Electronic Supplementary Information

Ring-Opening Metathesis Polymerization of Cyclooctene Derivatives with Chain Transfer Agents derived from Glycerol Carbonate

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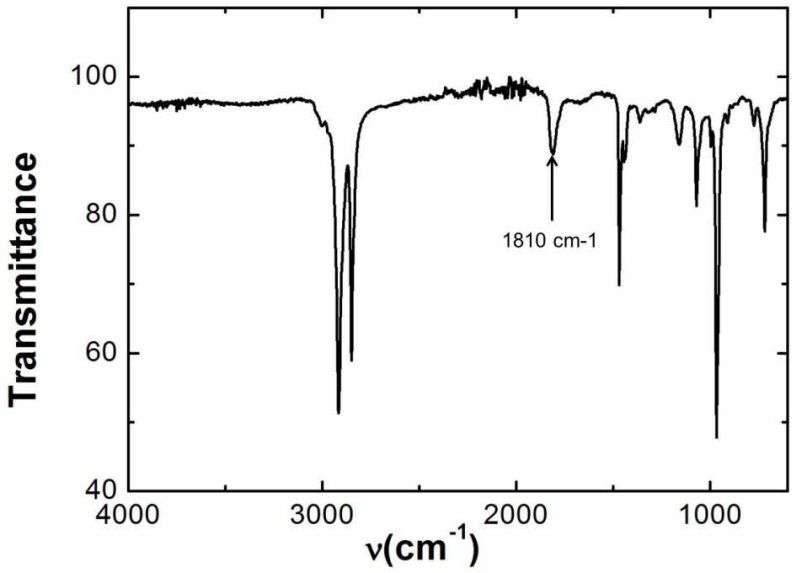

Figure S1. FT-IR spectrum (ATR) of an α,ω-di(**GC**)-PCOE synthesized from the ROMP of COE in the presence of **1** (Table 1, entry 1).

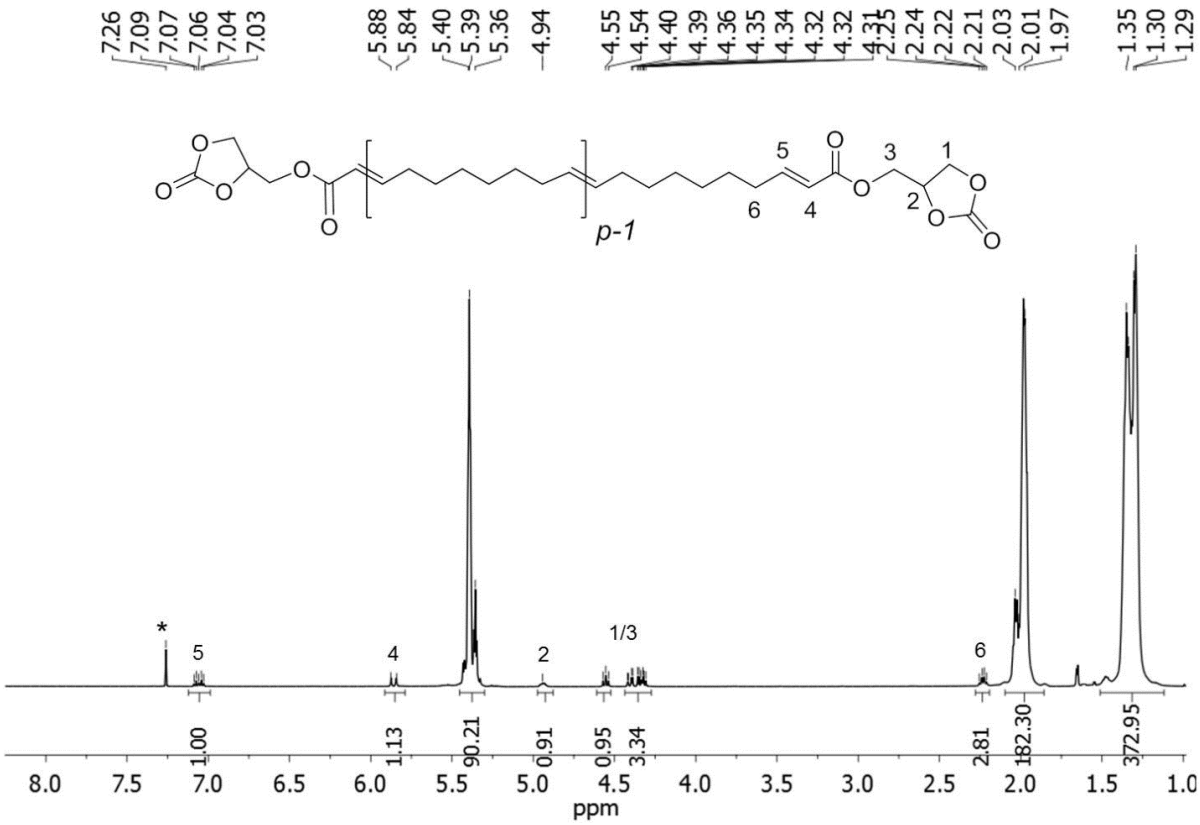

Figure S2. ^{1}H NMR spectrum ($CDCl_3$, 500 MHz, 298 K) of an α,ω-di(**GC**)-PCOE (Table 1, entry 3). δ_{ppm}: repeating unit: 5.36, 1.97, 1.29, chain-end groups: 7.03 (m, *CH*=CH-CO_2), 5.84 (m, CH=*CH*-CO_2), 4.94 (broad signal, CH_2-C*H*-CH_2OCOO), 4.55–4.32 (m, *CH_2*-CH-CH_2OCOO and CH_2-CH-*CH_2*OCOO) (* stands for residual solvent resonance).

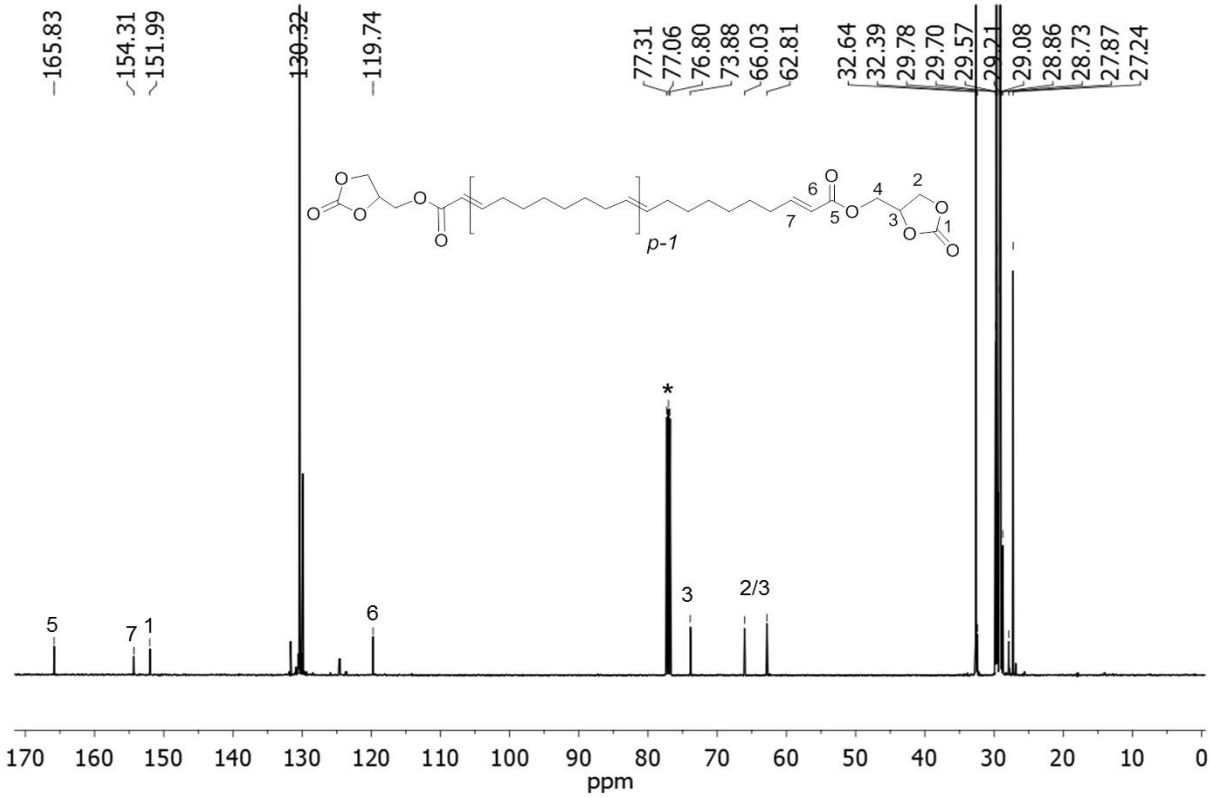

Figure S3. $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 100 MHz, 298 K) of an α,ω-di(**GC**)-PCOE (Table 1, entry 3). δ_{ppm}: repeating unit: 130.3, 129.9, 32.6, 29.8–27.2, chain-end groups: 165.8 (OC=O), 154.3 (O=COO), 152.0 (*CH*=CH-COO), 119.7 (CH=*CH*-COO), 73.9 (CH_2-*CH*-CH_2OCOO), 66.0, 62.8 (*CH_2*-CH-CH_2OCOO and CH_2-CH-*CH_2*OCOO) (* stands for residual solvent resonance).

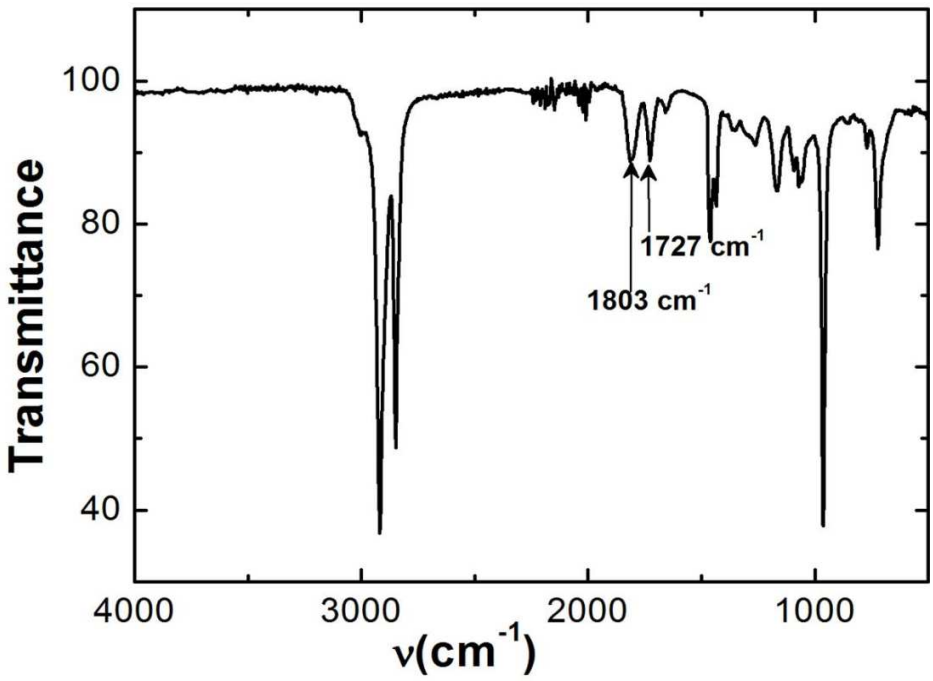

Figure S4. FT-IR spectrum (ATR) of an α,ω-di(**GC**)-PCOE synthesized from the ROMP of COE in the presence of **2** (Table 1, entry 3).

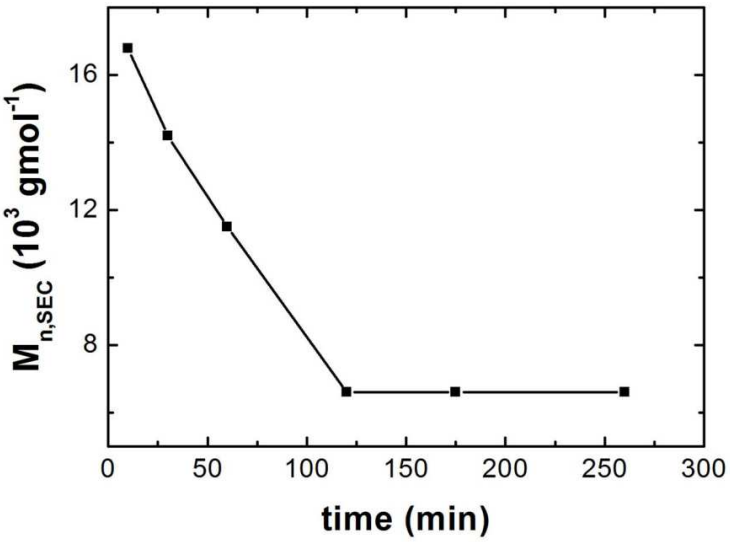

Figure S5. Variation of the molar mass of PCOE obtained in the presence of **2** as a function of time (Table 1, entry 3).

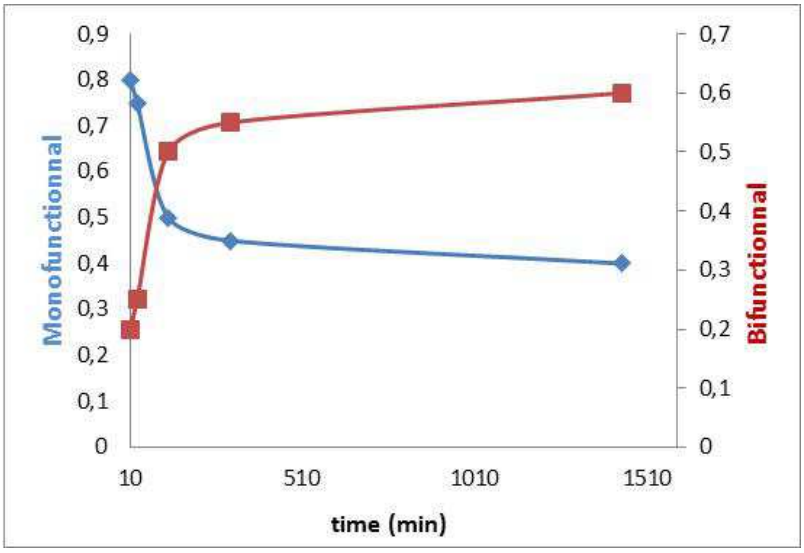

Figure 6. ^{1}H NMR monitoring of the formation of α-**GC**,ω-vinyl-PCOE (monofunctional, ◆) and α,ω-di(**GC**)-PCOE (bifunctional, ■) during the ROMP of COE in the presence of **2** and DCM as solvent of reaction.

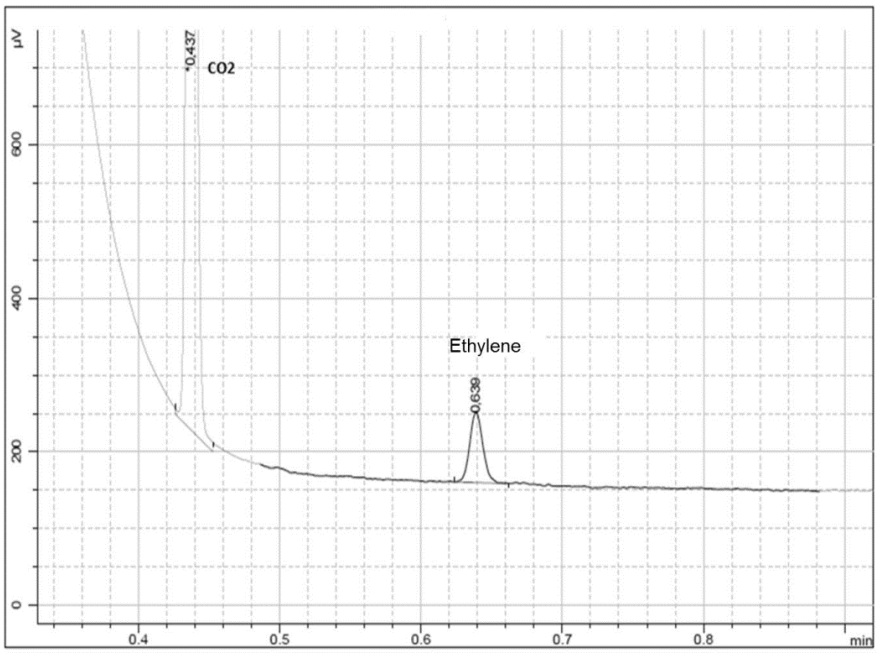

Figure S7. Gas chromatogram showing the ethylene released during the ROMP of COE in the presence of **2** (Table 1, entry 3).

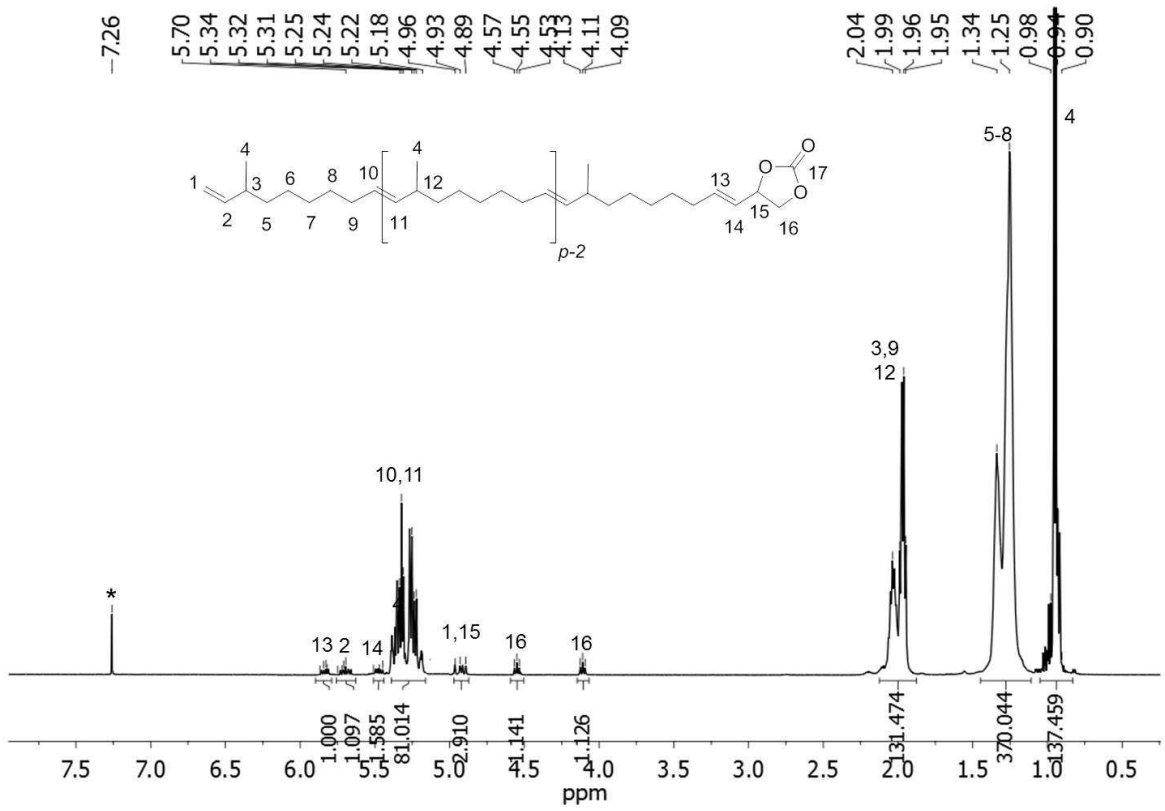

Figure S8. ^{1}H NMR spectrum ($CDCl_3$, 500 MHz, 298 K) of an α-**GC**,ω-vinyl-P(3-Me-COE) prepared from **1** (Table 1, entry 5). δ_{ppm}: repeating unit: 5.39–5.18, 2.04-1.95, 1.34, 1.25, 0.94, chain-end groups: 5.87 (m, *CH*=CH-CH-OCO_2), 5.75 (m, CH=*CH*-CH-OCO_2), 5.45 (CH_2=*CH*-CH), 4.89 (m, *CH_2*=CH-CH and CH=CH-*CH*-OCO_2), 4.57–4.09 (CH-*CH_2*-OCOO), 2.04 (m, CH_2=CH-*CH*) (* stands for residual solvent resonance).

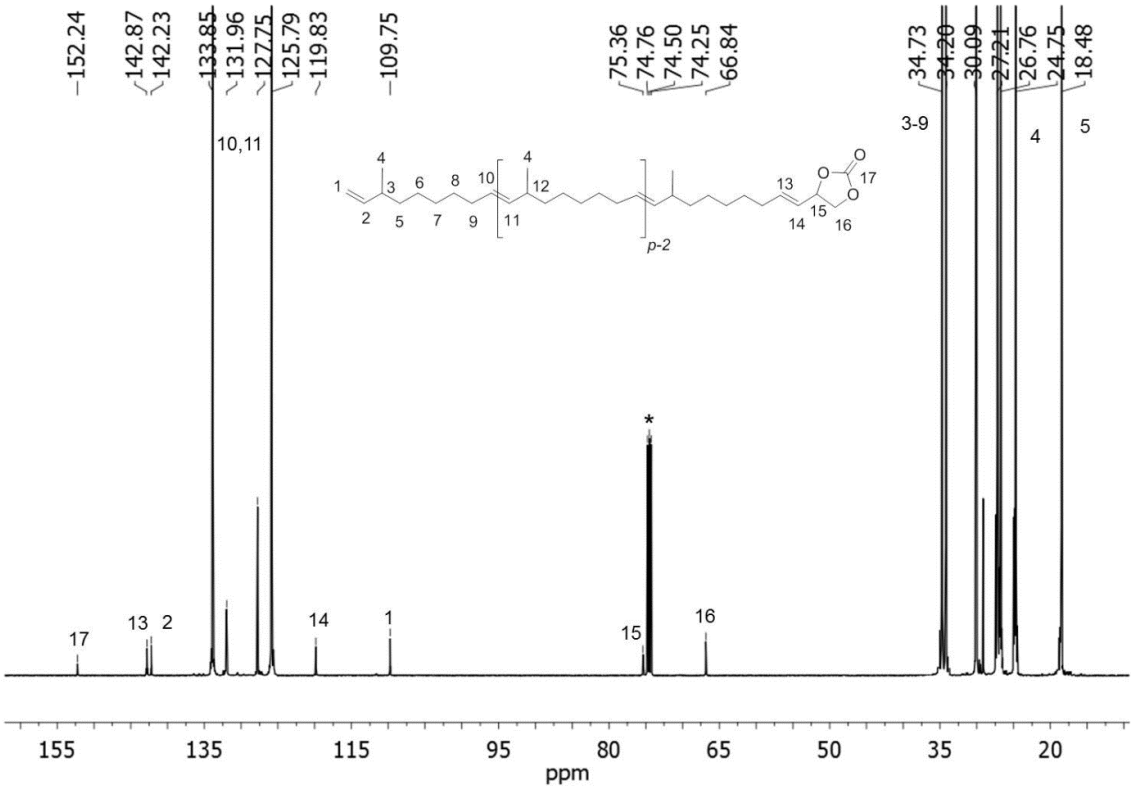

Figure S9. $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 100 MHz, 298 K) of an α-**GC**,ω-vinyl-P(3-Me-COE) prepared from **1** (Table 1, entry 5). δ_{ppm}: repeating unit: 133.8, 132.0, 127.7, 125.8, 34.7-27.7, 18.5. Chain-end groups: 152.2 (O=COO), 142.9 (*CH*=CH-CHOCOO), 142.2 (CH_2=*CH*-CH), 119.8 (CH=*CH*-CHOCOO), 109.7 (*CH_2*=CH-CH), 75.4 (CH=CH-*CH*OCOO), 66.8 (CH-*CH_2*-OCOO) (* stands for residual solvent resonance).

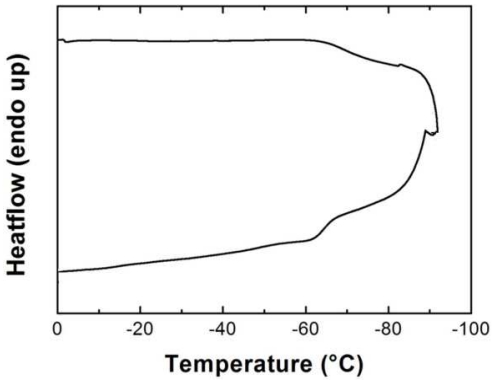

Figure S10. DSC thermogram (second heating cycle) of an α-**GC**,ω-vinyl-P(3-Me-COE) prepared from **1** (T_g = –64 °C) synthesized from the ROMP of 3-Me-COE in the presence of **1** (Table 1, entry 5).

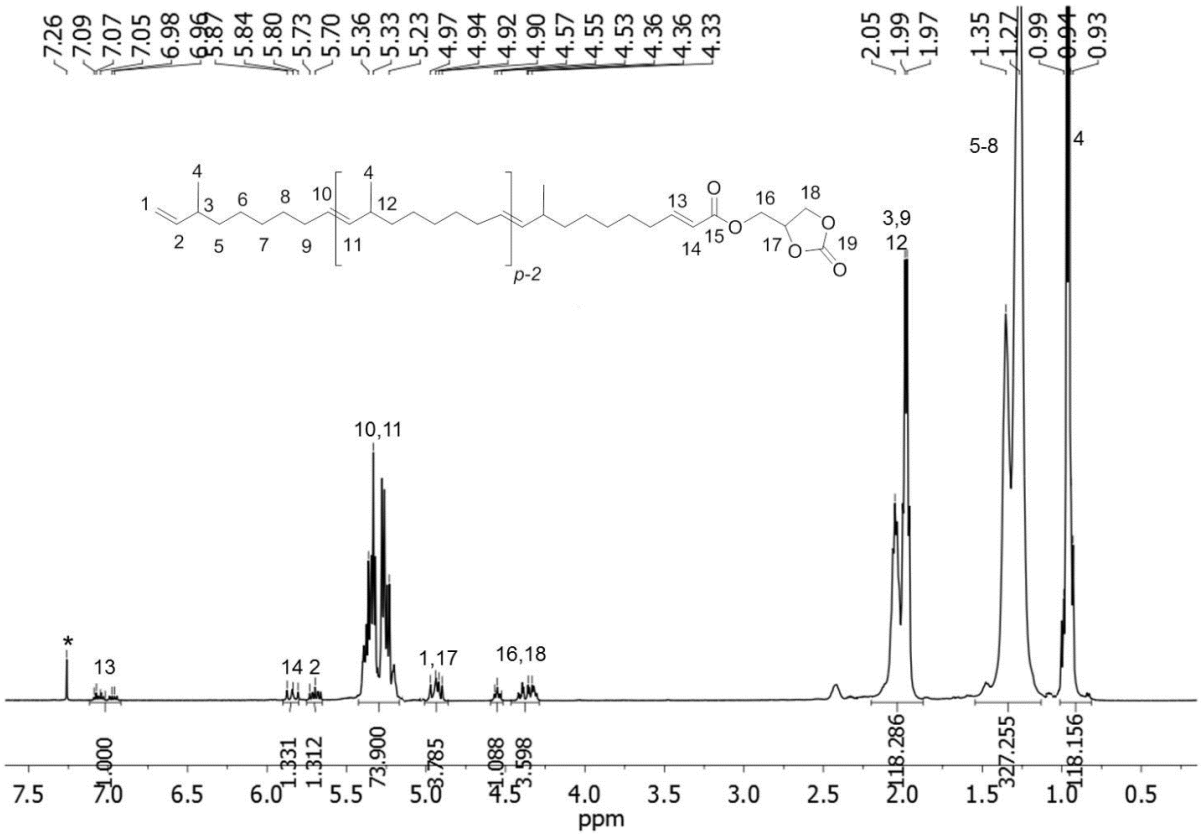

Figure S11. ^{1}H NMR spectrum ($CDCl_3$, 500 MHz, 298 K) of an α-**GC**,ω-vinyl-PCOE prepared from **2** (Table 1, entry 7). δ_{ppm}: repeating unit: 5.39-5.20, 2.04–1.97, 1.34, 1.25, 0.94. Chain-end groups: 6.94 (m, *CH*=CH-CO_2), 5.80 (m, CH=*CH*-CO_2), 5.66 (m, CH_2=*CH*-CH), 4.90 (m, *CH_2*=CH-CH and CH=CH-*CH*-OCO_2), 4.57–4.33 (m, *CH_2*-CH-CH_2OCOO and CH_2-CH-*CH_2*OCOO), 2.05 (m, CH_2=*CH*-CH) (* stands for residual solvent resonance).

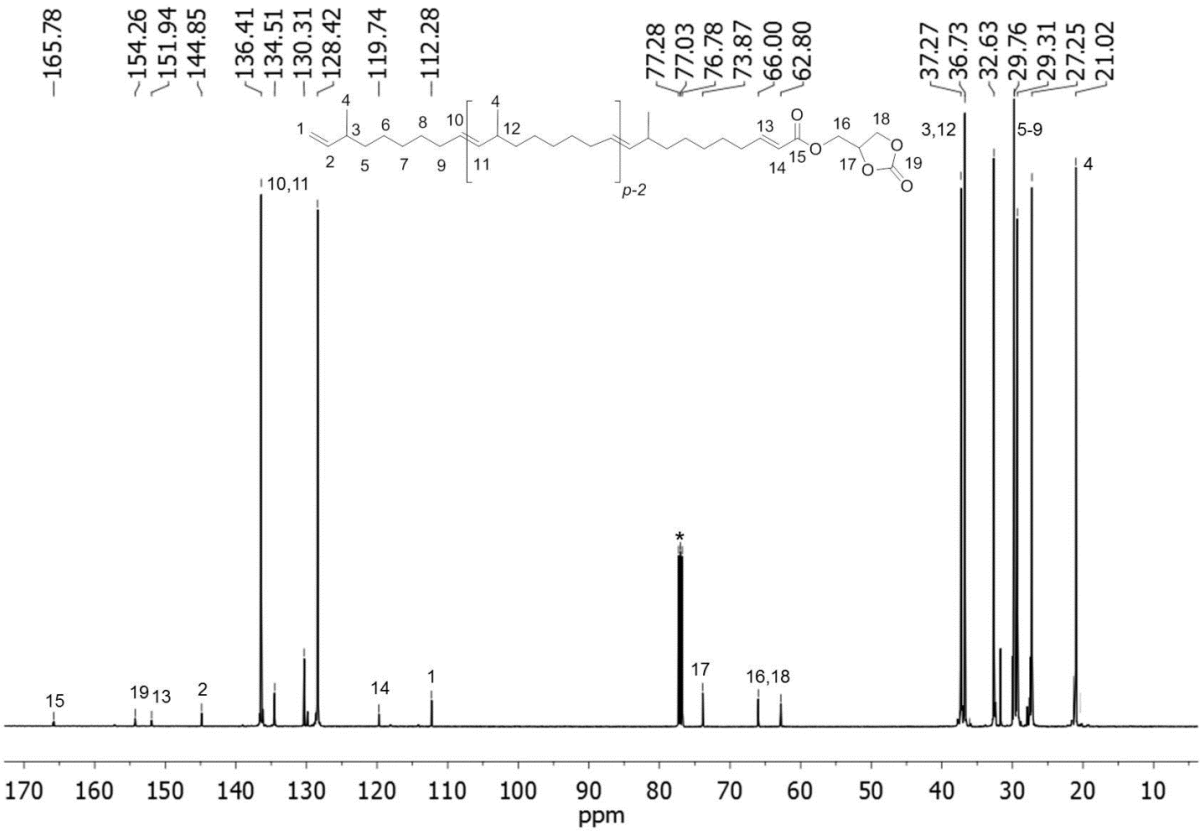

Figure S12. $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 100 MHz, 298 K) of an α-**GC**,ω-vinyl-P(3-Me-COE) prepared from **2** (Table 1, entry 7). δ_{ppm}: repeating unit: 136.4, 134.5, 130.3, 128.4, 37.3–27.2, 21.0. Chain-end groups: 165.8 (OC=O), 154.3 (O=COO), 151.9 (*CH*=CH-COO), 144.8 (CH_2=*CH*-CH), 119.7 (CH=*CH*-COO), 112.3 (*CH_2*=CH-CH), 73.9 (CH_2-*CH*-CH_2OCOO), 66.0, 62.8 (*CH_2*-CH-CH_2OCOO and CH_2-CH-*CH_2*OCOO) (* stands for residual solvent resonance).

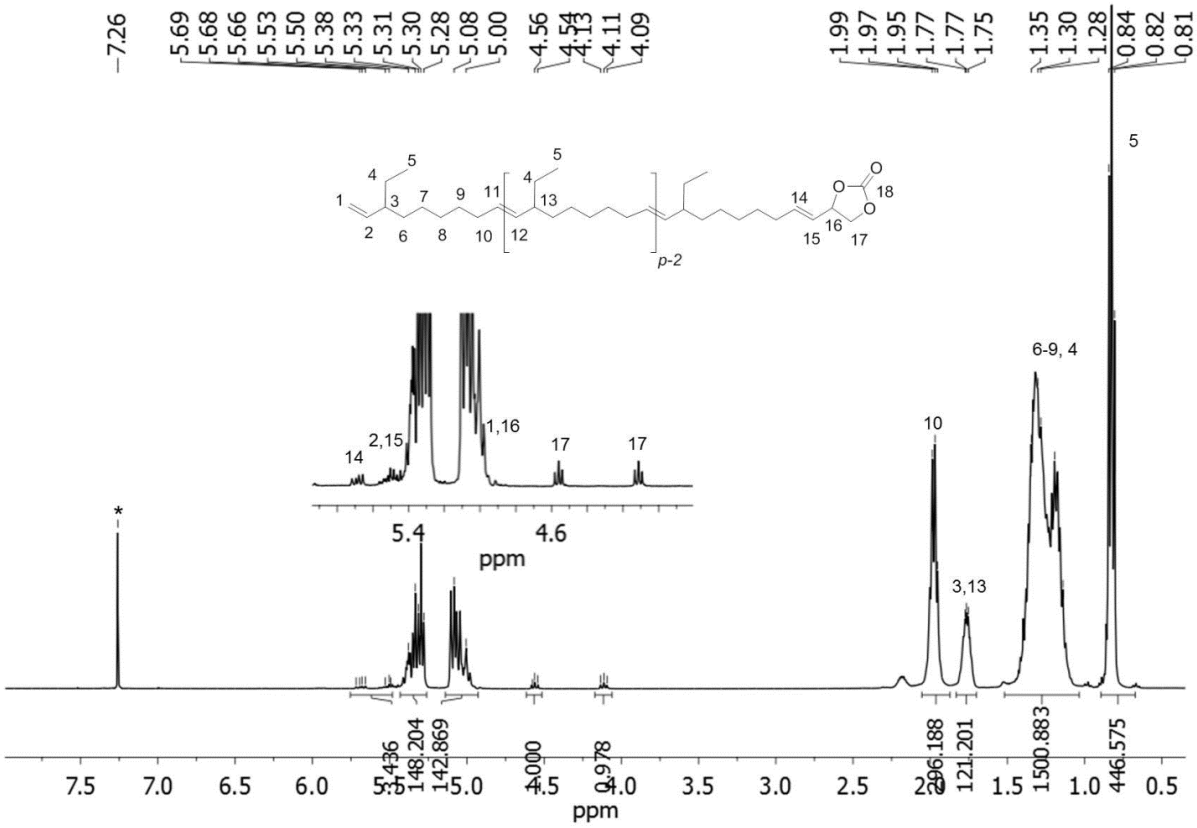

Figure S13. ^{1}H NMR spectrum ($CDCl_3$, 500 MHz, 298 K) of an α-**GC**,ω-vinyl-P(3-Et-COE) prepared from **1** (Table 1, entry 9). δ_{ppm}: repeating unit: 5.38–5.00, 1.99-1.95, 1.75, 1.35–1.28, 0.81. Chain-end groups: 5.66 (m, *CH*=CH-CH-OCO_2), 5.50 (m, CH=*CH*-CH-OCO_2), 5.45 (CH_2=*CH*-CH and CH=*CH*-CH-OCO_2), 5.00 (m, *CH_2*=CH-CH, and CH=CH-*CH*-OCO_2), 4.57–4.09 (CH-*CH_2*-OCOO), 1.75 (m, CH_2=CH-*CH*) (* stands for residual solvent resonance).

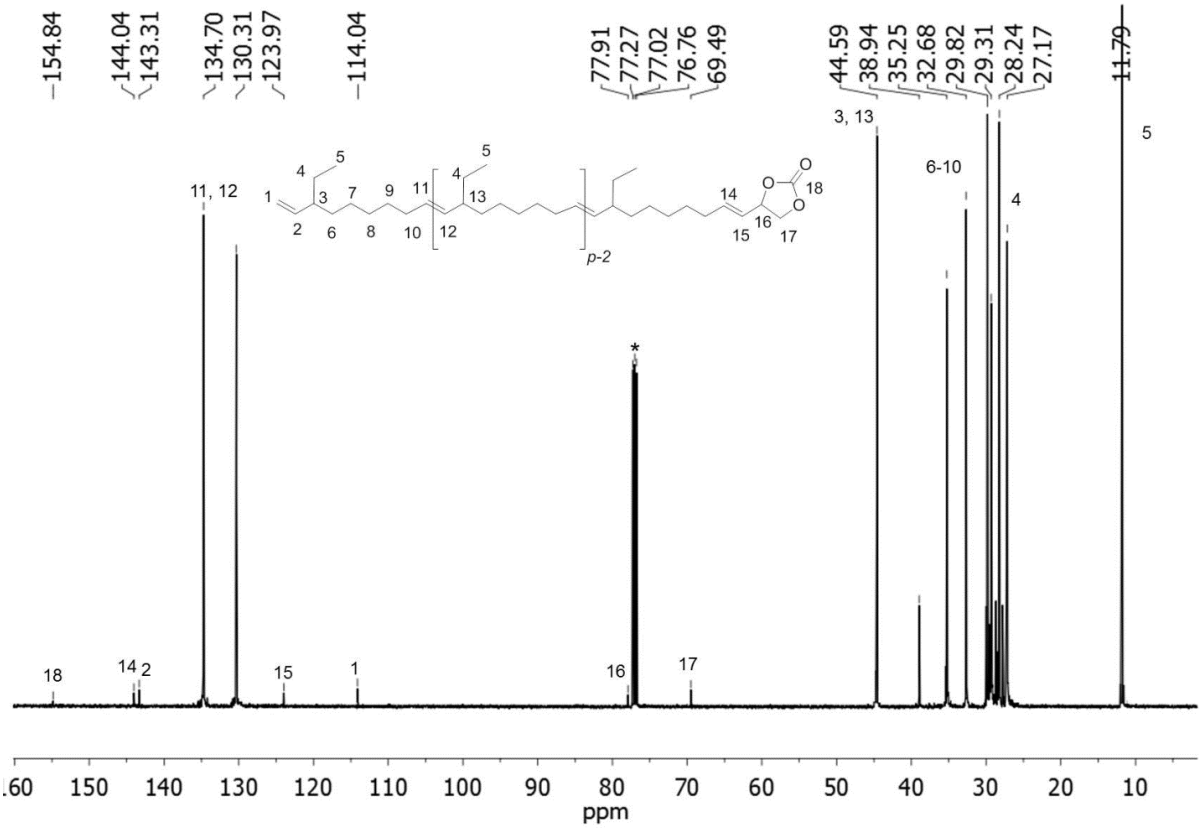

Figure S14. $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 100 MHz, 298 K) of an α-**GC**,ω-vinyl-P(3-Et-COE) prepared from **1** (Table 1, entry 9). δ_{ppm}: repeating unit: 134.7, 130.3, 40.6, 38.9–27.2, 11.8. Chain-end groups: 154.8 (O=COO), 144.0 (*CH*=CH-CHOCOO), 143.3 (CH_2=*CH*-CH), 124.0 (CH=*CH*-CHOCOO), 114.0 (*CH_2*=CH-CH), 77.9 (CH=CH-*CH*OCOO), 69.5 (CH-*CH_2*-OCOO) (* stands for residual solvent resonance).

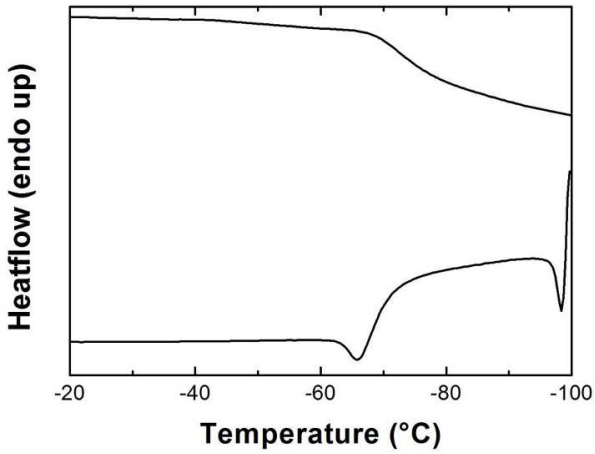

Figure S15. DSC thermogram (second heating cycle) of an α-**GC**,ω-vinyl-P(3-Et-COE) (T_g = –69 °C) synthesized from the ROMP of 3-Et-COE in the presence of **1** (Table 1, entry 9).

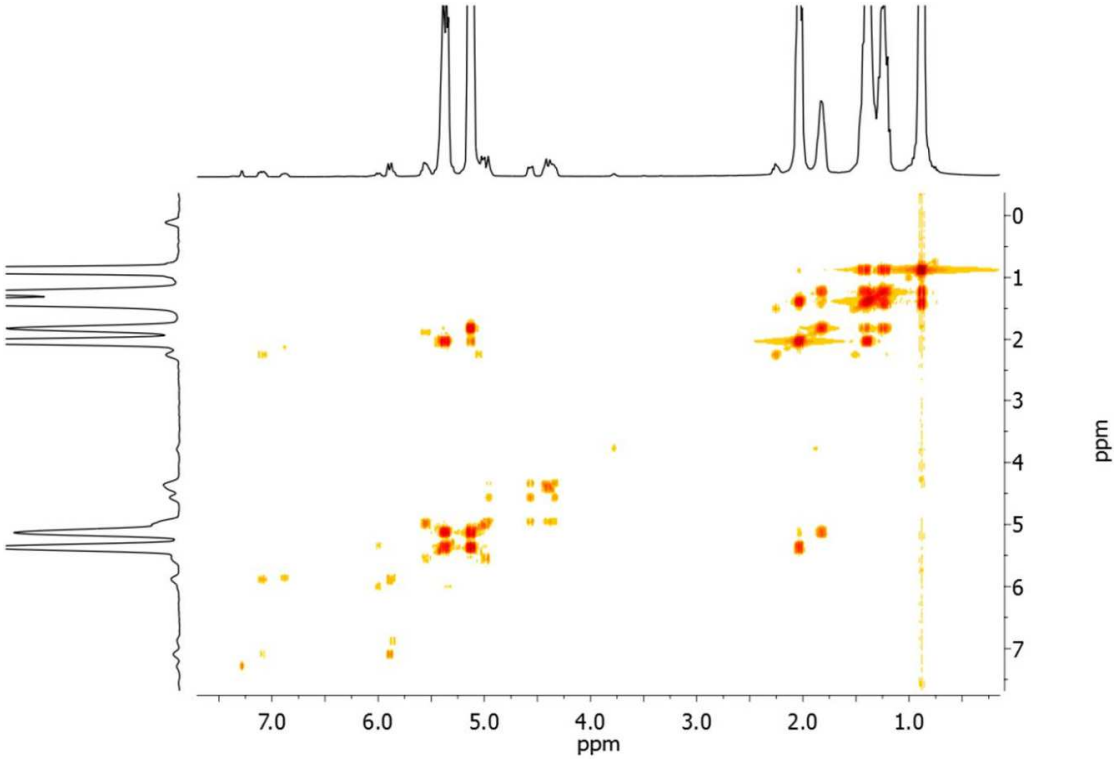

Figure S16. ^{1}H-^{1}H COSY NMR spectrum ($CDCl_3$, 500 MHz, 298 K) of an α-**GC**,ω-vinyl-P(3-Et-COE) prepared from **2** (Table 1, entry 11).

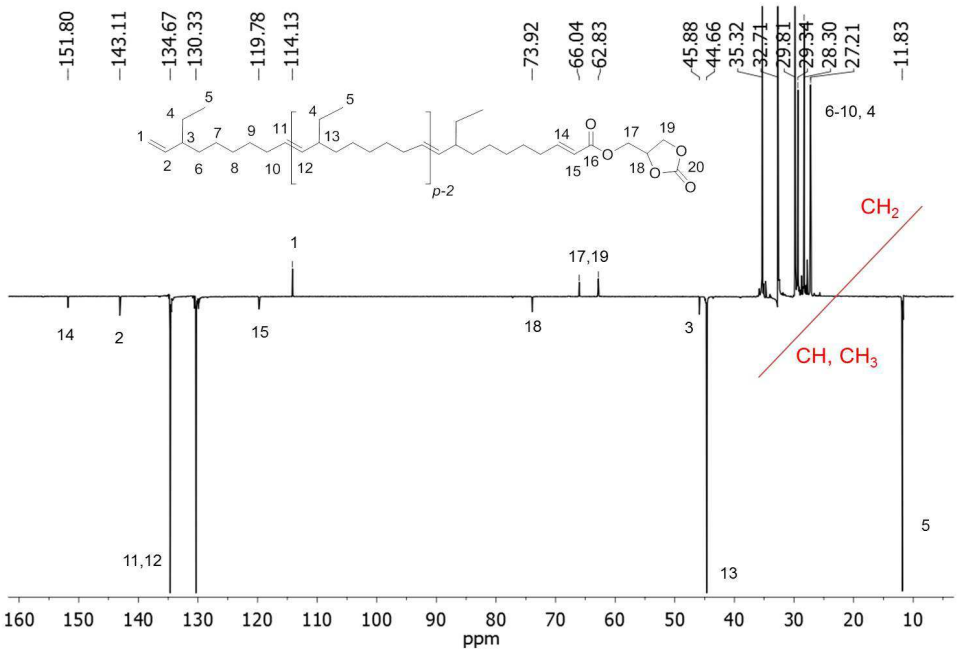

Figure S17. $^{13}C\{^{1}H\}$ (DEPT 135) NMR spectrum ($CDCl_3$, 50 MHz, 298 K) of an α-**GC**,ω-vinyl-P(3-Et-COE) prepared from **2** (Table 1, entry 11). δ_{ppm}: repeating unit: 134.7, 130.3, 44.7, 35.3–27.2, 11.8. Chain-end groups: 151.8 (*CH*=CH-COO), 143.1 (CH_2=*CH*-CH), 119.8 (CH=*CH*-COO), 114.1 (*CH_2*=CH-CH), 73.9 (CH_2-*CH*-CH_2OCOO), 66.0, 62.8 (*CH_2*-CH-CH_2OCOO and CH_2-CH-*CH_2*OCOO), 45.9 (CH_2=CH-*CH*).

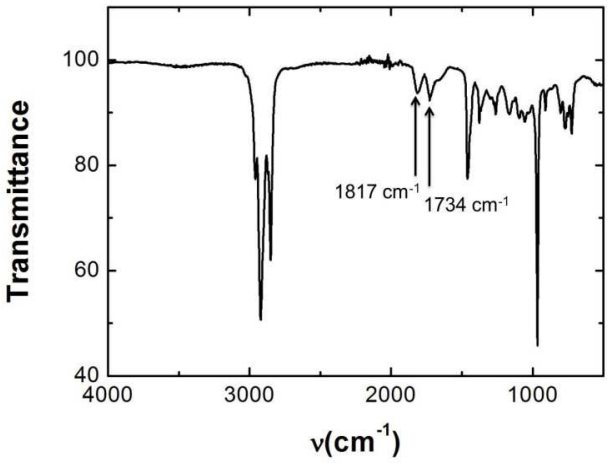

Figure S18. FT-IR spectrum (ATR) of an α-**GC**,ω-vinyl-P(3-Et-COE) synthesized from the ROMP of 3-Et-COE in the presence of **2** (Table 1, entry 11).

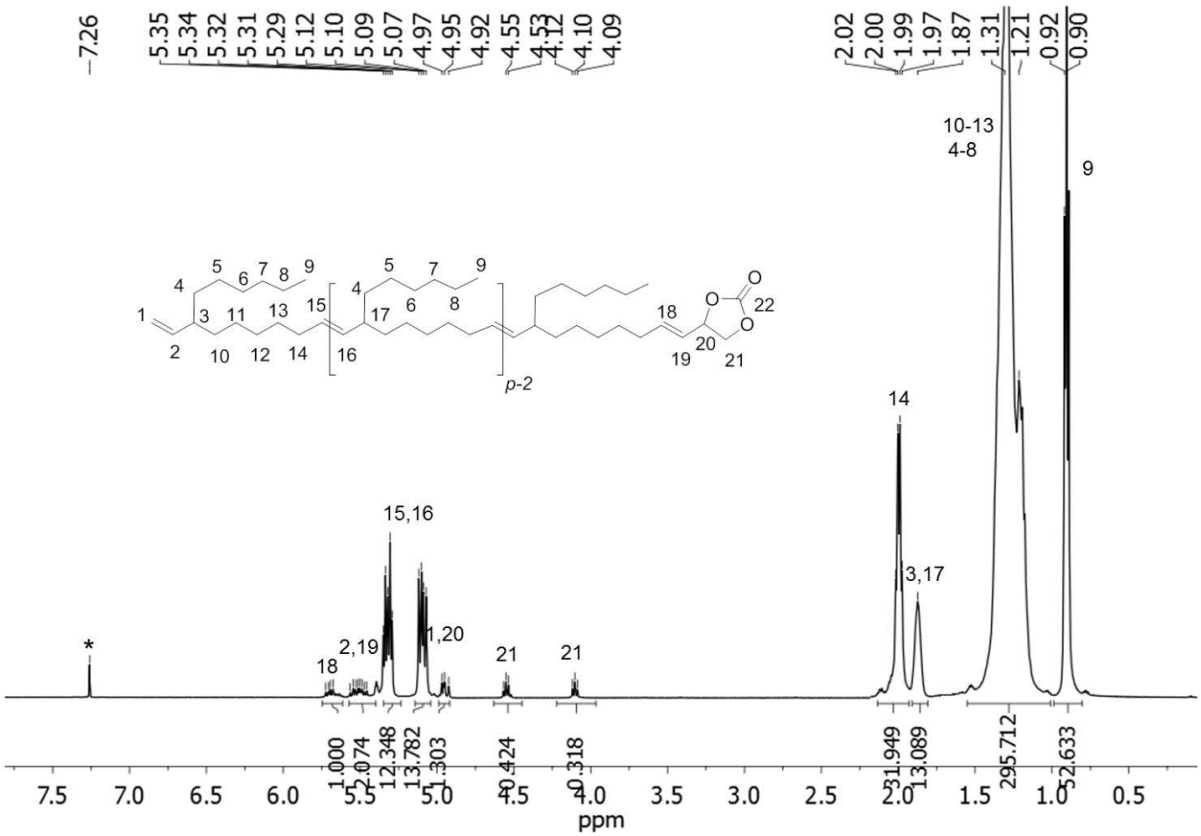

Figure S19. ^{1}H NMR spectrum ($CDCl_3$, 500 MHz, 298 K) of an α-**GC**,ω-vinyl-P(3-*n*-hexyl-COE) prepared from **1** (Table 1, entry 13). δ_{ppm}: repeating unit: 5.34–5.07, 2.02-1.97, 1.87, 1.31–1.21, 0.90. Chain-end groups: 5.68 (m, *CH*=CH-CO_2), 5.46 (m, CH=*CH*-CH-OCO_2 and CH=*CH*-CH-OCO_2), 5.00 (m, CH_2=CH-CH, and CH=CH-*CH*-OCO_2), 4.57–4.09 (CH-CH_2-OCOO), 1.87 (m, CH_2=CH-*CH*) (* stands for residual solvent resonance).

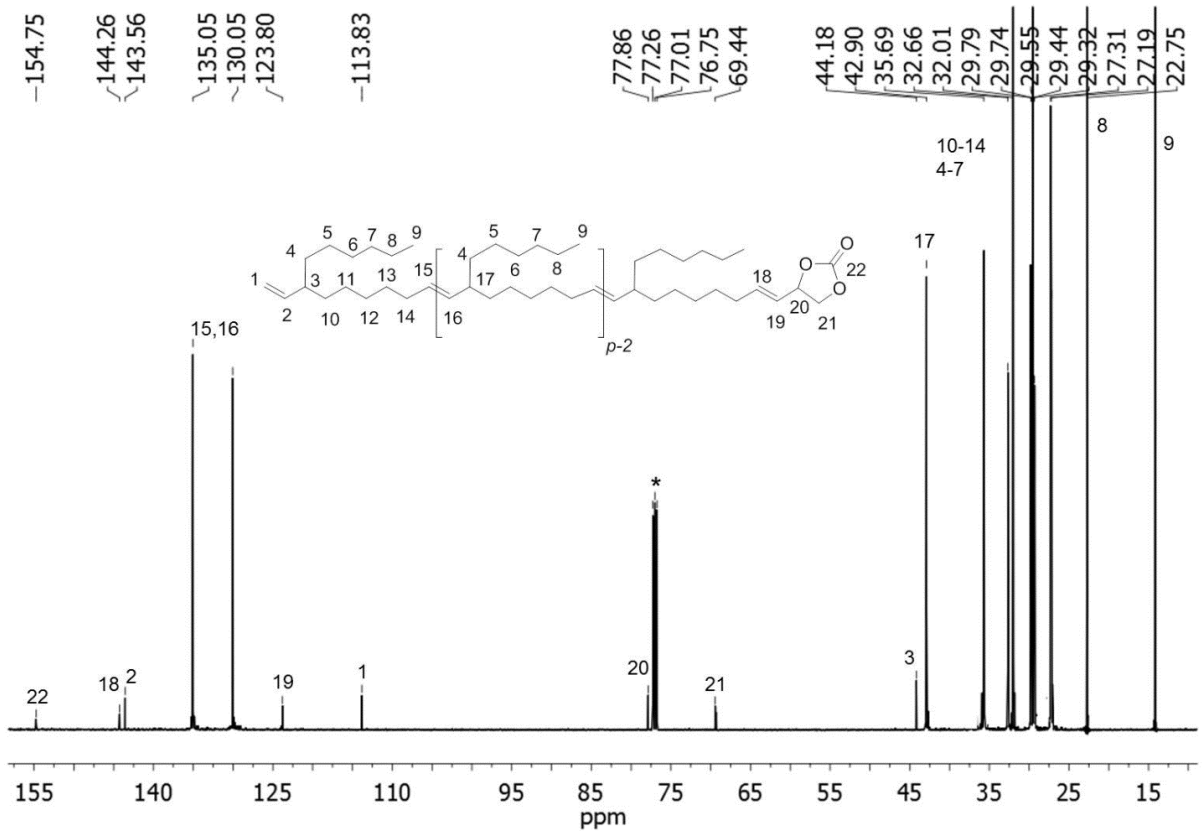

Figure S20. $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 100 MHz, 298 K) of an α-**GC**,ω-vinyl-P(3-*n*-hexyl-COE) prepared from **1** (Table 1, entry 13). δ_{ppm}: repeating unit: 135.0, 130.0, 42.9, 35.7–22.7, 14.1. Chain-end groups: 154.7 (O=COO), 144.3 (*CH*=CH-CHOCOO), 143.6 (CH_2=*CH*-CH), 123.8 (CH=*CH*-CHOCOO), 113.8 (CH_2=CH-CH), 77.9 (CH=CH-*CH*OCOO), 69.5 (CH-CH_2-OCOO), 44.2 (CH_2=CH-*CH*) (* stands for residual solvent resonance).

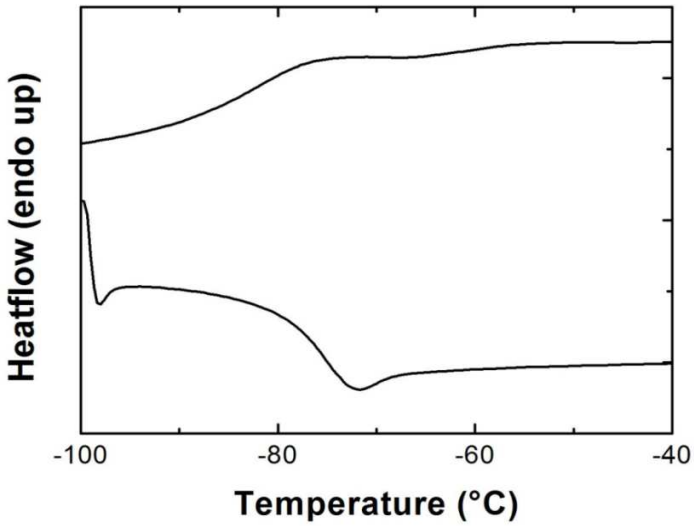

Figure S21. DSC thermogram (second heating cycle) of an α-**GC**,ω-vinyl–P(3-*n*-hexyl-COE) (T_g = –77 °C) synthesized from the ROMP of 3-*n*-hexyl-COE in the presence of **1** (Table 1, entry 13).

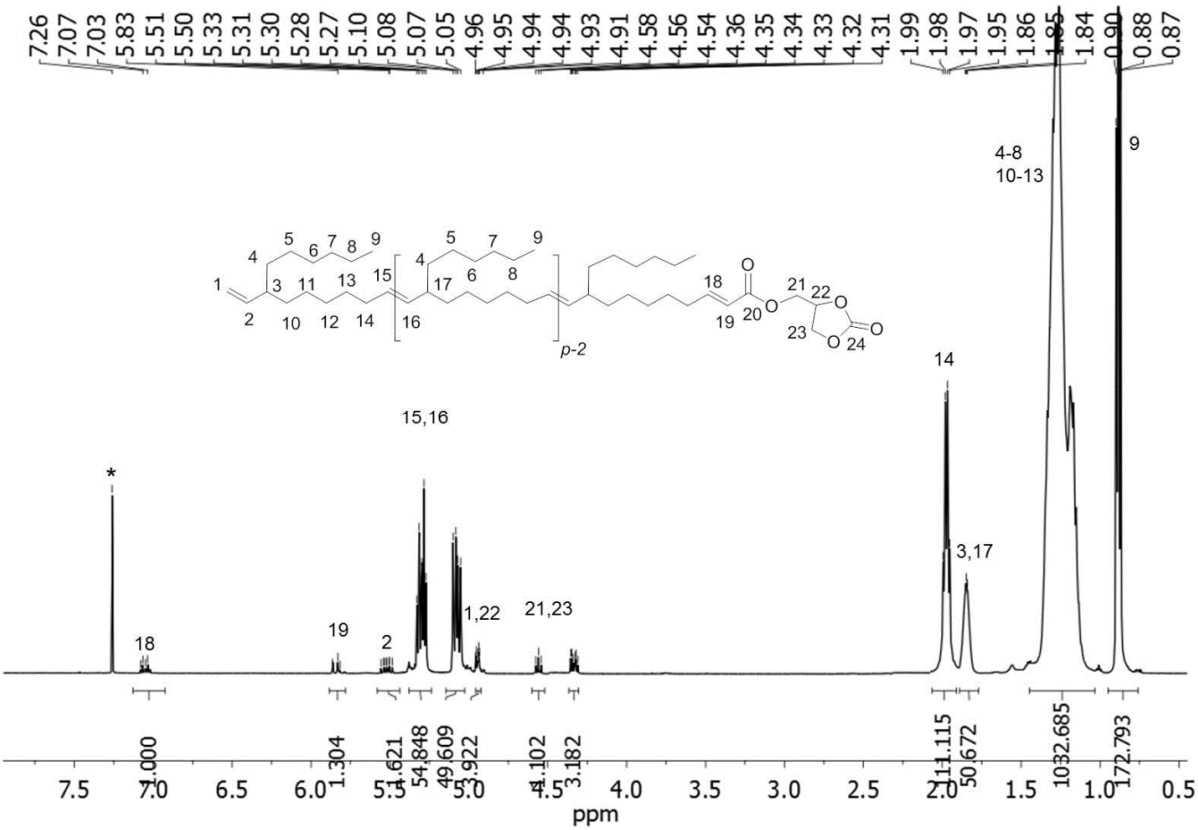

Figure S22. ^{1}H NMR spectrum ($CDCl_3$, 500 MHz, 298 K) of an α-**GC**,ω-vinyl-P(3-*n*-hexyl-COE) prepared from **2** (Table 1, entry 15). δ_{ppm}: repeating unit: 5.33–5.05, 1.99, 1.84, 1.33-1.15, 0.87. Chain-end groups: 7.03 (m, *CH*=CH-CO_2), 5.82 (m, CH=*CH*-CO_2), 5.48 (m, CH_2=*CH*-CH), 4.91 (m, *CH_2*=CH-CH, and CH=CH-*CH*-OCO_2), 4.58–4.31 (m, *CH_2*-CH-CH_2OCOO and CH_2-CH-*CH_2*OCOO), 1.84 (m, CH_2=*CH*-CH) (* stands for residual solvent resonance).

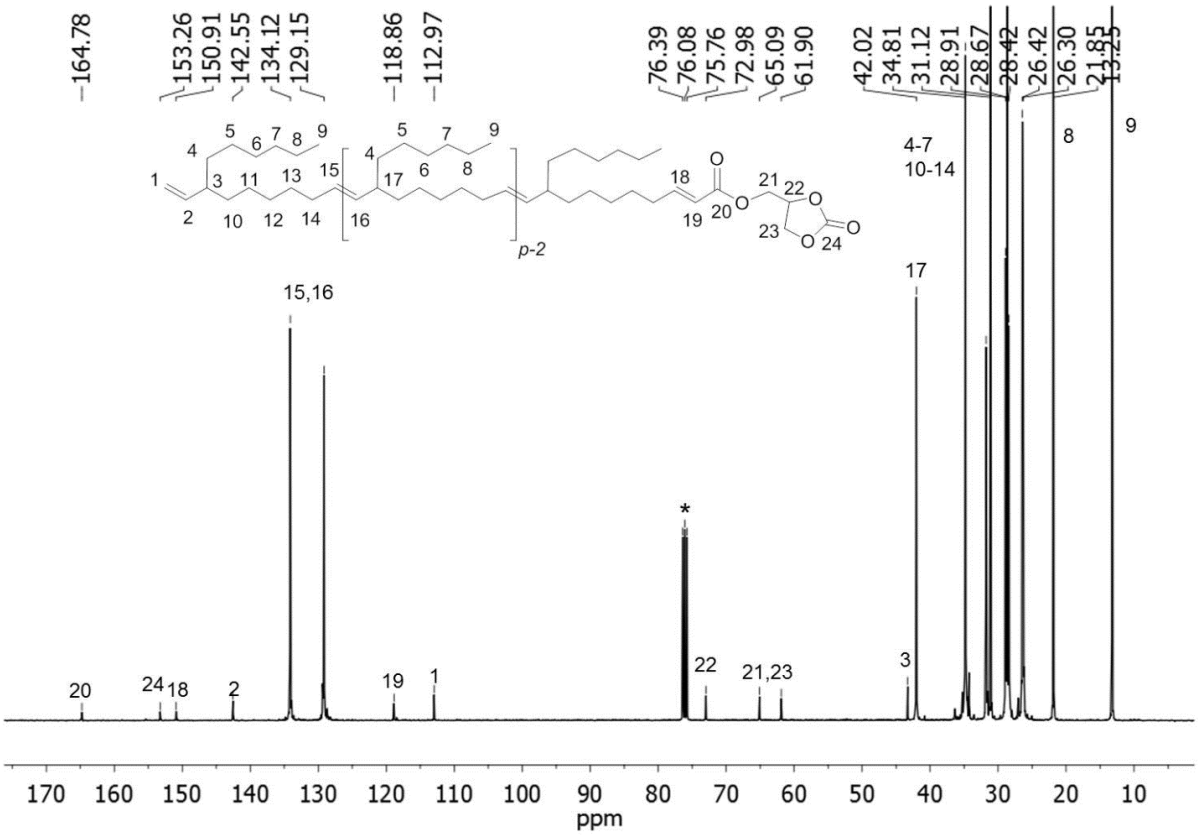

Figure S23. $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 100 MHz, 298 K) of an α-**GC**,ω-vinyl-P(3-*n*-hexyl-COE) prepared from **2** (Table 1, entry 15). δ_{ppm}: repeating unit: 134.1, 129.1, 42.0, 34.8–21.8, 13.2. Chain-end groups: 164.8 (OC=O), 153.3 (O=COO), 150.9 (*CH*=CH-COO), 142.5 (CH_2=*CH*-CH), 118.9 (CH=*CH*-COO), 112.9 (*CH_2*=CH-CH), 73.0 (CH_2-*CH*-CH_2OCOO), 65.1, 61.9 (*CH_2*-CH-CH_2OCOO and CH_2-CH-*CH_2*OCOO), 43.3 (CH_2=CH-*CH*) (* stands for residual solvent resonance).

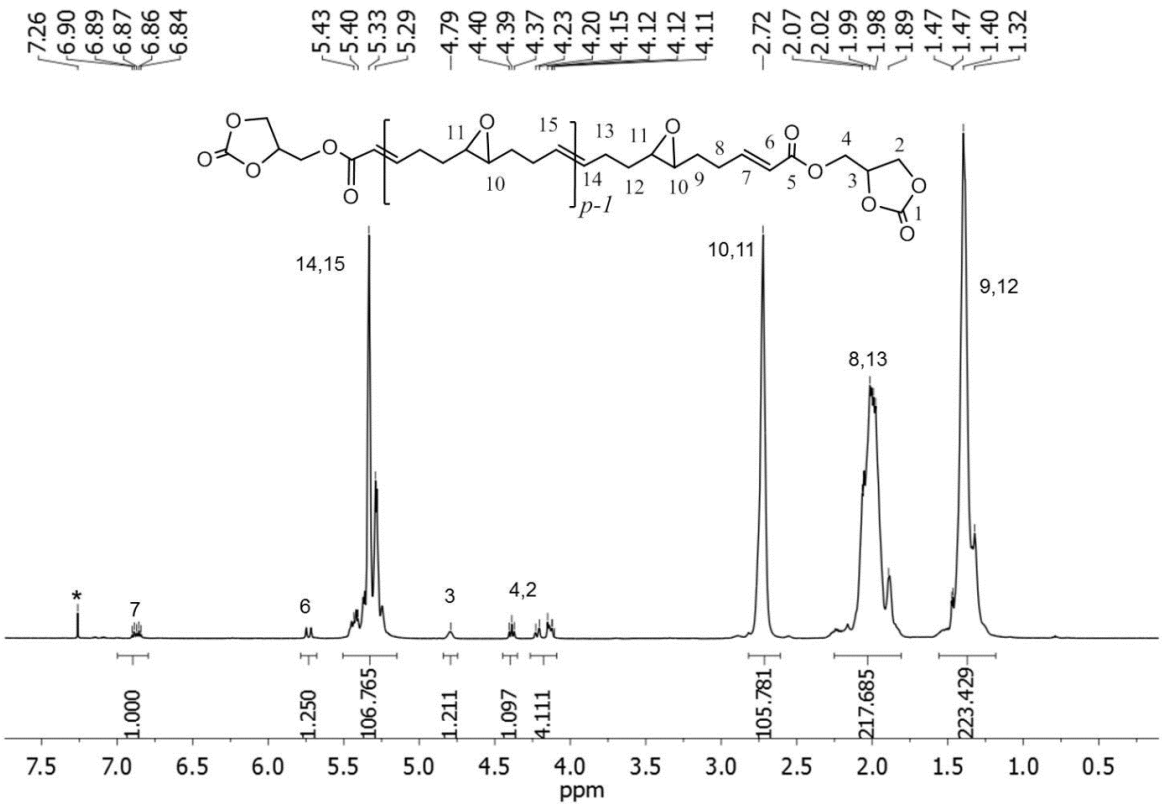

Figure S24. ^{1}H NMR spectrum ($CDCl_3$, 500 MHz, 298 K) of an α,ω-di(**GC**)-P(5,6-epoxy-COE) prepared from **2** (Table 1, entry 18). δ_{ppm}: repeating unit: 5.43-5.29, 2.72, 2.07–1.89, 1.47-1.32 chain-end groups: 6.84 (m, *CH*=CH-CO_2), 5.72 (m, CH=*CH*-CO_2), 4.79 (broad signal, CH_2-C*H*-CH_2OCOO), 4.40–4.11 (m, *CH_2*-CH-CH_2OCOO and CH_2-CH-*CH_2*OCOO) (* stands for residual solvent resonance).

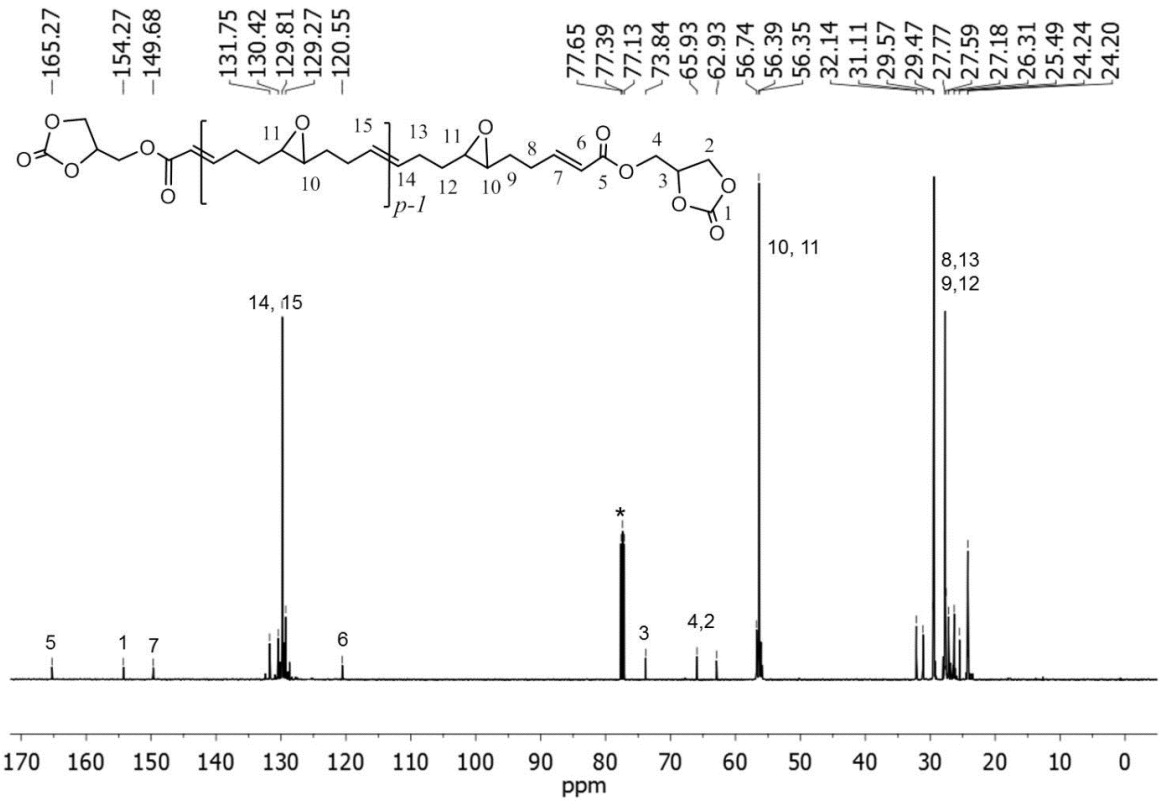

Figure S25. $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 100 MHz, 298 K) of an α,ω-di(**GC**)-P(5,6-epoxy-COE) prepared from **2** (Table 1, entry 18). δ_{ppm}: repeating unit: 131.7–129.3, 56.7, 32.1–24.2, chain-end groups: 165.3 (OC=O), 154.3 (O=COO), 149.7 (*CH*=CH-COO), 120.5 (CH=*CH*-COO), 73.8 (CH_2-*CH*-CH_2OCOO), 65.9, 62.9 (*CH_2*-CH-CH_2OCOO and CH_2-CH-*CH_2*OCOO) (* stands for residual solvent resonance).

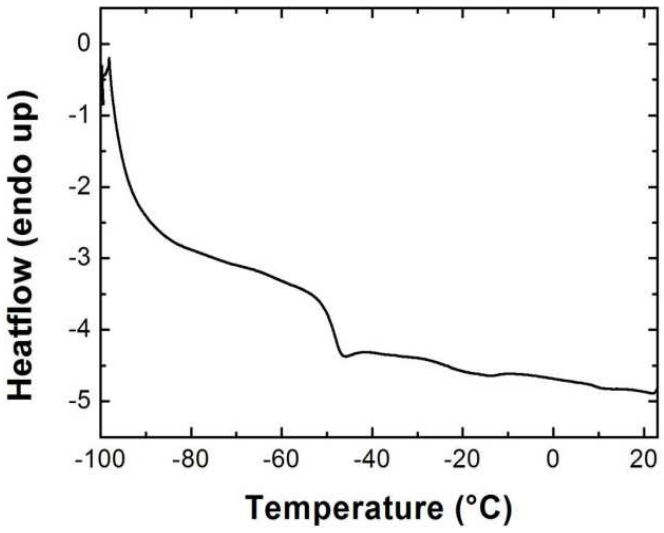

Figure S26. DSC thermogram (second heating cycle) of an α,ω-di(**GC**)-P(5,6-epoxy-COE) (T_g = –48 °C) synthesized from the ROMP of 5,6-epoxy-COE in the presence of **2** (Table 1, entry 18).

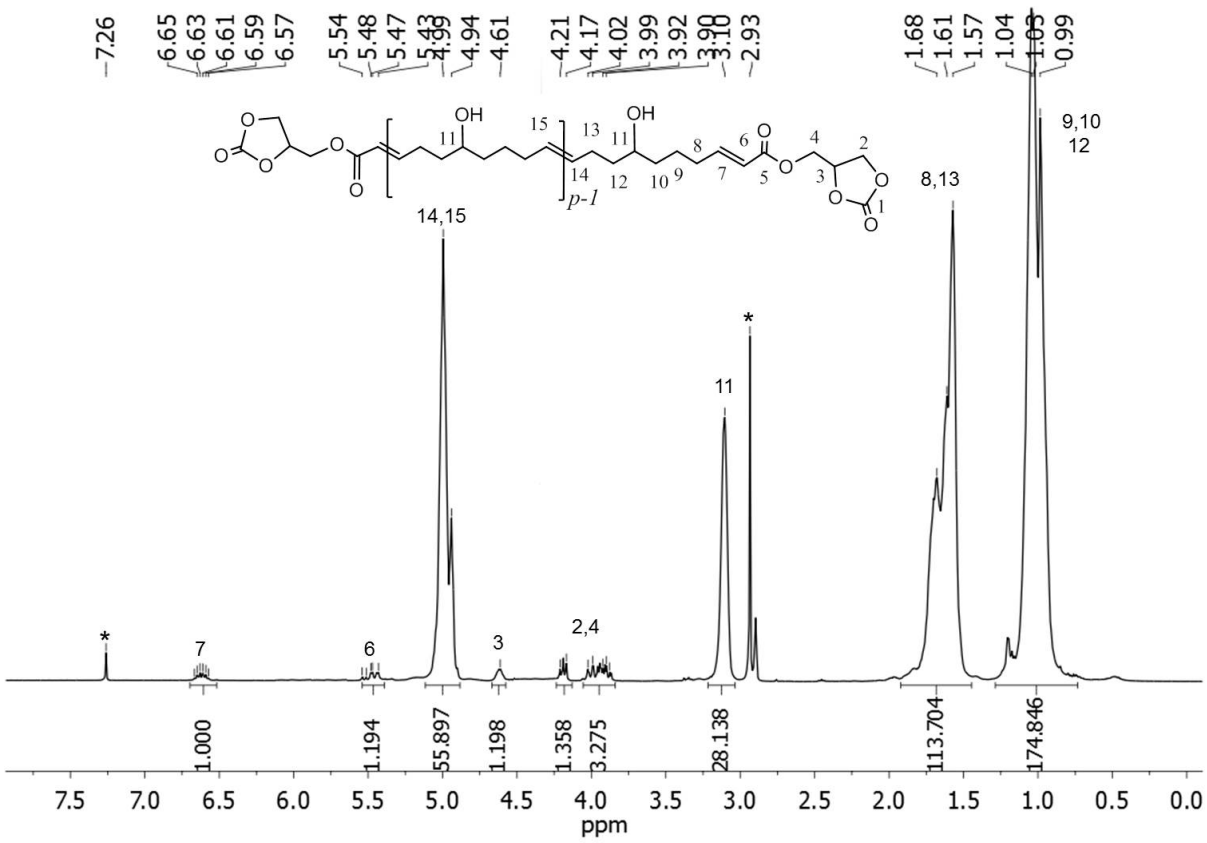

Figure S27. ^{1}H NMR spectrum ($CDCl_3/CD_3OD$, 500 MHz, 298 K) of an α,ω-di(**GC**)-P(5-OH-COE) prepared from **2** (Table 1, entry 19). δ_{ppm}: repeating unit: 4.99, 4.94, 3.10, 1.68, 1.61, 1.57, 1.04–0.99, chain-end groups: 6.57 (m, *CH*=CH-CO_2), 5.43 (m, CH=*CH*-CO_2), 4.61 (broad peak, CH_2-C*H*-CH_2OCOO), 4.21–3.90 (m, *CH_2*-CH-CH_2OCOO and CH_2-CH-*CH_2*OCOO) (* stands for residual solvent resonance).

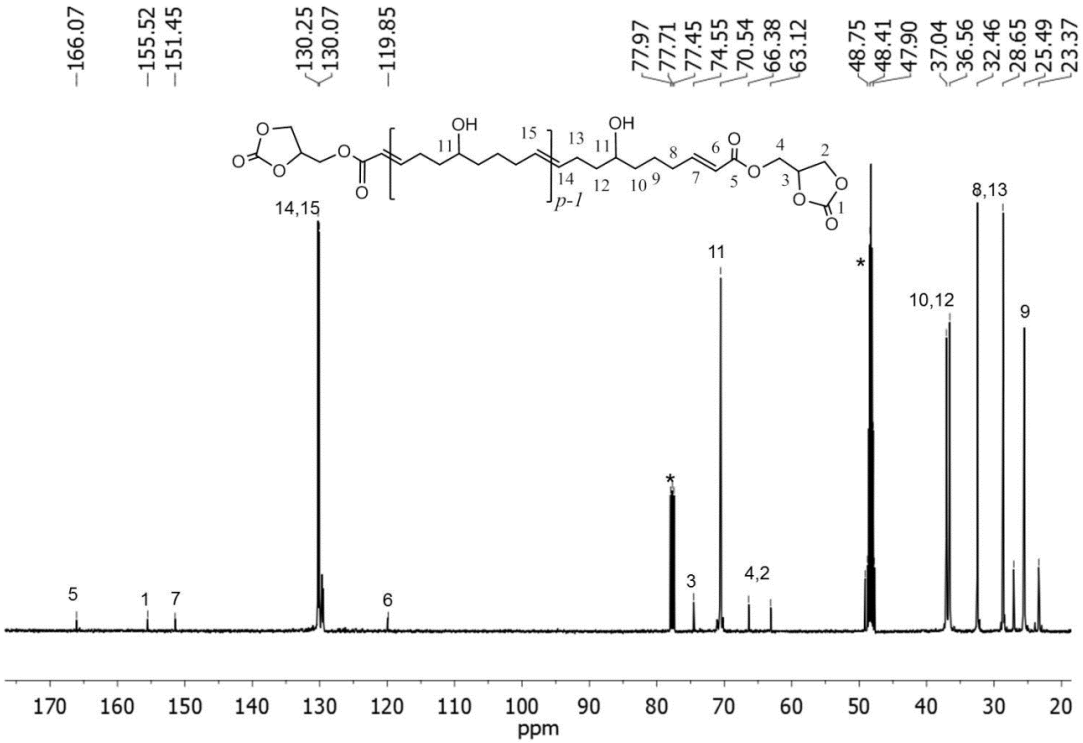

Figure S28. $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3/CD_3OD$, 100 MHz, 298 K) of an α,ω-di(**GC**)-P(5-OH-COE) prepared from **2** (Table 1, entry 19). δ_{ppm}: repeating unit: 130.2–130.1, 70.5, 37.0, 36.6, 32.5, 28.6, 25.5, 23.4, chain-end groups: 166.1(OC=O), 155.5 (O=COO), 151.4 (*CH*=CH-COO), 119.8 (CH=*CH*-COO), 74.5 (CH_2-*CH*-CH_2OCOO), 66.4, 63.1 (*CH_2*-CH-CH_2OCOO and CH_2-CH-*CH_2*OCOO) (* stands for residual solvent resonance).

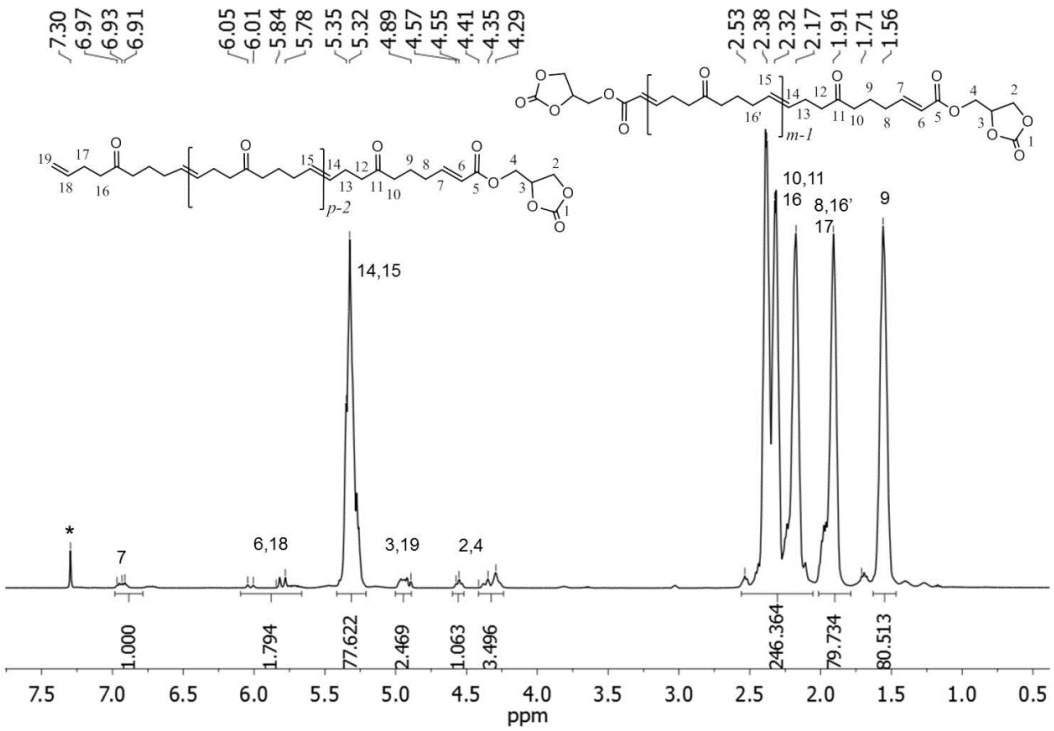

Figure S29. ^{1}H NMR spectrum ($CDCl_3$, 500 MHz, 298 K) of a mixture of α,ω-di(**GC**)-P(5-O=COE) and α-**GC**,ω-vinyl-P(5-O=COE) prepared from **2** (Table 1, entry 20). δ_{ppm}: repeating unit: 5.35, 5.32, 2.53, 2.38, 2.32, 2.17, 1.91, 1.71, 1.56, chain-end groups: 6.91 (m, *CH*=CH-CO_2), 6.05–5.78 (m, CH=*CH*-CO_2 and CH_2=*CH*-CH_2), 4.89 (broad signal, CH_2-C*H*-CH_2OCOO and *CH_2*=CH-CH_2), 4.57–4.29 (m, *CH_2*-CH-CH_2OCOO and CH_2-CH-*CH_2*OCOO) (* stands for residual solvent resonance).

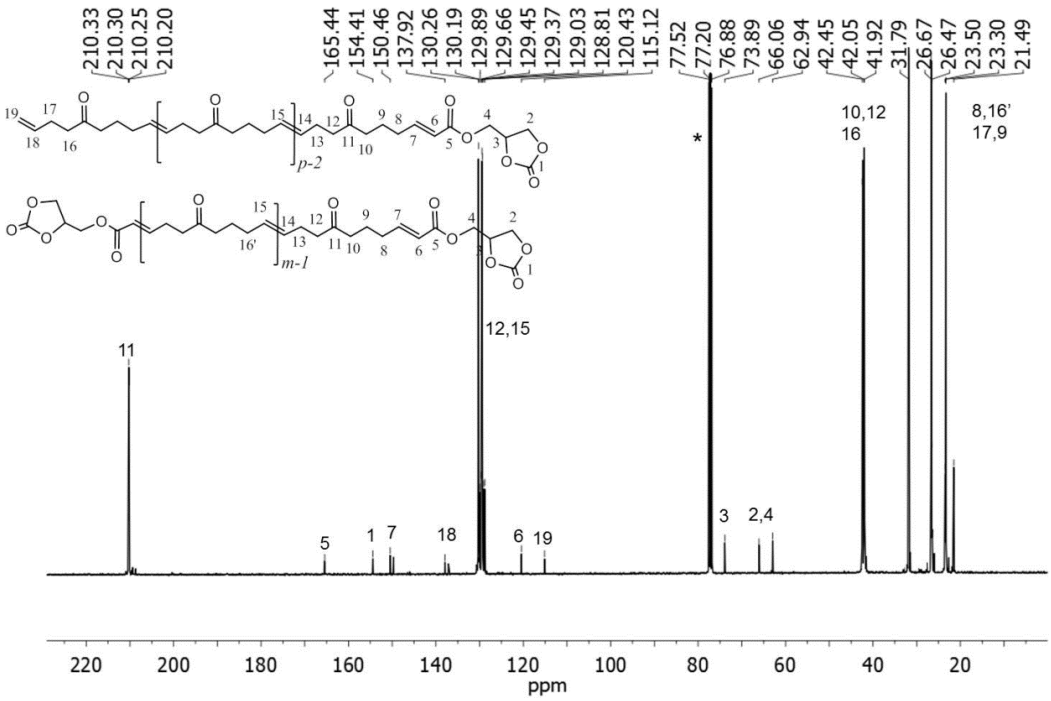

Figure S30. $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 100 MHz, 298 K) of a mixture of α,ω-di(**GC**)-P(5-O=COE) and α-**GC**,ω-vinyl-P(5-O=COE) prepared from **2** (Table 1, entry 20). δ_{ppm}: repeating unit: 210.2, 130.3–128.8, 42.4–41.9, 31.8, 26.7, 26.5, 23.5, 23.3, 21.5, chain-end groups: 165.4 (OC=O), 154.4 (O=COO), 150.5 (*CH*=CH-COO), 137.9 (CH_2=*CH*-CH_2), 120.4 (CH=*CH*-COO), 115.1 (*CH_2*=CH-CH_2), 73.9 (CH_2-*CH*-CH_2OCOO), 66.1, 62.9 (*CH_2*-CH-CH_2OCOO and CH_2-CH-*CH_2*OCOO) (* stands for residual solvent resonance).