

Schiff Bases Derived from 6-Amino-2*H*-chromen-2-one. Synthesis and ¹H NMR Spectra

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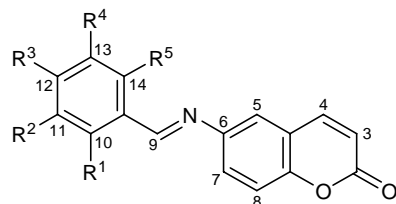
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Abstract—A number of 6-arylmethylideneamino-2*H*-chromen-2-ones were synthesized by reaction of 6-amino-2*H*-chromen-2-one with aromatic and heterocyclic aldehydes. A linear relation was revealed between the chemical shifts of the azomethine CH=N proton and protons in the chromene ring, on the one hand, and Hammett constants σ of the *para* substituents, on the other. Formation of intramolecular hydrogen bond in *ortho*-hydroxy derivatives induces a downfield shift of signals from protons in positions 3–5, 7, and 8 and CH=N proton (9-H) and upfield shift of the *o*-H signal (14-H).

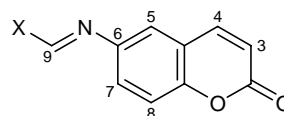
Compounds of the coumarin series are fluorescent dyes and materials for dye lasers [1–4]. These compounds include *N*-arylmethylidene derivatives (Schiff bases) of 6-amino-2*H*-chromen-2-one, which were reported by us previously [5]. In order to study in detail their spectral parameters with regard to the nature of substituent in the arylmethylidene fragment, we have synthesized a number of new Schiff bases belonging to this series.

Compounds **I–XXXVIII** were obtained by condensation of the corresponding aldehydes with 6-amino-2*H*-chromen-2-one in anhydrous alcohol or dioxane in the presence of a catalytic amount of piperidine on heating for 6 h under reflux. 6-Arylmethylideneamino-2*H*-chromen-2-ones **I–XXXII** were synthesized from

substituted benzaldehydes, and Schiff bases **XXXIII–XXXVIII**, from polycyclic and heterocyclic aldehydes. The products were isolated and purified by standard procedures. They were yellow to orange crystalline substances. The structure of compounds **I–XXXVIII** was confirmed by the ¹H NMR spectra (see Experimental), and physical constants of previously described compounds **II**, **III**, **X**, and **XV** coincided with published data [5–7]. The ¹H NMR spectra of the newly synthesized compounds were recorded from 0.08 M solutions in DMSO-*d*₆ at 25°C. It seemed to be reasonable to compare their spectral parameters (i.e., chemical shifts and coupling constants) and correlate these parameters with their structure, specifically with the nature of R¹–R⁵ substituents in the phenyl ring.



I–XXXII



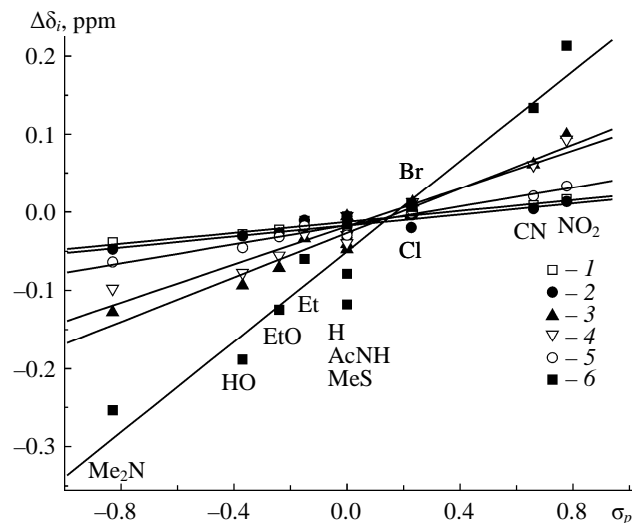
XXXIII–XXXVII

I, R³ = Et₂N; **II**, R³ = Me₂N; **III**, R³ = HO; **IV**, R³ = EtO; **V**, R³ = MeS; **VI**, R³ = Et; **VII**, R³ = AcNH; **VIII**, R³ = 5-carboxy-1-methylpyrazol-3-yl; **IX**, R³ = BzO; **X**, R³ = H; **XI**, R³ = Cl; **XII**, R³ = Br; **XIII**, R³ = CN; **XIV**, R³ = O₂N; **XV**, R¹ = HO; **XVI**, R¹ = EtO; **XVII**, R¹ = F; **XVIII**, R¹ = Cl; **XIX**, R¹ = O₂N; **XX**, R¹ = R³ = Me; **XXI**, R² = R³ = R⁴ = MeO; **XXII**, R² = MeO, R³ = HO; **XXIII**, R² = MeO, R³ = PrO; **XXIV**, R² = MeO, R³ = BzO; **XXV**, R² = MeO, R³ = *p*-FBzO; **XXVI**, R¹ = MeO, R⁴ = Br; **XXVII**, R¹ = HO, R² = R⁴ = Cl; **XXVIII**, R² = O₂N; **XXIX**, R² = O₂N, R³ = Cl; **XXX**, R¹ = Cl, R⁴ = O₂N; **XXXI**, R¹ = F, R⁵ = Cl; **XXXII**, R² = MeO, R³ = 5-carboxy-1-methylpyrazol-3-yl; **XXXIII**, X = 2-hydroxy-1-naphthyl; **XXXIV**, X = 9-anthryl; **XXXV**, X = 3-pyridyl; **XXXVI**, X = 2-hydroxy-6-methylquinolin-3-yl; **XXXVII**, X = 2-methylindol-3-yl; **XXXVIII**, X = 1,2-dimethylindol-3-yl; Rⁱ = H unless otherwise stated.

In our belief, the most interesting series are *para*-substituted compounds **I–XIV** ($R^3 \neq H$) and *ortho*-substituted 6-arylmethylideneamino-2*H*-chromen-2-ones **XV–XIX** ($R^1 \neq H$). For these compounds we examined the effect of the corresponding substituent (R^3 or R^1) on the chemical shifts δ_i of protons in the coumarin fragment ($i = 3–5, 7, 8$) and proton at the azomethine bond (9-H, $i = 9$). We previously showed [8] that the effect of a substituent on the chemical shifts of remote protons may be appreciable even at a distance of 15 interatomic bonds. Our data indicate that the chemical shifts δ_i of each of the six examined protons ($i = 3–5, 7–9$) correlate with electronic properties of the R^3 substituent. For the sake of convenience, we shall consider the difference $\Delta\delta_i$ between the chemical shifts of the i th proton in compounds with $R^3 \neq H$ and the same proton in benzaldehyde derivative **X** ($R^3 = H$). It is seen that the shorter the distance between H^i and R^3 , the stronger the effect of the latter on $\Delta\delta_i$. As expected, the largest $\Delta\delta_i$ values are observed for the nearest 9-H proton, and the smallest (lower by an order of magnitude), for the most distant 3-H proton. The $\Delta\delta_i$ values for 4-H, 5-H, 7-H, and 8-H occupy an intermediate place between $\Delta\delta_3$ and $\Delta\delta_9$.

We anticipated the existence of a correlation between $\Delta\delta_i$ and Hammett substituent constants σ_p . These correlations are shown in figure (σ_p values were taken from [9]). It is seen that $\Delta\delta_i$ is linearly related to σ_p for each i th proton in the series of *para*-substituted compounds **II–VII** and **X–XIV**; the correlation coefficients R for 5-H, 7-H, 8-H, and 9-H are equal to 0.97, and for 3-H and 4-H, to 0.93 and 0.89, respectively. We can conclude that the chemical shifts δ_i of 3-H–5-H and 7-H–9-H are linear in the donor–acceptor power of the *para*-substituent (R^3), which is characterized by the Hammett constant σ_p . The slope (b) of the straight lines in figure can be regarded as the parameter ρ in the Hammett equation. It reflects the sensitivity of each particular proton to the effect of the R^3 substituent. The coefficient b in the linear regression $y = a + bx$ ($y = \Delta\delta_i$, $x = \sigma_p$, a and b are coefficients) is minimal for the most distant protons, 3-H and 4-H ($b = 0.035$), while the correlation for 9-H is characterized by the maximal value of b (0.289). The values of b for 5-H, 7-H, and 8-H are 0.142, 0.122, and 0.061, respectively.

We compared the δ_i values for *ortho*-substituted Schiff bases **XV–XIX** with those found for their analogs having the same substituent in the *para* position ($R^1 = R^3$). It is known that most substituents located in the *ortho* and *para* positions (R^1_o and R^3_p) with respect to a reaction center exert similar effects on the



Correlations between the differences in the chemical shifts $\Delta\delta_i$ of substituted and unsubstituted Schiff bases and Hammett constants σ_p for 6-arylmethylideneamino-2*H*-chromen-2-ones **II–VII** and **X–XIV**: (1) $\Delta\delta_3$, (2) $\Delta\delta_4$, (3) $\Delta\delta_5$, (4) $\Delta\delta_7$, (5) $\Delta\delta_8$, (6) $\Delta\delta_9$.

latter (in our case, on δ_i). Here, the larger the distance from the reaction center (in our case, i -H) to R , the more similar the above effects [10]. In fact, as follows from the data for compounds **IV** and **XVI** ($R = EtO$), **XI** and **XVIII** ($R = Cl$), and **XIV** and **XIX** ($R = NO_2$), $\Delta\delta_o$ and $\Delta\delta_p$ are approximately equal for the most distant protons, 8-H and especially 3-H: the difference does not exceed 0.025 ppm. The difference $\Delta\delta_{o,p}$ for 4-H, 5-H, and 7-H is larger; it ranges from 0.03 to 0.06 ppm. The $\Delta\delta_{o,p}$ values for 5-H and 7-H (which are located most closely to R^1 or R^3), are negative for **IV/XVI** and **XIV/XIX** and maximal in absolute value, while the corresponding values for more distant 3-H, 4-H, and 8-H protons are positive and minimal. The difference $\Delta\delta_{o,p}^o$ is greater by an order of magnitude (0.09 to 0.37 ppm) and is positive. These data suggest a direct effect of the *ortho* substituent on the nearby 9-H proton.

A specific series consists of *ortho*-hydroxy Schiff bases **XV**, **XXVII**, and **XXXIII**. In the 1H NMR spectra of these compounds, the 5-H and 7-H signals are displaced upfield to a considerable extent (δ 7.7–7.8 ppm). On the other hand, the 14-H signal in the spectra of **XV** and **XXVII** appears strongly upfield, as compared to all other *ortho*- and polysubstituted compounds where $R^1 \neq OH$. The 9-H signal of *ortho*-hydroxy derivatives **XV** and **XXVII** is displaced downfield relative to the corresponding signals of the other *ortho*-substituted compounds where $R^1 \neq OH$. Signals from the more distant 3-H, 4-H, and 8-H

protons in *ortho*-hydroxy compounds **XV**, **XXVII**, and **XXXIII** are also displaced downfield relative to the signals from analogous protons in *para*-hydroxy derivative **III**, and the difference $\Delta\delta_{o-p}$ is 0.03–0.05 ppm. Thus for the pair of hydroxy derivatives **III** and **XV** all $\Delta\delta_{o-p}$ values are greater than those for the pairs with other substituents R^1 and R^3 (EtO, Cl, NO_2). A possible reason is formation of intramolecular hydrogen bond $\text{O-H}\cdots\text{H}$ which induces, on the one hand, downfield shift of the 3-H–5-H and 7-H–9-H signals (as well as of the OH signal to δ 12.8–15.5 ppm) and, on the other, upfield shift of the *ortho*-proton signal (14-H). Presumably, just the formation of H-chelate ring is responsible for the above displacement of the 3-H–9-H signals in the spectra of *ortho*-hydroxy-substituted Schiff bases **XV**, **XXVII**, **XXXIII**. The ^1H NMR spectra of Schiff bases **XXXIII**–**XXXVIII** derived from polycyclic and heterocyclic aldehydes are characterized by upfield (**XXXVII**, **XXXVIII**; δ_3 6.40–6.41, δ_4 7.97–7.98 ppm) or downfield shift of the 3-H and 4-H signals (**XXXIV**; δ_3 6.49, δ_4 8.09 ppm).

As concerns proton–proton coupling constants in compounds **I**–**XXXVIII**, a fairly strong interaction between 5-H and 7-H in the coumarin fragment should be noted for all the examined compounds. The $^4J_{5,7}$ values range from 1.1 Hz for compound **VI** to 2.5 Hz for **V** and **XXVII**; this parameter was used as a criterion for assignment of the corresponding signals in the ^1H NMR spectra of **I**–**XXXVIII**. The coupling constants between 3-H and 4-H ($^3J = 9.4, 9.9$ Hz) are generally larger than those between 7-H and 8-H ($^3J = 8.5, 9.0$ Hz). An exception is the coupling constant $^3J_{7,8} = 7.9$ Hz for compound **XIII**.

EXPERIMENTAL

The ^1H NMR spectra were recorded on a Bruker spectrometer operating at 400 MHz in a pulse mode; tetramethylsilane was used as internal reference, and $\text{DMSO}-d_6$, as solvent. The coupling constants were measured with an accuracy of ± 0.1 Hz (the data are given only for the coumarin fragment). The progress of reactions and the purity of products were monitored by TLC on Silufol UV-254 plates using benzene–acetone (10:1) as eluent; spots were visualized under UV light.

6-Arylmethylideneamino-2H-chromen-2-ones I–XXXVIII (general procedure). A mixture of 10 mmol of 6-amino-2H-chromen-2-one, 10 mmol of the corresponding aldehyde, and a few drops of piperidine in 50 ml of anhydrous ethanol was heated for 6 h under reflux. The mixture was cooled to room temperature

and left to stand for 12 h, and the precipitate was filtered off. An additional amount of the product can be isolated by evaporation of the mother liquor. The products were purified by recrystallization from ethanol (compounds **I–VI**), ethanol–DMF (1:1) (**XI**, **XII**, **XVII**, **XIX**, **XXII**), or DMF (**VII–X**, **XIII–XV**, **XX**, **XXI**, **XXIII**–**XXXVIII**) or by reprecipitation from ethanol with hexane (**XVI**, **XVIII**).

6-(4-Diethylaminobenzylideneamino)-2H-chromen-2-one (I). Yield 2.43 g (76%), mp 162–163°C. ^1H NMR spectrum, δ , ppm (J , Hz): 6.413 d (1H, 3-H, $^3J = 9.5$), 7.979 d (1H, 4-H, $^3J = 9.6$), 7.439 d (1H, 5-H, $^4J = 2.0$), 7.404 d.d (1H, 7-H, $^3J = 8.9$, $^4J = 2.0$), 7.320 d (1H, 8-H, $^3J = 8.7$), 8.357 s (1H, 9-H), 7.683 d (2H, 10-H, 14-H), 6.900 d (2H, 11-H, 13-H), 3.443 q (4H, 2CH_2), 1.174 t (6H, 2CH_3). Found, %: C 74.83; H 6.13; N 8.54. $\text{C}_{20}\text{H}_{20}\text{N}_2\text{O}_2$. Calculated, %: C 74.98; H 6.29; N 8.74.

6-(4-Dimethylaminobenzylideneamino)-2H-chromen-2-one (II). Yield 2.19 g (75%), mp 198–199°C. ^1H NMR spectrum, δ , ppm (J , Hz): 6.416 d (1H, 3-H, $^3J = 9.5$), 7.979 d (1H, 4-H, $^3J = 9.5$), 7.449 d (1H, 5-H, $^4J = 1.8$), 7.414 d.d (1H, 7-H, $^3J = 8.7$, $^4J = 1.8$), 7.326 d (1H, 8-H, $^3J = 8.6$), 8.388 s (1H, 9-H), 7.718 d (2H, 10-H, 14-H), 6.736 d (2H, 11-H, 13-H), 3.061 s (6H, 2CH_3).

6-(4-Hydroxybenzylideneamino)-2H-chromen-2-one (III). Yield 1.70 g (64%), mp 243–244°C. ^1H NMR spectrum, δ , ppm (J , Hz): 6.426 d (1H, 3-H, $^3J = 9.7$), 7.996 d (1H, 4-H, $^3J = 9.5$), 7.483 d (1H, 5-H, $^4J = 2.0$), 7.434 d.d (1H, 7-H, $^3J = 8.7$, $^4J = 2.1$), 7.344 d (1H, 8-H, $^3J = 8.6$), 8.453 s (1H, 9-H), 7.740 d (2H, 10-H, 14-H), 6.852 d (2H, 11-H, 13-H), 9.933 s (1H, OH).

6-(4-Ethoxybenzylideneamino)-2H-chromen-2-one (IV). Yield 1.96 g (67%), mp 195–196°C. ^1H NMR spectrum, δ , ppm (J , Hz): 6.432 d (1H, 3-H, $^3J = 9.8$), 8.000 d (1H, 4-H, $^3J = 9.6$), 7.505 d (1H, 5-H, $^4J = 2.3$), 7.456 d.d (1H, 7-H, $^3J = 8.6$, $^4J = 2.4$), 7.358 d (1H, 8-H, $^3J = 8.7$), 8.517 s (1H, 9-H), 7.852 d (2H, 10-H, 14-H), 6.988 d (2H, 11-H, 13-H), 4.121 q (2H, CH_2), 1.428 t (3H, CH_3). Found, %: C 73.59; H 4.93; N 4.52. $\text{C}_{18}\text{H}_{15}\text{NO}_3$. Calculated, %: C 73.71; H 5.15; N 4.78.

6-(4-Methylsulfanylbenzylideneamino)-2H-chromen-2-one (V). Yield 2.15 g (73%), mp 156–157°C. ^1H NMR spectrum, δ , ppm (J , Hz): 6.428 d (1H, 3-H, $^3J = 9.7$), 7.994 d (1H, 4-H, $^3J = 9.7$), 7.536 d (1H, 5-H, $^4J = 2.5$), 7.482 d.d (1H, 7-H, $^3J = 8.8$, $^4J = 2.5$), 7.362 d (1H, 8-H, $^3J = 8.8$), 8.563 s (1H, 9-H), 7.846 d

(2H, 10-H, 14-H), 7.316 d (2H, 11-H, 13-H), 2.547 s (3H, CH₃). Found, %: C 68.89; H 4.23; N 4.58; S 10.72. C₁₇H₁₃NO₂S. Calculated, %: C 69.13; H 4.44; N 4.74; S 10.86.

6-(4-Ethylbenzylideneamino)-2H-chromen-2-one (VI). Yield 1.94 g (70%), mp 168–169°C. ¹H NMR spectrum, δ, ppm (*J*, Hz): 6.443 d (1H, 3-H, ³*J* = 9.8), 8.016 d (1H, 4-H, ³*J* = 9.7), 7.543 d (1H, 5-H, ⁴*J* = 1.1), 7.483 d.d (1H, 7-H, ³*J* = 8.6, ⁴*J* = 1.4), 7.372 d (1H, 8-H, ³*J* = 8.9), 8.582 s (1H, 9-H), 7.837 d (2H, 10-H, 14-H), 7.321 d (2H, 11-H, 13-H), 2.714 q (2H, CH₂), 1.271 t (3H, CH₃). Found, %: C 77.72; H 5.28; N 4.87. C₁₈H₁₅NO₂. Calculated, %: C 77.96; H 5.45; N 5.05.

6-(4-Acetaminobenzylideneamino)-2H-chromen-2-one (VII). Yield 2.11 g (69%), mp 232–234°C. ¹H NMR spectrum, δ, ppm (*J*, Hz): 6.436 d (1H, 3-H, ³*J* = 9.5), 8.008 d (1H, 4-H, ³*J* = 9.5), 7.529 d (1H, 5-H, ⁴*J* = 2.0), 7.472 d.d (1H, 7-H, ³*J* = 8.8, ⁴*J* = 2.0), 7.360 d (1H, 8-H, ³*J* = 8.7), 8.524 s (1H, 9-H), 7.830 d (2H, 10-H, 14-H), 7.718 d (2H, 11-H, 13-H), 2.086 s (3H, CH₃), 10.088 s (1H, NH). Found, %: C 70.24; H 4.46; N 9.02. C₁₈H₁₄N₂O₃. Calculated, %: C 70.58; H 4.61; N 9.15.

6-[4-(5-Carboxy-1-methylpyrazol-3-yl)benzylideneamino]-2H-chromen-2-one (VIII). Yield 2.80 g (75%), mp 194–195°C. ¹H NMR spectrum, δ, ppm (*J*, Hz): 6.444 d (1H, 3-H, ³*J* = 9.6), 8.013 d (1H, 4-H, ³*J* = 9.6), 7.571 d (1H, 5-H, ⁴*J* = 2.0), 7.514 d.d (1H, 7-H, ³*J* = 8.7, ⁴*J* = 2.0), 7.381 d (1H, 8-H, ³*J* = 8.7), 8.673 s (1H, 9-H), 8.044 d (2H, 10-H, 14-H), 7.381 d (2H, 11-H, 13-H), 7.541 d (1H, 4-H, pyrazolyl), 7.073 d (1H, 5-H, pyrazolyl) 4.182 s (3H, CH₃). Found, %: C 67.35; H 3.87; N 11.03. C₂₁H₁₅N₃O₄. Calculated, %: C 67.56; H 4.05; N 11.25.

6-(4-Benzoyloxybenzylideneamino)-2H-chromen-2-one (IX). Yield 2.58 g (70%), mp 216–217°C. ¹H NMR spectrum, δ, ppm (*J*, Hz): 6.444 d (1H, 3-H, ³*J* = 9.6), 8.017 d (1H, 4-H, ³*J* = 9.6), 7.586 s (1H, 5-H), 7.519 d (1H, 7-H, ³*J* = 8.5), 7.389 m (1H, 8-H), 8.682 s (1H, 9-H), 8.052 d (2H, 10-H, 14-H), 7.389 d (2H, 11-H, 13-H), 8.168 d (2H, *o*-H), 7.586 d.d (2H, *m*-H) 7.719 t (1H, *p*-H). Found, %: C 74.63; H 3.88; N 3.58. C₂₃H₁₅NO₄. Calculated, %: C 74.79; H 4.09; N 3.79.

6-Benzylideneamino-2H-chromen-2-one (X). Yield 1.69 g (68%), mp 151–152°C. ¹H NMR spectrum, δ, ppm (*J*, Hz): 6.449 d (1H, 3-H, ³*J* = 9.5), 8.021 d (1H, 4-H, ³*J* = 9.8), 7.571 s (1H, 5-H, ⁴*J* = 2.3), 7.384 d (1H, 8-H, ³*J* = 8.7), 8.636 s (1H, 9-H),

7.952 d (2H, 10-H, 14-H), 7.520 m (4H, 7-H, 11-H, 12-H, 13-H).

6-(4-Chlorobenzylideneamino)-2H-chromen-2-one (XI). Yield 1.96 g (69%), mp 192–193°C. ¹H NMR spectrum, δ, ppm (*J*, Hz): 6.455 d (1H, 3-H, ³*J* = 9.5), 8.007 d (1H, 4-H, ³*J* = 9.5), 7.573 d (1H, 5-H, ⁴*J* = 2.3), 7.516 d.d (1H, 7-H, ³*J* = 8.8, ⁴*J* = 2.3), 7.388 d (1H, 8-H, ³*J* = 8.7), 8.653 s (1H, 9-H), 7.946 d (2H, 10-H, 14-H), 7.516 d (2H, 11-H, 13-H). Found, %: C 67.59; H 3.27; Cl 12.39; N 4.75. C₁₆H₁₀ClNO₂. Calculated, %: C 67.74; H 3.55; Cl 12.50; N 4.94.

6-(4-Bromobenzylideneamino)-2H-chromen-2-one (XII). Yield 2.36 g (72%), mp 188–189°C. ¹H NMR spectrum, δ, ppm (*J*, Hz): 6.454 d (1H, 3-H, ³*J* = 9.5), 8.023 d (1H, 4-H, ³*J* = 9.5), 7.589 d (1H, 5-H, ⁴*J* = 1.9), 7.524 d.d (1H, 7-H, ³*J* = 9.0, ⁴*J* = 1.9), 7.391 d (1H, 8-H, ³*J* = 9.0), 8.648 s (1H, 9-H), 7.881 d (2H, 10-H, 14-H), 7.668 d (2H, 11-H, 13-H). Found, %: C 58.38; H 2.87; Br 24.17; N 4.06. C₁₆H₁₀BrNO₂. Calculated, %: C 58.56; H 3.07; Br 24.35; N 4.27.

6-(4-Cyanobenzylideneamino)-2H-chromen-2-one (XIII). Yield 2.06 g (75%), mp 250–251°C. ¹H NMR spectrum, δ, ppm (*J*, Hz): 6.463 d (1H, 3-H, ³*J* = 9.5), 8.031 d (1H, 4-H, ³*J* = 9.5), 7.638 s (1H, 5-H), 7.572 d (1H, 7-H, ³*J* = 7.9), 7.410 d (1H, 8-H, ³*J* = 7.9), 8.775 s (1H, 9-H), 7.908 d (2H, 10-H, 14-H), 8.120 d (2H, 11-H, 13-H). Found, %: C 74.29; H 3.47; N 10.04. C₁₇H₁₀N₂O₂. Calculated, %: C 74.45; H 3.67; N 10.21.

6-(4-Nitrobenzylideneamino)-2H-chromen-2-one (XIV). Yield 2.23 g (76%), mp 242–243°C. ¹H NMR spectrum, δ, ppm (*J*, Hz): 6.471 d (1H, 3-H, ³*J* = 9.9), 8.040 d (1H, 4-H, ³*J* = 9.9), 7.676 c (1H, 5-H), 7.605 d (1H, 7-H, ³*J* = 9.4), 7.423 d (1H, 8-H, ³*J* = 9.4), 8.855 s (1H, 9-H), 8.205 d (2H, 10-H, 14-H), 8.348 d (2H, 11-H, 13-H). Found, %: C 65.13; H 3.21; N 9.39. C₁₆H₁₀N₂O₄. Calculated, %: C 65.31; H 3.43; N 9.52.

6-(2-Hydroxybenzylideneamino)-2H-chromen-2-one (XV). Yield 1.75 g (66%), mp 170–171°C. ¹H NMR spectrum, δ, ppm (*J*, Hz): 6.469 d (1H, 3-H, ³*J* = 9.5), 8.035 d (1H, 4-H, ³*J* = 9.5), 7.740 d (1H, 5-H, ⁴*J* = 2.3), 7.663 d.d (1H, 7-H, ³*J* = 8.8, ⁴*J* = 2.3), 7.427 d (1H, 8-H, ³*J* = 8.8), 8.964 s (1H, 9-H), 6.949 d (1H, 11-H), 7.383 d.d (1H, 12-H), 6.928 d.d (1H, 13-H), 7.605 d (1H, 14-H), 12.816 s (1H, OH).

6-(2-Ethoxybenzylideneamino)-2H-chromen-2-one (XVI). Yield 2.05 g (70%), mp 173–175°C. ¹H NMR spectrum, δ, ppm (*J*, Hz): 6.442 d (1H, 3-H, ³*J* = 9.7), 8.029 d (1H, 4-H, ³*J* = 9.5), 7.474 d (1H, 5-H, ⁴*J* = 2.1), 7.420 d.d (1H, 7-H, ³*J* = 8.7, ⁴*J* = 2.1),

7.367 d (1H, 8-H, $^3J = 8.6$), 8.886 s (1H, 9-H), 7.015 d (1H, 11-H), 7.457 d.d (1H, 12-H), 7.068 d.d (1H, 13-H), 8.046 d (1H, 14-H), 4.170 q (2H, CH₂), 1.451 t (3H, CH₃). Found, %: C 73.52; H 4.93; N 4.63. C₁₈H₁₅NO₃. Calculated, %: C 73.71; H 5.15; N 4.78.

6-(2-Fluorobenzylideneamino)-2H-chromen-2-one (XVII). Yield 2.0 g (75%), mp 145–146°C. ¹H NMR spectrum, δ, ppm (*J*, Hz): 6.442 d (1H, 3-H, $^3J = 9.5$), 8.021 d (1H, 4-H, $^3J = 9.6$), 7.597 d (1H, 5-H, $^4J = 2.2$), 7.509 d.d (1H, 7-H, $^3J = 8.7$, $^4J = 2.2$), 7.377 d (1H, 8-H, $^3J = 8.7$), 8.824 s (1H, 9-H), 7.246 d (1H, 11-H), 7.561 d.d (1H, 12-H), 7.307 d.d (1H, 13-H), 8.138 d (1H, 14-H). Found, %: C 71.75; H 3.62; F 6.97; N 5.11. C₁₆H₁₀FNO₂. Calculated, %: C 71.91; H 3.77; F 7.11; N 5.24.

6-(2-Chlorobenzylideneamino)-2H-chromen-2-one (XVIII). Yield 1.93 g (68%), mp 181–183°C. ¹H NMR spectrum, δ, ppm (*J*, Hz): 6.458 d (1H, 3-H, $^3J = 9.5$), 8.046 d (1H, 4-H, $^3J = 9.5$), 7.597 s (1H, 5-H), 7.518 d (1H, 7-H, $^3J = 8.5$), 7.411 d (1H, 8-H, $^3J = 8.5$), 8.933 s (1H, 9-H), 7.327 d (1H, 11-H), 7.530 d.d (1H, 12-H), 7.365 d.d (1H, 13-H), 8.213 d (1H, 14-H). Found, %: C 67.59; H 3.37; Cl 12.37; N 4.79. C₁₆H₁₀ClNO₂. Calculated, %: C 67.74; H 3.55; Cl 12.50; N 4.94.

6-(2-Nitrobenzylideneamino)-2H-chromen-2-one (XIX). Yield 2.21 g (75%), mp 210–211°C. ¹H NMR spectrum, δ, ppm (*J*, Hz): 6.462 d (1H, 3-H, $^3J = 9.6$), 8.066 d (1H, 4-H, $^3J = 9.8$), 7.625 d (1H, 5-H, $^4J = 2.2$), 7.548 d.d (1H, 7-H, $^3J = 8.7$, $^4J = 2.2$), 7.420 d (1H, 8-H, $^3J = 8.7$), 8.951 s (1H, 9-H), 7.858 d (1H, 11-H), 7.769 d.d (1H, 12-H), 8.092 d.d (1H, 13-H), 8.265 d (1H, 14-H). Found, %: C 65.12; H 3.26; N 9.33. C₁₆H₁₀N₂O₄. Calculated, %: C 65.31; H 3.43; N 9.52.

6-(2,4-Dimethylbenzylideneamino)-2H-chromen-2-one (XX). Yield 2.49 g (90%), mp 155–156°C. ¹H NMR spectrum, δ, ppm (*J*, Hz): 6.431 d (1H, 3-H, $^3J = 9.6$), 7.997 d (1H, 4-H, $^3J = 9.7$), 7.525 d (1H, 5-H, $^4J = 2.5$), 7.470 d.d (1H, 7-H, $^3J = 8.8$, $^4J = 2.5$), 7.356 d (1H, 8-H, $^3J = 8.8$), 8.768 s (1H, 9-H), 7.063 s (1H, 11-H), 7.093 d (1H, 13-H), 7.906 d (1H, 14-H), 2.366 s (3H, CH₃), 2.584 s (3H, CH₃). Found, %: C 77.65; H 5.35; N 4.92. C₁₈H₁₅NO₂. Calculated, %: C 77.96; H 5.45; N 5.05.

6-(3,4,5-Trimethoxybenzylideneamino)-2H-chromen-2-one (XXI). Yield 3.12 g (92%), mp 194–195°C. ¹H NMR spectrum, δ, ppm (*J*, Hz): 6.437 d (1H, 3-H, $^3J = 9.4$), 7.993 d (1H, 4-H, $^3J = 9.6$), 7.525 d (1H, 5-H, $^4J = 2.1$), 7.471 d.d (1H, 7-H, $^3J = 8.7$, $^4J = 2.2$), 7.368 d (1H, 8-H, $^3J = 8.6$), 8.513 s (1H,

9-H), 7.219 s (2H, 10-H, 14-H), 3.781 s (3H, CH₃), 3.891 s (6H, 2CH₃). Found, %: C 66.85; H 4.93; N 4.02. C₁₉H₁₇NO₅. Calculated, %: C 67.25; H 5.05; N 4.13.

6-(4-Hydroxy-3-methoxybenzylideneamino)-2H-chromen-2-one (XXII). Yield 2.63 g (89%), mp 193–194°C. ¹H NMR spectrum, δ, ppm (*J*, Hz): 6.414 d (1H, 3-H, $^3J = 9.4$), 7.970 d (1H, 4-H, $^3J = 9.4$), 7.468 s (1H, 5-H), 7.427 d (1H, 7-H, $^3J = 8.5$), 7.334 d (1H, 8-H, $^3J = 8.5$), 8.418 s (1H, 9-H), 7.511 s (1H, 10-H), 6.860 d (1H, 13-H), 7.259 d (1H, 14-H), 3.893 s (3H, OCH₃), 9.519 s (1H, OH). Found, %: C 68.89; H 4.25; N 4.67. C₁₇H₁₃NO₄. Calculated, %: C 69.15; H 4.44; N 4.74.

6-(3-Methoxy-4-propoxybenzylideneamino)-2H-chromen-2-one (XXIII). Yield 2.63 g (78%), mp 197–198°C. ¹H NMR spectrum, δ, ppm (*J*, Hz): 6.439 d (1H, 3-H, $^3J = 9.3$), 8.003 d (1H, 4-H, $^3J = 9.5$), 7.539 s (1H, 5-H), 7.463 d (1H, 7-H, $^3J = 8.7$), 7.370 d (1H, 8-H, $^3J = 8.2$), 8.491 s (1H, 9-H), 7.514 s (1H, 10-H), 6.990 d (1H, 13-H), 7.366 d (1H, 14-H), 4.000 t (2H, OCH₂), 3.882 s (3H, OCH₃), 1.831 m (2H, CH₂), 1.062 t (3H, CH₃). Found, %: C 71.02; H 5.53; N 3.98. C₂₀H₁₉NO₄. Calculated, %: C 71.20; H 5.68; N 4.15.

6-(4-Benzoyloxy-3-methoxybenzylideneamino)-2H-chromen-2-one (XXIV). Yield 3.27 g (82%), mp 198–199°C. ¹H NMR spectrum, δ, ppm (*J*, Hz): 6.451 d (1H, 3-H, $^3J = 9.5$), 8.024 d (1H, 4-H, $^3J = 9.7$), 7.564 m (5H, 5-H, 7-H, 14-H, *m*-H), 7.394 d (1H, 8-H, $^3J = 8.8$), 8.651 s (1H, 9-H), 7.751 s (1H, 10-H), 7.299 d (1H, 13-H), 3.907 s (3H, CH₃), 8.150 d (2H, *o*-H), 7.713 t (1H, *p*-H). Found, %: C 71.89; H 4.15; N 3.43. C₂₄H₁₇NO₅. Calculated, %: C 72.17; H 4.29; N 3.51.

6-[4-(4-Fluorobenzoyloxy)-3-methoxybenzylideneamino]-2H-chromen-2-one (XXV). Yield 3.46 g (83%), mp 198–199°C. ¹H NMR spectrum, δ, ppm (*J*, Hz): 6.448 d (1H, 3-H, $^3J = 9.6$), 8.017 d (1H, 4-H, $^3J = 9.6$), 7.575 d (1H, 5-H, $^4J = 2.3$), 7.515 d.d (1H, 7-H, $^3J = 8.8$, $^4J = 2.3$), 7.389 d (1H, 8-H, $^3J = 8.8$), 8.644 s (1H, 9-H), 7.746 s (1H, 10-H), 7.570 m (1H, 14-H), 7.300 m (3H, 13-H, *m*-H), 3.902 s (3H, OCH₃), 8.210 m (2H, *o*-H). Found, %: C 68.89; H 3.69; F 4.43; N 3.19. C₂₄H₁₆FNO₅. Calculated, %: C 69.06; H 3.86; F 4.55; N 3.36.

6-(5-Bromo-2-methoxybenzylideneamino)-2H-chromen-2-one (XXVI). Yield 3.37 g (94%), mp 184–185°C. ¹H NMR spectrum, δ, ppm (*J*, Hz): 6.441 d (1H, 3-H, $^3J = 9.6$), 8.021 d (1H, 4-H, $^3J = 9.5$), 7.526 d (1H, 5-H, $^4J = 2.5$), 7.456 d.d (1H, 7-H, $^3J = 8.7$, $^4J = 2.5$), 7.372 d (1H, 8-H, $^3J = 8.7$), 8.838 s (1H, 9-H),

7.093 d (1H, 11-H), 7.591 d.d (1H, 12-H), 8.144 d (1H, 14-H), 3.928 s (3H, OCH₃). Found, %: C 56.69; H 3.21; Br 21.98; N 3.78. C₁₇H₁₂BrNO₃. Calculated, %: C 57.01; H 3.38; Br 22.31; N 3.91.

6-(2-Hydroxy-3,5-dichlorobenzylideneamino)-2H-chromen-2-one (XXVII). Yield 2.97 g (89%), mp 230–231°C. ¹H NMR spectrum, δ, ppm (*J*, Hz): 6.491 d (1H, 3-H, ³*J* = 9.4), 8.050 d (1H, 4-H, ³*J* = 9.6), 7.818 d (1H, 5-H, ⁴*J* = 2.5), 7.736 d.d (1H, 7-H, ³*J* = 8.8, ⁴*J* = 2.5), 7.468 d (1H, 8-H, ³*J* = 8.7), 9.068 s (1H, 9-H), 7.541 s (1H, 12-H), 7.672 s (1H, 14-H), 14.010 s (1H, OH). Found, %: C 57.23; H 2.49; Cl 20.93; N 4.02. C₁₆H₉Cl₂NO₃. Calculated, %: C 57.51; H 2.71; Cl 21.22; N 4.19.

6-(3-Nitrobenzylideneamino)-2H-chromen-2-one (XXVIII). Yield 2.23 g (76%), mp 214–215°C. ¹H NMR spectrum, δ, ppm (*J*, Hz): 6.459 d (1H, 3-H, ³*J* = 7.9), 8.021 d (1H, 4-H, ³*J* = 8.3), 7.646 s (1H, 5-H), 7.584 d (1H, 7-H, ³*J* = 7.6), 7.405 d (1H, 8-H, ³*J* = 7.9), 8.851 s (1H, 9-H), 8.766 s (1H, 10-H), 7.792 d.d (1H, 13-H), 8.344 d (2H, 12-H, 14-H). Found, %: C 64.98; H 3.15; N 9.33. C₁₆H₁₀N₂O₄. Calculated, %: C 65.31; H 3.43; N 9.52.

6-(4-Chloro-3-nitrobenzylideneamino)-2H-chromen-2-one (XXIX). Yield 2.53 g (78%), mp 247–248°C. ¹H NMR spectrum, δ, ppm (*J*, Hz): 6.449 d (1H, 3-H, ³*J* = 9.4), 8.003 d (1H, 4-H, ³*J* = 9.4), 7.626 s (1H, 5-H), 7.567 d (1H, 7-H, ³*J* = 8.2), 7.397 d (1H, 8-H, ³*J* = 8.2), 8.797 s (1H, 9-H), 8.531 s (1H, 10-H), 7.831 d (1H, 13-H), 8.221 d (1H, 14-H). Found, %: C 58.29; H 2.59; Cl 10.65; N 8.34. C₁₆H₉ClN₂O₄. Calculated, %: C 58.46; H 2.76; Cl 10.79; N 8.52.

6-(2-Chloro-5-nitrobenzylideneamino)-2H-chromen-2-one (XXX). Yield 2.99 g (91%), mp 262–263°C. ¹H NMR spectrum, δ, ppm (*J*, Hz): 6.475 d (1H, 3-H, ³*J* = 9.6), 8.056 d (1H, 4-H, ³*J* = 9.5), 7.737 d (1H, 5-H, ⁴*J* = 2.0), 7.632 d.d (1H, 7-H, ³*J* = 8.7, ⁴*J* = 2.0), 7.433 d (1H, 8-H, ³*J* = 8.7), 8.998 s (1H, 9-H), 7.853 d (1H, 11-H), 8.356 d.d (1H, 12-H), 8.961 d (1H, 14-H). Found, %: C 58.32; H 2.63; Cl 10.63; N 8.31. C₁₆H₉ClN₂O₄. Calculated, %: C 58.46; H 2.76; Cl 10.79; N 8.52.

6-(2-Chloro-6-fluorobenzylideneamino)-2H-chromen-2-one (XXXI). Yield 2.20 g (73%), mp 164°C. ¹H NMR spectrum, δ, ppm (*J*, Hz): 6.453 d (1H, 3-H, ³*J* = 9.5), 8.043 d (1H, 4-H, ³*J* = 9.5), 7.577 d (1H, 5-H, ⁴*J* = 2.5), 7.490 d.d (1H, 7-H, ³*J* = 8.7, ⁴*J* = 2.5), 7.403 d (1H, 8-H, ³*J* = 8.7), 8.777 s (1H, 9-H), 7.275 m (1H, 11-H), 7.540 m (1H, 12-H), 7.395 m (1H, 13-H). Found, %: C 63.42; H 2.83; Hlg 17.85; N 4.23.

C₁₆H₉ClFNO₂. Calculated, %: C 63.70; H 3.01; Cl 11.75; F 6.30; N 4.64.

6-[3-Methoxy-4-(5-carboxy-1-methylpyrazolyl)-benzylideneamino]-2H-chromen-2-one (XXXII). Yield 2.78 g (69%), mp 215–217°C. ¹H NMR spectrum, δ, ppm (*J*, Hz): 6.451 d (1H, 3-H, ³*J* = 9.5), 8.032 d (1H, 4-H, ³*J* = 9.5), 7.550 m (4H, 5-H, 7-H, 14-H; 4-H, pyrazolyl), 7.393 d (1H, 8-H, ³*J* = 8.7), 8.651 s (1H, 9-H), 7.751 s (1H, 10-H), 7.301 d (1H, 13-H), 7.059 d (1H, 5-H, pyrazolyl), 4.176 s (3H, NCH₃), 3.922 s (3H, OCH₃). Found, %: C 65.32; H 4.12; N 10.18. C₂₂H₁₇N₃O₅. Calculated, %: C 65.51; H 4.25; N 10.42.

6-(2-Hydroxy-1-naphthylmethylideneamino)-2H-chromen-2-one (XXXIII). Yield 2.33 g (74%), mp 220–221°C. ¹H NMR spectrum, δ, ppm (*J*, Hz): 6.477 d (1H, 3-H, ³*J* = 9.6), 8.028 d (1H, 4-H, ³*J* = 9.5), 7.937 d (1H, 5-H, ⁴*J* = 2.4), 7.843 d.d (1H, 7-H, ³*J* = 8.8, ⁴*J* = 2.4), 7.437 d (1H, 8-H, ³*J* = 8.8), 9.714 s (1H, 9-H), 7.045 d (1H, 3-H, naphthyl), 7.60 m (4H, 4-H, 5-H, 6-H, 7-H, naphthyl), 8.469 d (1H, 8-H, naphthyl), 15.464 s (1H, OH). Found, %: C 76.12; H 4.05; N 4.35. C₂₀H₁₃NO₃. Calculated, %: C 76.18; H 4.16; N 4.44.

6-(9-Anthrylmethylideneamino)-2H-chromen-2-one (XXXIV). Yield 3.0 g (86%), mp 247–248°C. ¹H NMR spectrum, δ, ppm (*J*, Hz): 6.486 d (1H, 3-H, ³*J* = 9.5), 8.094 d (1H, 4-H, ³*J* = 9.8), 7.822 d (1H, 5-H, ⁴*J* = 2.5), 7.740 d.d (1H, 7-H, ³*J* = 8.7, ⁴*J* = 2.5), 7.472 d (1H, 8-H, ³*J* = 8.7), 9.838 s (1H, 9-H), 8.718 s (1H, 10-H, anthryl), 8.894 d (2H, 1-H, 8-H, anthryl), 7.612 d.d (2H, 2-H, 7-H, anthryl), 7.555 d.d (2H, 3-H, 6-H, anthryl), 8.131 d (2H, 4-H, 5-H, anthryl). Found, %: C 82.35; H 4.17; N 3.79. C₂₄H₁₅NO₂. Calculated, %: C 82.51; H 4.33; N 4.01.

6-(3-Pyridylmethylideneamino)-2H-chromen-2-one (XXXV). Yield 1.95 g (78%), mp 162–163°C. ¹H NMR spectrum, δ, ppm (*J*, Hz): 6.446 d (1H, 3-H, ³*J* = 9.5), 8.011 d (1H, 4-H, ³*J* = 9.4), 7.601 s (1H, 5-H), 7.523 m (2H, 7-H; 5-H, pyridyl), 7.385 d (1H, 8-H, ³*J* = 8.8), 9.032 s (1H, 9-H), 8.662 d (1H, 4-H, pyridyl), 8.300 d (1H, 6-H, pyridyl), 8.736 s (1H, 2-H, pyridyl). Found, %: C 71.89; H 3.87; N 10.98. C₁₅H₁₀N₂O₂. Calculated, %: C 71.99; H 4.03; N 11.19.

6-(2-Hydroxy-6-methylquinolin-3-ylmethylideneamino)-2H-chromen-2-one (XXXVI). Yield 2.31 g (70%), mp 331–332°C. ¹H NMR spectrum, δ, ppm (*J*, Hz): 6.438 d (1H, 3-H, ³*J* = 9.1), 8.051 d (1H, 4-H, ³*J* = 9.4), 7.599 s (1H, 5-H), 7.508 d (1H, 7-H, ³*J* = 9.0), 7.380 d (1H, 8-H, ³*J* = 9.0), 8.865 s (1H, 9-H), 8.574 s (1H, 4-H, quinolyl), 7.542 s (1H, 5-H,

quinolyl), 7.262 d (1H, 7-H, quinolyl), 7.346 d (1H, 8-H, quinolyl), 2.404 s (3H, CH₃), 12.029 s (1H, OH). Found, %: C 72.57; H 4.07; N 8.26. C₂₀H₁₄N₂O₃. Calculated, %: C 72.72; H 4.27; N 8.48.

6-(2-Methylindol-3-ylmethylideneamino)-2H-chromen-2-one (XXXVII). Yield 1.75 g (58%), mp 215–216°C. ¹H NMR spectrum, δ, ppm (*J*, Hz): 6.406 d (1H, 3-H, ³*J* = 9.4), 7.984 d (1H, 4-H, ³*J* = 9.4), 7.587 s (1H, 5-H), 7.456 d (1H, 7-H, ³*J* = 8.5), 7.330 d (1H, 8-H, ³*J* = 8.5), 8.737 s (1H, 9-H), 7.356 d (1H, 4-H, indolyl), 7.125 d.d (1H, 5-H, indolyl), 7.094 d.d (1H, 6-H, indolyl), 8.334 d (1H, 7-H, indolyl), 2.676 s (3H, CH₃), 11.557 s (1H, NH). Found, %: C 75.34; H 4.32; N 9.06. C₁₉H₁₄N₂O₂. Calculated, %: C 75.48; H 4.67; N 9.27.

6-(1,2-Dimethylindol-3-ylmethylideneamino)-2H-chromen-2-one (XXXVIII). Yield 1.99 g (63%), mp 219–220°C. ¹H NMR spectrum, δ, ppm (*J*, Hz): 6.402 d (1H, 3-H, ³*J* = 9.4), 7.970 d (1H, 4-H, ³*J* = 9.4), 7.490 s (1H, 5-H), 7.479 d (1H, 7-H, ³*J* = 8.5), 7.399 d (1H, 8-H, ³*J* = 8.5), 8.765 s (1H, 9-H), 7.325 d (1H, 4-H, indolyl), 7.146 d.d (1H, 5-H, indolyl), 7.195 d.d (1H, 6-H, indolyl), 8.395 d (1H, 7-H, indolyl), 3.754 s (3H, NCH₃), 2.682 s (3H, CH₃). Found, %: C 75.73; H 4.89; N 8.73. C₂₀H₁₆N₂O₂. Calculated, %: C 75.93; H 5.10; N 8.85.

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