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Ultrasound healable shape memory dynamic polymers

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Methods

Materials. Unless otherwise stated, all solvents and reagents were obtained from commercial suppliers with the highest purity available and used without further purification. Polycaprolactone diol (Perstorp, Capa2402, Mn=4,000 g mol^{-1}) was dried under vacuum at 110 °C for 12 h prior to use. Anhydrous tetrahydrofuran (THF) and 1,4-dioxane were obtained by distillation over sodium benzophenone. Compound **4**, **6** and **7** were synthesized using reported procedures[1,2] with some modifications. All reactions were carried out under an inert atmosphere of oxygen-free N_2 unless otherwise stated.

General characterizations. The ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker 400 (400 MHz) spectrometer. All chemical shifts were reported in parts per million (ppm) downfield from TMS using the residual protonated solvent as an internal standard (d_6-DMSO, ^1H 2.50 ppm and ^{13}C 39.7 ppm). DSC experiments were carried out under nitrogen atmosphere on TA Instruments DSCQ2000 at a heating rate of 5 °C min^{-1}. Dynamic Mechanical Thermal Analysis (DMTA) experiments were performed on a TA Instruments Q-800 instrument system in the dual cantilever mode. The storage modulus (G'), loss modulus (G'') and loss factor (tanδ) were measured from −100 to 100 °C under a nitrogen atmosphere at a heating rate of 3 °C min^{-1}. The strain amplitude used was 50 μm and the test frequency was 1 Hz. Surface temperatures were determined with a FLIR Systems infrared camera (Thermovision A20, Sweden). Dynamic rheological measurements were carried out in a dynamic rheometer (Bohlin Gemini 2000, Malvern, British) in constant-strain mode by controlling the strain at 1%. The diameter of the plate was 25 mm, and the gap was about 1 mm. All of the samples were tested from 60 to 180 °C at a heating rate of 3 °C min^{-1} in the frequency of 1 Hz.

Experimental setup. The general apparatus was assembled as shown in Figure S1.

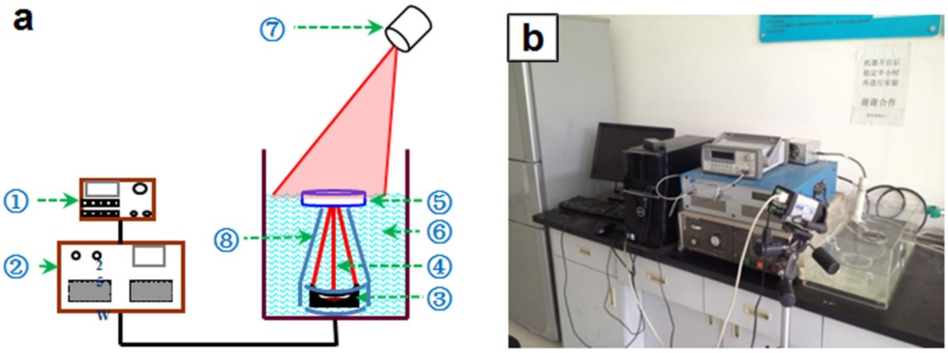

Fig. S1 Schematic illustration for experimental setup (a) and photo of the used high intensity focused ultrasound (HIFU) apparatus (b). ①: Arbitrary waveform generator, ②: RF power amplifier, ③: Acoustic lens transducer, ④: Ultrasound beams, ⑤: Polymer sample, ⑥: Water bath, ⑦: Infrared camera, ⑧: Transducer shell.

The high intensity focused ultrasound (HIFU) apparatus comprises three main components: an arbitrary waveform generator (Agilent 33220A Function Generator), a RF power amplifier (A150, Electronics & innovation) and an acoustic lens transducer (H-101, Sonic Concept, USA). The acoustic lens transducer with a high acoustic focal pressure within a long focal volume of Φ1.26 mm × 11 mm and a geometric focal length of 62.6 mm was mounted at the bottom of a tank filled with water and the beams of ultrasound were pointed upwards and focused on a specified spot. The ultrasound power output can be adjusted in the range of 0~150 W and the frequency of ultrasound is 1.1 MHz.

Synthetic Procedures.

Synthesis of 4,10-Dioxatricyclo[5.2.1.0^{2,6}]dec-8-ene-3,5-dione (compound 1). A solution of maleic anhydride (20 g, 204 mmol) in 50 mL anhydrous dioxane was charged to a flame dried 100 mL round-bottom flask with a magnetic stir bar. Furan (15 mL) was added via syringe and the solution was allowed to stir at room temperature for 30 min. The flask was sealed with a rubber plug and the mixture was kept still overnight. The product precipitated out of solution and was collected via vacuum filtration and washed with diethyl ether. The colorless crystals were 100% exo-addition product by NMR analysis and used without further purification. Yield 93.7%; mp 114–116 °C; ^{1}H NMR (400 MHz, d$_6$-DMSO, 298 K) δ (ppm) 6.580 (s, 2H), 5.349 (s, 2H), 3.311 (s, 2H); ^{13}C NMR (100 MHz, d$_6$-DMSO, 298 K) δ (ppm) 171.83, 137.11, 81.938, 49.356; FT-IR (KBr) ν=3095.3, 3033.4, 2997.2, 1860.8, 1790.4, 1226.9 cm^{-1}.

Synthesis of 4-(2-Hydroxyethyl)-10-oxa-4-azatricyclo[5.2.1.0^{2,6}]dec-8-ene-3,5-dione (compound 2). The anhydride **1** (5.00 g, 30.1 mmol) was suspended in MeOH (7 mL) in a flame dried 50 mL three-neck round-bottom flask with a magnetic stir bar and reflux condenser. The solution was purged with nitrogen for 10 minutes in an ice bath, after which ethanolamine (1.84 g, 30.1 mmol) in 3 mL MeOH was added dropwise via a dropping funnel. The resulting solution was allowed to stir for 5 min at 0 °C, then turned dark orange and was refluxed for 24 h. The flask was cooled to room temperature, and after 2 h the product began to crystallize. The mixture was stored in a freezer overnight, and the precipitate was collected by vacuum filtration. The resulting white crystals were washed with 2-propanol and used without further purification. Yield 70.5%; mp 134–137 °C; ^{1}H NMR (400 MHz, d$_6$-DMSO, 298 K) δ (ppm) 6.552 (s, 2H), 5.123 (s, 2H), 4.799 (s, 1H), 3.417 (s, 4H), 2.928 (s, 2H); ^{13}C NMR (100 MHz, d$_6$-DMSO, 298 K) δ (ppm) 176.72, 136.67, 80.518, 57.489, 47.349, 40.828; FT-IR (KBr) ν=3477.3, 3095.2, 2971.7, 2936.0, 2894.6, 1768.3, 1696.0 cm^{-1}.

Synthesis of 1-(2-Hydroxyethyl)-1*H*-pyrrole-2,5-dione (compound 3). To a flame dried 100 mL round-bottom flask equipped with a stir bar and vigreaux condenser was charged with compound **2** (4.18g, 20.0 mmol) and toluene (50 mL). The reaction was refluxed overnight. The resulting mixture was hot filtered, and the product crystallized from solution upon cooling. The colorless solid was collected via vacuum filtration, washed with diethyl ether and used without further purification. Yield 92.4%; mp 70–72 °C; ^{1}H NMR (400 MHz, d$_6$-DMSO, 298 K) δ (ppm) 7.014 (s, 2H), 4.793 (s, 1H), 3.456 (s, 4H); ^{13}C NMR (100 MHz, d$_6$-DMSO, 298 K) δ (ppm) 171.31, 134.65, 58.145, 40.147; FT-IR (KBr) ν=3445.9, 3275.4, 3108.4, 2964.1, 2932.9, 2880.2, 1711.9, 1406.3, 1158.7 cm^{-1}.

Synthesis of 1-(Hydroxymethyl)-10-oxatricyclo[5.2.1.0^{2,6}]dec-8-ene-3,5-dione-2-aminoethanol (compound 4). Compound **3** (1.41g, 10.0 mmol), high purity benzene (20 mL) and freshly distilled furfuryl alcohol (0.99g, 10.1 mmol) were added to a 100 mL round-bottom flask equipped with a magnetic stir bar and reflux condenser. The reaction was refluxed for 24 h, during which the product precipitated. The resulting mixture was cooled to room temperature. The product was collected via vacuum filtration and washed with diethyl ether. Yield 88.0%; mp 110–115 °C; ^{1}H NMR (400 MHz, d$_6$-DMSO, 298 K) δ (ppm) 6.504 (br, 2H), 5.076 (s, 1H), 4.956 (t, 1H), 4.792 (t, 1H), 4.020 (dd, 1H), 3.670 (dd, 1H), 3.402 (br, 4H), 3.032 (d, 1H), 2.869 (d, 1H); ^{13}C NMR (100 MHz, d$_6$-DMSO, 298 K) δ (ppm) 176.71, 175.28, 138.39, 136.76, 91.930, 80.461, 59.209, 57.581, 50.219, 48.036, 40.851; FT-IR (KBr) ν=3434.0, 3083.2, 2948.6, 1696.0, 1404.1, 1188.7, 1037.9 cm^{-1}.

Synthesis of N-(2,3-dihydroxy-propyl)-10-oxa-4-aza-tricyclo[5.2.1.0^{2,6}]-dec-8-ene-3,5-dione (compound 5). The anhydride **1** (5.00 g, 30.1 mmol) was suspended in EtOH (7.5 mL) in a flame dried 50 mL three-neck round-bottom flask with a magnetic stir bar and reflux condenser. A solution of 3-amino-1,2-propanediol (2.74 g, 30.1 mmol) in EtOH (2 mL) was added drop wise to the reaction system via a dropping funnel. The resulting mixture was refluxed at 85 °C for 12 hours, during which the solution turned orange and then the product began to precipitate. After the reaction, the mixture was stored in a freezer overnight, and the crystal was collected by vacuum filtration and washed with diethyl ether. The product was dried under vacuum and used without further purification. Yield 54.5%; ^{1}H NMR (400 MHz, d_6-DMSO, 298 K) δ (ppm) 6.550 (s, 2H), 5.126 (s, 2H), 4.805 (s, 1H), 4.586 (s, 1H), 3.672 (m, 1H), 3.349 (d, 2H), 3.277 (d, 2H), 2.928 (s, 2H); ^{13}C NMR (100 MHz, d_6-DMSO, 298 K) δ (ppm) 176.60, 136.46, 80.312, 68.054, 63.882, 47.151, 41.753; FT-IR (KBr) ν=3396.7, 2999.2, 2935.1, 2894.5, 1768.7, 1696.2, 1436.5, 1404.8, 1339.8, 1189.1, 1062.9, 883.1 cm^{-1}.

Synthesis of N-(2,3-dihydroxypropyl)maleimide (compound 6). To a flame dried 100 mL round-bottom flask equipped with a stir bar and vigreaux condenser was charged with compound **5** (4.78g, 20.0 mmol) and toluene (50 mL). The reaction was refluxed overnight. The resulting mixture was hot filtered, and the product crystallized from solution upon cooling. The colorless solid was collected via vacuum filtration, washed with petroleum ether and used without further purification. Yield 83.6%; ^{1}H NMR (400 MHz, d_6-DMSO, 298 K) δ (ppm) 7.000 (s, 2H), 4.873 (d, 1H), 4.645 (t, 1H), 3.682 (m, 1H), 3.422 (d, 2H), 3.345 (m, 2H); ^{13}C NMR (100 MHz, d_6-DMSO, 298 K) δ (ppm) 171.64, 134.89, 68.922, 64.504, 41.612; FT-IR (KBr) ν=3500.2, 3411.0, 3102.8, 2942.9, 2892.1, 1702.3, 1444.2, 1412.7, 1330.1, 1166.8, 1101.4, 1050.4 cm^{-1}.

Synthesis of 1,6-hexamethylene-bis(2-furanylmethylcarbamate) (compound 7). A flame dried 100 mL three-necked flask equipped with magnetic stirrer, thermometer, and condenser was charged with furfuryl alcohol (9.80 g, 0.10 mol), anhydrous THF (50mL) and dibutyltin dilaurate (0.50 g). The solution was purged with dry nitrogen for 10 minutes and 1,6-hexamethylene diisocyanate (HDI, 8.40 g, 0.05 mol) was added dropwise via a dropping funnel under vigorous stirring. The reaction mixture was maintained for 30 min at room temperature and stirred for 4 h at 50 °C. Then the resulting white product was recrystallized from methanol. Yield 88.4%; mp 101–103

°C; ^{1}H NMR (400 MHz, d_6-DMSO, 298 K) δ (ppm) 7.654 (d, 2H), 7.225 (m, 2H), 6.444 (d, 4H), 4.983 (s, 4H), 2.957 (m, 4H), 1.356 (s, 4H), 1.214 (s, 4H); ^{13}C NMR (100 MHz, d_6-DMSO, 298 K) δ (ppm) 155.92, 150.49, 143.53, 110.82, 110.38, 57.431, 40.404, 29.605, 26.130; FT-IR (KBr) ν=3327.9, 3048.2, 2940.2, 2864.2, 1687.1, 1534.4, 1469.3, 1338.8, 1262.2 cm^{-1}.

Synthesis of polymers. The PU−FM and the control polymers were synthesized according to Scheme 1. Typically, the synthesis of PU−FM$_{20}$ is as follows. Firstly, a precursor **8** was synthesized by the reaction of PCL and MDI (1:2) at 80 °C under nitrogen atmosphere for 2 h. The precursor **8** (13.50 g, 3.00 mmol), compound **4** (0.8960 g, 3.75 mmol) and hexamethylene diisocyanate trimer (tri-HDI) (0.2520 g, 0.50 mmol) were dissolved in anhydrous 1,4-dioxane (15 mL). The mixture was degassed under reduced pressure and then cast into Teflon molds. Polymerization reaction and evaporation of the solvent took place at 80 °C under nitrogen atmosphere for 96 h. The polymer was further dried under vacuum to obtain a pale yellow non-transparent solid. The samples of PU−BM$_{20}$ and PU′−FM′$_{20}$ were prepared through the similar procedures by using the following monomer molar ratios respectively: (1) [tri-HDI]:[compound **8**]:[1,4-benzenedimethanol (BM)]=8:48:60; (2) [compound **6**]:[compound **7**]:[compound **8**]=5:1:5. After demolding, all the polymers were kept in a desiccator to avoid moisture.

Table S1 The component of PU−FM with different crosslinking index.

Sample	PU−FM$_{20}$	PU−FM$_{30}$	PU−FM$_{40}$	PU−FM$_{50}$
[tri-HDI] : [**8**] : [**4**]	8 : 48 : 60	12 : 42 : 60	16 : 36 : 60	20 : 30 : 60
ρ	20%	30%	40%	50%

The crosslinking index ρ (for PU−FM) and ρ' (for PU′−FM′), are defined as:

$$\rho = 100\%\frac{3N_{tri-HDI}}{2N_4} \qquad \rho' = 100\%\frac{4N_7}{2N_{MDI}} = 100\%\frac{4N_7}{2(2N_8)}$$

where $N_{\text{tri-HDI}}$, N_4 , N_7, N_{MDI} and N_8 are the mole number of tri-HDI, compound **4**, compound **7**, MDI, and compound **8** respectively. Note that: for PU′−FM′, (1) the mole number of hydroxyl groups which serve as cross-linkages is equal to $4N_7$; (2) according to the synthesis procedures, N_{MDI} is equal to $2N_8$.

Morphology characterization. Small-angle X-ray scattering (SAXS) experiments were performed at the beamline BL16B1 at Shanghai Synchrotron Radiation Facility (SSRF), China, using the third generation of synchrotron radiation light sources. The energy of the X-ray radiation was 10 keV and the wavelength of the radiation source is 0.124 nm. The scattering patterns were collected by a Mar165 CCD detector (Diamond Light Source, Oxfordshire, UK), which had a resolution of 2048×2048 pixels (pixel size=80×80 μm^2). The image acquisition time was 200 s and the sample-to-detector distance was 2030 mm. All the images were corrected for background scattering, air scattering and beam fluctuations. The two-dimensional data sets were azimuthally averaged to give intensity as a function of the magnitude of the scattering vector, q, where $q=4\pi \sin(\theta)/\lambda$ and 2θ is the scattering angle. The long period (d_{long}) was calculated with the Bragg equation: $d_{\text{long}}=2\pi/q_{\max}$ (nm), in which $q_{\max}$ corresponds to the peak position in the scattering curves (i.e., $I(q)q^2$ vs. q). Sections for AFM were prepared by ultramicrotomy using a Leica UCT ultracryomicrotome and the AFM data were collected on a Nano Scope MultiMode Ⅲa AFM (Veeco Instruments, USA) in a tapping mode. 3D images in Figure 3 were collected with a VHX-1000C Digital Microscope (Keyence, Japan).

Mechanical testing. The mechanical properties of PU−FM and the control polymers were measured using an Instron 5567 machine (USA) with a 500 mm min^{-1} strain rate at 25 °C. In order to clearly show the process of HIFU-triggered crack closure assisted healing of PU−FM and obtain a better healing efficiency, the test samples were tailored using a gauge dimension: 35 mm × 8 mm, thickness of 3.0-3.2 mm measured for each sample with a digital vernier caliper. Each measurement was repeated at least three times. Young's modulus was determined from the initial slope of the stress–strain curves.

HIFU-triggered shape memory assisted healing. As shown in Figure S2, samples of PU−FM and the control polymers were cut and bent to obtain a crack with ~50% of the sheet width and an angle of ~10° between two cut scars. Using the HIFU apparatus setup shown in Figure S1, the localized and directed control of shape memory assisted healing of the damaged samples were investigated by exposure of samples to the HIFU focus.

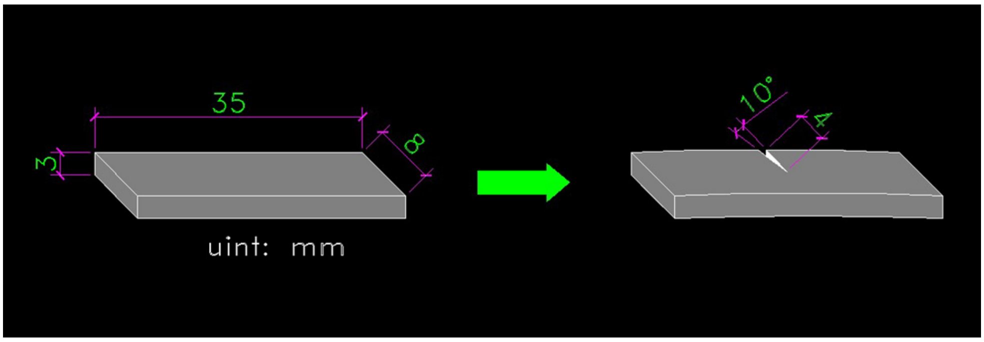

Fig. S2 Schematic illustration of the dimensions of the sample plates used for stress-strain experiments and of the damaged samples for HIFU-triggered shape memory assisted healing experiments.

HIFU-triggered dynamic exchange reactions of low molecular weight model compounds. Ultrasound-responsive dynamic exchange reactions were carried out directly in screw-cap NMR tubes equipped into the HIFU apparatus. The ^1H NMR spectra were recorded on a Bruker 400 (400 MHz) spectrometer, and chemical shifts were recorded in parts per million (ppm) downfield from TMS using the residual protonated solvent as an internal standard (d_6-DMSO, ^1H 2.50 ppm). Equimolar amounts of furan-maleimide Diels-Alder adduct **4** and maleimide **9** were dissolved in 0.5 mL of d_6-DMSO in a screw-cap NMR tube to give a 0.1 mol L^{-1} solution. The top of the NMR tube was then wrapped tightly in Teflon tape. An initial ^1H NMR spectrum was obtained at 25 °C immediately after sample preparation and taken as time = 0 h. The second ^1H NMR spectrum was obtained after the sample had been kept at 25 °C for 120 h. The NMR tube was then exposed to the HIFU focal spot, and the third ^1H NMR spectrum was obtained after the sample exposing to HIFU treatment for 60 min.

Temperature-dependent FTIR characterization of the dynamic polymers. The temperature-dependent absorbance FTIR spectra of PU−FM_{20} were recorded with a 4 cm^{-1} spectral resolution on a Nicolet-IS10 (Thermo Electron Co., USA) spectrometer by signal averaging 20 scans. Two pieces of microscope KBr windows, which have no absorption bands in the MIR region, were used to prepare a transmission cell. Variable-temperature spectra, controlled by a temperature control instrument including programmed heating cell and circulating water jacket cooling system, were collected between 30 and 150 °C with a heating rate of 5 °C min^{-1}.

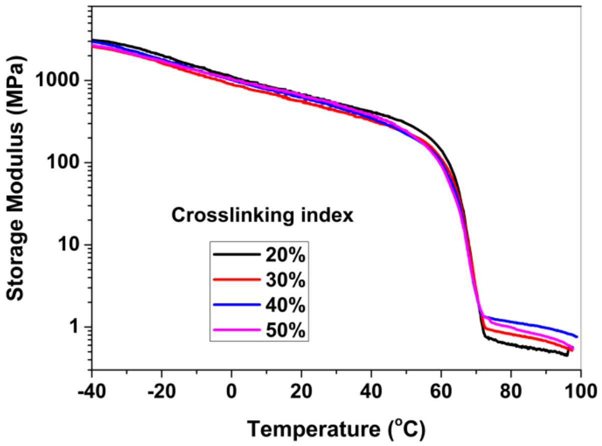

Fig. S3 Dynamic Mechanical Thermal Analysis (DMTA) traces of PU−FM. Experiments were conducted under N_2 at a heating rate of 3 °C min^{-1} and a frequency of 1 Hz.

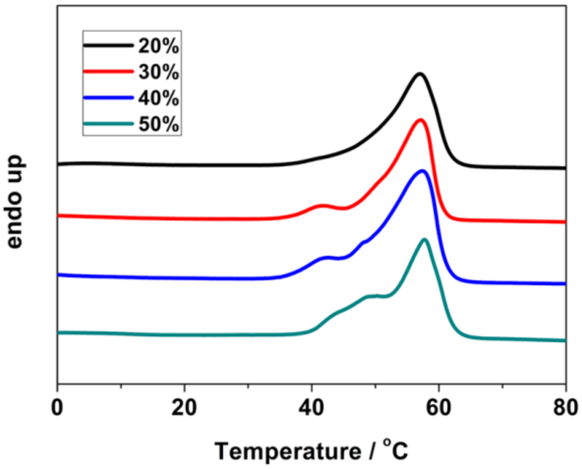

Fig. S4 Differential scanning calorimetry (DSC) traces of PU−FM, showing the T_m of PCL segments in PU−FM ranging from 57 to 60 °C. Experiments were conducted at a heating rate of 5 °C min^{-1} under nitrogen atmosphere.

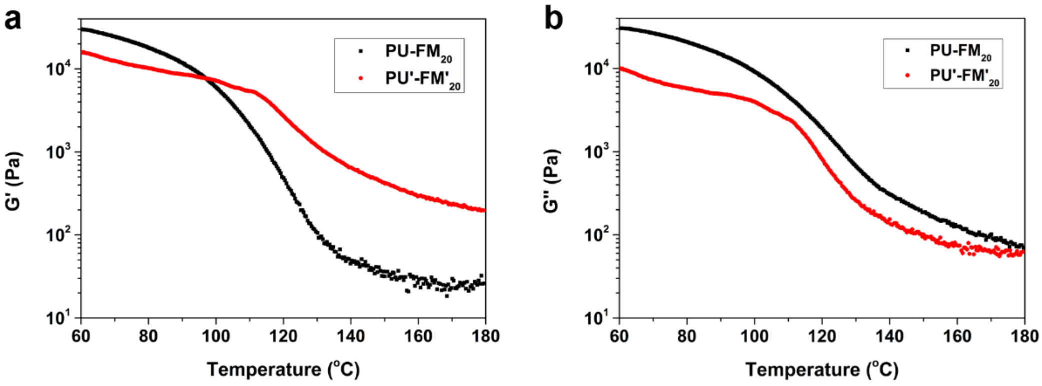

Fig. S5 (a) Elastic modulus (storage modulus G′) and (b) viscous modulus (loss modulus G″) versus temperature at a fixed frequency of 1 Hz.

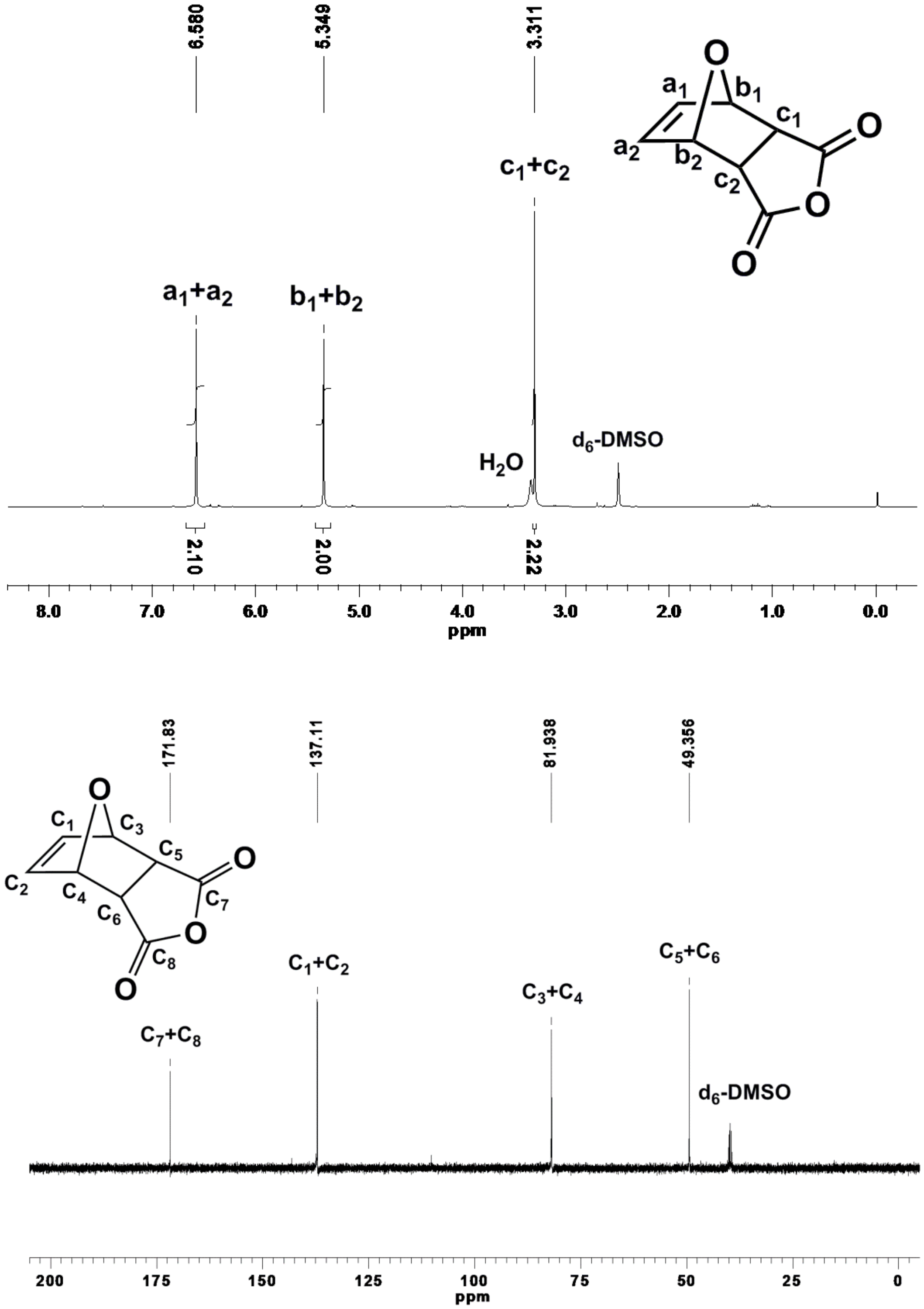

Fig. S6 ^{1}H (top) and ^{13}C (bottom) NMR spectra of 4,10-dioxatricyclo[5.2.1.0^{2,6}]dec-8-ene-3,5-dione.

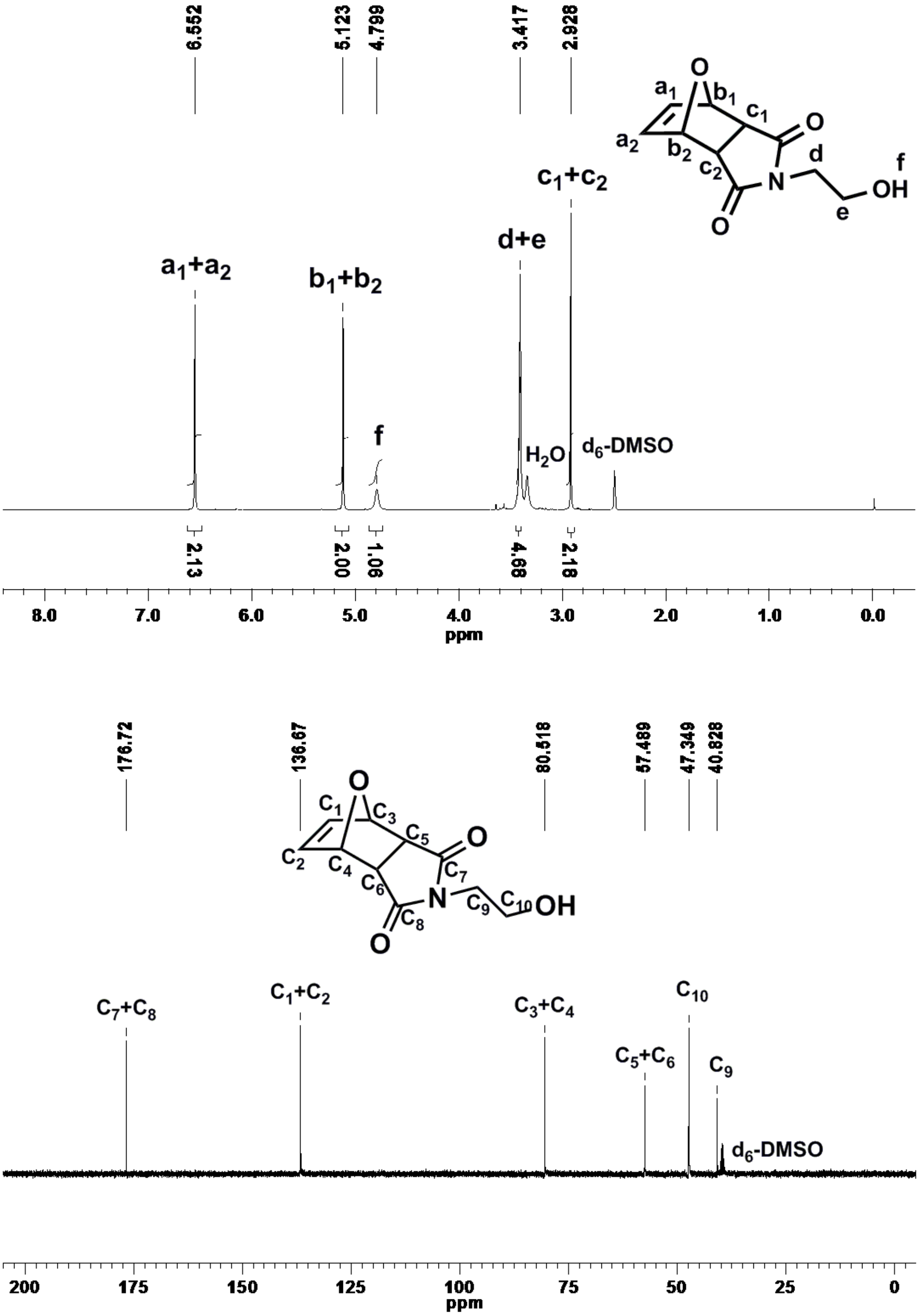

Fig. S7 ^1H (top) and ^{13}C (bottom) NMR spectra of 4-(2-hydroxyethyl)-10-oxa-4-azatricyclo [5.2.1.0^{2,6}]dec-8-ene-3,5-dione.

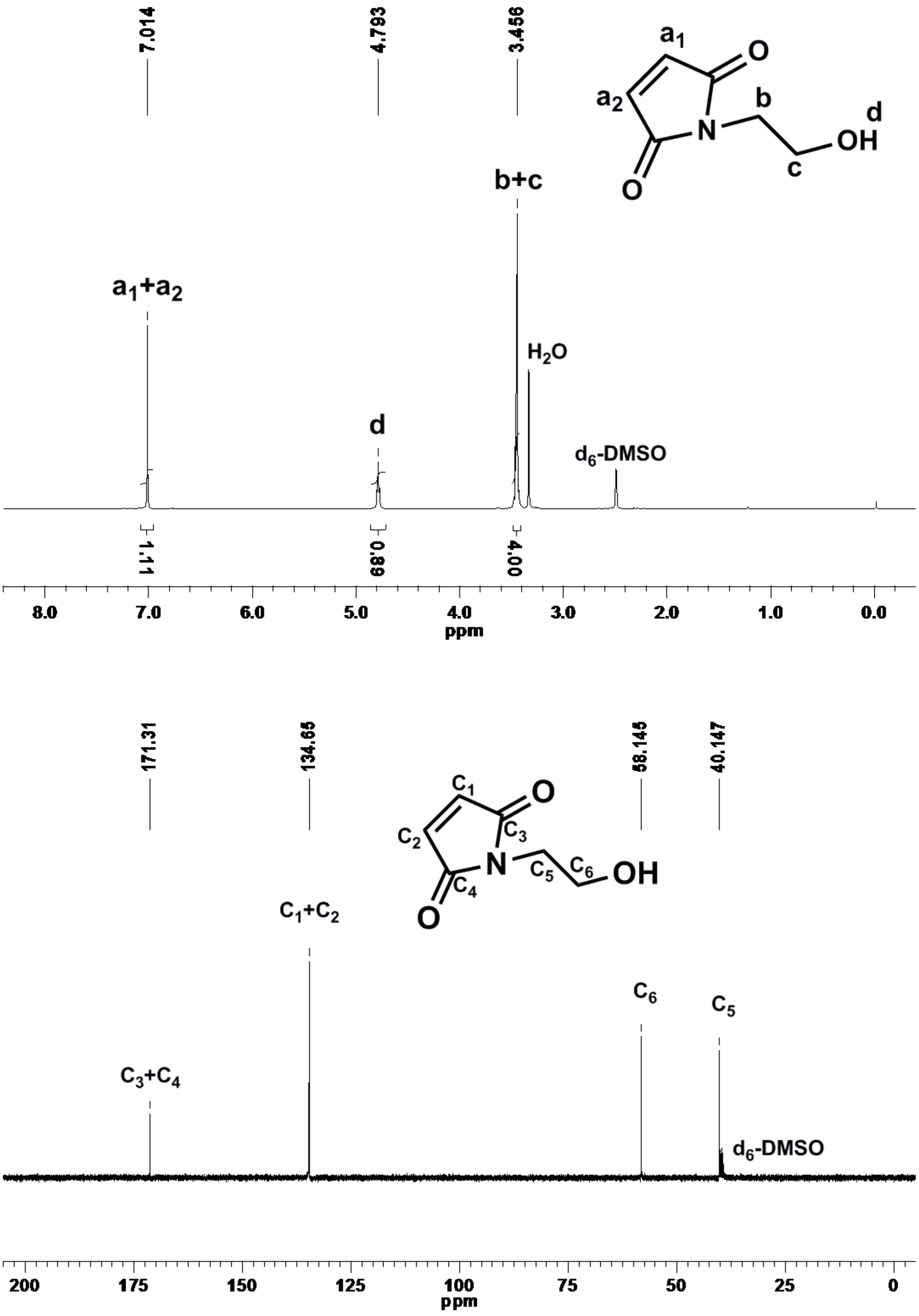

Fig. S8 ^{1}H (top) and ^{13}C (bottom) NMR spectra of 1-(2-hydroxyethyl)-1*H*-pyrrole-2,5-dione.

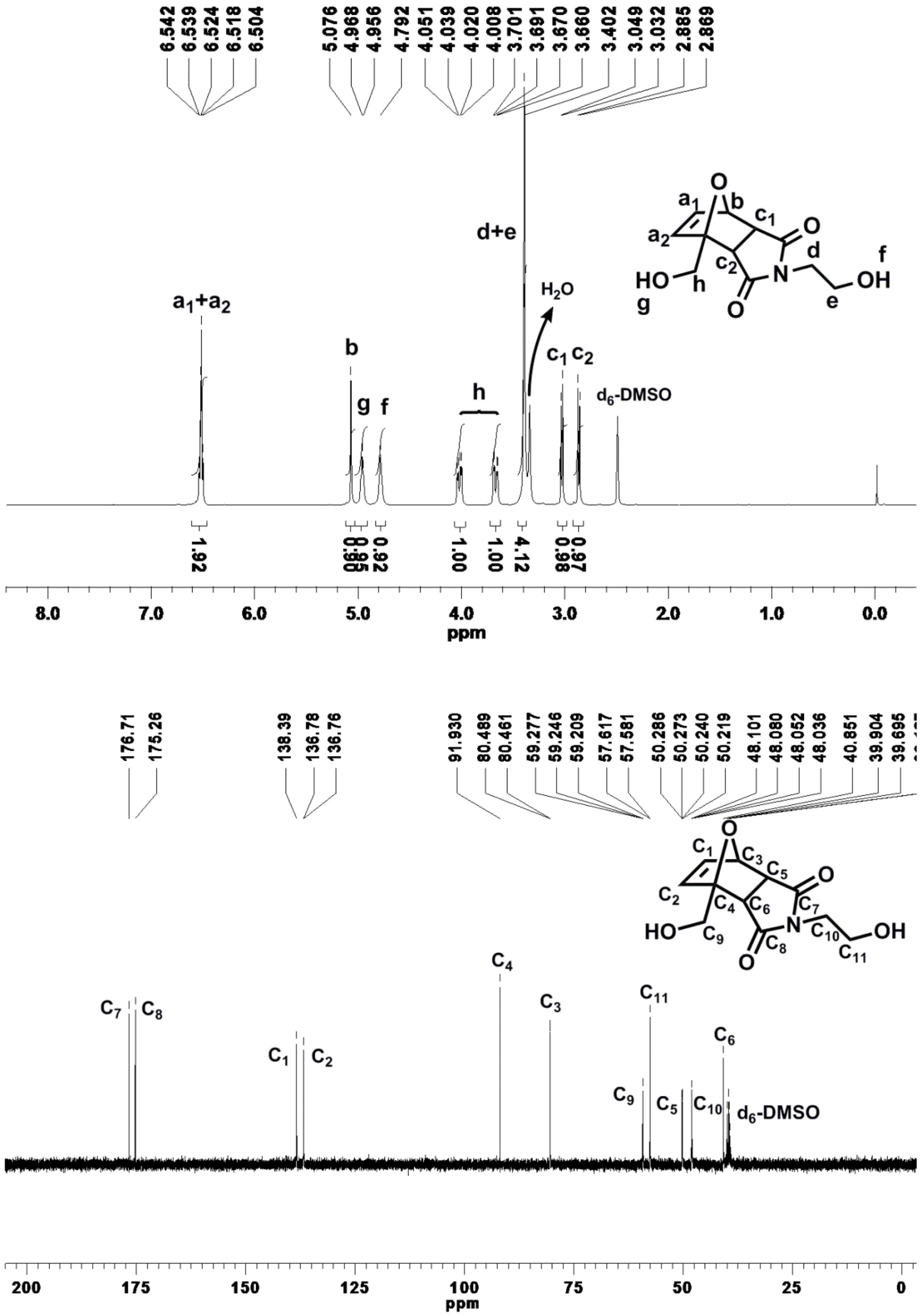

Fig. S9 ^1H (top) and ^{13}C (bottom) NMR spectra of 1-(hydroxymethyl)-10-oxatricyclo [5.2.1.0^{2,6}]dec-8-ene-3,5-dione-2-aminoethanol.

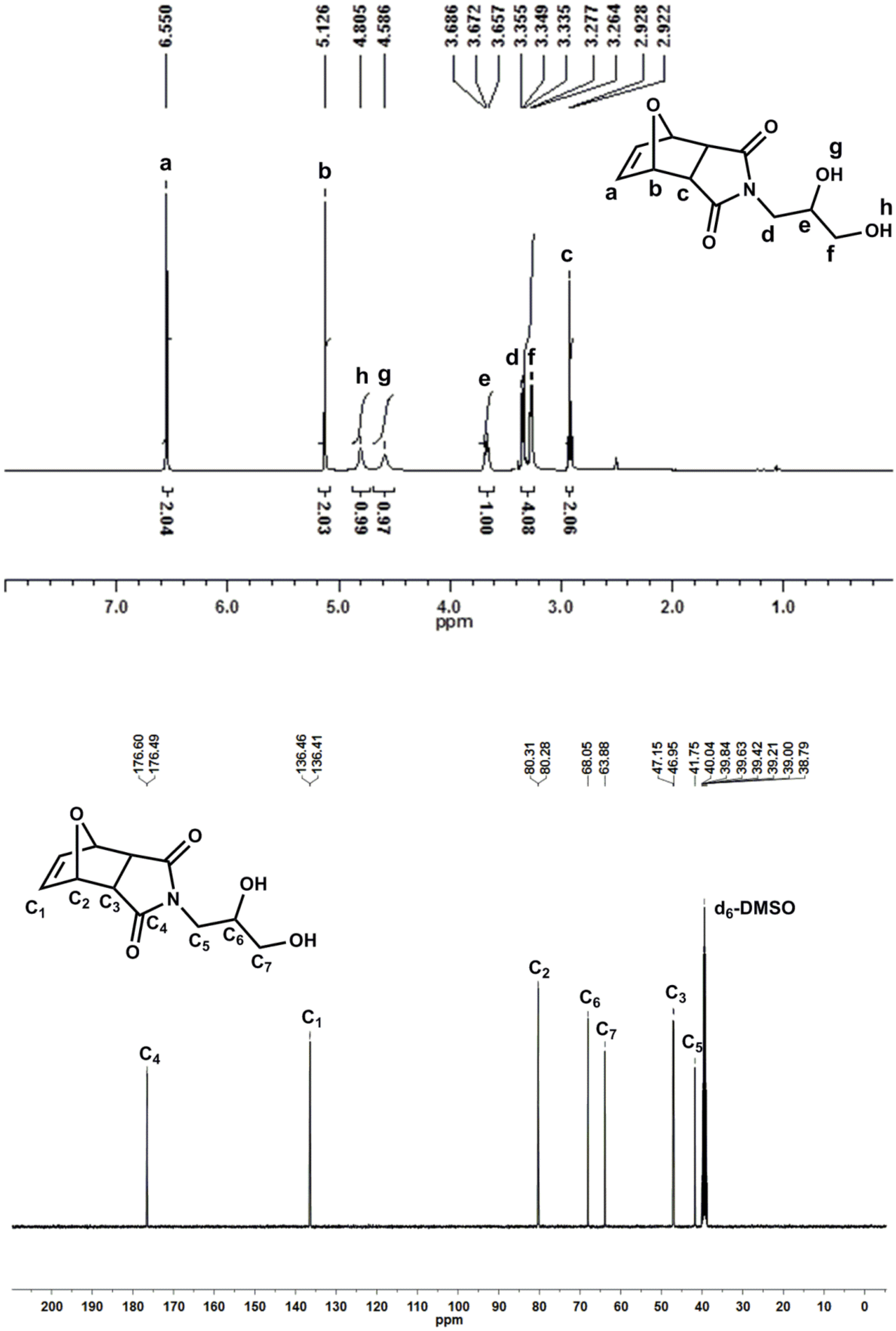

Fig. S10 ^{1}H (top) and ^{13}C (bottom) NMR spectra of N-(2,3-dihydroxy-propyl)-10-oxa-4- aza-tricyclo[5.2.1.0^{2,6}]-dec-8-ene-3,5-dione.

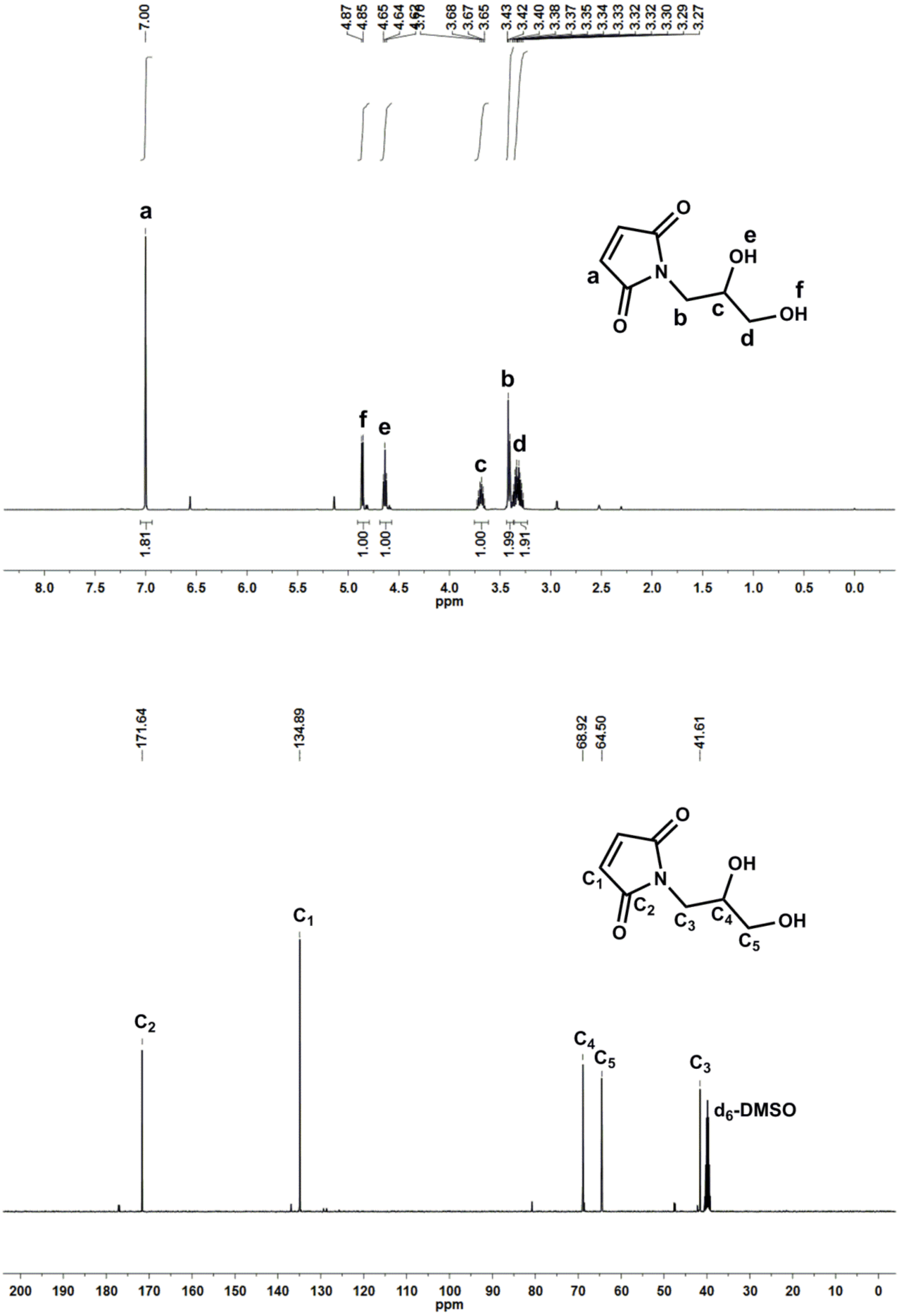

Fig. S11 ^{1}H (top) and ^{13}C (bottom) NMR spectra of N-(2,3-dihydroxypropyl)maleimide.

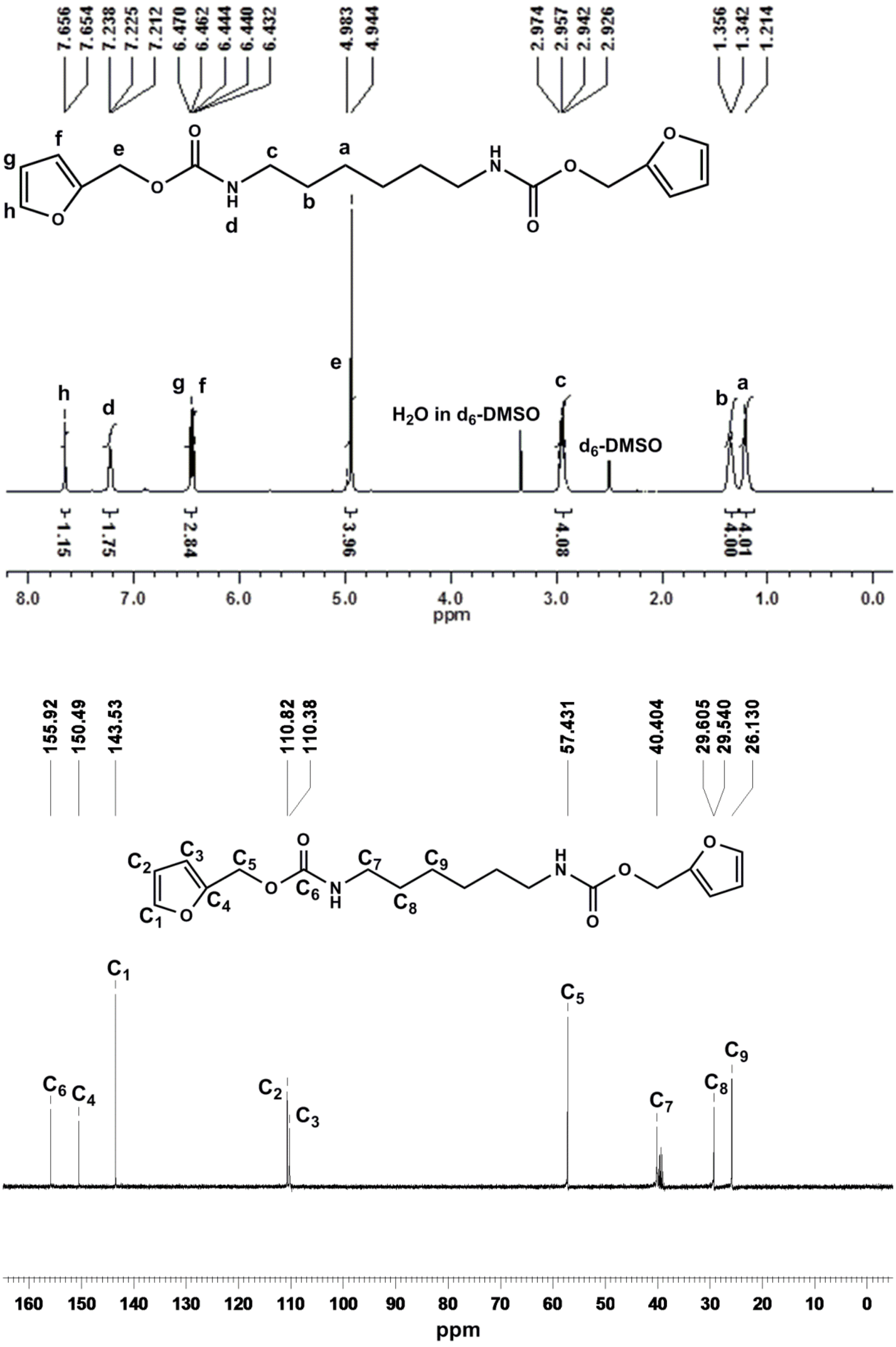

Fig. S12 ^1H (top) and ^{13}C (bottom) NMR spectra of 1,6-hexamethylene-bis (2-furanylmethylcarbamate).

Supporting Movie Legend:

Movie S1 records the process of HIFU-triggered shape memory assisted healing of PU−FM. The damaged samples were prepared as shown in Figure S2 and then exposed to the HIFU focal spot for a period of time under a given HIFU power output.

Movie S2 shows the experiment for HIFU-triggered reshuffling or dynamic exchange reaction of the low molecular weight DA model compounds.

References

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