Aluminum Complexes with Bidentate N,N-Dialkylaniline–arylamido Ligands: Synthesis, Structures, and Catalytic Properties for Efficient Ring-Opening **Polymerization of ε-Caprolactone**

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A number of Al complexes bearing bidentate N,N-dialkylaniline-arylamido ligands, ortho-(ArNCH₂)C₆H₄NR₂AlMe₂ $(R = Me, Ar = 2,6 \text{-} i Pr_2 C_6 H_3, \textbf{ 3a}; 2,6 \text{-} Et_2 C_6 H_3, \textbf{ 3b}; 2,6 \text{-}$ $Me_2C_6H_{3}$, **3c**; 4-MeC_6H_4, **3d**; Ph, **3e**; and R = Et, Ar = 2,6 $iPr_2C_6H_3$, **3f**; 2,6-Me₂C₆H₃, **3g**; Ph, **3h**), have been synthesized from the reaction of the corresponding free ligands, or $tho-(ArNHCH_2)C_6H_4NR_2$ (R = Me, Ar = 2,6-*i*Pr₂C₆H₃, **2a**; 2,6-Et₂C₆H₃, **2b**; 2,6-Me₂C₆H₃, **2c**; 4-MeC₆H₄, **2d**; Ph, **2e**; and R = Et, Ar = $2,6-iPr_2C_6H_3$, **2f**; $2,6-Me_2C_6H_3$, **2g**; Ph, **2h**), with AlMe₃ (1 equiv.). All complexes were characterized by ¹H

and ¹³C NMR spectroscopy and elemental analysis. Singlecrystal X-ray diffraction analysis of complexes 3c and 3e revealed that these Al complexes have a distorted tetrahedral geometry around the metal center. All complexes were found to be efficient catalysts for the ring-opening polymerization of ε -caprolactone (CL) in the presence of benzyl alcohol, and complexes **3a-h** catalyze the polymerization of CL in a living fashion.

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Introduction

The synthesis of $poly(\varepsilon$ -caprolactone) (PCL) and poly-(lactide) (PLA) as well as their copolymers have received considerable attention because of their potential applications in medicine, pharmaceutics, and tissue engineering such as delivery medium for the controlled release of drugs, scaffolds, and the delivery of antibodies and genes.^[1] The signal-site metal complex catalyzed ring-opening polymerization (ROP) of ε -caprolactone (CL) is the major method used to synthesize PCL due to its good control over the molecular weight of the polymerization product.^[2] A number of main-group and transition-metal complexes, including magnesium,^[3] calcium,^[4] aluminum,^[5] titanium,^[6] iron,^[7] zinc,^[8] tin,^[9] and rare-earth metal^[10] complexes supported by various ligands have been reported to be efficient catalysts for the ROP of CL. Among these catalysts, Al complexes are the most intensely studied catalysts due to their high Lewis acidity. A series of salicylaldimine-aluminum complexes have been reported by Nomura and coworkers that are efficient catalysts for the ROP of CL, and the catalytic activity of this type of complexes was found to increase with increasing steric bulk of their ligands.^[11] Recently, our group reported a similar type of Al catalysts with N-arylanilido-arylimine ligands.^[12] The catalytic activity of this type of catalysts was found to decrease with an increase in the steric hindrance of the ligands. To further modify the ligand and examine the steric effect of the ligand, we have developed a number of new Al complexes bearing bidentate N,N-dialkylaniline-arylamido ligands. From a structural point of view, the steric hindrance of the new ligands should be moderate in comparison to those of the salicylaldimine ligands and the N-arylanilido-arylimine ligands. The new Al complexes were found to be efficient catalysts for the ROP of CL in the presence of benzyl alcohol (BnOH). In this paper, we wish to report the synthesis of the Al complexes ortho-(ArNCH₂)- $C_6H_4NR_2AlMe_2$ (R = Me, Ar = 2,6-*i*Pr₂C₆H₃, 3a; 2,6-Et₂C₆H₃, **3b**; 2,6-Me₂C₆H₃, **3c**; 4-MeC₆H₄, **3d**; Ph, **3e**; and $R = Et, Ar = 2,6-iPr_2C_6H_3, 3f; 2,6-Me_2C_6H_3, 3g; Ph, 3h$ as well as their catalytic properties for the ROP of CL.

Results and Discussion

Synthesis and Spectroscopic Characterization of the Free Ligands and Their Al Complexes

Al complexes **3a-h** were synthesized from the reaction of corresponding free ligands ortho-(ArNHCH₂)C₆H₄NR₂ (R = Me, Ar = $2,6-i\Pr_2C_6H_3$, **2a**; $2,6-Et_2C_6H_3$, **2b**; $2,6-Et_2C_6H_3$, $Me_2C_6H_3$, **2c**; 4-MeC₆H₄, **2d**; Ph, **2e**; and R = Et, Ar = 2,6 $iPr_2C_6H_3$, **2f**; 2,6-Me₂C₆H₃, **2g**; Ph, **2h**) with AlMe₃ (1 equiv.), as shown in Scheme 1. ortho-Dimethylaminobenzaldehyde (A) and ortho-diethylaminobenzaldehyde (B) were prepared by treatment of N,N-dimethylaniline and N,N-diethylaniline with nBuLi (1 equiv.), followed by reac-



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tion with DMF. Preligands **1a**–**h** were synthesized by condensation between **A** or **B** and a substituted aniline in methanol. Reduction of preligands **1a**–**h** with LiAlH₄ in ethyl ether gave free ligands **2a**–**h**. Among these compounds, **1d**, **1e**, **1h**, and **2e** have been reported previously.^[13] All new compounds were characterized by ¹H and ¹³C NMR spectroscopy along with elemental analyses. The ¹H NMR spectra of preligands **1a–c** and **1f–g** exhibit a resonance in the range of $\delta = 8.50-8.80$ ppm for the imino N=CH proton, with the corresponding ¹³C NMR resonance around $\delta =$ 160 ppm. The NH resonance in free ligands **2a–d** and **2f–h** appears at characteristically middle field about $\delta =$ 3.90 ppm.



Scheme 1. Synthetic procedure of ligands 2a-h and complexes 3a-h.

Al complexes **3a–h** were obtained in good yields by alkane elimination reaction as shown in Scheme 1. The reaction of free ligands **2a–h** with AlMe₃ (1.0 equiv.) affords Al complexes **3a–h**. The disappearance of the N–H signal of the free ligands and the appearance of the resonances for the protons of AlMe₂ ($\delta = -0.60$ to -1.04 ppm) for complexes **3a–h** in high-field regions in the ¹H NMR spectra demonstrate the formation of the desired complexes. Complexes **3a–h** were all characterized by ¹H and ¹³C NMR spectroscopy and elemental analyses. As mentioned above, the ¹H NMR spectra of complexes **3a–h** all exhibit characteristic resonances for the protons of AlMe₂, with the corresponding ¹³C NMR resonances for the carbon atoms of the AlMe₂ group in the regions of $\delta = -9.78$ to -10.51 ppm for **3a–h**.

X-ray Crystallographic Analysis

The molecular structure of complex 3c is shown in Figure 1. Selected bond lengths and angles for 3c are given in Table 1. X-ray analysis revealed that the Al center of complex 3c adopts a distorted tetrahedral geometry with the metal center chelated by the amine and amido nitrogen atoms of the bidentate ligand. The six-membered chelating ring has a legless chair geometry and the aluminum atom occupies the top position of the backrest. The torsion angle between the plane of N1-A1-N2 and the plane of C6-C7-N1 is 57.6°, which is an indication of how far the Al atom is out of the plane of the aniline backbone. The N1-Al-N2 angle [94.23(12)°] in the complex is close to those in related known Al complexes.^[14] The Al-N2 (amido) distance [1.809(3) Å] is shorter than the Al-N1 (amine) distance [2.027(3) Å], which indicates the Al-N (amine) coordination bond character.



Figure 1. The molecular structure of complex 3c. Thermal ellipsoids are shown at the 30% probability level. Hydrogen atoms are omitted for clarity.

Complex 3e crystallizes with two independent molecules (assigned as 3e1 and 3e2) in an asymmetric unit cell. The structure of molecule 3e1 is shown in Figure 2, and the structures of both molecules 3e1 and 3e2 are given in Figure S1 (Supporting Information). The two molecules have similar conformation and structural parameters. Selected bond lengths and angles for 3e are given in Table 1. The structural feature around the Al atom in 3e is similar to that in 3c, adopting a distorted tetrahedral geometry with the four-coordinate metal center chelated by the amine and amido nitrogen atoms of the bidentate ligand. The torsion angles between the plane of N1–Al–N2 and the plane of C6–C7–N1 are 55.5 and 57.2° for 3e1 and 3e2, respectively.

Table 1. Selected bond lengths [Å] and angles [°] for 3c and 3e.

Complex 3c							
Al–N1 2.027(3)		N2-Al-C1	114.52(16)				
Al-N2	1.809(3)	C1-Al-C2	113.7(2)				
Al-C2	1.959(4)	N1-A1-N2	94.23(12)				
Al-C1	1.952(4)	N1-A1-C2	103.22(15)				
C5-N2	1.450(4)	N1-A1-C1	108.94(16)				
N2-Al-C1	119.06(16)						
Complex 3e1		Complex 3e2					
All-N1	2.032(2)	A12-N3	2.035(2)				
A11-N2	1.863(2)	A12-N4	1.860(2)				
Al1-C16	1.963(2)	A12-C33	1.961(2)				
Al1-C17	1.968(2)	A12-C34	1.965(2)				
C9-N2	1.459(3)	C26-N4	1.464(3)				
N2-A11-C16	114.77(10)	N4-A12-C33	114.31(10)				
N2-Al1-C17	115.25(10)	N4-A12-C34	114.81(10)				
C16-Al1-C17	115.98(11)	C33-A12-34	116.74(11)				
N1-A11-N2	95.82(8)	N3-A12-N4	96.46(8)				
N1-Al1-C16	106.43(10)	N3-A12-C33	106.97(10)				
N1-A11-C17	105.52(10)	N3-A12-C34	104.47(10)				

The N1–Al–N2 bond angles [95.82(8) and 96.46(8)° for **3e1** and **3e2**, respectively] are slightly larger than that in **3c**. As seen in **3c**, the Al–N2 (amido) distances [1.863(2) and 1.860(2) Å] are also shorter than the Al–N1 (amine) distances [2.032(2) and 2.035(2) Å] in **3e**. Both the Al–N1 and Al–N2 distances in **3e** are longer than those in **3c**. The observed differences in the bond lengths and angles between **3c** and **3e** may simply result from the packing force, as it cannot be reasonably explained otherwise.



Figure 2. The molecular structure of one (3e1) of the two independent complexes present in the crystals of 3e. Thermal ellipsoids are shown at the 30% probability level. Hydrogen atoms are omitted for clarity.

Ring-Opening Polymerization of ϵ -Caprolactone Initiated by 3a–e

Complexes **3a–h** were systematically investigated for the ROP of CL. Representative experimental results are summarized in Table 2. Complexes **3a–h** all show high reactivity for catalyzing the ROP of CL in the presence of BnOH,

whereas no reaction takes place in the absence of BnOH (Table 2, Entries 1–5). The ortho-(ArNCH₂)C₆H₄NMe₂-AlMe₂ complexes 3a-e were synthesized and studied as catalysts for the ROP of CL first and it was found that their catalytic activity under the same conditions is in the order of 3a > 3b > 3c > 3d > 3e (Table 2, Entries 6–10). These results indicate that increasing the steric hindrance of the aryl group at the amido N atom in the ligands of these complexes can considerably increase their catalytic activity. A similar phenomenon has been observed in the salicylaldimine-aluminum catalyst system.^[11] However, reverse results were obtained with the bulky N-arylanilido-arylimine Al catalyst system.^[12] To systematically examine and correctly understand the steric effect of the ligands on the catalytic activity of the new type of complexes, ortho-(ArNCH₂)-C₆H₄NEt₂AlMe₂ complexes **3f-h** were then synthesized and their catalytic properties for the ROP of CL was studied. It is interesting to find that the catalytic activities of these complexes increases first and then decreases with an increase in the steric hindrance of the aryl group at the amido N atom in their ligands (Table 2, Entries 25-27). These results indicate that catalysts of this type require their ligands with adequate steric hindrance to show the highest catalytic activity. A too-bulky ligand may block the coordination and insertion of the monomer, whereas a less-bulky ligand might allow the coordination of the ester linkages in the polymer chain. For complexes 3a-e, the NMe₂ group is small in size, which results in these complexes requiring a bulky aryl group at the amido N atom in their ligands to demonstrate good catalytic activity. To examine the effect of reaction conditions on the catalytic activity of the new catalyst system, polymerization experiments under different conditions were conducted with complex 3a in the presence of BnOH. The role of BnOH in the ROP of CL has been studied and reported previously.^[12,15] Under similar conditions, the catalytic activity of 3a was observed to change obviously with the change in the BnOH/Al molar ratio, and the highest catalytic activity was obtained with a BnOH/Al molar ratio of 2:1. It was found that the number-averaged degree of polymerization (DP_n) of the obtained polymers (calculated by ¹H NMR) is close to the CL/BnOH molar ratio, and the molecular weight (M_n) of the polymers determined by gel permeation chromatography is proportional to the CL/BnOH molar ratio (Figure 3). Similar results have previously been reported for other initiator systems,^[12,16] which have been described as "immortal" polymerization. The polymerization reaction was also examined at different reaction temperatures and the reactivity of complex 3a was found to increase noticeably from 20 to 70 °C. When the polymerization reaction was carried out at 20 °C for different times, it was found that the DP_n and M_n values of the obtained polymers increase linearly with an increase in polymer yields. These results demonstrate the "living" character of the polymerization process with BnOH as a co-initiator. In comparison with related known initiator systems, the reactivity of the present system is similar to that of the N-arylanilido-arylimine Al catalyst system.^[12] The ¹H NMR spectrum of a typical PCL sample shows the pres-

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Table 7	$R_{1n\sigma}$	nolymerization	of g-ca	prolactone	initiated b	\mathbf{w} com	nleyes	- 39_h [4]
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Entry	Cat.	[BnOH]/[Al]/[CL]	Temp. [°C]	Time	Yield [%] ^[b]	TOF ^[c]	$\mathrm{DP}_n^{[\mathrm{d}]}$	$M_n^{[e]} \times 10^3$	$M_n(\text{SEC})^{[f]} \times 10^3$	M_n (theor) ^[g] $ imes 10^3$	$M_{\rm w}/M_n^{\rm [e]}$
1	3a	0:1:100	70	24 h	0	_	_	_	_	_	_
2	3b	0:1:100	70	24 h	0	_	_	_	_	_	_
3	3c	0:1:100	70	24 h	0	_	_	_	_	_	_
4	3d	0:1:100	70	24 h	0	_	_	_	_	_	_
5	3e	0:1:100	70	24 h	0	_	_	_	_	_	_
6	3a	2:1:100	70	3 min	96.5	1930	49	11.8	6.6	5.6	1.24
7	3b	2:1:100	70	4 min	94.3	1414	53	12.7	7.1	5.5	1.18
8	3c	2:1:100	70	4.7 min	95.1	1214	56	13.4	7.5	5.5	1.25
9	3d	2:1:100	70	6.5 min	96.7	892	47	11.4	6.3	5.6	1.20
10	3e	2:1:100	70	7 min	95.8	821	51	12.3	6.9	5.4	1.12
11	3a	0.5:1:100	70	18 min	93.2	311	197	37.9	21.2	21.4	1.35
12	3a	1:1:100	70	14 min	95.7	409	97	19.1	10.7	11.0	1.41
13	3a	4:1:100	70	10 min	92.6	556	27	7.51	4.2	2.7	1.56
14	3a	2:1:100	50	7 min	94.9	813	55	13.2	7.4	5.5	1.32
15	3a	2:1:100	20	12 min	93.4	467	48	11.6	6.5	5.4	1.28
16	3a	2:1:200	70	5 min	96.2	2308	99	21.4	12.0	11.1	1.35
17	3a	2:1:300	70	7 min	98.1	2522	159	26.0	14.6	16.9	1.72
18	3a	2:1:400	70	9.3 min	96.3	2485	203	39.7	22.2	22.1	1.51
19	3a	2:1:450	70	12.7 min	95.3	2026	225	43.7	24.5	24.6	1.74
20	3a	2:1:400	20	9 min	46.5	1240	95	20.3	11.4	10.7	1.16
21	3a	2:1:400	20	18 min	70.2	936	146	28.5	16.0	16.1	1.18
22	3a	2:1:400	20	27 min	85.0	755	175	33.8	18.9	19.5	1.19
23	3a	2:1:400	20	36 min	92.4	616	187	35.2	19.7	21.2	1.24
24	4	0:1:100	70	3 min	97.1	1942	50	11.4	6.4	5.6	1.36
25	3f	2:1:100	70	5.5 min	92.1	1005	46	11.1	6.2	5.4	1.27
26	3g	2:1:100	70	5 min	94.6	1135	52	12.5	7.0	5.5	1.19
27	3h	2:1:100	70	8 min	95.2	714	54	12.9	7.2	5.5	1.26

[a] Polymerization conditions: catalyst (0.19 mmol), [CL] = 1 \times in toluene. [b] Isolated yield. [c] Mole of CL consumed per mol of catalyst per hour. [d] The number-averaged degree of polymerization calculated by ¹H NMR spectroscopy. [e] The molecular weight obtained from GPC analysis. [f] SEC values of precipitated polymer samples corrected with the coefficient 0.56. [g] Calculated for one growing polymer chain with M_n (theor) = {[ε -CL]₀/[BnOH]₀ × 114 × (conversion)+ 108}.

ence of a benzyl ester group at $\delta = 5.12$ ppm (singlet, CH_2Ph) as the initiating chain end. These results suggest that BnOH reacts first with the alkyl Al complexes to form the LAl-OBn complexes as the catalytic active species. To further confirm that the benzyloxyaluminum complex acts as the active catalyst, benzyloxyaluminum complex 4 was synthesized by reaction of 3a with BnOH (2 equiv.) and used as catalyst for the ROP of CL (Figure 4A). It was found that complex 4 shows similar catalytic activity to the catalyst system of 3a/BnOH (1:2). The formation of Al- $[O(CH_2)_5C=O]_nOCH_2Ph$ intermediates during the polymerization was confirmed by ¹H NMR spectroscopy (Figure 4B), in which the signals of the methylene protons (c, d, e, and f) of the polymer appear at $\delta = 4.22, 2.46, 1.81,$ 1.54 ppm, and the sharp signal at $\delta = 5.27$ ppm arises from the ending benzyl CH₂ group.

On the basis of the above results, a mechanism for the present polymerization system, similar to the one proposed previously for the *N*-arylanilido–arylimine Al catalyst system,^[12] can be proposed as shown in Scheme 2. The benzyl-oxyaluminum complexes are the active catalysts that are produced by the reaction of the alkylaluminum complexes with BnOH. The polymerization reaction takes place by repeated coordination of the CL monomer to the metal center and insertion into the Al–O bond to form the polymerization intermediates LAl–OP (where P refers to the polymer chain). Free polymers can be released by the addition of



Figure 3. Plot of Mn vs. [CL]/[BnOH] for the ROP of CL catalyzed by complex **3a**/BnOH in toluene at 70 °C.

BnOH or acetic acid. BnOH acts as a chain initiator as well as a chain transfer reagent in the polymerization procedure. During the polymerization, excess BnOH (if any) would react with the polymerization intermediates LAl–OP to replace the –OP groups and form the free polymers and new active species. The formed shorter chain polymers would also react with the polymerization intermediates with longer polymer chains to produce longer chain free poly-



Figure 4. ¹H NMR spectra of (A) complex 4 in CDCl₃, and (B) the reaction mixture of complex 4 and CL in CDCl₃ at room temperature.

mers and new polymerization intermediates. Finally, the polymerization reaction stops when the monomer is totally consumed.



Scheme 2. The proposed mechanism for the ROP of CL.

Conclusions

In conclusion, several Al complexes supported by bidentate *N*,*N*-dimethylaniline–arylamido ligands and *N*,*N*-diethylaniline–arylamido ligands have been synthesized in good yields by the reaction of free ligands 2a-h with AlMe₃ (1.0 equiv.). All complexes were fully characterized by ¹H and ¹³C NMR spectroscopy along with elemental analyses. The structures of 3c and 3e were determined by X-ray crystallography, and the structural analysis revealed that the Al center of these complexes adopts a distorted tetrahedral ge-

ometry with the metal center chelated by the amine and amido nitrogen atoms of their bidentate ligands. Complexes 3a-h are all efficient catalysts for the ROP of CL in the presence of benzyl alcohol and catalyze the polymerization of CL in a living fashion. The catalytic activity of complexes 3a-e increases with an increase in the steric bulk of the aryl groups at the amido N atom in the N,N-dimethylaniline-arylamido ligands, whereas the catalytic activity of complexes 3f-h increases first and then decreases with an increase in the steric bulk of the aryl groups in the N,Ndiethylaniline-arylamido ligands. In addition, the catalytic activity of these catalyst systems increases with an increase in polymerization temperature from 20 to 70 °C and also changes with the BnOH/Al molar ratio with the highest catalytic activity being observed at the BnOH/Al molar ratio of 2:1. Benzyloxyaluminum complex 4 was synthesized and tested as the active catalyst for the ROP of CL, which supports the proposed mechanism for the polymerization.

Experimental Section

General: All reactions were performed using standard Schlenk techniques in an atmosphere of high-purity nitrogen or glove-box techniques. Toluene, hexane, and Et_2O were dried by heating at reflux over sodium and benzophenone and then distilled under nitrogen prior to use. C_6D_6 and CDCl₃ were dried with CaH₂ for 48 h and vacuum-transferred into an air-free flask. *n*BuLi and AlMe₃ were purchased from Aldrich and used as received. Compounds **1d**, **1e**, and **2e** were prepared according to a literature procedure.^[11] ¹H and ¹³C NMR spectra were measured using a Varian Mercury-300 NMR spectrometer. Elemental analyses were performed with a Perkin–Elmer 2400 analyzer. GPC measurements were performed with a Waters-410 system using CH₂Cl₂ as the eluent (flow rate: 1 mL min⁻¹, at 25 °C). Molecular weights and molecular weight distributions were calculated using polystyrene as standard.

ortho-C₆H₄(NMe₂)CHO (A): After removal of the solvent of nBuLi (79 mL, 79 mmol), N,N-dimethylaniline (10 mL) was added at 0 °C with stirring, gently heating to 80 °C for 24 h, during which a yellow solid was formed. DMF (6.0 mL) in Et₂O (40 mL) was added to the mixture at 0 °C. After stirring for 12 h, the reaction was quenched with H₂O (30 mL), and the organic phase was separated, washed with brine, and dried with magnesium sulfate. The solvent was removed in vacuo to give the crude product as a vellow oil. Pure product was obtained by column chromatography (10% ethyl acetate in hexanes) as a yellow oil (9.2 g, 78%). C₉H₁₁NO (149.19): calcd. C 72.46, H 7.43, N 9.39; found C 72.38, H 7.38, N 9.26. ¹H NMR (300 MHz, CDCl₃, 293 K): δ = 10.22 (s, 1 H, CHO), 7.75 (d, 1 H, Ph-H), 7.46 (d, 1 H, Ph-H), 7.06 (d, 1 H, Ph-H), 7.01 (t, 1 H, Ph-H), 2.92 (s, 6 H, NCH₃) ppm. ¹³C{¹H} NMR (75 MHz, $CDCl_3$, 293 K): $\delta = 191.05$, 155.66, 134.49, 130.81, 126.89, 120.49, 117.51, 45.42 ppm.

ortho-C₆H₄(NEt₂)CHO (B): Under an atmosphere of nitrogen, *n*BuLi (35 mL, 35 mmol) was added dropwise to a stirred Et₂O solution (50 mL) of *N*,*N*-diethylaniline (5 mL) in the presence of TMEDA (5 mL). The mixture was gently heated to reflux for 24 h. DMF (3.1 mL) in Et₂O (20 mL) was added to the mixture at 0 °C. After stirring for 12 h, the reaction was quenched with H₂O (30 mL), and the organic phase was separated, washed with brine, and dried with magnesium sulfate. The solvent was removed in vacuo to give the crude product as a yellow oil. Pure product was

obtained by column chromatography (dichloromethane/hexane, 2:1) as a yellow oil (1.7 g, 30%). $C_{11}H_{15}NO$ (177.24): calcd. C 74.54, H 8.53, N 7.90; found C 74.49, H 8.50, N 7.94. ¹H NMR (300 MHz, CDCl₃, 293 K): $\delta = 10.36$ (s, 1 H, CHO), 7.82 (d, 1 H, Ph-*H*), 7.49 (t, 1 H, Ph-*H*), 7.17 (d, 1 H, Ph-*H*), 7.07 (d, 1 H, Ph-*H*), 3.18 (q, 4 H, NCH₂CH₃), 1.06 (t, 6 H, NCH₂CH₃) ppm. ¹³C{¹H} NMR (75 MHz, CDCl₃, 293 K): $\delta = 191.72$, 154.34, 134.02, 128.60, 122.54, 122.15, 121.47, 48.72, 12.09 ppm.

ortho-C₆H₄(NMe₂)CH=NC₆H₃iPr₂-2,6 (1a): A solution of *ortho*-C₆H₄(NMe₂)CHO (2.24 g, 15.0 mmol) and 2,6-diisopropylaniline (2.83 mL, 15.0 mmol) in MeOH (20 mL) was stirred at room temperature for 12 h. The mixture was then cooled to 0 °C for a couple of hours to precipitate the product. The precipitate was collected on a filter and washed with cool MeOH (5 mL) to give the product as a yellow crystalline material (3.7 g, 80%). C₂₁H₂₈N₂ (308.46): calcd. C 81.77, H 9.15, N 9.08; found C 81.74, H 9.14, N 9.12. ¹H NMR (300 MHz, CDCl₃, 293 K): *δ* = 8.58 (s, 1 H, *CH*=N), 8.24 (d, 1 H, Ph-*H*), 7.47 (t, 1 H, Ph-*H*), 7.03–7.16 (m, 5 H, Ph-*H*), 3.04 [m, 2 H, *CH*(CH₃)₂], 2.81 (s, 6 H, NCH₃), 1.20 [d, 12 H, CH(CH₃)₂] ppm. ¹³C{¹H} NMR (75 MHz, CDCl₃, 293 K): *δ* = 160.26, 154.46, 149.26, 137.21, 131.25, 128.74, 127.62, 123.36, 122.42, 122.25, 118.24, 45.27, 27.30, 22.08 ppm.

ortho-C₆H₄(NMe₂)CH=NC₆H₃Et₂-2,6 (1b): A mixture of *ortho*-C₆H₄(NMe₂)CHO (3.13 g, 21.0 mmol) and 2,6-diethylaniline (3.46 mL, 21.0 mmol) in MeOH (20 mL) was stirred for 12 h. The solvent was removed in vacuo to give the crude product as a yellow oil. Pure product was obtained by column chromatography (5% ethyl acetate in hexanes) as a yellow solid (4.95 g, 84%). C₁₉H₂₄N₂ (280.41): calcd. C 81.38, H 8.63, N 9.99; found C 81.35, H 8.60, N 10.05. ¹H NMR (300 MHz, CDCl₃, 293 K): δ = 8.59 (s, 1 H, CH=N), 8.16 (d, 1 H, Ph-H), 7.44 (t, 1 H, Ph-H), 7.04–7.15 (m, 5 H, Ph-H), 2.78 (s, 6 H, NCH₃), 2.52 (q, 4 H, CH₂CH₃), 1.16 (t, 6 H, CH₂CH₃) ppm. ¹³C{¹H} NMR (75 MHz, CDCl₃, 293 K): δ = 171.89, 156.03, 142.46, 136.86, 136.79, 136.14, 129.06, 125.80, 116.01, 115.01, 114.73, 56.84, 18.67, 8.24 ppm.

ortho-C₆H₄(NMe₂)CH=NC₆H₃Me₂-2,6 (1c): This compound was prepared in the same way as described above for 1a with *ortho*-C₆H₄(NMe₂)CHO (2.98 g, 20.0 mmol) and 2,6-dimethylaniline (2.44 mL, 20.0 mmol) as starting materials. The product (3.94 g, 78%) was obtained as a yellow powder. C₁₇H₂₀N₂ (252.35): calcd. C 80.91, H 7.99, N 11.10; found C 80.88, H 8.07, N 11.05. ¹H NMR (300 MHz, CDCl₃, 293 K): δ = 8.56 (s, 1 H, CH=N), 8.17 (d, 1 H, Ph-*H*), 7.44 (t, 1 H, Ph-*H*), 7.14–6.95 (m, 5 H, Ph-*H*), 2.79 (s, 6 H, NC*H*₃), 2.16 (s, 6 H, C*H*₃) ppm. ¹³C{¹H} NMR (75 MHz, CDCl₃, 293 K): δ = 161.36, 154.59, 151.79, 131.62, 128.82, 127.96, 127.81, 126.91, 123.25, 122.34, 118.23, 45.50, 18.28 ppm.

ortho-C₆H₄(NEt₂)CH=NC₆H₃*i*Pr₂-2,6 (1f): This compound was prepared in the same way as described above for 1a with B (0.890 g, 5.0 mmol) and 2,6-diisopropylaniline (0.94 mL, 5.0 mmol) as starting materials. The product (1.13 g, 67%) was obtained as a yellow powder. C₂₃H₃₂N₂ (336.51): calcd. C 82.09, H 9.58, N 8.32; found C 82.13, H 9.54, N 8.33. ¹H NMR (300 MHz, CDCl₃, 293 K): δ = 8.69 (s, 1 H, CH=N), 8.24 (d, 1 H, Ph-*H*), 7.47 (t, 1 H, Ph-*H*), 7.03–7.16 (m, 5 H, Ph-*H*), 3.05 [m, 2 H, C*H*(CH₃)₂], 3.05 (m, 4 H, NC*H*₂CH₃), 1.19 [d, 12 H, CH(C*H*₃)₂], 0.96 (t, 6 H, NCH₂C*H*₃) ppm. ¹³C{¹H} NMR (75 MHz, CDCl₃, 293 K): δ = 161.19, 152.45, 150.12, 137.88, 132.84, 132.80, 132.76, 131.57, 127.80, 124.02, 123.06, 48.88, 27.98, 23.70, 12.39 ppm.

ortho-C₆H₄(NEt₂)CH=NC₆H₃Me₂-2,6 (1g): This compound was prepared in the same way as described above for 1a with B (1.06 g, 6.0 mmol) and 2,6-dimethylaniline (0.73 mL, 6.0 mmol) as starting materials. The product (1.33 g, 79%) was obtained as a yellow pow-

der. C₁₉H₂₄N₂ (280.41): calcd. C 81.38, H 8.63, N 9.99; found C 81.41, H 8.67, N 9.92. ¹H NMR (300 MHz, CDCl₃, 293 K): δ = 8.67 (s, 1 H, CH=N), 8.20 (d, 1 H, Ph-*H*), 7.45 (t, 1 H, Ph-*H*), 7.20–6.95 (m, 5 H, Ph-*H*), 3.08 (q, 4 H, NCH₂CH₃), 2.16 (s, 6 H, CH₃), 0.99 (t, 6 H, NCH₂CH₃) ppm. ¹³C{¹H} NMR (75 MHz, CDCl₃, 293 K): δ = 161.87, 152.31, 152.10, 132.35, 131.48, 128.00, 127.76, 127.18, 123.57, 123.39, 122.46, 48.64, 18.43, 12.33 ppm.

ortho-C₆H₄(NMe₂)CH₂NHC₆H₃iPr₂-2,6 (2a): A solution of Li-AlH₄ (0.681 g, 18.0 mmol) in Et₂O (10 mL) was added to a solution of 1a (3.70 g, 12.0 mmol) in Et₂O (30 mL) at 0 °C. The mixture was warmed to room temperature and stirred for 5 h. The reaction was quenched with cooled H₂O (20 mL), and the organic phase was separated, washed with brine, and dried with magnesium sulfate. The solvent was removed in vacuo to give the crude product as a yellow oil. Pure product was obtained by distillation under reduced pressure as a yellow solid (2.83 g, 76%). C₂₁H₃₀N₂ (310.48): calcd. C 81.24, H 9.74, N 9.02; found C 81.27, H 9.73, N 9.00. ¹H NMR $(300 \text{ MHz}, \text{CDCl}_3, 293 \text{ K}): \delta = 7.42 \text{ (d, 1 H, Ph-}H), 7.28 \text{ (t, 1 H, Ph-}H)$ Ph-H), 7.21 (d, 1 H, Ph-H), 7.05-6.11 (m, 4 H, Ph-H), 4.07 (s, 2 H, CH₂N), 3.89 (br., 1 H, NH), 3.40 [m, 2 H, CH(CH₃)₂], 2.72 (s, 6 H, NCH₃), 1.25 [d, 12 H, CH(CH₃)₂] ppm. ¹³C{¹H} NMR $(75 \text{ MHz}, \text{ CDCl}_3, 293 \text{ K}): \delta = 152.83, 143.58, 142.67, 135.16,$ 129.69, 128.16, 124.01, 123.62, 123.49, 120.01, 53.05, 45.30, 27.49, 24.34 ppm.

ortho-C₆H₄(NMe₂)CH₂NHC₆H₃Et₂-2,6 (2b): This compound was prepared in the same way as described above for **2a** with **1b** (3.53 g, 12.6 mmol) and LiAlH₄ (0.720 g, 18.9 mmol) as starting materials. The product (2.92 g, 82%) was obtained as a yellow solid. C₁₉H₂₆N₂ (282.42): calcd. C 80.80, H 9.28, N 9.92; found C 80.83, H 9.26, N 9.91. ¹H NMR (300 MHz, CDCl₃, 293 K): δ = 7.47 (d, 1 H, Ph-*H*), 7.30 (t, 1 H, Ph-*H*), 7.22 (d, 1 H, Ph-*H*), 7.08–6.98 (m, 4 H, Ph-*H*), 4.15 (s, 2 H, C*H*₂N), 3.87 (br., 1 H, NH), 2.74 (s, 6 H, NC*H*₃), 2.54 (q, 4 H, C*H*₂CH₃), 1.27 (t, 6 H, CH₂C*H*₃) ppm. ¹³C{¹H} NMR (75 MHz, CDCl₃, 293 K): δ = 152.75, 145.34, 136.76, 129.61, 128.04, 126.59, 125.93, 123.82, 122.69, 119.80, 51.25, 45.22, 24.21, 15.05 ppm.

ortho-C₆H₄(NMe₂)CH₂NHC₆H₃Me₂-2,6 (2c): This compound was prepared in the same way as described above for 2a with 1c (2.95 g, 11.7 mmol) and LiAlH₄ (0.670 g, 17.6 mmol) as starting materials. The product (2.02 g, 68%) was obtained as a yellow oil. C₁₇H₂₂N₂ (254.37): calcd. C 80.27, H 8.72, N 11.01; found C 80.30, H 8.70, N 11.00. ¹H NMR (300 MHz, CDCl₃, 293 K): δ = 7.39 (d, 1 H, Ph-*H*), 7.26 (t, 1 H, Ph-*H*), 7.17 (d, 1 H, Ph-*H*), 7.05 (t, 1 H, Ph-*H*), 6.99 (d, 2 H, Ph-*H*), 6.82 (t, 1 H, Ph-*H*), 4.17 (s, 2 H, C*H*₂N), 3.87 (br., 1 H, N*H*), 2.72 (s, 6 H, NC*H*₃), 2.30 (s, 6 H, C*H*₃) ppm. ¹³C{¹H} NMR (75 MHz, CDCl₃, 293 K): δ = 152.70, 146.41, 134.95, 129.78, 128.71, 128.71, 128.04, 123.65, 121.83, 119.65, 49.38, 45.18, 18.35 ppm.

ortho-C₆H₄(NMe₂)CH₂NHC₆H₄Me-4 (2d): This compound was prepared in the same way as described above for **2a** with **1d** (2.57 g, 10.8 mmol) and LiAlH₄ (0.610 g, 16.2 mmol) as starting materials. The product (2.05 g, 79%) was obtained as a yellow oil. C₁₆H₂₀N₂ (240.34): calcd. C 79.96, H 8.39, N 11.66; found C 79.90, H 8.38, N 11.72. ¹H NMR (300 MHz, CDCl₃, 293 K): δ = 7.37 (d, 1 H, Ph-*H*), 7.26–6.97 (m, 5 H, Ph-*H*), 6.62 (d, 2 H, Ph-*H*), 4.40 (s, 2 H, CH₂N), 3.92 (br., 1 H, N*H*), 2.76 (s, 6 H, NC*H*₃), 2.24 (s, 3 H, CH₃) ppm. ¹³C{¹H} NMR (75 MHz, CDCl₃, 293 K): δ = 152.36, 146.24, 133.34, 129.63, 129.23, 127.82, 126.44, 123.28, 119.15, 113.06, 44.94, 44.84, 20.37 ppm.

ortho-C₆H₄(NEt₂)CH₂NHC₆H₃*i*Pr₂-2,6 (2f): This compound was prepared in the same way as described above for 2a with 1f (1.01 g, 3.0 mmol) and LiAlH₄ (0.17 g, 4.5 mmol) as starting materials. The



product (0.84 g, 83%) was obtained as a yellow oil. $C_{23}H_{34}N_2$ (338.53): calcd. C 81.60, H 10.12, N 8.28; found C 81.53, H 10.15, N 8.32. ¹H NMR (300 MHz, CDCl₃, 293 K): δ = 7.46 (d, 1 H, Ph-H), 7.28 (t, 1 H, Ph-H), 7.21–7.12 (m, 5 H, Ph-H), 4.10 (s, 2 H, CH₂N), 3.53 (br., 1 H, NH), 3.42 [m, 2 H, CH(CH₃)₂], 3.06 (q, 4 H, NCH₂CH₃), 1.24 [d, 12 H, CH(CH₃)₂], 1.03 (t, 6 H, NCH₂CH₃) ppm. ¹³C{¹H} NMR (75 MHz, CDCl₃, 293 K): δ = 142.93, 137.39, 129.53, 128.31, 124.16, 123.75, 123.55, 123.07, 122.75, 118.50, 52.46, 48.30, 27.52, 24.37, 12.20 ppm.

ortho-C₆H₄(NEt₂)CH₂NHC₆H₃Me₂-2,6 (2g): This compound was prepared in the same way as described above for 2a with 1g (1.12 g, 4.0 mmol) and LiAlH₄ (0.23 g, 6.0 mmol) as starting materials. The product (1.02 g, 91%) was obtained as a yellow oil. C₁₉H₂₆N₂ (282.42): calcd. C 80.80, H 9.28, N 9.92; found C 80.83, H 9.23, N 9.94. ¹H NMR (300 MHz, CDCl₃, 293 K): δ = 7.45 (d, 1 H, Ph-*H*), 7.26 (t, 1 H, Ph-*H*), 7.19 (m, 2 H, Ph-*H*), 7.01 (d, 2 H, Ph-*H*), 6.84 (t, 1 H, Ph-*H*), 4.18 (s, 2 H, CH₂N), 3.68 (br., 1 H, NH), 3.08 (q, 4 H, NCH₂CH₃), 2.38 (s, 6 H, CH₃), 1.06 (t, 6 H, NCH₂CH₃) ppm. ¹³C{¹H} NMR (75 MHz, CDCl₃, 293 K): δ = 146.70, 137.80, 129.96, 129.60, 128.85, 127.61, 124.30, 123.10, 121.95, 118.03, 65.64, 48.76, 18.56, 12.52 ppm.

ortho-C₆H₄(NEt₂)CH₂NHC₆H₅ (2h): This compound was prepared in the same way as described above for **2a** with **1h** (1.39 g, 5.5 mmol) and LiAlH₄ (0.31 g, 8.3 mmol) as starting materials. The product (1.22 g, 87%) was obtained as a yellow oil. C₁₇H₂₂N₂ (254.37): calcd. C 80.27, H 8.72, N 11.01; found C 80.21, H 8.75, N 11.04. ¹H NMR (300 MHz, CDCl₃, 293 K): δ = 7.37 (d, 1 H, Ph-*H*), 7.25–7.17 (m, 4 H, Ph-*H*), 7.06 (t, 1 H, Ph-*H*), 6.66 (m, 3 H, Ph-*H*), 4.40 (s, 2 H, C*H*₂N), 3.65 (br., 1 H, N*H*), 3.02 (q, 4 H, NCH₂CH₃), 1.05 (t, 6 H, NCH₂CH₃) ppm. ¹³C{¹H} NMR (75 MHz, CDCl₃, 293 K): δ = 148.58, 136.04, 129.12, 127.36, 123.93, 122.62, 118.28, 117.08, 113.61, 112.8, 48.01, 44.69, 12.62 ppm.

ortho-C₆H₄(NMe₂)(CH₂NC₆H₃*i*Pr₂-2,6)AlMe₂ (3a): AlMe₃ (1.0 M in toluene, 2.0 mL, 2.0 mmol) was added to a solution of **2a** (0.62 g, 2.0 mmol) in toluene (20 mL) at -10 °C with stirring. The reaction mixture was gently heated to 80 °C for 24 h. After removal of the solvent, the product was recrystallized from hexane to give the desired complex as a colorless crystalline solid (0.62 g, 84%). C₂₃H₃₅AlN₂ (366.52): calcd. C 75.37, H 9.63, N 7.64; found C 75.40, H 9.61, N 7.65. ¹H NMR (300 MHz, CDCl₃, 293 K): δ = 7.32 (m, 3 H, Ph-*H*), 7.02 (m, 1 H, Ph-*H*), 6.94–6.93 (m, 2 H, Ph-*H*), 6.71 (m, 1 H, Ph-*H*), 4.45 (s, 2 H, CH₂N), 3.95 [m, 2 H, CH(CH₃)₂], 2.41 (s, 6 H, NCH₃), 1.41 [q, 12 H, CH(CH₃)₂], -0.63 (s, 6 H, AlCH₃) ppm. ¹³C{¹H} NMR (75 MHz, CDCl₃, 293 K): δ = 149.12, 147.93, 145.99, 136.09, 130.60, 127.60, 127.16, 124.87, 124.11, 118.74, 60.74, 44.91, 27.52, 26.23, 25.15, -9.97 ppm.

ortho-C₆H₄(NMe₂)(CH₂NC₆H₃Et₂-2,6)AlMe₂ (3b): This compound was prepared in the same way as described above for 3a with 2b (0.62 g, 2.2 mmol) and AlMe₃ (2.2 mL, 2.2 mmol) as starting materials. The product (0.65 g, 87%) was obtained as a colorless crystalline solid. C₂₁H₃₁AlN₂ (338.47): calcd. C 74.52, H 9.23, N 8.28; found C 74.39, H 9.32, N 8.34. ¹H NMR (300 MHz, CDCl₃, 293 K): δ = 7.32–7.28 (m, 3 H, Ph-*H*), 6.99–6.94 (m, 3 H, Ph-*H*), 6.71 (m, 1 H, Ph-*H*), 4.38 (s, 2 H, CH₂N), 3.0 (q, 4 H, CH₂CH₃), 2.40 (s, 6 H, NCH₃), 1.38 (t, 6 H, CH₂CH₃), -0.63 (s, 6 H, AlCH₃) ppm. ¹³C{¹H} NMR (75 MHz, CDCl₃, 293 K): δ = 149.64, 146.00, 144.21, 136.13, 130.69, 127.52, 127.10, 126.68, 124.27, 118.73, 59.37, 45.02, 24.50, 16.38, –9.90 ppm.

ortho-C₆H₄(NMe₂)(CH₂NC₆H₃Me₂-2,6)AlMe₂ (3c): This compound was prepared in the same way as described above for 3a with 2c (0.46 g, 1.8 mmol) and AlMe₃ (1.8 mL, 1.8 mmol) as starting

materials. The product (0.50 g, 89%) was obtained as a colorless crystalline solid. $C_{19}H_{27}AIN_2$ (310.41): calcd. C 73.52, H 8.77, N 9.02; found C 73.50, H 8.75, N 9.00. ¹H NMR (300 MHz, C₆D₆, 293 K): δ = 7.25 (d, 2 H, Ph-*H*), 7.13 (t, 1 H, Ph-*H*), 6.93 (m, 3 H, Ph-*H*), 6.69 (m, 1 H, Ph-*H*), 4.32 (s, 2 H, C*H*₂N), 2.52 (s, 6 H, NC*H*₃), 2.36 (s, 6 H, C*H*₃), -0.65 (s, 6 H, AIC*H*₃) ppm. ¹³C{¹H} NMR (75 MHz, C₆D₆, 293 K): δ = 150.81, 1415.98, 138.29, 136.26, 130.74, 129.03, 127.40, 127.05, 123.84, 118.62, 57.19, 44.94, 19.57, -9.78 ppm.

ortho-C₆H₄(NMe₂)(CH₂NC₆H₄Me-4)AlMe₂ (3d): This compound was prepared in the same way as described above for 3a with 2d (0.72 g, 3.0 mmol) and AlMe₃ (3.0 mL, 3.0 mmol) as starting materials. The product (0.82 g, 92%) was obtained as a colorless crystalline solid. C₁₈H₂₅AlN₂ (296.39): calcd. C 72.94, H 8.50, N 9.45; found C 72.96, H 8.45, N 9.48. ¹H NMR (300 MHz, CDCl₃, 293 K): δ = 7.37–7.28 (m, 6 H, Ph-*H*), 7.00 (d, 1 H, Ph-*H*), 6.69 (d, 1 H, Ph-*H*), 4.49 (s, 2 H, CH₂N), 2.92 (s, 6 H, NCH₃), 2.25 (s, 3 H,CH₃), -0.85 (s, 6 H, AlCH₃) ppm. ¹³C{¹H} NMR (75 MHz, CDCl₃, 293 K): δ = 151.93, 145.32, 134.62, 131.78, 129.62, 128.45, 127.64, 123.77, 118.61, 114.38, 53.87, 44.91, 20.52, –10.20 ppm.

ortho-C₆H₄(NMe₂)(CH₂NC₆H₅)AlMe₂ (3e): This compound was prepared in the same way as described above for **3a** with **2e** (0.56 g, 2.5 mmol) and AlMe₃ (2.5 mL, 2.5 mmol) as starting materials. The product (0.66 g, 93%) was obtained as a colorless crystalline solid. C₁₇H₂₃AlN₂ (282.36): calcd. C 72.31, H 8.21, N 9.92; found C 72.35, H 8.25, N 9.83. ¹H NMR (300 MHz, CDCl₃, 293 K): δ = 7.37–7.30 (m, 4 H, Ph-*H*), 7.20 (t, 2 H, Ph-*H*), 6.77 (d, 2 H, Ph-*H*), 6.62 (t, 1 H, Ph-*H*), 4.50 (s, 2 H, CH₂N), 2.93 (s, 6 H, NCH₃), -0.84 (s, 6 H, AlCH₃) ppm. ¹³C{¹H} NMR (75 MHz, CDCl₃, 293 K): δ = 154.03, 154.01, 134.13, 131.53, 128.79, 128.27, 127.41, 118.37, 114.66, 114.26, 53.39, 44.64, –10.51 ppm.

ortho-C₆H₄(NEt₂) (CH₂NC₆H₃iPr₂-2,6)AlMe₂ (3f): This compound was prepared in the same way as described above for **3a** with **2f** (0.34 g, 1.0 mmol) and AlMe₃ (1.0 mL, 1.0 mmol) as starting materials. The product (0.36 g, 92%) was obtained as a colorless crystalline solid. C₂₅H₃₉AlN₂ (394.57): calcd. C 76.10, H 9.96, N 7.10; found C 76.15, H 9.93, N 7.18. ¹H NMR (300 MHz, CDCl₃, 293 K): δ = 7.51 (d, 1 H, Ph-*H*), 7.36 (m, 3 H, Ph-*H*), 7.24–7.11 (m, 3 H, Ph-*H*), 4.35 (s, 2 H, CH₂N), 3.69 [m, 2 H, CH(CH₃)₂], 3.50 (m, 4 H, NCH₂CH₃), 1.25 [d, 12 H, CH(CH₃)₂], 1.19 (t, 6 H, NCH₂CH₃), -1.04 (s, 6 H, AlCH₃) ppm. ¹³C{¹H} NMR (75 MHz, CDCl₃, 293 K): δ = 149.52, 142.84, 135.82, 130.81, 129.45, 127.56, 126.67, 124.31, 123.15, 121.69, 60.81, 44.40, 27.14, 25.92, 24.38, 9.20, -8.52 ppm.

ortho-C₆H₄(NEt₂) (CH₂NC₆H₃Me₂-2,6)AlMe₂ (3g): This compound was prepared in the same way as described above for 3a with 2g (0.42 g, 1.5 mmol) and AlMe₃ (1.5 mL, 1.5 mmol) as starting materials. The product (0.44 g, 87%) was obtained as a colorless crystalline solid. C₂₁H₃₁AlN₂ (338.47): calcd. C 74.52, H 9.23, N 8.28; found C 74.48, H 9.27, N 8.23. ¹H NMR (300 MHz, CDCl₃, 293 K): δ = 7.32 (d, 1 H, Ph-*H*), 7.29 (t, 1 H, Ph-*H*), 7.24 (m, 2 H, Ph-*H*), 7.05 (d, 2 H, Ph-*H*), 6.91 (t, 1 H, Ph-*H*), 4.34 (s, 2 H, CH₂N), 3.55 (m, 4 H, NCH₂CH₃), 2.31 (s, 6 H, CH₃), 1.20 (t, 6 H, NCH₂CH₃), -1.03 (s, 6 H, AlCH₃) ppm. ¹³C{¹H} NMR (75 MHz, CDCl₃, 293 K): δ = 150.84, 143.42, 138.32, 136.09, 130.89, 128.20, 126.94, 126.59, 123.02, 121.66, 57.30, 44.40, 19.18, 9.06, -8.25 ppm.

ortho-C₆H₄(NEt₂) (CH₂NC₆H₅)AlMe₂ (3h): This compound was prepared in the same way as described above for 3a with 2h (0.51 g, 2.0 mmol) and AlMe₃ (2.0 mL, 2.0 mmol) as starting materials. The product (0.52 g, 84%) was obtained as a colorless crystalline solid. C₁₉H₂₇AlN₂ (310.41): calcd. C 73.52, H 8.77, N 9.02; found C 73.56, H 8.73, N 9.07. ¹H NMR (300 MHz, CDCl₃, 293 K): δ =

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7.37–7.23 (m, 4 H, Ph-*H*), 7.17 (t, 2 H, Ph-*H*), 6.75–6.63 (m, 3 H, Ph-*H*), 4.43 (s, 2 H, CH₂N), 3.42 (m, 4 H, NCH₂CH₃), 1.15 (t, 6 H, NCH₂CH₃) –0.79 (s, 6 H, AlCH₃) ppm. $^{13}C{^1H}$ NMR (75 MHz, CDCl₃, 293 K): δ = 146.88, 135.25, 131.90, 129.27, 128.92, 127.61, 127.15, 114.76, 114.67, 90.49, 53.96, 47.48, 10.23, –8.24 ppm.

ortho-C₆H₄(NMe₂)(CH₂NC₆H₃*i*Pr₂-2,6)Al-(OCH₂C₆H₅)₂ (4): To a solution of **3a** (0.37 g, 1.0 mmol) in toluene (20 mL) was added BnOH (1.0 M in toluene, 2.0 mL, 2.0 mmol) at –10 °C. The reaction mixture was allowed to gently warm to room temperature and stirred for 1 h. After removal of the solvent, the crude product was recrystallized from *n*-hexane to give the pure product as a colorless crystalline solid (0.50 g, 90%). C₃₅H₄₃AlN₂O₂ (550.71): calcd. C 76.33, H 7.87, N 5.09; found C 76.28, H 7.83, N 5.16. ¹H NMR (300 MHz, CDCl₃, 293 K): δ = 7.46–7.08 (m, 17 H, Ph-*H*), 5.01 (s, 4 H, OC*H*₂), 4.08 (s, 2 H, C*H*₂N), 3.42 [m, 2 H, C*H*(CH₃)₂], 2.74 (s, 6 H, NC*H*₃), 1.28 [d, 12 H, CH(C*H*₃)₂] ppm. ¹³C{¹H} NMR (75 MHz, C₆D₆, 293 K): δ = 152.87, 143.63, 142.69, 130.05, 129.69, 128.73, 128.68, 128.21, 128.15, 124.01, 123.60, 123.49, 120.02, 90.35, 67.15, 53.01, 45.31, 27.50, 24.34 ppm.

General Procedure for the Polymerization of CL: To a rapidly stirred solution of CL in toluene (the amounts of CL and toluene were calculated based on the conditions given in Table 2) was added a solution of a catalyst (0.19 mmol) and appropriate amount of BnOH in toluene (5 mL) under a nitrogen atmosphere at the desired temperature. After the reaction mixture was stirred for a prescribed period or until the reaction mixture became very viscous and could not be stirred, the reaction was quenched by the addition of an excess amount of aqueous acetic acid (1.0 N). The polymer was then precipitated by adding MeOH (100 mL) into the mixture, collected on a frit, washed with MeOH (3×10 mL), and dried in vacuo up to a constant weight.

Crystal Structure Determination: Single crystals of 3c and 3e suitable for X-ray structural analysis were obtained from n-hexane at

Table 3. Crystal data and structural refinements details for 3c and 3e.

	3c	3e			
Formula	C ₁₉ H ₂₇ AlN ₂	C ₁₇ H ₂₃ AlN ₂			
Fw	310.41	282.35			
Crystal system	orthorhombic	monoclinic			
Space group	$P2_{1}2_{1}2_{1}$	$P2_1/c$			
<i>a</i> [Å]	7.9459(16)	17.3507(13)			
b [Å]	15.360(3)	12.5371(9)			
c [Å]	15.453(3)	16.7569(12)			
	90	90			
β[°]	90	117.9610(10)			
γ [°]	90	90			
$V[Å^3]$	1886.0(7)	3219.6(4)			
Z	4	8			
D_{calcd} [gcm ⁻³]	1.093	1.165			
F(000)	672	1216			
Θ range for data collection	3.17 to 27.48°	1.33 to 26.03°			
Limiting indices	$-10 \le h \le 9$	$-21 \le h \le 21$			
-	$-19 \le k \le 19$	$-15 \le k \le 6$			
	$-19 \le l \le 19$	$-20 \le l \le 20$			
No. of data/restraints/parameters	4224/0/205	6344/0/369			
Goodness-of-fit on F^2	0.911	1.023			
Final R indices $I > 2\sigma(I)$	$R_1^{[a]} = 0.0594$	$R_1^{[a]} = 0.0549$			
	$wR_2^{[b]} = 0.0816$	$wR_2^{[b]} = 0.1214$			
R indices (all data)	$R_1^{[a]} = 0.1714$	$R_1^{[a]} = 0.0811$			
~ /	$wR_2^{[b]} = 0.1067$	$wR_2^{[b]} = 0.1345$			
R _{int}	0.1456	0.0414			
[a] $R_1 = \Sigma F_0 - F_c / \Sigma F_0 $. [b] $wR_2 = \{\Sigma w (F_0^2 - F_c^2)^2 / \Sigma w (F_0^2)^2\}^{1/2}$.					

-20 °C. Diffraction data of 3c were collected at 293 K with a Rigaku R-AXIS RAPID IP diffractometer equipped with graphitemonochromated Mo- K_{α} radiation ($\lambda = 0.71073$ Å). Diffraction data of 3e was collected at 293 K with a Bruker SMART-CCD diffractometer equipped with graphite-monochromated Mo- K_{α} radiation ($\lambda = 0.71073$ Å). Details of the crystal data, data collections, and structure refinements are summarized in Table 3. The structures were solved by direct methods and refined by full-matrix least-squares on F2. All non-hydrogen atoms were refined anisotropically and the hydrogen atoms were included in idealized position. All calculations were performed using the SHELXTL^[17] crystallographic software packages. CCDC-703530 (for 3c) and -703531 (for 3e) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/ data_request/cif.

Supporting Information (see footnote on the first page of this article): Molecular structure of **3e**.

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