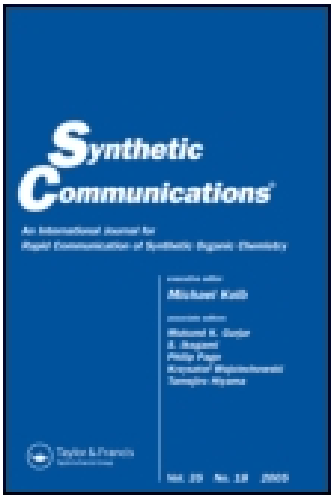

Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry

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Leila Benmaktouf [a], Houcine Ammar [a], Yves Le Bigot [b] & Souhir Abid [a]

[a] Laboratoire de Chimie Appliquée: Hétérocycles, Corps Gras et Polymères, Faculté des Sciences, Université de Sfax, Sfax, Tunisia

[b] Laboratoire de Génie Chimique, ENSIACET, Toulouse, France

Published online: 03 Mar 2011.

To cite this article: Leila Benmaktouf, Houcine Ammar, Yves Le Bigot & Souhir Abid (2011) Synthesis of New Iminocoumarins Bearing Parabanic Moieties, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 41:7, 1017-1026, DOI: 10.1080/00397911003710562

To link to this article: http://dx.doi.org/10.1080/00397911003710562

Synthetic Communications®, 41: 1017–1026, 2011

ISSN: 0039-7911 print/1532-2432 online
DOI: 10.1080/00397911003710562

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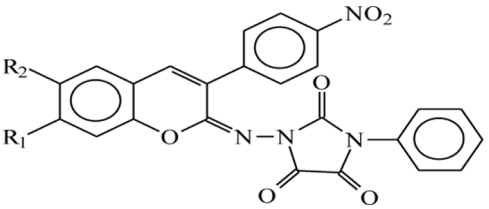
Leila Benmaktouf,[1] Houcine Ammar,[1] Yves Le Bigot,[2] and Souhir Abid[1]

[1]*Laboratoire de Chimie Appliquée: Hétérocycles, Corps Gras et Polymères, Faculté des Sciences, Université de Sfax, Sfax, Tunisia*
[2]*Laboratoire de Génie Chimique, ENSIACET, Toulouse, France*

GRAPHICAL ABSTRACT



Abstract *The synthesis of novel substituted 3-*p*-nitro-phenyliminocoumarins and corresponding* N*-ureaiminocoumarins is described. The condensation of these materials with oxalyl chloride leads to the corresponding* N*-parabanic iminocoumarins, which have not previously been described, in moderate or good yields and high selectivity. The structures were characterized by Fourier transform infrared,* ^{1}H *and* ^{13}C *NMR, and elemental analysis.*

Keywords *N*-Hydrazonochromene; iminocoumarin; Knoevenagel condensation; Schmidt reaction

INTRODUCTION

In the past decade, the synthesis, characterization, and properties of 2-iminocoumarin derivatives have been studied intensively. This considerable attention of investigators to these products is connected on the one hand to their high reactivity toward both electrophiles and nucleophiles and on the other hand to their many applications in agricultural and pharmacological industries. For example, some 3-hetaryl coumarins and iminocoumarins have been proposed as anticancer,[1] anti-asthmatic,[2] antibacterial,[3] and antiallergic[4] agents. Iminocoumarins can be

Received January 4, 2010.
Address correspondence to Souhir Abid, Laboratoire de Chimie Appliquée: Hétérocycles, Corps Gras et Polymères, Faculté des Sciences de Sfax, 3000 Sfax, Tunisia. E-mail: abidsouhir@yahoo.fr

also used as fluorescent dyes, and their optical properties depend strongly on the nature and the position of substituents.[5–9]

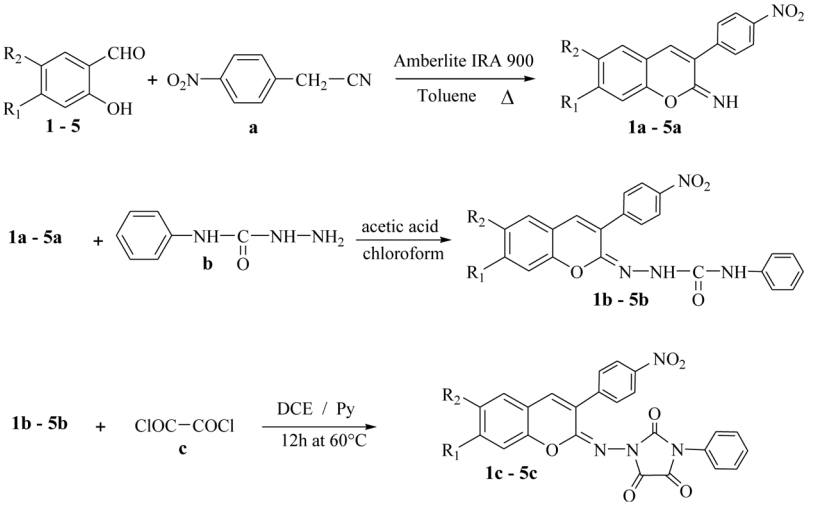
This wide range of applications has stimulated great research on the preparation, reactivity, and properties of iminocoumarins. It was reported that 2-iminocoumarins are highly versatile precursors used for the synthesis of several polycyclic compounds. Bilokin et al. have described the use of 2-iminocoumarin-3-carboxamides as starting reagents in the synthesis of 3-hetaryl coumarins.[10,11] Gorobets et al. have studied the reaction of 3-thiazolyl-2-iminocoumarins with amine and hydrazide derivatives under acid catalysis conditions to obtain the corresponding N-substituted iminocoumarins.[12] Using aromatic aldehydes as electrophilic reagents, benzopyranopyrimidines or imidazolyl coumarins were obtained depending on the structure of starting materials.[13] Volmajer et al. have developed the synthesis of *N*-hydrazonochromenes via condensation of 2-iminocoumarin-3-carbonitriles with hydrazine derivatives such as phenylhydrazine, 2-hydrazinopyridine, or *N*-phenylhydrazinecarboxamide.[14] In our previous work, we showed that 3-cyano-2-iminicoumarins reacted with electrophiles such as ethylchloroformate, isocyanates, acylchlorides, and thioisocyanates, leading to the corresponding *N*-substituted iminicoumarins.[7,15,16] Reaction of *N*-ethoxycarbonyl derivatives with amines or hydrazides as *N*-nucleophiles led to benzopyranopyrimidines,[15,17] whereas hydrazine reagents gave 3-hetaryl coumarins.[18] Bis-iminocoumarins can be obtained by the Schmidt reaction using diamines as reagents.[19]

In view of these findings, it appears that a satisfactory combination of coumarinic or iminocoumarinic moieties and nitrogen-containing heterocycle constitutes an original way to develop organic materials of special interest. It seems that the structure of the heterocycle and its position in iminocoumarin substrate might present a decisive role in both biological and optical properties. Given the potential importance of this family of compounds and the extensive experience of our laboratories in the field of heterocyclic-based coumarins and iminocoumarins, we decided to study the synthesis of a novel class of organic functional materials bearing iminocoumarin and parabanic groups. To the best of our knowledge, no reports on this family of iminocoumarin derivatives have appeared in the literature. In the present paper, we describe the synthesis of several 3-*p*-nitro-phenyliminocoumarins followed by their transformation into *N*-parabanic derivatives.

RESULTS AND DISCUSSION

The synthetic procedure leading to *N*-parabanic iminocoumarins included, as shown in Scheme 1, three steps: (i) condensation of *p*-nitrobenzyl cyanide with substituted salicylaldehydes to obtain the corresponding iminocoumarins **1a–5a** followed by (ii) introduction of urea function in the *N*-position in acidic medium and then (iii) its conversion to parabanic heterocycle by treatment with oxalyl chloride.

When the first step was carried out with homogenous catalyst such as piperidine according to our previous procedure,[15] iminocoumarins **1a–5a** were obtained in moderate yields (10–20%). The use of resin Amberlite IRA 900 proved more suitable for the synthesis of these iminocoumarins. This catalyst was not only of interest because of its advantage in term of yields (Table 1) but also because it offered



Scheme 1. General pathway for synthesis of the 2-*N*-parabanic iminocoumarins.

considerable advantages essential to preventing undesirable side reactions such as hydrolysis from converting iminocoumarins to the corresponding coumarins in homogenous medium.[15,16] Fourier transform infrared (FTIR), ^{1}H and ^{13}C NMR, and elemental analysis confirmed the expected structures.

The coupling, by Schmidt reaction, of **1a–5a** compounds with 4-phenylsemicarbazide **b**, carried out at room temperature in a mixture of chloroform and glacial acetic acid, led in the second step to *N*-ureaiminocoumarins **1b–5b** following the *N*-nucleophilic attack of imidic carbon center (Table 1). The substituents in the starting iminocoumarins **1a–5a** proved to have a significant effect on the reaction course.

Table 1. Synthesis of compounds **1a–5a**, **1b–5b**, and **1c–5c**

Compounds	R_1	R_2	Yields (%)	Times (h)
1a	H	H	58 (13[a])	8
2a	H	Br	50 (10[a])	8
3a	$N(Et)_2$	H	73 (16[a])	6
4a	H	MeO	82 (16[a])	6
5a	MeO	H	75 (20[a])	6
1b	H	H	66	2
2b	H	Br	92	0.5
3b	N(Et)2	H	38	4
4b	H	MeO	90	2
5b	MeO	H	30	4
1c	H	H	88	12
2c	H	Br	95	12
3c	$N(Et)_2$	H	46	12
4c	H	MeO	78	12
5c	MeO	H	65	12

[a]Yields obtained with piperidine as catalyst.

Hence, in the case of the 2-iminocoumarins bearing a bromo or methoxy group in the 6-position, the reaction occurred in almost quantitative yields (compounds **2b, 4b**). However, the presence of a donor substituent in position 7 led to a dramatic decrease in yield (compounds **3b, 5b**), which can be attributed to the low electrophilic reactivity of imidic carbon.

The expected structures **1b–5b** were clearly confirmed by the spectroscopic analyses showing the presence of urea function (ν C=O: 1706 cm^{-1}; δ NH: 8.41 and 10.19 ppm; δ CO: 152 ppm in compound **1b**).

The cyclocondensations of **1b–5b** with oxalyl chloride **c**, carried out in the presence of pyridine, started in a heterogeneous system because of their insolubility in 1,2-dichloroethane (DCE). The mixture became homogeneous with the progress of the reaction because of the increased solubility of the parabanic ring once it was formed. In this case, the use of pyridine was important because it acts both as catalyst activating chloroformyl functions and at the same time as acid acceptor. The progress of the reaction was followed by the changes in the FTIR spectra of samples withdrawn at regular intervals from the reaction media, which showed a decrease of the absorption bands characteristic of the urea group and the appearance of an absorption band in the region of 1770 cm^{-1} assigned to the parabanic ring resulting from the intermolecular cyclisation. Moreover, all *N*-parabanic iminocoumarins **1c–5c** exhibit ^{1}H NMR spectra in good agreement with their expected structures. Particularly, the absence of original peaks arising from the NHCONH group is a clear indication that the cyclocondensation reaction had gone to completion. Table 1 shows the yields of isolated *N*-parabanic iminocoumarins **1c–5c**.

CONCLUSION

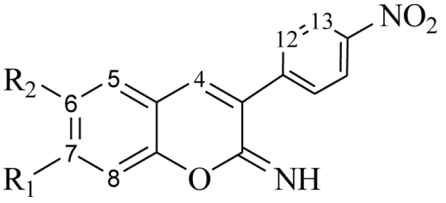
We have presented a facile route for the formation of novel iminocoumarins bearing parabanic rings by the reaction of *N*-ureaiminocoumarins derivatives with oxalyl chloride in the presence of pyridine and ethylene chloride as solvent. The *N*-ureaiminocoumarins derivatives were obtained by reaction of iminocoumarins derivatives with *N*-nucleophiles under acid catalysis. The method developed in this work is particularly interesting for the simplicity of providing this family of iminocoumarin compouds in good yield with high selectivity.

EXPERIMENTAL

Aldehydes **1–5**, *p*-nitrobenzyl cyanide **a**, 4-phenylsemicarbazide **b**, and oxalyl chloride **c** are commercial products. Solvents (toluene, chloroform) were purified by standard technique and redistilled prior to their use. Catalyst IRA 900 was conditioned and then used. The melting points were determined on an Electrothermal 9100 apparatus. IR spectra were obtained on a Jasco FTIR 420 instrument using KBr pellets. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker WP 200 spectrometer at 300 MHz and 75.0 MHz respectively, in $CDCl_3$ or dimethylsulfoxide (DMSO-d_6), with tetramethylsilane (TMS) as internal standard (chemical shifts in ppm). Elemental microanalysis were performed on a EA 1112 analyser from CE Instruments.

General Procedure for the Synthesis of Iminocoumarins (1a–5a)

A mixture of aldehydes **1–5** (20 mmol), IRA 900 resin (2 g, 20 mmol OH^-), and toluene (25 mL) were introduced in a 250-mL, three-necked flask equipped with a condenser and stirred for 3 h at 85 °C under a nitrogen atmosphere. After that, the *p*-nitrobenzyl cyanide **a** (20 mmol) was added and the mixture was refluxed for an appropriate time (Table 1). After completion of the reaction, the organic phase was separated from the solid catalyst and concentrated under reduced pressure. The solid phase was recrystallized from toluene (compound **1a, 3a**) or from ethyl acetate (compounds **2a, 4a–5a**).



Data

3-(*p*-Nitrophenyl)iminocoumarin (1a). IR (KBr) (cm^{-1}): $\nu = 1651$ (C=N), 3297 (NH). ^1H NMR (DMSO-d_6) (ppm): $\delta = 6.91$–7.58 (m, 4H, Ar), 7.93 (d, 2H, H_{12}, $J^3 = 8.7$ Hz), 8.23 (s, 1H, H_4), 8.32 (d, 2H, H_{13}, $J^3 = 8.7$ Hz), 8.58 (br, 1H, NH). ^{13}C NMR (DMSO-d_6) (ppm): $\delta = 108.0$, 116.6, 119.7, 120.8, 124.8, 127.2, 128.4, 130.5, 133.7, 140.8, 147.6, 153.5, 157.7. Mp (°C) = 182. Calculated for $C_{15}H_{10}N_2O_3$: C, 67.67%; H, 3.76; N, 10.53. Found: C, 67.73%; H, 3.81; N, 10.49.

6-Bromo-3-(*p*-nitrophenyl)iminocoumarin (2a). IR (KBr) (cm^{-1}): $\nu = 1653$ (C=N), 3288 (NH). ^1H NMR (DMSO-d_6) (ppm): $\delta = 6.93$ (d, 1H, H_8, $J^3 = 8.7$ Hz), 7.50 (dd, 1H, H_7, $J^3 = 8.7$ Hz, $J^4 = 2.4$ Hz), 7.66 (d, 1H, H_5, $J^4 = 2.4$ Hz), 7.94 (d, 2H, H_{12}, $J^3 = 8.7$ Hz), 8.13 (s, 1H, H_4), 8.30 (d, 2H, H_{13}, $J^3 = 8.7$ Hz), 8.76 (br, 1H, NH). ^{13}C NMR (DMSO-d_6) (ppm): $\delta = 109.4$, 110.3, 117.4, 118.6, 122.8, 124.7, 127.2, 130.4, 135.6, 140.2, 140.4, 147.6, 156.9. Mp (°C) = 222. Calculated for $C_{15}H_9BrN_2O_3$: C, 52.17%; H, 2.60; N, 8.11. Found: C, 52.28; H, 2.64; N, 7.95.

7-Diethylamino-3-(*p*-nitrophenyl)iminocoumarin (3a). IR (KBr) (cm^{-1}): $\nu = 1650$ (C=N), 3291 (NH). ^1H NMR ($CDCl_3$) (ppm): $\delta = 1.21$ (t, 6H, CH_3, $J^3 = 7.2$), 3.41 (q, 4H, CH_2, $J^3 = 7.2$), 6.35 (d, 1H, H_8, $J^4 = 2.4$ Hz), 6.46 (dd, 1H, H_6, $J^3 = 8.7$ Hz, $J^4 = 2.4$ Hz), 7.18 (d, 1H, H_5, $J^3 = 8.7$ Hz), 7.54 (s, 1H, H_4), 7.83 (d, 2H, H_{12}, $J^3 = 8.7$ Hz), 8.24 (d, 2H, H_{13}, $J^3 = 8.7$ Hz), 8.28 (s, 1H, NH). ^{13}C NMR ($CDCl_3$) (ppm): $\delta = 12.5$, 44.8, 96.7, 107.6, 108.4, 121.2, 123.6, 128.9, 129.0, 136.1, 144.1, 150.5, 155.7, 159.6, 164.0. Mp (°C) = 120. Calculated for $C_{19}H_{19}N_3O_3$: C, 67.65%; H, 5.63; N, 12.46. Found: C, 68.02%, H, 5.64; N, 12.55.

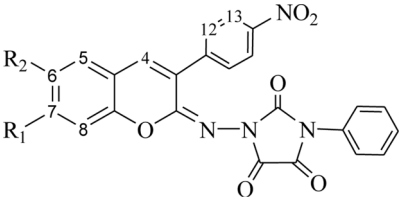
6-Methoxy-3-(*p*-nitrophenyl)iminocoumarin (4a). IR (KBr) (cm^{-1}): $\nu = 1647$ (C=N), 3293 (NH). ^1H NMR (DMSO-d_6) (ppm): $\delta = 3.75$ (s, 3H, CH_3O), 6.92 (d, 1H, H_8, $J^3 = 9$ Hz), 7.01 (dd, 1H, H_7, $J^3 = 9$ Hz, $J^4 = 3$ Hz), 7.59

(d, 1H, H_5, $J^4 = 3$ Hz), 7.93 (d, 2H, H_{12}, $J^3 = 9$ Hz), 8.20 (s, 1H, H_4), 8.31 (d, 2H, H_{13}, $J^3 = 9$ Hz), 8.48 (br, 1H, NH). ^{13}C NMR (DMSO-d_6) (ppm): $\delta = 56.1$, 112.1, 116.2, 118.4, 120.3, 123.5, 124.9, 127.2, 128.6, 143.5, 147.4, 147.8, 155.4, 162.3. Mp (°C) = 210. Calculated for $C_{16}H_{12}N_2O_4$: C, 64.86%; H, 4.05, N, 9.46. Found: C, 65.03%; H, 4.04; N, 9.22.

7-Methoxy-3-(*p*-nitrophenyl)iminocoumarin (5a). IR (KBr) (cm^{-1}): $\nu = 1648$ (C=N), 3276 (NH). ^{1}H NMR (DMSO-d_6) (ppm): $\delta = 3.77$ (s, 3H, CH_3O), 6.51 (d, 1H, H_8, $J^4 = 2.1$ Hz), 6.59 (dd, 1H, H_6, $J^3 = 8.7$ Hz, $J^4 = 2.1$ Hz), 7.89 (d, 2H, H_{12}, $J^3 = 8.7$ Hz), 8.06 (d, 1H, H_5, $J^3 = 8.7$ Hz), 8.16 (s, 1H, H_4), 8.29 (d, 2H, H_{13}, $J^3 = 8.7$ Hz), 8.45 (s, 1H, NH). ^{13}C NMR (DMSO-d_6) (ppm): $\delta = 55.8$, 101.4, 104.0, 106.9, 114.0, 118.7, 124.9, 126.7, 129.4, 130.3, 141.1, 147.1, 160.1, 164.1 Mp (°C) = 208. Calculated for $C_{16}H_{12}N_2O_4$: C, 64.86%; H, 4.05; N, 9.46. Found: C, 65.02%; H, 4.03; N, 9.24.

General Procedure for the Synthesis of *N*-Ureaiminocoumarins (1b–5b)

4-phenylsemicarbazide (3 mmol) was added with 5 ml of acetic acid to a stirred mixture of iminocoumarins (3 mmol) and chloroform (25 ml). The mixture was stirred for an appropriate time (Table 1) at room temperature. A red or orange solid was precipitated from the reaction mixture and was collected by filtration. It was recrystallized from an appropriate solvent.



Data

1-[3-(*p*-Nitrophenyl)-2H-chromen-2-ylidene]-4-phenylsemicarbazide (1b). IR (KBr) (cm^{-1}): $\nu = 1710$ (C=O), 3378 (NH). ^{1}H NMR (DMSO-d_6) (ppm): $\delta = 6.94$–7.54 (m, 9H, Ar), 7.47 (s, 1H, H_4), 8.03 (d, 2H, H_{12}, $J^3 = 8.7$ Hz), 8.32 (d, 2H, H_{13}, $J^3 = 8.7$ Hz), 8.41 (br, 1H, NH) 10.11 (br, 1H, NH). ^{13}C NMR (DMSO-d_6) (ppm): $\delta = 109.3$, 115.1, 117.9, 119.6, 121.4, 122.2, 124.1, 126.8, 128.3, 128.6, 131.1, 133.6, 139.9, 141.4, 147.3, 152.9, 157.6, 157.9. Mp (°C) ≥ 260. Calculated for $C_{22}H_{16}N_4O_4$: C, 66%; H, 4; N, 14. Found: C, 65.62%; H, 4.03; N, 14.08.

1-[3-(*p*-Nitrophenyl)-6-bromo-2H-chromen-2-ylidene]-4-phenylsemicarbazide (2b). IR (KBr) (cm^{-1}): $\nu = 1706$ (C=O), 3378 (NH).^{1}H NMR (DMSO-d_6) (ppm): $\delta = 6.98$–7.42 (m, 5H, Ar), 7.28 (d, 1H, H_8, $J^3 = 8.7$ Hz), 7.4 (s, 1H, H_4), 7.61 (dd, 1H, H_7, $J^3 = 8.7$ Hz, $J^4 = 2.4$ Hz), 7.74 (d, 1H, H_5, $J^4 = 2.4$ Hz), 8.01 (d, 2H, H_{12}, $J^3 = 9$ Hz), 8.31 (d, 2H, H_{13}, $J^3 = 9$ Hz), 8.41 (br, 1H, NH), 10.19 (br, 1H, NH). ^{13}C NMR (DMSO-d_6) (ppm): $\delta = 116.1$, 117.7, 119.0, 122.7, 122.8, 123.8, 129.0, 129.3, 130.0, 130.3, 130.6, 130.7, 133.7, 139.3, 142.1, 147.8, 151.4,

152.7. Mp (°C) = 222. Calculated for $C_{22}H_{15}BrN_4O_4$: C, 55.11%; H, 3.13%; N, 11.69. Found: C, 55.32%; H, 3.08; N, 11.73.

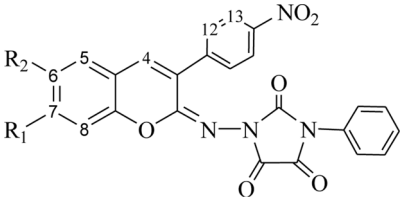
1-[3-(*p*-Nitrophenyl)-7-(diethylamino)-2H-chromen-2-ylidene]-4-phenylsemicarbazide (3b). IR (KBr) (cm^{-1}): $\nu = 1715$ (C=O), 3378 (NH). ^1H NMR ($CDCl_3$) (ppm): $\delta = 1.25$ (t, 6H, CH_3, $J^3 = 6.9$), 3.43 (q, 4H, CH_2, $J^3 = 6.9$), 6.45 (d, 1H, H_8, $J^4 = 2.1$ Hz), 6.48 (dd, 1H, H_6, $J^3 = 8.4$ Hz, $J^4 = 2.1$ Hz), 7.03–7.41 (m, 5H, Ar), 7.15 (d, 1H, H_5, $J^3 = 8.4$ Hz), 7.03 (s, 1H, H_4), 7.81 (br, 1H, NH), 7.83 (d, 2H, H_{12}, $J^3 = 9$ Hz), 8.23 (br, 1H, NH), 8.30 (d, 2H, H_{13}, $J^3 = 9$ Hz), ^{13}C NMR ($CDCl_3$) (ppm): $\delta = 12.9$, 45.2, 97.3, 108.3, 108.5, 119.5, 121.2, 123.7, 123.8, 129.4, 129.6, 132.5, 138.3, 142.7, 143.5, 147.5, 150.6, 153.2, 153.4, 154.3 Mp (°C) ≥ 260. Calculated for $C_{26}H_{25}N_5O_4$: C, 66.24%; H, 5.30; N, 14.85. Found: C, 66.17%; H, 5.22; N, 14.95.

1-[3-(*p*-Nitrophenyl)-6-methoxy-2H-chromen-2-ylidene]-4-phenylsemicarbazide (4b). IR (KBr) (cm^{-1}): $\nu = 1676$ (C=O), 3372 (NH). ^1H NMR (DMSO-d_6) (ppm): $\delta = 3.76$ (s, 3H, CH_3O), 6.96–7.43 (m, 5H, Ar), 7.03 (dd, 1H, H_7, $J^3 = 9.6$ Hz, $J^4 = 3$ Hz), 7.06 (d, 1H, H_8, $J^3 = 9.6$ Hz), 7.28 (d, 1H, H_5, $J^4 = 3$ Hz), 7.40 (s, 1H, H_4), 8.00 (d, 2H, H_{12}, $J^3 = 8.7$ Hz), 8.30 (d, 2H, H_{13}, $J^3 = 8.7$ Hz), 8.38 (br, 1H, NH), 10.04 (br, 1H, NH). ^{13}C NMR (DMSO-d_6) (ppm): $\delta = 55.9$, 112.1, 116.3, 117.3, 118.8, 120.8, 122.5, 123.6, 128.0, 129.1, 130.4, 131.3, 139.3, 141.5, 142.3, 146.3, 147.5, 152.6, 155.8. Mp (°C) ≥ 260. Calculated for $C_{23}H_{18}N_4O_5$: C, 64.18%; H, 4.18; N, 13.02. Found: C, 64.27%; H, 4.11; N, 12.96.

1-[3-(*p*-Nitrophenyl)-7-methoxy-2H-chromen-2-ylidene]-4-phenylsemicarbazide (5b). IR (KBr) (cm^{-1}): $\nu = 1711$, 3359. ^1H NMR (DMSO-d_6) (ppm): $\delta = 3.83$ (s, 3H, CH_3O), 6.83 (dd, 1H, H_6, $J^3 = 8.4$ Hz, $J^4 = 2.4$ Hz), 6.95 (d, 1H, H_5, $J^3 = 8.4$ Hz), 7.00 (d, 1H, H_8, $J^4 = 2.4$ Hz), 7.24–7.47 (m, 5H, Ar), 7.46 (s, 1H, H_4), 8.02 (d, 2H, H_{12}, $J^3 = 8.7$ Hz), 8.31 (d, 2H, H_{13}, $J^3 = 8.7$ Hz), 8.43 (br, 1H, NH), 10.09 (br, 1H, NH). ^{13}C NMR (DMSO-d_6) (ppm): $\delta = 55.3$, 101.1, 105.7, 115.7, 119.0, 124.1, 125.2, 126.8, 127.9, 128.8, 129.5, 130.2, 138.6, 145.3, 146.1, 154.0, 158.0, 161.2, 172.5. Mp (°C) = 150. Calculated for $C_{23}H_{18}N_4O_5$: C, 64.18%; H, 4.18; N, 13.02. Found: C, 64.22%; H, 4.22; N, 13.06.

General Procedure for the Synthesis of *N*-Parabanic Iminocoumarins 1c–5c

To a stirred mixture of *N*-ureaiminocoumarins (1.5 mmol) in 25 ml of ethylene chloride containing 0.5 ml of pyridine, 2.25 g of oxalyl chloride were added dropwise for 0.5 h at room temperature. The reaction mixture was then stirred for 12 h at 60 °C. A yellow solid was precipitated from the reaction mixture and collected by filtration. It was recrystallized from an appropriate solvent.



Data

***N*-(3′-Phenylparabanic acid)-3-(*p*-nitrophenyl)iminocoumarin (1c).** IR (KBr) (cm^{-1}): $\nu = 1739$, 1773. ^1H NMR (DMSO-d_6) (ppm): $\delta = 7.37$–7.77 (m, 9H, Ar), 8.02 (d, 2H, H_{12}, $J^3 = 8.7$ Hz), 8.09 (s, 1H, H_4), 8.33 (d, 2H, H_{13}, $J^3 = 8.7$ Hz), ^{13}C NMR (DMSO-d_6) (ppm): $\delta = 116.2$, 119.6, 121.2, 123.6, 124.8, 125.5, 125.8, 127.2, 129.5, 130.7, 130.8, 132.7, 138.6, 141.5, 147.6, 151.4, 153.1, 155.4, 156.9, 158.6. Mp (°C) ≥ 260. Calculated for $C_{24}H_{14}N_4O_6$: C, 63.43%; H, 3.08; N, 12.33. Found: C, 63.77%; H, 2.95, N, 12.13.

***N*-(3′-Phenylparabanic acid)-6-bromo-3-(*p*-nitrophenyl)iminocoumarin (2c).** IR (KBr) (cm^{-1}): $\nu = 1721$, 1742, 1772. ^1H NMR (DMSO-d_6) (ppm): $\delta = 7.42$–8.86 (m, 13H, Ar). ^{13}C NMR (DMSO-d_6) (ppm): $\delta = 117.2$, 118.4, 121.7, 123.6, 126.8, 127.1, 129.1, 129.4, 130.8, 131.3, 134.9, 137.2, 141.1, 143.9, 144.2, 147.8, 150.5, 153.0, 155.8, 158.1. Mp (°C) ≥ 260. Calculated for $C_{24}H_{13}BrN_4O_6$: C, 54.03%; H, 2.44; N, 10.50. Found: C, 54.11%; H, 2.41; N, 10.41.

***N*-(3′-Phenylparabanic acid)-7-(diethylamino)-3-(*p*-nitrophenyl)iminocoumarin (3c).** IR (KBr) (cm^{-1}): $\nu = 1723$, 1744, 1790. ^1H NMR ($CDCl_3$) (ppm): $\delta = 1.18$ (t, 6H, CH_3, $J^3 = 7.2$), 3.40 (q, 4H, CH_2, $J^3 = 7.2$), 6.48 (d, 1H, H_8, $J^4 = 2.4$ Hz), 6.58 (dd, 1H, H_6, $J^3 = 9$ Hz, $J^4 = 2.4$ Hz), 7.30 (d, 1H, H_5, $J^3 = 9$ Hz), 7.36–8.77 (m, 5H, Ar), 7.76 (s, 1H, H_4), 7.86 (d, 2H, H_{12}, $J^3 = 6.9$ Hz), 8.23 (d, 2H, H_{13}, $J^3 = 6.9$ Hz), ^{13}C NMR ($CDCl_3$) (ppm): $\delta = 12.4$, 44.6, 98.1, 106.2, 110.3, 121.8, 123.9, 124.3, 125.9, 128.1, 128.3, 129.2, 133.0, 137.1, 143.6, 148.2, 149.1, 150.3, 152.4, 155.8, 156.3, 159.9. Mp (°C) = 174. Calculated for $C_{28}H_{23}N_5O_6$: C, 64%; H, 4.38; N, 13.33. Found: C, 63.78%; H, 4.29; N, 13.52.

***N*-(3′-Phenylparabanic acid)-6-methoxy-3-(*p*-nitrophenyl)iminocoumarin (4c).** IR (KBr) (cm^{-1}): $\nu = 1735$, 1761, 1772. ^1H NMR (DMSO-d_6) (ppm): $\delta = 3.80$ (s, 3H, CH_3O), 7.20 (dd, 1H, H_7, $J^3 = 9$ Hz, $J^4 = 3$ Hz), 7.31 (d, 1H, H_5, $J^4 = 3$ Hz), 7.40 (d, 1H, H_8, $J^3 = 9$ Hz), 7.46–7.57 (m, 5H, Ar), 8.03 (s, 1H, H_4), 8.01 (d, 2H, H_{12}, $J^3 = 8.7$ Hz), 8.33 (d, 2H, H_{13}, $J^3 = 8.7$ Hz), ^{13}C NMR (DMSO-d_6) (ppm): $\delta = 56.1$, 112.0, 117.3, 119.5, 120.2, 123.6, 125.8, 127.2, 129.1, 129.4, 130.80, 130.86, 138.6, 141.5, 145.8, 147.6, 150.7, 153.2, 156.0, 156.5, 158.8. Mp (°C) ≥ 260. Calculated for $C_{25}H_{16}N_4O_7$: C, 61.98%; H, 3.30; N, 11.57. Found: C, 62.09%; H, 3.36; N, 11.48.

***N*-(3′-Phenylparabanic acid)-7-methoxy-3-(*p*-nitrophenyl)iminocoumarin (5c).** IR (KBr) (cm^{-1}): $\nu = 1733$, 1759, 1771. ^1H NMR (DMSO-d_6) (ppm): $\delta = 3.81$ (s, 3H, CH_3O), 6.95 (dd, 1H, H_6, $J^3 = 8.3$ Hz, $J^4 = 2.1$ Hz), 7.15 (d, 1H, H_5, $J^3 = 8.3$ Hz), 7.25 (d, 1H, H_8, $J^4 = 2.1$ Hz), 7.42–7.63 (m, 5H, Ar), 7.56 (s, 1H, H_4), 8.12 (d, 2H, H_{12}, $J^3 = 8.7$ Hz), 8.30 (d, 2H, H_{13}, $J^3 = 8.7$ Hz). ^{13}C NMR (DMSO-d_6) (ppm): $\delta = 56.2$, 104.5, 109.3, 116.1, 120.5, 123.8, 124.7, 125.9, 127.9, 128.6, 129.1, 132.0, 138.4, 142.0, 146.9, 149.1, 151.3, 154.6, 159.4, 160.1, 161.2. Mp (°C) ≥ 260. Calculated for $C_{25}H_{16}N_4O_7$: C, 61.98%; H, 3.30, N, 11.57. Found: C, 62.07%; H, 3.34; N, 11.46.

ACKNOWLEDGMENTS

The authors acknowledge the Ministry of Higher Education, Scientific Research, and Technology in Tunisia for their financial support. They also thank Pr. Rachid El Gharbi for his useful discussions about this work.

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