Electronic Supplementary Material (ESI) for Materials Advances.


# Supplementary data

## Fabrication of photoluminescent nanoparticles from carbazole-derived chalcones: a study of optical properties, cell biomarking, and metabolism

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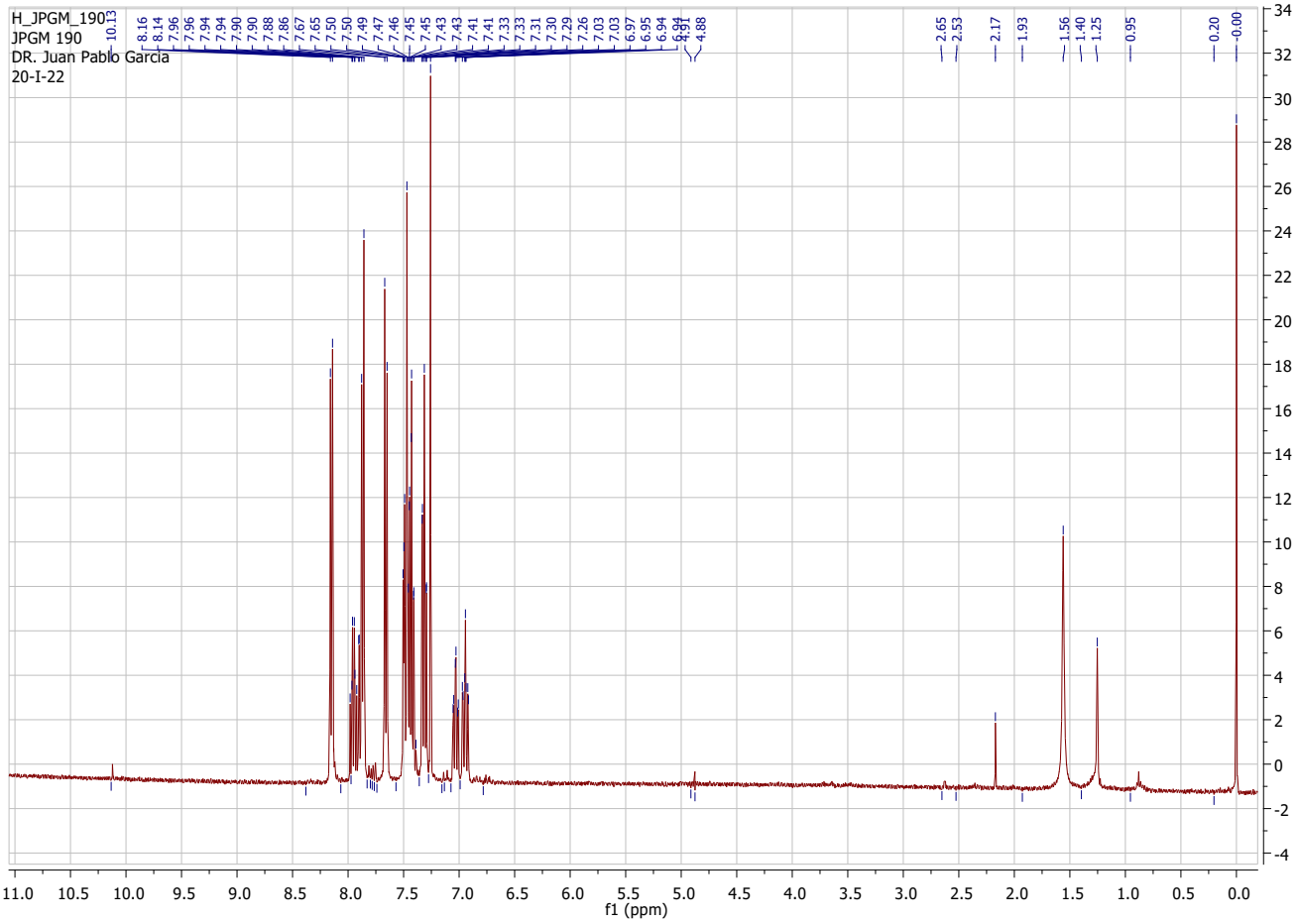
### Chalcone synthesis

The synthesis of the chalcones was carried out by means of the Claisen-Schmidt condensation reaction (Scheme 1), in a flask 0.486 mmol of N-(4-formylphenyl)carbazole and 0.486 mmol of the corresponding acetophenone were placed, to the mixture were added 30 mL of EtOH and 0.1 mL of a KOH 10% solution as catalyst, the mixture was stirred and heated to 65 °C, the reaction was monitored using thin layer chromatography and was terminated when the reagents had been consumed. . The solvent was removed by rotary evaporation and the solid purified by recrystallization using a 70:30 EtOH-ethyl acetate mixture.

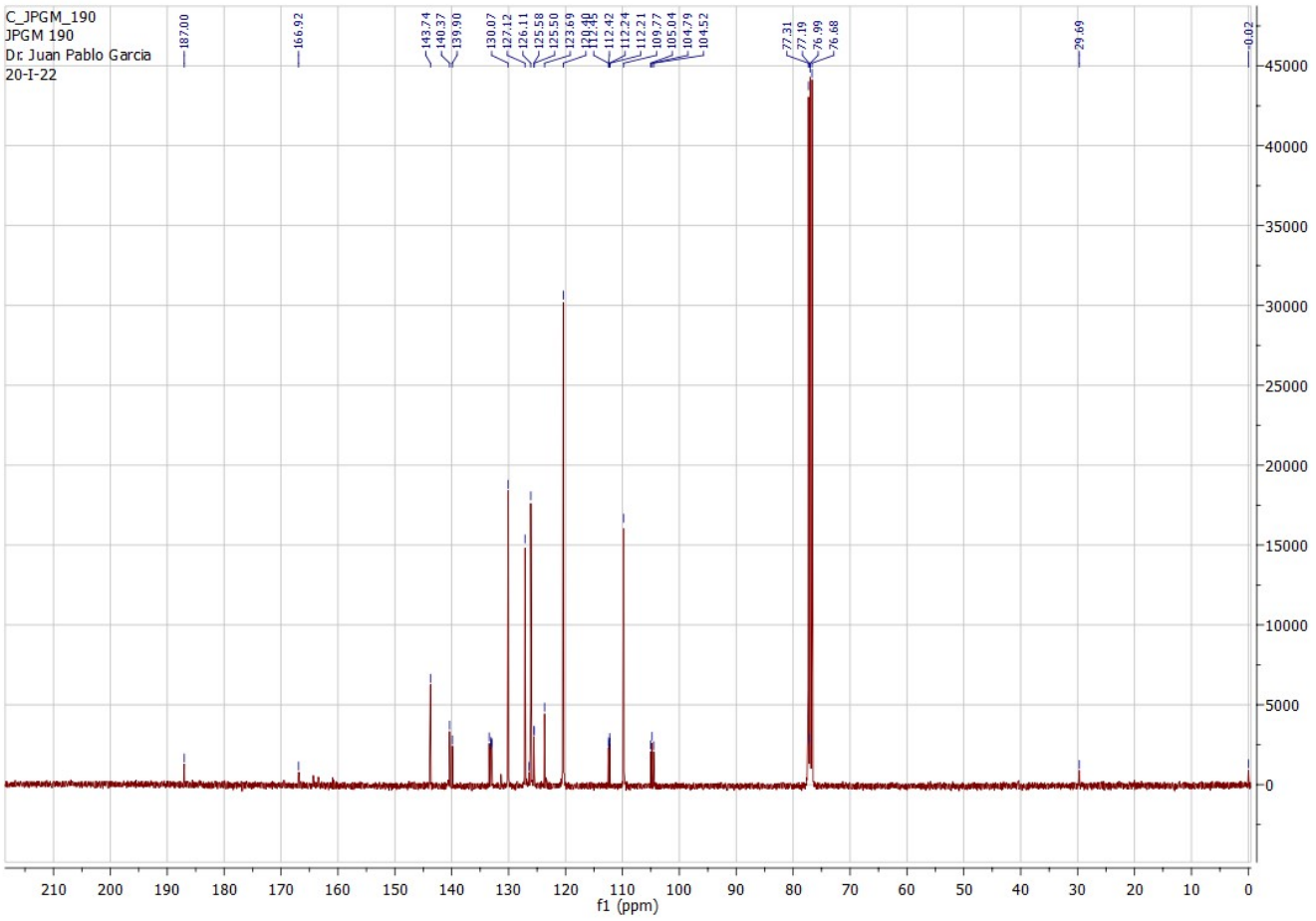
(2E)-3-[4-(9H-carbazol-9-yl)phenyl]-1-(2,4-difluorophenyl)prop-2-en-1-one (M1). In a 50 mL round bottom flask, 0.486 mmol of N-(4-formylphenyl)carbazole and 0.486 mmol of 2,4-difluoroacetophenone dissolved in 30 mL of ethanol were placed, obtaining a yellow solid, 88.9% yield (mechanochemical synthesis). Melting point: 167.4-168.6 °C, FTIR $cm^{-1}$, 1663 (C=O); 1595, 1516, 1450 (C=C-C), 1364, 1334 (C-N); 1140, 1096, 1038 (C-F). $^{1}$H-NMR ($CDCl_3$): 7.03 (td 1H), 6.94(ddd, 1H), 7.95 (dt, 1H), 7.41 (d, *J*=15.4 Hz, 1H), 7.68 (d, *J*=15.4 Hz, 1H), 7.89 (d, *J*=7.86 Hz, 2H), 7.51 (d, 2H), 7.59 (d, 2H), 7.26-7.23 (m, 2H), 7.32 (d, *J*=6.6 Hz, 2H), 8.15 (d, *J*=6.6 Hz, 2H)$^{13}$C-NMR ($CDCl_3$): δ 143.3, 120.4, 140.7, 123.7, 123.4, 143.3, 190.9, 120.5, 143.7, 133.4, 130.11, 123.7, 140, 140.3, 109.7, 127.1, 126.1, 120.5, 120.8.

(2E)-3-[4-(9H-carbazol-9-yl)phenyl]-1-(3,4-difluorophenyl)prop-2-en-1-one (M2). In a 50 mL round bottom flask, 0.486 mmol of N-(4-formylphenyl)carbazole and 0.486 mmol of 3,4-difluoroacetophenone dissolved in 30 mL of ethanol were placed, obtaining a yellow solid,

yield 95.8% (mechanochemical synthesis). Melting point: 166.5-167.9 °C, FTIR $cm^{-1}$, 1666 (C=O); 1586, 1512, 1480, 1450 (C=C-C), 1364, 1336 (C-N); 1109, 1029 (C-F). $^{1}$H-NMR ($CDCl_3$): 7.41-7.53 (m, 1H), 7.28-7.36 (m, 1H), 7.84-7.94 (m, 1H), 7.53 (d, *J*=15.7 Hz, 1H), 7.92 (d, *J*=17.7 Hz, 1H), 7.89 (d, *J*=8.25 Hz, 2H), 7.66 (d, *J*=8.25 Hz, 2H), 7.44 (m), 7.33 (d, *J*=7.75 Hz, 2H), 8.15 (d, *J*=7.75 Hz, 2H)$^{13}$C-NMR ($CDCl_3$): δ 117.2, 149.6, 117.9, 125.4, 135.8, 187.5, 120.5, 144.6, 133.3, 130.16, 123.8, 140.1, 140.3, 109.8, 127.2, 126.2, 125.5, 121.3




**Spectrum 1.** $^{1}$H-NMR ($CDCl_3$) spectrum of M1.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JPGM 190
Dr. Juan Pablo Garcia
20-I-22
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112.24
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200
190
180
170
160
150
140
130
120
110
100
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50
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10
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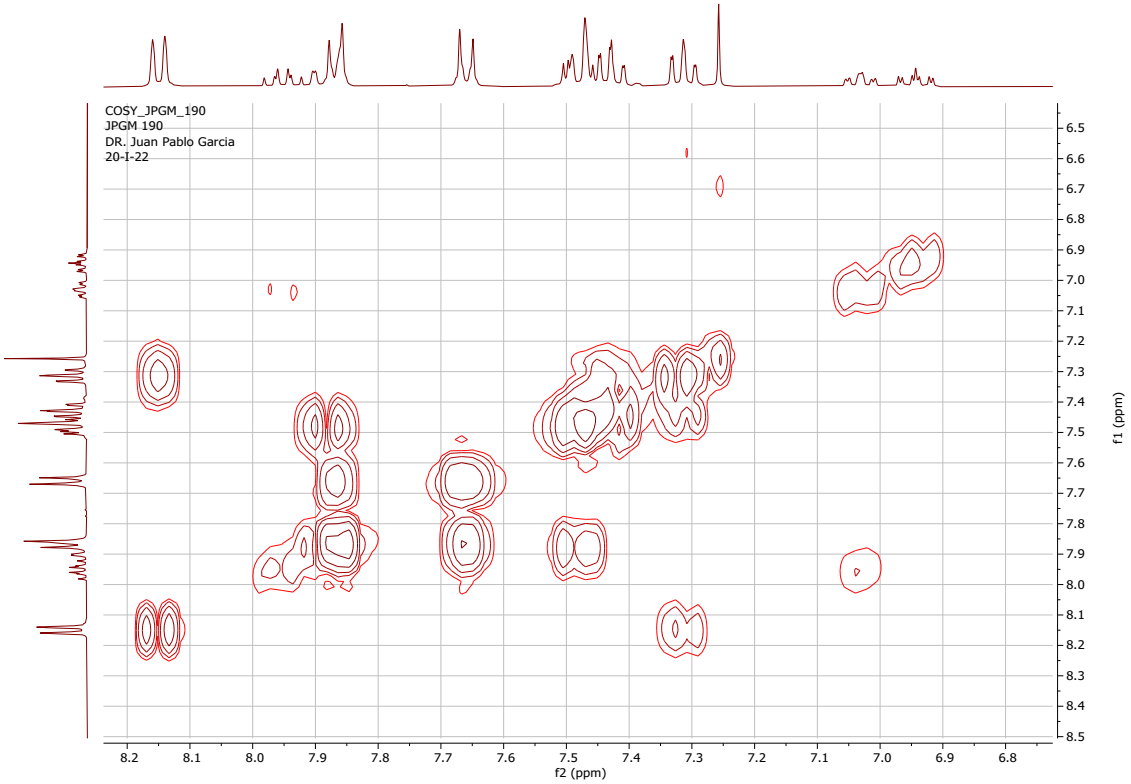
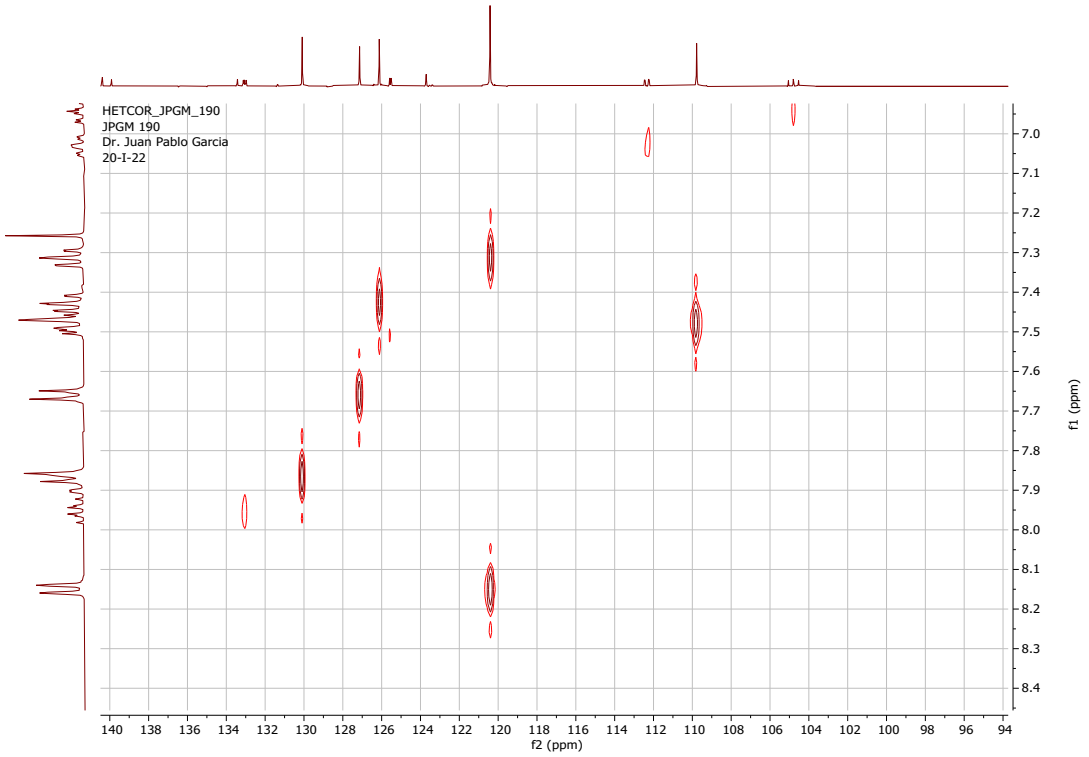
f1 (ppm)

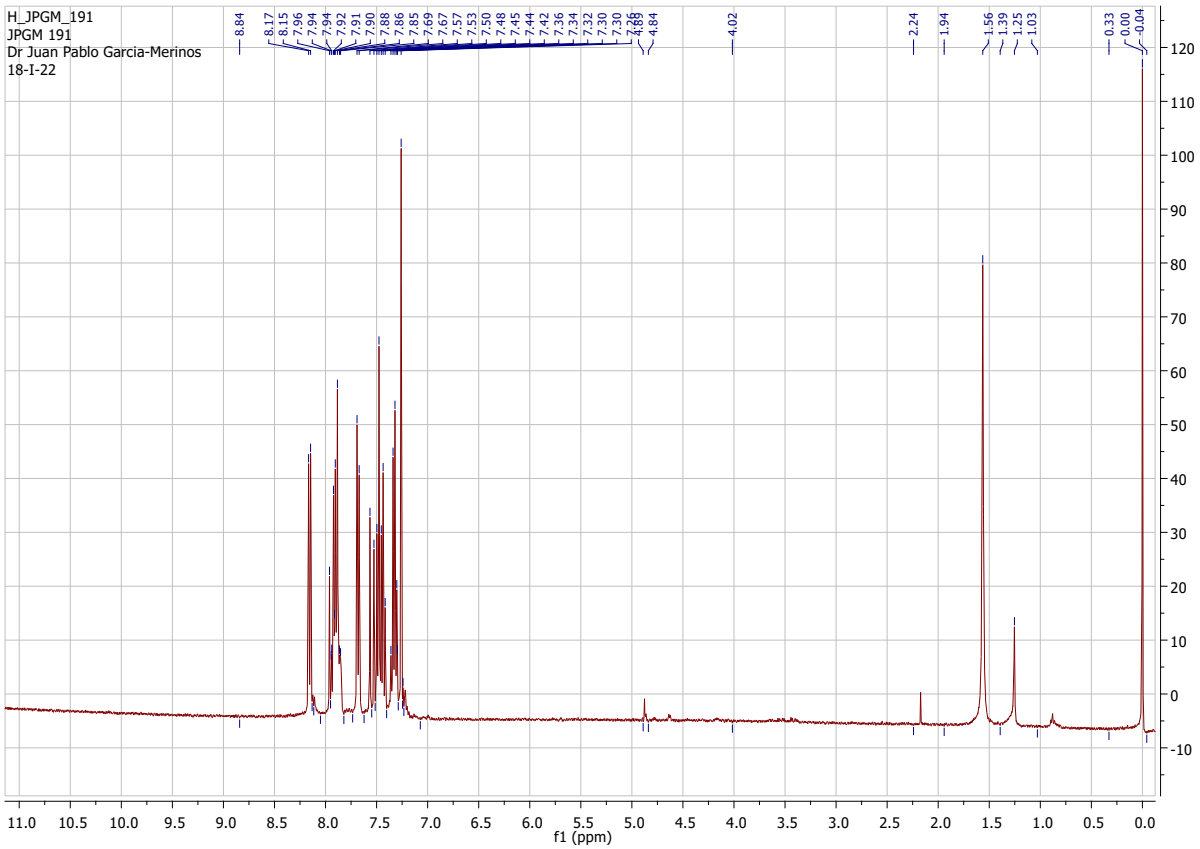
**Spectrum 2.** $^{13}$C-NMR ($CDCl_3$) spectrum of M1.



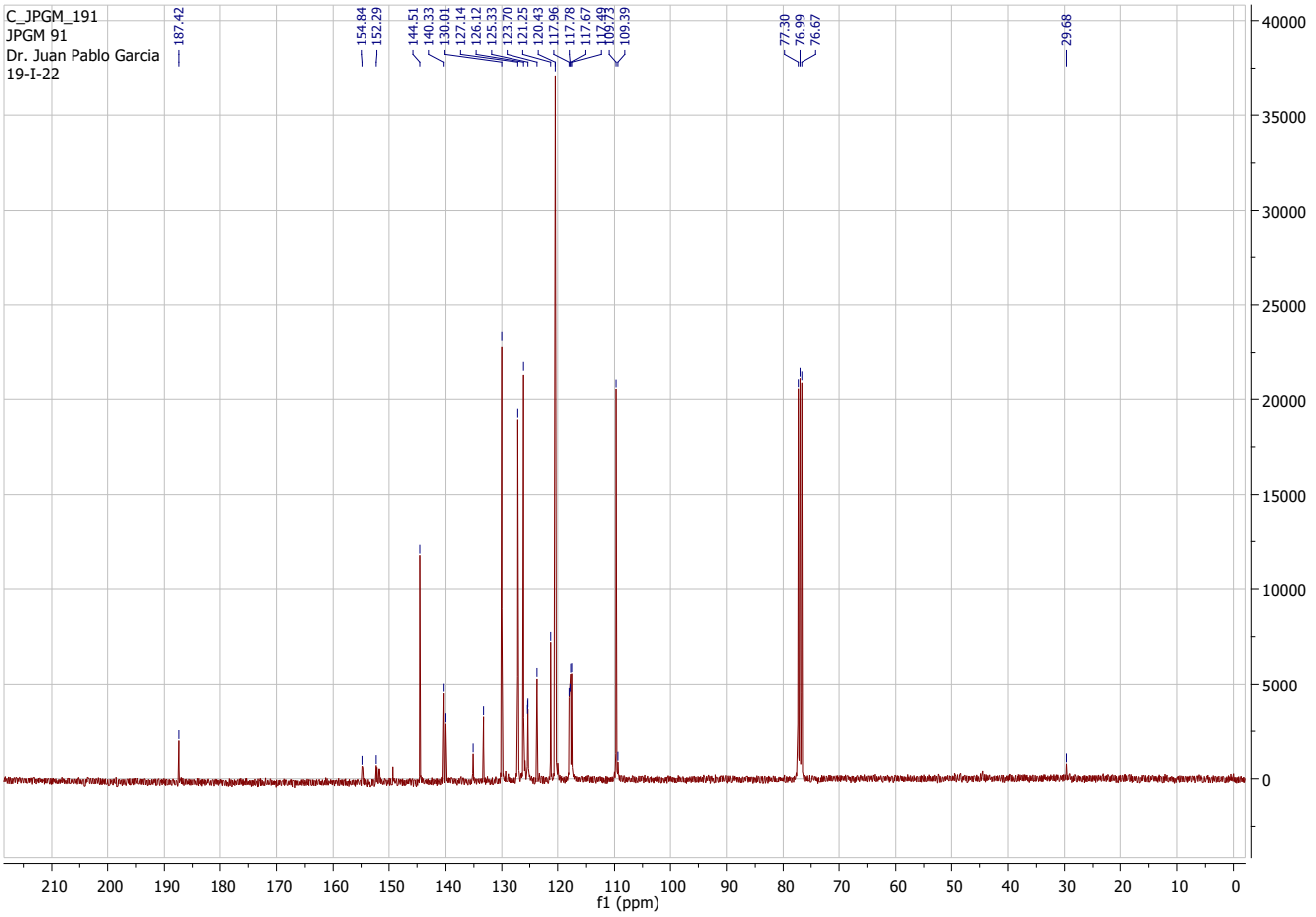

**Spectrum 3.** $^{1}$H -$^{1}$H COSY spectrum of M1.



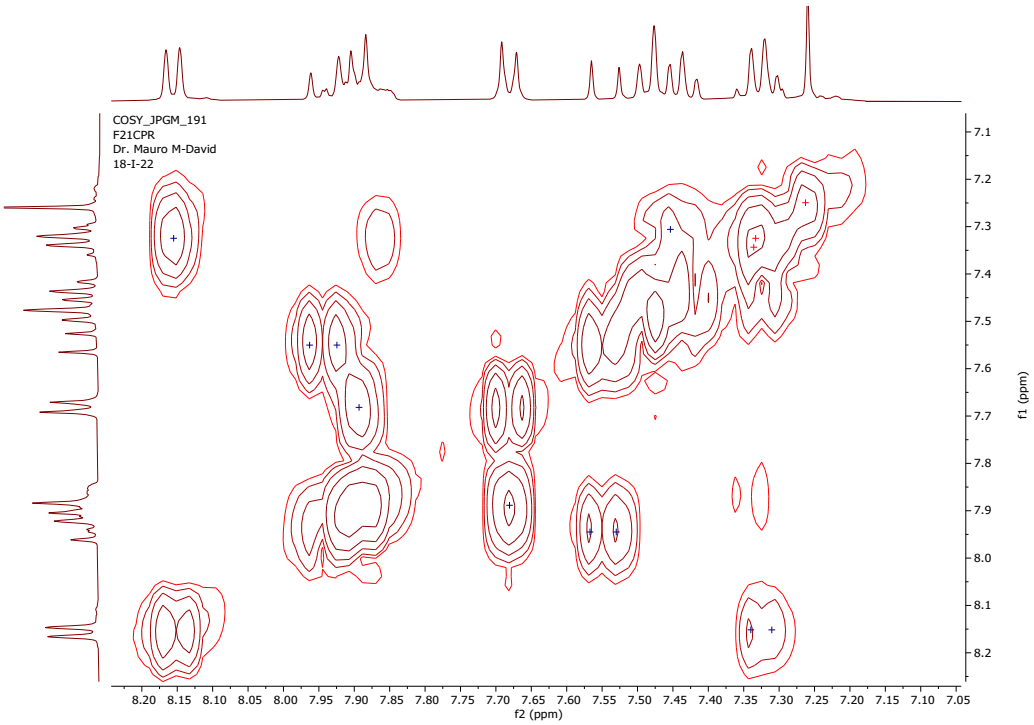

**Spectrum 4.** $^{1}H$ -$^{13}C$ HETCOR spectrum of M1.



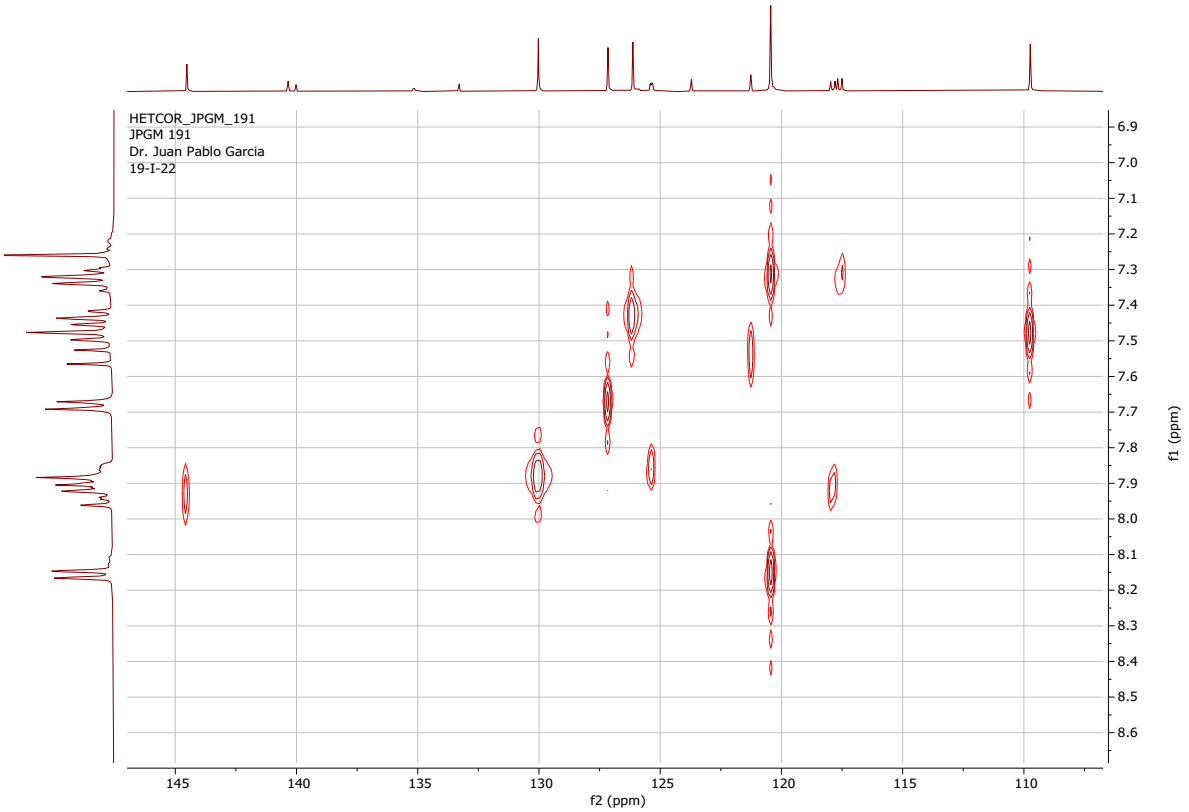

**Spectrum 5.** $^{1}$H-NMR ($CDCl_3$) spectrum of M2.



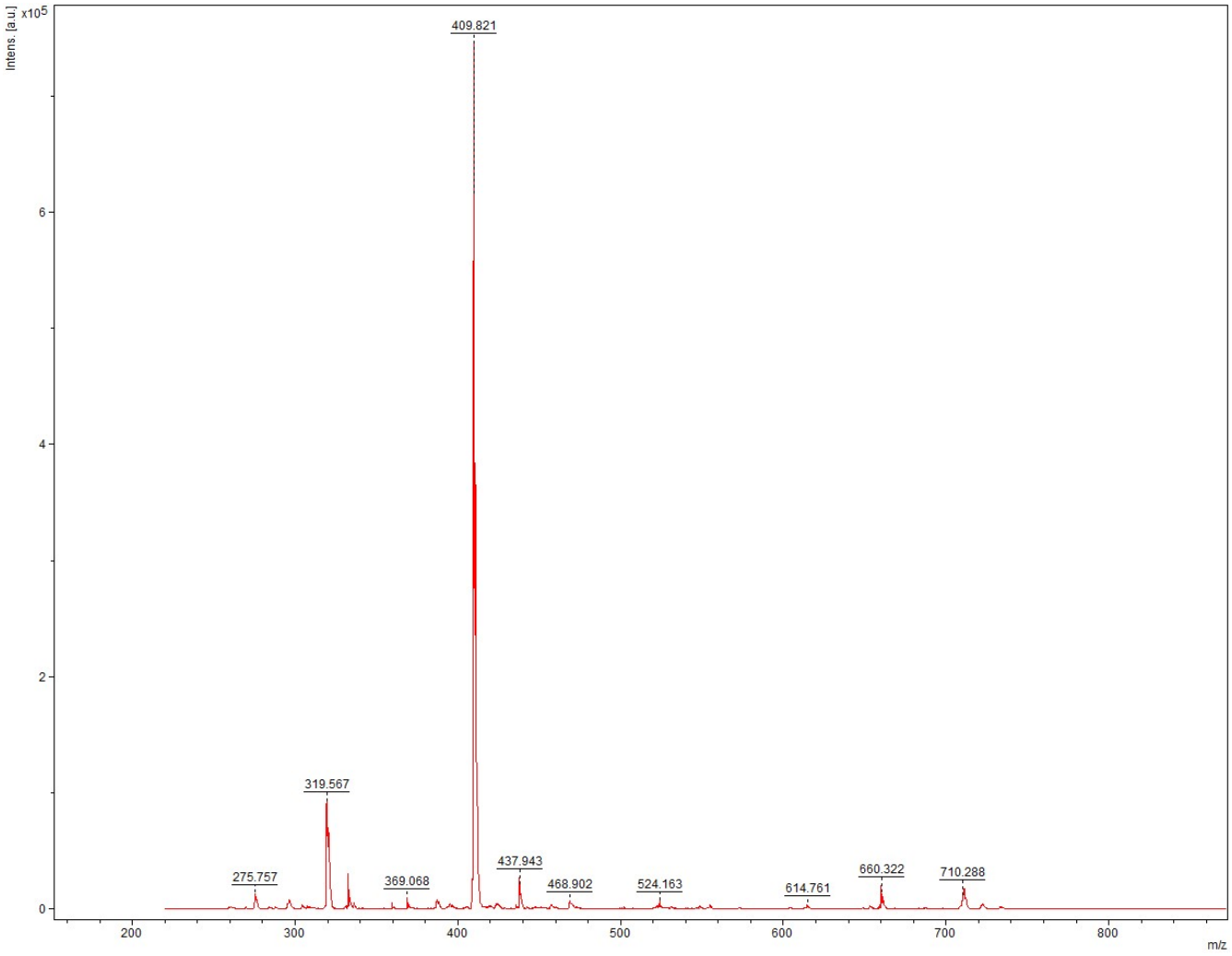

**Spectrum 6.** $^{13}$C-NMR ($CDCl_3$) spectrum of M2.



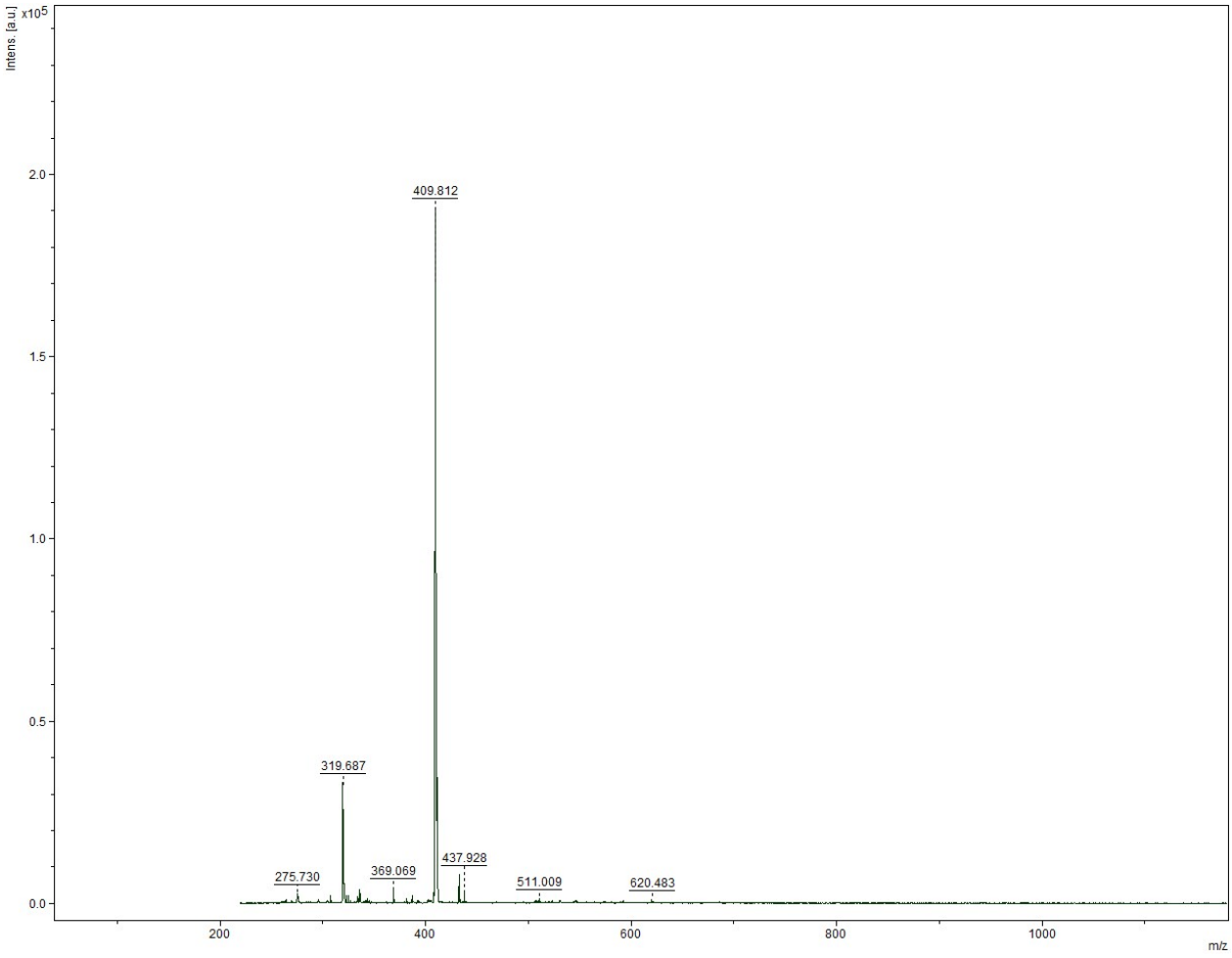

**Spectrum 7.** $^{1}H$ -$^{1}H$ COSY spectrum of M2.




**Spectrum 7.** $^{1}H$ -$^{13}C$ HETCOR spectrum of M2.




**Spectrum 8**. HRMS for M1




**Spectrum 8**. HRMS of M2

## Solvatochromism

Solutions at a concentration of $1\times10^{-4}$ M of **M1** and **M2** were prepared in: acetonitrile, methanol, ethanol, acetone, propanol, methylene chloride, THF, ethyl acetate, chloroform, chlorobenzene, ethyl acetate, ethyl ether, toluene, dioxane and hexane HPLC grade; its absorption spectrum and its emission spectrum were obtained. The interaction of the solvent in the photoluminescence was studied in terms of the Lippert-Mataga equation.

**Aggregation Induced Emission Enhancement**

In order to evaluate whether the molecules M1 and M2 exhibited the AIEE effect, a $1\times10^{-3}$ M solution in THF of M1 and M2 was prepared as stock solutions. Vials were numbered from 1 to 10, adding different ratios of THF-water to each one with 1 mL syringes, sonicating for 10 minutes, for later reading in the JENWAY 7315 Spectrophotometer and in the fluorescence spectrophotometer.

**Nanoparticles fabrication by microemulsión method**

The manufacture of M1 and M2 nanoparticles was carried out by the microemulsion method for fluorophores reported (2016). Three different concentrations (0.11, 0.22 and 0.44 g) of two different surfactants (Aerosol-OT and Triton X-100) were tested; the surfactant and 300 µL of 1-butanol were dissolved in THF-$H_2O$.

Then, 1.2 mL of the fluorophore dissolved in THF was added to a concentration of $1 \times 10^{-3}$ M. Half an hour later, 100 µL of pure triethoxyvinylsilane (VTES) were added to the system, stirring for 1 hour. Finally, the doped nanoparticles were precipitated by adding 20 µL of aminopropyltriethoxyslane (APTES) shaking for 20 hours and centrifuged at 1000 rpm for 10 minutes.

To remove excess surfactant, the suspension obtained was dialyzed with a 14 KDa cellulose membrane for 24 hours. Finally, to eliminate larger particles, the suspension was filtered with a 0.22 µm microfilter.

**Evaluation of cell staining capacity and study of cell metabolism**

Colon and breast cancer cell lines were purchased by ATCC microbiologics. For cellular authentication, a comprehensive analysis report interprets both karyotypically cancer cell lines, this includes an electropherogram supporting the allele calls at each locus, known reference profiling against the ATCC human STR database and a comprehensive interpretation of results, this done by the provider. For samples with human blood, statements that appropriate ethics committee approval and informed written consent of all participants were obtained by the Faculty of Chemical Sciences of the Autonomous University of Coahuila (Number protocol: P-FCQ-H-01-09-21-2). To obtain monocyte culture, a human blood sample was centrifuged for 30 min at 4000 rpm containing 2 mL of

ficol. Subsequently, the supernatant (plasma) was removed, and the cells deposited at the solid-liquid interface were extracted. Said cells were then deposited in a conical tube to be washed with PBS 1X, centrifuging them for 10 min and discarding the supernatant. After that, the extracted cells were transferred to a Falcon tube where RPMI culture medium was added in a ratio of 10.44 g per liter of solution and 20 µL of penicillin-streptomycin antibiotic. The cells were incubated at 37 °C, morphologically identified by light microscopy and counted in a Neubauer chamber to obtain cell cultures with a density of 30,000 cells/mL.

For fibroblast culture, they were extracted from a fragment of porcine skin of a recently slaughtered animal which was granted by the municipal slaughterhouse and following the NOM-062-ZOO-1999 recommendations. Porcine skin and subcutaneous fat were scraped and recovered to a mass of 15 g. Subsequently, triplicate washes were performed with 25 mL of sterile PBS 1X for 10 min, shaking with the help of a vortex. The tissue was then recovered and was minced with 100 mL of sterile PBS 1X. 45 mL of the mixture was placed in a Falcon tube and 5 mL of trypsin 1X, 500 µL of collagenase solution (14 units) and 10 µL of penicillin-streptomycin antibiotic were added for proteolytic degradation of extracellular matrix, and it was stirred for 1 h at 37 °C. Said medium was minced again to later be centrifuged for 5 min to rescue the cell button. Finally, to prepare the culture medium, the rescued cells were mixed with 1.044 g of DMEM culture medium (Dulbecco's Modified Eagle's Medium), 10 µL of antibiotic and adjusted to a final volume of 50 mL with sterile PBS 1X. The cells were incubated at 37 °C, morphologically identified by light microscopy and counted in a Neubauer chamber to obtain cell cultures with a density of 30,000 cells/mL.

Hemolysis test: For samples with human blood, statements that appropriate ethics committee approval and informed written consent of all participants were obtained by the Faculty of Chemical Sciences of the Autonomous University of Coahuila (Number protocol: P-FCQ-H-01-09-21-2). A tube of human blood was centrifuged at 3000 rpm, at a temperature of 5 °C for 15 minutes, then the supernatant was removed, and 3 washes were made with Alsever's solution. For the preparation of the erythrocyte solution, a 100 µL aliquot of centrifuged blood was taken and 10 mL of Alsever was added. Finally, they were kept frozen until the moment of use. In 1.5 mL Eppendorf tubes, 150 µL of each type NPs suspension and 112 µL of erythrocyte solution were placed; subsequently, the volume of each tube was made up with Alsever solution. They were incubated for 1 h at 37 °C with orbital shaking at 100 rpm. The tubes were then centrifuged for 1 minute at 1000 rpm. Aliquots of 200 µL were taken and added to a microplate. The absorbance of the samples was measured at 415 nm and the percentage of hemolysis was measured with the equation 1 (eq. 1):

$$Hemolysis\ (\%) = \left(\frac{A_h - A_{Cn}}{A_{Cp} - A_{Cn}}\right) * 100 \quad (eq.\ 1)$$

Where: $A_h$, $A_{Cn}$ y $A_{Cp}$ are the absorbances for samples, negative control (Alsever's solution) and positive control (water), respectively.

Cell viability: The metabolic activity of human monocytes, porcine dermis fibroblasts and human colon and breast cancer cells being in contact with each type NPs suspension was evaluated by the MTT assay. The cells were cultured in RPMI (mononuclear cells) or DMEM (fibroblasts and cancer cells) medium supplemented with 10 wt.% fetal bovine serum (FBS, Corning) and antibiotics (Sigma-Aldrich) in a humidified atmosphere containing 5% $CO_2$ and 95% air at 37°C. For this, 150 µL of cell suspension (30 000 cells/mL) were seeded over 100 µL of each NPs suspension in polystyrene culture plates and incubated by 24 and 72 h at 37 °C. PBS-1X was used as the positive control. At the evaluation time, 15 µL of 3-(4,5-dimetilthiazol-2-yl)-2,5-diphenyltetrazolium) solution (1 wt.% in sterilized PBS-1X) was added and incubated for 2 h more. After that, 2 mL of propan-2-ol was added to dissolve the resulting blue formazan crystals. Aliquots of 200 µL were taken from the liquid medium and the absorbance was measured at 560 nm (ThermoScientific MultiSkan Sky UV-Vis spectrophotometer). Cell viability was calculated using Equation 2 (eq. 2):

$$\text{Cell viability (\%)} = (A_{sample}/A_{control}) * 100 \quad \text{(eq. 2)}$$

Where $A_{sample}$ and $A_{control}$ represent the absorbances for each sample or formulation and PBS-1X, respectively. Values less than 60% cell viability are considered cytotoxic.

Cell proliferation: In this assay, there were observed stained cells with the live/dead fluorescent reagent containing calcein-AM and ethidium homodimer, growing in contact with each type of NPs suspension. For this, 1 mL of cell culture (30 000 cell) was mixed with 1 mL of each type of NPs suspension and incubated at 37 °C for 48 h. After incubation, cells were stained with the live/dead fluorescent reagent. PBS-1X was used as control for comparison. Stained cells were transferred to a slide and were inspected with a VELAB VE-146YT fluorescence microscope using an objective with 40 magnifications (40X). Excitation of samples was conducted with a green LASER (λ=532 nm, for ethidium homodimer and λ=427 nm, for calcein). To appreciate the effect of anticancer phototherapy, samples with cancer cell lines were exposed to 230 nm UV light for 1 h.

Staining of the nanoparticles with chalcones for induced cell selectivity: 1 mL of each type of NPs suspension was stained using 300 µL of rhodamine-b (300 ppm), the mixture was vortexed for 5 minutes and incubated at 37 °C for 3 h; subsequently, the NPs were washed 3 times with sterile PBS 1X to remove excess rhodamine-b. Subsequently, the NPs stained with rhodamine were dispersed in 1 mL of cell suspension of cancer cell lines (colon and breast) and incubated for 24 h at 37 °C to achieve internalization of the stained NPs in the cells. The cells were centrifuged and washed with sterile PBS 1X and observed under a fluorescence microscope (VELAB VE-146YT), using red laser (λ=532 nm) for rhodamine excitation, in order to appreciate the biomarker effect.

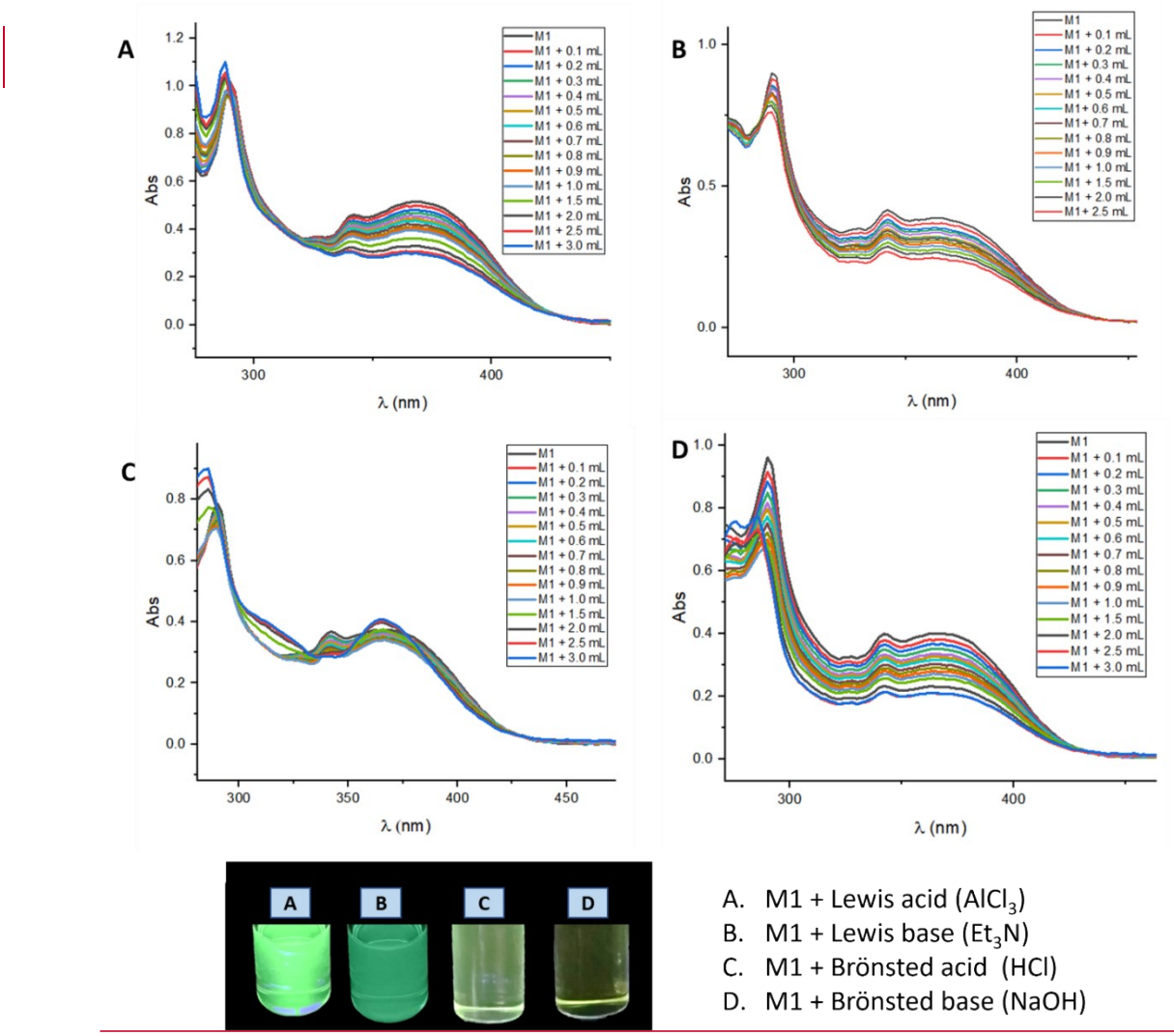



**Figure S1**. Absorption spectra of M1 titrations with Lewis and Brönsted acids and bases.

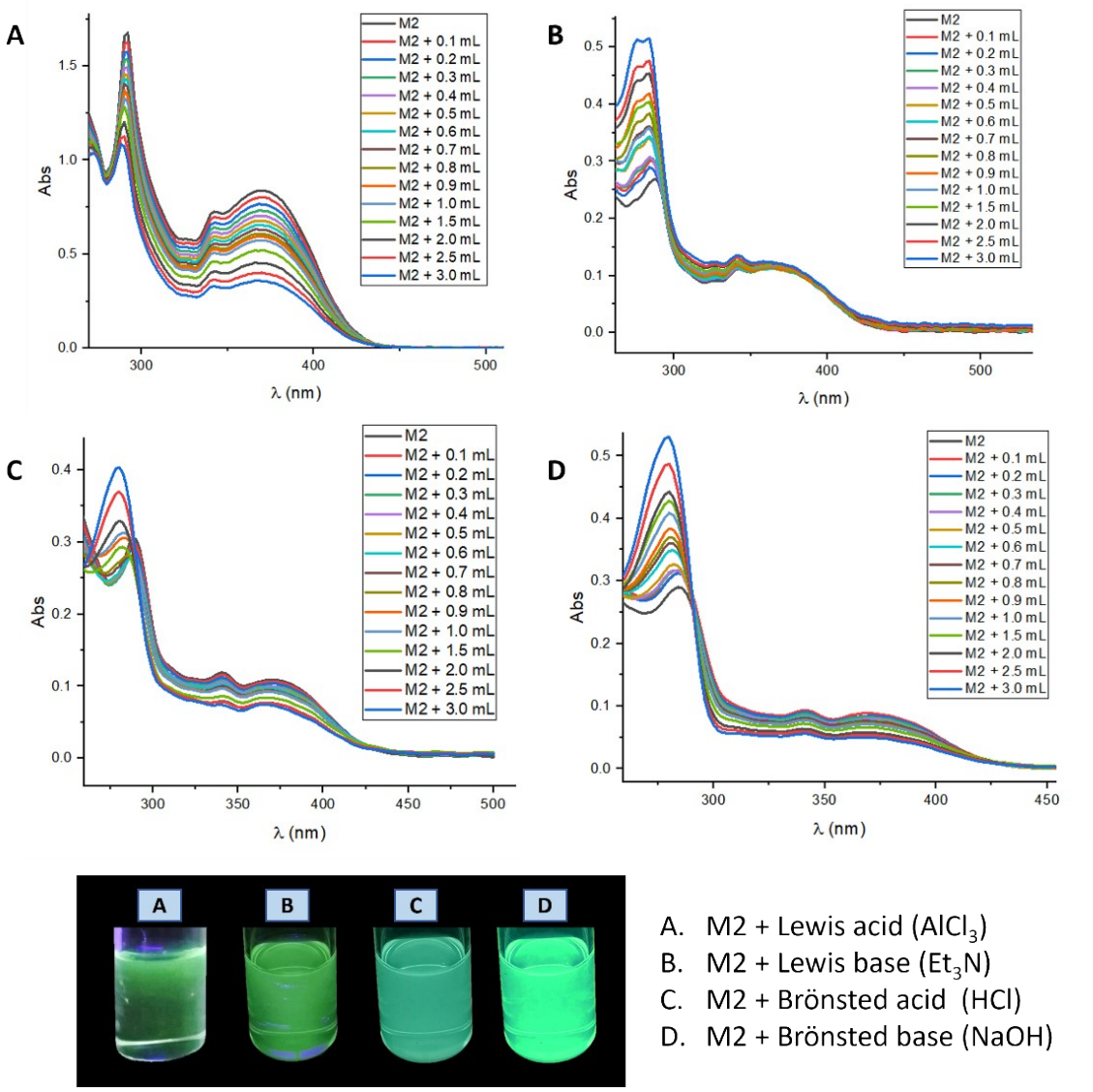
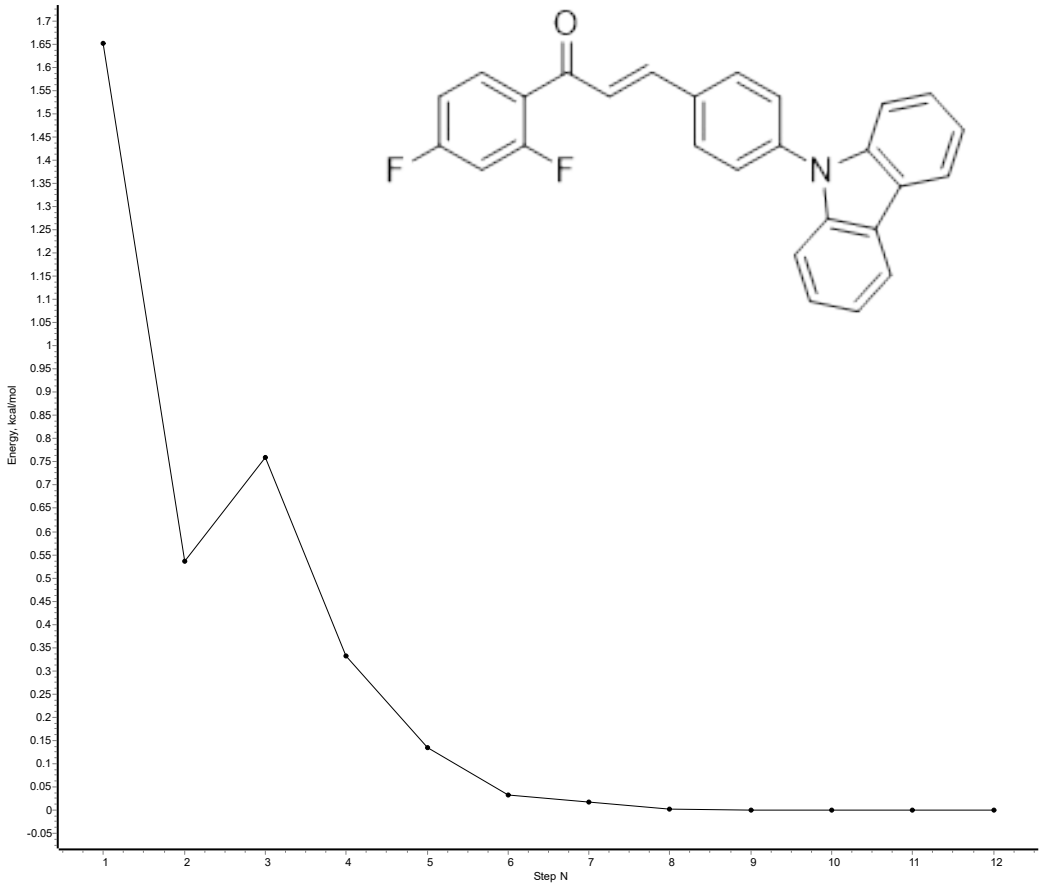



**Figure S2**. Absorption spectra of M2 titrations with Lewis and Brönsted acids and bases.

**Computational modeling**

Molecular modeling was performed in the GaussView program. All calculations were carried out in GAUSSIAN 09, using the B3Lyp functional. All CHON atoms were represented by the bases 6-31G(d,). The energies were calculated in the gas phase until its structural optimization at 298.15 K. A frequency analysis of all the structures was carried out during the optimization to rule out that the structure was not a local minimum.

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| 477.4919 | 1.0712 |
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| 1350.1734 | 2.4505 |

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| 3220.8562 | 7.5648 |
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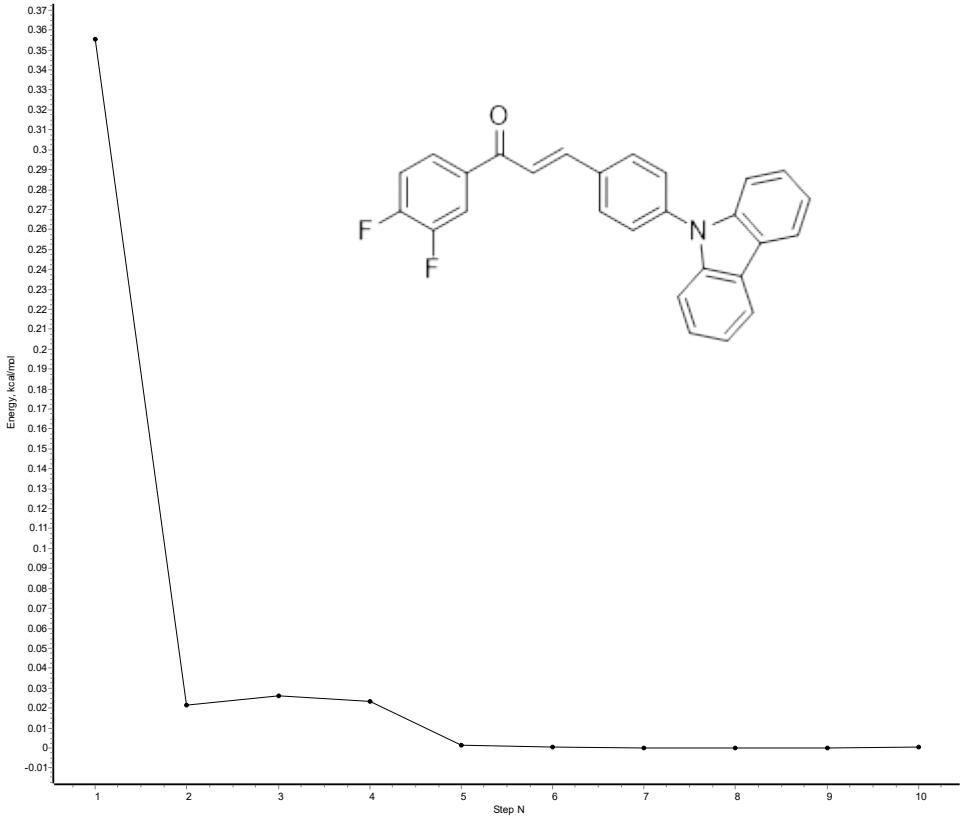


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| 104.1941 | 0.2535 |
| 119.1143 | 1.0153 |
| 122.0441 | 2.1365 |
| 137.0168 | 4.0409 |
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| 166.969 | 8.6971 |
| 200.0101 | 0.6566 |
| 215.8994 | 1.0093 |
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| | |
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| 294.2872 | 3.9284 |
| 297.0411 | 0.1687 |
| 325.8583 | 3.6559 |
| 355.4782 | 0.4431 |
| 370.8006 | 1.983 |
| 389.3807 | 6.4919 |
| 421.4469 | 8.1859 |
| 428.3826 | 5.3208 |
| 436.5167 | 3.6673 |
| 439.7121 | 7.0195 |
| 448.5152 | 1.8311 |
| 461.069 | 10.2056 |
| 468.43 | 0.6977 |
| 514.9445 | 7.0964 |
| 524.3195 | 3.9556 |
| 536.4549 | 6.257 |
| 569.4636 | 12.9281 |
| 577.2888 | 2.4948 |
| 582.7794 | 0.53 |
| 590.3008 | 17.4122 |
| 619.2265 | 16.9839 |
| 627.8097 | 0.6075 |
| 637.2014 | 7.9574 |
| 658.6282 | 5.9554 |
| 659.4842 | 7.2355 |
| 674.4915 | 0.6795 |
| 712.7986 | 7.0384 |
| 717.6316 | 9.5221 |
| 733.53 | 0.1866 |
| 740.4368 | 17.231 |
| 755.9252 | 4.8684 |
| 759.9228 | 22.2543 |
| 764.9724 | 79.2732 |
| 774.4441 | 0.5649 |
| 789.7073 | 2.8262 |
| 796.9529 | 35.2827 |
| 840.683 | 35.5871 |
| 845.1319 | 2.8155 |
| 852.4576 | 18.0736 |
| 867.9055 | 1.7652 |

| | |
|---|---|
| 869.4447 | 4.2808 |
| 873.3544 | 0.9895 |
| 901.811 | 29.0833 |
| 907.6961 | 15.3793 |
| 931.9458 | 1.2528 |
| 932.4698 | 3.8026 |
| 933.1708 | 1.0465 |
| 942.2664 | 5.9823 |
| 955.5046 | 4.5426 |
| 966.0265 | 5.5298 |
| 968.0558 | 1.716 |
| 970.6563 | 0.5355 |
| 974.4219 | 0.5791 |
| 977.3616 | 1.0297 |
| 1022.0685 | 2.5952 |
| 1034.0579 | 42.302 |
| 1036.3634 | 1.3298 |
| 1051.6301 | 2.4022 |
| 1059.604 | 6.9641 |
| 1090.1169 | 38.4757 |
| 1131.7941 | 10.9705 |
| 1146.1482 | 99.3958 |
| 1149.2163 | 19.5007 |
| 1152.0196 | 6.7429 |
| 1186.5168 | 4.2933 |
| 1193.7562 | 0.0845 |
| 1203.865 | 64.2615 |
| 1221.2002 | 96.3305 |
| 1227.0693 | 169.087 |
| 1246.6279 | 10.4956 |
| 1256.0029 | 82.1048 |
| 1266.2975 | 35.3982 |
| 1270.1352 | 17.6313 |
| 1299.0805 | 4.6311 |
| 1309.3739 | 62.8985 |
| 1330.3587 | 13.3447 |
| 1338.1936 | 277.4556 |
| 1344.2879 | 360.5067 |
| 1350.1986 | 2.0508 |
| 1357.7438 | 22.1682 |
| 1358.4701 | 8.4358 |

| | |
|---|---|
| 1379.8754 | 25.464 |
| 1386.0466 | 129.22 |
| 1391.1347 | 2.2549 |
| 1402.4258 | 100.8188 |
| 1459.1337 | 25.1572 |
| 1467.1324 | 35.5555 |
| 1491.8956 | 268.7536 |
| 1503.5347 | 29.8359 |
| 1524.1509 | 32.2841 |
| 1535.5763 | 14.2392 |
| 1562.9811 | 186.2691 |
| 1564.3713 | 123.5225 |
| 1611.1129 | 18.0549 |
| 1632.641 | 0.052 |
| 1634.7858 | 2.3902 |
| 1646.897 | 85.2156 |
| 1653.8957 | 21.7394 |
| 1657.7731 | 318.3324 |
| 1664.2342 | 44.3074 |
| 1675.4364 | 0.4722 |
| 1688.5589 | 68.2219 |
| 1727.3149 | 258.0494 |
| 1750.52030 | 0.047 |
| 3176.6582 | 5.2872 |
| 3185.4262 | 0.308 |
| 3186.5235 | 1.3553 |
| 3188.9135 | 10.6492 |
| 3192.6049 | 19.0881 |
| 3194.0205 | 13.0988 |
| 3195.4915 | 7.9884 |
| 3206.3036 | 9.9697 |
| 3208.7222 | 34.0528 |
| 3209.6124 | 49.4861 |
| 3218.5613 | 10.1424 |
| 3220.6472 | 7.524 |
| 3221.0608 | 2.3399 |
| 3222.9911 | 9.8311 |
| 3224.4491 | 4.7303 |
| 3236.4341 | 1.2918 |
| 3236.6705 | 2.4362 |