

*Supporting information for*

**Hexacyclotetradecenes as polycyclic fused *exo*-norbornene monomers:  
Synthesis of cyclic olefin copolymers via Ti-catalyzed controlled  
polymerization**

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Table S1. Attempted ROMP of **1**.

entry	catalyst		solvent <sup>a</sup>	temp. °C	time h	yield <sup>b</sup> %
	type	mol%				
1	G1	1	DCM	25	18	0
2	G1	1	toluene	25	18	0
3	G2	1	toluene	25	18	0
4	G2	1	bulk	-20	18	0
5	G2	10	toluene	25	72	0
6	G3	1	toluene	25	18	0
7	G3	1	bulk	25	18	0
8	G3	1	bulk	-20	18	0
9	G3	10	toluene	25	72	0
10	HG2	1	DCM	25	18	0
11	HG2	2	toluene	40	18	0

<sup>a</sup>[**1**] = 0.25 M (in toluene and in DCM). <sup>b</sup>after reprecipitation into MeOH

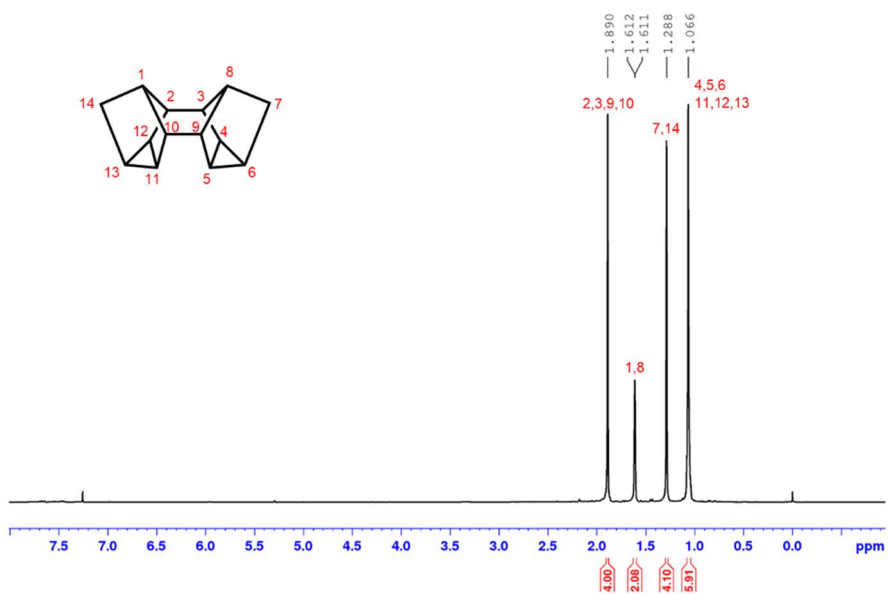


Figure S1. <sup>1</sup>H NMR spectrum of Binor-S

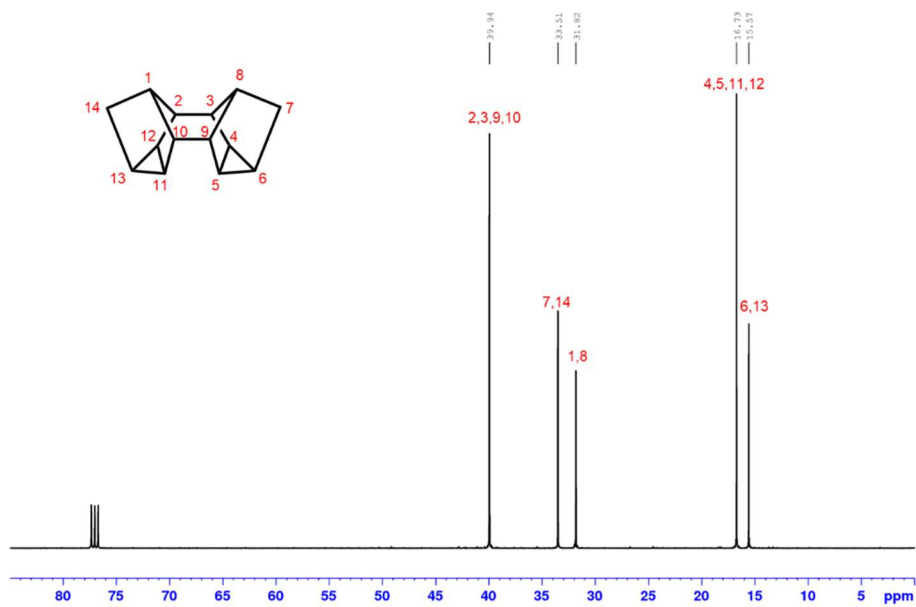


Figure S2. <sup>13</sup>C NMR spectrum of Binor-S

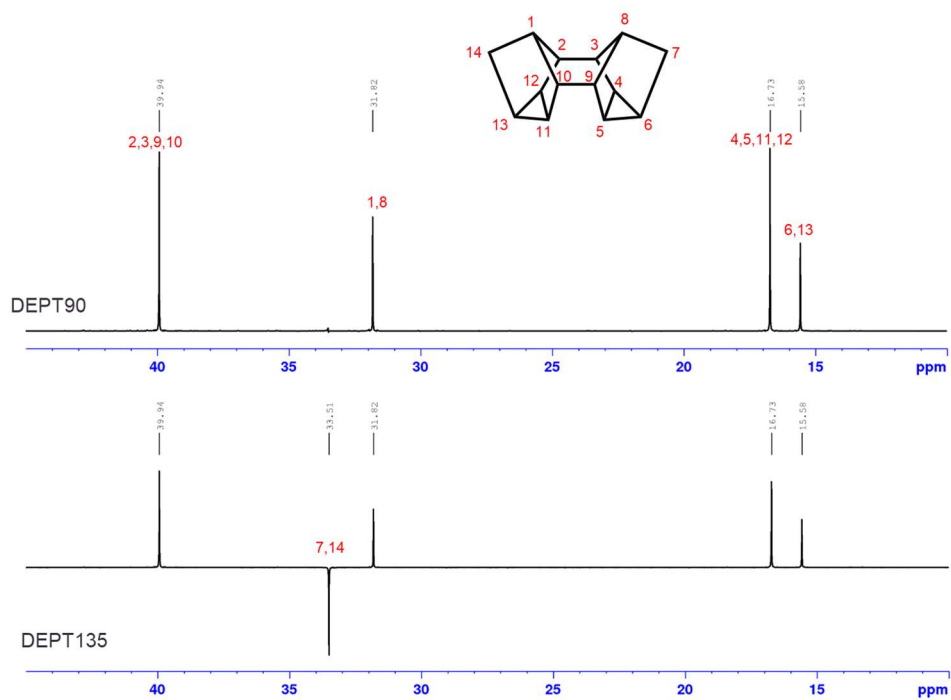


Figure S3. DEPT90 and DEPT135 NMR spectra of Binor-S

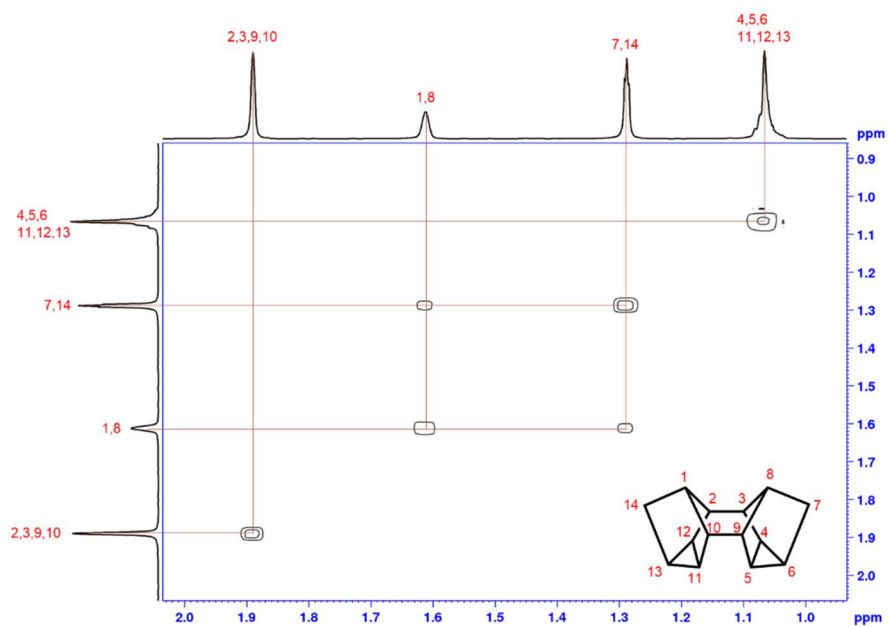


Figure S4.  $^1\text{H}$ - $^1\text{H}$  COSY NMR spectrum of Binor-S

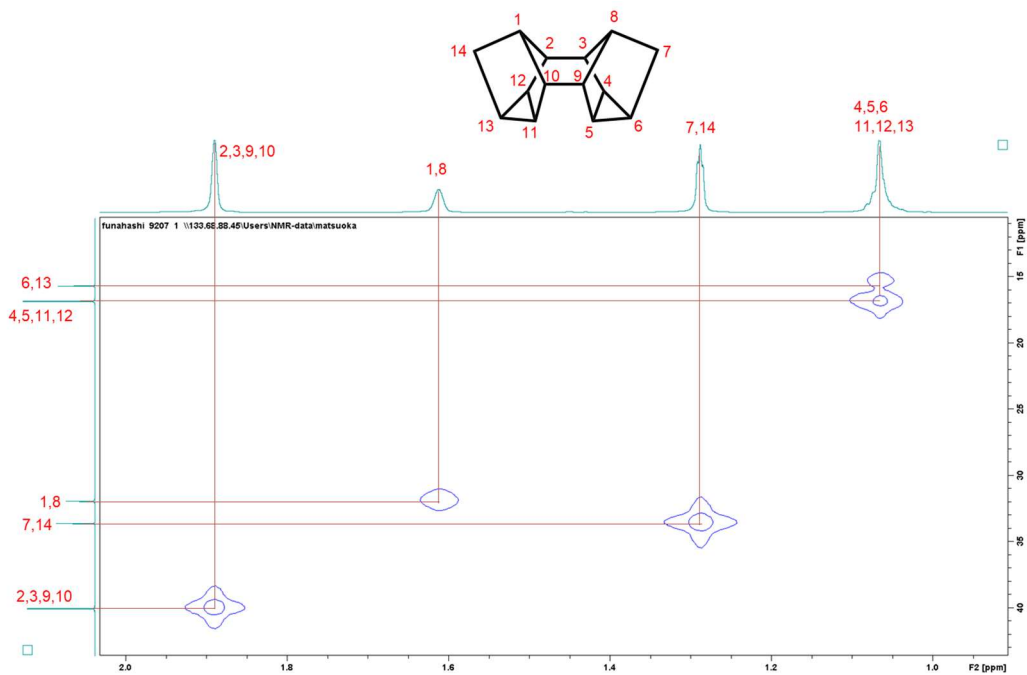


Figure S5. HMQC NMR spectrum of Binor-S

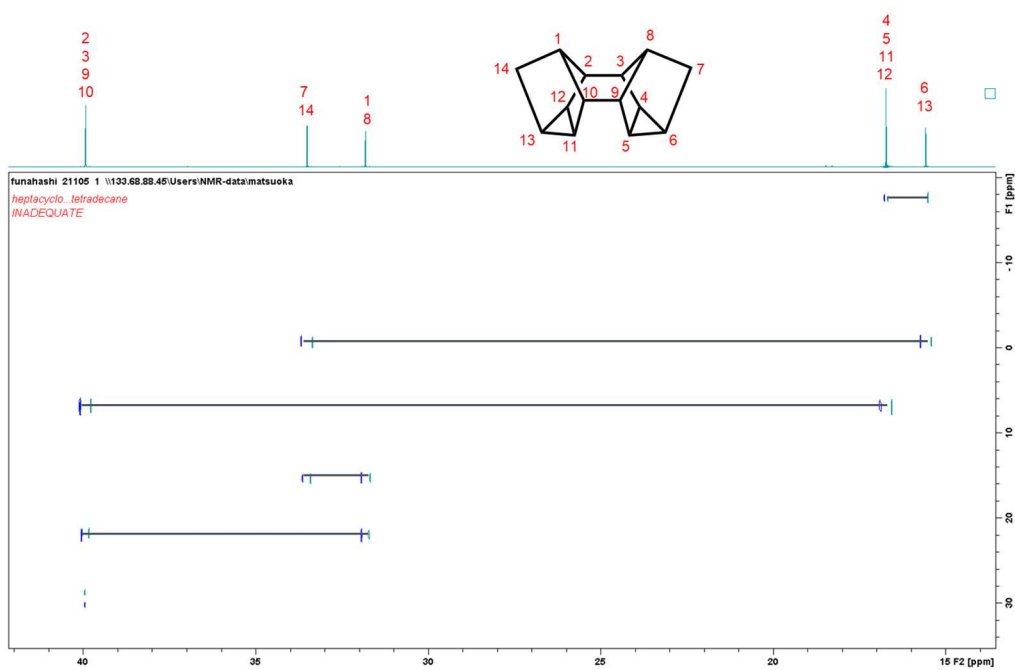


Figure S6.  $^{13}\text{C}$  INADEQUATE NMR spectrum of Binor-S

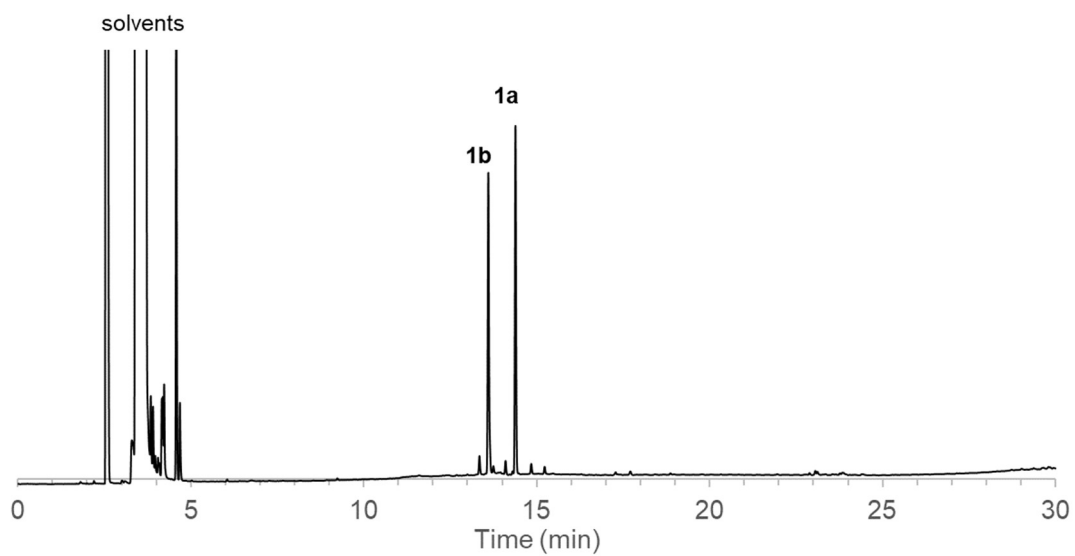


Figure S7. GC chromatogram of **1a** and **1b**.

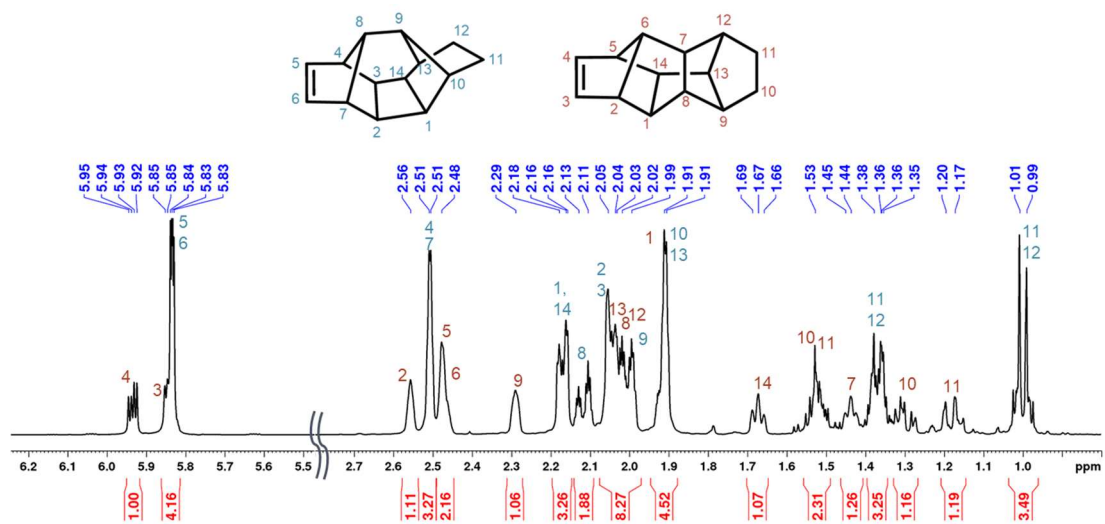


Figure S8.  $^1\text{H}$  NMR spectrum of **1a** and **1b**

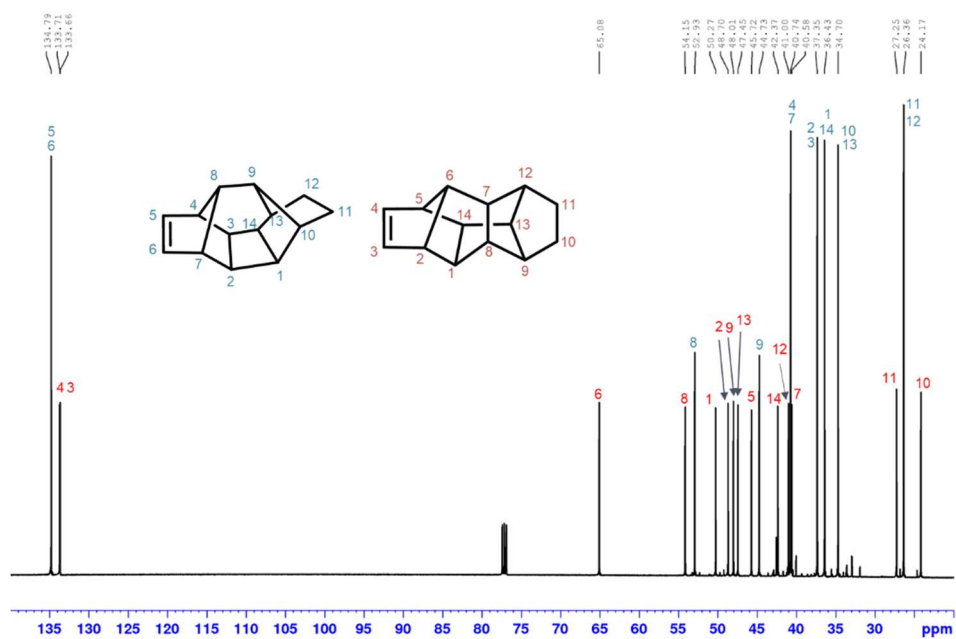


Figure S9.  $^{13}\text{C}$  NMR spectrum of **1a** and **1b**

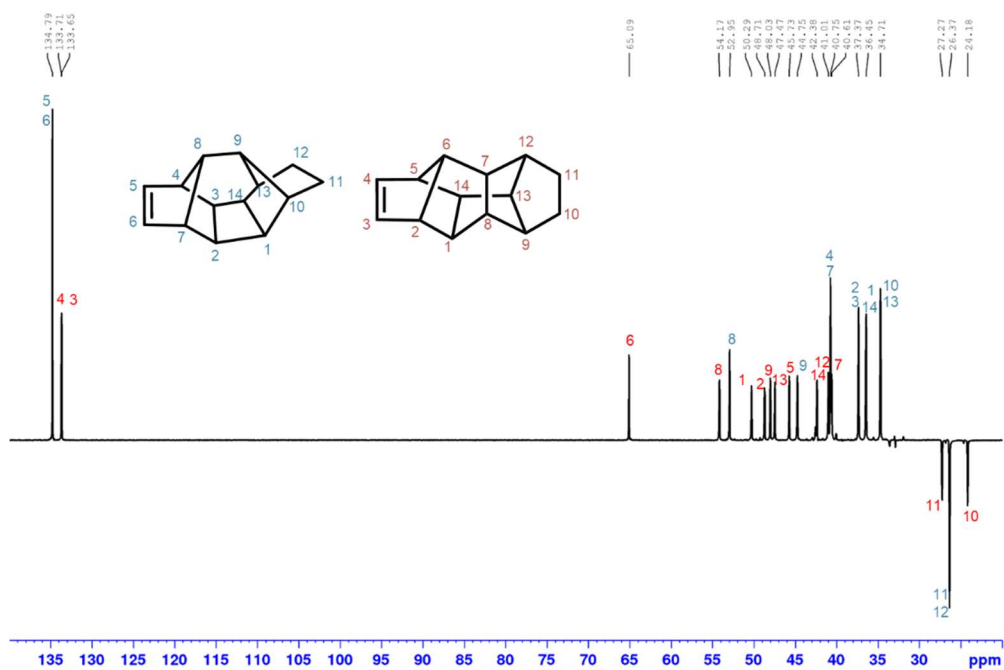


Figure S10. DEPT135 NMR spectrum of **1a** and **1b**



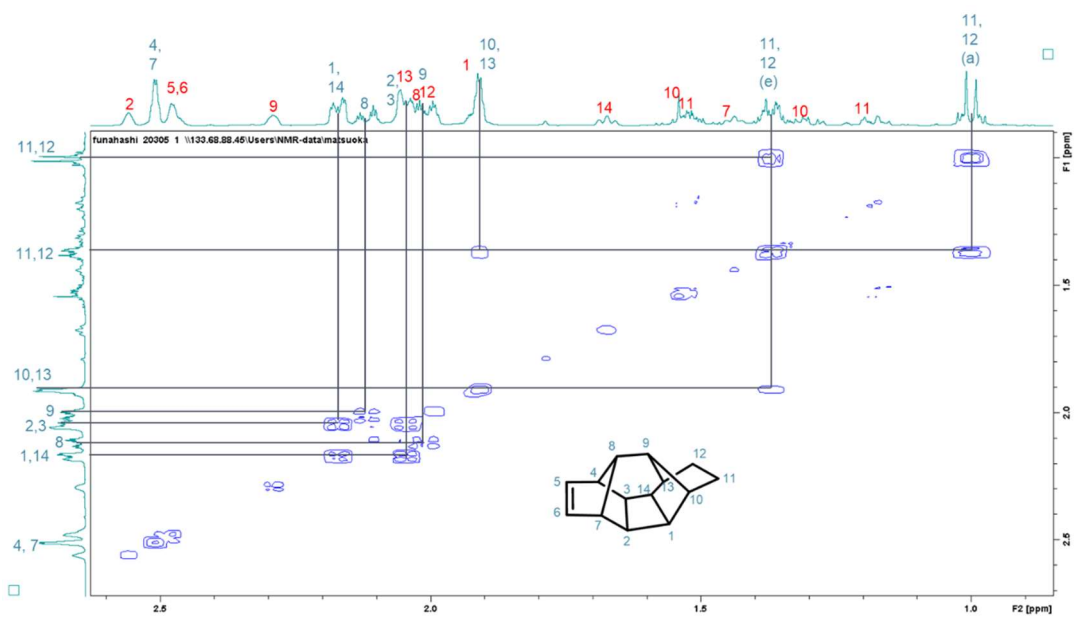


Figure S11.  $^1\text{H}$ - $^1\text{H}$  COSY NMR spectrum of **1a** and **1b** (correlation of **1a**)

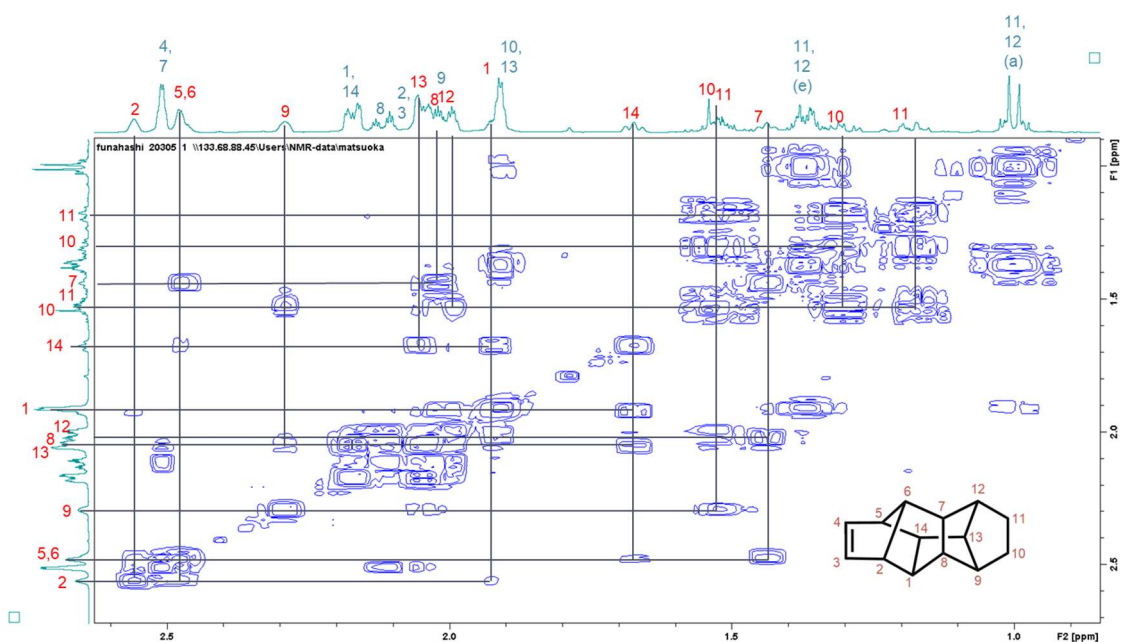


Figure S12.  $^1\text{H}$ - $^1\text{H}$  COSY NMR spectrum of **1a** and **1b** (correlation of **1b**)

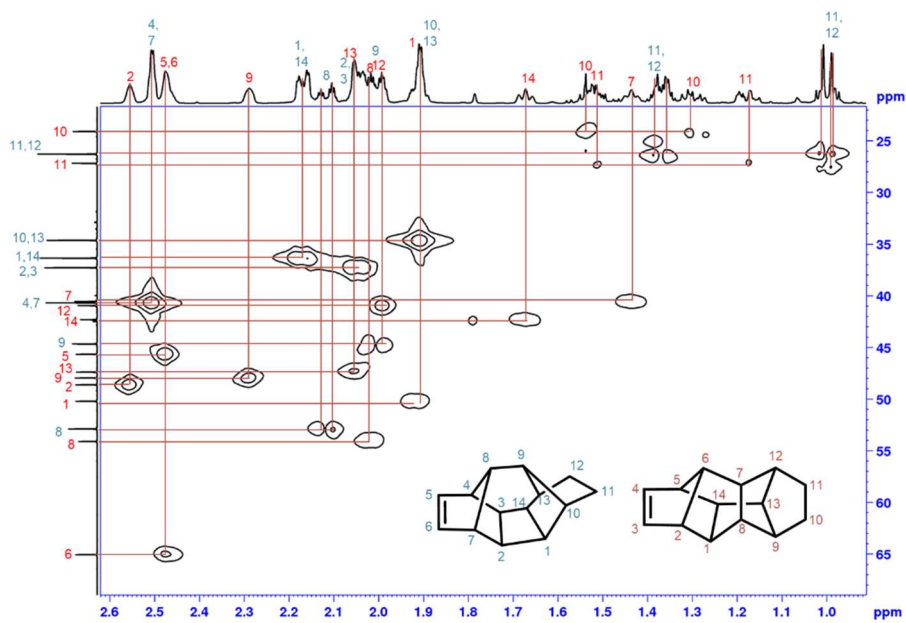


Figure S13. HMQC NMR spectrum of **1a** and **1b**

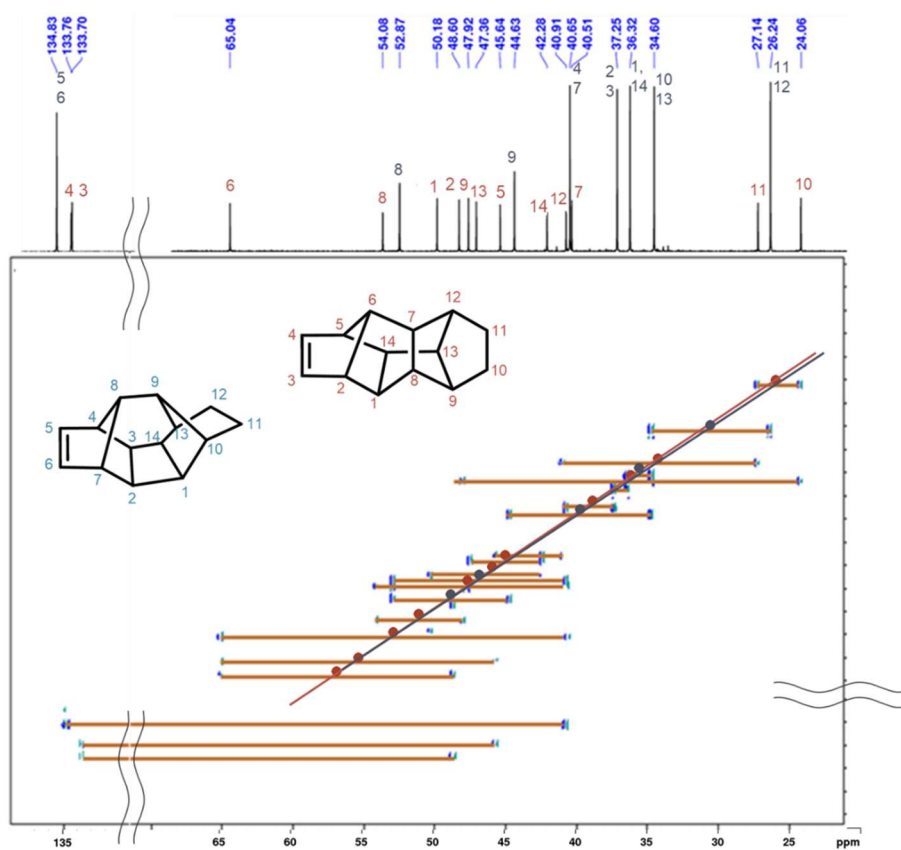


Figure S14.  $^{13}\text{C}$  INADEQUATE NMR spectrum of **1a** and **1b**

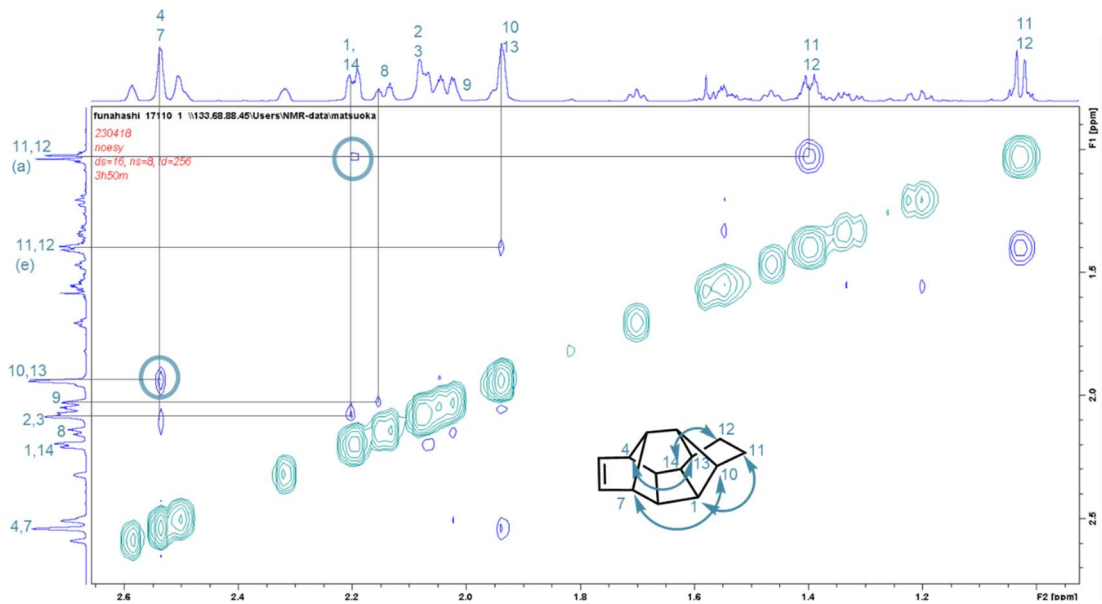


Figure S15. NOESY NMR spectrum of **1a** and **1b** (correlation of **1a**)

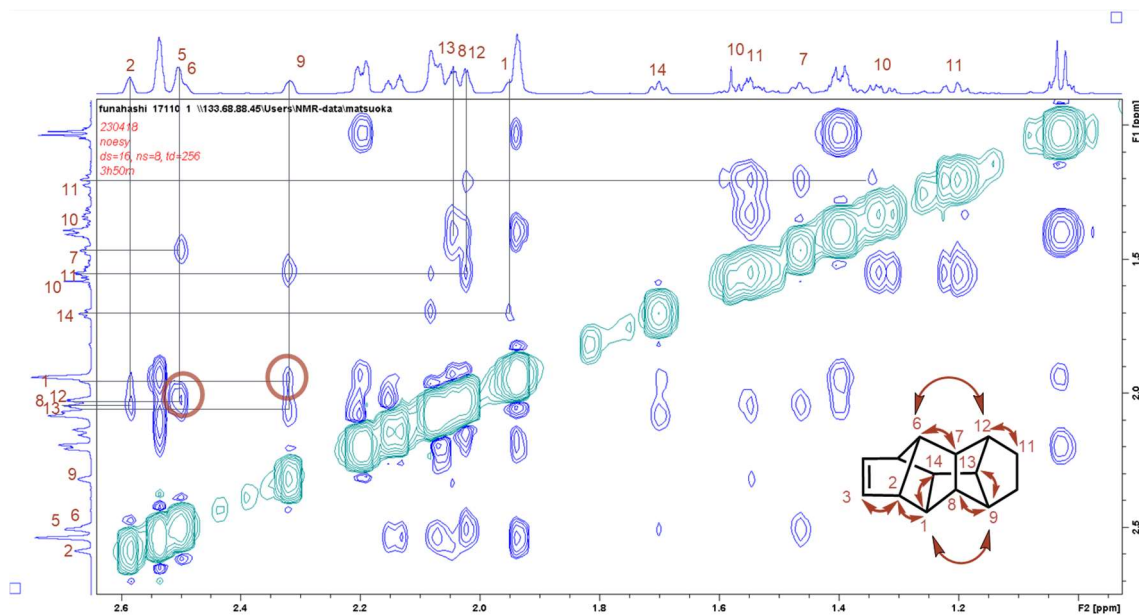


Figure S16. NOESY NMR spectrum of **1a** and **1b** (correlation of **1b**)

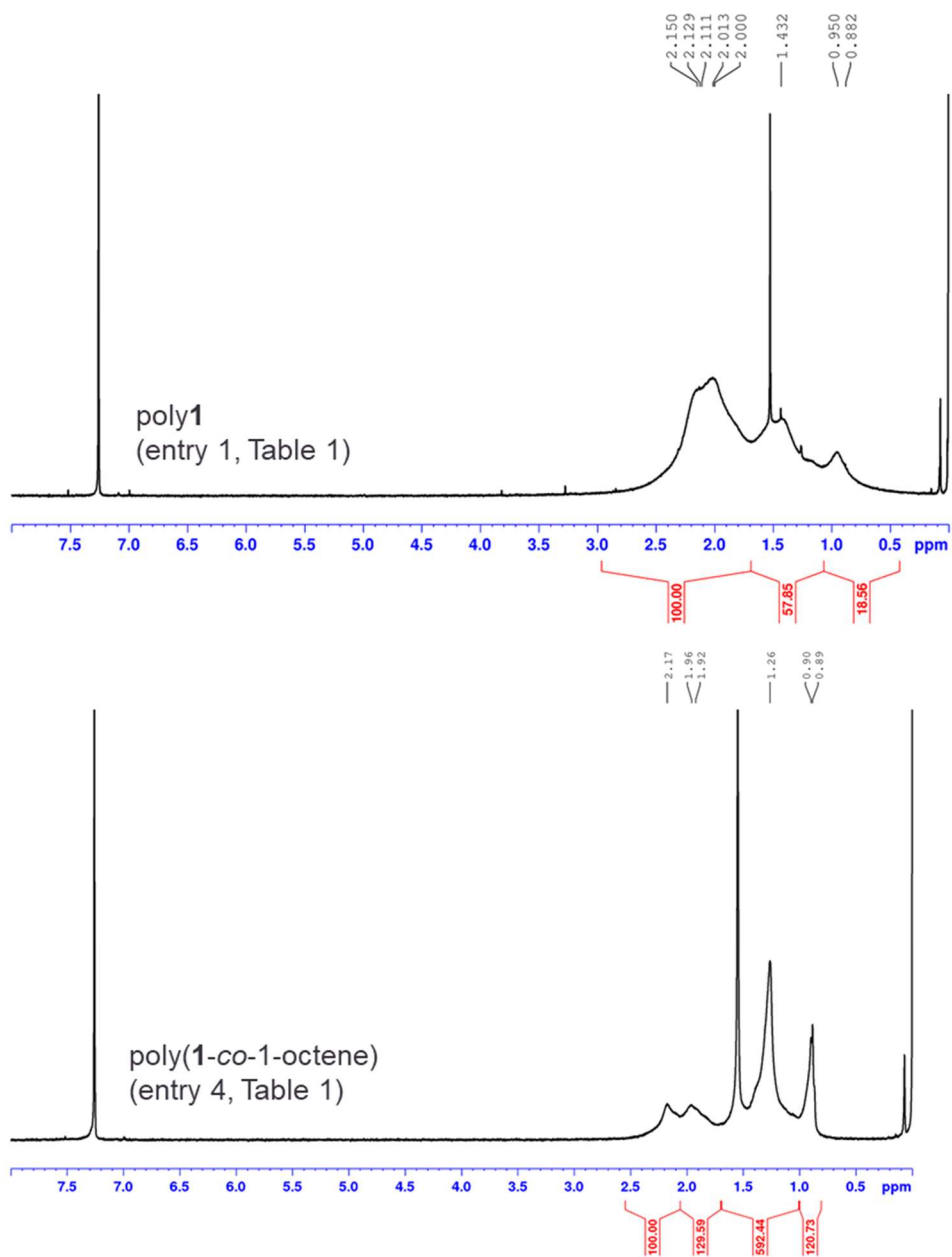


Figure S17.  $^1\text{H}$  NMR spectra of poly1 and poly(1-co-1-octene)

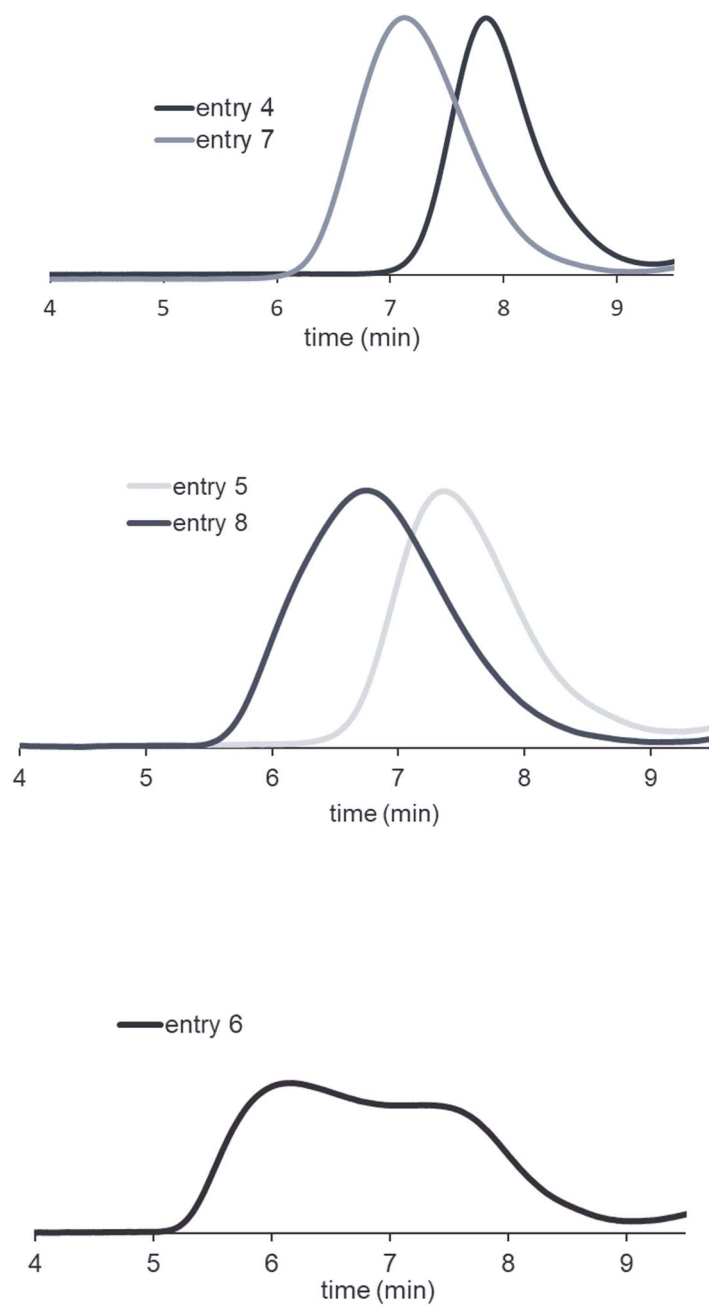


Figure S18. SEC chromatograms of poly(**1-co-1**-octene) (entries 4, 5, 7, and 8) and poly(1-octene) (entry 6).

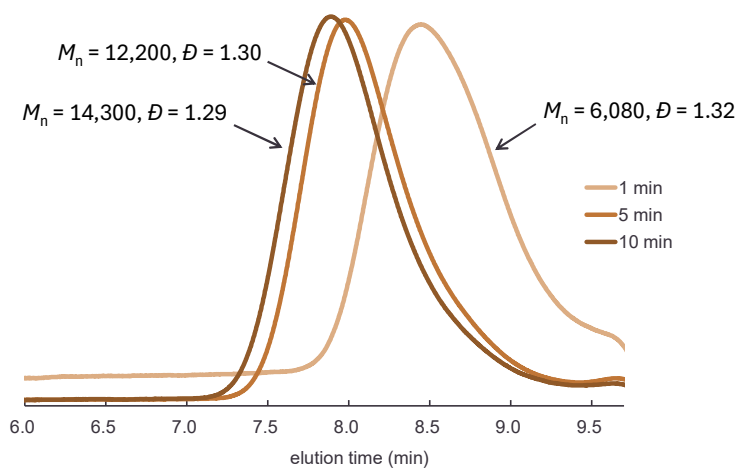


Figure S19. SEC chromatograms and molecular weight data of poly(**1-co-1-octene**) (Figure 2C).

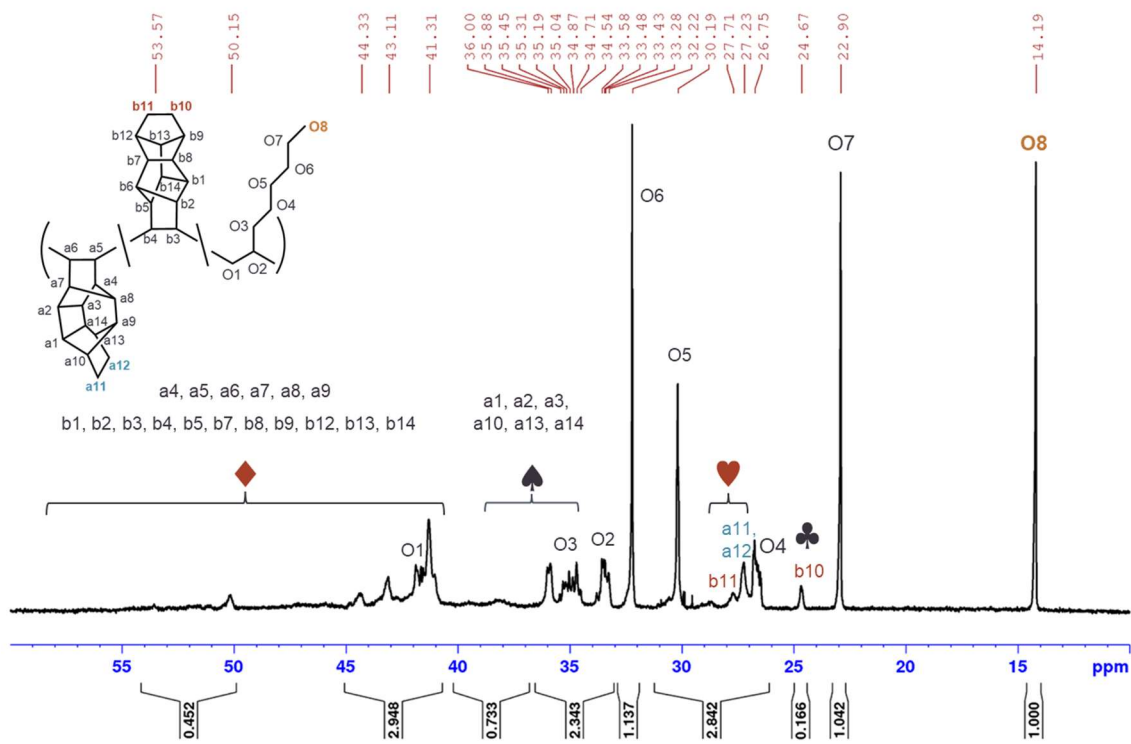


Figure S20.  $^{13}\text{C}$  NMR spectrum of poly(**1-co-1-octene**) (entry 8, Table 1)

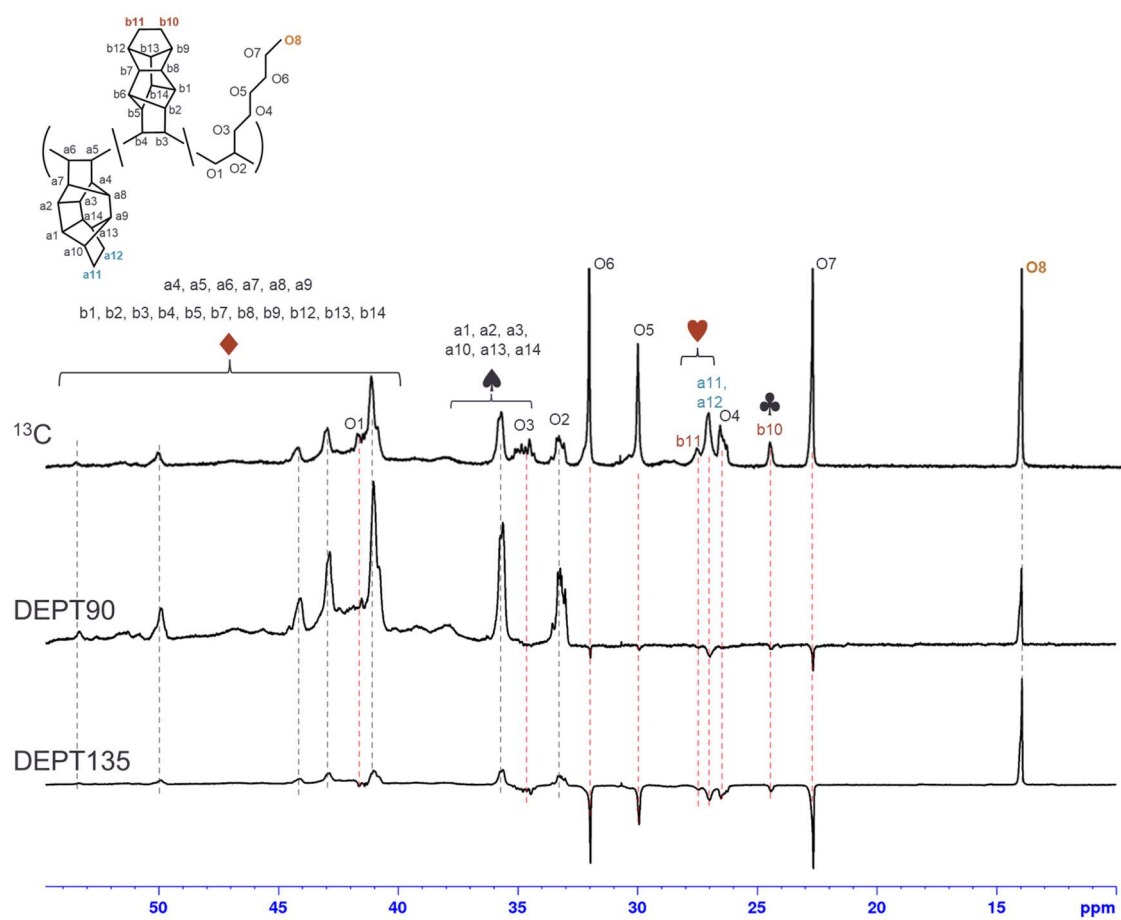


Figure S21.  $^{13}\text{C}$ , DEPT90, and DEPT135 NMR spectrum of poly(1-co-1-octene) (entry 7, Table 1)

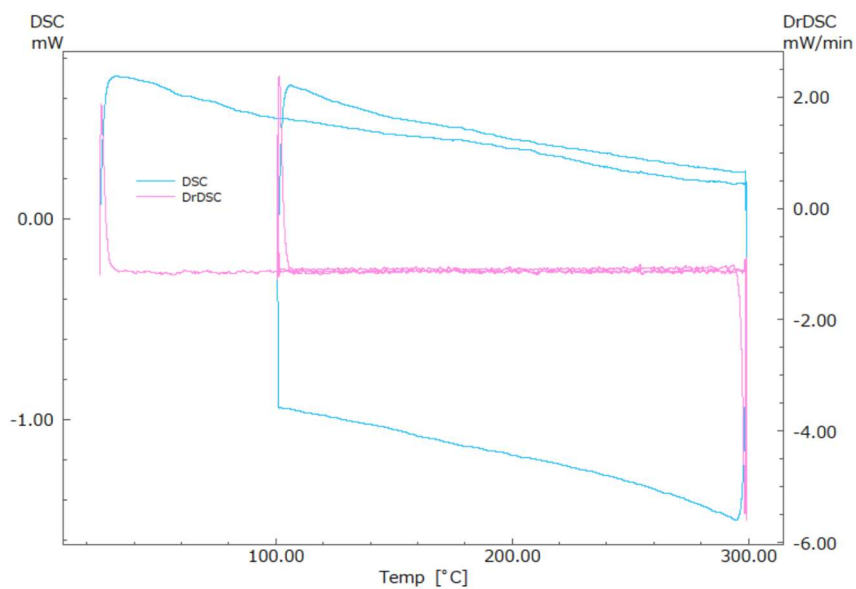


Figure S22. DSC profile of poly1 (entry 1, Table 1).

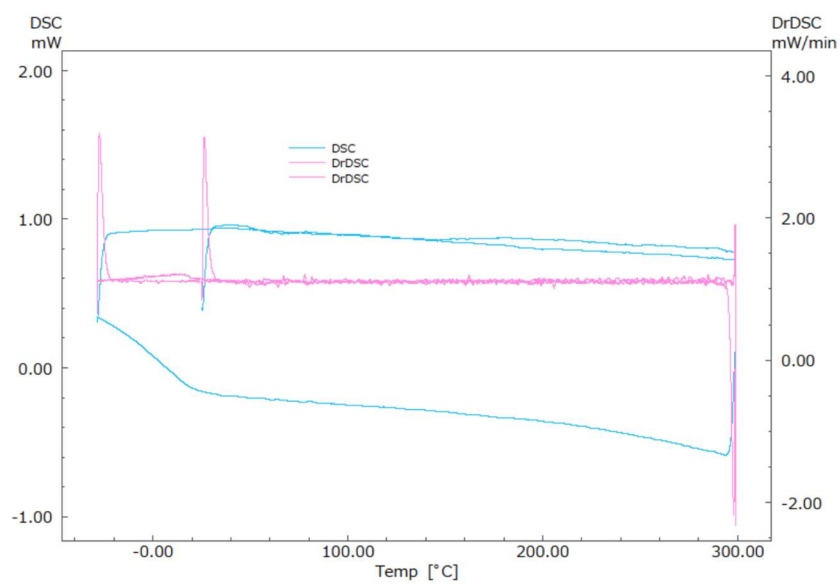


Figure S23. DSC profile of poly(1-co-1-octene) (entry 4, Table 1).



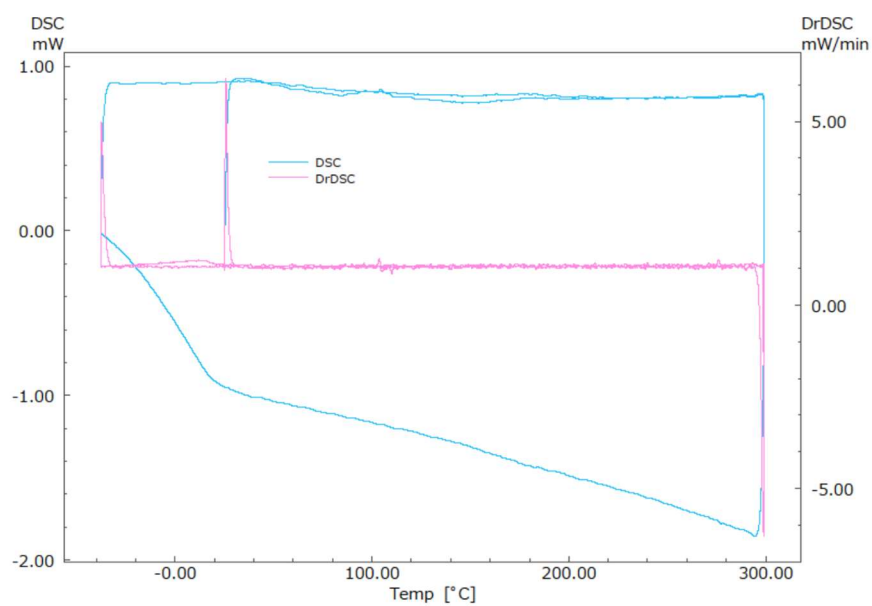


Figure S24. DSC profile of poly(1-co-1-octene) (entry 5, Table 1).

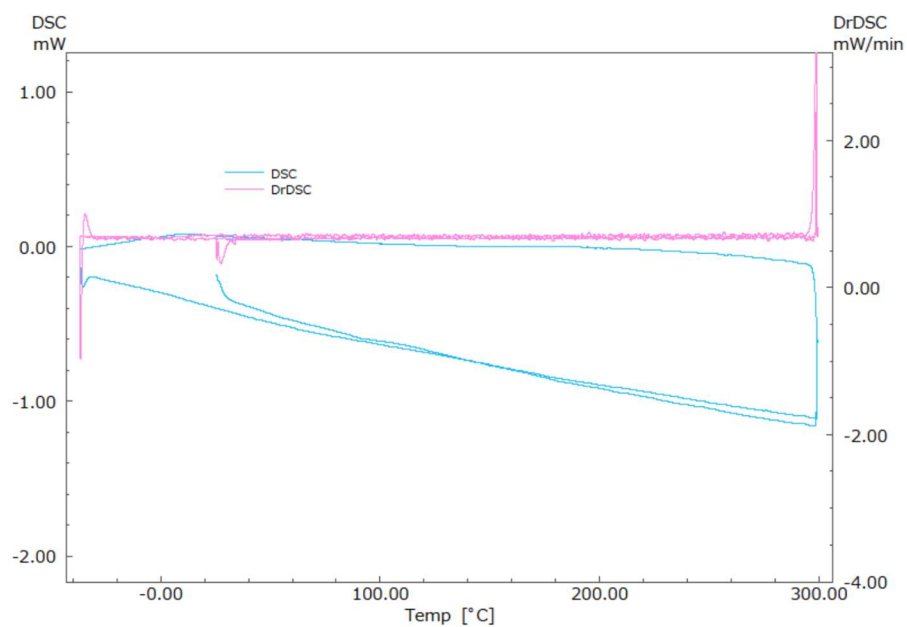


Figure S25. DSC profile of poly(1-co-1-octene) (entry 8, Table 1).

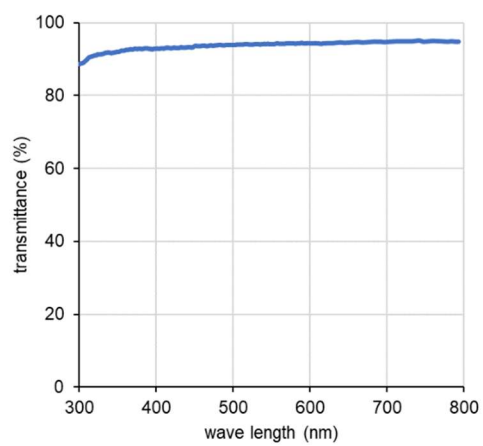


Figure S26. UV-vis spectrum of poly(1-co-1-octene) (thickness of 86 μm) (entry 4, Table 1)