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(Coumarin-3-yl)-benzoates as a Series of New Fluorescent Compounds: Synthesis, Characterization and Fluorescence Properties in the Solid State

Sosso Siaka[1], Jules Yoda[1,2], Abdoulaye Djandé[1,*], Bruno Coulomb[3]

[1]Laboratory of Molecular Chemistry and Materials, Organic Chemistry and Phytochemistry Team, University Ouaga I Pr Joseph KI-Zerbo, Burkina Faso
[2]Department of Medicine, Traditional Phamacopees and Pharmacy, Institute for Health Sciences Research, Ouagadougou, Burkina Faso
[3]Laboratory of Environmental Chemistry, Department of Chemistry, UMR 7376, Team TRAME, Aix-Marseille University, France

Abstract (Coumarin-3-yl)-benzoates, a series of coumarin derivatives were designed, synthesized and characterized as fluorescent compounds. The structural assignments of these compounds were examined based on their corresponding FT-IR, ESI-MS, and ^{1}H- and ^{13}C-NMR spectral data in addition to their crystal structures determined by X-ray diffractometry. The fluorescence spectra, recorded in the solid state, have been investigated. The effects of various substituents R on fluorescence properties were examined. As a result, compound **2c** with an electron-donating substituent (R = *t*-Bu) exhibited the strongest fluorescence intensity whereas compound **2f** with an electron-withdrawing group (R = CN) presented the weakest one.

Keywords (Coumarin-3-yl)-benzoates, Synthesis, Characterization, Fluorescence, Solid state, Substituents R

1. Introduction

Fluorescent compounds play an important role in solid state lighting, solar energy conversion and as biomarkers in the life sciences [1-6]. As an important group of organic heterocycles, coumarin derivatives have been found to possess a wide range of pharmacological and biological activities, which can display among others, insecticidal [7], antibacterial [8], anti-HIV [9, 10], anticancer [11, 12], anticoagulant [13] and antioxidant [14] activities.

Furthermore, coumarin derivatives, possessing a heterocyclic skeleton with a ring oxygen on a carbonyl group, are well-known fluorescence dyes for their high photoluminescence quantum efficiencies. A number of coumarins have been synthesized and explored the possibility of their application to electro-optic materials, such as laser dyes, fluorescent probes or labels, solar collector systems, organic scintillators and photoelectronic sensitizers. [15-19]

In the current work described here, synthesis and structural analysis of six 3-substituted coumarin derivatives, presenting at that position an ester function (compounds **2**), were undertaken. Fluorescence properties of these (coumarin-3-yl)-benzoates, in the solid state, were then reported.

So, the title compounds were synthesized according to a described convenient method, in satisfactory yields, from chroman-2,3-dione and acyl chloride in the presence of triethylamine (TEA).

Their molecular structures were characterized by the means of FT-IR, ^{1}H and ^{13}C NMR and ESI-MS spectrometries and were additionally determined by X-ray diffractometry.

The fluorescence spectra were recorded in solid-state, in order to examine the unique effects of different substitutions on fluorescence emission.

2. Experimental Section

2.1. Synthesis and Characterization of Compounds 2

2.1.1. Synthesis

(Coumarin-3-yl)-benzoates were synthesized from chroman-2,3-dione, *the ketone tautomeric form* of 3-hydroxycoumarin, by *O*-acylation with acyl chlorides in the presence of TEA as shown below. (Scheme 1). We used HSAB theory of Pearson [20] in the choice of TEA as base. According to this principle, to obtain best yields with hard acids like benzoyl chlorides, it is necessary to use a hard base like triethylamine (TEA). Further, the preferable solvents were ethers: diethyl ether or tetrahydrofuran (THF), at reflux.

* Corresponding author:
djandeabdou@yahoo.fr (Abdoulaye Djandé)
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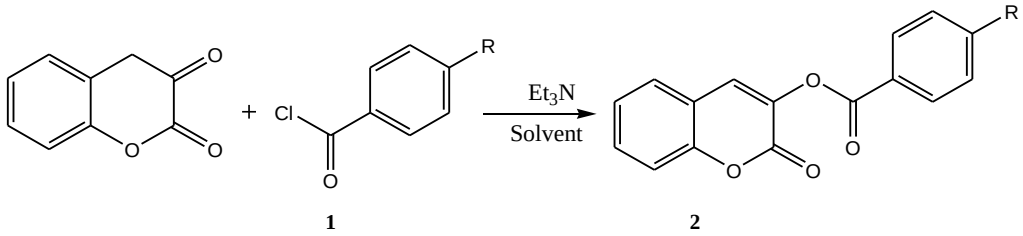


1 **2**

R = H: Solvent = Diethyl ether;
Other cases: Solvent = THF.

2a: R = H; **2b**: R = CH_3; **2c**: R = *t*-Bu; **2d**: R = Cl; **2e**: R = F; **2f**: R = CN.

Scheme 1. Preparation of (coumarin-3-yl)-benzoates

Synthesis and crystallization (compound **2a**)

To a solution of benzoyl chloride (6.17 mmol) in dried diethyl ether (25 mL) was added dried TEA (3.2 mL; 3.6 molar equivalents) and chroman-2,3-dione (1 g ; 6.17 mmol) by small portions over 30 min, under strong stirring. The reaction mixture was left under agitation for 2 h at room temperature and then refluxed for 2 h. The obtained solution was poured in a separating funnel containing 40 ml of chloroform and washed with diluted hydrochloric acid solution until the pH was 2-3. The organic phase was extracted, washed with water to neutrality, dried using MgSO4 and the solvent removed. The crude product was filtered off with suction, washed with petroleum ether and recrystallized from a solvent mixture of chloroform–hexane (1/3, V/V) to offer yellow crystals **2a**.

Synthesis and crystallization (compounds **2b, 2c, 2d, 2e, 2f**)

To a solution of the corresponding 4-substitutedbenzoyl chloride (6.17 mmol) in dried THF (40 mL) was added dried TEA (2.6 mL; 3 molar equivalents) and chroman-2,3-dione (1 g; 6.17 mmol) by small portions over 30 min, under high speed stirring. The mixture was then refluxed for 4 h and poured into 40 mL of chloroform. The resulting solution was acidified with diluted hydrochloric acid until the pH was 2–3. The organic layer was extracted, washed with water to neutrality, dried over MgSO4. The resulting precipitate was filtered off with suction, washed with petroleum ether and recrystallized from a solvent mixture of chloroform-hexane (1/3, V/V) to afford desired crystals **2**.

2.1.2. Materials and Measurement

Melting points were determined in capillary tubes on a Stuart SMP 11 apparatus and are uncorrected.

IR spectra were recorded on a Bruker IFS 66 / S Fourier Transform Infrared spectrometer (FT-IR), driven by the OPUS 6.5 software and using the ATR (Attenuated Total Reflection) technique.

^{1}H and **^{13}C (+ DEPT 135) NMR spectra** were recorded on a BRUKER AMX spectrometer at 400 or 600 MHz and 100 MHz respectively, using TMS as internal standard (chemical shifts in δ values, J in Hz).

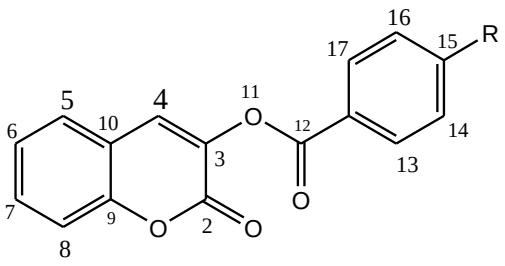
Mass spectra were obtained on a 3200 QTRAP (Applied Biosystems SCIEX) spectrometer equipped with a pneumatically assisted air pressure ionization (API) source.

All the compounds were analyzed by **X-ray diffractometry**. In this study, we highlight the crystallographic data that justify their 3D structures. Data were collected by the X scan technique at 293 and 298 K on an Agilent SuperNova Dual diffractometer with an Atlas S2 detector, using Cu*Kα* radiation (λ = 1.54184 Å) and MoKα (λ = 0.71073 Å), and were corrected for Lorentz and polarization effects. The structures were solved by direct methods which revealed the positions of all non-hydrogen atoms, and were refined on F^2 by a full-matrix least-squares procedure using anisotropic displacement parameters. The program used to solve structure was SHELXS97 [21]. The program used to refine the structures was SHELXL2013 [22]. All hydrogen atoms were located from difference Fourier maps and were refined isotropically. Molecular graphics were generated with Platon [23]. Finally, the software used to prepare material for publications was publCIF [24].

A summary of the crystals data, experimental details, and refinements results is given below in the crystal structure Determination.

It's the occasion for us to signalize that the crystal structures of compounds **2a**, **2c**, **2d**, **2e** have previously been published by our research team [25-28] and the crystal structure of compound **2b** by M J Matos and al. [29], but in this last case data were measured on a Bruker APEX2 [26] at 100 K using radiation (λ = 0.71073Å).

2.1.3. Characterization



Scheme 2. Numbered structure of compounds **2**

2.1.3.1. (Coumarin-3-yl)-benzoate (2a)

Yield: 84%; **^{1}H-NMR** (DMSO-d6; 400 MHz): 7.43 (t, 1H, J = 8 Hz, H-15); 7.50 (d, 1H, J = 8 Hz, H-8); 7.65 (d, 3H, J = 8 Hz, H-5; H-14 and H-16); 7.77 (t, 2H, J = 8 Hz, H-6

and H-7); 8.13 (d, 2H, J = 4 Hz, H-13 and H-17); 8.21 (s, 1H, H-4). **^{13}C-NMR** (DMSO-d6; 100 MHz): 116.24 (C-8); 118.30 (C-10); 125.14 (C-4); 127.58 (C-12); 128.51 (C-6); 129.12 (C-14 et C-16); 129.94 (C-13 and C-17); 131.60 (C-5); 132.09 (C-7); 134.59 (C-15); 135.48 (C-3); 151.61 (C-9); 156.08 (C-11); 163.59 (C-2). **DEPT 135°**: 116.24 (C-8); 125.14 (C-4); 128.51 (C-6); 129.12 (C-14 and C-16); 129.94 (C-13 et C-17); 131.60 (C-5); 132.09 (C-7); 134.59 (C-15). **IR** (cm^{-1}): 1742.3 (C=O, ester); 1728.4 (C=O, lactone); 1607 (C=C); 3046.5 (C-H, aromatic ring); 1250.5 (C–O, ester); 1098.3 (C–O, lactone). **ESI-MS** $[M+H]^+$: 267.

***Crystal structure Determination* (2a)**

Chemical formula: $C_{16}H_{10}O_4$; Formula weight: 266.24; Crystal description: prism, yellow; Melting point (K): 423-426; Crystal system: Triclinic; space group: P1; Temperature (K): 298; Wavelength (Å): 0.71073; Unit cell dimensions: a = 6.9243 (6) Å , b =7.7262 (8) Å , c = 11.8168 (6) Å , α = 84.550 (6)°, β = 81.852 (6)°, γ = 83.023 (8)°; Volume (Å ^{3}): 619.22 (9); Z = 2; Radiation type: MoKα; Absorption coefficient (mm^{-1}): 0.10; Density (Mg m^{-3}): 1.428; F(000): 276; Crystal size (mm): 0.34 x 0.12 x 0.06; 7628 measured reflections; 2283 independent reflections; *R*int = 0.039; $R[F^2 > 2\sigma(F^2)]$ = 0.051; *wR* (F^2) = 0.159; *S* = 1.04; 2283 reflections; 221 parameters.

2.1.3.2. (Coumarin-3-yl)-4-mehylbenzoate (2b)

Yield: 93 %; **^{1}H-NMR** ($CDCl_3$; 400 MHz): 2.47 (s, 3H, CH_3); 7.33 (d, 2H, J = 7,5 Hz, H-6 and H-8); 7.37 (d, 1H, J = 7.4 Hz, H-7); 7.43 (d, 1H, J = 7.6 Hz, H-5); 7.52 (d, 2H, J = 8.1 Hz, H-14 and H-16); 7.66 (s, 1H, H-4); 8.1 (d, 2H, J = 8.2 Hz, H-13 and H-17). **^{13}C-NMR** ($CDCl_3$; 100 MHz): 21.82 (C-18); 116.71 (C-8); 118.61 (C-10); 124.9 (C-4); 125.41 (C-12); 127.86 (C-6); 129.41 (C-14 and C-16); 130.61 (C-13 and C-17); 130.96 (C-5); 131.14 (C-7); 136.54 (C-3); 145.17 (C-15) ; 152.12 (C-9); 156.73 (C-11); 164.09 (C-2). **DEPT135°**: 21.82 (C-18); 116.71 (C-8); 124.9 (C-4); 127.86 (C-6); 129.41 (C-14 and C-16); 130.61 (C-13 and C-17); 130.96 (C-5); 131.14 (C-7). **IR** (cm^{-1}): 1744.3 (C=O, ester); 1726.4 (C=O, lactone); 1611.2 (C=C); 3054.9 (C-H, aromatic ring); 2960 (C-H, aliphatic); 1248.7 (C–O, ester); 1097.8 (C–O, lactone). **ESI-MS**: $[M+H]^+$: 281.

***Crystal structure Determination* (2b)**

Chemical formula: $C_{17}H_{12}O_4$; Formula weight: 280.27; Crystal description: prism, colourless; Melting point (K): 443-445; Crystal system: Triclinic; space group: P -1; Temperature (K): 293(2); Wavelength (Å): 0.71073; Unit cell dimensions: a = 6.8221(2) Å , b = 7.1714(3) Å , c = 14.1270(6) Å, α = 93.239(4)°, β = 92.492(3)°, γ = 101.299(3)°; Volume (Å ^{3}): 675.62(5); Z = 2; Radiation type: MoKα; Absorption coefficient (mm^{-1}): 0.10; Density (Mg m^{-3}): 1.378; F(000): 292; Crystal size (mm): 0.44 x 0.28 x 0.28; 9533 measured reflections; 2866 independent reflections; *R*int = 0.017; $R[F^2 > 2\sigma(F^2)]$ = 0.047; *wR* (F^2) = 0.133; *S* = 1.07; 2866 reflections; 190 parameters.

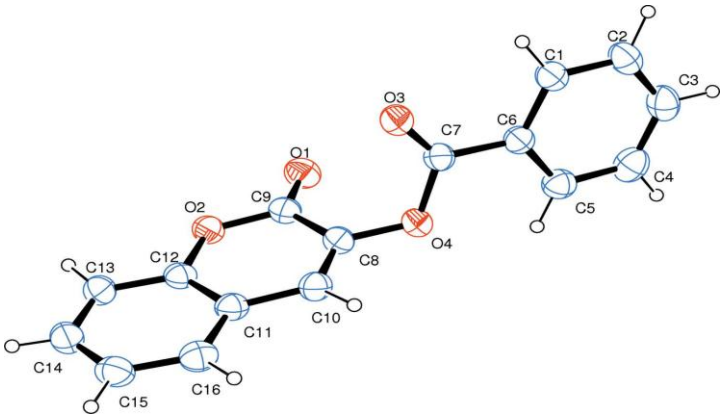


Figure 1. Molecular structure of compound **2a**. Displacement ellipsoids are drawn at the 50% probability level. H atoms are shown as spheres of arbitrary radius

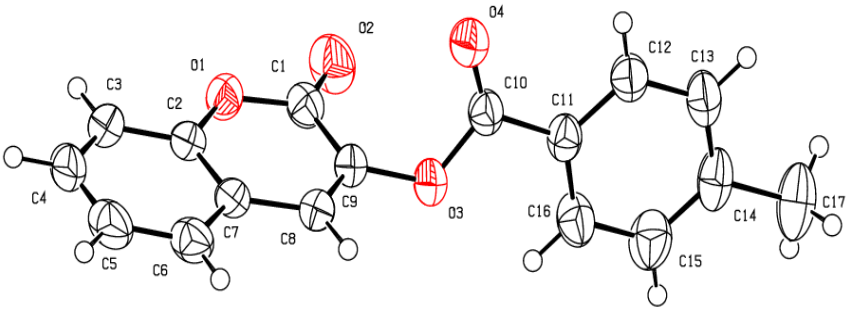


Figure 2. Molecular structure of compound **2b** with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level

2.1.3.3. (coumarin-3-yl)-4-tertiobutylbenzoate (2c)

Yield: 84%; **^{1}H-NMR** (DMSO-d6; 600 MHz):1.2019 (s, 9H, 3CH_3); 7.4229 (d, 1H, J = 6.6 Hz, H-7); 7.44855 (d, 1H, J = 9.9 Hz, H-5); 7.5001 (d, 2H, J = 7.92 Hz, H-6 and H-8); 7.6457 (d, 2H, J = 7.44 Hz, H-14 and H-16); 7.8154 (d, 2H, J = 7.08 Hz, H-13 and H-17); 8.0473 (s, 1H, H-4). **^{13}C-NMR** (DMSO-d6; 400 MHz): 30.73 (CH_3); 39.04 (C-18); 116.39 (C-8); 118.36 (C-10); 124.87 (C-12); 125.34 (C-4); 126.02 (C-14 and C-16); 128.54 (C-6); 130.49 (C-13 and C-17); 131.61 (C-5); 132.07 (C-7); 135.56 (C-3); 151.74 (C-9); 156.15 (C-11); 157.90 (C-15); 163.53 (C-2). **DEPT 135°**: 30.73 (CH_3); 116.39 (C-8); 125.34 (C-4); 126.02 (C-14 and C-16); 128.54 (C-6); 130.49 (C-13 and C-17); 131.61 (C-5); 132.07 (C-7). **IR** (cm^{-1}): 1726.6 (C=O, ester); 1705.3 (C=O, lactone); 1603.1 (C=C); 3046.4 (C-H, aromatic ring); 2913.8 (C-H, aliphatic); 1269.4 (C–O, ester), 1091.8 (C–O, lactone). **ESI-MS**: $[M+H]^+$: 323.

Crystal structure Determination (2c)

Chemical formula: $C_{20}H_{18}O_4$; Formula weight: 322.34; Crystal description: Prism, colorless; Melting point (K): 410-413 K; Crystal system: Monoclinic; space group: *C*2/*c*; Temperature (K): 298; Wavelength (Å): λ = 0.71073; Unit cell dimensions: *a* = 22.8977 (5) Å , *b* = 5.9947 (1) Å , *c* = 24.0352 (7)Å ; β = 93.297 (2)°; Volume (Å ^{3}): 3293.73(13); Z = 8; Radiation type: Mo$K\alpha$; Absorption coefficient (mm^{-1}): 0.09; Density (Mg m^{-3}): 1.300; F(000): 1360; Crystal size (mm): 0.34 x 0.12 x 0.06; 19994 measured reflections; 3005 independent reflections; *R*int = 0.031; $R[F^2 > 2\sigma(F^2)]$ = 0.048; $wR(F^2)$ = 0.127; *S* = 1.12; 3005 reflections; 290 parameters.

2.1.3.4. (Coumarin-3-yl)-4-chlorobenzoate (2d)

Yield: 70%; **^{1}H-NMR** (Acetone-d6; 400 MHz): 7.32 (d, 2H, J = 7.95 Hz, H-6 and H-8); 7.44 (d, 1H, J = 7.6 Hz, H-7); 7.52 (d, 2H, J = 8.2 Hz, H-14 and H-16); 7.63 (d, 1H, J = 7.5 Hz, H-5); 7.91 (s, 1H, H-4); 8.07 (d, 2H, J = 8.4 Hz, H-13 and H-17). **^{13}C-NMR** (Acetone-d6; 100 MHz): 116.35 (C-8); 116.67 (C-10); 125.05 (C-4); 127.16 (C-12); 128.47 (C-6); 128.68 (C-5); 129.25 (C-14 and C-16); 131.82 (C-13 and C-17); 136.25 (C-3); 140.14 (C-15); 151.5 (C-7); 152.3 (C-9); 157.5 (C-11); 162.92 (C-2). **DEPT135°**: 116.35 (C-8); 125.05 (C-4); 128.47 (C-6); 128.68 (C-5); 129.25 (C-14 and C-16); 131.82 (C-13 and C-17); 151.5 (C-7). **IR** (cm^{-1}): 1746.4 (C=O, ester), 1724.9 (C=O, lactone), 1592 (C=C); 3052.7 (C-H, aromatic ring); 1249.4 (C–O, ester); 1092.1 (C–O, lactone); 750 (C-Cl). **ESI-MS** $[M+H]^+$: 301.

***Crystal structure Determination* (2d)**

Chemical formula: $C_{16}H_9ClO_4$; Formula weight: 300.68; Crystal description: Prism, colourless; Melting point (K): 478-479; Crystal system: Triclinic; space group: P1; Temperature (K): 293; Wavelength (Å): λ = 1.54184; Unit cell dimensions: *a* = 6.7866 (4) Å ; *b* = 7.1789 (3)Å , *c* = 14.0981 (5) Å ; α = 94.098 (3)°; β = 93.461 (4)° ;γ = 106.154 (4)°; Volume (Å ^{3}): 655.75 (5); Z = 2; Radiation type: Cu$K\alpha$; Absorption coefficient (mm^{-1}): 2.72; Density (Mg m^{-3}): 1.523; F(000): 308; Crystal size (mm): 0.12 × 0.12 × 0.08; 7634 measured reflections; 2409 independent reflections; *R*int = 0.022; $R[F^2 > 2\sigma(F^2)]$ = 0.039; *wR* (F^2) = 0.106; *S* = 1.05; 2409 reflections; 190 parameters.

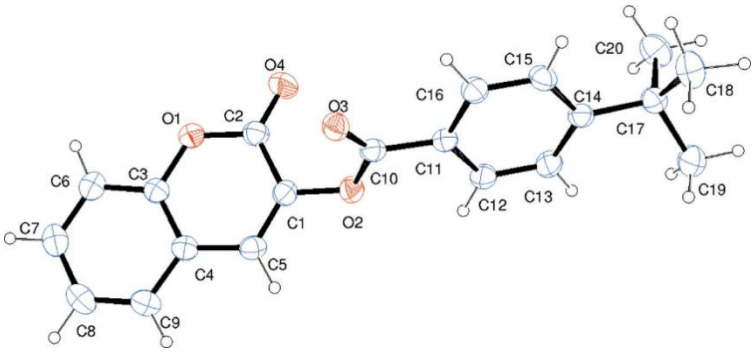


Figure 3. Molecular structure of compound **2c** with atom labelling. Displacement ellipsoids are drawn at the 30% probability level

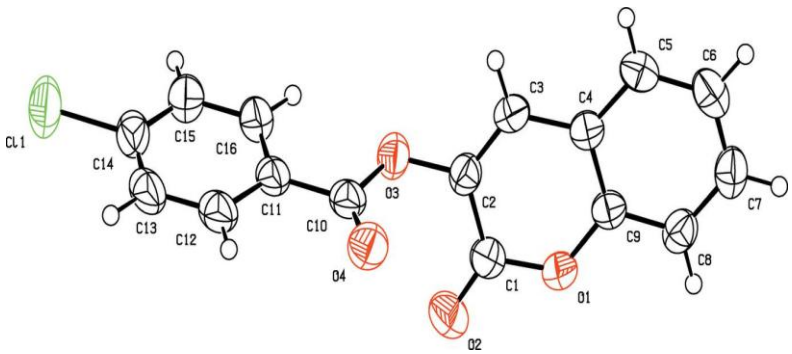


Figure 4. Molecular structure of compound **2d** with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level

2.1.3.5. (Coumarin-3-yl)-4-fluorobenzoate (2e)

Yield: 80 %; **^{1}H-NMR** (DMSO-d6; 600MHz): 7.43125 (d, 1H, J = 7.26 Hz, H-8); 7.4716 (t, 1H, J = 8.82 Hz, H-6); 7.51165 (d, 2H, J = 8.34 Hz, H-14 and H-16); 7.6645 (t, 1H, J = 8.58 Hz, H-7); 7.76295 (d, 1H, J = 9 Hz, H-5); 8.1940(s,1H,H-4); 8.2088 (d, 2H, J = 8.76 Hz, H-13 and H-17). **^{13}C-NMR** (DMSO-d6; 100 MHz): 116.36 (C-14 and C-16); 116.50 (C-8); 118.28 (C-10); 125.21 (C-4); 128.57 (C-6); 131.7 (C-5); 132.19 (C-7); 133.10 (C-13 and C-17); 135.39 (C-12); 151.63 (C-3); 156.07 (C-9); 162.66 (C-11); 165.00 (C-2); 166.88 (C-15). **DEPT 135°**: 116.36 (C-14 and C-16); 116.50 (C-8); 125.21 (C-4); 128.57 (C-6); 131.7 (C-5); 132.19 (C-7); 133.10 (C-13 and C-17). **IR** (cm^{-1}): 1746.4 (C=O, ester); 1724.0 (C=O, lactone); 1604.4 (C=C); 3059.5 (C-H, aromatic); 1245.4 (C–O, ester); 1099.1 (C–O, lactone); 1151 (C-F). **ESI-MS**: $[M+H]^+$: 285.

***Crystal structure Determination* (2e)**

Chemical formula: $C_{16}H_9FO_4$; Formula weight: 284.23; Crystal description: prism, colourless; Melting point (K): 452-454; Crystal system: Triclinic; space group: P1; Temperature (K): 293; Wavelength (Å): λ = 1.54184; Unit cell dimensions: a = 6.8116 (2) Å , b = 7.2402 (2) Å , c = 13.4826 (3) Å , α = 96.943 (2)°, β = 90.862 (2)°, γ = 106.139 (2)°; Volume (Å ^{3}): 633.21 (3); Z = 2; Radiation type: Cu$K\alpha$; Absorption coefficient (mm^{-1}): 1.00; Density (Mg m^{-3}): 1.491; F(000): 292; Crystal size (mm): 0.36 × 0.26 × 0.16; 12676 measured reflections; 2358 independent reflections; Rint = 0.017; $R[F^2 > 2\sigma(F^2)]$ = 0.036; $wR(F^2)$ = 0.100; S = 1.09; 2358 reflections; 191 parameters.

2.1.3.6. (Coumarin-3-yl)-4-cyanobenzoate (2f)

Yield: 67%; **^{1}H-NMR** ($CDCl_3$; 400MHz): 7.32 (d, 1H, J = 7.7 Hz, H-8); 7.39 (d, 1H, J = 7.92 Hz, H-6); 7.51 (d, 1H, J = 7.98 Hz, H-7); 7.60 (d, 1H, J = 8.01 Hz, H-5); 7.68 (s, 1H, H-4); 7.80 (d, 2H, J = 8.1 Hz, H-14 and H-16); 8.3 (d, 2H, J = 8.2 Hz, H-13 and H-17). **^{13}C-NMR** ($CDCl_3$; 100 MHz): 114.7 (C15); 116.87 (C-8); 117.85 (C-18); 125.09(C-4); 127.99(C-6); 128.44(C-10); 130.97(C-5); 131.17 (C-13 and C-17); 131.59 (C-7); 132.46 (C-14 and C-16); 133.99 (C-12); 137.30 (C-3); 151.06 (C-9); 159.34 (C-11); 161.46 (C-2). **DEPT135°**: 116.87 (C-8); 125.09(C-4); 127.99(C-6); 130.97(C-5); 131.17(C-13 and C-17); 131.59 (C-7); 132.46 (C-14 and C-16). **IR** (cm^{-1}): 1745.8 (C=O, ester); 1722.7 (C=O, lactone); 1606.2 (C=C); 3064 (C-H, aromatic ring); 1239.6 (C–O, ester); 1106.0 (C–O, lactone); 2236 (CN). **ESI-MS** $[M+H]^+$: 292.

***Crystal structure Determination* (2f)**

Chemical formula: $C_{17}H_9NO_4$; Formula weight: 291.25; Crystal description: prism, yellow; Melting point (K): 517-519; Crystal system: Triclinic; space group: P1; Temperature (K): 298; Wavelength (Å): 1.54184; Unit cell dimensions: a = 6.8063 (2)Å , b = 7.2205 (3)Å , c = 13.7047 (5) Å, α = 86.960 (3)°, β = 87.210 (3)°, γ = 78.852 (3)°; Volume (Å ^{3}): 659.37 (4); Z = 2; Radiation type: CuKα; Absorption coefficient (mm^{-1}): 0.89; Density (Mg m^{-3}): 1.4670 (1); F(000): 300; Crystal size (mm): 0.44 x 0.12 x 0.02; 8043 measured reflections; 2416 independent reflections; Rint =0.026; $R[F^2 > 2\sigma(F^2)]$ = 0.037; $wR(F^2)$ = 0.111; S = 1.03; 2159 reflections; 200 parameters.

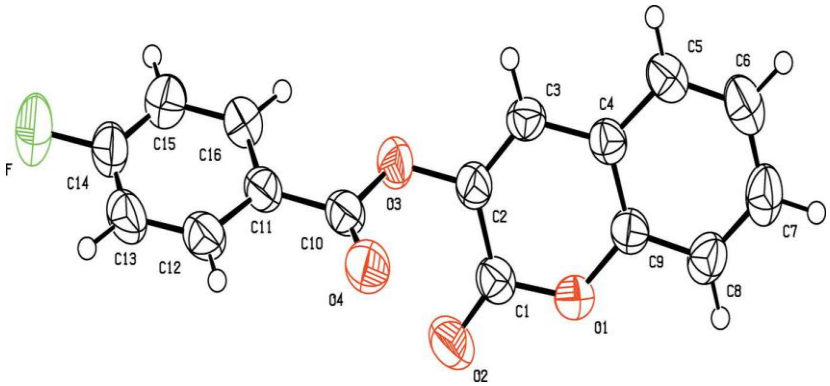


Figure 5. Molecular structure of compound **2e** with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level

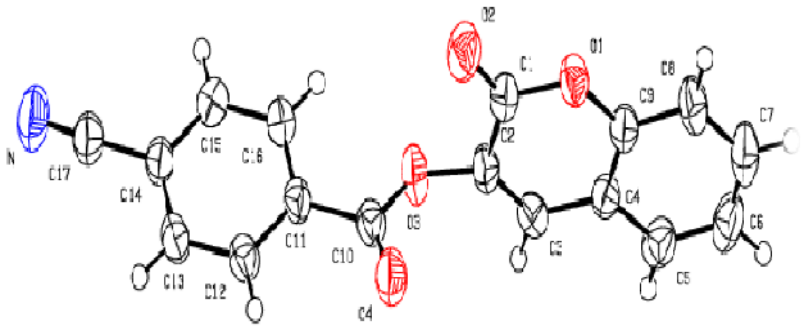


Figure 6. Molecular structures of compound **2f** with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50 % probability level

2.2. Fluorescence Spectra

The fluorescence spectra of compounds **2** were recorded in the solid state on a SAFAS Xenius fluorimeter equipped with a temperature controlled 10-cell auto sampler for liquid analysis and an **optic nose** for **solid analysis**. Spectra acquisition were performed in 2D (Excitation-Emission Matrices). The fluorescence spectra were recorded using excitation into the maximum of the longest wavelength absorption band program. All compounds were excited at their respective maximum excitation wavelength.

3. Results and Discussion

3.1. Characterization

Compounds **2** were prepared in high to acceptable yields (65% – 91%), by an O-acylation reaction of chroman-2,3-dione (tautomer of 3-hydroxycoumarin) with the corresponding benzoyl chloride (Scheme 1).

Examination of the information obtained from the NMR spectra enabled us to assign the chemical shifts of the different protons and carbons for all compounds. The FT-IR spectra of compounds **2** showed their main characteristic absorption bands (C=O, lactone); (C=O, ester); (C=C); (C-H Aromatic ring); (C–O, lactone); (C–O, ester)…

The molecular structures of all compounds were resolved by X-ray diffractometry and are shown in the different ORTEP structures obtained, with the atomic numbering scheme used.

As it can be observed, all the molecules under study adopted some similar aspects in the conformation of the crystal. Coumarin nucleus and aromatic ring attached to the ester bridge in each molecule are planar, as expected. The main difference between the molecular structures of compounds **2** is the dihedral angle between coumarin ring system and the benzene ring: **2a**: 83.58(9)°; **2b**: 79.64(5)°; **2c**: 57.55(9)°; **2d**: 73.95(8)°; **2e**: 70.18(6)°; **2f**: 87.35(5)°.

For all compounds, the C-O-C-C torsion angle and the dihedral angles between the coumarin cycle and the benzoate group also vary with steric hindrance.

In the different structures, intramolecular bonds, valence bonds and stacking modes (C-H ... π; π ... π) have been observed, connecting the molecules in a three-dimensional supramolecular framework [25-28]. The analysis of the crystallographic data provides further evidence on the results of the structural characterization of the compounds **2**.

3.2. Fluorescence Properties

The different bands are characterized by the position of the maximum emission, analyzed through the wavelength (λ_F) and the fluorescence intensity (I_F). The results are reported in the table below (table 2).

Table 2. Excitation wavelengths (λ_{Ex}), emission wavelengths (λ_F) and fluorescence intensities (I_F)

Compound	R	λ_{Ex} (nm)	λ_F (nm)	I_F (a.u)
2a	**H**	460	509	99.32
2b	**CH_3**	460	509	99.35
2c	***t*-Bu**	460	525	100.06
2d	**Cl**	445	510	99.49
2e	**F**	445	510	98.74
2f	**CN**	460	460	27.65

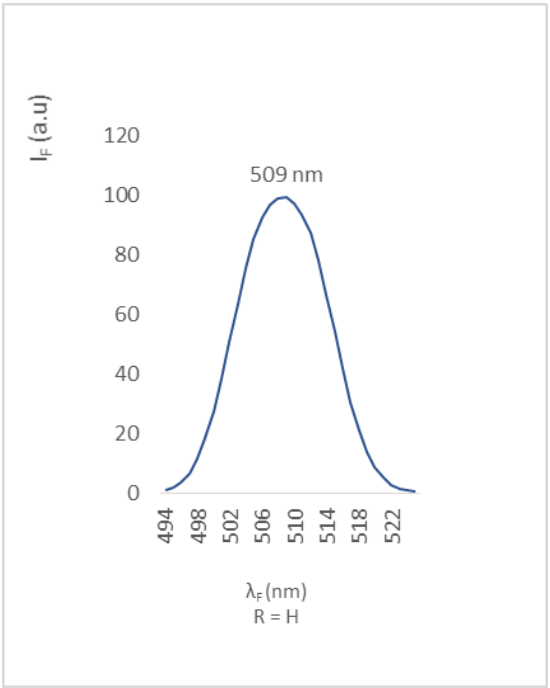


Figure 7. Fluorescence emission of compound **2a**

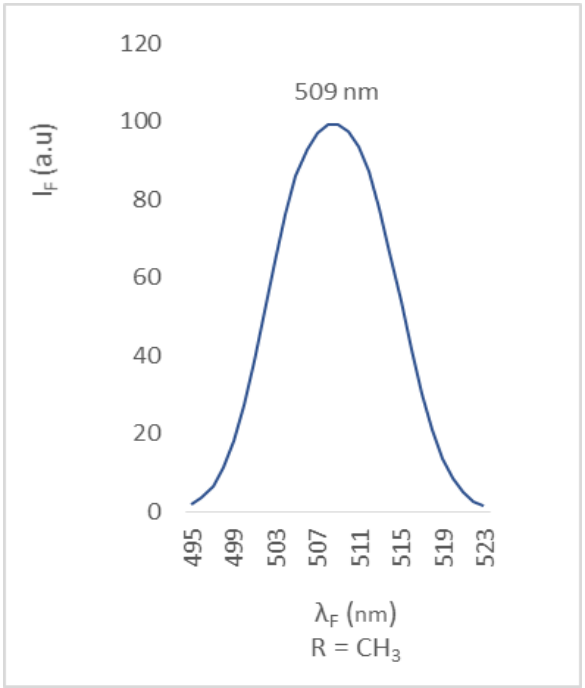


Figure 8. Fluorescence emission of compound **2b**

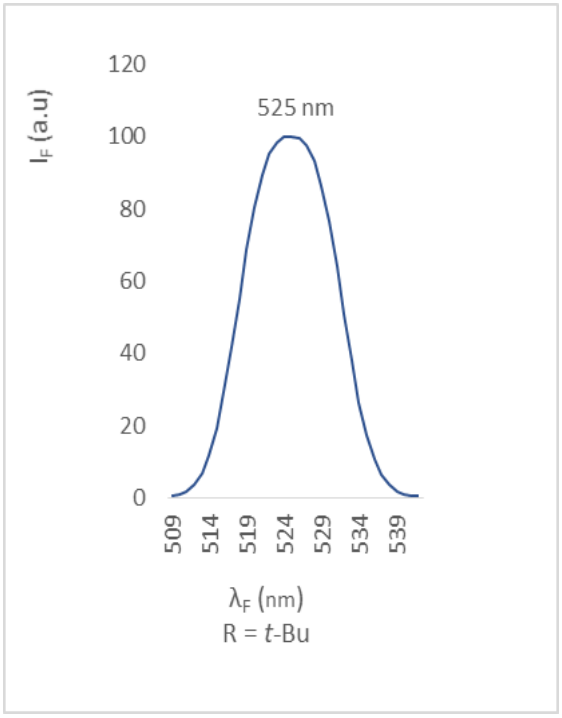


Figure 9. Fluorescence emission of compound **2c**

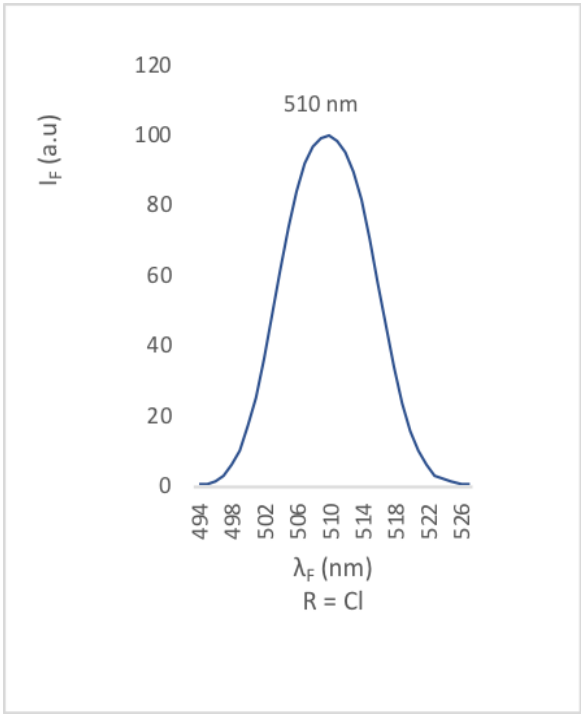


Figure 10. Fluorescence emission of compound **2d**

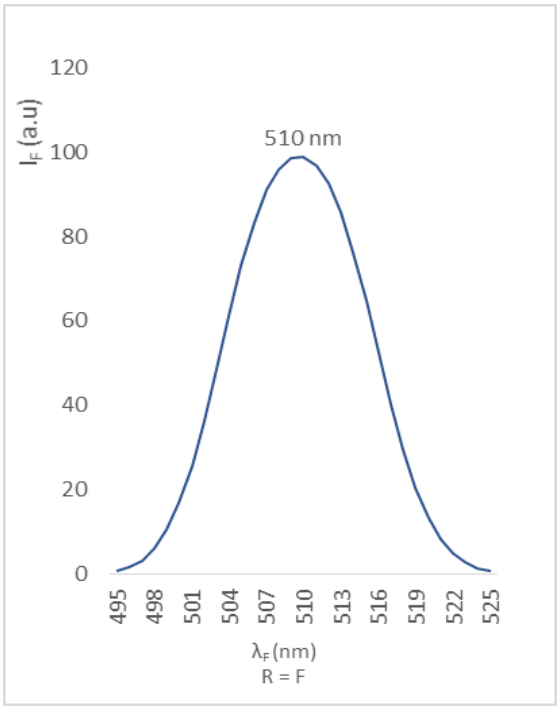


Figure 11. Fluorescence emission of compound **2e**

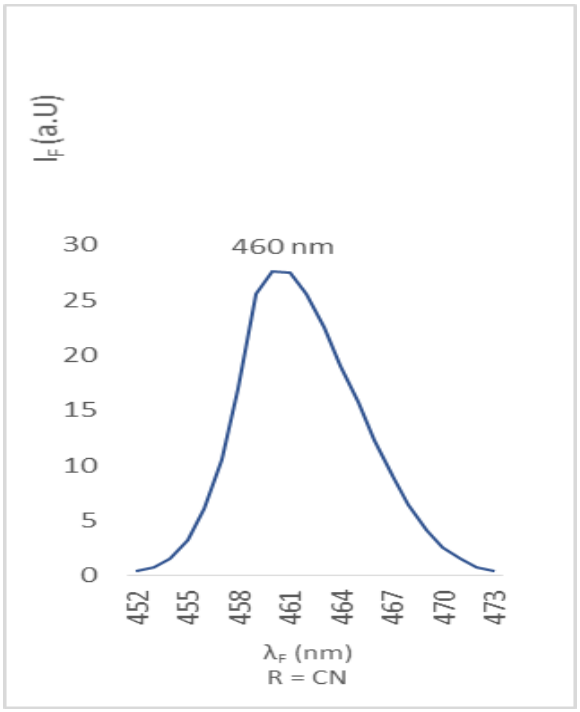


Figure 12. Fluorescence emission of compound **2f**

All the synthesized compounds **2** exhibited fluorescence emission with wavelength ranging from 460 to 525 nm. Nevertheless, we observed that there is a clear relationship between the electronic nature of the substituent R at the para position of carbonyl group and fluorescence emission:

- Compounds **2a** (R = H); **2b** (R = CH_3) and **2c** (R = *t*-Bu) including substituting groups R with varying electron donating ability exhibited strong fluorescence at a longer wavelength i.e. 509-525 nm. The fluorescence intensity was as high as the electron donating ability was great. So, it was significantly high in the case of compound **2c**.
- On the other hand, the compounds **2d**: (R = Cl); **2e**: (R = F) and **2f** (R = CN) including substituting groups R with varying electron-withdrawing ability exhibited strong to weak fluorescence at a shorter wavelength i.e.

460-510 nm. The greater was the electron withdrawing character, the weaker was the fluorescence intensity. Thus, it was pronouncedly weak in the case of compound **2f**.

These results are in agreement with studies observed by Djandé et al and Yasameen et al [30-31] who observed respectively that 4-acyl-isochroman-1,3-diones and coumarin derivatives substituted an electron-donating group favor the efficiency of fluorescence emission while electron-withdrawing groups performed the opposite effect [30, 31].

4. Conclusions

A series of 3-substituted coumarin derivatives (compounds 2a-2f) were successfully synthesized and the proposed structures were determined by spectral analysis performed by IR, NMR, and ESI-MS and confirmed by X-ray diffractometry.

Fluorescence properties of these (coumarin-3-yl)-benzoates were studied in the solid state. The fluorescence emission was influenced by the electronic nature of the substituting group R. In summary, all the compounds exhibited intense fluorescence except compound **2f**, due to the great electron-withdrawing ability of its substituent cyano (R = CN).

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REFERENCES

[1] Zhao Y. R., Zheng Q., Dakin K. Xu., K., Martinez M. L., Li W-H. New Caged Coumarin Fluorophores with Extraordinary Uncaging Cross Sections Suitable for Biological Imaging Applications. *J. Amer. Chem. Soc*. 2004, 126, 4653-4663.

[2] Geddes, C. D. et al., Metal-Enhanced Fluorescence (MEF) Due to Silver Colloids on a Planar Surface: Potential Applications of Indocyanine Green to in Vivo Imaging. *J. Phys. Chem.* 2003, A. 107, 3443–3449.

[3] Noginov, M. A. et al. Demonstration of a spaser-based nanolaser. *Nature* 2009, 460, 1110–1112.

[4] Seidel, J., Grafstroem, S., Eng, L. Stimulated emission of surface plasmons at the interface. *Phys. Rev. Lett* 2005, 94, 177401.

[5] Oulton, R.F. Surface plasmon lasers: sources of nanoscopic light. *Materials Today* 2012, 15, 26–34.

[6] Aslan, K., Leonenko, Z., Lakowicz, J. R., Geddes, C. D. Annealed silver-island films for applications in metal-enhanced fluorescence: interpretation in terms of radiating plasmons, *J. Fluoresc.* 2005, 15, 643–654.

[7] Oliva, A., Meepagala, K.M., Wedge, D.E., Harries, D., Hale, A.L., Aliotta, G., Duke, S.O. Synthesis and insecticidal activity of new 4-hydroxy-2H-1-benzopyran-2-one derivatives. *J. Agric. Food. Chem.* 2003, 51 (4), 890–896.

[8] Cravotto, G., Tagliapietra, S., Cappello, R., Palmisano, G., Curini, M., Boccalini. Long-chain 3-Acyl-4-hydroxycoumarins: Structure and antibacterial activity. *Arch. Pharm.* (Weinheim, Ger.) 2006, 339 (3), 129–132.

[9] Huang, L.; Yuan, X.; Yu, D.; Lee, K.; Ho Chen, C. Mechanism of action and resistant profile of anti-HIV-1 coumarin derivatives. *Virology* 2005, 332, 623–628.

[10] Olmedo, D.; Sancho, R.; Bedoya, L.M.; López-Pérez, J.L.; Olmo, E.; Muñoz, E.; Alcamí, J.; Gupta, M.P.; Feliciano, A.S. 3-phenylcoumarins as inhibitors of HIV-1 replication. *Molecules* 2012, 17, 9245–9257.

[11] Bi, J., Chen, Z., Su, W. Synthesis and antitumor activity of novel coumarin derivatives via a three-component reaction in water. *Chin. J. Chem.* 2013, 31 (4), 507–514.

[12] Zhi Qiang, D., Shi, J.B., Song, B.A., Liu, X.H. Novel 2 Hchromen derivatives: design, synthesis and anticancer activity. *Roy. Soc. Chem. Adv.* 2014, 4 (11), 5607–5617.

[13] S.A., Sethumadhavan, S. Synthesis, anticoagulant and PIVKA-II induced by new 4-hydroxycoumarin derivatives. *Bioorg. Med. Chem.* 2010, 18 (10), 3371–3378.

[14] Bailly F., Maurin C., Teissier E., Vezin H., Cotelle P. Antioxidant properties of 3-hydroxycoumarin derivatives. Bioorganic & Medicinal Chemistry 2004, 12 (21), 5611–5618.

[15] Graciet, J.C. New coumarin type dyes for optical data recording. *Eur. Pat. Appl.* 2005, EP 1516895 A1 0323.

[16] Harishkumar, H. N.; Mahadevan K. M.; Masagalli, J.N. Facile synthesis of 2-(1,3-benzoxazol/benzothiazol-2-yl)-3H-benzo[f]chromen-3-one as blue fluorescent brighteners. *S. Afr. J. Chem*, 2012, 65, 5-9.

[17] Murata, C.; Masuda, T.; Kamochi, Y.; Todoroki, K.; Yoshida, H.; Nohta, H.; Yamaguchi, M.; Takadate, A. Improvement of fluorescence characteristics of coumarins ; synthesis and fluorescence properties of 6-methoxycoumarin and benzocoumarin derivatives as novel fluorophores emitting in the longer wavelength region and their application to analytical reagents. *Chem. Pharm. Bull.* 2005, 53(7), 750758.

[18] Zhou, S. H.; Jia, J. H.; Gao, J. R.; Han, L.; Li, Y. J.; Sheng, W. J. The one-pot synthesis and fluorimetric study of 3-(2-benzothiazolyl)-coumarins. *Dyes and Pigments* 2010, 86, 123-128.

[19] Moeckli, P. Preparation of some new red fluorescent 4-cyanocoumarin dyes. *Dyes and Pigments.* 1980, 1, 3-15.

[20] R. G. Pearson *J. Amer. Chem. Soc.* 1963, 85, 3583.

[21] Sheldrick, G. M. *Acta Cryst.* 2008, A64, 112–122.

[22] Sheldrick, G. M. *Acta Cryst.* 2015, C71, 3–8.

[23] Spek, A. L. *Acta Cryst.* D65, 2009, 148–155.

[24] Westrip, S. P. *J. Appl. Cryst.* 2010, 43, 920–925.

[25] Konan René Kambo, Siaka Sosso, Abdoulaye Djandé, Rita Kakou-Yao and Abodou Jules Tenon. 2-Oxo-2H-chromen-3-yl 4-tert-butylbenzoate. *IUCrData*. 1 2016, x161633.

[26] Konan René Kambo, Siaka Sosso, F. Mansilla-Koblavi, Abdoulaye Djandé and Rita Kakou-Yao. 2-Oxo-2H-chromen-3-yl benzoate. IUCrData. 2 2017, x170663.

[27] Ziki, E., Sosso, S., Mansilla-Koblavi, F., Djandé, A. and Kakou-Yao, R. Crystal structure of 2-oxo-2H- chromen-3-yl 4-chlorobenzoate and Hirshfeld surface analysis. *Acta Cryst*. 2017, E73, 45–47.

[28] Eric Ziki, Siaka Sosso, Lamine Cissé, Guy Euloge Bany, Abdoulaye Djandé and Rita Kakou-Yao. 2-Oxo-2H-chromen-3-yl 4-fluorobenzoate. *IUCr Data*. 2 2017, x170550.

[29] Maria J. Matos, Eugenio Uriarte, Lourdes Santana, Santiago Vilar. Synthesis, NMR characterization, X-ray structural analysis and theoretical calculations of amide and ester derivatives of the coumarin scaffold. *Journal of Molecular Structure* 2014, 1041, 144–150.

[30] Djandé A., Cisse L., Kaboré L., Saba A., Tine A. and Aycard J. P. Synthesis and fluorescence properties of 4-acylisochroman-1,3-diones, *Heterocyclic communications* 2008, 14 (4) 23.

[31] Yasameen K. Al-Majedy, Ahmed A. Al-Amiery, Abdul Amir H. Kadhum, Abu Bakar Mohamad. 4-Hydroxycoumarins as New Fluorescent Compounds: Synthesis and Characterization. *American Journal of Chemistry* 2015, 5(3A): 48-51.