Electronic Supplementary Information

For

Force induced strengthening of a mechanochromic polymer based on naphthalene fused cyclobutane mechanophore

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Experimental section

Materials and measurements

Unless otherwise stated, all reagents and solvents were obtained from Aladdin Co. Ltd. And used without further purification. Unless otherwise noted, all reactions were carried out under ambient atmosphere.

^{1}H NMR was recorded on 400 MHz (Bruker ARX300) and ^{13}C NMR spectra were recorded on Bruker 100 MHz spectrometer at room temperature with $CDCl_3$ or d6-DMSO as the solvents and tetramethylsilane (TMS) as the internal standard. Electrospray ionization (ESI) mass spectra were obtained on a Finnigan LCQ Advantage ion trap mass spectrometer (ThermoFisher Corporation). Thermogravimetric Analysis (TGA) was carried out on Neyzsch Instrument TG 209 F1. Fluorescence spectra measurements were performed on a Shimadzu RF-5301PC spectroflurophotometer. Absorption spectra were determined on a Pgeneral UV-Vis TU-1901 spectrophotometer. Uniaxial tensile tests were performed on TMA Q400. Specimens were cut in a rectangle shape using a normalized cutter with a central part of 30 mm in length, 5 mm in width. The number average molecular weights (Mn), weight average molelular weight (Mw) and polydispersities (PDI) were measured by GPC on a Waters 150 instrument equipped with 10^3, 10^4 and 10^5 Å Waters Ultrastyragel columns and using THF (1.0 mL/min) as the eluent at 25 °C. Calibration was against polystyrene standards.

Molecular Simulation

All Density Functional Theory (DFT) calculations were performed using the ORCA version 2.8 program package.[S1] Structure optimization was performed based on the Density Function Theory (DFT). Following each optimization, the vibrational frequencies were calculated to make sure that all the optimized structures were the stable geometric structures. The basis set used here was B3LYP. The transition states were located using Synchronous Transit-guided Quasi-Newton (STQN) method[S2]. Transition states are

characterized by having exactly one vibrational mode with an imaginary frequency. They are located on so-called first order saddle points on the potential energy surface, which is local maxima in exactly one direction (the reaction pathway), and a local minima in all other directions.

Ultrasound Sonication

Ultrasound experiments were performed with a 11.5 mm (diameter) titanium solid probe (Scientz). For typical sonication experiment, polymers were dissolved in THF with a concentration of 4 mg/mL. The solution was then transferred to a 3-necked cell in an ice bath and sparged with nitrogen for 30 min. A pulse sequence of 2s on/2s off was applied to the solution at a power of 8.7 W/cm^2. The temperature of the system was maintained at 0-5 °C. The sonication was carried out under a nitrogen atmosphere.

Aliquots (1 mL, 4 mg/mL) at given time were removed from the cell for GPC and UV-Vis test. After sonication, the residual solution was precipitated by methanol and redissolved in CDCl$_3$ (~ 20 mg/mL) for ^{1}H NMR measurement.
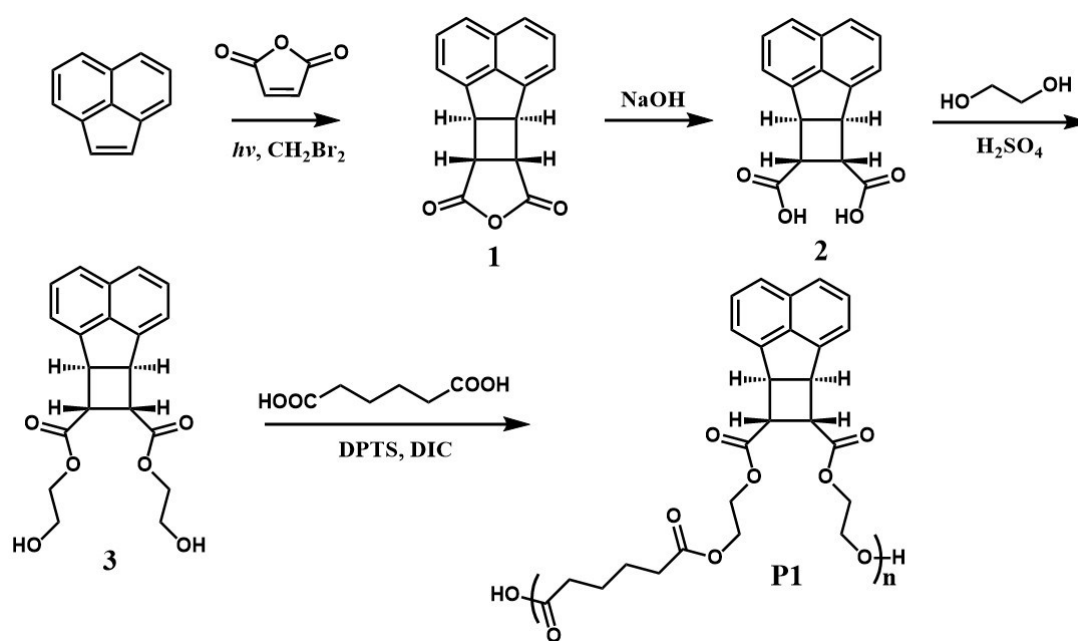

Figure S1 Synthetic route of naphthalene fused cyclobutane (**NCD**) mechanophore and the related polyester **P1** carrying **NCD** on its backbone.

Synthesis of compound 2

A solution of acenaphthylene (8.0 g, 52.6 mmol) and maleic anhydride (15.0 g, 153.1 mmol) in 150 mL dibromomethane was irradiated for 48 h. The insoluble substance was filtrated. Evaporation of the filtrate left a solid residue, which was treated with 150 mL diethyl ether to dissolve unreacted reactants. The ether-insoluble residue was recrystallized from benzene to give compound **1**. The compound 1 was added to a solution of 40 mL 1.5 N methanolic KOH. After refluxed for 2 h, the reaction mixture was poured into ice bath and acidified with concentrated hydrochloric acid. The precipitate was filtered, dried, and recrystallized from acetone to give the

target compound **2** (2.5 g, yield: 44 %).

^{1}H NMR (400 MHz, d_6-DMSO): δ 12.6 (s, 2H), 7.73 (d, 2H), 7.52 (t, 2H), 7.37 (d, 2H), 4.35 (d, 2H), 3.13 (d, 2H). ^{13}C NMR (100 MHz, d_6-DMSO): δ 174.0, 146.8, 139.9, 132.0, 128.8, 123.7, 120.0, 47.3, 44.7. ESI-MS (m/z): Calculated for $C_{16}H_{12}O_4$ (M+H$^+$): 269.07, found (M+H$^+$): 269.08.

Synthesis of compound 3

Compound **2** (2.0 g, 7.5 mmol) and catalyst concentrated H_2SO_4 (0.5 mL) was added to the 40 mL glycol. After the mixture was refluxed for 4 h, the solution was poured into 100 mL water and extracted with dichloromethane. The extract was dried with Na_2SO_4 and evaporated to give the crude product. After recrystallization from ethyl acetate, the target compound **3** (2.2 g, yield: 81 %) was obtained.

^{1}H NMR (400 MHz, CDCl$_3$): δ 7.67 (d, 2H), 7.48 (t, 2H), 7.35 (d, 2H), 4.53 (d, 2H), 4.40 (m, 2H), 4.23 (m, 2H), 3.86 (m, 4H), 3.32 (d, 2H), 2.73 (s, 2H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 168.3, 140.7, 135.1, 127.3, 123.6, 119.1, 115.1, 62.2, 56.0, 42.4, 40.1. ESI-MS (m/z): Calculated for $C_{20}H_{20}O_6$ (M+H$^+$): 357.13, found (M+H$^+$): 357.13.

Synthesis of polyester P1

Compound 3 (0.419 g, 1.25 mmol, 1 eq.), adipic acid (0.183 g, 1.25 mmol, 1 eq.) and dimethylaminopyridinium toluenesulfonate (0.146 g, 0.5 mmol, 0.4 eq.) were added to a 10 mL flask. 2 mL dry CH_2Cl_2 was added by using a syringe. The solution was stirred at room temperature until solution became homogeneous. *N,N*-diisopropylcarbodiimide (0.58 mL, 3.75 mmol, 3 eq.) was added to the mixture by using a syringe. The solution was stirred at room temperature for 96 h. The mixture was precipitated twice from CH_2Cl_2 into MeOH to afford a light yellow solid **P1** (0.53 g, yield: 88 %).

Synthesis of reference compound R1
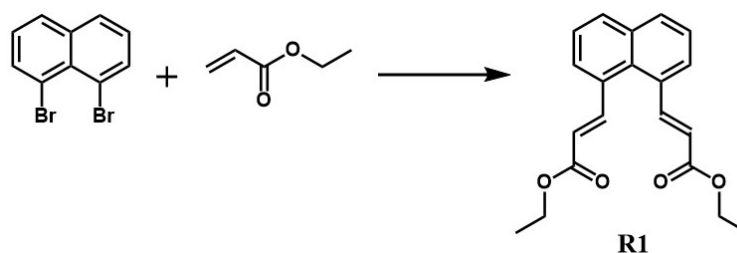
A 50 mL Schlenk tube was charged with a mixture of 1,8-dibromonaphthalene (1.5 g, 5.24 mmol), PdCl$_2$(PPh$_3$)$_2$ (0.368 g, 0.0088 mmol, 6mg), ethyl acrylate (2.79 mL,26.2 mmol), and NEt$_3$ (1.82 mL, 13.1 mmol) in DMF (30 mL) under nitrogen. The flask was sealed under nitrogen after three vacuum/nitrogen cycles, heated to 80 °C for 2 days, and then concentrated under vacuum. The crude was dissolved in CH_2Cl_2, washed with brine (40 mL×5), dried over Na_2SO_4, and concentrated in vacuo. The product was purified by column chromatography (silica gel, hexanes/ethyl acetate = 10:1) yielded **R1** as a yellow solid (1.67 g, 83%).

^{1}H NMR (400 MHz, CDCl$_3$): δ 8.32 (d, 2H), 7.86 (d, 2H), 7.58 (d, 2H), 7.46 (t, 2H), 6.30 (d, 2H), 4.25 (q, 4H), 1.32 (t, 6H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 166.3, 146.8, 134.4, 133.7, 130.6, 130.0, 128.2, 125.9, 120.0, 60.5, 14.2. ESI-MS (m/z): Calculated for

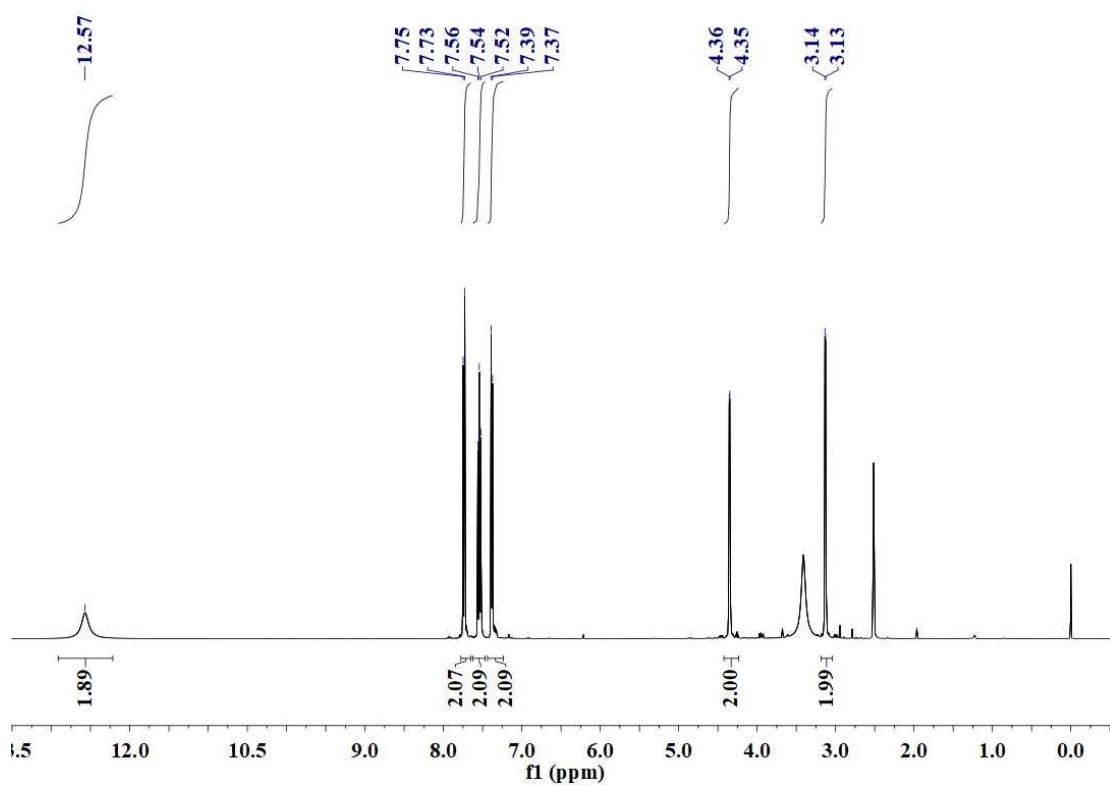$C_{20}H_{20}O_4$ (M+H$^+$): 325.14, found (M+H$^+$): 325.14.

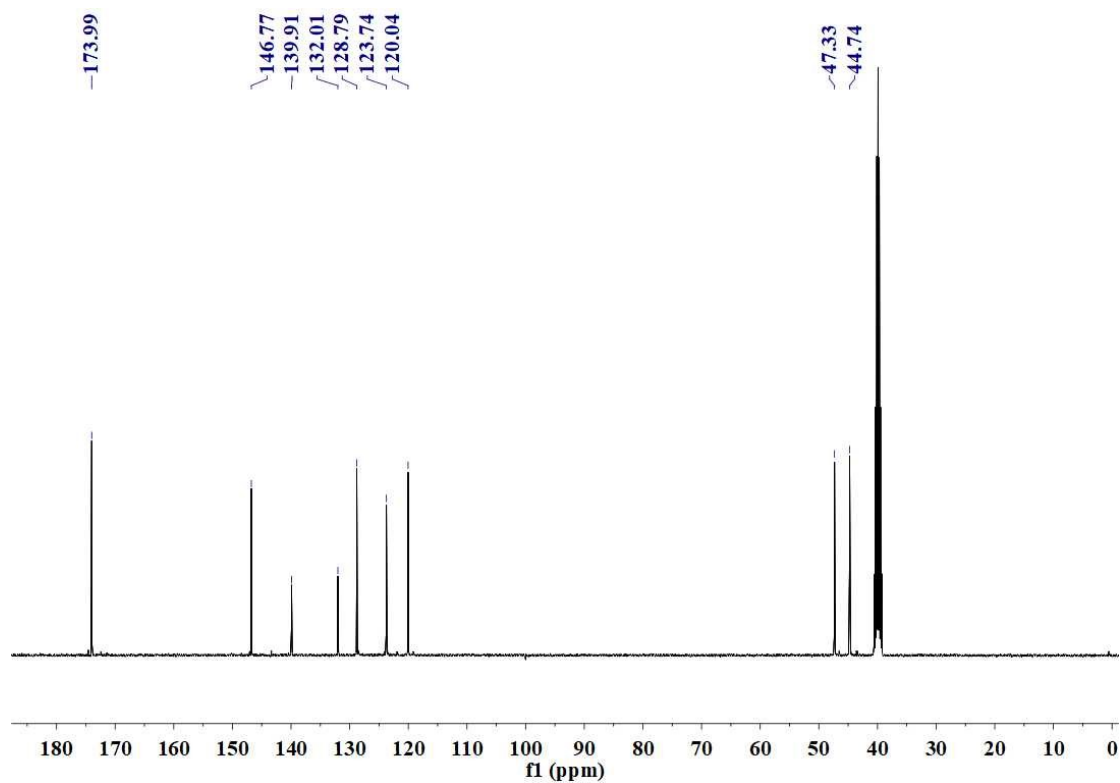**Figure S2** ^{1}H NMR spectrum of compound **2** in d$_6$-DMSO.

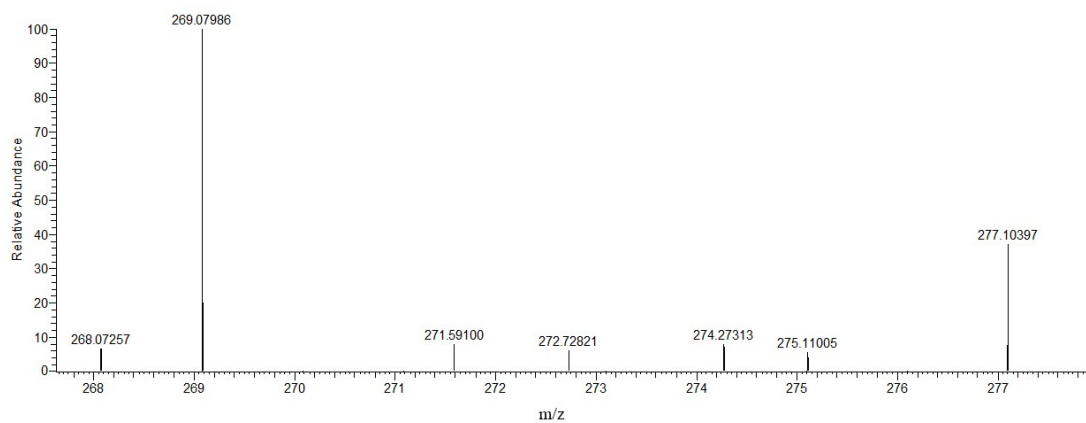**Figure S3** ^{13}C NMR spectrum of compound **2** in d$_6$-DMSO.

Figure S4 ESI mass spectrum of compound **2.**
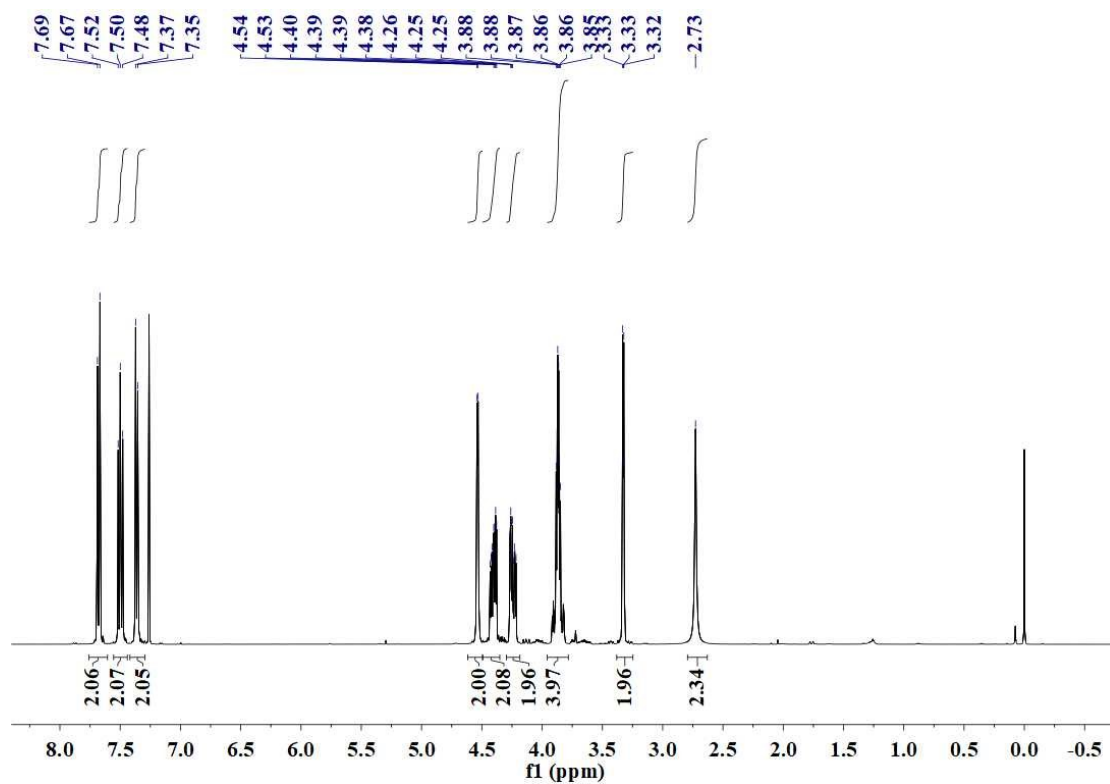

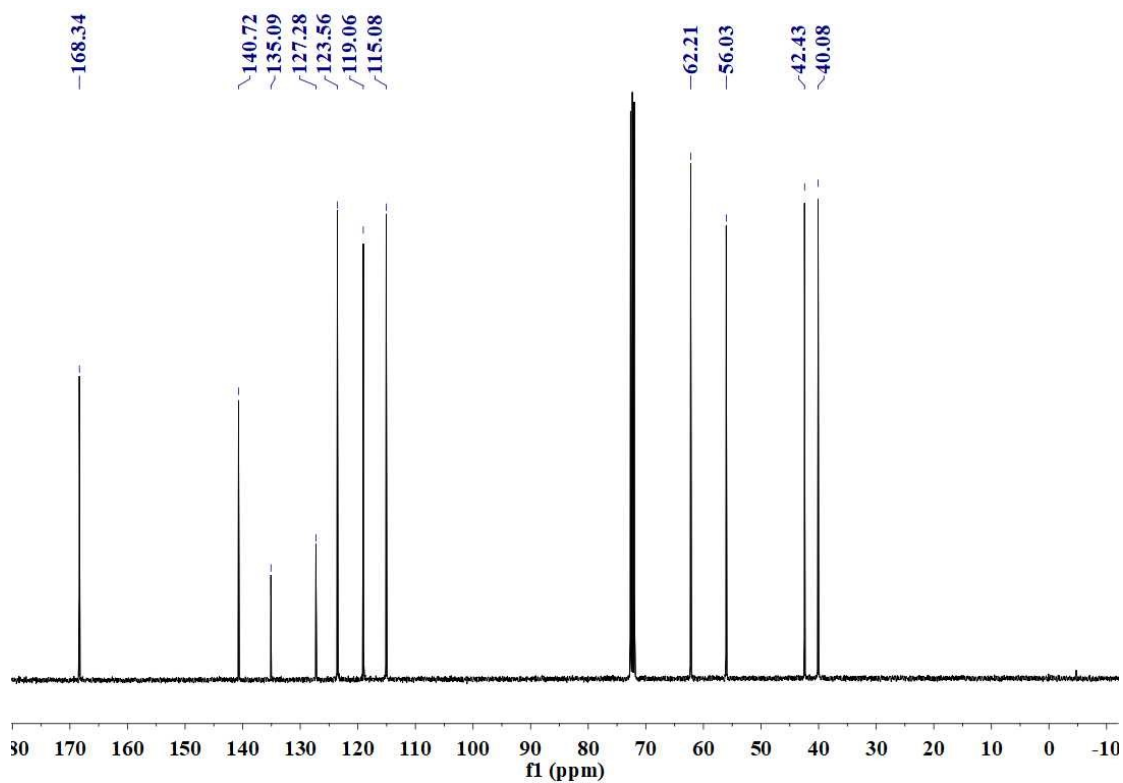**Figure S5** ^{1}H NMR spectrum of compound **3** in CDCl$_3$.

Figure S6 ^{13}C NMR spectrum of compound **3** in CDCl$_3$.
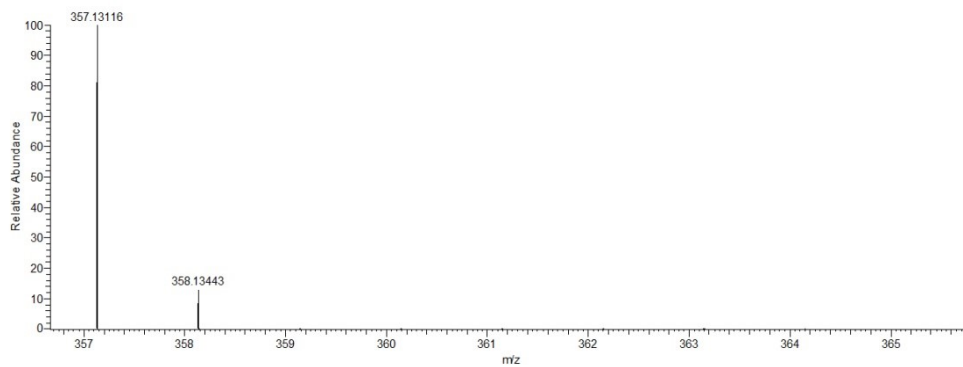

Figure S7 ESI mass spectrum of compound **3**.
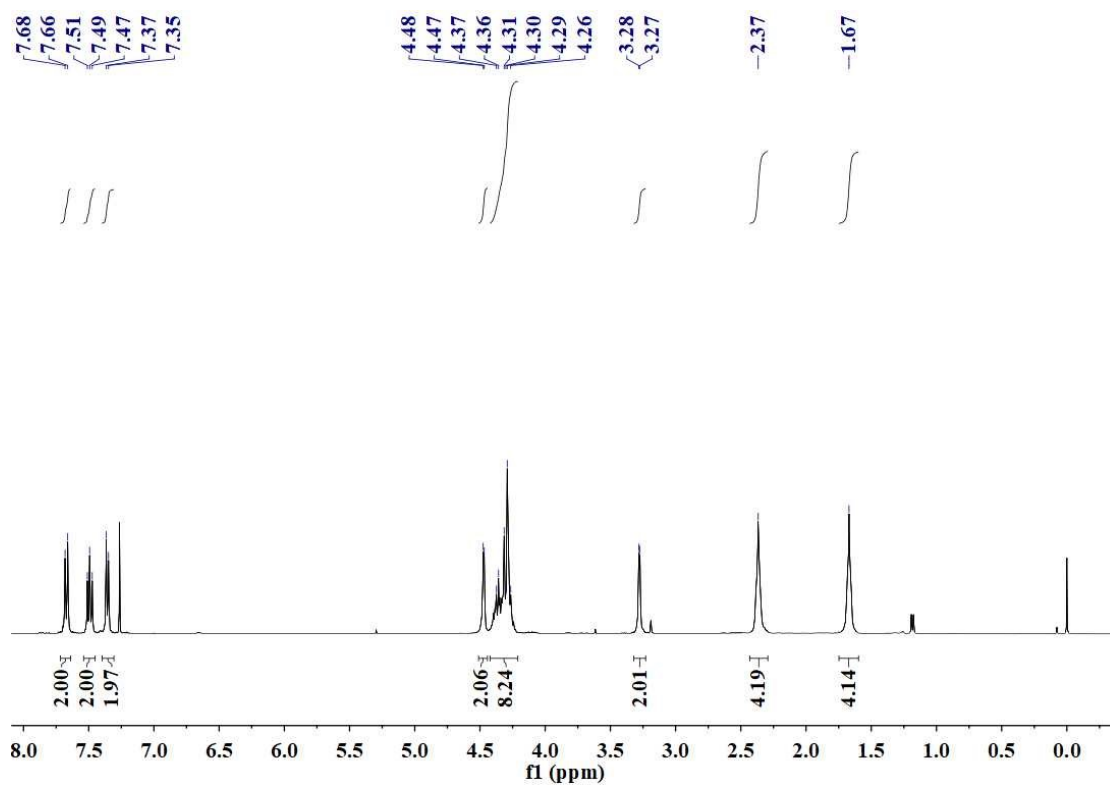
Figure S8 ^{1}H NMR spectrum of **P1** in CDCl$_3$.
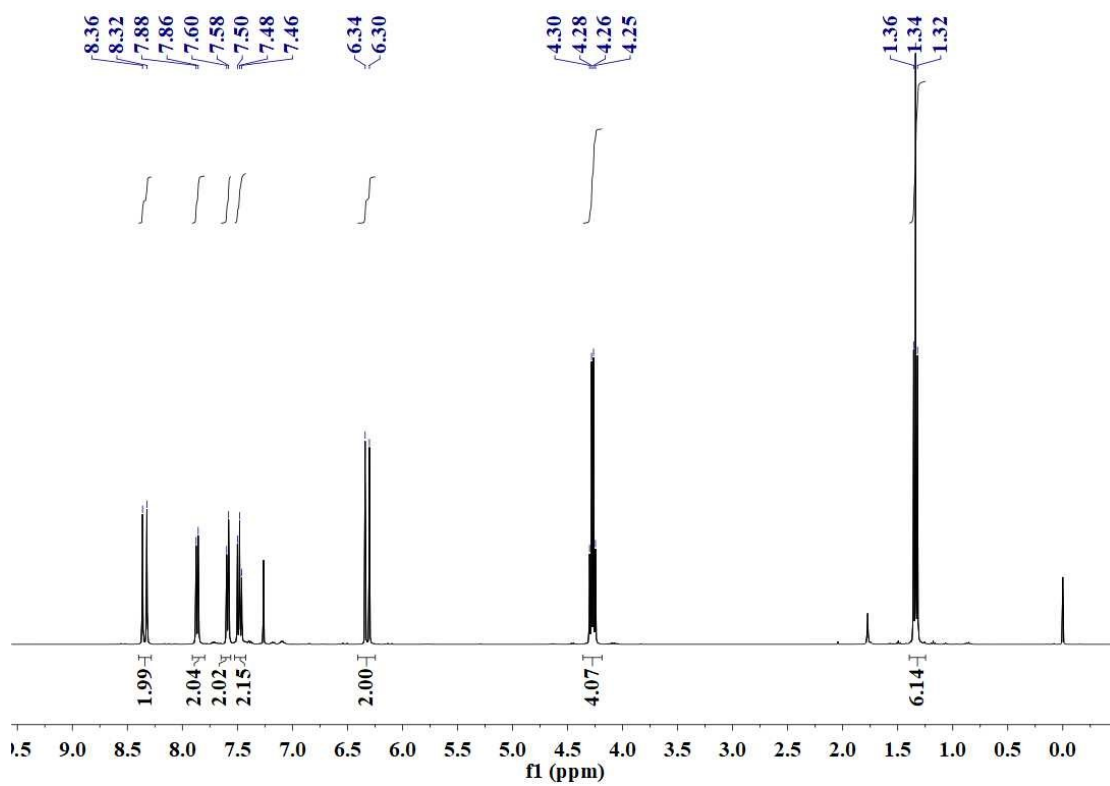

Figure S9 ^{1}H NMR spectrum of the reference compound **R1** in CDCl$_3$.
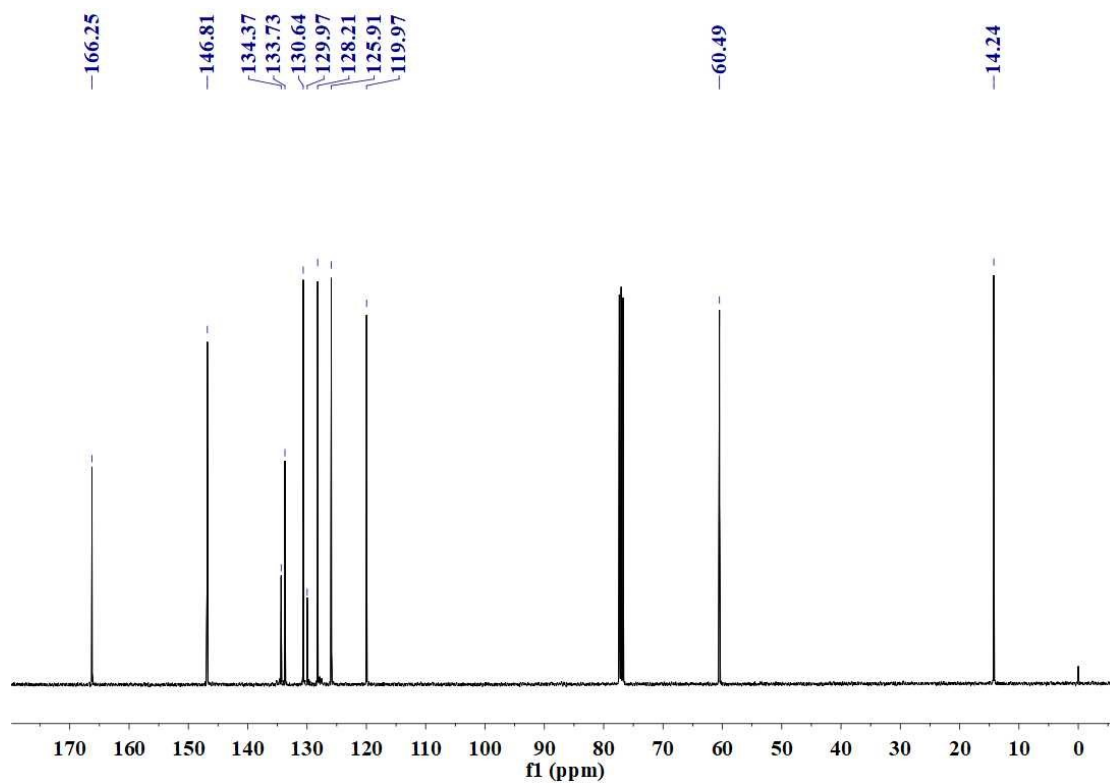
Figure S10 ^{13}C NMR spectrum of the reference compound **R1** in CDCl$_3$.

166.25

146.81
134.37
133.73
130.64
129.97
128.21
125.91
119.97
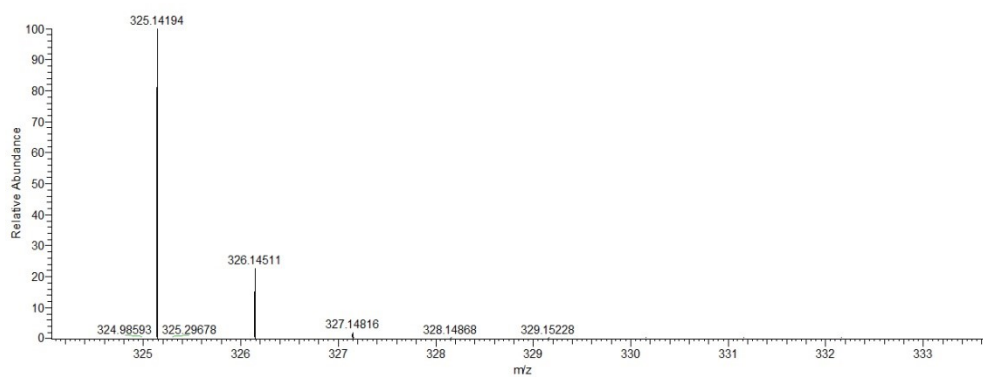
60.49

14.24

Figure S11 ESI mass spectrum of reference compound **R1**.
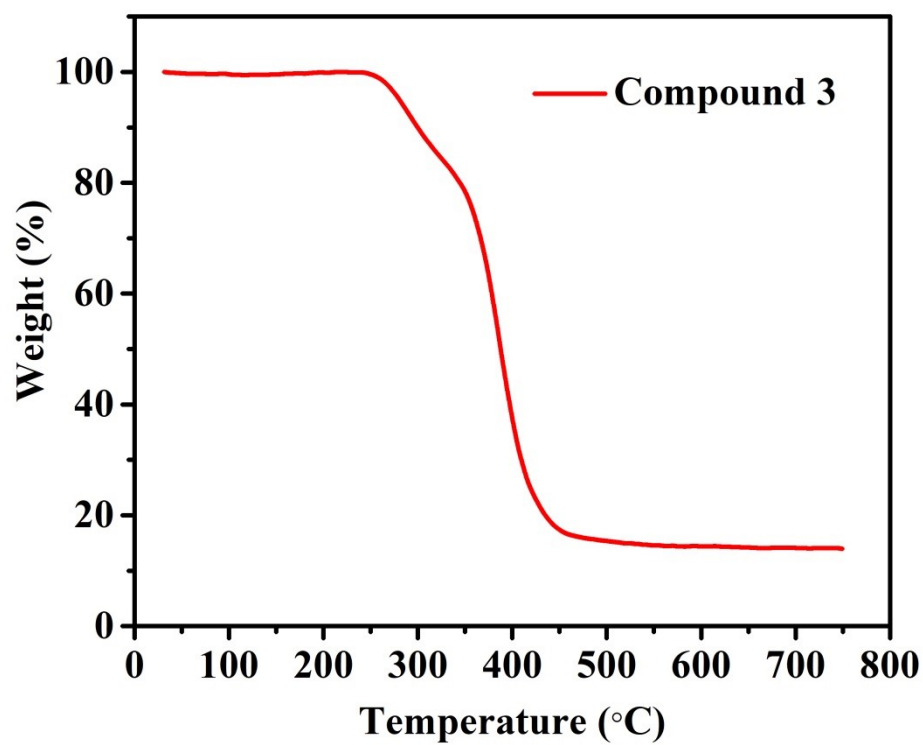
Figure S12 TG curve of the compound **3** in nitrogen atmosphere.
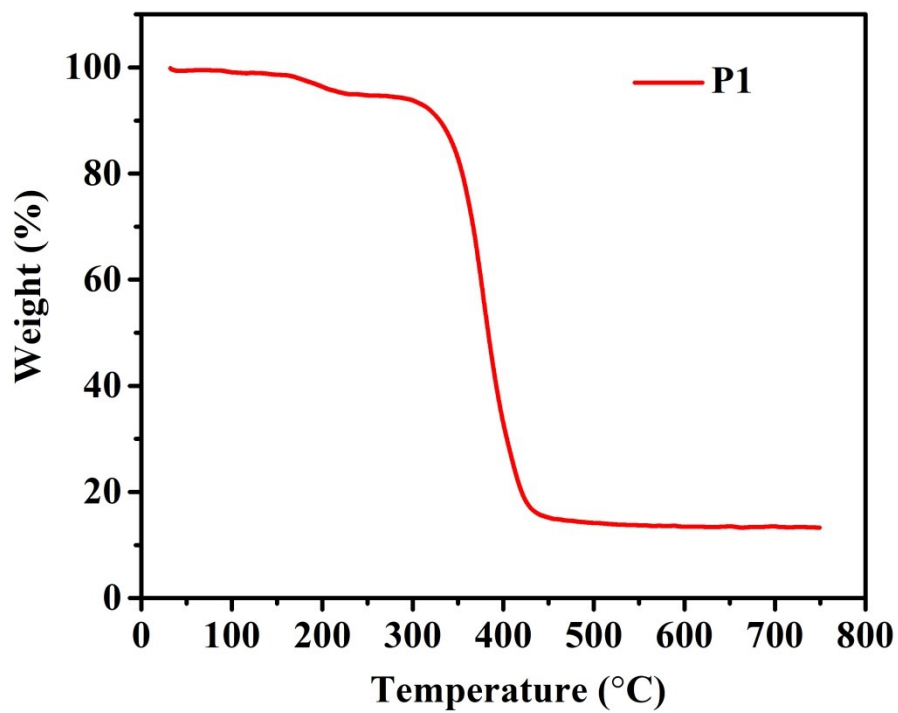

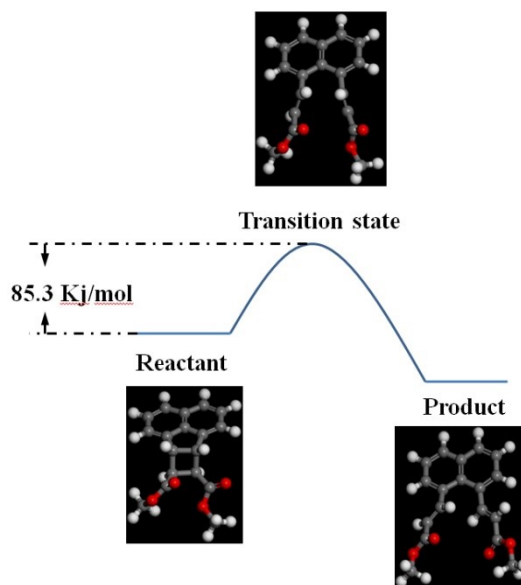**Figure S13** TG curve of the **P1** in nitrogen atmosphere.

Figure S14 Transition state search for the transformation of *exo*-**NCD** mechanophore to *trans,trans* isomer (the energy barrier for the transformation was calculated to be 85.3Kj/mol).

Structure optimization

To assess the possible release length of the NCD during sonication, we performed geometry optimization calculations for the mechanophore and three retro cycloaddition products. Any unnecessary side groups were omitted to save calculation time. The distances between two oxygens (d_{o-o}) on the ester groups were measured for all of the optimized structures (Fig. S15). The value of d_{o-o} for R2 was 3.5 Å and increased to 6.8 Å (*trans*, *trans*-R2), 7.5 Å (*trans*, *cis*-R2) and 7.8 Å (*cis*, *cis*-R2) after sonication. The calculated stored length for R2 was comparable to those of most of the previous reported systems, such as gem-dibromocyclopropane (<2 Å) and bicyclo[3.2.0]heptane (~4 Å), which demonstrated its potential ability in dissipating strain energy to lower the risk of chain fracture.
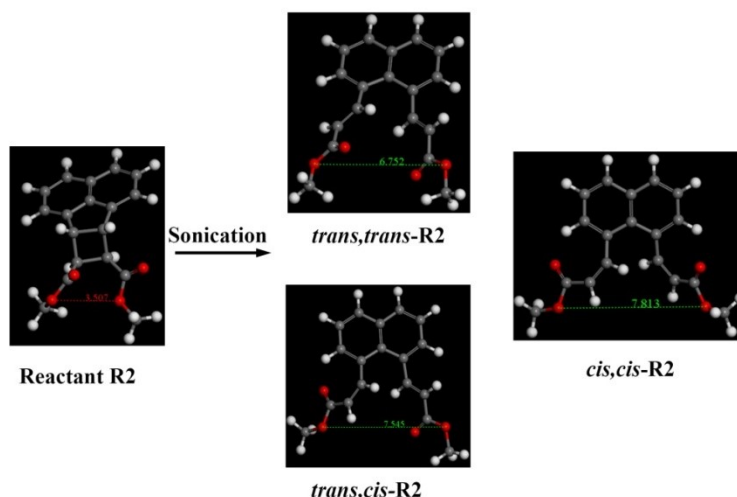
Figure S15 Theoretical calculation of the elongation of the distance between the two ester O atoms before and after the force-induced retro-cycloaddition reaction. The distances were measured to be 3.5 Å, 6.8 Å, 7.5 Å, and 7.8 Å for modal molecules R2, *trans,trans*-R2, *trans,cis*-R2 and *cis,cis*-R2, respectively.
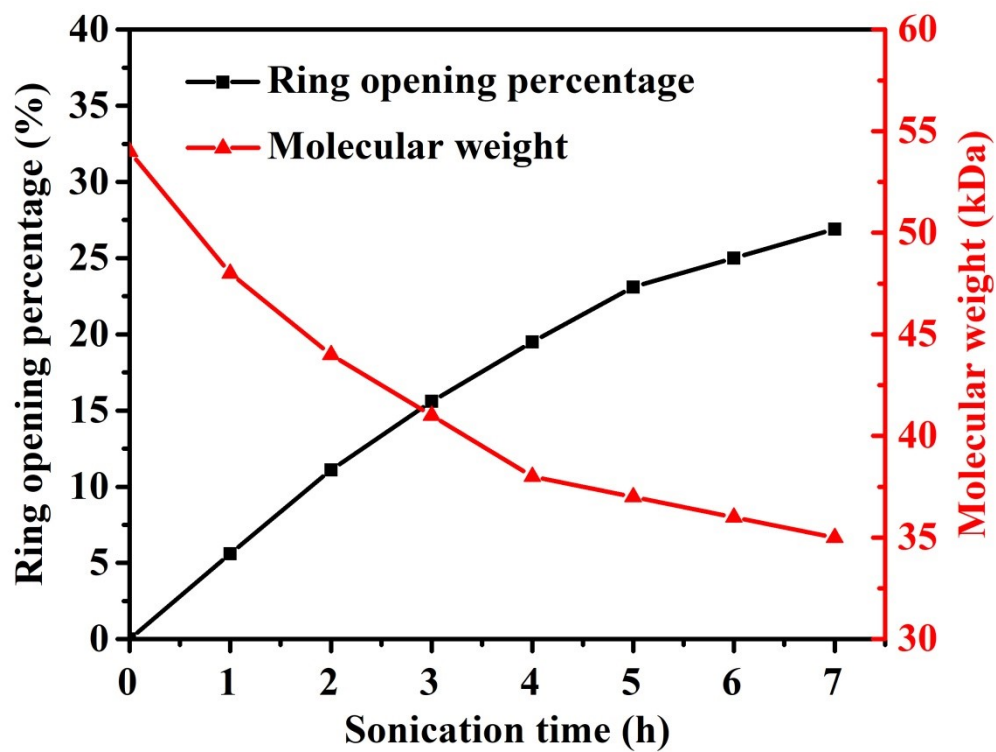
Figure S16 Ring opening percentage of **P1** as a function of sonication time. Molecular weight degradation due to nonspecific chain scission (red) occurs due to high flow forces experienced in pulsed ultrasound.
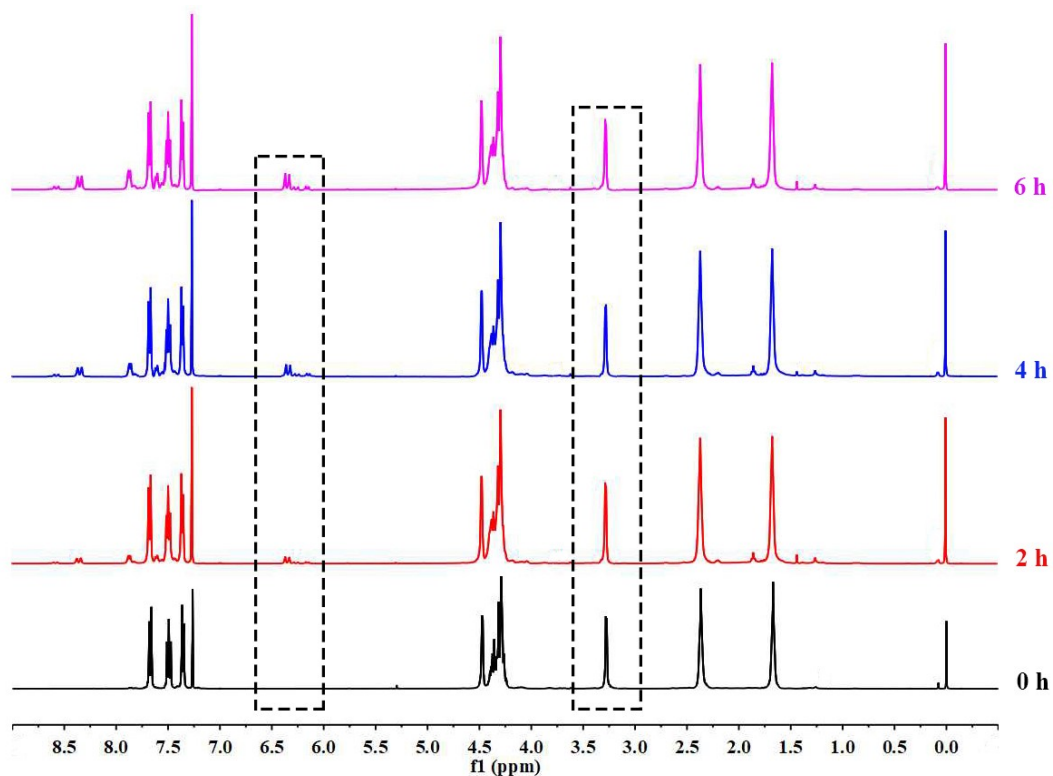
Figure S17 ^{1}H NMR spectra of **P1** as a function of sonication time. The ring opening ratio in **P1** was calculated according to the integral of the proton on vinyl ($\sim$6.38 ppm) and cyclobutane ($\sim$3.37 ppm).
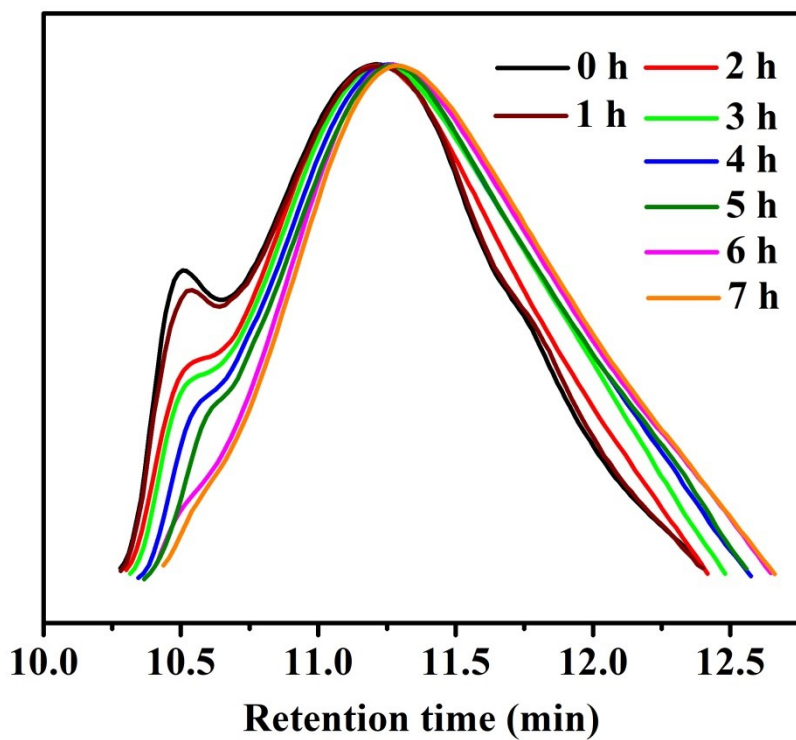
Figure S18 GPC traces of **P1** with different sonication time.

Table S1 Molecular parameters of the polymers

Entry	Sonication time	M_n (KDa)	M_w (KDa)	PDI
P1	0 h	54	115	2.13
P1	1 h	48	99	2.06
P1	2 h	44	83	1.88
P1	3 h	41	73	1.78
P1	4 h	38	64	1.69
P1	5 h	37	61	1.65
P1	6 h	36	57	1.57
P1	7 h	35	54	1.55
P2	0 h	13	30	2.32
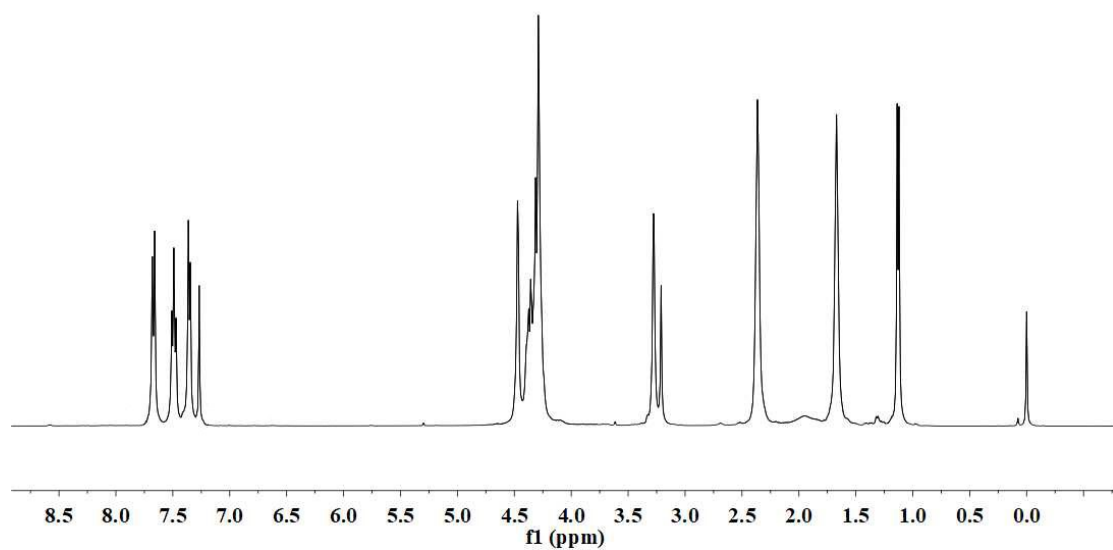
Figure S19 ^{1}H NMR spectrum of **P2** with low molecular weight after sonication for 3 h (8.7 W/cm^{-2}, 2 s on and 2 s off). No change in spectrum was observed.
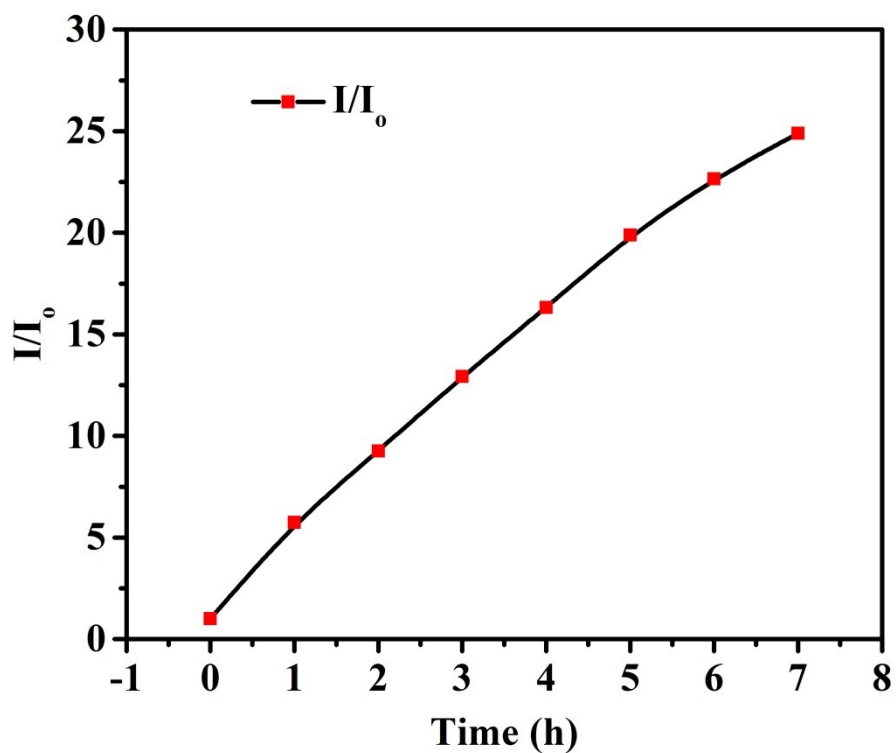
Figure S20 Fluorescent intensity increment at 423 nm for **P1** as a function of the sonication time.
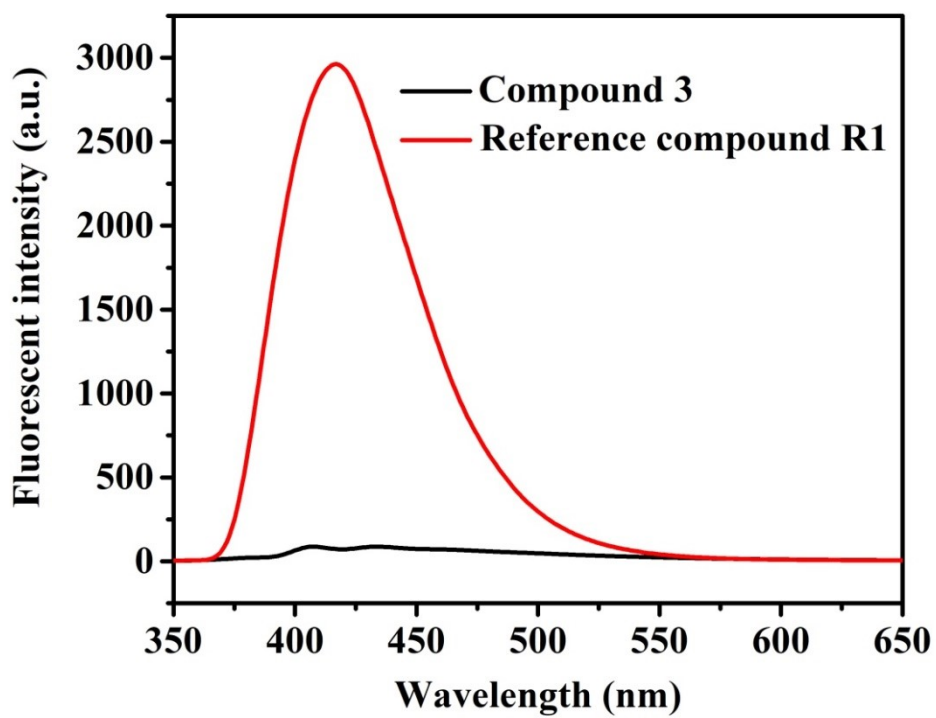
Figure S21 Fluorescent spectra of the compound **3** and **R1** (excitation wavelength: 340 nm).
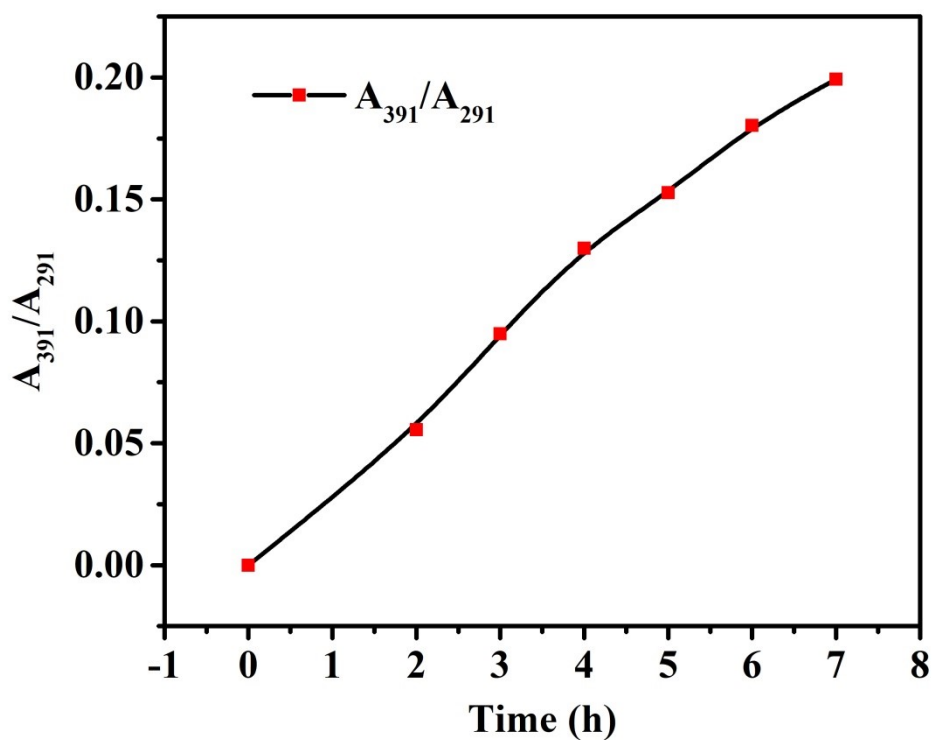
Figure S22 Absorbance ratio of 391 nm and 291 nm as a function of sonication time.
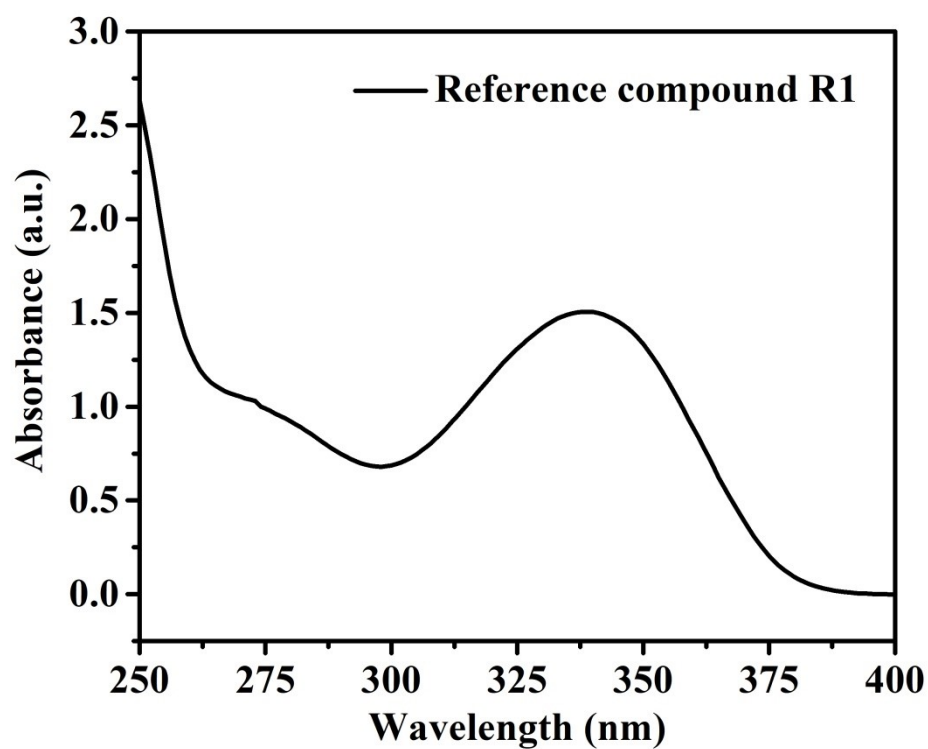
Figure S23 Absorbance spectrum of the reference compound **R1**.
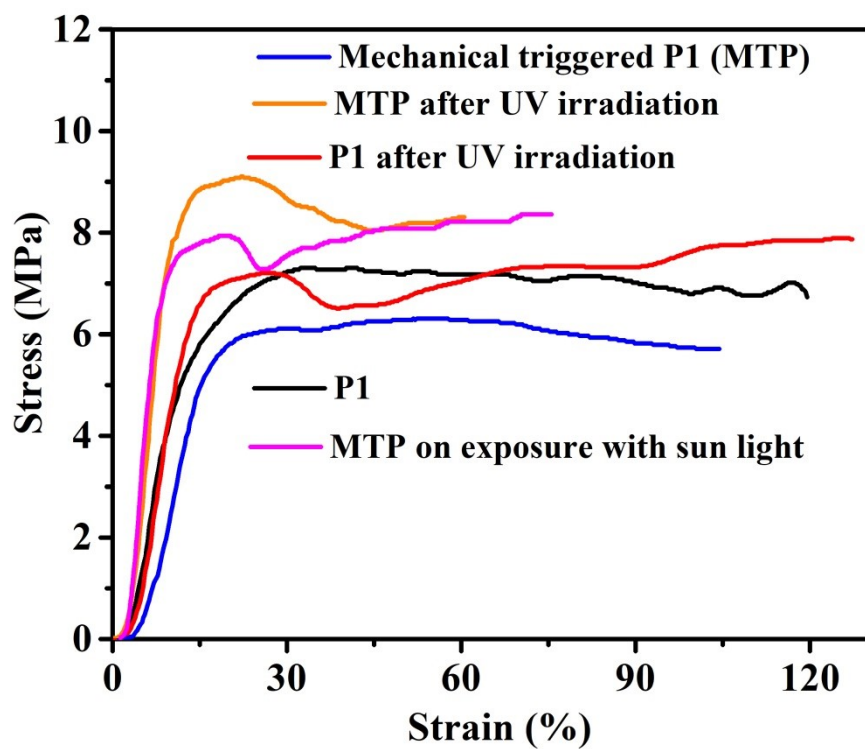
Figure S24 Stress-strain curves for the **P1** with different conditions. The tensile samples of mechanical triggered P1 (MTP) were prepared by casting a **P1** solution sonicated for 6 h. The times for UV irradiation and sunlight exposure were both 1 h.
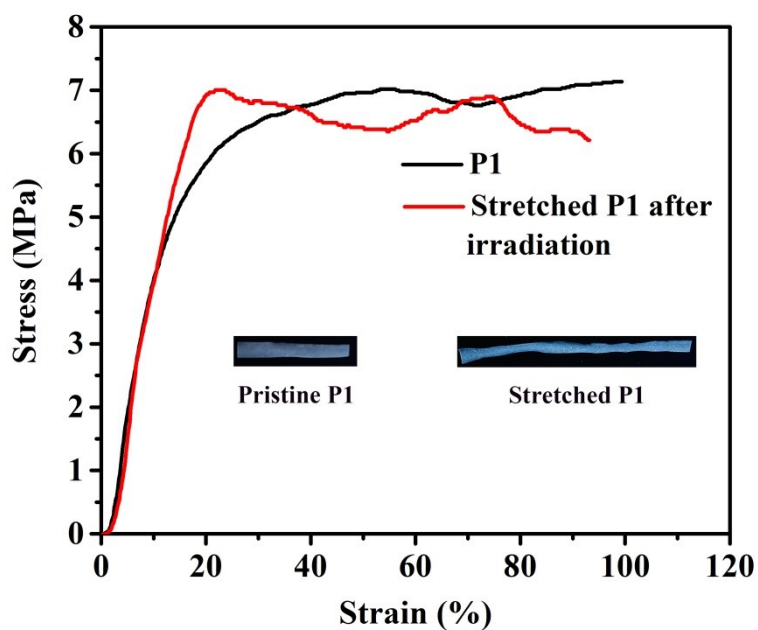
Figure S25 Stress-strain curves for the **P1** and stretched **P1** after UV irradiation. The inserts showed the fluorescent images of **P1** before and after stretching with hand.
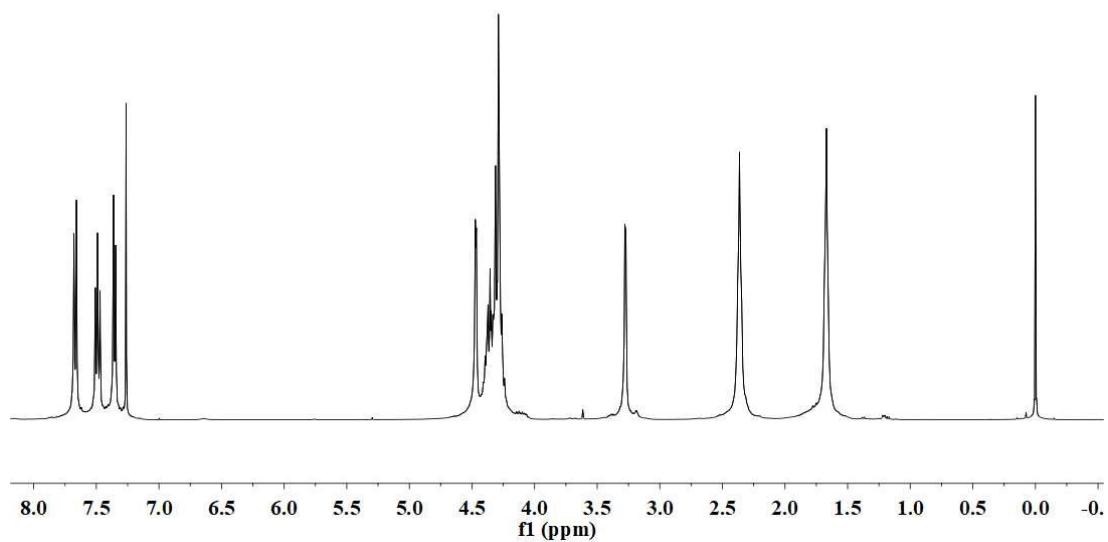
Figure S26 ^{1}H NMR spectrum of the stretched **P1** in CDCl$_3$. The vinyl protons originated from ring opened **NCD** could hardly be seen from ^{1}H NMR spectrum.

Figure S27 Fluorescent spectra of sonicated P1 under the irradiation of UV light (340 nm, 2.1 mW/cm^2)
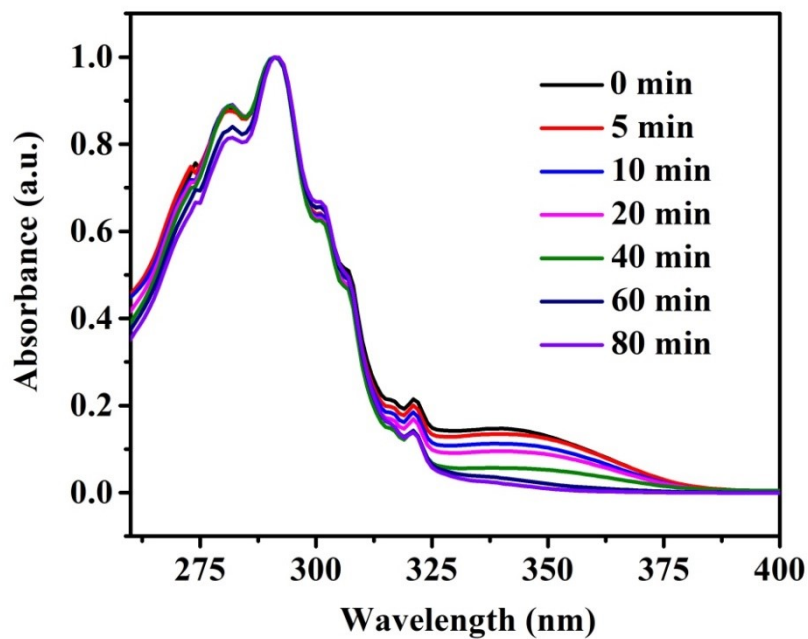
Figure S28 Absorption spectra of sonicated P1 under the irradiation of UV light (340 nm, 2.1 mW/cm^2)
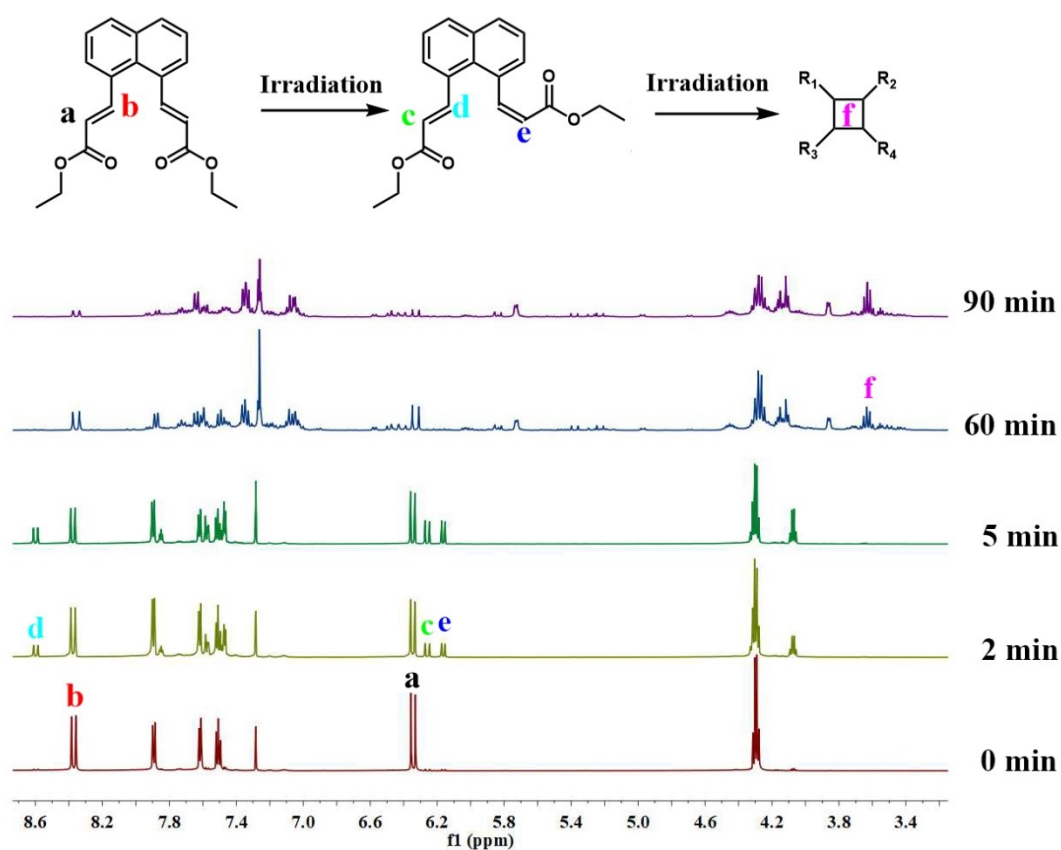
Figure S29 ^{1}H NMR spectra of reference compound **R1** as a function of irradiation time (340 nm, 2.1 mW/cm^2).

The coordinates for the optimized structure of modal molecules **R2**

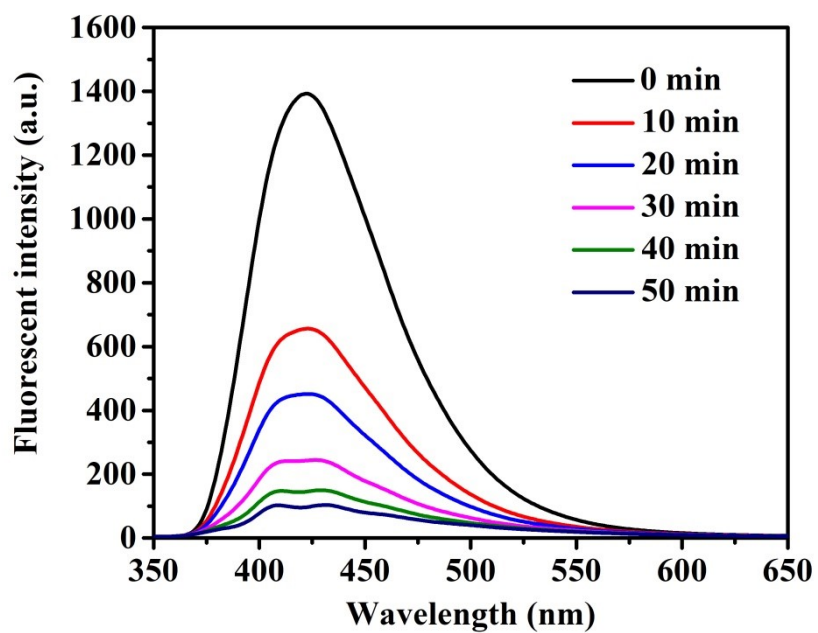| 1	C	-2.989353	1.629017	2.306448
2	C	-2.640800	0.479563	1.547443
3	C	-1.304106	0.169015	1.386152
4	C	-0.331295	1.007662	1.978743
5	C	-0.653471	2.149070	2.752951
6	C	-2.035716	2.441298	2.901254
7	C	0.444740	2.868551	3.298231
8	C	1.743368	2.447220	3.056948
9	C	2.041533	1.311458	2.253522
10	C	0.995464	0.590161	1.712649
11	C	-0.599576	-0.966809	0.683570
12	H	-4.046400	1.873391	2.429371
13	H	-3.428424	-0.140436	1.114917
14	H	-2.345027	3.309056	3.487898
15	H	0.261957	3.758113	3.903629
16	H	2.571887	3.008274	3.494123
17	H	3.080562	1.032360	2.070476
18	C	0.928653	-0.606722	0.796876
19	C	-0.516861	-0.883897	-0.892049
20	C	0.932303	-0.297470	-0.732447
21	C	-0.548168	-2.260008	-1.524067
22	O	-1.403294	-2.514569	-2.564366
23	C	-2.199191	-1.470415	-3.155465
24	O	0.144844	-3.173494	-1.117113
25	C	2.074273	-0.857746	-1.548516
26	O	3.176228	-1.132470	-1.112287
27	O	1.724689	-0.956753	-2.863806
28	C	2.762425	-1.489506	-3.721754
29	H	-0.893683	-1.958302	1.051357
30	H	1.597927	-1.436604	1.050830
31	H	-1.228621	-0.181233	-1.335204
32	H	0.906608	0.787584	-0.912936
33	H	-2.940697	-1.075794	-2.446263
34	H	-2.723541	-1.950862	-3.988897
35	H	-1.571857	-0.655934	-3.544756
36	H	3.653783	-0.849487	-3.684426
37	H	2.331250	-1.497668	-4.727611
38	H	3.027586	-2.505611	-3.405426

Sum of atomic energies is -996.64365 Ha.

The coordinates for the optimized structure of *trans,trans*-**R2**

1	C	-3.979517	1.943898	-0.342339

2	C	-3.280586	0.732454	-0.200765
3	C	-1.896575	0.691955	-0.027236
4	C	-1.151988	1.923513	-0.051003
5	C	-1.888762	3.157857	-0.081291
6	C	-3.297607	3.138390	-0.243875
7	C	-1.204375	4.392938	0.053903
8	C	0.167659	4.427432	0.188421
9	C	0.904395	3.232306	0.111835
10	C	0.286084	1.989647	-0.039925
11	C	-1.277495	-0.587405	0.330401
12	C	-1.654630	-1.805695	-0.115673
13	C	-1.011273	-3.030467	0.385643
14	O	-1.452105	-4.114781	-0.332910
15	C	-0.822101	-5.362559	0.022497
16	O	-0.199074	-3.111371	1.296441
17	C	1.121649	0.821288	-0.328771
18	C	2.361180	0.587441	0.156073
19	H	-5.062865	1.931121	-0.469349
20	H	-3.841560	-0.201164	-0.144885
21	H	-3.832274	4.089643	-0.282753
22	H	-1.786359	5.316748	0.043163
23	H	0.692322	5.377728	0.292929
24	H	1.993826	3.280470	0.090220
25	H	-0.469021	-0.559269	1.065501
26	H	-2.406880	-1.932179	-0.894773
27	H	0.264976	-5.299831	-0.124667
28	H	-1.258487	-6.109823	-0.649306
29	H	-1.028070	-5.614962	1.071004
30	H	0.726120	0.093447	-1.041812
31	H	2.815898	1.215887	0.922344
32	C	3.146162	-0.575021	-0.285933
33	O	4.297874	-0.664980	0.457903
34	C	5.132153	-1.797188	0.137133
35	O	2.854093	-1.362375	-1.175031
36	H	5.468766	-1.746414	-0.906910
37	H	4.583341	-2.735773	0.292206
38	H	5.985104	-1.732906	0.821590

Sum of atomic energies is -996.6455728 Ha

The coordinates for the optimized structure of *trans,cis*-**R2**.

1	C	-4.139220	0.962106	0.566646
2	C	-3.261943	-0.132305	0.491396
3	C	-1.904429	0.020960	0.202625
4	C	-1.388448	1.336194	-0.077206

5	C	-2.283521	2.454254	0.068733
6	C	-3.648541	2.237616	0.385683
7	C	-1.803275	3.776387	-0.110787
8	C	-0.486045	4.007779	-0.441773
9	C	0.380680	2.922707	-0.654178
10	C	-0.037366	1.602360	-0.502153
11	C	-1.047978	-1.162688	0.305073
12	C	-1.403971	-2.423168	-0.031492
13	C	-0.487913	-3.551665	0.193366
14	O	-1.057676	-4.720354	-0.252951
15	C	-0.225218	-5.886804	-0.083262
16	O	0.631426	-3.497965	0.685445
17	C	0.844794	0.523823	-0.960149
18	C	2.183831	0.337950	-0.851899
19	H	-5.188937	0.799448	0.815220
20	H	-3.629789	-1.128363	0.738754
21	H	-4.302273	3.105475	0.489804
22	H	-2.501483	4.606281	0.014822
23	H	-0.117331	5.025657	-0.576364
24	H	1.398014	3.112012	-0.986745
25	H	-0.047922	-1.029945	0.724976
26	H	-2.362522	-2.647891	-0.499983
27	H	0.727514	-5.759655	-0.613669
28	H	-0.797539	-6.717391	-0.508995
29	H	-0.020638	-6.062010	0.981313
30	H	0.328138	-0.251366	-1.534124
31	H	2.610812	-0.530899	-1.352420
32	C	3.155930	1.101191	-0.052510
33	O	4.389338	0.499713	-0.166435
34	C	5.432696	1.134755	0.599481
35	O	2.969164	2.090301	0.643702
36	H	5.566591	2.177147	0.279299
37	H	6.335986	0.549647	0.400615
38	H	5.189063	1.118705	1.670143

Sum of atomic energies is -996.6392238 Ha.

The coordinates for the optimized structure of *cis,cis*-**R2**

1	C	-3.809878	0.875625	0.597990
2	C	-2.921792	-0.209338	0.509684
3	C	-1.554700	-0.025183	0.295263
4	C	-1.053178	1.311687	0.073701
5	C	-1.957507	2.414095	0.262436
6	C	-3.329998	2.165903	0.520140
7	C	-1.478312	3.746653	0.177359

8	C	-0.152999	4.001622	-0.106479
9	C	0.720796	2.934721	-0.375346
10	C	0.299738	1.606154	-0.324100
11	C	-0.613300	-1.122235	0.517681
12	C	-0.663345	-2.477078	0.405122
13	C	1.161902	0.564093	-0.894420
14	C	2.503755	0.359910	-0.862062
15	H	-4.870327	0.690814	0.770024
16	H	-3.296755	-1.220291	0.645510
17	H	-4.000186	3.018116	0.652170
18	H	-2.180813	4.568842	0.332244
19	H	0.212900	5.026590	-0.170801
20	H	1.742545	3.144160	-0.680967
21	H	0.345978	-0.769975	0.905030
22	H	0.228597	-3.015170	0.727339
23	H	0.613187	-0.153569	-1.513249
24	H	2.896129	-0.462568	-1.461562
25	C	3.524692	1.028046	-0.039881
26	O	4.743277	0.430829	-0.287058
27	C	5.839195	0.934994	0.501938
28	O	3.387497	1.938720	0.765726
29	H	5.981396	2.010948	0.334799
30	H	6.717224	0.372551	0.165895
31	H	5.657314	0.758991	1.570808
32	C	-1.693896	-3.367762	-0.140466
33	O	-1.189187	-4.652154	-0.159563
34	C	-2.087671	-5.641449	-0.696001
35	O	-2.820967	-3.103778	-0.542001
36	H	-1.531103	-6.585074	-0.674683
37	H	-2.377738	-5.386545	-1.723402
38	H	-2.992471	-5.711895	-0.078816

Sum of atomic energies is -996.6307202 Ha.

References

[S1] Neese, F.; ORCA-an ab initio, Density Functional and Semiempirical Program Package Version 2.8 2011, Universität Bonn, Bonn, Germany.

[S2] Peng, C. Y., Ayala, P. Y., Schlegel, H. B. & Frisch, M. J. Using redundant internal coordinates to optimize equilibrium geometries and transition states. J. Comput. Chem. 17, 1996, 49-56.