

## Supplementary Material

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### Self-assembly, concomitant photochemical processes, and improvement of the yield of [2+2] photoreactions from supramolecular arrays via mechanochemical assistance.

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**Figure 2.** Monitoring of the isomerisation of H<sub>2</sub>Mal to H<sub>2</sub>Fu in presence of 2Cl-Stb by <sup>1</sup>H NMR spectroscopy as a function of time and the solvent; <sup>1</sup>H NMR spectra in DMSO-D<sub>6</sub> (a) and MeOD (b) at room temperature, respectively.

**Figure S3.** (a) <sup>1</sup>H NMR spectra of compound **1** before (bottom) and after UV-irradiation for 3 days at 350 nm (b) and 302 nm (c), respectively. (b) <sup>1</sup>H NMR spectrum of the photoproduct isolated from the irradiation of **1**, containing *rctt*-1,3-bis(4-pyridyl)-2,4-bis(2-chlorophenyl)cyclobutane (2-Cl-dpcb).

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of **2** after UV-irradiation for 5 days and co-ground with 40% of fresh 2,2'-bpe for 30 min and a third exposure to UV-irradiation for 2 days.

**Figure S5.** (a) Comparison of the  $^1\text{H}$  NMR spectra of compound **3** after UV irradiation for 3 days at 302 nm and the mixture after a second grinding-irradiation step (additional UV-irradiation for 2 days). (b) Representative  $^1\text{H}$  NMR spectrum of the photoproduct isolated from the irradiation of **2** and **3**, containing *rctt*-tetrakis(2-pyridyl)cyclobutane (2,2'-tpcb).

**Figure S6.** Comparison of the  $^1\text{H}$  NMR spectra of compound **4** after UV irradiation for 3 days at 302 nm and the mixture after a second grinding-irradiation step (additional irradiation for 2 days). *Trans* 3-(3-pyridyl)acrylic acid (3HPA) and *rctt*-3,4-bis(3-pyridyl)-cyclobutane-1,2-dicarboxylic acid *head to head* (3-bpcd).

## 1. Experimental Section

All reagents were obtained from commercial sources and used without further purification. The elemental analysis (C, H, N) was performed on a model EA1108 Fisons elemental analyzer. The FT-IR spectra were recorded from KBr discs, using a Nicolet Magna-IR 560 spectrophotometer. XRPD patterns were recorded on a Bruker D8 Diffractometer with Cu(K $\alpha$ ) (1.5418 Å) radiation, with a scan speed of 2 deg/min. The  $^1\text{H}$  NMR spectra were recorded on a Bruker AVANCE-300 Spectrometer in DMSO-D $_6$  or MeOD.

**Preparation of (1).** A solution of *trans*-2'-chloro-4-stilbazole (**2Cl-Stb**) (200 mg, 1 mmol) in 20 mL of methanol was added to 25 mL of a solution of maleic acid (**H<sub>2</sub>Mal**) (128 mg, 1 mmol) and allowed to stir for 15 min. Slow evaporation of the resulting solutions at room temperature gave crystals of good quality for X-ray single crystal analysis. Yield based on 2Cl-Stb: 85% (pale yellow prisms). The XRD pattern showed that **1** can also be obtained as a highly pure single-phase by direct liquid-assisted co-grinding of the starting compounds for a period of 45-60 min (Fig 1(a)). IR (cm $^{-1}$ ):  $\nu(\text{N-H, O-H})$ : 3200,  $\nu(\text{O-H})_{\text{acid}}$ : 3000-2000 (C=O) $_{\text{acid}}$ : 1706,  $\nu(\text{COO}^-)$ : 1624  $\nu(\text{C=C, C=N,})$ : 1600-1485,  $\nu(\text{COO})$ : 1456-1360,  $\nu(\text{=C-H})$ : 996.

**Preparation of (2).** A solution of 2,2'-bpe (200 mg, 1 mmol) in 20 mL of methanol was added to 25 mL of a solution of fumaric acid (**H<sub>2</sub>Fu**) (287 mg, 2 mmol) and allowed to stir for 15 min. Slow evaporation of the resulting solution at room temperature gave crystals of good quality for X-ray single crystal analysis. Yield based on 2,2'-bpe: 75% (pale yellow prisms). The XRD pattern showed that **2** can be also obtained as a highly pure single-phase via liquid-assisted grinding for a period of 45-60 min (Fig 1(b)). IR (cm $^{-1}$ ):  $\nu(\text{O-H})$ : 3600-2900,  $\nu(\text{C=O})_{\text{acid}}$ : 1700,  $\nu(\text{COO}^-)$ : 1609-1568,  $\nu(\text{C=C, C=N})_{2,2'\text{-bpe}}$ : 1600-1476,  $\nu(\text{COO}^-)$ : 1456-1330,  $\nu(\text{O-H})$ : 1245,  $\nu(\text{=C-H})$ : 979.

**Preparation of (3).** Compound **3** was prepared according to previously published procedure<sup>5a</sup> and can also be obtained as a highly pure single-phase by direct liquid-assisted co-grinding of the starting compounds for a period of 45-60 min (See PXRD pattern, Fig S4 and S5). IR (cm $^{-1}$ ):  $\nu(\text{O-H})$ : 3600-2900,  $\nu(\text{C=O})$ : 1700,  $\nu(\text{C=C})_{\text{acid}}$ : 1645,  $\nu(\text{C=C, C=N})_{2,2'\text{-bpe}}$ : 1600-1476,  $\nu(\text{C-O})$ : 1244,  $\nu(\text{=C-H})$ : 985.

### Solid state reactivity.

The reactivity of compounds **1-4** was studied upon irradiation with UV light. A powdered crystalline sample (100 mg) and crystals of **1-4** were irradiated at different wavelengths (302 and 356 nm) during 3-5 days. The irradiated samples were characterised by  $^1\text{H}$  NMR spectroscopy for monitoring the respective topochemical transformations. These compounds were isolated from an extraction with  $\text{CH}_2\text{Cl}_2$  after the neutralization of the acid component with NaOH in either case.

*rctt*-1,3-bis(4-pyridyl)-2,4-bis(2-chlorophenyl)cyclobutane (2-Cl-dpcb).

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ),  $\delta_{\text{H}}$ (ppm),  $J$  (Hz): 8.33( $\text{H}_a$ , d,  $J_{ab} = 4.5$ ,  $J_{ab'} = 1.6$ ), 7.31( $\text{H}_c$ , dd,  $J_{cd} = 7.7$ ,  $J_{ce} = 1.6$ ), 7.22( $\text{H}_f$ , dd;  $J_{fe} = 8.3$ ,  $J_{fd} = 2.5$ ), 7.16( $\text{H}_e$ , ddd,  $J_{ef} = 7.6$ ,  $J_{ed} = 7.5$ ,  $J_{ec} = 1.5$ ), 7.07( $\text{H}_d$ , ddd,  $J_{dc} = 9.93$ ,  $J_{ed} = 6.80$ ,  $J_{df} = 2.91$ ), 4.79( $\text{H}_g$ , m,  $J_{gh'} = 8.5$ ,  $J_{gh} = 2.0$ ), and 4.57( $\text{H}_h$ , m,  $J_{hg'} = 8.5$ ,  $J_{hg} = 2.5$ ).

*rctt*-tetrakis(2-pyridyl)cyclobutane isomer (2,2'-tpcb)

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ),  $\delta_{\text{H}}$ (ppm),  $J$  (Hz): 8.42( $\text{H}_a$ , ddd,  $J_{ab} = 4.8$ ,  $J_{ac} = 1.0$ ), 7.36( $\text{H}_b$ , td;  $J_{bc} = 7.7$ ,  $J_{bd} = 1.84$ ), 6.9( $\text{H}_c$ , ddd;  $J_{cd} = 7.8$ ), 7.07( $\text{H}_d$ , dd), and 5.13( $\text{H}_e$ , s).

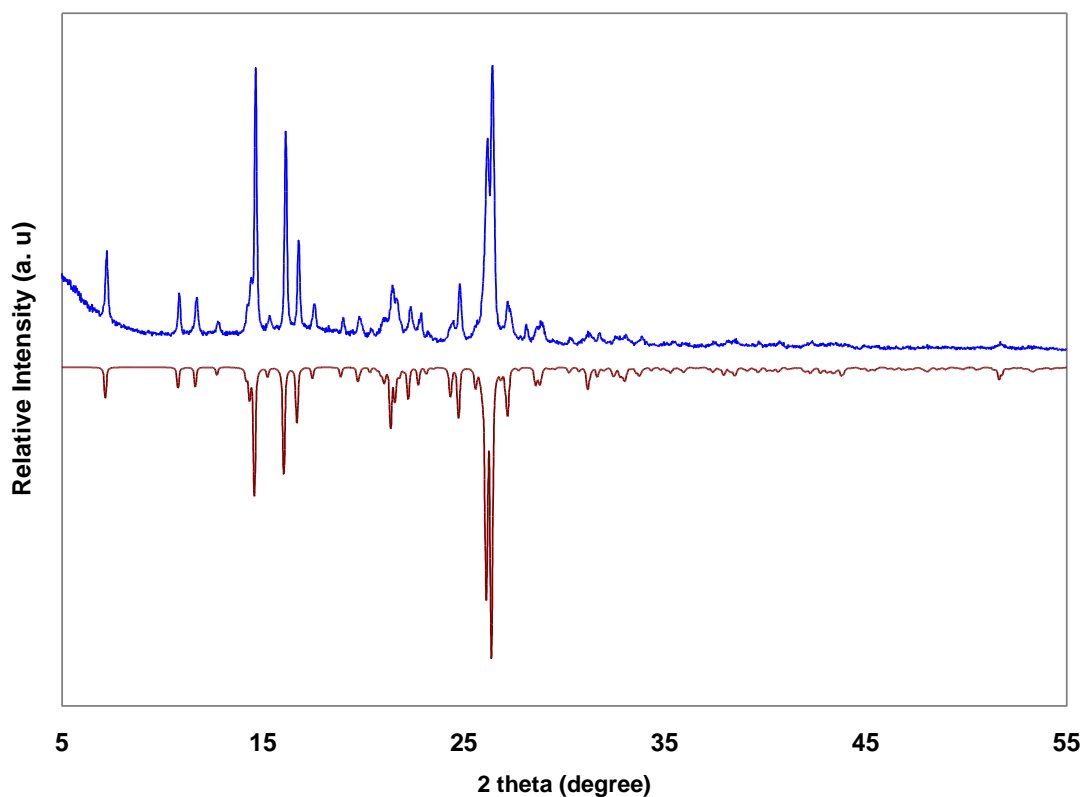
*rctt*-3,4-bis(3-Pyridyl)-1,2-bis(carboxylic)cyclobutane.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ),  $\delta_{\text{H}}$ (ppm),  $J$ (Hz): 8.24( $\text{H}_c$ , d,  $J_{cf} = 14.7$ ), 7.46( $\text{H}_a$ , m,  $J_{ab} = 7.8$ ,  $J_{ab} = 1.6$ ), 7.10( $\text{H}_b$ , m;  $J_{ab} = 4.6$ ), 4.31( $\text{H}_c$ , m,  $J_{cd} = 6.3$ ) and 3.90( $\text{H}_d$ , m,  $J_{dc} = 6.1$ ).

**Crystal structure determination.** Intensity data were recorded at room temperature on a Rigaku AFC-7S diffractometer equipped with a CCD bidimensional detector using monochromated  $\text{Mo}(\text{K}\alpha)$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). An empirical absorption correction (multi-scan) was applied using the package CrystalClear.<sup>13</sup> The structures were solved by Direct Methods and refined by full-matrix least-squares on  $F^2$  using the SHELXTL-PLUS package.<sup>14</sup> Hydrogen atoms on the carbon atoms were placed at fixed positions using the HFIX instruction. H-atoms on carboxylic groups were found from the Difference Fourier map. They were refined with isotropic displacement parameters set to  $1.2 \times U_{\text{eq}}$  of the attached atom.

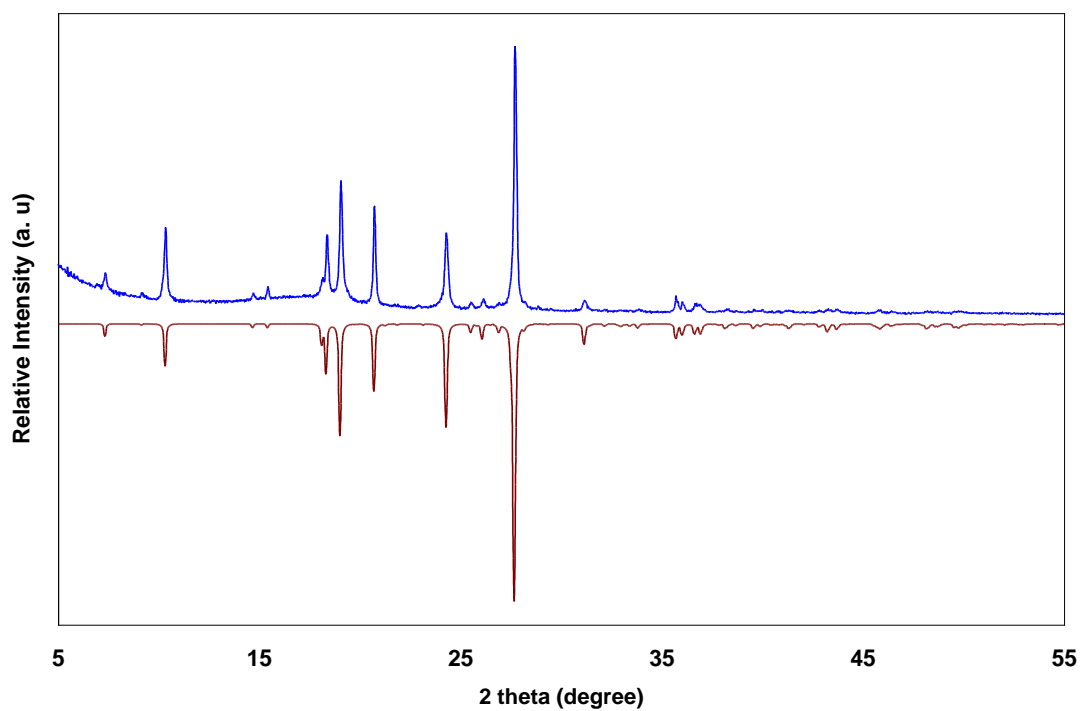
## 2. References

13. CrystalClear, 2005. Rigaku Corporation, Tokyo, Japan.
14. Sheldrick, G. M, Acta Cryst. 2008, A64, 112.

**Figure S1.** (a) Powder XRD patterns from a ground mixture of 2Cl-Stb, H<sub>2</sub>Mal and H<sub>2</sub>Fu for 45 min (blue) and simulated from single crystal structure of **1** (red). (b) PXRD patterns from a ground mixture of 2,2'-bpe and H<sub>2</sub>Fu for 45 min (blue) and simulated from single crystal structure of **2** (red).

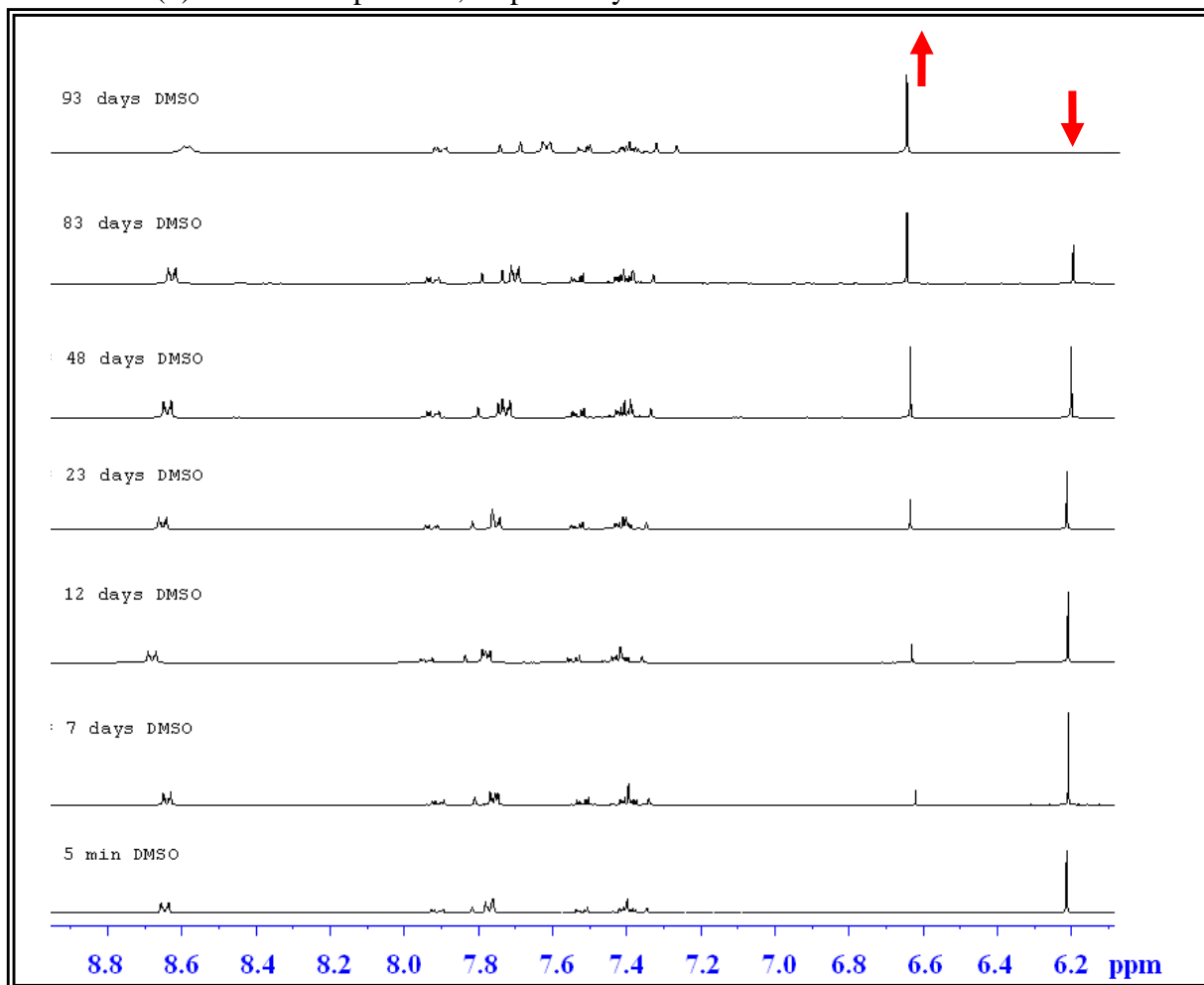


(a)



(b)

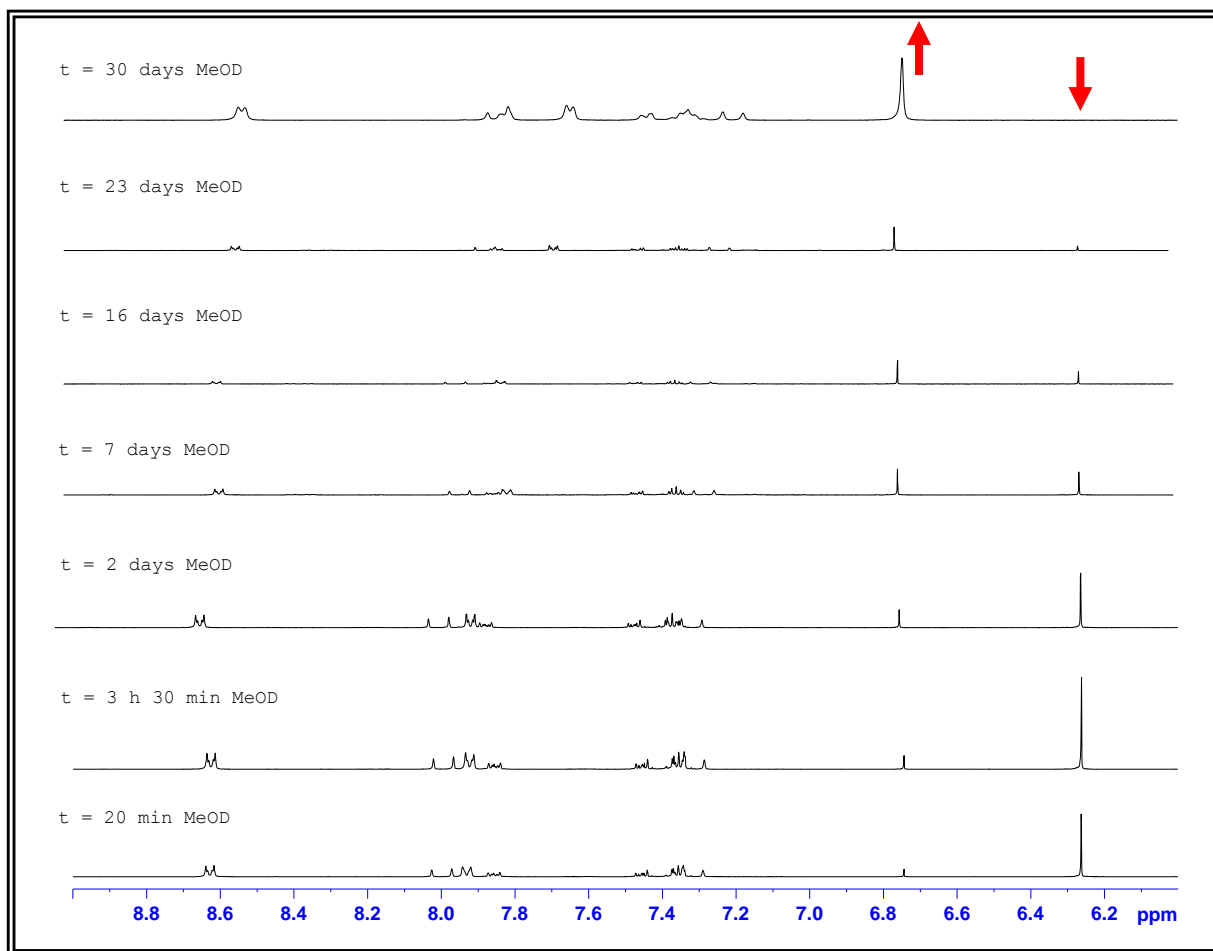
**Figure 2.** Monitoring of the isomerisation of H<sub>2</sub>Mal to H<sub>2</sub>Fu in presence of 2Cl-Stb by <sup>1</sup>H NMR spectroscopy as a function of time and the solvent; <sup>1</sup>H NMR spectra in DMSO-D<sub>6</sub> (a) and MeOD (b) at room temperature, respectively.



(a)

**Table 1.** Values of the degree *cis-trans* isomerisation of H<sub>2</sub>Mal into H<sub>2</sub>Fu estimated by <sup>1</sup>H-NMR spectroscopy as a function of time in DMSO-D<sub>6</sub>

Time (days)	H <sub>2</sub> Mal (%)	H <sub>2</sub> Fu (%)
0	100	0
7	88.75	11.24
12	78.68	21.32
23	72.89	27.10
48	51.57	48.42
83	36.43	63.53
93	0	100

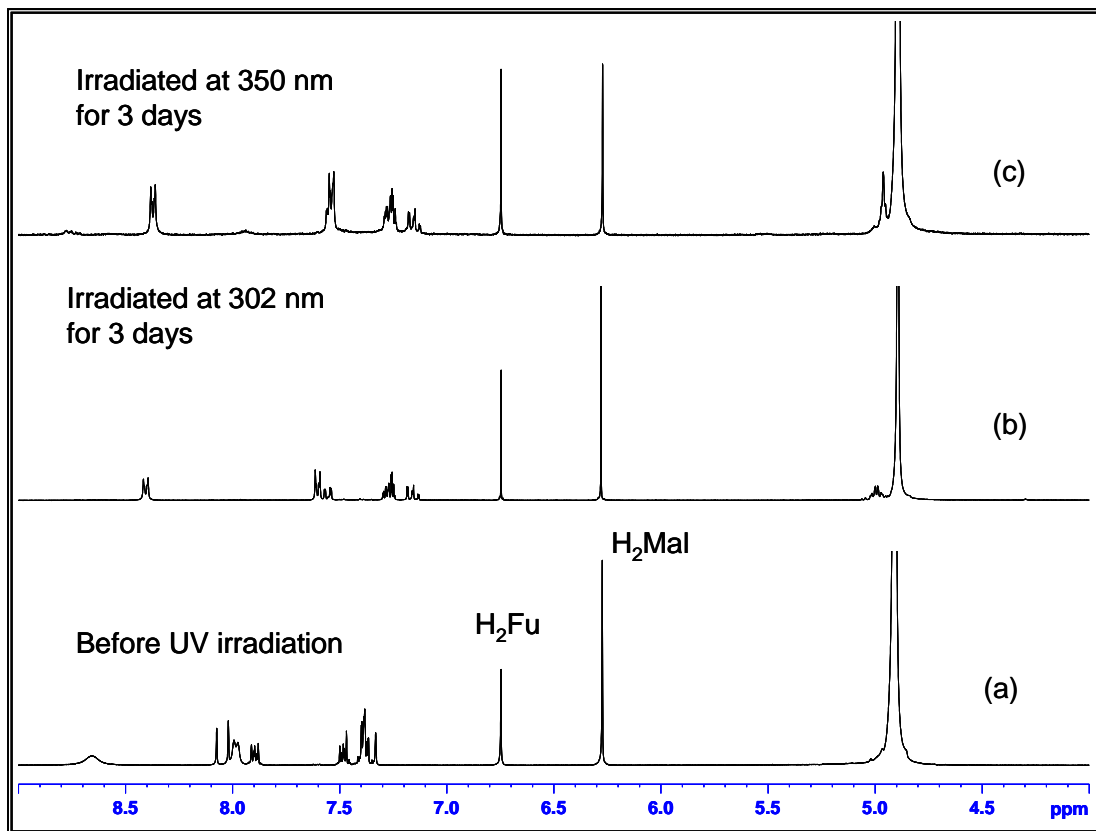


(b)

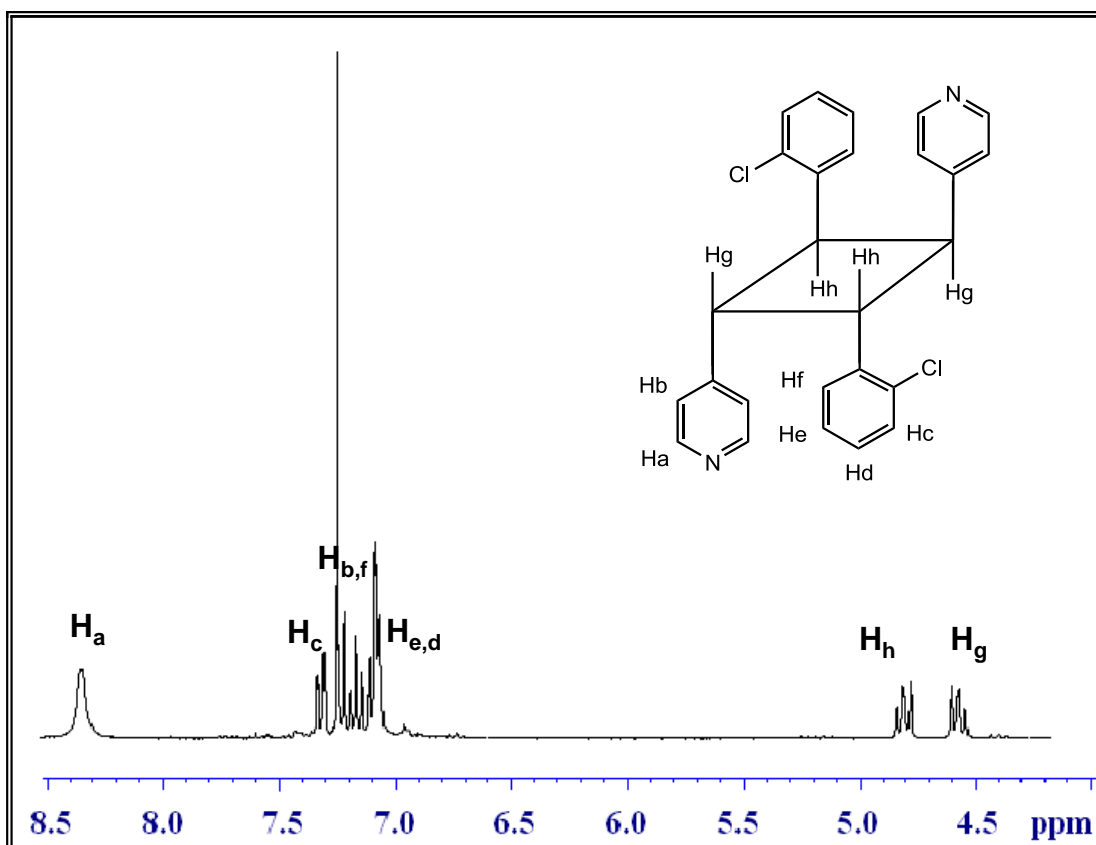
**Table 2.** Degree of *cis-trans* isomerisation of  $\text{H}_2\text{Mal}$  to  $\text{H}_2\text{Fu}$  estimated by  $^1\text{H-NMR}$  spectroscopy as a function of time in MeOD

Time (days)	$\text{H}_2\text{Mal}$ (%)	$\text{H}_2\text{Fu}$ (%)
0.014	92.00	8.00
0.15	89.56	10.43
2	74.89	25.11
7	53.94	46.05
16	33.76	66.23
23	13.45	86.55
30	0	100

**Figure S3.** (a)  $^1\text{H}$  NMR spectra of compound **1** before (bottom) and after UV-irradiation for 3 days at 350 nm (b) and 302 nm (c), respectively. (b)  $^1\text{H}$  NMR spectrum of the photoproduct isolated from the irradiation of **1**, containing *rac*-1,3-bis(4-pyridyl)-2,4-bis(2-chlorophenyl)cyclobutane (2-Cl-dpcb).



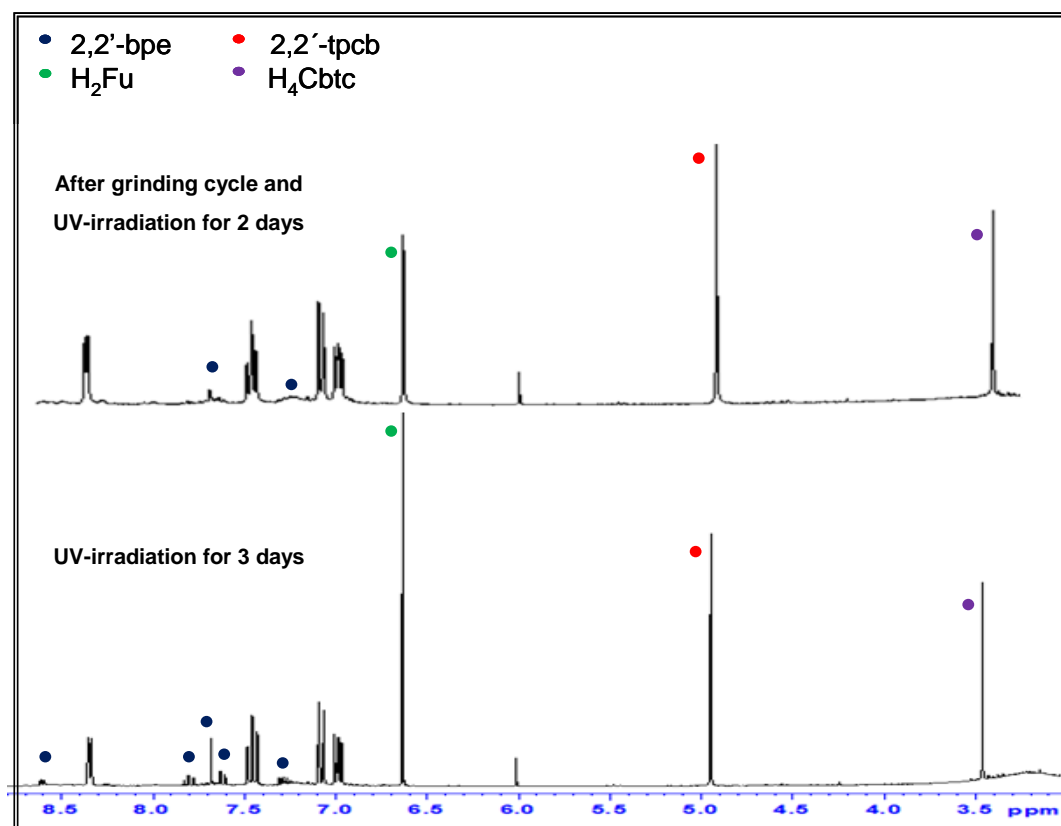
(a)



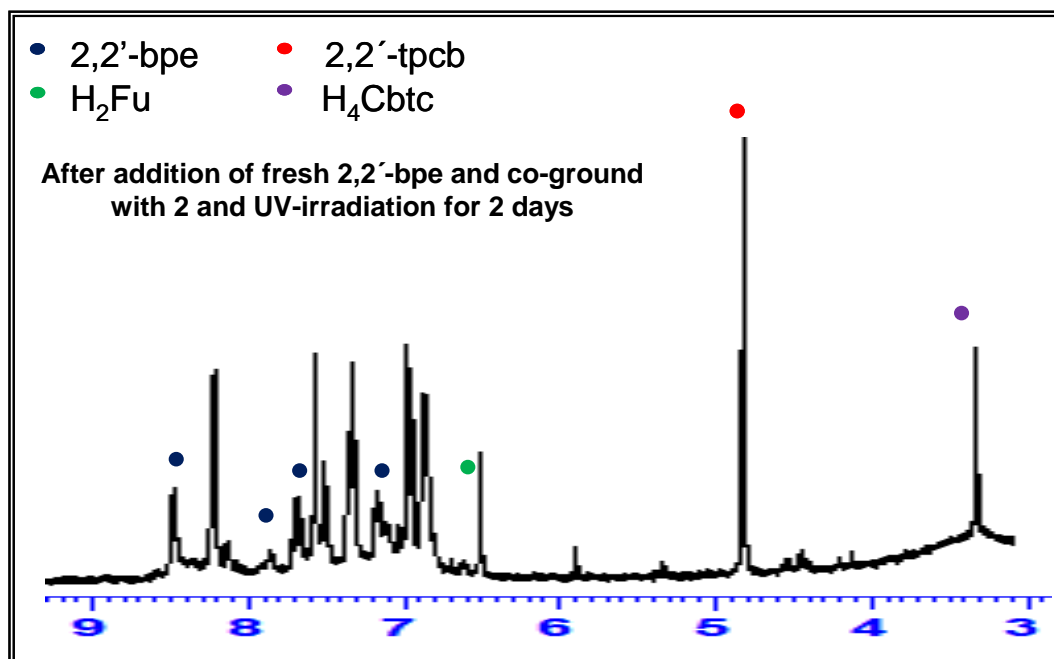
(b)



**Figure S4.** (a) Comparison of the  $^1\text{H}$  NMR spectra of the mixture of 2,2'-tpcb and  $\text{H}_4\text{Cbtc}$  obtained from the photoreaction of compound **2** after irradiation for 3 days and the mixture after a second grinding-irradiation step (additional UV-irradiation for 2 days). (b)  $^1\text{H}$  NMR spectrum of the mixture of **2** after UV-irradiation for 5 days and co-ground with 40% fresh 2,2'-bpe for 30 min and a third exposure to UV-irradiation for 2 days.

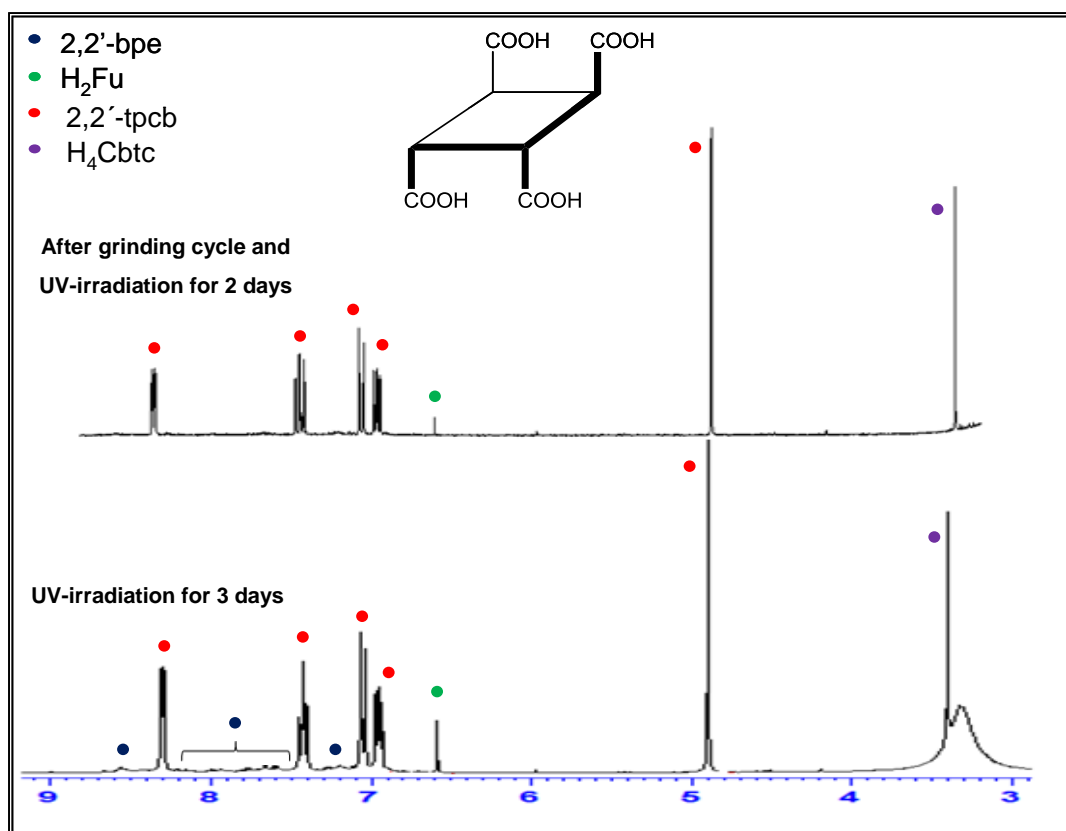


(a)

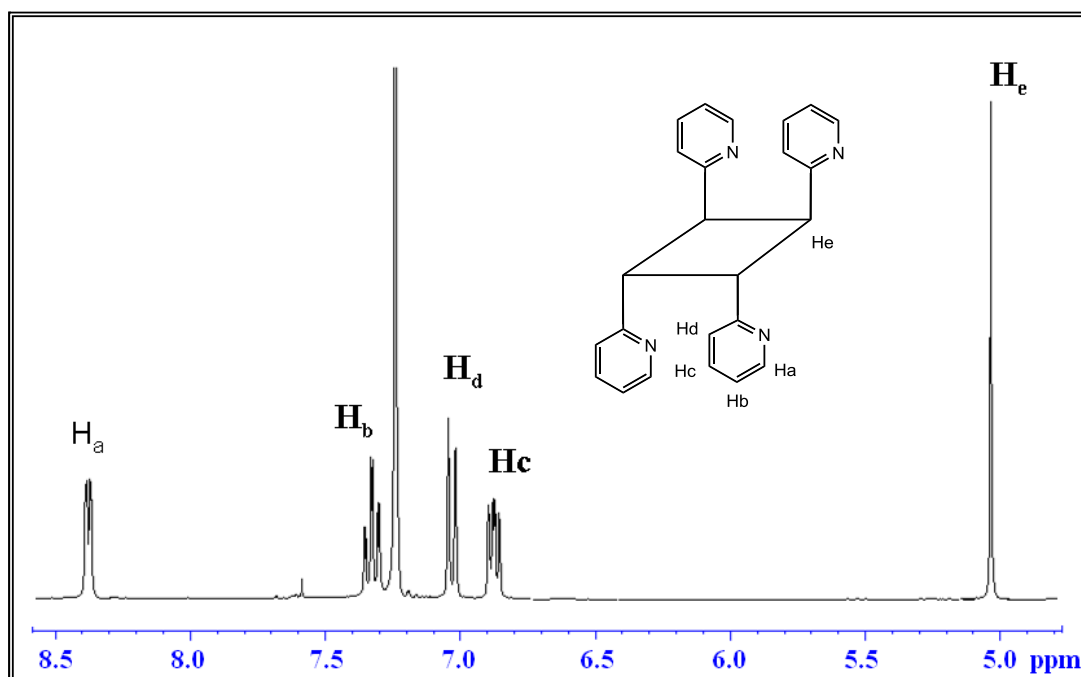


(b)

**Figure S5.** (a) Comparison of the  $^1\text{H}$  NMR spectra of compound **3** after UV irradiation for 3 days at 302 nm and the mixture after a second grinding-irradiation step (additional UV-irradiation for 2 days). (b) Representative  $^1\text{H}$  NMR spectrum of the photoproduct isolated from the irradiation of **2** and **3**, containing *rac*-tetrakis(2-pyridyl)cyclobutane (2,2'-tpcb).



(a)



(b)

**Figure S6.** Comparison of the  $^1\text{H}$  NMR spectra of compound **4** after UV irradiation for 3 days at 302 nm and the mixture after a second grinding-irradiation step (additional irradiation for 2 days). *Trans* 3-(3-pyridyl)acrylic acid (3HPA) and *rac*-3,4-bis(3-pyridyl)-cyclobutane-1,2-dicarboxylic acid (3-bpcd).

