Supporting Information

Controlled keto-enol tautomerism of coumarin containing β-ketodithioester by its encapsulation in cucurbit[7]uril.

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Contents **Page**

Figure S1A. ^{1}H NMR spectrum for **CAM1** alone in DMSO-d_6. S-3

Figure S1B. ^{1}H NMR spectrum for **CAM1** alone in CD_3CN. S-3

Figure. S2. ^{13}C NMR spectrum for **CAM1** alone in DMSO-d_6. S-4

Figure S3. HRMS of **CAM1** (2mM) in water-DMSO (99:1, v/v) solution. S-4

Figure S4A. ^{1}H NMR spectrum for **CAM2** alone in DMSO-d_6. S-5

Figure S4B. ^{1}H NMR spectrum for **CAM2** alone in CD_3CN. S-5

Figure S5. ^{13}C NMR spectrum for **CAM2** alone in DMSO-d_6. S-6

Figure S6. ^{13}C NMR-DEPT spectrum for **CAM2** alone in DMSO-d_6. S-6

Figure S7. COSY spectrum of **CAM2** alone in DMSO-d_6. S-7

Figure S8. ^{1}H-HMQC spectrum of **CAM2** alone in DMSO-d_6. S-7

Figure S9. ^{1}H-HMBC spectrum of **CAM2** alone in DMSO-d_6. S-8

Figure S10. HRMS-ESI of **CAM2** (2 mM) in water-DMSO (99:1, v/v) solution. S-8

Figure S11. Normalized UV-vis absorption spectra of; A) coumarin-derivative **CAM1** dye (2 μM) and B) coumarin-derivative dye **CAM2** (4 μM), in different solvents. S-9

Figure S12. Comparison of partial ^{1}H NMR spectra for: A) **CAM1** alone in CD_3CN/D_2O and B) **CAM1** and CB7 (3 eq.). S-9

Figure S13. Comparison of partial ^{1}H NMR spectra for: A) **CAM1** alone in CD_3CN/D_2O and B) **CAM1** and CB7 (3 eq.). S-10

Figure S14. Comparison of partial ^{1}H NMR spectra (400 MHz) for: A) Intermediate **2** alone in CD_3CN/D_2O and B) Intermediate **2** and CB7 (3 eq.). S-10

Figure S15. ESI mass spectra of a 1:10 molar ratio in aqueous solution of coumarin-derivative **CAM1** and CB7, respectively. S-11

Figure S16. Normalized excitation and emission spectra of dyes: A) **CAM1** and (B) **CAM2**, in aqueous solutions. S-11

Figure S17. Job plot for the complexes **CAM1-CB7** and **CAM2-CB7** S-12

Figure S18. HRMS-ESI of a 1:10 molar ratio in aqueous solution of coumarin-derivative A) **CAM1** and CB7, and B) **CAM2** and CB7, respectively. S-12

Figure S19. Comparison of partial ^{1}H NMR spectra (200 MHz) for: A) **CAM2** alone in CD_3CN/D_2O, B) **CAM2** and CB7 (3 eq.) and C) **CAM2** and β-CD (3 eq.). S-13

Figure S20. A) Fluorescence spectra of **CAM1** with increasing concentrations of CB7. Inset shows the fluorescence titration of **CAM1** with CB7. B) Determination of the effective binding constant by fitting data to a 1:1 host:guest model. S-13

Table S1. Binding energy from docking studies for **CAM1** and **CAM2** in CB7 and β-CD. S-14

A)

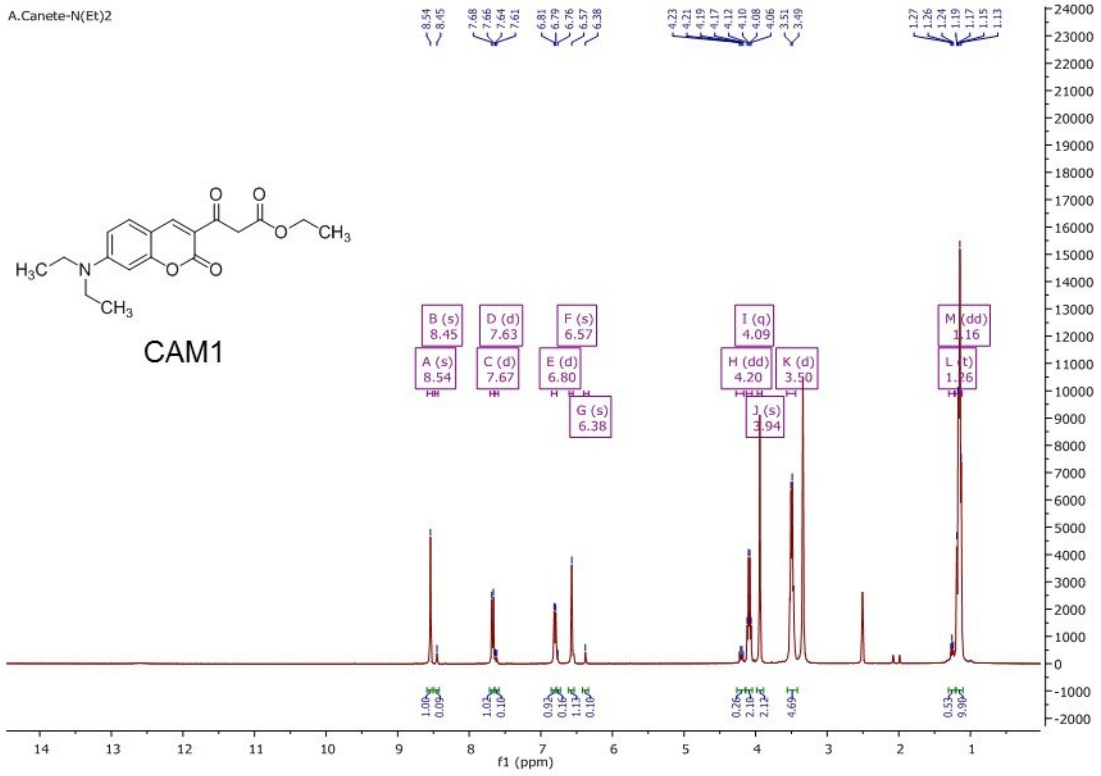

Figure S1A. ^{1}H NMR spectrum (400 MHz) for **CAM1** alone in DMSO-d_6.

B)

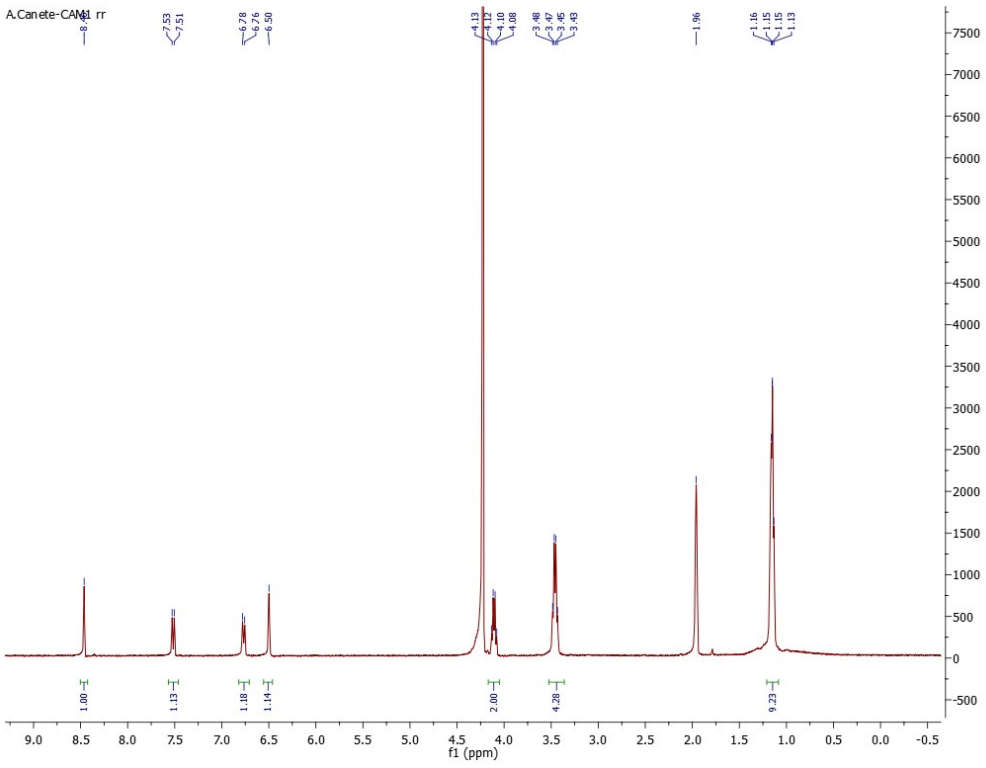

Figure S1B. ^{1}H NMR spectrum (400 MHz) for **CAM1** alone in CD_3CN.

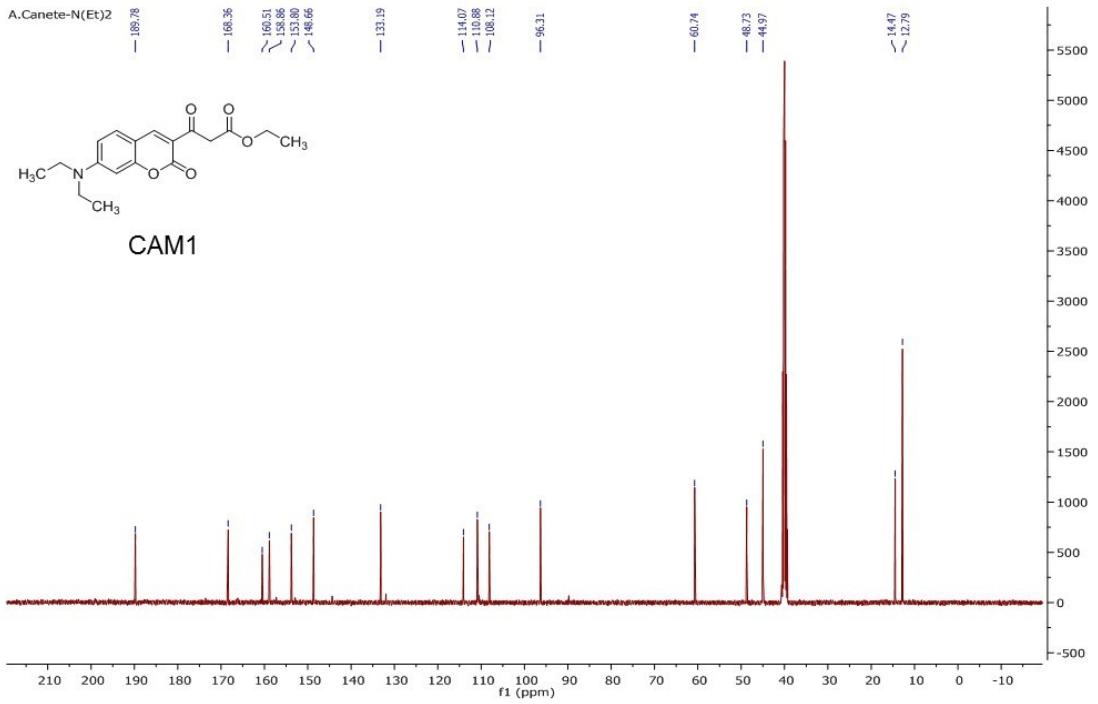

Figure S2. ^{13}C NMR spectrum (400 MHz) for **CAM1** alone in DMSO-d_6.

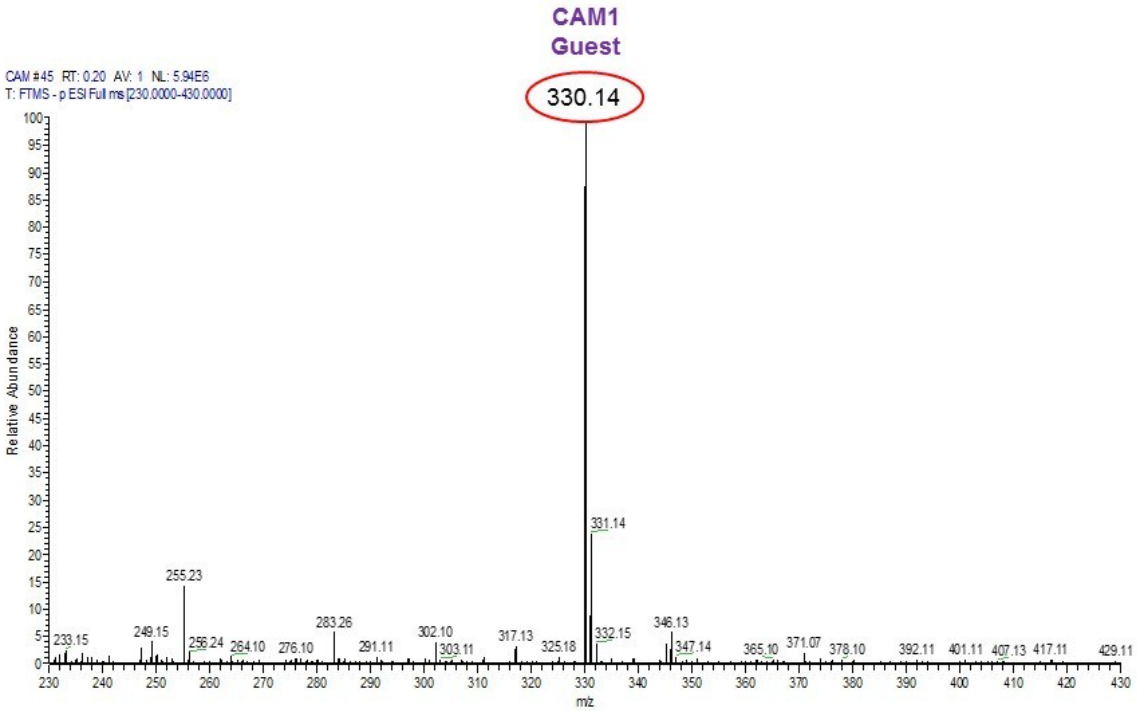

Figure S3. HRMS (ESI, negative mode) of **CAM1** (2mM) in water-DMSO (99:1, v/v) solution.

A)

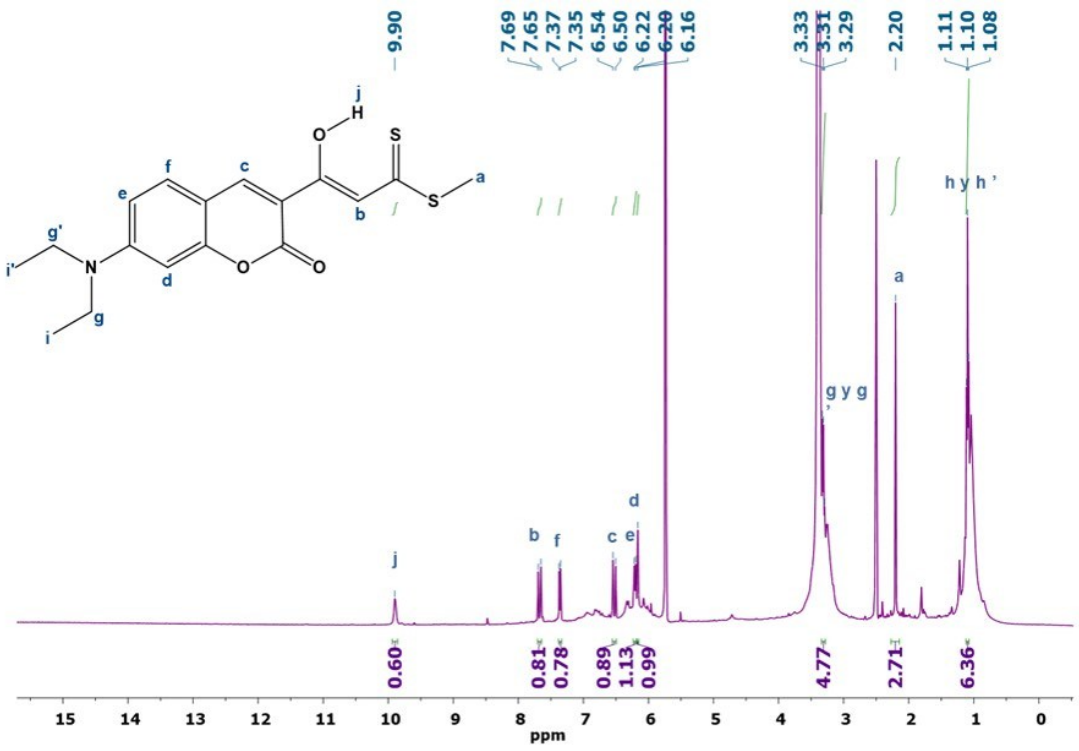

Figure S4A. ^{1}H NMR spectrum (400 MHz) for **CAM2** alone in DMSO-d_6.

B)

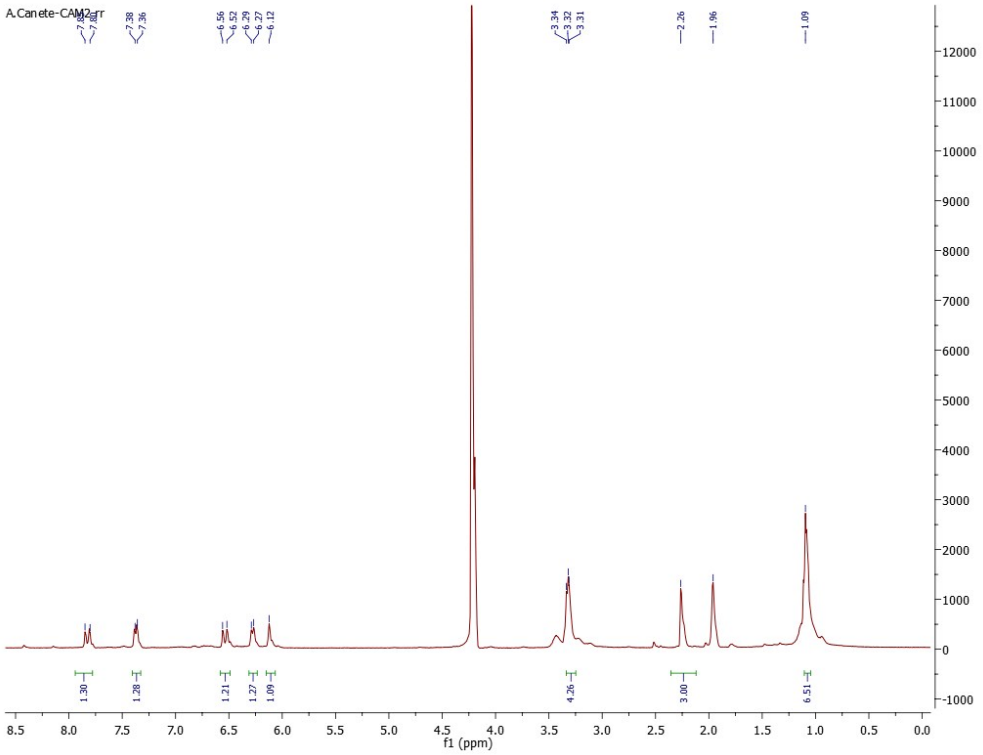

Figure S4B. ^{1}H NMR spectrum (400 MHz) for **CAM2** alone in CD_3CN.

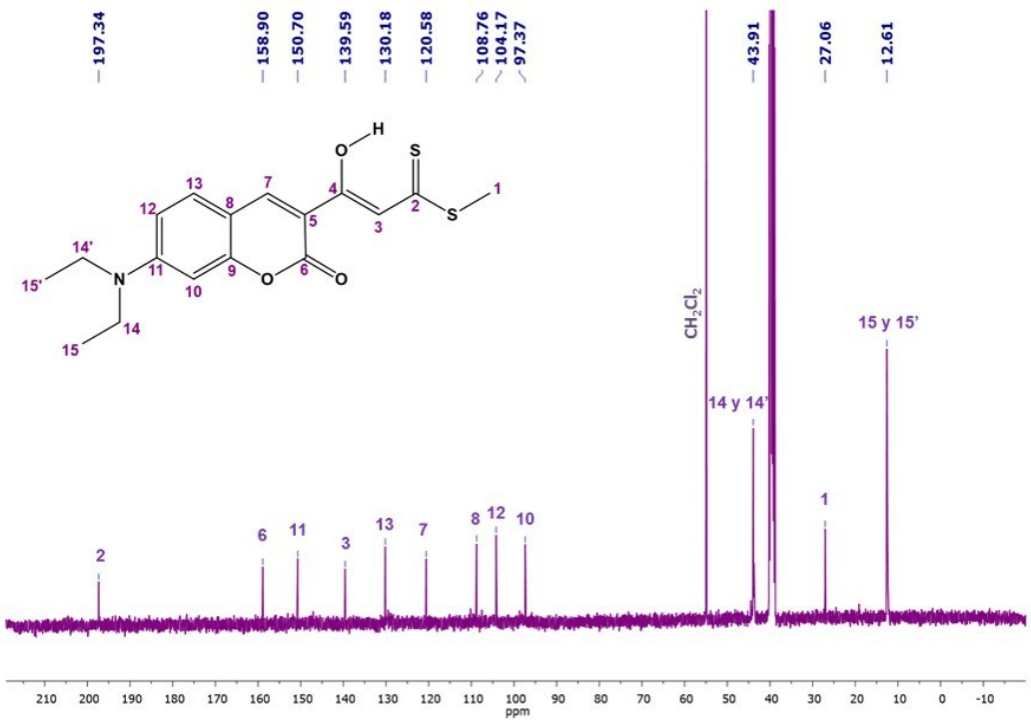

Figure S5. ^{13}C NMR spectrum (400 MHz) for **CAM2** alone in DMSO-d_6.

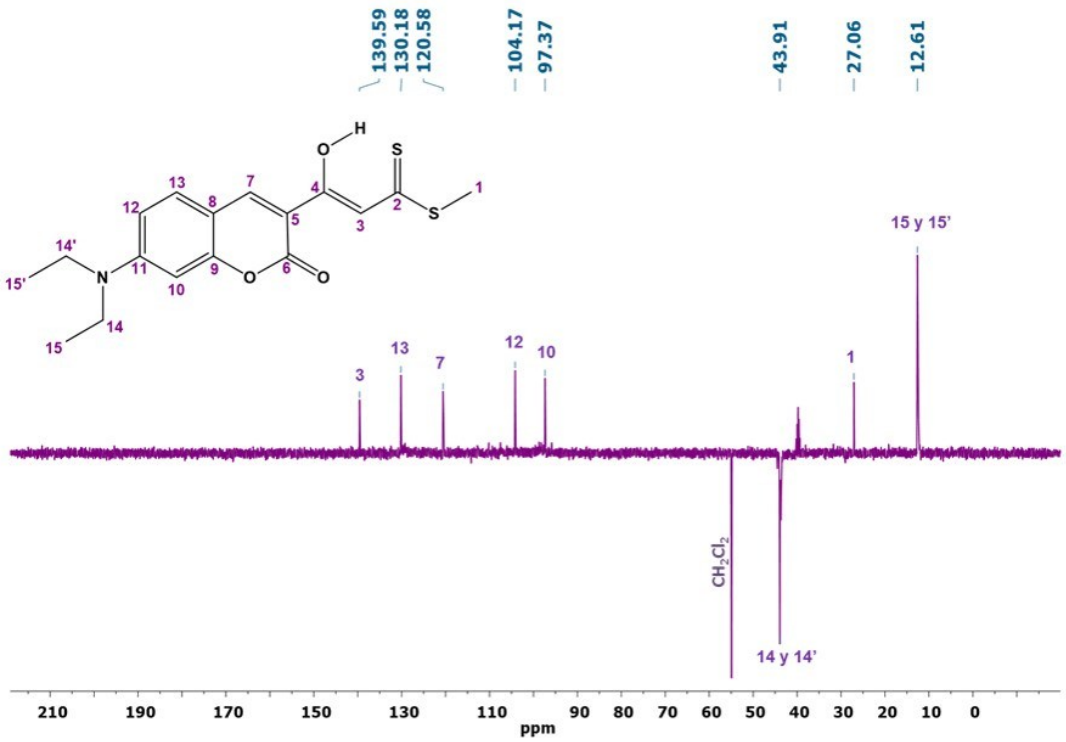

Figure S6. ^{13}C NMR-DEPT spectrum (101 MHz) for **CAM2** alone in DMSO-d_6.

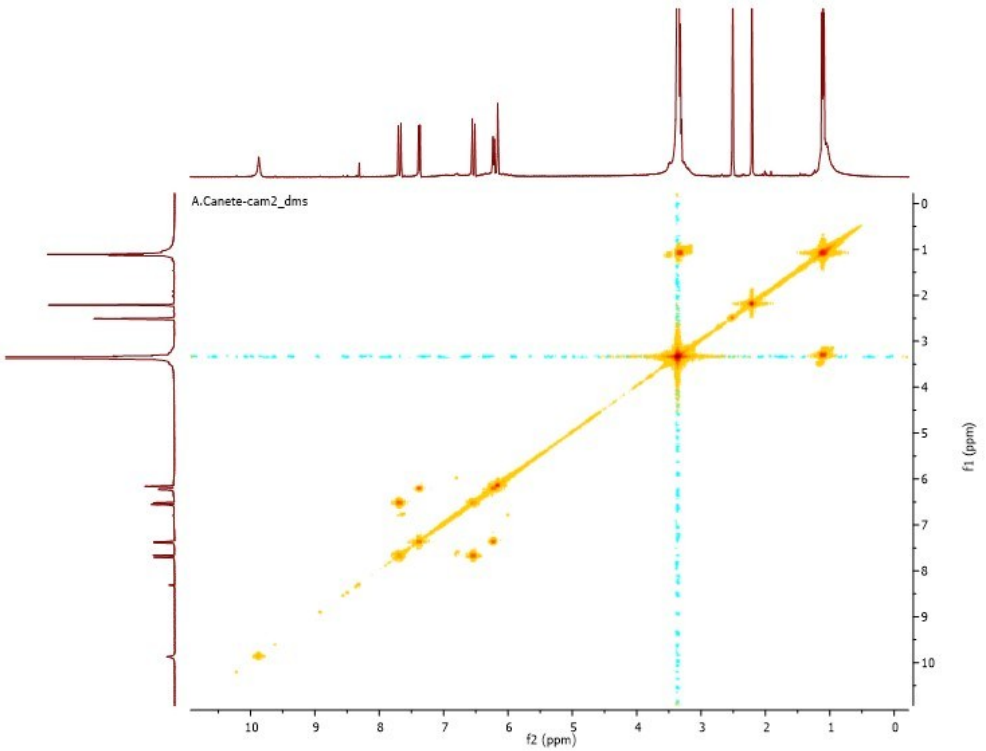

Figure S7. COSY spectrum (400 MHz) of **CAM2** alone in DMSO-d_6.

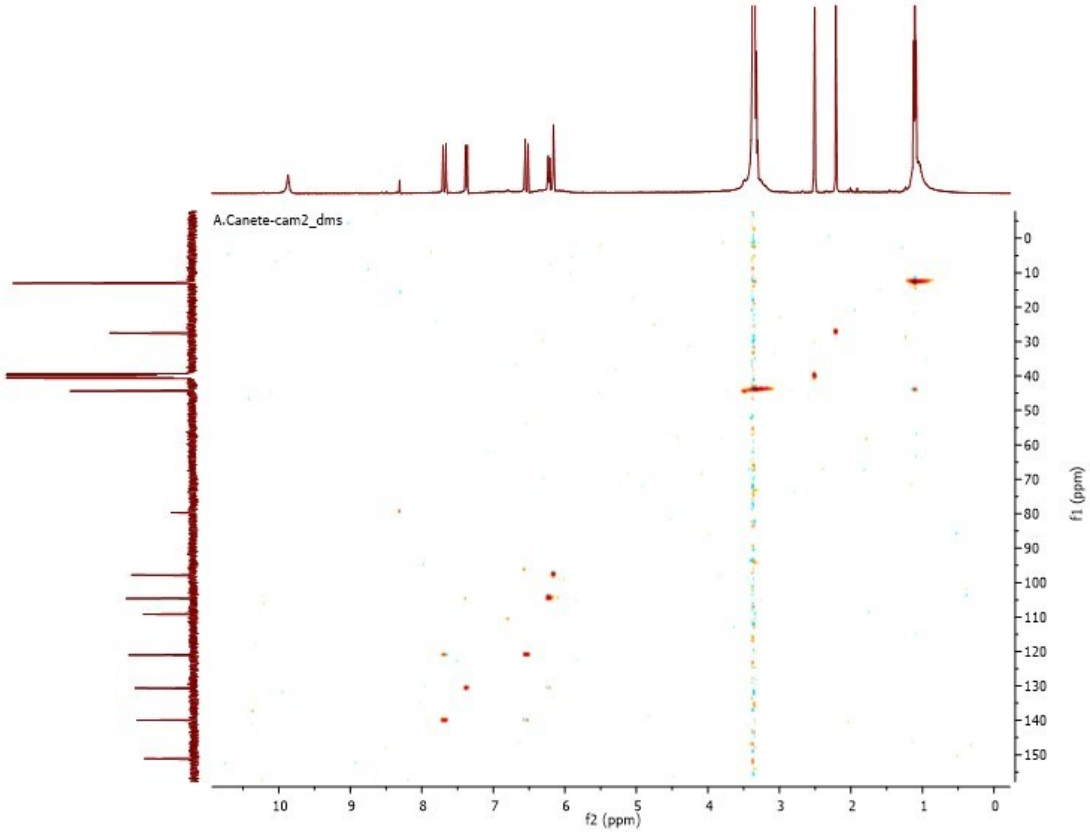

Figure S8. ^{1}H-HMQC spectrum (400 MHz) of **CAM2** alone in DMSO-d_6.

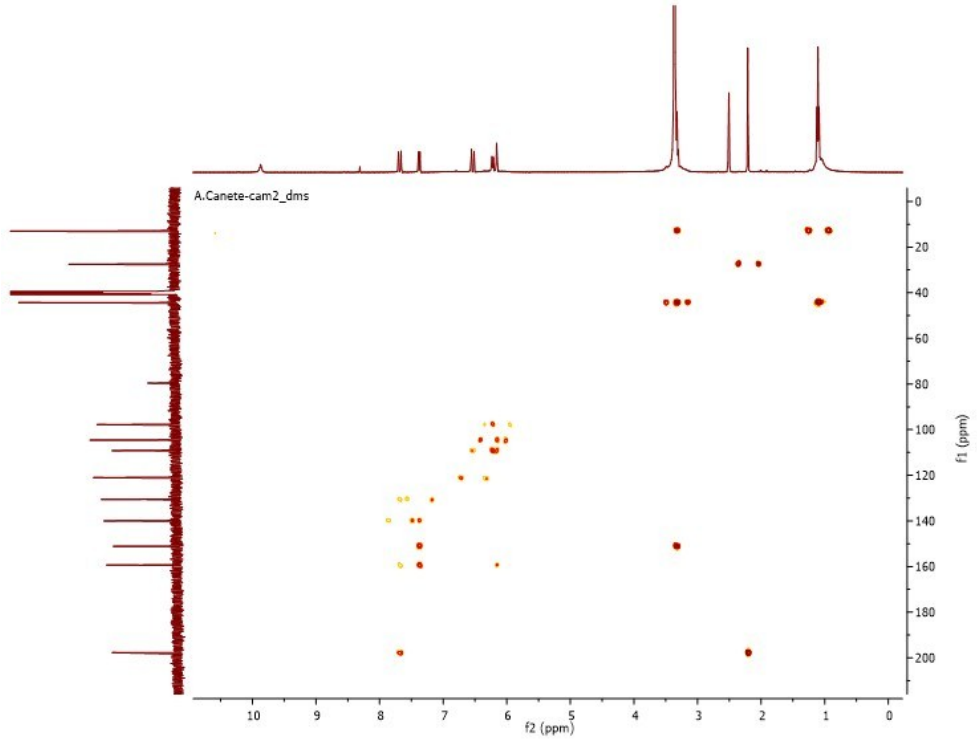

Figure S9. ^{1}H-HMBC spectrum (400 MHz) of **CAM2** alone in DMSO-d_6.

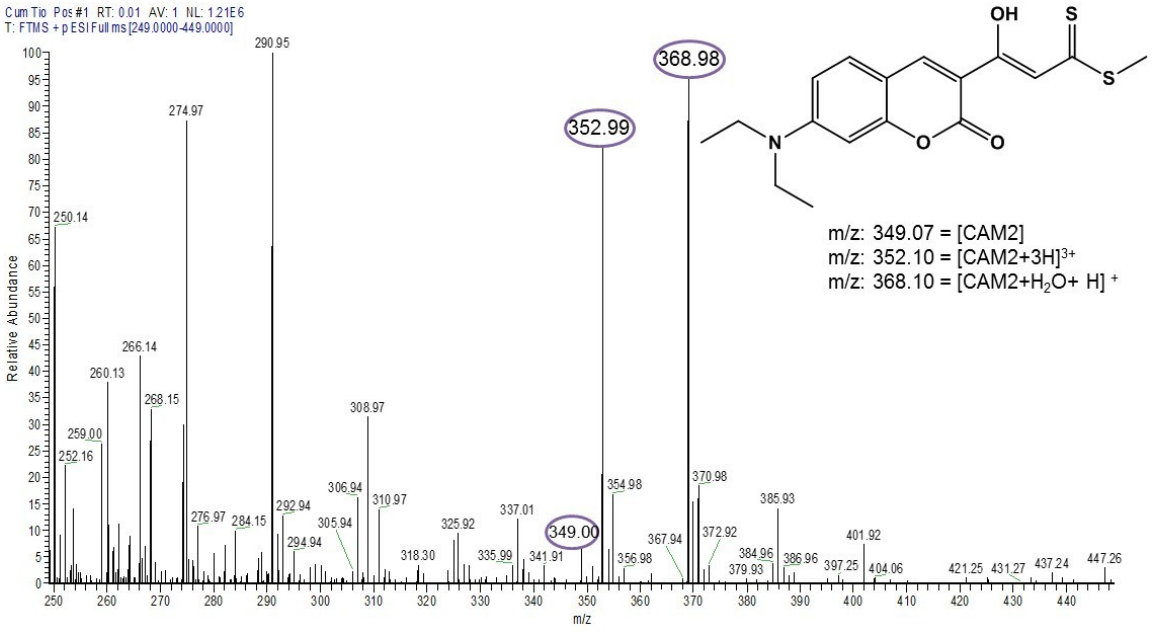

Figure S10. HRMS-ESI (positive mode) of **CAM2** (2mM) in water-DMSO (99:1, v/v) solution.

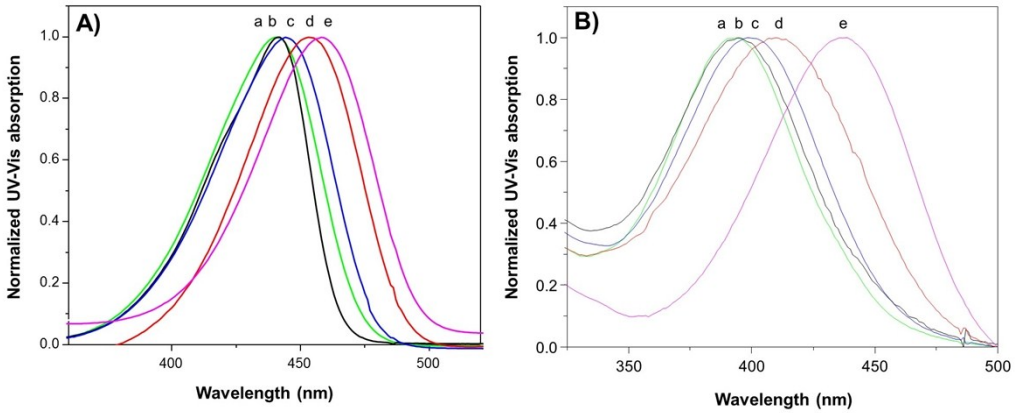

Figure S11. Normalized UV-vis absorption spectra of: A) coumarin-derivative **CAM1** dye (2 μM) and B) coumarin-derivative dye **CAM2** (4 μM) in chloroform (a), DMSO (b), ethanol (c), aqueous solution (d) and with CB7 (100 μM) in aqueous solution (e).

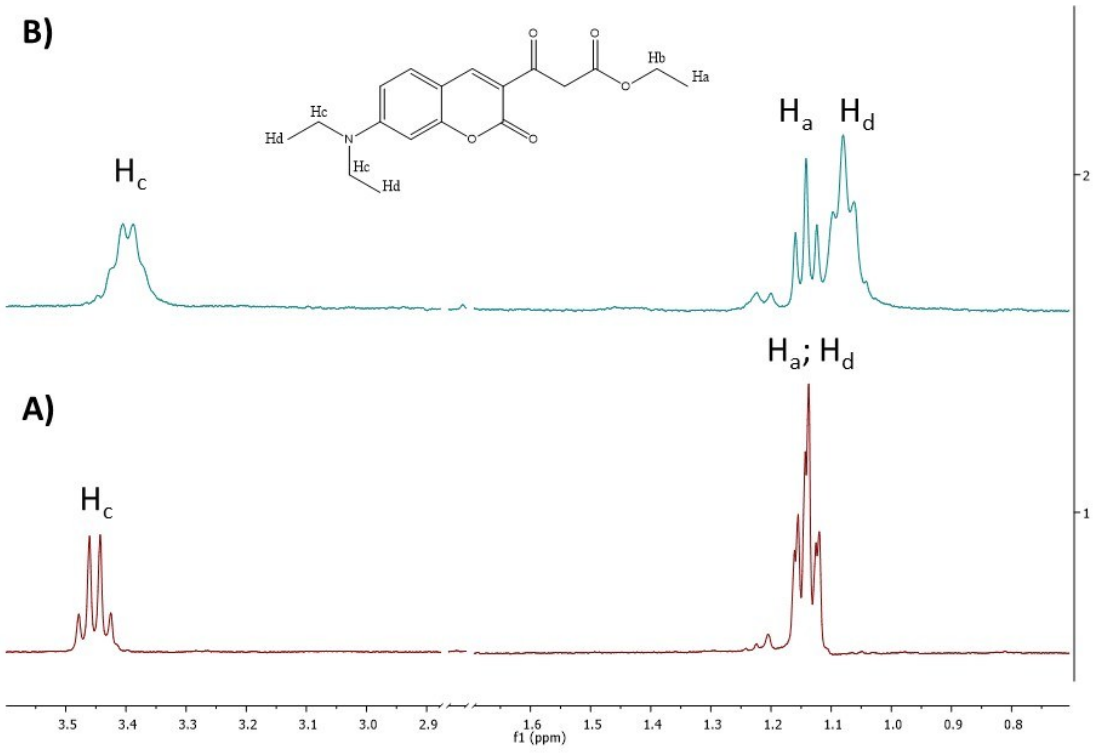

Figure S12. Comparison of partial ^{1}H NMR spectra (400 MHz) for: A) **CAM1** alone in CD_3CN/D_2O and B) **CAM1** and CB7 (3 eq.).

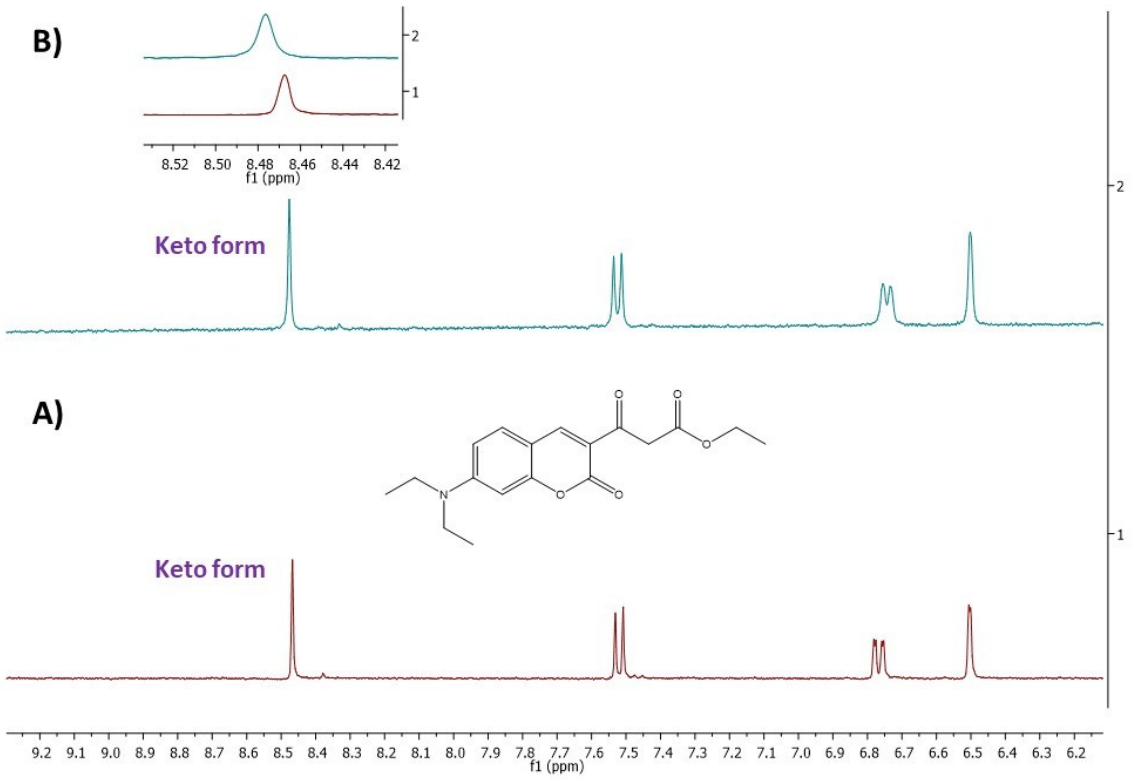

Figure S13. Comparison of partial ^{1}H NMR spectra (400 MHz) for: A) **CAM1** alone in CD_3CN/D_2O and B) **CAM1** and CB7 (3 eq.).

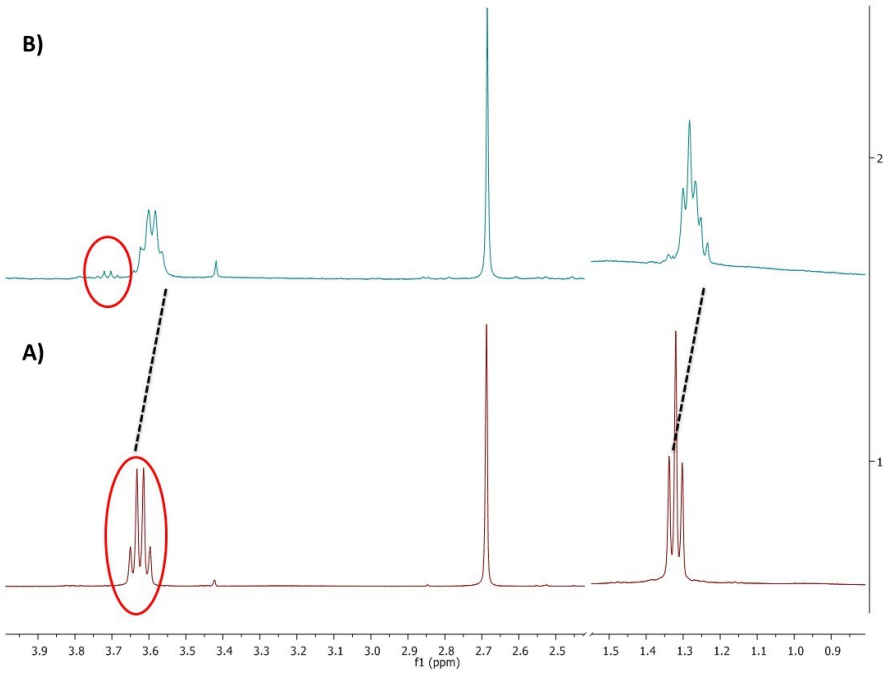

Figure S14. Comparison of partial ^{1}H NMR spectra (400 MHz) for: A) Intermediate **2** alone in CD_3CN/D_2O and B) Intermediate **2** and CB7 (3 eq.).

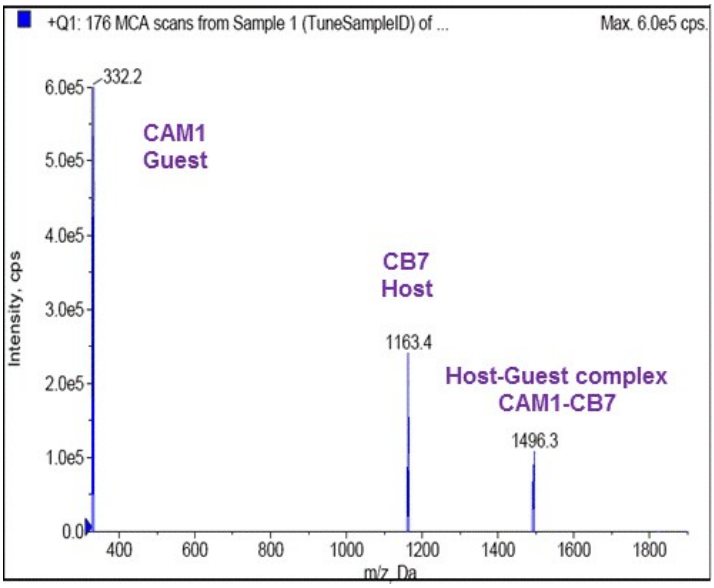

Figure S15. ESI mass spectra of a 1:10 molar ratio in aqueous solution of coumarin-derivative **CAM1** and CB7, respectively.

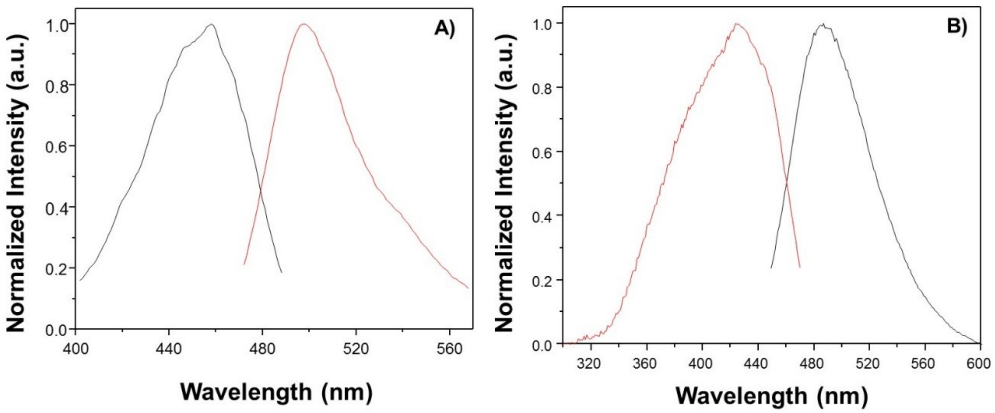

Figure S16. Normalized excitation and emission spectra of coumarin-derivative dyes: A) **CAM1** (5 μM) and B) **CAM2** (5 μM), excitation and emission slits of 5 nm were used. All spectra were carried out in aqueous solutions.

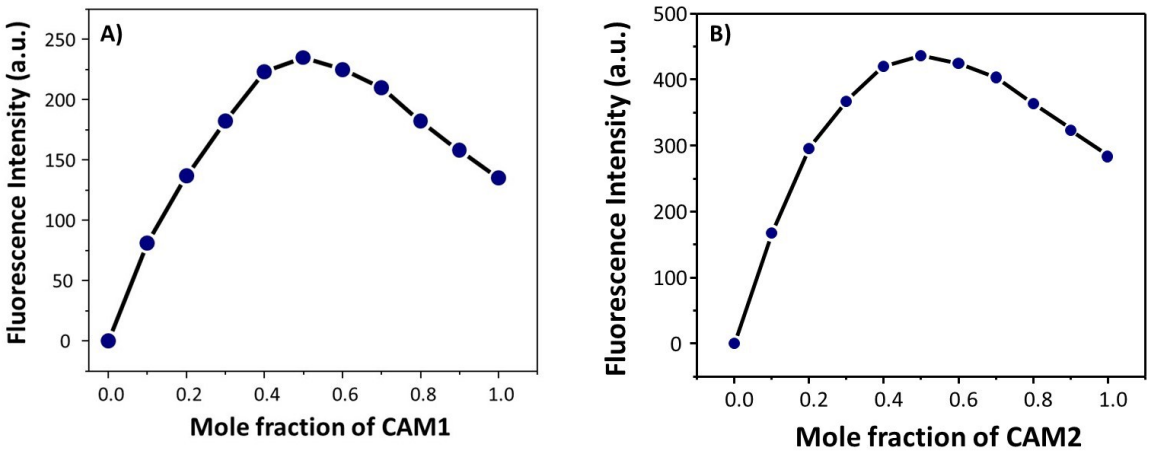

Figure S17. Job plot for the complexes **CAM1**-CB7 (λ_{exc} = 460 nm; λ_{em} = 500 nm) (A) and **CAM2**-CB7 (B) (λ_{exc} = 420 nm; λ_{em} = 490 nm).

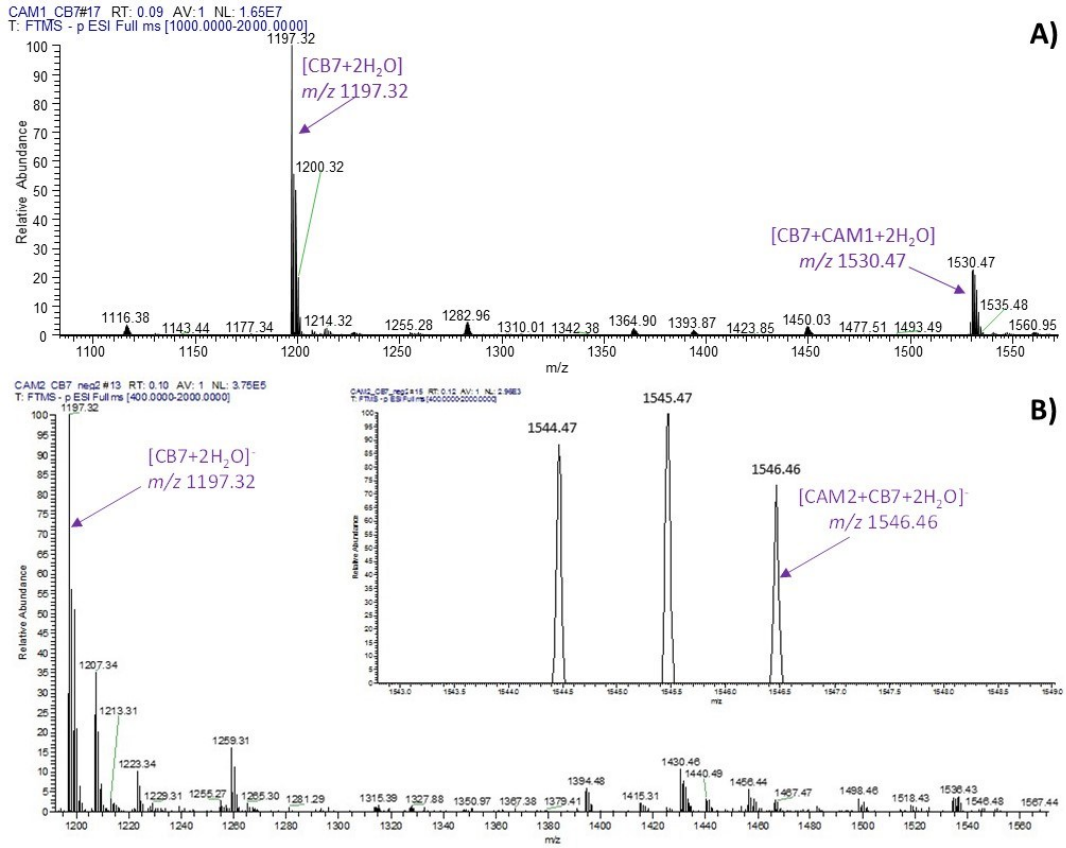

Figure S18. HRMS-ESI (negative mode) of a 1:10 molar ratio in aqueous solution of coumarin-derivative A) **CAM1** and CB7, and B) **CAM2** and CB7.

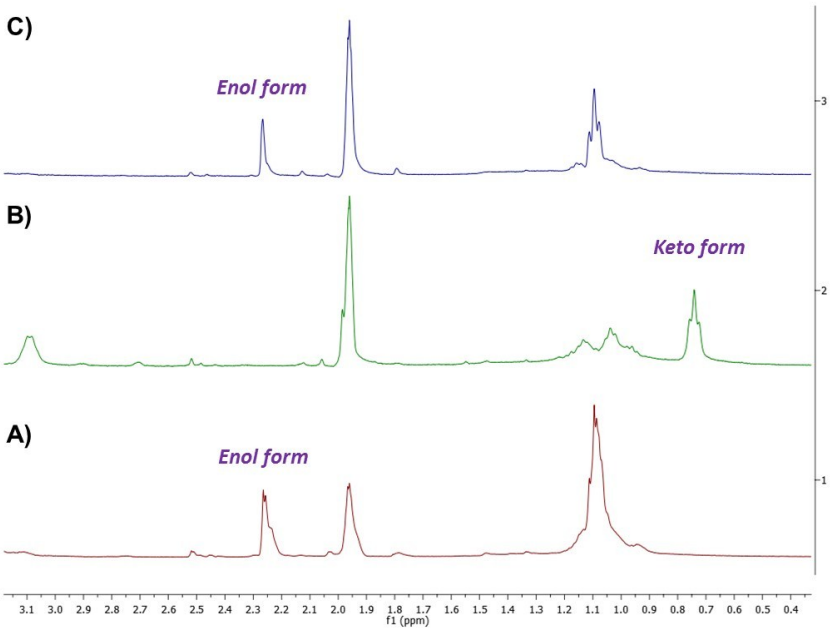

Figure S19. Comparison of partial ^{1}H NMR spectra (400 MHz) for: A) **CAM2** alone in CD_3CN/D_2O, B) **CAM2** and CB7 (3 eq.) and C) **CAM2** and β-CD (3 eq.).

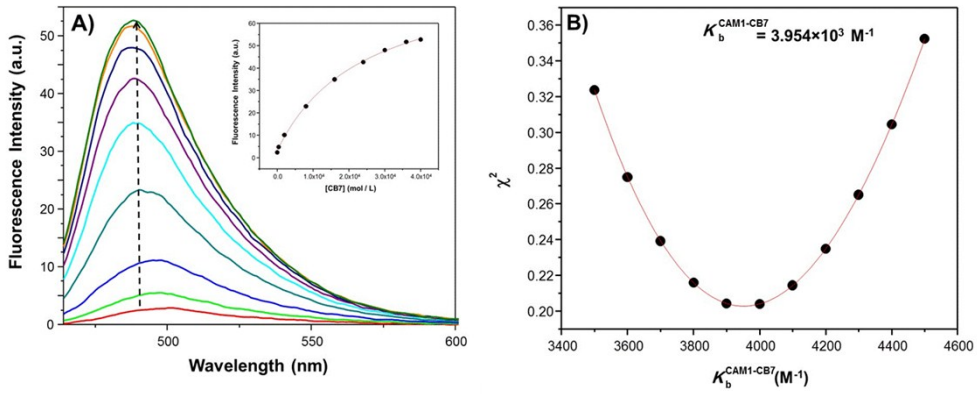

Figure S20. A) Fluorescence spectra of the coumarin-derivative **CAM1** (5 µM) with increasing concentrations of CB7 (5-400 µM). Inset shows the fluorescence titration of 5 µM **CAM1** with CB7 in aqueous solution. B) The effective binding constant was determined as $K_{CAM1CB7}$ = 3.95 × 10^3 M^{-1} by fitting data to the 1:1 host:guest model. Excitation and emission slits of 5 nm were used.

Table S1. Binding energy from docking studies for **CAM1** and **CAM2** in CB7 and β-CD.

Guest	Binding Energy (kcal/mol)	
	CB7	**β-CD**
CAM1	-1.2	-0.6
CAM2	-2.1	-1.6