

Supplementary material

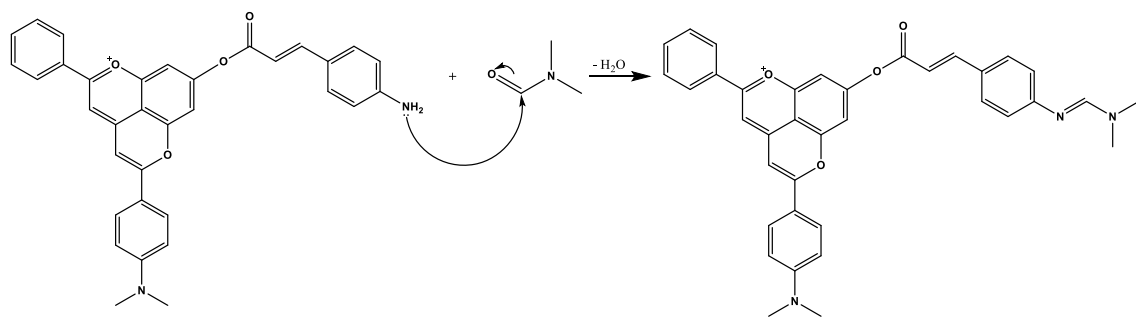
Functionalization of 7-hydroxy-pyranoflavylium: synthesis of new dyes with extended chromatic stability.

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Keywords: 7-hydroxy-pyranoflavylium; 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride; ester bond; coupling chemistry; cinnamic acids



Scheme S1: Nucleophilic addition of a primary amine present in dye 2 to the carbonyl group of the solvent (DMF) resulting in a side-product with $[\text{M}^+]$ m/z 582 and a maximum absorption wavelength of 570 nm.

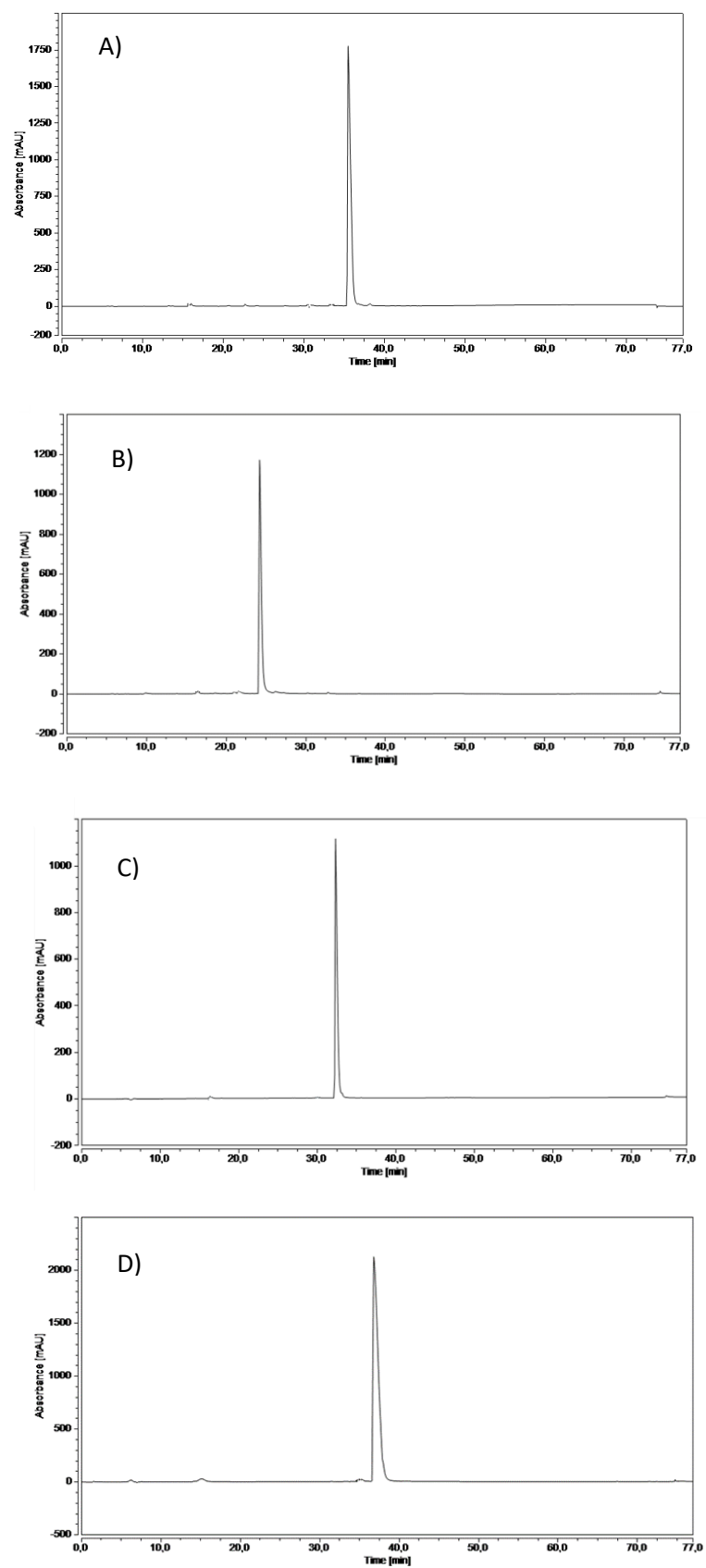


Figure S1 - HPLC chromatograms obtained at a wavelength maximum of each dye. Dye 1 (A), Dye 2 (B), dye 3 (C) and dye 4 (D).

Dye_1#86-115 RT: 1.30-1.75 AV: 30 NL: 3.57E6

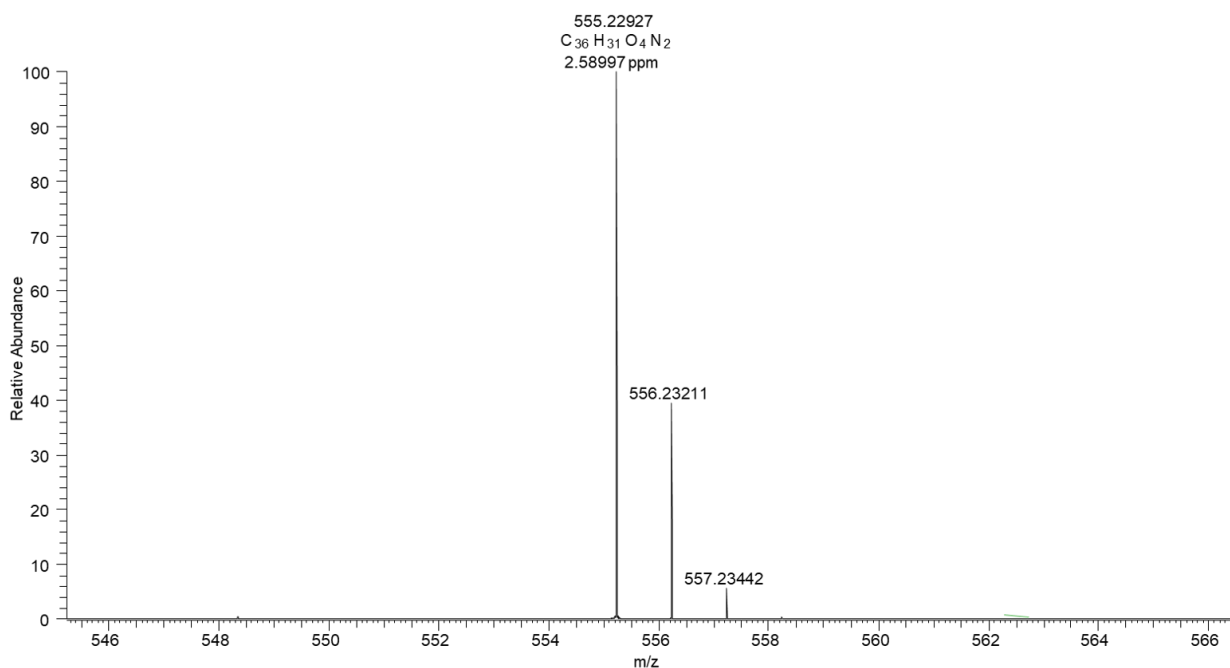


Figure S2: HRMS analysis performed in the positive-ion mode of the new ester compound formed during the esterification reaction of amino-based 7-hydroxyl-pyranoflavylum and 4-dimethyl amino cinnamic acid.

Dye_2#13-29 RT: 0.19-0.47 AV: 17 NL: 3.02E7

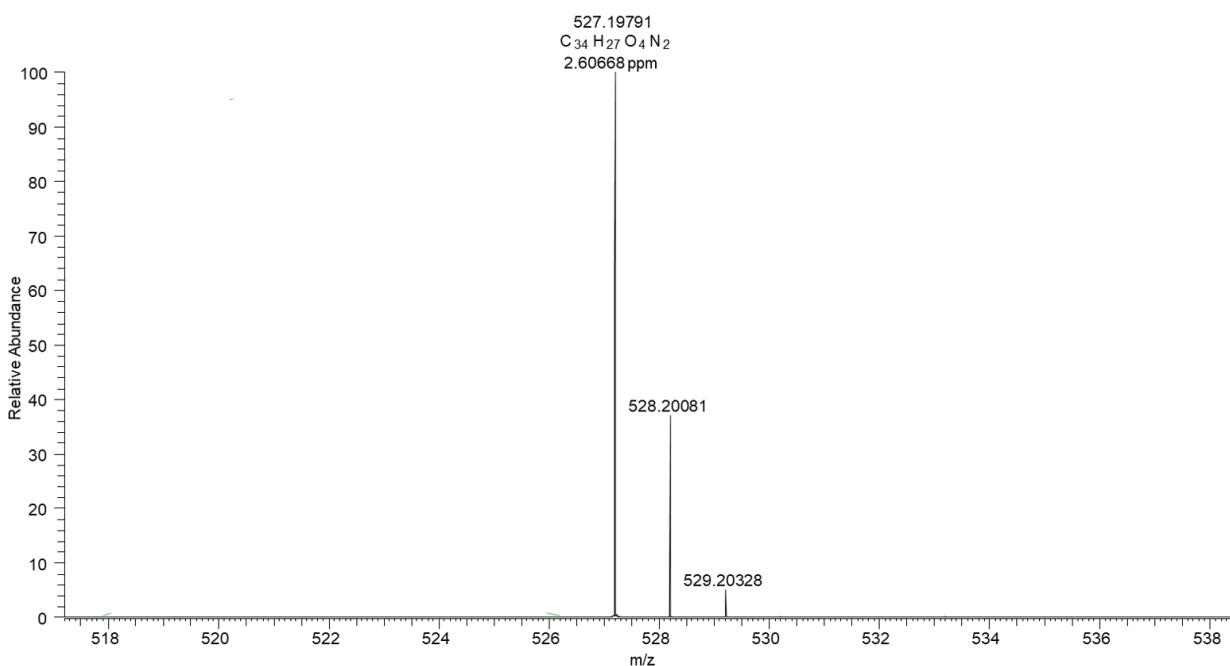


Figure S3: HRMS analysis performed in the positive-ion mode of the new ester compound formed during the esterification reaction of amino-based 7-hydroxyl-pyranoflavylum and 4-amino cinnamic acid.

Dye_3#50-78 RT: 1.35-1.87 AV: 20 NL: 1.23E8

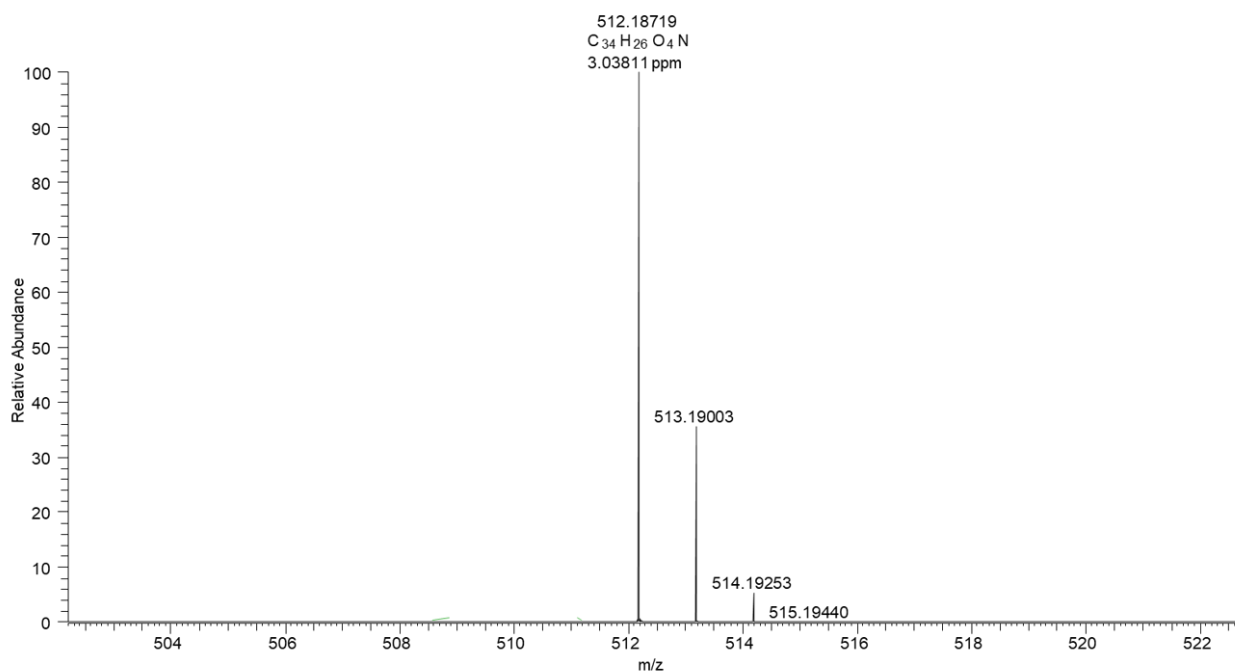


Figure S4: HRMS analysis performed in the positive-ion mode of the new ester compound formed during the esterification reaction of amino-based 7-hydroxyl-pyranoflavylum and trans-cinnamic acid.

Dye_4#75-95 RT: 2.04-2.48 AV: 17 NL: 1.87E8

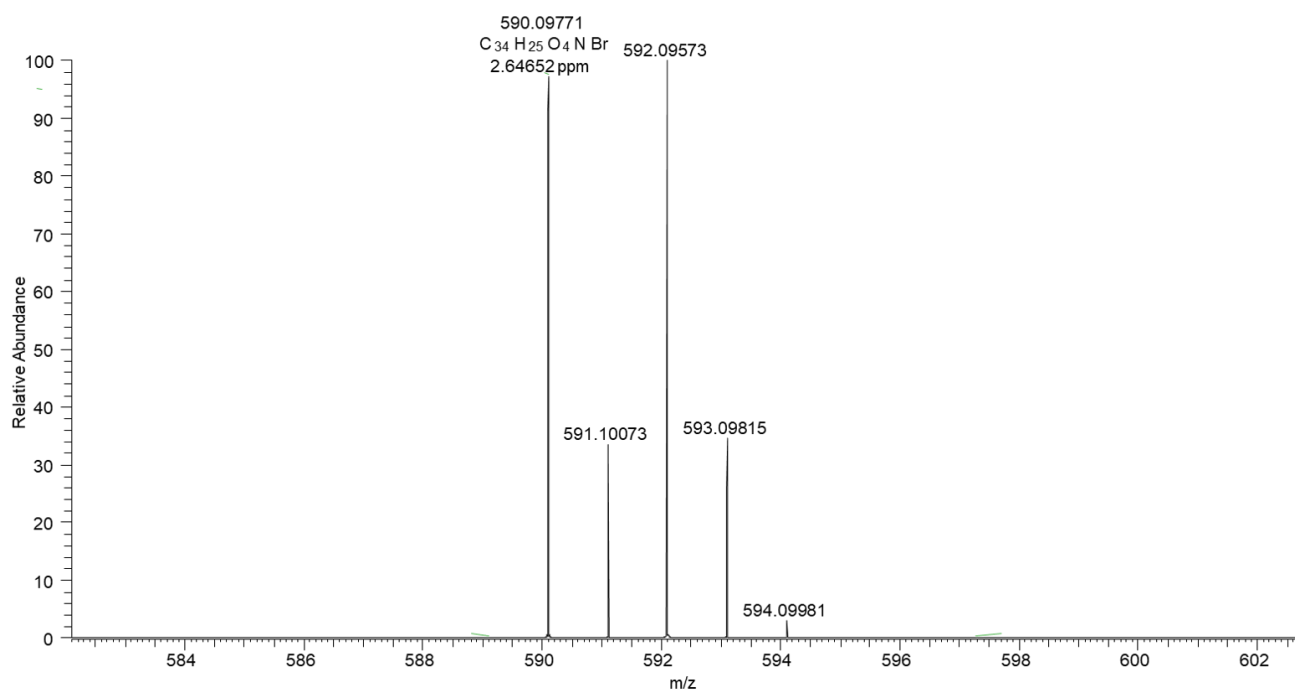


Figure S5: HRMS analysis performed in the positive-ion mode of the new ester compound formed during the esterification reaction of amino-based 7-hydroxyl-pyranoflavylum and 4-bromo cinnamic acid.

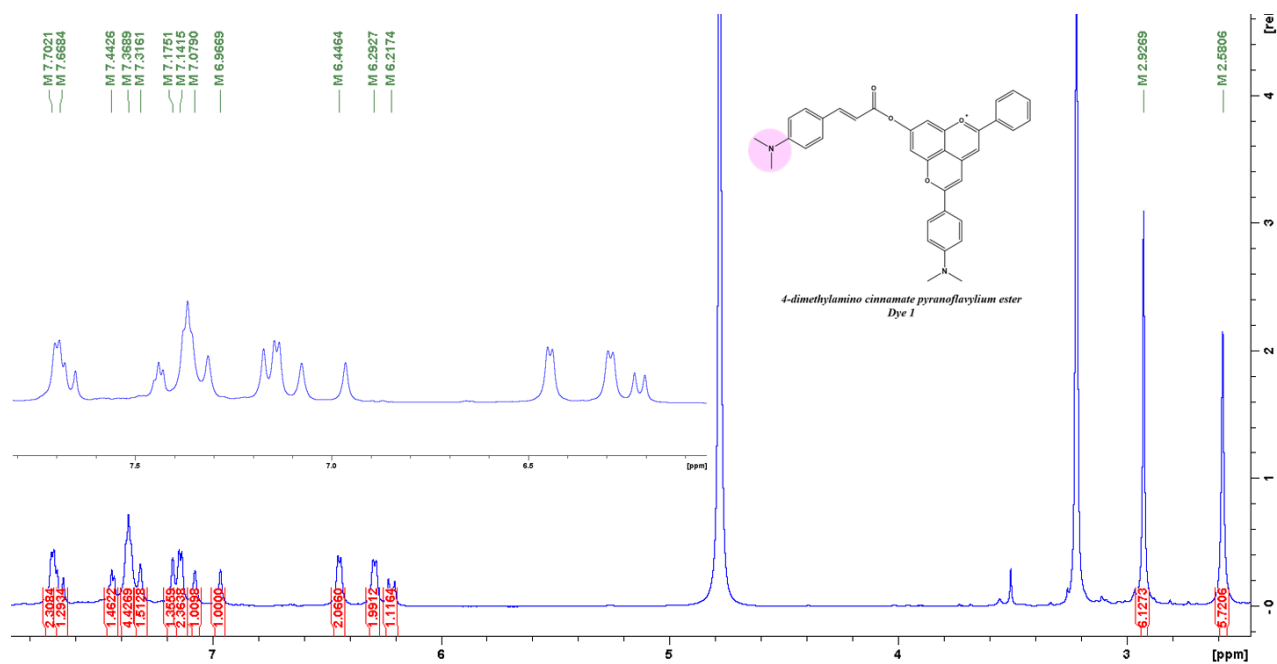


Figure S6 - ¹H-NMR spectrum in methanol deuterated of 4-dimethylamino cinnamate pyranoflavylum ester (Dye 1)

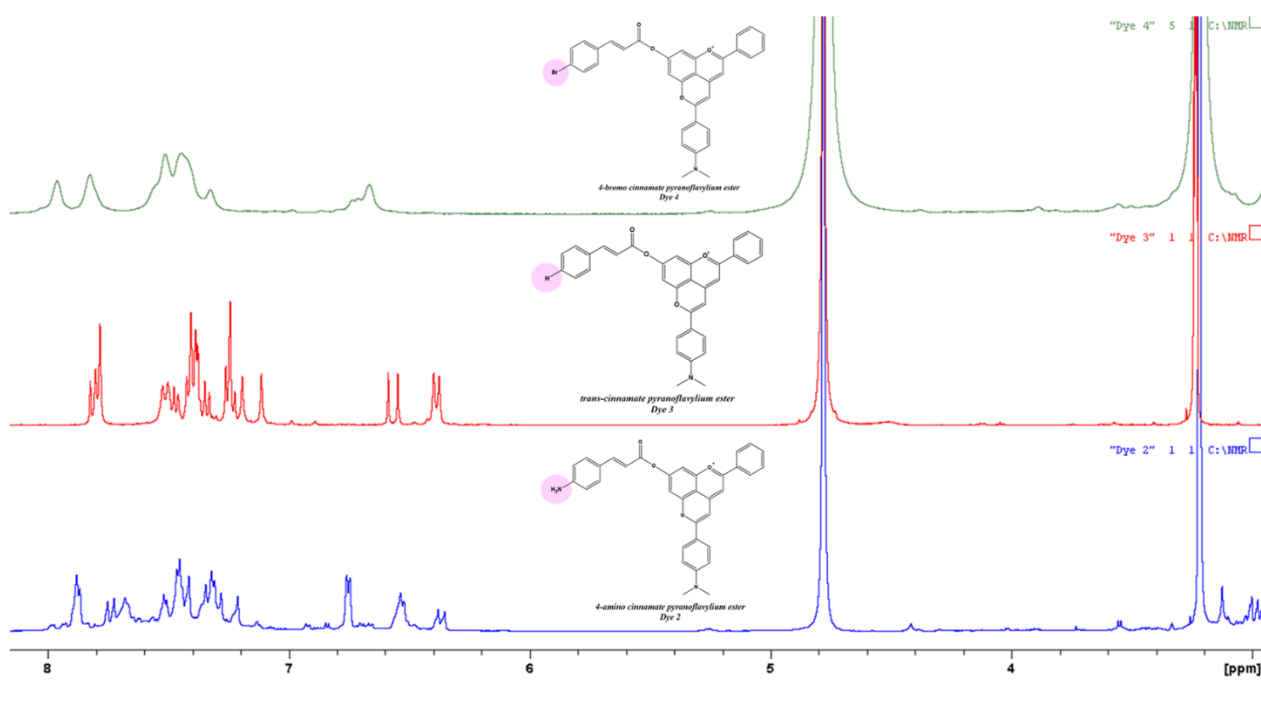


Figure S7 - ¹H NMR spectra in methanol deuterated of 4-amino cinnamate pyranoflavylum ester (Dye 2 - blue), trans-cinnamate pyranoflavylum ester (Dye 3 - red) and 4-bromo cinnamate pyranoflavylum ester (Dye 4 - green)

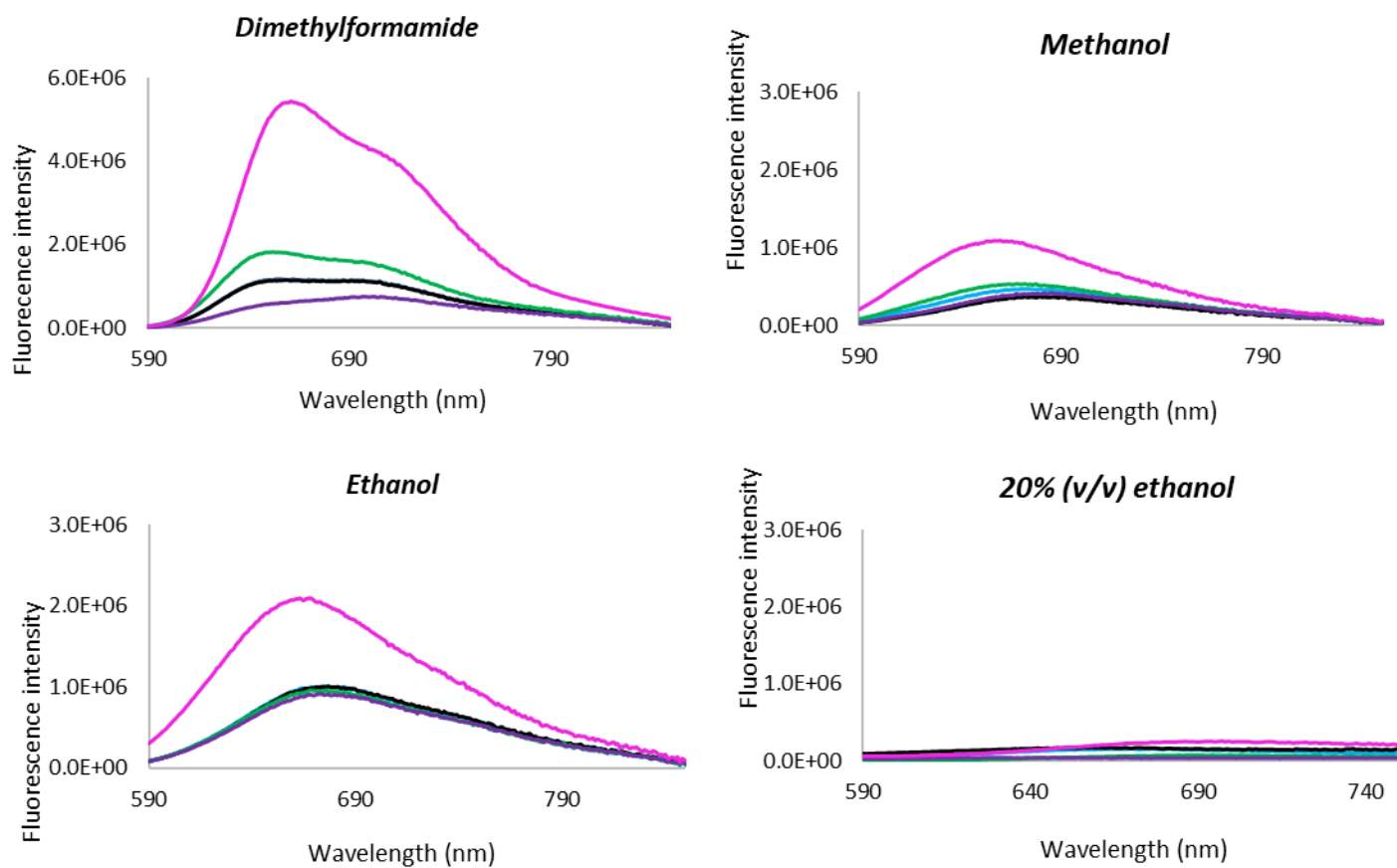


Figure S8 - Fluorescence spectra for the pigments in different solvents. Pink: 7-hydroxyl pyranoflavylum precursor. Purple: dye 1; Green: dye 2; Blue: dye 3 and Black: dye 4.

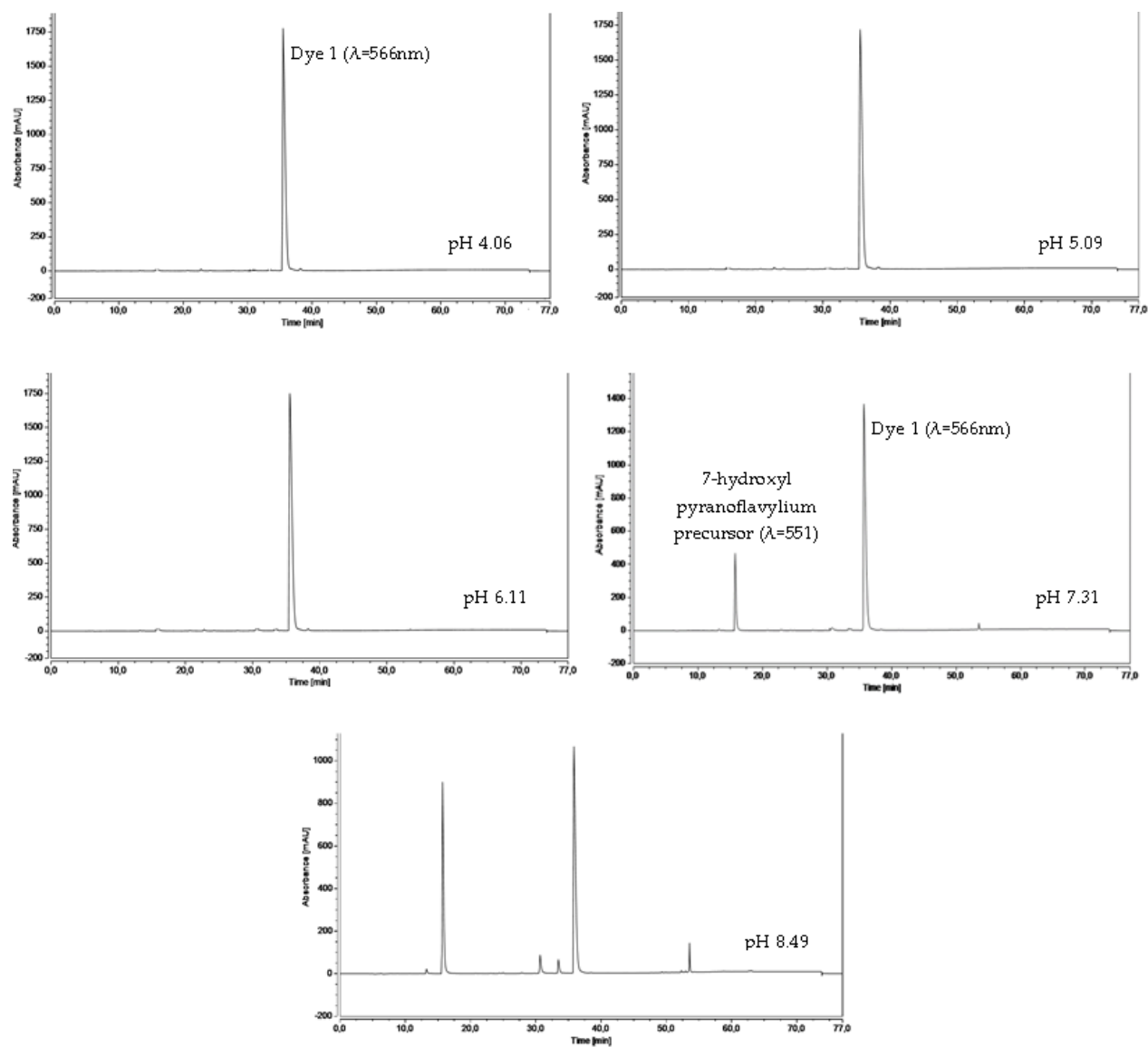


Figure S9 – HPLC chromatograms for dye 1 (4-dimethylamino pyranoflavylium cinnamate ester) in aqueous solution with 50% (v/v) ethanol/water at different pH values after 27 hours at room temperature.