Supporting Information for

α,ω-Bis(Trialkoxysilyl) Difunctionalized Polycyclooctenes from Ruthenium-Catalyzed Chain-Transfer Ring-Opening Metathesis Polymerization

Figure S1. ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298 K) of CTA **2**

Figure S2. $^{13}C\{^{1}H\}$ NMR spectrum (125 MHz, $CDCl_3$, 298 K) of CTA **2**

Figure S3. ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298 K) of CTA **3-OEt**

Figure S4. $^{13}C\{^{1}H\}$ NMR spectrum (125 MHz, $CDCl_3$, 298 K) of CTA **3-OEt**

Figure S5. ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298 K) of CTA **isom-4**

Figure S6. $^{13}C\{^{1}H\}$ NMR spectrum (125 MHz, $CDCl_3$, 298 K) of CTA **isom-4**

Figure S7. ESI-HR mass spectrum of CTA **isom-4**

Figure S8. FTIR spectrum of CTA **isom-4**

Figure S9. ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298 K) of CTA **5**

Figure S10. $^{13}C\{^{1}H\}$ NMR spectrum (125 MHz, $CDCl_3$, 298 K) of CTA **5**

Figure S11. ESI-HR mass spectrum of CTA **5**

Figure S12. FTIR spectrum of CTA **5**

Figure S13. ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298 K) of CTA **6**

Figure S14. $^{13}C\{^{1}H\}$ NMR spectrum (125 MHz, $CDCl_3$, 298 K) of CTA **6**

Figure S15. ESI-HR mass spectrum of CTA **6**

Figure S16. FTIR spectrum of CTA **6**

Figure S17. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, $CDCl_3$, 298 K) of a crude polymer prepared by ROMP/CM of COE using **G2** and CTA **2.**

Figure S18. ^{1}H-^{1}H COSY NMR spectrum (500 MHz, $CDCl_3$, 298 K) of a crude polymer prepared by ROMP/CM of COE using **G2** and CTA **2.**

Figure S19. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of a **CNF** PCOE sample isolated from a crude polymer prepared by ROMP/CM of COE using **G2** and CTA **1** (Table 1, entry 1)

Figure S20. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, $CDCl_3$, 298 K) of a **CNF** PCOE sample isolated from a crude polymer prepared by ROMP/CM of COE using **G2** and CTA **1** (Table 1, entry 1)

Figure S21. SEC traces of PCOE samples prepared from the ROMP/CM of COE using **G2** catalyst and CTAs **2** or **5** in CH_2Cl_2 at 40 °C for 24 h (Table 2, entries 10, 16, 20).

Figure S22. DEPT 135 $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, $CDCl_3$, 298 K) of a crude polymer sample prepared by ROMP/CM of COE using **G2** and CTA **2** (Table 1, entry 2).

Figure S23. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of **CNF** PCOE isolated from a crude polymer prepared by ROMP/CM of COE using **G2** and CTA **2** (Table 2, entry 10)

Figure S24. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, $CDCl_3$, 298 K) of **CNF** PCOE isolated from a crude polymer prepared by ROMP/CM of COE using **G2** and CTA **2** (Table 2, entry 10)

Figure S25. ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298 K) of a crude polymer prepared by ROMP/CM of COE using **G2** and CTA **3-OMe** (Table 1, entry 4).

Figure S26. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, $CDCl_3$, 298 K) of a crude polymer prepared by ROMP/CM of COE using **G2** and CTA **3-OMe** (Table 1, entry 4).

Figure S27. ESI-HRMS spectrum, ionized with Na^+, of a crude polymer prepared by ROMP/CM of COE using **G2** and CTA **3-OMe** (Table 1, entry 4).

Figure S28. FTIR spectrum of a crude polymer prepared by ROMP/CM of COE using **G2** and CTA **3-OMe** (Table 1, entry 4).

Figure S29. ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298 K) of a crude polymer prepared by ROMP/CM of COE using **G2** and CTA **3-OEt** (Table 1, entry 7).

Figure S30. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, $CDCl_3$, 298 K) of a crude polymer prepared by ROMP/CM of COE using **G2** and CTA **3-OEt** (Table 1, entry 7).

Figure S31. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, $CDCl_3$, 298 K) of a crude polymer prepared by ROMP/CM of COE using **G2** and CTA **4** (Table 1, entry 8).

Figure S32. FTIR spectrum of a crude polymer prepared by ROMP/CM of COE using **G2** and CTA **4** (Table 1, entry 8).

Figure S33. MALDI-ToF mass spectrum (DCTB matrix, sodium ionizing salt: NaI) of a crude polymer prepared by ROMP/CM of COE using **G2** and CTA **4** (Table 1, entry 8), showing the presence of DF PCOE; see top zoomed region and the corresponding middle and bottom simulations for $n = 7$.

Figure S34. ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298 K) of a crude polymer sample prepared by ROMP/CM of COE using **G2** and CTA **5** (Table 1, entry 10).

Figure S35. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, $CDCl_3$, 298 K) of a crude polymer prepared by ROMP/CM of COE using **G2** and CTA **5** (Table 1, entry 10).

Figure S36. ^{1}H-^{13}C HMQC NMR spectrum (125 MHz, $CDCl_3$, 298 K) of a crude polymer prepared by ROMP/CM of COE using **G2** and CTA **5** (Table 1, entry 10).

Figure S37. FTIR spectrum of a crude polymer prepared by ROMP/CM of COE using **G2** and CTA **5** (Table 1, entry 10).

Figure S38. MALDI-ToF mass spectrum (DCTB matrix, sodium ionizing salt: NaI) of a crude polymer prepared by ROMP/CM of COE/CTA **5** using **G2** (Table 1, entry 10), showing

the presence of DF PCOE; see top zoomed region and the corresponding middle and bottom simulations

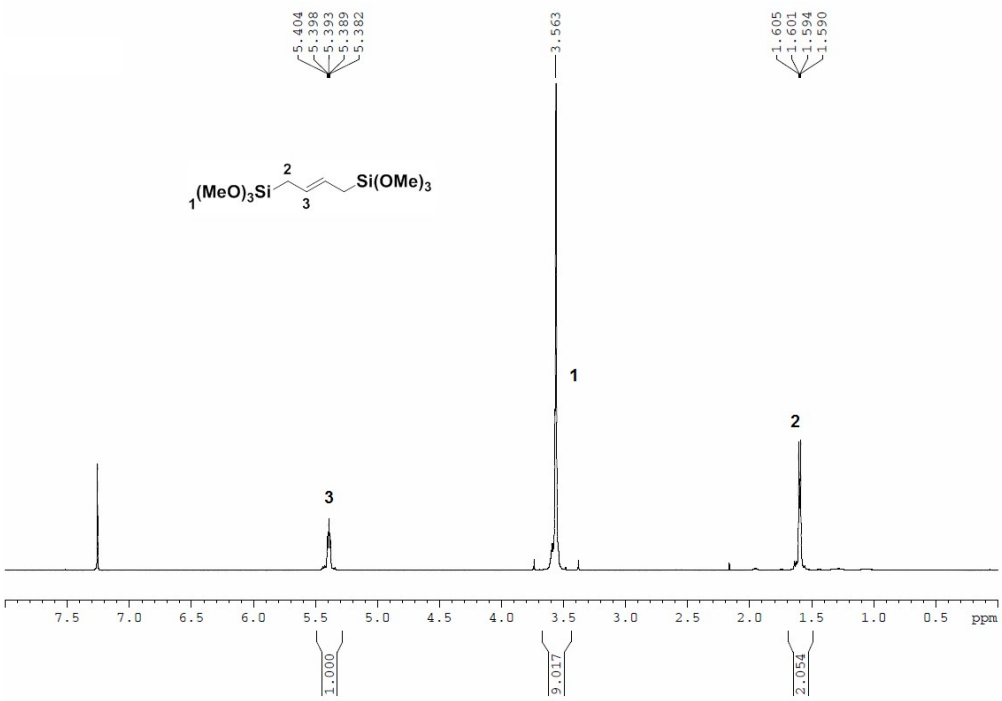

Figure S1. ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298 K) of CTA **2**

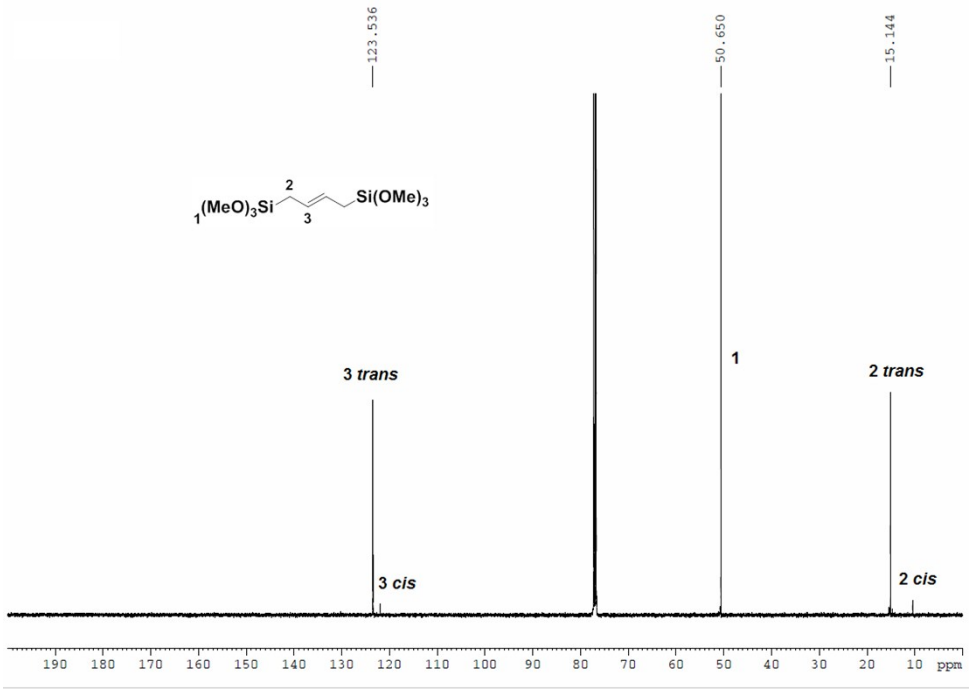

Figure S2. $^{13}C\{^{1}H\}$ NMR spectrum (125 MHz, $CDCl_3$, 298 K) of CTA **2**

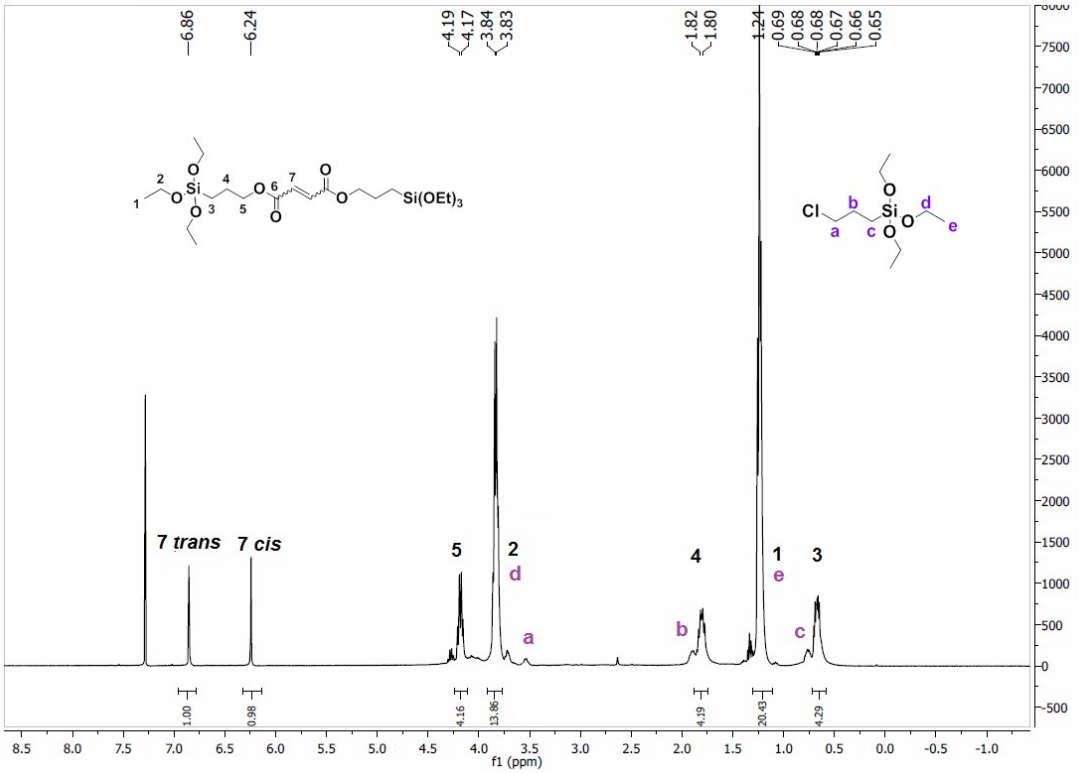

Figure S3. ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298 K) of CTA **3-OEt**

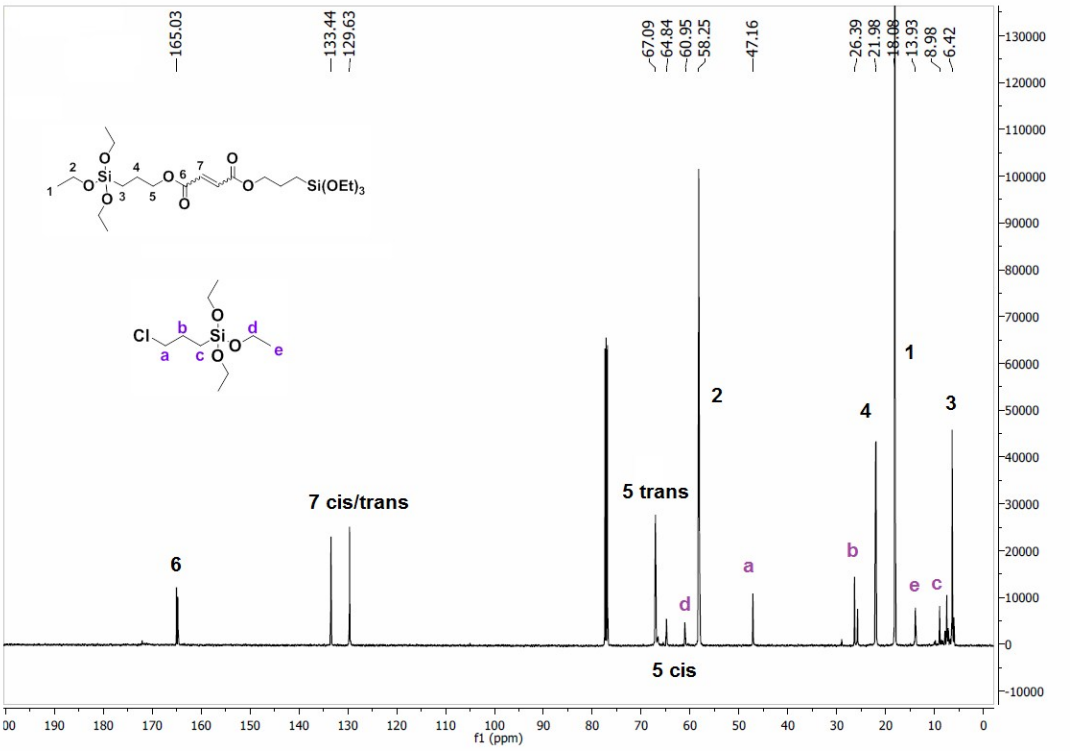

Figure S4. $^{13}C\{^{1}H\}$ NMR spectrum (125 MHz, $CDCl_3$, 298 K) of CTA **3-OEt**

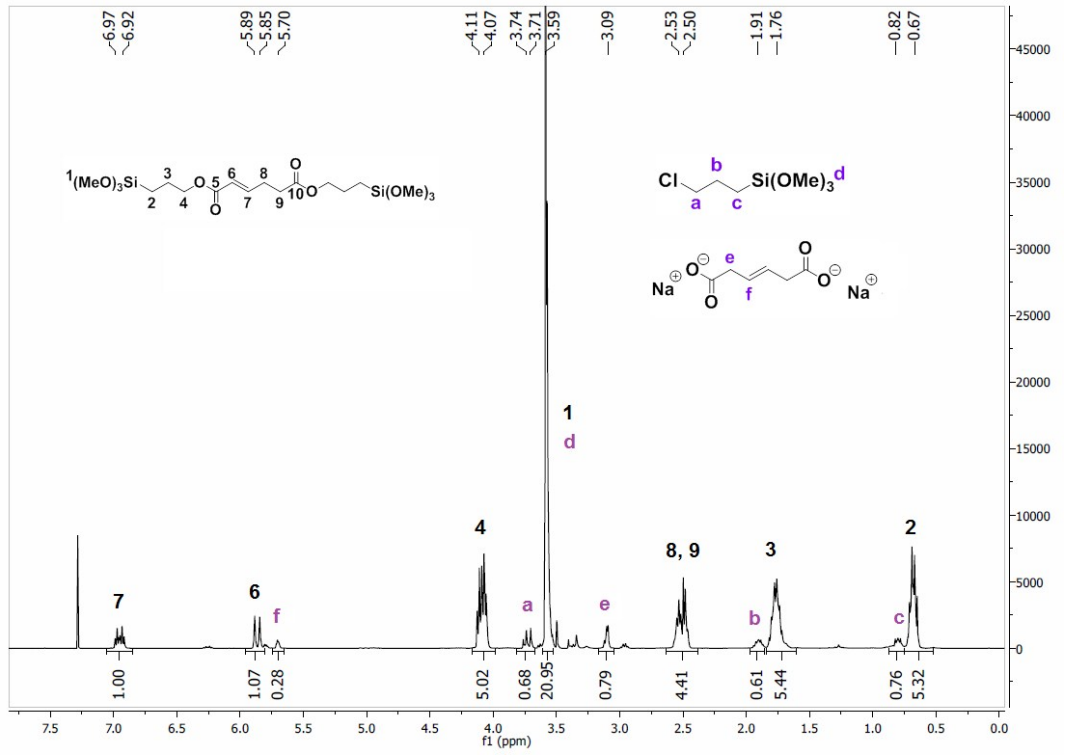

Figure S5. ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298 K) of CTA **isom-4**

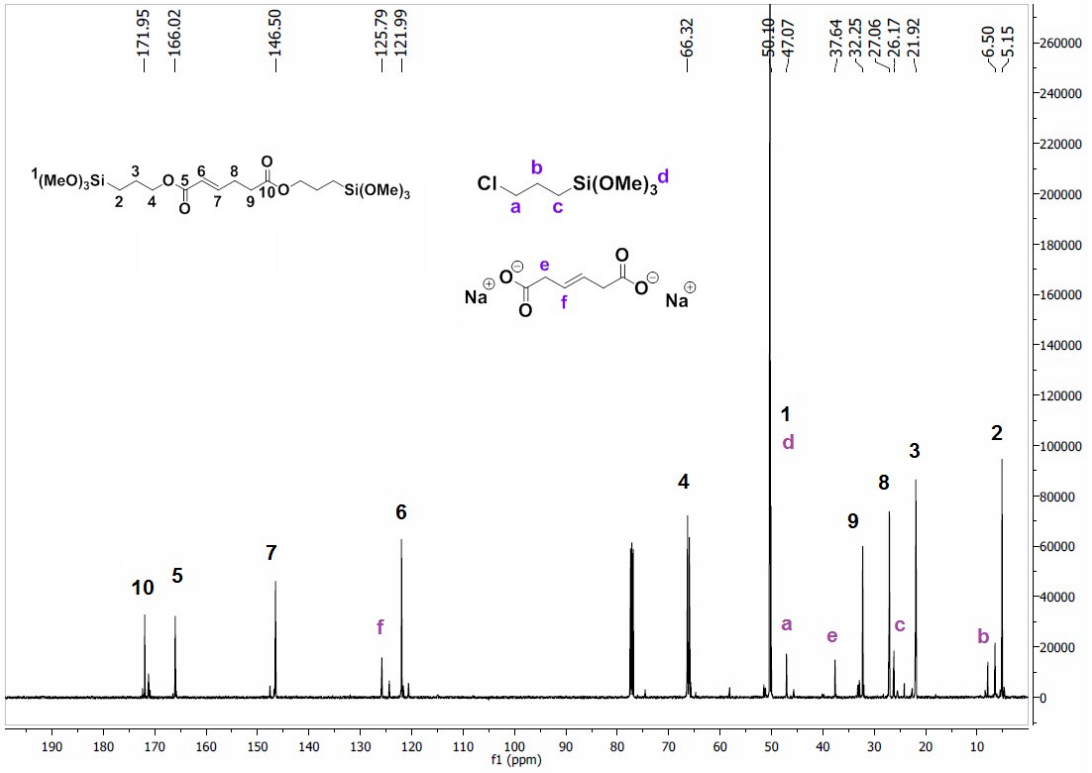

Figure S6. $^{13}C\{^{1}H\}$ NMR spectrum (125 MHz, $CDCl_3$, 298 K) of CTA **isom-4**

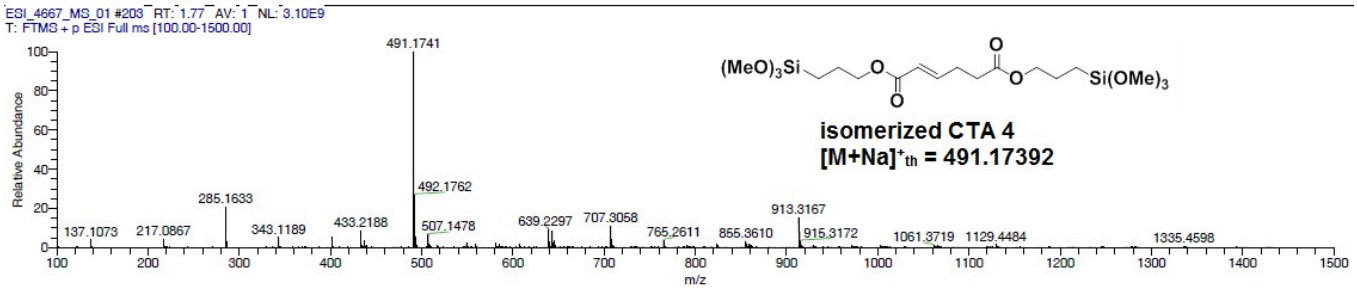

Figure S7. ESI-HR mass spectrum of CTA **isom-4**

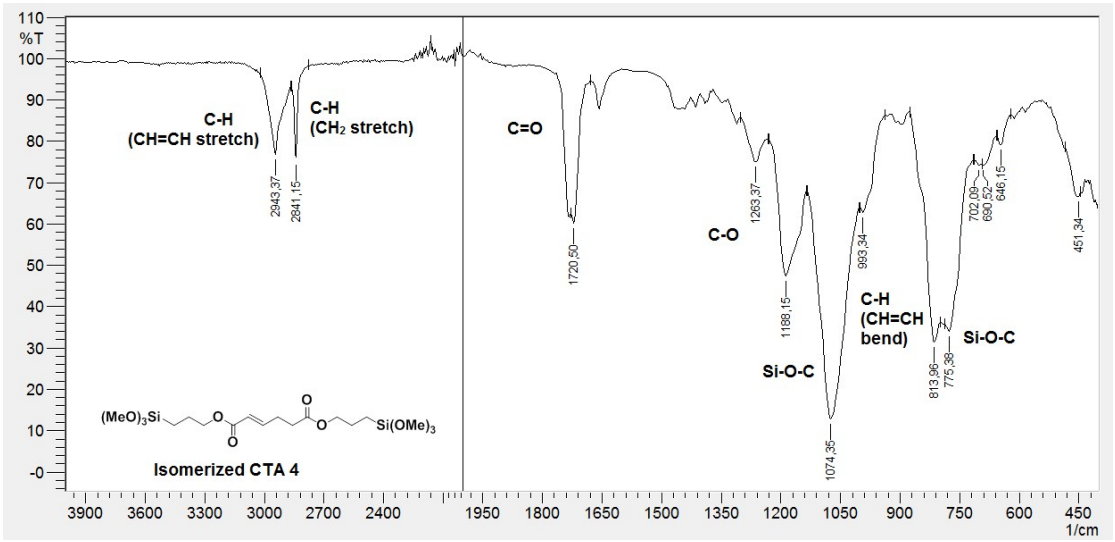

Figure S8. FTIR spectrum of CTA **isom-4**

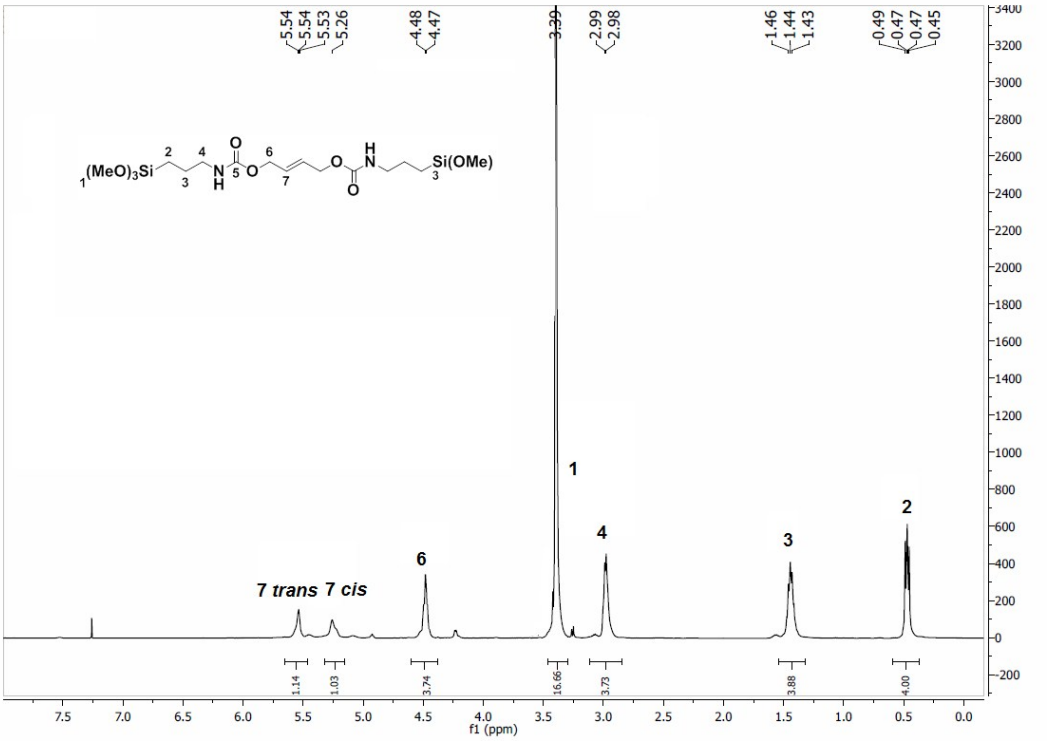

Figure S9. ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298 K) of CTA **5**

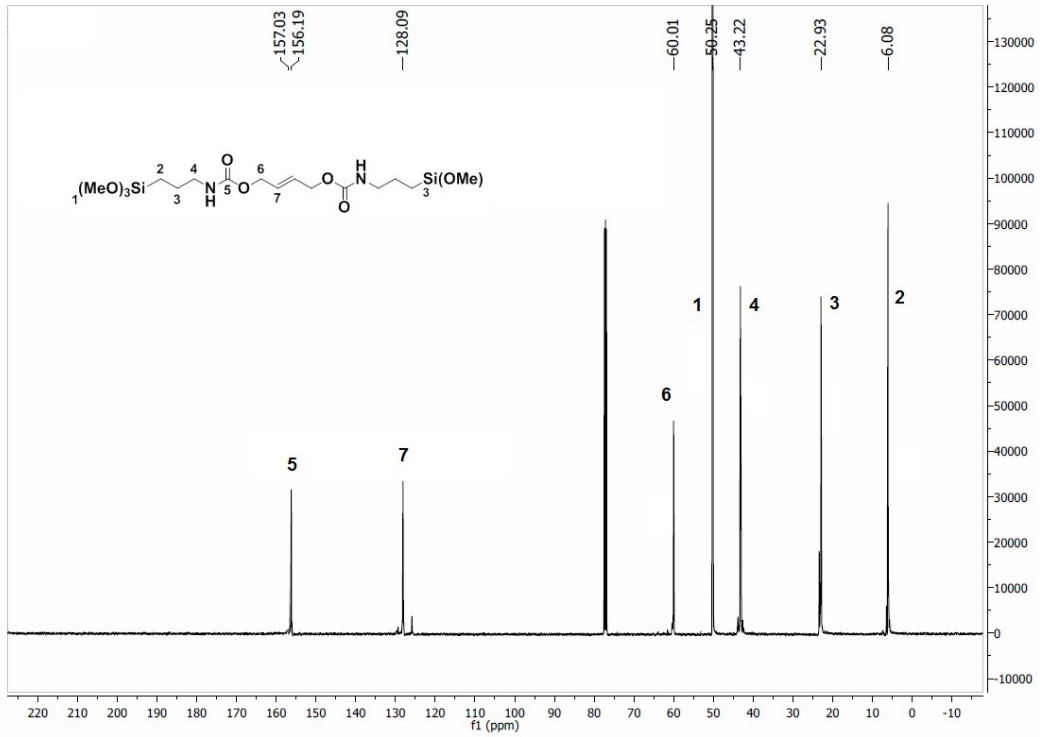

Figure S10. $^{13}C\{^{1}H\}$ NMR spectrum (125 MHz, $CDCl_3$, 298 K) of CTA **5**

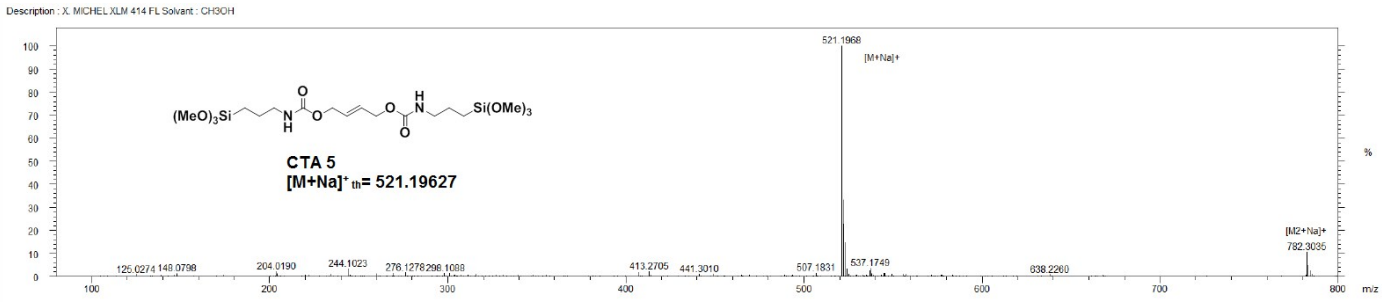

Figure S11. ESI-HR mass spectrum of CTA **5**

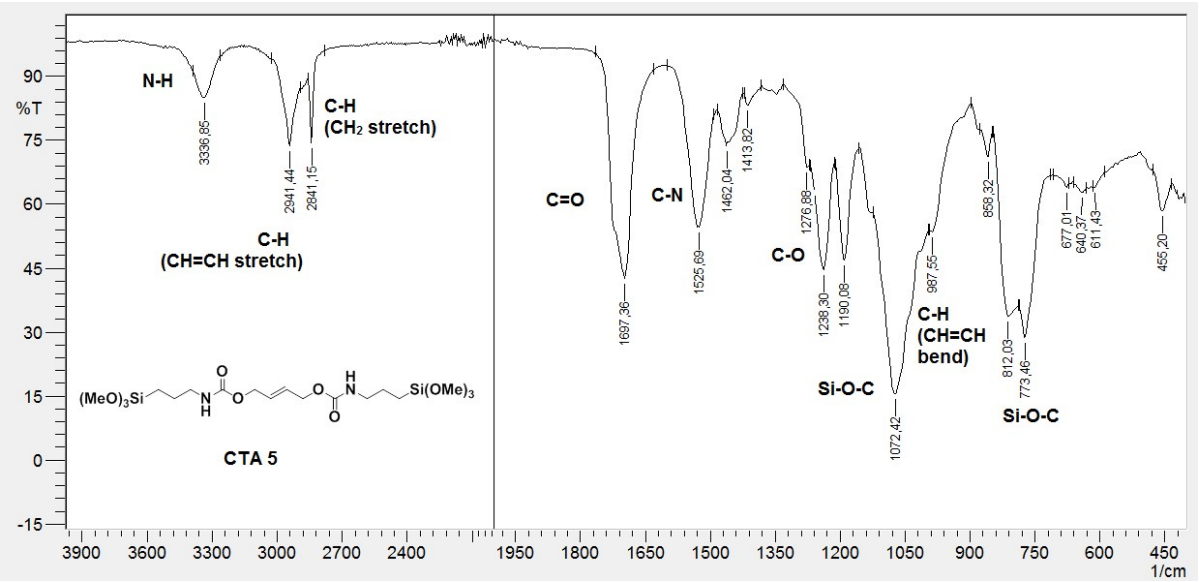

Figure S12. FTIR spectrum of CTA **5**

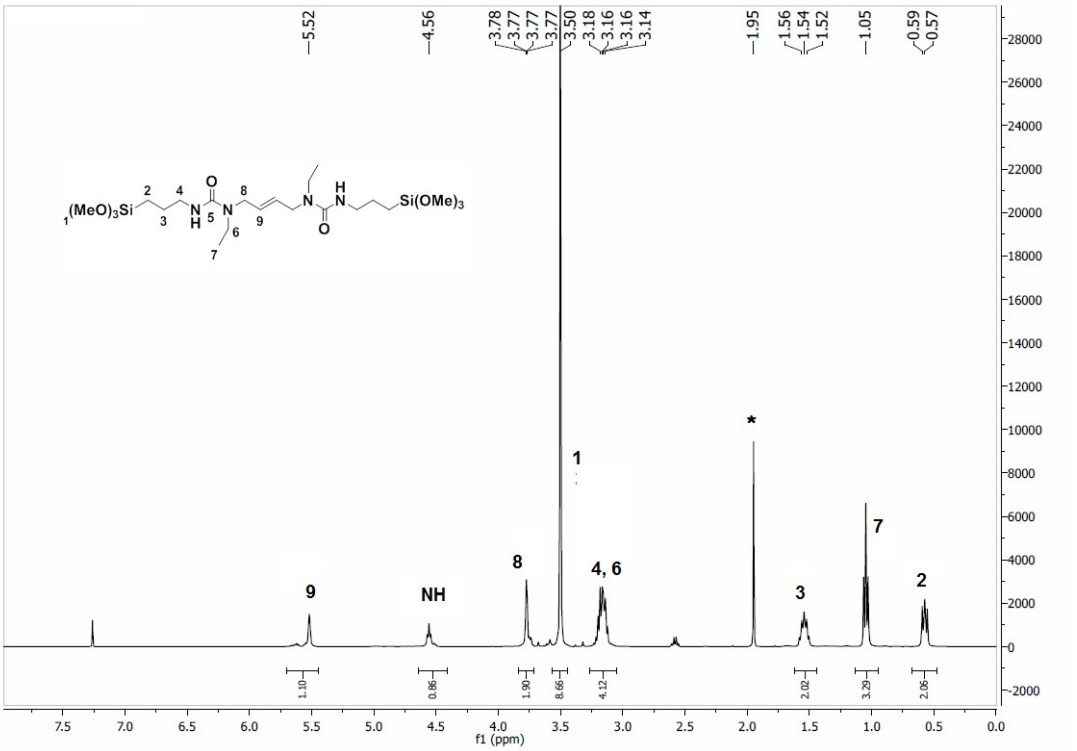

Figure S13. ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298 K) of CTA **6**

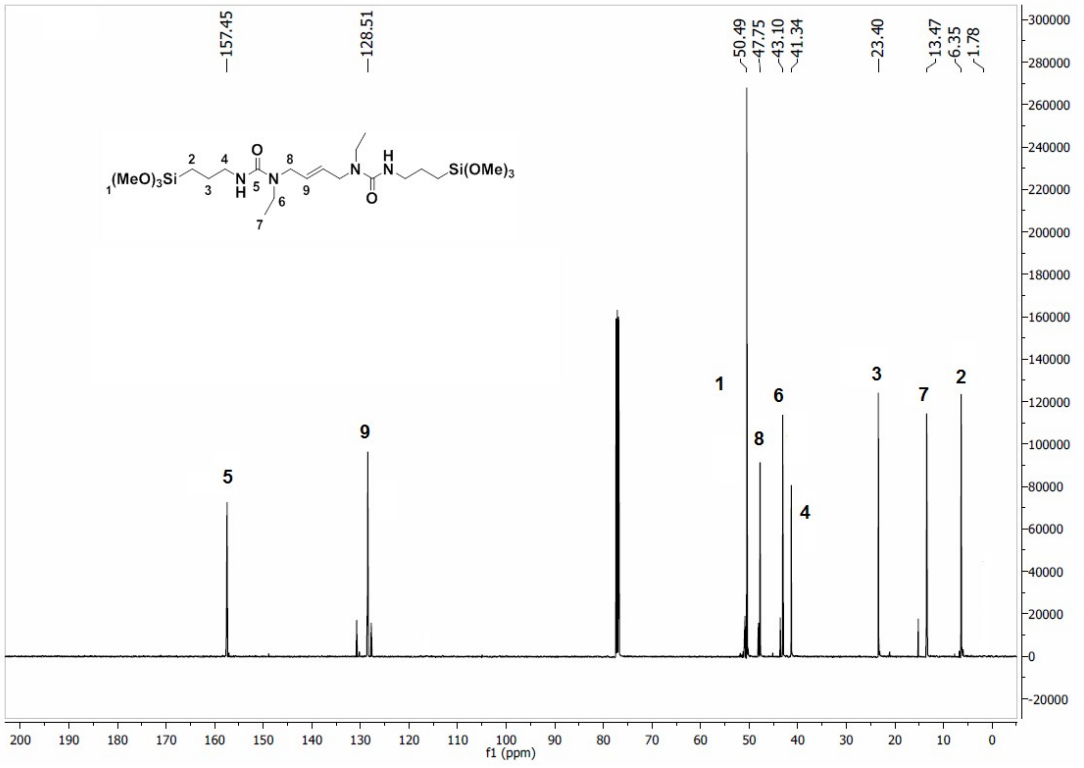

Figure S14. $^{13}C\{^{1}H\}$ NMR spectrum (125 MHz, $CDCl_3$, 298 K) of CTA **6**

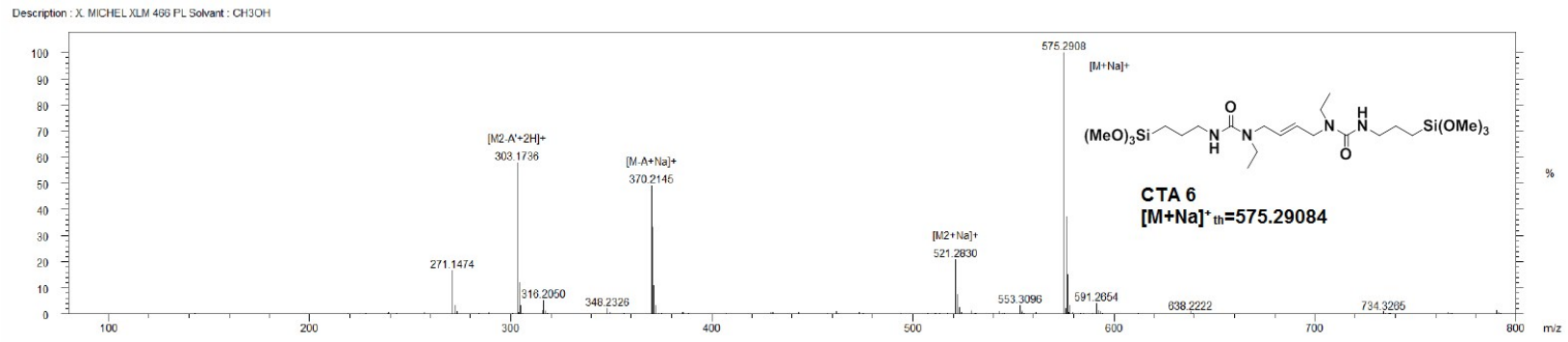

Figure S15. ESI-HR mass spectrum of CTA **6**

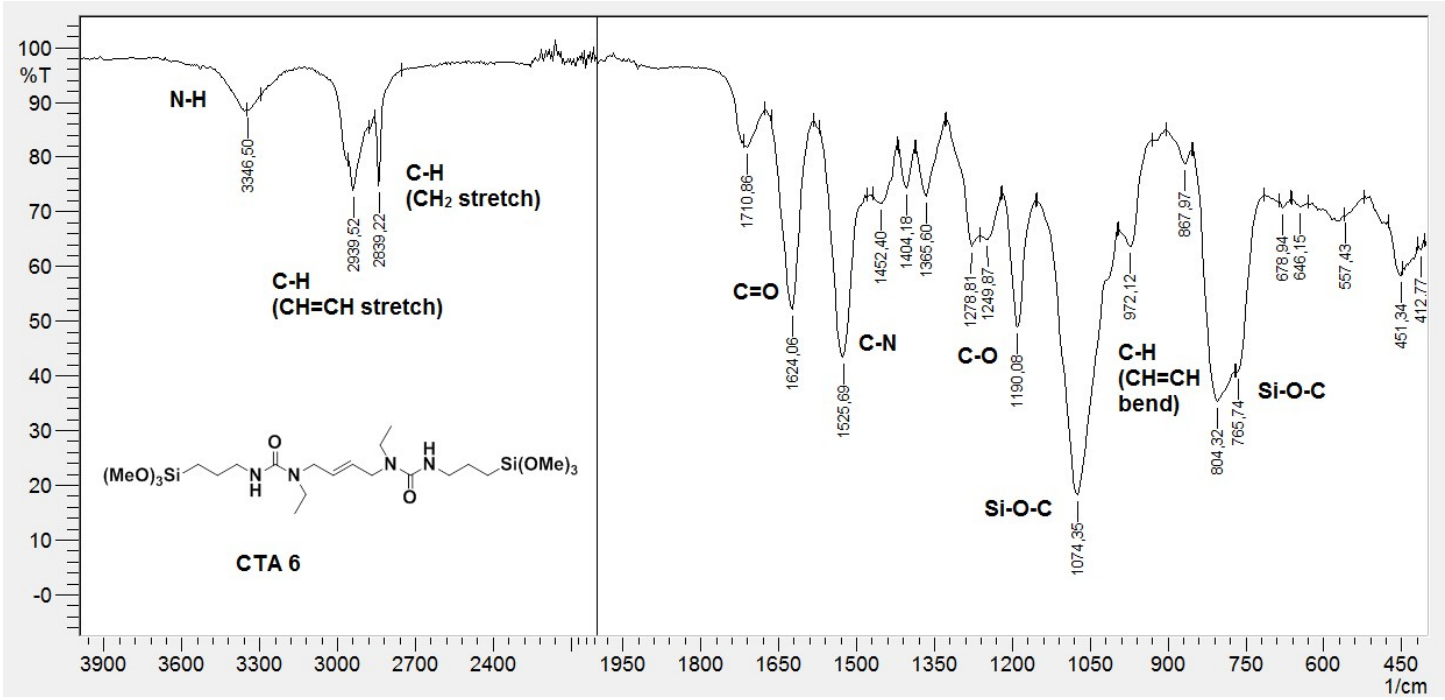

Figure S16. FTIR spectrum of CTA **6**

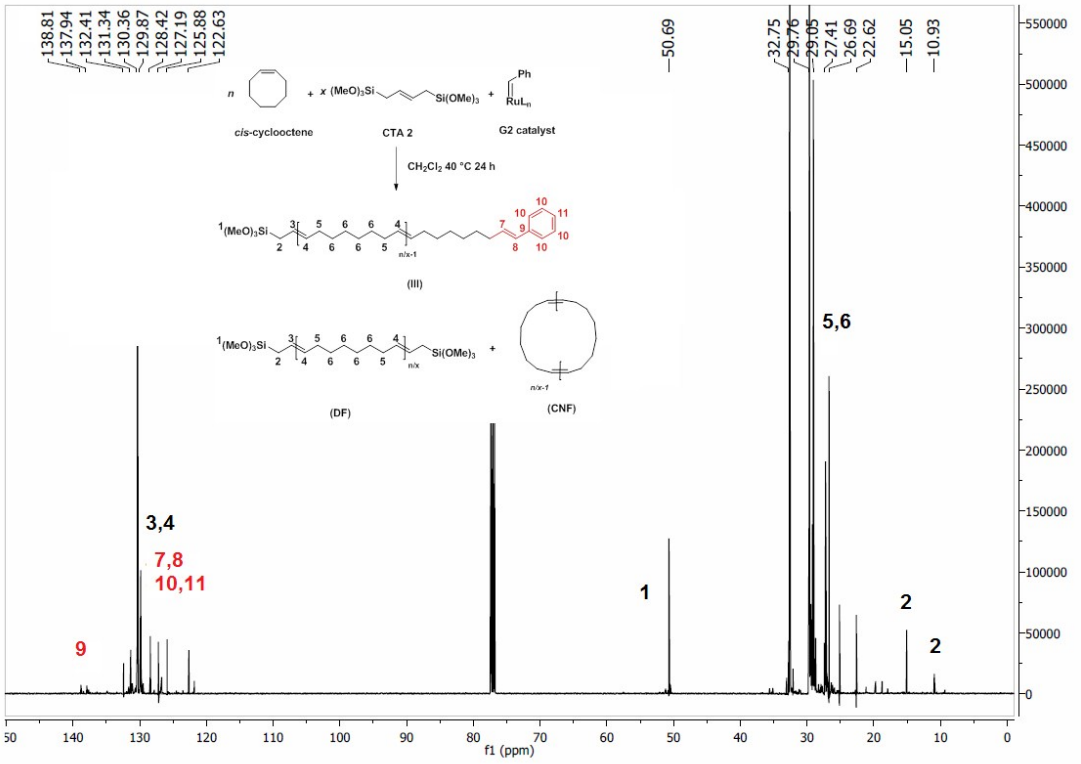

Figure S17. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, $CDCl_3$, 298 K) of a crude polymer prepared by ROMP/CM of COE using **G2** and CTA **2.**

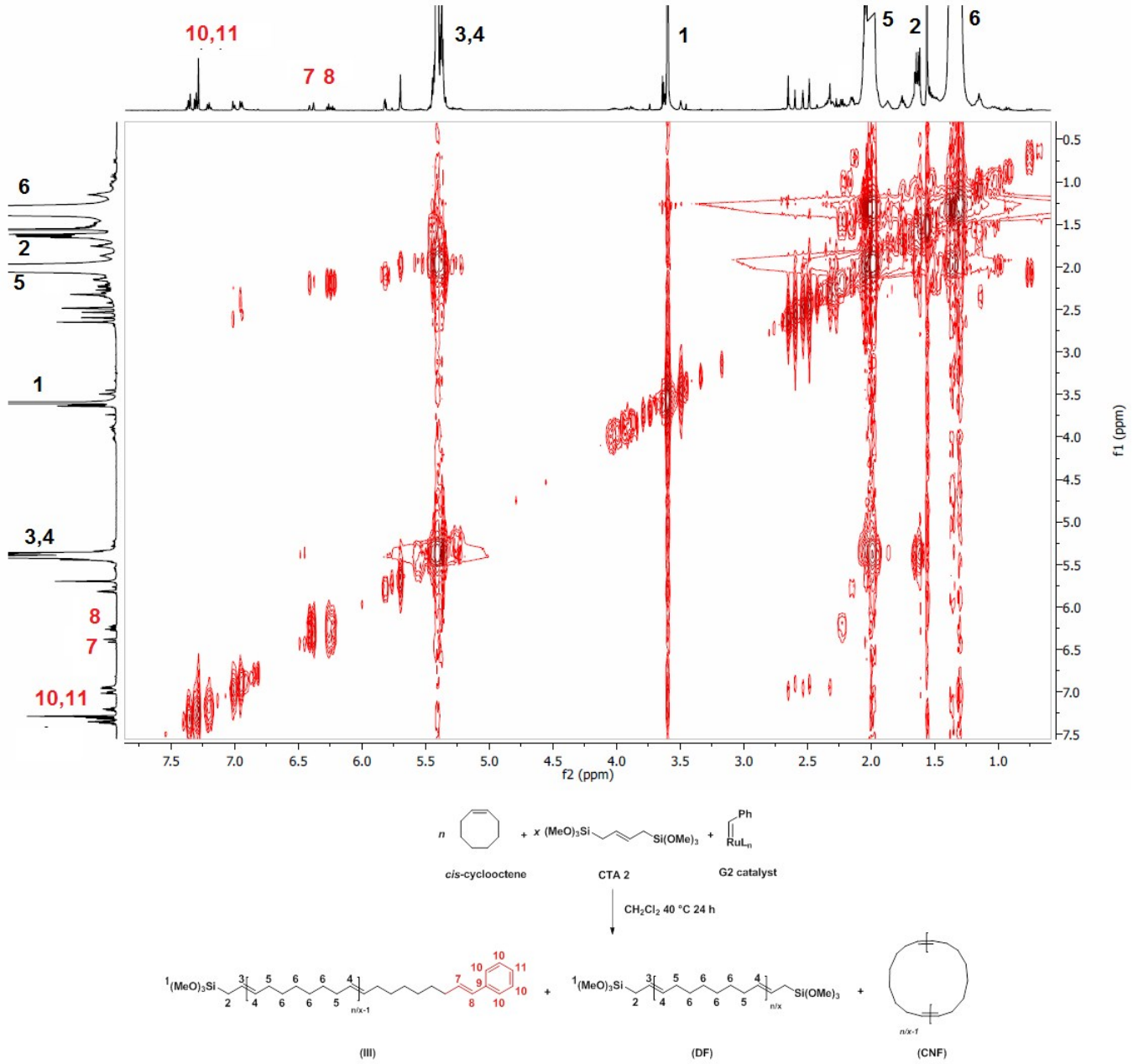

Figure S18. ^{1}H-^{1}H COSY NMR spectrum (500 MHz, $CDCl_3$, 298 K) of a crude polymer prepared by ROMP/CM of COE using **G2** and CTA **2.**

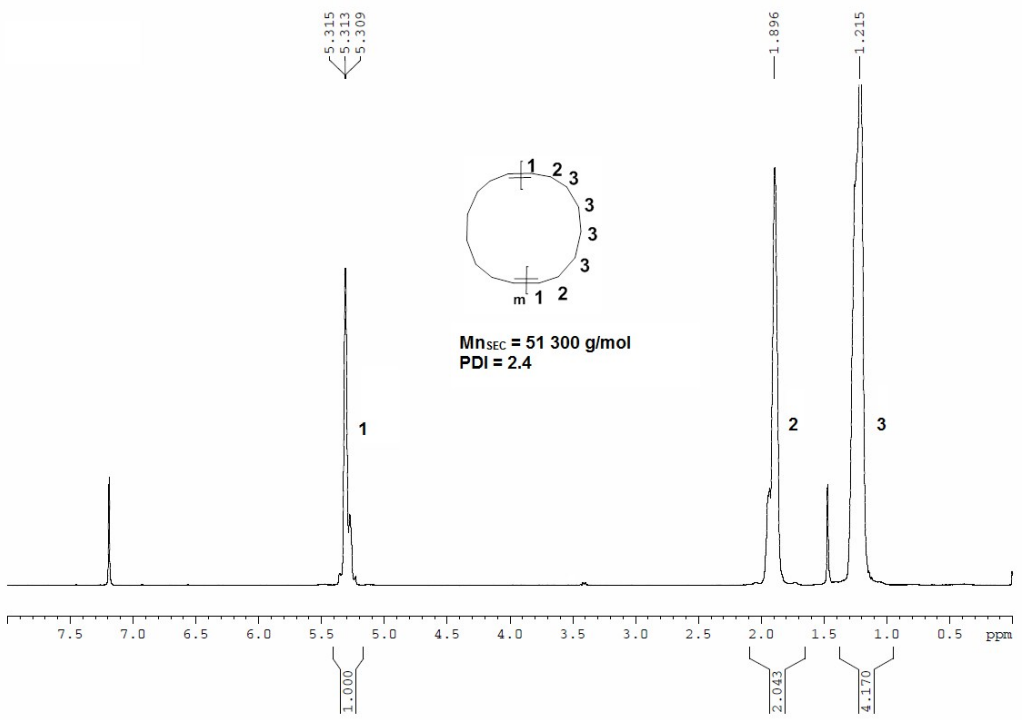

Figure S19. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of a **CNF** PCOE sample isolated from a crude polymer prepared by ROMP/CM of COE using **G2** and CTA **1** (Table 1, entry 1)

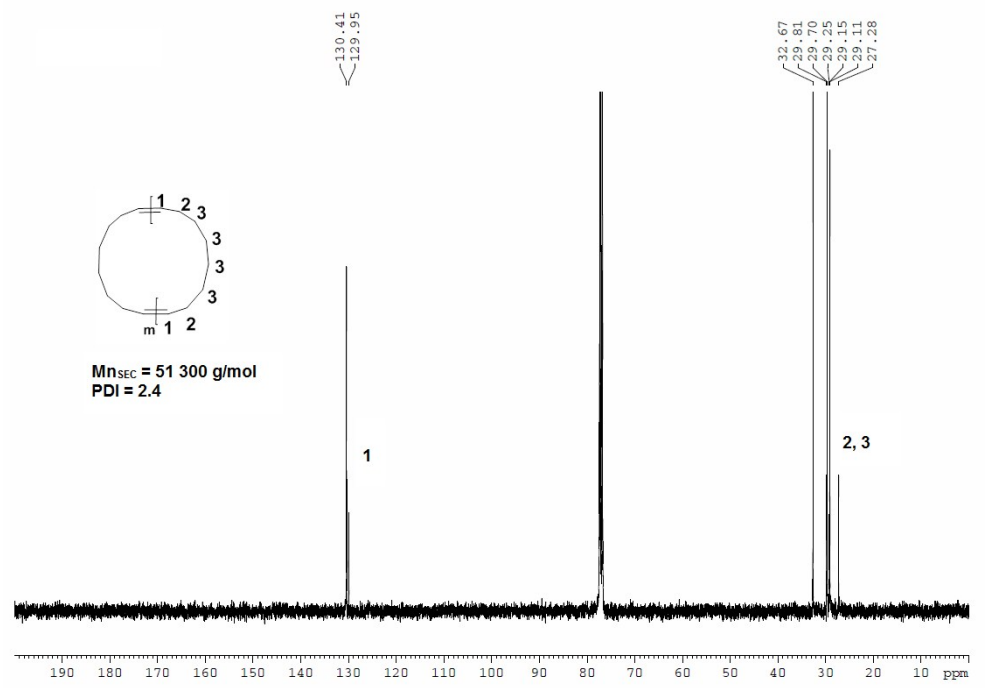

Figure S20. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, $CDCl_3$, 298 K) of a **CNF** PCOE sample isolated from a crude polymer prepared by ROMP/CM of COE using **G2** and CTA **1** (Table 1, entry 1)

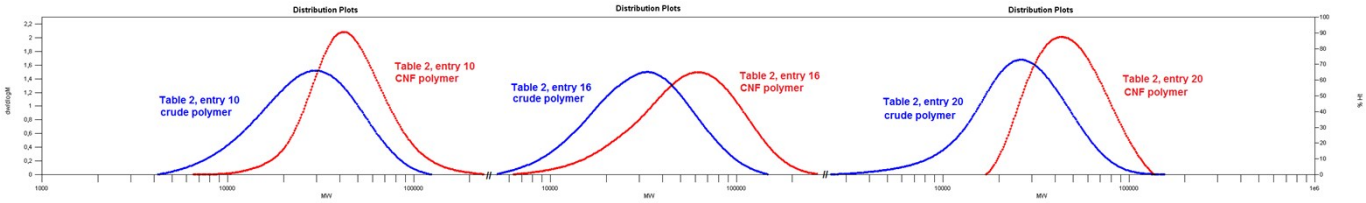

Figure S21. SEC traces of PCOE samples prepared from the ROMP/CM of COE using **G2** catalyst and CTAs **2** or **5** in CH_2Cl_2 at 40 °C for 24 h (Table 2, entries 10, 16, 20).

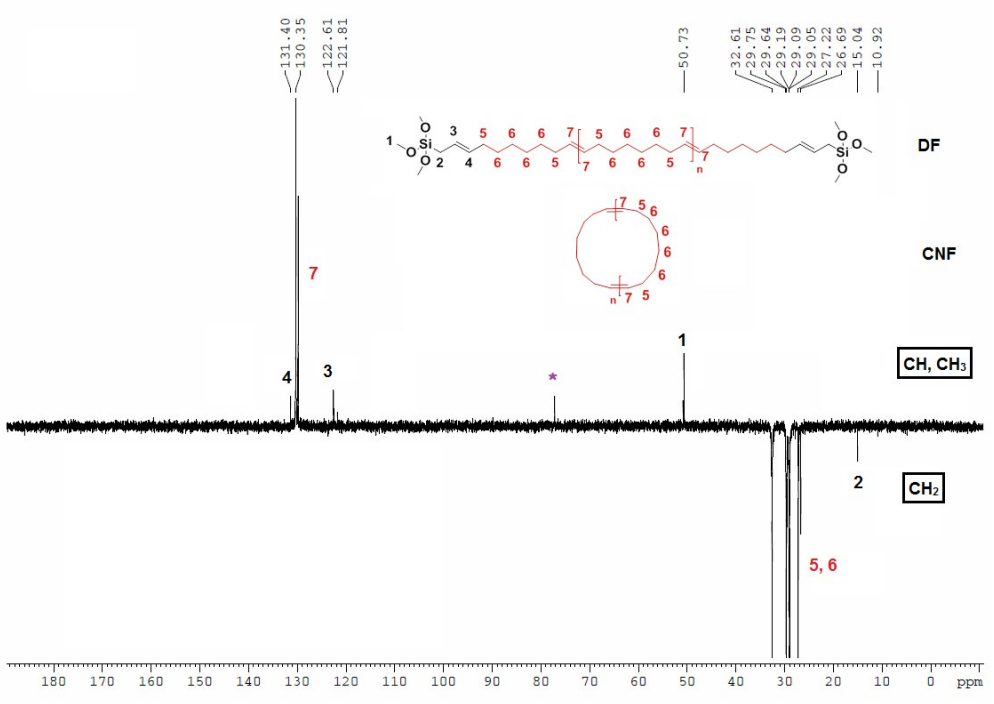

Figure S22. DEPT 135 $^{13}C\{^1H\}$ NMR spectrum (100 MHz, $CDCl_3$, 298 K) of a crude polymer sample prepared by ROMP/CM of COE using **G2** and CTA **2** (Table 1, entry 2).

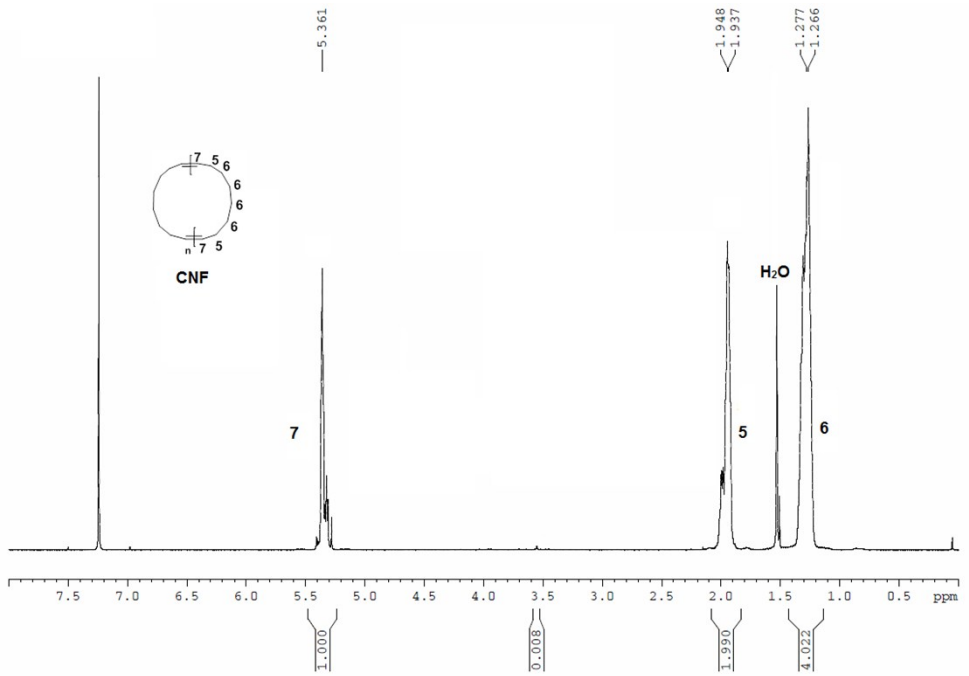

Figure S23. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of **CNF** PCOE isolated from a crude polymer prepared by ROMP/CM of COE using **G2** and CTA **2** (Table 2, entry 10)

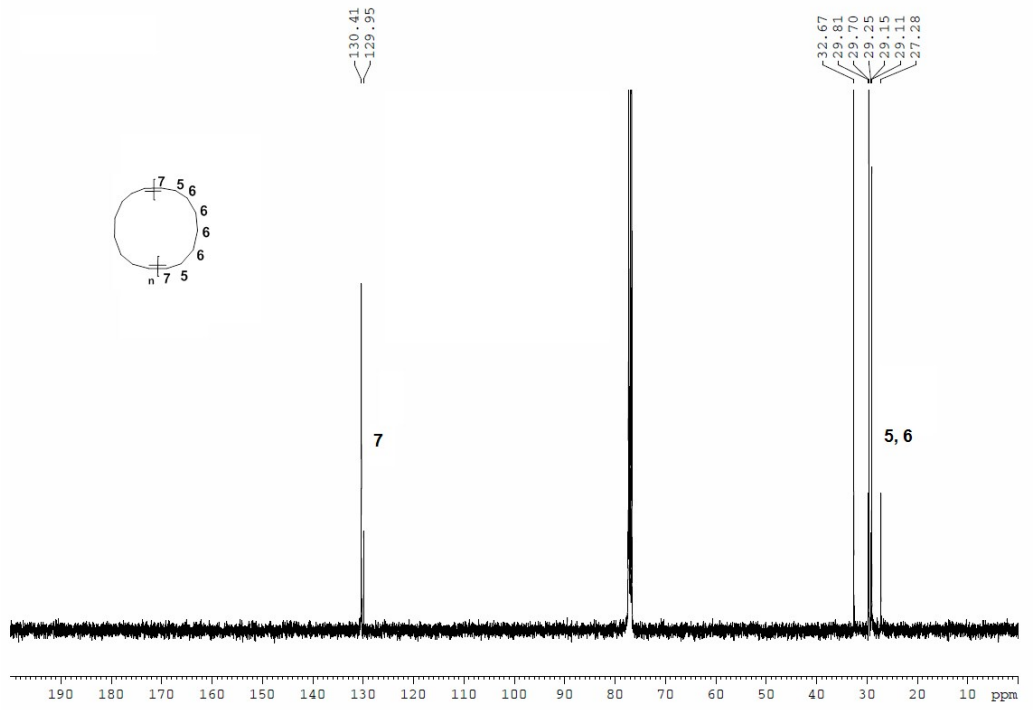

Figure S24. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, $CDCl_3$, 298 K) of **CNF** PCOE isolated from a crude polymer prepared by ROMP/CM of COE using **G2** and CTA **2** (Table 2, entry 10).

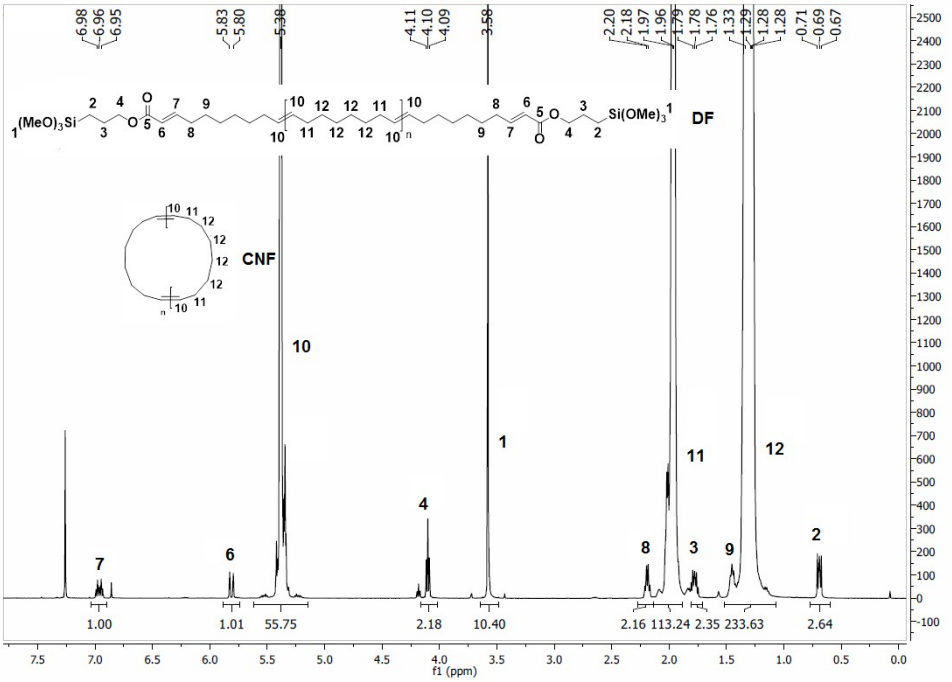

Figure S25. ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298 K) of a crude polymer prepared by ROMP/CM of COE using **G2** and CTA **3-OMe** (Table 1, entry 4).

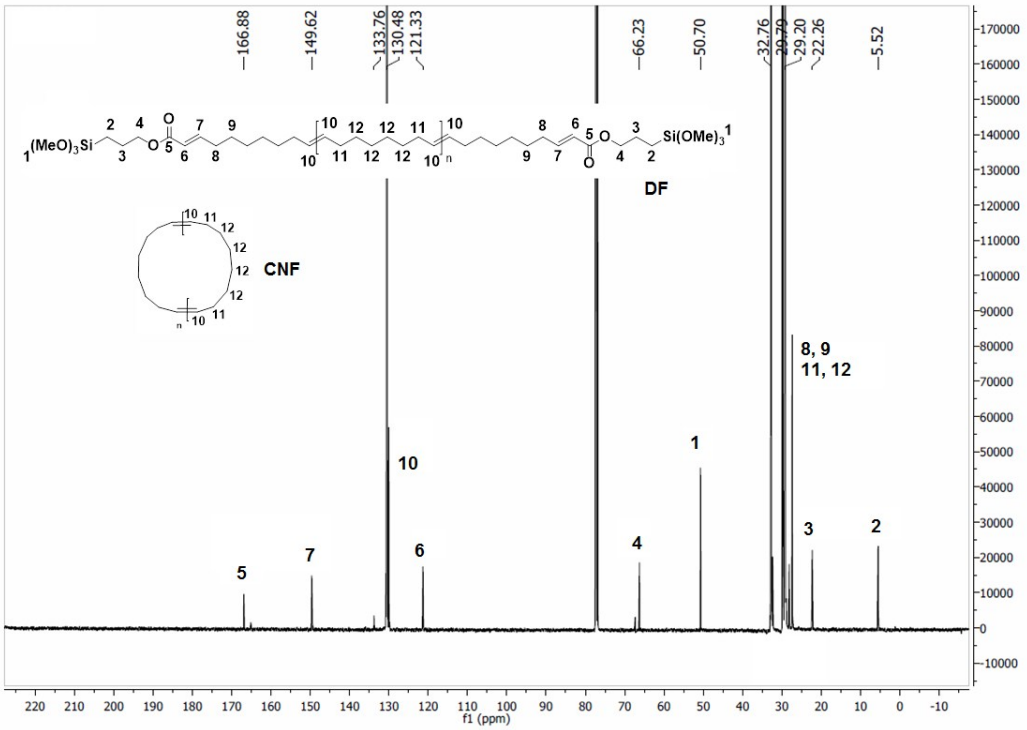

Figure S26. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, $CDCl_3$, 298 K) of a crude polymer prepared by ROMP/CM of COE using **G2** and CTA **3-OMe** (Table 1, entry 4).

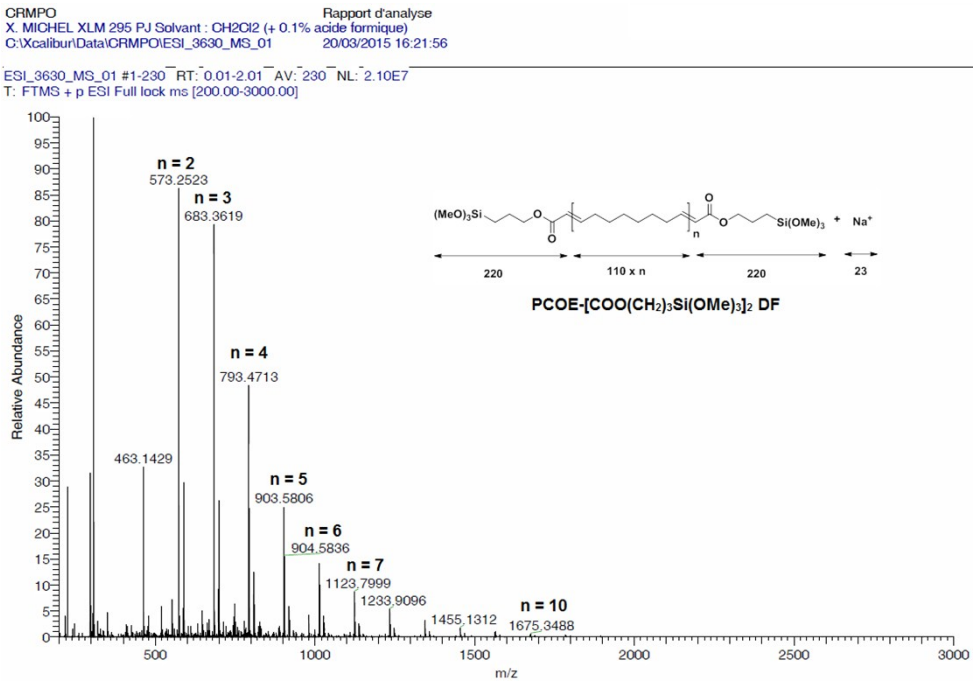

Figure S27. ESI-HRMS spectrum, ionized with Na^+, of a crude polymer prepared by ROMP/CM of COE using **G2** and CTA **3-OMe** (Table 1, entry 4).

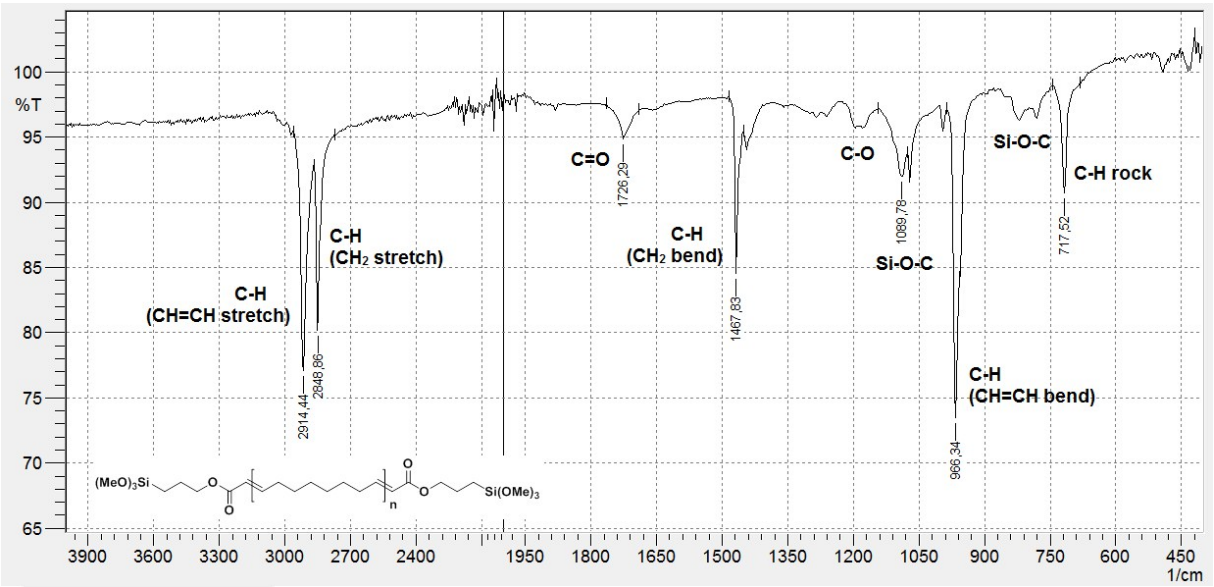

Figure S28. FTIR spectrum of a crude polymer prepared by ROMP/CM of COE using **G2** and CTA **3-OMe** (Table 1, entry 4).

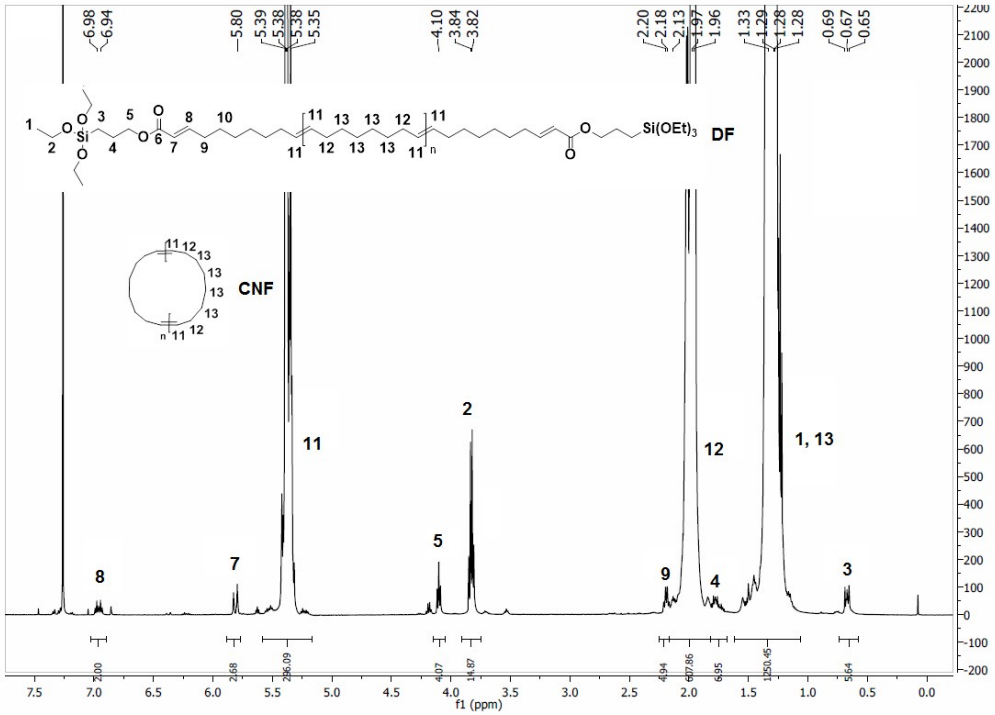

Figure S29. ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298 K) of a crude polymer prepared by ROMP/CM of COE using **G2** and CTA **3-OEt** (Table 1, entry 7).

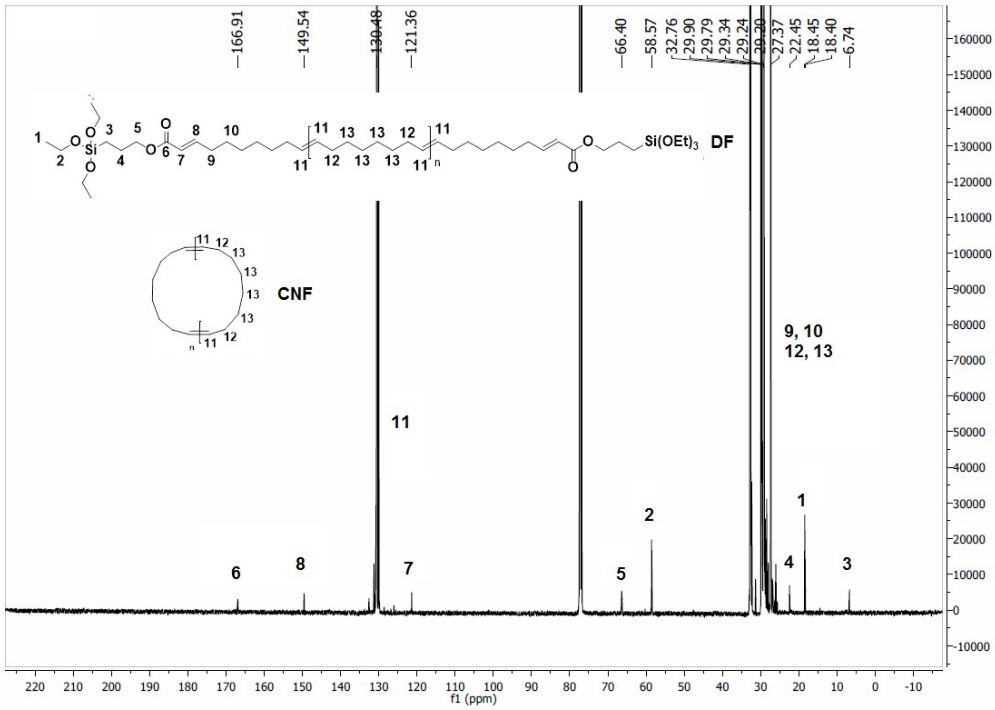

Figure S30. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, $CDCl_3$, 298 K) of a crude polymer prepared by ROMP/CM of COE using **G2** and CTA **3-OEt** (Table 1, entry 7).

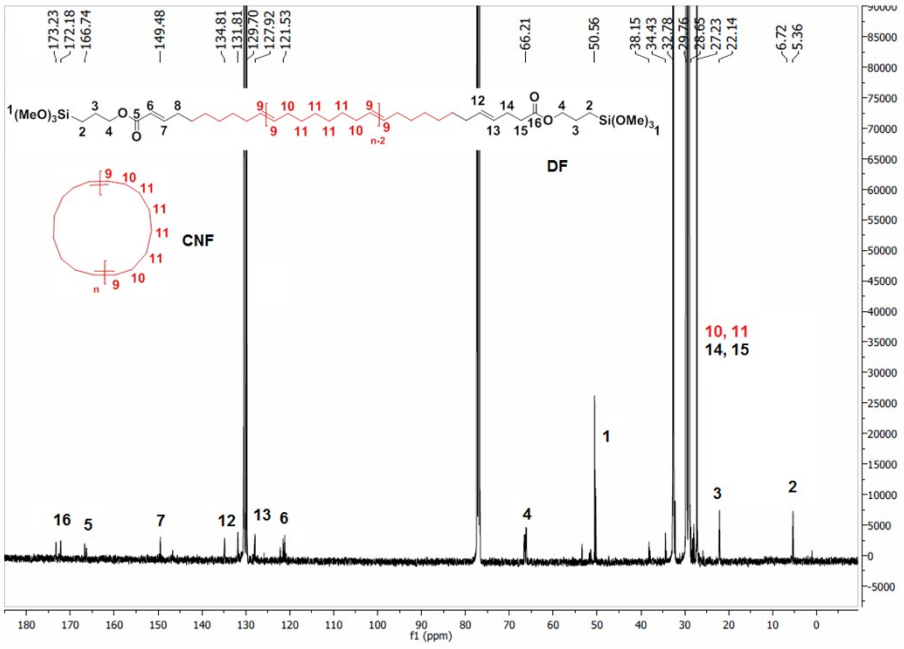

Figure S31. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, $CDCl_3$, 298 K) of a crude polymer prepared by ROMP/CM of COE using **G2** and CTA **4** (Table 1, entry 8).

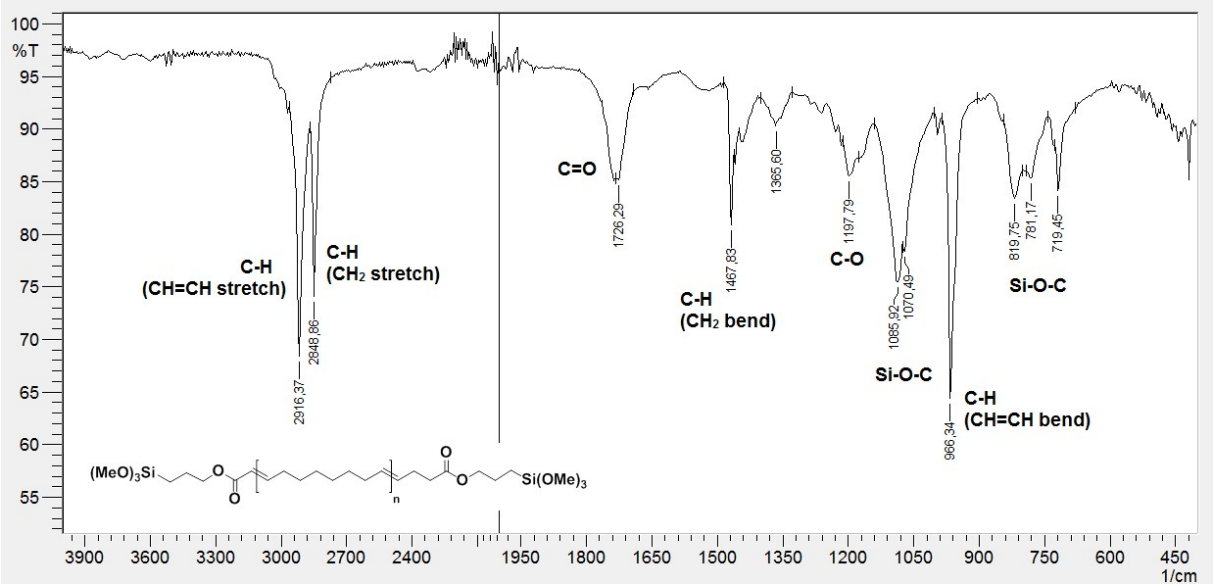

Figure S32. FTIR spectrum of a crude polymer prepared by ROMP/CM of COE using **G2** and CTA **4** (Table 1, entry 8).

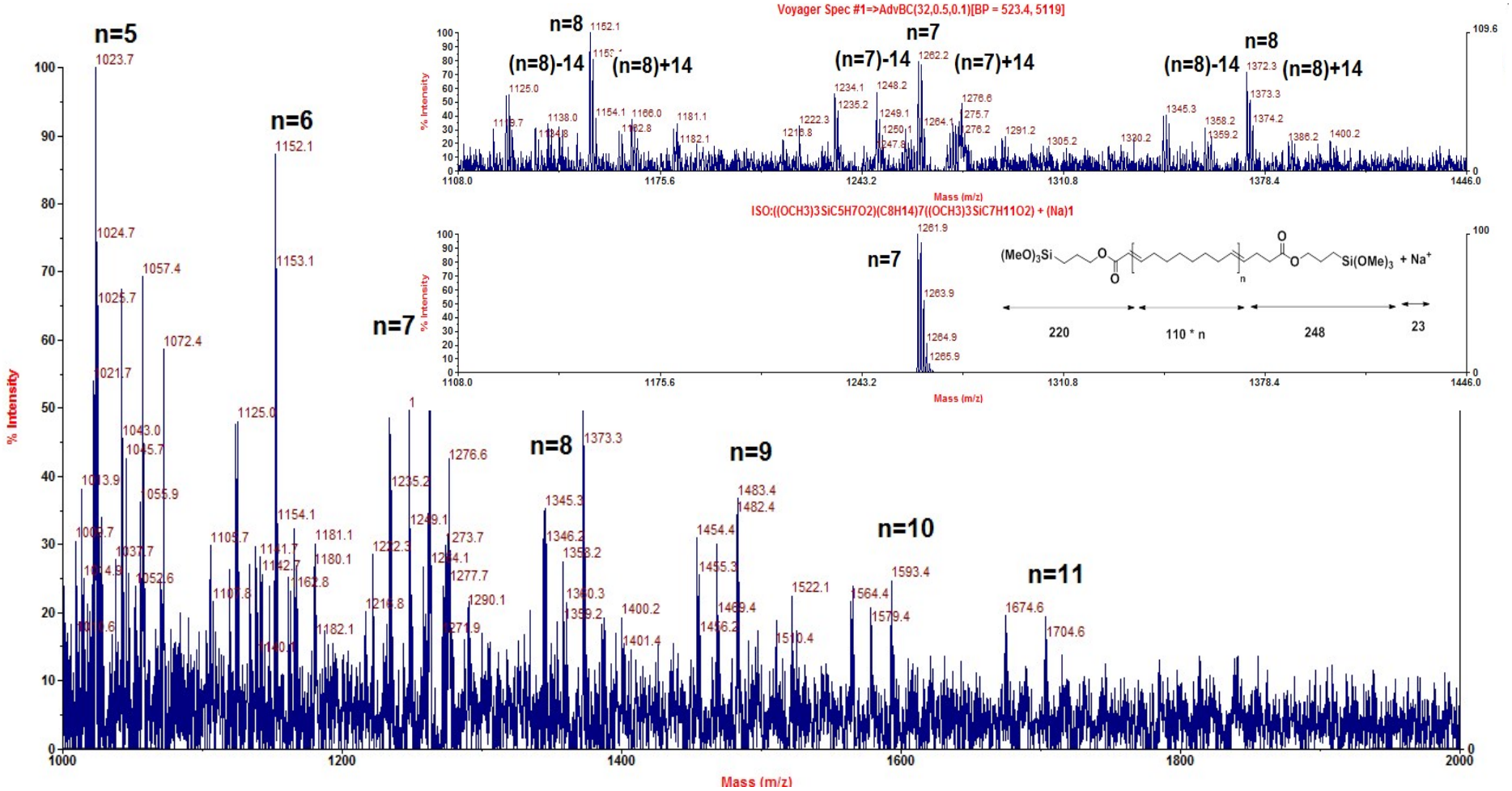

Figure S33. MALDI-ToF mass spectrum (DCTB matrix, sodium ionizing salt: NaI) of a crude polymer prepared by ROMP/CM of COE using **G2** and CTA **4** (Table 1, entry 8), showing the presence of DF PCOE; see top zoomed region and the corresponding middle and bottom simulations for $n = 7$.

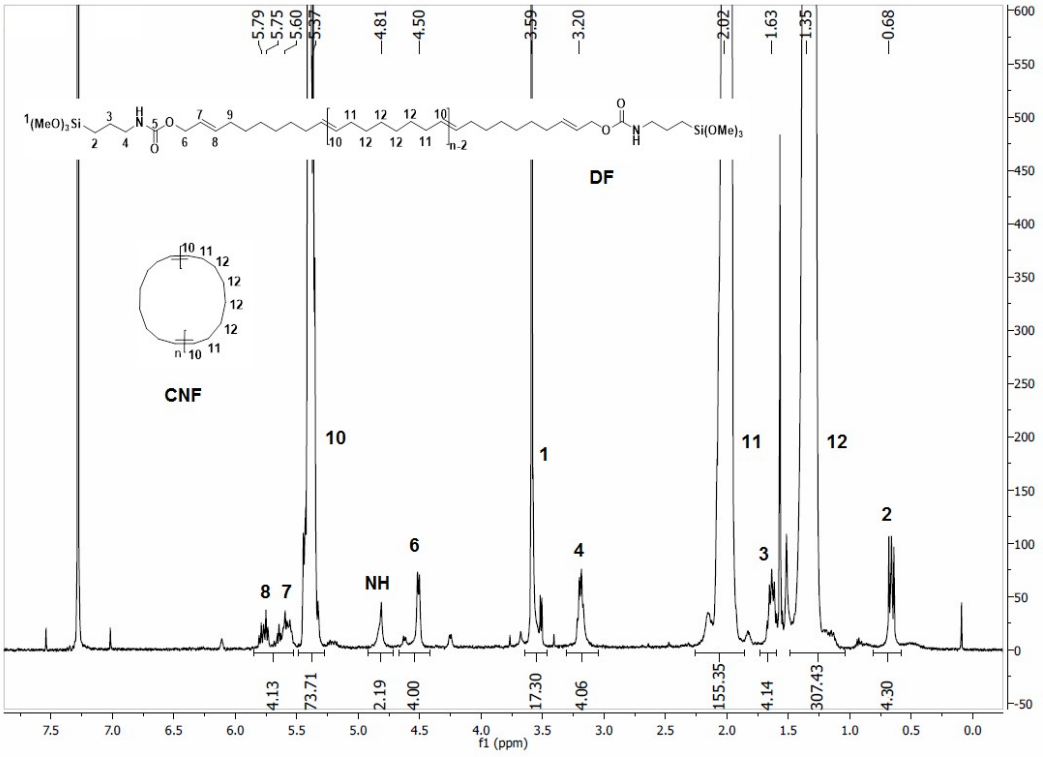

Figure S34. ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298 K) of a crude polymer sample prepared by ROMP/CM of COE using **G2** and CTA **5** (Table 1, entry 10).

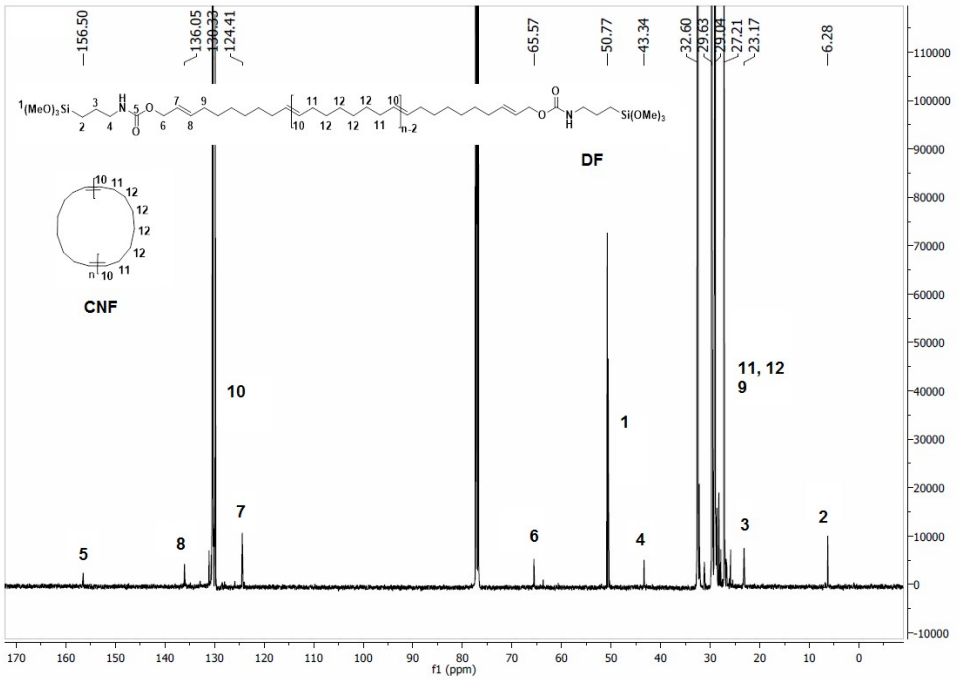

Figure S35. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, $CDCl_3$, 298 K) of a crude polymer prepared by ROMP/CM of COE using **G2** and CTA **5** (Table 1, entry 10).

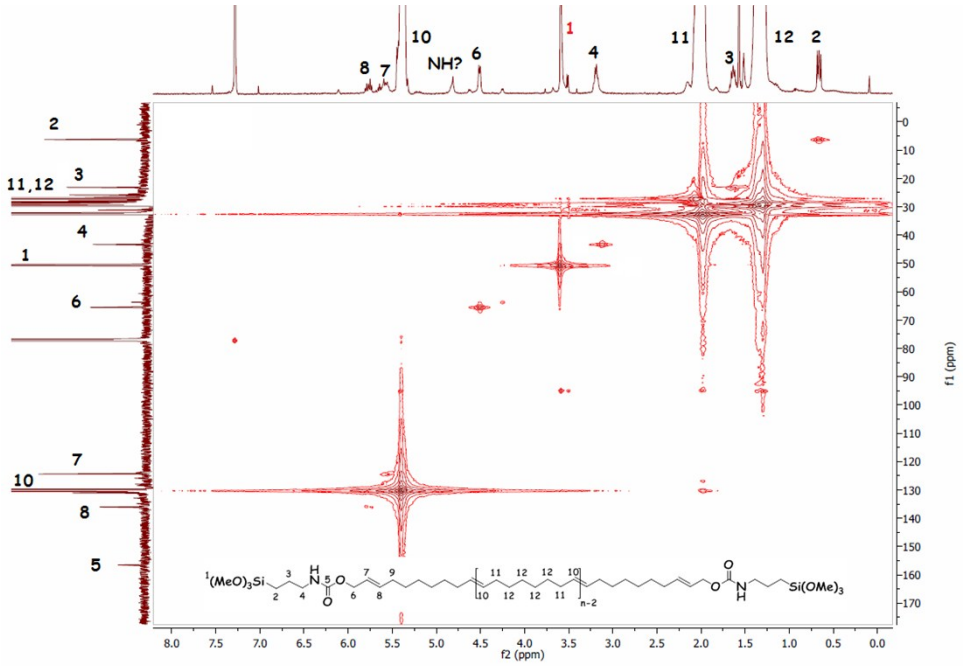

Figure S36. ^{1}H-^{13}C HMQC NMR spectrum (125 MHz, $CDCl_3$, 298 K) of a crude polymer prepared by ROMP/CM of COE using **G2** and CTA **5** (Table 1, entry 10).

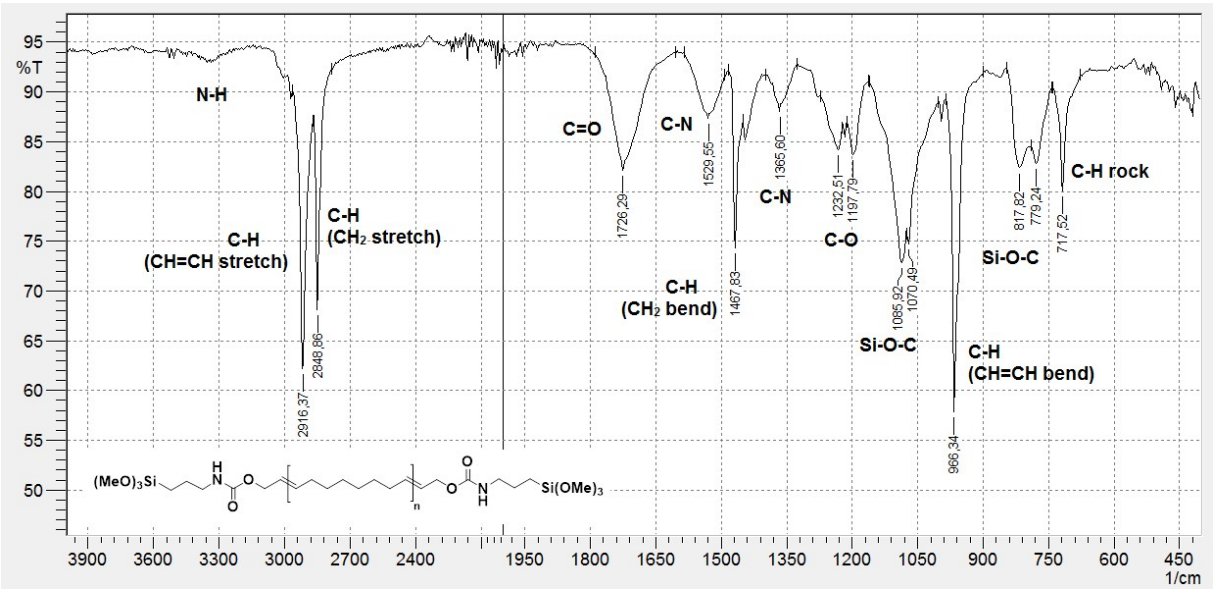

Figure S37. FTIR spectrum of a crude polymer prepared by ROMP/CM of COE using **G2** and CTA **5** (Table 1, entry 10).

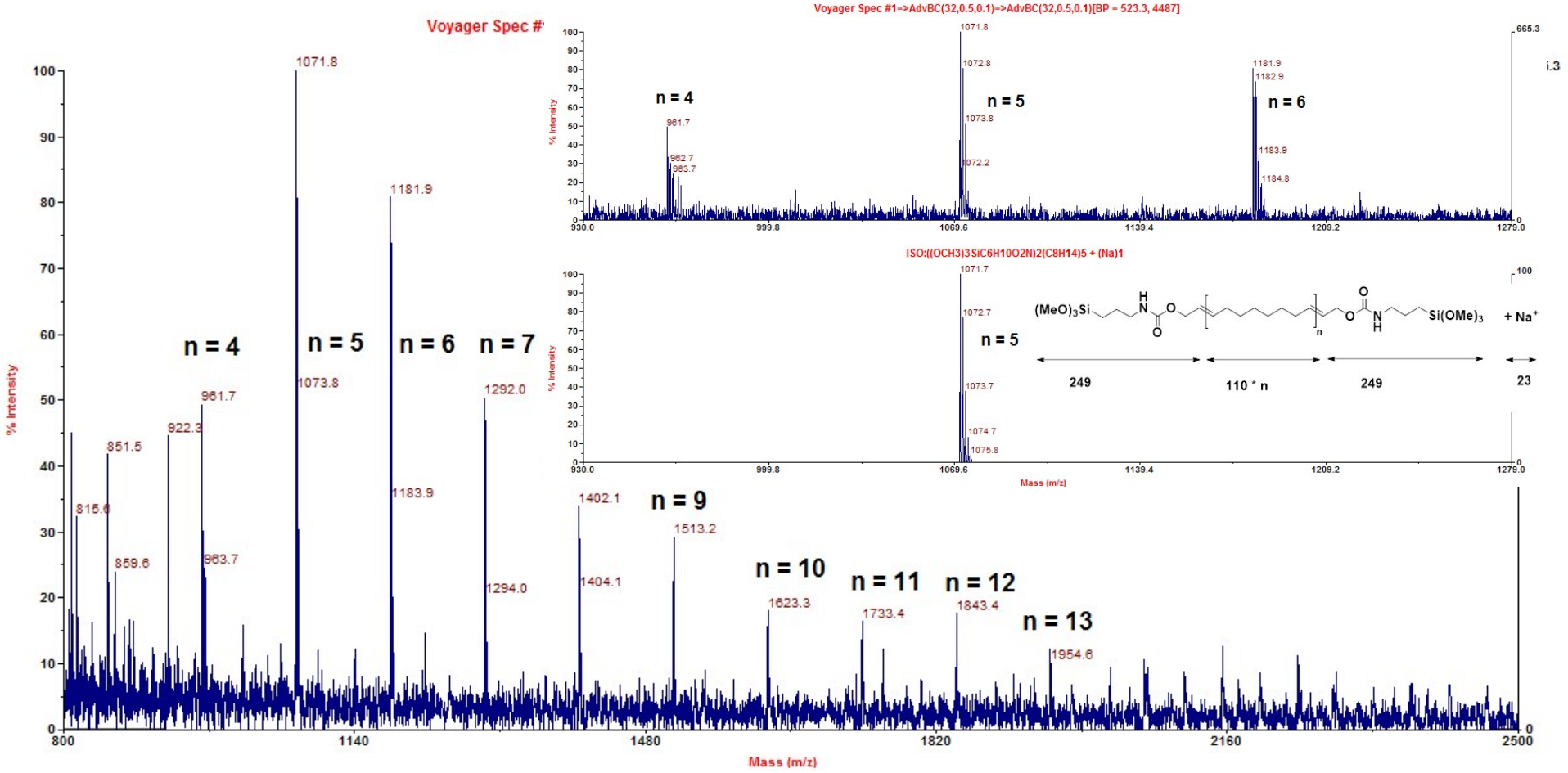

Figure S38. MALDI-ToF mass spectrum (DCTB matrix, sodium ionizing salt: NaI) of a crude polymer prepared by ROMP/CM of COE/CTA **5** using **G2** (Table 1, entry 10), showing the presence of DF PCOE; see top zoomed region and the corresponding middle and bottom simulations for n = 5.