

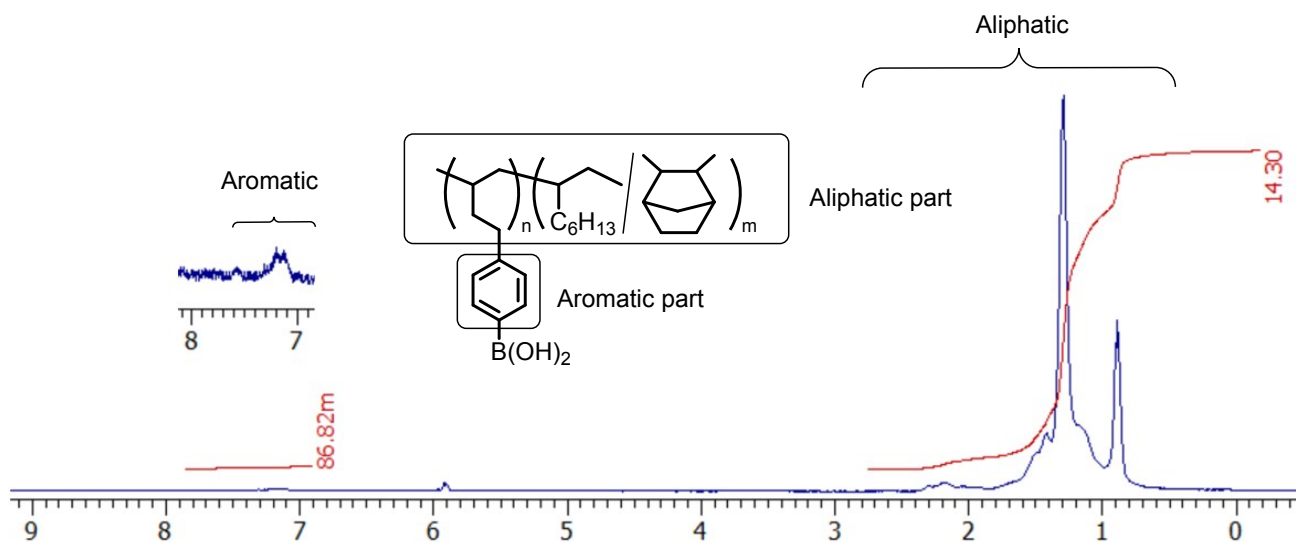
# Supporting Information

## Effect of the number of arms on the mechanical properties of star-shaped cyclic olefin copolymer

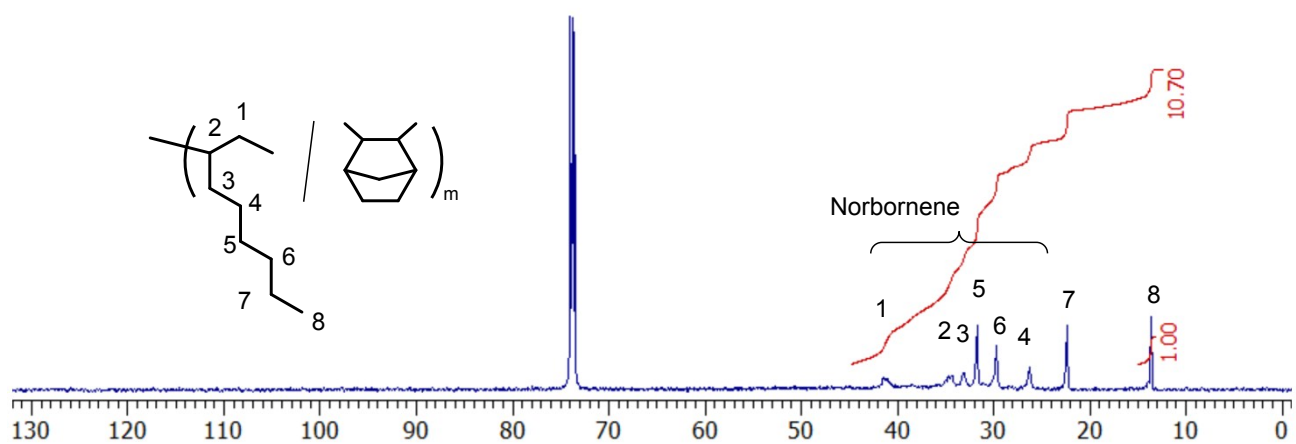
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**Figure S1.**  $^1\text{H}$  NMR spectrum of end-functionalized poly(norbornene-co-1-octene) (500 MHz, 130 °C, in  $\text{C}_2\text{D}_2\text{Cl}_4$ ).



**Figure S2.**  $^{13}\text{C}$  NMR spectrum of end-functionalized poly(norbornene-co-1-octene) (125 MHz, 130 °C, in  $\text{C}_2\text{D}_2\text{Cl}_4$ ).

### Calculation Method for the number of boronic acid per polymer chain.

Using the  $^{13}\text{C}$  NMR spectrum in Figure S2, content of 1-octene in COC ( $f_{\text{oct}}$ ) is described as followings:

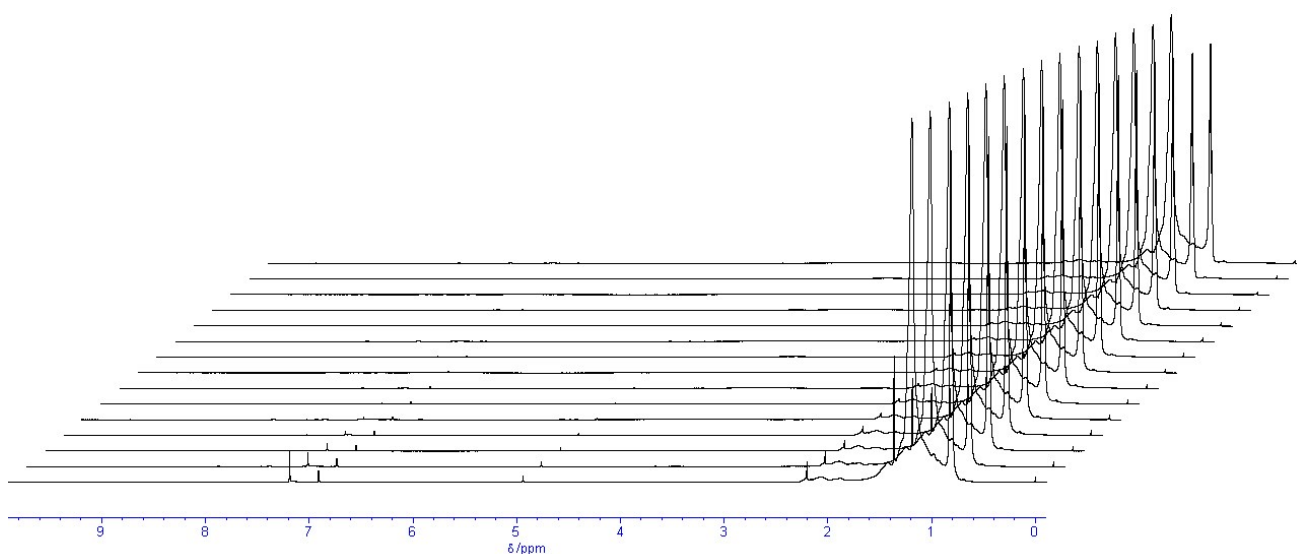
$$I = 8 I_{\text{oct}} + 7 I_{\text{oct}} (1-f_{\text{oct}})/f_{\text{oct}} = I_{\text{oct}} + 7 (I_{\text{oct}}/f_{\text{oct}})$$

where  $I$  represent whole integral ratio and  $I_{\text{oct}}$  is integral ratio of the peak at 13.6 ppm, which is assigned to C8 carbon of 1-octene unit.  $f_{\text{oct}}$  can be calculated to be 0.72, showing that the average number of protons per one hydrocarbon unit is  $16*0.72+10*0.28 \approx 14.3$ . Using the molecular weight of both monomers, the polymerization degree at  $M_n = 33000$  can therefore be  $33000/(94*0.28+112*0.72) \approx 310$ .

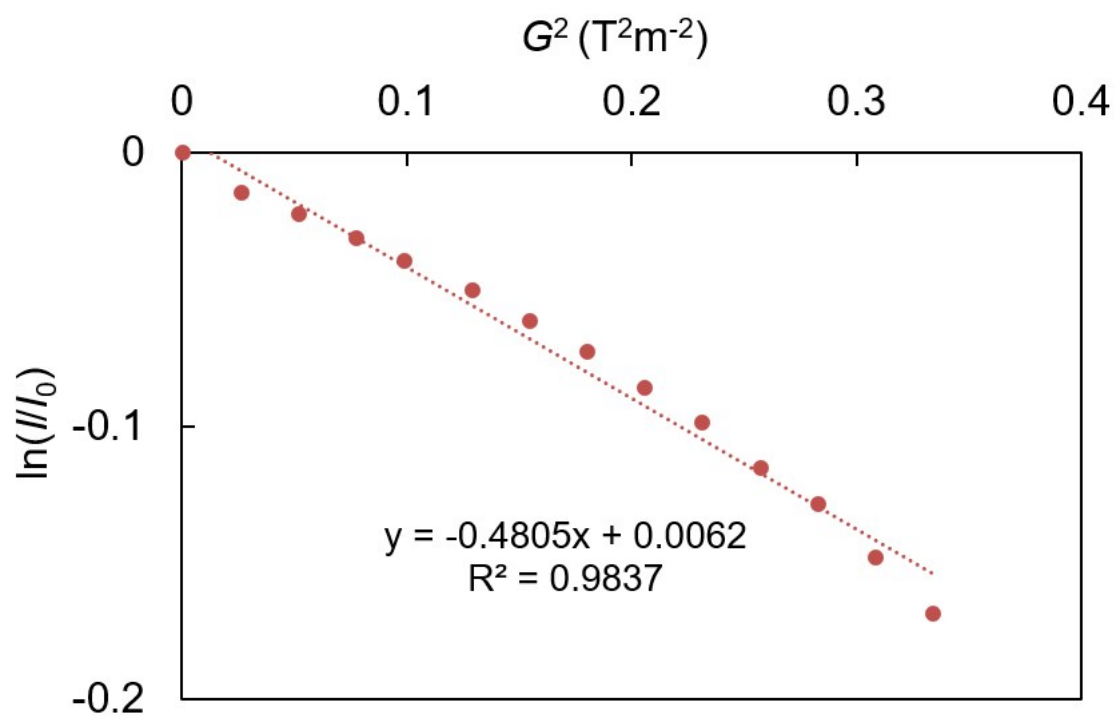
Number of boronic acid ( $N$ ) in the COC is calculated using the following equation and  $^1\text{H}$  NMR spectrum:

$$N = (I_{\text{aro}} / 4) / (I_{\text{ali}} / 14.3 / 310) = 77.5 I_{\text{aro}} / (I_{\text{ali}} / 14.3)$$

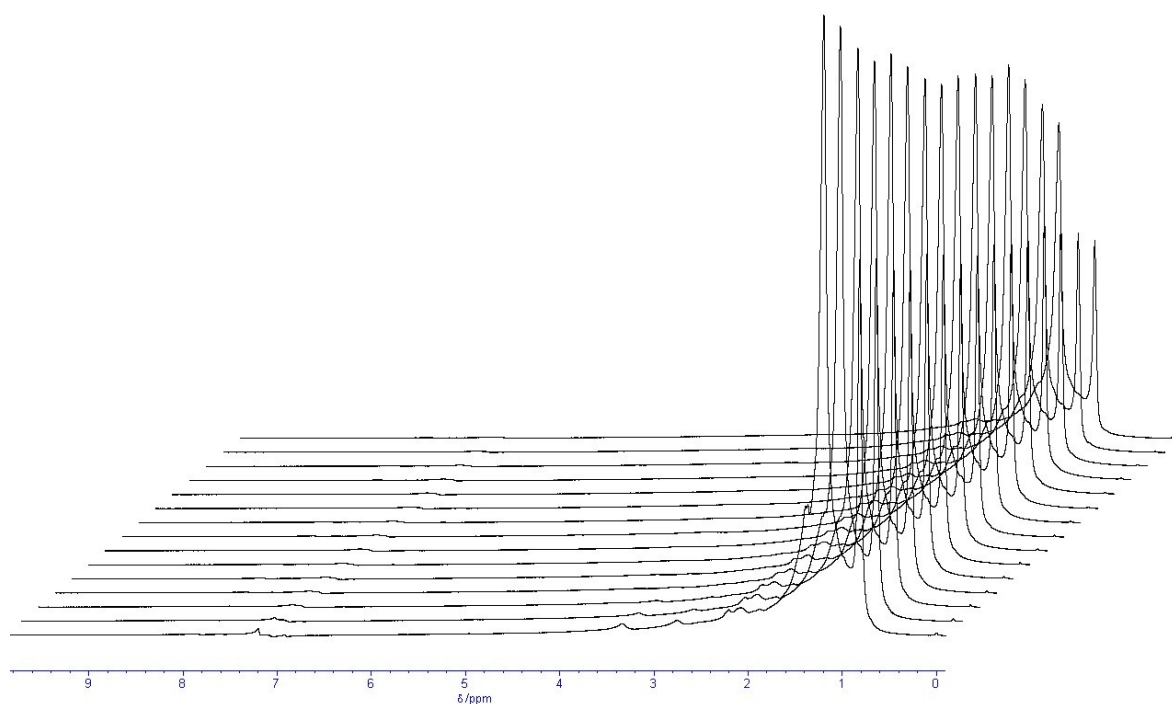
where  $I_{\text{ali}}$  is the integral ratio of aliphatic region and  $I_{\text{aro}}$  is that of aromatic region. Here  $N$  is calculated to be  $77.5*0.087 = 6.7$  from Figure S1.



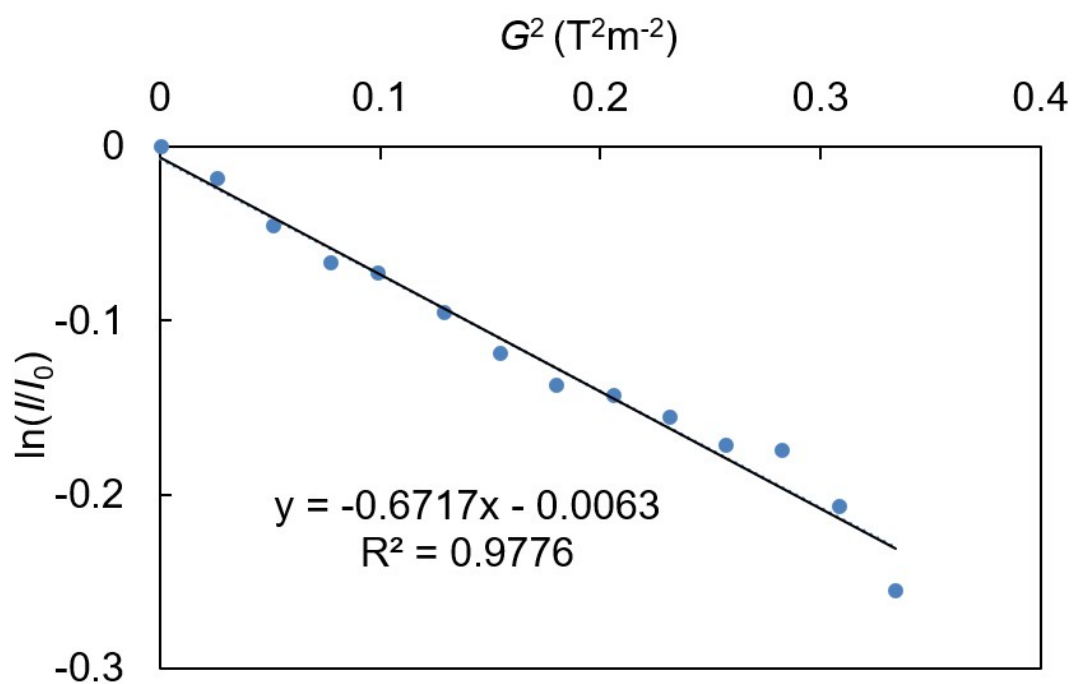
**Figure S3.** Full array DOSY NMR spectra of end-functionalized poly(norbornene-co-1-octene) without additive (500 MHz, 25 °C,  $\delta = 2$  ms,  $\Delta = 50$  ms, in  $\text{CDCl}_3$ ).



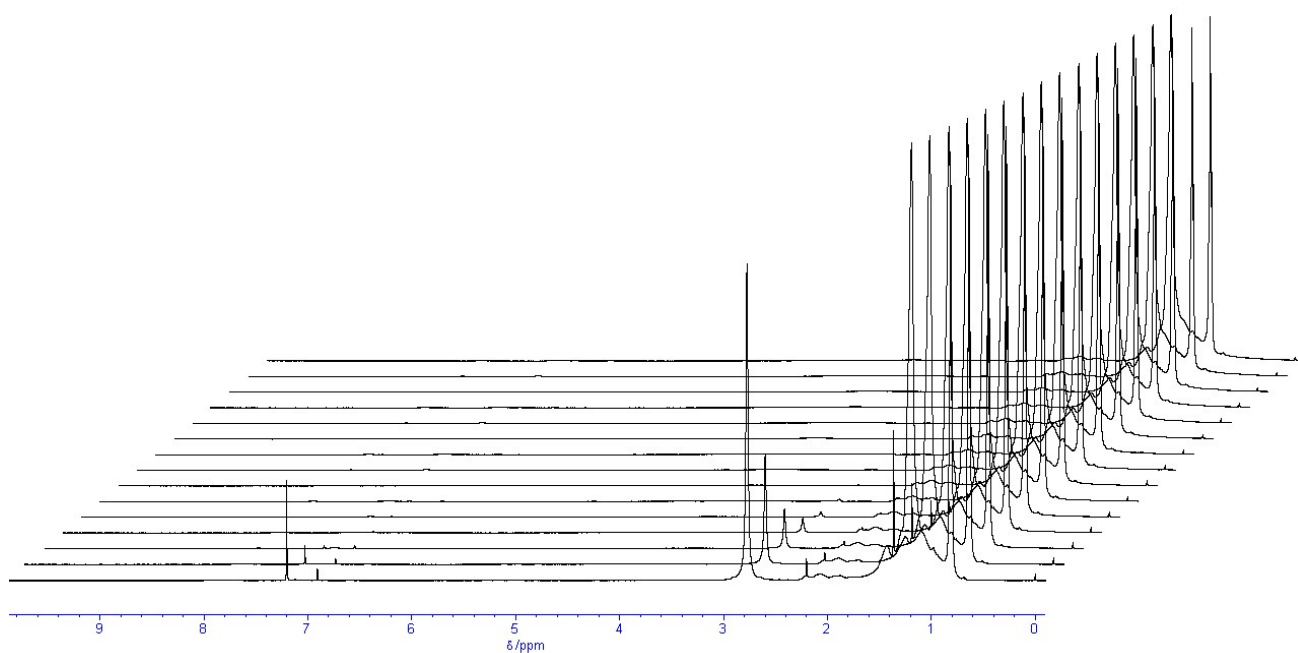
**Figure S4.** Plots of peak intensity ratio at 1.2 ppm ( $I/I_0$ ) versus gradient strength ( $G$ ) on DOSY NMR spectra of end-functionalized poly(norbornene-co-1-octene) without additive.



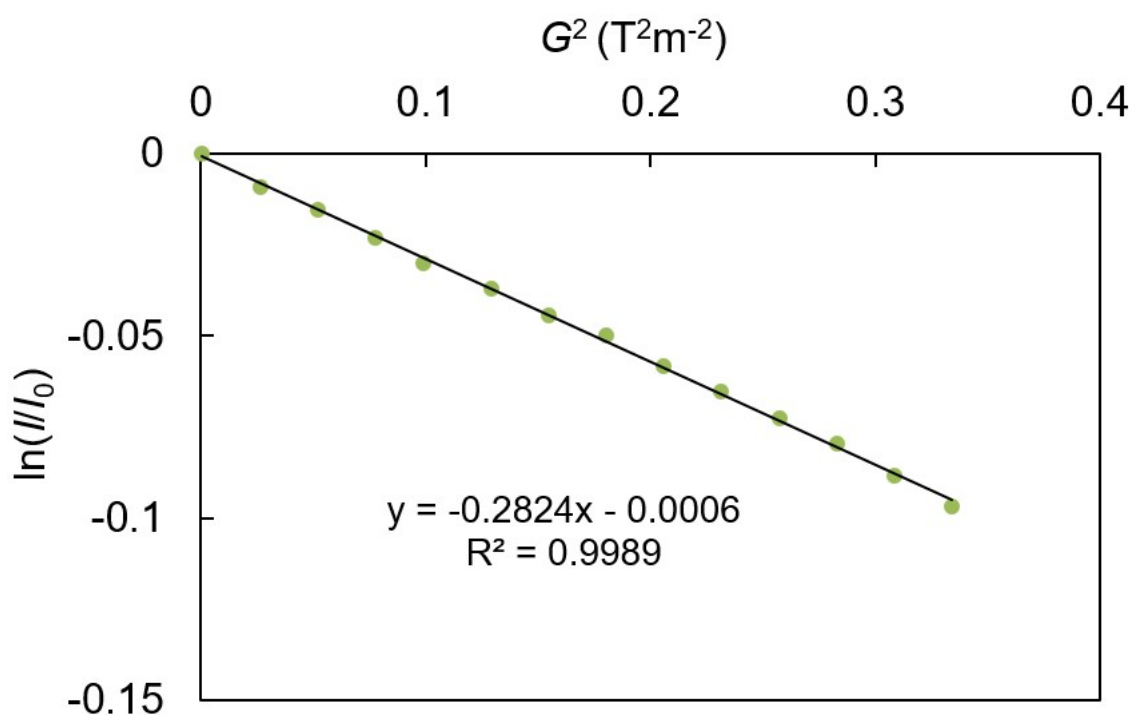
**Figure S5.** Full array DOSY NMR spectra of end-functionalized poly(norbornene-co-1-octene) treated with **4a** (500 MHz, 25 °C,  $\delta = 2$  ms,  $\Delta = 50$  ms, in  $\text{CDCl}_3$ ).



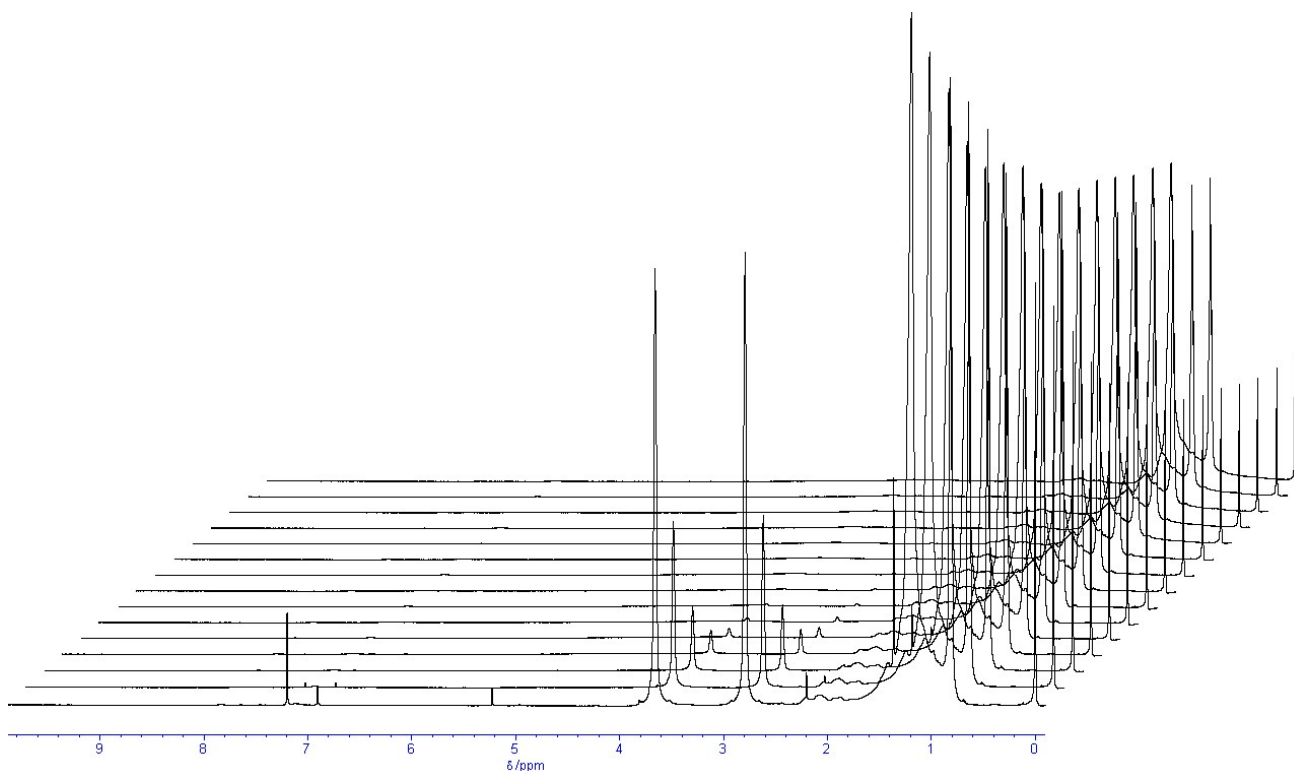
**Figure S6.** Plots of peak intensity ratio at 1.2 ppm ( $I/I_0$ ) versus gradient strength ( $G$ ) on DOSY NMR spectra of end-functionalized poly(norbornene-co-1-octene) treated with **4a**.



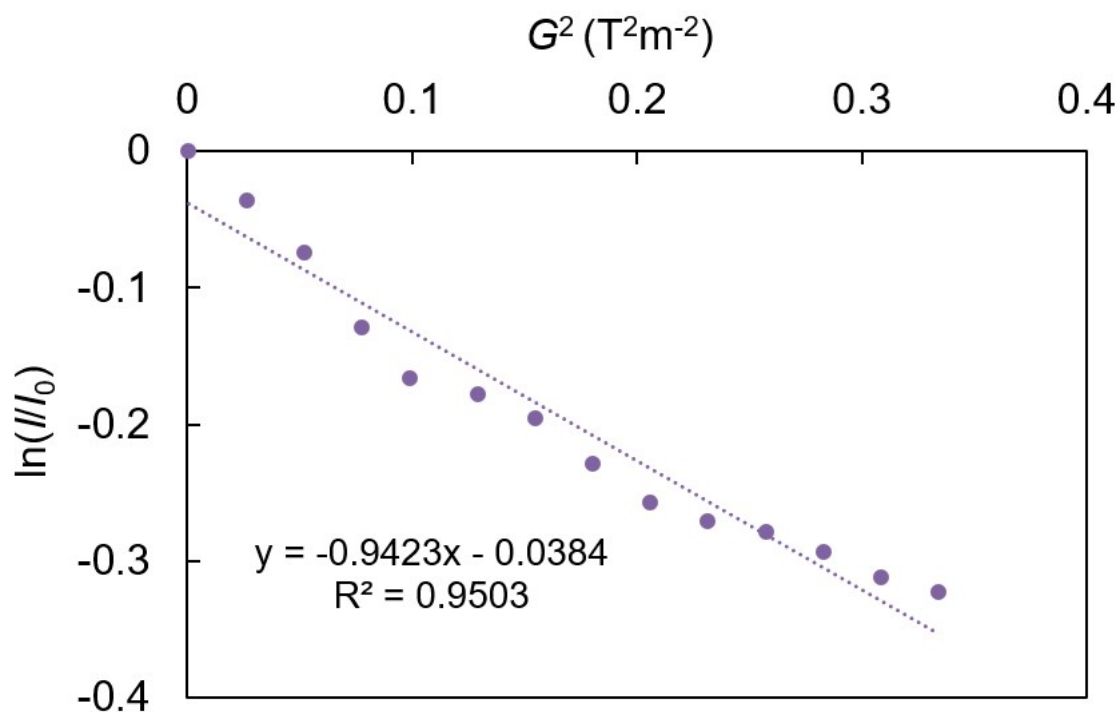
**Figure S7.** Full array DOSY NMR spectra of end-functionalized poly(norbornene-co-1-octene) treated with **4b** (500 MHz, 25 °C,  $\delta = 2$  ms,  $\Delta = 100$  ms, in  $\text{CDCl}_3$ ).



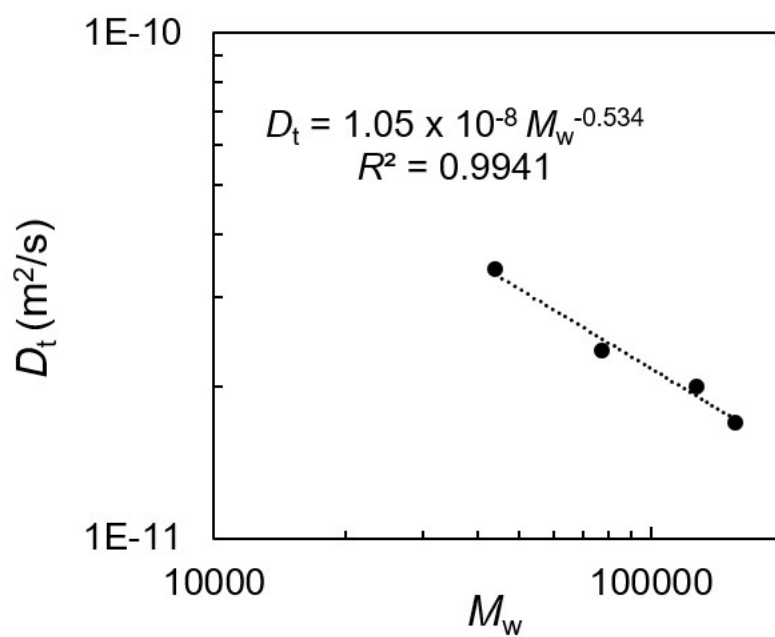
**Figure S8.** Plots of peak intensity ratio at 1.2 ppm ( $I/I_0$ ) versus gradient strength ( $G$ ) on DOSY NMR spectra of end-functionalized poly(norbornene-co-1-octene) treated with **4b**.



**Figure S9.** Full array DOSY NMR spectra of end-functionalized poly(norbornene-co-1-octene) treated with **4c** (500 MHz, 25 °C,  $\delta = 2.8$  ms,  $\Delta = 100$  ms, in  $\text{CDCl}_3$ ).

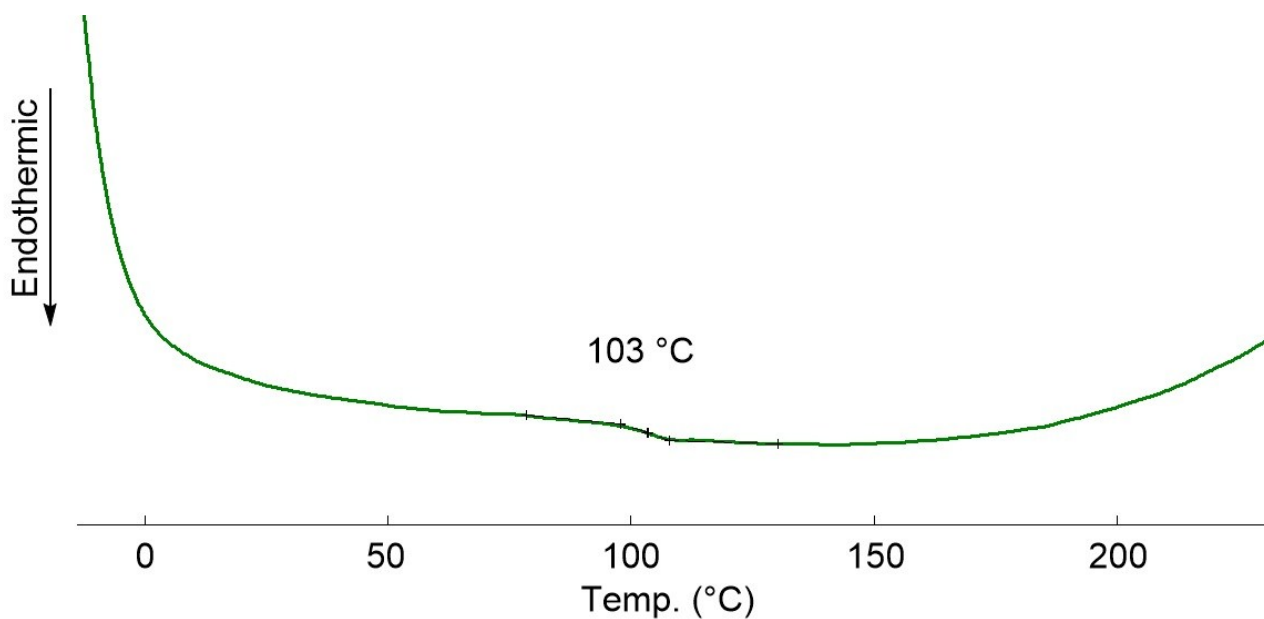


**Figure S10.** Plots of peak intensity ratio at 1.2 ppm ( $I/I_0$ ) versus gradient strength ( $G$ ) on DOSY NMR spectra of end-functionalized poly(norbornene-co-1-octene) treated with **4c**.

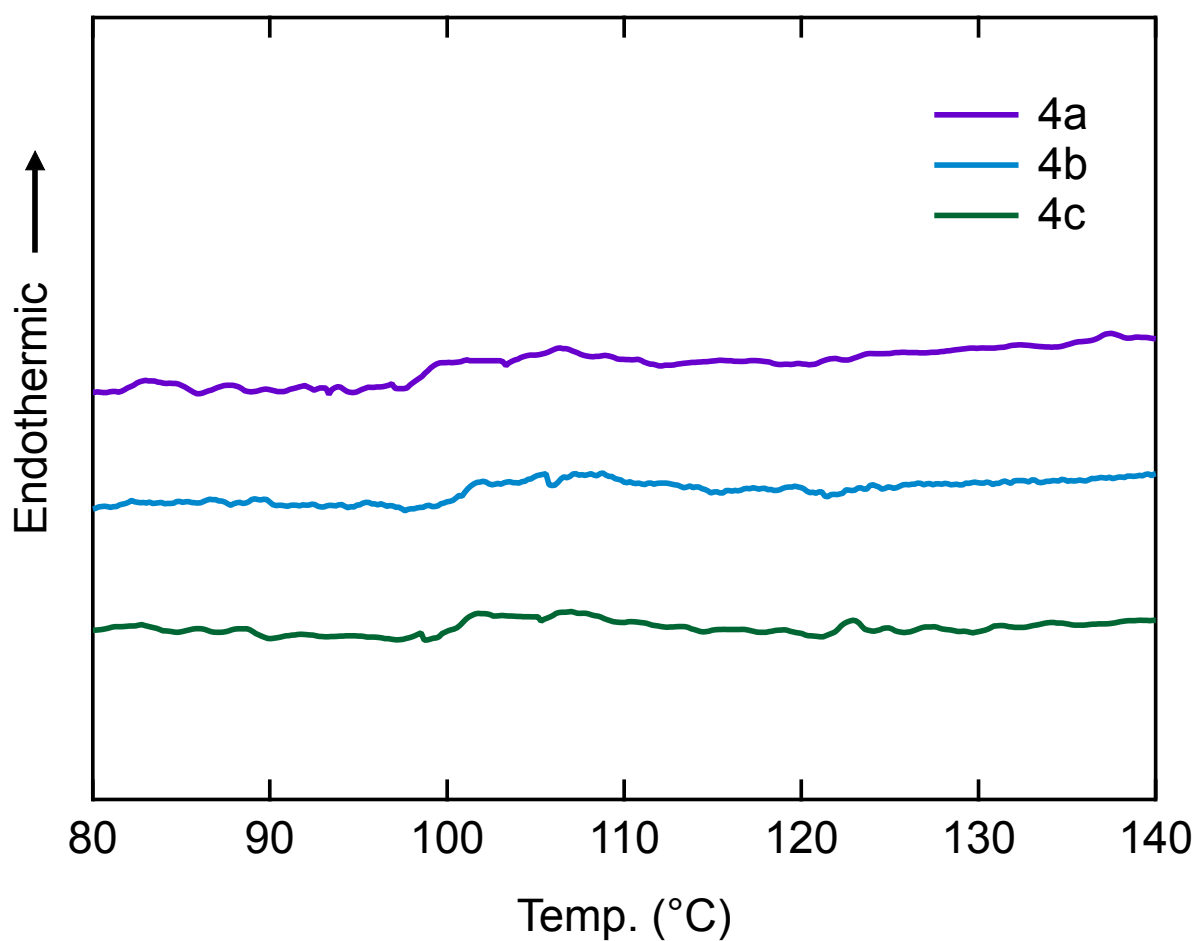


**Figure S11.** Relationship between diffusion coefficient ( $D_t$ ) and molecular weight ( $M_w$ ) of the end-functionalized poly(norbornene-co-1-octene)s treated with various amines.

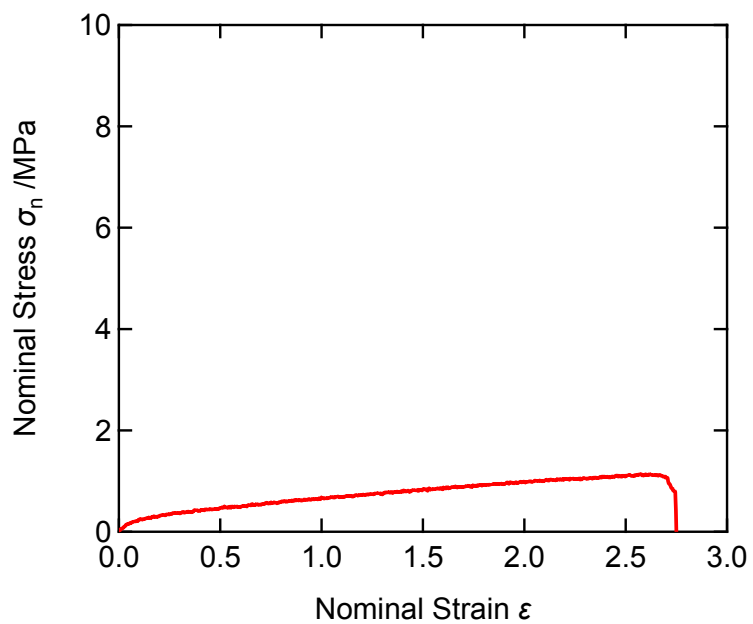




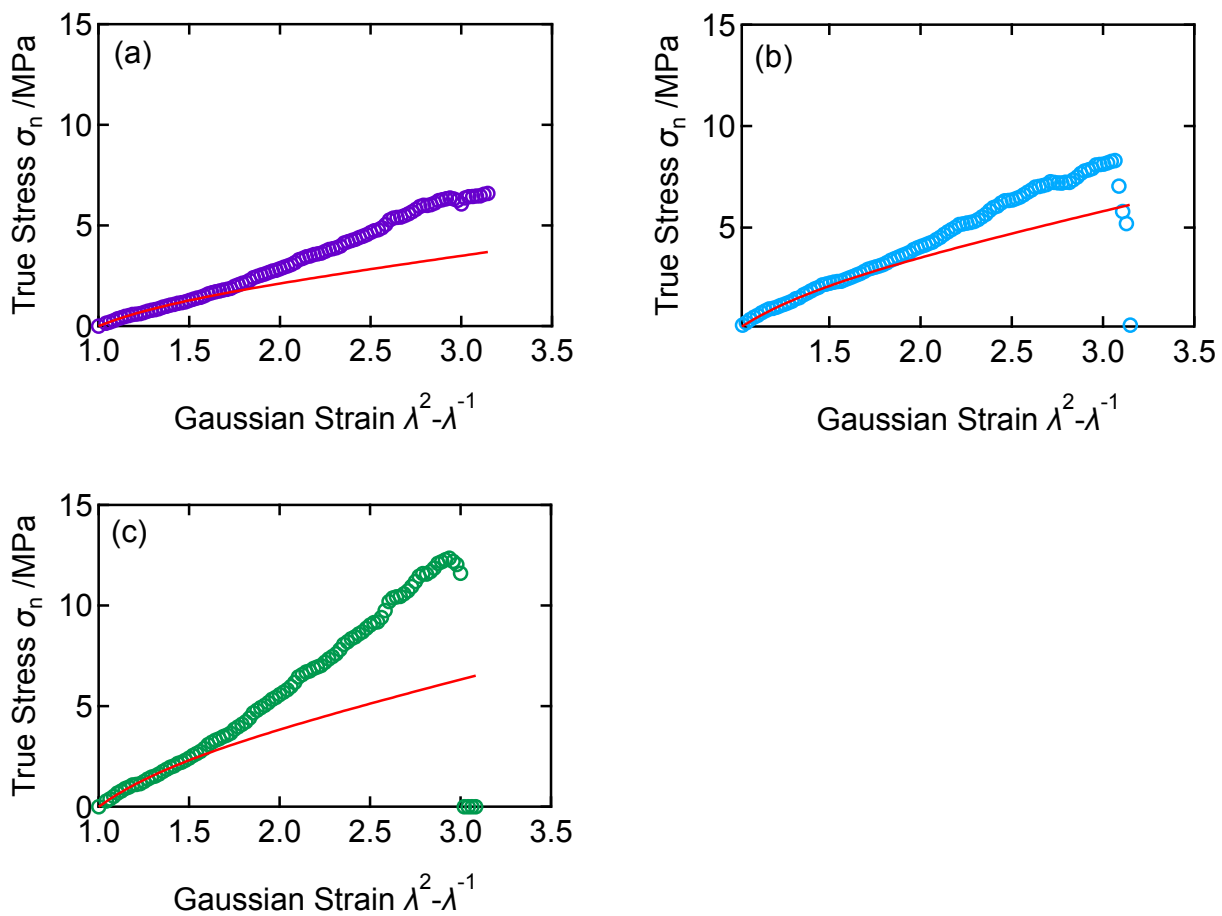
**Figure S12.** DSC thermograms of end-functionalized poly(norbornene-co-1-octene) without additive.



**Figure S13.** DSC thermograms of end-functionalized poly(norbornene-co-1-octene)s treated with **4a-4c**.



**Figure S14.** Nominal stress–strain curve of linear end-functionalized poly(norbornene-co-1-octene) with  $M_n = 74 \times 10^3$  and  $M_w/M_n = 1.24$ . The glass transition temperature is 150 °C.



**Figure S15.** True stress–Gaussian strain curves (circles) with fitting data of affine-network model (red line) for end-functionalized poly(norbornene-co-1-octene)s treated with (a) **4a**, (b) **4b**, and (c) **4c**.