Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting information for:

Regioselective cross metathesis for block and heterotelechelic polymer synthesis

Madalyn R. Radlauer, Megan E. Matta, and Marc A. Hillmyer*

Department of Chemistry, University of Minnesota, Minneapolis, MN 55455-0431

* Corresponding author: hillmyer@umn.edu

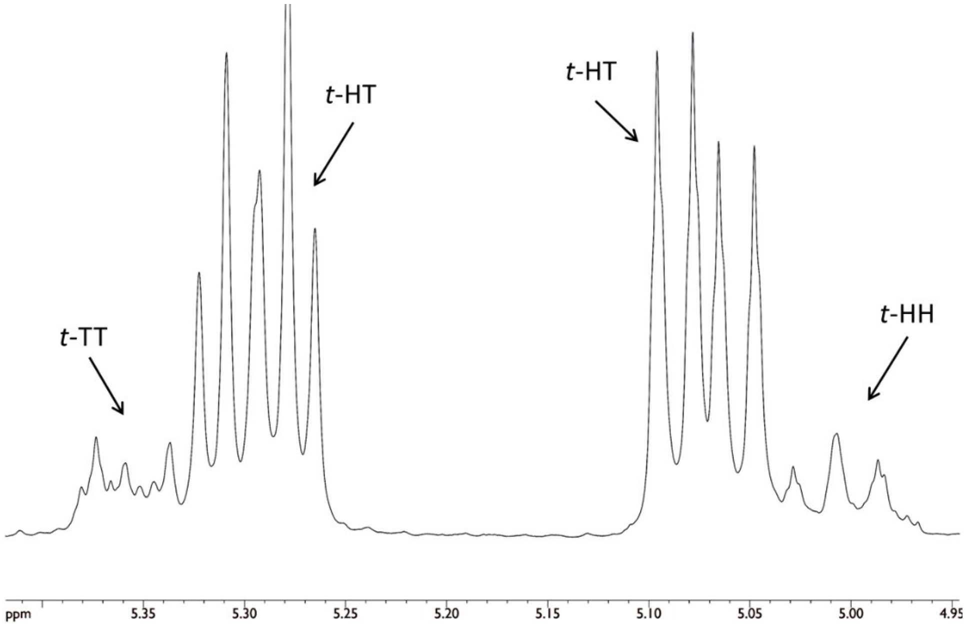

Figure S1. Assignment of *trans*-tail-to-tail (*t*-TT), *trans*-head-to-head (*t*-HH), and *trans*-head-to-tail (*t*-HT) olefinic peaks in the ^{1}H NMR spectrum of poly(3EtCOE).

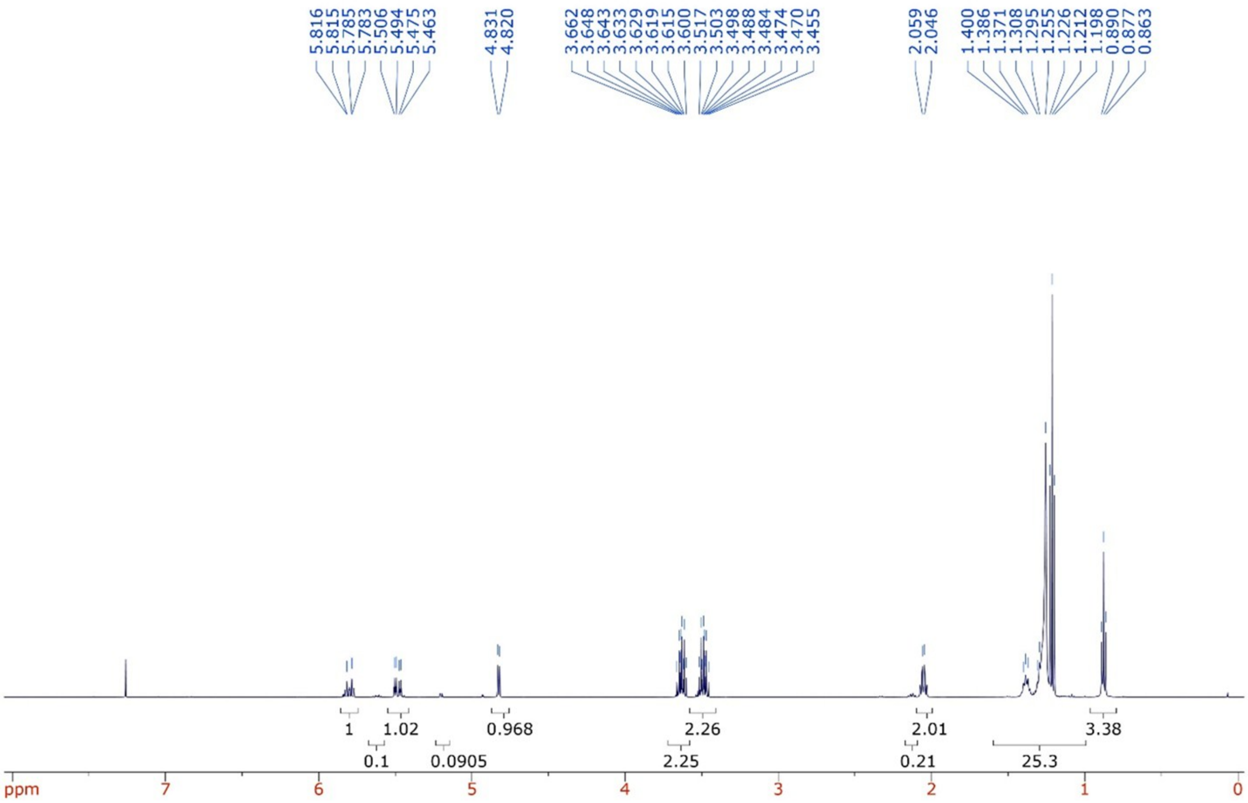

Figure S2. ^{1}H NMR spectrum of 1,1-diethoxytridec-2-ene with a 10:1 E/Z ratio.

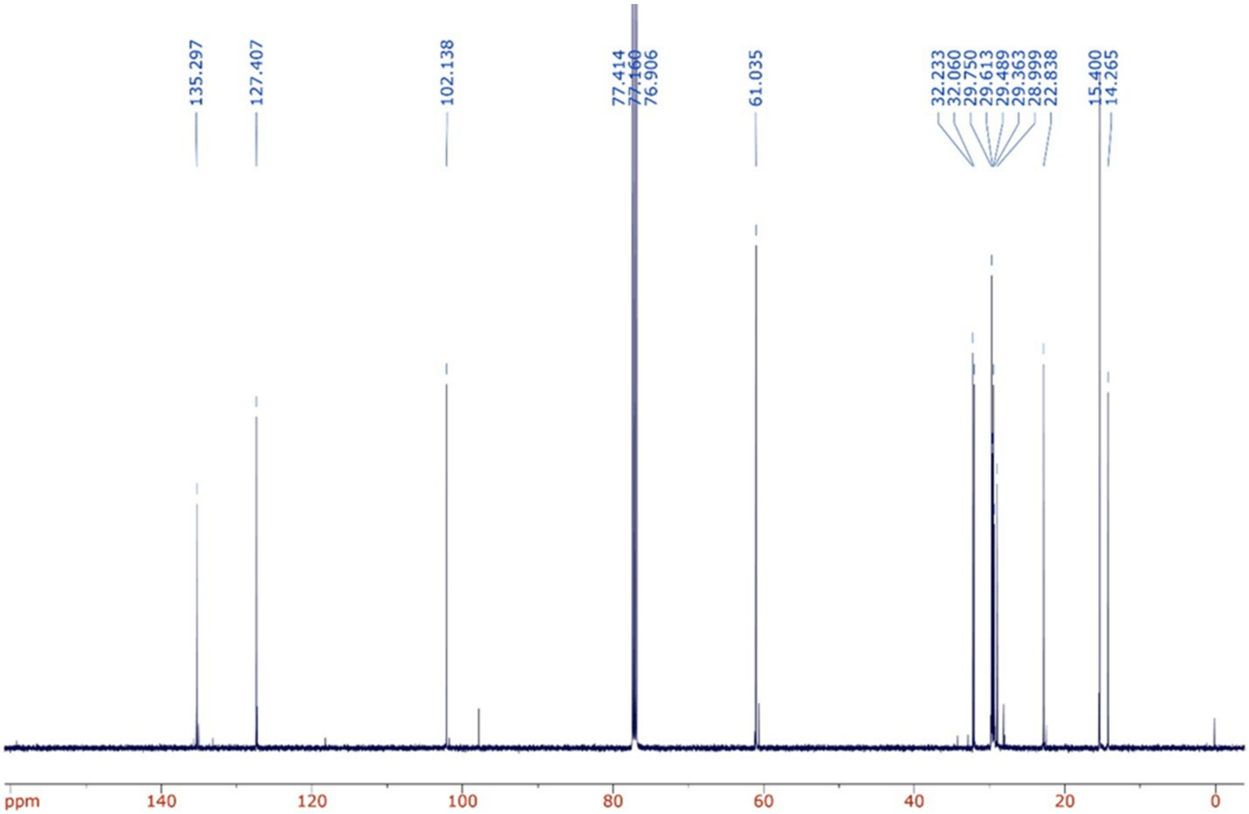

Figure S3. ^{13}C NMR spectrum of 1,1-diethoxytridec-2-ene with a 10:1 E/Z ratio.

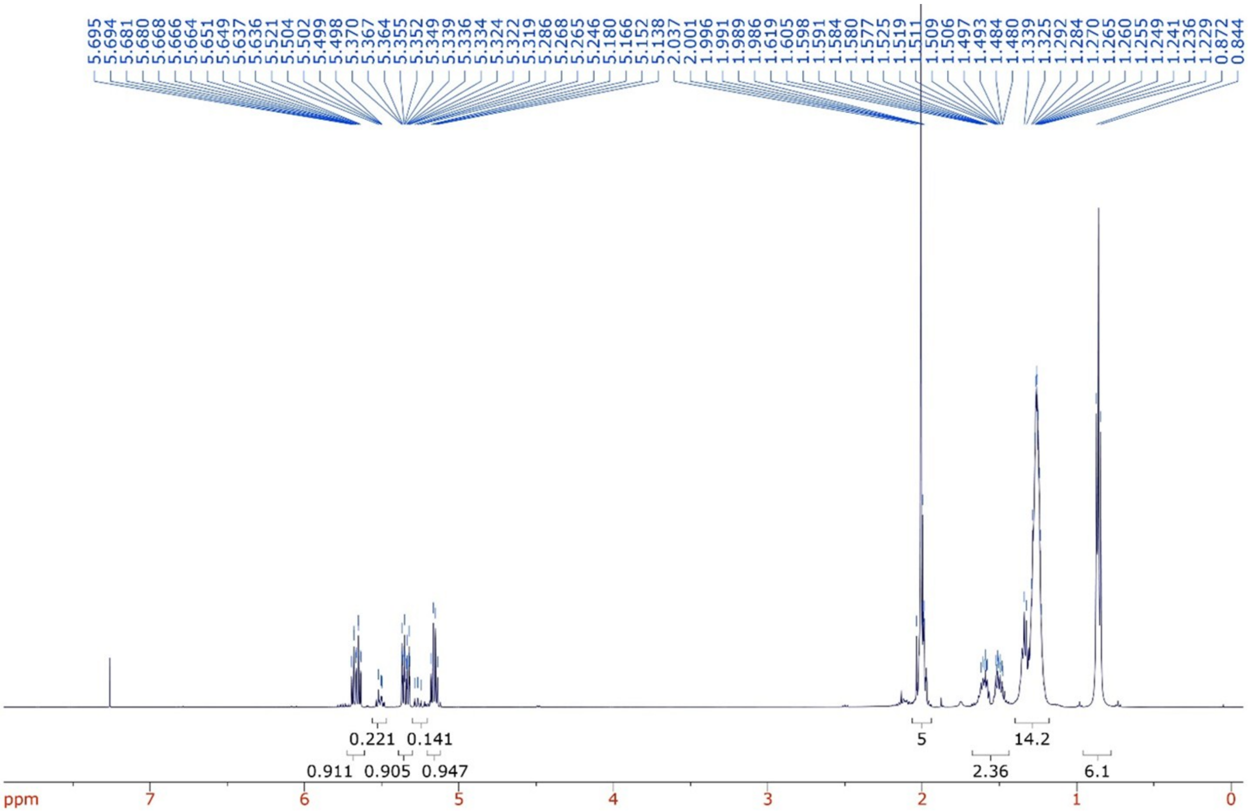

Figure S4. ^{1}H NMR spectrum of 7-tetradecen-6-yl acetate with a 4:1 E/Z ratio.

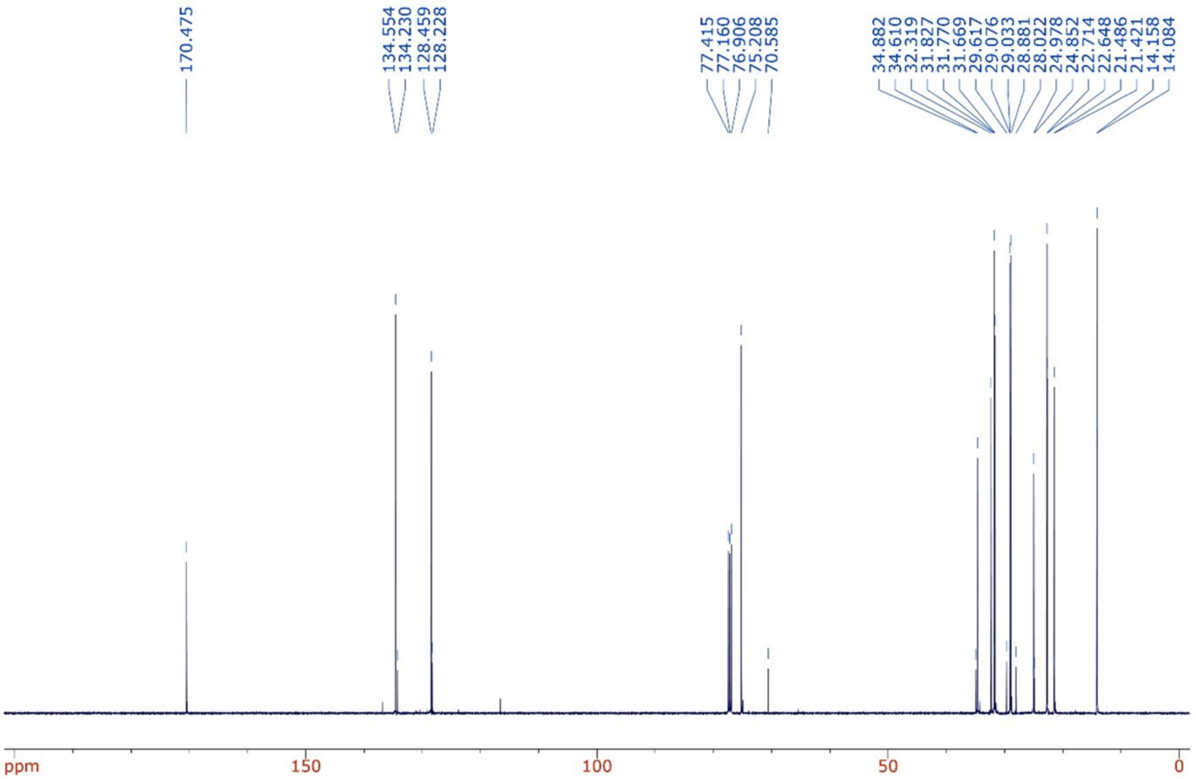

Figure S5. ^{13}C NMR spectrum of 7-tetradecen-6-yl acetate with a 4:1 E/Z ratio.

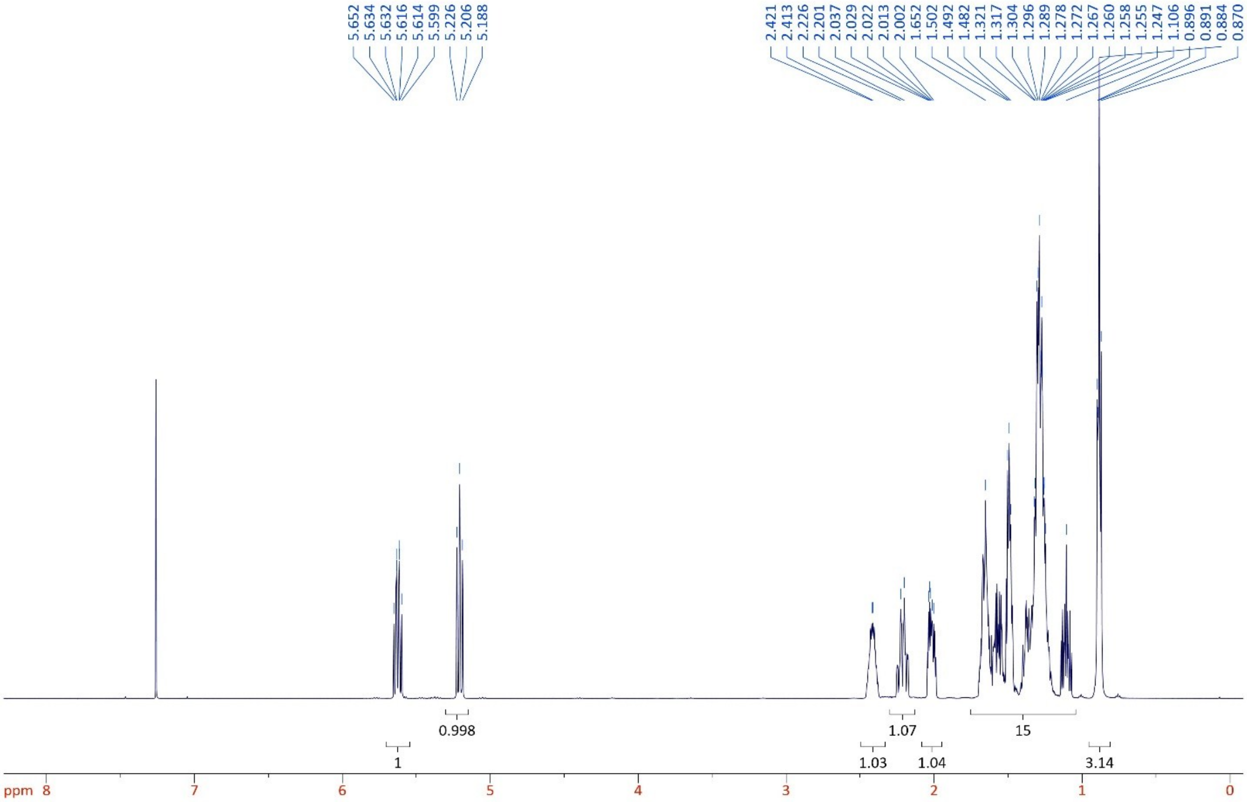

Figure S6. ^{1}H NMR spectrum of 3-n-butyl-cyclooctene (3nBuCOE).

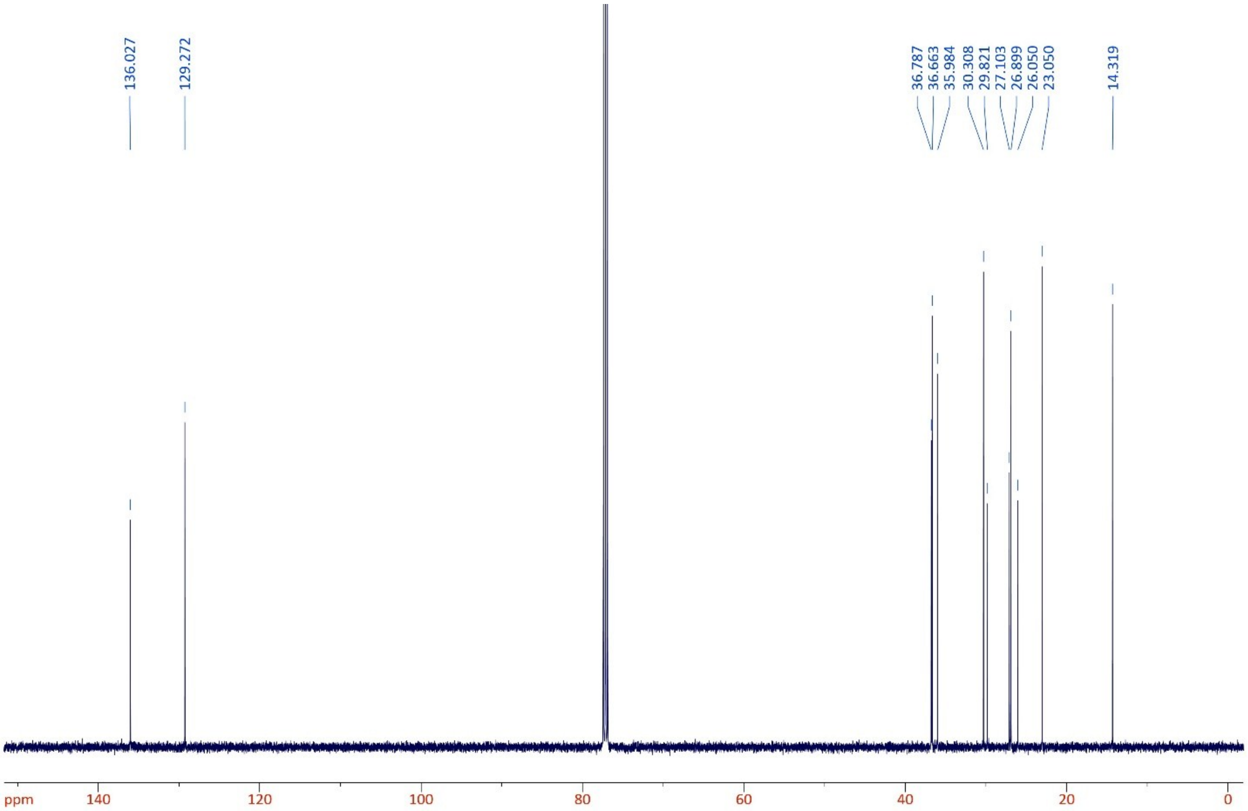

Figure S7. ^{13}C NMR spectrum of 3nBuCOE.

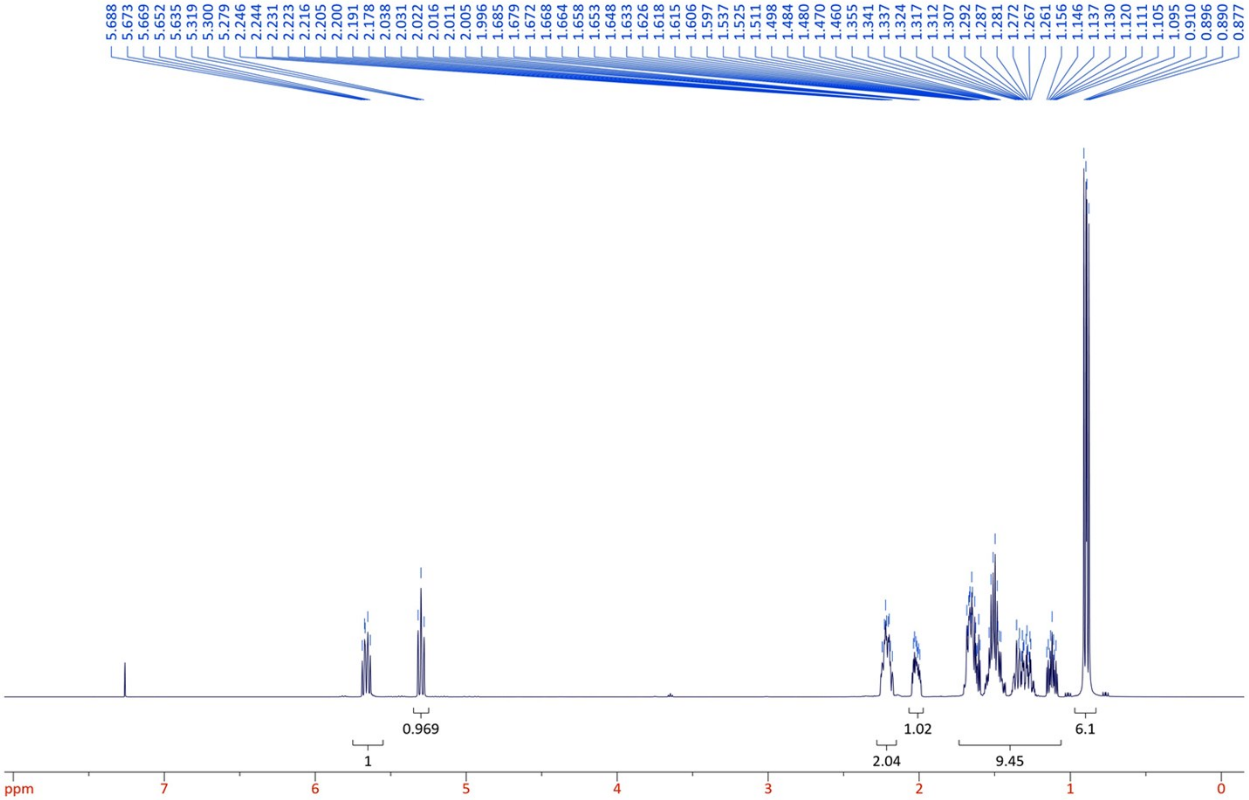

Figure S8. ^{1}H NMR spectrum of 3-isopropyl-cyclooctene (3iPrCOE).

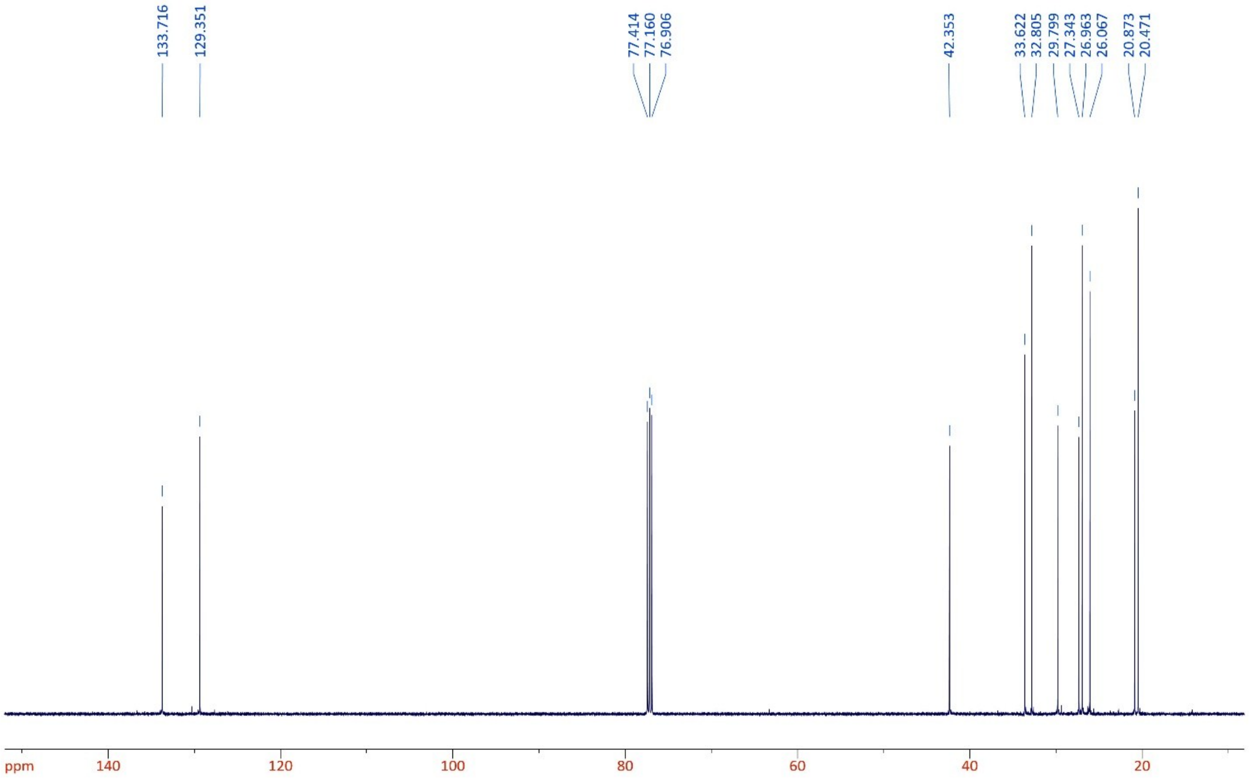

Figure S9. ^{13}C NMR spectrum of 3iPrCOE.

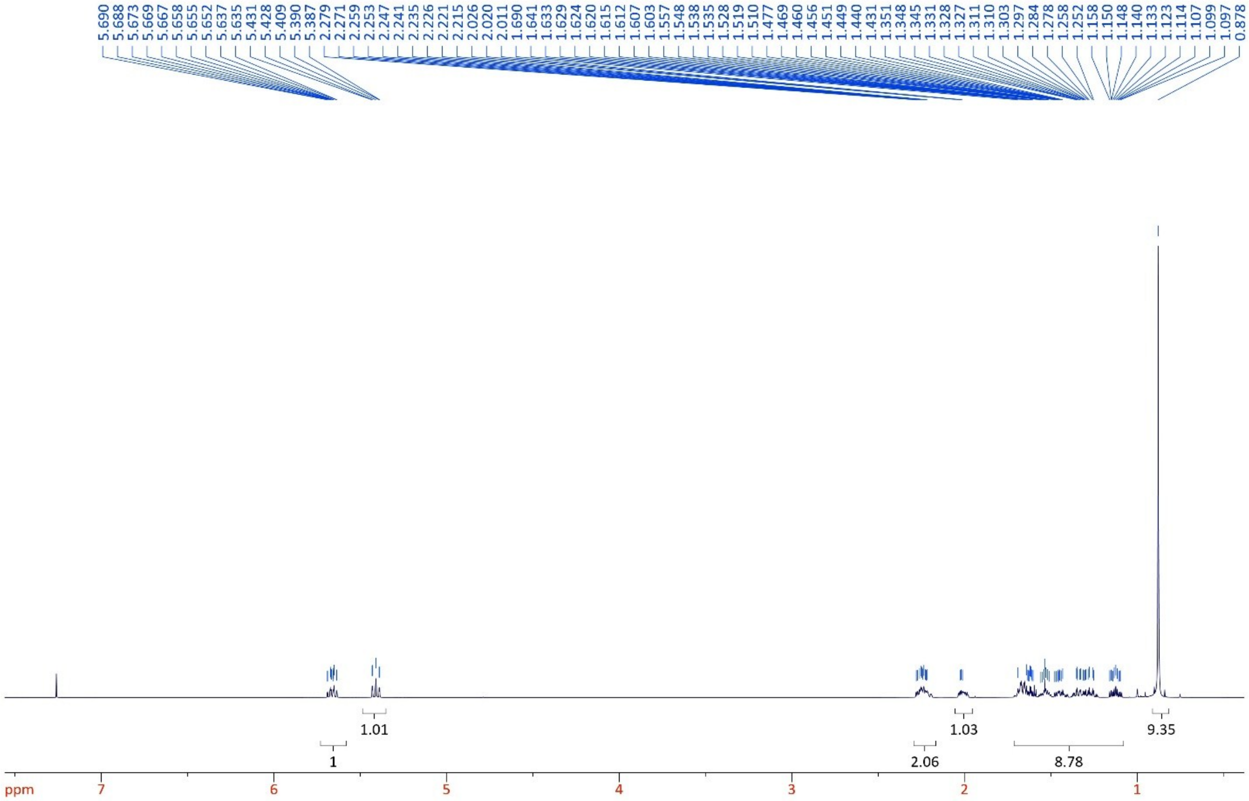

Figure S10. ^{1}H NMR spectrum of 3-*tert*-butyl-cyclooctene (3tBuCOE).

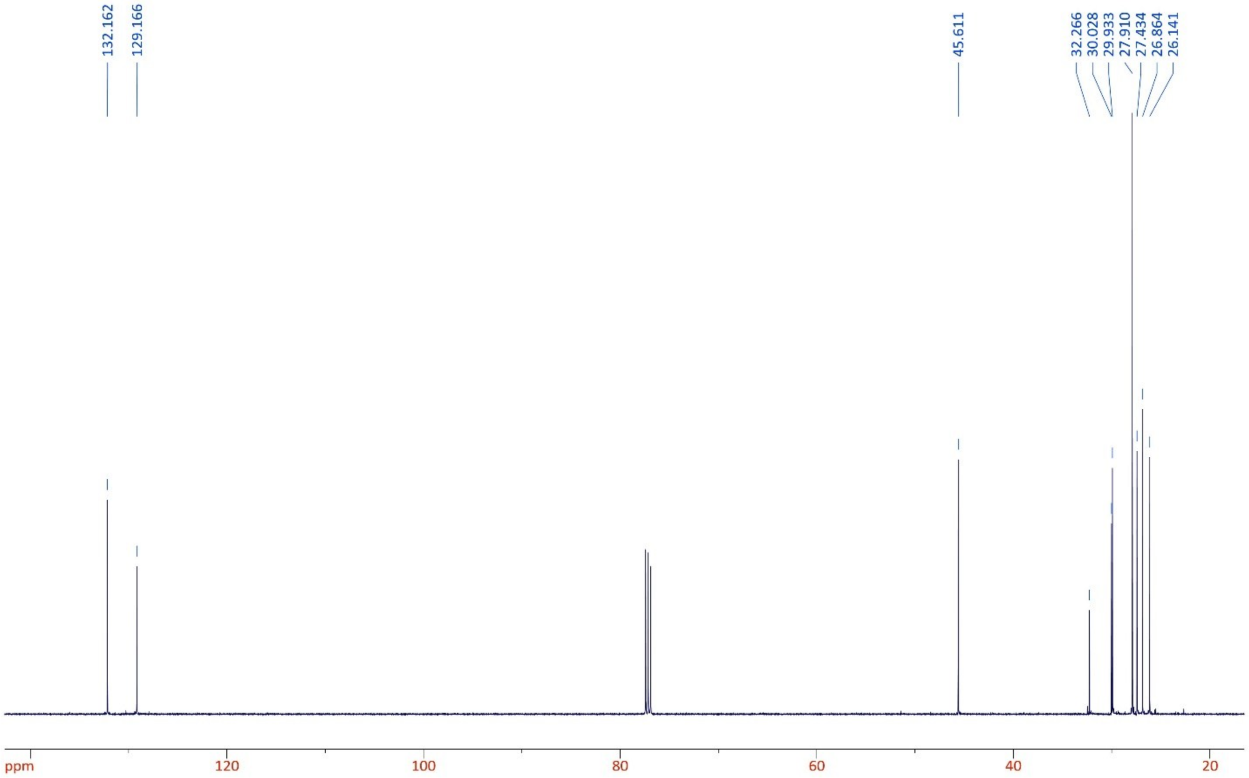

Figure S11. ^{13}C NMR spectrum of 3tBuCOE.

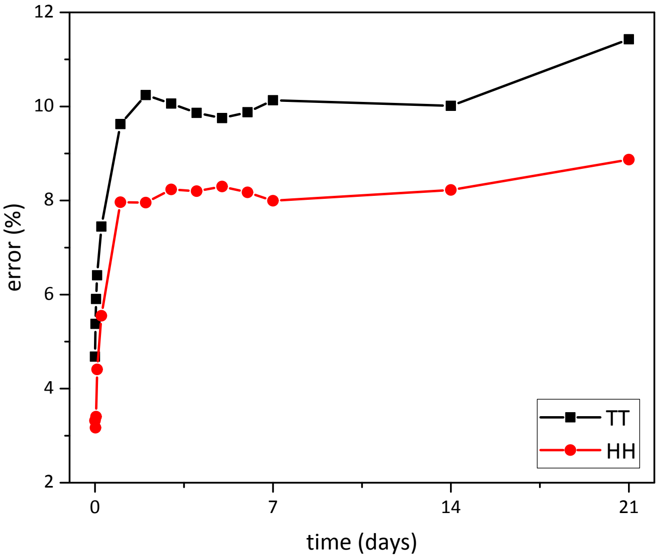

Figure S12. Cross metathesis (CM) of two poly(3EtCOE)s of M_n = 4 kg mol^{-1} and M_n = 65 kg mol^{-1} monitoring the *t*-TT (black) and *t*-HH (red) percent error values over 3 weeks with ^{1}H NMR spectroscopy.

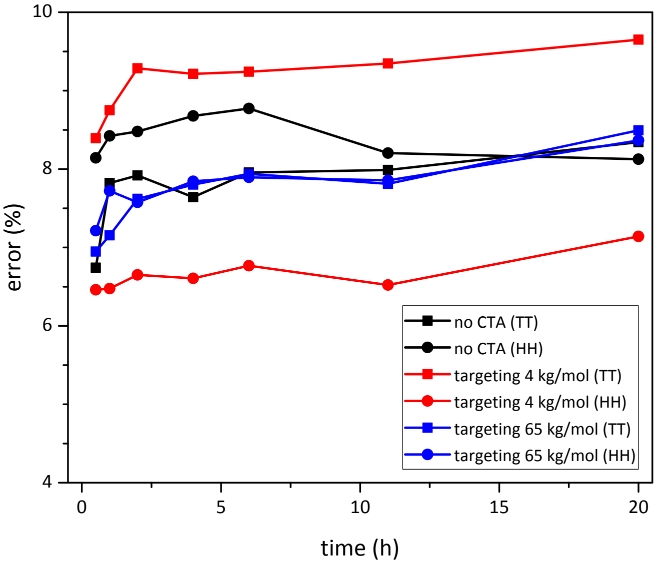

Figure S13. Evolution of *t*-TT and *t*-HH error over 20 h during the ring opening metathesis polymerization (ROMP) of 3EtCOE monitored with ^{1}H NMR spectroscopy.

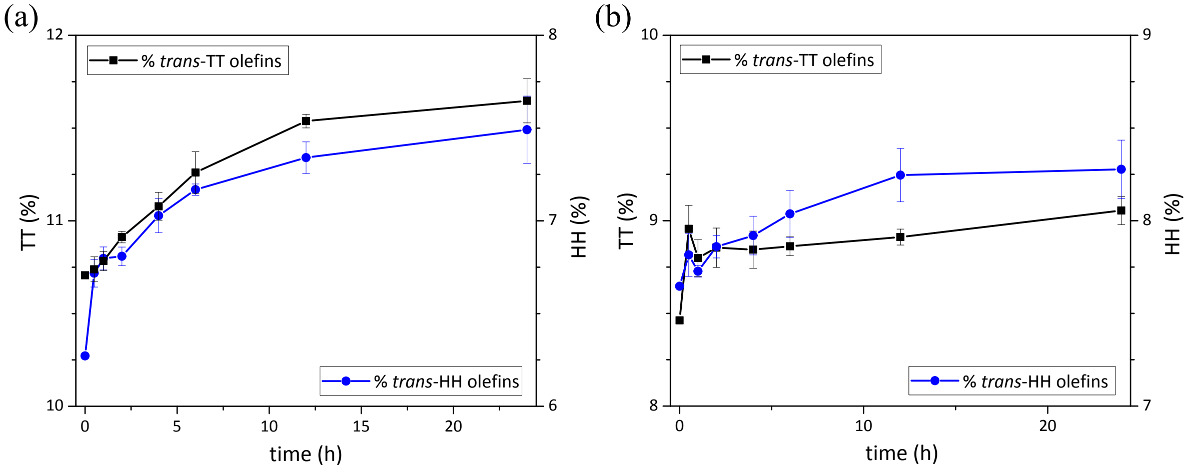

Figure S14. Evolution of *t*-TT and *t*-HH error over 24 h during the CM of 6.7 kg mol^{-1} poly(3EtCOE) (a) and 60 kg mol^{-1} poly(3EtCOE) (b) monitored with ^{1}H NMR spectroscopy.

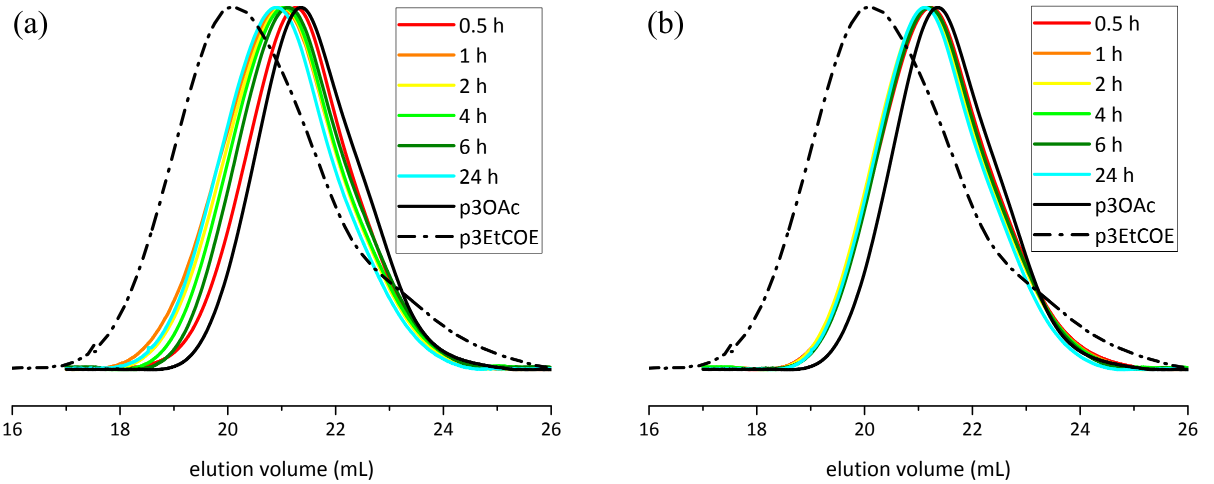

Figure S15. SEC traces (RI) of starting poly(3EtCOE) and poly(3OAcCOE) (M_n = 65 kg mol^{-1} and M_n = 27 kg mol^{-1}, black) and the post-CM products (M_n = 34 kg mol^{-1} and M_n = 30 kg mol^{-1}) using G2 (a) and G3 (b), respectively, from 0.5 to 24 h.

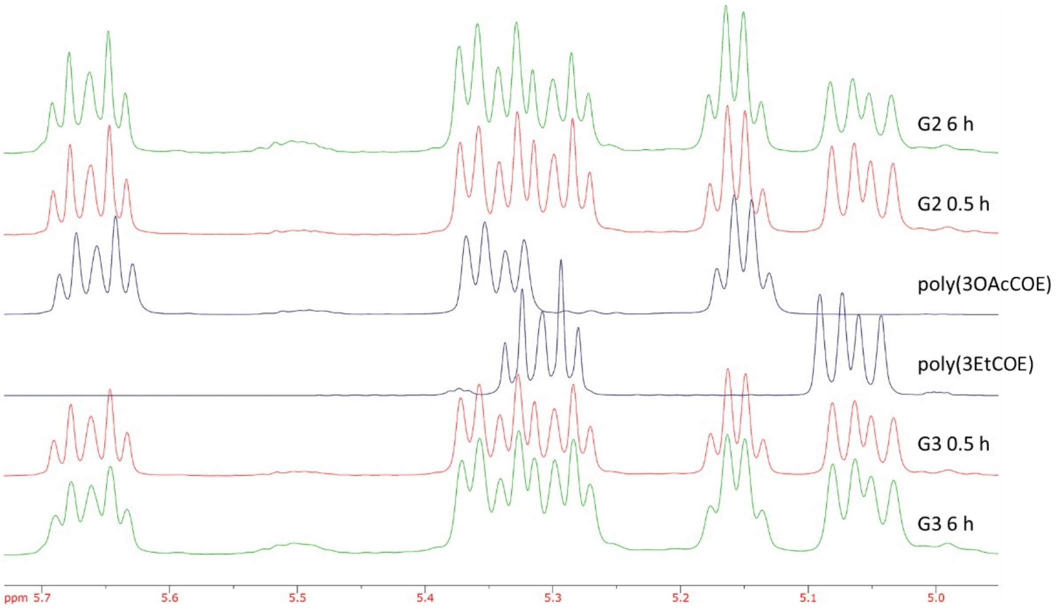

Figure S16. ^{1}H NMR spectra of poly(3EtCOE) and poly(3OAcCOE) and the post-CM products with G2 and G3.

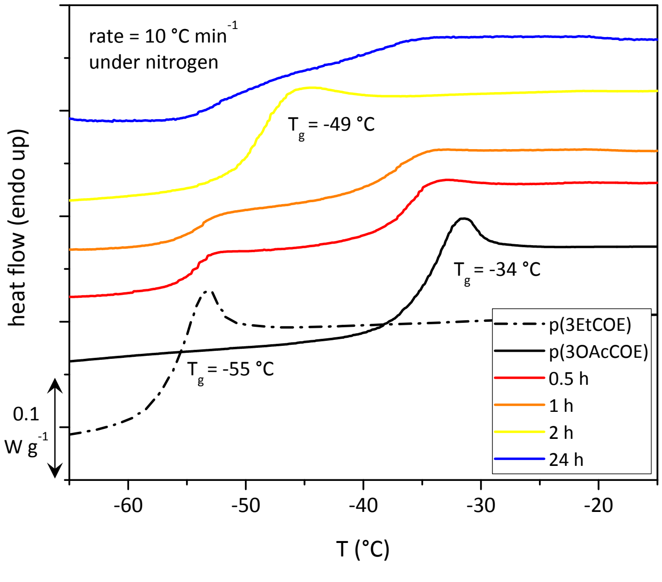

Figure S17. Repetition of the CM experiment between poly(3EtCOE) and poly(3OAcCOE) in the presence of G2 from Figure 3b showing that the changes in the DSC traces are reproducible. DSC traces of the starting polymers are shown in black and the post-CM products at 0.5, 1, 2, and 24 h are shown in color.

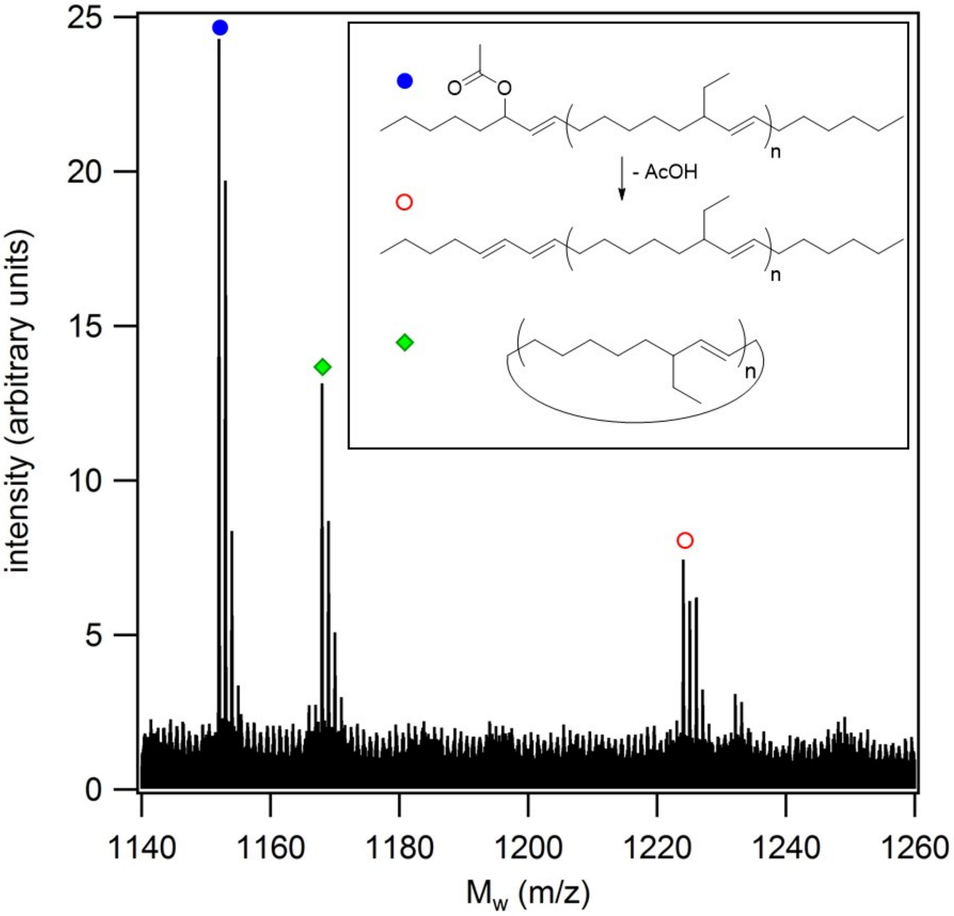

Figure S18. Zoomed in portion of Figure 6, the MALDI-TOF mass spectrum of the oligomers made from ROMP of 3EtCOE using **CTA-2** (M_n = 1.4 kg mol^{-1}) (5 h reaction time). The spectrum was acquired with the reflector positive acquisition method and the reflector default processing method using 3600 shots/spot and using 1 µL of the DCTB:$Cu(NO_3)_2$ matrix (20 mg DCTB to 0.1 mg $Cu(NO_3)_2$ in 1 mL tetrahydrofuran (THF)) and 0.5 µL of the sample solution (2 mg in 1 mL THF) per sample (DCTB = *trans*-2-[3-(4-*tert*-Butylphenyl)-2-methyl-2-propenylidene]malononitrile).

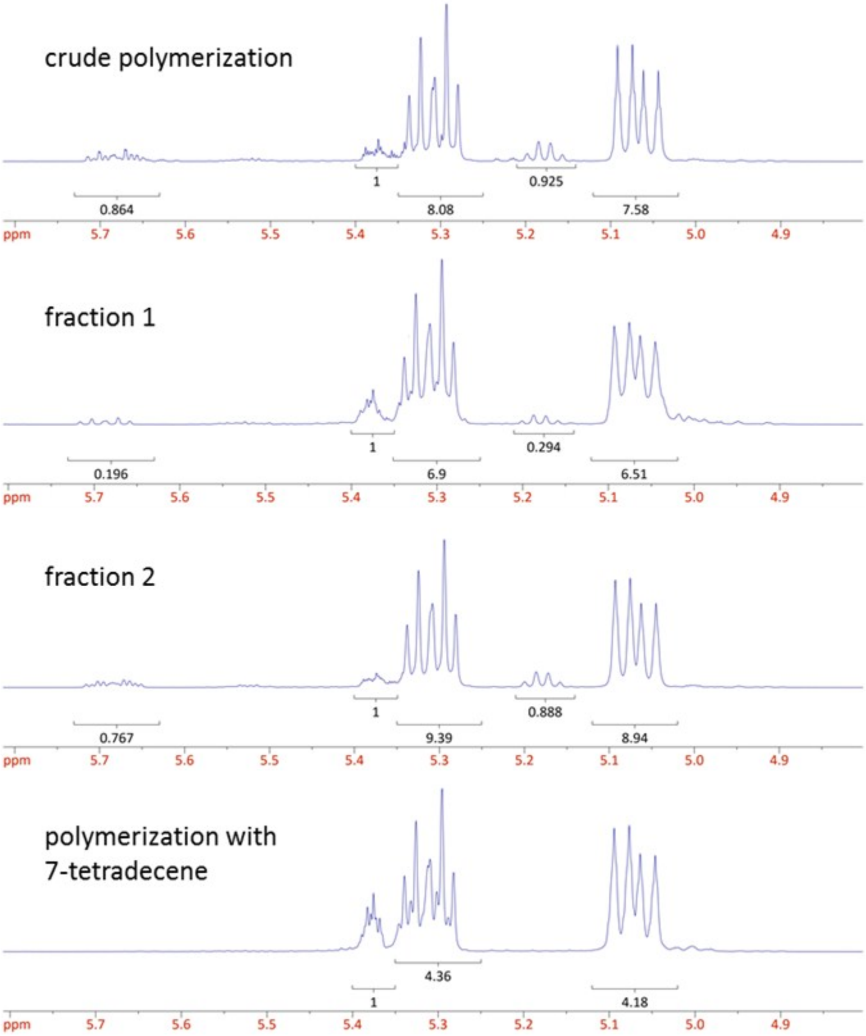

Figure S19. ^{1}H NMR spectra of the starting material and fractions of the column on the oligomers made by ROMP of 3EtCOE with 7-tetradecen-6-yl acetate (5 h reaction time).

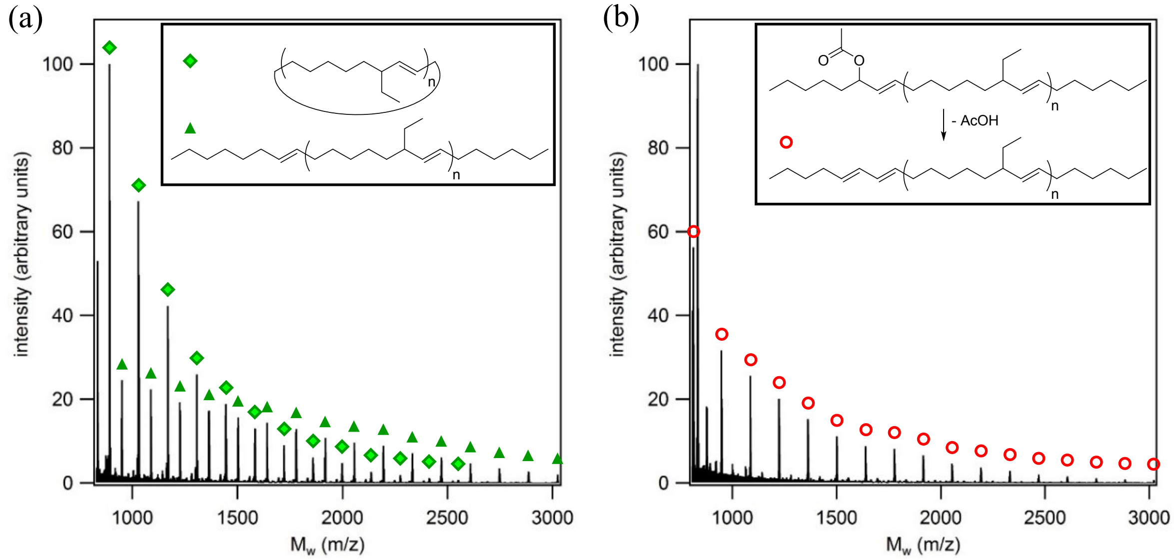

Figure S20. MALDI-TOF mass spectra of the first (non-polar; a) and second (more polar; b) column fractions of the oligomers made by ROMP of 3EtCOE with 7-tetradecen-6-yl acetate (5 h reaction time). No peaks corresponding to cyclic or homotelechelic oligomers are observed in the second fraction.

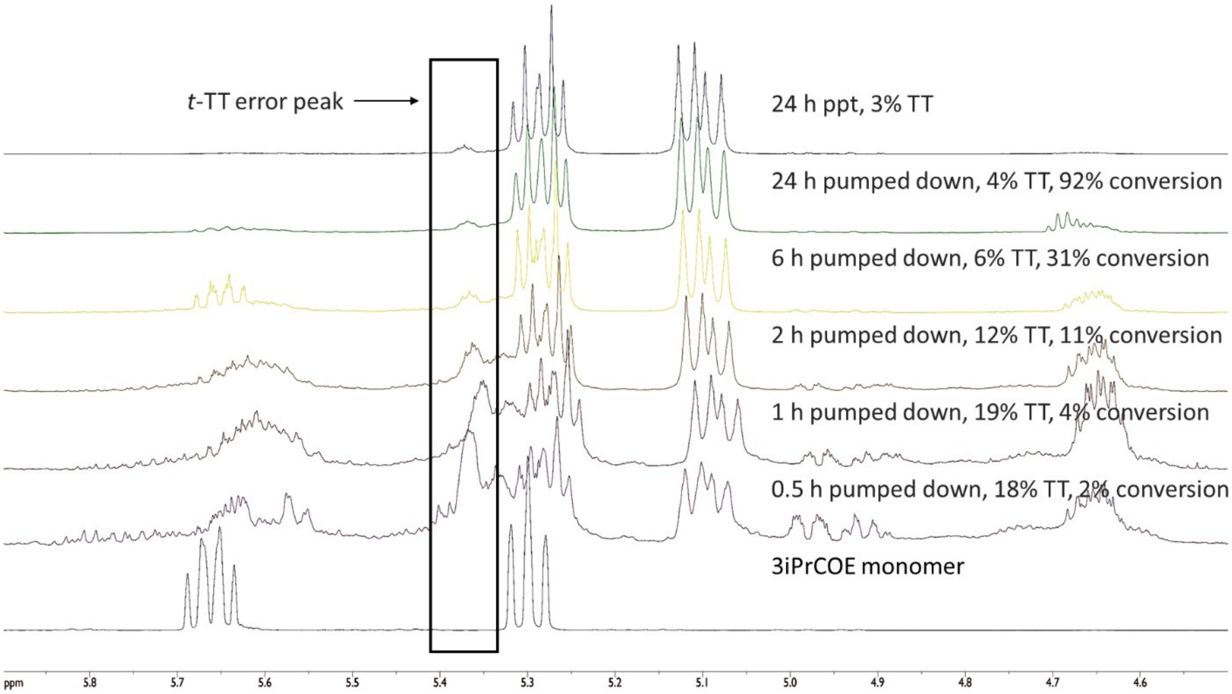

Figure S21. ^{1}H NMR spectra of the ROMP of 3iPrCOE monitored over 24 h.