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Ring-Opening Polymerization of *rac*-Lactide with Aluminum Chiral Anilido-Oxazolinate Complexes

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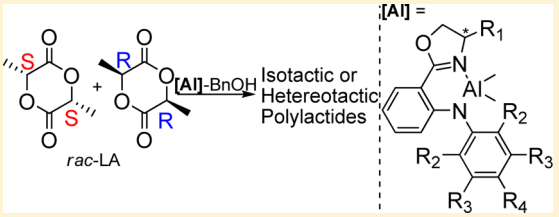
Supporting Information

ABSTRACT: A series of dimethylaluminum complexes (L^{1a-i})$AlMe_2$ (**2a–i**, where HL^{1a-i} = 2-(2′-ArNH)phenyl-4-R_1-oxazoline) bearing chiral, bidentate anilido-oxazolinate ligands have been prepared and characterized. Six of the complexes, in the presence of an alcohol cocatalyst, are shown to be active initiators for the stereoselective ring-opening polymerization of *rac*-lactide in toluene solution and under bulk conditions, yielding polylactides with a range of tacticity from slightly isotactic to moderately heterotactic. The reactivity and selectivity of these catalysts are discussed on the basis of the effect of their substituents.

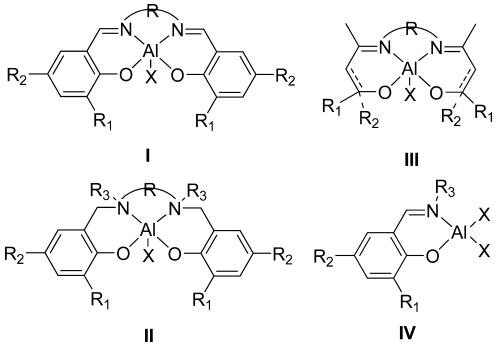


INTRODUCTION

Synthetic aliphatic polyesters, such as polylactide (PLA), and their copolymers have attracted considerable attention due to their biocompatibility and biodegradability.[1] These features are important in biomedical applications, such as drug delivery and tissue engineering,[2] and in agricultural and packaging applications.[3] Furthermore, PLA is derived from renewable resources and is considered a viable alternative to petrochemical-based materials. Although PLA can be produced by the polycondensation of lactic acids, the ring-opening polymerization (ROP) of lactide (LA) with an initiator/catalyst is the method of choice because it offers a higher degree of reaction control.[1] Due to the presence of two chiral centers in a lactide monomer, a range of microstructures, including atactic, isotactic, heterotactic, and syndiotactic, are possible for PLA derived from lactide. The tacticity has a significant effect on the physical and thermal properties of bulk materials. For example, atactic PLA is amorphous, while isotactic PLA is a crystalline polymer that melts at ∼170 °C.[4] Alongside the structure of lactide monomers, catalysts play a vital role in determining the stereo outcome of ROP. Much effort has currently been devoted to the design and synthesis of single-site catalysts/initiators for the ROP of *rac*-lactide with high activities and stereoselectivities.[5]

A wide array of catalytic systems for the ROP of lactides have been developed in the literature, ranging from homoleptic metal salts such as Sn(Octanoate)$_2$, Ca[N(SiMe$_3$)$_2$]$_2$, and Sc(OTf)$_3$ in combination with alcohols as chain transfer reagents[6] to well-defined single-site catalysts such as Zn and Mg complexes supported by β-diketiminate[7] and Y and Sc complexes supported by pyridine-diamide type ligands.[8] In particular, group 13 metal complexes are of special interest because of their effective stereo control and low toxicity.[9] The pioneering works by Spassky[10] in the control of PLA microstructure showed that a chiral salen aluminum complex (Scheme 1; **I**, where R = (*R*)-2,2′-binaphthyl, R_1 = R_2 = H, X = OMe) was highly isoselective for the ROP of *rac*-lactide. This system was further exploited[11] and expanded to other salen species,[12] their reduced derivatives such as salan (**II**; Scheme 1)[13] and salalen,[14] and related N_2O_2 (**III**; Scheme 1) and N_4 type ligands.[15] These initiators typically feature a five-coordinate aluminum center supported by dianionic, tetradentate ligands. A range of stereoselectivity has been achieved, from highly isospecific to highly heterospecific, even by simply varying the substituent groups in the same ligand framework.[13a] Al complexes supported by related bidentate half-salen ligands are usually four-coordinate (**IV**; Scheme 1) and exert less stereocontrol for the ROP of *rac*-lactide.[16] Al complexes supported by bidentate ligands can take on a pentacoordinate

Scheme 1. Examples of Stereoselective Al-Based Initiators for the ROP of *rac*-Lactide



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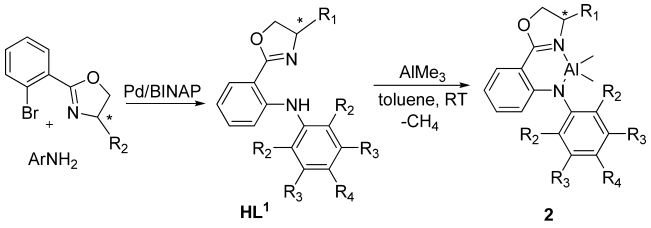
geometry and induce high isoselectivity.[17] It should also be mentioned that initiators based on heavier group 13 elements have been shown to be stereoselective for the ROP of *rac*-lactide.[18]

Bidentate and monoanionic β-diketiminate ligands are analogous to the half-salen ligands and have been successfully employed in ROP reactions.[5a,19] We have been interested in a chiral variation derived from the anilido-oxazolinate framework[20] and turned our attention to aluminum complexes incorporating these chiral ligands. The achiral version of the anilido-oxazolinate aluminum complexes in the ROP of L-lactide has been reported.[21] It is expected that the new chiral complexes are active initiators for the ROP of *rac*-lactide and may induce appreciable stereoselectivity to control the microstructure of the product. Herein we report a series of dimethylaluminum complexes and their application as initiators for the ROP of *rac*-lactide. Both hetero- and isotactic selectivities could be achieved by modulation of the substituent groups.

RESULTS AND DISCUSSION

Ligands. As mentioned earlier, the bidentate anilido-oxazolinate ligands (**HL^1**; Scheme 2) can be viewed as chiral variations of the conventional β-diketiminate ligands. The oxazoline ring is conveniently formed from chiral amino alcohols and 2-bromobenzaldehyde, and the coupling between oxazolines and anilines using a palladium-catalyzed amination protocol gave the ligands as orange oily or crystalline materials in good to high yields (69−88%). In addition to addressing the question if the chiral version could induce stereoselectivity in the ROP of *rac*-lactide, this particular series of ligands was targeted to investigate the steric and electronic influences of the substituents (see Scheme 2), because such factors may drastically affect the stereoselectivity toward the ROP of *rac*-lactide.[13a] The stereogenic center is introduced at the oxazoline R_1 position and is expected to exert a substantial steric influence. The aniline R_3 and R_4 positions are mostly electronic. On the other hand, the R_2 position is in closer proximity to the metal center, in comparison to the *ortho* position in related bidentate half-salen ligands (see the R_1 group in **IV** in Scheme 1), and it can also influence the metal center electronically. On the basis of these considerations, (*S*)-^{i}Pr, (*R*)-Ph, and (*R*)-^{i}Bu at the R_1 position and a methyl group at the R_2 position were incorporated to test the effect of steric factors on the reactivity and selectivity of the catalysts. A trifluoromethyl group on the R_3 position and a methoxy group on the R_4 position were used to probe the electronic effect.

Scheme 2. Preparation of Ligands and Their Aluminum Complexes



	R_1	R_2	R_3	R_4
a	(*S*)-^{i}Pr	H	H	H
b	(*S*)-^{i}Pr	Me	H	H
c	(*R*)-Ph	H	H	H
d	(*R*)-Ph	Me	H	H
e	(*R*)-^{i}Bu	H	H	H
f	(*R*)-^{i}Bu	Me	H	H
g	(*S*)-^{i}Pr	H	CF_3	H
h	(*S*)-^{i}Pr	H	H	OMe
i	(*S*)-^{i}Pr	OPh, H	H	H

Synthesis and Characterization of Aluminum Complexes. Reaction of the free ligands **HL^1** with 1.2 equiv of $AlMe_3$ in toluene at ambient temperature yielded the dimethylaluminum complexes **2a−i** (Scheme 2). The compounds were normally isolated as yellow powders in good yields (68−87%). Characterization by ^{1}H NMR and ^{13}C NMR revealed the formation of the expected dimethylaluminum complexes and was consistent with the mononuclear structures. For instance, the NH peak of the free ligand (around 10 ppm) disappeared upon reaction, and the ^{1}H NMR signals for the oxazoline moiety shift downfield in comparison to that in the free ligands, indicative of the formation of a six-membered chelate ring. Furthermore, two separate singlets in the upfield region around −1 ppm were observed and attributed to the aluminum methyl ($AlMe_2$) protons. These observations are in agreement with the unsymmetrical nature of the complexes, and the two methyl groups are nonequivalent. The latter is

Table 1. Polymerization of *rac*-Lactide with Al Complexes 2a−i[a]

entry	cat.	cat. loading (mol %)	time (h)	conversn (%)[b]	M_n[c]	M_n[d]	M_w/M_n[d]	P_r/P_m[e]
1	**2a**	2	24	96	6.92	7.7 (4.4)	1.20	P_r = 0.69
2	**2a**	0.5	48	97	28.0	12.1 (7.0)	1.45	P_r = 0.51
3	**2b**	2	24	15				
4	**2c**	2	24	95	6.85	10.8 (6.3)	1.23	P_m = 0.60
5[f]	**2c**	2	20	95	6.85	7.7 (4.5)	1.29	P_m = 1.0
6	**2d**	2	24	12				P_r = 0.53
7	**2e**	2	24	95	6.85	8.3 (4.8)	1.28	P_r = 0.74
8	**2e**	1	48	98	14.1	23.6 (13.7)	1.69	
9[g]	**2e**	1	48	40				
10	**2f**	2	24	12				
11	**2g**	2	24	95	6.85	4.9 (2.8)	1.64	P_m = 0.57
12	**2h**	2	24	93	6.70	9.7 (5.6)	1.25	P_r = 0.62
13	**2i**	2	24	98	7.06	9.0 (5.2)	1.53	P_r = 0.61

[a]Reaction conditions: see the Experimental Section for details. [b]Monomer conversion determined by ^{1}H NMR spectroscopy. [c]Calculated molecular weight based on conversion: $[LA]_0/[Al]_0 \times$ (conversn %) × 144. [d]Experimental molecular weight determined by GPC vs polystyrene standards. The values in parentheses are corrected by a factor of 0.58.[23] [e]Probability of racemic (P_r) or meso (P_m) enchainment, determined by homonuclear decoupled ^{1}H NMR spectroscopy. [f]L-Lactide was used. [g]Reaction was carried out in THF at 60 °C.

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Table 2. Polymerization of *rac*-Lactide with Al Complexes under Bulk Conditions[a]

entry	cat.	cat. loading (mol %)	time (h)	conversn (%)[b]	M_n[c]	M_n[d]	M_w/M_n[d]	P_r/P_m[e]
1	**2a**	2	1.5	74	5.33	3.9 (2.3)	1.74	P_r = 0.52
2	**2a**	0.25	1.0	81	46.7	23.1 (13.4)	1.45	P_r = 0.52
3	**2c**	0.25	1.0	65	37.5	13.1 (7.6)	2.02	P_m = 0.61
4	**2e**	0.25	1.0	61	35.2	4.2 (2.5)	1.82	P_r = 0.57
5	**2f**	0.25	2.0	31	17.9	19.6 (11.3)	1.95	P_r = 0.60
6	**2g**	0.25	2.0	78	44.9	35.6 (20.6)	2.99	P_m = 0.57
7	**2i**	0.25	1.5	75	43.2	207 (120)	1.84	P_r = 0.58

[a]Reaction conditions: see the Experimental Section for details. [b]Monomer conversion determined by ^{1}H NMR spectroscopy. [c]Calculated molecular weight based on conversion: $[LA]_0/[Al]_0 \times$ (conversn %) × 144. [d]Experimental molecular weight determined by GPC vs polystyrene standards. The values in parentheses are corrected by a factor of 0.58. [e]Probability of racemic (P_r) or meso (P_m) enchainment, determined by homonuclear decoupled ^{1}H NMR spectroscopy.

relevant in the context of stereoselective catalysis, as the growing polymer chain will occupy one of the two likely coordination sites during polymerization. In complexes **2b**,**d**,**f**, two singlets corresponding to the two *o*-methyl groups on the aniline phenyl moiety were observed, indicative of restricted rotation due to the steric bulk of *o*-methyl groups. In line with these observations, two sets of ^{1}H and ^{13}C NMR signals were observed for compound **2i**, in which a bulky phenoxy group occupies one of the *ortho* positions (R_2 in Scheme 2), presumably due to the presence of a pair of isomers with *anti* and *syn* configurations. The ratio of ∼1.5 remains largely unchanged upon dilution or heating to 60 °C.[22] We were also able to obtain crystals of **2d** for single-crystal X-ray diffraction analysis, which confirmed the mononuclear, distorted-tetrahedral geometry around the aluminum center, despite the low quality of the data (see Figure S14 and Table S1, Supporting Information).[22] Attempts to obtain pentacoordinate Al complexes of the formula $(L)_2AlMe$ by using a 2:1 ratio of ligand to $AlMe_3$ have been unsuccessful.

Polymerization of *rac*-Lactide. The aluminum complexes were tested as initiators for *rac*-lactide ROP, and the results are summarized in Table 1. The polymerizations were typically conducted in dry toluene at 80 °C with concentrations of *rac*-lactide (0.50 M), catalyst (10 mM), and benzyl alcohol, BnOH (10 mM). The reaction progress was monitored by taking regular aliquots which were analyzed by ^{1}H NMR spectroscopy. Under catalytic conditions, it was generally assumed that benzyl alcohol reacted with the dimethylaluminum compound to generate an alkoxide complex that initiated the polymerization reaction. However, such a (L)Al(Me)(OBn) complex could not be clearly identified in the stoichiometric reaction between 1 equiv of benzyl alcohol and **2a**. When 2 equiv of BnOH was employed in the catalytic reaction, the conversion of *rac*-lactide was very poor, likely due to demetalation of the Al catalyst by excess alcohol. In the absence of an exogenous alcohol, these complexes led to very little conversion of lactide. Mixing of stoichiometric amounts of compound **2c** and *rac*-LA showed no sign of reaction. Complexes **2b**,**d**,**f** with 2,6-dimethyl substituents were not effective; less than 15% conversion was observed after 24 h (entries 3, 6, and 10, Table 1), while the rest of the aluminum catalysts achieved >93% conversion under identical conditions. Presumably the steric bulk played a considerable role in inhibiting the polymerization.[21] However, in the case of **2i**, where only one R_2 substituent (see Scheme 2) was present, reactivity was observed comparable to that of unsubstituted complexes (entry 13). Furthermore, experiments conducted in THF at 60 °C were much slower than in toluene, likely due to the coordinating nature of THF and lower temperatures (entry 9). When an L-lactide was employed with **2c**, a perfectly isotactic PLA (PLLA) with P_m = 1 was obtained and no epimerization was detected (entry 5). The observed molecular weights of PLA are typically lower than or close to the calculated values based on conversions, and the molecular weight distributions are somewhat broad (1.2−1.7). MALDI-TOF mass spectrometry (Figure S7, Supporting Information) analysis of the polymer generated by **2c** revealed the presence of the benzyloxy end group, supporting the alkoxide as the initiating group. Furthermore, the presence of a series of peaks separated by a mass unit of 72 indicates considerable transesterification during the polymerization.

One of our main goals was to investigate if these chiral catalysts could induce stereoselectivity in the ROP of *rac*-lactide. Thus, the microstructure (or tacticity) of the resulting PLA, in particular the probability of isotactic enchainment at the diad level, P_m, was assessed by integration of the methine region of the homonuclear decoupled ^{1}H NMR spectrum (Table 1). It is noteworthy that a range of stereoselectivities was observed. While two of the initiators (**2c**,**g**) lead to isotactic enrichment, the remaining initiators lead to heterotactic enrichment. Among this series of catalysts, **2c** showed the highest isoselectivity (P_m = 0.61), while **2a** (P_r = 0.69) and **2e** (P_r = 0.74) were heterotactically inclined. Apparently the electron-withdrawing ability and the bulkiness of the phenyl group at R_1 may be responsible for the increase in isoselectivity. Compound **2g** also exhibited a slight isotactic bias (P_m = 0.57), which again was attributed to the presence of a strong electron-withdrawing group at R_3. On the basis of these considerations, **2i** with a phenoxy group at the R_2 position was expected to have high heteroselectivity. However, a P_r value of 0.58 was observed. This might be accounted for by the presence of *anti* and *syn* isomers of **2i**. Although the stereoselectivity observed was not particularly high, the findings here are interesting because the change of selectivity was due to the variation of substituents on R_1, R_3, and R_4 in the similar initiator structures. Such a strategy of modulation of tacticity by changing substituents has been utilized in other aluminum[13] and zirconium[24] systems.

We also tested representative catalysts under bulk/melt conditions at 130 °C, since such conditions require no solvent and allow high temperature and high monomer concentration, leading to shorter reaction time and higher turnover frequency.[25] Selected results are summarized in Table 2. Indeed, these aluminum compounds functioned as initiators for ROP of *rac*-lactides with low catalyst loads (0.25 mol %) and much shorter reaction times (1.0−1.5 h). In addition, the alcohol cocatalyst was not required under bulk conditions and

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therefore not employed in the above runs. The actual nature of initiating groups is likely to be external nucleophilic impurities. Even **2f** with the bulky 2,6-dimethylphenyl group showed a higher conversion (31% vs 12% in solution). The molecular weights were typically lower than the theoretical values (except for **2i**, where a much higher M_n was obtained) and the molecular weight distributions tended to be broader than the solution polymerizations. This may be due to diffusional constraints imposed by the elevated viscosities found in bulk polymerizations, particularly at high conversions. However, the conversion of *rac*-lactide in these reactions seems to reach a plateau of around 70−80%. One likely reason is that the mobility of the monomer is reduced due to viscosity-induced diffusional constraint, and the reaction slows down considerably. Another interesting observation is the variation of selectivity as judged by P_m. For example, **2a**,**e** showed a moderate heteroselectivity under normal solution conditions but became essentially nonselective under bulk conditions. In contrast, the isoselectivity for **2c**,**g** remained the same under both normal and bulk conditions.

To further probe the catalyst factors that may influence the activity in ROP of *rac*-lactide, the polymerization kinetics were monitored for the six active initiators (**2a**,**c**,**e**,**g**−**i**) in combination with 1 equiv (vs Al) of BnOH. All of them showed a first-order dependence on lactide concentration up to 80% conversion, as judged by the linear relationship of $\ln([LA]_0/[LA]_t)$ versus time (Figure 1). The pseudo-first-order rate constants, k_{obs}, were obtained from the slope of these linear plots and are given in Table 3. Among the six Al complexes, the apparent first-order rate constants follow the order **2a** > **2h** > **2e** ≈ **2g** ≈ **2i** > **2c**. The trend can be understood, at least in part, on the basis of steric and electronic considerations. In the **2a**,**g**−**i** series, where the oxazoline moiety is the same, both the electron-withdrawing groups at R_3 and electron-donating groups at R_4 result in lowered reactivity, which may suggest a delicate sensitivity of reactivity vs Lewis acidity of the metal center.[26] The enhanced Lewis acidity induced by electron-withdrawing groups may lead to preferred coordination of lactide monomer, but it could also inhibit the subsequent insertion step. It is also worth noting that the two catalysts (**2c**,**g**) with a preference for isotacticity are less active catalysts. In addition, kinetic measurements for the polymerization of L-lactide by **2c** revealed rates very similar to those for *rac*-lactide. Analogous kinetic results have been observed for a highly isoselective aluminum complex.[12a]

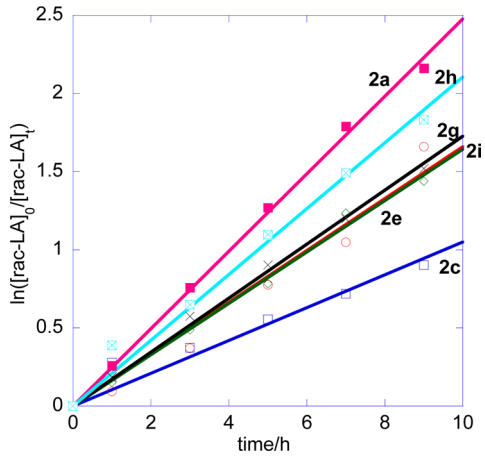

Figure 1. Semilogarithmic plot of *rac*-lactide conversion vs time catalyzed by complexes **2** in toluene at 80 °C.

Table 3. Apparent Rate Constants (k_{obs}) for the Polymerization of *rac*-Lactide[a]

entry	cat.	k_{obs} (h^{-1})	entry	cat.	k_{obs} (h^{-1})
1	**2a**	0.248 (±0.009)	5	**2g**	0.173 (±0.006)
2	**2c**	0.11 (±0.04)	6	**2h**	0.21 (±0.04)
3[b]	**2c**	0.09 (±0.02)	7	**2i**	0.17 (±0.06)
4	**2e**	0.16 (±0.01)			

[a]The kinetic experiments were run in the presence of 1 equiv of BnOH (vs Al catalysts); see Experimental section for details. [b]L-Lactide was used.

CONCLUSIONS

In conclusion, a series of aluminum complexes containing chiral, bidentate anilido-oxazolinate ligands have been synthesized and characterized. These complexes were tested in the ring-opening polymerization of *rac*-lactide in the presence of benzylic alcohol, and six of them were effective in promoting the polymerization, while the other three with 2,6-dimethylphenyl substituents showed low catalytic reactivity. The microstructure of the resulting polylactides ranged from slightly isotactic to moderately heterotactic. The reactivity and selectivity can be roughly understood on the basis of steric and electronic factors of substituents on several specific positions of the ligand framework. Taken together, these results indicate that electron-withdrawing groups on this series of aluminum compounds tend to give slower, but isoselective, catalysts for the ROP of *rac*-LA. Studies further delineating these factors in catalysis are underway.

EXPERIMENTAL SECTION

General Considerations. All reactions that involved compounds sensitive to air and/or moisture were carried out under a dry nitrogen atmosphere using freshly dried solvents and standard Schlenk line and glovebox techniques. All chemicals were purchased from commercial sources. Toluene, hexanes, and THF were distilled under nitrogen from Na/benzophenone. $CDCl_3$ was dried over CaH_2, distilled, and degassed prior to use. *rac*-LA was recrystallized from dry toluene, sublimed under vacuum, and stored under a dry nitrogen atmosphere.

NMR spectra were recorded on a Bruker AVANCE-500 NMR spectrometer (^1H, and ^{13}C) and referenced to the residual solvent peak. *J* values are given in Hz. Gel permeation chromatography (GPC) analysis was performed on a Varian Prostar instrument, using a PLgel 5 μm Mixed-D column, a Prostar 355 RI detector, and THF as eluent at a flow rate of 1 mL/min (20 °C). Polystyrene standards were used for calibration. Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS) spectra were obtained on Applied Biosystems/MD SCIEX 4800 equipment using α-cyano-4-hydroxycinnamic acid as a matrix and 5 mM sodium acetate as an ionization agent. The HR-MS was performed using high-resolution time-of-flight G1969A instrumentation (Agilent). The optical rotation was measured on a Jasco P-2000 polarimeter with a 589 nm light source at 23 °C.

Synthesis of Ligands. Similar ligands have been obtained previously;[20] the following example is typical. To a round-bottom flask were added 2-bromobenzaldehyde (6.5 mmol), 1 equiv of amino alcohol, and 25 mL of toluene. After the mixture was stirred for 24 h, K_3PO_4 (19.5 mmol) and NBS (13.0 mmol) were added and stirring was continued for 5 h at room temperature. After filtration, the mixture was washed three times with $NaHCO_3$ and H_2O. The organic fraction was dried with Na_2SO_4 and purified by column to the give the oxazoline precursors. The product was mixed with 120 mol % of

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aniline, 5 mol % of $Pd(OAc)_2$, 5 mol % of *rac*-BINAP, 140 mol % of sodium *tert*-butoxide, and 15 mL of dry toluene in a Schlenk flask under nitrogen. The mixture was heated to 100 °C for 48 h and then filtered and purified by column. The desired ligands were usually obtained as yellow-orange oils ($\mathbf{HL^{1a-c}}$ and $\mathbf{HL^{1e-h}}$) or crystalline solids ($\mathbf{HL^{1d}}$ and $\mathbf{HL^{1i}}$) in ∼66−89% yields. Characterizations of $\mathbf{HL^{1b,d,f}}$ have been reported previously.[20]

*(4S)-4,5-Dihydro-2-(2′-anilinophenyl)-4-isopropyloxazole (**HL^1a**).* Yield: 1.0 g (3.57 mmol), 86%. ^{1}H NMR ($CDCl_3$, 298 K): δ 10.55 (1H, s, N*H*), 7.73 (1H, d, Ar*H*), 7.28 (4H, m, Ar*H*), 7.20 (2H, d, Ar*H*), 6.97 (1H, t, Ar*H*), 4.29 (1H, m, NCH(R)CH_2O), 4.05 (1H, m, NC*H*(R)CH_2O), 3.96 (1H, m, NCH(R)CH_2O), 1.71 (1H, m, C*H*CH_3), 0.97 (3H, d, CHCH_3), 0.88 (3H, d, CHCH_3). ^{13}C NMR ($CDCl_3$, 298 K): δ 163.75 (*C*═N), 145.73, 141.74, 132.09, 130.12, 129.51, 122.77, 121.55, 117.10, 113.28, 110.59, 73.16 (NCH(R)-CH_2O), 69.28 (NCH(R)CH_2O), 33.59 (*C*HMe$_2$), 19.24 (CH*Me*$_2$), 19.02 (CH*Me*$_2$). GC/MS: *m*/*z* 280.0 $[M]^+$, 237.0 (100), 206.9, 193.9, 179.9, 166.9. HRMS (EI^+): *m*/*z* calcd for $C_{18}H_{21}N_2O$ $[M + H]^+$ 281.16539; found 281.16457.

*(4R)-4,5-Dihydro-2-(2′-anilinophenyl)-4-phenyloxazole (**HL^1c**).*[27] Yield: 304 mg (0.968 mmol), 88%. ^{1}H NMR ($CDCl_3$, 298 K): δ 10.39 (1H, s, N*H*), 7.80 (1H, d, Ar*H*), 7.22 (6H, m, Ar*H*), 7.17−7.15 (3H, m, Ar*H*), 7.08 (2H, t, Ar*H*), 6.96 (1H, t, Ar*H*), 6.69 (1H, t, Ar*H*), 5.39 (1H, m, NCH(R)CH_2O), 4.63 (1H, m, NC*H*(R)CH_2O), 4.06 (1H, m, NCH(R)CH_2O). ^{13}C NMR ($CDCl_3$, 298 K): δ 165.25, 146.25, 142.69, 141.44, 132.48, 130.40, 129.45, 128.97, 127.78, 126.73, 123.21, 122.32, 117.11, 113.36, 110.10, 73.31 (NCH(R)CH_2O), 70.32 (NCH(R)CH_2O). GC/MS: *m*/*z* 314 $[M]^+$, 283, 205, 194 (100), 167, 91. HRMS (EI^+): *m*/*z* calcd for $C_{21}H_{18}N_2O$ $[M]^+$ 314.14191; found 314.14866.

*(4R)-4,5-Dihydro-2-(2′-anilinophenyl)-4-isobutyloxazole (**HL^1e**).* Yield: 254 mg (0.861 mmol), 86%. ^{1}H NMR ($CDCl_3$, 298 K): δ 10.48 (1H, s, N*H*), 7.73 (1H, d, Ar*H*), 7.26 (4H, m, Ar*H*), 7.18 (2H, t, Ar*H*), 6.97 (1H, t, Ar*H*), 6.67 (1H, t, Ar*H*), 4.35 (2H, m, NCH(R)CH_2O), 3.82 (1H, t, NC*H*(R)CH_2O), 1.80 (1H, m CH_2CH), 1.59 (1H, m, CH_2CH), 1.36 (1H, m, CH_2C*H*), 0.93 (6H, m, CHCH_3). ^{13}C NMR ($CDCl_3$, 298 K): δ 163.45, 145.54, 141.49, 131.86, 129.90, 129.27, 122.66, 121.56, 116.93, 113.11, 110.44, 71.48 (NC*H*(R)CH_2O), 65.17 (NCH(R)CH_2O), 45.65 (CH_2CHMe$_2$), 25.84 (CH_2C*H*Me$_2$), 22.98 (CH_2CH*Me*$_2$), 22.64 (CH_2CH*Me*$_2$). GC/MS: *m*/*z* 294 $[M]^+$ (100), 263, 237, 194, 167, 139. HRMS (EI^+): *m*/*z* calcd for $C_{19}H_{23}N_2O$ $[M + H]^+$ 295.18104; found 295.18182.

*(4S)-4,5-Dihydro-2-(2′-(3,5-bis(trifluoromethyl)anilino)phenyl)-4-isopropyloxazole (**HL^1g**).* Yield: 670 mg (1.61 mmol), 87%. ^{1}H NMR ($CDCl_3$, 298 K): δ 11.00 (1H, s, N*H*), 7.74 (1H, d, Ar*H*), 7.50 (2H, s, Ar*H*), 7.30−7.27 (3H, m, Ar*H*), 6.80 (1H, t, Ar*H*), 4.28 (1H, m, NCH(R)CH_2O), 4.04 (1H, m, NC*H*(R)CH_2O), 3.95 (1H, m, NCH(R)CH_2O), 1.70 (1H, m,C*H*CH_3), 0.93 (3H, d, CHCH_3), 0.84 (3H, d, CHCH_3). ^{13}C NMR ($CDCl_3$, 298 K): δ 163.66, 143.79, 143.49, 133.01, 132.74, 132.40, 130.50, 124.66, 122.48, 119.65, 118.89, 114.82, 114.30, 112.59, 72.99 (NCH(R)CH_2O), 69.47 (NCH(R)CH_2O), 33.47 (*C*HMe$_2$), 19.14 (CH*Me*$_2$), 18.88 (CH*Me*$_2$). GC/MS: *m*/*z* 416 $[M]^+$, 373 (100), 345, 316, 291, 234, 182. HRMS (EI^+): *m*/*z* calcd for $C_{20}H_{19}N_2OF_6$ $[M + H]^+$ 417.14016; found 417.14115.

*(4S)-4,5-Dihydro-2-(2′-(4-methoxyanilino)phenyl)-4-isopropyloxazole (**HL^1h**).* Yield: 558 mg (1.79 mmol), 84%. ^{1}H NMR ($CDCl_3$, 298 K): δ 10.36 (1H, s, N*H*), 7.80 (1H, d, Ar*H*), 7.22 (3H, d, Ar*H*), 7.11 (1H, d, Ar*H*); 6.93 (2H, d, Ar*H*), 6.70 (1H, t, Ar*H*), 4.38 (1H, t, NCH(R)CH_2O), 4.15 (1H, m, NC*H*(R)CH_2O), 4.06 (1H, t, NCH(R)CH_2O), 3.83 (3H, s, ArO*Me*), 1.82 (1H, m, C*H*CH_3), 1.06 (3H, d, CHCH_3), 0.96 (3H, d, CHCH_3). ^{13}C NMR ($CDCl_3$, 298 K): δ 163.36 (*C*═N), 156.28, 147.33, 134.47, 132.13, 130.03, 125.10, 116.19, 114.76, 112.46, 109.58, 73.08 (NCH(R)CH_2O), 69.10 (NCH(R)CH_2O), 55.75 (ArO*Me*), 33.50 (*C*HMe$_2$), 19.26 (CH*Me*$_2$), 18.97 (CH*Me*$_2$). GC/MS: *m*/*z* 310 $[M]^+$ (100), 267, 237, 209, 182, 154. HRMS (EI^+): *m*/*z* calcd for $C_{19}H_{23}N_2O_2$ $[M + H]^+$ 311.17595; found 311.17612.

*(4S)-4,5-Dihydro-2-(2′-(2-phenoxyanilino)phenyl)-4-isopropyloxazole (**HL^1i**).* Yield: 659 mg (1.77 mmol), 88%. ^{1}H NMR ($CDCl_3$, 298 K): δ 10.63 (1H, s, N*H*), 7.79 (1H, d, Ar*H*), 7.63 (3H, d, Ar*H*), 7.46(1H, d, Ar*H*), 7.29(2H, m, Ar*H*), 7.11(1H, m, Ar*H*), 7.03(2H, m, Ar*H*), 6.97(4H, m, Ar*H*), 6.78(1H, m, Ar*H*), 4.31 (1H, t, NC*H*(R)CH_2O), 4.00 (2H, m, NCH(R)CH_2O), 1.65 (1H, m, C*H*CH_3), 0.93 (3H, d, CHCH_3), 0.85 (3H, d, CHCH_3). ^{13}C NMR ($CDCl_3$, 298 K): δ 163.33 (*C*═N), 157.78, 148.29, 144.95, 133.89, 131.84, 130.12, 129.69, 124.08, 122.89, 122.71, 120.92, 120.40, 118.20, 117.50, 113.75, 111.59, 73.15 (NCH(R)CH_2O), 69.18 (NCH(R)CH_2O), 33.29 (*C*HMe$_2$), 19.17 (CH*Me*$_2$), 18.86 (CH*Me*$_2$). GC/MS: *m*/*z* 372 $[M]^+$, 329, 299, 286 (100), 245, 209, 167. HRMS (EI^+): *m*/*z* calcd for $C_{24}H_{25}N_2O_2$ $[M + H]^+$ 373.19160; found 373.18851.

Synthesis of Aluminum Complexes. In a typical procedure, ligand $\mathbf{HL^1}$ (1.0 mmol) was mixed with 1.2 or 1.5 equiv of $AlMe_3$ in toluene. The mixture was stirred under nitrogen at room temperature for 12 h. After removal of toluene in vacuo, the resulting yellow-orange residue was extracted multiple times with dry hexanes and combined. The solvent was then removed in vacuo at low temperature, affording the product as a yellow powder. The products can be further purified by recrystallization from a dichloromethane−hexane solution.

*(**L^1a**)AlMe$_2$ (**2a**).*[28] Yield: 315 mg (0.935 mmol), 69%. $[\alpha]_D$ = +359° (*c* 1.5, toluene). ^{1}H NMR ($CDCl_3$, 298 K): δ 7.67 (1H, d, *J* = 10, Ar*H*), 7.39 (2H, m, Ar*H*), 7.19 (1H, t, *J* = 10, Ar*H*), 7.09 (3H, m, Ar*H*), 6.45 (2H, m, Ar*H*), 4.44 (3H, m, NC*H*(R)CH_2O), 2.33 (1H, m, C*H*Me$_2$), 0.99 (3H, d, *J* = 10, CH(CH_3)$_2$), 0.91 (3H, d, J =10, J = CH(CH_3)$_2$), −0.86 (3H, s, Al*Me*), −0.89 (3H, s, Al*Me*). ^{13}C NMR ($CDCl_3$, 298 K): δ 169.87 (*C*═N), 157.07, 147.12, 135.32, 130.74, 129.94, 128.33, 124.81, 117.21, 113.75, 105.04, 67.90 (NCH(R)CH_2O), 67.57 (NCH(R)CH_2O), 29.94 (*C*HMe$_2$), 19.51 (CH*Me*$_2$), 14.33 (CH*Me*$_2$), −7.77 (AlCH$_3$), −9.93 (AlCH$_3$).

*(**L^1b**)AlMe$_2$ (**2b**).*[28] Yield: 252 mg (0.690 mmol), 69%. $[\alpha]_D$ = +96.7° (*c* 0.667, toluene). ^{1}H NMR ($CDCl_3$, 298 K): δ 7.70 (1H, d, *J* = 10, Ar*H*), 7.12 (2H, m, Ar*H*), 7.08 (2H, m, Ar*H*), 6.45 (1H, t, *J* = 5, Ar*H*), 6.05 (1H, d, *J* = 5, Ar*H*), 4.48 (3H, m, NC*H*(R)CH_2O), 2.35 (1H, m, C*H*Me$_2$), 2.12 (3H, s, Ar*Me*), 2.10 (3H, s, Ar*Me*), 0.99 (3H, d, *J* = 10, CH(CH_3)$_2$), 0.90 (3H, d, *J* = 10, CH(CH_3)$_2$), −0.88 (3H, s, Al*Me*), −0.93 (3H, s, Al*Me*). ^{13}C NMR ($CDCl_3$, 298 K): δ 169.99, (*C*═N), 156.16, 143.21, 137.05, 136.82, 135.77, 130.98, 128.92, 128.87, 125.41, 116.19, 113.63, 104.50, 67.75 (NCH(R)CH_2O), 67.54 (NCH(R)CH_2O), 29.89 (*C*HMe$_2$), 19.44 (CH*Me*$_2$), 18.69 (ArCH$_3$), 18.64 (ArCH$_3$), 14.27 (CH*Me*$_2$), −8.25 (AlCH$_3$), −8.96 (AlCH$_3$).

*(**L^1c**)AlMe$_2$ (**2c**).* Yield: 200 mg (0.539 mmol), 53%. $[\alpha]_D$ = −422° (*c* 3.86, toluene). ^{1}H NMR ($CDCl_3$, 298 K): δ 7.77 (1H, d, *J* = 10, Ar*H*), 7.5−7.3 (7H, m, Ar*H*), 7.15 (2H, m, Ar*H*); 7.05 (2H, m, Ar*H*), 6.50 (1H, t, *J* = 10, Ar*H*), 6.43 (1H, d, *J* = 10, Ar*H*), 5.36 (1H, m, NC*H*(R)CH_2O), 4.96 (1H, m, NCH(R)CH_2O), 4.57 (1H, m, NCH(R)CH_2O), −0.94 (3H, s, Al*Me*), −1.55 (3H, s, Al*Me*). ^{13}C NMR ($CDCl_3$, 298 K): δ 170.18 (*C*═N), 157.33, 146.94, 138.47, 135.68, 130.88, 129.95, 129.43, 129.35, 128.24 128.05, 124.86, 117.32, 113.84, 104.59, 75.28 (NCH(R)CH_2O), 66.98 (NC*H*(R)CH_2O), −9.00 (*Me*Al), −9.79 (*Me*Al). Anal. Calcd for $C_{23}H_{23}N_2OAl$: C, 74.58; H, 6.26; N, 7.56. Found: C, 74.20; H 6.33; N, 7.55.

*(**L^1d**)AlMe$_2$ (**2d**).* Yield: 98.4 mg (0.247 mmol), 50%. $[\alpha]_D$ = −162° (*c* 2.62, toluene). ^{1}H NMR ($CDCl_3$, 298 K): δ 7.80 (1H, d, *J* = 10, Ar*H*), 7.40 (3H, m, Ar*H*), 7.35 (2H, m, Ar*H*), 7.09 (3H, m, Ar*H*), 7.04 (1H, m, Ar*H*), 6.49 (1H, t, *J* = 10, Ar*H*), 6.06 (1H, d, *J* = 10, Ar*H*), 5.37 (1H, m, NCH(R)CH_2O), 5.01 (1H, m, NC*H*(R)CH_2O), 4.58 (1H, m, NCH(R)CH_2O), 2.11 (3H, s, Ar*Me*), 2.04 (3H, s, Ar*Me*), −0.92 (3H, s, Al*Me*), −1.62 (3H, s, Al*Me*). ^{13}C NMR ($CDCl_3$, 298 K): δ 170.30 (*C*═N), 156.42, 143.05, 138.86, 136.97, 136.68, 136.00, 131.06, 129.34, 128.83, 127.91, 125.38, 116.26, 113.68, 104.11, 75.38 (NCH(R)CH_2O), 66.94 (NCH(R)CH_2O), 18.58 (*Me*Ph), −9.08 (*Me*Al), −9.46 (*Me*Al). Anal. Calcd for $C_{25}H_{27}N_2OAl$: C, 75.35; H, 6.83; N, 7.03. Found: C, 77.33; H, 7.18; N, 7.08.

*(**L^1e**)AlMe$_2$ (**2e**).* Yield: 245 mg (0.698 mmol), 67%. $[\alpha]_D$ = −388° (*c* 1.73, toluene). ^{1}H NMR ($CDCl_3$, 298 K):): δ 7.68 (1H, d, *J* = 10, Ar*H*), 7.38 (2H, m, Ar*H*), 7.19 (1H, m, Ar*H*), 7.11 (3H, m, Ar*H*), 6.45 (2H, m, Ar*H*), 4.72 (1H, m, NC*H*(R)CH_2O), 4.41 (1H, m, NCH(R)CH_2O), 4.23 (1H, m, NCH(R)CH_2O), 1.95 (1H, m, C*H*CH_3), 1.62 (2H, m, CH_2CH), 0.99 (6H, m, CH(CH_3)$_2$), −0.85 (3H, s, Al*Me*), −0.90 (3H, s, Al*Me*). ^{13}C NMR ($CDCl_3$, 298 K): δ

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169.72, 157.12, 147.17, 135.36, 130.71, 129.99, 128.34, 124.84, 117.25, 113.81, 105.22, 73.21 (NCH(R)CH_2O), 62.01 (NCH(R)CH_2O), 44.06 (CH_2CHMe_2), 25.94 (CH_2CHMe_2), 23.91 ($CHMe_2$), 21.70 ($CHMe_2$), −6.85 (*Me*Al), −9.98 (*Me*Al). Anal. Calcd for $C_{21}H_{27}N_2OAl$: C, 71.98; H, 7.77; N, 7.99. Found: C, 70.64; H, 7.34; N, 7.59.[28]

(L[1f])AlMe$_2$ (2f). Yield: 343 mg (0.905 mmol), 90%. $[\alpha]_D$ = −150° (*c* 2.1, toluene). ^{1}H NMR ($CDCl_3$, 298 K): δ 7.71 (1H, d, *J* = 10, Ar*H*), 7.15 (3H, m, Ar*H*), 7.08 (1H, d, *J* = 10, Ar*H*), 6.45 (1H, t, *J* = 10, Ar*H*), 6.05 (1H, d, *J* = 10, Ar*H*), 4.73 (1H, m, NC*H*(R)CH_2O), 4.42 (1H, m, NCH(R)CH_2O), 4.25 (1H, m, NCH(R)CH_2O), 2.12 (3H, s, Ar*Me*), 2.10 (3H, s, Ar*Me*), 1.96 (1H, m, C*H*CH_3), 1.62 (2H, m,CH_2CH), 1.00 (6H, m, CHCH_3), −0.88 (3H, s, Al*Me*), −0.89 (3H, s, Al*Me*). ^{13}C NMR ($CDCl_3$, 298 K): δ 169.79 (*C*═N), 156.05, 143.15, 137.08, 136.73, 135.69, 130.81, 128.93, 128.83, 125.37, 116.13, 113.59, 104.66, 73.18 (NCH(R)CH_2O), 61.94 (NCH(R)CH_2O), 44.05 (C$CHCH_3$), 25.91 (CHCH_2CH), 24.00 (CH*Me*), 21.70 (CH*Me*), 18.76 (*Me*Ph), −7.17 (*Me*Al), −9.28 (*Me*Al). Anal. Calcd for $C_{23}H_{31}N_2OAl$: C, 72.99; H, 8.26; N, 7.40. Found: C, 72.76; H, 8.47; N, 7.19.

(L[1g])AlMe$_2$ (2g).[28] Yield: 224 mg (0.474 mmol), 95%. $[\alpha]_D$ = +304° (*c* 1.77, toluene). ^{1}H NMR ($CDCl_3$, 298 K): δ 7.65 (1H, d, *J* = 5, Ar*H*), 7.52 (1H, s, Ar*H*), 7.46 (2H, s, Ar*H*), 7.14 (1H, m, Ar*H*), 6.55 (1H, t, *J* = 5, Ar*H*), 6.48 (1H, d, *J* = 5, Ar*H*), 4.44 (2H, m, NCH(R)CH_2O), 4.34 (1H, m, NC*H*(R)CH_2O), 2.23 (1H, m, C*H*CH_3), 0.91 (3H, d, *J* = 5, CHCH_3), 0.82 (3H, d, *J* = 5, CHCH_3), −0.92 (3H, s, Al*Me*), −0.97 (3H, s, Al*Me*). ^{13}C NMR ($CDCl_3$, 298 K): δ 169.96 (*C*═N), 155.60, 150.27, 135.90, 133.20 (quartet, CF_3), 131.14, 127.58, 124.81, 122.53, 117.84, 117.41, 116.20, 107.31, 68.14 (NCH(R)CH_2O), 68.08 (NCH(R)CH_2O), 30.03 ($CHMe_2$), 19.37 ($CHMe_2$), 14.38 ($CHMe_2$), −7.88 ($AlCH_3$), −10.30 ($AlCH_3$).

(L[1h])AlMe$_2$ (2h). Yield: 308 mg (0.839 mmol), 84%. $[\alpha]_D$ = +187° (*c* 2.03, toluene). ^{1}H NMR ($CDCl_3$, 298 K): δ 7.66 (1H, d, *J* = 10, Ar*H*), 7.11 (1H, m, Ar*H*), 6.98 (4H, m, Ar*H*), 6.43 (1H, t, *J* = 10, Ar*H*), 6.38 (1H, d, *J* = 10, Ar*H*), 4.48 (3H, m, NC*H*(R)CH_2O), 3.86 (3H, s, ArO*Me*), 2.33 (1H, m, C*H*CH_3), 0.99 (3H, d, *J* = 10, CHCH_3), 0.90 (3H, d, *J* = 10, CHCH_3), −0.87 (3H, s, Al*Me*), −0.89 (3H, s, Al*Me*). ^{13}C NMR ($CDCl_3$, 298 K): δ 170.22 (*C*═N), 157.67, 156.22, 141.25, 135.69, 130.75, 129.56, 117.12, 116.91, 113.68, 104.89, 68.06 (NCH(R)CH_2O), 67.64 (OCH_3), 58.28 (NCH(R)CH_2O), 30.01 (C$CHCH_3$), 19.57 (CH*Me*), 14.37 (CH*Me*), −8.37 (*Me*Al), −9.90 (*Me*Al). Anal. Calcd for $C_{21}H_{27}N_2O_2Al$: C, 68.83; H, 7.43; N, 7.64. Found: C, 68.36; H, 7.62; N, 7.50.

(L[1i])AlMe$_2$ (2i). Yield: 381 mg (0.888 mmol), 86%. $[\alpha]_D$ = +468° (*c* 2.5, toluene). The compound exists as two isomers in ∼1.5:1.0 ratio, presumably the anti and syn isomers due to the orientation of the *o*-PhO group. ^{1}H NMR ($CDCl_3$, 298 K): *anti*-**2i**, δ 7.47 (1H, d, *J* = 5, Ar*H*), 6.58 (1H, d, *J* = 10, Ar*H*), 6.52 (2H, d, *J* = 10, *o*-C_6H_5O), 6.48 (m, 1H, Ar*H*), 4.02 (m, 1H, oxazoline−C*H*), 2.12 (m, 1H, C*H*Me_2), 0.85 (d, 3H, *J* = 5, CHMe_2), 0.76 (d, 3H, *J* = 5, CHMe_2), −0.91 (s, 3H, Al*Me*), −1.06 (s, 3H, Al*Me*); *syn*-**2i**, δ 7.56 (1H, d, *J* = 10, Ar*H*), 6.80 (1H, d, *J* = 5, Ar*H*), 6.70 (2H, d, *J* = 5, *o*-C_6H_5O), 6.48 (m, 1H, Ar*H*), 2.18 (m, 1H, C*H*Me_2), 0.85 (d, 3H, *J* = 5, CHMe_2), 0.66 (d, 3H, *J* = 5, CHMe_2), −0.87 (s, 3H, Al*Me*), −1.06 (s, 3H, Al*Me*). The rest of the signals at δ 7.22−6.82 for aromatic protons and at δ 4.42−4.20 for oxazoline protons show considerable overlap and are not resolved. ^{13}C NMR ($CDCl_3$, 298 K): *anti*-**2i**, δ 169.29 (*C*═N), 157.08 (*ipso*-*C*), 155.54 (*ipso*-*C*), 151.32 (*ipso*-*C*), 139.04 (*ipso*-*C*), 134.58, 129.87, 129.03 (*m*-C_6H_5O), 128.81, 124.88, 124.68, 122.17, 121.07, 119.13, 118.38 (*o*-C_6H_5O), 115.03, 107.22 (*ipso*-*C*), 67.95, 67.81, 30.05 ($CHMe_2$), 19.35 ($CHMe_2$), 14.49 ($CHMe_2$), −7.51 (Al*Me*), −11.16 (Al*Me*); *syn*-**2i**, δ 169.37 (*C*═N), 156.54 (*ipso*-*C*), 156.03 (*ipso*-*C*), 152.79 (*ipso*-*C*), 138.90 (*ipso*-*C*), 134.65, 130.16, 129.61 (*m*-C_6H_5O), 127.92, 124.35, 124.07, 123.47, 119.80 (*o*-C_6H_5O), 119.03, 118.63, 114.91, 107.07 (*ipso*-*C*), 68.16, 67.69, 29.80 ($CHMe_2$), 19.48 ($CHMe_2$), 14.30 ($CHMe_2$), −8.78 (Al*Me*), −9.53 (Al*Me*). Anal. Calcd for $C_{26}H_{29}N_2O_2Al$: C, 72.88; H, 6.82; N, 6.54. Found: C, 72.70; H, 6.76; N, 6.43.

Polymerization of *rac*-Lactide. A typical solution polymerization procedure was exemplified by the following: *rac*-lactide (0.71 g, 4.9 mmol), benzyl alcohol (10.3 μL, 0.10 mmol), Al complex (0.10 mmol), and toluene (8.0 mL) were placed in a Schlenk flask. The reaction mixture was heated in an oil bath preset at 80 °C. The conversion of *rac*-lactide was monitored by periodically taking samples via ^{1}H NMR spectroscopic analyses. Typical conversions were 92−99% after 24 h (except for compounds **2b**,**d**,**f**). At the end of the reaction, the polymer was isolated by precipitation from a CH_2Cl_2 solution. The tacticity was determined by a homonuclear decoupled ^{1}H NMR spectrum in the methine region (5.25−5.15 ppm), which can be assigned according to the literature.[29]

The bulk polymerization was performed by heating *rac*-lactide (2.84 g, 19.8 mmol) and an Al catalyst (0.050 mmol) in a Schlenk flask under nitrogen with an oil bath preset at 130 °C. The heating was discontinued when the melt became very viscous and stirring stopped, usually within 2 h. The resulting reaction mixture was analyzed by ^{1}H NMR spectroscopy to determine the conversion of lactide and tacticity of PLA.

Kinetic Runs. A Schlenk flask was loaded with *rac*-lactide, Al catalyst (2 mol %), benzyl alcohol (2 mol %, 1 equiv vs catalyst), and toluene such that [*rac*-LA] = 0.50 M under nitrogen. The flask was then heated to 80 °C via an oil bath. At preset time intervals, an aliquot (0.1 mL) was withdrawn and quenched with MeOH or CH_2Cl_2. The solvent was then removed in vacuo, and the conversion of lactide was determined by ^{1}H NMR spectroscopy. The apparent first-order rate constants were obtained by the slope of linear fit of semilogarithmic plot of *rac*-lactide conversion vs time, using the KaleidaGraph program (version 4.0).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Text, figures, and tables giving experimental details, representative ^{1}H and ^{13}C NMR spectra of aluminum complexes, MALDI MS of a PLA sample, and structural data for **2d**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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