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POLYMER SUPPORTED REAGENTS: NOVEL METHODOLOGY FOR SELECTIVE AND GENERAL SYNTHESIS OF IMINOCOUMARINS

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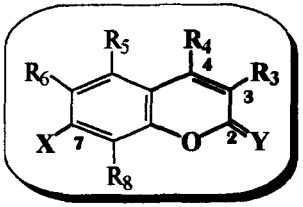
Abstract : A selective synthesis of iminocoumarins *3* was accomplished, starting from salicylaldehydes *1* and nitriles *2*, by the use of Amberlite IRA 900 resin as a polymeric solid support. The possibility of using various arylacetonitriles enhances the synthetic versatility of this strategy.

The performances required for fluorescent dyes, especially for their use in dye lasers, have induced many chemists to synthesize new molecules possessing optimal photophysical properties (1). Among these compounds, coumarin derivatives (①,Y=O) constitute very important classes of laser dyes and have been



Donor-acceptor benzopyran ① dyes with X group as donor and pyran heterocyclic moiety (include Y site) as acceptor

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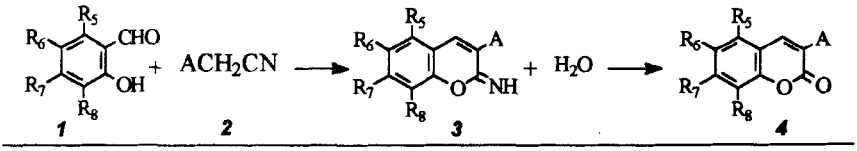
the subject of extensive investigation (2). The laser performances of these dyes were discussed, outlining important implications connected with the electronic affinity of the pyran acceptor moiety. In this context, considerable interest has been manifested in the functionalization of pyran heterocyclic moiety (R_3 = H, CN, CO_2Et; R_4 = H, CF_3, CH_3), more particularly in the synthesis of high emissive dyes (3-5). In order to achieve this study and to prove the relationship between photophysical properties and pyran acceptor capability, according to the nature of Y site (Y= O and Y= NH), it was the aim of our work to synthesize the iminocoumarin compounds (①, Y= NH). We therefore investigated the possibility to prepare such compounds starting from salicylaldehydes *1*/nitriles *2* system.

Attempts on the synthesis of iminocoumarins *3* starting from salicylaldehydes *1*/ nitriles *2* system gave unpromising results in classical Knoevenagel conditions: From arylacetonitriles (A = aryl), neither were attempts to condense *1* to *2* successful. From activated nitriles (A= CN, $CONH_2$, COC_5H_6), coumarins *4* was the major resulted product in this condensation, as illustrated in scheme 1 (6-7). With a view to solving this problem, a recent attempt, involving the Knoevenagel reaction between 2-hydroxy-1-benzylideneanilines and nitriles *2*, has been proposed (8).This method is, however, not free from drawbacks: difficult availability of starting materials and lack of generality.

Scheme 1: *Condensation between salicylaldehydes 1 and activated nitriles 2 using the classical Knoevenagel conditions.*



1 *2* *3* *4*

Taking these facts into consideration, we were interested in developing an efficient synthetic route to iminocoumarins *3* by the extension of our preceding strategy (9). Herein, we report a successful utilization of salicylaldehydes *1*/nitriles *2* system as a convenient starting materials for a selective synthesis of novel iminocoumarin derivatives. The key feature of this strategy is the use of strong anion exchange resin as a polymeric solid support (10-12).

The synthetic procedure was accomplished in three-steps as follow (see scheme 2):

(i) ***Preparation of polymer supported phenate anions*** **(II)***:* Treatment of salicylaldehydes *1* with Amberlite IRA 900 (under its OH^- form) in cyclohexane solvent by the use of a Dean-Stark water separator, afforded the polymer supported phenate anions (II) (resin beads become yellow).

(ii) ***Reaction of nitriles 2 with polymer supported reagents*** **(II):** Nitriles *2* are combined with phenate resin beads (II), under reflux conditions, leading to the polymer supported anions (III) formation (resin beads become red).

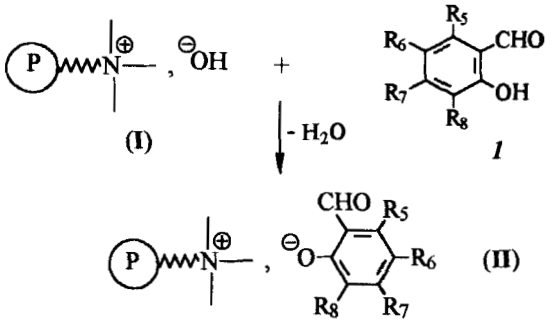
(iii) ***Deblock of the iminocoumarins 3 from the resin:*** Treatment of resin beads (III) by elution with chloroform, afforded the iminocoumarins *3*.

The use of Amberlite IRA 900 resin beads as a solid support offers a practical alternative to the classical Knoevenagel methods. Using our procedure, the iminocoumarins *3* are generated in situ with no presence of free water and their hydrolyze do not take place. As a result, the addition of salicylaldehydes *1* to nitriles *2* provided access to desired iminocoumarins *3* with excellent selectivities.

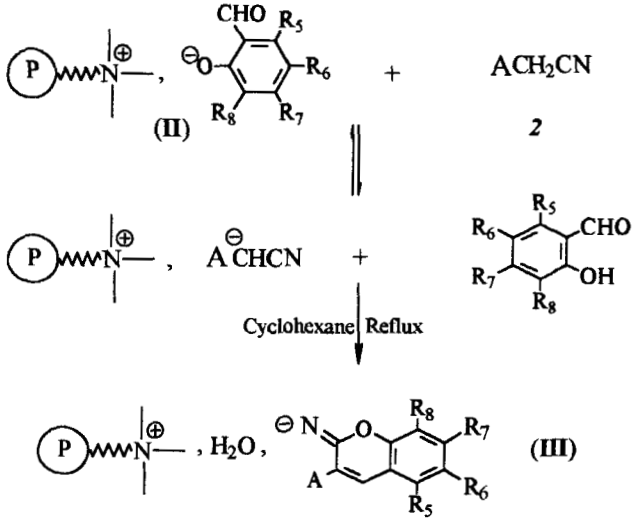
The possibility of using various arylacetonitriles enhances the versatility of this strategy and allows the preparation of novel 3-Aryliminocoumarins compounds *3a-l* in good yields, as illustrated in table 1.

***Scheme 2** : Selective synthesis of iminocoumarins 3 using salicylaldehydes 1 and nitriles 2 as starting materials.*

First step: *Preparation of Polymer Supported Phenate anions* (II).



Second Step: *Reaction of Nitriles 2 with polymer supported* reagents (II).



Third Step: *Deablock of iminocoumarins 3 from the resin.*

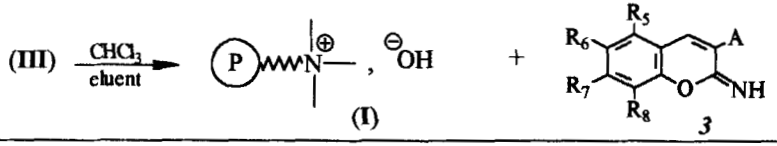
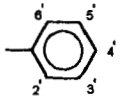
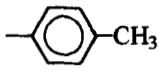
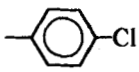
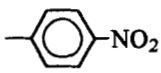
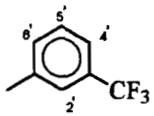
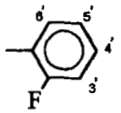
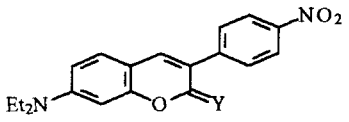


Table 1: *Preparation of iminocoumarins* ***3a-n*** starting *from Salicylaldehydes 1 and Nitriles 2.*

Product	Salicylaldehydes *1*				Nitriles *2*	Time (h)	Yield* (%)
	R_5	R_6	R_7	R_8	A		
3a	H	H	H	H		8	90
3b	H	OMe	H	H		8	85
3c	OMe	H	OMe	H		36	80
3d	H	H	H	H		20	60
3e	OMe	H	OMe	H		48	50
3f	H	H	H	H		4	92
3g	H	Cl	H	H		6	90
3h	OMe	H	OMe	H		15	85
3i	OMe	H	OMe	H		2	90
3j	H	H	NEt_2	H		6	40
3k	OMe	H	OMe	H		15	85
3l	OMe	H	OMe	H		17	80
3m	H	H	H	H	CN	1	95
3n	H	H	H	H	$CONH_2$	1	90

* Yields estimated by GC using a non-polar column (Varian OV 101) and corrected after separation of pure product.

To prove the synthetic utility of these compounds, preliminary fluorescence spectroscopic analysis revealed their competitive behavior. For example, in hexane, the iminocoumarin ***3j*** shows a high 'Green-Yellow' fluorescence efficiency, while its corresponding coumarin ***4j*** is photophysically inert.



3j: Y= NH / ***4j***: Y= O

In order to confirm the synthetic utility of iminocoumarin ***3*** derivatives, we show in a forthcoming paper (13), the ready availability of these compounds as starting

Table 2. *^{1}H NMR chemical shift of iminocoumarin **3b** and its corresponding coumarin **4b**.*

Y= NH ♣			Y= O		
Proton	δ (ppm)	Coupling (Hz)	Proton	δ (ppm)	Coupling (Hz)
H-4	**7.03**	s	H-4	**7.73**	s
H-5	6.72	d J_{54}= 2.9	H-5	6.95	d J_{54}= 2.9
H-7	6.87	dd J_{78}= 9.0 J_{75}= 2.9	H-7	7.08	dd J_{78}= 9.0 J_{75}= 2.9
H-8	7.01	d J_{78}= 9.0	H-8	7.26	d J_{78}= 9.0
H-3',4',5'	7.34-7.44	♠	H-3',4',5'	7.38-7.46	♠
H-2',6'	7.50-7.52	♠	H-2',6'	7.70-7.66	♠

♣The imine proton signal appeared as a large delocalized band (7-8 ppm). This band can be seated in evidence by integration ratios of aromatic proton system and methoxy proton.

♠ Unresolved ^{3}J coupling.

materials for the preparation of new benzopyran ① dyes (Y= NR; R = alkyl, aryl, heterocyclyl, NHC_6H_5, $NHCOCH_3$, etc).

Standard spectroscopic data of each compound are consistent with the proposed structure: Absorption bands in the IR spectrum at [3330, 3300 (ν_{N-H})] and [1640-1635 ($\nu_{C=N}$)] were appropriate for the imine group (C_2=N-H). In ^{13}C NMR spectra, C_2 signal appeared as a broad line at 160-161 (the width of this line at half-height was 90 Hz). In the ^1H NMR spectra, δH_4 of iminocoumarins ***3*** appeared at lower fields than their corresponding coumarins ***4***, with a difference of about 0.7 ppm (see table 2 and experimental). The ^{13}C NMR spectra show that C_4 carbon resonance of 133.7 / 128.7 was shifted about 6.7 ppm down field when compared with their corresponding coumarins (see table 3 and experimental).

EXPERIMENTAL SECTION

Melting points were taken using a Kofler hot-stage apparatus and are uncorrected. IR spectra were obtained on a Perkin - Elmer 782 spectrophotometer (3500-2500 cm^{-1}). UV spectra were measured in EtOH using a shimadzu 2100 spectrophotometer (500-290 nm). ^1H and ^{13}C NMR spectra were recorded with a Bruker AC 300 spectrometer at 300.1 MHz and 75.4 MHz respectively, in $CDCl_3$, with TMS as internal standard. Samples for the ^{13}C NMR measurements were prepared by dissolving 0.15 g of the substrate in 1.5 mL of $CDCl_3$ (for detecting the C-2 signal, we should use a more concentrated solution: 1g of the substrate in 1.5 mL of $CDCl_3$). Elemental analyses were determined using a Carbo-Erba 1106 elemental analyzer. All used products are of commercial origin and used without further purification.

Table 3. *^{13}C NMR chemical shift assignment and ^{13}C-^{1}H coupling of iminocoumarin **3b** and its corresponding coumarin **4b**.*

Y = NH			Y = O		
Carbon	δ (ppm)	Coupling (Hz)	Carbon	δ (ppm)	Coupling (Hz)
C-2	160.8	broad line (W = 90 Hz)♣	C-2	160.6	d J_{24}= 10.0
C-3	130.4	t $J_{32'}$=$J_{36'}$= 3.1	C-3	128.4	t $J_{32'}$=$J_{36'}$= 3.0
C-4	**132.8**	dd J_{44}= 163.0 / J_{45}= 5.2	C-4	**139.6**	dd J_{44}= 161.8 / J_{45}= 5.4
C-5	110.2	td J_{55}= 160.0 J_{45}= J_{57}= 4.4	C-5	109.8	td J_{55}= 160.1 J_{45}= J_{57}= 4.5
C-6	155.0	m	C-6	156.0	m
C-7	116.8	dd J_{77}= 162.0 / J_{57}= 5.6	C-7	119.0	dd J_{77}= 163 / J_{57}= 5.5
C-8	115.9	d J_{88}= 163.9	C-8	117.3	d J_{88}= 165.3
C-9	147.0	m	C-9	147.8	m
C-10	119.8	d $J_{10\text{-}8}$= 5.2	C-10	119.9	d $J_{10\text{-}8}$= 5.3
C-1'	136.0	td $J_{1'4}$= 4.3 / $J_{1'2'}$= $J_{1'6'}$= 6.0	C-1'	134.6	td $J_{1'4}$= 4.9 / $J_{1'2'}$= $J_{1'6'}$= 7.0
C-2',6'	128.4*	•	C-2',6'	128.4°	•
C-3',5'	128.4*	♣	C-3',5'	128.3°	♣
C-4'	128.4*	•	C-4'	128.7	t $J_{4'2'}$= $J_{4'6'}$= 7.5
		$^{1}J_{2'3'}$= 160.0			$^{1}J_{2'3'}$= 160.0

* Superimposed lines.
• W: The half-height line width.
° Assignments could be exchanged.
♣ Unresolved ^{3}J coupling.

General Procedure for the selective synthesis of iminocoumarins 3a-n:

Under nitrogen atmosphere, a mixture of the aldehyde *1* (0.02 mol), Amberlite IRA 900 resin (9g, 0.02 mol OH^-) and cyclohexane (25 mL) was refluxed with the use of a Dean-Stark water separator. Acid-base reaction progress between Amberlite IRA 900 resin and aldehyde *1* was monitored by G.C thechnique.

After completion of this reaction, the nitrile *2* (0.02 mol) was added and the mechanically stirred mixture was refluxed during the time indicated in table 1.

After that, the reaction mixture was separated from the solid catalyst.

* Treatment of the resin beads by elution with chloroform, allows the recuperation of 90% from the synthesized iminocoumarin *3*.

* The organic phase was then evaporated under reduced pressure, leading to the recuperation of the resting iminocoumarin *3* (10%).

Finally, the obtained iminocoumarin *3* was purified by crystallizing with the hexane. The purity of the synthesized compounds was examined by spectroscopic investigations in addition to elemental analyses.

3-Phenyliminocoumarin *3a*.

mp 100-103°C; IR ($CHCl_3$, νcm^{-1}) 3326, 3296 (NH), 1642 (C=N), 1595 (C=C); IR (KBr, νcm^{-1}) 3255 (NH), 1648 (C=N), 1600 (C=C); UV λ_{max} 329, 292 nm; ^1H NMR δ 7.64-7.25 (8H, m); 7.15-7.06 (3H, m, 4,6,8-H); ^{13}C NMR δ 115.6, 120.0 (q), 123.5, 127.5, 128.6, 128.6, 128.8, 130.5 (q), 130.6, 133.3, 136.3 (q), 153.2 (q); Elemental analysis: Found (%): C, 81.29; H, 4.79; N, 5.88; Calcd for $C_{15}H_{11}ON$ (%): C, 81.42; H, 5.01; N, 6.33.

6- Methoxy-3-phenyliminocoumarin *3b*.

mp 136-138°C; IR ($CHCl_3$, νcm^{-1}) 3338, 3296 (NH), 1643 (C=N), 1600,1580

(C=C); IR (KBr, νcm^{-1}) 3274 (NH), 1643 (C=N), 1600,1577 (C=C); UV λ_{max} 356, 292 nm; ^1H NMR δ 7.52-7.50 (2H, m, 2',6'-H); 7.44-7.34 (3H, m, 3',4',5'-H); 7.03 (1H, s, 4-H); 7.01 (1H, d, J_{78}= 9.0 Hz, 8-H); 6.87 (1H, dd, J_{78}= 9.0 Hz and J_{75}= 2.9 Hz, 7-H); 6.72 (1H, d, J_{54}= 2.9 Hz, 5-H); ^{13}C NMR δ 55.7 ($O\underline{C}H_3$), 110.2, 115.9, 116.8, 119.8 (q), 128.4, 128.4, 128.4, 130.4 (q), 132.8, 136.0 (q), 147.0 (q), 155.0 (q); Elemental analysis: Found (%): C, 76.57; H, 5.31; N, 5.25; Calcd for $C_{16}H_{13}O_2N$ (%): C, 76.47; H, 5.21; N, 5.57.

5,7-Dimethoxy-3-phenyliminocoumarin *3c*.

mp 152-154°C; IR ($CHCl_3$, νcm^{-1}) 3338, 3302 (NH), 1644 (C=N), 1615,1605,1580 (C=C); UV λ_{max} 344 nm; ^1H NMR δ 7.52 (2H, m, 2',6'-H), 7.43 (1H, s, 4-H), 7.41-7.37 (3H, m, 3', 4', 5'-H), 6.29 (1H, d, J_{68}=2.1 Hz, 6-H or 8-H); 6.17 (1H, d, J_{68}=2.1 Hz, 8-H or 6-H), 3.83 (3H, s, $OC\underline{H}_3$); 3.81 (3H, s, $OC\underline{H}_3$); ^{13}C NMR δ 55.7 ($O\underline{C}H_3$), 55.8 ($O\underline{C}H_3$), 92.5, 93.8, 104.2 (q), 125.3 (q), 128.2, 128.5, 128.6, 128.7, 136.9 (q), 155.2 (q), 156.7(q), 162.6 (q); Elemental analysis: Found (%): C, 72.37; H, 5.31; N, 5.25; Calcd for $C_{17}H_{15}O_3N$ (%): C, 72.58; H, 5.37; N, 4.98.

3-(4'-Methylphenyl)iminocoumarin *3d*.

mp 107-109°C; IR ($CHCl_3$, νcm^{-1}) 3335, 3295 (NH), 1643 (C=N), 1605,1592 (C=C); UV λ_{max} 334, 304 nm; ^1H NMR δ 7.70-7.40 (1H, large band, N$\underline{H}$), 7.40-7.38 (2H, m, 2',6'-H), 7.31-7.18 (4H, m, 5, 7, 3',5'-H), 7.10-7.02 (3H, m, 4, 6, 8-H), 2.34 ($C\underline{H}_3$); ^{13}C NMR δ 20.9 ($\underline{C}H_3$), 115.1, 119.6 (q), 123.0, 127.0, 128.0, 129.0, 130.0, 130.0 (q), 132.4, 132.9 (q), 138.3(q), 152.6 (q); Elemental analysis: Found (%): C, 81.57; H, 5.70; N, 5.64; Calcd for $C_{16}H_{13}ON$ (%): C, 81.67; H, 5.57; N, 5.95.

5,7-Dimethoxy-3-(4'-methylphenyl)iminocoumarin *3e*.

mp 128-130°C; IR ($CHCl_3$, νcm^{-1}) 3338, 3300 (NH), 1645 (C=N), 1615,1605,1585 (C=C); UV λ_{max} 340, 297 nm; ^1H NMR δ 7.42 (2H, d, $J_{2',3'}$=7.7 Hz, 2', 6'-H), 7.41 (1H, s, H-4), 7.22 (2H, d, $J_{2',3'}$=7.7 Hz, 3',5'-H), 6.32 (1H, d, J_{68}=2.1 Hz, 6-H or 8-H), 6.18 (1H, d, J_{68}=2.1 Hz, 8-H or 6-H), 3.82 (3H, s, OCH_3); 3.81 (3H, s, OCH_3), 2.38 (3H, s, CH_3); ^{13}C NMR δ 21.1 (CH_3), 55.6 (OCH_3), 55.7 (OCH_3), 92.4, 93.7, 104.1 (q), 125.2 (q),127.9, 128.2, 129.2, 133.9 (q), 138.0 (q), 155.0 (q), 156.6(q), 162.3(q); Elemental analysis: Found (%): C, 73.00; H, 6.00; N, 4.38; Calcd for $C_{18}H_{17}O_3N$ (%): C, 73.20; H, 5.80; N, 4.74.

3-(4'-Chlorophenyl)iminocoumarin *3f*.

mp 121-124°C; IR ($CHCl_3$, νcm^{-1}) 3339, 3297 (NH), 1649 (C=N), 1601,1593 (C=C); UV λ_{max} 333, 293 nm; ^1H NMR δ 7.65-7.40 (5H, m, 2', 3', 5', 6'-H and NH), 7.37-7.28 (2H, m, 5, 7-H), 7.18-7.05 (3H, m, 4, 6, 8-H); ^{13}C NMR δ 115.5, 119.8 (q), 123.6, 127.6, 128.8, 129.8 (q), 130.1, 130.8, 133.7, 134.6 (q), 134.8 (q), 153.2 (q); Elemental analysis: Found (%): C, 70.10; H, 4.00; N, 5.22; Calcd for $C_{15}H_{10}ONCl$ (%): C, 70.45; H, 3.94; N, 5.47.

6-Chloro-3-(4'-chlorophenyl)iminocoumarin *3g*.

mp 175-176°C; IR ($CHCl_3$, νcm^{-1}) 3346, 3298(NH), 1646 (C=N), 1597 (C=C); UV λ_{max} 342, 293 nm; ^1H NMR δ 7.65-7.45 (3H, m, 2', 6'-H and NH); 7.40 (2H, d, $J_{2',3'}$= 8.7 Hz, 3', 5'-H), 7.32 (1H, d, J_{57}= 2.3 Hz, 5-H), 7.29 (1H, dd, J_{78}= 8.7 Hz and J_{57}= 2.3 Hz, 7-H); 7.08 (1H, d, J_{78}= 8.7 Hz, 8-H), 7.05 (1H, s, 4-H); ^{13}C NMR δ 117.0, 120.9 (q), 126.8 , 128.8 (q), 129.0, 130.2, 130.7, 130.8 (q), 132.3, 134.2 (q), 135.1 (q), 151.6 (q); Elemental analysis: Found (%): C, 62.25; H, 3.22; N, 4.59; Calcd for $C_{15}H_9ONCl_2$ (%): C, 62.09; H, 3.12; N, 4.82.

5,7-Dimethoxy-3-(4'-chlorophenyl)iminocoumarin *3h*.

mp 162-164°C; IR ($CHCl_3$, νcm^{-1}) 3339, 3298 (NH), 1646 (C=N), 1606 (C=C); UV λ_{max} 345 nm, ^1H NMR δ 7.52 (2H, d, $J_{2',3'}$= 8.0 Hz, 2',6'-H), 7.43 (1H, s, 4-H); 7.38 (2H, d, $J_{2',3'}$= 8.0 Hz, 3', 5'-H); 6.26 (1H, d, J_{68}= 2.1 Hz, 6-H or 8-H); 6.16 (1H, d, J_{68}= 2.1 Hz, 8-H or 6-H), 3.83 (3H, s, $OC\underline{H}_3$), 3.81(3H, s, $OC\underline{H}_3$); ^{13}C NMR δ 55.5 ($OC\underline{H}_3$), 55.7 ($OC\underline{H}_3$), 92.2, 93.6, 103.9 (q), 124.0 (q), 128.5, 128.7, 129.9, 133.6 (q), 135.2 (q), 155.1 (q), 156.6 (q), 162.5 (q); Elemental analysis: Found (%): C, 64.7; H, 4.83; N, 4.08; Calcd for $C_{17}H_{14}O_3NCl$ (%): C, 64.66; H, 4 47; N, 4.43.

5,7-Dimethoxy-3-(4'-nitrophenyl)iminocoumarin *3i*.

mp 204-206°C, IR ($CHCl_3$, νcm^{-1}) 3344, 3301 (NH), 1650 (C=N), 1606 (C=C); UV λ_{max} 370 nm, ^1H NMR δ 8.25 (2H, d, $J_{2',3'}$= 8.9 Hz, 3',5'-H), 7.85 (2H, d, $J_{2',3'}$= 8.9 Hz, 2',6'-H), 7.61 (1H, s, H-4); 6.30 (1H, d, J_{68}= 2.1 Hz, 6-H or 8-H); 6.22 (1H, d, J_{68}= 2.1 Hz, 8-H or 6-H); 3.90 (3H, s, $OC\underline{H}_3$); 3.86 (3H, s, $OC\underline{H}_3$); ^{13}C NMR δ 55.8 ($OC\underline{H}_3$); 55.9 ($OC\underline{H}_3$), 92.3, 94.0, 103.9 (q), 123.2 (q), 123.5, 129.5, 130.6, 143.7 (q), 147.1 (q), 155.6 (q), 157.1 (q), 163.3 (q); Elemental analysis: Found (%): C, 62.63; H, 4.17; N, 8.39; Calcd for $C_{17}H_{14}O_5N_2$ (%): C, 62.57; H, 4.32; N, 8.58.

7-Diethylamino-3-(4'-nitrophenyl)iminocoumarin *3j*.

mp 157-161°C; IR ($CHCl_3$, νcm^{-1}) 3338, 3300 (NH), 1643 (C=N), 1603, 1592 (C=C); UV λ_{max} 428 nm; ^1H NMR δ 8.27 (2H, d, $J_{2',3'}$= 9.0 Hz, 3',5'-H); 8.15 (1H, d, J_{56}= 9.3 Hz, 5-H); 8.14 (1H, s, 4-H); 7.79 (2H, d, $J_{2',3'}$= 9 Hz, 2',6'-H); 6.39 (1H, dd, J_{65}= 9.3 Hz and J_{68}=2.4 Hz, 6-H); 6.20 (1H, d, J_{86}= 2.4 Hz, 8-H), 2.50 (4H, q, J=3.2 Hz, $C\underline{H}_2$); 1.14 (6H, t, J=3.2 Hz, $C\underline{H}_3$); ^{13}C NMR δ 12.5 ($\underline{C}H_3$); 44.0 ($\underline{C}H_2$); 96.3, 104.5, 108.3 (q), 119.4 (q), 124.3, 125.0, 128.6, 139.3,

142.4 (q), 145.5 (q), 151.9 (q), 160.0 (q); Elemental analysis: Found (%): C, 67.56; H, 5.83; N,12.30; Calcd for $C_{19}H_{19}O_3N_3$ (%): C, 67.64; H, 5.67; N, 12.45.

5,7-Dimethoxy-3-(3'-trifluoromethylphenyl)iminocoumarin *3k*.

mp 134-135°C; IR (KBr, νcm^{-1}) 3292 (NH), 1654 (C=N), 1616, 1580 (C=C); UV λ_{max} 346 nm; ^1H NMR δ 7.86 (1H, s, 2'-H); 7.83 (1H, d, $^3J_{5',6'}$= 7.1 Hz, 6'-H), 7.60 (1H, d, $^3J_{4',5'}$= 7.8 Hz, 4'-H), 7.55 (1H, dd, $^3J_{5',6'}$= 7.1 Hz and $^3J_{4',5'}$= 7.8 Hz, 5'-H), 7.54 (1H, s, 4-H); 6.30 (1H, d, J_{68}= 2.1 Hz, 6-H or 8-H); 6.20 (1H, d, J_{68}= 2.1 Hz, 8-H or 6-H); 3.86 (3H, s, $OC\underline{H}_3$); 3.84 (3H, s, $OC\underline{H}_3$); ^{13}C NMR δ 55.67 ($O\underline{C}H_3$); 55.80 ($O\underline{C}H_3$), 92.3, 94.0, 104.0 (q), 122.2 (q, J= 24 Hz), 123.0 (q, J= 273 Hz),124.0 (q), 124.7 (J= 20 Hz), 125.6 (J= 20 Hz), 128.7, 129.5, 132.1, 137.7 (q), 155.5 (q), 156.9 (q), 162.9 (q); Elemental analysis: Found (%): C, 62.17; H, 4.54; N, 3.65; Calcd for $C_{18}H_{14}O_3NF_3$ (%): C, 62.42; H, 4.07; N, 4.04.

5,7-Dimethoxy-3-(2'-fluorophenyl)iminocoumarin *3l*.

mp 136-137°C; IR (KBr, νcm^{-1}) 3273 (NH), 1651 (C=N), 1623, 1607, 1578 (C=C); UV λ_{max} 338 nm; ^1H NMR δ 7.48 (1H, s, 4-H); 7.44-7.33 (2H, m); 7.21-7.11 (2H, m); 6.25 (1H, d, J_{68}= 2.0 Hz, 6-H or 8-H); 6.19 (1H, d, J_{68}= 2.0 Hz, 8-H or 6-H); 3.84(3H, s, $OC\underline{H}_3$); 3.82 (3H, s, $OC\underline{H}_3$); ^{13}C NMR δ 55.7 ($O\underline{C}H_3$); 55.8 ($O\underline{C}H_3$), 92.6, 93.9, 103.8 (q), 116.0 (J=20 Hz), 121.7 (q, J= 8Hz), 124.2 (q), 124.3 (J=3.5 Hz), 130.1 (J=8Hz), 130.7, 131.5 (d, J=2.5 Hz), 155.6 (q), 156.9 (q), 162.1 (q, J=248 Hz), 162.9 (q); Elemental analysis: Found (%): C, 68.69; H, 4.88; N, 4.44; Calcd for $C_{17}H_{14}O_3NF$ (%): C, 68.45; H, 4.73; N, 4.69.

3-Cyanoiminocoumarin *3m*.

mp 198-201°C [lit[14]: 183-185°C]; IR ($CHCl_3$, νcm^{-1}) 3332, 3280 (NH), 2222, 2180 (CN), 1650 (C=N), 1605, 1580 (C=C); [lit[14]: IR (Nujol, νcm^{-1}) 3333, 2222,

1652]; UV λ_{max} 348, 304, 293 nm; Elemental analysis: Found (%): C, 70.67; H, 3.66; N, 16.39; Calcd for $C_{10}H_6ON_2$ (%): C, 70.58; H, 3.55; N, 16.46.

3-Amidoiminocoumarin *3n*.

mp 195-198°C [lit[14]: 180-190°C]; IR ($CHCl_3$, vcm^{-1}) 3338, 3296, 1655, 1644,1600 1578; [lit[14]: IR (Nujol, vcm^{-1}) 3333, 1666]; UV λ_{max} 342, 305, 290 nm; Elemental analysis: Found (%): C, 63.73; H, 4.41; N, 14.57; Calcd for $C_{10}H_8O_2N_2$ (%): C, 63.82; H, 4.28; N, 14.88.

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