Supporting information for

CHARACTERIZATION OF AMINE STABILIZED CdSe/ZnS CORE-SHELL QUANTUM DOTS BY MEANS OF TRIARYLPYRYLIUM DYES

Alicia Beltrán, M. Isabel Burguete, Santiago V. Luis,* Francisco Galindo,*

Universitat Jaume I, Departamento de Química Inorgánica y Orgánica, Avda. Sos Baynat ,s/n 12071, Castellón de la Plana, Spain

Email: luiss@uji.es, francisco.galindo@uji.es

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Experimental section

Materials and instruments

All commercially available reagents and solvents were used as received. Hexadecylamine (HDA), compound **1c** and HDA-stabilized QDs (Lumidot, emissive at 480 nm) in toluene solution (5mg/mL) were purchased from Aldrich.

Fourier Transform Infrared (FT-IR) spectra were acquired using a FT-IR-6200 type A JASCO spectrometer, with 4 cm^{-1} resolution and 50 scans accumulation. ^{1}H and ^{13}C NMR spectra were recorded on a Varian INOVA 500 MHz spectrometer (500 MHz for ^{1}H and 125 MHz for ^{13}C). A Q-TOF Premier mass spectrometer with an electrospray source (Waters, Manchester, UK) has been used. UV–Vis absorption spectra were recorded in a Hewlett–Packard 8453 apparatus. Steady-state fluorescence spectra were recorded in a Spex Fluorog 3-11 equipped with a 450 W xenon lamp. Time-resolved fluorescence was recorded using an IBH-5000U apparatus using pulsed 372 nm and 464 nm NanoLEDs as excitation sources. Compound **2d** was used as a reference for the determination of emission quantum yields (reported value in acetonitrile: 0.97).[1]

Synthetic procedures and characterizations

Compound 1a. 2 equivalents of $BF_3 \cdot OEt_2$ (3.36 ml; 26.64 mmol) were added to a solution of 4-formyl benzoic acid (2 g; 13.32 mmol) and 2 equivalents of acetophenone (3.12 ml; 26.64 mmol) in anhydrous toluene. The clear solution was refluxed for 2 h. After cooling to room temperature, acetone was added and the solution was poured into excess ether (200 ml).

(1231 mg, 21%).IR (ATR)(cm^{-1}) 3201, 3109, 1711, 1619, 1493; ^{1}H NMR (500 MHz, DMSO-d_6) δ(ppm) 9.20 (s, 2H), 8.66 (d, J = 11.7 Hz, 2H), 8.59 (d, J = 7.7 Hz, 4H), 8.24 (d, J = 9.9 Hz, 2H), 7.88 (t, J = 7.3 Hz, 2H), 7.80 (t, J = 7.6 Hz, 4H);^{13}C NMR (125 MHz, DMSO-d_6) δ(ppm) 171.0, 166.8, 164.5, 136.6, 136.3, 135.7, 130.6, 130.4, 129.5, 129.4, 129.2, 116.4; HRMS(ESI-TOF)$^+$ calculated for $C_{24}H_{17}O_3^+$ (M^+)(m/z): 353,1178; experimental (M^+)(m/z): 353,1169

Compound 1b. 2 equivalents of $BF_3 \cdot OEt_2$ (1.36 ml; 10.70 mmol) were added to a solution of 4-bromobenzaldehyde (1 g; 5.35 mmol) and 2 equivalents of acetophenone (1.26 ml; 10.70 mmol) in anhydrous toluene. The clear solution was refluxed for 2 h. After cooling to room temperature, acetone was added and the solution was poured into excess ether (200 ml).

(306 mg, 12%).IR (ATR)(cm^{-1}): 3076, 1619, 1579, 1496; ^{1}H NMR (500 MHz, DMSO-d_6) δ(ppm) 9.13 (s, 2H), 8.57 (d, J = 7.6 Hz, 4H), 8.52 (d, J = 8.3 Hz, 2H), 7.97 (dd, J = 17.5, 7.4 Hz, 2H), 7.88 (dd, J = 23.7, 16.7 Hz, 2H), 7.77 (dd, J = 22.4, 15.1 Hz, 4H);^{13}C NMR (125 MHz, DMSO-d_6) δ(ppm) 170.7, 164.3, 135.6, 133.4, 132.2, 132.0, 130.4, 130.4, 129.5, 129.3, 115.5; HRMS(ESI-TOF)$^+$ calculated for $C_{23}H_{16}BrO^+$ (M^+)(m/z): 387.0385; experimental (M^+)(m/z): 387.0386

Compound 1d. 2 equivalents of $BF_3 \cdot OEt_2$ (0.953 ml; 7.52 mmol) were added to a solution of 4-metoxybenzaldehyde (0.522 g; 3.76 mmol) and 2 equivalents of acetophenone (0.886 ml; 7.52 mmol) in anhydrous toluene. The clear solution was refluxed for 2 h. After cooling to room temperature, acetone was added and the solution was poured into excess ether (200 ml).

[1] G. Haucke, P. Czerney, F. Cebulla, *Ber. Bunsenges. Phys. Chem.* **1992**, 96 880

(722 mg, 45%).IR (ATR)(cm^{-1}): 2942, 1591, 1489, 1453; ^{1}H NMR (500 MHz, CH_3CN-d_3) δ(ppm) 8.62 (s, 2H), 8.40 (d, 6H), 7.86 (m, 2H), 7.78 (t, J = 7.5 Hz, 4H), 7.32 (d, J = 12.1 Hz, 2H), 3.99 (s, 3H);^{13}C NMR (125 MHz, CH_3CN-d_3) δ(ppm) 169.7, 166.7, 164.5, 134.9, 132.6, 129.9, 129.2, 128.4, 124.5, 115.9, 113.6, 56.1; HRMS(ESI-TOF)$^+$ calculated for $C_{24}H_{19}O_2^+$ (M^+)(m/z): 339.1385; experimental (M^+)(m/z): 339.1387

Compound 2a. 2 equivalents of $BF_3{\cdot}OEt_2$ (1.70 mL, 13.32 mmol) were added to a solution of 4-formyl benzoic acid (1 g; 6.66 mmol) and 2 equivalents of 4-metoxyacetophenone (2 g; 13.32 mmol) in anhydrous toluene. The clear solution was refluxed for 2 h. After cooling to room temperature, acetone was added and the solution was poured into excess ether (200 ml).

(670 mg, 20%).IR (ATR)(cm^{-1}): 3124, 3012, 1680, 1600, 1572, 1488; ^{1}H NMR (500 MHz, DMSO-d_6) δ(ppm) 8.90 (s, 2H), 8.54 (dd, J = 15.3, 8.3 Hz, 6H), 8.20 (d, J = 7.6 Hz, 2H), 7.29 (d, J = 8.3 Hz, 4H), 3.94 (s, 6H); ^{13}C NMR (125 MHz, DMSO-d_6) δ(ppm) 187.7, 167.3, 163.9, 142.1, 139.4, 132.4, 131.5, 130.7, 130.1, 129.2, 124.7, 114.5, 56.1, 56.0; HRMS(ESI-TOF)$^+$ calculated for $C_{26}H_{21}O_5^+$ (M^+)(m/z): 413.1389; experimental (M^+)(m/z): 413.1380

Compound 2b. 2 equivalents of $BF_3{\cdot}OEt_2$ (1.6 ml; 10.70 mmol) were added to a solution of 4-bromobenzaldehyde (1 g; 5.35 mmol) and 2 equivalents of 4-metoxyacetophenone (1.61 g, 10.70 mmol) in anhydrous toluene. The clear solution was refluxed for 2 h. After cooling to room temperature, acetone was added and the solution was poured into excess ether (200 ml).

(1020 mg, 36%).IR (ATR)(cm^{-1}): 3074, 1592, 1487, 1451; ^{1}H NMR (500 MHz, DMSO-d_6) δ(ppm) 8.86 (s, 2H), 8.48 (d, J = 13.3 Hz, 4H), 8.43 (d, J = 8.4 Hz, 2H), 7.98 (dd, J = 21.8, 8.7 Hz, 2H), 7.27 (d, J = 8.8 Hz, 4H), 3.96 (s, 6H); ^{13}C NMR (125 MHz, DMSO-d_6) δ(ppm) 169.5, 165.4, 162.4, 133.1, 132.3, 131.8, 131.5, 129.5, 121.8, 115.9, 113.1, 56.1; HRMS(ESI-TOF)$^+$ calculated for $C_{25}H_{20}BrO_3^+$ (M^+)(m/z): 447.0596; experimental (M^+)(m/z): 447.0594

Compound 2c. 2 equivalents of $BF_3{\cdot}OEt_2$ (1.18 ml; 9.32 mmol) were added to a solution of benzaldehyde (0.5 g; 4.66 mmol) and 2 equivalents of 4-metoxyacetophenone (1.41 g; 9.32 mmol) in anhydrous toluene. The clear solution was refluxed for 2 h. After cooling to room temperature, acetone was added and the solution was poured into excess ether (200 ml).

(250 mg, 12%).IR (ATR)(cm^{-1}): 3077, 2940, 1600, 1491, 1457; ^{1}H NMR (500 MHz, DMSO-d_6) δ(ppm) 8.83 (s, 2H), 8.48 (t, J = 8.8 Hz, 6H), 7.80 (t, J = 6.8 Hz, 1H), 7.73 (t, J = 7.1 Hz, 2H), 7.26 (d, J = 8.3 Hz, 4H), 3.90 (s, 6H); ^{13}C NMR (125 MHz, DMSO-d_6) δ(ppm) 169.4, 165.3, 163.7, 135.0, 133.2, 131.5, 130.1, 130.0, 121.8, 115.9, 113.1, 56.6, 56.5; HRMS(ESI-TOF)$^+$ calculated for $C_{25}H_{21}O_3^+$ (M^+)(m/z): 369.1491; experimental (M^+)(m/z): 369.1494

Compound 2d. 2 equivalents of $BF_3{\cdot}OEt_2$ (0.953 ml; 7.52 mmol) were added to a solution of 4-metoxybenzaldehyde (0.522 g; 3.76 mmol) and 2 equivalents of 4-metoxyacetophenone (1.41g; 7.52 mmol) in anhydrous toluene. The clear solution was refluxed for 2 h. After cooling to room temperature, acetone was added and the solution was poured into excess ether (200 ml).

(550 mg, 30%).IR (ATR)(cm^{-1}): 2942, 1594, 1488, 1460; ^{1}H NMR (500 MHz, CH_3CN-d_3) δ(ppm) 8.57 – 7.91 (m, 7H), 7.45 – 7.08 (m, 7H), 3.97 (s, 9H); ^{13}C NMR (125 MHz, CH_3CN-d_3) δ(ppm) 168.6, 165.3, 162.7, 131.8, 130.7, 130.6, 124.7, 121.3, 115.6, 115.5, 111.2, 55.9; HRMS(ESI-TOF)$^+$ calculated for $C_{26}H_{23}O_4^+$ (M^+)(m/z): 399.1596; experimental (M^+)(m/z): 399.1599

Fluorometric and absorption studies

Measurements with QDs. Compounds **1a-d** and **2a-d** were dissolved in acetonitrile to obtain 10 μM solutions. These solutions were titrated by adding increasing volumes of the commercial solution of QDs. The fluorescence intensities of the resulting solution were measured after 2 minutes of reaction, with excitation at the corresponding absorption maxima of each compound.

Measurements with hexadecylamine. Compounds **1a-d** and **2a-d** were dissolved in acetonitrile to obtain 10 μM solutions. These solutions were titrated by adding increasing volumes of the stock solution of hexadecylamine in toluene. The fluorescence intensities of the resulting solution were measured after 2 minutes of reaction, with excitation at the corresponding absorption maxima of each compound.

Quantitative determination. Fluorescence tests were performed using pyrylium salts **1a-d**. Increasing amounts of these compounds were added to 5 μL of commercial solution of quantum dots in 1 mL of acetonitrile. The fluorescence intensities of the resulting solution were measured after 2 minutes of reaction, with excitation at the corresponding absorption maxima of each compound.

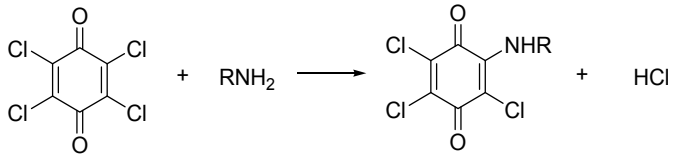
HRMS-QTOF measurements

Two types of samples were prepared. One was prepared using 1 mL of 10 μM solution of pyrylium salts **1a-d** and 5 μL of commercial solution of QDs, and the control sample was prepared using 1 equivalent of hexadecylamine and pyrylium salts **1a-d**.

Analysis using chloranil.[2]

Chloranil reacts with a variety of primary, secondary and tertiary, aliphatic, and aromatic amines at room temperature. Here, we use this procedure to confirm the usefulness of the new method presented and based on pyrylium salts.

800 μL of propanol and 200 μL of a 5% solution of chloranil in 1,4-dioxane were mixed. Increasing amounts of hexadecylamine stock solution were added to create a calibration curve. After each addition, the sample was fully mixed and then the increase in absorbance with time was measured by UV-vis spectrophotometry. The spectra were registered after 10 minutes of reaction. For QDs, 5 μL of commercial solution of nanoparticles were added to the chloranil stock and the UV-vis absorption spectrum was recorded after 10 minutes. This experiment was repeated 10 times to calculate standard deviation of this method.



Scheme 1. Reaction of primary amines with chloranil

[2] (a) R.E. Smith, W.R. Davis, *Anal.Chem.*, **1984**, 56, 2345-2349,(b) P.C. Dwlvedl, A.K. Banga, *J.Phys. Chem.* **1981**, 56, 2345-2349

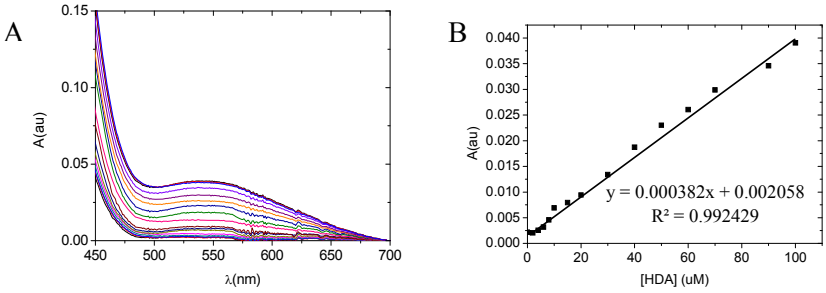


Figure S1 A) Absorption spectra obtained by adding incrreasing amounts of hexadecylamine (from a 1 mM stock solution in toluene) to a chloranil solution (1,4-dioxane and propanol). B) Calibration curve (λ_{abs}=540 nm).

NMR, FTIR,HRMS spectra
Compound 1a

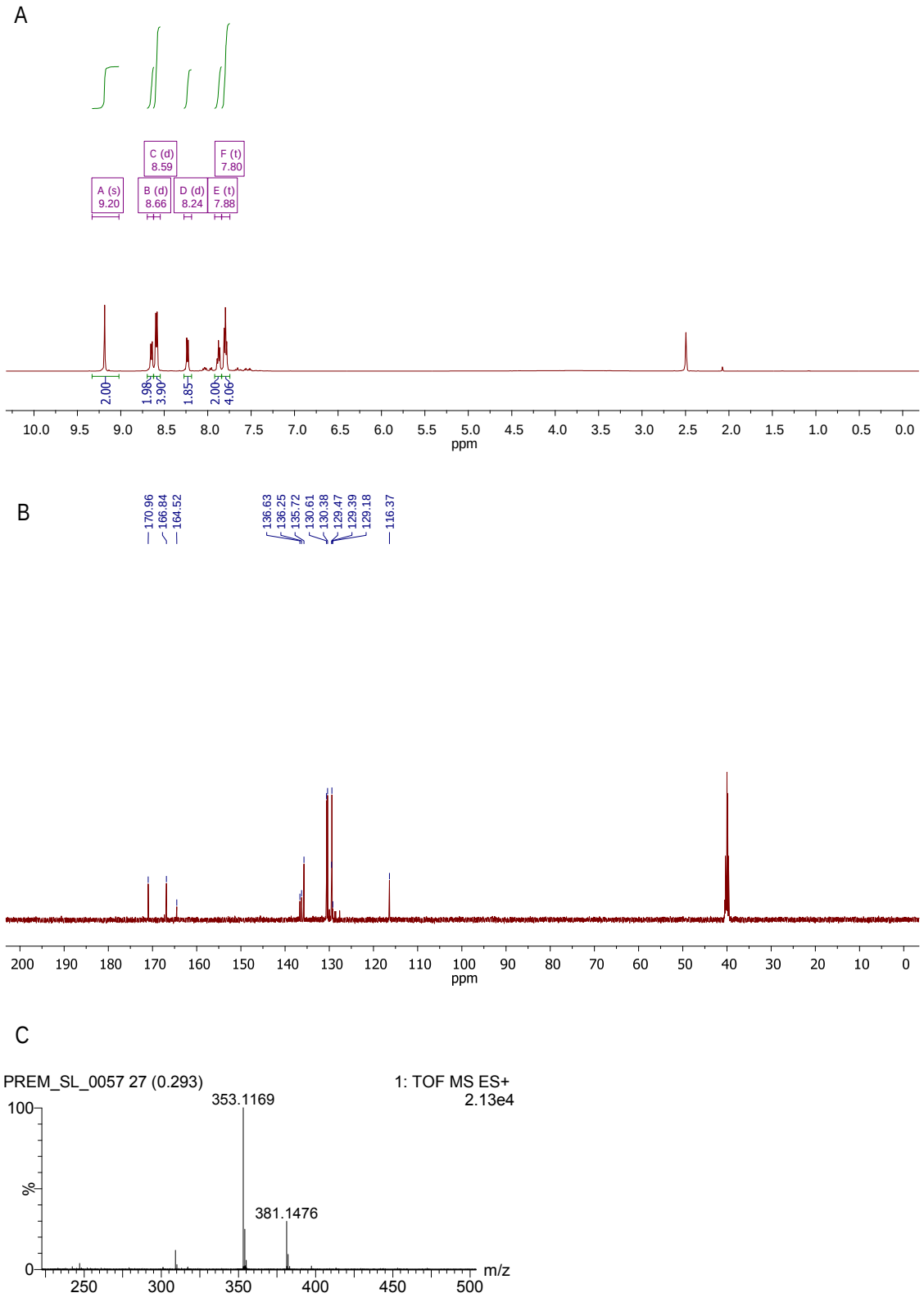


Figure S2. A) ^{1}H NMR (DMSO-d_6) spectra of compound **1a**; B) ^{13}C NMR (DMSO-d_6) spectra of compound **1a**; C) HRMS spectra of compound **1a**.

Compound 1b

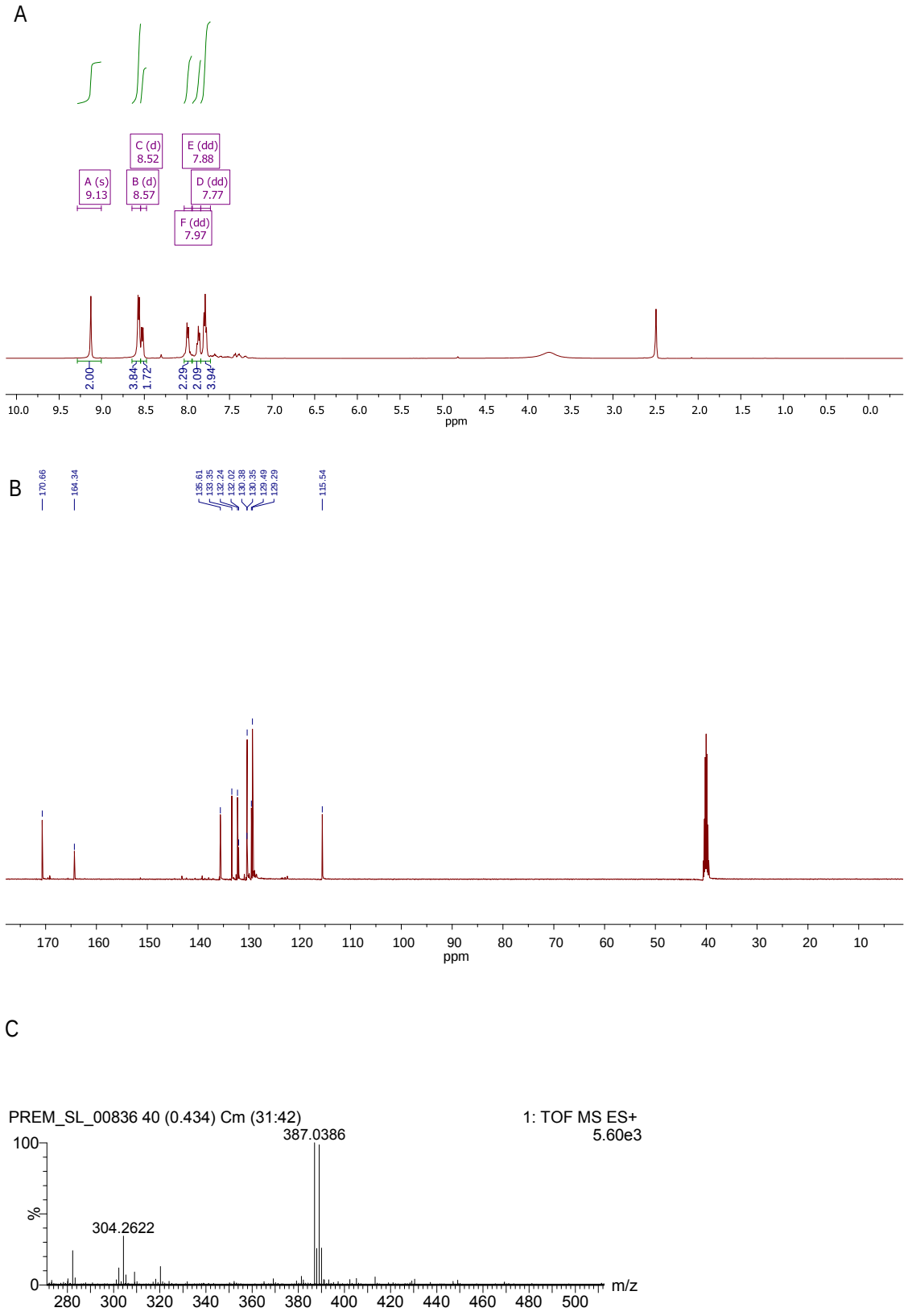


Figure S3. A) ^{1}H NMR (DMSO-d_6) spectra of compound **1b**; B) ^{13}C NMR (DMSO-d_6) spectra of compound **1b**; C) HRMS spectra of compound **1b**.

Compound 1c

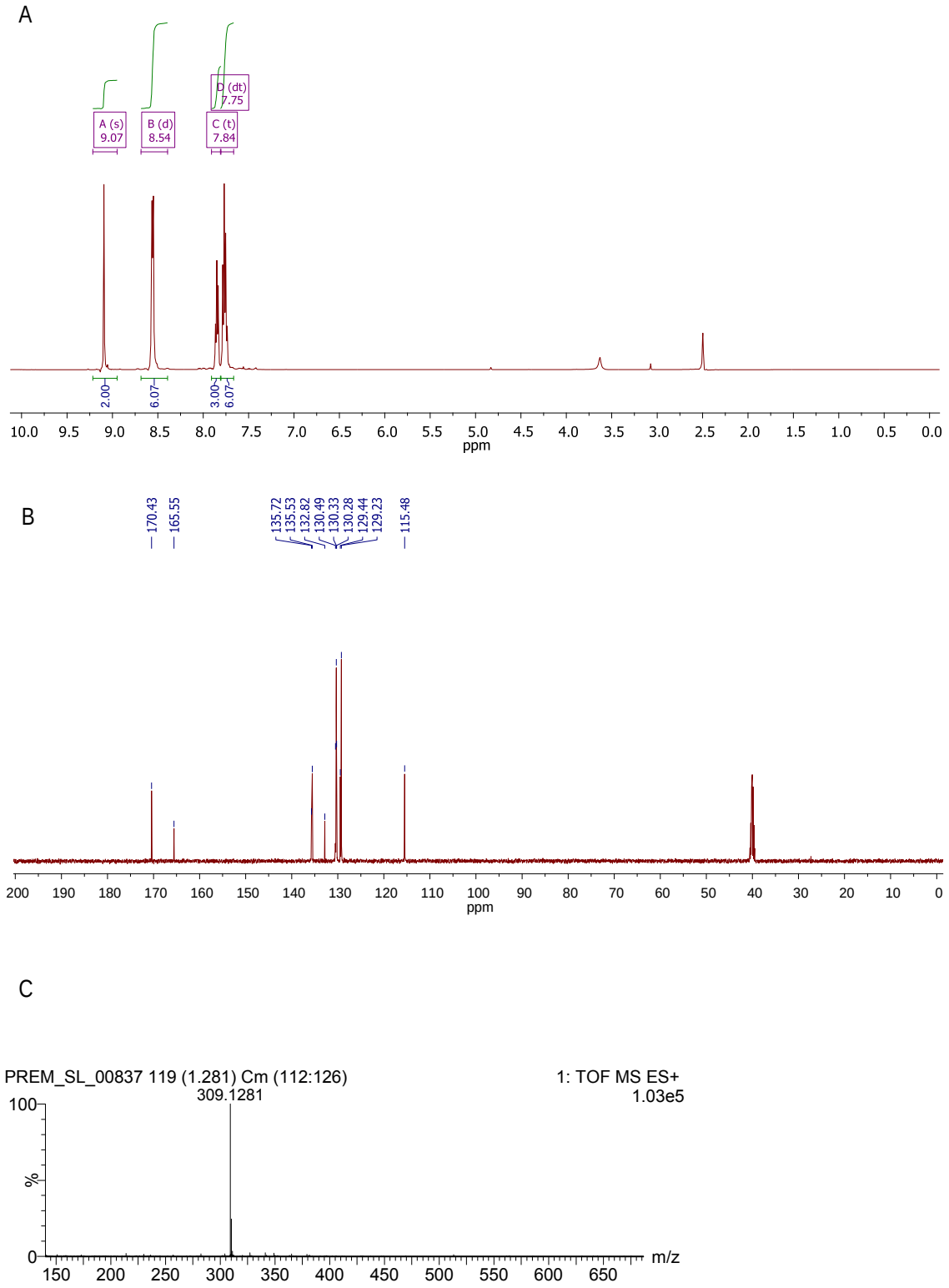


Figure S4. A) ^{1}H NMR (DMSO-d_6) spectra of compound **1c**; B) ^{13}C NMR (DMSO-d_6) spectra of compound **1c**; C) HRMS spectra of compound **1c**.

Compound 1d

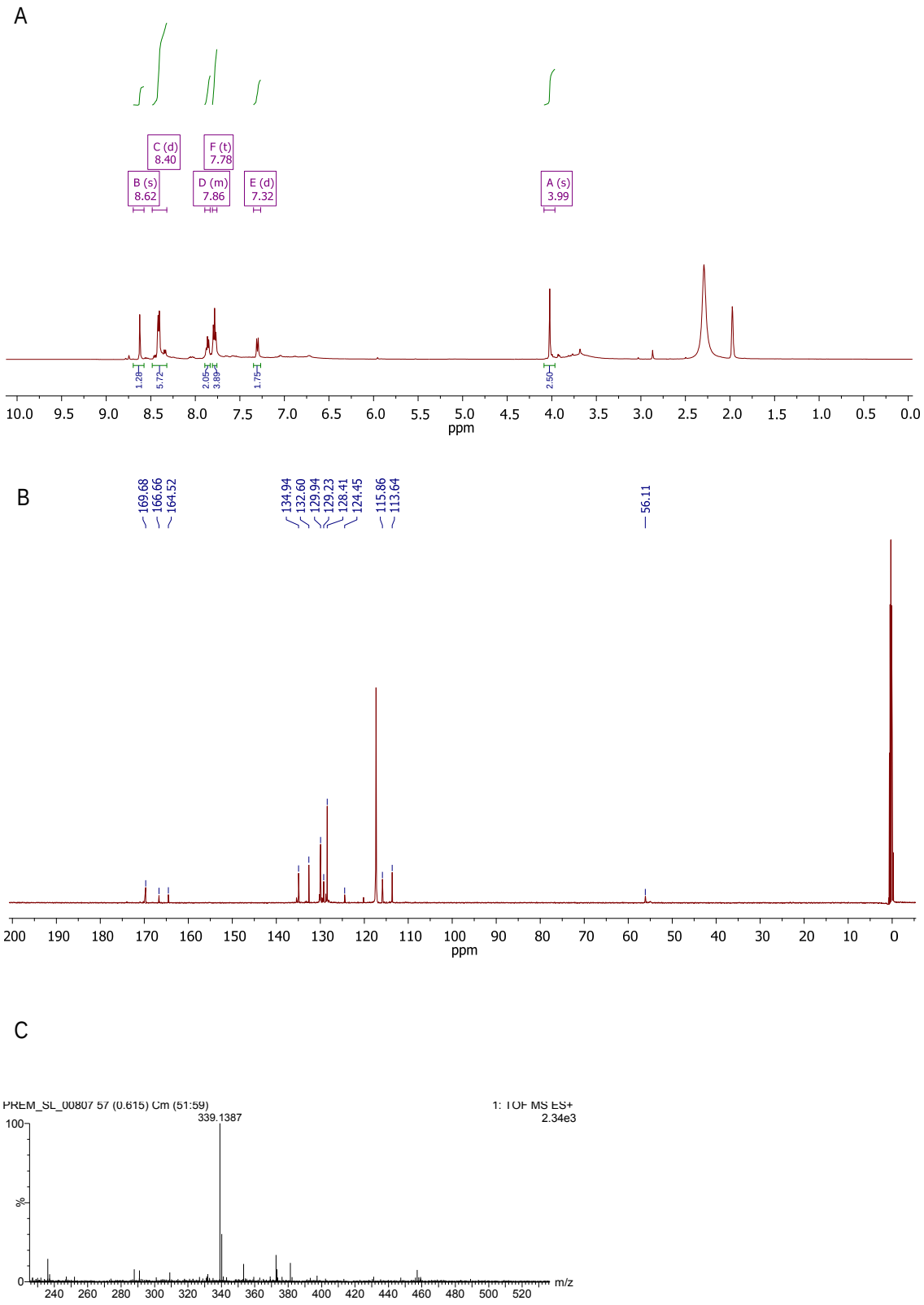


Figure S5. A) ^{1}H NMR (CH_3CN-d_3) spectra of compound **1d**; B) ^{13}C NMR (CH_3CN-d_3) spectra of compound **1d**; C) HRMS spectra of compound **1d**.

Compound 2a

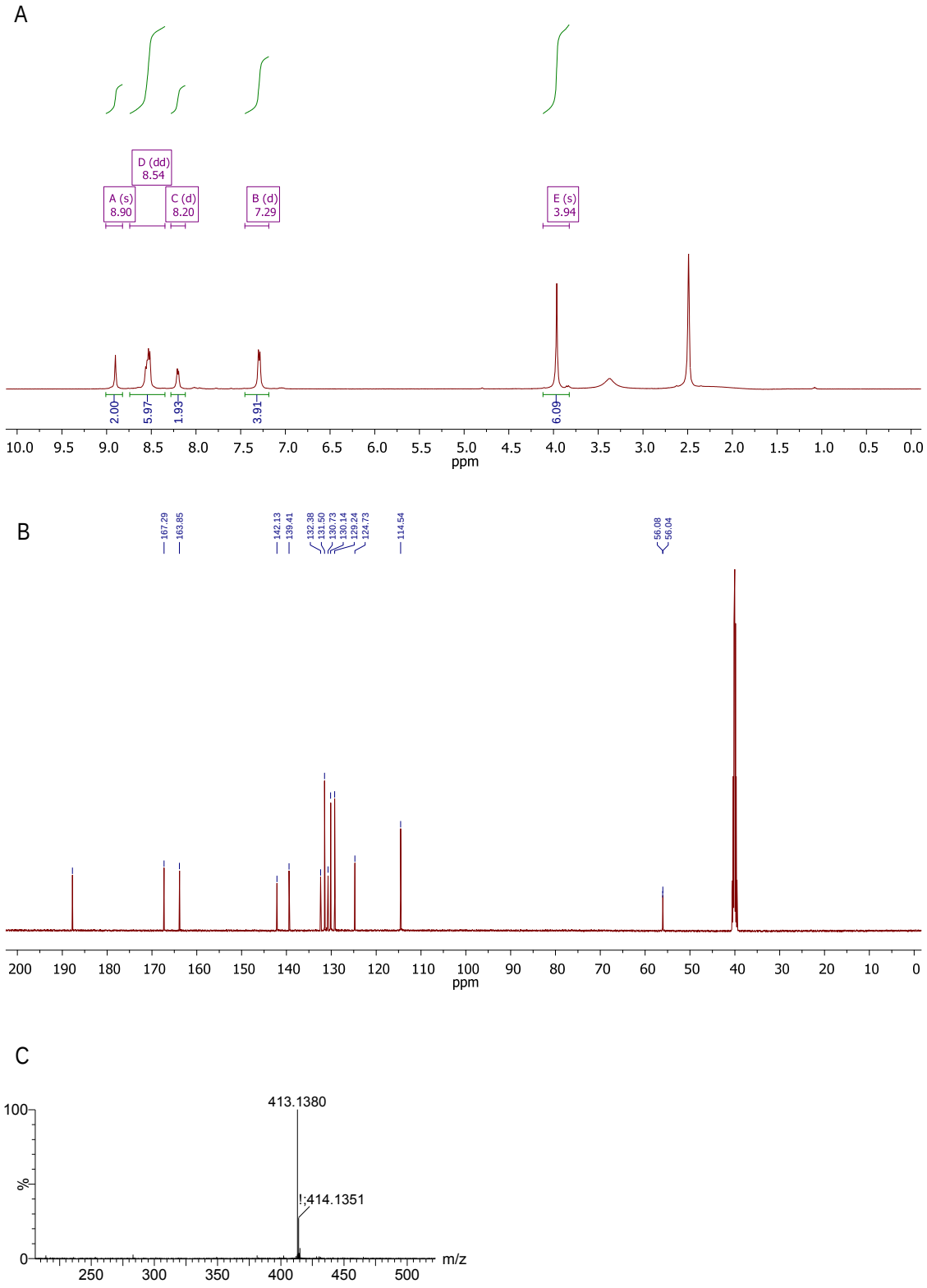


Figure S6. A) ^{1}H NMR (DMSO-d_6) spectra of compound **2a**; B) ^{13}C NMR (DMSO-d_6) spectra of compound **2a**; C) HRMS spectra of compound **2a**.

Compound 2b

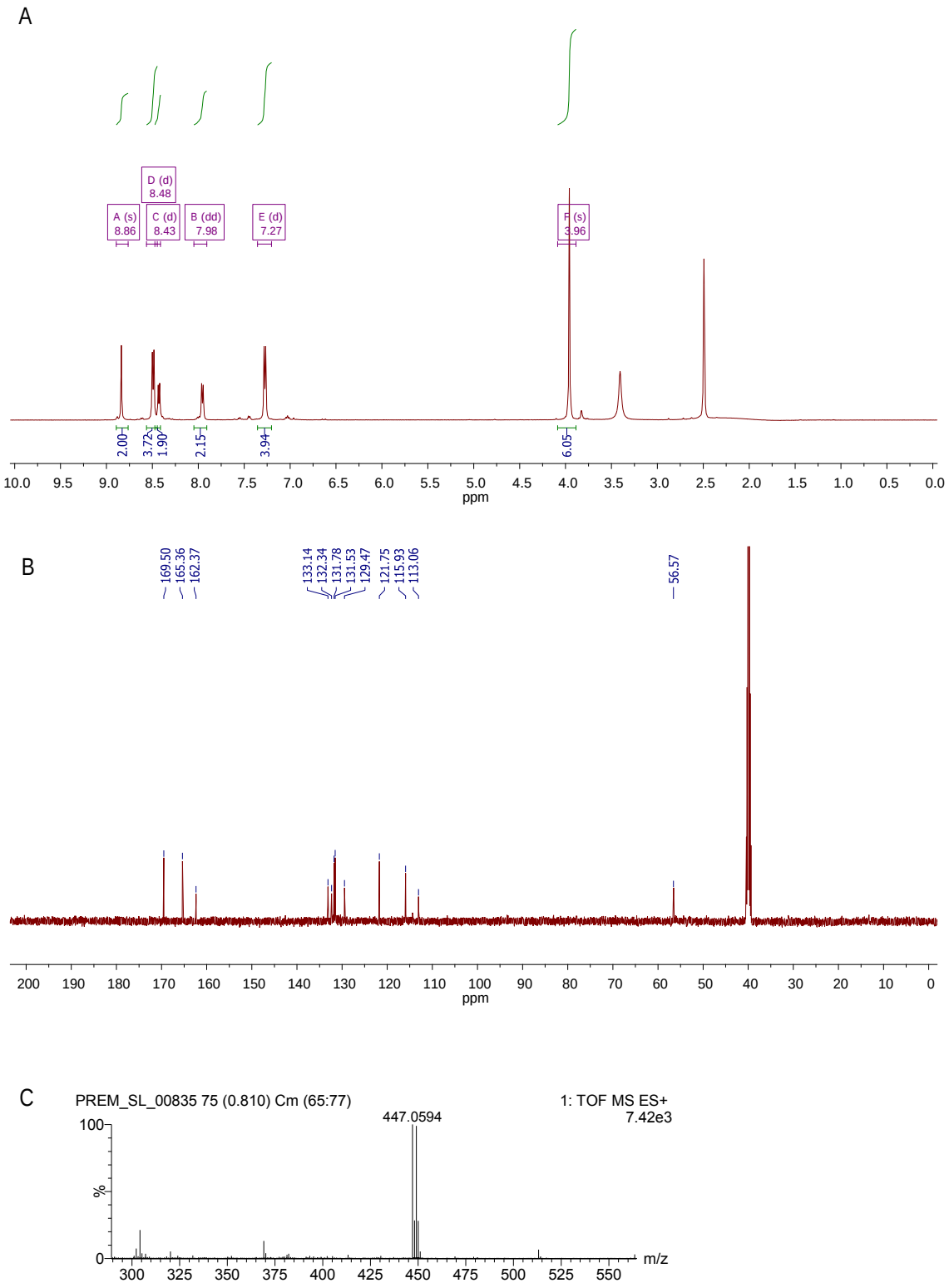


Figure S7. A) ^{1}H NMR (DMSO-d_6) spectra of compound **2b**; B) ^{13}C NMR (DMSO-d_6) spectra of compound **2b**; C) HRMS spectra of compound **2b**.

Compound 2c

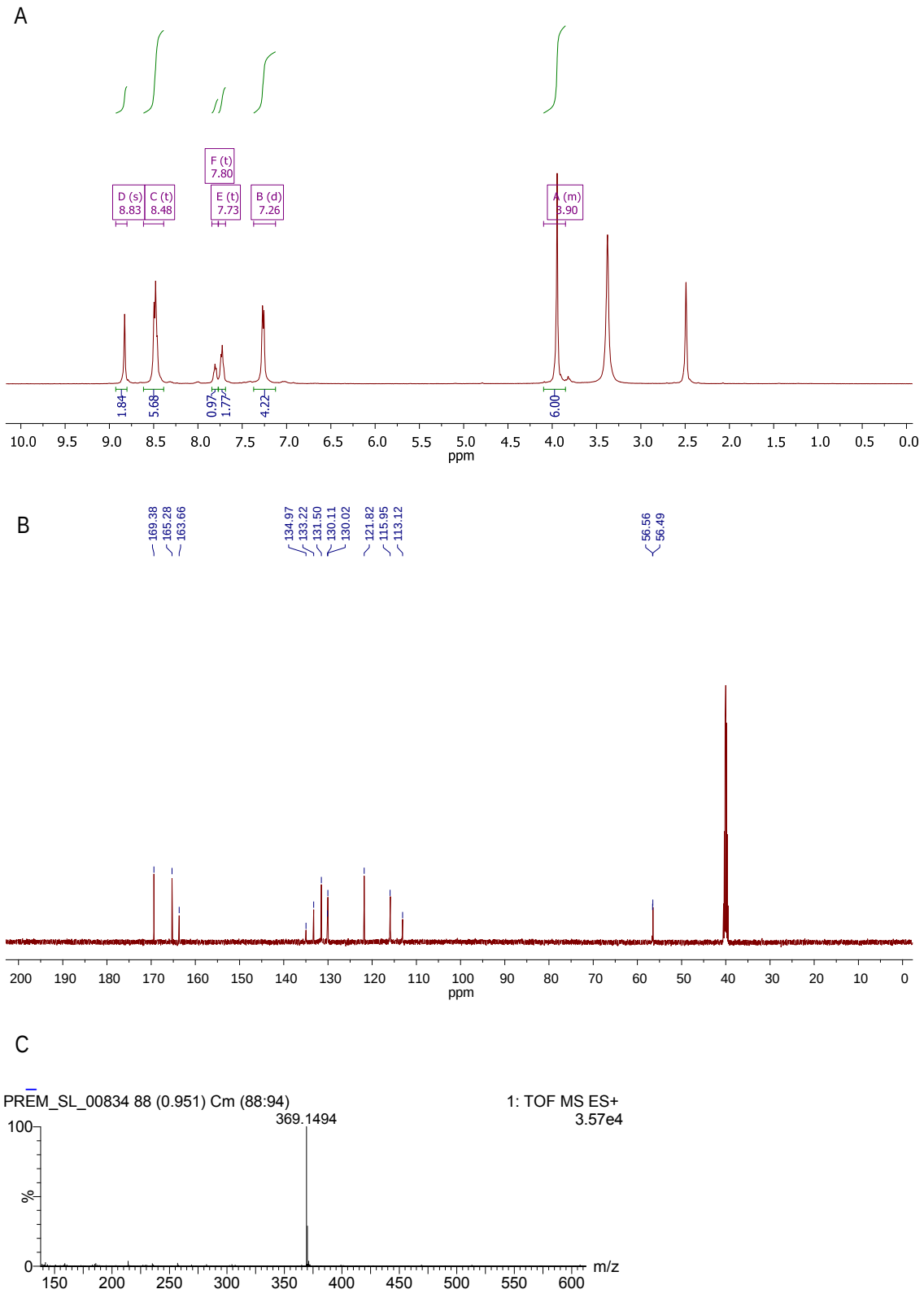


Figure S8. A) ^{1}H NMR (DMSO-d_6) spectra of compound **2c**; B) ^{13}C NMR (DMSO-d_6) spectra of compound **2c**; C) HRMS spectra of compound **2c**.

Compound 2d

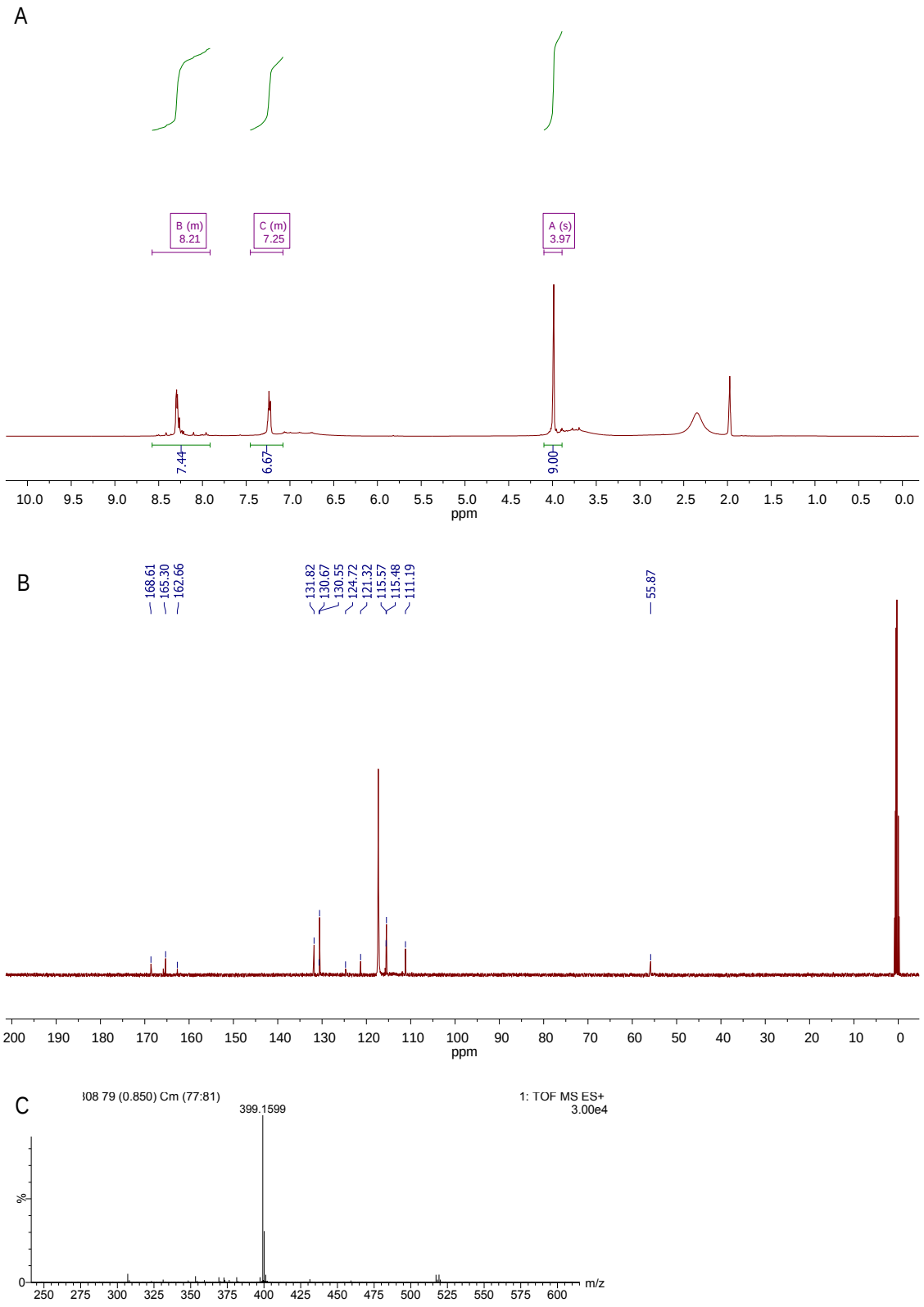


Figure S9. A) ^{1}H NMR (CH_3CN-d_3) spectra of compound **2d**; B) ^{13}C NMR (CH_3CN-d_3) spectra of compound **2d**; C) HRMS spectra of compound **2d**

Fluorescence and absorption spectra

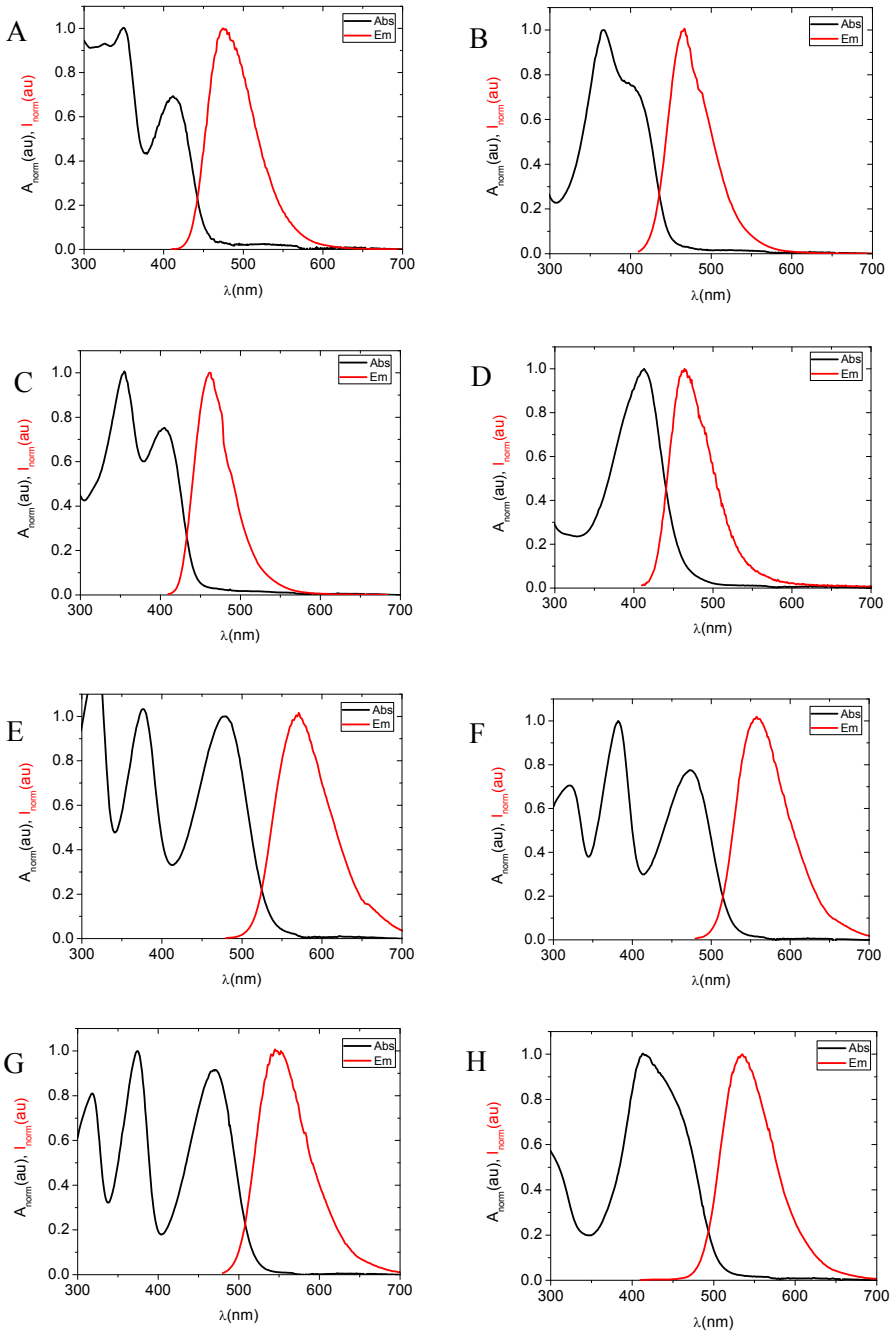


Figure S10 Normalized absorption and emission spectra of 10 µM solutions in acetonitrile of the diferent compounds: A) **1a**, B) **1b**, C) **1c**, D) **1d**, E)**2a**, F) **2b**, G) **2c**, H) **2d**.

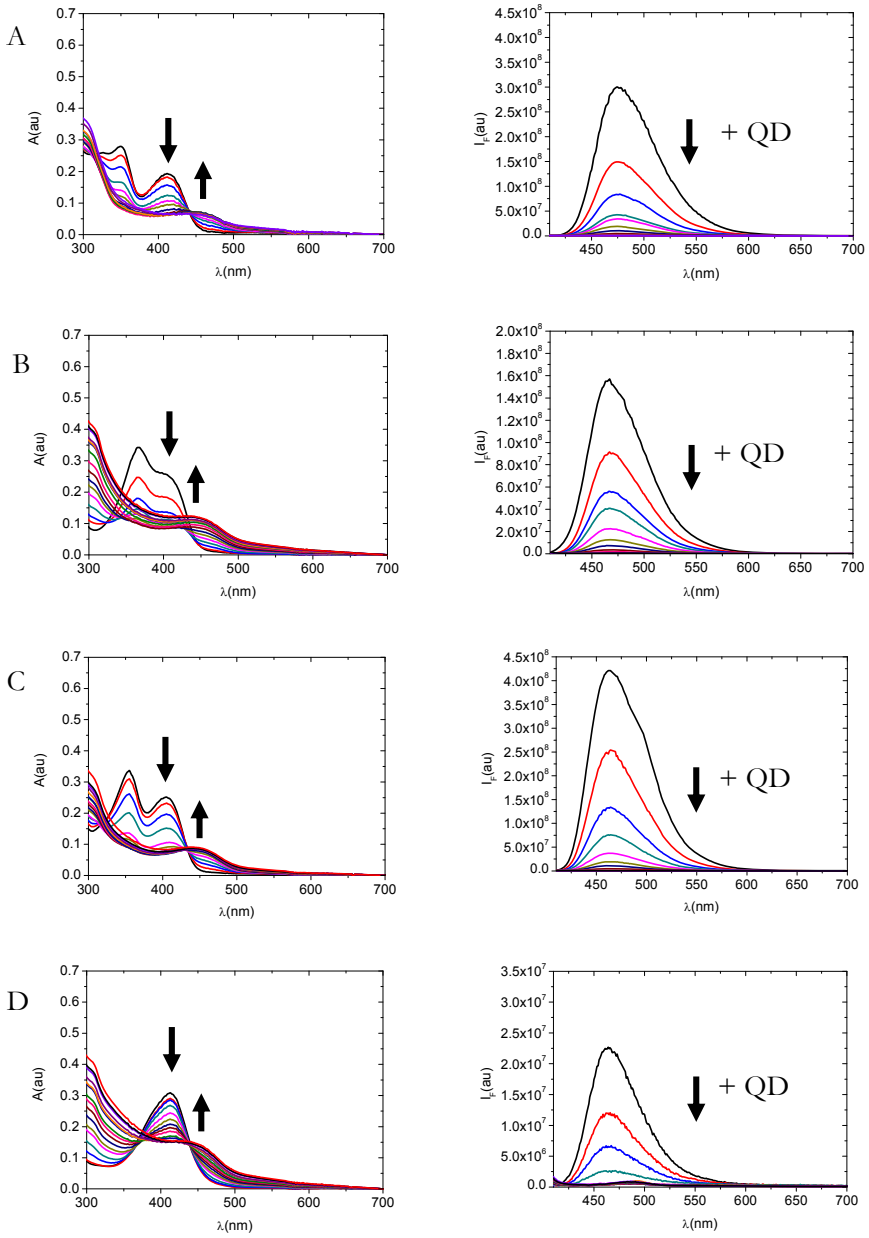


Figure S11 Left: Absorption spectra of compounds **1a-d** (10 μM) in acetonitrile in the presence of increasing amounts of QDs. Right: Emission spectra of compounds **1a-d** (10 μM) in acetonitrile in the presence of increasing amounts of QDs. A) Compound **1a**, B) Compound **1b**, C) Compound **1c**, D) Compound **1d**. λexc = 400 nm.

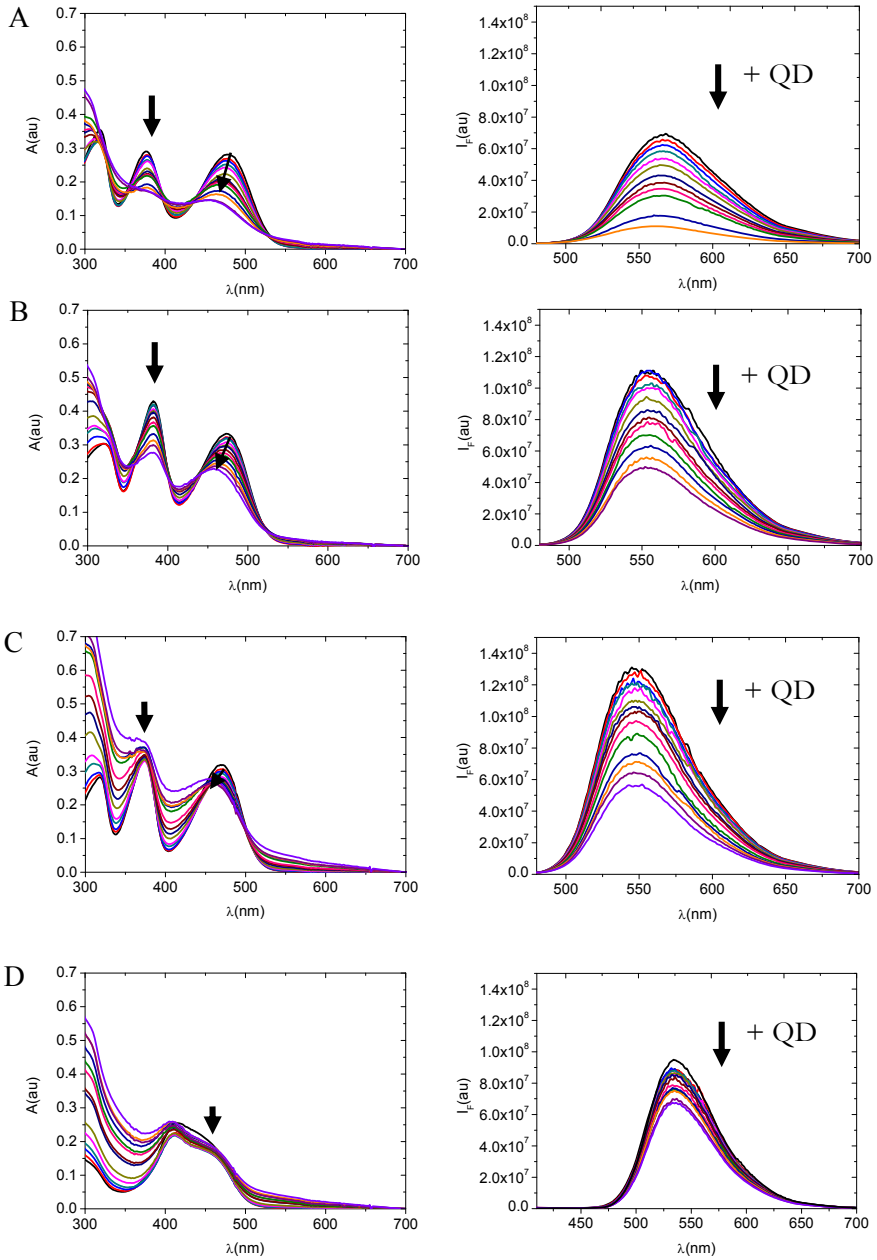


Figure S12 Left: Absorption spectra of compounds **2a-d** (10 μM) in acetonitrile in the presence of increasing amounts of QDs. Right: Emission spectra of compounds **2a-d** (10 μM) in acetonitrile in the presence of increasing amounts of QDs. A) Compound **2a**, B) Compound **2b**, C) Compound **2c**, D) Compound **2d**. λexc = 470 nm for **2a-c** and λexc = 400 nm for **2d**)

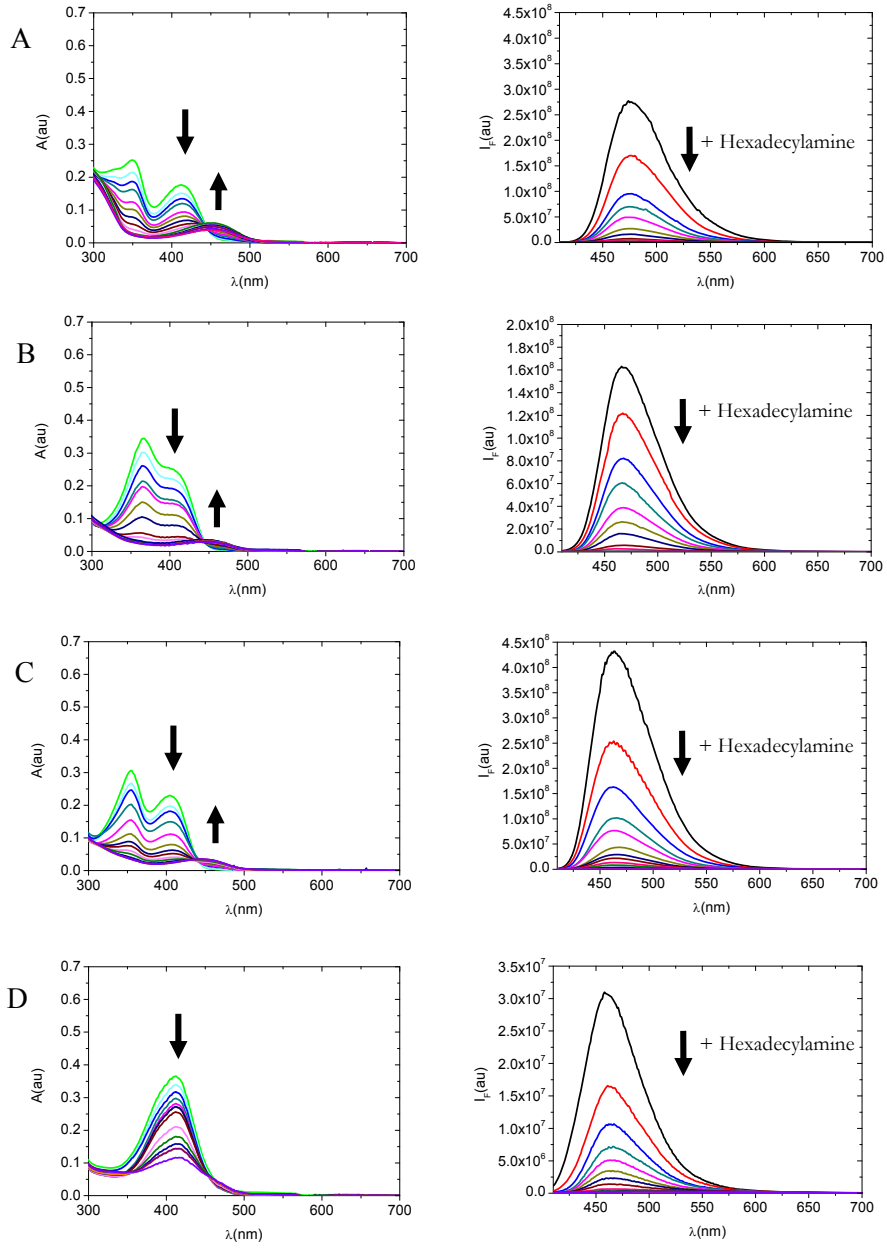


Figure S13 Left: Absorption spectra of compounds **1a-d** (10 μM) in acetonitrile in the presence of increasing amounts of hexadecylamine (HDA). **Right**: Emission spectra of compounds **1a-d** (10 μM) in acetonitrile in the presence of increasing amounts of hexadecylamine (HDA). A) Compound **1a**, B) Compound **1b**, C) Compound **1c**, D) Compound **1d**. λexc = 400 nm.

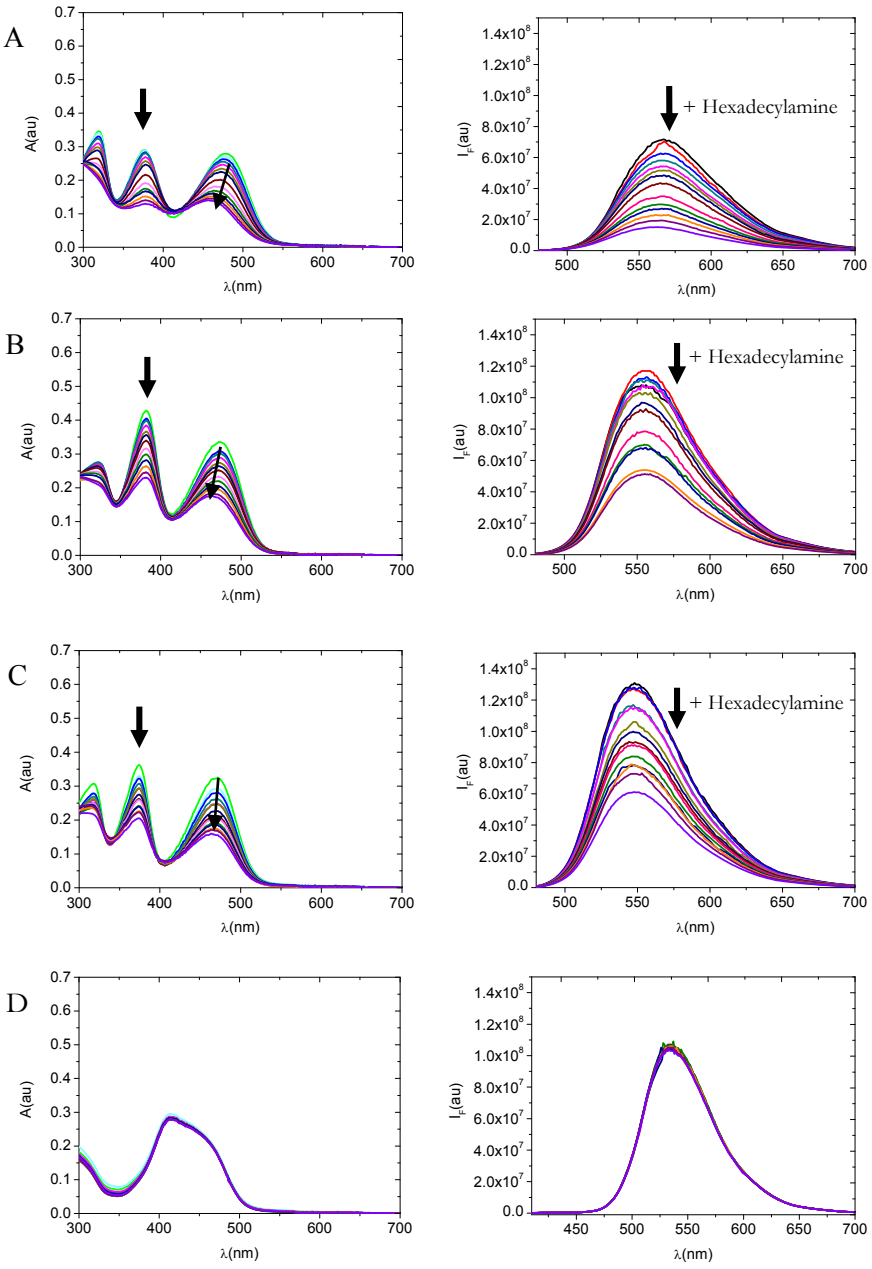


Figure S14 Left: Absorption spectra of compounds **2a-d** (10 μM) in acetonitrile in the presence of increasing amounts of hexadecylamine (HDA). **Right**: Emission spectra of compounds **2a-d** (10 μM) in acetonitrile in the presence of increasing amounts of hexadecylamine (HDA). A) Compound **2a**, B) Compound **2b**, C) Compound **2c**, D) Compound **2d**. λexc = 470 nm for **2a-c** and λexc = 400 nm for **2d**.

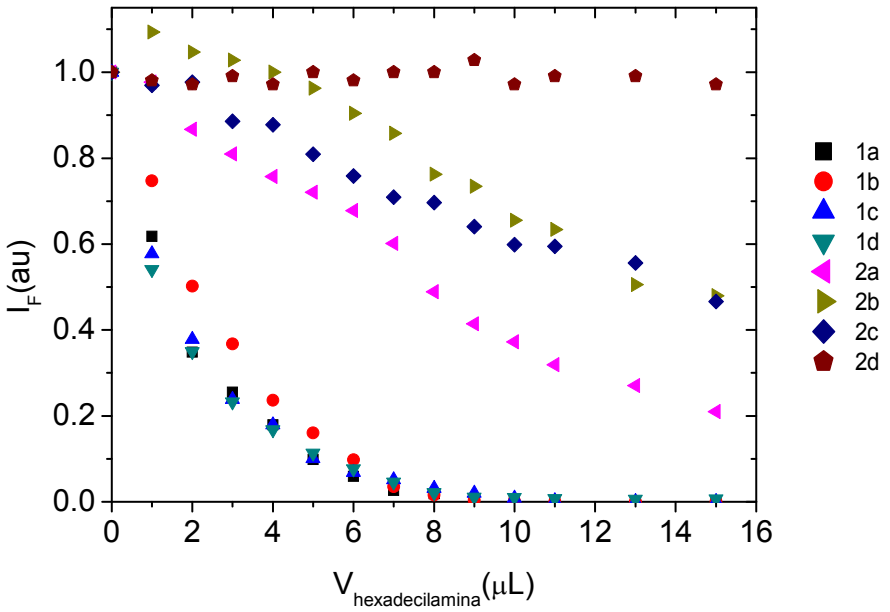


Figure S15 Variation of the fluorescence intensity of the 2,4,6-triarylpyrylium salts **1a-d**, **2a-d** (10 μM) in acetonitrile in the presence of increasing amounts of hexadecylamine, from a stock solution (1 mM) in toluene.

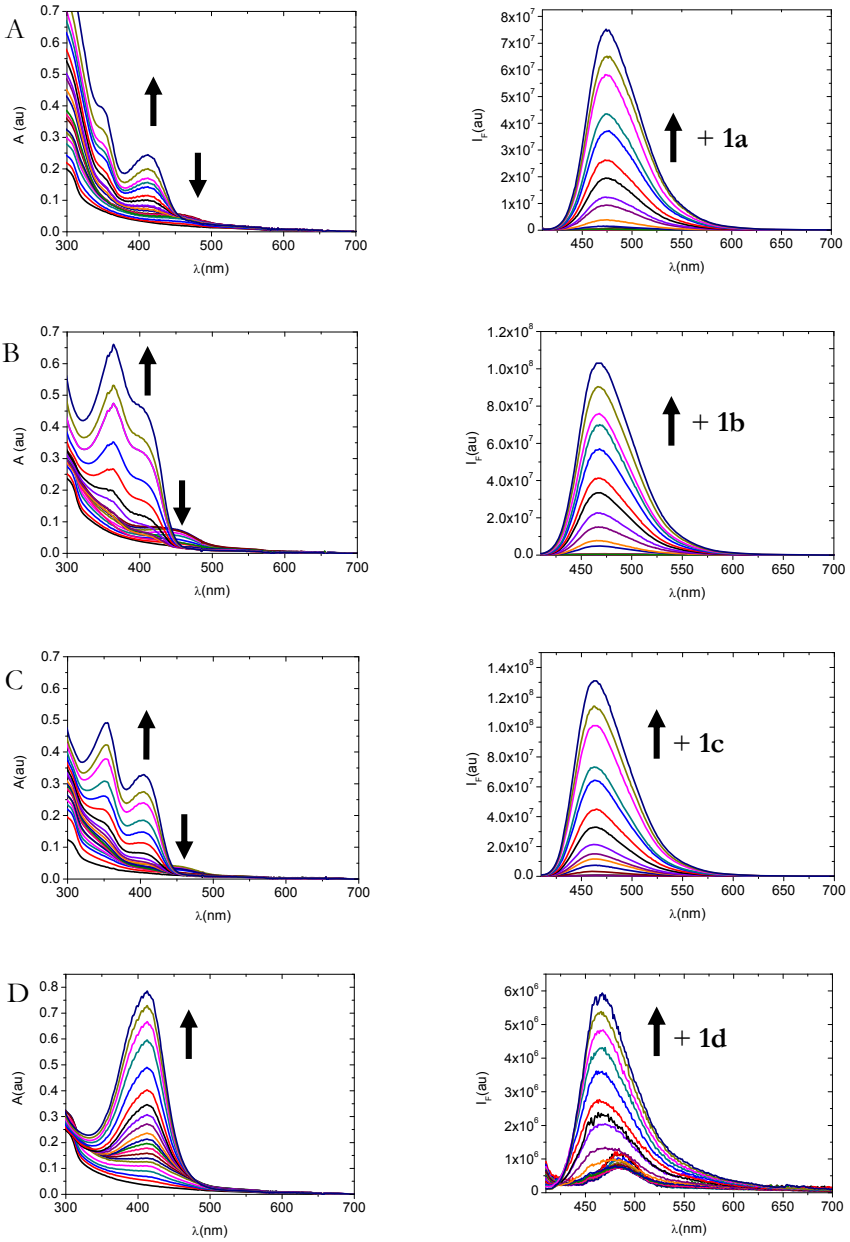


Figure S16 Left: Absorption spectra. Compounds **1a-d** in acetonitrile in the presence of 5 µL of QD commercial solution (with increasing amounts of the pyrylium salt). **Right**: Emission spectra. Compounds **1a-d** in acetonitrile in the presence of 5 µL of QD commercial solution (with increasing amounts of the pyrylium salt). A) Compound **1a**, B) Compound **1b**, C) Compound **1c**, D) Compound **1d**. λexc = 400 nm.

HRMS-QTOF spectra of pyrylium salts in the presence of Quantum Dots or hexadecylamine.

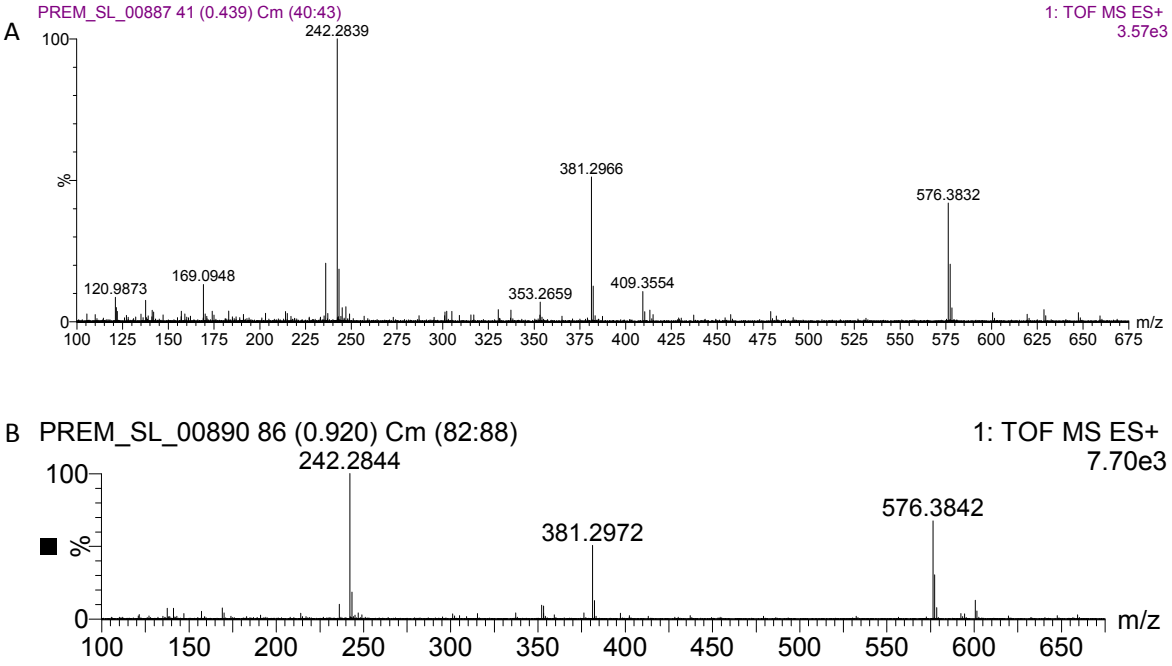


Figure S17. A) HRMS-QTOF spectra of compound **1a** in acetonitrile and in the presence of 5 µL of QDs; B) HRMS-QTOF spectra of compound **1a** in acetonitrile and in the presence of 1 equivalent of hexadecylamine.

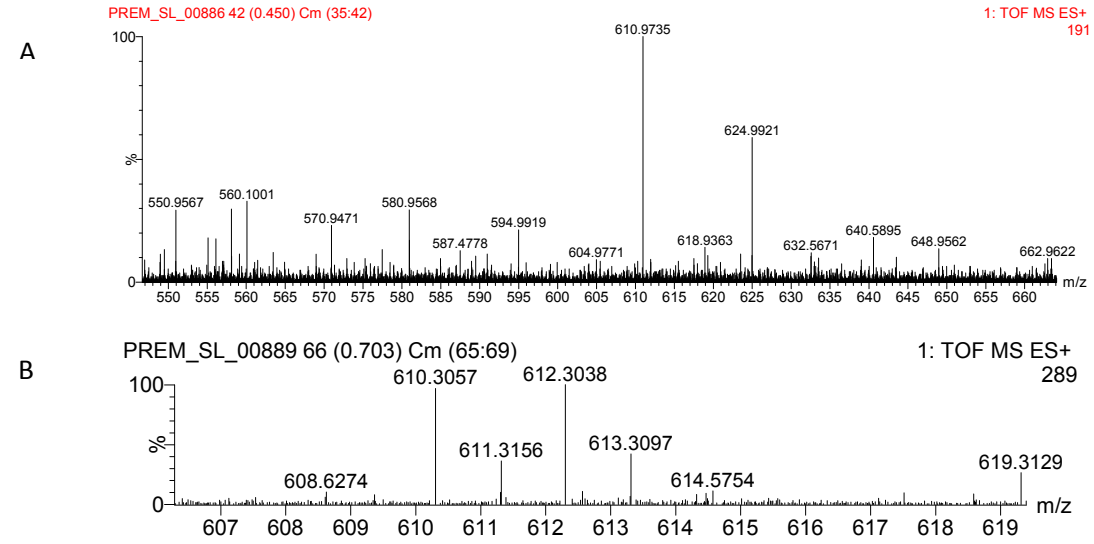


Figure S18 A) HRMS-QTOF spectra of compound **1b** in acetonitrile and in the presence of 5 µL of QDs; B) HRMS-QTOF spectra of compound **1b** in acetonitrile and in the presence of 1 equivalent of hexadecylamine.

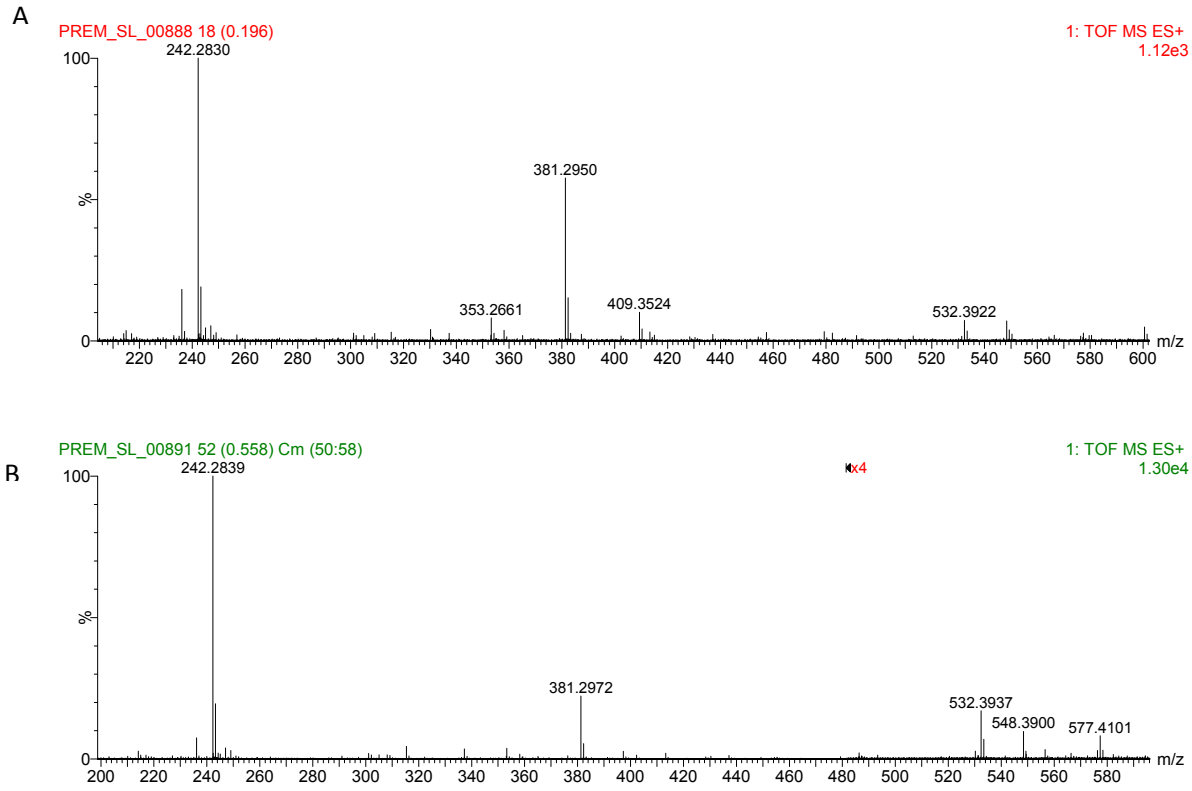


Figure S19. A) HRMS-QTOF spectra of compound **1c** in acetonitrile and in the presence of 5 µL of QDs; B) HRMS-QTOF spectra of compound **1c** in acetonitrile and in the presence of 1 equivalent of hexadecylamine.

Crystallographic data

*Compound **1a** (perchlorate salt described in ref. 3)*

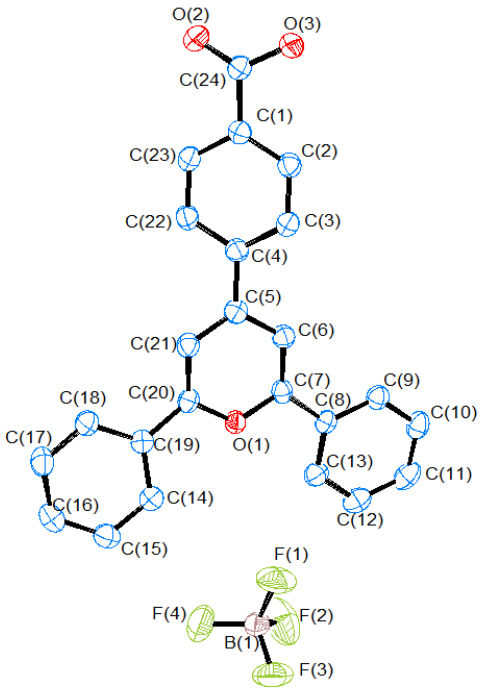


Figure S20 X-ray structure for compound **1a.**

[3] T. M. Krygowski, R. Anulewicz, B. Pniewska, P. Milart, *J. Phys. Org. Chem.* **1991,** 4, 121.

Table S1 Crystal data and structure refinement for compound **1a**.

Identification code	str1578
Empirical formula	$C_{24}H_{17}BF_4O_3$
Formula weight	440.18
Temperature/K	148(80)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	7.1387(3)
b/Å	16.6302(5)
c/Å	17.1016(6)
α/°	90
β/°	100.004(4)
γ/°	90
Volume/Å^3	1999.39(12)
Z	4
ρ_{calc}mg/mm^3	1.462
m/mm^{-1}	1.023
F(000)	904.0
Crystal size/mm^3	0.4568 × 0.0682 × 0.0627
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection	7.47 to 129.566
Index ranges	$-8 \leq h \leq 6$, $-19 \leq k \leq 19$, $-19 \leq l \leq 20$
Reflections collected	15751
Independent reflections	3341 [R_{int} = 0.0381, R_{sigma} = 0.0249]
Data/restraints/parameters	3341/0/353
Goodness-of-fit on F^2	1.034
Final R indexes [I>=2σ (I)]	R_1 = 0.0442, wR_2 = 0.1190
Final R indexes [all data]	R_1 = 0.0521, wR_2 = 0.1275
Largest diff. peak/hole / e Å^{-3}	0.48/-0.26

*Compound **1b***

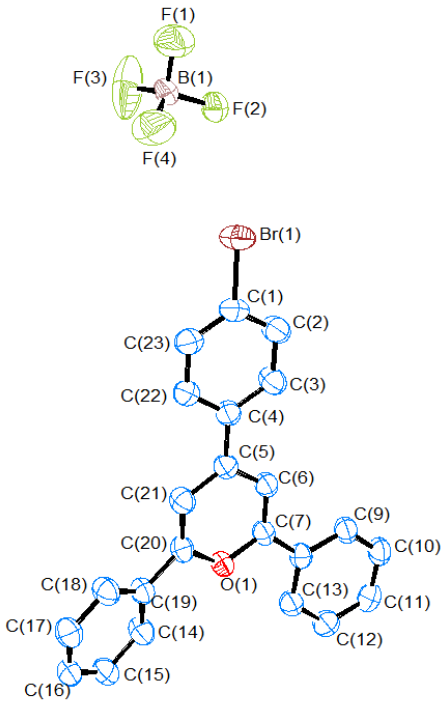


Figure S21. X-ray structure for compound **1b**.

Table S2 Crystal data and structure refinement for compound **1b**.

Identification code	str1520
Empirical formula	$C_{23}H_{16}BBrF_4O$
Formula weight	475.08
Temperature/K	298
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	13.5265(4)
b/Å	9.8137(3)
c/Å	15.2162(4)
α/°	90
β/°	95.234(3)
γ/°	90
Volume/Å^3	2011.44(11)
Z	4
ρ_{calc}mg/mm^3	1.569
m/mm^{-1}	3.225
F(000)	952.0
Crystal size/mm^3	0.295 × 0.041 × 0.034
Radiation	Cu Kα (λ = 1.5418)
2Θ range for data collection	8.376 to 145.496
Index ranges	$-16 \leq h \leq 16$, $-11 \leq k \leq 11$, $-18 \leq l \leq 18$
Reflections collected	18214
Independent reflections	3939[R(int) = 0.0879]
Data/restraints/parameters	3939/0/271
Goodness-of-fit on F^2	1.406
Final R indexes [I>=2σ (I)]	R_1 = 0.0731, wR_2 = 0.3008
Final R indexes [all data]	R_1 = 0.1284, wR_2 = 0.3129
Largest diff. peak/hole / e Å^{-3}	1.13/-0.77