Dihydrofurocoumarinones - new useful intermediates for substituted and condensed furocoumarins

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(received 02 May 00; accepted 21 Sep 00; published on the web 29 Sep 00)

DOI: http://dx.doi.org/10.3998/ark.5550190.0001.408

Abstract

Survey of new synthetic paths to substituted and condensed furocoumarins, perspective compounds for photochemotherapy is given. These furocoumarin syntheses are based on the use of dihydrofurocoumarinones as convenient synthons. Both dihydrofuro[2,3-h]coumarin-9-ones and dihydrofuro[2,3-g]coumarin-6-ones became available via the unusual Fries rearrangement of 7-hydroxycoumarin chloroacetates. Substitution and keto-enol reactions of dihydrofurocoumarinones followed by aromatization of dihydrofuranone moiety are key steps of substituted and condensed furo[2,3-h]- and furo[2,3-g]coumarins synthesis.

We have already characterized in our previous papers many of the compounds listed in the survey. The structures of new compounds are proved by mass spectral, 1H NMR spectral and elemental analysis data

Keywords: Dihydrofurocoumarinones, furocoumarins, Fries rearrangement, dihydrofuranone aromatization.

Introduction

Furocoumarin derivatives, natural photosensitive compounds have been found to be useful for medical treatment of skin diseases [1,2]. Furocoumarin/ultraviolet therapy, known as photopheresis, has recently been used for treatment of cutaneous T cell lymphoma, Sezary syndrome and related diseases [3,4]. Photochemotherapeutic effect of furocoumarins is based on intercalation of the furocoumarin molecule between pyrimidine bases of the microorganism DNA. The intercalation is then followed by the UV light activated cycloaddition reactions of furocoumarin with pyrimidine bases. These [2+2] photocycloaddition reactions provide thus a cross-link of DNA and prevent a microorganism reproduction.

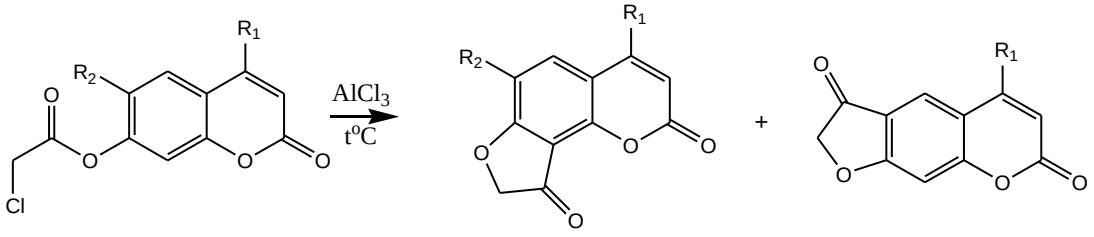
Psoralens, linear furocoumarins have two active sites in the [2+2] photocycloaddition reactions: pyrone ring and furan ring double bonds. This kind difunctionality of furocoumarins has been suggested to be a reason of undesirable side effects of their photoreactions with DNA, which lead to mutagenicity and carcinogenicity[5].

Angelicins, angular furocoumarins show monofunctional properties in their interaction with DNA. They have the only reactive double bond - pyrone ring one. [2+2] Photocycloaddition reactions with furan double bond have been considered as the hindered ones with angelicin derivatives by steric reasons. In spite of their monofunctionality, angelicins possess highly effective phototherapeutic properties. For example, 6,9-dimethyl- and 4,6,9-trimethylangelicins have been shown to be more reactive than psoralens [6-11]. Moreover, angular furocoumarins do not show undesirable side effects and do not have skin toxicity as well [2]. Therefore, syntheses of new psoralen and angelicin derivatives have been intensively studied along last years for purposes of photochemotherapy [[12-19].

We have earlier found dihydrofurocoumarin-9-ones to be very useful intermediates for substituted and condensed furocoumarin synthesis [20-28]. Survey of our previous studies and unpublished results is given in this paper.

Discussion

7-Chloroacetoxycoumarins 1a-d undergo unusual Fries rearrangement with dihydrofuro[2,3-h]coumarin-9-ones 2a-d formation (Scheme 1)



1 a-d **2 a-d** **3 a,b**

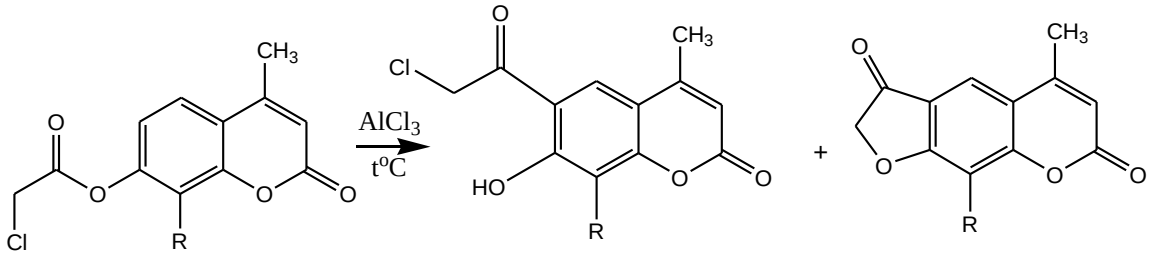
a: R_1=R_2=H; **b:** R_1=Me, R_2=H; **c:** R_1=Me, R_2=Cl; **d:** R_1=Me, R_2=Et

Scheme 1

Good yield of dihydrofuro[2,3-h]coumarin-9-ones 2a-d (up to 70%) and no any notable amount of dihydrofuro[2,3-g]coumarin-6-ones 3 have been found when the rearrangement was carried out at temperature 115-120°C.

Nevertheless, linear compounds – dihydrofuro[2,3-g]coumarin-6-ones 5a,b were the predominant products when starting 7-chloroacetoxycoumarins 4a,b contained a substituent at position 8 (Scheme 2) [22].

6-Chloroacetyl-7-hydroxy-4-methyl-8-R-coumarins 6a,b have also been found in the reaction mixtures. They seem to be the key intermediates in the unusual way of Fries rearrangement of 7-hydroxycoumarin chloroacetates.

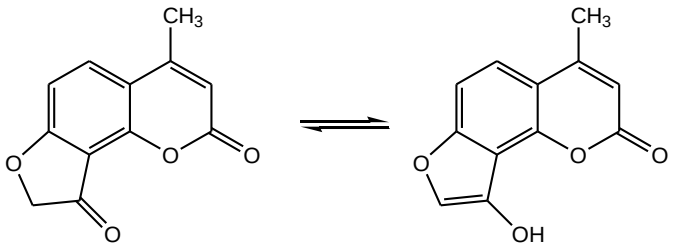


4 a,b **6 a,b** **5 a,b**

R: **a**, Me; **b**, Et

Scheme 2

Continuing our studies of these $AlCl_3$-catalyzed reactions we have found conditions when linear cyclizations take place even with substrates which have no any substituents at the position 8. For example, ratio of linear/angular products of 7-chloroacetoxycoumarins 1a,b rearrangement (Scheme 1) depends upon the reaction temperature in certain extent. Although angular derivatives 2a,b are the only products when the rearrangement goes at the temperature 115°C, yields of linear isomers - dihydrofuro[2,3-g]coumarin-6-ones 3a,b increase (up to 25%) when reaction temperature is getting higher (till 130°C). Dihydrofuro[2,3-g]coumarin-6-ones 3a, b can be isolated and purified by column chromatography and recrystallization.
Dihydrofuro[2,3-h]coumarin-9-ones 2a, b undergo keto-enol tautomeric transformations (Scheme 3).



2b, keto **2b,** enol

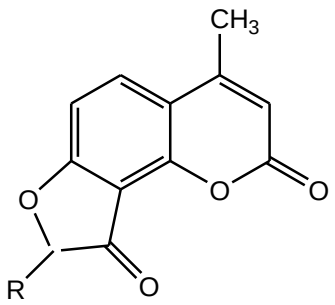
Scheme 3

Analyzing 4-methyldihydrofuro[2,3-h]coumarin-9-one 2b reactivity, we have studied its equilibrium transformations in more detail. Electron absorption spectra of 2b in CCl_4-MeOH mixtures have been recorded and an isosbestic point has been registered. Positions of the longest-

wavelength absorption bands in the UV spectra have been found at 330 nm in methanol and at 285 nm in CCl_4. We have assigned the band at 330 nm to the enol form absorption, since its PPP CI–calculated position is located at 328 nm. Both semiempirical and nonempirical quantum chemical calculations showed the keto form to be a predominant one. The difference between formation energies of keto and enol forms has been found equal to –10.57 and –8.82 kcal/mol by AM1 and PM3 calculations respectively.

Keto-enol tautomeric transformation of 4-methyldihydrofuro[2,3-h]coumarin-9-one 2b turned to be a key way of many its reactions. We have carried out chlorination and bromination of the compound 2b with a good yield [24]. For example, treatment of 2b by bromine in acetic acid or 1,4-dioxane provides its mono- and dibromination.

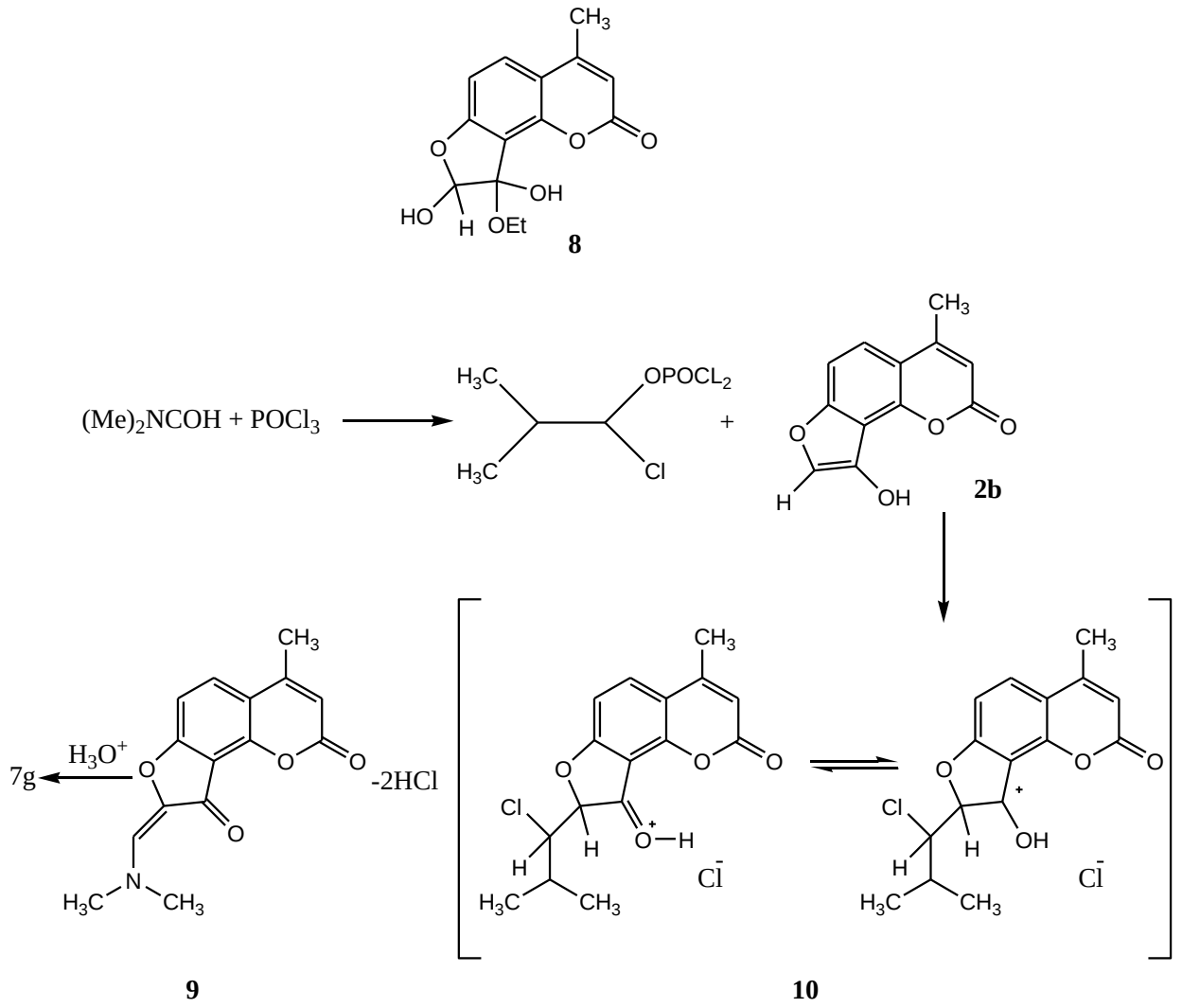
Halogen atoms at position 8 of dihydrofuro[2,3-h]coumarin-9-ones 7a, b have been found to be rather reactive in nucleophilic substitution. 8-Bromo-derivative 7b has been transformed to 8-hydroxy-, 8-acetoxy- and 8-methoxydihydrofuro[2,3-h]coumarin-9-ones (compounds 7c, 7d, 7e respectively).



R: **a**, Cl; **b**, Br; c, OH; **d**, OCOMe; **e**, OMe; **g**, CHO

For example, 8-hydroxy-derivative 7c has been prepared by two procedures. Treatment of 7b by AgOH in presence of acetone-water provided 7c formation with 35% yield[24]. On the other hand, hydrolysis of 7d in ethanol-water in presence of HCl gave semiacetal 8 as a main product.

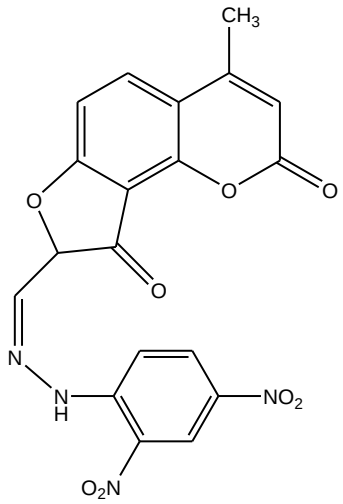
Synthesis of 8-formyl-4-methyldihydrofuro[2,3-h]coumarin-9-one 7g has been carried out by Vilsmeier-Haack reaction with isolation of dimethylamine 9 as an intermediate product instead of oxonium chloride 10. The following Scheme can be suggested for explanation of the results (Scheme 4).



Scheme 4

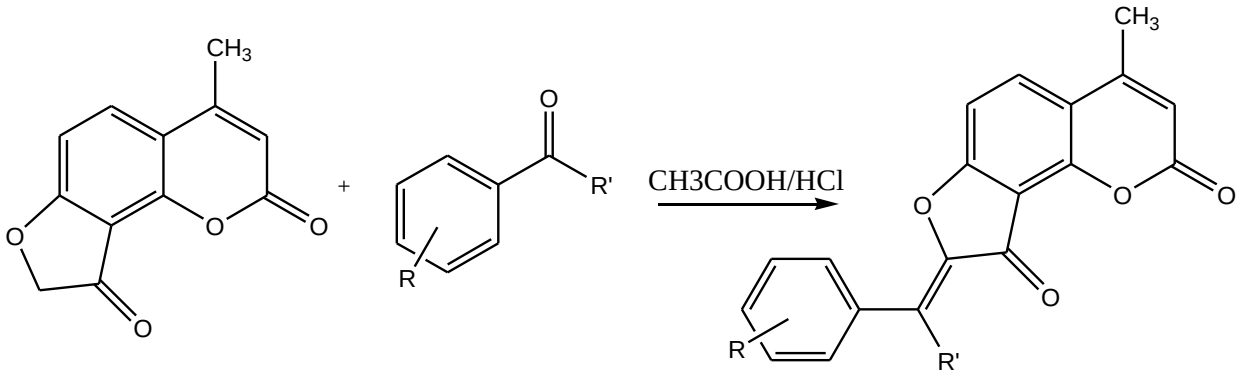
In spite of low solubility in many solvents, dimethylamine 9 is easily hydrolyzed in weak acidic solutions with the formyl-derivative 7g formation. When hydrolysis has been carried out in presence of concentrated sulfuric acid, decarbonylation of the 7g took place with formation of 2b. The compound 7g is also decarbonylated under long heating. The loss of CO is also a main way of molecular ion fragmentation under mass spectrum recording.

8-Formyl function is the most reactive carbonyl group of the compound 7g. Its 2,4-dinitrophenylhydrazone 11 has been obtained in mild conditions with the quantitative yield.



11

4-Methyldihydrofuro[2,3-h]coumarin-9-one 2b undergoes easily condensations with aldehydes and ketones in acetic acid in the presence of HCl (Scheme 5). According to the spectral data, condensation products 12 a-h have a croton-type structure [24].

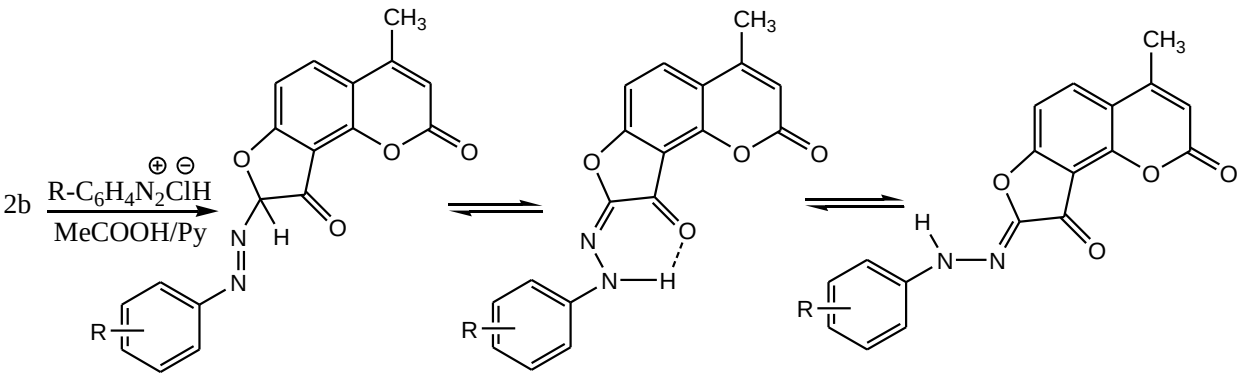


12 a-h

a-g: R'=H; **a**, R+H; **b**, R=4-Br; **c**, R=4-Me_2N; **d**, R=4-OH, 3-OMe;
e, R=2-NO_2; **f**, R=2-OH; **g**, R=4-NO_2; **h**, R=R'=Me

Scheme 5

Dihydrofuro[2,3-h]coumarin-9-ones undergo azocoupling reactions as well. For example, compound 2b reacts with aryldiazonium chlorides in acetic acid in the presence of pyridine with formation of 8-arylazo-4-methyldihydrofuro[2,3-h]coumarin-9-ones 13a-n (Scheme 6).



13 a-p: R: **a**, H; **b**, 4-OMe; **c**, Cl; **d**, NO_2, **e**, 4-Me; **f**, 4-Cl; g, 2-NO_2; **h**, 2-NO_2-4-NO_2; **i**, 4-NEt_2; **j**, 2-Et; **k**, 3-Et; **l**, 4-Et; **m**, 2-Me-3-Me; **n**, 2-Me; **o**, 4-Br; **p**, 3-NO_2

Scheme 6

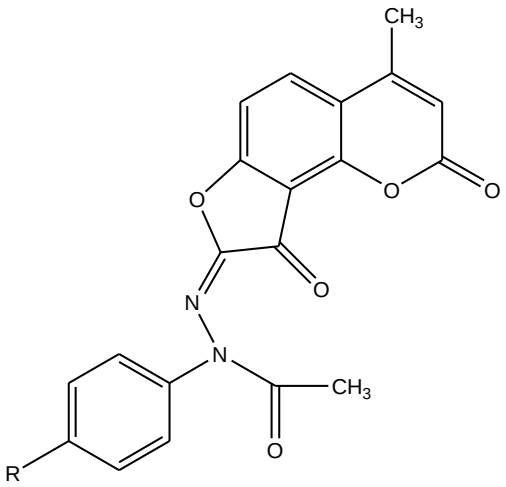
We have studied azo-quinone hydrazone tautomeric transformations of the compounds 13 with use of electron absorption spectra and quantum chemical calculations, both semiempirical and nonempirical. Hydrazone tautomeric forms have been found to be the predominant ones. For example, a good correlation between calculated by the PPP CI method and experimental positions (λ max) of the longest-wavelength absorption bands has been found when anti-isomer of quinone hydrazone form used as a model in the calculations [25] (Table 1).

Calculated by the PPP CI method and experimental positions (λ max) of the longest-wavelength absorption bands of the compounds 13 a-d.

N-H Singlet signal at 11.0-11.3 ppm in the 1H NMR spectra and characteristic peaks in the mass spectra approve quinone hydrazone tautomeric form of the azocompounds 13. NH-Function in the compounds 13 has been acetylated [25] with formation of N-acetyl quinone hydrazones 14.

Table 1

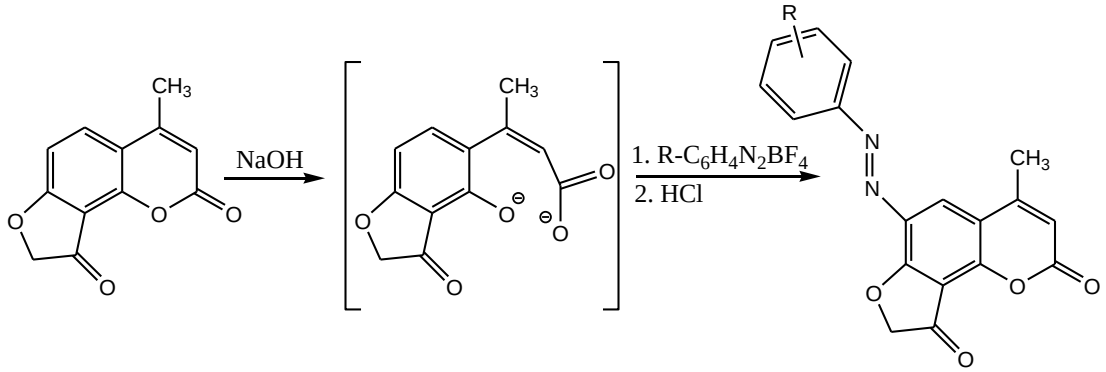
Compd number	R	λ max,exp.	λmax, antiform (calculated)	λmax,syn form (calculated)
13a	H	428	429	392
13b	OMe	451	444	405
13c	Cl	430	432	396
13d	NO2	431	433	394



14 a-e

R: **a**, H; **b**, 4-OMe; **c**, 4-Br; **d**, 4-Cl; **e**, 4-Me

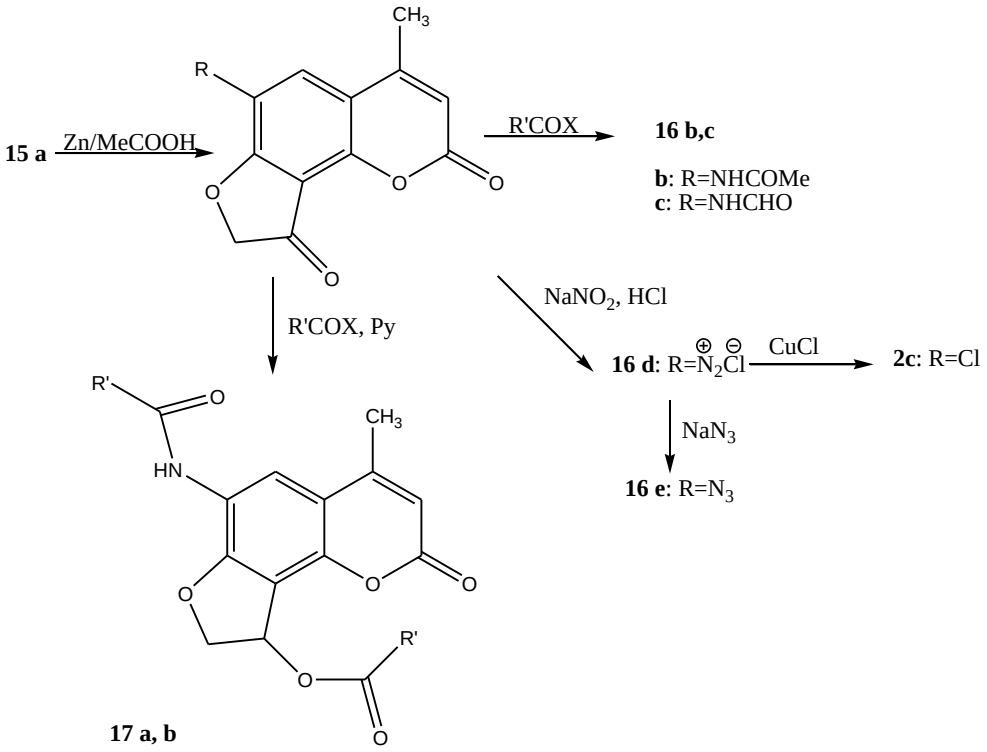
Dihydrofuro[2,3-h]coumarin-9-ones can also undergo azocoupling reactions at position 6. It happens when reactions with aryldiazonium tetrafluoroborates are carried out in the presence of sodium hydroxide. For example, R-substituted phenyldiazonium tetrafluoroborates and 2b react with formation of azocoupling products 15a-e, 4-methyl-6-(R-phenylazo)dihydrofuro[2,3-h]coumarin-9-ones with a very good yield. The regioselectivity is due to lactone ring opening in the presence of strong base. The formed phenoxide ion (Scheme 7) reacts with electrophiles at position 6.



R: **a**, H; **b**, 4-OMe; **c**, 4-NO_2; **d**, 3-Et; **e**, 4-NMe_2 **15 a-e**

Scheme 7

Resonance stabilization of the intermediate σ-complex is much facilitated along azocoupling reaction with the lactone open form. The final acidification recovers cyclic form of coumarin moiety with 6-arylazo-4-methyldihydrofuro[2,3-h]coumarin-9-ones 15a-e formation.



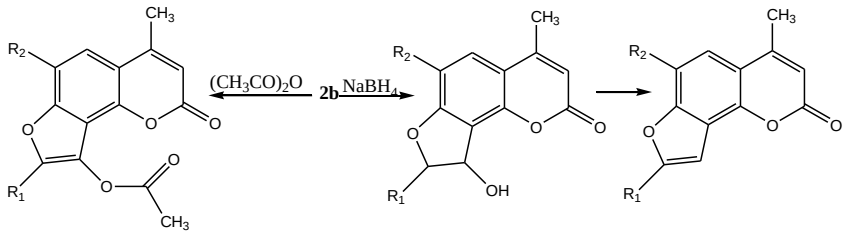
Scheme 8

On opposite to the compounds 13a-n, azocoupling products 15a-e possess an azo tautomeric form. Therefore, compounds 15a-e has been easily reducted. For example, reduction of azo function in azocompound 15a leads to 6-amino-4-methyldihydrofuro[2,3-h]coumarin-9-one 16a with a very good yield. Transformations of the amino function in it, followed by aromatization of the dihydrofuranone ring provides a series of new angelicin derivatives [27] (Scheme 8).

For example, amino function of 16a is readily acylated. Thus, treatment of 16a by acetic anhydride under heating provides 6-acetamido-4-methyldihydrofuro[2,3-h]coumarin-9-one 16b formation. Treatment of 16a by acetic anhydride in presence of pyridine provides both N- and O-acetylation with formation of 6-acetamido-9-acetoxy-4-methylangelicin 17a. Similar, benzoylation of 16a by benzoyl chloride in presence of pyridine gives 6-benzamido-9-benzoyloxy-4-methylangelicin 17b. Heating of 16a in formic acid gives 6-formamido-4-methyldihydrofuro[2,3-h]coumarin-9-one 16c.

Amine 16a undergoes diazotization under treatment with sodium nitrite and hydrochloric acid. The product of diazotization, 4-methyldihydrofuro[2,3-h]coumarin-9-one–6-diazonium chloride 16d transforms to 6-chloro-4-methyldihydrofuro[2,3-h]coumarin-9-one 16e via the Sandmeyer reaction and to 6-azido-4-methyldihydrofuro[2,3-h]coumarin-9-one 16f under treatment with sodium azide.

Both 4-methyldihydrofuro[2,3-h]coumarin-9-ones 2a, b (unsubstituted in furanone and benzene rings) and their 8- and 6-substituted derivatives undergo rather easily transformation to the proper angelicins. That kind of transformation has been done by two procedures: 1) reduction of furanone moiety followed by dehydration of the resulted alcohols 18 into angelicins 19 as a final products; 2) O-acetylation of dihydrofuranone enol form with formation of 9-acetoxyangelicins 20. Alcohols 18, angelicins 19, and 9-acetoxyangelicins 20 are listed on the Scheme 9.



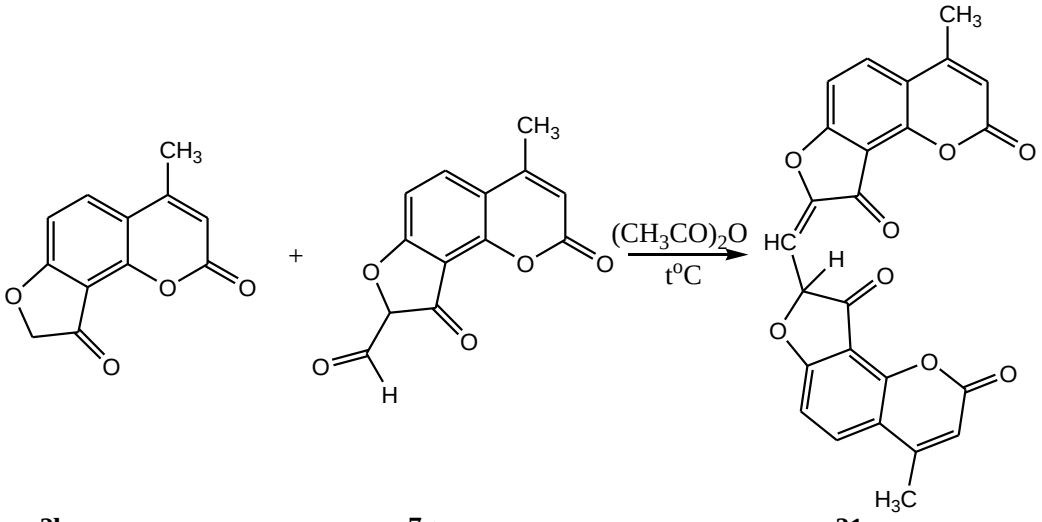
20 **18** **19**

Scheme 9

18:	**a**: R_1=H; R_2=Cl	19:	**a**: R_1=H; R_2=Cl
	b: R_1=H; R_2=Et		**b**: R_1=H; R_2=Et
	c: R_1=H; R_2=4-Me_2N-$C_6H_4N_2$		**c**: R_1=H; R_2=3,5-$Me_2C_3HN_2$
	d: R_1=H; R_2=NH_2		**d**: R_1=H; R_2=NH_2
	e: R_1=H; R_2=$NHCOCH_3$		**e**: R_1=H; R_2=CH_3CONH
	f: R_1=H; R_2=NHCHO		**f**: R_1=H; R_2=NHCHO
	g: R_1=H; R_2=N_3		**g**: R_1=H; R_2=N_3
	b: R_1=H; R_2=Et		**h**: R_1=H; R_2=4-CH_3-$C_6H_4SO_2NH$
			i: R_1=H; R_2=4-OH-C_6H_4CHN
20:	**a**: R_1=R_2=H		**j**: R_1=H; R_2=$NHNH_2$
	b: R_1=H; R_2=Et		**k**: R_1=H; R_2=4-O_2N-C_6H_4-CHNNH
	c: R_1=Cl; R_2=H		**l**: R_1=H; R_2=4-HO-C_6H_4-CHNNH
	d: R_1=Br; R_2=H		**m**: R_1=H; R_2=4-Me_2N-C_6H_4-N_2
	e: R_1=H; R_2=PhN=N-		
	f: R_1=H; R_2=4-MeO-C_6H_4-N=N-		
	g: R_1=H; R_2=4-NO_2-C_6H_4-N=N-		
	h: R_1=COMe; R_2=H		
	i: R_1=COMe; R_2=NHCHO		
	j: R_1=H; R_2=NHCHO		

There are some comments to the acetylation procedure. When acetylation is carried out by acetic anhydride in the presence of potassium acetate, 9-acetoxy-derivatives 20 are the final products. When compound 2b is treated by acetic anhydride in presence of sulfuric acid or pyridine, both O-acetylation and C-acetylation take place with formation of diacetyl-derivative 20h.

Acetylation of 7g provides rather an unusual result. Dimer 21 has been isolated as a main product. The following steps of aldehyde 7g transformation can be suggested: 7g undergoes partly decarbonylation along the acetylation procedure. The formed amount of 2b reacts then with the starting aldehyde 7g via croton condensation with formation of 21 (Scheme 10).

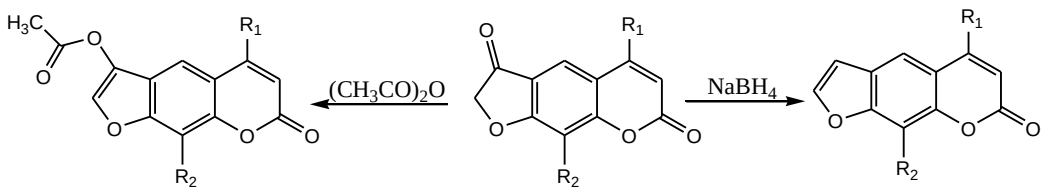


2b **7g** **21**

Scheme 10

Linear dihydrofuro[2,3-g]coumarin-6-ones 3 and 5 seem to undergo keto-enol transformations as well. Nevertheless an isosbestic points have not been seen in their electron absorption spectra when CCl_4-MeOH mixtures are used as solvents. We have found the differences between formation energies of keto and enol tautomeric forms of 3b to be much higher, when compared with that of the 2b tautomeric forms: -15.72 and –12.57 kcal/mol by AM1 and PM3 calculations respectively. Keto form of 3b turns to be relatively more stable one. Nevertheless dihydrofuro[2,3-g]coumarin-6-ones seem to be similar in reactivity to dihydrofuro[2,3-h]coumarin-9-ones.

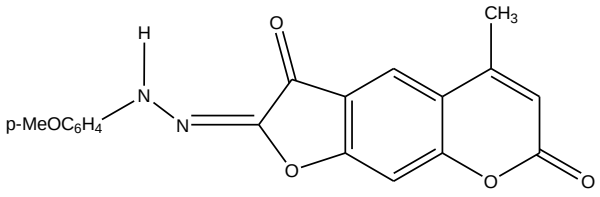
Linear dihydrofuro[2,3-g]coumarin-6-ones undergo also transformation to psoralen derivatives. Compounds 3b and 5a have been transformed into psoralens 22 and 23 by reduction/dehydration and acetylation procedures respectively (Scheme 11).



23: R_1=R_2=Me **3b**: R_1=Me, R_2=H **22**: R_1=Me, R_2=H
5a: R_1=R_2=Me

Scheme 11

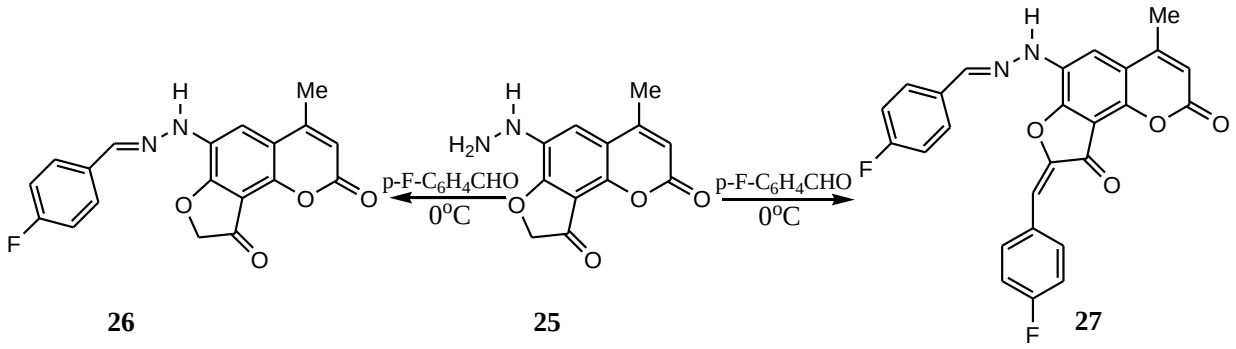
4-Methyldihydrofuro[2,3-g]coumarin-6-one undergoes an azocoupling reaction at position 7 in the presence of weak acid. In accordance with spectral data, 4-methyl-6-(4'-metoxyphenylazo)dihydrofuro[2,3-g]coumarin-6-one 24 possesses an quinone hydrazone tautomeric form.



24

Diazocompound 16d has been reducted with formation of hydrazine derivative 25. Hydrazine 25 is sensitive to heating. Its preparation goes with a good yield if temperature of the reaction is below –10°C. If temperature of the reduction is higher, the reaction is accompanied by formation of amine 16a and traces of coumarinone 2b.

Hydrazine 25 reacts readily with benzaldehydes [27]. However, regioselectivity of these reactions depends also upon the temperature. For example, hydrazone 26 has smoothly been prepared along condensation of 25 with 4-fluorobenzaldehyde in acetic acid at temperature O°C. At higher temperature condensation with 4-fluorobenzaldehyde takes place also at position 8 (methylene group of dihydrofuranone ring). Bis-benzylidene derivative 27 is a product of the reaction (Scheme 12).



26 **25** **27**

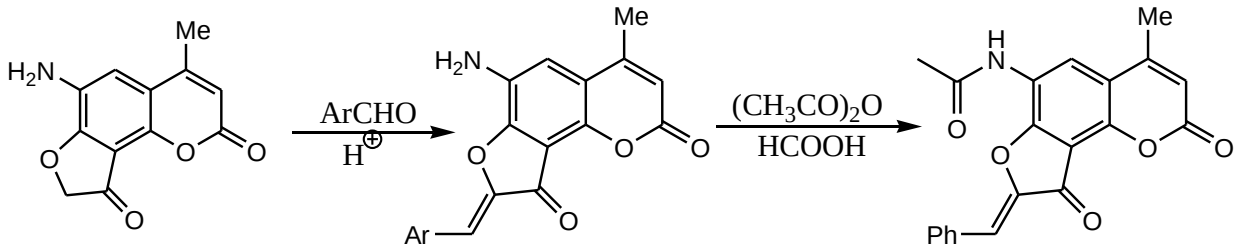
Scheme 12

Position 8 seems to be rather reactive in the amine 16a. If condensations of amine 16a with benzaldehyde, pentafluorobenzaldehyde and 3,4,5-tris(methoxy)benzaldehyde take place in acetic acid in the presence of concentrated hydrochloric acid, reactions go at the position 8 only (leaving 6-amino function untouched) with formation of C-benzylidene derivatives 28a-c respectively.

These derivatives are analogues of C-benzylidene derivatives, which we have earlier studied in more detail [24]. C-H-Bond seems to be more nucleophilic in these conditions than the 6-amino function.

Moreover, pentafluorobenzaldehyde, the most active benzaldehyde reacts only at the position 8 of 16a in the presence of HCI. One can suggest, N-protonation decreases concentration of the active form of amin 16a. Benzylidene derivative 28a undergoes easily an acetylation and formylation in standard procedures with formation of compounds 29a, b respectively (Scheme 13).

Diazotization of 6-amino-4-methylangelicin 19, followed by reduction of the resulted diazocompound gave 6-hydrazino-4-methylangelicin 30. This derivative turned to become as a key compound in new pyrrolo[2,3-f]furo[2,3-h]coumarins synthesis via indole cyclization by Fisher [26]. The respective hydrazones 31, 33, 35 and pyrrolo[2,3-f]furo[2,3-h]coumarins 32, 34 and 36 are listed below on the Scheme 14.

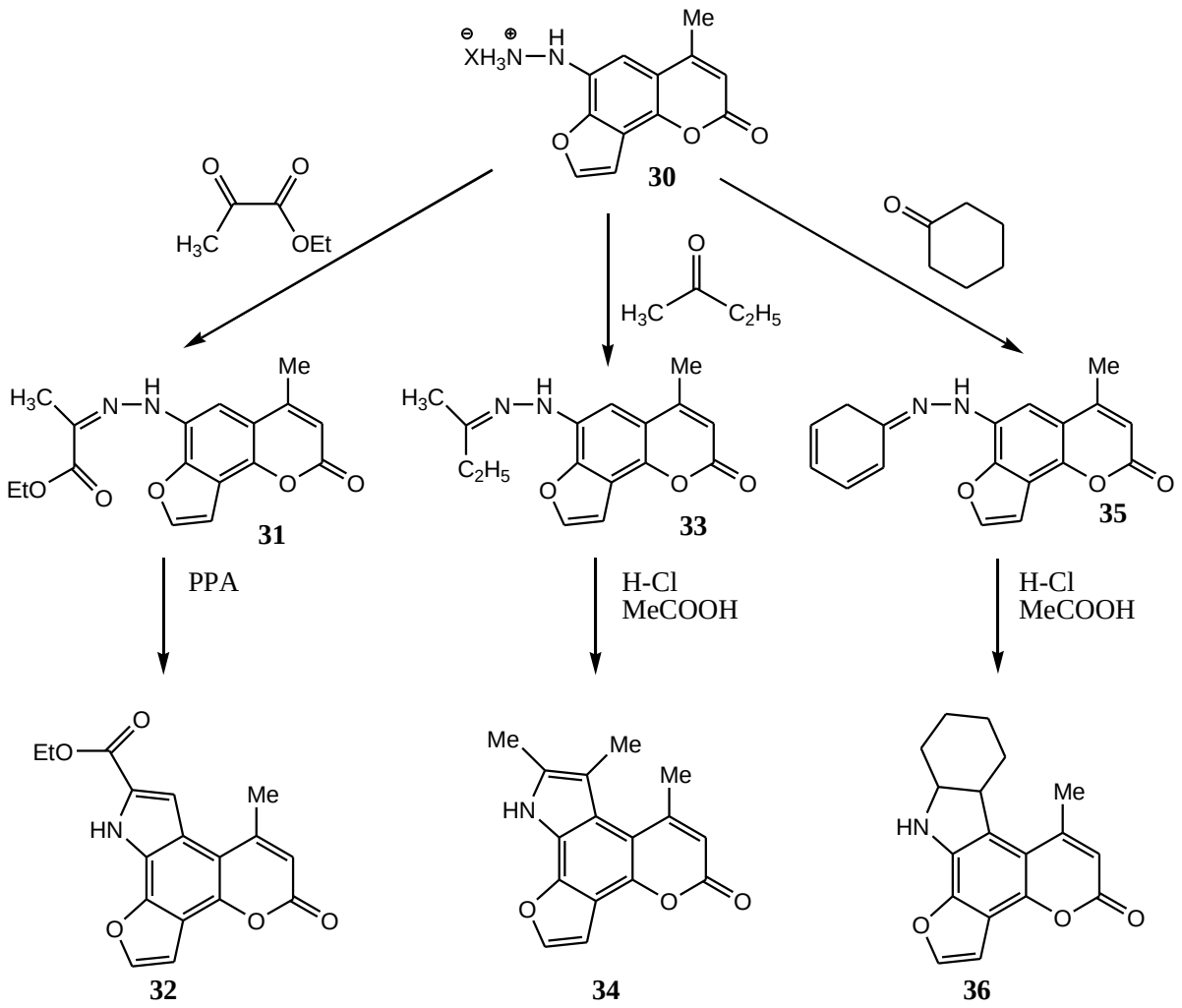


16a

28 a: Ar=Ph
b: Ar=C_6F_5
c: Ar=3,4,5-$(MeO)_3C_6H_2$-

29 a: R=Me
b: R=H

Scheme 13



Scheme 14

Experimental Section

General Procedures. 1H NMR spectra were recorded on a Varian Gemini-200 spectrometer at 200 MHz in acetone-d_6, DMSO-d_6 or $CDCI_3$ solutions using TMS as internal standard. Chemical shifts are given in ppm.

Mass spectra were scanned on a SSQ-710 (Finnigan MAT) spectrometer at the energy of ionizing electrons equal to 70 ev.

Electron absorption spectra were recorded on a spectrophotometer "Specord-UV/VIS" using CCl_4, methanol or ethanol solutions.

Fries rearrangement of 7-chloroacetoxycoumarins 1a-d, 4a,b.

The mixture of 7-chloroacetoxycoumarin 1 or 4 (0.016 mol) and anhydrous aluminium chloride (0.052 mol) was heated in an oil bath at 115-120^{o}C for 25-35 min. The cooled reaction mixture

was poured into cold dilute HCl. The crude solid, thus obtained, was washed with water and recrystallized from glacial acetic acid. Compounds 2 a-d were thus obtained. The filtrate was evaporated and compound 3b was obtained by column chromatography (silica gel 40/100, $CHCl_3$) and recrystallization from glacial acetic acid.

6-Chloro-4-methyldihydrofuro[2,3-h]coumarin-9-one (**2c).** yield=20%, light yellow crystals, mp 244-245°C. 1H NMR (acetone-d_6; δ, ppm; J, Hz): 2.53 (d, 3H, 4-Me, $J_{Me,3}$ =1.2), 4.96 (s, 2H, -CH_2-), 6.31 (q, 1H, 3-H, $J_{3,Me}$ =1.2), 8.14 (s, 1H, 5-H).
MS (m/z, %): 250/252 (1Cl)(M+, 100), 222/224 (1Cl)(-CO, 84), 193/195 (1Cl), (-CO,-HCO, 59), 149/151 (1Cl)(-2CO,-HCO,17).
Anal. calc. for $C_{12}H_7O_4Cl$: C 57.48, H 2.79; found: C 57.23, H 2.91.
6-Ethyl-4-methyldihydrofuro[2,3-h]coumarin-9-one (2d). yield=75%, light yellow crystals, mp 243-244°C. 1H NMR (acetone-d_6; δ, ppm; J, Hz): 1.29 (t, 3H, Me, $J_{Me,-CH2-}$ =7.7), 2.50 (d, 3H, 4-Me, $J_{Me,3}$ =1.2), 2.76 (q, 2H, -CH_2-, $J_{-CH2-,Me}$ =7.7), 4.85 (s, 2H, -CH_2-), 6.21 (q, 1H, 3-H, $J_{3,Me}$ =1.2), 7.91 (s, 1H, 5-H).
MS (m/z, %): 244 (M+,100), 216 (-CO, 85), 187 (-CO, - HCO, 20), 229 (-Me, 79), 201 (-Me, -CO, 98), 173 (-Me, -2CO, 26).
Anal. calc. for $C_{14}H_{12}O_4$: C 68.85, H 4.92; found: C 68.79, H 4.98.
4-Methyldihydrofuro[2,3-g]coumarin-9-one (3b). yield=15%, light yellow crystals, mp 234-236°C. 1H NMR (DMSO-d_6, δ, ppm; J, Hz): 2.47 (d, 3H,4-Me, $J_{Me,3}$ =1.1), 4.91 (s, 2H, CH_2), 6.34 (q, 1H, 3-H, $J_{3,Me}$ =1.1), 7.28 (s, 1H, 9-H), 8.05 (s, 1H, 5-H).
MS (m/z, %): 216 (M+,100), 188 (-CO, 52), 159 (-CO,-HCO, 59), 131 (-2CO, -HCO,18).
Anal. calc. for $C_{12}H_8O_4$: C 66.67, H 3.73; found: C 66.79, H 3.88.
8,9-Dihydroxy-9-ethoxy-4-methyl-8,9-dihydrofuro[2,3-h]coumarin (8). Mixture of 8-acetoxy-4-methyldihydrofuro[2,3-h]coumarin-9-one (0.4g, 0.0014 mol) 5 ml of ethanol and 5 ml of HCl stir intensively for 4 hrs. at 20°C and pour into water. The product was extracted by $CHCl_3$ and purified by column chromatography (silica gel 40/100, $CHCl_3$), compound 8, yield=10%, white crystals, mp 155-156°C. 1H NMR (acetone-d_6; δ, ppm; J, Hz): 1.16 (t, 3H, Me, $J_{Me,-CH2-}$ =7.4), 2.43 (d, 3H, 4-Me, $J_{Me,3}$ =1.2), 4.18 (q, 2H, -CH_2-, $J_{-CH2-,Me}$ =7.4), 4.96 (d, 1H, 8-OH, $J_{8-OH,8-H}$ =5.0), 5.81 (d, 1H, $J_{8-H,8-OH}$ =5.0), 6.11 (q, 1H, 3-H, $J_{3,Me}$ =1.2), 6.91 (d, 1H, 6-H, $J_{6,5}$ =8.9), 7.61 (d, 1H, 5-H, $J_{5,6}$ =8.9), 9.54 (s, 1H, 9-OH).
MS (m/z, %): 278 (M+,20), 205 (- O=C-OEt, 100), 176 (- O=C-OEt, - HCO, 6), 260 (- H_2O, 5), 232 (- EtOH, 6).
Anal. calc. for $C_{14}H_{14}O_6$: C 60.43, H 5.07; found: C 60.29, H 5.07.
8-(*N*,*N*-Dimethylaminomethylideno)-4-methyldihydrofuro[2,3-h]coumarin-9-one (9). Phosphorous oxychloride (2.3 ml) was added drop by drop to DMFA (2 ml) at 10°C. Solution of compound 2b (4g, 0.018 mol) in 25 ml of DMFA and 75 ml dioxane was added then to the $POCl_3$-DMFA mixture. Reaction mixture was heated then for 2 hrs on water bath. The precipitate was filtered off, washed by water and hot acetone (3 times). Compound 9, yield=90%, yellow crystals, mp 266-267°C. 1H NMR (DMSO-d_6, δ, ppm; J, Hz): 2.45 (d, 3H, 4-Me, $J_{Me,3}$

=1.2), 3.29 (s, 6H,-N(Me)$_2$, 6.33 (q, 1H, 3-H, J $_{3,Me}$ =1.2), 7.24 (s, 1H, =CH-N), 7.35 (d, 1H, 6-H, J $_{6,5}$ =8.8), 7.91 (d, 1H, 5-H, J $_{5,6}$ =8.8).
MS (m/z, %): 271 (M+, 20), 256 (- Me, 25), 242 (- HCO, 7), 214 (- HCO, - CO, 10).
Anal. calc. for $C_{15}H_{13}NO_4$: C 66.41, H 4.83, N 5.16; found: C 66.52, H 4.70, N 5.00.

8-Formyl-4-methyldihydrofuro[2,3-h]coumarin-9-one (7g). Reaction mixture of the compound 9 synthesis was poured into water (700ml) and heated then for 5-7 min at 80-90ºC. The solution was left for a night, the formed precipitate was then filtered off and recrystallized from acetone.
Compound 7g, yield=50%, yellow crystals, mp 275ºC(decomp.). 1H NMR ($CDCl_3$, δ, ppm; J, Hz): 2.50 (d, 3H, 4-Me, J $_{Me,3}$ =1.2), 6.33 (q, 1H, 3-H, J $_{3,Me}$ =1.2), 7.17 (s, 1H,8-H), 7.38 (d, 1H, 6-H, J $_{6,5}$ =8.9), 7.75 (d, 1H, 5-H, J $_{5,6}$ =8.9), 9.88 (s, 1H, - COH).
MS (m/z, %): 244 (M+, 100), 216 (- CO, 65), 215 (- HCO, 34), 187 (- CO, - HCO, 17), 159 (- HCO,- 2CO,16).
Anal. calc. for $C_{13}H_8O_5$: C 63.94, H 3.30; found: C 63.84, H 3.36

8-Formyl-4-methyldihydrofuro[2,3-h]coumarin-9-one, 2,4-dinitrophenyl-hydrazone (11). Solution of 2,4-dinitrophenylhydrazine (0.49g, 0.002 mol) in glacial acetic acid (30 ml) was added to suspension of compound 7g in glacial acetic acid (50 ml). Reaction mixture was then stirred for 1 hr at 20ºC and 1 hr at 60-80ºC. The formed precipitate was filtered off and recrystallized from acetone.
Compound 11, yield=95%, dark red crystals, mp 261-262ºC. 1H NMR (acetone-d_6, δ, ppm; J, Hz): 2.50 (d, 3H, 4-Me, J $_{Me,3}$ =1.2), 6.39 (q, 1H, 3-H, J $_{3,Me}$ =1.2), 7.59 (d, 1H, 6-H, J $_{6,5}$ =8.9), 7.78 (d, 1H, 5-H, J $_{5,6}$ =8.9), 7.98 (d, 1H, 6'-H, J $_{6',5'}$ =9.6), 8.43 (dd, 1H, 5'-H, J $_{5',6'}$ =9.6, J $_{5',3'}$ =2.6), 8.84 (s, 1H, -CH=), 8.88 (d, 1H, 3'-H, J $_{3',5'}$ =2.6), 10.6 (s,1H,OH), 11.74 (s, 1H, NH).
MS (m/z, %): 424 (M+, 27), 202 (- CH-CH=N-NH-$C_6H_3(NO_2)_2$, 40), 174 (- CH-CH=N-NH-$C_6H_3(NO_2)_2$, - CO, 100), 215 (- CH=N-NH-$C_6H_3(NO_2)_2$, 13), 171 (- CH=N-NH-$C_6H_3(NO_2)_2$,- CO_2, 33).
Anal. calc. for $C_{19}H_{12}N_4O_8$: C 53.78, H 2.85, N 13.20; found: C 53.69, H 2.91, N 13.21.

Croton condensation of 2b with aldehydes. Synthesis of 8-(R-benzylideno)-4-methyldihydrofuro[2,3-h]coumarin-9-ones (12). Compound 2b (0.5g, 0.0023 mol), glacial acetic acid (12 ml), conc. HCl (6 ml) and R-benzaldehyde (0.019 mol) were heated for 1 hr under reflux. Precipitate was filtered off and recrystallized from DMSO.

8-(4′-Bromobenzylideno)-4-methyldihydrofuro[2,3-h]coumarin-9-one(12b). yield=85%, yellow crystals, mp 335-336ºC. 1H NMR (DMSO-d_6, δ, ppm; J, Hz): 2.47 (d, 3H, 4-Me, J $_{Me,3}$ =1.2), 6.36 (q, 1H, 3-H, J $_{3,Me}$ =1.2), 6.96 (s, 1H, =(Ph)C-H), 7.48 (d, 1H, 6-H, J $_{6,5}$ =9.0), 7.70 (d, 2H, 2'-H, J $_{2',3'}$ =8.5), 7.92 (d, 2H, 3'-H, J $_{3',2'}$ =8.5), 8.16 (d, 1H, 5-H, J $_{5,6}$ =9.0).
MS (m/z, %): 382/384, (1Br), (M+, 79), 303 (- Br, 100), 353/355, (1Br), (- HCO, 11), 275 (- Br, - CO, 18).
Anal. calc. for $C_{19}H_{11}BrO_4$: C 59.55, H 2.89; Br 20.85; found: C 59.40, H 2.99, Br 20.69.

8-(4′-*N*,*N*-Dimethylaminobenzylideno)-4-methyldihydrofuro[2,3-h]coumarin-9-one (12c). yield=87%, yellow crystals, mp 315-317°C. 1H NMR (DMSO-d_6, δ, ppm; J, Hz): 2.47 (d, 3H, 4-Me, $J_{Me,3}$ =0.9), 3.04 (s, 6H, $N(Me)_2$), 6.33 (q, 1H, 3-H, $J_{3,Me}$ =0.9), 6.82 (d, 2H, 3'-H, $J_{3',2'}$ =9.0), 6.91 (s, 1H, =(Ph)C-H), 7.44 (d, 1H, 6-H, $J_{6,5}$ =8.7), 7.85 (d, 2H, 2'-H, $J_{2',3'}$ =9.0), 8.08 (d, 1H, 5-H, $J_{5,6}$ =8.7).

MS (m/z, %): 347 (M+, 100), 346(- H, 22), 319 (- CO, 2), 290 (- CO, - HCO, 22).

Anal. calc. for $C_{21}H_{17}NO_4$: C 72.61, H 4.93, N 4.03; found: C 72.50, H 4.72, N 4.21.

8-(4'-Hydroxy-3′-methoxybenzylideno)-4-methyldihydrofuro[2,3-h]coumarin-9-one (12d). yield=85%, yellow crystals, mp 330-331°C. 1H NMR (DMSO-d_6, δ, ppm; J, Hz): 2.44 (d, 3H, 4-Me, $J_{Me,3}$ =0.9), 3.86 (s, 3H, OMe), 6.35 (q, 1H, 3-H, $J_{3,Me}$ =0.9), 6.85 (d, 1H, 5'-H, $J_{5',6'}$ =8.5) 6.90 (s, 1H, =(Ph)C-H), 7.48 (d, 1H, 6-H, $J_{6,5}$ =9.0), 7.49 (dd, 1H, 6'-H, $J_{6',5'}$ =8.5, $J_{6',2'}$ =0.9), 7.54 (d, 1H, 2'-H, $J_{2',6'}$ =0.9), 8.09 (d, 1H, 5-H, $J_{5,6}$ =9.0), 9.94 (s, 1H, OH).

MS (m/z, %): 350 (M+, 100), 333(- OH, 16), 319 (- OMe, 14).

Anal. calc. for $C_{20}H_{14}NO_6$: C 68.57, H 4.03; found: C 68.50, H 4.02.

8-(2′-Nitrobenzylideno)-4-methyldihydrofuro[2,3-h]coumarin-9-one (12e). yield=86%, yellow crystals, mp 312-313°C. 1H NMR (DMSO-d_6, δ, ppm; J, Hz): 2.50 (d, 3H, 4-Me, $J_{Me,3}$ =0.9), 6.38 (q, 1H, 3-H, $J_{3,Me}$ =0.9), 7.21 (s, 1H, =(Ph)C-H), 7.41 (d,1H, 6-H, $J_{6,5}$ =8.0), 7.70 (m, 1H, 4'-H), 7.87 (m, 1H, 5'-H), 8.11-8.23 (m, 3H, 3'-H, 6'-H, 5-H).

MS (m/z, %): 349 (M+, 17), 332(- OH, 17), 319 (- NO, 100), 303 (- NO_2, 98), 275 (- NO_2, -CO, 98).

Anal. calc. for $C_{19}H_{11}NO_6$: C 65.33, H 3.17, N 4.01; found: C 65.21, H 3.03, N 4.17.

8-(2′-Hydroxybenzylideno)-4-methyldihydrofuro[2,3-h]coumarin-9-one(12f). yield=87%, yellow crystals, mp 296-297°C. 1H NMR (DMSO-d_6, δ, ppm; J, Hz): 2.47 (d, 3H, 4-Me, $J_{Me,3}$ =0.9), 6.35 (q, 1H, 3-H, $J_{3,Me}$ =0.9), 6.95 (s, 1H, =(Ph)C-H), 6.97 (d, 1H, 3'-H, $J_{3',4'}$ =8.0), 7.29 (m, 1H, 4'-H, 5'-H), 7.46 (d, 1H, 6-H, $J_{6,5}$ =9.0), 8.11 (d, 1H, 6'-H, $J_{6',5'}$ =8.0), 8.12 (d, 1H, 5-H, $J_{5,6}$ =9.0), 10.21 (s, 1H, OH).

MS (m/z, %): 320 (M+, 81), 303(- OH, 23), 202 (-OH, - C=C-Ph, 100), 174 (- OH, - C=C-Ph, -CO, 93).

Anal. calc. for $C_{19}H_{12}O_5$: C 71.24, H 3.78; found: C 71.10, H 3.60.

8-(4′-Nitrobenzylideno)-4-methyldihydrofuro[2,3-h]coumarin-9-one (12g). yield=85%, yellow crystals, mp 354-355°C. 1H NMR (DMSO-d_6, δ, ppm; J, Hz): 2.50 (d, 3H, 4-Me, $J_{Me,3}$ =0.9), 6.38 (q, 1H, 3-H, $J_{3,Me}$ =0.9), 7.08 (s, 1H, =(Ph)C-H), 7.50 (d, 1H, 6-H, $J_{6,5}$ =9.0), 8.18 (d, 2H, 2'-H, $J_{2',3'}$ =8.5), 8.23 (d, 1H, 5-H, $J_{5,6}$ =9.0). 8.30 (d, 2H, 3'-H, $J_{3',2'}$ =8.5)

MS (m/z, %): 349 (M+, 100), 332(- OH, 16), 303(- NO_2, 20), 302 (- HNO_2, 57), 274 (- HNO_2, -CO, 98).

Anal. calc. for $C_{19}H_{11}NO_6$: C 65.33, H 3.17, N 4.01; found: C 65.21, H 3.03, N 4.17.

8-(4′, α-Dimethylbenzylideno)-4-methyldihydrofuro[2,3-h]coumarin-9-one(12h). yield=86%, yellow crystals, mp 263-264°C. 1H NMR (DMSO-d_6, δ, ppm; J, Hz): 2.40 (s, 3H, p-Me), 2.50 (d, 3H, 4-Me, $J_{Me,3}$ =1.0), 2.69 (s, 3H, =(Ph)C-Me), 6.26 (q, 1H, 3-H, $J_{3,Me}$ =1.0), 7.20 (d, 1H, 6-H,

$J_{6,5}$ =8.5), 7.65 (d, 2H, 2'-H, $J_{2',3'}$ =8.4), 7.30 (d, 2H, 3'-H, $J_{3',2'}$ =8.5), 8.06 (d, 1H, 5-H, $J_{5,6}$ =8.5).

MS (m/z, %): 332, (M+, 86), 331 (- H, 90), 317, (- Me, 100), 289 (- Me, - CO, 7).

Anal. calc. for $C_{21}H_{16}O_4$: C 75.89, H 4.85; found: C 75.80, H 4.99.

Synthesis of 8-(R-arylazo)-4-methyldihydrofuro[2,3-h]coumarin-9-ones 13. A mixture of compound 2b (0.00093 mol), glacial acetic acid (10 ml), pyridine (1 ml) and R-phenyldiazonium chloride was mixed for 8 hrs, washed then 3 times by acetone and recrystallized from DMCO.

4-Methyl-8-(4'-methylphenylazo)-4-methyldihydrofuro[2,3-h]coumarin-9-one13e, yield= 80%, red crystals, mp 296-298°C. 1H NMR (DMSO-d_6, δ, ppm; J, Hz): 2.26 (s, 3H, 4'-Me), 2.47 (d, 3H, 4-Me, $J_{Me,3}$ =1.1), 6.40 (q, 1H, 3-H, $J_{3,Me}$ =1.1), 7.24 (d, 2H, 3'-H, 5'-H, $J_{3'2'}$=$J_{5',6'}$ =8.4), 7.28 (d, 2H, 2'-H, 6'-H, $J_{2',3'}$=$J_{6',5'}$ =8.4), 7.37 (d, 6-H, $J_{6,5}$ =8.6), 8.11 (d, 1H, 5-H, $J_{5,6}$ =8.6), 11.01 (s, 1H, NH).

MS (m/z, %): 334 (M+, 100), 203 (-4-MeC_6H_4-N=N-C, 24), 174 (-4-MeC_6H_4-N=N-C, - HCO, 24).

Anal. calc. for $C_{19}H_{14}N_2O_4$: C 68.26, H 4.22, N 8.38; found: C 68.32, H 4.34, N 8.41.

4-Methyl-8-(4′-chlorophenylazo)-4-methyldihydrofuro[2,3-h]coumarin-9-one (13f). yield= 85%, orange crystals, mp 320-322°C. 1H NMR (DMSO-d_6, δ, ppm; J, Hz): 2.48 (d, 3H, 4-Me, $J_{Me,3}$ =1.1), 6.42 (q, 1H, 3-H, $J_{3,Me}$ =1.1), 7.36 (m, 4H, 2'-H, 3'-H, 5'-H, 6'-H), 7.38 (d, 1H, 6-H, $J_{6,5}$ =8.6), 8.14 (d, 1H, 5-H, $J_{5,6}$ =8.6), 11.15 (s, 1H, NH).

MS (m/z, %): 354/356 (1Cl) (M+, 100), 319 (-Cl, 5), 291 (-Cl,- CO, 5), 202 (-4-ClC_6H_4-N=N-C, 44), 174 (-4-ClC_6H_4-N=N-C, - CO, 66).

Anal. calc. for $C_{18}H_{11}ClN_2O_4$: C 60.94, H 3.13, Cl 9.99, N 7.90; found: C 60.84, H 3.23, Cl9.89 N 7.80.

4-Methyl-8-(2′-nitrophenylazo)-dihydrofuro[2,3-h]coumarin-9-one (13g). yield= 81%, yellow crystals, mp 350°C. 1H NMR (DMSO-d_6, δ, ppm; J, Hz): 2.48 (d, 3H, 4-Me, $J_{Me,3}$ =1.1), 6.44 (q, 1H, 3-H, $J_{3,Me}$ =1.1), 7.17 (s, 1H, 4'-H), 7.56 (d, 6-H, $J_{6,5}$ =8.8), 7.81 (m, 1H, 5'-H), 7.92 (m, 1H, 6'-H), 8.22 (d, 1H, 5-H, $J_{5,6}$ =8.8), 11.03 (s, 1H, NH).

MS (m/z, %): 365 (M+, 64), 203 (-2-$NO_2C_6H_4$-N=N-C, 90), 202 (-2-$NO_2C_6H_4$-NH-N=C, 63), 174 (-2-$NO_2C_6H_4$-N=N=C, -HCO, 100), 174 (-2-$NO_2C_6H_4$-NH-N=C, -CO, 100), 146 (-2-$NO_2C_6H_4$-NH-N=C, -2CO, 16), 145 (-2-$NO_2C_6H_4$-NH-N=C, -CO, -HCO,10).

Anal. calc. for $C_{18}H_{11}N_3O_6$: C 59.18, H 3.04, N 11.50; found: C 59.26, H 3.30, N 11.37.

4-Methyl-8-(2′4′-dinitrophenylazo)-4-methyldihydrofuro[2,3-h]coumarin-9-one (13h). yield= 80%, yellow crystals, mp 350°C. 1H NMR (DMSO-d_6, δ, ppm; J, Hz): 2.50 (d, 3H, 4-Me, $J_{Me,3}$ =1.1), 6.41 (q, 1H, 3-H, $J_{3,Me}$ =1.1), 7.56 (d, 6-H, $J_{6,5}$ =8.8), 7.20 (d, 1H, 6'-H, $J_{6',5'}$ =9.4), 8.31 (d, 1H, 5-H, $J_{5,6}$ =8.8), 8.61 (dd, 1H, 5'-H, $J_{5',6'}$ =9.4, $J_{5',3'}$ =2.6), 9.03 (d, 1H, 3'-H, $J_{3',5'}$=2.6), 11.38 (s, 0.62H, NH), 13.65 (s, 0.38H, OH).

MS (m/z, %): 410 (M+, 42), 202 (-2-NO_2-4-$NO_2C_6H_3$, 70), 174 (-2-NO_2-4-$NO_2C_6H_3$, -CO, 100).

Anal. calc. for $C_{18}H_{10}N_4O_8$: C 52.69, H 2.46, N 13.66; found: C 52.50, H 2.41, N 13.66.

4-Methyl-8-(4′-diethylaminophenylazo)-4-methyldihydrofuro[2,3-h]coumarin-9-one (13i). yield= 85%, red crystals, mp 350°C. 1H NMR (DMSO-d_6, δ, ppm; J, Hz): 1.07 (t, 3H, Me, $J_{Me,-}$

$_{CH2-}$ =7.5), 2.49 (d, 3H, 4-Me, J $_{Me,3}$ =1.1), 3.51 (q, 2H, -CH2-, J$_{-CH2-,Me}$ =7.5), 6.41 (q, 1H, 3-H, J $_{3,Me}$ =1.1), 7.38 (d, 6-H, J $_{6,5}$ =8.9), 7.51 (m, 4H, 2'-H, 3'-H, 5'-H, 6'-H), 8.14 (d, 1H, 5-H, J $_{5,6}$ =8.9), 11.24 (s, 1H, NH).
MS (m/z, %): 391 (M+, 2).
Anal. calc. for $C_{22}H_{21}N_3O_4$: C 67.51, H 5.41, N 10.73; found: C 67.82, H 5.54, N 10.62.

4-Methyl-8-(2′-ethylphenylazo)-4-methyldihydrofuro[2,3-h]coumarin-9-one (13j). yield=70%, red crystals, mp 350°C. 1H NMR (DMSO-d_6, δ, ppm; J, Hz): 1.40 (t, 3H, Me, J $_{Me,-CH2-}$ =7.5), 2.50 (d, 3H, 4-Me, J $_{Me,3}$ =1.1), 2.90 (q, 2H, -CH_2-, J$_{-CH2-,Me}$ =7.5), 6.41 (q, 1H, 3-H, J $_{3,Me}$ =1.1), 7.52 (m, 4H, 3'-H, 4'-H, 5'-H, 6'-H), 7.22 (d, 6-H, J $_{6,5}$ =8.9), 8.02 (d, 1H, 5-H, J $_{5,6}$ =8.9), 10.00 (s, 0.6H, NH), 12.20 (s, 0.4H, OH).
MS (m/z, %): 348 (M+, 100).
Anal. calc. for $C_{20}H_{16}N_2O_4$: C 68.96, H 4.63, N 8.04; found: C 68.76, H 4.57, N 8.27.

4-Methyl-8-(3′-ethylphenylazo)-4-methyldihydrofuro[2,3-h]coumarin-9-one (13k). yield=70%, red crystals, mp 350°C. 1H NMR (DMSO-d_6, δ, ppm; J, Hz): 1.25 (t, 3H, Me, J $_{Me,-CH2-}$ =7.5), 2.50 (d, 3H, 4-Me, J $_{Me,3}$ =1.1), 2.60 (q, 2H, -CH_2-, J$_{-CH2-,Me}$ =7.5), 6.31 (q, 1H, 3-H, J $_{3,Me}$ =1.1), 7.22 (m, 4H, 2'-H, 4'-H, 5'-H, 6'-H), 7.31 (d, 6-H, J $_{6,5}$ =8.9), 8.02 (d, 1H, 5-H, J $_{5,6}$ =8.9), 10.90 (s, 1H, NH).
MS (m/z, %): 348 (M+, 100), 202 (-3-$C_2H_5C_6H_4$-NH-N=CH, 24).
Anal. calc. for $C_{20}H_{16}N_2O_4$: C 68.96, H 4.63, N 8.04; found: C 68.81, H 4.47, N 8.15.

4-Methyl-8-(4′-ethylphenylazo)-4-methyldihydrofuro[2,3-h]coumarin-9-one (13l). yield=75%, red crystals, mp 280-282°C. 1H NMR (DMSO-d_6, δ, ppm; J, Hz): 1.2 (t, 3H, Me, J $_{Me,-CH2-}$ =7.5), 2.40 (d, 3H, 4-Me, J $_{Me,3}$ =1.1), 2.60 (q, 2H, -CH_2-, J$_{-CH2-,Me}$ =7.5), 6.40 (q, 1H, 3-H, J $_{3,Me}$ =1.1), 7.16 (d, 2H, 3'-H, 5'-H, J $_{3',2'}$=J $_{5',6'}$ =8.5), 7.30 (d, 2H, 2'-H, 6'-H, J $_{2',3'}$=J $_{6',5'}$ =8.5), 7.36 (d, 6-H, J $_{6,5}$ =8.9), 8.10 (d, 1H, 5-H, J $_{5,6}$ =8.9), 11.02 (s, 1H, NH).
MS (m/z, %): 348 (M+, 64), 203 (-4-$C_2H_5C_6H_4$-NH-N=CH, 26), 202 (-4-$C_2H_5C_6H_4$-NH-N=C, 36), 174 (-4-$C_2H_5C_6H_4$-NH-N=CH, CO, 77), , 146 (-4-$C_2H_5C_6H_4$-NH-N=C, -2CO, 13).
Anal. calc. for $C_{20}H_{16}N_2O_4$: C 68.96, H 4.63, N 8.04; found: C 68.86, H 4.50, N 8.17.

4-Methyl-8-(2′,3′-dimethylphenylazo)-4-methyldihydrofuro[2,3-h]coumarin-9-one (13m). yield=70%, red crystals, mp 278-280°C. 1H NMR (DMSO-d_6, δ, ppm; J, Hz): 2.51 (d, 3H, 4-Me, J $_{Me,3}$ =1.1), 3.30 (s, 6H, 2'-Me, 3'-Me), 6.40 (q, 1H, 3-H, J $_{3,Me}$ =1.1), 6.35-6.91 (m, 3H, 4'-H, 5'-H, 6'-H), 7.41 (d, 6-H, J $_{6,5}$ =8.8), 8.21 (d, 1H, 5-H, J $_{5,6}$ =8.8), 9.81 (s, 1H, NH).
MS (m/z, %): 348 (M+, 100).
Anal. calc. for $C_{20}H_{16}N_2O_4$: C 68.96, H 4.63, N 8.04; found: C 68.81, H 4.70, N 8.27.

4-Methyl-8-(2′-methylphenylazo)-4-methyldihydrofuro[2,3-h]coumarin-9-one (13n). yield=70%, red crystals, mp 350°C. 1H NMR (DMSO-d_6, δ, ppm; J, Hz): 2.35 (s, 3H, 2'-Me), 2.50 (d, 3H, 4-Me, J $_{Me,3}$ =1.1), 6.41 (q, 1H, 3-H, J $_{3,Me}$ =1.1), 6.96-8.10, (m, 4H, 3'-H, 4'-H, 5'-H, 6'-H), 7.42 (d, 6-H, J $_{6,5}$ =8.9), 8.12 (d, 1H, 5-H, J $_{5,6}$ =8.9), 9.75 (s, 1H, NH).
MS (m/z, %): 334 (M+, 100).
Anal. calc. for $C_{19}H_{14}N_2O_4$: C 68.26, H 4.22, N 8.38; found: C 6.98, H 4.09, N 8.43.

4-Methyl-8-(4′-bromophenylazo)-4-methyldihydrofuro[2,3-h]coumarin-9-one (13o). yield= 85%, orange crystals, mp 350ºC. 1H NMR (DMSO-d_6, δ, ppm; J, Hz): 2.49 (d, 3H, 4-Me, $J_{Me,3}$ =1.1), 6.42 (q, 1H, 3-H, $J_{3,Me}$ =1.1), 7.32 (d, 2H, 2'-H, 6'-H, $J_{2',3'}=J_{6',5'}$ =9.1), 7.40 (d, 1H, 6-H, $J_{6,5}$ =8.8), 7.50 (d, 2H, 3'-H, 5'-H, $J_{3',2'}=J_{5',6'}$ =9.1), 8.13 (d, 1H, 5-H, $J_{5,6}$ =8.8), 11.14 (s, 1H, NH).

MS (m/z, %): 398/400 (1Br) (M+, 100), 202 (-4-BrC_6H_4-N=N-C, 33), 174 (-4-BrC_6H_4-N=N-C, -CO, 77).

Anal. calc. for $C_{18}H_{11}BrN_2O_4$: C 54.16, H 2.78, Br 20.02, N 7.02; found: C 54.25, H 2.67, Br 20.34 N 7.34.

4-Methyl-8-(3′-nitrophenylazo)-4-methyldihydrofuro[2,3-h]coumarin-9-one (13p), yield= 81%, yellow crystals, mp 350ºC. 1H NMR (DMSO-d_6, δ, ppm; J, Hz): 2.48 (d, 3H, 4-Me, $J_{Me,3}$ =1.1), 6.42 (q, 1H, 3-H, $J_{3,Me}$ =1.1), 7.40 (d, 6-H, $J_{6,5}$ =8.9), 7.61 (m, 1H, 5'-H), 7.22 (d, 1H, 6'-H, $J_{6',5'}$ =8.0), 7.76 (d, 1H, 4'-H, $J_{4',5'}$ =8.0), 8.12 (s, 1H, 2'-H), 8.17 (d, 1H, 5-H, $J_{5,6}$=8.9), 11.30 (s, 1H, NH).

MS (m/z, %): 365 (M+, 100), 202 (-3-$NO_2C_6H_4$-NH-N=C, 63), 174 (-3-$NO_2C_6H_4$-NH-N=C, -CO, 94).

Anal. calc. for $C_{18}H_{11}N_3O_6$: C 59.18, H 3.04, N 11.50; found: C 59.28, H 3.24, N 11.30.

Synthesis of 4-methyldihydrofuro[2,3-h]coumarin-8,9-diones, 8-(N-acetyl-N-aryl) hydrazones 14.

A solution of compound 13 (0.00026 mol) in acetic anhydride (6 ml) and pyridine (6 ml) was stirred for 1 hr at 50ºC and poured then into water (50 ml). The product was filtered off and recrystallized from acetic anhydride.

4-Methyldihydrofuro[2,3-h]coumarin-8,9-dione,8-*N*-acetyl-*N*-(4′-chlorophenyl) hydrazone 14d, yield=75%, yellow crystals, mp 320-322ºC. 1H NMR (DMSO-d_6, δ, ppm; J, Hz): 2.41 (d, 3H, 4-Me, $J_{Me,3}$ =1.1), 2.63 (s, 3H, Ac), 6.27 (q, 1H, 3-H, $J_{3,Me}$ =1.1), 7.22 (dd, 2H, 2'-H, 6'-H, $J_{2',3'}=J_{6',5'}$ =8.8, $J_{2',6'}$=2.1), 7.45 (dd, 2H, 3'-H, 5'-H, $J_{3',2'}=J_{5',6'}$=8.8, $J_{3',5'}$ =2.1), 6.66 (d, 1H, 6-H, $J_{6,5}$ =8.4), 7.77 (d, 1H, 5-H, $J_{5,6}$ =8.4).

MS (m/z, %): 396/398 (1Cl) (M+, 7), 354/356 (1Cl), (-CH_2=C=O, 100), 203 (- CH_2=C=O, -4-ClC_6H_4-N=N-C, 31), 202 (-CH_2=C=O, -4-ClC_6H_4-NH-N=CH, 24), 174 (-CH_2=C=O,-4-ClC_6H_4-NH-N=C, - CO, 31), 174 (- CH_2=C=O, - 4-ClC_6H_4-N=N-C, - HCO, 31)

Anal. calc. for $C_{20}H_{13}ClN_2O_5$: C 60.54, H 3.30, Cl 8.93, N 7.06; found: C 60.44, H 3.41, Cl 8.89 N 6.83

4-Methyldihydrofuro[2,3-h]coumarin-8,9-dione,8-*N*-acetyl-*N*-(4′-methylphenyl) hydrazone (14e). yield=80%, yellow crystals, mp 286-288ºC. 1H NMR (DMSO-d_6, δ, ppm; J, Hz): 2.40 (s, 3H, 4'-Me), 2.41 (d, 3H, 4-Me, $J_{Me,3}$ =1.1), 2.42 (s, 3H, NAc), 2.63 (s, 3H, Ac), 6.38 (q, 1H, 3-H, $J_{3,Me}$ =1.1), 7.24 (m, 4H, 2'-H, 3'-H, 5'-H, 6'-H,), 6.72 (d, 1H, 6-H, $J_{6,5}$ =8.6), 8.01 (d, 1H, 5-H, $J_{5,6}$ =8.6).

MS (m/z, %): 376 (M+, 2), 334 (-CH_2=C=O, 100).

Anal. calc. for $C_{21}H_{16}N_2O_5$: C 67.02, H 4.28, N 7.44; found: C 66.85, H 4.02, N 7.52.

Synthesis of 6-(*R*-phenylazo)-4-methyldihydrofuro[2,3-h]coumarin-9-ones (15 a-e). Compound 2b (0.00046 mol) was dissolved in 3%-solution of NaOH at 80°C and cooled then till room temperature. R-Phenyldiazonium tetrafluoroborate (0.00046 mol) was then added to the prepared solution of 2b. After stirring for 30 min reaction mixture was acidified. The precipitate was filtered off and recrystallized from chloroform.

6-**(3′-Ethylphenylazo)-4-methyldihydrofuro[2,3-h]coumarin-9-one 15d,** yield =70%, yellow crystals, mp 350°C. 1H NMR (DMSO-d_6, δ, ppm; J, Hz): 1.33 (t, 3H, Me, $J_{Me,-CH2-}$ =7.5), 2.51 (d, 3H, 4-Me, $J_{Me,3}$ =1.1), 2.78 (q, 2H, -CH_2-, $J_{-CH2-,Me}$ =7.5), 6.31 (q, 1H, 3-H, $J_{3,Me}$ =1.1), 7.53 (m, 4H, 2'-H, 4'-H, 5'-H, 6'-H), 8.25 (c, 1H, 5-H).

MS (m/z, %): 348 (M+, 100), 215 (-3-$C_2H_5C_6H_4$-N=N, 40).

Anal. calc. for $C_{20}H_{16}N_2O_4$: C 68.96, H 4.63, N 8.04; found: C 68.81, H 4.47, N 8.15.

4-Methyl-6-(4′-dimethylaminophenylazo)dihydrofuro[2,3-*h*]coumarin-9-one (15e). yield= 85%, red crystals, mp 350°C. 1H NMR (DMSO-d_6, δ, ppm; J, Hz): 2.50 (d, 3H, 4-Me, $J_{Me,3}$ =1.1), 3.13 (s, 6H, Me_2N), 4.89 (s, 2H, CH_2), 6.27 (q, 1H, 3-H, $J_{3,Me}$ =1.1), 6.75 (d, 2H, 3'-H, 5'-H, $J_{3',2'}$=$J_{5',6'}$=9.1), 7.91 (d, 2H, 2'-H, 6'-H, $J_{2',3'}$=$J_{6',5'}$=9.1), 8.18 (s,1H, 5-H).

MS (m/z, %): 363 (M+, 100).

Anal. calc. for $C_{20}H_{17}N_3O_4$: C 66.11, H 4.72, N 11.56; found: C 68.82, H 4.54, N 8.21.

6-Acetamido-4-methyldihydrofuro[2,3-*h*]coumarin-9-one (16b). 6-Amino-4-methyldihydrofuro[2,3-h]coumarin-9-one 16a (0.0004 mol) and acetic anhydride (10 ml) were heated for 10 min and cooled then until a precipitate formed.

The product was recrystallized from acetic acid, white crystals, yield=90%, mp 279-281°C. 1H NMR (DMSO-d_6, δ, ppm; J, Hz): 2.38 (d, 3H, 4-Me, $J_{Me,3}$ =1.1), 2.13 (s, 3H, Ac), 4.98 (s, 2H,CH_2), 6.33 (q, 1H, 3-H, $J_{3,Me}$ =1.1), 8.52 (s,1H,5-H), 9.99 (s, 1H, NH).

MS (m/z, %): 273 (M+, 90), 231 (-CH_2=C=O, 100), 203 (-CH_2=C=O, - CO, 65), 175 (-CH_2=C=O, -2CO, 47), 147 (- CH_2=C=O, -3CO, 6), 146 (- CH_2=C=O, -2CO, - HCO, 10), 118 (-CH_2=C=O, -3CO, - HCO, 16).

Anal. calc. for $C_{14}H_{11}NO_5$: C 61.54, H 4.06, N 5.13; found: C 61.50, H 4.15, N 5.12.

6-Formamido-4-methyldihydrofuro[2,3-*h*]coumarin-9-one (16c). 6-Amino-4-methyldihydrofuro[2,3-h]coumarin-9-one 16a (0.0004 mol) and formic acid (5 ml) were heated for 10 min and cooled then until a precipitate formed. The product was recrystallized from acetic acid, white crystals, yield=90%, mp 279-281°C. 1H NMR (DMSO-d_6, δ, ppm; J, Hz): 2.40 (d, 3H, 4-Me, $J_{Me,3}$ =1.1), 5.01 (s, 2H,CH_2), 6.35 (q, 1H, 3-H, $J_{3,Me}$ =1.1), 8.38 (s, 1H, CH), 8.69 (s, 1H, 5-H), 10.32 (s, 1H, NH).

MS (m/z, %): 259 (M+, 100), 231 (- CO, 20), 203 (- 2CO, 23), 175 (- 3CO, 36).

Anal. calc. for $C_{13}H_9NO_5$: C 60.24, H 3.50, N 5.40; found: C 60.20, H 3.55, N 5.39.

6-Azido-4-methyldihydrofuro[2,3-*h*]coumarin-9-one (16e). To the solution of 4-methyldihydrofuro[2,3-h]coumarin-9-one 6-diazonium chloride 16d (0.0011 mol) was added sodium azide (0.0015 mol). The precipitate was filtered off, dried and recrystallized from DMFA, yellow crystals, yield=40%, mp 204°C. 1H NMR (DMSO-d_6, δ, ppm; J, Hz): 2.41 (d, 3H, 4-Me, $J_{Me,3}$ =1.1), 4.82 (s, 2H,CH_2), 6.25 (q, 1H, 3-H, $J_{3,Me}$ =1.1), 7.37 (s, 1H, 5-H).

MS (m/z, %): 257 (M+, 15), 229 (- CO, 100).
Anal. calc. for $C_{12}H_7N_3O_4$: C 56.04, H 2.74, N 16.34; found: C 56.10, H 2.81, N 16.27.

6-Acetamido-9-acetoxy-4-methylfuro[2,3-*h*]coumarin (17a). 6-Amino-4-methyldihydrofuro[2,3-h]coumarin-9-one 16a (0.0004 mol), acetic anhydride (10 ml) and pyridine (5 ml) were heated for 20 min and cooled then until a precipitate formed. The product was recrystallized from acetic anhydride, white crystals, yield=80%, mp 228-230ºC. 1H NMR (DMSO-d_6, δ, ppm; J, Hz): 2.41 (s, 3H, OAc), 2.44 (d, 3H, 4-Me, $J_{Me,3}$ =1.1), 2.16 (s, 3H, Ac), 6.39 (q, 1H, 3-H, $J_{3,Me}$= 1.1), 7.09 (s, 1H, 5-H), 8.32 (s, 1H, 8-H), 10.16 (s, 1H, NH).
MS (m/z, %): 315 (M+, 24), 273 (-CH_2=C=O, 100), 231 (- 2CH_2=C=O, 74), 203 (- 2CH_2=C=O, - CO, 16), 202 (- 2CH_2=C=O, - HCO, 13).
Anal. calc. for $C_{16}H_{13}NO_6$: C 60.95, H 4.16, N 4.44; found: C 60.72, H 3.90, N 4.58.

6-Benzamido-9-benzoyloxy-4-methylfuro[2,3-*h*]coumarin (17b). 6-Amino-4-methyldihydrofuro[2,3-h]coumarin-9-one 16a (0.0004 mol), benzoyl chloride (0.007 mol), pyridine (1 ml) and chloroform (8 ml) were heated for 1 hr and cooled then until a precipitate formed. The product was recrystallized from chloroform, white crystals, yield=75%, mp 208-210ºC. 1H NMR (DMSO-d_6, δ, ppm; J, Hz): 2.48 (d, 3H, 4-Me, $J_{Me,3}$ =1.1), 6.36 (q, 1H, 3-H, $J_{3,Me}$ =1.1), 7.57-8.30 (m, 10H, H-Phenyls), 8.50 (s, 1H, 5-H), 7.91 (s, 1H, 8-H), 10.60 (s, 1H, NH).
MS (m/z, %): 439 (M+, 100), 334 (- PhCO, 20).
Anal. calc. for $C_{26}H_{17}NO_6$: C 60.95, H 4.16, N 4.44; found: C 60.72, H 3.90, N 4.58.

9-Hydroxy-4-methyldihydrofuro[2,3-*h*]counarins 18 a-g. Substituted 4-methyldihydrofuro[2,3-h]coumarin-9-one (0.0014 mol) and NaBH4 (2 mol) were stirred in methanol (20 ml) for 2 hrs at room temperature and poured then into water (30 ml). The precipitate was recrystallized from alcohol.

6-Chloro-9-hydroxy-4-methyldihydrofuro[2,3-*h*]coumarin (18a). light yellow crystals, yield=85%, mp 235-237ºC. 1H NMR (DMSO-d_6, δ, ppm; J, Hz): 2.47 (d, 3H, 4-Me, $J_{Me,3}$ =1.2), 4.63 (dd, 1H, 8a-H, J_{hem} =10.6, $J_{8\text{-}a,9}$ =2.2), 4.82 (dd, 1H, 8b-H, J_{hem} =10.6, $J_{8b,9}$ =6.2), 5.17 (d, 1H, 9-OH, $J_{9\text{-}OH,9}$= 6.0), 5.76 (ddd, 1H, 9-H, $J_{9,8b}$ =6.2, $J_{9,9\text{-}OH}$ =6.0, $J_{9,8a}$ =2.2), 6.19 (q, 1H, 3-H, $J_{3,Me}$ =1.2), 7.66 (s, 1H, 5-H).
MS (m/z, %): 252/254, (1 Cl), (M+, 100), 224/226, (1Cl), (- CO, 25), 195/197, (1 Cl), (- CO, - H2O, 23), 237/239, (1Cl), (- Me, 10).
Anal. calc. for $C_{12}H_9ClO_4$: C 57.05, H 3.59, Cl 14.03; found: C 57.22, H 3.72, Cl 14.18.

6-Ethyl-9-hydroxy-4-methyldihydrofuro[2,3-h]coumarin (18b). light yellow crystals, yield=85%, mp 205-206ºC. 1H NMR (DMSO-d_6, δ, ppm; J, Hz): 1.23 (t, 3H, Me, $J_{Me,CH2}$ =7.5), 2.44 (d, 3H, 4-Me, $J_{Me,3}$ =1.2), 4.56 (dd, 1H, 8a-H, J_{hem} =10.7, $J_{8\text{-}a,9}$ =2.2), 4.72 (dd, 1H, 8b-H, J_{hem} =10.7, $J_{8b,9}$ =6.2), 4.98 (d, 1H, 9-OH, $J_{9\text{-}OH,9}$ =5.0), 5.68 (ddd, 1H, 9-H, $J_{9,8b}$ =6.2, $J_{9,9\text{-}OH}$ =5.0, $J_{9,8a}$ =2.2), 6.09 (q, 1H, 3-H, $J_{3,Me}$ =1.2), 7.52 (s, 1H, 5-H).
MS (m/z, %): 246 (M+, 100), 218 (- CO, 20), 231 (- Me, 56), 203 (- Me, - CO, 27).
Anal. calc. for $C_{14}H_{14}O_4$: C 68.28, H 5.73; found: C 68.22, H 5.79.

Synthesis of 4-methyl-6-R-furo[2,3-h]coumarins 19. Compound 18 (0.00137 mol), dioxane (10 ml) and 20% H_2SO_4 (5 ml) were heated at 50°C for 1 hr and poured then into water. The precipitate was filtered off and recrystallized from chloroform.

6-Chloro-4-methylfuro[2,3-*h*]coumarin (19a). light yellow crystals, yield=80%, mp 209-210°C. 1H NMR (acetone-d_6, δ, ppm; J, Hz): 2.57 (d, 3H, 4-Me, $J_{Me,3}$ =1.0), 6.35 (q, 1H, 3-H, $J_{3,Me}$ =1.0), 7.29 (d, 1H, 9-H, $J_{9,8}$ =2.2), 7.77 (s, 1H, 5-H), 8.11 (d, 1H, 8-H, $J_{8,9}$ =2.2).

MS (m/z, %): 234/236, (1CI), (M+, 97), 206/208, (1Cl), (-CO, 100), 205/207, (1Cl), (-HCO, 85), 171 (- CO, - CI, 37).

Anal. calc. for $C_{12}H_7ClO_3$: C 61.41, H 2.98; found: C 61.62, H 3.18.

6-Ethyl-4-methylfuro[2,3-*h*]coumarin (19b). light yellow crystals, yield=83%, mp 182-183°C. 1H NMR (DMSO-d_6, δ, ppm; J, Hz): 1.36 (t, 3H, Me, $J_{Me,CH2}$ =7.4), 2.54 (d, 3H, 4-Me, $J_{Me,3}$ =1.0), 2.99 (q, 2H,-CH_2-, $J_{-CH2-,Me}$ =7.4), 6.26 (q, 1H, 3-H, $J_{3,Me}$ =1.0), 7.18 (d, 1H, 9-H, $J_{9,8}$ =2.2), 7.54 (s, 1H, 5-H), 7.99 (d, 1H, 8-H, $J_{8,9}$ =2.2).

MS (m/z, %): 228 (M+, 94), 200 (- CO, 49), 185 (- CO, - Me, 100), 213 (- Me, 84).

Anal. calc. for $C_{14}H_{12}O_3$: C 73.68, H 5.26; found: C 73.28, H 5.13.

Synthesis of acetoxyfurocoumarins 20a-j, 23. A substituted dihydrofurocoumarinone (0.005 mol), acetic anhydride (20 ml) and potassium acetate (0.0025 mol) were heated at 120°C for 1 hr. The reaction mixture was filtered and excess of acetic anhydride was distilled off. The precipitate was filtered off and recrystallized from acetone.

9'-Acetoxy-4-methylfuro[2,3-*h*]coumarin (20a). white crystals, yield =70%, mp 164-166°C. 1H NMR ($CDCl_3$, δ, ppm; J, Hz): 2.48 (s, 3H, OAc), 2.49 (d, 3H, 4-Me, $J_{Me,3}$ =0.9), 6.28 (q, 1H, 3-H, $J_{3,Me}$ =0.9), 7.39 (d, 1H, 6-H, $J_{6,5}$= 8.8), 7.54 (d, 1H, 5-H, $J_{5,6}$ =8.8), 7.90 (s, 1H, 8-H).

MS (m/z, %): 258 (M+, 20), 216 (-CH_2=C=O, 100), 188 (- CH_2=C=O, - CO, 30), 187 (- CH_2=C=O, - HCO, 10), 160 (- CH_2=C=O, - 2 CO, 18).

Anal. calc. for $C_{14}H_{10}O_5$: C 65.12, H 3.90, ; found: C 65.32, H 3.80.

9-Acetoxy-6-ethyl-4-methylfuro[2,3-*h*]coumarin (20b). white crystals, yield=70%, mp 213-214°C. 1H NMR ($CDCl_3$, δ, ppm; J, Hz): 1.36 (t, 3H, Me, $J_{Me,-CH2-}$ =7.4), 2.48 (s, 3H, OAc), 2.49 (d, 3H, 4-Me, $J_{Me,3}$ =0.9), 2.94 (q, 2H, -CH_2-, $J_{-CH2-,Me}$ =7.4), 6.25 (q, 1H, 3-H, $J_{3,Me}$ =0.9), 7.30 (s, 1H, 5-H), 7.88 (s, 1H, 8-H).

MS (m/z, %): 286 (M+, 15), 244 (-CH_2=C=O, 100), 229 (- CH_2=C=O, - Me, 14), 216 (- CH_2=C=O, - CO, 7), 188 (- CH_2=C=O, - 2CO, 13).

Anal. calc. for $C_{16}H_{14}O_5$: C 67.13, H 4.93, ; found: C 67.42, H 4.90.

9′-Acetoxy-8-chloro-4-methylfuro[2,3-*h*]coumarin (20c). white crystals, yield =70%, mp 210-211°C. 1H NMR ($CDCl_3$, δ, ppm; J, Hz): 2.51 (s, 3H, OAc), 2.46 (d, 3H, 4-Me, $J_{Me,3}$ =0.9), 6.25 (q, 1H, 3-H, $J_{3,Me}$ =0.9), 7.32 (d, 1H, 6-H, $J_{6,5}$ =8.8), 7.50 (d, 1H, 5-H, $J_{5,6}$ =8.8).

MS (m/z, %): 292/294 (1Cl) (M+, 17), 250/252 (1Cl) (-CH_2=C=O, 100), 222/224 (- CH_2=C=O, - CO, 9), 221/223 (1Cl) (- CH_2=C=O, - HCO, 8).

Anal. calc. for $C_{14}H_9ClO_5$: C 57.40, H 3.07, Cl 12.13 ; found: C 57.32, H 3.03, Cl 12.18.

9′-Acetoxy-8-bromo-4-methylfuro[2,3-*h*]coumarin (20d). white crystals, yield =75%, mp 225-227ºC. 1H NMR ($CDCl_3$, δ, ppm; J, Hz): 2.51 (s, 3H, OAc), 2.46 (d, 3H, 4-Me, $J_{Me,3}$ =0.9), 6.25 (q, 1H, 3-H, $J_{3,Me}$ =0.9), 7.34 (d, 1H, 6-H, $J_{6,5}$ =8.8), 7.49 (d, 1H, 5-H, $J_{5,6}$=8.8).
MS (m/z, %): 336/338 (1Br) (M+, 12), 294/296 (1Br) (-CH_2=C=O, 100), 266/268 (1Br) (-CH_2=C=O, - CO, 7), 238/240 (1Br) (- CH_2=C=O, - 2CO, 23), 159 (- CH_2=C=O, -2CO, -Br, 33).
Anal. calc. for $C_{14}H_9BrO_5$: C 49.83, H 2.67, Br 23.70 ; found: C 49.88, H 2.69, Br 23.70.
9′-Acetoxy-8-acetyl-4-methylfuro[2,3-*h*]coumarin (20h). white crystals, yield= 65%, mp 195-196ºC. 1H NMR ($CDCl_3$, δ, ppm; J, Hz): 2.58 (s, 3H, OAc), 2.49 (d, 3H, 4-Me, $J_{Me,3}$ =0.9), 2.59 (s, 3H, Ac), 6.29 (q, 1H, 3-H, $J_{3,Me}$ =0.9), 7.45 (d, 1H, 6-H, $J_{6,5}$=8.8), 7.70 (d, 1H, 5-H, $J_{5,6}$ =8.8).
MS (m/z, %): 300 (M+, 7), 258 (-CH_2=C=O, 100), 230 (- CH_2=C=O, - CO, 20), 243 (-CH_2=C=O, - Me, 39), 215 (- CH_2=C=O, - Me-C=O, 9).
Anal. calc. for $C_{16}H_{12}O_6$: C 64.00, H 4.03; found: C 64.17, H 3.93.
8-(4′-Methyldihydrofuro[2′,3′-*h*]coumarin-9′-one-8′-methylideno) -4-methyldi hydrofuro[2,3-h]coumarin-9-one (21). Compound 7g (0.002 mol) and acetic anhydride (20 ml) were heated at 130ºC for 2 hrs. The precipitate was filtered off and washed with hot acetone. Compound 21, yellow crystals, yield =45%, mp 308ºC (decomp.). 1H NMR (DMSO-d_6, δ, ppm; J, Hz): 2.55 (d, 3H, 4-Me, $J_{Me,3}$ =1.2), 2.57 (d, 3H, 4'-Me, $J_{Me,3'}$ =0.9), 6.29 (q, 1H, 3-H, $J_{3,Me}$ =1.2), 6.44 (q, 1H, 3'-H, $J_{3',Me}$ =0.9), 6.96 (s, 1H, =C-H), 7.49 (d, 1H, 6-H, $J_{6,5}$ =9.0), 7.67 (d, 1H, 6'-H, $J_{6',5'}$ =8.8), 7.91 (d, 1H, 5'-H, $J_{5',6'}$= 8.8), 8.23 (d, 1H, 5-H, $J_{5,6}$ =9.0).
MS (m/z, %): 442 (M+, 100), 425(- OH, 10), 414(- CO, 5), 385 (- CO, -HCO, 7).
Anal. calc. for $C_{25}H_{14}O_8$: C 67.88, H 3.19; found: C 67.93, H 3.28
4-Methylfuro[2,3-*g*]coumarin (22). Compound 3b (0.001 mol), $NaBH_4$ (0.0011 mol) and ethanol (7ml) were stirred at room temperature for 2 hrs. The mixture was then acidified by phosphorous acid and heated under boiling for 1 hr. The precipitate was filtered off and recrystallized from ethanol. Compound 22, white crystals, yield =65%, mp 200ºC. 1H NMR (DMSO-d_6, δ, ppm; J, Hz): 2.49 (d, 3H,4-Me, $J_{Me,3}$=1.1), 6.43 (q, 1H, 3-H, $J_{3,Me}$=1.1), 7.07 (dd, 1H, 6-H, $J_{6,7}$=2.5, $J_{6,5}$=0.8), 7.67 (d, 1H, 5-H, $J_{5,6}$=0.8), 8.07 (s, 1H, 9-H), 8.08 (d, 1H, 7-H, $J_{7,6}$ =2.5).
MS (m/z, %): 200 (M+,100).
Anal. calc. for $C_{12}H_8O_3$: C 72.00, H 4.03; found: C 71.79, H 3.88.
6-Acetoxy-4,9-dimethylfuro[2,3-*g*]coumarin (23). white crystals, yield =73%, mp 195-196ºC. 1H NMR ($CDCl_3$, δ, ppm; J, Hz): 2.42 (s, 3H, 9-Me), 2.52 (d, 3H, 4-Me, $J_{Me,3}$=1.2), 2.59 (s, 3H, OAc),6.28 (q, 1H, 3-H, $J_{3,Me}$=1.2), 7.62 (s, 1H, 5-H,), 8.11 (s, 1H, 7-H).
MS (m/z, %): 272 (M+, 24), 230 (- CH_2=C=O, 100), 202 (- CH_2=C=O, -CO, 22), 201 (-CH_2=C=O, - HCO, 15).
Anal. calc. for $C_{14}H_{10}O_5$: C 65.12, H 3.90; found: C 65.39, H 3.88.
4-Methyl-7-(4′-methoxyphenylazo)dihydrofuro[2,3-*g*]coumarin (24). This compound has been prepared similarly to preparation of the compounds 13

Red crystals, yield =70%, mp 280-282°C. 1H NMR ($CDCl_3$, δ, ppm; J, Hz): 2.48 (d, 3H,4-Me, $J_{Me,3}$=1.1), 3.81 (s, 3H, 4'-OMe), 6.31 (q, 1H, 3-H, $J_{3,Me}$=1.1), 6.92 (d, 2H, 3'-H, 5'-H, $J_{3',2'}$=$J_{5',6'}$=9.0), 7.22 (d, 2H, 2'-H, 6'-H, $J_{2',3'}$=$J_{6',5'}$=9.0), 8.12 (s, 1H, 5-H), 8.33 (s, 1H, NH).
MS (m/z, %): 350 (M+,100), 335 (- Me, 7.3), 203 (- 4-$MeOC_6H_4$-N==N=C, 12), 174 (- 4-$MeOC_6H_4$-N==N=C, -HCO, 10).
Anal. calc. for $C_{19}H_{14}N_2O_5$: C 65.14, H 4.03; N 8.00; found: C 65.22, H 4.31, N 8.31.

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