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PAPER

Zinc complexes supported by claw-type aminophenolate ligands: synthesis, characterization and catalysis in the ring-opening polymerization of *rac*-lactide†

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A series of zinc silylamido complexes bearing claw-type multidentate aminophenolate ligands, [LZnN(SiMe$_3$)$_2$] (L = –OAr^1-CH$_2$N[(CH$_2$)$_n$NR$_2$]CH$_2$Ar^2, n = 2 or 3; R = Me or Et (**1a–3a**, **5a**, **7a** and **8a**); L = –OC$_6$H$_2$-4,6-^{t}Bu$_2$-2-CH$_2$N[(CH$_2$)$_2$OMe]$_2$ (**9a**)), have been synthesized *via* the reaction of Zn[N(SiMe$_3$)$_2$]$_2$ and 1 equiv. of corresponding aminophenol. The reaction of Zn[N(SiMe$_3$)$_2$]$_2$ with the proligand **L^{6}H** (2-{*N*-(2-methoxybenzyl)-*N*-[3-(*N*′,*N*′-dimethylamino)propyl]aminomethyl}-4-methyl-6-tritylphenol) resulted in the formation of bisphenolate zinc complex **6** regardless of the stoichiometric ratio of the two starting materials. Complex **4b** with an initiating group of 3-*tert*-butyl-2-methoxy-5-methylbenzyloxy was obtained and further studied *via* the X-ray diffraction method to be monomeric. Zinc ethyl complex **2c** was also prepared from the reaction of ZnEt$_2$ and 1 equiv. of proligand **L^{2}H** as the representative complex with an alkyl initiating group. All zinc silylamido complexes efficiently initiated the ring-opening polymerization of *rac*-lactide in the presence or absence of isopropanol at ambient temperature. The steric and electronic characteristics of the ancillary ligands significantly influenced the polymerization performance of the corresponding zinc complexes. The introduction of bulky *ortho*-substituents on the phenoxy moiety resulted in an apparent decrease of catalytic activity while a slightly enhanced isotactic selectivity. Meanwhile, the elongation of the pendant amine arm to three-carbon-atom linkage led to significant decline of the catalytic activity in the absence of isopropanol. The zinc ethyl complex **2c** was not such an efficient initiator as the silylamido ones, but the alkoxy complex **4b** gave an obviously faster and better controlled polymerization when compared to the zinc silylamido complexes.

Introduction

Polylactides (PLAs) produced from renewable resources, have been studied intensively due to their biocompatible, biodegradable properties and potential as attractive alternatives for commercial olefinic materials.[1–6] Among the methods nowadays adopted to obtain PLAs with high molecular weight and specific stereo-microstructure, the ring-opening polymerization (ROP) of lactides initiated by single-site metal complexes is particularly emphasized.[7–12,13] For a well-defined metal complex L$_m$MR (L$_m$ = multidentate ligand; M = central metal; R = initiating group), both the character of the central metal such as radius and electronegativity, and the steric hindrance and the electronic effect brought by the ancillary ligand, contribute to the active site with specific interspace and electronic effect, which significantly influence the polymerization process.[14] The physical, mechanical and thermal properties of polylactide are highly dependent on the polymer's tacticity,[8,9,15,16] and the stereocomplexed PLA produced from a blend of poly-L-LA and poly-D-LA has a T_m value up to 230 °C.[17–19] It is believed that forming a stereocomplexed PLA from *rac*-LA at the molecular level *via* a catalytic process will afford the material with superior processing properties. Thus controlling the microstructure of PLA with the aim to get stereocomplexed PLA from *rac*-LA has become an attractive research spot.[13,20] Researchers all over the world endeavor to explore catalysts possessing good biocompatibility, high activity and excellent stereoselectivity, especially isotactic selectivity for the ROP of *rac*-LA.

The "non-properties" such as colorless, odorless and non-toxicity of zinc[21] make it a superior candidate in functioning as a catalytic center,[22] and its complexes are usually efficient catalysts for the ROP of lactides, as included in a recent review[12] and other literatures.[20,23–51] In terms of controlling the stereo-microstructure of the resultant PLA, some discrete zinc complexes display high heterotactic or low to moderate isotactic selectivity

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†Electronic supplementary information (ESI) available: CCDC reference number 845892 for **4b**. CIF file for zinc complex **4b**, ^{1}H NMR spectra of oligomers of *rac*-LA by **2a**/^{i}PrOH, **4b**, **4b**/^{i}PrOH, the ESI-TOF spectra of oligomer of *rac*-LA obtained by complex **2a**, the methine region of homonuclear decoupled ^{1}H NMR spectrum of poly(*rac*-LA) prepared with **1a** in the presence of ^{i}PrOH in toluene. See DOI: 10.1039/c2dt11767c

in the ROP of *rac*-lactide.[42,49–52] The desired high isotactic selectivity is only available for aluminum complexes bearing Salen-type[53–56] or similar ligands.[47,57,58] Although versatile multidentate ligands such as β-diketiminate,[59,60] phenoxy-amine,[33,43,61,62] phenoxy-imine[20,39,41,63–66] have been extensively developed to complex with zinc, the factors either electronic or steric of the ancillary ligand which may induce high isotactic selectivity in the ROP of *rac*-lactide is undiscovered.

Previously we reported that upon coordination with a zinc ion, an unsymmetrical monoanionic aminophenolate ligand could construct a scorpionate tripodal geometry around the metal center, providing relatively easily adjustable steric hindrance and electronic effect.[48] The variation of the substituents on the phenyl moieties led to moderate stereoselectivity switching from heterotactic bias to isotactic bias, indicating that the steric protection is still not sufficient for the stereoselective coordination/insertion of lactide monomers. Herein we further modified the ancillary ligands either by elongating the pendant amine arm or by introducing a more bulky amino group. A series of zinc silylamino complexes, representative zinc benzyloxy or zinc ethyl complexes bearing such unsymmetrical monoanionic aminophenolate ligands were obtained and evaluated for the ring-opening polymerization of *rac*-lactide.

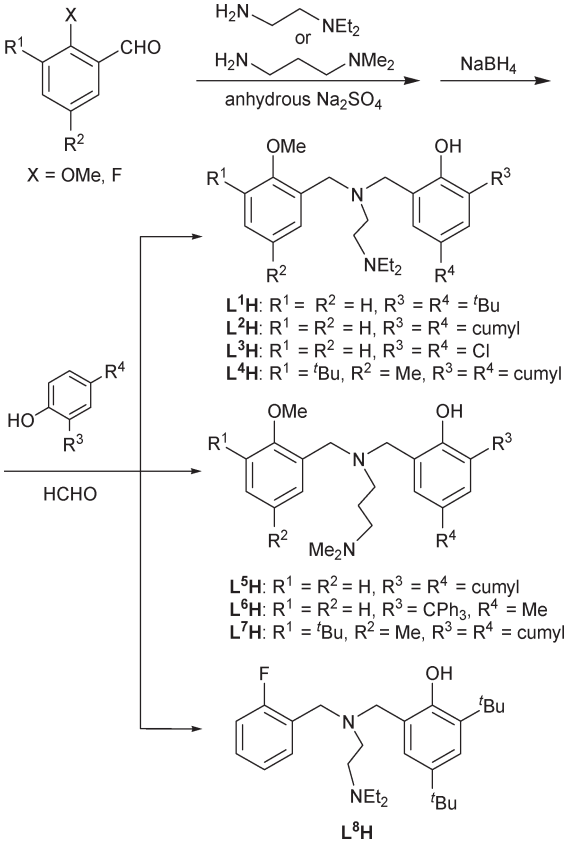
Results and discussion

Synthesis and characterization of zinc complexes

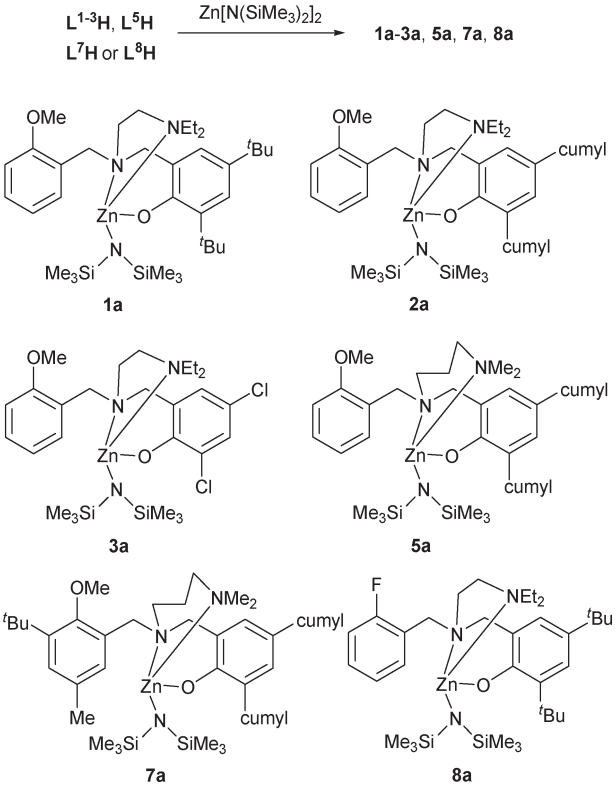
The claw-type multidentate amino-phenol proligands $\mathbf{L^{1–8}H}$ with different pendant amine arms ($–NCH_2CH_2NEt_2$ or $–NCH_2CH_2CH_2NMe_2$) were synthesized according to our previous methods as illustrated in Scheme 1.[48] Analytically pure $\mathbf{L^{1–3}H}$ and $\mathbf{L^{5–8}H}$ could be obtained by column chromatography, while $\mathbf{L^4H}$ was only obtained as a mixture contaminated with 1/6 equiv. of 3-*tert*-butyl-2-methoxy-5-methylbenzyl alcohol, a reduction product of the starting arylaldehyde, due to their very similar polarities.

The obtained proligands $\mathbf{L^{1–3}H}$ and $\mathbf{L^{5–8}H}$ were then used to complex with $Zn[N(SiMe_3)_2]_2$ in the ratio of 1 : 1 at ambient temperature, zinc silylamido complexes **1a–3a**, **5a**, **7a** and **8a** could be isolated successfully as colorless, air/moisture sensitive crystalline solids in moderate yields (Scheme 2). From the reaction of $\mathbf{L^6H}$ and $Zn[N(SiMe_3)_2]_2$, only the bis-ligated complex **6**, without a silylamido group, could be isolated (Scheme 3), which is hardly soluble in common hydrocarbon solvents. In comparison, all the silylamido complexes were smoothly dissolvable in hexane or a mixture of hexane and toluene. Particularly, complexes **2a** and **3a** with cumyl or chloro substituents also possess enough solubility in hydrocarbon solvents, which is in contrast to their analogues with a pendant $–NCH_2CH_2NMe_2$ group in the ligand framework.[48]

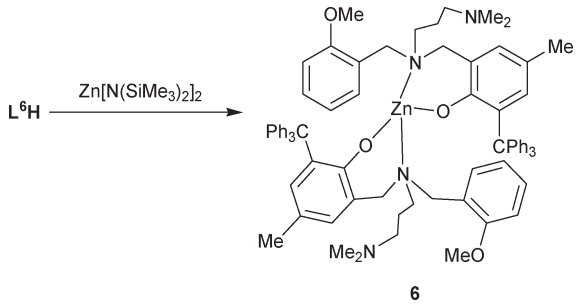
With the expectation that the zinc silylamido complex bearing ligand $\mathbf{L^4}$ might be isolated from the reaction of $Zn[N(SiMe_3)_2]_2$ and the impure $\mathbf{L^4H}$ (containing 1/6 equiv. of 3-*tert*-butyl-2-methoxy-5-methylbenzyl alcohol), a similar amine elimination reaction was carried out. After work-up, the target complex **4a** co-crystallized with another colorless substance **4b**, which was proved to be a product of **4a** with 3-*tert*-butyl-2-methoxy-5-methylbenzyl alcohol (Scheme 4). Tediously fractional



Scheme 1



Scheme 2



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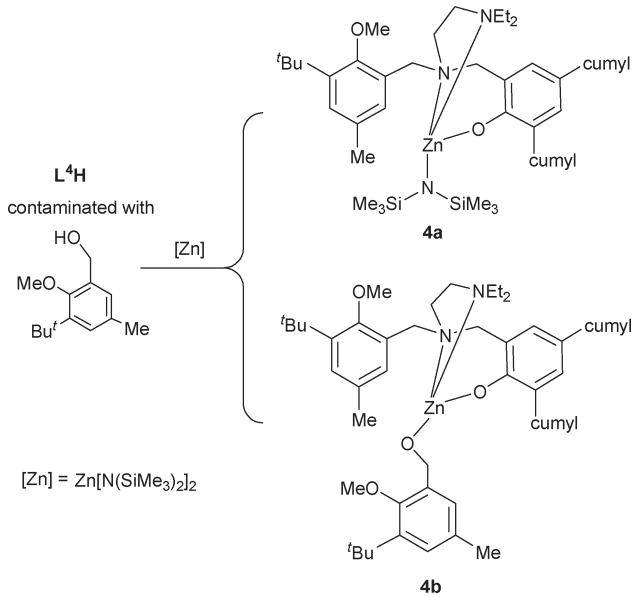
Scheme 3



Scheme 4

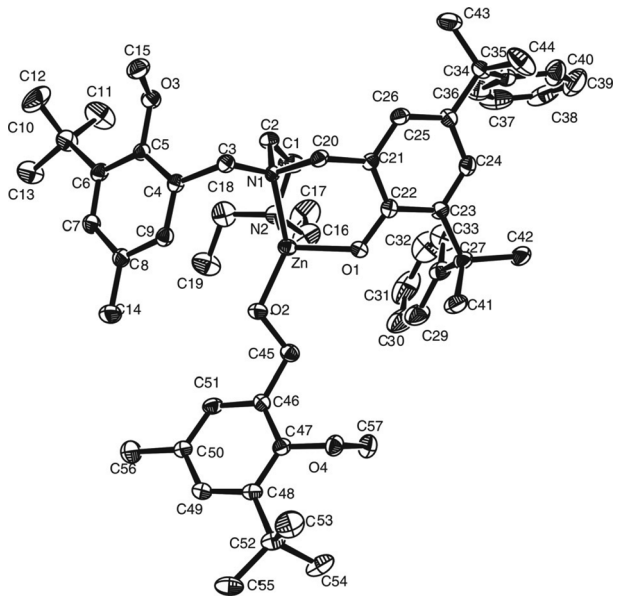
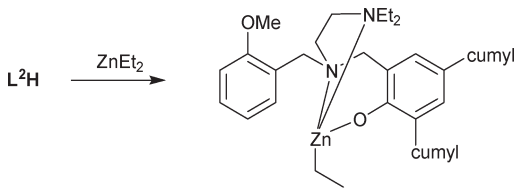
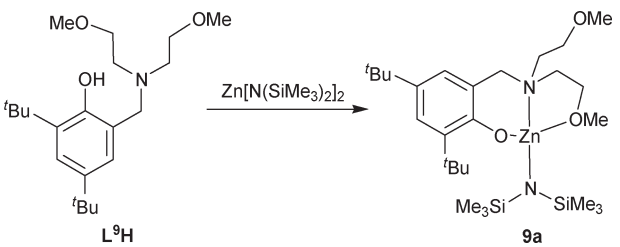


Fig. 1 ORTEP diagram of the molecular structure of complex **4b**. Thermal ellipsoids are drawn at the 20% probability level. Hydrogen atoms are omitted for clarity. Selected bond distances: Zn–O2 1.863 Å, Zn–O1 1.939 Å, Zn···O3 5.263 Å and Zn···O4 5.382 Å, Zn–N1 2.097 Å, Zn–N2 2.109 Å; selected angles: O2–Zn–O1 11.16°, O2–Zn–N1 134.74°, O1–Zn–N1 97.43°, O2–Zn–N2 113.55°, O1–Zn–N2 110.65°, N1–Zn–N2 86.11°.



2c

Scheme 5



Scheme 6

crystallization failed to afford **4a** in pure form, however, from the mother liquor analytically pure complex **4b** could be isolated as cubic colorless crystals, which was further characterized *via* X-ray diffraction study (Fig. 1, *vide post*).

With the aim to own complexes that permit the comparison of the effect of different initiating groups and ligand frameworks on the polymerization process, we further synthesized zinc ethyl complex **2c** *via* the treatment of **L^{2}H** with 1 equiv. of diethyl zinc (Scheme 5), and zinc silylamido complex **9a** bearing a less bulk aminophenolate ligand {–OC_6H_2-4,6-^{t}Bu_2-2-CH_2N[$(CH_2)_2$OMe]$_2$} (**L^{9}H** was prepared according to the literature[67]) *via* the amine elimination route (Scheme 6).

The stoichiometric structures of all the complexes except for complex **6** were confirmed on the basis of ^{1}H and ^{13}C NMR spectroscopy as well as elemental analysis. The very poor solubility of complex **6** either in C_6D_6 or in $CDCl_3$ hampered further structural characterization. Similar to our previous report,[48] in the ^{1}H NMR spectra (C_6D_6) of all the zinc complexes with exclusion of **9a**, the two protons of the methylene group in each Ar-CH_2-N unit are inequivalent and give rise to two doublets as compared to one singlet for the proligand; the proton resonances of the pendant amine arm (both N$(CH_2)_n$N and NCH_2CH_3 moieties) also exhibit unidentifiable coupling modes. All these suggest the participation of all three nitrogen donors in the coordination with the zinc center. While for **9a**, one singlet accounting for two protons of Ar-CH_2-N unit is displayed, and four multiplets with each representing two protons of the two NCH_2CH_2OMe groups were observed, which possibly indicates some fluxional coordination behavior of the two ether arms in solution. The coordination of the aryl-methoxy group to the metal center in complexes **1a–3a**, **5a** and **7a** is excluded based on the slight change of the corresponding chemical shifts of

methoxy protons between complex and proligand. As for complex **8a**, the existence of a weak interaction between the fluorine atom and the zinc center was studied with ^{19}F NMR spectroscopy, however, a chemical-shift difference of 3.48 ppm in ^{19}F NMR (**L^{8}H**, −118.49 ppm *vs.* complex **8a**, −115.01 ppm) might suggest nothing.

Molecular structure of 4b

Single crystals of complex **4b** suitable for X-ray structural determination were obtained from a saturated solution of hexane–toluene mixture at room temperature. An ORTEP drawing of the molecular structure of complex **4b** is given in Fig. 1. Although bearing a substituted benzyloxy group, complex **4b** possesses a monomeric structure in the solid state. The zinc atom is coordinated by three heteroatom donors of the tetradentate ligand and one 3-*tert*-butyl-2-methoxy-5-methylbenzyloxy group adopting a distorted tetrahedral geometry. Similar to the results from Lin,[24] Chisholm[68] and our previous work,[48] both the ether functional groups have no coordination interaction with the zinc center as evidenced by the long distances of Zn···O3 = 5.263 Å and Zn···O4 = 5.382 Å. The bond distances of Zn–N1 and Zn–N2 are 2.097 Å and 2.109 Å respectively, both falling into the range of Zn–N coordinating bond lengths reported for common zinc complexes[29,48,51,69,70] (2.058–2.324 Å), which are however shorter than their silylamido analogues.[48] The angles of O2–Zn–O1 = 111.16(14)°, O2–Zn–N1 = 134.74(15)° and O2–Zn–N2 = 113.55(16)° deviate significantly from the normal value of 109.37°, obviously due to the constrains imposed by the multi-coordination mode of the ligand.

Ring-opening polymerization of *rac*-lactide

Polymerization with zinc silylamido complexes. The ring-opening polymerizations of *rac*-LA employing zinc silylamido complexes **1a–3a**, **5a**, **7a–9a** as initiators were examined systematically. As shown in Table 1, all of the zinc silylamido complexes alone are efficient initiators for the ROP of *rac*-LA either in toluene or in THF at ambient temperature. In each case, high conversion could be reached within hours when the [*rac*-LA]$_0$: [Zn]$_0$ ratio is 200. PLAs with high molecular weighs and narrow to moderate molecular weight distributions (M_w/M_n = 1.07–1.74) could be obtained.

Compared to our previous results,[48] zinc silylamido complexes **1a–3a**, **5a**, **7a** and **8a**, either with a pendant diethylamino group or elongated three-carbon pendant amino arm, display significantly lower catalytic activities for the ROP of *rac*-LA. It takes around 2–8 h for the monomer conversions up to 98%, whereas their analogues with a pendant $NCH_2CH_2NMe_2$ group accomplish the polymerization within 1 h under the identical conditions.[48] For complexes with the same substituents on the phenyl rings, complex **2a** with a pendant $NCH_2CH_2NEt_2$ group is more active than complex **5a** with a pendant $NCH_2CH_2CH_2NMe_2$ group (Table 1, runs 5, 7 *vs.* runs 12, 14), suggesting the prominent influence of the chain length. Such drastic influence of one-carbon-elongation was also observed for other metal complex systems, such as Salen–Al complexes,[71–73] thioalkanediylbisphenolate rare earth metal complexes.[74–77]

Besides, several structure–activity trends similar to our previous results[48] can be drawn from the comparison of the polymerization runs in Table 1. It is found that the catalytic activity obviously decreases when the ^{t}Bu groups on the

Table 1 ROP of *rac*-LA initiated by zinc silylamido complexes[a]

Run	Cat.	[*rac*-LA]$_0$: [Zn]$_0$: [^{i}PrOH]$_0$	Solvent	*T*/°C	*t*/min	Conv.[b] (%)	10^{-4} $M_{n,calcd.}$[c]	10^{-4} M_n[d]	PDI[d]	P_m[e]
1	**1a**	200 : 1 : 0	Tol.	25	150	90	2.59	9.43[f]	1.34[f]	0.61
2		200 : 1 : 1	Tol.	25	45	96	2.77	4.60	1.44	0.61
3		200 : 1 : 0	THF	25	120	92	2.65	6.38	1.39	0.60
4		200 : 1 : 1	THF	25	45	78	2.25	1.89	1.41	0.58
5	**2a**	200 : 1 : 0	Tol.	24	180	95	2.74	9.34	1.55	0.65
6		200 : 1 : 1	Tol.	24	60	98	2.82	4.74	1.46	0.65
7		200 : 1 : 0	THF	25	120	89	2.56	—	—	—
8		200 : 1 : 0	THF	28	75	91	2.62	11.25	1.42	0.65
9		200 : 1 : 1	THF	25	75	95	2.74	6.15	1.42	0.65
10	**3a**	200 : 1 : 0	Tol.	25	120	98	2.82	2.85	1.57	0.51
11		200 : 1 : 1	Tol.	25	30	99	2.85	1.69	1.47	0.53
12	**5a**	200 : 1 : 0	Tol.	25	430	82	2.36	5.13	1.43	0.58
13		200 : 1 : 1	Tol.	25	45	93	2.68	2.49	1.73	0.58
14		200 : 1 : 0	THF	25	300	96	2.77	2.16[f]	2.05[f]	0.58
15		200 : 1 : 1	THF	25	45	83	2.39	1.98[f]	1.69[f]	0.55
16	**7a**	200 : 1 : 0	Tol.	27	480	98	2.82	2.65	1.43	0.63
17		200 : 1 : 1	Tol.	27	45	99	2.85	2.45	1.43	0.61
18		200 : 1 : 0	THF	25	330	96	2.77	1.19[f]	1.42[f]	0.61
19		200 : 1 : 1	THF	25	45	62	1.78	1.10[f]	1.36[f]	0.59
20	**8a**	200 : 1 : 0	Tol.	25	180	83	2.39	4.78	1.48	0.60
21		200 : 1 : 1	Tol.	25	45	99	2.85	2.73	1.54	0.60
22		200 : 1 : 0	THF	24	120	83	2.39	6.95	1.55	0.61
23		200 : 1 : 1	THF	24	45	83	2.39	2.98	1.32	0.61
24	**9a**	200 : 1 : 0	Tol.	25	20	98	2.82	9.37	1.32	0.39
25		200 : 1 : 1	Tol.	25	10	99	2.85	2.55	1.07	0.39

[a] [*rac*-LA]$_0$ = 1.0 M, [Zn]$_0$ = 0.005 M. [b] Determined by ^{1}H NMR spectroscopy. [c] $M_{n,calcd}$ = ([*rac*-LA]$_0$/[Zn]$_0$) × 144.13 × Conv.%. [d] Determined by GPC, Waters M515 pump, 25 °C, 1 mL min^{-1}, PS as standards. [e] P_m is the probability of forming a new *m*-dyad, determined by homonuclear decoupled ^{1}H NMR spectroscopy. [f] Determined by GPC, Waters 1515 pump, 35 °C, 1 mL min^{-1}, PS as standards.

phenoxy unit are replaced by cumyl groups with the rest of the ancillary ligand remaining unchanged (**1a** *vs.* **2a**, Table 1). Namely, bulky substituents of the phenoxy moiety, especially at the *ortho*-position, tend to hinder the approach of a monomer to the central metal and are disadvantageous to the catalytic activity. Introduction of halogens on the ancillary ligand was reported to have an inconsistent influence on the polymerization rate.[50,51] The conclusion drawn from our study is that the catalytic activity will increase when chlorine atoms are substituted at the *ortho*- and *para*-positions of the phenoxy moiety (**3a**, Table 1), which is in accordance with the results of tetradentate Salan– or Salen–Al complexes,[78,79] but conflicts with those of tridentate Schiff-base zinc and magnesium complexes,[50,51] bis(aminophenolato) aluminum complexes,[80] and aminophenolate titanium, zirconium complexes.[81] Substituents on the phenyl ether moiety have a slight influence on the catalytic activity when compared with those on the phenoxy unit. Complex **7a** with *ortho*-^{t}Bu group shows parallel activity to **5a** without any *ortho*-substitution on the phenyl ether moiety.

The particularity of the fluorine atom usually causes compounds to have unpredictable properties, it is also the case for complex **8a** with fluoro instead of methoxy group on one phenyl ring. In comparison with the methoxy analogue **1a**, complex **8a** displays declined activity for the ROP of *rac*-LA either in toluene or THF in the absence of isopropanol (Table 1, runs 1, 3 *vs.* runs 20, 22). Although the interaction of fluoro to the central metal is not conclusive from ^{19}F NMR spectroscopy, fluxional coordination of the fluoro to the zinc center might be suggested to be responsible for the decrease of the activity.[82]

Among these silylamido zinc complexes, complex **9a** indicates the highest activity, and a monomer conversion of up to 98% could be achieved within 10 min in toluene at 25 °C. It is apparent that when less steric hindrance is imposed by the ligand framework the catalytic activity is significantly enhanced.

From the ^{1}H NMR spectra of the resultant polymer samples obtained by these zinc silylamido complexes, no clear end-groups could be distinguished. Whereas, in the ESI-TOF mass spectrum of an oligomer obtained by complex **2a** with [*rac*-LA]$_0$: [Zn]$_0$ = 10 : 1, a series of signals end-capped with N(SiMe$_3$)$_2$ and a hydroxy group do dominant (see Fig. 2), indicative of the initiation with the N(SiMe$_3$)$_2$ group and therefore a coordination–insertion polymerization by a single-site catalyst. Still, the intra- and intermolecular transesterifications are inevitable, as evident from the ESI-TOF mass spectrum.

This series of zinc silylamido complexes give overall elevated isotactic stereoselectivities for the ROP of *rac*-lactide compared to our previous work.[48] Except for complexes **3a** and **9a**, all the complexes produce polylactide with a slightly isotactic bias (P_m = 0.55–0.65). Complex **2a** with sterically demanding cumyl groups shows the highest preference for isotactic dyad enchainment, the P_m value of the polymer sample is up to 0.65 at ambient temperature. Moreover, it is found that the polymerization of L-LA by **2a** proceeds faster than that of *rac*-LA, also implying a sequential insertion preference of lactide monomer with same chirality.

The slight increase in isotactic stereoselectivity promoted us to study complex **2a** in more detail. Polymerization conditions, such as polymerization time, temperature, monomer to initiator ratio, different solvents (toluene, THF, dichloromethane), and so on, were varied to study the influence on the isotactic selectivity of **2a** (see Table S1†). However, no apparent improvement in isotactic selectivity could be observed.

Polymerization with zinc alkoxy complexes. Upon addition of isopropanol, the activities of all zinc silylamido complexes increased significantly. The influence of ligand framework and substituents became less profound and the activities of all complexes were somewhat close to one another, which promoted us to study the real active species. The typical NMR-scale reaction of complex **2a** with isopropanol in 1 : 1 ratio indicated that the zinc isopropoxide complex "L^{2}ZnO^{i}Pr" was generated quantitively (Fig. 3). To acquire some information about the ROP of *rac*-lactide initiated by the *in situ* generated zinc isopropoxide, the NMR-scale polymerization was also conducted with [*rac*-LA]$_0$: [**2a**]$_0$: [^{i}PrOH]$_0$ = 10 : 1 : 1. The polymerization started instantaneously and the active oligomer could be identified unambiguously (Fig. 4), which did not decompose even with the addition of the second equiv. of isopropanol. Small amount of free ligand **L^{2}H** appeared until 7 equiv. of isopropanol was added. The O^{i}Pr group end-capping on the obtained oligomer

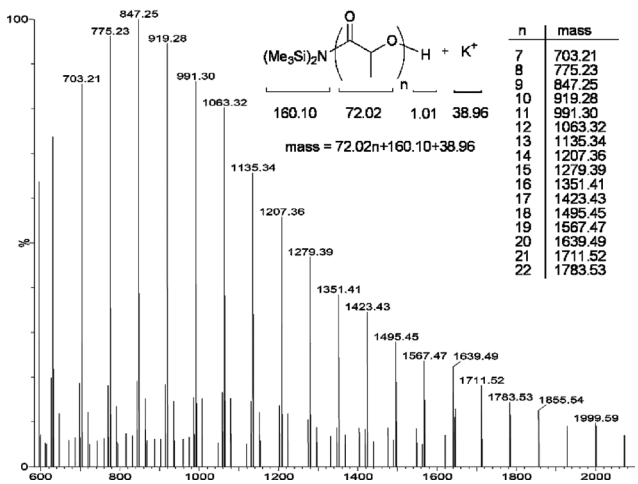


Fig. 2 ESI-TOF mass spectrum of the oligomer of *rac*-LA obtained with **2a** ([*rac*-LA]$_0$: [**2a**]$_0$ = 10 : 1, in toluene).

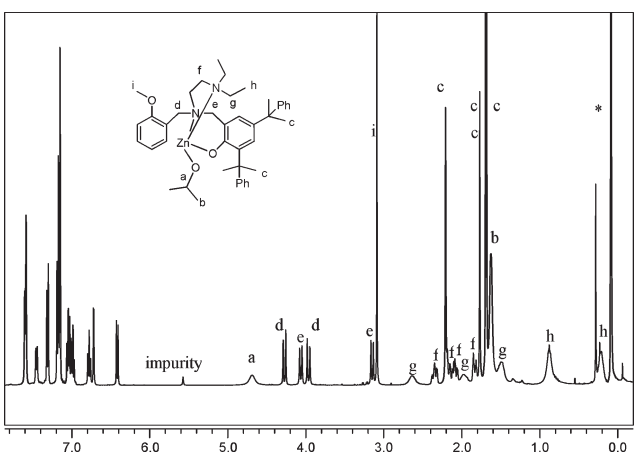


Fig. 3 ^{1}H NMR spectrum (C_6D_6, 400 MHz) of zinc isopropoxide complex generated *in situ* from the reaction of **2a** and isopropanol ([Zn]$_0$: [^{i}PrOH]$_0$ = 10 : 1, at ambient temperature; *, free HN(SiMe$_3$)$_2$).

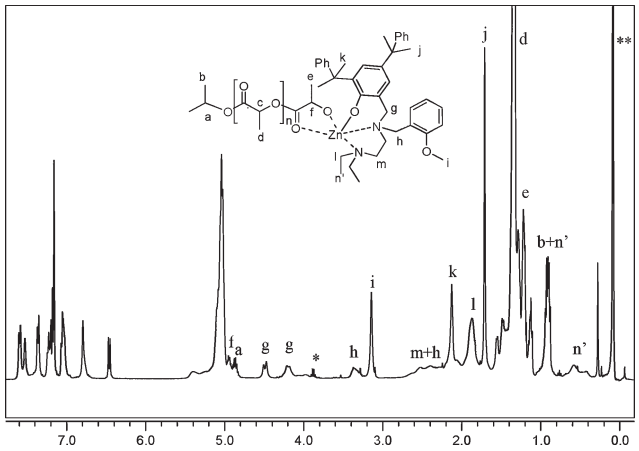


Fig. 4 ^{1}H NMR spectrum (400 MHz, C_6D_6) of active *rac*-lactide oligomer by **2a**/^{i}PrOH ([*rac*-LA]$_0$: [Zn]$_0$: [^{i}PrOH]$_0$ = 10 : 1 : 1, at 25 °C; *, monomer; **, free $HN(SiMe_3)_2$).

could be distinctly observed (See ESI, Fig. S1†). All these suggest that the reaction of zinc silylamido complex with isopropanol *in situ* generates the well-defined zinc isopropoxide complex, which behaves as a single-site initiator for the coordination/insertion polymerization of *rac*-lactide.

Without the addition of isopropanol, zinc ethyl complex **2c** could hardly initiate the ROP of *rac*-LA at ambient temperature (Table 2). Even in the presence of isopropanol, it still took more than 48 h for complex **2c** to gain high monomer conversion up to 96%. From our previous study,[48] it is known that at ambient temperature the reaction of such zinc ethyl complex with alcohol is unexpectedly slow. Thus, polymerization of *rac*-lactide at elevated temperature of 60 °C was conducted. To our surprise, either in the presence or in the absence of isopropanol, complex **2c** shows sufficient catalytic activity for the ROP of *rac*-LA, which is in contrast to our previous results. High monomer conversions could be achieved within relatively short periods (Table 2, runs 3 and 4).

Benzyloxy complex **4b**, although possessing bulky groups on both phenyl moieties, displays higher activity than zinc silylamido complex **2a** with a similar ligand framework. As depicted in Fig. 5, when the monomer conversions are lower than 89%, a linear relationship of molecular weight *versus* monomer conversion could be obtained by complex **4b** alone, and the resultant PLA samples have relatively low PDI = 1.14–1.31, suggesting a well-controlled polymerization process by **4b**. The ^{1}H NMR spectra of oligomer samples obtained by **4b** show that the polymers are systematically end-capped with 3-*tert*-butyl- 2-methoxy-5-methylbenzyloxy group and a hydroxy group (See ESI, Fig. S3†), giving evidence that the benzyloxy group in **4b** acts as an efficient initiating group for the polymerization of lactide. In the presence of isopropanol, the polymerization rate by **4b** keeps constant, and the polymerization affords PLA with nearly half of the theoretical molecular weight. Both end groups of O^{i}Pr and substituted benzyloxy could be identified in the ^{1}H NMR spectra of the polymer samples (See ESI, Fig. S3†). Obviously, the excess isopropanol acts as a chain transfer reagent instead.

The bis-ligated complex **6** shows neglectable catalytic activity for the polymerization of *rac*-lactide even in the presence of isopropanol with the polymerization time extended to 4 days. As general observed, the aroxy group is not nucleophilic enough to initiate the ring-opening polymerization of cyclic esters.

From Tables 1 and 2, it is further concluded that the initiating group has no essential influence on the stereoselectivity of the corresponding zinc complex. In most of the cases, the isotacticity of the resultant polymer is unchanged regardless of the presence or absence of isopropanol. The slight deviation of P_m values in some cases is mainly due to the transesterification during the polymerization process, which becomes significant in the case of complex **2c** due to the quite low polymerization rate.

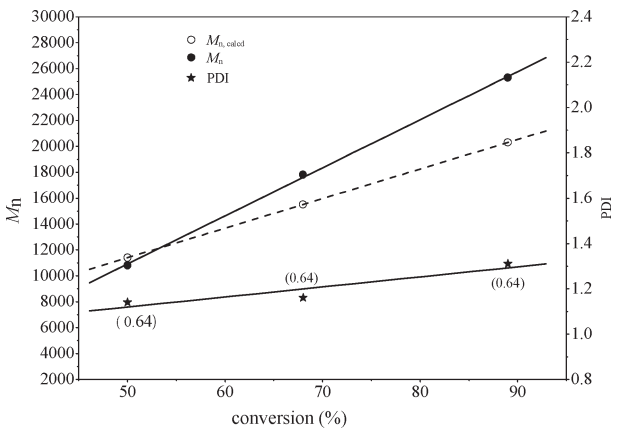


Fig. 5 The relationship of M_n, PDI of PLA sample *versus* monomer conversion catalyzed by complex **4b** ([*rac*-LA]$_0$ = 0.79 M, [*rac*-LA]$_0$: [**4b**]$_0$ = 158 : 1, 24 °C, in toluene; with P_m values in parentheses).

Table 2 ROP of *rac*-LA catalyzed by zinc complexes **2c** and **4b**[a]

Run	Cat.	[*rac*-LA]$_0$: [Zn]$_0$: [^{i}PrOH]$_0$	*T*/°C	*t*/h	Conv.[b] (%)	10^{-4} $M_{n,calcd.}$[c]	10^{-4} M_n[d]	PDI[d]	P_m[e]
1	**2c**	200 : 1 : 0	26	72	10	0.29	—	—	—
2		200 : 1 : 1	26	48	96	2.77	2.47	1.36	0.59
3		200 : 1 : 0	60	72	92	2.65	7.23[f]	1.39[f]	0.61
4		200 : 1 : 1	60	12	90	2.59	4.20	1.35	0.61
5	**4b**	200 : 1 : 0	25	0.75	92	2.65	4.09	1.39	0.62
6		200 : 1 : 1	25	0.75	90	1.29	1.02	1.11	0.62

[a] [*rac*-LA]$_0$ = 1 M, [Zn]$_0$ = 0.005 M. [b] Determined by ^{1}H NMR spectroscopy. [c] $M_{n,calcd}$ = ([*rac*-LA]$_0$/[Zn]$_0$) × 144.13 × Conv.%. [d] Determined by GPC, Waters M515 pump, 25 °C, 1 mL min^{-1}, PS as standards. [e] P_m is the probability of forming a new *m*-dyad, determined by homonuclear decoupled ^{1}H NMR spectroscopy. [f] Determined by GPC, Waters 1515 pump, 35 °C, 1 mL min^{-1}, PS as standards.

Conclusions

A series of zinc silylamido complexes, zinc ethyl complex and zinc benzyloxy complex, ligated with claw-type multidentate aminophenolate ligand were obtained and evaluated for the ROP of *rac*-lactide. All of the zinc silylamido complexes efficiently initiated the ROP of *rac*-LA at ambient temperature, with the initiating group $N(SiMe_3)_2$ end-capping the polymer chain as evidenced in the ESI-TOF mass spectrum. The introduction of bulky *ortho*-substituents on the phenoxy ring resulted in an apparent decrease of the catalytic activity while a slightly enhanced isotactic selectivity (P_m up to 0.65 at ambient temperature). Replacement of the dimethylamino group with a diethylamino group and introduction of a longer pendant amine arm both led to a dramatic decline of the catalytic activity in the absence of isopropanol. Benzyloxy complex **4b** alone could initiate a well-controlled polymerization (conv. < 89%), whereas the zinc ethyl complex **2c** was not so efficient as the silylamido or alkoxy analogues, showed low activity for lactide polymerization even in the presence of isopropanol at room temperature, but proved to be more active at elevated temperature.

Experimental

General considerations and materials

All manipulations were carried out under a dry argon atmosphere using standard Schlenk-line or glove-box techniques. Toluene, petroleum ether and *n*-hexane were refluxed over sodium benzophenone ketyl prior to use. Benzene-d_6, chloroform-*d* and other reagents were carefully dried and stored in glove-box. Zn $[N(SiMe_3)_2]_2$,[83] 3-*tert*-butyl-5-methyl-2-methoxybenzaldehyde[84] and 4,6-di(*tert*-butyl)-2-[*N*,*N*-di(2-methoxyethyl)aminomethyl] phenol ($\mathbf{L^9H}$)[67] were prepared according to the literature methods. *rac*-Lactide (Aldrich) was sublimed twice under vacuum at 80 °C. Isopropanol was dried over calcium hydride prior to distillation. All other chemicals were commercially available and used after appropriate purification. Glassware and vials used in the polymerization were dried in an oven at 120 °C overnight and exposed to a vacuum–argon cycle three times.

NMR spectra were recorded on Bruker AVANCE-400 and Bruker AVANCE-500 spectrometers at 25 °C (^{1}H: 400, 500 MHz; ^{13}C: 100 MHz) unless otherwise stated. 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. Spectroscopic analyses of polymers were performed in $CDCl_3$. Gel permeation chromatography (GPC) analyses were carried out on a Waters instrument (M515 pump, Optilab Rex injector) in THF at 25 °C, or a Waters instrument (1515 pump, Waters 2414 RI) in THF at 35 °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}).

Synthesis of proligands

4,6-Di-*tert*-butyl-2-{*N*-(2-methoxybenzyl)-*N*-[2-(*N*′,*N*′-diethyl amino)ethyl]aminomethyl}-phenol ($\mathbf{L^1H}$). The solution of *N*,*N*-diethylethane-1,2-diamine (2.32 g, 20.0 mmol) and 2-methoxybenzaldehyde (2.72 g, 20.0 mmol) in methanol (20 mL) were heated to reflux for 24 h. After cooling to room temperature, sodium borohydride (1.51 g, 40.0 mmol) was added slowly to the above yellow solution and the resultant mixture was stirred for another 3 h at 50 °C. The reaction mixture was extracted with methylene dichloride, and the combined organic phase was dried over anhydrous $MgSO_4$. After removal of the solvent by rotary evaporation, a viscous yellow oil was obtained, to which was added the solution of paraformaldehyde (0.72 g, 24 mmol) and 2,4-di-*tert*-butylphenol (4.13 g, 20.0 mmol) in methanol (20 mL), and then stirred at 80 °C for 12 h. The mixture was cooled and concentrated under vacuum to give an oil, which was purified by column chromatography (silica gel 100 mesh, petroleum ether/ethyl acetate = 4 : 1) to afford a light yellow oil after removal of all the volatiles (4.78 g, 52.6%). Found: C, 76.51; H, 10.26; N, 6.10. Calc. for $C_{29}H_{46}N_2O_2$: C, 76.60; H, 10.20; N, 6.16%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.76 (br, 1H, O*H*), 7.28 (d, 2H, J = 7.2 Hz, Ar*H*), 7.21 (d, 1H, J = 2.4 Hz, Ar*H*), 6.96–6.87 (m, 3H, Ar*H*), 3.90 (s, 3H, OCH_3), 3.79 (s, 2H, Ar–CH_2N), 3.75 (s, 2H, NCH_2–Ar), 2.63–2.58 (m, 2H, NCH_2CH_2N), 2.54–2.50 (m, 2H, NCH_2CH_2N), 2.39 (q, 4H, J = 7.2 Hz, NCH_2CH_3), 1.46 (s, 9H, C(CH_3)$_3$), 1.31 (s, 9H, C(CH_3)$_3$), 0.91 (t, 6H, J = 7.2 Hz, NCH$_2CH_3$); ^{13}C NMR (100 MHz, $CDCl_3$): 158.3, 154.4, 140.2, 135.6, 131.6, 128.9, 126.0, 123.8, 122.8, 122.2, 120.4, 110.5 (all Ar*C*), 59.0 (OCH_3), 55.3 (N–CH_2–Ar), 53.9 (Ar–CH_2–N), 50.8 (NCH_2CH_2N), 50.1 (NCH$_2CH_2$N), 47.4 (NCH_2CH_3), 35.0 (*C*(CH_3)$_3$), 34.2 (*C*(CH_3)$_3$), 31.8 (C(CH_3)$_3$), 29.7 (C(CH_3)$_3$), 11.6 (NCH$_2CH_3$).

4,6-Dicumyl-2-{*N*-(2-methoxybenzyl)-*N*-[2-(*N*′,*N*′-diethyl amino) ethyl]aminomethyl}-phenol ($\mathbf{L^2H}$). The procedure was same as that of $\mathbf{L^1H}$, except that 2,4-dicumylphenol (6.61 g, 20.0 mmol) was used to afford ligand $\mathbf{L^2H}$ as a light yellow oil (6.14 g, 53.0%). Found: C, 80.91; H, 8.76; N, 4.75. Calc. for $C_{39}H_{50}N_2O_2$: C, 80.93; H, 8.71; N, 4.84%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.36 (s, 1H, O*H*), 7.29 (m, 4H, Ar*H*), 7.25–7.17 (m, 7H, Ar*H*), 7.15–7.12 (m, 1H, Ar*H*), 6.58 (d, 1H, J = 7.6 Hz, Ar*H*), 6.84–6.78 (m, 3H, Ar*H*), 3.68 (s, 3H, OCH_3), 3.63 (s, 2H, Ar–CH_2N), 3.59 (s, 2H, NCH_2–Ar), 2.45 (m, 2H, NCH_2CH_2N), 2.30 (m, 6H, NCH_2CH_2N, NCH_2CH_3), 1.71 (s, 6H, C(CH_3)$_2$Ph), 1.70 (s, 6H, C(CH_3)$_2$Ph), 0.84 (t, 6H, J = 6.8 Hz, NCH$_2CH_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.0, 155.1, 152.9, 152.6,140.4, 139.4, 132.6, 129.3, 128.6, 127.8, 127.3, 127.2, 126.9, 126.4, 125.5, 125.4, 124.0, 121.3, 111.1 (all Ar*C*), 58.5 (*C*H$_3$O–Ar), 55.4 (Ar–*C*H$_2$N), 53.7 (N*C*H$_2$–Ar), 51.5 (N*C*H$_2$CH$_2$N), 51.0 (NCH$_2$*C*H$_2$N), 47.6 (N*C*H$_2$CH$_3$), 43.4 (*C*(CH_3)$_2$Ph), 43.1 (*C*(CH_3)$_2$Ph), 32.1 (C(*C*H$_3$)$_2$Ph), 30.4 (C(*C*H$_3$)$_2$Ph), 12.5 (NCH$_2$*C*H$_3$).

4,6-Dichloro-2-{*N*-(2-methoxybenzyl)-*N*-[2-(*N*′,*N*′-diethyl amino) ethyl]aminomethyl}-phenol ($\mathbf{L^3H}$). The procedure was same as that of $\mathbf{L^1H}$, except that 2,4-dichlorophenol (3.26 g, 20.0 mmol) was used to afford ligand $\mathbf{L^3H}$ as a white solid (3.32 g, 40.4%). Found: C, 61.34; H, 6.80; N, 6.71. Calc. for $C_{21}H_{28}Cl_2N_2O_2$: C, 61.31; H, 6.86; N, 6.81%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.22–7.24 (m, 2H, Ar*H*), 7.17 (d, 1H, J = 7.2 Hz, Ar*H*), 6.86–6.84 (m, 2H, Ar*H*), 6.83 (d,1H, J = 8.0 Hz, Ar*H*), 3.79 (s, 3H, OCH_3), 3.68 (s, 2H, Ar–CH_2N), 3.63 (s, 2H,

NCH_2–Ar), 2.58 (*quasi* s, 4H, NCH_2CH_2N), 2.30 (q, 4H, J = 7.2 Hz, NCH_2CH$_3$), 0.95 (t, 6H, J = 7.2 Hz, NCH$_2$CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.2, 153.1, 131.6, 129.2, 128.5, 127.5, 125.9, 125.1, 122.6, 121.7, 120.3, 110.5 (all Ar*C*), 56.4 (*C*H$_3$O–Ar), 55.2 (Ar–*C*H$_2$N), 53.3 (N*C*H$_2$–Ar), 50.4 (N*C*H$_2$CH$_2$N), 49.7 (NCH$_2$*C*H$_2$N), 46.5(N*C*H$_2$CH$_3$), 11.1 (NCH$_2$*C*H$_3$).

4,6-Dicumyl-2-{*N*-(3-*tert*-butyl-2-methoxy-5-methylbenzyl)-*N*-[2-(*N*′,*N*′-diethylamino)ethyl]aminomethyl}-phenol (L^{4}H). The procedure was same as that of **L^{1}H**, except that 3-*tert*-butyl-2-methoxy-5-methylbenzaldehyde (4.13 g, 20.0 mmol) was used in the first step and 2,4-dicumylphenol (6.61 g, 20.0 mmol) was used in the last step to afford ligand **L^{4}H** as a light yellow oil: in pure form (~20 mg), as a mixture of **L^{4}H** and 1/6 equiv. of 3-*tert*-butyl-2-methoxy-5-methylbenzyl alcohol (4.70 g, 36.2%). For the pure **L^{4}H**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.18 (s, 1H, O*H*), 7.26–7.24 (m, 4H, Ar*H*), 7.23–7.20 (m, 4H, Ar*H*), 7.18 (s, 1H, Ar*H*), 7.16–7.14 (m, 1H, Ar*H*), 7.07 (t, 1H, J = 6.8 Hz, Ar*H*), 6.96 (s, 1H, Ar*H*), 6.81 (s, 1H, Ar*H*), 6.78 (s, 1H, Ar*H*), 3.57 (s, 3H, OCH_3), 3.53 (s, 2H, Ar–CH_2N), 3.50 (s, 2H, NCH_2–Ar), 2.36 (br s, 4H, NCH_2CH_2N), 2.25 (q, 4H, J = 7.2 Hz, NCH_2CH$_3$), 2.18 (s, 3H, Ar–CH_3), 1.69 (s, 6H, C(CH_3)$_2$Ph), 1.68 (s, 6H, C(CH_3)$_2$Ph), 1.35 (s, 9H, C(CH_3)$_3$), 0.81 (t, 6H, J = 7.2 Hz, NCH$_2$CH_3).

4,6-Dicumyl-2-{*N*-(2-methoxybenzyl)-*N*-[3-(*N*′,*N*′-dimethyl amino)propyl]aminomethyl}-phenol (L^{5}H). The procedure was same as that of **L^{1}H**, except that 2,4-dicumylphenol (6.61 g, 20.0 mmol) and *N*,*N*-dimethylpropane-1,3-diamine (3.06 g, 30.0 mmol) were used to afford ligand **L^{5}H** as a light yellow oil (3.61 g, 32.5%). Found: C, 81.04; H, 8.61; N, 4.95. Calc. for $C_{38}H_{48}N_2O_2$: C, 80.81; H, 8.57; N, 4.96%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27–7.26 (m, 4H, Ar*H*), 7.22–7.15 (m, 7H, Ar*H*), 7.12–7.09 (m, 1H, Ar*H*), 6.91 (dd, 1H, J = 7.6, 1.6 Hz, Ar*H*), 6.80–6.77 (m, 2H, Ar*H*), 6.70 (d, 1H, J = 2.0 Hz, Ar*H*), 3.65 (s, 3H, Ar–OCH_3), 3.59 (s, 2H, Ar–CH_2N), 3.54 (s, 2H, Ar–CH_2N), 2.33 (t, 2H, J = 6.0 Hz, NCH_2CH$_2$CH$_2$N), 2.10 (s, 6H, N(CH_3)$_2$), 2.04 (t, 2H, J = 6.0 Hz, NCH$_2$CH$_2$CH_2N), 1.67 (s, 6H, C(CH_3)$_2$Ph), 1.64 (s, 6H, C(CH_3)$_2$Ph), 1.50 (quintet, 2H, J = 6.0 Hz, NCH$_2$CH_2CH$_2$N); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.2, 154.0, 151.8, 151.6, 139.6, 135.1, 131.8, 128.9, 127.9, 127.7, 126.9, 125.8, 125.6, 125.4, 124.7, 122.0, 120.4, 110.4 (all Ar*C*), 58.5 (*C*H$_3$O–Ar), 57.7 (Ar–*C*H$_2$N), 55.2 (N*C*H$_2$–Ar), 52.7 (N*C*H$_2$CH$_2$CH$_2$N), 51.2 (NCH$_2$CH$_2$*C*H$_2$N), 45.5 (N(*C*H$_3$)$_2$), 42.6 (*C*(CH$_3$)$_2$Ph), 42.1 (*C*(CH$_3$)$_2$Ph), 31.3 (C(*C*H$_3$)$_2$Ph), 29.6 (C(*C*H$_3$)$_2$Ph), 24.2 (NCH$_2$*C*H$_2$CH$_2$N).

2-{*N*-(2-Methoxybenzyl)-*N*-[3-(*N*′,*N*′-dimethylamino)propyl] aminomethyl}-4-methyl-6-tritylphenol (L^{6}H). The procedure was same as that of **L^{1}H**, except that *N*,*N*-dimethylpropane-1,3-diamine (3.06 g, 30.0 mmol) and 4-methyl-2-tritylphenol (7.01 g, 20.0 mmol) were used to afford ligand **L^{6}H** as a white solid (5.27 g, 45.1%). Found: C, 81.85; H, 7.60; N, 4.73. Calc. for $C_{40}H_{44}N_2O_2$: C, 82.15; H, 7.58; N, 4.79%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.20–7.18 (m, 9H, Ar*H*), 7.16–7.14 (m, 4H, Ar*H*), 7.12–7.10 (m, 3H, Ar*H*), 6.85–6.73 (m, 5H, Ar*H*), 3.63 (s, 2H, Ar–CH_2N), 3.54 (s, 3H, Ar–OCH_3), 3.50 (s, 2H, Ar–CH_2N), 2.29 (t, 2H, J = 6.0 Hz, NCH_2CH$_2$CH$_2$N), 2.14 (s, 3H, Ar–CH_3), 2.12 (s, 6H, N(CH_3)$_2$), 2.02 (t, 2H, J = 6.0 Hz, NCH$_2$CH$_2$CH_2N), 1.47 (quintet, 2H, J = 6.0 Hz, NCH$_2$CH_2CH$_2$N). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.1, 154.3, 146.3, 133.6, 131.6, 131.3, 130.6, 128.8, 128.6, 127.0, 126.3, 125.3, 125.2, 122.5, 120.5, 110.3 (all Ar*C*), 63.3 (*C*Ph$_3$), 58.2 (Ar–OCH_3), 57.5 (Ar–*C*H$_2$), 55.1 (Ar–*C*H$_2$), 52.3 (N*C*H$_2$CH$_2$CH$_2$N), 51.0 (NCH$_2$CH$_2$*C*H$_2$N), 45.3 (N*C*H$_3$), 23.8 (NCH$_2$*C*H$_2$CH$_2$N), 21.0 (Ar–*C*H$_3$).

4,6-Dicumyl-2-{*N*-(3-*tert*-butyl-2-methoxy-5-methylbenzyl)-*N*-[3-(*N*′,*N*′-dimethylamino)propyl]aminomethyl}-phenol (L^{7}H). The procedure was same as that of **L^{1}H**, except that 3-*tert*-butyl-2-methoxy-5-methylbenzaldehyde (4.34 g, 20.0 mmol), 2,4-dicumylphenol (6.61 g, 20.0 mmol) and *N*,*N*-dimethylpropane-1,3-diamine (3.06 g, 30.0 mmol) were used to afford ligand **L^{7}H** as a light yellow oil (6.41 g, 48.2%). Found: C, 81.10; H, 9.76; N, 4.17. Calc. for $C_{43}H_{58}N_2O_2$: C, 81.34; H, 9.21; N,4.41%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25 (s, 2H, Ar*H*), δ 7.24 (s, 2H, Ar*H*), 7.19–7.17 (m, 5H, Ar*H*), 7.15–7.12 (m, 1H, Ar*H*), 7.09–7.04 (m, 1H, Ar*H*), 6.96 (d, 1H, J = 2.0 Hz, Ar*H*), 6.75 (d, 1H, J = 2.0 Hz, Ar*H*), 6.74 (d, 1H, J = 2.4 Hz, Ar*H*), 3.59 (s, 2H, Ar–CH_2N), 3.58 (s, 3H, Ar–OCH_3) 3.51 (s, 2H, Ar–CH_2N), 2.28 (t, 2H, J = 6.0 Hz, NCH_2CH$_2$CH$_2$N), 2.16 (s, 3H, Ar–CH_3), 2.08 (s, 6H, N(CH_3)$_2$), 2.02 (t, 2H, J = 6.0 Hz, NCH$_2$CH$_2$CH_2N), 1.66 (s, 12H, C(CH_3)$_2$Ph), 1.52 (quintet, 2H, J = 6.0 Hz, NCH$_2$CH_2CH$_2$N), 1.33 (s, 9H, C(CH_3)$_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.8, 154.0, 151.6, 151.5,142.4, 139.8, 135.1, 132.8, 130.5, 129.8, 127.8, 128.0, 127.7, 126.9, 125.9, 125.8, 125.5, 125.0, 124.9, 122.0 (all Ar*C*), 62.5 (ArOCH_3), 58.6 (Ar–*C*H$_2$N), 57.6 (Ar–*C*H$_2$N), 51.6 (N*C*H$_2$CH$_2$CH$_2$N), 51.1 (NCH$_2$CH$_2$*C*H$_2$N), 45.3 (N*C*H$_3$), 42.4 (*C*(CH$_3$)$_2$Ph), 42.1 (*C*(CH$_3$)$_2$Ph), 34.9 (*C*(CH$_3$)$_3$), 31.1 (C(*C*H$_3$)$_3$), 29.5 (C(*C*H$_3$)$_2$Ph), 23.7 (NCH$_2$*C*H$_2$CH$_2$N), 21.1 (Ar–*C*H$_3$).

4,6-Di-*tert*-butyl-2-{*N*-(2-fluorobenzyl)-*N*-[2-(*N*′,*N*′-diethyl amino)ethyl]aminomethyl}-phenol (L^{8}H). The procedure was same as that of **L^{1}H**, except that 2-fluorobenzaldehyde (2.48 g, 20.0 mmol) was added in the first step and 2,4-*tert*-butylphenol (6.61 g, 20.0 mmol) was used in the last step to afford ligand **L^{8}H** as a light yellow oil (3.16 g, 35.7%). Found: C, 75.93; H, 9.70; N, 6.15. Calc. for $C_{28}H_{43}FN_2O$: C, 75.97; H, 9.79; N, 6.33%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.41 (br, 1H, O*H*), 7.33 (t, 1H, J = 7.2 Hz, Ar*H*), 7.26–7.20 (m, 2H, Ar*H*), 7.09 (t, 1H, J = 7.2 Hz, Ar*H*), 7.02 (t, 1H, J = 9.2 Hz, Ar*H*), 6.89 (d, 1H, J = 2.4 Hz, Ar*H*), 3.77 (s, 2H, Ar-CH_2N), 3.69 (s, 2H, NCH_2-Ar), 2.59 (s, 4H, NCH_2CH_2N), 2.41 (q, 4H, J = 7.2 Hz, NCH_2CH$_3$), 1.46 (s, 9H, C(CH_3)$_3$), 1.30 (s, 9H, C(CH_3)$_3$), 0.95 (t, 6H, J = 7.2 Hz, NCH$_2$CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): 161.6 (d, J_{FC} = 244.7 Hz), 154.1, 140.4, 135.8, 132.2 (d, J_{FC} = 4.2 Hz), 129.2 (d, J_{FC} = 8.2 Hz), 124.9 (d, J_{FC} = 4.2 Hz), 124.2, 124.1 (d, J_{FC} = 3.5 Hz), 123.1, 121.9, 115.3 (d, J_{FC} = 22.3 Hz) (all Ar*C*), 58.2 (Ar–*C*H$_2$N), 51.0 (N*C*H$_2$–Ar), 50.7 (N*C*H$_2$CH$_2$N), 50.2 (NCH$_2$*C*H$_2$N), 46.9 (N*C*H$_2$CH$_3$), 35.1 (*C*(CH$_3$)$_3$), 34.2 (C(*C*H$_3$)$_3$), 31.8 (C(*C*H$_3$)$_3$), 29.7 (C(*C*H$_3$)$_3$), 11.6 (NCH$_2$*C*H$_3$). ^{19}F NMR (376 MHz, C_6D_6): −118.49.

Synthesis of zinc complexes

[(L^1)ZnN(SiMe$_3$)$_2$] (1a). The ligand **L^{1}H** (0.455 g, 1.00 mmol) was added slowly to a solution of Zn[N(SiMe$_3$)$_2$]$_2$

(0.385 g, 1.00 mmol) in light petroleum ether (20 mL). The solution was stirred at room temperature for 24 h and filtered. All the volatiles of the clear light yellow filtrate were removed to give a foam-like matter, which was further dried under vacuum for half an hour and then dissolved with the proper amount of hexane and kept at −40 °C to give colorless crystals (413 mg, 60.8%). Found: C, 61.94; H, 9.31; N, 6.20. Calc. for $C_{35}H_{63}N_3O_2Si_2Zn$: C, 61.87; H, 9.35; N, 6.18%. ^{1}H NMR (400 MHz, C_6D_6): δ 7.56 (s, 1H, Ar*H*), 7.07 (t, 1H, J = 8.0 Hz, Ar*H*), 6.98 (d, 1H, J = 7.2 Hz, Ar*H*), 6.77 (t, 1H, J = 7.2 Hz, Ar*H*), 6.73 (d, J = 2.0 Hz, 1H, Ar*H*), 6.46 (d, 1H, J = 8.0 Hz, Ar*H*), 4.54 (d, 1H, J = 14.0 Hz, Ar–CH_2N), 4.32 (d, 1H, J = 12.0 Hz, Ar–CH_2N), 4.18 (d, 1H, J = 14.0 Hz, NCH_2–Ar), 3.43 (d, 1H, J = 12.0 Hz, NCH_2–Ar), 3.15 (s, 3H, OCH_3), 2.62–2.41 (m, 7H, NCH_2CH_2N, NCH_2CH$_3$), 2.12–2.08 (m, 1H, NCH_2CH$_3$), 1.80 (s, 9H, C(CH_3)$_3$), 1.29 (s, 9H, C(CH_3)$_3$), 0.42–0.81 (br m, 6H, NCH$_2$CH_3), 0.59 (s, 18H, N(Si(CH_3)$_3$)$_2$); ^{13}C NMR (100 MHz, C_6D_6): δ 165.4, 159.0, 138.0, 134.7, 134.4, 130.4, 126.6, 124.8, 121.0, 120.7, 111.4 (all Ar*C*), 60.5 (*C*H$_3$OAr), 55.0 (Ar–*C*H$_2$N), 53.5 (N*C*H$_2$–Ar), 50.1 (N*C*H$_2$CH$_2$N), 45.6 (NCH$_2$*C*H$_2$N), 36.0 (N*C*H$_2$CH$_3$), 34.1 (*C*(CH$_3$)$_3$), 32.2 (*C*(CH$_3$)$_3$), 30.6 (C(*C*H$_3$)$_3$), 23.1 (N(CH$_2$*C*H$_3$)$_2$), 7.5 (N(Si(CH$_3$)$_3$)$_2$).

[(L^2)ZnN(SiMe$_3$)$_2$] (2a). Following a procedure similar to that described for **1a**, **L^{2}H** (0.579 g, 1.00 mmol) was treated with Zn [N(SiMe$_3$)$_2$]$_2$ (0.385 g, 1.00 mmol) in toluene (20 mL) at room temperature to obtain a foam-like matter. Recrystallization with a solvent mixture of hexane and toluene afforded colorless needle-like crystals (455 mg, 56.6%). Found: C, 67.50; H, 8.26; N, 4.93. Calc. for $C_{45}H_{67}N_3O_2Si_2Zn$: C, 67.26; H, 8.40; N, 5.23%. ^{1}H NMR (400 MHz, C_6D_6): δ 7.58 (d, 2H, J = 7.6 Hz, Ar*H*), 7.57 (s, 1H, Ar*H*), 7.25 (dd, 2H, J = 7.6, 0.8 Hz, Ar*H*), 7.20–7.16 (m, 2H, Ar*H*), 7.14–7.12 (m, 2H, Ar*H*), 7.04–6.98 (m, 3H, Ar*H*), 6.84 (dd, 1H, J = 7.6, 0.8 Hz, Ar*H*), 6.71–6.67 (m, 2H, Ar*H*), 6.39 (d, 1H, J = 8.4 Hz, Ar*H*), 4.47 (d, 1H, J = 14.0 Hz, Ar–CH_2N), 4.24 (d, 1H, J = 12.4 Hz, NCH_2–Ar), 4.08 (d, 1H, J = 14.0 Hz, Ar–CH_2N), 3.36 (d, 1H, J = 12.4 Hz, NCH_2–Ar), 3.08 (s, 3H, OCH_3), 2.45–2.40 (m, 2H, NCH_2CH_2N), 2.20 (s, 3H, C(CH_3)$_2$Ph), 2.31–2.16 (m, 2H, NCH_2CH_2N), 2.10–1.80 (m, 2H, NCH_2CH$_3$), 1.79–1.71 (m, 5H, C(CH_3)$_2$Ph, NCH_2CH$_3$), 1.66 (s, 3H, C(CH_3)$_2$Ph), 1.60 (s, 3H, C(CH_3)$_2$Ph), 0.70–0.32 (br, 6H, NCH$_2$CH_3), 0.53 (s, 18H, N(Si(CH$_3$)$_3$)$_2$, overlapped with the signal of NCH$_2$CH_3); ^{13}C NMR (100 MHz, C_6D_6): δ 165.4, 158.9, 153.0, 152.2, 137.5, 134.4, 133.4, 130.3, 129.0, 128.2, 127.9, 127.3, 127.1, 125.5, 124.5, 120.9, 120.6, 120.5, 111.3 (all Ar*C*), 60.2 (*C*H$_3$O–Ar), 54.9 (Ar–*C*H$_2$N), 52.9 (N*C*H$_2$–Ar), 49.7 (N*C*H$_2$CH$_2$N), 44.2 (NCH$_2$*C*H$_2$N), 42.8 (N(*C*H$_2$CH$_3$)), 42.3 (*C*(CH$_3$)$_2$Ph), 34.1 (*C*(CH$_3$)$_2$Ph), 31.4 (C(*C*H$_3$)$_2$Ph), 31.3 (C(*C*H$_3$)$_2$Ph), 26.6 (N(CH$_2$*C*H$_3$)), 7.5 (N(Si(CH$_3$)$_3$)$_2$).

[(L^2)ZnEt] (2c). The ligand **L^{2}H** (0.579 g, 1.00 mmol) was dissolved in toluene (20 mL), to this solution was added diethyl zinc (1.00 mL, 1.00 mmol, 1 M in hexane). The resultant light yellow mixture was stirred for 24 h at room temperature. Evaporation of all the volatiles *in vacuo* afforded white solids, which were further dried under vacuum for several hours. The solids were then recrystallized with hexane and kept at −39 °C to give colorless crystals (571 mg, 81.2%). Found: C, 73.25; H, 8.10; N, 4.17. Calc. for $C_{41}H_{54}N_2O_2Zn\cdot(3/8\ C_6H_{14})$: C, 73.72; H, 8.48; N, 3.98%. ^{1}H NMR (400 MHz, C_6D_6): δ 7.63–7.60 (m, 3H, Ar*H*), 7.39 (d, 2H, J = 7.2 Hz, Ar*H*), 7.21–7.18 (m, 4H, Ar*H*), 7.07 (m, 3H, Ar*H*), 6.97 (d, 1H, J = 7.2 Hz, Ar*H*), 6.83 (s, 1H, Ar*H*), 6.74 (t, 1H, J = 7.2 Hz, Ar*H*), 6.43 (d, 1H, J = 8.2 Hz, Ar*H*), 4.20 (d, 1H, J = 14.0 Hz, Ar–CH_2N), 3.81 (d, 1H, J = 14.0 Hz, Ar–CH_2N), 3.56 (d, 1H, J = 12.4 Hz, NCH_2–Ar), 3.29 (d, 1H, J = 12.4 Hz, NCH_2–Ar), 3.09 (s, 1H, OCH_3), 2.52–2.48 (m, 1H, NCH_2CH_2N), 2.23 (s, 3H, C(CH_3)$_2$Ph), 2.09–2.02 (m, 7H, NCH_2CH$_3$, NCH_2CH_2N), 1.88 (s, 3H, C(CH_3)$_2$Ph), 1.75 (s, 6H, C(CH_3)$_2$Ph), 1.69 (t, 3H, J = 8.0 Hz, ZnCH$_2$CH_3), 0.57 (t, 6H, J = 6.8 Hz, NCH$_2$CH_3), 0.47–0.34 (m, 2H, ZnCH_2CH$_3$); ^{13}C NMR (100 MHz, C_6D_6): δ 165.6, 158.8, 153.2, 153.0, 137.8, 134.5, 133.3, 129.9, 128.8, 128.1, 127.6, 127.3, 127.1, 126.2, 125.5, 124.3, 122.2, 121.5, 120.6, 111.1 (all Ar*C*), 57.4 (*C*H$_3$O–Ar), 54.8 (Ar–*C*H$_2$N), 52.5 (N*C*H$_2$–Ar), 50.2 (N*C*H$_2$CH$_2$N), 47.6 (NCH$_2$*C*H$_2$N), 42.8 (N*C*H$_2$CH$_3$), 42.6 (N*C*H$_2$CH$_3$), 32.1 (*C*(CH$_3$)$_2$Ph), 31.9 (*C*(CH$_3$)$_2$Ph), 31.7 (C(*C*H$_3$)$_2$Ph), 31.5 (C(*C*H$_3$)$_2$Ph), 27.6 (C(*C*H$_3$)$_2$Ph), 23.0 (C(*C*H$_3$)$_2$Ph), 14.3 (NCH$_2$*C*H$_3$), 14.0 (NCH$_2$*C*H$_3$), 8.6 (ZnCH$_2$*C*H$_3$), −1.1 (Zn*C*H$_2$CH$_3$).

[(L^3)ZnN(SiMe$_3$)$_2$] (3a). An analogous method to that of **1a** was utilized, except that **L^{3}H** (0. 411 g, 1.00 mmol) was used to give colorless granular crystals (419 mg, 65.9%). Found: C, 50.49; H, 7.12; N, 6.74. Calc. for $C_{27}H_{45}Cl_2N_3O_2Si_2Zn$: C, 50.98; H, 7.13; N, 6.61%. ^{1}H NMR (400 MHz, C_6D_6): δ 7.45 (d, 1H, J = 2.4 Hz, Ar*H*), 7.11 (t, 1H, J = 8.0 Hz, Ar*H*), 6.94 (dd, 1H, J = 7.2, 1.2 Hz, Ar*H*), 6.83 (t, 1H, J = 7.2 Hz, Ar*H*), 6.49 (d, 1H, J = 8.0 Hz, Ar*H*), 6.44 (d, 1H, J = 2.4 Hz, Ar*H*), 4.35 (d, 1H, J = 14.0 Hz, NCH_2–Ar), 4.06 (d, 1H, J = 12.8 Hz, Ar–CH_2N), 4.01 (d, 1H, J = 14.0 Hz, NCH_2–Ar), 3.17 (s, 3H, OCH_3), 3.01 (d, 1H, J = 12.8 Hz, Ar–CH_2N), 2.52–2.46 (m, 3H, NCH_2CH_2N), 2.28–2.22 (m, 1H, NCH_2CH_2N), 2.18–2.14 (m, 1H, NCH_2CH$_3$), 2.06–2.03 (m, 1H, NCH_2CH$_3$), 1.83–1.79 (m, 1H, NCH_2CH$_3$), 0.74 (t, 6H, J = 7.2 Hz, CH$_2$CH_3), 0.65–0.63 (m, 1H, NCH_2CH$_3$), 0.55 (s, 18H, N(Si(CH_3)$_3$)$_2$); ^{13}C NMR (100 MHz, C_6D_6): δ 162.0, 158.7, 134.0, 130.6, 130.2, 129.4, 125.6, 123.7, 120.9, 120.1, 116.6, 111.3 (all Ar*C*), 58.5 (*C*H$_3$O–Ar), 55.0 (Ar–*C*H$_2$N), 53.9 (N*C*H$_2$–Ar), 51.8 (N*C*H$_2$CH$_2$N), 46.6 (NCH$_2$*C*H$_2$N), 32.0 (N*C*H$_2$CH$_3$), 23.1 (NCH$_2$*C*H$_3$), 7.2 (N(Si(*C*H$_3$)$_3$)$_2$).

{(L^4)Zn[(3-*tert*-butyl-2-methoxy-5-methylbenzyloxy]} (4b). ***Method A*:** The impure ligand **L^{4}H** [containing **L^{4}H** (0.649 g, 1.00 mmol) and 3-*tert*-butyl-2-methoxy-5-methylbenzyl alcohol (0.037 g, 1/6 mmol)] was added slowly to a solution of Zn [N(SiMe$_3$)$_2$]$_2$ (0.385 g, 1.00 mmol) in toluene (20 mL) and the solution was stirred for 24 h at room temperature. The second portion of 3-*tert*-butyl-2-methoxy-5-methylbenzyl alcohol (0.187 g, 5/6 mmol) was added to the above solution and stirred for another 24 h. After filtration, the filtrate was evaporated to dryness to give foam-like solids, which was dried under vacuum for half an hour. The resultant solids were dissolved with proper amount of hexane and kept at −39 °C to give colorless crystals (570 mg, 61.3%). ***Method B*:** The mixture of impure ligand **L^{4}H** [containing **L^{4}H** (0.649 g, 1.00 mmol) and 3,5-di-*tert*-butyl-2-methoxybenzyl alcohol (0.037 g, 1/6 mmol)] was added slowly

to a solution of $Zn[N(SiMe_3)_2]_2$ (0.385 g, 1.00 mmol) in toluene (20 mL), and then 3,5-di-*tert*-butyl-2-methoxybenzyl alcohol (0.187 g, 5/6 mmol) was added. The obtained solution was stirred for 24 h at room temperature and filtered. After a similar work-up procedure, colorless crystals were obtained (277 mg, 30.1%). Found: C, 74.48; H, 8.66; N, 3.11. Calc. for $C_{57}H_{78}N_2O_4Zn$: C, 74.36; H, 8.54; N, 3.04%. ^{1}H NMR (400 MHz, C_6D_6): δ 7.92 (s, 1H, Ar*H*), 7.61 (s, 1H, Ar*H*), 7.60 (d, 2H, J = 7.2 Hz, Ar*H*, partially overlapped), 7.46 (br s, 1H, Ar*H*), 7.35 (d, 2H, J = 7.2 Hz, Ar*H*), 7.21–7.17 (m, 5H, Ar*H*), 7.07–7.04 (m, 2H, Ar*H*), 6.99 (t, 1H, J = 7.2 Hz, Ar*H*), 6.81 (d, 1H, J = 0.8 Hz, Ar*H*), 5.56 (s, 2H, Ar–CH_2O), 4.06 (d, 1H, J = 13.6 Hz, Ar–CH_2N), 3.91 (s, 3H, OCH_3), 3.74 (d, 1H, J = 12.4 Hz, NCH_2–Ar), 3.55 (d, 1H, J = 13.6 Hz, Ar–CH_2N), 3.27 (s, 3H, OCH_3), 3.13 (d, 1H, J = 12.4 Hz, NCH_2–Ar), 2.55–2.50 (m, 1H, NCH_2CH_2N), 2.36 (s, 3H, Ar–CH_3), 2.24 (s, 3H, Ar–CH_3), 2.21 (s, 3H, C(CH_3)$_2$Ph), 2.16–2.13 (m, 1H, NCH_2CH_2N), 2.04–1.84 (m, 1H, NCH_2CH_2N), 1.99–1.83 (m, 1H, NCH_2CH_2N), 1.84 (s, 3H, C(CH_3)$_2$Ph), 1.74 (s, 3H, C(CH_3)$_2$Ph), 1.72 (s, 3H, C(CH_3)$_2$Ph), 1.68–1.64 (m, 4H, NCH_2CH$_3$), 1.52 (s, 9H, C(CH_3)$_3$), 1.32 (s, 9H, C(CH_3)$_3$), 0.76–0.74 (m, 3H, NCH$_2$CH_3), 0.29–0.28 (m, 3H, NCH$_2$CH_3); ^{13}C NMR (100 MHz, C_6D_6): δ 165.5, 157.8, 155.8, 152.9, 152.4, 142.8, 141.2, 138.1, 134.3, 134.3, 133.4, 131.7, 129.8, 128.9, 128.8, 128.1, 127.9, 127.6, 127.2, 127.1, 126.8, 126.5, 125.5, 125.4, 124.4, 121.4 (all Ar*C*), 65.2 (Ar–*C*H$_2$O), 62.8 (*C*H$_3$O–Ar), 62.1 (*C*H$_3$O–Ar), 60.1 (N*C*H$_2$–Ar), 53.9 (Ar–*C*H$_2$N), 50.6 (N*C*H$_2$CH$_2$N), 46.7 (NCH$_2$*C*H$_2$N), 42.7 (*C*(CH$_3$)$_2$Ph), 42.6 (*C*(CH$_3$)$_2$Ph), 35.2 (*C*(CH$_3$)$_3$), 35.0 (*C*(CH$_3$)$_3$), 32.0 (C(*C*H$_3$)$_2$Ph), 31.9 (C(*C*H$_3$)$_2$Ph), 31.5 (C(*C*H$_3$)$_2$Ph), 31.4 (C(*C*H$_3$)$_3$), 31.3 (C(*C*H$_3$)$_3$), 27.5 (C(*C*H$_3$)$_2$Ph), 23.0 (NCH$_2$*C*H$_3$), 21.6 (Ar–*C*H$_3$), 21.0 (Ar–*C*H$_3$).

[(L^5)ZnN(SiMe$_3$)$_2$] (5a). An analogous method to that of **1a** was utilized, except that **L^{5}H** (0.565 g, 1.00 mmol) was used to give a white crystalline solid (453 mg, 56.4%). Found: C, 67.20; H, 8.48; N, 5.24. Calc. for $C_{45}H_{68}N_3O_2Si_2Zn$: C, 67.17; H, 8.52; N, 5.22%. ^{1}H NMR (400 MHz, C_6D_6): δ 7.55 (d, 1H, J = 1.8 Hz, Ar*H*), 7.41 (d, 2H, J = 7.6 Hz, Ar*H*), 7.31 (d, 2H, J = 7.6 Hz, Ar*H*), 7.12 (d, 2H, J = 7.8 Hz, Ar*H*), 7.08 (d, 2H, J = 7.3 Hz, Ar*H*), 7.04–6.95 (m, 3H, Ar*H*), 6.80 (d, 1H, J = 6.8 Hz, Ar*H*), 6.75 (d, 1H, J = 1.8 Hz, Ar*H*), 6.70 (t, 1H, J = 7.3 Hz, Ar*H*), 6.41 (d, 1H, J = 8.0 Hz, Ar*H*), 4.41 (br d, 1H, J = 13.0 Hz, Ar–CH_2N), 4.25 (d, 1H, J = 13.5 Hz, Ar–CH_2N), 4.07 (br d, 1H, J = 13.0 Hz, Ar–CH_2N), 3.42 (d, 1H, J = 13.5 Hz, Ar–CH_2N), 3.11 (s, 3H, Ar–OCH_3), 2.52 (t, 1H, J = 12.0 Hz, NCH_2CH$_2$CH_2N), 2.30–2.20 (m, 1H, NCH_2CH$_2$CH_2N), 2.18 (s, 3H, C(CH_3)$_2$Ph), 1.82–1.67 (m, 6H, N(CH_3)$_2$), 1.63 (s, 3H, C(CH_3)$_2$Ph), 1.61 (s, 6H, C(CH_3)$_2$Ph), 1.60–1.52 (m, 2H, NCH$_2$CH_2CH$_2$N), 1.35 (dd, 1H, J = 12.0, 5.6 Hz, NCH_2CH$_2$-CH_2N), 0.74 (br d, 1H, NCH_2CH$_2$CH_2N), 0.43 (s, 18H, N(Si(CH_3)$_3$)$_2$); ^{13}C NMR (100 MHz, C_6D_6): δ 163.0, 159.1, 154.7, 152.7, 137.5, 134.9, 133.7, 130.4, 128.1, 127.3, 127.2, 126.3, 125.5, 124.6, 120.7, 120.4, 119.6, 110.3 (all, Ar*C*), 61.2 (*C*H$_3$O–Ar), 60.9 (Ar–*C*H$_2$N), 54.9 (N*C*H$_2$–Ar), 53.0(N*C*H$_2$-CH$_2$CH$_2$N), 50.3 (NCH$_2$CH$_2$*C*H$_2$N), 43.0 (N(*C*H$_3$)$_2$), 42.4 (C(*C*H$_3$)$_2$Ph), 31.6 (C(*C*H$_3$)$_2$Ph), 31.5 (C(*C*H$_3$)$_2$Ph), 26.7 (C(*C*H$_3$)$_2$Ph), 22.1 (NCH$_2$*C*H$_2$CH$_2$N), 7.5 (N(Si(*C*H$_3$)$_3$)$_2$).

[L$^6_2$Zn] (6). The ligand **L^{6}H** (0.585 g, 1.00 mmol) was added slowly to a solution of $Zn[N(SiMe_3)_2]_2$ (0.385 g, 1.00 mmol) in light petroleum ether (20 mL). The solution was stirred for 24 h at room temperature and plenty of white solids precipitated. After filtration and drying under vacuum, the white solids were dissolved with toluene (more than 45 mL) and kept at −39 °C to afford a white powder (0.468 g, 75.9%). Found: C, 78.31; H, 6.99; N, 4.51. Calc. for $C_{80}H_{86}N_4O_4Zn\cdot(C_7H_8)$: C, 77.93; H, 7.03; N, 4.54%. MS (*m*/*z*): 647 (40, [M − L]$^+$); 632 (57, [M − L − CH$_3$]$^+$); 584 (6, L$^+$); 525 (74, {M − L − [*o*-MeOC$_6$H$_4$CH$_2$]}$^+$); 463 (70, {L − [*o*-MeOC$_6$H$_4$CH$_2$]}$^+$); 361 (100, {L − [*o*- MeOC$_6$H$_4$CH$_2$] − N(CH$_2$)$_3$N(CH$_3$)$_2$}$^+$); 285 (61, {M − L − [*o*-Ph$_3$C-*o*-CH$_2$-*p*-CH$_3$C$_6$H$_2$O]$^+$}; 269 (46, {M − L − [*o*-Ph$_3$C-*o*-CH$_2$-*p*-CH$_3$C$_6$H$_2$O] − CH$_3$}$^+$).

[(L^7)ZnN(SiMe$_3$)$_2$] (7a). An analogous method to that of **1a** was utilized, except that **L^{7}H** (0. 762 g, 1.00 mmol) was used to give a white crystalline solid (530 mg, 51.3%). Found: C, 67.68; H, 8.80; N, 4.64. Calc. for $C_{49}H_{76}N_3O_2Si_2Zn$: C, 68.38; H, 8.90; N, 4.88%. ^{1}H NMR (400 MHz, C_6D_6): δ 7.51 (d, 1H, J = 2.4 Hz, Ar*H*), 7.41–7.39 (m, 2H, Ar*H*), 7.30–7.27 (m, 2H, Ar*H*), 7.11–7.05 (m, 5H, Ar*H*), 7.00–6.94 (m, 2H, Ar*H*), 6.71 (d, 1H, J = 2.4 Hz, Ar*H*), 6.64 (d, 1H, J = 1.6 Hz, Ar*H*), 4.53 (d, 1H, J = 13.2 Hz, Ar–CH_2N), 4.20 (d, 1H, J = 14.0 Hz, NCH_2–Ar), 4.03 (d, 1H, J = 13.2 Hz, Ar–CH_2N), 3.40 (s, 3H, Ar–OCH_3), 3.40 (d, 1H, J = 14.0 Hz, NCH_2–Ar, partially overlapped), 2.53–2.45 (m, 1H, NCH_2CH$_2$CH_2N), 2.17 (s, 3H, Ar–CH_3), 2.16–2.08 (m, 2H, NCH_2CH$_2$CH_2N), 2.08 (s, 3H, C(CH_3)$_2$Ph), 1.80–1.66 (m, 6H, N(CH_3)$_2$), 1.61 (s, 3H, C(CH_3)$_2$Ph), 1.59 (s, 3H, C(CH_3)$_2$Ph), 1.57 (s, 3H, C(CH_3)$_2$Ph), 1.41–1.38 (m, 1H, NCH_2CH$_2$CH_2N), 1.36 (s, 9H, C(CH_3)$_3$), 1.30–1.26 (dd, J = 12.8, 4.8 Hz, 1H, NCH_2CH$_2$CH_2N), 0.67 (dt,1H, J = 16, 4.8 Hz, NCH_2CH$_2$CH_2N), 0.44 (s, 18H, N(Si(CH_3)$_3$)$_2$); ^{13}C NMR (100 MHz, C_6D_6): δ 162.8, 158.6, 154.7, 152.5, 143.6, 137.5, 133.9, 133.4, 132.5, 129.5, 127.2, 126.3, 125.4, 124.6, 123.9, 120.4 (all Ar*C*), 63.1 (*C*H$_3$O–Ar), 61.4 (Ar–*C*H$_2$N), 54.1 (N*C*H$_2$–Ar), 49.3 (N*C*H$_2$CH$_2$CH$_2$N), 48.3 (N*C*H$_2$CH$_2$CH$_2$N), 47.8 (NCH$_3$), 42.9 (*C*(CH$_3$)$_2$Ph), 42.4 (*C*(CH$_3$)$_2$Ph), 35.7 (*C*(CH$_3$)$_3$), 35.0 (C(*C*H$_3$)$_2$Ph), 31.5 (C(*C*H$_3$)$_2$Ph), 31.4 (C(*C*H$_3$)$_2$Ph), 31.2(C(*C*H$_3$)$_3$), 26.4 (C(*C*H$_3$)$_2$Ph), 22.1 (CH$_2$*C*H$_2$CH$_2$), 21.1 (*C*H$_3$–Ar), 7.5 (N(Si(*C*H$_3$)$_3$)$_2$).

[(L^8)ZnN(SiMe$_3$)$_2$] (8a). An analogous method to that of **2a** was utilized, except that **L^{8}H** (0.443 g, 1.00 mmol) was used to give colorless granular crystals (408 mg, 61.2%). Found: C, 61.25; H, 9.09; N, 6.28. Calc. for $C_{34}H_{60}FN_3OSi_2Zn$: C, 61.19; H, 9.06; N, 6.30%. ^{1}H NMR (400 MHz, C_6D_6): δ 7.56 (d, 1H, J = 2.0 Hz, Ar*H*), 6.94 (t, 1H, J = 7.2 Hz, Ar*H*), 6.86 (m, 1H, Ar*H*), 6.78–6.70 (m, 3H, Ar*H*), 4.48 (d, 1H, J = 14.0 Hz, Ar–CH_2N), 4.15 (d, 1H, J = 12.4 Hz, Ar–CH_2N), 4.07 (d, 1H, J = 14.0 Hz, NCH_2–Ar), 3.32 (d, 1H, J = 12.4 Hz, NCH_2–Ar), 2.73–2.13 (m, 6H, NCH_2CH_2N, NCH$_2$CH_3), 2.11–1.93 (m, 1H, NCH_2CH$_3$), 1.78 (s, 9H, C(CH_3)$_3$), 1.46–1.35 (m, 1H, NCH_2CH$_3$), 1.30 (s, 9H, C(CH_3)$_3$), 0.95–0.61 (br, 3H, NCH$_2$CH_3), 0.60–0.10 (br, 3H, NCH$_2$CH_3), 0.55 (s, 18H, N(Si(CH_3)$_3$)$_2$), overlapped with the signal of NCH$_2$CH_3). ^{13}C NMR (100 MHz, C_6D_6): δ 165.2, 162.3(d, J_{FC} = 243.8 Hz), 138.1, 134.9 (t, J_{FC} = 3.2 Hz), 134.8, 130.9 (d, J_{FC} = 8.4 Hz),

126.5, 125.0, 124.5(d, J_{FC} = 3.4 Hz), 120.2, 119.2(d, J_{FC} = 15.8 Hz), 115.8 (d, J_{FC} = 23.1 Hz) (all Ar*C*), 60.3 (*C*H$_3$O–Ar), 52.9 (Ar–*C*H$_2$N), 49.7 (N*C*H$_2$CH$_2$N), 46.1 (NCH$_2$*C*H$_2$N), 36.0 (N*C*H$_2$CH$_3$), 34.1 (*C*(CH$_3$)$_3$), 32.2 (C(*C*H$_3$)$_3$), 30.6 (C(*C*H$_3$)$_3$), 7.5 (N(Si(*C*H$_3$)$_3$)$_2$).^{19}F NMR (376 MHz, C_6D_6): −115.01.

[(L^9)ZnN(SiMe$_3$)$_2$] (9a). An analogous method to that of **1a** was utilized, except that **L^{9}H** (0.352 g, 1.00 mmol) was used to give granular colorless crystals (343 mg, 59.5%). Found: C, 56.48; H, 9.46; N, 4.92. Calc. for $C_{27}H_{54}N_2O_3Si_2Zn$: C, 56.27; H, 9.44; N, 4.86%. ^{1}H NMR (400 MHz, C_6D_6): δ 7.54 (s, 1H, Ar*H*), 6.77 (s, 1H, Ar*H*), 3.41 (s, 2H, Ar-C*H*$_2$N), 3.00– 2.95 (m, 2H, NCH$_2$C*H*$_2$O), 2.89 (s, 6H, OC*H*$_3$), 2.89–2.85 (m, 2H, NC*H*$_2$C*H*$_2$O), 2.66–2.59 (m, 2H, NC*H*$_2$CH$_2$O), 2.31–2.28 (m, 2H, NC*H*$_2$CH$_2$O), 1.76 (s, 9H, C(C*H*$_3$)$_3$), 1.42 (s, 9H, C(C*H*$_3$)$_3$), 0.45 (s, 18H, N(Si(C*H*$_3$)$_3$)$_2$); ^{13}C NMR (100 MHz, C_6D_6): δ 164.5, 138.0, 135.6, 124.9, 124.5, 121.7 (All, Ar-*C*), 69.2 (NCH$_2$*C*H$_2$O), 62.3 (NCH$_2$*C*H$_2$O), 59.0 (*C*H$_3$O), 57.8 (*C*H$_3$O), 35.8 (N*C*H$_2$CH$_2$O), 34.1 (*C*(CH$_3$)$_3$), 32.3 (N*C*H$_2$CH$_2$O), 30.3 (C(*C*H$_3$)$_3$), 6.2 (N(Si(*C*H$_3$)$_3$)$_2$).

X-Ray crystallography

Suitable crystals of complex **4b** for X-ray diffraction analysis were obtained from the saturated toluene/hexane mixture at room temperature. Diffraction data were collected on a Bruker AXSD 8 diffractometer with graphite-monochromated Mo-Kα (λ = 0.71073 Å) radiation. All data were collected at 20 °C using the ϕ and ω-scan techniques. The structure was 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 were done by Bruker SMART, and reduction were done by Bruker SHELXTL. The structure solution and refinement were performed by SHELXS-97[87] and SHELXL-97[88] respectively. Molecular structure was generated using ORTEP program.[89] Formula of **4b**: $C_{57}H_{78}N_2O_4Zn\cdot(0.5\ C_6H_{14})$; Crystal system, Triclinic; Space group: $P\bar{1}$; Unit cell dimensions: a = 14.726(2) Å, b = 14.998(2) Å, c = 15.817(2) Å, α = 63.485 (3)°, β = 67.435(3)°, γ = 75.481(3)°, Z = 2.

Typical polymerization experiments

In a Braun Labstar glove-box, an initiator solution from a stock solution in THF or toluene was injected sequentially to a series of 20 mL vials loaded with *rac*-lactide and suitable amounts of dry solvent. After specified time intervals, each vial was taken out of the glove-box; an aliquot was withdrawn and quenched quickly with petroleum ether, the reaction mixture was quenched at the same time by adding excess amount of petroleum ether and one drop of water. All the volatiles in the aliquots were removed and the residue was subjected to monomer conversion determination which was monitored by integration of monomer *vs.* polymer methine or methyl resonances in ^{1}H NMR ($CDCl_3$, 400 MHz). The precipitates collected from the bulk mixture were dried in air, dissolved with dichloromethane and sequentially precipitated into petroleum ether. The obtained polymer was further dried in a vacuum oven at 50 °C for 16 h. Each reaction was used as one data point. In the cases where isopropanol was used, the solution of initiator was injected to the solution of *rac*-lactide in toluene or THF to which isopropanol was added. Otherwise the procedures were the same.

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