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Synthesis and Transformations of 3-Allyl-7,10-dimethyl-2-sulfanylidene-2,3,5,6-tetrahydrospiro[benzo[*h*]quinazoline-5,1′-cyclopentan]-4(1*H*)-one

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Abstract—Ethyl 4′-amino-5′,8′-dimethyl-1′*H*-spiro[cyclopentane-1,2′-naphthalene]-3′-carboxylate reacted with allyl isothiocyanate to give 3-allyl-7,10-dimethyl-2-sulfanylidene-2,3,5,6-tetrahydrospiro[benzo[*h*]quinazoline-5,1′-cyclopentan]-4(1*H*)-one. Reactions of the latter with alkyl halides and hydrazine hydrate and subsequent transformations of the products afforded a series of new benzo[*h*]quinazoline derivatives containing an allyl group in the 3-position.

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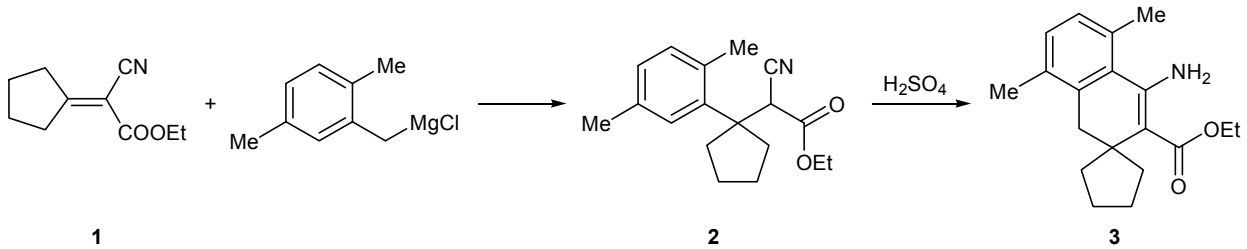
Spiro-fused benzo[*h*]quinazoline derivatives are known to exhibit antitumor [1–5] and psychotropic activity [6, 7]. The goal of the present work was to synthesize a spiro benzo[*h*]quinazoline compound, 7,10-dimethyl-3-(prop-2-en-1-yl)-2-sulfanylidene-2,3,5,6-tetrahydrospiro[benzo[*h*]quinazoline-5,1′-cyclopentan]-4(1*H*)-one (**4**) and study its transformations. For this purpose, an efficient procedure has been developed for the synthesis of key precursor **3**, β-amino ester of the dihydronaphthalene series, which is the base compound for the preparation of dihydrobenzo[*h*]quinazolines spiro fused to cyclopentane ring. Enamino ester **3** was synthesized by acid-catalyzed cyclization of ethyl 2-cyano-2-[1-(2,5-dimethylbenzyl)cyclopentyl]acetate (**2**) which was prepared in turn by reaction of 2,5-dimethylbenzylmagnesium chloride with ethyl 2-cyano-2-cyclopentylideneacetate (**1**) [8] (Scheme 1).

With the goal of obtaining new heterocyclic spiro systems containing a benzo[*h*]quinazoline fragment, amino ester **3** was brought into reaction with allyl isothiocyanate. According to [9], benzoyl isothiocyanate reacted with an analog of ester **3** to give a thiourea derivative [9]. Prolonged heating of **3** with allyl isothiocyanate resulted in intramolecular cyclization of the primary addition product with formation of 7,10-dimethyl-3-(prop-2-en-1-yl)-2-sulfanylidene-2,3,5,6-tetrahydrospiro[benzo[*h*]quinazoline-5,1′-cyclopentan]-4(1*H*)-one (**4**) (Scheme 2). Presumably, the reaction involved intramolecular proton transfer to the carbonyl group with simultaneous elimination of ethanol (Scheme 2). The ^{1}H NMR spectrum of **4** displayed a signal at δ 11.40–11.48 ppm from the NH proton of the quinazoline fragment, and protons of the allyl group resonated at δ 5.00, 5.26–5.38, and 5.82–6.00 ppm.

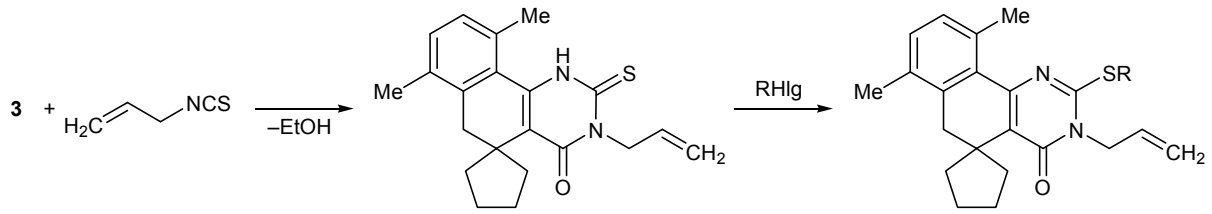
The alkylation of **4** with alkyl halides in anhydrous ethanol afforded the corresponding alkylsulfanyl derivatives **5a**–**5e** (Scheme 2) containing an allyl group in the 3-position of the quinazoline ring. Compounds **5a**–

Scheme 1.



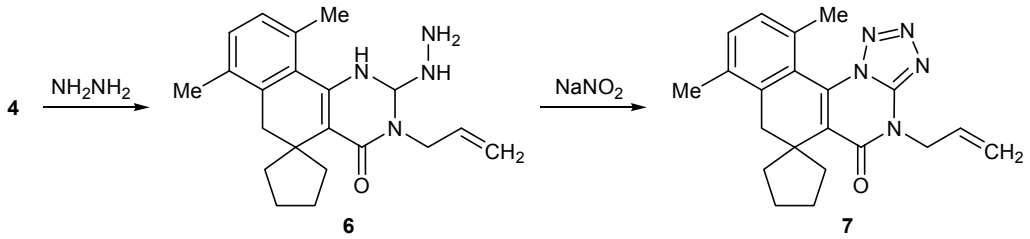
1 **2** **3**

Scheme 2.



R = Me (**a**), Et (**b**), $H_2NC(O)CH_2$ (**c**), CH_2=$CHCH_2$ (**d**), $PhCH_2$ (**e**); Hlg = Cl, I.

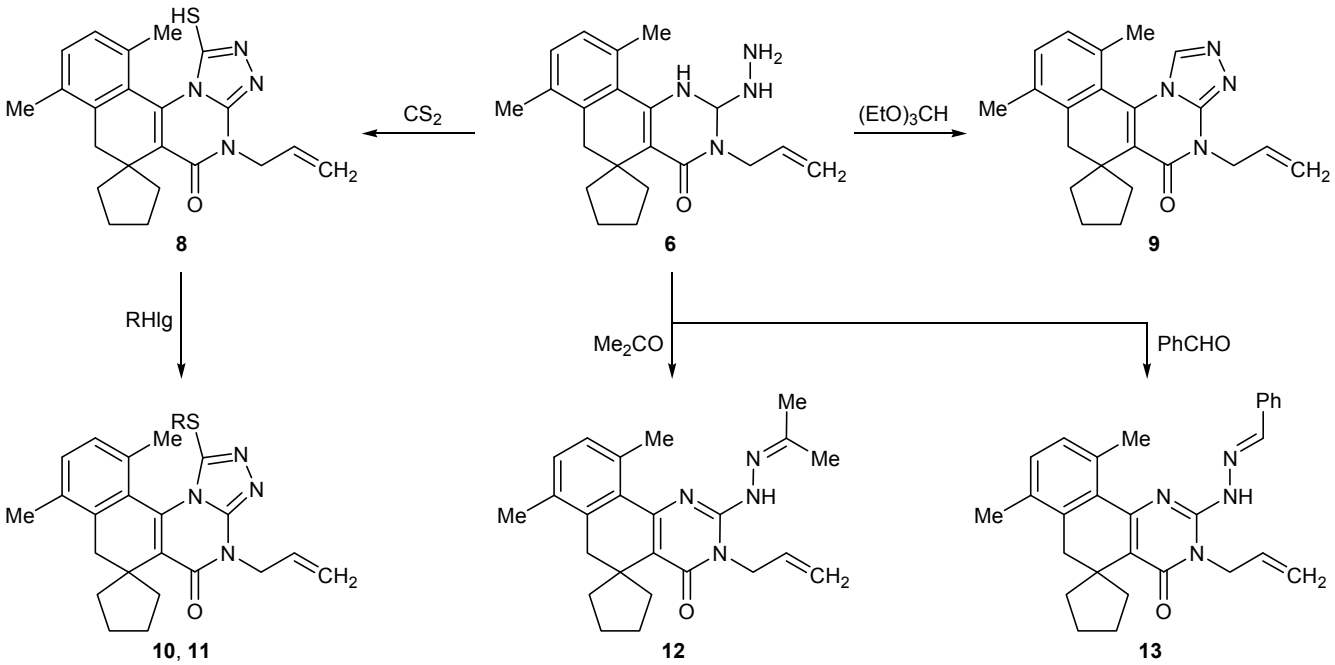
Scheme 3.



5e were isolated as high-melting colorless crystalline solids readily soluble in DMSO and DMF, poorly soluble in chloroform, ethyl acetate, ethanol, and aromatic hydrocarbons, and insoluble in alkanes, diethyl ether, and water.

The reaction of **4** with hydrazine hydrate gave hydrazinyl-substituted derivative **6** which underwent cyclization to fused tetrazole **7** on treatment with sodium nitrite in acetic acid (Scheme 3). Heterocyclization of **6** with carbon disulfide in pyridine led to the formation of sulfanyltriazole **8**, whereas the reaction of **6** with triethyl orthoformate under reflux for 3 days produced 1,2,4-triazole derivative **9** (Scheme 4). Sulfanyltriazole **8** was alkylated with benzyl chloride and chloroacetamide in anhydrous ethanol to obtain alkylsulfanyl derivatives **10** and **11**. Hydrazones **12** and **13** were synthesized by reaction of **6** with acetone and benzaldehyde, respectively (Scheme 4).

Scheme 4.



10, R = $PhCH_2$; **11**, R = $H_2NC(O)CH_2$.

EXPERIMENTAL

The IR spectra were recorded in mineral oil on a UR-20 spectrometer. The ^{1}H NMR spectra were measured on a Varian Mercury 300 instrument at 300 MHz in DMSO-d_6 using tetramethylsilane as internal standard. The melting points were determined on a Boetius melting point apparatus. Analytical thin-layer chromatography was performed on Silufol UV-254 plates using chloroform–ethanol (1:1) as eluent; spots were visualized by treatment with iodine vapor.

Ethyl 2-cyano-2-{[1-(2,5-dimethylphenyl)-methyl]cyclopentyl}acetate (2). A solution of 6.60 g (40 mmol) of cyano ester **1** in 40 mL of anhydrous benzene was added to a slightly boiling solution of Grignard reagent prepared from 1.51 g (63 mmol) of magnesium and 6.18 g (40 mmol) of 2,5-dimethylbenzyl chloride in 40 mL of anhydrous diethyl ether. The mixture was stirred for 2 h at 42–45°C and cooled with ice water, 20% sulfuric acid was added dropwise, and the mixture was stirred at room temperature until complete decomposition of the magnesium complex. The organic phase was separated, the aqueous phase was extracted with diethyl ether, and the extract was combined with the organic phase, washed twice with water, and dried over magnesium sulfate. The solvent was distilled off, and the residue was distilled through a 10-cm column under reduced pressure. Yield 10.4 g (87%), bp 190–192°C (3 mm), R_f 0.43. IR spectrum, ν, cm^{-1}: 2260 (C≡N), 1750 (C=O), 1610 (C=C$_{arom}$). ^{1}H NMR spectrum, δ, ppm: 1.29 t (3H, J = 7.1 Hz), 1.30–1.56 m (8H, C_5H_8), 2.34 s (3H, CH_3), 2.48 s (3H, CH_3), 2.47 s (2H, C**H**$_2$C$_6$H$_3$), 3.30 m (1H), 4.15–4.20 q (2H, OCH_2, J = 7.1 Hz), 6.93 d (1H, C_6H_3, J = 7.8 Hz), 7.02 d (1H, C_6H_3, J = 7.8 Hz), 7.06 d (1H, C_6H_3, J = 7.8 Hz). Found, %: C 76.34; H 8.46; N 4.74. $C_{19}H_{25}NO_2$. Calculated, %: C 76.22; H 8.42; N 4.68.

Ethyl 4′-amino-5′,8′-dimethyl-1*H*-spiro[cyclopentane-1,2′-naphthalene]-3′-carboxylate (3). Concentrated sulfuric acid, 8 mL, was added at 25–30°C to 4.78 g (16 mmol) of ester **2** on cooling with water. The mixture was stirred for 3 h at room temperature and poured onto 120 g of crushed ice. The precipitate was filtered off and washed with water, 60 mL of water and 6 mL of aqueous ammonia were added, and the mixture was extracted with diethyl ether. The extract was evaporated, and the residue was recrystallized from ethanol–water (2:1). Yield 3.44 g (72%), mp 110°C, R_f 0.48. IR spectrum, ν, cm^{-1}: 3000–3200 (NH), 1760 (C=O), 1605 (C=C$_{arom}$). ^{1}H NMR spectrum, δ, ppm: 1.34 t (3H, CH_3, J = 7.1 Hz), 1.38–1.90 m (8H, C_5H_8), 2.34 s (3H, CH_3), 2.48 s (3H, CH_3), 2.51 s (2H, CH_2), 4.17 q (2H, OCH_2, J = 7.1 Hz), 6.68 br.s (2H, NH_2), 6.90 d (1H, C_6H_2, J = 7.8 Hz), 6.98 d (1H, C_6H_2, J = 7.8 Hz). Found, %: C 76.30; H 8.56; N 4.80. $C_{19}H_{25}NO_2$. Calculated, %: C 76.22; H 8.42; N 4.68.

7,10-Dimethyl-3-(prop-2-en-1-yl)-2-sulfanylidene-2,3,5,6-tetrahydrospiro[benzo[*h*]quinazoline-5,1′-cyclopentan]-4(1*H*)-one (4). A mixture of 5.42 g (20 mmol) of compound **3** and 2.26 g (20 mmol) of allyl isothiocyanate was refluxed for 18 h. A solution of 1.84 g (33 mmol) of potassium hydroxide in 150 mL of water and 150 mL of ethanol was added, and the mixture was refluxed for 5 h. The mixture was cooled and acidified with 10% aqueous HCl to a weakly acidic reaction, and the precipitate was filtered off, washed with water, dried, and recrystallized from anhydrous ethanol. Yield 5.98 g (85%), mp 165°C, R_f 0.53. IR spectrum, ν, cm^{-1}: 3300–3450 (NH), 1665 (C=O), 1585 (C=C$_{arom}$). ^{1}H NMR spectrum, δ, ppm: 1.20–1.36 m (2H), 1.56–1.69 m (2H), 1.75–1.88 m (2H), 2.06–2.16 m (2H) (C_5H_8); 2.29 s (3H, CH_3), 2.56 s (3H, CH_3), 2.66 s (2H, CH_2), 4.98 br.d (NCH_2, J = 5.8 Hz), 5.19 d.q (1H, =CH_2, J = 10.2, 1.3 Hz), 5.31 d.q (1H, =CH_2, J = 17.1, 1.3 Hz), 5.96 d.d.t (1H, =CH, J = 17.1, 10.2, 5.8 Hz); 6.98 d and 7.11 d (1H each, C_6H_2, J = 7.8 Hz), 11.47 br.s (1H, NH). Found, %: C 71.30; H 6.66; N 7.80; S 9.00. $C_{21}H_{24}N_2OS$. Calculated, %: C 71.55; H 6.86; N 7.95; S 9.10.

Compounds 5a–5e (*general procedure*). A mixture of 3.12 g (10 mmol) of thione **4**, 0.56 g (10 mmol) of potassium hydroxide, and 60 mL of anhydrous ethanol was refluxed for 30 min, 1.22 g (10 mmol) of the corresponding alkyl halide was added, and the mixture was refluxed for 8 h more. The mixture was cooled and diluted with 10 mL of water, and the precipitate was filtered off and recrystallized from ethanol.

7,10-Dimethyl-2-(methylsulfanyl)-3-(prop-2-en-1-yl)-5,6-dihydrospiro[benzo[*h*]quinazoline-5,1′-cyclopentan]-4(3*H*)-one (5a). Yield 5.98 g (85%), mp 165°C, R_f 0.51. IR spectrum, ν, cm^{-1}: 1665 (C=O), 1610 (C=C$_{arom}$). ^{1}H NMR spectrum, δ, ppm: 1.22–1.73 m (8H, C_5H_8), 1.34 t (3H, CH_3, J = 7.3 Hz), 2.34 s (3H, CH_3), 2.58 s (3H, CH_3), 2.82 br.s (2H, CH_2), 4.63 br.d (2H, NCH_2, J = 5.7 Hz), 5.21–5.99 m (2H, =CH_2), 5.90 d.d.t (1H, =CH, J = 17.1, 10.3, 5.7 Hz), 5.96 d.d.t (1H, =CH, J = 17.1, 10.2, 5.8 Hz), 6.94 d and 7.01 d (1H each, 8-H, 9-H, J = 7.8 Hz). Found, %: C 72.30; H 7.10; N 7.50; S 8.70. $C_{22}H_{26}N_2OS$. Calculated, %: C 72.09; H 7.15; N 7.64; S 8.75.

2-(Ethylsulfanyl)-7,10-dimethyl-3-(prop-2-en-1-yl)-5,6-dihydrospiro[benzo[*h*]quinazoline-5,1′-cyclopentan]-4(3*H*)-one (5b). Yield 5.98 g (85%), mp 165°C, R_f 0.53. IR spectrum, ν, cm^{-1}: 1665 (C=O), 1610 (C=C_{arom}). ^1H NMR spectrum, δ, ppm: 1.20–1.80 m (8H, C_5H_8), 2.34 s (3H, CH_3), 2.58 s (3H, CH_3), 2.82 br.s (2H, CH_2), 4.42 q (2H, C**H**$_2$CH$_3$, *J* = 7.3 Hz), 4.63 br.d (2H, NCH_2, *J* = 5.7 Hz), 5.21–5.99 m (2H, =CH_2), 5.90 d.d.t (1H, =CH, *J* = 17.1, 10.3, 5.7 Hz), 5.96 d.d.t (1H, =CH, *J* = 17.1, 10.2, 5.8 Hz), 6.92 d and 7.03 d (1H each, 8-H, 9-H, *J* = 7.7 Hz). Found, %: C 72.30; H 7.30; N 7.46; S 8.50. $C_{23}H_{28}N_2OS$. Calculated, %: C 72.59; H 7.42; N 7.36; S 8.43.

2-[7,10-Dimethyl-4-oxo-3-(prop-2-en-1-yl)-3,4,5,6-tetrahydrospiro[benzo[*h*]quinazoline-5,1′-cyclopentan]-2-ylsulfanyl]acetamide (5c). Yield 2.87 g (75%), mp 165°C, R_f 0.42. IR spectrum, ν, cm^{-1}: 1660 (C=O), 1605 (C=C_{arom}). ^1H NMR spectrum, δ, ppm: 1.20–1.75 m (8H, C_5H_8), 2.34 s (3H, CH_3), 2.58 s (3H, CH_3), 2.82 br.s (2H, CH_2), 3.89 q (2H, SCH_2, *J* = 7.3 Hz), 6.90 d and 7.01 d (1H each, 8-H, 9-H, *J* = 7.8 Hz), 7.19 s (2H, $CONH_2$, *J* = 7.8 Hz). Found, %: C 67.30; H 6.60; N 10.46; S 7.50. $C_{23}H_{27}N_3O_2S$. Calculated, %: C 67.45; H 6.65; N 10.26; S 7.83.

7,10-Dimethyl-3-(prop-2-en-1-yl)-2-(prop-2-en-1-ylsulfanyl)-5,6-dihydrospiro[benzo[*h*]quinazoline-5,1′-cyclopentan]-4(3*H*)-one (5d). Yield 2.87 g (75%), mp 165°C, R_f 0.58. IR spectrum, ν, cm^{-1}: 1660 (C=O), 1620 (C=N), 1605 (C=C_{arom}). ^1H NMR spectrum, δ, ppm: 1.20–1.75 m (8H, C_5H_8), 2.34 s (3H, CH_3), 2.48 s (3H, CH_3), 2.82 br.s (2H, CH_2), 3.54 q (2H, SCH_2, *J* = 7.3 Hz), 4.98 s (2H, NCH_2), 5.08–5.16 m (2H, =CH_2), 6.08 d.d.t (1H, =CH, *J* = 17.1 Hz), 6.90 d and 7.01 d (1H each, 8-H, 9-H, *J* = 7.8 Hz). Found, %: C 73.30; H 7.30; N 7.46; S 8.10. $C_{24}H_{28}N_2OS$. Calculated, %: C 73.43; H 7.19; N 7.14; S 8.17.

2-(Benzylsulfanyl)-7,10-dimethyl-3-(prop-2-en-1-yl)-5,6-dihydrospiro[benzo[*h*]quinazoline-5,1′-cyclopentan]-4(3*H*)-one (5e). Yield 5.98 g (85%), mp 165°C, R_f 0.47. IR spectrum, ν, cm^{-1}: 1670 (C=O), 1600 (C=C_{arom}). ^1H NMR spectrum, δ, ppm: 1.31–1.45 m (2H), 1.59–1.72 m (2H), 1.78–1.92 m (2H), 2.12–2.23 m (2H) (C_5H_8); 2.29 s (3H, CH_3), 2.63 s (3H, CH_3), 2.68 s (2H, CH_2), 4.50 s (2H, SCH_2), 4.63 br.d (2H, NCH_2, *J* = 5.7 Hz), 5.21–5.99 m (2H, =CH_2), 5.90 d.d.t (1H, =CH, *J* = 17.1, 10.3, 5.7 Hz), 5.96 d.d.t (1H, =CH, *J* = 17.1, 10.2, 5.8 Hz), 6.92 d and 7.03 d (1H each, 8-H, 9-H, *J* = 7.7 Hz), 7.20–7.35 m (5H, C_6H_5). ^{13}C NMR spectrum, δ_C, ppm: 19.1 (CH_3), 23.6 (CH_3), 25.3 (2C, CH_2), 34.7 (2C, CH_2), 35.4 (SCH_2), 38.6 (CH_2), 43.0, 45.6 (NCH_2), 118 (=CH_2), 123.6, 127.0 (CH), 128.1 (2C, Ph), 128.6 (2C, Ph), 129.6 (CH), 130.4 (CH), 130.6 (CH), 130.7, 131.6, 133.3, 134.9, 136.3, 154.2, 155.8, 159.2. Found, %: C 75.79; H 6.80; N 6.46; S 7.10. $C_{28}H_{30}N_2OS$. Calculated, %: C 75.98; H 6.83; N 6.33; S 7.24.

2-Hydrazinyl-7,10-dimethyl-3-(prop-2-en-1-yl)-5,6-dihydrospiro[benzo[*h*]quinazoline-5,1′-cyclopentan]-4(3*H*)-one (6). A mixture of 3.52 g (10 mmol) of compound **4** and 16 mL of hydrazine hydrate was heated for 15 h. When the reaction was complete, the precipitate was filtered off, washed with water, and recrystallized from anhydrous butan-1-ol. Yield 3.00 g (87%), mp 175°C, R_f 0.53. IR spectrum, ν, cm^{-1}: 3300–3450 (NH), 1665 (C=O), 1585 (C=C_{arom}). ^1H NMR spectrum, δ, ppm: 1.25–1.36 m (2H), 1.55–1.68 m (2H), 1.74–1.88 m (2H), 2.10–2.33 m (2H) (C_5H_8); 2.27 s (3H, CH_3), 2.63 s (2H, CH_2), 2.69 s (3H, CH_3), 4.10 br.s (2H, NH_2), 4.56 br.d (2H, NCH_2, *J* = 5.4 Hz), 5.14 d.q (1H, =CH_2, *J* = 10.3, 1.3 Hz), 5.21 d.q (1H, =CH_2, *J* = 17.2, 1.3 Hz), 5.83 d.d.t (1H, =CH, *J* = 17.2, 10.3, 5.4 Hz), 6.89 d and 6.97 d (1H each, 8-H, 9-H, *J* = 7.7 Hz), 7.88 br.s (1H, NH). Found, %: C 71.80; H 7.39; N 16.00. $C_{21}H_{26}N_4O$. Calculated, %: C 71.97; H 7.48; N 15.99.

8,11-Dimethyl-4-(prop-2-en-1-yl)-4*H*-spiro-[benzo[*h*]tetrazolo[1,5-*a*]quinazoline-6,1′-cyclopentan]-5(7*H*)-one (7). A solution of 1.8 g of sodium nitrite in 36 mL of water was added dropwise at room temperature to a solution of 3.50 g (10 mmol) of hydrazine **6** in 60 mL of glacial acetic acid. The mixture was stirred for 30 min, and the precipitate was filtered off and washed with water. Yield 2.67 g (74%), mp 190°C, R_f 0.53. IR spectrum, ν, cm^{-1}: 1670 (C=O), 1605 (C=C_{arom}). ^1H NMR spectrum, δ, ppm: 1.20–1.75 m (8H, C_5H_8), 2.32 s (3H, CH_3), 2.51 s (3H, CH_3), 2.81 br.s (2H, CH_2), 4.86 br.d (2H, NCH_2, *J* = 5.4 Hz), 5.19 d.q (1H, =CH_2, *J* = 10.3, 1.3 Hz), 5.22 d.q (1H, =CH_2, *J* = 17.2, 1.3 Hz), 5.87 d.d.t (1H, =CH, *J* = 17.2, 10.3, 5.4 Hz), 6.97 d and 7.10 d (1H each, 9-H, 10-H, *J* = 7.8 Hz). Found, %: C 69.60; H 6.31; N 19.00. $C_{21}H_{23}N_5O$. Calculated, %: C 69.78; H 6.41; N 19.38.

8,11-Dimethyl-4-(prop-2-en-1-yl)-1-sulfanyl-4*H*-spiro[benzo[*h*][1,2,4]triazolo[4,3-*a*]quinazoline-6,1′-cyclopentan]-5(7*H*)-one (8). A mixture of 3.50 g (10 mmol) of hydrazine **6**, 11 mL of pyridine, and

11 mL of carbon disulfide was stirred for 18 h at 115–118°C. Excess pyridine and carbon disulfide were distilled off, and the residue was recrystallized from butan-1-ol. Yield 2.97 g (76%), mp 255°C, R_f 0.59. IR spectrum, ν, cm^{-1}: 1670 (C=O), 1600 (C=C_{arom}). ^1H NMR spectrum, δ, ppm: 1.20–1.75 m (8H, C_5H_8), 2.34 s (3H, CH_3), 2.53 s (3H, CH_3), 2.80 br.s (2H, CH_2), 4.84 br.d (2H, NCH_2, J = 5.4 Hz), 5.17 d.q (1H, =CH_2, J = 10.3, 1.3 Hz), 5.21 d.q (1H, =CH_2, J = 17.2, 1.3 Hz), 5.86 d.d.t (1H, =CH, J = 17.2, 10.3, 5.4 Hz), 6.97 d and 7.10 d (1H each, 9-H, 10-H, J = 7.8 Hz), 13.05 s (1H, SH). Found, %: C 67.49; H 6.36; N 14.77; S 8.07. $C_{22}H_{24}N_4OS$. Calculated, %: C 67.32; H 6.16; N 14.27; S 8.17.

8,11-Dimethyl-4-(prop-2-en-1-yl)-4*H*-spiro-[benzo[*h*][1,2,4]triazolo[4,3-*a*]quinazoline-6,1′-cyclopentan]-5(7*H*)-one (9). A mixture of 3.50 g (10 mmol) of compound **6** and 12 mL of triethyl orthoformate was heated for 20 h at 145–146°C. Excess triethyl orthoformate was distilled off, and the residue was recrystallized from butan-1-ol. Yield 2.80 g (78%), mp 245°C, R_f 0.46. IR spectrum, ν, cm^{-1}: 1675 (C=O), 1605 (C=C_{arom}). ^1H NMR spectrum, δ, ppm: 1.22–1.73 m (8H, C_5H_8), 2.34 s (3H, CH_3), 2.58 s (3H, CH_3), 2.82 br.s (2H, CH_2), 4.86 br.d (2H, NCH_2, J = 5.4 Hz), 5.19 d.q (1H, =CH_2, J = 10.3, 1.3 Hz), 5.22 d.q (1H, =CH_2, J = 17.2, 1.3 Hz), 5.87 d.d.t (1H, =CH, J = 17.2, 10.3, 5.4 Hz), 6.97 d and 7.10 d (1H each, 9-H, 10-H, J = 7.8 Hz), 8.87 s (1H, 1-H). Found, %: C 73.52; H 6.34; N 15.40. $C_{22}H_{24}N_4O$. Calculated, %: C 73.31; H 6.71; N 15.54.

Compounds 10 and 11 (*general procedure*). A mixture of 3.92 g (10 mmol) of compound **8** and 0.56 g (10 mmol) of potassium hydroxide in 60 mL of anhydrous ethanol was refluxed for 30 min, 10 mmol of benzyl chloride or chloroacetamide was added, and the mixture was refluxed for 8 h more. The mixture was cooled and diluted with 10 mL of water, and the precipitate was filtered off and recrystallized from ethanol.

2-[8,11-Dimethyl-5-oxo-4-(prop-2-en-1-yl)-4,5,6,7-tetrahydrospiro[benzo[*h*][1,2,4]triazolo-[4,3-*a*]quinazoline-6,1′-cyclopentan]-1-ylsulfanyl]-acetamide (10). Yield 3.18 g (76%), mp 222°C, R_f 0.58. IR spectrum, ν, cm^{-1}: 1670 (C=O), 1600 (C=C_{arom}). ^1H NMR spectrum, δ, ppm: 1.20–1.75 m (8H, C_5H_8), 2.34 s (3H, CH_3), 2.53 s (3H, CH_3), 2.80 br.s (2H, CH_2), 4.84 br.d (2H, NCH_2, J = 5.4 Hz), 5.17 d.q (1H, =CH_2, J = 10.3, 1.3 Hz), 5.21 d.q (1H, =CH_2, J = 17.2, 1.3 Hz), 5.86 d.d.t (1H, =CH, J = 17.2, 10.3, 5.4 Hz), 6.97 d and 7.10 d (1H each, 9-H, 10-H, J = 7.8 Hz). Found, %: C 67.49; H 6.36; N 14.77; S 8.07. $C_{22}H_{24}N_4OS$. Calculated, %: C 67.32; H 6.16; N 14.27; S 8.17.

1-(Benzylsulfanyl)-8,11-dimethyl-4-(prop-2-en-1-yl)-4*H*-spiro[benzo[*h*][1,2,4]triazolo[4,3-*a*]quinazoline-6,1′-cyclopentan]-5(7*H*)-one (11). Yield 4.14 g (86%), mp 140°C, R_f 0.57. IR spectrum, ν, cm^{-1}: 1665 (C=O), 1605 (C=C_{arom}). ^1H NMR spectrum, δ, ppm: 1.20–1.75 m (8H, C_5H_8), 2.34 s (3H, CH_3), 2.53 s (3H, CH_3), 2.80 br.s (2H, CH_2), 4.50 (2H, SCH_2), 4.63 br.d (2H, NCH_2, J = 5.7 Hz), 5.21 d.q (1H, =CH_2, J = 10.3, 1.3 Hz), 5.29 d.q (1H, =CH_2, J = 17.2, 1.3 Hz), 5.90 d.d.t (1H, =CH, J = 17.1, 10.3, 5.7 Hz), 6.92 d and 7.03 d (1H each, 9-H, 10-H, J = 7.7 Hz), 7.20–7.35 m (5H, C_6H_5). Found, %: C 67.49; H 6.36; N 14.77; S 8.07. $C_{22}H_{24}N_4OS$. Calculated, %: C 67.32; H 6.16; N 14.27; S 8.17.

Compounds 12 and 13 (*general procedure*). Acetone or benzaldehyde, 10 mmol, was added to a solution of 3.40 g (10 mmol) of hydrazine **6** in 100 mL of benzene, and the mixture was refluxed for 6 h. The solvent was distilled off, 50 mL of water was added to the residue, and the precipitate was filtered off and recrystallized from ethanol.

7,10-Dimethyl-2-[2-(propan-2-ylidene)hydrazinyl]-3-(prop-2-en-1-yl)-5,6-dihydrospiro[benzo-[*h*]quinazoline-5,1′-cyclopentan]-4(3*H*)-one (12). Yield 3.43 g (88%), mp 140°C, R_f 0.59. IR spectrum, ν, cm^{-1}: 1610 (C=C_{arom}), 1670 (C=O). ^1H NMR spectrum, δ, ppm: 1.27–1.88 m (8H, C_5H_8), 2.28 s (3H, CH_3), 2.34 s (3H, CH_3), 2.48 s (3H, CH_3), 2.65 br.s (2H, CH_2), 2.69 s (3H, CH_3), 4.56 br.d (2H, NCH_2, J = 6.1, 1.4 Hz), 5.25 d.q (1H, =CH_2, J = 10.4, 1.4 Hz), 5.55 d.q (1H, =CH_2, J = 17.0, 1.4 Hz), 5.91 d.d.t (1H, =CH, J = 17.0, 10.4, 6.1 Hz), 6.99 d (1H) and 7.18 d (1H each, 8-H, 9-H, J = 17.8 Hz), 9.59 br.s (1H, NH). Found, %: C 73.61; H 7.54; N 14.45. $C_{24}H_{30}N_4O$. Calculated, %: C 73.81; H 7.74; N 14.35.

2-[(2-Benzylidene)hydrazinyl]-7,10-dimethyl-3-(prop-2-en-1-yl)-5,6-dihydrospiro[benzo[*h*]quinazoline-5,1′-cyclopentan]-4(3*H*)-one (13). Yield 3.67 g (84%), mp 142°C, R_f 0.48. IR spectrum, ν, cm^{-1}: 1665 (C=O), 1605 (C=C_{arom}). ^1H NMR spectrum, δ, ppm: 1.35–1.60 m (8H, C_5H_8), 2.34 s (3H, CH_3), 2.48 s (3H, CH_3), 2.53 br.s (2H, CH_2), 4.69 br.d (2H, NCH_2, J = 5.7 Hz), 5.20 d.q (1H, =CH_2, J = 10.3, 1.3 Hz), 5.25 d.q (1H, =CH_2, J = 17.2, 1.3 Hz), 5.87 d.d.t (1H, =CH, J = 17.1, 10.3, 5.7 Hz), 6.88 d and 6.94 d (1H each, 8-H, 9-H, J = 7.7 Hz), 7.52–

7.83 m (5H, C_6H_5), 8.36 s (1H, N=CH), 9.59 br.s (1H, NH). Found, %: C 76.61; H 6.54; N 12.47. $C_{24}H_{30}N_4O$. Calculated, %: C 76.68; H 6.89; N 12.78.

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