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Synthesis of heterocyclic chromenes via Buchwald C–N coupling and the substituent effect on their photochromic properties

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ABSTRACT

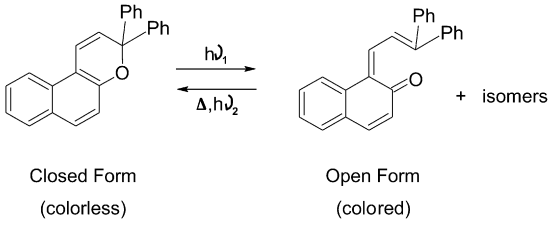
Synthesis of series of new heterocyclic [2]*H*- and [3]*H*-chromenes via Buchwald C–N coupling is described. Introduction of heterocyclic substituent to 6-position of benzopyrans and in 8-position of naphthopyrans led to significant bathochromic shift (up to 154 nm) in the spectra of their open forms. Substituted benzopyrans display high colorability values along with acceptable resistance to fatigue. By using judicious substituents, the absorption range of this type of pyrans can be tuned according to the nature of the heterocyclic unit, and the photochromic properties of pyrans could be adjusted to desired values.

1. Introduction

Chromenes are of special interest as photochromic compounds[1] due to their photo-induced reversible electrocyclic opening of the pyran ring (Scheme 1).

[2]*H*- and [3]*H*-Chromenes represent an important class of molecules[2,3] being the main subunits in numerous natural and biologically active compounds. They are widely adopted for fabrication of opto-electronic devices and ophthalmic lenses.[4] Development of chromenes with programmed photochromic properties is of foremost importance.

The absorption of the merocyanine ring-opened form depends strongly on the substituents.[5] The incorporation of heterocyclic units into chromene molecules may lead to the enhancement of its photochemical properties as well as to their more extended application. This raises a possibility of synthesis of chromenes with particular photochromic properties by the introduction of various substituents. However, this approach faces two problems. First, the dependence of the photochromic properties of heterocyclic substituents has not been profoundly investigated. Secondly, the repertoire of electron-donating substituents was limited due to the complexity of the synthetic methods. This paper describes the important issue of chromene research—the development of novel synthetic conditions enabling to introduce the electron-donating substituents to chromenes.



Scheme 1. Photo-induced reversible electrocyclic opening of the pyran ring.

2. Results and discussion

Recently, Buchwald developed powerful methodology[6–9] for the amination of aryl halides. Palladium-promoted cross-coupling reactions have been widely applied for the functionalization of variety of cyclic secondary amines. However, the reaction of Buchwald has not been employed for electron-donating substituents' introduction to the chromene molecules. We have previously employed this strategy for the synthesis of various aminochromenes.[10,11] Prompted by our studies dealing with the palladium-catalyzed C–N coupling of bromopyrans we became interested in determining whether a related process could be used for the rapid buildup of diverse heterocyclic chromenes from potentially simple starting materials. Starting from pyrans **1**–**4**[12,13] containing the bromine-group available for modification (Scheme 2), we prepared a library of pyran-heterocyclic tandems using morpholine, piperidine, pyrrolidine, and pyrrole.

The coupling was carried out in the presence of tris(dibenzilideneacetone)dipalladium(0) (2 mol %), 2-(di-*t*-butylphosphino)-biphenyl (4 mol %), aryl halide (0.9 equiv), amine (1 equiv),

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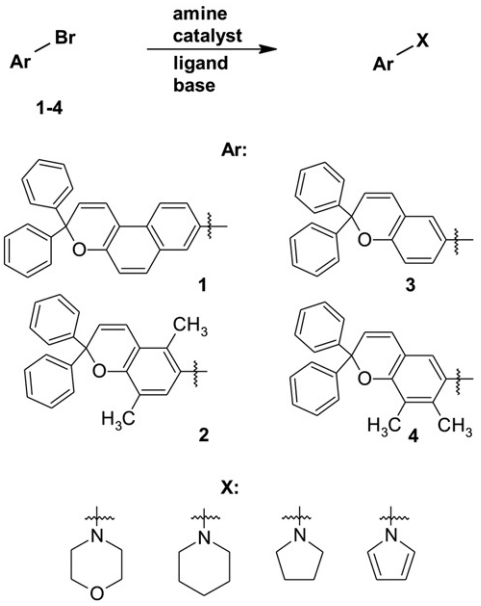


Scheme 2. Synthesis of heterocyclic chromenes.

Table 1
Palladium-catalyzed coupling of chromenes with morpholine, piperidine and pyrrolidine

Entry	ArBr	Amine	Yield, %	Time/h
1	**1**	Morpholine	73	24
2	**1**	Piperidine	86	20
3	**1**	Pyrrolidine	87	40
4	**2**	Morpholine	84	24
5	**2**	Piperidine	81	4
6	**2**	Pyrrolidine	79	1.5
7	**3**	Morpholine	87	20
8	**3**	Piperidine	75	24
9	**3**	Pyrrolidine	94	40
10	**4**	Morpholine	83	20
11	**4**	Piperidine	71	36
12	**4**	Pyrrolidine	89	64
13	**1**	Pyrrole	49[a]	49
14	**2**	Pyrrole	33[a]	2.5
15	**3**	Pyrrole	46[a]	4

[a] t=40 °C.

sodium tertbutoxide (1.4 equiv) in refluxing toluene (1 mL/mmol) under argon. In most cases chromene-bromides **1**–**4** were found to be rather reactive under the general conditions (entries 4–6, Table 1).

Good to excellent yields were observed for arylbromides coupled with saturated heterocyclic amines (entries **1**–**12**). Extension of this chemistry to include pyrrole as substrate appeared to be less successful. After a few tests, we noticed that better yields in this case could be achieved when low temperature is applied (40 °C) (entries **13**–**15**). Rise of reaction temperature to 80 °C leads to rapid disappearance of starting material (about 30 min) and to simultaneous increase in by-products formation.

The structure of one of the target compounds was determined by X-ray crystallographic analysis[14] (Fig. 1). Morpholine derivative of **2** (entry **4**) has unit cells that contain two crystallographically independent, but virtually structurally identical molecules in asymmetric crystal unit.

The electronic absorption spectra of the new naphthopyrans and benzopyrans were monitored[15] without and under UV irradiation. Both series exhibit photochromic properties at room temperature (Fig. 2).

Main absorption bands (in the region 300 nm to 700 nm) are collected in Tables 2 and 3 (naphthopyrans) and Tables 4 and 5 (benzopyrans, demonstrated measurable levels of absorption under given[15] irradiation conditions). In each case the results are compared to the unsubstituted parent compounds[16,17] (Scheme 3).

As stated before,[18] the introduction of *N*-containing heterocycle at the C8 position of 3,3-diphenyl-3*H*-naphtho[2,1-*b*]pyrans led to a global bathochromic shift in the spectra of the open forms (Table 2). As we expected, novel heterocyclic naphthopyrans exhibit an imposing displacement of maximum-absorption wavelength ($\Delta\lambda_2$) at long wave region up to 120 nm (**NP4**) after irradiation by UV light. An intensive band appears also in the UV region (344–359 nm) showing a slight hypsochromic shift according to the nature of the 8-substituent. It can be noticed that regarding to the closed forms, the far UV absorption band is sensitive to this substitution, the higher shift being obtained also for **NP4** (31 nm) (Table 3).

Concerning the benzopyran series (Tables 4 and 5), it appears that the open form of the parent compound (**P1**) compared to the naphthopyran one (**NP1**), shows a bathochromic shift at the λ_{max} (482 nm instead 432 nm) but also the presence of a second band in the near visible range (420 nm).

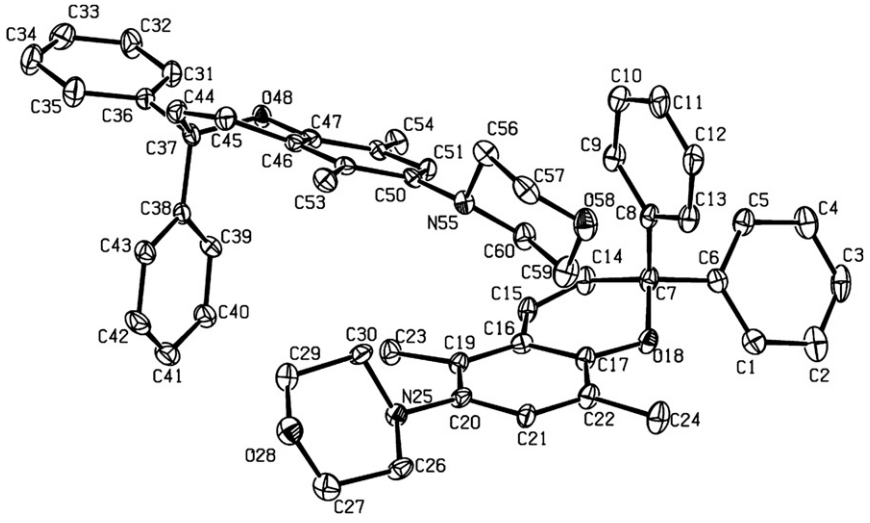


Figure 1. The molecular structure of the crystalline compound **4**.

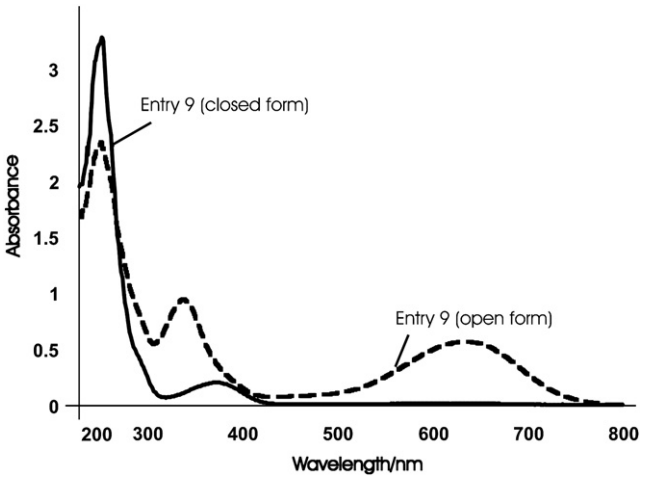
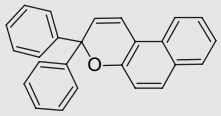
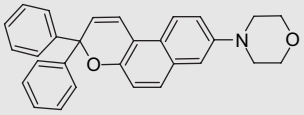
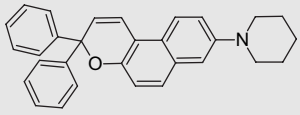
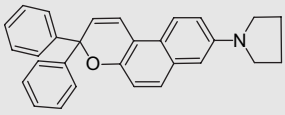
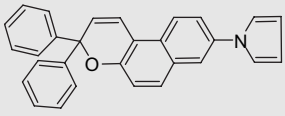


Figure 2. Absorption spectra of entry **9** under dark and irradiated conditions (acetonitrile solutions, $C=0.84\times10^{-5}$ M).

Table 2
Absorption properties of the open forms of naphthopyrans

Entry	Structure	λ_{max}, nm	$\Delta\lambda_1$, $\Delta\lambda_2$, nm (shift of λ_{max})
NP1		360, 432	—, —
NP2		344, 503	−16, 71
NP3		353, 524	−7, 92
NP4		359, 552	−1, 120
NP5		360, 462	0, 30

When the benzopyran ring is substituted by a nitrogenated heterocycle in the 6-position (**P2**–**P4**), the λ_{max} of the open form is shifted to the red, the maximum being observed with a pyrrolidine ring (+154 nm). Curiously, at the same time, the UV range absorption band of this open form is shifted toward shorter wavelengths (about −70 nm).

Adding of two methyl groups in 7 and 8-positions seems to minimize these effects, the higher shift of the λ_{max} is +93 nm for **DMP4**, while the absorption in the UV range is quasi unchanged. The benzopyran series seems to be very interesting allowing higher bathochromic displacement than the naphthopyran one. For instance, in the pyrrolidine ring λ_{max} is 552 nm for naphthopyran and 636 nm for benzopyran. Moreover, depending on the added substitutions, a wide covering of the visible range (from 400 nm to 600 nm or moreover) can be expected, which is interesting for the design of efficient photochromic lenses.

Table 3
Absorption properties of the closed forms of naphthopyrans

Entry	λ_{max}, nm	$\Delta\lambda$
NP1	369	—
NP2	372	3
NP3	381	12
NP4	400	31

Table 4
Absorption properties of the open forms of benzopyrans

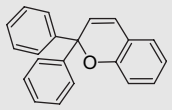
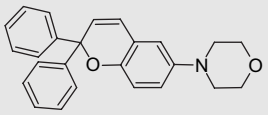
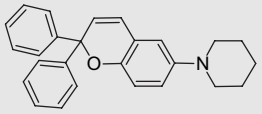
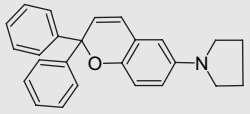
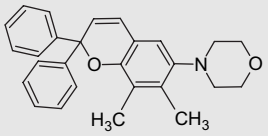
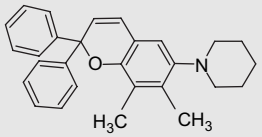
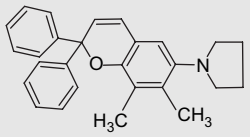
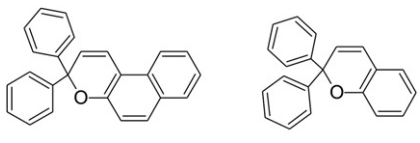
Entry	Structure	λ_{max}, nm	$\Delta\lambda_1$, $\Delta\lambda_2$, nm
P1		420, 482	—, —
P2		336, 555	−84, 73
P3		331, 567	−89, 85
P4		336, 636	−84, 154
DMP2		399, 527	−21, 45
DMP3		397, 539	−23, 57
DMP4		413, 575	−7, 93

Table 5
Absorption properties of the closed forms of benzopyrans

Entry	λ_{max}, nm	$\Delta\lambda$
P1	320	—
P2	344	24
P3	341	21
P4	318	−2
DMP2	327	7
DMP3	330	10
DMP4	336	16



Scheme 3. Unsubstituted parent compounds.

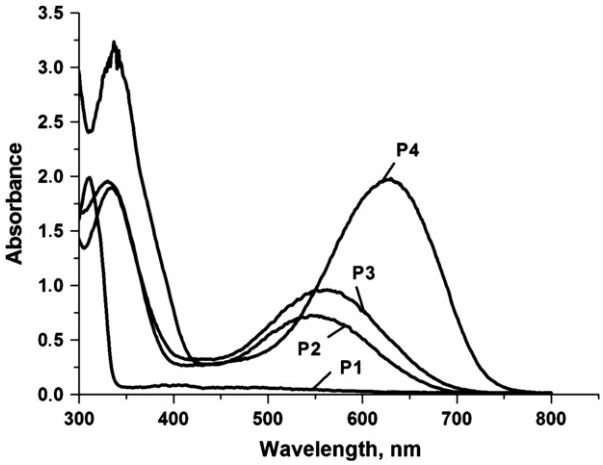


Figure 3. Absorption spectra of **P1**-**P4** under irradiated conditions (toluene, 20 °C, $C=5\times10^{-4}$ M).

Table 6
Resistance to fatigue ($t_{A0/2}$) for benzopyrans **P1**–**P4** (5×10^{-4} M in toluene, 20 °C)

Entry	($t_{A0/2}$) min	$f(t_{A0/2})$[a]
P1	123.0	—
P2	160.1	1.3
P3	140.4	1.41
P4	35.6	0.28

[a] $f(t_{A0/2})$=ratio pertaining to the resistance to fatigue with respect to the parent compound **P1**.

The open forms of compounds **P2**–**P4** show the high corresponding colorability values (Fig. 3) comparing to parent benzopyran **P1**. It is possible to conclude that the heterocyclic constituent at 6-position of benzopyrans stabilizes the photogenerated open forms.

The resistance to fatigue (photodegradation) of benzopyrans **P1**–**P4** under continuous UV irradiation was also evaluated (Table 6). We found that the values for the time required to reach 50% of the initial value ($t_{A0/2}$) for **P2** and **P3** is higher than one of the parent compound **P1**. Unfortunately pyrrolidine substituted benzopyran **P4** displayed the decrease of its fatigue resistance ($f(t_{A0/2})<1$).

Compounds **P2** and **P3** show a good compromise between colorability and photodegradation, they could be useful in applications relating to photochromic lenses.

3. Conclusions

Synthesis of new heterocyclic naphthopyrans and benzopyrans by Buchwald palladium-catalyzed C–N coupling was efficiently accomplished. Both series reveal photochromic properties at room temperature in solution. Introduction of heterocyclic constituent to 6-position of benzopyrans and in 8-position of naphthopyrans leads to global bathochromic shift in the spectra of their open forms. Some of the substituted benzopyrans display high colorability values along with good resistance to fatigue. These results show that by using judicious substituents the absorption range of this type of pyrans can be tuned according to the nature of the heterocyclic constituent on the benzopyran subunit, and the photochromic properties could be adjusted to desired values. The properties of this series of new chromenes open the new prospects for their applications, they would be a good basis for elaboration of opto-electronic devices and ophthalmic lenses.

4. Experimental

4.1. General

Glassware used in the reactions described below was dried for a minimum of 12 h in an oven at 120 °C. ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker AC-250 at 250 MHz and 62.5 MHz, respectively. Chemical shifts are reported in parts per million (δ) relative to the nondeuterated solvent peak. Coupling constants (J values) are expressed in hertz (Hz), and spin multiplicities are indicated by the following symbols: s (singlet), d (doublet), t (triplet), q (quadruplet), m (multiplet). Silica TLC was conducted on precoated aluminum sheets (60 F_{254}) with a 0.2 mm thickness (Aldrich Chemical Co.). Solvents and starting compounds were obtained from commercial sources (Acros, Sigma and Aldrich). Photochemical measurements were performed in acetonitrile solutions ($C=0.84\times10^{-5}$ M) of spectrometric grade at 20E. The analysis cell was placed in sample chamber in *Cary 50 Scan* spectrophotometer. Solutions were stirred continuously during experiments. *An Oriel-150-W-high-pressure* Xe lamp was used for irradiation, 134 mW/cm^2. Mass spectrometry analyses were carried out on a 3200 QTRAP (Applied Biosystems SCIEX).

4.1.1. General procedure for the amination reactions

A Schlenk flask was charged with aryl halide (0.9 mmol), amine (1 mmol), sodium tertbutoxide (1.4 mmol), tris(dibenzilideneacetone)dipalladium(0) (2 mol %), 2-(di-*t*-butylphosphino)biphenyl (4 mol %) in toluene (1 mL/mmol) under argon. The flask was immersed in an 80 EC oil bath with stirring until the starting material had been completely consumed as judged by GC analysis. The solution was allowed then to cool to room temperature, taken up in ether and filtered. The solution was concentrated to dryness under reduced pressure. The crude material was purified by column chromatography with cyclohexane–acetone (90:10).

*4.1.1.1. 4-(3,3-Diphenyl-3H-benzo[f]chromen-8-yl)morpholine (**1**).* ^{1}H NMR (250.13 MHz, $CDCl_3$): δ=3.17 (t, J=4.74 Hz, 4H), 3.86–3.90 (m, 4H), 6.24 (d, J=9.96 Hz, 1H), 7.01 (d, J=2.37 Hz, 1H), 7.13 (d, J=9.00 Hz, 1H), 7.16–7.21 (m, 3H), 7.26–7.32 (m, 5H), 7.44–7.52 (m, 5H), 7.85 (d, J=9.16 Hz, 1H). ^{13}C NMR (62.90 MHz, $CDCl_3$): δ=50.12 (2×CH_2), 66.96 (2×CH_2), 82.32 (OC), 111.36 (CH=), 114.15 (C), 118.73 (CH=), 119.66 (CH=), 119.82 (CH=), 122.42 (CH=), 124.86 (C), 127.02 (4×CH=), 127.48 (2×CH=), 127.99 (CH=), 128.07 (4×CH=), 128.62 (CH=), 130.25 (C), 144.90 (2×C), 147.54 (C), 149.05 (C). HRMS calcd for $C_{29}H_{25}NO_2$ 419.1885, found 419.1876. ESI-MS: m/z=420 $[M+H]^+$.

*4.1.1.2. 1-(3,3-Diphenyl-3H-benzo[f]chromen-8-yl)piperidine (**2**).* ^{1}H NMR (250.13 MHz, $CDCl_3$): δ=1.42–1.48 (m, 2H), 1.57–1.66 (m, 4H), 2.89–2.93 (m, 4H), 6.17 (d, J=10.11 Hz, 1H), 6.62 (s, 1H), 6.75 (d, J=10.11 Hz, 1H), 7.11–7.24 (m, 6H), 7.35–7.36 (m, 4H). ^{13}C NMR (62.90 MHz, $CDCl_3$): δ=24.24 (CH_2), 25.85 (2×CH_2), 51.40 (2×CH_2), 82.20 (OC), 111.78 (CH=), 114.09 (C), 118.40 (CH=), 119.74 (CH=), 121.14 (CH=), 122.04 (CH=), 124.49 (C), 126.98 (4×CH=), 127.39 (2×CH=), 127.79 (C), 128.01 (4×CH=), 128.52 (CH=), 130.35 (CH=), 136.45 (C), 144.93 (2×C), 148.78 (C). Mp=178–179 °C; HRMS calcd for $C_{30}H_{27}NO$ 417.2093, found 417.2081. ESI-MS: m/z=418 $[M+H]^+$.

*4.1.1.3. 1-(3,3-Diphenyl-3H-benzo[f]chromen-8-yl)pyrrolidine (**3**).* ^{1}H NMR (250.13 MHz, $CDCl_3$): δ=1.94–1.99 (m, 4H), 3.28 (br s, 4H), 6.17 (d, J=9.95 Hz, 1H), 6.61 (s, 1H), 6.93 (d, J=8.56 Hz, 1H), 7.03 (d, J=8.78 Hz, 1H), 7.12–7.25 (m, 7H), 7.39–7.43 (m, 5H), 7.75 (d, J=9.14 Hz, 1H). ^{13}C NMR (62.90 MHz, $CDCl_3$): δ=25.43 (2×CH_2), 47.92 (2×CH_2), 82.10 (OC), 114.15 (CH=), 116.34 (CH=), 118.57 (CH=), 119.46 (C), 119.97 (CH=), 122.24 (CH=), 126.99 (CH=), 127.05

(4×CH═), 127.37 (2×CH═), 127.67 (CH═), 128.02 (4×CH═), 128.16 (C), 131.03 (C), 144.60 (C), 145.12 (2×C), 147.40 (C). HRMS calcd for $C_{29}H_{25}NO$ 403.1936, found 403.1927. ESI-MS: m/z=404 $[M+H]^+$.

*4.1.1.4. 4-(5,8-Dimethyl-2,2-diphenyl-2H-chromen-6-yl)morpholine (**4**).* ^{1}H NMR (250.13 MHz, $CDCl_3$): δ=2.24 (s, 3H), 2.26 (s, 3H), 2.75–2.79 (m, 4H), 3.78–3.82 (m, 4H), 6.17 (d, J=9.96 Hz, 1H), 6.71 (s, 1H), 6.82 (d, J=10.11 Hz, 1H), 7.20–7.33 (m, 6H), 7.42–7.46 (m, 4H). ^{13}C NMR (62.90 MHz, $CDCl_3$): δ=12.98 (CH_3), 16.38 (CH_3), 53.38 (2×CH_2), 68.02 (2×CH_2), 81.76 (OC), 120.66 (C), 122.07 (CH═), 122.36 (CH═), 123.45 (C), 127.10 (C), 127.27 (4×CH═), 127.73 (2×CH═), 128.50 (4×CH═), 129.10 (CH═), 144.91 (C), 146.00 (2×C), 147.33 (C). Mp 129–130 °C; HRMS calcd for $C_{27}H_{27}NO_2$ 397.2042, found 397.2037. ESI-MS: m/z=398 $[M+H]^+$.

*4.1.1.5. 1-(5,8-Dimethyl-2,2-diphenyl-2H-chromen-6-yl)piperidine (**5**).* ^{1}H NMR (250.13 MHz, $CDCl_3$): δ=1.56–1.60 (m, 3×CH_2), 2.15 (s, 3H), 2.18 (s, 3H), 2.61–2.62 (m, 4H), 6.17 (d, J=10.11 Hz, 1H), 6.62 (s, 1H), 6.75 (d, J=10.11 Hz, 1H), 7.11–7.24 (m, 6H), 7.35–7.36 (m, 4H). ^{13}C NMR (62.90 MHz, $CDCl_3$): δ=12.56 (CH_3), 15.93 (CH_3), 24.41 (CH_2), 26.72 (2×CH_2), 54.08 (2×CH_2), 81.27 (OC), 120.07 (C), 121.82 (CH═), 121.87 (CH═), 122.62 (C), 126.55 (C), 126.85 (4×CH═), 127.15 (2×CH═), 128.01 (4×CH═), 128.37 (CH═), 145.70 (2×C), 146.15 (C), 146.31 (C). Mp 126–128 °C; HRMS calcd for $C_{28}H_{29}NO$ 395.2249, found 395.2253. ESI-MS: m/z=396 $[M+H]^+$.

*4.1.1.6. 1-(5,8-Dimethyl-2,2-diphenyl-2H-chromen-6-yl)pyrrolidine (**6**).* ^{1}H NMR (250.13 MHz, $CDCl_3$): δ=1.76–1.81 (m, 4H), 2.15 (s, 3H), 2.18 (s, 3H), 2.84–2.88 (m, 4H), 6.10 (d, J=9.95 Hz, 1H), 6.62 (s, 1H), 6.74 (d, J=9.95 Hz, 1H), 7.11–7.25 (m, 6H), 7.36–7.39 (m, 4H). ^{13}C NMR (62.90 MHz, $CDCl_3$): δ=15.84 (CH_3), 18.06 (CH_3), 29.39 (2×CH_2), 54.06 (2×CH_2), 83.24 (OC), 122.16 (CH═), 122.37 (C), 123.93 (CH═), 124.60 (C), 127.25 (C), 128.93 (4×CH═), 129.27 (2×CH═), 130.08 (4×CH═), 130.67 (CH═), 144.58 (C), 147.78 (2×C), 147.88 (C). HRMS calcd for $C_{27}H_{27}NO$ 381.2093, found 381.2089. ESI-MS: m/z=382 $[M+H]^+$.

*4.1.1.7. 4-(-2,2-Diphenyl-2H-chromen-6-yl)morpholine (**7**).* ^{1}H NMR (250.13 MHz, $CDCl_3$): δ=3.03–3.07 (m, 4H), 3.86 (t, J=4.74 Hz, 4H), 6.23 (d, J=9.79 Hz, 1H), 6.62 (d, J=6.95 Hz, 1H), 6.64 (s, 1H), 6.76 (dd, J=2.84, 8.69 Hz, 1H), 6.91 (d, J=8.69 Hz, 1H), 7.25–7.49 (m, 10H). ^{13}C NMR (62.90 MHz, $CDCl_3$): δ=50.55 (2×CH_2), 66.97 (2×CH_2), 82.30 (OC), 114.71 (CH═), 116.89 (CH═), 117.86 (CH═), 121.44 (C), 123.66 (CH═), 126.97 (4×CH═), 127.40 (2×CH═), 128.04 (4×CH═), 129.66 (CH═), 144.87 (2×C), 145.84 (2×C), 146.63 (C). Mp 155–156 °C; HRMS calcd for $C_{25}H_{23}NO_2$ 369.1729, found 369.1731. ESI-MS: m/z=370 $[M+H]^+$.

*4.1.1.8. 1-(2,2-Diphenyl-2H-chromen-6-yl)piperidine (**8**).* ^{1}H NMR (250.13 MHz, $CDCl_3$): δ=1.42–1.48 (m, 2H), 1.57–1.66 (m, 4H), 2.89–2.93 (m, 4H), 6.10 (d, J=9.80 Hz, 1H), 6.50 (d, J=9.80 Hz, 1H), 6.56 (d, J=2.52 Hz, 1H), 6.66–6.70 (m, 1H), 6.76 (d, J=8.69 Hz, 1H), 7.12–7.26 (m, 6H), 7.32–7.37 (m, 4H). ^{13}C NMR (62.90 MHz, $CDCl_3$): δ=24.14 (CH_2), 26.09 (2×CH_2), 52.17 (2×CH_2), 82.30 (OC), 115.79 (CH═), 116.73 (CH═), 118.93 (CH═), 121.31 (C), 123.90 (CH═), 127.05 (4×CH═), 127.39 (2×CH═), 128.06 (4CH═), 129.30 (CH═), 145.07 (2×C), 146.36 (C), 147.02 (C). HRMS calcd for $C_{26}H_{25}NO$ 367.1936, found 367.1931. ESI-MS: m/z=368 $[M+H]^+$.

*4.1.1.9. 1-(2,2-Diphenyl-2H-chromen-6-yl)pyrrolidine (**9**).* ^{1}H NMR (250.13 MHz, $CDCl_3$): δ=1.84–1.88 (m, 4H), 3.08–3.13 (m, 4H), 6.11 (d, J=9.80 Hz, 1H), 6.17 (d, J=2.69 Hz, 1H), 6.30 (dd, J=2.85, 8.69 Hz, 1H), 6.41 (d, J=9.79 Hz, 1H), 6.76 (d, J=8.53 Hz, 1H), 7.11–7.25 (m, 6H), 7.33–7.38 (m, 4H). ^{13}C NMR (62.90 MHz, $CDCl_3$): δ=24.34 (2×CH_2), 47.06 (2×CH_2), 80.92 (OC), 108.47 (CH═), 111.53 (CH═), 115.98 (CH═), 120.67 (C), 123.18 (CH═), 126.01 (4×CH═), 126.23 (2×CH═), 126.96 (4×CH═), 128.70 (CH═), 142.20 (C), 142.30 (C), 144.14 (2×C). HRMS calcd for $C_{25}H_{23}NO$ 353.1780, found 353.1782. ESI-MS: m/z=354 $[M+H]^+$.

*4.1.1.10. 4-(7,8-Dimethyl-2,2-diphenyl-2H-chromen-6-yl)morpholine (**10**).* ^{1}H NMR (250.13 MHz, $CDCl_3$): δ=2.14 (s, 3H), 2.19 (s, 3H), 2.71–2.75 (m, 4H), 3.74–3.78 (m, 4H), 6.04 (d, J=9.63 Hz, 1H), 6.53 (d, J=9.96 Hz, 1H), 6.55 (s, 1H), 7.18–7.28 (m, 6H), 7.37–7.41 (m, 4H). ^{13}C NMR (62.90 MHz, $CDCl_3$): δ=12.37 (CH_3), 14.24 (CH_3), 52.97 (2×CH_2), 67.54 (2×CH_2), 82.31 (OC), 114.81 (CH═), 118.43 (C), 124.01 (CH═), 125.24 (C), 126.85 (4×CH═), 127.26 (2×CH═), 127.86 (C), 128.05 (4×CH═), 133.64 (CH═), 144.76 (C), 145.61 (2×C), 146.58 (C). HRMS calcd for $C_{27}H_{27}NO_2$ 397.2042, found 397.2044. ESI-MS: m/z=398 $[M+H]^+$.

*4.1.1.11. 1-(7,8-Dimethyl-2,2-diphenyl-2H-chromen-6-yl)piperidine (**11**).* ^{1}H NMR (250.13 MHz, $CDCl_3$): δ=1.47–1.55 (m, 6H), 2.04 (s, 3H), 2.10 (s, 3H), 2.56–2.57 (m, 4H), 5.94 (d, J=9.64 Hz, 1H), 6.41–6.45 (m, 2H), 7.09–7.20 (m, 6H), 7.29–7.33 (m, 4H). ^{13}C NMR (62.90 MHz, $CDCl_3$): δ=12.37 (CH_3), 14.28 (CH_3), 24.40 (CH_2), 26.92 (2×CH_2), 54.11 (2×CH_2), 82.20 (OC), 114.69 (CH═), 118.20 (C), 124.19 (CH═), 124.89 (C), 126.82 (4×CH═), 127.14 (2×CH═), 127.49 (C), 127.96 (4×CH═), 133.58 (C), 145.71 (2×C), 145.99 (C), 146.40 (C). HRMS calcd for $C_{28}H_{29}NO$ 395.2249, found 395.2242. ESI-MS: m/z=396 $[M+H]^+$.

*4.1.1.12. 1-(7,8-Dimethyl-2,2-diphenyl-2H-chromen-6-yl)pyrrolidine (**12**).* ^{1}H NMR (250.13 MHz, $CDCl_3$): δ=1.76–1.81 (m, 4H), 2.09 (s, 3H), 2.16 (s, 3H), 2.83–2.87 (m, 4H), 6.00 (d, J=9.63 Hz, 1H), 6.48 (d, J=10.11 Hz, 1H), 6.50 (s, 1H), 7.10–7.24 (m, 6H), 7.35–7.38 (m, 4H). ^{13}C NMR (62.90 MHz, $CDCl_3$): δ=12.38 (CH_3), 15.42 (CH_3), 24.25 (2×CH_2), 52.01 (2×CH_2), 82.21 (OC), 113.08 (CH═), 118.14 (C), 124.33 (CH═), 125.07 (C), 126.90 (4×CH═), 127.20 (2×CH═), 127.70 (CH═), 128.03 (4×CH═), 132.38 (C), 142.79 (C), 145.63 (C), 145.81 (2×C). HRMS calcd for $C_{27}H_{27}NO$ 381.2093, found 381.2087. ESI-MS: m/z=382 $[M+H]^+$.

*4.1.1.13. 1-(3,3-Diphenyl-3H-benzo[f]chromen-8-yl)-1H-pyrrole (**13**).* ^{1}H NMR (250.13 MHz, $CDCl_3$): δ=6.34 (d, J=9.95 Hz, 1H), 6.41–6.42 (m, 2H), 7.19–7.20 (m, 2H), 7.26–7.40 (m, 8H), 7.51–7.61 (m, 5H), 7.67–7.70 (m, 2H), 8.03 (d, J=9.00 Hz, 1H). ^{13}C NMR (62.90 MHz, $CDCl_3$): δ=81.67 (OC), 109.44 (2×CH═), 113.21 (C), 117.40 (CH═), 118.36 (CH═), 118.59 (2×CH═), 119.92 (CH═), 121.09 (C), 122.08 (CH═), 126.05 (4×CH═), 126.67 (2×CH═), 126.82 (C), 127.00 (4×CH═), 127.34 (CH═), 128.46 (CH═), 128.66 (CH═), 135.57 (C), 143.72 (2×C), 149.42 (C). Mp 186–190 °C; HRMS calcd for $C_{29}H_{21}NO$ 399.1623, found 399.1617. ESI-MS: m/z=400 $[M+H]^+$.

*4.1.1.14. 1-(5,8-Dimethyl-2,2-diphenyl-2H-chromen-6-yl)-1H-pyrrole (**14**).* ^{1}H NMR (250.13 MHz, $CDCl_3$): δ=1.94 (s, 3H), 2.21 (s, 3H), 6.15–6.17 (m, 3H), 6.59–6.60 (m, 2H), 6.76 (d, J=10.11 Hz, 1H), 6.84 (s, 1H), 7.20–7.33 (m, 6H), 7.37–7.41 (m, 4H). ^{13}C NMR (62.90 MHz, $CDCl_3$): δ=11.95 (CH_3), 14.55 (CH_3), 80.73 (OC), 107.20 (2×CH═), 118.65 (C), 119.91 (CH═), 121.44 (2×CH═), 122.40 (C), 125.74 (4×CH═), 126.44 (2×CH═), 126.96 (C), 127.10 (4×CH═), 127.95 (CH═), 128.04 (CH═), 130.20 (C), 144.11 (2×C), 148.76 (C). HRMS calcd for $C_{27}H_{23}NO$ 377.1780, found 377.1775. ESI-MS: m/z=378 $[M+H]^+$.

*4.1.1.15. 1-(2,2-Diphenyl-2H-chromen-6-yl)-1H-pyrrole (**15**).* ^{1}H NMR (250.13 MHz, $CDCl_3$): δ=6.17 (d, J=9.97 Hz, 1H), 6.20 (t, J=2.21 Hz, 2H), 6.54 (d, J=9.79 Hz, 1H), 6.85–6.87 (m, 3H), 6.93 (d, J=2.53 Hz, 1H), 7.04 (dd, J=2.69, 8.53 Hz, 1H), 7.15–7.26 (m, 5H), 7.27–7.28 (m, 1H), 7.32–7.36 (m, 4H). ^{13}C NMR (62.90 MHz, $CDCl_3$): δ=81.27 (OC), 109.81 (2×CH═), 117.24 (CH═), 119.23 (CH═), 119.64 (2×CH═),

121.74 (C), 122.10 (CH═), 122.91 (CH═), 127.01 (4×CH═), 127.68 (2×CH═), 128.21 (4×CH═), 130.20 (CH═), 134.89 (C), 144.55 (2×C), 150.47 (C). Mp 100–102 °C; HRMS calcd for $C_{25}H_{19}NO$ 349.1467, found 349.1461. ESI-MS: m/z=350 $[M+H]^+$.

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