Electronic Supplementary Material (ESI) for Polymer Chemistry.


# Electronic Supplementary Information

# Synthesis and click chemistry of a new class of biodegradable polylactide towards tunable thermo-responsive biomaterials

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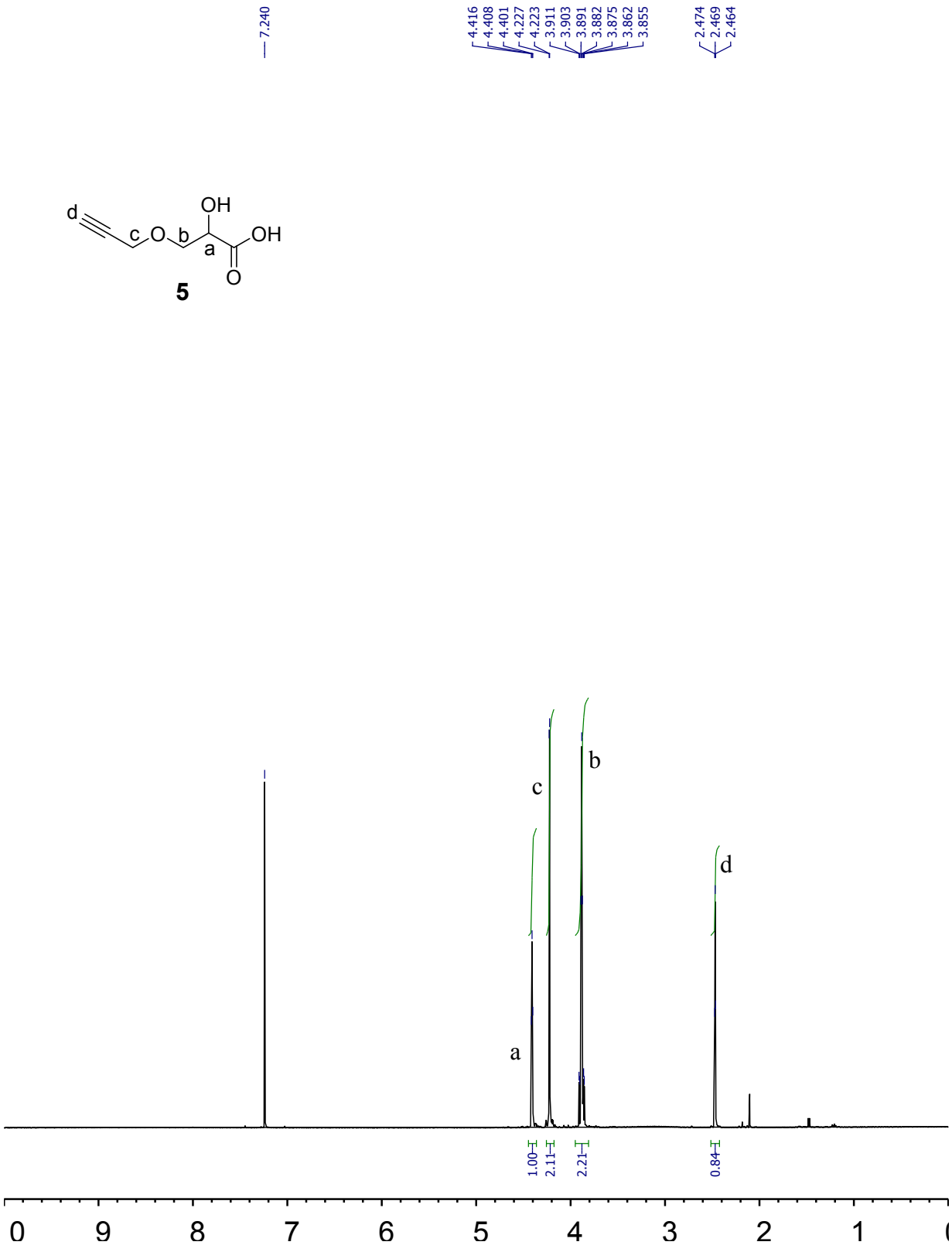



**Fig. S1** $^{1}$H NMR spectrum of **5** ($CDCl_3$, 500 MHz).

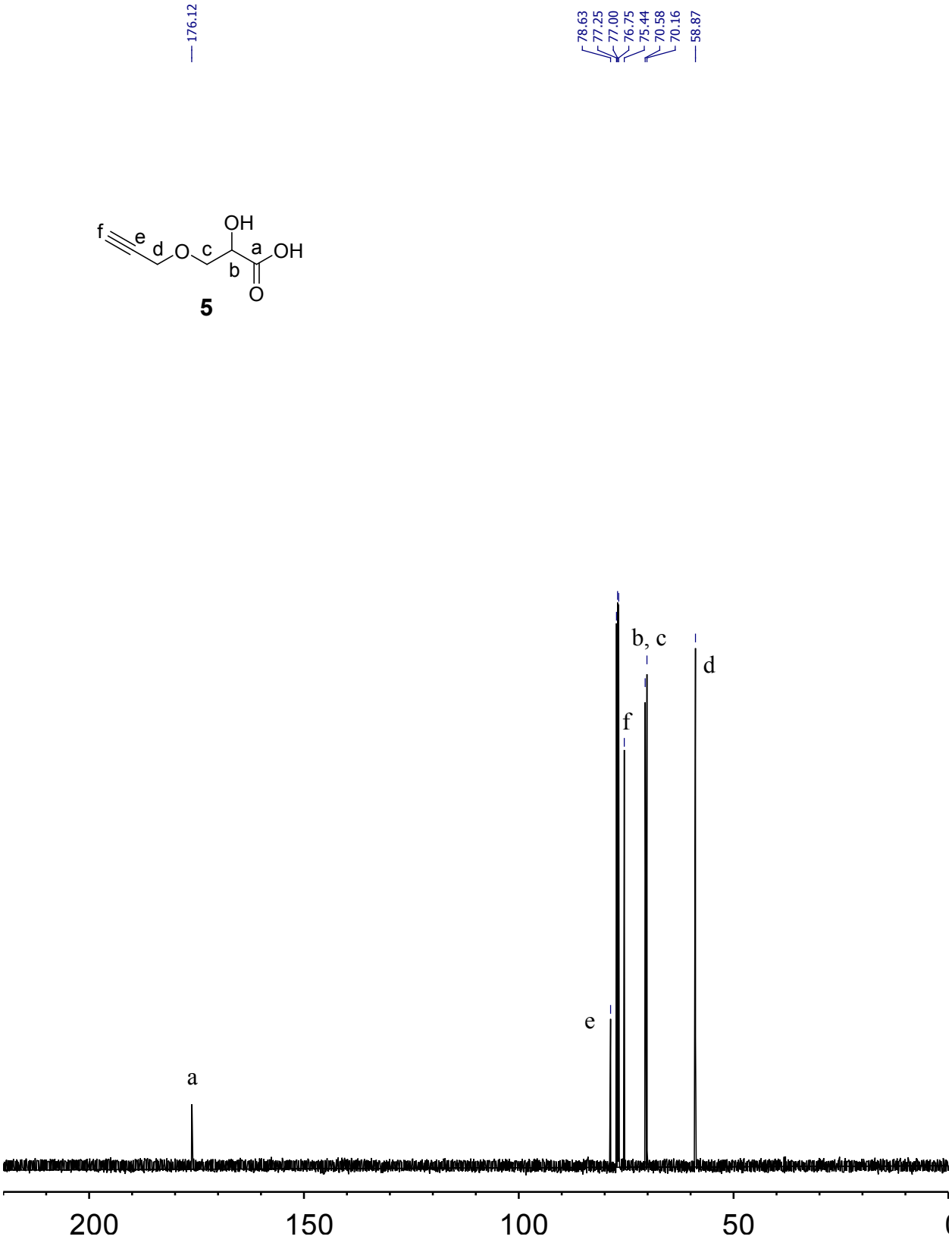



**Fig. S2** $^{13}C$ NMR spectrum of **5** ($CDCl_3$, 125 MHz).

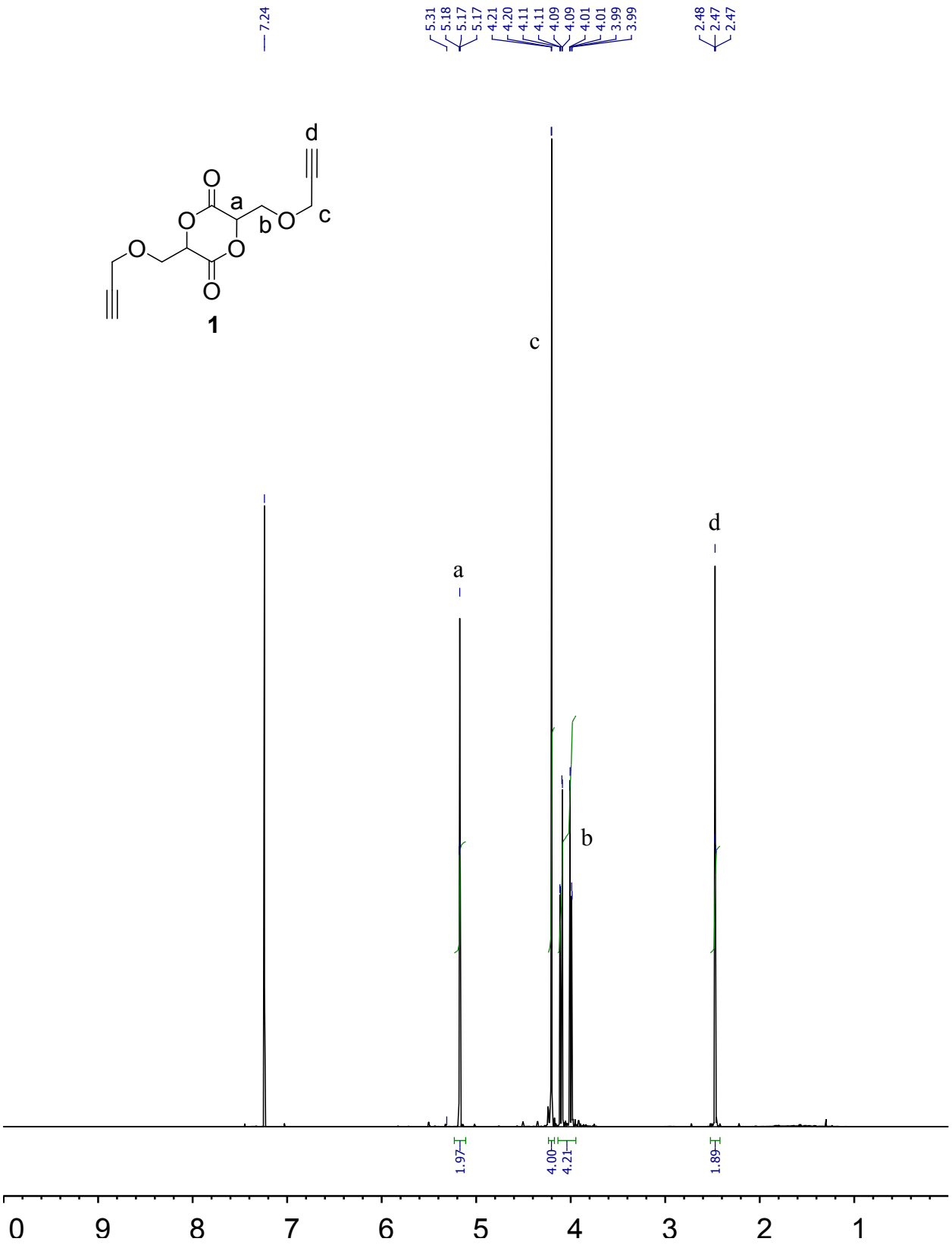



**Fig. S3** $^{1}$H NMR spectra of monomer **1** ($CDCl_3$, 500 MHz).

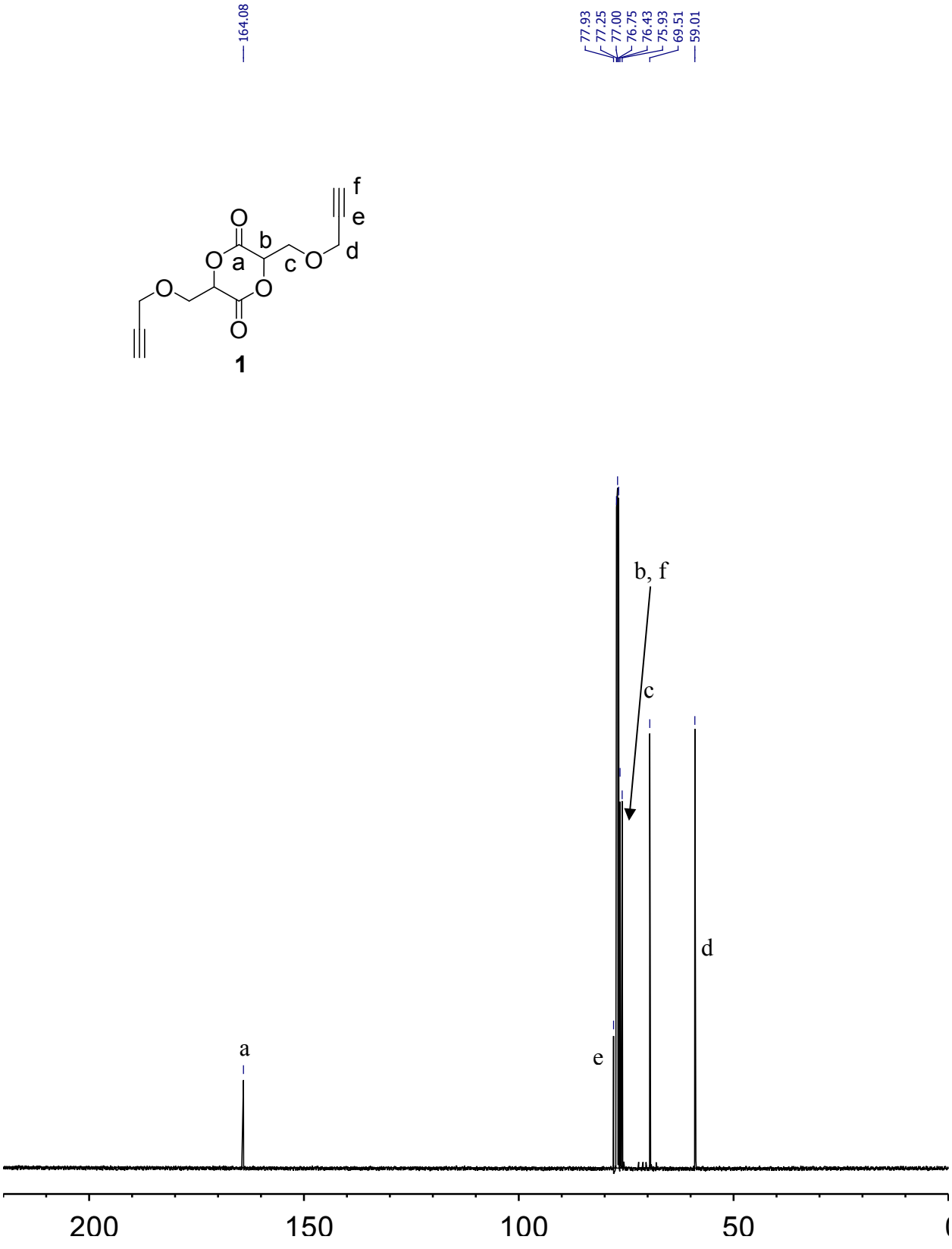



**Fig. S4** $^{13}C$ NMR spectra of monomer **1** ($CDCl_3$, 125 MHz).

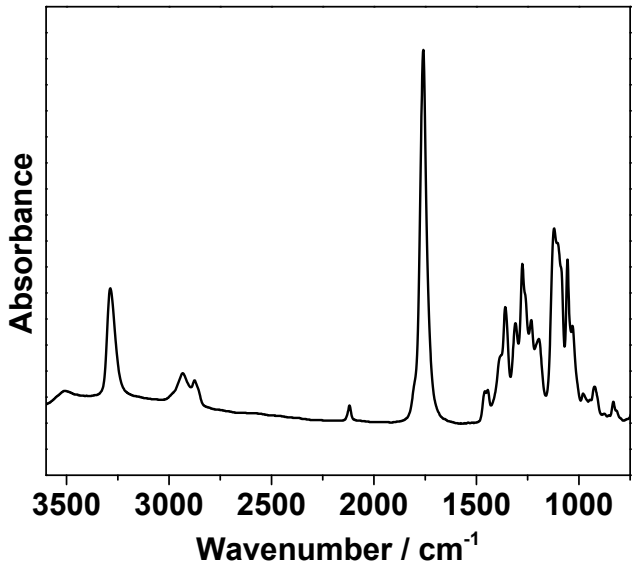



**Fig. S5** FT-IR spectrum of monomer **1**.

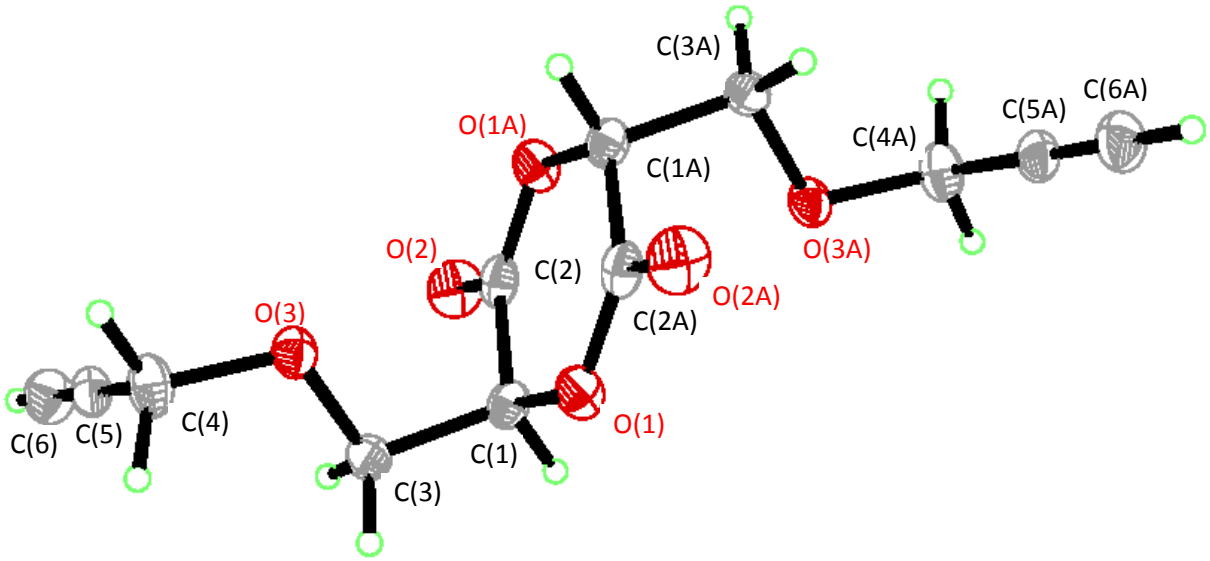



**Fig. S6** Molecular drawing of **1** with 50% thermal ellipsoids from X-ray crystallography.

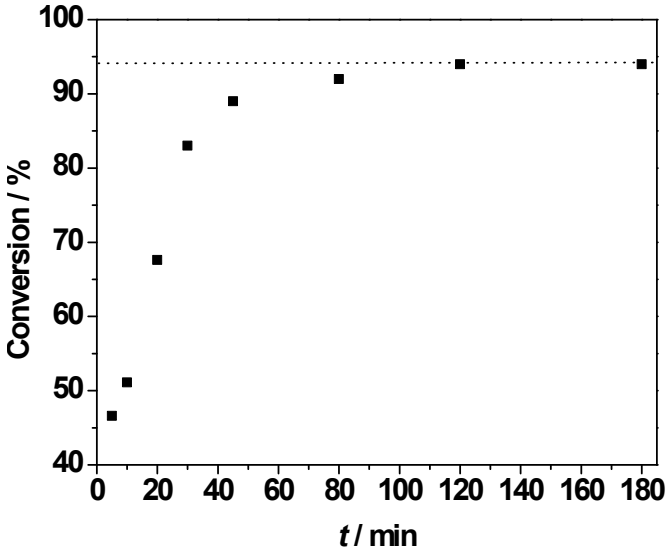
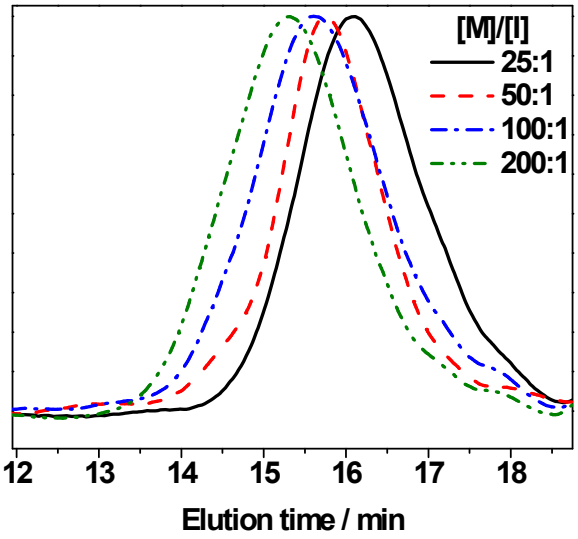



**Fig. S7** Percent conversion for the bulk polymerization of **1**. Conditions: 130 °C, [**1**]:[$Sn(Oct)_2$]:[TBBA] = 50:1:1.




| [M]/[I] | 25 | 50 | 100 | 200 |
|---|---|---|---|---|
| $M_n$ (g/mol, GPC) | 9900 | 10100 | 11400 | 17200 |
| PDI | 1.48 | 1.46 | 1.55 | 1.60 |

**Fig. S8** GPC curves of polymers **P1** from bulk polymerization of **1** with different [M]/[I] ratios (130 °C).

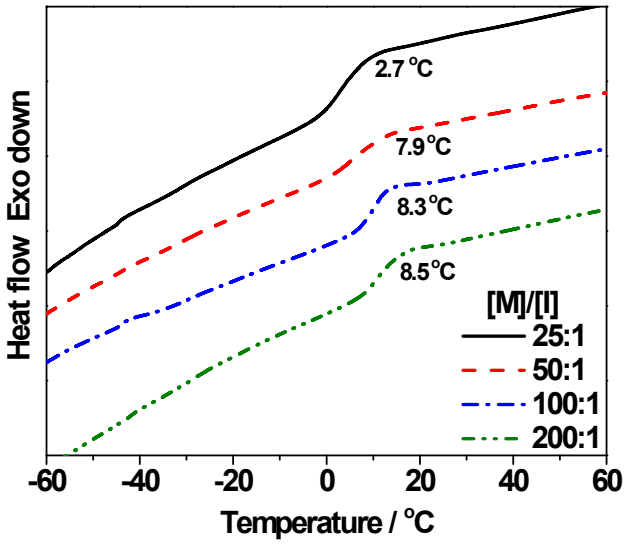
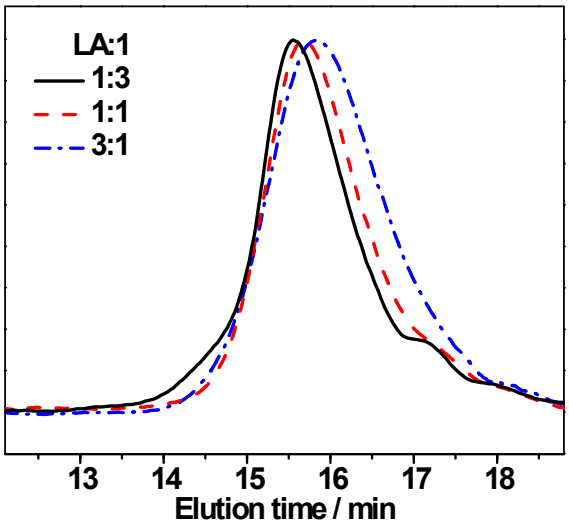



**Fig. S9** DSC traces of homopolymers (**P1**) from bulk polymerization of **1** with different [M]/[I] ratios. (second heating scans, 10 °C/min in $N_2$)




| Ratio of **LA:1** | 1:3 | 1:1 | 3:1 |
|---|---|---|---|
| $M_n$ (g/mol, GPC) | 12300 | 10200 | 8900 |
| PDI | 1.41 | 1.45 | 1.53 |

**Fig. S10** GPC curves of copolymers **P(1-*co*-LA)** from bulk polymerization of **1** and **LA** with different feed ratios of **1** to **LA** ([M]/[I] = 100, 130 °C).

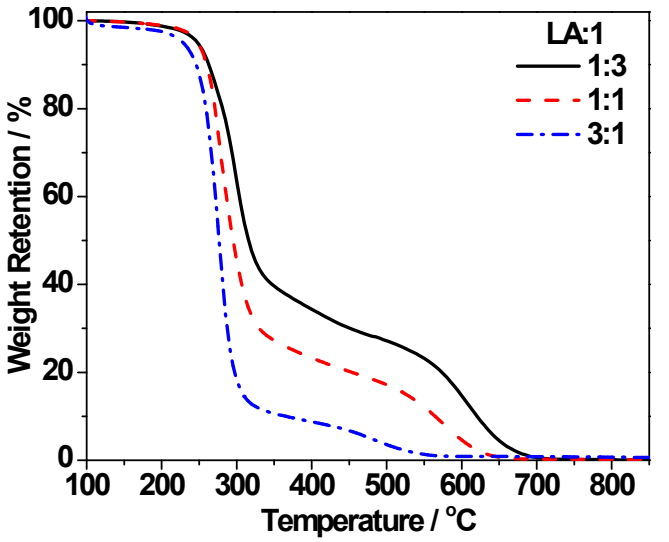



**Fig. S11** TGA curves of **P(1-*co*-LA)** with different feed ratios of **LA** to **1**. Conditions: 130 °C, [**M**]:[$Sn(Oct)_2$]:[TBBA] = 100:1:1.

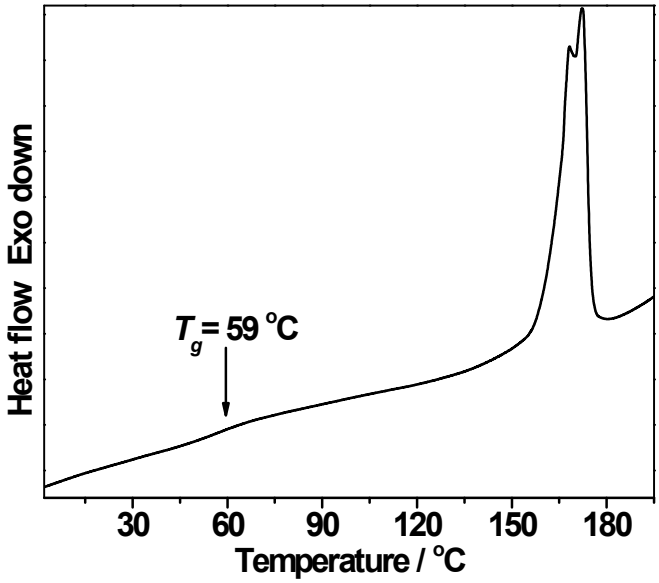



**Fig. S12** DSC trace of PLLA. (second heating scan, 10 °C/min in $N_2$)

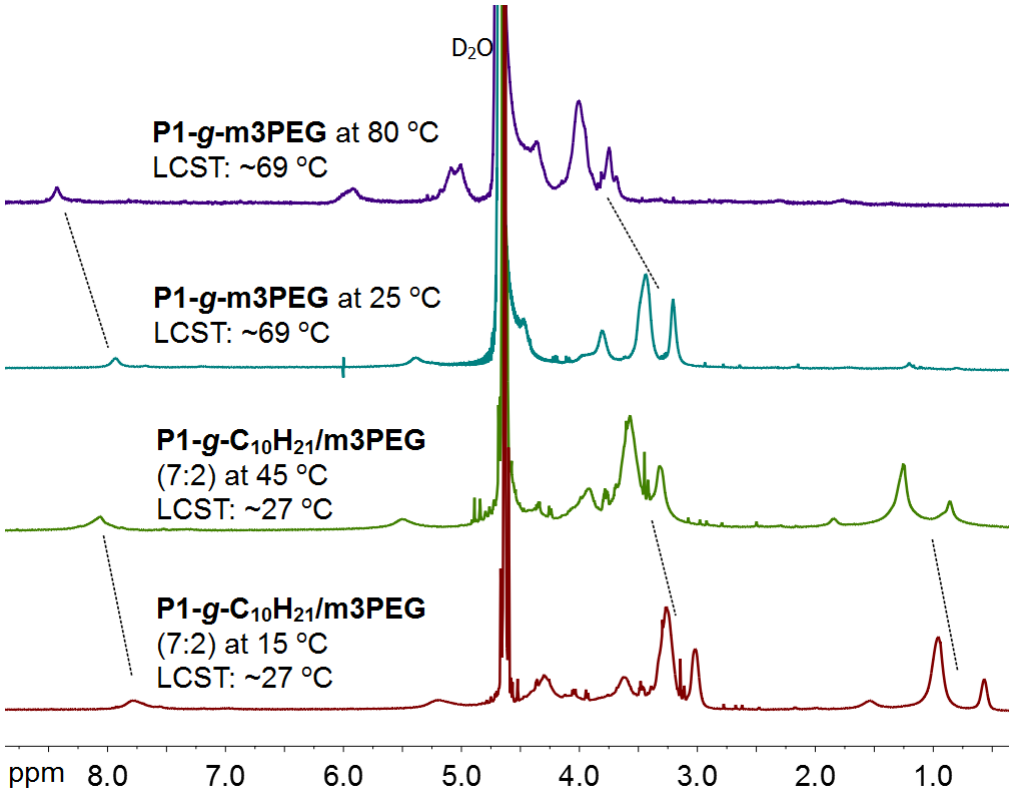



**Fig. S13** 500 MHz $^1$H NMR spectra of **P1-*g*-m3PEG** and **P1-*g*-$C_{10}H_{21}$/m3PEG** (7 : 2 feed ratio of m3PEG$N_3$ : $C_{10}H_{21}N_3$) at temperatures below and above their LCST. Solvent: $D_2O$. The broken line denotes the significant changes of chemical shifts.

**Table S1** Bulk polymerization data of monomer **1** at different conversions[a]

| Time/min | Conversion[b] | $M_n$ (g/mol, GPC)[c] | PDI[c] | $X_n$[d] | $X_{n,\ theoretical}$[e] |
|---|---|---|---|---|---|
| 5 | 46.6% | 8300 | 1.15 | 29 | 24 |
| 10 | 51.1% | 8600 | 1.18 | 32 | 26 |
| 20 | 67.9% | 9200 | 1.20 | 37 | 34 |
| 30 | 83% | 10300 | 1.50 | 43 | 41 |

[a] Using $Sn(Oct)_2$ as a catalyst and TBBA as an initiator at 130 °C. [b] Measured by $^1$H NMR. [c] Measured by GPC in THF. [d] Determined from $^1$H NMR using end group analysis. [e] Calculated from [M]/[I] and corrected for conversion.