.4 (C2), 151.3 (N=CH), 159.7 (C Ar), 160.2 (C4). Found, %: C 74.31; H 6.77; N 11.73. $C_{29}H_{32}N_4O_2$. Calculated, %: C 74.33; H 6.88; N 11.96.

3-Allyl-2-(2-(4-chlorobenzylidene)hydrazinyl)-*3H*-spiro[benzo[h]quinazoline-5,1'-cycloheptan]-4(*6H*)-one (Ar=4-ClC_6H_4) **(10).** Yield 1.5 *g* (40%) of **9,** mp 171-173°C, R_f 0.77 (ethyl acetate-benzene, 1:5). IR spectrum, *ν*, cm^{-1}: 1600 (C=C arom); 1614 (C=N); 1666 (C=O); 3371 (NH). ^{1}H NMR spectrum (300 MHz, DMSO-d6/CCl_4 1/3), δ, ppm: 1.30-1.42 (m, 2H, cycloheptane), 1.44-1.71 (m, 6H, cycloheptane), 1.72-1.86 (m, 2H, cycloheptane), 2.22-2.34 (m, 2H, cycloheptane), 2.89 (s, 2H, C*6*H_2), 4.62 (dt, 2H, J=7.0, 1.2, $\underline{CH_2}$-CH=CH_2), 5.15 (dq, 1H, J=10.1, 1.2, CH_2-CH=$\underline{CH_2}$), 5.28 (dq, 1H, J=17.0, 1.2, CH_2-CH=$\underline{CH_2}$), 5.93 (ddt, 1H, J=17.0, 10.1, 7.0, CH_2-$\underline{CH}$=CH_2), 7.24-7.31 (m, 1H, Ar), 7.36-7.46 (m, 4H, Ar), 7.53-7.60 (m, 1H, Ar), 7.72-7.79 (m, 2H, Ar), 8.31 (s, 1H, N=CH), 9.65 (s, 1H, NH). ^{13}C NMR spectrum (75 MHz, DMSO-d6/CCl_4 1/3), δ, ppm: 23.9 (2×CH_2 cycloheptane), 29.5 (2×CH_2 cycloheptane), 36.0 (2×CH_2 cycloheptane), 38.9 (C*5*), 40.5 (C*6*H_2), 41.6 ($\underline{CH_2}$-CH=CH_2), 114.3 (C4_a), 116.9 (CH_2-CH=$\underline{CH_2}$), 121.2 (CH Ar), 126.1 (C Ar), 126.6 (CH Ar), 128.1 (2×CH Ar), 128.2 (CH Ar), 128.2 (2×CH Ar), 130.4 (CH Ar), 131.9 (C Ar), 133.5 (CH_2-$\underline{CH}$=CH_2), 134.1 (C Ar), 136.8 (C Ar), 139.5 (C10_b), 50.1 (N=CH), 150.2 (C*2*), 159.5 (C*4*). Found, %: C 71.21; H 6.36; Cl 7.69; N11.56. $C_{28}H_{29}ClN_4O$. Calculated, %: C 71.10; H 6.18; Cl 7.50; N 11.84.

3-Allyl-2-(2-(3-hydroxy-4-methoxybenzylidene)hydrazinyl)-*3H*-spiro[benzo[h]quinazoline-5,1'-cycloheptan]-4(*6H*)-one (Ar=3-OH-4-$CH_3OC_6H_3$) **(11).** Yield 3.7 *g* (95%) of **11,** mp 185-187°C, R_f 0.63 (ethyl acetate-benzene, 1:5). IR spectrum, *ν*, cm^{-1}: 1023 (C-O-C); 1600 (C=C arom); 1614 (C=N); 1673 (C=O); 3150-3250 (NH); 3352 (OH). ^{1}H NMR spectrum (300 MHz, DMSO-d6/CCl_4 1/3), δ, ppm: 1.30-1.42 (m, 2H, cycloheptane), 1.44-1.71 (m, 6H, cycloheptane), 1.72-1.86 (m, 2H, cycloheptane), 2.22-2.34 (m, 2H, cycloheptane), 2.89 (s, 2H, C*6*H_2), 3.87 (s, 3H, O-CH_3), 4.59 (dt, 2H, J=7.0, 1.2, $\underline{CH_2}$-CH=CH_2), 5.14 (dq, 1H, J=10.1, 1.2, CH_2-CH=$\underline{CH_2}$), 5.27 (dq, 1H, J=17.0, 1.2, CH_2-CH=$\underline{CH_2}$), 5.93 (ddt, 1H, J=17.0, 10.1, 7.0, CH_2-$\underline{CH}$=CH_2), 6.86 (d, 1H J=8.2, Ar), 7.04 (dd, 1H J=8.2, 1.8, Ar), 7.23-7.31 (m, 1H, Ar), 7.29 (d, 1H J=1.8, Ar), 7.39-7.50 (m, 2H, Ar), 7.55-7.61 (m, 1H, Ar), 8.18 (s, 1H, N=CH), 8.73 (s, 1H, OH), 9.59 (s, 1H, NH). ^{13}C NMR spectrum (75 MHz, DMSO-d6/CCl_4 1/3), δ, ppm: 23.9 (2×CH_2 cycloheptane), 29.6 (2×CH_2 cycloheptane), 36.2 (2×CH_2 cycloheptane), 38.9 (C*5*), 40.6 (C*6*H_2), 41.5 ($\underline{CH_2}$-CH=CH_2), 55.2 (OCH_3), 111.3 (CH Ar), 112.8 (CH Ar), 113.7 (C4_a), 116.8 (CH_2-CH=$\underline{CH_2}$), 119.5 (CH Ar), 120.9 (CH Ar), 126.3 (C Ar), 126.9 (CH Ar), 127.9 (C Ar), 128.2 (CH Ar), 130.4 (CH Ar), 132.1 (CH_2-$\underline{CH}$=CH_2), 136.8 (C Ar), 139.4 (C10_b), 146.7 (C Ar), 149.1 (C Ar), 149.4 (C*2*), 151.7 (N=CH), 159.8 (C*4*). Found, %: C 72.01; H 6.59; N 11.43. $C_{29}H_{32}N_4O_3$. Calculated, %: C 71.88; H 6.66; N 11.56.

3-Allyl-2-(2-(4-hydroxy-3-methoxybenzylidene)hydrazinyl)-*3H*-spiro[benzo[h]quinazoline-5,1'-cycloheptan]-4(*6H*)-one (Ar=4-OH-3-

$CH_3OC_6H_3$) **(12).** Yield 3.7 *g* (96 %) of **12,** mp 173-175°C, R_f 0.58 (ethyl acetate-benzene, 1:5). IR spectrum, *ν, cm*$^{-1}$: 1000 (C-O-C); 1602 (C=C arom); 1624 (C=N); 1669 (C=O); 3150-3326 (NH, OH). ^{1}H NMR spectrum (300 MHz, DMSO-d6/CCl_4 1/3), δ, ppm: 1.30-1.42 (m, 2H, cycloheptane), 1.44-1.71 (m, 6H, cycloheptane), 1.72-1.86 (m, 2H, cycloheptane), 2.22-2.34 (m, 2H, cycloheptane), 2.89 (s, 2H, C*6*H_2), 3.92 (s, 3H, O-CH_3), 4.59 (dt, 2H, J=7.0, 1.2, $\underline{CH_2}$-CH=CH_2), 5.14 (dq, 1H, J=10.1, 1.2, CH_2-CH=$\underline{CH_2}$), 5.26 (dq, 1H, J=17.0, 1.2, CH_2-CH=$\underline{CH_2}$), 5.93 (ddt, 1H, J=17.0, 10.1, 7.0, CH_2-$\underline{CH}$=CH_2), 6.80 (d, 1H, J=8.2, Ar), 7.07 (dd, 1H, J=8.2, 1.8, Ar), 7.25-7.30 (m, 1H, Ar), 7.35-7.45 (m, 2H, Ar), 7.39 (d, 1H, J=1.8, Ar), 7.57-7.62 (m, 1H, Ar), 8.20 (s, 1H, N=CH), 8.89 (s, 1H, OH), 9.71 (s, 1H, NH). ^{13}C NMR spectrum (75 MHz, DMSO-d6/CCl_4 1/3), δ, ppm: 23.9 (2×CH_2 cycloheptane), 29.6 (2×CH_2 cycloheptane), 36.1 (2×CH_2 cycloheptane), 38.9 (C*5*), 40.6 (C*6*H_2), 41.5 ($\underline{CH_2}$-CH=CH_2), 54.9 (OCH_3), 109.3 (CH Ar), 113.6 (C*4*$_a$), 115.0 (CH Ar), 116.7 (CH_2-CH=$\underline{CH_2}$), 120.9 (CH Ar), 121.4 (CH Ar), 126.2 (CH Ar), 126.3 (C Ar), 126.5 (C Ar), 128.2 (CH Ar), 130.3 (CH Ar), 132.1 (CH_2-$\underline{CH}$=CH_2), 136.9 (C Ar), 139.4 (C*10*$_b$), 147.5 (C Ar), 148.6 (C Ar), 149.4 (C*2*), 151.6 (N=CH), 159.8 (C*4*). Found, %: C 71.96; H 6.59; N 11.73. $C_{29}H_{32}N_4O_3$. Calculated, %: C 71.88; H 6.66; N 11.56.

3-Allyl-2-(2-(3,4,5-trimethoxybenzylidene)hydrazinyl)-*3H*-spiro[benzo[h]quinazoline-5,1'-cycloheptan]-4(*6H*)-one (Ar=3,4,5-(4-$CH_3O)_3C_6H_2$) **(13).** Yield 3.4 *g* (80%) of **13,** mp 179-181°C, R_f 0.61 (ethyl acetate-benzene, 1:1:5). IR spectrum, *ν, cm*$^{-1}$: 1001 (C-O-C); 1590 (C=C arom); 1621 (C=N); 1665 (C=O); 3150-3360 (NH, OH). ^{1}H NMR spectrum (300 MHz, DMSO-d6/CCl_4 1/3), δ, ppm: 1.30-1.42 (m, 2H, cycloheptane), 1.44-1.71 (m, 6H, cycloheptane), 1.72-1.86 (m, 2H, cycloheptane), 2.23-2.35 (m, 2H, cycloheptane), 2.89 (s, 2H, C*6*H_2), 3.77 (s, 3H, O-CH_3), 3.90 (s, 6H, 2×(O-CH_3)), 4.61 (dt, 2H, J=7.0, 1.2, $\underline{CH_2}$-CH=CH_2), 5.16 (dq, 1H, J=10.1, 1.2, CH_2-CH=$\underline{CH_2}$), 5.27 (dq, 1H, J=17.0, 1.2, CH_2-CH=$\underline{CH_2}$), 5.94 (ddt, 1H, J=17.0, 10.1, 7.0, CH_2-$\underline{CH}$=CH_2), 7.04 (s, 2H, Ar), 7.26-7.31 (m, 1H, Ar), 7.33-7.44 (m, 2H, Ar), 7.57-7.62 (m, 1H, Ar), 8.23 (s, 1H, N=CH), 9.79 (s, 1H, NH). ^{13}C NMR spectrum (75 MHz, DMSO-d6/CCl_4 1/3), δ, ppm: 23.9 (2×CH_2 cycloheptane), 29.5 (2×CH_2 cycloheptane), 36.1 (2×CH_2 cycloheptane), 38.9 (C*5*), 40.5 (C6H_2), 41.5 ($\underline{CH_2}$-CH=CH_2), 55.2 (2×(O-CH_3)), 59.6 (OCH_3), 104.1 (2×CH Ar), 113.9 (C4$_a$), 116.8 (CH_2-CH=$\underline{CH_2}$), 121.0 (CH Ar), 126.23 (C Ar), 126.4 (CH Ar), 128.2 (CH Ar), 130.1 (C Ar), 130.4 (CH Ar), 132.0 (CH_2-$\underline{CH}$=CH_2), 136.9 (C Ar), 139.1 (CH Ar), 139.5 (C10$_b$), 150.1 (C2), 150.8 (N=CH), 152.8 (2×C Ar), 159.7(C4). Found, %: C 70.61; H 6.69; N 10.53. $C_{31}H_{36}N_4O_4$. Calculated, %: C 70.43; H 6.86; N 10.60.

4-Allyl-*4H*-spiro[benzo[h][1,2,4]triazolo[4,3-a]quinazoline-6,1'-cycloheptan]-5(*7H*)-one (14). The mixture of 2.1 *g* (6 *mmol)* of 3-allyl-2-hydrazinyl-*3H*-spiro[benzo[h]quinazoline-5,1'-cycloheptan]-4(*6H*)-one (**6**),

and 15 *ml* of ethylorthoformate was boiled for 15 hrs with a backflow condenser. After distillation of ethylorthoformate excess, the precipitate was recrystallized from butanol. Yield 1.0 *g* (46%) of **14,** mp 148-150°C, R_f 0.65 (ethyl acetate-benzene, 1:1). IR spectrum, *ν, cm*$^{-1}$: 1600 (C=C arom); 1624 (C=N); 1666 (C=O). ^{1}H NMR spectrum (300 MHz, DMSO-d6/CCl_4 1/3), δ, ppm: 1.24-1.36 (m, 2H, CH_2 cycloheptane), 1.44-1.88 (m, 8H, 4×CH_2 cycloheptane), 2.22-2.34 (m, 2H, CH_2 cycloheptane), 2.92 (s, 2H, C*7*H_2), 4.77 (dt, 2H, J=5.4, 1.5, CH_2-CH=CH_2), 5.25 (dq, 1H, J=10.3, 1.5, CH_2-CH=CH_2), 5.38 (dq, 1H, J=17.3, 1.5, CH_2-CH=CH_2), 6.01 (ddt, 1H, J=17.3, 10.3, 5.4, CH_2-CH=CH_2), 7.33-7.51 (m, 3H, 3×CH Ar), 7.82-7.87 (m, 1H, CH Ar), 8.97 (s, 1H, C*1*H). ^{13}C NMR spectrum (75 MHz, DMSO-d6/CCl_4 1/3), δ, ppm: 24.0 (2×CH_2 cycloheptane), 29.3 (2×CH_2 cycloheptane), 34.5 (2×CH_2 cycloheptane), 40.2 (C*6*), 40.5 (C*7*H_2), 44.3 (CH_2-CH=CH_2), 118.4 (CH_2-CH=CH_2), 124.2 (C*5$_a$*), 124.4 (CH Ar), 125.3 (C Ar), 126.8 (CH Ar), 128.3 (CH Ar), 130.6 (CH_2-CH=CH_2), 130.7 (CH Ar), 135.3 (C*1*H), 136.3 (C Ar), 136.7 (C*11$_b$*), 147.9 (C*3$_a$*), 157.2 (C=O). Found, %: C 73.18; H 6.59; N 15.73. $C_{22}H_{24}N_4O$. Calculated, %: C 73.31; H 6.71; N 15.54.

4-Allyl-1-mercapto-*4H*-spiro[benzo[h][1,2,4]triazolo[4,3-a]quinazoline-6,1'-cycloheptan]-5(*7H*)-one (15). The mixture of 2.1 *g* (6 *mmol)* of 3-allyl-2-hydrazinyl-3H-spiro[benzo[h]quinazoline-5,1'-cycloheptan]-4(*6H*)-one (**6**), 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 10% chlorohydric acid up to pH=3.0-3.5. The precipitate was filtered and recrystallized from butanol. Yield 1.9 *g* (81%) of **15,** mp >250°C, R_f 0.60 (ethyl acetate-benzene, 1:5). IR spectrum, ν, *cm*$^{-1}$: 1600 (C=C arom); 1632 (C=N); 1673 (C=O). ^{1}H NMR spectrum (300 MHz, DMSO-d6/CCl_4 1/3), δ, ppm: 1.20-2.00 (m, 10H, 5×CH_2 cycloheptane), 2.72-3.16 (m, 2H, CH_2 cycloheptane), 2.91 (s, 2H, C*7*H_2), 4.60 (dt, 2H, J=5.4, 1.5, CH_2-CH=CH_2), 5.23 (dq, 1H, J=10.3, 1.5, CH_2-CH=CH_2), 5.34 (dq, 1H, J=17.3, 1.5, CH_2-CH=CH_2), 5.94 (ddt, 1H, J=17.3, 10.3, 5.4, CH_2-CH=CH_2), 7.14-7.23 (m, 2H, 2×CH Ar), 7.82-7.87 (m, 1H, CH Ar), 7.53-7.58 (m, 1H, CH Ar), 13.81 (s, 1H, SH). ^{13}C NMR spectrum (75 MHz, DMSO-d6/CCl_4 1/3), δ, ppm: 24.0 (2×CH_2 cycloheptane), 28.9 (2×CH_2 cycloheptane), 28.9 (2×CH_2 cycloheptane), 40.1 (C6), 41.3 (C7H_2), 43.8 (CH_2-CH=CH_2), 118.5 (CH_2-CH=CH_2), 123.7 (CH Ar), 124.0 (C5$_a$), 126.5 (CH Ar), 129.0 (C Ar), 129.3 (CH Ar), 129.8 (CH Ar), 130.3 (CH_2-CH=CH_2), 134.8 (C Ar), 139.2 (C11$_b$), 145.4 (C3$_a$), 156.7 (C1), 162.5 (C=O). Found, %: C 67.18; H 6.33; N 14.38. S 8.04. $C_{22}H_{24}N_4OS$. Calculated, %: C 67.32; H 6.16; N 14.27; S 8.17.

4-Allyl-1-(methylthio)-*4H*-spiro[benzo[h][1,2,4]triazolo[4,3-a]quinazoline-6,1'-cycloheptan]-5(*7H*)-one (16). The mixture of 3.92 *g* (10 *mmol*) of 4-allyl-1-mercapto-*4H*-spiro[benzo[h][1,2,4]triazolo-[4,3-a]quinazoline-6,1'-cycloheptan]-5(*7H*)-one (**15**), 0.56 *g* (10 *mmol*) of

KOH, 30 *ml* of absolute ethanol was boiled in round bottom flask with a backflow condenser for 30 *min*. Then 1.7 *g* (12 *mmol*) of methyl iodide was added and continued to boil 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 3.6 *g* (89%) of **16,** mp 180-182°C, R_f 0.60 (ethyl acetate-benzene, 1:1). IR spectrum, ν, cm^{-1}: 1595 (C=C arom); 1612 (C=C); 1662 (C=O). ^{1}H NMR spectrum (300 MHz, DMSO-d6/CCl_4 1/3), δ, ppm: 0.86-2.20 (brs, 11H, cycloheptane), 2.61 (s, 3H, CH_3), 2.64-3.24 (brs, 3H, 1×CH cycloheptane, C*7*H_2), 4.74 (dt, 2H, J=7.0, 1.2, $\underline{CH_2}$-CH=CH_2), 5.25 (dq, 1H, J=10.1, 1.2, CH_2-CH=$\underline{CH_2}$), 5.38 (dq, 1H, J=17.0, 1.2, CH_2-CH=$\underline{CH_2}$), 6.00 (ddt, 1H, J=17.0, 10.1, 7.0, CH_2-$\underline{CH}$=CH_2), 7.28-7.37 (m, 2H, Ar), 7.38-7.46 (m, 2H, Ar). ^{13}C NMR spectrum (75 MHz, DMSO-d6/CCl_4 1/3), δ, ppm: 16.6 (CH_3), 23.9 (2×CH_2 cycloheptane), 29.2 (brs, 2×CH_2 cycloheptane), 37.2 (brs, 2×CH_2 cycloheptane), 40.0 (C*7*H_2), 41.4 (C*6*), 44.1 ($\underline{CH_2}$-CH=CH_2), 118.5 (CH_2-CH=$\underline{CH_2}$), 124.9 (C*5*$_a$), 125.3 (C*1*), 125.3 (CH Ar), 126.6 (C Ar), 127.6 (CH Ar), 130.6 (2×CH Ar), 135.6 (CH_2-$\underline{CH}$=CH_2), 137.1 (C Ar), 143.8 (C*11*$_b$), 149.5 (C*3*$_a$), 156.7 (C*5*). Found, %: C 68.11; H 6.63; N 13.63. S 8.04. $C_{23}H_{26}N_4OS$. Calculated, %: C 67.95; H 6.45; N 13.78; S 7.89.

4-Allyl-1-(ethylthio)-*4H*-spiro[benzo[h][1,2,4]triazolo[4,3-a]quinazoline-6,1'-cycloheptan]-5(*7H*)-one (17). Similarly, from 3.92 *g* (10 *mmol*) of 4-allyl-1-mercapto-*4H*-spiro[benzo[h][1,2,4]tri-azolo[4,3-a]quinazoline-6,1'-cycloheptan]-5(*7H*)-one (**15**) and 1.7 *g* (11 *mmol*) of ethyl iodide, 2.9 *g* (69%) of **17** was obtained: mp 130-132°C, R_f 0.66 (ethyl acetate-benzene, 1:1). IR spectrum, ν, cm^{-1}: 1600 (C=C arom); 1613 (C=C); 1660 (C=O). ^{1}H NMR spectrum (300 MHz, DMSO-d6/CCl_4 1/3), δ, ppm: 0.86-2.20 (brs, 11H, cycloheptane), 1.34 (t, 3H, J=7.3, CH_2-$\underline{CH_3}$), 2.64-3.24 (brs, 3H, 1×CH cycloheptane, C*7*H_2), 3.16 (q, 2H, J=7.3, $\underline{CH_2}$-CH_3), 4.74 (dt, 2H, J=7.0, 1.2, $\underline{CH_2}$-CH=CH_2), 5.25 (dq, 1H, J=10.1, 1.2, CH_2-CH=$\underline{CH_2}$), 5.39 (dq, 1H, J=17.0, 1.2, CH_2-CH=$\underline{CH_2}$), 6.00 (ddt, 1H, J=17.0, 10.1, 7.0, CH_2-$\underline{CH}$=CH_2), 7.27-7.46 (m, 4H, Ar). ^{13}C NMR spectrum (75 MHz, DMSO-d6/CCl_4 1/3), δ, ppm: 14.0 (CH_2-$\underline{CH_3}$), 23.9 (2×CH_2 cycloheptane), 28.5 ($\underline{CH_2}$-CH_3), 29.3 (brs, 2×CH_2 cycloheptane), 37.2 (brs, 2×CH_2 cycloheptane), 40.1 (C*7*H_2), 41.4 (C*6*), 44.2 ($\underline{CH_2}$-CH=CH_2), 118.5 (CH_2-CH=$\underline{CH_2}$), 125.0 (C*5*$_a$), 125.2 (C*1*), 125.3 (CH Ar), 126.7 (C Ar), 127.6 (CH Ar), 130.6 (2×CH Ar), 135.6 (CH_2-$\underline{CH}$=CH_2), 137.2 (C Ar), 142.9 (C*11*$_b$), 149.4 (C*3*$_a$), 156.7 (C*5*). Found, %: C 68.71; H 6.59; N 13.49; S 7.77. $C_{24}H_{28}N_4OS$. Calculated, %: C 68.54; H 6.71; N 13.32; S 7.62.

4-Allyl-1-(allylthio)-*4H*-spiro[benzo[h][1,2,4]triazolo[4,3-a]quinazoline-6,1'-cycloheptan]-5(*7H*)-one (18). Similarly, from 3.92 *g* (10 *mmol*) of 4-allyl-1-mercapto-*4H*-spiro[benzo[h][1,2,4]triazolo[4,3-a]quinazoline-6,1'-cycloheptan]-5(*7H*)-one (**15**) and 1.21 *g* (10 *mmol*) of allyl bromide, 2.5 *g*(58 %) of **18** was obtained: mp 129-131°C, R_f 0.67 (ethyl

acetate-benzene, 1:1). IR spectrum, ν, cm^{-1}: 1600 (C=C arom); 1615 (C=C); 1660 (C=O). ^{1}H NMR spectrum (300 MHz, DMSO-d6/CCl_4 1/3), δ, ppm: 0.84-2.18 (brs, 11H, cycloheptane), 2.62-3.22 (brs, 3H, 1×CH cycloheptane, C*7*H_2), 3.77 (dt, 2H, J=7.0, 1.2, S-$\underline{CH_2}$-CH=CH_2), 4.74 (dt, 2H, J=7.0, 1.2, N-$\underline{CH_2}$-CH=CH_2), 5.07 (dq, 1H, J=10.1, 1.2, S-CH_2-CH=$\underline{CH_2}$), 5.20 (dq, 1H, J=17.0, 1.2, S-CH_2-CH=$\underline{CH_2}$), 5.25 (dq, 1H, J=10.1, 1.2, N-CH_2-CH=$\underline{CH_2}$), 5.38 (dq, 1H, J=17.0, 1.2, CH_2-CH=$\underline{CH_2}$), 5.86 (ddt, 1H, J=17.0, 10.1, 7.0, S-CH_2-$\underline{CH}$=CH_2), 5.99 (ddt, 1H, J=17.0, 10.1, 7.0, CH_2-$\underline{CH}$=CH_2), 7.28-7.47 (m, 4H, Ar). ^{13}C NMR spectrum (75 MHz, DMSO-d6/CCl_4 1/3), δ, ppm: 23.9 (2×CH_2 cycloheptane), 28.6 (brs, 2×CH_2 cycloheptane), 37.1 (brs, 2×CH_2 cycloheptane), 37.1 (S-$\underline{CH_2}$-CH=CH_2), 40.0 (C*7*H_2), 41.3 (C*6*), 44.1 (N-$\underline{CH_2}$-CH=CH_2), 118.4 (N-CH_2-CH=$\underline{CH_2}$), 118.5 (S-CH_2-CH=$\underline{CH_2}$), 125.0 (C*5*$_a$), 125.2 (C*1*), 125.3 (CH Ar), 126.7 (C Ar), 127.6 (CH Ar), 130.5 (CH Ar), 130.6 (CH Ar), 132.1 (S-CH_2-$\underline{CH}$=CH_2), 135.6 (N-CH_2-$\underline{CH}$=CH_2), 137.2 (C Ar), 142.4 (C*11*$_b$), 149.4 (C*3*$_a$), 156.7 (C*5*). Found, %: C 69.60; H 6.71; N 13.13; S 7.58. $C_{25}H_{28}N_4OS$. Calculated, %: C 69.41; H 6.52; N 12.95; S 7.41.

4-Allyl-1-(benzylthio)-*4H*-spiro[benzo[h][1,2,4]triazolo[4,3-a]quinazoline-6,1'-cycloheptan]-5(*7H*)-one (19). Similarly, from 3.92 *g* (10 *mmol*) of 4-allyl-1-mercapto-*4H*-spiro[benzo[h][1,2,4]triazolo[4,3-a]quinazoline-6,1'-cycloheptan]-5(*7H*)-one (**15**) and 1.27 *g* (10 *mmol*) of chloromethyl-benzene, 4.2 *g* (87%) of **19** was obtained: mp 165-166ºC, R_f 0.75 (ethyl acetate-benzene, 1:1). IR spectrum, ν, cm^{-1}: 1595 (C=C arom); 1612 (C=C); 1660 (C=O). ^{1}H NMR spectrum (300 MHz, DMSO-d6/CCl_4 1/3), δ, ppm: 0.80-2.14 (brs, 11H, cycloheptane), 2.54-3.14 (brs, 3H, 1×CH cycloheptane, C7H_2), 4.28 (brs, 2H, S-CH_2), 4.73 (dt, 2H, J=7.0, 1.2, $\underline{CH_2}$-CH=CH_2), 5.26 (dq, 1H, J=10.1, 1.2, CH_2-CH=$\underline{CH_2}$), 5.38 (dq, 1H, J=17.0, 1.2, CH_2-CH=$\underline{CH_2}$), 6.00 (ddt, 1H, J=17.0, 10.1, 7.0, CH_2-$\underline{CH}$=CH_2), 7.12-7.43 (m, 9H, Ar). ^{13}C NMR spectrum (75 MHz, DMSO-d6/CCl_4 1/3), δ, ppm: 23.9 (2×CH_2 cycloheptane), 28.6 (brs, 2×CH_2 cycloheptane), 37.0 (brs, 2×CH_2 cycloheptane), 39.8 (C7H_2), 41.2 (C6), 41.2 (S-CH_2), 44.1 ($\underline{CH_2}$-CH=CH_2), 118.4 (CH_2-CH=$\underline{CH_2}$), 125.0 (C5$_a$), 125.2 (C1), 125.2 (CH Ar), 126.6 (C Ar), 126.4 (CH Ar), 127.6 (CH Ar),127.8 (2×CH Ar), 128.5 (2×CH Ar), 130.5 (CH Ar), 130.5 (CH Ar), 135.5 (CH_2-$\underline{CH}$=CH_2), 135.8 (C Ar), 137.1 (C Ar), 142.5 (C11$_b$), 149.4 (C3$_a$), 156.6 (C5). Found, %: C 72.11; H 6.13; N 11.50; S 6.46. $C_{29}H_{30}N_4OS$. Calculated, %: C 72.17; H 6.27; N 11.61; S 6.64.

3-ԱԼԻԼ-ՍՊԻՐՈ[ԲԵՆԶՈ[h]ԽԻՆԱԶՈԼԻՆ-5,1'-ՑԻԿԼՈՀԵՊՏԱՆԻ] ՆՈՐ ԱԾԱՆՑՅԱԼՆԵՐԻ ՍԻՆԹԵԶԸ

Ա. Ս. ԱՅՎԱԶՅԱՆ

3-Ալիլ-2-թիօքսո-2,3-դիհիդրո-1H-սպիրո[բենզո[h]խինազոլին-5,1'-ցիկլոհեպտան]-4(6H)-ոնի կոնդենսմամբ 2-բրոմ-ֆենիլէթանոնի և տարբեր կառուցվածքի 2-թիօքսոբենզո[h]խինազոլինների հետ սինթեզվել են 3-ալիլ-2-((2-օքսո-2-ֆենիլէթիլ)թիո)-3H-սպիրո[բենզո[h]խինազոլին-5,1'-ցիկլոհեպտան]-4(6H)-ոն, 2-((3-ալիլ-4-օքսո-4,6-դիհիդրո-3H-սպիրո[բենզո[h]խինազոլին-5,1'-ցիկլոհեպտան]-2-իլ)թիո)մեթիլ-5,5-դիմեթիլ-5,6-դիհիդրոբենզո[h]խինազոլին-4(3H)-ոն, 2-((3-ալիլ-4-օքսո-4,6-դիհիդրո-3H-սպիրո[բենզո-[h]խինազոլին-5,1'-ցիկլոհեպտան]-2-իլ)թիո)մեթիլ-5-էթիլ-5-մեթիլ-5,6-դիհիդրոբենզո[h]խինազոլին-4(3H)-ոն և 3-ալիլ-2-((4-օքսո-4,6-դիհիդրո-3H-սպիրո[բենզո[h]խինազոլին-5,1'-ցիկլոհեպտան]-2-իլ)մեթիլ)թիո-3H-սպիրո[բենզո[h]խինազոլին-5,1'-ցիկլոպենտան]-4(6H)-ոն: 3-Ալիլ-2-հիդրազինիլ-3H-սպիրո[բենզո[h]խինազոլին-5,1'-ցիկլոհեպտան]-4(6H)-ոնի փոխարկումներով սինթեզվել են N'-(3-ալիլ-4-օքսո-4,6-դիհիդրո-3H-սպիրո[բենզո[h]խինազոլին-5,1'-ցիկլոհեպտան]-2-իլ)բենզոհիդրազիդ, N-[2-(3-ալիլ-4-օքսո-4,6-դիհիդրո-3H-սպիրո[բենզո[h]խինազոլին-5,1'-ցիկլոհեպտան]-2-իլ)հիդրազինոկարբոնոթիոիլ]բենզամիդ, 2-(արիլիդեն-հիդրազինիլ)-3-ալիլ-3H-սպիրո[բենզո[h]խինազոլին-5,1'-ցիկլոհեպտան]-4(6H)-ոն, 4-ալիլ-4H-սպիրո[բենզո[h][1,2,4]տրի-ազոլո[4,3-a]խինազոլին-6,1'-ցիկլոհեպտան]-5(7H)-ոն և 4-ալիլ-1-մերկապտո-4H-սպիրո[բենզո[h][1,2,4]տրիազոլո[4,3-a]խինազոլին-6,1'-ցիկլոհեպտան]-5(7H)-ոն: Վերջինս տարբեր կառուցվածքի հալոգենիդներով ալկիլացնելով փոխարկվել է 1-ալկիլթիոածանցյալների:

СИНТЕЗ НОВЫХ ПРОИЗВОДНЫХ 3-АЛЛИЛ-СПИРО[БЕНЗО[h]ХИНАЗОЛИН-5,1'-ЦИКЛОГЕПТАНА]

А. С. АЙВАЗЯН

Научно-технологический центр органической и фармацевтической химии
НАН Республики Армения
Армения, 0014, Ереван, пр. Азатутяна. 26
Тел.: +374 10 288 443 E-mail: ani.ayvazyan17@mail.ru

В результате конденсации 3-аллил-2-тиоксо-2,3-дигидро-*1H*-спиро[бензо[h]хиназолин-5,1'-циклогептан]-4(*6H*)-она с фенацилбромидом и 2-тиоксобензо[h]хиназолинами различного строения синтезированы 2-метилтиопроизводные спиро[бензо[h]хиназолин-5,1'-циклогептана]. Превращениями 3-аллил-2-гидразинил-*3H*-спиро[бензо[h]хиназолин-5,1'-циклогептан]-4(*6H*)-она синтезированы бензгидразид, гидразинокарбонотиоилбензамид, арилиденгидразиды спиробензо[h]хиназолинового ряда, а также 4-алил-*4H*-спиро[бензо[h][1,2,4]триазоло[4,3-a]хиназолин-6,1'-циклогептан]-5(*7H*)-он и 4-алил-1-меркапто-*4H*-спиро[бензо[h][1,2,4]триазоло[4,3-a]хиназолин-6,1'-циклогептан]-5(*7H*)-он. Последний алкилированием с различными галогенидами переведен в 1-алкилтиопроизводные.

REFERENCES

[1] *Shafi S.S., Kumar S.S. //* Intern. J. Chem.Tech. Res. (USA), 2015, v. 8, №1, p. 164.
[2] *Wu L., Zhang Ch.* // RSC Advances, 2016, Issue 34, №6, p. 287555.

[3] *Nowak M., Fornal E., Kontek R., Sroczyński D., Jóźwiak A., Augustowska E., Warpas A., Adamczyk M., Malinowski Z.* // ARKIVOC. 2018, part vii, 0-0. *The Free Internet J. Org. Chem.* Published on line 10-13-2018.

[4] *Keshari A.K., Singh A.K., Raj V., Rai A., Trivedi P., Ghosh B., Kumar U., Rawat A., Kumar D., Saha S. //* Drug Des. Devel. Ther., 2017, v. 11, p. 1623.

[5] *Kantin G.P., Krasavin M. //* Chem. Heterocycl. Compd., 2016**,** v. 52, №11, p. 918.

[6] *Kamela M.M., Zagharyb W.A., Al-Wablic R.I., Anwara M.M.*// Egyptian Pharm. J., 2016, v.15, p. 98.

[7] *Pozharskii A.F., Ozeryanskii V.A., Mikshiev V.Y., Antonov A.S., Chernyshev A.V., Metelitsa A.V., Borodkin G.S., Fedik N.S., Dyablo O.V.* // J. Org. Chem., 2016, v. 81, №13, 5574.

[8] *Mikshiev V.Y., Antonov A.S., Pozharskii A.F.* // Org. Lett., 2016, v.18, №12, 2872.

[9] *Sahoo M. Jena., Daf S., Kumar S.* // Genomics Inform., 2016, September, 14(3), p. 104.

[10] *Rui J., Xu X., Yang Y., Huang J., HWang Xu.Sh. //* Chem. Ind. Forest Prod., 2016, v. 36, №4, p. 2872.

[11] *Malinowski Z., Fornal E., Warpas A., Nowak M.* // Monatsh. Chem., 2018, v. 49, Issue 11, p. 1999.

[12] *Ebied M.Y., Zaghary W.A., Amin K.M., Hammad Sh.F.J.//* Adv. Pharm. Res., 2017, v. 1, №4, p. 216.

[13] *Markosyan A.I., Dilanyan S.V., Arsenyan F.H., Sukasyan R.S., Gharibjanyan B.T.*// Chem. Pharm. J. (Moscow), 2010, v. 44, №3, p. 3.

[14] *Kantin G.P., Krasavin M.* // Chem. Heterocycl. Compd., 2016, v. 52, №11, p. 918.

[15] *Wu L., Zhang Ch.* // RSC Advances, 2016, Issue 34, №6, p. 287555.

[16] *Gomha S.M., Abbas E.M.H., Farghaly T.A.* // J. Het. Chem., 2017, v.54, p. 610.

[17] *Markosyan A., Gabrielyan S. // 3*-nd International congress on technology – engineering & science (Icontes) – 09-10 Feb. 2017, Kuala Lumpur, Malaysia. Abstract book, p. 244.

[18] *Markosyan A.I., Hakopyan Kh.S., Gabrielyan S.H., Mamyan S.S., Ayvazyan A.G., Arsenyan F.H., Muradyan R.E.* // Electronic J. Nat. Sci. NAS RA, 2018, v. 30, Issue 2, p. 39.

[19] *Markosyan A.I., Hayrapetyan K.K., Gabrielyan S.H., Mamyan S.S., Arsenyan F.H., Авакимян Дж.А., Muradyan R.E.*// Chem. J. of Armenia, 2018, т. 71, №3, с. 368.

[20] *Markosyan A.I., Hakopyan Kh.S., Ayvazyan A.S., Mamyan S.S., Ayvazyan A.G., Tamazyan R.A., Arsenyan F.H., Stepanyan H.M.* // Chem. J. of Armenia, 2018, v. 71, №4, p. 596.

[21] *Markosyan A.I., Ayvazyan A.S., Gabrielyan S.H., Mamyan S.S.* // Chem. J. of Armenia, 2019, v. 72, №4, p. 469.

[22] *Markosyan A.I., Ayvazyan A.S., Gabrielyan S.H., Makaryan G.M., Mamyan S.S.*// Electronic J. Nat. Sci. NAS RA, 2020, v. 34, Issue 1, p. 22.

[23] *Markosyan A.I., Hayrapetyan K.K., Gabrielyan S.H., Shirinyan V.Z., Mamyan S.S., Avakimyan J.A., Stepanyan H.M.* // J. Org. Chem. (Moscow), 2018, v. 54, №4, p. 604.

[24] *Markosyan A.I., Dilanyan S.V.* // Electronic J. Nat. Sci. NAS RA, 2006, v. 7, №2, p. 15.

[25] *Markosyan A.I., Hovhannisyan M.H., Kuroyan R.H., Sukasyan R.S., Arzanunts E.M., Sarkisyan I.S.*// Chem.-pharm. J. (Moscow), 1991, v.25, №8, p.26.