Synthesis and structure of new 3-pyrazolinylcoumarins and 3-pyrazolinyl-2-quinolones

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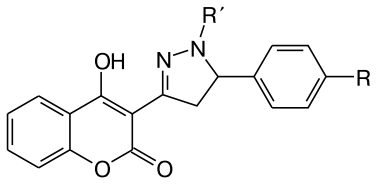
The reactions of substituted 3-cinnamoyl-4-hydroxycoumarins and 3-cinnamoyl-4-hydroxy-2-quinolones with different phenylhydrazines gave 3-hetaryl-1*H*-4,5-dihydropyrazoles. The product structures were studied by ^{1}H NMR spectroscopy and mass spectrometry. 4-Hydroxy-3-pyrazolinylcoumarins exist in DMSO as two tautomers (4-enol and chromane-2,4-dione), while 4-hydroxy-3-pyrazolinyl-2-quinolones exist only in the enol form.

Key words: 1*H*-4,5-dihydropyrazoles, 4-hydroxycoumarin, 4-hydroxy-2-quinolone, aldol condensation, tautomerism.

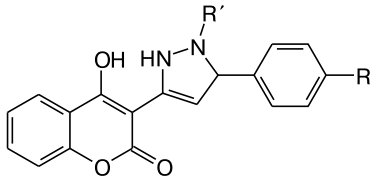
Derivatives of Δ^1-pyrazolines (1*H*-4,5-dihydropyrazoles) find extensive use as optical bleachers and fluorescent dyes.[1] Their spectral properties depend appreciably on the nature of substituents in positions 1 and 3. In particular, 1,3,5-triaryl-1*H*-4,5-dihydropyrazoles are distinguished by high fluorescence with a quantum yield of more than 0.8.[2—5] Many pyrazolines also show various pharmacological properties.[6—12] Some of these compounds have neuroleptic, analgesic, antiinflammatory, or antipyretic properties and some other exhibit antidepressant effect and antibacterial activity. Some pyrazoline derivatives are used as pesticides, fungicides, and insecticides.

3-Hetaryl-1*H*-4,5-dihydropyrazoles arouse particular interest because the properties determined by the pyrazoline fragment are combined with the features of the corresponding hetarene.[13,14] Therefore, it should be noted that 3-(4-hydroxy-3-coumarinyl)-1*H*-4,5-dihydropyrazoles are structural analogs of 3-substituted 4-hydroxycoumarins some representatives of which are effective blood anticoagulants.

Meanwhile, the knowledge concerning 3-coumarinyl-1*H*-4,5-dihydropyrazoles is scarce, while data on their 2-quinolone analogs are totally missing. Only some 3-(3-coumarinyl)-1*H*-4,5-dihydropyrazoles have been prepared from the coumarin analogs of chalcones.[15—17] Thus 5-aryl-3-(3-coumarinyl)-1*H*-4,5-dihydropyrazoles were synthesized by the reaction of 3-cinnamoyl-4-hydroxycoumarins with hydrazine hydrate and phenylhydrazine in the presence of piperidine in ethanol.[15] However, the reliability of these results was not confirmed by spectral data; moreover, the authors failed to choose between two possible isomeric structures (**A** and **B**).



A



B

Results and Discussion

The small number of works dealing with the synthesis and study of 3-coumarinyl-1*H*-4,5-dihydropyrazoles is due to poor reproducibility of the synthesis of coumarin analogs of chalcones by condensation of 3-acetyl-4-hydroxycoumarin with aromatic aldehydes. Carrying out this reaction in the presence of catalytic amounts of 10% NaOH without a solvent[18] and in chloroform in the presence of piperidine[19] was reported. We were unable to accomplish condensation in the presence of sodium hydroxide, while the reaction in the presence of piperidine proved to be non-versatile and was reproduced only in low yields and only for some aldehydes.

Previously,[20] we found that under acid catalysis, the boron difluoride complex of 3-acetyl-4-hydroxycou-

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marin **1** is smoothly converted into coumarin analogs of chalcones **2** in which the lactone fragment of the coumarin nucleus is distinguished by enhanced stability against hydrolysis. In the subsequent study of the reactivity of complex **1**, we obtained new coumarin analogs of chalcones **2** using acetic acid (in the presence of catalytic amounts of sulfuric acid) or acetic anhydride as the solvent (Scheme 1). Boron complexes of chalcone analogs **3** are formed as direct condensation products.

The success of the synthesis of 3-cinnamoyl-4-hydroxycoumarins according to Scheme 1 is due to the properties of the 3-acetyl-4-hydroxycoumarin boron difluoride complex. As shown previously,[21] the complexation of 3-acetyl-4-hydroxycoumarin with BF_3 increases considerably the C=O bond length (from 1.252 to 1.285 Å) and shortens the C(=O)—CH_3 bond (from 1.492 to 1.476 Å). These changes in the bond lengths correspond to the structural change of the acetyl group toward enolization, which leads to an increase in the reaction rate between the enol formed and aldehyde.

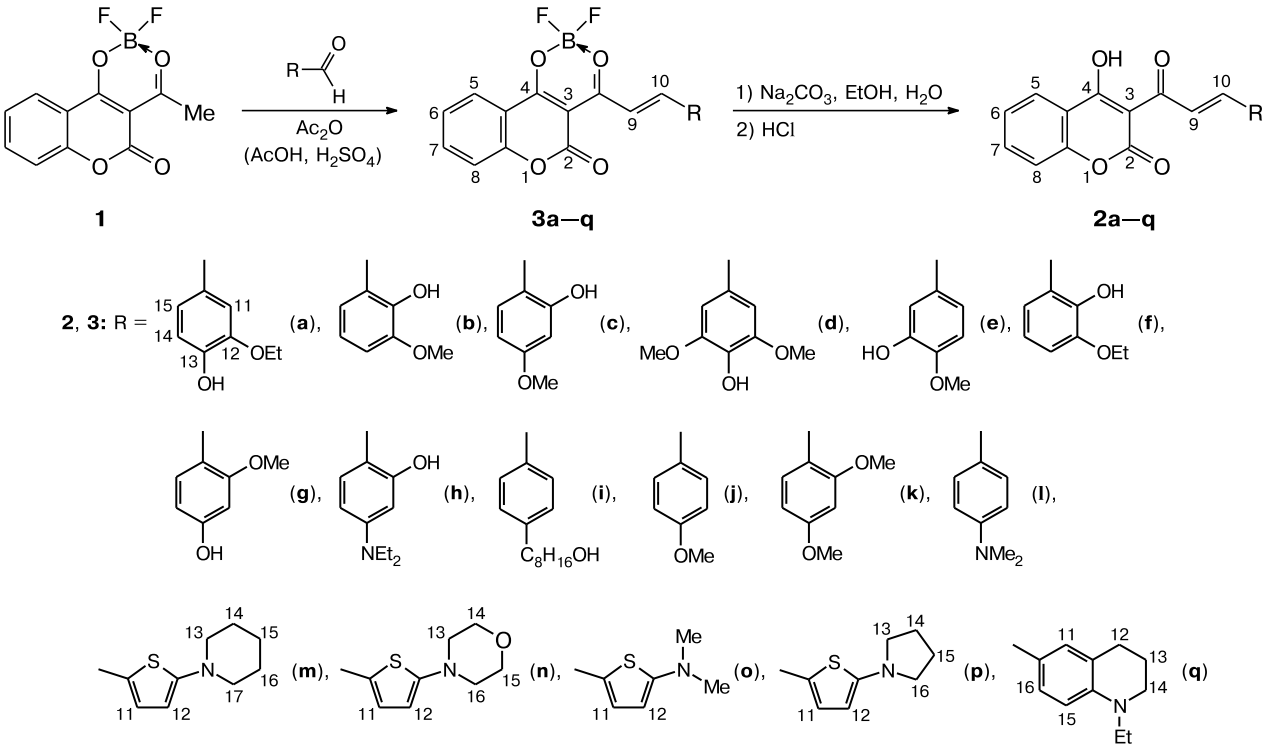
The reaction of substituted 3-cinnamoyl-4-hydroxycoumarins **2** with substituted phenyl- and hetarylhydrazines in isopropyl alcohol smoothly gives 1,5-diaryl-3-(4-hydroxy-3-coumarinyl)-1*H*-4,5-dihydropyrazoles **4** (Scheme 2).

All new compounds were characterized by the ^{1}H NMR spectra, mass spectra, and elemental analysis data. The ^{1}H NMR spectra of compounds **2a—q** exhibit signals at δ 7.5—8.5 for H(9) and H(10) protons with spin-spin coupling constants of 15.2—15.7 Hz; this corresponds to the *E*-configuration of the crotonic condensation products **2**. The ^{1}H NMR spectra of compounds **4a—n** exhibit also signals for protons at C(9) and C(10) as doublets of doublets or multiplets.

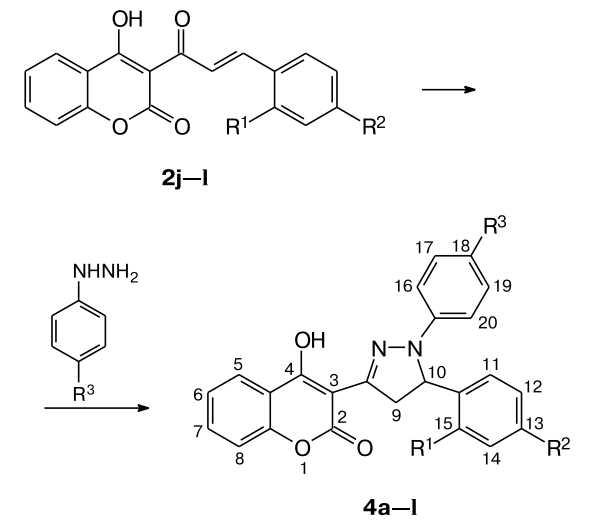
Compounds **4a,f** have been described previously;[15] however, their spectral characteristics were not reported and our data on the melting points of these compounds do not coincide with published data.

Since both the spectral properties and the biological activities of 3-substituted 4-hydroxycoumarins are determined by the type of tautomeric form in which they exist, we studied the dependence of chemical shifts in the ^{1}H NMR spectra of new 1,5-diaryl-3-(4-hydroxy-3-coumarinyl)-1*H*-4,5-dihydropyrazoles **4a—n** on the solvent. The spectra recorded in deuterated DMSO and chloroform attest to the ability of 3-(4-hydroxy-3-coumarinyl)-1*H*-4,5-dihydropyrazoles to exist in at least two tautomeric forms. Thus the ^{1}H NMR spectrum of pyrazoline **4b** recorded in a nonpolar solvent ($CDCl_3$) exhibits only one low-field signal (δ 13.98), which belongs to the hydroxyl group present in the enol form **C** of pyrazoline **4** (Fig. 1). In the ^{1}H NMR spectrum of pyrazoline **4b** recorded in a polar solvent (DMSO), an additional signal corresponding to the NH group appears at δ 10.32 apart from the OH signal (δ 13.74). From comparison of the integral intensities of these signals, one can conclude that

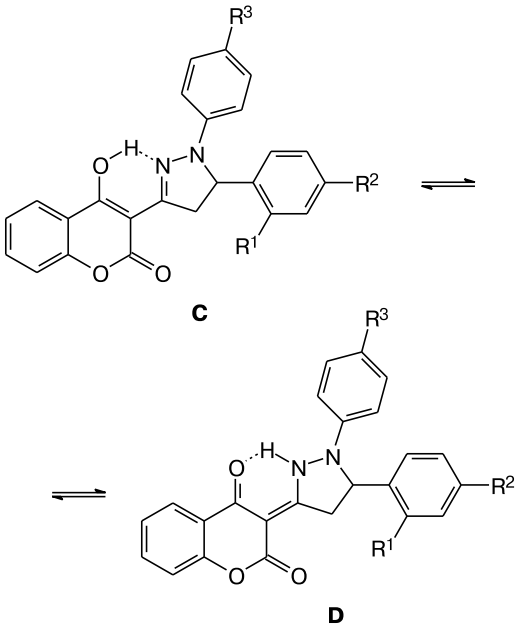
Scheme 1



Scheme 2



Scheme 3



4	R^1	R^2	R^3	**4**	R^1	R^2	R^3
a	H	OMe	H	**g**	OMe	OMe	F
b	H	OMe	F	**h**	OMe	OMe	Me
c	H	OMe	Me	**i**	OMe	OMe	NO_2
d	H	OMe	OMe	**j**	H	NMe_2	H
e	H	OMe	NO_2	**k**	H	NMe_2	F
f	OMe	OMe	H	**l**	H	NMe_2	OMe

4: R = H (**m**), OMe (**n**)

compound **4b** exists in DMSO as chromane-2,4-dione **D** by 45% and as enol **C** by 55%.

According to results of AM1 semiempirical quantum chemical calculations, the interconversions of the tautomers **C** and **D** of 3-(4-hydroxy-3-coumarinyl)-1*H*-4,5-dihydropyrazoles are most probable as the difference between their formation enthalpies is small (1—3 kcal mol^{-1}). The formation enthalpies ΔH_f° of the tautomers of compounds **4a—l** imply that chromane-2,4-dione **D** is the most stable form (Scheme 3), as the calculated enthalpy of its formation is the lowest almost for all structures. Pyrazolines **4e** and **4i** containing a *p*-nitrophenyl substituent at N(1) are exceptions. The difference between the formation energies of tautomers **C** and **D** decreases for these pyrazolines to 6.27—6.38 kcal mol^{-1}.

2-Quinolone analogs of compounds **4** were obtained in the same way (Scheme 4). As we reported previously,[22] acid-catalyzed reactions of boron difluoride complex of 3-acetyl-4-hydroxy-1-methyl-2-quinolone with aromatic and heterocyclic aldehydes afford boron difluoride complexes of 3-cinnamoyl-substituted derivatives of 4-hydroxy-2-quinolone in high yields. They are hydrolyzed to give heterocyclic analogs of chalcones **5a,b** in a quantitative yield.

Compounds **5a,b** react with phenylhydrazine in acetic acid or with phenylhydrazine hydrochlorides in isopro-

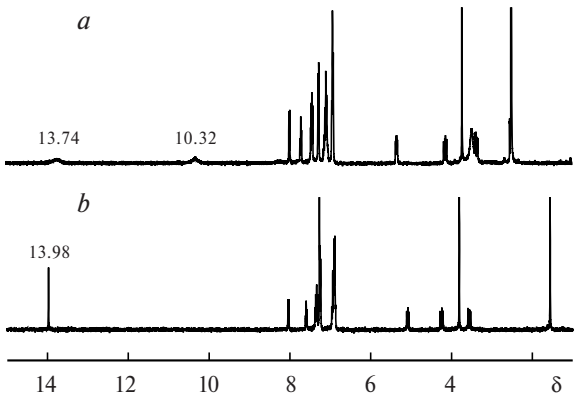
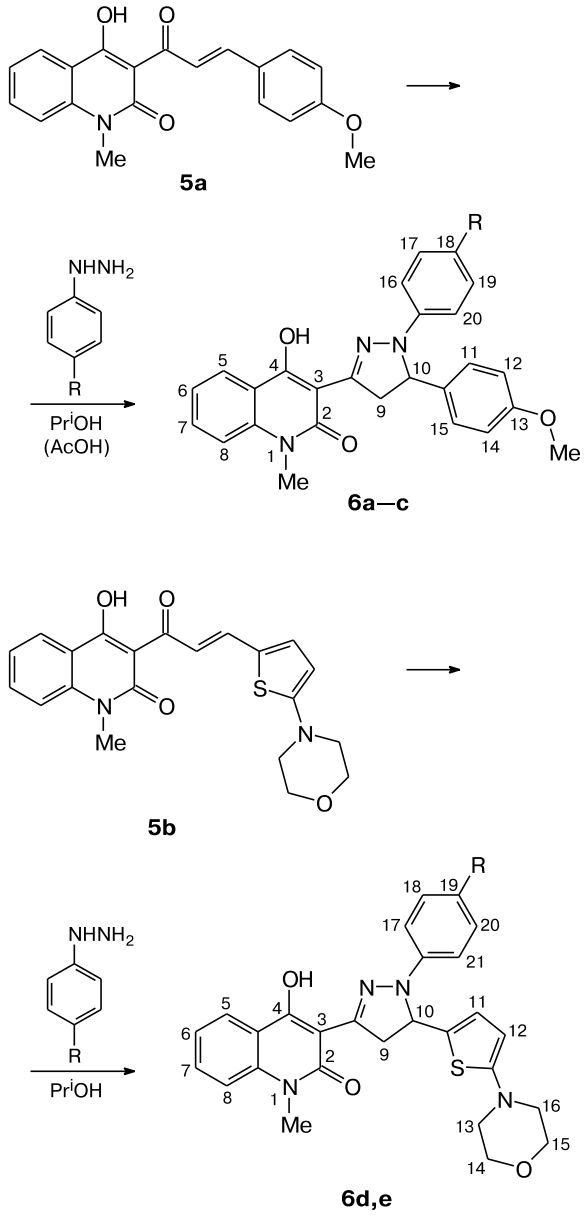


Fig. 1. ^{1}H NMR spectra of compound **4b** recorded in DMSO-d_6 (*a*) and $CDCl_3$ (*b*).

Scheme 4



6: R = H (**a**), F (**b**, **d**), OMe (**c**, **e**)

pyl alcohol in the presence of KOH to give compounds **6a—e** in high yields (see Scheme 4). The structures of obtained compounds were proved by NMR spectroscopy, mass spectrometry, and elemental analysis. The ^{1}H NMR spectra of all compounds exhibit a narrow signal at δ 13.5 for the hydroxyl proton, the signal position and form remaining invariable for different solvents (DMSO-d_6 and $CDCl_3$). This fact indicates that unlike coumarin analogs **4a—l**, compounds **6a—e** are by 100% the hydroxy form in these solvents. As the spectra of compounds **4a—l**, the ^{1}H NMR spectra of compounds **6a—e** contain signals for three protons (2 H(9) and H(10)) typical of 5-substituted pyrazolines as doublets of doublets with δ of 3.5 to 6.0.

Experimental

^{1}H NMR spectra were recorded on a Bruker WP-400 SY spectrometer (400 MHz) with Me_4Si as the internal standard. LC/MS analysis was performed on a PE SCIEX API165 spectrometer (ELSD UV254) with a Synergi 2u Hydro-RP Mercury column (20×2.0 mm).

Condensation of boron complex 1 with aldehydes. ***A.*** A solution of aldehyde (4 mmol) in acetic anhydride (2 mL) was added at 60 °C to a solution of boron difluoride complex of 3-acetyl-4-hydroxycoumarin **1** [21] (4 mmol) in acetic anhydride (10 mL). The mixture was heated for 30 min at 90 °C. After cooling, the precipitate was filtered off, washed on the filter with acetic acid, dried, and recrystallized from acetic acid.

B. A solution of aldehyde (4 mmol) in acetic acid (2 mL) was added at 60 °C to a solution of boron complex **1** (4 mmol) in glacial acetic acid (6 mL), and then concentrated H_2SO_4 (0.5 mL) was added. The mixture was refluxed for 30 min. After cooling, the precipitate was filtered off, washed on the filter with acetic acid, and dried in air.

4-Difluoroboryloxy-3-[(*E*)-3-(3-ethoxy-4-hydroxyphenyl)-prop-2-enoyl]coumarin (3a). Yield 79% (method *B*), m.p. 160—162 °C. ^{1}H NMR ($CDCl_3$), δ: 1.50 (t, 3 H, $OCH_2C\underline{H}_3$, J = 7.2 Hz); 4.26 (q, 2 H, $OC\underline{H}_2CH_3$, J = 7.2 Hz); 7.05 (d, 1 H, H(12), J = 8.2 Hz); 7.23—7.51 (m, 3 H, H(6), H(8), H(15)); 7.80 (m, 1 H, H(7)); 8.26 (d, 1 H, H(5), J = 6.9 Hz); 8.42 (d, 1 H, H(10), J = 15.4 Hz); 8.47 (d, 1 H, H(9), J = 15.4 Hz); 9.15 (s, 1 H, OH). MS, m/z (I_{rel} (%)): 400 (75). Found (%): C, 59.83; H, 3.81. $C_{20}H_{15}BF_2O_6$. Calculated (%): C, 60.00; H, 3.75.

4-Difluoroboryloxy-3-[(*E*)-3-(2-hydroxy-3-methoxyphenyl)-prop-2-enoyl]coumarin (3b). Yield 87% (method *B*), m.p. 228—230 °C. ^{1}H NMR ($CDCl_3$), δ: 4.26 (s, 3 H, OCH_3); 7.20—7.38 (m, 5 H, H(6), H(8), H(12), H(14), H(15)); 7.76 (m, 1 H, H(7)); 8.15 (d, 1 H, H(5), J = 6.8 Hz); 8.32 (m, 2 H, H(9), H(10)); 9.25 (s, 1 H, OH). MS, m/z (I_{rel} (%)): 386 (85). Found (%): C, 59.21; H, 3.24. $C_{19}H_{13}BF_2O_6$. Calculated (%): C, 59.07; H, 3.37.

4-Difluoroboryloxy-3-[(*E*)-3-(2-hydroxy-4-methoxyphenyl)-prop-2-enoyl]coumarin (3c). Yield 61% (method *B*), m.p. 120—122 °C. ^{1}H NMR ($CDCl_3$), δ: 3.94 (s, 3 H, OCH_3); 6.12 (s, 1 H, H(12)); 7.06—7.31 (m, 4 H, H(6), H(8), H(11), H(14)); 7.81 (m, 1 H, H(7)); 8.07 (d, 1 H, H(5), J = 6.4 Hz); 8.21 (m, 2 H, H(9), H(10)); 9.42 (s, 1 H, OH). MS, m/z (I_{rel} (%)): 386 (70). Found (%): C, 58.91; H, 3.45. $C_{19}H_{13}BF_2O_6$. Calculated (%): C, 59.07; H, 3.37.

4-Difluoroboryloxy-3-[(*E*)-3-(4-hydroxy-3,5-dimethoxyphenyl)prop-2-enoyl]coumarin (3d). Yield 65% (method *B*), m.p. 230—232 °C. ^{1}H NMR ($CDCl_3$), δ: 3.95 (s, 6 H, 2 OCH_3); 7.09 (s, 2 H, H(11), H(15)); 7.41 (m, 2 H, H(6), H(8)); 7.84 (m, 1 H, H(7)); 7.96 (d, 1 H, H(5), J = 6.5 Hz); 8.41 (d, 1 H, H(10), J = 15.2); 8.47 (d, 1 H, H(9), J = 15.2); 9.26 (s, 1 H, OH). MS, m/z (I_{rel} (%)): 416 (82). Found (%): C, 57.51; H, 3.74. $C_{20}H_{15}BF_2O_7$. Calculated (%): C, 57.69; H, 3.61.

4-Difluoroboryloxy-3-[(*E*)-3-(3-hydroxy-4-methoxyphenyl)-prop-2-enoyl]coumarin (3e). Yield 78% (method *B*), m.p. 175—177 °C. ^{1}H NMR ($CDCl_3$), δ: 4.05 (s, 3 H, OCH_3); 6.84 (s, 1 H, H(15)); 7.09 (d, 1 H, H(12), J = 7.8 Hz); 7.24—7.39 (m, 3 H, H(6), H(8), H(11)); 7.76 (m, 1 H, H(7)); 7.96 (d, 1 H, H(5), J = 6.5 Hz); 8.41 (d, 1 H, H(10), J = 15.2 Hz); 8.47 (d, 1 H, H(9), J = 15.2 Hz); 9.26 (s, 1 H, OH). MS, m/z (I_{rel} (%)): 386 (75). Found (%): C, 59.19; H, 3.45. $C_{19}H_{13}BF_2O_6$. Calculated (%): C, 59.07; H, 3.37.

4-Difluoroboryloxy-3-[(*E*)-3-(3-ethoxy-2-hydroxyphenyl)-prop-2-enoyl]coumarin (3f). Yield 64% (method *B*), m.p. 189—191 °C. ^{1}H NMR ($CDCl_3$), δ: 2.94 (t, 3 H, $OCH_2C\underline{H}_3$, J = 7.4 Hz); 3.98 (q, 2 H, $OC\underline{H}_2CH_3$, J = 7.4 Hz); 7.02—7.36 (m, 5 H, H(6), H(8), H(13), H(14), H(15)); 7.62 (m, 1 H, H(7)); 7.91 (d, 1 H, H(5), J = 6.4 Hz); 8.09 (m, 2 H, H(9), H(10)); 8.31 (s, 1 H, OH). MS, m/z (I_{rel} (%)): 400 (95). Found (%): C, 59.79; H, 3.81. $C_{20}H_{15}BF_2O_6$. Calculated (%): C, 60.01; H, 3.75.

4-Difluoroboryloxy-3-[(*E*)-3-(4-hydroxy-2-methoxyphenyl)-prop-2-enoyl]coumarin (3g). Yield 87% (method *B*), m.p. 228—230 °C. ^{1}H NMR ($CDCl_3$), δ: 4.23 (s, 3 H, OCH_3); 7.17—7.41 (m, 5 H, H(6), H(8), H(12), H(14), H(15)); 7.75 (m, 1 H, H(7)); 8.13 (d, 1 H, H(5), J = 6.8 Hz); 8.31 (m, 2 H, H(9), H(10)); 9.23 (s, 1 H, OH). MS, m/z (I_{rel} (%)): 386 (85). Found (%): C, 59.18; H, 3.49. $C_{19}H_{13}BF_2O_6$. Calculated (%): C, 59.07; H, 3.37.

4-Difluoroboryloxy-3-{(*E*)-3-[4-(*N*,*N*-diethylamino)-2-hydroxyphenyl]prop-2-enoyl}coumarin (3h). Yield 58% (method *A*), m.p. 182—184 °C. ^{1}H NMR ($CDCl_3$), δ: 1.27 (t, 6 H, 2 $CH_2C\underline{H}_3$); 3.48 (q, 4 H, 2 $C\underline{H}_2CH_3$); 6.43 (s, 1 H, H(12)); 6.64 (d, 1 H, H(14), J = 9.3 Hz); 7.32 (m, 2 H, H(6), H(8)); 7.73 (m, 2 H, H(7), H(15)); 8.21 (d, 1 H, H(5), J = 9.3 Hz); 8.34 (d, 1 H, H(10), J = 15.4 Hz); 8.53 (d, 1 H, H(9), J = 15.4 Hz); 8.87 (s, 1 H, OH). MS, m/z (I_{rel} (%)): 411 (65). Found (%): C, 64.81; H, 4.71; N, 3.49. $C_{22}H_{20}BF_2NO_4$. Calculated (%): C, 64.23; H, 4.87; N, 3.41.

4-Difluoroboryloxy-3-{(*E*)-3-[4-(7-hydroxyoctyl)phenyl]prop-2-enoyl}coumarin (3i). Yield 82% (method *B*), m.p. 149—151 °C. ^{1}H NMR ($CDCl_3$), δ: 2.43 (m, 14 H, $CH_2C_7\underline{H}_{14}$); 3.96 (t, 2 H, $C\underline{H}_2C_7H_{14}$, J = 6.1 Hz); 6.89 (d, 2 H, H(11), H(15), J = 8.3 Hz); 7.32 (m, 2 H, H(6), H(8)); 7.65 (m, 3 H, H(7), H(12), H(14)); 8.03 (m, 3 H, H(5), H(9), H(10)); 8.87 (s, 1 H, OH). MS, m/z (I_{rel} (%)): 468 (75). Found (%): C, 66.45; H, 3.71. $C_{26}H_{27}BF_2O_5$. Calculated (%): C, 66.67; H, 3.63.

4-Difluoroboryloxy-3-[(*E*)-3-(4-methoxyphenyl)prop-2-enoyl]coumarin (3j). Yield 84% (method *B*), m.p. 194—196 °C (*cf.* Ref. 20: m.p. 194—196 °C).

4-Difluoroboryloxy-3-[(*E*)-3-(2,4-dimethoxyphenyl)prop-2-enoyl]coumarin (3k). Yield 76% (method *B*), m.p. 272—274 °C (*cf.* Ref. 20: m.p. 273—274 °C).

4-Difluoroboryloxy-3-{(*E*)-3-[4-(*N*,*N*-dimethylamino)phenyl]-prop-2-enoyl}coumarin (3l). Yield 87% (method *A*), m.p. 331—333 °C (*cf.* Ref. 20: m.p. 332—333 °C).

4-Difluoroboryloxy-3-[(*E*)-3-(5-piperidino-2-thienyl)prop-2-enoyl]coumarin (3m). Yield 67% (method *A*), m.p. 303—305 °C. ^{1}H NMR ($CDCl_3$), δ: 1.62 (m, 6 H, H(14), H(15), H(16)); 3.83 (t, 4 H, H(13), H(17), J = 9.2 Hz); 7.13 (d, 1 H, H(12), J = 5.5 Hz); 7.19 (d, 1 H, H(10), J = 14.8 Hz); 7.44 (m, 2 H, H(6), H(8)); 7.78 (m, 1 H, H(7)); 7.97 (d, 1 H, H(5), J = 6.9 Hz); 8.12 (d, 1 H, H(11), J = 5.5 Hz); 8.29 (d, 1 H, H(9), J = 14.8 Hz). MS, m/z (I_{rel} (%)): 429 (82). Found (%): C, 58.41; H, 4.32; N, 3.15. $C_{21}H_{18}BF_2NO_4S$. Calculated (%): C, 58.74; H, 4.20; N, 3.26.

4-Difluoroboryloxy-3-[(*E*)-3-(5-morpholino-2-thienyl)prop-2-enoyl]coumarin (3n). Yield 65% (method *A*), m.p. 321—323 °C. ^{1}H NMR ($CDCl_3$), δ: 3.82 (m, 8 H, H(13), H(14)), H(15), H(16)); 7.07 (d, 1 H, H(12), J = 5.1 Hz); 7.26 (d, 1 H, H(10), J = 12.9 Hz); 7.44 (m, 2 H, H(6), H(8)); 7.78 (m, 1 H, H(7)); 7.98 (d, 1 H, H(5), J = 6.8 Hz); 8.11 (d, 1 H, H(11), J = 5.1 Hz); 8.35 (d, 1 H, H(9), J = 12.9 Hz). MS, m/z (I_{rel} (%)): 431 (65). Found (%): C, 55.32; H, 3.58; N, 3.17. $C_{20}H_{16}BF_2NO_5S$. Calculated (%): C, 55.68; H, 3.71; N, 3.25.

4-Difluoroboryloxy-3-{(*E*)-3-[5-(*N*,*N*-dimethylamino)-2-thienyl]prop-2-enoyl}coumarin (3o). Yield 63% (method *A*), m.p. 308—310 °C. ^{1}H NMR ($CDCl_3$), δ: 3.43 (s, 6 H, 2 CH_3); 6.97 (d, 1 H, H(12), J = 5.1 Hz); 7.23 (d, 1 H, H(10), J = 12.9 Hz); 7.42 (m, 2 H, H(6), H(8)); 7.78 (m, 1 H, H(7)); 7.97 (d, 1 H, H(5), J = 6.5 Hz); 8.10 (d, 1 H, H(11), J = 5.1 Hz); 8.29 (d, 1 H, H(9), J = 12.9 Hz). MS, m/z (I_{rel} (%)): 389 (76). Found (%): C, 55.81; H, 3.52; N, 3.69. $C_{18}H_{14}BF_2NO_4S$. Calculated (%): C, 55.53; H, 3.60; N, 3.60.

4-Difluoroboryloxy-3-[(*E*)-3-(5-pyrrolidino-2-thienyl)prop-2-enoyl]coumarin (3p). Yield 79% (method *A*), m.p. 310—312 °C. The ^{1}H NMR spectrum could not be recorded due to poor solubility in $CDCl_3$. MS, m/z (I_{rel} (%)): 401 (65). Found (%): C, 59.71; H, 3.92. $C_{20}H_{16}BF_2O_4S$. Calculated (%): C, 59.85; H, 3.99.

4-Difluoroboryloxy-3-[(*E*)-3-(1-ethyl-1,2,3,4-tetrahydroquinolin-6-yl)prop-2-enoyl]coumarin (3q). Yield 83% (method *A*), m.p. 252—254 °C. ^{1}H NMR ($CDCl_3$), δ: 1.29 (t, 3 H, $CH_2C\underline{H}_3$, J = 7.4 Hz); 2.01 (q, 2 H, $C\underline{H}_2CH_3$, J = 7.4 Hz); 2.77 (m, 2 H, H(14)); 3.52 (m, 4 H, H(12), H(13)); 6.64 (d, 1 H, H(15), J = 8.8 Hz); 7.23—7.45 (m, 2 H, H(11), H(16)); 7.56 (m, 2 H, H(6), H(8)); 7.74 (m, 1 H, H(7)); 8.22 (m, 2 H, H(6), H(10)); 8.48 (d, 1 H, H(9), J = 15.1 Hz). MS, m/z (I_{rel} (%)): 423 (80). Found (%): C, 65.38; H, 4.79; N, 3.26. $C_{23}H_{20}BF_2NO_4$. Calculated (%): C, 65.25; H, 4.73; N, 3.31.

Hydrolysis of boron complexes 3 (general procedure). Boron complex **3** (0.5 g) was dissolved in ethanol (5 mL) in a single-neck flask equipped with a reflux condenser. Water (5 mL) and a 5—10-fold molar excess of Na_2CO_3 were added. The mixture was heated at reflux until the color of the boron complex disappeared. Then the reaction mixture was cooled and carefully acidified. The precipitate was filtered off, washed, and dried.

4-Hydroxy-3-[(*E*)-3-(3-ethoxy-4-hydroxyphenyl)prop-2-enoyl]coumarin (2a). Yield 96%, m.p. 123—125 °C (*cf.* Ref. 23: m.p. 125 °C).

4-Hydroxy-3-[(*E*)-3-(2-hydroxy-3-methoxyphenyl)prop-2-enoyl]coumarin (2b). Yield 97%, m.p. 150—153 °C. ^{1}H NMR (DMSO-d_6), δ: 3.84 (s, 3 H, OCH_3); 6.89 (m, 1 H, H(14)); 7.08 (d, 1 H, H(13), J = 7.4 Hz); 7.24 (d, 1 H, H(15), J = 7.9 Hz); 7.43 (m, 2 H, H(6), H(8)); 7.82 (m, 1 H, H(7)); 8.07 (d, 1 H, H(5), J = 6.5 Hz); 8.36 (m, 2 H, H(9), H(10)); 9.66 (s, 1 H, OH(11)); 18.21 (s, 1 H, OH(4)). MS, m/z (I_{rel} (%)): 338 (93). Found (%): C, 67.72; H, 4.25. $C_{19}H_{14}O_6$. Calculated (%): C, 67.45; H, 4.14.

4-Hydroxy-3-[(*E*)-3-(2-hydroxy-4-methoxyphenyl)prop-2-enoyl]coumarin (2c). Yield 95%, m.p. 184—186 °C. ^{1}H NMR (DMSO-d_6), δ: 3.81 (s, 3 H, OCH_3); 6.57 (m, 2 H, H(12), H(14)); 7.42 (m, 3 H, H(6), H(8), H(15)); 7.59 (d, 1 H, H(10), J = 15.7 Hz); 7.82 (m, 2 H, H(7), H(9)); 8.04 (d, 1 H, H(5), J = 6.9 Hz); 8.31 (s, 1 H, OH(11)); 18.6 (s, 1 H, OH(4)). MS, m/z (I_{rel} (%)): 338 (89). Found (%): C, 67.91; H, 4.29. $C_{19}H_{14}O_6$. Calculated (%): C, 67.45; H, 4.14.

4-Hydroxy-3-[(*E*)-3-(4-hydroxy-3,5-dimethoxyphenyl)prop-2-enoyl]coumarin (2d). Yield 98%, m.p. >350 °C. ^{1}H NMR (DMSO-d_6), δ: 3.57 (s, 6 H, 2 OCH_3); 6.72 (s, 2 H, H(11), H(15)); 7.41—7.63 (m, 5 H, H(6), H(7), H(8), H(9), H(10)); 7.94 (d, 1 H, H(5), J = 7.9 Hz); 8.20 (s, 1 H, OH(13)); 18.92 (s, 1 H, OH(4)). MS, m/z (I_{rel} (%)): 368 (95). Found (%): C, 65.43; H, 4.26. $C_{20}H_{16}O_7$. Calculated (%): C, 65.22; H, 4.35.

4-Hydroxy-3-[(*E*)-3-(3-hydroxy-4-methoxyphenyl)prop-2-enoyl]coumarin (2e). Yield 96%, m.p. 119—120 °C. ^{1}H NMR (DMSO-d_6), δ: 3.85 (s, 3 H, OCH_3); 6.84 (d, 1 H, H(12), J = 8.7 Hz); 7.13 (d, 1 H, H(11), J = 8.7 Hz); 7.28 (m, 3 H, H(6), H(8), H(15)); 7.63 (m, 1 H, H(7)); 7.94 (d, 1 H, H(10), J = 15.3 Hz); 8.05 (d, 1 H, H(4), J = 7.6 Hz); 8.22 (d, 1 H, H(9), J = 15.3 Hz); 9.14 (s, 1 H, OH(13)); 17.63 (s, 1 H, OH(4)). MS, m/z (I_{rel} (%)): 338 (95).

Found (%): C, 67.73; H, 4.02. $C_{19}H_{14}O_6$. Calculated (%): C, 67.45; H, 4.14.

3-[(*E*)-3-(3-Ethoxy-2-hydroxyphenyl)prop-2-enoyl]-4-hydroxycoumarin (2f). Yield 95%, m.p. 199—201 °C. ^{1}H NMR (DMSO-d_6), δ: 1.37 (t, 3 H, $OCH_2C\underline{H}_3$, J = 6.9 Hz); 4,10 (q, 2 H, $OC\underline{H}_2CH_3$, J = 6.9 Hz); 6.87 (m, 1 H, H(14)); 7.08 (d, 1 H, H(13), J = 8.3 Hz); 7.22 (d, 1 H, H(15), J = 7.9 Hz); 7.43 (m, 2 H, H(6), H(8)); 7.81 (m, 1 H, H(7)); 8.04 (d, 1 H, H(5), J = 6.9 Hz); 8,35 (m, 2 H, H(9), H(10)); 9,48 (s, 1 H, OH(11)); 18,06 (s, 1 H, OH(4)). MS, m/z (I_{rel} (%)): 352 (90). Found (%): C, 68.35; H, 4.41. $C_{20}H_{16}O_6$. Calculated (%): C, 68.18; H, 4.55.

4-Hydroxy-3-[(*E*)-3-(4-hydroxy-2-methoxyphenyl)prop-2-enoyl]coumarin (2g). Yield 97%, m.p. 150—153 °C. ^{1}H NMR (DMSO-d_6), δ: 3.81 (s, 3 H, OCH_3); 6.87 (s, 1 H, H(12)); 7.05 (d, 1 H, H(14), J = 7.4 Hz); 7.22 (d, 1 H, H(15), J = 7.9 Hz); 7.41 (m, 2 H, H(6), H(8)); 7.80 (m, 1 H, H(7)); 8.04 (d, 1 H, H(4), J = 6.5 Hz); 8.33 (m, 2 H, H(9), H(10)); 9.64 (s, 1 H, OH(11)); 18.22 (s, 1 H, OH(4)). MS, m/z (I_{rel} (%)): 338 (93). Found (%): C, 67.29; H, 4.07. $C_{19}H_{14}O_6$. Calculated (%): C, 67.45; H, 4.14.

3-{(*E*)-3-[4-(*N*,*N*-Diethylamino)-2-hydroxyphenyl]prop-2-enoyl}-4-hydroxycoumarin (2h). Yield 92%, m.p. 194—196 °C. ^{1}H NMR (DMSO-d_6), δ: 1.10 (t, 6 H, 2 $CH_2C\underline{H}_3$, J = 6.9 Hz); 3.41 (q, 4 H, 2 $C\underline{H}_2CH_3$, J = 6.9 Hz); 6.25 (s, 1 H, H(12)); 6.46 (d, 1 H, H(14), J = 8.3 Hz); 7.41 (m, 3 H, H(6), H(8), H(15)); 7.76 (m, 1 H, H(7)); 8.02 (d, 1 H, H(5), J = 7.8 Hz); 8.11 (d, 1 H, H(10), J = 15.2 Hz); 8.40 (d, 1 H, H(9), J = 15.2 Hz); 10.53 (s, 1 H, OH(11)); 17.69 (s, 1 H, OH(4)). MS, m/z (I_{rel} (%)): 363 (95). Found (%): C, 72.21; H, 6.03; N, 3.71 $C_{22}H_{21}NO_4$. Calculated (%): C, 72.42; H, 5.91; N, 3.86.

4-Hydroxy-3-{(*E*)-3-[4-(7-hydroxyoctyl)phenyl]prop-2-enoyl}coumarin (2i). Yield 95%, m.p. 99—101 °C. ^{1}H NMR (DMSO-d_6), δ: 2.48 (m, 14 H, $CH_2C_7\underline{H}_{14}$); 4.06 (t, 2 H, $C\underline{H}_2C_7H_{14}$, J = 6.7 Hz); 7.07 (d, 2 H, H(12), H(14), J = 8.1 Hz); 7.41 (m, 2 H, H(6), H(8)); 7.76 (m, 3 H, H(7), H(11), H(15)); 8.09 (m, 3 H, H(5), H(9), H(10)); 9.12 (s, 1 H, OH); 18.61 (s, 1 H, OH(4)). MS, m/z (I_{rel} (%)): 420 (85). Found (%): C, 74.43; H, 6.77. $C_{26}H_{28}O_5$. Calculated (%): C, 74.29; H, 6.67.

4-Hydroxy-3-[(*E*)-3-(4-methoxyphenyl)prop-2-enoyl]coumarin (2j). Yield 96%, m.p. 185—186 °C (*cf.* Ref. 18: m.p. 184 °C).

3-[(*E*)-3-(2,4-Dimethoxyphenyl)prop-2-enoyl]-4-hydroxycoumarin (2k). Yield 98%, m.p. 143—144 °C (*cf.* Ref. 20: m.p. 143—144 °C).

3-{(*E*)-3-[4-(Dimethylamino)phenyl]prop-2-enoyl}-4-hydroxycoumarin (2l). Yield 97%, m.p. 214—215 °C (*cf.* Ref. 20: m.p. 212—215 °C).

4-Hydroxy-3-[(*E*)-3-(5-piperidino-2-thienyl)prop-2-enoyl]-coumarin (2m). Yield 98%, m.p. 225—227 °C. ^{1}H NMR (DMSO-d_6), δ: 1.73 (m, 6 H, H(14), H(15), H(16)); 3.58 (t, 4 H, H(13), H(17), J = 9.4 Hz); 6.57 (d, 1 H, H(12), J = 5.5 Hz); 7.36 (m, 3 H, H(6), H(8), H(11)); 7.70 (m, 2 H, H(7), H(10)); 7.98 (d, 1 H, H(5), J = 7.9 Hz); 8.22 (d, 1 H, H(9), J = 14.3 Hz); 18.65 (s, 1 H, OH). MS, m/z (I_{rel} (%)): 381 (75). Found (%): C, 66.02; H, 5.07; N, 3.79. $C_{21}H_{19}NO_4S$. Calculated (%): C, 66.14; H, 4.99; N, 3.67.

4-Hydroxy-3-[(*E*)-3-(5-morpholino-2-thienyl)prop-2-enoyl]-coumarin (2n). Yield 91%, m.p. 284—286 °C. ^{1}H NMR (DMSO-d_6), δ: 3.63 (m, 8 H, H(13), H(14), H(15), H(16)); 6.49 (d, 1 H, H(12), J = 4.6 Hz); 7.36 (m, 3 H, H(6), H(8), H(10)); 7.73 (m, 2 H, H(7), H(11)); 7.97 (d, 1 H, H(5), J = 6.9 Hz); 8.23 (d, 1 H, H(9), J = 14.8 Hz); 17.81 (s, 1 H, OH). MS, m/z (I_{rel} (%)): 383 (95). Found (%): C, 62.88; H, 4.28; N, 3.79. $C_{20}H_{17}NO_5S$. Calculated (%): C, 62.66; H, 4.44; N, 3.66.

4-Hydroxy-3-{(*E*)-3-[5-(*N*,*N*-dimethylamino)-2-thienyl]prop-2-enoyl}coumarin (2o). Yield 96%, m.p. 244—246 °C. ^{1}H NMR (DMSO-d_6), δ: 3.27 (s, 6 H, 2 CH_3); 6.43 (d, 1 H, H(12), J = 4.6 Hz); 7.37 (m, 3 H, H(6), H(8), H(10)); 7.72 (m, 2 H, H(7), H(11)); 7.98 (d, 1 H, H(5), J = 9.7 Hz); 8.23 (d, 1 H, H(9), J = 14.3 Hz); 18.87 (s, 1 H, OH). MS, m/z (I_{rel} (%)): 341 (85). Found (%): C, 63.51; H, 4.29; N, 4.16. $C_{18}H_{15}NO_4S$. Calculated (%): C, 63.34; H, 4.40; N, 4.11.

4-Hydroxy-3-[(*E*)-3-(5-pyrrolidino-2-thienyl)prop-2-enoyl]-coumarin (2p). Yield 98%, m.p. 225—227 °C. ^{1}H NMR (DMSO-d_6), δ: 2.13 (m, 4 H, H(13), H(16)); 3.44 (m, 4 H, H(14), H(15)); 5.91 (d, 1 H, H(12), J = 4.6 Hz); 7.16—7.38 (m, 3 H, H(6), H(8), H(11)); 7.62 (m, 2 H, H(7), H(10); 8.05 (d, 1 H, H(5), J = 6.5 Hz); 8.19 (d, 1 H, H(9), J = 15.2 Hz); 17.63 (s, 1 H, OH). MS, m/z (I_{rel} (%)): 367 (70). Found (%): C, 65.29; H, 4.58; N, 3.74. $C_{20}H_{17}NO_5S$. Calculated (%): C, 65.40; H, 4.63; N, 3.81.

3-[(*E*)-3-(1-Ethyl-1,2,3,4-tetrahydroquinolin-6-yl)prop-2-enoyl]-4-hydroxycoumarin (2q). Yield 96%, m.p. 194—196 °C. ^{1}H NMR (DMSO-d_6), δ: 1.20 (t, 3 H, $CH_2C\underline{H}_3$, $J \approx 7$ Hz); 1.98 (q, 2 H, $C\underline{H}_2CH_3$, $J \approx 7$ Hz); 2.79 (m, 2 H, H(13)); 3.41 (m, 4 H, H(12), H(14)); 6.58 (d, 1 H, H(15), J = 8.6 Hz); 7.29 (m, 2 H, H(11), H(16)); 7.44 (m, 2 H, H(6), H(8)); 7.63 (m, 1 H, H(7)); 8.12 (m, 3 H, H(5), H(9), H(10)); 18.75 (s, 1 H, OH). MS, m/z (I_{rel} (%)): 375 (85). Found (%): C, 73.48; H, 5.66; N, 3.79. $C_{23}H_{21}NO_5S$. Calculated (%): C, 73.60; H, 5.60; N, 3.73.

Synthesis of 4-hydroxy-3-pyrazolinylcoumarins 4 (general procedure). A 3—4-fold molar excess of phenylhydrazine hydrochloride and KOH (0.3 g) were added at reflux to a suspension of 3-cinnamoyl-4-hydroxycoumarin **2** (0.5 g) in isopropyl alcohol (30 mL). The mixture was refluxed for 1 h, cooled, and filtered. The resulting precipitate was recrystallized from alcohol.

4-Hydroxy-3-[5-(4-methoxyphenyl)-1-phenyl-4,5-dihydro-1*H*-pyrazol-3-yl]coumarin (4a). Yield 73%, m.p. 181—183 °C (*cf.* Ref. 15: m.p. 196 °C). ^{1}H NMR (DMSO-d_6), δ: 3.36 (dd, 1 H, H(9), J = 18.4 Hz, J = 6.9 Hz); 3.74 (s, 3 H, OCH_3); 4.18 (dd, 1 H, H(9), J = 18.4 Hz, J = 12.0 Hz); 5.35 (dd, 1 H, H(10), J = 6.9 Hz, J = 12.0); 6.81 (m, 1 H, H(18)); 6.87—6.93 (m, 4 H, H(11), H(12), H(14), H(15)); 7.24—7.30 (m, 4 H, H(16), H(17), H(19), H(20)); 7.41 (m, 2 H, H(6), H(8)); 7.69 (m, 1 H, H(7)); 7.99 (d, 1 H, H(5), J = 6.8 Hz); 14.10 (s, 1 H, OH). MS, m/z (I_{rel} (%)): 412 (95). Found (%): C, 72.69; H, 4.93; N, 6.22. $C_{25}H_{20}N_2O_4$. Calculated (%): C, 72.82; H, 4.85; N, 6.10.

4-Hydroxy-3-[5-(4-methoxyphenyl)-1-(4-fluorophenyl)-4,5-dihydro-1*H*-pyrazol-3-yl]coumarin (4b). Yield 78%, m.p. 204—206 °C. ^{1}H NMR (DMSO-d_6), δ: 3.38 (dd, 1 H, H(9), J = 18.9 Hz, J = 8.7 Hz); 3.71 (s, 3 H, OCH_3); 4.12 (dd, 1 H, H(9), J = 18.9 Hz, J = 12.3 Hz); 5.30 (dd, 1 H, H(10), J = 8.7 Hz, J = 12.30 Hz); 6.54—7.45 (m, 10 H, H(6), H(8), H(11), H(12), H(14), H(15), H(16), H(17), H(19), H(20)); 7.68 (m, 1 H, H(7)); 7.98 (d, 1 H, H(5), J = 7.0 Hz); 10.31 (s, 0.45 H, NH); 13.88 (s, 0.55 H, OH). MS, m/z (I_{rel} (%)): 430 (80). Found (%): C, 69.18; H, 4.23; N, 6.72. $C_{25}H_{19}FN_2O_4$. Calculated (%): C, 69.76; H, 4.45; N, 6.51.

4-Hydroxy-3-[5-(4-methoxyphenyl)-1-(4-tolyl)-4,5-dihydro-1*H*-pyrazol-3-yl]coumarin (4c). Yield 77%, m.p. 215—217 °C. ^{1}H NMR (DMSO-d_6), δ: 2.19 (s, 3 H, CH_3); 3.35 (dd, 1 H, H(9), J = 18.9 Hz, J = 8.2 Hz); 3.70 (s, 3 H, OCH_3); 4.13 (dd, 1 H, H(9), J = 18.9 Hz, J = 12.3 Hz); 5.36 (dd, 1 H, H(10), J = 8.0 Hz, J = 12.3 Hz); 6.84—6.92 (m, 4 H, H(11), H(12), H(14), H(15)); 7.06 (d, 2 H, H(17), H(19), J = 8.3 Hz); 7.27 (d, 2 H, H(16), H(20), J = 8.3 Hz); 7.44 (m, 2 H, H(6), H(8)); 7.69 (m, 1 H, H(7)); 7.98 (d, 1 H, H(5), J = 7.4 Hz); 14.05 (s, 1 H, OH). MS,

m/z (I_{rel} (%)): 426 (85). Found (%): C, 73.68; H, 5.43; N, 6.39. $C_{26}H_{22}N_2O_4$. Calculated (%): C, 73.23; H, 5.20; N, 6.57.

4-Hydroxy-3-[1,5-di(4-methoxyphenyl)-4,5-dihydro-1*H*-pyrazol-3-yl]coumarin (4d). Yield 79%, m.p. 199—201 °C. ^{1}H NMR (DMSO-d_6), δ: 3.37 (dd, 1 H, H(9), J = 18.9 Hz, J = 9.7 Hz); 3.68, 3.72 (both s, 3 H each, OCH_3); 4.13 (dd, 1 H, H(9), J = 18.9 Hz, J = 11.7 Hz); 5.21 (dd, 1 H, H(10), J = 9.7 Hz, J = 11.78 Hz); 6.86 (m, 6 H, H(11), H(12), H(14), H(15), H(17), H(19)); 7.38 (m, 4 H, H(6), H(8), H(16), H(20)); 7.69 (m, 1 H, H(7)); 7.98 (d, 1 H, H(5), J = 8.2 Hz); 13.86 (s, 1 H, OH). MS, *m/z* (I_{rel} (%)): 442 (95). Found (%): C, 71.01; H, 5.13; N, 6.18. $C_{26}H_{22}N_2O_5$. Calculated (%): C, 70.58; H, 5.01; N, 6.33.

4-Hydroxy-3-[5-(4-methoxyphenyl)-1-(4-nitrophenyl)-4,5-dihydro-1*H*-pyrazol-3-yl]coumarin (4e). Yield 72%, m.p. 261—263 °C. ^{1}H NMR (DMSO-d_6), δ: 3.43 (dd, 1 H, H(9), J = 19.4 Hz, J = 6.1 Hz); 3.63 (s, 3 H, OCH_3); 4.18 (dd, 1 H, H(9), J = 19.4 Hz, J = 11.7 Hz); 5.15 (dd, 1 H, H(10), J = 6.1 Hz, J = 11.7 Hz); 6.94—7.26 (m, 6 H, H(11), H(12), H(14), H(15), H(16), H(20)); 7.48 (m, 2 H, H(6), H(8)); 7.71 (m, 1 H, H(7)); 8.08—8.14 (m, 3 H, H(5), H(17), H(19)); 13.82 (s, 1 H, OH). MS, *m/z* (I_{rel} (%)): 457 (90). Found (%): C, 65.32; H, 4.29; N, 9.31. $C_{25}H_{19}N_3O_6$. Calculated (%): C, 65.64; H, 4.19; N, 9.19.

3-[5-(2,4-Dimethoxyphenyl)-1-phenyl-4,5-dihydro-1*H*-pyrazol-3-yl]-4-hydroxycoumarin (4f). Yield 61%, m.p. 202—203 °C (*cf.* Ref. 15: m.p. 218 °C). ^{1}H NMR (DMSO-d_6), δ: 3.30 (dd, 1 H, H(9), J = 18.8 Hz, J = 6.7 Hz); 3.75, 3.90 (both s, 3 H each, OCH_3); 4.15 (dd, 1 H, H(9), J = 18.8 Hz, J = 12.4 Hz); 5.40 (dd, 1 H, H(10), J = 6.7 Hz, J = 12.4 Hz); 6.30 (d, 1 H, H(12), J = 7.8 Hz); 6.52 (s, 1 H, H(14)); 6.80 (m, 3 H, H(16), H(17), H(19)); 6.90 (d, 1 H, H(11), J = 7.8 Hz); 7.16 (m, 2 H, H(16), H(20)); 7.30 (m, 2 H, H(6), H(8)); 7.60 (m, 1 H, H(7)); 7.94 (d, 1 H, H(5), J = 6.8 Hz); 13.95 (s, 1 H, OH). MS, *m/z* (I_{rel} (%)): 442 (90). Found (%): C, 70.52; H, 5.06; N, 6.28. $C_{26}H_{22}N_2O_5$. Calculated (%): C, 70.58; H, 5.01; N, 6.33.

3-[5-(2,4-Dimethoxyphenyl)-1-(4-fluorophenyl)-4,5-dihydro-1*H*-pyrazol-3-yl]-4-hydroxycoumarin (4g). Yield 74%, m.p. >350 °C. ^{1}H NMR (DMSO-d_6), δ: 3.63 (dd, 1 H, H(9), J = 18.4 Hz, J = 12.4 Hz); 3.74, 3.85 (both s, 3 H each, OCH_3); 4.07 (dd, 1 H, H(9), J = 18.4 Hz, J = 6.4 Hz); 5.45 (dd, 1 H, H(10), J = 6.4 Hz, J = 12.4 Hz); 6.46 (d, 1 H, H(12), J = 8.3 Hz); 6.63 (s, 1 H, H(14)); 6.73—7.11 (m, 5 H, H(11), H(16), H(17), H(19), H(20)); 7.44 (m, 2 H, H(6), H(8)); 7.71 (m, 1 H, H(7)); 8.00 (d, 1 H, H(5), J = 7.4 Hz); 14.18 (s, 1 H, OH). MS, *m/z* (I_{rel} (%)): 460 (73). Found (%): C, 67.61; H, 4.73; N, 6.19. $C_{26}H_{21}FN_2O_5$. Calculated (%): C, 67.82; H, 4.60; N, 6.08.

3-[5-(2,4-Dimethoxyphenyl)-1-(4-tolyl)-4,5-dihydro-1*H*-pyrazol-3-yl]-4-hydroxycoumarin (4h). Yield 75%, m.p. >350 °C. ^{1}H NMR (DMSO-d_6), δ: 2.17 (s, 3 H, CH_3); 3.39 (dd, 1 H, H(9), J = 18.9 Hz, J = 7.7 Hz); 3.71, 3.78 (both s, 3 H each, OCH_3); 4.09 (dd, 1 H, H(9), J = 18.9 Hz, J = 12.3 Hz); 5.46 (dd, 1 H, H(10), J = 7.7 Hz, J = 12.3 Hz); 6.41 (d, 1 H, H(12), J = 8.5 Hz); 6.65 (s, 1 H, H(14)); 6.77 (d, 1 H, H(11), J = 8.5 Hz); 7.02—7.14 (m, 4 H, H(16), H(17), H(19), H(20)); 7.46 (m, 2 H, H(6), H(8)); 7.71 (m, 1 H, H(7)); 8.01 (d, 1 H, H(5), J = 7.9 Hz); 14.27 (s, 1 H, OH). MS, *m/z* (I_{rel} (%)): 456 (75). Found (%): C, 71.22; H, 5.49; N, 6.21. $C_{27}H_{24}N_2O_5$. Calculated (%): C, 71.04; H, 5.30; N, 6.14.

3-[5-(2,4-Dimethoxyphenyl)-1-(4-nitrophenyl)-4,5-dihydro-1*H*-pyrazol-3-yl]-4-hydroxycoumarin (4i). Yield 71%, m.p. 225—227 °C. ^{1}H NMR (DMSO-d_6), δ: 3.61 (dd, 1 H, H(9), J = 19.48 Hz, J = 5.64 Hz); 3.75, 3.88 (both s, 3 H each, OCH_3); 4.20 (dd, 1 H, H(9), J = 19.4 Hz, J = 11.8 Hz); 4.58 (dd, 1 H, H(10), J = 5.6 Hz, J = 11.8 Hz); 6.36 (d, 1 H, H(12), J = 8.2 Hz); 6.50 (s, 1 H, H(14)); 6.84 (d, 2 H, H(16), H(20), J = 9.0 Hz); 7.35—7.44 (m, 3 H, H(6), H(8), H(11)); 7.57 (m, 1 H, H(7)); 8.06—8.15 (m, 3 H, H(5), H(17), H(19)); 13.60 (s, 1 H, OH). MS, *m/z* (I_{rel} (%)): 487 (80). Found (%): C, 64.24; H, 4.18; N, 8.53. $C_{26}H_{21}N_3O_7$. Calculated (%): C, 64.06; H, 4.34; N, 8.62.

3-{5-[4-(*N*,*N*-Dimethylamino)phenyl]-1-phenyl-4,5-dihydro-1*H*-pyrazol-3-yl}-4-hydroxycoumarin (4j). Yield 54%, m.p. 229—231 °C. ^{1}H NMR (DMSO-d_6), δ: 2.93 (s, 6 H, $(CH_3)_2$); 3.57 (dd, 1 H, H(9), J_{gem} = 18.96 Hz, J_{vic} = 6.28 Hz); 4.19 (dd, 1 H, H(9), J_{gem} = 18.96 Hz, J_{vic} = 12.30 Hz); 5.12 (dd, 1 H, H(10), J_{cis} = 6.28 Hz, J_{trans} = 12.30 Hz); 6.68 (d, 2 H, H(12), H(14), J = 8.41 Hz); 6.85 (m, 1 H, H(18)); 6.96 (m, 2 H, H(17), H(19)); 7.13—7.25 (m, 4 H, H(11), H(15), H(16), H(20)); 7.30 (m, 2 H, H(6), H(8)); 7.56 (m, 1 H, H(7)); 8.02 (d, 1 H, H(5), J = 7.32 Hz); 14.11 (s, 1 H, OH). MS, *m/z* (I_{rel} (%)): 425 (100). Found (%): C, 73.38; H, 5.48; N, 9.82. $C_{26}H_{23}N_3O_3$. Calculated (%): C, 73.40; H, 5.45; N, 9.88.

3-{5-[4-(*N*,*N*-Dimethylamino)phenyl]-1-(4-fluorophenyl)-4,5-dihydro-1*H*-pyrazol-3-yl}-4-hydroxycoumarin (4k). Yield 74%, m.p. >350 °C. ^{1}H NMR (DMSO-d_6), δ: 2.54 (s, 6 H, 2 CH_3); 3.03 (dd, 1 H, H(9), J = 18.9 Hz, J = 8.7 Hz); 4.05 (dd, 1 H, H(9), J = 18.9 Hz, J = 12.3 Hz); 5.23 (dd, 1 H, H(10), J = 8.7 Hz, J = 12.3 Hz); 6.68 (d, 2 H, H(12), H(14), J = 8.3 Hz); 6.84—7.06 (m, 6 H, H(11), H(15), H(16), H(17), H(19), H(20)); 7.42 (m, 2 H, H(6), H(8)); 7.69 (m, 1 H, H(7)); 7,98 (d, 1 H, H(5), J = 6.4 Hz); 14.47 (s, 1 H, OH). MS, *m/z* (I_{rel} (%)): 443 (65). Found (%): C, 70.21; H, 5.09; N, 9.31. $C_{26}H_{22}FN_3O_3$. Calculated (%): C, 70.42; H, 5.00; N, 9.48.

3-{5-[4-(*N*,*N*-Dimethylamino)phenyl]-1-(4-methoxyphenyl)-4,5-dihydro-1*H*-pyrazol-3-yl}-4-hydroxycoumarin (4l). Yield 77%, m.p. 175—177 °C. ^{1}H NMR (DMSO-d_6), δ: 2.91 (s, 6 H, 2 CH_3); 3.35 (dd, 1 H, H(9), J = 18.9 Hz, J = 9.2 Hz); 3.62 (s, 3 H, OCH_3); 4.12 (dd, 1 H, H(9), J = 18.9 Hz, J = 11.7 Hz); 5.11 (dd, 1 H, H(10), J = 9.2 Hz, J = 11.7 Hz); 6.63—6.92 (m, 6 H, H(11), H(12), H(14), H(15), H(17), H(19)); 7.17 (d, 2 H, H(16), H(20), J = 9.3 Hz); 7.38 (m, 2 H, H(6), H(8)); 7.65 (m, 1 H, H(7)); 7.96 (d, 1 H, H(5), J = 7.3 Hz); 14.06 (s, 1 H, OH). MS, *m/z* (I_{rel} (%)): 455 (65). Found (%): C, 71.40; H, 5.39; N, 9.12. $C_{27}H_{25}N_3O_4$. Calculated (%): C, 71.19; H, 5.53; N, 9.22.

3-[5-(Benzothiazol-2-yl)-1-(4-methoxyphenyl)-4,5-dihydro-1*H*-pyrazol-3-yl]-4-hydroxycoumarin (4m). Yield 79%, m.p. 241—243 °C. ^{1}H NMR (DMSO-d_6), δ: 3.47 (dd, 1 H, H(9), J = 18.8 Hz, J = 12.4 Hz); 3.69 (s, 3 H, OCH_3); 4.22 (dd, 1 H, H(9), J = 18.8 Hz, J = 6.7 Hz); 5.69 (dd, 1 H, H(10), J = 6.7 Hz, J = 12.4 Hz); 6.88 (d, 2 H, H(12), H(14), J = 8.3 Hz); 7.13 (m, 1 H, H(17)); 7.31 (m, 3 H, H(11), H(15), H(19)); 7.46 (m, 3 H, H(6), H(8), H(18)); 7.76 (m, 1 H, H(7)); 7.82 (d, 1 H, H(16), J = 7.8 Hz); 8.02 (d, 1 H, H(5), J = 7.8 Hz). MS, *m/z* (I_{rel} (%)): 469 (70). Found (%): C, 66.21; H, 4.14; N, 8.69. $C_{26}H_{19}N_3O_4S$. Calculated (%): C, 66.52; H, 4.05; N, 8.96.

3-[5-(Benzothiazol-2-yl)-1-(2,4-dimethoxyphenyl)-4,5-dihydro-1*H*-pyrazol-3-yl]-4-hydroxycoumarin (4n). Yield 74%, m.p. 225—227 °C. ^{1}H NMR (DMSO-d_6), δ: 3.39 (dd, 1 H, H(9), J = 18.9 Hz, J = 12.4 Hz); 3.68, 3.82 (both s, 3 H each, OCH_3); 4.11 (dd, 1 H, H(9), J = 18.9 Hz, J = 6.3 Hz); 5.71 (dd, 1 H, H(10), J = 6.3 Hz, J = 12.4 Hz); 6.45 (d, 1 H, H(12), J = 8.2 Hz); 6.64 (s, 1 H, H(14)); 6.97 (d, 1 H, H(11), J = 8.2 Hz); 7.12 (m, 1 H, H(17)); 7.25 (m, 1 H, H(18)); 7.43 (m, 3 H, H(6), H(8), H(19)); 7.67 (m, 1 H, H(7)); 7.84 (d, 1 H, H(16), J = 7.9); 8.01 (d, 1 H, H(5), J = 8.2 Hz). MS, *m/z* (I_{rel} (%)): 487 (85). Found (%):

C, 64.33; H, 4.14; N, 8.49. $C_{26}H_{21}N_3O_5S$. Calculated (%): C, 64.06; H, 4.31; N, 8.62.

Synthesis of 4-hydroxy-3-pyrazolinyl-2-quinolones 6. ***A.*** 3-cinnamoyl-4-hydroxy-2-quinolone **5a** (0.5 g) was dissolved on heating in acetic acid (30 mL), and a 3—4-fold molar excess of phenylhydrazine was added to the resulting solution. The mixture was refluxed for 30 min. After cooling, the precipitate was filtered off and recrystallized from alcohol.

4-Hydroxy-3-[5-(4-methoxyphenyl)-1-phenyl-4,5-dihydro-1*H*-pyrazol-3-yl]-1-methylquinolin-2-(1*H*)-one (6a). Yield 87%, m.p. 198—199 °C. ^{1}H NMR ($CDCl_3$), δ: 3.65 (m, 4 H, NMe, H(9)); 3.72 (s, 3 H, OCH_3); 4.27 (dd, 1 H, H(9), J = 18.5 Hz, J = 12.0 Hz); 5.18 (dd, 1 H, H(10), J = 7.5 Hz, J = 12.0 Hz); 6.82—6.90 (m, 3 H, H(12), H(14), H(18)); 6.96 (m, 2 H, H(11), H(15)); 7.20—7.36 (m, 6 H, H(6), H(8), H(16), H(17), H(20), H(21)); 7.62 (m, 1 H, H(7)); 8.22 (d, 1 H, H(5), J = 7.9 Hz); 13.70 (s, 1 H, OH). MS, m/z (I_{rel} (%)): 425 (90). Found (%): C, 73.29; H, 5.34; N, 9.94. $C_{26}H_{23}N_3O_3$. Calculated (%): C, 73.40; H, 5.45; N, 9.88.

B. A 3—4-fold molar excess of phenylhydrazine hydrochloride and KOH (0.3 g) were added at reflux to a suspension of 3-cinnamoyl-4-hydroxy-2-quinolone **5a,b** (0.5 g) in isopropyl alcohol (30 mL) and the mixture was refluxed for 1 h. After cooling, the reaction mixture was filtered off. The resulting precipitate was recrystallized from alcohol.

4-Hydroxy-3-[5-(4-methoxyphenyl)-1-(4-fluorophenyl)-4,5-dihydro-1*H*-pyrazol-3-yl]-1-methylquinolin-2(1*H*)-one (6b). Yield 79%, m.p. 207—208 °C. ^{1}H NMR ($CDCl_3$), δ: 3.60 (m, 4 H, NMe, H(9)); 3.78 (s, 3 H, OCH_3); 4.23 (dd, 1 H, H(9), J = 18.7 Hz, J = 12.1 Hz); 5.06 (dd, 1 H, H(10), J = 8.0 Hz, J = 12.1 Hz); 6.80—7.48 (m, 10 H, H(6), H(8), H(11), H(12), H(14), H(15), H(16), H(17), H(19), H(20)); 7.48 (m, 1 H, H(7)); 8.20 (d, 1 H, H(5), J = 8.0 Hz); 13.60 (s, 1 H, OH). MS, m/z (I_{rel} (%)): 443 (85). Found (%): C, 70.34; H, 4.92; N, 9.36. $C_{26}H_{22}FN_3O_3$. Calculated (%): C, 70.42; H, 5.00; N, 9.48.

3-[1,5-Bis(4-methoxyphenyl)-4,5-dihydro-1*H*-pyrazol-3-yl]-4-hydroxy-1-methylquinolin-2(1*H*)-one (6c). Yield 74%, m.p. 176—177 °C. ^{1}H NMR ($CDCl_3$)б δ: 3.52 (m, 4 H, NMe, H(9)); 3.70 (m, 6 H, OCH_3); 4.30 (dd, 1 H, H(9), J = 18.4 Hz, J = 12.0 Hz); 5.06 (dd, 1 H, H(10), J = 8.6 Hz, J = 11.6 Hz); 6.70—7.06 (m, 10 H, H(6), H(8), H(11), H(12), H(14), H(15), H(16), H(17), H(19), H(20)); 7.62 (m, 1 H, H(7)); 8.14 (d, 1 H, H(5), J = 8.2 Hz); 13.70 (s, 1 H, OH). MS, m/z (I_{rel} (%)): 455 (90). Found (%): C, 71.08; H, 5.47; N, 9.20. $C_{27}H_{25}N_3O_4$. Calculated (%): C, 71.19; H, 5.53; N, 9.22.

{1-(4-Fluorophenyl)-3-[5-(5-morpholino-2-thienyl)]-4,5-dihydro-1*H*-pyrazol-3-yl}-4-hydroxy-1-methylquinolin-2(1*H*)-one (6d). Yield 85%, m.p. 190—191 °C. ^{1}H NMR ($CDCl_3$), δ: 3.02 (m, 4 H, H(14), H(15)); 3.60 (s, 3 H, NMe, H(9)); 3.70—3.86 (m, 5 H, H(9), H(13), H(16)); 4.15 (dd, 1 H, H(9), J = 18.0 Hz, J = 11.8 Hz); 5.08 (dd, 1 H, H(10), J = 8.2 Hz, J = 12.0 Hz); 5.95 (d, 1 H, H(12), J = 3.1 Hz); 6.70 (d, 1 H, H(11), J = 3.1 Hz); 6.82 (m, 4 H, H(17), H(18), H(20), H(21)); 7.25—7.32 (m, 2 H, H(6), H(8)); 7.60 (m, 1 H, H(7)); 8.15 (d, 1 H, H(5), J = 8.0 Hz); 13.55 (s, 1 H, OH). MS, m/z (I_{rel} (%)): 504 (95). Found (%): C, 64.15; H, 5.02; N, 11.19. $C_{27}H_{25}FN_4O_3S$. Calculated (%): C, 64.27; H, 4.99; N, 11.10.

4-Hydroxy-3-[1-(4-methoxyphenyl)-5-(5-morpholino-2-thienyl)-4,5-dihydro-1*H*-pyrazol-3-yl]-1-methylquinolin-2(1*H*)-one (6e). Yield 82%, m.p. 186—187 °C. ^{1}H NMR ($CDCl_3$), δ: 3.10 (m, 4 H, H(14), H(15)); 3.62 (s, 3 H, NMe); 3.72—3.90 (m, 8 H, OMe, H(9), H(13), H(16)); 4.20 (dd, 1 H, H(9), J = 17.8 Hz, J = 11.6 Hz); 5.12 (dd, 1 H, H(10), J = 8.3 Hz, J = 11.8 Hz); 5.95 (d, 1 H, H(12), J = 2.8 Hz); 6.70 (d, 1 H, H(11), J = 2.8 Hz); 6.82 (d, 2 H, H(18), H(20), J = 8.0 Hz); 7.05 (d, 2 H, H(17), H(21), J = 8.0); 7.26—7.35 (m, 2 H, H(6), H(8)); 7.60 (m, 1 H, H(7)); 8.18 (d, 1 H, H(5), J = 7.6 Hz); 13.72 (s, 1 H, OH). MS, m/z (I_{rel} (%)): 516 (85). Found (%): C, 65.21; H, 5.39; N, 10.77. $C_{28}H_{28}N_4O_4S$. Calculated (%): C, 65.10; H, 5.46; N, 10.84.

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