Table S1. Crystal data and structure refinements**.**

	Diol-2HSA@280K-325nm, 48 mW He/Cd laser	
	Before-exposure	1min-exposure
Crystal data		
Chemical formula	$C_{42}H_{38}O_6$	
M_r	638.72	
Cell setting, space group	Triclinic, *P*-1	
Temperature (K)	280 (2)	
a (Å)	8.6391 (2)	8.6677 (3)
b (Å)	9.7902 (3)	9.9558 (4)
c (Å)	11.4484 (3)	11.1736 (4)
α (°)	89.882 (2)	92.263 (1)
β (°)	110.116 (1)	110.567 (1)
γ (°)	105.694 (3)	107.697 (2)
V (Å^3)	870.90 (4)	848.39 (6)
Z	1	
D_x (Mg m^{-3})	1.218	1.250
Radiation type	Mo $K\alpha$	
μ (mm^{-1})	0.08	
Crystal form, colour	Block, colorless	
Crystal size (mm)	0.12 × 0.05 × 0.04	
Data collection		
Diffractometer	CCD area detector	
Data collection method	phi and ω scans	
Absorption correction	Empirical (using intensity measurements)	
T_{min}	0.990	
T_{max}	0.997	
No. of measured, independent and observed reflections	9026, 3418, 2560	6842, 3329, 2305
Criterion for observed reflections	$I > 2\sigma(I)$	
R_{int}	0.027	0.022
θ_{max} (°)	26.0	
Refinement		
Refinement on	F^2	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.040, 0.106, 1.02	0.043, 0.111, 1.01
No. of relections	3418 reflections	3329 reflections
No. of parameters	225	
H-atom treatment	Refined independently	
Weighting scheme	Calculated	$w = 1/[\sigma^2(F_o^2) + (0.0519P)^2 + 0.1114P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$	<0.0001	<0.0001
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.14, –0.21	0.19, –0.19
Reaction results		
conversion ratio(%)	0	100

	Diol-2HSA@280K-337nm, nitrogen laser	
	Before-exposure	1000 laser pulses exposure, ~150mJ total,
Crystal data		
Chemical formula	$C_{42}H_{38}O_6$	
M_r	638.72	
Cell setting, space group	Triclinic, *P*-1	
Temperature (K)	280 (2)	
a (Å)	8.6394 (2), ,	8.6465 (2)
b (Å)	9.7970 (2)	9.8126 (2)
c (Å)	11.4362 (3)	11.4267 (3)
α (°)	89.852 (1)	90.012 (3)
β (°)	110.013 (2)	110.117 (2)
γ (°)	105.768 (1)	105.952 (4)
V (Å^3)	870.88 (4)	870.46 (4)
Z	1	
D_x (Mg m^{-3})	1.218	
Radiation type	Mo $K\alpha$	
μ (mm^{-1})	0.08	
Crystal form, colour	Block, colorless	
Crystal size (mm)	0.14 × 0.06 × 0.04	
Data collection		
Diffractometer	CCD area detector	
Data collection method	phi and ω scans	
Absorption correction	Empirical (using intensity measurements)	
T_{min}	0.989	0.989
T_{max}	0.997	0.997
No. of measured, independent and observed reflections	11527, 3418, 2995	11635, 3424, 2835
Criterion for observed reflections	$I > 2\sigma(I)$	
R_{int}	0.017	0.017
θ_{max} (°)	26.0	
Refinement		
Refinement on	F^2	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.038, 0.098, 1.04	0.036, 0.095, 0.98
No. of relections	3418 reflections	3424 reflections
No. of parameters	225	242
H-atom treatment	Refined independently	Constrained to parent site
Weighting scheme	Calculated $w = 1/[\sigma^2(F_o^2) + (0.0436P)^2 + 0.2023P]$ where $P = (F_o^2 + 2F_c^2)/3$	
$(\Delta/\sigma)_{max}$	<0.0001	<0.0001
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.22, –0.20	0.21, –0.17
Reaction results		
conversion ratio(%)	0	7.96(18)

	Diol-2HSA@90K-325nm, 48 mW He/Cd laser			
	Before-exposure	1h-exposure	3h-exposure	8h-exposure
Crystal data				
Chemical formula	$C_{42}H_{38}O_6$			
M_r	638.72			
Cell setting, space group	Triclinic, *P*-1			
Temperature (K)	90 (2)			
a (Å)	8.5870 (3)	8.5938 (3)	8.5943 (3)	8.5959 (4)
b (Å)	9.6052 (2)	9.6260 (3)	9.6258 (4)	9.6271 (4)
c (Å)	11.3407 (1)	11.3346 (4)	11.3318 (4)	11.3333 (5)
α (°)	90.0309 (6)	90.1378 (5)	90.1441 (6)	90.1271 (9)
β (°)	109.7910 (9)	109.8917 (6)	109.9089 (5)	109.9222 (6)
γ (°)	105.4502 (8)	105.6692 (5)	105.7044 (7)	105.7201 (5)
V (Å^3)	844.07 (4)	844.32 (5)	843.86 (5)	844.12 (6)
Z	1			
D_x (Mg m^{-3})	1.257	1.256	1.257	1.256
Radiation type	Mo $K\alpha$			
μ (mm^{-1})	0.08			
Crystal form, colour	Block, colorless			
Crystal size (mm)	0.10 × 0.06 × 0.04			
Data collection				
Diffractometer	CCD area detector			
Data collection method	phi and ω scans			
Absorption correction	Empirical (using intensity measurements)			
T_{min}	0.992			
T_{max}	0.997			
No. of measured, independent and observed reflections	11072, 3317, 3062	8782, 3318, 2901	6651, 3308, 2834	6724, 3310, 2832
Criterion for observed reflections	$I > 2\sigma(I)$			
R_{int}	0.015	0.018	0.018	0.017
θ_{max} (°)	26.0			
Refinement				
Refinement on	F^2			
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.031, 0.080, 1.05	0.036, 0.090, 1.10	0.039, 0.096, 1.14	0.039, 0.095, 1.13
No. of relections	3317 reflections	3318 reflections	3308 reflections	3310 reflections
No. of parameters	225	242		
H-atom treatment	Refined independently	Constrained to parent site		
Weighting scheme	Calculated $w = 1/[\sigma^2(F_o^2) + (0.0335P)^2 + 0.3327P]$ where $P = (F_o^2 + 2F_c^2)/3$			
$(\Delta/\sigma)_{max}$	0.001	0.002	<0.0001	<0.0001
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.29, –0.25	0.19, –0.23	0.23, –0.23	0.23, –0.23
Reaction results				
conversion ratio(%)	0	5.64(16)	6.32(17)	6.44(17)

Computer programs: *Bruker APEXII*; *Bruker SAINT*; *SHELXS-97* (Sheldrick, 1990); *SHELXL-97* (Sheldrick, 1997); *Bruker SHELXTL*.

Table S2. Hydrogen bonds distances at 280 K.

D–H···A	d(D···A)/Å	<DHA/°	D–H···A	d(D···A)/Å	<DHA/°
O(1)-H(1O)···O(2)	2.680(2)	178(2)	O(3)-H(3O)···O(1)	2.734(2)	168(2)
a) -x+1, -y, -z+1					

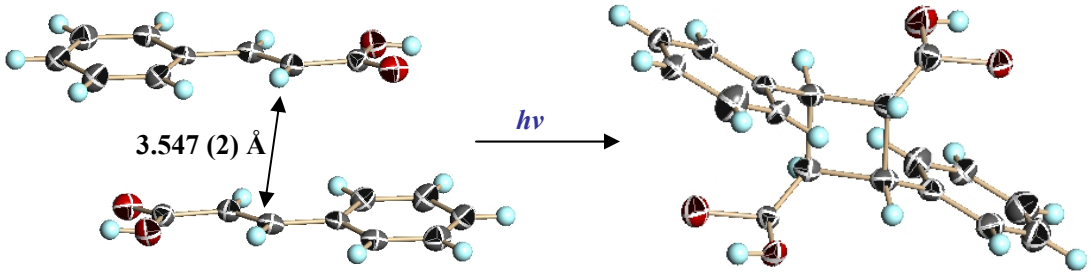

Figure S1. Perspective views showing the photoreaction of α-cinnamic acid at 90 K (355nm excitation). 50% probability displacement ellipsoids are shown.