Supplementary Information
for

Molecular Cage Promoted Aerobic Oxidation or Photo-Induced Rearrangement of Spiroepoxy Naphthalenone

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Content

1. General

Unless otherwise stated, all chemicals and solvents were purchased from commercial companies (Adamas, J&K Scientific, and Sigma-Aldrich. etc) and used without further purification. Anhydrous solvents were distilled according to standard procedures.[S1] Deuterated solvents were purchased from Adamas and J&K. 1D and 2D-NMR were measured on a Bruker Biospin Avance III (400 MHz) spectrometer or JNM-ECZ600R/S1 (600 MHz) spectrometer. ^{1}H-NMR chemical shifts were determined with tetramethylsilane (TMS) or respect to residual signals of the deuterated solvents used (δ = 4.79 for D_2O in ^{1}H NMR). The photoreactors used in this research were bought from Wuhan Geao Instruments Science & Technology Co., Ltd (China) (Purple LEDs, light intensity = 37.4 mw/cm^2, λ_{max} = 390 nm; Blue LEDs, λ_{max} = 450 nm; 1 W for every light bulb; every Schlenk tube was irradiated by 6 light bulbs from the side). Gas chromatography mass spectrometry (GC-MS) analyses were performed on a Shimadzu GCMS-QP2010SE instrument. ESI-TOF-MS were recorded on Impact II UHR-TOF from Bruker. Data analysis was conducted with the Bruker Data Analysis software (Version 4.3) and simulations were performed with the Bruker Isotope Pattern software. UV-vis adsorption spectra were recorded on UV-2700 UV-Visible spectrophotometer from SHIMADZU Corporation.

Stokes-Einstein equation:

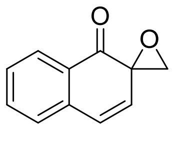
$$D = \frac{K_b T}{6\pi\eta r}$$

was applied to estimate the dynamic radius of complexes in solution. D is diffusion coefficient obtained from DOSY spectrum, K_b is Boltzmann constant, T is the absolute temperature, viscosity η, and r is the estimated dynamic radius.

2. Synthesis procedure

Ligand synthesis and cage **1** assembly were following previous reported procedures.[S2]

Substrate **2** was prepared according to literature reported.[S3] To a solution of 173.0 mg (1.0 mmol) of 1-hydroxy-2-hydroxymethylnaphthalene in 2.0 mL THF was added dropwise 5.0 mL (1.5 mmol) of a 0.3 M aqueous solution of $NaIO_4$. The reaction mixture was stirred for 12 h in room temperature, then partitioned between dichloromethane and water. The organic phase was dried over anhydrous Na_2SO_4, filtered and evaporated. Further purified on silica gel via column chromatography (EtOAc: Petroleum ether = 3:7).



Spiroepoxy Naphthalenone **(2)** was prepared following literature reported[S3] as a white solid (115.2 mg, 0.35 mmol, 66.9 % yield). Analytical data: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, J = 7.8 Hz, 1H), 7.65 (t, J = 7.5 Hz, 1H), 7.43 (t, J = 7.5 Hz, 1H), 7.34 (d, J = 7.5 Hz, 1H), 6.91 (d, J = 9.9 Hz, 1H), 5.93 (d, J = 9.9 Hz, 1H), 3.46 (d, J = 7.6 Hz, 1H), 3.17 (d, J = 7.6 Hz, 1H).; ^{13}C NMR: (101 MHz, $CDCl_3$): δ 193.4, 137.5, 135.1, 131.4, 131.1, 129.4, 128.5, 128.1, 126.9, 57.7, 55.8;

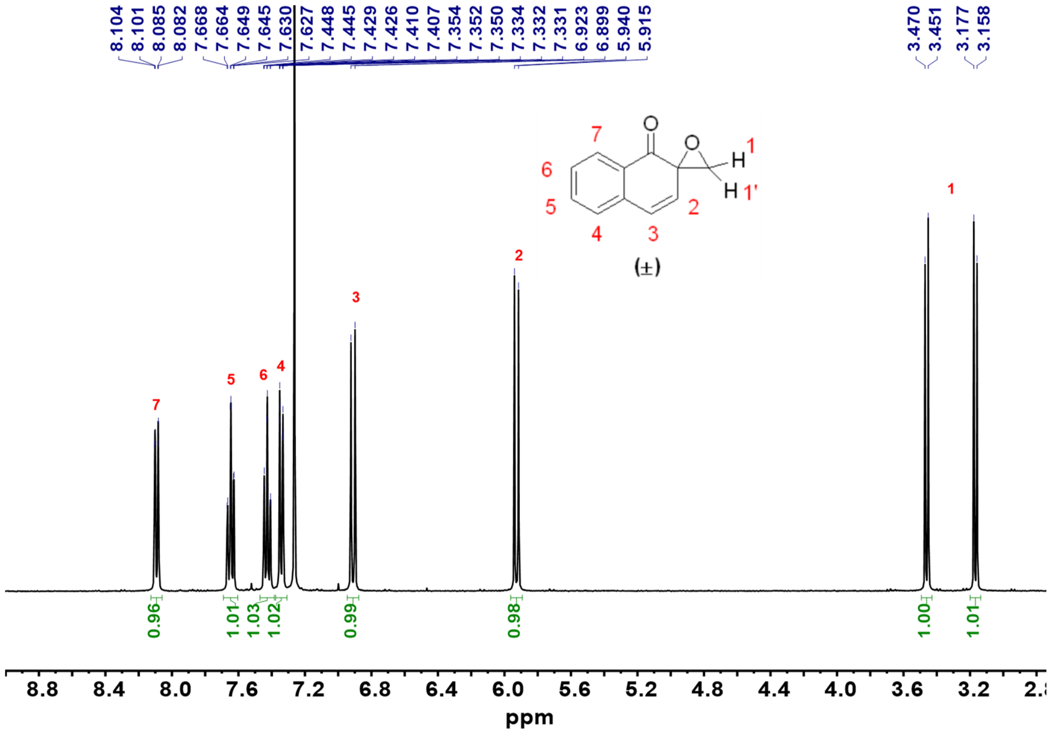


Figure S1 ^{1}H NMR spectrum of **2**. (400 MHz, CDCl$_3$, 298 K)

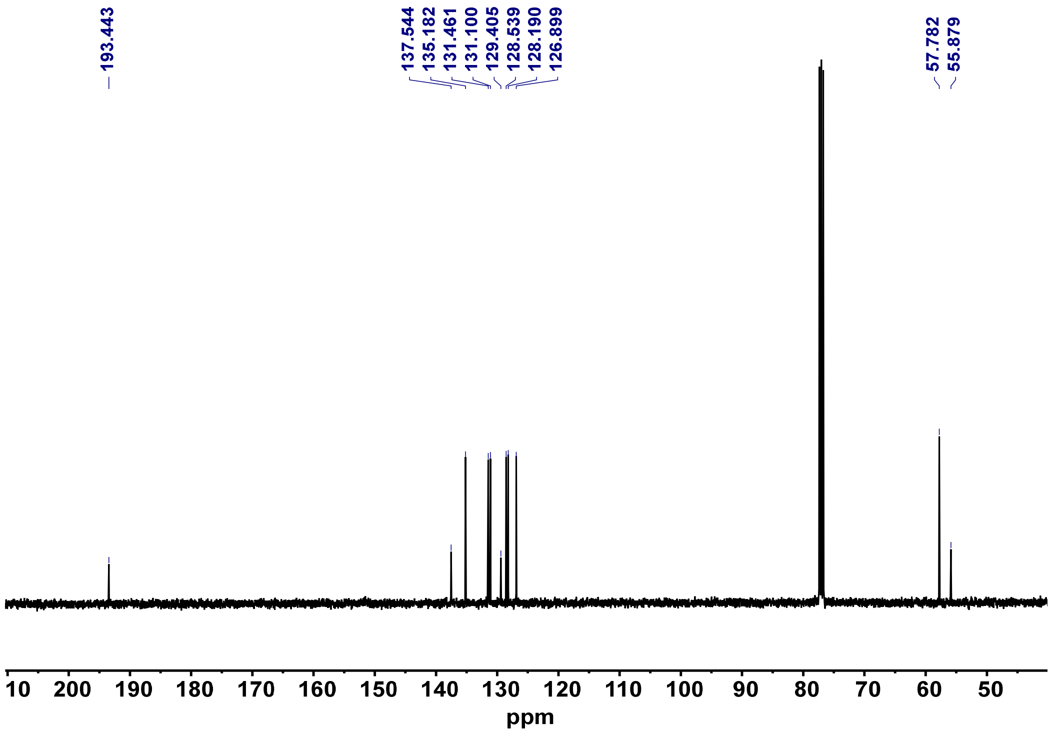
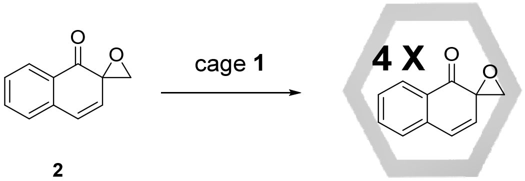


Figure S2 ^{13}C NMR spectrum of **2**. (101 MHz, CDCl$_3$, 298 K)

3. Host-Guest studies

3.1 Encapsulation



2

Excess amount of **2** were directly added into the solution of cage **1** in D_2O, the mixture was stirred for 30 min before subjected to NMR measurement. All the NMR spectra were tested after insoluble substrates removed by filtration. ([**1**] = 2.5×10^{-3} mM)

Physical data of $(\mathbf{2})_4\subset\mathbf{1}$: ^1H NMR (400 MHz, D_2O) δ 9.45 (d, *J* = 6.0 Hz, 8H), 9.41 (d, *J* = 6.4 Hz, 8H), 9.32 (d, *J* = 6.0 Hz, 8H), 8.91 (d, *J* = 6.4 Hz, 8H), 8.67 (d, *J* = 5.8 Hz, 8H), 8.62 (d, *J* = 5.8 Hz, 7H), 8.03 (s, 8H), 6.18 (m, 4H), 6.02 (m, 16H), 5.71 (d, J = 7.5 Hz, 4H), 5.32 (d, J = 9.7 Hz, 4H), 4.44 (d, J = 9.7 Hz, 4H), 3.12 (m, 16H), 2.65(m, 48H), 2.03 (m, 8H).

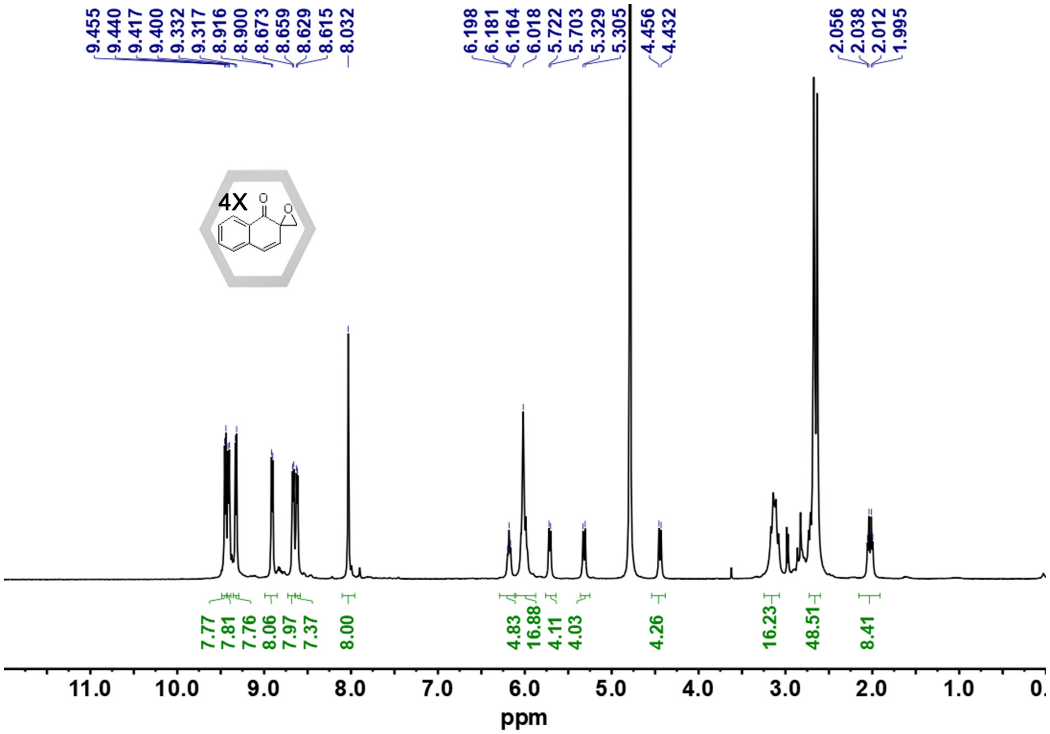


Figure S3 ^1H NMR spectrum of $(\mathbf{2})_4\subset\mathbf{1}$. (400 MHz, D_2O, 298 K, [**1**] = 2.5 × 10^{-3} mM)

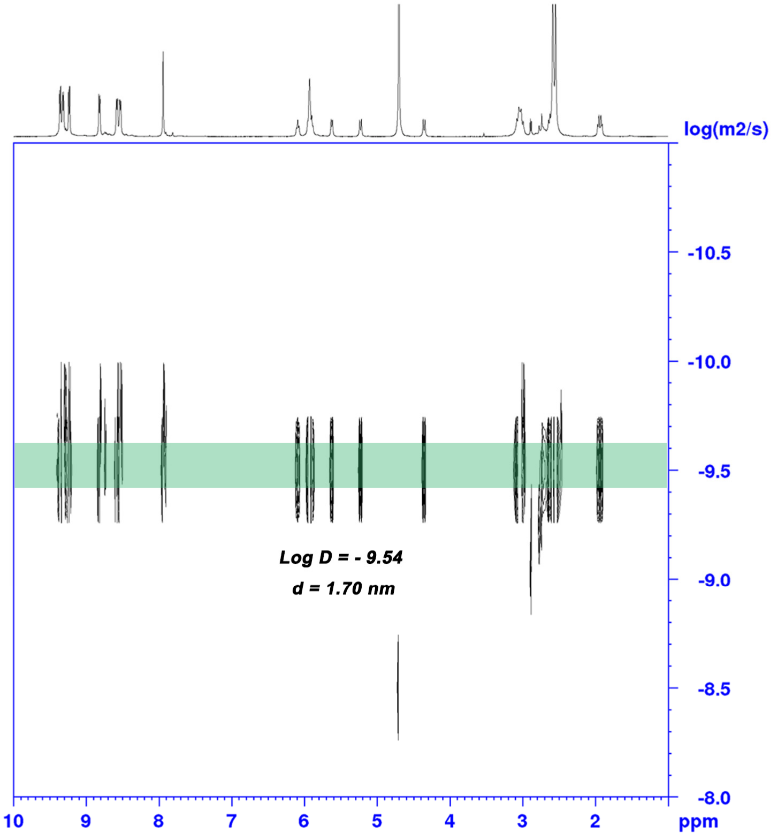
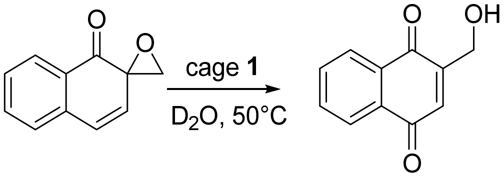


Figure S4 ^{1}H DOSY spectrum of ($\mathbf{2}$)$_4$$\subset$$\mathbf{1}$. (400 MHz, D_2O, 298 K, [**1**] = 2.5 × 10^{-3} mM)

4. Procedure for cage catalyzed reaction from 2 to 3:



An excess amount of **2** was suspended in a D_2O solution (1.0 mL) of cage **1** (2.5×10^{-3} mmol; 2.5 mM), and the solution was stirred at room temperature for 30 min. After filtration, the quantitative formation of inclusion complex ($\mathbf{2}$)$_4$$\subset$$\mathbf{1}$ was confirmed by ^{1}H NMR. Host-guest complex solution was stirred for 2 h at 50°C. After extraction with $CDCl_3$ for three times, product **4** was obtained with > 99% yield, as determined by NMR analysis with inner standard (1,3,5-Trimethoxybenzene, 1×10^{-3} mM).

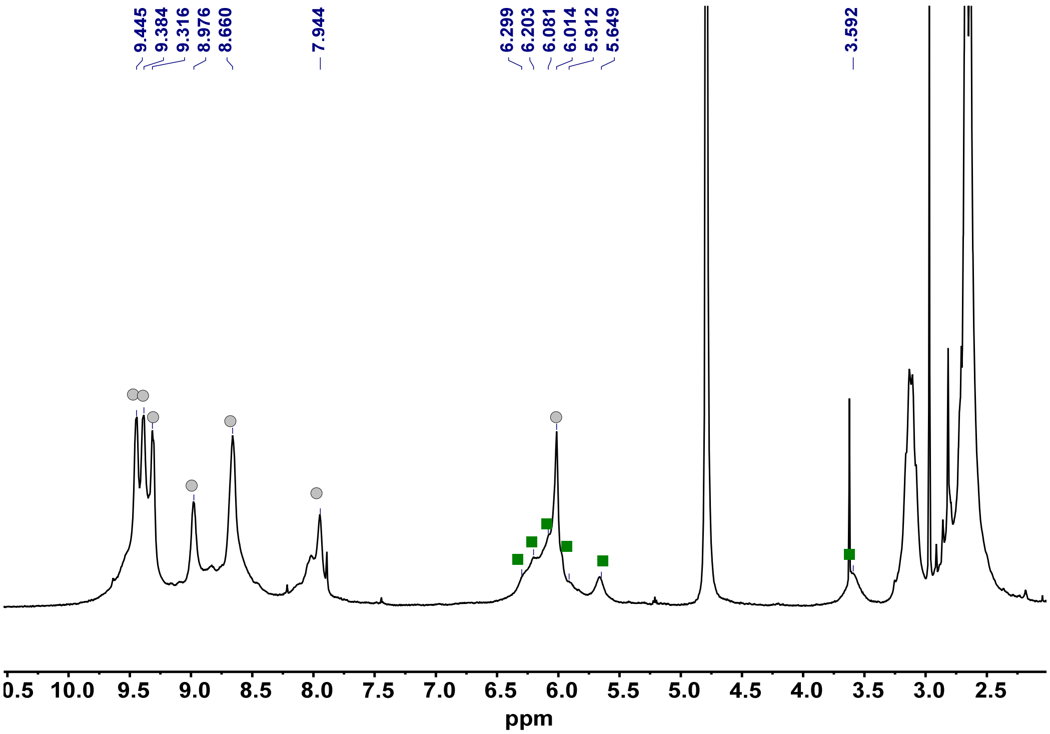


Figure S5 ^{1}H NMR (400 MHz, 298 K, D_2O) spectrum of $(\mathbf{2})_4\subset\mathbf{1}$ after heating at 50 °C for 2 h.

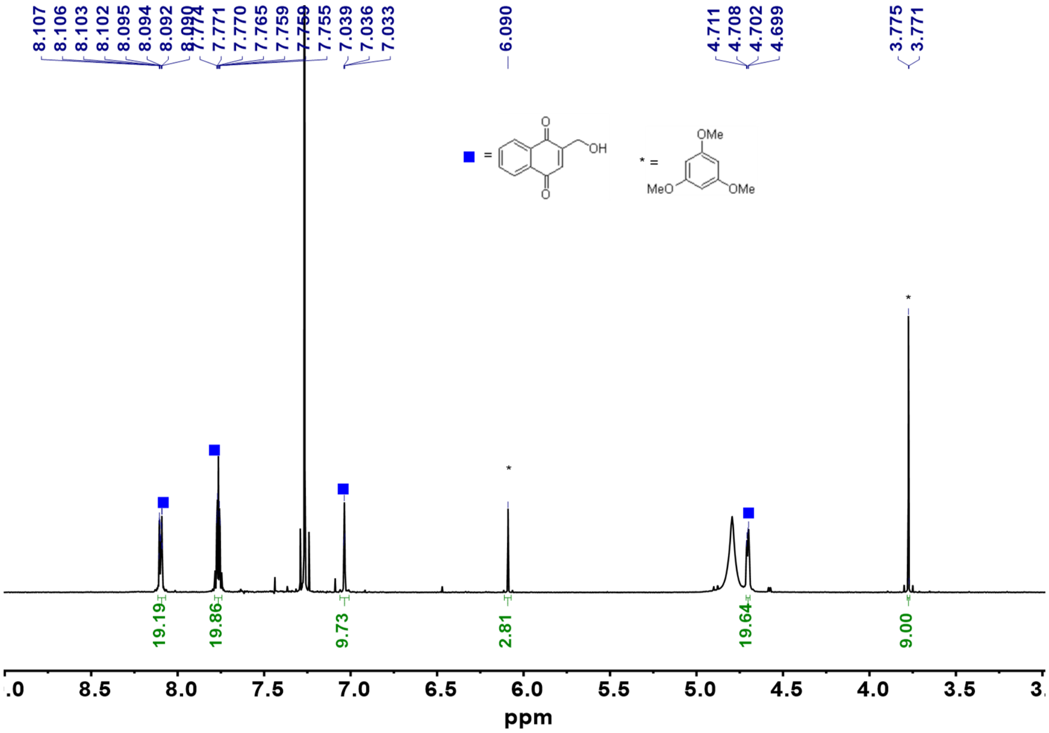


Figure S6 ^{1}H NMR (600 MHz, 298 K, $CDCl_3$) spectrum of extraction solution from $(\mathbf{2})_4\subset\mathbf{1}$ after heating at 50 °C for 2 h. (1,3,5-Trimethoxybenzene, 1×10^{-3} mM)

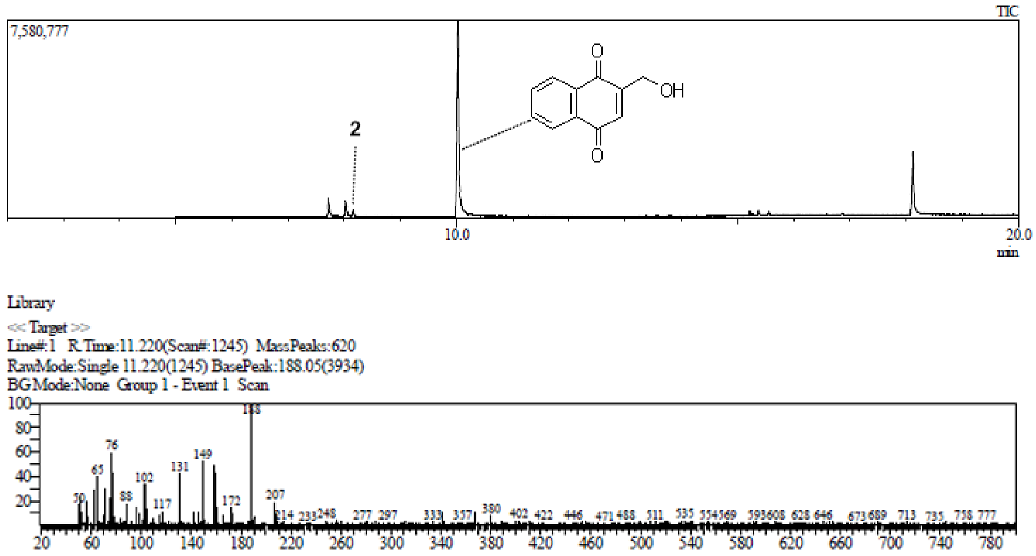


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Figure S7 Overlay of GC-MS spectra for indication of **3** promoted by cage **1** ($CHCl_3$).

Inhibitor competition:

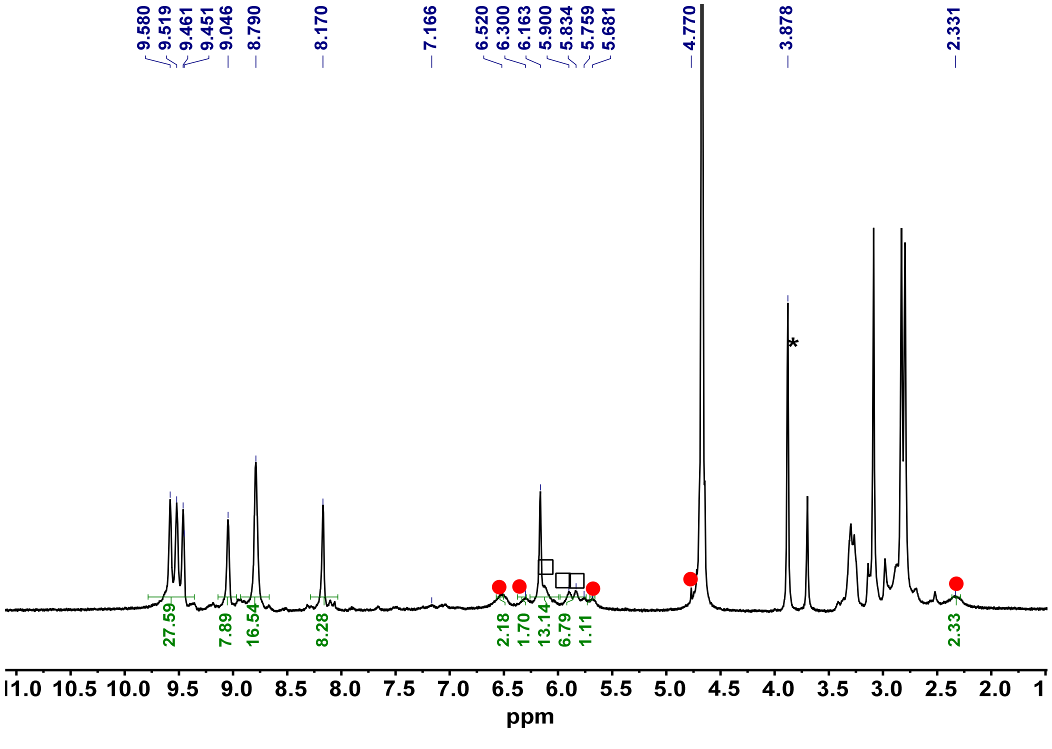


Figure S8 ^1H NMR spectra of the mixture of $(BPh_4^-)\subset 1$ and 2 in D_2O. (600 MHz, D_2O, 328 K, ●: 2, □: BPh_4^-, *: 1,4-Dioxane)

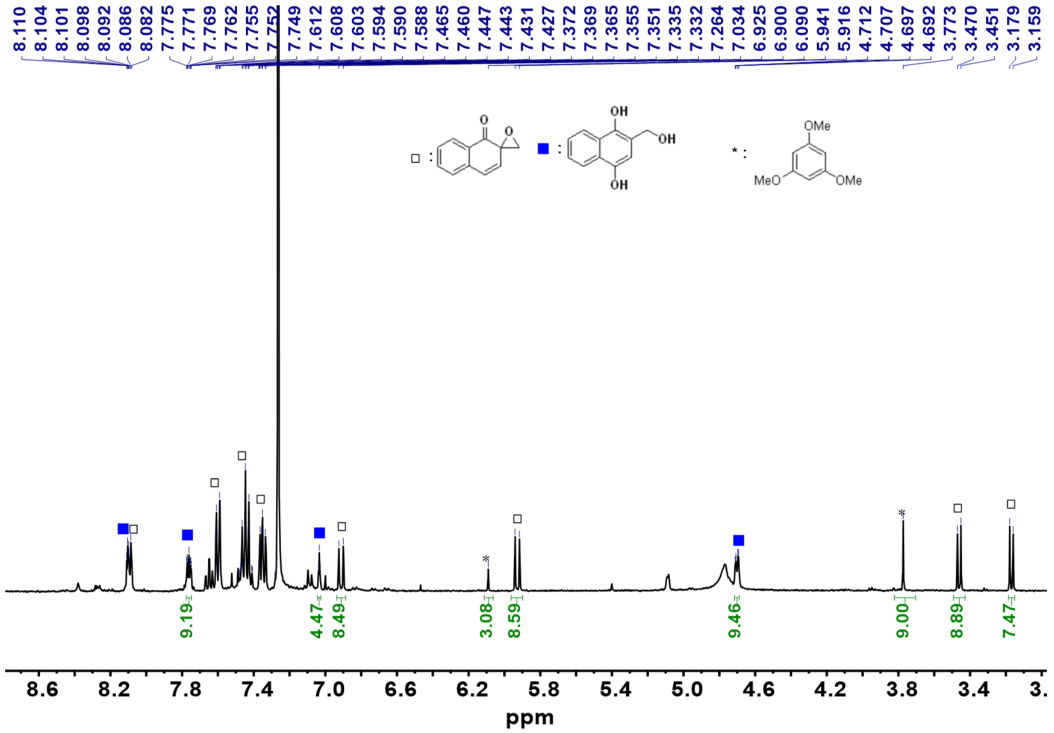
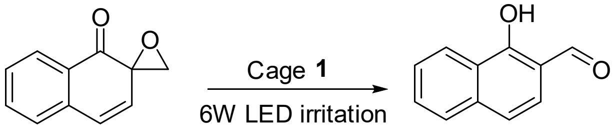


Figure S9 ^{1}H NMR (400 MHz, 298 K, $CDCl_3$) spectrum of extraction solution from mixture of (BPh_4^-)⊂**1** and **2** after heating at 50 °C for 2 h. (1,3,5-Trimethoxybenzene, 1×10^{-3} mM)

5. Procedure for LEDs/cage promoted rection from 2 to 4:



2 **4**

Procedure A: **2** (1.7 mg; 1.0×10^{-2} mmol) was solved into $CHCl_3$ and irradiated by purpure LEDs for two hours. Product 4 was obtained almost quantitatively detected by ^{1}H NMR.

Procedure B: **2** (1.7 mg; 1.0×10^{-2} mmol) was suspended in a D_2O solution (1.0 mL) of cage **1** (2.5×10^{-3} mmol; 2.5 mM), and the solution was stirred at room temperature for 30 min under an atmosphere of N_2. After mixture solution became clear, host-guest complex solution was stirred for 8 h at r.t. in a schlenk tube with blue-LED (6W) irradiation under an N_2 atmosphere. The color of solution changed gradually from yellow to orange. After extraction with $CDCl_3$, product **4** was obtained in 90% yield, as determined by NMR analysis with inner standard (1,3,5-Trimethoxybenzene, 1×10^{-3} mM).

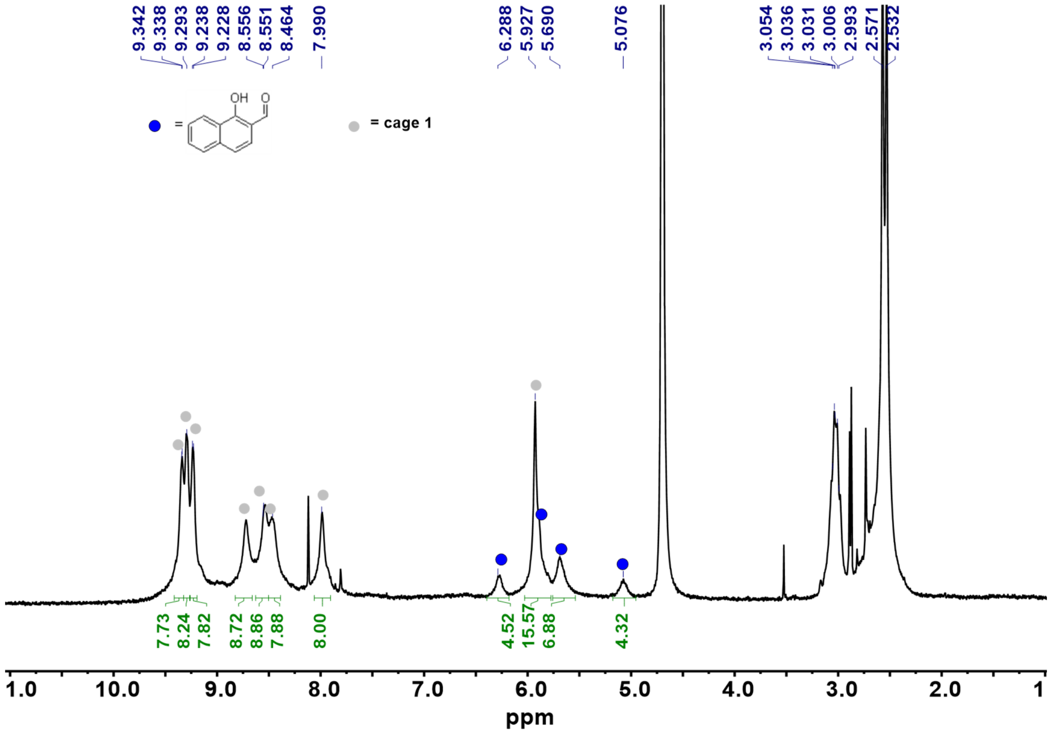


Figure S11 ^{1}H NMR of $(\mathbf{2})_4\subset\mathbf{1}$ after irradiation by blue-LEDs for 8 h under N_2 atmosphere. (400 MHz, 298 K, D_2O)

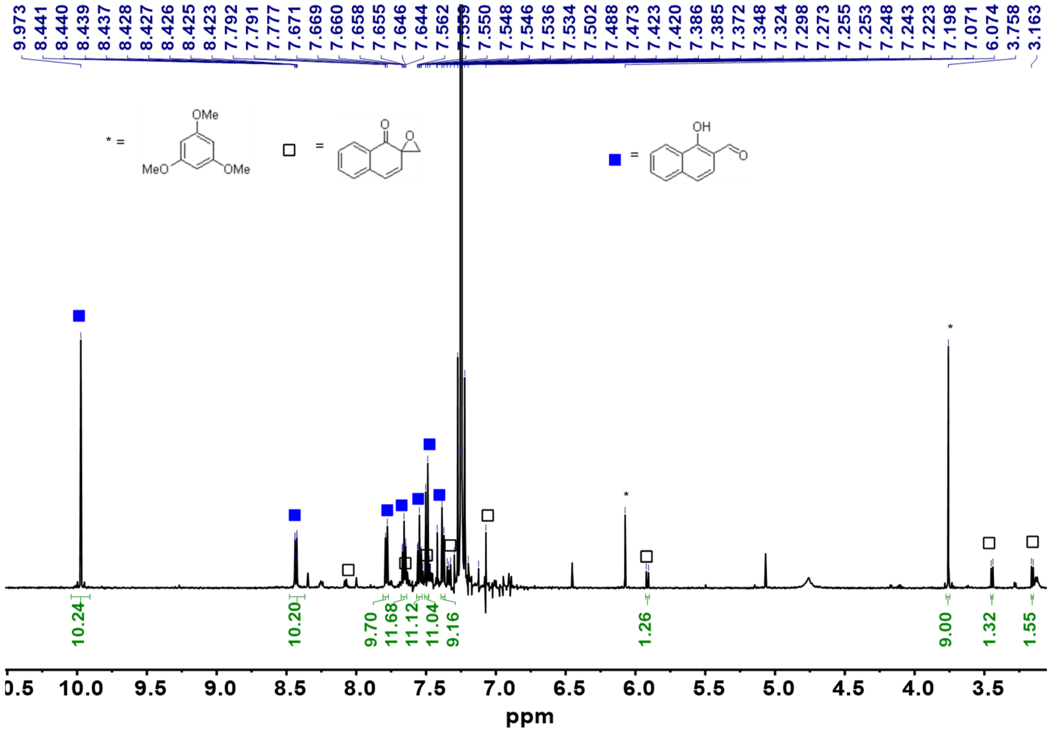


Figure S12 ^{1}H NMR (400 MHz, 298 K, $CDCl_3$) spectrum of extraction solution from previous solution. (1,3,5-Trimethoxybenzene, 1×10^{-3} mM)

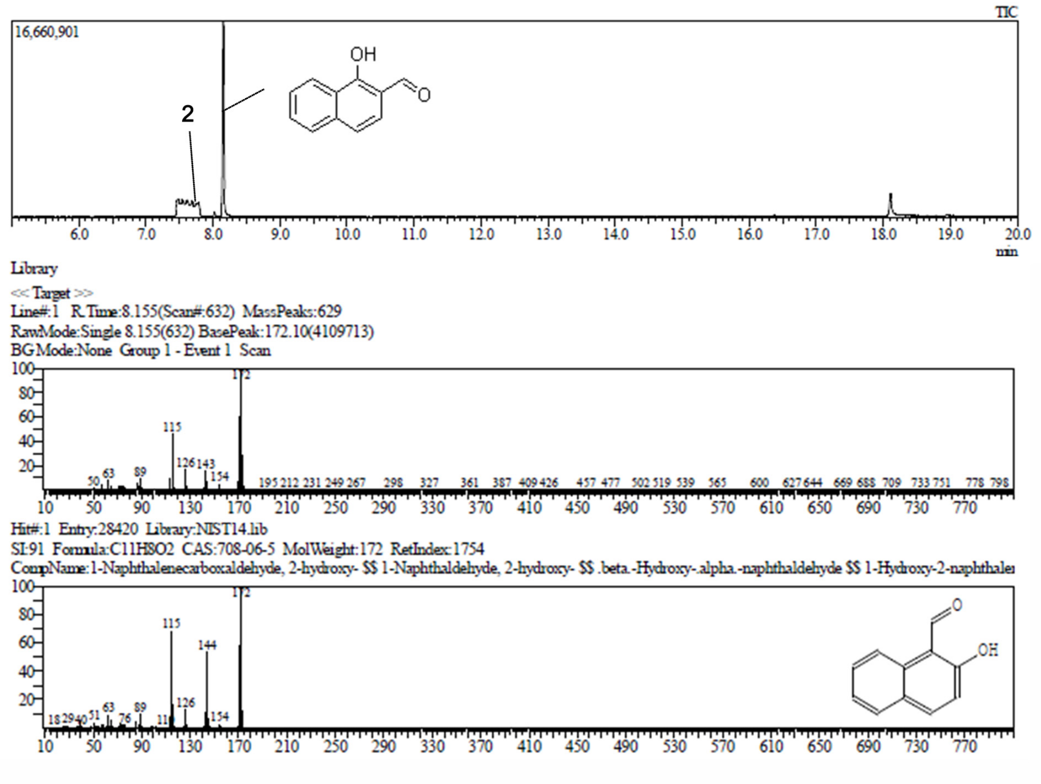


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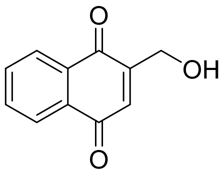
Figure S13 Overlay of GC-MS spectra for indication of **4** promoted by cage **1** ($CHCl_3$).

6. NMR Spectra of Products 3 and 4:



brown solid, ^1H NMR (600 MHz, $CDCl_3$) δ 2.34 (br s,1H), 4.67 (s, 2H), 6.99 (t, *J* = 1.8 Hz, 1H), 7.73 (m, 2H), 8.06 ppm (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 60.0, 126.3, 132.0, 133.4, 133.8, 134.1, 149.0, 185.0, 185.4. NMR Data is corresponding to previous literature.[S4] HRMS (ESI): calcd for $C_{11}H_8O_3$ $(M-H)^-$ 187.0405, found 187.0401.

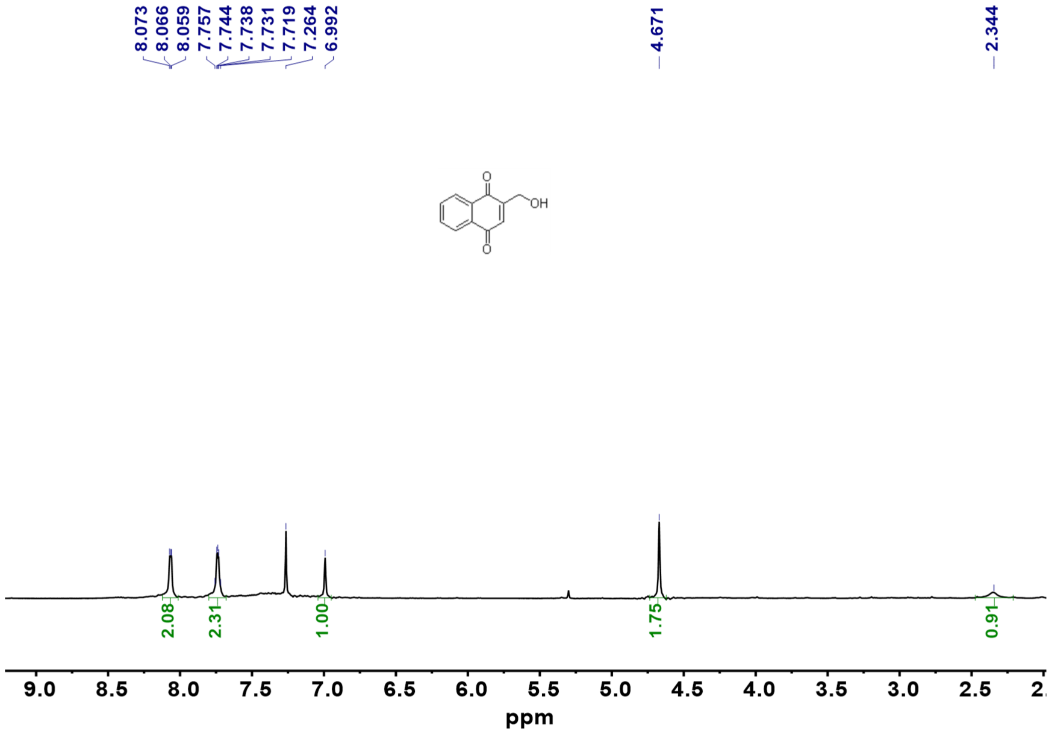


Figure S14 ^{1}H NMR spectrum of **3**. (600 MHz, 298 K, $CDCl_3$)

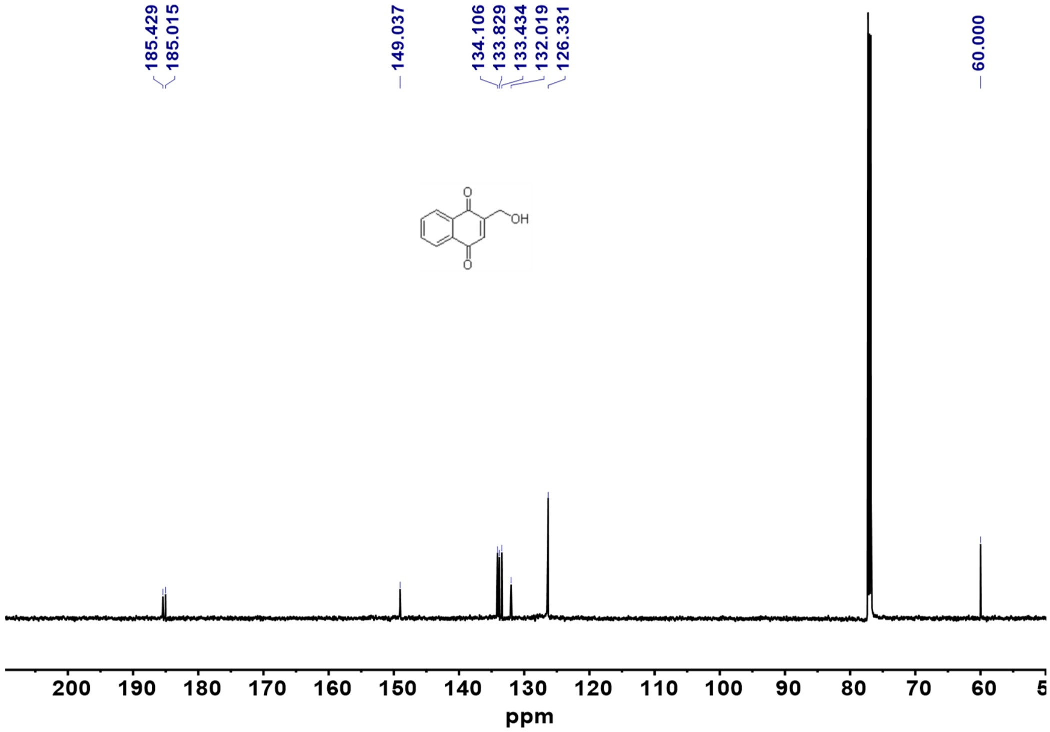
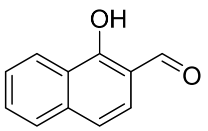


Figure S15 ^{13}C NMR spectrum of **3**. (151 MHz, 298 K, $CDCl_3$)



yellow solid, ^{1}H NMR (600 MHz, $CDCl_3$) δ 12.66 (1H, s), 9.97 (1H, s), 8.44 (1H, br d, *J*=8.3 Hz),7.79 (1H, d, *J*=8.3Hz), 7.67 (1H, dd, *J*=8.3, 1.5 Hz), 7.56 (1H, dd, *J*=8.3, 1.5Hz), 7.49 (1H, d, *J*=8.3Hz), 7.36 (1H, d, *J*=8.3 Hz). ^{13}C NMR (151 MHz, $CDCl_3$) δ 196.4, 161.9, 137.5, 130.6, 127.6, 126.5, 126.2, 124.5, 124.3, 119.4, 114.3.

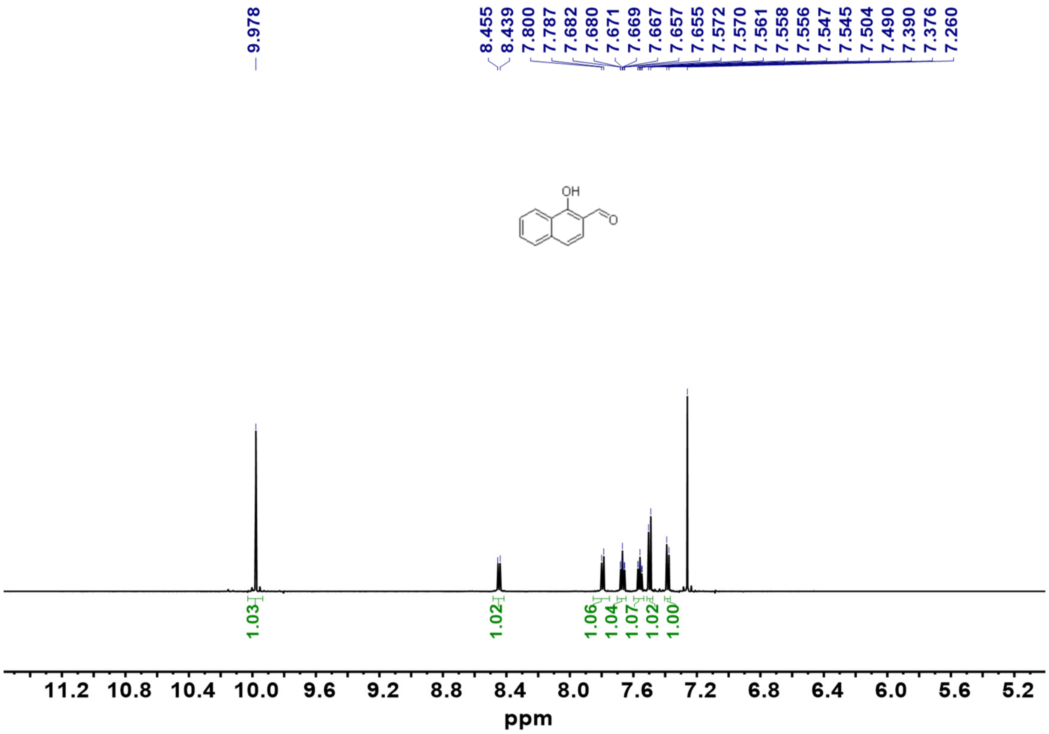


Figure S16 ^{1}H NMR spectrum of **4** (600 MHz, 298 K, $CDCl_3$)

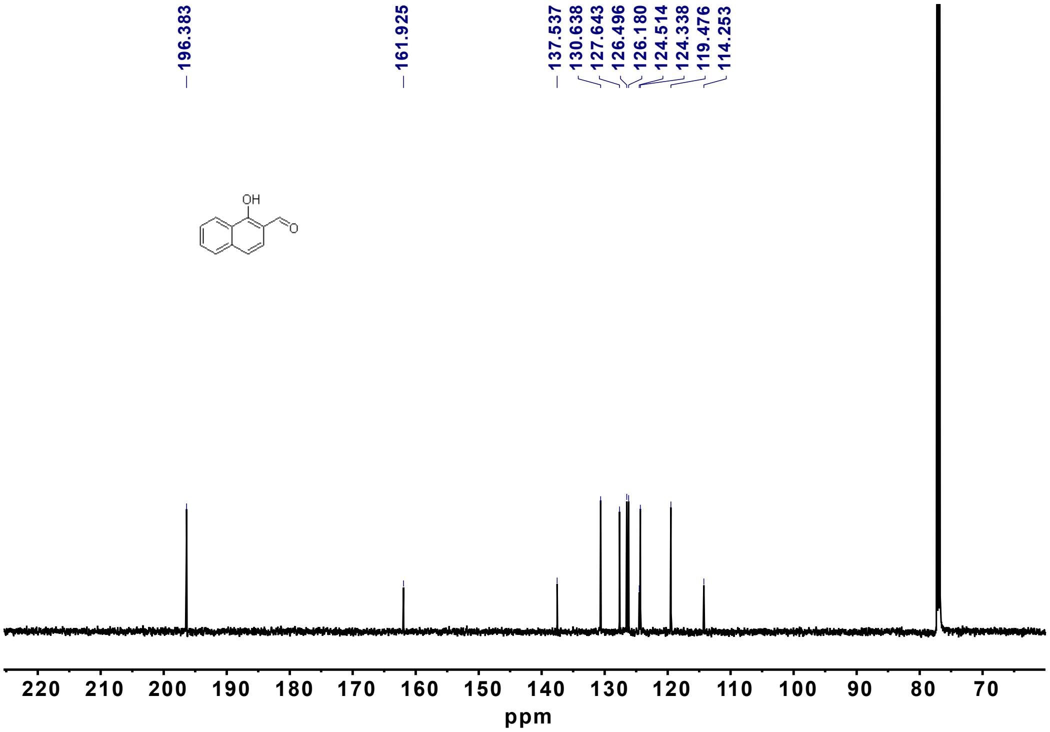


Figure S17 ^{13}C NMR spectrum of **4** (151 MHz, 298 K, $CDCl_3$)

7. Proposed Mechanism

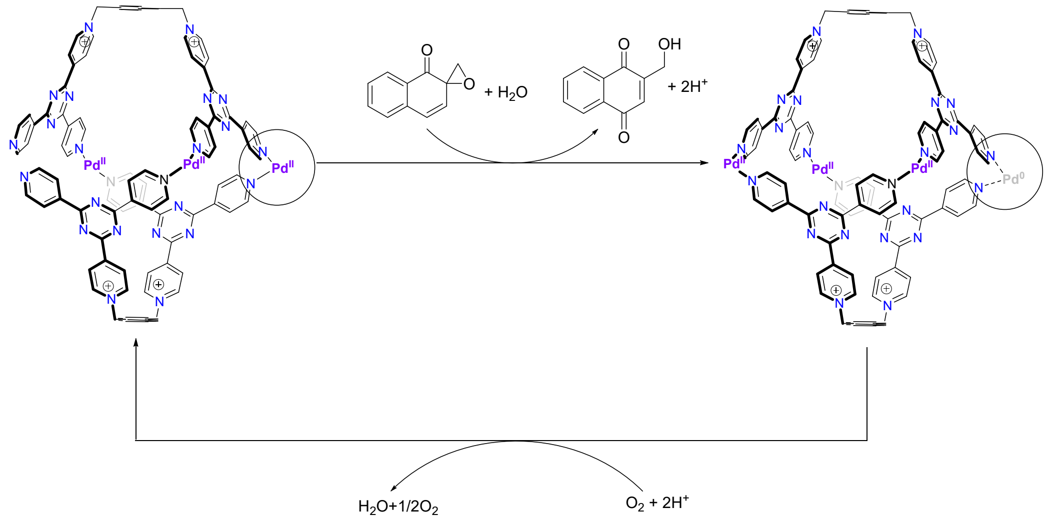


Figure S18 Proposed a possible mechanism of the conversion from **2** to **3**.

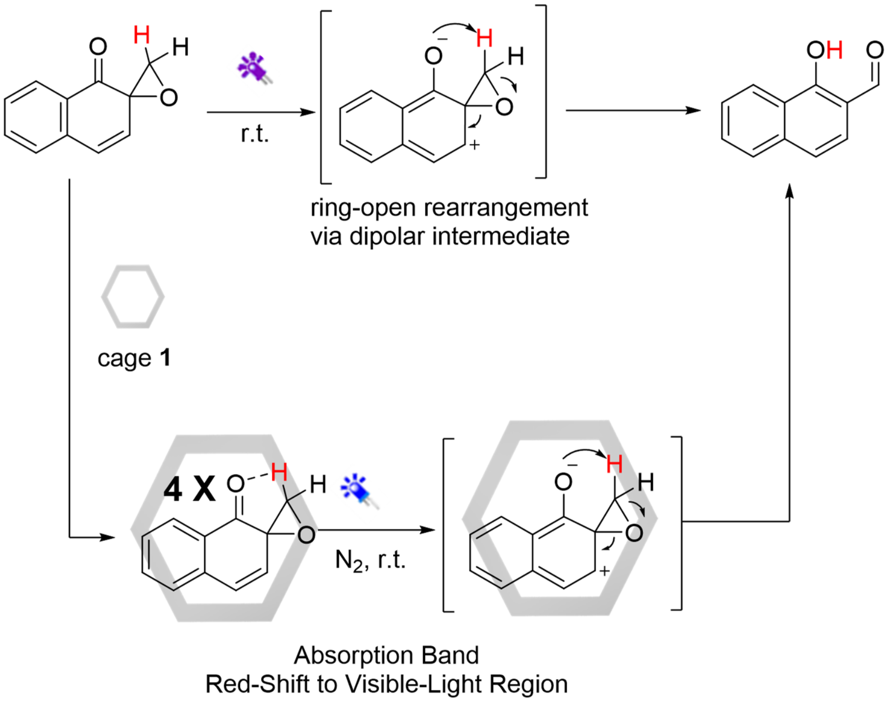


Figure S19 Proposed mechanism of the conversion from **2** to **4** with LEDs irradiation.

8. X-Ray Data

X-ray crystallography analysis of single crystal was performed on a Bruker D8 VENTURE photon II diffractometer with Iμs 3.0 microfocus X-ray source diffractometer. Data reduction was performed with the APEX-III software. Structures were solved by direct methods and refined by full-matrix least squares on *F2* with anisotropic displacement using the SHELX software package.[S5] In the structure of host-guest complex, solvent molecules were highly disordered and could not be reasonably located. These residual intensities were removed by PLATON/SQUEEZE routine.[S6] Crystal data and final refinement details for the structures are reported in Table S3.

Crystal data for host-guest complex of product **3** and cage **1** (mo_cpm353d): Space group I_4, a = 38.791(3) Å, b = 38.791(3); c = 32.719(3) Å, V = 49234(9) Å^3, Z = 8, T = 200 K. Anisotropic least squares refinement based on 19292 independent merged reflections (R_{int}= 0.1052) converged at residual wR^2 = 0.2384 for all data; residual R_1 = 0.0708 for 59016 observed data [$I > 2\sigma (I)$], and goodness of fit (GOF) =1.009. CCDC: 2065411.

Table S3. Crystal data and structure refinement of mo_cpm353d

Identification code	mo_cpm353d	
Empirical formula	$C_{145} H_{152} B F_4 N_{32} O_9 Pd_4$	
Formula weight	2999.40	
Temperature	200(2) K	
Wavelength	0.71073 Å	
Crystal system	Tetragonal	
Space group	I_4	
Unit cell dimensions	a = 38.791(3) Å	α= 90°.
	b = 38.791(3) Å	β= 90°.
	c = 32.719(3) Å	γ = 90°.
Volume	49234(9) Å^3	
Z	8	
Density (calculated)	0.809 Mg/m^3	
Absorption coefficient	0.330 mm^{-1}	
F(000)	12344	
Crystal size	0.5 x 0.3 x 0.3 mm^3	
Theta range for data collection	2.206 to 18.847°.	
Index ranges	-35<=h<=35, -34<=k<=34, -29<=l<=29	
Reflections collected	59016	
Independent reflections	19292 [R(int) = 0.1052]	
Completeness to theta = 18.847°	99.6 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	19292 / 2260 / 1429	
Goodness-of-fit on F^2	1.009	
Final R indices [I>2sigma(I)]	R_1 = 0.0708, wR^2 = 0.1713	
R indices (all data)	R_1 = 0.1958, wR^2 = 0.2384	
Absolute structure parameter	0.58(7)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.573 and -0.353 e.Å^{-3}	

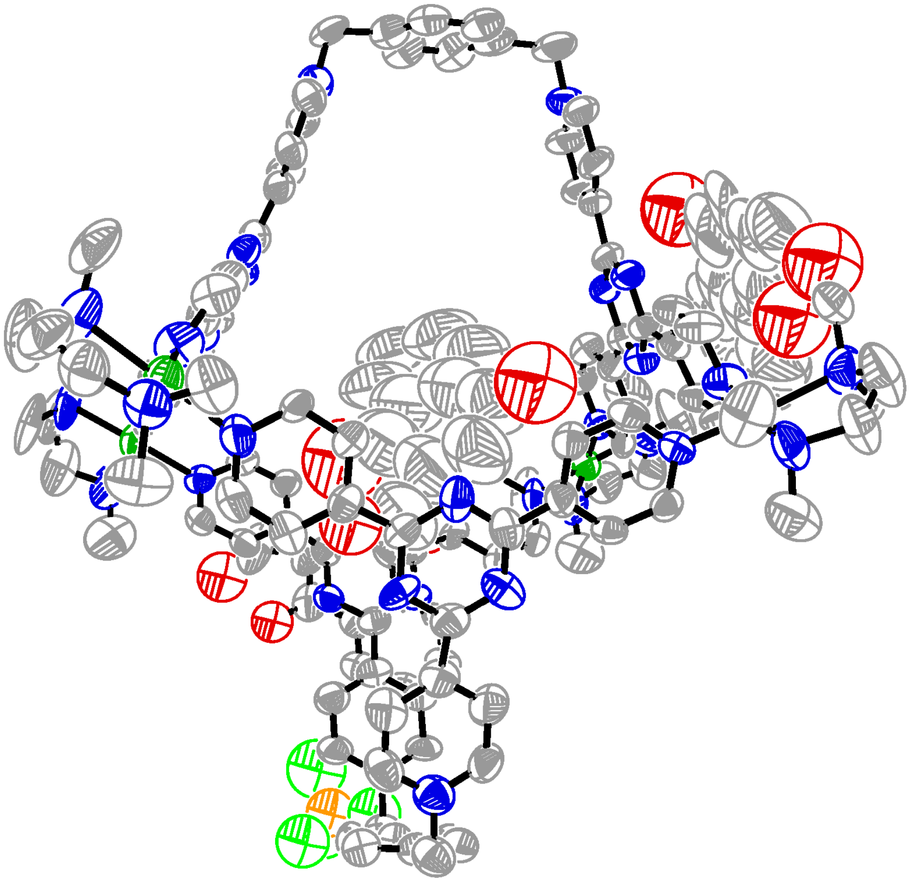


Figure S20 Ortep drawing of the asymmetric unit in the crystal structure of host-guest complex of product **3** and cage **1** at 30% probability level.

9. Mass spectrum

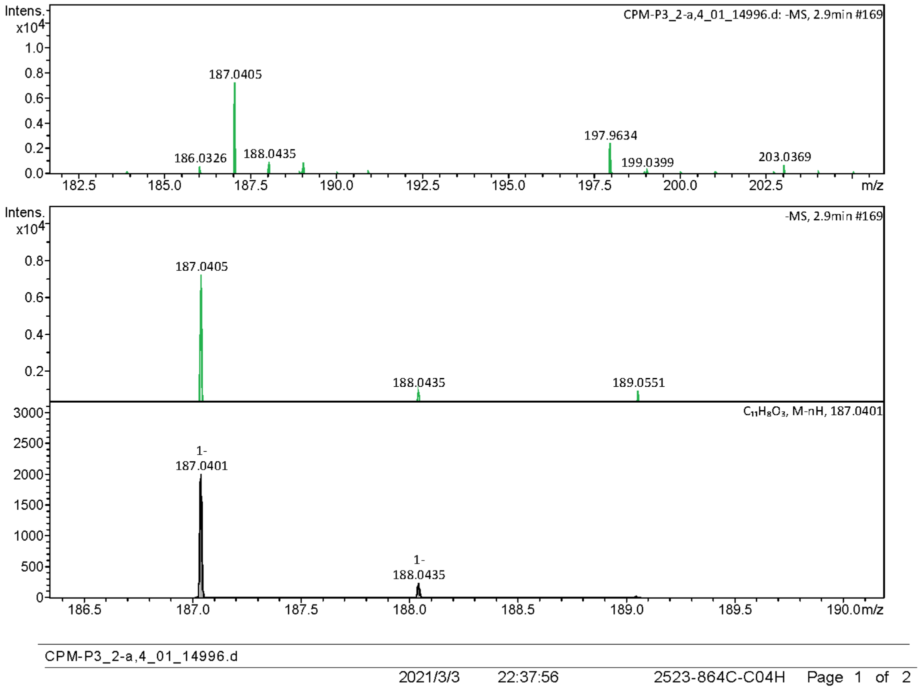


Figure S21 ESI-TOF Mass spectrum of product **3**.

Reference:

[1] Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, 1518-1520.

[2] S.-C. Li, L.-X. Cai, L.-P. Zhou, F. Guo, Q.-F. Sun, *Sci. China Chem.* **2019**, 713-718.

[3] a) Tius, M. A.; Reddy, N. K., *Syn. Comm.* **1994**, 859-869. b) McLaughlin, M. F.; Massolo, E.; Liu, S.; Johnson, J. S. *J. Am. Chem. Soc.* **2019**, 2645-2651.

[4] Balzer, B. L.; Cazanoue, M.; Finn, M., *J. Am. Chem. Soc.* **1992**, 8735-8736.

[5] Sheldrick, G. *Acta Crystallogr. Sect. C* **2015**, 3-8.

[6] Spek A. L. *J. Appl. Crystallogr*. **2003**, 7-13.