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Supporting Information

(Bipyridine bisphenolate)-aluminum/onium salt pair: A highly active binary catalysts for ringopening polymerization of lactide with improved thermostability and protic tolerance

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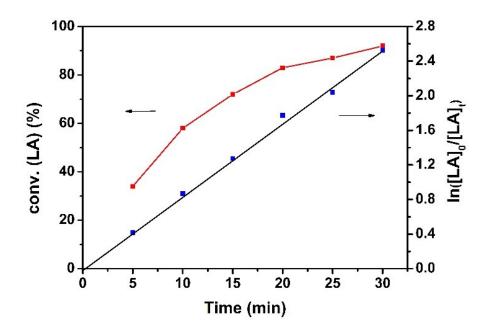


Figure S1. The polymerization kinetic plot for ring-opening polymerization.

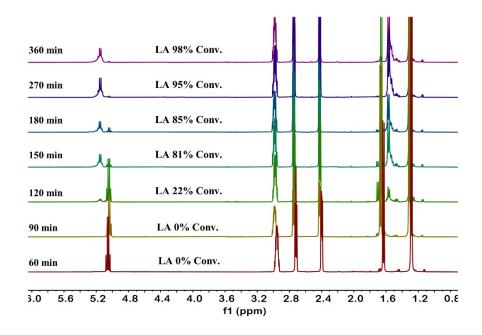


Figure S2. The ¹H NMR spectra of the LA polymerization mixture by using PPNCl as catalyst.

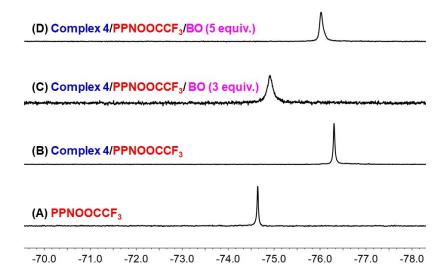


Figure S3. The *in situ* ¹⁹F NMR spectra of the cocatalyst (**A**), Al/cocatalyst pair (**B**), Al/cocatalyst/BO and Al/cocatalyst/BO (C and D).

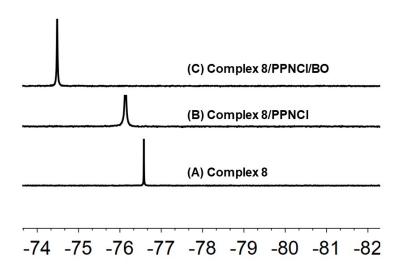


Figure S4. The ¹⁹F NMR spectra for the complex **8** (A), complex **8**/PPNCl (molar ratio =1:1) and complex **8**/PPNCl/BO mixtures (1:1:3).

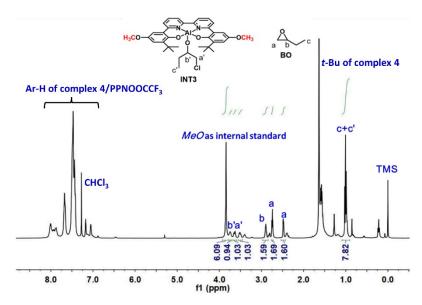


Figure S5. ¹H NMR peak assignments of complex 4/PPNOOCCF₃ combination with BO (molar ratio=1:1:3).

Table S1. Selected chemical shifts corresponding to the representative signal for alkoxides and their integral analysis (data were extracted from figure S4).

Compound	Representative peaks	δ (ppm)	Integral
DO.	a (<i>CH2</i> CH-O)	2.77-2.72	3.29
		2.53-2.43	
ВО	b (СН2 <i>СН</i> -О)	2.98-2.84	1.59
	c (<i>CH3</i> CH2-)	1.13-0.90	4.80
INT3A	<i>CH3</i> O-Ar	3.93-3.79	6.09
	a' (<i>CH2</i> CH-O)	3.68-3.59	2.06
		3.56-3.45	
	b' (CH2 <i>CH</i> -O)	3.77-3.70	0.94
	c'(<i>CH3</i> CH2-)	1.13-0.90	3.00

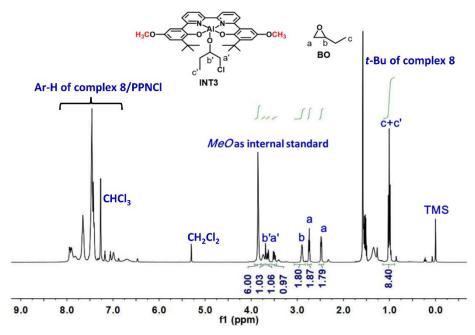


Figure S6. ¹H NMR peak assignments of complex **8**/PPNCl combination with BO (molar ratio=1:1:3).

Table S2. Selected chemical shifts corresponding to the representative signal for alkoxides and their integral analysis (data were extracted from figure S5).

Compound	Representative peaks	δ (ppm)	Integral
ВО	a (<i>CH2</i> CH-O)	2.77-2.72	3.66
		2.53-2.43	
DU	b (CH2 <i>CH</i> -O)	1.13-0.90	1.80
	c (<i>CH3</i> CH2-)	1.13-0.90	5.40
	<i>CH3</i> O-Ar	3.93-3.79	6.00
	a' (<i>CH2</i> CH-O)	3.68-3.59	2.03
INT3A		3.56-3.45	
	b' (CH2 <i>CH</i> -O)	3.77-3.70	1.03
	c' (<i>CH3</i> CH2-)	1.13-0.90	3.00

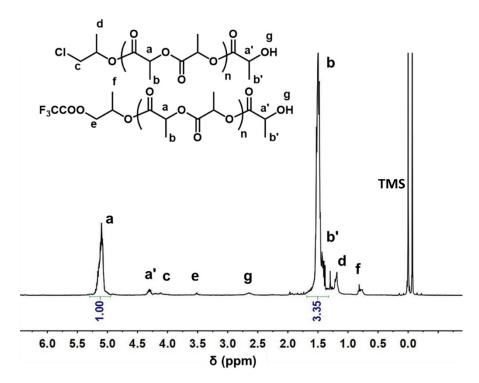


Figure S7. The ¹H NMR spectrum of the PLA obtained by **8**/PPNCl.

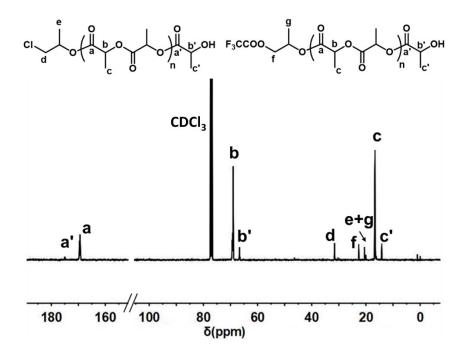


Figure S8. The ¹³C NMR spectrum of the PLA obtained by 8/PPNCl.

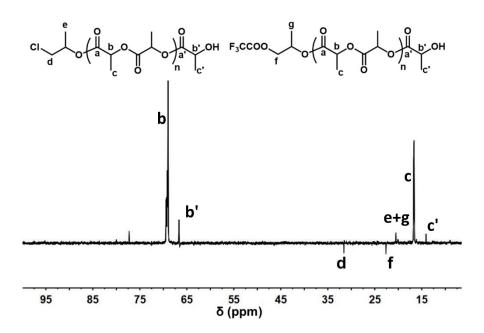


Figure S9. The DEPT(135) spectrum of the PLA obtained by 8/PPNCl.

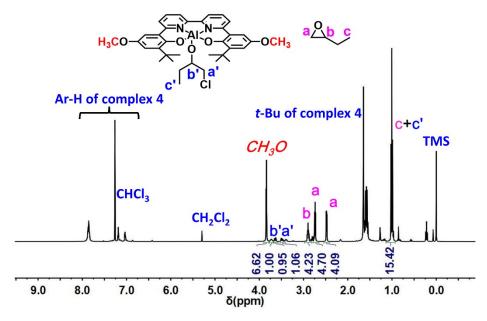


Figure S10. ¹H NMR peak assignments of complex 4 combination with BO (molar ratio=1:5).