Furo[3,4-b]chromones, and not pyrano[3,4-b]chromones are obtained by the reaction of 3-formylchromones with isocyanides.

Ana G. Neo,* Leda Garrido, Jesús Díaz,* Stefano Marcaccini, and Carlos F. Marcos*

*Laboratorio de Química Orgánica y Bioorgánica (L.O.B.O.). Departamento de Química Orgánica e Inorgánica. Facultad de Veterinaria. Universidad de Extremadura. 10071 Cáceres, Spain.

Dipartimento di Chimica ‘Ugo Schiff’, Università di Firenze. 50019 Sesto Fiorentino FI. Italy

E-mail: cfernan@unex.es

General techniques
General procedure for the cycloaddition of formylchromones and isocyanides
Spectroscopic data of compounds 3a-j
Synthesis of compound 8
Spectroscopic data of compound 8
Synthesis of compound 10
Spectroscopic data of compound 10

Spectra:
NMR spectra of compound 3f
1H-NMR of compound 3a
13C-NMR of compound 3a
1H-NMR of compound 3b
13C-NMR of compound 3b
1H-NMR of compound 3c
13C-NMR of compound 3c
1H-NMR of compound 3d
13C-NMR of compound 3d
1H-NMR of compound 3e
13C-NMR of compound 3e
1H-NMR of compound 3g
13C-NMR of compound 3g
1H-NMR of compound 3h
1H-NMR of compound 3i
1H-NMR of compound 3j
1H-NMR of compound 8
13C-NMR of compound 8
1H-NMR of compound 10
13C-NMR of compound 10
**General Techniques.** Melting points are uncorrected. IR spectra were recorded as KBr pellets using a Bruker Vector 22 FT-IR spectrometer. Proton and carbon-13 nuclear magnetic resonance ($^1$H NMR or $^{13}$C NMR) spectra were obtained on a Bruker 400 MHz spectrometer. Bidimensional NMR spectra were obtained on a Bruker 600 MHz spectrometer. Mass spectra (MS) were recorded with a Varian 1200 spectrometer using Electronic Impact (EI, 70 eV). High Resolution Mass Spectra (HRMS) were recorded with a Micromass Autospec spectrometer, with EI or CI. Tetrahydrofurane was freshly distilled from sodium/benzophenone. Isocyanides were purchased from Aldrich. All experiments were carried out under nitrogen inert atmosphere. Liquid reagents were measured using Gilson positive-displacement micropipettes with disposable tips and pistons. Thin layer chromatography was performed on aluminium plates coated with Merck Kieselgel 60 GF-254 silica gel, using 254 nm UV light or a mixture of $p$-anisaldehyde (2.5%), acetic acid (1%) and H$_2$SO$_4$ (3.4%) in 95% ethanol, as developer. Flash column chromatography was performed as described by Still et al.\(^1\) employing silica gel Merck 60 (230-400 mesh). Experiments under microwave irradiation were performed in closed vials, using a focused single-mode microwave reactor CEM Discover BenchMate.

General procedure for the cycloaddition of formylchromones and isocyanides. Isocyanide 2a-g (2.5 mmol) was added to a solution of formyl chromone 1a-d (5 mmol) in dry THF (5 mL). The resulting solution was refluxed under N₂ for 5 to 8 h, until all the starting materials were consumed, as judged by tlc. The reaction mixture was cooled to 0 ºC. The precipitate was collected by filtration and washed with 2-propanol and hexanes. In some cases, the mother liquors were concentrated and purified by column chromatography (SiO₂, gradient of hexane-EtOAc) to obtain a second batch of product.

Spectroscopic data of compounds 3a-j.

1-[1-(4-Oxo-4H-1-benzopyran-3-yl)-meth-(Z)-ylidene]-3-[(Z)-pentylimino]-1,3-dihydrofuro[3,4-b][1]benzopyran-9-one (3a). (55%) obtained as a yellow solid; mp 216-217 ºC; IR (cm⁻¹) 1676, 1649, 1615, 1487, 1465; ¹H-NMR (400 MHz, CDCl₃) δ 8.71 (s, 1H), 8.32 (dd, 1H, J₁ = 8.0, J₂ = 1.4 Hz), 8.27 (dd, 1H, J₁ = 8.0, J₂ = 1.4 Hz), 7.74 (dd, 1H, J₁ = 8.5, J₂ = 7.0, J₃ = 1.6 Hz), 7.67 (d, 1H, J = 8.0 Hz), 7.61 (dd, 1H, J₁ = 8.5, J₂ = 7.0, J₃ = 1.6 Hz), 7.49 (bdd, 1H, J₁ = 8.0, J₂ = 7.1 Hz), 7.44 (d, 1H, J = 8.3 Hz), 7.38 (bdd, 1H, J₁ = 7.9, J₂ = 7.4 Hz), 7.14 (s, 1H), 3.72 (t, 2H, J = 7.1 Hz), 1.83 (m, 2H), 1.45 (m, 4H), 0.95 (t, 3H, J = 7.1 Hz); ¹³C-NMR (100 MHz, CDCl₃) δ 174.8 (C), 172.2 (C), 156.2 (CH), 155.9 (C), 155.7 (C), 155.7 (C), 148.0 (C), 143.9 (C), 134.7 (CH), 133.6 (CH), 126.4 (CH), 126.1 (CH), 125.2 (CH), 124.6 (C), 123.5 (C), 120.0 (C), 119.4 (C), 119.0 (CH), 118.0 (CH), 97.1 (CH), 49.2 (CH₂), 30.1 (CH₂), 29.7 (CH₂), 22.5 (CH₂), 14.0 (CH₃); MS (EI) m/z (%) 427 (M⁺, 71), 384 (71), 370 (56), 356 (57), 343 (100), 328, (35), 237 (12), 208 (26), 180 (22), 121 (29), 92 (25), 77 (11); HRMS (EI) Calcd for C₂₆H₂₁NO₅: 427.1420. Found: 427.1409.

3-[(Z)-Cyclohexylimino]-1-[1-(4-oxo-4H-1-benzopyran-3-yl)-meth-(Z)-ylidene]-1,3-dihydrofuro[3,4-b][1]benzopyran-9-one (3b). (75%) obtained as a yellow solid; mp 274-276 ºC; IR (cm⁻¹) 1676, 1615, 1566, 1488, 1466, 1105, 758; ¹H-NMR (400 MHz, CDCl₃) δ 8.71 (s, 1H), 8.32 (dd, 1H, J₁ = 8.0, J₂ = 1.6 Hz), 8.28 (dd, 1H, J₁ = 8.0, J₂ = 1.6 Hz), 7.74 (ddd, 1H, J₁ = 6.7, J₂ = 6.7, J₃ = 1.6 Hz), 7.69 (bd, 1H, J = 7.3 Hz), 7.64 (dd, 1H, J₁ = 7.0, J₂ = 7.0, J₃ = 1.6 Hz), 7.49 (ddd, 1H, J₁ = 6.9, J₂ = 6.9, J₃ = 1.6 Hz), 7.46 (bd, 1H, J = 8.7 Hz), 7.40 (dd, 1H, J₁ = 6.8, J₂ = 6.8, J₃ = 1.6 Hz), 7.15 (s, 1H), 3.92 (m, 1H), 1.96-1.33 (m, 10H); ¹³C-NMR (100 MHz, CDCl₃) δ 175.0 (C), 173.3 (C), 156.3 (C), 155.8 (C), 155.7 (CH), 153.0 (C), 147.0 (C), 144.0 (C), 134.7 (CH), 133.7 (CH), 126.5 (CH), 126.5 (CH), 126.1 (CH), 125.3 (CH), 124.7 (C), 123.6 (C), 120.1 (C), 119.6 (C), 119.0 (CH), 118.0 (CH), 97.0 (CH), 58.1 (CH), 33.5 (CH₂), 25.6 (CH₂), 24.9 (CH₃); MS (EI) m/z (%) 439 (M⁺, 60), 357 (55), 329 (74), 237 (100), 198 (60), 59 (51) 120 (62), 92 (42); HRMS (EI) Calcd for C₂₇H₂₁NO₅: 439.1420. Found: 439.1415.
3-[(Z)-tert-Butylimino]-1-[1-(4-oxo-4\(H\)-1-benzopyran-3-yl)-meth-(Z)-ylidene]-1,3-dihydro-furo[3,4-b][1]benzopyran-9-one (3c). (54%) obtained as a yellow solid; mp 309-310 °C; IR (cm\(^{-1}\)) 1713, 1673, 1651, 1566, 1464, 976, 760; \(^1\)H-NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.74 (s, 1H), 8.35 (dd, 1H, \(J_1 = 8.0, J_2 = 1.5 \text{ Hz}\)), 8.31 (dd, 1H, \(J_1 = 8.0, J_2 = 1.6 \text{ Hz}\)), 7.76 (dd, 1H, \(J_1 = 8.5, J_2 = 6.7, J_3 = 1.6 \text{ Hz}\)), 7.68 (dd, 1H, \(J_1 = 8.6, J_2 = 8.6, J_3 = 1.6 \text{ Hz}\)), 7.51 (dd, 1H, \(J_1 = 8.1, J_2 = 6.7, J_3 = 1.5 \text{ Hz}\)), 7.49 (bd, 1H, \(J = 8.3 \text{ Hz}\)), 7.43 (bdd, 1H, \(J_1 = 7.9, J_2 = 7.2 \text{ Hz}\)), 7.16 (s, 1H), 1.56 (s, 9H); 13C-NMR (100 MHz, CDCl\(_3\)) \(\delta\) 175.1 (C), 172.4 (C), 156.3 (C), 155.8 (C), 155.5 (CH), 153.7 (C), 153.7 (C), 144.6 (C), 144.3 (C), 134.6 (CH), 133.7 (CH), 126.5 (CH), 126.1 (CH), 125.4 (CH), 124.7 (C), 123.7 (C), 119.5 (C), 119.3 (C), 119.1 (CH), 118.1 (CH), 96.8 (CH), 55.9 (C), 29.9 (CH\(_3\)); MS (EI) \(m/z\) (%) 413 (M\(^+\), 11), 357 (100), 329 (73), 237 (77), 198 (37), 159 (34), 120 (42), 92 (35); HRMS (EI) Calcd for C\(_{25}\)H\(_{19}\)NO\(_5\): 413.1263. Found: 413.1247.

3-[(Z)-Benzylimino]-1-[1-(4-oxo-4\(H\)-1-benzopyran-3-yl)-meth-(Z)-ylidene]-1,3-dihydro-furo[3,4-b][1]benzopyran-9-one (3d). (56%) obtained as a yellow solid; mp 238 °C (dec.); IR (cm\(^{-1}\)) 1674, 1649, 1614, 1564, 1485, 1466, 1120, 759; \(^1\)H-NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.70 (s, 1H), 8.36 (dd, 1H, \(J_1 = 8.0, J_2 = 1.6 \text{ Hz}\)), 8.31 (dd, 1H, \(J_1 = 8.0, J_2 = 1.6 \text{ Hz}\)), 7.77 (ddd, 1H, \(J_1 = 7.8, J_2 = 7.8, J_3 = 1.6 \text{ Hz}\)), 7.68 (m, 2H), 7.51 (m, 1H), 7.50 (m, 2H), 7.42 (m, 3H), 7.31 (bdd, 1H, \(J_1 = 7.4, J_2 = 7.4 \text{ Hz}\)), 7.23 (s, 1H), 4.96 (bs, 2H); 13C-NMR (100 MHz, CDCl\(_3\)) \(\delta\) 175.0 (C), 172.3 (C), 156.3 (C), 156.0 (CH), 155.8 (C), 152.8 (C), 149.0 (C), 144.0 (C), 138.6 (C), 134.8 (CH), 133.8 (CH), 128.7 (CH), 127.9 (CH), 127.4 (CH), 126.5 (CH), 126.5 (CH), 126.3 (CH), 125.4 (CH), 124.7 (C), 123.6 (C), 120.4 (C), 119.4 (C), 119.0 (CH), 118.1 (CH), 97.9 (CH), 52.9 (CH\(_2\)); MS (EI) \(m/z\) (%) 447 (M\(^+\), 60), 356 (66), 328 (29), 249 (26), 208 (28), 91 (100); HRMS (EI) Calcd for C\(_{28}\)H\(_{17}\)NO\(_5\): 447.1107. Found: 447.1109.

[9-Oxo-1-[1-(4-oxo-4\(H\)-1-benzopyran-3-yl)-meth-(Z)-ylideneamino]-acetic acid tert-butyl ester (3e). (10-30%) obtained as a yellow solid; mp 224 °C (dec.); IR (cm\(^{-1}\)) 1748, 1673, 1640, 1612, 1563, 1489, 1460, 1161, 757; \(^1\)H-NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.77 (s, 1H), 8.32 (d, 1H, \(J_1 = 8.0, J_2 = 1.6 \text{ Hz}\)), 8.26 (d, 1H, \(J_1 = 7.8 \text{ Hz}\)), 7.76 (t, 1H, \(J = 7.6 \text{ Hz}\)), 7.67-7.58 (m, 2H), 7.51 (t, 1H, \(J = 7.5 \text{ Hz}\)), 7.45-7.38 (m, 2H), 7.18 (s, 1H), 4.46 (s, 2H), 1.55 (s, 9H); 13C-NMR (100 MHz, CDCl\(_3\)) \(\delta\) 174.79 (C), 172.10 (C), 168.16 (C), 156.18 (CH), 155.72 (C), 152.38 (C), 150.54 (C), 143.76 (C), 134.86 (CH), 133.71 (CH), 126.43 (CH), 120.4 (C), 119.4 (C), 119.0 (CH), 118.1 (CH), 97.9 (CH), 52.9 (CH\(_2\)); MS (EI) \(m/z\) (%) 447 (M\(^+\), 60), 356 (66), 328 (29), 249 (26), 208 (28), 91 (100); HRMS (EI) Calcd for C\(_{28}\)H\(_{17}\)NO\(_5\): 447.1107. Found: 447.1109.
126.23 (CH), 125.38 (CH), 124.64 (C), 123.54 (C), 120.49 (C), 119.18 (C), 119.00 (CH), 118.06 (CH), 98.45 (CH), 82.1 (C), 51.20 (CH_2), 28.05 (CH_3); MS (EI) m/z (%) 471 (M^+, 25), 415 (37), 370 (100), 342 (32), 314 (56), 250 (38), 121 (77); HRMS (EI) Calcd for C_{27}H_{21}NO_{7}: 471.1318. Found: 471.1308.

7-Methyl-1-[1-(6-methyl-4-oxo-4H-1-benzopyran-3-yl)-meth-(Z)-ylidene]-3-[(Z)-pentylimino]-1,3-dihydro-furo[3,4-b][1]benzopyran-9-one (3f). (61%) obtained as a yellow solid; mp 230-231 °C; IR (cm\(^{-1}\)) 1676, 1618, 1484, 816; \(^{1}\)H-NMR (400 MHz, CDCl_3) \(\delta = 8.69\) (bs, 1H, CH-2'), 8.09 (bs, 1H, CH-8), 8.05 (bs, 1H, CH-5'), 7.56 (d, 1H, \(J = 8.5\) Hz, CH-5), 7.53 (dd, 1H, \(J_1 = 8.5, J_2 = 2.1\) Hz, CH-6), 7.42 (dd, 1H, \(J_1 = 8.5, J_2 = 2.1\) Hz, CH-7'), 7.34 (d, 1H, \(J = 8.5\) Hz, CH-8'), 7.13 (bs, 1H, CH-9'), 3.72 (t, 2H, \(J = 7.0\) Hz, \(-\text{CH}_2-(\text{CH}_2)_3\text{CH}_3\)), 2.48 (s, 3H, C7-CH_3), 2.44 (s, 3H, C6'-CH_3), 1.82 (m, 2H, \(-\text{CH}_2-\text{CH}_2-(\text{CH}_2)_2\text{CH}_3\)), 1.47 (m, 2H, \(\text{-CH}_2\text{CH}_2\text{CH}_3\)), 1.43 (m, 2H, \(\text{-CH}_2\text{CH}_2\text{CH}_3\)), 0.95 (t, 3H, \(J = 7.2\) Hz, \(-\text{CH}_2\text{CH}_2\text{CH}_3\)); 13C-NMR (100 MHz, CDCl_3) \(\delta = 174.9\) (C=O 4'), 172.3 (C=O 9), 155.8 (CH-2'), 154.5 (C-4a), 154.0 (C-8a'), 152.6 (C-3a), 148.2 (C-3), 143.9 (C-1), 136.3 (C-7), 135.8 (CH-6), 135.3 (C-6'), 134.8 (CH-7'), 125.8 (CH-5'), 124.3 (C-8a), 123.2 (C-4a'), 119.9 (C-9a), 119.2 (C-3'), 118.6 (CH-5), 117.8 (CH-8'), 97.1 (CH-9'), 49.1 (\(-\text{CH}_2-(\text{CH}_2)_3\text{CH}_3\)), 30.2 (\(-\text{CH}_2\text{CH}_2\text{CH}_3\)), 29.7 (\(-\text{CH}_2\text{CH}_2\text{CH}_3\)), 22.5 (\(-\text{CH}_2\text{CH}_2\text{CH}_3\)), 2.49 (s, 3H, 2 x ArCH_3), 1.47 (m, 2H, \(\text{-CH}_2\text{CH}_2\text{CH}_3\)), 0.95 (t, 3H, \(J = 7.2\) Hz, \(-\text{CH}_2\text{CH}_2\text{CH}_3\)); MS (EI) m/z (%) 455 (M^+, 73), 412 (56), 398 (60), 384 (54), 371 (100), 222 (23), 134 (41); HRMS (EI) Calcd for C_{28}H_{25}NO_{5}: 455.1733. Found: 455.1741.

3-[(Z)-Cyclohexylimino]-7-methyl-1-[1-(6-methyl-4-oxo-4H-1-benzopyran-3-yl)-meth-(Z)-ylidene]-1,3-dihydro-furo[3,4-b][1]benzopyran-9-one (3g). (59%) obtained as a yellow solid; mp 303-306 °C; IR (cm\(^{-1}\)) 1675, 1653, 1618, 1482, 1109, 815; \(^{1}\)H-NMR (400 MHz, CDCl_3) \(\delta = 8.71\) (s, 1H), 8.12 (bs, 1H), 8.09 (bs, 1H), 7.60 (d, 1H, \(J = 8.6\) Hz), 7.55 (dd, 1H, \(J_1 = 8.6, J_2 = 2.2\) Hz), 7.49 (dd, 1H, \(J_1 = 8.6, J_2 = 2.2\) Hz), 7.38 (d, 1H, \(J = 8.5\) Hz), 7.18 (s, 1H), 3.91 (m, 1H), 2.49 (s, 3H), 2.47 (s, 3H), 2.47-1.48 (m, 10H); \(^{13}\)C-NMR (100 MHz, CDCl_3) \(\delta = 175.12\) (C), 155.68 (CH), 154.69 (C), 154.14 (C), 152.90 (C), 147.22 (C), 144.08 (C), 136.37 (CH), 135.87 (C), 135.36 (C), 135.00 (CH), 125.91 (CH), 125.87 (CH), 124.47 (C), 123.38 (C), 120.10 (C), 119.45 (C), 118.85 (CH), 117.90 (CH), 58.13 (CH), 33.53 (CH_2), 25.61 (CH_2), 24.88 (CH_2), 20.97 (CH_3); MS (EI) m/z (%) 467 (M^+, 79), 384 (53), 357 (54), 251 (35), 212 (30), 173 (31), 134 (100); HRMS (EI) Calcd for C_{29}H_{23}NO_5: 467.1733. Found: 467.1748.
7-Chloro-1-[1-(6-chloro-4-oxo-4H-1-benzopyran-3-yl)-meth-(Z)-ylidene]-3-[Z]-cyclohexylimino]-1,3-dihydro-furo[3,4-b][1]benzopyran-9-one (3h). (69%) obtained as a yellow solid; mp 303 °C (dec.); IR (cm⁻¹) 1675, 1655, 1604, 1561, 1463, 1106, 997;¹H-NMR (400 MHz, CDCl₃) δ 8.71 (s, 1H), 8.25 (d, 1H, J = 11.6 Hz), 8.24 (d, 1H, J = 12.5 Hz), 7.68 (m, 2H), 7.60 (dd, 1H, J₁ = 8.8, J₂ = 2.4 Hz), 7.45 (d, 1H, J = 8.9 Hz), 7.09 (s, 1H), 3.93 (m, 1H), 2.00-1.27 (m, 10 H); MS (EI) m/z (%) 509 (M⁺ + 2, 8), 508 (M⁺ + 1, 5), 507 (M⁺, 11), 425 (12), 397 (15), 271 (60), 232 (59), 193 (65), 154 (100); HRMS (EI) Calcd for C₂₇H₁₉Cl₂NO₅: 507.0640. Found: 507.0631.

Due to the low solubility of 3h in most common solvents, we were unable to obtain a good ¹³C-NMR spectrum.

3-[Z]-Benzyylimino]-7-chloro-1-[1-(6-chloro-4-oxo-4H-1-benzopyran-3-yl)-meth-(Z)-ylidene]-1,3-dihydro-furo[3,4-b][1]benzopyran-9-one (3i). (55%) obtained as a yellow solid; mp 262-263 °C (dec.); IR (cm⁻¹) 1673, 1656, 1610, 1561, 1464, 1283, 1114, 820;¹H-NMR (400 MHz, CDCl₃) δ 8.70 (s, 1H), 8.30 (d, 1H, J = 14.9 Hz), 8.29 (d, 1H, J = 14.9 Hz), 7.74 (dd, 1H, J₁ = 8.9, J₂ = 2.5 Hz), 7.65 (m, 2H), 7.42 (m, 2H), 7.34 (m, 1H), 7.19 (s, 1H), 4.97 (bs, 2H); MS (EI) m/z (%) 517 (M⁺ + 2, 2), 516 (M⁺ + 1, 2), 515 (M⁺, 3), 424 (8), 283 (7), 155 (6), 126 (5), 91 (100); HRMS (EI) Calcd for C₂₈H₁₅Cl₂NO₅: 515.0327. Found: 515.0325.

Due to the low solubility of 3i in most common solvents, we were unable to obtain a good ¹³C-NMR spectrum.

7-Bromo-1-[1-(6-bromo-4-oxo-4H-1-benzopyran-3-yl)-meth-(Z)-ylidene]-3-[Z]-cyclohexylimino]-1,3-dihydro-furo[3,4-b][1]benzopyran-9-one (3j). (60%) obtained as a yellow solid; mp 332-334 °C; IR (cm⁻¹) 1675, 1656, 1602, 1558, 1481, 1458, 1285, 1111, 997;¹H-NMR (400 MHz, CDCl₃) δ 8.73 (s, 1H), 8.48 (d, 1H, J = 11 Hz), 8.45 (d, 1H, J = 11 Hz), 7.86 (dd, 1H, J₁ = 8.9 Hz, J₂ = 2.4 Hz), 7.80 (dd, 1H, J₁ = 8.9 Hz, J₂ = 2.4 Hz), 7.63 (d, 1H, J = 8.9 Hz), 7.43 (d, 1H, J = 8.9 Hz), 7.15 (s, 1H), 3.93 (m, 1H), 2.00-1.24 (m, 10H); MS (EI) m/z (%) 599 (M⁺ + 2, 5), 598
(M+ + 1, 5), 597 (M+, 10), 515 (9), 486 (27), 276 (27), 237 (31), 198 (100); HRMS (EI) Calcd for C_{27}H_{19}Br_8: 596.9609. Found: 596.9604.

Due to the low solubility of 3j in most common solvents, we were unable to obtain a good 13C-NMR spectrum.

**Synthesis of 4-Oxo-3-(2-(4-oxo-4H-chromen-3-yl)acetyl)-N-pentyl-4H-chromene-2-carboxamide (8).** To a suspension of 3a (0.2 mmol) in ethanol (2 mL), 300 μL of 10% aqueous HCl was added. The resulting mixture was heated at 70-80 °C for 2 hours. The reaction was then cooled to rt, H2O (10 mL) was added and the organic phase was extracted with CH2Cl2, dried (Na2SO4) and concentrated. The residue was purified by flash chromatography (silica gel, hexane-EtOAc gradient), giving the compound 8 (24%) as a yellow solid; mp 205-207 ºC dec.; IR (cm⁻¹) 3706, 1796, 1664, 1631, 1664, 1105, 758; ¹H NMR (400 MHz, CDCl3) δ 8.32 (dd, J1 = 8.2, J2= 1.4 Hz, 1H), (dd, J1 = 8.3, J2= 1.2 Hz, 1H), 7.78 – 7.70 (m, 3H), 7.55 – 7.45 (m, 2H), 7.43 (t, J = 13.4 Hz, 1H), 6.87 (bs, 1H), 3.67 (ddd, J 1 = 19.6, J 2 = 12.7, J 3 = 7.4 Hz, 2H), 3.58 (t, J = 13.4 Hz, 1H), 3.50 (ddd, J1 = 19.6, J2 = 12.7, J3 = 7.4 Hz, 2H), 3.10 (d, J = 14.4 Hz, 1H), 1.36 (dd, J = 12.7, 8.6 Hz, 4H), 0.91 (t, J = 6.0 Hz, 3H); 13C NMR (101 MHz, CDCl3) δ 180.20 (C), 172.92 (C), 160.63 (C), 156.49 (C), 156.04 (C), 155.79 (C), 154.35 (CH), 134.37 (CH), 127.44 (C), 126.22 (CH), 126.06 (CH), 125.89 (C), 125.71 (CH), 123.22 (C), 119.53 (C), 119.04 (CH), 118.16 (CH), 90.11 (C), 40.21 (CH2), 36.52 (CH2), 29.44 (CH2), 28.53 (CH2), 22.36 (CH3), 14.00 (CH3); MS (CI) m/z (%) 446 (M⁺+1, 100), 429 (48), 389 (11), 363 (16), 361 (67), 286 (15).

**Synthesis of (Z)-1-((4-Oxo-4H-chromen-3-yl)methylene)-2-pentyl-1,2-dihydrochromeno[2,3-c]pyrrole-3,9-dione (10).** Method A. To a suspension of 3a (0.1 mmol) in ethanol (1 mL), 300 μL of 35% aqueous HCl was added. The mixture was irradiated in a microwave reactor at 110 ºC for 1 minute. The reaction was cooled to rt and the solid was filtered and washed with EtOH, yielding compound 10 as a practically pure yellow solid (65%); mp 265-267 ºC; IR (cm⁻¹) 3420, 1797, 1707, 1679, 1640, 1612, 1462, 1300, 1194, 761; ¹H NMR (500 MHz, CDCl3) δ 8.31 (d, J = 7.7 Hz, 1H), 8.23 (d, J = 7.6 Hz, 1H), 7.90 (s, 1H), 7.79 – 7.67 (m, 3H), 7.59 (d, J = 8.4 Hz, 1H), 7.52 – 7.43 (m, 2H), 6.73 (s, 1H), 4.00 (t, J = 7.4 Hz, 2H), 1.88 – 1.74 (m, 2H), 1.49 – 1.38 (m, 4H), 0.96 (t, J = 6.4 Hz, 3H); ¹³C NMR (101 MHz, CDCl3) δ 176.53 (C), 171.70 (C), 159.33 (C), 156.33 (C), 155.85 (CH), 155.55 (C), 155.12 (C), 134.53 (CH), 133.70 (CH), 131.88 (C), 129.66 (CH), 126.19 (CH), 126.12 (CH), 125.47 (CH), 125.28 (C), 123.86 (C), 119.70 (C), 118.78 (CH), 118.42 (CH), 118.11 (C), 107.73 (CH), 40.26 (CH2), 29.03 (CH2), 28.54 (CH2), 22.37 (CH2), 13.98 (CH3); MS (CI) m/z (%) 446 (M⁺+1, 100), 429 (48), 389 (11), 363 (16), 361 (67), 286 (15).

**Method B.** Alternatively, when a suspension of 0.05 mmol of 8 in 1 mL of EtOH and 300 μL of 35% HCl was irradiated in a microwave reactor at 110 ºC for 1 minute, compound 10 was obtained quantitatively.
NMR SPECTRA OF

3f