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Divergence of Polycondensation by a Tandem Reaction Based on Sequential Conjugate Substitutions

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Electric Supplementary Information

Experiments

Instruments

^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ (Across Organics) on AVANCE 400 (Bruker) and AVANCE NEO (Bruker) spectrometers. Chemical shifts in ^{1}H and ^{13}C NMR spectra were referred to the signal of tetramethylsilane (TMS) and solvent ($CDCl_3$), respectively. Molecular weight and its distributions were determined at 40 °C by size-exclusion chromatography (SEC) on an EXTREMA chromatograph (JASCO) equipped with two SEC columns [PL-gel, Mixed C (300 mm _7.5 mm), Polymer Laboratories], using tetrahydrofuran (THF, Wako Pure Chemical Industries, for HPLC grade) as an eluent (flow rate = 0.8 mL min^{-1}), and calibrated against standard polystyrene (PS) samples (TSK-gel oligomer kit, Tosoh, M_n: 1.03×10^6, 3.89×10^5, 1.82×10^5, 3.68×10^4, 1.36×10^4, 5.32×10^3, 3.03×10^3, 8.73×10^2) and detected with UV (UV-4070, JASCO) and RI (RI-4030, JASCO) detectors. Differential scanning calorimetry (DSC) were measured with a Shimadzu DSC-60 differential scanning calorimeter (scan rate = 10 °C/min) under a N_2 atmosphere (flow rate = 50 mL/min). IR spectra were recorded on a Cary 630 FTIR spectrometer equipped with an attenuated total reflection attachment (single reflection). Thermogravimetric /differential thermal analyses (TG/DTA) was carried out from room temperature to 500 °C at a heating rate of 10 °C with Rigaku Thermo plus II TG8120 under an N_2 atmosphere.

Materials

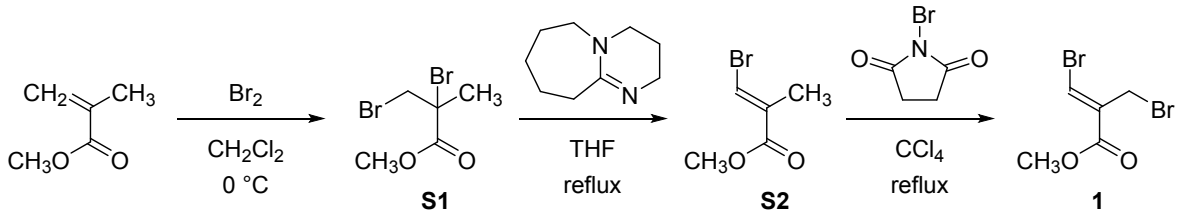
Methyl methacrylate, *N*-bromosuccinmide (NBS), triethylamine (Et_3N), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), 1,4-diazabicyclo[2.2.2]octane (DABCO), deuterochloroform ($CDCl_3$) and 1,10-decanedithiol were purchased from Tokyo Chemical Industry Co., Ltd. Sodium thiosulfate (Na_2SO_3) was purchased from Yoneyama Yakuhin Kogyo Co, Ltd. Bromide, *N,N*-diisopropylethylamine (iPr_2NEt), sodium sulfate (Na_2SO_4), chloroform ($CHCl_3$), dichloromethane (CH_2Cl_2), tetrachloromethane (CCl4), tetrahydrofuran (THF), acetonitrile (CH_3CN) and *N,N*-dimethylformamide (DMF) were purchased from Wako Pure Chemical Industries, Ltd.

Synthesis

Methyl 2,3-dibromopropionate (**S1**)[1]: A liquid of bromine (80 g, 0.50 mol) was added dropwise via an addition funnel to a solution of methyl methacrylate (50.16 g, 0.50 mol) in CH_2Cl_2 (200 mL) at 0 °C. The reaction mixture was stirred at 0 °C for 3 h and at room temperature for additional 3 h. *Sat.* $Na_2S_2O_3$ aq. (150 mL) was added to the reaction mixture and stirred at room temperature for 15 min. The layers were separated, and the aqueous layer was extracted with CH_2Cl_2 (20 mL × 3). The organic layers were combined and washed with H_2O (150 mL) and brine (150 mL). The combined organic layer was dried over Na_2SO_4 and concentrated to yield crude **S1** (182 g, yield: 148%). The crude **S1** was used in the next reaction without further purification.

Methyl β-bromo-methacrylate (**S2**)[1]: A solution of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (83.84 g,0.55 mol) in THF (150 mL) was added dropwise to a solution of **S1** (182.71 g) in THF (150 mL) at room temperature. The reaction mixture was refluxed for 2 h. After cooling to room temperature, H_2O (150 mL) was added and the aqueous layer was extracted with EtOAc (50 mL × 3). The organic layers were combined and washed with 1 M HCl aq. (100 mL), H_2O (100 mL) and brine (100 mL). The combined organic layer was dried over Na_2SO_4 and concentrated. The residue oil was purified by distillation under reduced pressure (bp: 47.0 °C / 10 mmHg) to yield **S2** as colorless oil (33.92 g, Yield: 37.6%). ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 26 °C): δ/ppm 7.46 (1H, s, =CHBr), 3.72 (3H, s, OCH_3), 1.98 (2H, s, CH_2).

Methyl β-bromo-α-(bromomethyl)acrylate (**1**)[2]: A solution of *N*-bromosuccinimide (16.98 g, 95.4 mmol) in CCl_4 (20.0 mL) was added to a solution of **S2** (15.0 g, 83.8 mmol) in CCl_4 (80.0 mL). The reaction mixture was refluxed for overnight. The precipitate was removed by filtration, and the filtrate was concentrated and distilled under reduced pressure (bp: 52.2 °C / 0.66 mmHg) to yield **1** as colorless oil (18.49 g, Yield: 85.6%). ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 26 °C): δ/ppm 7.70 (1H, s, =CHBr),4.28 (2H, s, CH_2Br), 3.82 (3H, s, OCH_3).



Scheme S1. The synthesis of β-bromo-α-(bromomethyl)acrylate (1).

Molecular Mechanics Calculation

Molecular mechanics (MM) simulation was performed by Spartan 16' ver. 1.1.0. The initial geometry of **8a** was optimized under MMFF force field, and the conformer distribution were searched under MMFF force field. The results of found conformers were described in Table S2. Similar simulations were performed for **8b**, but same results to **8a** were obtained as they were interconvertible. Similar simulations were also performed for **8c** and **8d**, and the results were summarized in Table S3.

Table S1 Tandem polymerization of **1** and **4**.

Entry[a]	Base	Solvent (Volume [mL])	Temp. [°C]	Yield [%]	M_n[b]	Đ[b]	Composition[c] [%]		
							E	***Z***	***Y***
1	K_2CO_3	CH_3CN (0.75)	25	>99	4000	2.3	51	47	2
2	K_2CO_3	CH_3CN (0.75)	80	82	36000	5.6	24	76	0
3	K_2CO_3	DMF (0.75)	25	>99	12800	3.4	24	76	0
4	K_2CO_3	DMF (0.75)	80	>99	8000	3.4	19	81	0
5	Et_3N	$CHCl_3$ (0.75)	25	93	4200	3.6	21	15	64
6	iPr_2NEt	$CHCl_3$ (0.75)	25	>99	3200	2.2	42	54	4
7	DABCO	$CHCl_3$ (0.75)	25	90	9200	1.7	3	5	92
S1	Li_2CO_3	DMF (0.75)	25	>99	800	1.8	49	46	5
S2	Na_2CO_3	DMF (0.75)	25	>99	3200	2.0	30	69	1
S3	Cs_2CO_3	DMF (0.75)	25	96	9600	2.4	25	75	0
S4	K_2CO_3	DMF (0.25)	25	>99	4800	1.9	32	67	1
S5	K_2CO_3	DMF (0.375)	25	>99	5700	2.0	30	70	0
S6	K_2CO_3	DMF (1.50)	25	>99	11400	2.7	21	79	0
S7	K_2CO_3	DMF (2.25)	25	>99	7200	3.4	19	81	0

[a] **1**: 0.750 mmol, $[\mathbf{1}]_0/[\mathbf{4}]_0/[\text{base}]_0$ = 1/1.0/2.1, solvent: 0.75 mL, 24h. [b] Determined by SEC (polystyrene standard, THF, 40 °C), as shown Fig. S5-S18. [c]Calculated by ^{1}H NMR spectrum.

Table S2. Stable conformers of intermediate **8a** and **8b** suggested by molecular mechanics (MMFF) calculation.

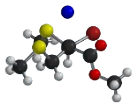
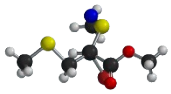
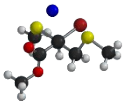
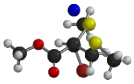
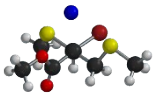
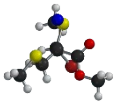
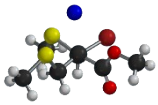
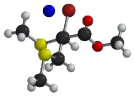
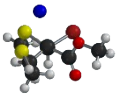
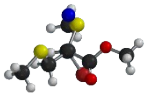
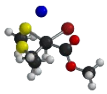
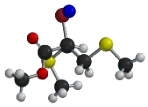
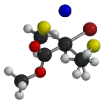
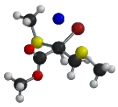
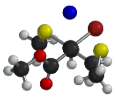
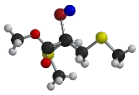
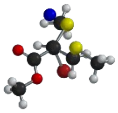
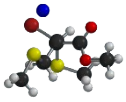
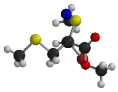
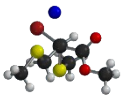
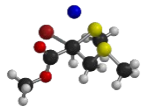
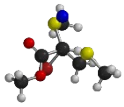
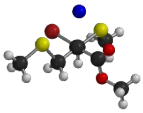
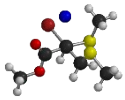
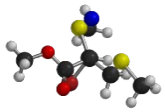
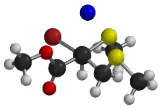
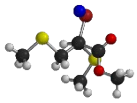
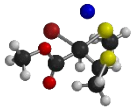
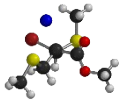
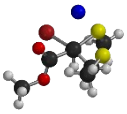
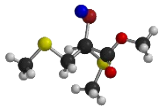
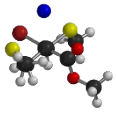
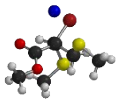
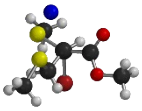
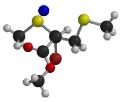
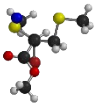
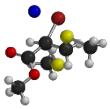
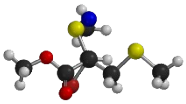
Entry	Model	Energy [kJ/mol]	∠⊖ - C/C-Br [°]	Memo	Entry	Model	Energy [kJ/mol]	∠⊖ - C/C-Br [°]	Memo
1		-933.41	62.10		11		-904.88	146.17	
2		-932.98	63.27		12		-904.30	158.56	**8a**
3		-932.81	59.49		13		-902.79	140.64	
4		-932.74	64.55		14		-899.88	38.13	
5		-926.76	68.48		15		-899.78	144.91	
6		-926.63	65.39		16		-894.80	-12.61	
7		-924.21	59.30		17		-894.63	43.30	
8		-924.12	55.82		18		-894.10	-15.73	
9		-908.60	162.87	**8b**	19		-893.96	-37.62	
10		-906.94	142.91		20		-892.07	-46.26	

Table S3. Stable conformers of intermediate **8c** and **8d** suggested by molecular mechanics (MMFF) calculation.

Entry	Model	Energy [kJ/mol]	∠⊖ - C/C-Br [°]	Memo	Entry	Model	Energy [kJ/mol]	∠⊖ - C/C-Br [°]	Memo
1		-933.41	-62.10		11		-902.79	-140.64	
2		-932.98	-63.27		12		-899.88	-38.13	
3		-932.81	-59.49		13		-899.78	-144.91	
4		-932.74	-64.55		14		-894.80	12.61	
5		-926.76	-68.48		15		-894.63	-43.30	
6		-926.63	-65.39		16		-894.10	15.73	
7		-924.21	-59.30		17		-893.96	37.62	
8		**-908.60**	**-162.87**	**8c**	18		-893.77	-156.83	
9		-906.94	**-142.91**	**8d**	19		-892.07	46.26	
10		-904.88	-146.17				-933.41	-62.10	

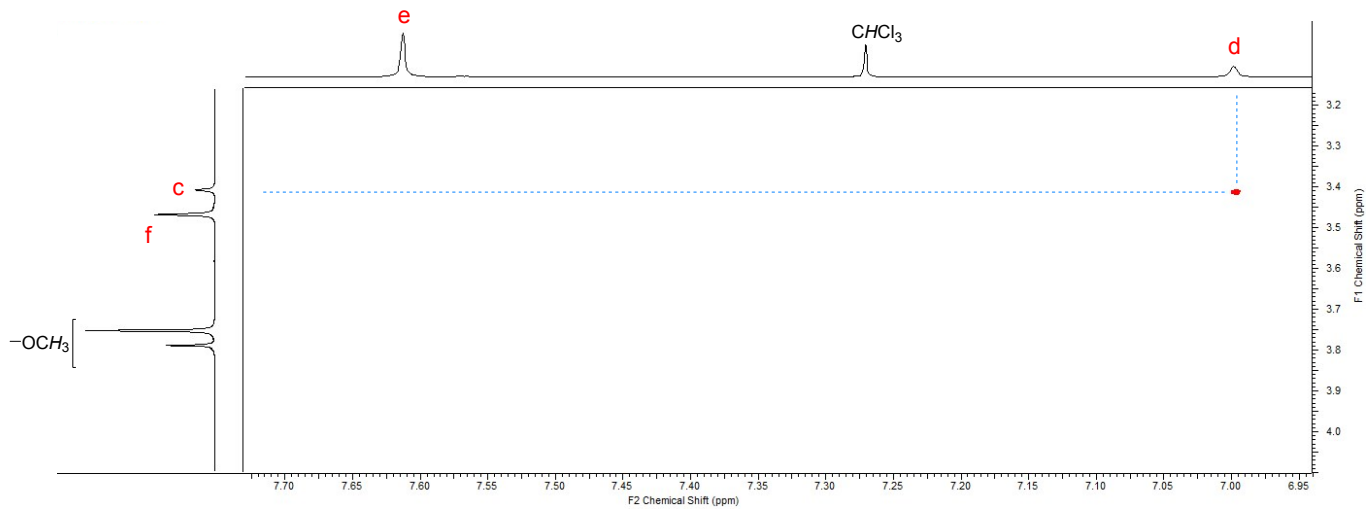


Fig. S1. The NOESY spectrum of the product in Entry 4 (400 MHz, $CDCl_3$, 25 °C).

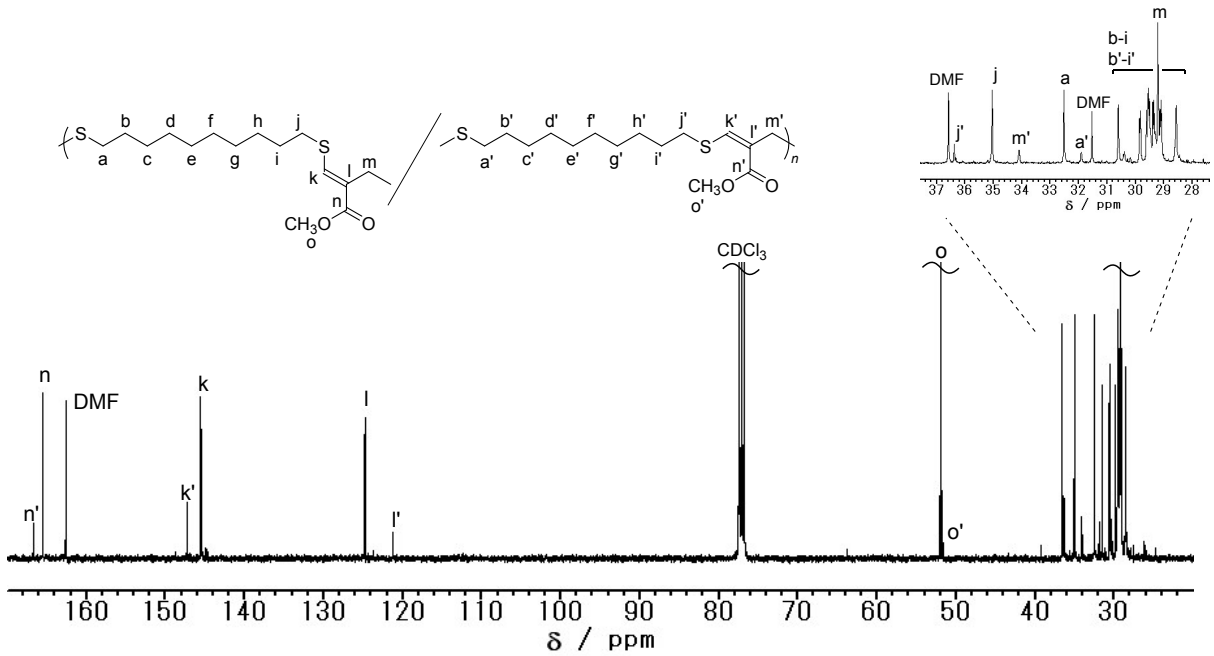


Fig. S2. The ^{13}C NMR spectrum of the product in Entry S7. (100 MHz, $CDCl_3$, 25 °C).

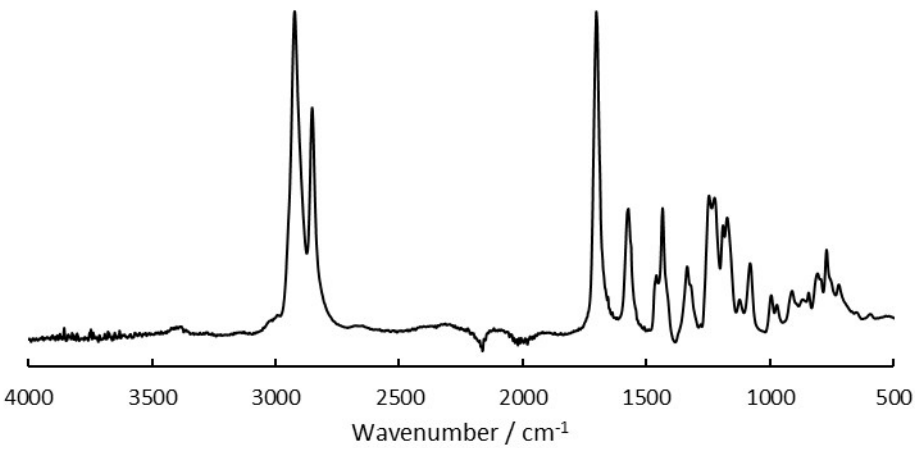


Fig. S3. IR spectrum of the product in Entry 2.

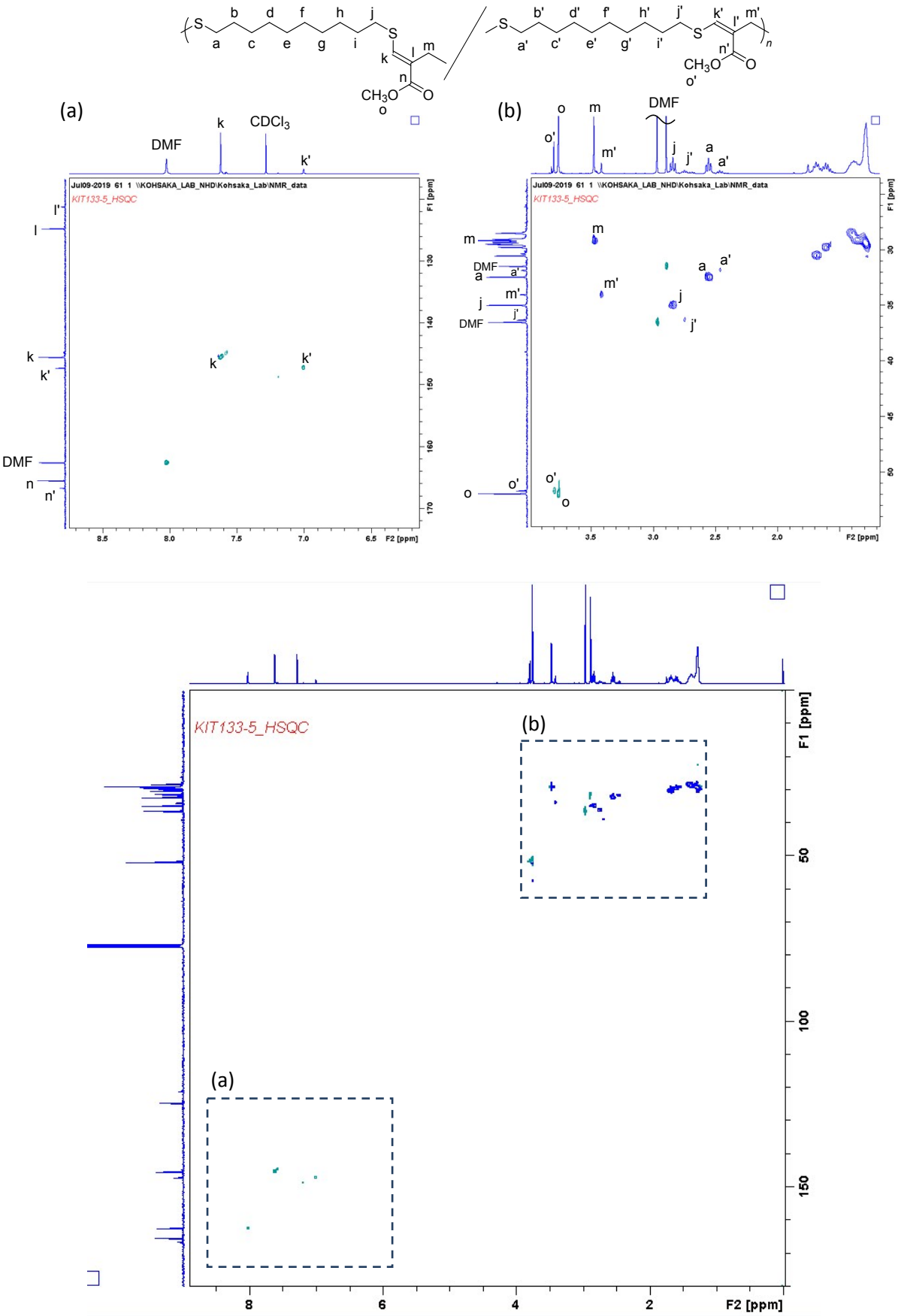


Fig. S4. The HSQC spectrum of the product in Entry S7. (400 MHz, CDCl3, 25 °C).

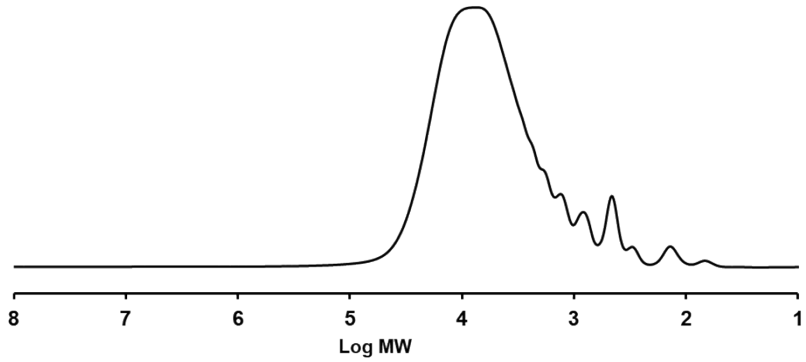


Fig. S5. SEC curve of the product in Entry 1 (THF, 40 °C, PS standards).

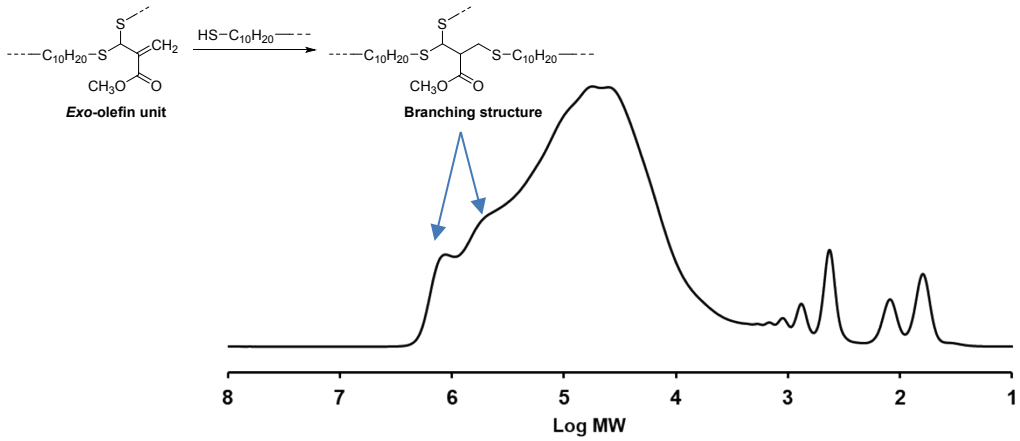


Fig. S6. SEC curve of the product in Entry 2 (THF, 40 °C, PS standards).

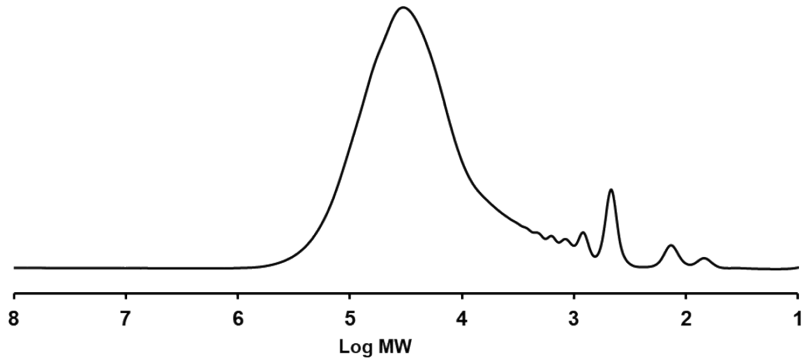


Fig. S7. SEC curve of the product in Entry 3 (THF, 40 °C, PS standards).

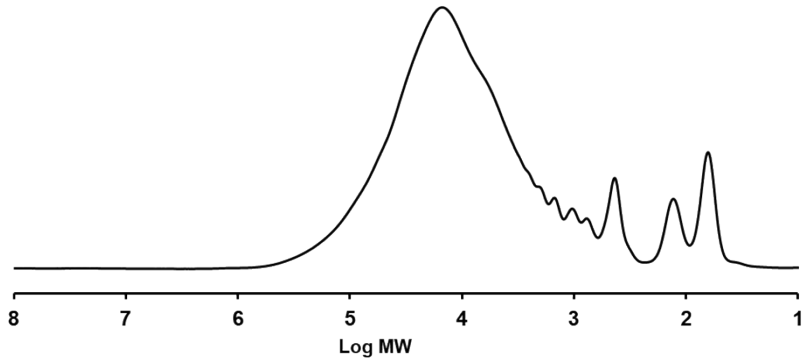


Fig. S8. SEC curve of the product in Entry 4 (THF, 40 °C, PS standards).

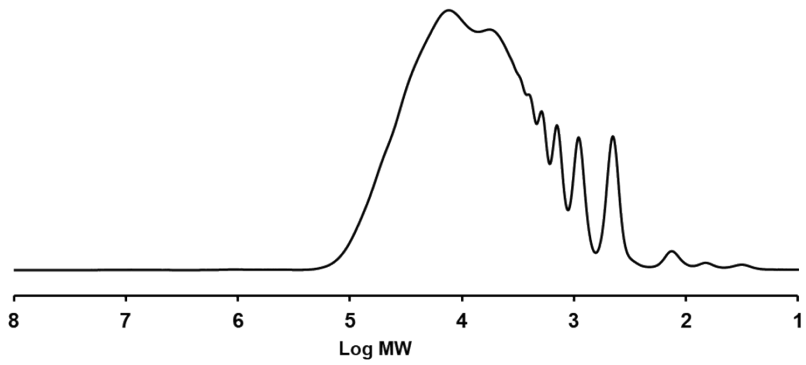


Fig. S9. SEC curve of the product in Entry 5 (THF, 40 °C, PS standards).

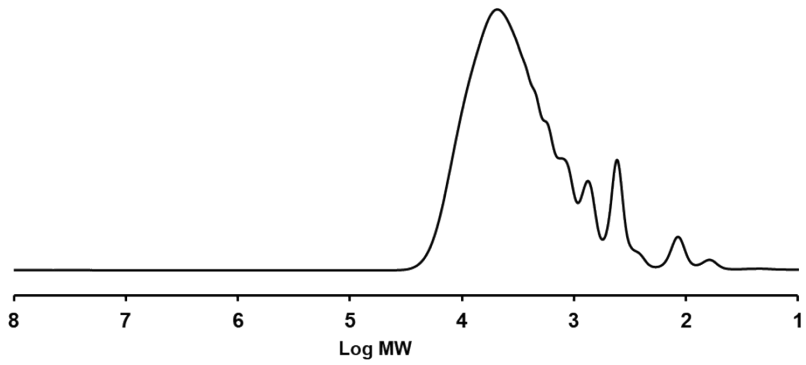


Fig. S10. SEC curve of the product in Entry 6 (THF, 40 °C, PS standards).

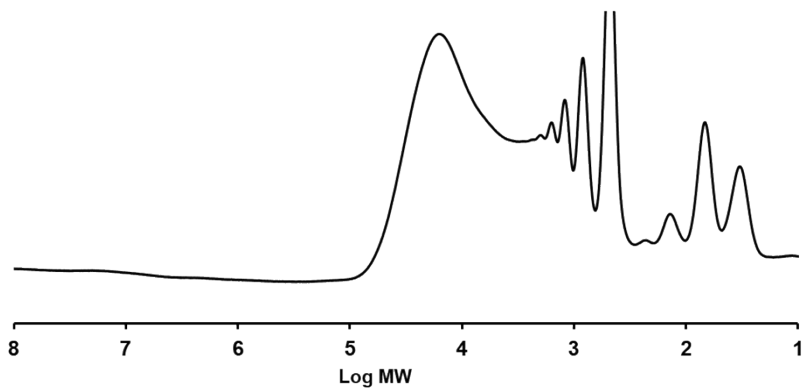


Fig. S11. SEC curve of the product in Entry 7 (THF, 40 °C, PS standards).

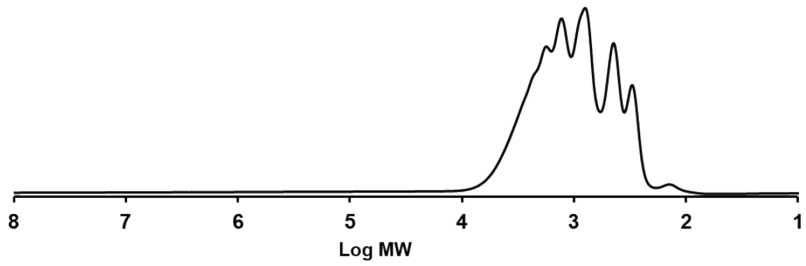


Fig. S12. SEC curve of the product in Entry S1 (THF, 40 °C, PS standards).

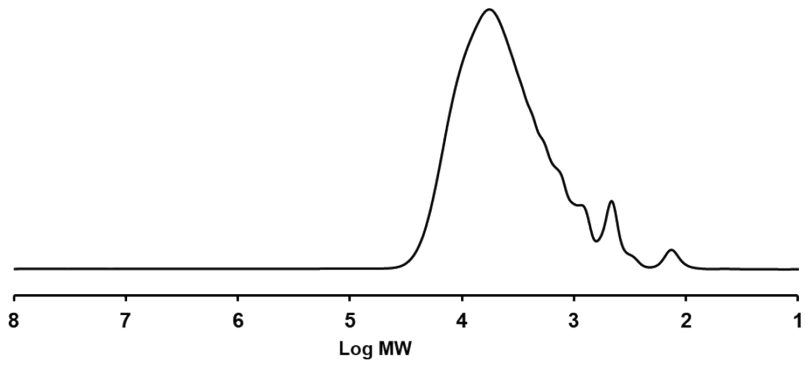


Fig. S13. SEC curve of the product in Entry S2 (THF, 40 °C, PS standards).

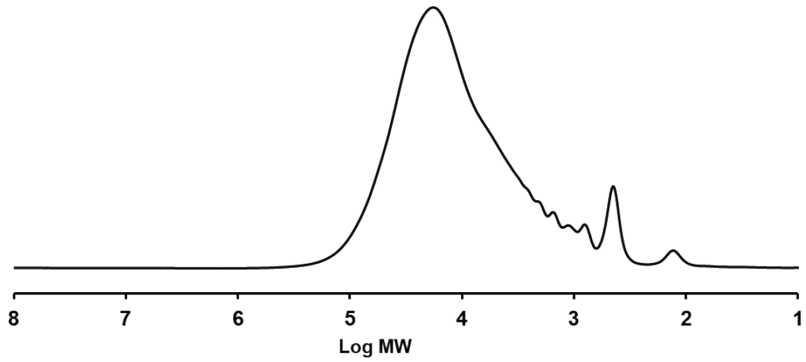


Fig. S14. SEC curve of the product in Entry S3 (THF, 40 °C, PS standards).

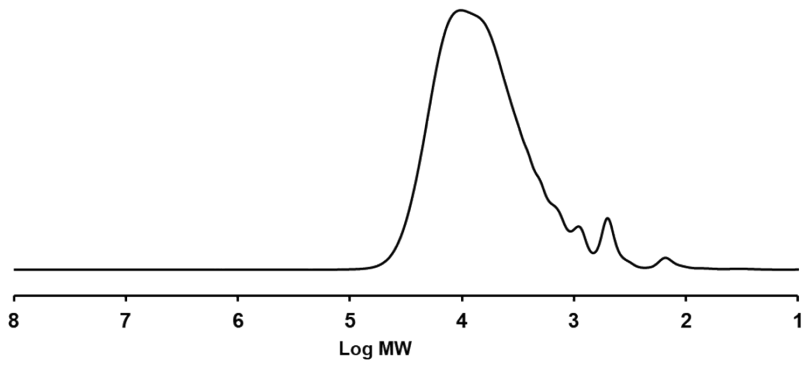


Fig. S15. SEC curve of the product in Entry S4 (THF, 40 °C, PS standards).

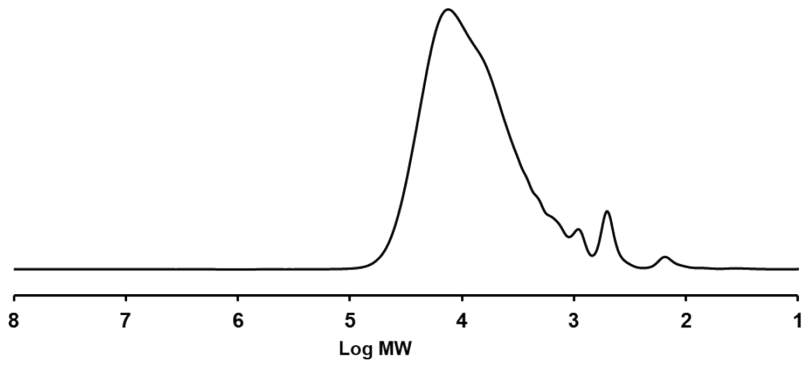


Fig. S16. SEC curve of the product in Entry S5 (THF, 40 °C, PS standards).

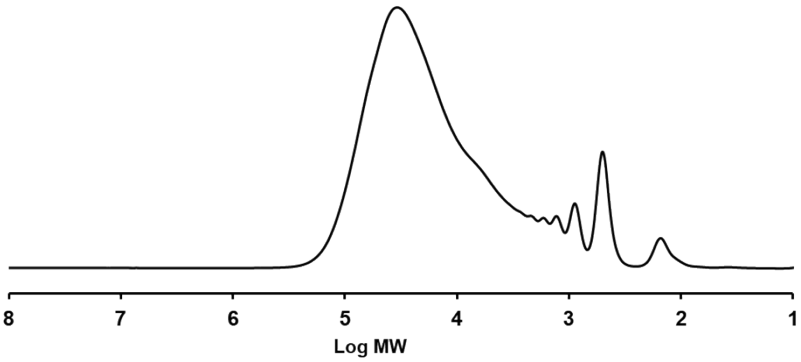


Fig. S17. SEC curve of the product in Entry S6 (THF, 40 °C, PS standards).

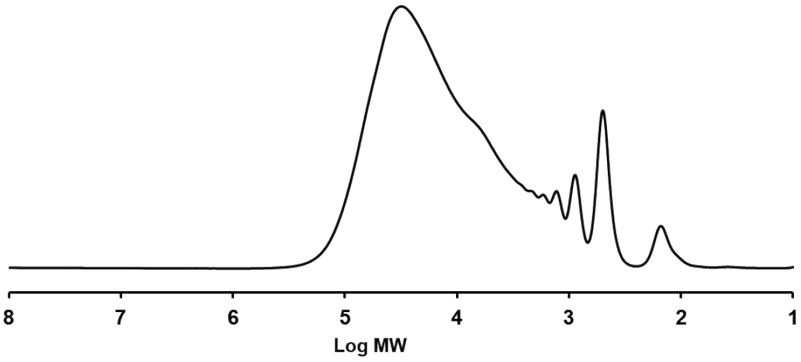


Fig. S18. SEC curve of the product in Entry S7 (THF, 40 °C, PS standards).

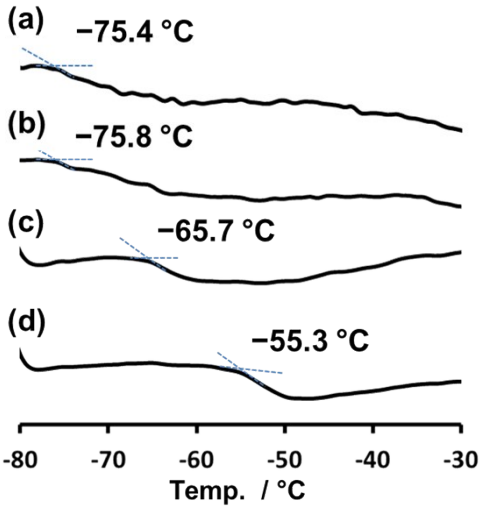


Fig. S19. DSC curves of the product in (a) Entry 1, (b) Entry 3, (c) Entry 5 and (d) Entry 7.

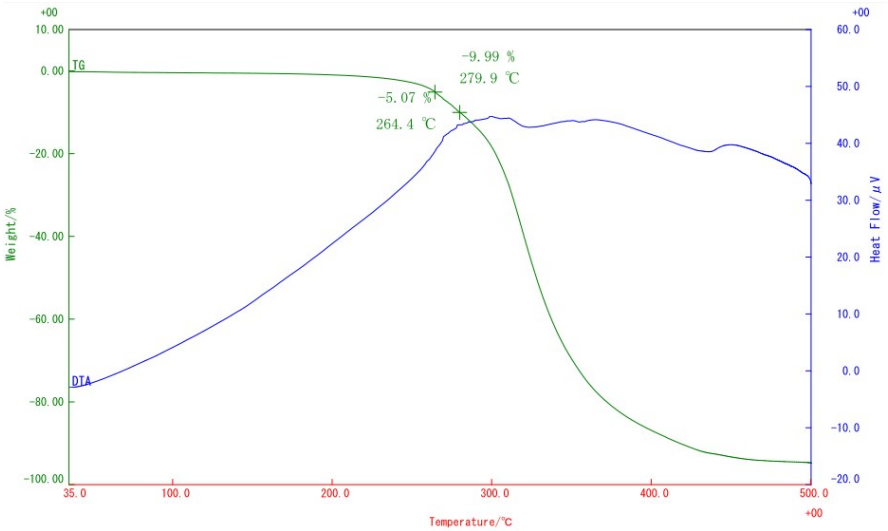


Fig. S20. TG/DTA curves of the product in Entry 1.

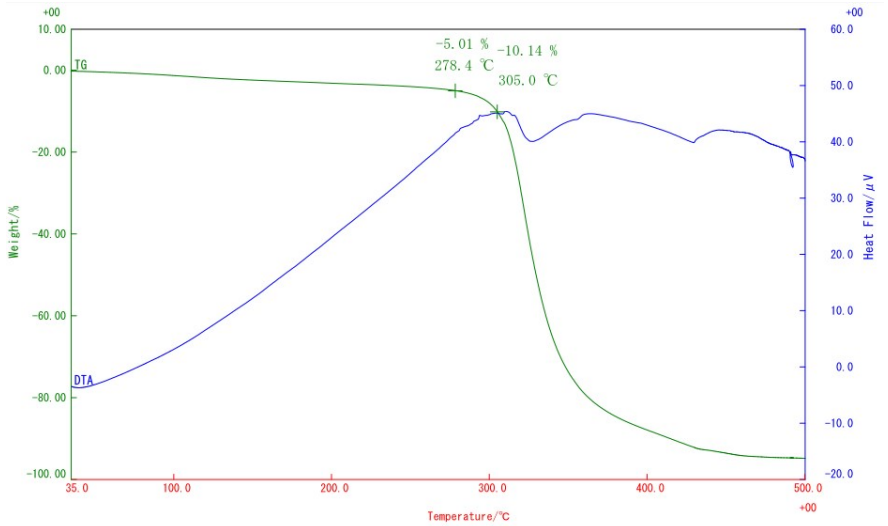


Fig. S21. TG/DTA curves of the product in Entry 3.

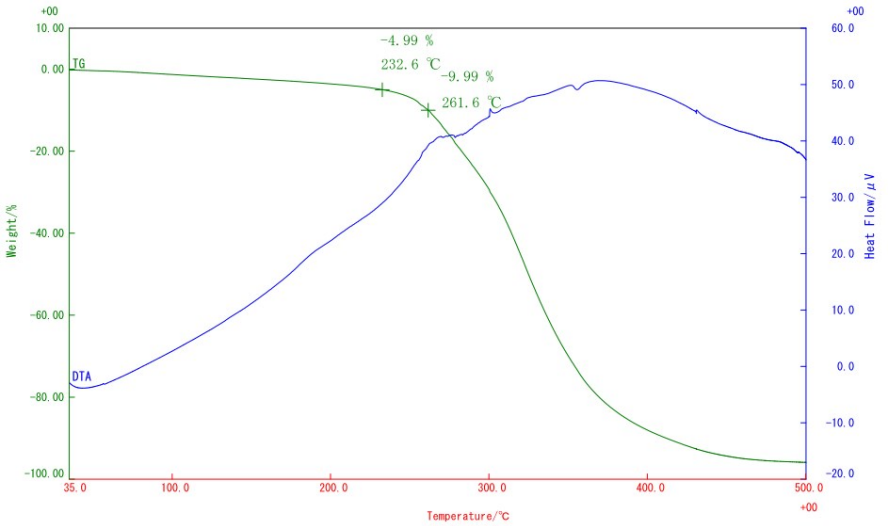


Fig. S22. TG/DTA curves of the product in Entry 3.

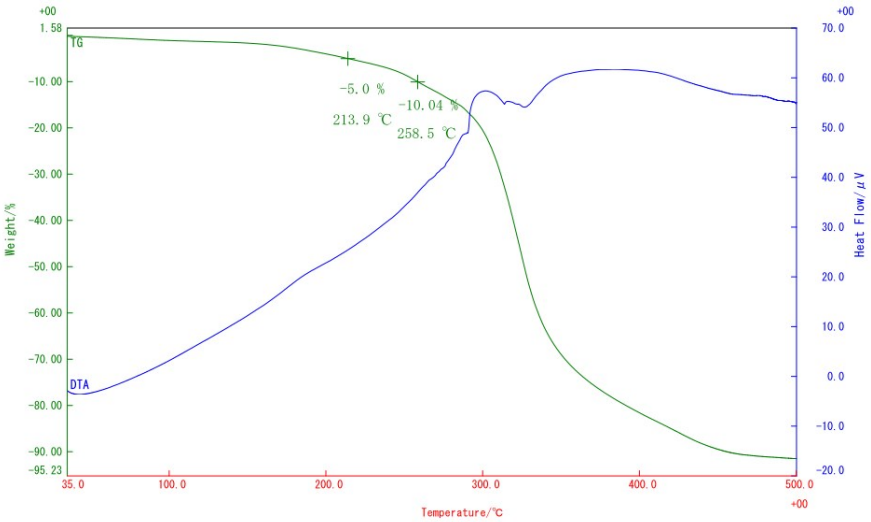


Fig. S23. TG/DTA curves of the product in Entry 7.

References

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2 D. Gopal and K. Rajagopalan, *Tetrahedron Lett.*, 1987, 28, 5327.