Supporting Information

Living ring-opening homo- and copolymerization of *ε*-caprolactone and *L*-lactide by cyclic β-ketiminato aluminum complexes

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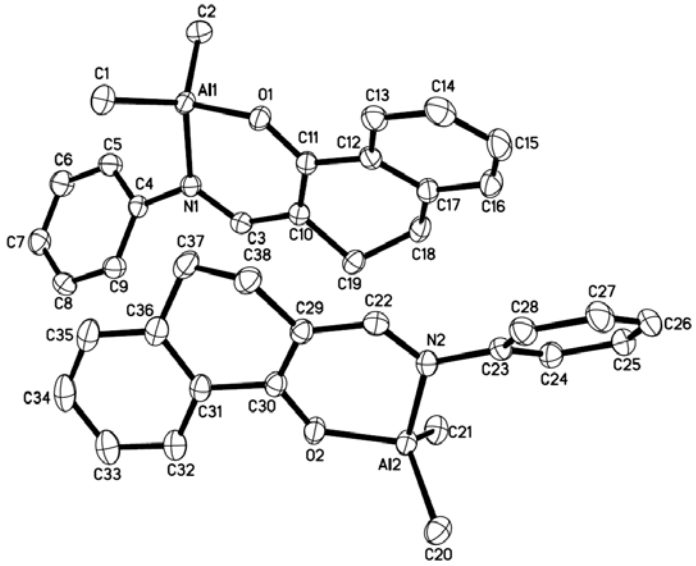

Fig. S1 Molecular structure of complex **3b** with thermal ellipsoids at 30% probability level. Hydrogen atoms are omitted for clarity.

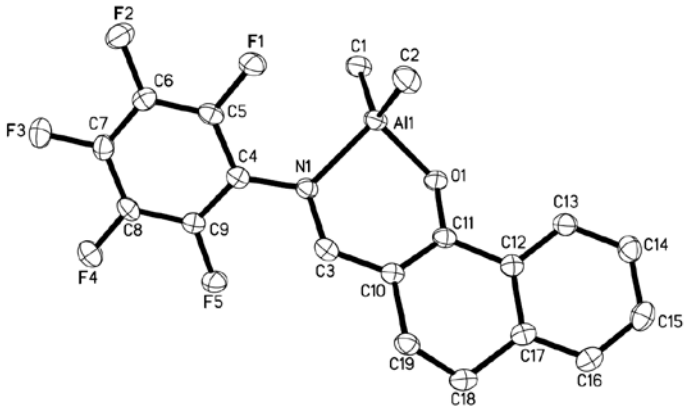

Fig. S2 Molecular structure of complex **3c** with thermal ellipsoids at 30% probability level. Hydrogen atoms are omitted for clarity.

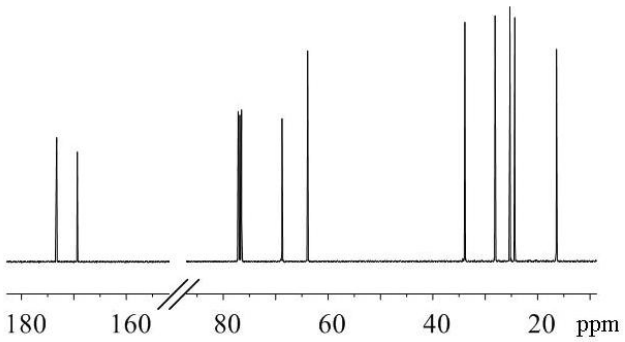

Fig. S3 ^{13}C NMR spectrum of PCL-*b*-PLLA copolymer by catalyst **3a** (entry 1, Table 3).

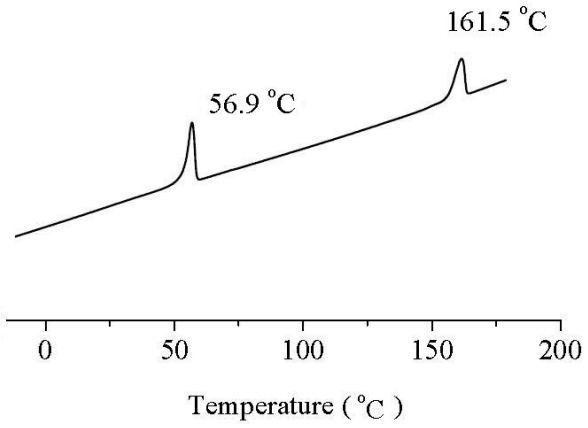

Fig. S4 DSC curve of PCL-*b*-PLLA copolymer by catalyst **3a** (entry 1, Table 3).

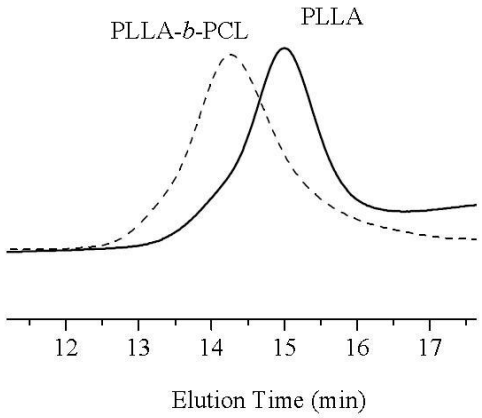

Fig. S5 GPC curves of PLLA and PLLA-*b*-PCL prepared by catalyst **3c**.

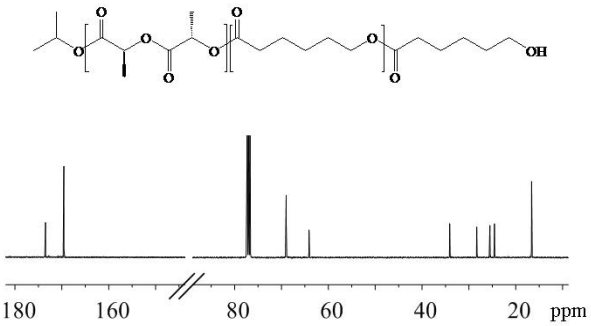

Fig. S6 ^{13}C NMR spectrum of PLLA-*b*-PCL copolymer by catalyst **3c** (entry 2, Table 3).

Table S1. Crystal data and structure refinements of complexes **3a-c.**

	3a	**3b**	**3c**
Empirical formula	$C_{25}H_{32}AlNO$	$C_{19}H_{20}AlNO$	$C_{19}H_{15}AlF_5NO$
Formula weight	389.50	305.34	395.30
Crystal system	monoclinic	triclinic	monoclinic
Space group	P2(1)/c	P-1	P2(1)/c
a (Å)	9.8106(8)	9.1373(5)	7.9649(7)
b (Å)	14.5843(12)	14.8039(8)	15.0918(13)
c (Å)	17.0062(13)	14.8329(8)	15.0663(13)
α (°)	90.00	117.5840(10)	90.00
β (°)	104.4090(10)	94.5200(10)	102.838(2)
γ (°)	90.00	104.3280(10)	90.00
V (Å^3), Z	2356.7(3), 4	1678.77(16), 4	1765.8(3), 4
$Density_{calcd}$ (Mg/m^3)	1.098	1.208	1.487
Absorption coefficient (mm^{-1})	0.100	0.122	0.174
F(000)	840	648	808
Crystal size/mm	0.30 ×0.16×0.08	0.33×0.25×0.18	0.31×0.23×0.14
θ range for data collection (°)	1.87 to 26.03	1.59 to 26.03	1.93 to 25.04
Reflections collected	13004	9262	10242
Independent reflections	4614 (R_{int}= 0.0303)	6483 (R_{int}= 0.0217)	3110 (R_{int}= 0.0439)
Data/restraints/ parameters	4614/0/259	6483/0/401	3110 /0/246
Goodness-of-fit on F^2	1.027	1.022	1.015
Final R indices [I>2σ (I)]: R1, wR2	0.0495, 0.1138	0.0552, 0.1200	0.0446, 0.0976
Largest diff. Peak and hole (e Å^{-3})	0.337 and -0.180	0.276 and -0.214	0.234 and -0.208