Supporting information

for

Macromolecular Engineering via Ring-Opening Polymerization (2): L-Lactide/Trimethylene Carbonate Copolymerization – Kinetic and Microstructural Control via Catalytic Tuning

Contents

[(BDI)Zn{N(SiMe$_3$)$_2$}]/BnOH, (middle spectra) P(LLA-*grad*-TMC) gradient copolymers and (bottom spectrum) a P(LLA-*ran*-TMC) random copolymer prepared by simultaneous loading of L-LA and TMC with various catalyst/BnOH systems in toluene at 110 °C (Table 1, entries 9, 2 and 15).

Figure S10. Details of the ^{1}H NMR spectra (CDCl$_3$, 500 MHz, 23 °C) of (top spectra) true P(TMC-*b*-LLA) block copolymers prepared by sequentially loading of TMC (1st) and L-LA (2nd) with the [(BDI)Zn{N(SiMe$_3$)$_2$}] / BnOH, (middle spectrum) a P(LLA-*grad*-TMC) gradient copolymer and (bottom spectrum) a P(LLA-*ran*-TMC) random copolymer prepared by simultaneous loading of L-LA and TMC with various catalyst/BnOH systems in toluene at 110 °C (Table 1, entries 2 and 15).

Figure S11 ^{13}C{^{1}H} NMR spectrum (CDCl$_3$, 125 MHz, 23 °C) of a P(LLA-*ran*-TMC) random copolymer prepared by simultaneous loading of L-LA and TMC with the TBD/BnOH system in toluene at 100 °C over 1h45 (Table 1, entry 15).

Figure S12. SEC trace of a copolymer prepared from the [(BDI)Zn{N(SiMe$_3$)$_2$}]/BnOH system ($M_{n,SEC}$ = 15 000 g.mol^{-1}, $Đ_M$ = 1.5) (Table 1, entry 3).

Figure S13. SEC trace of a copolymer prepared from the Yb(OTf)$_3$/BnOH system ($M_{n,SEC}$ = 13 600 g.mol^{-1}, $Đ_M$ = 1.3) (Table 1, entry 9).

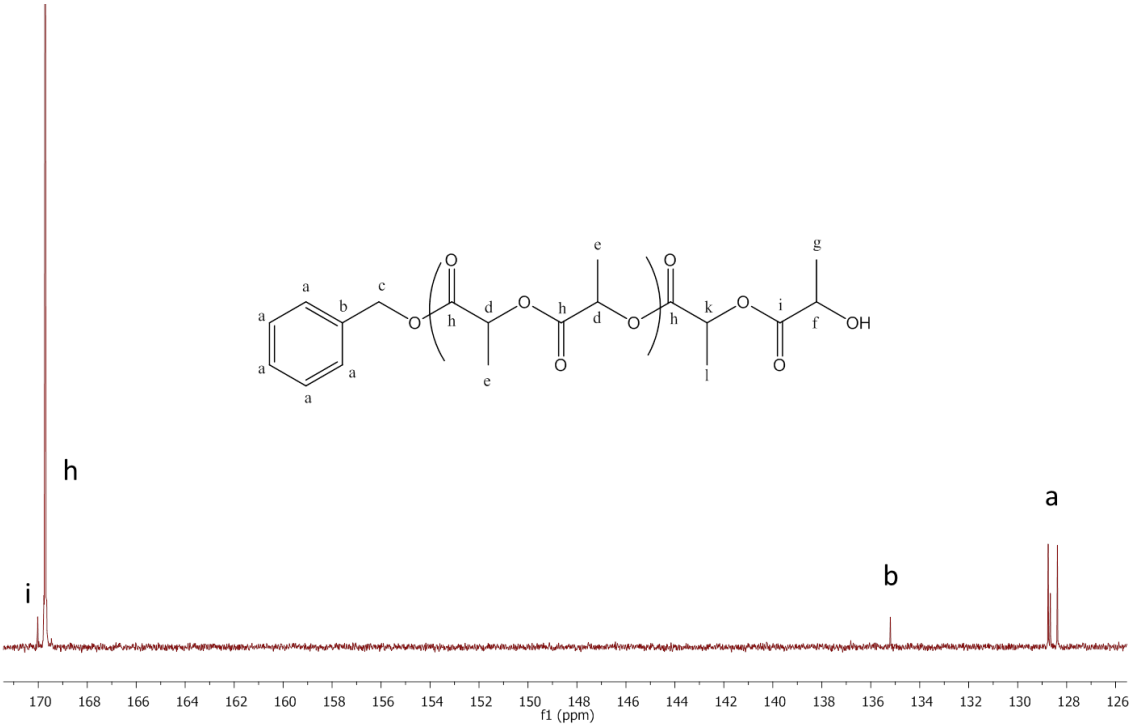

Figure S1. Details of the low field region of the $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 125 MHz, 23 °C) of a PLLA homopolymer synthesized from the [(BDI)Zn{$N(SiMe_3)_2$}]/BnOH system ($M_{n,SEC}$ = 5 000 g.mol^{-1}).

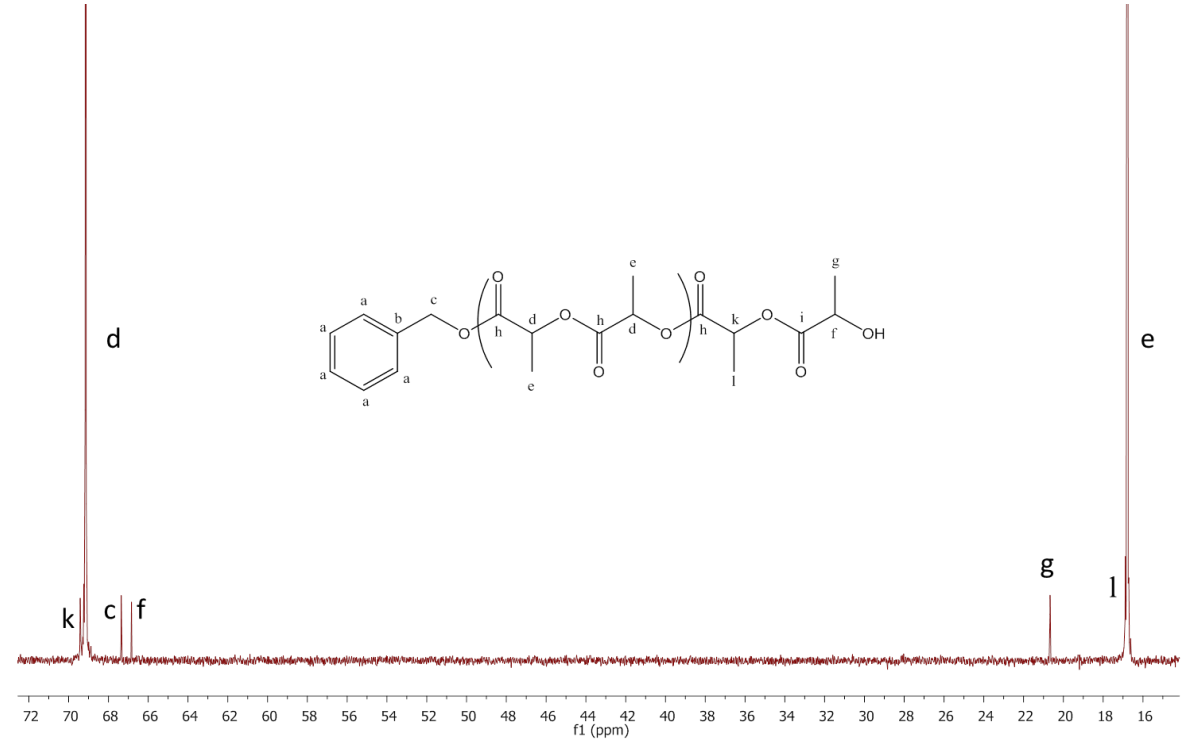

Figure S2. Details of the high field region of the $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 125 MHz, 23 °C) of a PLLA homopolymer synthesized from the [(BDI)Zn{$N(SiMe_3)_2$}]/BnOH system ($M_{n,SEC}$ = 5 000 g.mol^{-1}).

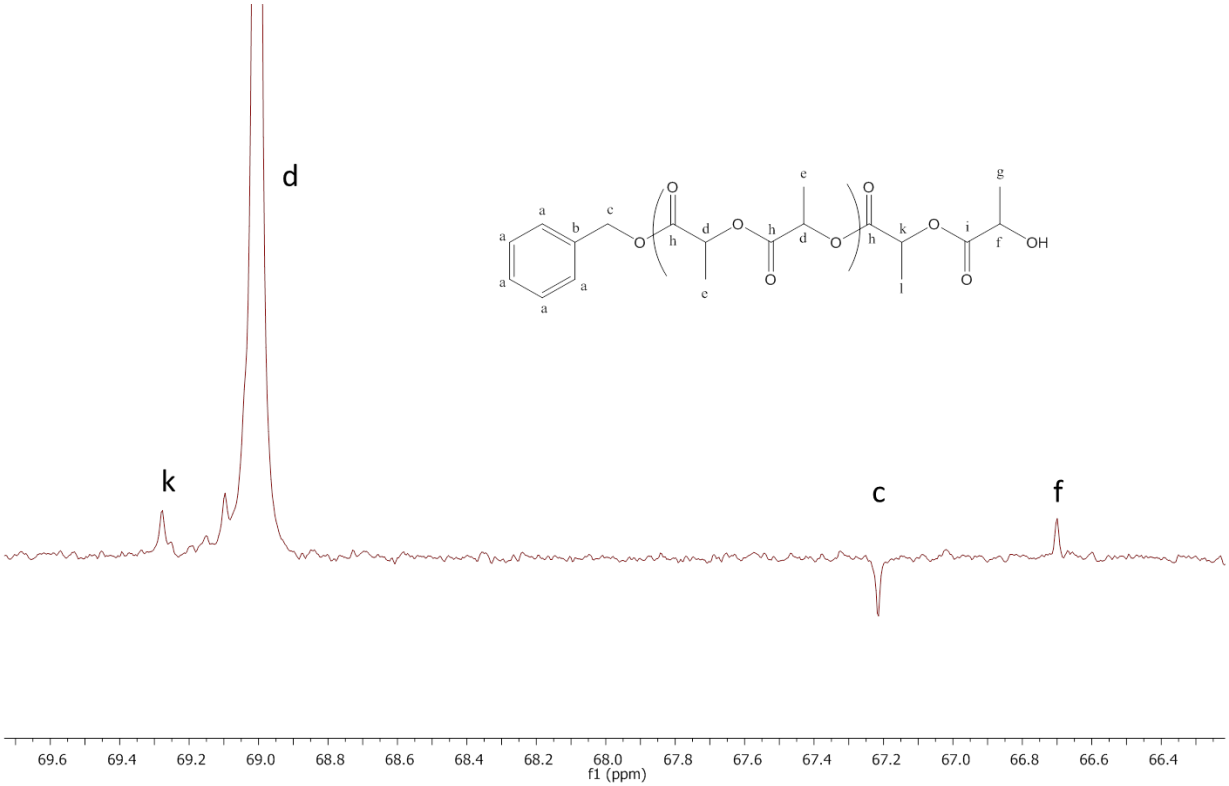

Figure S3. Details of the high field region of the DEPT ^{13}C NMR spectrum ($CDCl_3$, 125 MHz, 23 °C) of a PLLA homopolymer synthesized from the [(BDI)Zn{$N(SiMe_3)_2$}]/BnOH system ($M_{n,SEC}$ = 5 000 g.mol^{-1}).

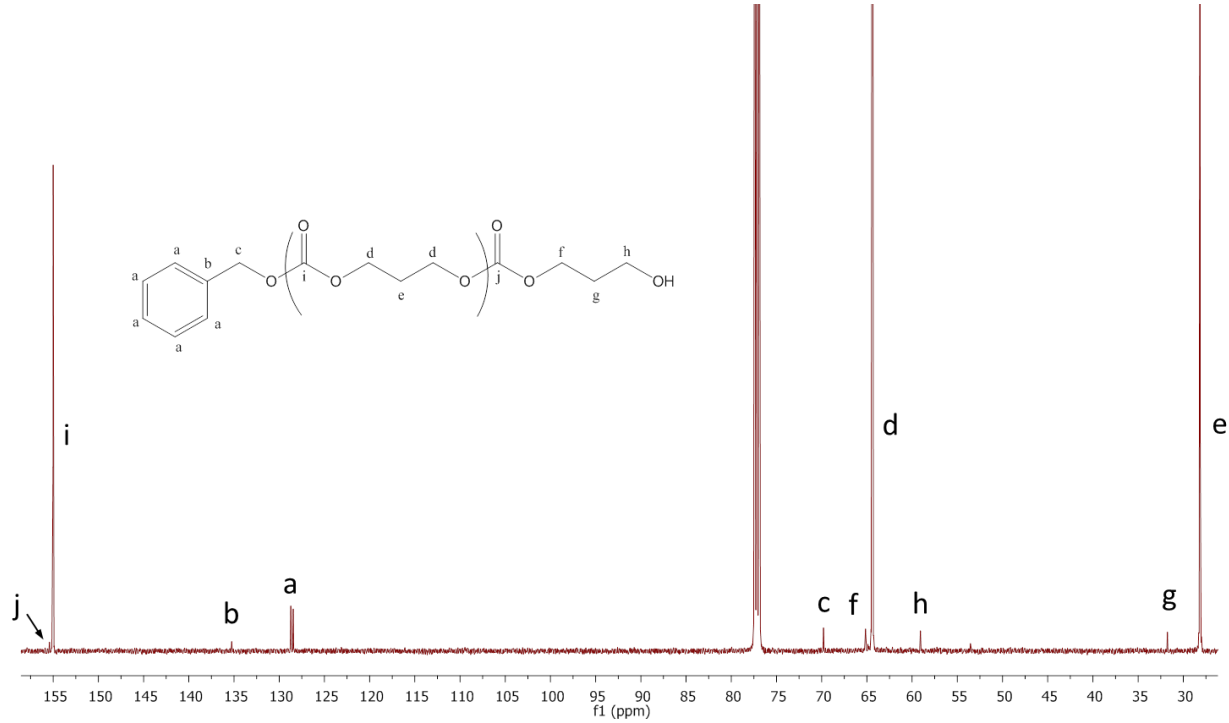

Figure S4. $^{13}C\{^1H\}$ NMR spectrum ($CDCl_3$, 125 MHz, 23 °C) of a PTMC homopolymer synthesized from the [(BDI)Zn{$N(SiMe_3)_2$}]/BnOH system ($M_{n,SEC}$ = 5 000 g.mol^{-1}).

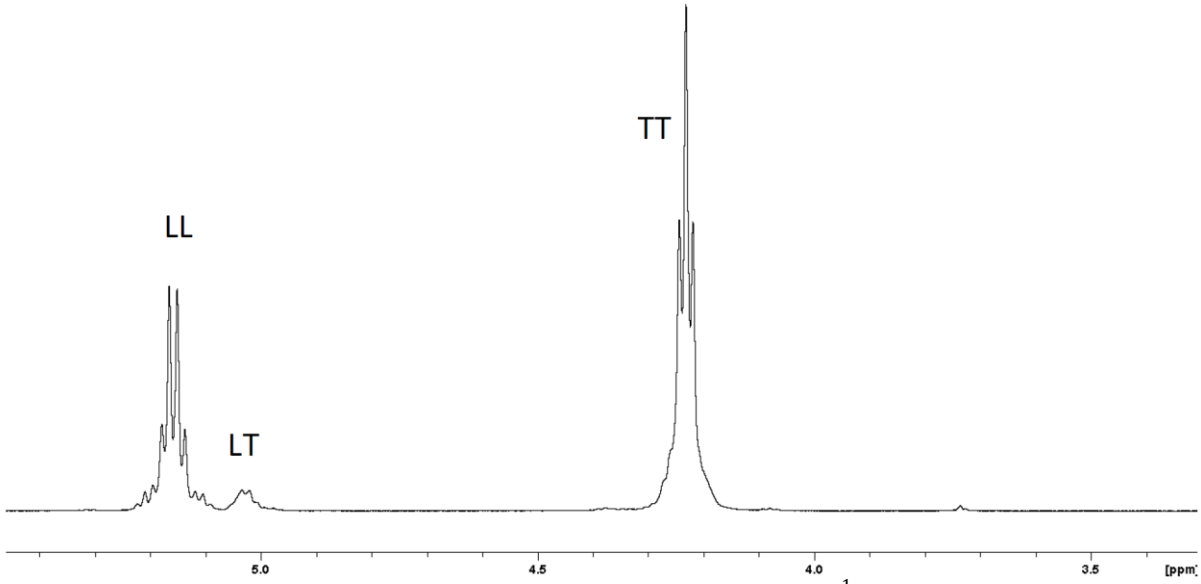

Figure S5. Details of the methylene and methine region of the ^{1}H NMR spectrum ($CDCl_3$, 500 MHz, 23 °C) of a P(LLA-*grad*-TMC) gradient copolymer ($M_{n,SEC}$ = 13 400 g.mol^{-1}) prepared with the [(BDI)Zn{N(SiMe$_3$)$_2$}]/BnOH system in toluene at 110 °C (Table 1, entry 2), with assignment of resonances.

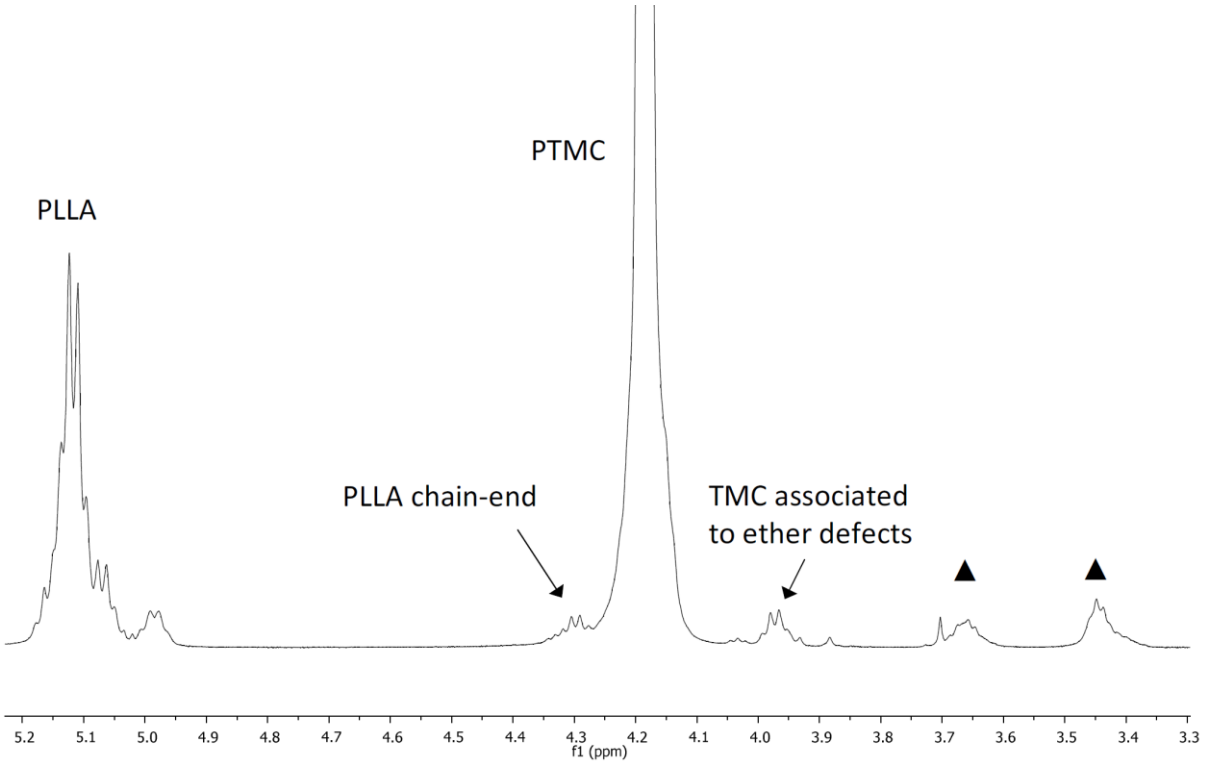

Figure S6. Details of the methylene and methine region of the ^{1}H NMR spectrum ($CDCl_3$, 500 MHz, 23 °C) of a P(LLA-*grad*-TMC) gradient copolymer ($M_{n,SEC}$ = 10 200 g.mol^{-1}) prepared with the Al(OTf)$_3$/BnOH system in toluene at 110 °C (Table 1, entry 5), showing resonances (▲) characteristic of ether units resulting from partial decarboxylation.

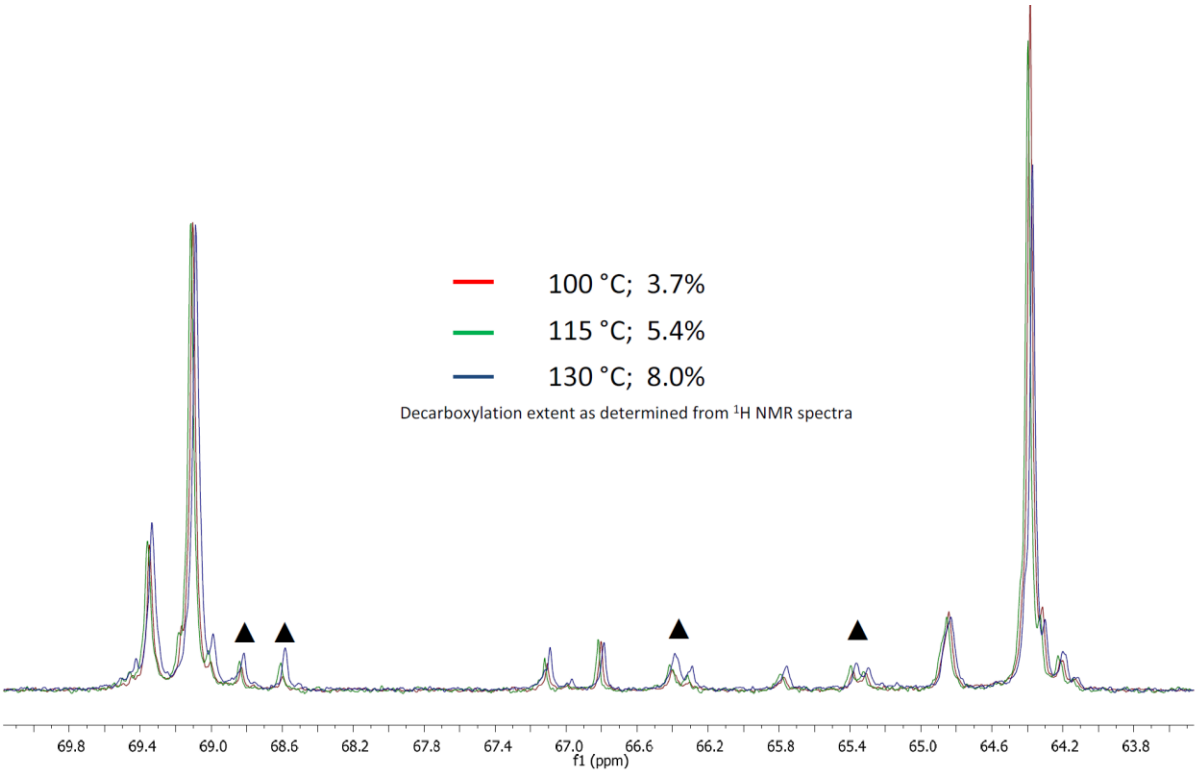

Figure S7. Details of the methine and methylene region of the $^{13}C\{^{1}H\}$ NMR spectra ($CDCl_3$, 125 MHz, 23 °C) of P(LLA-*grad*-TMC) gradient copolymers prepared with the $Al(OTf)_3$/BnOH system in toluene at 100, 115 and 130 °C, showing evolution of resonances characteristic (▲) of ether units resulting from partial decarboxylation.

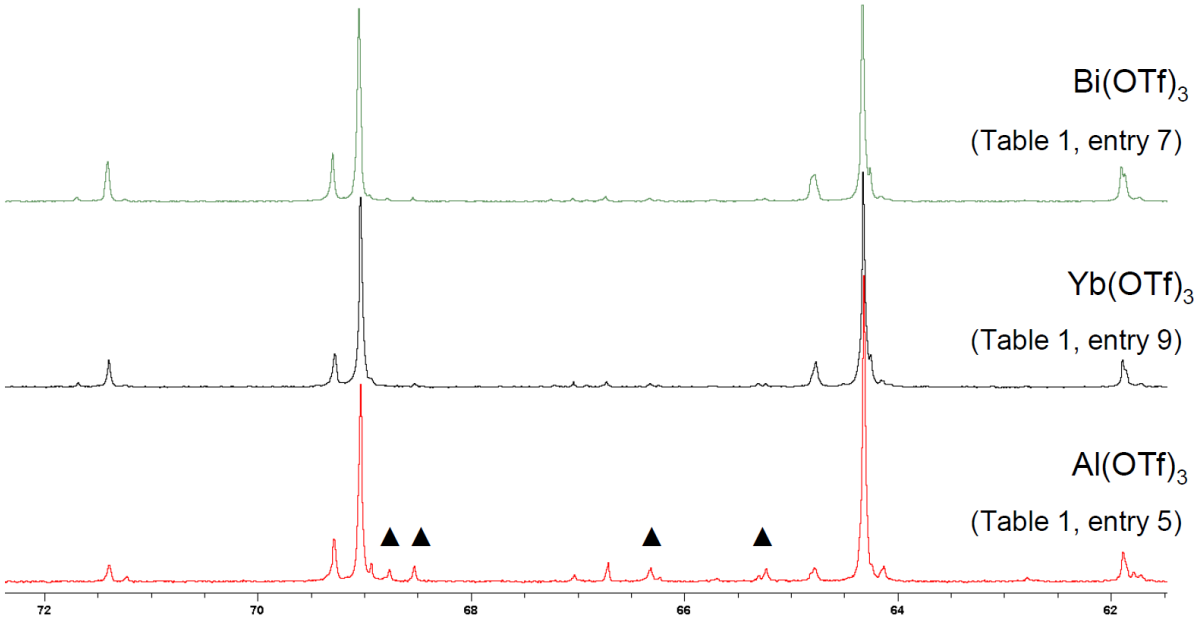

Figure S8. Details of the methine and methylene region of the $^{13}C\{^{1}H\}$ NMR spectra ($CDCl_3$, 125 MHz, 23 °C) of P(LLA-*grad*-TMC) gradient copolymers prepared with the $M(OTf)_3$/BnOH systems in toluene at 110 °C, showing resonances characteristic of ether units resulting from partial decarboxylation.

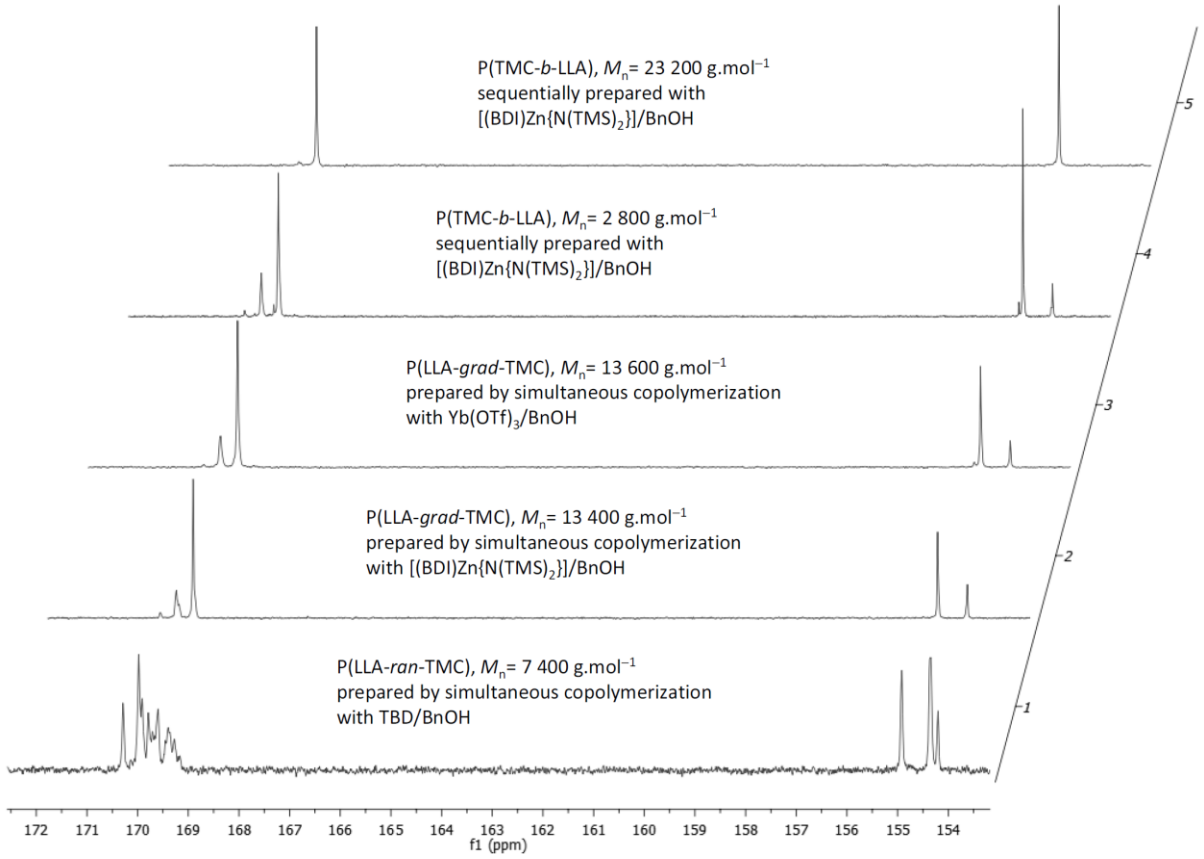

Figure S9. Details of the carbonyl region of the $^{13}C\{^{1}H\}$ NMR spectra ($CDCl_3$, 125 MHz, 23 °C) of (top spectra) true P(TMC-*b*-LLA) block copolymers ($M_{n,SEC}$ = 23 200 and 2 800 g.mol^{-1}) prepared by sequentially loading of TMC (1st) and L-LA (2nd) with the [(BDI)Zn{N(SiMe$_3$)$_2$}]/BnOH, (middle spectra) P(LLA-*grad*-TMC) gradient copolymers and (bottom spectrum) a P(LLA-*ran*-TMC) random copolymer prepared by simultaneous loading of L-LA and TMC with various catalyst/BnOH systems in toluene at 110 °C (Table 1, entries 9, 2 and 15).

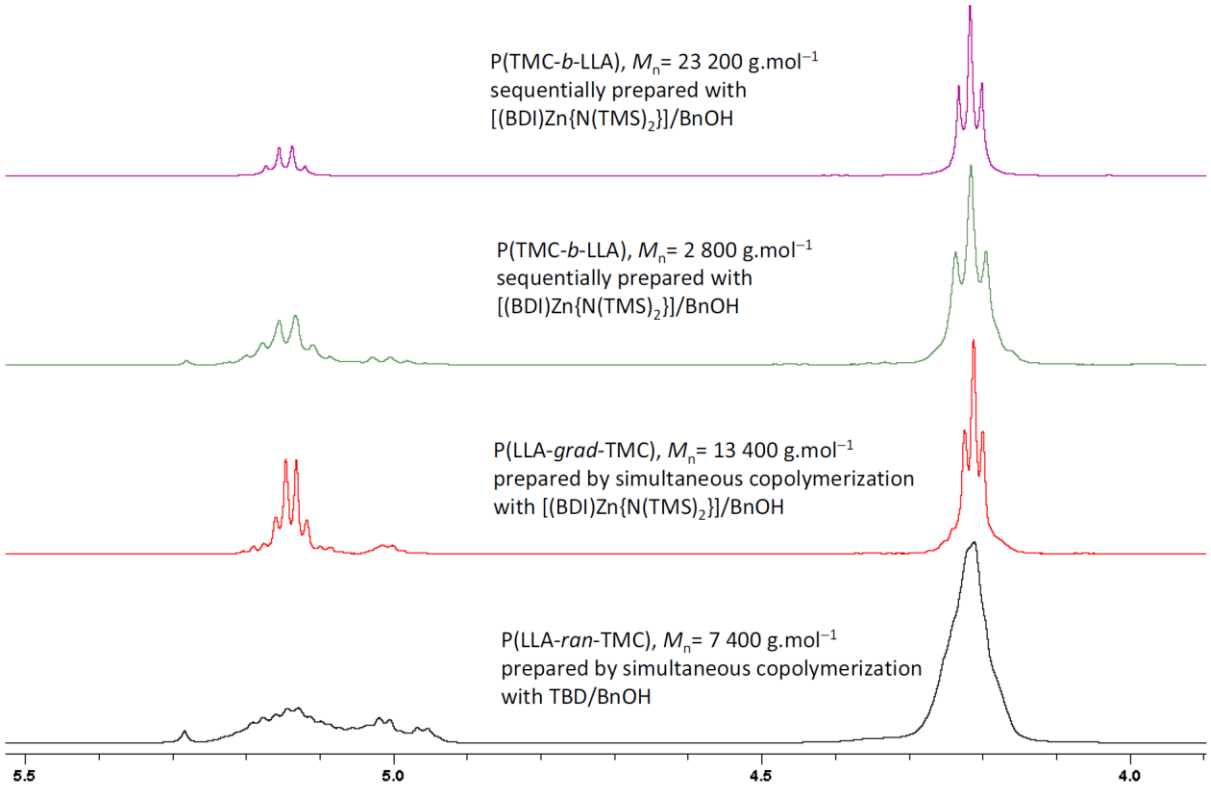

Figure S10. Details of the ^{1}H NMR spectra ($CDCl_3$, 500 MHz, 23 °C) of (top spectra) true P(TMC-*b*-LLA) block copolymers prepared by sequentially loading of TMC (1st) and L-LA (2nd) with the [(BDI)Zn{N(SiMe$_3$)$_2$}]/BnOH, (middle spectrum) a P(LLA-*grad*-TMC) gradient copolymer and (bottom spectrum) a P(LLA-*ran*-TMC) random copolymer prepared by simultaneous loading of L-LA and TMC with various catalyst/BnOH systems in toluene at 110 °C (Table 1, entries 2 and 15).

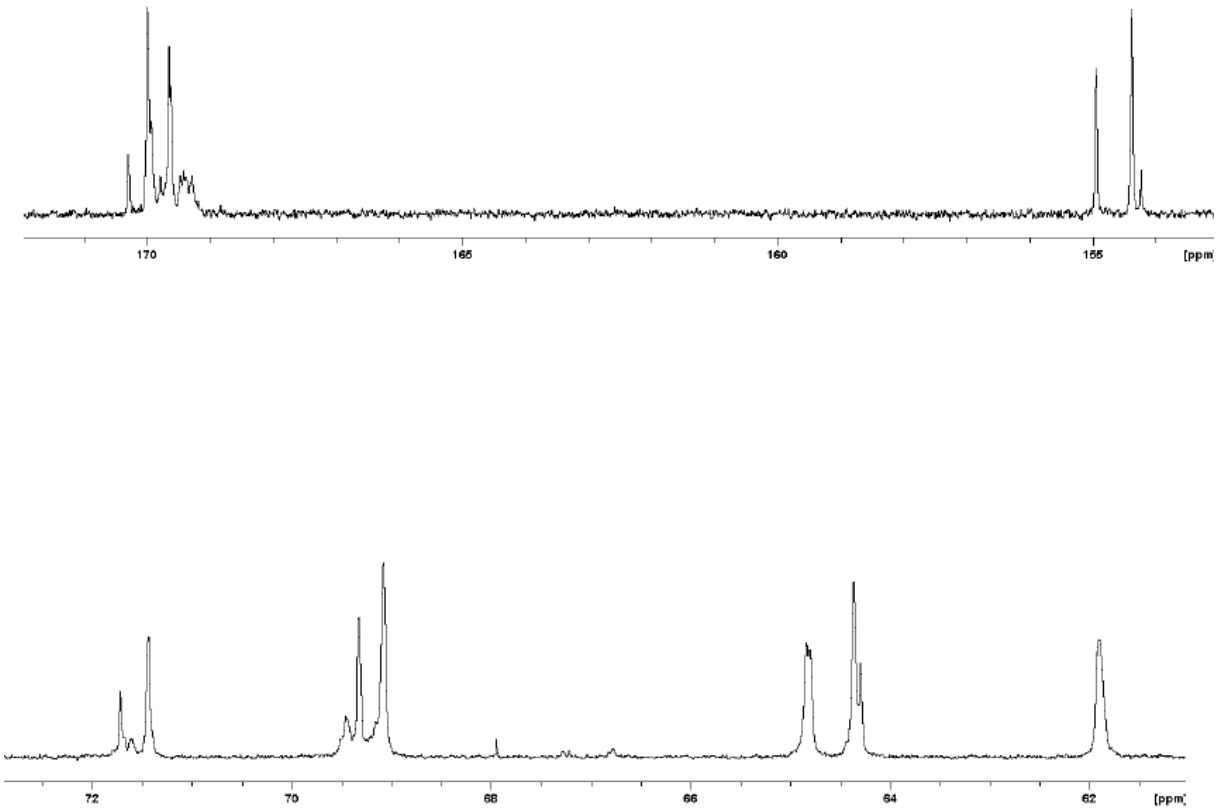

Figure S11. $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 125 MHz, 23 °C) of a P(LLA-*ran*-TMC) random copolymer prepared by simultaneous loading of L-LA and TMC with the TBD/BnOH system in toluene at 100 °C over 1h45 (Table 1, entry 12).

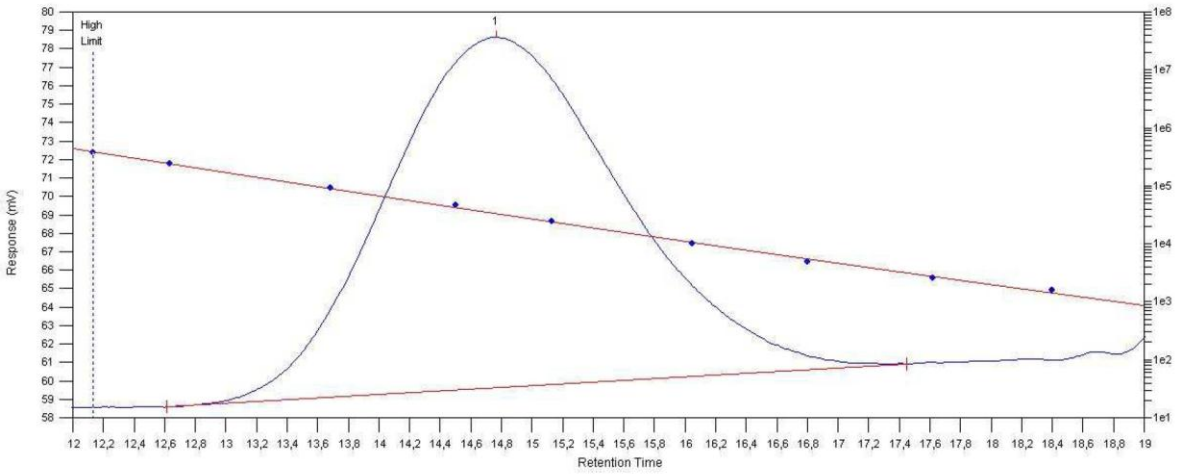

Figure S12. SEC trace of a copolymer prepared from the [(BDI)Zn{N(SiMe$_3$)$_2$}]/BnOH system ($M_{n,SEC}$ = 15 000 g.mol^{-1}, $Đ_M$ = 1.5) (Table 1, entry 3).

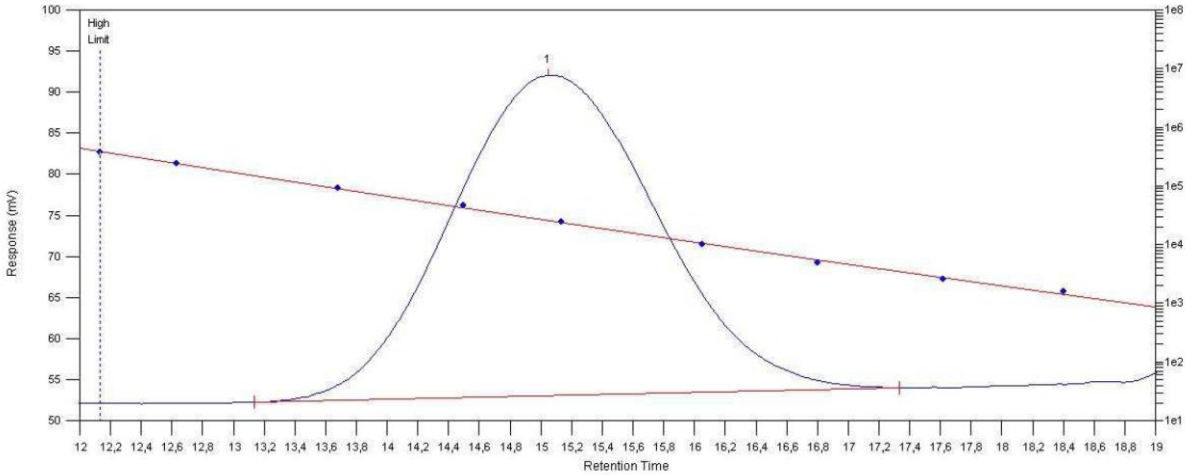

Figure S13. SEC trace of a copolymer prepared from the Yb(OTf)$_3$/BnOH system ($M_{n,SEC}$ = 13 600 g.mol^{-1}, $Đ_M$ = 1.3) (Table 1, entry 9).