A solid-state trimerisation of a diene diacid affords a bicyclobutane: reactant structure from X-ray powder data and product separation and structure determination *via* co-crystallisation.

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Supplementary data

Content:

Materials:

(*E*,*E*)-2,5-dimethylmuconic acid (98%, Alfa Aesar), 4,4-bipyridine (98%, Aldrich Chemical Co.), and *N*,*N*-dimethylformamide (ACS reagent, ≥ 99.8%, Sigma-Aldrich) were used as received.

Methods:

NMR Studies

Products were characterized by using Avance-400 and Avance-600 Bruker NMR spectrometers (Billerica, MA) operating at 400 and 600 MHz, respectively, using deuterated dimethyl sulfoxide (DMSO-d_6) as solvent. ^{1}H and ^{13}C chemical shifts were referenced with the residual proton and carbon-13 chemical shifts of the solvent (DMSO-d_6, ^{1}H, 2.5 ppm; ^{13}C, 39.5 ppm). Fractions with milligram quantities of the product were characterized with a battery of one- and two-dimensional homonuclear and heteronuclear experiments [^{1}H, ^{13}C, ^{13}C-DEPT, and correlated spectroscopy (COSY), nuclear Overhauser effect spectroscopy (NOESY), heteronuclear multiple quantum coherence (HMQC) and heteronuclear multiple bond correlation (HMBC)]. Gradient-assisted versions of the pulse sequences were used for all the 2D experiments. Inverse detection probe was used for all the 2D heteronuclear 2D experiments. Typical parameters for the NMR experiments were as follows: ^{1}H (TD, 64k; NS, 4k), ^{13}C (TD, 128k; NS, 10000), 1D COSY (TD, 2k; TD1, 256; NS, 32; DS, 32), NOESY (TD, 2k; TD1, 256; NS, 32; DS, 32; mixing times, 0.5, 1.0, 1.5, and 2.0s), ^{13}C-^{1}H HMQC (TD, 2k; TD1, 256; NS, 32; DS, 128)and ^{13}C-^{1}H HMBC (TD, 2k; TD1, 256; NS, 64; DS, 128). TD, NS, and DS refer to time domain data points, number of scans, and dummy scans, respectively. Relaxation delay was set to 4s for all the 2D experiments. All of the NMR data were processed with TOPSPIN 1.3 suite of software programs. One-dimensional ^{1}H data were processed with zero-filling to 64k data points and 0.2 Hz exponential line broadening, whereas ^{13}C spectra were processed with zero-filling to 128k data points and 1.0 Hz of exponential line broadening. The 2D NMR data were processed with the zero-filling to 2048 points and 1024 points in acquisition and second dimension, respectively. Relative numbers of proton signals multiplied by the integral areas were used for the quantification.

Single-crystal X-ray Diffraction

Single-crystal X-ray diffraction studies of (**2a**)·2(4,4'-dipy)·2DMF were performed on a Nonius Kappa CCD diffractometer. Data collection was conducted at 150 K using MoK$_\alpha$ radiation (λ = 0.71073 Å). A total of 491 diffraction images were collected in two phi scans (frame-exposure times: 60 s and 240 s) and four omega scans (frame-exposure times: 240 s) with 2.0º per-frame rotations. Data reduction was accomplished using the *HKL Denzo* and *HKL Scalepack* programs (Otwinowski & Minor, 1997). The structure was fully solved *via* direct methods using *SHELXS-97* (Sheldrick, 2008). Refinement by full-matrix least-squares based on F^2 was performed utilizing *SHELXL-97* (Sheldrick, 2008). All hydrogen atoms were refined in geometrically constrained riding positions.

Powder X-ray Diffraction

Structure solution of **1** by powder X-ray diffraction (PXRD) was accomplished on a Bruker D8 Advance powder diffractometer, Cu$K\alpha_1$ radiation from a primary Ge(111)-Johannson monochromator, Våntag-1 position sensitive detector with 6° angle opening; step mode with

0.0085° per step. The sample was gently crushed in an agate mortar into a fine powder and packed in 0.5 mm borosilicate glass capillary. The capillary was rotated during data collection for better particle statistics. High-resolution pattern of **1** was collected in the angle region from 4° to 75° in 2θ and the total data collection time was 18 h. Rietveld refinement was performed using restraints on bond lengths and valence angles as well as planarity restraints. All calculations (indexing, structure solution by simulated annealing in direct space and Rietveld refinement) were performed using the program Topas, version 4.1 (Bruker-AXS, Karlsruhe, Germany).

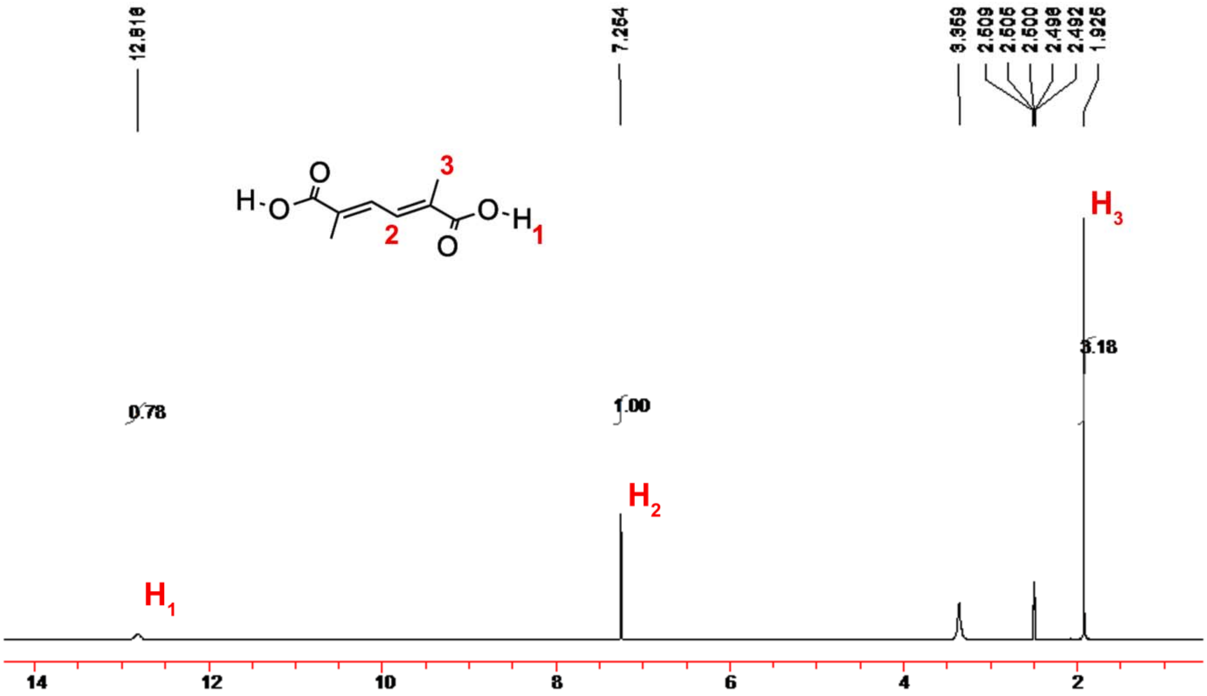


Figure S1. ^{1}H NMR spectrum of **1** before photoreaction.

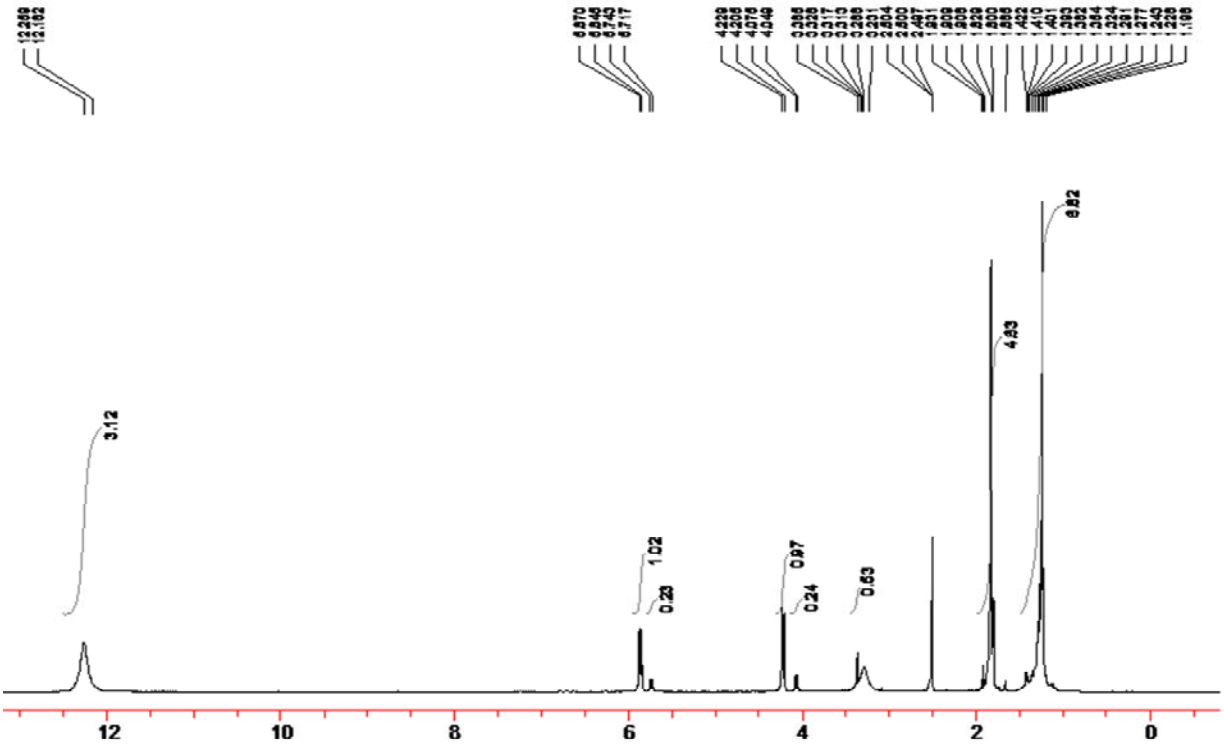


Figure S2. ^{1}H NMR spectrum of **1** after 60 hours of UV-irradiation (400 MHz).

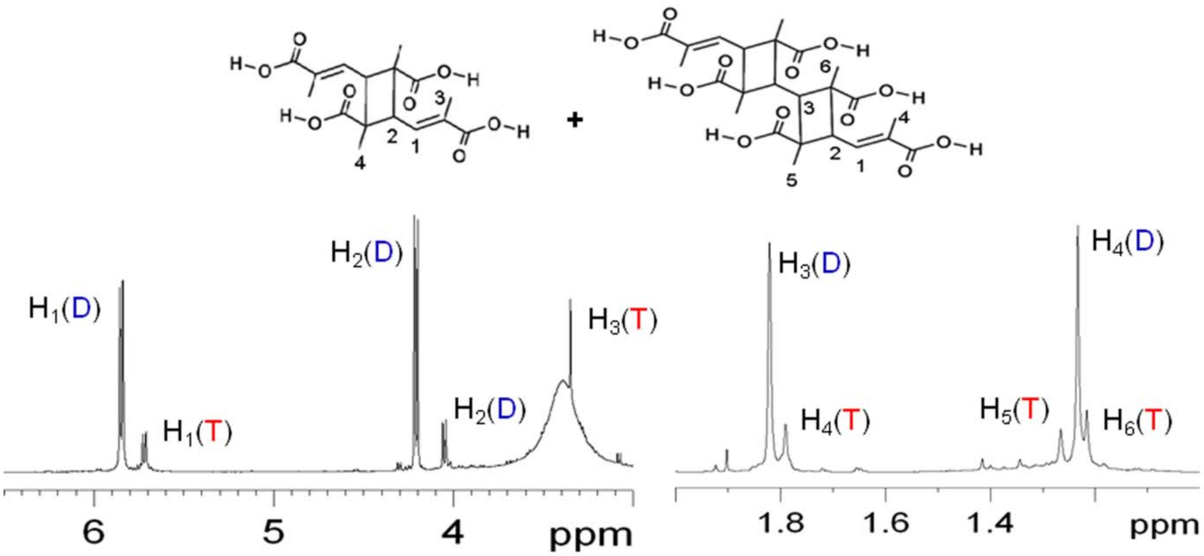


Figure S3. ^{1}H NMR assignment of **1** after 60 hours of UV-irradiation (600 MHz).

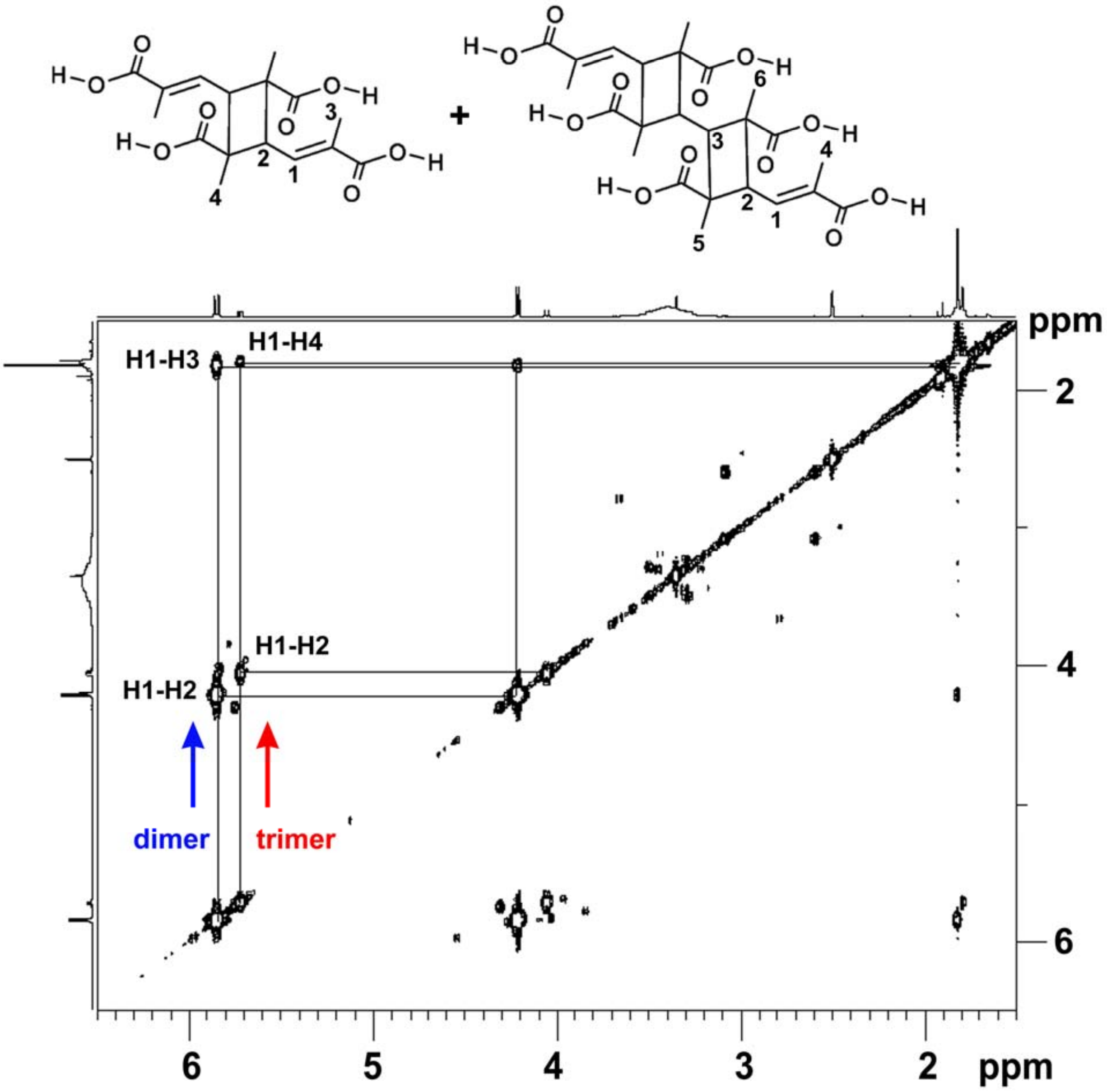


Figure S4. ^{1}H-^{1}H COSY cross section of the mixture containing **2a** and **2b** in DMSO-d_6.

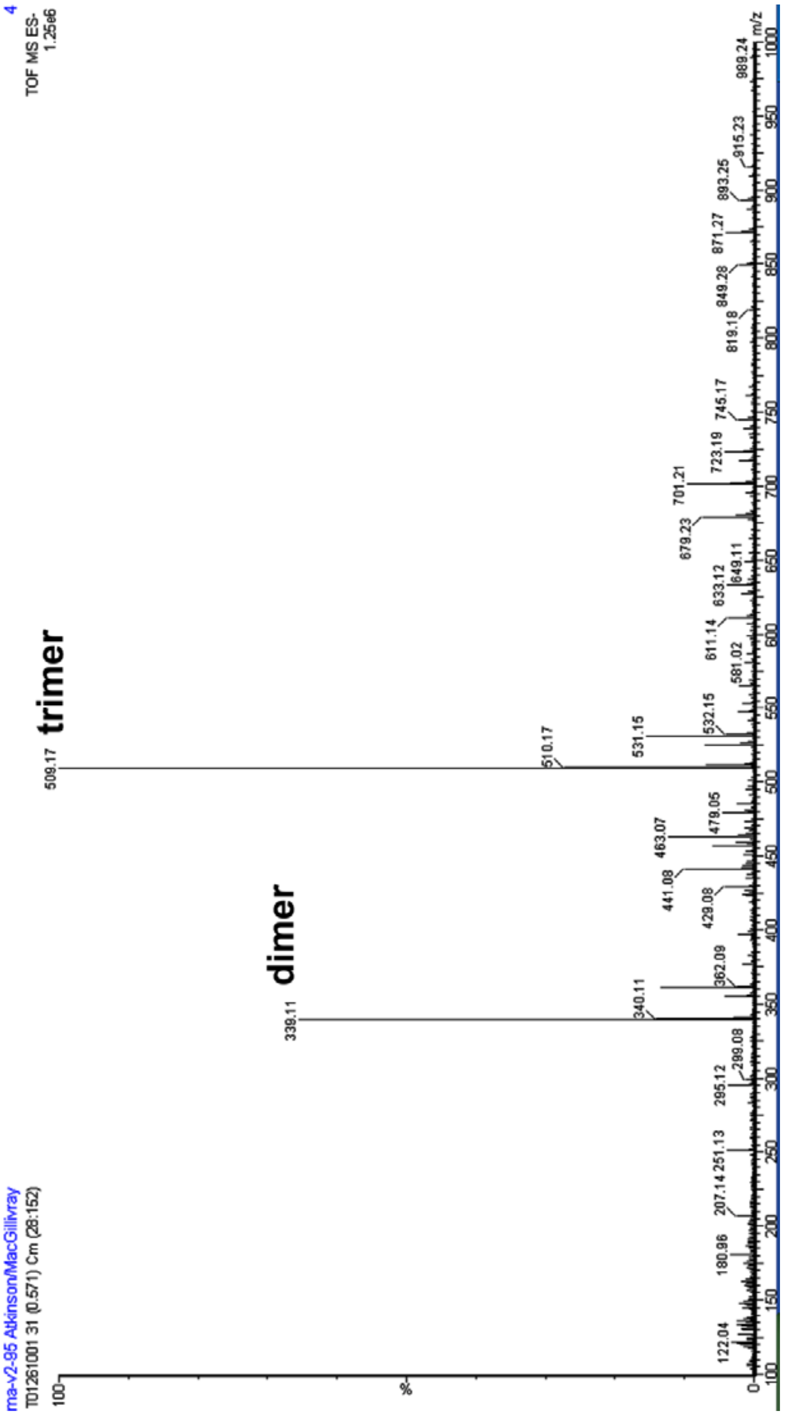


Figure S5. ESI-Mass Spectrum of photoreacted **1** after 60 hours. The fragment at 339.11 m/z represents **2b**. The fragment at 509.17 m/z represents **2a**.

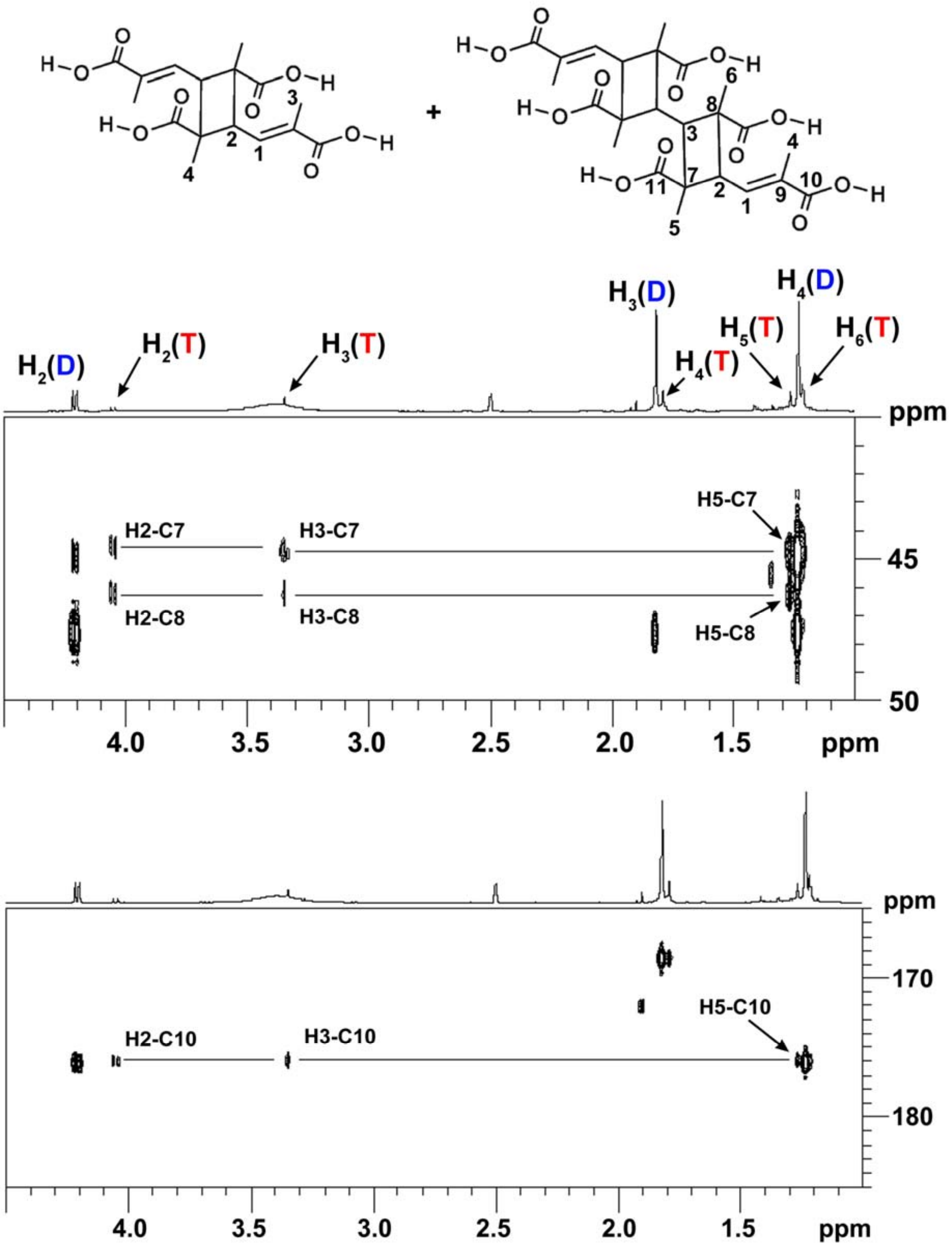


Figure S6. ^{1}H-^{13}C HMBC spectral cross sections of **2a** and **2b** photoreacted mixture. The singlet proton at 3.35 ppm displays correlations with C5, C7, and C8 of **2a**.

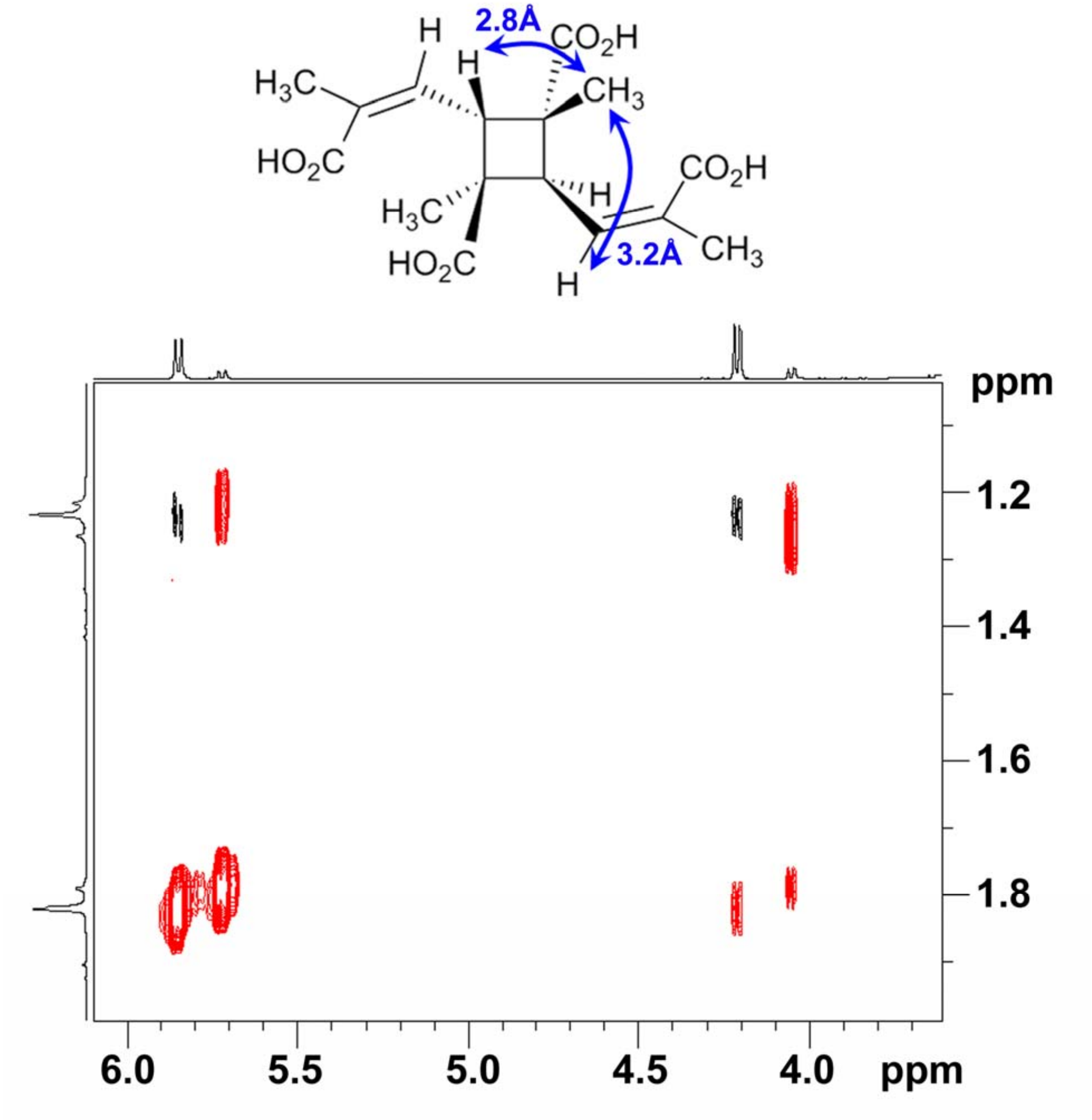


Figure S7. 2D NOESY spectrum cross section of **2b** showing magnetization transfer between the cyclobutyl methyl group with the cyclobutyl proton (*r* = 2.8Å) and the olefinic proton (*r* = 3.2Å). The cross peaks in "red" are of the same sign as the diagonal peaks and arise due to the incomplete cancelation of residual J-cross peaks.

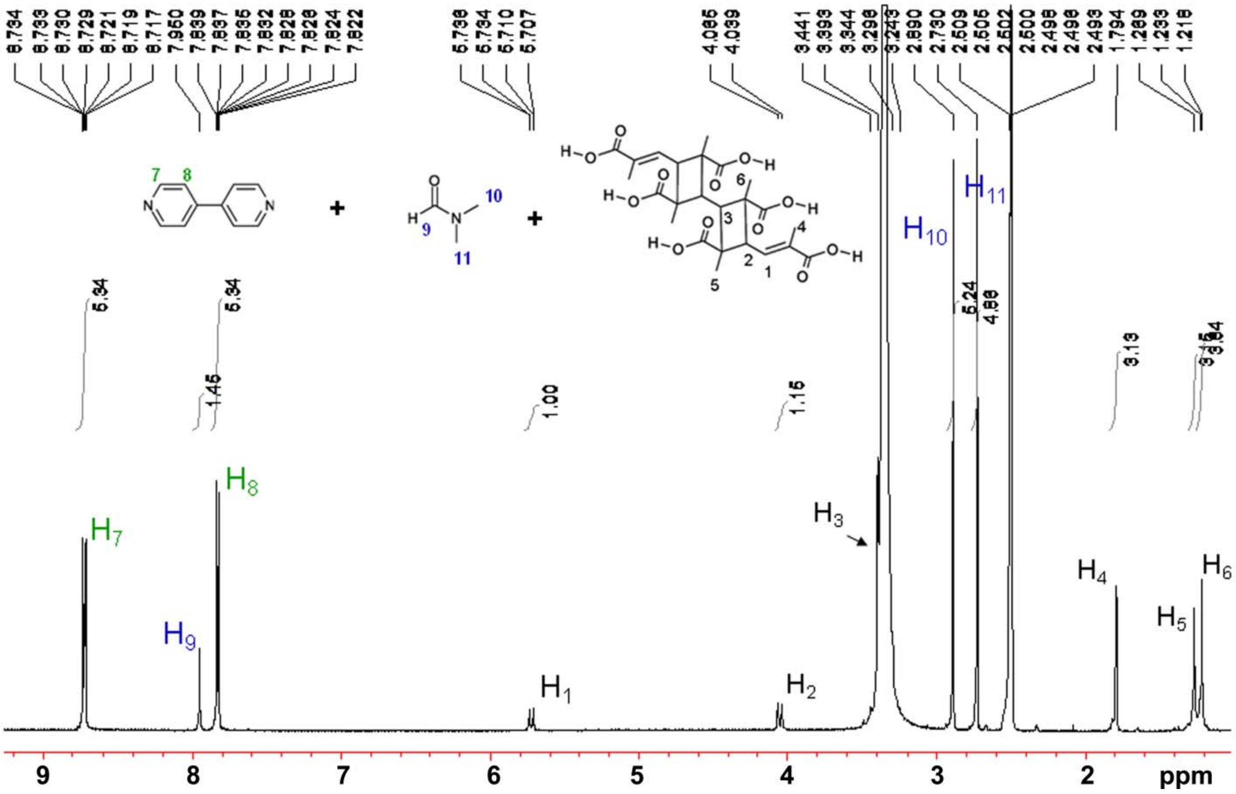
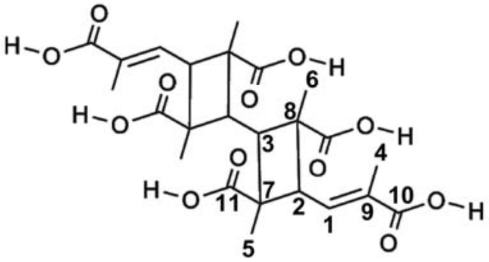


Figure S8. ^{1}H NMR spectra of co-crystal (**2a**)·2(4,4'-dipy)·2DMF.

Table S1. Chemical shifts of trimer **2a.**



Atom Position	^{1}H	^{13}C
1	5.72	134.5
2	4.04	44.6
3	3.35	44.5
4	1.79	20.79
5	1.26	19.9
6	1.21	19.9
7		44.7
8		46.3
9		131.1
10		168.6
11		176.1

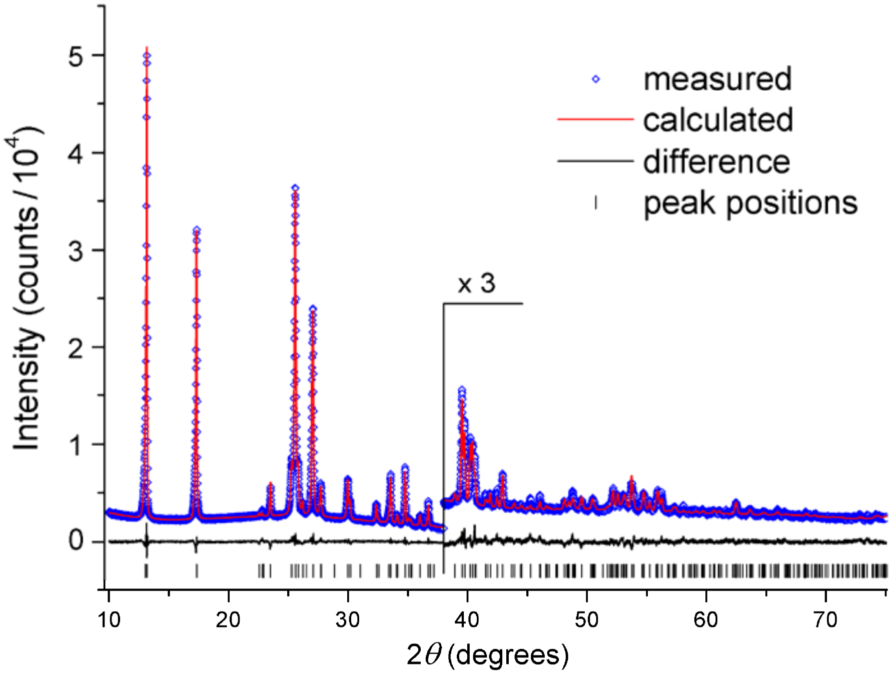


Figure S9. Rietveld-refinement plot of **1**. The high angle region is enlarged for clarity.

Table S2. Crystallographic and Rietveld refinement details for **1**.

Compound	**1**
Molecular formula	$C_8H_{10}O_4$
Formula weight (in g/mol)	170.17
Space group	$P2_1/$
a / Å	3.8984(1)
b / Å	7.8794(1)
c / Å	13.5148(4)
β / °	95.965(2)
V / Å^3	412.88(1)
Z	2
Calc. density (g cm^{-3})	1.369
Temperature (K)	293
Wavelength (Å)	1.5406
R_{exp} (%)[*]	2.19
R_{p} (%)[*]	2.82
R_{wp} (%)[*]	3.763
gof[*]	1.72
$R(F^2)$ (%)[*]	1.40
Starting angle (° 2θ)	5
Final angle (° 2θ)	75
Step width (° 2θ)	0.00853
Scan time	18 h
No. of variables	74
CCDC deposition number	780278

[*] as defined in Topas, version 4.1, Bruker-AXS, Karlsruhe, Germany

Table S3. Crystallographic details for (**2a**)·2(4,4'-dipy)·2DMF.

Compound	(**2a**)·2(4,4'-dipy)·2DMF
Chemical formula	$C_{24}H_{30}O_{12}{\cdot}2(C_{10}H_8N_2){\cdot}2(C_3H_7NO)$
Formula Mass	969.04
Crystal system	Triclinic
a/Å	8.1654(9)
b/Å	11.7147(13)
c/Å	13.1518(14)
α/°	86.292(5)
β/°	77.546(5)
γ/°	78.982(5)
Unit cell volume/$Å^3$	1205.4(2)
Temperature/K	150(2)
Space group	$P\bar{1}$
No. of formula units per unit cell, *Z*	1
No. of reflections measured	8199
No. of independent reflections	4236
R_{int}	0.0182
Final R_1 values ($I > 2\sigma(I)$)	0.0462
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.1239
Final R_1 values (all data)	0.0576
Final $wR(F^2)$ values (all data)	0.1294
CCDC deposition number	780279