

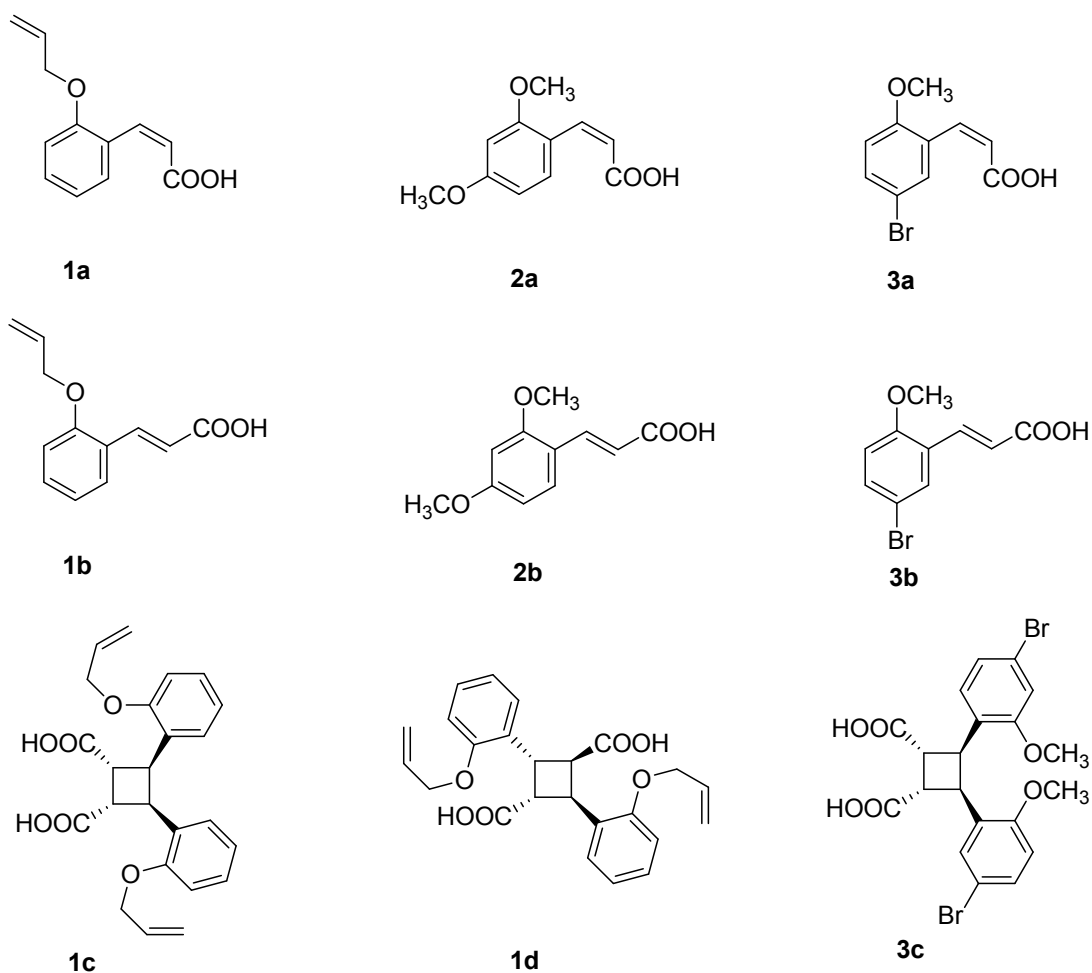
Electronic Supplementary Information

Solid-state photochemistry of *cis*-cinnamic acids: A competition between [2+2] addition and *cis-trans* isomerization

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Scheme S1: Structure of molecules investigated in this study.

Experimental

Synthesis of 2-allyloxy-*cis*-cinnamic acid (**1a**)¹

Powdered potassium hydroxide (5.76 g, 102.64 mmol) was added to a solution of coumarin (1 g, 6.843 mmol) dissolved in 20 mL of DMSO and the mixture was stirred at room temperature for 2 h under nitrogen atmosphere. Allylbromide (0.59 mL, 6.843 mmol) was added to the reaction mixture over a period of one min. and continued the stirring for 10 min. The mixture was poured into ice water and then acidified (pH <3) with hydrochloric acid. The solid was filtered, air dried and recrystallized from hexanes.

Yield 62%; White solid; Known compound.² m.p. 82-84 °C (lit. 82-83 °C)

¹H NMR (500 MHz, DMSO-d₆) δ: 4.59 (d, J=5.1 Hz, 2H), 5.26 (dd, J=10.6, 1.3 Hz, 1H), 5.40 (dd, J=17.3, 1.6 Hz, 1H), 5.95 (d, J=12.5 Hz, 1H), 6.01-6.08 (m, 1H), 6.90 (t, J=7.5 Hz, 1H), 6.99 (d, J=8.3 Hz, 1H), 7.05 (d, J=12.5 Hz, 1H), 7.27-7.31 (m, 1H), 7.46-7.47 (m, 1H), 12.32 (s, 1H)

¹³C NMR (125 MHz, DMSO-d₆) δ: 68.9, 112.4, 117.8, 120.3, 121.6, 124.5, 130.6, 130.7, 134.0, 137.1, 156.2, 167.8

HRMS (ESI) calcd for C₁₂H₁₁O₃ [M-H]⁻203.0714, found 203.0723.

Synthesis of 2,4-dimethoxy-*cis*-cinnamic acid (2a)¹

Powdered potassium hydroxide (4.78 g, 85.2 mmol) was added to a solution of 7-methoxycoumarin (1 g, 5.6802 mmol) dissolved in 20 mL of DMSO and the mixture was stirred at room temperature for 2 h under nitrogen atmosphere. Methyl iodide (0.354 mL, 5.6802 mmol) was added to the reaction mixture over a period of one min. and continued the stirring for 10 min. The mixture was poured into ice water and then acidified (pH <3) with hydrochloric acid. The solid was filtered, air dried and recrystallized from ethanol.

Yield 76%; White solid; Known compound.³ m.p. 142-144 °C

¹H NMR (500 MHz, DMSO-d₆) δ: 3.79 (s, 3H), 3.80 (s, 3H), 5.80 (d, J=12.6 Hz, 1H), 6.51 (dd, J=8.6, 2.4 Hz, 1H), 6.56 (d, J=2.3 Hz, 1H), 6.97 (d, J=12.6 Hz, 1H), 7.63 (d, J=8.6 Hz, 1H), 12.17 (s, 1H)

¹³C NMR (125 MHz, DMSO-d₆) δ: 55.8, 55.9, 98.2, 105.1, 116.7, 118.9, 131.9, 136.8, 158.9, 161.9, 168.0

HRMS (ESI) calcd for C₁₁H₁₁O₄ [M-H]⁻207.0663, found 207.0673.

Synthesis of 5-bromo-2-methoxy-*cis*-cinnamic acid (3a)¹

6-bromocoumarin was synthesized following the literature procedure.⁴

Powdered potassium hydroxide (3.74 g, 66.6548 mmol) was added to a solution of 6-bromocoumarin (1 g, 4.4437 mmol) dissolved in 20 mL of DMSO and the mixture was stirred at room temperature for 2 h under nitrogen atmosphere. Methyl iodide (0.277 mL, 4.4437 mmol) was added to the reaction mixture over a period of one min. and continued the stirring for 10 min. The mixture was poured into ice water and then acidified (pH <3) with hydrochloric acid. The solid was filtered, air dried and recrystallized from ethanol.

Yield 53%; White solid; Known compound.² m.p. 161-162 °C (lit. 161-162 °C)

¹H NMR (500 MHz, DMSO-d₆) δ: 3.78 (s, 3H), 5.99 (d, J=12.5 Hz, 1H), 6.94 (d, J=12.5 Hz, 1H), 6.99 (d, J=8.9 Hz, 1H), 7.46-7.49 (m, 1H), 7.59 (d, J=2.2 Hz, 1H), 12.48 (s, 1H)

¹³C NMR (125 MHz, DMSO-d₆) δ: 56.3, 111.6, 113.6, 122.9, 126.5, 132.7, 132.9, 135.6, 156.5, 167.5

HRMS (ESI) calcd for C₁₀H₈BrO₃ [M-H]⁻254.9662, found 254.9675.

Synthesis of 2-allyloxy-*trans*-cinnamic acid (1b)

Powdered potassium hydroxide (5.127 g, 91.3743 mmol) was added to a solution of 2-hydroxy-*trans*-cinnamic acid (1 g, 6.0916 mmol) dissolved in 20 mL of DMSO and the mixture was stirred at room temperature for 2 h under nitrogen atmosphere. Allyl bromide (0.527 mL, 6.0916 mmol) was added to the reaction mixture over a period of one min. and continued the stirring for 10 min. The mixture was poured into ice water and then acidified (pH <3) with hydrochloric acid. The solid was filtered, air dried and recrystallized from ethanol and water (1:1) mixture.

Yield 72%; White solid; Known compound⁵. m.p. 121-123 °C (lit. 121-123 °C)

¹H NMR (500 MHz, DMSO-d₆) δ: 4.66 (d, J=5 Hz, 2H), 5.29 (dd, J=10.5, 1.3 Hz, 1H), 5.42 (dd, J=17.2, 1.5 Hz, 1H), 6.05-6.13 (m, 1H), 6.52 (d, J=16.2 Hz, 1H), 6.96 (t, J=7.5 Hz, 1H), 7.08 (d, J=8.3 Hz, 1H), 7.36-7.39 (m, 1H), 7.68-7.69 (m, 1H), 7.86 (d, J=16.2 Hz, 1H), 12.34 (s, 1H)

¹³C NMR (125 MHz, DMSO-d₆) δ: 69.1, 113.3, 118.2, 119.8, 121.3, 123.1, 128.9, 132.1, 133.9, 139.1, 157.1, 168.4

HRMS (ESI) calcd for C₁₂H₁₁O₃ [M-H]⁻203.0714, found 203.0723.

Synthesis of 2,4-dimethoxy-*trans*-cinnamic acid (2b)

2,4-dimethoxy-*trans*-cinnamic acid was synthesized via two steps. In the first step, 7-methoxycoumarin was converted to 2-hydroxy-4-methoxy-*trans*-cinnamic acid following the literature procedure⁶. In the second step, 2-hydroxy-4-methoxy-*trans*-cinnamic acid was then converted to 2,4-dimethoxy-*trans*-cinnamic acid using the procedure below.

Powdered potassium hydroxide (4.34 g, 77.2479 mmol) was added to a solution of 2-hydroxy-4-methoxy-*trans*-cinnamic acid (1 g, 5.1499 mmol) dissolved in 20 mL of DMSO and the mixture was stirred at room temperature for 2 h under nitrogen atmosphere. Methyl iodide (0.32 mL, 5.1499 mmol) was added to the reaction mixture over a period of one min. and continued the stirring for 10 min. The mixture was poured into ice water and then acidified (pH <3) with hydrochloric acid. The solid was filtered, air dried and recrystallized from ethanol.

Yield 56%; White solid; Known compound refer to literature reference⁷. m.p. 187-189 °C ;

¹H NMR (500 MHz, DMSO-*d*₆) δ: 3.82 (s, 3H), 3.86 (s, 3H), 6.37 (d, J=16.1 Hz, 1H), 6.57 (dd, J=8.6, 2.3 Hz, 1H), 6.61 (d, J=2.3 Hz, 1H), 7.61 (d, J=8.6 Hz, 1H), 7.75 (d, J=16.1 Hz, 1H), 12.09 (s, 1H);

¹³C NMR (125 MHz, DMSO-*d*₆) δ: 55.9, 56.2, 98.8, 106.6, 115.9, 116.8, 130.4, 139.2, 159.8, 162.9, 168.6;

HRMS (ESI) calcd for C₁₁H₁₁O₄ [M-H]⁻207.0663, found 207.0676.

Synthesis of 5-bromo-2-methoxy-*trans*-cinnamic acid (3b)

5-bromo-2-hydroxy-*trans*-cinnamic acid was synthesized by treating 5-bromo-salicylaldehyde with Wittig reagent⁸ followed by base hydrolysis. 5-bromo-2-hydroxy-*trans*-cinnamic acid was converted to 5-bromo-2-methoxy-*trans*-cinnamic acid by using the procedure below.

Powdered potassium hydroxide (3.463 g, 61.7157 mmol) was added to a solution of 5-bromo-2-hydroxy-*trans*-cinnamic acid (1 g, 4.1144 mmol) dissolved in 20 mL of DMSO and the mixture was stirred at room temperature for 2 h under nitrogen atmosphere. Methyl iodide (0.256 mL, 4.1144 mmol) was added to the reaction mixture over a period of one min. and continued the stirring for 10 min. The mixture was poured into ice water and then acidified (pH < 3) with hydrochloric acid. The solid was filtered, air dried and recrystallized from ethanol.

Yield 80%; White solid; Known compound refer to literature reference⁵. m.p. 226-229 °C (lit. 225-228 °C);

¹H NMR (500 MHz, DMSO-*d*₆) δ: 3.86 (s, 3H), 6.59 (d, J=16.2 Hz, 1H), 7.05 (d, 8.9 Hz, 1H), 7.54-7.56 (m, 1H), 7.73 (d, J=16.2 Hz, 1H), 7.88 (d, J=2 Hz, 1H), 12.44 (s, 1H);

¹³C NMR (125 MHz, DMSO-*d*₆) δ: 56.5, 112.8, 114.5, 121.3, 125.2, 130.9, 134.3, 137.5, 157.3, 168.1;

HRMS (ESI) calcd for C₁₀H₈BrO₃ [M-H]⁻254.9662, found 254.9678.

Isolation of dimers from reaction mixture upon completion

Dimers from reaction mixture were isolated by filtration and column purification. After irradiating the samples for longer hours (4 or 5 days), all the sample was collected and 3 ml of chloroform and 2 or 3 mL of ethyl acetate were added. Monomers (*cis*- or *trans*-cinnamic acid derivatives) and truxinic acid derivatives were dissolved in ethyl acetate but truxillic acid derivatives were insoluble. So, they were separated by filtration followed by washing and drying. Filtrate was purified by column chromatography using hexane and ethyl acetate.

2,2'-diallyloxy- α -truxillic acid (1d)

Yield 44%; White solid; Known compound.² m.p. 238-240 °C (lit. 237-238 °C) (THF and toluene (9:1) solvent mixture).

^1H NMR (500 MHz, DMSO- d_6) δ : 3.75-3.79 (m, 2H), 4.46-4.49 (m, 2H), 4.51-4.55 (m, 4H), 4.58-4.62 (m, 4H), 5.26 (dd, $J=10.6, 1.3$ Hz, 2H), 5.44 (dd, $J=17.3, 1.5$ Hz, 2H), 6.04-6.12 (m, 2H), 6.92-6.95 (m, 4H), 7.18-7.21 (m, 2H), 7.26 (d, $J=7$ Hz, 2H), 11.94 (s, 1H)

^{13}C NMR (125 MHz, DMSO- d_6) δ : 21.5, 36.6, 45.1, 68.9, 112.3, 117.2, 120.7, 125.8, 127.5, 128.2, 128.3, 128.7, 129.4, 134.4, 137.8, 156.6, 173.9

HRMS (ESI) calcd for $\text{C}_{24}\text{H}_{23}\text{O}_6$ $[\text{M}-\text{H}]^-$ 407.1500, found 407.1498.

2,2'-diallyloxy- β -truxinic acid (1c)

Yield 48%; White solid; m.p. 160-163 °C (acetone and toluene (9:1) solvent mixture);

^1H NMR (500 MHz, DMSO- d_6) δ : 3.79 (quasi d, $J=6.15$ Hz, 2H), 4.24-4.28 (m, 2H), 4.34-4.38 (m, 2H), 4.47 (quasi d, $J=6.15$ Hz, 2H), 5.22 (dd, $J=10.6, 1.5$ Hz, 2H), 5.34 (dd, $J=17.3, 1.6$ Hz, 2H), 5.94-6.01 (m, 2H), 6.65-6.71 (m, 4H), 6.96-6.99 (m, 2H), 7.05-7.07 (m, 2H), 12.27 (s, 1H);

^{13}C NMR (125 MHz, DMSO- d_6) δ : 39.6, 42.8, 68.4, 111.5, 117.1, 120.0, 127.6, 128.3, 128.5, 134.3, 156.2, 174.8;

HRMS (ESI) calcd for $\text{C}_{24}\text{H}_{23}\text{O}_6$ $[\text{M}-\text{H}]^-$ 407.1500, found 407.1487.

5,5'-dibromo-2,2'-dimethoxy- α -truxillic acid

Yield 14%; White solid; Known compound refer to literature reference² (lit. 313-314 °C)

^1H NMR (500 MHz, DMSO- d_6) δ : 3.73-3.77 (m, 8H), 4.32-4.36 (m, 2H, α, α' -H), 6.94 (d, $J=8.8$ Hz, 2H), 7.34 (d, $J=3$ Hz, 2H), 7.38-7.41 (m, 2H), 12.1 (s, 2H)

HRMS (ESI) calcd for $\text{C}_{20}\text{H}_{17}\text{Br}_2\text{O}_6$ $[\text{M}-\text{H}]^-$ 510.9397, found 510.9408.

5,5'-dibromo-2,2'-dimethoxy- β -truxinic acid (3c)

Yield 26%; White solid; Known compound refer to literature reference.² m.p. 240-243 °C (lit. 241-244 °C) (Dioxane and water (1:1) solvent mixture);

^1H NMR (500 MHz, DMSO-d_6) δ : 3.55 (s, 6H), 3.85 (quasi d, $J=6.05$ Hz, 2H), 4.3 (quasi d, $J=5.95$ Hz, 2H), 6.63 (d, $J=8.75$ Hz, 2H), 7.16-7.21 (m, 4H), 12.35 (s, 2H)

^{13}C NMR (125 MHz, DMSO-d_6) δ : 39.6, 41.9, 55.6, 111.6, 112.4, 130.3, 130.4, 131.2, 156.4, 174.7

HRMS (ESI) calcd for $\text{C}_{20}\text{H}_{17}\text{Br}_2\text{O}_6$ $[\text{M-H}]^-$ 510.9397, found 510.943.

Irradiation Procedure

Irradiations were performed using a 450 W medium pressure mercury arc lamp placed in a water-cooled Pyrex immersion well. Light emitted from a Hanovia lamp was filtered through Pyrex (transmission $\lambda \geq 290$ nm). About 4-5 mg of powdered cinnamic acid derivatives were spread uniformly between two Pyrex glass plates sealed with parafilm and irradiated. The plates were turned around every 20 min. The irradiation samples were dissolved in DMSO-d_6 and photo reactions were monitored by ^1H NMR. After completion of reaction, photo products were isolated and characterized by ^1H NMR, mass spec. and X-ray structural determination.

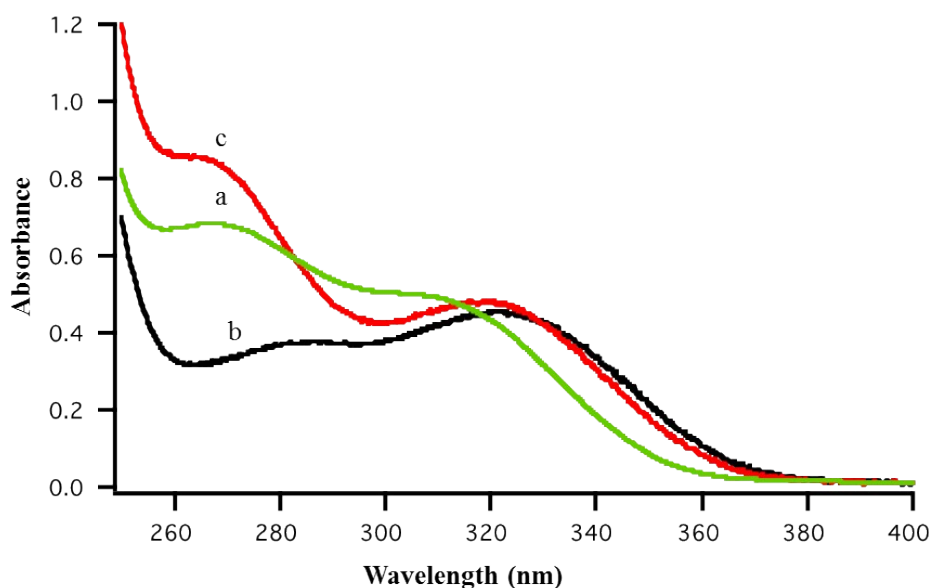


Figure S1. UV spectra of a) 2-allyloxy-*cis*-cinnamic acid (green) b) 2,4-dimethyl-*cis*-cinnamic acid (black) and c) 5-bromo-2-methoxy-*cis*-cinnamic acid (red) in chloroform (10^{-4} M).

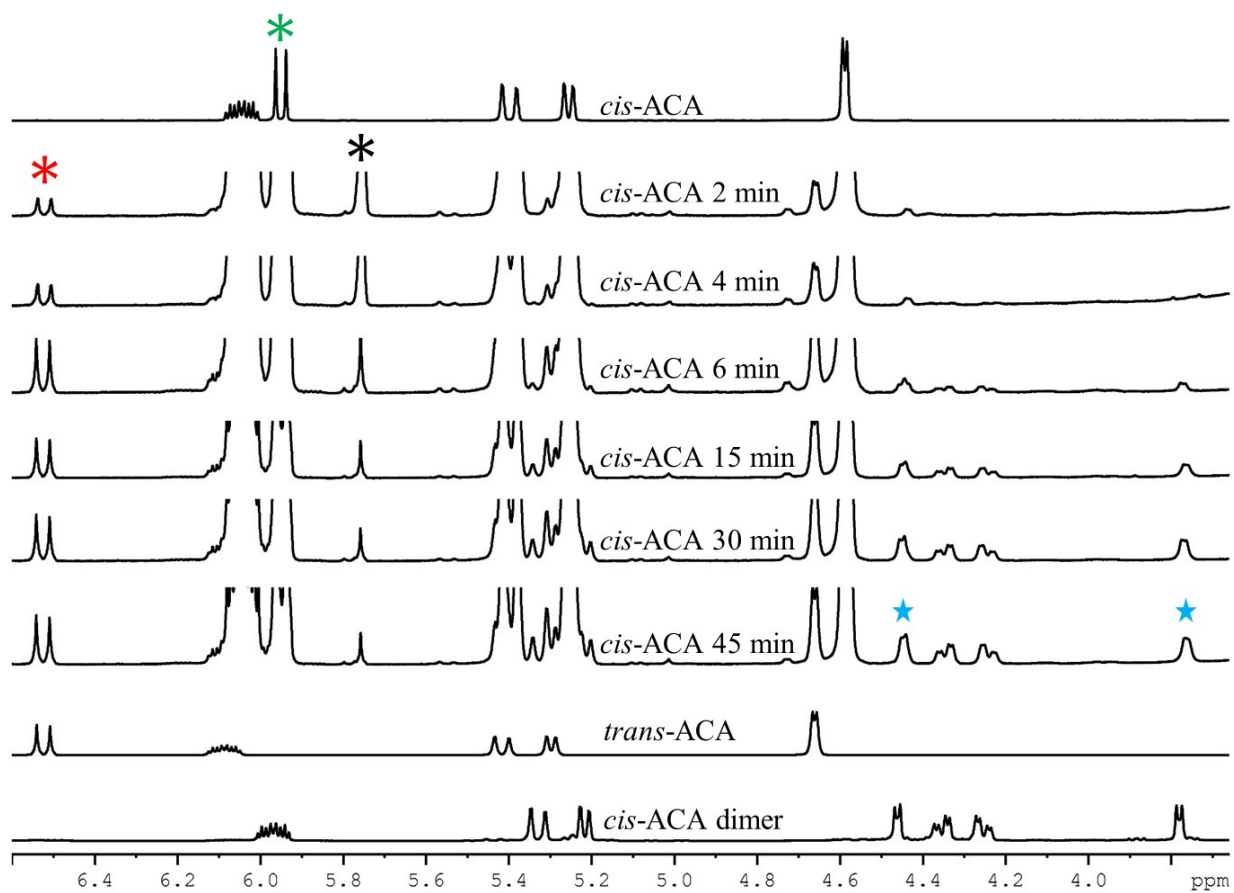


Figure S2. ^1H NMR (500 MHz, $\text{DMSO}-d_6$) of 2-allyloxy-*cis*-cinnamic acid reaction monitoring at different intervals of time. *, *, * and * indicate *cis*-proton, *trans*-proton, dichloromethane solvent traces and head to head (H-H) dimer protons respectively.

Irradiation time in minutes	<i>trans</i> -isomer formation (%)	dimer (head to head) formation (%)	<i>cis</i> -depletion (%)
0	0	0	100
2	2.5	1.2	96.3
4	3.4	1.5	95.1
6	4.4	2	93.6
15	8	5	87
30	7.5	6.2	86.3
45	8	8	84

Table T1. Percent conversion of 2-allyloxy-*cis*-cinnamic acid for various min. upon irradiation (calculated by integration of ¹H NMR peaks).

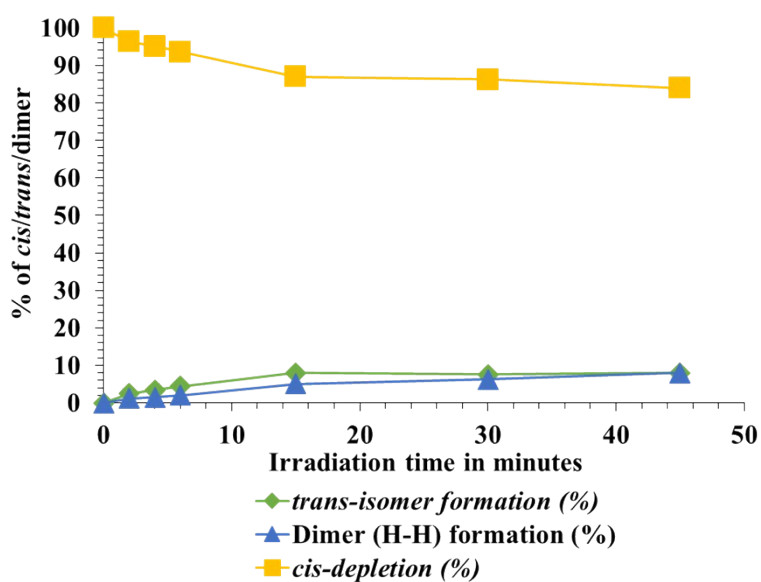


Figure S3. Graphical representation of percent conversion of 2-allyloxy-*cis*-cinnamic acid for various min. upon irradiation.

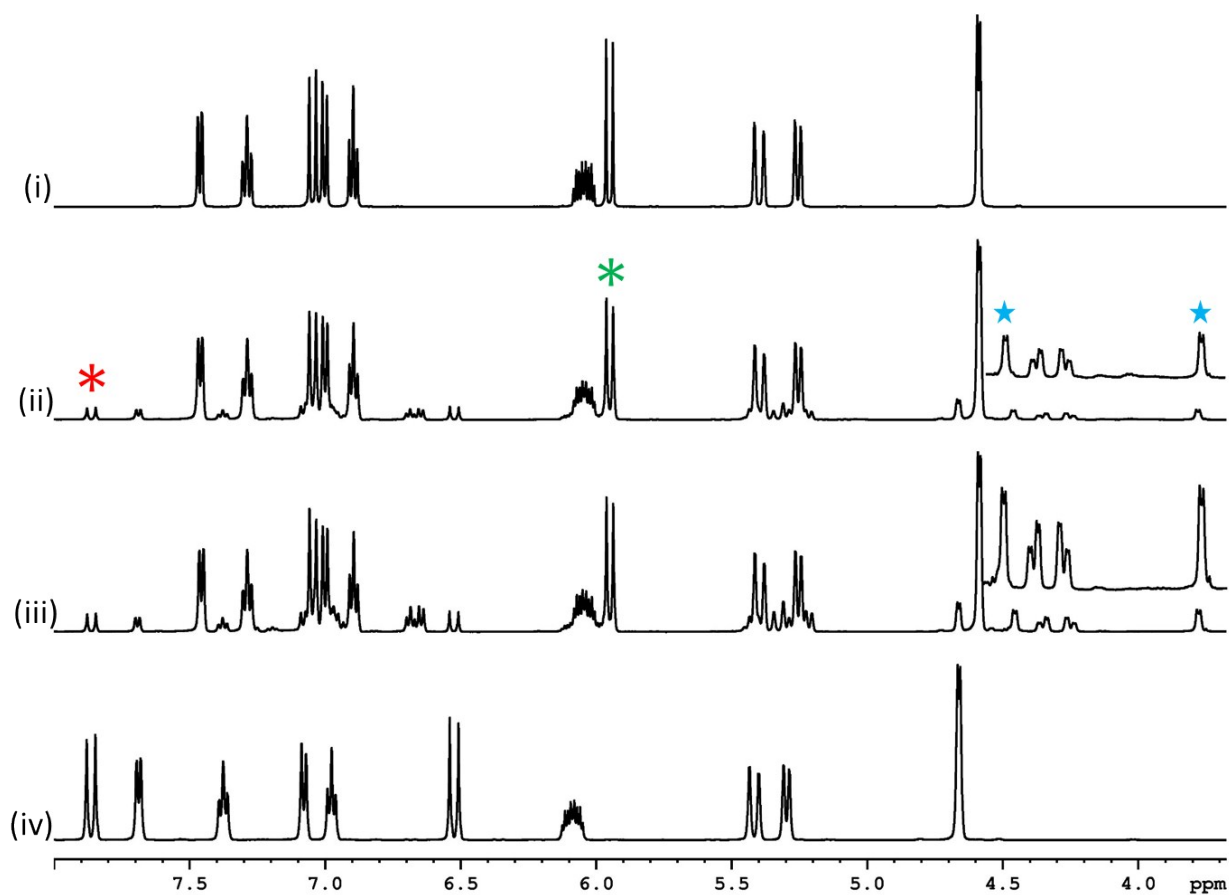


Figure S4. (i) ^1H NMR (500 MHz, $\text{DMSO-}d_6$) of 2-allyloxy-*cis*-cinnamic acid before irradiation, (ii) after irradiation of 2-allyloxy-*cis*-cinnamic acid for 6 min. (iii) after irradiation of 2-allyloxy-*cis*-cinnamic acid for 45 min. (iv) 2-allyloxy-*trans*-cinnamic acid before irradiation. \ast , \ast and \star indicate *cis*-proton, *trans*-proton and head to head (H-H) dimer protons respectively.

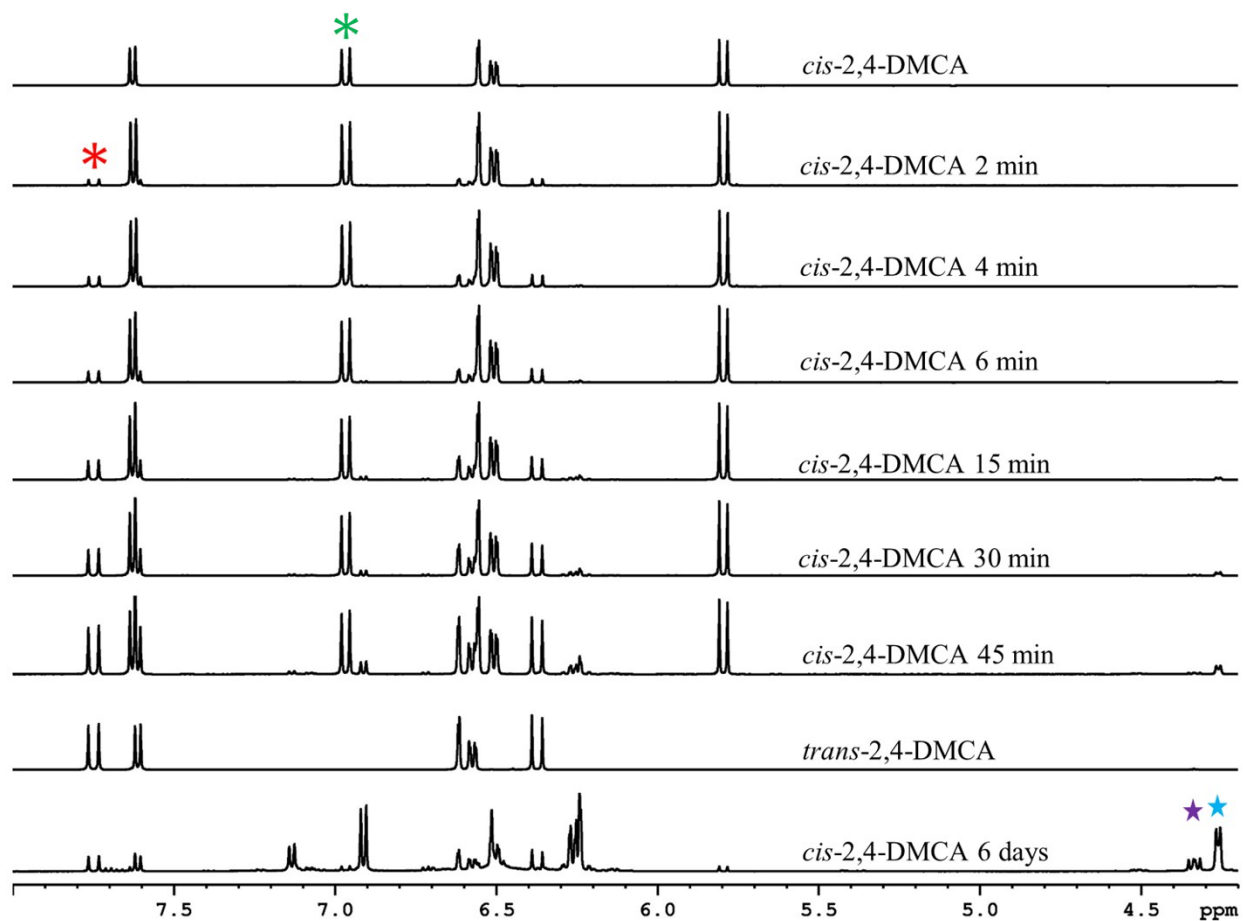


Figure S5. ^1H NMR (500 MHz, $\text{DMSO}-d_6$) of 2,4-dimethoxy-*cis*-cinnamic acid reaction monitoring at different intervals of time. \ast , \ast , \ast and \ast indicate *cis*-proton, *trans*-proton, head-head (H-H) dimer protons and head-tail (H-T) dimer protons respectively.

Irradiation time (min)	<i>trans</i> -isomer formation (%)	dimer (H-H) formation (%)	dimer (H-T) formation (%)	<i>cis</i> -isomer depletion (%)
0	0	0	0	100
2	8	0	0	92
4	13	1.7	0	85.3
6	15	2	1	82
15	23	4	1.2	71.8
30	28	6	2	64
45	36	10	3	51

Table T2. Percent conversion of 2,4-dimethoxy-*cis*-cinnamic acid for various min. upon irradiation (calculated by integration of ¹H NMR peaks).

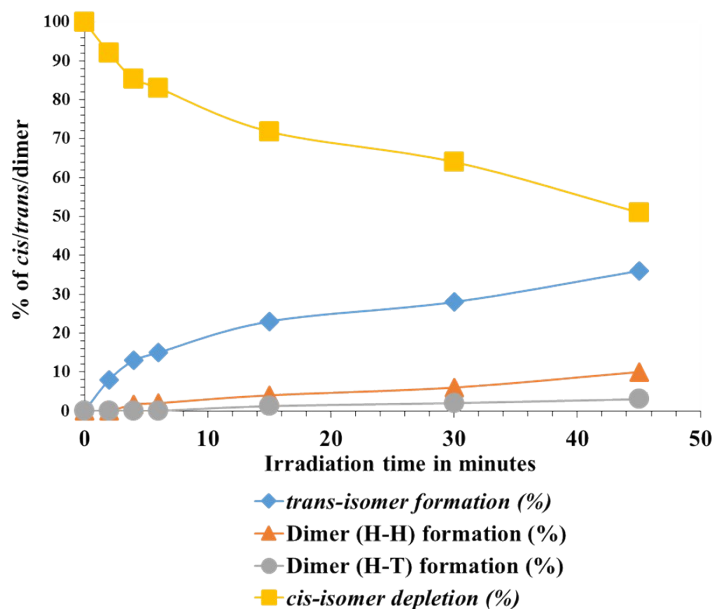


Figure S6. Graphical representation of percent conversion of 2,4-dimethoxy-*cis*-cinnamic acid for various min. upon irradiation.

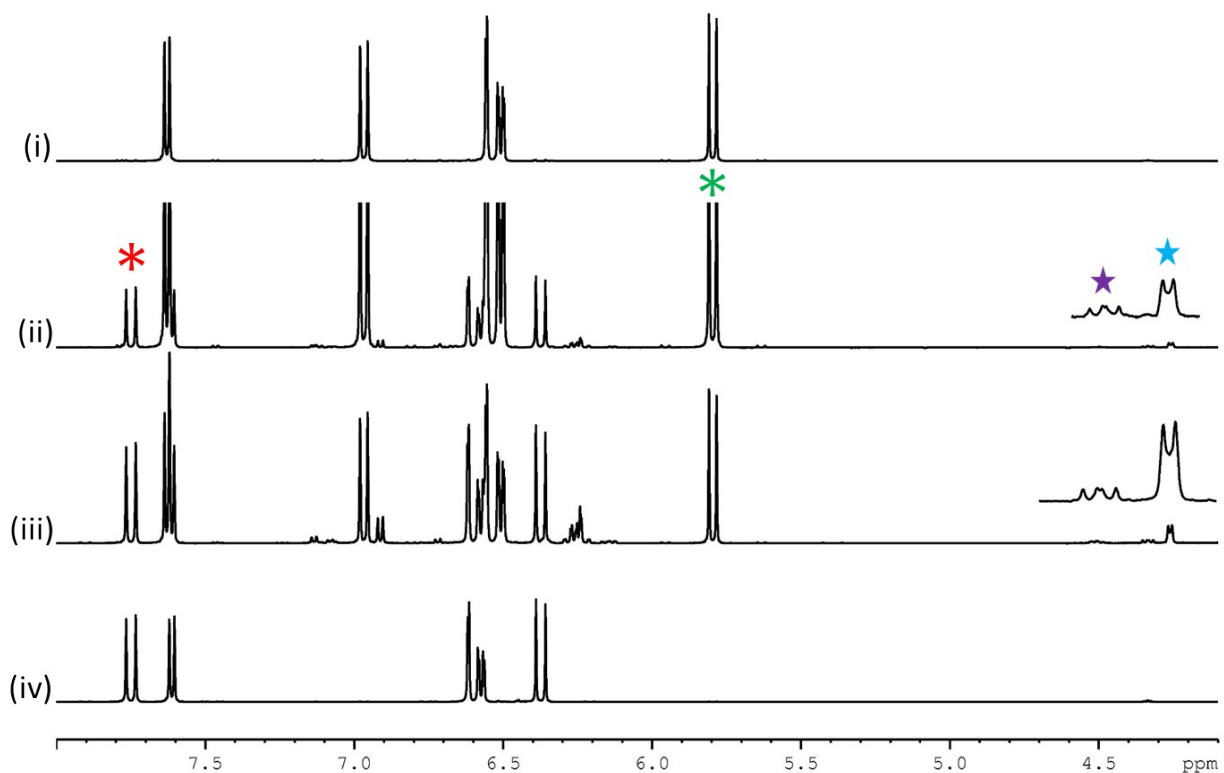


Figure S7. (i) ^1H NMR (500 MHz, $\text{DMSO-}d_6$) of 2,4-dimethoxy-*cis*-cinnamic acid before irradiation, (ii) after irradiation of 2,4-dimethoxy-*cis*-cinnamic acid for 6 min. (iii) after irradiation of 2,4-dimethoxy-*cis*-cinnamic acid for 45 min. (iv) 2,4-dimethoxy-*trans*-cinnamic acid before irradiation. \ast , \ast , \star and \star indicate *cis*-proton, *trans*-proton, head-head (H-H) dimer protons and head-tail (H-T) dimer protons respectively.

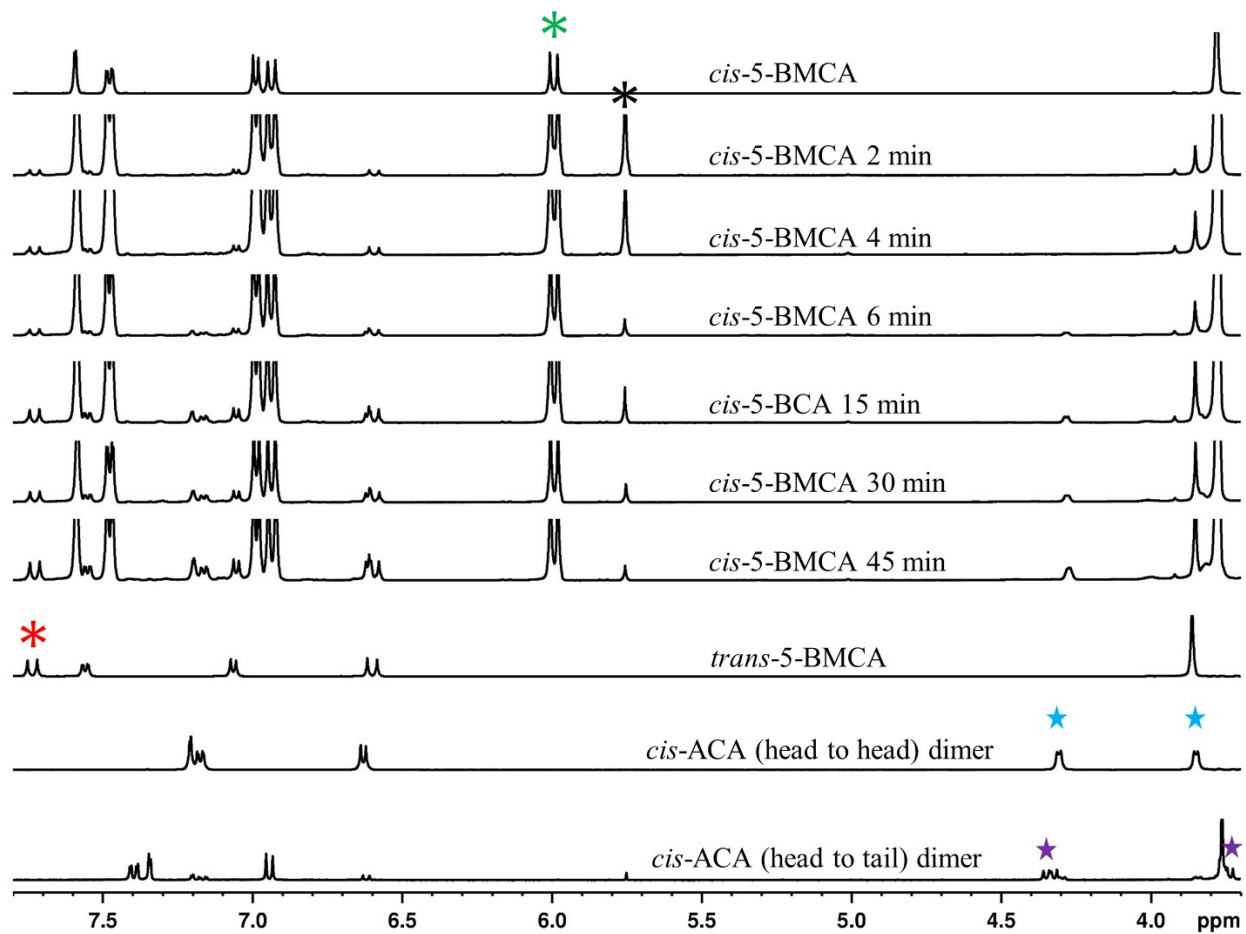


Figure S8. ^1H NMR (500 MHz, DMSO-d_6) of 5-bromo-2-methoxy-*cis*-cinnamic acid reaction monitoring at different intervals of time. ★, ★, ★, ★ and ★ indicate *cis*-proton, *trans*-proton, dichloromethane solvent traces, head to head (H-H) dimer protons and head to tail (H-T) dimer protons respectively.

Irradiation time (min)	<i>trans</i> -isomer formation (%)	dimer (H-H) formation (%)	dimer (H-T) formation (%)	<i>cis</i> -isomer depletion (%)
0	0	0	0	100
2	4	0	0	96
4	4.4	0	0	95.6
6	6	3.4	0	90.6
15	8	4.2	0	87.8
30	11	9	1.3	78.7
45	12.4	10.4	1.5	75.7

Table T3. Percent conversion of 5-bromo-2-methoxy-*cis*-cinnamic acid for various min. upon irradiation (calculated by integration of ¹H NMR peaks).

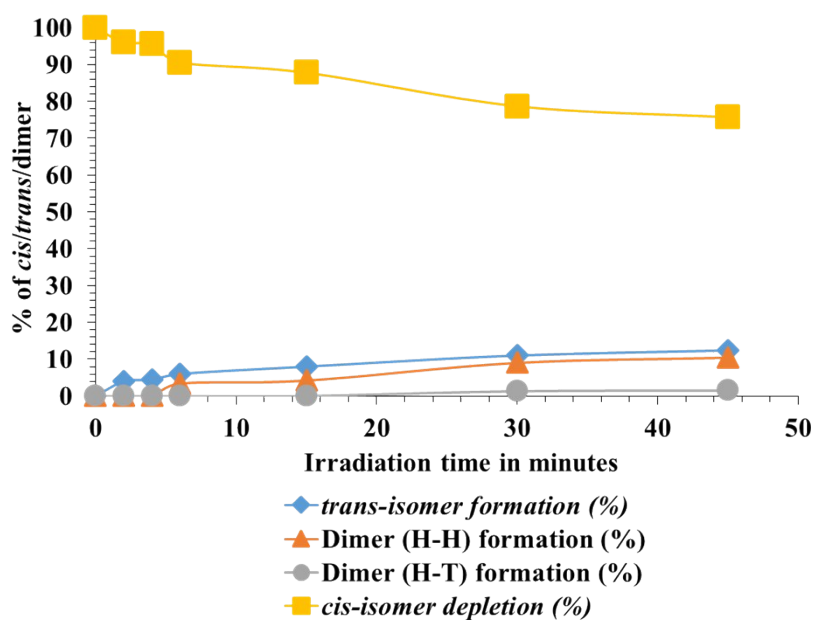


Figure S9. Graphical representation of percent conversion of 5-bromo-2-methoxy-*cis*-cinnamic acid for various min. upon irradiation.

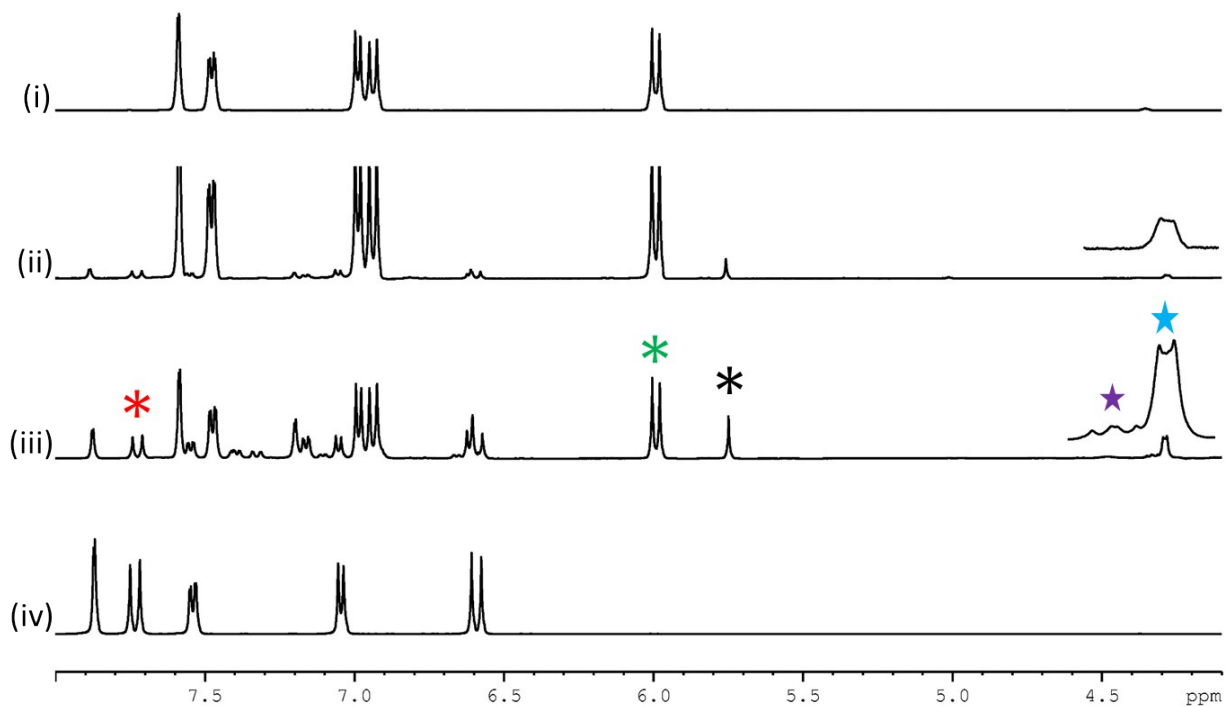


Figure S10. (i) ^1H NMR (500 MHz, $\text{DMSO-}d_6$) of 5-bromo-2-methoxy-*cis*-cinnamic acid before irradiation, (ii) after irradiation of 5-bromo-2-methoxy-*cis*-cinnamic acid for 6 min. (iii) after irradiation of 5-bromo-2-methoxy-*cis*-cinnamic acid for 45 min. (iv) 5-bromo-2-methoxy-*trans*-cinnamic acid before irradiation. \star , \star , \star , \star and \star indicate *cis*-proton, *trans*-proton, dichloromethane solvent traces, head to head (H-H) dimer protons and head to tail (H-T) dimer protons respectively.

Crystallographic Analyses

Each data crystal was glued onto the end of a thin glass fiber. X-ray intensity data were measured by using a Bruker SMART APEX2 CCD-based diffractometer using Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$).⁹ The raw data frames were integrated with the SAINT+ program by using a narrow-frame integration algorithm.⁹ Corrections for Lorentz and polarization effects were also applied with SAINT+. An empirical absorption correction based on the multiple measurement of equivalent reflections was applied using the program SADABS. All structures were solved by a combination of direct methods and difference Fourier syntheses, and refined by full-matrix least-squares on F^2 , by using the SHELXTL software package.¹⁰ All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were placed in geometrically idealized positions and included as standard riding atoms during the least-squares refinements. Crystal data, data collection parameters and results of the analyses are listed in Tables 4, 5 and 6.

Colorless single crystals of 2-allyloxy-*cis*-cinnamic acid (**1a**) suitable for x-ray diffraction analyses obtained by evaporation of hexane and 2 drops of dichloromethane, crystallized in the monoclinic crystal system. The systematic absences in the intensity data were consistent with the unique space group $P2_1/n$.

Colorless single crystals of 2-allyloxy-*trans*-cinnamic acid (**1b**) suitable for x-ray diffraction analyses obtained by evaporation of ethanol and water (1:1) solvent mixture, crystallized in the triclinic crystal system. The space group $P\bar{1}$ was assumed and confirmed by the successful solution and refinement of the structure. PLATON checkcif indicates a shorter than usual contact between riding H atoms H11 and H12B of 1.85 \AA , suggest that the reflection data are not good enough to allow reasonable location of H atoms to be determined, however, it is clear by NMR that it is an allyloxy group.

Colorless single crystals of 2,2'-diallyloxy- β -truxinic acid (**1c**) suitable for x-ray diffraction analyses obtained by evaporation of acetone and toluene (9:1) solvent mixture, crystallized in the triclinic crystal system. The space group $P\bar{1}$ was assumed and confirmed by the successful solution and refinement of the structure. Half a molecule of toluene from the crystallization solvent cocrystallized with the complex. The solvent molecule is disordered about an inversion center and was modeled using geometric restraints.

Colorless single crystals of 2,2'-diallyloxy- α -truxillic acid (**1d**) suitable for x-ray diffraction analyses obtained by evaporation of tetrahydrofuran and toluene (9:1) solvent mixture, crystallized in the triclinic crystal system. The space group $P\bar{1}$ was assumed and confirmed by the successful solution and refinement of the structure. With $Z = 1$, the molecule is crystallographically centrosymmetrical. One molecule of toluene from the crystallization solvent also cocrystallized with the complex. For the disordered toluene component, the benzene rings were refined as a rigid hexagon with $d(\text{C-C}) = 1.39 \text{ \AA}$.

Colorless single crystals of 5-bromo-2-methoxy-*cis*-cinnamic acid (**3a**) suitable for x-ray diffraction analyses obtained by evaporation of ethanol solvent, crystallized in the monoclinic crystal system. The systematic absences in the intensity data were consistent with the unique space group $P2_1/n$.

Colorless single crystals of 5-bromo-2-methoxy-*trans*-cinnamic acid (**3b**) suitable for x-ray diffraction analyses obtained by evaporation of ethanol solvent, crystallized in the monoclinic crystal system. The systematic absences in the intensity data were consistent with either of the space groups Cc or $C2/c$, the latter of which was confirmed by the successful solution and refinement of the structure.

Colorless single crystals of 5,5'-dibromo-2,2'-dimethoxy- β -truxinic acid (**3c**) suitable for x-ray diffraction analyses obtained by evaporation of dioxane and water (1:1) solvent mixture, crystallized in the triclinic crystal system. The space group $P\bar{1}$ was assumed and confirmed by the successful solution and refinement of the structure. Two molecules of water and half a molecule of dioxane is present in the asymmetric crystal unit. The dioxane molecule is slightly disordered and was not modeled using geometric restraints.

Colorless single crystals of 2,4-dimethoxy-*cis*-cinnamic acid (**2a**) and 2,4-dimethoxy-*trans*-cinnamic acid (**2b**) suitable for x-ray diffraction analyses obtained by evaporation of ethanol solvent and ethanol solvent respectively, crystallized in the triclinic crystal system. The space group $P\bar{1}$ was assumed and confirmed by the successful solution and refinement of the structure.

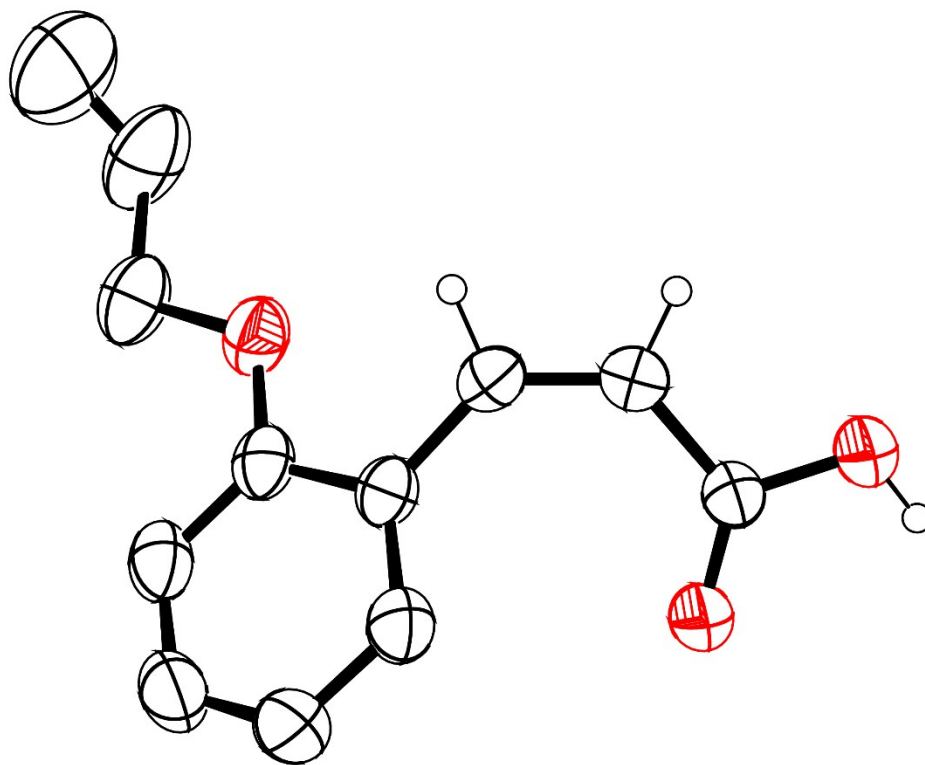


Figure S11. An ORTEP of the molecular structure of 2-allyloxy-*cis*-cinnamic acid (**1a**) showing 40 % probability thermal ellipsoids.

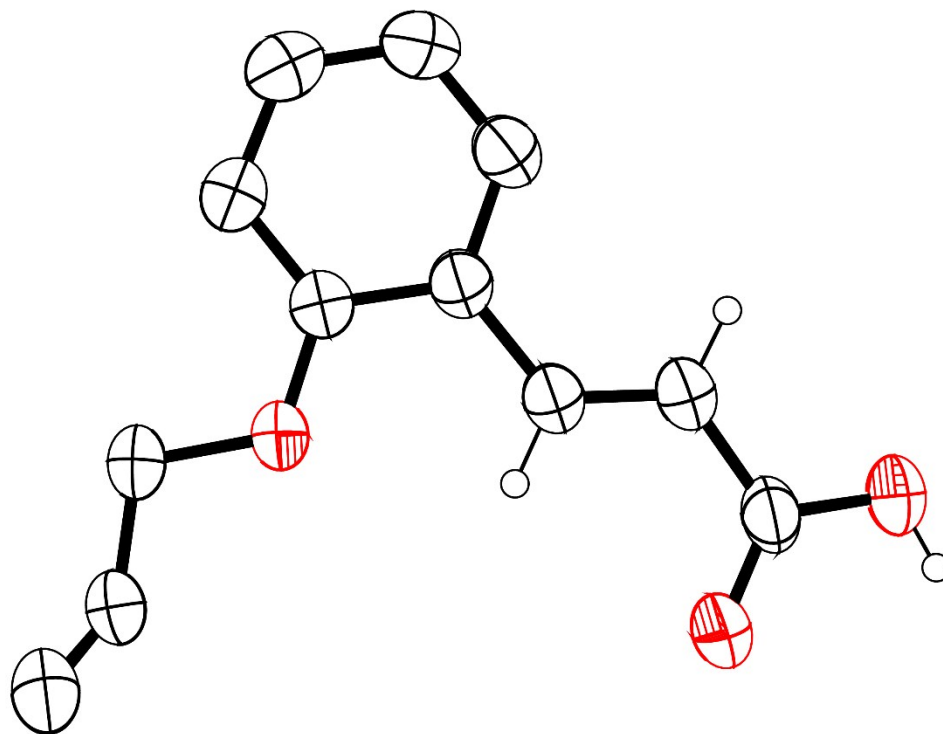


Figure S12. An ORTEP of the molecular structure of 2-allyloxy-*trans*-cinnamic acid (**1b**) showing 40 % probability thermal ellipsoids.

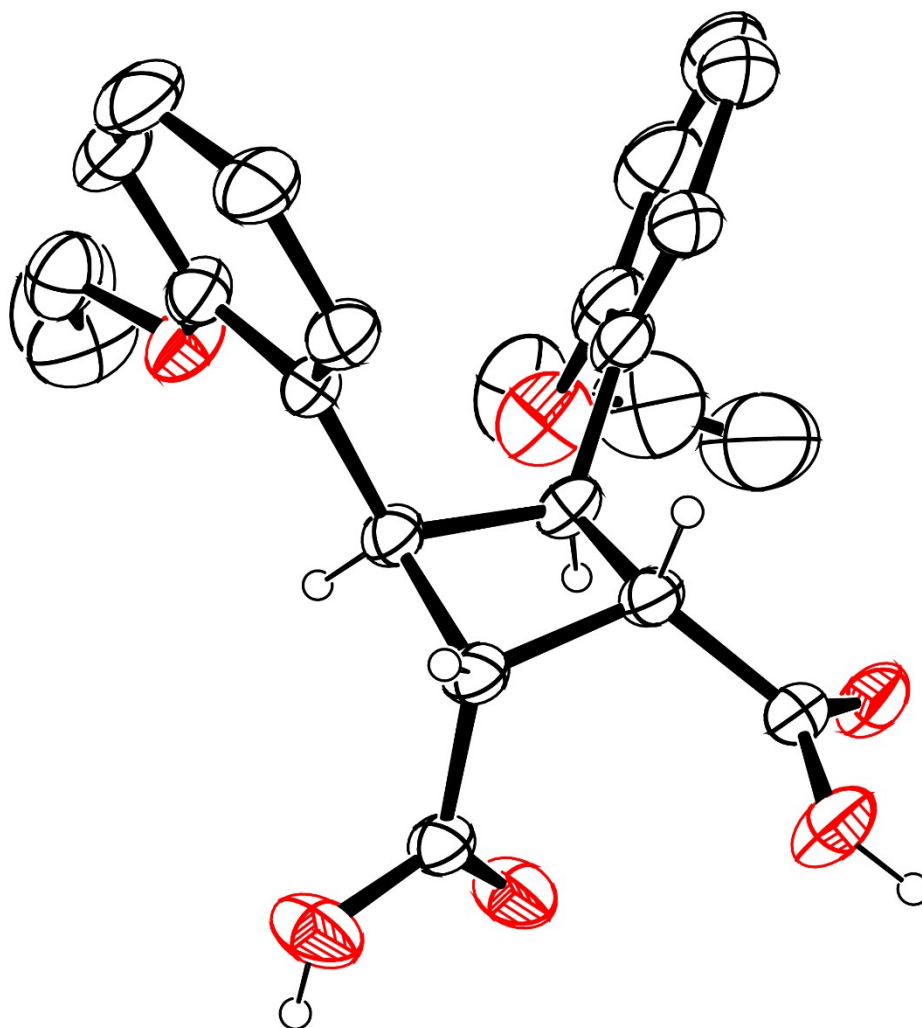


Figure S13. An ORTEP of the molecular structure of 2,2'-diallyloxy-β-truxinic acid (**1c**) showing 40 % probability thermal ellipsoids.

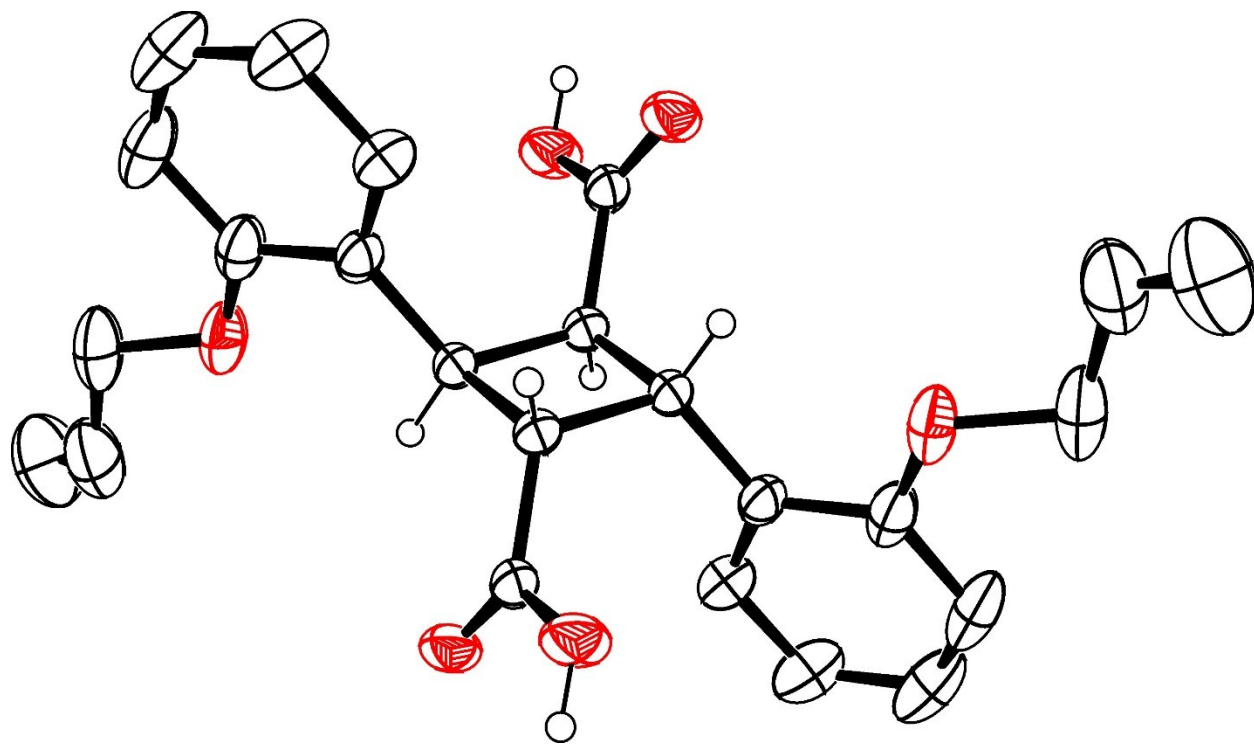


Figure S14. An ORTEP of the molecular structure of 2,2'-diallyloxy- α -truxillic acid (**1d**) showing 40 % probability thermal ellipsoids.

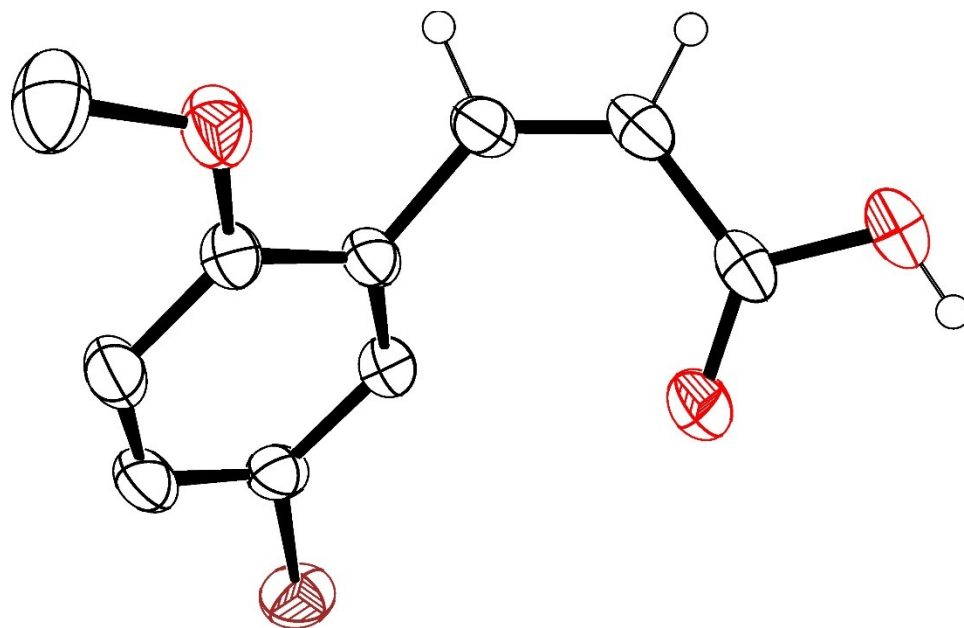


Figure S15. An ORTEP of the molecular structure of 5-bromo-2-methoxy-*cis*-cinnamic acid (**3a**) showing 40 % probability thermal ellipsoids.

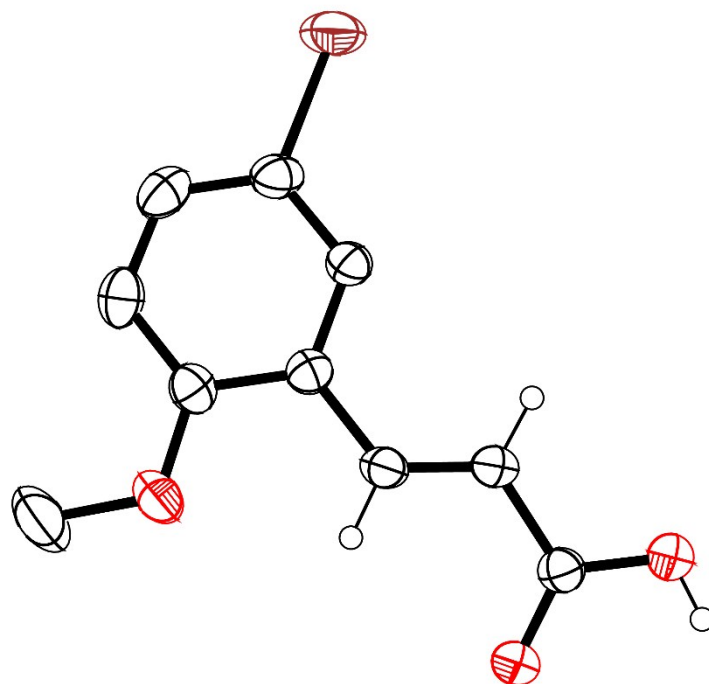


Figure S16. An ORTEP of the molecular structure of 5-bromo-2-methoxy-*trans*-cinnamic acid (**3b**) showing 40 % probability thermal ellipsoids.

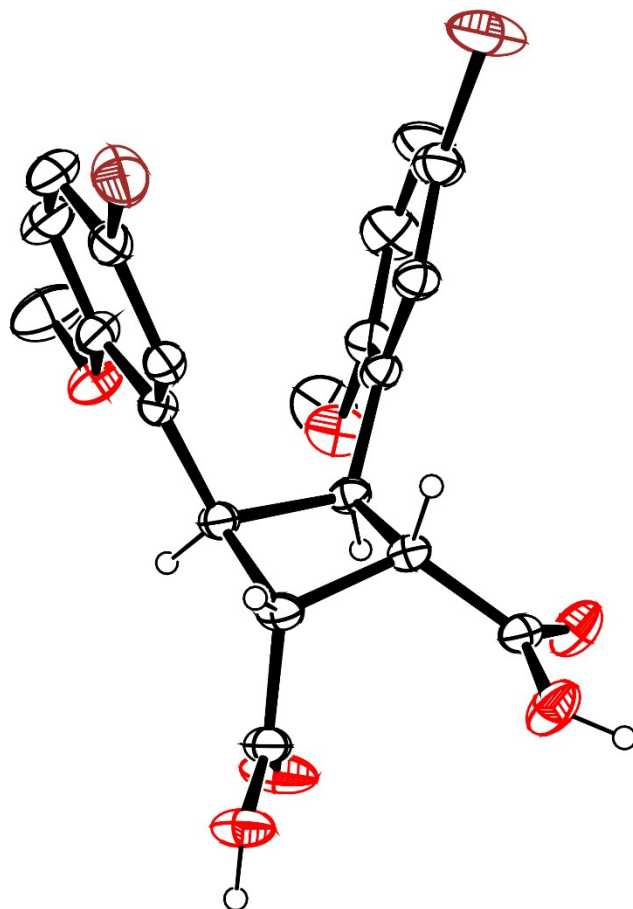


Figure S17. An ORTEP of the molecular structure of 5,5'-dibromo-2,2'-dimethoxy- β -truxinic acid (**3c**) showing 30 % probability thermal ellipsoids.

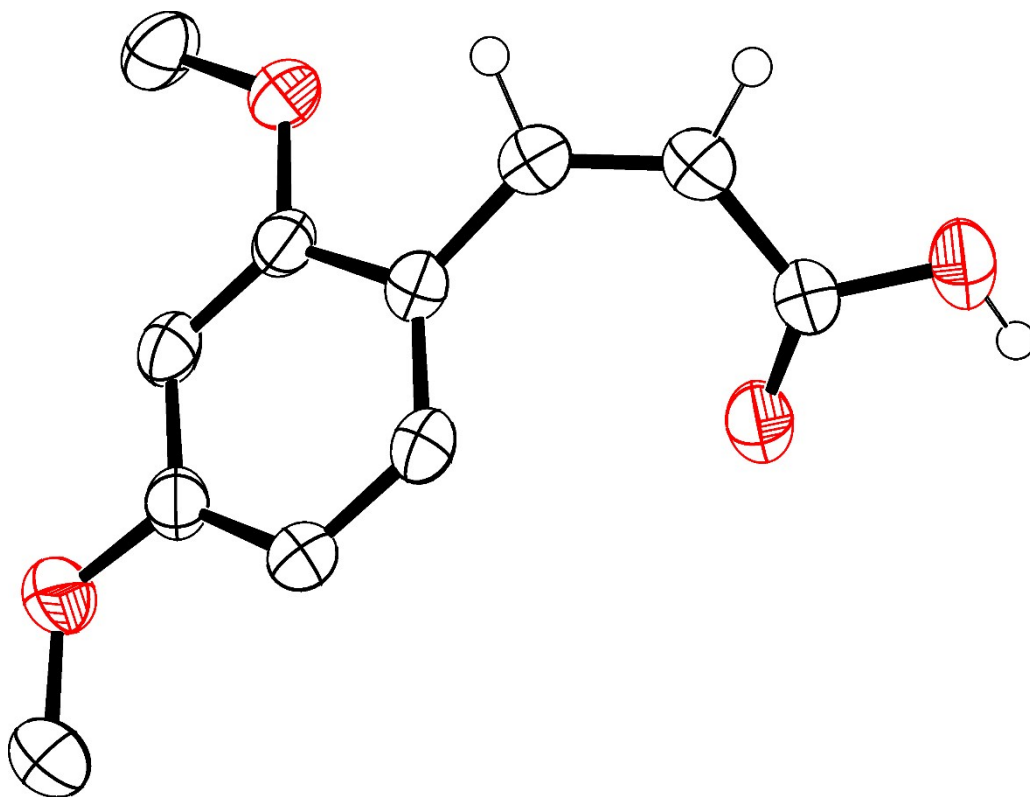


Figure S18. An ORTEP of the molecular structure of 2,4-dimethoxy-*cis*-cinnamic acid (**2a**) showing 50 % probability thermal ellipsoids.

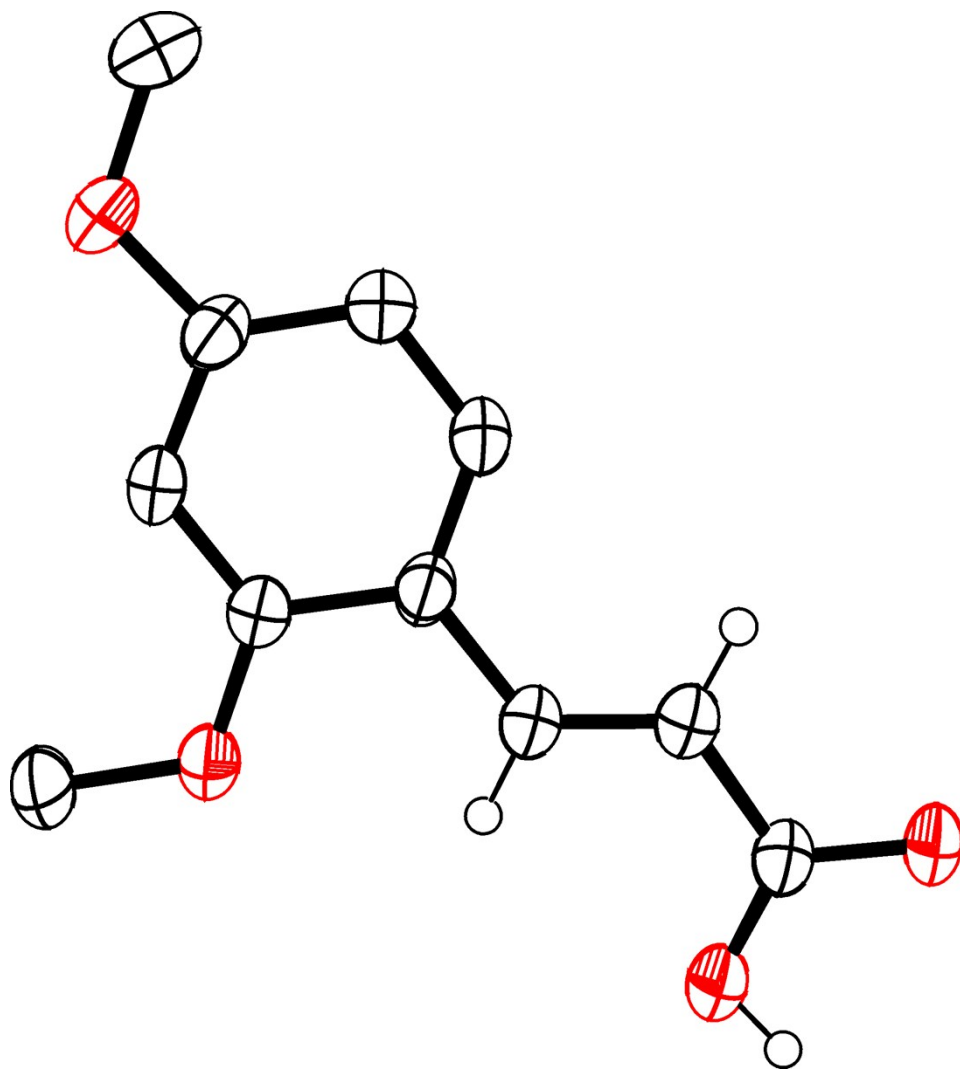


Figure S19. An ORTEP of the molecular structure of 2,4-dimethoxy-*trans*-cinnamic acid (**2b**) showing 50 % probability thermal ellipsoids.

Table T4. Crystallographic Data for Compounds 1a, 1b, 1c and 1d.

	1a	1b	1c	1d
Empirical formula	C ₁₂ H ₁₂ O ₃	C ₁₂ H ₁₂ O ₃	C ₂₄ H ₂₄ O ₆ •½C ₇ H ₈	C ₂₄ H ₂₄ O ₆ •C ₇ H ₈
Formula weight	204.22	204.22	454.50	500.56
Crystal system	Monoclinic	Triclinic	Triclinic	Triclinic
Lattice parameters				
<i>a</i> (Å)	4.0982(3)	7.7380(6)	9.9527(5)	8.3783(4)
<i>b</i> (Å)	13.3942(9)	8.1099(6)	10.3401(5)	9.3392(5)
<i>c</i> (Å)	20.0019(14)	10.0048(8)	12.2625(6)	9.5107(5)
α (deg)	90	71.822(1)	82.4210(8)	75.719(1)
β (deg)	91.125(1)	84.921(1)	83.5482(9)	82.633(1)
γ (deg)	90	64.415(1)	82.2157(9)	69.677(1)
V (Å ³)	1097.73(13)	537.24(7)	1233.65(11)	675.55(6)
Space group	<i>P</i> 2 ₁ / <i>n</i> (#14)	<i>P</i> $\bar{1}$ (#2)	<i>P</i> $\bar{1}$ (#2)	<i>P</i> $\bar{1}$ (#2)
Z value	4	2	2	1
ρ _{calc} (g / cm ³)	1.236	1.262	1.224	1.230
μ (Mo Kα) (mm ⁻¹)	0.089	0.090	0.086	0.085
Temperature (K)	296(2)	296(2)	296(2)	296(2)
2Θ _{max} (°)	50.00	50.00	50.00	56.00
No. Obs. (I > 2σ(I))	1625	1521	3690	2827
No. Parameters	138	138	325	191
Goodness of fit	1.055	1.062	1.042	1.045
Max. shift in cycle	0.000	0.000	0.018	0.000
Residuals*:R1; wR2	0.0554; 0.1640	0.0617; 0.1697	0.0668; 0.1925	0.0483; 0.1307
Absorption Correction, Max/min	Multi-scan 0.9912/0.9587	Multi-scan 0.7461/0.6867	Multi-scan 0.7466/0.6854	Multi-scan 0.7460/0.7014
Largest peak in Final Diff. Map (e ⁻ / Å ³)	0.473	0.369	0.543	0.299

$$*R = \frac{\sum_{hkl} (|F_{obs}| - |F_{calc}|)}{\sum_{hkl} |F_{obs}|}; R_w = \left[\frac{\sum_{hkl} w(|F_{obs}| - |F_{calc}|)^2}{\sum_{hkl} wF_{obs}^2} \right]^{1/2},$$

$$w = 1/\sigma^2(F_{obs}); GOF = \left[\frac{\sum_{hkl} w(|F_{obs}| - |F_{calc}|)^2}{(n_{data} - n_{vari})} \right]^{1/2}.$$

Table T5. Crystallographic Data for Compounds 2a and 2b.

	2a	2b
Empirical formula	C ₁₁ H ₁₂ O ₄	C ₁₁ H ₁₂ O ₄
Formula weight	208.21	208.21
Crystal system	Triclinic	Triclinic
Lattice parameters		
<i>a</i> (Å)	3.9208(2)	7.5522(9)
<i>b</i> (Å)	11.0581(7)	8.1546(10)
<i>c</i> (Å)	12.1034(7)	8.9900(11)
α (deg)	79.857(1)	91.546(2)
β (deg)	86.846(1)	111.209(2)
γ (deg)	80.343(1)	94.653(2)
<i>V</i> (Å ³)	509.07(5)	513.50(11)
Space group	<i>P</i> $\bar{1}$ (#2)	<i>P</i> $\bar{1}$ (#2)
<i>Z</i> value	2	2
ρ_{calc} (g / cm ³)	1.358	1.347
μ (Mo K α) (mm ⁻¹)	0.104	0.103
Temperature (K)	296	296
2 Θ_{max} (°)	54.0	54.0
No. Obs. (<i>I</i> > 2 σ (<i>I</i>))	1930	1636
No. Parameters	140	139
Goodness of fit	1.046	1.032
Max. shift in cycle	0.001	0.000
Residuals*:R1; wR2	0.0390; 0.1037	0.0484; 0.1301
Absorption Correction, Max/min	Multi-scan 0.7461/0.7073	Multi-scan 0.7460/0.5947
Largest peak in Final Diff. Map (e ⁻ / Å ³)	0.253	0.224

* $R = \sum_{\text{hkl}} (| | F_{\text{obs}} | - | F_{\text{calc}} | |) / \sum_{\text{hkl}} | F_{\text{obs}} |$; $R_w = [\sum_{\text{hkl}} w (| F_{\text{obs}} | - | F_{\text{calc}} |)^2 / \sum_{\text{hkl}} w F_{\text{obs}}^2]^{1/2}$,
 $w = 1/\sigma^2(F_{\text{obs}})$; $\text{GOF} = [\sum_{\text{hkl}} w (| F_{\text{obs}} | - | F_{\text{calc}} |)^2 / (n_{\text{data}} - n_{\text{vari}})]^{1/2}$.

Table T6. Crystallographic Data for Compounds 3a, 3b and 3c.

	3a	3b	3c
Empirical formula	C ₁₀ H ₉ O ₃ Br	C ₁₀ H ₉ O ₃ Br	C ₂₀ H ₁₈ O ₆ Br ₂ •½C ₄ H ₈ O ₂ •2H ₂ O
Formula weight	257.08	257.08	594.25
Crystal system	Monoclinic	Monoclinic	Triclinic
Lattice parameters			
<i>a</i> (Å)	15.7172(9)	18.770(2)	9.0513(5)
<i>b</i> (Å)	4.0206(2)	4.7420(5)	10.3906(5)
<i>c</i> (Å)	17.5023(10)	23.122(3)	14.5614(7)
α (deg)	90	90	108.141(1)
β (deg)	114.595(1)	90.860(1)	102.794(1)
γ (deg)	90	90	94.194(1)
V (Å ³)	1005.67(10)	2057.7(4)	1254.09(11)
Space group	<i>P</i> 2 ₁ / <i>n</i> (#14)	<i>C</i> 2/ <i>c</i> (#15)	<i>P</i> $\bar{1}$ (#2)
Z value	4	8	2
ρ _{calc} (g / cm ³)	1.698	1.660	1.574
μ (Mo Kα) (mm ⁻¹)	4.064	3.973	3.279
Temperature (K)	296(2)	296(2)	296(2)
2Θ _{max} (°)	59.98	51.00	55.99
No. Obs. (I > 2σ(I))	2226	1593	4618
No. Parameters	129	129	318
Goodness of fit	1.036	1.075	1.031
Max. shift in cycle	0.004	0.001	0.001
Residuals*:R1; wR2	0.0362; 0.0912	0.0443; 0.1043	0.0482; 0.1227
Absorption Correction, Max/min	Multi-scan 0.6867/0.2176	Multi-scan 0.7457/0.5269	Multi-scan 0.7461/0.4641
Largest peak in Final Diff. Map (e ⁻ / Å ³)	0.575	1.025	0.767

*R = $\sum_{hkl} (|F_{obs}| - |F_{calc}|) / \sum_{hkl} |F_{obs}|$; R_w = $[\sum_{hkl} w(|F_{obs}| - |F_{calc}|)^2 / \sum_{hkl} w F_{obs}^2]^{1/2}$,
w = $1/\sigma^2(F_{obs})$; GOF = $[\sum_{hkl} w(|F_{obs}| - |F_{calc}|)^2 / (n_{data} - n_{vari})]^{1/2}$.

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