------ Supporting Information ------

Scalable preparation and property investigation of a *cis*-cyclobutane-1,2dicarboxylic acid from β -*trans*-cinnamic acid

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1. Material and methods

Commercial trans-Cinnamic acid (Alfa Aesar, 99+%, Catalog No.: A13538, Lot: U08D059 and 10162461, Matheson Coleman & Bell Manufacturing Chemists, Catalog No. or Lot: CX1690, and Acros Organic, 98+%, Catalog No.: 158575000, Lot #: A0356181.) was used as received. All solvents, purchased from Alfa Aesar, Aldrich, and Acros Organics, were used without further purification. The irradiation source was EIKO 15526 F15T8/BL Fluorescent Blacklight Bulb (wavelength: 365 nm). No quartz glassware is required for the photoreaction. The round-bottom flask, beaker, Erlenmeyer flask, and glass vial (XB15288-65) used in the photoreaction were purchased from Chemglass and VWR. Melting points were measured on a DigiMelt MPA160 apparatus from Stanford Research Systems (SRS) without correction. ¹H and ¹³C{¹H} NMR data were recorded on a Bruker AVANCE 500 MHz spectrometer. ¹H NMR data were reported as follows: chemical shift (ppm), s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, m = multiplet, coupling constant (Hz), and integration. FT-IR spectra were acquired on a Thermo Scientific Nicolet iS5 FT-IR spectrometer. UV-Vis spectra were recorded on a Beckman DU400 UV/vis spectrometer. Calorimetric curves were recorded on a Perkin Elmer Jade DSC at a ramping rate of 10 °C/min. Thermogravimetric analysis (TGA) was performed on a TA SDT Q600 instrument at a ramping rate of 20 °C/min in argon or nitrogen atmosphere. Single crystal X-ray data were recorded on a Bruker Apex X-Ray Diffractometer with Mo K α (λ = 0.71073 Å). X-ray Powder Diffraction (XRD) was performed on an X'PERT-PRO X-ray diffractometer (PANalytical, Netherlands) equipped with a 3 KW copper tube X-ray generator of $\lambda = 0.1541$ nm under 40 mA and 45 KV. Spectra were collected at room temperature in a 20 range of 3~35° at a scanning rate of 3°/min.

1.1. Preparation of β -trans-cinnamic acid and CBDA-4

Commercial trans-cinnamic acid (5.0 g) was added into a 20 mL glass vial. The vial was covered with a small piece of glass and placed in a preheated oven at 180 °C for 30 minutes. The vial containing the melted *trans*- cinnamic acid was moved to a fume hood and allowed to cool down to room temperature. The trans-cinnamic acid in the vial was then dissolved by adding 5 mL DMF. The brownish DMF solution was sonicated for 30 mins and then filtered. The filtrate was added dropwise for 10 mins into a 500 mL round-bottom flask containing 240 mL of ice-water with vigorous stirring, or injected into the ice-water with stirring by using a syringe. It is important that the DMF solution must be added directly into the water, rather than added onto the ice that floats on the top of the water when it was not stirred fast enough. At this step, the trans-cinnamic acid was precipitated out as a white powder, which was the β crystal form (m.p.: 133.2 – 134.0 °C) suspended in the ice-water mixture, confirmed by PXRD. About 100 mL ice was then added into the mixture and the flask was placed between 6 blacklight bulbs for irradiation (Two round-bottom flasks, 5.0 g x 2 cinnamic acid, can be irradiated at the same time as shown in Figure S12a). The lamps should be kept as close to the flask as possible and the reaction mixture should be stirred vigorously. The ice in the mixture melted gradually in about 3 hours, and the photoreaction was further carried out for 68 hours with stirring at room temperature and monitored by ¹H NMR.

Afterwards, the mixture was filtered and washed with 5 mL of ethanol to give CBDA-4 (4.43 g, 89 %) as a white powder. m.p. 207.6 – 208.6 °C. ¹H NMR (500 MHz, DMSO-*d*₆): δ 12.46 (s, 2H), 6.99 ~ 7.09 (m, 10H), 4.22 (d, *J* = 4.5 Hz, 2H), 3.81 (d, *J* = 4.5 Hz, 2H) ppm; ¹³C NMR (125 MHz, DMSO-*d*₆): δ 174.3, 139.6, 128.2, 128.0, 126.2, 44.8, 42.9.

The ¹H NMR and ¹³C spectra of the residue from the filtrate of the CBDA-4 photoreaction were also collected after solvent evaporation and are shown in the end of Figure S2. The residue contained a small amount of *trans*-cinnamic acid, *cis*-cinnamic acid, DMF, and CBDA-4.

For the 50 g scale photoreaction, *trans*-cinnamic acid was added into a 250 mL Erlenmeyer flask. The flask was covered with a small piece of glass and placed in a preheated oven at 180 °C for 30 minutes. The flask containing the melted trans-cinnamic acid was moved to a fume hood and allowed to cool down to room temperature. The trans-cinnamic acid in the flask was then dissolved by adding 50 mL DMF. The brownish DMF solution was sonicated for 30 mins and then filtered. The filtrate was added dropwise for 30 mins into a 4000 mL beaker containing 2400 mL of ice-water with vigorous stirring. It is important that the DMF solution must be added directly into the water, rather than added onto the ice that floats on the top of the water when it was not stirred fast enough. At this step, the *trans*-cinnamic acid was precipitated out as a white powder, which was the β crystal form suspended in the ice-water mixture. About 1000 mL ice was then added into the mixture and the beaker was placed between 16 blacklight bulbs for irradiation (A picture of the reaction is shown in Figure S12b). The lamps should be kept as close to the flask as possible and the reaction mixture should be stirred vigorously. The ice in the mixture melted gradually in about 3 hours, and the photoreaction was further carried out for about 7 days with stirring at room temperature and monitored by ¹H NMR. Afterwards, the mixture was filtered to give CBDA-4 (42.3 g, 85 %) as a white powder. In case the powder contains a tiny amount of unreacted trans-cinnamic acid, it can be washed with a small amount of ethanol, in which transcinnamic acid has much higher solubility than CBDA-4.

1.2. A control experiment

Commercial *trans*-cinnamic acid (100 mg) was dissolved in 20 mL of acetonitrile. After 20 mins of sonication, the mixture was filtered into a 20 mL glass vial. The vial was capped and placed in front of six blacklight bulbs. The solution was irradiated for four days with stirring. Next, the mixture was concentrated, and the residue was checked by using NMR. ¹H and ¹³C NMR spectra showed a mixture of *trans*-cinnamic acid and *cis*-cinnamic acid. There was no CBDA-4 or CBDA-1 formed (Figure S4).

1.3.Thermocleavage experiments

Experiment I: A sample of 10 mg CBDA-4 was placed in a NMR tube. The NMR tube with the sample was put into a sand-bath and heated to 300 °C for 30 minutes and then cooled down to room temperature. ¹H NMR spectrum of this crude sample of the thermocleavage reaction was taken directly with DMSO- d_6 as a solvent showing that the conversion to *trans*-cinnamic acid was about 85 % (Figure S5 top).

Experiment II: A sample of 0.5 g CBDA-4 was scattered into a sublimation apparatus with water condenser. The sublimation apparatus was put into a sand-bath and heated to 300 °C under argon protection. After 15 minutes, the transparent crystals were scraped off the water condenser

to give *trans*-cinnamic acid (0.3 g, 60%). The residue was confirmed as *trans*-cinnamic acid and several other decomposed products (Figure S5 bottom).

1.4. Recrystallization of CBDA-4

A sample of CBDA-4 (100 mg) was dissolved in 10 mL of acetonitrile and two drops of acetic acid. The mixture was sonicated for 30 mins and filtered into a 20 mL glass vial. The vial was placed uncovered into a fume hood. One week later, high-quality single crystals were obtained as colorless plates.

1.5. Powder-XRD sample preparation

The white precipitate from the procedure described in section 1.1 of the supporting information was filtered and air-dried. PXRD confirmed that it is the "head-to-head" packing of *trans*-cinnamic acid, which is β -*trans*-cinnamic acid (Figure S8).

All four commercial *trans*-cinnamic acid products used (Alfa Aesar, 99+%, Catalog No.: A13538, Lot: U08D059 and 10162461, Matheson Coleman & Bell Manufacturing Chemists, Catalog No. or Lot: CX1690, and Acros Organic, 98+%, Catalog No.: 158575000, Lot #: A0356181) were confirmed as α -trans-cinnamic acid.

1.6. Melting point measurement

Melting points were measured on a DigiMelt MPA160 apparatus from Stanford Research Systems (SRS) at a heating rate of 2 °C/min. Averages of three experiments were reported in the manuscript and the details are listed in the following table. The melting points of β -trans-cinnamic acid and α -trans-cinnamic acid were measured using the same DigiMelt MPA160 apparatus.

Entry	<i>β-trans</i> -cinnamic acid (°C)	<i>α-trans</i> -cinnamic acid (°C)	CBDA-4 (°C)
1	133.1 - 133.7	133.6 - 134.5	207.8 - 208.8
2	133.4 - 134.3	133.4 - 134.4	207.3 - 208.2
3	133.2 - 134.1	133.5 - 134.2	207.8 - 208.9
Average	133.2 – 134.0	133.5 – 134.4	207.6 - 208.6

- 2. Spectra of NMR, FT-IR and UV-Vis
- 2.1. NMR spectra of *trans*-cinnamic acid, CBDA-4, and the residue from the filtrate



Figure S1 ¹H (top) and ¹³C (bottom) NMR spectra of the starting material *trans*-cinnamic acid in DMSO- d_6 .



Figure S2 ¹H (top), ¹³C (middle), and DEPT135 (bottom) NMR spectra of CBDA-4 in DMSO- d_6 .



Figure S2 continued DEPT90 (top) and COSY (bottom) NMR spectra of CBDA-4 in DMSO- d_6 .



Figure S2 continued ¹H (top) and ¹³C (bottom) NMR spectra of the residue from the filtrate of the CBDA-4 photoreaction in DMSO- d_6 . The residue from the procedure described in section 1.1 of the supporting information contained a small amount of *trans*-cinnamic acid, *cis*-cinnamic acid, DMF, and CBDA-4.

2.2. NMR spectra of CBDA-1 and isomerization of *trans*-cinnamic acid for comparison



Figure S3 ¹H (top) and ¹³C (bottom) NMR spectra of CBDA-1 in DMSO-*d*₆ for comparison.



Figure S4 ¹H (top) and ¹³C (bottom) NMR of *trans*- and *cis*-cinnamic acid in DMSO-*d*₆ from the control experiment for comparison.





Figure S5 The crude ¹H NMR spectrum of the mixture after thermocleavage reaction of CBDA-4 showing about 85 % conversion to *trans*-cinnamic acid (top). The ¹H NMR spectrum of the thermocleavage reaction residue after sublimation, which contains *trans*-cinnamic acid and several other decomposed products (bottom). The spectra were taken with DMSO- d_6 at room temperature.



2.4. FT-IR spectra of β -trans-cinnamic acid, α -trans-cinnamic acid, CBDA-4, and CBDA-1

Figure S6 IR spectra of β -trans-cinnamic acid (top) and α -trans-cinnamic acid (bottom).



Figure S6 continued IR spectra of CBDA-4 (top) and CBDA-1 (bottom) for comparison.

2.5. UV-Vis spectrum of CBDA-4



Figure S7 UV-Vis absorbance of CBDA-4.

3. Crystal data of CBDA-4



 Table S1. Crystal data of CBDA-4

Crystal	CBDA-4
CCDC #	1857653
Formula	$C_{18}H_{16}O_4$
FW	296.31
Crystal size [mm]	$0.600 \times 0.450 \times 0.300$
Crystal system	Monoclinic
Space group	$P2_1/c$
a (Å)	16.2829(11)
b (Å)	5.5494(3)
c (Å)	16.4604(10)
a (°)	90
β (°)	113.418(4)
γ (°)	90
$V(A^3)$	1364.85(15)
Temp. (K)	100(2)
Ζ	4
ρcalc (g·cm⁻³)	1.442
μ (mm ⁻¹)	0.102
Radiation type	MoKa ($\lambda = 0.71073$)
F(000)	624
Reflections collected	10087
Independent reflections	2451
R1/wR2 (I $\geq 2\sigma$) (%)	3.30/12.84
R1/wR2 (all data) (%)	3.62/13.95



Figure S8 Powder-XRD of β -trans-cinnamic acid and α -trans-cinnamic acid. Simulation data were obtained from X-ray single crystal data of β -trans-cinnamic acid^a and α -trans-cinnamic acid^b

a). I. Abdelmoty, V. Buchholz, L. Di, C. Guo, K. Kowitz, V. Enkelmann, G. Wegner and B. M. Foxman, *Cryst. Growth Des.*, 2005, **5**, 2210-2217.

b). Z. Wang, B. Miller, M. Mabin, R. Shahni, Z. D. Wang, A. Ugrinov and Q. R. Chu, *Sci. Rep.*, 2017, 7, 13704.

5. DSC curves of β -trans-cinnamic acid and α -trans-cinnamic acid



Figure S9 DSC curves of β -trans-cinnamic acid and α -trans-cinnamic acid. DSC was recorded from 30 °C to 170 °C with a heating rate of 10 °C ·min⁻¹ under N₂ atmosphere.

6. DSC data of CBDA-4



Figure S10 DSC curve of CBDA-4 to compare with the one stopped at 300 °C in the manuscript. DSC was recorded from 30 °C to 400 °C with a heating rate of 10 °C \cdot min⁻¹ under N₂ atmosphere.

7. TGA and DTG curves of CBDA-4



Figure S11 TGA and DTG curves of CBDA-4 recorded from 50 °C to 600 °C with a heating rate of 20 °C \cdot min⁻¹ under N₂ atmosphere.

8. Images of the photoreactions



Figure S12 (a) Image of the photoreaction (5 g x 2 scale) using 6 blacklight bulbs and two roundbottom flasks. (The lamps should be kept as close to the flask as possible and the reaction mixture should be stirred vigorously.)



Figure S12 continued (b) Image of the 50 g scale photoreaction using 16 blacklight bulbs and a 4000 mL beaker (four bulbs in front of the beaker were removed in this picture for clarity).