

## Supporting Information for

# One-Pot Cascade Polymerization Based on Addition Reaction of Electrophilic Selenium Reagent to Alkene

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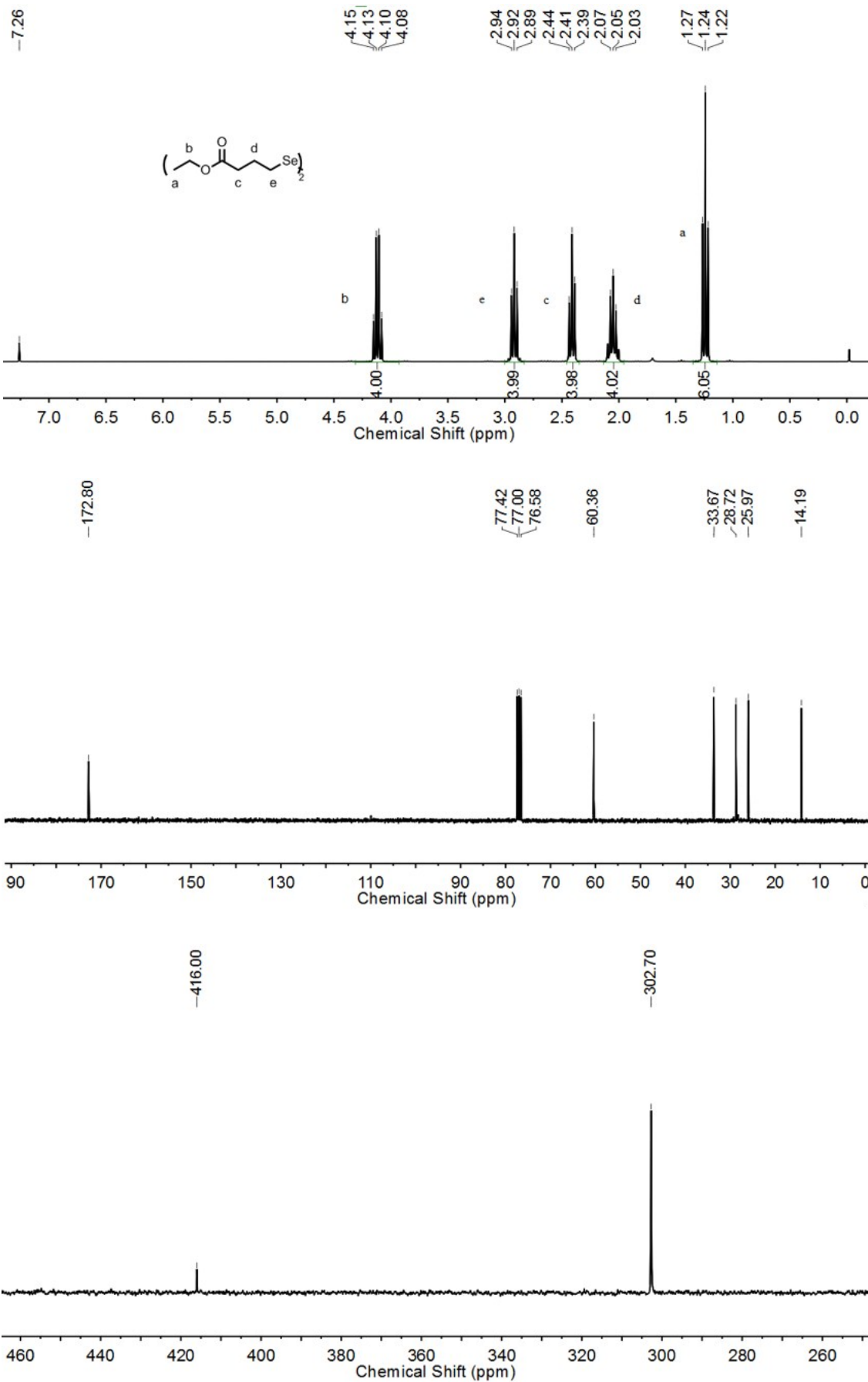


Fig. S1 <sup>1</sup>H, <sup>13</sup>C, and <sup>77</sup>Se NMR spectra of diethyl  $\gamma$ ,  $\gamma'$ -diselenodibutyrate.

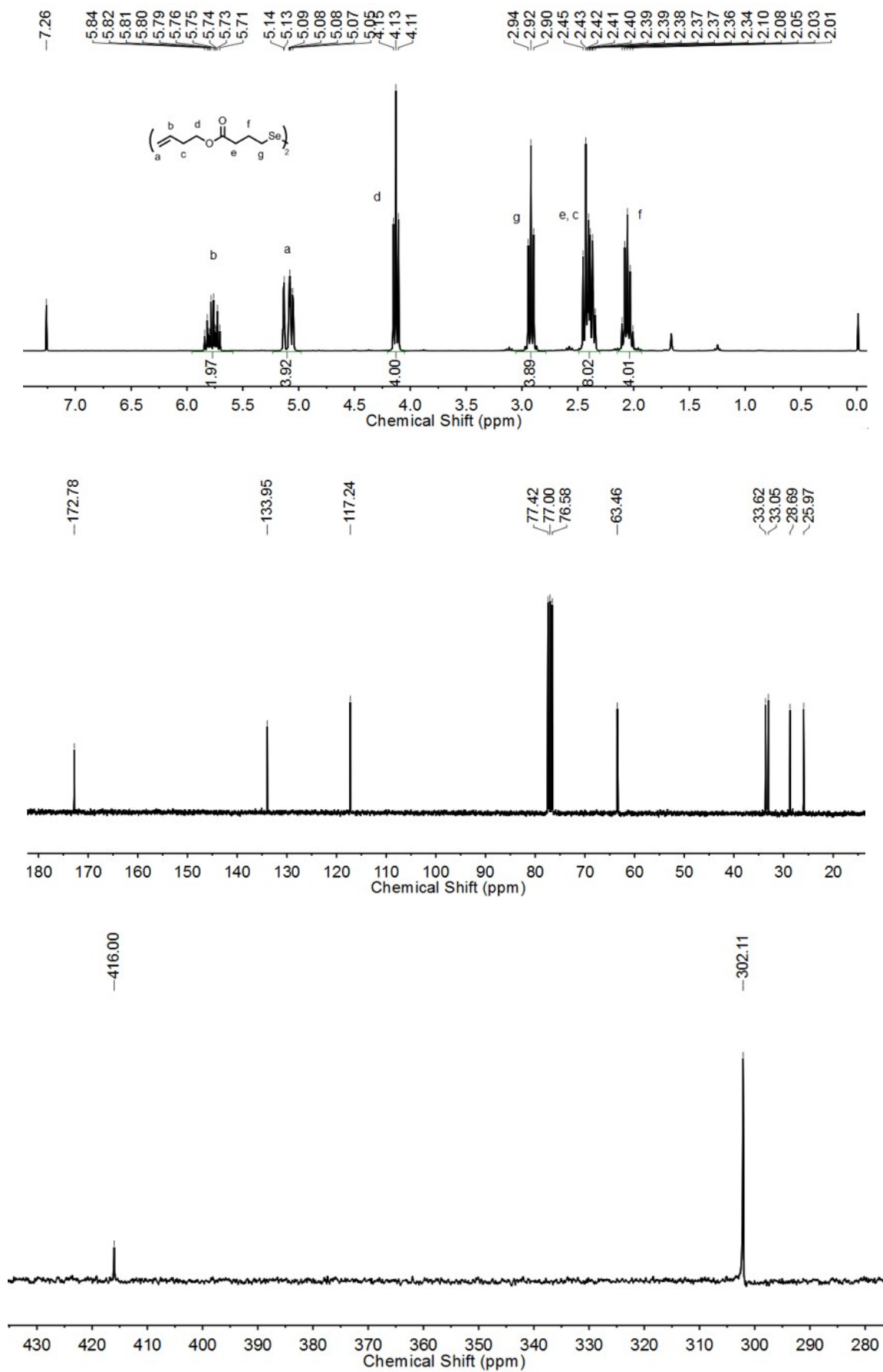


Fig. S2 <sup>1</sup>H, <sup>13</sup>C, and <sup>77</sup>Se NMR spectra of di(but-3-en-1-yl) γ, γ'-diselenodibutyrate.



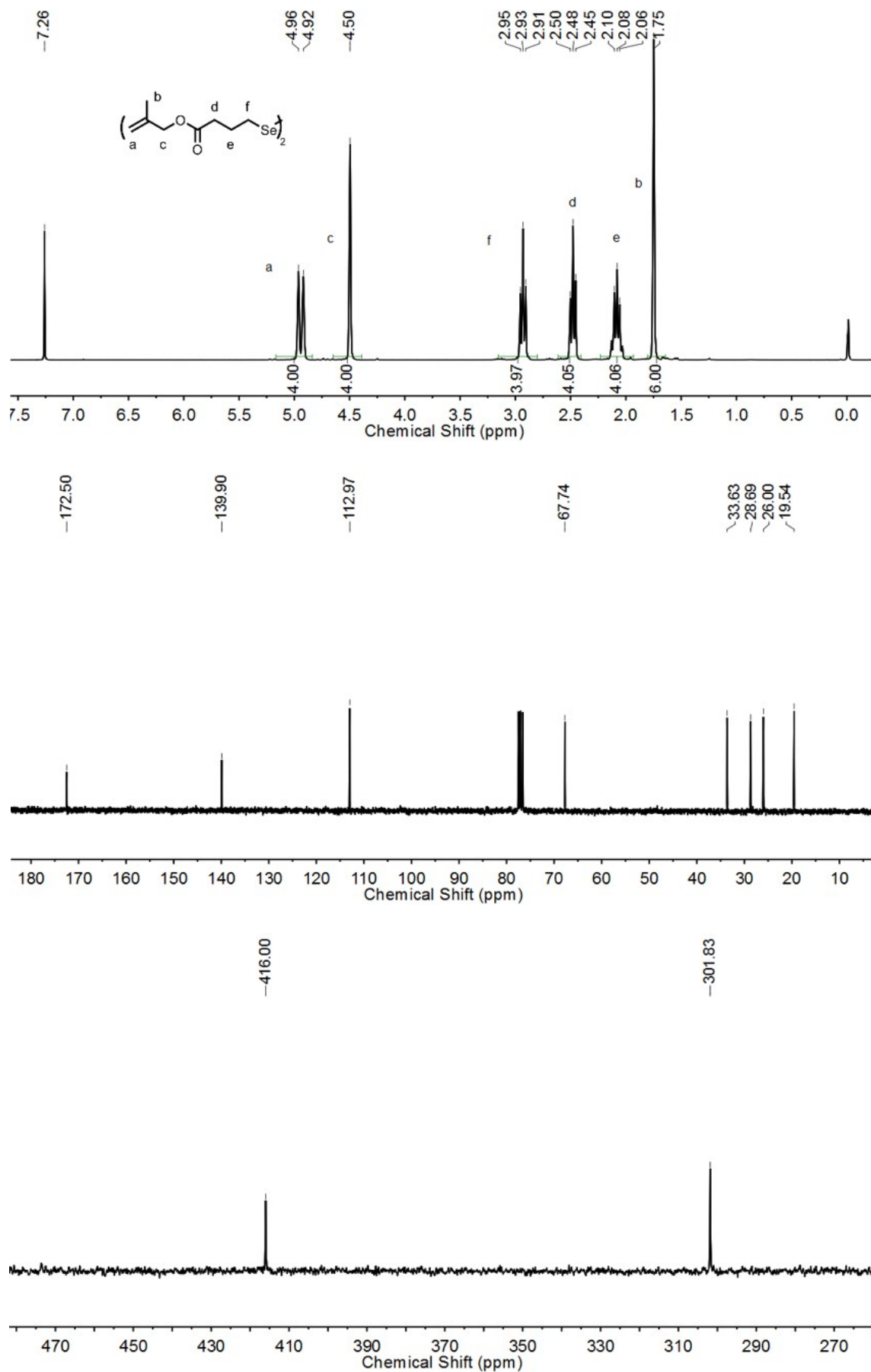


Fig. S4 <sup>1</sup>H, <sup>13</sup>C, and <sup>77</sup>Se NMR spectra of di(2-methylallyl) γ, γ'-diselenodibutyrate.



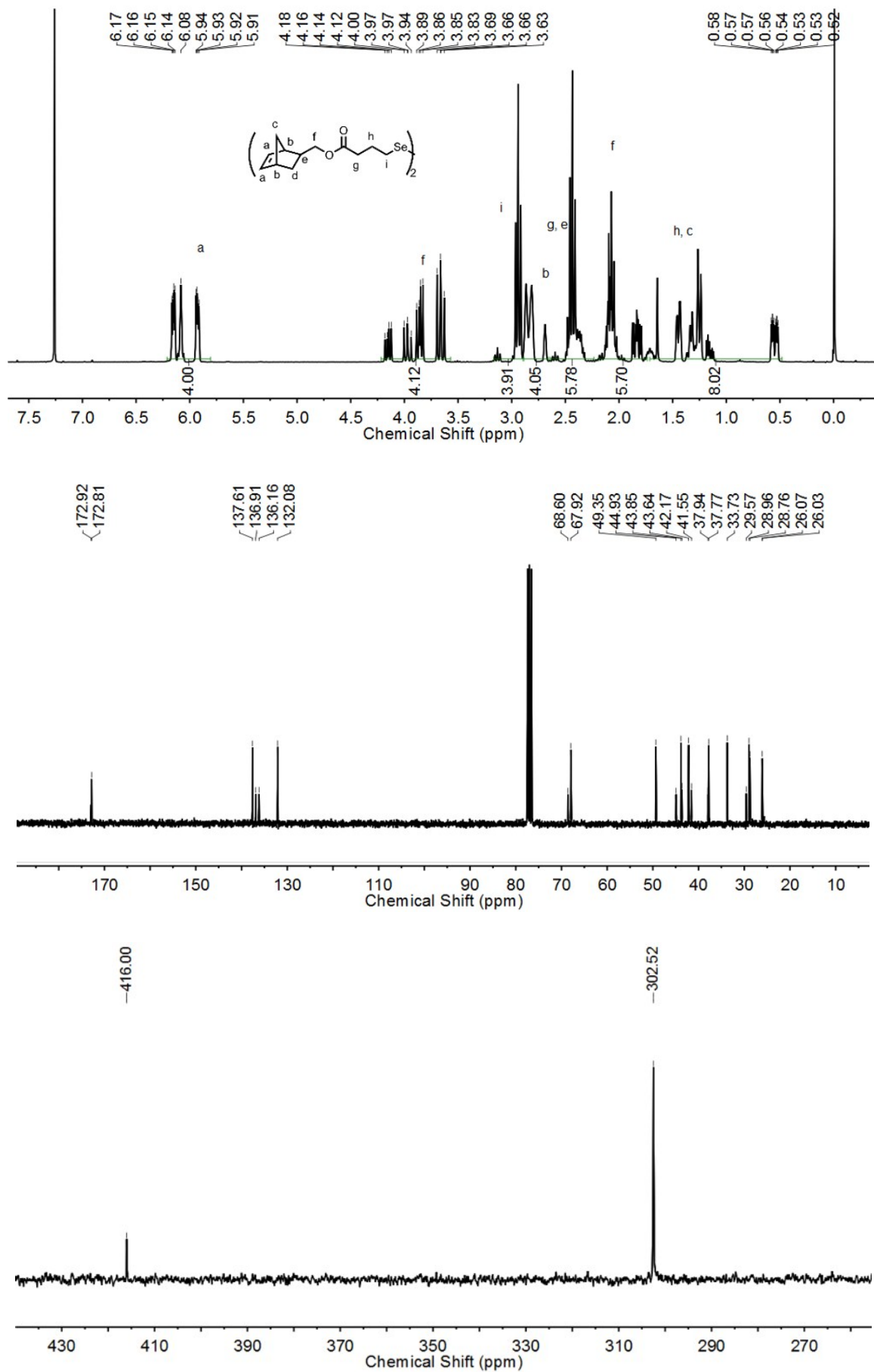


Fig. S6  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{77}\text{Se}$  NMR spectra of di(bicyclo[2.2.1]hept-5-en-2-ylmethyl)  $\gamma, \gamma'$ -diselenodibutyrate.

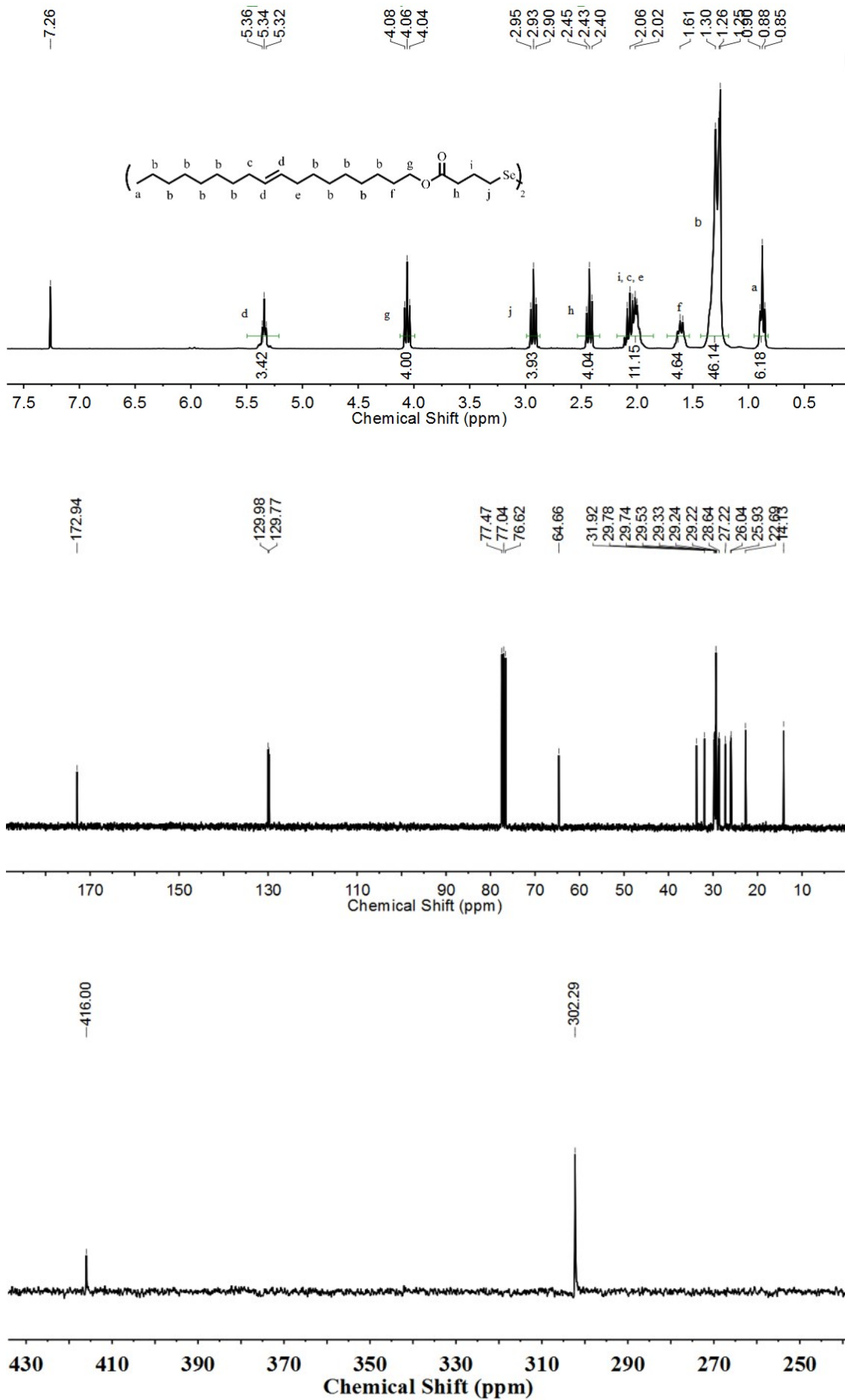


Fig. S7 <sup>1</sup>H, <sup>13</sup>C, and <sup>77</sup>Se NMR spectra of di(9-octadecen-1-yl) γ, γ'-diselenodibutyrate.



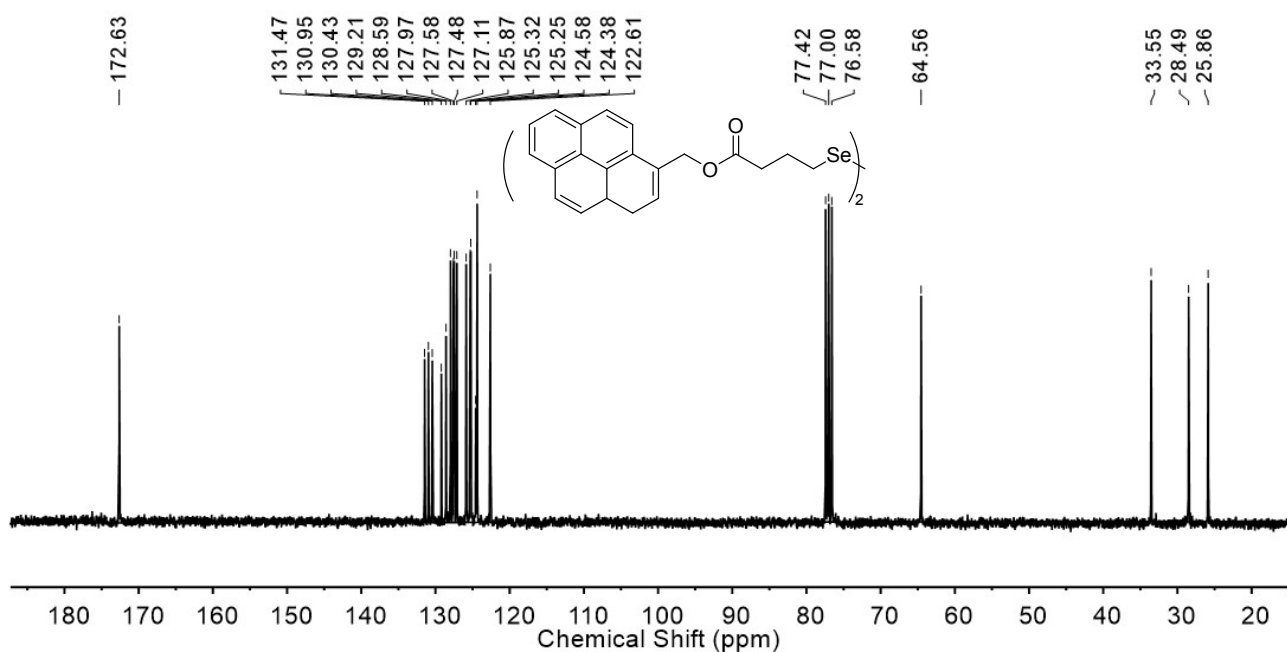
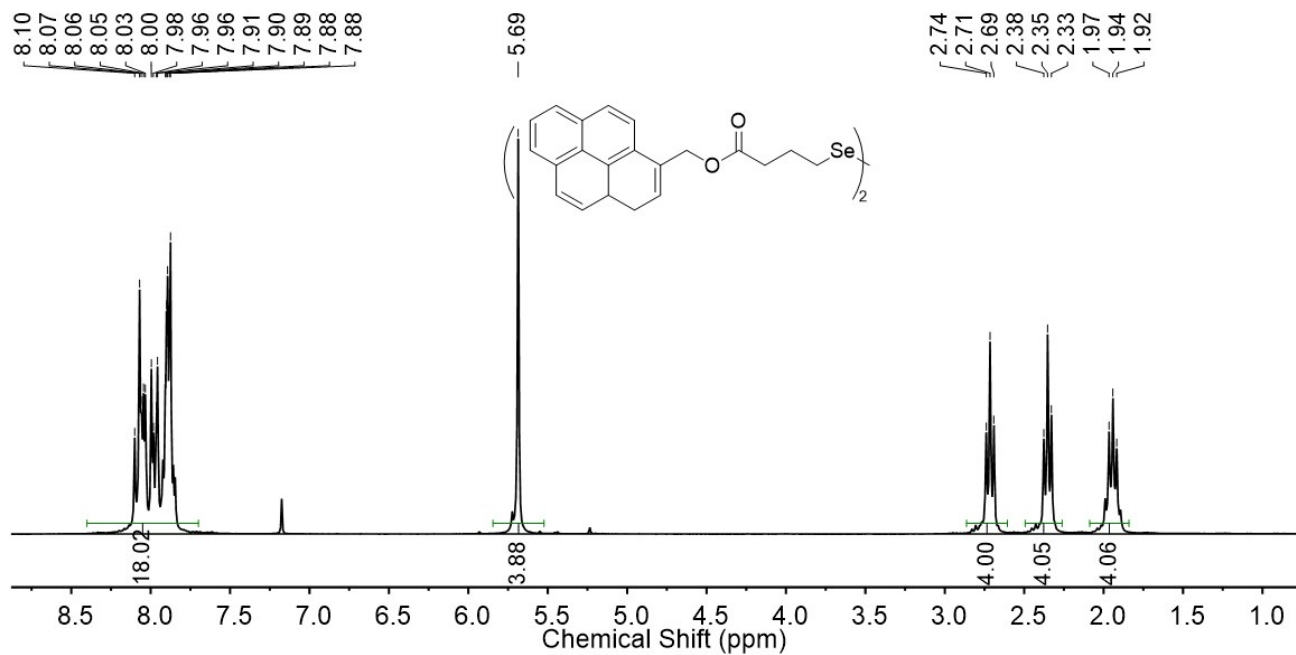


Fig. S8 <sup>1</sup>H and <sup>13</sup>C NMR spectra of di(pyren-1-ylmethyl)  $\gamma$ ,  $\gamma'$ -diselenodibutyrate.



## Model reaction of electrophilic selenium-promoted additions of nucleophiles to 1-hexene

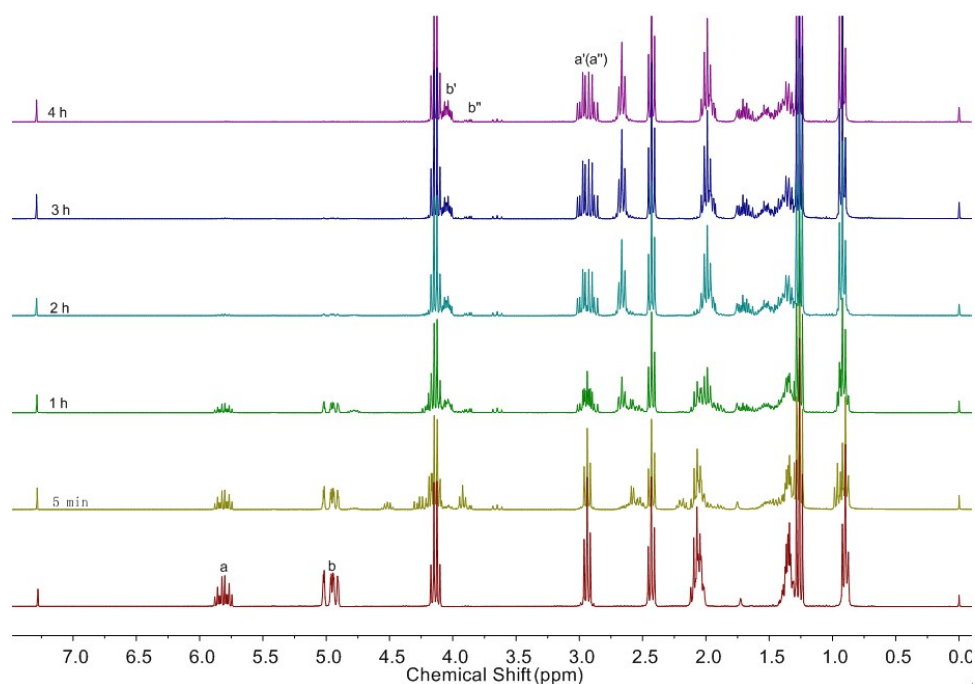
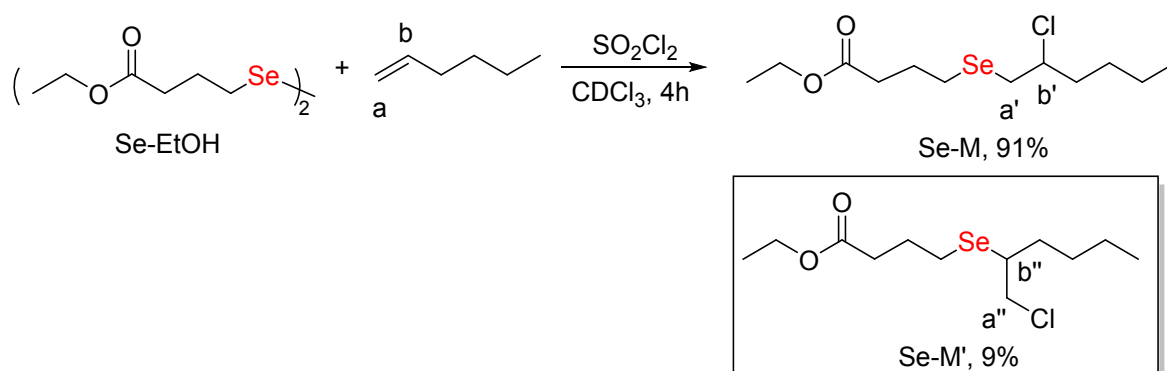


Fig. S10  $^1\text{H}$  NMR spectra of the reaction solution with the molar ratio of [diethyl  $\gamma, \gamma'$ -diselenodibutyrate] $_0$  : [1-hexene] $_0$  : [sulfonyl chloride] $_0$  = 1:1:1 at room temperature in  $\text{CDCl}_3$ . The chemoselective conversions were determined using  $^1\text{H}$  NMR spectra by comparing the integrated characteristic signals of proton  $b'$  (4.01 ppm) and  $b''$  (3.86 ppm).

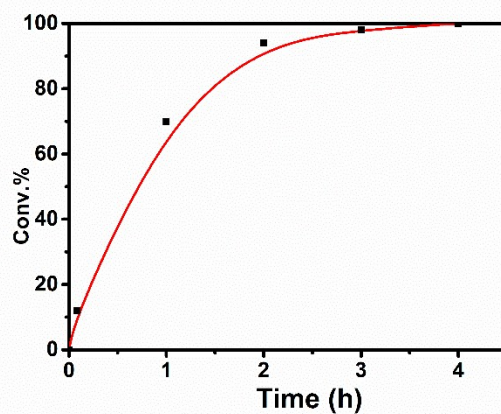


Fig. S11 Plot of conversion versus time for the one pot reaction of diethyl  $\gamma, \gamma'$ -diselenodibutyrate, 1-hexene, and sulfonyl chloride according to Fig. S10.

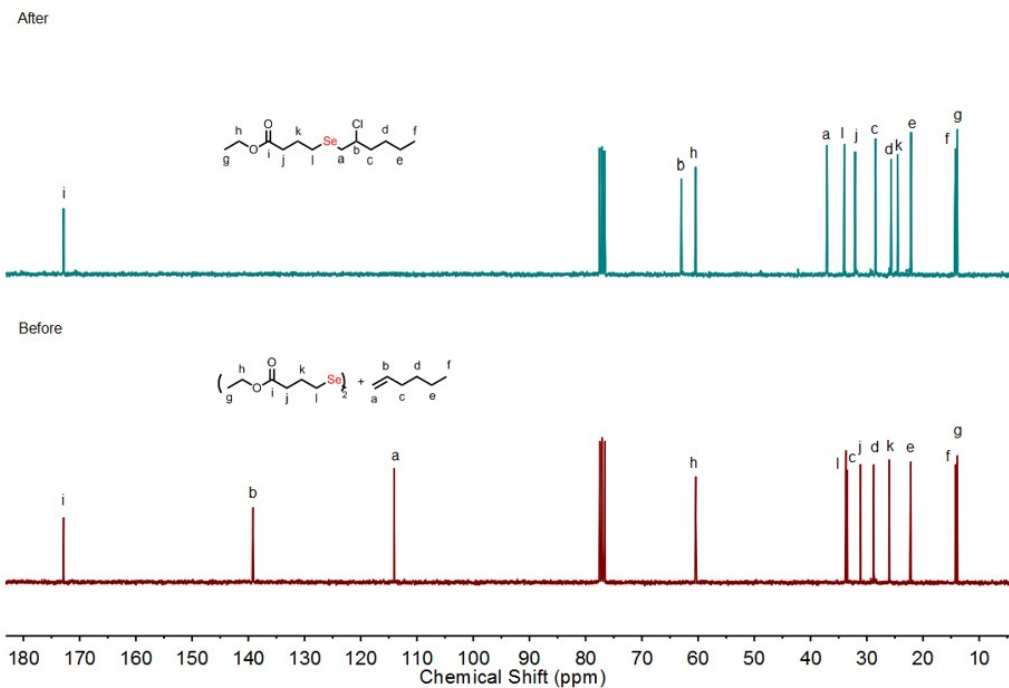


Fig. S12  $^{13}\text{C}$  NMR spectra of the mixture of diethyl  $\gamma, \gamma'$ -diselenodibutyrates and 1-hexene before and after the addition of sulfonyl chloride in  $\text{CDCl}_3$ .

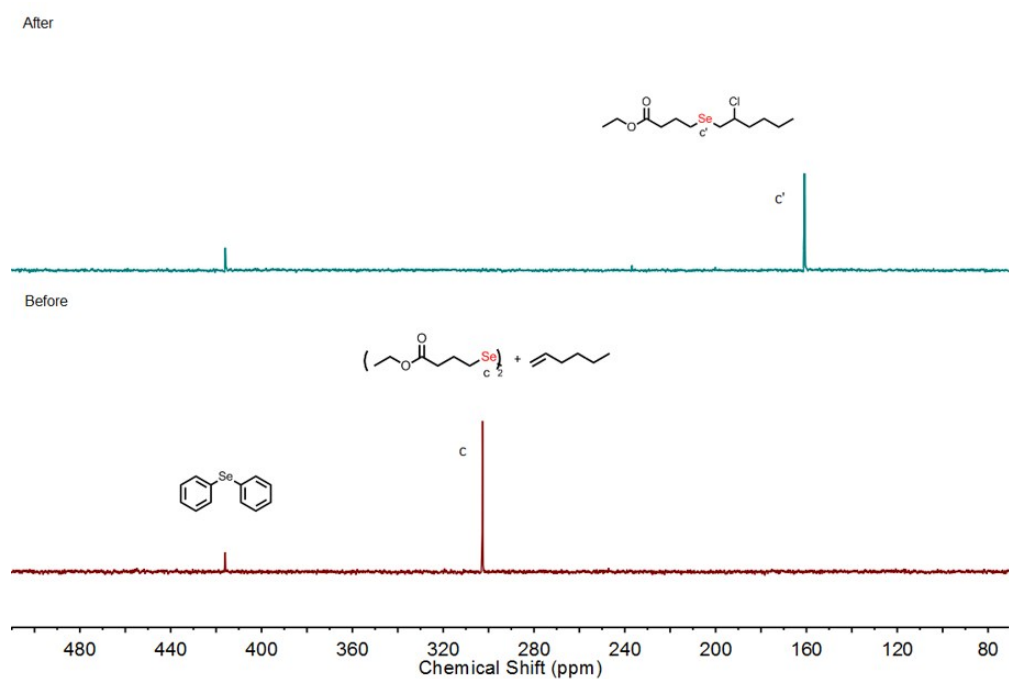


Fig. S13  $^{77}\text{Se}$  NMR spectra of the mixture of diethyl  $\gamma, \gamma'$ -diselenodibutyrates and 1-hexene before and after the addition of sulfonyl chloride in  $\text{CDCl}_3$ .

## One-pot stepwise polymerization of the electrophilic selenium reagents to alkenes

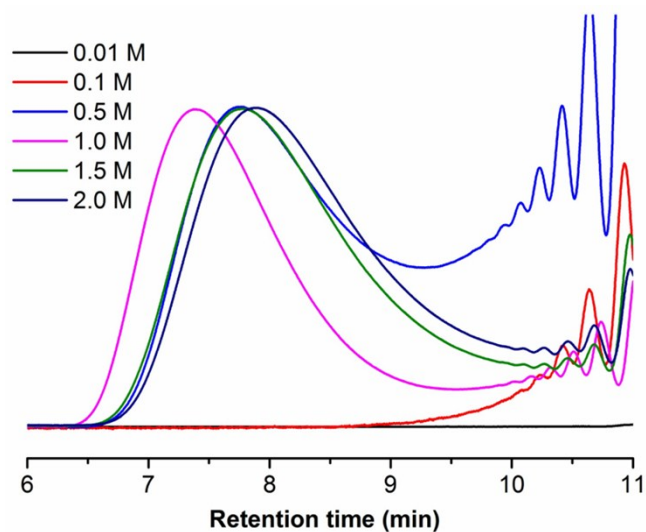


Fig. S14 SEC curves of polymer PSe-2 obtaining in different monomer concentration.

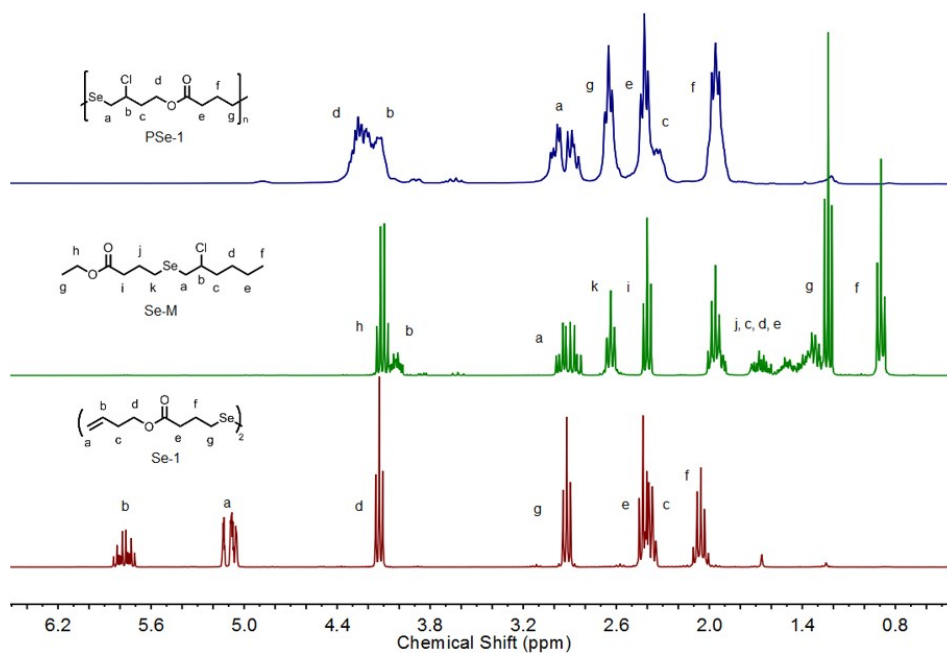


Fig. S15 <sup>1</sup>H NMR spectra of polymer PSe-1, model compound Se-M, and monomer Se-1.

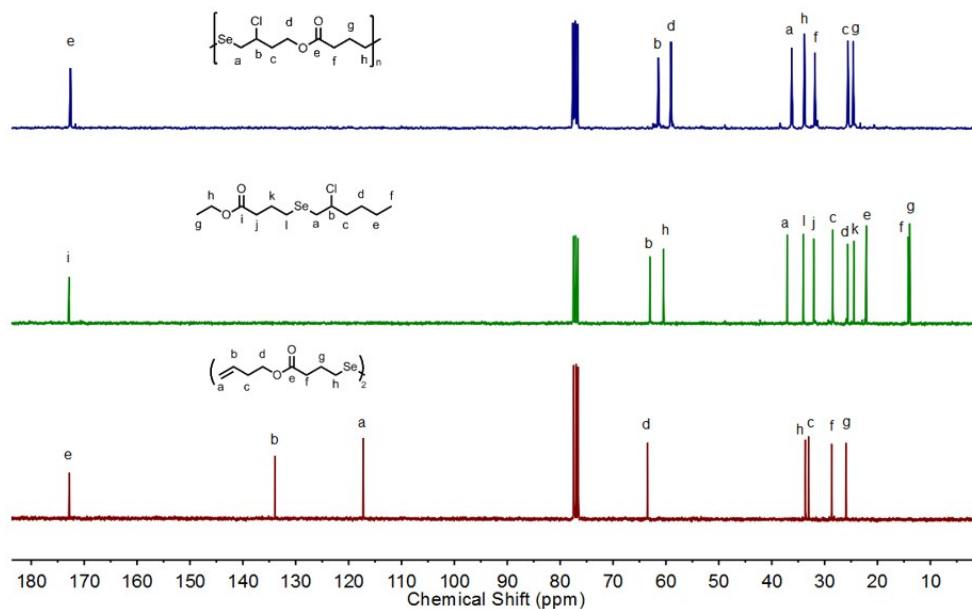


Fig. S16  $^{13}\text{C}$  NMR spectra of polymer PSe-1, model compound Se-M, and monomer Se-1.

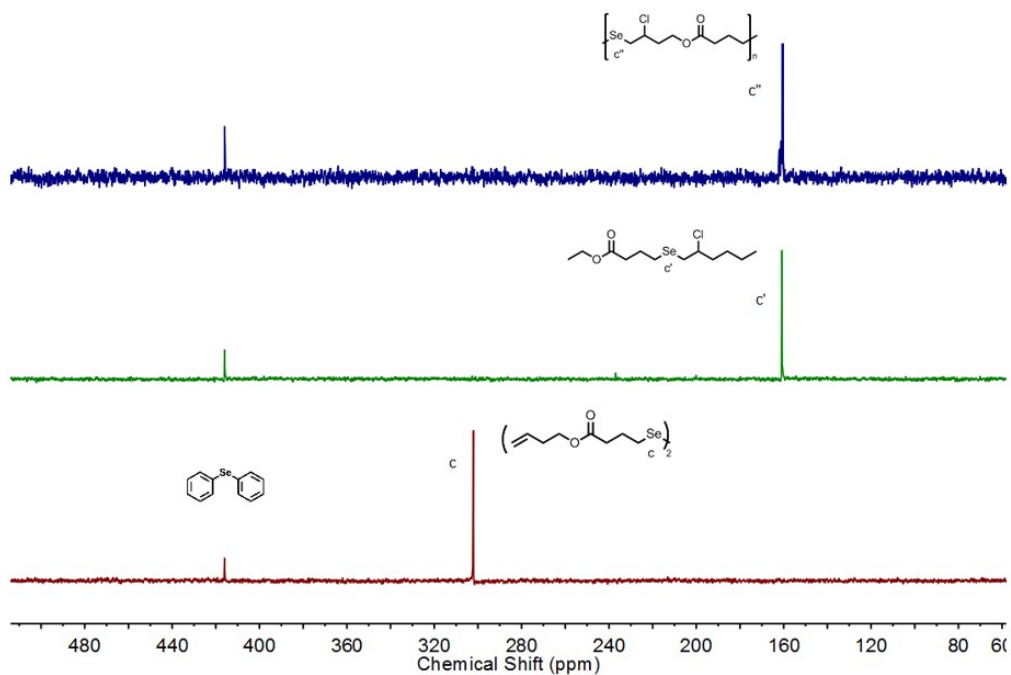


Fig. S17  $^{77}\text{Se}$  NMR spectra of polymer PSe-1, model compound Se-M, and monomer Se-1.

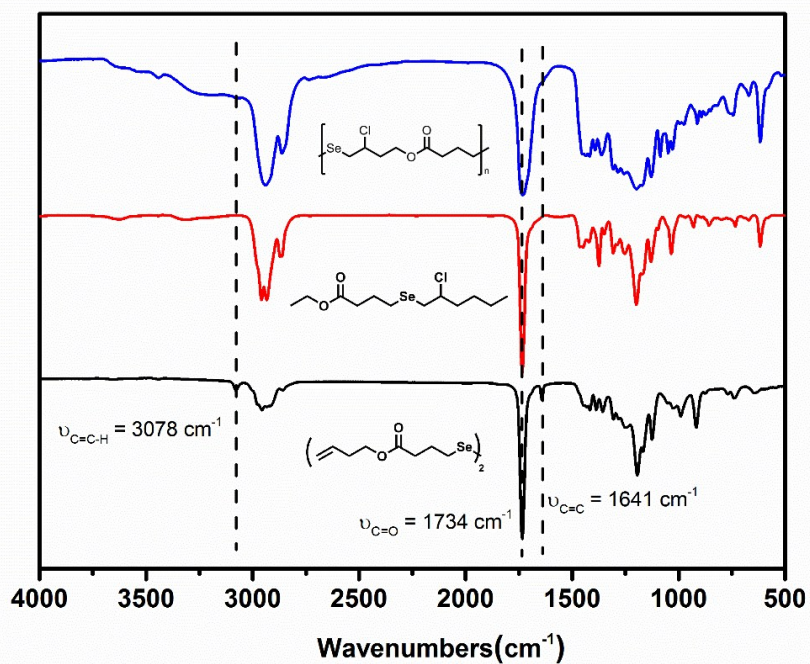


Fig. S18 FTIR spectra of polymer PSe-1, model compound Se-M, and monomer Se-1.

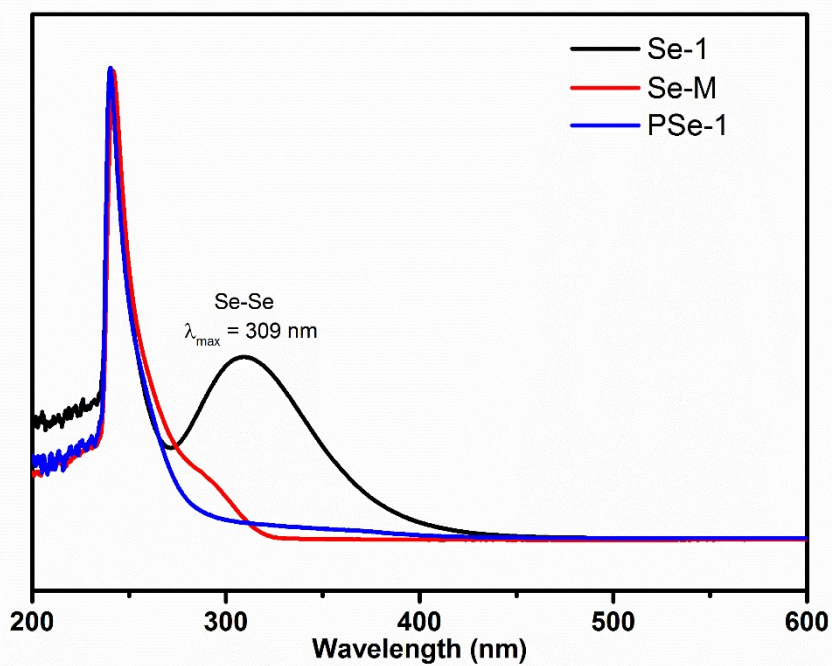


Fig. S19 UV spectra of monomer Se-1, model compound Se-M, and polymer PSe-1.

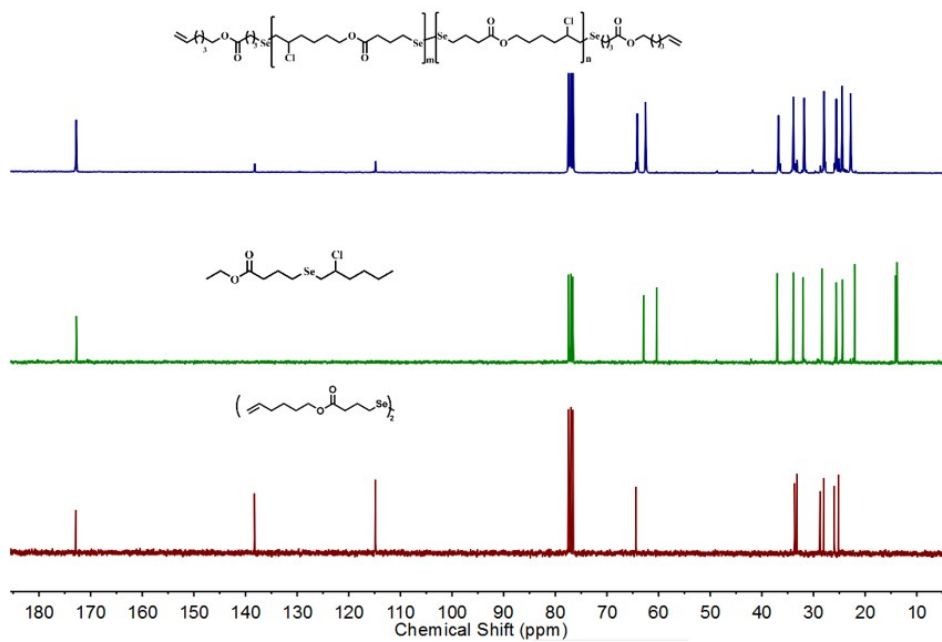


Fig. S20.  $^{13}\text{C}$  NMR spectra of polymer PSe-2, model compound Se-M, and monomer Se-2.

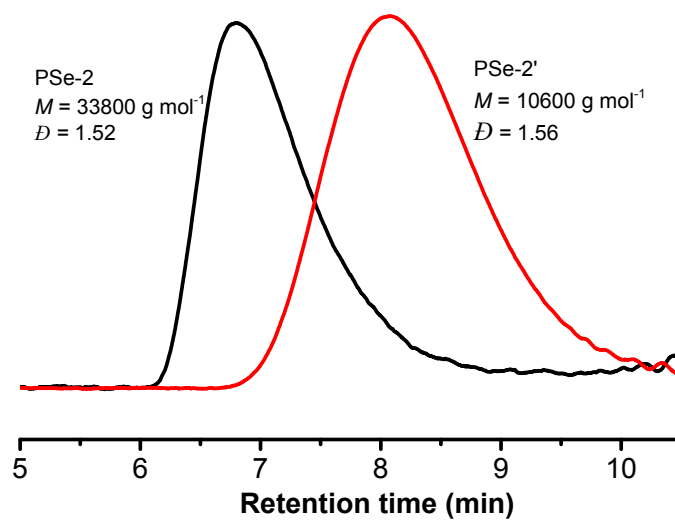


Fig. S21. SEC curves of PSe-2 and PSe-2' obtained with different molar ratio of  $[\text{Se-2}]_0 : [\text{SO}_2\text{Cl}_2]_0$  (1:1 for PSe-2, 1:0.97 for PSe-2' ) after 24 hours in  $\text{CDCl}_3$ .



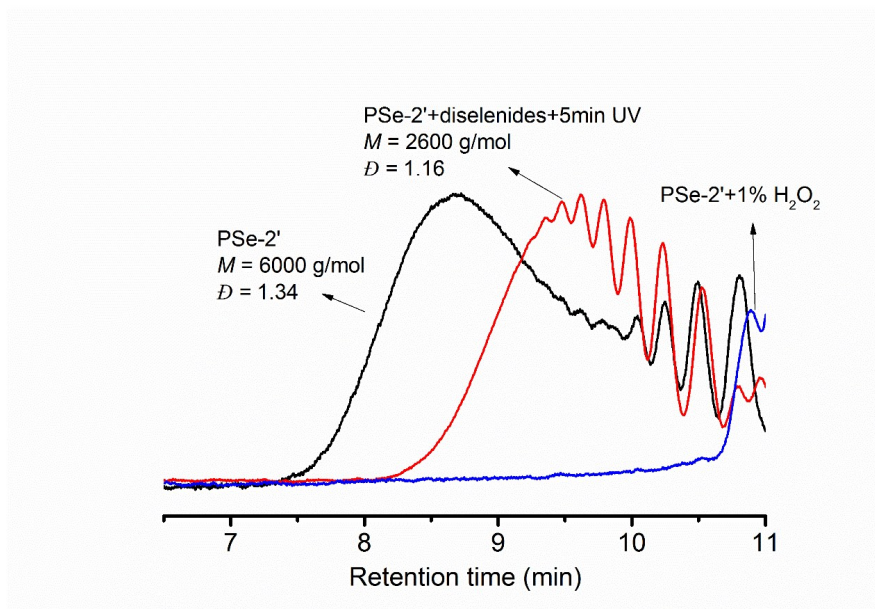


Fig. S22 SEC curves of PSe-2' before and after treating with diphenyl diselenide under irradiation for 5 min.

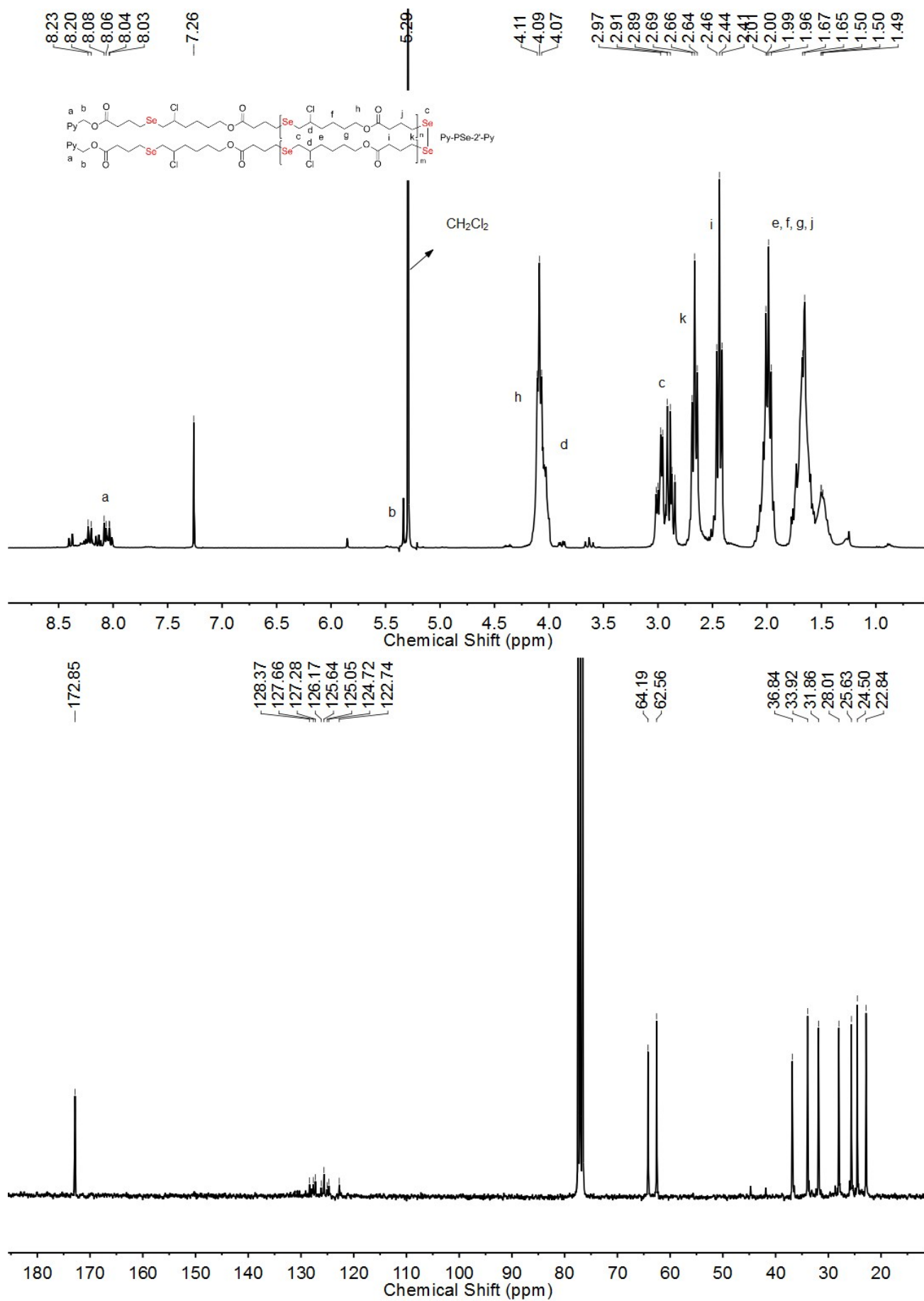


Fig. S23 <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of polymer Py-PSe-2'-Py

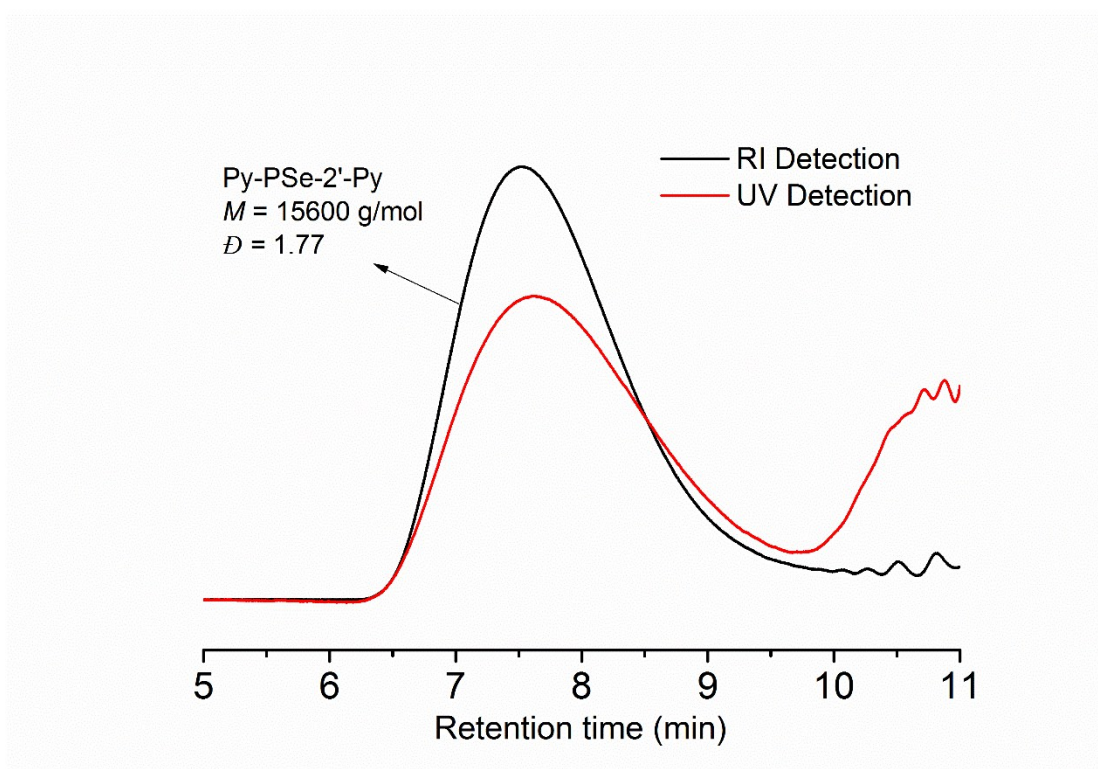


Fig. S24 SEC curves of Py-PSe-2'-Py which was measured by RI detection and UV detection at the wavelength of 340 nm.

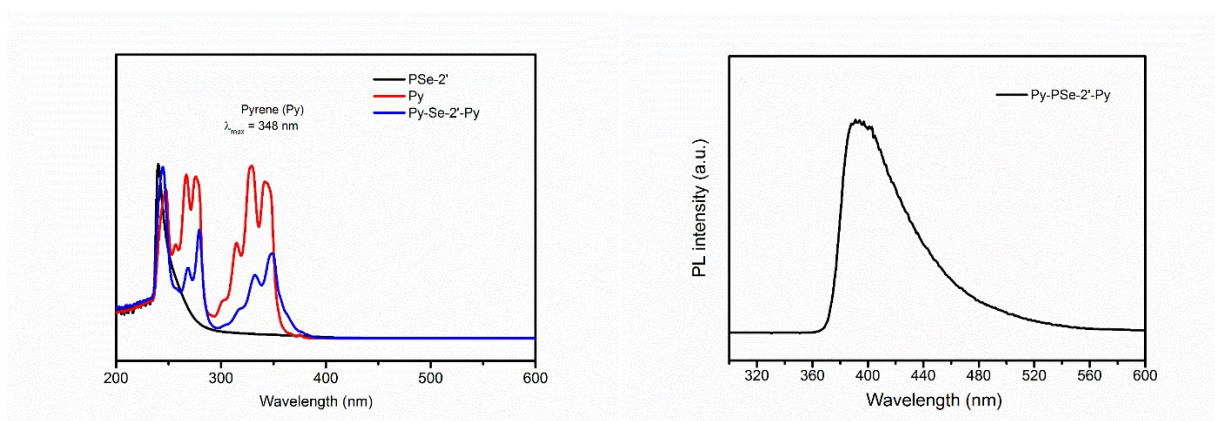


Fig. S25 a) UV spectra of monomer PSe-2', Py, and Py-PSe-2'-Py. b) Photoluminescence (PL) Properties of Py-PSe-2'-Py in  $\text{CHCl}_3$ . Concentration:  $0.5 \mu\text{M}$ .  $\lambda_{ex} = 390$  nm.

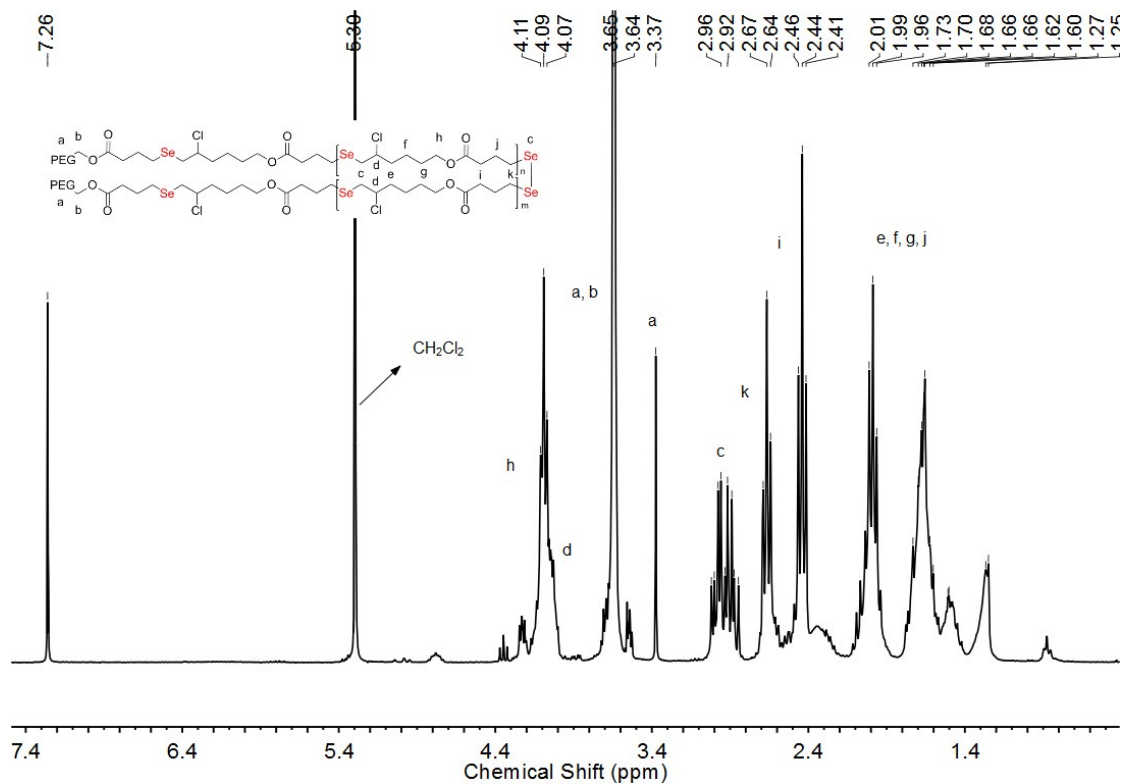


Fig. S26 <sup>1</sup>H NMR spectrum of polymer PEG-PSe-2'-PEG in CDCl<sub>3</sub>

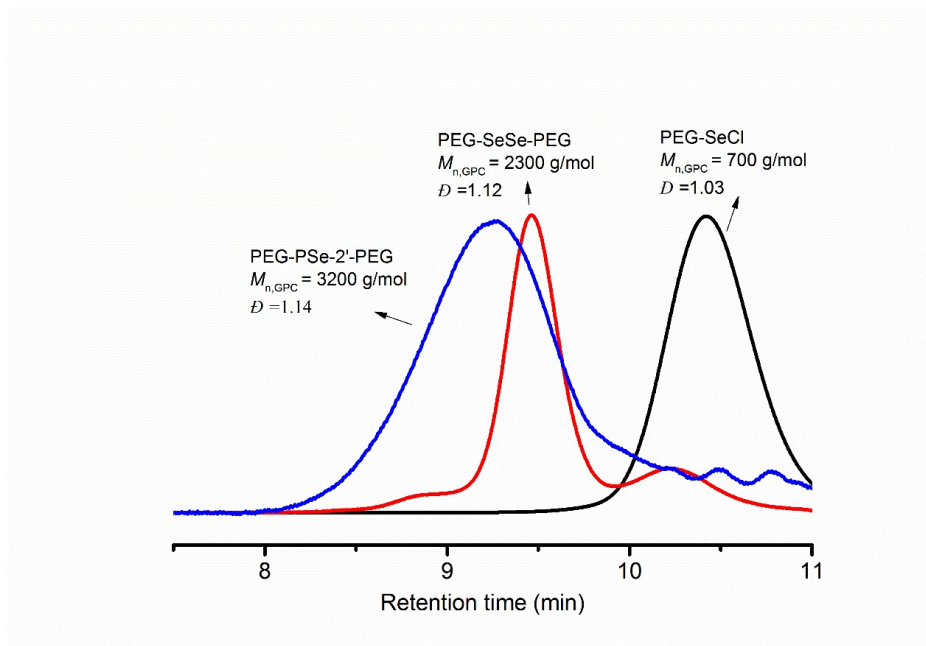


Fig. S27 SEC curves of PEG-SeCl, PEG-SeSe-PEG and PEG-PSe-2'-PEG obtaining with the molar ratio of [Se-2]<sub>0</sub> : [PEG-SeSe-PEG]<sub>0</sub> = 10:1 after 24 hours in CH<sub>2</sub>Cl<sub>2</sub>.

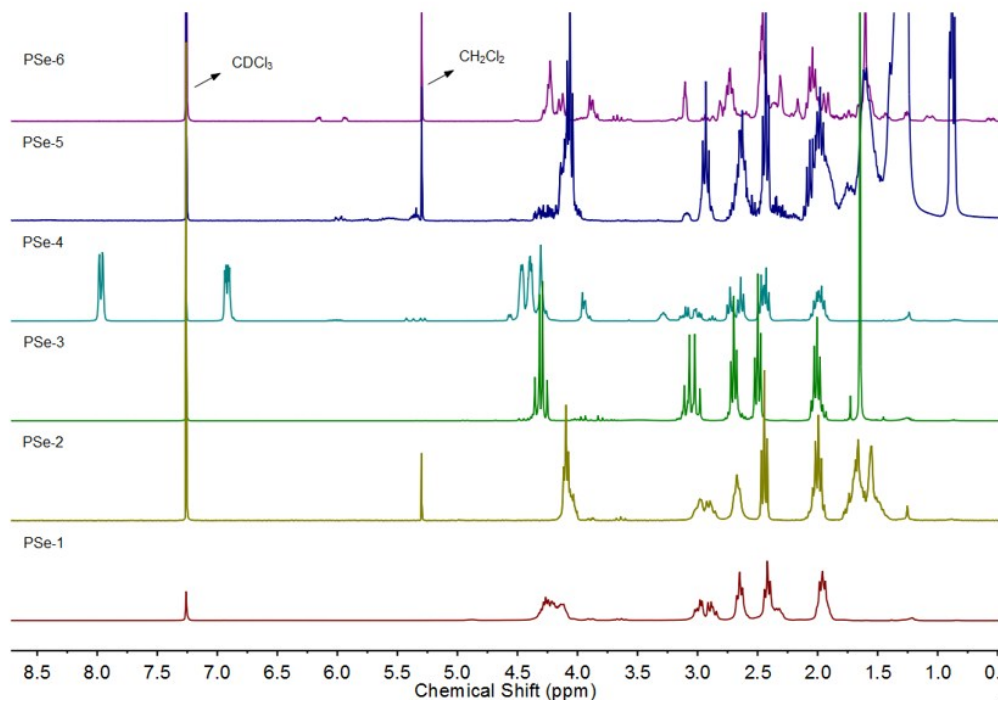


Fig. S28 <sup>1</sup>H NMR spectra of PSe-1, PSe-2, PSe-3, PSe-4, PSe-5 and PSe-6.

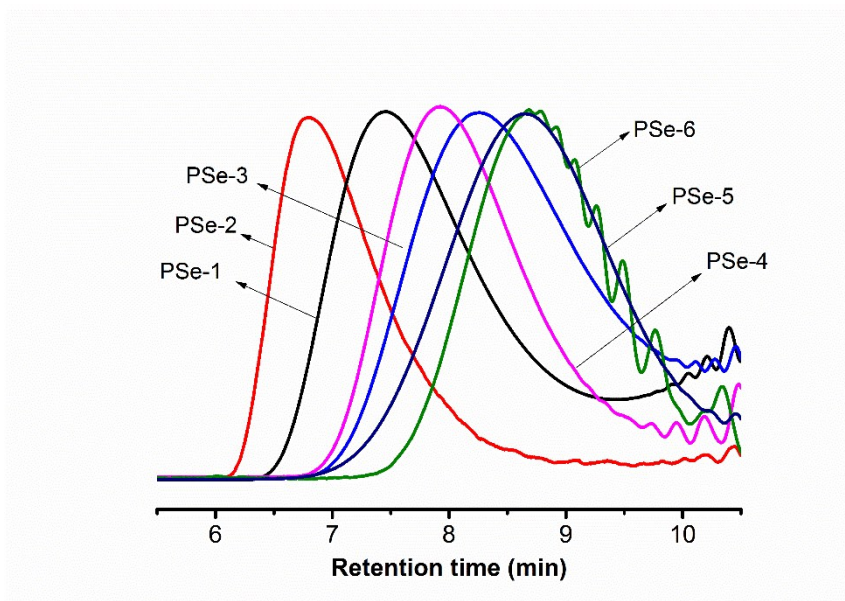


Fig. S29 SEC spectra of PSe-1, PSe-2, PSe-3, PSe-4, PSe-5, PSe-6.

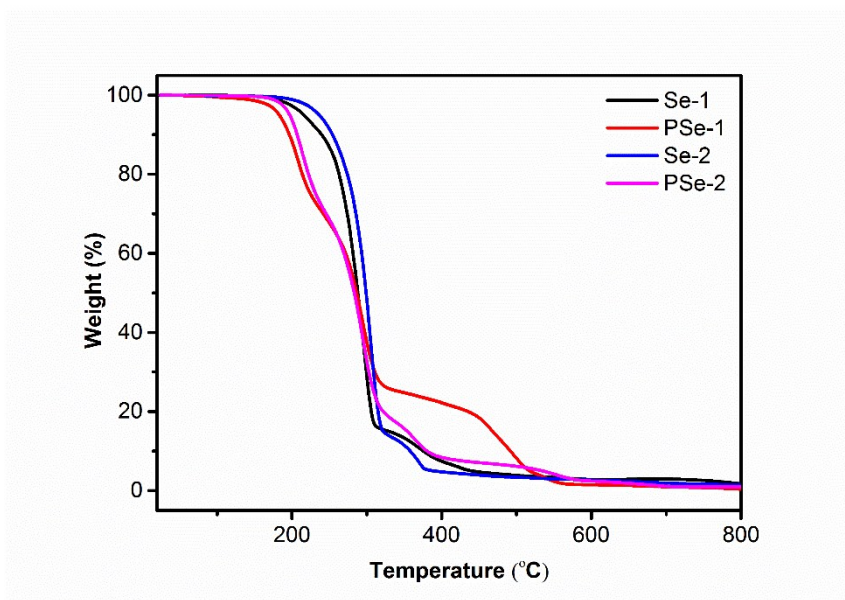


Fig. S30 TGA spectra of Se-1, PSe-1, Se-2, and PSe-2.

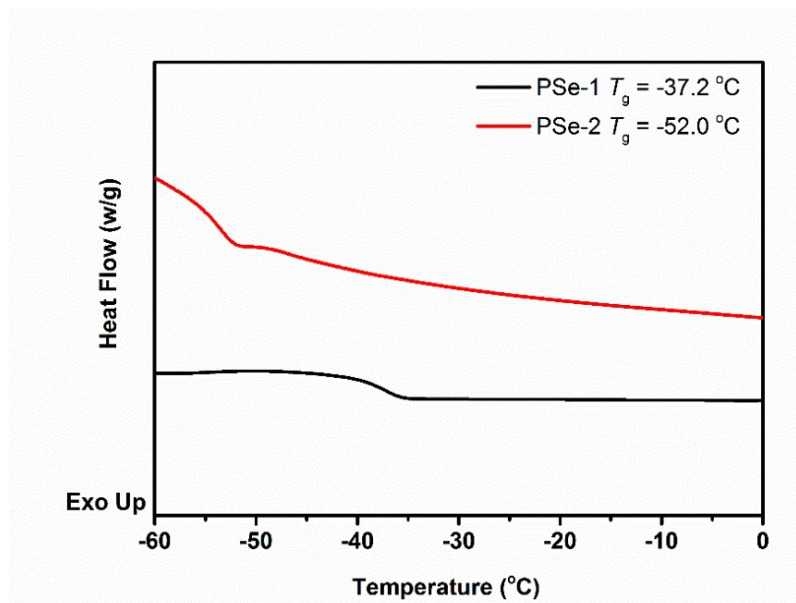


Fig. S31 DSC spectra of PSe-1 and PSe-2 at a ramp rate of  $10$  °C  $\text{min}^{-1}$ .