Supporting information for

Functionalized Cyclic Olefin Copolymers: Chemoselective Polymerization of Cyclopropane-Containing Norbornadiene Dimer using Titanium Catalyst and Post-Polymerization Modification

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General

All reactions and polymerizations were performed under a nitrogen atmosphere using a grove box or Schlenck technique.

Materials

1[1], **2**[2], and Al^{i}Bu(BHT)$_2$[3] were synthesized according to the previous report. 1-Octene (TCI, >99%), *m*-xylene (Wako, 98%), and 2-(2-ethoxyethoxy)ethanol (Wako, >98%) were distilled from CaH_2 under reduced pressure and stored with molecular sieves 3Å. $^{i}Bu_3Al$ (Wako, 1.0 mol/L in toluene), 2,6-di-*tert*-butyl-*p*-cresol (TCI, >99%), $[Ph_3C][B(C_6F_5)_4]$ (TCI, >98%), Tf_2NH (TCI, >99%), butyric acid (TCI, >99%), benzoic acid (Kishida, >99.5%), methyl glycolate (TCI, >98%), methanol (Wako, super dehydrated, water <10 ppm, >99.8%), toluene (Wako, deoxidized, oxygen <1 ppm, water <10 ppm, >99.5%) were used as received.

Copolymerization of **1** with 1-octene (entry 5, Table 1)

To a two-necked round-bottomed flask, Al^{i}Bu(BHT)$_2$ (0.5 mL, 0.20 mmol, 0.4 mol/L in toluene), **1** (498 mg, 2.70 mmol), 1-octene (303 mg, 2.70 mmol), and toluene (27 mL) were added and stirred at 0 °C. To the flask, the solutions of **2** (7.4 mg, 20 μmol) in toluene (1 mL) and $[Ph_3C][B(C_6F_5)_4]$ (19 mg, 20 μmol) in toluene (1 mL) were added via syringes in this order to initiate the polymerization, and the mixture was stirred at 0 °C for 1 h. The polymerization was quenched by adding MeOH (5 mL). The reprecipitation into MeOH (140 mL)/HCl aq (10 mL, 2 mol/L) afforded poly(**1**-*co*-1-octene) (745 mg, 93 %) as a white solid.

To estimate the conversions and the polymer molecular weights during the polymerization, the polymerizations were conducted in the presence of dodecane (0.40 g, 2.3 mmol) as an internal standard. One aliquot (~10 μL) was taken from the polymerization mixture via a syringe and added into MeOH/$CHCl_3$ (one drop/1 mL). After stirring with a metal scavenger (R-Cat-Sil TA (KANTO)) followed by filtration, the obtained solution was analyzed by gas chromatography. After evaporation of the solvent, the polymer sample was dissolved in $CHCl_3$ solution and then subjected to SEC measurement.

The composition of **1** was estimated using the following equation, where I_{O7}, I_{O8}, and I_{cy} indicate the ^{13}C NMR integral ratios of O7, O8, and cyclopropane moiety (C4, C5, C6', C4', C5', and C6), respectively.

Composition of **1** (mol%) = $(I_{cy}/3)/((I_{O7} + I_{O8})/2 + I_{cy}/3)\times100$

PPM of poly(**1**-*co*-1-octene) with *m*-xylene or toluene

To a solution of Tf_2NH (5.7 mg, 20 μmol, 0.1 equivalent relative to the cyclopropane moiety) in *m*-xylene (1.5 mL), a solution of poly(**1**-*co*-1-octene) (60 mg, run 5 in Table 1) in *m*-xylene (1.5 mL) was added at 50 °C. The reaction mixture was stirred at 50 °C for 30 min. The reaction was quenched by adding $NaHCO_3$ aq. The reprecipitation into methanol afforded poly**3a** (56 mg) in 70 % yield. The PPM with toluene was similarly performed.

PPM of poly(**1**-*co*-1-octene) with carboxylic acids or methyl glycolate

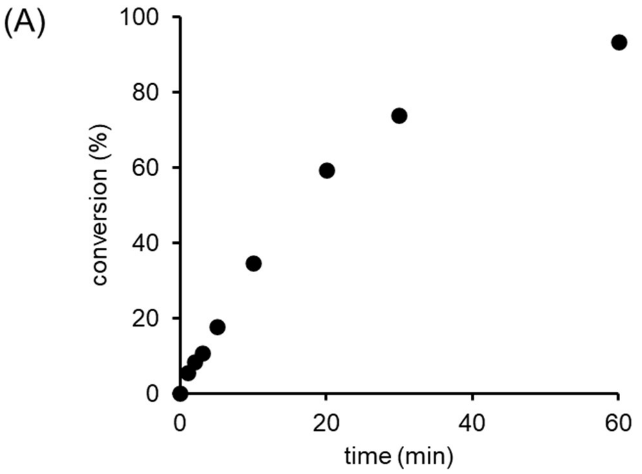
To a solution of Tf_2NH (5.7 mg, 20 μmol, 0.1 equivalent relative to the cyclopropane moiety) in $CHCl_3$ (1.5 mL), a solution of poly(**1**-*co*-1-octene) (60 mg, run 5 in Table 1) and butyric acid (89 mg, 1.0 mmol) in $CHCl_3$ (1.5 mL) was added at 50 °C. The reaction mixture was stirred at 50 °C for 30 min. The reaction was quenched by adding $NaHCO_3$ aq. The reprecipitation into methanol afforded poly**3c** (71 mg) in 93 % yield. The PPMs with benzoic acid and methyl glycolate were similarly performed.

PPM of poly(**1**-*co*-1-octene) with methanol or 2-(2-ethoxyethoxy)ethanol

To a solution of Tf_2NH (57 mg, 0.20 mmol, equimolar relative to the cyclopropane moiety) in $CHCl_3$ (1.5 mL), a solution of poly(**1**-*co*-1-octene) (60 mg, run 5 in Table 1) in $CHCl_3$ (1.5 mL) was added at 50 °C, and the mixture was stirred at 50 °C for 10 min. To this mixture, methanol (33 mg, 1.0 mmol) was added, and the mixture was stirred at 50 °C for 30 min. The reaction was quenched by adding $NaHCO_3$ aq. The reprecipitation into methanol afforded poly**3f** (58 mg) in 87 % yield. The PPM with 2-(2-ethoxyethoxy)ethanol was similarly performed.

Instrumentation

Unless otherwise noted, ^1H and ^{13}C NMR spectra were obtained on a Bruker Avance III HD spectrometer (400 MHz for ^1H, 100 MHz for ^{13}C). DEPT135 NMR spectra of **1**, poly**1**, and poly(**1**-*co*-1-octene)s were obtained on Bruker AVANCE III equipped with a cryoprobe (500 MHz for ^1H, 125 MHz for ^{13}C). ^1H and ^{13}C NMR spectra of poly**1** and poly(**1**-*co*-1-octene)s (Figures 3(B) and 3(C)) were obtained on Bruker AVANCE III with a cryoprobe (900 MHz for ^1H, 225 MHz for ^{13}C) in 1,1,2,2-tetrachloroethane-d_2 ($C_2D_2Cl_4$) at 130 °C. The ^{13}C NMR measurement was conducted using an inverse-gated decoupling technique with a repetition delay of 4 s and a number of scans of 1024 in the presence of $Cr(acac)_3$ as a relaxation agent (0.05 M). The chemical shifts were referenced to tetramethylsilane (TMS) in $CDCl_3$ (0.00 ppm for ^1H) and the residual solvent peak of $CDCl_3$ (77.10 ppm for ^{13}C) and $C_2D_2Cl_4$ (6.00 ppm for ^1H, 74.47 ppm for ^{13}C). The conversions were estimated by gas chromatography (GC) using a GC-2014 (Shimadzu) instrument equipped with a flame ionization detector and a ZB-5 fused-silica capillary column (Zebron) using dodecane as an internal standard. The SEC measurements were performed using a JASCO EXTREMA system with a RI-4035 (JASCO) detector using $CHCl_3$ as the eluent at 40 °C with a flow rate of 0.3 mL/min. Two HK-404L (Shodex) columns were equipped and calibrated against polystyrene standards. TGA measurements were performed on a DTG-60 (Shimadzu) instrument with a heating rate of 10 °C/min under a nitrogen atmosphere.



(B)

time	conv of **1**	$10^{-3}M_n$	$10^{-3}M_p$	$Đ$
min	%			
0	0	-	-	-
1	5	-	-	-
2	8	-	-	-
3	11	-	-	-
5	18	-	3.3	-
10	35	8.8	7.1	1.19
20	59	10.2	9.9	1.23
30	74	12.5	13.6	1.25
60	93	16.9	15.7	1.27

Figure S1. Supplementary data of the polymerization of **1** (Figure 1, under the conditions of run 1 in Table 1).
(A) Time versus conversion plot, and (B) molecular weight data against conversion. The conversions were estimated using GC.

Table S1. Supplementary data of the copolymerization of **1** with 1-octene (Figure 2)

time	conversion (%)		$10^{-3}M_n$	*Đ*
min	**1**	1-octene		
0	0	0	-	-
5	41	15	10	1.25
10	77	38	19	1.19
15	100	66	26	1.26
20	100	100	31	1.33
25	100	100	32	1.36

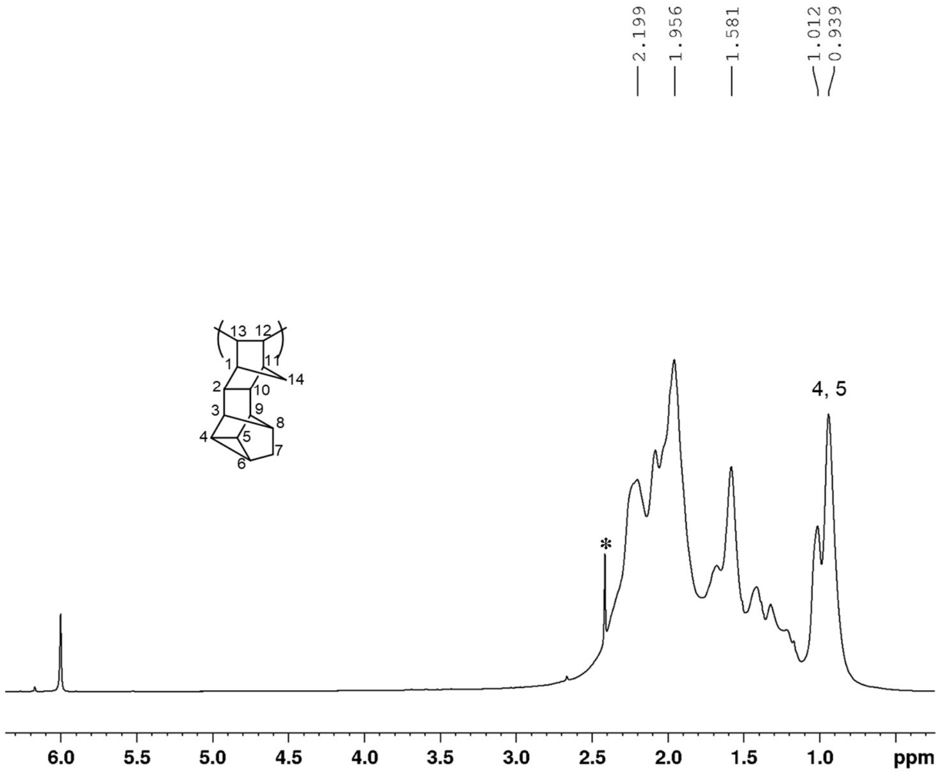


Figure S2. ^{1}H NMR spectrum of poly**1** (CD_2Cl_4, 130 °C) (run 2, Table 1).

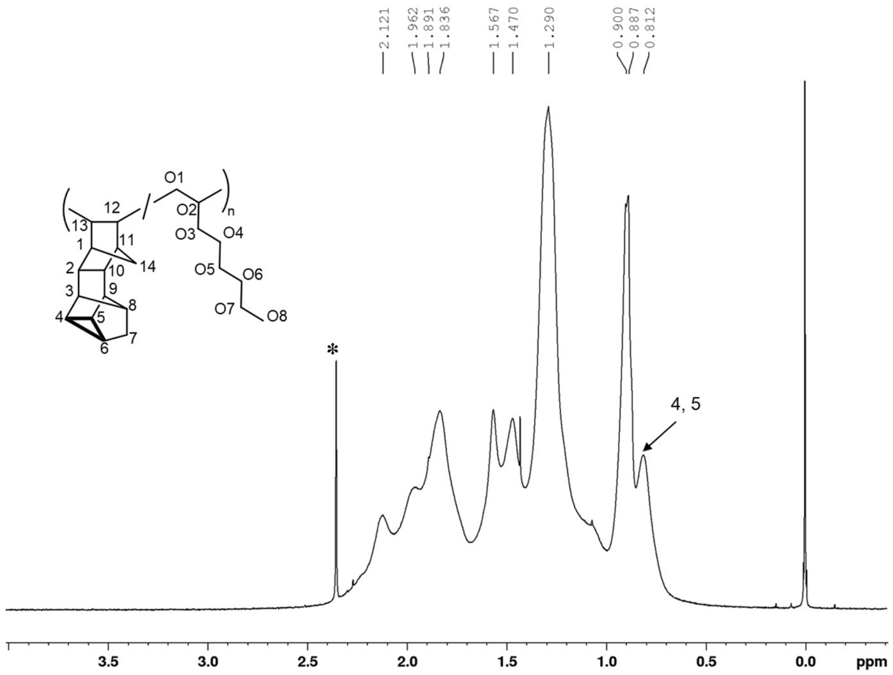


Figure S3. ^{1}H NMR spectrum of poly(**1**-*co*-1-octene) ($CDCl_3$) (run 5, Table 1).

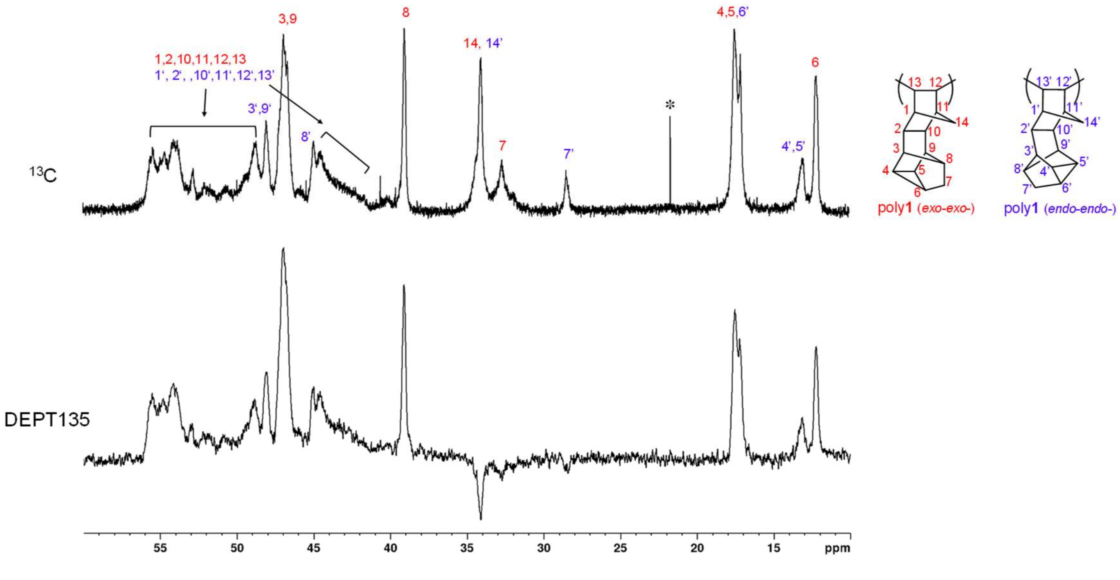


Figure S4. DEPT135 NMR spectrum of poly**1** (run 2, Table 1) compared with the corresponding ^{13}C NMR spectrum (Figure 3(B)) (CD_2Cl_4).

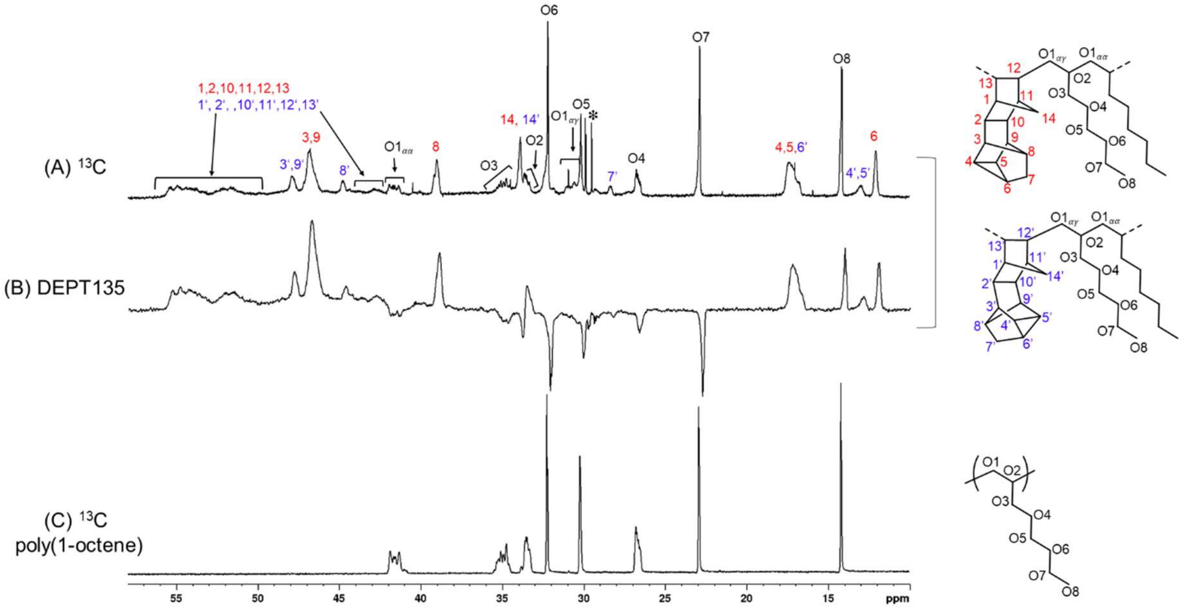


Figure S5. (A) ^{13}C NMR and (B) DEPT135 NMR spectra of poly(**1**-*co*-1-octene) (run 5, Table 1) compared with (C) ^{13}C NMR spectrum of poly(1-octene) (CD_2Cl_4).

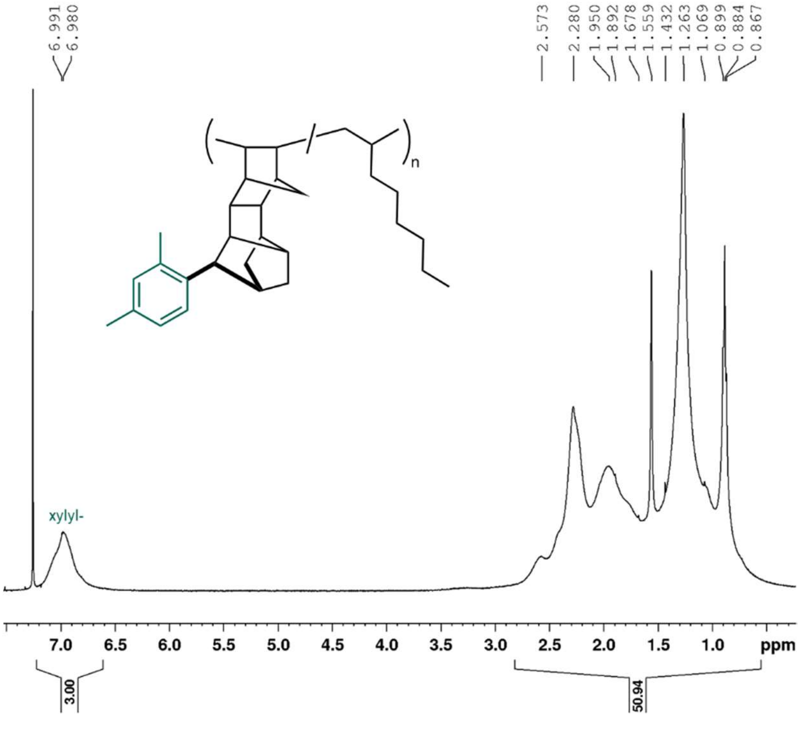


Figure S6. ^{1}H NMR spectrum of poly**3a** ($CDCl_3$).

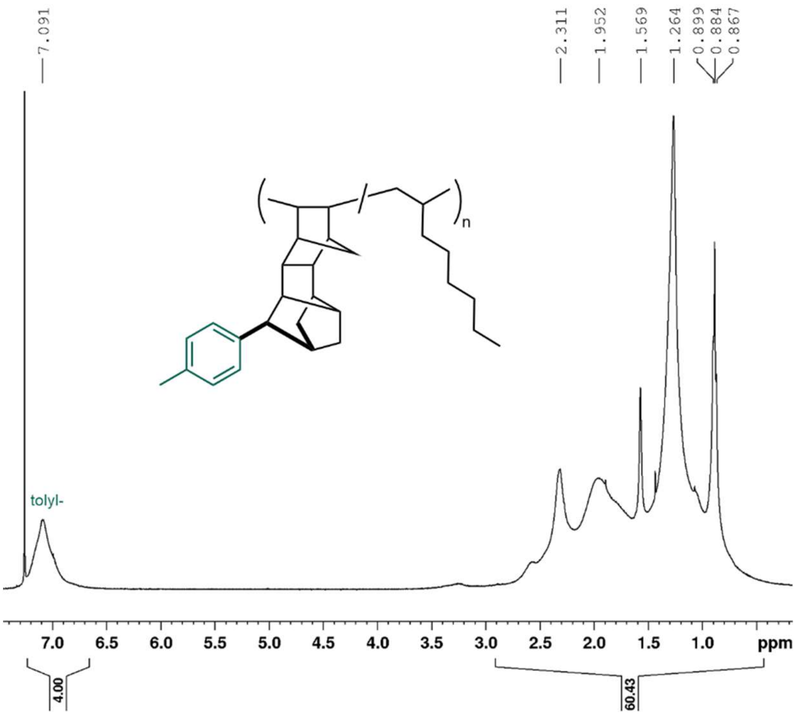


Figure S7. ^{1}H NMR spectrum of poly**3b** ($CDCl_3$).

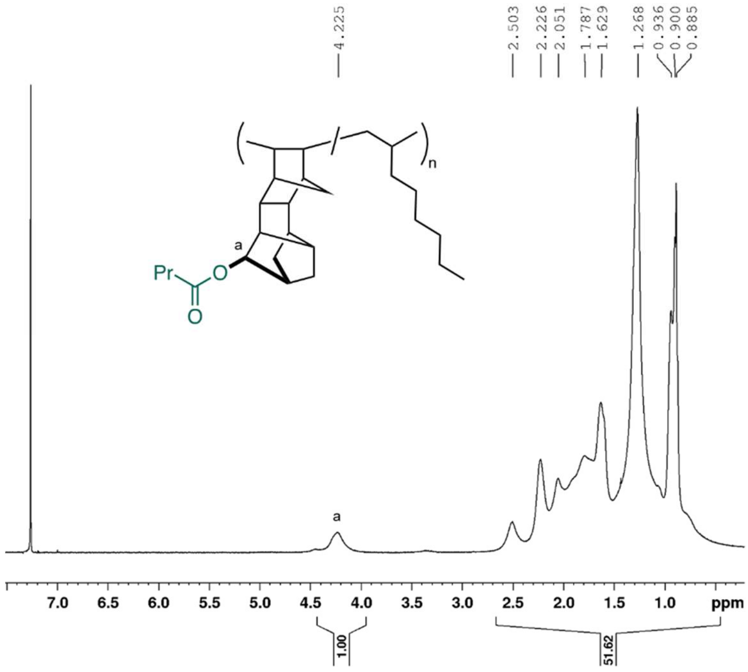


Figure S8. ^{1}H NMR spectrum of poly**3c** ($CDCl_3$).

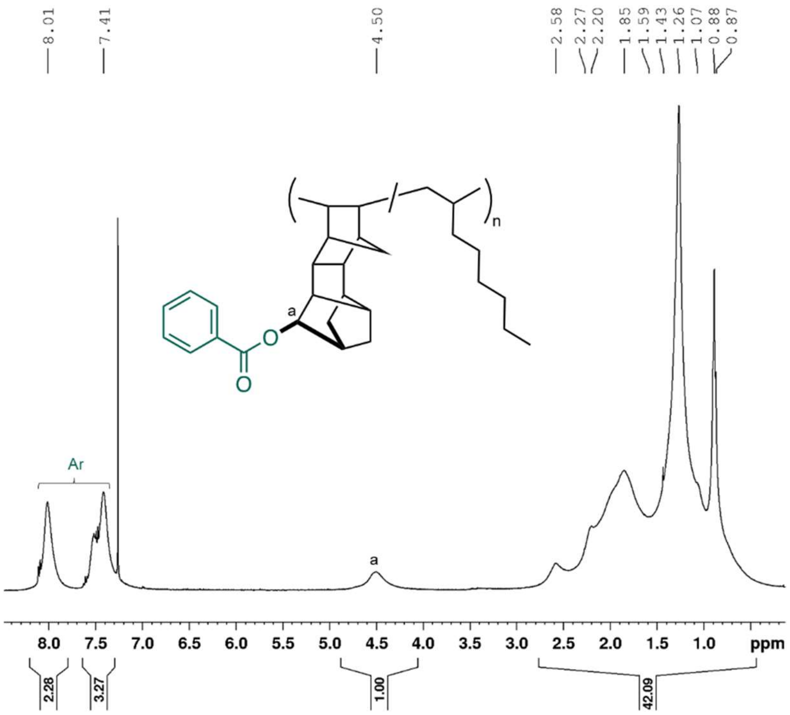


Figure S9. ^{1}H NMR spectrum of poly**3d** ($CDCl_3$).

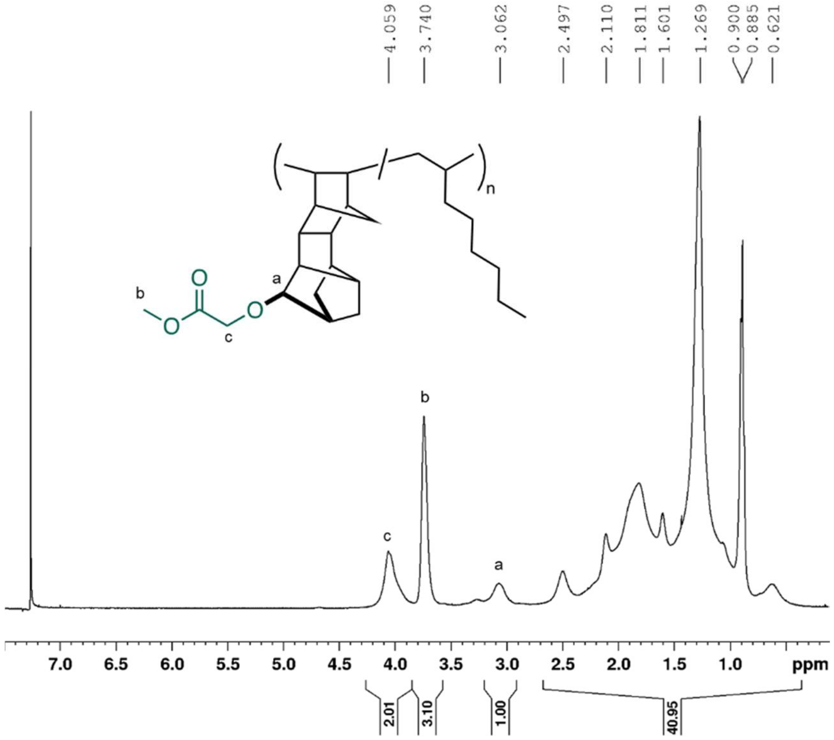


Figure S10. ^{1}H NMR spectrum of poly**3e** ($CDCl_3$).

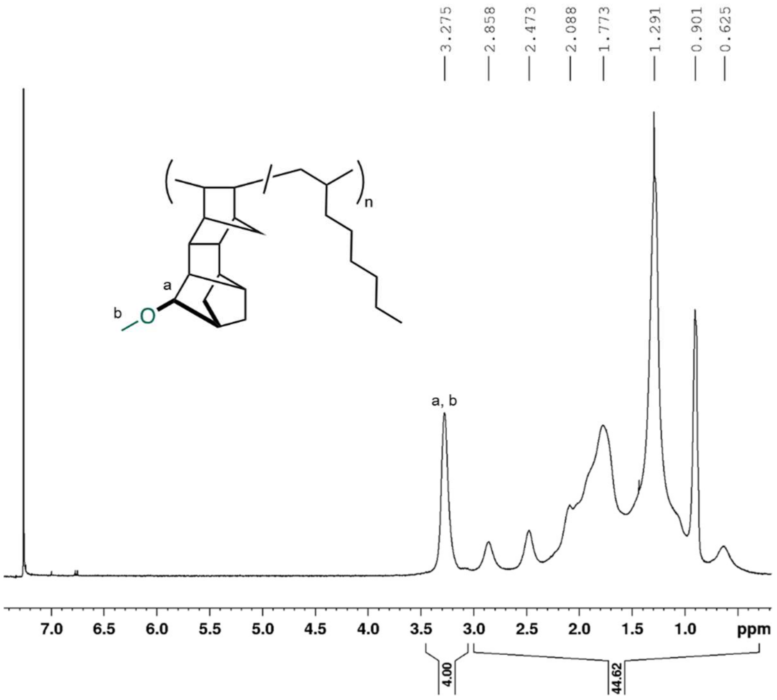


Figure S11. ^{1}H NMR spectrum of poly**3f** ($CDCl_3$).

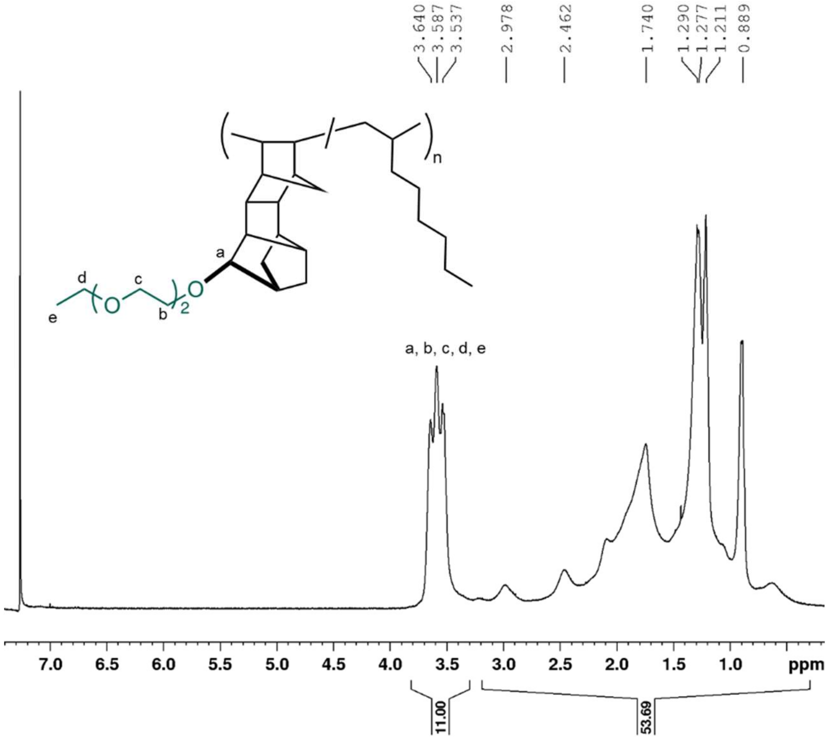


Figure S12. ^{1}H NMR spectrum of poly**3g** ($CDCl_3$).

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