

Supporting Information for

**Poly(β -keto enol ether) Prepared by Three-Component Polycondensation of Bis(diazoketone),
Bis(1,3-diketone), and Tetrahydrofuran: Mild Acid-Degradable Polymers to Afford
Well-Defined Low Molecular Weight Components**

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Experimental

Materials.

$\text{Rh}_2(\text{OAc})_4$ (Azmax, 99%), 1,3-diphenyl-1,3-propanedione **2** (FUJIFILM Wako Pure Chemical, >98%), NaH (Nacalai Tesque, abt. 60% oil suspension), CaH_2 (Nacalai Tesque, >90.0%), Na_2SO_4 (Nacalai Tesque, >98.5%), methanol (Yoneyama Yakuhin Kogyo, 99%), chloroform (Junsei Chemical, 99%), dichloromethane (Junsei Chemical, 99%), and hydrochloric acid (Nacalai Tesque, 35-37%) were used as received. Acetone (FUJIFILM Wako Pure Chemical, 99%) was dried over CaH_2 and used without further purification. Tetrahydrofuran (THF, Kanto Chemical, > 99.5%, dehydrated Super Plus grade) was further purified using Glass Contour MINI (Nikko Hansen & Co.). Diazoacetophenone (**1**),¹ 4,4-dimethyl-1-phenylpentane-1,3-dione (**6**),² 3,3'-(1,4-Phenylene)bis(1-phenylpropane-1,3-dione) (**X1**),^{3,4} 1,1'-(1,4-Phenylene)bis-3,3-dimethylpentane-1,3-dione (**X2**),⁴ 1,2-Bis[(4-diazoacetylphenyl)dimethylsilyl]ethane (**A1**),⁵ and 4,4'-Bis(diazoacetyl)biphenyl (**A2**)⁶ were prepared according to the literatures. **Caution!** Extra care must be taken for preparation and handling of the diazoacetates because of their potential explosiveness.

Model reactions.

Three-component coupling of 1, 2 and THF (Scheme 3). Under a N_2 atmosphere, a THF (3.0 mL) solution of **2** (0.128 g, 0.571 mmol) and $\text{Rh}_2(\text{OAc})_4$ (2.60 mg, 5.89×10^{-3} mmol) ($[\text{2}]/[\text{Rh}] = 48.5$, Rh; 2.06 mol%) was placed in a Schlenk tube, and the solution was maintained at 25 °C by using an oil bath with a thermo-controller. A THF (2.7 mL) solution of **1** (0.100 g, 0.684 mmol) was added to the solution, and the resulting mixture was stirred at 25 °C for 13 h. After volatiles were removed under reduced pressure, CH_2Cl_2 and H_2O were added, and the organic layer was separated by using a separatory funnel. The organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified with preparative size-exclusion chromatography (SEC) using CHCl_3 as eluent, to afford 0.199 g (0.480 mmol, 84% yield) of **3** as pale orange oil.

Acid-catalyzed decomposition of 3 (Scheme 3). An acetone (19.2 mL) solution of **3** (0.192 g, 0.463 mmol) was placed in a round bottomed flask equipped with a three-way cock. After 2 drops of 1 M HCl/MeOH was added to the solution, the mixture was stirred at room temperature for 12 h. After CH_2Cl_2 and H_2O were added to the mixture, an organic layer was separated using a separatory funnel. After the organic layer was dried over Na_2SO_4 and concentrated under reduced pressure, the resulting residue was subjected to preparative SEC with CHCl_3 as eluent, yielding **2** (99.9 mg, 0.445 mmol, 96% yield) and **4** (91.6 mg, 0.440 mmol, 95% yield, a yellow solid).

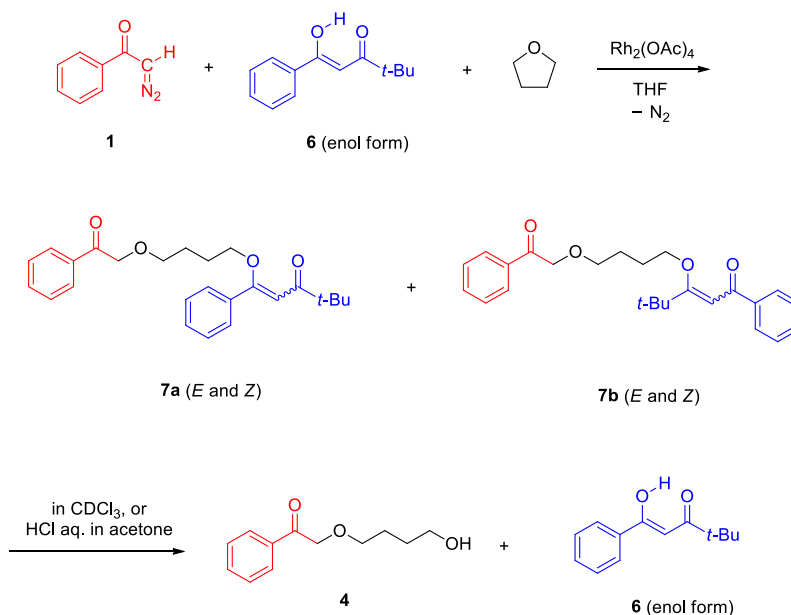
4: ^1H NMR (500 MHz, CDCl_3 , δ): 7.93 (d, $J = 7.8$ Hz, 2H, *o*-Ph-H), 7.59 (t, $J = 7.5$ Hz, 1H, *p*-Ph-H), 7.47 (t, $J = 7.8$ Hz, 2H, *m*-Ph-H), 4.77 (s, 2H, $\text{C}=\text{O}-\text{CH}_2-\text{O}$), 3.69 (t, $J = 6.0$ Hz, $\text{O}-\text{CH}_2-\text{CH}_2$), 3.64 (t, $J = 5.8$ Hz, $\text{O}-\text{CH}_2-\text{CH}_2$), 2.04 (br, 1H, OH), 1.78 (quintet, 2H, $\text{O}-\text{CH}_2-\text{CH}_2-\text{CH}_2$), 1.71 (quintet, 2H, $\text{O}-\text{CH}_2-\text{CH}_2-\text{CH}_2$). ^{13}C NMR (125 MHz, CDCl_3 , δ): 196.56 (C=O), 134.82 (Ph), 133.67 (Ph), 128.79 (Ph), 127.88 (Ph), 73.68 ($\text{O}-\text{CH}_2$), 71.84 ($\text{O}-\text{CH}_2$), 62.34 ($\text{O}-\text{CH}_2$), 29.61 ($-\text{CH}_2-\text{CH}_2-\text{CH}_2$), 26.39 ($-\text{CH}_2-\text{CH}_2-\text{CH}_2$). Anal. Calcd for $\text{C}_{12}\text{H}_{16}\text{O}_3 \cdot 0.3\text{H}_2\text{O}$: C, 67.46; H, 7.83. Found: C, 67.93, H, 7.91.

Three-component coupling of 1, X1 and THF (Scheme 5). The reaction of **1** (0.121 g, 0.828 mmol) with **X1** (0.127 g, 0.343 mmol) catalyzed by $\text{Rh}_2(\text{OAc})_4$ (1.64 mg, 3.71×10^{-3} mmol, $[\text{X1}]/[\text{Rh}] = 46.2$) was carried out in a similar procedure as described above for the reaction of **1** with **2**. The product **5** (0.235 g, 0.313 mmol, 91% yield) was obtained as a pale yellow

solid.

Acid-catalyzed decomposition of 5 (Scheme 5). Decomposition of **5** (0.257 g, 0.342 mmol) was carried out in a similar procedure as for **3**, yielding **4** (0.121 g, 0.581 mmol, 85% yield) and **X1** (0.0993 g, 0.268 mmol, 78% yield) after isolation using preparative-SEC.

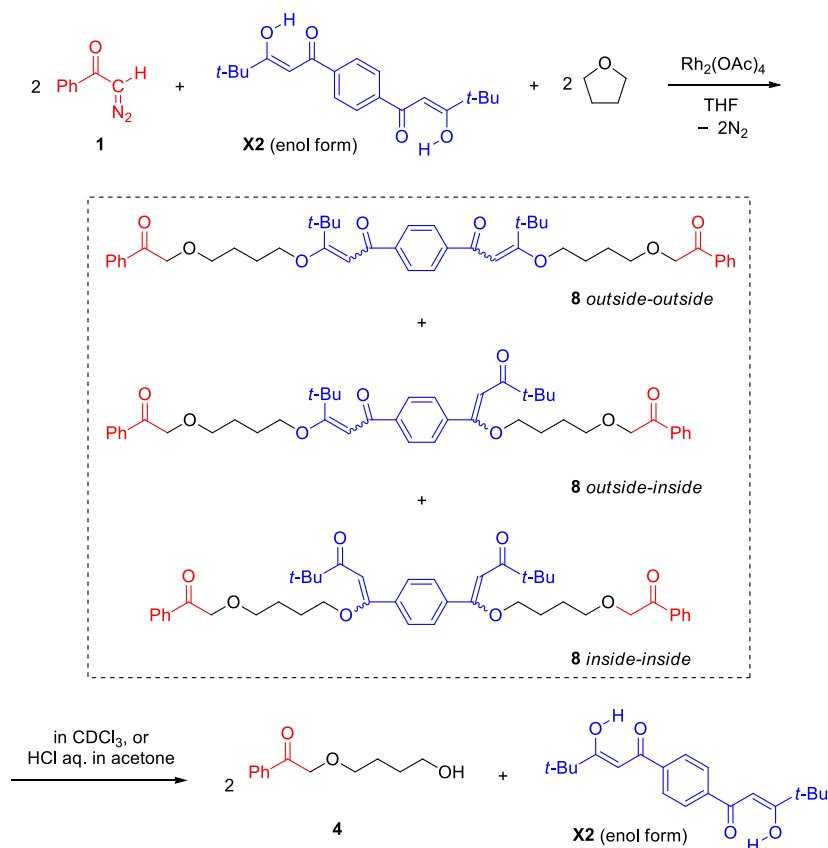
Three-component coupling of 1, 6 and THF (Scheme S1). The reaction of **1** (0.101 g, 0.691 mmol) with **6** (0.123 g, 0.602 mmol) catalyzed by $\text{Rh}_2(\text{OAc})_4$ (2.68 mg, 6.07×10^{-3} mmol, $[\mathbf{6}]/[\text{Rh}] = 49.6$) was carried out in a similar procedure as described above for the reaction of **1** with **2**. The product **7** (0.196 g, 0.497 mmol, 84% yield) was obtained as pale orange oil.



Scheme S1. Model reaction of **1** with **6** in THF followed by acid-catalyzed decomposition.

Acid-catalyzed decomposition of 7 (Scheme S1). Decomposition of **7** (0.186 g, 0.471 mmol) was carried out in a similar manner as for **3**, yielding **4** (0.0900 g, 0.432 mmol, 92% yield) and **6** (0.0704 g, 0.345 mmol, 73% yield) after isolation using preparative-SEC.

Three-component coupling of 1, X2 and THF (Scheme S2). The reaction of **1** (0.103 g, 0.705 mmol) with **X2** (0.0941 g, 0.285 mmol) catalyzed by $\text{Rh}_2(\text{OAc})_4$ (3.02 mg, 6.84×10^{-3} mmol, $[\mathbf{X2}]/[\text{Rh}] = 20.8$) was carried out in a similar procedure as described above for the reaction of **1** with **2**. The product **8** (0.194 g, 0.273 mmol, 96% yield) was obtained as a yellow solid.



Scheme S2. Model reaction of **1** with **X2** in THF followed by acid-catalyzed decomposition.

Acid-catalyzed decomposition of 8 (Scheme S2). Decomposition of **8** (0.184 g, 0.259 mmol) was carried out in a similar manner as for **3**, yielding **4** (0.0743 g, 0.357 mmol, 69% yield) and **X2** (0.0689 g, 0.208 mmol, 80% yield) after isolation using preparative-SEC.

Polymerization

As a representative example for the three-component polycondensation, the procedure for Rh-catalyzed polymerization of **A1** with **X1** in THF (run 2 in Table 1) is described below.

Under a N_2 atmosphere, a THF (2.5 mL) solution of **A1** (0.110 g, 0.253 mmol) was placed in a Schlenk tube, and the temperature of the solution was kept at 25 °C with an oil bath with a thermo-controller. A THF (2.2 mL) solution of **X1** (0.0854 g, 0.231 mmol) was added to the Schlenk tube using a syringe, and the mixture was stirred at 25 °C for 13 h. After volatiles were removed under reduced pressure, CH_2Cl_2 and H_2O were added to the residue and the organic layer was separated by using a separatory funnel. The organic layer was dried over Na_2SO_4 , and the volatiles were removed under reduced pressure. The residue was subjected to preparative SEC with CHCl_3 as an eluent to yield poly(**A1'**-**X1**-THF) (0.108 g, 53% yield) as a yellow solid.

The polymerization of **A1** with **X2** in THF and **A2** with **X1** in THF were carried out in a similar manner.

Degradation

Degradation of poly(A1'-X1-THF). An acetone (14.8 mL) solution of poly(A1'-X1-THF) (70.4 mg, 7.88×10^{-5} mol of the repeating unit) was placed in a round bottomed flask with a three-way cock, and the solution was kept at 25 °C using an oil bath with a thermo-controller. At 25 °C, three drops of 1 M HCl aq. was added to the solution with stirring. After the resulting mixture was stirred at 25 °C for 13 h, CH₂Cl₂ and H₂O were added to the residue and the organic layer was separated by using a separatory funnel. The organic layer was dried over Na₂SO₄, and the volatiles were removed under reduced pressure. The residue was subjected to preparative SEC with CHCl₃ as an eluent to yield **d-A1'** (36.2 mg, 6.48×10^{-5} mol, 82% yield, an orange solid) and **X1** (26.4 mg, 7.13×10^{-5} mol, 91% yield).

d-A1': ¹H NMR (500 MHz, CDCl₃, δ): 7.85 (d, *J* = 8.5 Hz, 4H, Ph-H), 7.54 (d, *J* = 8.5 Hz, 2H, Ph-H), 4.76 (s, 4H, C[=O]-CH₂-O), 3.69 (t, *J* = 6.0 Hz, 4H, O-CH₂-CH₂), 3.64 (t, *J* = 6.0 Hz, 4H, O-CH₂-CH₂), 2.31 (br, 2H, OH), 1.78 (quintet, 4H, O-CH₂-CH₂-CH₂-), 1.71 (quintet, 4H, O-CH₂-CH₂-CH₂-), 0.61 (s, 2H, Si-CH₂), 0.24 (s, 12H, Si-CH₃). ¹³C NMR (125 MHz, CDCl₃, δ): 196.84 (C=O), 146.91 (Ph), 135.16 (Ph), 134.17 (Ph), 126.95 (Ph), 73.95 (O-CH₂), 72.07 (O-CH₂), 62.75 (O-CH₂), 29.98 (-CH₂-CH₂-CH₂-), 26.70 (-CH₂-CH₂-CH₂-), 7.82 (Si-CH₂), -3.56 (Si-CH₃). Anal. Calcd for C₃₀H₄₆O₆Si₂: C, 64.48; H, 8.30. Found: C, 64.41, H, 8.51.

Degradation of poly(A1'-X2-THF) was carried out in a similar procedure as for poly(A1'-X1-THF). The degradation of poly(A1'-X2-THF) (59.0 mg, 6.91×10^{-5} mol of the repeating unit) in acetone (11.9 mL) with 2 drops of 1 M HCl aq. at 25 °C for 12 h afforded **d-A1'** (36.1 mg, 6.45×10^{-5} mol, 93% yield) and **X2** (21.6 mg, 6.54×10^{-5} mol, 95% yield).

For degradation of poly(A2'-X1-THF), because of the low solubility of both the starting polymer and the product **d-A2'** in acetone, CHCl₃ was used as a solvent for the degradation and the extraction of the product. Degradation of poly(A2'-X1-THF) (126 mg, 1.68×10^{-4} mol of the repeating unit) in 25.1 mL of CHCl₃ with 2 drops of 1M HCl aq. afforded **d-A2'** (34.8 mg, 8.39×10^{-5} mol, 50% yield, an orange oil) and **X1** (50.5 mg, 1.36×10^{-4} mol, 81% yield).

d-A2': ¹H NMR (500 MHz, DMSO-*d*₆, δ): 8.03 (d, *J* = 8.0 Hz, 4H, Ph-H), 7.90 (d, *J* = 8.5 Hz, 4H, Ph-H), 4.85 (s, 4H, C[=O]-CH₂-O), 4.40 (t, *J* = 5.3 Hz, 2H, -OH), 3.52 (t, *J* = 6.5 Hz, 4H, O-CH₂-CH₂), 3.41 (quartet, 4H, HO-CH₂-CH₂), 1.59 (quintet, 4H, O-CH₂-CH₂-CH₂-), 1.48 (quintet, 4H, O-CH₂-CH₂-CH₂-). ¹³C NMR (125 MHz, DMSO-*d*₆, δ): 196.54 (C=O), 143.41 (Ph), 134.38 (Ph), 128.52 (Ph), 127.30 (Ph), 73.26 (O-CH₂), 70.71 (O-CH₂), 60.52 (O-CH₂), 29.17 (-CH₂-CH₂-CH₂-), 25.93 (-CH₂-CH₂-CH₂-). Anal. Calcd for C₂₄H₃₀O₆: C, 69.55; H, 7.28. Found: C, 69.19, H, 6.96.

Measurements.

The number-average molecular weight (*M_n*) and polydispersity ratio [weight-average molecular weight/number-average molecular weight (*M_w*/*M_n*)] were measured by means of SEC on a Jasco-ChromNAV system equipped with a differential refractometer detector using THF as eluent at a flow rate of 1.0 mL/min at 40 °C, calibrated with 6 poly(methyl methacrylate) (PMMA) standards (Shodex M-75; *M_p* = 2400-212000, *M_w*/*M_n* < 1.1) and dibutyl sebacate (molecular weight = 314.5). The columns used for the SEC analyses was a combination of Styragel HR4 and HR2 (Waters; exclusion limit molecular weight = 600 kDa and 20 kDa for polystyrene, respectively; column size = 300 mm × 7.8 mm i.d.; average particle size = 5 μm).

Purification by preparative recycling SEC was performed on a JAI LC-918R equipped with a combination of columns of a JAIGEL-3H and a JAIGEL-2H (Japan Analytical Industry; exclusion limit molecular weight = 70 kDa and 5 kDa for polystyrene, respectively; column size = 600 mm × 20 mm i.d.) using CHCl₃ as eluent at a flow rate of 3.8 mL/min at room temperature. ¹H (500 MHz) and ¹³C (126 MHz) NMR spectra were recorded on a Bruker Avance III HD 500 spectrometer in CDCl₃ or DMSO-*d*₆ at room temperature or at 50 °C. The glass transition temperature (*T*_g) of polymers was determined by differential scanning calorimetry (DSC; Seiko Instruments Inc., EXSTAR DSC6000) in the range from −100 °C to 100 °C for product polymers. The heating and cooling rates were 10 °C/min. The *T*_g of the polymers was defined as the temperature of the midpoint of a heat capacity change on the second heating scan. Thermogravimetric analysis was performed with Exstar TG/DTA6200 (Seiko Instruments). The experiments were carried out with about 5 mg of a sample under a nitrogen atmosphere at a heating rate of 10 °C/min. Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF-MS) analyses were performed on a JMS-S3000 (JEOL, spiral mode) using dithranol as a matrix and sodium trifluoroacetate as an ion source. Elemental analyses were performed on a YANAKO CHN Corder MT-5.

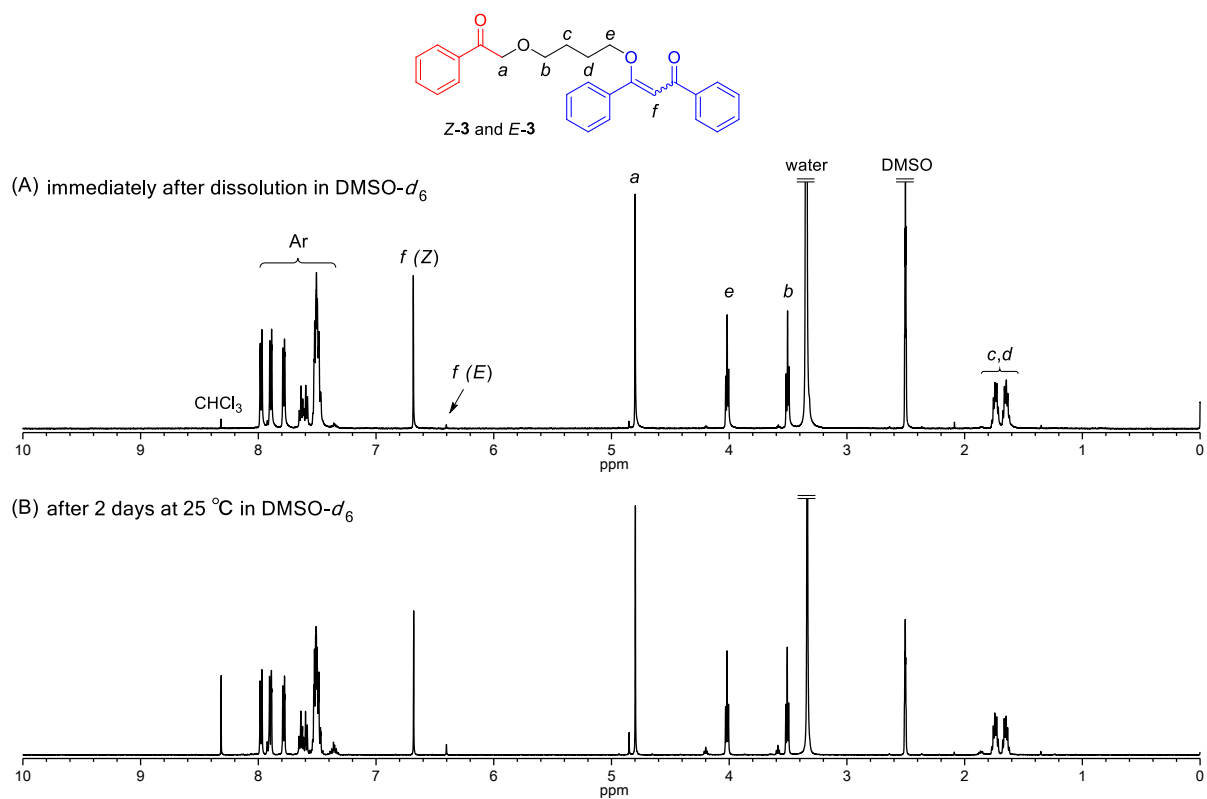


Figure S1. ^1H NMR spectra of **3** recorded in DMSO- d_6 .

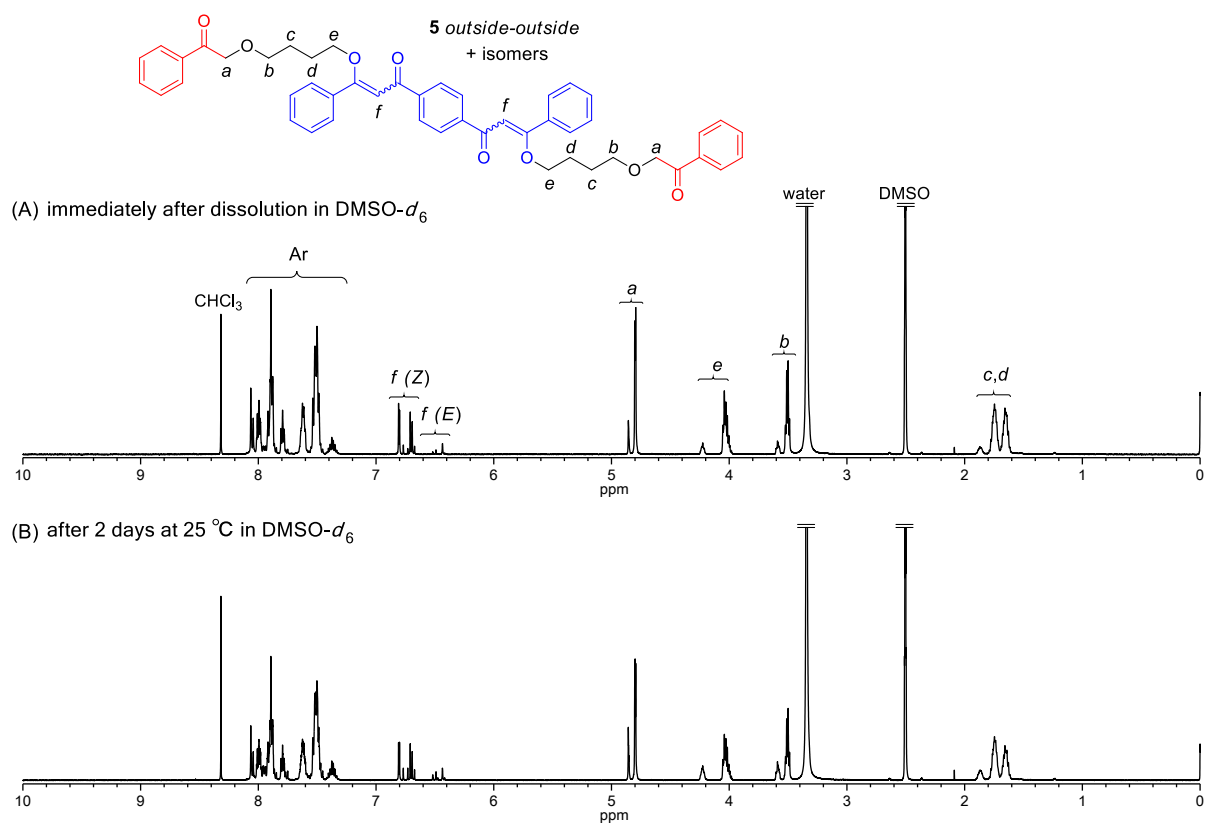


Figure S2. ^1H NMR spectra of **5** recorded in DMSO- d_6 .

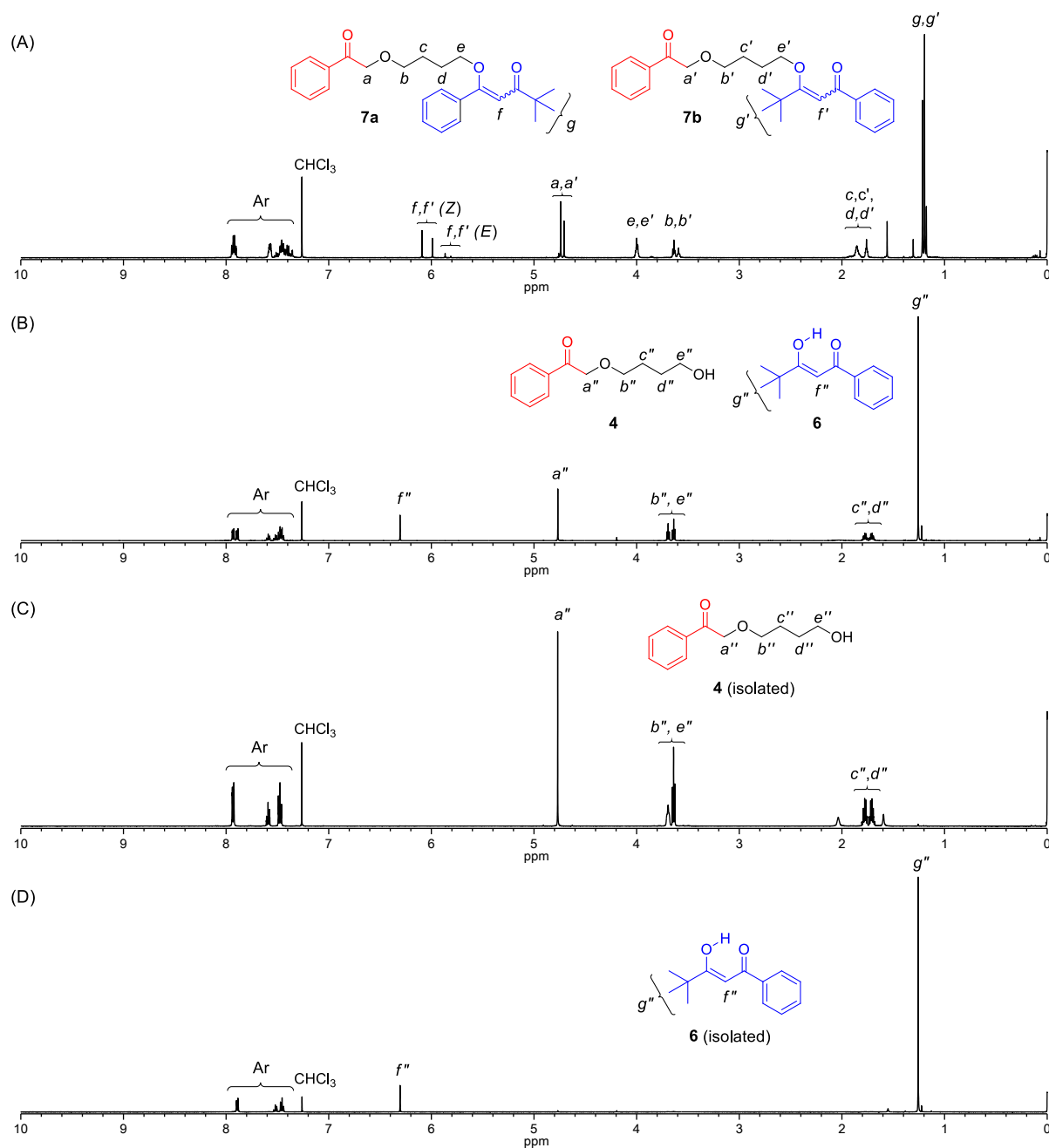


Figure S3. ¹H NMR spectra of (A) **7a** and **7b**, (B) the acid-catalyzed decomposition products of **7a** and **7b** without isolation after standing in CDCl₃ at 25 °C for 5 days, (C) isolated **4**, and (D) isolated **6**. In addition to *E*- and *Z*-C=C-derived isomers, the asymmetry of **6** brings about the presence of additional isomers as illustrated in Scheme S1 as **7a** and **7b**, which should result in the more complex signal appearance of vinylic-Hs in the ¹H NMR spectrum.

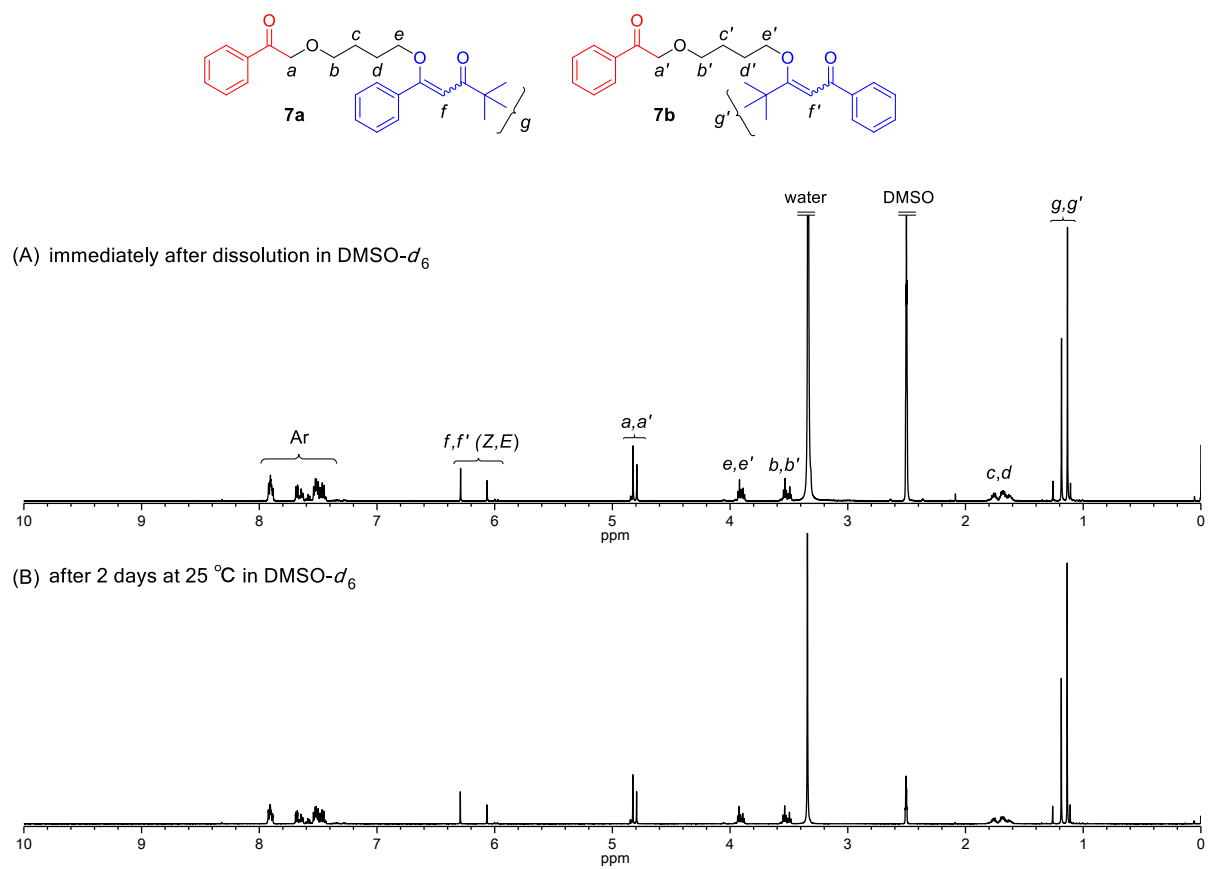


Figure S4. ^1H NMR spectra of **7a** and **7b** recorded in DMSO- d_6 .

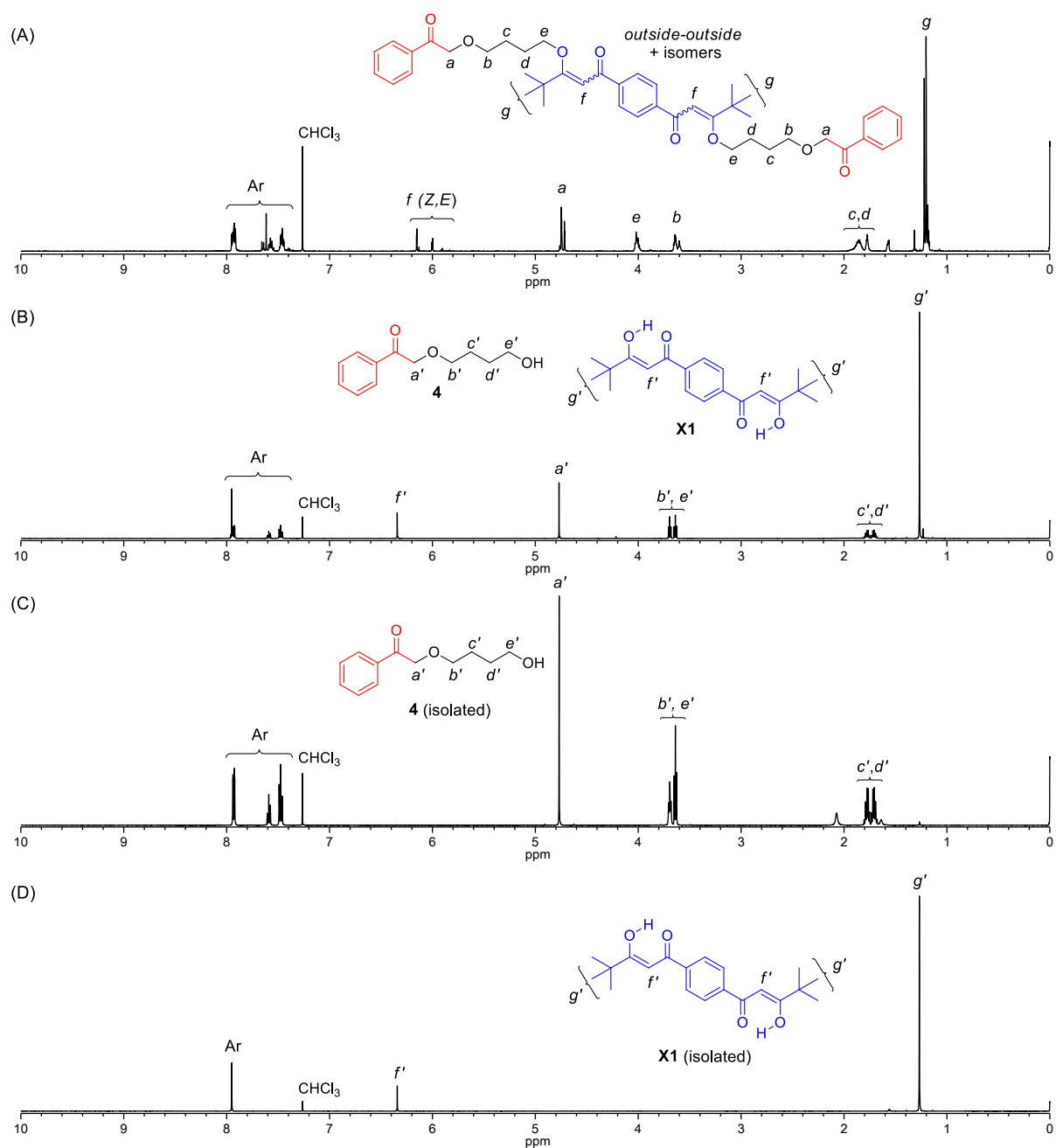


Figure S5. ^1H NMR spectra of (A) the product obtained from **1**, **6**, and THF, (B) the acid-catalyzed decomposition products without isolation after standing in CDCl_3 at 25 °C for 5 days, (C) isolated **4**, and (D) isolated **X1**.

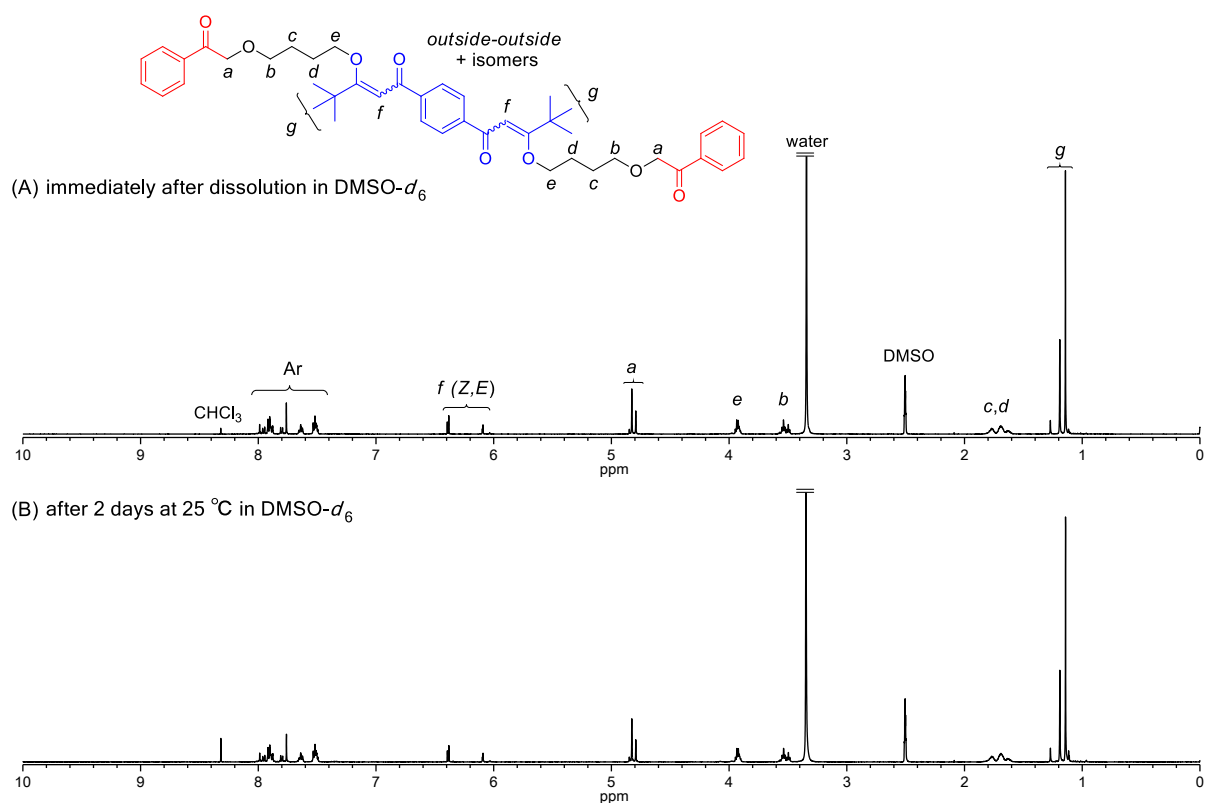


Figure S6. ^1H NMR spectra of the product obtained from 1, 6, and THF recorded in $\text{DMSO}-d_6$.

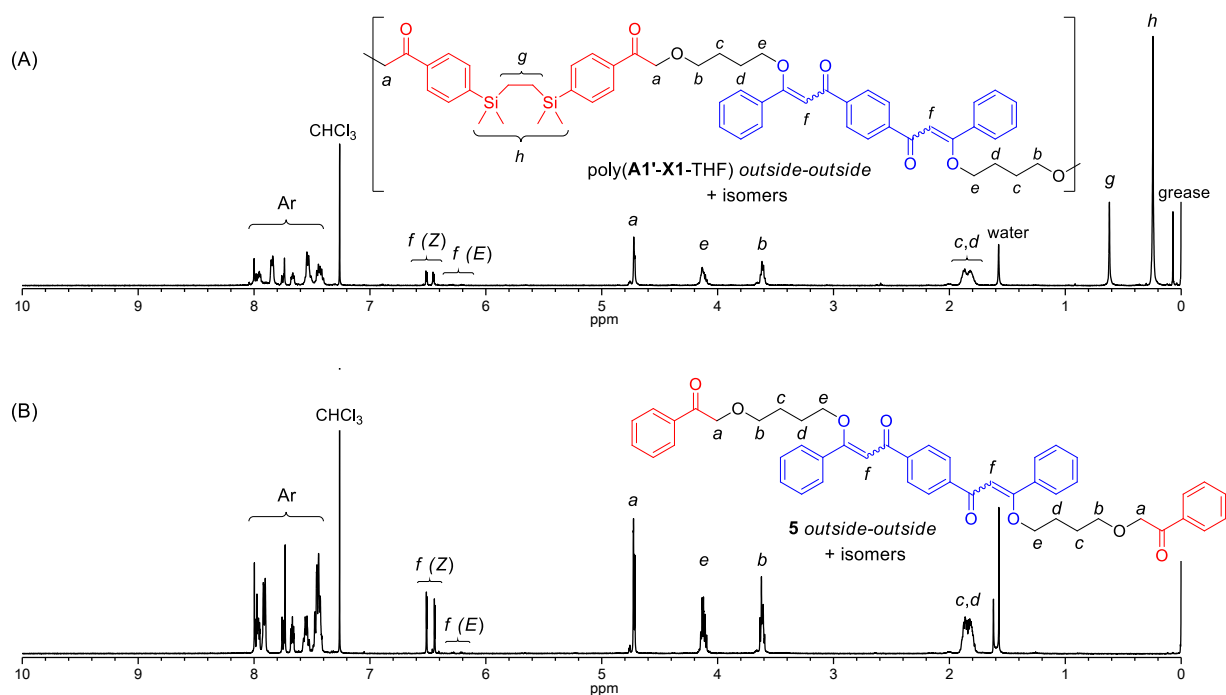


Figure S7. NMR spectra of (A) poly(A1'-X1-THF) (Figure 3A) and (B) 5 (Figure 2A).

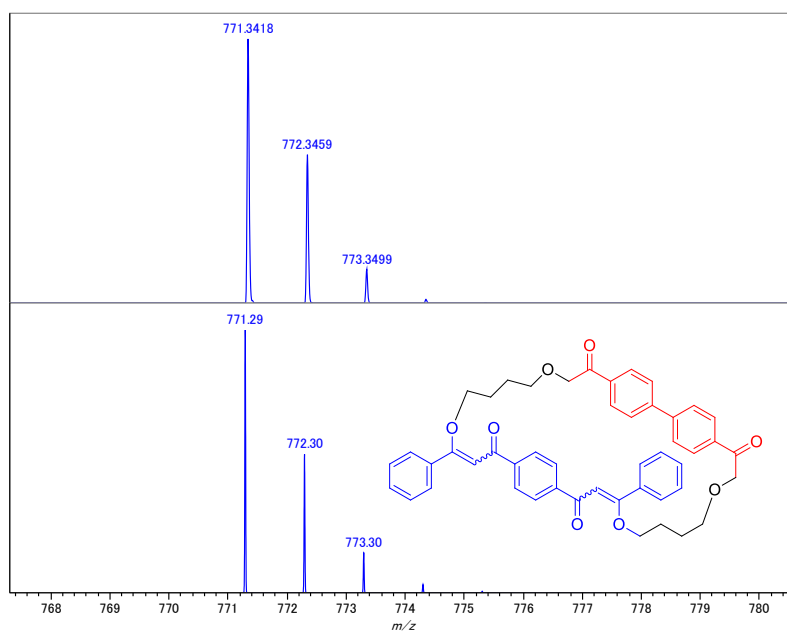


Figure S8. MALDI-TOF-MS spectrum of a cyclic oligomer (upper) and its theoretical isotopic distribution of a Na-adduct (lower).

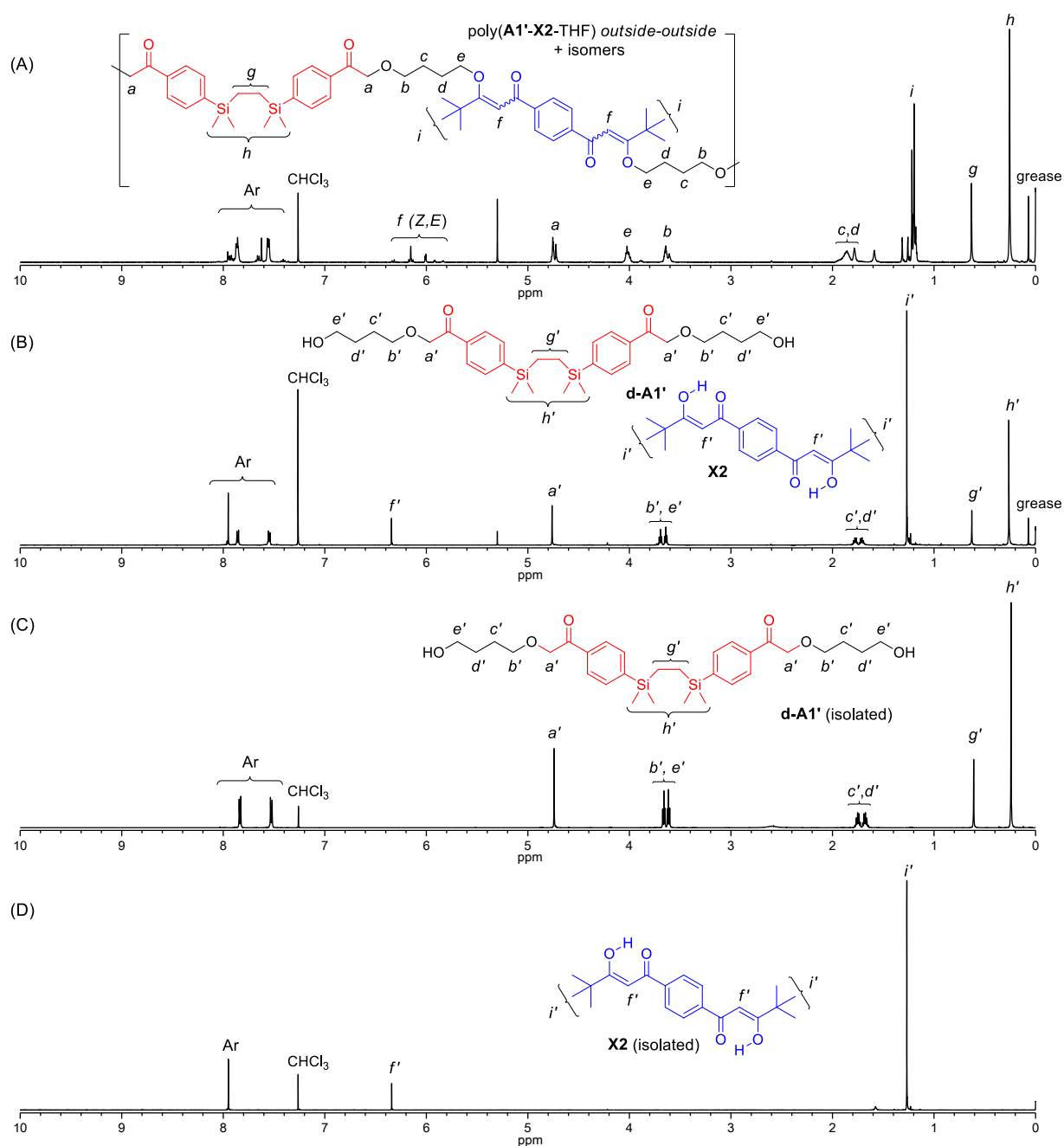


Figure S9. ^1H NMR spectra of (A) poly(A1'-X2-THF) (Table 1, run 5), (B) the acid-catalyzed decomposition products of poly(A1'-X2-THF) without isolation after standing in CDCl_3 at 25°C for 5 days, (C) isolated d-A1', and (D) isolated X2.

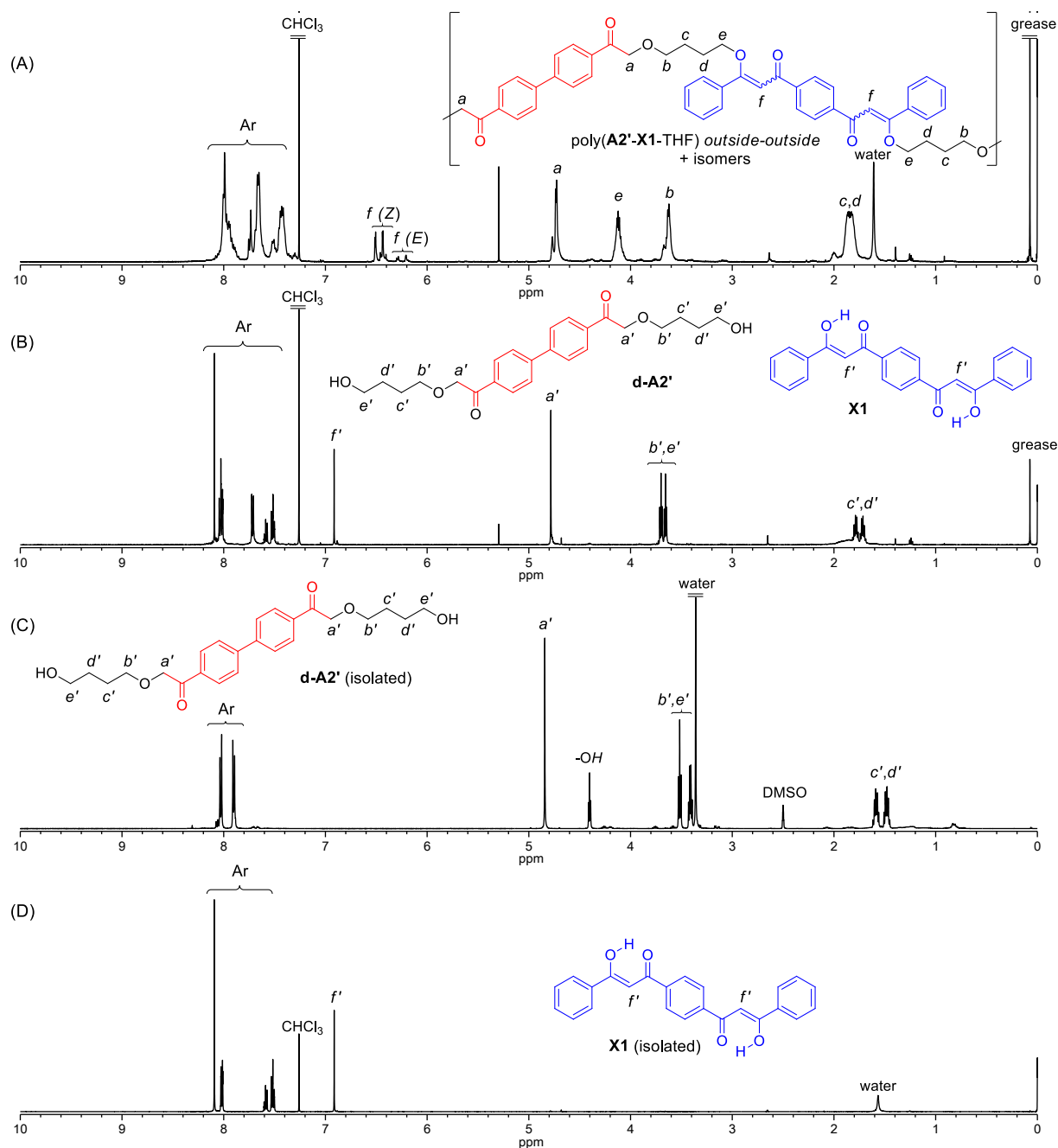


Figure S10. ^1H NMR spectra of (A) poly(A2'-X1-THF) ($M_n = 14400$, $M_w/M_n = 1.91$), (B) the acid-catalyzed decomposition products of poly(A2'-X1-THF) without isolation after standing in CDCl_3 at 25°C for 5 days, (C) isolated d-A2', and (D) isolated X1 (The NMR spectrum of d-A2' was recorded in $\text{DMSO}-d_6$ due to its low solubility toward CDCl_3 , while the mixture of d-A2' and X1 was soluble in CDCl_3).

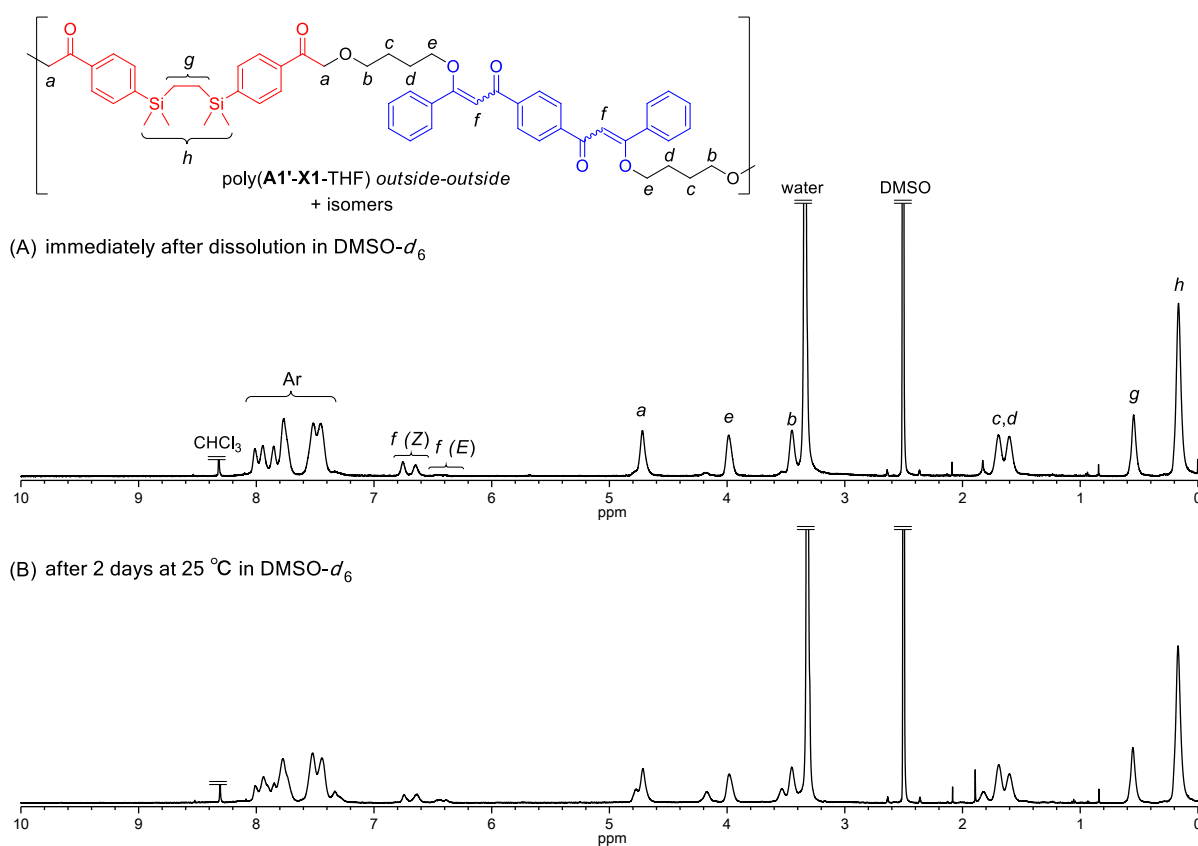


Figure S11. ^1H NMR spectra of poly(A1'-X1-THF) recorded in $\text{DMSO}-d_6$ (The NMR spectrum slightly changed after 2 days. This should be attributed to the fact that stereoselectivity of the β -keto enol ether linkage in the original polymer slightly changed with the assistance of trace of acid.).

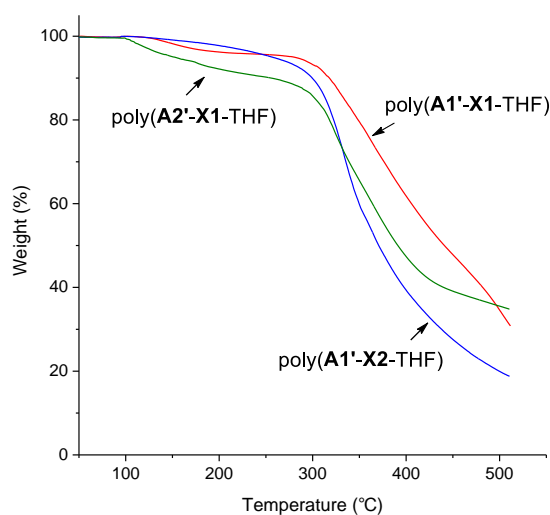


Figure S12. Thermogravimetric analysis results of poly(A1'-X1-THF) ($M_n = 32100$, $M_w/M_n = 1.44$), poly(A1'-X2-THF) ($M_n = 42800$, $M_w/M_n = 2.48$), and poly(A2'-X1-THF) ($M_n = 14700$, $M_w/M_n = 4.33$).

References

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