Proceedings

Synthesis and Photophysical Characterization of 2'-Aminochalcones [†]

Cátia I. C. Esteves [1], Luís F. B. Fontes [1,2], A. Filipa N. Borges [1], João Rocha [2], Artur M. S. Silva [1] and Samuel Guieu [1,2]

[1] LAQV-REQUIMTE; catiaiesteves@ua.pt (C.I.C.E.); email1@gmail.com (L.F.B.F.); email2@gmail.com (A.F.N.B.); email3@gmail.com (A.M.S.S.); email4@gmail.com (S.G.)

[2] CICECO-Aveiro Institute of Materials, Universidade de Aveiro, Campus de Santiago, 3810-193 Aveiro, Portugal; sguieu@ua.pt

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Abstract: Chalcones present biological activity and therefore they are currently studied for their therapeutic potential. They have shown antitumor, anti-inflammatory, antifungal and antibacterial properties. These compounds occur in Nature as secondary metabolites of plants and are precursors of flavonoids biosynthesis. Generally, they are not luminescent, but derivatives with some particular patterns of substitution can present fair quantum yields. Excited State Intramolecular Proton Transfer (ESIPT) is a particular case of tautomerization, and some molecules can exhibit ESIPT fluorescence if their structures incorporate an intramolecular hydrogen bonding interaction between a hydrogen donor (-OH or -NH) and a hydrogen acceptor. If the dye is fluorescent, emission from both tautomers may be observed, leading to a dual emission. The chalcones with a strong push-pull character, compounds **2c**, **3c** and **4c**, presented dual emission of keto-enol tautomerism as a consequence of ESIPT.

Keywords: aminochalcones; Excited State Intramolecular Proton Transfer; synthesis; fluorescence

1. Introduction

Chalcone (1,3-diphenylprop-2-en-1-one) is an aromatic ketone, where the two aromatic nuclei are joined by an α,β-unsaturated carbonyl bridge, which forms the central nucleus of a variety of important biological compounds [1]. Chalcone exists as *trans* (*E*)- or *cis* (*Z*)-isomers, with the most stable and predominant stereoisomer being the (*E*)-isomer [2]. There are several method for the synthesis of chalcones being the Claisen-Schmidt condensation the classic method [3]. Chalcones and their derivatives have been extensively studied because of their wide range of applicability [4]. Chalcones have several applications such as anti-inflammatory, Reference [5] anti-HIV, Reference [6] antibacterial, Reference [7] anticancer, Reference [8] antituberculosis, Reference [9] antileishmanial, Reference [10] therapeutical activity, Reference [11] among others.

Structural changes in chalcone derivatives can modify different optical properties such as refractive index, absorption magnitude and spectral position, as well as the optical energy gap [4]. These examples indicate that structurally modified chalcones can exhibit variable physical properties.

Within this class of compounds, 2'-aminochalcone derivatives still represent a recent field of investigation [12]. They have antitumor activity [13] and have been shown to be photoprotectors [14].

Generally, they are not luminescent, but derivatives with some particular patterns of substitution can present fair quantum yields [15].

Excited State Intramolecular Proton Transfer (ESIPT) is a particular case of tautomerization, and molecules can exhibit ESIPT fluorescence if their structures incorporate an intramolecular hydrogen bonding interaction between a hydrogen donor (-OH or -NH) and a hydrogen acceptor [16]. The

intramolecular hydrogen bond plays a crucial role in the proton transfer process [17]. If the dye is fluorescent, emission from both tautomers may be observed, leading to a dual emission [18]. ESIPT fluorophores have some beneficial photophysical properties such as intense luminescence, photostability and an unusually large Stokes Shift [3]. The proton-transfer tautomer emits fluorescence at longer wavelengths and will result in larger Stokes shifts.

ESIPT is a system with four energy levels (L→L*→E*→E). The two forms of the chalcone (L and ESIPT form) are in equilibrium (Scheme 1). In the ground state, the chalcone is in the L form. After absorption of a photon, the L* suffers an ESIPT tautomerization equilibrium to the E*, and both tautomers can emit light. After relaxation to the E form, the chalcone goes back to the keto form through reverse proton transfer (RPT). This equilibrium may be influenced by the environment of the chalcone, especially the polarity and proticity of the solvent, leading to different proportion of both tautomers, and therefore to different emission intensities in the two bands when dual emission is observed. As such, these fluorophores may found applications as molecular probes, giving an insight into the properties of their environment, for example the polarity of an organelle.
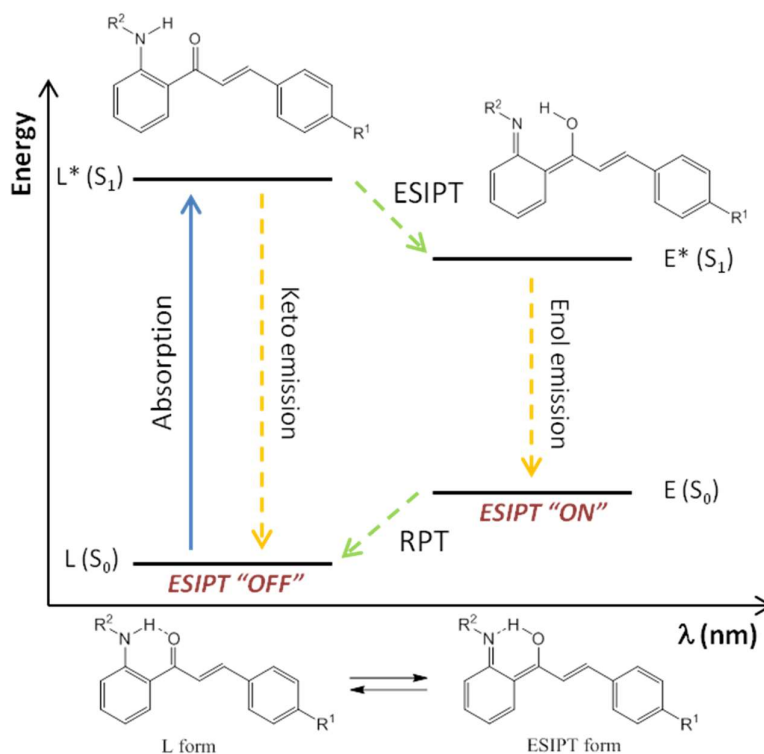
Scheme 1. Description of the ESIPT process [16].

Here, we report the synthesis and photophysical characterizations of 2′-aminochalcones, substituted with electron donating or withdrawing groups, which could be used as markers to study the environment of cellular organelles.

2. Experimental

2.1. General Procedure for the Synthesis of 2′-Aminochalcones 2a-c

The 2′-aminochalcone derivatives were obtained via aldol condensation reaction of 2′-aminoacetophenone (2 mmoL) with the appropriate substituted benzaldehyde **1a-c** (2 mmoL) catalyzed by potassium hydroxide (4 mmoL) in methanol (5 mL). The reaction mixture was stirred at 60 °C overnight followed by addition of H_2O (100 mL), the pH was adjusted to 3–4 with dilute HCl and the solution extracted with CH_2Cl_2 (3 × 30 mL). The organic layer was collected, dried over

anhydrous sodium sulfate, and the solution was concentrated to dryness. The resulting oil was purified by silica gel column chromatography, using dichloromethane as eluent.

2.1.1. (E)-1-(2-aminophenyl)-3-(4-methylphenyl)prop-2-en-1-one (**2a**)

The product was isolated as a yellow solid (1.139 g, 4.81 mmoL, 80%). M.p. = 91–92 °C. ^{1}H NMR (300 MHz, CDCl$_3$) δ = 2.39 (s, 3H, CH$_3$), 6.44 (br s, 2H, NH$_2$), 6.71 (d, *J* = 8.1 Hz, 1H, H-3), 6.72 (dt, *J* = 8.1 and 1.2 Hz, 1H, H-4), 7.22 (d, *J* = 8.1 Hz, 2H, H-3′,5′), 7.30 (dt, *J* = 8.1 Hz, 1.2 Hz, 1H, H-4), 7.54 (d, *J* = 8.1 Hz, 2H, H-2′,6′), 7.61 (d, *J* = 15.6 Hz, 1H, α-H), 7.78 (d, *J* = 15.3 Hz, 1H, β-H), 7.89 (dd, *J* = 8.1 and 1.2 Hz, 1H, H-6) ppm. ^{13}C NMR (75 MHz, CDCl$_3$) δ = 21.6 (CH$_3$), 115.8 (C-5), 117.4 (C-3), 119.2 (C-1), 122.1 (α-C), 128.4 (C-2′,6′), 129.7 (C-3′,5′), 131.1 (C-6), 132.6 (C-1′), 134.3 (C-4), 140.6 (C-4′), 143.0 (β-C), 151.2 (C-2), 191.8 (CO) ppm. MS *m/z* (ESI %): 238.1 ([M+H]$^+$); HMRS: *m/z* (ESI) calc. for C$_{16}$H$_{16}$NO 238.1226, found 238.1230. UV/Vis (CHCl$_3$, nm): λ_{max} (log ε) = 317 (4.59).

2.1.2. (E)-1-(2-aminophenyl)-3-(4-methoxyphenyl)prop-2-en-1-one (**2b**)

The product was isolated as a dark yellow solid (0.214 g, 0.81 mmoL, 43%). M.p. = 68–69 °C. ^{1}H NMR (300 MHz, CDCl$_3$) δ = 3.81 (s, 3H, OCH$_3$), 6.25 (br s, 2H, NH$_2$), 6.65–6.70 (m, 2H, H-3 and H-5), 6.90 (d, *J* = 8.8 Hz, 2H, H-3′,5′), 7.26 (dt, *J* = 8.4 and 1.5 Hz, 1H, H-4), 7.48 (d, *J* = 15.6 Hz, 1H, α-H), 7.56 (d, *J* = 8.8 Hz, 2H, H-2′,6′), 7.71 (d, *J* = 15.6 Hz, 1H, β-H), 7.84 (dd, *J* = 8.4 and 1.5 Hz, 1H, H-6) ppm. ^{13}C NMR (75 MHz, CDCl$_3$) δ = 55.4 (OCH$_3$), 114.4 (C-3′,5′), 115.8 (C-5), 117.3 (C-3), 119.3 (C-1), 120.8 (α-C), 128.0 (C-1′), 130.0 (C-2′,6′), 130.9 (C-6), 134.1 (C-4), 142.8 (β-C), 151.0 (C-2), 161.3 (C-4′), 191.8 (CO) ppm. MS *m/z* (ESI %): 254.1 ([M+H]$^+$); HMRS: *m/z* (ESI) calc. for C$_{16}$H$_{16}$NO$_2$ 254.1176, found 254.1172. UV/Vis (CHCl$_3$, nm): λ_{max} (log ε) = 333 (4.51).

2.1.3. (E)-1-(2-aminophenyl)-3-[4-(dimethylamino)phenyl]prop-2-en-1-one (**2c**)

The product was isolated as an orange solid (1.210 g, 4.51 mmoL, 75%). M.p. = 120–121 °C. ^{1}H NMR (300 MHz, CDCl$_3$) δ = 3.00 (s, 6H, N(CH$_3$)$_2$), 6.26 (br s, 2H, NH$_2$), 6.67 (d, *J* = 8.7 Hz, 2H, H-3′,5′), 6.66–6.71(m, 2H, H-3 and H-5), 7.25 (dt, *J* = 8.1 and 1.2 Hz, 1H, H-4), 7.41 (d, *J* = 15.4 Hz, 1H, α -H), 7.52 (d, *J* = 8.7 Hz, 2H, H-2′,6′), 7.73 (d, *J* = 15.4 Hz, 1H, β -H), 7.86 (dd, *J* = 8.1 and 1.2 Hz, 1H, H-6) ppm. ^{13}C NMR (75 MHz, CDCl$_3$) δ = 40.2 (N(CH$_3$)$_2$), 111.9 (C-3′,5′), 115.8 (C-5), 117.3 (C-3), 117.9 (α -C), 119.9 (C-1), 123.0 (C-1′), 130.2 (C-2′,6′), 130.8 (C-6), 133.7 (C-4), 144.0 (β -C), 150.7 (C-2), 151.8 (C-4′), 192.0 (CO) ppm. MS *m/z* (ESI %): 267.1 ([M+H]$^+$); HMRS: *m/z* (ESI) calc. for C$_{17}$H$_{19}$N$_2$O 267.1492, found 267.1499. UV/Vis (CHCl$_3$, nm): λ_{max} (log ε) = 418 (4.59).

2.2. General Procedure for the Synthesis of 2′-(methanesulfonylamino)chalcones **3a-c**

2′-Aminochalcone derivatives **2a-c** (1 mmoL), methane sulfonyl chloride (1 mmoL) and triethylamine (1 mmoL) in dichloromethane (5 mL) were stirred overnight at room temperature. Following the addition of H$_2$O (50 mL), the pH was neutralized with dilute HCl and the solution extracted with CH$_2$Cl$_2$ (3 × 20 mL). The organic layer was collected, dried over anhydrous sodium sulfate, and the solution was concentrated to dryness. The resulting solid was purified by silica gel column chromatography, using dichloromethane as eluent.

2.2.1. (E)-N-{2-[3-(4-methylphenyl)acryloyl]phenyl}methanesulfonamide (**3a**)

The product was isolated as a yellow solid (0.148 g, 0.47 mmoL, 56%) M.p. = 125–126 °C. ^{1}H NMR (300 MHz, CDCl$_3$) δ = 2.40 (s, 3H, CH$_3$), 3.06 (s, 3H, SO$_2$CH$_3$), 7.21 (dt, *J* = 7.8 and 1.2 Hz, 1H, H-5), 7.24 (d, *J* = 8.4 Hz, 2H, H-3′,5′), 7.55 (d, *J* = 15.5 Hz, 1H, α -H), 7.56 (d, *J* = 8.4 Hz, 2H, H-2′,6′), 7.57 (dt, *J* = 7.8 and 1.2 Hz, 1H, H-4), 7.79 (dd, *J* = 8.4 and 1.2 Hz, 1H, H-3), 7.83 (d, *J* = 15.5 Hz, 1H, β -H), 8.03 (dd, *J* = 7.8 and 1.2 Hz, 1H, H-6), 11.27 (br s, 1H, NH) ppm. ^{13}C NMR (75 MHz, CDCl$_3$) δ = 21.6 (CH$_3$), 40.1 (SO$_2$CH$_3$), 118.8 (C-3), 120.7 (α -C), 122.8 (C-5), 123.6 (C-1′), 128.8 (C-2′,6′), 129.8 (C-3′,5′), 131.1 (C-6), 131.7 (C-2), 134.8 (C-4), 140.6 (C-1), 141.8 (C-4′), 146.4 (β -C), 192.7 (CO) ppm. MS *m/z* (ESI %): 316.1 ([M+H]$^+$); HMRS: *m/z* (ESI) calc. for C$_{17}$H$_{18}$NO$_3$S 316.1002, found 316.1008. UV/Vis (CHCl$_3$, nm): λ_{max} (log ε) = 336 (4.56).

2.2.2. (E)-N-{2-[3-(4-methoxyphenyl)acryloyl]phenyl}methanesulfonamide (**3b**)

The product was isolated as a yellow solid (0.109 g, 0.33 mmoL, 42%). M.p. = 135–136 °C. ^{1}H NMR (300 MHz, CDCl$_3$) δ = 3.06 (s, 3H, SO$_2$CH$_3$), 3.86 (s, 3H, OCH$_3$), 6.94 (d, *J* = 8.7 Hz, 2H, H-3',5'), 7.21 (dt, *J* = 8.1 and 1.2 Hz, 1H, H-5), 7.46 (d, *J* = 15.3 Hz, 1H, α-H), 7.56 (dt, *J* = 8.1 and 1.2 Hz, 1H, H-4), 7.60 (d, *J* = 8.7 Hz, 2H, H-2',6'), 7.77 (dd, *J* = 8.1 and 1.2 Hz, 1H, H-3), 7.81 (d, *J* = 15.3 Hz, 1H, β-H), 8.03 (dd, *J* = 8.1 and 1.2 Hz, 1H, H-6), 11.32 (br s,1H, NH) ppm. ^{13}C NMR (75 MHz, CDCl$_3$) δ = 40.1 (SO$_2$CH$_3$), 50.5 (OCH$_3$), 114.6 (C-3',5'), 118.8 (C-3), 119.3 (α-C), 122.8 (C-5), 123.7 (C-1), 127.2 (C-1'), 130.6 (C-2',6'), 131.0 (C-6), 134.7 (C-4), 140.6 (C-2), 146.2 (β-C), 162.2 (C-4'), 192.6 (CO) ppm. MS *m/z* (ESI %): 332.1 ([M+H]$^+$); HMRS: *m/z* (ESI) calc. for C$_{17}$H$_{18}$NO$_4$S 332.0951, found 332.0965. UV/Vis (CHCl$_3$, nm): λ$_{max}$ (log ε) = 361 (4.57).

2.2.3. (E)-N-{2-[3-(4-(dimethylamino)phenyl)acryloyl]phenyl}methanesulfonamide (**3c**)

The product was isolated as a red solid (0.142 g, 0.41 mmoL, 55%). M.p. = 155–156 °C. ^{1}H NMR (300 MHz, CDCl$_3$) δ = 3.03 (s, 3H, SO$_2$CH$_3$), 3.06 (s, 6H, N(CH$_3$)$_2$), 6.69 (d, *J* = 8.8 Hz, 2H, H-3',5'), 7.19 (dt, *J* = 8.1 and 1.2 Hz, 1H, H-5), 7.36 (d, *J* = 15.0 Hz, 1H, α-H), 7.53 (dt, *J* = 8.1 and 1.2 Hz, 1H, H-4), 7.55 (d, *J* = 8.8 Hz, 2H, H-2',6'), 7.77 (dd, *J* = 8.1 and 1.2 Hz, 1H, H-3), 7.83 (d, *J* = 15.0 Hz, 1H, β-H), 8.02 (dd, *J* = 8.1 and 1.2 Hz, 1H, H-6), 11.40 (br s, 1H, NH) ppm. ^{13}C NMR (75 MHz, CDCl$_3$) δ = 39.9 (SO$_2$CH$_3$), 40.1 (N(CH$_3$)$_2$), 111.8 (C-3',5'), 116.0 (α-C), 119.1 (C-3), 122.1 (C-1'), 122. 8 (C-5), 124.5 (C-1), 130.7 (C-6), 131.0 (C-2',6'), 134.1 (C-4), 140.3 (C-2), 147.5 (β-C), 152.5 (C-4'), 192.4 (CO) ppm. MS *m/z* (ESI %): 345.1 ([M+H]$^+$); HMRS: *m/z* (ESI) calc. for C$_{18}$H$_{21}$N$_2$O$_3$S 345.1267, found 345.1263. UV/Vis (CHCl$_3$, nm): λ$_{max}$ (log ε) = 439 (4.65).

2.3. General Procedure for the Synthesis of 2′-(Acetylamino)Chalcones **4a-c**

2′-Aminochalcone derivatives **2a-c** (1 mmol), acetyl chloride (1 mmoL) and triethylamine (1 mmoL) in dichloromethane (5 mL) were stirred overnight at room temperature. Following the addition of H$_2$O (50 mL), the pH was neutralized with dilute HCl and the solution extracted with CH$_2$Cl$_2$ (3 × 20 mL). The organic layer was collected, dried over anhydrous sodium sulfate, and the solution was concentrated to dryness. The resulting solid was purified by silica gel column chromatography, using dichloromethane as eluent.

2.3.1. (E)-N-{2-[3-(4-methylphenyl)acryloyl]phenyl}acetamide (**4a**)

The product was isolated as a yellow solid (0.118 g, 0.42 mmoL, 84%). M.p. = 121–122 °C. ^{1}H NMR (300 MHz, CDCl$_3$) δ = 2.25 (s, 3H, COCH$_3$), 2.41 (s, 3H, CH$_3$), 7.16 (dt, *J* = 8.2 and 1.2 Hz, 1H, H-5), 7.25 (d, *J* = 8.4 Hz, 2H, H-3',5'), 7.52 (d, *J* = 15.6 Hz, 1H, α-H), 7.55 (d, J = 8.4 Hz, 2H, H-2',6'), 7.56 (dt, *J* = 8.2 and 1.2 Hz, 1H, H-4), 7.79 (d, *J* = 15.6 Hz, 1H, β-H), 7.97 (dd, *J* = 8.2 and 1.2 Hz, 1H, H-3), 8.70 (d, *J* = 8.2 Hz, 1H, H-6), 11.55 (br s, 1H, NH) ppm. ^{13}C NMR (75 MHz, CDCl$_3$) δ = 21.6 (CH$_3$), 25.5 (COCH$_3$), 121.2 (C-6), 121.8 (α-C), 122.4 (C-5), 123.5 (C-1), 128.7 (C-2',6'), 129.8 (C-3',5'), 130.5 (C-3), 131.9 (C-1'), 134.6 (C-4), 141.0 (C-2), 141.6 (C-4'), 145.8 (β-C), 169.4 (COCH$_3$), 193.5 (CO) ppm. MS *m/z* (ESI %): 280.1 ([M+H]$^+$); HMRS: *m/z* (ESI) calc. for C$_{18}$H$_{18}$NO$_2$ 280.1332, found 280.1337. UV/Vis (CHCl$_3$, nm): λ$_{max}$ (log ε) = 334 (4.49).

2.3.2. (E)-N-{2-[3-(4-methoxyphenyl)acryloyl]phenyl}acetamide (**4b**)

The product was isolated as a yellow solid (0.101 g, 0.34 mmoL, 43%). M.p. = 121–122 °C. ^{1}H NMR (300 MHz, CDCl$_3$) δ = 2.23 (s, 3H, COCH$_3$), 3.84 (s, 3H, OCH$_3$), 6.93 (d, *J* = 8.7 Hz, 2H, H-3',5'), 7.13 (dt, *J* = 8.1 and 1.2 Hz, 1H, H-5), 7.42 (d, *J* = 15.6 Hz, 1H, α -H), 7.53 (dt, *J* = 8.1 and 1.2 Hz, 1H, H-4), 7.59 (d, *J* = 8.7 Hz, 2H, H-2',6'), 7.76 (d, *J* = 15.6 Hz, 1H, β -H), 7.94 (dd, *J* = 8.1 and 1.2 Hz, 1H, H-3), 8.69 (dd, *J* = 8.1 and 1.2 Hz, 1H, H-6) 11.58 (br s, 1H, NH) ppm. ^{13}C NMR (75 MHz, CDCl$_3$) δ = 25.5 (COCH$_3$), 55.4 (OCH$_3$), 114.5 (C-3',5'), 120.3 (α -C), 121.1 (C-6), 122.4 (C-5), 123.6 (C-1), 127.3 (C-1'), 130.4 (C-3), 130.5 (C-2',6'), 134.4 (C-4), 140.9 (C-2), 145.5 (β -C), 162.0 (C-4'), 169.3 (CO CH$_3$), 193.3 (CO) ppm. MS *m/z* (ESI %): 296.1 ([M+H]$^+$); HMRS: *m/z* (ESI) calc. for C$_{18}$H$_{18}$NO$_3$ 296.1281, found 296.1272. UV/Vis (CHCl$_3$, nm): λ$_{max}$ (log ε) = 359 (4.54).

2.3.3. (E)-N-{2-[3-(4-(dimethylamino)phenyl)acryloyl]phenyl}acetamide (**4c**)

The product was isolated as an orange solid (0.162 g, 0.52 mmoL, 66%). M.p. = 129–131 °C. ^{1}H NMR (300 MHz, CDCl$_3$) δ = 2.23 (s, 3H, COCH$_3$), 3.04 (s, 6H, N(CH$_3$)$_2$), 6.67 (d, *J* = 8.7 Hz, 2H, H-3′,5′), 7.13 (dt, *J* = 8.1 and 1.2 Hz, 1H, H-5), 7.34 (d, *J* = 15.3 Hz, 1H, α-H), 7.51 (dt, *J* = 8.1 and 1.2 Hz, 1H, H-4), 7.54 (d, *J* = 8.7 Hz, 2H, H-2′,6′), 7.78 (d, *J* = 15.3 Hz, 1H, β-H), 7.95 (dd, *J* = 8.1 and 1.2 Hz, H-3), 8.68 (dd, *J* = 8.1 and 1.2 Hz, 1H, H-6), 11.66 (br s, 1H, NH) ppm. ^{13}C NMR (75 MHz, CDCl$_3$) δ = 25.5 (COCH$_3$), 3.04 (N(CH$_3$)$_2$), 111.8 (C-3′,5′), 117.2 (α-C), 121.0 (C-6), 122.3 (C-1′), 122.3 (C-5), 124.3 (C-1), 130.2 (C-3), 130.8 (C-2′,6′), 133.8 (C-4), 140.7 (C-2), 146.8 (β-C), 152.3 (C-4′), 169.3 (COCH$_3$), 193.2 (CO) ppm. MS *m/z* (ESI %): 309.2 ([M+H]$^+$); HMRS: *m/z* (ESI) calc. for C$_{19}$H$_{21}$N$_2$O$_2$ 309.1598, found 309.1595. UV/Vis (CHCl$_3$, nm): λ_{max} (log ε) = 432 (4.61).

2.4. Photophysical Characterization of 2′-aminochalcones 2, 3 and 4

Solutions of 2′-aminochalcones **2a-c**, **3a-c** and **4a-c** (10^{-4} to 10^{-6} M) were prepared in solvents with different character (polar-apolar, protic-aprotic), and their absorption and emission spectra were recorded. Relative fluorescence quantum yields were calculated using fluorescein (Φ_F = 0.95 in NaOH 0.1 M) and anthracene (Φ_F = 0.27 in ethanol) as standard [19].

3. Results and Discussion

3.1. Synthesis

The synthetic route chosen to obtain the 2′-aminochalcones comprised two steps (Scheme 1). First, the aminochalcones were synthesized by base-catalyzed aldol condensation using potassium hydroxide, in 43–80% yields. Then, the electron-withdrawing groups are introduced to obtain the final compounds **3** (sulfonamide formation) and **4** (acylation), in 42–84% yields. All new compounds were fully characterized by ^{1}H-NMR, ^{13}C-NMR and MS.
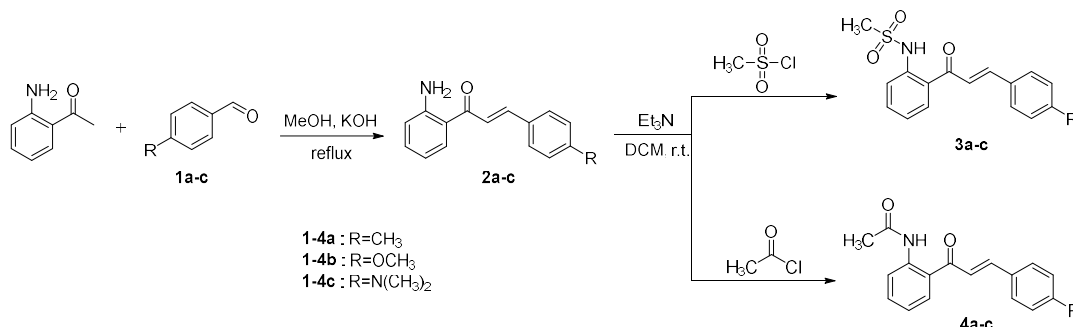
Scheme 2. Synthesis of the 2′-aminochalcones **2a-c**, **3a-c** and **4a-c**.

The main features of the ^{1}H NMR spectra of compounds **2**, **3** and **4** are the signals corresponding to the vinylic protons of their characteristic α,β-unsaturated moieties. The protons H-α and H-β appear at δ 7.34–7.61 and 7.71–7.83 ppm, respectively, as two doublets with a coupling constant of ca. 15 Hz, which indicates a (*E*)-configuration for the vinylic system. Another important characteristic of the ^{1}H NMR spectra of **3** and **4** is a singlet with high frequency values (δ 11.27–11.66 ppm) attributed to 2′-NH$_2$, due to the intramolecular hydrogen bond with the carbonyl group. This signal is not observed for compounds **2a-c** that have a broad singlet with lower frequency values, between 6.25 and 6.44 ppm.

3.2. Photophysical Study of 2′-Aminochalcones 2, 3 and 4

The photophysical properties of the chalcones **2a-c**, **3a-c** and **4a-c** were evaluated. First, the absorption and emission spectra of all compounds were measured in acetonitrile (Figures 1 and 2). The 2′-aminocalcones **2-4** show low to moderate fluorescence quantum yields, and large Stokes' shifts

(5058–9883 cm^{-1}) (Table 1). The influence of the electron-donating group is observed, and compounds **2c**, **3c** and **4c** bearing a dimethylamino substituent present a red shift on the absorption and emission maxima. They are also more emissive, with higher quantum yields of 0.03–0.35. For some compounds, the emission profile is not symmetric, and a second emission band appears with a lower intensity. This is consistent with the ESIPT proposed model.

Table 1. UV-visible absorption and emission data for 2′-aminochalcones **2**, **3** and **4** in organic solvents of different character, with π^* values by Kamlet and Taft [20].

Cpd	Solvent (π^*)	UV/Vis		Fluorescence		
		λ_{max} (nm)	log ε	λ_{em} (nm)	Stokes' Shift (cm^{-1})	Φ_F
2a	Diethyl ether (0.27)	308	4.58	---	---	---
	Chloroform (0.58)	317	4.59	459	9759	<0.01
	ACN (0.75)	311	4.57	449	9883	<0.01
	DMSO (1.00)	317	4.57	460	9807	<0.01
2b	Diethyl ether (0.27)	324	4.51	---	---	---
	Chloroform (0.58)	333	4.51	455	8052	<0.01
	ACN (0.75)	327	4.52	448	8260	<0.01
	DMSO (1.00)	335	4.52	454	7824	<0.01
2c	Diethyl ether (0.27)	404	4.58	493	4468	<0.01
	Chloroform (0.58)	418	4.59	497/532	3803/5126	0.03
	ACN (0.75)	418	4.57	540	5405	0.03
	DMSO (1.00)	429	4.58	540	4792	0.03
3a	Diethyl ether (0.27)	329	4.57	417/441	6414/7719	<0.01
	Chloroform (0.58)	336	4.56	440	7035	<0.01
	ACN (0.75)	333	4.59	438	7199	<0.01
	DMSO (1.00)	332	4.58	413/438	5907/7289	<0.01
3b	Diethyl ether (0.27)	354	4.53	---	---	---
	Chloroform (0.58)	361	4.57	454	5674	<0.01
	ACN (0.75)	358	4.50	445	5461	<0.01
	DMSO (1.00)	363	4.52	455	5570	<0.01
3c	Diethyl ether (0.27)	424	4.62	---	---	---
	Chloroform (0.58)	439	4.66	535	4087	0.10
	ACN (0.75)	437	4.60	561	5058	0.10
	DMSO (1.00)	445	4.61	557	4519	0.11
4a	Diethyl ether (0.27)	325	4.51	---	---	---
	Chloroform (0.58)	334	4.49	440	7213	<0.01
	ACN (0.75)	326	4.49	432	7527	<0.01
	DMSO (1.00)	327	4.50	458	8747	<0.01
4b	Diethyl ether (0.27)	349	4.53	---	---	---
	Chloroform (0.58)	359	4.54	437	4972	<0.01
	ACN (0.75)	352	4.51	431	5207	<0.01
	DMSO (1.00)	352	4.52	437	5526	<0.01
4c	Diethyl ether (0.27)	417	4.59	492	3656	<0.01
	Chloroform (0.58)	432	4.61	553	5065	0.32
	ACN (0.75)	428	4.60	556	5379	0.35
	DMSO (1.00)	437	4.60	558	4962	0.36

Considering the results obtained in acetonitrile, the photophysical properties of 2′-aminochalcones **2**, **3** and **4** were evaluated in other organic solvents presenting different polarity. The solvents tested were dimethylsulfoxide, chloroform and diethyl ether, as examples of solvents with different polarity and proticity, with π^* values determined by Kamlet and Taft,[20] indicating the

ability of a particular solvent to stabilize a charge or a dipole due to its dielectric effect, normalized between cyclohexane ($\pi^* = 0$) and DMSO ($\pi^* = 1$). The collected data revealed similar *maxima* wavelengths of absorption, but some differences in the emission *maxima* wavelengths (two *maxima* can be observed in some solvents, for compounds **2c**, **3a**, **3c** and **4c**) and the fluorescence quantum yield do not vary significantly (Table 1). The general trend revealed that 2'-aminochalcone **4c** (*para*-position of ring B with dimethylamine and in ring A the acetyl-protected amine group) is the most fluorescent (with Φ_F in the range of 0.32–0.36).

The absorption and emission spectra of **2c** and **4c** in different solvent are presented in figures 3 and 4. For both compounds, a small shift is observed in the absorption spectra in different solvents, probably due to the solvatochromism expected for push-pull dyes. Two emission bands are clearly visible for **2c**, with variable intensities depending on the solvent. They are less obvious for **4c**. In diethyl ether (less polar solvent), the band at shorter wavelengths is predominant, corresponding to the L form (Scheme 1). In DMSO and ACN (more polar), the band at longer wavelengths is predominant, corresponding to the E form. In Chloroform, both bands are present, witnessing the ESIPT equilibrium. These bands are probably merged into a single one for **4c**.
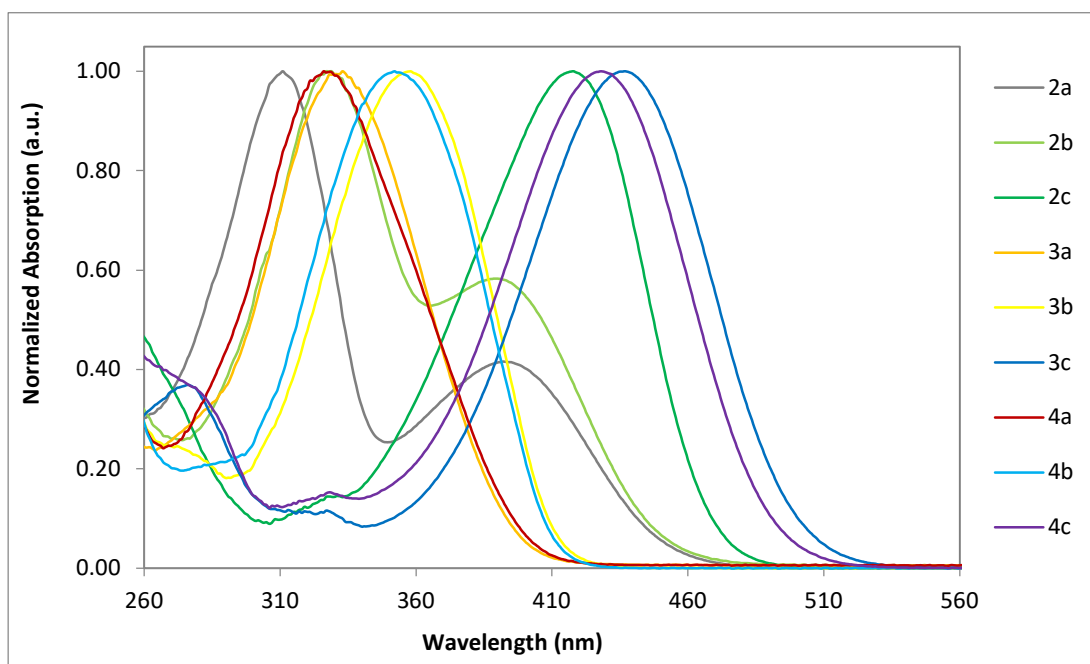
Figure 1. Normalized absorption spectra of 2'aminochalcones **2**, **3** and **4** in acetonitrile.
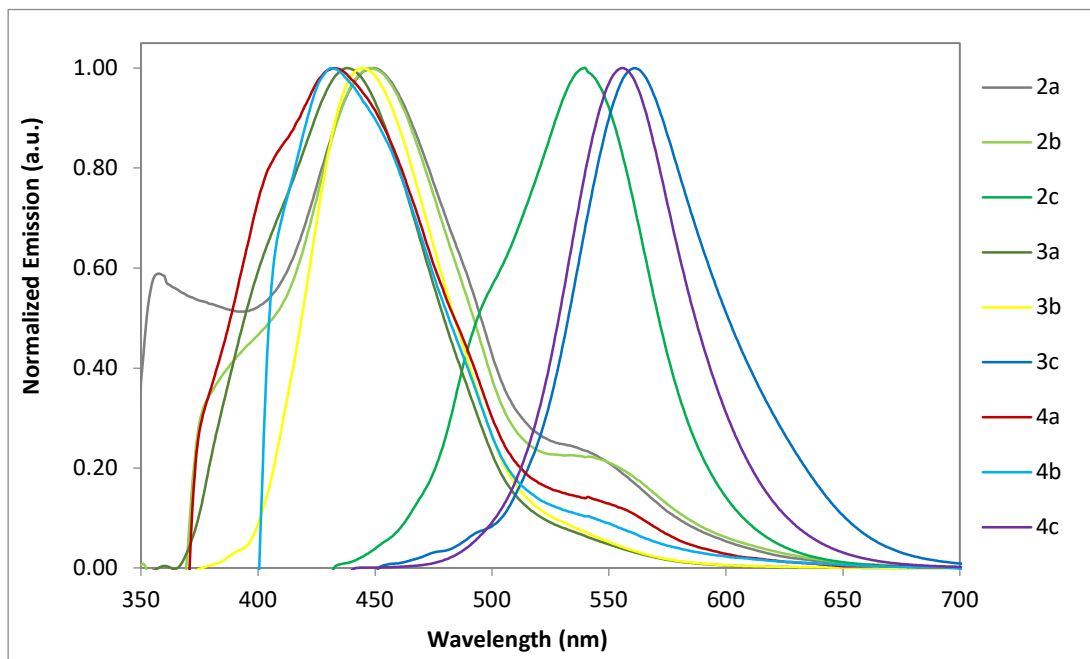
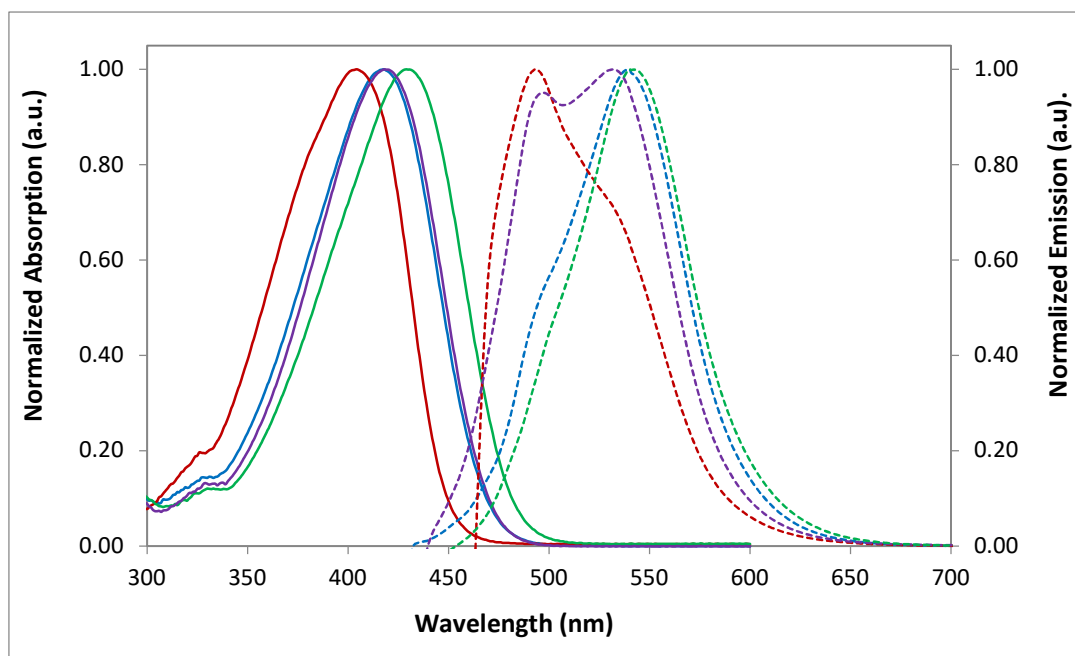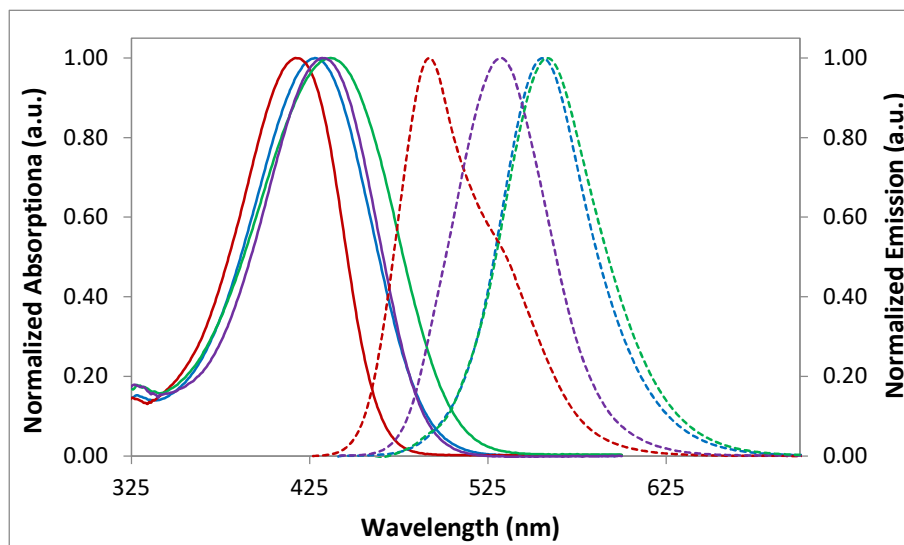**Figure 2.** Normalized emission spectra of 2'aminochalcones **2**, **3** and **4** in acetonitrile.

Figure 3. Normalized absorption and emission spectra of chalcone **2c** in –acetonitrile, –diethyl ether, –chloroform and—dimethyl sulfoxide (λ_{exc} = 418 nm, 404nm, 418 nm and 429 nm respectively (absorption, full line; emission, dotted line).

Figure 4. Normalized absorption and emission spectra of chalcone **4c** in −acetonitrile, −diethyl ether, −chloroform and—dimethyl sulfoxide (λ_{exc} = 428 nm, 417 nm, 432 nm and 437 nm respectively (absorption, full line; emission, dotted line).

4. Conclusions

The 2'aminochalcones **2**, **3** and **4** are emissive, especially derivatives **c** (*N,N*-dimethylamine as a substituent) with moderate fluorescence *quantum* yields (Φ_F = 0.03 for **2c**; Φ_F = 0.10 for **3c**; Φ_F = 0.35 for **4c**) and large Stokes' shifts (5405, 5058 and 5379 cm^{-1}, respectively) in acetonitrile. Compound **4c** (acetyl group as a substituent on the amine) displayed the highest fluorescence. Fluorophores **2c** and **4c** present an interesting ESIPT, with a dual emission. The intensity of each emission band is strongly influenced by the solvent and witnesses a dramatic shift in the ESIPT equilibrium. These compounds could therefore find applications as molecular probes of organelles polarity, and this study is on-going.

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