Electronic supplementary information

Supramolecular Photochemistry of Encapsulated Caged *ortho*-Nitrobenzyl Triggers

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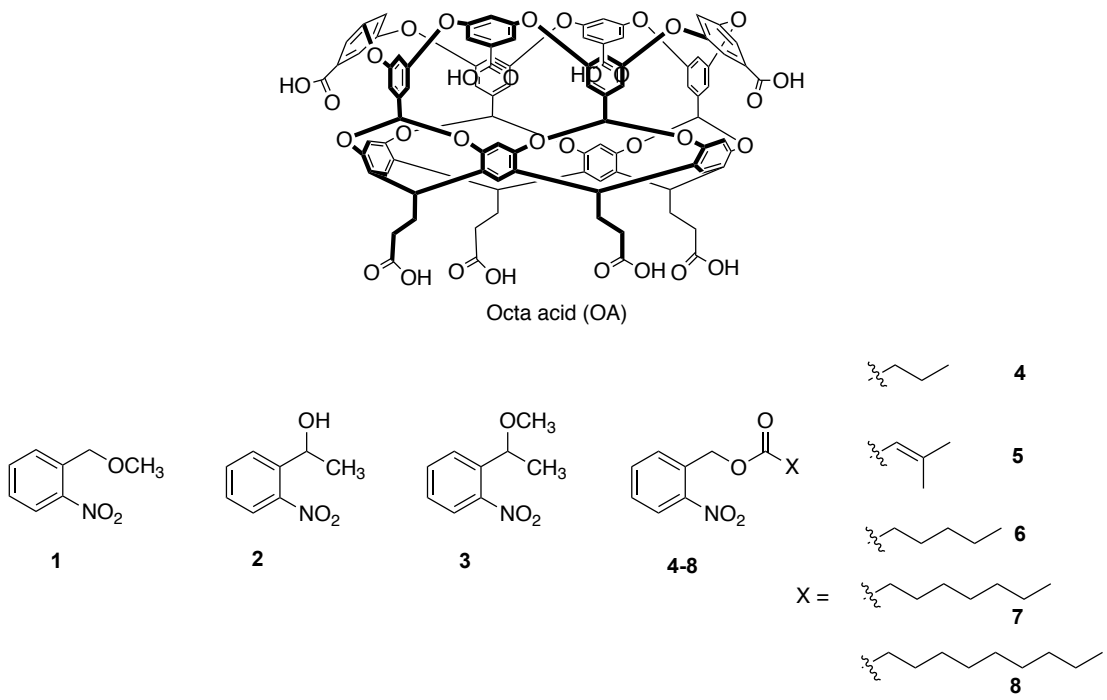

Scheme 1. Structures of water-soluble octa acid (OA) cavitand and oNB triggers (**1**-**8**).

2. Characterization spectra

2.1 ^{1}H NMR spectra of oNB esters 4 - 8

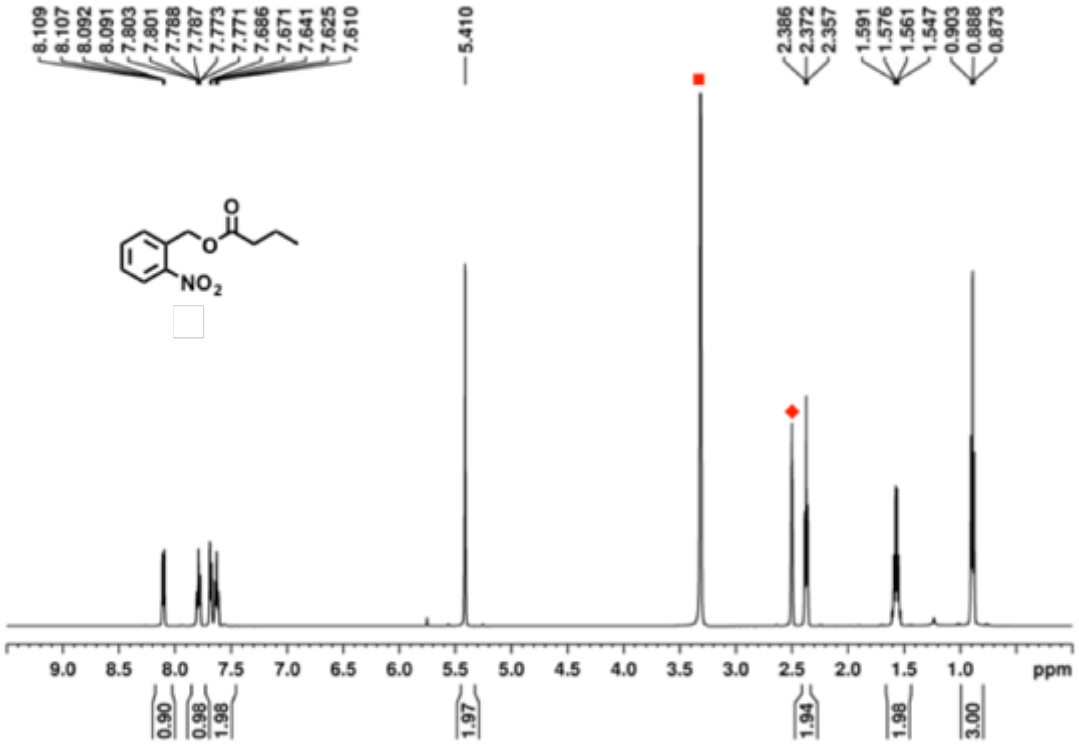

Figure S1. ^{1}H NMR (500 MHz) spectrum of **4** in DMSO-d_6. ■ and ♦ indicate the residual solvent peak of water and DMSO-d_6, respectively.

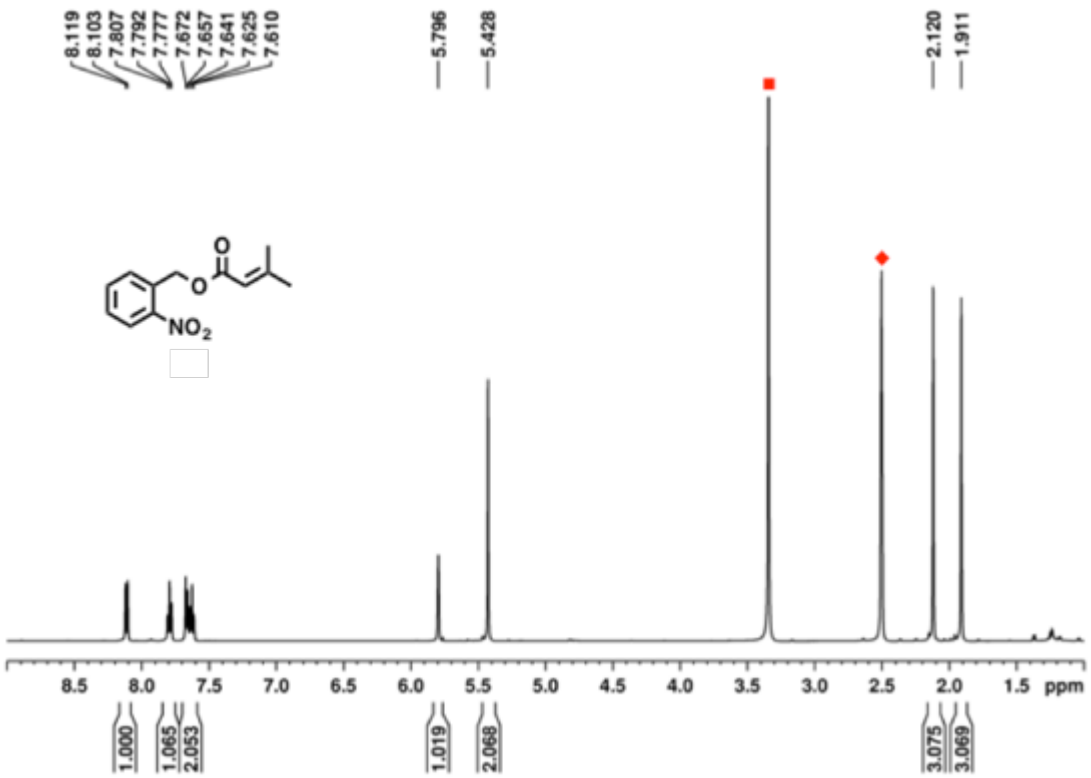

Figure S2. ^{1}H NMR (500 MHz) spectrum of **5** in DMSO-d_6. ■ and ♦ indicate the residual solvent peaks of water and DMSO-d_6, respectively.

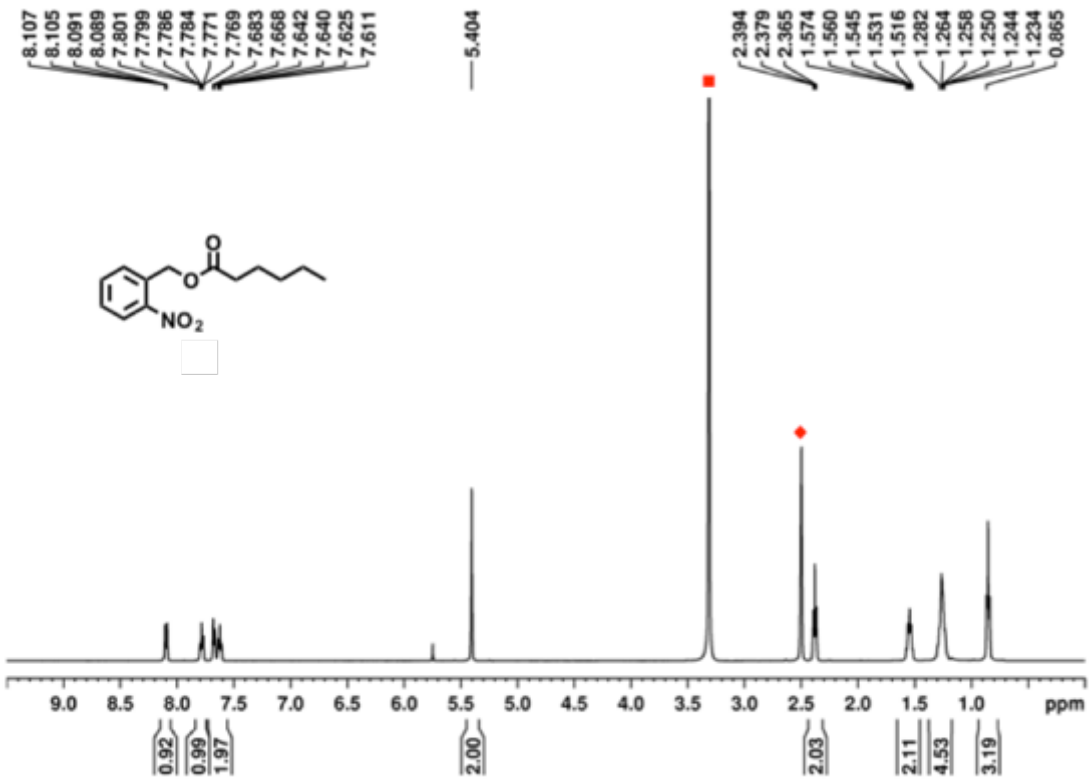

Figure S3. ^{1}H NMR (500 MHz) spectrum of **6** in DMSO-d_6. ■ and ♦ indicate the residual solvent peaks of water and DMSO-d_6, respectively.

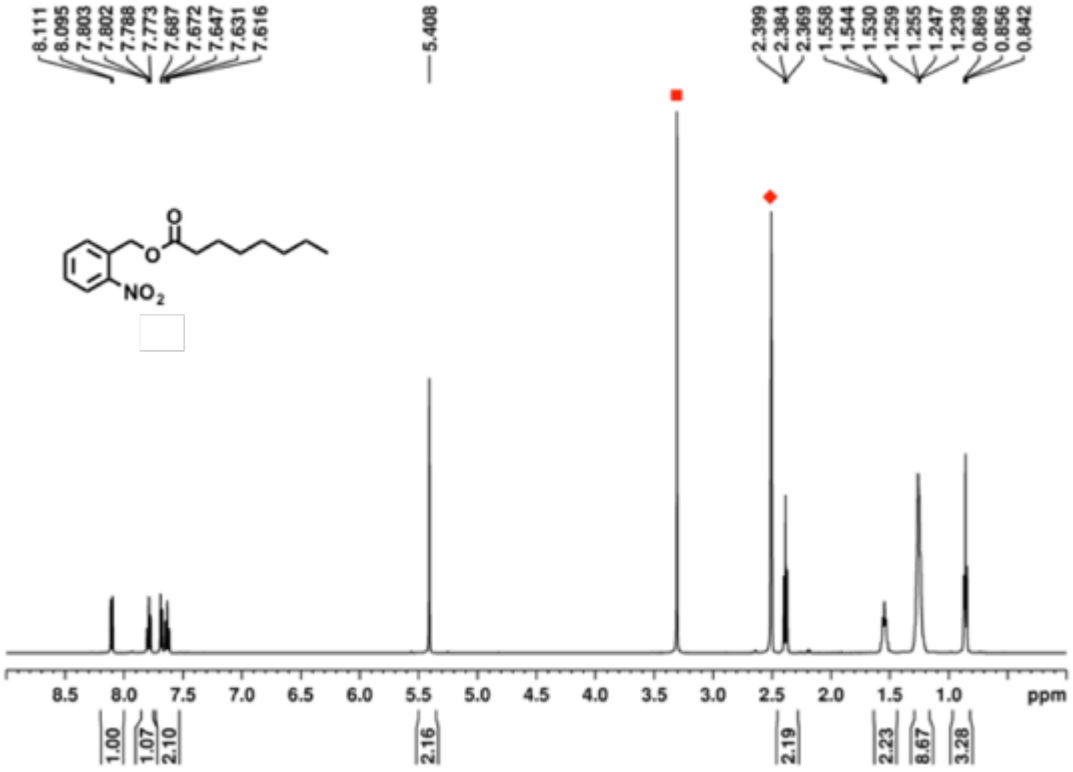

Figure S4. ^{1}H NMR (500 MHz) spectrum of **7** in DMSO-d_6. ■ and ♦ indicate the residual solvent peaks of water and DMSO-d_6, respectively.

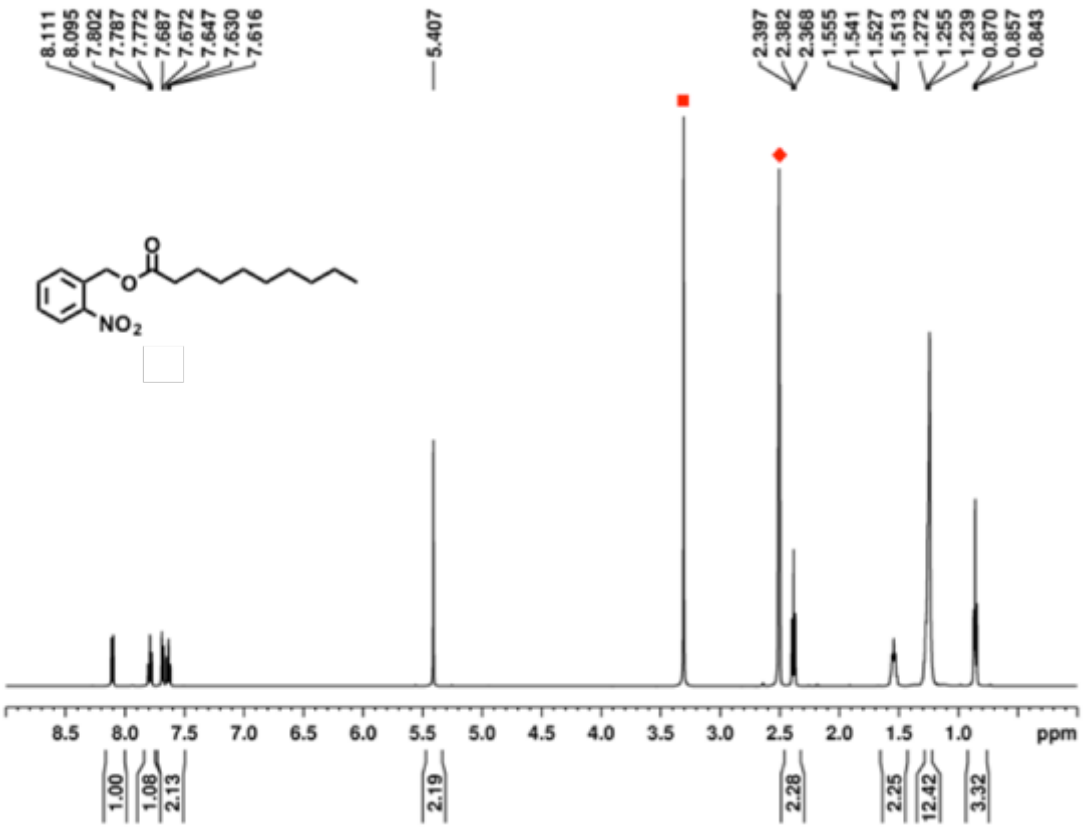

Figure S5. ^{1}H NMR (500 MHz) spectrum of **8** in DMSO-d_6. ■ and ♦ indicate the residual solvent peak of water and DMSO-d_6, respectively.

2.2 ESI-MS spectra of oNB esters 4-8

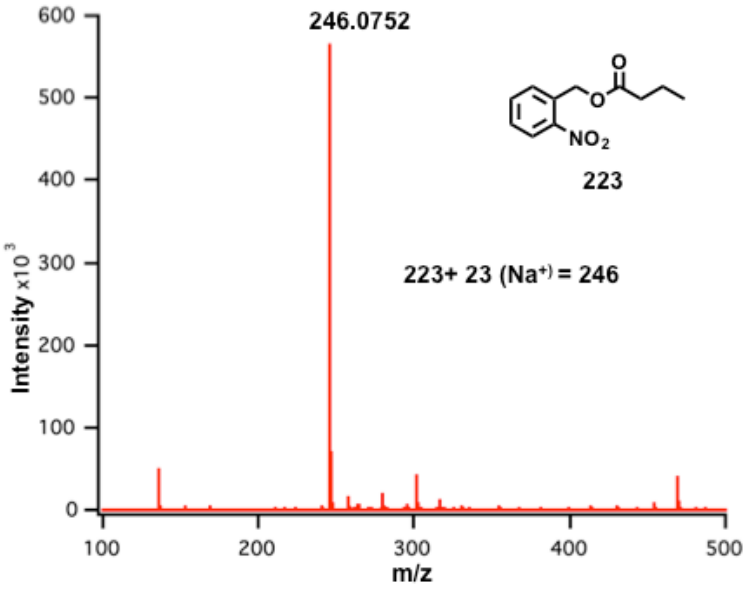

Figure S6. ESI-MS full scan spectrum of **4** in methanol-chloroform (50:50) containing 0.1% formic acid.

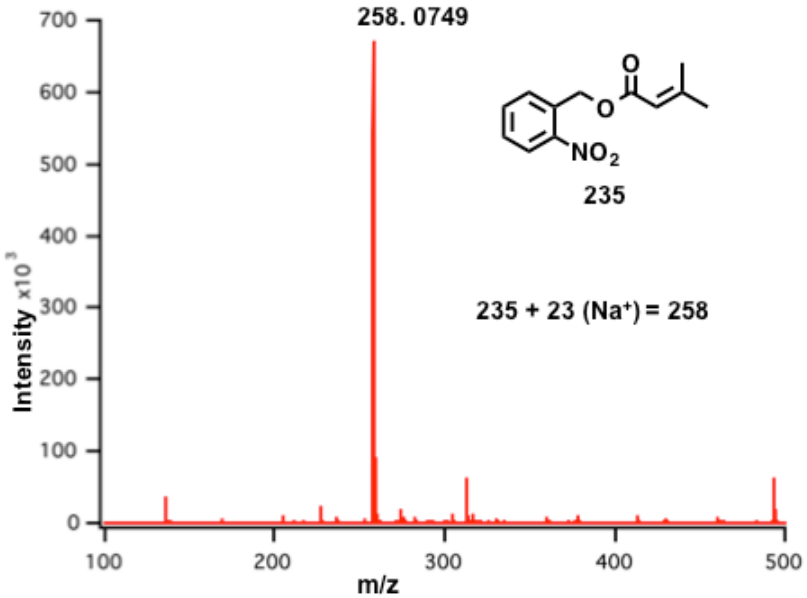

Figure S7. ESI-MS full scan spectrum of **5** in methanol-chloroform (50:50) containing 0.1% formic acid.

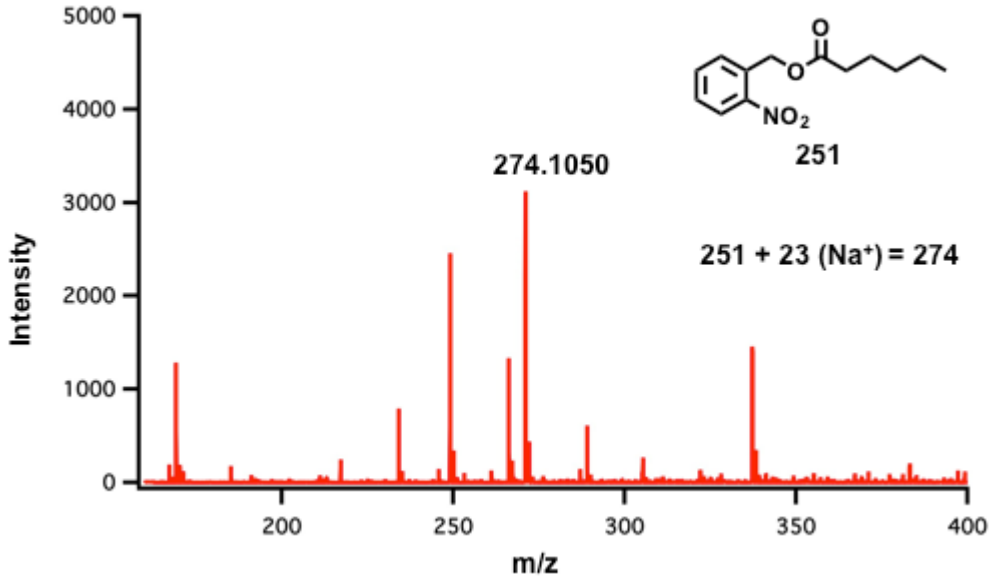

Figure S8. ESI-MS full scan spectrum of **6** in methanol-chloroform (50:50) containing 0.1% formic acid.

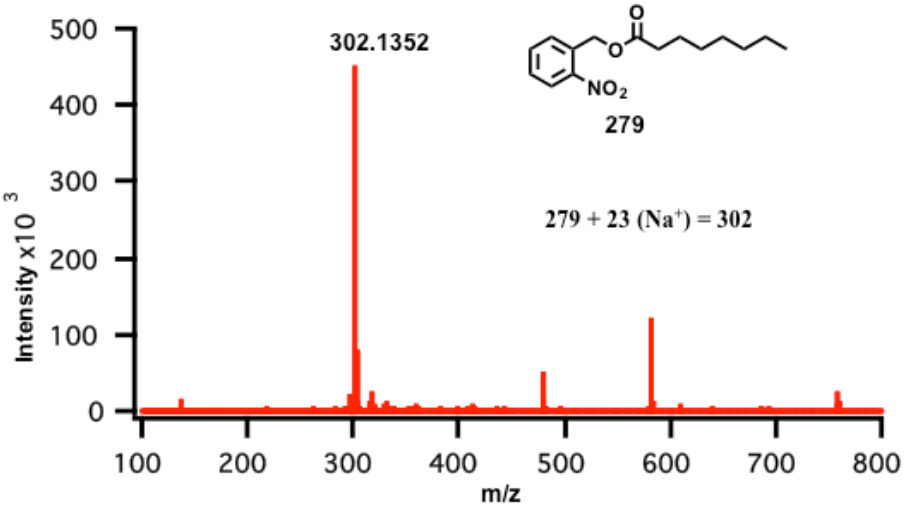

Figure S9. ESI-MS full scan spectrum of **7** in methanol-chloroform (50:50) containing 0.1% formic acid.

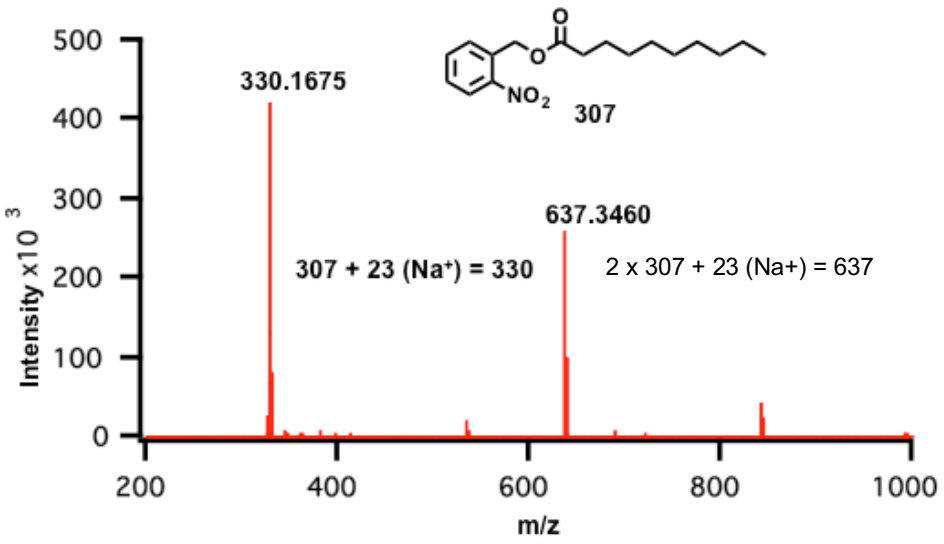

Figure S10. ESI-MS full scan spectrum of **8** in methanol-chloroform (50:50) containing 0.1% formic acid.

2.3 Absorption spectra of O-NB triggers 1 - 8 in water in the presence and absence of octa acid.

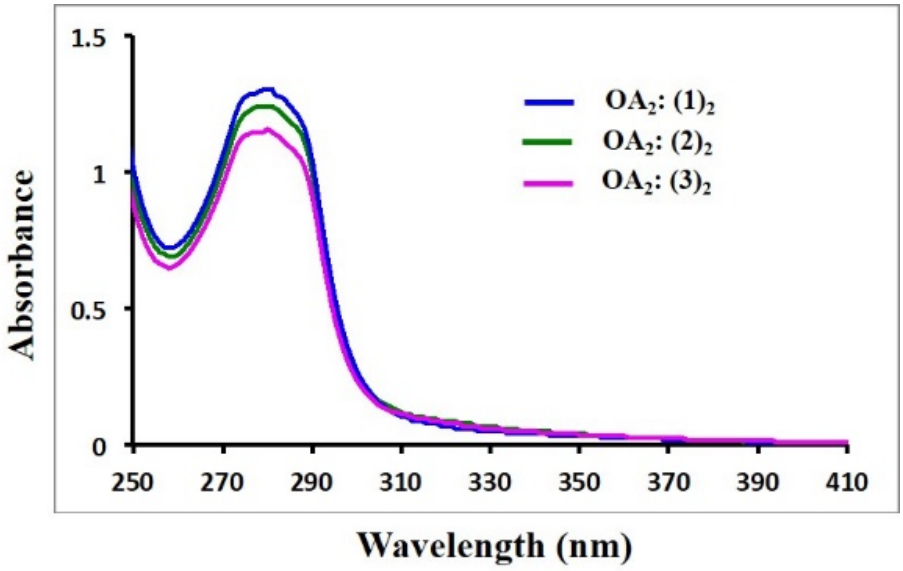

Figure S11. Absorption spectra of complexes of (**1-3**) with OA; $(OA)_2$: $(\mathbf{1})_2$ (blue); $(OA)_2$: $(\mathbf{2})_2$ (green); $(OA)_2$: $(\mathbf{3})_2$ (purple); [**1-3**] = 50 μM, [OA] = 50 μM in borate buffer.

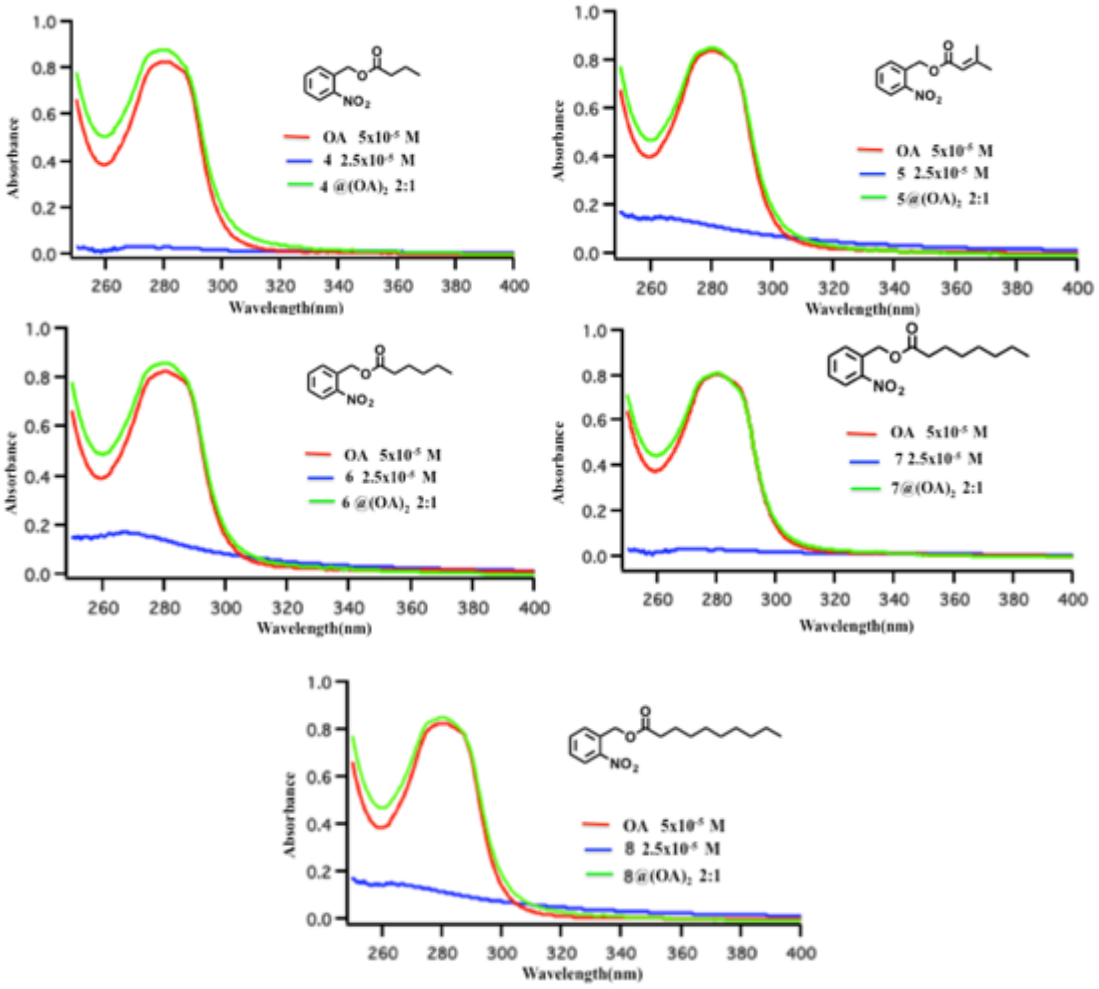

Figure S12. UV-Vis spectra of OA (red), guest (blue) and guest@$(OA)_2$ (green) at [guest] = 25 μM, [OA] = 50 μM in $Na_2B_4O_7$ buffer/H_2O).

2.4 ^{1}H NMR titration spectra of octa acid with guests 1 - 8, 2D-COSY NMR spectra of the complexes

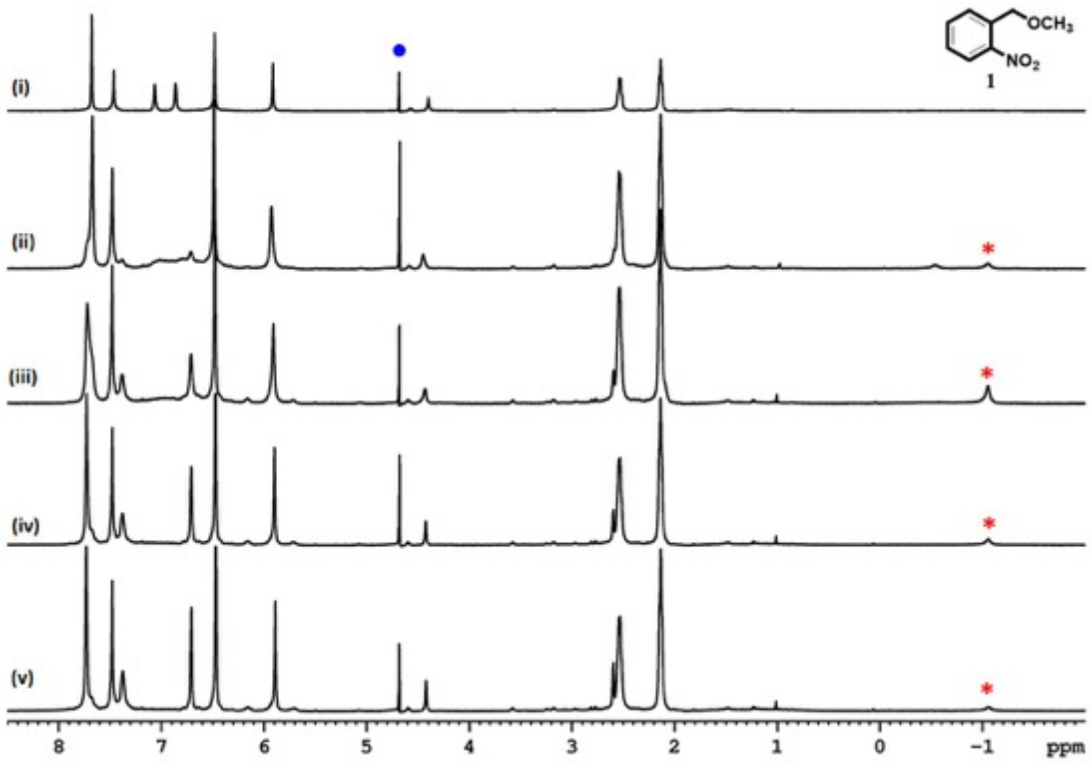

Figure S13. ^{1}H NMR (500 MHz) spectra of (i) OA(1 mM) in 10 mM $Na_2B_4O_7$ buffer/D_2O; (ii) **1**@OA ([OA] = 1 mM), [**1**] = 0.25 mM); (iii) **1**@OA ([OA] = 1 mM), [**1**] = 0.5 mM); (iv) **1**@OA ([OA] = 1 mM), [**1**] = 0.75 mM); (v) **1**@OA ([OA] = 1 mM), [**1**] = 1 mM); "*" indicates the bound guest proton peak and "●"represent the residual D_2O.

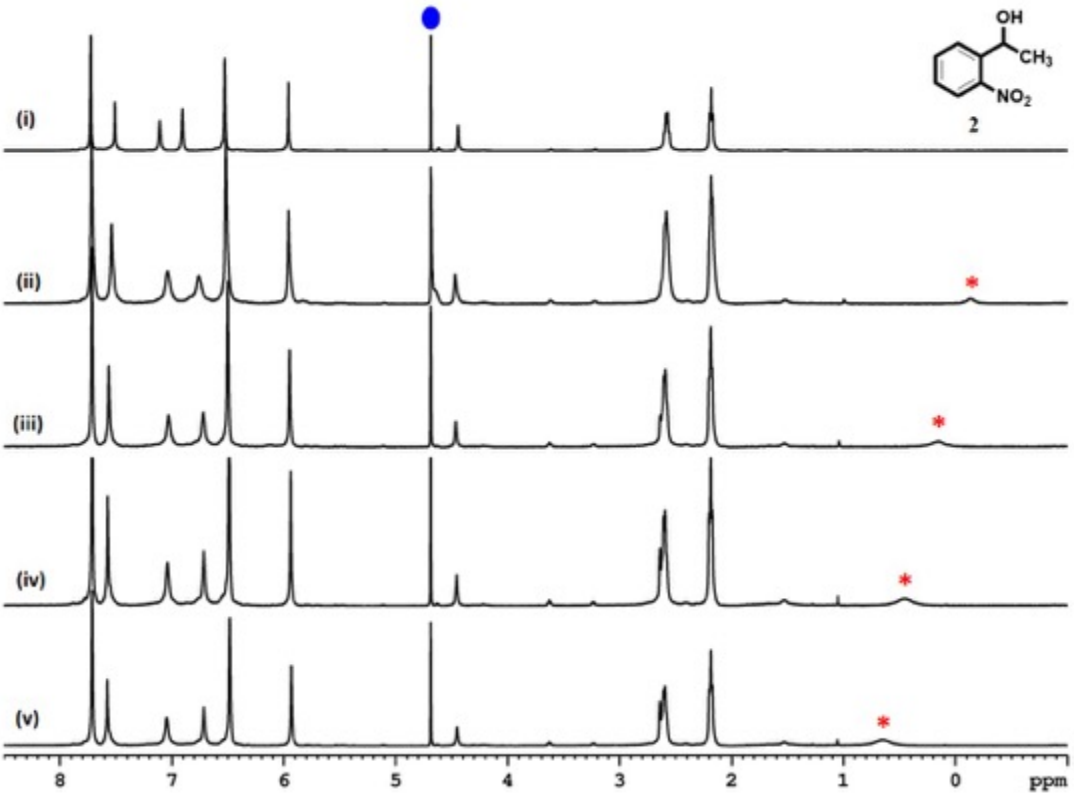

Figure S14. ^{1}H NMR (500 MHz) spectra of (i) OA(1 mM) in 10 mM $Na_2B_4O_7$ buffer/D_2O; (ii) **2**@OA ([OA] = 1 mM), [**2**] = 0.25 mM); (iii) **2**@OA ([OA] = 1 mM), [**2**] = 0.5 mM); (iv) **2**@OA ([OA] = 1 mM), [**2**] = 0.75 mM); (v) **2**@OA ([OA] = 1 mM), [**2**] = 1 mM); "*" indicates the bound guest proton peak and "●"represent the residual D_2O.

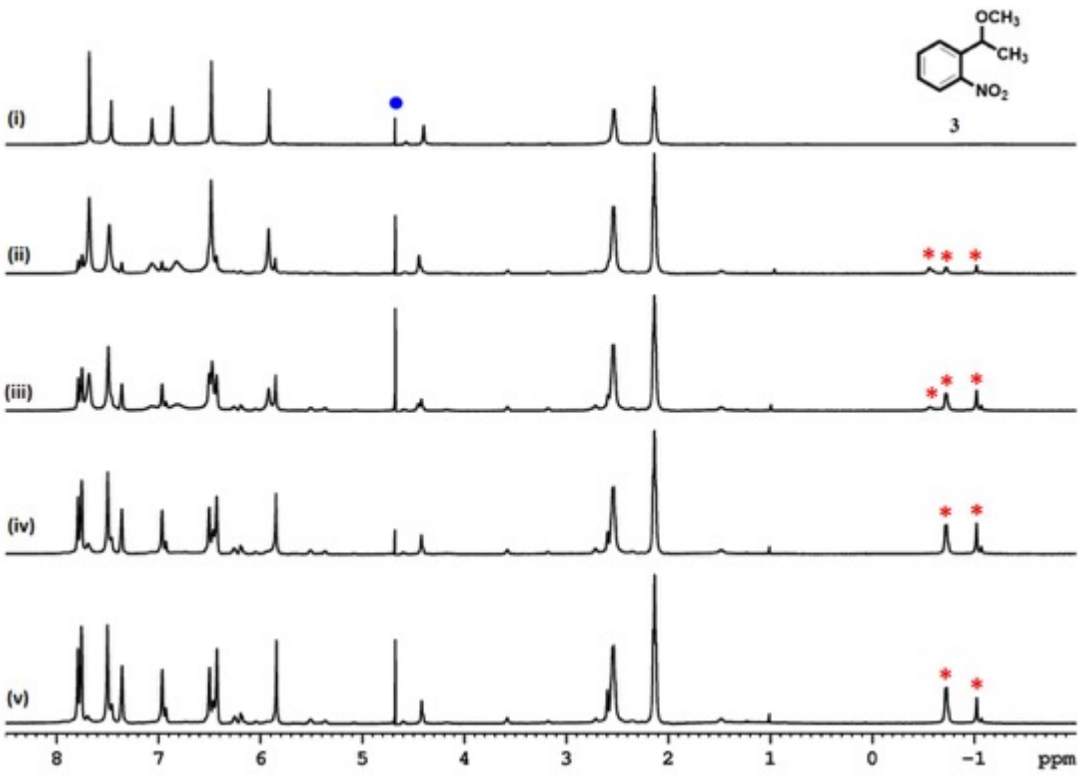

Figure S15. ^{1}H NMR (500 MHz) spectra of (i) OA(1 mM) in 10 mM $Na_2B_4O_7$ buffer/D_2O; (ii) **3**@OA ([OA] = 1 mM), **[3]** = 0.25 mM); (iii)**3**@OA ([OA] = 1 mM), [**3**] = 0.5 mM); (iv) **3**@OA ([OA] = 1 mM), [**3**] = 0.75 mM); (v) **3**@OA ([OA] = 1 mM), [**3**] = 1 mM); "*" indicates the bound guest proton peak and "●"represent the residual D_2O.

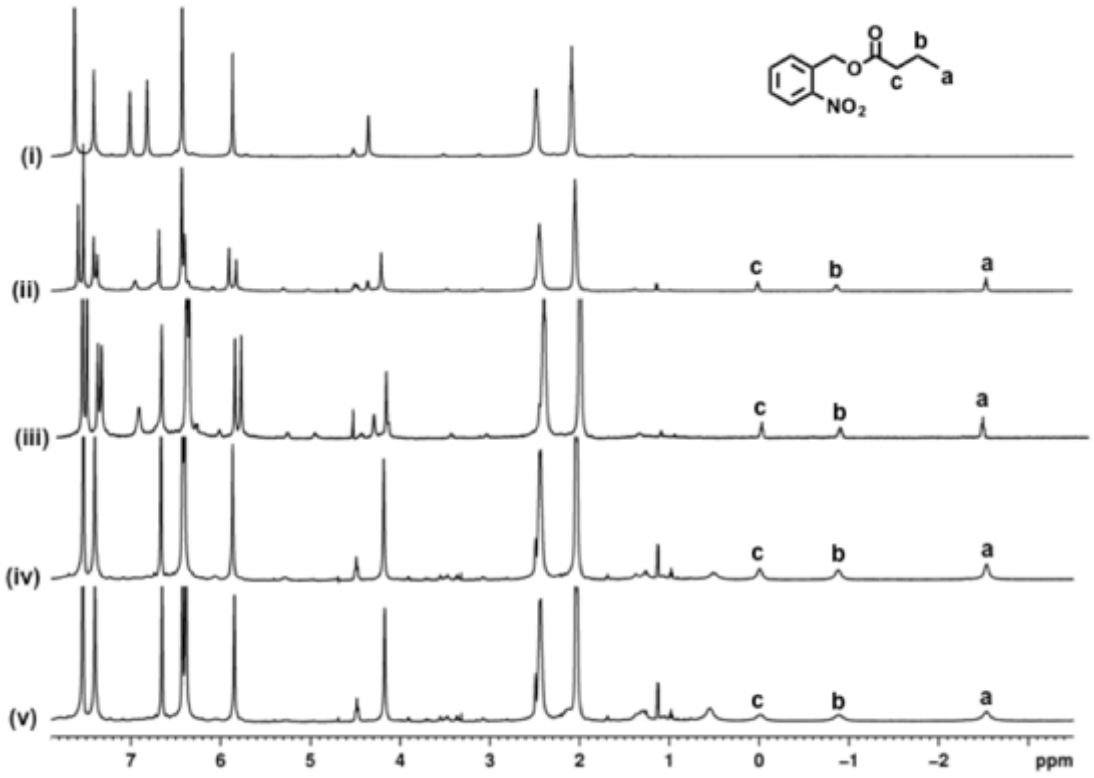

Figure S16. ^{1}H NMR (500 MHz, 10 mM $Na_2B_4O_7$ buffer/D_2O, pH = 8.7) spectra of (i) OA ([OA] = 1 mM) (ii) **1**@OA (OA=1 mM, [**4**] = 0.25 mM); (iii) **4**@OA (OA=1 mM, [**4**] = 0.5 mM); (iv) **4**@OA (OA=1 mM, [**4**] = 0.75 mM); (v) **4**@OA (OA=1 mM, [**4**] = 1.0 mM). "a-c" indicate the OA bound guest aliphatic proton peaks.

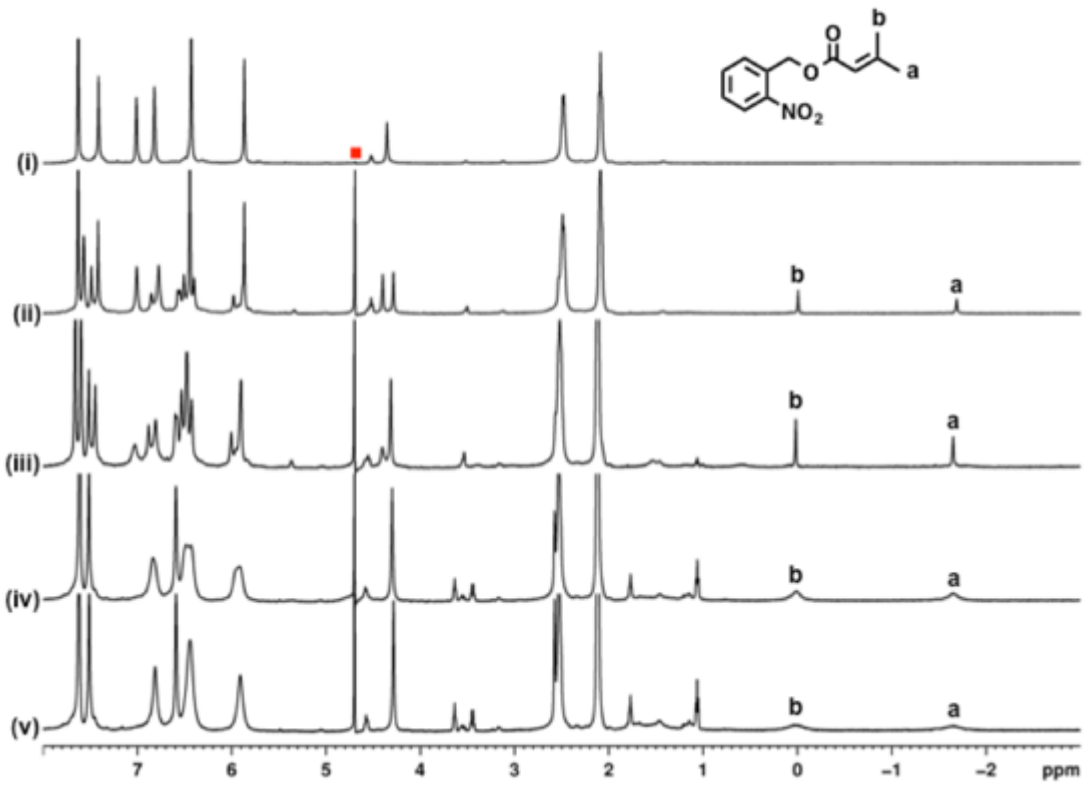

Figure S17. ^{1}H NMR (500 MHz, 10 mM $Na_2B_4O_7$ buffer/D_2O, pH = 8.7) spectra of (i) OA ([OA] = 1 mM) (ii) **5**@OA (OA=1 mM, [**5**] = 0.25 mM); (iii) **5**@OA (OA=1 mM, [**5**] = 0.5 mM); (iv) **5**@OA (OA=1 mM, [**5**] = 0.75 mM); (v) **5**@OA (OA=1 mM, [**5**] = 1.0 mM). ▪ indicates the residual solvent peak of water. "a and b" indicate the OA bound guest aliphatic proton peaks.

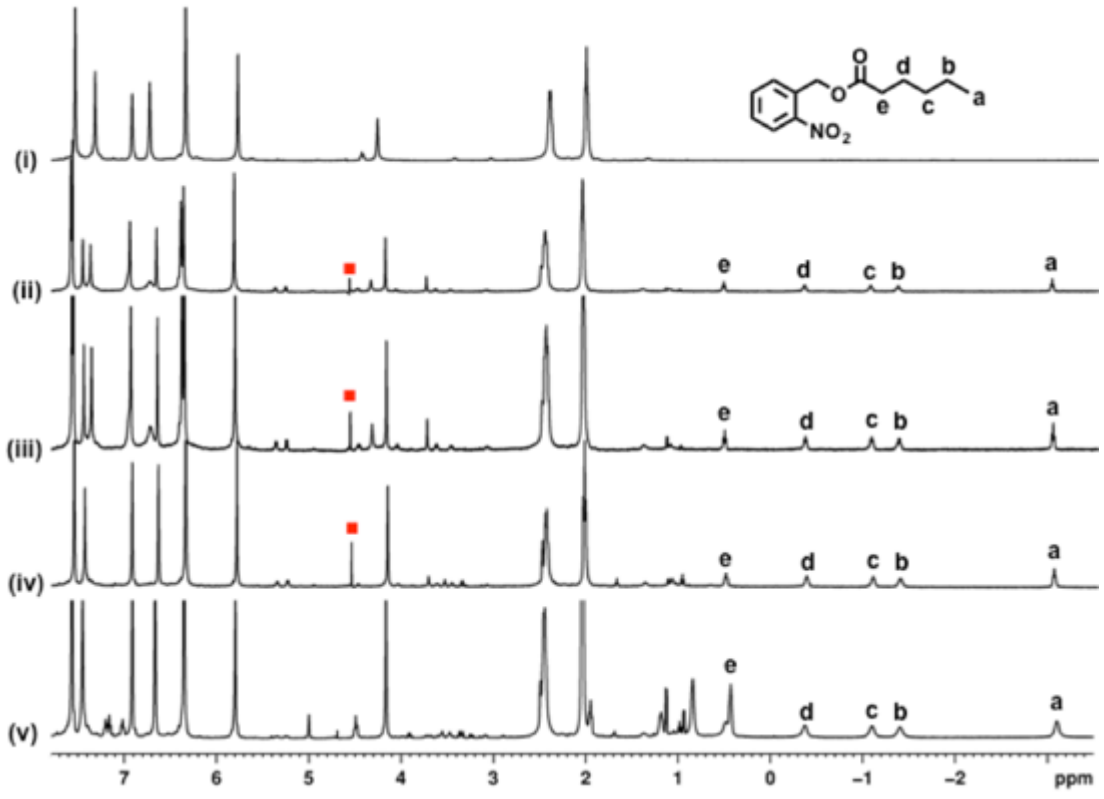

Figure S18. ^{1}H NMR (500 MHz, 10 mM $Na_2B_4O_7$ buffer/D_2O, pH = 8.7) spectra of (i) OA ([OA] = 1 mM) (ii) **6**@OA (OA=1 mM, [**6**] = 0.25 mM); (iii) **6**@OA (OA=1 mM, [**6**] = 0.5 mM); (iv) **6**@OA (OA=1 mM, [**6**] = 0.75 mM); (v) **6**@OA (OA=1 mM, [**6**] = 1.0 mM). ▪ indicates the residual solvent peak of water. "a-e" indicate the OA bound guest aliphatic proton peaks.

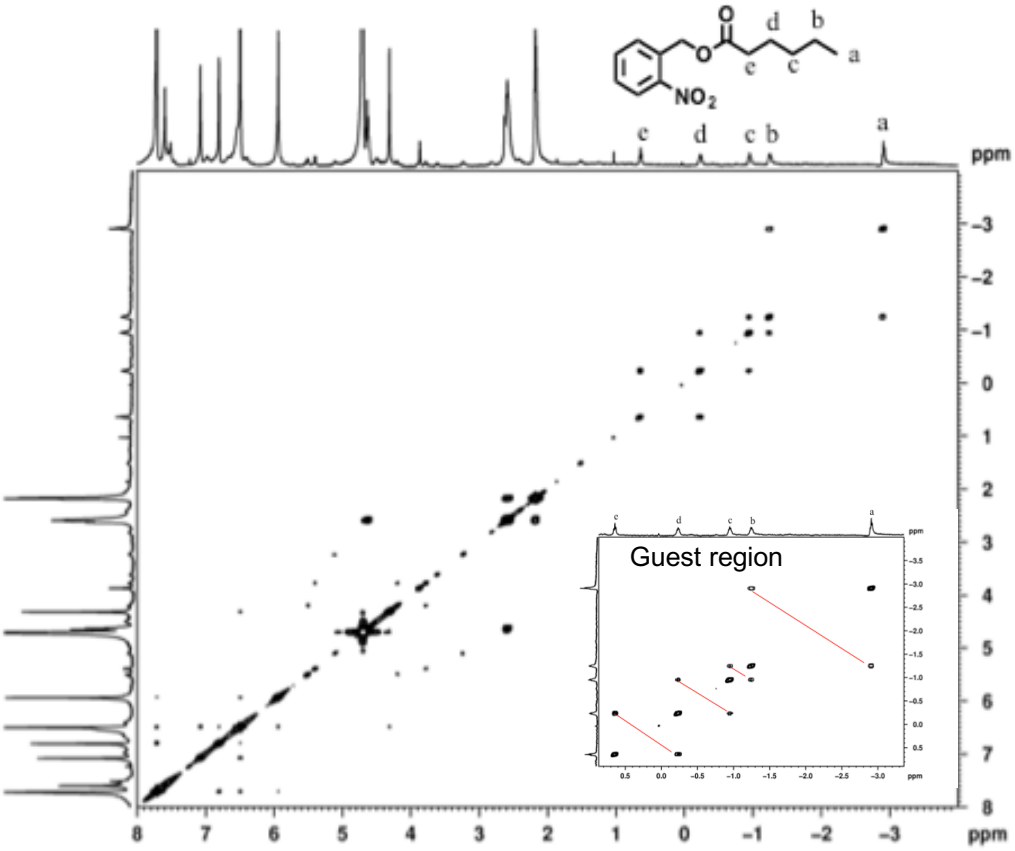

Figure S19. ^{1}H-NMR (500 MHz) COSY spectra of complex **6**@$(OA)_{2}$.. "a-e" indicate the OA bound guest aliphatic proton peaks.

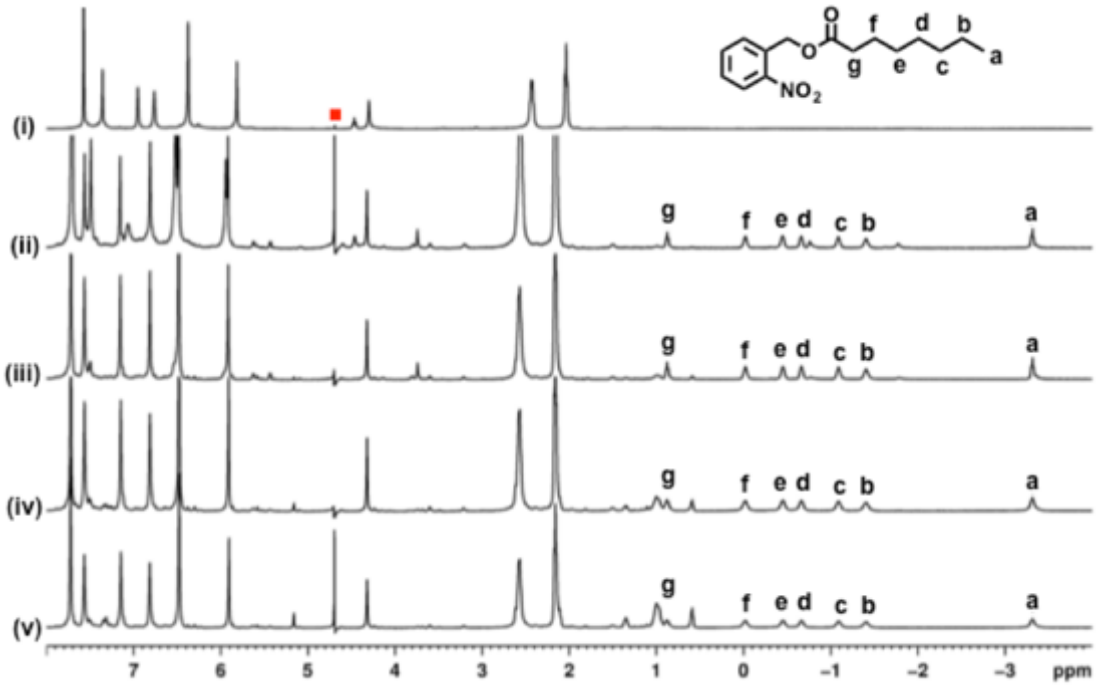

Figure S20. ^{1}H NMR (500 MHz, 10 mM $Na_2B_4O_7$ buffer/D_2O, pH = 8.7) spectra of (i) OA ([OA] = 1 mM) (ii) **7**@OA (OA=1 mM, [**7**] = 0.25 mM); (iii) **7**@OA (OA=1 mM, [**7**] = 0.5 mM); (iv) **7**@OA (OA=1 mM, [**7**] = 0.75 mM); (v) **7**@OA (OA=1 mM, [**7**] = 1.0 mM). ▪ indicates the residual solvent peak of water. "a-g" indicate the OA bound guest aliphatic proton peaks.

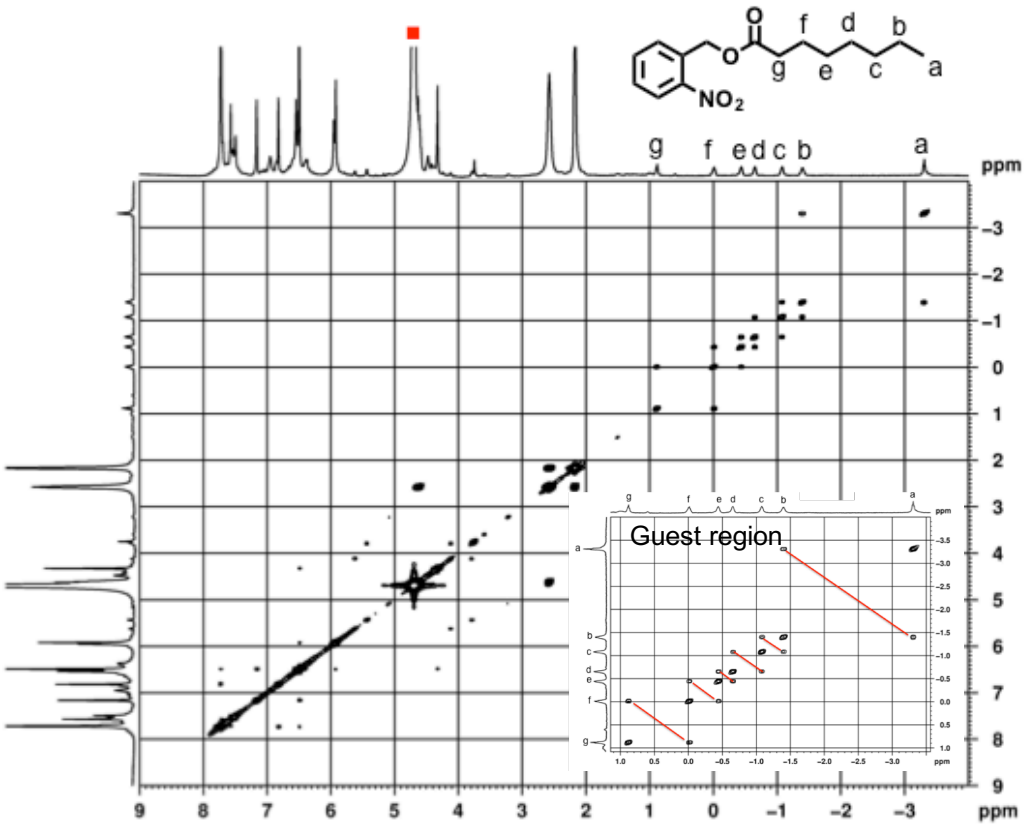

Figure S21. ^{1}H NMR (500 MHz) COSY spectra of complex **7**@$(OA)_{2.}$. "a-g" indicate the OA bound guest aliphatic proton peaks.

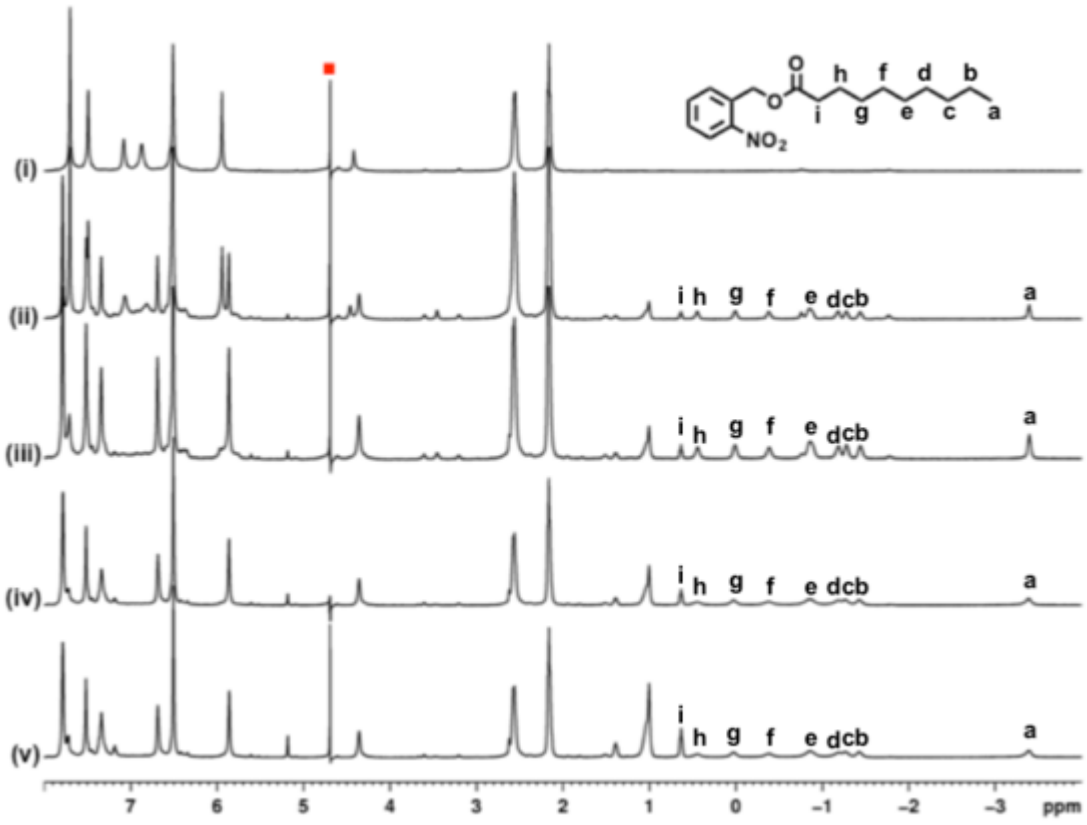

Figure S22. ^{1}H NMR (500 MHz, 10 mM $Na_2B_4O_7$ buffer/D_2O, pH = 8.7) spectra of (i) OA ([OA] = 1 mM) (i) **8**@OA (OA=1 mM, [**8**] = 0.25 mM); (ii) **8**@OA (OA=1 mM, [**8**] = 0.5 mM); (iii) **8**@OA (OA=1 mM, [**8**] = 0.75 mM); (iv) **8**@OA (OA=1 mM, [**8**] = 1.0 mM). ▪ indicates the residual solvent peak of water.

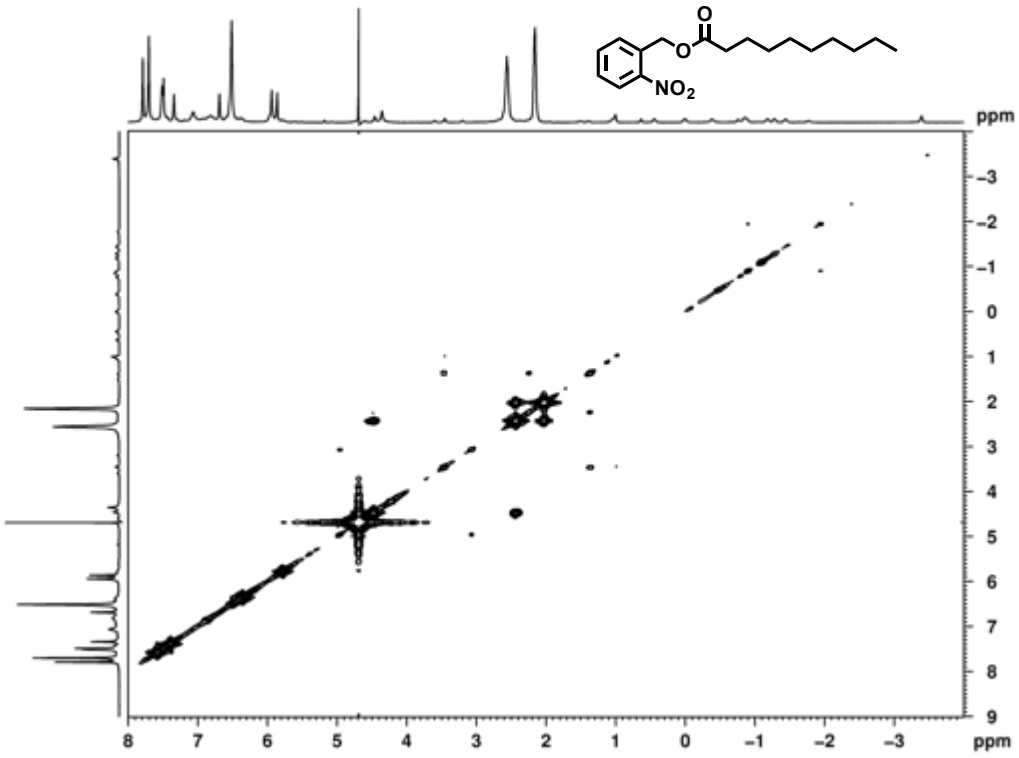

Figure S23. ^{1}H NMR (500 MHz) COSY spectra of complex **8**@$(OA)_2$

2.5 ^{1}H NMR spectra of irradiated samples

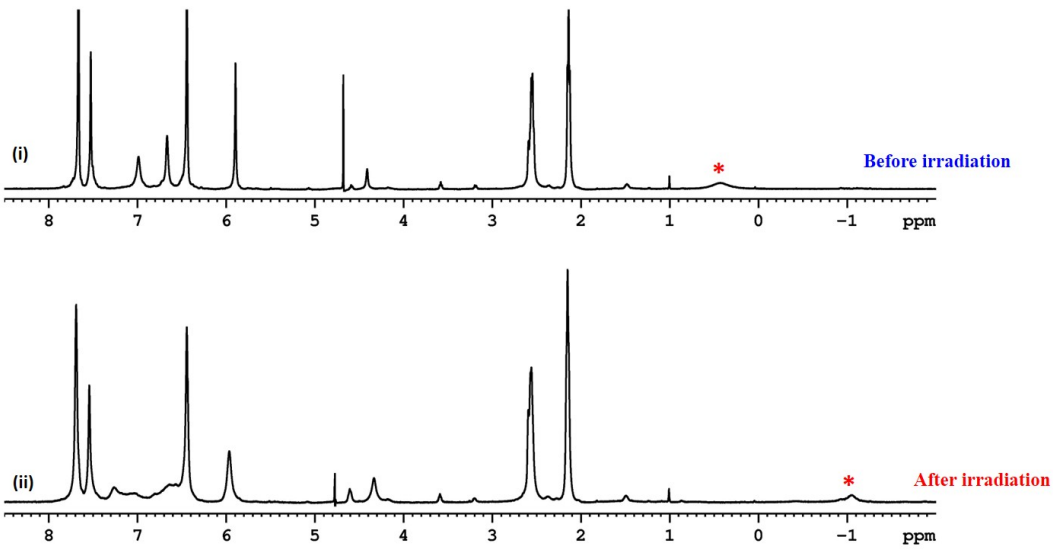

Figure S24. ^{1}H NMR (500 MHz) spectra of (i) **2_2@OA_2** before irradiation; (ii) **2_2@OA_2** after 30 min irradiation.

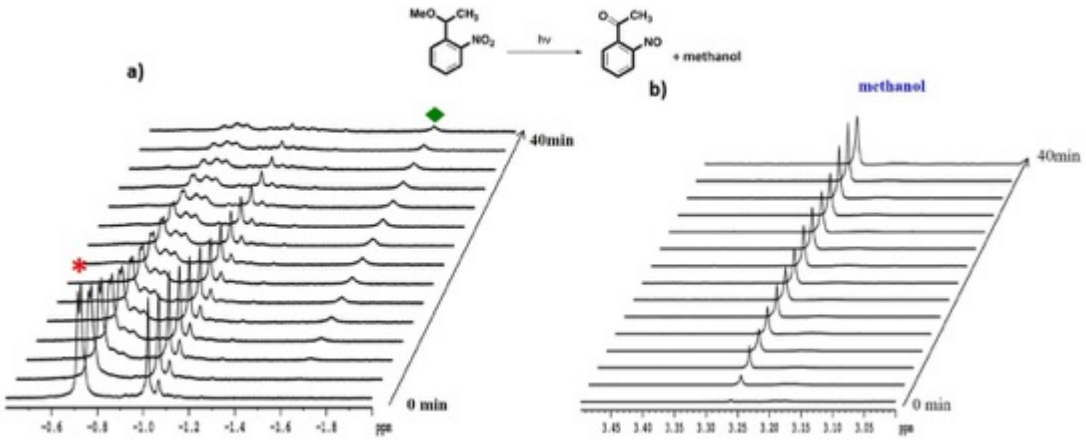

Figure S25. Progress of reaction as followed by ^{1}H NMR (500 MHz upon photolysis of **3_2@OA_2** a) disappearance of methyl proton; b) formation of photoproduct (methanol) with time.

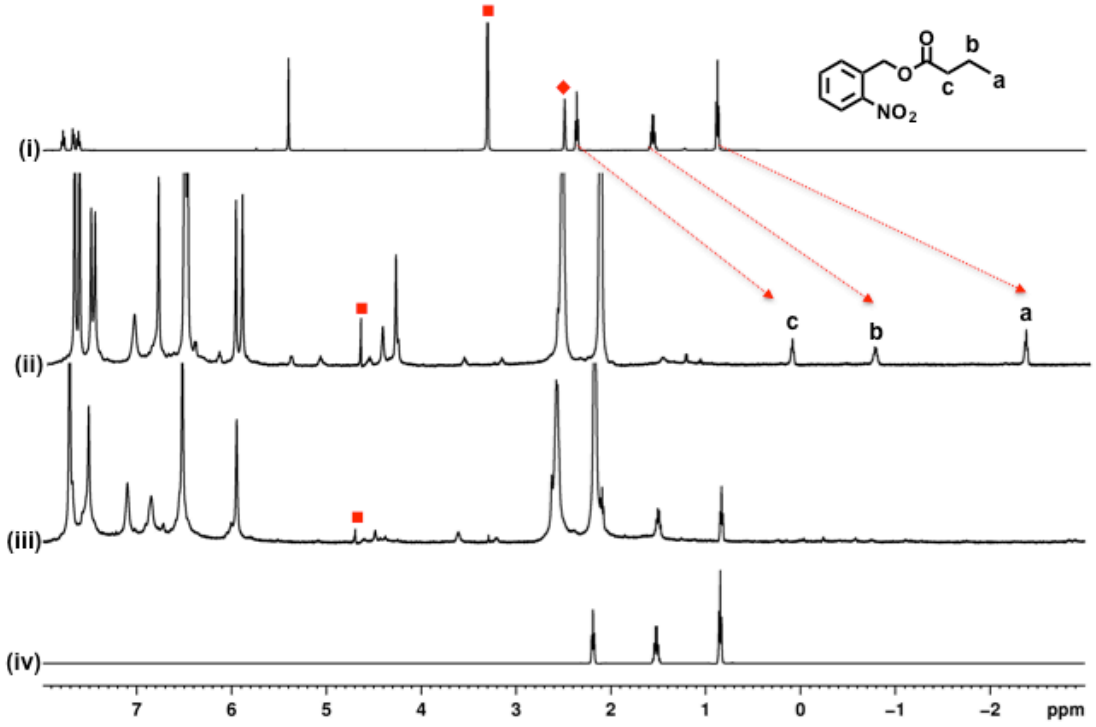

Figure S26. ^{1}H NMR spectra (500 MHz, 10 mM $Na_2B_4O_7$ buffer/D_2O, pH = 8.7) of (i) **4** in DMSO-d_6, (ii) **4**@$(OA)_2$ ([OA] = 1 mM and [**4**] = 0.5 mM), (iii) 2.5 h irradiation of (ii) at ($\lambda \geq 300$ nm), (iv) butyric acid in $Na_2B_4O_7$ buffer/D_2O. Symbols ◆ and ■ indicates the residual solvent peaks of DMSO-d_6 and water, respectively. "a-c" indicate the OA bound guest aliphatic proton peaks.

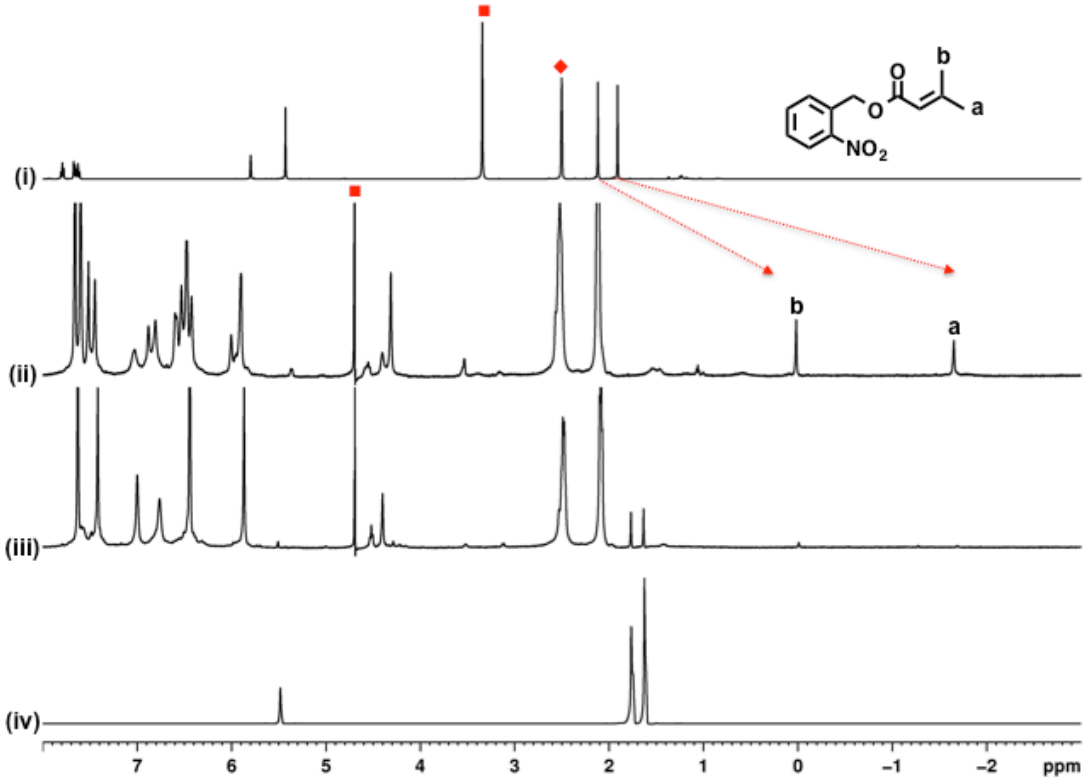

Figure S27. ^{1}H NMR spectra (500 MHz, 10 mM $Na_2B_4O_7$ buffer/D_2O, pH = 8.7) of (i) **5** in DMSO-d_6, (ii) **5**@$(OA)_2$ ([OA] = 1 mM and [**5**] = 0.5 mM), (iii) 2 h irradiation of (ii) at ($\lambda \geq 300$ nm), (iv) 3,3 dimethylacrylic acid in $Na_2B_4O_7$ buffer/D_2O. Symbols ◆ and ■ indicates the residual solvent peaks of DMSO-d_6 and water, respectively. "a and b" indicate the OA bound guest aliphatic proton peaks.

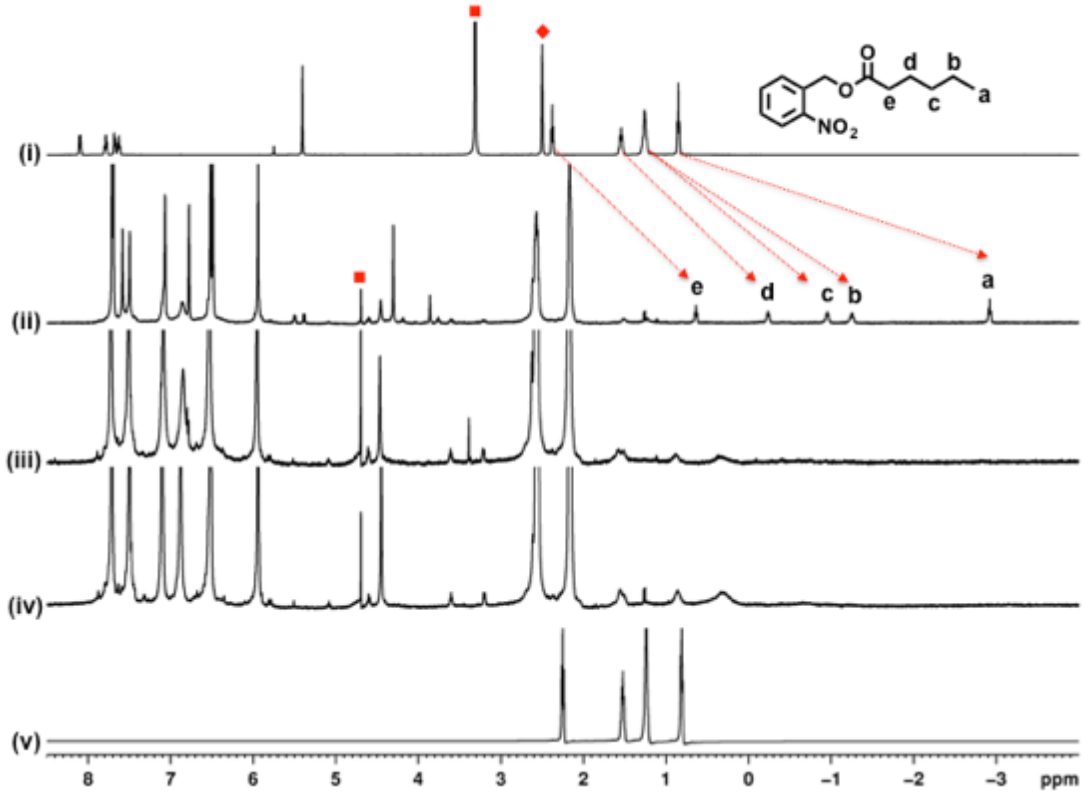

Figure S28. ^{1}H NMR spectra (500 MHz, 10 mM $Na_2B_4O_7$ buffer/D_2O, pH = 8.7) of (i) **6** in DMSO-d_6 (ii) **6**@$(OA)_2$ ([OA] = 1 mM and [**6**] = 0.5 mM); (iii) 4 h irradiation of (ii) at ($\lambda \geq 300$ nm); (iv) hexanoic acid@OA **(**[OA]=1mM, [hexanoic acid] = 0.25 mM); (v) hexanoic acid in $Na_2B_4O_7$ buffer/D_2O. Symbols ◆ and ■ indicate the residual solvent peaks of DMSO-d_6 and water, respectively. "a-e" indicate the OA bound guest aliphatic proton peaks.

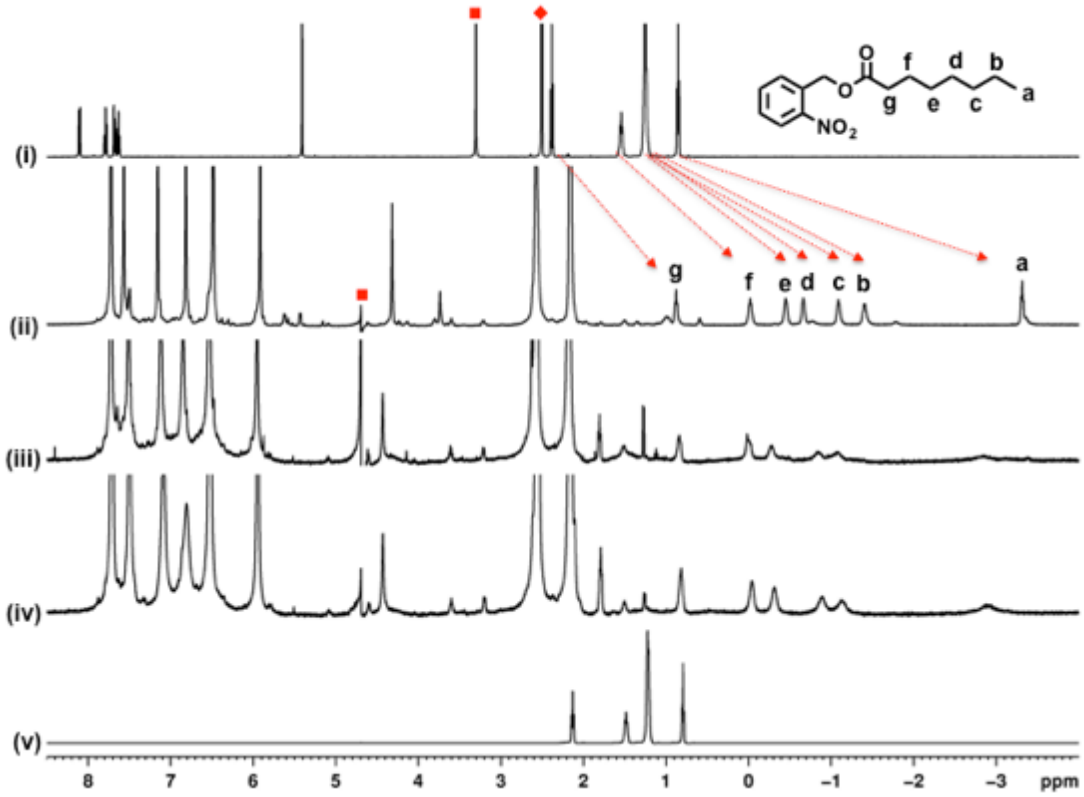

Figure S29. ^{1}H NMR spectra (500 MHz, 10 mM $Na_2B_4O_7$ buffer/D_2O, pH = 8.7) of (i) **7** in DMSO-d_6 (ii) **7**@$(OA)_2$ ([OA] = 1 mM and [**7**] = 0.5 mM); (iii) 5 h irradiation of (ii) at ($\lambda \geq 300$ nm); (iv) octanoic acid@OA **(**[OA]=1mM, [octanoic acid] = 0.25 mM); (v) octanoic acid in $Na_2B_4O_7$ buffer/D_2O. Symbols ◆ and ■ indicate the residual solvent peaks of DMSO-d_6 and water, respectively. "a-g" indicate the OA bound guest aliphatic proton peaks.

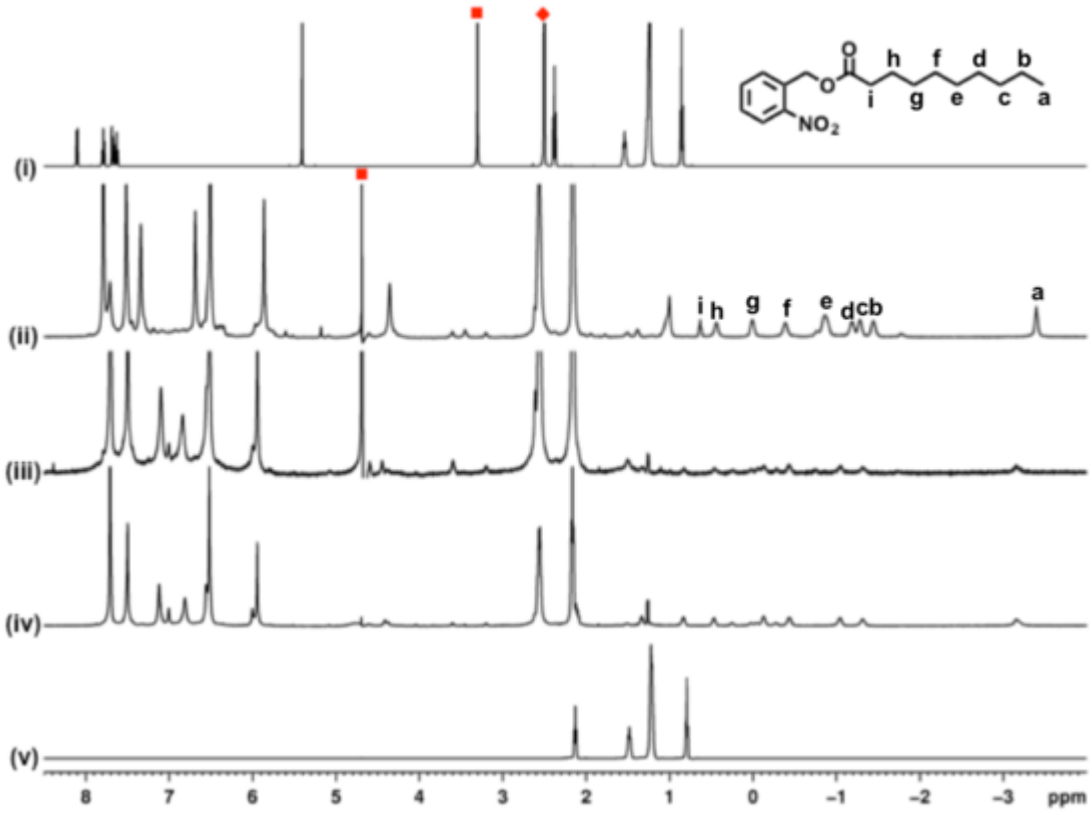

Figure S30. ^{1}H-NMR spectra (500 MHz, 10 mM $Na_2B_4O_7$ buffer/D_2O, pH = 8.7) of (i) **8** in DMSO-d_6 (ii) **8**@$(OA)_2$ ([OA] = 1 mM and [**8**] = 0.5 mM); (iii) 5 h irradiation of (ii) at ($\lambda \geq 300$ nm); (iv) decanoic acid@OA **(**[OA] = 1mM, [decanoic acid] = 0.25 mM); (v) decanoic acid in $Na_2B_4O_7$ buffer/D_2O. Symbols ◆ and ■ indicate the residual solvent peaks of DMSO-d_6 and water, respectively.

2.6 LC-DAD-MS profiles and fragmentation spectra of selected triggers and products

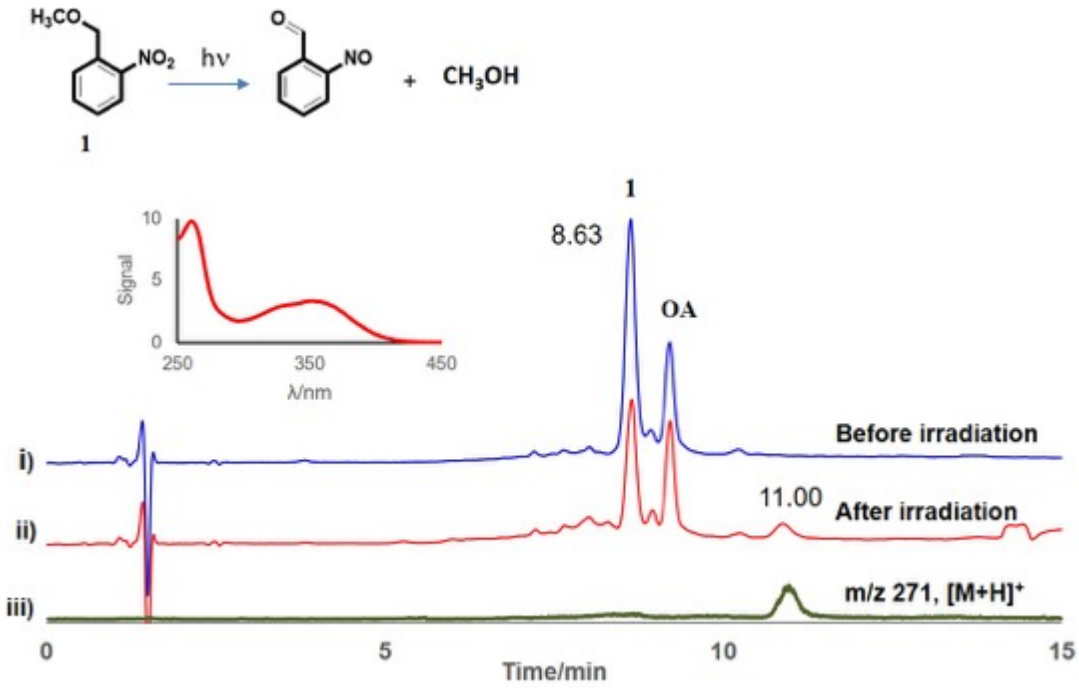

Figure S31. LC−DAD and LC−MS traces of **1**@OA (0.5 mM : 1 mM) in borate buffer (10 mM). (i) LC−DAD trace at 320 nm before irradiation, (ii) LC−DAD trace at 320 nm after 2 minutes irradiation (λ > 300 nm), (iii) single ion trace at m/z 271, assigned to $[M + H]^+$ of dimer of 2-nitrosobenzaldehyde.[5] The insert shows the UV spectrum of compound with 11.00 minutes retention time.

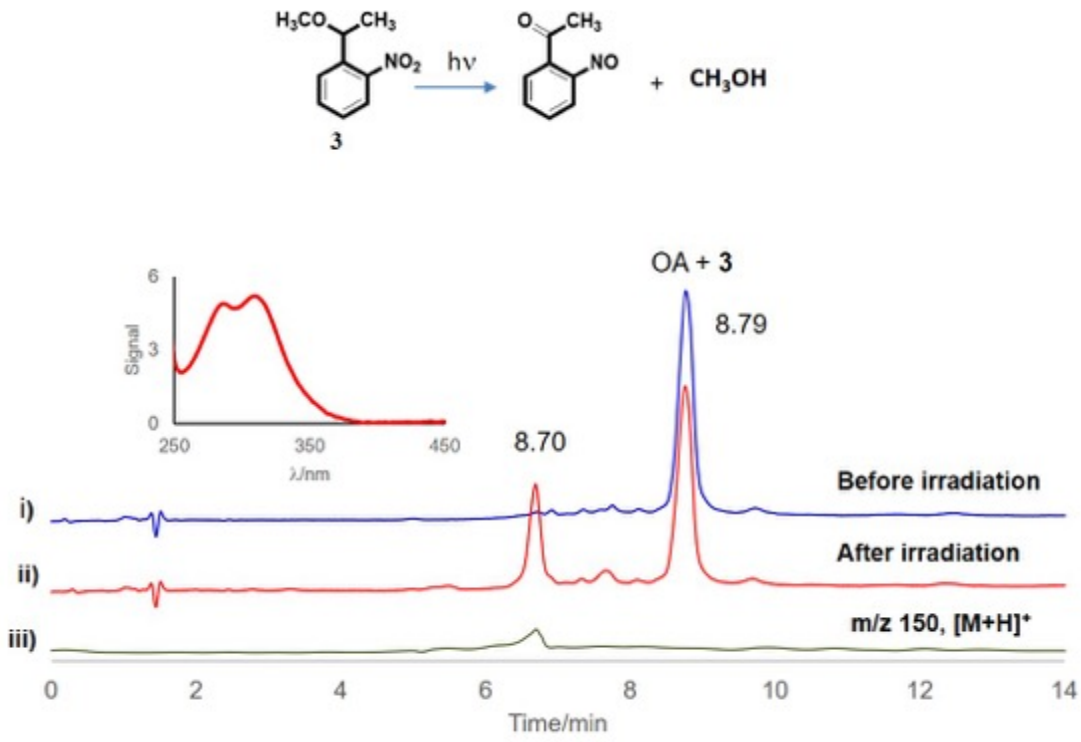

Figure S32. LC−DAD and LC−MS traces of **3**@OA (0.5 mM : 1 mM) in borate buffer (10 mM). (i) LC−DAD trace at 320 nm before irradiation, (ii) LC−DAD trace at 320 nm after 2 minutes irradiation (λ > 300 nm), (iii) single ion trace at m/z 150, assigned to $[M + H]^+$ of 2-nitrosoacetophenone.[1] The insert shows the UV spectrum of compound with 8.70 minutes retention time.

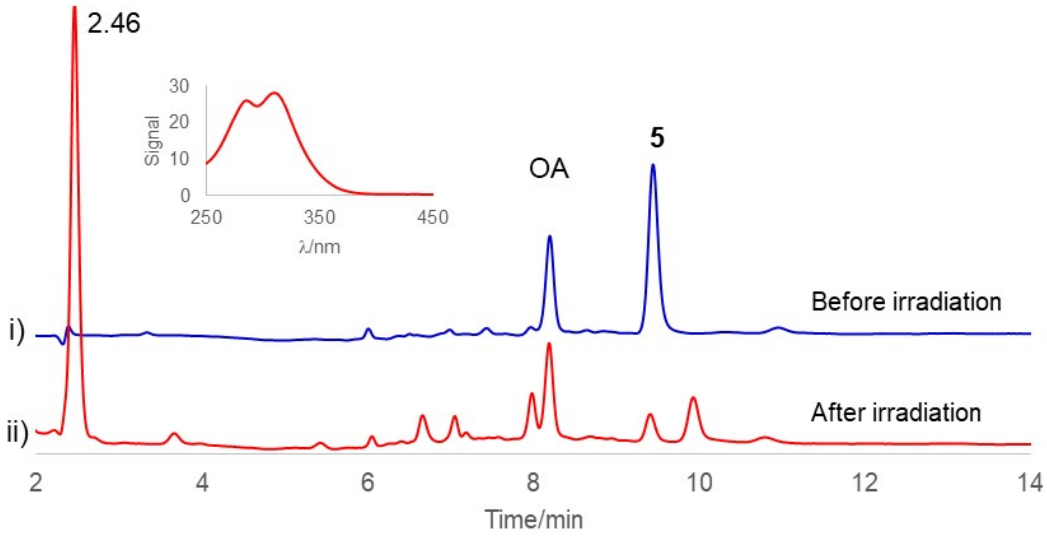

Figure S33. LC−DAD traces of **5**@OA (0.5 mM : 1 mM) in borate buffer (10 mM). (i) LC−DAD trace at 320 nm before irradiation, (ii) LC−DAD trace at 320 nm after 2 minutes irradiation (λ > 300 nm). The insert shows the UV spectrum of compound with 2.46 minutes retention time, assigned to *o*-nitrosobenzaldehyde.[5]

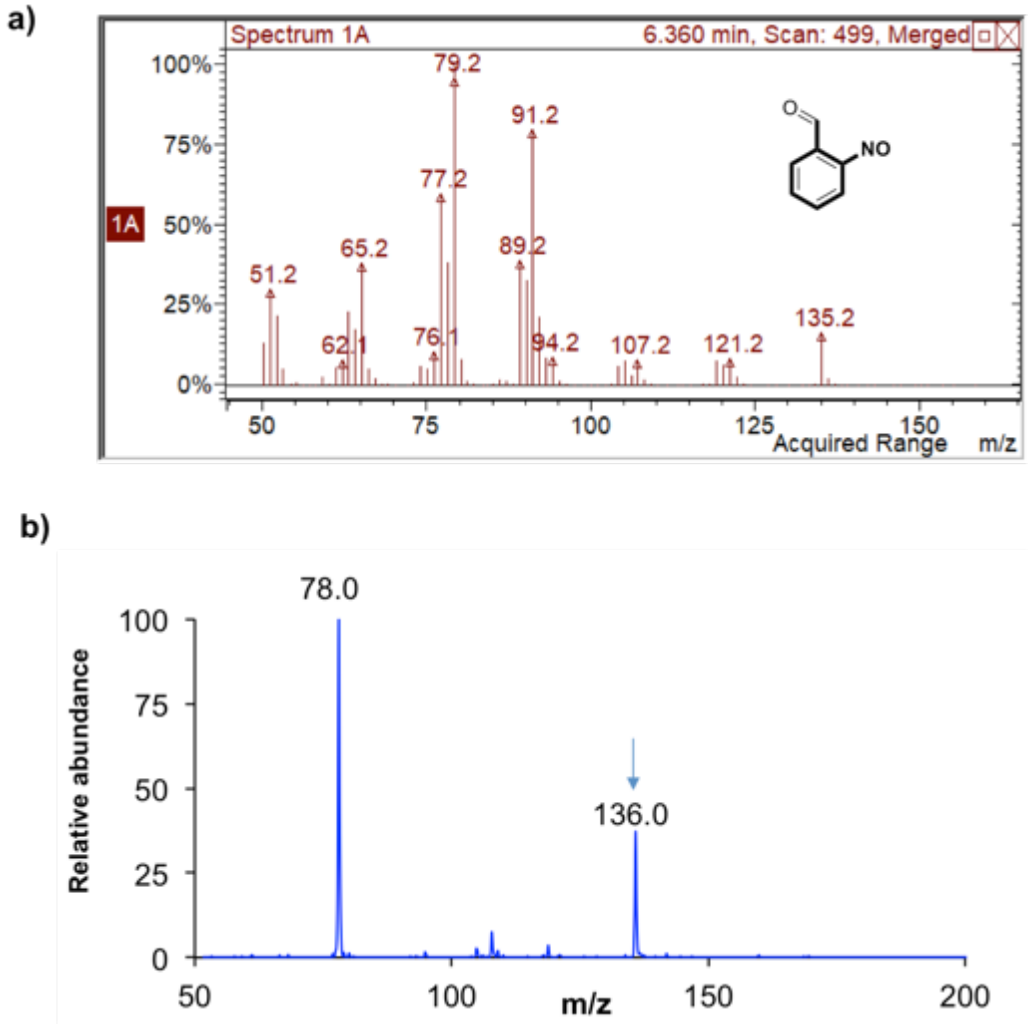

Figure S34. EI (electron impact), **a)**, and ESI-MS^2, **b)**, spectra of 2-nitrosobenzaldehyde.

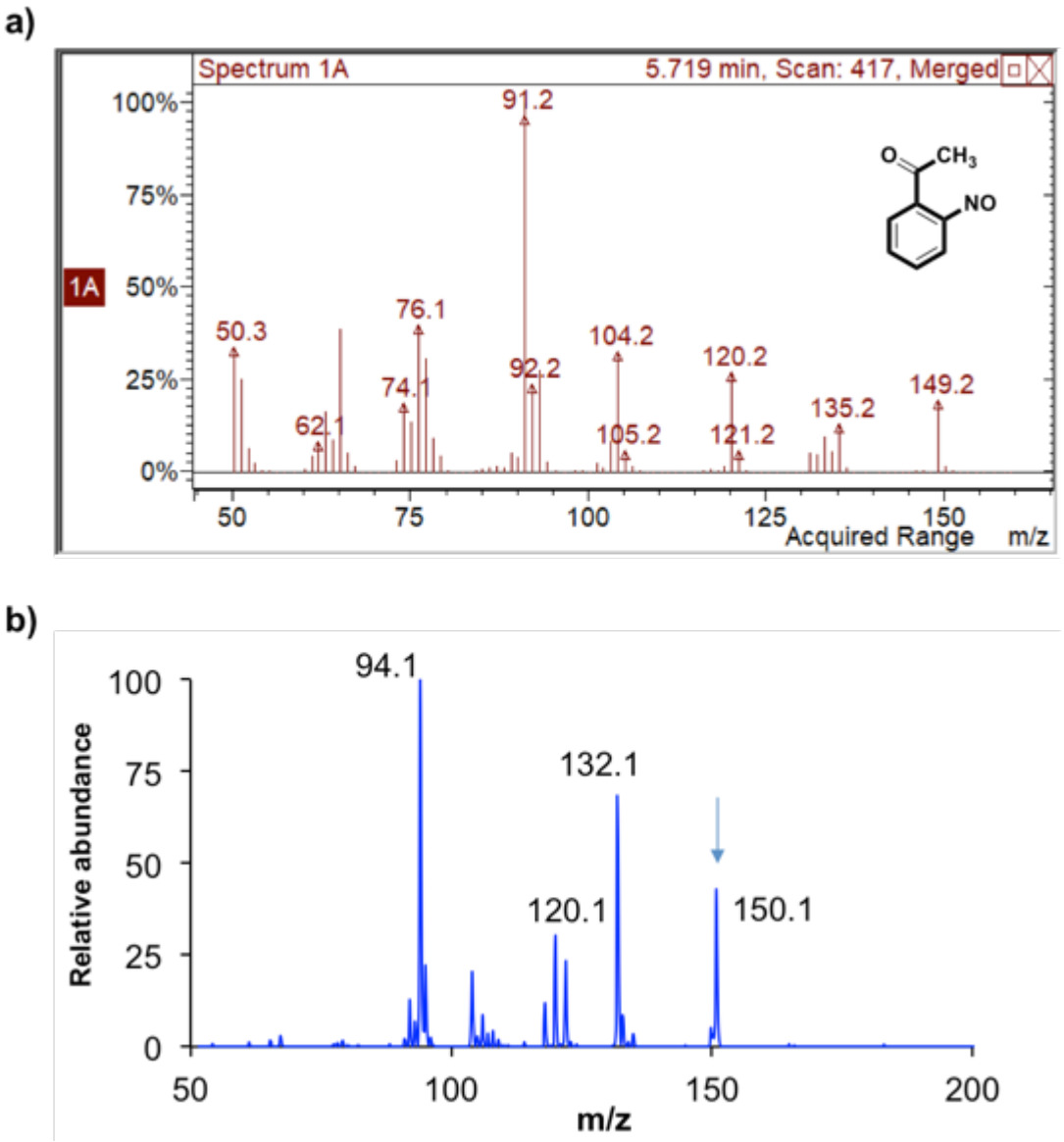

Figure S35. EI (electron impact), **a)**, and ESI-MS^2, **b)**, spectra of 2-nitroso acetophenone.