Electronic Supplementary Information

Organoaluminium complexes of *ortho*-, *meta*-, *para*-anisidines: Synthesis, structural studies and ROP of *ε*-caprolactone (and *rac*-lactide).

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Table S1. Screening of the known [1, 2] complexes $Me_2Al[O\text{-}2\text{-}tBu\text{-}6\text{-}(RN{=}CH)C_6H_3]$ (R = *t*Bu (**4**), C_6F_5 (**5**))

Entry	Cat.	CL:X[b]:BnOH	*T*/◦C	*t*/min	m/g	Yield (%)	M_n*10^{-4} [c]	PDI
1	4	250:01:01	50	30	0.00	00.0	N/A	N/A
2	4	250:01:01	60	30	0.00	00.0	N/A	N/A
3	4	250:01:01	60	60	0.27	9.0	1.77	1.22
4	5	250:01:01	50	30	2.25	78.0	3.23	1.23
5	5	250:01:01	60	30	2.71	94.2	3.89	1.53
6	5	250:01:01	60	60	2.73	94.7	5.01	1.89

[a] Conditions: 20 μmol of cat.; 1.0 M *ε*-CL toluene solution. [b] X=Al-anisidine complexes [c] GPC data in THF *vs* polystyrene standards.

References

[1] N. Iwasa, M. Fujiki and K. Nomura, *J. Mol. Cat. A, Chem.,* 2008, **292**, 67.

[2] J. Liu, N. Iwasa and K. Nomura, *Dalton Trans.,* 2008, 3978.

PCL data:

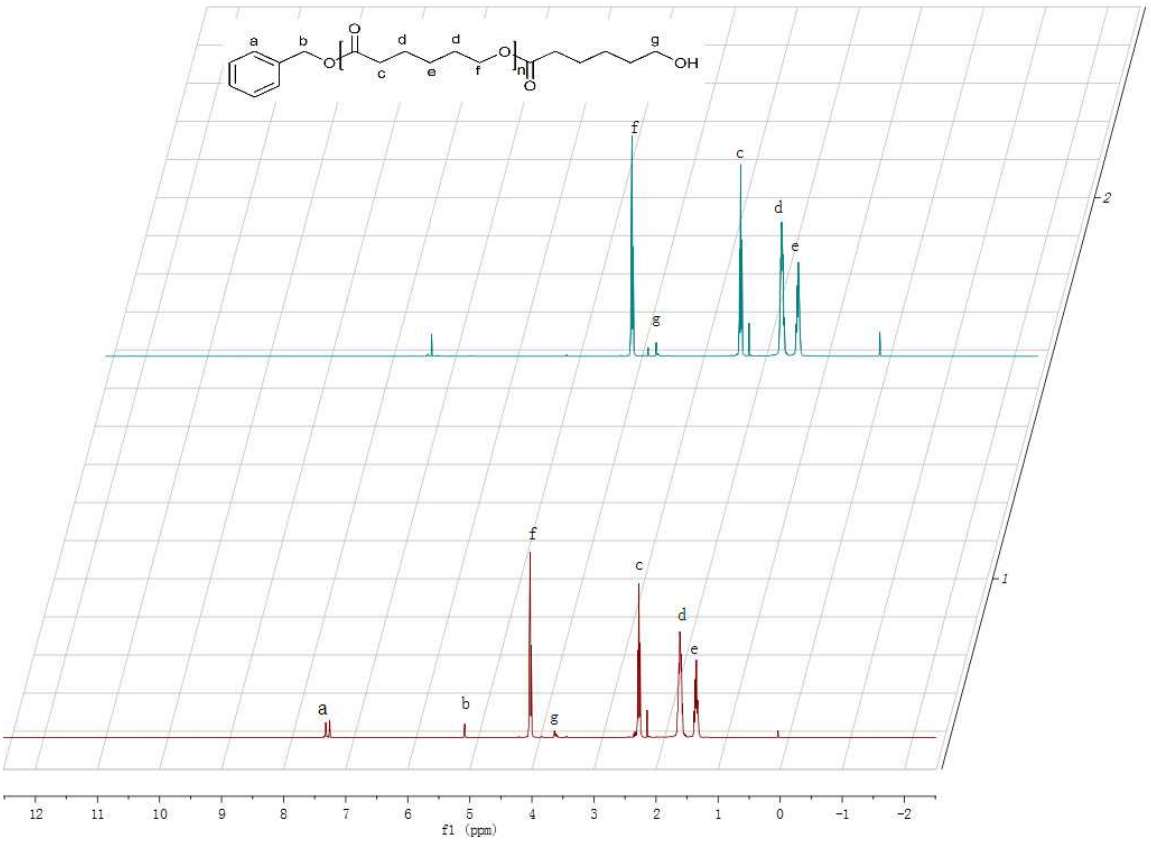

Figure S1. ^{1}H NMR spectrum of PCL in $CDCl_3$ catalyzed by aluminium complexes (1) pre-catalyst **3** with BnOH (Table 2, entry 3); (2) pre- catalyst **1** with BnOH (Table 2, entry 1).

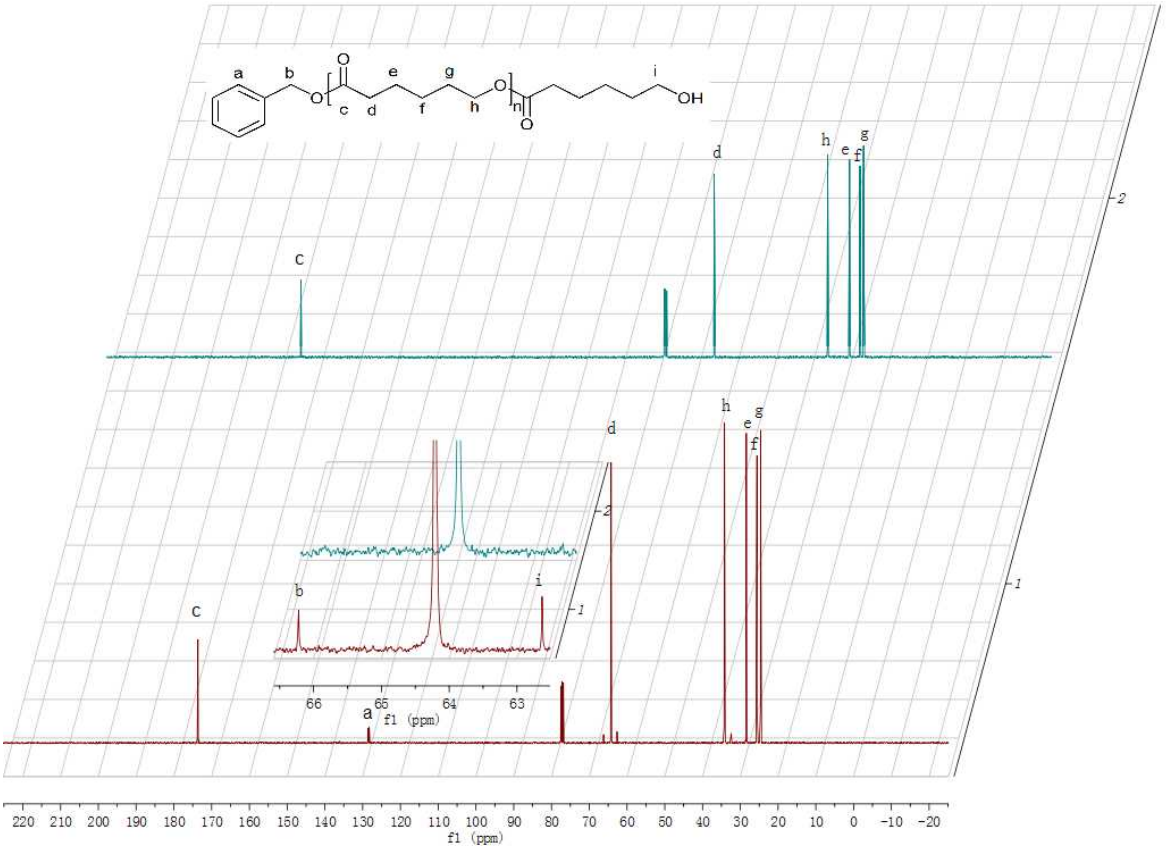

Figure S2. ^{13}C NMR spectrum of PCL in $CDCl_3$ catalyzed by aluminium complexes (1) pre-catalyst **3** with BnOH (Table 2, entry 3); (2) pre- catalyst **1** with BnOH (Table 2, entry 1).

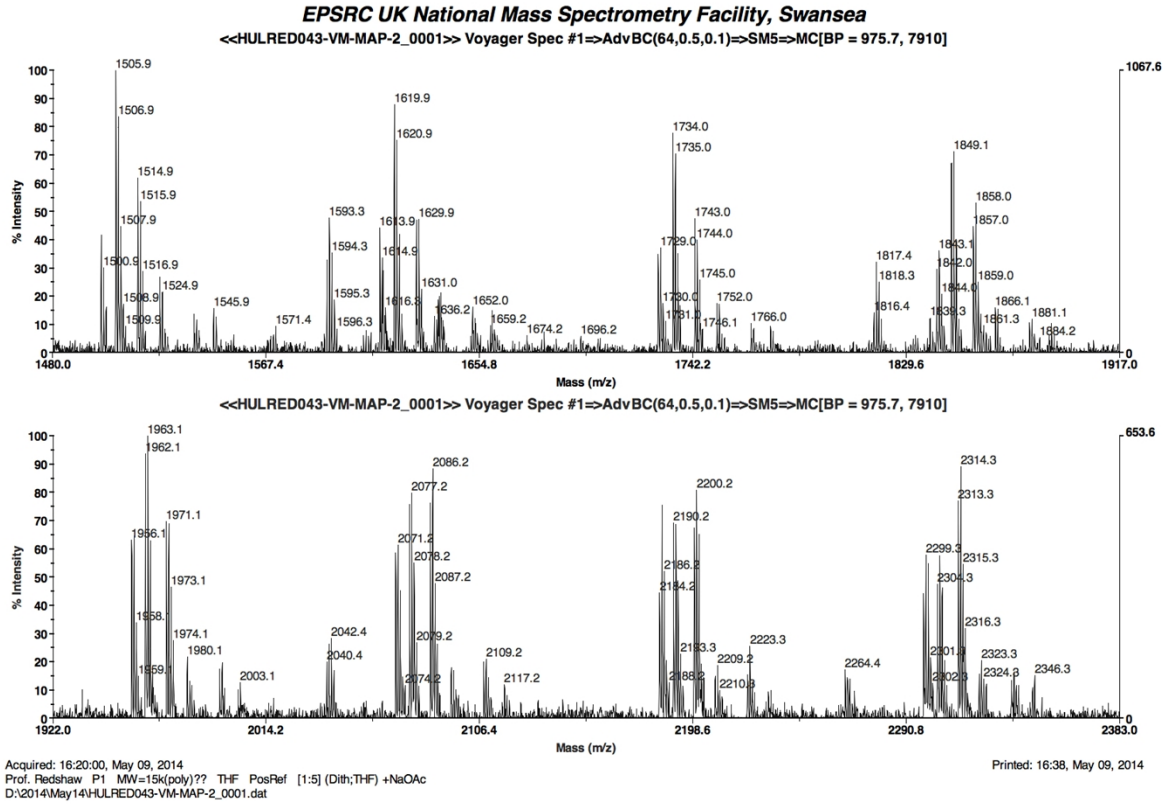

Figure S3. MALDI-TOF mass spectrum of PCL initiated by **1** in toluene at 80 °C, [CL]/[**1**]/[BnOH] = 50:1:1 (Table 2, entry 1). 114.14*n + 1+1 for H-(CL)n-H and 114.14*n + 1 + 22+1 for H-(CL)n-H •Na+.

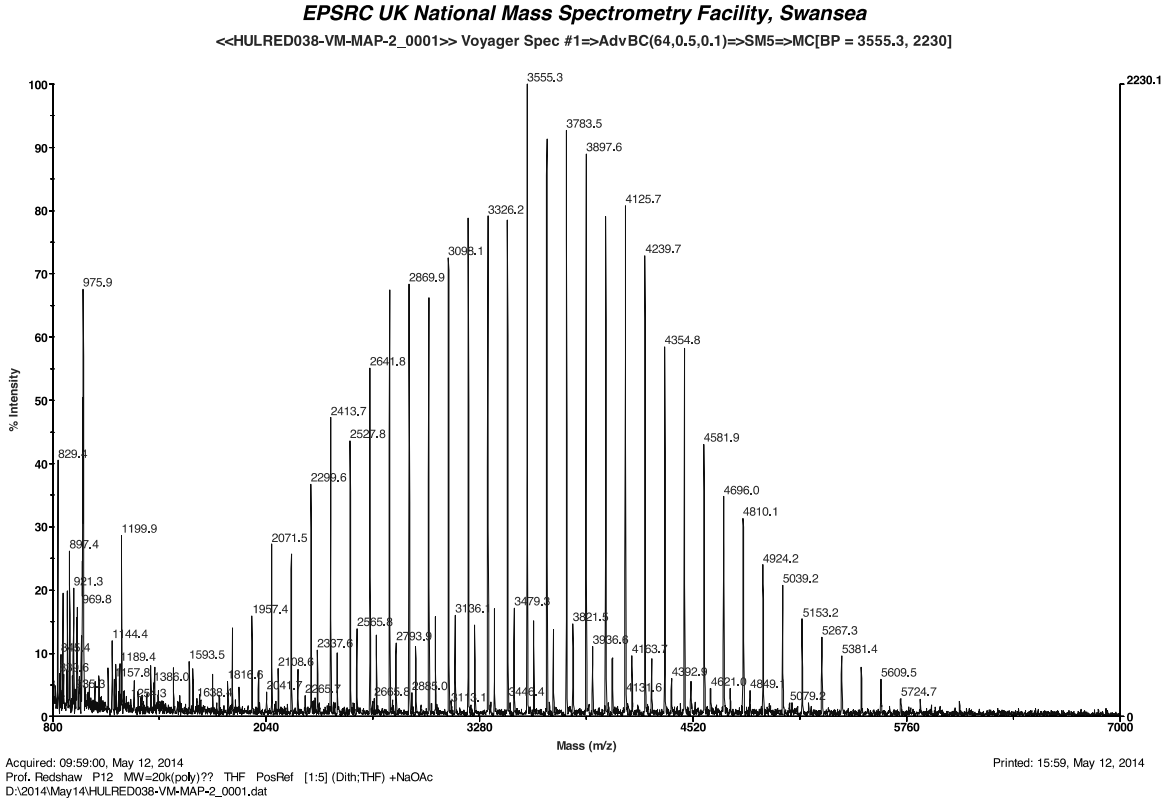

Figure S4. MALDI-TOF mass spectrum of PCL initiated by **3** in toluene at 80 °C, [CL]/[**3**]/[BnOH] = 50:1:1 (Table 2, entry 3). 114.14*n + 108 for BnO-(CL)n-H, 114.14*n + 108 +1 for BnO-(CL)n-H and 114.14*n + 108 + 1 + 22 for BnO-(CL)n-H •Na^+.

PLA data:

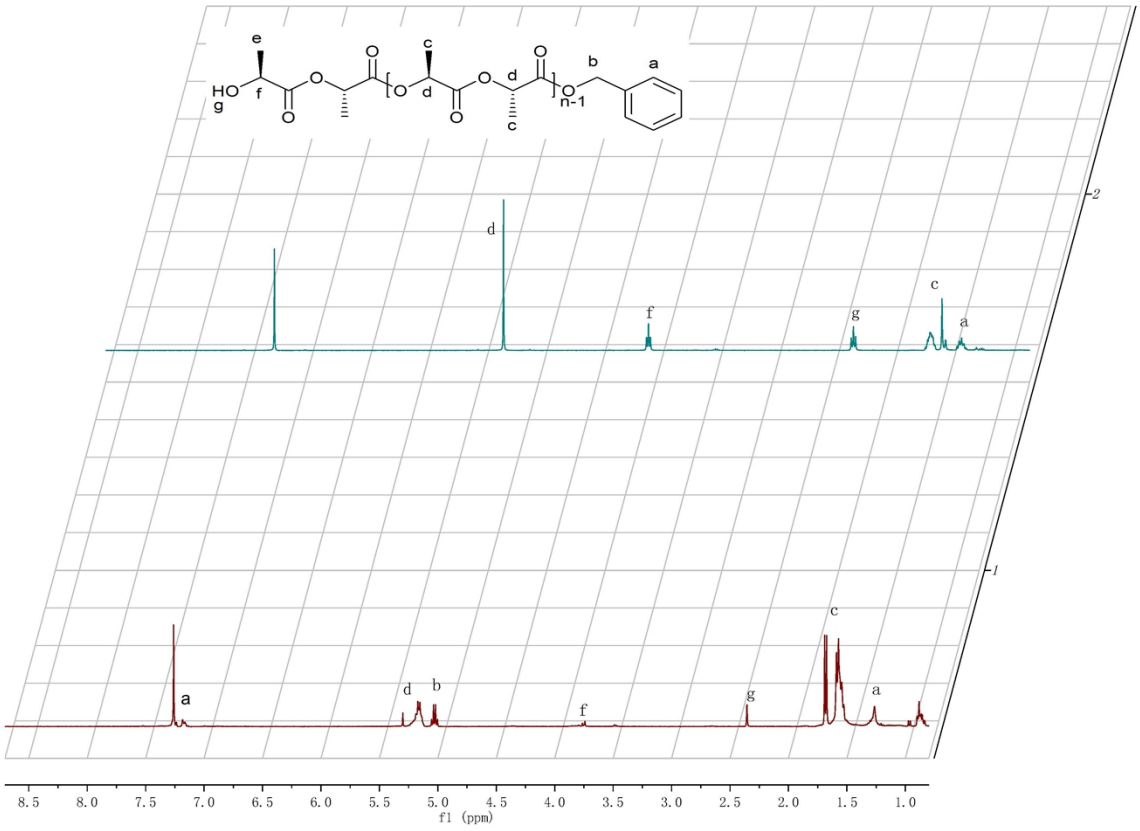

Figure S5. ^{1}H NMR spectrum of PLA in $CDCl_3$ catalyzed by aluminium complexes (1) pre-catalyst **3** with BnOH (Table 3, entry 3); (2) pre- catalyst **1** with BnOH (Table 3, entry 1).

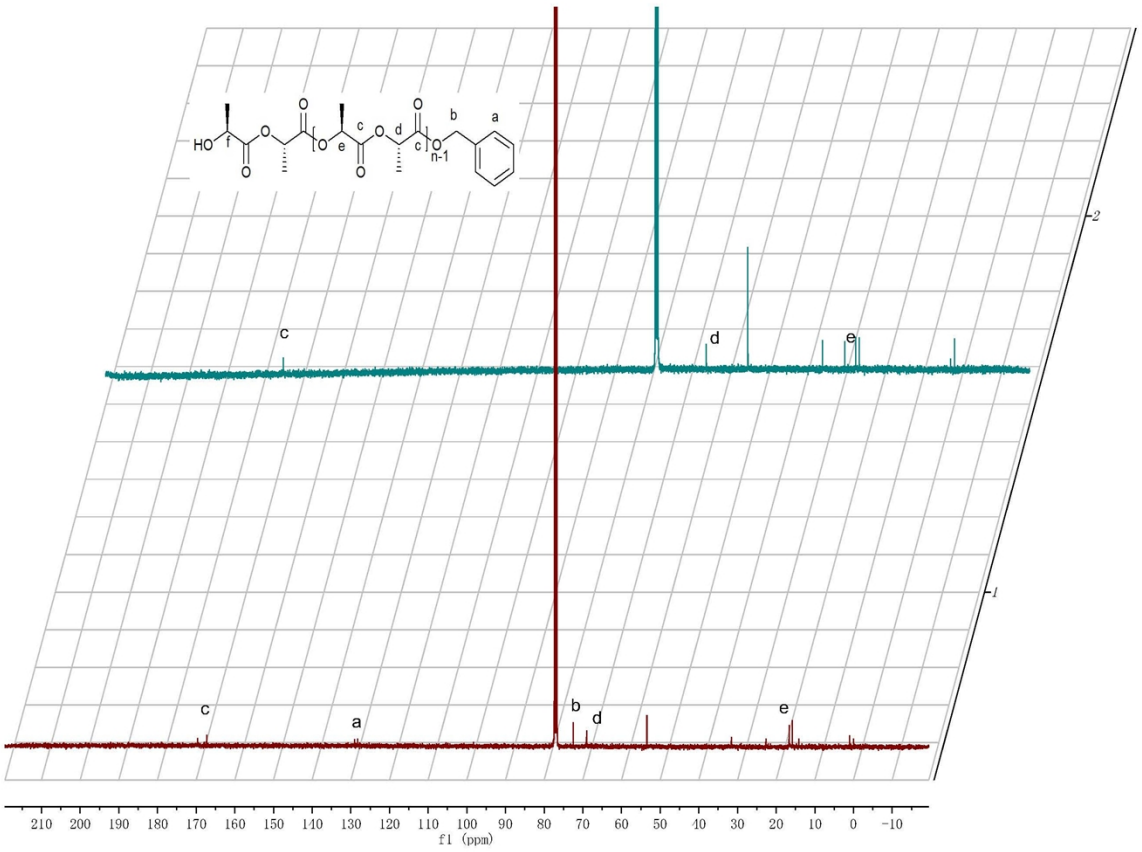

Figure S6. ^{13}C NMR spectrum of PLA in $CDCl_3$ catalyzed by aluminium complexes (1) pre-catalyst **3** with BnOH (Table 3, entry 3); (2) pre- catalyst **1** with BnOH (Table 3, entry 1).

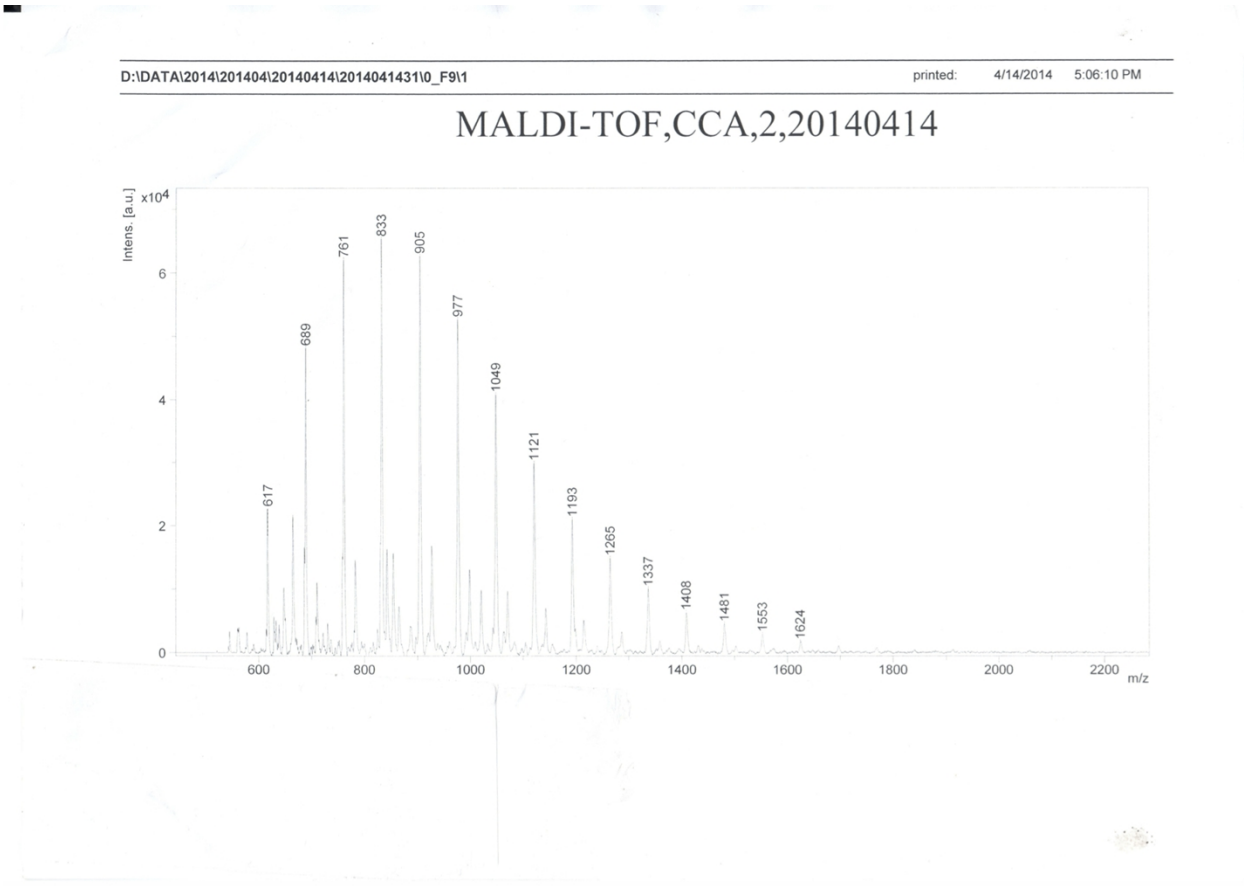

Figure S7. MALDI-TOF mass spectrum of PLA initiated by **1** in toluene at 80 °C, [LA]/[**1**]/[BnOH] = 50:1:1 (Table 2, entry 3). 72*n for (LA)n, 72*n + 17 +1 for H-(CL)n-OH and 72*n + 1 + 17 + 22 for HO-(CL)n-OH •Na+.

Crystallographic ESI:

Table S2*: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)*

	x	*y*	*z*	U_{iso}*/U_{eq}
Al1	1.08048 (5)	0.06059 (3)	0.42625 (4)	0.02465 (12)
C1	1.29966 (19)	0.07116 (12)	0.38918 (18)	0.0455 (4)
H1A	1.3425	0.1194	0.4410	0.068*
H1B	1.3146	0.0826	0.2947	0.068*
H1C	1.3514	0.0167	0.4134	0.068*
C2	0.9618 (2)	0.15396 (10)	0.33853 (15)	0.0406 (4)
H2A	0.8560	0.1524	0.3700	0.061*
H2B	0.9634	0.1450	0.2425	0.061*
H2C	1.0072	0.2108	0.3596	0.061*
Al2	0.89498 (4)	0.15546 (3)	0.64521 (4)	0.02493 (12)
C3	0.67643 (18)	0.16515 (12)	0.61058 (19)	0.0449 (4)
H3A	0.6540	0.1432	0.5215	0.067*
H3B	0.6454	0.2265	0.6169	0.067*
H3C	0.6200	0.1306	0.6759	0.067*
C4	1.02308 (19)	0.26028 (10)	0.64616 (16)	0.0386 (4)
H4A	1.1310	0.2432	0.6460	0.058*
H4B	1.0014	0.2947	0.7257	0.058*
H4C	1.0009	0.2954	0.5673	0.058*
N1	1.01412 (12)	0.05318 (7)	0.60956 (10)	0.0214 (2)
C5	1.11476 (15)	0.05089 (8)	0.72176 (13)	0.0240 (3)
C6	1.26312 (17)	0.01775 (11)	0.72173 (16)	0.0358 (3)
H6	1.3002 (19)	-0.0065 (12)	0.6424 (18)	0.041 (5)*
C7	1.3508 (2)	0.01877 (14)	0.83642 (19)	0.0502 (4)
H7	1.458 (3)	-0.0032 (15)	0.835 (2)	0.070 (7)*
C8	1.2934 (2)	0.05267 (13)	0.95245 (19)	0.0517 (5)
H8	1.355 (3)	0.0550 (13)	1.028 (2)	0.061 (6)*
C9	1.1461 (2)	0.08549 (11)	0.95679 (16)	0.0401 (4)
H9	1.110 (2)	0.1087 (12)	1.031 (2)	0.044 (5)*
C10	1.06115 (16)	0.08400 (9)	0.84211 (13)	0.0267 (3)
O1	0.91176 (11)	0.11744 (6)	0.83040 (9)	0.0284 (2)

C11	0.8464 (2)	0.16334 (12)	0.94228 (16)	0.0436 (4)
H11A	0.8373	0.1233	1.0175	0.065*
H11B	0.7450	0.1855	0.9183	0.065*
H11C	0.9128	0.2123	0.9668	0.065*

Table S3: *Geometric parameters (Å, º) for **1***

Al1—N1	1.9454 (11)	C4—H4B	0.9800
Al1—C1	1.9618 (16)	C4—H4C	0.9800
Al1—N1^{i}	1.9626 (11)	N1—C5	1.4343 (16)
Al1—C2	1.9759 (16)	C5—C6	1.3940 (19)
C1—H1A	0.9800	C5—C10	1.3993 (19)
C1—H1B	0.9800	C6—C7	1.388 (2)
C1—H1C	0.9800	C6—H6	0.942 (19)
C2—H2A	0.9800	C7—C8	1.378 (3)
C2—H2B	0.9800	C7—H7	1.00 (2)
C2—H2C	0.9800	C8—C9	1.384 (3)
Al2—N1	1.9164 (11)	C8—H8	0.94 (2)
Al2—C3	1.9491 (16)	C9—C10	1.375 (2)
Al2—C4	1.9583 (16)	C9—H9	0.89 (2)
Al2—O1	1.9645 (10)	C10—O1	1.4089 (16)
C3—H3A	0.9800	O1—C11	1.4498 (16)
C3—H3B	0.9800	C11—H11A	0.9800
C3—H3C	0.9800	C11—H11B	0.9800
C4—H4A	0.9800	C11—H11C	0.9800
N1—Al1—C1	118.73 (7)	H4B—C4—H4C	109.5
N1—Al1—N1^{i}	89.82 (4)	C5—N1—Al2	101.82 (8)
C1—Al1—N1^{i}	116.76 (6)	C5—N1—Al1	124.73 (8)
N1—Al1—C2	108.15 (6)	Al2—N1—Al1	107.15 (5)
C1—Al1—C2	111.57 (8)	C5—N1—Al1^{i}	112.45 (8)
N1^{i}—Al1—C2	109.82 (6)	Al2—N1—Al1^{i}	122.08 (6)
Al1—C1—H1A	109.5	Al1—N1—Al1^{i}	90.18 (4)
Al1—C1—H1B	109.5	C6—C5—C10	116.51 (13)
H1A—C1—H1B	109.5	C6—C5—N1	125.37 (12)
Al1—C1—H1C	109.5	C10—C5—N1	118.12 (11)
H1A—C1—H1C	109.5	C7—C6—C5	120.57 (15)

H1B—C1—H1C	109.5	C7—C6—H6	121.6 (10)
Al1—C2—H2A	109.5	C5—C6—H6	117.8 (10)
Al1—C2—H2B	109.5	C8—C7—C6	120.84 (16)
H2A—C2—H2B	109.5	C8—C7—H7	119.1 (13)
Al1—C2—H2C	109.5	C6—C7—H7	120.0 (13)
H2A—C2—H2C	109.5	C7—C8—C9	120.32 (15)
H2B—C2—H2C	109.5	C7—C8—H8	120.0 (14)
N1—Al2—C3	124.23 (7)	C9—C8—H8	119.7 (13)
N1—Al2—C4	111.07 (6)	C10—C9—C8	117.97 (15)
C3—Al2—C4	119.99 (8)	C10—C9—H9	121.5 (12)
N1—Al2—O1	84.10 (4)	C8—C9—H9	120.5 (12)
C3—Al2—O1	105.34 (7)	C9—C10—C5	123.79 (14)
C4—Al2—O1	101.35 (6)	C9—C10—O1	124.37 (13)
Al2—C3—H3A	109.5	C5—C10—O1	111.82 (11)
Al2—C3—H3B	109.5	C10—O1—C11	118.59 (12)
H3A—C3—H3B	109.5	C10—O1—Al2	104.78 (8)
Al2—C3—H3C	109.5	C11—O1—Al2	124.75 (9)
H3A—C3—H3C	109.5	O1—C11—H11A	109.5
H3B—C3—H3C	109.5	O1—C11—H11B	109.5
Al2—C4—H4A	109.5	H11A—C11—H11B	109.5
Al2—C4—H4B	109.5	O1—C11—H11C	109.5
H4A—C4—H4B	109.5	H11A—C11—H11C	109.5
Al2—C4—H4C	109.5	H11B—C11—H11C	109.5
H4A—C4—H4C	109.5		
Al2—N1—C5—C6	-149.30 (13)	C8—C9—C10—C5	0.3 (2)
Al1—N1—C5—C6	-28.53 (18)	C8—C9—C10—O1	-177.97 (15)
Al1^{i}—N1—C5—C6	78.35 (15)	C6—C5—C10—C9	0.2 (2)
Al2—N1—C5—C10	31.04 (13)	N1—C5—C10—C9	179.93 (13)
Al1—N1—C5—C10	151.81 (10)	C6—C5—C10—O1	178.71 (12)
Al1^{i}—N1—C5—C10	-101.30 (12)	N1—C5—C10—O1	-1.60 (17)
C10—C5—C6—C7	-0.3 (2)	C9—C10—O1—C11	5.6 (2)
N1—C5—C6—C7	-179.98 (15)	C5—C10—O1—C11	-172.89 (12)
C5—C6—C7—C8	-0.2 (3)	C9—C10—O1—Al2	150.16 (13)
C6—C7—C8—C9	0.7 (3)	C5—C10—O1—Al2	-28.30 (13)
C7—C8—C9—C10	-0.8 (3)		

Symmetry code: (i) -*x*+2, -*y*, -*z*+1.

Computing details

Data collection: Bruker *SMART*; cell refinement: Bruker *SAINT*; data reduction: Bruker *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2013* (Sheldrick, 2013); molecular graphics: Bruker *SHELXTL*; software used to prepare material for publication: Bruker SHLXTL.

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Crystal structure data for 2, [1,3-(Me_3AlOMe),NHC_6H_4(μ-Me_2Al)]$_2$

Table S4*: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)*

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
Al1	0.10328 (7)	0.23031 (2)	0.24514 (4)	0.03661 (14)	
C1	0.0038 (4)	0.20683 (19)	0.0999 (2)	0.1045 (12)	
H1A	-0.0591	0.2432	0.0653	0.157*	
H1B	-0.0867	0.1724	0.1056	0.157*	
H1C	0.1075	0.1932	0.0560	0.157*	
C2	0.2618 (3)	0.16702 (9)	0.3221 (2)	0.0657 (6)	
H2A	0.3396	0.1454	0.2702	0.099*	
H2B	0.1814	0.1363	0.3569	0.099*	
H2C	0.3434	0.1878	0.3776	0.099*	
C3	-0.0613 (3)	0.27828 (9)	0.33687 (16)	0.0502 (5)	
H3A	0.0100	0.2919	0.4028	0.075*	
H3B	-0.1670	0.2518	0.3568	0.075*	
H3C	-0.1096	0.3153	0.2970	0.075*	
Al2	-0.16176 (6)	0.50037 (2)	0.06428 (4)	0.02861 (12)	
C4	-0.2646 (2)	0.42041 (8)	0.11129 (14)	0.0415 (4)	
H4A	-0.2262	0.4131	0.1877	0.062*	
H4B	-0.2170	0.3863	0.0668	0.062*	
H4C	-0.4024	0.4217	0.1031	0.062*	
C5	-0.2780 (3)	0.57926 (9)	0.10839 (14)	0.0489 (5)	
H5A	-0.3871	0.5886	0.0593	0.073*	
H5B	-0.1862	0.6135	0.1052	0.073*	
H5C	-0.3190	0.5752	0.1828	0.073*	
O1	0.29435 (16)	0.29244 (5)	0.20935 (10)	0.0393 (3)	
C6	0.28894 (19)	0.35790 (6)	0.23110 (12)	0.0284 (3)	
C7	0.3731 (2)	0.37992 (8)	0.32619 (13)	0.0368 (4)	
H7	0.430 (3)	0.3531 (10)	0.3743 (17)	0.058 (6)*	
C8	0.3700 (2)	0.44410 (8)	0.34407 (12)	0.0370 (4)	
H8	0.423 (3)	0.4610 (9)	0.4092 (16)	0.048 (5)*	
C9	0.2873 (2)	0.48476 (7)	0.26802 (12)	0.0291 (3)	
H9	0.286 (2)	0.5283 (8)	0.2814 (14)	0.034 (4)*	
C10	0.20219 (17)	0.46144 (6)	0.17198 (10)	0.0220 (3)	

C11	0.20196 (19)	0.39665 (6)	0.15402 (11)	0.0241 (3)	
H11	0.148 (2)	0.3801 (8)	0.0914 (14)	0.033 (4)*	
C12	0.4534 (3)	0.27389 (8)	0.14719 (19)	0.0551 (5)	
H12A	0.4446	0.2946	0.0761	0.083*	
H12B	0.4520	0.2281	0.1371	0.083*	
H12C	0.5708	0.2864	0.1863	0.083*	
N1	0.11473 (16)	0.50315 (5)	0.09261 (10)	0.0247 (2)	
H1	0.139 (3)	0.5401 (9)	0.1111 (14)	0.036 (5)*	
C13	0.0205 (6)	0.4644 (2)	0.5270 (3)	0.0517 (9)	0.5
C14	-0.1146 (14)	0.4629 (4)	0.4467 (8)	0.0459 (15)	0.5
H14	-0.1782	0.4247	0.4284	0.055*	0.5
C15	-0.1607 (7)	0.5198 (2)	0.3896 (4)	0.0637 (11)	0.5
H15	-0.2569	0.5199	0.3333	0.076*	0.5
C16	-0.0679 (13)	0.5731 (3)	0.4155 (9)	0.085 (2)	0.5
H16	-0.0991	0.6105	0.3765	0.101*	0.5
C17	0.0698 (10)	0.5749 (3)	0.4962 (6)	0.0910 (18)	0.5
H17	0.1353	0.6129	0.5132	0.109*	0.5
C18	0.1138 (16)	0.5178 (4)	0.5552 (10)	0.067 (2)	0.5
H18	0.2070	0.5177	0.6132	0.080*	0.5
C19	0.0676 (16)	0.4033 (4)	0.5835 (8)	0.103 (3)	0.5
H19A	-0.0476	0.3845	0.6097	0.155*	0.5
H19B	0.1568	0.4112	0.6452	0.155*	0.5
H19C	0.1244	0.3743	0.5326	0.155*	0.5

Table S5*: Geometric parameters (Å, º) for (**2**)*

Al1—C3	1.9541 (19)	C7—H7	0.90 (2)
Al1—C1	1.957 (2)	C8—C9	1.384 (2)
Al1—O1	1.9600 (11)	C8—H8	0.94 (2)
Al1—C2	1.968 (2)	C9—C10	1.3938 (19)
C1—H1A	0.9800	C9—H9	0.940 (17)
C1—H1B	0.9800	C10—C11	1.3941 (18)
C1—H1C	0.9800	C10—N1	1.4385 (16)
C2—H2A	0.9800	C11—H11	0.916 (17)
C2—H2B	0.9800	C12—H12A	0.9800
C2—H2C	0.9800	C12—H12B	0.9800
C3—H3A	0.9800	C12—H12C	0.9800

C3—H3B	0.9800	N1—Al2^{i}	1.9807 (13)
C3—H3C	0.9800	N1—H1	0.833 (19)
Al2—C4	1.9490 (16)	C13—C14	1.344 (9)
Al2—C5	1.9577 (18)	C13—C18	1.351 (8)
Al2—N1	1.9802 (12)	C13—C19	1.503 (8)
Al2—N1^{i}	1.9807 (13)	C14—C15	1.430 (9)
Al2—Al2^{i}	2.8573 (8)	C14—H14	0.9500
C4—H4A	0.9800	C15—C16	1.340 (8)
C4—H4B	0.9800	C15—H15	0.9500
C4—H4C	0.9800	C16—C17	1.362 (11)
C5—H5A	0.9800	C16—H16	0.9500
C5—H5B	0.9800	C17—C18	1.441 (11)
C5—H5C	0.9800	C17—H17	0.9500
O1—C6	1.4173 (17)	C18—H18	0.9500
O1—C12	1.451 (2)	C19—H19A	0.9800
C6—C7	1.372 (2)	C19—H19B	0.9800
C6—C11	1.3803 (19)	C19—H19C	0.9800
C7—C8	1.382 (2)		
C3—Al1—C1	117.58 (12)	C6—C7—C8	117.59 (14)
C3—Al1—O1	102.74 (7)	C6—C7—H7	120.6 (14)
C1—Al1—O1	100.87 (10)	C8—C7—H7	121.8 (14)
C3—Al1—C2	114.98 (9)	C7—C8—C9	121.16 (14)
C1—Al1—C2	116.07 (15)	C7—C8—H8	120.2 (12)
O1—Al1—C2	100.48 (7)	C9—C8—H8	118.6 (12)
Al1—C1—H1A	109.5	C8—C9—C10	120.37 (14)
Al1—C1—H1B	109.5	C8—C9—H9	120.1 (11)
H1A—C1—H1B	109.5	C10—C9—H9	119.5 (11)
Al1—C1—H1C	109.5	C9—C10—C11	118.88 (12)
H1A—C1—H1C	109.5	C9—C10—N1	120.92 (12)
H1B—C1—H1C	109.5	C11—C10—N1	120.20 (12)
Al1—C2—H2A	109.5	C6—C11—C10	118.85 (13)
Al1—C2—H2B	109.5	C6—C11—H11	120.5 (10)
H2A—C2—H2B	109.5	C10—C11—H11	120.6 (10)
Al1—C2—H2C	109.5	O1—C12—H12A	109.5
H2A—C2—H2C	109.5	O1—C12—H12B	109.5
H2B—C2—H2C	109.5	H12A—C12—H12B	109.5

Al1—C3—H3A	109.5	O1—C12—H12C	109.5
Al1—C3—H3B	109.5	H12A—C12—H12C	109.5
H3A—C3—H3B	109.5	H12B—C12—H12C	109.5
Al1—C3—H3C	109.5	C10—N1—Al2	119.57 (9)
H3A—C3—H3C	109.5	C10—N1—Al2^{i}	123.58 (9)
H3B—C3—H3C	109.5	Al2—N1—Al2^{i}	92.33 (5)
C4—Al2—C5	119.59 (9)	C10—N1—H1	108.4 (12)
C4—Al2—N1	110.93 (6)	Al2—N1—H1	105.6 (12)
C5—Al2—N1	110.76 (7)	Al2^{i}—N1—H1	105.1 (12)
C4—Al2—N1^{i}	109.97 (7)	C14—C13—C18	122.2 (7)
C5—Al2—N1^{i}	113.43 (6)	C14—C13—C19	117.1 (6)
N1—Al2—N1^{i}	87.67 (5)	C18—C13—C19	120.7 (7)
C4—Al2—Al2^{i}	118.97 (6)	C13—C14—C15	118.7 (6)
C5—Al2—Al2^{i}	121.42 (7)	C13—C14—H14	120.6
N1—Al2—Al2^{i}	43.84 (4)	C15—C14—H14	120.6
N1^{i}—Al2—Al2^{i}	43.83 (4)	C16—C15—C14	119.9 (7)
Al2—C4—H4A	109.5	C16—C15—H15	120.0
Al2—C4—H4B	109.5	C14—C15—H15	120.0
H4A—C4—H4B	109.5	C15—C16—C17	121.7 (8)
Al2—C4—H4C	109.5	C15—C16—H16	119.2
H4A—C4—H4C	109.5	C17—C16—H16	119.2
H4B—C4—H4C	109.5	C16—C17—C18	118.4 (7)
Al2—C5—H5A	109.5	C16—C17—H17	120.8
Al2—C5—H5B	109.5	C18—C17—H17	120.8
H5A—C5—H5B	109.5	C13—C18—C17	119.0 (9)
Al2—C5—H5C	109.5	C13—C18—H18	120.5
H5A—C5—H5C	109.5	C17—C18—H18	120.5
H5B—C5—H5C	109.5	C13—C19—H19A	109.5
C6—O1—C12	113.30 (11)	C13—C19—H19B	109.5
C6—O1—Al1	126.35 (9)	H19A—C19—H19B	109.5
C12—O1—Al1	120.17 (10)	C13—C19—H19C	109.5
C7—C6—C11	123.14 (14)	H19A—C19—H19C	109.5
C7—C6—O1	118.79 (13)	H19B—C19—H19C	109.5
C11—C6—O1	118.06 (13)		
C12—O1—C6—C7	-92.52 (18)	N1—C10—C11—C6	179.25 (12)
Al1—O1—C6—C7	92.40 (15)	C9—C10—N1—Al2	-113.06 (13)

C12—O1—C6—C11	86.21 (18)	C11—C10—N1—Al2	66.56 (15)
Al1—O1—C6—C11	-88.88 (15)	C9—C10—N1—Al2^{i}	131.30 (12)
C11—C6—C7—C8	-0.3 (2)	C11—C10—N1—Al2^{i}	-49.08 (16)
O1—C6—C7—C8	178.37 (13)	C18—C13—C14—C15	0.0 (18)
C6—C7—C8—C9	-0.9 (2)	C19—C13—C14—C15	-178.8 (8)
C7—C8—C9—C10	1.1 (2)	C13—C14—C15—C16	0.9 (13)
C8—C9—C10—C11	0.0 (2)	C14—C15—C16—C17	-0.5 (13)
C8—C9—C10—N1	179.60 (13)	C15—C16—C17—C18	-0.6 (13)
C7—C6—C11—C10	1.3 (2)	C14—C13—C18—C17	-1.2 (18)
O1—C6—C11—C10	-177.35 (11)	C19—C13—C18—C17	177.6 (8)
C9—C10—C11—C6	-1.12 (19)	C16—C17—C18—C13	1.5 (14)

Symmetry code: (i) -*x*, -*y*+1, -*z*.

Computing details

Data collection: Bruker *SMART*; cell refinement: Bruker *SAINT*; data reduction: Bruker *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2013* (Sheldrick, 2013); molecular graphics: Bruker *SHELXTL*; software used to prepare material for publication: Bruker *SHELXTL*.

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Crystal data and structure refinement for 3, [1,4-(Me_3AlOMe),NHC_6H_4(μ-Me_2Al)]$_2$

Table S6: Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å$^2\times 10^3$) for **3**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Al(2)	1790(1)	5570(1)	671(1)	24(1)
C(1)	2002(3)	-4085(2)	-3638(2)	41(1)
C(2)	-940(3)	-1814(2)	-3734(2)	39(1)
C(3)	2588(3)	-1929(2)	-5565(2)	46(1)
O(1)	3012(2)	-990(1)	-2573(1)	27(1)
C(12)	4982(3)	-1051(2)	-2344(2)	39(1)
C(6)	2522(2)	349(2)	-2149(2)	25(1)
C(7)	2739(3)	1267(2)	-2924(2)	28(1)
C(8)	2184(3)	2553(2)	-2523(2)	28(1)
C(9)	1417(2)	2917(2)	-1368(2)	23(1)
C(10)	1246(2)	1970(2)	-592(2)	26(1)
C(11)	1809(2)	682(2)	-990(2)	26(1)
N(1)	792(2)	4237(1)	-983(1)	24(1)
Al(1)	1502(1)	-2335(1)	-4044(1)	28(1)
C(4)	3009(3)	4690(2)	1912(2)	39(1)
C(5)	3041(3)	7237(2)	316(2)	35(1)

Table S7: Bond lengths [Å] and angles [°] for **3**.

Al(2)-C(5)	1.9582(19)	N(1)-H(1)	0.867(15)
Al(2)-C(4)	1.959(2)	C(4)-H(4A)	0.9800
Al(2)-N(1)#1	1.9809(15)	C(4)-H(4B)	0.9800
Al(2)-N(1)	1.9851(16)	C(4)-H(4C)	0.9800
C(1)-Al(1)	1.975(2)	C(5)-H(5A)	0.9800
C(1)-H(1A)	0.9800	C(5)-H(5B)	0.9800
C(1)-H(1B)	0.9800	C(5)-H(5C)	0.9800
C(1)-H(1C)	0.9800		
C(2)-Al(1)	1.962(2)	C(5)-Al(2)-C(4)	119.69(9)
C(2)-H(2A)	0.9800	C(5)-Al(2)-N(1)#1	111.54(7)
C(2)-H(2B)	0.9800	C(4)-Al(2)-N(1)#1	111.68(8)
C(2)-H(2C)	0.9800	C(5)-Al(2)-N(1)	110.06(8)
C(3)-Al(1)	1.973(2)	C(4)-Al(2)-N(1)	112.02(8)
C(3)-H(3A)	0.9800	N(1)#1-Al(2)-N(1)	87.24(6)
C(3)-H(3B)	0.9800	Al(1)-C(1)-H(1A)	109.5
C(3)-H(3C)	0.9800	Al(1)-C(1)-H(1B)	109.5
O(1)-C(6)	1.422(2)	H(1A)-C(1)-H(1B)	109.5
O(1)-C(12)	1.459(2)	Al(1)-C(1)-H(1C)	109.5
O(1)-Al(1)	1.9851(14)	H(1A)-C(1)-H(1C)	109.5
C(12)-H(12A)	0.9800	H(1B)-C(1)-H(1C)	109.5
C(12)-H(12B)	0.9800	Al(1)-C(2)-H(2A)	109.5
C(12)-H(12C)	0.9800	Al(1)-C(2)-H(2B)	109.5
C(6)-C(11)	1.371(2)	H(2A)-C(2)-H(2B)	109.5
C(6)-C(7)	1.379(2)	Al(1)-C(2)-H(2C)	109.5
C(7)-C(8)	1.389(2)	H(2A)-C(2)-H(2C)	109.5
C(7)-H(7)	0.9500	H(2B)-C(2)-H(2C)	109.5
C(8)-C(9)	1.390(2)	Al(1)-C(3)-H(3A)	109.5
C(8)-H(8)	0.9500	Al(1)-C(3)-H(3B)	109.5
C(9)-C(10)	1.402(2)	H(3A)-C(3)-H(3B)	109.5
C(9)-N(1)	1.440(2)	Al(1)-C(3)-H(3C)	109.5
C(10)-C(11)	1.393(2)	H(3A)-C(3)-H(3C)	109.5
C(10)-H(10)	0.9500	H(3B)-C(3)-H(3C)	109.5
C(11)-H(11)	0.9500	C(6)-O(1)-C(12)	113.54(14)
N(1)-Al(2)#1	1.9809(15)	C(6)-O(1)-Al(1)	120.28(10)

C(12)-O(1)-Al(1)	119.52(11)	C(1)-Al(1)-O(1)	101.08(8)
O(1)-C(12)-H(12A)	109.5	Al(2)-C(4)-H(4A)	109.5
O(1)-C(12)-H(12B)	109.5	Al(2)-C(4)-H(4B)	109.5
H(12A)-C(12)-H(12B)	109.5	H(4A)-C(4)-H(4B)	109.5
O(1)-C(12)-H(12C)	109.5	Al(2)-C(4)-H(4C)	109.5
H(12A)-C(12)-H(12C)	109.5	H(4A)-C(4)-H(4C)	109.5
H(12B)-C(12)-H(12C)	109.5	H(4B)-C(4)-H(4C)	109.5
C(11)-C(6)-C(7)	121.85(16)	Al(2)-C(5)-H(5A)	109.5
C(11)-C(6)-O(1)	118.86(15)	Al(2)-C(5)-H(5B)	109.5
C(7)-C(6)-O(1)	119.28(14)	H(5A)-C(5)-H(5B)	109.5
C(6)-C(7)-C(8)	118.69(15)	Al(2)-C(5)-H(5C)	109.5
C(6)-C(7)-H(7)	120.7	H(5A)-C(5)-H(5C)	109.5
C(8)-C(7)-H(7)	120.7	H(5B)-C(5)-H(5C)	109.5
C(7)-C(8)-C(9)	121.16(15)		
C(7)-C(8)-H(8)	119.4		
C(9)-C(8)-H(8)	119.4		
C(8)-C(9)-C(10)	118.71(15)		
C(8)-C(9)-N(1)	120.67(14)		
C(10)-C(9)-N(1)	120.62(14)		
C(11)-C(10)-C(9)	120.17(15)		
C(11)-C(10)-H(10)	119.9		
C(9)-C(10)-H(10)	119.9		
C(6)-C(11)-C(10)	119.41(15)		
C(6)-C(11)-H(11)	120.3		
C(10)-C(11)-H(11)	120.3		
C(9)-N(1)-Al(2)#1	122.13(11)		
C(9)-N(1)-Al(2)	122.38(11)		
Al(2)#1-N(1)-Al(2)	92.76(6)		
C(9)-N(1)-H(1)	106.2(15)		
Al(2)#1-N(1)-H(1)	106.3(12)		
Al(2)-N(1)-H(1)	105.2(12)		
C(2)-Al(1)-C(3)	118.46(10)		
C(2)-Al(1)-C(1)	115.59(10)		
C(3)-Al(1)-C(1)	115.19(10)		
C(2)-Al(1)-O(1)	99.36(8)		
C(3)-Al(1)-O(1)	102.71(8)		

Symmetry transformations used to generate equivalent atoms:

#1 -x,-y+1,-z

Table S8: Anisotropic displacement parameters ($Å^2 \times 10^3$)for **3**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Al(2)	24(1)	19(1)	29(1)	4(1)	1(1)	5(1)
C(1)	51(1)	26(1)	43(1)	7(1)	-2(1)	6(1)
C(2)	32(1)	40(1)	44(1)	7(1)	1(1)	6(1)
C(3)	61(2)	45(1)	36(1)	11(1)	16(1)	12(1)
O(1)	25(1)	20(1)	35(1)	3(1)	2(1)	7(1)
C(12)	25(1)	30(1)	59(1)	6(1)	0(1)	7(1)
C(6)	23(1)	19(1)	30(1)	3(1)	0(1)	5(1)
C(7)	31(1)	25(1)	29(1)	5(1)	10(1)	6(1)
C(8)	32(1)	23(1)	30(1)	9(1)	5(1)	4(1)
C(9)	23(1)	18(1)	28(1)	4(1)	1(1)	4(1)
C(10)	30(1)	25(1)	26(1)	6(1)	6(1)	5(1)
C(11)	26(1)	22(1)	31(1)	9(1)	2(1)	4(1)
N(1)	27(1)	19(1)	26(1)	6(1)	5(1)	5(1)
Al(1)	31(1)	23(1)	29(1)	6(1)	3(1)	6(1)
C(4)	43(1)	33(1)	40(1)	7(1)	-5(1)	12(1)
C(5)	32(1)	29(1)	41(1)	4(1)	4(1)	0(1)

Table S9. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($Å^2 \times 10^3$) for **3**.

	x	y	z	U(eq)
H(1A)	2890	-4489	-4192	61
H(1B)	854	-4719	-3794	61
H(1C)	2509	-3915	-2725	61
H(2A)	-1042	-923	-3938	59
H(2B)	-1110	-1748	-2821	59
H(2C)	-1887	-2508	-4287	59
H(3A)	1980	-2581	-6354	69
H(3B)	3905	-2012	-5475	69
H(3C)	2419	-994	-5620	69
H(12A)	5648	-466	-2817	58
H(12B)	5225	-1999	-2646	58
H(12C)	5395	-729	-1414	58
H(7)	3257	1024	-3716	34
H(8)	2331	3195	-3047	33
H(10)	746	2206	208	32
H(11)	1700	40	-463	31
H(4A)	3909	4146	1493	58
H(4B)	2089	4088	2206	58
H(4C)	3638	5394	2658	58
H(5A)	2871	8034	993	53
H(5B)	2521	7343	-529	53
H(5C)	4357	7166	305	53
H(1)	1020(20)	4660(20)	-1586(16)	42

Table S10: Torsion angles [°] for **3**.

C(12)-O(1)-C(6)-C(11)	-100.72(19)
Al(1)-O(1)-C(6)-C(11)	108.03(16)
C(12)-O(1)-C(6)-C(7)	80.6(2)
Al(1)-O(1)-C(6)-C(7)	-70.61(19)
C(11)-C(6)-C(7)-C(8)	-1.2(3)
O(1)-C(6)-C(7)-C(8)	177.38(17)
C(6)-C(7)-C(8)-C(9)	-0.3(3)
C(7)-C(8)-C(9)-C(10)	1.4(3)
C(7)-C(8)-C(9)-N(1)	-177.99(17)
C(8)-C(9)-C(10)-C(11)	-1.1(3)
N(1)-C(9)-C(10)-C(11)	178.26(17)
C(7)-C(6)-C(11)-C(10)	1.5(3)
O(1)-C(6)-C(11)-C(10)	-177.12(16)
C(9)-C(10)-C(11)-C(6)	-0.3(3)
C(8)-C(9)-N(1)-Al(2)#1	121.14(16)
C(10)-C(9)-N(1)-Al(2)#1	-58.2(2)
C(8)-C(9)-N(1)-Al(2)	-121.12(16)
C(10)-C(9)-N(1)-Al(2)	59.5(2)
C(5)-Al(2)-N(1)-C(9)	116.67(14)
C(4)-Al(2)-N(1)-C(9)	-19.08(15)
N(1)#1-Al(2)-N(1)-C(9)	-131.38(14)
C(5)-Al(2)-N(1)-Al(2)#1	-111.95(8)
C(4)-Al(2)-N(1)-Al(2)#1	112.30(9)
N(1)#1-Al(2)-N(1)-Al(2)#1	0.0
C(6)-O(1)-Al(1)-C(2)	-34.88(13)
C(12)-O(1)-Al(1)-C(2)	175.57(13)
C(6)-O(1)-Al(1)-C(3)	87.29(13)
C(12)-O(1)-Al(1)-C(3)	-62.26(14)
C(6)-O(1)-Al(1)-C(1)	-153.45(12)
C(12)-O(1)-Al(1)-C(1)	57.00(14)

Symmetry transformations used to generate equivalent atoms:

#1 -x,-y+1,-z