

## Supplementary Material

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### A novel example of double reactivity by either photochemical [2+2] or thermal additions of an ionic organic supramolecular assembly

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**Figure S3.** (a) Monitoring structural changes of the photoreaction of **1** by Powder X-Ray Diffraction at different UV-irradiation time periods.

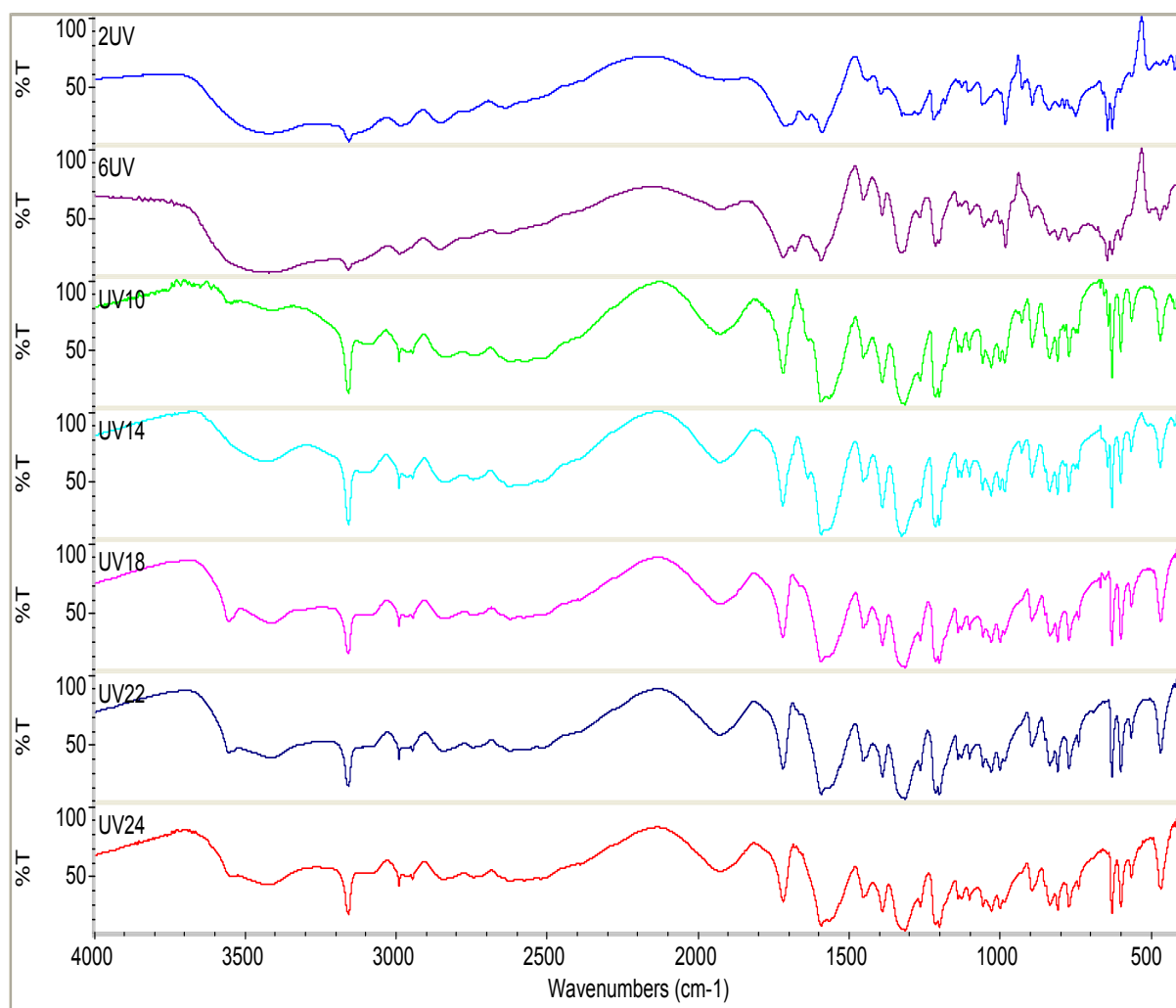
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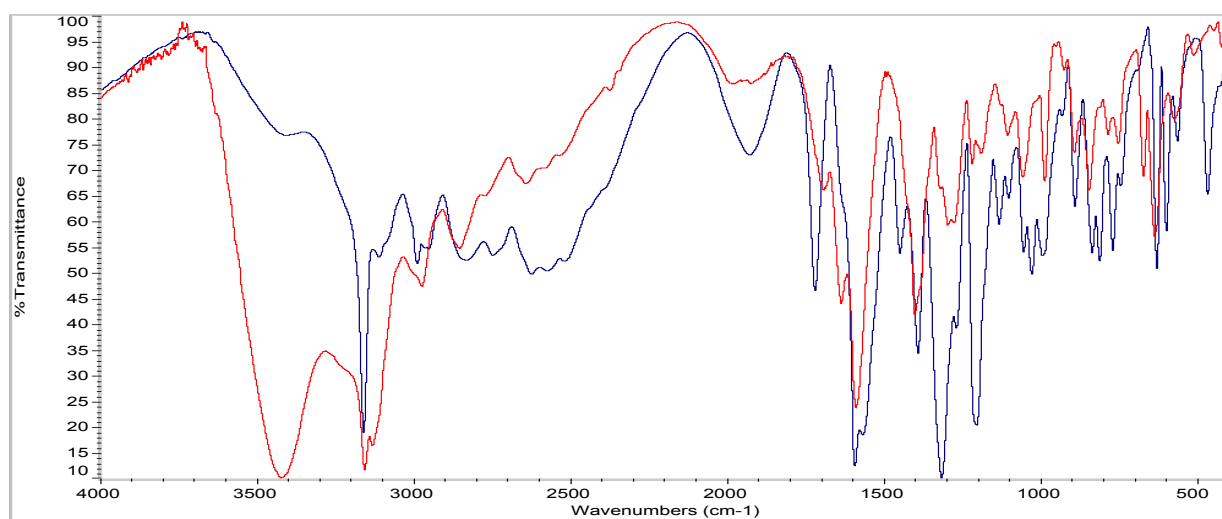
**Figure S6.** Comparison of the <sup>1</sup>H NMR spectra of compound **1** in DMSO-D<sub>6</sub> after UV irradiation for 2 days at 254 nm and after heating under hydrothermal conditions at 140 and 190 °C for 2 days, showing the isomerisation of *rectt* to *rtct*-isomer. (b) The <sup>1</sup>H NMR spectrum of [(*rectt*-H<sub>2</sub>Cbtc<sup>2-</sup>)(Im<sup>+</sup>)<sub>2</sub>]: (**2**) in DMSO-D<sub>6</sub> after heating under hydrothermal conditions at 120 °C for 2 days.

**Figure S7.** The <sup>1</sup>H NMR spectrum of compound **1** in DMSO-D<sub>6</sub> after UV irradiation for 2 days at 254 nm and heated under hydrothermal conditions at 120 °C for 2 days, showing the isomerisation of *rectt* to *rectt* and *rtct*-isomers together with the products of the thermal ring cleavage (Maleic and Fumaric acid) and traces of hydroamination product.

**Figure S1. Figure S1.** (a) Monitoring the photoreaction of **1** by FT-IR at different UV-irradiation time periods. (b) Comparison of the FT-IR spectra of **1** before (blue) and after the photoreaction for 24 h (red), respectively.

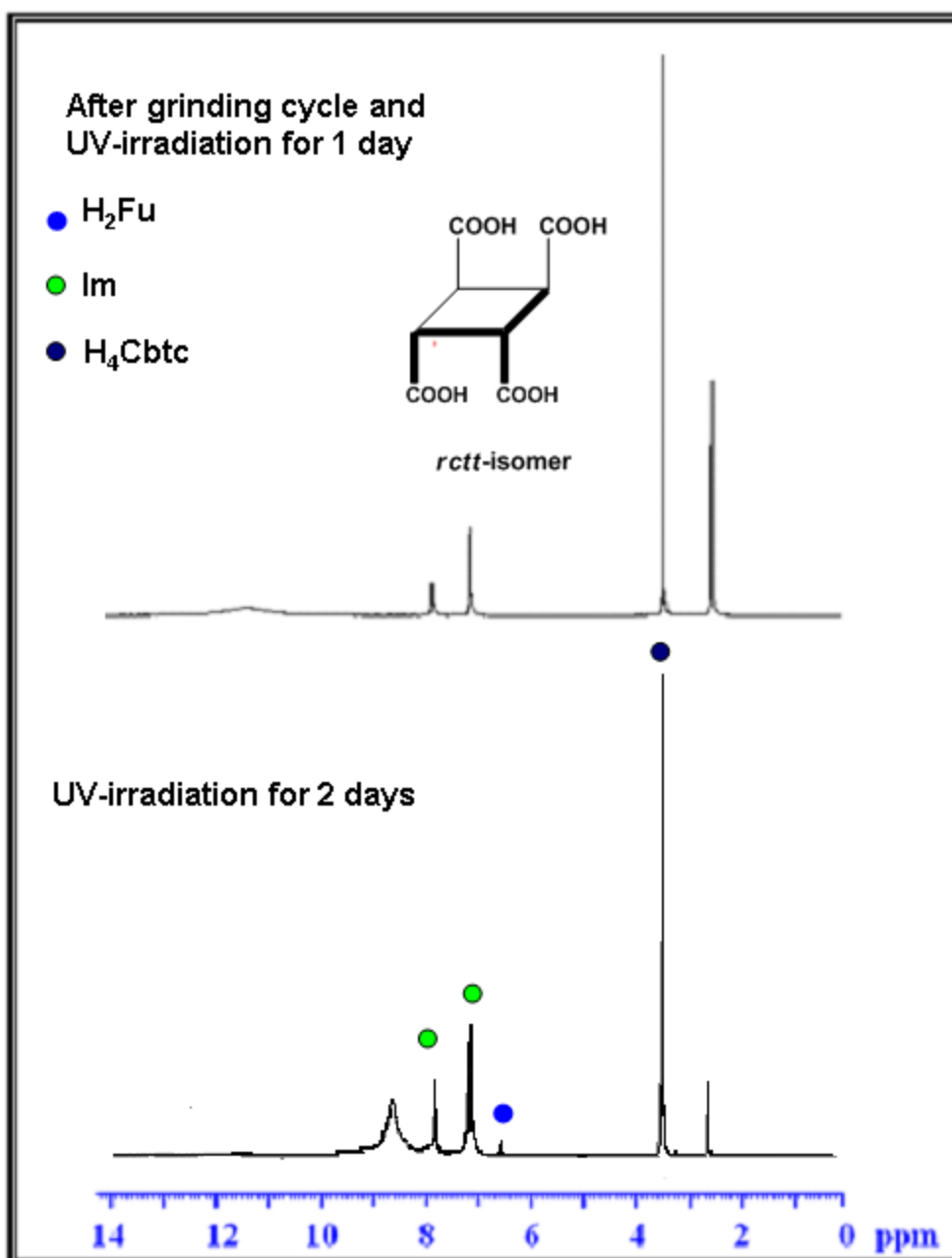


**(a)**

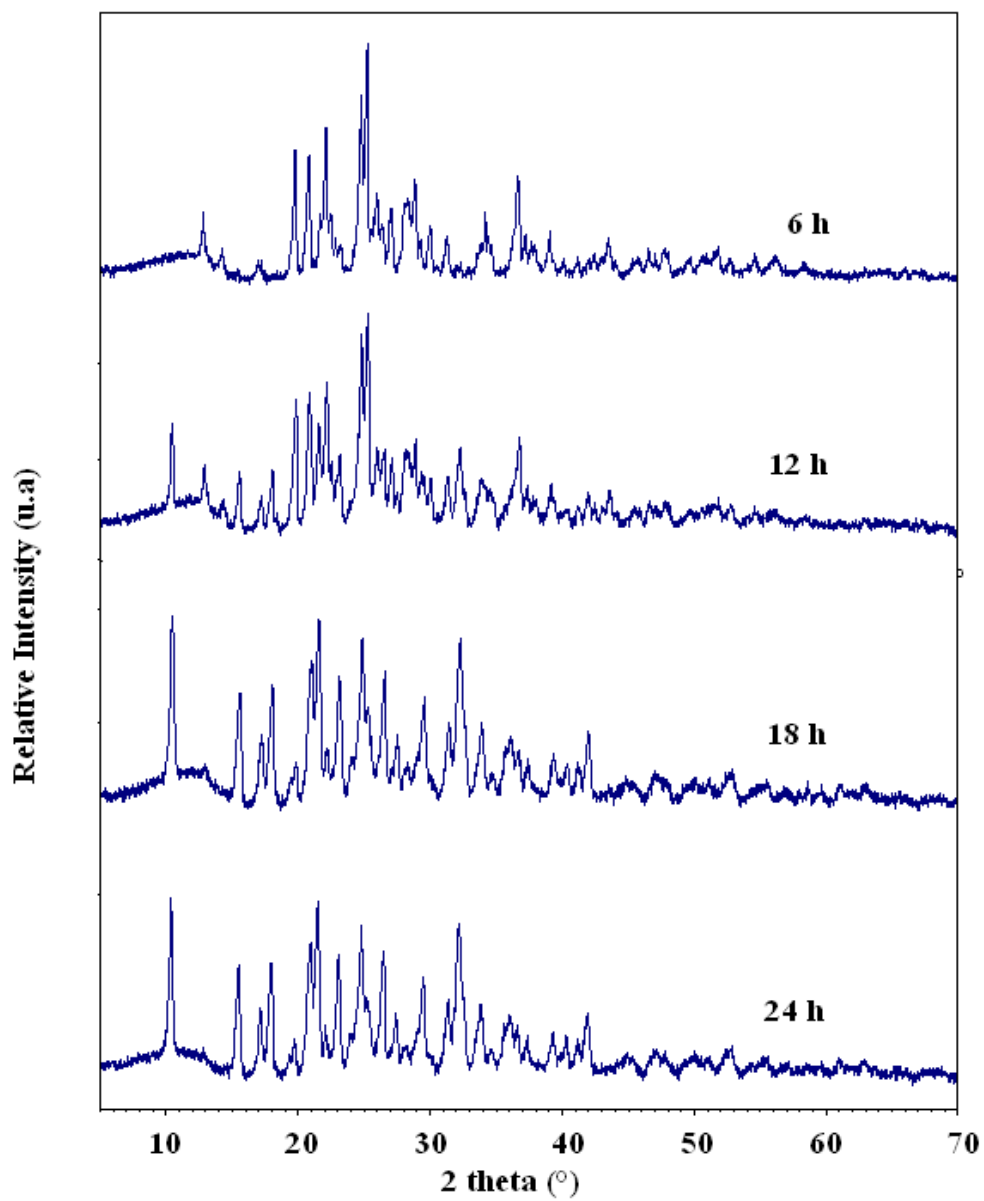


**(b)**

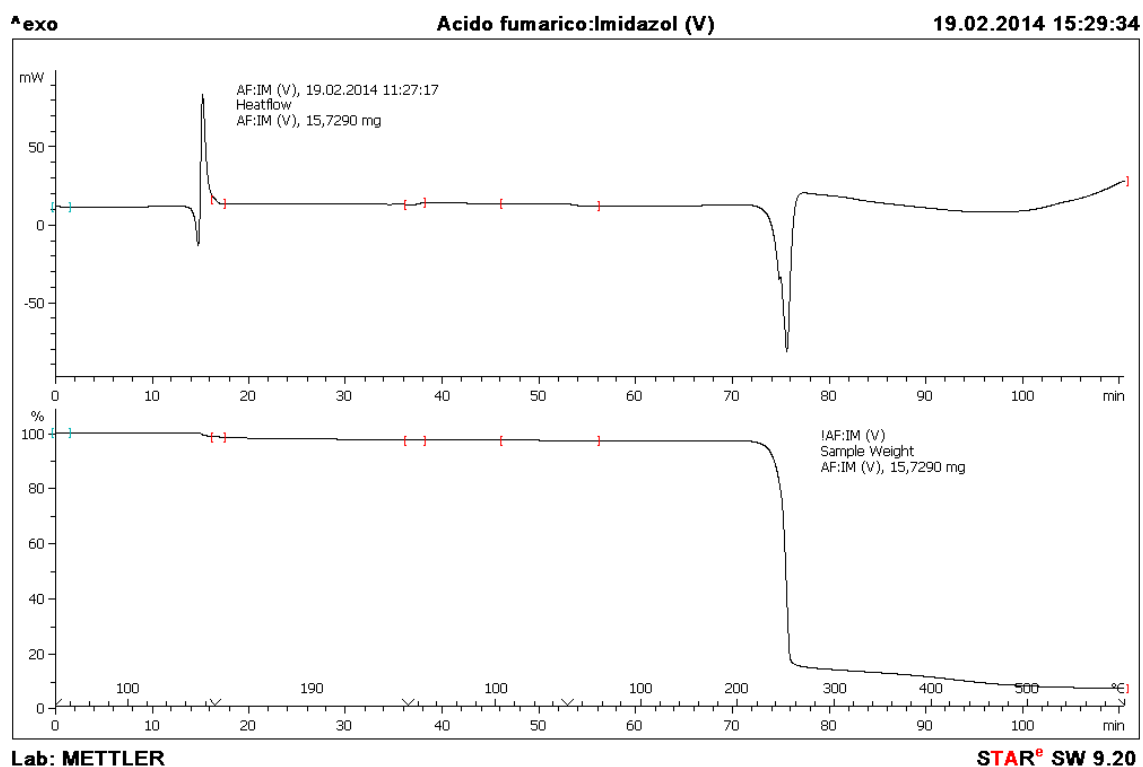
**Figure S2.** Comparison of the  $^1\text{H}$  NMR spectra obtained from the photoreaction of compound **1** after irradiation for 48 h and the mixture after a second grinding-irradiation step (additional UV-irradiation for 1 day).



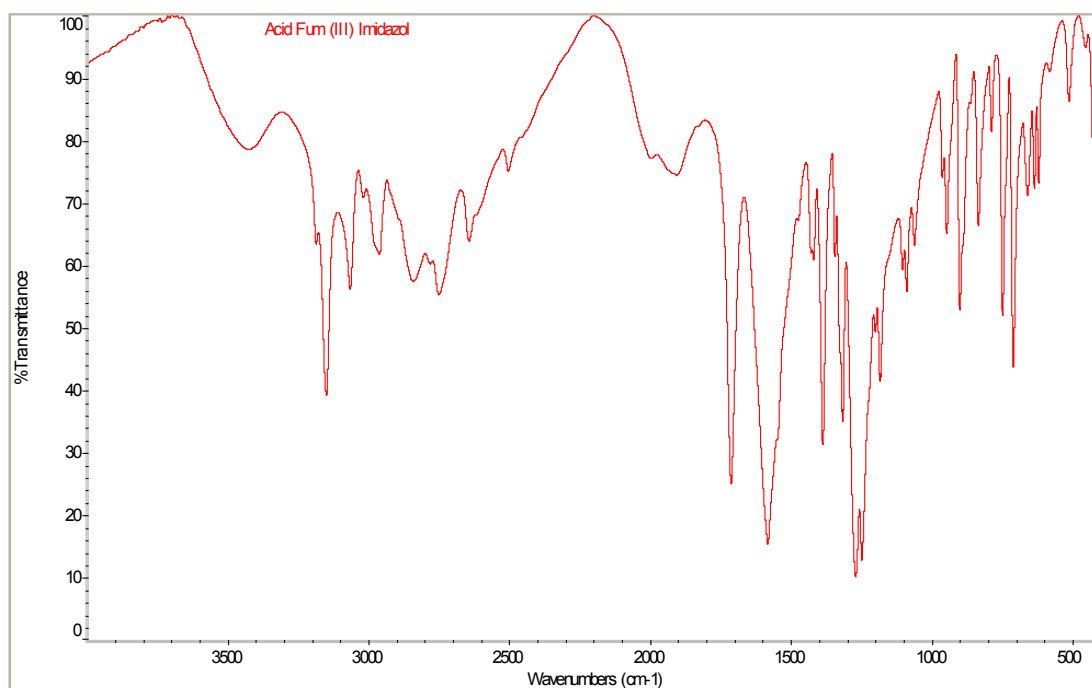
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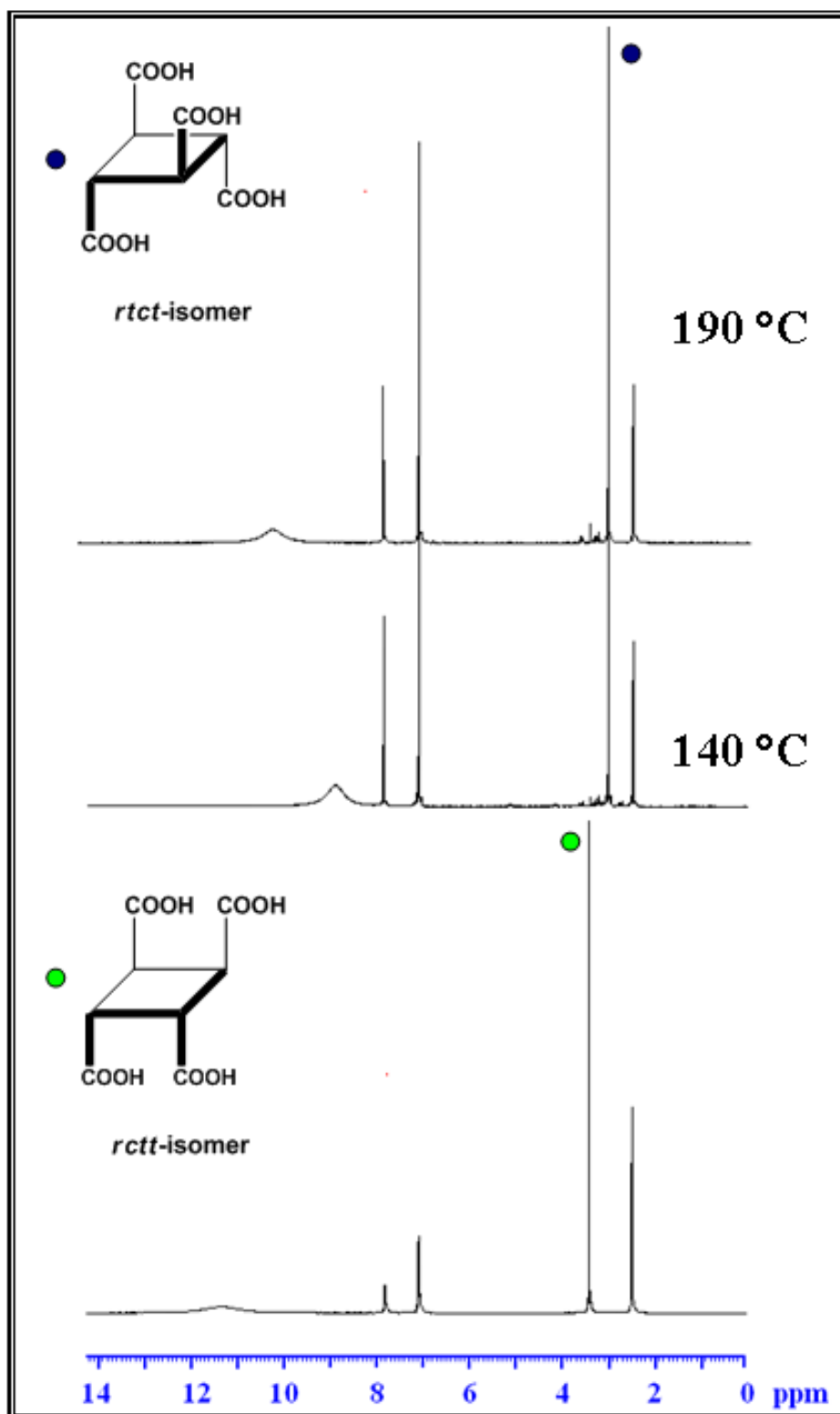
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**Figure S5.** FT-IR spectrum of **1** fresh heated in the solid state upon nitrogen atmosphere at 190 °C for 30 min



**Figure S6. (a)** Comparison of the  $^1\text{H}$  NMR spectra of compound **1** in DMSO after UV irradiation for 2 days at 254 nm and after heating under hydrothermal conditions at 140 and 190  $^\circ\text{C}$  for 2 days, showing the isomerisation of *rtct* to *rtct*-isomer. (b)



**Figure S7.** The  $^1\text{H}$  NMR spectrum of compound **1** in  $\text{DMSO-}D_6$  after UV irradiation for 2 days at 254 nm and heated under hydrothermal conditions at 120 °C for 2 days, showing the isomerisation of *rttt* to *rcct* and *rtct*-isomers together with the products of the thermal ring cleavage (Maleic and Fumaric acid) and traces of hydroamination product.

