

Supporting Information for

**A dual-initiating organic frustrated Lewis pair catalyst for living polymerizations of
(bio)acrylates to facilitate the synthesis of metal-free multiblock copolymers**

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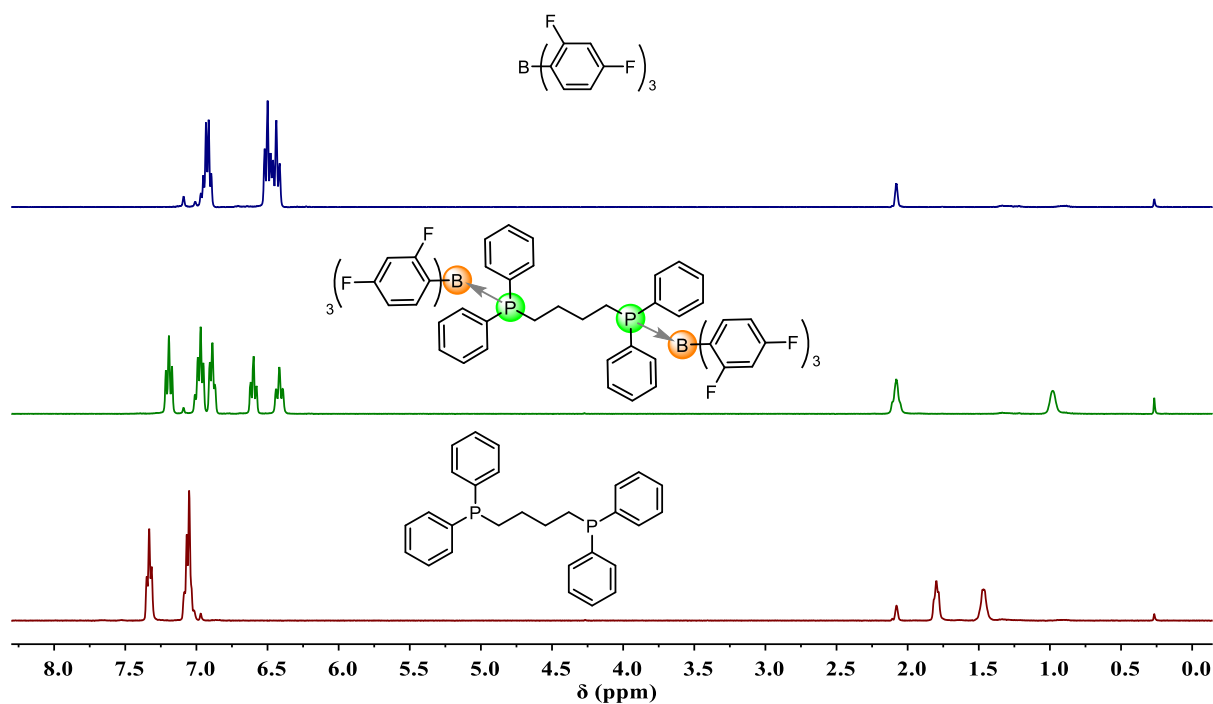


Figure S1. ^1H NMR spectra (toluene- d_8 , RT): (top) $\text{B}(\text{2,4-F}_2\text{C}_6\text{H}_3)_3$; (middle) $\text{DPPh}_2 \rightarrow \text{B}(\text{2,4-F}_2\text{C}_6\text{H}_3)_3$ CLA; (bottom) DPPh_2 .

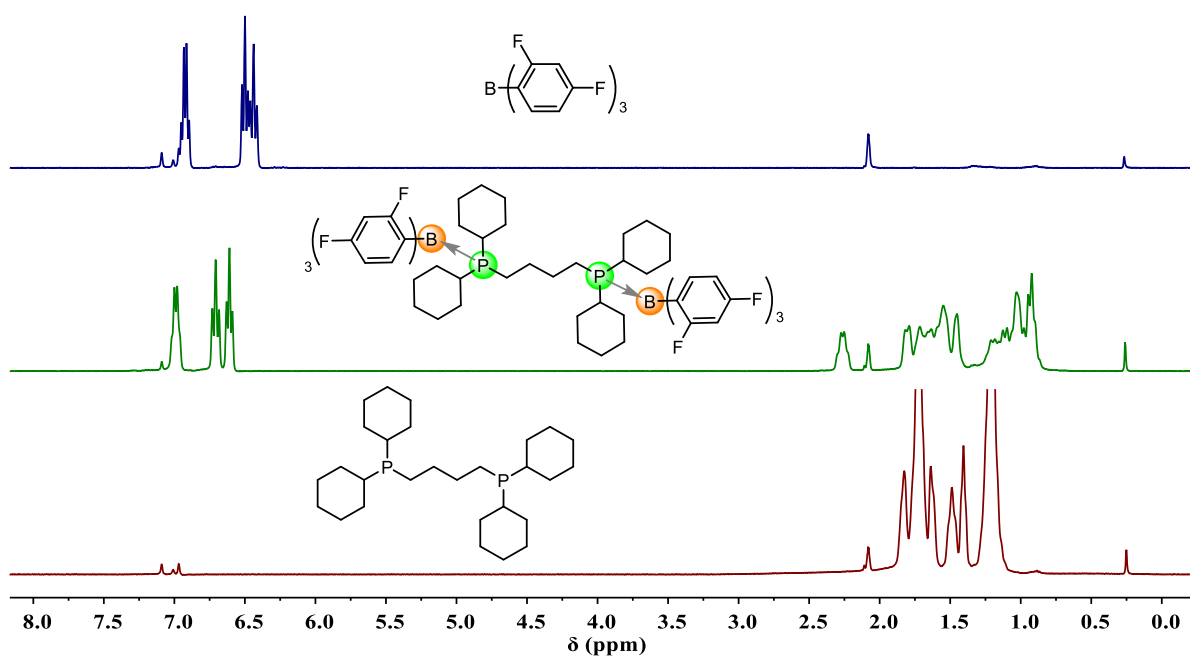


Figure S2. ^1H NMR spectra (toluene- d_8 , RT): (top) $\text{B}(\text{2,4-F}_2\text{C}_6\text{H}_3)_3$; (middle) $\text{DPCy}_2 \rightarrow \text{B}(\text{2,4-F}_2\text{C}_6\text{H}_3)_3$ CLA; (bottom) DPCy_2 .

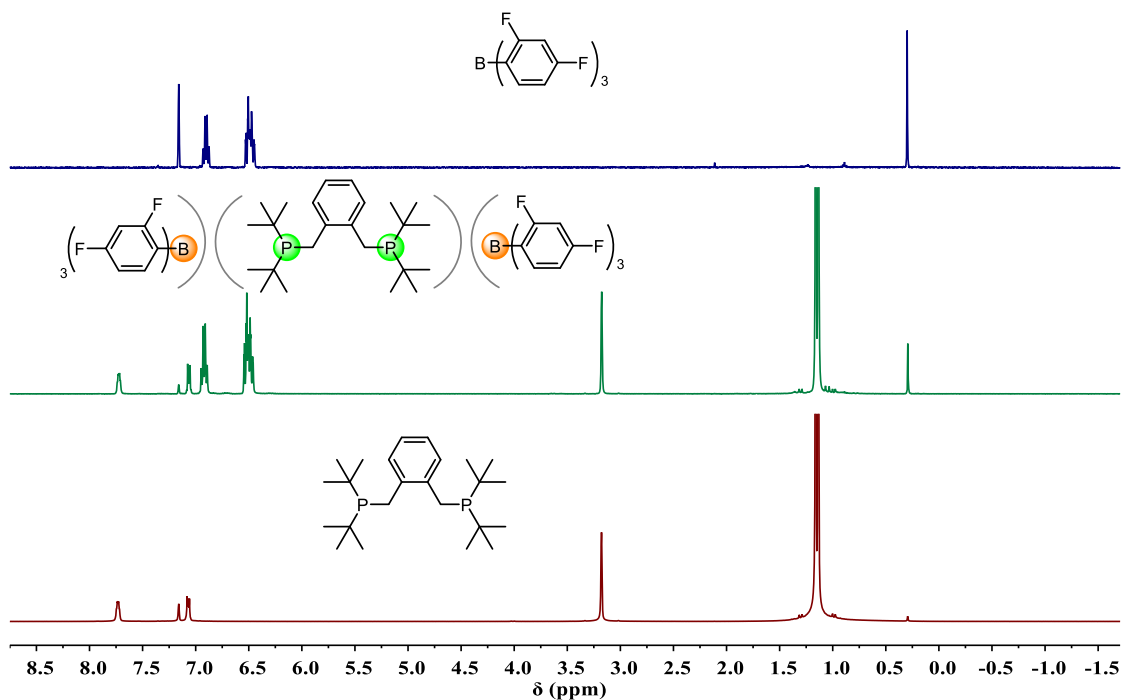


Figure S3. ^1H NMR spectra (benzene- d_6 , RT): (top) $\text{B}(2,4\text{-F}_2\text{C}_6\text{H}_3)_3$; (middle) $\text{DP}'\text{Bu}_2/\text{B}(2,4\text{-F}_2\text{C}_6\text{H}_3)_3$ FLP; (bottom) $\text{DP}'\text{Bu}_2$.

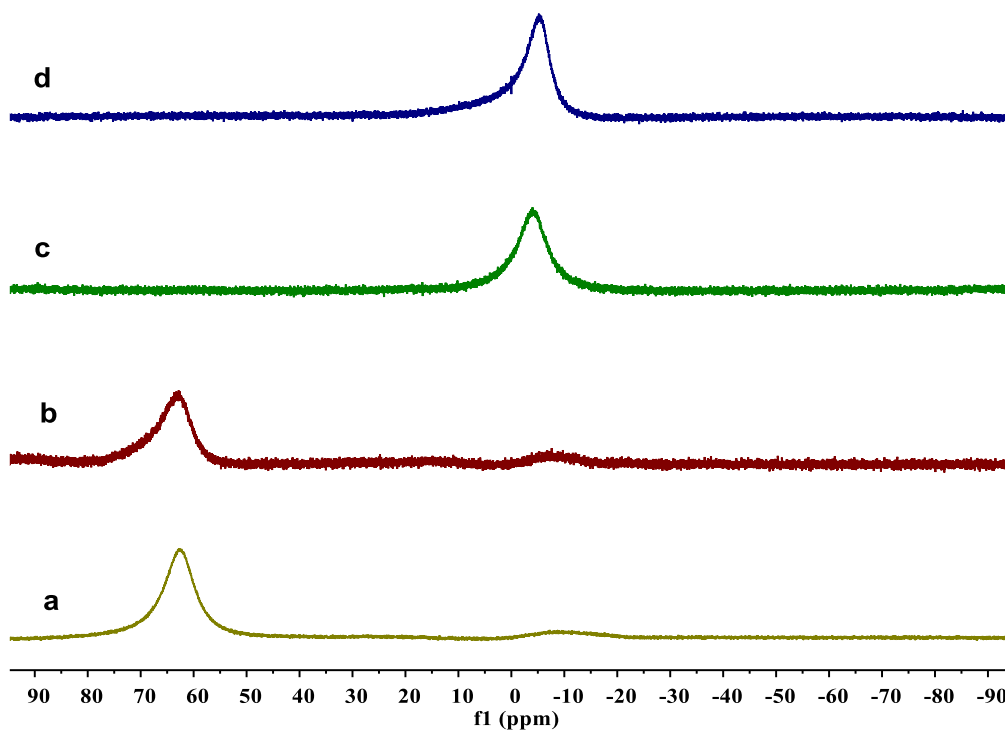


Figure S4. ^{11}B NMR spectra (toluene- d_8 , RT) of $\text{B}(2,4\text{-F}_2\text{Ph})_3$ (a), $\text{DP}'\text{Bu}_2/\text{B}(2,4\text{-F}_2\text{C}_6\text{H}_3)_3$ FLP (b), $\text{DPPH}_2 \rightarrow \text{B}(2,4\text{-F}_2\text{C}_6\text{H}_3)_3$ CLA (c), and $\text{DPCy}_2 \rightarrow \text{B}(2,4\text{-F}_2\text{C}_6\text{H}_3)_3$ CLA (d).

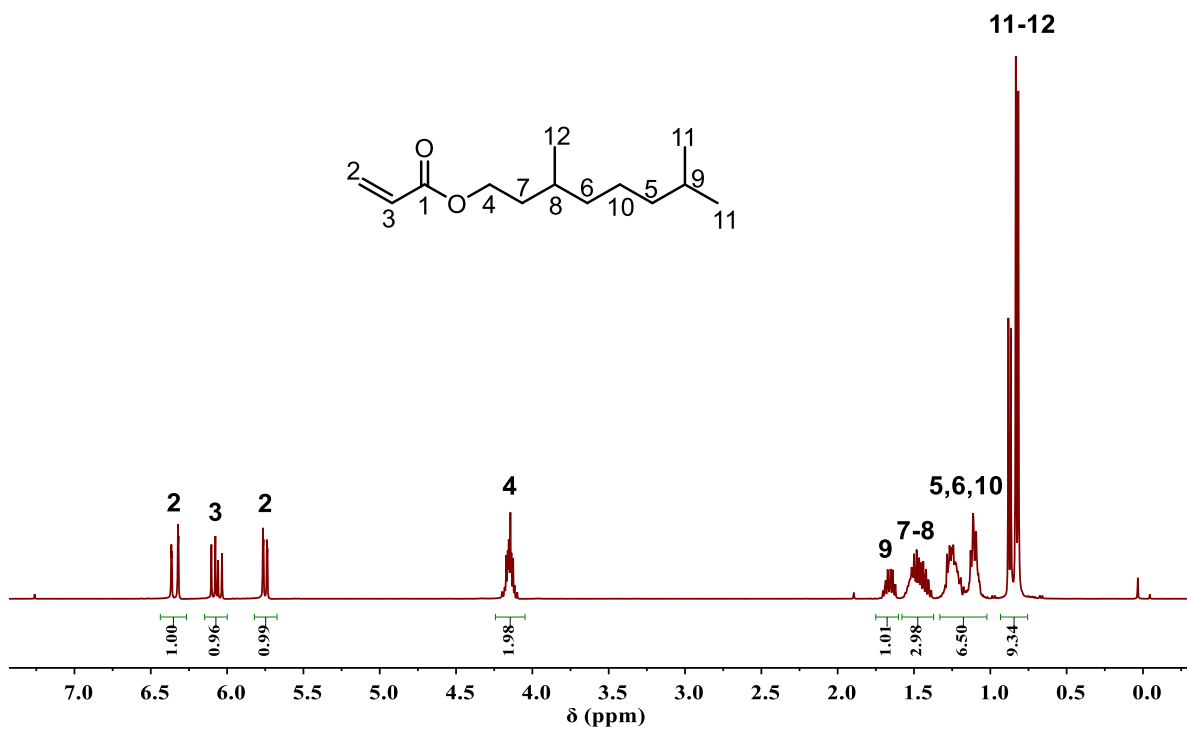


Figure S5. ¹H NMR spectrum (CDCl₃) of THGA.

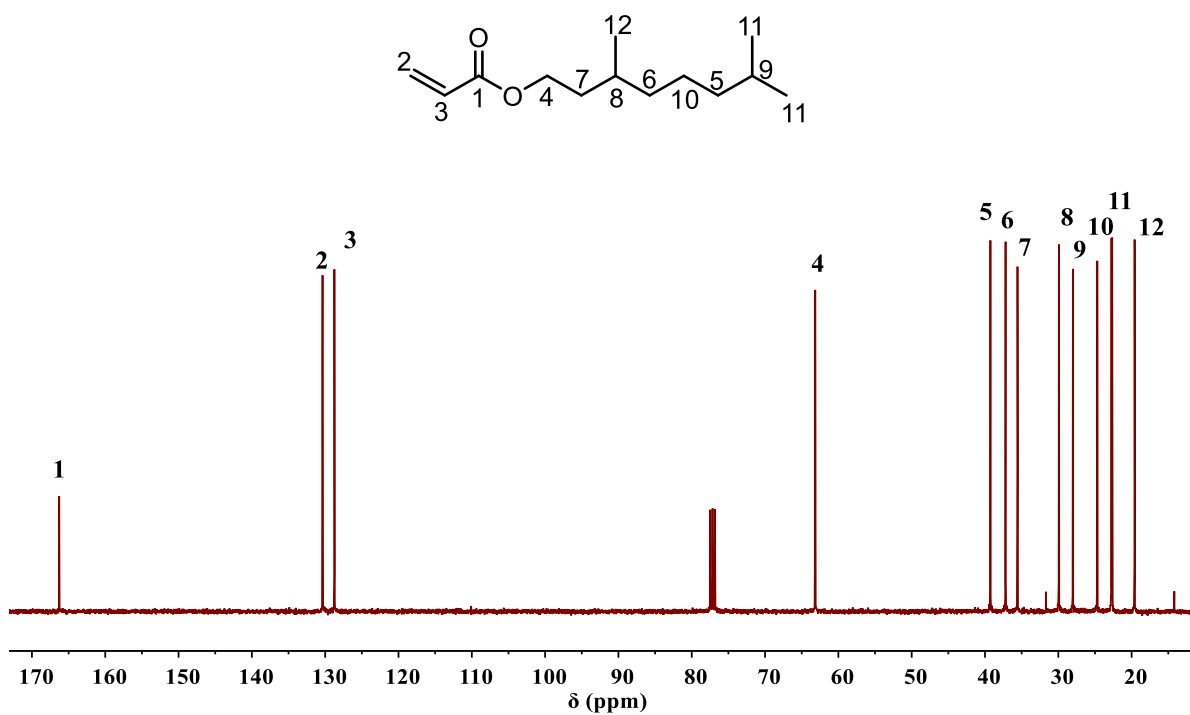


Figure S6. ¹³C NMR spectrum (CDCl₃) of THGA.

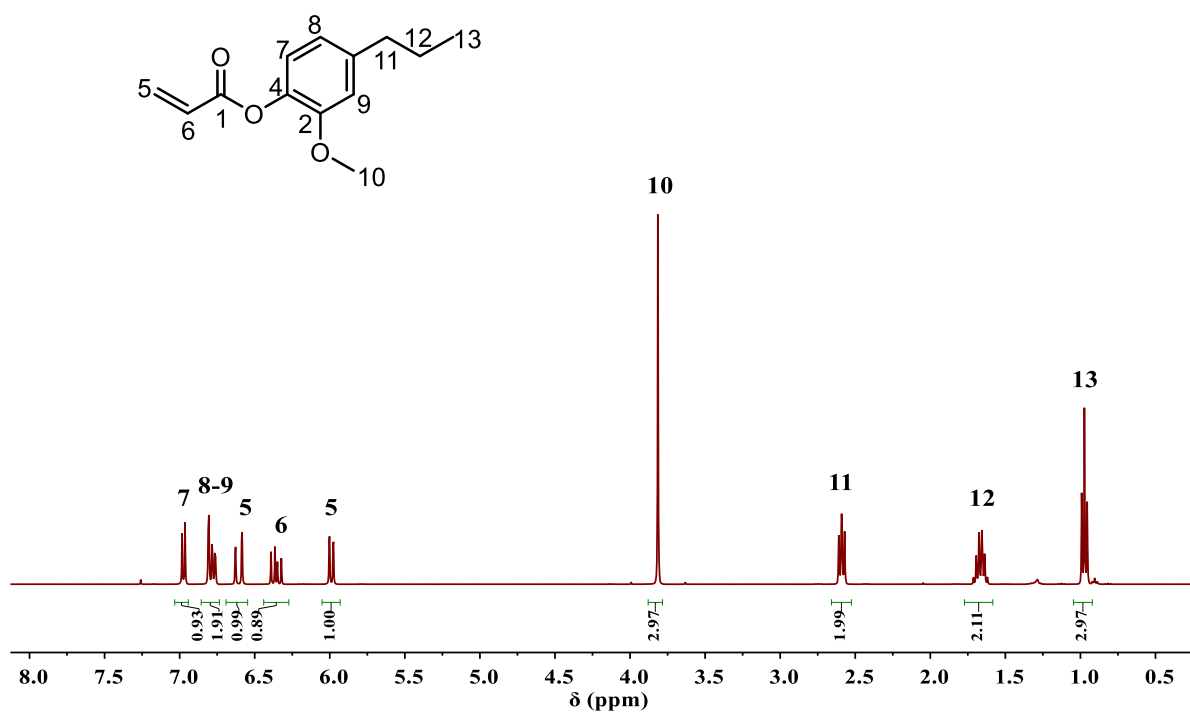


Figure S7. ^1H NMR spectrum (CDCl_3) of 4pGA.

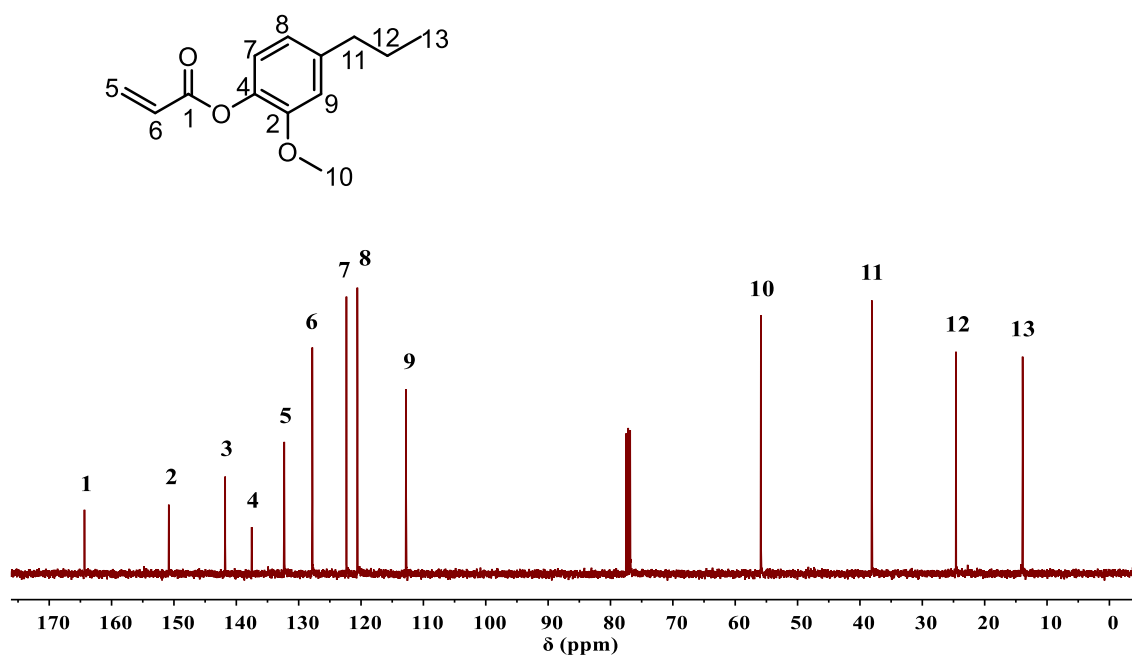


Figure S8. ^{13}C NMR spectrum (CDCl_3) of 4pGA.

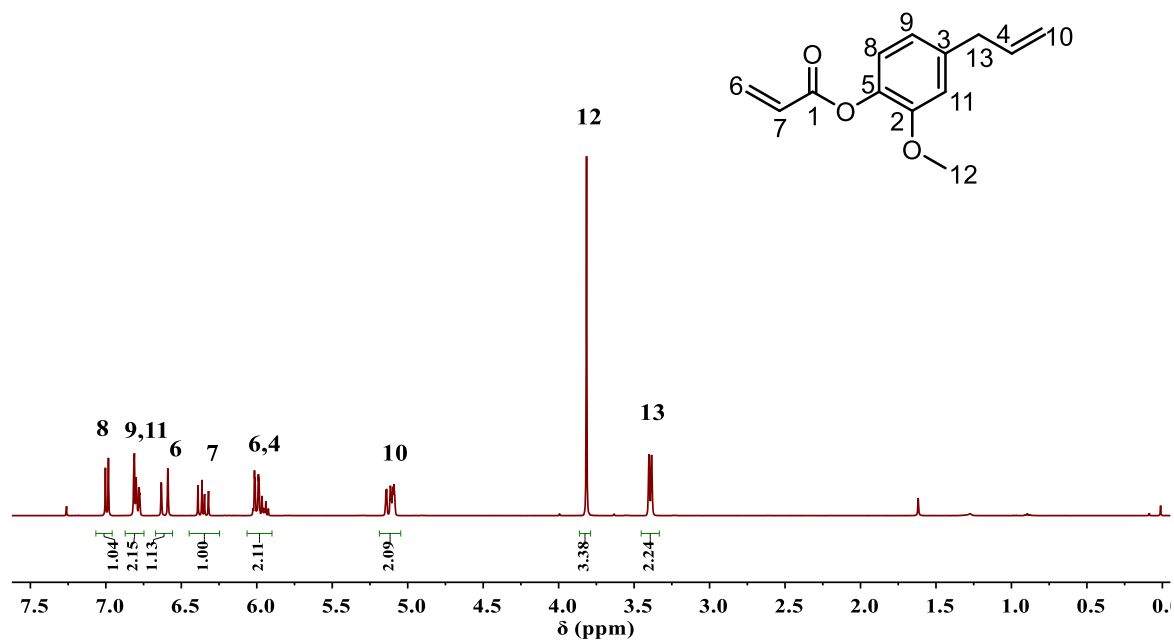


Figure S9. ^1H NMR spectrum (CDCl_3) of 4aGA.

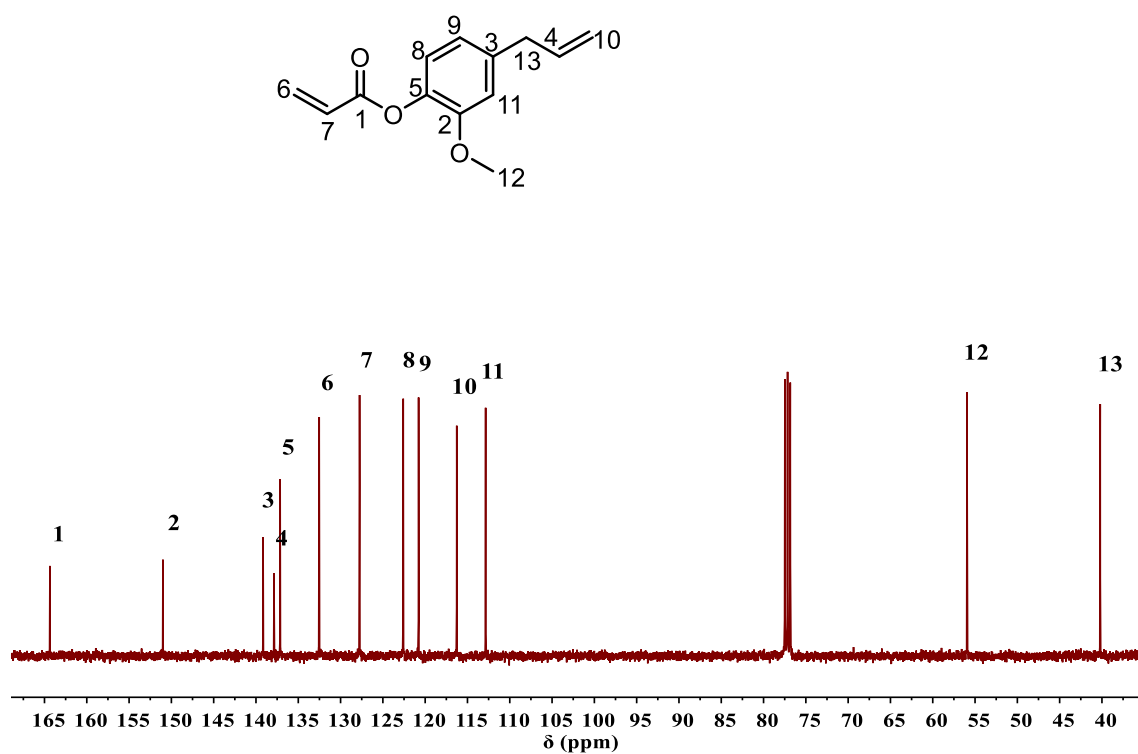


Figure S10. ^{13}C NMR spectrum (CDCl_3) of 4aGA.

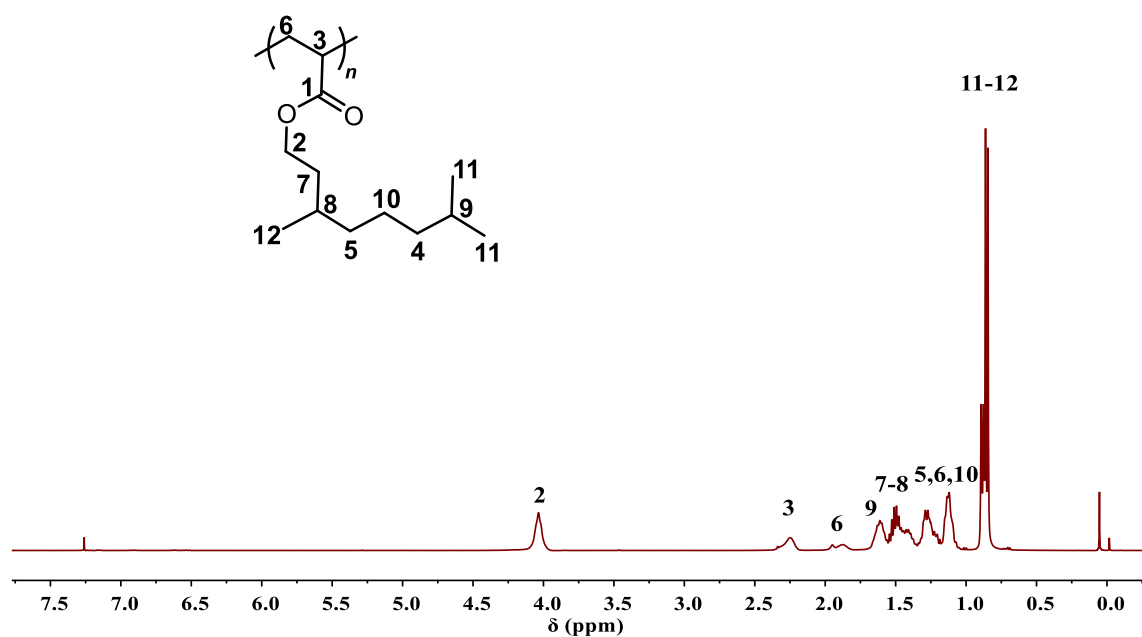


Figure S11. ^1H NMR spectrum (CDCl_3 , RT) of PTHGA (Table 1, Run 15).

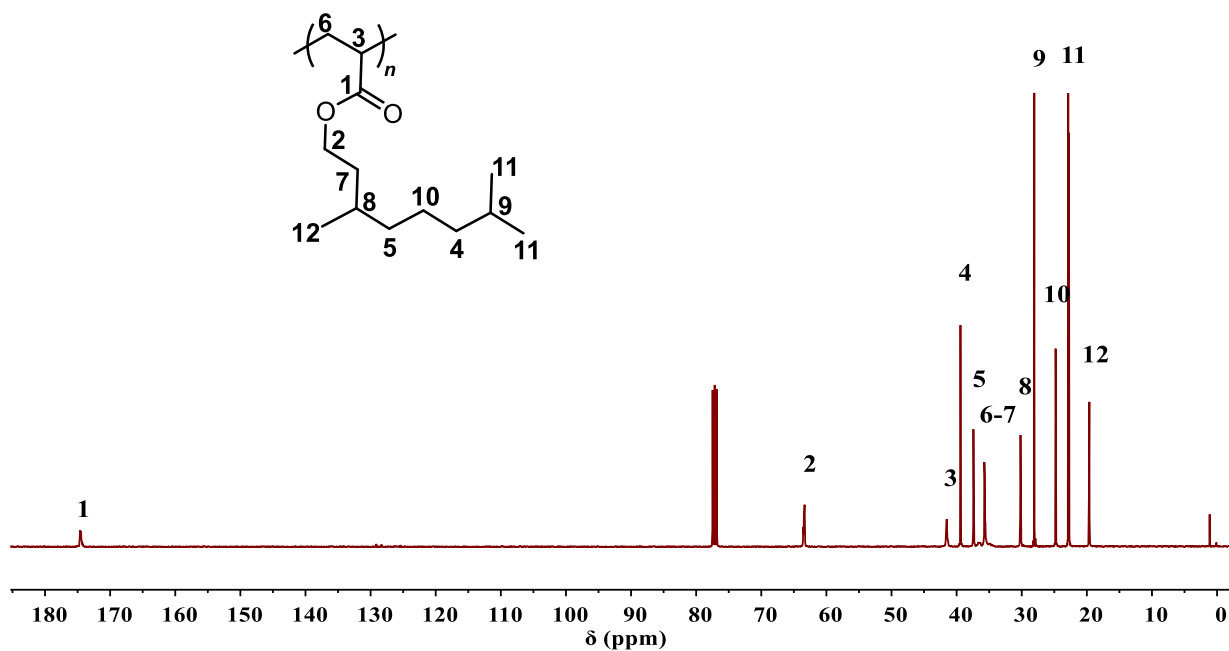


Figure S12. ^{13}C NMR spectrum (CDCl_3 , RT) of PTHGA (Table 1, Run 15).

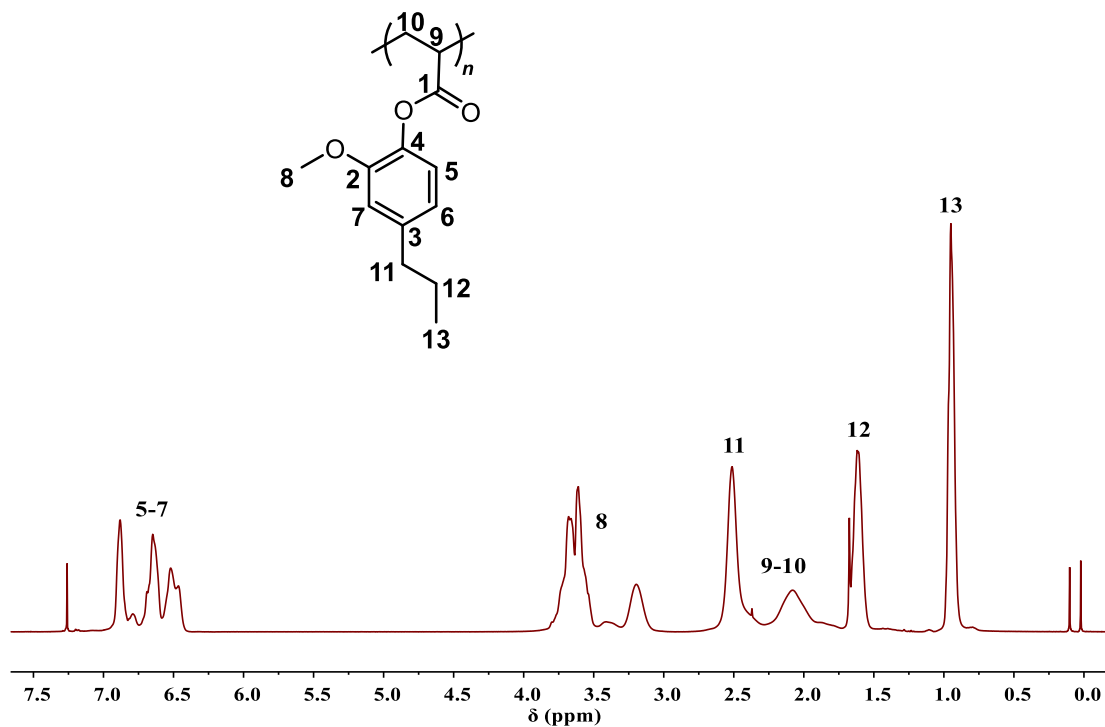


Figure S13. ^1H NMR spectrum (CDCl₃, RT) of P4pGA (Table 1, Run 11).

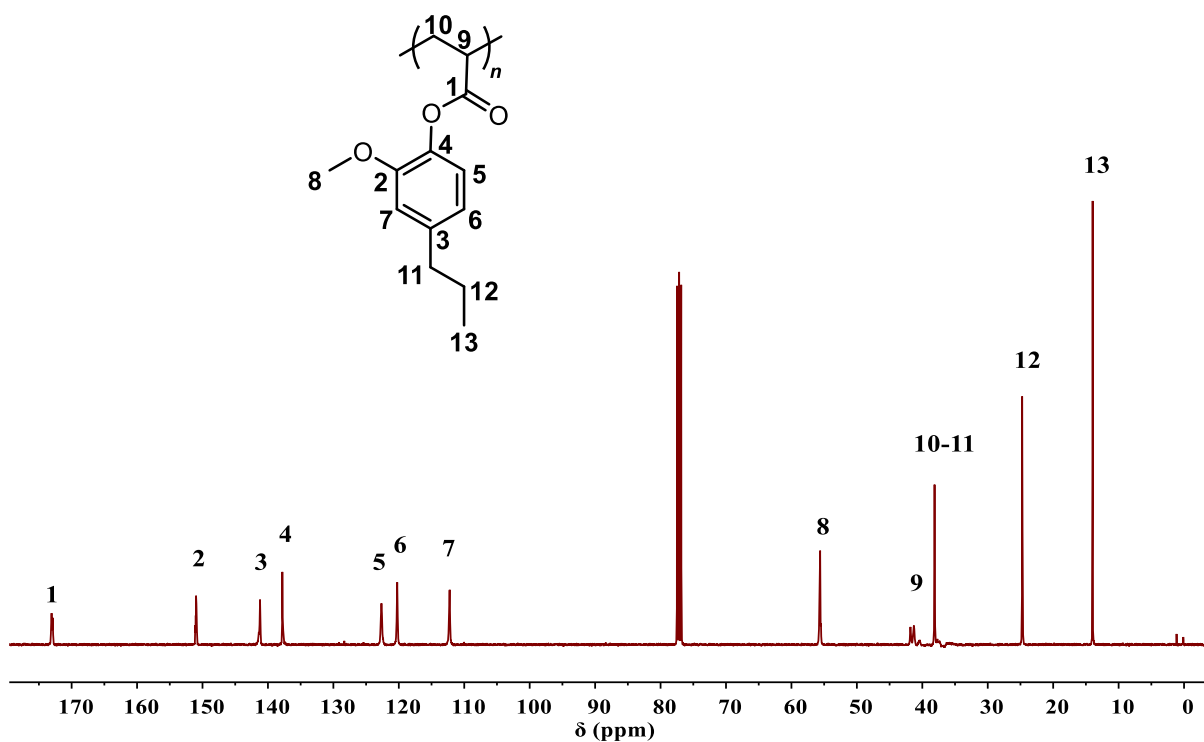


Figure S14. ^{13}C NMR spectrum (CDCl₃, RT) of P4pGA (Table 1, Run 11).

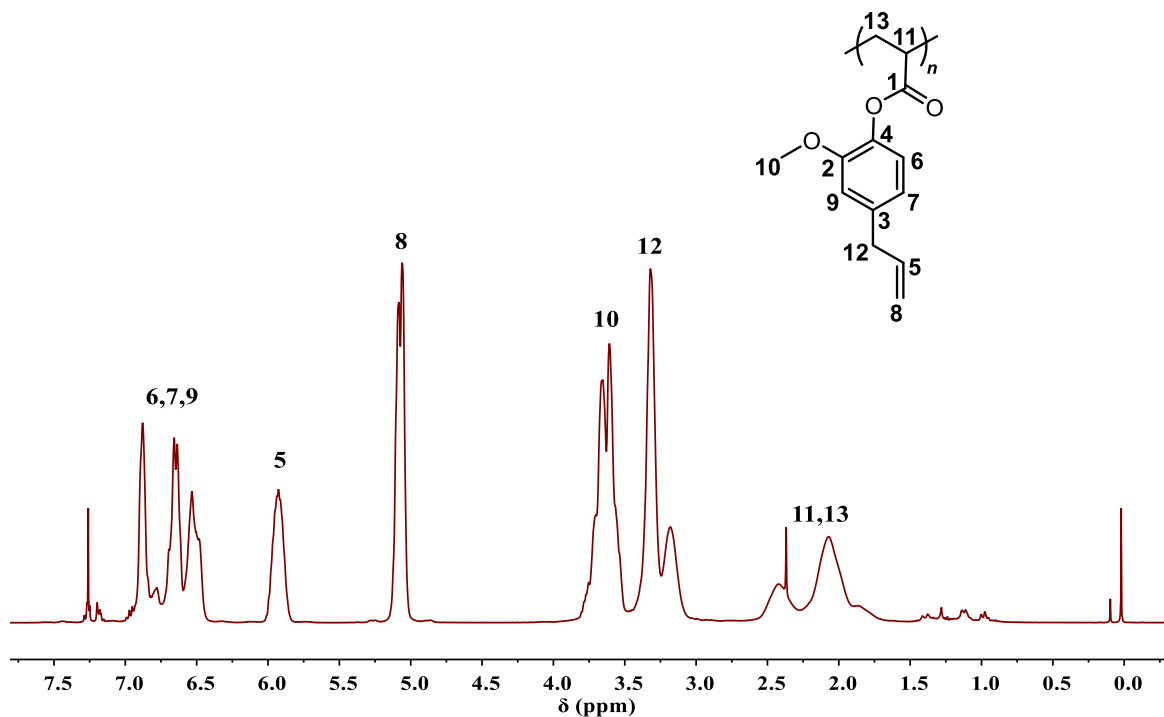


Figure S15. ¹H NMR spectrum (CDCl₃, RT) of P4aGA (Table 1, Run 13).

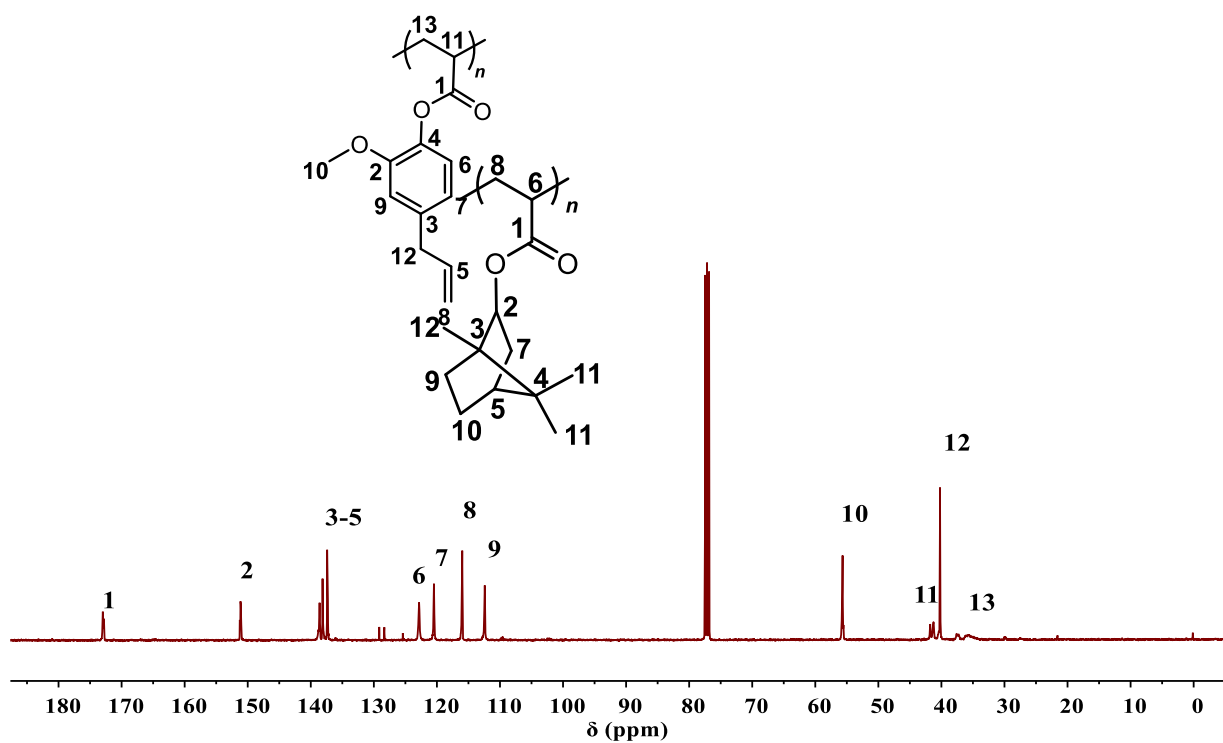


Figure S16. ¹³C NMR spectrum (CDCl₃, RT) of P4pGA (Table 1, Run 13).

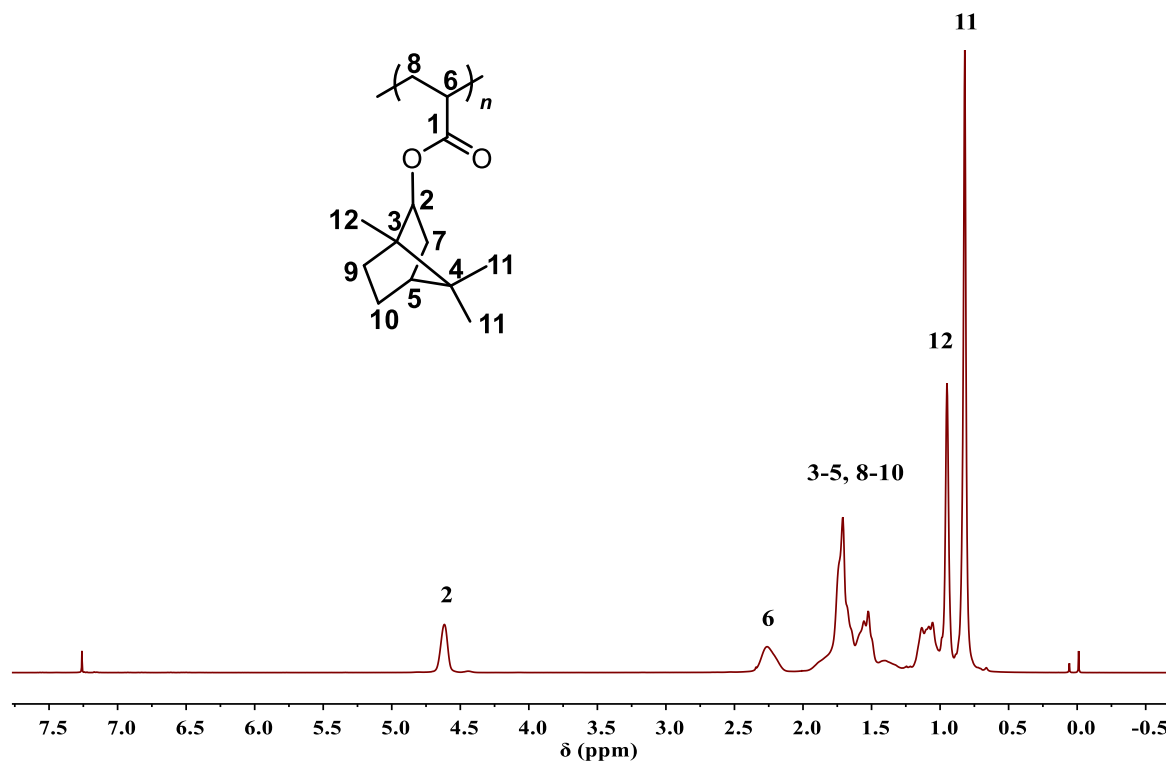


Figure S17. ¹H NMR spectrum (CDCl₃, RT) of PIBOA (Table 1, Run 17).

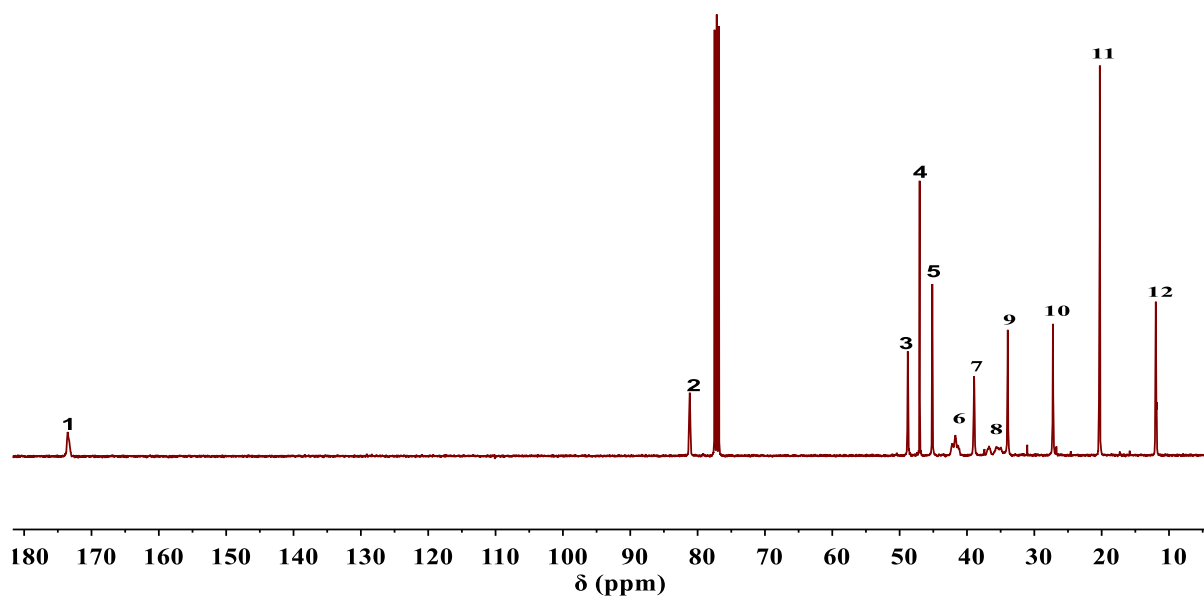


Figure S18. ¹³C NMR spectrum (CDCl₃, RT) of PIBOA (Table 1, Run 17).

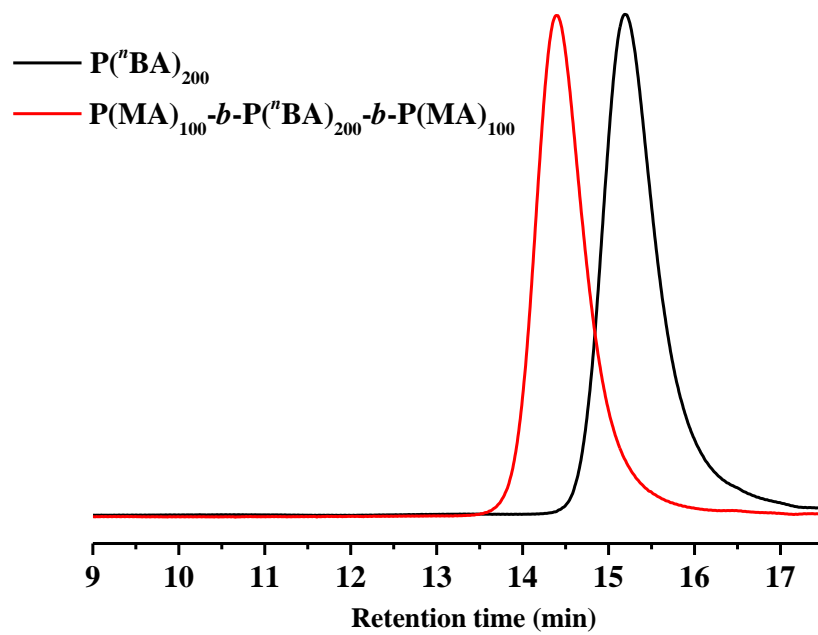


Figure S19. GPC curves of PⁿBA homopolymer ($M_n = 30.2$ kg/mol, $D = 1.09$), and PMA-*b*-PⁿBA-*b*-PMA triblock copolymer ($M_n = 38.4$ kg/mol, $D = 1.09$).