# β-Diketiminate aluminium complexes: synthesis, characterization and ring-opening polymerization of cyclic esters†

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A series of aluminium alkyl complexes (BDI)$AlEt_2$ (**3a–m**) bearing symmetrical or unsymmetrical β-diketiminate ligand (BDI) frameworks were obtained from the reaction of triethyl aluminium and the corresponding β-diketimine. The monomeric structure of the aluminium complex **3k** was confirmed by an X-ray diffraction study, which shows that the aluminium center is coordinated by both of the nitrogen donors of the chelating diketiminate ligand and the two ethyl groups in a distorted tetrahedral geometry. Attempt to synthesize β-diketiminate aluminium alkoxide complexes by the reactions of monochloride complex "(BDI-**2a**)AlMeCl" (**4**) with alkali salts of 2-propanol gave unexpectedly an aluminoxane [(BDI-**2a**)AlMe]$_2$(μ-O) (**7**) as characterized by X-ray diffraction methods. Complexes **3a–m** and [(2,6-$^i$Pr$_2$C$_6$H$_3$NCMe)$_2$HC]$AlEt_2$ (**8**) were found to catalyze the ring-opening polymerization (ROP) of ε-caprolactone with moderate activities. The steric and electronic characteristics of the ancillary ligands have a significant influence on the polymerization performance of the corresponding aluminium complexes. The introduction of electron-donating substituents at the *para*-positions of the aryl rings in the ligand resulted in an apparent decrease in catalytic activity. Complex **3h** showed the highest activity among the investigated aluminium complexes due to the high electrophilicity of the metal center induced by the *meta*-trifluoromethyl substituents on the aryl rings. The increase of steric hindrance of the ligand by introducing *ortho*-substituents onto the phenyl moieties also resulted in a decrease in the catalytic activity. Although the viscosity average molecular weights ($M_\eta$) of the obtained poly(caprolactone)s increased with the enhancement of monomer conversion, the ROPs of ε-caprolactone initiated by complexes **3a–m** and **8** were not well-controlled, as judged from the broad molecular weight distributions (PDI = 1.66–3.74, $M_w/M_n$) of the obtained polymers and the nonlinear relationship of molecular weight *versus* monomer conversion.

## Introduction

Poly(ε-caprolactone) (PCL) and poly(lactide) (PLA) as well as their copolymers are the most important synthetic biodegradable polymers, and have attracted considerable attention mainly due to their biomedical and pharmaceutical applications.[1–6] In industry PCL and PLA are synthesized by ring-opening polymerizations (ROPs) using tin(II) bis(2-ethylhexanoate) ($SnOct_2$) as catalyst. Although $Sn(Oct)_2$ has been accepted as a food additive by the U.S. FDA, the toxicity associated with most tin compounds is a considerable drawback in the case of biomedical applications.[5] So researchers all over the world endeavor to explore novel well-defined catalysts which possess the characteristics of good biocompatibility, high catalytic activity and excellent stereoselectivity.

In recent years, aluminium bis(phenolate)-based complexes have proved to be efficient for the ROP of cyclic esters in the presence of alcohol, mainly due to their great success in: (1) initiating living ring-opening polymerization, producing polymers with well-controlled molecular weight and narrow molecular weight distribution; (2) stereocontrolled polymerization of chiral monomers such as lactides, for example Salen or Salen supporting aluminium complexes exhibit excellent stereoselectivity as well as reasonable catalytic activities in the polymerization of *rac*-lactide and *meso*-lactide.[7–11] Besides the aluminium bis(phenolate) systems, aluminium amide complexes have also proved to be active in the ROP of cyclic esters. Chakraborty and Chen[12] synthesized neutral three-coordinate chelating diamide aluminium complexes, which produced telechelic PCLs with high molecular weights up to $1.21 \times 10^6$ Da. Comparatively, aluminium complexes bearing purely nitrogen-containing polydentate ligands and their application in ROP of cyclic esters are still less investigated. Nevertheless, nitrogen-containing ligands prove to benefit other metals well. Coates *et al.* and Gibson *et al.* reported a series of zinc and magnesium complexes supported by β-diketiminate ligands, with zinc β-diketiminate complexes polymerizing *rac*-lactide to heterotactic PLA ($P_r = 0.94$ at 0 °C),[13] and *meso*-lactide to syndiotactic PLA ($P_r = 0.76$ at 0 °C).[13] On the other hand, the magnesium β-diketiminate complexes were extremely active for the polymerization of *rac*-lactide, polymerizing 500 equiv. of monomer up to 96% conversion in less than 5 min at 20 °C.[14] Based on the success with zinc and magnesium metals, Chisholm's group[15] synthesized β-diketiminate calcium complexes, which showed high

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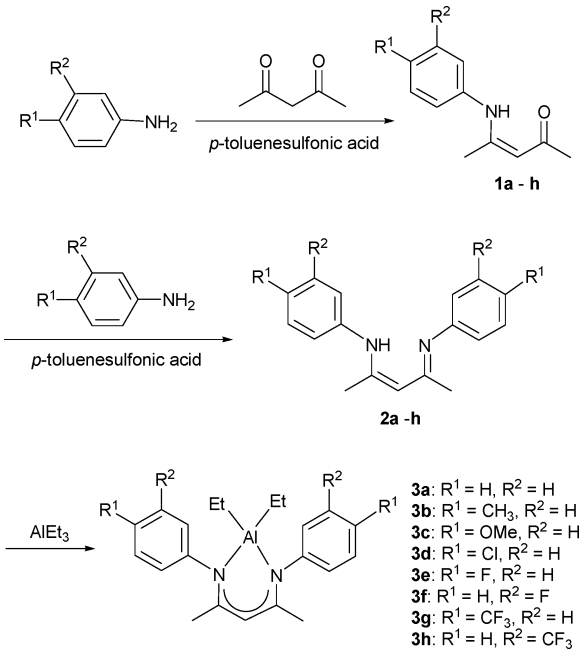
activity but hardly any stereoselectivity in the ROP of *rac*-lactide.

Aluminium complexes with β-diketiminate ligands have been reported extensively.[16–36] To the best of our knowledge, the studies of these complexes described in the literature are however limited to rearrangement reactions,[16–20] being employed as cocatalysts/active species for olefin polymerizations,[21–24] synthetic methodologies,[25–36] and have not yet been extended to act as initiators for the polymerization of cyclic esters; furthermore, nearly all of the β-diketiminate ligands involved possess a symmetrical structure.[37] β-diketimines as versatile ligands, allowing easy modulation of steric and electronic factors by varying the amide moieties,[14,38–44] would be ideal ligand sets for the design of novel aluminium-based catalysts/initiators for the polymerization of cyclic esters. It is conceivable that β-diketiminate aluminium complexes will possess catalytic activity for the ROP of cyclic esters due to the high Lewis acidity of the metal center that accounts for effective monomer activation *via* σ-bond coordination.[12] As a monoanionic bidentate ligand, β-diketiminate ligands tend to adopt a planar configuration when bonded to a metal atom, and construct an achiral metal center for most of the divalent or trivalent metals if the β-diketiminate itself is symmetric. Therefore it is desired to introduce some unsymmetrical features into the ligand framework in order to construct metal complexes capable of initiating stereoselective polymerization of chiral monomers. Herein we report on the synthesis of a series of aluminium diethyl complexes ligated by symmetrical or unsymmetrical β-diketiminate ligands, and their catalytic behavior for ROPs of cyclic esters. The steric and electronic effects of ligands on the polymerization of ε-caprolactone were explored. As far as we know, this is the first time that β-diketiminate aluminium complexes have been reported as initiators for the ring-opening polymerization of cyclic esters.

## Results and discussion

### Synthesis of β-diketiminate aluminium complexes

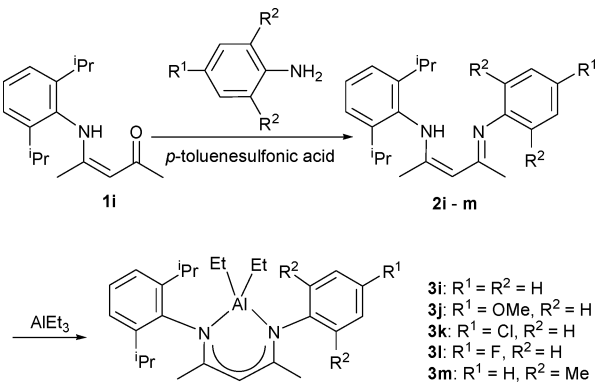
With the aim of unravelling the effect of the catalyst/initiator structure parameters on polymerization activity, various substituents such as alkyl, alkoxy, halide were adopted to obtain β-diketiminate ligands containing N-aryl moieties with differing electron-donating abilities. As depicted in Scheme 1, the symmetrical β-diketimines **2a–h** were synthesized in two steps using classic literature procedures:[14] (1) condensation of 2,4-pentanedione with one equiv. of primary aromatic amine in toluene, with *para*-toluenesulfonic acid as catalyst, afforded the enaminoketone intermediate **1**; (2) another equiv. of the same aromatic amine was pre-treated with *para*-toluenesulfonic acid in a 1 : 1 ratio for 3 h to afford *para*-toluenesulfonate, which was then reacted with the corresponding enaminoketone **1** to give β-diketimines **2a–h** in reasonable yields. In the second step, the one-pot reaction of enaminoketone, aromatic amine and *para*-toluenesulfonic acid failed to give any target product; the reaction of enaminoketone with the *para*-toluenesulfonic acid took place instead, preventing further reaction with the aromatic amine. The reactions of ligands **2a–h** with triethyl aluminium in a 1 : 1 molar ratio in *n*-hexane readily generated the four-coordinated aluminium complexes **3a–h** (Scheme 1), proceeding along with the elimination of 1 equiv. of




**Scheme 1**

ethane. Pale yellow crystals were obtained in each case in moderate to good yields after recrystallization from aliphatic solvents.

Similar two-step condensation reactions were adopted to synthesize the unsymmetrical β-diketimines. Successful synthesis was limited to the reactions of 4-(2,6-diisopropylphenyl)amino-3-penten-2-one (**1i**) with the corresponding aromatic amines (Scheme 2). The condensation of enaminoketones having smaller *ortho*-substituents than 2-propyl with the studied primary aromatic amines led to mixtures of all three possible β-diketiminates, which however are too similar to be separated from one another. Similar results have been reported by Park and Marshall.[42] Possibly a steric bulky group such as 2-propyl is essential to create sufficient space encumbrances to restrain the exchange reactions between the two different amine moieties involved in the structure. In contrast to symmetrical β-diketimines, the pretreatment of aromatic amine with *para*-toluenesulfonic acid is not necessary for the synthesis of unsymmetrical ligands **2i–m**, most likely due to the presence of bulky 2-propyl groups which block the reaction of **1i** with *para*-toluenesulfonic acid. Aluminium complexes **3i–m**



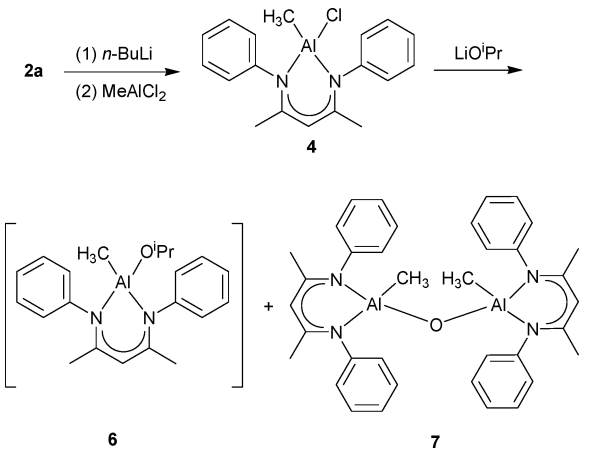

**Scheme 2**

with unsymmetrical β-diketimine were synthesized accordingly *via* the reactions of ligands **2i–m** with triethyl aluminium.

The $^1$H NMR spectra indicate that, for aluminium complexes **3a–d**, **3g–h** the chemical environments of both aromatic rings as well as the two backbone methyl groups are identical. In contrast, aluminium complexes **3i–m** with unsymmetrical β-diketiminate ligands exhibit different resonances for them in $^1$H NMR spectra. The chemical shifts of the γ-C*H* in complexes **3a–h** are about 4.9 ppm, almost the same as those in the neutral β-diketimines. For complexes **3i–m**, the chemical shifts of the γ-C*H* move to lower field significantly. One signal is displayed for the methine protons of 2-propyl groups in complexes **3i–m**, but restricted rotation about the N–aryl bonds gives rise to two separated doublets for the –CH(C$H_3$)$_2$ methyl groups. In addition, $^1$H NMR spectra of aluminium complexes **3i–m** reveal two diastereotopic methene protons in each ethyl group (Al-$CH_2$CH$_3$) which resonate at about $\delta$ −0.37 ppm as two separate multipeaks of dq mode,[45] suggesting that the bulky *ortho*-2-propyl substituents restrict the free rotation of the phenyl moiety on the NMR time scale.[45,46]

Further attempts to synthesize the corresponding alkoxide complexes were carried out by reacting the β-diketiminate aluminium diethyl complex **3e** with 2-propanol in toluene. No reaction occurred even under reflux conditions for long time, or using excess 2-propanol. The replacement of 2-propanol with the more acidic benzyl alcohol did not work either. Therefore an alternative salt metathesis route of treating a monochloride aluminium complex with LiO$^i$Pr was designed. In the first step β-diketimine **2a** was reacted with $Me_2AlCl$ to synthesize the monochloride aluminium complex (BDI-**2a**)AlMeCl (**4**). However, the reaction gave a mixture of monochloride complex (**4**) and dimethyl complex (**5**) in about a 1 : 2 molar ratio, which could hardly be separated from each other (Scheme 3). The elimination of hydrogen chloride seems even faster under the reaction conditions, possibly due to the presence of β-diketimine acting as a base. In consequence of this fact, a two-step salt metathesis route was adopted as outlined in Scheme 4. Monochloride aluminium complex **4**[47] could be obtained in moderate yield from the reaction of the lithium salt of **2a** and $MeAlCl_2$; the sequential treatment of **4** with LiO$^i$Pr gave a white solid after workup, however it was shown to be a mixture by $^1$H NMR spectroscopy. In addition to one set of resonances assignable to "[(BDI-**2a**)AlMe(O$^i$Pr)]" (**6**),[48] another set of resonances accounting for an unknown structure was also displayed, which was later characterized as an aluminoxane complex [(BDI-**2a**)AlMe]$_2$(μ-O) (**7**) by an X-ray diffraction study (*vide infra*). Due to the similar solubility of **6** and **7**, further separation processes failed to give analytically pure products. In consideration of the better reactivity of the sodium salt than the lithium one, NaO$^i$Pr was reacted with complex **4**. This strategy however could not improve the reaction to give aluminium isopropoxide **6**; instead, unexpectedly, only complex **7** was isolated as colorless crystals in high yield.[49]

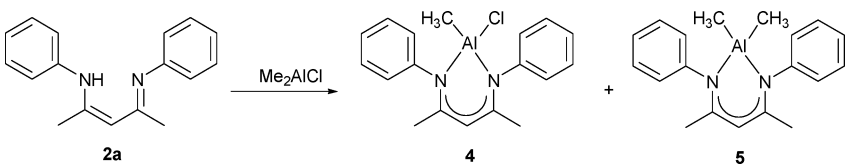



**Scheme 4**

Alumoxanes as potential active catalysts and cocatalysts for the polymerization of a wide range of organic monomers have attracted much attention from chemists.[50–53] In most of the cases, the alumoxanes were prepared by stoichiometric hydrolysis of aluminium alkyls or hydride with water or water contained in hydrated metal salts.[34,36,54,55] Reaction of aluminium alkyls or hydride with reactive oxygen-containing inorganic or organic substrates, such as alkali metal oxides,[56] anhydrous lithium hydroxide,[57] siloxanes,[58] or carboxylate acid,[59] also provided effective synthetic approaches to well-characterized alumoxanes.[60,61] More recently, Roesky and co-workers reported the stoichiometric hydrolysis of the aluminium–halide bond in aluminium β-diketiminate complexes LAlMeCl to afford aluminoxanes,[22,24] however a complicated system of KOH/$H_2$O/KH in liquid ammonia and toluene, or a strong nucleophilic reagent such as N-heterocyclic carbene acting as hydrogen halide acceptor, are essentially required to fulfill the transformation under mild conditions.[34,62–64] Simple treatment of LAlMeCl with water in THF only led to complete hydrolysis yielding an insoluble aluminium oxide or hydroxide under elimination of β-diketimine.[64] In view of the selective formation of complex **7** in good yield in this work, the possibility that it was produced by the contamination of moisture was therefore excluded. Although the mechanism is not clear at the present stage, it is conceivable that the alkali salt may take part in the reaction and play an important role. As we know, this is the first example that an alkali salt of an alcohol may have promoted the selective transformation of aluminium monohalide to an alumoxane complex.

### Crystal structure of aluminium complexes 3k and 7

Single crystals of aluminium complexes **3k** and **7** suitable for X-ray diffraction measurement were obtained by slowly cooling a saturated *n*-hexane solution to −20 °C and 0 °C respectively.




**Scheme 3**

**Table 1** Crystal data and structure refinement details for **3k** and **7**

| | **3k** | **7** |
|---|---|---|
| Empirical formula | $C_{27}H_{38}AlClN_2$ | $C_{36}H_{40}Al_2N_4O$ |
| Formula weight | 453.02 | 598.68 |
| $T$/K | 293(2) | 293(2) |
| Wavelength/Å | 0.71073 | 0.71073 |
| Crystal size/mm | 0.50 × 0.49 × 0.25 | 0.48 × 0.36 × 0.30 |
| Crystal system | Monoclinic | Orthorhombic |
| Space group | *P*2(1)/*n* | *Pbca* |
| $a$/Å | 12.3283(13) | 15.5268(11) |
| $b$/Å | 10.2992(10) | 19.5571(15) |
| $c$/Å | 21.520(2) | 22.6748(17) |
| $\alpha$/° | 90.00 | 90.00 |
| $\beta$/° | 93.270(2) | 90.00 |
| $\gamma$/° | 90.00 | 90.00 |
| Volume/Å$^3$ | 2727.9(5) | 6885.4(9) |
| $Z$ | 4 | 8 |
| Calcd density/Mg m$^{-3}$ | 1.103 | 1.155 |
| Absorp coeff/mm$^{-1}$ | 0.188 | 0.117 |
| $F$(000) | 976 | 2544 |
| $\theta$ range for data collection/° | 1.86 to 27.00 | 1.80 to 27.00 |
| Limiting indices | $-15<=h<=14$, $-6<=k<=13$, $-27<=l<=25$ | $-19<=h<=16$, $-23<=k<=24$, $-28<=l<=28$ |
| Reflns collected/unique | 15695/5952 [$R$(int) = 0.1071] | 38829/7492 [$R$(int) = 0.0968] |
| Max. and min. transmn | 1.00000 and 0.76883 | 1.00000 and 0.75196 |
| Data/restrains/parameters | 5952/0/288 | 7492/0/395 |
| Goodness-of-fit on $F^2$ | 0.882 | 0.789 |
| Final $R$ indices [$I > 2\sigma(I)$] | $R_1 = 0.0550$, $wR_2 = 0.1364$ | $R_1 = 0.0512$, $wR_2 = 0.1159$ |
| $R$ Indices (all data) | $R_1 = 0.0932$, $wR_2 = 0.1505$ | $R_1 = 0.1337$, $wR_2 = 0.1356$ |
| Largest diff. peak and hole/e Å$^{-3}$ | 0.266 and −0.204 | 0.319 and −0.185 |

**Table 2** Selected bond distances (Å) and angles (°) for complex **3k**

| | | | |
|---|---|---|---|
| Al–N(1) | 1.9062(16) | Al–N(2) | 1.9223(16) |
| Al–C(24) | 1.960(2) | Al–C(26) | 1.964(2) |
| N(1)–C(1) | 1.334(3) | N(2)–C(3) | 1.329(2) |
| C(1)–C(2) | 1.386(3) | C(2)–C(3) | 1.390(3) |
| C(1)–C(4) | 1.506(3) | C(3)–C(5) | 1.508(3) |
| N(1)–C(6) | 1.441(2) | N(2)–C(12) | 1.454(2) |
| N(1)–Al–N(2) | 94.50(7) | C(24)–Al–C(26) | 115.59(11) |
| N(1)–Al–C(24) | 113.48(10) | N(2)–Al–C(24) | 112.68(9) |
| N(1)–Al–C(26) | 105.58(9) | N(2)–Al–C(26) | 112.90(9) |

**Table 3** Selected bond distances (Å) and angles (°) for complex **7**

| | | | |
|---|---|---|---|
| Al(1)–N(1) | 1.904(2) | Al(2)–N(3) | 1.909(2) |
| Al(1)–N(2) | 1.912(2) | Al(2)–N(4) | 1.902(2) |
| Al(1)–O(1) | 1.6797(18) | Al(2)–O(1) | 1.6807(18) |
| Al(1)–C(18) | 1.942(3) | Al(2)–C(36) | 1.934(3) |
| N(1)–Al(1)–N(2) | 94.69(10) | N(3)–Al(2)–N(4) | 95.46(11) |
| Al(1)–O–Al(2) | 168.90(12) | | |

Crystallographic data, results of structure refinements, and selected bond lengths and angles are summarized in Tables 1, 2 and 3.

As shown in Fig. 1, being surrounded by two nitrogen donors of the chelating β-diketiminate ligand and two ethyl groups, the aluminium center in complex **3k** possesses a distorted tetrahedral geometry with the bite angle of N(1)–Al–N(2) (94.50(7)°) significantly smaller than the regular tetrahedral angle of 109.28°, which however falls into the normal range of 86.76–100.04° for the tetracoordinate β-diketiminate metal complexes.[24,27,45,46,65–68] The C(24)–Al–C(26) angle of 115.59(11)° is comparable to those observed in symmetrical β-diketiminate aluminium complexes [(4-MeC$_6$H$_4$NCMe)$_2$HC]AlMe$_2$ (115.4(2)°)[25] and [(2,6-$^i$Pr$_2$C$_6$H$_3$NCMe)$_2$HC]AlMe$_2$ (117.4(1)°).[16] The N1–C1–C2–C3–N2 backbone of the ligand in complex **3k** is essentially planar with the aluminium center deviating from it by 0.5595 Å. This value tends to be sensitive to the steric bulkiness of the *ortho*-substituents of the phenyl moieties in the β-diketiminate ligand, since deviations of 0.33 Å and 0.72 Å have been observed for [(4-MeC$_6$H$_4$NCMe)$_2$HC]AlMe$_2$ and [(2,6-$^i$Pr$_2$C$_6$H$_3$NCMe)$_2$HC]AlMe$_2$ respectively. Obviously the more bulky the *ortho*-substituents, the larger the deviation of the aluminium center from the backbone plane will be. The very close bond lengths of N(1)–C(1) (1.334(3) Å) and N(2)–C(3) (1.329(2) Å), as well as C(1)–C(2) (1.386(3) Å) and C(2)–C(3) (1.390(3) Å) indicate the multiple bond character and significant delocalization in these bonds. The two aryl rings have similar orientations towards the ligand backbone, with the dihedral angle of 78.15° formed by the 2,6-diisopropylphenyl ring and that of 80.74° by

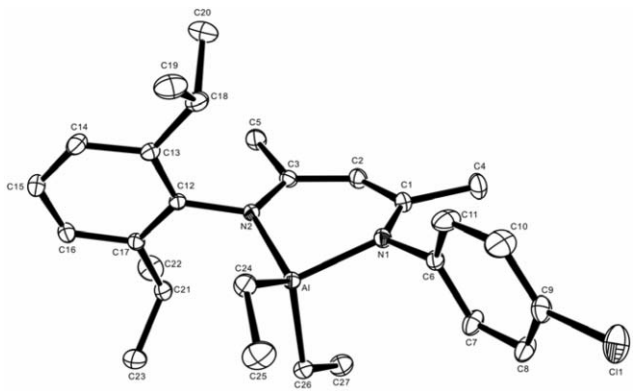



**Fig. 1** ORTEP diagram of the molecular structure of (BDI-**2k**)AlEt$_2$ (**3k**). Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

the 4-chlorophenyl ring. The two Al–N bond lengths (Al–N(1) = 1.9062(16), Al–N(2) = 1.9223(16) Å) in **3k** are almost identical, with the Al–N(2) (N-phenyl-2,6-diisopropyl) bond length slightly elongated by about 0.02 Å. The rather long Al···C (C1, C2, C3) contacts (2.849–3.147 Å) and the orientation of the chelate ring N1–C1–C2–C3–N2 exclude any π interaction between the β-diketiminate ligand and the metal center in **3k**, just as has been reported for β-diketiminate aluminium or zinc complexes.[13,14,16,25]

The X-ray structural analysis (Fig. 2) of compound **7** unambiguously indicated the formation of an Al(1)–O–Al(2) unit and its nearly linear structure, with this angle (168.90(12)°) being smaller than that in the pentafluoro-substituted complex $\{HC[(CMe)(NC_6F_5)]_2AlMe\}_2(\mu\text{-}O)$ (174.42(11)°),[34] but significantly larger than the one in $\{HC[(CMe)(2,6\text{-}^iPrNC_6H_3)]_2\text{-}AlOH\}_2(\mu\text{-}O)$ (143.84(16)°).[62] In complex **7** each aluminium center adopts a distorted tetrahedral geometry constructed by two nitrogen atoms of the ligand, a methyl group and one (μ-O) unit. The Al–O bond lengths (1.6797(18), 1.6807(18) Å) are slightly shorter than those in $\{HC[(CMe)(NC_6F_5)]_2AlMe\}_2(\mu\text{-}O)$ (1.689(2), 1.685(2) Å), possibly resulting from the smaller Al(1)–O–Al(2) angle.[34] The two Al–C bonds are in *trans*-position relative to the Al(1)–O–Al(2) plane, with the bond lengths (avg. 1.938(3) Å) slightly shorter than those in $\{HC[(CMe)(NC_6F_5)]_2AlMe\}_2(\mu\text{-}O)$ (avg 1.956(2) Å).[34] Besides, other structural features such as the N–Al–N bond angles (94.69(10)°, 95.46(11)°) are comparative to those in **3k** and other reported β-diketiminate dialkyl aluminium complexes.[16,25]

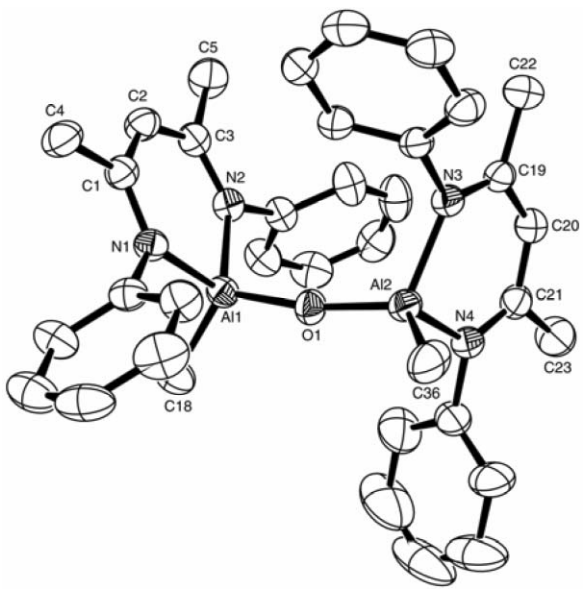



**Fig. 2** ORTEP diagram of the molecular structure of [(BDI-**2a**)-AlMe]$_2$(μ-O) (**7**). Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity.

### Ring-opening polymerization of *rac*-lactide

As we have mentioned that the corresponding aluminium alkoxides could not be generated from the reaction of this series of β-diketiminate aluminium complexes and alcohol, complex **3e** was added directly to a solution of *rac*-lactide (*rac*-LA) in toluene at 80 °C with an [Al]/[*rac*-LA] ratio of 1 : 100. However no polymer could be isolated after long reaction times of more than 10 d, implying that neither the Al–N bonding nor the Al–alkyl bonding in these complexes is active enough to initiate the ring opening polymerization of lactide monomer. Lewiński *et al.*[70] found that the complex $[Me_2Al(\mu\text{-}OCH_2CH_2OMe)]_2$ was inactive towards polymerization of lactide at 40 °C in $CH_2Cl_2$; after introducing the bulky *tert*-butyl group, the complex $[^tBu_2Al(\mu\text{-}OCH_2CH_2OMe)]_2$ was effective for the ROP of lactide at 40 °C. The authors suggested that the different chelating extent of the lactide monomer with the metal center in these two cases could be responsible for the inverse catalytic behavior. It is reasonable that the inactivity of our complexes for the ROP of lactide might also be due to the strong chelation of lactide with aluminium, which suppressed the further insertion of incoming monomer, although the chelate species was not obtained.

### Ring-opening polymerization of ε-caprolactone

β-Diketiminate aluminium complexes **3a–m** as well as the previously reported bulky aluminium complex $[(2,6\text{-}^iPr_2C_6H_3NCMe)_2HC]AlEt_2$ (**8**) however do initiate the ring-opening polymerization of ε-caprolactone (ε-CL) in toluene at 80 °C. The polymerization results are listed in Table 4, all complexes displayed moderate activities for the polymerization of ε-caprolactone, and the structure of the ancillary ligands has a significant influence on the polymerization behavior of the corresponding aluminium complexes.

Comparing the polymerization runs performed for 9 h in Table 4, several structure–activity trends may be drawn. It is found that for aluminium complexes **3a–h** with symmetrical β-diketiminate ligands, the electronic nature of the *para*- or *meta*-substituents of the phenyl groups exerts great influence on the ROP of ε-CL. A clear decreasing tendency of catalytic activity is found for complexes **3a–c** in the order **3a** (*p*-H) > **3b** (*p*-Me) > **3c** (*p*-OMe) (runs 1, 3, 5), indicating that electron-donating substituents at the *para*-position are a disadvantage to the catalytic activity. The introduction of electron-donating groups on the phenyl rings decreases the electrophilicity of the aluminium center through the chelating π-system of the ancillary ligand, and is thus unfavorable for the coordination/insertion of the cyclic ester monomer and leads to a decrease in activity.[71] Based on this point of view, complexes **3d** and **3e** bearing electron-withdrawing *para*-chloro or -fluoro substituents are expected to display increased activities. However the polymerization experiments gave inverse results. Complexes **3d** (*p*-Cl) and **3e** (*p*-F) show much lower activity compared with the unsubstituted complex **3a**, and complex **3d** is slightly more active than **3e** (runs 1, 7, 9). Nevertheless, when a fluorine atom was introduced at the *meta*-position of the phenyl moieties, complex **3f** does show higher activity than **3a** (run 11 *vs.* 1). The influence of halogen substitution at the ancillary ligands on the polymerization performance of the corresponding metal catalysts/initiators for cyclic esters has been investigated in other cases,[36,72–75] but conflicting results are usually obtained. A decrease in catalytic activity was observed for bis(phenolato)bis(amine) aluminium complexes with *para*-bromo substitution at the phenoxy moieties;[72] whereas a great improvement in activity was obtained for salen–aluminium complexes with *para*-chloro substitution.[36,73] When halide-substituted amine-phenolate ligands were employed with Group IV metals, the opposite influence was found for

**Table 4** Ring-opening polymerization of ε-CL initiated by aluminium complexes **3a–m** and **8**[a]

| Run | Cat. | Time/h | Conv.[b] (%) | $M_{Cald}$[c] | $M_\eta$[d] ($10^4$) | $M_w$[f] ($10^4$) | $M_w/M_n$[f] |
|---|---|---|---|---|---|---|---|
| 1 | **3a** | 9 | 73 | 8322 | 11.2 | | |
| 2 | | 17 | 89 | 10 146 | 12.5 | | |
| 3 | **3b** | 9 | 62 | 7068 | 6.20 | | |
| 4 | | 17 | 92 | 10 488 | 7.54 | | |
| 5 | **3c** | 9 | 50 | 5700 | 4.13 | | |
| 6 | | 24 | 85 | 9690 | 6.58 | 3.48 | 2.06 |
| 7 | **3d** | 9 | 57 | 6498 | 4.02 | | |
| 8 | | 17 | 89 | 10 146 | 5.32 | | |
| 9 | **3e** | 9 | 49 | 5586 | 5.65 | 3.18 | 3.74 |
| 10 | | 17 | 92 | 10 488 | 9.50 | | |
| 11 | **3f** | 9 | 86 | 9804 | 11.3 | 5.52 | 2.48 |
| 12 | | 17 | 96 | 10 944 | 10.2 | | |
| 13 | **3g** | 7 | 74 | 8436 | 7.66 | 5.35 | 1.66 |
| 14 | | 9 | 91 | 10 374 | 8.39 | | |
| 15 | **3h** | 7 | 85 | 9690 | 6.98 | | |
| 16 | | 9 | 93 | 10 602 | 7.85 | | |
| 17 | **3i** | 9 | 30 | 3420 | 4.41 | | |
| 18 | | 56 | 74 | 8436 | 5.10 | | |
| 19 | **3j** | 9 | 11 | 1254 | [e] | | |
| 20 | | 48 | 82 | 9348 | 3.73 | | |
| 21 | **3k** | 9 | 23 | 2622 | [e] | | |
| 22 | | 48 | 91 | 10 374 | 3.44 | | |
| 23 | **3l** | 9 | 18 | 2052 | 2.72 | | |
| 24 | | 48 | 90 | 10 260 | 5.04 | 4.27 | 2.42 |
| 25 | **3m** | 240 | 72 | 8208 | 3.22 | | |
| 26 | **8** | 240 | 6.9 | 786 | 0.23 | | |

[a] $[\varepsilon\text{-CL}]_0/[Al]_0 = 100$, $[\varepsilon\text{-CL}]_0 = 1.0$ M, toluene, 80 °C. [b] Determined by $^1$H NMR spectroscopy. [c] $M_{Cald} = ([\varepsilon\text{-CL}]_0/[Al]_0) \times 114 \times$ conv.%. [d] Viscosity measurements, in DMF, 30 °C. [e] Not enough sample available for the measurement. [f] Determined by gel permeation chromatography, calibrated with polystyrene standards in THF, $M_w' = M_{w,GPC} \times 0.56$.[69]

titanium and zirconium complexes.[74] Obviously, the effect of halogen substitution on activity is considerably complicated. Halogen atoms, especially fluorine, being strongly electronegative are considered to display marked electron-withdrawing characteristics, but the lone pair in the p-orbital of the halogen atom can also lead to an electron-donating conjugated effect *via* p–π bonding to its *para*- and *ortho*-positions when introduced to a phenyl ring. From a comparison of catalytic activities of complexes **3d–f**, it seems that the lower activity of complexes **3d** and **3e** should be attributed to this electron-donating conjugated effect. In order to exclude the conjugated effect of the *para*-halogen substitution and verify the influence of an electron-withdrawing group, the trifluoromethyl group was introduced to the *para*- or *meta*-position of the phenyl rings. As expected, complexes **3g**, **3h** exhibit significantly higher activities for the ROP of ε-CL; and **3h** shows the highest activity among these β-diketiminate aluminium complexes; high conversion up to 93% was obtained within 9 h. With the aim of having a detailed understanding of the influence of these substituents on the polymerization processes, such as initiation, chain propagation, kinetic experiments were carried out for complexes **3a**, **3e**, **3f**, and **3g**. Semilogarithmic plots ($\ln\{([CL]_0 - [CL]_{eq})/([CL]_t - [CL]_{eq})\}$ *versus* time), typical of slow initiation, were observed in all cases (Fig. S1–S4, see ESI†). However, due to the lack of a method to determine accurately the concentration of active initiators at specified time intervals, this study finally failed to give believable results.†

A similar electronic influence of substituent on polymerization was also found for aluminium complexes **3i–m** with unsymmetrical β-diketiminate ligands. In the case of complex **3j**, introducing a methoxy group to the *para*-position of the aromatic ring led to a decrease in catalytic activity (run 19). Complexes **3k** and **3l** with *para*-halogen substitution display lower polymerization activities (runs 21 and 23) than the unsubstituted complex **3i**. In general, aluminium complexes **3i–l** with unsymmetrical β-diketiminate ligands show much lower catalytic activity when compared with complexes **3a–h**, the bulky *ortho*-2-propyl groups in one of the aryl rings remarkably block the coordination sphere of the metal center and restrain the coordination/insertion of the monomer. The unfavorable steric influence of the *ortho*-substitution is also incorporated into complexes **3m** and **8** (runs 25 and 26), only low to moderate monomer conversion was reached after long polymerization times of 240 h. Due to the difficulty encountered in the synthesis of the unsymmetrical β-diketiminate ligands with less steric hindrance than 2-propyl at the *ortho*-positions, further study concerning the steric and electronic cooperative effect on the ROP of ε-CL is restricted. It should also be pointed that with the advancement of the polymerizations, the monomer conversions were not able to reflect the real activities of the aluminium complexes due to the quite high viscosity of the reaction solution in some cases, which significantly restricted the effective monomer diffusion and coordination/insertion.

Molecular weight information of all poly(ε-caprolactone) samples was obtained by viscosity measurements and in selected cases by gel permeation chromatography (GPC). As shown in Table 4, in general, with the increase of monomer conversion, the viscosity-average molecular weights ($M_\eta$) of the polymer samples increase. The $M_\eta$ of all the polymers deviate considerably from the theoretical values (calculated with the assumption that each aluminium

center initiates one polymer chain). The poorly controlled nature of the ROP of ε-CL by these aluminium complexes is also indicated by the broad molecular weight distributions (MWD = 1.66–3.74) of the polymer samples *via* GPC analysis. Similar results were observed by Chakraborty and Chen when diamide aluminium complexes [N^N]AlR (N^N = ArN(CH$_2$)$_3$NAr) were used to catalyze the ROP of ε-CL.[12]

In order to understand the polymerization mechanism of ε-CL by aluminium complexes **3a–m**, ε-CL was polymerized with complex **3c** as initiator at the molar ratio of [ε-CL]/[Al] = 20 : 1 under the same conditions. The $^1$H NMR spectrum of the purified oligomer, obtained at 34% monomer conversion, indicates the existence of a tiny peak at 3.65 ppm which is assignable to the methene protons (–C*H*$_2$–) adjacent to a terminal hydroxyl group, suggesting a linear structure of the oligomer instead of cyclic. The molecular weight of more than 11 000 estimated from $^1$H NMR spectroscopy however hampers a detailed end-group analysis with ESI or MALDI-TOF spectrometry.[70] Due to the fact that complexes **3a–m** are hardly sensitive to oxygen/moisture and are inert to alcohol, the possibility of any impurity initiating the polymerization is excluded.

Based on an activity comparison between ketoiminate aluminium complexes (OCMeCHCMeNAr)$_2$AlR (R = Me, Et) and their corresponding chloride complexes, Huang *et al.*[46] assumed that Al–alkyl bonding is responsible for the initiation in the ROP of ε-CL. Nevertheless, no further evidence was observed to confirm it. Lewiński and co-workers even reported that, in the presence of dioxygen, methylaluminium(bisphenoxide) might be oxidized to give Al–OMe species which finally led to poly(ε-CL)s end-capped with a methoxy group.[76,77] The *in situ* $^1$H NMR polymerizations of ε-CL in the presence of [N^N]AlMe conducted by Chakraborty and Chen[12] however evidenced retaining the methyl group at the aluminium center and the initiation step involving monomer insertion into an Al–N bond. Since no characteristic signals of terminal ethyl (COC*H*$_2$C*H*$_3$) or ethoxy (COOC*H*$_2$C*H*$_3$) groups could be observed in the $^1$H NMR spectrum of the oligomer sample by complex **3c**, we suggest that, similar to the results of Chakraborty and Chen,[12] the ROP of ε-CL by complexes **3a–m** and **8** were most likely initiated by one of the Al–N bonds. After quenching with normal methanol, the terminal amide was hydrolyzed[78–80] and polymers with hydroxyl and carboxyl as terminals were obtained.

Compared to an alkoxy group, the initiation by an amide group is rather slow, which usually leads to a broad molecular weight distribution of the obtained polymer.[12] In complexes **3a–m**, the two Al–N bonds are averaged due to the delocalization of the β-diketiminate framework, it is clear that these Al–N bonds are even more inert than usual Al–amido bonds. After insertion of the first monomer into an Al–N bond, an Al–O bond is formed and sequentially induces a fast propagation of the polymer chain. The rather slow initiation step combined with quite fast chain propagation thus results in PCLs with significant deviation of experimental molecular weights from the theoretical values and broad molecular weight distributions as well. On the other hand, the bulky *ortho*-2-propyl groups at one of the aromatic rings in complexes **3i–m** obviously hindered the coordination/insertion of the monomer to the aluminium center, leading to a decrease in propagation rate. As a result, the $M_\eta$ of polymers produced by complexes **3i–m** are generally smaller than those obtained by complexes **3a–h** bearing less hindered β-diketiminate ligands at similar monomer conversions.

## Experimental

### General considerations

All manipulations were carried out under a dry argon atmosphere using standard Schlenk techniques unless otherwise indicated. Toluene and *n*-hexane were refluxed over sodium benzophenone prior to use. Chloroform-*d* was dried over calcium hydride. ε-Caprolactone (ACROS ORGANICS, 99%) was dried over $CaH_2$ for 1 d at 80 °C, then vacuum distilled and stored under argon. *n*-BuLi (2.3 M in *n*-hexane) was purchased from Chemetall. $AlEt_3$ (Fluka, 99%), $Me_2AlCl$ (supplied by Nanjing University, China) and $MeAlCl_2$ (Aldrich, 1.0 M in *n*-hexane) were used as received. Enaminoketones **1a–i**,[41,81] β-diketimines **2a**,[39] **2b**,[39] **2g**,[82] **2i**,[41] **2k**,[83] and [(2,6-$^i$Pr$_2$C$_6$H$_3$NCMe)$_2$HC]AlEt$_2$ (**8**)[16] were synthesized according to the published procedures. NMR spectra were recorded on Bruker AVANCE-500 and AVANCE-300 spectrometers with $CDCl_3$ as solvent ($^1$H: 500 MHz; $^{13}$C: 125 MHz and 75 MHz). Chemical shifts for $^1$H and $^{13}$C NMR spectra were referenced internally using the residual solvent resonances and reported relative to tetramethylsilane (TMS). Elemental analyses were performed on an EA-1106 instrument. The intrinsic viscosity of poly(ε-caprolactone) was measured with an Ubbelohde viscometer in *N*,*N*-dimethylformamide (DMF) at 30 °C. The viscosity average molecular weight of PCL was calculated according to the equation:[84] $[\eta]\ (dL/g) = 1.91 \times 10^{-4} M_\eta^{0.73}$. Gel permeation chromatography (GPC) analyses were carried out on a Waters instrument (M515 pump, Optilab Rex injector) in THF at 25 °C, at a flow rate of 1 mL min$^{-1}$. Calibration standards were commercially available narrowly distributed linear polystyrene samples that cover a broad range of molar masses ($10^3 < M < 2 \times 10^6$ g mol$^{-1}$).

### Syntheses

**2-(4-Methoxyphenyl)amino-4-(4-methoxyphenyl)imino-2-pentene (2c).** To a stirred solution of 4-methoxyaniline (6.150 g, 50.00 mmol) in 80 mL of toluene was added *para*-toluenesulfonic acid monohydrate (9.510 g, 50.00 mmol), and the mixture was stirred for 3 h at room temperature, then 4-(4-methoxyphenyl)amino-3-penten-2-one (**1c**) (10.26 g, 50.00 mmol) was added to it. A Dean–Stark apparatus was attached and the mixture was heated to reflux for 24 h. The reaction mixture was cooled and dried under reduced pressure to give a yellow solid. The obtained solid was treated with diethyl ether (100 mL), water (100 mL) and sodium carbonate (10.60 g, 100.0 mmol), and kept stirring. After complete dissolution, the aqueous phase was separated and extracted with diethyl ether. The combined organic phases were dried over $MgSO_4$ and rotary evaporated to dryness under reduced pressure to afford a yellow solid. Yellow crystals of **2c** (11.95 g, 77%) were obtained after recrystallization from methanol (Found: C, 73.55; H, 7.25; N, 9.06. Calc. for $C_{19}H_{22}N_2O_2$: C, 73.52; H, 7.14; N, 9.03%); mp 93.5–94.5 °C; $\delta_H$ (500 MHz, $CDCl_3$): 1.96 (s, 6H, C*H*$_3$), 3.79 (s, 6H, OC*H*$_3$), 4.84 (s, 1H, $\gamma$-C*H*), 6.85 (d, $^3J$ = 8.7 Hz, 4H, *o*-Ar-*H*), 6.91 (d, $^3J$ = 8.7 Hz, 4H, *m*-Ar-*H*), 12.57 (br s, 1H, N*H*); $\delta_C$ (75 MHz, $CDCl_3$): 20.7 (C*Me*),

55.5 (O*Me*), 96.4 (*C*H), 114.1 (Ar-*C*), 124.3 (Ar-*C*), 138.9 (Ar-*C*), 156.1 (Ar-*C*), 160.2 (N*C*Me).

**2-(4-Chlorophenyl)amino-4-(4-chlorophenyl)imino-2-pentene (2d).** β-Diketimine **2d** was synthesized by the same procedure as **2c**. 9.510 g (50.00 mmol) of *para*-toluenesulfonic acid monohydrate, 6.380 g (50.00 mmol) of 4-chloroaniline, and 10.48 g (50.00 mmol) of 4-(4-chlorophenyl)amino-3-penten-2-one (**1d**) were used to give **2d** (11.80 g, 74%) as yellow crystals (Found: C, 63.94; H, 5.09; N, 8.86. Calc. for $C_{17}H_{16}Cl_2N_2$: C, 63.96; H, 5.05; N, 8.78%); mp 86–87 °C; $\delta_H$ (500 MHz, $CDCl_3$): 1.98 (s, 6H, C$H_3$), 4.89 (s, 1H, $\gamma$-C*H*), 6.88 (d, $^3J = 8.7$ Hz, 4H, *o*-Ar-*H*), 7.25 (d, $^3J = 8.7$ Hz, 4H, *m*-Ar-*H*), 12.59 (br s, 1H, N*H*); $\delta_C$ (75 MHz, $CDCl_3$): 20.9 (C*Me*), 97.9 (*C*H), 123.8 (Ar-*C*), 128.6 (Ar-*C*), 128.9 (Ar-*C*), 144.1 (Ar-*C*), 159.8 (N*C*Me).

**2-(4-Fluorophenyl)amino-4-(4-fluorophenyl)imino-2-pentene (2e).** β-Diketimine **2e** was synthesized by the same procedure as **2c**. 9.510 g (50.00 mmol) of *para*-toluenesulfonic acid monohydrate, 5.561 g (50.00 mmol) of 4-fluoroaniline, and 9.650 g (50.00 mmol) of 4-(4-fluorophenyl)amino-3-penten-2-one (**1e**) were used to give **2e** (10.73 g, 75%) as yellow crystals (Found: C, 71.36; H, 5.63; N, 9.80. Calc. for $C_{17}H_{16}F_2N_2$: C, 71.31; H, 5.63; N 9.78%); mp 69–70 °C; $\delta_H$ (500 MHz, $CDCl_3$): 1.95 (s, 6H, C$H_3$), 4.87 (s, 1H, $\gamma$-C*H*), 6.88–6.93 (m, 4H, *o*-Ar-*H*), 6.96–7.01 (m, 4H, *m*-Ar-*H*), 12.53 (br s, 1H, N*H*); $\delta_C$ (75 MHz, $CDCl_3$): 20.7 (C*Me*), 97.1 (*C*H), 115.5 (Ar-*C*), 115.6 (Ar-*C*), 124.3 (Ar-*C*), 141.7 (Ar-*C*), 157.9 (Ar-*C*), 160.2 (Ar-*C*), 161.1 (N*C*Me).

**2-(3-Fluorophenyl)amino-4-(3-fluorophenyl)imino-2-pentene (2f).** β-Diketimine **2f** was synthesized by the same procedure as **2c**. 9.510 g (50.00 mmol) of *para*-toluenesulfonic acid monohydrate, 5.561 g (50.00 mmol) of 3-fluoroaniline and 9.650 g (50.00 mmol) of 4-(3-fluorophenyl)amino-3-penten-2-one (**1f**) were used to give **2f** (7.292 g, 51%) as light yellow crystals (Found: C, 71.27; H, 5.60; N, 9.84. Calc. for $C_{17}H_{16}F_2N_2$: C, 71.31; H, 5.63; N, 9.78%); mp 31–32 °C; $\delta_H$ (500 MHz, $CDCl_3$): 2.02 (s, 6H, C$H_3$), 4.90 (s, 1H, $\gamma$-C*H*), 6.71 (m, 6H, *o*-, *m*-Ar-*H*), 7.22 (d, $^3J = 8.0$ Hz, 1H, *p*-Ar-*H*), 7.25 (d, $^3J = 8.0$ Hz, 1H, *p*-Ar-*H*), 12.64 (br s, 1H, N*H*); $\delta_C$ (75 MHz, $CDCl_3$): 21.0 (C*Me*), 98.4 (*C*H), 109.2 (Ar-*C*), 109.6 (Ar-*C*), 109.8 (Ar-*C*), 110.1 (Ar-*C*), 118.1 (Ar-*C*), 118.5 (Ar-*C*), 129.9 (Ar–*C*), 130.1 (Ar–*C*), 147.3 (Ar–*C*), 147.5 (Ar–*C*), 159.7 (Ar–*C*), 161.5 (Ar–*C*), 164.8 (N*C*Me).

**2-(3-Trifluoromethylphenyl)amino-4-(3-trifluoromethylphenyl)-imino-2-pentene (2h).** To a stirred solution of 3-trifluoromethylaniline (8.056 g, 50.00 mmol) in 80 mL of toluene was added *para*-toluenesulfonic acid monohydrate (9.510 g, 50.00 mmol). The mixture was stirred for 3 h at room temperature, then 4-(3-trifluoromethylphenyl)amino-3-penten-2-one (**1h**) (12.15 g, 50.00 mmol) was added to it. A Dean–Stark apparatus was attached and the mixture was heated to reflux for 24 h. The reaction mixture was cooled and all the volatiles were evacuated under reduced pressure to give a yellow solid. The obtained solid was treated with diethyl ether (100 mL), water (100 mL) and sodium carbonate (10.60 g, 100.0 mmol), and kept stirring until dissolution was complete. The aqueous phase was separated and extracted with diethyl ether. The combined organic phase was dried over $MgSO_4$ and concentrated under reduced pressure. The obtained residue was distilled to afford **2h** as a yellow oil (12.56 g, 65%); bp 128–130 °C (0.3 Torr); $\delta_H$ (500 MHz, $CDCl_3$,): 2.05 (s, 6H, C$H_3$), 4.96 (s, 1H, $\gamma$-C*H*), 7.12 (d, $^3J = 8.0$ Hz, 2H, *o*-Ar-*H*), 7.21 (s, 2H, *o*-Ar-*H*), 7.32 (d, $^3J = 8.0$ Hz, 2H, *p*-Ar-*H*), 7.41 (t, $^3J = 8.0$ Hz, 2H, *m*-Ar-*H*), 12.71 (br s, 1H, N*H*).

**2-(2,6-Diisopropylphenyl)amino-4-(4-methoxyphenyl)imino-2-pentene (2j).** 9.510 g (50.00 mmol) of *para*-toluenesulfonic acid monohydrate, 6.160 g (50.00 mmol) of 4-methoxyaniline, 12.97 g (50.00 mmol) of 4-(2,6-diisopropylphenyl)amino-3-penten-2-one (**1i**), and 80 mL of toluene were combined in a round bottomed flask. A Dean–Stark apparatus was attached and the mixture was heated to reflux for 24 h. The reaction mixture was cooled and dried under reduced pressure to give a yellow solid. The obtained solid was treated with diethyl ether (100 mL), water (100 mL) and sodium carbonate (10.60 g, 100.0 mmol), and kept stirring. After complete dissolution, the aqueous phase was separated and extracted with diethyl ether. The combined organic phases were dried over $MgSO_4$ and rotary evaporated to dryness under reduced pressure to afford a yellow solid. Yellow crystals of **2j** (13.85 g, 76%) were obtained after recrystallization from methanol (Found: C, 79.21; H, 8.95; N, 7.69. Calc. for $C_{24}H_{32}N_2O$: C, 79.08; H, 8.85; N, 7.68%); mp 104–105 °C; $\delta_H$ (500 MHz, $CDCl_3$): 1.13 (d, $^3J = 6.9$ Hz, 6H, -CH(C$H_3$)$_2$), 1.20 (d, $^3J = 6.9$ Hz, 6H, -CH(C$H_3$)$_2$), 1.69 (s, 3H, C$H_3$), 2.00 (s, 3H, C$H_3$), 2.97 (sept, $^3J = 6.9$ Hz, 2H, -C*H*(CH$_3$)$_2$), 3.78 (s, 3H, OC$H_3$), 4.84 (s, 1H, $\gamma$-C*H*), 6.82 (d, $^3J = 8.8$ Hz, 2H, *o*-Ar-*H*), 6.90 (d, $^3J = 8.8$ Hz, 2H, *m*-Ar-*H*), 7.06–7.13 (m, 3H, *m*-, *p*-Ar-*H*), 12.61 (br s, 1H, N*H*); $\delta_C$ (75 MHz, $CDCl_3$): 20.5 (C*Me*), 21.3 (C*Me*), 22.7 (CH*Me*$_2$), 24.1 (CH*Me*$_2$), 28.3 (*C*HMe$_2$), 55.5 (O*Me*), 95.1 (*C*H), 114.1 (Ar-*C*), 122.9 (Ar-*C*), 124.0 (Ar-*C*), 124.8 (Ar-*C*), 136.6 (Ar-*C*), 140.2 (Ar-*C*), 143.6 (Ar-*C*), 156.2 (Ar-*C*), 156.8 (N*C*Me), 163.6 (N*C*Me).

**2-(2,6-Diisopropylphenyl)amino-4-(4-fluorophenyl)imino-2-pentene (2l).** β-Diketimine **2l** was synthesized by the same procedure as **2j**. 9.510 g (50.00 mmol) of *para*-toluenesulfonic acid monohydrate, 5.561 g (50.00 mmol) of 4-fluoroaniline and 12.97 g (50.00 mmol) of 4-(2,6-diisopropylphenyl)amino-3-penten-2-one (**1i**) were used to give **2l** (12.86 g, 73%) as colorless crystals (Found: C, 78.33; H, 8.30; N, 7.99. Calc. for $C_{23}H_{29}FN_2$: C, 78.37; H, 8.29; N, 7.95%); mp 100.5–101.5 °C; $\delta_H$ (500 MHz, $CDCl_3$): 1.13 (d, $^3J = 6.9$ Hz, 6H, -CH(C$H_3$)$_2$), 1.21 (d, $^3J = 6.9$ Hz, 6H, -CH(C$H_3$)$_2$), 1.70 (s, 3H, C$H_3$), 1.99 (s, 3H, C$H_3$), 3.00 (sept, $^3J = 6.9$ Hz, 2H, -C*H*(CH$_3$)$_2$), 4.87 (s, 1H, $\gamma$-C*H*), 6.78–6.80 (m, 2H, *o*-Ar-*H*), 6.93–6.96 (m, 2H, *m*-Ar-*H*), 7.13 (s, 3H, *m*-, *p*-Ar-*H*), 12.57 (br s, 1H, N*H*); $\delta_C$ (75 MHz, $CDCl_3$): 20.7 (C*Me*), 20.9 (C*Me*), 22.7 (CH*Me*$_2$), 24.3 (CH*Me*$_2$), 28.3 (*C*HMe$_2$), 95.5 (*C*H), 115.3 (Ar-*C*), 115.6 (Ar-*C*), 123.0 (Ar-*C*), 124.1 (Ar-*C*), 124.2 (Ar-*C*), 125.0 (Ar-*C*), 141.4 (Ar-*C*), 141.7 (Ar-*C*), 157.6 (Ar-*C*), 158.8 (Ar-*C*), 160.8 (N*C*Me), 162.1 (N*C*Me).

**2-(2,6-Diisopropylphenyl)amino-4-(2,6-dimethylphenyl)imino-2-pentene (2m).** β-Diketimine **2m** was synthesized by the same procedure as **2j**. 9.510 g (50.00 mmol) of *para*-toluenesulfonic acid monohydrate, 6.090 g (50.00 mmol) of 2,6-dimethylaniline and 12.97 g (50.00 mmol) of 4-(2,6-diisopropylphenyl)amino-3-penten-2-one (**1i**) were used to give **2m** (12.87 g, 71%) as colorless crystals (Found: C, 82.91; H, 9.43; N, 7.71. Calc. for $C_{25}H_{34}N_2$: C, 82.82; H, 9.45; N, 7.73%); mp 93–94 °C; $\delta_H$ (500 MHz, $CDCl_3$): 1.12 (d, $^3J = 6.9$ Hz, 6H, -CH(C$H_3$)$_2$), 1.23 (d, $^3J = 6.9$ Hz, 6H, -CH(C$H_3$)$_2$), 1.70 (s, 3H, C$H_3$), 1.71 (s, 3H, C$H_3$), 2.15 (s, 6H, Ar-C$H_3$), 3.09 (sept, $^3J = 6.9$ Hz, 2H, -C*H*(CH$_3$)$_2$), 4.88 (s, 1H,

$\gamma$-C*H*), 6.94 (t, $^3J$ = 7.4 Hz, 1H, *p*-Ar-*H*), 7.04 (d, $^3J$ = 7.4 Hz, 2H, *m*-Ar-*H*), 7.13 (m, 3H, *m*-, *p*-Ar-*H*), 12.28 (br s, 1H, N*H*); $\delta_C$ (75 MHz, $CDCl_3$): 18.3 (Ar-*Me*), 20.6 (C*Me*), 22.9 (CH*Me*$_2$), 24.5 (CH*Me*$_2$), 28.5 (*C*HMe$_2$), 93.3 (*C*H), 123.1 (Ar-*C*), 124.0 (Ar-*C*), 125.7 (Ar-*C*), 127.9 (Ar-*C*), 131.5 (Ar-*C*), 139.8 (Ar-*C*), 143.1 (Ar-*C*), 144.8 (Ar-*C*), 160.2 (N*C*Me), 162.0 (N*C*Me).

**(BDI-2a)AlEt$_2$ (3a).** A solution of $AlEt_3$ (0.457 g, 4.000 mmol) in 10 mL of *n*-hexane was added dropwise to a solution of β-diketimine **2a** (1.001 g, 4.000 mmol) in 20 mL of *n*-hexane at 0 °C with rapid stirring. The reaction solution was then stirred overnight at room temperature and filtered. The filtrate was concentrated under vacuum to approximate 2 mL. **3a** deposited after 24 h at −40 °C as yellow crystals (1.003 g, 75%) (Found: C, 75.30; H, 8.18; N, 8.39. Calc. for $C_{21}H_{27}AlN_2$: C, 75.42; H, 8.14; N, 8.38%); mp 63–64 °C; $\delta_H$ (500 MHz, $CDCl_3$): −0.36 (q, $^3J$ = 8.1 Hz, 4H, AlC*H*$_2$CH$_3$), 0.75 (t, $^3J$ = 8.1 Hz, 6H, AlCH$_2$C*H*$_3$), 1.83 (s, 6H, C*H*$_3$), 4.86 (s, 1H, $\gamma$-C*H*), 7.06 (d, $^3J$ = 7.4 Hz, 4H, *o*-Ar-*H*), 7.21 (t, $^3J$ = 7.4 Hz, 2H, *p*-Ar-*H*), 7.35 (t, $^3J$ = 7.4 Hz, 4H, *m*-Ar-*H*); $\delta_C$ (75 MHz, $CDCl_3$): 0.2 (Al*C*H$_2$CH$_3$), 9.1 (AlCH$_2$*C*H$_3$), 23.0 (C*Me*), 96.7 (*C*H), 125.7 (Ar-*C*), 126.1 (Ar-*C*), 129.1 (Ar-*C*), 145.7 (Ar-*C*), 168.3 (N*C*Me).

**(BDI-2b)AlEt$_2$ (3b).** Complex **3b** was synthesized using the same procedure as for complex **3a**. 0.457 g (4.000 mmol) of $AlEt_3$ and 1.113 g (4.000 mmol) of β-diketimine **2b** were used to obtain **3b** (1.015 g, 70%) as yellow crystals (Found: C, 76.12; H, 8.63; N, 7.67. Calc. for $C_{23}H_{31}AlN_2$: C, 76.21; H, 8.62; N 7.73%); mp 86–87 °C; $\delta_H$ (500 MHz, $CDCl_3$): −0.37 (q, $^3J$ = 8.1 Hz, 4H, AlC*H*$_2$CH$_3$), 0.77 (t, $^3J$ = 8.1 Hz, 6H, AlCH$_2$C*H*$_3$), 1.82 (s, 6H, C*H*$_3$), 2.35 (s, 6H, Ar-C*H*$_3$), 4.82 (s, 1H, $\gamma$-C*H*), 6.93 (d, $^3J$ = 8.0 Hz, 4H, *o*-Ar-*H*), 7.15 (d, $^3J$ = 8.0 Hz, 4H, *m*-Ar-*H*); $\delta_C$ (75 MHz, $CDCl_3$): 0.3 (Al*C*H$_2$CH$_3$), 9.2 (AlCH$_2$*C*H$_3$), 21.0 (Ar-*Me*), 23.0 (C*Me*), 96.4 (*C*H), 125.8 (Ar-*C*), 129.6 (Ar-*C*), 135.2 (Ar-*C*), 143.1 (Ar-*C*), 168.4 (N*C*Me).

**(BDI-2c)AlEt$_2$ (3c).** Complex **3c** was synthesized using the same procedure as for complex **3a**. 0.457 g (4.000 mmol) of $AlEt_3$ and 1.241 g (4.000 mmol) of β-diketimine **2c** were used to obtain **3c** (1.231 g, 78%) as yellow crystals (Found: C, 70.32; H, 7.84; N, 7.07. Calc. for $C_{23}H_{31}AlN_2O_2$: C, 70.03; H, 7.92; N, 7.10%); mp 82–83 °C; $\delta_H$ (500 MHz, $CDCl_3$): −0.38 (q, $^3J$ = 8.1 Hz, 4H, AlC*H*$_2$CH$_3$), 0.76 (t, $^3J$ = 8.1 Hz, 6H, AlCH$_2$C*H*$_3$), 1.80 (s, 6H, C*H*$_3$), 3.81 (s, 6H, Ar-OC*H*$_3$), 4.81 (s, 1H, $\gamma$-C*H*), 6.87 (dt, $^3J$ = 8.9 Hz, $^4J$ = 2.2 Hz, 4H, *o*-Ar-*H*), 6.95 (dt, $^3J$ = 8.9 Hz, $^4J$ = 2.2 Hz, 4H, *m*-Ar-*H*); $\delta_C$ (75 MHz, $CDCl_3$): 0.2 (Al*C*H$_2$CH$_3$), 9.2 (AlCH$_2$*C*H$_3$), 22.9 (C*Me*), 55.4 (O*Me*), 96.3 (*C*H), 114.2 (Ar-*C*), 126.9 (Ar-*C*), 138.6 (Ar-*C*), 157.4 (Ar-*C*), 168.8 (N*C*Me).

**(BDI-2d)AlEt$_2$ (3d).** Complex **3d** was synthesized using the same procedure as for complex **3a**. 0.457 g (4.000 mmol) of $AlEt_3$ and 1.276 g (4.000 mmol) of β-diketimine **2d** were used to obtain **3d** (1.258 g, 78%) as yellow crystals (Found: C, 62.31; H, 6.29; N, 6.99. Calc. for $C_{21}H_{25}AlCl_2N_2$: C, 62.54; H, 6.25; N, 6.95%); mp 96–98 °C; $\delta_H$ (500 MHz, $CDCl_3$): −0.37 (q, $^3J$ = 8.0 Hz, 4H, AlC*H*$_2$CH$_3$), 0.75 (t, $^3J$ = 8.0 Hz, 6H, AlCH$_2$C*H*$_3$), 1.82 (s, 6H, C*H*$_3$), 4.88 (s, 1H, $\gamma$-C*H*), 6.98 (d, $^3J$ = 8.2 Hz, 4H, *o*-Ar-*H*), 7.33 (d, $^3J$ = 8.2 Hz, 4H, *m*-Ar-*H*); $\delta_C$ (75 MHz, $CDCl_3$): $\delta$ 0.2 (Al*C*H$_2$CH$_3$), 9.2 (AlCH$_2$*C*H$_3$), 23.1 (C*Me*), 97.3 (*C*H), 127.7 (Ar-*C*), 129.6 (Ar-*C*), 129.7 (Ar-*C*), 131.5 (Ar-*C*), 168.6 (N*C*Me).

**(BDI-2e)AlEt$_2$ (3e).** Complex **3e** was synthesized using the same procedure as for complex **3a**. 0.457 g (4.000 mmol) of $AlEt_3$ and 1.144 g (4.000 mmol) of β-diketimine **2e** were used to obtain **3e** (1.182 g, 80%) as yellow crystals (Found: C, 68.10; H, 6.74; N, 7.51. Calc. for $C_{21}H_{25}AlF_2N_2$: C, 68.09; H, 6.80; N, 7.56%); mp 91–93 °C; $\delta_H$ (500 MHz, $CDCl_3$): −0.40 (q, $^3J$ = 8.1, 4H, AlC*H*$_2$CH$_3$), 0.73 (t, $^3J$ = 8.1 Hz, 6H, AlCH$_2$C*H*$_3$), 1.81 (s, 6H, C*H*$_3$), 4.86 (s, 1H, $\gamma$-C*H*), 6.96–7.06 (m, 8H, *o*-, *m*-Ar-*H*); $\delta_C$ (75 MHz, $CDCl_3$): 0.1 (Al*C*H$_2$CH$_3$), 9.1 (AlCH$_2$*C*H$_3$), 23.0 (C*Me*), 96.9 (*C*H), 115.8 (Ar-*C*), 116.1 (Ar-*C*), 127.5 (Ar-*C*), 141.5 (Ar-*C*), 159.1 (Ar-*C*), 162.4 (Ar-*C*), 168.9 (N*C*Me).

**(BDI-2f)AlEt$_2$ (3f).** Complex **3f** was synthesized using the same procedure as for complex **3a**. 0.457 g (4.000 mmol) of $AlEt_3$ and 1.144 g (4.000 mmol) of β-diketimine **2f** were used to obtain **3f** (0.738 g, 50%) as yellow crystals (Found: C, 68.00; H, 6.72; N, 7.63. Calc. for $C_{21}H_{25}AlF_2N_2$: C, 68.09; H, 6.80; N, 7.56%); mp 45–46 °C; $\delta_H$ (500 MHz, $CDCl_3$): −0.35 (q, $^3J$ = 8.1 Hz, 4H, AlC*H*$_2$CH$_3$), 0.76 (t, $^3J$ = 8.1 Hz, 6H, AlCH$_2$C*H*$_3$), 1.86 (s, 6H, C*H*$_3$), 4.90 (s, 1H, $\gamma$-C*H*), 6.79 (d, $^3J$ = 8.2 Hz, 2H, *o*-Ar-*H*), 6.85 (d, $^3J$ = 7.8 Hz, 2H, *o*-Ar-*H*), 6.94 (t, $^3J$ = 8.2 Hz, 2H, *p*-Ar-*H*), 7.32 (q, $^3J$ = 7.8 Hz, 2H, *m*-Ar-*H*); $\delta_C$ (75 MHz, $CDCl_3$): 0.1 (Al*C*H$_2$CH$_3$), 9.1 (AlCH$_2$*C*H$_3$), 23.0 (C*Me*), 97.3 (*C*H), 112.7 (Ar-*C*), 113.0 (Ar-*C*), 113.3 (Ar-*C*), 113.5 (Ar-*C*), 121.8 (Ar-*C*), 121.9 (Ar-*C*), 130.2 (Ar-*C*), 130.3 (Ar-*C*), 147.2 (Ar-*C*), 147.4 (Ar-*C*), 161.4 (Ar-*C*), 164.7 (Ar-*C*), 168.6 (N*C*Me).

**(BDI-2g)AlEt$_2$ (3g).** A solution of $AlEt_3$ (0.514 g, 4.000 mmol) in 10 mL of toluene was added dropwise to a solution of β-diketimine **2g** (1.545 g, 4.000 mmol) in 20 mL of toluene at 0 °C with rapid stirring. The reaction solution was stirred overnight at room temperature and at 60 °C for 48 h, then was concentrated under vacuum to afford an orange-yellow sticky solid. 10 mL of *n*-hexane was added and the slightly turbid solution was filtered. The filtrate was concentrate under reduced pressure to approximate 3 mL. **3g** deposited after 24 h at −40 °C as yellow crystals (1.072 g, 57%) (Found: C, 58.47; H, 5.41; N, 5.95. Calc. for $C_{23}H_{25}AlF_6N_2$: C, 58.72; H, 5.36; N, 5.95%); mp 73–74 °C; $\delta_H$ (500 MHz, $CDCl_3$): −0.37 (q, $^3J$ = 8.1 Hz, 4H, AlC*H*$_2$CH$_3$), 0.74 (t, $^3J$ = 8.1 Hz, 6H, AlCH$_2$C*H*$_3$), 1.84 (s, 6H, C*H*$_3$), 4.95 (s, 1H, $\gamma$-C*H*), 7.17 (d, $^3J$ = 8.3 Hz, 4H, *o*-Ar-H), 7.64 (d, $^3J$ = 8.3 Hz, 4H, *m*-Ar-H); $\delta_C$ (125 MHz, $CDCl_3$): 0.1 (Al*C*H$_2$CH$_3$), 9.0 (AlCH$_2$*C*H$_3$), 23.1 (C*Me*), 97.8 (*C*H), 124.1 (q, $^1J_{C\text{-}F}$ = 270.0 Hz, *C*F$_3$), 126.4 (Ar-*C*), 128.1 (q, $^2J_{C\text{-}C\text{-}F}$ = 32.4 Hz, Ar-*C*), 146.1 (Ar-*C*), 168.7 (N*C*Me).

**(BDI-2h)AlEt$_2$ (3h).** Complex **3h** was synthesized using the same procedure as for complex **3a**. 0.457 g (4.000 mmol) of $AlEt_3$ and 1.545 g (4.000 mmol) of β-diketimine **2h** were used to obtain **3h** (1.279 g, 68%) as yellow crystals (Found: C, 58.96; H, 5.22; N, 5.78. Calc. for $C_{23}H_{25}AlF_6N_2$: C, 58.72; H, 5.36; N, 5.95%); mp 79–80 °C; $\delta_H$ (500 MHz, $CDCl_3$): −0.38 (q, $^3J$ = 8.1 Hz, 4H, AlC*H*$_2$CH$_3$), 0.73 (t, $^3J$ = 8.1 Hz, 6H, AlCH$_2$C*H*$_3$), 1.84 (s, 6H, C*H*$_3$), 4.95 (s, 1H, $\gamma$-C*H*), 7.25 (m, 2H, *o*-Ar-H), 7.32 (s, 2H, *o*-Ar-H), 7.47–7.50 (m, 4H, *m*-, *p*-Ar-H); $\delta_C$ (125 MHz, $CDCl_3$): $\delta$ 0.1 (Al*C*H$_2$CH$_3$), 8.8 (AlCH$_2$*C*H$_3$), 23.1 (C*Me*), 97.7 (*C*H), 122.6 (Ar-*C*), 122.9 (Ar-*C*), 123.7 (q, $^1J_{C\text{-}F}$ = 270.0 Hz, *C*F$_3$), 129.4 (Ar-*C*), 129.7 (Ar-*C*), 131.8 (q, $^2J_{C\text{-}C\text{-}F}$ = 32.4 Hz, Ar-*C*), 146.1 (Ar-*C*), 168.7 (N*C*Me).

**(BDI-2i)AlEt$_2$ (3i).** Complex **3i** was synthesized using the same procedure as for complex **3a**. 0.457 g (4.000 mmol) of $AlEt_3$ and

1.338 g (4.000 mmol) of β-diketimine **2i** were used to obtain **3i** (1.155 g, 69%) as colorless crystals (Found: C, 77.57; H, 9.41; N, 6.54. Calc. for $C_{27}H_{39}AlN_2$: C, 77.47; H, 9.39; N, 6.69%); mp 67–68 °C; $\delta_H$ (500 MHz, $CDCl_3$): −0.41 (dq, $^2J$ = 14.3 Hz, $^3J$ = 8.1 Hz, 2H, $AlCH_2CH_3$), −0.32 (dq, $^2J$ = 14.3 Hz, $^3J$ = 8.1 Hz, 2H, $AlCH_2CH_3$), 0.73 (t, $^3J$ = 8.1 Hz, 6H, $AlCH_2CH_3$), 1.17 (d, $^3J$ = 6.8 Hz, 6H, -CH($CH_3$)$_2$), 1.20 (d, $^3J$ = 6.8 Hz, 6H, -CH($CH_3$)$_2$), 1.77 (s, 3H, $CH_3$), 1.91 (s, 3H, $CH_3$), 3.08 (sept, $^3J$ = 6.8 Hz, 2H, -$CH$(CH$_3$)$_2$), 5.12 (s, 1H, γ-$CH$), 7.00 (d, $^3J$ = 7.3 Hz, 2H, *o*-Ar-*H*), 7.14 (d, $^3J$ = 7.3 Hz, 2H, *m*-Ar-*H*), 7.20 (m, 2H, *p*-Ar-*H*), 7.34 (t, $^3J$ = 7.7 Hz, 2H, *m*-Ar-*H*); $\delta_C$ (75 MHz, $CDCl_3$): δ −0.1 ($AlCH_2CH_3$), 9.6 ($AlCH_2CH_3$), 22.8 (C*Me*), 23.3 (C*Me*), 24.6 (CH*Me*$_2$), 24.9 (CH*Me*$_2$), 27.8 (*C*HMe$_2$), 99.0 (*C*H), 123.8 (Ar-*C*), 125.3 (Ar-*C*), 125.7 (Ar-*C*), 126.4 (Ar-*C*), 129.0 (Ar-*C*), 141.0 (Ar-*C*), 143.9 (Ar-*C*), 146.2 (Ar-*C*), 167.3 (N*C*Me), 169.5 (N*C*Me).

**(BDI-2j)AlEt$_2$ (3j).** Complex **3j** was synthesized using the same procedure as for complex **3a**. 0.457 g (4.000 mmol) of $AlEt_3$ and 1.458 g (4.000 mmol) of β-diketimine **2j** were used to obtain **3j** (1.310 g, 73%) as yellow crystals (Found: C, 74.89; H, 9.33; N, 6.11. Calc. for $C_{28}H_{41}AlN_2O$: C, 74.96; H, 9.21; N, 6.24%); mp 90–91 °C; $\delta_H$ (500 MHz, $CDCl_3$): −0.41 (dq, $^2J$ = 14.1 Hz, $^3J$ = 8.1 Hz, 2H, $AlCH_2CH_3$), −0.33 (dq, $^2J$ = 14.1 Hz, $^3J$ = 8.1 Hz, 2H, $AlCH_2CH_3$), 0.73 (t, $^3J$ = 8.1 Hz, 6H, $AlCH_2CH_3$), 1.17 (d, $^3J$ = 6.8 Hz, 6H, -CH($CH_3$)$_2$), 1.19 (d, $^3J$ = 6.8 Hz, 6H, -CH($CH_3$)$_2$), 1.76 (s, 3H, $CH_3$), 1.90 (s, 3H, $CH_3$), 3.09 (sept, $^3J$ = 6.8 Hz, 2H, -$CH$(CH$_3$)$_2$), 3.80 (s, 3H, O$CH_3$), 5.09 (s, 1H, γ-$CH$), 6.90 (m, 4H, *o*-, *m*-Ar-*H*), 7.13 (d, $^3J$ = 7.3 Hz, 2H, *m*-Ar-*H*), 7.20 (t, $^3J$ = 7.3 Hz, 1H, *p*-Ar-H); $\delta_C$ (75 MHz, $CDCl_3$): −0.1 ($AlCH_2CH_3$), 9.7 ($AlCH_2CH_3$), 20.5 (C*Me*), 21.2 (C*Me*), 24.1 (CH*Me*$_2$), 24.6 (CH*Me*$_2$), 27.8 (*C*HMe$_2$), 55.4 (O*Me*), 98.7 (*C*H), 114.2 (Ar-*C*), 123.8 (Ar-*C*), 126.3 (Ar-*C*), 126.5 (Ar-*C*), 139.0 (Ar-*C*), 141.1 (Ar-*C*), 144.0 (Ar-*C*), 157.2 (Ar-*C*), 167.9 (N*C*Me), 169.3 (N*C*Me).

**(BDI-2k)AlEt$_2$ (3k).** Complex **3k** was synthesized using the same procedure as for complex **3a**. 0.457 g (4.000 mmol) of $AlEt_3$, and 1.475 g (4.000 mmol) of β-diketimine **2k** were used to obtain **3k** (1.359 g, 75%) as yellow crystals (Found: C, 71.78; H, 8.49; N, 6.12. Calc. for $C_{27}H_{38}AlClN_2$: C, 71.58; H, 8.45; N, 6.18%); mp 91–92 °C; $\delta_H$ (500 MHz, $CDCl_3$): −0.41 (dq, $^2J$ = 14.3 Hz, $^3J$ = 8.2 Hz, 2H, $AlCH_2CH_3$), −0.33 (dq, $^2J$ = 14.3 Hz, $^3J$ = 8.2 Hz, 2H, $AlCH_2CH_3$), 0.73 (t, $^3J$ = 8.2 Hz, 6H, $AlCH_2CH_3$), 1.09 (d, $^3J$ = 6.8 Hz, 6H, -CH($CH_3$)$_2$), 1.12 (d, $^3J$ = 6.8 Hz, 6H, -CH($CH_3$)$_2$), 1.77 (s, 3H, $CH_3$), 1.91 (s, 3H, $CH_3$), 3.03 (sept, $^3J$ = 6.8 Hz, 2H, -$CH$(CH$_3$)$_2$), 5.13 (s, 1H, γ-$CH$), 6.93 (dt, $^3J$ = 8.6 Hz, $^4J$ = 2.0 Hz, 2H, *o*-Ar-*H*), 7.13 (d, $^3J$ = 7.3 Hz, 2H, *m*-Ar-*H*), 7.21 (t, $^3J$ = 7.3 Hz, 1H, *p*-Ar-*H*), 7.31 (dt, $^3J$ = 8.6 Hz, $^4J$ = 2.0 Hz, 2H, *m*-Ar-*H*); $\delta_C$ (75 MHz, $CDCl_3$): −0.3 ($AlCH_2CH_3$), 9.6 ($AlCH_2CH_3$), 22.9 (C*Me*), 23.3 (C*Me*), 24.5 (CH*Me*$_2$), 24.6 (CH*Me*$_2$), 27.9 (*C*HMe$_2$), 99.3 (*C*H), 123.9 (Ar-*C*), 126.5 (Ar-*C*), 127.1 (Ar-*C*), 129.2 (Ar-*C*), 130.9 (Ar-*C*), 140.8 (Ar-*C*), 143.7 (Ar-*C*), 144.8 (Ar-*C*), 167.0 (N*C*Me), 170.1 (N*C*Me).

**(BDI-2l)AlEt$_2$ (3l).** Complex **3l** was synthesized using the same procedure as for complex **3a**. 0.457 g (4.000 mmol) of $AlEt_3$ and 1.409 g (4.000 mmol) of β-diketimine **2l** were used to obtain **3l** (1.327 g, 76%) as yellow crystals (Found: C, 74.47; H, 8.61; N, 6.54. Calc. for $C_{27}H_{38}AlFN_2$: C, 74.28; H, 8.77; N, 6.42%); mp 82–83 °C; $\delta_H$ (500 MHz, $CDCl_3$): −0.41 (dq, $^2J$ = 14.3 Hz, $^3J$ = 8.1 Hz, 2H, $AlCH_2CH_3$), −0.33 (dq, $^2J$ = 14.3 Hz, $^3J$ = 8.1 Hz, 2H, $AlCH_2CH_3$), 0.72 (t, $^3J$ = 8.1 Hz, 6H, $AlCH_2CH_3$), 1.16 (d, $^3J$ = 6.8 Hz, 6H, -CH($CH_3$)$_2$), 1.19 (d, $^3J$ = 6.8 Hz, 6H, -CH($CH_3$)$_2$), 1.77 (s, 3H, $CH_3$), 1.89 (s, 3H, $CH_3$), 3.06 (sept, $^3J$ = 6.8 Hz, 2H, -$CH$(CH$_3$)$_2$), 5.12 (s, 1H, γ-$CH$), 6.96 (dt, $^3J$ = 8.5 Hz, $^4J$ = 2.0 Hz, 2H, *o*-Ar-*H*), 7.13 (d, $^3J$ = 8.2 Hz, 2H, *m*-Ar-*H*), 7.21 (t, $^3J$ = 8.2 Hz, 1H, *p*-Ar-*H*), 7.30 (dt, $^3J$ = 8.5 Hz, $^4J$ = 2.0 Hz, 2H, *m*-Ar-*H*); $\delta_C$ (75 MHz, $CDCl_3$): −0.2 ($AlCH_2CH_3$), 9.6 ($AlCH_2CH_3$), 22.8 (C*Me*), 23.3 (C*Me*), 24.5 (CH*Me*$_2$), 24.6 (CH*Me*$_2$), 27.9 (*C*HMe$_2$), 99.0 (*C*H), 115.7 (Ar-*C*), 116.0 (Ar-*C*), 123.9 (Ar-*C*), 126.4 (Ar-*C*), 127.0 (Ar-*C*), 127.1 (Ar-*C*), 140.9 (Ar-*C*), 142.1 (Ar-*C*), 142.2 (Ar-*C*), 143.8 (Ar-*C*), 158.9 (Ar-*C*), 162.1 (Ar-*C*), 167.5 (N*C*Me), 169.9 (N*C*Me).

**(BDI-2m)AlEt$_2$ (3m).** Complex **3m** was synthesized using the same procedure as for complex **3a**. 0.457 g (4.000 mmol) of $AlEt_3$ and 1.450 g (4.000 mmol) of β-diketimine **2m** were used to obtain **3m** (1.250 g yield 70%) as colorless crystals (Found: C, 77.40; H, 10.15; N, 6.37. Calc. for $C_{29}H_{43}AlN_2$: C, 77.98; H, 9.70; N, 6.27%); mp 88–90 °C; $\delta_H$ (500 MHz, $CDCl_3$): −0.37 (m, 4H, $AlCH_2CH_3$), 0.70 (t, $^3J$ = 8.1 Hz, 6H, $AlCH_2CH_3$), 1.15 (d, $^3J$ = 6.8 Hz, 6H, -CH($CH_3$)$_2$), 1.23 (d, $^3J$ = 6.8 Hz, 6H, -CH($CH_3$)$_2$), 1.73 (s, 3H, $CH_3$), 1.79 (s, 3H, $CH_3$), 2.27 (s, 6H, Ar–$CH_3$), 3.26 (sept, $^3J$ = 6.8 Hz, 2H, -$CH$(CH$_3$)$_2$), 5.08 (s, 1H, γ-$CH$), 7.02–7.08 (m, 3H, *m*-, *p*-Ar-*H*), 7.16 (d, $^3J$ = 7.8 Hz, 2H, *m*-Ar-*H*), 7.22 (t, $^3J$ = 7.8 Hz, 1H, *p*-Ar-*H*); $\delta_C$ (75 MHz, $CDCl_3$): 0.9 ($AlCH_2CH_3$), 9.2 ($AlCH_2CH_3$), 18.4 (Ar-*Me*), 22.7 (C*Me*), 23.5 (C*Me*), 24.8 (CH*Me*$_2$), 24.9 (CH*Me*$_2$), 27.6 (*C*HMe$_2$), 97.7 (*C*H), 124.1 (Ar-*C*), 125.6 (Ar-*C*), 126.5 (Ar-*C*), 128.6 (Ar-*C*), 133.5 (Ar-*C*), 140.9 (Ar-*C*), 143.6 (Ar-*C*), 144.2 (Ar-*C*), 168.7 (N*C*Me), 170.2 (N*C*Me).

**Generation of "(BDI-2a)AlMeCl" (4).** To a solution of ligand **2a** (1.000 g, 4.000 mmol) in 10 mL of toluene was added dropwise *n*-BuLi (2.3 M, 1.74 mL, 4.000 mmol) at −78 °C. The mixture was stirred and allowed to warm to ambient temperature. After being stirred for an additional 12 h, the solution was cooled to −78 °C and $MeAlCl_2$ (1.0 M, 4.00 mL, 4.000 mmol) was added. The resulting solution was allowed to warm to ambient temperature. and stirred overnight. After workup, the insoluble LiCl was removed by filtration, the filtrate was condensed to about 4 mL. **4** was deposited after 24 h at −20 °C as pale yellow crystals (0.925 g, 71%). $\delta_H$ (500 MHz, $CDCl_3$): −0.98 (s, 3H, Al-$CH_3$), 1.87 (s, 6H, $CH_3$), 5.12 (s, 1H, γ-$CH$), 7.16–7.39 (m, 10H, Ar-*H*).

**Reaction of complex 4 with LiO$^i$Pr.** To a solution of 2-propanol (0.240 g, 4.000 mmol) in 10 mL of toluene was added dropwise *n*-BuLi (2.30 M, 1.74 mL, 4.000 mmol) at −78 °C. The mixture was stirred and allowed to warm to ambient temperature. After being stirred for an additional 12 h, the solution was added dropwise to a solution of complex **4** (1.300 g, 4.000 mmol) in 10 mL of toluene at 0 °C. The resulting solution was allowed to warm to r.t. and was stirred overnight. After workup, the insoluble LiCl was removed by filtration, the filtrate was condensed to about 5 mL. 0.670 g white solid was deposited after 24 h at 0 °C. The $^1H$ NMR spectrum indicated that the isolated solid was a mixture of **6** and **7**.

**Reaction of complex 4 with NaO$^i$Pr.** To a suspension of sodium (0.083 g, 3.600 mmol) in 10 mL of toluene was added dropwise 2-propanol (0.106 g, 1.800 mmol) at 0 °C. The mixture was stirred and allowed to warm to ambient temperature. After being stirred

for an additional 12 h, the solution was filtered into a solution of complex **4** (0.588 g, 1.800 mmol) in 10 mL of toluene at 0 °C. The resulting solution was allowed to warm to room temperature and stirred overnight. After workup, the solvent was removed under vacuum, then 30 mL of *n*-hexane was added and the insoluble residue was removed by filtration, the filtrate was condensed to about 15 mL. Complex **7** was deposited at 0 °C after 24 h as colorless crystals (0.296 g, 55%). $\delta_H$ (500 MHz, $CDCl_3$): −1.34 (s, 6H, Al-C$H_3$), 1.83 (s, 12H, C$H_3$), 4.95 (s, 2H, $\gamma$-C$H$), 6.92 (d, $^3J$ = 7.4 Hz, 8H, *o*-Ar-$H$). 7.10 (t, $^3J$ = 7.4 Hz, 4H, *p*-Ar-$H$), 7.20 (t, $^3J$ = 7.4 Hz, 8H, *m*-Ar-$H$). EI-MS: $m/z$ (%) 583 (100, [$M^+$ − Me]).

### Typical polymerization procedure

To a solution of ε-caprolactone (ε-CL) in toluene kept at 80 °C, a solution of β-diketiminate aluminium complex **3a** in toluene was injected. The concentration of ε-CL was 1 M. 1 mL of polymerization aliquots were withdrawn at appropriate time intervals under the protection of argon and quenched with methanol. After removal of the volatiles, the residue was subjected to $^1$H NMR analysis. Monomer conversion was determined by observing the integration of monomer *vs.* polymer methylene resonance in the $^1$H NMR ($CDCl_3$, 500 MHz) spectrum. The polymer was purified by dissolving the crude samples in $CH_2Cl_2$ and precipitating into methanol. The obtained polymers were further dried in a vacuum oven at 60 °C for 24 h. The dry polymer samples were subjected to viscosity measurements and in selected cases analyzed by GPC.

### X-Ray diffraction measurements

The crystallographic data for complexes **3k** and **7** were collected on a Bruker AXSD8 diffractometer with graphite-monochromated Mo-Kα ($\lambda$ = 0.71073 Å) radiation. All data were collected at 20 °C using omega-scan techniques. The structures of **3k** and **7** were solved by direct methods and refined using Fourier techniques. An absorption correction based on SADABS was applied.[85] All non-hydrogen atoms were refined by full-matrix least-squares on $F^2$ using the SHELXTL program package.[86] Hydrogen atoms were located and refined by the geometry method. The cell refinement, data collection, and reduction were done using Bruker SAINT.[87] The structure solution and refinement were performed with SHELXS-97[88] and SHELXL-97[89] respectively. For further crystal data and details of measurements see Tables 1, 2 and 3. Molecule structures were generated using ORTEP.[90]

## Conclusions

Aluminum complexes **3a–m** supported by symmetrical or unsymmetrical β-diketiminate ligands were synthesized readily *via* alkane elimination reactions. The molecular structure of complex **3k** was further confirmed by X-ray diffraction techniques. In the presence of alkali salt of 2-propanol, a monochloride aluminium complex bearing a β-diketiminate ligand was transformed unexpectedly to the aluminoxane complex **7** *via* an unknown mechanism, which may provide a new strategy to the preparation of alumoxanes. β-Diketiminate aluminium complexes **3a–m** were inactive for the polymerization of *rac*-lactide. However these complexes did prove to be efficient initiators for the ring-opening polymerization of ε-caprolactone. This is the first time that β-diketiminate aluminium complexes have been applied to catalyze the ROP of cyclic esters. The effect of the ligand substituents on the ROP of ε-caprolactone is significant. In general, electron-donating substituents at the *para*-position of the phenyl rings decrease the electrophilicity of the aluminium center, and are unfavorable for the coordination and insertion of ε-caprolactone monomers. The introduction of fluorine atoms to the *meta*-positions of the phenyl rings improved the catalytic activity; whereas the *para*-fluoro substituent led to an inverse result. $CF_3$ substitution at either the *para*- or *meta*-position of the phenyl rings improved the activity of the corresponding aluminium complex, with the *meta*-$CF_3$ substituted complex **3h** showing the highest catalytic activity among the investigated β-diketiminate aluminium complexes. In addition, increasing the steric hindrance of the *ortho*-substituents on the aryl ring also resulted in a decrease in catalytic activity. The ROP of ε-caprolactone initiated by β-diketiminate aluminium complexes **3a–m** are not well-controlled, the measured molecular weights deviate significantly from the theoretical values. End group analysis of the obtained oligomer sample excludes the possibility that the polymerization is initiated from the Al–alkyl bond; the Al–amido moiety is most likely the active site for initiation.

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48 Spectroscopic data for **6** selected from $^1$H NMR analysis of the mixture. $\delta_H$ (500 MHz, $CDCl_3$): −1.34 (s, 3H, Al-C$H_3$), 0.90 (d, $^3J$ = 6.0 Hz, 6H, OCH(C$H_3$)$_2$), 1.85 (s, 6H, C$H_3$), 3.81 (sept, $^3J$ = 6.0 Hz, 1H, OC*H*(CH$_3$)$_2$), 5.00 (s, 1H, $\gamma$-C*H*), 7.10–7.35 (m, 10H, Ar-*H*).
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