Amidinate aluminium complexes: synthesis, characterization and ring-opening polymerization of *rac*-lactide†

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A series of aluminium alkyl complexes {PhC(NR′)(NR″)}AlR_2 (**4a–n**, R′ = 2,6-^{i}Pr$_2$C$_6$H$_3$, 2,6-Me$_2$C$_6$H$_3$; R″ = aryl groups with various *ortho*-, *para*- or *meta*-substituents, *tert*-butyl; R = methyl, ethyl) bearing non-symmetrically *N*-substituted benzamidinate ligands were synthesized *via* the reaction of trialkylaluminium and the corresponding benzamidine proligands. Complex **5** bearing symmetric amidinate ligand was also obtained for comparison purposes. The X-ray diffraction studies of complexes **4b**, **4c** and **5** show in each case a distorted tetrahedral geometry around the aluminium center. All the amidinate aluminium complexes were found to catalyze the ring-opening polymerization (ROP) of *rac*-lactide 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-withdrawing substituents at the *ortho*-positions of *N*-phenyl ring of the ligands resulted in an obvious increase in catalytic activity. Complex **4b** showed the highest activity among the investigated aluminium complexes due to the high electrophilicity of the metal center induced by the *ortho*-chloro substituents on the phenyl ring. The existence of *ortho*-substituents of small steric bulkiness is also beneficial for the increase of activity of these catalysts. However, further increase of steric hindrance of the ligands by introducing bulky *ortho*-substituents onto the phenyl moieties resulted in a decrease of activity and an increase in the isotactic bias of the obtained polylactides. The broad molecular weight distributions (PDI = 1.13–2.02) of the polymer samples indicated that the ROP of *rac*-lactide initiated by these complexes was not well-controlled.

Introduction

Polylactide (PLA) prepared from renewable sources is considered as an important material which exhibits unique properties, such as biodegradability and bioassimilability, and has widely potential applications in biomedical, pharmaceutical and agricultural fields.[1–4] Recently, using PLA as a new environmental-friendly thermoplastic and an alternative material for polyolefinic products of petroleum industry has attracted great attention of researchers both in academy and industry. To get polylactide with appropriate properties, different polymerization methods based on coordination, anionic and cationic catalysts have been explored. Among them, coordination polymerization of lactides undoubtedly is more attractive because of its better controllability over the polymerization process. Ring-opening polymerization of *rac*-lactide initiated by discrete metal complexes of Al, Ca, Mg, Zn, Sn, Fe and rare-earth metals is an efficient way to produce PLAs with high molecular weights as well as various tacticities.[5–18] Aluminium complexes, especially those bearing salen ligands and their derivatives, play an important role in the ROP of *rac*-lactide among these catalysts. The rare cases of highly isotactic polylactides prepared from *rac*-lactide were achieved by using aluminium complexes with salen-type ligands.[19–28] Apart from bisphenolate-type ligands, ligands containing pure nitrogen donors were also used to complex with aluminium. Bertrand *et al.*[7] synthesized aluminium complexes featuring tridentate diamidoamine ligands and investigated their catalytic performance for lactide polymerization. Only upon being converted *in situ* into alkoxides by initiating prepolymerization of propylene oxide could these complexes initiate the ROP of lactides with low activities. Not long ago, we reported some examples of β-diketiminate aluminium complexes, but they could only initiate the polymerization of ε-caprolactone and showed no activity for lactide polymerization.[29]

Recently, considerable attention has been given to aluminium complexes supported by various amidinate ligands for the fact that the coordination environment of the metal center can be easily modified by attaching substituents of various steric and electronic properties. Jordan *et al.*[30–32] reported the synthesis and structural analysis of aluminium complexes [RC(NR′)$_2$]$AlMe_2$ (R = Me, ^{t}Bu; R′ = ^{i}Pr, Cy, Ad), while amidinate ligands containing terphenyl group on the backbone carbon and the corresponding dialkylaluminium complexes were synthesized by the groups of Arnold and Clyburne.[33,34] Junk *et al.* also reported the synthesis of a dimethylaluminium complex featuring the bulky *N*,*N*′-bis(2,6-diisopropylphenyl)-4-toluamidinate ligand.[35] To the best of our knowledge, most of the amidinate aluminium complexes were explored mainly for studying the synthetic

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† Electronic supplementary information (ESI) available: Schematic presentation of the core structures of amidinate aluminium complexes, ^{1}H NMR spectra of ligand **3a**, complex **4a** and complex **4a** with isopropanol, ^{1}H NMR spectra of *rac*-LA polymerization initiated by complex **4c**, homonuclear decoupled ^{1}H NMR spectrum of the methine region of PLA, ESI-TOF mass spectrum of *rac*-lactide oligomer and summary of crystallographic data for **4b**, **4c** and **5**. CCDC reference numbers 772424–772426. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c0dt00272k

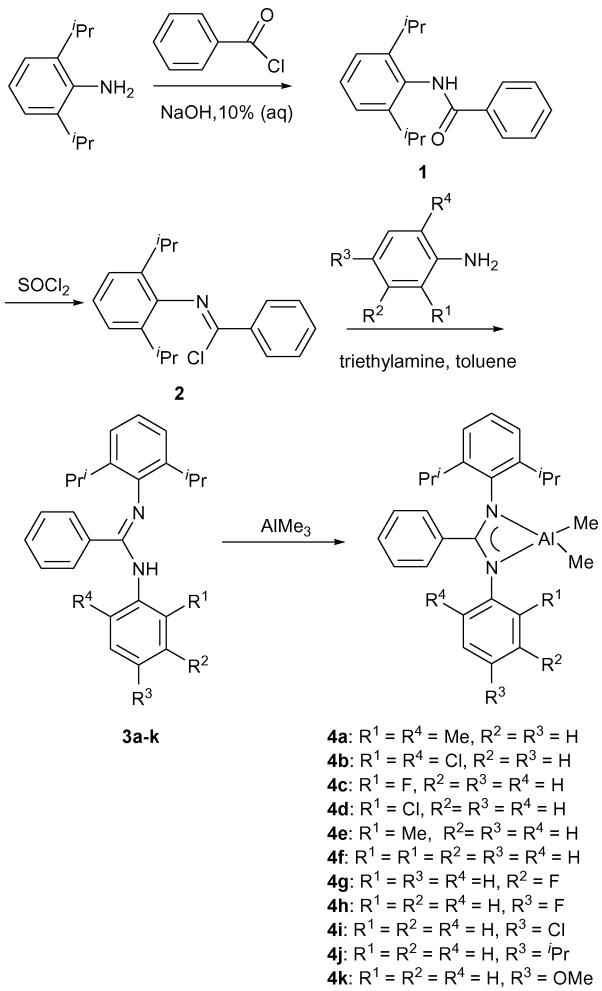
methodologies,[30,31,33–45] as catalysts for olefin polymerization,[46–49] or for other non-catalytic applications,[50] and have not yet been used as initiators for the ROP of cyclic esters such as lactides and ε-caprolactone. Due to the high Lewis acidity of the unsaturatedly coordinated metal center which should facilitate the coordination and activation of substrates, it is conceivable that amidinate aluminium complexes may possess catalytic activity for the ROP of lactide. At present, in most of the situations the amidinate ligands involved all bear two identical N-moieties and only a few examples of complexes bearing amidinate ligands with two different N-moieties were reported.[51] In further exploring the use of amidinate ligands for the development of stereoselective initiators for the ROP of *rac*-lactide, herein we report the synthesis of a range of aluminium complexes supported by non-symmetrically N-substituted amidinate ligands and their catalytic behavior towards *rac*-lactide polymerization, supposing that the unsymmetric coordinate surrounding of the aluminium center formed by the non-symmetrical ligands might induce some enantiomorphic site control over the monomer coordination/insertion during the polymerization process.

Results and discussion

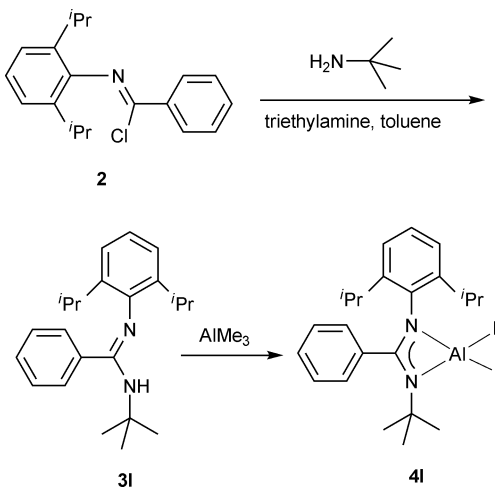
Synthesis and structure of amidinate aluminium complexes

A convenient method used to synthesize amidinate aluminium complex is to use carbodiimide as precursor to react directly with alkylaluminium, which is however limited by the non-symmetrical carbodiimide sources when adopted to prepare metal complexes featuring non-symmetrical amidinate ligands where different N- and N′-substituents are involved. To form a potential chiral environment around the metal center, especially in the catalytically active state, it is considered to attach different substituents at two nitrogen atoms. Using imidoyl chloride as an intermediate to react with diverse aromatic or aliphatic amines affords us a way to synthesize a variety of non-symmetrical amidine proligands whose structure could be tuned easily from steric and electronic aspects.[51–54] As shown in Scheme 1, addition of benzoyl chloride to a mixture of 10% NaOH and 2,6-diisopropylaniline followed by chlorination with thionyl chloride and treatment with aryl amine yielded the corresponding amidine compounds.[52,54] Benzamidines **3a–k** were reacted with $AlMe_3$ to afford the amidinate aluminium complexes **4a–k** which were isolated as off-white or light-yellow crystals from hexane or toluene in moderate yields. The monomeric structures of these amidinate aluminium complexes were further confirmed by X-ray diffraction studies. It should be noted that an excess amount of $AlMe_3$ was adopted to facilitate the conversion of the proligand in each case. The reaction of the benzamidine proligand and $AlMe_3$ in 1 : 1 ratio normally resulted in low conversion even under more forcing conditions such as refluxing in toluene, which raised problems to sequential purification.

Benzamidine compound **3l** bearing *N*-alkyl substituents, synthesized easily *via* the reaction of *N*-(2,6-diisopropylphenyl)benzylimidoyl chloride and *tert*-butylamine, was also treated with excess $AlMe_3$ to afford complex **4l** as colorless crystals in moderate yield (Scheme 2). The high solubility of complex **4l**, possibly induced by the introduction of *tert*-butyl groups, made it difficult to crystallize even in *n*-hexane.

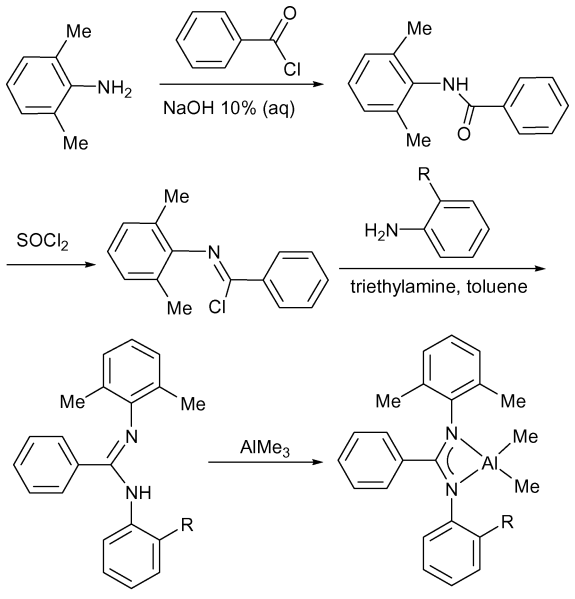


Scheme 1



Scheme 2

To minimize the steric congestion around the metal center, we also synthesized *N*-(2,6-dimethylphenyl)-*N*′-(2-methylphenyl)-benzamidine (**3m**), *N*-(2,6-dimethylphenyl)-*N*′-phenylbenzamidine (**3n**), and the related aluminium complexes **4m–n** *via* similar procedures (Scheme 3). On the other hand, the



Scheme 3

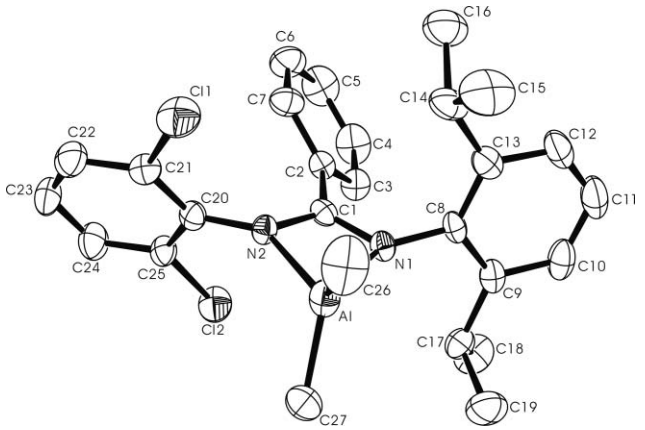


Fig. 1 ORTEP diagram of the molecular structure of [{PhC(*N*-2,6-^{i}Pr$_2$C$_6$H$_3$)(*N*-2,6-Cl$_2$C$_6$H$_3$)}AlMe$_2$] (**4b**). Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Al–N1 1.949(4), Al–N2 1.950(4), N1–C1 1.331(5), N2–C1 1.356(5), Al–C26 1.945(5), Al–C27 1.937(6), N1–C8 1.432(5), N2–C20 1.402(5); N1–Al–N2 68.44(15), Al–N1–C1 91.4(3), Al–N2–C1 90.6(3), Al–N1–C8 142.4(3), Al–N2–C20 142.0(3), N1–C1–N2 109.4(4), N1–C1–C2 126.1(4), N2–C1–C2 124.4(4), C2–C1–Al 178.7(3), C26–Al–C27 120.4(3).

synthesis of the proligand *N*,*N*′-bis(2,6-diisopropylphenyl)-benzamidine[52] and the related aluminium dimethyl complex **5** provided us with the example that bears the maximum steric congestion around the metal center among these complexes.

Though amidinate aluminium dimethyl complexes **4a–n** and **5** were synthesized successfully, the reaction of these amidines with triethylaluminium did not readily afford analytically pure diethyl analogues except for **4a′**, [{PhC(*N*-2,6-^{i}Pr$_2$C$_6$H$_3$)(*N*-2,6-Me$_2$C$_6$H$_3$)}AlEt$_2$], due to the difficulty encountered in the purification process.[34] Even with the employment of a large excess of AlEt$_3$ the amidine compounds could not be converted completely to the desired aluminium complexes; in most of the cases the residual ligands co-crystallized with the target aluminium complexes and could not be excluded cleanly even after repeated recrystallization from *n*-hexane.

The ^{1}H NMR spectra of amidine proligands obtained in this work are generally complicated due to the presence of isomers or possible interconversion between *Z-syn* and *E-syn* isomers that occurs on the NMR time scale,[55] which makes a precise assignment of all the resonances difficult. The resonances become simplified in the ^{1}H NMR spectra of the corresponding aluminium complexes as delocalization occurs when the amidine proligand coordinates with the aluminium center. For instance, in the ^{1}H NMR spectrum of **3a**, there are three singlets at 2.36, 2.13, 2.03 ppm accounting for the aromatic methyl groups and four doublets at 1.36, 1.24, 1.02, 0.91 ppm accounting for the isopropylmethyl groups. Only one singlet at 2.21 ppm accounting for the aromatic methyl and two doublets at 1.17, 0.86 ppm accounting for isopropyl-methyls are observed in the ^{1}H NMR spectrum of complex **4a**.

As depicted in Fig. 1, complex **4b** is monomeric with distorted tetrahedral geometry at the aluminium center. The Al atom and the chelating N1–C1–N2 moiety of the amidinate ligand construct a nearly coplanar four-membered metallacycle (the torsion angle of N1–Al–N2–C1 = 2.0°). The aryl rings are oriented perpendicular to the metallacycle (angles between aryl and metallacycle planes are 76.44 and 75.06°). The slight difference between bond distances of N1–Al [1.949(4) Å] and N2–Al [1.950(4) Å] as well as N1–C1 [1.331(5) Å] and N2–C1 [1.356(5) Å] in complex **4b** demonstrates a well delocalized system. By comparison with the related *N*-alkyl or -aryl substituted amidinate aluminium complexes, the non-symmetrical substitution mode in the amidinate ligand does have a certain influence on the molecular structure of **4b**, as indicated by the larger $\Delta_{C\text{-}N}$ value of 0.025 Å ($\Delta_{C\text{-}N}$ = 0.001–0.017 Å for symmetric systems).[31,32,34] Furthermore, the electronegative 2,6-dichloro substitution shortens the bond distance of N2–C20 and gives rise to elongated Al–N bonds (1.950(4) *vs.* 1.912–1.940 Å). The other bond lengths and angles are however comparable to the reported amidinate aluminium complexes.

The introduction of *ortho*-F substitution in complex **4c** dramatically changes the orientation of the related aryl group, which is approximately parallel to the metallacycle plane (N1–Al–N2–C1) rather than perpendicular (angle between the two planes is 14.315°, Fig. 2). A weak interaction between the fluorine atom and the aluminium center with a distance of 2.7936 Å could be observed which can be compared with the sum of the metal radius r_m(Al) and fluorine van der Waals radius r_v(F) [r_m(Al) + r_v(F) = 1.43 + 1.40 =2.83 Å], and is considered to be responsible for the unusual array of the aryl group. The interaction also forces the whole amidinate ligand to move towards it, as indicated by the significant difference between the two Al–N bonds (1.9701(14) *vs.* 1.9290(14) Å) in comparison with those in **4b** and other amidinate aluminium complexes.[31,32,34] This deviation of amidinate ligand also leads to smaller N1–Cl–N2 and Al–N1–C1 angles as well as a bigger Al–N2–C1 angle. Moreover, in contrast to complex **4b**, where the electron withdrawing *ortho*-Cl substituents result in the elongated Al–N bonds, the weak F···Al interaction in **4c** shortens the corresponding Al–N2 bond and counteracts the electron withdrawing effect of the *ortho*-F substituent on it.

As shown in Fig. 3, complex **5** possesses C_2-symmetry with the axis located along C2–C1···Al; the chelating nitrogen donors and

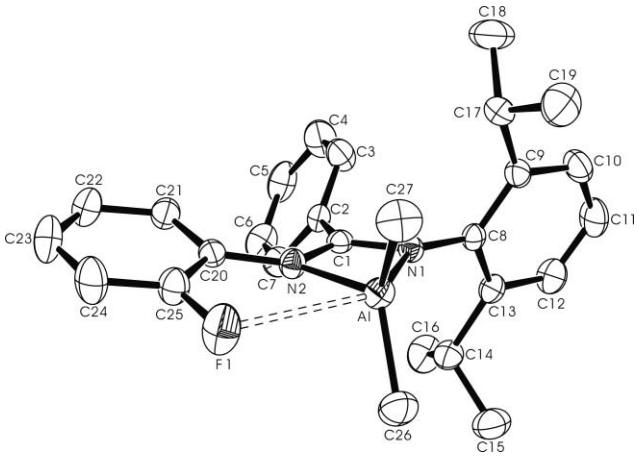


Fig. 2 ORTEP diagram of the molecular structure of [{PhC(*N*-2,6-$^{i}Pr_2C_6H_3$)(*N*-2-FC_6H_4)}$AlMe_2$] (**4c**). Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Al–N1 1.9701(14), Al–N2 1.9290(14), N1–C1 1.3269(19), N2–C1 1.340(2), Al–C26 1.944(2), Al–C27 1.943(2), N1–C8 1.427(2), N2–C20 1.401(2), F···Al 2.7936; N1–Al–N2 67.56(6), Al–N1–C1 91.09(10), Al–N2–C1 92.50(10), Al–N1–C8 142.57(10), Al–N2–C20 135.85(12), N1–C1–N2 108.79(14), N1–C1–C2 124.51(14), N2–C1–C2 126.62(14), C2–C1–Al 175.96(11), C26–Al–C27 120.77(11).

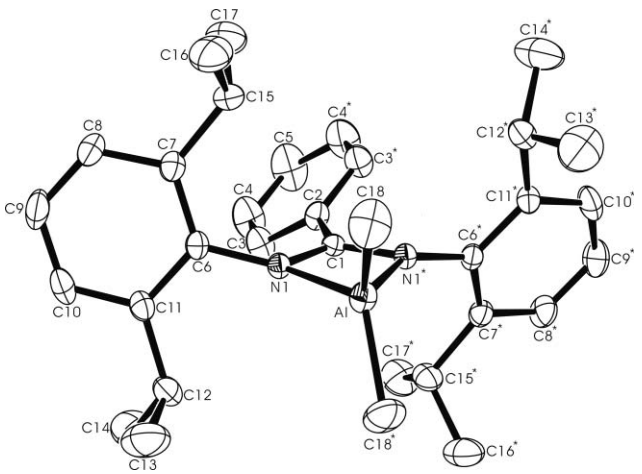


Fig. 3 ORTEP diagram of the molecular structure of complex [{PhC(*N*-2,6-$^{i}Pr_2C_6H_3)_2$}$AlMe_2$] (**5**). Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Al–N1 1.9381(18), Al–C18 1.945(3), C1–N1 1.334(2), N1–C6 1.426(2); N1–Al–N1* 68.61(9), Al–N1–C1 90.73(13), N1–C1–N1* 109.9(2), C2–C1–Al 179.999(1), N1–Al–C18 113.34(10), N1–Al–C18* 118.24(11).

aluminium metal center form a consummate plane evidenced by the torsion angle of N1–Al–N1*–C1 = 0°. The two C–N bond distances (1.334(2) Å), lying between the C–N bond distance in amidine (1.301 Å) and the C–N single-bond distance (1.47 Å), suggest a symmetric delocalization in the complex. The Al–N bond distance of [1.938(18) Å] and the bond distance of Al–CH_3 [1.945(3) Å] are comparable to the aluminium complex with bulky ligand [{4-MeC_6H_4C(2,6-$^{i}Pr_2C_6H_3N)_2$}$AlMe_2$].[35] The N1–C1–N1* angle of 109.9(2)° and the N1–Al–N1* bite angle of 68.61(9)° mean that the complex is more closed than the complex bearing a less bulky substituted group [$MeC(NC_6H_{11})_2$]$AlMe_2$ (110.4, 69°)[31] and more open than the complex bearing a more steric bulky group [*t*-BuC(*N*-2,6-$^{i}Pr_2C_6H_3)_2$]$AlMe_2$ (107.4, 68.15°).[32]

Ring-opening polymerization of *rac*-lactide with addition of alcohol

As for most of the aluminium complexes, the initiators adopted for lactide polymerization were generated by *in situ* alcoholysis of the complexes using isopropanol or benzyl alcohol[23,24,26–28,56–60] or released by the reaction of neutral proligand and aluminium alkoxide.[20,21,25,61–64] A toluene solution of amidinate aluminium complex **4a** was treated with two equiv. of isopropanol and used directly to initiate the ring-opening polymerization of *rac*-lactide at 70 °C. Rapid polymerization was observed and monomer conversion up to 78% could be reached within 4 h. The ^{1}H NMR spectrum of the obtained polylactide sample showed that the polymer chains were end-capped with isopropyl ester and a hydroxyl group, respectively.

In order to identify the actual active species, the reaction of complex **4a** and one equiv. of isopropanol was monitored by ^{1}H NMR spectroscopy in $CDCl_3$. Signals assignable to the free proligand **3a** were detected; besides, one multiple signals at 4.20 ppm and one doublet of doublet at 1.28 ppm appeared; the singlet accounting for Al–CH_3 in **4a** shifted to higher field as multiple signals ranging from –0.70 to –0.80 ppm. The integration ratio of them appeared to be 1: 6 : 6. Clearly, the alcoholysis reaction afforded the amine elimination product "$Me_2Al(O^{i}Pr)$" instead of the desired alkyl elimination one. As expected, the further addition of a second equiv. of isopropanol afforded "$MeAl(O^{i}Pr)_2$" as complicated aggregates. It is indisputable that the polymerization carried out with **4a**/isopropanol system was in fact initiated by the alkyl elimination products of "$Me_2Al(O^{i}Pr)$" or "$MeAl(O^{i}Pr)_2$" or "$Al(O^{i}Pr)_3$" depending on the [Al]/[^{i}PrOH] ratio. The instability of metal complex of N-containing ligand towards alcoholysis/enolysis was also observed by other groups.[65–67]

Aluminium complexes as single component initiators

Polymerization of *rac*-lactide initiated by benzamidinate aluminium complexes **4a–n** and **5** without addition of alcohol was carefully studied. The results showed that all the complexes displayed moderate activities for the ring-opening polymerization of *rac*-lactide when used as single component initiators, and the structure of the ancillary ligands had a significant influence on the polymerization behavior of the corresponding aluminium complexes.

Influence of ancillary ligand on catalytic activity

To facilitate comparing the effect of ancillary ligand on catalytic activities, amidinate aluminium complexes obtained in this work were divided into groups and are discussed separately.

For complexes **4a–f** all possessing one *N*-2,6-diisopropylphenyl group, the *ortho*-substituents on the other *N*-phenyl ring show obvious influence on the catalytic activity of the corresponding aluminium complex. As shown in Table 1, in contrast to most literature results, regardless of the electronic nature of the *ortho*-substituents, complexes **4a–e**

Table 1 Polymerization of *rac*-LA initiated by amidinate aluminium complexes with *ortho*-substituents on *N*-phenyl rings[a]

Run	Initiator	*t*/h	Conv.[b] (%)	$10^{-4}M_c$[c]	$10^{-4}M_\eta$[d]	$10^{-4}M_n'$[e]	M_w/M_n[e]	P_m[f]
1	**4a** (*o*-Me, Me)	12	57	0.82				0.63
2		24	86	1.24	2.96	2.20	1.93	
3	**4a′** (*o*-Me, Me)	48	60	0.86				0.60
4		72	83	1.20	2.53	2.26	1.38	
5	**4b** (*o*-Cl, Cl)	12	94	1.35	2.33	1.65	1.35	0.54
6	**4c** (*o*-F)	24	85	1.22	1.97	1.21	1.13	0.52
7	**4d** (*o*-Cl)	36	82	1.19	1.15	1.48	1.22	0.51
8	**4e** (*o*-Me)	48	88	1.26	1.65	2.60	1.36	0.51
9	**4f** (*N*-Ph)	48	64	0.92	1.74	1.64	1.31	
10		96	78	1.12				0.47
11	**4m** (*o*-Me)	24	77	1.11		1.47	1.20	0.53
12		48	91	1.31				
13	**4n** (*N*-Ph)	48	85	1.22	1.77	1.46	1.38	
14		72	96	1.38				0.51
15	**5** (*o*-^{i}Pr, ^{i}Pr)	48	59	0.85	1.45	1.60	1.34	0.65
16[g]		24	86	1.24	2.24	2.03	1.63	

[a] *Conditions*: [*rac*-LA]$_0$/[Al]$_0$ = 100, [*rac*-LA]$_0$ = 1.0 M, in toluene, 70 °C. [b] Determined by the integration ratio of the methine protons in monomer and polymer. [c] M_c = ([*rac*-LA]$_0$/[Al]$_0$) × 144.13 × conversion (%). [d] The intrinsic viscosity of polylactide was determined with an Ubbelohde viscosimeter at 25 °C in $CDCl_3$, and the viscosity average molecular weight (M_η) was calculated from the equation: $[\eta]$ (dL g^{-1}) = $2.21 \times 10^4 M_\eta^{0.77}$.[68] [e] The number average molecular weight (M_n) and molecular weight distribution (M_w/M_n) were determined by a gel permeation chromatograph, calibrated with polystyrene standards in THF, $M_n' = 0.58M_{n,GPC}$. [f] P_m is the probability of forming a new *m*-dyad, determined by homonuclear decoupled ^{1}H NMR. [g] 100 °C.

with various *ortho*-substituents all exhibit superior activities than **4f** without any substituent on one of the *N*-phenyl groups; and for the same substituent, methyl or chloro, the complex with *ortho*-disubstituted *N*-aryl group exhibits superior activity than the one with *ortho*-monosubstituted *N*-aryl group. That is, complex **4a** is more active than **4e** and complex **4b** is more active than **4d** (run 2 *vs.* 8, run 5 *vs.* 7). It is therefore conceived that the introduction of substituent at *ortho*-positions is favorable for the enhancement of catalytic activity and the steric effect may dominate.

To verify the steric effect of *ortho*-substituents of the *N*-aryl group, complexes **4m**, **4n** and **5** were obtained. The polymerization results show that a similar tendency as that of **4a–f** is also observed for complexes **4m** and **4n** possessing the *N*-2,6-dimethylphenyl group, with complex **4m** being more active than **4n** (Table 1). However, the increase of steric bulkiness of the *ortho*-substituents *via* introducing isopropyl groups is disadvantageous, lower activity than that of **4f** is observed for complex **5**, and complexes **4m** and **4n** are even more active than their *N*-2,6-diisopropyl analogues **4e** and **4f**, respectively.

When we reconsider complexes **4a–e**, it is found that the electronic nature of the *ortho*-substituents also shows a certain influence on the activity. In general the introduction of an electron withdrawing group leads to an enhancement of catalytic activity. Thus complex **4b** with *ortho*-dichloro substituents exhibits higher activity than complex **4a** with *ortho*-dimethyl substituents; complex **4c** with *ortho*-fluoro group on one of the *N*-phenyl groups displays the highest activity among complexes **4c–e** with *ortho*-monosubstitution. Nevertheless, the number of *ortho*-substituents seems more dominant than electronic effects, in comparison with **4a**, complex **4c** is less active.

The same fluoro substituent at different position of *N*-phenyl ring brings distinct influence on the activities of corresponding aluminium complexes **4c**, **4g** and **4h**, which are in the order of **4c** (*ortho*-F) > **4g** (*meso*-F) > **4h** (*para*-F) (Table 2). The fluorine atom, being strongly electronegative, is generally considered to display a marked electron-withdrawing effect, and this electron-withdrawing strength is attenuated with the distance. On the other hand the lone pair in the p-orbital of fluorine atom can also lead to an electron-donating conjugation effect *via* p–π bonding to its *para*- and *ortho*-positions when introduced to phenyl ring. It is reasonable that *ortho*-fluoro substitution will display the same extent of electron-donating conjugated effect as the *para*-fluoro substitution but stronger electron-withdrawing effect due to shorter distance; and the *meta*-fluoro substitution will only display an electron-withdrawing effect. As a result, the latter will often lead to highest activity, as we previously found for β-diketiminate aluminium complexes in the polymerization of ε-caprolactone.[29] In contrast to this, in this work complex **4c** (*ortho*-F) exhibits much higher activity than **4g** (*meta*-F) (run 6 *vs.* 17 in Table 2), which implies again some special effect of *ortho*-substitution. From X-ray diffraction study of complex **4c**, a close contact of the *ortho*-fluoro with aluminium center is observed. Likely, this might be responsible for the extraordinary activity in *rac*-lactide polymerization. A similar positive effect of *ortho*-fluoro substituent on the polymerization of ε-caprolactone was also observed for aluminium complexes bearing phenoxyimine ligands.[69]

In comparison with complexes **4a–e** and **4m–n** bearing various *ortho*-substituents on one *N*-aryl group, complexes **4h–k** with one *para*-substituted *N*-aryl group exhibit significant lower catalytic activities in the polymerization of *rac*-lactide (Table 2). On the evidence of the catalytic activities of complexes **4f**, **4j** and **4k**, the obvious tendency is that an electron-donating substituent introduced onto the *para*-position of the phenyl ring reduces the activity of the aluminium complexes. Complexes **4h**, **4i** possessing electron withdrawing halogen substituents, show comparable or even lower activity than **4f** in *rac*-lactide polymerization, possibly suggesting a dominant electron-donating conjugated effect of the halogen atom. Similarly, the electronic donating ability of *tert*-butyl towards the active metal center in complex **4l** may account for the low activity as well.

Table 2 Polymerization of *rac*-LA initiated by amidinate aluminium complexes with various *N*-aryl and *N*-alkyl groups[a]

Run	Initiator	*t*/h	Conv.[b] (%)	$10^{-4}M_c$[c]	$10^{-4}M_\eta$[d]	$10^{-4}M_n'$[e]	M_w/M_n[e]	P_m[f]
6	**4c** (*o*-F)	24	85	1.22	1.97	1.21	1.13	0.52
17	**4g** (*m*-F)	48	86	1.24	1.72	1.66	1.22	
18		72	93	1.33		1.93	1.56	0.52
19	**4h** (*p*-F)	48	61	0.87	1.68	1.45	1.23	
20		72	71	1.02	1.72			0.51
21	**4i** (*p*-Cl)	48	65	0.93	1.12			
22		72	75	1.08	3.30			0.50
23	**4j** (*p*-^{i}Pr)	48	60	0.86	1.51	1.31	1.25	
24		72	73	1.05	1.82			0.49
25	**4k** (*p*-OMe)	72	42	0.61	1.00	1.18	1.39	
26		96	47	0.68				0.51
27	**4l** (*N*-^{t}Bu)	72	51	0.73	3.33	2.02	1.46	
28		120	72	1.04				0.47

[a] *Conditions*: [*rac*-LA]$_0$/[Al]$_0$ = 100, [*rac*-LA]$_0$ = 1.0 M, in toluene, 70 °C. [b] Determined by the integration ratio of the methine protons in monomer and polymer. [c] M_c = ([*rac*-LA]$_0$/[Al]$_0$) × 144.13 × conversion (%). [d] The intrinsic viscosity of PLA was determined with an Ubbelohde viscosimeter at 25 °C in $CDCl_3$, and the viscosity average molecular weight (M_η) was calculated from the equation: $[\eta]$ (dL g^{-1}) = $2.21 \times 10^4 M_\eta^{0.77}$.[68] [e] The number average molecular weight (M_n) and molecular weight distribution (M_w/M_n) were determined by a gel permeation chromatograph, calibrated with polystyrene standards in THF, $M_n' = 0.58M_{n,GPC}$. [f] P_m is the probability of forming a new *m*-dyad, determined by homonuclear decoupled ^{1}H NMR spectroscopy.

From the above mentioned features, several unconventional aspects could be summarized: (1) regardless of the electronic nature, the presence of *ortho*-substituents of small steric bulk is benefit for the enhancement of catalytic activity; (2) the number of such group is also important; (3) based on these two conditions, an electron-withdrawing nature of substituent is more favored in comparison with electron donating one. It is therefore reasonable to hypothesize that the *ortho*-substituents of small steric bulkiness might exhibit some special effect during the polymerization process which is beneficial for the increase of activity of these catalysts.

Studies concerning mechanism and active species

Being different from the polymerization carried in the presence of alcohol, the polymerization initiated by these amidinate aluminium complexes alone was accompanied by the occurrence of a yellow solution. The whole system was very sensitive, although with strict exclusion of moisture and oxygen direct sampling from the polymerization solution led to partial deactivation of the remaining polymerization mixture. Thus sequential sampling at specified interval from a single polymerization solution failed to provide reasonable monomer conversion data and independent polymerization runs had to be used for each data point. To clarify whether a free radical mechanism was involved in the polymerization, controlled polymerization runs were carried out *via* two ways: (1) TEMPO serving as a free radical capture reagent was added to the polymerization mixture in the very beginning; (2) TEMPO was added to the polymerization mixture which had processed for a couple of hours. Both cases showed that the addition of TEMPO had no influence on the polymerization, the progress of monomer conversion with time during the polymerization was the same in each comparable run, thus excluding a possible free radical mechanism.

Polymerization of *rac*-lactide initiated by complex **4c** was further monitored by ^{1}H NMR spectroscopy in C_6D_6 at 60 °C with [*rac*-LA]/[Al] = 10. Upon mixing, the resonances accounting for complex **4c** only shifted slightly, while a considerable downfield shift of the methine proton resonance of *rac*-lactide from 3.79 ppm (free *rac*-lactide) to 3.94 ppm was observed, which further shifted to 4.13 ppm with the appearance of a new signal at 5.05 ppm assignable to PLA after 2 h at 60 °C. It seemed that, under the adopted conditions, all the monomer molecules tended to coordinate to the aluminium center and the interaction became even stronger with the consumption of lactide monomer. With the progress of polymerization, the resonances of the amidinate moiety could not be identified anymore due to significant broadening and overlapping; the methyl group attached to the aluminium atom displayed a group of signals in the region of –0.20 to –0.50 ppm but with reduced integral when referring to the sum of lactide monomer and polymer. No well-defined active species could be characterized during the polymerization. Based on the fact that no free amidine proligand was observed in the ^{1}H NMR spectra and the structure of amidinate ligand has considerable influence on the catalytic activity, we suggest that the amidinate segment may still bond to aluminium during the polymerization process.

In order to understand the possible initiation pathway, end-group analysis of obtained polymer samples through ^{1}H NMR spectroscopy were carried out thoroughly. Resonances of the methine proton at 4.35 ppm and hydroxyl group at 2.60 ppm in the ^{1}H NMR spectra of most polylactide samples could be recognized, indicating the linear structure of obtained polymers. The identification of the other end is not conclusive, neither aromatic protons of amidinate moiety nor acetyl protons resulting from Al-methyl initiation could be detected, giving no direct support for either Al–N and Al–R initiation pathways.

Through the *in situ* ^{1}H NMR polymerizations of ε-CL in the presence of diamino-aluminium complexes [N∧N]AlMe, Chakraborty and Chen observed the initiation step involving monomer insertion into an Al–N bond.[15] Very recently, Mountford and co-workers found that the ROP of *rac*-lactide by sulfonamide-supported aluminium complexes [Al($N_2^{Ts}N^R$)Et] (R = OMe, py) was initiated by monomer insertion to the Al–Et bond as evident by the existence of the EtC(O)CH(Me)O– end group as characterized by MALDI-TOF spectra.[70] The ESI-TOF mass spectrum of the oligomer sample obtained with [*rac*-LA]/[**4c**] = 10 at 70 °C however indicated the existence

of both MeC(O)CH(Me)O– and {PhC(*N*-2,6-$^{i}Pr_2C_6H_3$)(*N*-2-FC_6H_4)}C(O)CH(Me)O– ends, thus for amidinate aluminium alkyl complexes, both Al–N and Al–R initiation are possible, with Al–R initiation dominant.[71]

Characterization of polylactides

Determination of the stereochemical structure of PLA is achieved through inspection of the methine group of homonuclear decoupled ^{1}H NMR spectra of the resultant polymers. The predominant *mmm* tetrad peak indicates that the polymer produced by catalyst **4a** is slightly isotactic bias enriched ($P_m = 0.63$), where $[mmm] = [P_m^2 + (1 - P_m)^2 + P_m^3 + (1 - P_m)^3]/2$, $[mrm] = [P_m(1 - P_m) + P_m(1 - P_m)^2]/2$, $[mmr] = [rmm] = [rmr] = [P_m^2(1 - P_m) + P_m(1 - P_m)^2]/2$. The intensity of *rmr*, *mmr* and *mrm* tetrads relative to the *mmm* tetrad does not change with conversion, indicating a homogeneous distribution of isotactic sequences along the polymer chain. Except for complexes **4a** and **5**, the other catalysts only initiated polymerizations which afforded atactic polymers.

The results of homonuclear decoupled ^{1}H NMR spectroscopy indicate that *ortho*-substituents of *N*-phenyl rings studied in this work show slight influence on the ability of corresponding catalysts to control monomer insertion. For instance, changing the isopropyl substituents in complex **5** ($P_m = 0.65$) to hydrogen atoms in complex **4f** results in a decrease in isotactic bias ($P_m = 0.47$). It is suggested that steric bulky groups at the *ortho*-positions may block the coordination sphere of the metal center and restrict the monomer insertion direction, leading to higher regularity of polylactide microstructure, and low activities of aluminium complexes in polymerization.[28,29]

Molecular weight information of all polylactide samples is obtained by viscosity measurements and gel permeation chromatography (GPC). As shown in Tables 1 and 2, in general, with the increase of monomer conversion, the viscosity average molecular weights of the polymer samples increase. However, the deviation of the molecular weights M_η and M_n' from theoretical values (calculated with the assumption that each aluminium center initiates one polymer chain) and broad molecular weight distributions of polylactides, imply a slow initiation relative to chain propagation and possible deactivation of the active sites and transesterification may be inevitable.

Conclusion

Aluminium complexes **4a–n** and **5** supported by symmetrical or non-symmetrical amidinate ligands were synthesized *via* alkane elimination reactions. The structures of these complexes were characterized by ^{1}H NMR, ^{13}C NMR and EA. The molecular structures of complexes **4b**, **4c** and **5** were further confirmed by X-ray diffraction techniques. These complexes are proved to be efficient initiators for the ring-opening polymerization of *rac*-lactide. The effect of ligand substituents on polymerization is significant. In general, an electron-donating substituent at the *para*-position of the *N*-phenyl ring decreases the electrophilicity of the aluminium center and is unfavorable for the coordination and insertion of *rac*-lactide monomer, leading to lower catalytic activity of the corresponding aluminium complex. The introduction of electron-withdrawing substituents to the *ortho*-positions of *N*-phenyl ring improves the catalytic activity. Such enhancement of catalytic activity could also be achieved by introducing small alkyl groups to *ortho*-positions of the *N*-phenyl ring. However, further increase the steric hindrance of the *ortho*-substituents results in a decrease in catalytic activity and slight increase of isotactic bias in polymer chain. The ROP of *rac*-lactide initiated by amidinate aluminium complexes **4a–n** is not well-controlled, as demonstrated by the measured molecular weights deviating from the theoretical values.

Experimental

General considerations and materials

All reactions and manipulations involving air-sensitive complexes were carried out under argon atmosphere using standard Schlenk vacuum-line and glove-box techniques. Toluene and *n*-hexane were refluxed over sodium benzophenone prior to use. Chloroform-*d* was dried over calcium hydride. C_6D_6 was refluxed over sodium and distilled. $AlMe_3$ (2.0 M in toluene) was purchased from Aldrich and used as received. Neat $AlEt_3$ (commercial product) was dissolved in an appropriate amount of petroleum ether to give a 0.94 M solution. *N*-(2,6-Diisopropylphenyl)benzamide (**1**), *N*,*N*′-bis(2,6-diisopropylphenyl)benzamidine and proligand **3a** were synthesized according to the published procedures.[52–72] *rac*-Lactide (Aldrich) was recrystallized with dry toluene and sublimed once under vacuum at 80 °C.

Instruments and measurements

NMR spectra were recorded on Bruker AVANCE-500 and AVANCE-400 spectrometers with $CDCl_3$ or C_6D_6 as solvent (^{1}H: 500 MHz or 400 MHz; ^{13}C: 125 MHz or 100 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 polylactides was measured with an Ubbelohde viscometer in chloroform at 25 °C. 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. Single crystals suitable for X-ray diffraction studies were obtained from *n*-hexane for **4b**, **4c** and from toluene for **5** at –40 °C. The crystallographic data for complexes **4b**, **4c** and **5** 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 **4b**, **4c** and **5** were solved by direct methods and refined using Fourier techniques. An absorption correction based on SADABS was applied.[73] All non-hydrogen atoms were refined by full-matrix least-squares on F^2 using the SHELXTL program package.[74] Hydrogen atoms were located and refined by the geometry method. The cell refinement, data collection, and reduction were done using Bruker SAINT.[75] The structure solution and refinement were performed with SHELXS-97[76] and SHELXL-97[77] respectively. Molecule structures were generated using ORTEP III program.[78]

Synthesis of amidine compounds

***N*-(2,6-Diisopropylphenyl)-*N*′-(2,6-dichlorophenyl)benzamidine (3b).** *N*-(2,6-Diisopropylphenyl)benzamide (6.20 g, 22.0 mmol) was refluxed in $SOCl_2$ (6.5 mL) for 1 h at 80 °C, then the reaction

mixture was cooled to room temperature and excess $SOCl_2$ was evaporated off under vacuum. The residual $SOCl_2$ could be removed by adding toluene followed by further evaporating the mixture. To the obtained residue a mixture of 2,6-dichloroaniline (3.25 g, 20.0 mmol) and triethylamine (11 mL, 80 mmol) in toluene (30 mL) was added. The reaction mixture was refluxed for 20 h and then cooled to room temperature, washed with water, dried over $MgSO_4$ and concentrated. The crude product was purified by column chromatography using silica gel (petroleum ether–ethyl acetate = 20 : 1) and further recrystallized with ethanol to give **3b** as colorless crystals (3.27 g, 35%) (Found: C, 70.11; H, 6.55; N, 6.28. Calc. for $C_{25}H_{26}Cl_2N_2$: C, 70.59; H, 6.16; N, 6.59%); mp 116 °C; δ_H (500 MHz, $CDCl_3$, 25 °C) 7.53 (d, 2H, ^3J = 6.8 Hz, Ar-*H*), 7.34 (m, 4H, Ar-*H*), 7.26 (m, 2H, Ar-*H*), 7.05 (d, 2H, ^3J = 8.0 Hz, Ar-*H*), 6.64 (t, 1H, ^3J = 8.0 Hz, Ar-*H*), 5.93 (s, 0.85H, –N*H*), 5.71 (s, 0.15H, –N*H*), 3.66 [septet, 1.7H, ^3J = 6.8 Hz, –C*H*$(CH_3)_2$], 3.34 [septet, 0.3H, ^3J = 6.8 Hz, –C*H*$(CH_3)_2$], 1.41 [d, 5.1H, ^3J = 6.8 Hz, –CH(C*H*$_3)_2$], 1.24 [d, 5.1H, ^3J = 6.8 Hz, –CH(C*H*$_3)_2$], 1.05 [d, 0.9H, ^3J = 6.8 Hz, –CH(C*H*$_3)_2$], 0.93 [d, 0.9H, ^3J = 6.8 Hz, –CH(C*H*$_3)_2$]; δ_C (125 MHz, $CDCl_3$, 25 °C) 158.7 (*C*–N), 147.1 (Ar-*C*), 146.0 (Ar-*C*), 135.4 (Ar-*C*), 132.4 (Ar-*C*), 129.9 (Ar-*C*), 128.5 (Ar-*C*), 128.4 (Ar-*C*), 127.8 (Ar-*C*), 127.7 (Ar-*C*), 126.9 (Ar-*C*), 123.5 (Ar-*C*), 122.4 (Ar-*C*), 28.5 [–*C*H$(CH_3)_2$], 25.0 [–CH(*C*H$_3)_2$], 22.9 [–CH(*C*H$_3)_2$].

***N*-(2,6-Diisopropylphenyl)-*N*′-(2-fluorophenyl)benzamidine (3c).** The procedure was similar to that of compound **3b** except that *N*-(2,6-diisopropylphenyl)benzamide (3.60 g, 13.0 mmol) and *o*-fluoroaniline (1.1 g, 11.8 mmol) were used. Crystallization in ethanol–water afforded colorless crystals (3.16 g, 66%) (Found: C, 80.18; H, 7.24; N, 7.36. Calc. for $C_{25}H_{27}FN_2$: C, 80.18; H, 7.27; N, 7.48%); mp 118–119 °C; δ_H (400 MHz, $CDCl_3$, 25 °C) 7.62 (br s, 1H, Ar-*H*), 7.50–6.86 (m, 9H, Ar-*H*), 6.82–6.68 (m, 2H, Ar-*H*), 6.50 (br s, 0.4H, N–*H*), 6.13 (br s, 0.4H, N–*H*), 5.88 (s, 0.2H, N–*H*), 3.46 [septet, 0.4H, ^3J = 6.8 Hz, –C*H*$(CH_3)_2$], 3.16 [br s, 1.6H, –C*H*$(CH_3)_2$], 1.39 [br s, 1.2H, –CH(C*H*$_3)_2$], 1.41–1.06 [m, 9.6H, –CH(C*H*$_3)_2$], 0.95 [d, 1.2H, ^3J = 6.8 Hz, –CH(C*H*$_3)_2$]; δ_C (100 MHz, $CDCl_3$, 25 °C) 158.6 (*C*=N), 153.1 (br, Ar-*C*), 146.7 (Ar-*C*), 138.9 (br, Ar-*C*), 135.2 (Ar-*C*), 134.7 (Ar-*C*), 133.9 (d, $^1J_{C-F}$ = 245 Hz, Ar-*C*), 129.8 (Ar-*C*), 129.5 (Ar-*C*), 128.5 (Ar-*C*), 128.3 (Ar-*C*), 128.2 (d, $^2J_{C-F}$ = 17.9 Hz, Ar-*C*), 127.6 (Ar-*C*), 125.0 (Ar-*C*), 123.5 (Ar-*C*), 122.2 (d, $^3J_{C-F}$ = 7.3 Hz, Ar-*C*), 115.1 (d, $^2J_{C-F}$ = 20.8 Hz, Ar-*C*), 30.8 [–*C*H$(CH_3)_2$], 28.9 [–*C*H$(CH_3)_2$], 28.2 [–CH(*C*H$_3)_2$], 23.7 [br, –CH(*C*H$_3)_2$].

***N* - (2,6 - Diisopropylphenyl) - *N*′ - (2 - chlorophenyl)benzamidine (3d).** The procedure was similar to that of compound **3b** except that *N*-(2,6-diisopropylphenyl)benzamide (6.80 g, 24.3 mmol) and *o*-chloroaniline (2.4 mL, 23.0 mmol) were used. Crystallization with toluene afforded colorless crystals (6.2 g, 65%) (Found: C, 76.87; H, 7.10; N, 7.05. Calc. for $C_{25}H_{27}ClN_2$: C, 76.80; H, 6.96; N, 7.17%); mp 140–141 °C; δ_H (500 MHz, $CDCl_3$, 25 °C) 7.62 (br s, 1H, Ar-*H*), 7.45 (d, ^3J = 6.3 Hz, 1H, Ar-*H*), 7.34–6.50 (m, 10H, Ar-*H*), 6.43 (s, 0.4H, –N*H*), 6.30 (s, 0.4H, –N*H*), 5.84 (s, 0.2H, –N*H*), 3.54 [septet, 0.4H, ^3J = 6.5 Hz, –C*H*$(CH_3)_2$], 3.15 [m, 1.6H, –C*H*$(CH_3)_2$], 1.39 [br s, 1.2H, –CH(C*H*$_3)_2$], 1.41–1.04 [m, 9.6H, –CH(C*H*$_3)_2$], 0.94 [br s, 1.2H, ^3J = 6.5 Hz, –CH(C*H*$_3)_2$]; δ_C (125 MHz, $CDCl_3$, 25 °C) 157.5 (*C*=N), 152.9 (br, Ar-*C*), 148.7 (Ar-*C*), 146.9 (Ar-*C*), 143.3 (br, Ar-*C*), 138.7 (br, Ar-*C*), 137.3 (Ar-*C*), 134.9 (Ar-*C*), 130.0 (br, Ar-*C*), 129.7 (Ar-*C*), 129.2 (Ar-*C*), 128.5 (br, Ar-*C*), 127.8 (br, Ar-*C*), 126.7 (br, Ar-*C*), 124.1 (br, Ar-*C*), 123.6 (Ar-*C*), 122.3 (Ar-*C*), 28.9 [–*C*H$(CH_3)_2$], 28.3 [–CH(*C*H$_3)_2$], 23.8 [br, –CH(*C*H$_3)_2$].

***N* - (2,6 - Diisopropylphenyl) - *N*′ - (2 - methylphenyl)benzamidine (3e).** The procedure was similar to that of compound **3b** except that *N*-(2,6-diisopropylphenyl)benzamide (6.20 g, 22.0 mmol) and *o*-methylaniline (2.15 g, 20.0 mmol) was used. Crystallization in ethanol–water afforded colorless crystals (5.5 g, 75%) (Found: C, 84.15; H, 8.24; N, 7.43. Calc. for $C_{26}H_{30}N_2$: C, 84.28; H, 8.16; N, 7.56%); mp 142 °C; δ_H (500 MHz, $CDCl_3$, 25 °C) 7.56 (d, 2H, ^3J = 7.4 Hz, Ar-*H*), 7.36–7.30 (m, 4H, Ar-*H*), 7.20 (d, 2H, ^3J = 7.4 Hz, Ar-*H*), 7.12–7.06 (m, 1H, Ar-*H*), 6.88 (t, 1H, ^3J = 7.2 Hz, Ar-*H*), 6.84 (t, 1H, ^3J = 7.4 Hz, Ar-*H*), 6.45 (d, 1H, ^3J = 7.4 Hz, Ar-*H*), 5.87 (s, 1H, –N*H*), 3.48 [septet, 0.16H, ^3J = 6.7 Hz, –C*H*$(CH_3)_2$], 3.22 [septet, 1.84H, ^3J = 6.7 Hz, –C*H*$(CH_3)_2$], 2.15 (s, 2.76H, –C*H*$_3$), 2.11 (s, 0.24H, –C*H*$_3$), 1.25 [d, 11H, ^3J = 6.7 Hz, –CH(C*H*$_3)_2$], 1.02 [d, 0.5H, ^3J = 6.7 Hz, –CH(C*H*$_3)_2$], 0.94 [d, 0.5H, ^3J = 6.7 Hz, –CH(C*H*$_3)_2$]; δ_C (125 MHz, $CDCl_3$, 25 °C) 154.2 (*C*=N), 145.2 (Ar-*C*), 143.4 (Ar-*C*), 139.2 (Ar-*C*), 138.8 (Ar-*C*), 135.2 (Ar-*C*), 130.4 (Ar-*C*), 130.2 (Ar-*C*), 129.7 (Ar-*C*), 128.7 (Ar-*C*), 128.2 (Ar-*C*), 126.2 (Ar-*C*), 124.9 (Ar-*C*), 124.2 (Ar-*C*), 123.8 (Ar-*C*), 123.5 (Ar-*C*), 28.5 [–*C*H$(CH_3)_2$], 28.2 [–*C*H$(CH_3)_2$], 24.5 [–CH(*C*H$_3)_2$], 23.7 [–CH(*C*H$_3)_2$], 21.9 [–CH(*C*H$_3)_2$], 18.1 [–CH(*C*H$_3)_2$].

***N*-(2,6-Diisopropylphenyl)-*N*′-phenylbenzamidine (3f).** The procedure was similar to that of compound **3b** except that *N*-(2,6-diisopropylphenyl)benzamide (3 g, 10 mmol) and aniline (0.84 g, 9.0 mmol) were used. Crystallization in ethanol–water afforded colorless crystals (2.25 g, 63%) (Found: C, 83.81; H, 8.03; N 7.53. Calc. for $C_{25}H_{28}N_2$: C, 84.23; H, 7.92; N, 7.86%); mp 143–144 °C; δ_H (500 MHz, $CDCl_3$, 25 °C) 7.62 (s, 2H, Ar-*H*), 7.38–7.34 (m, 3H, Ar-*H*), 7.20 (s, 2H, Ar-*H*), 7.12–6.93 (m, 4H, Ar-*H*), 6.60 (br s, 2H, Ar-*H*), 6.23 (s, 1H, –N*H*), 3.16 [br s, 2H, –C*H*$(CH_3)_2$], 1.22 [d, 12H, ^3J = 6.8 Hz, –CH(C*H*$_3)_2$]; δ_C (125 MHz, $CDCl_3$, 25 °C) 153.8 (*C*=N), 143.4 (Ar-*C*), 140.1 (Ar-*C*), 139.1 (Ar-*C*), 135.1 (Ar-*C*), 129.7 (Ar-*C*), 128.9 (Ar-*C*), 128.7 (Ar-*C*), 128.7 (Ar-*C*), 128.3 (Ar-*C*), 123.8 (Ar-*C*), 123.57 (Ar-*C*), 122.5 (Ar-*C*), 28.2 [–*C*H$(CH_3)_2$], 23.9 [–CH(*C*H$_3)_2$], 23.5 [–CH(*C*H$_3)_2$].

***N* - (2,6 - Diisopropylphenyl) - *N*′ - (3-fluorophenyl)benzamidine (3g).** The procedure was similar to that of compound **3b** except that *N*-(2,6-diisopropylphenyl)benzamide (3.9 g, 14 mmol) and 3-fluoroaniline (1.4 g, 12 mmol) were used. Crystallization in ethanol–water afforded colorless crystals (2.7 g, 55%) (Found: C, 80.30; H, 7.13; N, 7.32. Calc. for $C_{25}H_{27}FN_2$: C, 80.18; H, 7.27; N, 7.48%); mp 108 °C; δ_H (500 MHz, $CDCl_3$, 25 °C) 7.63 (br s, 1H, Ar-*H*), 7.43–7.31 (m, 3H, Ar-*H*), 7.25–7.20 (m, 2H, Ar-*H*), 7.13 (br s, 1H Ar-*H*), 7.01 (d, 1H, ^3J = 6.4 Hz, Ar-*H*), 6.60 (b s, 1H, Ar-*H*), 6.47–6.24 (m, 3H, Ar-*H*), 5.80 (s, 1H, –N*H*), 3.71 [septet, 0.22H, ^3J = 6.7 Hz, –C*H*$(CH_3)_2$], 3.40 [septet, 0.32H, ^3J = 6.7 Hz, –C*H*$(CH_3)_2$], 3.12 [br s, 1.46H, –C*H*$(CH_3)_2$], 1.37 [br s, 0.96H, –CH(C*H*$_3)_2$], 1.27 [br s, 0.96H, –CH(C*H*$_3)_2$], 1.23 [d, 4.4H, ^3J = 6.7 Hz, –CH(C*H*$_3)_2$], 1.20 [d, 4.4H, ^3J = 6.7 Hz, –CH(C*H*$_3)_2$], 1.08 [d, 0.6H, ^3J = 6.7 Hz, –CH(C*H*$_3)_2$], 0.98 [d, 0.6H, ^3J = 6.7 Hz, –CH(C*H*$_3)_2$]; δ_C (125 MHz, $CDCl_3$, 25 °C) 153.2 (*C*=N), 146.5 (Ar-*C*), 138.9 (Ar-*C*), 134.7 (Ar-*C*), 130.1 (Ar-*C*), 129.8 (Ar-*C*), 129.7 (Ar-*C*), 129.6 (Ar-*C*), 128.7 , (Ar-*C*) 128.6 (Ar-*C*), 128.4

(Ar-*C*), 128.3 (Ar-*C*), 128.1 (Ar-*C*), 124.0 (Ar-*C*), 123.6 (Ar-*C*), 123.5 (Ar-*C*), 118.6 (Ar-*C*), 117.6 (Ar-*C*), 28.9 [–*C*H(CH$_3$)$_2$], 28.2 [–*C*H(CH$_3$)$_2$], 23.8 [–CH(*C*H$_3$)$_2$], 23.5 [–CH(*C*H$_3$)$_2$].

***N* - (2,6 - Diisopropylphenyl) - *N′* - (4 - fluorophenyl)benzamidine (3h).** The procedure was similar to that of compound **3b** except that *N*-(2,6-diisopropylphenyl)benzamide (6.75 g, 24.0 mmol) and 4-fluoroaniline (2.2 mL, 23 mmol) were used. Crystallization in ethanol–water afforded colorless crystals (5.7 g, 63%) (Found: C, 80.04; H, 7.29; N, 7.25. Calc. for $C_{25}H_{27}FN_2$: C, 80.18; H, 7.27; N, 7.48%); mp 110–112 °C; δ_H (500 MHz, $CDCl_3$, 25 °C) 7.71 (br s, 2H, Ar-*H*), 7.34–7.47 (m, 3H, Ar-*H*), 7.21–7.25 (m, 2H, Ar-*H*), 7.12 (m, 1H, Ar-*H*), 6.78 (br s, 1.6H, Ar-*H*), 6.69 (m, 0.4H, Ar-*H*), 6.60 (br s, 1.6H, Ar-*H*), 6.49 (m, 0.4H, Ar-*H*), 6.16 (s, 0.9H, –N*H*), 5.75 (s, 0.1H, –N*H*), 3.40 [septet, 0.2H, $^3J = 6.7$ Hz, –C*H*(CH$_3$)$_2$], 3.16 [septet, 1.8H, $^3J = 6.8$ Hz, –C*H*(CH$_3$)$_2$], 1.38–1.24 [m, 10.8H, –C*H*(CH$_3$)$_2$], 1.06 [d, $^3J = 6.8$ Hz, 0.6H, –CH(C*H*$_3$)$_2$], 0.97 [d, $^3J = 6.8$ Hz, 0.6H, –CH(C*H*$_3$)$_2$]; δ_C (125 MHz, $CDCl_3$, 25 °C) 153.9 (*C*=N), 146.5 (Ar-*C*), 143.3 (Ar-*C*), 139.2 (Ar-*C*), 136.3 (Ar-*C*), 134.9 (Ar-*C*), 129.8 (Ar-*C*), 129.0 (Ar-*C*), 128.8 (Ar-*C*), 128.6 (Ar-*C*), 128.5 (Ar-*C*), 128.4 (Ar-*C*), 124.6 (d, $^3J_{C-F} = 6.2$ Hz, Ar-*C*), 123.9 (Ar-*C*), 123.6 (Ar-*C*), 115.5 (d, Ar-*C*, $^2J_{C-F} = 22.5$ Hz), 28.9 [–CH(*C*H$_3$)$_2$], 28.2 [–*C*H(CH$_3$)$_2$], 23.9 [–CH(*C*H$_3$)$_2$], 23.5 [–CH(*C*H$_3$)$_2$].

***N*-(2,6-Diisopropylphenyl)-*N′*-(4-chlorophenyl)benzamidine (3i).** The procedure was similar to that of compound **3b** except that *N*-(2,6-diisopropylphenyl)benzamide (7.0 g, 25 mmol) and 4-chloroaniline (2.9 g, 23 mmol) were used. Crystallization in toluene afforded colorless crystals (6.3 g, 69%) (Found: C, 76.84; H, 7.11; N, 7.10. Calc. for $C_{25}H_{27}ClN_2$: C, 76.80; H, 6.96; N, 7.17%); mp 131–132 °C; δ_H (500 MHz, $CDCl_3$, 25 °C) 7.71 (br s, 1H, Ar-*H*), 7.35–7.40 (m, 4H, Ar-*H*), 6.90–7.23 (m, 5H, Ar-*H*), 6.47–6.90 (m, 2H, Ar-*H*), 6.18 (s, 0.85H, –N*H*), 5.79 (s, 0.15H, –N*H*), 3.39 [septet, 0.3H, $^3J = 6.6$ Hz, –C*H*(CH$_3$)$_2$], 3.13 [septet, 1.7H, $^3J = 6.6$ Hz, –C*H*(CH$_3$)$_2$], 1.20–1.16 [m, 10.2H, –CH(C*H*$_3$)$_2$], 1.07 [d, 0.9H, $^3J = 6.6$ Hz, –CH(C*H*$_3$)$_2$], 0.97 [d, 0.9H, $^3J = 6.6$ Hz, –CH(C*H*$_3$)$_2$]; δ_C (125 MHz, $CDCl_3$, 25 °C) 153.4 (*C*=N), 146.5 (Ar-*C*), 143.6 (Ar-*C*), 139.1 (Ar-*C*), 134.7 (Ar-*C*), 130.0 (Ar-*C*), 129.6 (Ar-*C*), 128.9 (Ar-*C*), 128.7 (Ar-*C*), 128.5 (Ar-*C*), 128.2 (Ar-*C*), 124.0 (Ar-*C*), 123.6 (Ar-*C*), 29.0 [–*C*H(CH$_3$)$_2$], 28.3 [–*C*H(CH$_3$)$_2$], 24.0 [–CH(*C*H$_3$)$_2$), 23.6 [–CH(*C*H$_3$)$_2$]. ESI-MS *m*/*z* (%): 446 (M^+), 264 (100, [2,6-^{i}Pr$_2$C$_6$H$_3$N=CC$_6$H$_5$]$^+$).

***N*-(2,6-Diisopropylphenyl)-*N′*-(4-isopropylphenyl)benzamidine (3j).** The procedure was similar to that of compound **3b** except that *N*-(2,6-diisopropylphenyl)benzamide (6.7 g, 24 mmol) and 4-isopropylaniline (3.1 mL, 23 mmol) were used. Crystallization in ethanol–water afforded colorless crystals (5.1 g, 56%) (Found: C, 84.35; H, 8.77; N, 6.84. Calc. for $C_{28}H_{34}N_2$: C, 84.37; H, 8.60; N, 7.03%); mp 90–91 °C; δ_H (500 MHz, $CDCl_3$, 25 °C) 7.61 (d, 2H, $^3J = 6.0$ Hz, Ar-*H*), 7.33–7.38 (m, 3H, Ar-*H*), 7.20 (d, 2H, $^3J = 6.8$ Hz, Ar-*H*), 7.12 (m, 1H, Ar-*H*), 6.91 (d, 2H, $^3J = 7.0$ Hz, Ar-*H*), 6.52 (d, 2H, $^3J = 7.0$ Hz, Ar-*H*), 6.18 (s, 1H, –N*H*), 3.16 [septet, 1.4H, $^3J = 6.8$ Hz, –C*H*(CH$_3$)$_2$], 2.75 [septet, 0.6H, $^3J = 6.8$ Hz, –C*H*(CH$_3$)$_2$], 1.23 [d, 8.4H, $^3J = 6.8$ Hz, –CH(C*H*$_3$)$_2$], 1.14 [d, 3.6 H, $^3J = 6.1$ Hz, –CH(C*H*$_3$)$_2$]; δ_C (125 MHz, $CDCl_3$, 25 °C) 154.0 (*C*=N), 144.2 (Ar-*C*), 143.5 (Ar-*C*), 139.2 (Ar-*C*), 137.9 (Ar-*C*), 135.3 (Ar-*C*), 129.6 (Ar-*C*), 129.0 (Ar-*C*), 128.9 (Ar-*C*), 128.3 (Ar-*C*), 126.7 (Ar-*C*), 123.6 (Ar-*C*), 122.7 (Ar-*C*), 33.4 [–*C*H(CH$_3$)$_2$], 28.2 [–*C*H(CH$_3$)$_2$], 24.0 [–CH(*C*H$_3$)$_2$], 23.6 [–CH(*C*H$_3$)$_2$].

***N*-(2,6-Diisopropylphenyl)-*N′*-(4-methoxylphenyl)benzamidine (3k).** The procedure was similar to that of compound **3b** except that *N*-(2,6-diisopropylphenyl)benzamide (6.7 g, 24 mmol) and 4-methoxylaniline (2.80 g, 22.6 mmol) were used. Crystallization in toluene afforded colorless crystals (6.3 g, 68%) (Found: C, 80.59; H, 8.05; N, 7.11. Calc. for $C_{26}H_{30}N_2O$: C, 80.79; H, 7.82; N, 7.25%); mp 114–115 °C; δ_H (500 MHz, $CDCl_3$, 25 °C) 7.58 (d, 2H, $^3J = 6.8$ Hz, Ar–H), 7.31–7.36 (m, 3H, Ar-*H*), 7.20 (d, 2H, $^3J = 7.3$ Hz, Ar-*H*), 7.09–7.12 (m, 1H, Ar-*H*), 6.60 (m, 4H, Ar-*H*), 6.11 (s, 1H, –N*H*), 3.69 (s, 3H, –OC*H*$_3$), 3.19 [septet, 2H, $^3J = 6.8$ Hz, –C*H*(CH$_3$)$_2$], 1.23 [d, 12H, $^3J = 6.8$ Hz, –C*H*(CH$_3$)$_2$]; δ_C (100 MHz, $CDCl_3$, 25 °C) 156.3 (*C*=N), 154.3 (Ar-*C*), 143.5 (Ar-*C*) 139.3 (Ar-*C*), 135.2 (Ar-*C*), 133.3 (Ar-*C*), 129.5 (Ar-*C*), 129.0 (Ar-*C*), 128.2 (Ar-*C*), 125.0 (Ar-*C*), 123.7 (Ar-*C*), 123.5 (Ar-*C*), 114.0 (Ar-*C*), 55.4 (O*C*H$_3$), 28.2 [–*C*H(CH$_3$)$_2$], 24.0 [–CH(*C*H$_3$)$_2$], 23.6 [–CH(*C*H$_3$)$_2$].

***N*-(2,6-Diisopropylphenyl)-*N′*-(*tert*-butyl)benzamidine (3l).** The procedure was similar to that of compound **3b** except that *N*-(2,6-diisopropylphenyl)benzamide (8.0 g, 28 mmol) and *t*-butylamine (2.5 g, 33 mmol) were used to react at 50 °C for 72 h. Crystallization in ethanol–water afforded light yellow crystals (6.1 g, 65%) (Found: C, 82.22; H, 9.40; N, 8.31. Calc. for $C_{23}H_{32}N_2$: C, 82.09; H, 9.58; N, 8.32%) mp 88 °C; δ_H (500 MHz, $CDCl_3$, 25 °C) 7.16 (m, 5H, Ar-*H*), 6.92 (br s, 2H, Ar-*H*), 6.85 (br s, 1H, Ar-*H*), 4.39 (s, 1H, –N*H*), 3.07 [septet, 2H, $^3J = 6.8$ Hz, –C*H*(CH$_3$)$_2$], 1.56 [s, 9H, –C(*CH*$_3$)$_3$], 1.12 [d, 6H, $^3J = 6.8$ Hz, –CH(C*H*$_3$)$_2$], 0.94 [d, 6H, $^3J = 6.8$ Hz, –CH(C*H*$_3$)$_2$]; δ_C (125 MHz, $CDCl_3$, 25 °C) 152.7 (*C*=N), 146.1 (Ar-*C*), 138.2 (Ar-*C*), 136.5 (Ar-*C*), 128.7 (Ar-*C*), 127.8 (Ar-*C*), 127.7 (Ar-*C*), 122.3 (Ar-*C*), 121.3 (Ar-*C*), 51.6 [–*C*(CH$_3$)$_3$], 28.9 [–*C*H(CH$_3$)$_2$], 28.1 [–C(*C*H$_3$)$_3$], 24.4 [–CH(*C*H$_3$)$_2$], 21.9 [–CH(*C*H$_3$)$_2$].

***N*-(2,6-Dimethylphenyl)-*N*-(2-methylphenyl)benzamidine (3m).** The procedure was similar to that of compound **3b**.[52] *N*-(2,6-Dimethylphenyl)benzamide (5.10 g, 22 mmol) and 2-methylaniline (2.14 ml, 20 mmol) were used according to the method used before. Distillation and crystallization the crude product afforded light yellow crystals (1.66 g, 53%) (Found: C, 84.14; H, 7.02; N, 8.87. Calc. for $C_{22}H_{22}N_2$: C, 84.04; H, 7.05; N, 8.91%); mp 82 °C; δ_H (400 MHz, $CDCl_3$, 25 °C) 7.60 (d, 1.3H, $^3J = 7.2$ Hz, Ar-*H*), 7.49 (d, 0.4H, $^3J = 7.2$ Hz, Ar-*H*), 7.37–7.29 (m 3.5H, Ar-*H*), 7.10 (t, 2.4H, $^3J = 7.2$ Hz, Ar-*H*), 7.03 (d, 0.4H, $^3J = 7.2$ Hz, Ar-*H*), 6.96–6.86 (m, 3.3H, Ar-*H*), 6.52 (d, 0.7H, $^3J = 8.0$ Hz, Ar-*H*), 5.91 (s, 1H, –N*H*), 2.38 (s, 0.7H, Ar–C*H*$_3$), 2.29 (s, 4.5H, Ar–C*H*$_3$), 2.18 (s, 2.4H, Ar–C*H*$_3$), 2.16 (s, 1.4H, Ar–C*H*$_3$); δ_C (100 MHz, $CDCl_3$, 25 °C) 153.8 (*C*=N), 145.8 (Ar-*C*), 139.4 (Ar-*C*), 134.8 (Ar-*C*), 130.4 (Ar-*C*), 130.2 (Ar-*C*), 129.7 (Ar-*C*), 128.6 (Ar-*C*), 128.5 (Ar-*C*), 128.3 (Ar-*C*), 128.1 (Ar-*C*), 126.2 (Ar-*C*), 124.9 (Ar-*C*), 124.3 (Ar-*C*), 123.0 (Ar-*C*), 18.6 (Ar-*C*H$_3$), 17.9 (Ar-*C*H$_3$) , 17.8 (Ar-*C*H$_3$).

***N*-(2,6-Dimethylphenyl)-*N′*-phenylbenzamidine (3n).** The procedure was similar to that of compound **3m**.[52] *N*-(2,6-Dimethylphenyl)benzamide (2.5 g, 10.3 mmol) and aniline (0.96 g, 10.3 mmol) were used according to the method used before. Crystallization in ethanol–water afforded light yellow crystals (1.5 g, 51%) (Found: C, 84.09; H, 6.63; N, 9.13. Calc. for $C_{21}H_{20}N_2$: C, 83.96; H, 6.71; N, 9.33%); mp 84 °C; δ_H (500 MHz, $CDCl_3$, 25 °C) 7.76–7.66 (m, 2H, Ar-*H*), 7.39–7.31 (m, 4H, Ar-*H*), 7.09

(br s, 3H, Ar-*H*), 6.93–6.89 (m, 2H, Ar-*H*), 6.64 (d, 1H, ^3J = 6.3 Hz, Ar-*H*), 6.18 (s, 1H, –N*H*), 2.23 (s, 4.3H, Ar–CH_3), 2.18 (s, 0.7H, Ar–CH_3), 2.10 (s, 1H, Ar–CH_3). δ_C (125 MHz, $CDCl_3$, 25 °C) 153.7 (*C*=N), 146.0 (Ar-*C*), 140.3, (Ar-*C*) 135.1 (Ar-*C*), 129.9 (Ar-*C*), 129.6 (Ar-*C*), 129.1 (Ar-*C*), 128.8 (Ar-*C*), 128.4 (Ar-*C*), 128.3 (Ar-*C*), 123.5 (Ar-*C*), 123.2 (Ar-*C*), 122.6 (Ar-*C*), 18.0 (Ar-*C*H_3).

Synthesis of amidinate aluminium complexes

[{PhC(*N*-2,6-^{i}Pr$_2$C$_6$H$_3$)(*N*-2,6-Me$_2$C$_6$H$_3$)}AlMe$_2$] (4a). To a solution of trimethyl aluminium (2.3 mL, 4.6 mmol, 2 M in toluene) in toluene (30 mL), compound **3a** (1.48 g, 3.86 mmol) was added slowly over a period of half an hour. Instantaneous evolution of methane and almost full dissolution of the suspension were observed. The colorless reaction solution was kept stirring for 24 h at 70 °C. After removal of all volatiles under vacuum, the obtained solids were crystallized from *n*-hexane at –40 °C to afford colorless crystals (0.95 g, 57%) (Found: C, 79.11; H, 8.39; N, 6.37. Calc. for $C_{29}H_{37}AlN_2$: C, 79.05; H, 8.46; N, 6.36%); mp 120 °C; δ_H (500 MHz, $CDCl_3$, 25 °C) 7.15 (tt, 1H, ^3J = 7.8 Hz, ^4J = 1.0 Hz, Ar-*H*), 7.10 (dd, 1H, ^3J = 8.5 Hz, ^3J = 7.0 Hz, Ar-*H*), 7.03–6.98 (m, 4H, Ar-*H*), 6.96 (m, 2H, Ar-*H*), 6.92–6.89 (m, 3H, Ar-*H*), 3.25 [septet, 2H, ^3J = 6.8 Hz, –C*H*(CH$_3$)$_2$], 2.21 (s, 6H, –CH_3), 1.17 [d, 6H, ^3J = 6.8 Hz, –CH(CH_3)$_2$], 0.86 [d, 6H, ^3J = 6.8 Hz, –CH(CH_3)$_2$], –0.50 [s, 6H, –Al(CH_3)$_2$]; δ_C (125 MHz, $CDCl_3$, 25 °C) 171.9 (*C*=N), 143.8 (Ar-*C*) 141.5 (Ar-*C*), 137.9 (Ar-*C*), 133.4 (Ar-*C*), 130.5 (Ar-*C*), 129.6 (Ar-*C*), 129.2 (Ar-*C*), 128.2 (Ar-*C*), 127.7 (Ar-*C*), 125.4 (Ar-*C*), 124.5 (Ar-*C*), 123.5 (Ar-*C*), 28.2 [–*C*H(CH$_3$)$_2$], 25.6 (–*C*H$_3$), 22.8 [–CH(*C*H$_3$)$_2$], 19.1 [CH(*C*H$_3$)$_2$], –9.7 [–Al(*C*H$_3$)$_2$].

[{PhC(*N*-2,6-^{i}Pr$_2$C$_6$H$_3$)(*N*-2,6-Me$_2$C$_6$H$_3$)}AlEt$_2$] (4a′). The procedure was similar to that of complex **4a**, except that proligand **3a** (1.53 g, 3.98 mmol) and a solution of triethyl aluminium (5.12 mL, 4.8 mmol, 0.94 M in petroleum ether) were used. Crystallization of the crude product from *n*-hexane for several times afforded colorless crystals (0.76 g, 41%) (Found: C, 78.84; H, 8.31; N, 6.27. Calc. for $C_{31}H_{41}AlN_2$: C, 79.45; H, 8.82; N, 5.98%); mp 91 °C; δ_H (500 MHz, C_6D_6 25 °C) 7.03 (m, 3H, Ar-*H*), 6.98 (m, 2H, Ar–H), 6.86–6.83 (m, 3H, Ar-*H*), 6.62 (m, 1H, Ar–H), 6.57 (m, 2H, Ar-*H*), 3.54 [septet, 2H, ^3J = 6.8 Hz, –C*H*(CH$_3$)$_2$], 2.28 (s, 6H, –CH_3), 1.39 [t, 6H, ^3J = 8.0 Hz, –Al(CH$_2$CH_3)$_2$], 1.28 [d, 6H, ^3J = 6.8 Hz, –CH(CH_3)$_2$], 0.91 [d, 6H, ^3J = 6.8 Hz, –CH(CH_3)$_2$], 0.61 [qd, 2H, ^3J = 8.0 Hz, ^2J = 3.0 Hz, –Al(CH_2CH$_3$)$_2$]; δ_C (125 MHz, $CDCl_3$, 25 °C) 172.1 (*C*=N), 143.5 (Ar-*C*), 141.6 (Ar-*C*), 138.0 (Ar-*C*), 133.1 (Ar-*C*), 130.5 (Ar-*C*), 129.6 (Ar-*C*), 129.2 (Ar-*C*), 128.2 (Ar-*C*), 127.7 (Ar-*C*), 125.4 (Ar-*C*), 124.4 (Ar-*C*), 123.4 (Ar-*C*), 28.2 [–*C*H(CH$_3$)$_2$], 25.5 (–*C*H$_3$), 22.8 [–CH(*C*H$_3$)$_2$], 19.1 [–CH(*C*H$_3$)$_2$], 8.8 [–Al(CH$_2$*C*H$_3$]$_2$, –0.06 [–Al(*C*H$_2$CH$_3$)$_2$].

[{PhC(*N*-2,6-^{i}Pr$_2$C$_6$H$_3$)(*N*-2,6-Cl$_2$C$_6$H$_3$)}AlMe$_2$] (4b). The procedure was similar to that of complex **4a**, except that proligand **3b** (0.53 g, 1.2 mmol) and a solution of trimethyl aluminium (0.9 mL, 1.8 mmol, 2 M in toluene) were used. Crystallization of the crude product from *n*-hexane afforded colorless crystals (0.35 g, 62%) (Found: C, 67.44; H, 6.37; N, 5.85. Calc. for $C_{27}H_{31}AlCl_2N_2$: C, 67.36; H, 6.49; N, 5.82%); mp 116 °C; δ_H (400 MHz, $CDCl_3$, 25 °C) 7.22 (d, 2H, ^3J = 8.0 Hz, Ar-*H*), 7.18 (tt, 1H, ^3J = 7.2 Hz, ^4J = 1.8 Hz, Ar-*H*), 7.12 (dd, 1H, ^3J = 8.6 Hz, ^3J = 6.6 Hz, Ar-*H*), 7.07–7.00 (m, 6H, Ar-*H*), 6.92 (t, 1H, ^3J = 8.0 Hz, Ar-*H*), 3.33 [septet, 2H, ^3J = 6.8 Hz, –C*H*(CH$_3$)$_2$], 1.18 [d, 6H, ^3J = 6.8 Hz, –CH(CH_3)$_2$], 0.86 [d, 6H, ^3J = 6.8 Hz, –CH(CH_3)$_2$], –0.47 [s, 6H, –Al(CH_3)$_2$]; δ_C (125 MHz, $CDCl_3$, 25 °C) 173.1 (*C*=N), 143.8 (Ar-*C*), 139.7 (Ar-*C*), 137.1 (Ar-*C*), 132.3 (Ar-*C*), 130.7 (Ar-*C*), 129.5 (Ar-*C*), 128.3 (Ar-*C*), 127.3 (Ar-*C*), 125.9 (Ar-*C*), 125.4 (Ar-*C*), 123.5 (Ar-*C*), 28.0 [–*C*H(CH$_3$)$_2$], 25.6 [–CH(*C*H$_3$)$_2$], 22.9 [–CH(*C*H$_3$)$_2$], –9.9 [–Al(*C*H$_3$)$_2$]; *Crystal data* for **4b**: $C_{27}H_{31}AlCl_2N_2$, M_r = 481.42, monoclinic, space group *C*2/*c*, *a* = 24.771(4), *b* = 14.720(2), *c* = 17.004(2) Å, β = 118.966(3)°, *V* = 5424.8(13) Å^3, *Z* = 8, D_c = 1.179 Mg m^{-3}, μ = 0.288 mm^{-1}, 13973 reflections measured and 5054 reflections unique, final R_1 = 0.0638, wR_2 = 0.1276 ($I > 2\sigma(I)$).

[{PhC(*N*-2,6-^{i}Pr$_2$C$_6$H$_3$)(*N*-2-FC$_6$H$_4$)}AlMe$_2$] (4c). The procedure was similar to that of complex **4a**, except that proligand **3c** (1.38 g, 3.68 mmol) and a solution of trimethyl aluminium (2.7 mL, 5.4 mmol, 2 M in toluene) were used. Crystallization of the crude product from *n*-hexane afforded colorless crystals (0.68 g, 44%) (Found: C, 75.29; H, 7.58; N, 6.58. Calc. for $C_{27}H_{32}AlFN_2$: C, 75.32; H, 7.49; N, 6.51%); mp 121–122 °C; δ_H (400 MHz, $CDCl_3$, 25 °C) 7.28 (tt, 1H, ^3J = 7.2 Hz, ^4J = 2.0 Hz, Ar-*H*), 7.17 (td, 2H, ^3J = 7.2 Hz, ^4J = 1.6 Hz, Ar-*H*), 7.13–7.09 (m, 3H Ar-*H*), 7.03–6.97 (m, 3H, Ar-*H*), 6.90–6.84 (m, 1H, Ar-*H*), 6.79 (td, 1H, ^3J = 8.0 Hz, ^4J = 1.2 Hz, Ar-*H*), 6.54 (td, 1H, ^3J = 8.0 Hz, ^4J = 1.6 Hz, Ar-*H*). 3.21 [septet, 2H, ^3J = 6.8 Hz, –C*H*(CH$_3$)$_2$], 1.15 [d, 6H, ^3J = 6.8 Hz, –C*H*(CH$_3$)$_2$], 0.87 [d, 6H, ^3J = 6.8 Hz, –CH(CH_3)$_2$], –0.51 [s, 6H, –Al(CH_3)$_2$]; δ_C (100 MHz, $CDCl_3$, 25 °C) 171.5 (*C*=N), 155.7 (d, $^1J_{F-C}$ = 243.2 Hz, Ar-*C*), 143.7 (Ar=*C*), 137.1 (Ar=*C*), 131.8 (d, $^3J_{F-C}$ = 10.5 Hz, Ar-*C*), 130.8 (Ar-*C*), 129.2 (Ar-*C*), 129.1 (Ar-*C*), 128.3 (Ar-*C*), 125.9 (Ar-*C*), 123.8 (Ar-*C*), 123.7 (Ar-*C*), 123.5 (Ar-*C*), 123.1 (Ar-*C*), 115.7 (d, $^2J_{F-C}$ = 20.5 Hz, Ar-*C*), 28.2 [–*C*H(CH$_3$)$_2$], 25.7 [–CH(*C*H$_3$)$_2$], 22.9 [–CH(*C*H$_3$)$_2$], –10.9 [–Al(*C*H$_3$)$_2$]; *Crystal data* for **4c**: $C_{27}H_{32}AlFN_2$, M_r = 430.53, triclinic, space group $P\bar{1}$, *a* = 9.005(7), *b* = 10.674(8), *c* = 14.0804(11) Å, α = 69.3390(10), β = 83.1210(10), γ = 83.9360(10)°, *V* = 1254.22(17) Å^3, *Z* = 2, D_c = 1.140 Mg m^{-3}, μ = 0.104 mm^{-1}, 7464 reflections measured and 5331 reflections unique, final R_1 = 0.0511, wR_2 = 0.1349 ($I > 2\sigma(I)$).

[{PhC(*N*-2,6-^{i}Pr$_2$C$_6$H$_3$)(*N*-2-ClC$_6$H$_4$)}AlMe$_2$] (4d). The procedure was similar to that of complex **4a**, except that proligand **3d** (1.04 g, 2.66 mmol) and a solution of trimethyl aluminium (1.7 mL, 3.4 mmol, 2 M in toluene) were used. Crystallization of the crude product from *n*-hexane afforded colorless crystals (0.54 g, 45%); (Found: C, 72.67; H, 7.21; N, 6.35. Calc. for $C_{27}H_{32}AlClN_2$: C, 72.55; H, 7.22; N, 6.27%); mp 106–107 °C; δ_H (500 MHz, $CDCl_3$, 25 °C) 7.34 (m, 1H, Ar-*H*), 7.27 (tt, 1H, ^3J = 7.5 Hz, ^4J = 1.0 Hz, Ar-*H*), 7.15 (t, 2H, ^3J = 8.0 Hz, Ar-*H*), 7.11 (t, 1H, ^3J = 7.9 Hz, Ar-*H*), 7.07 (d, 2H, ^3J = 7.9 Hz, Ar-*H*), 7.03 (d, 2H, ^3J = 7.5 Hz, Ar-*H*), 6.85 (m, 2H, Ar-*H*), 6.45 (m, 1H, Ar-*H*), 3.19 [septet, 2H, ^3J = 6.8 Hz, –C*H*(CH$_3$)$_2$], 1.17 [d, 6H, ^3J = 6.8 Hz, –CH(CH_3)$_2$], 0.87 (d, 6H, ^3J = 6.8 Hz, –CH(CH_3)$_2$), –0.51 [s, 6H, –Al(CH_3)$_2$]; δ_C (100 MHz, $CDCl_3$, 25 °C) 171.5 (*C*=N), 143.5 (Ar-*C*), 141.0 (Ar-*C*), 137.0 (Ar-*C*), 130.9 (Ar-*C*), 129.7 (Ar-*C*), 129.6 (Ar-*C*), 129.0 (Ar-*C*), 128.3 (Ar-*C*), 127.3 (Ar-*C*), 126.6 (Ar-*C*), 125.9 (Ar-*C*), 124.4 (Ar-*C*), 123.5 (Ar-*C*), 123.1 (Ar-*C*),

28.1 [–$CH(CH_3)_2$], 25.6 [–$CH(CH_3)_2$], 22.9 [–$CH(CH_3)_2$], –10.2 [–$Al(CH_3)_2$].

[{PhC(*N*-2,6-^{i}Pr$_2$C$_6$H$_3$)(*N*-2-MeC$_6$H$_4$)}AlMe$_2$] (4e). The procedure was similar to that of complex **4a**, except that proligand **3e** (1.6 g, 4.3 mmol) and a solution of trimethyl aluminium (2.6 mL, 4.6 mmol, 2 M in toluene) were used. Crystallization of the crude product from *n*-hexane afforded off-white crystals of **4e** (0.78 g, 42%) (Found: C, 78.39; H, 8.34; N, 6.41. Calc. for $C_{28}H_{35}AlN_2$: C, 78.84; H, 8.27; N, 6.57%); mp 81–82 °C; δ_H (500 MHz, $CDCl_3$, 25 °C) 7.18 (t, 1H, ^3J = 7.5 Hz, Ar-*H*), 7.14 (d, 1H, ^3J = 7.5 Hz, Ar-*H*), 7.10 (t, 1H, ^3J = 7.5 Hz, Ar-*H*), 7.06 (t, 2H, ^3J = 7.8 Hz, Ar-*H*), 7.02 (d, 2H, ^3J = 7.5 Hz, Ar-*H*), 6.96 (d, 2H, ^3J = 7.8 Hz, Ar–H), 6.90 (m, 2H, Ar–H), 6.55 (dd, 1H, ^3J = 7.5 Hz, ^4J = 1.5 Hz, Ar-*H*), 3.26 [septet, 2H, ^3J = 6.8 Hz, –$CH(CH_3)_2$], 2.33 (s, 3H, Ar–CH_3), 1.16 [d, 6H, ^3J = 6.8 Hz, –$CH(CH_3)_2$], 0.86 [d, 6H, ^3J = 6.8 Hz, –$CH(CH_3)_2$], –0.52 [s, 6H, –$Al(CH_3)_2$]; δ_C (125 MHz, $CDCl_3$, 25 °C) 172.0 (*C*=N), 143.7 (Ar-*C*), 142.8 (Ar-*C*), 137.6 (Ar-*C*), 131.9 (Ar-*C*), 130.5 (Ar-*C*), 130.4 (Ar-*C*), 129.9 (Ar-*C*), 129.1 (Ar-*C*), 127.9 (Ar-*C*), 126.1 (Ar-*C*), 125.6 (Ar-*C*), 125.5 (Ar-*C*), 123.6 (Ar-*C*), 123.5 (Ar-*C*), 28.2 [–$CH(CH_3)_2$], 25.7 (Ar-CH_3), 22.8 [–$CH(CH_3)_2$], 19.2 [–$CH(CH_3)_2$], –10.3 [–$Al(CH_3)_2$].

[{PhC(*N*-2,6-^{i}Pr$_2$C$_6$H$_3$)(*N*-Ph)}AlMe$_2$] (4f). The procedure was similar to that of complex **4a**, except that proligand **3f** (1.0 g, 2.8 mmol) and a solution of trimethyl aluminium (1.7 mL, 3.3 mmol, 2 M in toluene) were used. Crystallization of the crude product from *n*-hexane afforded light yellow crystals (0.78 g, 42%) (Found: C, 78.55; H, 8.10; N, 6.74. Calc. for $C_{27}H_{33}AlN_2$: C, 78.61; H, 8.06; N, 6.79%); mp 112 °C; δ_H (500 MHz, $CDCl_3$, 25 °C) 7.24 (t, 1H, ^3J = 7.5 Hz, Ar-*H*), 7.15–7.08 (m, 5H, Ar-*H*), 7.05 (d, 2H, ^3J = 8.0 Hz, Ar-*H*), 7.00 (d, 2H, ^3J = 7.5 Hz, Ar-*H*), 6.94 (t, 1H, ^3J = 7.0 Hz, Ar-*H*), 6.70 (d, 2H, ^3J = 8.0 Hz, Ar-*H*), 3.22 [septet, 2H, ^3J = 6.8 Hz, –$CH(CH_3)_2$], 1.14 [d, 6H, ^3J = 6.8 Hz, –$CH(CH_3)_2$], 0.87 [d, 6H, ^3J = 6.8 Hz, –$CH(CH_3)_2$], –0.51 [s, 6H, –$Al(CH_3)_2$]; δ_C (125 MHz, $CDCl_3$, 25 °C) 171.3 (*C*=N), 143.8 (Ar-*C*), 143.6 (Ar-*C*), 137.2 (Ar-*C*), 130.5 (Ar–C), 129.7 (Ar-*C*), 128.7 (Ar-*C*), 128.72 (Ar-*C*), 128.1 (Ar-*C*), 125.7 (Ar-*C*), 123.4 (Ar-*C*), 123.3 (Ar-*C*), 122.7 (Ar-*C*), 28.1 [–$CH(CH_3)_2$], 25.7 [–$CH(CH_3)_2$], 22.8 [–$CH(CH_3)_2$], –10.8 [–$Al(CH_3)_2$].

[{PhC(*N*-2,6-^{i}Pr$_2$C$_6$H$_3$)(*N*-3-FC$_6$H$_4$)}AlMe$_2$] (4g). The procedure was similar to that of complex **4a**, except that the proligand **3g** (1.4 g, 3.7 mmol) and a solution of trimethyl aluminium (2.3 mL, 4.6 mmol, 2 M in toluene) were used. Crystallization of the crude product from *n*-hexane afforded colorless crystals (0.95 g, 60%) (Found: C, 75.66; H, 7.51; N, 6.45. Calc. for $C_{27}H_{32}AlFN_2$: C, 75.32; H, 7.49; N, 6.51%); mp 98 °C; δ_H (500 MHz, $CDCl_3$, 25 °C) 7.28 (tt, 1H, ^3J = 7.5 Hz, ^4J = 1.0 Hz Ar-*H*), 7.16 (t, 2H, ^3J = 8.0 Hz, Ar-*H*), 7.11 (dd, 1H, ^3J = 8.0 Hz, ^3J = 6.5 Hz, Ar-*H*), 7.09–7.04 (m, 3H, Ar-*H*), 7.02 (d, 2H, ^3J = 7.0 Hz, Ar-*H*), 6.64 (td, 1H, ^3J = 8.0 Hz, ^4J = 2.5 Hz, Ar-*H*), 6.47 (dd, 1H, ^3J = 8.0 Hz, ^4J = 1.5 Hz, Ar-*H*), 6.37 (dt, 1H, ^3J = 10.5 Hz, ^4J = 2.5 Hz, Ar-*H*), 3.18 [septet, 2H, ^3J = 7.0 Hz, –$CH(CH_3)_2$], 1.14 [d, 6H, ^3J = 7.0 Hz, –$CH(CH_3)_2$], 0.87 [d, 6H, ^3J = 7.0 Hz, –$CH(CH_3)_2$], –0.51 [s, 6H, –$Al(CH_3)_2$]; δ_C (125 MHz, $CDCl_3$, 25 °C) 171.52 (*C*=N), 162.8 (d, $^1J_{C-F}$ = 244 Hz), 145.4 (d, $^3J_{C-F}$ = 10 Hz) 143.7 (Ar-*C*), 136.9 (Ar-*C*), 130.8 (Ar-*C*), 129.7 (d, $^3J_{C-F}$ = 10 Hz, (Ar-*C*)), 129.6 (Ar-*C*), 128.5 (Ar-*C*), 128.3 (Ar-*C*), 125.9 (Ar-*C*), 123.5 (Ar-*C*), 118.9 (Ar-*C*), 110.1 (d, $^2J_{C-F}$ = 22 Hz, Ar-*C*), 109.5 (d,$^2J_{C-F}$ = 22 Hz Ar-*C*), 29.2 [–$CH(CH_3)_2$], 25.7 [–$CH(CH_3)_2$], 22.8 [–$CH(CH_3)_2$], –10.8 [–$Al(CH_3)_2$].

[{PhC(*N*-2,6-^{i}Pr$_2$C$_6$H$_3$)(*N*-4-FC$_6$H$_4$)}AlMe$_2$] (4h). The procedure was similar to that of complex **4a**, except that the proligand **3h** (1.14 g, 3.05 mmol) and a solution of trimethyl aluminium (1.9 mL, 3.8 mmol, 2 M in toluene) were used. Crystallization of the crude product from *n*-hexane afforded colorless crystals (0.43 g, 33%) (Found: C, 75.30; H, 7.41; N, 6.76. Calc. for $C_{27}H_{32}AlFN_2$: C, 75.32; H, 7.49; N, 6.51%); mp 112–114 °C; δ_H (500 MHz, $CDCl_3$, 25 °C) 7.26 (t, 1H, ^3J = 8.0 Hz, Ar–H), 7.14 (t, 2H, ^3J = 8.0 Hz, Ar-*H*), 7.09 (t, 1H, ^3J = 8.2 Hz, Ar-*H*), 7.02 (t, 4H, ^3J = 8.4 Hz, Ar-*H*), 6.82 (t, 2H, ^3J = 8.4 Hz, Ar-*H*), 6.67 (m, 2H, Ar-*H*), 3.22 [septet, 2H, ^3J = 6.8 Hz, –$CH(CH_3)_2$], 1.16 [d, 6H, ^3J = 6.8 Hz, –$CH(CH_3)_2$], 0.90 [d, 6H, ^3J = 6.8 Hz, –$CH(CH_3)_2$], –0.51 [s, 6H, –$Al(CH_3)_2$]; δ_C (100 MHz, $CDCl_3$, 25 °C) 171.4 (*C*=N), 158.9 (Ar-*C*, $^1J_{C-F}$ = 240 Hz), 143.8 (Ar-*C*), 139.8 (Ar-*C*), 139.8 (Ar-*C*), 137.2 (Ar-*C*), 130.6 (Ar-*C*), 129.8 (Ar-*C*), 128.5 (Ar-*C*), 128.2 (Ar-*C*), 125.8 (Ar-*C*), 124.6 (Ar-*C*), 124.5 (Ar-*C*), 123.5 (Ar-*C*), 115.5 (Ar-*C*, $^2J_{C-F}$ = 20 Hz), 28.2 [–$CH(CH_3)_2$], 25.7 [–$CH(CH_3)_2$], 22.8 [–$CH(CH_3)_2$], –10.8 [–$Al(CH_3)_2$].

[{PhC(*N*-2,6-^{i}Pr$_2$C$_6$H$_3$)(*N*-4-ClC$_6$H$_4$)}AlMe$_2$] (4i). The procedure was similar to that of complex **4a**, except that the proligand **3i** (1.10 g, 2.81 mmol) and a solution of trimethyl aluminium (1.8 mL, 3.6 mmol, 2 M in toluene) were used. Crystallization of the crude product from *n*-hexane afforded colorless crystals (0.73 g, 47%) (Found: C, 72.75; H, 7.43; N, 6.22. Calc. for $C_{27}H_{32}AlClN_2$: C, 72.55; H, 7.22; N, 6.27%); mp 104–105 °C; δ_H (500 MHz, $CDCl_3$, 25 °C) 7.27 (t, 1H, ^3J = 7.4 Hz, Ar-*H*), 7.15 (t, 2H, ^3J = 8.0 Hz, Ar-*H*), 7.09 (dd, 1H, ^3J = 8.5 Hz, ^3J = 7.0 Hz, Ar-*H*), 7.07–7.03 (m, 4H, Ar-*H*), 7.01 (d, 2H, ^3J = 7.5 Hz, Ar–H), 6.62 (d, 2H, ^3J = 8.5 Hz, Ar-*H*), 3.18 [septet, 2H, ^3J = 6.8 Hz, –$CH(CH_3)_2$], 1.15 [d, 6H, ^3J = 6.8 Hz, –$CH(CH_3)_2$], 0.88 [d, 6H, ^3J = 6.8 Hz, –$CH(CH_3)_2$], –0.53 [s, 6H, –$Al(CH_3)_2$]; δ_C (100 MHz, $CDCl_3$, 25 °C) 171.4 (*C*=N), 143.7 (Ar-*C*), 142.3 (Ar-*C*), 137.0 (Ar-*C*), 130.8 (Ar-*C*), 129.7 (Ar-*C*), 128.9 (Ar-*C*), 128.5 (Ar-*C*), 128.3 (Ar-*C*), 127.9 (Ar-*C*), 125.9 (Ar-*C*), 124.4 (Ar-*C*), 123.5 (Ar-*C*), 28.2 [–$CH(CH_3)_2$], 25.7 [–$CH(CH_3)_2$], 22.8 [–$CH(CH_3)_2$], –10.8 [$Al(CH_3)_2$]; ESI-MS *m*/*z* (%): 446 (trace, M^+), 390 (7, [M–$Al(CH_3)_2]^+$), 264 (100, [2,6-^{i}Pr$_2$C$_6$H$_3$N=$CC_6H_5]^+$).

[{PhC(*N*-2,6-^{i}Pr$_2$C$_6$H$_3$)(*N*-4-^{i}PrC$_6$H$_4$)}AlMe$_2$] (4j). The procedure was similar to that of complex **4a**, except that proligand **3j** (1.09 g, 2.74 mmol) and a solution of trimethyl aluminium (1.7 mL, 3.4 mmol, 2 M in toluene) were used. Crystallization of the crude product from *n*-hexane afforded colorless crystals (0.66 g, 53%) (Found: C, 78.97; H, 8.78; N, 6.14. Calc. for $C_{30}H_{39}AlN_2$: C, 79.26; H, 8.65; N, 6.16%); mp 107–108 °C; δ_H (500 MHz, $CDCl_3$, 25 °C) 7.24 (t, 1H, ^3J = 7.5 Hz, Ar-*H*), 7.13 (t, 2H, ^3J = 8.0 Hz, Ar-*H*), 7.08 (dd, 1H, ^3J = 8.5 Hz, ^3J = 7.0 Hz, Ar-*H*), 7.05 (d, 2H, ^3J = 8.5 Hz, Ar-*H*), 7.00 (d, 2H, ^3J = 8.0 Hz, Ar-*H*), 6.96 (d, 2H, ^3J = 8.0 Hz, Ar-*H*), 6.62 (d, 2H, ^3J = 8.5 Hz, Ar-*H*), 3.23 [septet, 2H, ^3J = 6.8 Hz, –$CH(CH_3)_2$], 2.79 [septet, 1H, ^3J = 6.8 Hz, –$CH(CH_3)_2$], 1.18 [d, ^3J = 6.8 Hz, 6H, –$CH(CH_3)_2$], 1.13 [d, 6H, ^3J = 6.8 Hz, –$CH(CH_3)_2$], 0.87 (d, 6H, ^3J = 6.8 Hz, –$CH(CH_3)_2$), –0.51 (s, 6H, –$Al(CH_3)_2$); δ_C (100 MHz, $CDCl_3$, 25 °C) 171.1 (*C*=N), 143.9 (Ar-*C*), 143.2 (Ar-*C*), 141.1 (Ar-*C*), 137.4 (Ar-*C*), 130.4 (Ar-*C*), 129.6 (Ar-*C*), 129.0 (Ar-*C*), 128.0 (Ar-*C*), 126.6 (Ar-*C*), 125.6 (Ar-*C*), 123.3 (Ar-*C*), 122.9 (Ar-*C*), 33.4 [–$CH(CH_3)_2$],

28.1 [–*C*H(CH$_3$)$_2$], 25.7 [–CH(*C*H$_3$)$_2$], 24.0 [–CH(*C*H$_3$)$_2$], 22.8 [–CH(*C*H$_3$)$_2$], –10.7 [–Al(*C*H$_3$)$_2$].

[{PhC(*N*-2,6-^{i}Pr$_2$C$_6$H$_3$)(*N*-4-MeOC$_6$H$_4$)}AlMe$_2$] (4k). The procedure was similar to that of complex **4a**, except that the proligand **3k** (1.20 g, 3.11 mmol) and a solution of trimethyl aluminium (1.9 mL, 3.8 mmol, 2 M in toluene) were used. Crystallization from *n*-hexane afforded light yellow crystals (0.79 g, 57%) (Found: C, 75.46; H, 8.19; N, 6.11. Calc. for $C_{28}H_{35}AlN_2O$: C, 75.99; H, 7.97; N, 6.33%); mp 121–123 °C; δ_H (500 MHz, $CDCl_3$, 25 °C) 7.23 (t, 1H, ^3J = 7.5 Hz, Ar-*H*), 7.12 (t, 2H, ^3J = 8.0 Hz, Ar-*H*), 7.07 (dd, 1H, ^3J = 8.0 Hz, ^3J = 6.5 Hz , Ar-*H*), 7.03 (d, 2H, ^3J = 7.5 Hz, Ar-*H*), 7.00 (d, 2H, ^3J = 7.5 Hz, Ar-*H*), 6.66 (m, 4H, Ar-*H*), 3.73 (s, 3H, OC*H*$_3$), 3.23 [septet, 2H, ^3J = 6.8 Hz, –C*H*(CH$_3$)$_2$], 1.15 [d, 6H, ^3J = 6.8 Hz, –CH(C*H*$_3$)$_2$], 0.87 [d, 6H, ^3J = 6.8 Hz, –CH(C*H*$_3$)$_2$], –0.51 [s, 6H, –Al(C*H*$_3$)$_2$]; δ_C (100 MHz, $CDCl_3$, 25 °C) 171.1 (*C*=N), 155.5 (Ar-*C*), 143.9 (Ar-*C*), 137.5 (Ar-*C*), 136.9 (Ar-*C*), 130.4 (Ar-*C*), 130.2 (Ar-*C*), 129.8 (Ar-*C*), 128.9 (Ar-*C*), 128.1 (Ar-*C*), 127.7 (Ar-*C*), 126.0 (Ar-*C*), 125.6 (Ar-*C*), 124.3 (Ar-*C*), 123.4 (Ar-*C*), 114.1 (Ar-*C*), 113.4 (Ar-*C*), 55.4 (O*C*H$_3$), 28.1 [*C*H(CH$_3$)$_2$], 25.7 [CH(*C*H$_3$)$_2$], 22.9 [CH(*C*H$_3$)$_2$], –10.8 [Al(*C*H$_3$)$_2$].

[{PhC(*N*-2,6-^{i}Pr$_2$C$_6$H$_3$)(*N*-^{t}Bu)}AlMe$_2$] (4l). The procedure was similar to that of complex **4a**, except that the proligand **3l** (1.1 g, 3.3 mmol) and a solution of trimethyl aluminium in toluene (2 mL, 4.0 mmol, 2 M in toluene) were used. Crystallization of the crude product from *n*-hexane for several times afforded colorless crystals (0.63 g, 50%); (Found: C, 76.24; H, 9.48; N, 7.03. Calc. for $C_{25}H_{37}AlN_2$: C, 76.49; H, 9.50; N, 7.14%); mp 130–131 °C; δ_H (500 MHz, $CDCl_3$, 25 °C) 7.20–7.18 (m, 3H, Ar-*H*), 7.13–7.11 (m, 2H, Ar-*H*), 6.94 (dd, 1H, ^3J = 8.5 Hz, ^3J = 6.0 Hz, Ar-*H*), 6.88 (d, 2H, ^3J = 8.0 Hz Ar-*H*), 3.28 [septet, 2H,^3J = 6.8 Hz, –C*H*(CH$_3$)$_2$], 1.16 [d, 6H, ^3J = 6.8 Hz, –CH(C*H*$_3$)$_2$], 1.14 (s, 9H, –C(C*H*$_3$)$_3$), 1.10 [d, 6H, ^3J = 6.8 Hz, –CH(C*H*$_3$)$_2$], –0.55 [s, 6H –Al(C*H*$_3$)$_2$]; δ_C (125 MHz, $CDCl_3$, 25 °C) 173.1 (*C*=N), 144.9 (Ar-*C*), 137.7 (Ar-*C*), 132.7 (Ar-*C*), 129.2 (Ar-*C*), 127.6 (Ar-*C*), 127.4 (Ar-*C*), 125.2 (Ar-*C*), 122.8 (Ar-*C*), 52.0 [–*C*(CH$_3$)$_3$], 32.2 [–*C*H(CH$_3$)$_2$], 28.1 [–C(*C*H$_3$)$_3$], 26.3 [–CH(C*H*$_3$)$_2$], 22.8 [–CH(C*H*$_3$)$_2$], –9.8 [Al(*C*H$_3$)$_2$].

[{PhC(*N*-2,6-Me$_2$C$_6$H$_3$)(*N*-2-MeC$_6$H$_4$)}AlMe$_2$] (4m). The procedure was similar to that of complex **4a**, except that proligand **3m** (1.0 g, 3.2 mmol) and a solution of trimethyl aluminium (2.3 mL, 4.6 mmol, 2 M in toluene) were used. Crystallization of the crude product from *n*-hexane afforded colorless crystals (0.43 g, 36%) (Found: C, 76.99; H, 7.24; N, 7.48. Calc. for $C_{24}H_{27}AlN_2$: C, 77.81; H, 7.35; N, 7.56%); mp 90 °C; δ_H (400 MHz, $CDCl_3$, 25 °C) 7.21 (t, 1H, ^3J = 7.2 Hz, Ar-*H*), 7.14 (d, 1H, ^3J = 6.4 Hz, Ar-*H*), 7.07 (t, 2H, ^3J = 7.6 Hz, Ar-*H*), 6.98 (d, 2H, ^3J = 7.6 Hz, Ar-*H*), 6.93–6.90 (m, 5H, Ar-*H*), 6.54 (d, 1H, ^3J = 7.2 Hz, Ar-*H*), 2.33 (s, 3H, Ar–C*H*$_3$), 2.20 (s, 6H, Ar–C*H*$_3$), –0.51 [s, 6H, –Al (C*H*$_3$)$_2$]; δ_C (100 MHz, $CDCl_3$, 25 °C) 171.8 (C=N), 142.7 (Ar-*C*), 141.1 (Ar-*C*), 133.5 (Ar-*C*), 132.2 (Ar-*C*), 130.5 (Ar-*C*), 130.4 (Ar-*C*), 129.8 (Ar-*C*), 128.9 (Ar-*C*), 128.1 (Ar-*C*), 127.9 (Ar-*C*), 126.1 (Ar-*C*), 125.4 (Ar-*C*), 124.7 (Ar-*C*), 123.7 (Ar-*C*), 19.1 (Ar-*C*H$_3$), –9.7 [–Al(*C*H$_3$)$_2$].

[{PhC(*N*-2,6-Me$_2$C$_6$H$_3$)(*N*-Ph)}AlMe$_2$] (4n). The procedure was similar to that of complex **4a**, except that proligand **3n** (1.3 g, 4.3 mmol) and a solution of trimethyl aluminium (2.6 mL, 5.2 mmol, 2 M in toluene) were used. Crystallization of the crude product from *n*-hexane afforded colorless crystals (0.42 g, 28%); (Found: C, 77.32; H, 6.97; N, 7.76. Calc. for $C_{23}H_{25}AlN_2$: C, 77.50; H, 7.07; N, 7.86%); mp 91–92 °C; δ_H (500 MHz, $CDCl_3$, 25 °C) 7.27 (br s, 1H, ^3J = 7.0 Hz, Ar-*H*), 7.14 (t, 2H, ^3J = 8.0 Hz, Ar-*H*), 7.11 (t, 2H, ^3J = 8.0 Hz, Ar-*H*), 7.07 (d, 2H, ^3J = 8.0 Hz, Ar-*H*), 6.95–6.90 (m, 4H, Ar-*H*), 6.69 (d, 2H, ^3J = 7.5 Hz, Ar-*H*), 2.18 (s, 6H, Ar–C*H*$_3$), –0.50 [s, 6H, Al(C*H*$_3$)$_2$]; δ_C (125 MHz, $CDCl_3$, 25 °C) 171.1 (*C*=N), 143.5 (Ar-*C*), 140.8 (Ar-*C*), 133.6 (Ar-*C*), 130.5 (Ar-*C*), 129.6 (Ar-*C*), 128.7 (Ar-*C*), 128.1 (Ar-*C*), 128.0 (Ar-*C*), 124.9 (Ar-*C*), 123.2 (Ar-*C*), 122.8 (Ar-*C*), 19.1 (Ar-*C*H$_3$), –10.1 [Al(*C*H$_3$)$_2$].

[{PhC(*N*-2,6-^{i}Pr$_2$C$_6$H$_3$)$_2$}AlMe$_2$] (5). The procedure was similar to that of complex **4a**, except that *N*,*N*′-bis(2,6-diisopropylphenyl)benzamidine (1.25 g, 2.86 mmol) and trimethyl aluminium (2.1 mL, 4.2 mmol, 2 M in toluene) were used. Crystallization of the crude product with toluene afforded colorless crystals (1.01 g, 72%); (Found: C, 79.03; H, 9.22; N 5.51. Calc. for $C_{33}H_{45}AlN_2$: C, 79.80; H, 9.13; N, 5.64%); mp 110–111 °C; δ_H (400 MHz, $CDCl_3$, 25 °C) 7.15–7.04 (m, 4H, Ar-*H*), 7.04 (br s, 2H, Ar-*H*), 7.02 (br s, 2H, Ar-*H*), 6.99 (t, 2H, ^3J = 8.0 Hz, Ar-*H*), 6.90 (d, 2H, ^3J = 8.0 Hz, Ar-*H*), 3.35 [septet, 4H, ^3J = 6.8 Hz, –C*H*(CH$_3$)$_2$], 1.19 [d, 12H, ^3J = 6.8 Hz, –CH(C*H*$_3$)$_2$], 0.86 [d, 12H, ^3J = 6.8 Hz, –CH(C*H*$_3$)$_2$], –0.50 [s, 6H, –Al(CH$_3$)$_2$]; δ_C (100 MHz, $CDCl_3$, 25 °C) 172 4 (*C*=N), 143.6 (Ar-*C*), 138.1 (Ar-*C*), 130.4 (Ar-*C*), 130.1 (Ar-*C*), 128.8 (Ar-*C*), 127.6 (Ar-*C*), 125.4 (Ar-*C*), 123.5 (Ar-*C*), 28.3 [–*C*H(CH$_3$)$_2$], 25.5 [–CH(*C*H$_3$)$_2$], 22.7 [–CH(*C*H$_3$)$_2$], –10.3 [–Al(*C*H$_3$)$_2$]; *Crystal data* for **5**: $C_{33}H_{45}AlN_2$, M_r = 496.69, trigonal, space group $P3_221$, $a = b$ = 14.948(8), c = 12.2099(10) Å, $\alpha = \beta$ = 90, γ = 120°, V = 2362.8(3) Å^3, Z = 3, D_c = 1.047 Mg m^{-3}, μ = 0.086 mm^{-1}, 13607 reflections measured and 3273 reflections unique, final R_1 = 0.0550, wR_2 = 0.1186 ($I > 2\sigma(I)$).

Typical polymerization procedure

To a solution of *rac*-lactide (167 mg, 1.16 mmol) in toluene (0.6 mL), a solution of aluminium amidinate complex (0.012 mmol) in toluene (0.5 mL) was added. The total volume was 1.1 mL. The mixture was then immersed into an oil bath of 70 °C for polymerization. The polymerization was quenched by addition of wet petroleum ether. After removal of the volatiles, the residue was subjected to ^{1}H NMR analysis. Monomer conversion was determined by observing the methine resonance integration of monomer *vs.* polymer in the ^{1}H NMR ($CDCl_3$, 400 MHz) spectrum. The purification of the polymer in each case was managed by dissolving the crude samples in CH_2Cl_2 and precipitating the polymer solution with methanol. The obtained polymers were further dried in a vacuum oven at 60 °C for 24 h. The polymer samples were subjected to viscosity measurements and in selected cases analyzed by GPC.

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