Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Synthesis and Polymerization of Cyclobutenyl-Functionalized Polylactide and Polycaprolactone: A Consecutive ROP/ROMP Route to Poly(1,4–butadiene)–*g*–Polyesters

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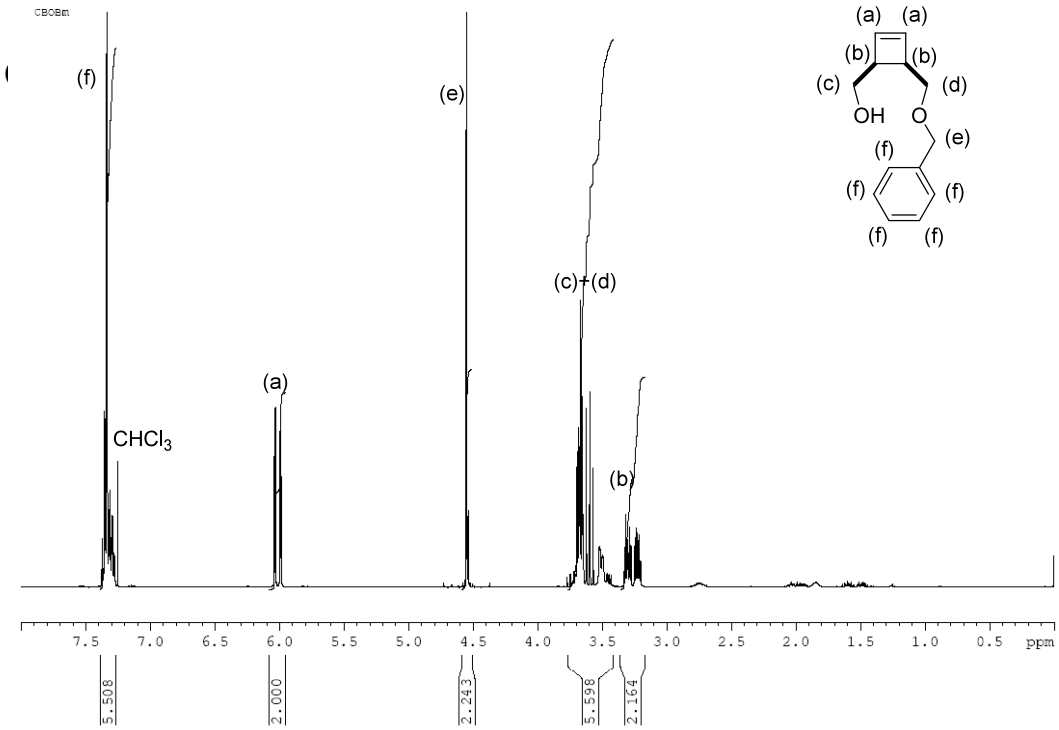
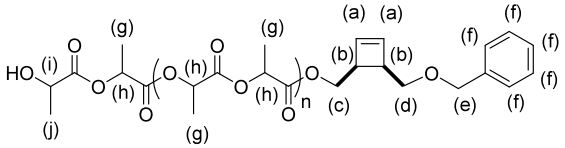


(B)



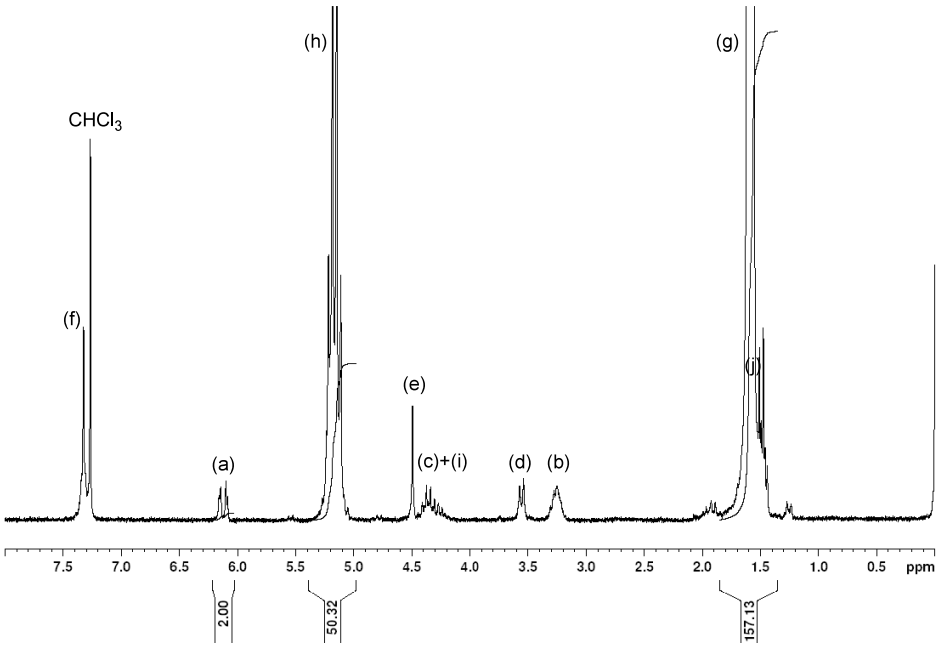


Figure S1. ^{1}H NMR spectra (200 MHz, $CDCl_3$, 25 °C) of (A) **3** and (B) the reaction mixture issued from the ROP of LA in DCM at 35 °C using inimer **3** as the initiator and TBD as the catalyst for a reaction time of 1 h (Table 1, run 1).

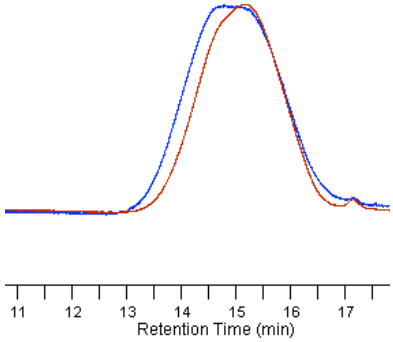


Figure S2. SEC traces in THF of the 3-PLA_{24} obtained by ROP using TBD as the catalyst after a reaction time of (A) 1 h (Table 1, run 1) and (B) 0.33 h (Table 1, run 2).

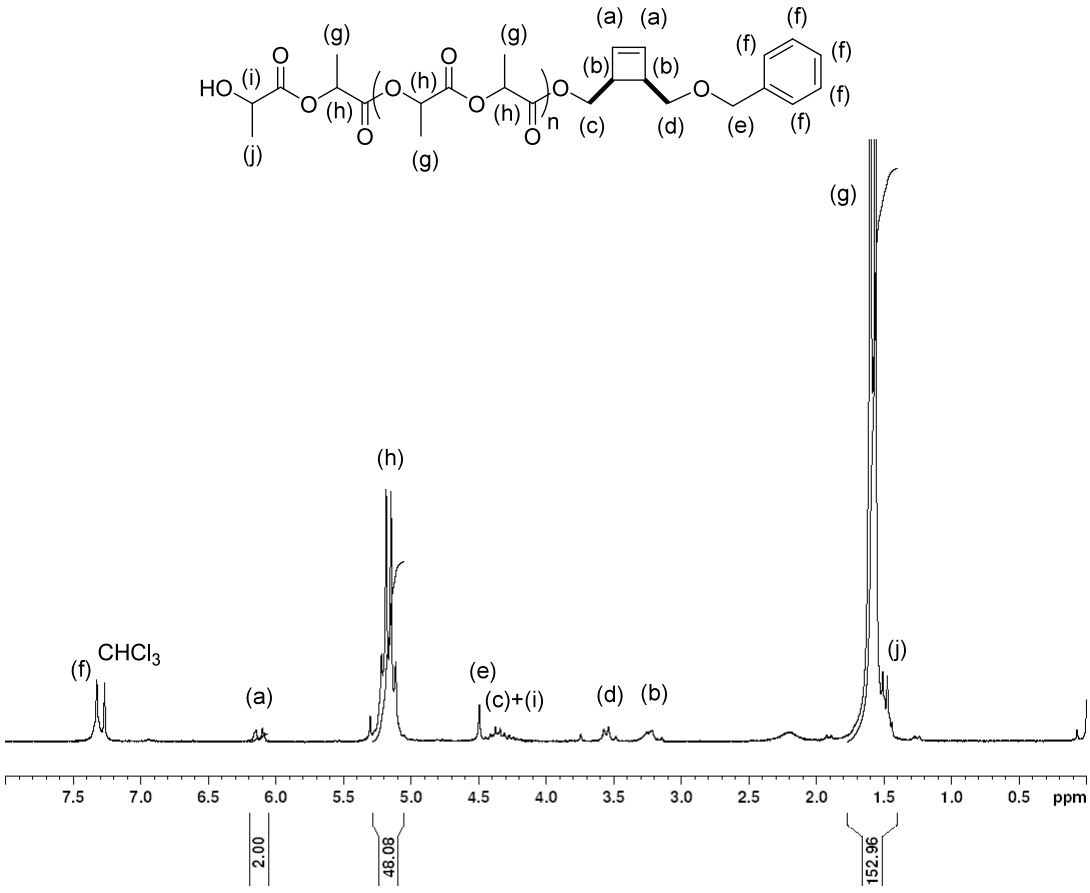


Figure S3. ^{1}H NMR spectrum (200 MHz, $CDCl_3$, 25 °C) of **3-PLA_{24}** issued from the ROP of LA in DCM at 35 °C using inimer **3** as the initiator and DMAP as the catalyst with a $[LA]_0/[\mathbf{2}]_0$ ratio of 14 (Table 1, run 4).

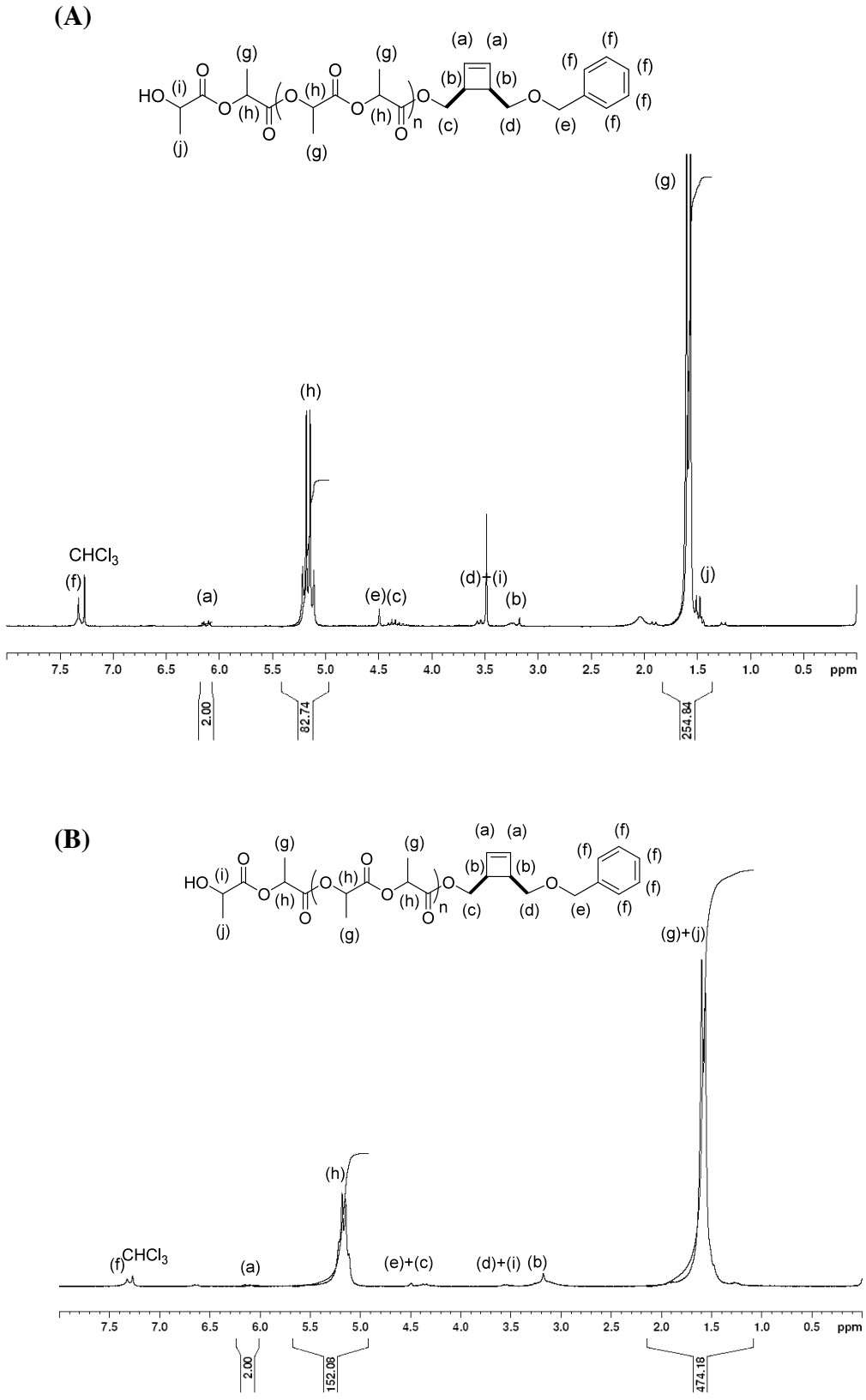


Figure S4. ^{1}H NMR spectra (200 MHz, $CDCl_3$, 25 °C) of **3-PLA** issued from the ROP of LA in DCM at 35 °C using inimer **3** as the initiator and DMAP as the catalyst with a $[LA]_0/[\mathbf{3}]_0$ ratio of (A) 35 (Table 1, run 5) and (B) 70 (Table 1, run 6).

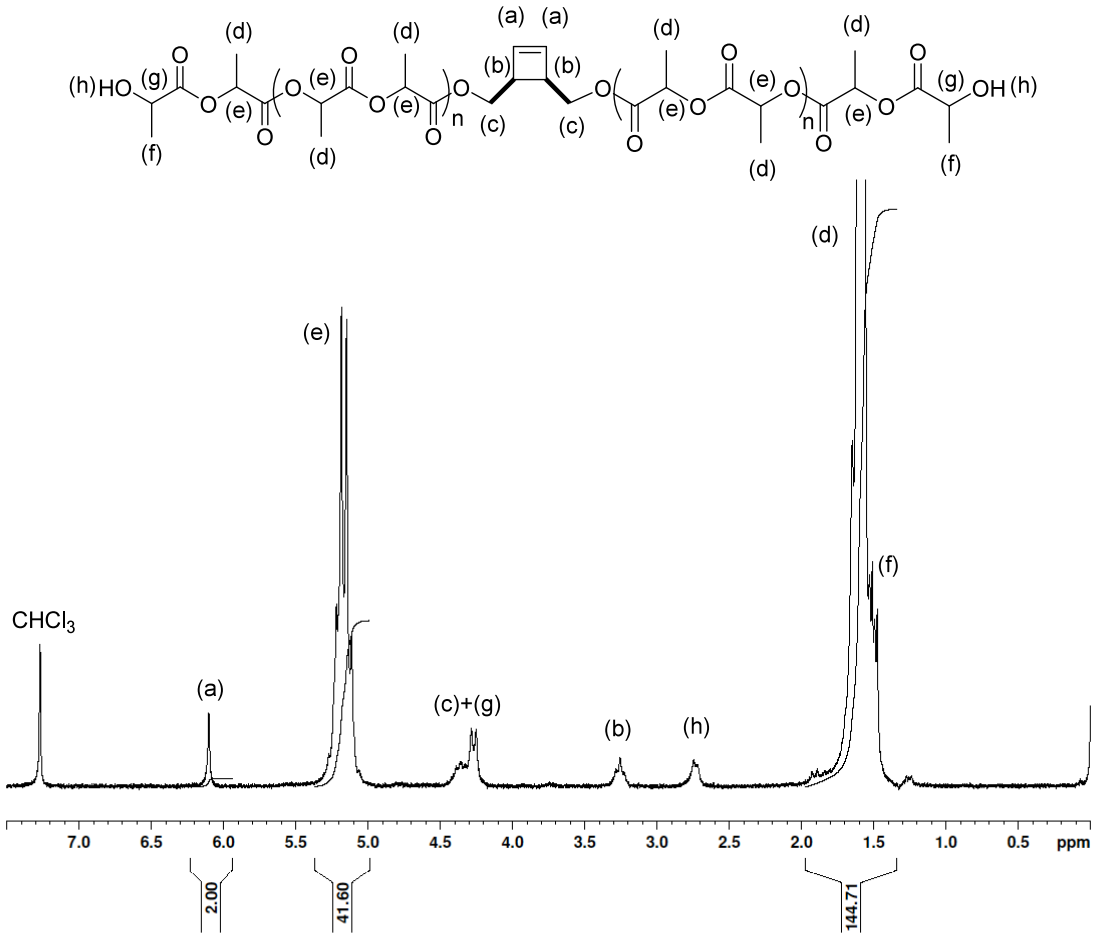


Figure S5. ^{1}H NMR spectrum (200 MHz, $CDCl_3$, 25 °C) of **2-PLA$_{20}$** issued from the ROP of LA in DCM at 35 °C using inimer **2** as the initiator and DMAP as the catalyst with a $[LA]_0/[\mathbf{2}]_0$ ratio of 14 (Table 1, run 7).

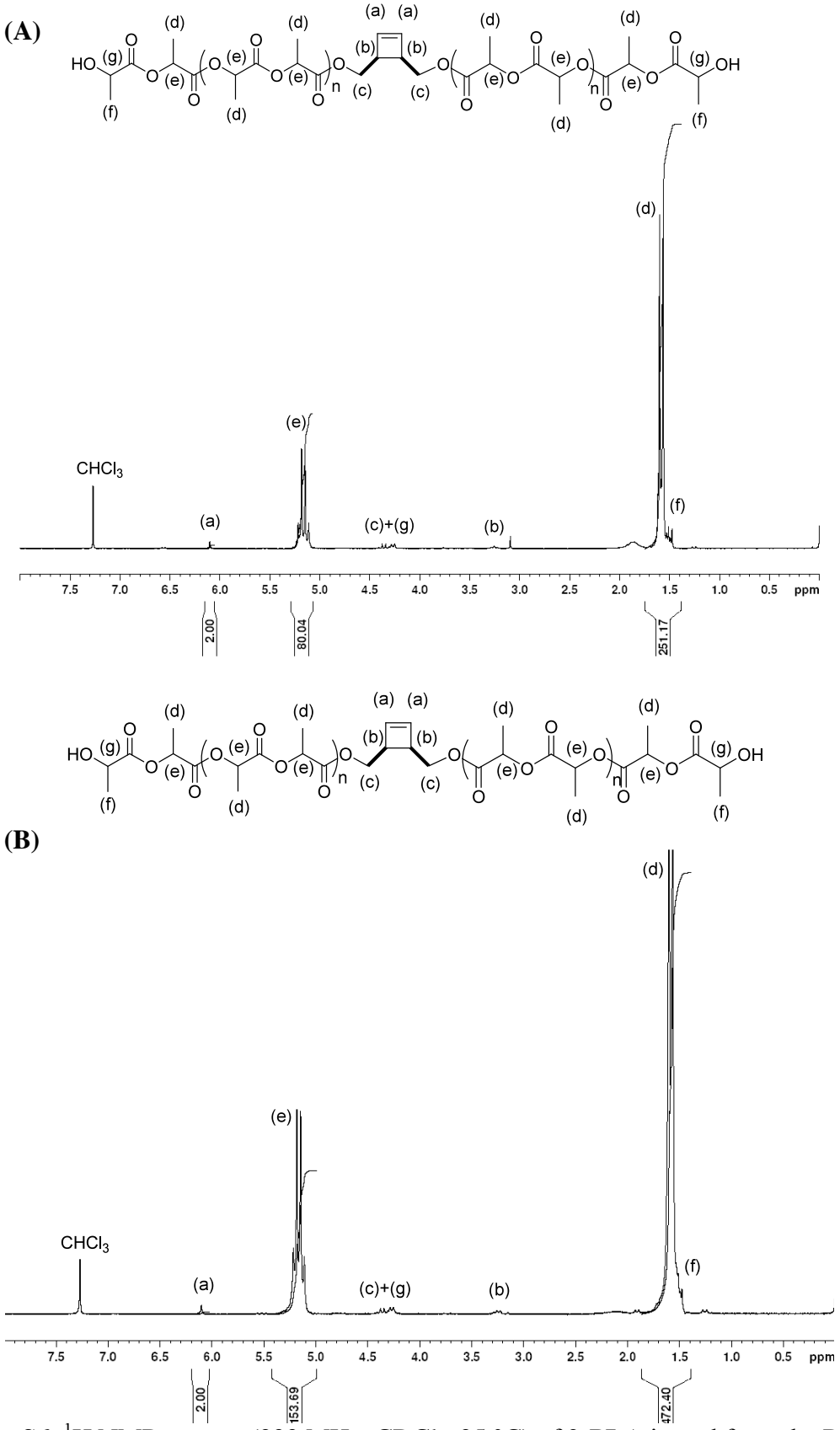


Figure S6. ^{1}H NMR spectra (200 MHz, $CDCl_3$, 25 °C) of **2-PLA** issued from the ROP of LA in DCM at 35 °C using inimer **2** as the initiator and DMAP as the catalyst with a $[LA]_0/[\mathbf{2}]_0$ ratio of (A) 35 (Table 1, run 8) and (B) 70 (Table 1, run 9).

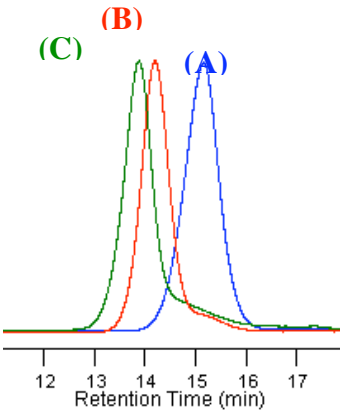


Figure S7. SEC traces for the (A) **2-PLA$_{20}$** (Table 1, run 7), (B) **2-PLA$_{40}$** (Table 1, run 8) and (C) **2-PLA$_{77}$** (Table 1, run 9).

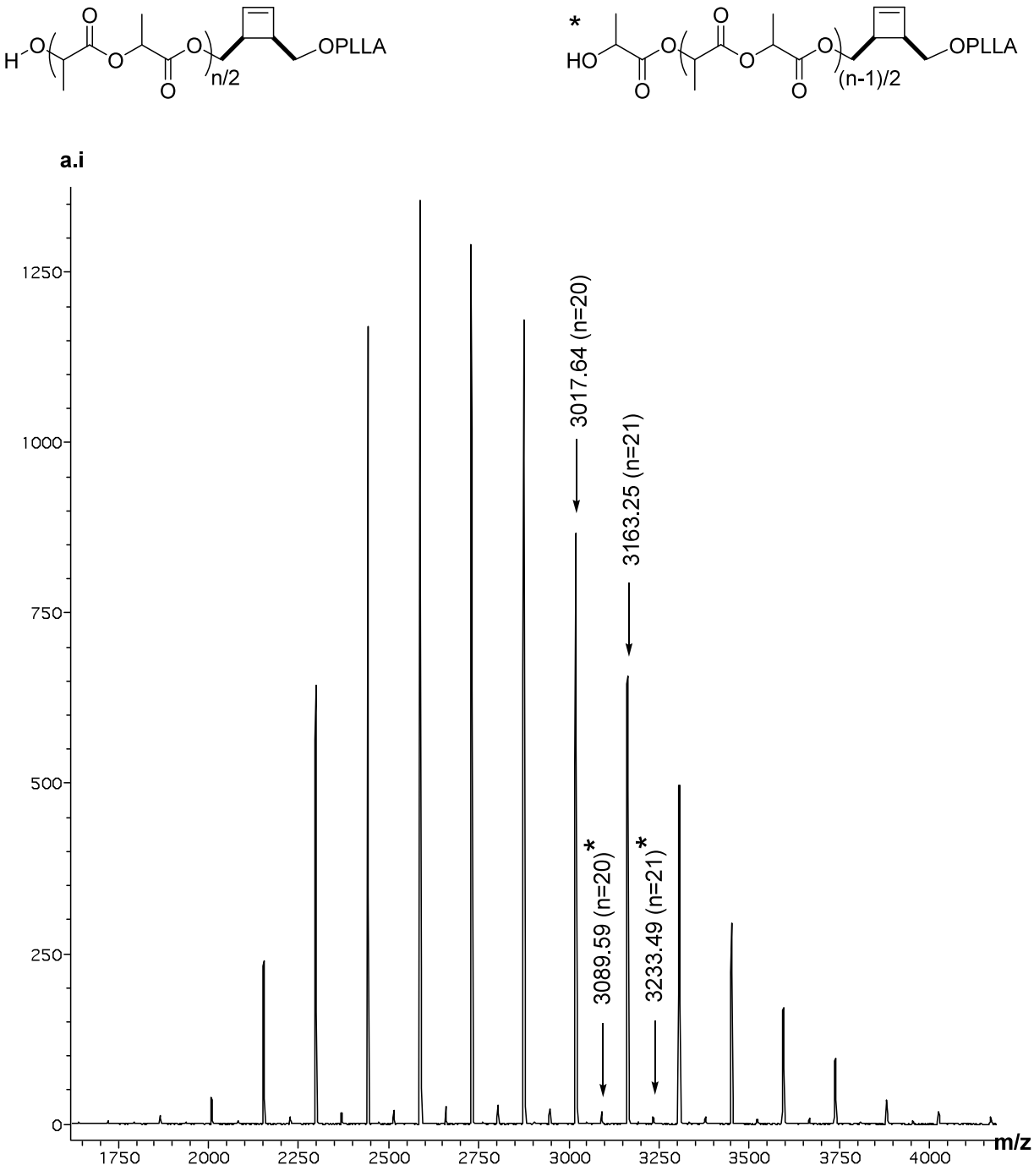


Figure S8. MALDI-TOF mass spectrum (matrix: DCTB + NaTFA) of the cyclobutenyl-functionalized PLA synthesized by ROP using inimer **2** as the initiator and DMAP as the catalyst in DCM at 35 °C with $[LA]_0/[\mathbf{2}]_0$ = 14/1 (Table 1, run 7).

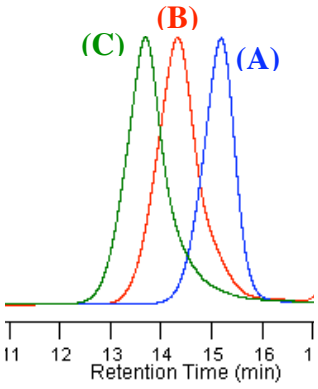


Figure S9. SEC traces for the (A) **2-PCL$_{19}$** (Table 2, run 1), (B) **2-PCL$_{47}$** (Table 2, run 2) and (C) **2-PCL$_{81}$** (Table 2, run 3).

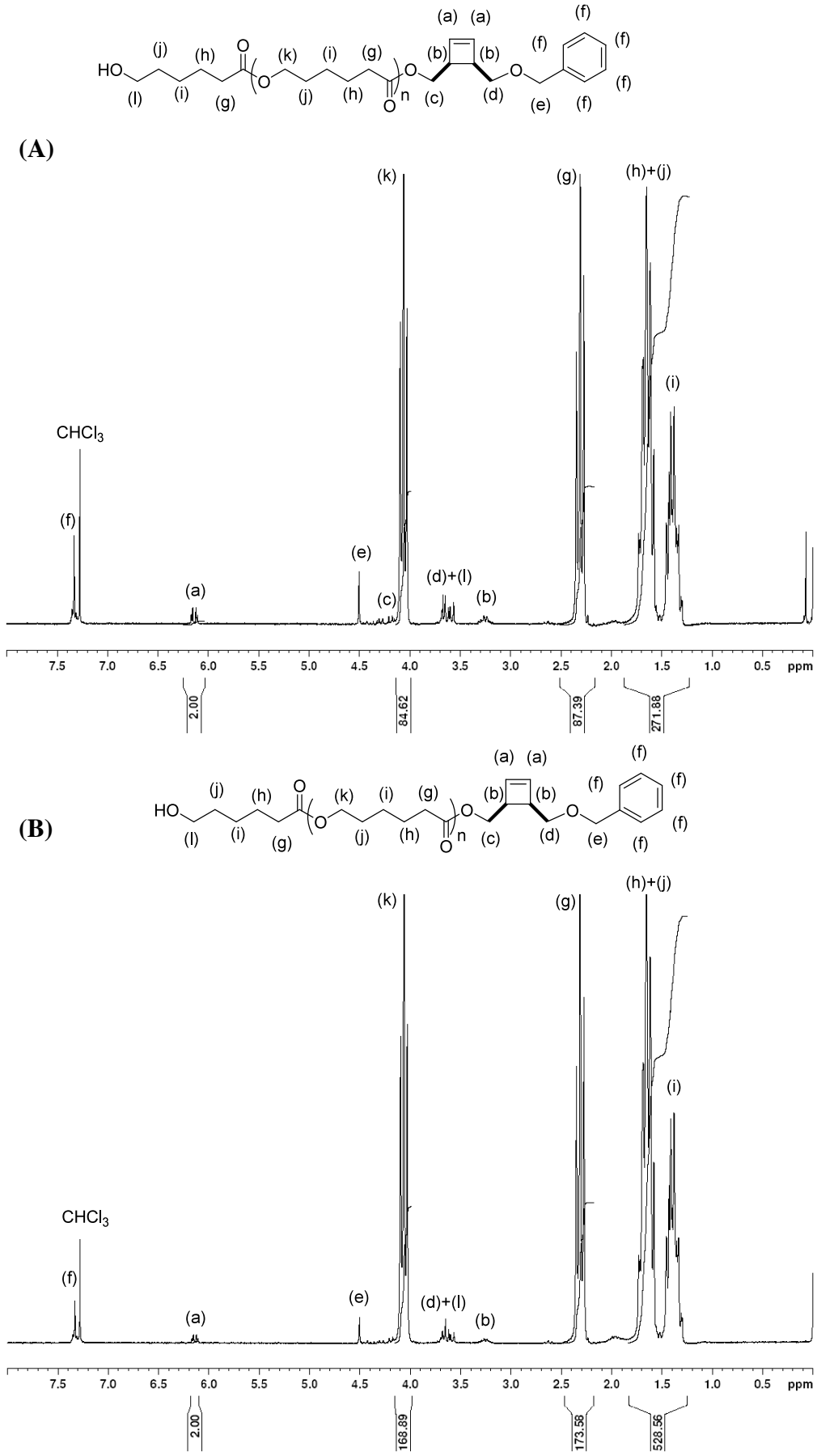


Figure S10. ^{1}H NMR spectra (200 MHz, $CDCl_3$, 25 °C) of **3-PCL** issued from the ROP of CL in toluene at 25 °C using inimer **3** as the initiator and TBD as the catalyst with a $[CL]_0/[\mathbf{3}]_0$ ratio of (A) 48 (Table 2, run 5) and (B) 96 (Table 2, run 7).

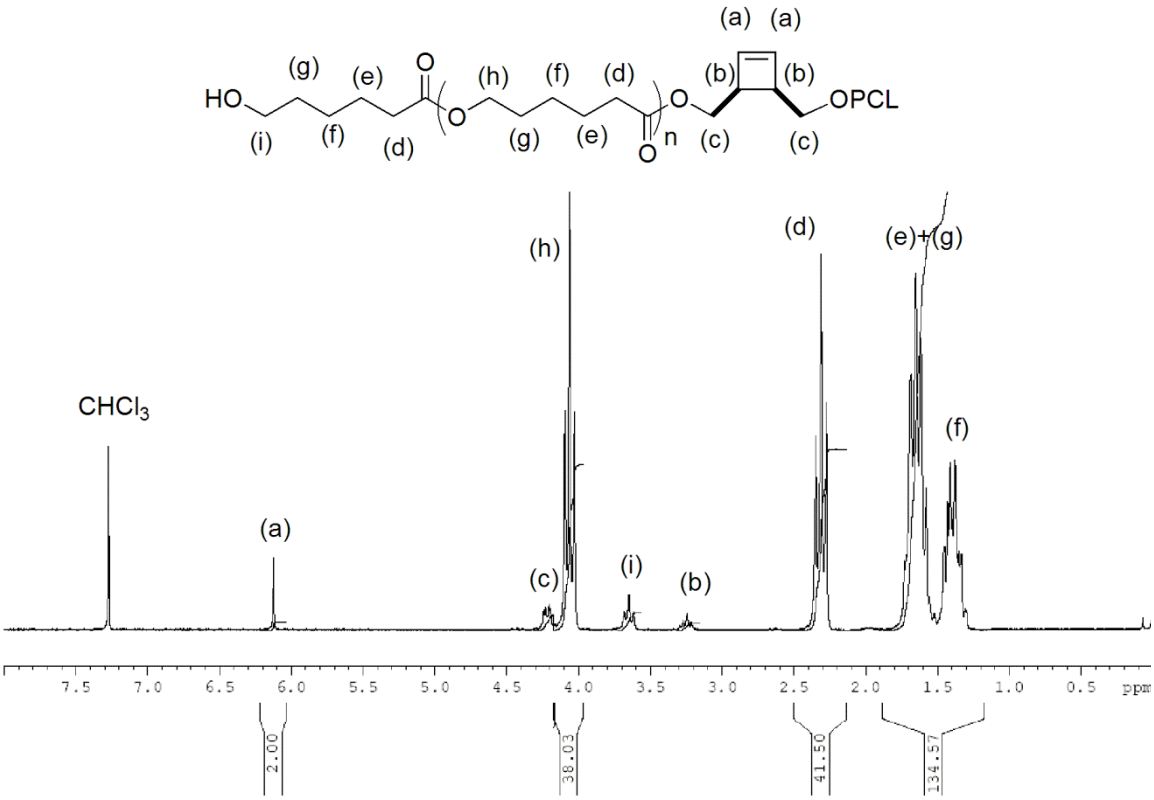


Figure S11. ^{1}H NMR spectrum (200 MHz, $CDCl_3$, 25 °C) of **2-PCL$_{19}$** issued from the ROP of CL in THF at 25 °C using inimer **2** as the initiator and TBD as the catalyst with a $[CL]_0/[\mathbf{2}]_0$ ratio of 18 (Table 2, run 1).

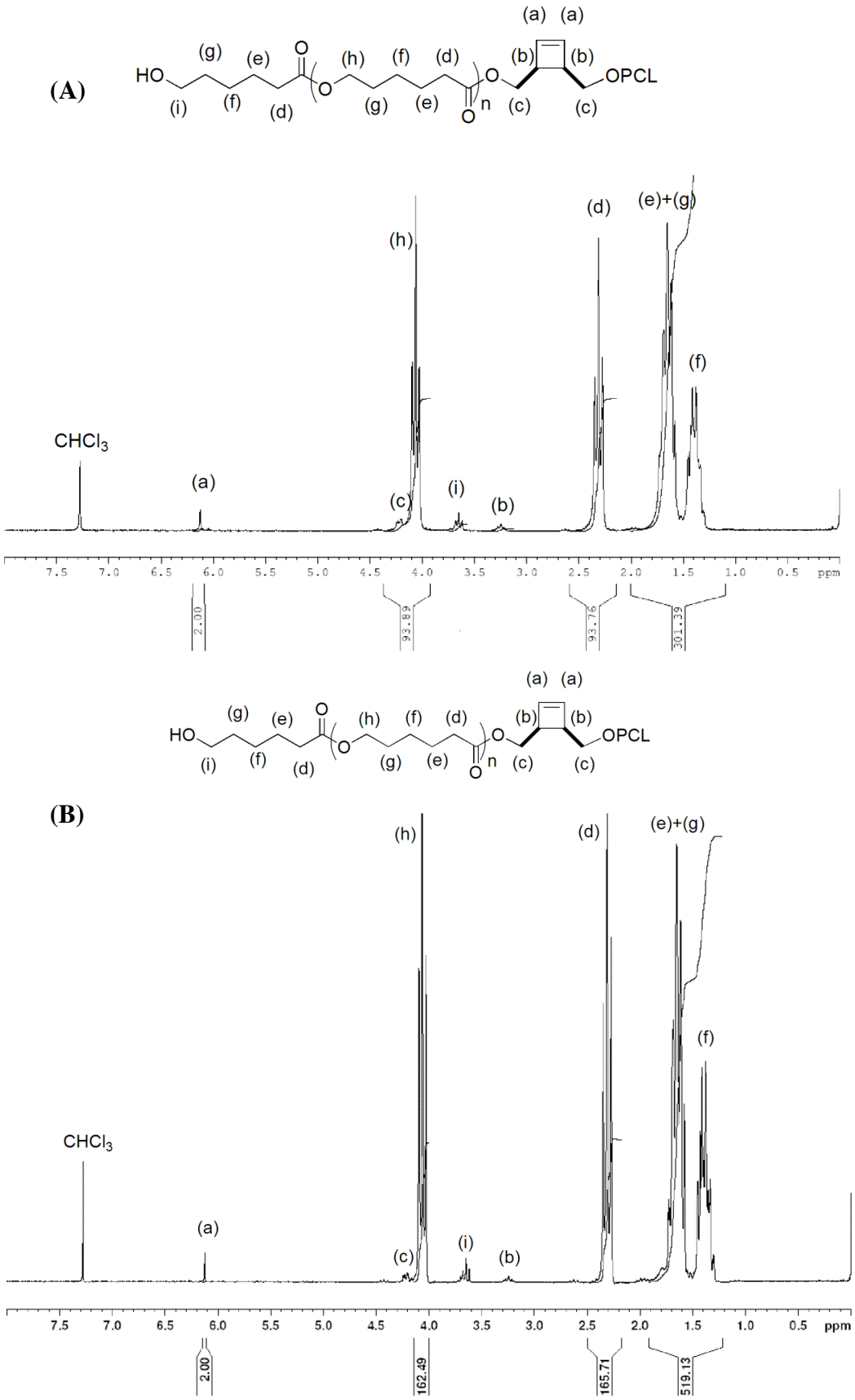


Figure S12. ^{1}H NMR spectra (200 MHz, $CDCl_3$, 25 °C) of **2-PCL** issued from the ROP of CL in toluene at 25 °C using inimer **2** as the initiator and TBD as the catalyst with a $[CL]_0/[\mathbf{2}]_0$ ratio of (A) 48 (Table 2, run 2) and (B) 96 (Table 2, run 3).

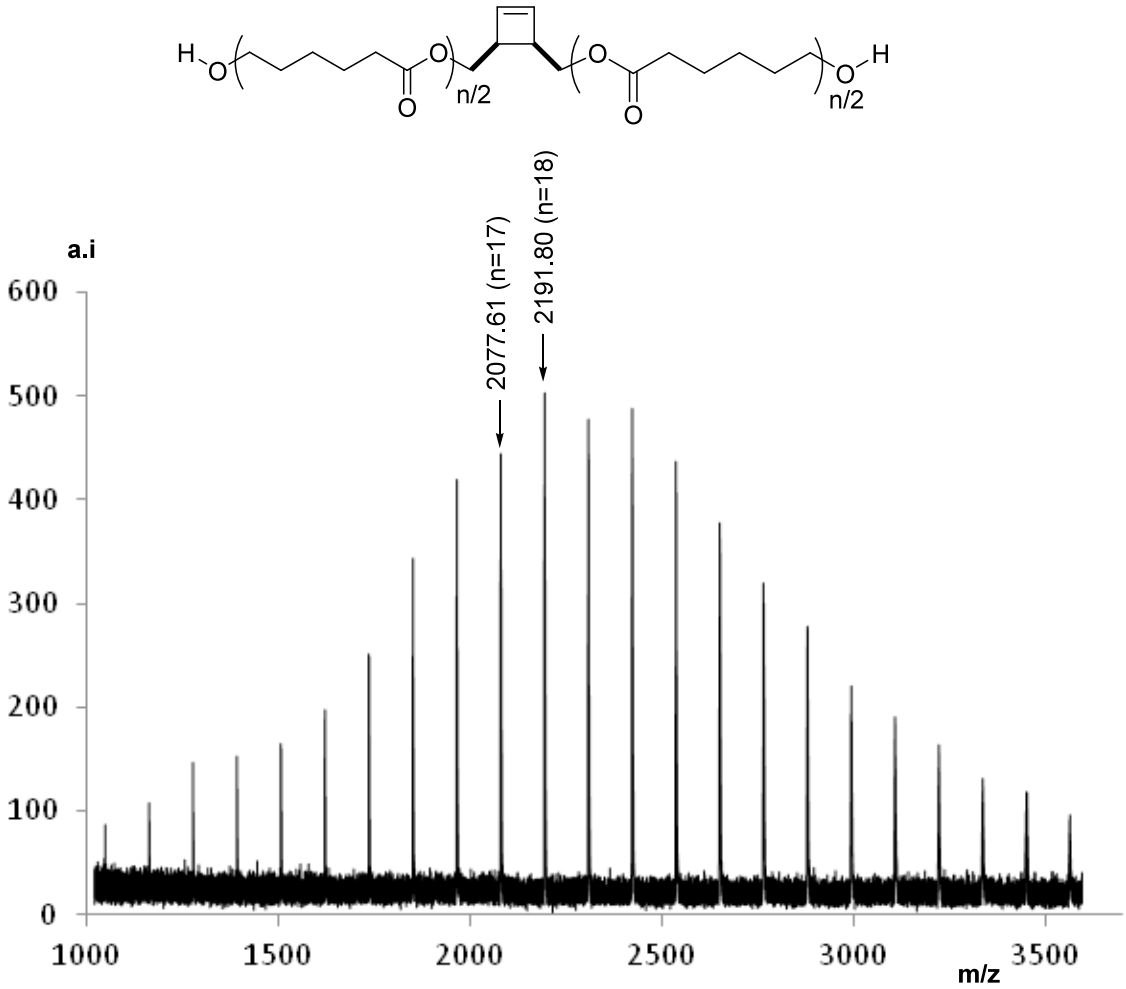


Figure S13. MALDI-TOF mass spectrum (matrix: DCTB + NaTFA) of the cyclobutenyl-functionalized PCL synthesized by ROP using inimer **2** as the initiator and TBD as the catalyst in THF at 25 °C with $[CL]_0/[\mathbf{2}]_0$ = 18/1 (Table 2, run 1).

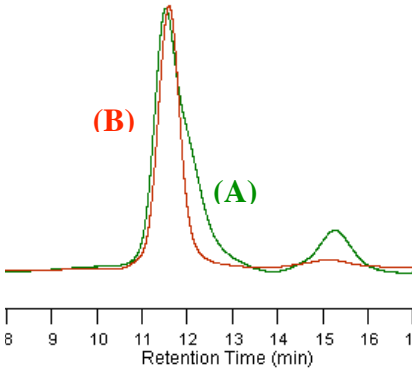


Figure S14. SEC traces for the (A) **PBu_{50}-*g*-3-PCL_{16}** without purification with a macromonomer concentration of 0.01 M (Table 3, run 2) and (B) **PBu_{100}-*g*-3-PCL_{16}** without purification with a macromonomer concentration of 0.04 M (Table 3, run 3).

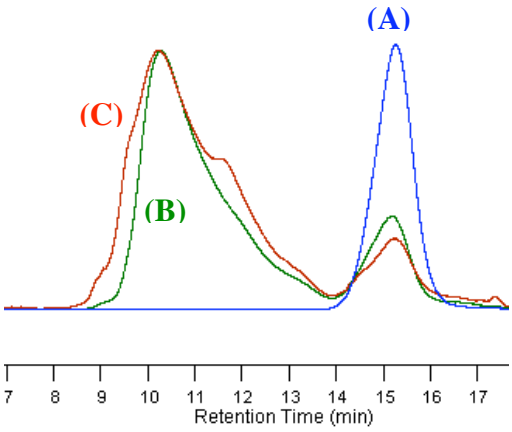


Figure S15. SEC traces for the (A) **3-PCL$_{16}$** (Table 2, run 4), (B) **PBu$_{100}$-*g*-3-PCL$_{16}$** without purification after a reaction time of 3h (Table 3, run 3) and (C) **PBu$_{100}$-*g*-3-PCL$_{16}$** without purification after a reaction time of 24h.

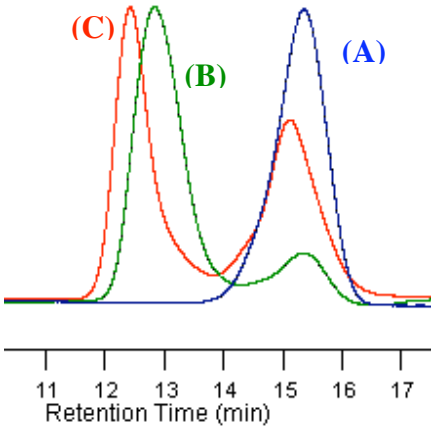


Figure S16. SEC traces for the (A) **3-PLA$_{24}$** (Table 1, run 3), (B) **PBu$_{10}$-*g*-3-PLA$_{24}$** without purification (Table 3, run 13) and (C) **PBu$_{50}$-*g*-3-PLA$_{24}$** without purification (Table 3, run 14).

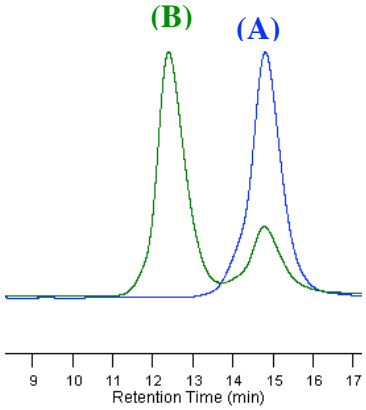


Figure S17. SEC traces for the (A) **3-PCL$_{42}$** (Table 2, run 5) and (B) **PBu$_{10}$-3-PCL$_{42}$** (Table 3, run 5).

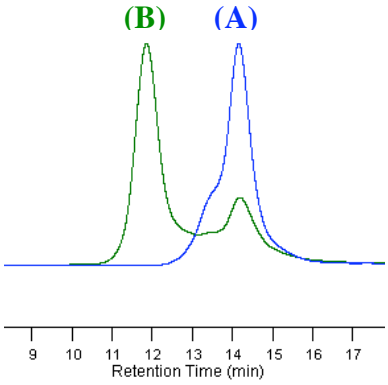


Figure S18. SEC traces for the (A) **3-PCL$_{84}$** (Table 2, run 6) and (B) **PBu$_{10}$-3-PCL$_{84}$** (Table 3, run 6).

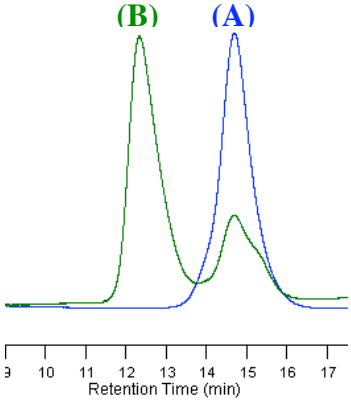


Figure S19. SEC traces for the (A) **3-PLA$_{41}$** (Table 1, run 5) and (B) **PBu$_{10}$-3-PLA$_{41}$** (Table 3, run 15).

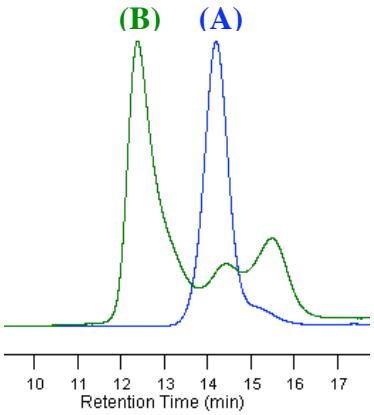


Figure S20. SEC traces for the (A) **2-PLA$_{40}$** (Table 1, run 8) and (B) **PBu$_{10}$-2-PLA$_{40}$** (Table 3, run 19).

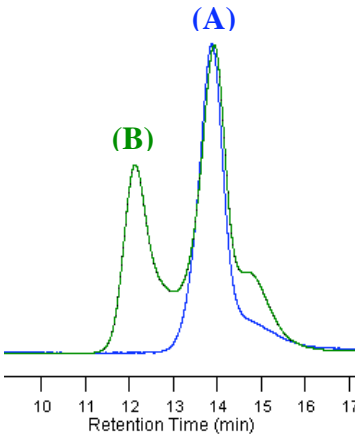


Figure S21. SEC traces for the (A) **2-PLA$_{77}$** (Table 1, run 9) and (B) **PBu$_{10}$-2-PLA$_{77}$** (Table 3, run 20).

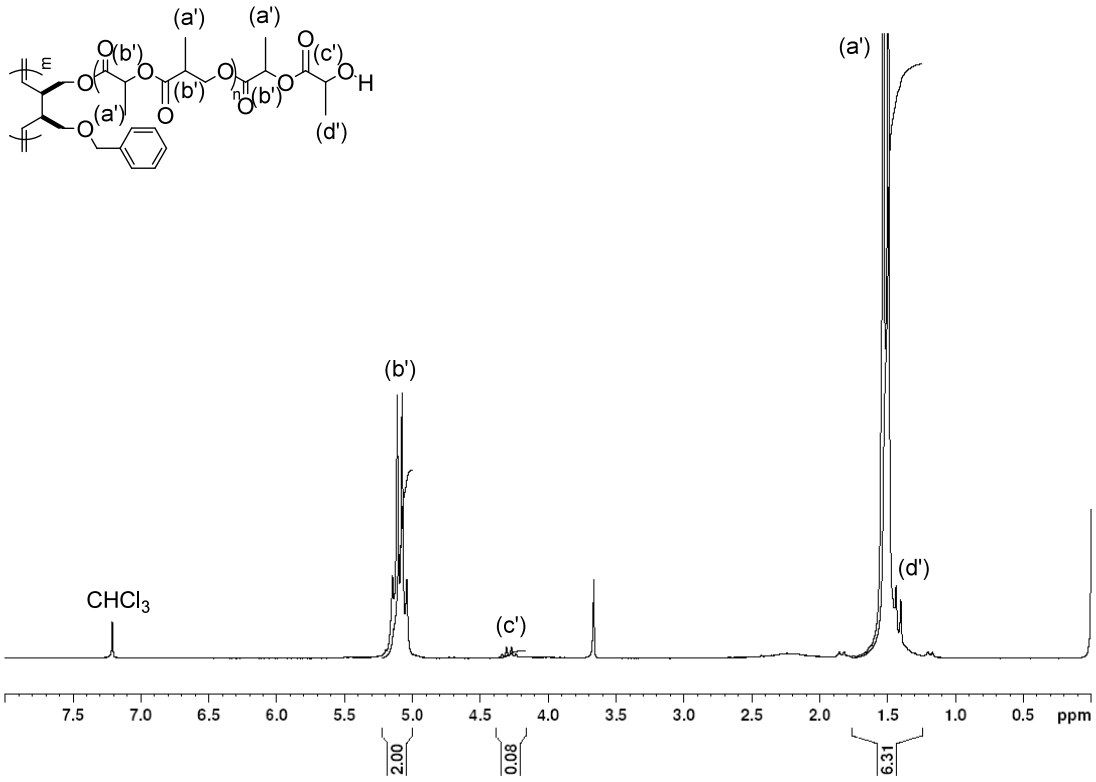


Figure S22. ^{1}H NMR spectrum (200 MHz, $CDCl_3$, 25 °C) of crude **PBu_{10}-*g*-3-PLA_{24}** issued from the ROMP of **3-PLA_{24}** in dichloroethane at 70 °C using **G2** as the catalyst for a reaction time of 3 h (Table 3, run 13).

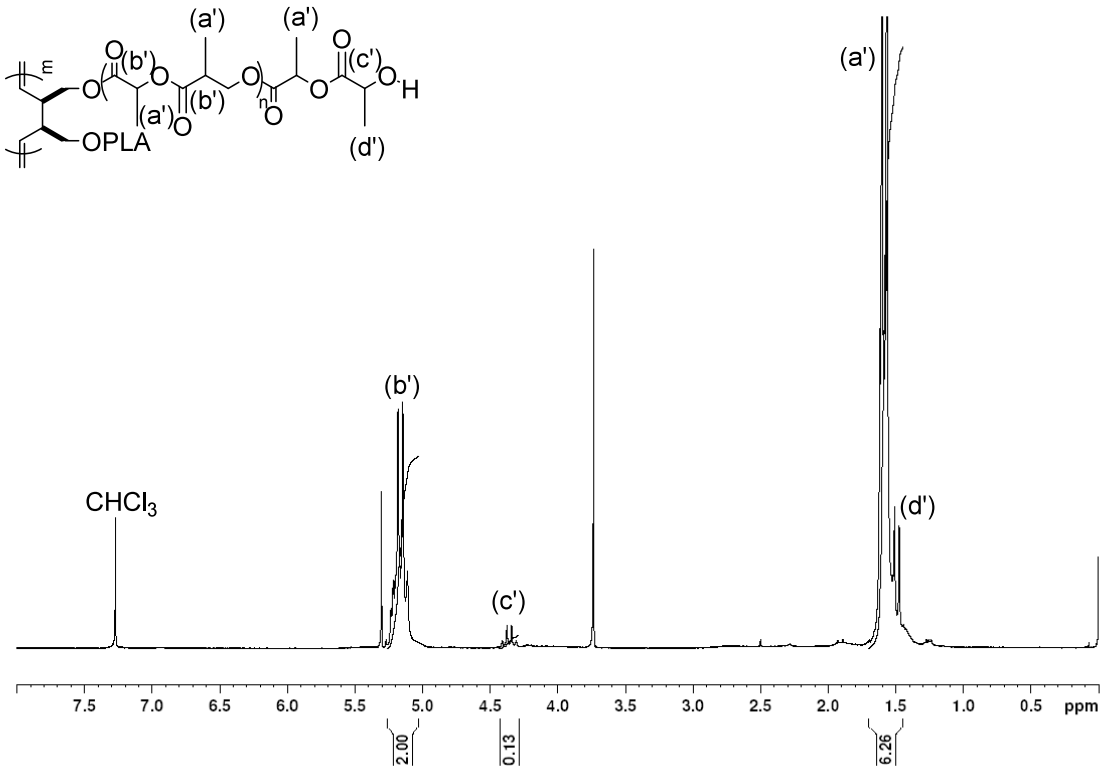


Figure S23. ^{1}H NMR spectrum (200 MHz, $CDCl_3$, 25 °C) of crude **PBu_{10}-*g*-2-PLA_{20}** issued from the ROMP of **2-PLA_{20}** in dichloroethane at 70 °C using **G2** as the catalyst for a reaction time of 3 h (Table 3, run 17).

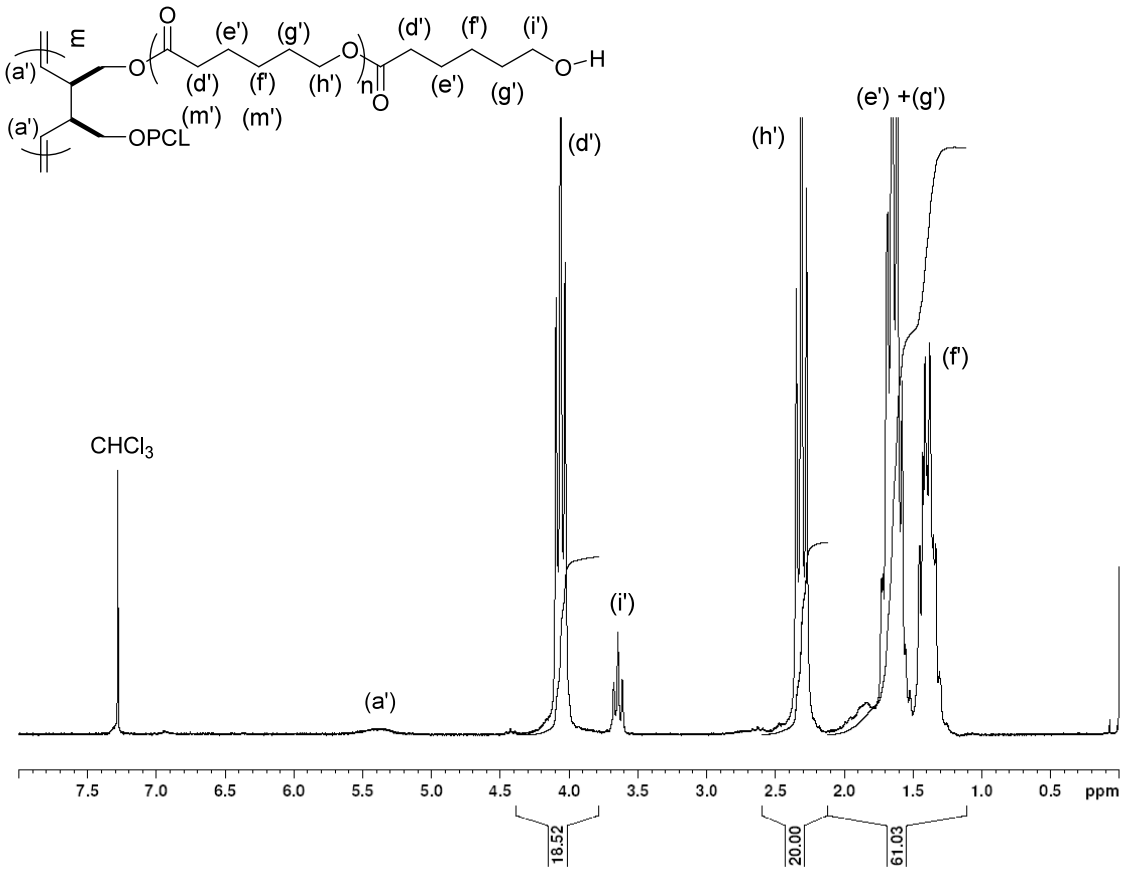


Figure S24. ^{1}H NMR spectrum (200 MHz, $CDCl_3$, 25 °C) of crude **PBu_{10}-*g*-2-PCL_{19}** issued from the ROMP of **2-PLA_{19}** in toluene at 70 °C using **G2** as the catalyst for a reaction time of 3 h (Table 3, run 7).