

Table S1. PMMA₃₀-OH initiated ring opening of lactide to prepare of PMMA-b-PLA copolymer^[a]

Run	Samples	Feed ^[b]	$M_{n\ th}(DA)^{[c]}$	$M_{n\ GPC}^{[d]}$	PDI	Conv.(%)	T_g
1	PMMA ₃₀ -OH	/	3347	3022	1.32	-	90
2	PMMA ₃₀ -b-PLA ₂₀	10	4787	4981	1.28	100	68
3	PMMA ₃₀ -b-PLA ₁₀₀	50	10547	11130	1.35	100	58
4	PMMA ₃₀ -b-PLA ₁₄₀	70	13427	14110	1.46	100	50

^[a] CH₂Cl₂ 2 mL, 25 °C, run 2, [LA]/DBU = 10:1, run 3, [LA]/DBU = 50:1, run 4, [LA]/DBU = 70:1, ^[b] Feeding ratio of [LA]/[OH], ^[c] $M_{n\ th} = ([LA]/[OH])_{Feed} \times M_{n\ LA} \times \text{conversion}(\%) + M_{n\ PMMA30-OH}$, where $M_{n\ LA}$ is the molecular weight of LA and $M_{n\ PMMA30-OH}$ is the molecular weight of $M_{n\ PMMA30-OH}$. ^[d] Determined by GPC against the standard monodispersed PMMA samples.

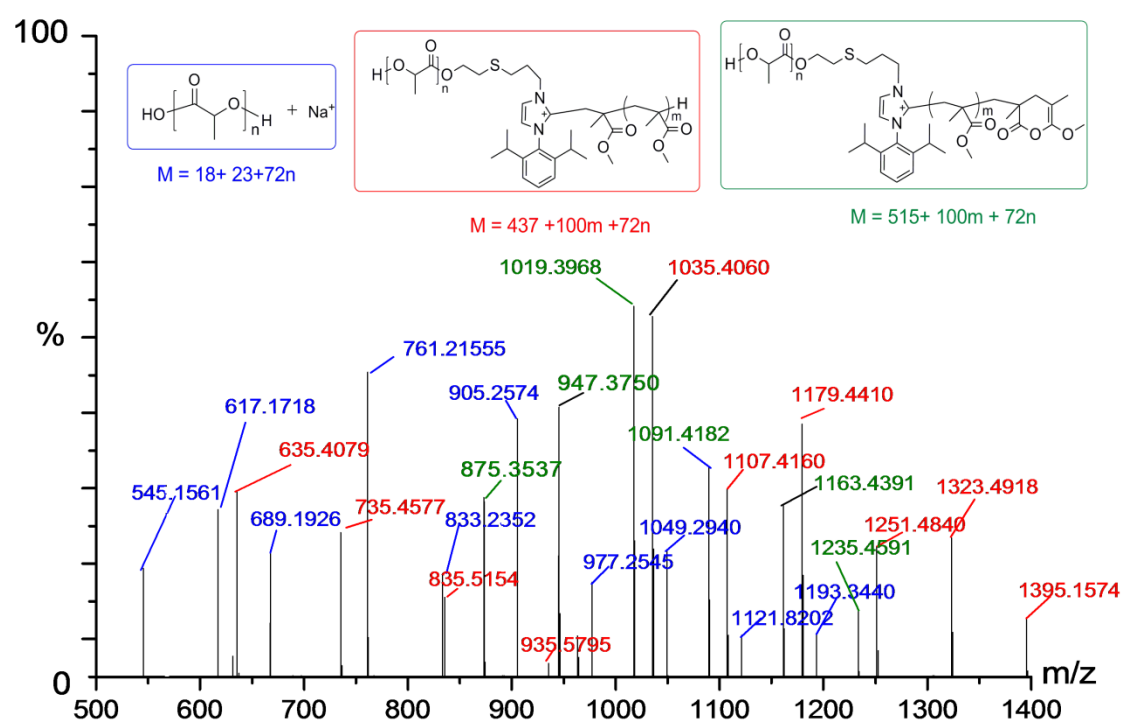


Figure S1. ESI-TOF MS spectrum of PMMA-b-PLA copolymer

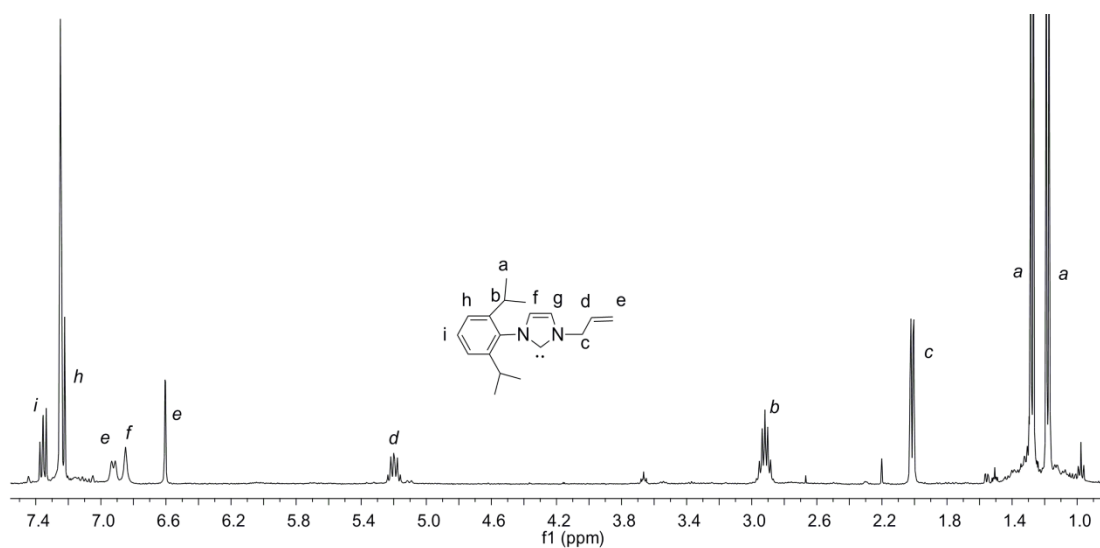


Figure S2. ¹H NMR spectrum of compound 3

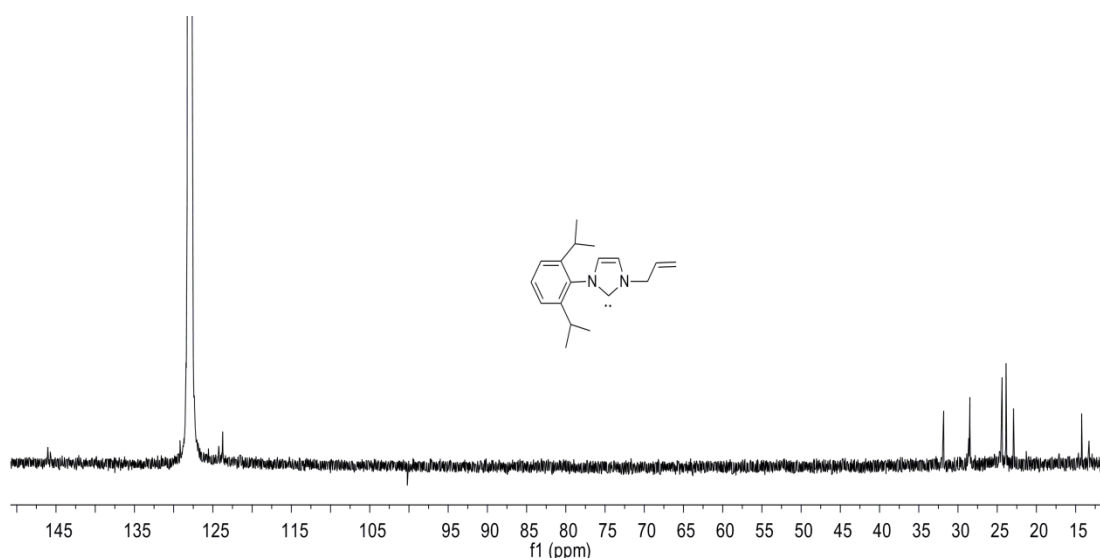


Figure S3. ¹³C NMR spectrum of compound 3

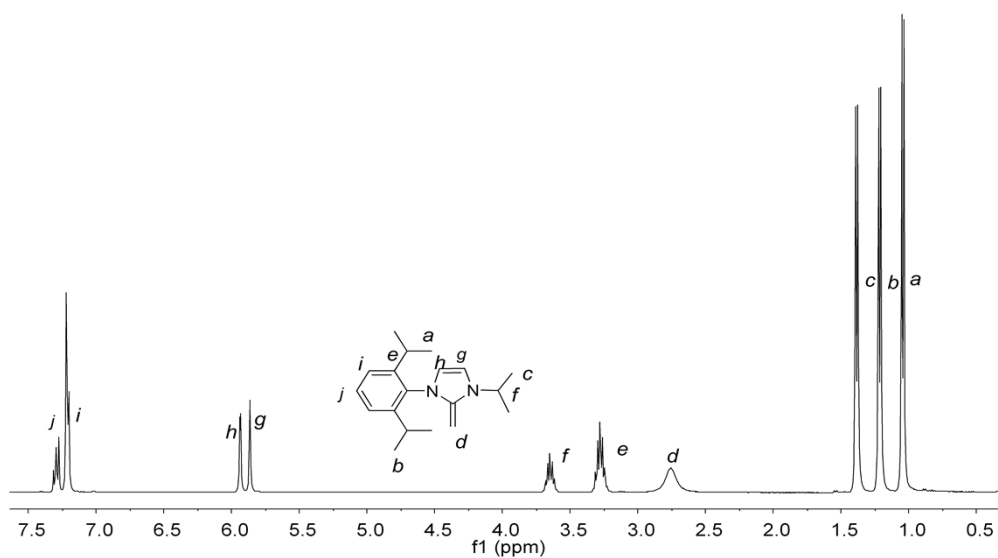


Figure S4. ¹H NMR spectrum of NHO

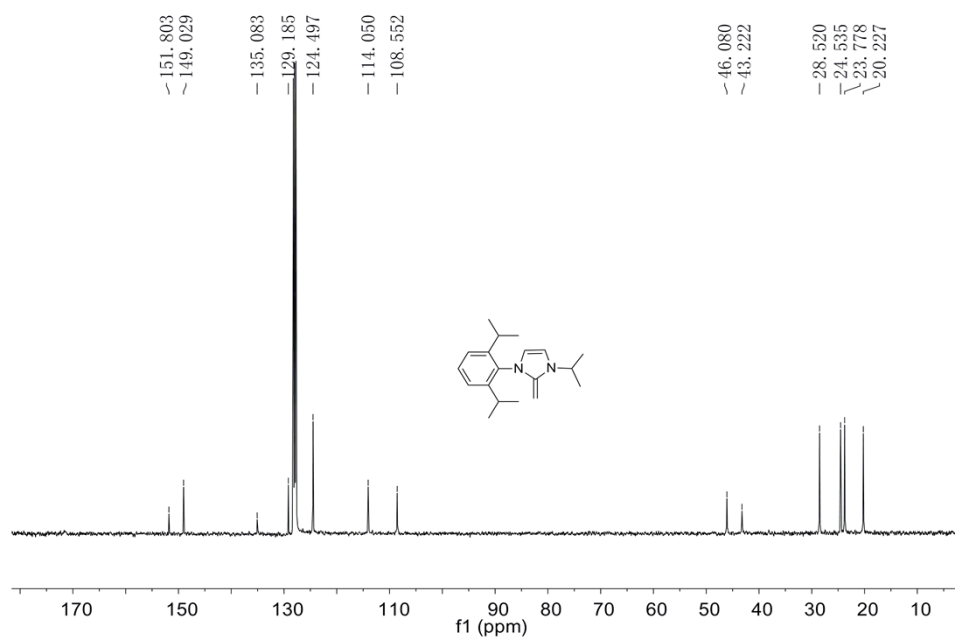


Figure S5. ¹³C NMR spectrum of NHO