-Supporting Information –

Mechanochemical Ring-Opening Metathesis Polymerization: Development, Scope, and Mechano-Exclusive Copolymer Synthesis

Gue Seon Lee,[a] Hyo Won Lee,[a] Hyun Sub Lee,[a] Taeyang Do,[a] Jean-Louis Do,[b] Jeewoo Lim,[c] Gregory I. Peterson,[d*] Tomislav Friščić,[b*] and Jeung Gon Kim[a,e*]

a) Department of Chemistry and Research Institute of Physics and Chemistry

Jeonbuk National University, Jeonju, 54896, Republic of Korea

E-mail: jeunggonkim@jbnu.ac.kr (J. G. Kim)

b) Department of Chemistry

McGill University, 801 Sherbrooke Street West H3A0B8 Montreal, Canada

E-mail: tomislav.friscic@mcgill.ca (T. Friščić)

c) Department of Chemistry and Research Institute for Basic Science

Kyung Hee University, Seoul 02447, Republic of Korea

d) Department of Chemistry

Inchon National University, Incheon, 22012, Republic of Korea

E-mail: gpeterson@inu.ac.kr (G. I. Peterson)

e) Institute of Advanced Composite Materials

Korea Institute of Science and Technology (KIST), Jeonbuk, 55324, Republic of Korea

1. General Considerations

All polymerization reactions were prepared under nitrogen atmosphere using a glove box to avoid contamination with moisture. All solvents were obtained as HPLC grade and dried over a mixture of pre-activated 3 Å molecular sieves and neutral alumina. Anhydrous solvents were prepared by drying them over a mixture of preactivated alumina and 3 Å molecular sieves.[1] The Grubbs **G3** was prepared according to a procedure in the literature.[2] Reagents from commercial sources were used without further purification. A Retsch Mixer Mill MM 400 instrument was used for the ball-milling experiments with a 10-mL zirconia vessel and zirconia balls with the diameters of 3, 5, 8, and 10 mm. A Teflon seal was placed between the vessel and the top closure.

2. Measurements

The ^{1}H-NMR spectra were measured by a Bruker AVANCE III HD-400 MHz Fourier transform NMR spectrometer at the Jeonbuk National University, department of chemistry shared facilities. Differential scanning calorimetry (DSC) measurements were recorded on TA Instruments DSC Q20 using a sealed aluminum pan/lid. The heating/cooling cycle from 0 ℃ to 250 ℃ at 10 ℃/min was repeated twice under an N_2 atmosphere. The heat flow of the second heating was used for the data acquisition. The size exclusion chromatography (SEC) system was composed of a Waters 2414 differential refractive index detector, a Waters 1515 isocratic pump, and a column heating module to determine the relative number-average molecular weight (M_n), and the weight-average molecular weight (M_w).

1) THF system: Shodex HK-403 and HK-404 L columns were eluted with HPLC grade tetrahydrofuran (THF) at 40 °C at 1.0 mL/min. A calibration curve was obtained with 16 monodispersed polystyrene standards (Alfa Aesar).

2) DMF system: Shodex LF804 column were eluted with HPLC grade dimethylfromamide (DMF) at 40 °C at 1.0 mL/min. A calibration curve was obtained with 13 monodispersed polystyrene standards (Alfa Aesar).

3) Water system: Shodex GF-510HQ column were eluted with HPLC grade water (0.02 wt% NaN_3) at 40 °C at 1.0 mL/min. A calibration curve was obtained with 12 monodispersed poly(ethylene oxide) standards (Agilent, EasyCal).

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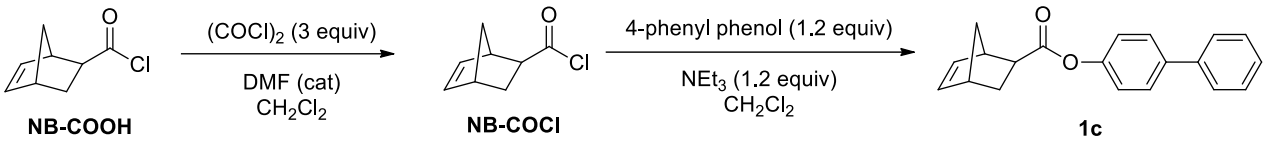
[1] D. B. G. Williams and M. Lawton, *J. Org. Chem.*, **2010**, *75*, 8351.

[2] M. S. Sanford, J. A. Love and R. H. Grubbs, *Organometallics*, **2001**, *20*, 5314

3. Monomer Synthesis

Monomers were prepared according to prior examples[3] except **1c**, **1e and 1i**.

3.1. Preparation of 1c



Oxalyl chloride (3.6 mL) was added slowly to the solution of NB-COOH (1.51 g, 10.9 mmol) and CH_2Cl_2 (10 mL) in a 100 mL round-bottom flask at 0 °C. After stirring for 1 h, the complete conversion to NB-COCl was confirmed by ^{1}H-NMR of an aliquot. The flask was placed under reduced pressure to afford a crude NB-COCl. CH_2Cl_2 (80 mL) was added to the crude NB-COCl, then the mixture was placed in an ice bath. 4-Phenyl phenol (2.23 g) and triethylamine (1.83 mL) were added in sequence. After 6 h, the mixture was washed with 1 N HCl (100 mL), water (100 mL), and brine (100 mL). The organic layer was dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by chromatography in silica gel (hexanes:EtOAc = 9:1) to give the desired products **1c** (0.771 g, 24% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.54 (m, 4H), 7.44 (dd, *J* = 10.3, 4.8 Hz, 2H), 7.35 (ddd, *J* = 7.3, 3.9, 1.2 Hz, 1H), 7.20 – 7.14 (m, 2H), 6.25 – 6.17 (m, 2H), 3.26 (s, 1H), 3.01 (s, 1H), 2.52 (ddd, *J* = 8.9, 4.4, 1.3 Hz, 1H), 2.13 – 2.06 (m, 1H), 1.64 (d, *J* = 8.6 Hz, 1H), 1.54 – 1.44 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.9, 150.4, 140.5, 138.9, 138.4, 135.7, 128.8, 128.2, 127.3, 127.1, 121.8, 46.9, 46.4, 43.4, 41.8, 30.6. High Resolution MS (EI) calcd for $C_{20}H_{18}O_2$ $[M]^+$, 290.1307; found, 290.1308.

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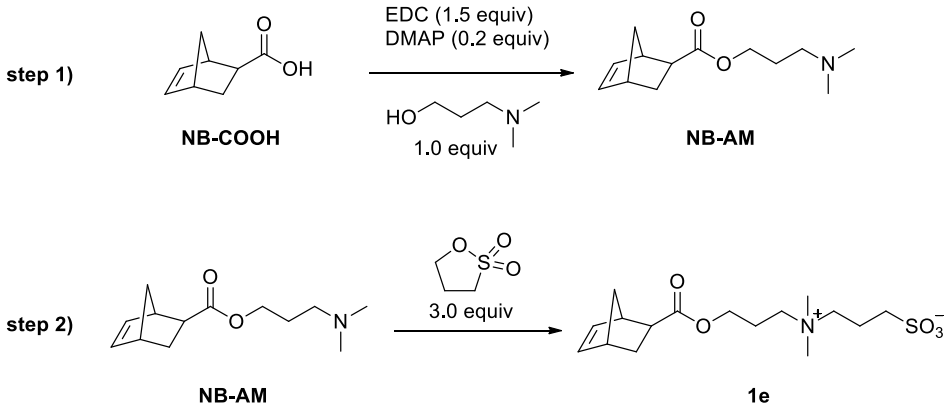
[3] Compound **1a**: A. M. Rush, D. A. Nelles, A. P. Blum, S. A. Barnhill, E. T. Tatro, G. W. Yeo and N. C. Gianneschi, *J. Am. Chem. Soc.*, **2014**, *136*, 7615; compound **1b**: S. C. Radzinski, J. C. Foster, R. C. Chapleski, Jr., D. Troya and J. B. Matson, *J. Am. Chem. Soc.*, **2016**, *138*, 22, 6998; compound **1d**: S. C. Radzinski, J. C. Foster and J. B. Matson, *Macromol. Rapid Commun.*, **2016**, *37*, 616; compound **1g**: S. Malfait, S. Gérard, R. Plantier-Royon, G. Mignani and C. Portella, *J. Fluorine Chem.*, **2011**, *132*, 760; **1h**: A. E. Levi, J. Lequieu, J. D. Horne, M. W. Bates, J. M. Ren, K. T. Delaney, G. H. Fredrickson and C. M. Bates, *Macromolecules*, **2019**, *52*, 1794; compound **1i**: S. Mukherjee, R. Xie, V. G. Reynolds, T. Uchiyama, A. E. Levi, E. Valois, H. Wang, M. L. Chabinyc and C. M. Bates, *Macromolecules*, **2020**, *53*, 1090.

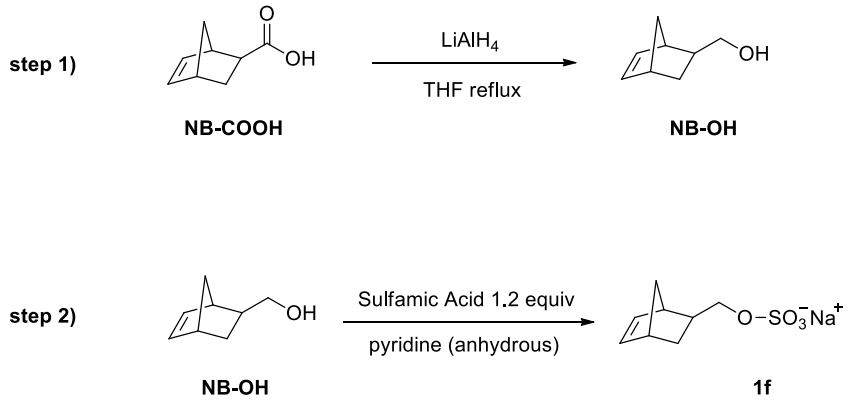
3.2. Preparation of 1e



Step 1: NB-COOH (1.0 g, 1.0 equiv), ethyl-3-(3-dimethylaminopropyl)carbodiimide) (EDC, 2.1 g, 1.5 equiv), 4-dimethylaminopyridine (DMAP, 0.18 g, 0.20 equiv), and 3-(dimethylamino)-1-propanol (0.85 mL, 1.0 equiv) were dissolved in CH_2Cl_2 (20 mL). After 12 h, the reaction mixture was washed with aq. $CuSO_4$ (X M, 100 mL), deionized water (100 mL), and brine (100 mL). The organic layer was dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure to give NB-AM (1.44 g, 89%).

Step 2: To a 20 mL vial, NB-AM (1.44g), 1,3-propanesultone (1.7 mL, 3.0 equiv) and MeCN (7 mL) were added. After stirring for 12 h, while precipitation **1e** was collected through filtration and dried in vacuo at 70 °C (0.96 g, 43%). ^{1}H NMR (400 MHz, D_2O) δ 6.23 (ddd, *J* = 19.5, 5.6, 3.0 Hz, 2H), 4.25 (t, *J* = 5.9 Hz, 2H), 3.57 – 3.45 (m, 4H), 3.17 (s, 6H), 3.12 – 3.06 (m, 1H), 3.02 (t, *J* = 7.2 Hz, 2H), 2.99 (s, 1H), 2.36 (ddd, *J* = 9.1, 4.5, 1.1 Hz, 1H), 2.32 – 2.17 (m, 4H), 1.86 (ddd, *J* = 11.8, 4.4, 3.8 Hz, 1H), 1.51 – 1.37 (m, 3H). ^{13}C NMR (100 MHz, D_2O) 179.0, 138.4, 135.7, 62.2, 61.6, 61.4, 50.8, 47.2, 46.1, 46.0, 42.9, 41.4, 30.1, 21.7, 18.1. High Resolution MS (FAB) calcd for $C_{16}H_{28}NO_5S$ $[M+H]^+$, 346.1688; found, 346.1690.

3.3. Preparation of 1f



Step 1: NB-OH was synthesized by following paper.[4] NB-OH (0.71 g 86%)

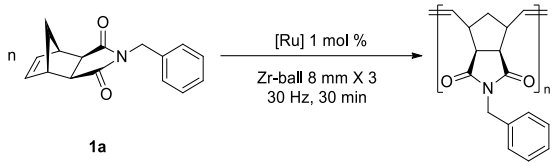
Step 2: To a 100 mL round bottom flask, NB-OH (0.71 g), sulfamic acid (0.67 g, 1.2 equiv) and anhydrous pyridine (13 mL) were added. After stirring for 16 h at 95 °C, the solution was cooled to room temperature. Methanol (40 mL) was added to the solution mixture. sat. aq. Na_2CO_3 was added dropwise and the solution was stirring for 30min. Na_2SO_4(s) was added and continued for a further stirring for 20 min. The resulting mixture was filtered and the solution was concentrated in vacuo for remove water. The crude product washed with CH_2Cl_2 and shaken. Then, while precipitation **1f** was collected through filtration and dried in vacuo at 70 °C (1.07 g, 83%). ^{1}H NMR (400 MHz, D_2O) δ 6.18 (s, 2H), 4.13 (dd, J = 9.7, 6.6 Hz, 1H), 3.99 (t, J = 9.4 Hz, 1H), 2.87 (s, 1H), 2.78 (s, 1H), 1.88 – 1.59 (m, 1H), 1.39 – 1.29 (m, 2H), 1.28 – 1.16 (m, 2H). ^{13}C NMR (100 MHz, D_2O) 137.45, 136.4, 73.4, 44.4, 43.2, 41.4, 38.0, 28.7. High Resolution MS (FAB+) calcd for $C_8H_{11}O_4SNa_2$ [M+Na], 249.0173; found, 249.0172.

[4] S. C. Radzinski, J. C. Foster and J. B. Matson, *Macromol. Rapid Commun.*, **2016**, *37*. 616.

4. ROMP Experiments

4.1. Initiator scope of ball-milling ROMP (Table 1)

Table S1. Raw data used for Table 1[a]



1a

Entry	[Ru]	Conv[b] (%)	M_n[c] (kg/mol)	M_w[c] (kg/mol)	$Đ$	E/Z[b]
1-1	G1	22	6.4	8.2	1.29	77/23
1-2		24	6.4	8.3	1.29	75/25
2-1	G2	98	14.3	24.4	1.70	57/43
2-2		98	13.8	23.0	1.67	57/43
3-1	G3	96	15.1	23.2	1.54	57/43
3-2		97	13.8	21.1	1.52	57/43
4-1	HG	98	20.7	43.4	2.10	57/43
4-2		98	21.8	46.7	2.14	57/43

[a]Reaction condition: **1a** (50 mg) and [Ru] = 1 mol% in a 10 mL zirconia jar with three zirconia balls (8 mm diameter). 30 Hz vibration for 30 minutes. [b]Determined by ^{1}H-NMR spectroscopy. [c]Determined by size exclusion chromatography (SEC) with polystyrene (PS) standards in tetrahydrofuran (THF) at 40 °C.

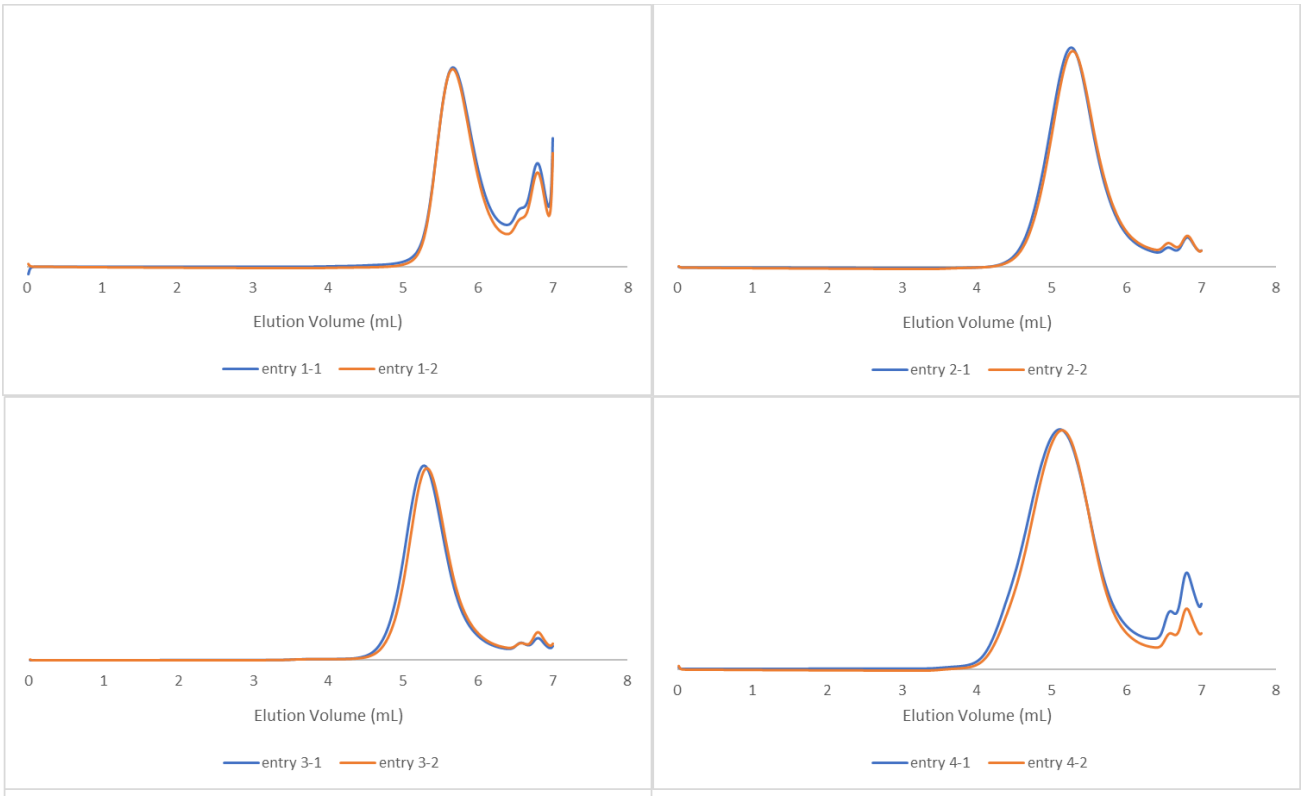
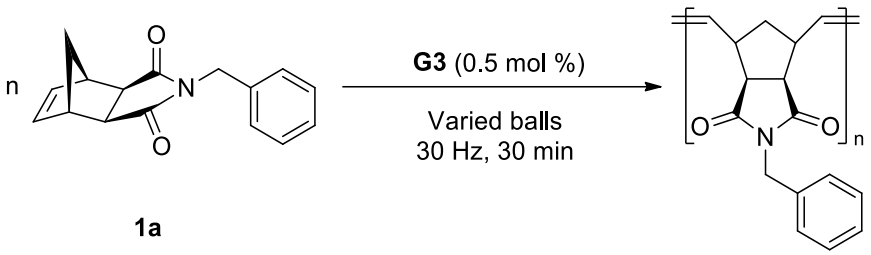


Figure S1. SEC diagrams of Table 1

4.2. Effect of the ball-milling parameters (Table 2)

Table S2. Raw data used for Table 2[a]



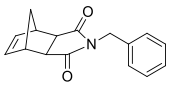
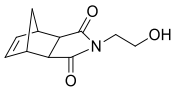
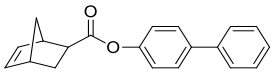
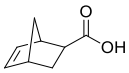
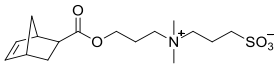
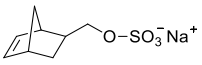
1a

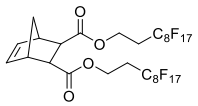
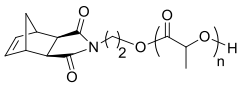
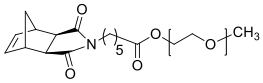
Entry	Balls	Conv[b] (%)	M_n[c] (kg/mol)	M_w[c] (kg/mol)	$Đ$
1-1	8 mm x 1	85	25.3	40.5	1.60
1-2		90	22.9	38.4	1.68
2-1	8 mm x 3	89	23.3	39.3	1.69
2-2		91	21.9	36.1	1.65
3-1	8 mm x 5	92	23.6	37.7	1.60
3-2		95	22.3	38.0	1.70
4-1	10 mm x 1	97	16.8	27.6	1.64
4-2		99	16.2	26.9	1.65
5-1	5 mm x 12	9	-	-	-
5-1		23	-	-	-
6-1	3 mm x 20	<5	-	-	-
6-1		<5	-	-	-
7-1	8 mm X3 (20 Hz)	16	-	-	-
7-2		24	-	-	-

[a] Reaction conditions: **1a** (50 mg) and **G3** in a 10 mL zirconia jar, followed by 30 Hz vibration for 30 min. [b] Determined using ^{1}H NMR spectroscopy. Conv.(%) = A portion of polymeric alkenes of total alkenes. [c] Determined using SEC with PS standards in THF at 40 °C.

4.3. Scope of the monomer in the solid-state ROMP (Table 3)

Table S3. Raw data used for Table 3[a]

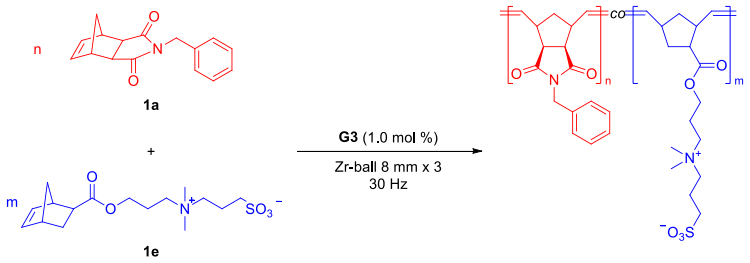
Entry	monomer	[M]/[G3]	Conv[b] (%)	M_n[c] (kg/mol)	M_w[c] (kg/mol)	$Đ$
1-1	 **1a**	100 (Neat)	96	15.1	23.2	1.54
1-2			97	13.8	21.1	1.52
2-1	 **1b**	100 (Neat)	98	70.3[d]	114[d]	1.62[d]
2-2			97	69.5[d]	127[d]	1.83[d]
3-1	 **1c**	100 (Neat)	90	17.9	27.6	1.54
3-2			91	18.4	28.1	1.53
4-1	 **1d**	100 (Neat)	99	N/A[e]	N/A[e]	N/A[e]
4-2			97	N/A[e]	N/A[e]	N/A[e]
5-1	 **1e**	100 (Neat)	86	5.4[f]	6.0[f]	1.12[f]
5-2			86	5.4[f]	6.1[f]	1.13[f]
5-3		100 H_2O (η = 0.4)	99	23.3[f]	30.7[f]	1.32[f]
5-4			99	26.1[f]	36.2[f]	1.39[f]
6-1	 **1f**	100 (Neat)	8	4.7[f]	4.8[f]	1.03[f]
6-2			9	4.7[f]	4.8[f]	1.03[f]
6-3[g]		100 H_2O (η = 0.4)	57	42.6[f]	60.0[f]	1.41[f]
6-4[g]			51	46.7[f]	65.5[f]	1.40[f]
6-5[g]		100 DMF (η = 0.4)	99	55.1[f]	70.9[f]	1.29[f]
6-6[g]			99	59.8[f]	80.4[f]	1.34[f]

7-1	 **1g**	50 THF/HFE[d] (1:1) (η = 0.4)	99	N/A[e]	N/A[e]	N/A[e]
7-2			99	N/A[e]	N/A[e]	N/A[e]
8-1[g]	 M_n (NMR) = 2.6 kg/mol **1h**	100 THF (η = 0.4)	96	94.7	125	1.31
8-2[g]			97	99.9	126	1.26
9-1[g]	 M_n (NMR) = 1.9 kg/mol **1i**	50 THF (η = 0.4)	94	65.0[d]	77.6[d]	1.19[d]
9-2[g]			92	79.8[d]	104[d]	1.30[d]
10-1[h]	 **1j**	100 (Neat)	99	26.4	65.3	2.47
10-2[h]			99	26.2	65.1	2.48

[a]Reaction conditions: monomer (50 mg), **G3**, and liquid (20 µL) in a 10 mL zirconia jar containing three zirconia balls (8 mm diameter), followed by 30 Hz vibration for 30 min. [b]Determined using ^{1}H NMR spectroscopy. [c]Determined using SEC with polystyrene standards in tetrahydrofuran at 40 °C. [d]Determined using SEC with polystyrene standards in dimethylformamide at 40 °C. [e] Products did not elude column. [f]Determined using SEC with poly(ethylene oxide) standards in H_2O at 40 °C. [g] Milling time = 60min. [h]**1j** (57 µL), **G3** in a 10 mL PTFE jar containing three zirconia balls

4.4. Copolymerizations of immiscible monomers with G3. (Table 4)

Table S4. Raw data used for Table 4[a]



Entry	n : m	LAG	Time (min)	Conv[c] **1a**/**1e**(%)	M_n (kg/mol)	M_w (kg/mol)	$Đ$
1-1[a]	10 : 1	THF (18.2 μL) + H_2O (1.8 μL)	30	97 / 99	14.3[d]	19.9[d]	1.40[d]
1-2[a]				95 / 99	14.0[d]	18.8[d]	1.35[d]
2-3[a]	4 : 1	THF (16 μL) + H_2O (4 μL)	30	99 / 99	14.0[d]	18.9[d]	1.35[d]
2-4[a]				99 / 99	14.0[d]	19.1[d]	1.37[d]
3-3[a]	2 : 1	THF (13.3 μL) + H_2O (6.7 μL)	30	99 / 99	15.5[d]	19.7[d]	1.27[d]
3-4[a]				99 / 99	15.5[d]	20.5[d]	1.32[d]
4-3[a]	1 : 2	THF (6.7 μL) + H_2O (13.3 μL)	30	99 / 99	14.2[e]	19.6[e]	1.38[e]
4-4[a]				99 / 99	14.2[e]	19.7[e]	1.39[e]
5-3[a]	1 : 4	THF (4 μL) + H_2O (16 μL)	30	99 / 99	17.5[e]	24.1[e]	1.38[e]
5-4[a]				99 / 99	17.2[e]	24.3[e]	1.41[e]
6-3[a]	1 : 10	THF (1.8 μL) + H_2O (18.2 μL)	30	99 / 99	18.4[e]	25.8[e]	1.40[e]
6-4[a]				99 / 99	17.7[e]	24.6[e]	1.39[e]

[a] Reaction conditions: **1a + 1e** (50 mg), **G3** (1.0 mol%), and liquid (20 μL) in a 10 mL zirconia jar containing three zirconia balls (8 mm diameter), followed by 30 Hz vibration. [b] Reaction conditions: **1a + 1e** (50mg), liquid (concentration 0.5 M) in a 1 mL V-shape vial [c] Determined using ^{1}H NMR spectroscopy. [d] Determined using SEC with polystyrene standards in tetrahydrofuran at 40 °C. [e] Determined using SEC with poly(ethylene oxide) standards in H_2O at 40 °C

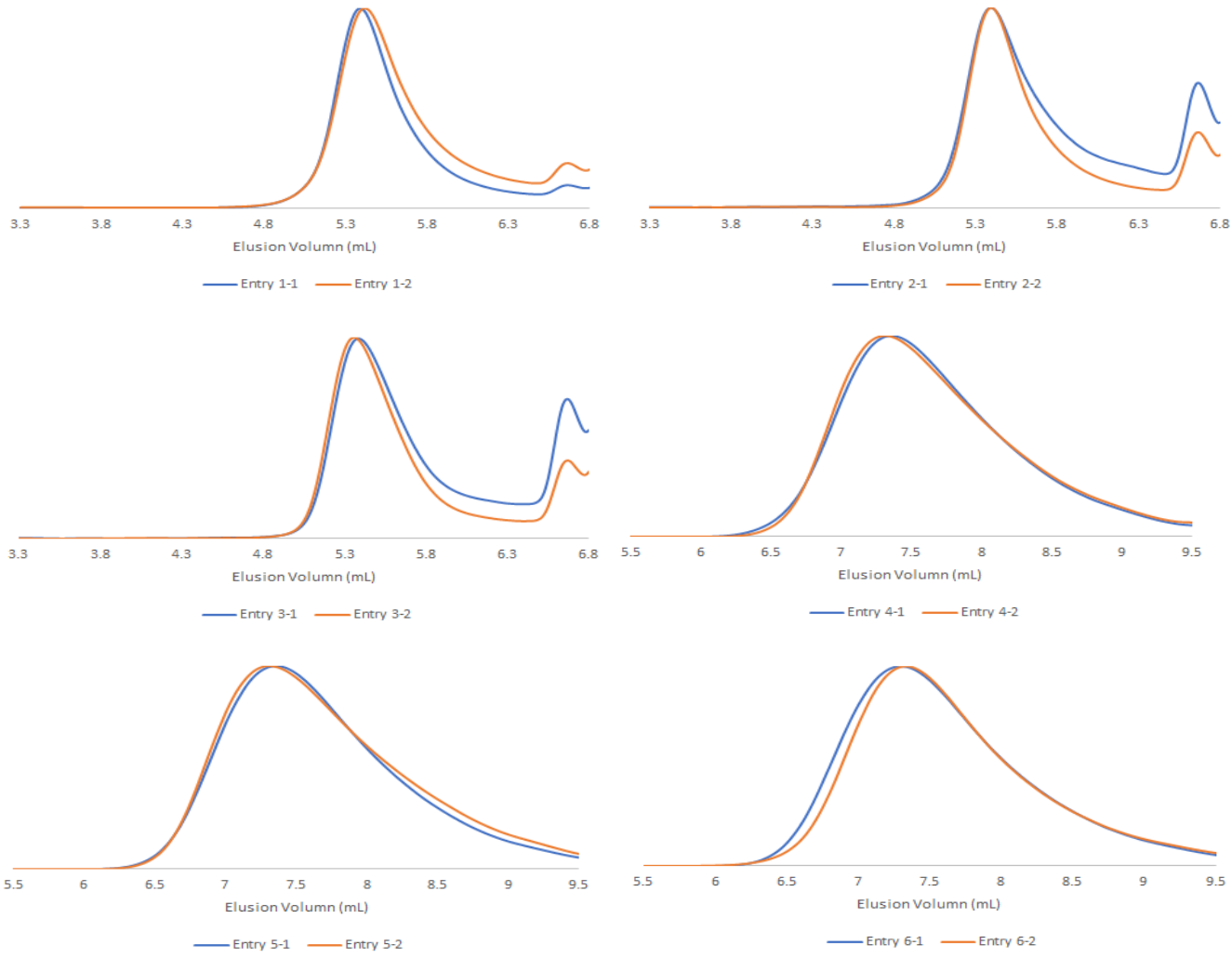


Figure S2. SEC diagrams of Table S4

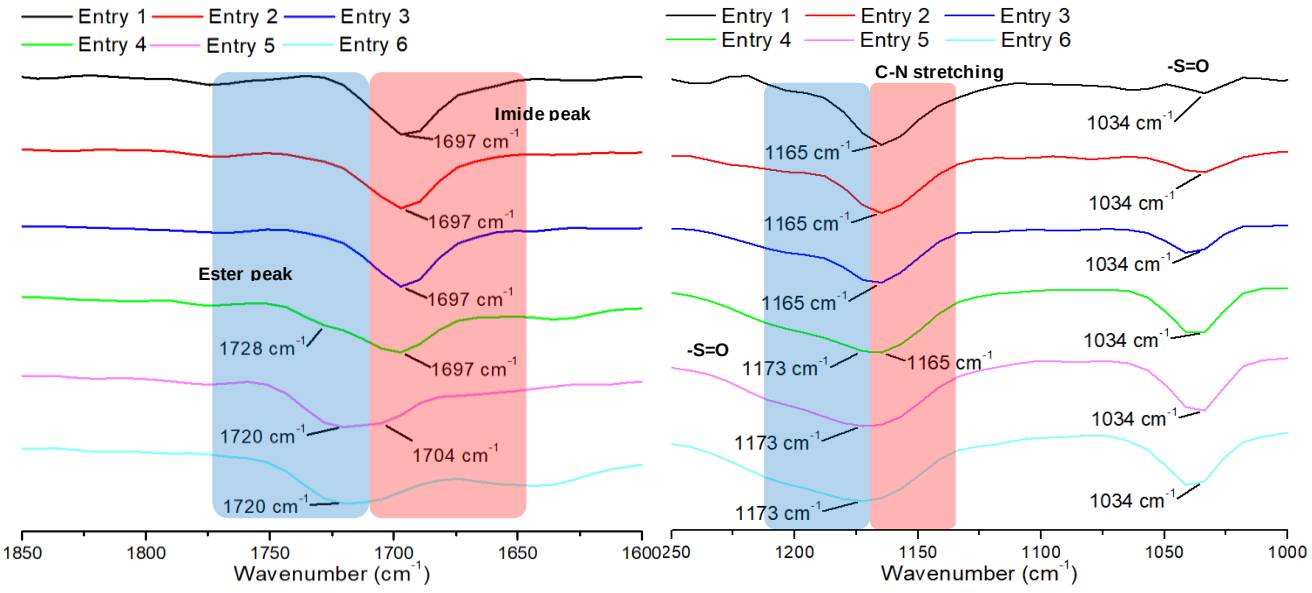


Figure S3. FT-IR spectra of Table S4.

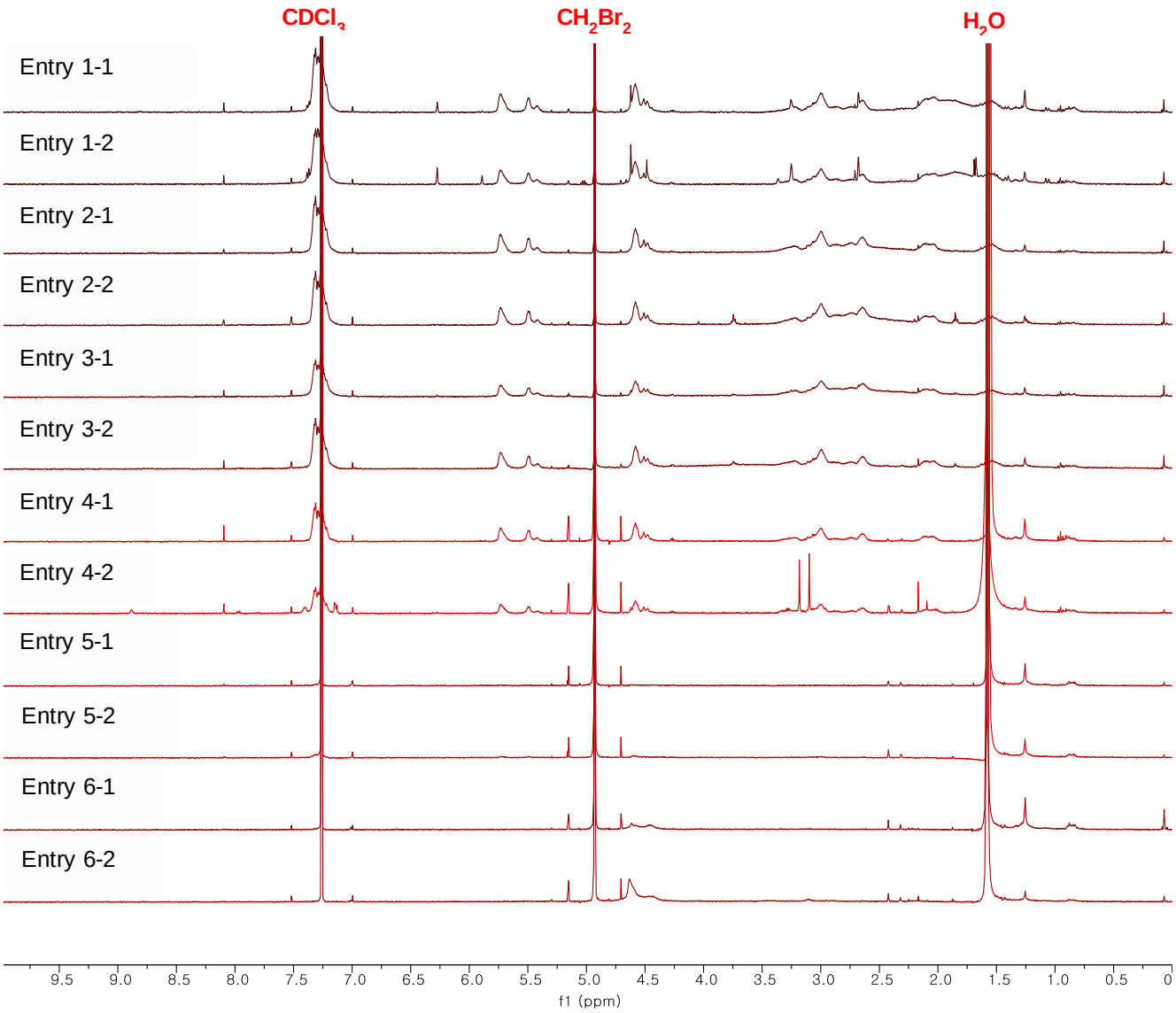


Figure S4. ^{1}H NMR spectrum of Table S4 (in $CDCl_3$)

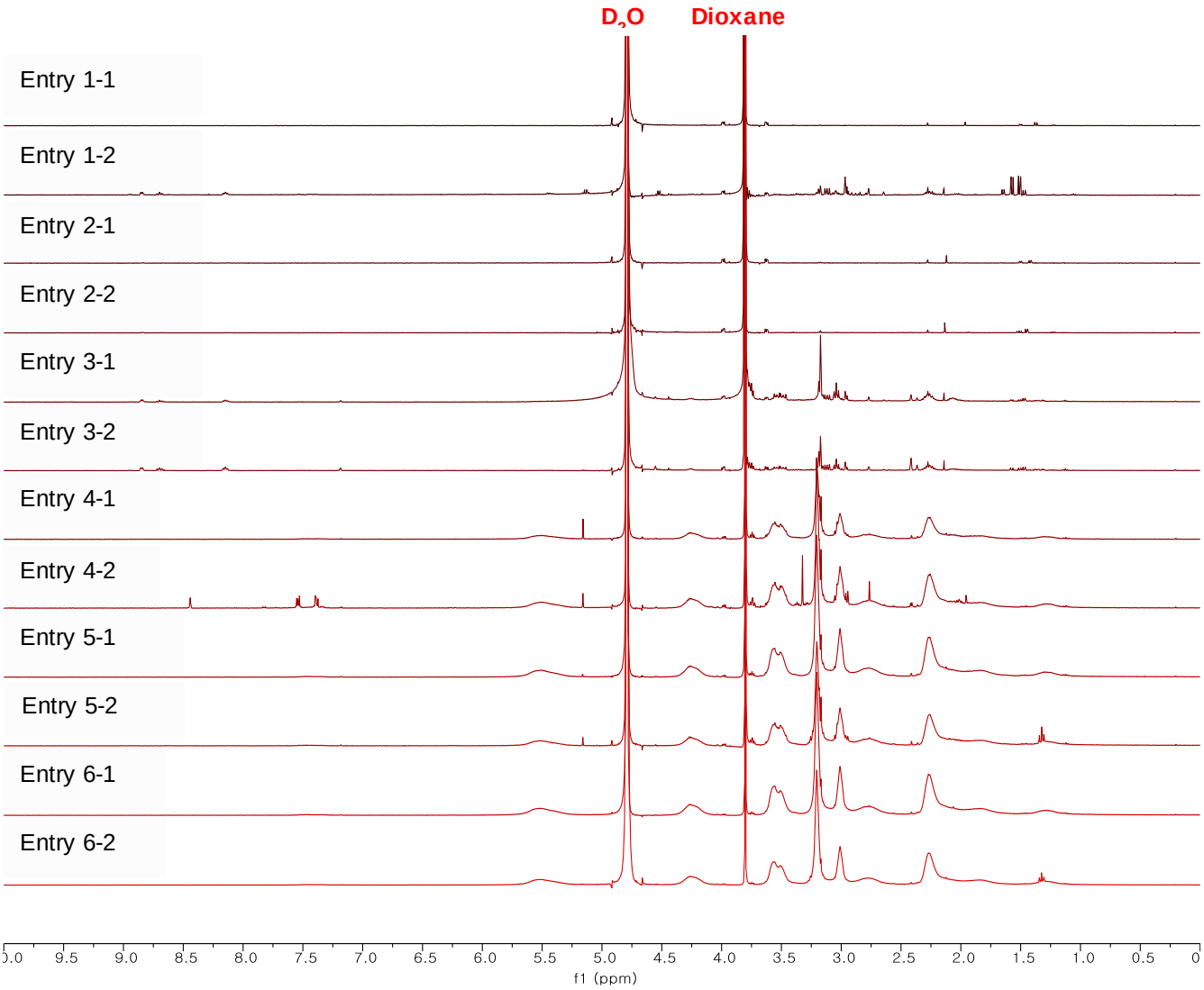


Figure S5. ^{1}H NMR spectrum of Table S4 (in D_2O)

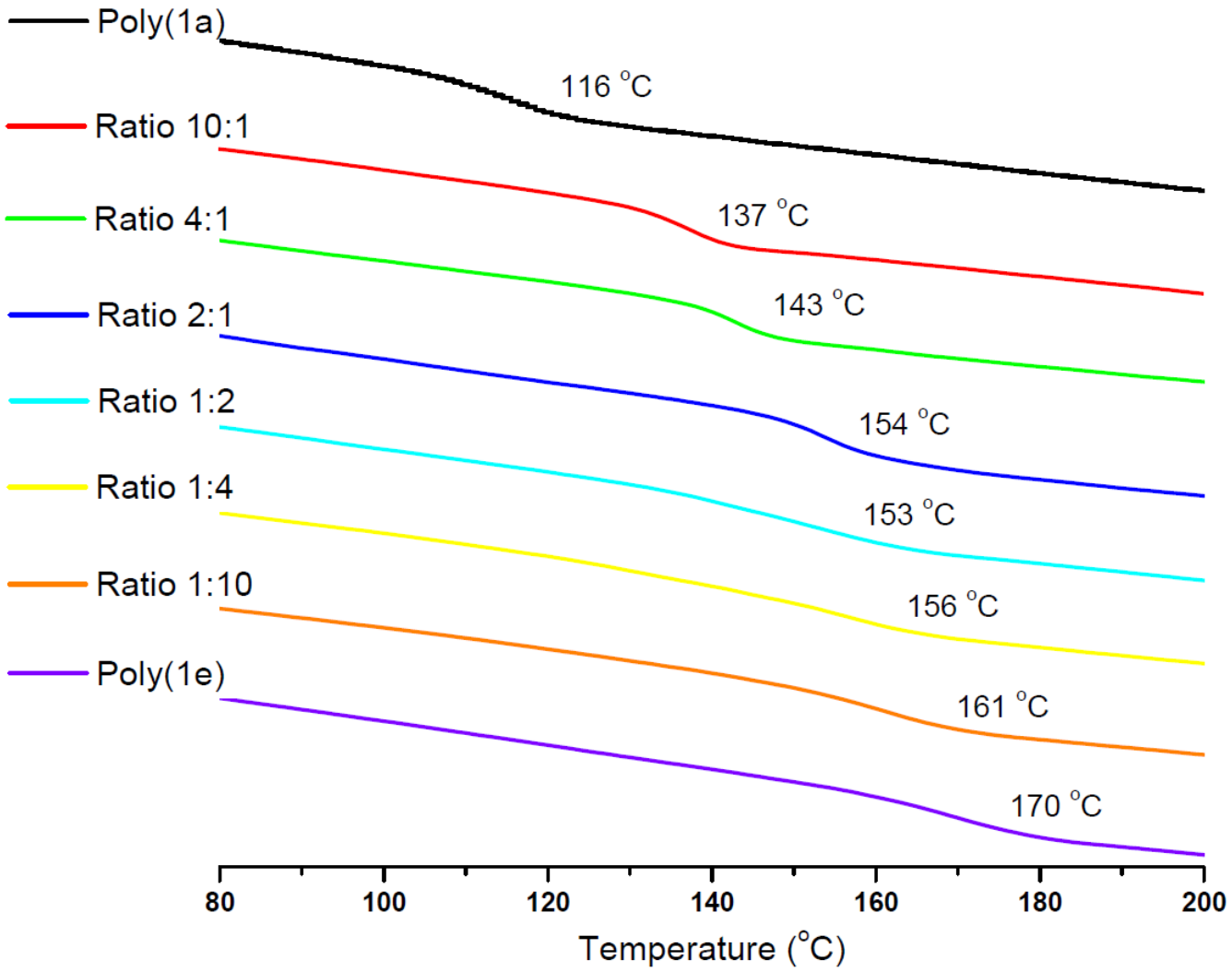


Figure S6. DSC thermograms of Poly(1a+1e) copolymer

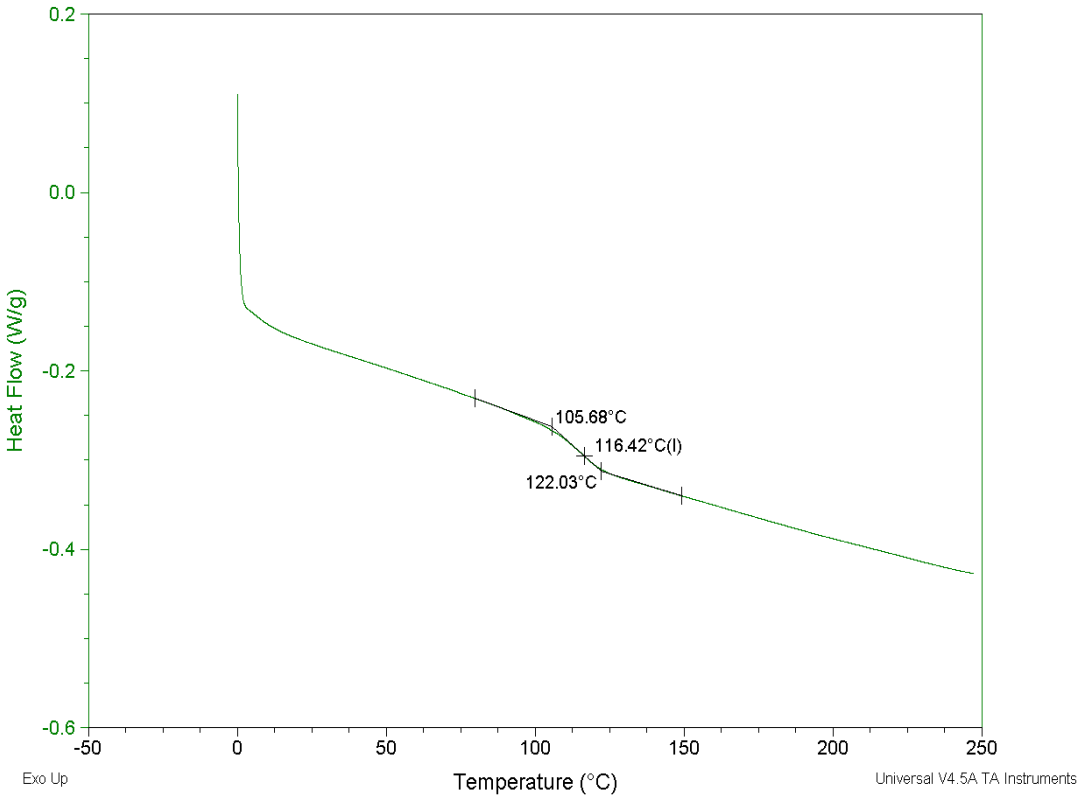


Figure S7. DSC Curve of Product of Table 1, entry 1

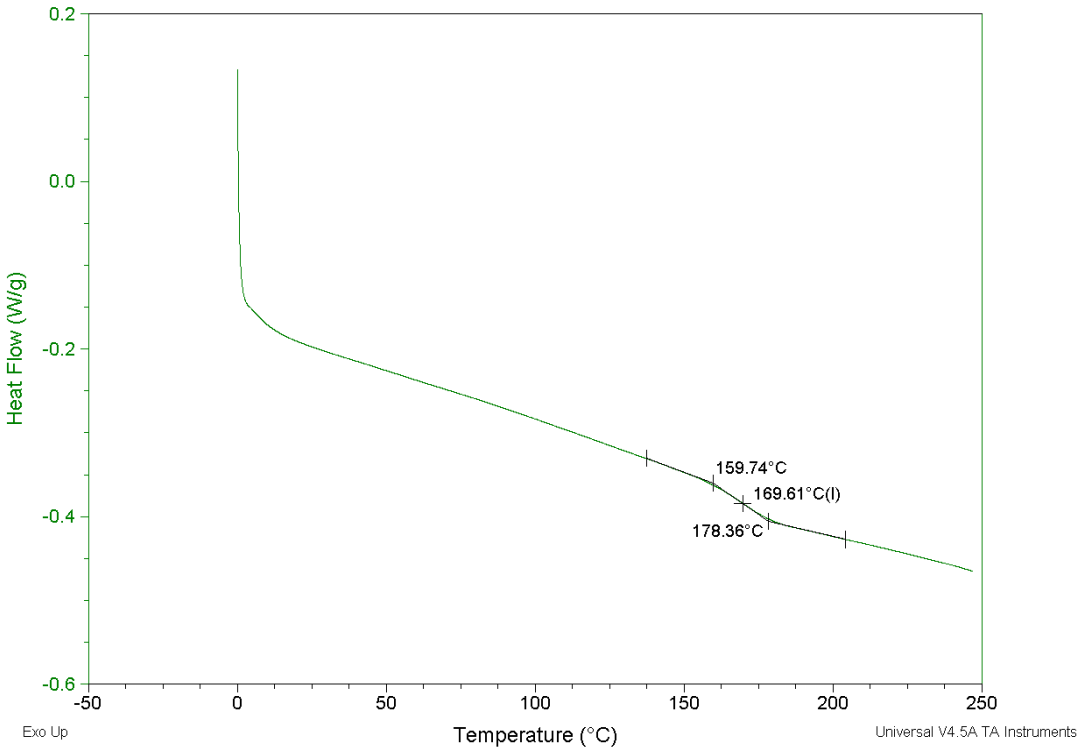


Figure S8. DSC Curve of Product of Table 3, entry 5

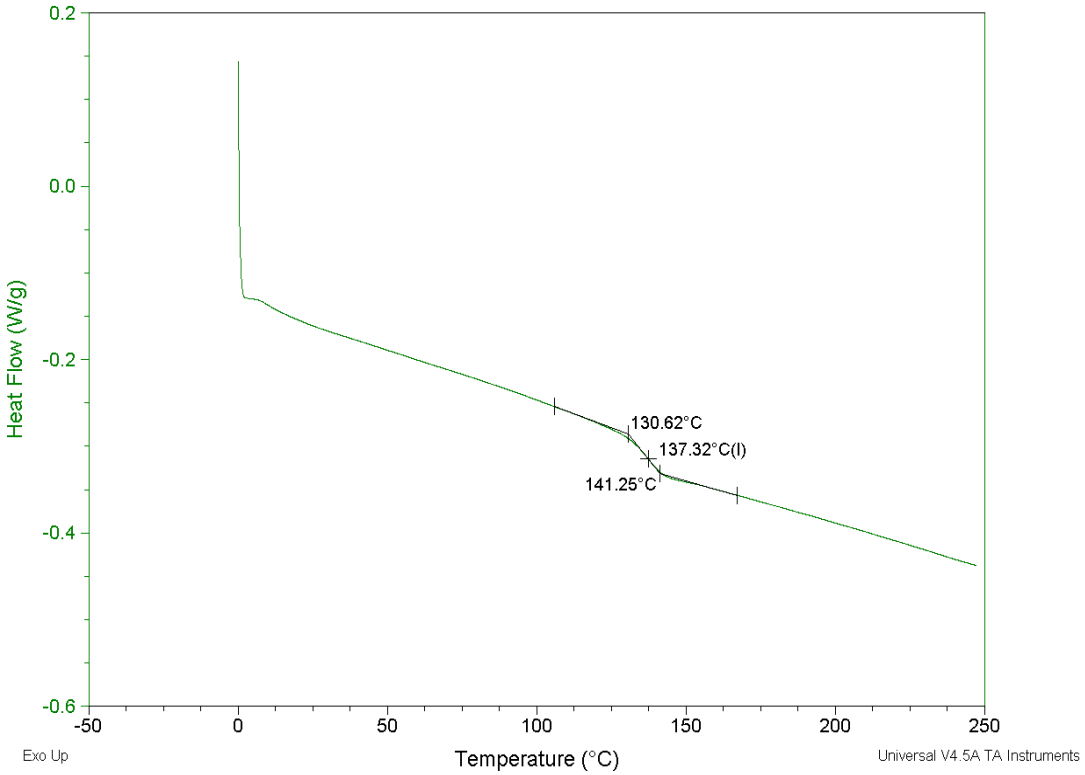


Figure S9. DSC Curve of Product of Table 4, entry 1

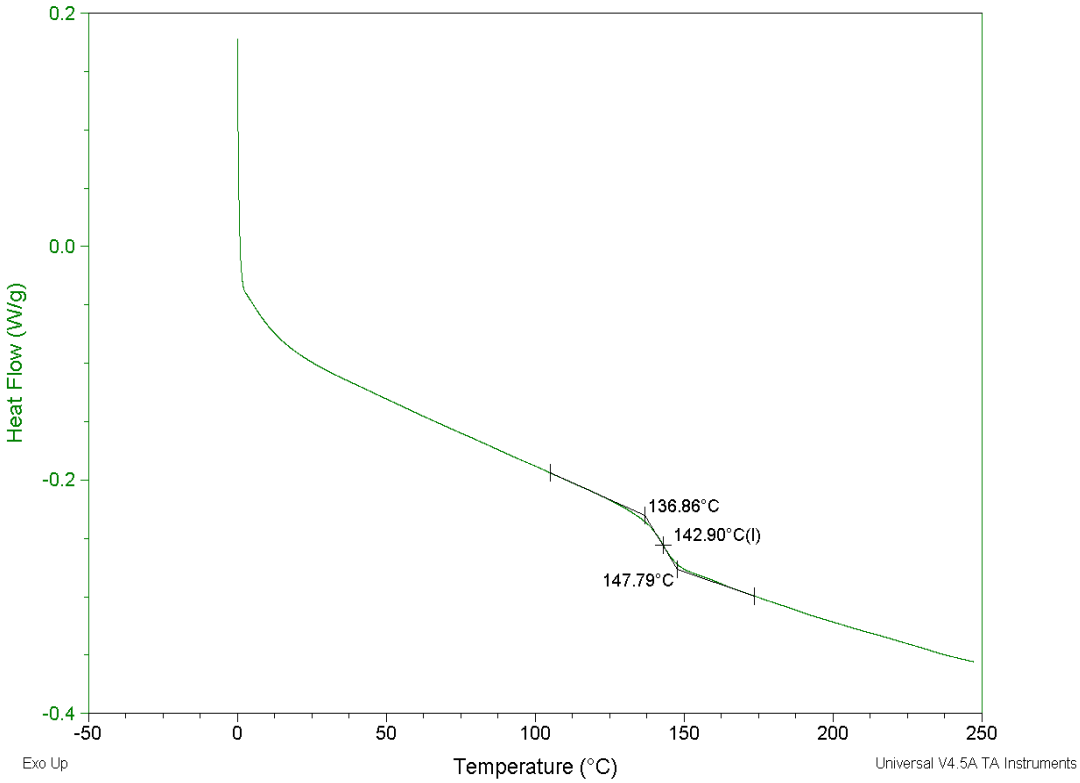


Figure S10. DSC Curve of Product of Table 4, entry 2

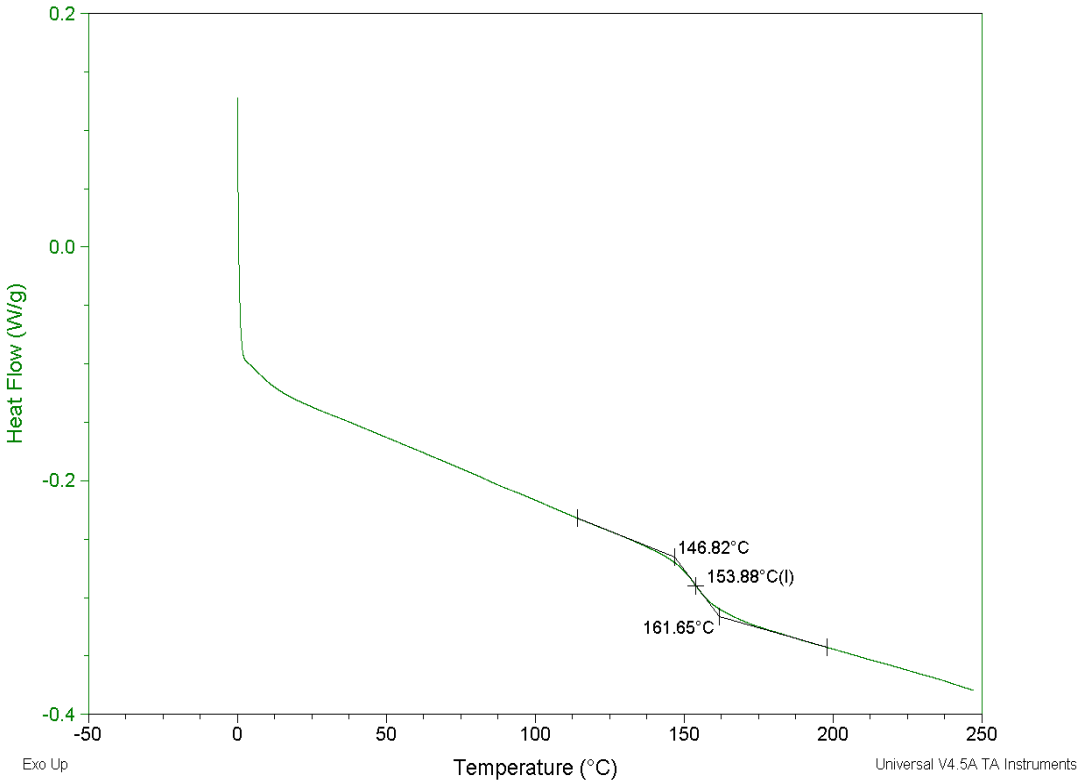


Figure S11. DSC Curve of Product of Table 4, entry 3

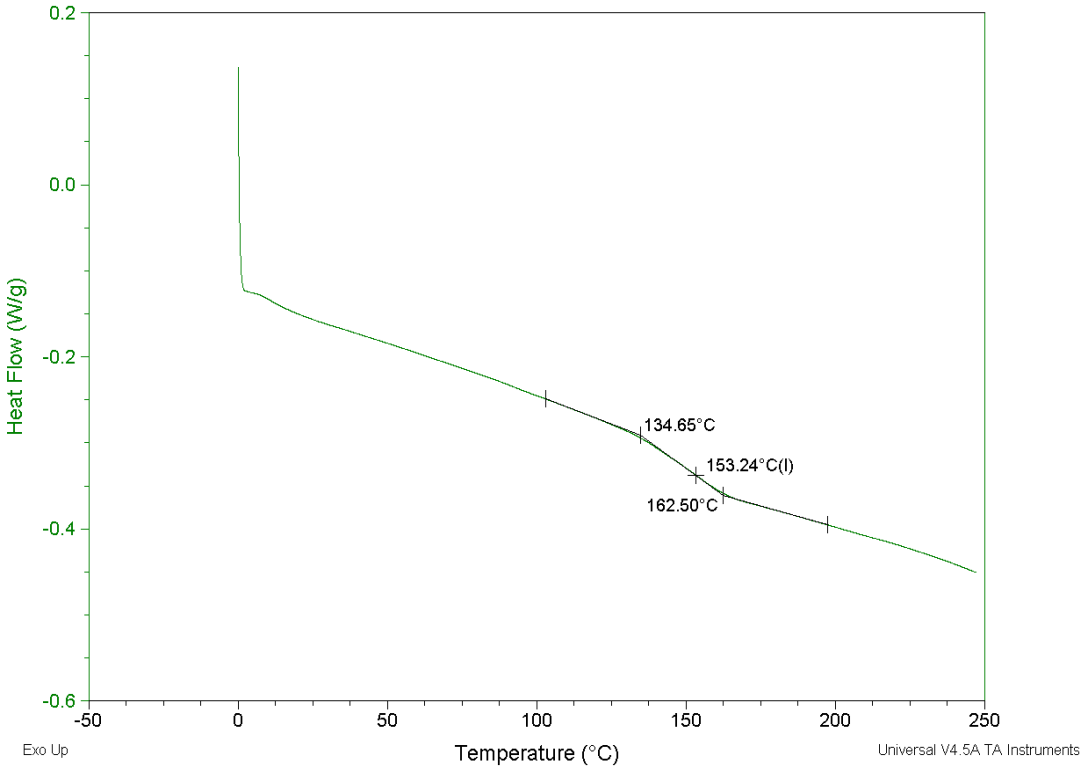


Figure S12. DSC Curve of Product of Table 4, entry 4

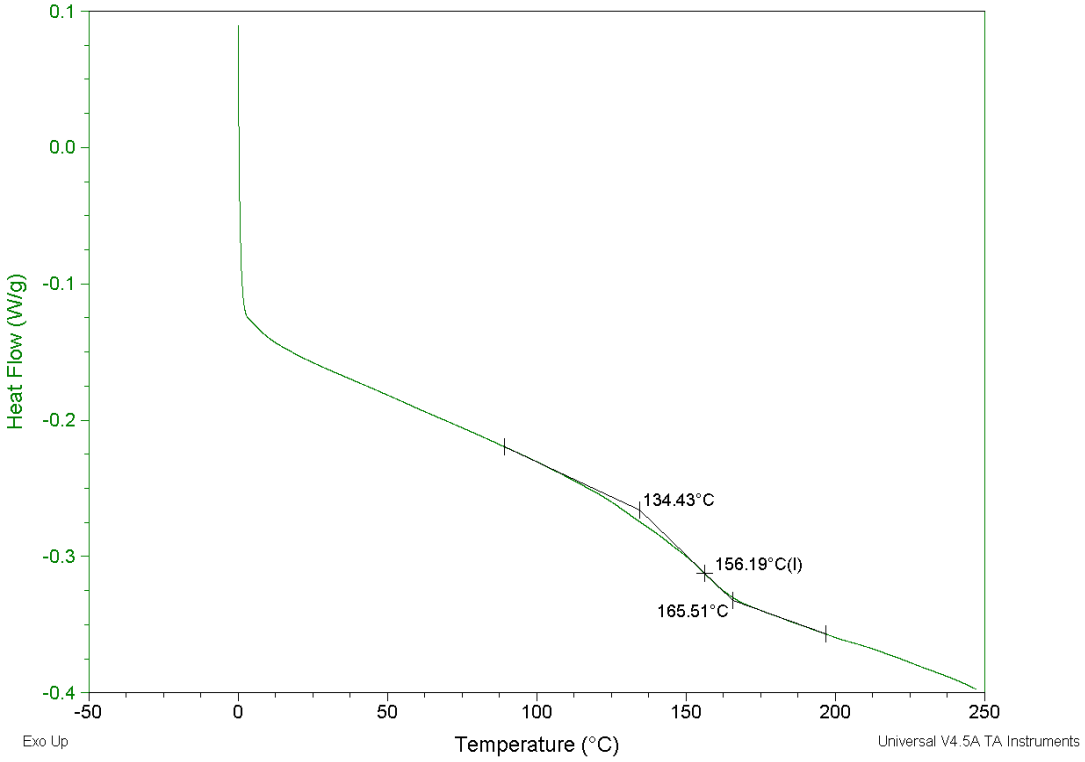


Figure S13. DSC Curve of Product of Table 4, entry 5

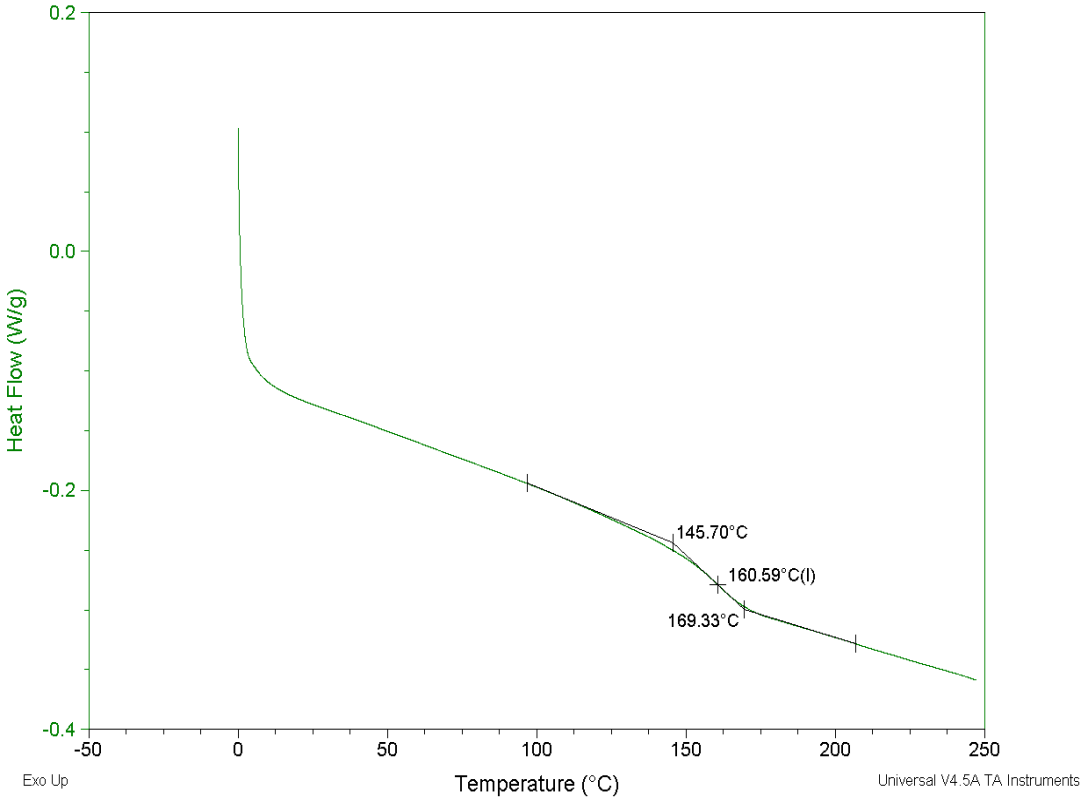
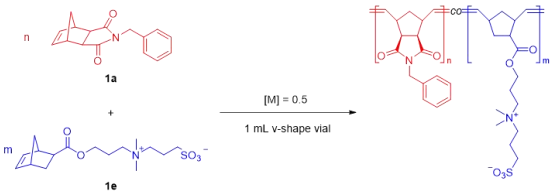


Figure S14. DSC Curve of Product of Table 4, entry 6



Entry	Solvent ratio		Major monomer	Minor monomer
	THF	H_2O	Step 1	Step 2
1 (10 : 1)	344 µL	38 µL	**1a** 44 mg Partially soluble	**1e** 6 mg Insoluble
2 (4 : 1)	294 µL	74 µL	**1a** 38 mg Partially soluble	**1e** 13 mg Insoluble
3 (2 : 1)	235 µL	117 µL	**1a** 30 mg Partially soluble	**1e** 20 mg Insoluble
4 (1 : 2)	106 µL	212 µL	**1e** 37 mg Soluble	**1a** 13 mg Insoluble
5 (1 : 4)	61 µL	245 µL	**1e** 42 mg Soluble	**1a** 7 mg Insoluble
6 (1 : 10)	27 µL	270 µL	**1e** 47 mg Soluble	**1a** 3 mg Insoluble

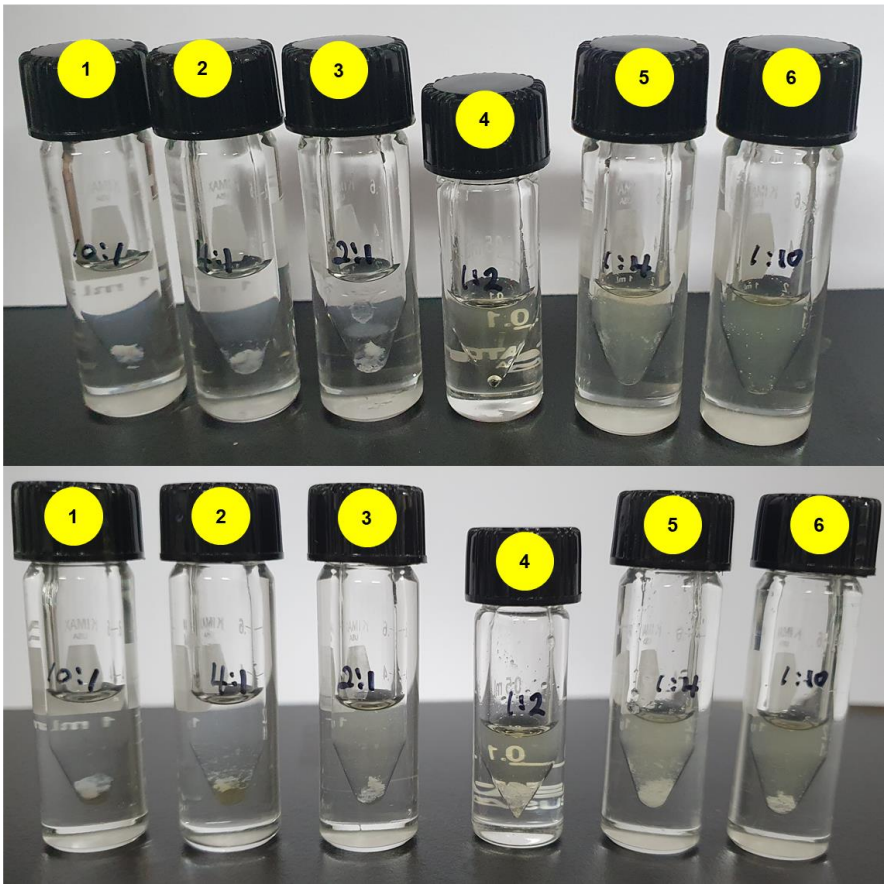
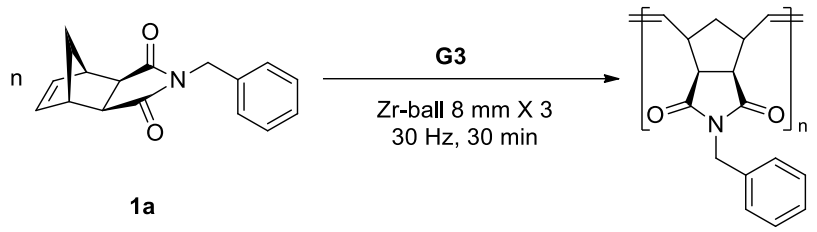


Figure S15. Solubility evaluation of monomer **1a** and **1e** in one solvent.

4.5. Conversion and number average molecular weight vs. ball-milling time (Figure 2)

Table S6. Raw data used for Figure 2



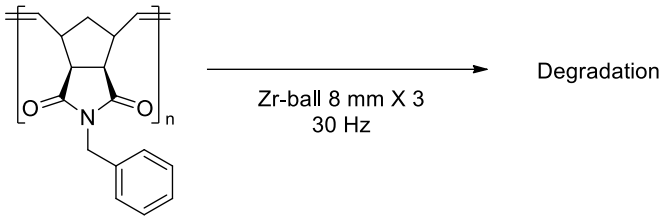
1a

[M]/G3 = 100					
Entry	Conv[b] (%)	M_n[c] (kg/mol)	M_w[c] (kg/mol)	*Đ*	E/Z[b]
5 min	42	16.2	52.8	3.25	51/49
	30	7.7	12.6	1.64	54/46
10 min	70	16.9	24.1	1.43	57/43
	64	13.3	20.5	1.54	56/44
30 min	90	16.8	24.1	1.44	57/43
	91	16.5	23.3	1.42	57/43
60 min	97	14.2	21.5	1.51	58/42
	95	14.2	21.5	1.51	57/43
[M]/G3 = 200					
Entry	Conv[b] (%)	M_n[c] (kg/mol)	M_w[c] (kg/mol)	*Đ*	E/Z[b]
5 min	26	13.5	23.1	1.71	56/44
	24	8.5	15.6	1.84	51/49
10 min	53	25.0	37.4	1.50	56/44
	53	23.5	36.2	1.54	56/44
30 min	89	23.3	39.4	1.69	56/44
	91	21.9	36.1	1.65	57/43
60 min	96	15.8	25.2	1.60	58/42
	94	16.6	26.6	1.61	57/43

[a]Reaction condition: **1a** (50 mg) and **G3** in a 10 mL zirconia jar with three zirconia balls (8 mm diameter). 30 Hz vibration. [b]Determined by ^{1}H-NMR spectroscopy. [c]Determined by size exclusion chromatography (SEC) with polystyrene (PS) standards in tetrahydrofuran (THF) at 40 °C.

4.6. Ball-milling induced degradation of poly-1a

Table S7. Degradation of Poly(1a)[a]



Poly-1a
50 mg

Entry	Time (min)	M_n[b] (kg/mol)	M_w[b] (kg/mol)	*Đ*
SM		33.0	38.6	1.17
1-1	10	24.8	47.9	1.93
1-2		26.2	50.5	1.93
2-2	20	20.1	40.5	2.02
2-2		22.2	44.5	2.00
3-1	30	17.2	35.3	2.05
3-2		19.1	39.7	2.08

[a]Reaction conditions: **Poly-1a** (50 mg) in a 10 mL zirconia jar containing three zirconia balls (8 mm diameter), followed by 30 Hz vibration. [b]Determined using SEC with polystyrene standards in tetrahydrofuran at 40 °C.

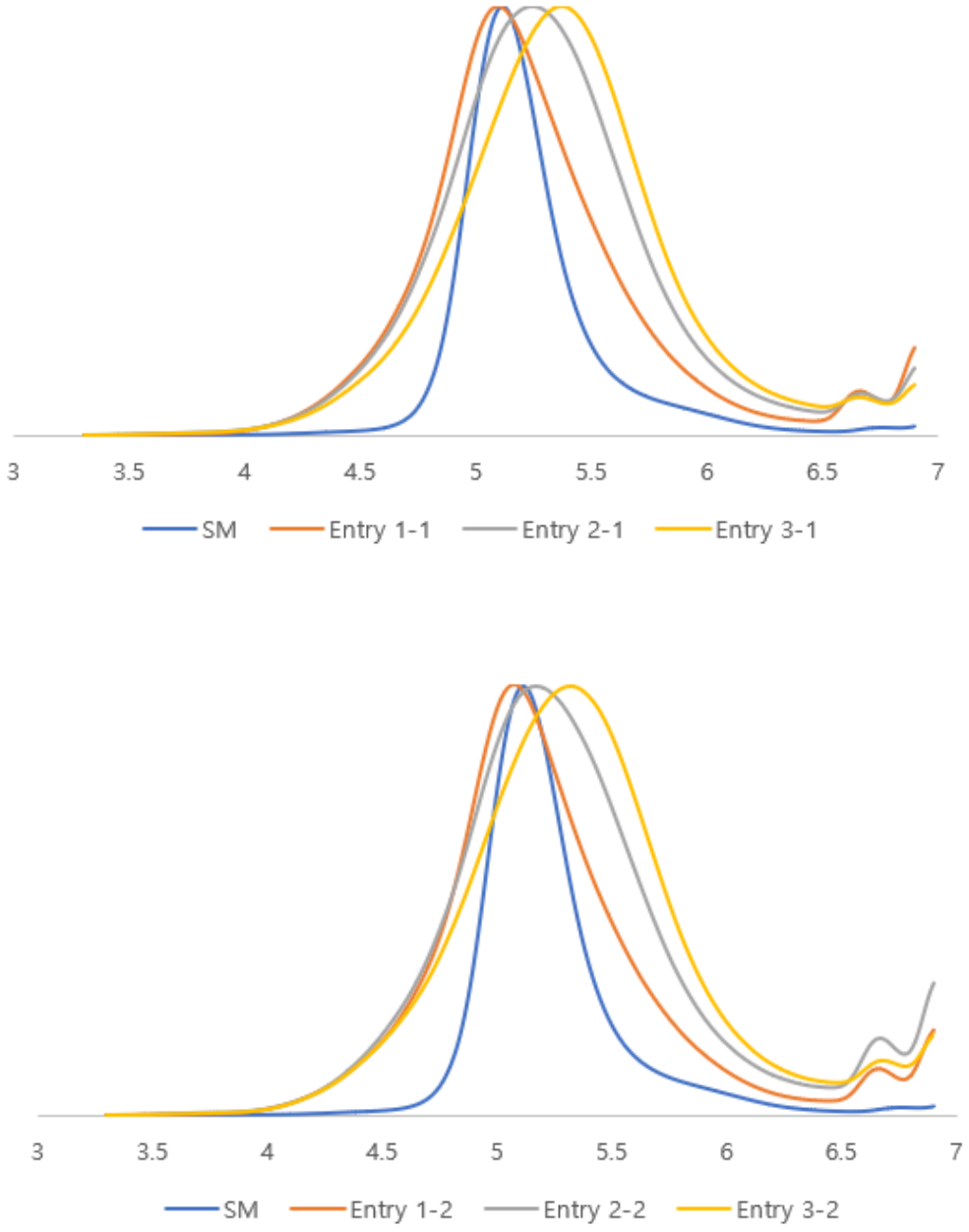
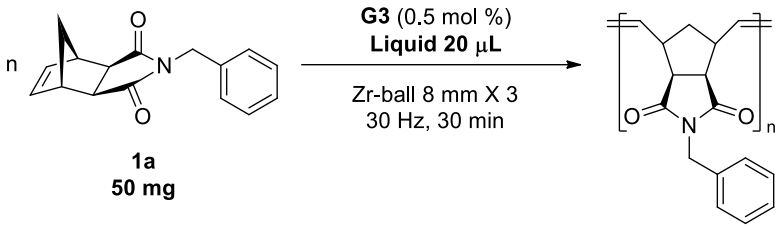


Figure S16. SEC diagrams of Table S7.

4.7. Effect of liquid-assisted grinding (Table 5)

Table S8. Raw data used for Table 5[a]



Entry	Liquid	Conv[b] (%)	M_n[c] (kg/mol)	M_w[c] (kg/mol)	M_p[c] (kg/mol)	$Đ$
1-1	None	89	23.3	39.3	35.0	1.69
1-2		91	21.9	36.1	32.4	1.65
2-1	Toluene	99	23.2	39.6	48.2	1.71
2-2		99	22.9	38.2	45.1	1.67
3-1	THF	97	27.0	45.6	56.5	1.69
3-2		95	24.3	43.6	55.0	1.79
4-1	DCE	99	30.3	42.6	45.5	1.41
4-2		99	34.3	44.2	46.7	1.29
5[d]	DCE (solution)	99	40.4	48.1	51.4	1.19
6[e]	DCE (20uL)	< 1	-	-	-	-

[a]Reaction condition: **1a** (50 mg), G3, and liquid (20 uL) in a 10 mL zirconia jar with three zirconia balls (8 mm diameter). 30 Hz vibration for 30 minutes. [b]Determined by ^{1}H-NMR spectroscopy. [c]Determined by size exclusion chromatography (SEC) with polystyrene (PS) standards in tetrahydrofuran (THF) at 40 ℃. [d]Reactions were proceeded in 0.4 mL solvent ([M] = 0.5 M) for 30 min in room temperature. [e]Reaction is proceeded in 20 uL solvent in V-shaped vial.

G3 cat + NB-Bn | Add 1,2-DCE | 5 min after the rxn | 30 min after the rxn

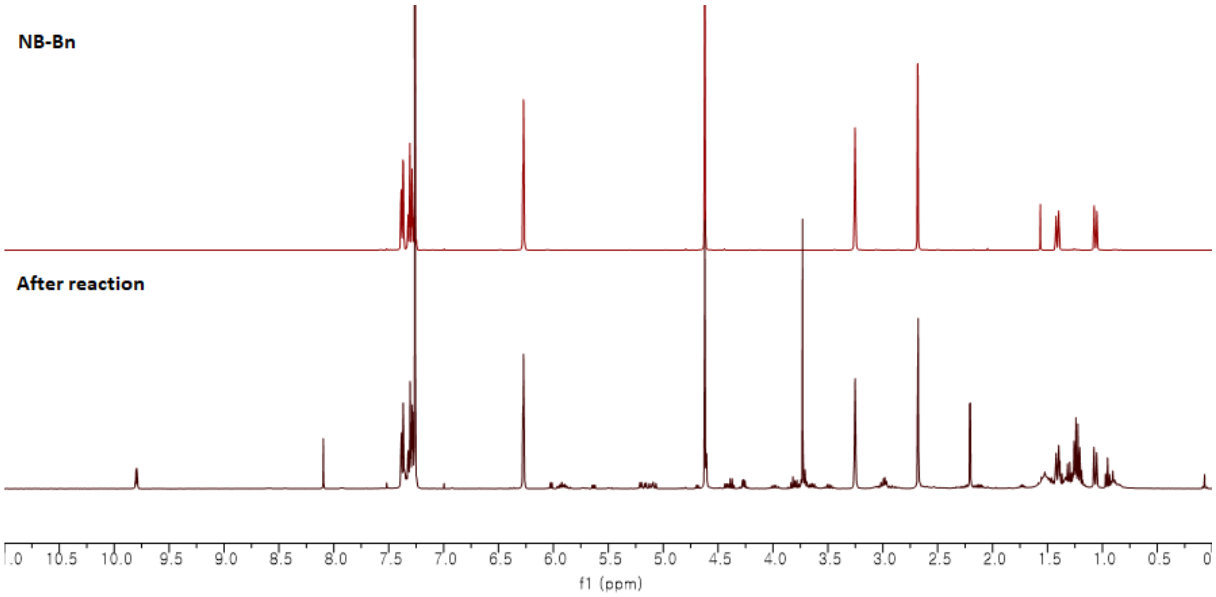
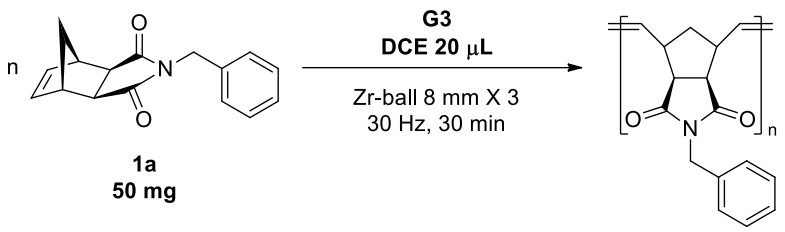


Figure S17. Reactions procedure of Table S8, En 6 and Crude NMR spectra.

4.8. Effect of liquid-assisted grinding (Figure 4)

Table S9. Raw data[a]



Entry	[1a]/[G3]	Conv[b] (%)	M_n[c] (kg/mol)	M_w[c] (kg/mol)	*Đ*
1-1	100	96	15.1	23.2	1.54
1-2		97	13.8	21.1	1.52
1-3		95	16.1	25.0	1.55
1-4		93	15.9	24.4	1.53
2-1	200	99	30.3	42.6	1.41
2-2		99	34.3	44.2	1.29
2-3		99	32.4	47.2	1.46
2-4		99	29.8	47.1	1.59
3-1	300	98	56.5	65.6	1.16
3-2		97	53.2	62.3	1.17
3-3		99	51.2	55.9	1.09
3-4		99	51.3	56.5	1.10

[a]Reaction condition: **1a** (50 mg), G3, and DCE (20 uL) in a 10 mL zirconia jar with three zirconia balls (8 mm diameter). 30 Hz vibration for 30 minutes. [b]Determined by ^{1}H-NMR spectroscopy. [c]Determined by size exclusion chromatography (SEC) with polystyrene (PS) standards in tetrahydrofuran (THF) at 40 ℃.

5. Copies of NMR Spectra

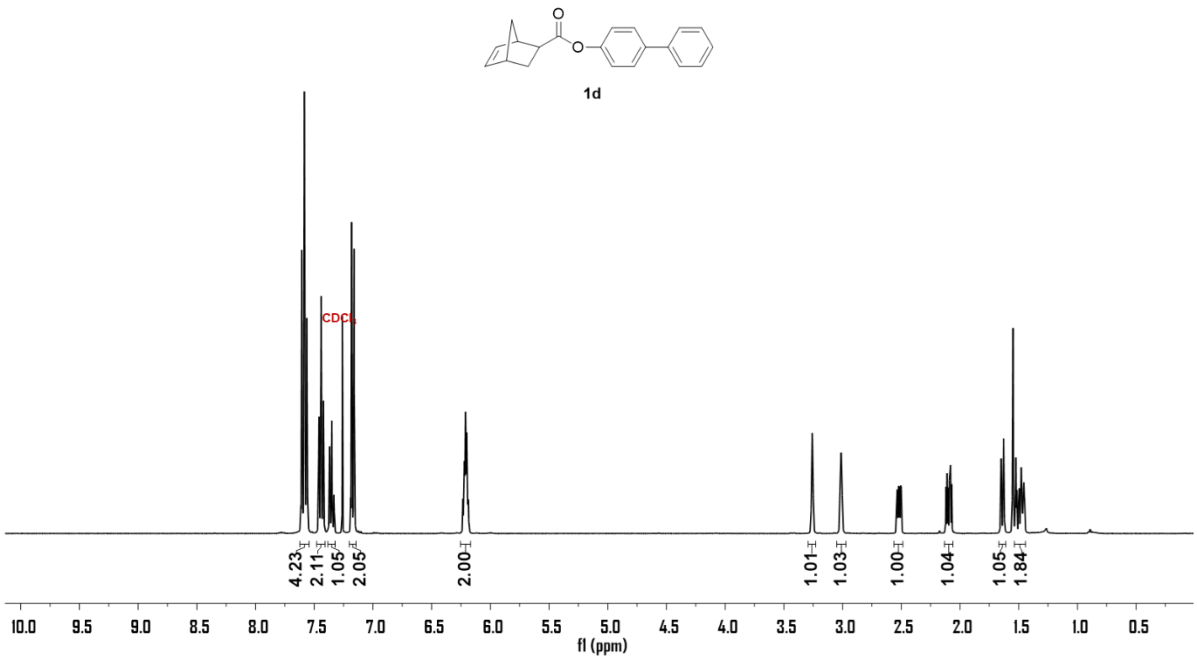


Figure S18. ^{1}H NMR spectrum of Compound 1d (in $CDCl_3$).

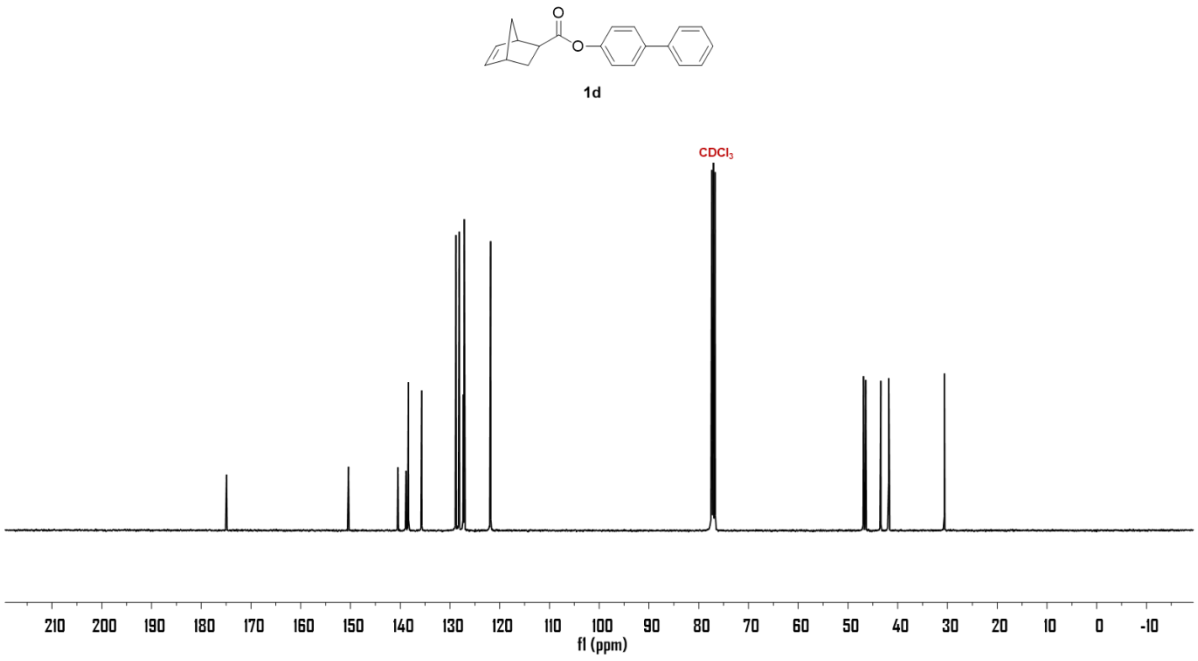


Figure S19. ^{13}C NMR spectrum of Compound 1d (in $CDCl_3$).

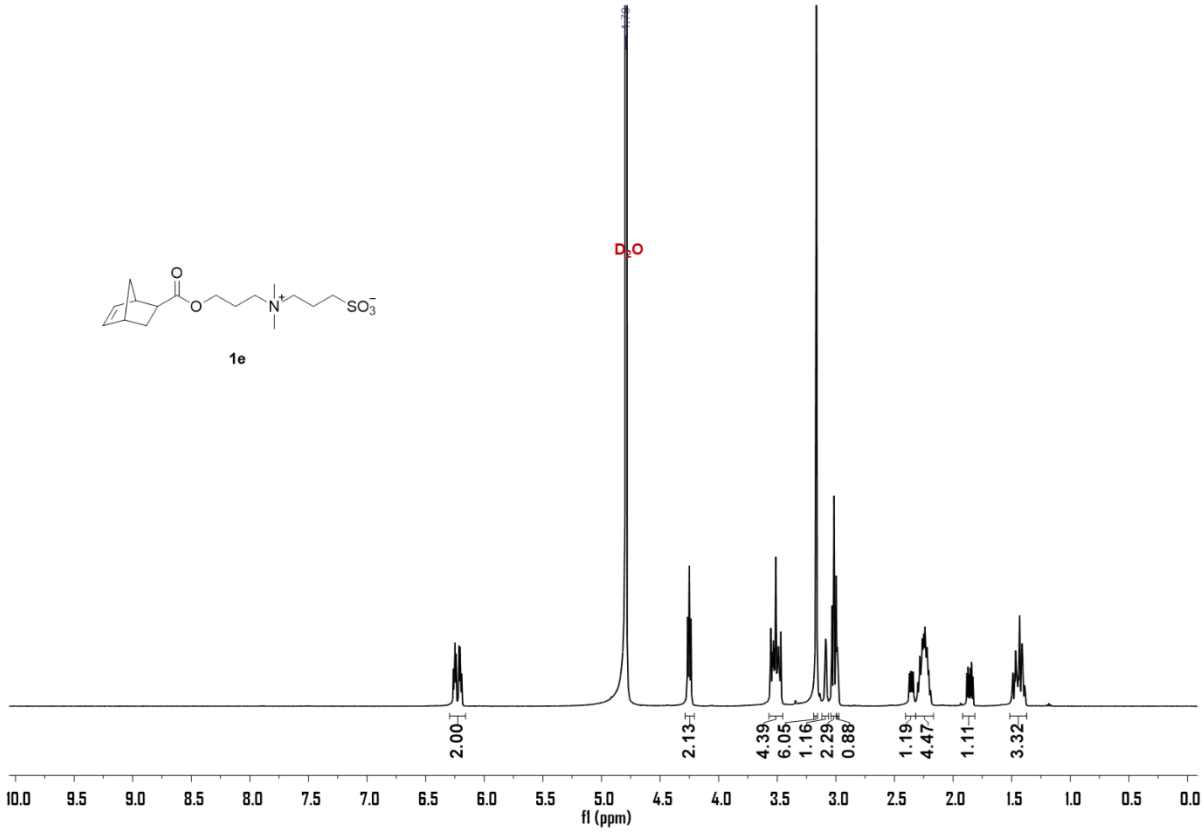


Figure S20. ^{1}H NMR spectrum of Compound 1e (in D_2O).

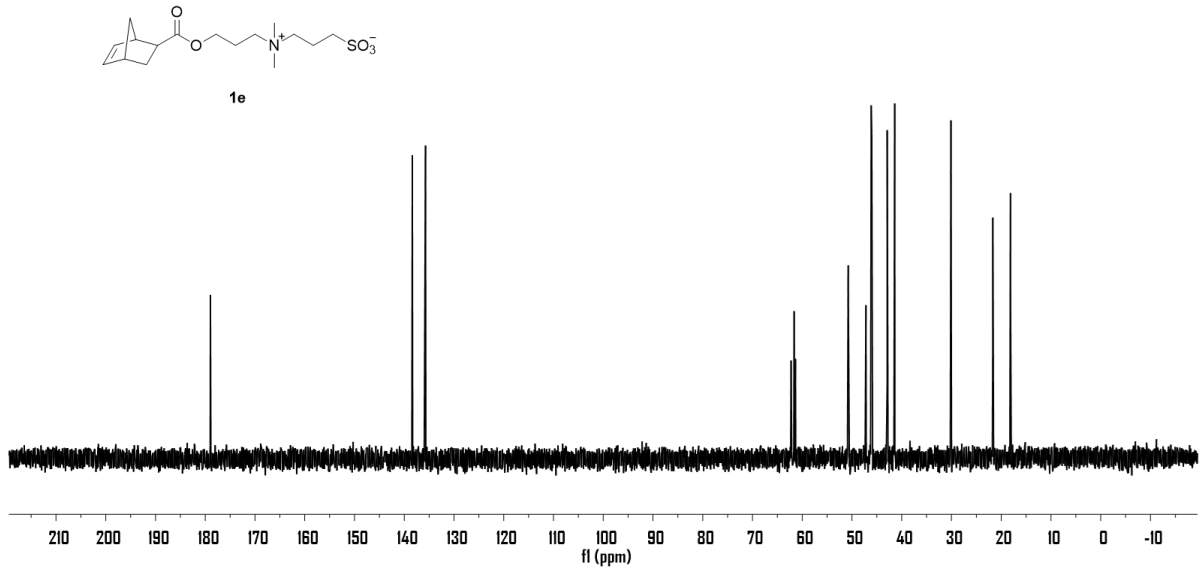


Figure S21. ^{13}C NMR spectrum of Compound 1e (in D_2O).

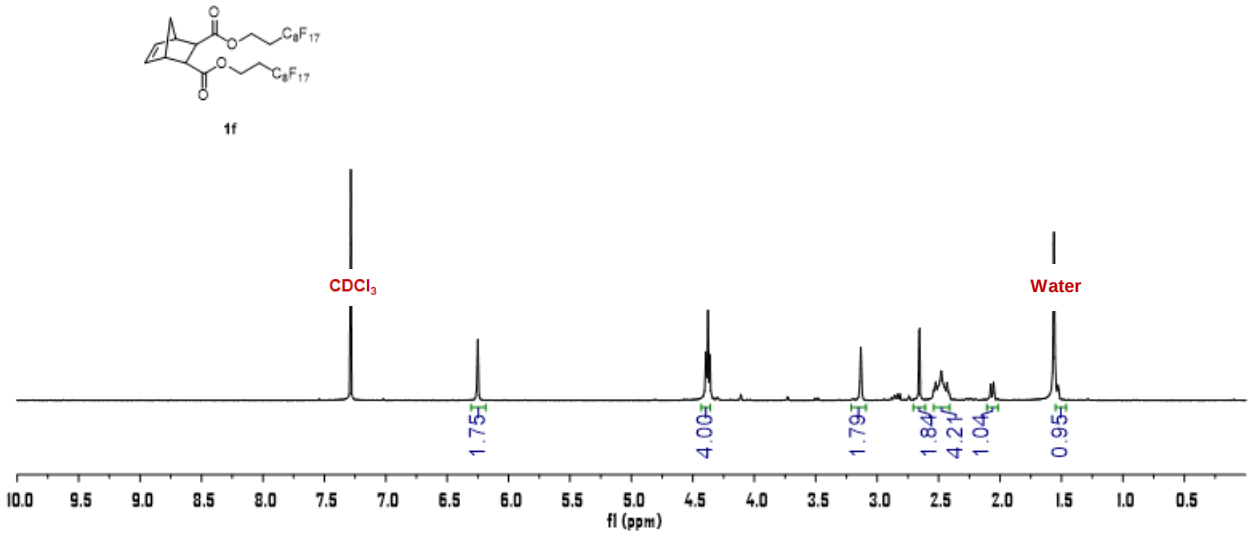


Figure S18. ^{1}H NMR spectrum of Compound 1f (in $CDCl_3$).

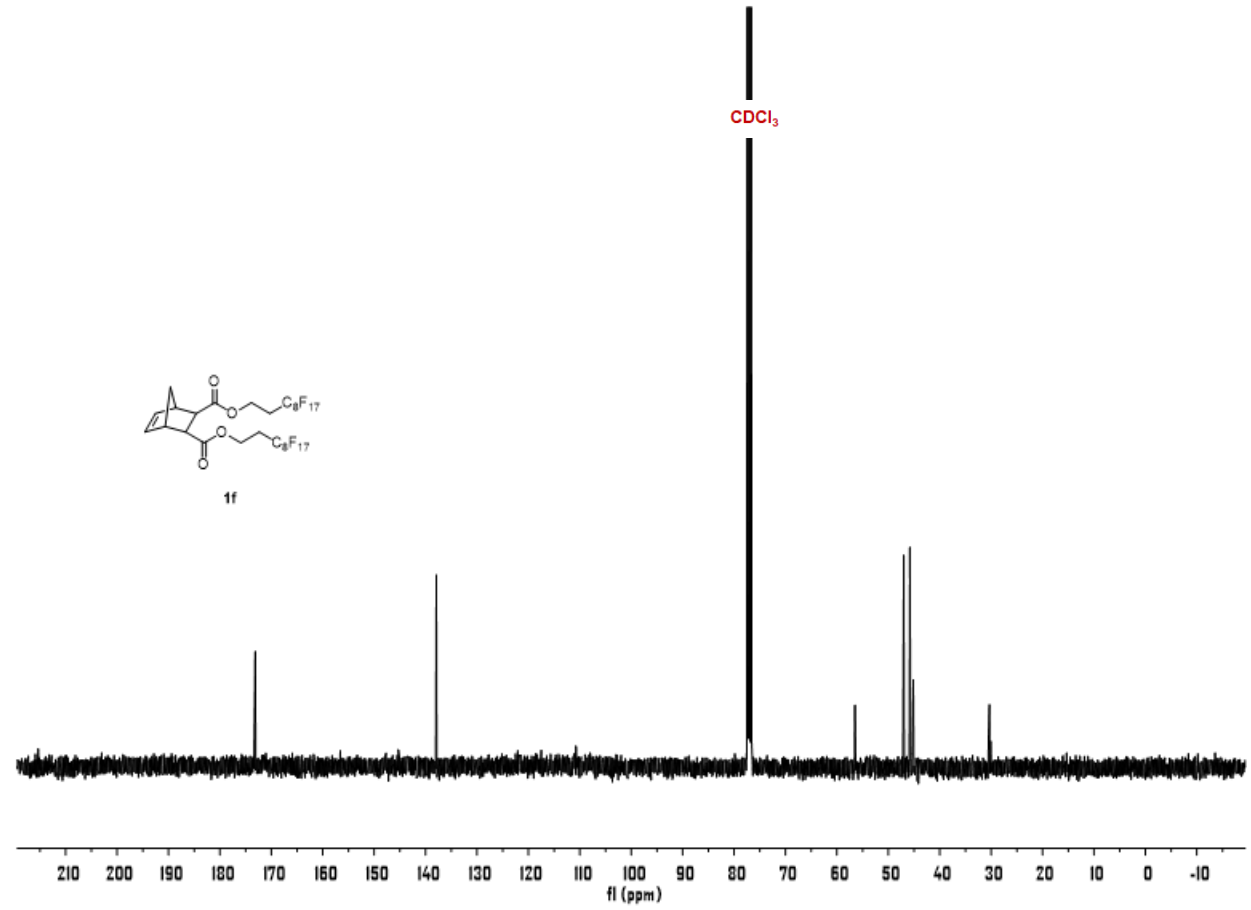


Figure S22. ^{13}C NMR spectrum of Compound 1f (in $CDCl_3$).

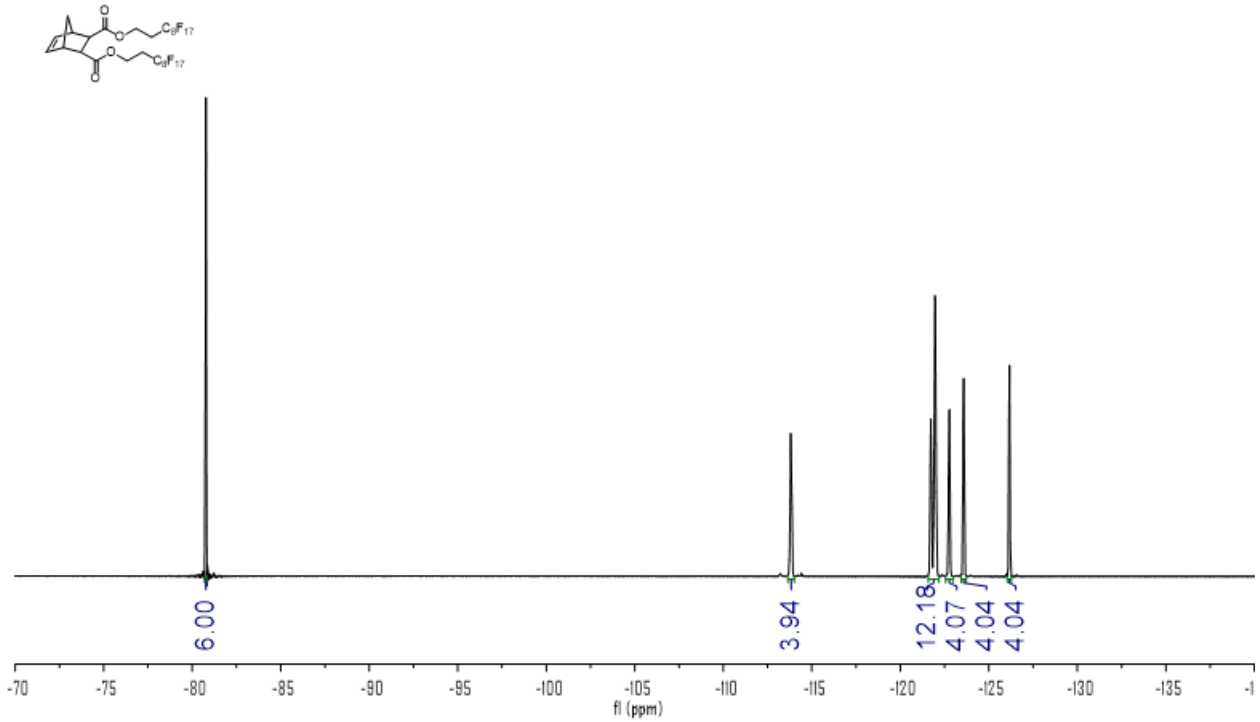


Figure S23. ^{19}F NMR spectrum of Compound 1f (in $CDCl_3$).

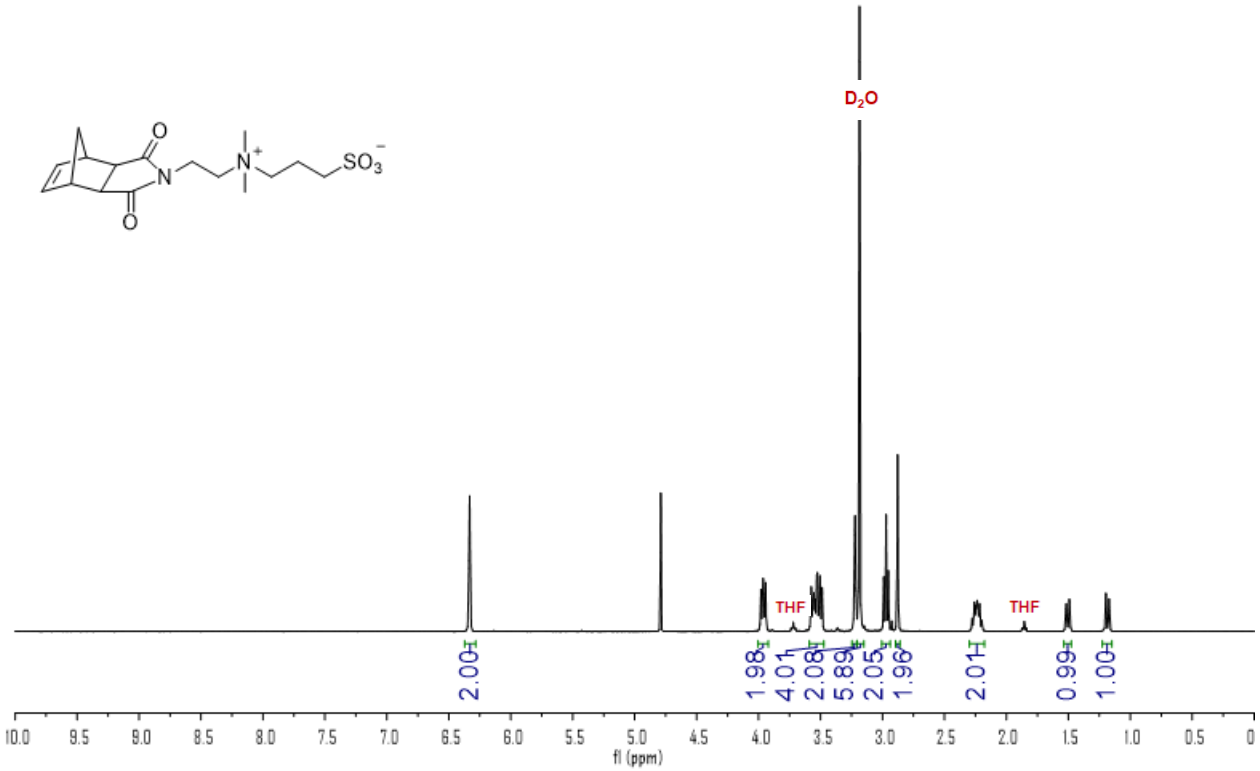


Figure S24. ^{1}H NMR spectrum of Compound 1i (in D_2O).

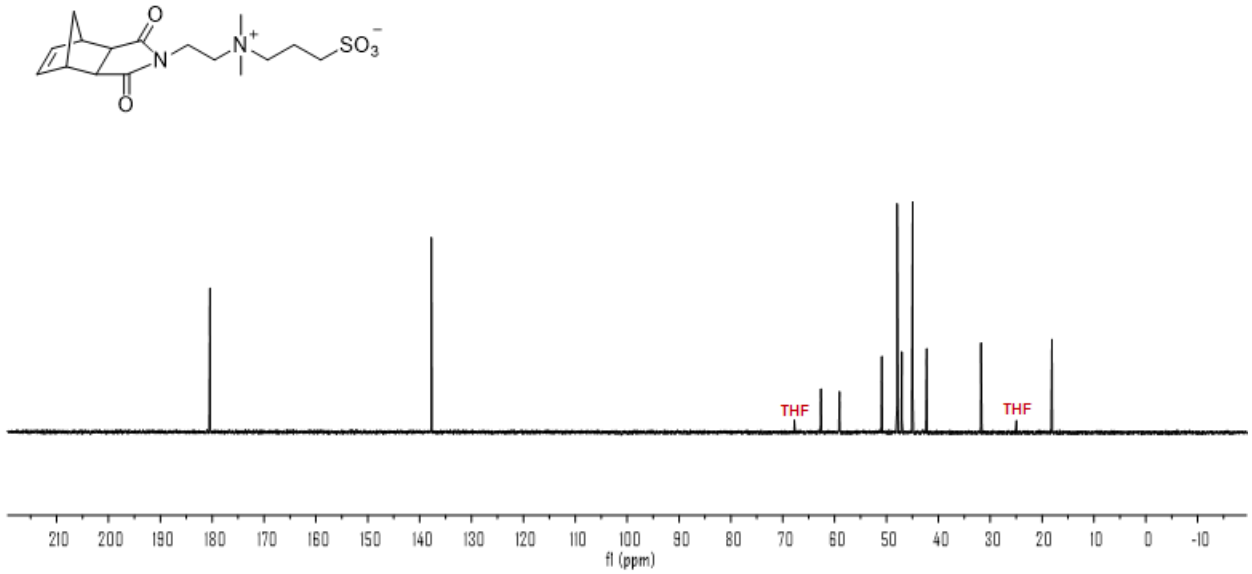


Figure S25. ^{13}C NMR spectrum of Compound 1i (in D_2O).

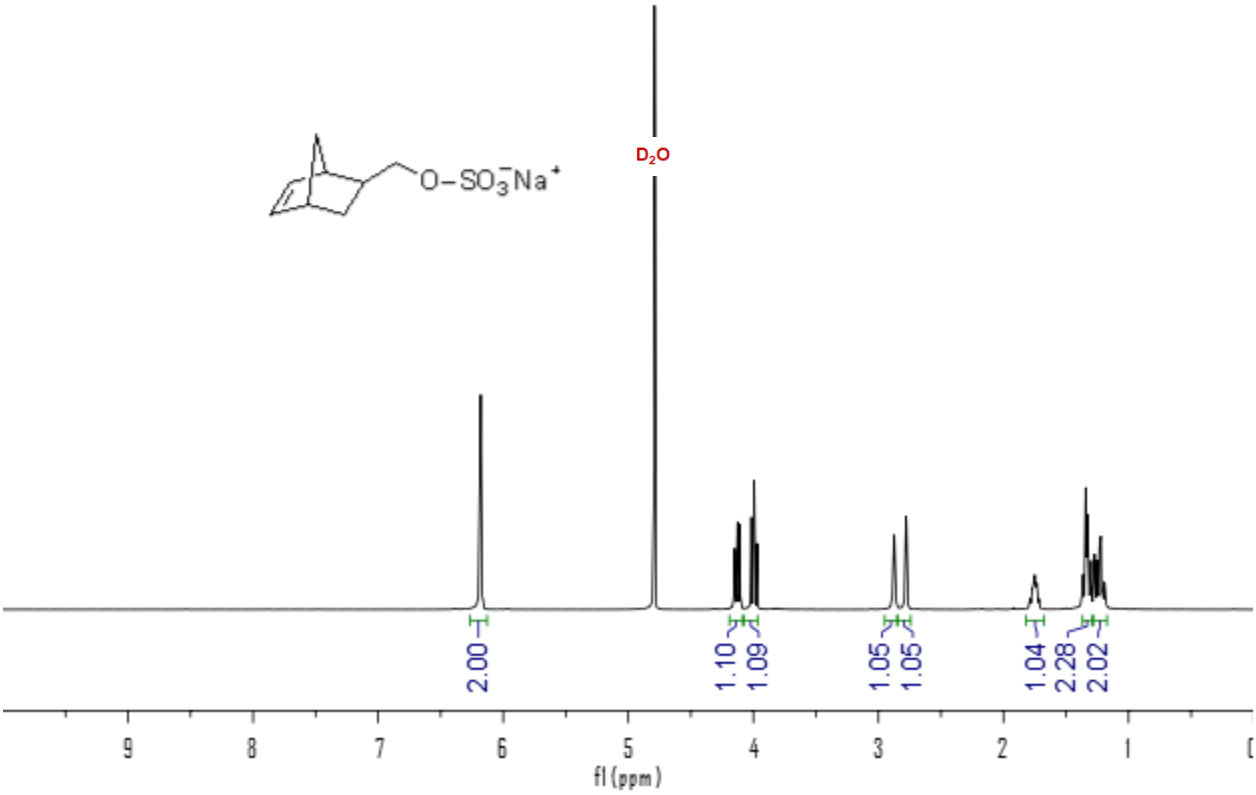


Figure S26. ^{1}H NMR spectrum of Compound 1f (in D_2O).

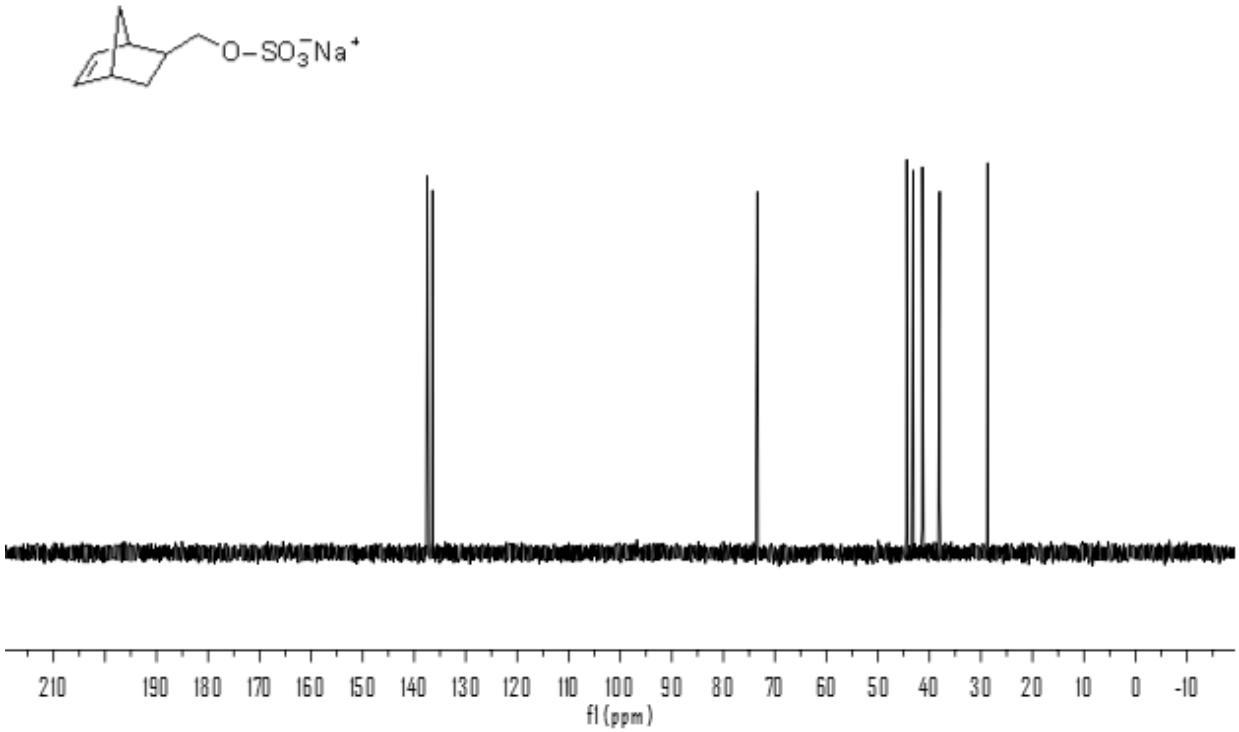


Figure S27. ^{13}C NMR spectrum of Compound 1f (in D_2O).

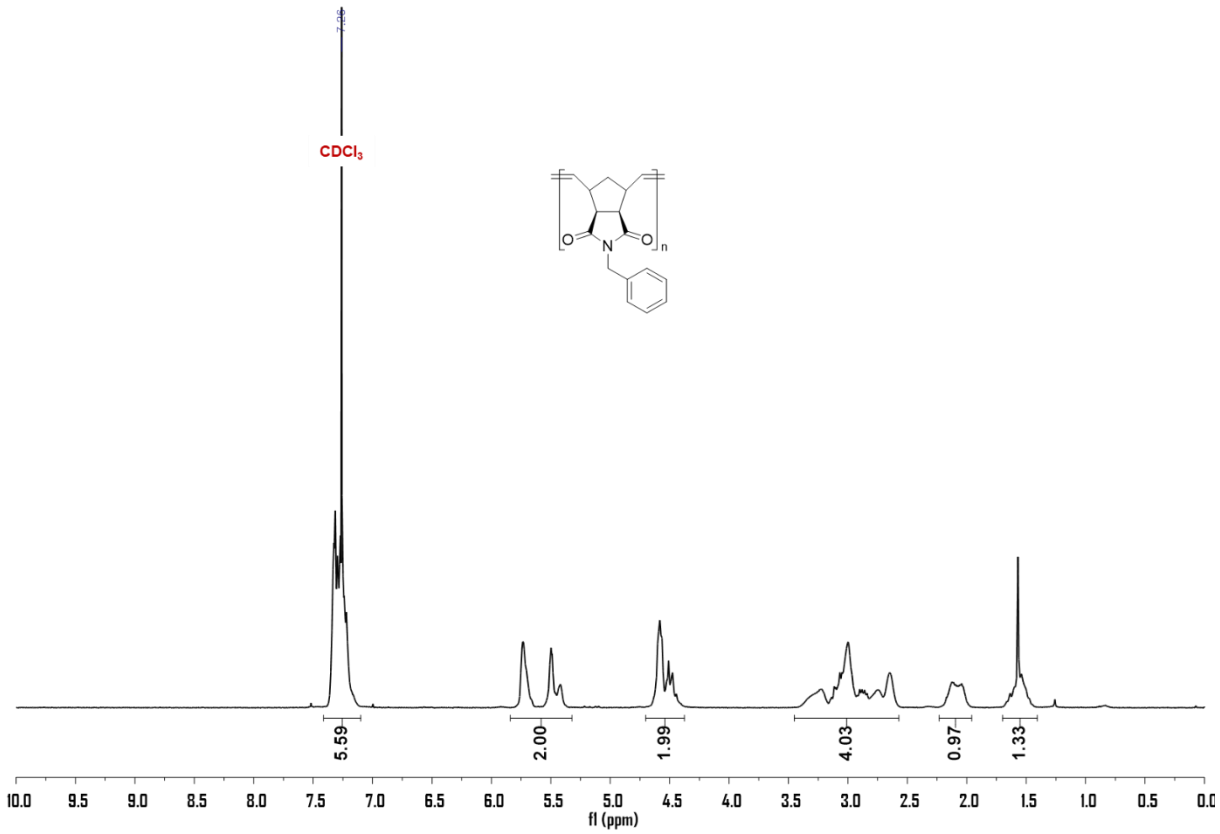


Figure S28. ^{1}H NMR spectrum of Product of Table 3, entry 1 (in $CDCl_3$).

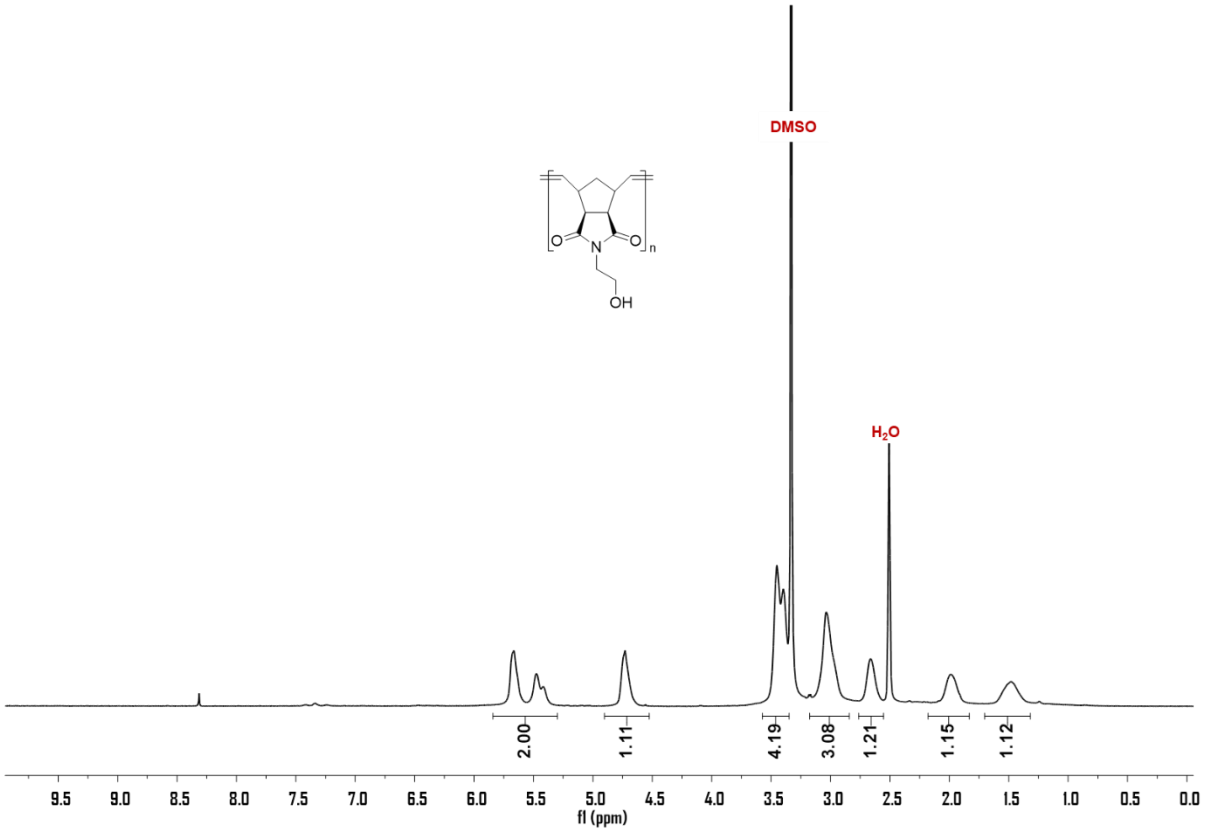


Figure S29. ^{1}H NMR spectrum of Product of Table 3, entry 2 (in DMSO-d_6).

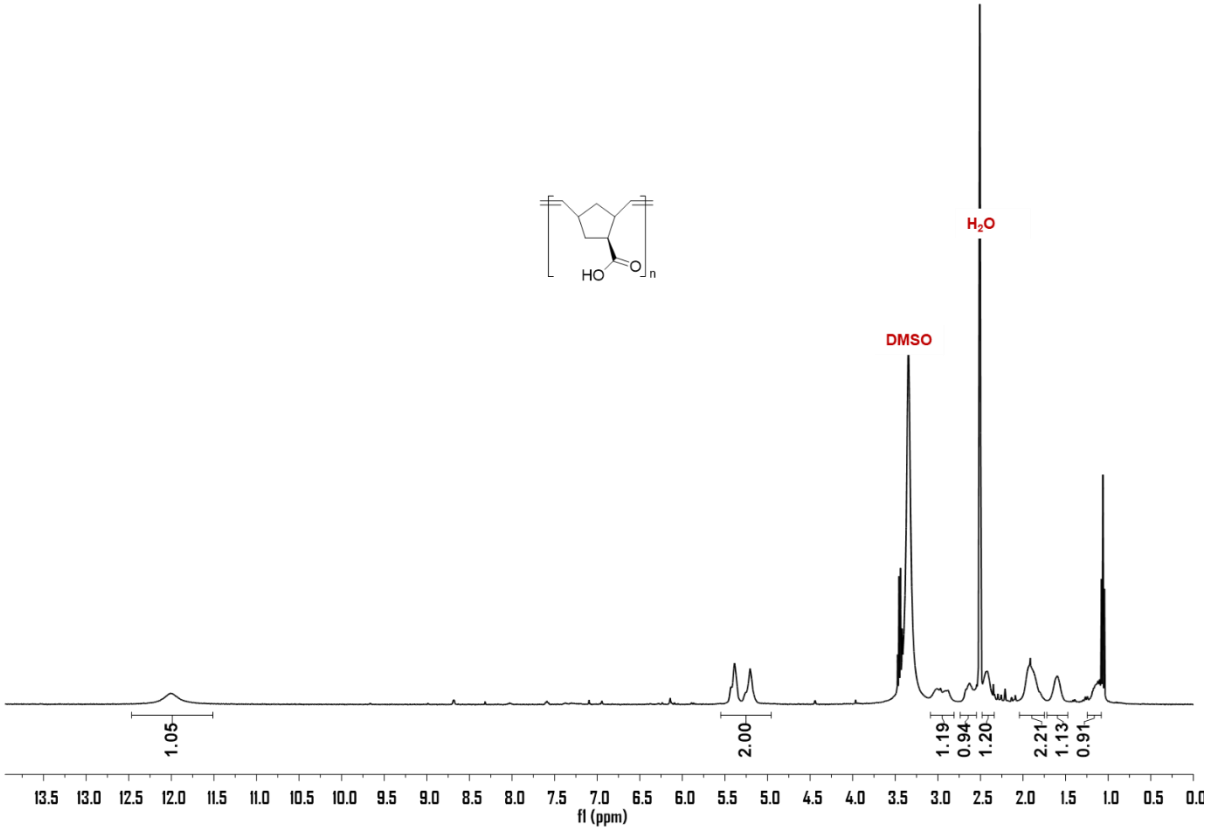


Figure S30. ^{1}H NMR spectrum of Product of Table 3, entry 3 (in DMSO-d_6).

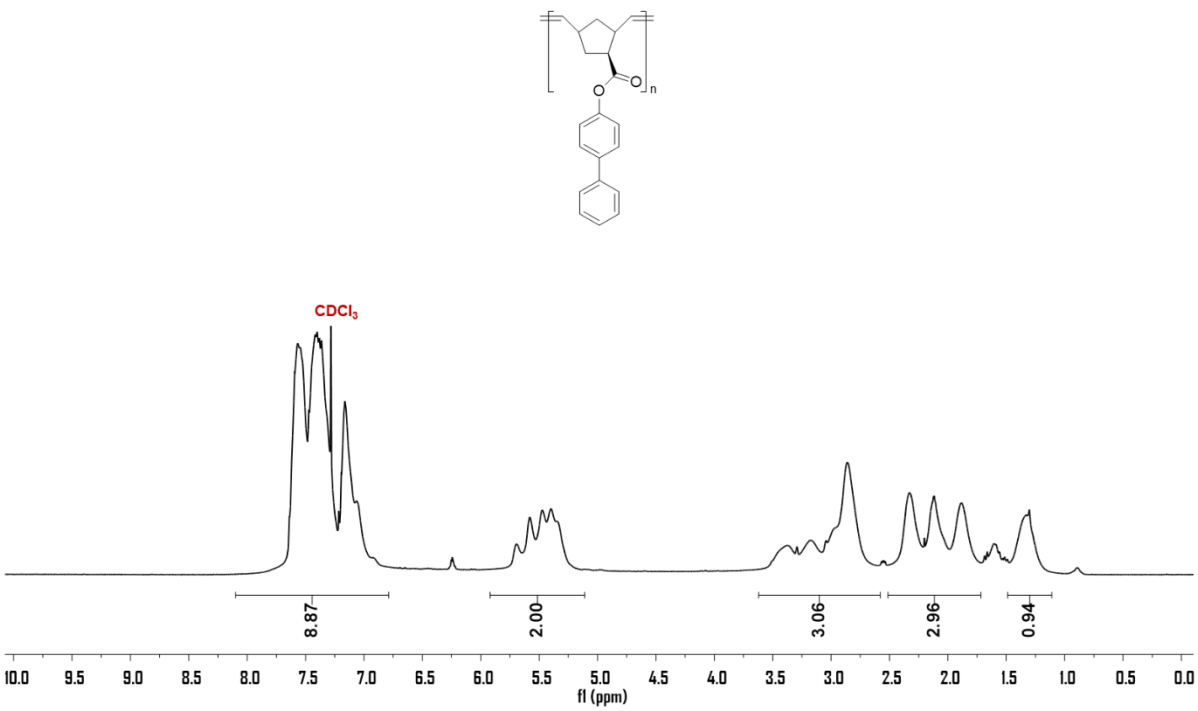


Figure S31. ^{1}H NMR spectrum of Product of Table 3, entry 4 (in $CDCl_3$).

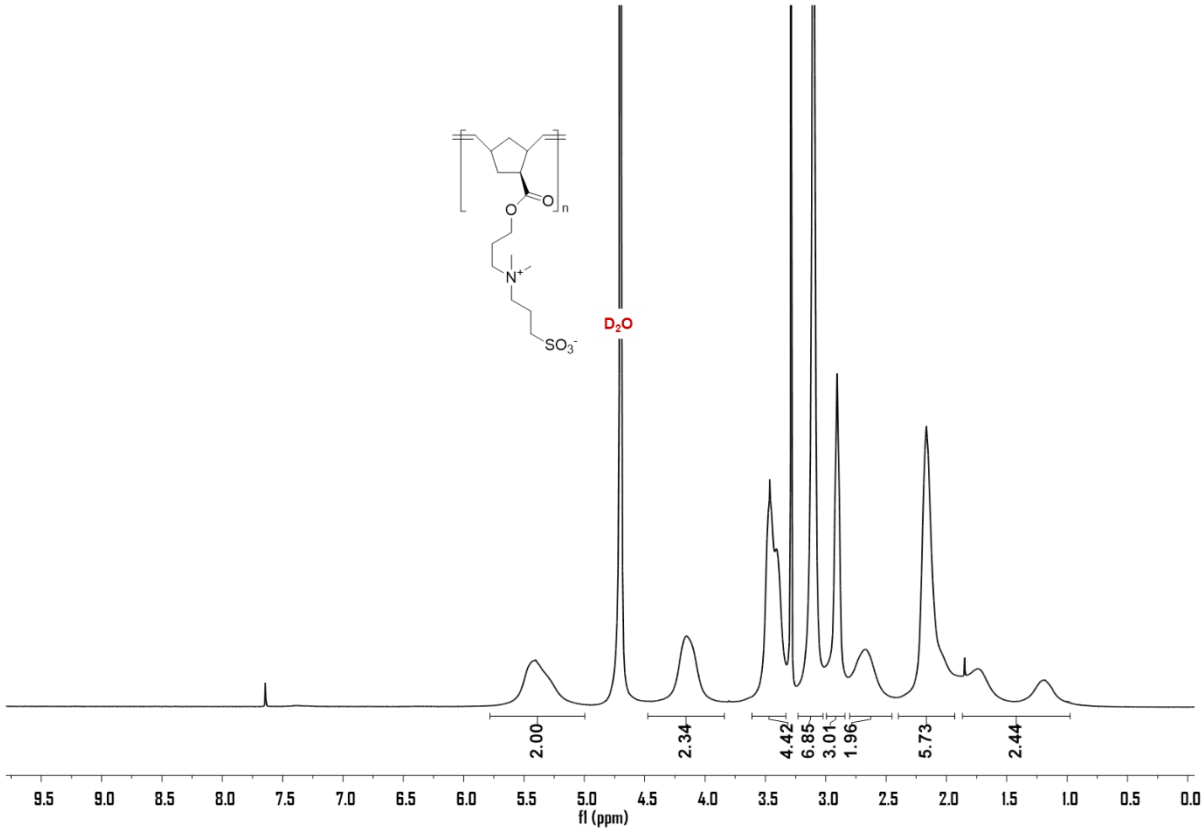


Figure S32. ^{1}H NMR spectrum of Product of Table 3, entry 5 (in D_2O).

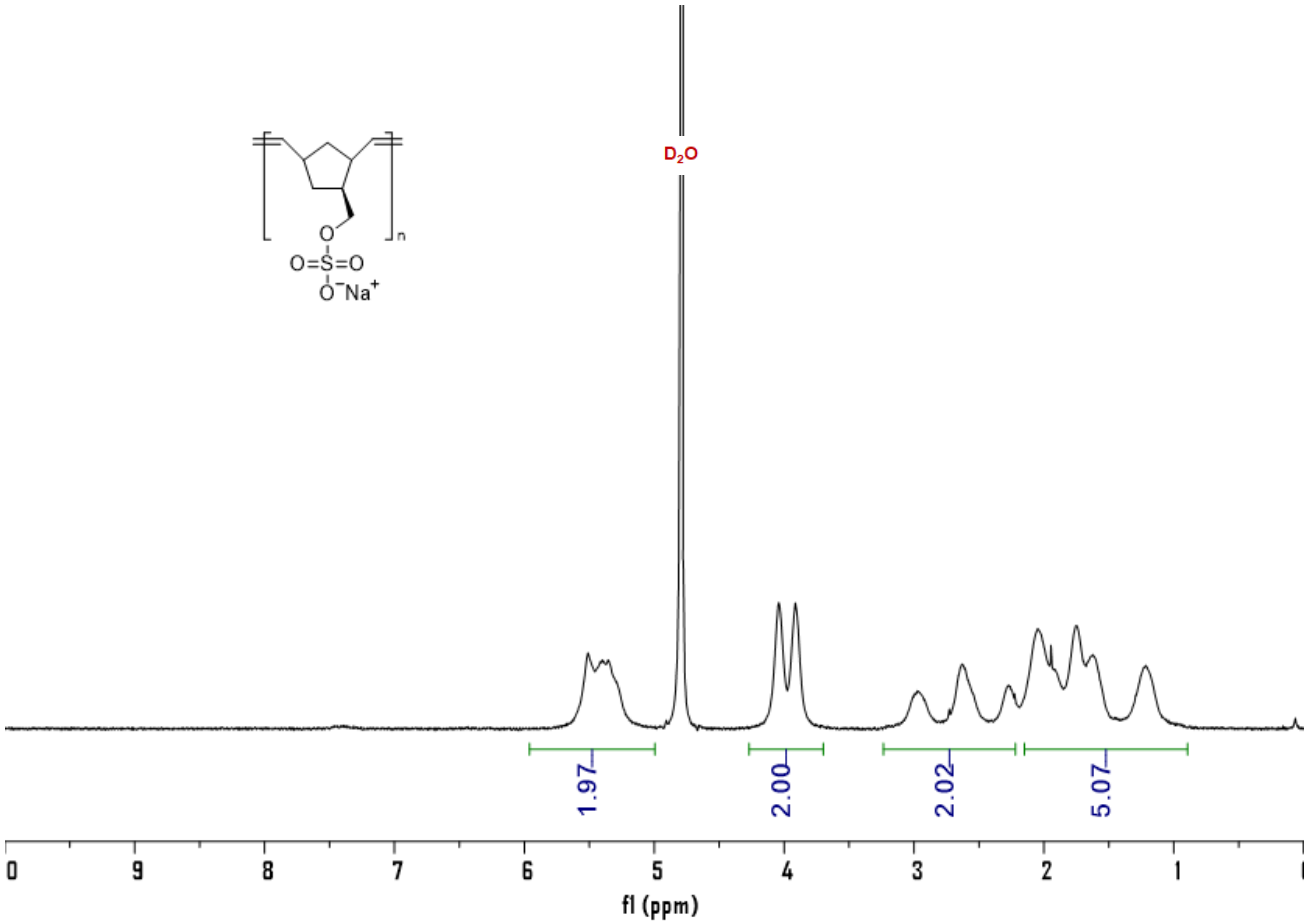


Figure S33. ^{1}H NMR spectrum of Product of Table 3, entry 6 (in D_2O).

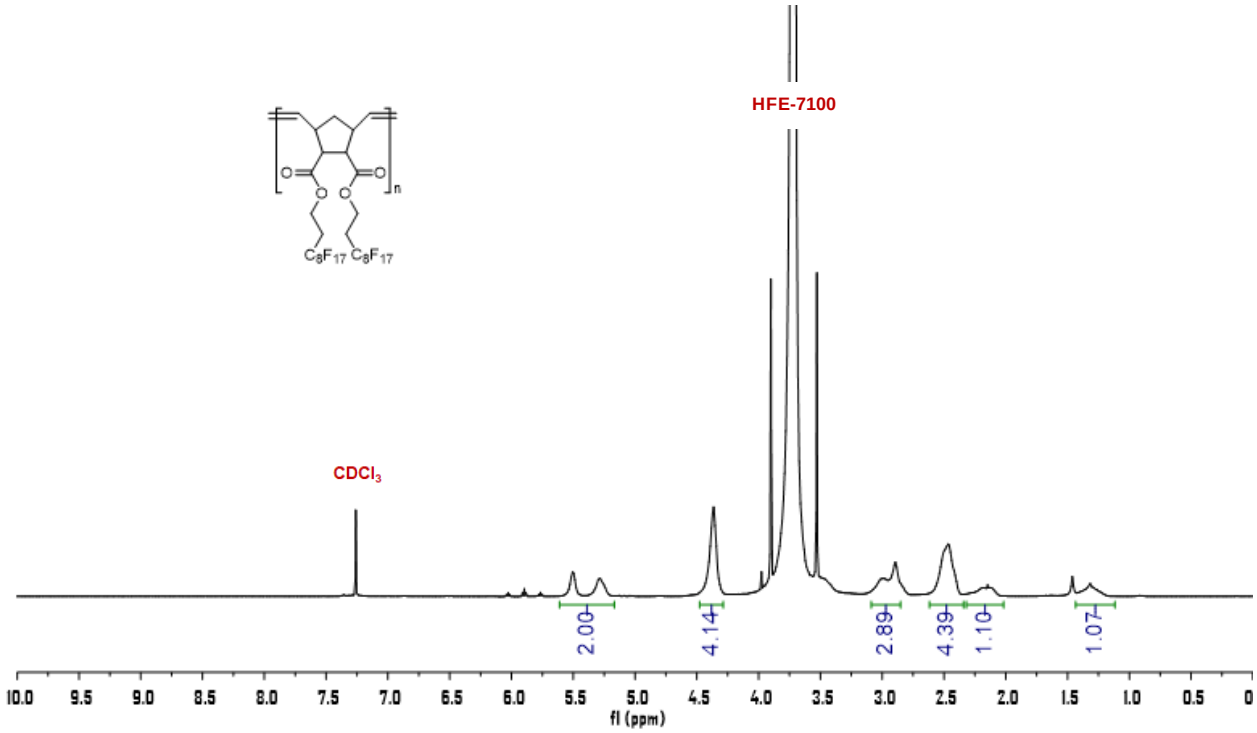


Figure S34. ^{1}H NMR spectrum of Product of Table 3, entry 7 (in $CDCl_3$).

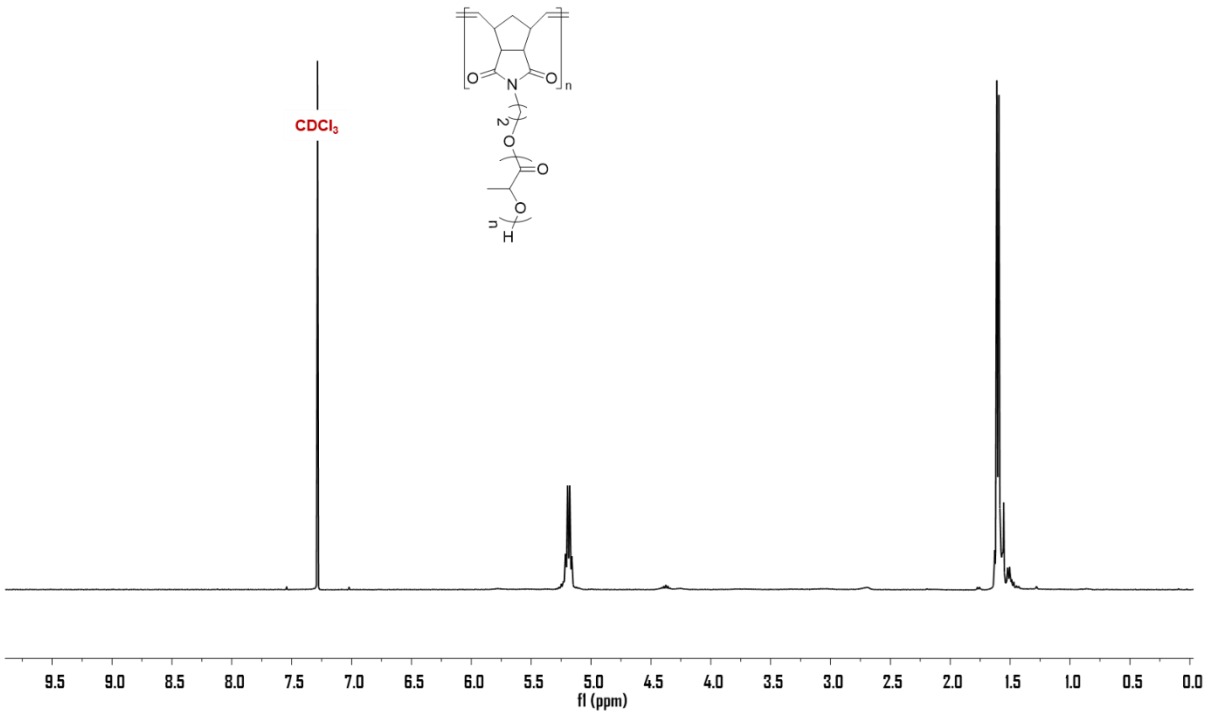


Figure S35. ^{1}H NMR spectrum of Product of Table 3, entry 8 (in $CDCl_3$).

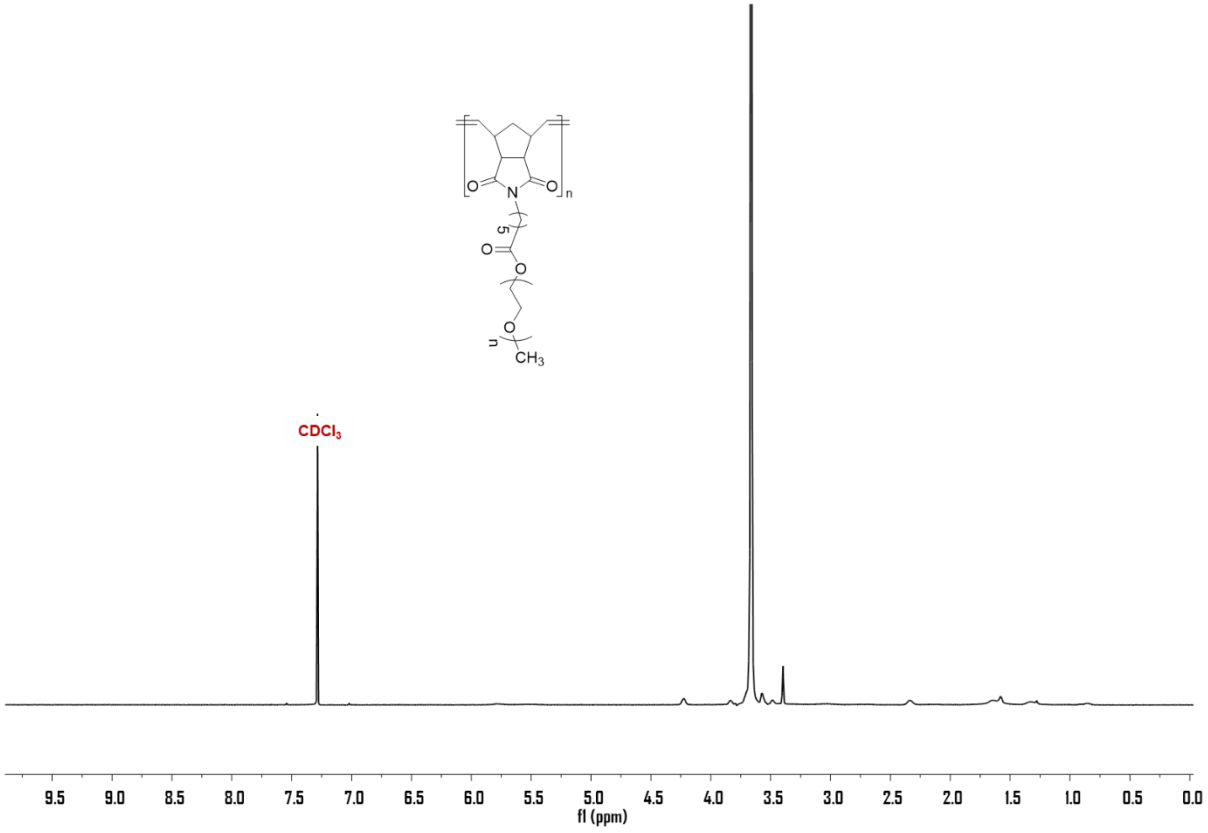


Figure S36. ^{1}H NMR spectrum of Product of Table 3, entry 9 (in $CDCl_3$).

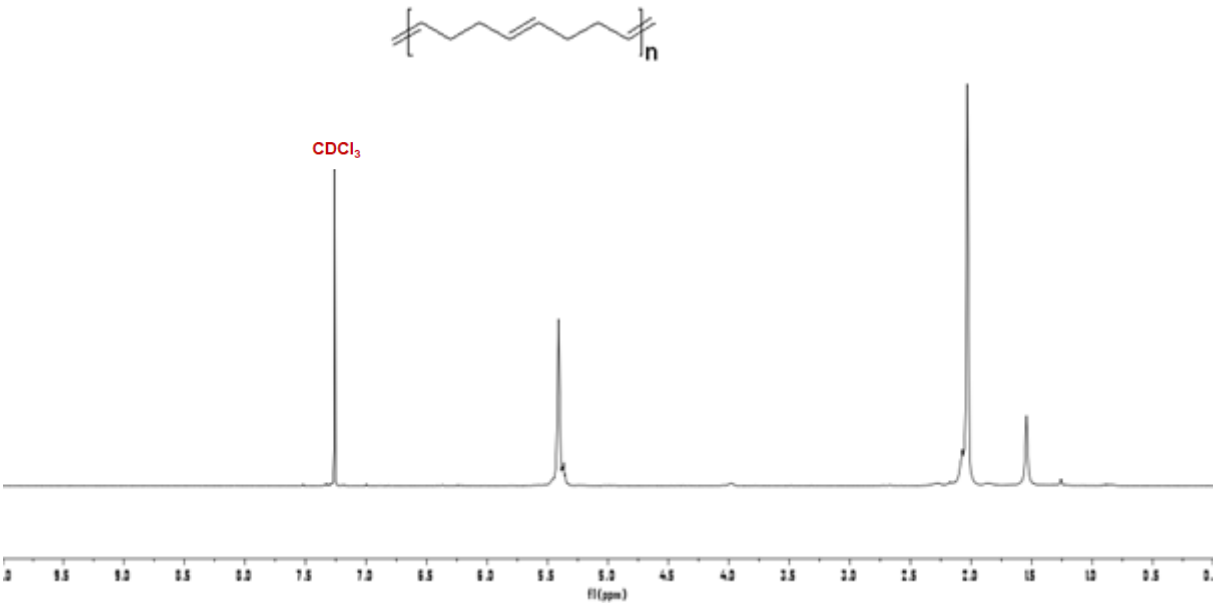


Figure S37. ^{1}H NMR spectrum of Product of Table 3, entry 10 (in $CDCl_3$).