Supplementary Material (ESI) for Dalton Transactions

Electronic Supplementary Information

Amidinate Aluminum Complexes: Synthesis, Characterization and Ring-Opening Polymerization of *rac*-Lactide

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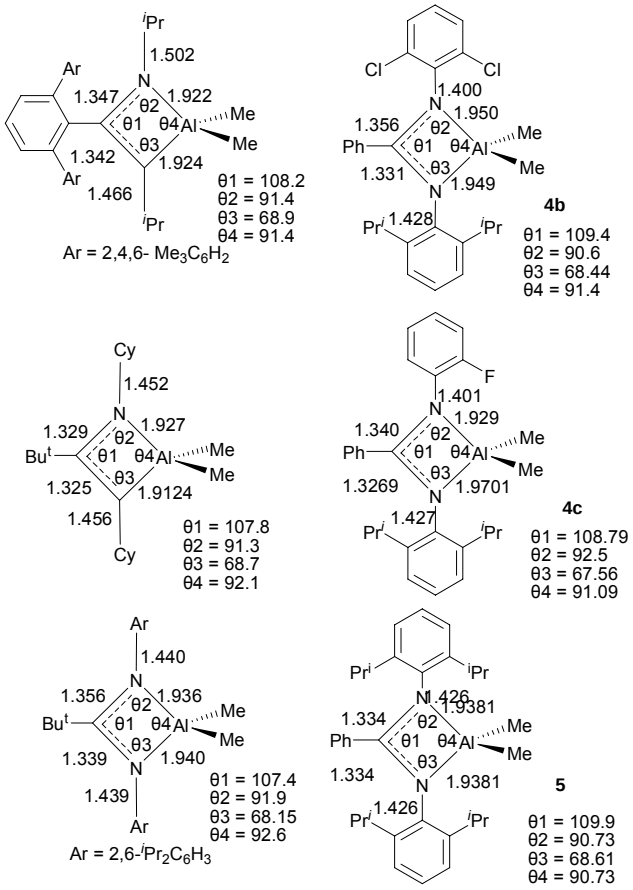


Figure S1. Schematic presentation of the core structures of amidinate aluminum complexes (angles (°), bond length (Å)).

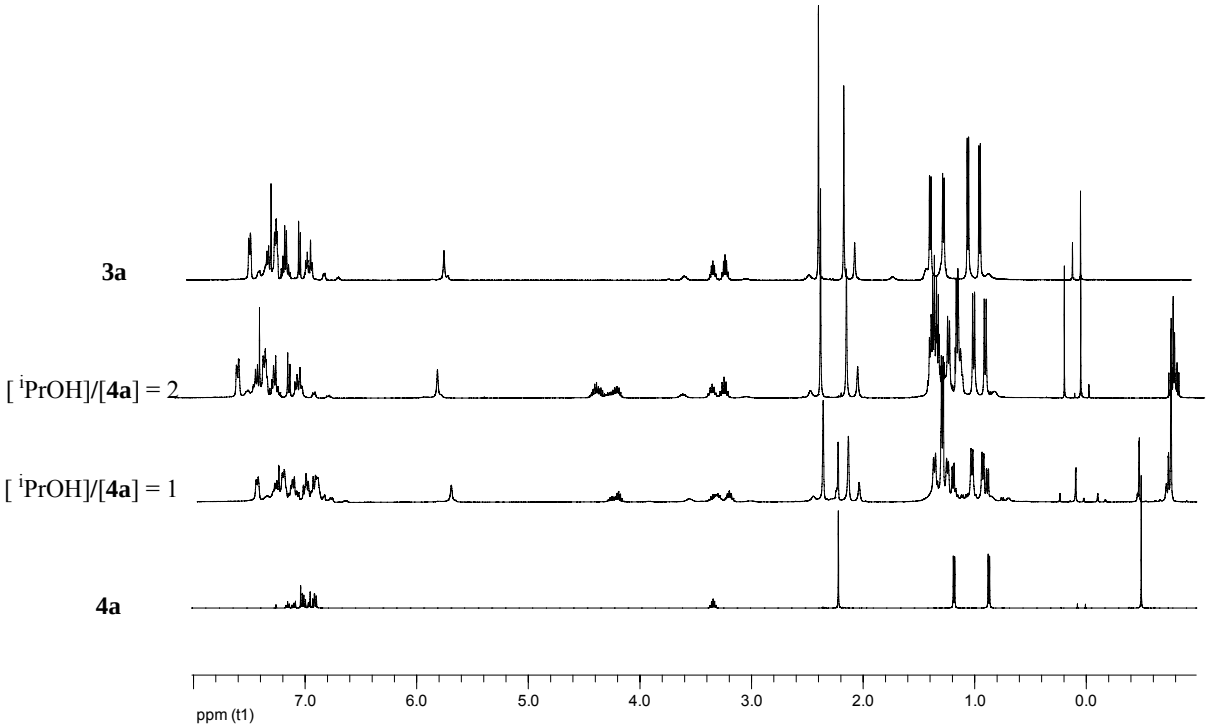


Figure S2. The ^{1}H NMR spectra of ligand **3a**, complex **4a** and complex **4a** with isopropanol ($CDCl_3$, 400 MHz).

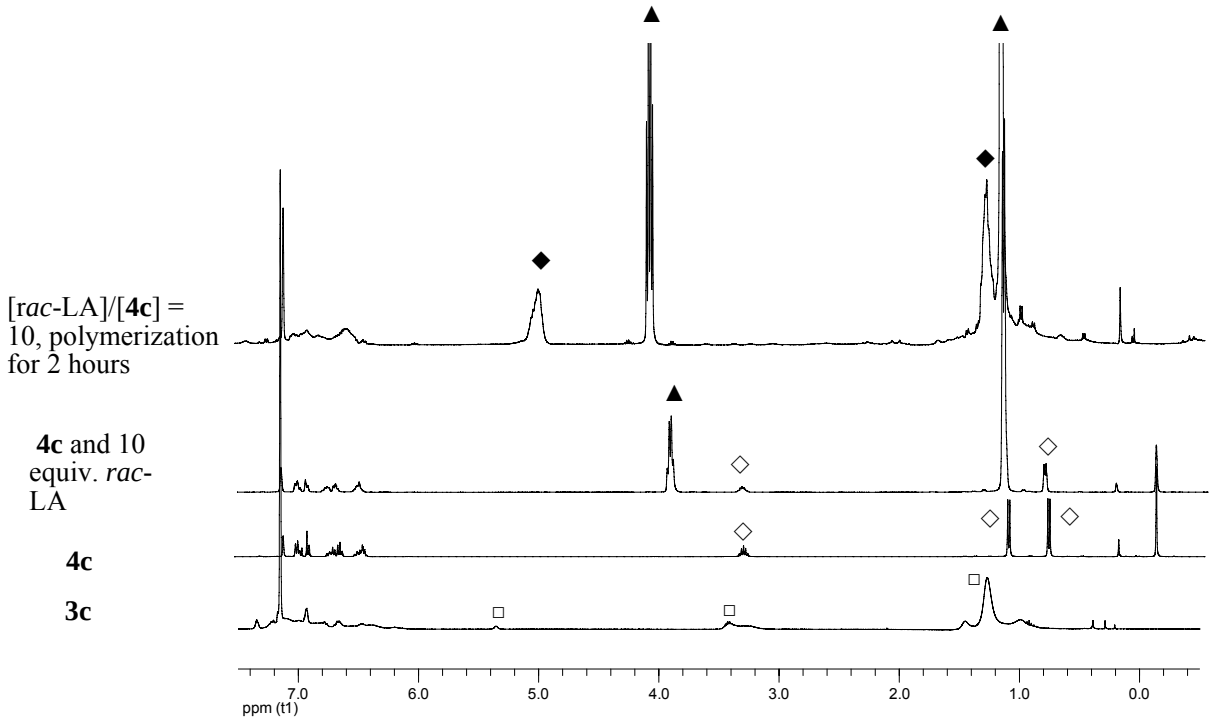


Figure S3. ^{1}H NMR spectra of *rac*-LA polymerization initiated by complex **4c** ($[rac\text{-LA}]_0/[Al]_0$ = 10, 70 °C, in C_6D_6) (□: The proton signals of ligand **3c**, ◇: The proton signals of complex **4c**, ▲: The proton signals of *rac*-lactide, ◆: The proton signals of poly-lactide).

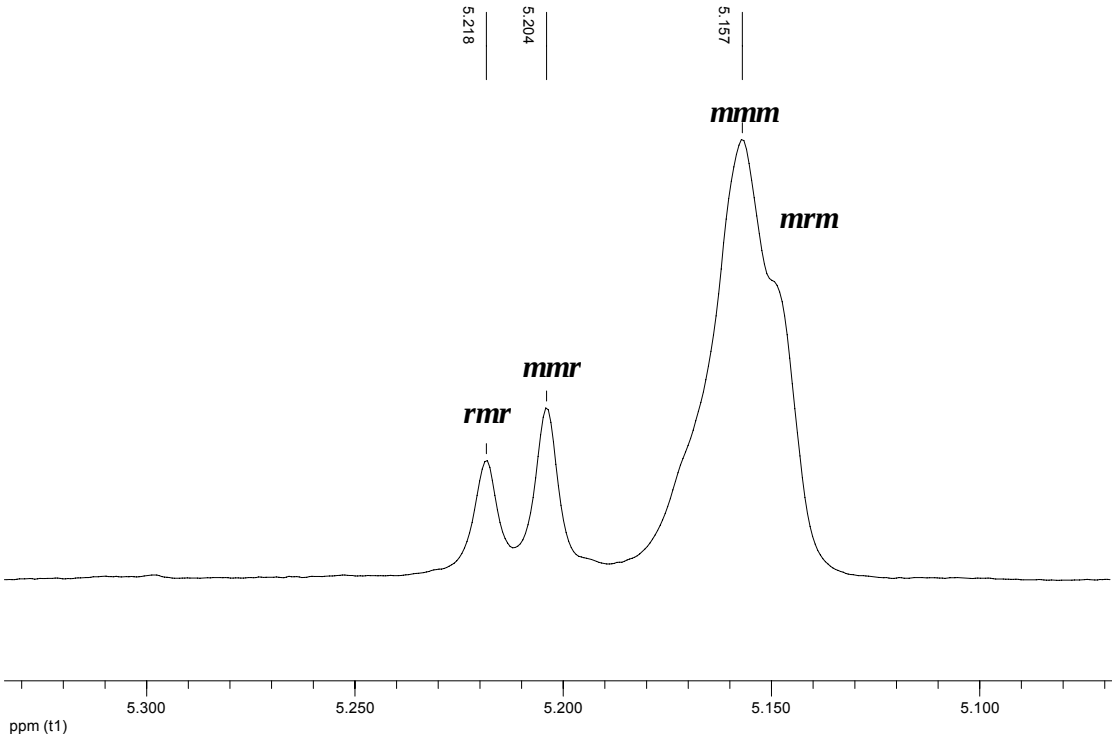
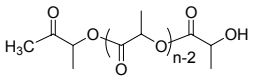
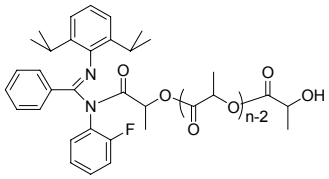


Figure S4. Homonuclear decoupled ^{1}H NMR spectrum of the methine region of PLA prepared with **4a**/*rac*-lactide at 70 °C for 12 h (500 MHz, $CDCl_3$).

= 16.05 + 72.07n



△ = 374.49 + 72.07n



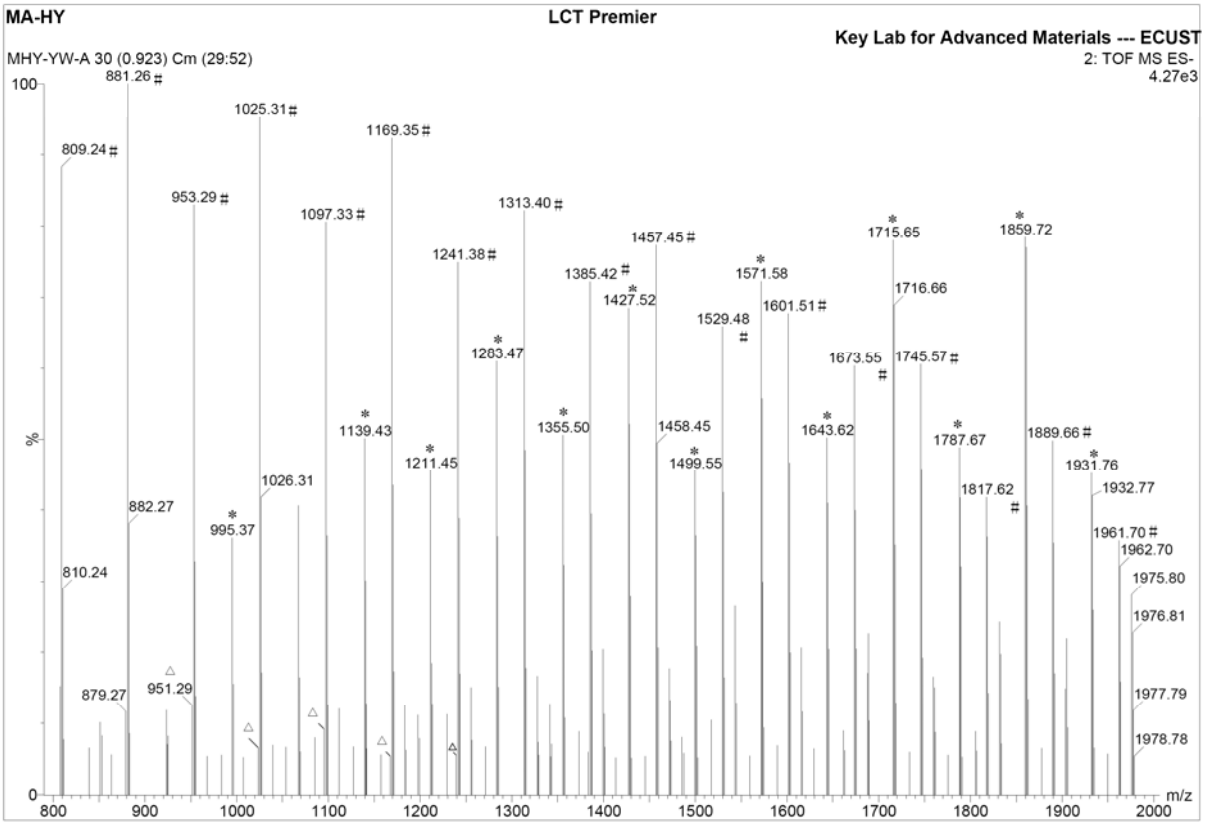


Figure S5. ESI-TOF mass spectrum of *rac*-lactide oligomer obtained with complex **4c** (in toluene at 70 °C, $[rac\text{-LA}]_0/[Al]_0 = 10$, $[rac\text{-LA}]_0 = 1$ mol/L).[a]

[a]: Currently, we have no reasonable explanation for the series marked with *, which correspond to oligomers end-caped with certain group having mass of 58 + 72.07m.

Table S1. The crystal data and structure refinement for complexes **4b**, **4c** and **5**

	4b	**4c**	**5**
Empirical formula	$C_{27}H_{31}AlCl_2N_2$	$C_{27}H_{32}AlFN_2$	$C_{33}H_{45}AlN_2$
Formula weight	481.42	430.53	496.69
Crystal size/mm	0.27 × 0.25 × 0.20	0.39 × 0.37 × 0.32	0.30 × 0.26 × 0.22
Crystal system	Monoclinic	Triclinic	Trigonal
Space group	C2/c	P-1	P3(2)21
a/Å	24.771(4)	9.005(7)	14.948 (8)
b/Å	14.720(2)	10.674(8)	14.948 (8)
c/Å	17.004(2)	14.0804(11)	12.2099(10)
α/°	90	69.3390(10)	90
ß/°	118.966(3)	83.1210(10)	90
γ/°	90	83.9360(10)	120
Volume/Å^3	5424.8(13)	1254.22(17)	2362.8(3)
Z	8	2	3
Calcd density (Mg/m^3)	1.179	1.140	1.047
Absorp coeff/mm^{-1}	0.288	0.104	0.086
F(000)	2032	460	810
θ range for data collection (°)	1.88 to 25.50	2.04 to 27.00	1.57 to 26.49
Limiting indices	$-29 \le h \le 28$	$-11 \le h \le 11$	$-18 \le h \le 16$
	$-15 \le k \le 17$	$-8 \le k \le 13$	$-18 \le k \le 18$
	$-20 \le l \le 19$	$-17 \le l \le 17$	$-15 \le l \le 15$
No. of reflns collected/unique	13973/5054	7464/5331	13607/3273
	(R_{int} = 0.1262)	(R_{int} = 0.0330)	(R_{int} = 0.0519)
Data/retrains/parameters	5054/0/296	5331/0/286	3273/0/170
Goodness-of-fit on F^2	0.842	1.019	1.118
Final *R* indices[I >2σ(I)]	R_1 = 0.0628	R_1 = 0.0511	R_1 = 0.0550
	wR_2 = 0.1218	wR_2 = 0.1349	wR_2 = 0.1186
R indices (all data)	R_1 = 0.1676	R_1 = 0.0676	R_1 = 0.0619
	wR_2 = 0.1488	wR_2 = 0.1444	wR_2 = 0.1219
Largest diff. peak and hole/e Å^{-3}	0.242 and –0.247	0.324 and –0.185	0.332 and –0.160

Table S2. The selected bond lengths (Å) and bond angles (°) for complex **5**

Al–N1	1.9381(18)	Al–C18	1.945(3)
C1–N1	1.334(2)	N1–C6	1.426(2)
N1–Al–N1*	68.61(9)	Al–N1–C1	90.73(13)
N1–C1–N1*	109.9(2)	C2–C1–Al	179.999(1)
N1–Al–C18	113.34(10)	N1–Al–C18*	118.24(11)

Table S3. The selected bond lengths (Å) and bond angles (°) for complexes **4b** and **4c**

	4b	**4c**
Al–N1	1.949(4)	1.9701(14)
Al–N2	1.950(4)	1.9290(14)
N1–C1	1.331(5)	1.3269(19)
N2–C1	1.356(5)	1.340(2)
Al–C26	1.945(5)	1.944(2)
Al–C27	1.937(6)	1.943(2)
N1–C8	1.432(5)	1.427(2)
N2–C20	1.402(5)	1.401(2)
F···Al	––	2.794
N1–Al–N2	68.44(15)	67.56(6)
Al–N1–C1	91.4(3)	91.09(10)
Al–N2–C1	90.6(3)	92.50(10)
Al–N1–C8	142.4(3)	142.57(10)
Al–N2–C20	142.0(3)	135.85(12)
N1–C1–N2	109.4(4)	108.79(14)
N1–C1–C2	126.1(4)	124.51(14)
N2–C1–C2	124.4(4)	126.62(14)
C2–C1–Al	178.7(3)	175.96(11)
C26–Al–C27	120.4(3)	120.77(11)
Al–N2–C20–C25	–84.8(6)	-17.1(2)
N2–C20–C25–Cl2	–7.7(6)	––
N2–C20–C25–F	––	–1.5(2)