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Study of Plant Coumarins: XIV.* Catalytic Amination of 7-Hydroxycoumarin Derivatives

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Abstract—Catalytic amination of 7-hydroxy-6-cyanocoumarin or 7-hydroxy-6-methoxycarbonylcoumarin triflates with substituted anilines, isoquinolin-5-amine, 1*H*-pyrazol-3-amine, or amino acids of penicillin series affords the corresponding 7-(*N*-substituted) aminocoumarins. In the amination of the mentioned triflates and also of peuruthenicine tosilate with 2-(piperidin-1-yl)aniline the catalytic system Pd(OAc)$_2$–BINAP has been efficient.

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Natural and synthetic coumarins are an important group of biologically active compounds whose range of therapeutical action depends essentially on the presence and the position of substituents. 7-Methoxycoumarins are inhibitors of macrophage NO-synthase [2, 3], the antiphlogistic action is found in 7-hydroxycoumarins [4], 7-aryl-substituted coumarins are considered as a new group of selective nonsteroid inhibitors of 17-β-hydroxy-steroid dehydrogenase type 1 (17β-HSD1) [5], and 7-amino-6-aryl-substituted coumarins are characterized as progesterone antagonists [6]. Coumarins with heterocyclic substituents in the aromatic ring may be utilized in the synthesis of antihypertensive [7], antimicrobial [8], and antitumor agents [9]. The derivatives of blue fluorescent dye, (*N*,*N*-dimethyl-7-aminocoumarin-4-yl)acetic acid, are used as fluorescent tags in biomedical visualization and the other branches of modern technology [10].

The preparation methods of 7-(*N*-substituted)-aminocoumarins are based on the aminophenols reaction with β-ketoesters in the presence of various condensation agents [11] or on the condensation of 4-*R*-amino-2-hydroxybenzaldehydes with ethyl nitroacetate [12]. Although recently the catalytic methods of building up the coumarin scaffold with the use of metal complex and organic catalysis found a significant application [13], the catalytic approach with respect to 7-substituted coumarins was utilized only in the synthesis of 7-aminocoumarin from 7-trifluoromethanesulfonyloxycoumarins [14, 15].

We recently developed a procedure for the synthesis of coumarins with aromatic, heterocyclic, or styryl substituents in the position C^7 by means of Pd-catalyzed cross-coupling of 6-methoxycarbonyl-7-(trifluoromethanesulfonyloxy)coumarin (**I**) [16]. Triflate **I** was prepared by the reaction of peuruthenicine (**II**) with trifluoromethanesulfonic anhydride in pyridine. In this study we carried out the catalytic synthesis of coumarins containing nitrogen functions in the position C^7 underlain by triflate **I** and 7-trifluoromethanesulfonyloxy-6-cyanocoumarin (**III**). Compound **III** was synthesized from available furocoumarin oreoselone (**IV**) along Scheme 1 including the Beckmann rearrangement of oreoselone (*E*)- and (*Z*)-oximes (**V**) followed by the reaction of the obtained 7-hydroxy-6-cyanocoumarin (**VI**) with trifluoromethane-sulfonic anhydride (Scheme 1).

Compounds **I** and **III** were brought into the cross-coupling reactions with substituted anilines, 1*H*-pyrazol-3-amine, or isoquinolin-5-amine catalyzed with palladium phosphine complexes (amination by Buchwald–Hartwig reaction) [17]. The reactions of coumarins **I** and **III** with 2-(piperidin-1-yl)aniline (**VIIa**), 2-(morpholin-4-yl)-5-(trifluoromethyl)aniline (**VIIb**), or 4-(methylsulfanyl)-3-(trifluoromethyl)ani-

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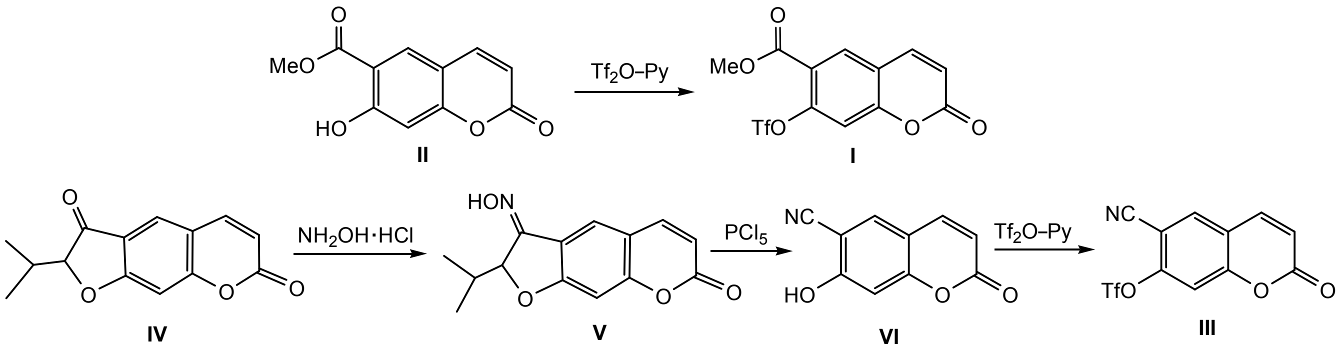
[*] For communication XIII, see [1].

Scheme 1.

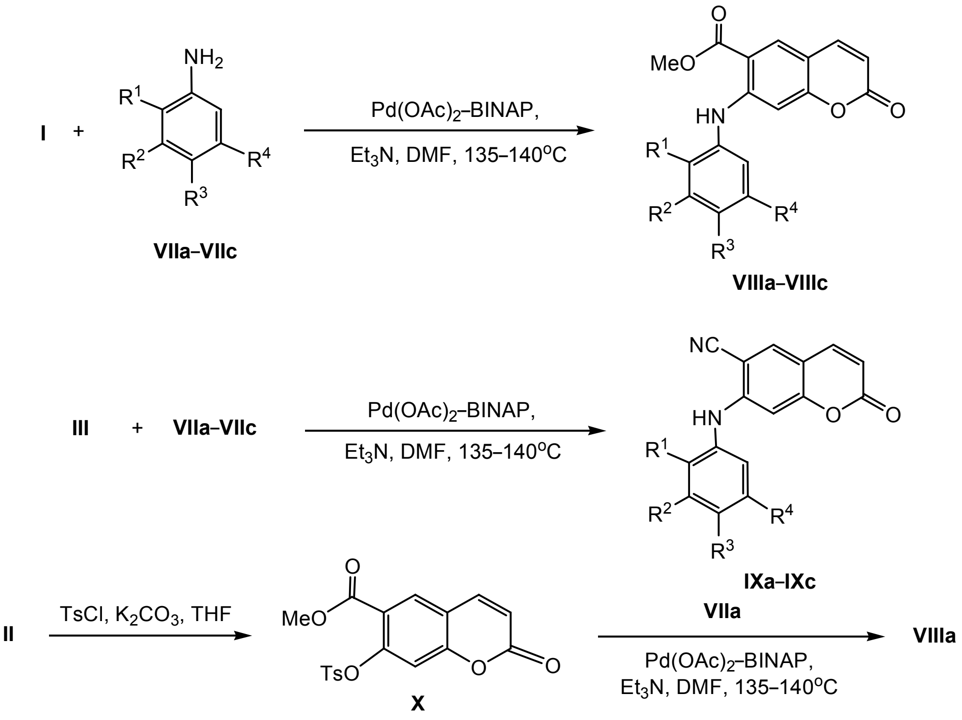


line (**VIIc**) were carried out under the conditions that we had developed for the catalytic amination of 2-isopropyl-3-(trifluoromethanesulfonyloxy)psoralen with aniline derivatives [solvent DMF, catalytic system Pd $(OAc)_2$–BINAP, 4 : 8 mol %, base triethylamine] [18]. To achieve a complete conversion of initial compounds **I** and **III** the temperature was raised to 135–140°C and the reaction time prolonged to 16 h. As a result we obtained 7-(arylamino)-6-methoxycarbonylcoumarins **VIIIa–VIIIc** (yield 63–71%) or 7-arylamino-6-cyanocoumarins **IXa–IXc** (yield 54–65%) isolated by column chromatography on silica gel (Scheme 2).

Only few instances of Pd-catalyzed amination of aryl tosylates and benzyl sulfonates are published [19]. We have established that the reaction of 7-tosyloxycoumarin (**X**) with 2-(piperidin-1-yl)aniline (**VIIa**) proceeds with the formation of amination product **VIIIa**, but the complete conversion of initial coumarin **X** requires a considerable prolongation of the reaction time (in 16 h the conversion has reached 50%).

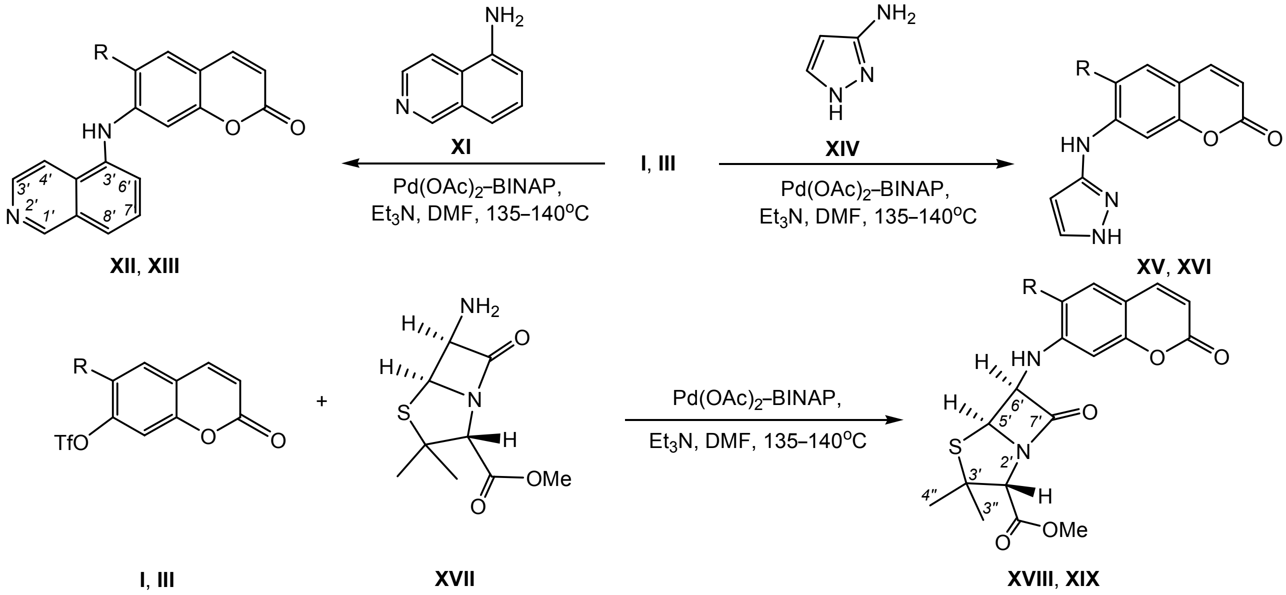
The catalytic amination of compounds **I** and **III** with isoquinoline-5-amine (**XI**) provided 7-[(isoquinolin-5-yl)-amino]coumarins **XII** and **XIII** (yield 63–64%) (Scheme 3). 7-(Trifluoromethanesul-fonyloxy)coumarins **I** and **III** with 3-amino-1*H*-pyrazole (**XIV**) afforded the corresponding 6-substituted 7-(1*H*-pyrazol-3-ylamino) coumarins **XV** and **XVI** (yield 44 and 72% respectively).

Scheme 2.



$R^1 = (CH_2)_5N$, $R^2 = R^3 = R^4 = H$ (**a**); R^1 = morpholin-4-yl, $R^2 = R^3 = H$, $R^4 = CF_3$ (**b**); $R^1 = R^4 = H$, $R^2 = CF_3$, $R^3 = SCH_3$ (**c**).

Scheme 3.



R = CO_2Me (**XII**, **XV**, **XVIII**), CN (**XIII**, **XVI**, **XIX**).

Aiming at the synthesis of lactam antibiotics with a coumarin fragment we examined the reaction of compounds **I** and **III** with methyl 6-aminopenicillanate (**XVII**). We thus obtained coumarinopenicillins **XVIII** and **XIX** (yield 65%). The combination in the same molecule of a coumarin and a β-lactam fragments seems promising in the light of modern trends in penicillins improvement by conjugation with peptides, catechols, and isochromans [20].

The composition and structure of compounds synthesized were established from spectral data and elemental analysis. IR spectra of 6-cyanocoumarins **III**, **IXa–IXc**, **XIII**, **XVI**, and **XIX** contain characteristic bands of stretching vibrations of cyano group (2226–2241 cm^{-1}). In the IR spectra of lactam derivative coumarins **XVIII** and **XIX** characteristic absorption bands of the carbonyl groups are observed at 1785, 1748–1740 (β-lactam), 1680–1726 (C=O of coumarin and COOMe) and of amino groups, at 3465–3478, 3412–3431 cm^{-1}.

^1H and ^{13}C NMR spectra of obtained compounds correspond to their assumed structure and contain a single set of the characteristic signals from the coumarin scaffold and the respective substituent. The special feature of compounds **XVIII** and **XIX** is the presence of the penicillin fragment. The protons of the lactam ring $H^{2',5',6'}$ in the ^1H NMR spectra give rise to signals at δ, ppm: 4.26 s (1H, $H^{2'}$), 4.60–4.68 d (1H, $H^{5'}$), and 5.26–5.48 d.d ($H^{6'}$, $J_{5',6'}$ 4.3–4.4 Hz).

Thus the catalytic amination of 7-hydroxycoumarin derivatives with diverse amines affords *N*-substituted 7-aminocoumarins that may be of interest like bioactive compounds.

EXPERIMENTAL**

NMR spectra were registered on spectrometers Bruker AV-300 [300.13 (^1H), 282.38 (^{19}F), 75.47 MHz (^{13}C)], AV-400 [400.13 (^1H), 100.78 MHz (^{13}C)], and AV-600 [600.30 (^1H), 150.96 MHz (^{13}C)]. Chemical shifts in the ^1H and ^{13}C spectra were measured with respect to the residual signals of solvent $CHCl_3$ (δ_H 7.24, δ_C 76.90 ppm); in ^{19}F spectra an internal reference C_6F_6 (δ_F 0.00 ppm) was used. The multiplicity of signals in ^{13}C NMR spectra was established by common procedures in the single resonance mode. IR spectra were recorded on a spectrophotometer Vector-22 from pellets with KBr. UV spectra were taken on a spectrophotometer HP 8453 UV Vis. Melting points were measured on a heating block Stuart SMF-38.

Elemental analysis was carried out on a CHN-analyzer Carlo Erba 1106.

Reaction products were isolated by column chromatography on silica gel Acros (0.035–0.070 mm)

** Analytic and spectral measurements were performed at the Chemical Services Center for general use of the Siberian Branch of the Russian Academy of Sciences.

or on aluminum oxide, eluents chloroform, chloroform–ethanol, 25 : 1.

Reaction progress was monitored by TLC on Silufol UV-254 plates, eluent chloroform–ethanol, 25 : 1, spots visualized with iodine vapor or under UV irradiation.

Solvents (DMF, THF, chloroform), and also Et$_3$N were purified by standard procedures.

Used in the study BINAP, tosyl chloride, 6-aminopenicillanic acid, and trifluoromethanesulfonic anhydride were purchased from Alfa Aesar.

Methyl 6-aminopenicillanate (**XVII**) was obtained by procedure [21], peuruthenicine triflate (**I**), by procedure [16], Pd(OAc)$_2$, by procedure [22], 7-hydroxy-6-cyanocoumarin (**VI**) was prepared by oreselone (**IV**) oximation [23] with subsequent rearrangement of oximes **V** by Beckmann reaction [24]. Spectral characteristics of compound **VI** were consistent with the published data [24].

2-Oxo-7-(trifluoromethanesulfonyloxy)-2*H*-chromene-6-carbonitrile (III). A solution of 500 mg (2.67 mmol) of 7-hydroxy-6-cyanocoumarin (**VI**) in 5 mL of pyridine was cooled to 0°C and at stirring under an argon atmosphere was added thereto within 15 min 1.35 mL (8.02 mmol) of trifluoromethanesulfonic anhydride. The mixture was warmed to room temperature and left standing for 2 days with intermittent stirring. It was quenched with 10 mL of water. The reaction product was extracted into dichloromethane (4 × 5 mL), the combined organic solutions were dried with MgSO$_4$ and evaporated, pyridine traces were removed by azeotropic distillation with benzene, the residue was crystallized from ethanol. Yield 510 mg (60%), mp 124–125°C (ethanol). IR spectrum, cm^{-1}: 3127, 3087, 3059, 2960, 2226, 1725, 1703, 1630, 1331, 1226, 1135, 1100, 960, 870, 750, 658, 601. UV spectrum (EtOH), λ_{max}, nm (log ε): 220 (3.99), 238 (4.20), 335 (4.11). ^{1}H NMR spectrum (CDCl$_3$), δ, ppm: 6.59 d (1H, H^3, *J* 9.8 Hz), 7.45 s (1H, H^8), 7.71 d (1H, H^4, *J* 9.8 Hz), 7.92 s (1H, H^5). ^{13}C NMR spectrum (CDCl$_3$), δ, ppm: 103.58 (C^6), 112.11 (C^3), 112.41 (C^{4a}), 116.43 (C^8), 118.9 (CN), 117.94, 118.47, 119.51, 120.04 (CF$_3$, *J* 146.3 Hz), 133.71 (C^5), 140.62 (C^4), 150.72 (C^7), 160.01 (C^2), 163.91 (C^{8a}). ^{19}F NMR spectrum (CDCl$_3$), δ, ppm: 89.70 (CF$_3$). Found, %: C 40.84; H 1.40; F 17.56; N 4.25; S 9.79. $C_{11}H_4F_3NO_5S$. Calculated, %: C 41.39; H 1.26; F 17.85; N 4.39; S 10.05.

Methyl 2-oxo-7-(tosyloxy)-2*H*-chromene-6-carboxylate (X). To a solution of 200 mg (0.91 mmol) of 6-methoxycarbonyl-7-hydroxycoumarin (**II**) in 3 mL of THF was added at stirring in succession 345 mg (1.82 mmol) of *p*-tolyenesulfonyl chloride and 579 mg (2.73 mmol) of K$_2$CO$_3$. The reaction mixture was heated to 60°C and kept at this temperature for 30 h. On the completion of the reaction (TLC monitoring by disappearance of the spot of initial coumarin **II**) the reaction mixture was evaporated to 1 mL, the residue was diluted with 5 mL of water, the reaction product was extracted into dichloromethane (4 × 5 mL). Yield 250 mg (73%), mp 145–146°C (chloroform). IR spectrum, cm^{-1}: 3053, 2937, 2739, 2677, 2492, 1722, 1624, 1599, 1441, 1379, 1320, 1286, 1219, 1178, 1132, 1105, 1040, 1013, 966, 926, 908, 818, 779, 750, 690, 667. UV spectrum (EtOH), λ_{max}, nm (log ε): 213 (3.89), 239 (4.13), 334 (4.09). ^{1}H NMR spectrum (CDCl$_3$), δ, ppm: 2.45 s (3H, CH$_3$), 3.84 s (3H, OCH$_3$), 6.43 d (1H, H^3, *J* 9.6 Hz), 6.90 s (1H, H^8), 7.37 d (2H, H$^{3',5'}$, *J* 8.2 Hz), 7.70 d (1H, H^4, *J* 9.6 Hz), 7.78 d (1H, H$^{2'}$, *J* 8.2 Hz), 7.88 d (1H, H$^{6'}$, *J* 8.2 Hz), 8.09 s (1H, H^5). ^{13}C NMR spectrum (CDCl$_3$), δ, ppm: 21.68 (CH$_3$), 52.04 (OCH$_3$), 112.19 (C^8), 117.27 (C^6), 117.46 (C^{4a}), 125.78 (C^3), 128.37 (C$^{2',6'}$), 128.70 (C^5), 129.94 (C$^{3',5'}$), 132.03 (C$^{1'}$), 142.21 (C$^{4'}$), 146.06 d (C^4), 149.90 (C^7), 156.15 (C^{8a}), 159.01 (C^2), 163.72 s (C=O при C^6). Found, %: C 57.30; H 3.63; S 8.86. $C_{18}H_{14}O_7S$. Calculated, %: C 57.75; H 3.77; S 8.57.

Methyl 2-oxo-7-[2-(piperidin-1-yl)phenylamino]-2*H*-chromene-6-carboxylate (VIIIa). *a*. To a solution of 100 mg (0.3 mmol) of peuruthenicine triflate (**I**) in 3 mL of DMF under an argon atmosphere was added in succession 106 mg (0.6 mmol) of 2-(piperidin-1-yl) aniline (**VIIa**), 4 mg (4 mo l%) of Pd(OAc)$_2$, 22 mg (8 mol %) of BINAP, 0.062 mL (0.3 mmol) of Et$_3$N. The reaction mixture was stirred for 8 h at 135–140°C [23], then it was poured in a Petri dish for evaporation in air. The residue was chromatographed on a column packed with silica gel (eluent chloroform), trace amount of reaction product and 90 mg of initial compound **VIIa** were isolated.

b. To a solution of 100 mg (0.3 mmol) of peuruthenicine triflate (**I**) in 3 mL of DMF under an argon atmosphere was added in succession 106 mg (0.6 mmol) of compound **VIIa**, 4 mg (4 mol %) of Pd (OAc)$_2$, 22 mg (8 mol %) BINAP, and 0.062 mL (0.3 mmol) of Et$_3$N. The reaction mixture was stirred for 16 h at 135–140°C (TLC monitoring), cooled, and poured in a Petri dish for evaporation in air. The column chromatography on slica gel (eluent chloroform) afforded 80 mg (71%) of compound **VIIIa**.

c. To a solution of 150 mg (0.4 mmol) of peuruthenicine tosylate (**X**) in 3 mL of DMF under an argon atmosphere was added 141 mg (0.8 mmol) of compound **VIIa**, 5 mg (4 mol %) of Pd(OAc)$_2$, 28 mg (8 mol %) of BINAP, and 0.081 mL (0.4 mmol) of Et$_3$N. The mixture was stirred for 16 h at 135–140°C. After the workup as described above we isolated 85 mg (56%) of compound **VIIIa** and 70 mg of initial compound **X**. Conversion 48%.

Compound VIIIa, mp 70–71°C (ethanol). IR spectrum, cm^{-1}: 3435, 3065, 2959, 1723, 1678, 1630, 1612, 1600, 1576, 1491, 1431, 1377, 1331, 1292, 1221, 1178, 1140, 1099, 1059, 1030, 962, 905, 878, 835, 785, 752. UV spectrum (EtOH), λ_{max}, nm (log ε): 222 (4.27), 240 (4.24), 275 (3.75), 285 (3.87), 311 (3.46). ^{1}H NMR spectrum (CDCl$_3$–CD$_3$OD), δ, ppm: 1.59 m (2H, H$^{3'',5''}$), 1.71 m (2H, H$^{3'',5''}$ and 2H, H$^{4''}$), 2.87 m (4H, H$^{2'',6''}$), 3.99 s (3H, OCH$_3$), 6.52 d (1H, H^3, *J* 9.7 Hz), 6.71 d (1H, H$^{3'}$, *J* 7.7 Hz), 6.74 d.d (1H, H$^{5'}$, *J* 7.2, 7.7 Hz), 6.92 d.d (1H, H$^{4'}$, *J* 7.2, 8.0 Hz), 6.99 d (1H, H$^{6'}$, *J* 8.0 Hz), 7.33 s (1H, H^8), 7.73 d (1H, H^4, *J* 9.7 Hz), 8.28 s (1H, H^5). ^{13}C NMR spectrum (CDCl$_3$–CD$_3$OD), δ, ppm: 24.13 (C$^{4''}$), 26.58 (C$^{3'',5''}$), 52.82 (C$^{2'',6''}$), 52.14 (OCH$_3$), 93.16 (C^8), 100.46, 100.51 (C$^{4a,3'}$), 108.39 (C^6), 111.83 (C$^{4'}$), 115.26 (C^3), 118.49 (C$^{6'}$), 119.69 (C$^{5'}$), 132.59 (C^5), 139.72 (C$^{1'}$), 141.41 (C$^{2'}$), 142.86 (C^4), 156.71 (C^7), 158.65 (C^{8a}), 161.33 (C^2), 162.92 (C=O). Found, %: C 70.09; H 5.67; N 6.99. C$_{22}$H$_{22}$N$_2$O$_4$. Calculated, %: C 69.83; H 5.86; N 7.40.

Methyl 7-{[2-(morpholin-4-yl)-5-(trifluoromethyl)phenyl]amino}-2-oxo-2*H*-chromene-6-carboxylate (VIIIb) was prepared by method *b* from 100 mg (0.3 mmol) of peuruthenicine triflate (**I**) and 152 mg (0.6 mmol) of 2-(morpholin-4-yl)-5-(trifluoromethyl)aniline (**VIIb**). Yield 85 mg (63%), mp 89–91°C (ethanol). IR spectrum, cm^{-1}: 3435, 3065, 2959, 1735, 1678, 1630, 1611, 1576, 1491, 1431, 1377, 1331, 1292, 1221, 1178, 1140, 1099, 1059, 1030, 962, 905, 878, 835, 785, 752. UV spectrum (EtOH), λ_{max}, nm (log ε): 239 (4.41), 274 (3.95), 285 (3.92), 309 (3.79). ^{1}H NMR spectrum (CDCl$_3$), δ, ppm: 2.84 m (4H, H$^{3'',5''}$), 3.76 m (4H, H$^{2'',6''}$), 3.89 s (3H, OCH$_3$), 4.58 br.s (1H, NH), 6.38 d (1H, H^3, *J* 9.6 Hz), 6.46 d (1H, H$^{3'}$, *J* 7.6 Hz), 6.87 d.d (1H, H$^{4'}$, *J* 7.6, 2.2 Hz), 6.91 d (1H, H$^{6'}$, *J* 2.2 Hz), 7.16 s (1H, H^8), 7.67 d (1H, H^4, *J* 9.6 Hz), 8.19 s (1H, H^5). ^{13}C NMR spectrum (CDCl$_3$), δ, ppm: 50.96 (C$^{3'',5''}$), 52.93 (OCH$_3$), 67.36 (C$^{2'',6''}$), 93.22 (C^8), 97.36 (C^{4a}), 110.60 (C^6), 111.67 (C^3), 114.67 (C$^{3'}$), 115.49 (C$^{6'}$), 116.47 (C$^{4'}$), 117.49 (C$^{5'}$), 119.49 q (CF$_3$, *J* 147.9 Hz), 132.67 (C^5), 141.74 (C$^{1'}$), 145.91 (C^4), 149.57 (C$^{2'}$), 156.72 (C^7), 158.37 (C^{8a}), 161.78 (C^2), 162.94 (C=O). Found, %: C 59.22; H 4.03; F 12.28; N 6.69. C$_{22}$H$_{19}$F$_3$N$_2$O$_5$. Calculated, %: C 58.93; H 4.27; F 12.71; N 6.25.

Methyl 7-{[4-methylsulfanyl-3-(trifluoromethyl)-phenyl]amino}-2-oxo-2*H*-chromene-6-carboxylate (VIIIc) was prepared by method *b* from 100 mg (0.3 mmol) of peuruthenicine triflate (**I**) and 124 mg (0.6 mmol) of 4-methylsulfanyl-3-(trifluoromethyl)-aniline (**VIIc**). Yield 90 mg (69%), mp 132–133°C (ethanol). IR spectrum, cm^{-1}: 3393, 3222, 3061, 2964, 1735, 1676, 1626, 1579, 1491, 1446, 1393, 1342, 1299, 1278, 1234, 1214, 1195, 1145, 1109, 1076, 1064, 948, 915, 903, 826, 797, 735. UV spectrum (EtOH), λ_{max}, nm (log ε): 226 (4.10), 245 (3.84), 288 (3.66), 325 (3.84), 335 (3.75). ^{1}H NMR spectrum (CDCl$_3$), δ, ppm: 2.39 s (3H, SCH$_3$), 3.99 s (3H, OCH$_3$), 4.58 br.s (1H, NH), 6.53 d (1H, H^3, *J* 9.6 Hz), 6.76 d.d (1H, H$^{6'}$, *J* 7.8, 2.2 Hz), 6.94 s (1H, H^8), 6.96 d (1H, H$^{2'}$, *J* 2.2 Hz), 7.32 d (1H, H$^{5'}$, *J* 7.8 Hz), 7.74 d (1H, H^4, *J* 9.6 Hz), 8.27 s (1H, H^5). ^{13}C NMR spectrum (CDCl$_3$), δ, ppm: 19.52 (SCH$_3$), 52.93 (OCH$_3$), 104.84 (C^8), 110.02 (C^{4a}), 111.89 (C^3), 112.08 (C^6), 113.18 (C$^{2'}$), 116.58 (C$^{4'}$), 121.45 q (CF$_3$, *J* 147.9 Hz), 125.54 (C$^{6'}$), 127.21 (C$^{5'}$), 132.67 (C^5), 134.52 (C$^{3'}$), 141.68 (C$^{1'}$), 145.35 (C^4), 156.79 (C^7), 158.45 (C^{8a}), 161.73 (C^2), 162.98 (C=O). Found, %: C 56.08; H 3.65; F 13.26; N 3.69; S 8.02. C$_{19}$H$_{14}$F$_3$NO$_4$S. Calculated, %: C 55.74; H 3.42; F 13.92; N 3.42; S 7.83.

2-Oxo-7-[2-(piperidin-1-yl)phenylamino]-2*H*-chromene-6-carbonitrile (IXa) was prepared by method *b* from 100 mg (0.3 mmol) of compound **III** and 106 mg (0.6 mmol) of compound **VIIa**, 4 mg (4 mol %) of Pd(OAc)$_2$, 22 mg (8 mol %) of BINAP, 0.062 mL (0.3 mmol) of Et$_3$N. Yield 60 mg (54%), mp 78–80°C (ethanol). IR spectrum, cm^{-1}: 3437, 3344, 3057, 2932, 2853, 2804, 2239, 1753, 1665, 1626, 1609, 1572, 1501, 1439, 1425, 1379, 1319, 1273, 1238, 1229, 1177, 1136, 1101, 1072, 1034, 918, 907, 870, 833, 777, 748, 698. UV spectrum (EtOH), λ_{max}, nm (log ε): 220 (4.39), 240 (4.18), 286 (3.74), 335 (2.76). ^{1}H NMR spectrum (CDCl$_3$–CD$_3$OD), δ, ppm: 1.53 m (2H, H$^{3'',5''}$), 1.63–1.74 m (2H, H$^{3'',5''}$ and 2H, H$^{4''}$), 2.79 m (4H, H$^{2'',6''}$), 6.55 d (1H, H^3, *J* 9.7 Hz), 6.70 d (1H, H$^{3'}$, *J* 7.7 Hz), 6.74 d.d (1H, H$^{5'}$, *J* 7.2, 7.7 Hz), 6.86 d.d (1H, H$^{4'}$, *J* 7.2, 8.0 Hz), 6.95 d (1H,

$H^{6'}$, *J* 8.0 Hz), 7.43 s (1H, H^{8}), 7.71 d (1H, H^{4}, *J* 9.7 Hz), 7.92 s (1H, H^{5}). ^{13}C NMR spectrum ($CDCl_3$–CD_3OD), δ, ppm: 24.09 ($C^{4''}$), 26.59 ($C^{3'',5''}$), 52.59, 53.02 ($C^{2'',6''}$), 103.41 (C^{6}), 109.51 (C^{4a}), 111.80 (C^{3}), 112.35 (C^{8}), 113.01 ($C^{3'}$), 113.96 ($C^{4'}$), 115.18 ($C^{6'}$), 118.68 (CN), 118.90 ($C^{5'}$), 123.98 ($C^{1'}$), 132.59 (C^{5}), 140.91 ($C^{2'}$), 141.38 (C^{4}), 156.86 (C^{7}), 159.46 (C^{8a}), 160.30 (C^{2}). Found, %: C 73.30; H 5.67; N 11.79. $C_{21}H_{19}N_3O_2$. Calculated, %: C 73.03; H 5.54; N 12.17.

7-{[2-(Morpholin-4-yl)-5-(trifluoromethyl)phenyl]-amino}-2-oxo-2*H*-chromene-6-carbonitrile (IXb) was prepared by method *b* from 100 mg (0.3 mmol) of compound **III** and 152 mg (0.6 mmol) of compound **VIIb**. Yield 80 mg (65%), mp 138–139°C (ethanol). IR spectrum, cm^{-1}: 3433, 3344, 3078, 3059, 2239, 1753, 1655, 1628, 1605, 1570, 1485, 1452, 1425, 1379, 1337, 1275, 1240, 1219, 1177, 1136, 1101, 1072, 995, 939, 916, 907, 870, 833, 777, 750, 698. UV spectrum (EtOH), λ_{max}, nm (log ε): 233 (4.54), 203 (4.47), 274 (3.96), 285 (3.93), 312 (3.86). ^{1}H NMR spectrum ($CDCl_3$–CD_3OD), δ, ppm: 2.86 m (4H, $H^{3'',5''}$), 3.78 m (4H, $H^{2'',6''}$), 6.48 d (1H, H^{3}, *J* 9.6 Hz), 6.54 d (1H, $H^{3'}$, *J* 7.8 Hz), 6.91 d.d (1H, $H^{4'}$, *J* 7.8, 2.0 Hz), 6.94 d (1H, $H^{6'}$, *J* 2.0 Hz), 7.41 s (1H, H^{8}), 7.73 d (1H, H^{4}, *J* 9.6 Hz), 7.94 s (1H, H^{5}). ^{13}C NMR spectrum ($CDCl_3$–CD_3OD), δ, ppm: 50.53, 50.66 ($C^{3'',5''}$), 67.11, 67.14 ($C^{2'',6''}$), 93.98 (C^{8}), 103.05 (C^{6}), 104.54 (C^{4a}), 111.66 (C^{3}), 105.84 ($C^{3'}$), 108.15 ($C^{6'}$), 118.77 (CN), 119.29 ($C^{4'}$), 125.12 q (CF_3, *J* 147.9 Hz), 129.65 ($C^{5'}$), 131.82 (C^{5}), 134.01 ($C^{1'}$), 141.08 (C^{4}), 142.54 ($C^{2'}$), 156.71 (C^{7}), 158.37 (C^{8a}), 160.04 (C^{2}). Found, %: C 60.20; H 4.03; F 13.63; N 9.98. $C_{21}H_{16}F_3N_3O_3$. Calculated, %: C 60.72; H 3.88; F 13.72; N 10.12.

7-{[4-Methylsulfanyl-3-(trifluoromethyl)phenyl]-amino}-2-oxo-2*H*-chromene-6-carbonitrile (IXc) was prepared by method *b* from 100 mg (0.3 mmol) of compound **III** and 124 mg (0.6 mmol) of compound **VIIc**. Yield 70 mg (57%), mp 139–140°C (ethanol). IR spectrum, cm^{-1}: 3431, 3061, 2230, 1760, 1705, 1624, 1504, 1483, 1439, 1394, 1327, 1286, 1263, 1240, 1223, 1157, 1130, 1030, 997, 908, 851, 826, 748, 725, 692. UV spectrum (EtOH), λ_{max}, nm (log ε): 225 (4.57), 236 (4.54), 325 (4.11). ^{1}H NMR spectrum ($CDCl_3$–CD_3OD), δ, ppm: 2.08 s (3H, SCH_3), 6.43 d (1H, H^{3}, *J* 9.6 Hz), 6.62 d.d (1H, $H^{6'}$, *J* 7.6, 1.8 Hz), 6.88 d (1H, $H^{2'}$, *J* 1.8 Hz), 6.94 s (1H, H^{8}), 7.26 d (1H, $H^{5'}$, *J* 7.6 Hz), 7.81 d (1H, H^{4}, *J* 9.6 Hz), 8.19 s (1H, H^{5}). ^{13}C NMR spectrum ($CDCl_3$–CD_3OD), δ, ppm: 20.12 (SCH_3), 98.22 (C^{6}), 103.69 (C^{8}), 112.39 (C^{4a}), 113.24 ($C^{4'}$), 113.88 (C^{3}), 115.72 ($C^{2'}$), 117.47 (CN), 125.88 q (CF_3, *J* 147.9 Hz), 129.66 ($C^{6'}$), 130.95 ($C^{5'}$), 134.00 (C^{5}), 134.47 ($C^{3'}$), 136.06 ($C^{1'}$), 143.17 (C^{4}), 158.17 (C^{7}), 160.83 (C^{8a}), 162.98 (C^{2}). Found, %: C 57.12; H 3.03; F 14.95; N 7.89; S 8.43. $C_{18}H_{11}F_3N_2O_2S$. Calculated, %: C 57.44; H 2.95; F 15.14; N 7.44; S 8.52.

Methyl 7-(isoquinolin-5-ylamino)-2-oxo-2*H*-chromene-6-carboxylate (XII). To a solution of 100 mg (0.3 mmol) of peuruthenicine triflate (**I**) in 3 mL of DMF under an argon atmosphere was added in succession 83 mg (0.6 mmol) of isoquinolin-5-amine (**XI**), 4 mg (4 mol %) of $Pd(OAc)_2$, 22 mg (8 mol %) of BINAP, 0.062 mL (0.3 mmol) of Et_3N. The reaction mixture was stirred for 16 h at 135–140°C (TLC monitoring), cooled, and poured in a Petri dish for evaporation in air. By column chromatography on silica gel (eluent chloroform) we isolated 70 mg (63%) of compound **XII**, mp 113–114°C (ethanol). IR spectrum, cm^{-1}: 3435, 3065, 3143, 1740, 1678, 1630, 1611, 1576, 1491, 1431, 1377, 1331, 1292, 1221, 1178, 1140, 1099, 1059, 1030, 962, 905, 878, 835, 780, 752. UV spectrum (EtOH), λ_{max}, nm (log ε): 225 (4.17), 240 (4.30), 275 (3.83), 285 (3.79), 311 (3.64). ^{1}H NMR spectrum ($CDCl_3$–CD_3OD), δ, ppm: 3.92 s (3H, OCH_3), 6.46 d (1H, H^{3}, *J* 9.7 Hz), 6.90 d.d (1H, $H^{6'}$, *J* 8.2, 1.6 Hz), 7.18 s (1H, H^{8}), 7.32 d.d (1H, $H^{7'}$, *J* 8.2, 7.6 Hz), 7.52 d (1H, $H^{4'}$, *J* 7.2 Hz), 7.60 d.d (1H, $H^{8'}$, *J* 7.6, 1.6 Hz), 7.71 d (1H, H^{4}, *J* 9.7 Hz), 8.20 c (1H, H^{5}), 8.32 d (1H, $H^{3'}$, *J* 7.2 Hz), 9.04 d (1H, $H^{1'}$). ^{13}C NMR spectrum ($CDCl_3$–CD_3OD), δ, ppm: 52.78 (OCH_3), 104.12 (C^{6}), 111.69 (C^{8}), 113.32 (C^{4a}), 114.76 (C^{3}), 117.54 ($C^{8'}$), 118.35 ($C^{6'}$), 120.56 ($C^{4'}$), 125.92 (C^{8a}), 128.11 ($C^{7'}$), 130.63 (C^{5}), 132.54 ($C^{4a'}$), 141.66 ($C^{5'}$), 142.35 (C^{4}), 144.74 ($C^{3'}$), 150.05 ($C^{1'}$), 151.95 (C^{7}), 158.45 (C^{8a}), 160.87 (C^{2}), 162.88 (C=O). Found, %: C 69.65; H 4.32; N 7.78. $C_{20}H_{14}N_2O_4$. Calculated, %: C 69.36; H 4.07; N 8.09.

7-(Isoquinolin-5-ylamino)-2-oxo-2*H*-chromene-6-carbonitrile (XIII) was similarly obtained from 100 mg (0.3 mmol) of compound **III** and 83 mg (0.6 mmol) of isoquinolin-5-amine (**XI**). Yield 60 mg (64%), mp 102–103°C (ethanol). IR spectrum, cm^{-1}: 3449, 3375, 3256, 2233, 1735, 1630, 1605, 1572, 1495, 1487, 1425, 1391, 1277, 1250, 1227, 1177, 1136, 1101, 1074, 1030, 916, 907, 870, 833, 800, 777, 750, 700. UV spectrum (EtOH), λ_{max}, nm (log ε): 220 (4.12), 239 (4.22), 274 (3.34), 285 (3.45), 324 (3.72). ^{1}H NMR spectrum ($CDCl_3$–CD_3OD), δ, ppm: 6.53 d (1H, H^{3}, *J* 9.7 Hz), 7.13 d.d (1H, $H^{6'}$, *J* 8.0, 1.6 Hz), 7.14 s (1H, H^{8}), 7.37 d.d (1H, H$^{7'}$, *J* 8.0, 7.6 Hz), 7.48 d (1H, H$^{4'}$, *J* 7.0 Hz), 7.56 d.d (1H, H$^{8'}$, *J* 7.6, 1.6 Hz), 7.87 d (1H, H^{4}, *J* 9.7 Hz), 8.12 c (1H, H^{5}), 8.23 d.d (1H, H$^{3'}$, *J* 7.0, 1.8 Hz), 8.77 d (1H, H$^{1'}$, *J* 1.8 Hz). ^{13}C NMR spectrum (CDCl$_3$–CD$_3$OD), δ, ppm: 102.78 (C^{6}), 111.47 (C^{8}), 112.13 (C^{4a}), 115.71 (C^{3}), 117.15 (C$^{8'}$), 118.20 (C$^{6'}$), 118.41 (C$^{4'}$), 118.99 (CN), 126.47 (C$^{8a'}$), 128.56 (C$^{7'}$), 130.38 (C^{5}), 132.61 (C$^{4a'}$), 140.30 (C$^{5'}$), 141.16 (C^{4}), 143.38 (C$^{3'}$), 148.11 (C$^{1'}$), 150.15 (C^{7}), 157.96 (C^{8a}), 160.88 (C^{2}). Found, %: C 73.14; H 3.26; N 13.59. $C_{19}H_{11}N_3O_2$. Calculated, %: C 72.84; H 3.54; N 13.41.

Methyl 2-oxo-7-[(1*H*-pyrazol-3-yl)amino]-2*H*-chromene-6-carboxylate (XV). To a solution of 100 mg (0.3 mmol) of peuruthenicine triflate (**I**) in 3 mL of DMF under an argon atmosphere was added in succession 50 mg (0.6 mmol) of 1*H*-pyrazol-3-amine (**XIV**), 4 mg (4 mol %) of Pd(OAc)$_2$, 22 mg (8 mol %) of BINAP, and 0.062 mL (0.3 mmol) of triethylamine. The reaction mixture was stirred for 16 h at 135–140°C (TLC monitoring), cooled, and poured in a Petri dish for evaporation in air. By column chromatography on silica gel (eluent chloroform) we isolated 50 mg (44%) of compound **XV**, mp 124–125°C (ethanol). IR spectrum, cm^{-1}: 3325, 3088, 3060, 2959, 2855, 1744, 1725, 1680, 1630, 1609, 1576, 1550, 1493, 1430, 1376, 1297, 1238, 1228, 1222, 1205, 1181, 1135, 1101, 1060, 1031, 961, 904, 885, 870, 844, 785, 772, 750, 658, 601. UV spectrum (EtOH), λ$_{\text{max}}$, nm (log ε): 232 (4.16), 274 (3.55), 285 (3.48), 311 (3.30). ^{1}H NMR spectrum (CDCl$_3$–CD$_3$OD), δ, ppm: 3.90 s (3H, OCH$_3$), 4.52 br.s (2H, NH), 6.05 d (1H, H$^{4'}$, *J* 1.9 Hz), 6.46 d (1H, H^{3}, *J* 9.7 Hz), 7.18 s (1H, H^{8}), 7.22 d (1H, H$^{5'}$, *J* 1.9 Hz), 7.72 d (1H, H^{4}, *J* 9.7 Hz), 8.21 s (1H, H^{5}). ^{13}C NMR spectrum (CDCl$_3$–CD$_3$OD), δ, ppm: 52.77 (OCH$_3$), 104.49 (C$^{4'}$), 111.68 (C^{4a}), 113.66 (C^{8}), 113.94 (C^{3}), 116.23 (C^{6}), 133.59 (C^{5}), 141.87 (C$^{5'}$), 142.90 (C^{4}), 149.38 (C^{7}), 156.52 (C$^{1'}$), 158.58 (C^{8a}), 160.76 (C^{2}), 162.93 (C=O). Found, %: C 58.86; H 3.95; N 14.56. $C_{14}H_{11}N_3O_4$. Calculated, %: C 58.95; H 3.89; N 14.73.

2-Oxo-7-[(1*H*-pyrazol-3-yl)amino]-2*H*-chromene-6-carbonitrile (XVI) was similarly obtained from 100 mg (0.3 mmol) of compound **III** and 50 mg (0.6 mmol) of 1*H*-pyrazol-3-amine (**XIV**). Yield 80 mg (72%), mp 124–125°C (ethanol). IR spectrum, cm^{-1}: 3339, 3245, 3148, 2233, 2220, 2855, 1725, 1702, 1690, 1627, 1630, 1598, 1552, 1492, 1430, 1416, 1398, 1323, 1270, 1254, 1231, 1173, 1138, 1118, 1030, 992, 856, 826, 819, 770, 763, 686, 638. UV spectrum (EtOH), λ$_{\text{max}}$, nm (log ε): 205 (4.08), 211 (4.07), 227 (4.05), 236 (4.07), 301 (3.45), 325 (3.61). ^{1}H NMR spectrum (CDCl$_3$), δ, ppm: 6.11 br.s (2H, NH and 1H, H$^{4'}$), 6.46 d (1H, H^{3}, *J* 9.7 Hz), 7.11 s (1H, H^{8}), 7.32 d (1H, H$^{5'}$, *J* 1.9 Hz), 7.81 d (1H, H^{4}, *J* 9.7 Hz), 8.28 s (1H, H^{5}). ^{13}C NMR spectrum (CDCl$_3$), δ, ppm: 102.48 (C^{6}), 104.51 (C$^{4'}$), 109.37 (C^{4a}), 113.25 (C^{8}), 113.84 (C^{3}), 118.99 (CN), 131.56 (C^{5}), 140.99 (C$^{5'}$), 142.51 (C^{4}), 143.97 (C^{7}), 155.16 (C$^{1'}$), 159.18 (C^{8a}), 161.54 (C^{2}). Found, %: C 61.93; H 3.70; N 22.66. $C_{13}H_8N_4O_2$. Calculated, %: C 61.90; H 3.20; N 22.21.

Methyl (2*R*,5*S*,6*S*)-3,3-dimethyl-6-[(6-methoxycarbonyl-2-oxo-2*H*-chromen-7-yl)amino]-7-oxo-4-thia-1-azabicyclo[3.2.0]heptane-2-carboxylate (XVIII). To a solution of 100 mg (0.3 mmol) of peuruthenicine triflate (**I**) in 3 mL of DMF under an argon atmosphere was added in succession 259 mg (0.6 mmol) of methyl 6-aminopenicillanate (**XVII**), 4 mg (4 mol %) of Pd(OAc)$_2$, 22 mg (8 mol %) of BINAP, and 0.062 mL (0.3 mmol) of triethylamine. The reaction mixture was stirred for 16 h at 135–140°C (TLC monitoring), cooled, and poured in a Petri dish for evaporation in air. By column chromatography on silica gel (eluent chloroform) we isolated 84 mg (65%) of viscous light-yellow oily compound **XVIII**. IR spectrum, cm^{-1}: 3465, 3412, 3143, 3065, 1785, 1740, 1678, 1630, 1611, 1526, 1495, 1431, 1375, 1331, 1292, 1221, 1178, 1140, 1099, 1059, 1030, 962, 930, 905, 878, 850, 780, 752, 728. UV spectrum (EtOH), λ$_{\text{max}}$, nm (log ε): 210 (4.21), 224 (4.17), 240 (4.30), 278 (3.83), 285 (3.79), 321 (3.64), 365 (3.02). ^{1}H NMR spectrum (CDCl$_3$–CD$_3$OD), δ, ppm: 1.33 s (3H, C$^{3''}$H$_3$), 1.52 s (3H, C$^{4''}$H$_3$), 3.71 s (3H, OCH$_3$), 3.92 s (3H, OCH$_3$), 4.26 s (1H, H$^{2'}$), 4.40 d (1H, NH, *J* 6.2 Hz), 4.60 d (1H, H$^{5'}$, *J* 4.4 Hz), 5.26 d.d (1H, H$^{6'}$, *J* 6.2, 4.4 Hz), 6.48 d (1H, H^{3}, *J* 9.7 Hz), 7.22 s (1H, H^{8}), 7.78 d (1H, H^{4}, *J* 9.7 Hz), 8.10 s (1H, H^{5}). ^{13}C NMR spectrum (CDCl$_3$–CD$_3$OD), δ, ppm: 27.24 (CH$_3$), 29.16 (CH$_3$), 51.75 (OCH$_3$), 52.36 (OCH$_3$), 63.54 (C$^{6'}$), 67.02 (C$^{5'}$), 68.08 (C$^{3'}$), 73.86 (C$^{2'}$), 111.69 (C^{8}), 113.65 (C^{4a}), 114.08 (C^{3}), 117.02 (C^{6}), 130.38 (C^{5}), 143.06 (C^{4}), 146.15 (C^{7}), 156.88 (C^{8a}), 160.91(C^{2}), 162.88 (C=O), 165.39 (C$^{7'}$), 170.12 (C=O при C$^{2'}$). Found, %: C 55.98; H 4.39; N 6.56. $C_{20}H_{20}N_2O_7S$. Calculated, %: C 55.55; H 4.66; N 6.48.

Methyl (2*R*,5*S*,6*S*)-3,3-dimethyl-6-[(6-cyano-2-oxo-2*H*-chromen-7-yl)amino]-7-oxo-4-thia-1-azabicyclo[3.2.0]heptane-2-carboxylate (XIX) was similarly obtained from 100 mg (0.3 mmol) of compound **III** and 259 mg (0.6 mmol) of compound

XVII. Yield 80 mg (65%), yellowish oily substance. IR spectrum, cm^{-1}: 3478, 3431, 3086, 3055, 2241, 1784, 1738, 1703, 1674, 1626, 1505, 1445, 1404, 1369, 1329, 1292, 1271, 1213, 1161, 1138, 1099, 1030, 926, 909, 854, 835, 755, 762, 748, 731. UV spectrum (EtOH), λ_{max}, nm (log ε): 210 (4.32), 220 (4.21), 237 (4.19), 298 (3.51), 326 (3.73), 371 (3.24). ^{1}H NMR spectrum ($CDCl_3$–CD_3OD), δ, ppm: 1.37 s (3H, $C^{3''}H_3$), 1.55 s (3H, $C^{4''}H_3$), 3.72 s (3H, OCH_3), 4.26 s (1H, $H^{2'}$), 4.31 d (1H, NH, *J* 6.2 Hz), 4.68 d (1H, $H^{5'}$, *J* 4.3 Hz), 5.48 d.d (1H, $H^{6'}$, *J* 6.2, 4.3 Hz), 6.40 d (1H, H^3, *J* 9.7 Hz), 7.11 s (1H, H^8), 7.82 d (1H, H^4, *J* 9.7 Hz), 8.12 s (1H, H^5). ^{13}C NMR spectrum ($CDCl_3$–CD_3OD), δ, ppm: 27.24 (CH_3), 29.16 (CH_3), 51.75 (OCH_3), 63.54 ($C^{6'}$), 67.02 ($C^{5'}$), 68.08 ($C^{3'}$), 73.86 ($C^{2'}$), 103.10 (C^6), 111.57 (C^8), 112.06 (C^{4a}), 113.27 (C^3), 118.11 (CN), 130.16 (C^5), 142.44 (C^4), 145.29 (C^7), 157.36 (C^{8a}), 161.11 (C^2), 165.26 ($C^{7'}$), 169.88 (C=O, $C^{2'}$). Found, %: C 57.35; H 4.67; N 10.31. $C_{19}H_{17}N_3O_5S$. Calculated, %: C 57.13; H 4.29; N 10.52.

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