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Serendipitous stereoselective synthesis of brand-new fluorescent dyes: (1*Z*)-3-(alkylimino)-1-[(chromone-3-yl)methylene]-1,3-dihydro-9*H*-furo[3,4-*b*]-chromen-9-one-type fluorophores with blue fluorescence emission properties

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ABSTRACT

The reactions of 3-formylchromones with alkyl isocyanides in dry dichloromethane at room temperature lead to new types of organic fluorophores (1*Z*)-3-(alkylimino)-1-[(chromone-3-yl)methylene]-1,3-dihydro-9*H*-furo[3,4-*b*]chromen-9-one, which exhibited strong blue emission in solution. The reactions involve a [4+1] cycloaddition followed by an activated electrophilic aromatic substitution at the furan ring and dehydration sequence.

1. Introduction

Fluorescence has been a major topic of recent research for photofunctional materials, and has found extensive applications in a variety of fields, such as solar energy collecting materials, laser chemistry, fluorescent probes, copy-preventing inks, and related areas.[1] Organic electroluminescent devices employing organic fluorophores as emitters have been the focus of considerable interest because of their possible applications as displays for mobile phones, personal computers, and televisions.[2] Organic fluorophores exhibiting strong blue, green, and red emissions are the most promising emitters for the fabrication of full-color electroluminescent devices.[3]

Again, fluorescence applications to biochemical measurements have increased dramatically, especially through the development of new fluorescent ligands.[4,5] The labeling of biomolecules with organic fluorophores for analytical applications is an attractive field of research. A protein bound to a fluorescent moiety is an important tool for conformational studies of protein–protein and ligand–receptor interactions. Among other applications, fluorogenic pre-column derivatizing agents for highly sensitive fluorescent detection in HPLC determinations, examined in view of sensitivity, separability, and short-run time have been reported.[6–8] Fluorescence allows qualitative and quantitative determinations to be performed easily and reliably by rapid and economic methods, with improved sensitivity and selectivity. Furthermore, labeling by fluorescent probes is an alternative to the use of radioactive compounds.

It is very important to design and develop new fluorescent chromophores, which have specific functionalities as new dye materials. By careful choice of molecular frame and functionality, it is possible to fine-tune the electronic properties of organic compounds.[9–12] The design and synthesis of brightly emissive molecules having a heterocyclic backbone and allowing for alterations in emission properties are a subject of current research in view of their potential applications as chemosensors and in optoelectronic devices.[13,14]

To the best of our knowledge, there are only few reports[15–20] on the synthesis of fused furochromones containing the furo[3,4-*b*]chromen skeleton, and very few of these compounds[18–20] are fluorescent products. The photoisomerization of 3-aroyl- and 3-(2-furoyl)-2-(2-furyl)-chromones has been shown to produce the corresponding 1-aryl- or L-(2-furyl)-furo[3,4-*b*]chromones as new photoluminescent compounds.[19,20]

Recently, the reaction of 3-formylchromones with tosylmethyl isocyanide (TOSMIC) in the presence of DBU in THF at room temperature leading to 2-tosyl-4-(2-hydroxybenzoyl)pyrroles, after in situ deformylation, has been reported.[21] As part of an ongoing research program on the development of new routes for the preparation of novel heterocyclic compounds,[22] in the present study, we

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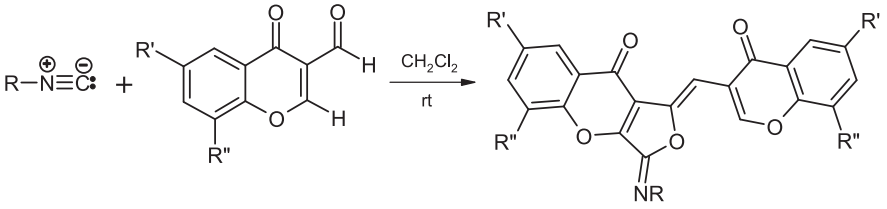
report our results on the one-pot pseudo three-component cascade transformation of 3-formylchromones and alkyl isocyanides into (1*Z*)-3-(alkylimino)-1-[(chromone-3-yl)methylene]-1,3-dihydro-9*H*-furo[3,4-*b*]chromen-9-ones, which is to our knowledge, the first example of the cascade assembly of this structure.

In a pilot experiment, it was observed that a solution of 3-formylchromone in anhydrous dichloromethane, when treated with a stoichiometric amount of *tert*-octyl isocyanide at room temperature afforded the (1*Z*)-3-(*tert*-octylimino)-1-[(4-oxo-4*H*-chromen-3-yl)methylene]-1,3-dihydro-9*H*-furo[3,4-*b*]chromen-9-one **3a** in 83% yield within 4 days and a half amount of *tert*-octyl isocyanide remaining unreacted.

Encouraged by this success, we successfully examined the reaction of 3-formylchromones (2 equiv) with other alkyl isocyanides (1 equiv) under similar conditions, furnishing the respective (1*Z*)-3-(alkylimino)-1-[(chromone-3-yl)methylene]-1,3-dihydro-9*H*-furo[3,4-*b*]chromen-9-ones **3a**–**o** in good yields. The optimized results are summarized in Table 1. The work-up involved simple filtration and washing with a small amount of acetone to provide the pure products. Compounds **3a**–**o** are stable yellow solids whose structures were established by IR, ^{1}H, ^{13}C NMR spectroscopy, and elemental analysis. For example, the ^{1}H NMR spectrum of **3a** exhibited five signals identified as *tert*-butyl protons (δ_H 1.05 ppm), geminal methyl groups (δ_H 1.61 ppm), methylene protons (δ_H 1.91 ppm), and two vinylic methine (δ_H 7.17 and 8.73 ppm) protons, along with multiplets for the aromatic hydrogens (δ_H 7.40–8.34 ppm). The ^{1}H decoupled ^{13}C NMR spectrum of **3a** showed 26 distinct resonances, which confirmed the proposed structure.

Table 1
Pseudo three-component condensation reactions of alkyl isocyanides and 3-formylchromone derivatives in dry dichloromethane



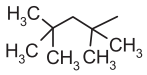
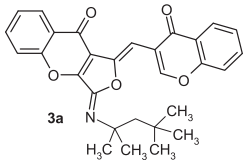
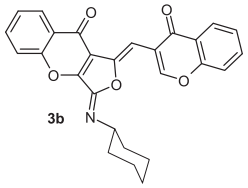
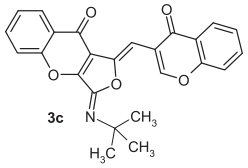
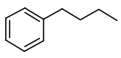
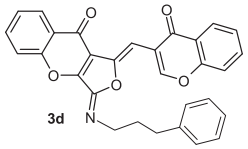
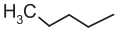
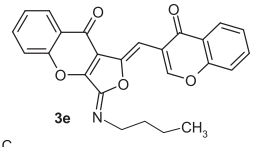
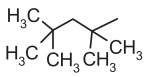
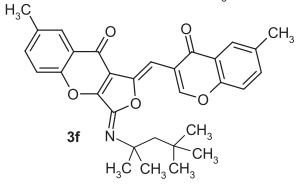
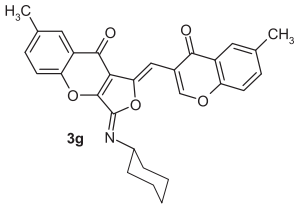
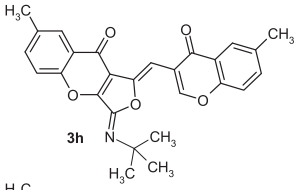
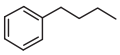
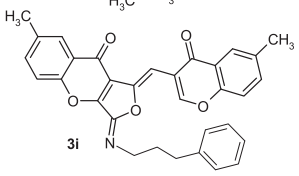
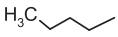
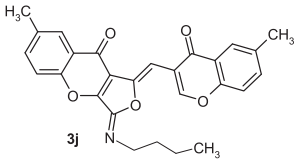
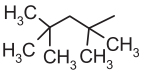
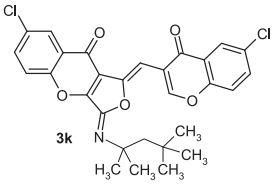
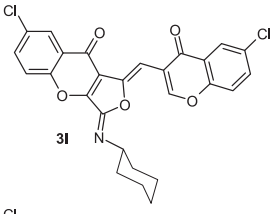
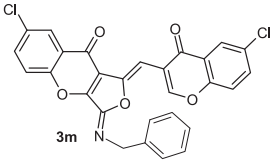
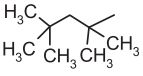
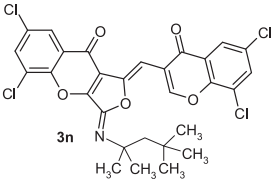
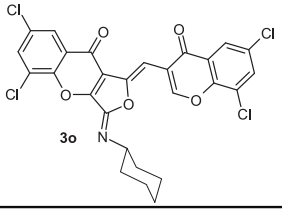
Entry	R	R′	R″	Product	Yield[a] (%)
1		H	H	 **3a**	83
2		H	H	 **3b**	89
3		H	H	 **3c**	82
4		H	H	 **3d**	90
5		H	H	 **3e**	77
6		CH_3	H	 **3f**	86

Table 1 (*continued*)

Entry	R	R′	R″	Product	Yield[a] (%)
7		CH_3	H	 **3g**	91
8		CH_3	H	 **3h**	84
9		CH_3	H	 **3i**	79
10		CH_3	H	 **3j**	93
11		Cl	H	 **3k**	88
12		Cl	H	 **3l**	91
13		Cl	H	 **3m**	62
14		Cl	Cl	 **3n**	90
15		Cl	Cl	 **3o**	94

[a] Refers to purified yield, which is >95% as determined by ^{1}H NMR spectroscopy.

Four 3-formylchromones and eight alkyl or aryl isocyanides were examined to study the generality and scope of the present protocol. The results show that the three-component reaction is quite general with 3-formylchromones affording the expected fused furochromones **3** in good yields. Also, we have found that the reactions proceed very efficiently with alkyl isocyanides, but the present method failed to furnish the expected fused furochromone derivatives with aryl isocyanides (2,6-dimethylphenyl isocyanide and 2-naphthyl isocyanide).

Although the mechanistic details of all the reactions are not known, the formation of these heterocycles tabulated in Table 1 can be rationalized by formation of a highly reactive fused 3-(alkylamino)-9*H*-furo[3,4-*b*]chromen-9-one intermediate **4** by the [4+1] cycloaddition reaction of alkyl isocyanide to 3-formylchromone followed by imine–enamine tautomerization. This attacks the formyl group of another 3-formylchromone leading to adduct **5**. Dehydration of the latter leads to the new compounds (1*Z*)-3-(alkylimino)-1-[(chromone-3-yl)methylene]-1,3-dihydro-9*H*-furo[3,4-*b*]chromen-9-ones **3** (Scheme 1).

In order to study whether the second equivalent of 3-formylchromones can be replaced with the other aldehydes, we carried out many parallel experiments. First, we examined the reaction of 6,8-dichloro-3-formylchromone (1 equiv), with cyclohexyl isocyanide (1 equiv) in the presence of 1 equiv of 4-nitrobenzaldehyde, in dry dichloromethane. A yellow solid precipitated from the reaction mixture when left to stand 4 days at room temperature. Structural elucidation by ^{1}H and ^{13}C NMR spectroscopy revealed this precipitate to be **3o** without the participation of 4-nitrobenzaldehyde and a half-stoichiometric amount of cyclohexyl isocyanide, which did not enter into the reaction. Also, our attempts to carry out this reaction under the same reaction conditions with other aromatic aldehydes, such as benzaldehyde or 4-(dimethylamino)benzaldehyde did not produce the expected products and these aromatic aldehydes remained totally unchanged and only product **3o** isolated. This remains an area for further investigations.

Compounds **3a**–**o** revealed very interesting photo-physical properties and spectacular fluorescence in solution (Fig. 1).

As shown in Fig. 2, the UV–vis spectra of these products in dichloromethane displayed similar absorption bands.

In summary, we have developed a simple and convenient one-pot, pseudo three-component reaction of alkyl isocyanides with 3-formylchromone derivatives to afford a new type of organic fluorophore, (1*Z*)-3-(alkylimino)-1-[(chromone-3-yl)methylene]-1,3-dihydro-9*H*-furo[3,4-*b*]chromen-9-ones. All the products prepared from this facile reaction were highly fluorescent exhibiting strong blue emission in solution and are expected to have important applications in material science and as DNA-intercalating agents.

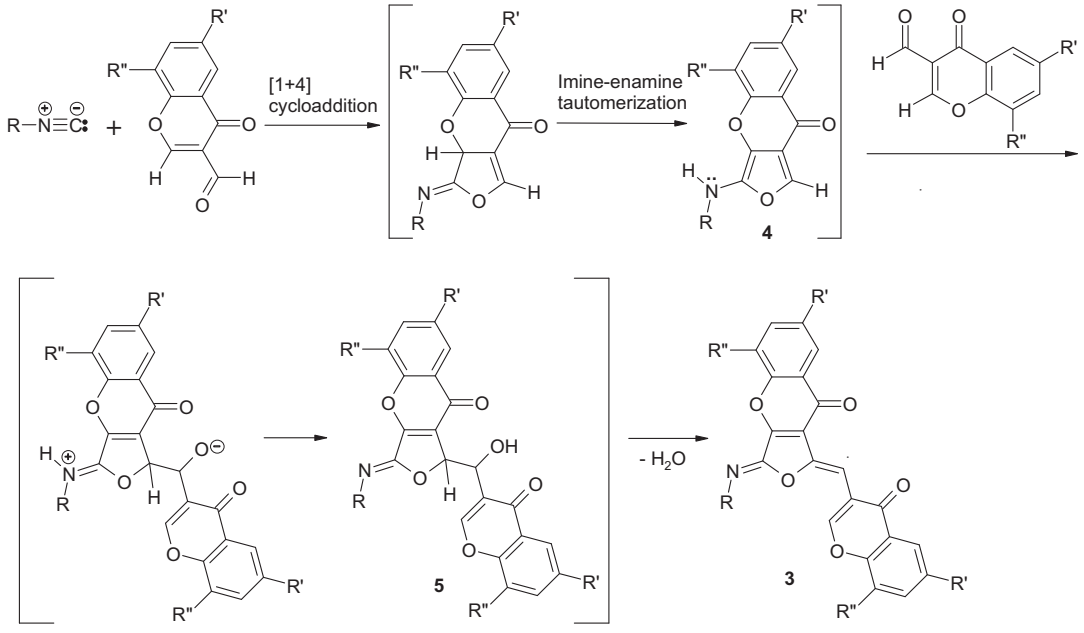
2. Experimental

2.1. General

Melting points were measured on a Büchi 535 apparatus and are uncorrected. Elemental analyses were performed using an Elementar Vario EL *III* instrument. FT-IR Spectra were recorded on a Bruker Equinox-55 spectrometer. UV–vis spectra were recorded on an Agilent HP 8453 Diode-Array spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DRX-400 Avance spectrometer at 400.13 and 100.77 MHz, respectively, with $CDCl_3$ as solvent and calibrated using residual undeuterated solvent as an internal reference. Chemical shifts are reported in parts per million (ppm) relative to TMS as internal reference. Analytical TLC was carried out on pre-coated plates (Merck silica gel 60 F_{254}) and visualized with UV light. All chemical reagents were obtained from Merck, Fluka or Acros and were used without further purification.

2.2. Typical procedure for preparation of (1*Z*)-1-[(4-oxo-4*H*-chromen-3-yl)methylene]-3-[(1,1,3,3-tetramethylbutyl)imino]-1,3-dihydro-9*H*-furo[3,4-*b*]chromen-9-one (3a)

To a magnetically stirred solution of 3-formylchromone (0.348 g, 2.0 mmol) in dry CH_2Cl_2 (10 mL) in a screw-capped vial, was added *tert*-octyl isocyanide (0.140 g, 1.0 mmol) via a syringe at room temperature (25 °C). The reaction mixture was then stirred for 4 days and the completion of reaction was confirmed by TLC (EtOAc/hexane 1:1). Then, the resulting solids were filtered and washed with acetone (5 mL) to yield **3a** as a yellow powder (0.390 g, 83%). The dried product thus obtained showed a single spot on TLC and was pure enough for all analytical purposes. Mp 267–269 °C; R_f (50% EtOAc/*n*-hexane) 0.67; IR (KBr) (ν_{max}, cm^{-1}): 1716, 1676, and 1649 (C=O), 1613 (C=C); ^{1}H NMR (400.1 MHz, $CDCl_3$): δ_H 1.05 (9H, s, C(CH_3)$_3$), 1.61 (6H, s, C(CH_3)$_2$, 1.91 (2H, s, CH_2)), 7.17 (1H, s, =CH–C), 7.40–8.34



Scheme 1. Possible mechanism for the formation of products **3**.

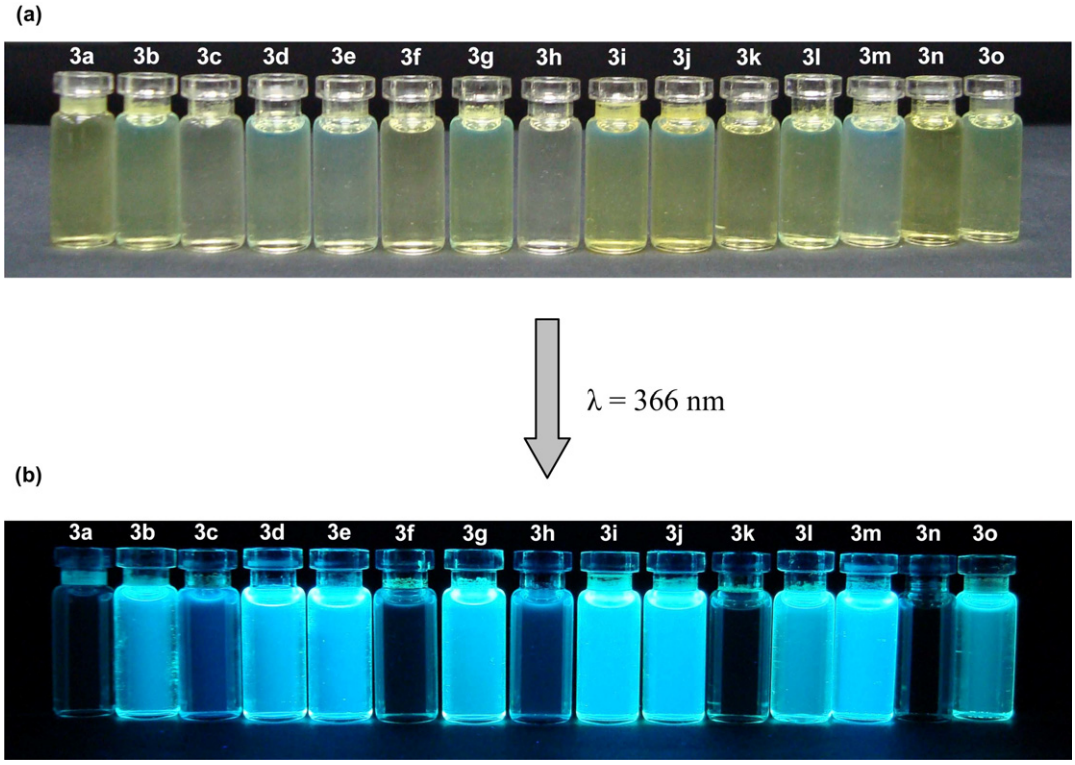


Fig. 1. Fluorescence of compounds **3a**–**o** in CH_2Cl_2 (a) before and (b) after UV exposure (λ=366 nm).

(8H, m, arom.), 8.73 (1H, s, =CH–O); ^{13}C NMR (100.7 MHz, $CDCl_3$): δ_C 175.18, 172.57, 156.57, 156.06, 155.85, 153.43, 144.94, 144.54, 134.87, 133.96, 126.73, 126.63, 126.36, 125.62, 124.92, 123.92, 119.64, 119.58, 119.50, 118.31, 97.86, 60.42, 54.94, 32.26, 31.81, 30.51. Anal. Calcd for $C_{29}H_{27}NO_5$ (469.52): C, 74.18; H, 5.80; N, 2.98%. Found: C, 74.47; H, 5.78; N, 2.96%.

*2.2.1. (1Z)-3-(Cyclohexylimino)-1-[(4-oxo-4H-chromen-3-yl)methylene]-1,3-dihydro-9H-furo[3,4-b]chromen-9-one (**3b**).* Yellow powder (0.392 g, 89%); mp 276–278 °C; R_f (50% EtOAc/*n*-hexane) 0.70; IR (KBr) (ν_{max}, cm^{-1}): 1699, 1671, and 1652 (C=O), 1610 (C=C); ^{1}H NMR (400.1 MHz, $CDCl_3$): δ_H 1.33–1.97 (10H, s, $5CH_2$), 3.90–3.94 (1H, m, NCH), 7.21 (1H, s, =CH–C), 7.40–8.37 (8H, m, arom.), 8.71 (1H, s, =CH–O); ^{13}C NMR (100.7 MHz, $CDCl_3$): δ_C 174.9, 172.2, 156.3, 155.9, 155.8, 152.5, 144.1, 134.8, 133.8, 126.8, 126.5, 126.2, 125.4, 124.7, 123.7, 120.4, 119.5, 119.2, 118.3, 118.1, 98.1, 58.2, 33.3, 25.5, 24.9. Anal. Calcd for $C_{27}H_{21}NO_5$ (439.45): C, 73.79; H, 4.82; N, 3.19%. Found: C, 73.63; H, 4.80; N, 3.21%.

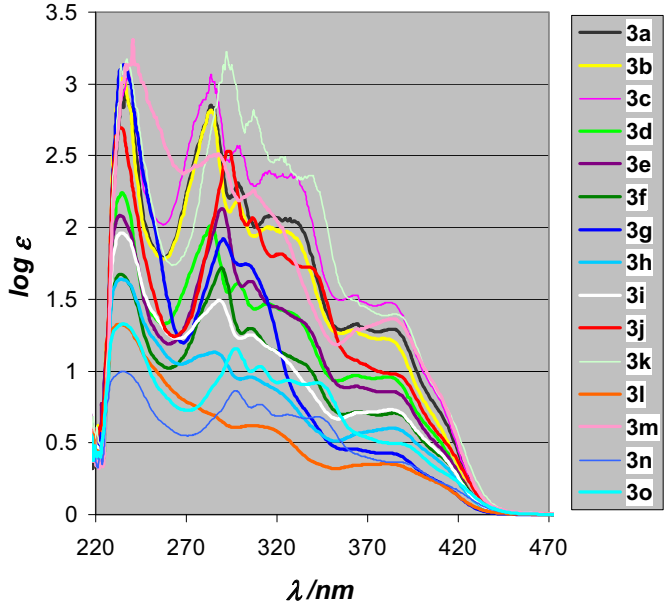


Fig. 2. UV–vis spectra of compounds **3a**–**o** in dichloromethane.

*2.2.2. (1Z)-3-(tert-Butylimino)-1-[(4-oxo-4H-chromen-3-yl)methylene]-1,3-dihydro-9H-furo[3,4-b]chromen-9-one (**3c**).* Yellow powder (0.340 g, 82%); mp 256–258 °C; R_f (50% EtOAc/*n*-hexane) 0.71; IR (KBr) (ν_{max}, cm^{-1}): 1713, 1671, and 1649 (C=O), 1609 (C=C); ^{1}H NMR (400.1 MHz, $CDCl_3$): δ_H 1.55 (9H, s, $C(CH_3)_3$), 7.15 (1H, s, =CH–C), 7.38–8.33 (8H, m, arom.), 8.71 (1H, s, =CH–O); ^{13}C NMR (100.7 MHz, $CDCl_3$): δ_C 175.2, 172.6, 156.5, 156.0, 155.7, 153.7, 145.1, 144.5, 134.8, 133.9, 126.7, 126.6, 126.3, 125.5, 124.9, 123.9, 119.6, 119.5, 119.4, 118.3, 97.4, 56.2, 30.1. Anal. Calcd for $C_{25}H_{19}NO_5$ (413.42): C, 72.63; H, 4.63; N, 3.39%. Found: C, 72.37; H, 4.64; N, 3.40%.

*2.2.3. (1Z)-1-[(4-Oxo-4H-chromen-3-yl)methylene]-3-[(3-phenylpropyl)imino]-1,3-dihydro-9H-furo[3,4-b]chromen-9-one (**3d**).* Yellow powder (0.428 g, 90%); mp 184–186 °C; R_f (50% EtOAc/*n*-hexane) 0.69; IR (KBr) (ν_{max}, cm^{-1}): 1699, 1673, and 1638 (C=O), 1610 (C=C); ^{1}H NMR (400.1 MHz, $CDCl_3$): δ_H 2.18 (2H, qui., $^3J_{HH}$ 7.1 Hz, $NCH_2CH_2CH_2Ph$), 2.81 (2H, t, $^3J_{HH}$ 7.1 Hz, $NCH_2CH_2CH_2Ph$), 3.74 (2H, t, $^3J_{HH}$ 7.1 Hz, $NCH_2CH_2CH_2Ph$), 5.28 (1H, s, =CH–C), 7.15–8.33 (13H, m, arom.), 8.55 (1H, s, =CH–O); ^{13}C NMR (100.7 MHz, $CDCl_3$): δ_C 175.1, 172.4, 156.5, 156.2, 156.0, 152.8, 144.1, 141.7, 135.0, 133.9, 128.7, 128.6, 126.7, 126.4, 126.1, 125.5, 124.9, 123.8, 120.5, 119.6, 119.2, 118.3, 97.8, 48.5, 33.7, 31.7. Anal. Calcd for $C_{30}H_{21}NO_5$ (475.49): C, 75.78; H, 4.45; N, 2.95%. Found: C, 76.01; H, 4.41; N, 2.96%.

*2.2.4. (1Z)-3-(Butylimino)-1-[(4-oxo-4H-chromen-3-yl)methylene]-1,3-dihydro-9H-furo[3,4-b]chromen-9-one (**3e**).* Yellow powder (0.319 g, 77%); mp 170–172 °C; R_f (50% EtOAc/*n*-hexane) 0.75; IR (KBr) (ν_{max}, cm^{-1}): 1795, 1701, 1671, and 1647 (C=O), 1611 (C=C);

^{1}H NMR (400.1 MHz, $CDCl_3$): δ_H 1.00 (3H, t, $^3J_{HH}$ 7.3 Hz, $NCH_2CH_2CH_2CH_3$), 1.50 (2H, sex., $^3J_{HH}$ 7.3 Hz, $NCH_2CH_2CH_2CH_3$), 1.80 (2H, qui., $^3J_{HH}$ 7.3 Hz, $NCH_2CH_2CH_2CH_3$), 3.73 (2H, t, $^3J_{HH}$ 7.3 Hz, $NCH_2CH_2CH_2CH_3$), 7.14 (1H, s, =CH–C), 7.36–8.31 (8H, m, arom.), 8.71 (1H, s, =CH–O); ^{13}C NMR (100.7 MHz, $CDCl_3$): δ_C 175.1, 172.4, 156.4, 156.1, 156.0, 152.9, 148.5, 144.2, 134.9, 133.9, 127.4, 126.7, 126.4, 125.5, 124.9, 123.8, 120.4, 119.7, 119.2, 118.3, 97.6, 49.1, 32.7, 20.9, 14.1. Anal. Calcd for $C_{25}H_{19}NO_5$ (413.42): C, 72.63; H, 4.63; N, 3.39%. Found: C, 72.40; H, 4.66; N, 3.37%.

*2.2.5. (1Z)-7-Methyl-1-[(6-methyl-4-oxo-4H-chromen-3-yl)methylene]-3-[(1,1,3,3-tetramethylbutyl)imino]-1,3-dihydro-9H-furo[3,4-b]chromen-9-one (**3f**).* Yellow powder (0.428 g, 86%); mp 277–279 °C; R_f (50% EtOAc/*n*-hexane) 0.66; IR (KBr) (ν_{max}, cm^{-1}): 1700, 1675, and 1652 (C=O), 1617 (C=C); ^{1}H NMR (400.1 MHz, $CDCl_3$): δ_H 1.04 (9H, s, $C(CH_3)_3$), 1.61 (6H, s, $C(CH_3)_2$), 1.91 (2H, s, CH_2), 2.46 and 2.48 (6H, 2s, $2CH_3$), 7.18 (1H, s, =CH–C), 7.36–8.10 (6H, m, arom.), 8.70 (1H, s, =CH–O); ^{13}C NMR (100.7 MHz, $CDCl_3$): δ_C 175.3, 172.6, 155.8, 154.9, 154.3, 153.2, 146.2, 145.1, 144.5, 136.6, 136.1, 135.7, 135.2, 126.0, 125.9, 124.6, 123.6, 119.5, 119.3, 119.2, 118.1, 98.1, 60.4, 54.9, 32.3, 31.8, 30.5, 21.2. Anal. Calcd for $C_{31}H_{31}NO_5$ (497.58): C, 74.83; H, 6.28; N, 2.81%. Found: C, 74.69; H, 6.31; N, 2.81%.

*2.2.6. (1Z)-3-(Cyclohexylimino)-7-methyl-1-[(6-methyl-4-oxo-4H-chromen-3-yl)methylene]-1,3-dihydro-9H-furo[3,4-b]chromen-9-one (**3g**).* Yellow powder (0.426 g, 91%); mp 306–308 °C; R_f (50% EtOAc/*n*-hexane) 0.70; IR (KBr) (ν_{max}, cm^{-1}): 1700, 1675, and 1651 (C=O), 1615 (C=C); ^{1}H NMR (400.1 MHz, $CDCl_3$): δ_H 1.23–1.96 (10H, s, $5CH_2$), 2.46 and 2.48 (6H, 2s, $2CH_3$), 3.88–3.93 (1H, m, NCH), 7.20 (1H, s, =CH–C), 7.36–8.10 (6H, m, arom.), 8.68 (1H, s, =CH–O); ^{13}C NMR (100.7 MHz, $CDCl_3$): δ_C 179.6, 177.1, 160.5, 159.3, 158.8, 157.7, 151.5, 148.7, 141.1, 140.9, 140.1, 139.9, 130.3, 130.1, 129.0, 127.8, 124.5, 123.9, 123.6, 122.9, 101.2, 64.1, 62.6, 42.8, 38.2, 36.0, 30.3, 29.4, 25.7. Anal. Calcd for $C_{29}H_{25}NO_5$ (467.51): C, 74.50; H, 5.39; N, 3.00%. Found: C, 74.68; H, 5.36; N, 3.00%.

*2.2.7. (1Z)-3-(tert-Butylimino)-7-methyl-1-[(6-methyl-4-oxo-4H-chromen-3-yl)methylene]-1,3-dihydro-9H-furo[3,4-b]chromen-9-one (**3h**).* Yellow powder (0.0.371 g, 84%); mp 298–300 °C; R_f (50% EtOAc/*n*-hexane) 0.74; IR (KBr) (ν_{max}, cm^{-1}): 1792, 1700, 1674, and 1651 (C=O), 1616 (C=C); ^{1}H NMR (400.1 MHz, $CDCl_3$): δ_H 1.53 (9H, s, $C(CH_3)_3$), 2.45 and 2.48 (6H, 2s, $2CH_3$), 7.14 (1H, s, =CH–C), 7.35–8.10 (6H, m, arom.), 8.70 (1H, s, =CH–O); ^{13}C NMR (100.7 MHz, $CDCl_3$): δ_C 175.4, 172.7, 155.6, 154.8, 154.3, 153.7, 145.0, 144.4, 136.5, 136.0, 135.6, 135.2, 126.0, 125.5, 125.2, 124.6, 123.5, 119.4, 119.0, 118.1, 97.1, 56.0, 30.1, 21.2, 21.1. Anal. Calcd for $C_{27}H_{23}NO_5$ (441.47): C, 73.46; H, 5.25; N, 3.17%. Found: C, 73.21; H, 5.20; N, 3.17%.

*2.2.8. (1Z)-7-Methyl-1-[(6-methyl-4-oxo-4H-chromen-3-yl)methylene]-3-[(3-phenylpropyl)imino]-1,3-dihydro-9H-furo[3,4-b]chromen-9-one (**3i**).* Yellow powder (0.398 g, 79%); mp 200–202 °C; R_f (50% EtOAc/*n*-hexane) 0.65; IR (KBr) (ν_{max}, cm^{-1}): 1703, 1675, and 1638 (C=O), 1619 (C=C); ^{1}H NMR (400.1 MHz, $CDCl_3$): δ_H 2.18 (2H, qui., $^3J_{HH}$ 7.1 Hz, $NCH_2CH_2CH_2Ph$), 2.46 and 2.49 (6H, 2s, $2CH_3$), 2.81 (2H, t, $^3J_{HH}$ 7.1 Hz, $NCH_2CH_2CH_2Ph$), 3.75 (2H, t, $^3J_{HH}$ 7.1 Hz, $NCH_2CH_2CH_2Ph$), 7.16–8.11 (12H, m, =CH–C, and arom.), 8.54 (1H, s, =CH–O); ^{13}C NMR (100.7 MHz, $CDCl_3$): δ_C 175.2, 172.5, 156.2, 154.8, 154.3, 144.1, 141.6, 136.7, 136.2, 135.7, 135.2, 128.7, 128.6, 128.4, 126.3, 126.1, 126.0, 124.6, 123.5, 119.3, 119.0, 118.2, 118.0, 117.8, 98.6, 48.3, 33.7, 31.6, 21.2. Anal. Calcd for $C_{32}H_{25}NO_5$ (503.54): C, 76.33; H, 5.00; N, 2.78%. Found: C, 76.16; H, 4.98; N, 2.76%.

*2.2.9. (1Z)-3-(Butylimino)-7-methyl-1-[(6-methyl-4-oxo-4H-chromen-3-yl)methylene]-1,3-dihydro-9H-furo[3,4-b]chromen-9-one (**3j**).* Yellow powder (0.439 g, 93%); mp 196–198 °C; R_f (50% EtOAc/*n*-hexane) 0.72; IR (KBr) (ν_{max}, cm^{-1}): 1701, 1672, and 1640 (C=O), 1609 (C=C); ^{1}H NMR (400.1 MHz, $CDCl_3$): δ_H 1.00 (3H, t, $^3J_{HH}$ 7.3 Hz, $NCH_2CH_2CH_2CH_3$), 1.50 (2H, sex., $^3J_{HH}$ 7.3 Hz, $NCH_2CH_2CH_2CH_3$), 1.80 (2H, qui., $^3J_{HH}$ 7.3 Hz, $NCH_2CH_2CH_2CH_3$), 2.45 and 2.48 (6H, 2s, $2CH_3$), 3.73 (2H, t, $^3J_{HH}$ 7.3 Hz, $NCH_2CH_2CH_2CH_3$), 7.19 (1H, s, =CH–C), 7.34–8.10 (6H, m, arom.), 8.71 (1H, s, =CH–O); ^{13}C NMR (100.7 MHz, $CDCl_3$): δ_C 175.2, 172.5, 156.2, 154.8, 154.3, 144.2, 136.7, 136.2, 135.6, 135.2, 126.9, 126.1, 126.0, 125.3, 124.6, 123.5, 119.4, 119.0, 118.0, 117.8, 98.2, 48.9, 32.6, 21.2, 20.9, 19.7, 14.1. Anal. Calcd for $C_{27}H_{23}NO_5$ (471.47): C, 73.46; H, 5.25; N, 3.17%. Found: C, 73.71; H, 5.28; N, 3.18%.

*2.2.10. (1Z)-7-Chloro-1-[(6-chloro-4-oxo-4H-chromen-3-yl)methylene]-3-[(1,1,3,3-tetramethylbutyl)imino]-1,3-dihydro-9H-furo[3,4-b]chromen-9-one (**3k**).* Yellow powder (0.474 g, 88%); mp 259–261 °C; R_f (50% EtOAc/*n*-hexane) 0.63; IR (KBr) (ν_{max}, cm^{-1}): 1709, 1675, and 1655 (C=O), 1606 (C=C); ^{1}H NMR (400.1 MHz, $CDCl_3$): δ_H 1.05 (9H, s, $C(CH_3)_3$), 1.58 (6H, s, $C(CH_3)_2$), 1.87 (2H, s, CH_2), 7.00 (1H, s, =CH–C), 7.39–8.22 (6H, m, arom.), 8.70 (1H, s, =CH–O); ^{13}C NMR (100.7 MHz, $CDCl_3$): δ_C 174.6, 172.0, 156.4, 155.4, 154.9, 154.8, 145.0, 143.4, 135.5, 134.7, 133.1, 132.1, 126.6, 126.5, 126.4, 125.3, 121.6, 120.7, 120.3, 119.8, 97.0, 60.7, 56.0, 32.9, 32.5, 31.2. Anal. Calcd for $C_{29}H_{25}Cl_2NO_5$ (538.41): C, 64.69; H, 4.68; N, 2.60%. Found: C, 64.90; H, 4.70; N, 2.63%.

*2.2.11. (1Z)-7-Chloro-1-[(6-chloro-4-oxo-4H-chromen-3-yl)methylene]-3-(cyclohexylimino)-1,3-dihydro-9H-furo[3,4-b]chromen-9-one (**3l**).* Yellow powder (0.463 g, 91%); mp 312–314 °C; R_f (50% EtOAc/*n*-hexane) 0.61; IR (KBr) (ν_{max}, cm^{-1}): 1697, 1674, and 1653 (C=O), 1604 (C=C); ^{1}H NMR (400.1 MHz, $CDCl_3$): δ_H 1.30–1.95 (10H, s, $5CH_2$), 3.88–3.93 (1H, m, NCH), 7.09 (1H, s, =CH–C), 7.42–8.25 (6H, m, arom.), 8.68 (1H, s, =CH–O); ^{13}C NMR (100.7 MHz, $CDCl_3$): δ_C 174.6, 171.8, 156.7, 155.4, 154.9, 153.9, 148.5, 144.8, 135.8, 134.9, 133.3, 132.2, 130.4, 126.7, 126.5, 125.3, 121.6, 120.9, 120.7, 120.4, 98.0, 59.1, 34.2, 26.3, 25.6. Anal. Calcd for $C_{27}H_{19}Cl_2NO_5$ (508.34): C, 63.79; H, 3.77; N, 2.76%. Found: C, 63.92; H, 3.75; N, 2.72%.

*2.2.12. (1Z)-3-(Benzylimino)-7-chloro-1-[(6-chloro-4-oxo-4H-chromen-3-yl)methylene]-1,3-dihydro-9H-furo[3,4-b]chromen-9-one (**3m**).* Yellow powder (0.321 g, 62%); mp 210–212 °C; R_f (50% EtOAc/*n*-hexane) 0.68; IR (KBr) (ν_{max}, cm^{-1}): 1700, 1669, and 1652 (C=O), 1607 (C=C); ^{1}H NMR (400.1 MHz, $CDCl_3$): δ_H 4.48 (2H, s, CH_2), 7.27–8.13 (12H, m, =CH–C, and arom.), 8.84 (1H, s, =CH–O); ^{13}C NMR (100.7 MHz, $CDCl_3$): δ_C 175.2, 172.8, 158.7, 155.4, 138.0, 137.8, 137.5, 136.6, 136.1, 133.5, 129.6, 129.4, 129.1, 128.6, 127.5, 126.9, 126.6, 126.2, 125.2, 125.1, 124.2, 119.7, 118.9, 118.6, 105.6, 60.3. Anal. Calcd for $C_{28}H_{15}Cl_2NO_5$ (516.32): C, 65.13; H, 2.93; N, 2.71%. Found: C, 65.35; H, 2.91; N, 2.68%.

*2.2.13. (1Z)-5,7-Dichloro-1-[(6,8-dichloro-4-oxo-4H-chromen-3-yl)methylene]-3-[(1,1,3,3-tetramethylbutyl)imino]-1,3-dihydro-9H-furo[3,4-b]chromen-9-one (**3n**).* Yellow powder (0.547 g, 90%); mp 274–276 °C; R_f (50% EtOAc/*n*-hexane) 0.51; IR (KBr) (ν_{max}, cm^{-1}): 1716, 1675, and 1656 (C=O), 1600 (C=C); ^{1}H NMR (400.1 MHz, $CDCl_3$): δ_H 1.09 (9H, s, $C(CH_3)_3$), 1.59 (6H, s, $C(CH_3)_2$), 1.79 (2H, s, CH_2), 6.96 (1H, s, =CH–C), 7.68, 7.76, 8.11, and 8.14 (4H, 4d, $^3J_{HH}$ 2.5 Hz, arom.), 8.74 (1H, s, =CH–O); ^{13}C NMR (100.7 MHz, $CDCl_3$): δ_C 174.1, 171.4, 156.2, 155.1, 151.5, 151.0, 145.3, 141.7, 135.6, 134.7, 132.8, 131.9, 127.4, 126.3, 126.0, 125.3, 125.2, 120.6, 119.7, 96.4, 60.5, 56.8, 33.0, 32.5, 30.9. Anal. Calcd for $C_{29}H_{23}Cl_4NO_5$ (607.30): C, 57.35; H, 3.82; N, 2.31%. Found: C, 57.16; H, 3.85; N, 2.29%.

*2.2.14. (1Z)-5,7-Dichloro-3-(cyclohexylimino)-1-[(6,8-dichloro-4-oxo-4H-chromen-3-yl)methylene]-1,3-dihydro-9H-furo[3,4-b]chromen-9-one (**3o**).* Yellow powder (0.543 g, 94%); mp 283–285 °C; R_f

(50% EtOAc/*n*-hexane) 0.50; IR (KBr) (ν_{max}, cm^{-1}): 1676 and 1653 (C=O), 1600 (C=C); ^1H NMR (400.1 MHz, $CDCl_3$): δ_H 1.30–2.13 (10H, s, $5CH_2$), 3.88–3.95 (1H, m, NCH), 7.05 (1H, s, =CH–C), 7.72, 7.79, 8.14, and 8.17 (4H, 4d, $^3J_{HH}$ 2.5 Hz, arom.), 8.73 (1H, s, =CH–O); ^{13}C NMR (100.7 MHz, $CDCl_3$): δ_C 174.1, 171.3, 156.4, 154.3, 151.5, 146.2, 145.0, 136.5, 135.8, 134.8, 133.0, 132.0, 127.4, 126.3, 126.1, 125.5, 125.4, 125.2, 120.9, 120.6, 97.3, 59.1, 34.1, 26.4, 25.4. Anal. Calcd for $C_{27}H_{17}Cl_4NO_5$ (577.23): C, 56.18; H, 2.97; N, 2.43%. Found: C, 56.40; H, 3.00; N, 2.45%.

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Supplementary data

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.tet.2011.01.033.

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