Influence of the side-chain characteristics on the aggregation-induced emission (AIE) properties of tetrasubsituted tetraphenylethylene (TPE)

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Supporting Information

Experimental

Chemicals

All the chemicals were purchased from Sigma-Aldrich Química S.A. (Madrid, Spain), and used without further purification. THF was dried over sodium and distilled before use.

General methods

The SEM, fluorescence microscopy, NMR and fluorescence spectroscopy techniques were employed to characterise the synthesised materials. The SEM images were obtained by a Hitachi S-4100 microscope (20 kV). The fluorescence images were obtained by a Leica DMR optical microscope. The ^{1}H and ^{13}C NMR spectra were recorded with the Bruker DPX300, 400AV and DRX500 spectrometers in the deuterated solvent, stated in each case as the lock, and in a residual solvent as the internal reference. The UV-vis spectra were recorded by a Shimazdu UV-2600 spectrophotometer using a 1-cm path length quartz cuvette. The emission spectra were recorded in a Varian Cary Eclipse fluorimeter using a 1-cm path length quartz cuvette. Quantum yields were measured using a Hamamatsu absolute quantum yield C9920.

Synthesis

Synthesis of 1,1,2,2-tetrakis(4-bromophenyl)ethene. Prepared according to the literature procedure.[13] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 (d, *J* = 8.4 Hz, 8H), 6.87 (d, *J* = 8.4 Hz, 8H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.61, 139.76, 132.87, 131.44, 121.42. Yield: 3.606 g, 62%.

Synthesis of 1,1,2,2-tetrakis(4-ethynylphenyl)ethene. A solution of 1,1,2,2-tetrakis(4-bromophenyl)ethene (1.296 g, 2.000 mmol) in toluene (15 mL) was prepared in a two-neck round flask. The flask was evacuated and flushed with argon 5 times. Dry triethylamine (45 mL) was injected through the septum. In an argon flow and with stirring, copper(I) iodide (0.159 g, 0.836 mmol) and tetrakis(triphenylphosphine)palladium(0) (0.467 g, 0.404 mmol) were added to the solution. With stirring, the reaction was heated to 60ºC and ethynyltrimethylsilane (2.12 mL, 15.0 mmol) was injected through the septum. After 15 min of stirring, the reaction was heated to 80ºC for 24 h in an argon atmosphere. After cooling, the reaction mixture was

filtered by gravity and the solvent was removed under reduced pressure. The obtained solid was dissolved in diethyl ether and a 1 M of TBAF solution in THF (3.4 mL, 3.4 mmol) was added. After 30 minutes of stirring at room temperature, the solvent was evaporated at reduced pressure and the crude was purified in a chromatography column using hexane/ethyl acetate (8:2) as an eluent. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.25 (d, J = 8.6 Hz, 8H), 6.94 (d, J = 8.6 Hz, 8H), 3.07 (s, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.41, 140.98, 131.93, 131.36, 120.86, 83.60, 77.94. Yield: 0.407 g, 52%.

Synthesis of 1,1,2,2-tetrakis(4-nitrophenyl)ethene. Prepared according to the literature procedure.[14] ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.8 Hz, 8H), 7.19 (d, *J* = 8.9 Hz, 8H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.49, 147.26, 141.69, 131.94, 124.10. Yield: 1.488 g, 96%.

Synthesis of 1,1,2,2-tetrakis(4-aminophenyl)ethene. Prepared according to the literature procedure.[15] ^{1}H NMR (300 MHz, DMSO-d_6) δ 6.57 (d, *J* = 8.5 Hz, 8H), 6.26 (d, *J* = 8.5 Hz, 8H), 4.84 (s, 8H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 146.04, 136.66, 132.91, 131.66, 113.12. Yield: 1.488 g, 96%.

Synthesis of 1,1,2,2-tetrakis(4-azidophenyl)ethene. Prepared according to the literature procedure.[16] ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.97 (d, *J* = 8.7 Hz, 8H), 6.79 (d, *J* = 8.8 Hz, 8H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.06, 139.55, 138.62, 132.83, 118.77. Yield: 1.748 g, 93%.

Synthesis of 1-dodecylazide. Prepared according to a literature procedure.[17] ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.25 (t, *J* = 7.0 Hz, 2H), 1.58 (q, *J* = 7.4 Hz, 2H), 1.42 – 1.20 (m, 20H), 0.88 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 51.62, 32.06, 29.77, 29.69, 29.63, 29.49, 29.30, 28.99, 26.87, 22.83, 14.22. ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.64, 143.46, 140.77, 132.08, 129.13, 125.36, 119.61, 50.57, 32.04, 29.73, 29.47, 29.15, 26.63, 22.82, 14.26. Yield: 0.493 g, 58%.

Synthesis of compound 1. To a solution of 1,1,2,2-tetrakis(4-ethynylphenyl)ethene (0.030 g, 0.071 mmol) in THF (2.0 mL), 1-dodecylazide (0.067 g, 0.318 mmol) and deionised water (1.0 mL) were added. Then a fresh solution of sodium ascorbate (0.012 g, 0.060 mmol) and copper(II) acetate monohydrate (0.0056 g, 0.028 mmol) in deionised water (1.0 mL) was added. The mixture was stirred for 12 h. Brine (8 mL) was added and the mixture was extracted with DCM (3 x 10 mL). Organic layers were combined, washed with brine (10 mL) and dried over anhydrous magnesium sulphate. The solvent was evaporated and the solid was washed with hexane. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.67 (s, 4H), 7.59 (d, *J* = 8.3 Hz, 8H), 7.14 (d, *J* = 8.3 Hz, 8H), 4.36 (t, *J* = 7.2 Hz, 8H), 1.91 (p, *J* = 7.4 Hz, 8H), 1.38–1.18 (m, 72H), 0.87 (t, *J* = 6.9 Hz, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.64, 143.46, 140.77, 132.08, 129.13, 125.36, 119.61, 50.57, 32.04, 29.73, 29.47, 29.15, 26.63, 22.82, 14.26. HRMS (ESI) for $C_{82}H_{120}N_{12}$ $[M+H]^+$, calcd: 1273.9837. Found: 1273.9844. Yield: 0.066 g, 73%.

General procedure for the synthesis of compounds 2-5. The desired alkyne (0.808 mmol) and deionised water (2.0 mL) were added to a solution of 1,1,2,2-tetrakis(4-azidophenyl)ethene (0.102 g, 0.206 mmol) in THF (4.0 mL). Then a fresh solution of sodium ascorbate (0.012 g, 0.060 mmol) and copper(II) acetate monohydrate (0.0056 g, 0.028 mmol) in deionised water (2.0 mL) was added and the mixture was stirred for 12 h. Brine (12 mL) was added and the mixture was extracted with DCM (3 x 15 mL). Organic layers were combined, washed with brine (10 mL) and dried over anhydrous magnesium sulphate. After evaporating the solvent, the desired products were obtained as high-purity yellow solids.

Synthesis of compound 2. Prepared according the general procedure shown above. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.68 (s, 4H), 7.55 (d, *J* = 8.6 Hz, 8H), 7.22 (d, *J* = 8.6 Hz, 8H), 2.78 (t, *J* = 7.7 Hz, 8H), 1.70 (p, *J* = 7.4 Hz, 8H), 1.41 (h, *J* = 7.3 Hz, 8H), 0.94 (t, *J* = 7.3 Hz, 12H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.38, 142.69, 140.31, 136.16, 132.62, 120.14, 118.72, 31.55, 25.41, 22.37, 13.91. HRMS (ESI) for $C_{50}H_{56}N_{12}$ $[M+H]^+$, calcd: 825.4829. Found: 825.4817. Yield: 0.1458 g, 88%.

Synthesis of compound 3. Prepared according the general procedure shown above. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.68 (s, 4H), 7.54 (d, *J* = 8.3 Hz, 8H), 7.20 (d, *J* = 8.4 Hz, 8H), 2.75 (t, *J* = 7.7 Hz, 8H), 1.70 (p, *J* = 7.5 Hz, 8H), 1.34 (m, 16H), 0.88 (t, *J* = 6.9 Hz, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.44, 142.70, 140.31, 136.17, 132.63, 120.15, 118.73, 31.49, 29.16, 25.70, 22.51, 14.09. HRMS (ESI) for $C_{54}H_{64}N_{12}$ $[M+H]^+$, calcd: 881.5455. Found: 881.5454. Yield: 0.2252 g, 87%.

Synthesis of compound 4. Prepared according the general procedure shown above. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.67 (s, 4H), 7.55 (d, *J* = 8.6 Hz, 8H), 7.21 (d, *J* = 8.6 Hz, 8H), 2.76 (t, *J* = 7.7 Hz, 8H), 1.70 (p, *J* = 7.2 Hz, 8H), 1.41–1.24 (m, 24H), 0.88 (t, *J* = 7.1 Hz, 12H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.46, 142.69, 140.31, 136.19, 132.63, 120.15, 118.72, 31.67, 29.44, 29.00, 25.75, 22.65, 14.17. HRMS (ESI) for $C_{58}H_{72}N_{12}$ $[M+H]^+$, calcd: 937.6081. Found: 937.6075. Yield: 0.1594 g, 84%.

Synthesis of compound 5. Prepared according the general procedure shown above. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.67 (s, 4H), 7.55 (d, *J* = 8.7 Hz, 8H), 7.22 (d, *J* = 8.6 Hz, 8H), 2.77 (t, *J* = 7.7 Hz, 8H), 1.70 (p, *J* = 7.5 Hz, 8H), 1.45–1.18 (m, 72H), 0.87 (t, *J* = 7.0 Hz, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.52, 142.72, 140.33, 136.21, 132.66, 120.19, 118.74, 32.04, 29.77, 29.68, 29.51, 29.47, 29.39, 25.79, 22.81, 14.25. HRMS (ESI) for $C_{82}H_{120}N_{12}$ $[M+H]^+$, calcd: 1273.9837. Found: 1273.9834. Yield: 0.2220 g, 86%.

Optical properties. PL emission spectra

To study the effect of the alkyl chain length on the fluorescence of the TPE derivatives, we did an array of mixtures THF/water and methanol/water of increasing polarity. The measured samples were prepared following this procedure: a 10^{-3} M stock solution in THF was prepared for each compound **1-5**. Then each 10^{-5} M solution was made in the quartz cell by adding the concentrated solution first, the organic solvent

second (THF or MeOH), and thirdly water. Mixtures were immediately measured after being prepared.

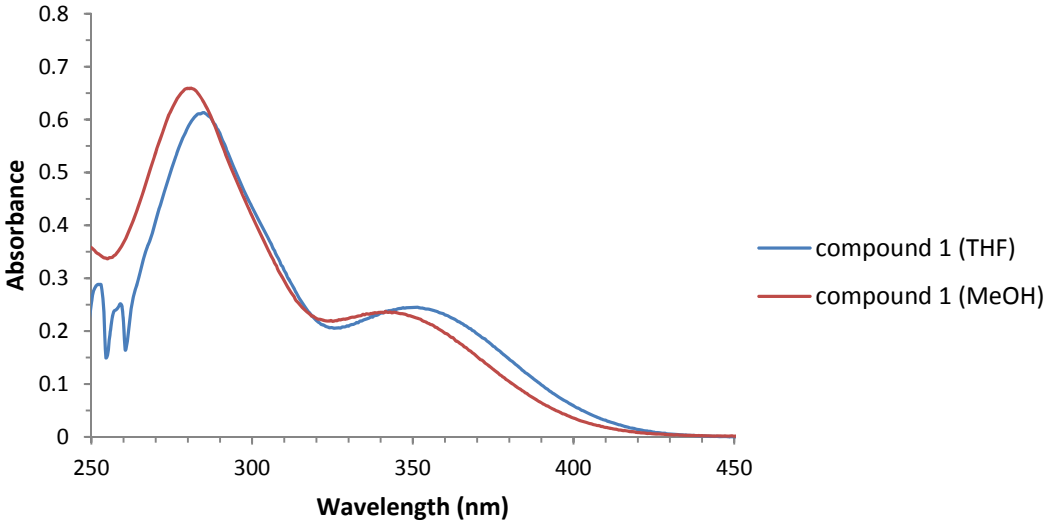

Figure S1. UV-vis spectrum of compound **1** (10^{-5} M) in THF and MeOH**.**

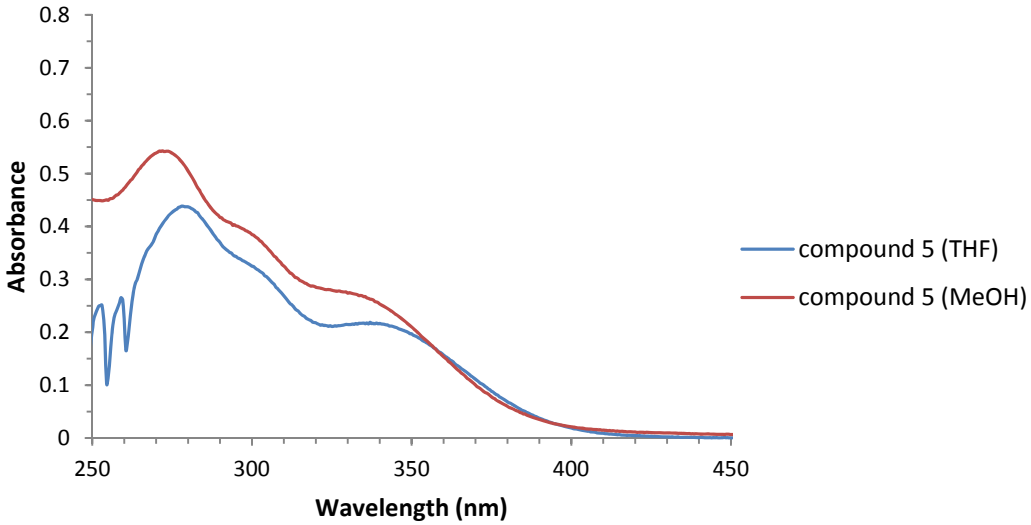

Figure S2. UV-vis spectrum of compound **5** (10^{-5} M) in THF and MeOH**.**

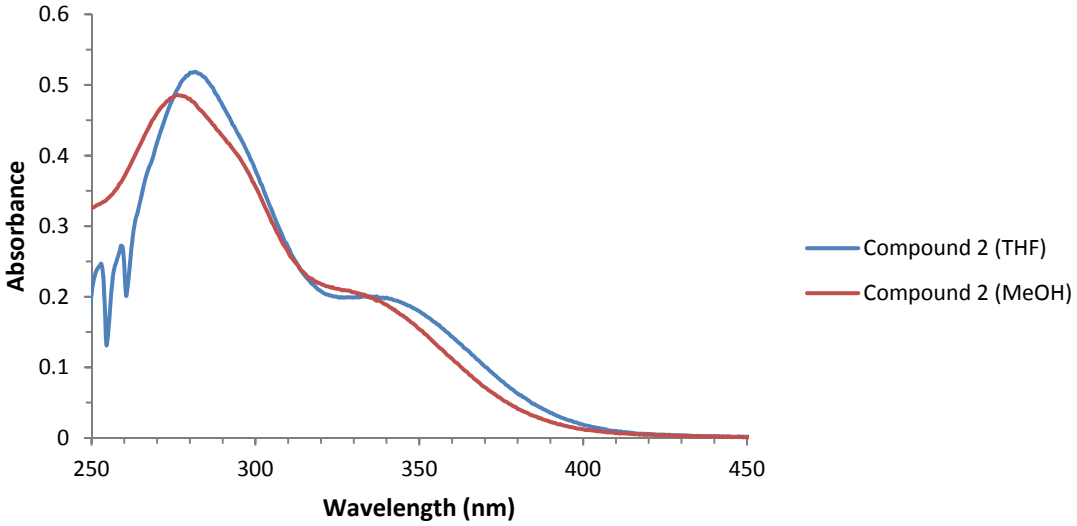

Figure S3. UV-vis spectrum of compound **2** (10^{-5} M) in THF and MeOH**.**

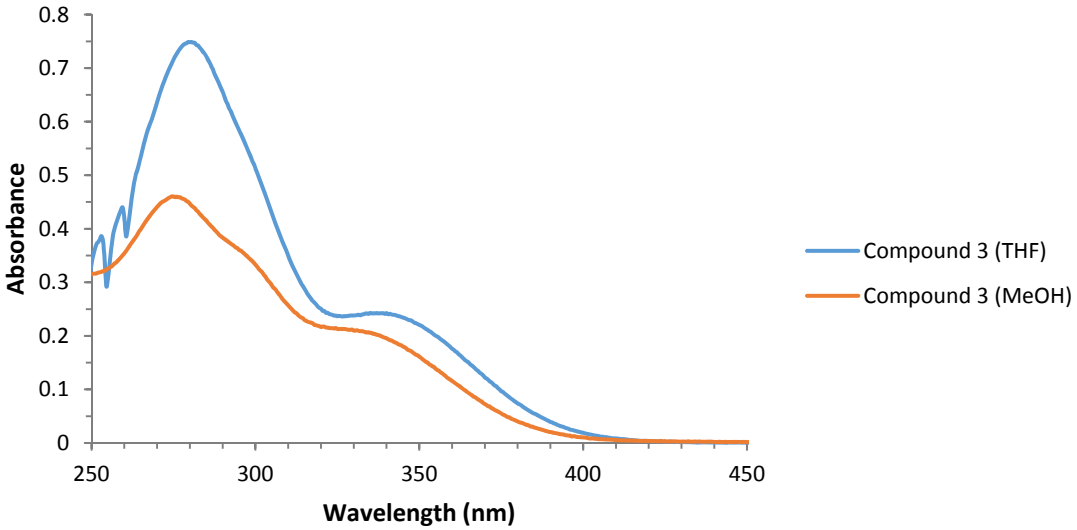

Figure S4. UV-vis spectrum of compound **3** (10^{-5} M) in THF and MeOH**.**

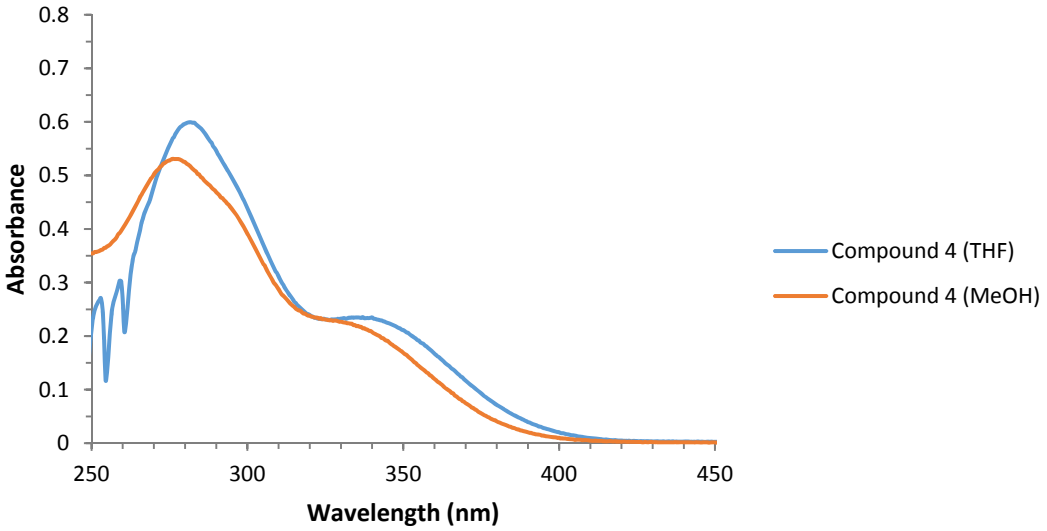

Figure S5. UV-vis spectrum of compound **4** (10^{-5} M) in THF and MeOH**.**

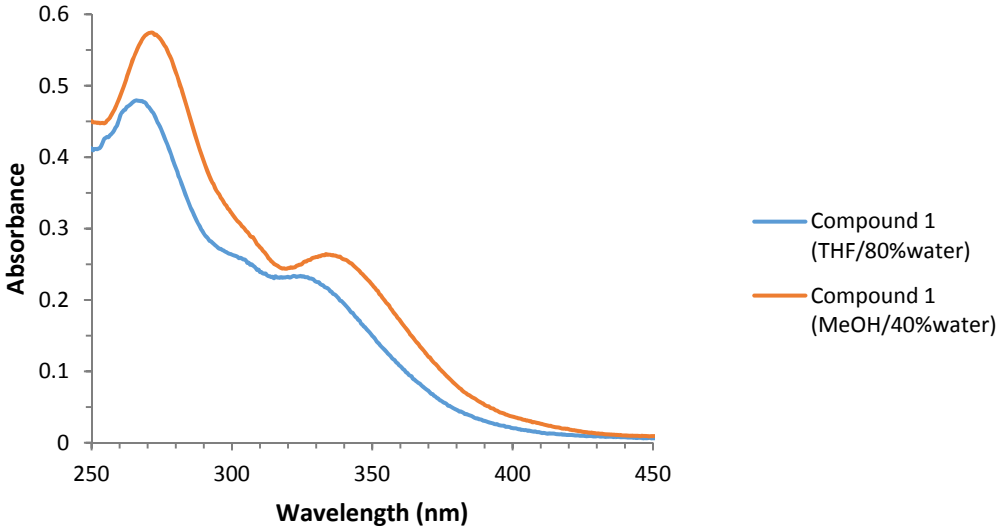

Figure S6. UV-vis spectrum of compound **1** (10^{-5} M) in THF/80% water and MeOH/40% water**.**

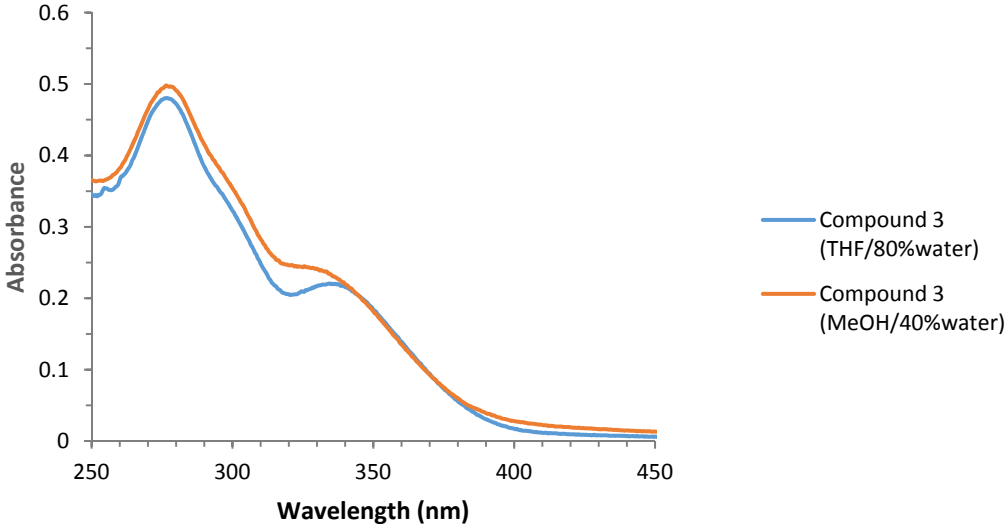

Figure S7. UV-vis spectrum of compound **3** (10^{-5} M) in THF/80%water and MeOH/40%water**.**

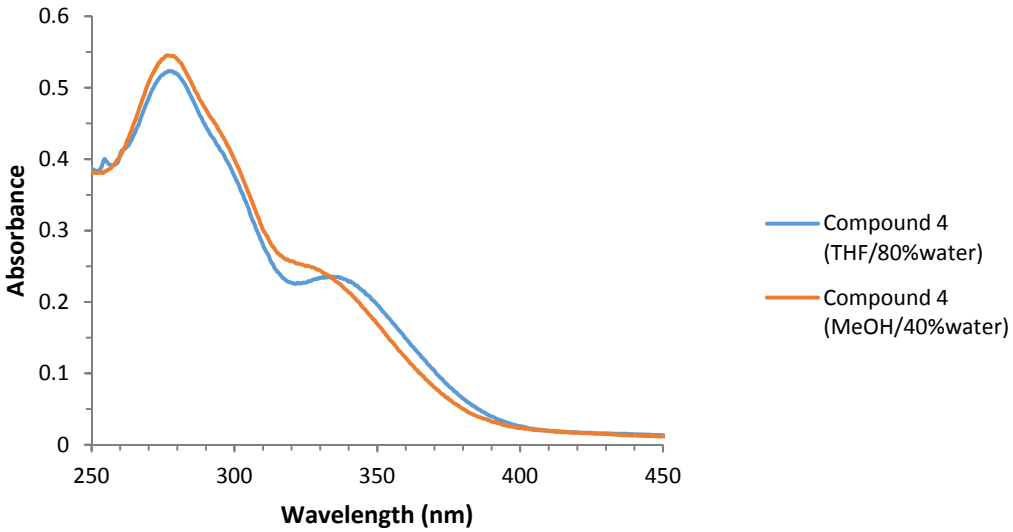

Figure S8. UV-vis spectrum of compound **4** (10^{-5} M) in THF /80%water and MeOH/40%water**.**

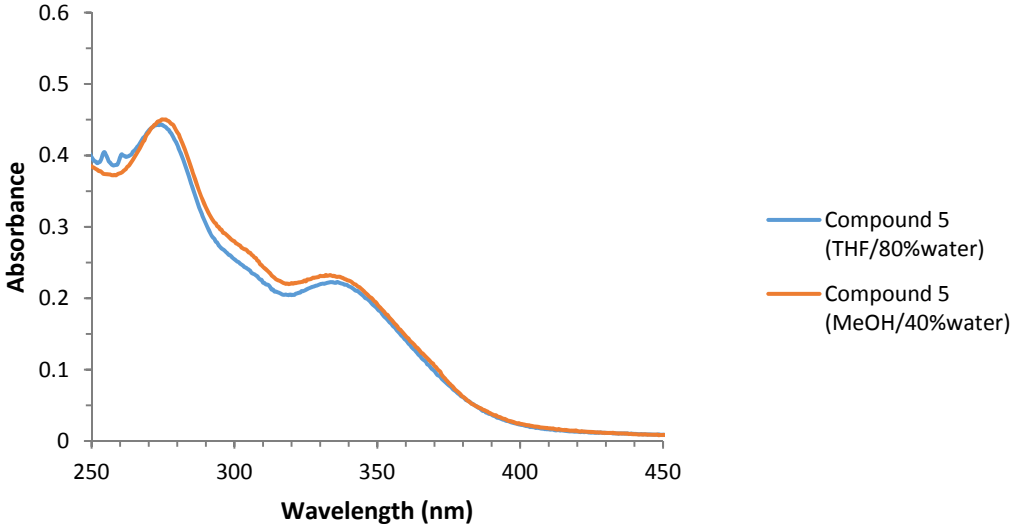

Figure S9. UV-vis spectrum of compound **5** (10^{-5} M) in THF/80%water and MeOH/40%water**.**

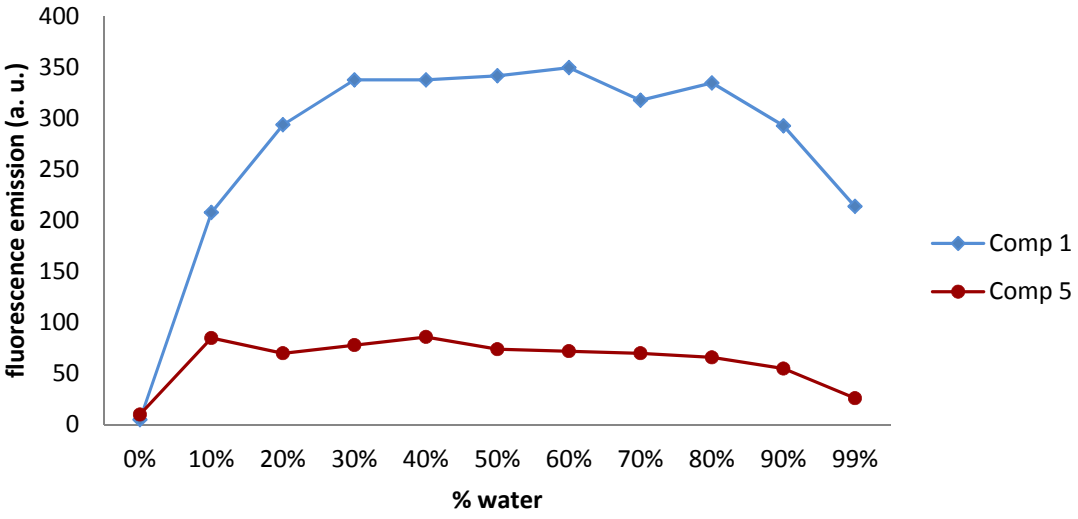

Figure S10. Enhancement of the fluorescence emission of compounds **1** and **5** *versus* f_w

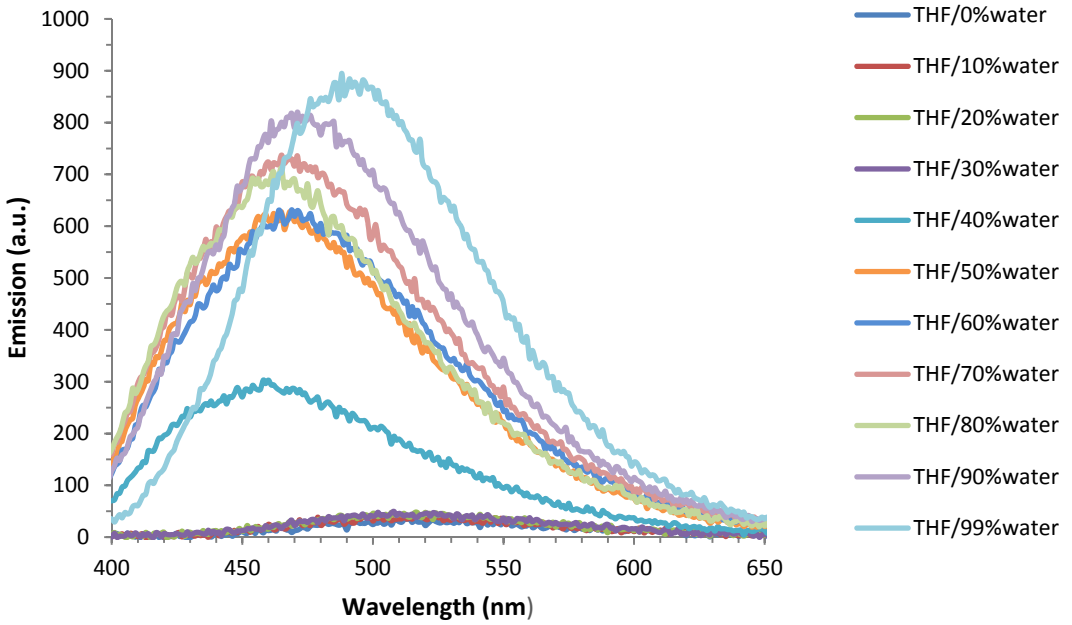

Figure S11. Steady-state fluorescence spectra of **1** (10^{-5} M) in THF/water (λ_{ex} = 350 nm, slits 5 nm/5 nm).

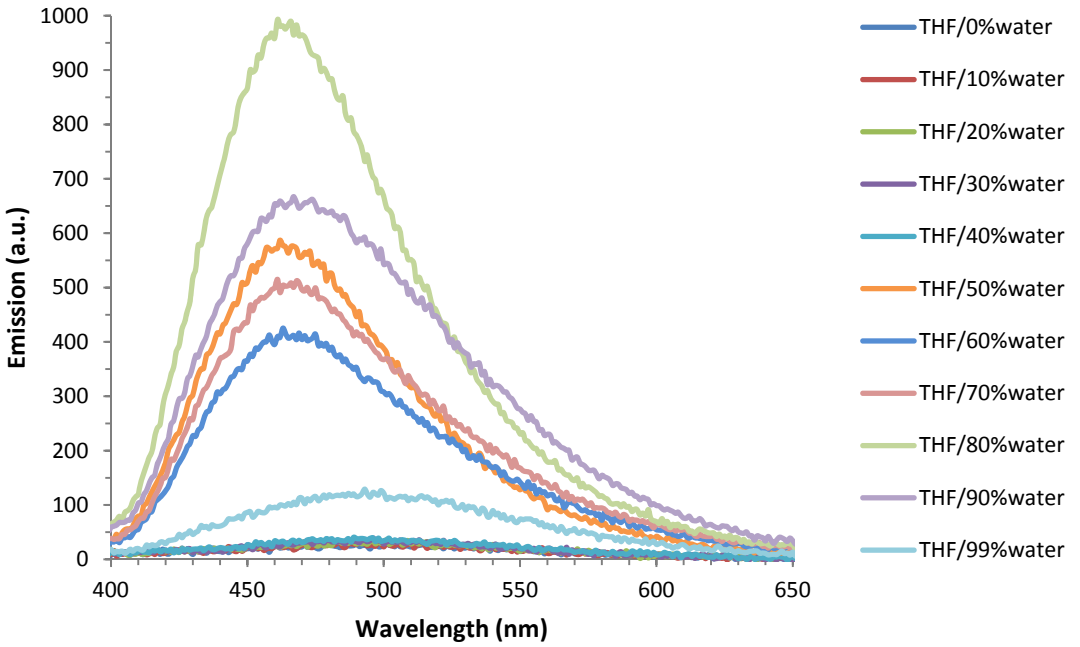

Figure S12. Steady-state fluorescence spectra of **5** (10^{-5} M) in THF/water (λ_{ex} = 350 nm, slits 5 nm/5 nm).

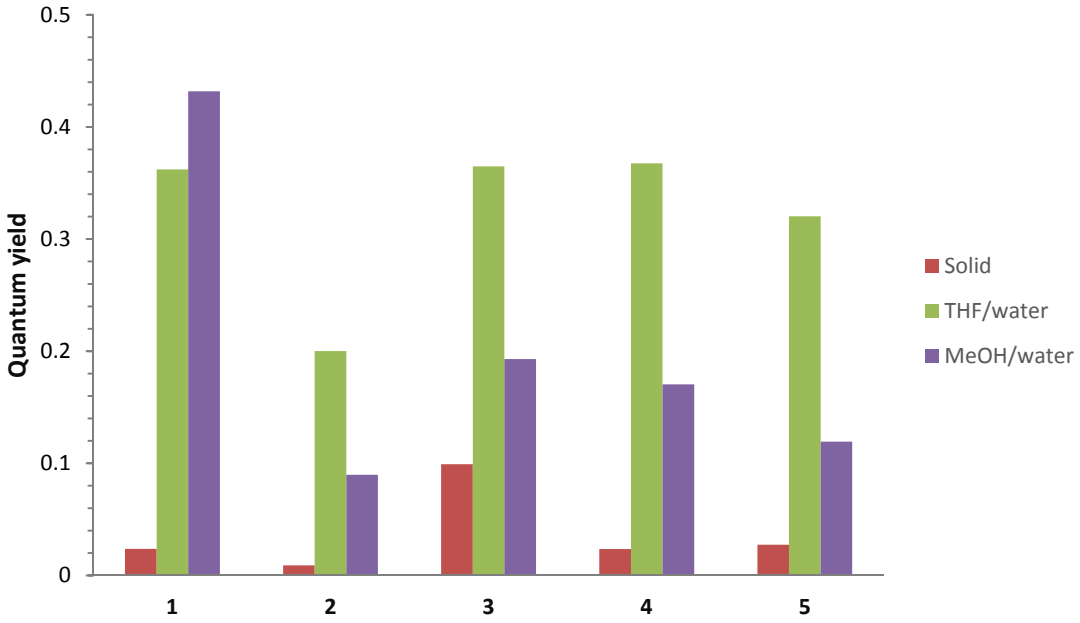

Figure S13. Comparative study for compounds **1**-**5** in solid state, THF and MeOH with increasing amounts of water. THF/water mixtures: **1** 99% water, **2** 90% water, **3 4 5** 80% water. MeOH/water mixtures: **1** 60% water, **2** 90% water, **3** 70% water, **4** 60% water, **5** 40% water.

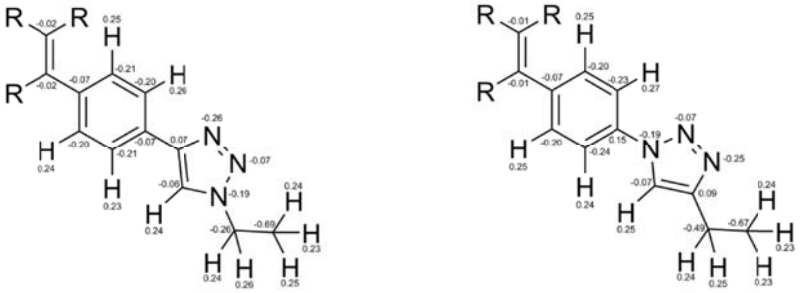

Figure S14. The formal charges estimated for the model compounds (left) for **1** and (right) for **5**.

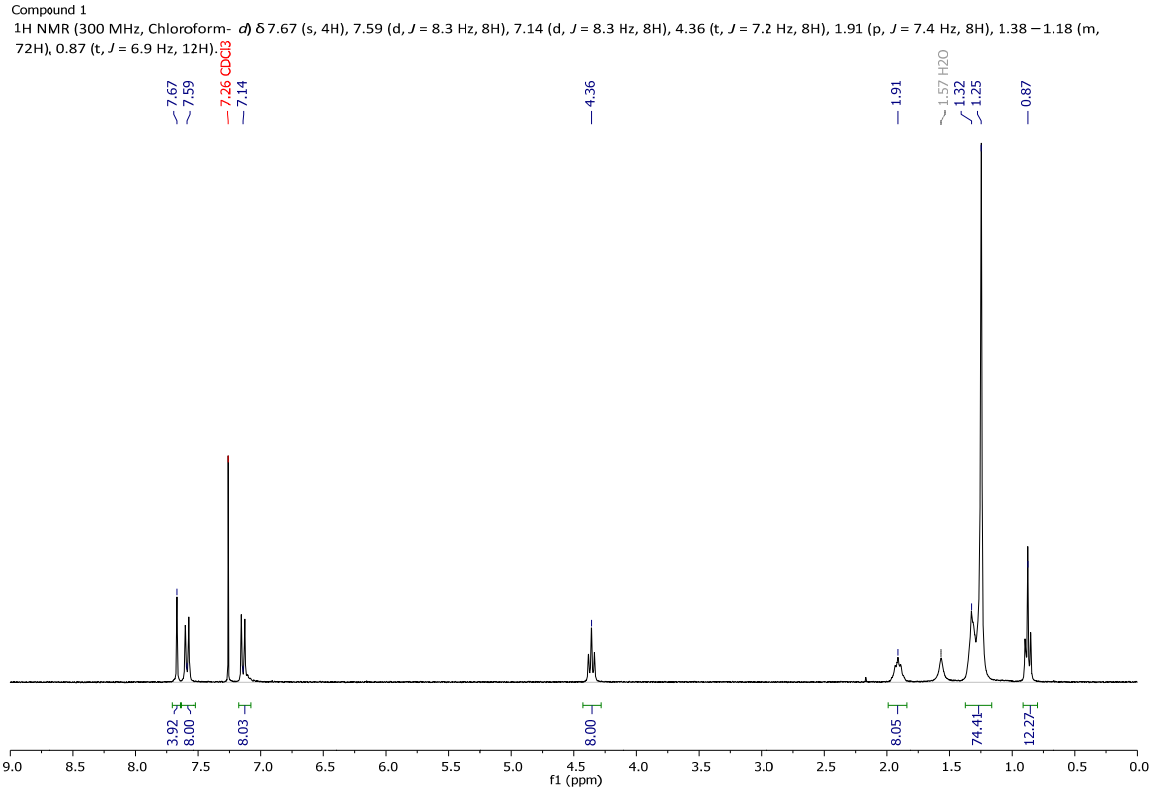

Figure S15. ^{1}H-NMR spectra of compound **1**.

Compound 1 ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.64, 143.46, 140.77, 132.08, 129.13, 125.36, 119.61, 50.57, 32.04, 29.73, 29.47, 29.15, 26.63, 22.82, 14.26.

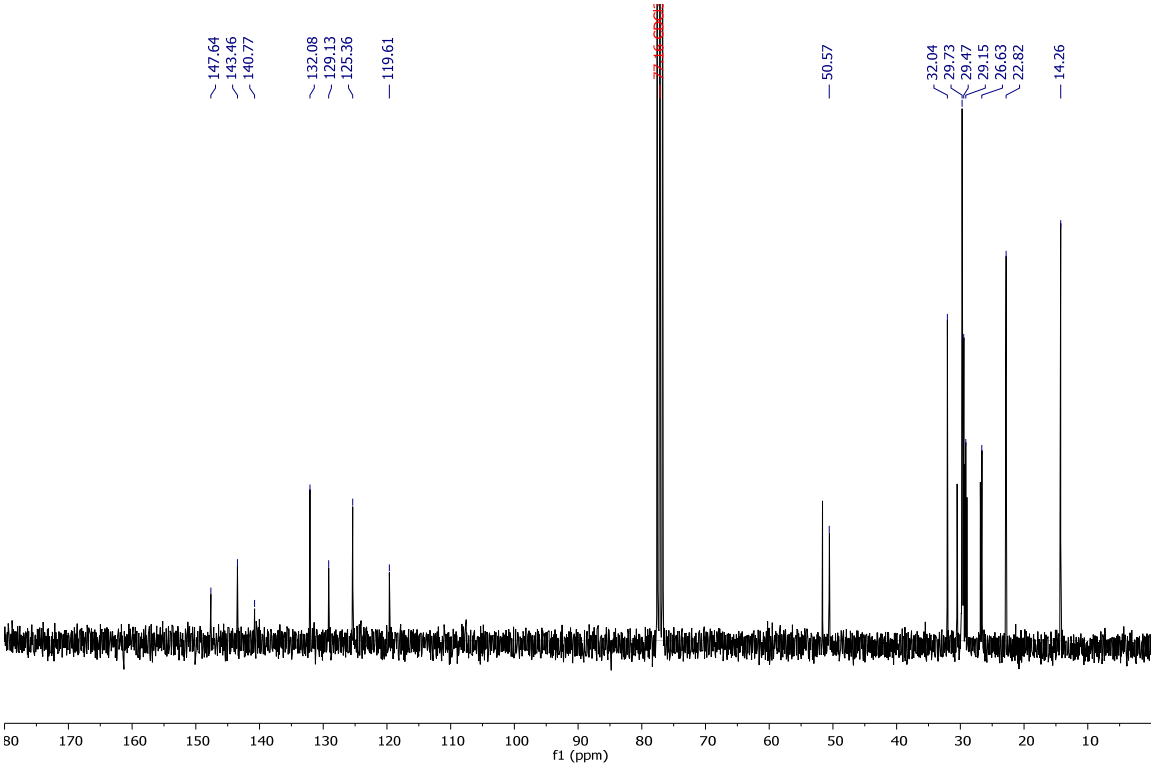

Figure S16. ^{13}C-NMR spectra of compound **1**.

Compound 2 ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.68 (s, 4H), 7.55 (d, *J* = 8.6 Hz, 8H), 7.22 (d, *J* = 8.6 Hz, 8H), 2.78 (t, *J* = 7.7 Hz, 8H), 1.70 (p, *J* = 7.4 Hz, 8H), 1.41 (h, *J* = 7.3 Hz, 8H), 0.94 (t, *J* = 7.3 Hz, 12H).

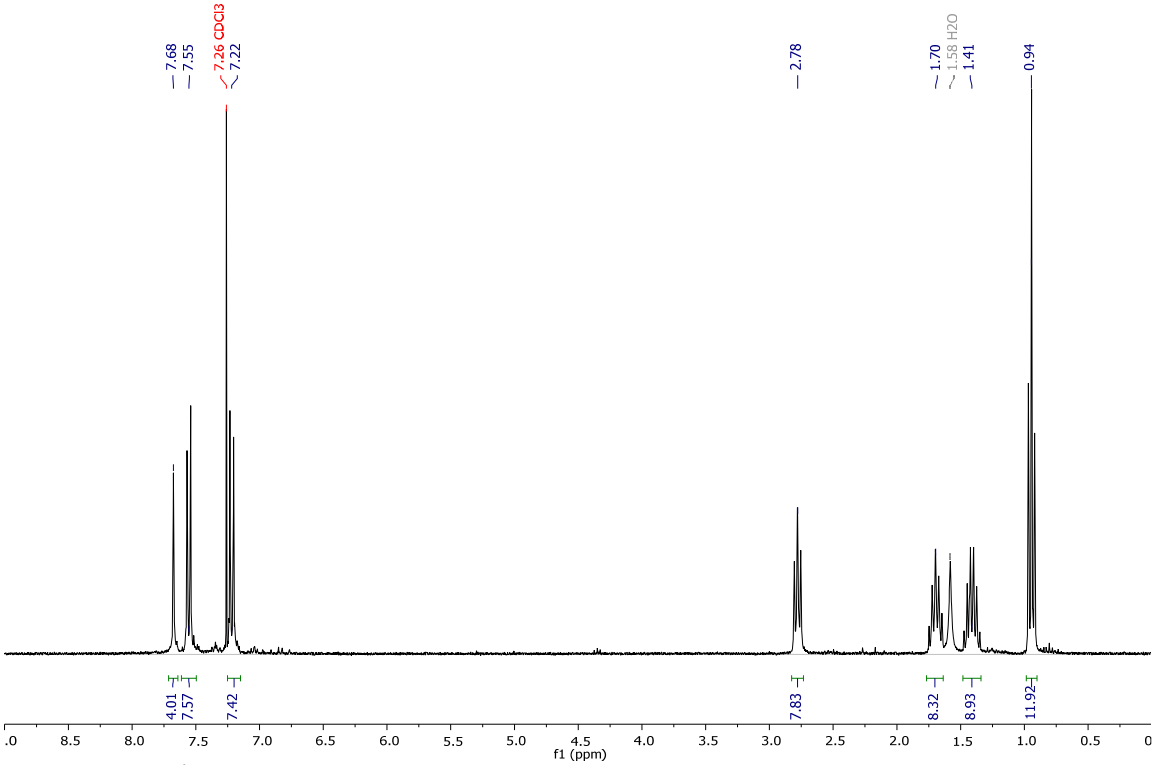

Figure S17. ^{1}H-NMR spectra of compound **2**.

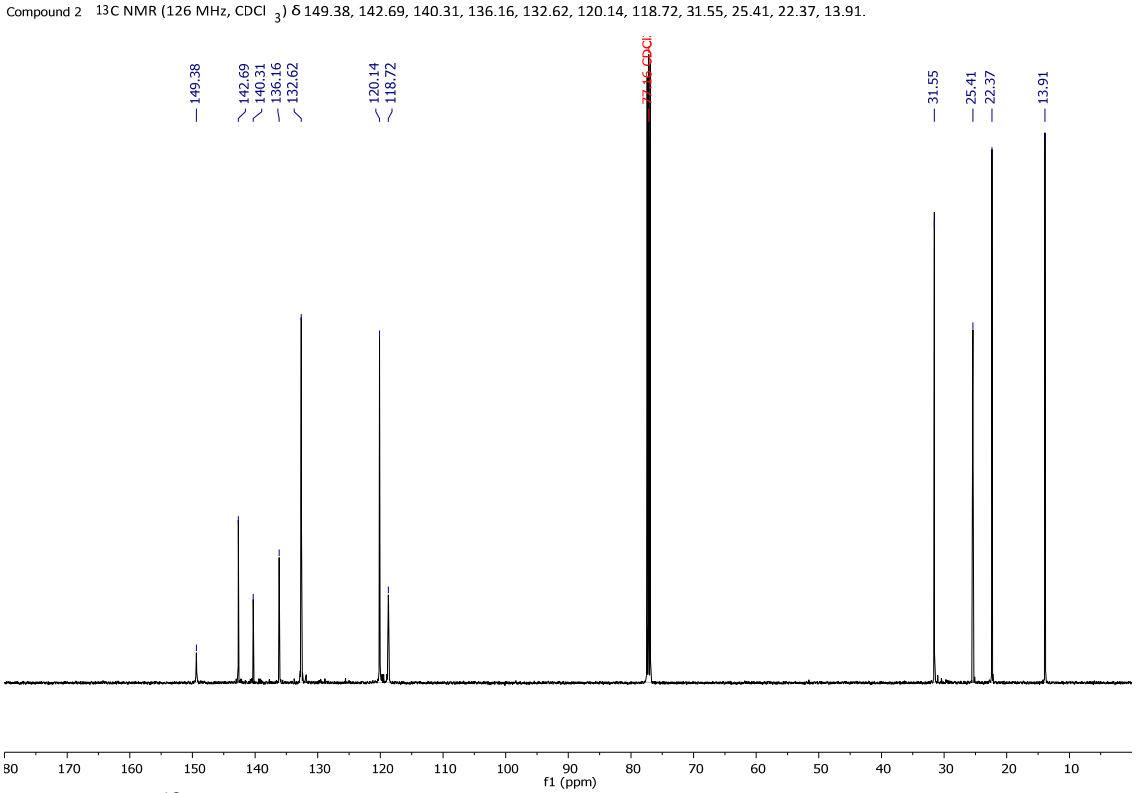

Figure S18. ^{13}C-NMR spectra of compound **2**.

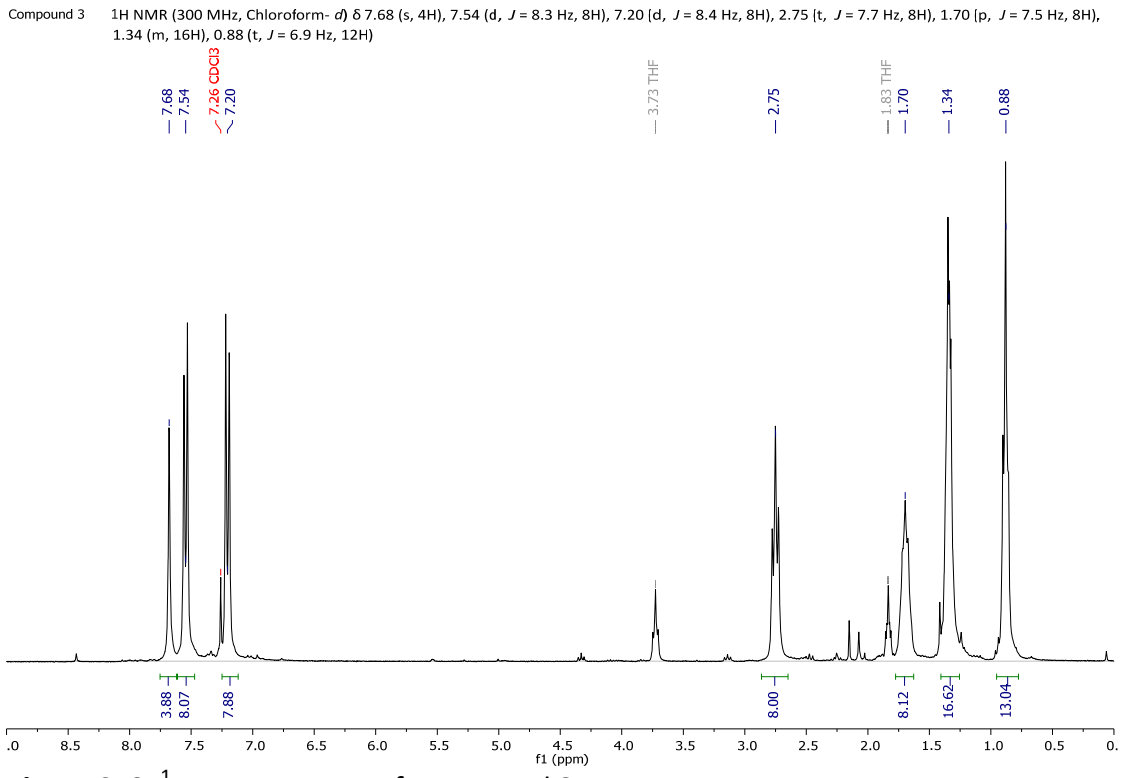

Figure S19. ^{1}H-NMR spectra of compound **3**.

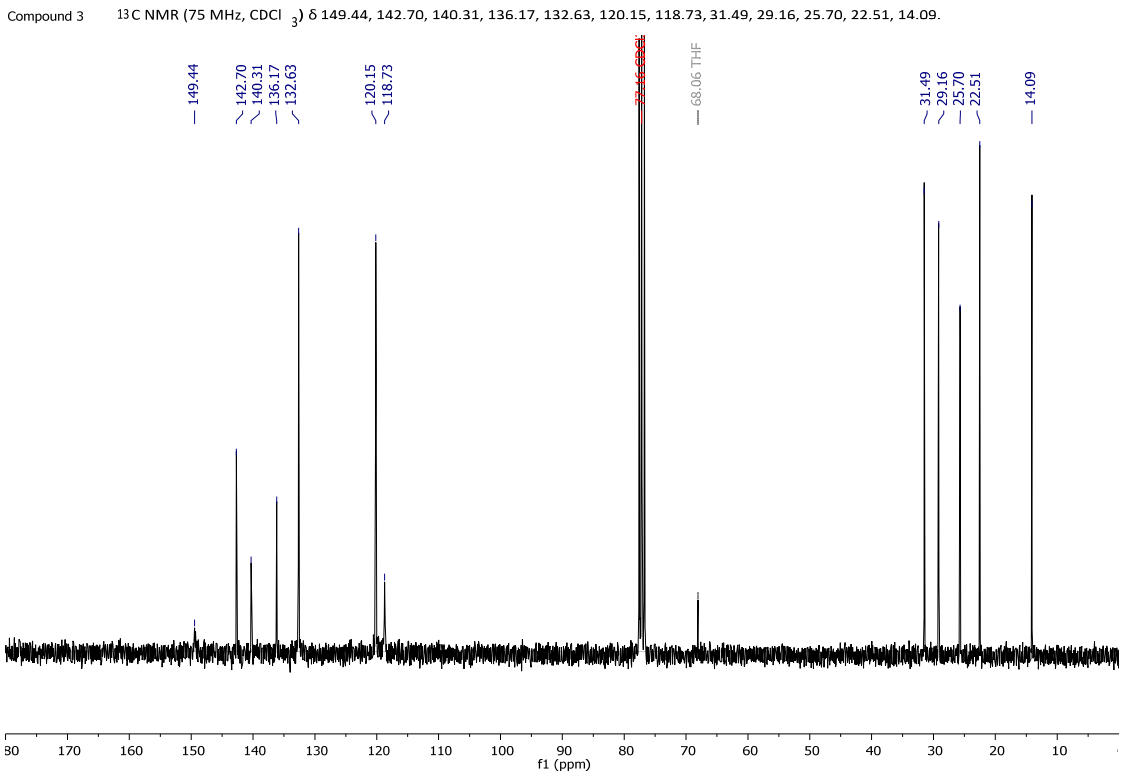

Figure S20. ^{13}C-NMR spectra of compound **3.**

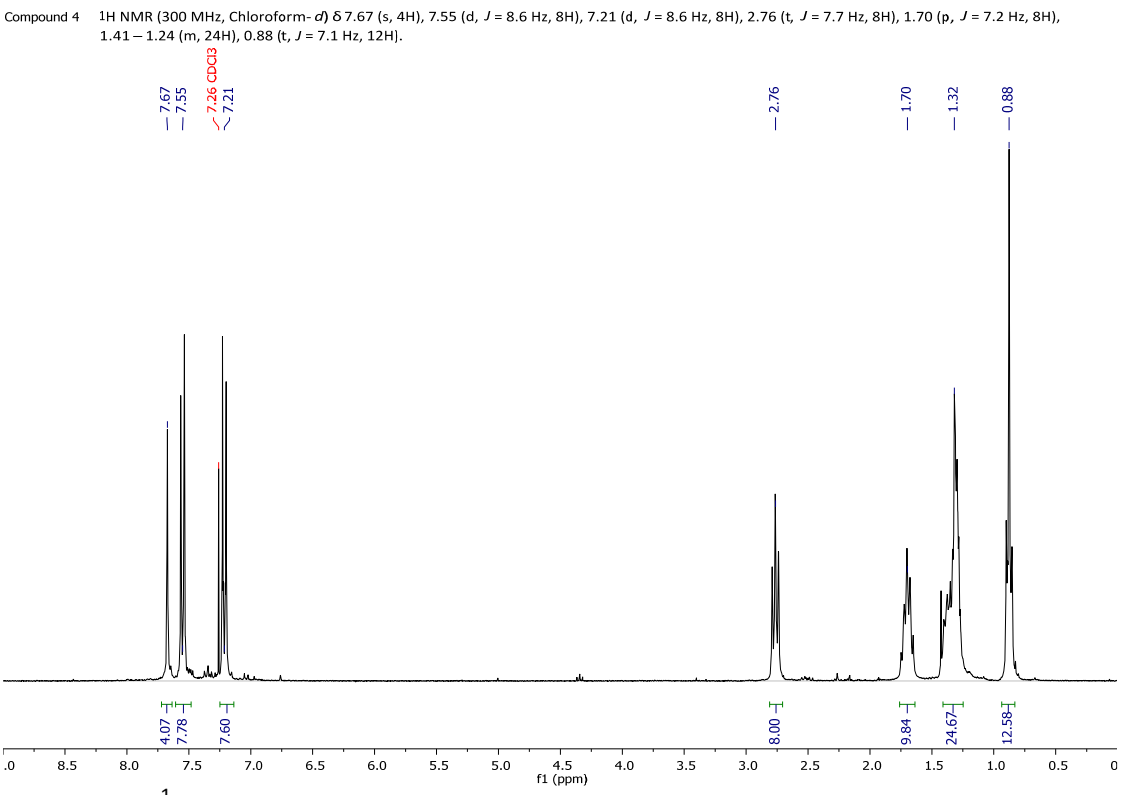

Figure S21. ^{1}H-NMR spectra of compound **4.**

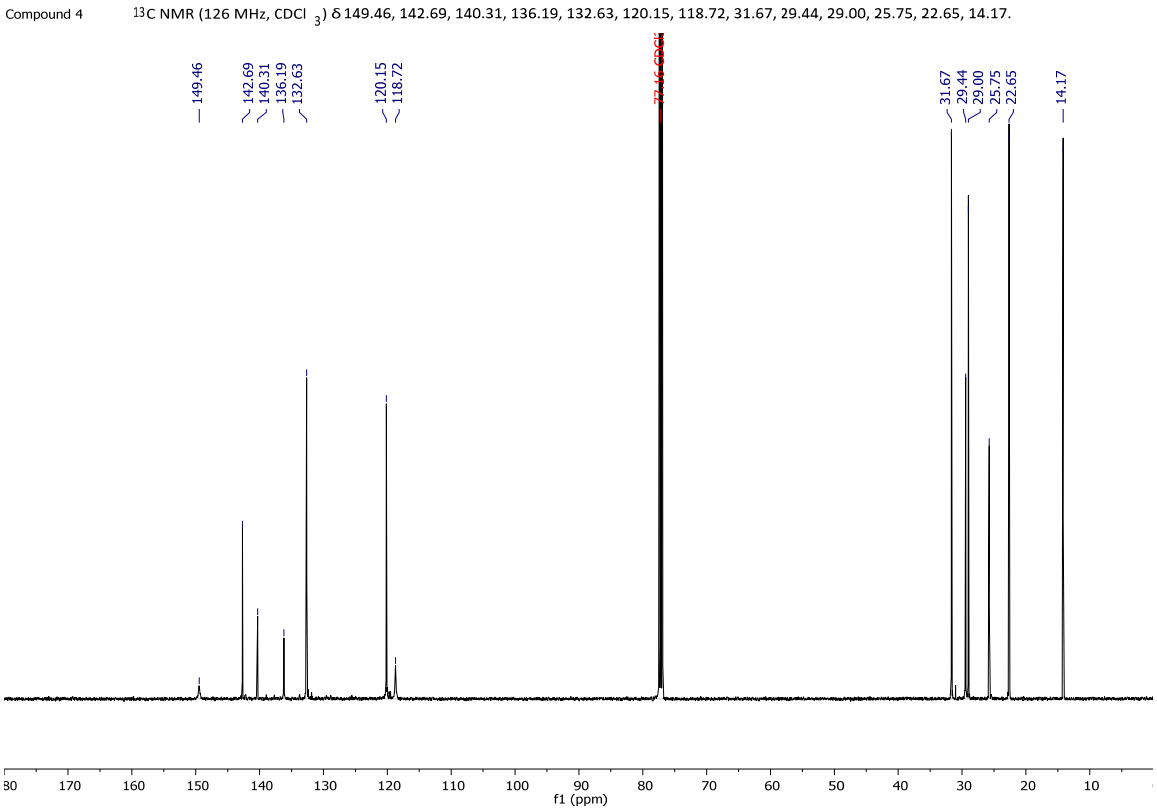

Figure S22. ^{13}C-NMR spectra of compound **4.**

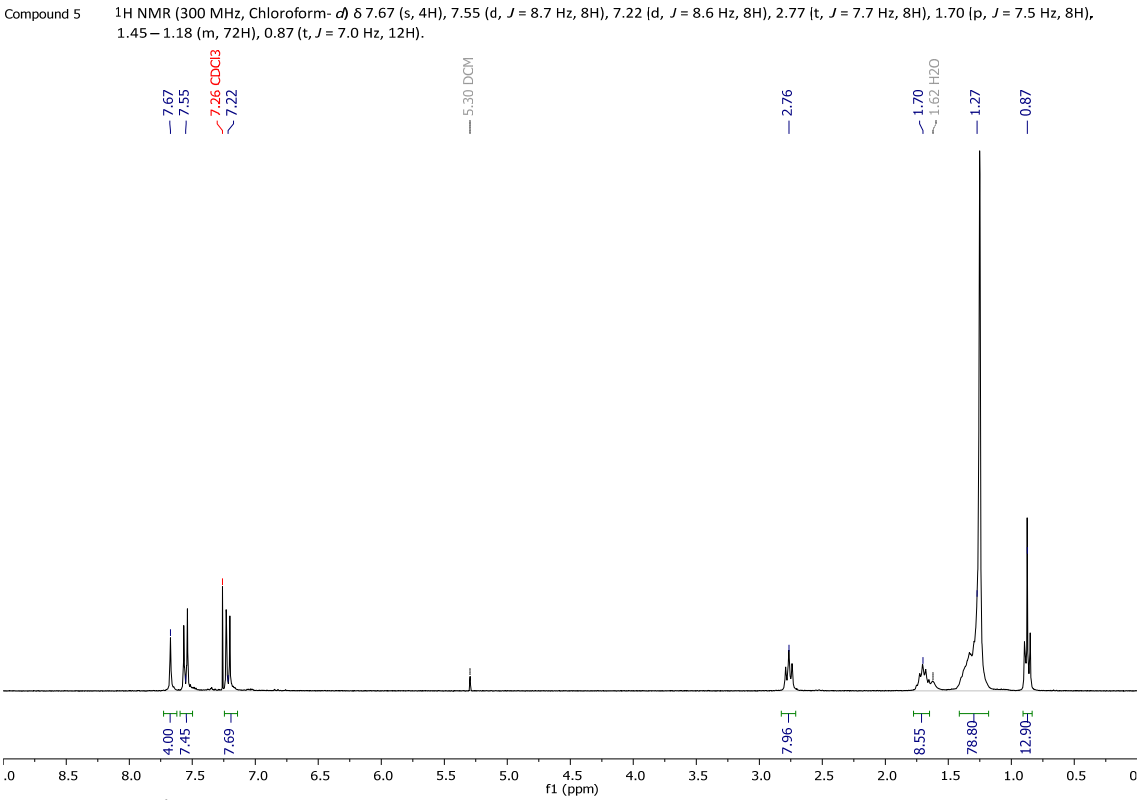

Figure S23. ^{1}H-NMR spectra of compound **5.**

Compound 5 ^{13}C NMR (75 MHz, CDCl$_3$) δ 149.52, 142.72, 140.33, 136.21, 132.66, 120.19, 118.74, 32.04, 29.77, 29.68, 29.51, 29.47, 29.39, 25.79, 22.81, 14.25.

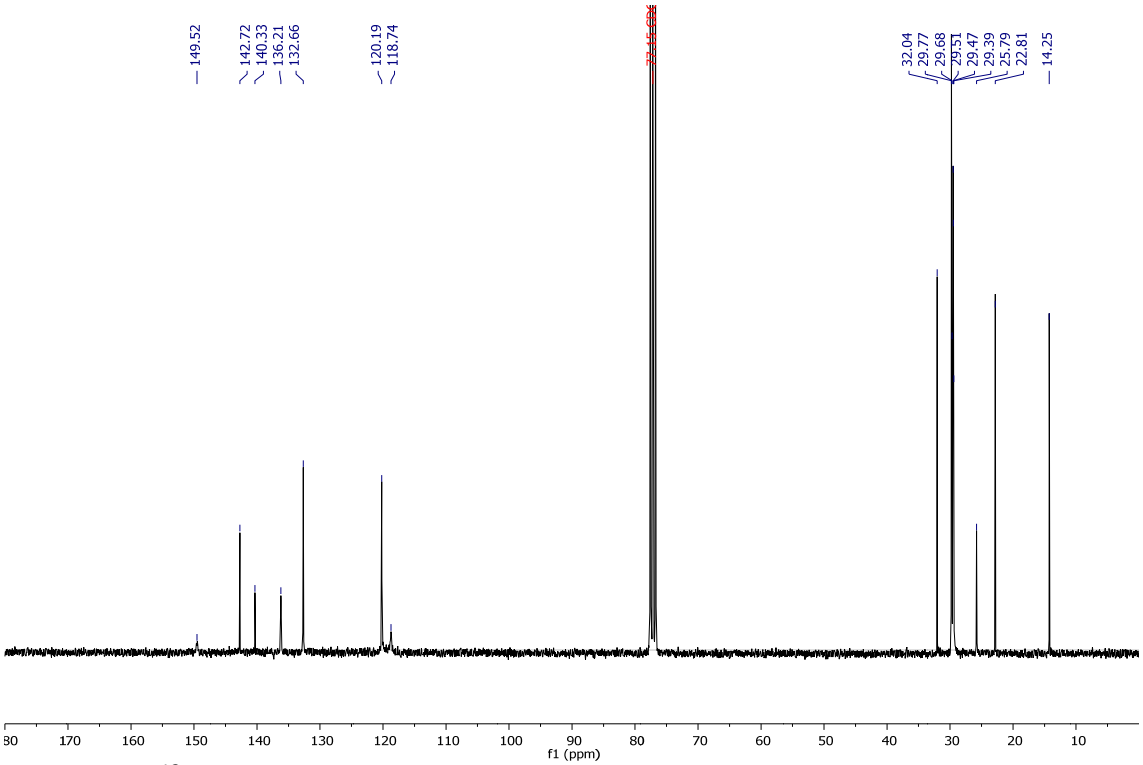

Figure S24. ^{13}C-NMR spectra of compound **5.**

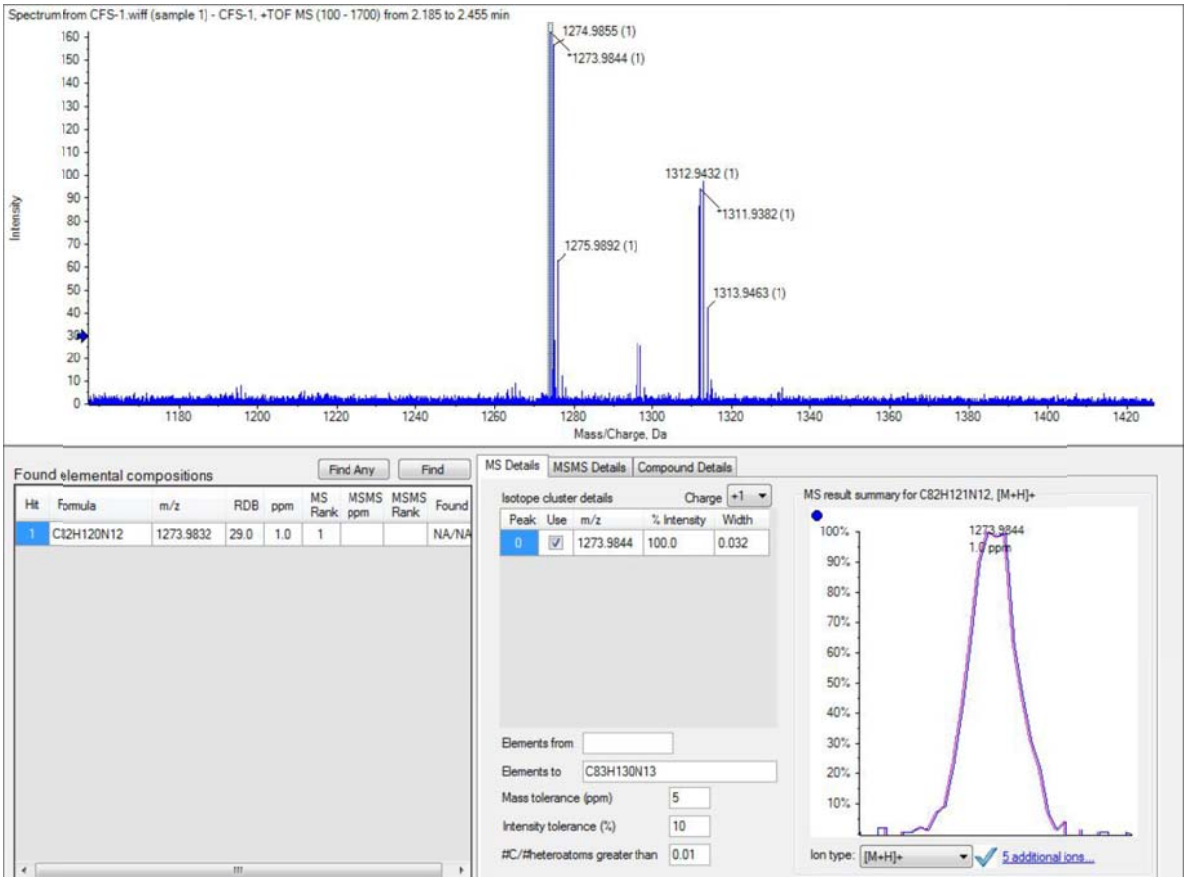

Figure S25. HRMS (ESI) for compound **1**.

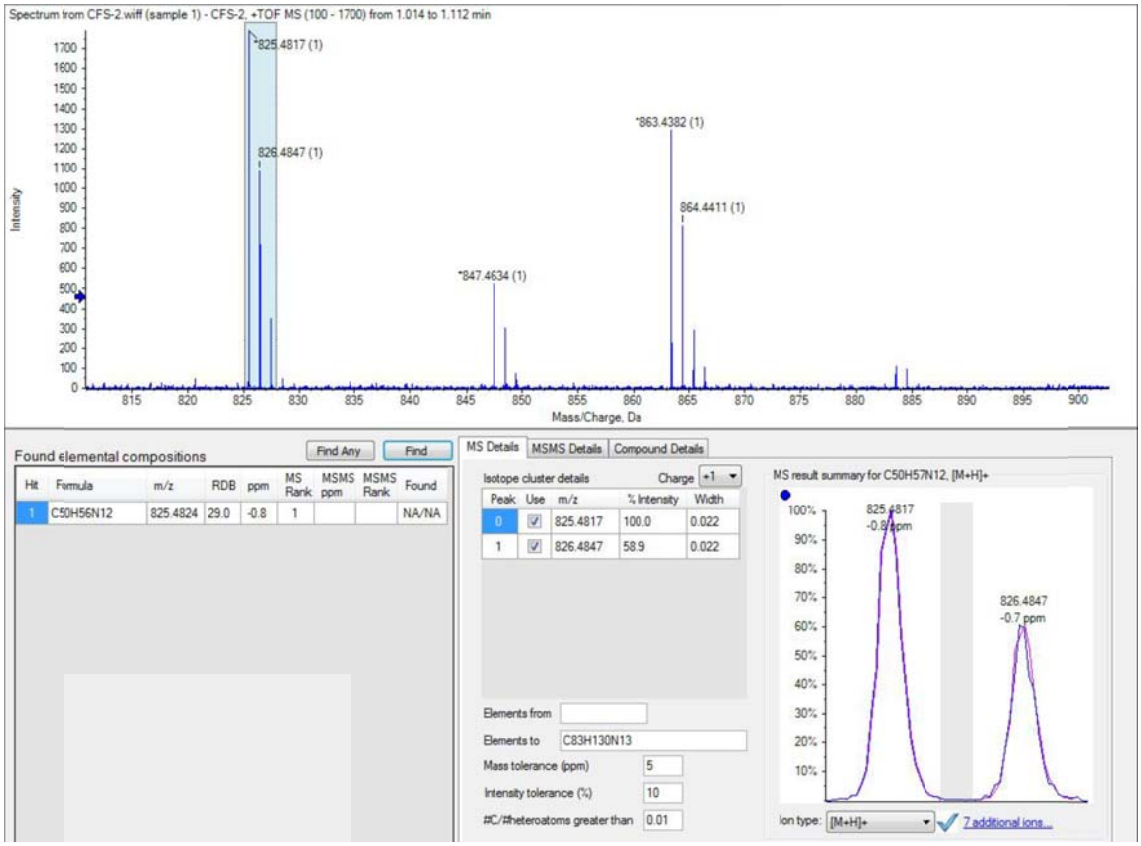

Figure S26. HRMS (ESI) for compound **2**.

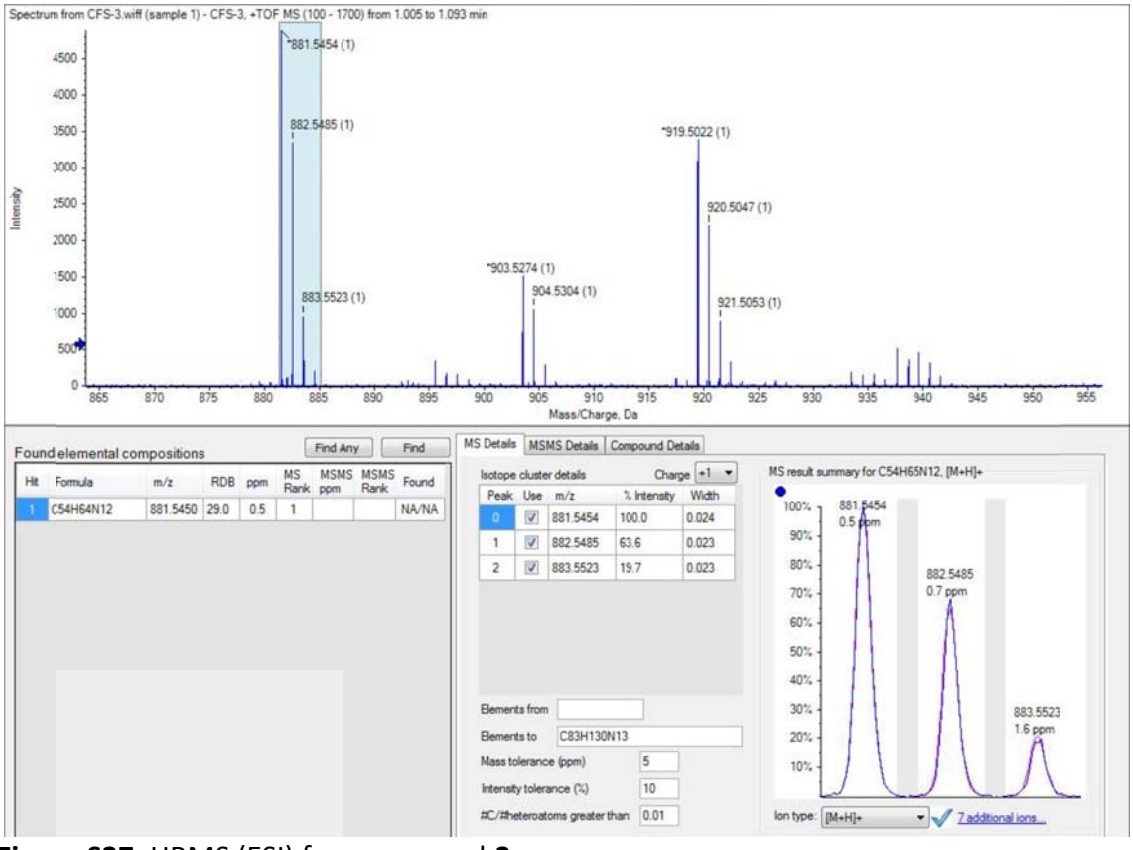

Figure S27. HRMS (ESI) for compound **3**.

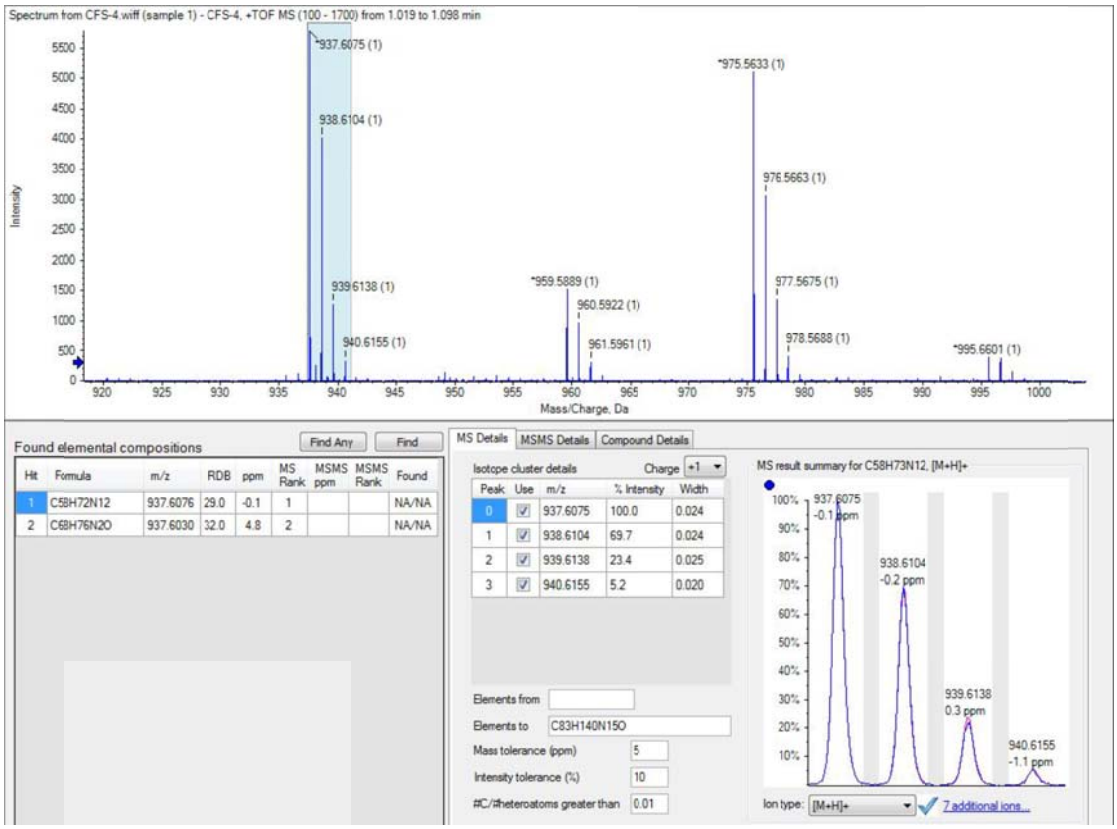

Figure S28. HRMS (ESI) for compound **4**.

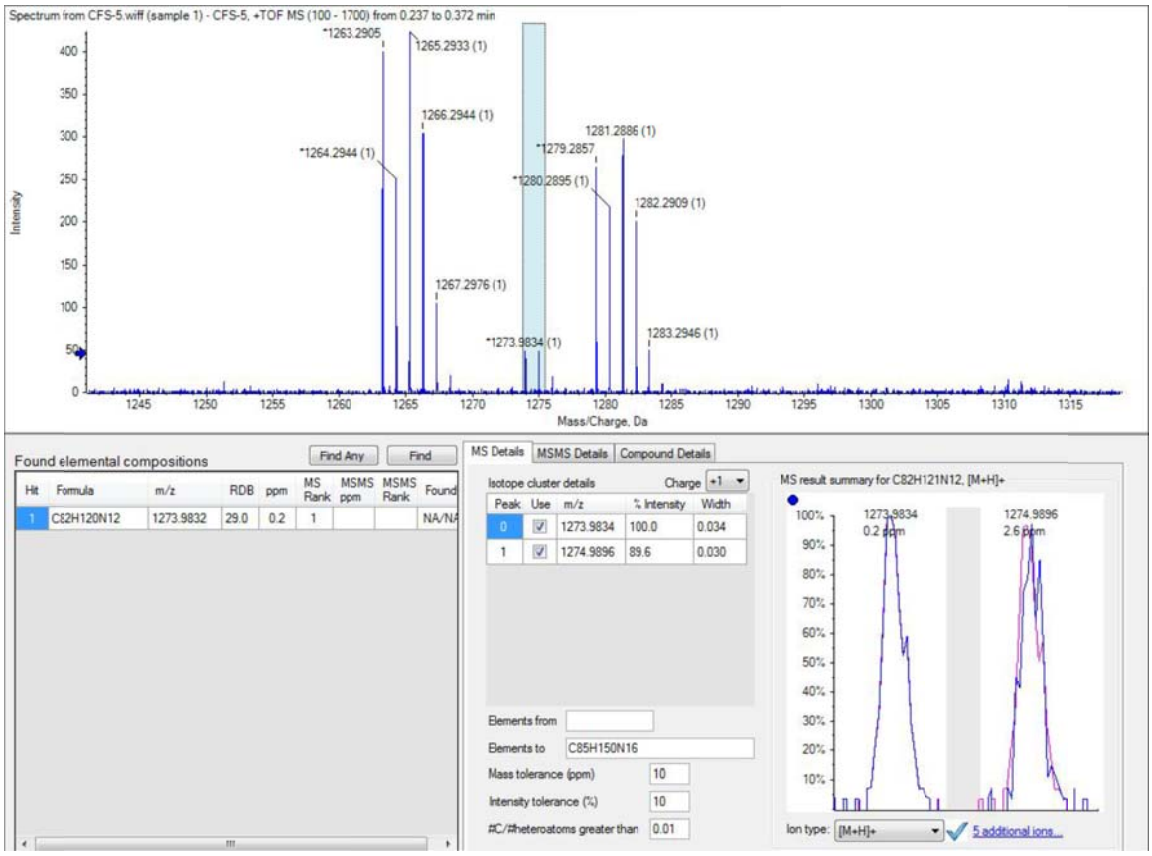

Figure S29. HRMS (ESI) for compound **5**.