

Diastereoselective guest-shape dependent [2+2]-photodimerization of 2-cyclopenten-1-one trapped within a metal-organic framework

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Supplementary information

Experimental details

Thieno[3,2b]thiophene-2,5-dicarboxylic acid (H_2ttcd) was synthesized according to the previously published procedure [1]. $Eu(NO_3)_3 \cdot 6H_2O$ (99.9% REO) was received from Dalchem. N,N-dimethylformamide (DMF, reagent grade) was supplied by Vekton. 2-cyclopenten-1-one (98%), 2-methyl-2-cyclopenten-1-one (98%) and 3-methyl-2-cyclopenten-1-one (>97%) were received from Sigma Aldrich. All the reagents were used as received without further purification. Synthesis of 1_{DMF} single crystals was carried out according to the previously published procedure [Ref. 8a in the MS].

Synthesis of 1_{cpo} . *Ca.* 5 mg of 1_{DMF} single crystals were decanted and immersed in 0.5 ml of 2-cyclopentenone (cpo) in a glass vial. The liquid was refreshed thrice with two days interval. After the immersing, single crystals suitable for SCXRD were selected for crystal structure determination.

Synthesis of 1_{2mcpo} single crystals. *Ca.* 5 mg of 1_{DMF} single crystals were decanted and immersed in 0.5 ml of 2-methyl-2-cyclopentenone (2mcpo) in a glass vial. The liquid was refreshed thrice with two days interval. After the immersing, single crystals suitable for SCXRD were selected for crystal structure determination.

Synthesis of 1_{3mcpo} single crystals. *Ca.* 5 mg of 1_{DMF} single crystals were decanted and immersed in 0.5 ml of 3-methyl-2-cyclopentenone (3mcpo) in a glass vial. The liquid was refreshed thrice with two days interval. After the immersing, single crystals suitable for SCXRD were selected for crystal structure determination.

Synthesis of 1_{bcpo} . Single crystal of 1_{cpo} was irradiated under $\lambda = 365$ nm right after SCXRD in a diffractometer camera without taking off from the crystal loop at $T = 150$ K. After 3 h irradiation, single crystal XRD experiment was repeated.

Synthesis of 1_{b2mcpo} . Single crystal of 1_{2mcpo} was taken to the crystal loop from 2mcpo liquor and irradiated under $\lambda = 365$ nm in a diffractometer camera at $T = 200$ K. After 14 h irradiation, single crystal XRD experiment was repeated.

Bulk UV irradiation of 1_{cpo} . 10 mg of carefully dried 1_{cpo} crystals were transferred into the bottom of *ca.* 5mm-wide glass tube, non-sealed in its top side. The tube bottom was placed into the isopropanol bath, continuously cooled by liquid nitrogen. After the isopropanol to be vastly thickened ($T \approx 190$ K), UV LED source was turned on in the open top of the tube. New N_2 portion was being added every 3-5 minutes to keep an approximately constant temperature during all the irradiation.

Diffraction data for single crystals of 1_{cpo} , 1_{2mcpo} , 1_{3mcpo} and 1_{bcpo} were collected on an automated Agilent Xcalibur diffractometer equipped with AtlasS2 area detector and graphite monochromator ($\lambda(MoK\alpha) = 0.71073$ Å). CrysAlisPro program package [2] was used for the integration, absorption correction and determination of unit cell parameters. Diffraction data for single crystals of 1_{b2mcpo} were collected on Bruker D8 Venture diffractometer equipped with PHOTON III area detector and Incoatec IuS3.0 microfocus X-ray tube with HELIOS multilayer mirror monochromator ($\lambda(MoK\alpha) = 0.71073$ Å). Bruker APEX, SAINT and SADABS software [3] was used for the integration, absorption correction and determination of unit cell parameters. Dual space algorithm (SHELXT [4]) was used for structure solution and full-matrix least squares technique (SHELXL [5]) was used for structure refinement. Anisotropic approximation was

applied for all atoms, except hydrogens. Positions of hydrogen atoms of organic ligands were calculated geometrically and refined in the riding model. Details for single crystal structure determination experiments and structure refinements are summarized in Table S1. CCDC 2219410–2219414 entries contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center at <https://www.ccdc.cam.ac.uk/structures/>.

Powder X-ray diffraction (PXRD) patterns were obtained at room temperature on a Shimadzu XRD-7000 diffractometer (Cu-K α radiation, $\lambda = 1.54178 \text{ \AA}$)

Solution UV/vis absorption spectra were recorded on OKB Spectr SF-2000 spectrophotometer.

Solid-state diffuse reflectance spectra (DRS) were recorded using Shimadzu UV-3101 spectrometer. The initial dependencies of the reflection of samples (R) on the wavelength were recalculated to the Kubelka-Munk function (M) by the equation: $M = (1 - R)^2/2R$.

^1H NMR spectra were recorded on a Bruker Advance 500 NMR spectrometer (500.13 Hz). For the preparation of solutions, ca. 10 mg of irradiated $\mathbf{1}_{\text{bcpo}}$ sample was immersed in 2.0 ml of d_6 -DMSO for 18 hours, then the liquid portion (ca. 0.6 ml) was carefully decanted. The solid was filtered from the rest of the solution and dried in air, then the second extraction cycle (18 hours, 2.0 mL of DMSO) was performed to analyze the residual guest contents in solid. No considerable cpo or bcpo peaks were found in the NMR spectra of the second extract (Figs. S7a and S8a).

UV irradiation of the crystals was performed using Hamamatsu C11924-211 UV-LED module with $\lambda_{\text{ex}} = 365 \text{ nm}$.

Table S1. Crystallographic data and structure refinement details for $\mathbf{1}_{\text{enone}}$ adducts.

	$\mathbf{1}_{\text{cpo}}$	$\mathbf{1}_{\text{bcpo}}$	$\mathbf{1}_{\text{2mcpo}}$	$\mathbf{1}_{\text{b2mcpo}}$	$\mathbf{1}_{\text{3mcpo}}$
Chemical formula	$\text{C}_{60}\text{H}_{56}\text{Eu}_2\text{N}_2\text{O}_{20}$ S_6	$\text{C}_{60}\text{H}_{56}\text{Eu}_2\text{N}_2\text{O}_{20}$ S_6	$\text{C}_{63}\text{H}_{67}\text{Eu}_2\text{N}_3\text{O}_{20}$ S_6	$\text{C}_{63}\text{H}_{67}\text{Eu}_2\text{N}_3\text{O}_{20}$ S_6	$\text{C}_{69}\text{H}_{69}\text{Eu}_2\text{N}_1\text{O}_{20}$ S_6
M_r , g/mol	1621.34	1621.34	1682.47	1682.47	1728.53
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic	Triclinic
Space group	P^{-1}	P^{-1}	P^{-1}	P^{-1}	P^{-1}
Temperature, K	150	150	170	200	170
a, \AA	11.2956(4)	11.4544(4)	11.8850(3)	11.9926 (5)	12.0510(3)
b, \AA	12.0825(5)	12.0514(4)	12.0883(3)	12.1214 (4)	12.0871(4)
c, \AA	13.0422(6)	13.0101(4)	13.0418(2)	13.0236 (5)	12.9978(3)
α , $^\circ$	101.757(4)	99.941(3)	99.461(2)	100.912 (1)	99.409(2)
β , $^\circ$	100.547(4)	100.886(3)	101.729(2)	101.849 (1)	101.617(2)
γ , $^\circ$	104.878(3)	108.091(3)	105.724(2)	105.290 (1)	101.594(2)
V, \AA^3	1631.28(12)	1624.16(10)	1717.39(7)	1726.83 (11)	1775.15(9)
Z	1	1	1	1	1
F(000)	812	812	848	848	872
$D_{\text{(calc.)}}$, $\text{g}\cdot\text{cm}^{-3}$	1.650	1.658	1.627	1.618	1.617
μ , mm^{-1}	2.17	2.18	2.07	2.05	2.00
Crystal size, mm	0.27×0.25 $\times 0.13$	0.27×0.25 $\times 0.13$	0.51×0.23 $\times 0.15$	$0.14 \times 0.09 \times$ 0.06	0.32×0.30 $\times 0.09$
θ range for data collection, $^\circ$	$1.9 < \theta <$ 25.4	$1.8 < \theta <$ 25.4	$2.1 < \theta <$ 25.4	$1.7 < \theta <$ 25.4	$2.1 < \theta <$ 25.0

No. of reflections: measured / independent / obs. [$I > 2\sigma(I)$]	12669 / 5978 / 5412	12730 / 5946 / 5267	14706 / 6292 / 5822	16712 / 6246 / 5743	18950 / 6254 / 5855
R_{int}	0.0221	0.0223	0.0305	0.0327	0.0391
Index ranges	$-13 \leq h \leq 13$ $-14 \leq k \leq 12$ $-15 \leq l \leq 12$	$-13 \leq h \leq 13$ $-14 \leq k \leq 13$ $-14 \leq l \leq 15$	$-14 \leq h \leq 14$ $-14 \leq k \leq 14$ $-15 \leq l \leq 15$	$-14 \leq h \leq 14$ $-14 \leq k \leq 14$ $-15 \leq l \leq 15$	$-14 \leq h \leq 14$ $-14 \leq k \leq 14$ $-15 \leq l \leq 15$
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0316$ $wR_2 = 0.0799$	$R_1 = 0.0353$ $wR_2 = 0.0890$	$R_1 = 0.0343$ $wR_2 = 0.0823$	$R_1 = 0.0353$ $wR_2 = 0.0767$	$R_1 = 0.0410$ $wR_2 = 0.1008$
Final R indices (all data)	$R_1 = 0.0376$ $wR_2 = 0.0824$	$R_1 = 0.0432$ $wR_2 = 0.0925$	$R_1 = 0.0384$ $wR_2 = 0.0845$	$R_1 = 0.0396$ $wR_2 = 0.0784$	$R_1 = 0.0475$ $wR_2 = 0.1042$
Goodness-of-fit on F^2	1.074	1.093	1.046	1.086	1.077
Largest diff. peak, hole, $e/\text{\AA}^3$	0.97, -0.92	1.10, -0.76	1.28, -1.26	1.05, -0.65	2.46, -1.18

Table S2. Bond lengths in Eu³⁺ coordination environment

		Structure					
Part of the capped square antiprism	O atoms	1_{DMF} [Ref. 8a in the MS]	1_{cpo}	1_{bcpo}	1_{2mcpo}	1_{b2mcpo}	1_{3mcpo}
Base square	Solvent	2.400(5) 2.407(5)	2.407(3) 2.436(3)	2.422(4) 2.424(4)	2.407(3) 2.453(3)	2.413(3) 2.465(3)	2.424(4) 2.450(4)
	κ^2 -COO	2.459(4) 2.489(4)	2.438(3) 2.478(3)	2.450(3) 2.478(3)	2.446(3) 2.467(3)	2.441(3) 2.472(3)	2.447(3) 2.488(3)
Upper square	κ^1, κ^1 -COO	2.388(4) 2.427(4)	2.402(3) 2.408(3)	2.393(3) 2.403(3)	2.410(3) 2.414(3)	2.406(3) 2.413(3)	2.397(3) 2.405(3)
	κ^2, κ^1 -COO	2.355(4) 2.450(4)	2.339(3) 2.450(3)	2.343(3) 2.454(3)	2.347(3) 2.462(3)	2.360(3) 2.473(3)	2.366(3) 2.446(3)
Cap	COO	2.675(4)	2.705(3)	2.700(3)	2.663(3)	2.663(3)	2.692(3)

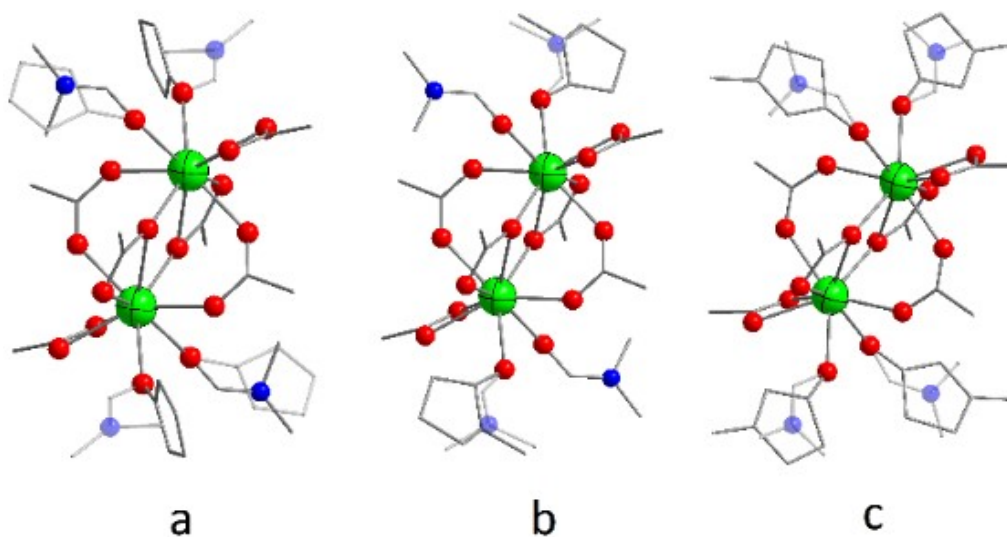


Figure S1. Binuclear carboxylate building blocks in the structure of $\mathbf{1}_{\text{cpo}}$ (a), $\mathbf{1}_{2\text{mcpo}}$ (b) and $\mathbf{1}_{3\text{mcpo}}$ (c). Eu atoms are green, O atoms are red, N atoms are blue, H atoms are not shown. Second positions of the disordered moieties are shown transparent.

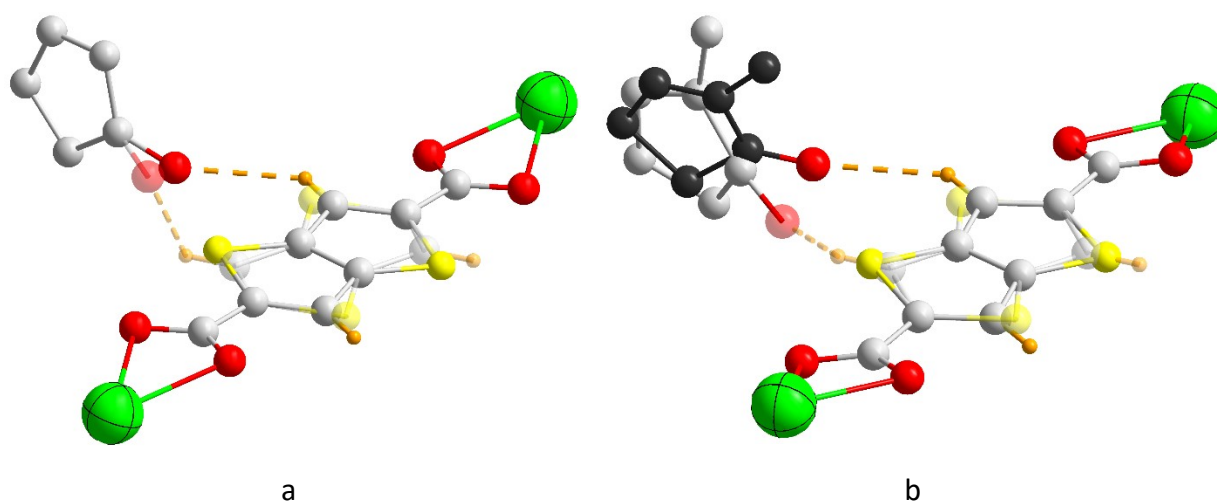


Figure S2. Contacts between guest substrate and ttdc ligand in $\mathbf{1}_{\text{cpo}}$ (a) and $\mathbf{1}_{2\text{mcpo}}$ (b). Eu atoms are green, O atoms are red, C atoms are grey, S atoms are yellow, H atoms and close O...H contacts are orange. Second positions of the disordered moieties are shown in different shades. Only H atoms of ttdc heterocyclic core are shown.

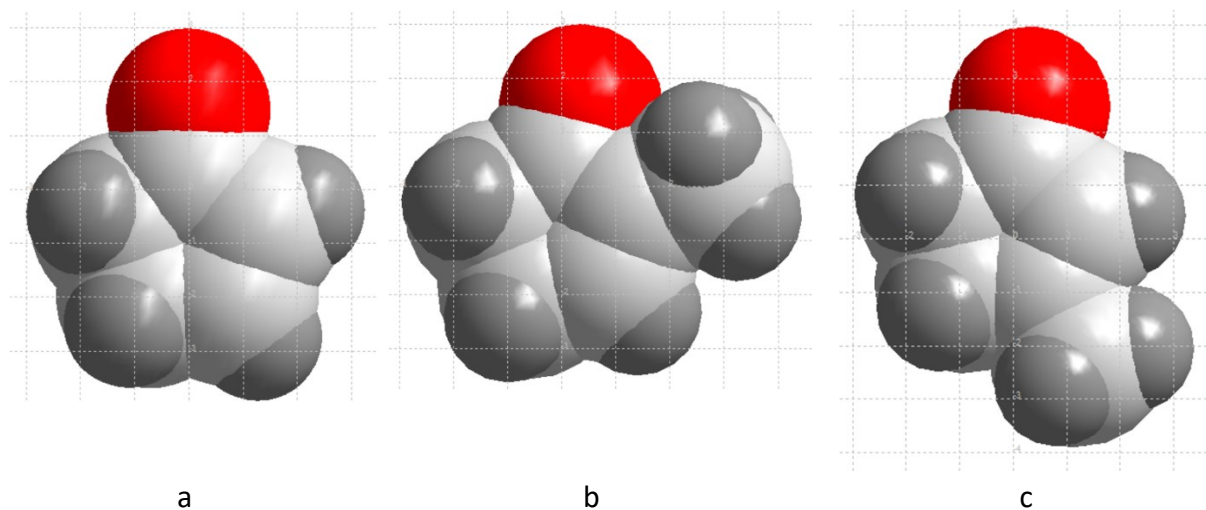


Figure S3. Space-filling representation of 2-cyclopenten-1-one (a), 2-methyl-2-cyclopenten-1-one (b) and 3-methyl-2-cyclopenten-1-one (c) with 1Å grid lines.

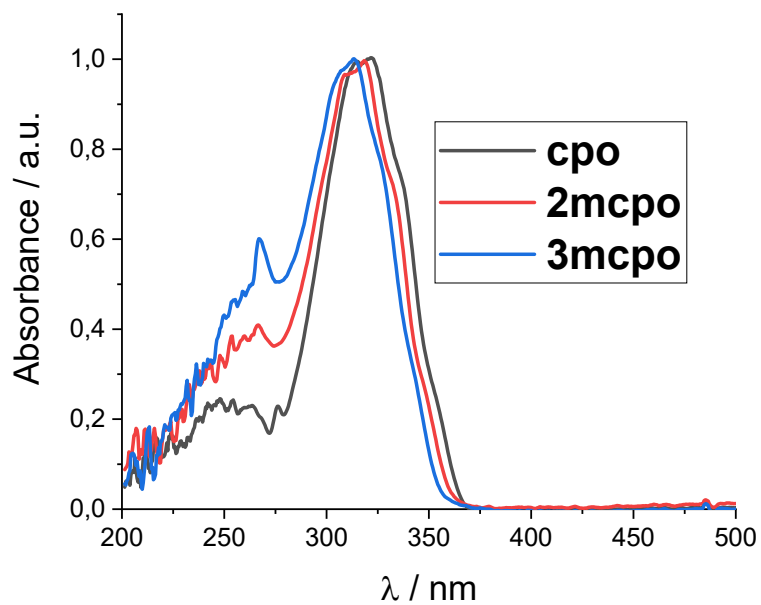


Figure S4. UV/vis spectra of ca. $4 \cdot 10^{-2}$ M solutions of cpo, 2mcpo and 3mcpo in DMF.

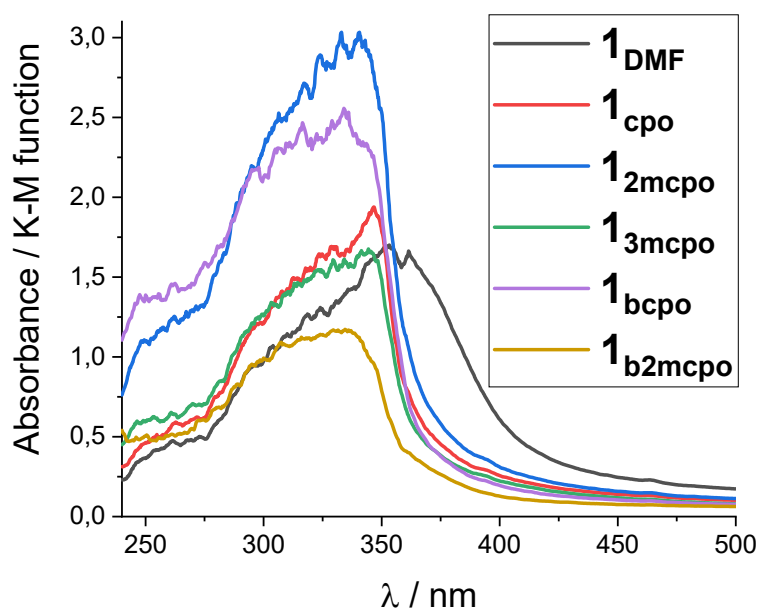


Figure S5. Solid-state diffuse reflectance spectra of initial 1_{DMF} , 1_{enone} adducts and irradiation products.

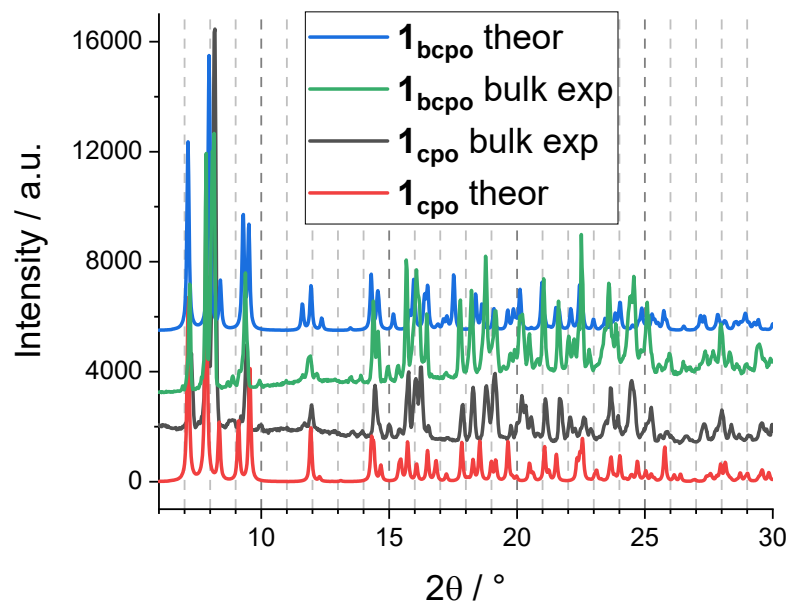


Figure S6. PXRD patterns of bulk initial 1_{cpo} and irradiated 1_{bcpo} samples, compared to the theoretical ones.

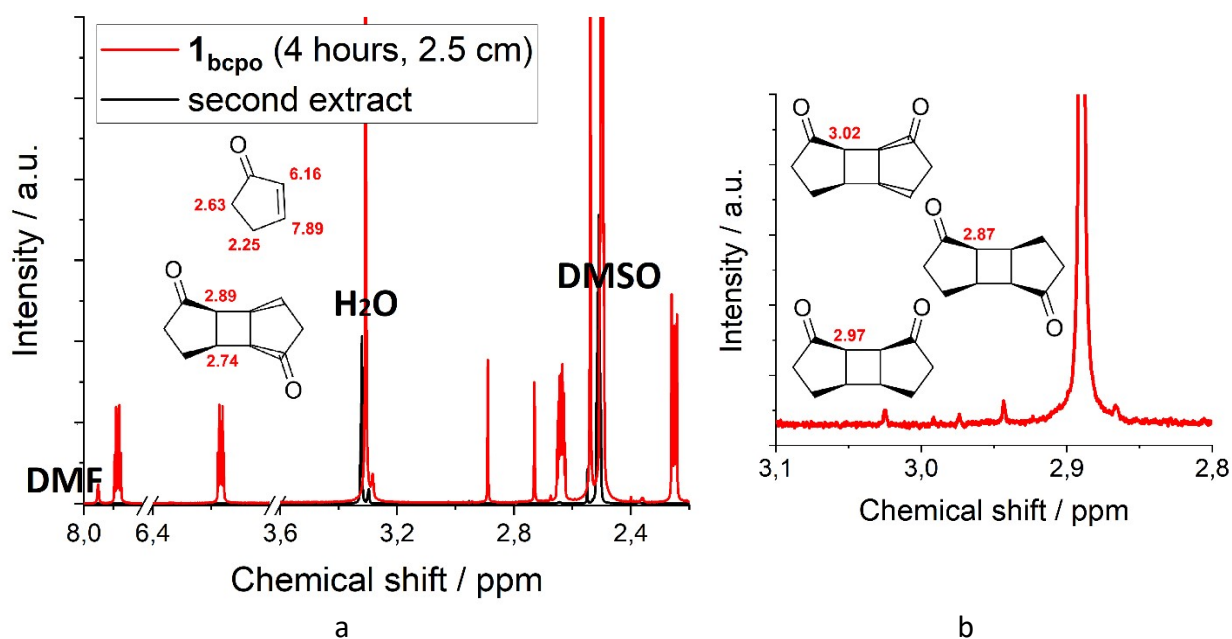


Figure S7. ^1H NMR spectrum of the reaction mixture after the irradiation, extracted from the bulk sample of $\mathbf{1}_{\text{bcpo}}$ twice by d_6 -DMSO. Irradiation characteristics: 4 hours, 2.5 cm distance between the sample and diode lamp (a). Enlarged part of the spectrum, showing area of cyclobutane protons, closest to C=O group. Y axis is 24 times scaled (b).

Table S2. Reaction characteristics for $\mathbf{1}_{\text{cpo}}$ after irradiation during 4 hours (see Fig. S7a). The distance between diode lamp and the sample was 2.5 cm.

Peak position, ppm	Integral area	Assignment
7.89	1.000	$\text{H}_{\text{C}=\text{C}}(\text{cpo})$
6.16	1.030	$\text{H}_{\text{C}=\text{C}}(\text{cpo})$
2.89	0.523	$\text{H}_{\text{cyclobutane}}(\text{bcpo})$
2.73	0.538	$\text{H}_{\text{cyclobutane}}(\text{bcpo})$

$$\text{Average cyclobutane protons' integral: } n_2 = \frac{0.523 + 0.538}{2} = 0.531$$

$$\text{Average C=C protons' integral: } n_1 = \frac{1.000 + 1.030}{2} = 1.015$$

$$\text{Yield of HT-anti bcpo: } \eta = \frac{n_2}{n_1 + n_2} = \frac{0.531}{1.015 + 0.531} = 34 \%$$

Table S3. Minor product peaks (see Fig. S7b).

Peak position, ppm	Integral area
3.02	0.008
2.97	0.007
2.94	0.009
2.87	0.009

0.523

Selectivity of HT-anti dimer formation: $s = \frac{0.523}{0.523 + 0.008 + 0.007 + 0.009 + 0.009} = 94 \%$

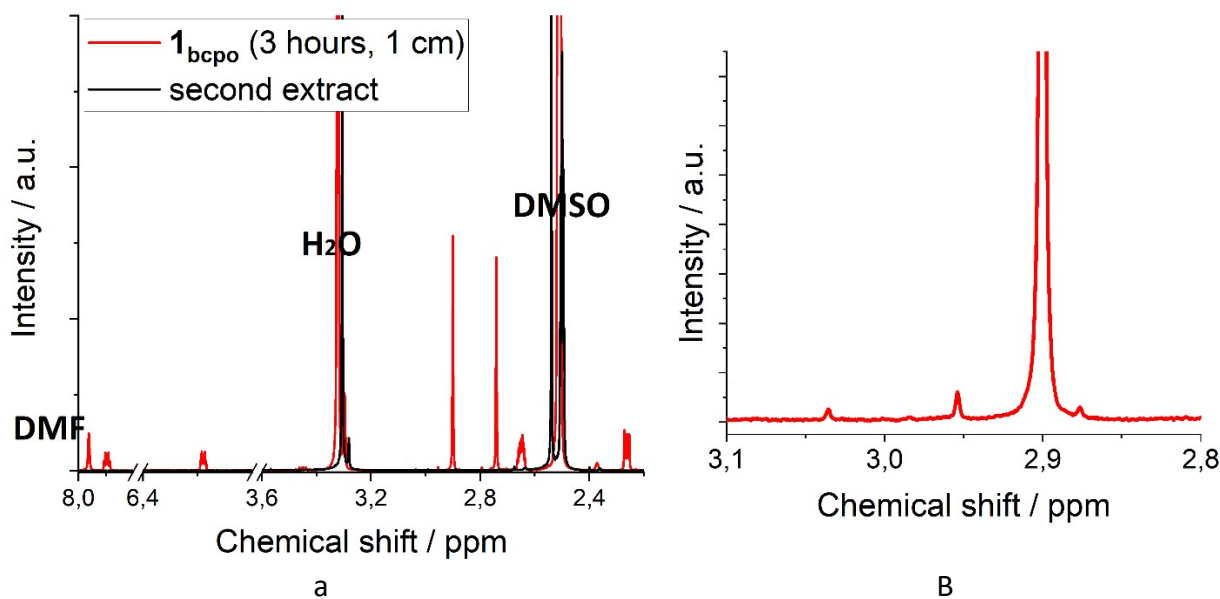


Figure S8. ¹H NMR spectrum of the reaction mixture after the irradiation, extracted from the bulk sample of **1bcpo** twice by d₆-DMSO. Irradiation characteristics: 3 hours, 1 cm distance between the sample and diode lamp (a). Enlarged part of the spectrum, showing area of cyclobutane protons, closest to C=O group. Y axis is 100 times scaled (b).

Table S4. Reaction characteristics for **1cpo** after irradiation during 3 hours (see Fig. S8a). The distance between diode lamp and the sample was 1 cm.

Peak position, ppm	Integral area	Assignment
7.89	1.000	H _{C=C} (cpo)
6.18	1.002	H _{C=C} (cpo)
2.90	3.610	H _{cyclobutane} (bcpo)
2.74	3.595	H _{cyclobutane} (bcpo)

$$\text{Average cyclobutane protons' integral: } n_2 = \frac{3.610 + 3.595}{2} = 3.603$$

$$\text{Average C=C protons' integral: } n_1 = \frac{1.000 + 1.002}{2} = 1.001$$

$$\text{Yield of HT-anti bcpo: } \eta = \frac{n_2}{n_1 + n_2} = \frac{3.603}{1.002 + 3.603} = 78 \%$$

Table S5. Minor products peaks (see Fig. S8b).

Peak position, ppm	Integral area
3.04	0.021
2.95	0.041

2.88	0.012
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3.610

Selectivity of HT-anti dimer formation: $s = \frac{3.610}{3.610 + 0.021 + 0.041 + 0.012} = 98 \%$

References

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