Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

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Version of record first published: 22 Feb 2010

To cite this article: Myriam Kammoun, Hamida Turki, Suzanne Fery-Forgues & Rachid El Gharbi (2010): Convenient Synthesis of a New Series of 3-Triazolonyl Iminocoumarins, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 40:6, 888-900

To link to this article: http://dx.doi.org/10.1080/00397910903026681

Synthetic Communications®, 40: 888–900, 2010

ISSN: 0039-7911 print/1532-2432 online
DOI: 10.1080/00397910903026681

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CONVENIENT SYNTHESIS OF A NEW SERIES OF 3-TRIAZOLONYL IMINOCOUMARINS

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3-Cyano-7-diethylamino-N-ethoxycarbonyl-iminocoumarin reacted with different hydrazines as N-nucleophiles to afford, in one step, a new series of 2-N-substituted 3-triazolonyl-iminocoumarins in good yields. In two cases, N-unsubstituted derivatives were also obtained. The structures of all the products obtained were confirmed by infrared, ^{1}H NMR, ^{13}C NMR, and elemental analysis. The optical properties of three of these compounds in dichloromethane and ethanol were reported.

Keywords: Iminocoumarin; spectroscopic properties; 3-triazolonyl iminocoumarin

INTRODUCTION

Coumarins (2-oxo-2*H*-1-benzopyrans) have been extensively investigated with regard to their interest as fluorescent dyes[1,2] and biologically active compounds.[3–5] The 2-imino analogs (2-imino-2*H*-1-benzopyrans) are less known and were considered for a long time as an intermediate in the synthesis of coumarins.[6] In the past decade, many articles dealing with their synthesis and reactivity have been published.[7–22] Some compounds of this family have found nice applications in the field of fluorescent sensors,[23,24] and others are promising antimicrobial agents.[25,26] Above all, the past few years have seen a burst of interest in these compounds because of their use as starting materials in elaborate condensed heterocyclic compounds[10–14] and functionalized coumarins[15–22] that may exhibit original biological activities. In particular, it seems that the presence of a hetaryl moiety on the 3-position of the coumarinic system induces specific activities,[27] and use of iminocoumarins is part of the best routes to access these compounds, which are quite difficult to obtain otherwise.

During the past few years, the synthesis and reactivity of 3-cyano-iminocoumarin and its derivatives have attracted our attention. O'Callaghan et al.

Received January 6, 2009.

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described the cyclization of 3-cyano-iminocoumarin into fused heterocycles under the action of C-nucleophilic reagent.[14] In a recent study dealing with ethoxycarbonylated cyano-iminocoumarins, we found that these compounds are convenient starting materials to provide polyheterocyclic systems when treated with various nucleophilic or electrophilic reagents. More precisely, we showed that they are readily recyclized by amines and hydrazides of carboxylic acids used as N-nucleophiles to give 2-oxo-2H-1-benzopyrano-[2,3-d]-pyrimidines bearing an arylamino or acylhydrazino fragment in the 4-position.[28,29] As a continuation of our studies, we investigate here the interaction of N-ethoxycarbonylated iminocoumarin with hydrazines to determine new synthetic capabilities. We chose to work with hydrazines that bear an arylhalogenated group because it has been known for long that coumarin derivatives provided with this type of substituent exhibit strong activity as anticoagulant rodenticides[30,31] and anti-inflammatory agents.[4,32] The present article describes an "unusual" reaction of 3-cyano-7-diethylamino-*N*-ethoxycarbonyl-iminocoumarin **1** with various hydrazines as an efficient way to obtain a new series of iminocoumarins containing a triazolonic heterocycle in the 3-position. To the best of our knowledge, triazolonyl iminocoumarins are unknown, and they might exhibit interesting biological activities. The optical properties of some of these new 3-hetaryl iminocoumarins are also described.

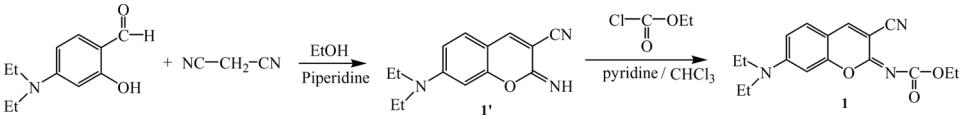
RESULTS AND DISCUSSION

Synthesis

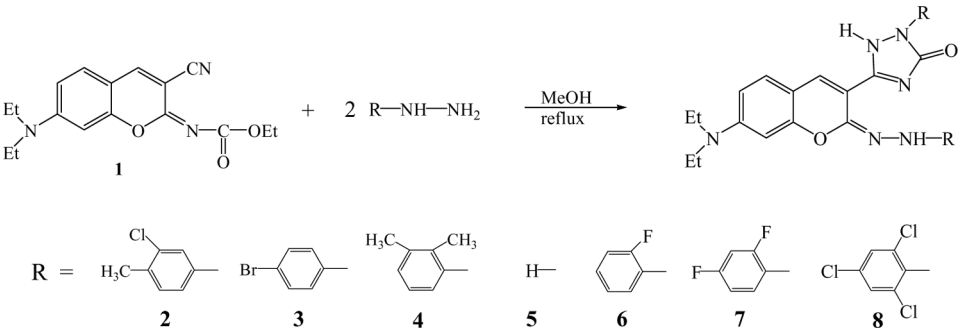
3-Cyano-iminocoumarin **1** was obtained by Knoevenagel protocol followed by *N*-ethoxycarbonylation as already described in previous work[28] and recalled in Scheme 1.

Then, the experimental conditions of the condensation of **1** with hydrazines were optimized. A detailed study was carried out using 3-chloro-4-tolylhydrazine. It showed that both compounds reacted in a 1:2 molar ratio by heating in absolute methanol to give the functionalized iminocoumarin **2** in one step in 85% yield (Scheme 2).

It must be noted that when the reaction was conducted in a 1:1 molar ratio, the same product was obtained but with a lower yield. Product **2** was isolated by simple filtration with high purity as confirmed by the ^{1}H NMR spectrum. The analytical data agreed with the formula $C_{29}H_{28}Cl_2N_6O_2$ in accordance with the structure of **2** established from Fourier transform infrared (FTIR) and NMR spectra. The FTIR spectrum showed the disappearance of the original peaks at 2214 and 1724 cm^{-1} arising from the C≡N and COOEt functions, respectively, as well as the appearance of absorption bands indicating the formation of the triazolonic heterocycle: NH (3200



Scheme 1.



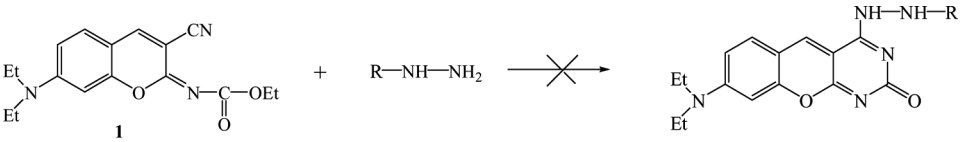
Scheme 2.

and 3350 cm^{-1}), C=N (1626 cm^{-1}), and C=O (1709 cm^{-1}). These characteristic absorptions are in accordance with the literature data related to triazolonic heterocycle (around 1640 cm^{-1} for C=N, 1705 cm^{-1} for C=O, and 3200 cm^{-1} for NH),[33] whereas absorption bands in pyrimidines analogs previously described[28] appeared at 1650 cm^{-1} (C=O) and 1570 cm^{-1} (C=N). The analysis of these spectroscopic data indicates that condensation of iminocoumarin **1** with hydrazines gave selectively the corresponding triazolonyl iminocoumarin, whereas reaction leading to benzopyranopyrimidines did not take place (Scheme 3).

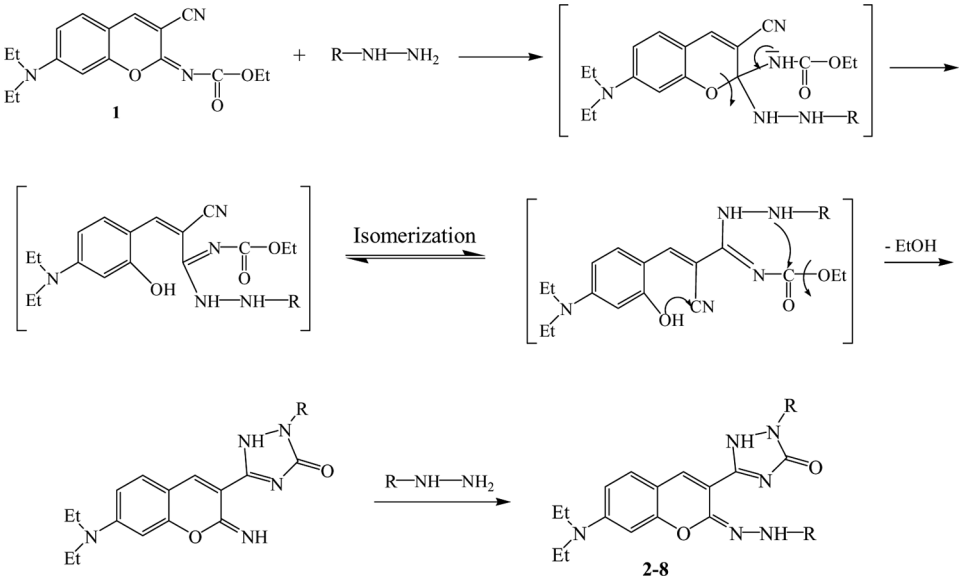
The structure of compound **2** was also confirmed by NMR spectroscopy. The ^{1}H NMR spectrum showed the peaks arising from two chlorotolyl groups at 1.13 and 7.02–7.43 ppm, which indicates that two molecules of hydrazine have reacted. The ^{1}H NMR and two-dimensional (2D) correlation spectra showed the presence of two resonances (9.46 and 12.10 ppm) related to NH, which were attributed by comparison with analogous structures reported in the literature: the peak at 12.10 ppm corresponds to the NH function of the triazolonic heterocycle (literature: 11 ppm),[34] and the resonance at 9.46 ppm is due to the NH function of the substituted amino group (literature: 9.5 ppm).[22]

We show in Scheme 4 a possible mechanism involving several steps: (i) the nucleophilic attack of hydrazine on the imidic function followed by the opening of the pyrane ring, (ii) the Z/E isomerization of the amidine intermediate, (iii) cyclizations to the iminocoumarin system and trizolonic heterocycle, and finally (iv) the interaction between the hydrazinic fragment and the carbonyl group, leading to the formation of the triazolonic heterocycle. The reaction does not stop at this stage but goes further to 2-*N*-substituted imincoumarins.[19,22]

Hydrazine itself and five hydrazines provided with a phenyl group bearing up to three substitutions behaved analogously when reacted with **1** under the same



Scheme 3.



Scheme 4.

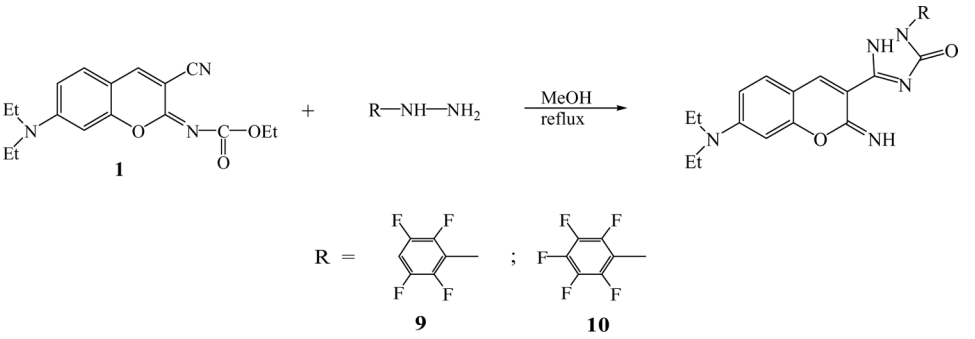
conditions. They all afforded the corresponding *N*-substituted triazolonyl-iminocoumarins (Scheme 2, Table 1). It can be noted that the reaction yield was particularly good for the aromatic hydrazines.

In contrast, hydrazines whose phenyl group was highly substituted by fluorine atoms reacted with **1** in a 1:1 molar ratio, leading to triazolonyl-iminocoumarins **9** and **10**, respectively, without any substitution on the imidic nitrogen atom (Scheme 5, Table 1). All attempts to obtain the corresponding *N*-substituted imino-coumarins using a molar ratio of 1:2 were unsuccessful, whatever the experimental conditions used.

Table 1. Synthesis of iminocoumarins **2–10**

Compound	Time (h)	Yield (%)	Mp (°C)
2	2	85	234
3	1.5	76	132
4	1.5	97	202
5	6	60	—[a]
6	2	90	249
7	2	70	245
8	8	85	210
9[b]	0.75	55	285
10[b]	3.5	43	256

[a]Decomposition temperature = 170 °C.
[b]Only N-unsubstituted compounds were obtained in all experiments.



Scheme 5.

Optical Properties

Coumarins make up a well-known family of fluorescent compounds. Iminocoumarins, which have almost the same aromatic system, also display interesting optical properties.[35–39] This is the reason why we had a cursory glance at the spectroscopic behavior of our compounds. Except for compound **5**, all the other compounds bear at least one phenyl group, and it can be noticed that this group is hardly involved in the electron conjugated system of the iminocoumarin structure. Consequently, the substitution of the phenyl group in the hydrazine function should have only a moderate influence upon the spectroscopic properties, via inductive or steric effect, and it can be expected that these compounds display similar behavior. Therefore, the optical properties were only measured on three of them, namely compounds **2**, **3**, and **10**. The results are gathered in Table 2. There were compared with those previously reported for 3-cyano-7-diethylamino-iminocoumarin **1′**.[35,36]

Compounds **2**, **3**, and **10** were poorly soluble in organic solvents. However, they could be studied in ethanol and dichloromethane at concentrations around 10^{-5} M for absorption and 10^{-6} M for fluorescence. In the visible spectrum, the absorption spectrum of the three compounds displayed only one band peaking around 450 nm, with an absorption tail extending until 560–580 nm. Therefore, the

Table 2. Maximum absorption wavelength (λ_{abs}), maximum excitation wavelength (λ_{ex}), maximum emission wavelength (λ_{em}), fluorescence lifetime (τ), and fluorescence quantum yield (Φ) of compounds **2**, **3**, and **10** in EtOH and CH_2Cl_2 (the values given for 3-cyano-7-diethylamino-iminocoumarin **1′** are from Refs. 35 and 36; sh = shoulder)

Compound	λ_{abs} (nm)	λ_{ex} (nm)	λ_{em} (nm)	τ (ns)	Φ
2 (EtOH)	450	440	498	1.5 ± 0.3	0.031 ± 0.003
2 (CH_2Cl_2)	458	447	496	2.0 ± 0.4	0.047 ± 0.005
3 (EtOH)	450	446	504	1.5 ± 0.3	0.054 ± 0.005
3 (CH_2Cl_2)	454	450	502	2.7 ± 0.2	0.11 ± 0.01
10 (EtOH)	444	441	504	0.7 ± 0.2	0.018 ± 0.002
10 (CH_2Cl_2)	450	450	520 (sh 500)	1.9 ± 0.5	0.019 ± 0.002
1′ (EtOH)	424	—	468	—	0.33 ± 0.02
1′ (CH_2Cl_2)	414 (sh 428)	414 (sh 429)	460 (sh 482)	2.9 ± 0.5	0.84 ± 0.02

small structural differences between these compounds did not lead to significant spectroscopic effect. In contrast, comparing the absorption spectra of compounds **10** and **1′** showed that the substitution of the cyano group by a hetaryl cycle induced a significant red shift of about 20 nm.

The three compounds were fluorescent. Normalized spectra in ethanol are given in Fig. 1. In ethanol, the three compounds displayed similar excitation spectra, as well as similar emission spectra, confirming that substitution on the imino group hardly changes the spectroscopic characteristics. This was also the case in dichloromethane, except that the emission spectrum of **10** slightly differed from that of the two other compounds (Table 2), a particularity that can be attributed to a specific solvent effect.

The excitation spectrum had the same shape as the absorption spectrum, but in most cases it was narrower and its maximum was slightly shifted to short wavelengths. This discrepancy suggests that despite careful filtration, the solutions still contained a small amount of undissolved compounds. These aggregates are visible on the red side of the absorption spectra but are not fluorescent. In fact, the excitation spectra did not vary with the emission wavelength, and conversely, the emission spectra were independent of the excitation wavelength. This indicates the presence of only one fluorescent species in each solution. The fluorescence quantum yields of the three hetaryl-iminocoumarins were measured, but the values lack precision because of the presence of undissolved material that contributes to absorption but not to fluorescence. Besides, an evolution of the fluorescence intensity with time was noticed for compound **3** in ethanol. It can be attributed either to dissolution of aggregates or to the decomposition of the compound toward a more fluorescent species. However, the quantum yield values clearly indicate that the hetaryliminocoumarins are much less fluorescent than **1′**, although all the lifetime values remained in the nanosecond range, close to that of compound **1′**. Substituting the cyano group by a triazolonyl group, which probably introduces $n \rightarrow \pi^*$ transitions, is thus particularly unfavorable to fluorescence. Finally, it can be pointed out that compounds **2**,

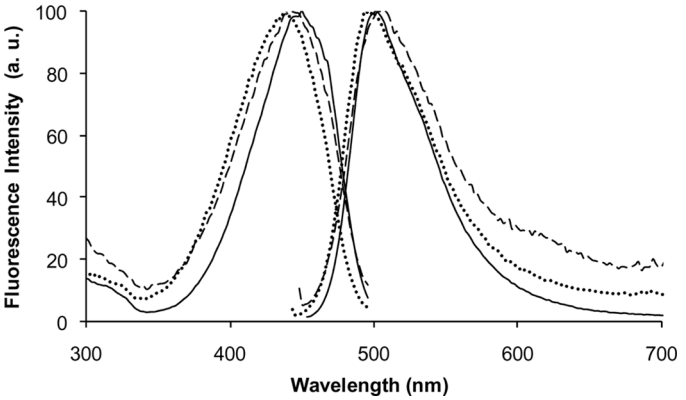


Figure 1. Normalized excitation and emission spectra of compounds **2** (dotted line), **3** (plain line), and **10** (broken line) in ethanol. For emission spectra, $\lambda_{ex} = \lambda_{abs}$ max. For excitation spectra, λ_{em} is set at the maximum intensity wavelength.

3, and **10** were slightly more fluorescent in dichloromethane than in ethanol, a behavior that has already been noticed for other iminocoumarins and is discussed elsewhere.[35]

CONCLUSION

In marked contrast with the results obtained when amines or hydrazides of carboxylic acids were used as nucleophilic reagents under similar conditions,[28,29] the recyclization of 3-cyano-7-diethylamino-N-ethoxycarbonyl-iminocoumarin by hydrazines did not lead to the expected benzopyranopyrimidines. In this case, the reaction followed an original mechanism leading to the corresponding 3-triazolonyl-iminocoumarins, substituted or not on the nitrogen atom of the imino group. The compounds obtained displayed no attractive optical properties. However, this work opens an interesting avenue for the synthesis of a new family of iminocoumarins that might exhibit particular biological properties. Besides, our synthesis allowed the easy introduction of an arylhalogenated group, borne by the triazolonyl group in the 3-position of the iminocoumarin heterocycle. The compounds thus obtained could be interesting intermediates to prepare analogs of 3-arylhalogenated-coumarins, knowing that many compounds of this series (for example, coumachlor)[30,31] have proved to be particularly active as pesticides.

EXPERIMENTAL

Hydrazines were commercially available from Aldrich. 3-Cyano-N-ethoxycarbonyl-7-diethylamino-iminocoumarin **1** was prepared as previously described.[28] Ethanol and dichloromethane (analytical grade) used for spectroscopic measurements were from VWR Prolabo and SDS, respectively. The melting points were determined on an Electrothermal 9100 apparatus. IR spectra were registered on a Jasco FTIR 420 spectrophotometer apparatus using KBr pellets. ^{1}H and ^{13}C NMR and CHcorr spectra were recorded on a Bruker WP 200 spectrometer operating at 300 and 75 MHz, respectively, in dimethylsulfoxide (DMSO-d_6) with tetramethylsilane (TMS) as internal standard (chemical shifts in ppm). Elemental microanalyses were preformed on a EA1112 analyser from CE Instruments at the Service Commun de Microanalyses de l'ENCIACET. Ultraviolet (UV)/vis absorption spectra were recorded on a Hewlett-Packard 8452A diode array spectrophotometer. Steady-state fluorescence work was performed on a Photon Technology International (PTI) Quanta Master 1 spectrofluorometer. All excitation and emission spectra were corrected. The fluorescence quantum yields (Φ) were determined using the classical formula: $\Phi = (A_s F_x n_x^2 \Phi_s)/(A_x F_s n_s^2)$ where A is the absorbance at the excitation wavelength, F is the area under the fluorescence curve, and n is the refractive index. Subscripts s and x refer the standard and the sample of unknown quantum yield, respectively. Coumarin 6 in ethanol ($\Phi = 0.78$) was taken as the standard.[40] Fluorescence decay was measured with the stroboscopic technique using a Strobe Master Fluorescence lifetime spectrophotometer from PTI. The excitation source was a flash lamp filled with a mixture of nitrogen and helium (30/70). Data were collected over 200 channels with a time base of 0.1 ns per channel. Analysis of fluorescence decay was performed using the multiexponential method software from

PTI. All spectrophotometric measurements were conducted in a thermostated cell at 25 °C. For spectroscopic work, compounds **2**, **3**, and **10** were purified by thin-layer chromatography (TLC) on silica plate using chloroform as the eluent. The solutions were carefully filtrated on paper filter before use.

General Procedure for the Synthesis of N-Substituted 3-Triazolonyl Iminocoumarins 2–8

A solution of 3-cyano-N-ethoxycarbonyl-7-diethylamino-iminocoumarin **1** (5 mmol) and hydrazine (10 mmol) in 30 ml of absolute methanol was refluxed during the time indicated in Table 1. After complete reaction, the *N*-substituted 3-hetaryl iminocoumarin obtained was separated by filtration and washed with methanol.

General Procedure for the Synthesis of 3-Hetaryl-iminocoumarins 9–10

A solution of 3-cyano-N-ethoxycarbonyl-7-diethylamino-iminocoumarin **1** (5 mmol) and hydrazine (5 mmol) in 30 ml of absolute methanol was refluxed during the time indicated in Table 1. After complete reaction, the simple 3-hetaryl iminocoumarin obtained was separated by filtration and washed with methanol.

Data

3-[1-(3-Chloro-4-tolyl)-5-oxo-2,5-dihydro-[1*H*]-[1,2,4]triazol-3-yl]-2-*N*-[3-chloro-4-tolylamino]-2-imino[2*H*]coumarin (2). Orange-brown solid, IR (cm^{-1}): $\nu = 1577$ (C=C), 1626 (C=N), 1709 (C=O), 3200 and 3350 (NH). ^1H NMR: $\delta = 1.13$ (t, $J = 6.9$ Hz, 6H, CH_3), $\delta = 2.19$ (s, 3H, CH_3), $\delta = 2.32$ (s, 3H, CH_3), 3.41 (q, $J = 6.9$ Hz, 4H, CH_2N), 6.50 (d, $J_{5,6} = 9.0$, 1H, H_6), 6.53 (s, 1H, H_8), 7.02 (d, $J = 8.1$ Hz, 1H, HAr), 7.12 (d, $J = 8.1$ Hz, 1H, HAr), 7.23 (d, $J = 8.1$ Hz, 2H, HAr), 7.42 (d, $J = 8.1$ Hz, 2H, HAr), 7.87 (d, $J_{5,6} = 9.0$ Hz, 1H, H_5), 8.08 (s, 1H, H_4), 9.46 (s, 1H, NH), 12.10 (s, 1H, NH). ^{13}C NMR: $\delta = 12.82$ ($2CH_3$), 19.01 (CH_3-Ar), 19.38 (CH_3-Ar), 44.43 ($2CH_2N$), 97.00 (C_6), 107.53 (C_{10}), 107.89 (C_3), 109.59 (C_8), 111.74 (CH-Ar), 112.79 (CH-Ar), 116.54 (C_5), 117.90 (C_4), 124.29 (C-CH_3(Ar)), 129.87 (CH-Ar), 130.30 (CH-Ar), 131.56 (CH-Ar), 131.90 (C-CH_3(Ar)), 131.91 (CH-Ar), 133.76 (C-Cl), 133.82 (C-Cl), 137.18 (C-N (Ar)), 138.16 (C-N (Ar)), 140.76 (C_7), 142.84 (C-Ar), 145.31 (NH-C=N), 150.47 (C_9), 152.43 (C_2), 154.77 (C=O). Calculated for $C_{29}H_{28}Cl_2N_6O_2$: C, 61.81; H, 5.01; N, 14.91%. Found: C, 61.46; H, 5.33; N, 14.35%.

3-[1-(4-Bromophenyl)-5-oxo-2,5-dihydro-[1*H*]-[1,2,4]triazol-3-yl]-2-*N*-[4-bromophenylamino]-2-imino[2*H*]coumarin (3). Orange-brown solid, IR (cm^{-1}): $\nu = 1587$ (C=C), 1622 (C=N), 1713 (C=O), 3271 and 3368 (NH). ^1H NMR: $\delta = 1.13$ (t, $J = 6.9$ Hz, 6H, CH_3), 3.39 (q, $J = 6.9$ Hz, 4H, CH_2N), 6.49 (dd, $J_{5,6} = 8.4$, $J_{6,8} = 1.8$ Hz, 1H, H_6), 6.53 (d, $J_{6,8} = 1.8$ Hz, 1H, H_8), 7.11 (d, $J = 8.7$ Hz, 2H, HAr), 7.33 (d, $J = 8.7$ Hz, 2H, HAr), 7.66 (d, $J = 8.7$ Hz, 2H, HAr), 7.95 (d, $J = 8.7$ Hz, 2H, HAr), 7.25 (d, $J_{5,6} = 8.4$ Hz, 1H, H_5), 7.41 (s, 1H, H_4), 8.30 (s, 1H,

NH), 9.53 (s, 1H, NH). ^{13}C NMR: δ = 11.55 ($2CH_3$), 43.17 ($2CH_2N$), 95.77 (C_8), 106.26 (C_{10}), 106.66 (C_6), 108.12 (C_3), 108.47 (C-Br), 113.50 (CH-Ar), 115.94 (C-Br), 118.69 (CH-Ar), 128.64 (C_5), 129.19 (C_4), 130.44 (CH-Ar), 130.99 (CH-Ar), 136.16 (C-N (Ar)), 137.26 (C-N (Ar)), 141.76 (C_7), 143.87 (NH-C=N), 149.21 (C_2), 151.17 (C_9), 153.54 (C=O). Calculated for $C_{27}H_{24}Br_2N_6O_2$: C, 51.94; H, 3.87; N, 13.46%. Found: C, 52.26; H, 3.49; N, 13.66%.

3-[1-(2,3-Dimethylphenyl)-5-oxo-2,5-dihydro-[1*H*]-[1,2,4]triazol-3-yl]-2-*N*-[2,3-dimethylphenylamino]-2-imino[2*H*]coumarin (4). Orange-brown solid, IR (cm^{-1}): ν = 1572 (C=C), 1619 (C=N), 1722 (C=O), 3289 and 3308 (NH). ^{1}H NMR: δ = 1.23 (t, J = 7.0 Hz, 6H, CH_3), δ = 2.33 (s, 6H, CH_3), δ = 2.35 (s, 6H, CH_3), 3.43 (q, J = 7.0 Hz, 4H, CH_2N), 6.36 (d, $J_{6,8}$ = 2.1 Hz, 1H, H_8), 6.44 (dd, $J_{5,6}$ = 8.7, $J_{6,8}$ = 2.1 Hz, 1H, H_6), 7.11 (d, $J_{5,6}$ = 8.7 Hz, 1H, H_5), 7.15–7.30 (m, 6 H, HAr), 7.65 (s, 1H, NH), 7.70 (s, 1H, H_4), 10.30 (s, 1H, NH). ^{13}C NMR: δ = 12.96 ($2CH_3$), 15.00 (CH_3Ar), 20.78 (CH_3Ar), 20.89 (CH_3Ar), 31.33 (CH_3Ar), 45.10 ($2CH_2N$), 97.27 (C_8), 108.35 (C_{10}), 108.48 (C_3), 108.66 (C_6), 111.21 (C_5), 120.24 (CAr), 122.44 (CH-Ar), 125.63 (CH-Ar), 126.51 (CH-Ar), 127.24 (CH-Ar), 128.25 (C_4), 129.88 (CH-Ar), 130.85 (CH-Ar), 134.79 (CAr), 135.82 (CAr), 137.31 (CAr), 138.76 (C-N (Ar)), 141.21 (C-N (Ar)), 141.79 (C_7), 142.74 (NH-C=N), 150.79 (C_2), 152.91 (C_9), 154.91 (C=O). Calculated for $C_{31}H_{34}N_6O_2$: C, 71.24; H, 6.56; N, 16.08. Found: C, 71.48; H, 6.37; N, 16.33.

3-(5-Oxo-2,5-dihydro-[1*H*]-[1,2,4]triazol-3-yl)-2-*N*-amino-2-imino[2*H*]-coumarin (5). Red solid, IR (cm^{-1}): ν = 1606 (C=C), 1647 (C=N), 1688 (C=O), 3300 and 3350 (NH). ^{1}H NMR: δ = 1.09 (t, J = 6.9 Hz, 6H, CH_3), 3.35 (q, J = 6.9 Hz, 4H, CH_2N), 5.71 (s, 2H, NH_2), 6.40 (d, $J_{5,6}$ = 8.7 Hz, 1H, H_6), 6.42 (s, 1H, H_8), 7.17 (d, $J_{5,6}$ = 8.7 Hz, 1H, H_5), 7.23 (s, 1H, H_4), 10.87 (s, 1H, NH), 11.55 (s, 1H, NH). ^{13}C NMR: δ = 12.94 ($2CH_3$), 44.46 ($2CH_2N$), 97.29 (C_6), 107.55 (C_8), 107.71 (C_{10}), 111.10 (C_3), 127.00 (C_4), 129.61 (C_5), 140.04 (C_7), 142.71 (NH-C=N), 150.09 (C_2), 154.87 (C_9), 155.65 (C=O). Calculated for $C_{15}H_{18}N_6O_2$: C, 57.31; H, 5.77; N, 26.74. Found: C, 57.40; H, 5.88; N, 26.42.

3-[1-(2-Fluorophenyl)-5-oxo-2,5-dihydro-[1*H*]-[1,2,4]triazol-3-yl]-2-*N*-[2-fluorophenylamino]-2-imino[2*H*]coumarin (6). Red-brown solid, IR (cm^{-1}): ν = 1580 (C=C), 1608 (C=N), 1708 (C=O), 3326 and 3350 (NH). ^{1}H NMR: δ = 1.16 (t, J = 6.9 Hz, 6H, CH_3), 3.44 (q, J = 6.9 Hz, 4H, CH_2N), 6.50 (dd, $J_{5,6}$ = 8.7, $J_{6,8}$ = 1.8 Hz, 1H, H_6), 6.66 (d, $J_{6,8}$ = 1.8 Hz, 1H, H_8), 6.70–6.85 (m, 2H, HAr), 7.02–7.20 (m, 4H, HAr), 7.40–7.50 (m, 2H, HAr), 7.28 (d, $J_{5,6}$ = 8.7, 1H, H_5), 8.43 (s, 1H, H_4), 8.80 (s, 1H, NH), 9.84 (s, 1H, NH). ^{13}C NMR: δ = 12.89 ($2CH_3$), 46.05 ($2CH_2N$), 97.45 (2CHAr), 98.14 (C_8), 105.85 (C_6), 108.02 (C_{10}), 108.66 (C_3), 114.70 (CHAr), 116.98 (CHAr), 117.2 (2CHAr), 121.50 (2CHAr), 126.00 (CHAr), 126.04 (CHAr), 129.78 (C-N(Ar)), 132.75 (C_5), 134.01 (C_4), 134.44 (C-N(Ar)), 144.74(C_7), 145.34 (C-F), 146.11 (NH-C=N), 149.65 (C-F), 153.72 (C_2), 154.65 (C_9), 157.89 (C=O). Calculated for $C_{27}H_{24}F_2N_6O_2$: C, 64.53; H, 4.81; N, 16.72%. Found: C, 64.49; H, 4.66; N, 16.75.

3-[1-(2,4-Difluorophenyl)-5-oxo-2,5-dihydro-[1*H*]-[1,2,4]triazol-3-yl]-2-*N*-[difluorophenylamino]-2-imino[2*H*]coumarin (7). Red-brown solid, IR (cm^{-1}): ν = 1587 (C=C), 1618 (C=N), 1711 (C=O), 3232 and 3312 (NH). ^{1}H NMR:

$\delta = 1.14$ (t, $J = 6.9$ Hz, 6H, CH_3), 3.48 (q, $J = 6.9$ Hz, 4H, CH_2N), 6.49 (dd, $J_{5,6} = 9$ Hz, $J_{6,8} = 1.8$ Hz, 1H, H_6), 6.61 (d, $J_{6,8} = 1.8$ Hz, 1H, H_8), 6.90–7.01 (m, 2H, HAr), 7.14–7.27 (m, 2H, HAr), 7.32–7.46 (m, 2H, HAr), 7.49 (d, $J_{5,6} = 9$ Hz, 1H, H_5), 8.39 (s, 1H, H_4), 8.72 (s, 1H, NH), 9.70 (s, 1H, NH). ^{13}C NMR: $\delta = 12.76$ ($2CH_3$), 44.84 ($2CH_2N$), 96.87 (C_8), 97.45 (2CHAr), 107.35 (C_6), 107.97 (C_{10}), 108.36 (C_3), 110.70 (2CHAr), 118.71 (CHAr), 118.73 (CHAr), 129.23 (C-N(Ar)), 129.77 (C-N(Ar)), 131.70 (C_5), 133.13 (C_4), 144.55 (C_7), 145.59 (NH-C=N), 149.73 (C-F), 152.33 (C-F), 153.57 (C-F), 153.60 (C-F), 153.64 (C_2), 154.33 (C_9), 157.86 (C=O). Calculated for $C_{27}H_{22}F_4N_6O_2$: C, 60.22; H, 4.12; N, 15.61. Found: C, 60.56; H, 4.13; N, 15.55%.

3-[1-(2,4,6-Trichlorophenyl)-5-oxo-2,5-dihydro-[1*H*]-[1,2,4]triazol-3-yl]-2-*N*-[2,4,6-trichlorophenylamino]-2-imino[2*H*]coumarin (8). Red-brown solid, IR (cm^{-1}): $\nu = 1587$ (C=C), 1618 (C=N), 1711 (C=O), 3232 and 3312 (NH). ^{1}H NMR: $\delta = 1.14$ (t, $J = 6.9$ Hz, 6H, CH_3), 3.41 (q, $J = 6.9$ Hz, 4H, CH_2N), 6.49 (dd, $J_{5,6} = 9$ Hz, $J_{6,8} = 1.8$ Hz, 1H, H_6), 6.64 (d, $J_{6,8} = 1.8$ Hz, 1H, H_8), 7.33 (d, $J_{5,6} = 9$ Hz, 1H, H_5), 7.59 (s, 1H, H_4), 7.65 (s, 2H, HAr), 7.94 (s, 2H, HAr), 8.28 (s, 1H, NH), 11.19 (s, 1H, NH). ^{13}C NMR: $\delta = 14.61$ (CH_3), 14.80 (CH_3), 46.39 ($2CH_2N$), 99.20 (C_8), 109.19 (C_6), 110.07 (C_{10}), 115.81 (C_3), 119.65 (C-Cl), 128.71 (C-Cl), 128.89 (C-Cl), 131.17 (2CH-Ar), 131.31 (2CH-Ar), 132.36 (C_5), 133.34 (C_4), 138.04 (C-Cl), 138.11 (C-Cl), 140.27 (C-Cl), 145.56 (C-N(Ar)), 152.80 (C-N(Ar)), 154.41 (C_7), 156.63 (NH-C=N), 160.40 (C_2), 160.89 (C_9), 161.38 (C=O). Calculated for $C_{27}H_{20}Cl_6N_6O_2$: C, 49.17; H, 2.99; N, 12.48. Found: C, 49.18; H, 2.93; N, 12.51.

3-[1-(2,3,5,6-Tetrafluorophenyl)-5-oxo-2,5-dihydro-[1*H*]-[1,2,4]triazol-3-yl]-2-imino[2*H*]coumarin (9). Red-brown solid, IR (cm^{-1}): $\nu = 1602$ (C=C), 1653 (C=N), 1737 (C=O), 3303 and 3372 (NH). ^{1}H NMR: $\delta = 1.35$ (t, $J = 6.9$ Hz, 6H, CH_3), 3.65 (q, $J = 6.9$ Hz, 4H, CH_2N), 6.80 (dd, $J_{5,6} = 6.9$, $J_{6,8} = 1.5$ Hz, 1H, H_6), 6.92 (d, $J_{6,8} = 1.5$ Hz, 1H, H_8), 7.36 (s, 1H, HAr), 7.60 (d, $J_{5,6} = 6.9$ Hz, 1H, H_5), 7.94 (s, 1H, H_4), 8.27 (s, 1H, NH), 9.33 (s, 1H, NH). ^{13}C NMR: $\delta = 13.44$ ($2CH_3$), 45.56 ($2CH_2N$), 96.05 (CHAr), 97.05 (C_8), 105.33 (C_6), 106.98 (C_{10}), 109.07 (C_3), 120.15 (C-N(Ar)), 128.89 (2C-F), 130.54 (C_5), 131.44 (C_4), 143.56 (C_7), 144.22 (NH-C=N), 147.77 (2C-F), 151.53 (C_2), 152.53 (C_9), 155.13 (C=O). Calculated for $C_{21}H_{17}F_4N_5O_2$: C, 56.38; H, 3.83; N, 15.65. Found: C, 56.49; H, 3.73; N, 15.45.

3-[1-(2,3,4,5,6-Pentafluoro-phenyl)-5-oxo-2,5-dihydro-[1*H*]-[1,2,4]triazol-3-yl]-2-imino[2*H*]coumarin (10). Red-brown solid, IR (cm^{-1}): $\nu = 1607$ (C=C), 1646 (C=N), 1745 (C=O), 3354 and 3390 (NH). ^{1}H NMR: $\delta = 1.35$ (t, $J = 6.9$ Hz, 6H, CH_3), 3.67 (q, $J = 6.9$ Hz, 4H, CH_2N), 6.82 (dd, $J_{5,6} = 6.9$ Hz, $J_{6,8} = 1.5$ Hz, 1H, H_6), 6.87 (d, $J_{6,8} = 1.5$ Hz, 1H, H_8), 7.62 (d, $J_{5,6} = 6.9$ Hz, 1H, H_5), 7.93 (s, 1H, H_4), 9.26 (s, 1H, NH), 11.60 (s, 1H, NH). ^{13}C NMR: $\delta = 12.64$ ($2CH_3$), 44.97 ($2CH_2N$), 96.95 (C_8), 106.25 (C_6), 107.32 (C_{10}), 108.76 (C_3), 116.10 (C-N(Ar)), 129.99 (C-F), 130.19 (C_5), 130.60 (C_4), 133.59 (2C-F), 136.89 (2C-F), 142.57 (C_7), 143.54 (NH-C=N), 151.22 (C_2), 152.04 (C_9), 154.49 (C=O). Calculated for $C_{21}H_{16}F_5N_5O_2$: C, 54.20; H, 3.47; N, 15.05. Found: C, 54.26; H, 3.33; N, 14.85.

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