Supporting Information

Photorelease of Incarcerated Caged Acids from Hydrophobic Coumaryl Esters into Aqueous Solution

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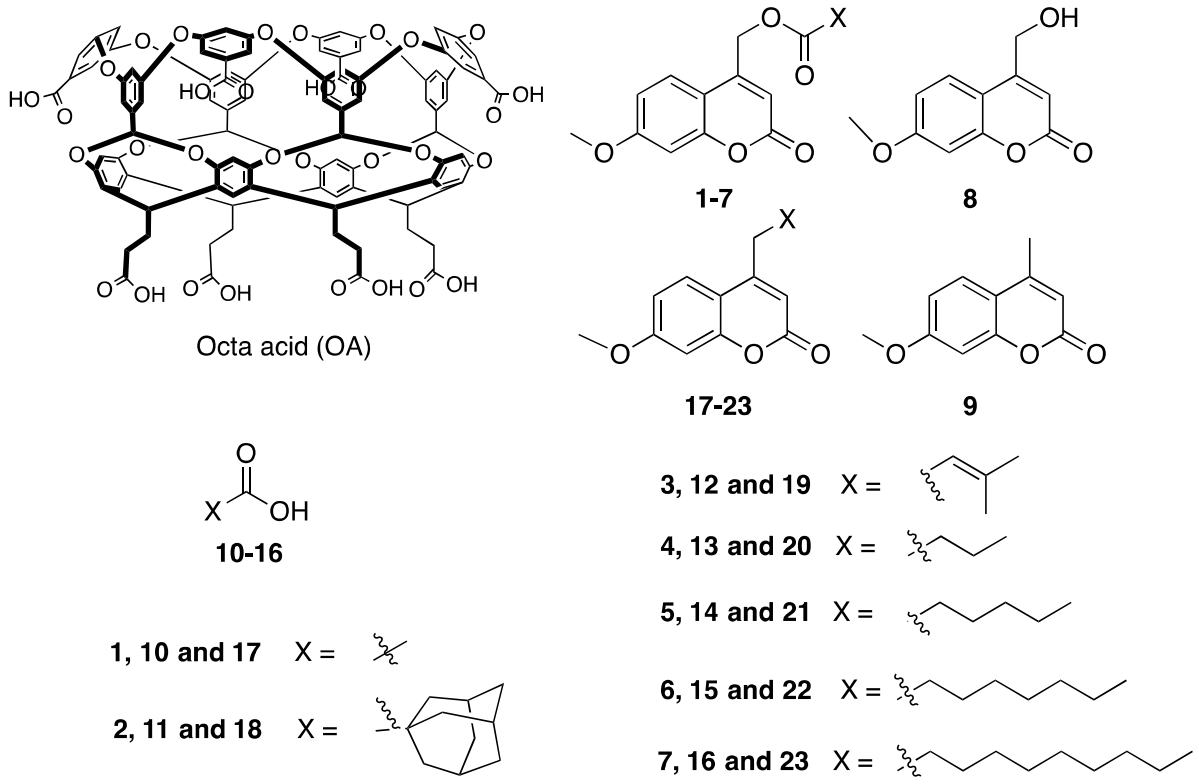
1. Structures of host, caged esters and primary photolysis products



Scheme S1. Structures of water-soluble octa acid (OA) cavitand, 7-methoxy-4-methylcoumaryl esters **1** – **7** and photoproducts **8**-**16**.

2. Synthesis and spectral data of caged esters

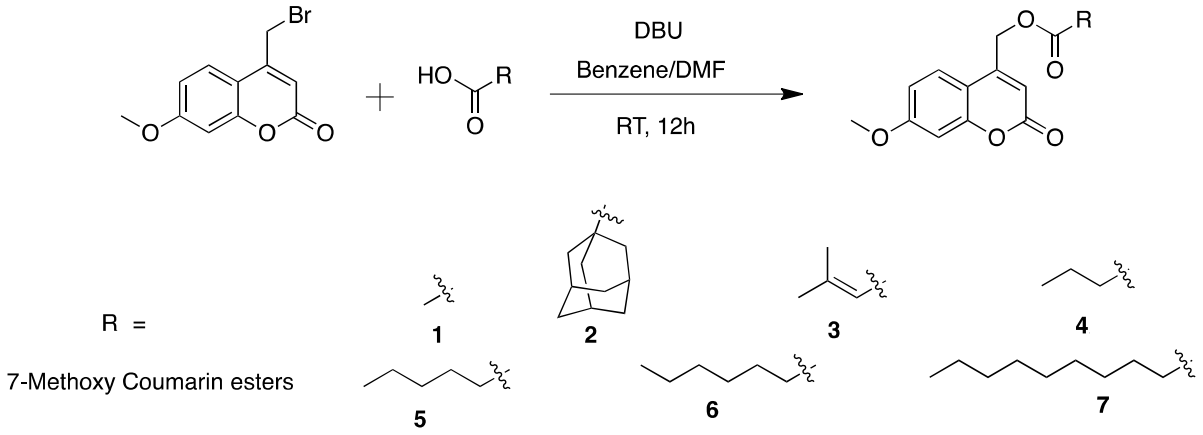
2.1 Materials

4-Bromomethyl-7-methoxycoumarin, 7-methoxy-4-methylcoumarin, acetic acid, 1-adamantanecarboxylic acid, 3,3-dimethylacrylic acid, butanoic acid, hexanoic acid, octanoic acid, and decanoic acid (Sigma-Aldrich/Alfa Aeser) were used as received. The host, octa acid (OA), was synthesized by following the literature procedure [1].

2.2 Synthesis of Coumaryl phototriggers 1 – 7 and photoproduct 8

(a) Synthesis of Coumaryl phototriggers 1 – 7

Each phototrigger was prepared by adding 0.4 mmol of 4-bromomethyl-7-methoxycoumarin and 0.5 mmol of the correspondent carboxylic acid to 15 mL of a 2:1 mixture of benzene:DMF in a 50 mL round bottomed flask. The mixture was stirred under N_2 until the solution became transparent. Then, 0.55 mmol of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) was added and the solution stirred for 12 h. The reaction mixture was poured into water, extracted with $CHCl_3$ (25 mL) and washed twice with aqueous $NaHCO_3$ solution (5%, 2x10 mL). The organic layer was dried over Na_2SO_4, concentrated and eluted through a silica gel column using $CHCl_3$ as the mobile phase to isolate the pure product as a light yellow solid. Phototriggers **1** – **7** were characterized by ^{1}H NMR, ^{13}C NMR and electrospray ionization mass spectrometry (ESI-MS). Photoproducts were isolated as yellow solid with the yields listed below. **1** : light yellow solid, 42 mg, 42 %; **2** : light yellow solid, 55 mg, 37 %; **3** : light yellow solid , 63 mg, 54 %; **4** : light yellow solid, 58 mg, 52 %; **5** : light yellow solid , 62 mg, 50 %; **6** : light yellow solid , 87 mg, 65 %; **7** : light yellow solid, 99 mg, 68 %



Scheme S2. Synthesis of 7-methoxy-4-methylcoumaryl esters **1** – **7**.

2.3 ^{1}H NMR and mass spectral data of synthesized 1-8

NMR and ESI-Mass spectra of Caged Esters: ^{1}H NMR (500 MHz) and ^{13}C-NMR (125 MHz) studies were carried out on a Bruker NMR spectrometer at 25 ^{0}C. Full scan ESI-MS spectra were obtained using a Bruker Daltonics microOTOF-QII. The synthesized compounds were solubilized in a mixture methanol-chloroform (50:50) containing 0.1 % formic acid. The ions were continuously generated by infusing the solutions (200 μL hr^{-1}) into the source, with the help of a syringe pump (KdScientific, model 601553, USA). Typical experimental conditions were as follows: capillary voltage, 4.5 kV; drying gas, 180 ºC at 4 L min^{-1}; nebulizer gas pressure, 0.3 bar; end plate offset -500 V. The Fragmentation ESI-

MS/MS spectra were obtained using Bruker Daltonics HCT *ultra* under positive and negative polarity. The ions were continuously generated by infusing the standards in acetonitrile (50 μM) or the irradiated samples prepared in aqueous ammonia, at 4 mL min^{-1} into the mass spectrometer source, with the help of a syringe pump (KdScientific, model 781100, USA). Typical experimental conditions were as follows: capillary voltage, 3.5 kV; capillary exit voltage (CE), 75 V; skimmer voltage, 40 V; drying gas, 300 ºC at 6 L min^{-1}; nebulizer gas pressure, 20 psi.

1: ^{1}H-NMR (500 MHz, DMSO) δ: 2.17 (s, 3H), 3.86 (s, 3H), 5.33 (d, *J* = 1Hz, 2H), 6.27 (s, 1H), 6.97 (did, *J* = 6.5 and 2Hz, 1H), 7.04 (d, *J* = 2.0 Hz, 1H), 7.66 (d, *J* = 9.0 Hz, 1H); ^{13}C-NMR (125 MHz, DMSO) δ: 27.9, 36.5, 38.8, 40.8, 55.5, 65.4, 114.0, 127.3, 130.1, 163.9, 177.2, 191.0; ESI-HRMS: Calculated for $C_{13}H_{12}0_5Na$ $[M+Na]^+$ 271.0577, observed: 271.0573.

2: ^{1}H-NMR (500 MHz, DMSO) δ: 1.69 (m, 6H), 1.89 (m, 6H), 1.99 (m, 3 H), 3.86 (s, 3H), 5.33 (s, 2H), 6.17 (s, 1H), 6.98 (dd, *J* = 6.5 and 2.5 Hz, 1H), 7.04 (d, *J* = 2.5 Hz,1H), 7.64 (d, *J* = 9.0 Hz, 1H); ^{13}C-NMR (125 MHz, DMSO-d_6) δ: 27.72, 36.28, 38.79, 56.45,61.54, 101.49, 109.24, 110.72, 112.86, 126.30, 151.22, 155.48, 160.37, 163.06, 176.23, 191.0; ESI-HRMS: Calculated for $C_{22}H_{24}O_5Na$ $[M+Na]^+$ 391.1516, observed: 391.1500.

3: ^{1}H-NMR (500 MHz, DMSO) δ: 1.92 (s, 3H), 2.14 (s, 3H), 3.85 (s, 3H), 5.35 (s, 2H), 5.87 (s, 1H), 6.20 (s, 1H), 6.98 (dd, *J* = 6.5 and 2Hz, 1H), 7.04 (d, *J* = 2.5 Hz,1H), 7.66 (d, *J* = 8.5 Hz, 1H); ^{13}C-NMR (125 MHz, DMSO) δ: 20.5, 27.4, 56.4, 60.9, 101.4, 109.3, 110.7, 112.8, 114.9, 126.2, 151.3, 155.4, 159.8, 160.4, 163.01, 185.37; ESI-HRMS: Calculated for $C_{16}H_{16}0_5$ Na $[M+Na]^+$ 311.0890, observed: 311.0896

4: ^{1}H-NMR (500 MHz, DMSO) δ: 0.91 (t, *J* = 7 Hz, 3H), 1.60 (m, 2H), 2.46 (t, *J* = 7 Hz, 2H), 3.87 (s, 3H), 5.36 (s, 2H), 6.25 (s, 1H), 6.98 (dd, *J* = 6 and 3Hz, 1H), 7.04 (d, *J* = 2.5 Hz,1H), 7.67 (d, *J* = 8.5 Hz, 1H); ^{13}C-NMR (125 MHz, DMSO) δ:13.87, 18.33, 35.53, 56.45, 61.49, 101.48, 109.45, 110.75, 112.82, 126.29, 151.04, 155.45, 160.40, 163.03, 172.79. ESI-HRMS: Calculated for $C_{15}H_{16}0_5Na$ $[M+Na]^+$ 299.0890, observed: 299.0876.

5: ^{1}H-NMR (500 MHz, DMSO) δ: 0.86 (t, *J* = 7 Hz, 3H), 1.23-1.28 (m, 2H), 1.29-1.33 (m, 2H), 2.47 (t, *J* = 7.5 Hz, 2H), 3.87 (s, 3H), 5.35 (s, 2H), 6.25 (s, 1H), 6.98 (dd, *J* = 6 and 2.5 Hz, 1H), 7.04 (d, *J* = 2.5 Hz, 1H), 7.67 (d, *J* = 8.5 Hz, 1H); ^{13}C-NMR (125 MHz, DMSO) δ: 14.35, 22.32, 24.52, 31.08, 33.64, 56.45, 61.51, 101.48, 109.50, 110.76, 112.81, 126.31,

151.03, 155.48, 160.39, 163.03, 172.92. ESI-HRMS: Calculated for $C_{17}H_{20}0_5Na$ $[M+Na]^+$ 327.1203, observed: 327.1218.

6: ^{1}H-NMR (500 MHz, DMSO) δ: 0.85 (t, *J* = 6.5 Hz, 3H), 1.23-1.26 (m, 8H), 1.55-1.58 (m, 2H), 2.47 (t, *J* = 7.5 Hz, 2H), 3.86 (s, 3H), 5.35 (s, 2H), 6.25 (s, 1H), 6.97 (dd, *J* = 6 and 2.5 Hz, 1H), 7.04 (d, *J* = 2.5 Hz, 1H), 7.66 (d, *J* = 9.0 Hz, 1H); ^{13}C-NMR (125 MHz, DMSO) δ: 14.37, 22.46, 24.84, 28.78, 28.83, 31.57, 33.68, 56.45, 61.52, 61.52, 101.47, 109.56, 110.76,112.81, 126.32, 151.01, 155.47, 160.39, 163.03, 172.92. ESI-HRMS: Calculated for $C_{19}H_{24}0_5Na$ $[M+Na]^+$ 355.1516, observed: 355.1529.

7: ^{1}H-NMR (500 MHz, DMSO) δ: 0.85 (t, *J* = 6.5 Hz, 3H), 1.25-1.23 (m, 12H), 1.55-1.58 (m, 2H), 2.47 (t, *J* = 7.5 Hz, 2H), 3.86 (s, 3H), 5.33 (s, 2H), 6.25 (s, 1H), 6.97 (dd, *J* = 6 and 2.5 Hz, 1H), 7.04 (d, *J* = 2.5 Hz, 1H), 7.66 (d, *J* = 9.0 Hz, 1H); ^{13}C-NMR (125 MHz, DMSO) δ: 14.39, 22.54, 24.83, 28.87, 29.08, 29.12, 29.30, 31.72, 33.69, 56.43, 61.51, 101.46, 109.56, 110.75, 112.79, 126.30, 150.99, 155.47, 160.38, 163.02, 172.91. ESI-HRMS: Calculated for $C_{21}H_{28}0_5Na$ $[M+Na]^+$ 383.1829, observed: 383.1841.

2.4 ^{1}H NMR, ^{13}C NMR , ESI-MS spectra of phototriggers

(a) ^{1}H and ^{13}C NMR Spectra, Mass spectra and fragmentation spectra of esters 1 – 7 and photoproduct 8.

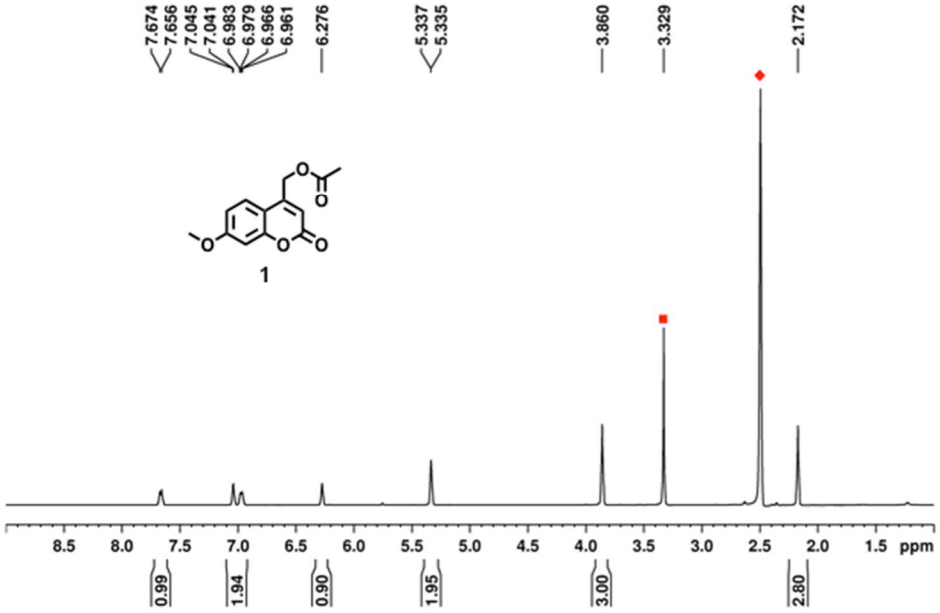


Figure S1. ^{1}H-NMR (500 MHz) spectrum of **1** in DMSO-d_6. ◆ and ■ indicate the residual solvent peaks of DMSO-d_6 and water, respectively.

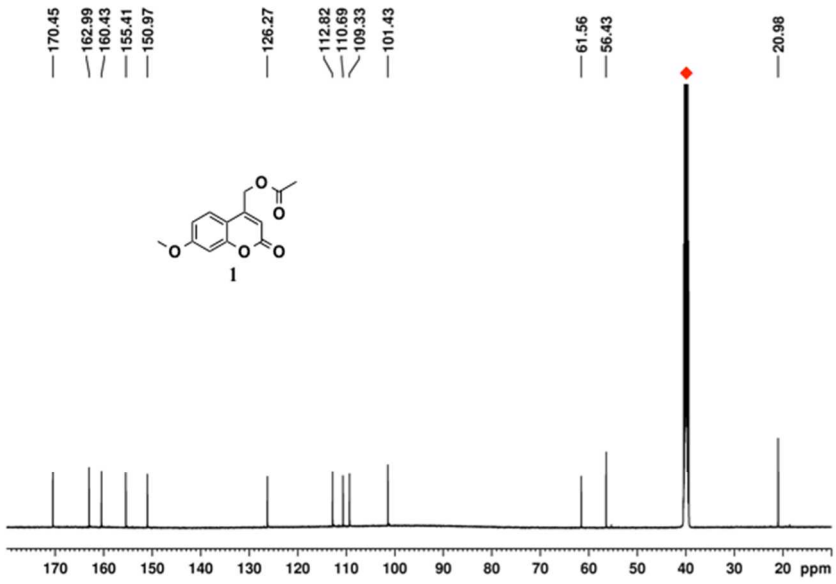


Figure S2. ^{13}C-NMR (125 MHz) spectrum of **1** in DMSO-d_6. ◆ indicates the residual solvent peak of DMSO-d_6.

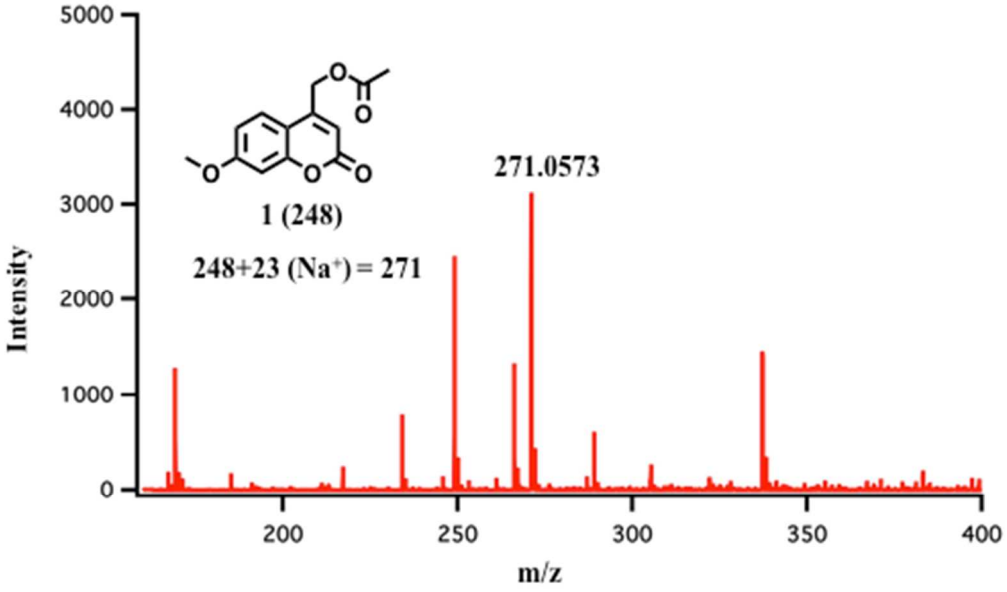


Figure S3. ESI mass spectrum of **1** in methanol-chloroform (50:50) containing 0.1 % formic acid.

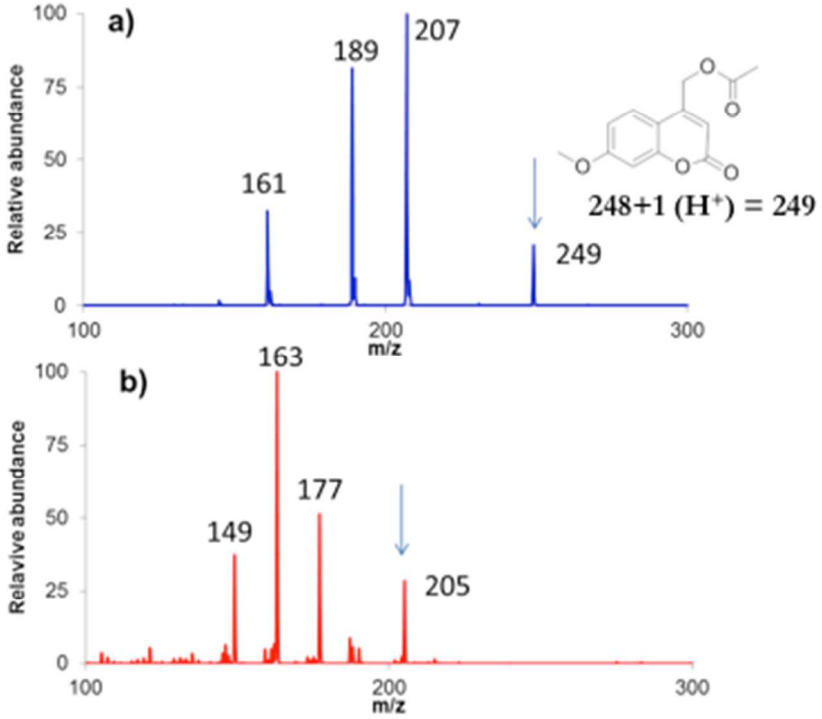


Figure S4. Fragmentation spectra of **1** (m/z 249), **a)**, and of m/z 205, **b)**. Spectrum **b)** was assigned to the decarboxylation photoproduct from the radical pair generated by initial homolysis of the CH_2-O bond of ester **1**. The arrows indicate the fragmented peaks.

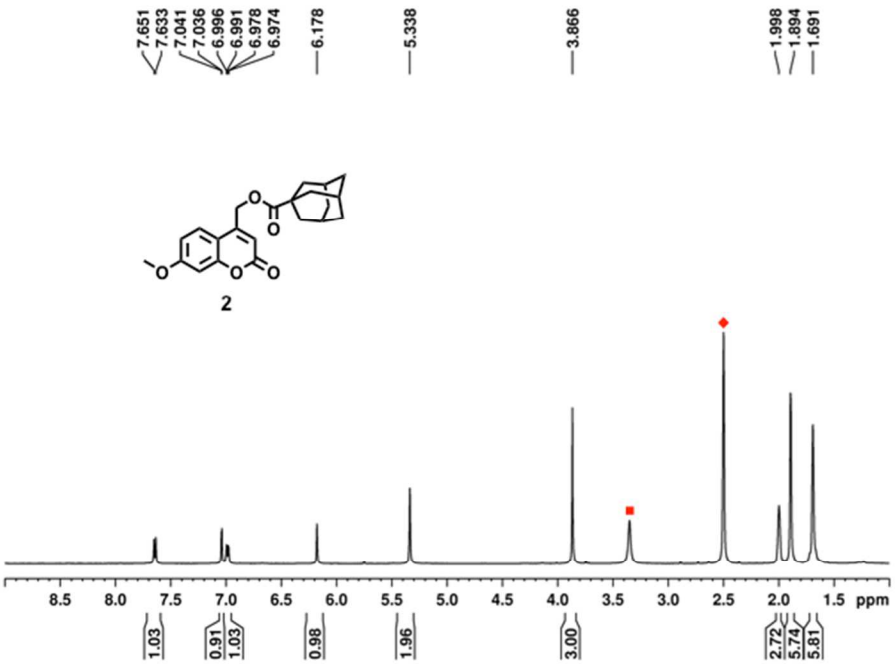


Figure S5. [1]H-NMR (500 MHz) spectrum of **2** in DMSO-d_6. ◆ and ■ indicate the residual solvent peaks of DMSO-d_6 and water, respectively.

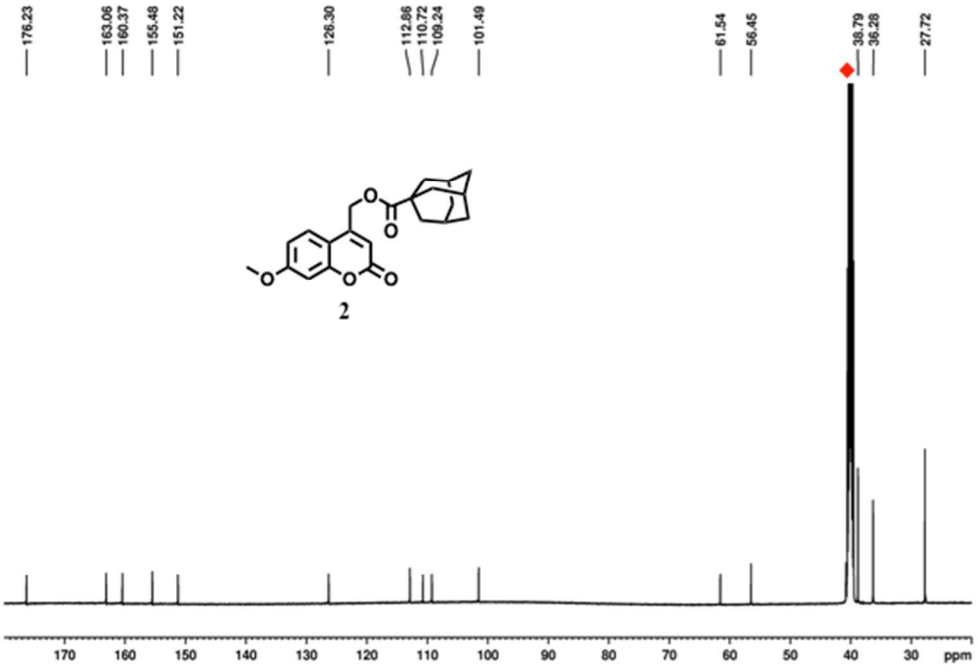


Figure S6. [13]C-NMR (125 MHz) spectrum of **2** in DMSO-d_6. ◆ indicates the residual solvent peak of DMSO-d_6.

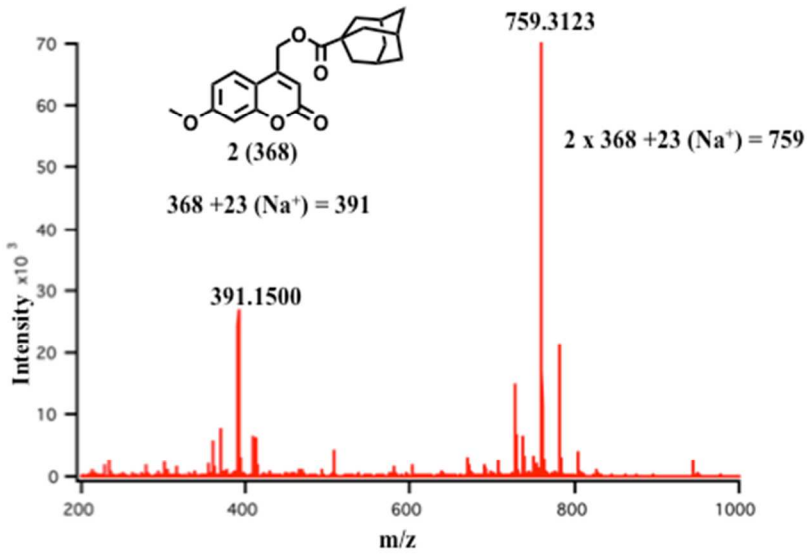


Figure S7. ESI mass spectrum of **2** in methanol-chloroform (50:50) containing 0.1 % formic acid.

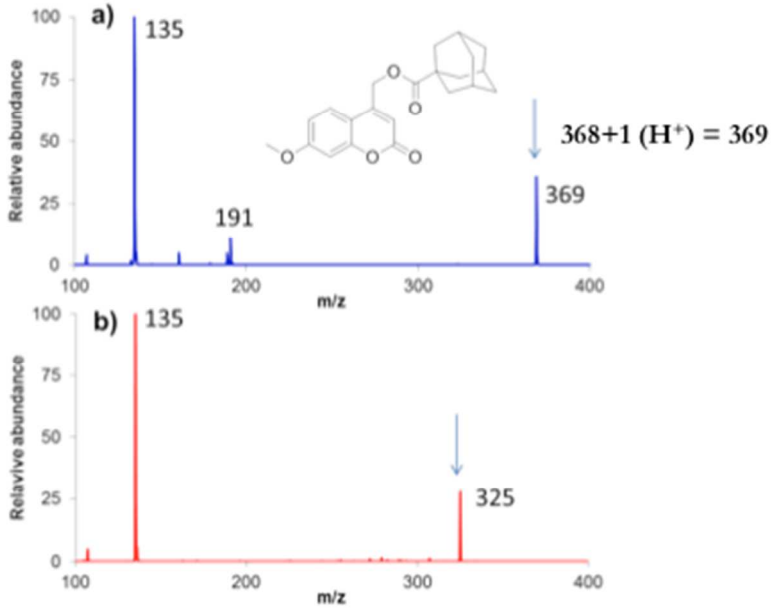


Figure S8. Fragmentation spectra of **2** (m/z 369), **a)**, and of m/z 325, **b)**. Spectrum **b)** was assigned to the decarboxylation photoproduct from the radical pair generated by initial homolysis of the CH_2-O bond of **2**. The arrows indicate the fragmented peaks.

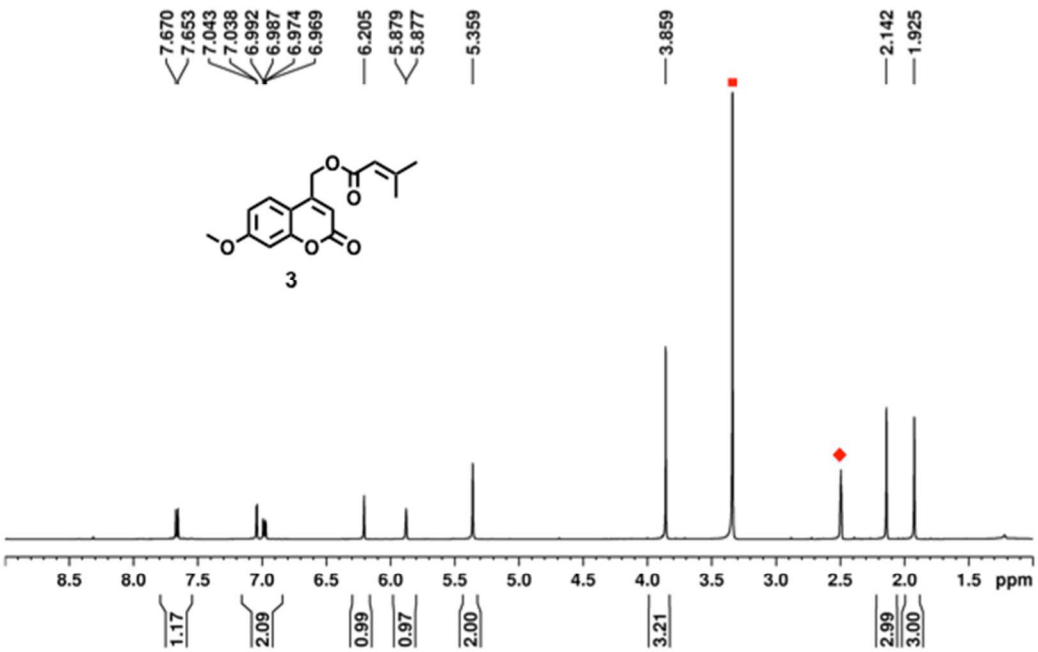


Figure S9. [1]H-NMR (500 MHz) spectrum of **3** in DMSO-d_6. ◆ and ■ indicate the residual solvent peaks of DMSO-d_6 and water, respectively.

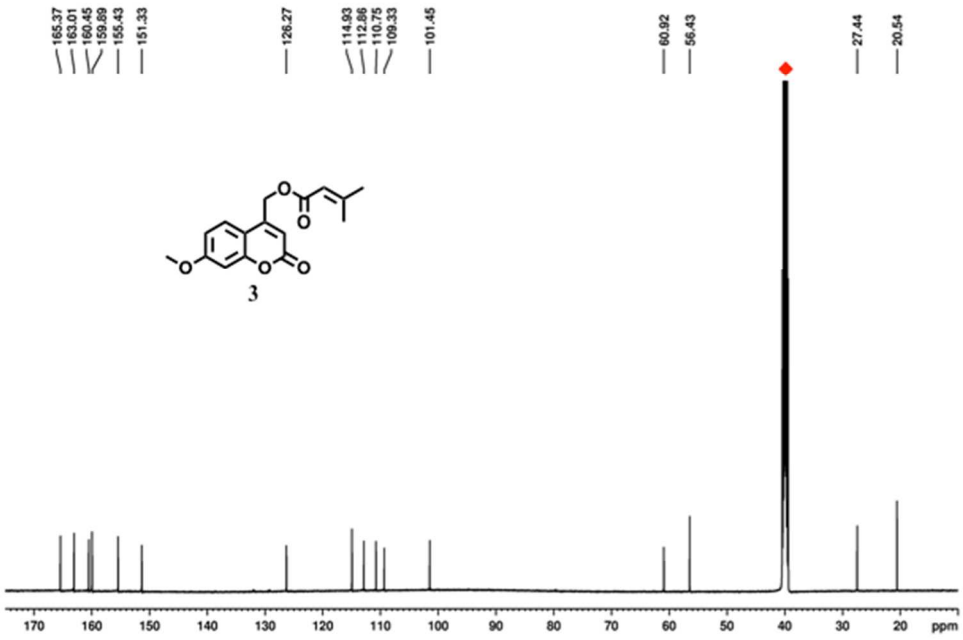


Figure S10. [13]C-NMR (125 MHz) spectra of **3** in DMSO-d_6. ◆ indicates the residual solvent peak of DMSO-d_6.

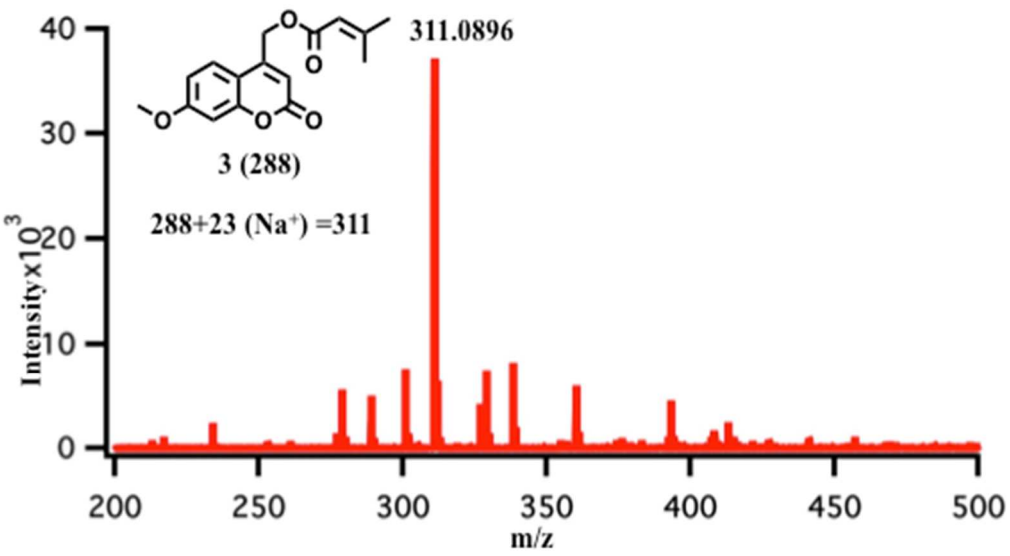


Figure S11. ESI mass spectrum of **3** in methanol-chloroform (50:50) containing 0.1 % formic acid.

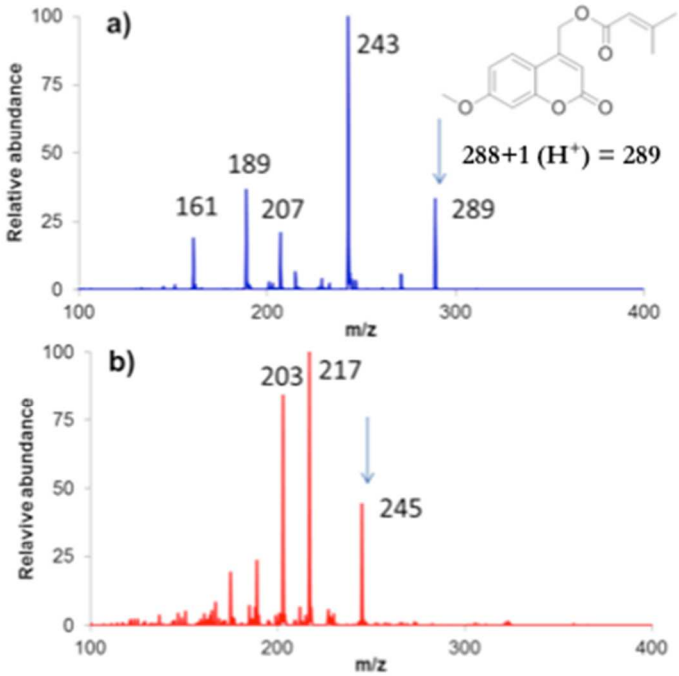


Figure S12. Fragmentation spectra of **3** (m/z 289), **a)**, and of m/z 245, **b)**. Spectrum **b)** was assigned the decarboxylation photoproduct from the radical pair generated by initial homolysis of the CH_2-O bond of **3**. The arrows indicate the fragmented peaks.

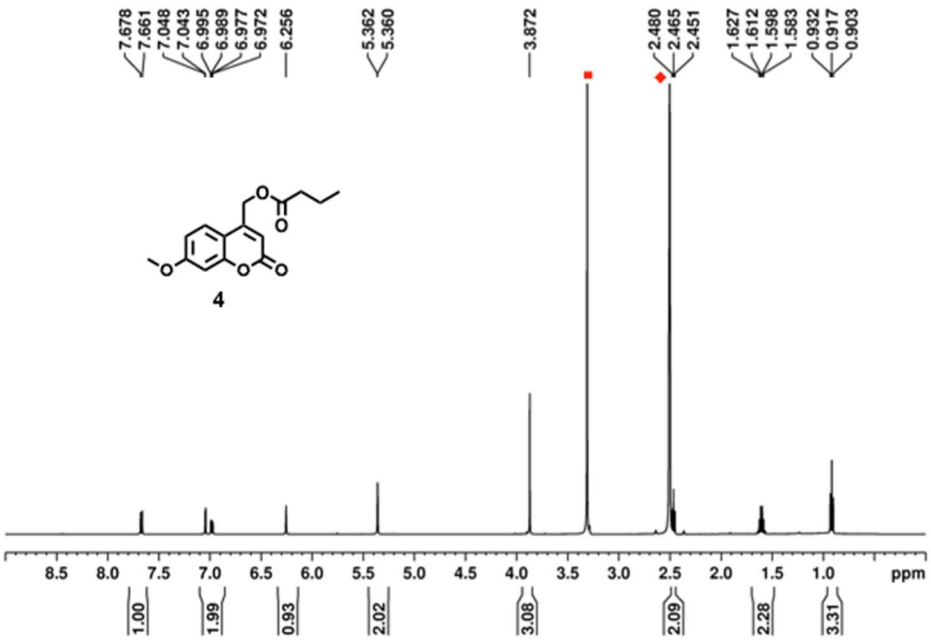


Figure S13. ^{1}H-NMR (500 MHz) spectrum of **4** in DMSO-d_6. ◆ and ■ indicate the residual solvent peaks of DMSO-d_6 and water, respectively.

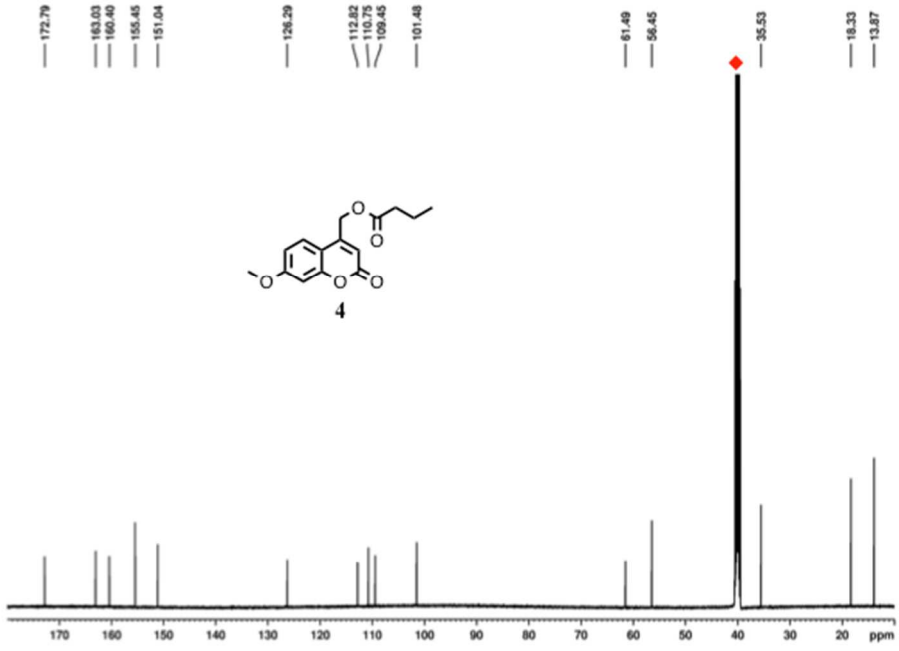


Figure S14. ^{13}C-NMR (125 MHz) spectrum of **4** in DMSO-d_6. ◆ indicates the residual solvent peak of DMSO-d_6.

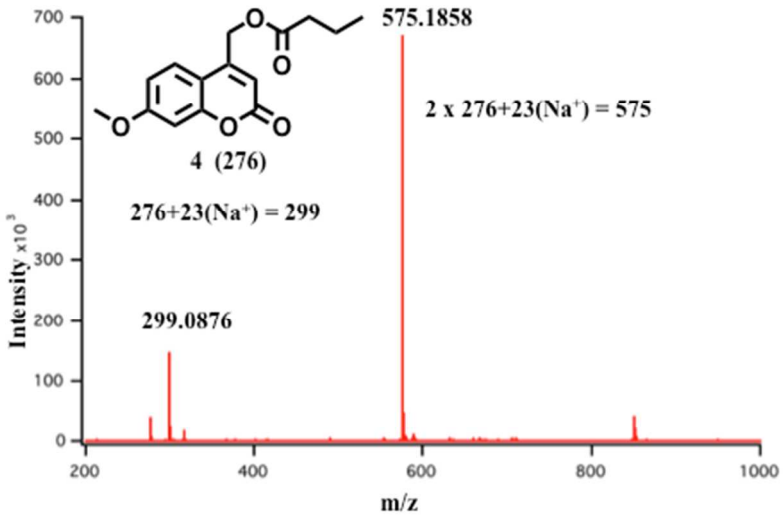


Figure S15. ESI mass spectrum of **4** in methanol-chloroform (50:50) containing 0.1 % formic acid.

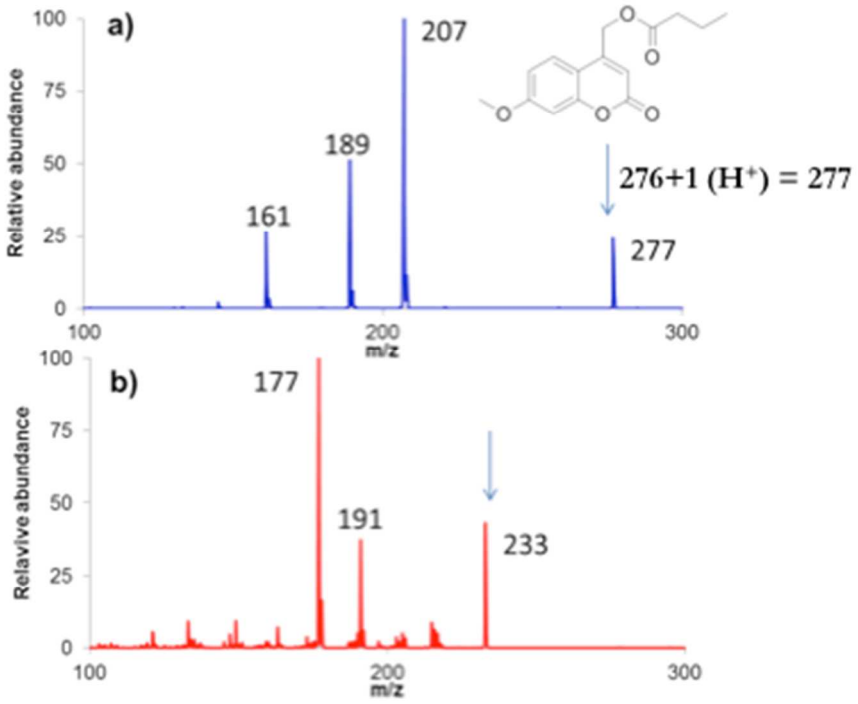


Figure S16. Fragmentation spectra of **4** (m/z 277), **a)**, and of m/z 233, **b)**. Spectrum **b)** was assigned to the decarboxylation photoproduct from the radical pair generated by initial homolysis of the CH_2-O bond of **4**. The arrows indicate the fragmented peaks.

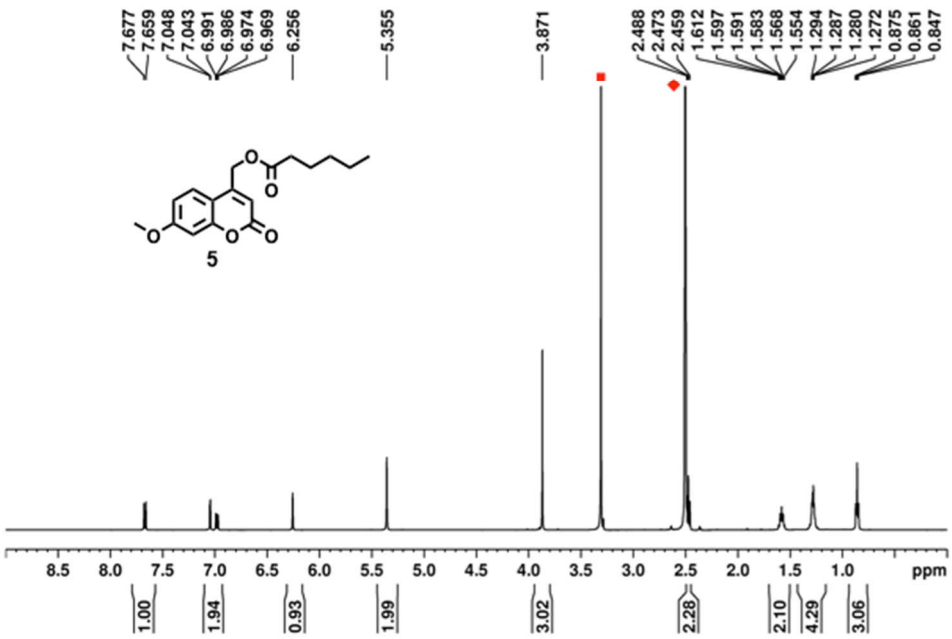


Figure S17. ^{1}H-NMR (500 MHz) spectrum of **5** in DMSO-d_6. ◆ and ■ indicate the residual solvent peaks of DMSO-d_6 and water, respectively.

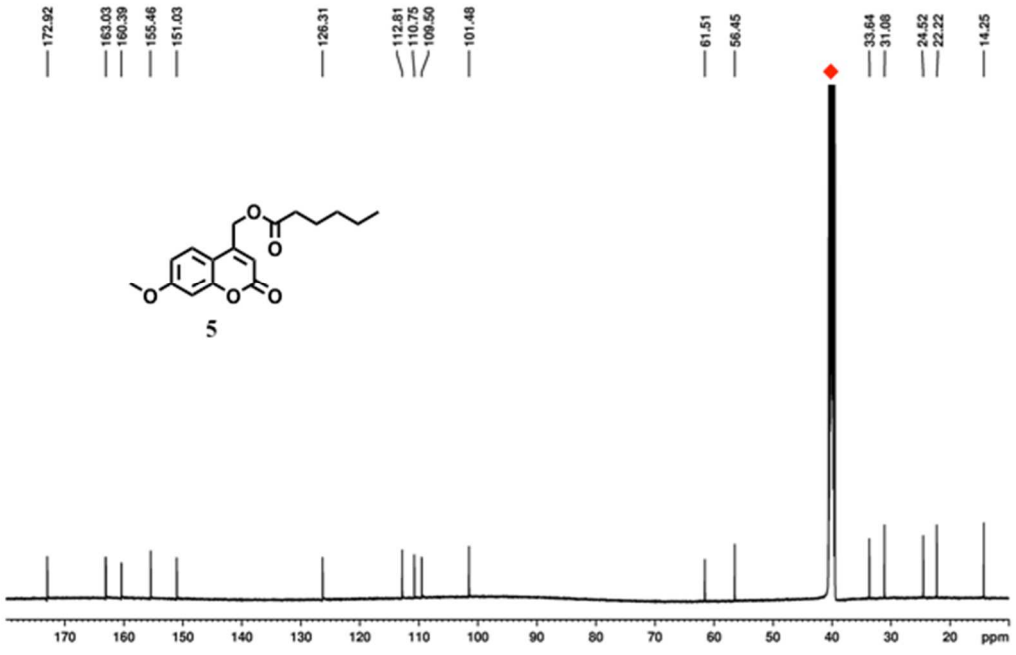


Figure S18. ^{13}C-NMR (125 MHz) spectrum of **5** in DMSO-d_6. ◆ indicates the residual solvent peak of DMSO-d_6.

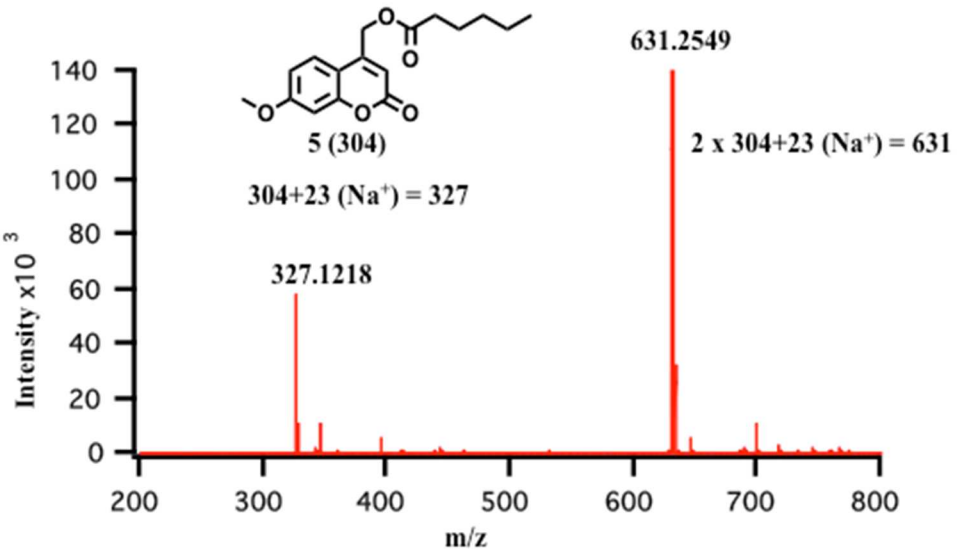


Figure S19. ESI mass spectrum of **5** in methanol-chloroform (50:50) containing 0.1 % formic acid.

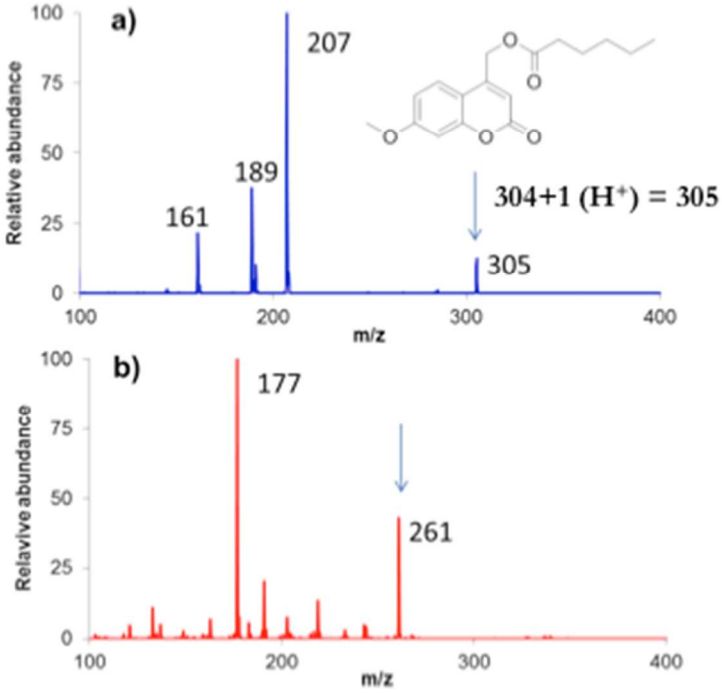


Figure S20. Fragmentation spectra of **5** (m/z 305), **a)**, and of m/z 261, **b)**. Spectrum **b)** was assigned to the decarboxylation photoproduct from the radical pair generated by initial homolysis of the CH_2-O bond of **5**. The arrows indicate the fragmented peaks.

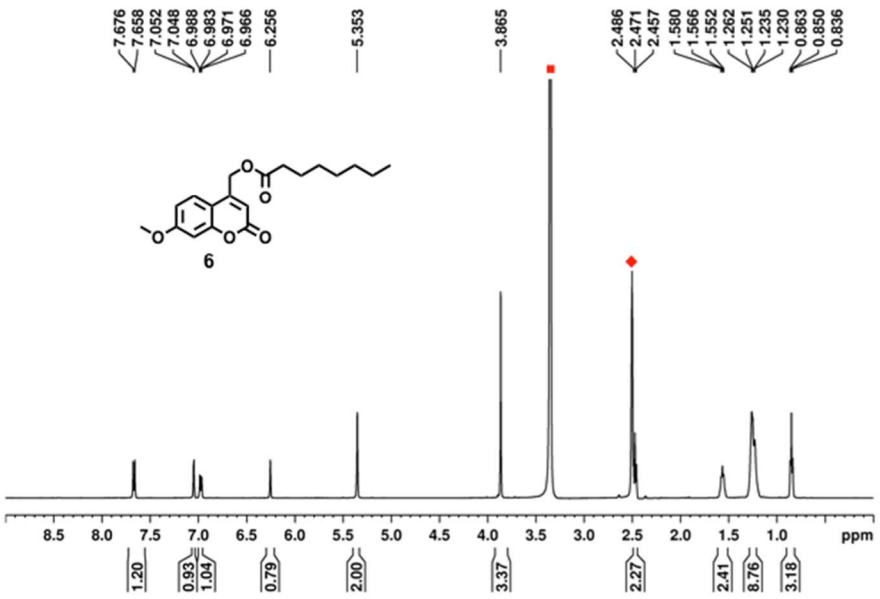


Figure S21. [1]H-NMR (500 MHz) spectrum of **6** in DMSO-d_6. ◆ and ■ indicate the residual solvent peak of DMSO-d_6 and water, respectively.

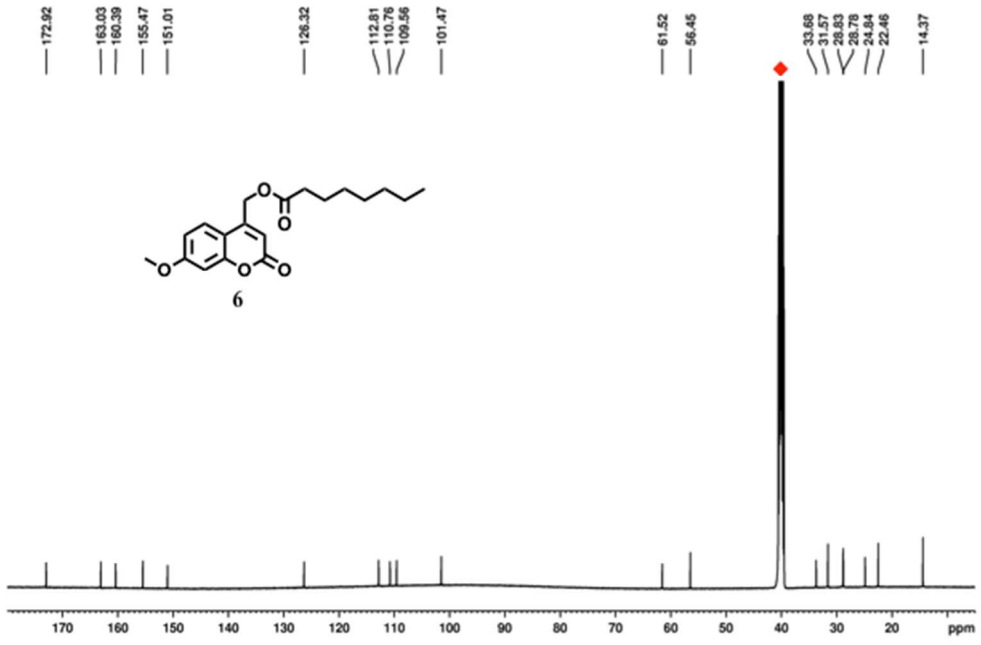


Figure S22. [13]C-NMR (125 MHz) spectra of **6** in DMSO-d_6. ◆ indicates the residual solvent peak of DMSO-d_6.

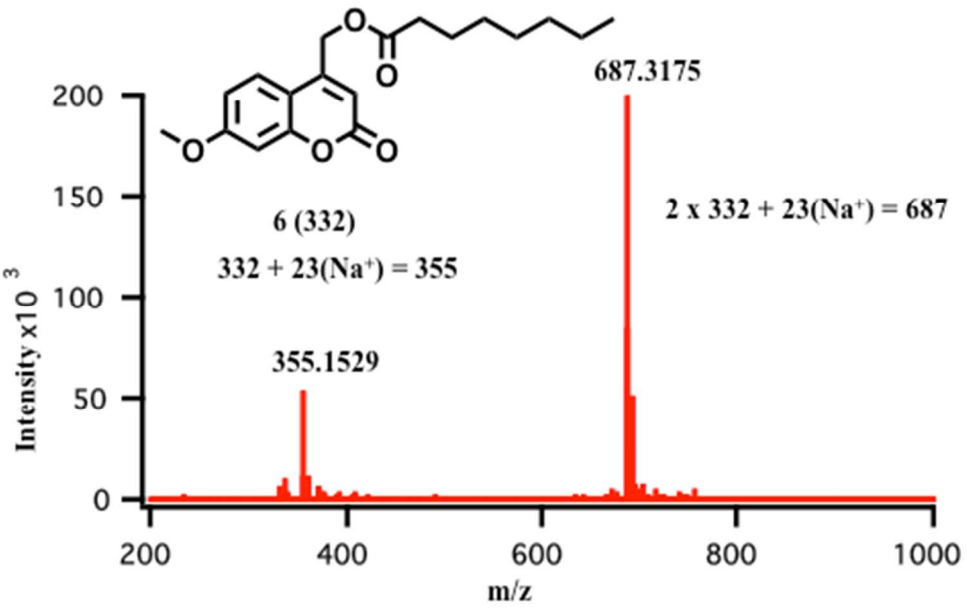


Figure S23. ESI mass spectrum of **6** in methanol-chloroform (50:50) containing 0.1 % formic acid.

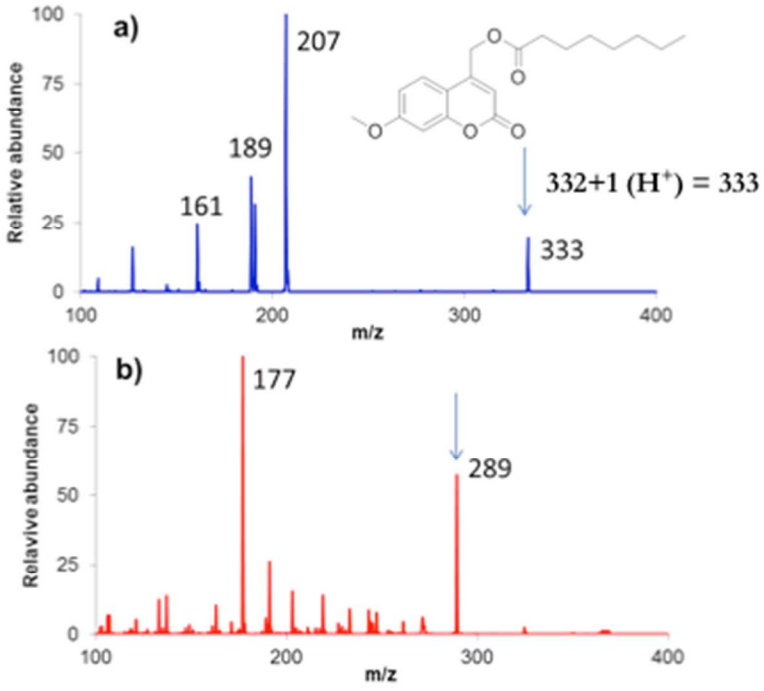


Figure S24. Fragmentation spectra of **6** (m/z 333), **a)**, and of m/z 289, **b)**. Spectrum **b)** was assigned to the decarboxylation photoproduct from the radical pair generated by initial homolysis of the CH_2-O bond of **6**. The arrows indicate the fragmented peaks.

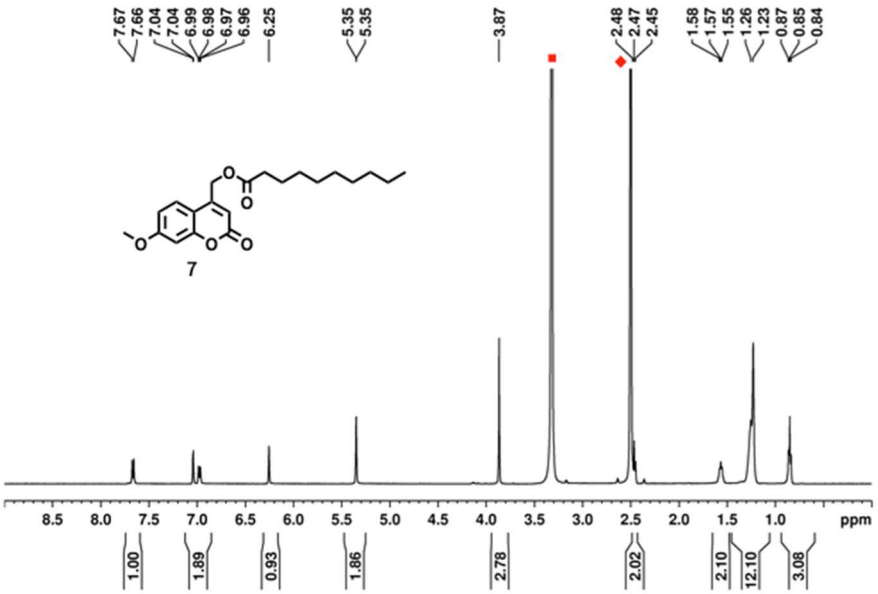


Figure S25. [1]H-NMR (500 MHz) spectrum of **7** in DMSO-d_6. ◆ and ■ indicate the residual solvent peaks of DMSO-d_6 and water, respectively.

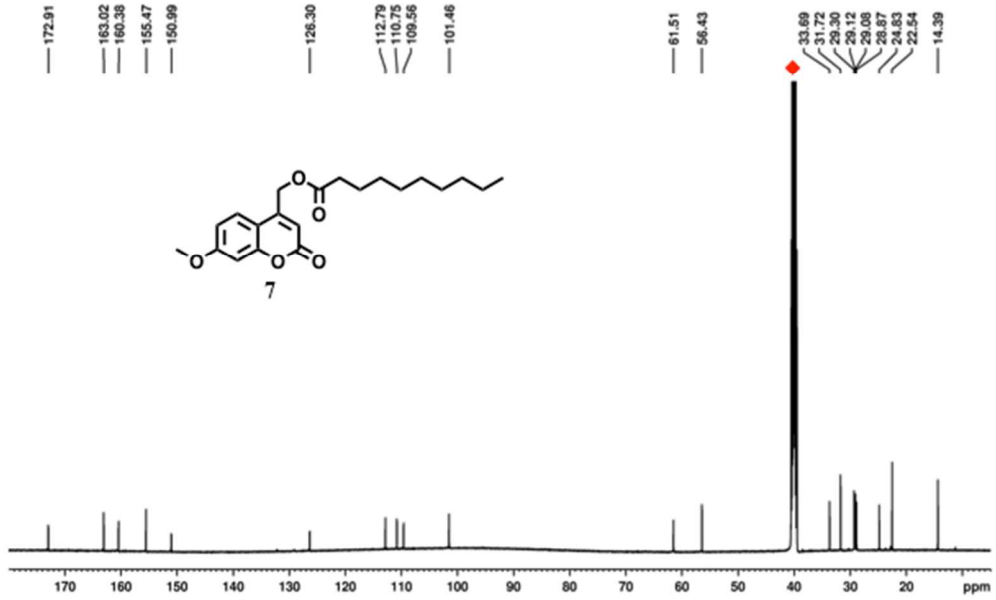


Figure S26. [13]C-NMR (125 MHz) spectra of **7** in DMSO-d_6. ◆ indicates the residual solvent peak of DMSO-d_6.

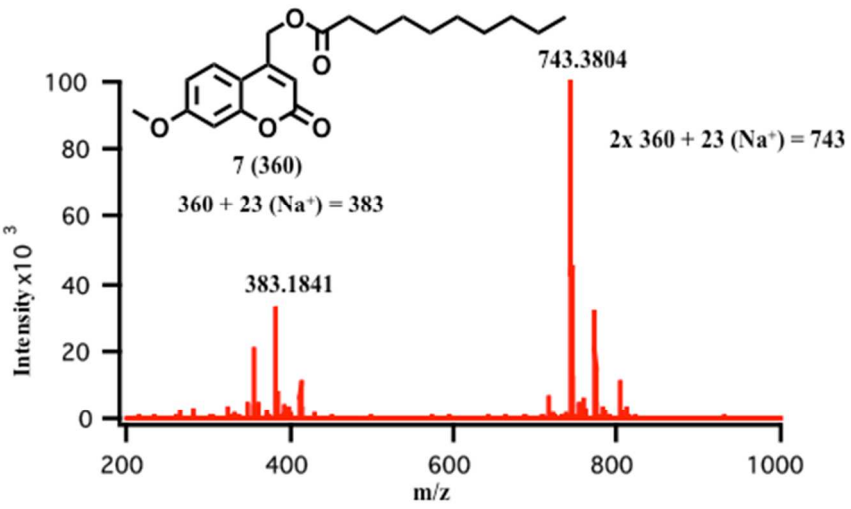


Figure S27. ESI mass spectrum of **7** in methanol-chloroform (50:50) containing 0.1 % formic acid.

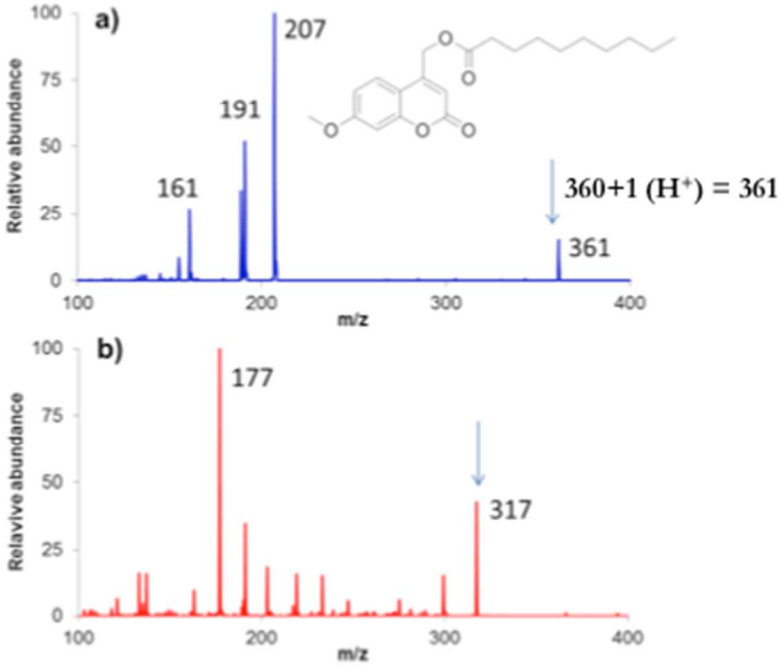
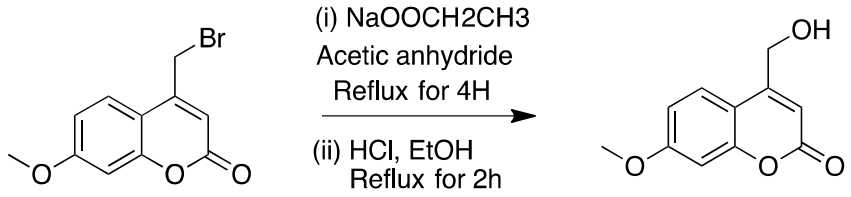


Figure S28. Fragmentation spectra of **7** (m/z 361), **a)**, and of m/z 317, **b)**. Spectrum **b)** was assigned to the decarboxylation photoproduct from the radical pair generated by initial homolysis of the CH_2-O bond of **7**. The arrows indicate the fragmented peaks.

(b) Synthesis of Photoproduct 8

7-methoxy-4-(hydroxymethyl)-2H-chromen-2-one was synthesized by following the literature procedure[2]. A mixture of 300 mg (1.11 mmol) of 4-bromomethyl-7-methoxy coumarin, and 900 mg (10.9 mmol) of sodium acetate in 8 mL of acetic anhydride was refluxed for 4 h. After filtration and washing of the residue with 5 mL of boiling acetic anhydride, the resulting filtrate was poured into ice-water after being cooled. The resulting white precipitate of 4-(acetoxymethyl)-7-methoxycoumarin was then refluxed in 15 mL of a 1:1 mixture of ethanol and hydrochloric acid for 2 h. After reaction the mixture was cooled to room temperature and filtered, yielding 70 mg of 7-methoxy-4-(hydroxymethyl)-2H-chromen-2-one as a white solid (yield: 30%). The product was characterized by ^{1}H NMR, ^{13}C NMR and ESI-MS. The product was obtained in 30% yield (70 mg).



Scheme S3. Synthesis of 7-methoxy-4-(hydroxymethyl)-2H-chromen-2-one (**8**).

8: ^{1}H-NMR (500 MHz, DMSO) δ: 4.73 (s, 3H), 5.60 (s, 1H), 6.30 (s, 1H), 6.94 (dd, J = 6.5 and 2.0 Hz, 1H), 7.0 (d, J = 2.5 Hz, 1H), 7.62 (d, J = 8.5 Hz, 1H); ^{13}C-NMR (125 MHz, DMSO) δ: 56.36, 59.55, 101.28, 107.86, 111.12, 112.60, 125.85, 155.28, 157.20, 160.95, 162.69. ESI-HRMS: Calculated for $C_{11}H_{10}0_4Na$ $[M+Na]^+$ 229.0471, observed: 229.0489.

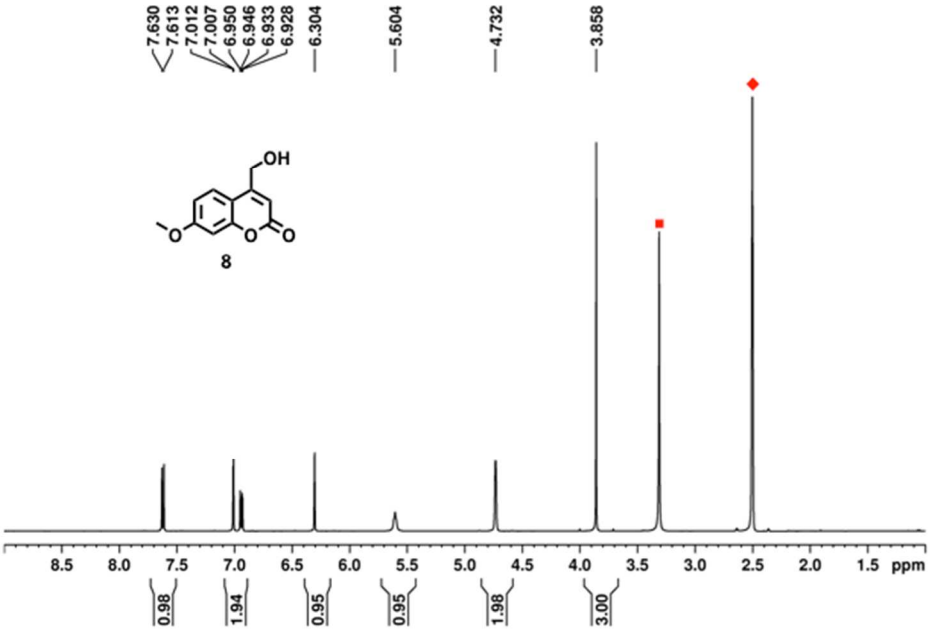


Figure S29. [1]H-NMR (500 MHz) spectrum of photoproduct **8** in DMSO-d_6. ◆ and ■ indicate the residual solvent peaks of DMSO-d_6 and water, respectively.

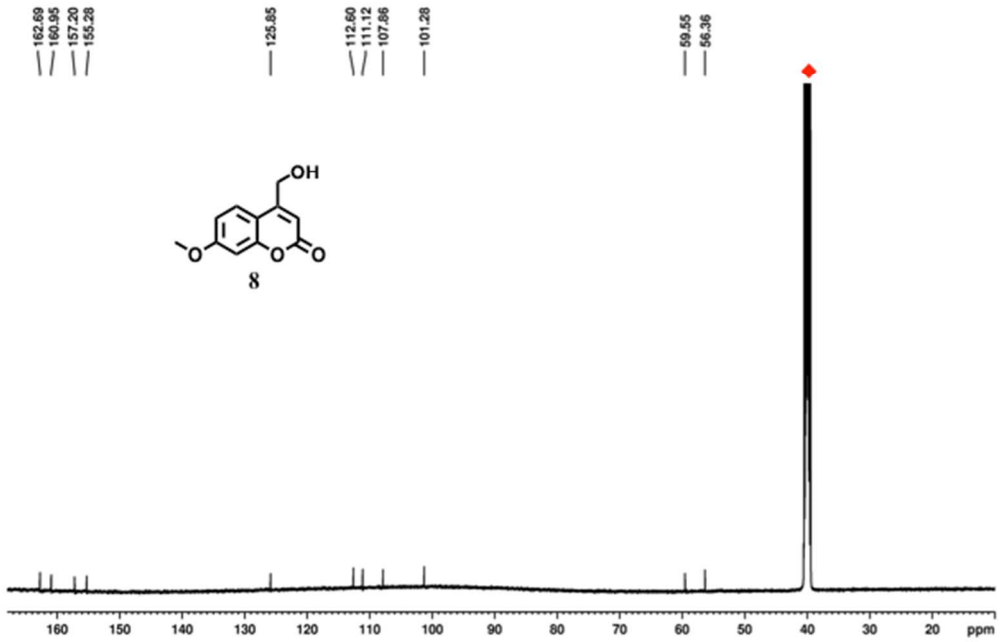


Figure S30. [13]C-NMR (125 MHz) spectra of photoproduct **8** in DMSO-d_6. ◆ indicates the residual solvent peak of DMSO-d_6.

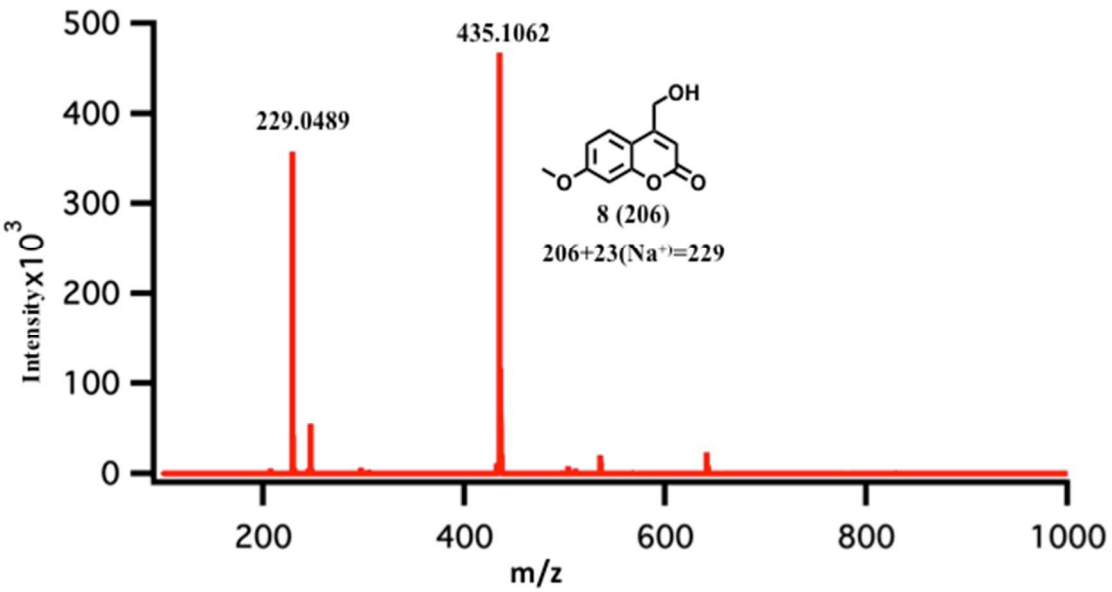


Figure S31. ESI mass spectrum of **8** in methanol-chloroform (50:50) containing 0.1 % formic acid.

3. Preparation and spectral characterization of host-guest complexes

3.1 Preparation of host-guest complexes of octa acid with phototriggers

UV-Vis spectra were recorded by using a UV-2600 UV-Vis Sspetrophotometer (Shimdazu) and the emission spectra were recorded using a FS920CDT Edinburgh fluorimeter. A 60 mM stock solution of the guest was prepared in DMSO, and 12 mL of $5x10^{-5}$ M of host (OA) solution was prepared at a pH 8.7 using 10 mM $Na_2B_4O_7$ buffer/H_2O. The solutions of the complexes were prepared by adding 5 µL of the 60 mM guest solution in DMSO-d_6 (which gave a final guest concentration of $2.5x10^{-5}$ M) to the prepared host solution ($5x10^{-5}$ M). After shaking the mixture manually for 2 min, the UV-Vis absorption and the emission spectra were recorded.

About 600 µL of a D_2O solution of host OA (1 mM OA in 10 mM $Na_2B_4O_7$, pH = 8.7) was placed in a NMR tube. Then 0.5 equivalent increments of guest solution (5 µL of a 60 mM solution in DMSO-d_6) were added. The ^1H NMR experiments were carried out after shaking the NMR tube for 2 min after each addition. Complex formation was monitored by the upfield shift of the aliphatic proton peaks of the guest.

3.2 UV-Visible absorbance and fluorescence spectra of 1-8

(a) Absorption spectra of coumaryl esters 1 – 7 and 7-methoxy-4-(hydroxymethyl)-2H-chromen-2-one (8) in water in the presence and absence of octa acid.

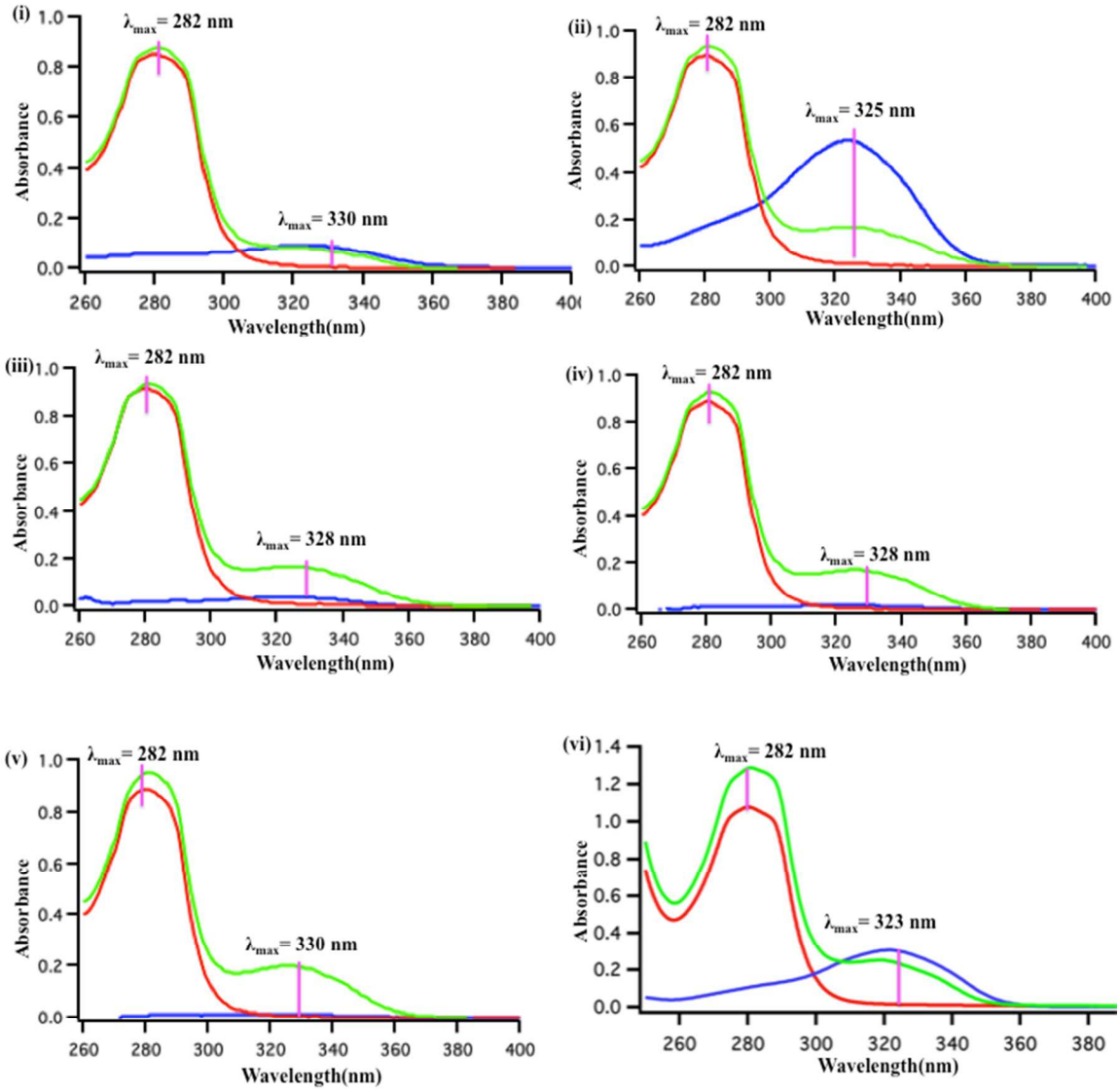


Figure S32. (i) UV-Vis absorption spectra of OA (red), **1** (blue) and **1**@$(OA)_2$ (green); (ii) UV-Vis spectra of OA (red), **3** (blue) and **3**@$(OA)_2$ (green) (iii) UV-Vis spectra of OA (red), **5** (blue) and **5**@$(OA)_2$ (green); (iv) UV-Vis spectra of OA (red), **6** (blue) and **6**@$(OA)_2$ (green) (v) UV-Vis spectra of OA (red), **7** (blue) and **7**@$(OA)_2$ (green) (vi) UV-Vis spectra

of OA (red), **8** (blue) and **8**@$(OA)_2$ (green) at [guest] = 50 μM, [OA] = 100 μM in $Na_2B_4O_7$ buffer/H_2O.

(b) Emission and excitation spectra of coumaryl esters 1 - 7 and 7-methoxy-4-(hydroxymethyl)-2H-chromen-2-one (8) in water in the presence and absence of octa acid.

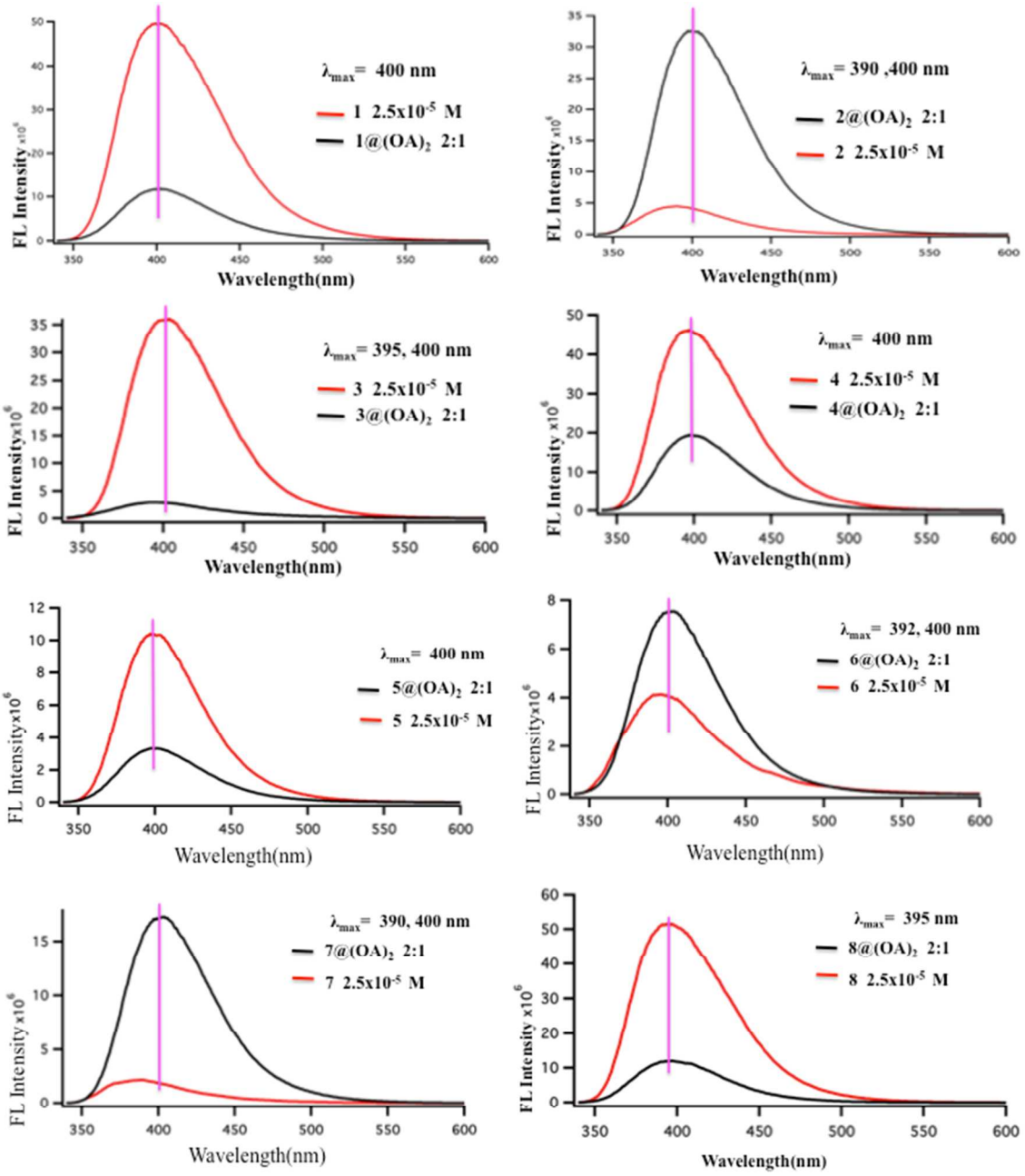


Figure S33. Emission spectra (λ_{exc}= 330 nm) of **1-8** (red) and corresponding H-G complexes with OA (black) at [**1-8**] =50 μM, [OA] = 100 μM in $Na_2B_4O_7$ buffer/H_2O).

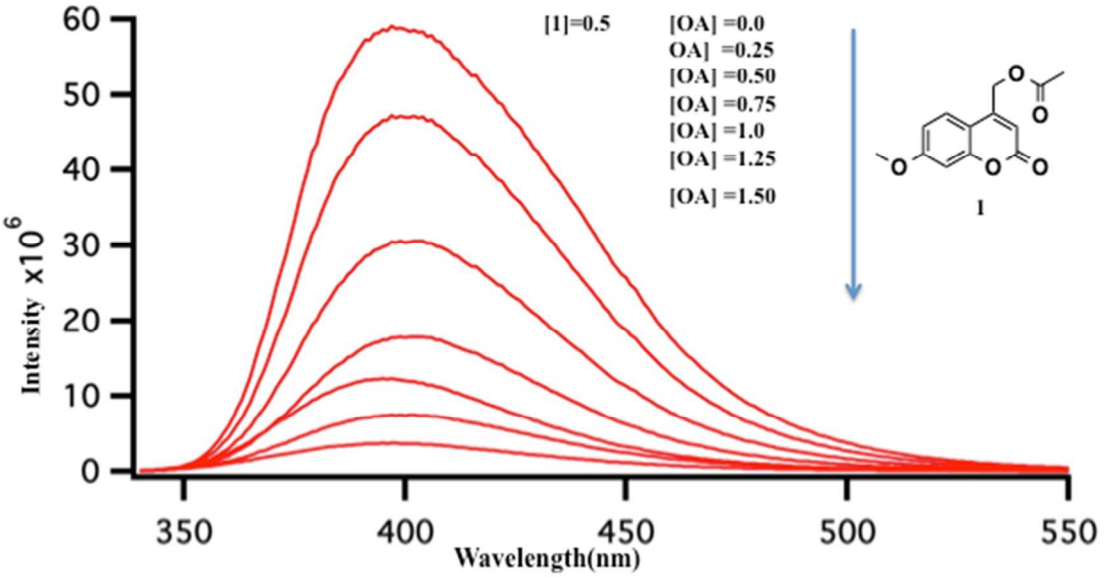


Figure S34. Emission (λ_{exc}= 330 nm) titration spectra of **1** with OA ([**1**] =50 μM, [OA]= increasing from top to bottom in $Na_2B_4O_7$ buffer/H_2O).

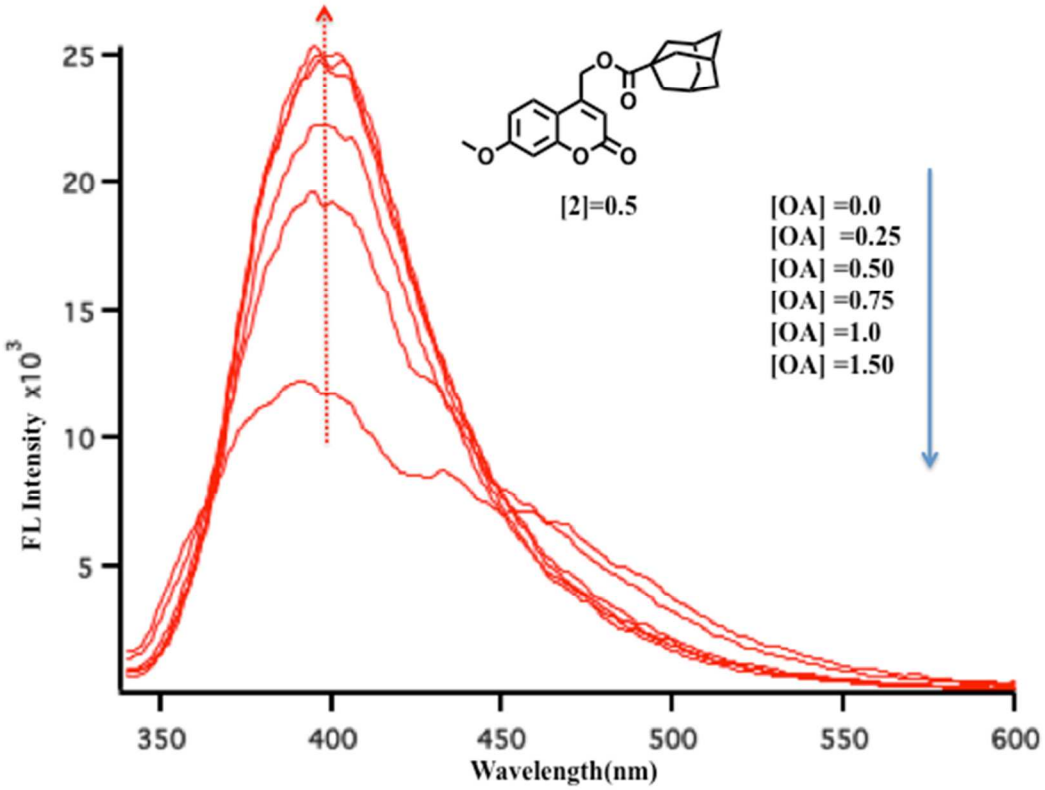


Figure S35. Emission (λ_{exc}= 330 nm) titration spectra of **2** with OA ([**2**] =50 μM, [OA] = increasing from bottom to top in $Na_2B_4O_7$ buffer/H_2O).

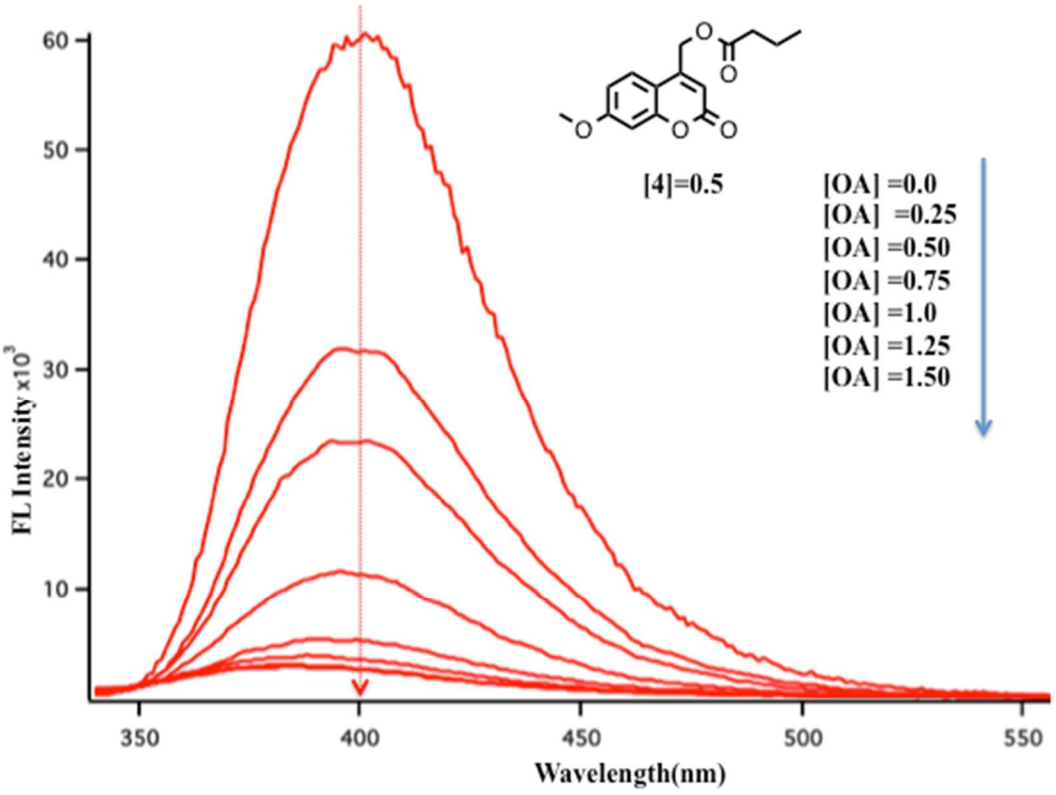


Figure S36. Emission (λ_{exc}= 330 nm) titration spectra of **4** with OA ([**4**] =50 μM, [OA] = increasing from top to bottom in $Na_2B_4O_7$ buffer/H_2O).

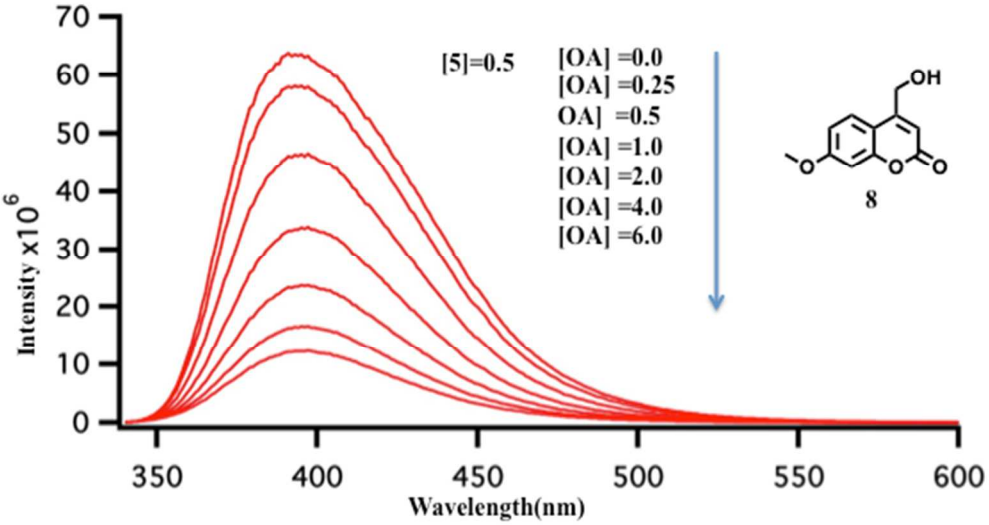


Figure S37. Emission (λ_{exc}= 330 nm) titration spectra of **8** with OA at ([**8**] =50 μM, [OA] = increasing from top to bottom in $Na_2B_4O_7$ buffer/H_2O).

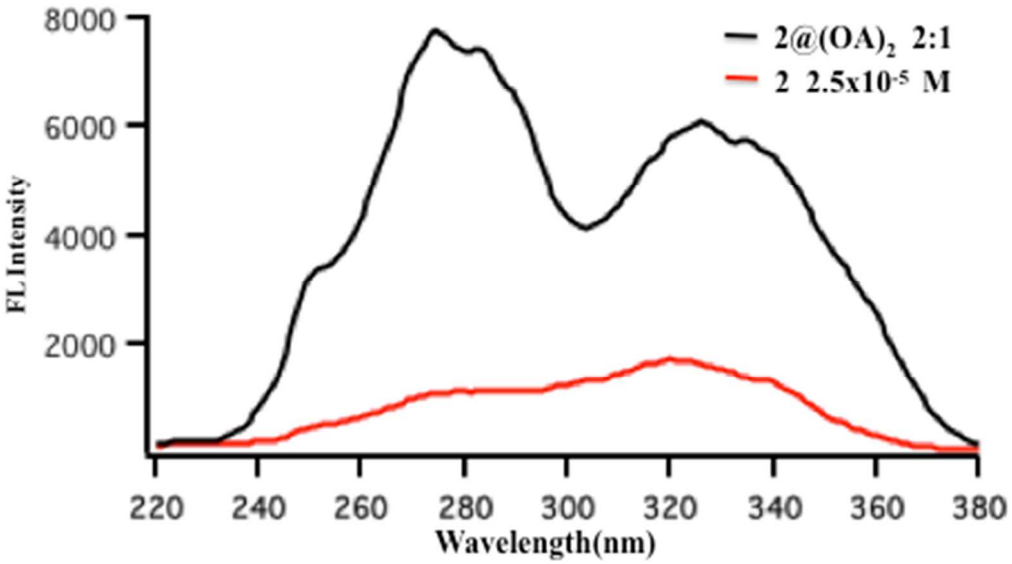


Figure S38. Excitation spectra (λ_{ems}= 400 nm) of **2** (red) and **2**@$(OA)_2$ black) at [**2**]=50 μM, [OA]= 100 μM in $Na_2B_4O_7$ buffer/H_2O).

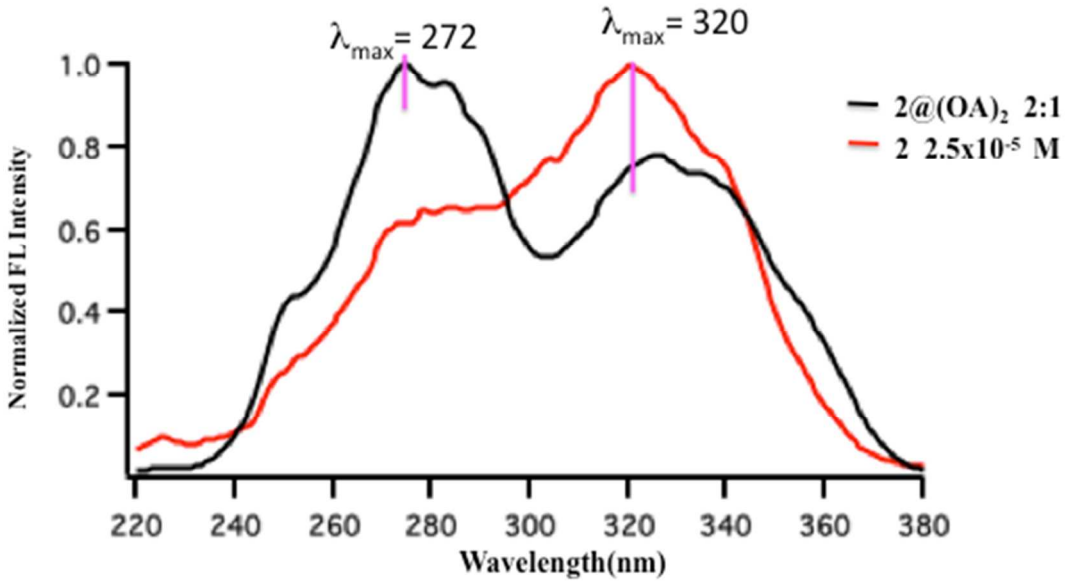


Figure S39. Normalized excitation spectra (λ_{ems}= 400 nm) of **2** (red) and **2**@$(OA)_2$ (black) at [**2**] =50 μM, [OA]= 100 μM in $Na_2B_4O_7$ buffer/H_2O). λ_{max}= 272 nm for OA and λ_{max}= 320 nm for **2**).

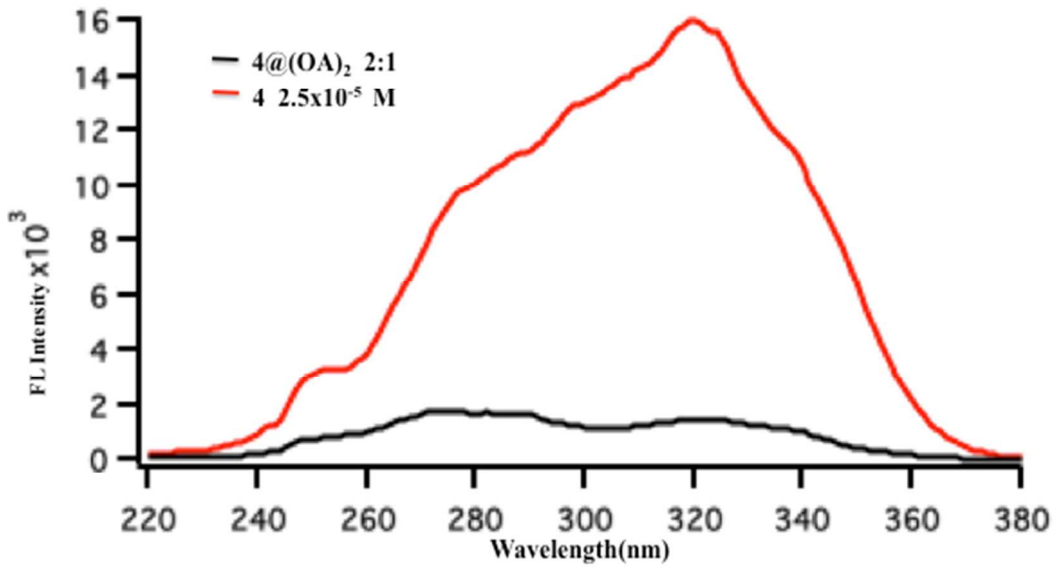


Figure S40. Excitation spectra (λ_{ems}= 400 nm) of **4** (red) and **4**@(OA)$_{2(}$, black) at [**4**] =50 μM, [OA] = 100 μM in $Na_2B_4O_7$ buffer/H_2O).

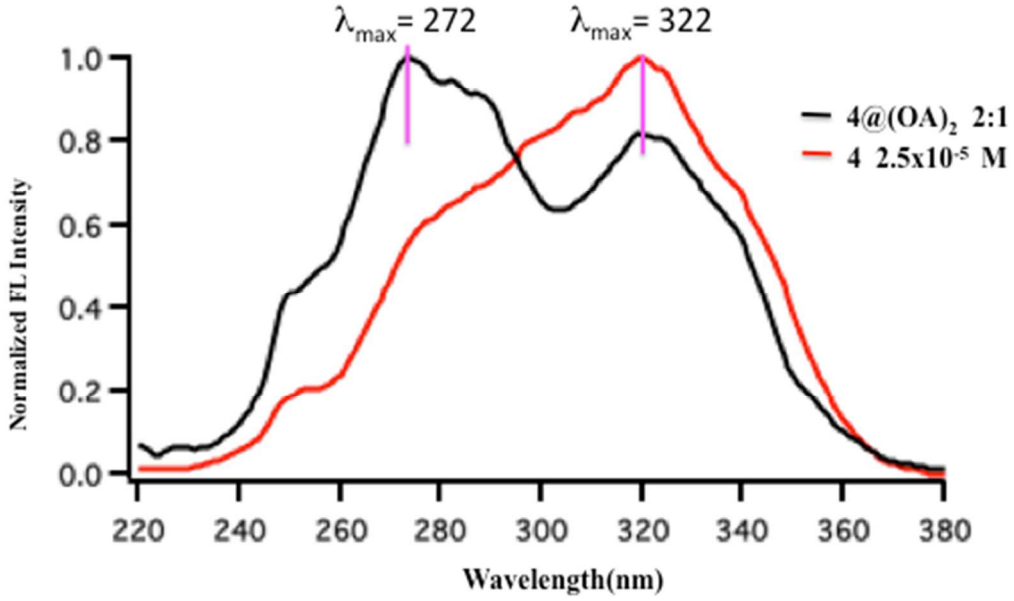


Figure S41. Normalized excitation spectra (λ_{ems}= 400 nm) of **4** (red) and **4**@(OA)$_2$ (black) at [**4**] =50 μM, [OA] = 100 μM in $Na_2B_4O_7$ buffer/H_2O). (λ_{max}= 272 nm of OA and λ_{max}= 322 nm of **4**).

3.3. [1]HNMR titration spectra of OA and compounds 1-8, and correspondent DOSY and COSY NMR spectra.

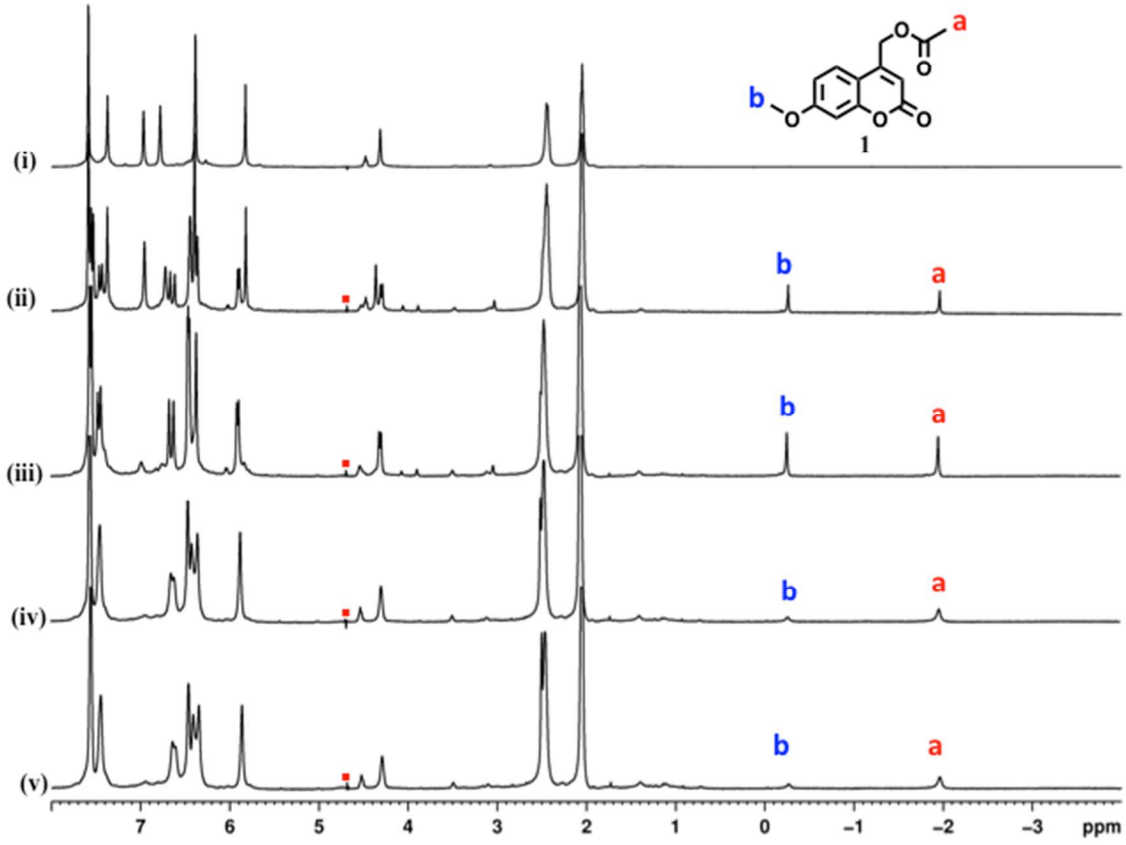


Figure S42. ^{1}H NMR (500 MHz, 10 mM $Na_2B_4O_7$ buffer/D_2O, pH = 8.7) spectra of (i) OA ([OA] = 1 mM) (ii) **1**@OA (OA=1 mM, [**1**] = 0.25 mM); (iii) **1**@OA (OA=1 mM, [**1**] = 0.5 mM); (iv) **1**@OA (OA=1 mM, [**1**] = 0.75 mM); (v) **1**@OA (OA=1 mM, [**1**] = 1.0 mM). ▪ indicates the residual solvent peak of water.

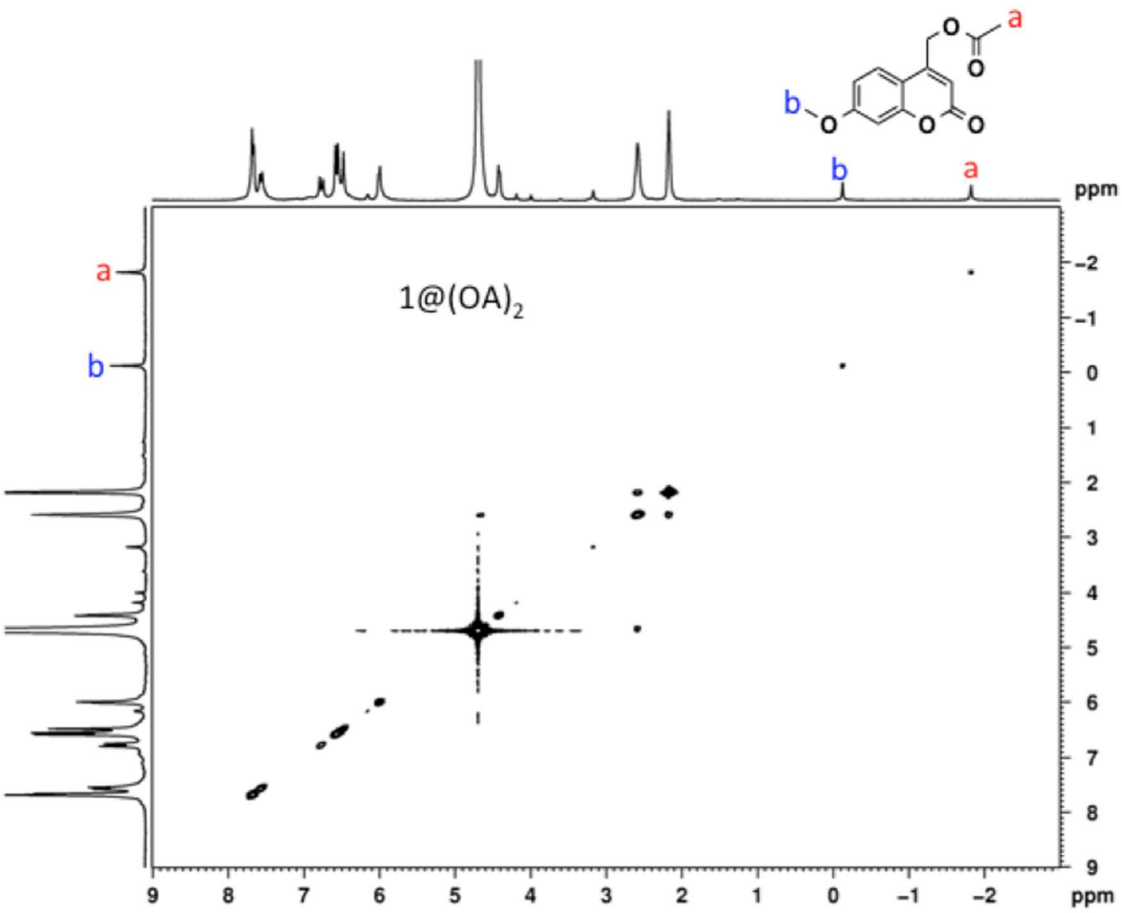


Figure S43. ^{1}H-NMR (500 MHz) COSY spectra of complex **1**@$(OA)_2$

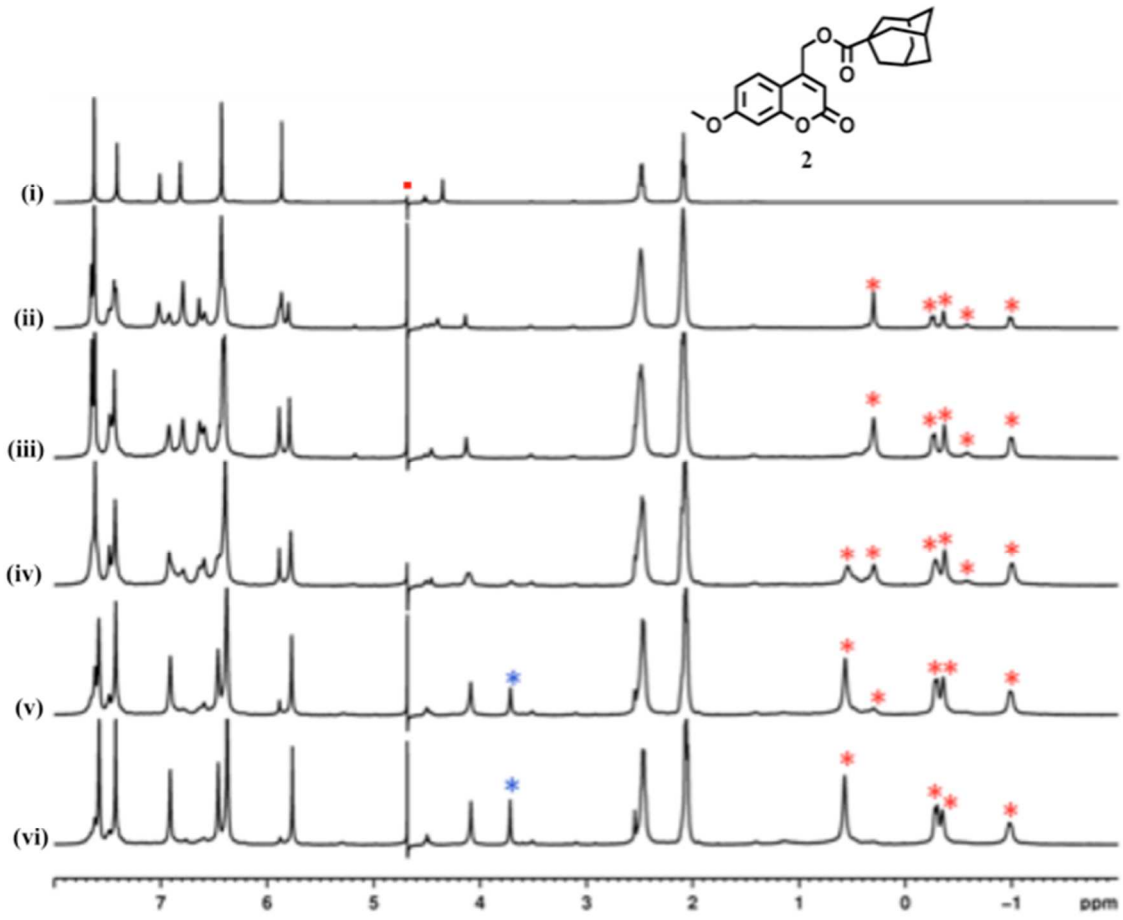


Figure S44. ^{1}H NMR (500 MHz, 10 mM $Na_2B_4O_7$ buffer/D_2O, pH = 8.7) (i) OA ([OA] = 1 mM) (ii) **2**@OA (OA=1 mM, [**2**] = 0.25 mM); (iii) **2**@OA (OA=1 mM, [**2**] = 0.5 mM); (iv) **2**@OA (OA=1 mM, [**2**] = 0.75 mM); (v) **2**@OA (OA=1 mM, [**2**] = 1.0 mM); (vi) **2**@OA (OA=1 mM, [**2**] = 1.5 mM). ▪ indicates the residual solvent peak of water.

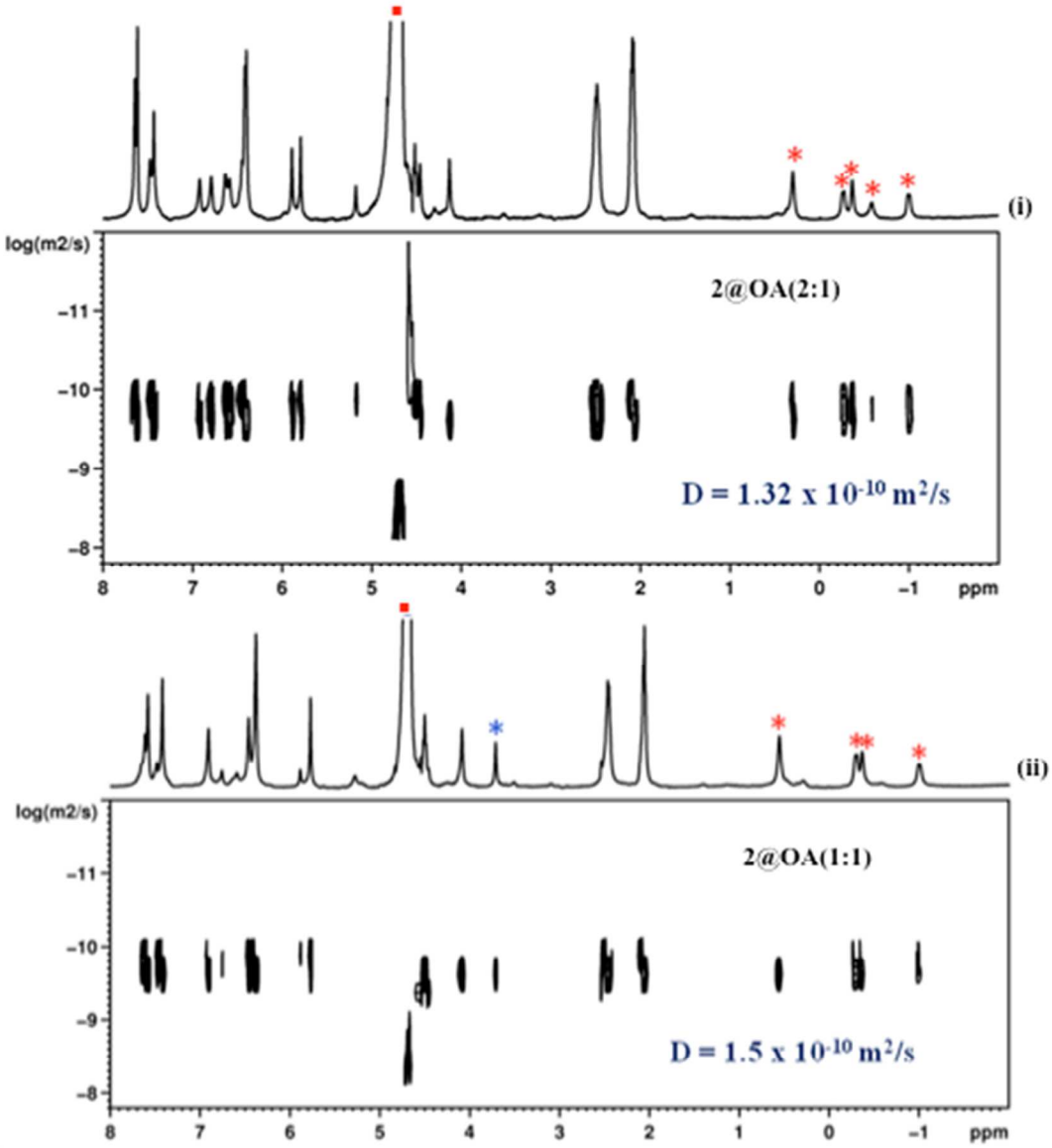


Figure S45. 2D DOSY NMR (500 MHz, 10 mM $Na_2B_4O_7$ buffer/D_2O, pH = 8.7) spectra of (i) **2**@$(OA)_2$ ([OA] = 1 mM and [**2**] = 0.5 mM) (ii) **2**@OA ([OA] = 1 mM and [**2**] = 1 mM) "*" indicates the OA bound guest **2** aliphatic proton peaks. "*" indicates the –OMe proton peak of **2** for **2**@OA (1:1) complex. ▪ indicates the residual solvent peak of water.

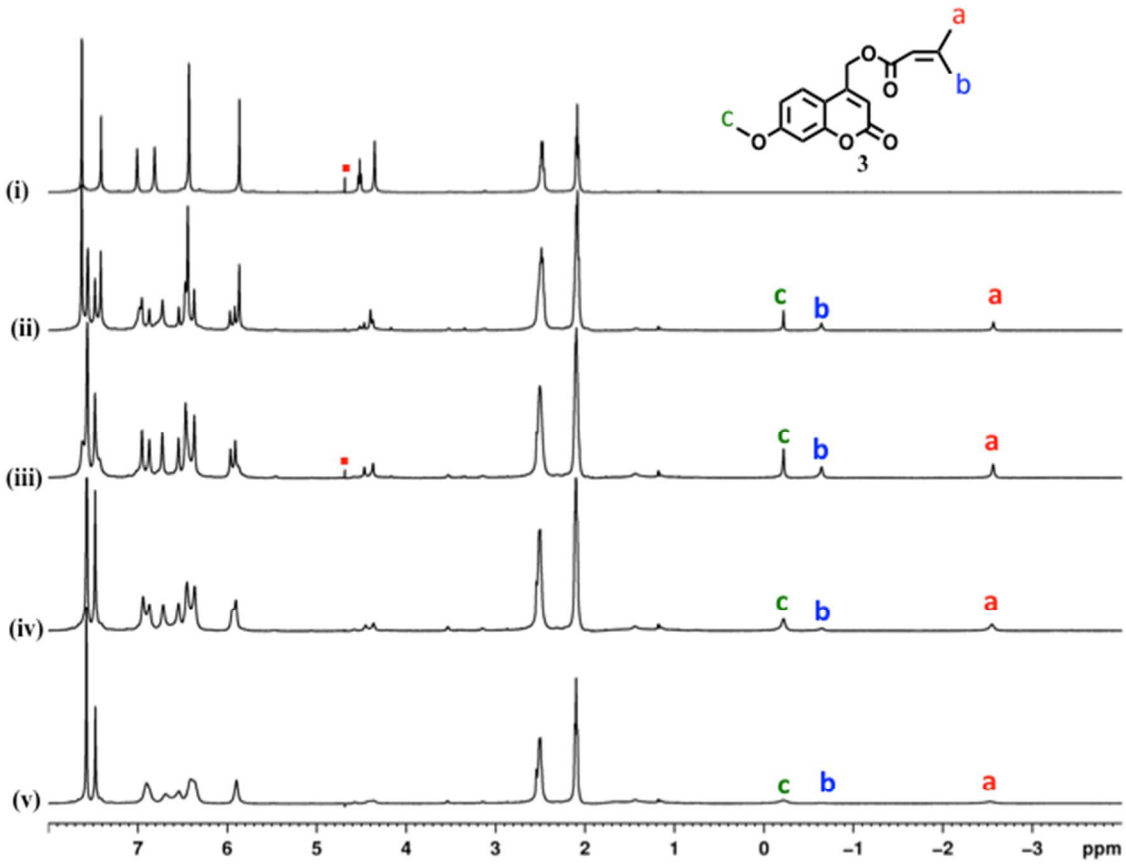


Figure S46. ^{1}H NMR (500 MHz, 10 mM $Na_2B_4O_7$ buffer/D_2O, pH = 8.7) spectra of (i) OA ([OA] = 1 mM); (ii) **3**@OA (OA=1 mM, [**3**] = 0.25 mM); (iii) **3**@OA (OA=1 mM, [**3**] = 0.5 mM); (iv) **3**@OA (OA=1 mM, [**3**] = 0.75 mM); (v) **3**@OA (OA=1 mM, [**3**] = 1 mM). ▪ indicates the residual solvent peak of water.

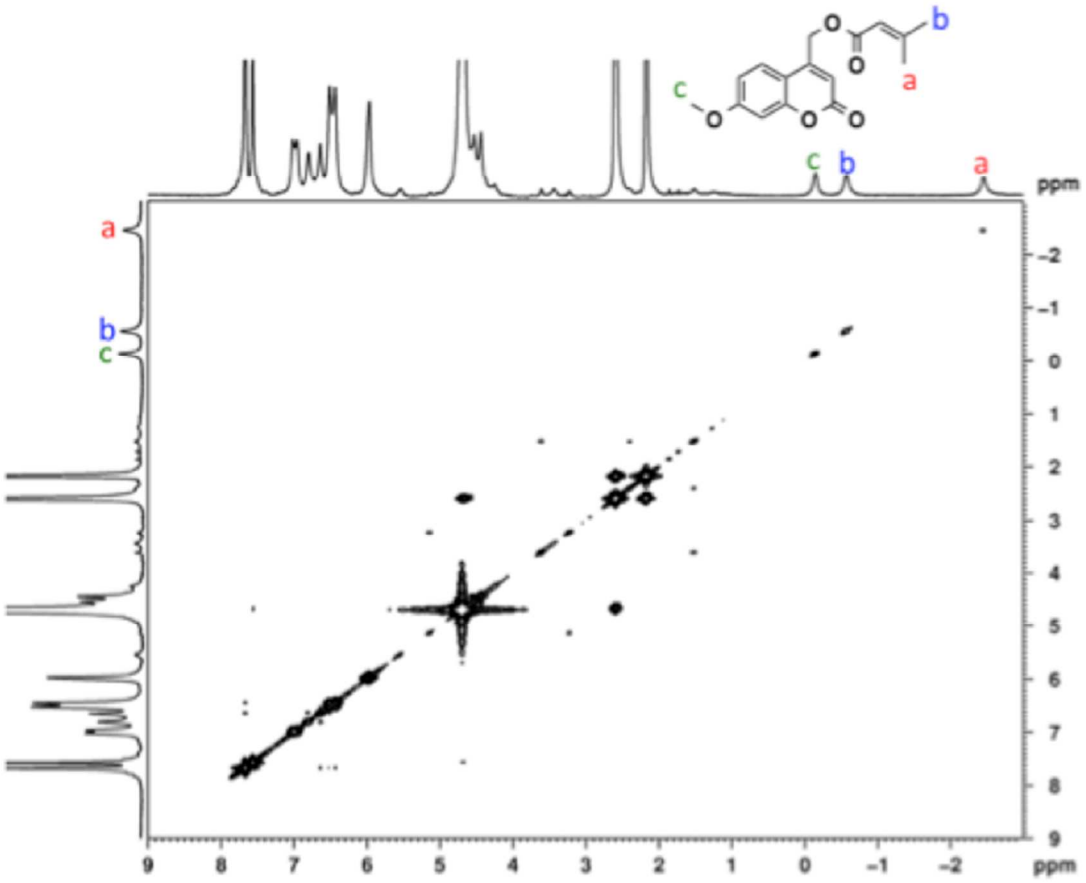


Figure S47. ^{1}H-NMR (500 MHz) COSY spectra of complex **3**@$(OA)_2$

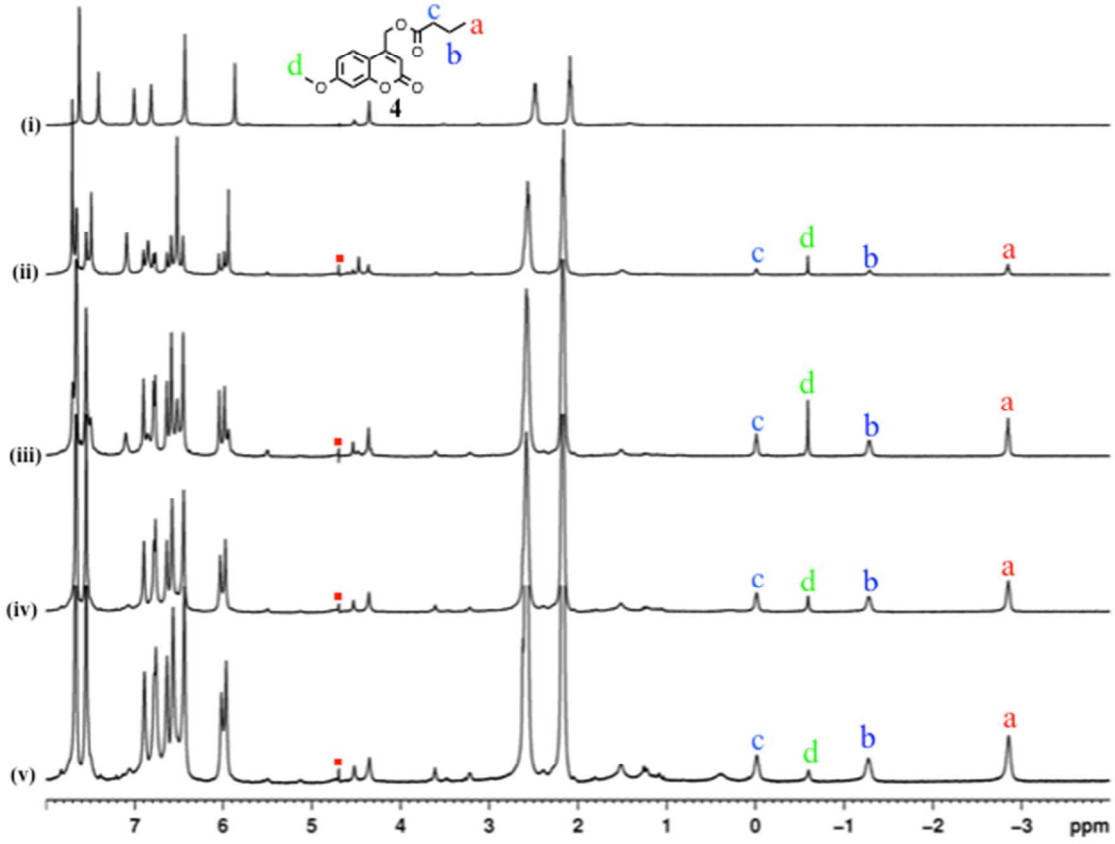


Figure S48. ^{1}H NMR (500 MHz, 10 mM $Na_2B_4O_7$ buffer/D_2O, pH = 8.7) spectra of (i) OA ([OA] = 1 mM); (ii) **4**@OA (OA=1 mM, [**4**] = 0.25 mM); (iii) **4**@OA (OA=1 mM, [**4**] = 0.5 mM); (iv) **4**@OA (OA=1 mM, [**4**] = 0.75 mM); (v) **4**@OA (OA=1 mM, [**4**] = 1 mM). ▪ indicates the residual solvent peak of water.

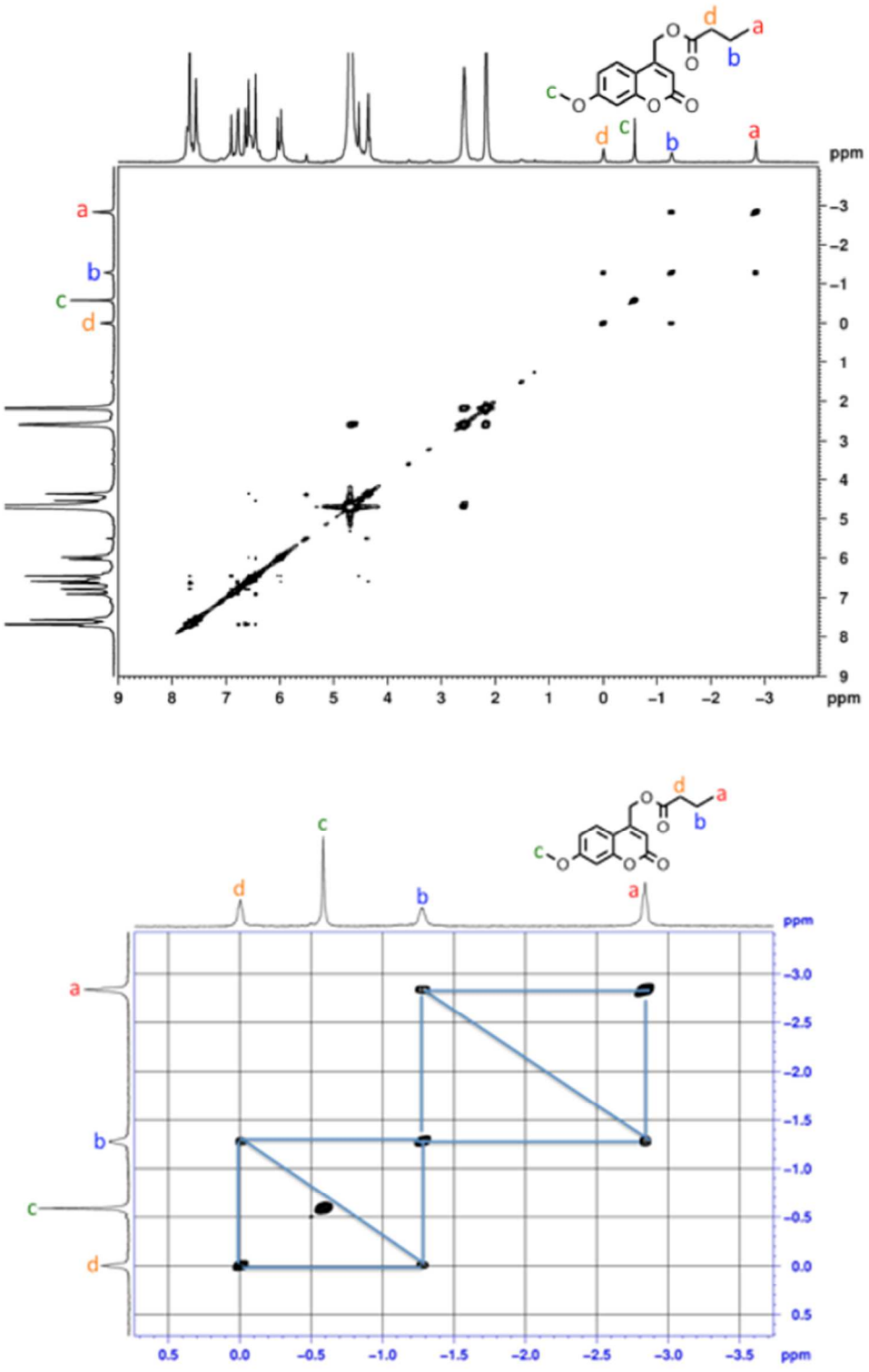


Figure S49 ^{1}H-NMR (500 MHz) COSY spectra of complex **4**@$(OA)_2$

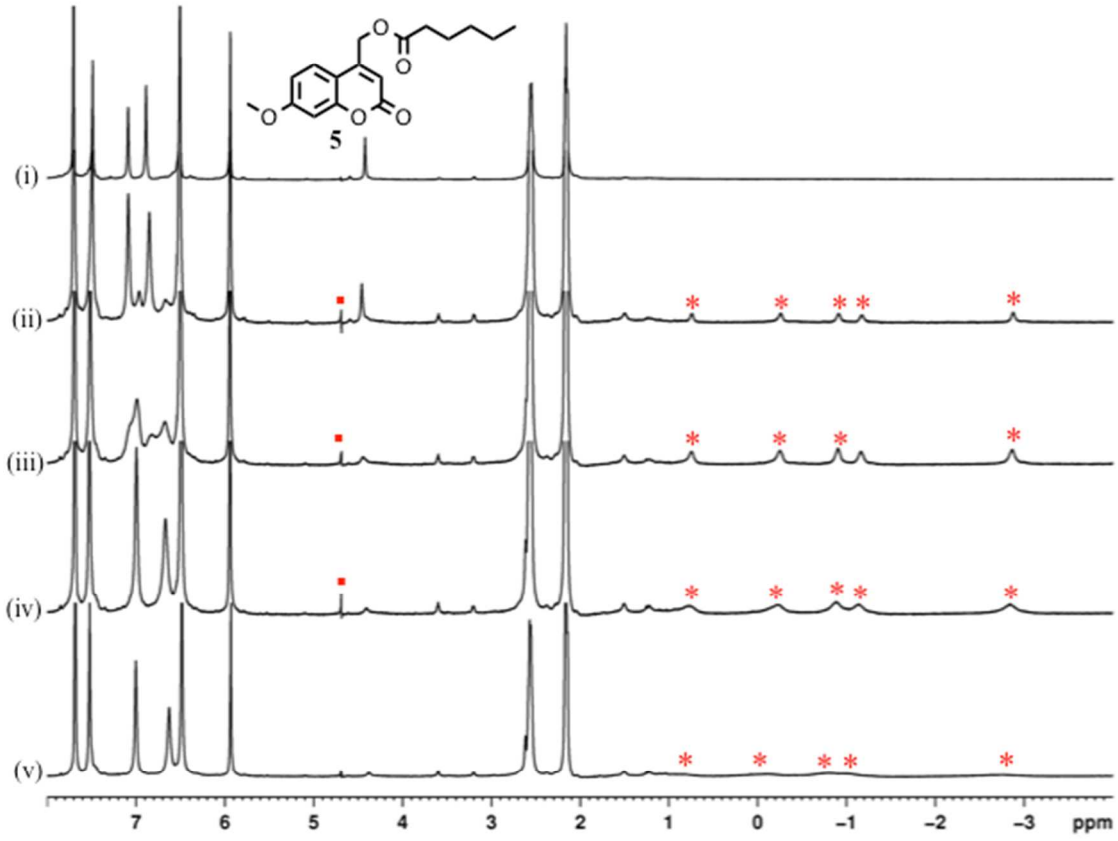


Figure S50. ^{1}H NMR (500 MHz, 10 mM $Na_2B_4O_7$ buffer/D_2O, pH = 8.7) spectra of (i) OA ([OA] = 1 mM); (ii) **5**@OA (OA=1 mM, [**5**] = 0.25 mM); (iii) **5**@OA (OA=1 mM, [**5**] = 0.5 mM); (iv) **5**@OA (OA=1 mM, [**5**] = 0.75 mM); (v) **5**@OA (OA=1 mM, [**5**] = 1 mM). ▪ indicates the residual solvent peak of water.

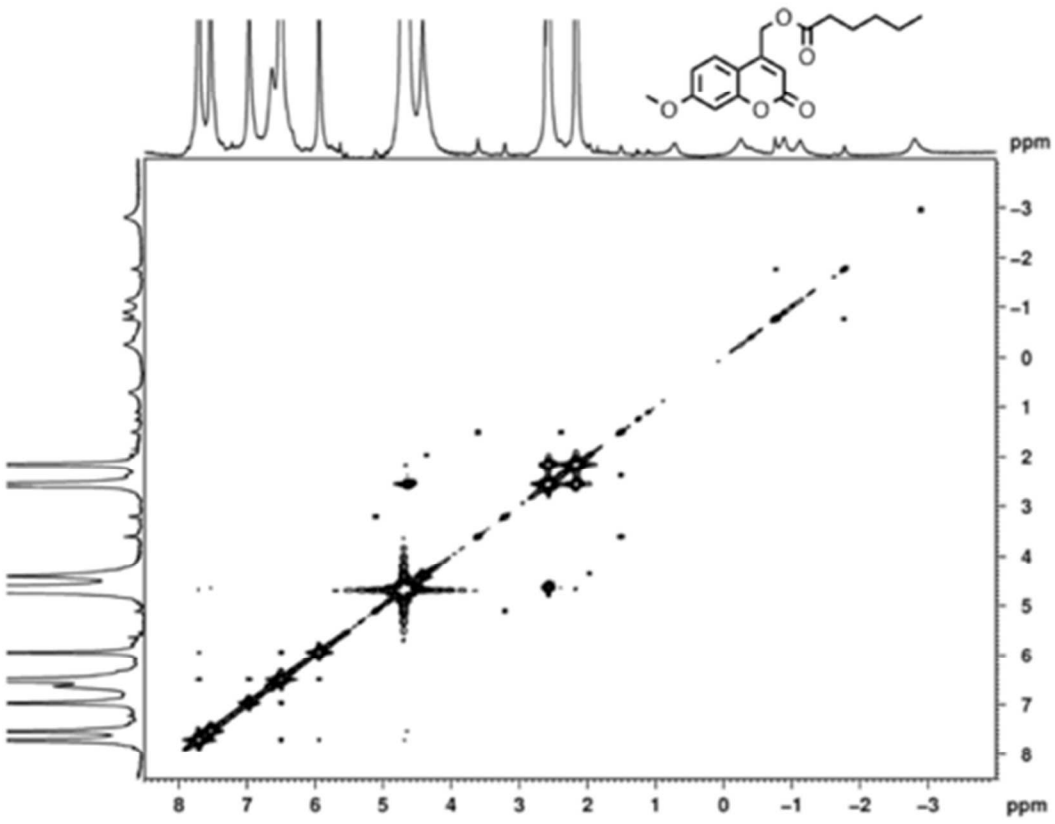


Figure S51 ^{1}H-NMR (500 MHz) COSY spectra of complex **5**@$(OA)_2$.

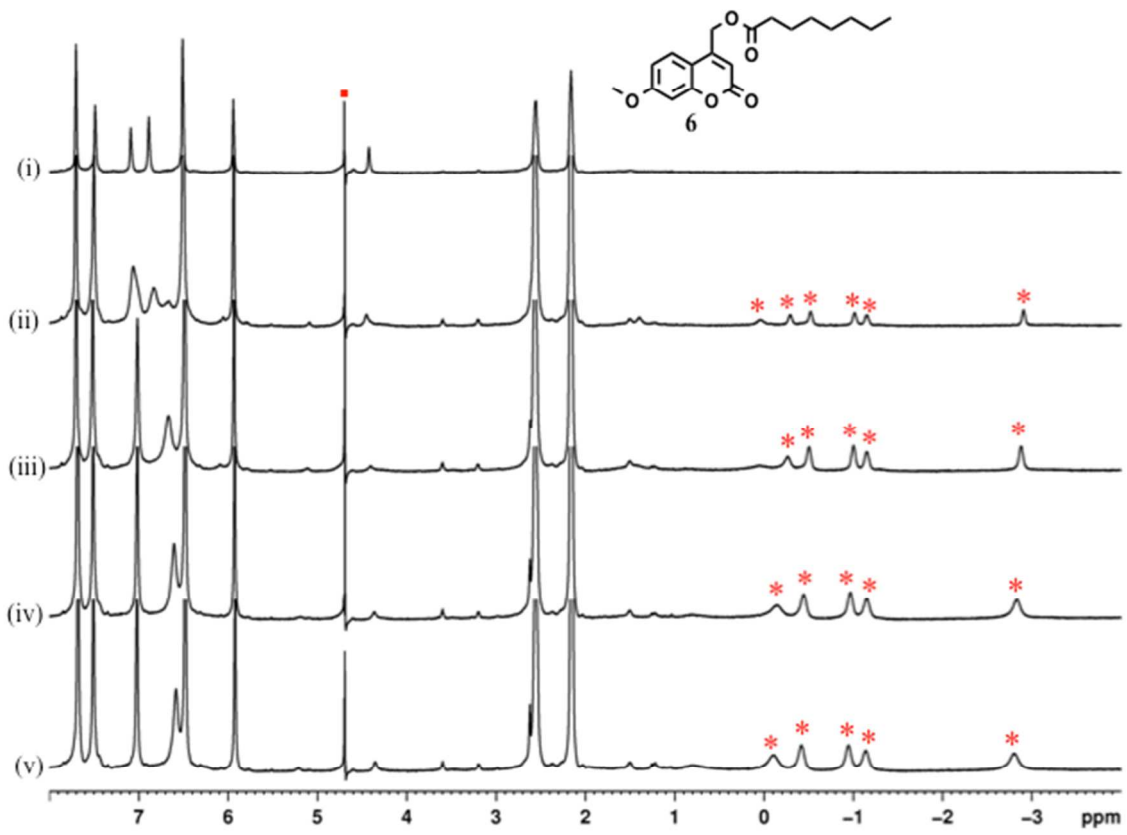


Figure S52. ^{1}H NMR (500 MHz, 10 mM $Na_2B_4O_7$ buffer/D_2O, pH = 8.7) spectra of (i) OA ([OA] = 1 mM); (ii) **6**@OA (OA=1 mM, [**6**] = 0.25 mM); (iii) **6**@OA (OA=1 mM, [**6**] = 0.5 mM); (iv) **6**@OA (OA=1 mM, [**6**] = 0.75 mM); (v) **6**@OA (OA=1 mM, [**6**] = 1 mM). ▪ indicates the residual solvent peak of water.

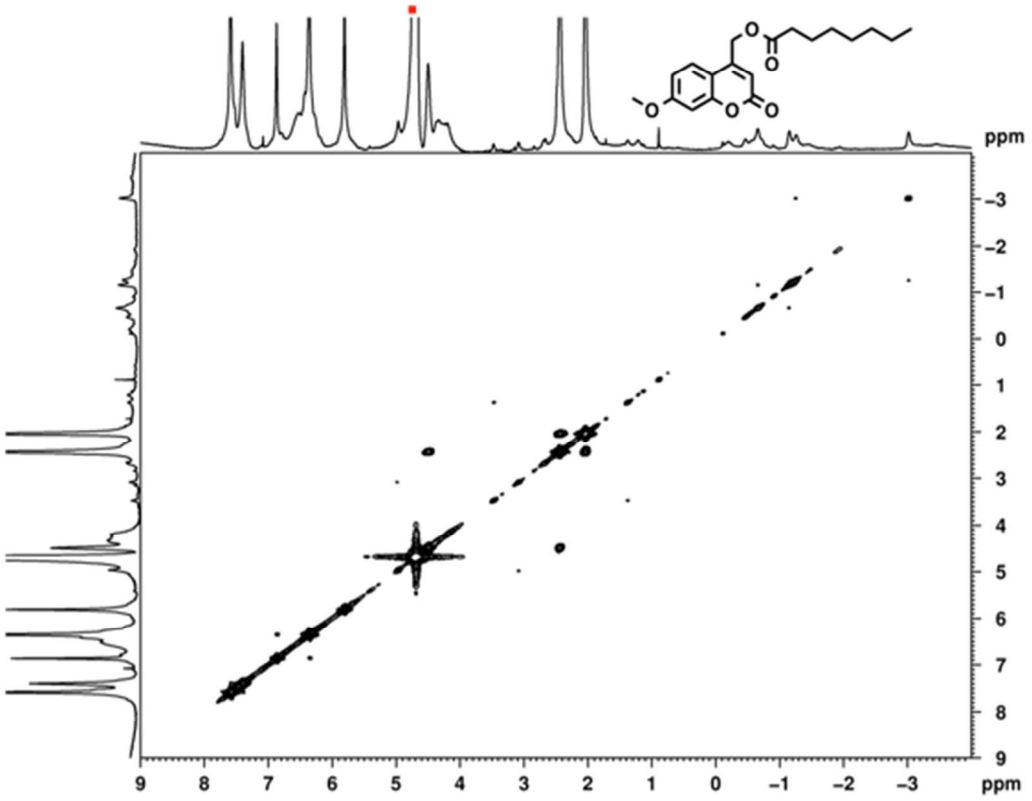


Figure S53. ^{1}H-NMR (500 MHz) COSY spectra of complex **6**@$(OA)_{2.}$

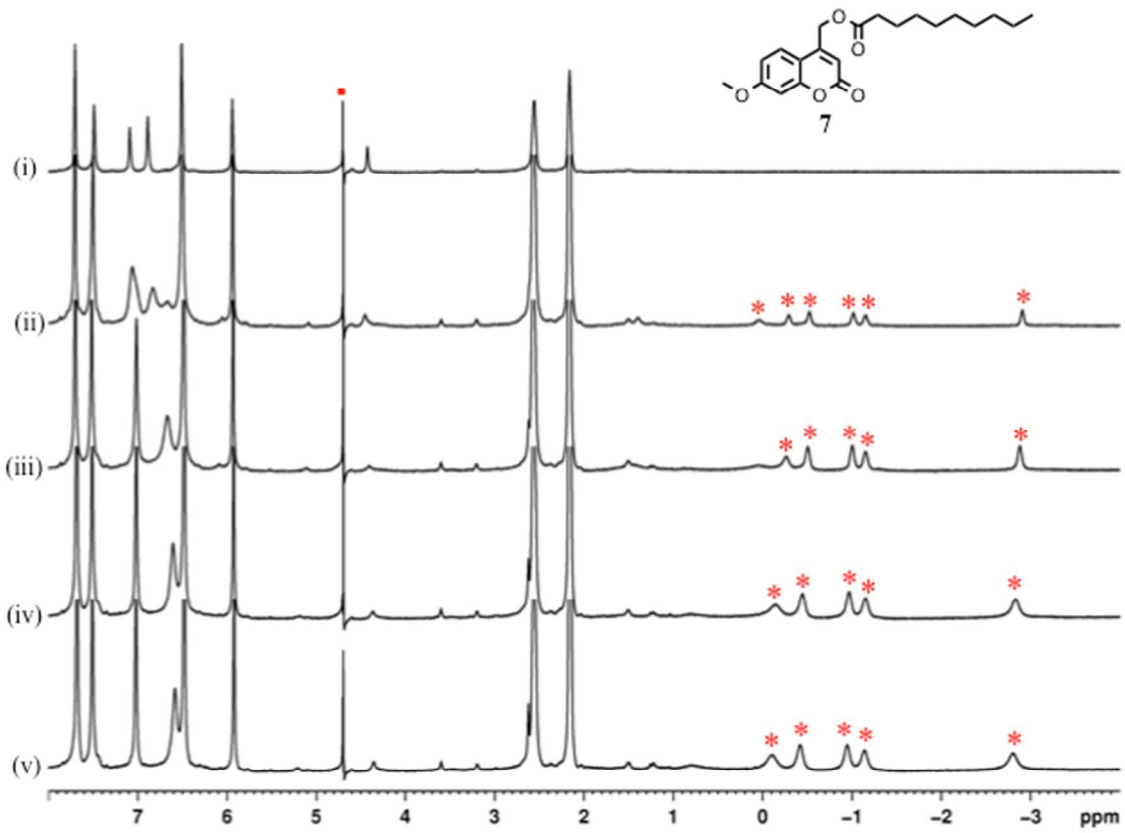


Figure S54. ^{1}H NMR (500 MHz, 10 mM $Na_2B_4O_7$ buffer/D_2O, pH = 8.7) spectra of (i) OA ([OA] = 1 mM); (ii) **7**@OA (OA=1 mM, [**7**] = 0.25 mM); (iii) **7**@OA (OA=1 mM, [**7**] = 0.5 mM); (iv) **7**@OA (OA=1 mM, [**7**] = 0.75 mM); (v) **7**@OA (OA=1 mM, [**7**] = 1 mM). ▪ indicates the residual solvent peak of water.

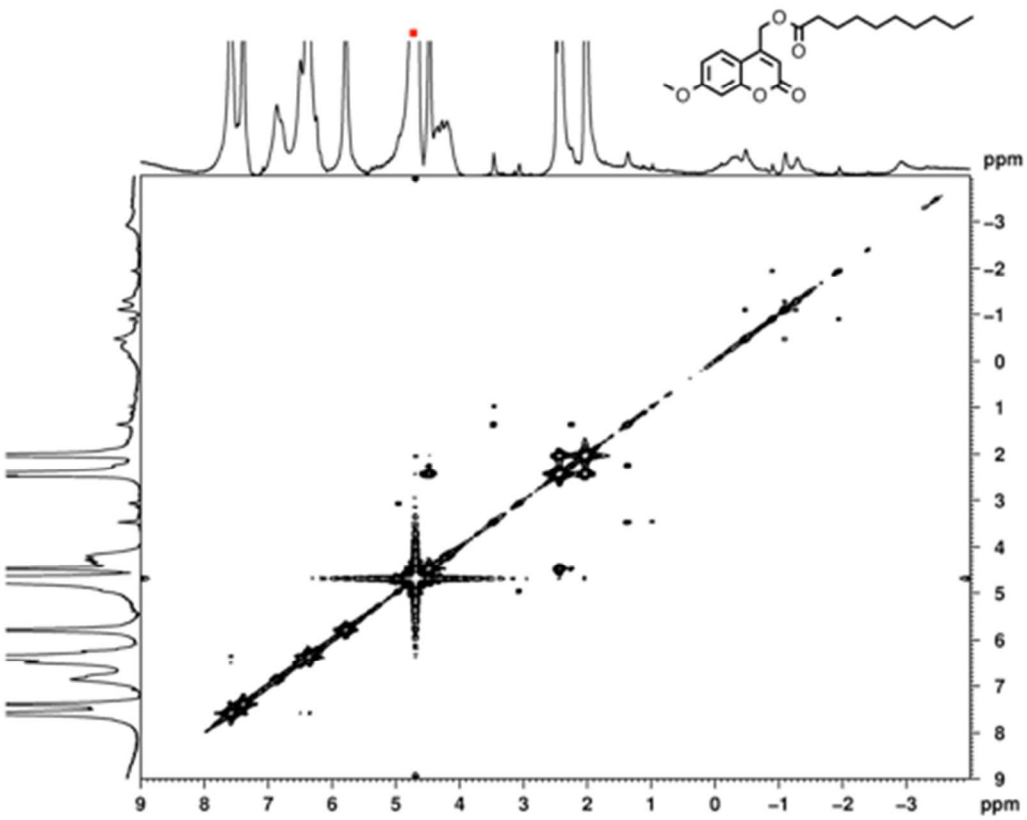


Figure S55 ^{1}H-NMR (500 MHz) COSY spectra of complex **7**@$(OA)_2$.

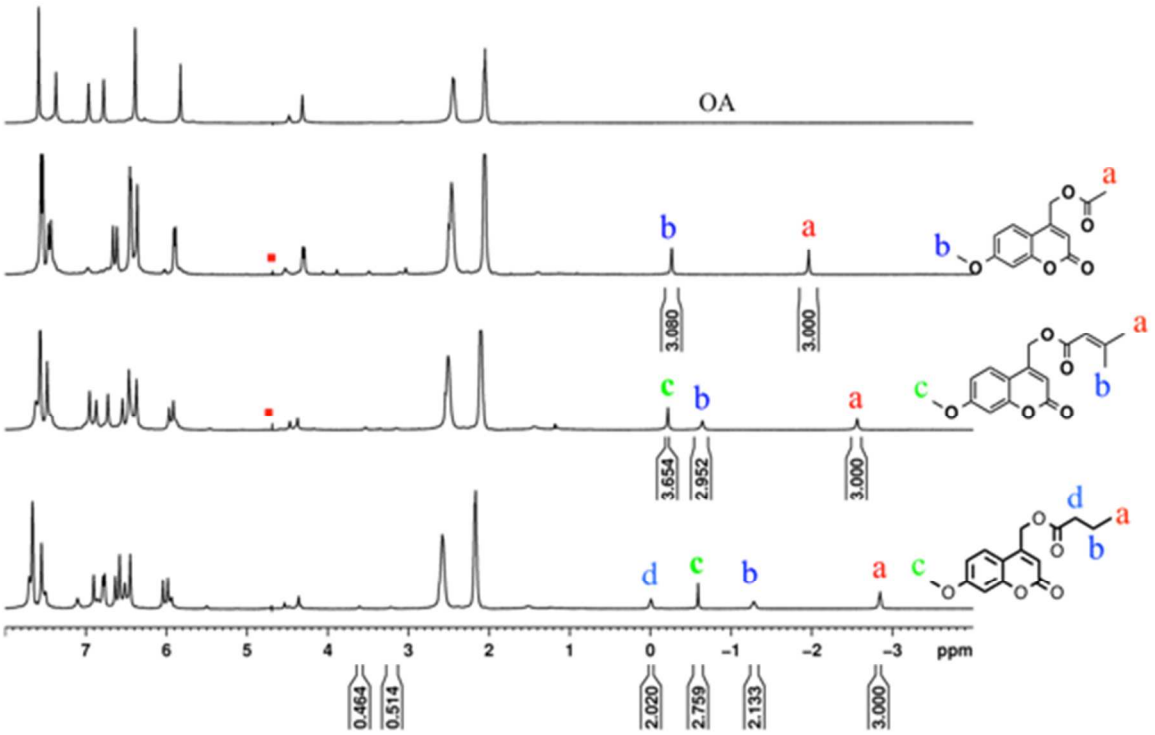


Figure S56. Integrated ^{1}H-NMR (500 MHz) spectra of complex **1**@$(OA)_2$, **3**@$(OA)_2$, and **4**@$(OA)_2$.

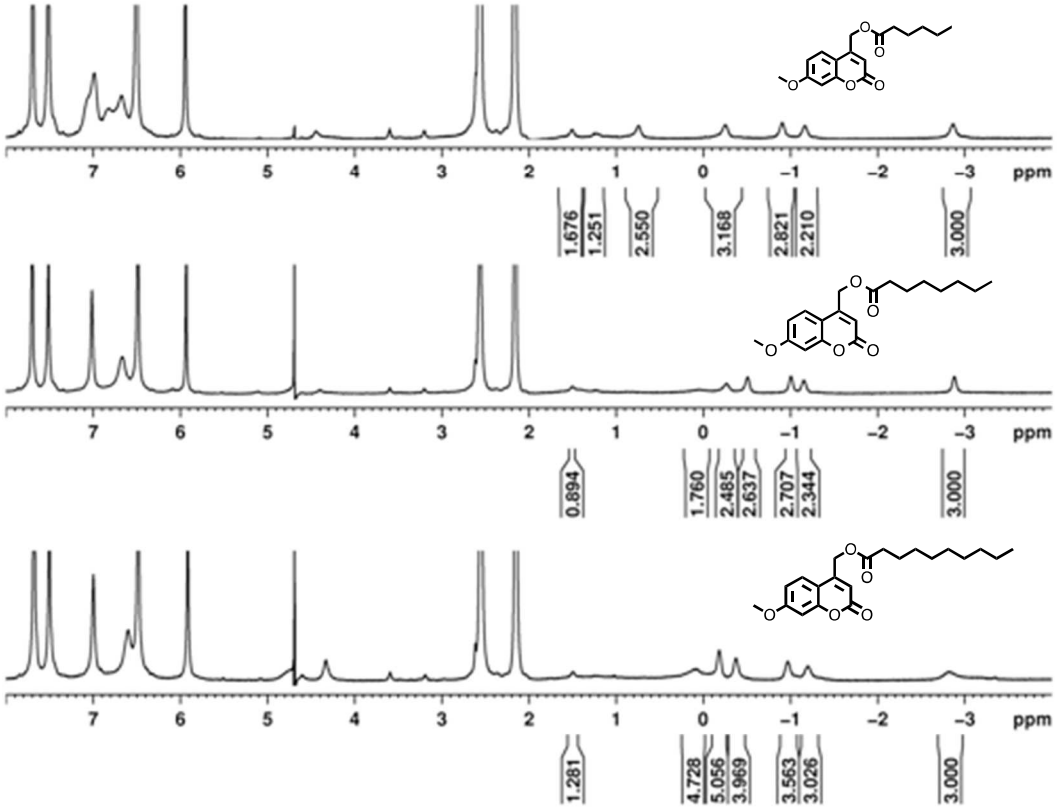


Figure S57. Integrated ^{1}H-NMR (500 MHz) spectra of complex **5**@$(OA)_2$, **6**@$(OA)_2$, and **7**@$(OA)_2$.

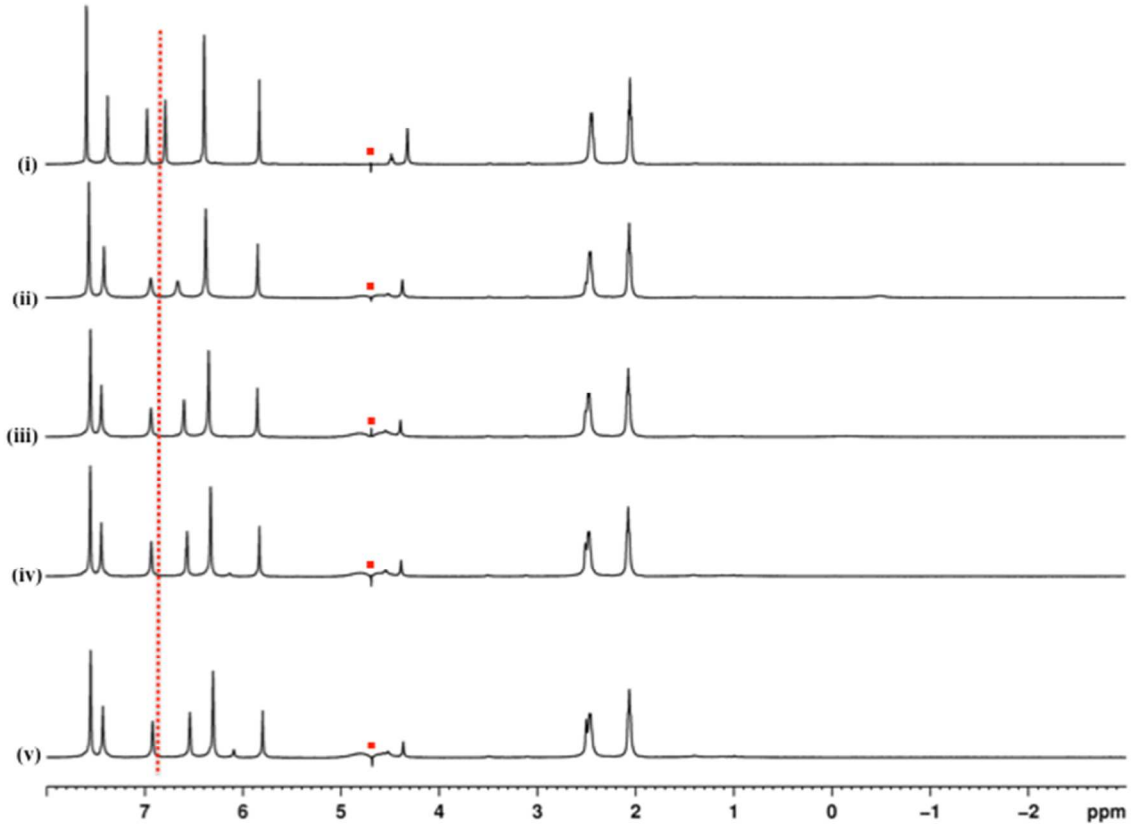


Figure S58. ^{1}H NMR (500 MHz, 10 mM $Na_2B_4O_7$ buffer/D_2O, pH = 8.7) spectra of (i) OA ([OA] = 1 mM) (ii) **8**@OA (OA=1 mM, [**8**] = 0.25 mM); (iii) **8**@OA (OA=1 mM, [**8**] = 0.5 mM); (iv)**8**@OA (OA=1 mM, [**8**] = 0.75 mM); (v) **8**@OA (OA=1 mM, [**8**] = 1.0 mM). ▪ indicates the residual solvent peak of water.

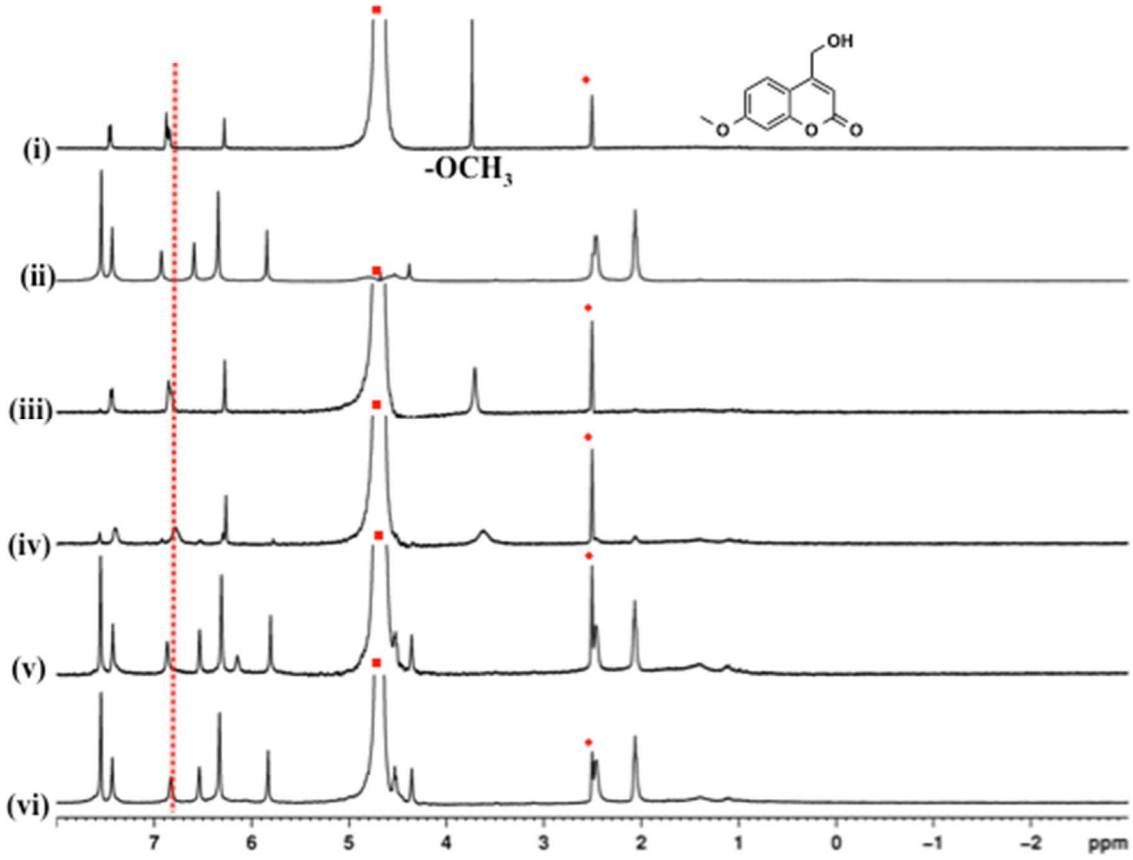


Figure S59. ^{1}H NMR (500 MHz, 10 mM $Na_2B_4O_7$ buffer/D_2O, pH = 8.7) spectra of (i) **8** ([8] = 0.5 mM, 0.5 mM); (ii) OA ([OA] = 1 mM) (iii) OA@ **8** ([**8**] = 0.5 mM, [OA]=0.01 mM); (iv) OA@ **8** ([**8**] = 0.5 mM, OA=0.03 mM); (v) OA@ **8** (([**8**] = 0.5 mM, [OA]=0.25 mM,); (vi) OA@ **8** ([**8**] = 0.5 mM, [OA=0.5 mM). ◆ and ■ indicate the residual solvent peaks of DMSO-d_6 and water, respectively.

4. Photolysis studies

4.1 Sample preparation and procedures

(a) Sample preparation for photochemical studies (monitored by ^{1}H NMR)

A 600 μL of 1 mM OA (10 mM $Na_2B_4O_7$ in D_2O, pH = 8.7) solution was placed in an NMR tube. Then 0.5 equivalents of guest (5 μL of a 60 mM solution in DMSO-d6) were added. After shaking the NMR tube for 5 min, the ^{1}H NMR was recorded to confirm the complex formation. The sample was then irradiated with UV light using a 450 W medium pressure mercury vapor lamp (Pyrex tubes, $\lambda \geq 300$ nm) and the progress of the reaction was monitored by ^{1}H NMR.

(b) Sample preparation for photochemical studies (monitored by fluorescence)

Stock solutions of each guest molecule were prepared in DMSO at 60 mM concentration. A 12 mL host (OA) solution at $5x10^{-5}$ M was also prepared using 10 mM $Na_2B_4O_7$ buffer/H_2O (pH = 8.7). The solutions of the complexes were prepared by adding 5 μL of a 60 mM guest solution in DMSO-d_6 (to make final guest concentration $2.5x10^{-5}$ M) to as prepared host solution ($5x10^{-5}$ M). After shaking the mixture (complex) manually for 2 min, the solution was placed in a quartz cuvette and irradiated with UV light using a 450 W medium pressure mercury vapor lamp ($\lambda \geq 300$ nm) and the progress of the reaction was monitored by fluorescence.

(c) Sample preparation for photochemical studies of products, monitored by liquid chromatography (LC) coupled to a diode array detector (DAD) and to a mass spectrometer (MS), LC-DAD-MS.

Irradiations of guests@OA_2 complexes were carried out using aqueous solutions of $Na_2B_4O_7$ (10 mM, pH = 8.7) containing 200 μM of the guest and 400 μM of the host and not degassed. These irradiations were performed using a high-pressure xenon lamp in conjunction with a water filter to prevent heating of the sample solution. An additional Pyrex filter was inserted to remove UV light below 300 nm. Irradiated samples for photoproduct analysis by ESI-MS/MS were prepared in 0.5 % aqueous ammonia.

(d) Identification and quantification studies of irradiated samples by Fluorescence, LC-DAD-MS, ESI-MS/MS and ^{1}H NMR)

Photoproducts of guests@OA_2 complexes were followed by LC-DAD with UV analysis at 280, 320, 330, 350 nm and by LC-MS under positive polarity or negative polarity. The identifications of 7-methoxy-4-(hydroxymethyl)-2*H*-chromen-2-one (**8**) and 7-methoxy-

4-methyl-2H-chromen-2-one (**9**) were made by injecting authentic standards. OA-coupling and decarboxylated ester photoproducts were assigned by a combination of UV (taken with the DAD), ESI-MS and ESI-MS/MS spectra and comparison with spectra of known compounds when available. The ESI-MS/MS spectra were obtained by direct injection (infusion).

Quantitative photoproduct analyses of 7-methoxy-4-(hydroxymethyl)-2H-chromen-2-one (**8**) and 7-methoxy-4-methyl-2H-chromen-2-one (**9**) were performed using calibrations curves prepared from DAD traces obtained at 320 nm. Quantitative estimations of OA-adduct products and decarboxylated trigger compounds were made by assuming the extinction coefficients at 350 nm were similar to the coumarin cage phototrigger and 7-methoxy-4-methyl-2H-chromen-2-one (**9**), respectively. Because OA-phototrigger coupling products have similar retention times or overlap with the OA signal, the concentrations of these products were estimated from traces at 350 nm, where OA does not absorb. 1-Adamantanecarboxylic acid, octanoic acid and decanoic acid were quantified by LC-MS, in the negative polarity mode by following the individual ions at m/z's 179, 143 and 171, respectively. The non-irradiated and irradiated solutions were directly injected into the LC-DAD-MS system without further processing. Acetic acid, 3,3-dimethylacrylic acid, butanoic acid and hexanoic acid were quantified by ^{1}H NMR**.** Here, the integral values were obtained before and after irradiation by taking one of the peaks of host molecule as a reference peak.

(e) ESI-MS and LC-MS analysis conditions

The ESI-MS spectra were obtained in the conditions reported in section 2.3. The LC-DAD-MS analysis was performed using an Agilent Technologies 1200 Series LC, equipped with a diode array detector and coupled to a Bruker Daltonics HCT *ultra*. A Hamilton PRP-1 reversed phase LC column (15.0 cm length, 2.1 mm internal diameter, 5 μm), stabilized at 25 °C was used. The mobile phase was comprise of acetonitrile (A) and water (B), both with 0.1 % of formic acid, and ethyl acetate (C). The gradient started with 52 % of A, 38 % of B and 10 % of C. The mobile phase composition was changed to 2 % of A, 73 % of B and 25 % of C in 5 minutes and kept at this composition for an additional 7 minutes. Finally, the system was allowed to return to the initial composition of the mobile phase (52 % of A, 38 % of B and 10 % of C) in 1 min and then stabilized for additional 5 minutes before the next run.

4.2 Fluorescence spectra of irradiated samples

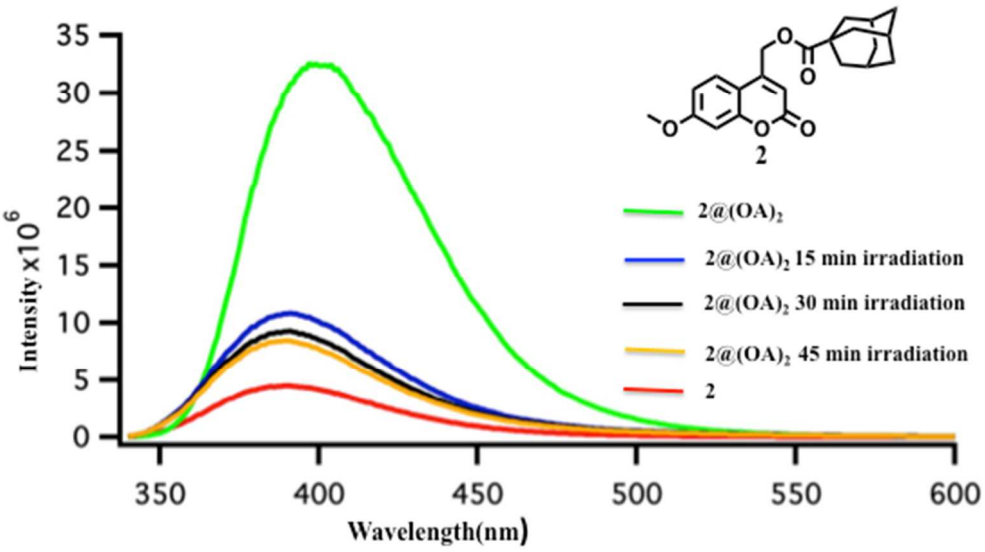


Figure S60. Emission spectra (λ_{exc}= 330 nm) of **2**@$(OA)_2$ as function of the irradiation time ([**2**] =50 μM, [OA] = 100 μM in $Na_2B_4O_7$ buffer/H_2O).

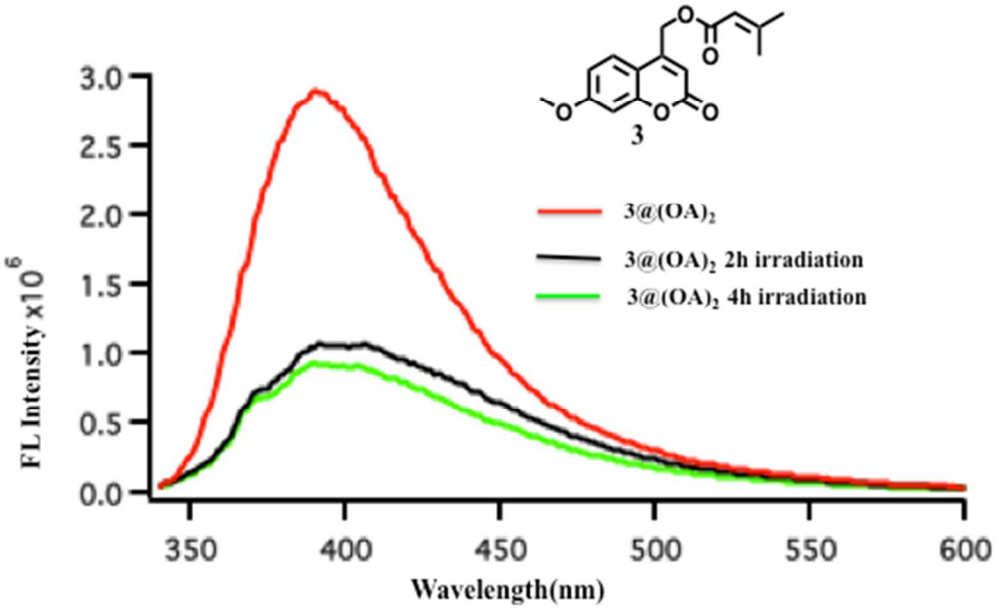


Figure S61. Emission spectra (λ_{exc}= 330 nm) of **3**@$(OA)_2$ as function of the irradiation time ([**3**] =50 μM, [OA] = 100 μM in $Na_2B_4O_7$ buffer/H_2O).

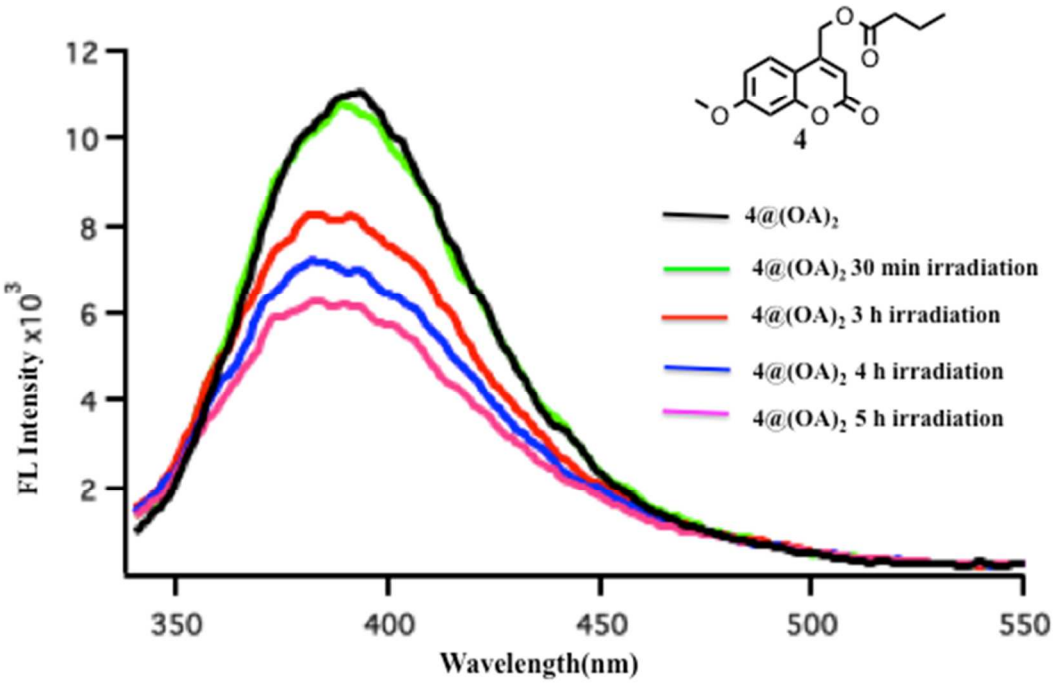


Figure S62. Emission spectra (λ_{exc}= 330 nm) of **4**@$(OA)_2$ as function of irradiation time ([**4**] =50 μM, [OA] = 100 μM in $Na_2B_4O_7$ buffer/H_2O).

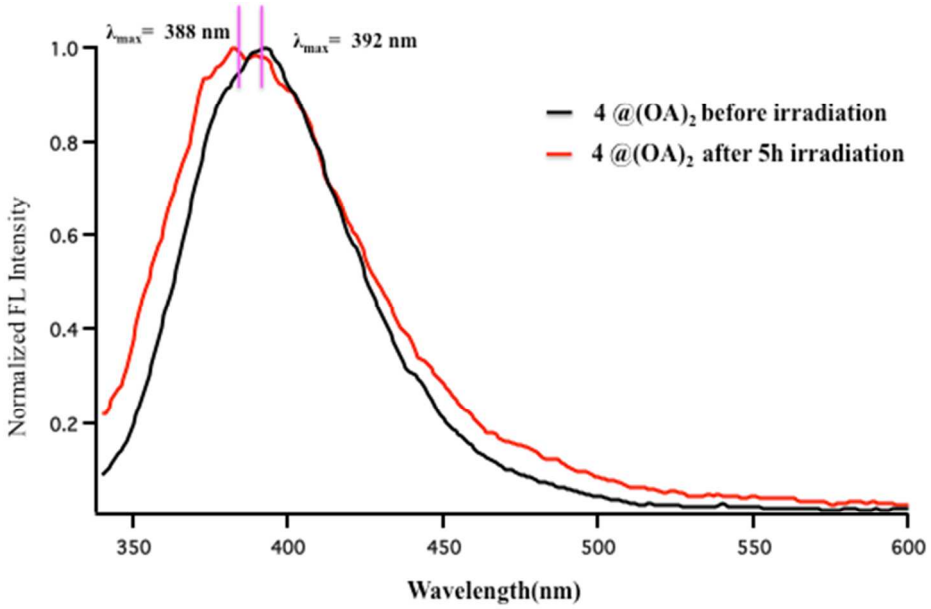


Figure S63. Normalized emission spectra (λ_{exc}= 330 nm) of **4**@$(OA)_2$ before irradiation (black) and after 5h irradiation (red) ([**4**]=50 μM, [OA]= 100 μM in $Na_2B_4O_7$ buffer/H_2O).

4.3 ^{1}H NMR spectra of irradiated samples

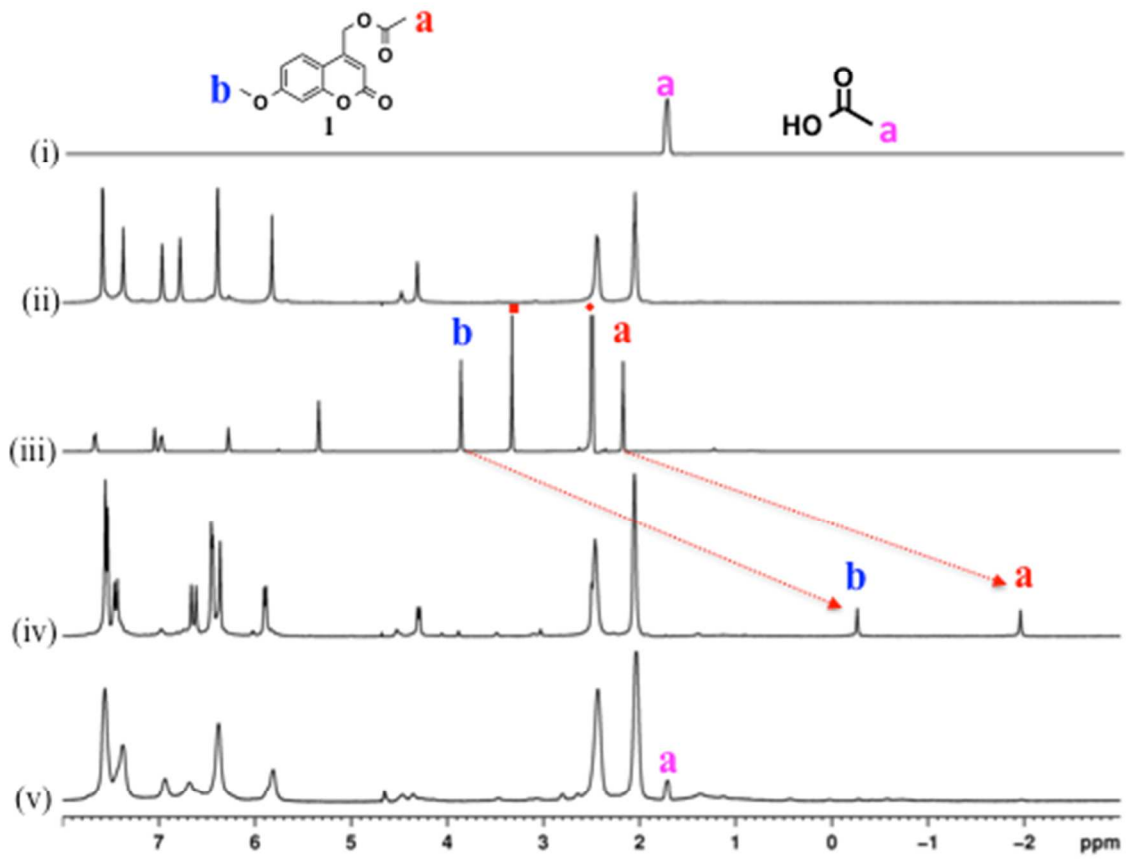


Figure S64. ^{1}H-NMR (500 MHz) spectra of (i) Acetic acid ([Acetic acid] = 0.5 mM) in 10 mM $Na_2B_4O_7$ buffer/D_2O, pH = 8.7; (ii) OA ([OA] = 1 mM) in 10 mM $Na_2B_4O_7$ buffer/D_2O, pH = 8.7; (iii) **1** in DMSO-d_6; (iv) **1**@$(OA)_2$ ([OA] = 1 mM and [**1**] = 0.5 mM) in 10 mM $Na_2B_4O_7$ buffer/D_2O, pH = 8.7); (v)) 70 min irradiation of ((iv)) ($\lambda \geq 300$ nm). ◆ and ■ indicate the residual solvent peaks of DMSO-d_6 and water, respectively.

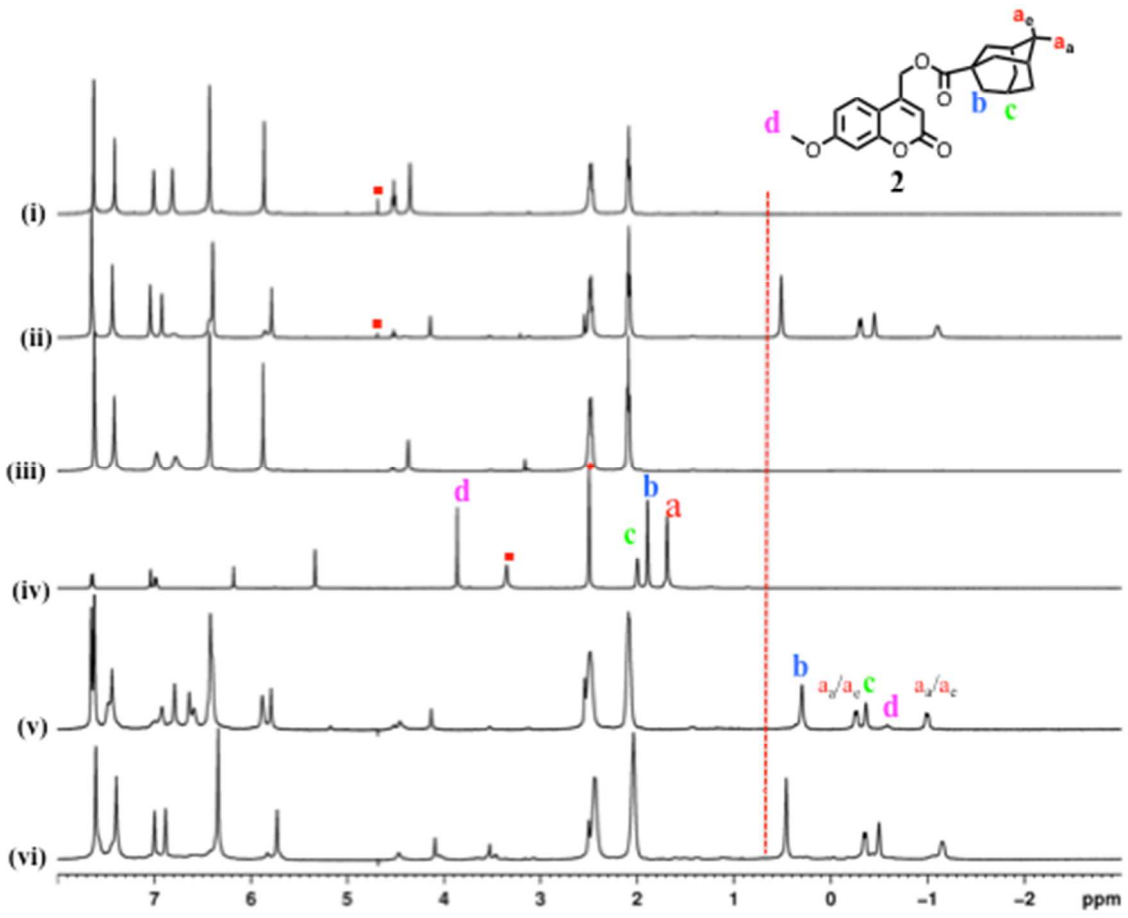


Figure S65. ^{1}H-NMR (500 MHz,) spectra of (i) OA ([OA]=1mM); (ii) 1-Adamantanecarboxylicacid@OA **(**[OA]=1mM, [1-Adamantane carboxylic acid] = 0.5 mM) in 10 mM $Na_2B_4O_7$ buffer/D_2O, pH = 8.7; (iii) **8**@OA (OA=1 mM, [**8**] = 0.5 mM) in 10 mM $Na_2B_4O_7$ buffer/D_2O, pH = 8.7; (iv) **2** in DMSO-d_6; (v) **2**@$(OA)_2$ ([OA] = 1 mM and [**2**] = 0.5 mM) in 10 mM $Na_2B_4O_7$ buffer/D_2O, pH = 8.7; (vi) after 30 min irradiation of ((v)) ($\lambda \geq$ 300 nm). ◆ and ■ indicate the residual solvent peaks of DMSO-d_6 and water, respectively.

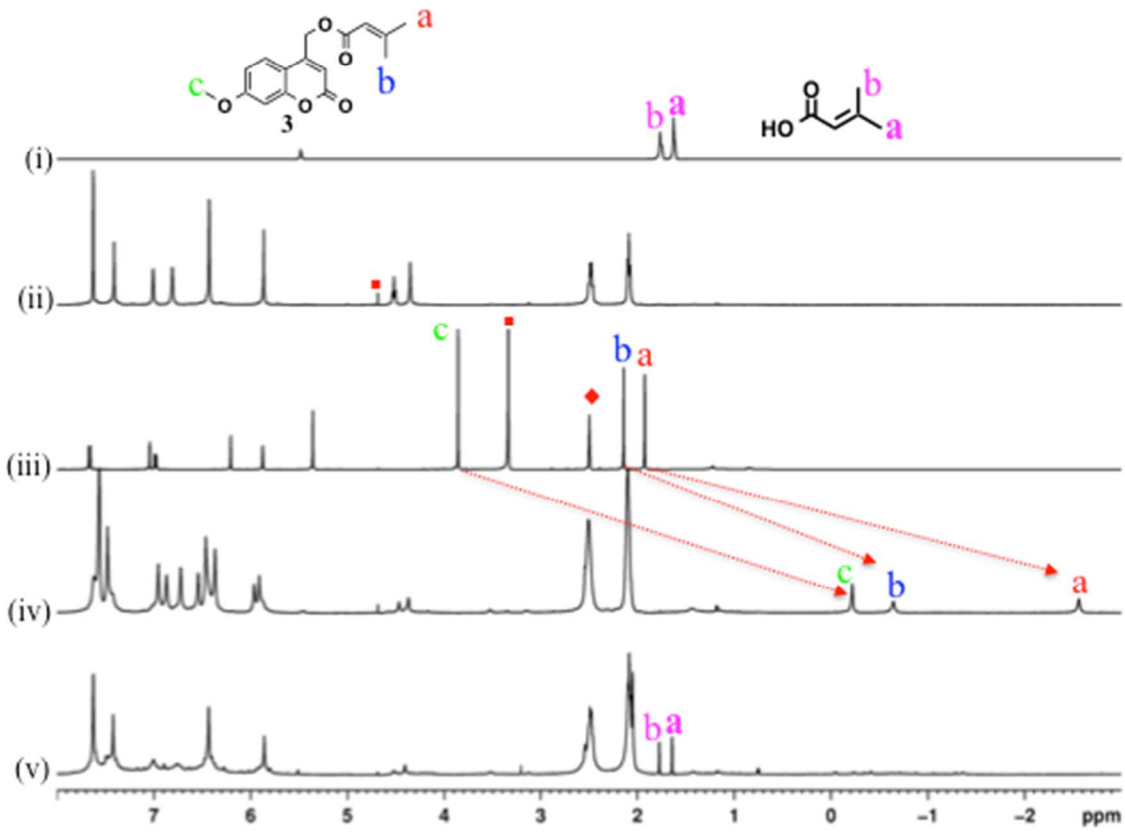


Figure S66. ^{1}H-NMR (500 MHz) spectra of (i) 3,3 dimethyl acrylic acid ([3,3 dimethyl acrylic acid] = 0.5 mM) **in** 10 mM $Na_2B_4O_7$ buffer/D_2O, pH = 8.7; (ii) OA ([OA] = 1 mM); (iii) **3** in DMSO-d_6; (iv) **3**@$(OA)_2$ ([OA] = 1 mM and [**3**] = 0.5 mM)); (v) after 4h irradiation of ((iv)) ($\lambda \geq 300$ nm). ◆ and ▪ indicate the residual solvent peaks of DMSO-d_6 and water, respectively.

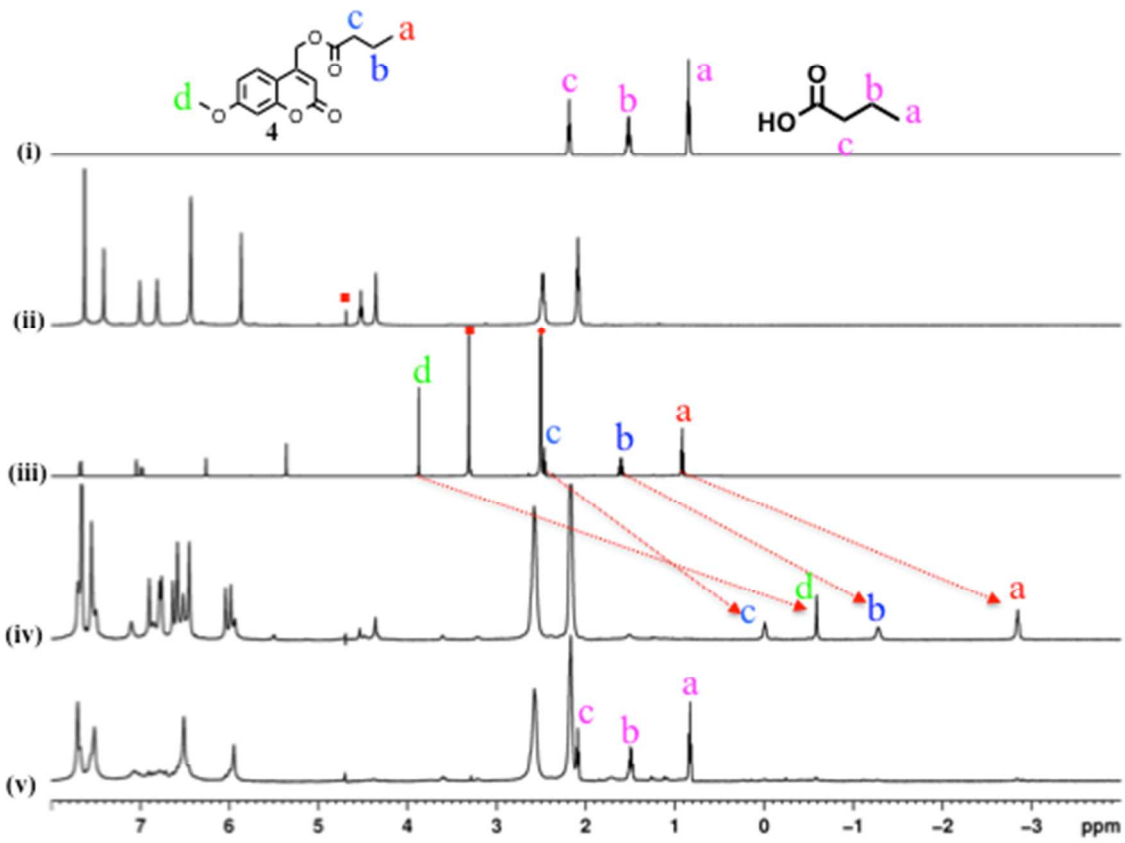


Figure S67. ^{1}H-NMR (500 MHz) spectra of (i) Butanoic acid ([Butanoic acid] = 0.5 mM) **in** 10 mM $Na_2B_4O_7$ buffer/D_2O, pH = 8.7; (ii) OA ([OA] = 1 mM) **in** 10 mM $Na_2B_4O_7$ buffer/D_2O, pH = 8.7; (iii) **4** in DMSO-d_6; (iv) **4**@$(OA)_2$ ([OA] = 1 mM and [**4**] = 0.5 mM) **in** 10 mM $Na_2B_4O_7$ buffer/D_2O, pH = 8.7; (v) after 5h irradiation of ((iv)) ($\lambda \geq 300$ nm). ◆ and ▪ indicate the residual solvent peaks of DMSO-d_6 and water, respectively.

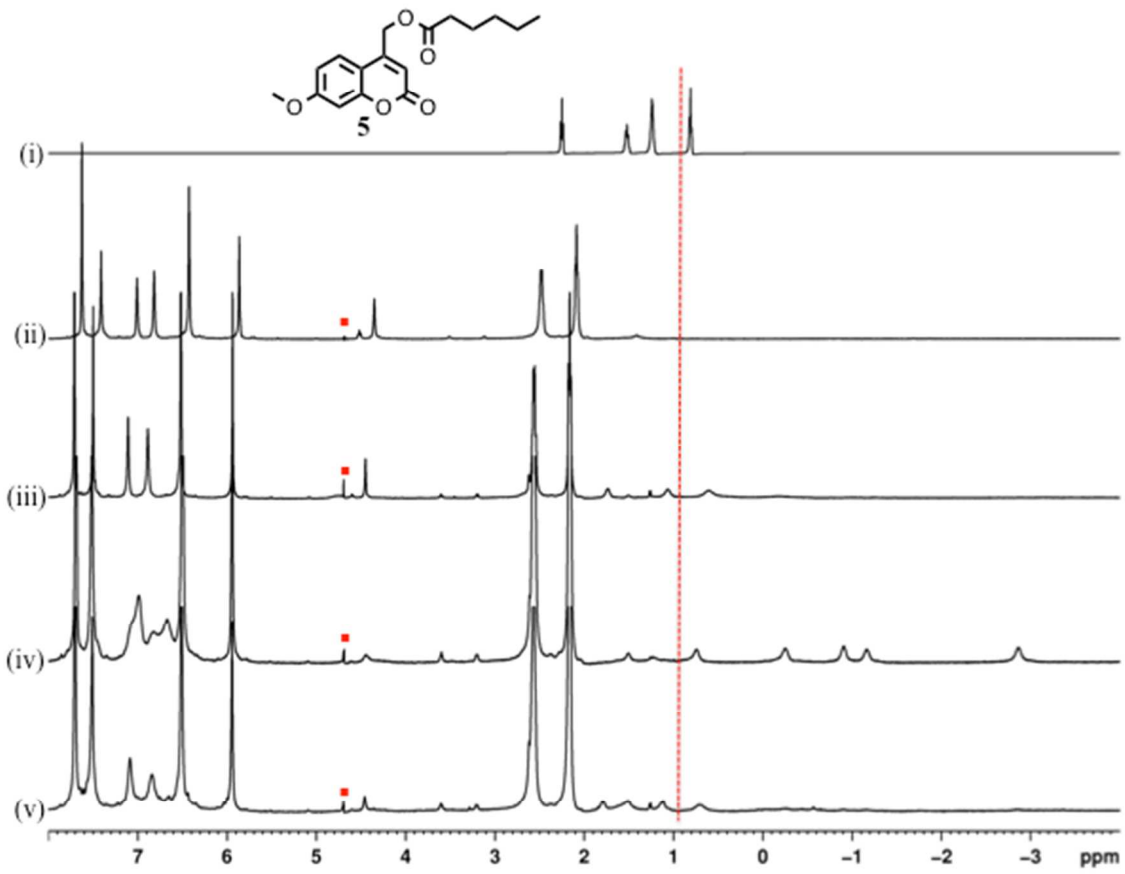


Figure S68. ^{1}H-NMR (500 MHz, 10 mM $Na_2B_4O_7$ buffer/D_2O, pH = 8.7) spectra of (i) Hexanoic acid (ii) OA ([OA] = 1 mM); (iii) Hexanoicacid (0.5 mM) + OA (1.0 Mm); (iv) **5**@$(OA)_2$ ([OA] = 1 mM and [**5**] = 0.5 mM)); (v) after 5h irradiation of ((iv)) ($\lambda \geq 300$ nm).▪ indicates the residual solvent peak of water.

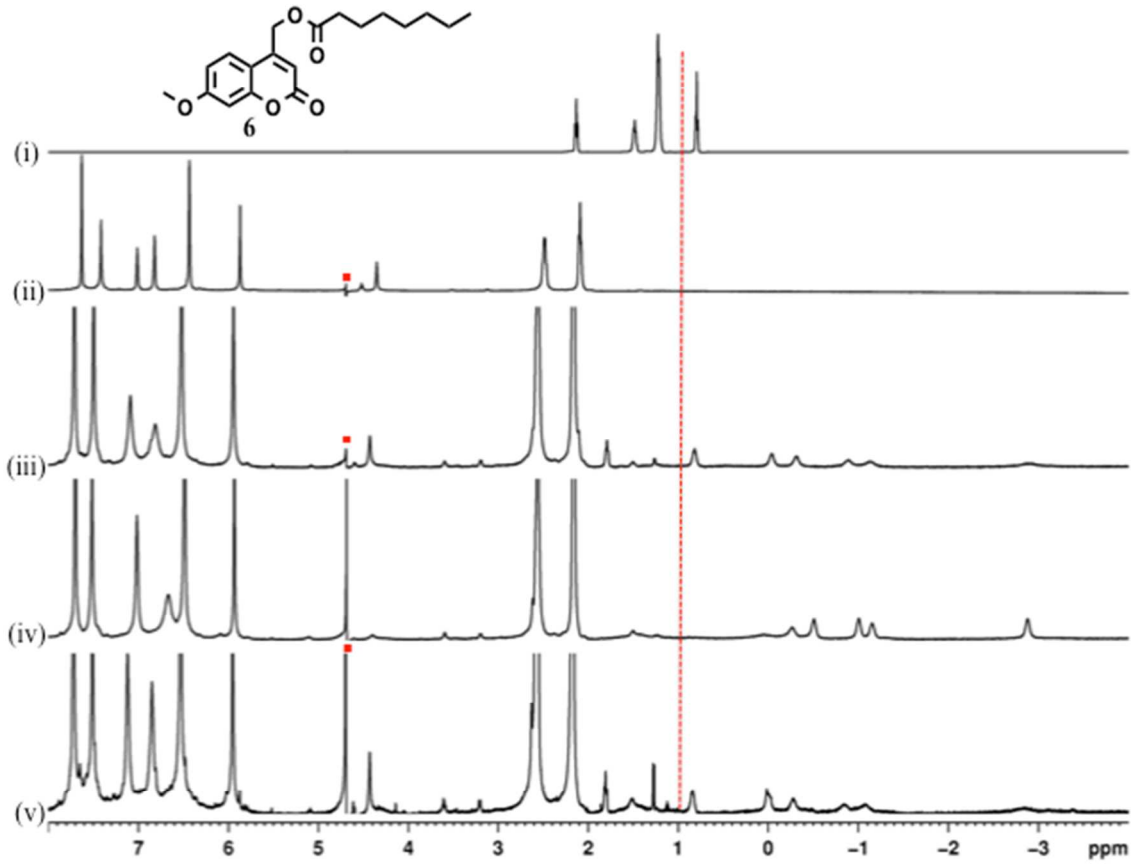


Figure S69. ^{1}H-NMR (500 MHz, 10 mM $Na_2B_4O_7$ buffer/D_2O, pH = 8.7) spectra of (i) Octanoic acid (ii) OA ([OA] = 1 mM); (iii) Octanoic acid (0.25 Mm) + OA (1.0 Mm); (iv) **6**@$(OA)_2$ ([OA] = 1 mM and [**6**] = 0.5 mM)); (v) after 5h irradiation of ((iv)) ($\lambda \geq 300$ nm). ▪ indicates the residual solvent peak of water.

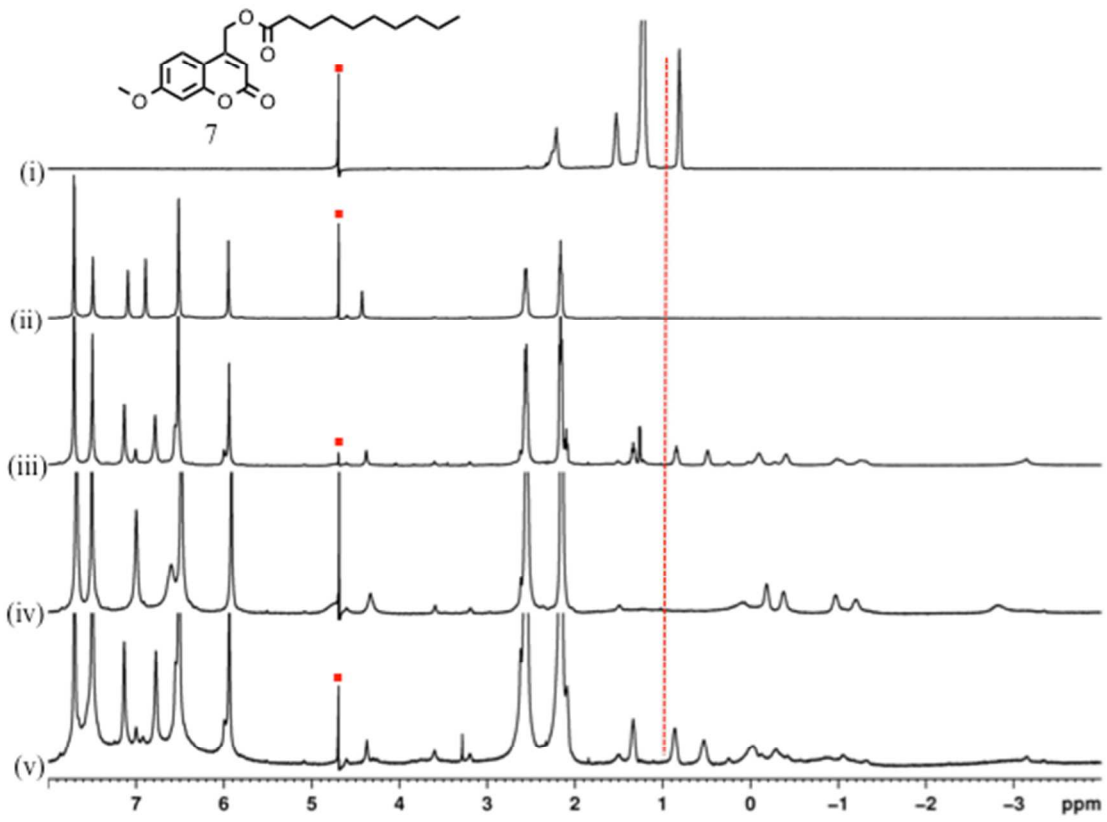


Figure S70. ^{1}H-NMR (500 MHz, 10 mM $Na_2B_4O_7$ buffer/D_2O, pH = 8.7) spectra of (i) Decanoic acid (ii) OA ([OA] = 1 mM); (iii) Decanoic acid (0.25 Mm) + OA (1.0 Mm); (iv) **7**@$(OA)_2$ ([OA] = 1 mM and [**7**] = 0.5 mM)); (v) after 6h irradiation of ((iv)) ($\lambda \geq 300$ nm). ▪ indicates the residual solvent peak of water.

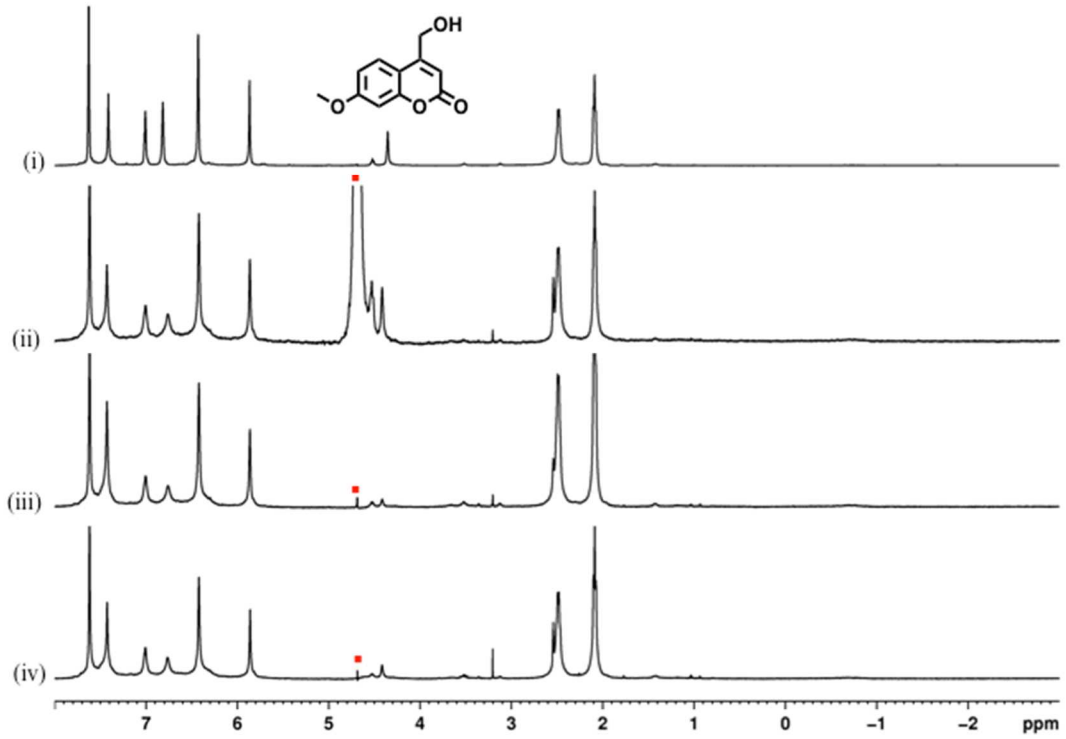


Figure S71. ^{1}H-NMR (500 MHz, 10 mM $Na_2B_4O_7$ buffer/D_2O, pH = 8.7) spectra of (i) OA ([OA] = 1 mM); (ii) **8**@$(OA)_2$ ([OA] = 1 mM and [**8**] = 0.5 mM); (iii)) 2h irradiation of ((ii)) ($\lambda \geq 300$ nm); (iii)) 4h irradiation of ((ii)) ($\lambda \geq 300$ nm).

4.4 ESI-MS and LC-MS of irradiated samples

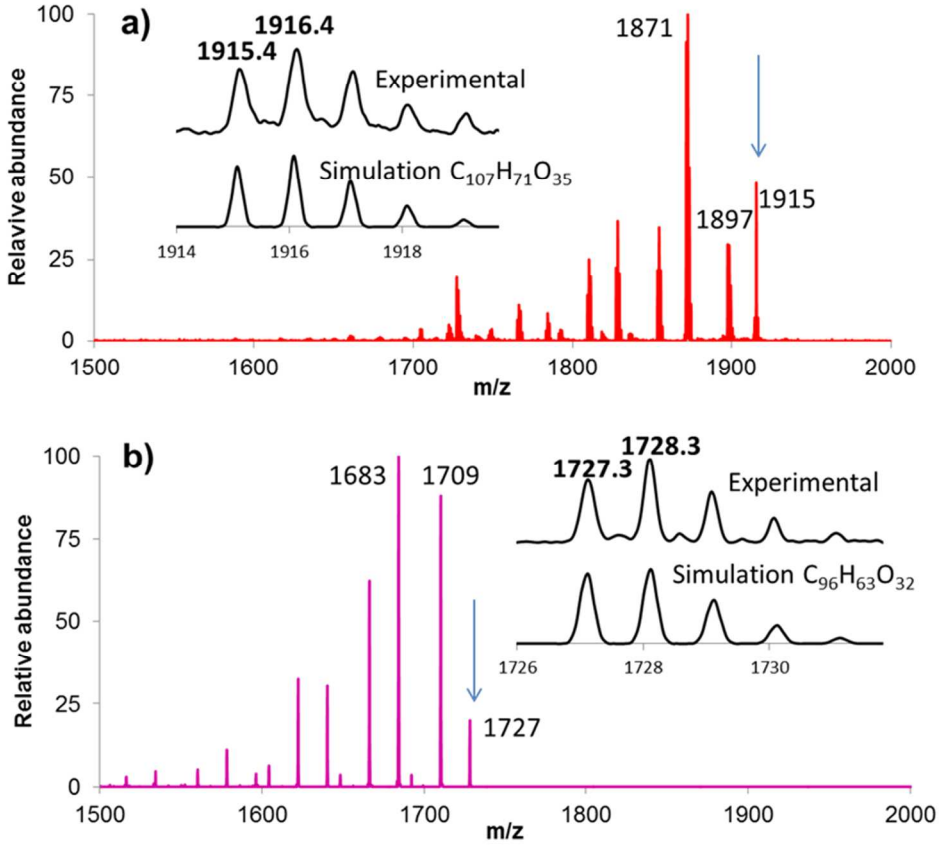


Figure S72. Fragmentation spectra of OA adduct with m/z 1915 ($[M-H]^-$), **a)**, and OA (m/z 1727, ([M-H]-), **b)**. The arrows indicate the fragmented ions. The inserts shows the experimental and simulated isotope patterns of fragmented peaks. $C_{96}H_{63}O_{32}$ is the deprotonated OA ion. $C_{107}H_{71}O_{35}$ corresponds to a deprotonated coupling product that is formed by the radical mechanism.

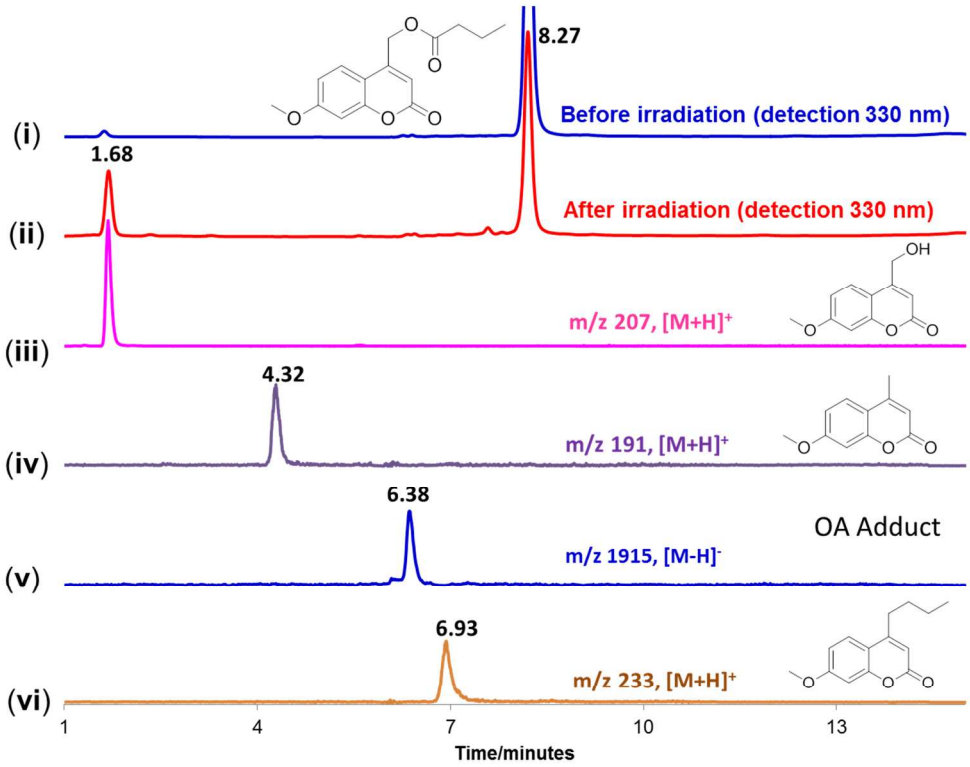


Figure S73. LC-DAD trace (330 nm) of **4**@OA_2, before irradiation, (**i**) and after irradiation (**ii**) followed by single ion mass chromatograms correspondent to main detected products. (**iii**) is the single ion trace at m/z 207, correspondent to the positive ion ($[M+H]^+$) of 7-methoxy-4-(hydroxymethyl)-2H-chromen-2-one (**8**); (**iv**) the single ion trace at m/z 191, correspondent to the positive ion ($[M+H]^+$) of 7-methoxy-4-methyl-2H-chromen-2-one (**9**); (**v**) the single ion trace at m/z 1915, correspondent to the negative ion ($[M-H]^-$) of a OA-Coumarin coupling product; (**vi**) the single ion trace at m/z 233, correspondent to the positive ion ($[M+H]^+$) of decarboxylated **4**.

References

1. Gibb, C. L. D.; Gibb, B. C. *J. Am. Chem. Soc.* **2004**, 126, 11408.

2. Eckardt, T.; Hagen, V.; Schade, B.; Schmidt, R.; Schweitzer, C.; Bendig, J. *J. Org. Chem*. **2002**, 67, 703-710.