Supplementary Information

Photo-driven anti-Markovnikov alkyne hydration in self-assembled hollow complexes

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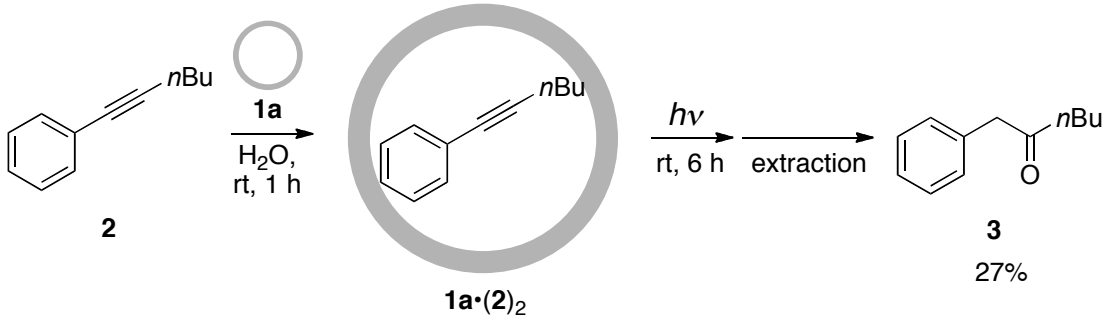
Materials and Instrumentations: ^{1}H NMR spectra were recorded on a Bruker DRX-500 (500 MHz) or a Bruker Avance 500 equipped with CP-TCI cryoprobe at 300 K. TMS or $CHCl_2CHCl_2$ ($CDCl_3$ solution) in a capillary served as an external standard (δ = 0 ppm for TMS or δ = 5.90 ppm for $CHCl_2CHCl_2$). GC-MS spectra were obtained on an Agilent 5973 inert Mass selective Detector equipped with a 6890N Network GC system and an EI source. Photoirradiation was carried out with a SEN LIGHTS CORP. HL400JH-3 400W high-pressure mercury lamp. Solvents and reagents were purchased from TCI Co., Ltd., WAKO Pure Chemical Industries Ltd., and Sigma-Aldrich Co. Deuterated H_2O was acquired from Cambridge Isotope Laboratories, Inc. and used as supplied for the complexation reactions and NMR measurements.

General procedure for photo-hydration of alkynes within cage 1: Arylalkynes (0.80 mmol) was suspended in a water solution (2.0 mL) of cage **1** (4.0×10^{-2} mmol; 20 mM) and the solution was stirred for 1 h at room temperature. After removing excess substrates by filtration, the formation of the host–guest complex was confirmed by ^{1}H NMR. The solution was degassed by freeze-pump-thaw method and filled with Ar, then irradiated with high-pressure mercury lamp (400 W) for 6 h at room temperature. After extraction with $CDCl_3$, the yields were determined by ^{1}H NMR analysis of the crude mixture. *The product structures were identified by ^{1}H NMR, GC-MS and comparison with authentic samples.*

Photo-hydration of 1-phenyl-1-hexyne (2) within cage 1a.



Physical data of 1a•(2)$_2$: ^{1}H NMR (500 MHz, D_2O, 300 K): d = –0.98 (t, J = 7.5 Hz, 3H, **2**), 0.22 (sextet, J = 7.0 2H, CH_2, **2**), 0.37 (quintet, J = 6.0 Hz, 2H, CH_2, **2**), 1.21 (t, J = 6.0 Hz, 2H, CH_2, **2**), 2.84 (s, 72H, CH_3, **1a**), 3.22 (s, 24H, CH_2, **1a**), 5.37 (d, J = 7.5 Hz, 2H, CH, **2**), 6.03 (t, J = 7.0 Hz, 2H, CH, **2**), 6.95 (t, J = 7.0 Hz, 1H, CH, **2**), 8.81 (d, J = 6.0 Hz, 24H, PyH_a, **1a**), 9.41 (d, J = 6.0 Hz, 24H, PyH_b, **1a**).

Physical data of 3: ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): d = 0.86 (t, J = 7.5 Hz, 3H, CH_3), 1.26 (sextet, J = 7.5 Hz, 2H, CH_2,), 1.53 (quintet, J = 8.0 Hz, 2H, CH_2,), 2.44 (t, J = 7.5 Hz, 2H, CH_2), 3.68 (s, 2H, CH_2), 7.20 (d, J = 7.0 Hz, 2H, CH), 7.26 (br, 1H, CH), 7.33 (t, J = 7.5 Hz, 2H, CH). MS (EI) m/z: 176 $[M]^+$, 91 $[M–C_4H_9CO]^{\bullet+}$, 85 $[M–C_6H_5CH_2]^{\bullet+}$.

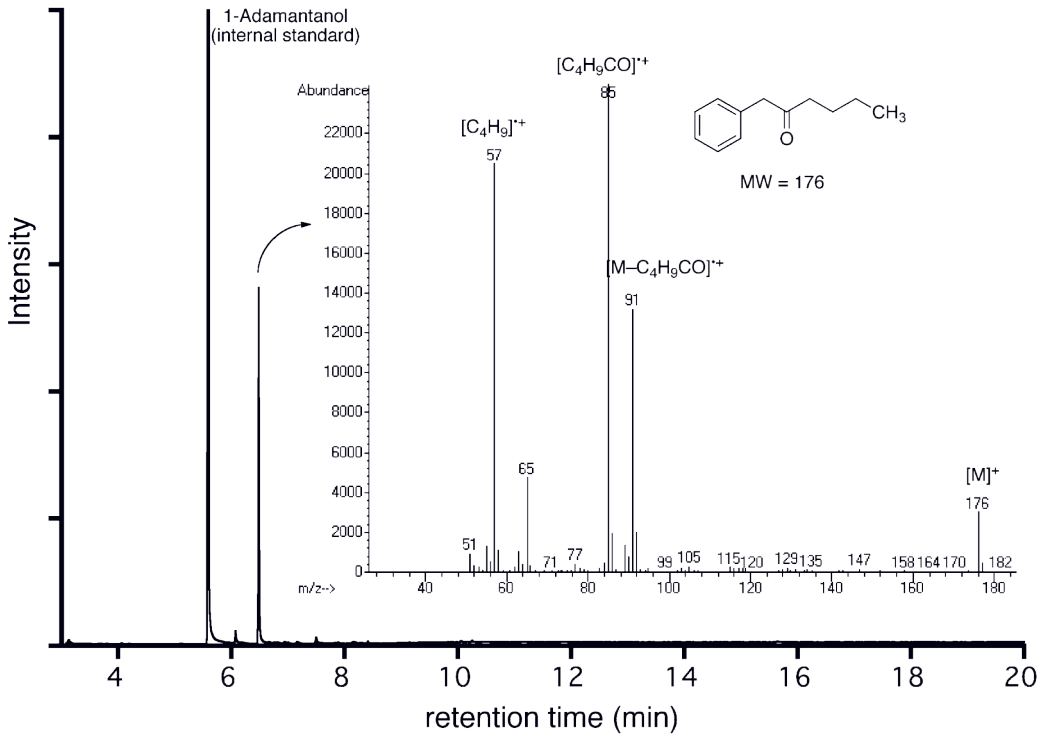


Fig. S1. GC and EI-MS spectra of **3** extracted from the reaction mixture (1-adamantanol: internal standard for GC-MS analysis).

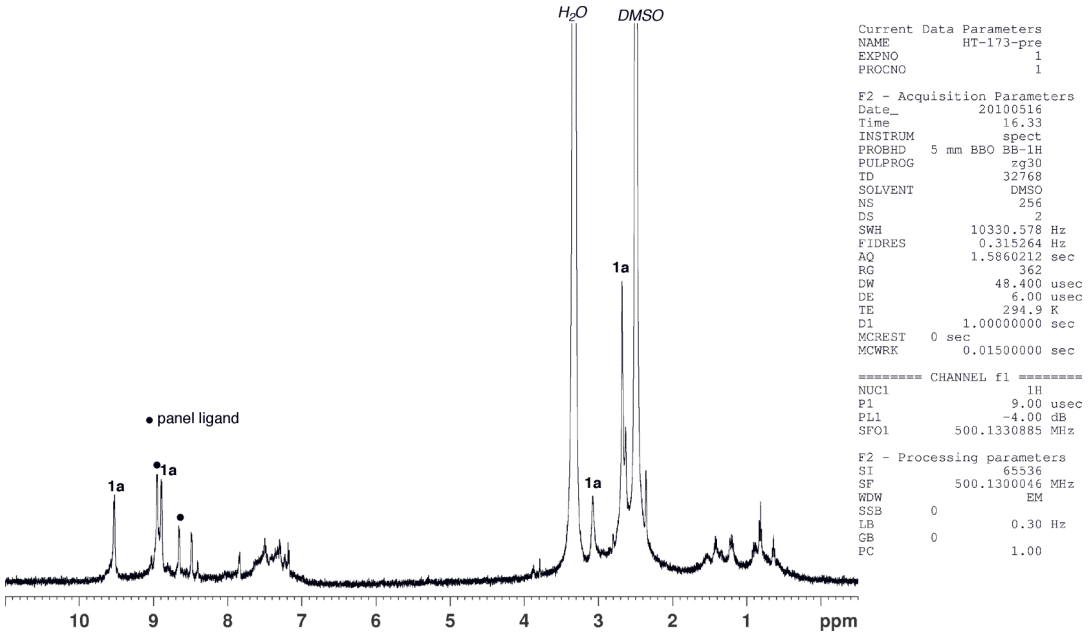
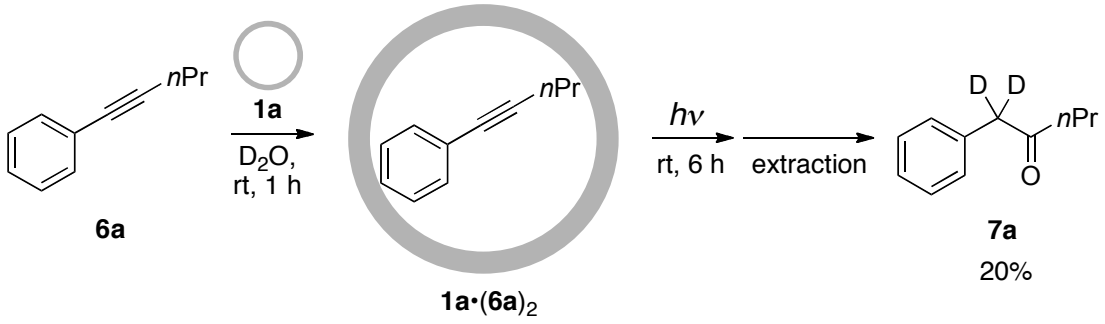


Fig. S2. ^{1}H NMR spectrum of the precipitated by-products after UV-light irradiation to inclusion complex **1a**•(**2**)$_2$. The precipitate was redissolved in DMSO-d_6. The broad signals could not be identified, but the Markovnikov adduct was not contained in the spectrum. Panel ligand of cage **1a** : 2,4,6-tri(4-pyridyl)-1,3,5-triazine.

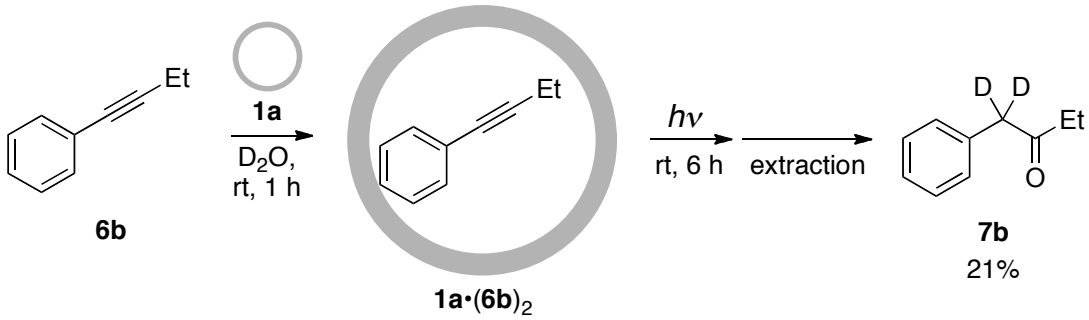
Photo-hydration of 1-phenyl-1-pentyne (6a) within cage 1a.



Physical data of 1a•(6a)$_2$: ^{1}H NMR (500 MHz, D_2O, 300 K): d = –0.56 (t, J = 8.0 Hz, 3H, **6a**), 0.44 (br, 2H, CH_2, **6a**), 1.22 (br, 2H, CH_2, **6a**), 2.81 (s, 72H, CH_3, **1a**), 3.19 (s, 24H, CH_2, **1a**), 5.12 (d, J = 7.0 Hz, 2H, CH, **6a**), 5.84 (t, J = 7.0 Hz, 2H, CH, **6a**), 6.66 (br, 1H, CH, **6a**), 8.76 (d, J = 4.5 Hz, 24H, PyH_a, **1a**), 9.36 (d, J = 4.0 Hz, 24H, PyH_b, **1a**).

Physical data of 7a: ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): d = 0.86 (t, J = 7.5 Hz, 3H, CH_3), 1.57 (sextet, J = 7.0 Hz, 2H, CH_2), 2.42 (t, J = 7.5 Hz, 2H, CH_2), 7.21 (d, J = 7.0 Hz, 2H, CH), 7.26 (br, 1H, CH), 7.33 (t, J = 7.5 Hz, 2H, CH). MS (EI) m/z: 164 $[M]^+$, 93 $[M–C_3H_7CO]^{\bullet+}$, 71 $[M–C_6H_5CD_2]^{\bullet+}$.

Photo-hydration of 1-phenyl-1-butyne (6b) within cage 1a.

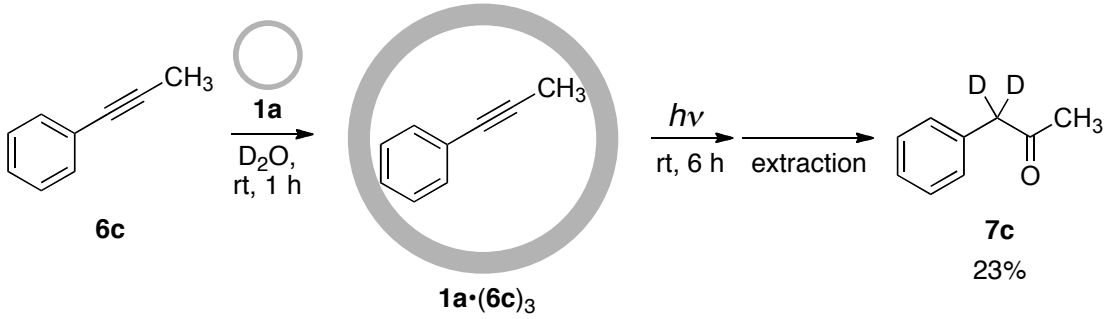


6b **1a•(6b)$_2$** **7b** 21%

Physical data of 1a•(6b)$_2$: ^{1}H NMR (500 MHz, D_2O, 300 K): d = –0.22 (t, J = 7.5 Hz, 3H, **6b**), 1.09 (q, J = 7.5 Hz, 2H, CH_2, **6b**), 2.76 (s, 72H, CH_3, **1a**), 3.16 (s, 24H, CH_2, **1a**), 5.06 (d, J = 7.5 Hz, 2H, CH, **6b**), 5.84 (t, J = 7.5 Hz, 2H, CH, **6b**), 6.18 (t, J = 7.5 Hz, 1H, CH, **6b**), 8.73 (d, J = 5.5 Hz, 24H, PyH_a, **1a**), 9.35 (d, J = 5.0 Hz, 24H, PyH_b, **1a**).

Physical data of 7b: ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): d = 1.02 (t, J = 7.5 Hz, 3H, CH_3), 2.47 (quartet, J = 7.5 Hz, 2H, CH_2), 2.42 (t, J = 7.5 Hz, 2H, CH_2), 7.21 (d, J = 7.5 Hz, 2H, CH), 7.26 (br, 1H, CH), 7.33 (t, J = 7.0 Hz, 2H, CH). MS (EI) m/z: 159 $[M]^+$, 93 $[M–CH_3CO]^{\bullet+}$, 57 $[M–C_6H_5CD_2]^{\bullet+}$.

Photo-hydration of 1-phenyl-1-pentyne (6c) within cage 1a.



6c **1a•(6c)$_3$** **7c** 23%

Physical data of 1a•(6c)$_3$: ^{1}H NMR (500 MHz, D_2O, 300 K): d = 1.05 (s, 3H, CH_3, **6c**), 2.81 (s, 72H, CH_3, **1a**), 3.20 (s, 24H, CH_2, **1a**), 5.18 (d, J = 8.0 Hz, 2H, CH, **6c**), 5.67 (t, J = 7.5 Hz, 2H, CH, **6c**), 5.84 (t, J = 7.5 Hz, 1H, CH, **6c**), 8.75 (d, J = 4.0 Hz, 24H, PyH_a, **1a**), 9.41 (d, J = 4.0 Hz, 24H, PyH_b, **1a**).

Physical data of 7c: ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): d = 2.15 (s, 3H, CH_3), 7.21 (d, J = 7.5 Hz, 2H, CH), 7.26 (br, 1H, CH), 7.34 (t, J = 7.0 Hz, 2H, CH). MS (EI) m/z: 136 $[M]^+$, 93 $[M–CH_3CO]^{\bullet+}$.

Photochemical reactions of benzyl ketone 3 (without cage 1a).

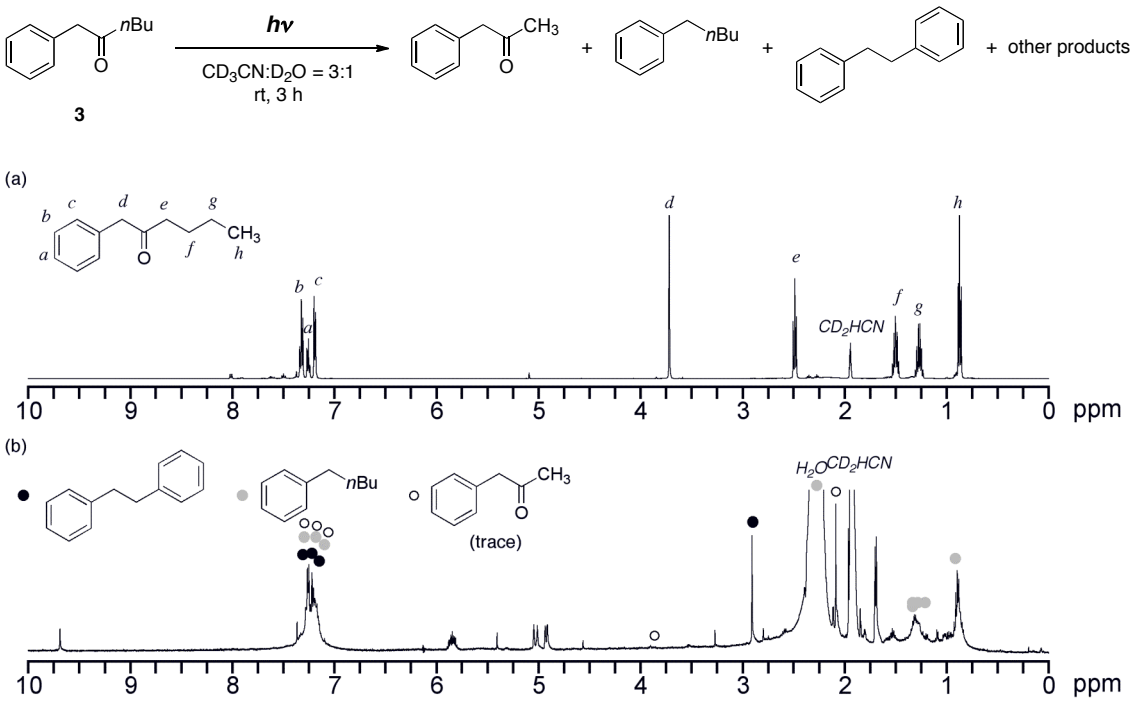
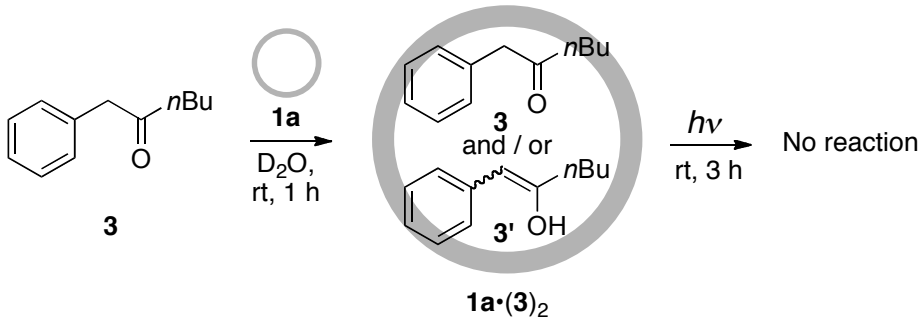


Fig. S3. ^{1}H NMR spectra (CD_3CN) of (a) benzyl ketone **3** and (b) the photoproducts. The photoproducts were identified by NMR and GC-MS.

Photochemical reactions of benzyl ketone 3 within cage 1a.



Physical data of 1a•(3)$_2$: ^{1}H NMR (500 MHz, D_2O, 300 K): d = –1.13 (sextet, J = 6.5 Hz, 2H, CH_2, **3**), –0.91 (t, J = 6.5 Hz, 3H, CH_3, **3**), –0.73 (quintet, J = 6.5 Hz, 2H, CH_2, **3**), 0.38 (t, J = 7.5 Hz, 3H, CH_3, **3'**), 0.58 (t, J = 6.5 Hz, 2H, CH_2, **3**), 0.89 (sextet, J = 7.5 Hz, 2H, CH_2, **3'**), 1.15 (quintet, J = 7.5 Hz, 2H, CH_2, **3'**), 1.67 (s, 2H, CH_2, **3**), 2.00 (t, J = 7.5 Hz, 2H, CH_2, **3'**), 2.88 (s, 72H, CH_3, **1a**), 3.28 (s, 24H, CH_2, **1a**), 5.25 (d, J = 7.0 Hz, 2H, CH, **3**), 5.47 (t, J = 7.0 Hz, 2H, CH, **3**), 5.74 (t, J = 6.0 Hz, 1H, CH, **3**), 5.96 (t, J = 7.5 Hz, 2H, CH, **3'**), 6.18 (t, J = 7.0 Hz, 1H, CH, **3'**), 6.26 (d, J = 7.5 Hz, 2H, CH, **3'**), 8.87 (d, J = 5.0 Hz, 24H, PyH_a, **1a**), 9.50 (d, J = 5.0 Hz, 24H, PyH_b, **1a**).

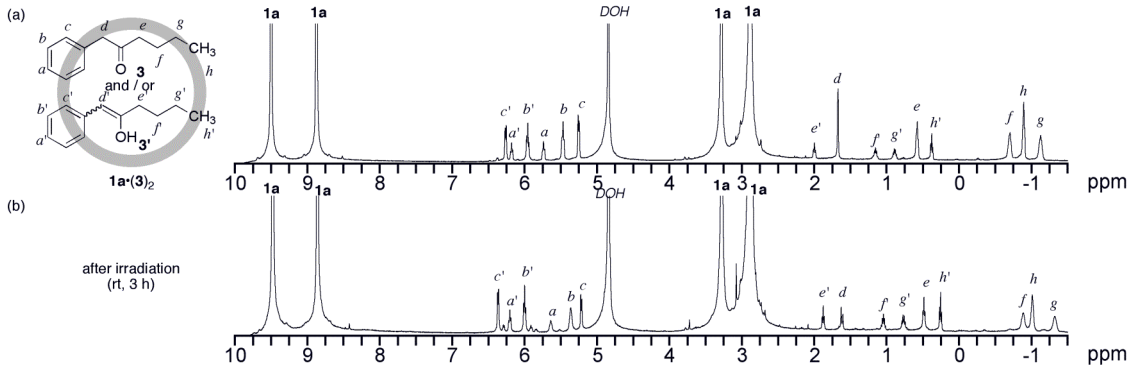
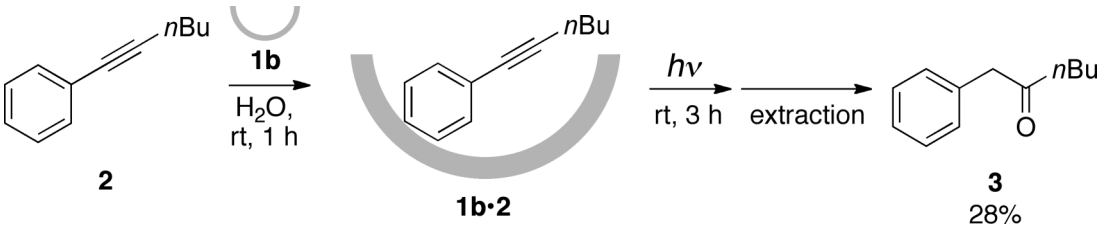


Fig. S4. ^{1}H NMR spectra (D_2O) of **1a•(3)**$_2$ (a) before and (b) after photoirradiation. Enol tautomer (**3'**) of benzyl ketone **3** also existed in cage **1a**. Although the ratio of **3** and **3'** changed and the benzylic protons (H_d) were deuterated during photoirradiation, the total amount of **3** and **3'** remained unchanged.

Photo-hydration of 2 within cage 1b.



Physical data of 1b•2: ^{1}H NMR (500 MHz, D_2O, 300 K): d = –0.20 (br, 5H, CH_2 and CH_3, **2**), –0.03 (br, 2H, CH_2, **2**), 0.46 (br, 2H, CH_2, **2**), 2.99–3.10 (m, 24H, CH_2, **1b**), 5.15 (br, 2H, CH, **2**), 5.42 (br, 2H, CH, **2**), 5.69 (br, 1H, CH, **2**), 7.93 (t, J = 7.0 Hz, 8H, PyH, **1b**), 7.97 (t, J = 7.0 Hz, 4H, PyH, **1b**), 9.05 (br, 8H, PyH, **1b**), 9.16 (d, J = 8.0 Hz, 4H, PyH, **1b**), 9.24 (d, 4H, J = 5.5 Hz PyH, **1b**), 9.33 (d, J = 5.5 Hz, 8H, PyH, **1b**), 9.71 (s, 4H, PyH, **1b**), 10.56 (s, 8H, PyH, **1b**).

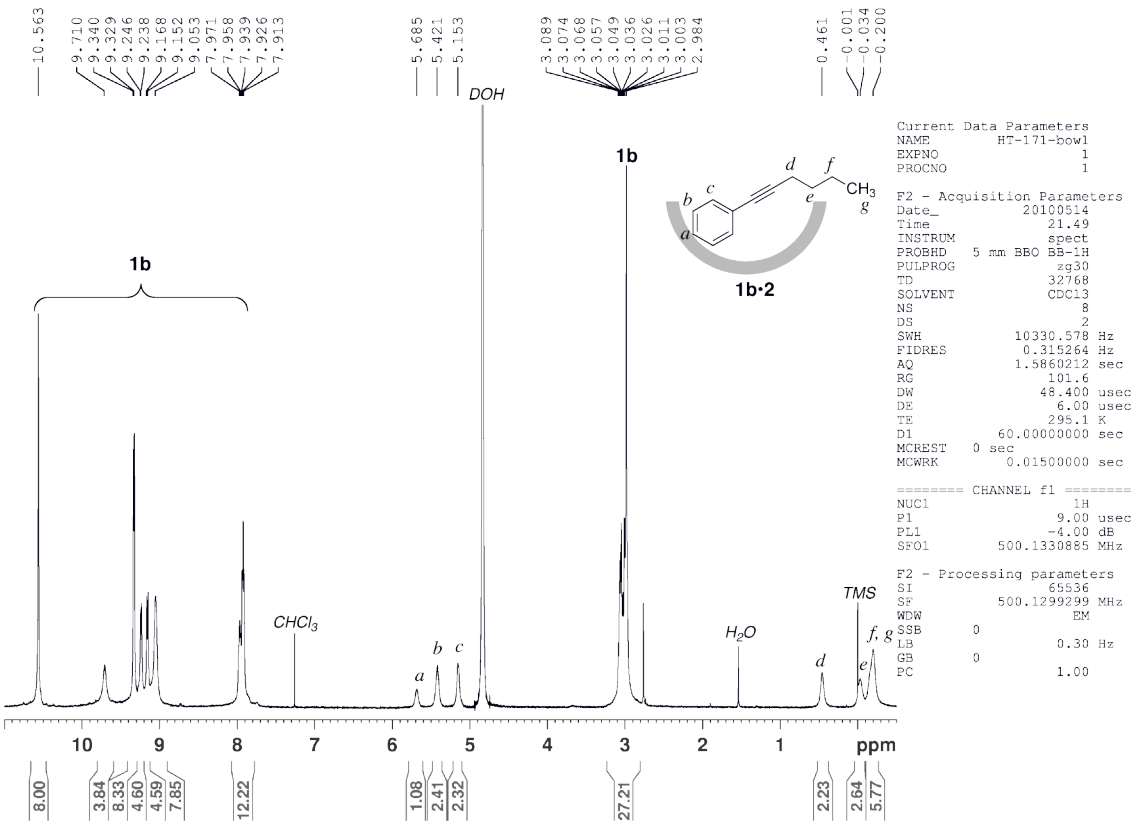


Fig. S5. ^{1}H NMR spectrum of **1b•2** (D_2O).

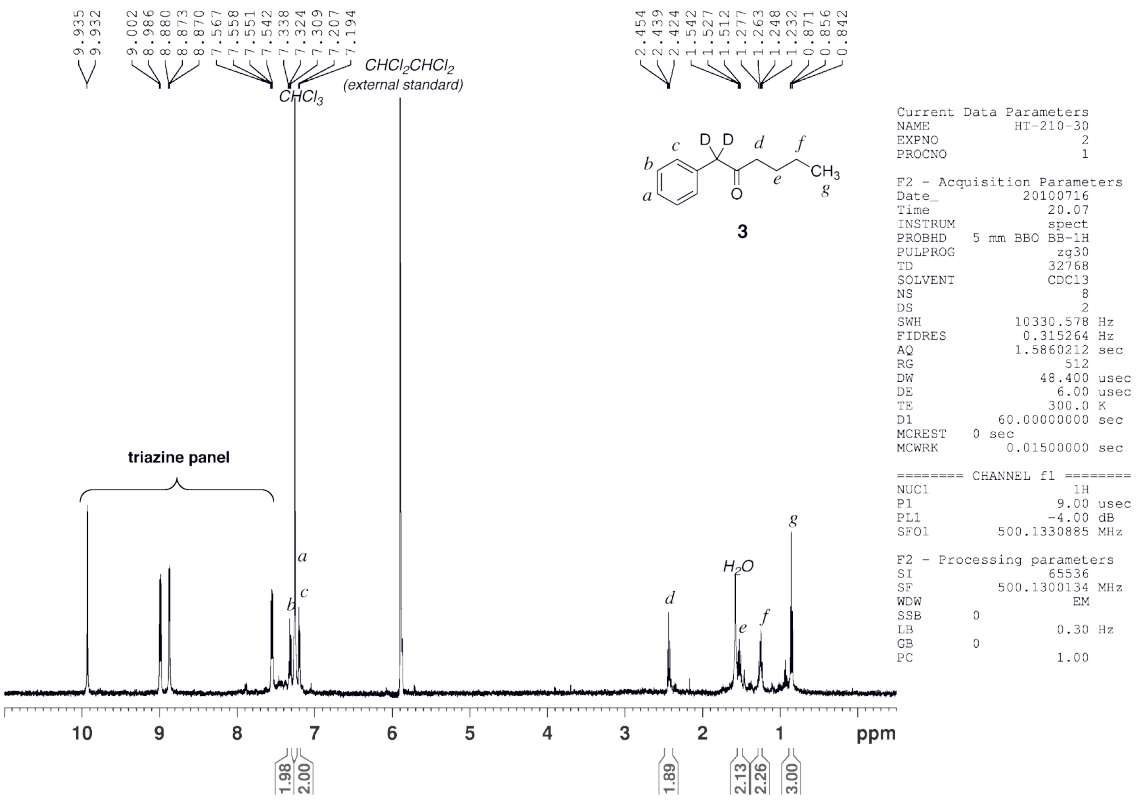
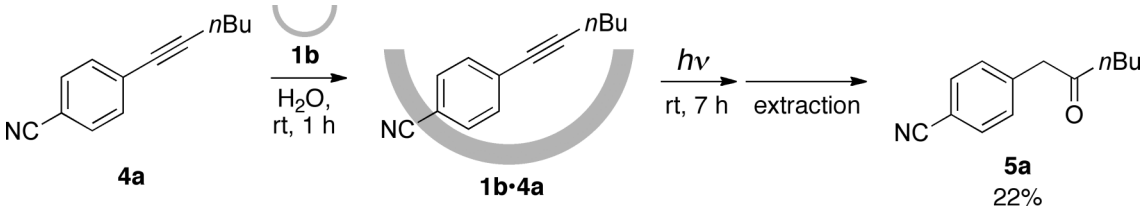


Fig. S6. ^{1}H NMR spectrum of **3** extracted from cage **1b** with $CDCl_3$ (reacted in D_2O solution).

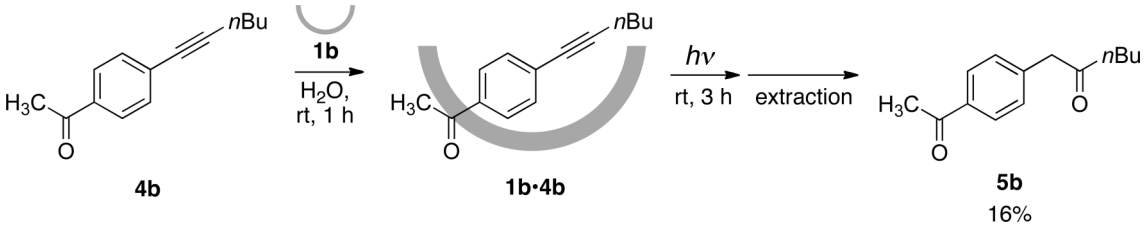
Photo-hydration of 4a within cage 1b.



Physical data of 1b•4a: ^{1}H NMR (500 MHz, D_2O, 300 K): d = 0.12 (br, 3H, CH_3, **4a**), 0.31 (br, 2H, CH_2, **4a**), 0.40 (br, 2H, CH_2, **4a**), 1.06 (br, 2H, CH_2, **4a**), 2.99–3.10 (m, 24H, CH_2, **1b**), 5.40 (br, 2H, CH, **4a**), 5.87 (br, 2H, CH, **4a**), 7.99 (t, J = 7.0 Hz, 8H, PyH, **1b**), 8.04 (t, J = 7.0 Hz, 4H, PyH, **1b**), 9.11 (d, J = 6.0 Hz, 8H, PyH, **1b**), 9.20 (d, J = 8.0 Hz, 4H, PyH, **1b**), 9.24 (d, 4H, J = 5.5 Hz PyH, **1b**), 9.39 (d, J = 5.5 Hz, 8H, PyH, **1b**), 9.76 (s, 4H, PyH, **1b**), 10.61 (s, 8H, PyH, **1b**).

Physical data of 5a: ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): d = 0.89 (t, J = 7.5 Hz, 3H, CH_3), 1.29 (sextet, J = 7.5 Hz, 2H, CH_2), 1.49 (quintet, J = 7.5 Hz, 2H, CH_2), 2.48 (t, J = 8.0 Hz, 2H, CH_2), 3.77 (s, 2H, CH_2), 7.31 (d, J = 9.0 Hz, 2H, CH), 7.62 (d, J = 9.0 Hz, 2H, CH). MS (EI) m/z: 201 $[M]^+$, 116 $[M–C_4H_9CO]^{\bullet+}$, 85 $[C_4H_9CO]^{\bullet+}$, 57 $[C_4H_9]^{\bullet+}$.

Photo-hydration of 4b within cage 1b.



Physical data of 1b•4b: ^{1}H NMR (500 MHz, D_2O, 300 K): d = 0.44 (br, 5H, CH_2 and CH_3, **4b**), 0.69 (br, 2H, CH_2, **4b**), 1.16 (br, 2H, CH_2, **4b**), 1.53 (br, 2H, CH_3, **4b**), 2.99–3.11 (m, 24H, CH_2, **1b**), 5.30 (br, 2H, CH, **4b**), 5.79 (br, 2H, CH, **4b**), 8.02 (t, J = 7.0 Hz, 8H, PyH, **1b**), 8.17 (t, J = 7.0 Hz, 4H, PyH, **1b**), 8.98 (d, J = 6.0 Hz, 8H, PyH, **1b**), 9.24 (d, J = 8.0 Hz, 4H, PyH, **1b**), 9.31 (d, 4H, J = 5.5 Hz PyH, **1b**), 9.44 (d, J = 5.0 Hz, 8H, PyH, **1b**), 9.60 (s, 4H, PyH, **1b**), 10.62 (s, 8H, PyH, **1b**).

Physical data of 5b: ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): d = 0.89 (t, J = 7.0 Hz, 3H, CH_3), 1.28 (sextet, J = 7.5 Hz, 2H, CH_2), 1.56 (quintet, J = 7.5 Hz, 2H, CH_2), 2.47 (t, J = 7.5Hz, 2H, CH_2), 2.60 (s, 3H, CH_3), 3.75 (s, 2H, CH_2), 7.30 (d, J = 8.0 Hz, 2H, CH), 7.93 (d, J = 7.5 Hz, 2H, CH). MS (EI) m/z: 218 $[M]^+$, 203 $[M–CH_3]^{\bullet+}$, 57 $[C_4H_9]^{\bullet+}$.