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Comparative study of lactide polymerization by zinc alkoxide complexes with a β-diketiminato ligand bearing different substituents

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ABSTRACT

A series of β-diketiminate zinc complexes has been synthesized and their reactivity for the ring-opening polymerization (ROP) of lactide has been studied. The reaction of β-diketimines (LH) with diethyl zinc forms the monomeric [LZnEt] complexes which further react with benzyl alcohol (BnOH) in toluene/hexane yielding dinuclear or trinuclear zinc complexes. These complexes have been characterized by single crystal X-ray diffraction, which showed the tri- and tetra-coordinated zinc complexes in which zinc atoms exhibit trigonal and tetrahedral geometry, respectively. All complexes have been tested as initiators for the ring-opening polymerization of lactide; they are all highly active. The rate of polymerization is heavily dependent on the *N*-aryl substituents with the order: alkyl group ~ alkoxy > halide group > nitro group. The β-diketiminate zinc complexes allow controlled ring-opening polymerization as shown by the linear relationship between the percentage conversion and the number-average molecular weight. On the basis of literature reports, a mechanism for ROP of lactide has been proposed.

1. Introduction

Poly(lactic acid) (PLA) [1], produced by the ring-opening polymerization (ROP) of lactide (LA), is a leading biodegradable and biocompatible polyester and has attracted considerable attention mainly because of its biomedical and pharmaceutical applications [2]. In industry, PLA is synthesized by ROP using tin(II) bis(2-ethylhexanoate) ($SnOct_2$) as a catalyst. Although $SnOct_2$ has been accepted as a food additive by the U.S. FDA, the toxicity associated with most tin compounds is a considerable drawback in the case of biomedical applications [1a]. So scientists all over the world are exploring novel, well-defined catalysts having the characteristics of good biocompatibility, high catalytic activity, and excellent stereoselectivity.

Nowadays, zinc complexes have been proven to be efficient catalysts for the ROP of lactide in the presence of alcohol, mainly due to their great successes in living ring-opening polymerization, producing polymers with well-controlled molecular weight and narrow molecular weight distribution [3]. Besides the zinc systems, metal alkoxides (*e.g.*, Al [4], Li [5], Mg [6], Fe [7], Sn [8], or Ti [9]) have also proven to be active in ROP of lactide. The neutral three-coordinate chelating diamide aluminum complexes were synthesized by Chakraborty and Chen [4j], which produced telechelic polycaprolactones (PCLs) with high molecular weights on the order of 10^6 Da. On the other hand, the magnesium β-diketiminate complexes were extremely active for the ROP of *rac*-lactide, with up to 80% conversion in less than 10 min at room temperature [10]. Based on the success with aluminum and magnesium metals, Chisholm's group [11] synthesized β-diketiminate calcium complexes with very high activity. Zinc complexes bearing polydentate ligands with nitrogen donors have been extensively studied for ROP of lactides. To the best of our knowledge, the substituent effects in the polymerization of LA by zinc complexes bearing β-diketiminate ligands have been previously studied by Coates and coworkers [3b,c,j]. However, these investigations were focused on the steric effects of the substituents on the N-aryl groups. Also, β-diketiminate ligands have emerged as one of the most versatile ligand classes in both main group and transition metal coordination chemistry [12]. Nearly all of the β-diketiminate ligands involved possess a symmetrical structure [12u], allowing facile modulation of steric and electronic factors [12v–y] and therefore they are ideal ligand sets for the design of novel zinc based catalysts/initiators for the ROP of lactide.

Herein, we report the synthesis of a series of zinc complexes ligated by symmetrical or unsymmetrical β-diketiminate ligands, and their catalytic behavior for the ROP of lactide. Specifically, the

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steric and electronic effects of these ligands on the polymerization of lactide were explored.

2. Results and discussion

2.1. Synthesis of β-diketiminate zinc complexes

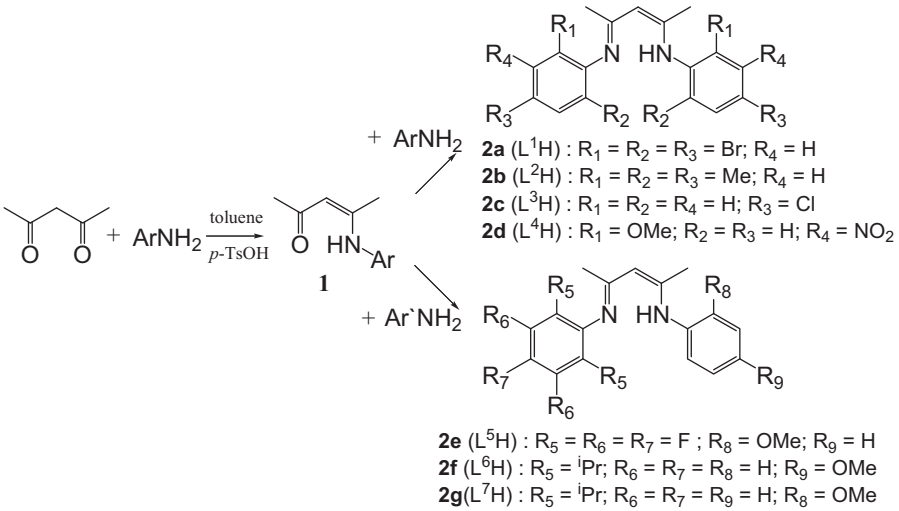
With the endeavor of assessing substituent effects on polymerization activity, various substituents such as alkyl, alkoxy, halo, and the nitro group were incorporated to obtain β-diketiminate ligands with different electron-donating and accepting abilities. The symmetrical β-diketimines **2a–d** (L^1H–L^4H) were synthesized in two steps as depicted in Scheme 1: (1) condensation of 2,4-pentanedione with one eq. of primary aromatic amine in toluene, with *p*-toluenesulfonic acid as catalyst, afforded the enaminoketone intermediate **1**; (2) another eq. of the same aromatic amine was pre-treated with *p*-toluenesulfonic acid in a 1:1 ratio to afford the *p*-toluenesulfonate ammonium salt, which was then reacted with the corresponding enaminoketone **1** to give β-diketimines **2a–d** in reasonable yields. In contrast, it is simpler to synthesize β-diketimines **2a–d**, with the same *N*-aryl substituents by refluxing 2.0 eq. of the primary aromatic amine with 2,4-pentanedione in toluene and *p*-toluenesulfonic acid as the catalyst. The reactions of ligands **2a–d** with diethyl zinc in a 1:1 molar ratio in *n*-hexane/toluene readily generated the tri-coordinated zinc complexes **3a–d** (Scheme 2), with the elimination of 1 eq. of ethane. Similar two-step condensation reactions were adopted to synthesize the unsymmetrical β-diketimines. Successful synthesis of **2e** (L^5H) was limited to the reaction of 4-(perfluorophenylamino)pent-3-en-2-one (**1e**) with 2-methoxyaniline by using *para*-toluenesulfonic acid as the catalyst. Also β-diketimines ligands **2f** and **2g** (L^6H–L^7H) were synthesized by the reaction of 4-(2,6-diisopropylphenyl)aminopent-3-en-2-one (**1f**) with the corresponding aromatic amines using *p*-toluenesulfonic acid as the catalyst (Scheme 1). Zinc complexes **3f** and **3g** with unsymmetrical β-diketimines were synthesized accordingly *via* the reactions of ligands **2f** and **2g** with diethyl zinc (Scheme 2).

The ^1H NMR spectra indicate that for zinc complexes **3a–d**, the chemical environments of both aromatic rings as well as the two backbone methyl groups are identical. Zinc complexes **3f** and **3g** with unsymmetrical β-diketiminate ligands exhibit separate resonances in the ^1H NMR spectra. The chemical shifts for the methine protons of the 2-propyl groups (–C**H**Me_2) in complexes **3f** and **3g** appear near 3.0 ppm, almost the same as those in the neutral β-diketimines, but because of restricted *N*-aryl bond rotation, there are two separate doublets for the methyl groups (–CH**Me**$_2$) in complexes **3f** and **3g**. In addition, ^1H NMR spectra of zinc complexes **3a–d** and **3f** and **3g** generally reveal two diastereotopic methylene protons in each ethyl group (Zn–C**H**$_2$$CH_3$), resonating at negative ppm, further implicating restricted *N*-aryl bond rotation.

Subsequently, attempts to synthesize the corresponding alkoxide complexes **4a–d** and **4f** and **4g** were carried out by reacting the β-diketiminate zinc ethyl complexes **3a–d** and **3f** and **3g** with 1.2 eq. of BnOH at 0 °C, respectively, (Scheme 2). But there are lots of impurities in **3a** reaction and it could not be purified. Fortunately the **3a** crystal was got and its structure was identified. A homoleptic complexes [$(L)_2Zn$] were observed by the NMR spectrum from the synthesis of **4f** and **4g**. It is believed that, in the presence of BnOH, LZnEt reacts with BnOH to yield LZnOBn and the disproportionation products, L_2Zn and $ZnOBn_2$. The disproportionation takes place when the functional groups of *N*-aryl substituents are not bulky and the similar situation was reported in the literature [12z]. The combination of 2 eq. of [LZnOBn] with $Zn(OBn)_2$ gives [L_2Zn_3(μ-$OBn)_4$]. The complex [$(L^5)_2Zn_2$(μ-$OBn)_2$] (**4e**) was formed by the direct reaction of ligand **2e** (L^5H) with diethyl zinc followed by the addition of BnOH; the structure of **4e** was confirmed by the NMR spectrum, and elemental analysis. The mononuclear complexes **3c** and **3d** undergo ligand redistribution to complexes **4i** and **4j** with the elimination of one eq. of diethyl zinc within 7 h and 2 days, respectively, due to the lack of steric bulk at the *N*-aryl *ortho* positions (Scheme 2). It is interesting to note that the complexes **4a–d** are dinuclear in nature whereas **4f** and **4g** are trinuclear. To understand this variation, we compared all of our complexes with the β-diketiminate Zn alkoxide complexes reported in the literature [3b–d,j] and concluded that, dinuclear complexes are produced when the ligands have alkyl groups at the *N*-aryl positions whereas, trinuclear zinc complexes are formed, when electron withdrawing groups are substituted in the 1- or 3- positions of pentenyl group following ^{i}propyl group at the 2,6 *N*-aryl positions. This may be due to π-resonance effect and/or electron donating effect of substituent. To clarify this, we prepared ligand **2f** (L^6H) with the OMe group at the *para* position, which produced trinuclear zinc complex. Following this result, we noted that β-diketiminate ligands **2a** (L^1H), **2c** (L^3H) and **2e** (L^5H), which have substituent groups bearing lone pairs of electrons (Br, Cl, F, and OMe), afford dinuclear complexes. This may be due to electron withdrawing groups Br and Cl in the case of **2a** and **2c**, respectively, and in case of **2e**, the *N*-pentafluorophenyl group is more electron-withdrawing than the OMe electron-donating group. For the synthesis of trinuclear complex, we prepared ligand **2b** (L^2H), which still produce dinuclear complex (**4b**), then we prepared the NMR tube with [$(L^2)_2Zn_2$(μ-$OBn)_2$] (**4b**) in benzene-d_6 and heat it at 60 °C for 4 days but no change in it. We heat the mixture with 1 eq. **4b** and 1 eq. $Zn_2(OBn)_2$ in THF at 80 °C for 4 days. From the NMR spectra, [$(L^2)_2Zn_3$(μ-$OBn)_4$] seems to appear but mixed with [$(L^2)_2Zn_2$(μ-$OBn)_2$] and we cannot purify it (supporting information Fig. 1). Thus finally we synthesize **2f** (L^6H) and **2g** (L^7H) with *N*-methoxyphenyl groups which produce trinuclear complexes **4f** and **4g** (Scheme 2), which conform by the NMR spectrum, elemental analysis and X-ray structural determination. Based on the above experiments, a generalized mechanistic scheme can be proposed (Scheme 3). Besides, [$(L^2)_2Zn_2$(μ-$OEt)_2$] (**4k**) can be synthesized from [L^2ZnEt] (**3b**) by react with O_2 (Scheme 4) which was supported by the literature review [13] and confirmed by X-ray structural determination. Zn alkylperoxides are the initial products of the auto-oxidation of alkylzinc compounds. Although it is certain that the final products are zinc alkoxides, the mechanisms by which these products are formed are uncertain. It is likely that reactions between alkylzinc compounds and alkylzinc peroxides are involved in the final reactions, since such a reaction has been observed independently.

2.2. Crystal structure of zinc complexes

Single crystals of zinc complexes **3f** [L^6ZnEt], **4a**[$(L^1)_2Zn_2$(μ-$OBn)_2$], **4b**[$(L^2)_2Zn_2$(μ-$OBn)_2$], and **4k**[$(L^2)_2Zn_2$(μ-$OEt)_2$] suitable for X-ray diffraction measurement were obtained. Crystallographic data, the results of structure refinements, and selected bond lengths and angles are summarized in Figs. 1–4 and supporting information Table 1. As shown in Fig. 1, being surrounded by two nitrogen donors of the chelating β-diketiminate ligand and one ethyl group, the zinc center in complex **3f** possesses a distorted trigonal geometry with bond angles 96.35°, 130.30°, and 133.30° for N(1)–Zn–N(2), N(1)–Zn–C(25), and N(2)–Zn–C(25), respectively. There are close interactions between Zn and N(1) (1.962 Å) as well as between Zn and N(2) (1.961 Å). The distance between Zn and C(25) is 1.949 Å. Metrical analysis reveals that **4a** (Fig. 2), **4b** (Fig. 3), **4k** (Fig. 4) are iso-structural-*i.e.*, distorted tetrahedral geometry with only slight variations in bond lengths and angles. In **4a**, the average O(1)–Zn(1)–O(1A) and N(1)–Zn–N(2) bond angles



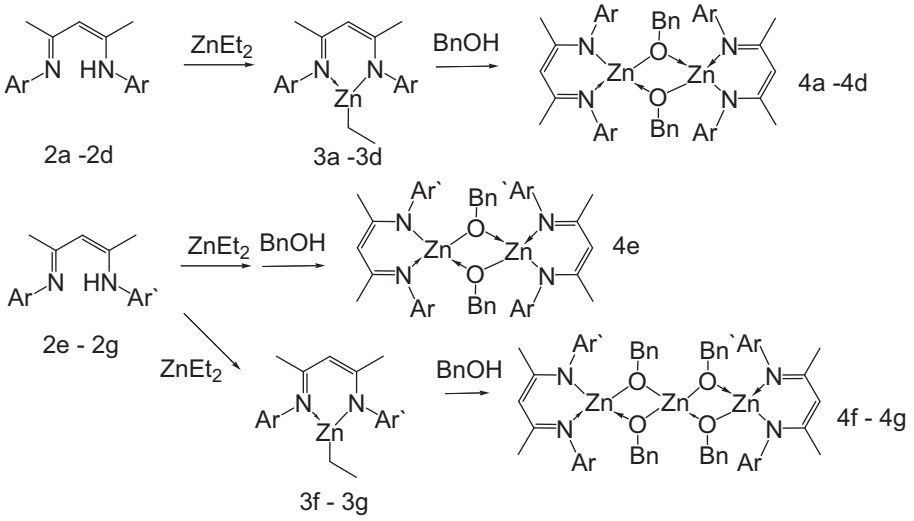
Scheme 1.

are 82.90° and 96.80°. The distances from Zn(1) to O(1), O(1A), N(1), and N(2) are 1.977, 1.959, 1.989 and 1.998 Å, respectively. In **4b**, the average O(1)–Zn(1)–O(2), O(1)–Zn(2)–O(2), N(1)–Zn–N(2), and N(3)–Zn–N(4) bond angles are 81.63°, 81.39°, 97.60°, and96.60, respectively. The distances from Zn(1) atom to O(1), O(2), N(1) and N(2) are 1.989, 1.956, 1.983 and 1.982 Å. The distances from Zn(2) atom to O(1), O(2), N(3) and N(4) are 1.960, 1.993, 1.997 and 2.001 Å and with bond angles of 82.91, 82.89,119.03 and 126.19. In **4k**, the Zn atoms with the average compressed O(1)-Zn(1)-O(2), O(1)-Zn(2)-O(2), N(1)-Zn-N(2) and N(3)-Zn-N(4) bond angles of 83.10°, 80.90°, 98.40° and 98.10°. The distance from Zn(1) atom to O(1), O(2), N(1) and N(2) are 1.985, 1.899, 1.938 and 1.934 Å. The distance from Zn(2) atom to O(1), O(2), N(3) and N(4) are 1.982, 1.989, 2.008 and 2.029 Å.

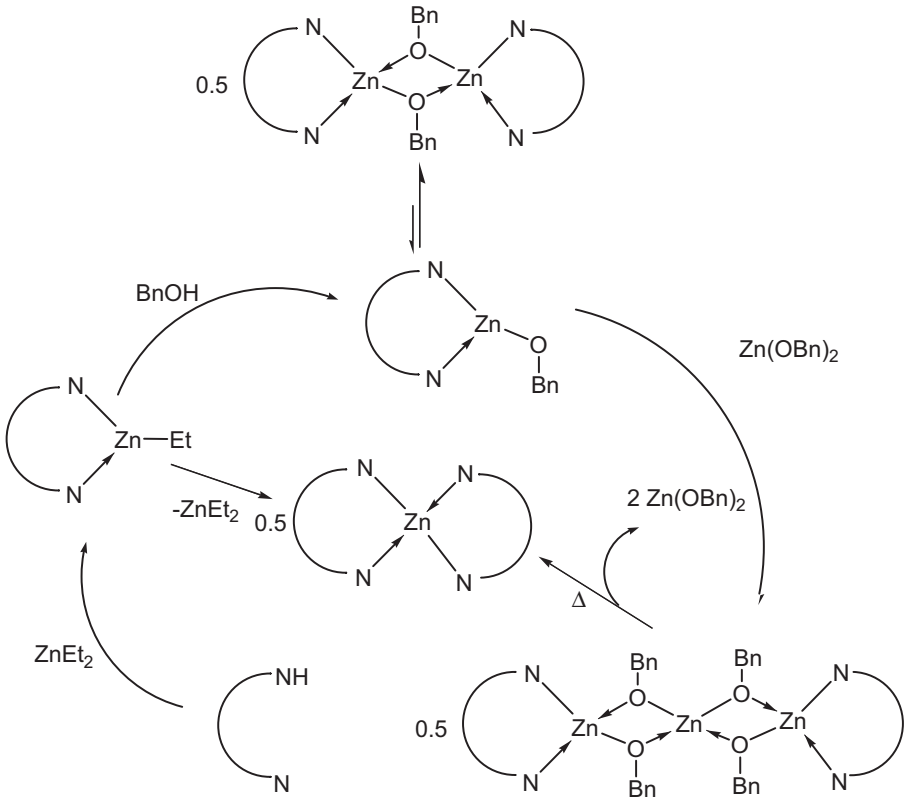
2.3. Ring-opening polymerization of L-lactide

β-Diketiminate Zn alkoxide complexes **3a**, **4b–g** as well as the previously reported zinc complex [3d] $(BDI\text{-}OMe)_2Zn_3(\mu\text{-}OBn)_4$, initiate the ring-opening polymerization of L-lactide (LA) in toluene at room temperature (for **3a** and **4d** the temperature is 100 °C and the concentration of **4d** is 1.25 mM because of the low solubility in toluene). The polymerization results are listed in Table 1, all complexes displayed good activities for the polymerization of L-lactide with narrow distribution and great control of molecular weight. The structures of the ancillary ligands have a significant influence on the polymerization behavior of the corresponding zinc complexes. The discrepancy between the calculated and observed $M_{n(nmr)}$ values is small except for **3a** and **4b**. The reasons for **3a** may be the initiator (BnOH) was additional and it needed time to exchange ethyl group for BnOH. It made the time delay for the alkoxide formation and brought about slightly broad PDI. Besides, few of the disproportionation made the part of BnOH unavailable and the M_n(nmr) value was higher than calculated with. The reason for **4b** may be the polymerization rate of **4b** was too fast to cause the transesterification.

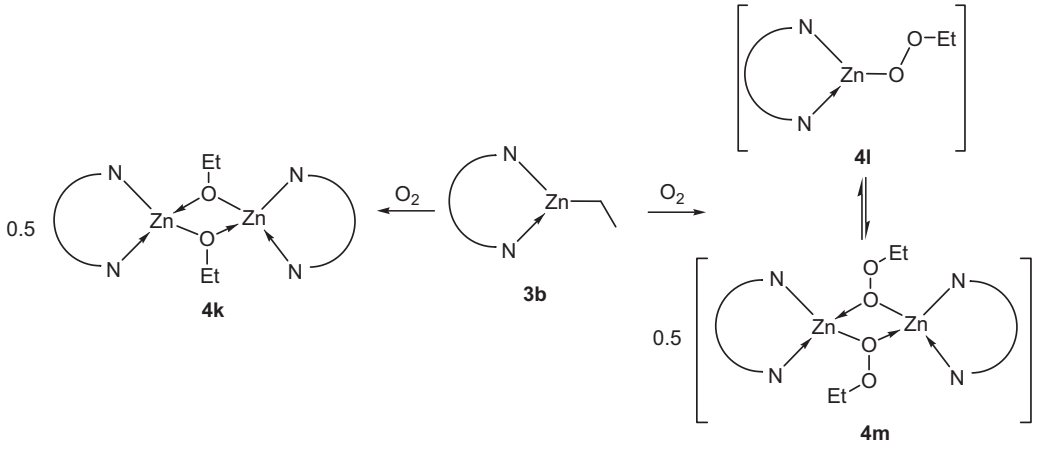
Comparing the polymerization runs performed in Table 1, several structure-activity trends may be drawn. It is found that for both zinc complexes with symmetrical or unsymmetrical β-diketiminate ligands, the electronic nature of the substituents of the phenyl groups exerts great influence on the ROP of L-LA. A clear increasing tendency of catalytic activity is found for complexes **4b**, **4f**, **4g** in the order **4b** > **4g** > **4f** (entry 2, 7, 6) with time, indicating that electron-donating substituents at the *ortho*-position are an advantage to the catalytic activity. The introduction of electron-donating groups on the phenyl rings decreases the lewis acidity of



Scheme 2.



Scheme 3. General proposed mechanism of zinc complex formation.

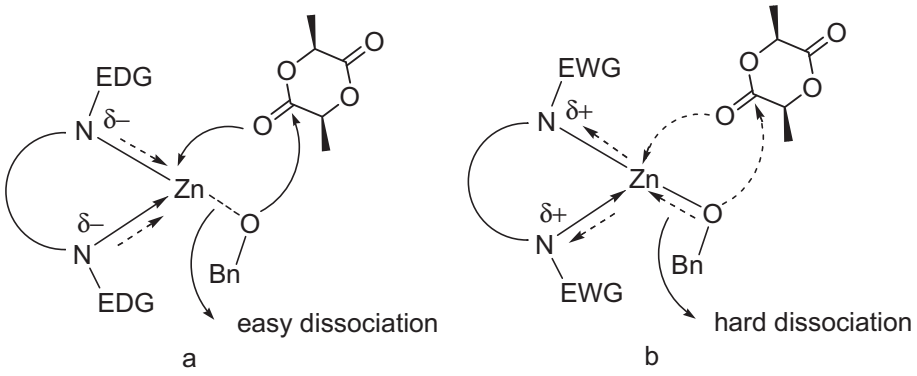


Scheme 4.

Table 1
β-Diketiminate Zn alkoxide complexes (2.5 mM) polymerized L-LA yielded PLA in toluene (20 mL) at room temperature and $[LA]_0/[cat.]$ ratio was 100:1.

Entry	Cat.	T (min)	t (°C)	PDI	M_n (GPC)[a]	M_n (calcd)[b]	M_n (nmr)[c]	Conv (%)
1	$[L^1ZnEt + BnOH]$[d](**3a**)	120	100	1.25	28,800	9500	12,500	87
2	$(L^2)_2Zn_2(\mu\text{-}OBn)_2$(**4b**)	2	R.T.	1.05	15,100	6900	9400	94
3	$(L^3)_2Zn_2(\mu\text{-}OBn)_2$(**4c**)	290	R.T.	1.05	10,000	6400	6700	87
4	$(L^4)_2Zn_2(\mu\text{-}OBn)_2$[e](**4d**)	360	100	1.09	17,200	12,500	11,600	86
5	$(L^5)_2Zn_2(\mu\text{-}OBn)_2$(**4e**)	120	R.T.	1.06	7700	7200	7800	99
6	$(L^6)_2Zn_3(\mu\text{-}OBn)_4$(**4f**)	5	R.T.	1.20	6800	3600	4400	96
7	$(L^7)_2Zn_3(\mu\text{-}OBn)_4$(**4g**)	3	R.T.	1.17	9000	3700	4300	99
8[f]	$(BDI\text{-}OMe)_2Zn_3(\mu\text{-}OBn)_4$	10	R.T.	1.09	9200	3500	4000	93

[a] Obtained from GPC analysis and calibrated by polystyrene standard.
[b] Calculated from the molecular weight of L-lactide × $[M]_o/[BnO^-]_o$ × conversion yield plus M_w(BnOH).
[c] Obtained from ^1H NMR analysis.
[d] In situ reaction of $[LA]/[BnOH] = 75$, $[L^1ZnEt] = 1.67$ mM, toluene 30 mL.
[e] $[LA]_0/[cat.]$ ratio was 200:1, $[(L^4)_2Zn_2(\mu\text{-}OBn)_2] = 1.25$ mM.
[f] It was reported on ref. [3h].



Scheme 5. Generalized mechanism for ROP of lactide (EDG = electron donating group and EWG = electron withdrawing group).

the zinc center through the chelating system of the ancillary ligand, which is favorable for the breaking of the Zn–alkoxide bond and leads to an increase in activity (Scheme 5a). Thus as can be seen in entries 2, 6, 7, 8, all complexes bearing electron donating groups on the *N*-aryl positions need less than 10 min for polymerization. Whereas, the entries for complexes bearing electron withdrawing groups (entries 1, 3, 4, 5) show that the ring opening rate is very slow. The lewis acidity of the zinc center is increased with electron withdrawing groups is strengthened, which causes the rate of polymerization to decrease (Scheme 5b). The rate of polymerization depends on the functional groups at the N-aryl positions in the following order: alkoxy ~ alkyl group > halide group > nitro group. The result is identical to literature report [3l,m,6f,g] and the principle is similar to acid dissociation constants of benzoic acid with rates of alkaline hydrolysis of ethyl benzoates [14]. Besides, the difference between the dinuclear and trinuclear complex is small for ROP of L-LA. It seems the electric effect is the key to control the catalytic rate.

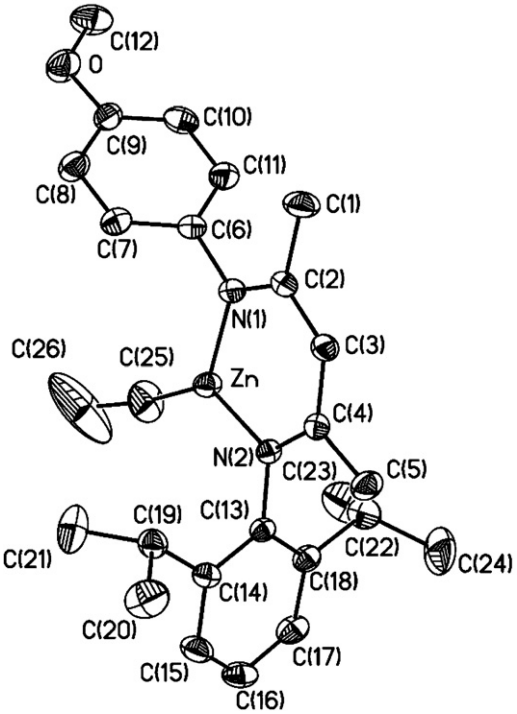


Fig. 1. ORTEP drawing of **3f** [L^{6}ZnEt] (non-hydrogen atoms) with ellipsoids drawn at the 20% probability level. Selected bond lengths (Å) and bond angles (deg): Zn–N(1) 1.962(3), Zn–N(2) 1.961(3), Zn–C(25) 1.949(5), N(1)–Zn–N(2) 96.35(12), N(1)–Zn–C(25) 130.30(2) and N(2)–Zn–C(25) 133.30(2).

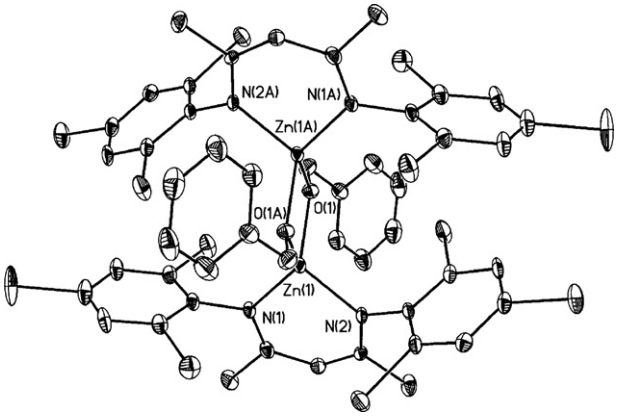


Fig. 2. ORTEP drawing of **4a** [$(L^1)_2Zn_2(\mu$-OBn$)_2$] (non-hydrogen atoms) with ellipsoids drawn at the 20% probability level. Selected bond lengths (Å) and bond angles (deg): Zn(1)–O(1) 1.977(5), Zn(1)–O(1A) 1.959(5), Zn(1)–N(1) 1.989(6), Zn(1)–N(2) 1.998(6), N(1)–Zn(1)–N(2) 96.80(3), O(1)–Zn(1)–O(1A) 82.90(2), Zn(1)–O(1)–Zn(1A) 97.10(2).

2.4. Kinetic studies of polymerization of L-lactide by *4e*

A kinetic study was performed in order to obtain reaction order in monomer and zinc complex for the polymerization of L-

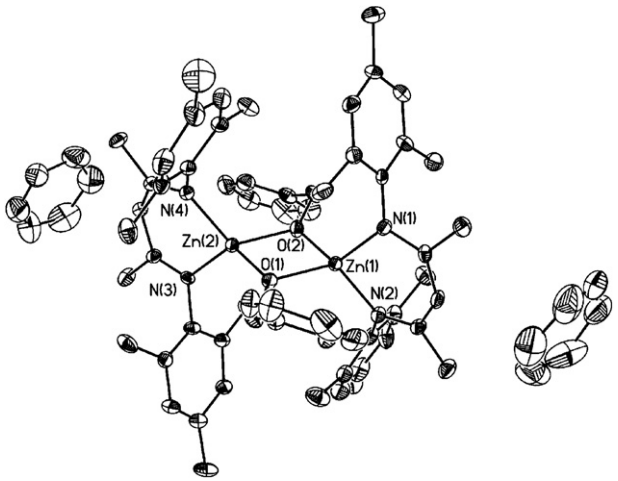


Fig. 3. ORTEP drawing of **4b** [$(L^2)_2Zn_2(\mu$-OBn$)_2$] (non-hydrogen atoms) with ellipsoids drawn at the 20% probability level. Selected bond lengths (Å) and bond angles (deg): Zn(1)–O(1) 1.989(5), Zn(1)–O(2) 1.956(5), Zn(1)–N(1) 1.983(6), Zn(1)–N(2) 1.982(6), Zn(2)–O(1) 1.960(5), Zn(2)–O(2) 1.993(5), Zn(2)–N(3) 1.997(6), Zn(2)–N(4) 2.001(6), N(1)–Zn(1)–N(2) 97.60(3), N(3)–Zn(2)–N(4) 96.60(3), O(1)–Zn(1)–O(2) 81.63(18), O(1)–Zn(2)–O(2) 81.39(19), Zn(1)–O(1)–Zn(2) 98.50(2), Zn(1)–O(2)–Zn(2) 98.50(2).

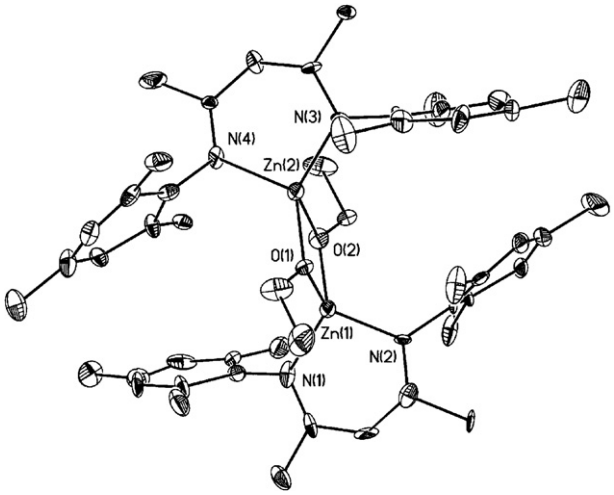


Fig. 4. ORTEP drawing of **4k** [$(L^2)_2Zn_2(\mu\text{-OEt})_2$] (non-hydrogen atoms) with ellipsoids drawn at the 20% probability level. Selected bond lengths (Å) and bond angles (deg): Zn(1)–O(1) 1.985(13), Zn(1)–O(2) 1.899(16), Zn(1)–N(1) 1.938(14), Zn(1)–N(2) 1.934(13), Zn(2)–O(1) 1.982(13), Zn(2)–O(2) 1.989(14), Zn(2)–N(3) 2.008(12), Zn(2)–N(4) 2.029(13), N(1)–Zn(1)–N(2) 98.40(6), N(3)–Zn(2)–N(4) 98.10(6), O(1)–Zn(1)–O(2) 83.10(5), O(1)–Zn(2)–O(2) 80.90(5), Zn(1)–O(1)–Zn(2) 96.70(6), Zn(1)–O(2)–Zn(2) 99.30(7).

lactide with compound **4e**. Conversion of L-lactide with time was recorded by ^{1}H NMR for different concentrations of **4e** at 25 °C until monomer consumption was completed ($[LA]_0/[\mathbf{4e}] = 200$; $[LA]_0 = 0.125$ M in toluene). To ascertain the kinetic order in [**4e**], the dependence of k_{obs} on $[LA]_0$ was analyzed. Plots of $\ln([LA]_0/[LA])$ vs time in a wide range of $[LA]_0$ are linear, showing polymerization proceeds with second-order dependence on monomer concentration (Fig. 5, $k_{obs} = 0.0286\ M^{-1}\ s^{-1}$). Therefore the rate of polymerization can be described as $-d[LA]/dt = k_{obs}[LA]^1$, where $k_{obs} = k[\mathbf{4e}]^x$ and k is the rate constant. Plotting $\ln k_{obs}$ vs ln[**4e**] lets us to determine x, the order in compound **4e** concentration. From the slope of the fitted line as shown in Fig. 6, the rate constant k is $8.37\ M^{-1}\ s^{-1}$. Therefore, on the basis of this analysis, $x = 1$. The reaction is both first order in compound **4e** and monomer concentrations, and the overall rate equation is $-d[LA]/dt = k[LA]^1[\mathbf{4e}]^1$. It is interesting to note that the rate law $-d[LA]/dt = k[LA]^1[\mathbf{4e}]^1$ is different than the rate law of $-d[LA]/dt = k[LA]^2[ini]^1$ found in the trinuclear initiator's system [3h]. The reason may be that the trinuclear complex is less sterically hindered than the dinuclear complex and allows two monomers to bond the active center.

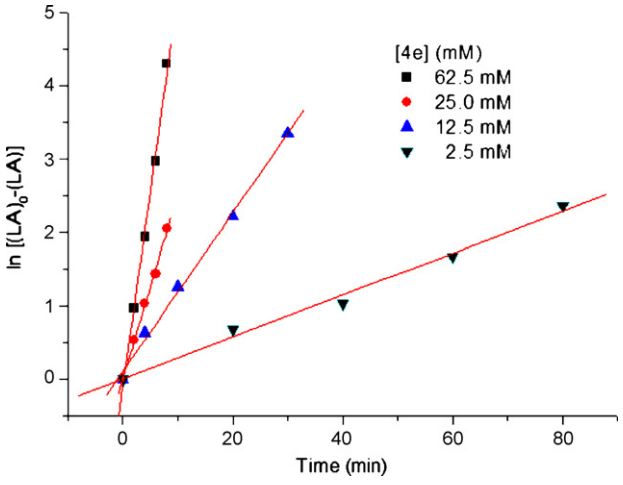


Fig. 5. First-order kinetic plots for L-LA polymerizations with time in toluene with different concentration of complex **4e** as an initiator.

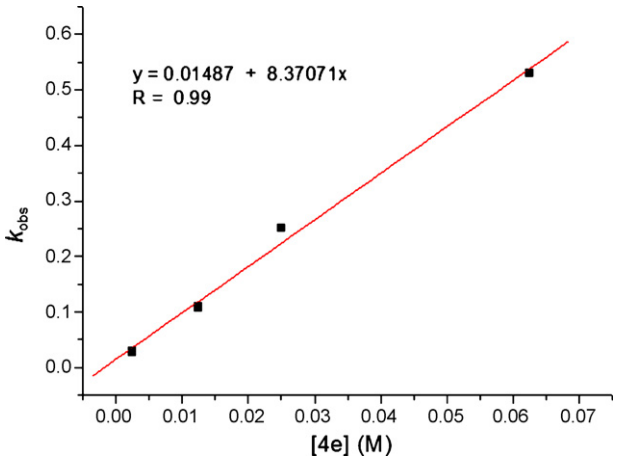


Fig. 6. Linear plot of k_{obs} vs [**4e**] for the polymerization of L-LA with $[LA]_0 = 0.125$ M in toluene. $k = 8.37\ M^{-1}\ s^{-1}$.

3. Conclusions

Zinc complexes **4a–j** supported by symmetrical or unsymmetrical β-diketiminate ligands were readily synthesized. The molecular structure of complex **3f**, **4a**, **4b** and **4k** were further confirmed by X-ray diffraction techniques. The effect of the ligand substituents on both the ROP of lactide and di- or trinuclear zinc structure is significant. It has been found that electron-donating substituents like methoxy group support the formation of trinuclear complexes. And also the electron-donating substituents at the phenyl rings decrease the electrophilicity of the zinc center as well as decrease the bond strength between zinc and BnO^-, and are favorable for the coordination and insertion of lactide monomers, whereas the electron withdrawing group gives the adverse effect. This effect changes the rate of polymerization.

4. Experimental

All manipulations were carried out under a dry nitrogen atmosphere. Solvents, benzyl alcohol, L-lactide and deuterated solvents were purified before uses. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Mercury-400 spectrometer with chemical shifts given in ppm from the internal TMS or center line of $CHCl_3$. Microanalyses were performed using a Heraeus CHN-O-RAPID instrument. The GPC measurements were performed on a Postnova PN1122 solvent delivery system with TriSEC GPC software using THF (HPLC grade) as an eluent. Molecular weight and molecular weight distributions were calculated using polystyrene as standard.

4.1. Synthesis of 2-((2,4,6-tribromophenyl)amino)-4-((2,4,6-tribromophenyl)imino)-2-pentene (L^1H) (**2a**)

2,4,6-Tribromoaniline (32.9 g, 100 mmol), 2,4-pentanedione (5.0 g, 50 mmol), and *p*-toluenesulfonic acid (0.30 mL) were refluxed in absolute toluene (30 mL) for 3 days. After being cooled to room temperature, the solution was passed through silica gel to remove *p*-toluenesulfonic acid and volatile materials were removed under vacuum to obtain a light yellow powder. The solid was then recrystallized from acetone at 0 °C to get white crystals. Yield: 14.3 g (40%). ^{1}H NMR ($CDCl_3$): δ 12.04 (1H, s, N**H**), 7.70 (4H, s, ArH), 5.05 (1H, s, β-CH), 1.81 (6H, s, C=CNC**H$_3$**) ppm. ^{13}C NMR ($CDCl_3$): δ 162.55 (C=N), 142.45, 134.22, 121.73, 118.03 (Ph), 95.22

(β-C), 21.03(C=CN**C**H_3) ppm. Anal. Calc. (found) for $C_{17}H_{12}Br_6N_2$: C 28.21 (28.42), H 1.67 (1.61), N 3.87 (3.94)%.

4.2. Synthesis of [L^1ZnEt] (**3a**)

To a suspension of (L^1H) (3.58 g, 5 mmol) in toluene (15 mL) was added diethyl zinc (7 mL, 7 mmol). After being stirred at 0 °C for 3 h, a light yellow solution was obtained. Volatile materials were removed in vacuo to yield a light yellow powder. Adding 30 mL hexane and washing the solid for 2 h, the white powder was collected by filtration. The white solid was dried in vacuo. Yield: 1.27 g (31%). ^{1}H NMR ($CDCl_3$): δ 7.74 (4H, s, ArH), 5.10 (1H, s, β-CH), 1.82 (6H, s, C=CNC**H$_3$**), 0.65 (3H, t, J = 8.0 Hz, ZnCH$_2$C**H$_3$**), −0.16 (2H, q, J = 8.0 Hz, ZnC**H$_2$**CH$_3$) ppm. ^{13}C NMR ($CDCl_3$): δ 167.87 (C=N), 146.02, 134.33, 121.58, 118.09 (Ph), 96.23 (β-C), 23.20 (C=CN**C**H$_3$), 11.48 (ZnCH$_2$**C**H$_3$), −3.10 (Zn**C**H$_2$CH$_3$) ppm. Anal. Calc. (found) for $C_{19}H_{16}Br_6N_2Zn$: C 27.93 (27.86), H 1.97 (1.92), N 3.43 (3.63)%.

4.3. Synthesis of [(L^1)$_2$Zn$_2$(μ-OBn)$_2$] (**4a**)

To a suspension of L^1ZnEt (2.04 g, 2.5 mmol) in toluene (15 mL) was added BnOH (0.31 mL, 3.0 mmol). When the mixture was stirred for 3 h, the resulting white powder was collected by filtration. After adding 15 mL toluene and 15 mL THF to the solid, the solution was stirred at 70 °C for 1 day and then filtrated. Colorless crystals appeared from the filtrate at −18 °C. NMR data showed a mixture of inseparable products. However, a single crystal suitable for X-ray diffraction analysis could be obtained.

4.4. Synthesis of 2-((2,4,6-trimethylphenyl)amino)-4-((2,4,6-trimethylphenyl)imino)-2-pentene (L^2-H) (**2b**)

The ligand was prepared as described in the literature [15].

4.5. Synthesis of [L^2ZnEt] (**3b**)

To a suspension of (L^2H) (3.34 g, 10 mmol) in hexane (15 mL) was added diethyl zinc (12 mL, 12 mmol). After being stirred at 0 °C for 3 h, a light yellow solution was obtained. Volatile materials were removed in vacuo to yield a yellow powder. After adding 15 mL n-hexane and stirred at 60 °C for 2 h, the solid redissoved in hexane. The light yellow powder was collected by filtration and dried in vacuo after the solution was kept at −18 °C for a week. Yield: 1.71 g (40%). ^{1}H NMR ($CDCl_3$): δ 6.87 (4H, s, ArH), 4.95 (1H, s, β-CH), 2.27 (6H, s, C=CNC**H$_3$**), 2.09 (12H, s, 2,6-(C**H$_3$**)$_2$Ph), 1.71 (6H, s, 4-C**H$_3$**Ph), 0.56 (3H, t, J = 8.0 Hz, ZnCH$_2$C**H$_3$**), −0.26 (2H, q, J = 8.0 Hz, ZnC**H$_2$**CH$_3$) ppm. ^{13}C NMR ($CDCl_3$): δ 166.63 (C=N), 145.19, 133.36, 130.68, 128.75 (Ph), 94.71 (β-C), 22.47 (C=CN**C**H$_3$), 20.82 (2,6-(**C**H$_3$)$_2$Ph), 18.53 (4-**C**H$_3$Ph), 11.39 (ZnCH$_2$**C**H$_3$), −3.53 (Zn**C**H$_2$CH$_3$) ppm. Anal. Calc. (found) for $C_{25}H_{34}N_2Zn$: C 70.17 (69.51), H 8.01 (7.56), N 6.55 (6.24)%.

4.6. Synthesis of [(L^2)$_2$Zn$_2$(μ-OBn)$_2$] (**4b**)

To a suspension of L^2ZnEt (1.07 g, 2.5 mmol) in hexane (15 mL) was added BnOH (0.31 mL, 3.0 mmol). When the mixture was stirred for 3 h, the resulting white powder was collected by filtration. After adding 15 mL of toluene to the solid, the solution was stirred for 15 min and then filtrated. The solid has been recrystallized from solvent hexane by placing at −18 °C for days and dried in vacuo. Colorless crystals appeared from the filtrate at −18 °C. Yield: 0.76 g (60%). ^{1}H NMR ($CDCl_3$): δ 7.11, 7.09, 6.99, 6.97, (5H, m, C$_6$**H$_5$**CH$_2$O), 6.74 (4H, s, ArH), 4.78 (1H, s, β-CH),4.42 (2H, s, PhC**H$_2$**O), 2.36 (6H, s, C=CNC**H$_3$**), 1.61 (12H, s, 2,6-(C**H$_3$**)$_2$Ph), 1.41 (6H, s, 4-C**H$_3$**Ph) ppm. ^{13}C NMR ($CDCl_3$): δ 167.54 (C=N),152.62 (MeO**C**CN), 145.49, 144.25, 132.34, 131.76, 128.93, 127.83, 127.57, 125.88 (Ph), 94.42 (β-C), 68.86 (Ph**C**H$_2$O), 23.02 (C=CN**C**H$_3$), 20.94 (4-**C**H$_3$Ph), 18.18 (2,6-(**C**H$_3$)$_2$Ph) ppm. Anal. Calc. (found) for $C_{60}H_{72}N_4O_2Zn_2$: C 71.23 (71.33), H 7.17 (6.86), N 5.54 (5.38)%.

4.7. Synthesis of 2-((4-chlorophenyl)amino)-4-((4-chlorophenyl)imino)-2-pentene (L^3H) (**2c**)

4-Chloroaniline (12.8 g, 100 mmol), 2,4-pentanedione (5.0 g, 50 mmol), and p-toluenesulfonic acid (0.30 mL) were refluxed in absolute toluene (30 mL) for 12 days. After being cooled to room temperature, the solution was passed through silica gel to remove p-toluenesulfonic acid. Volatile materials were removed under vacuum to give a yellow powder. The solid was recrystallized from ethanol at 0 °C to yield yellow crystals. Yield: 9.57 g (60%). ^{1}H NMR ($CDCl_3$): δ 12.60 (1H, s, N**H**), 7.21 (4H, d, J = 8.8 Hz, ClC(C**H**CH)$_2$CN), 6.84 (4H, d, J = 8.8 Hz, ClC(CHC**H**)$_2$CN), 4.87 (1H, s, β-CH), 1.95 (6H, s, C=CNC**H$_3$**) ppm. ^{13}C NMR ($CDCl_3$): δ 159.51 (C=N), 143.96, 128.70, 128.39, 123.57 (Ph), 97.83 (β-C), 20.65(C=CN**C**H$_3$) ppm. Anal. Calc. (found) for $C_{17}H_{16}Cl_2N_2$: C 63.96 (63.82), H 5.05 (5.24), N 8.78 (8.54)%.

4.8. Synthesis of [(L^3)$_2$Zn] (**4i**)

To a suspension of (L^3H) (3.19 g, 10 mmol) in hexane (15 mL) was added diethyl zinc (12 mL, 12 mmol). After being stirred at 0 °C for 3 h, a light yellow solution was obtained. Volatile materials were removed in vacuo to yield a yellow powder. From the presence of ethyl group signals in the NMR spectra the formation of L^3ZnEt could be deduced. However, disproportionation to (L^3)$_2$Zn over a period of 7 h at room temperature could be observed. Yield: 3.16 g (90%). ^{1}H NMR ($CDCl_3$): δ 7.13 (4H, d, J = 8.4 Hz, ClC(C**H**CH)$_2$CN), 6.49 (4H, d, J = 8.4 Hz, ClC(CHC**H**)$_2$CN), 4.54 (1H, s, β-CH), 1.75 (6H, s, C=CNC**H$_3$**) ppm. ^{13}C NMR ($CDCl_3$): δ 166.46 (C=N), 148.40, 129.67, 128.44, 125.52 (Ph), 96.15 (β-C), 23.04 (C=CNCH$_3$) ppm. Anal. Calc. (found) for $C_{108}H_{104}Cl_{12}N_{12}Zn_3$ (3 (L_3)$_2$Zn. 1 hexane): C 59.19 (59.19), H 4.78 (4.50), N 7.67 (7.31)%.

4.9. Synthesis of [(L^3)$_2$Zn$_2$(μ-OBn)$_2$] (**4c**)

To a suspension of L^3ZnEt (1.07 g, 2.5 mmol) was added BnOH (0.31 mL, 3.0 mmol) in hexane (15 mL). When the mixture was stirred for 3 h, the resulting light yellow powder was collected by filtration. The light yellow solid was dried in vacuo. Yield: 0.49 g (40%). ^{1}H NMR ($CDCl_3$): δ 7.17, 6.86, (5H, s, C$_6$**H$_5$**CH$_2$O), 7.07 (4H, d, J = 4.8 Hz, ClC(C**H**CH)$_2$CN), 6.43 (4H, d, J = 4.8 Hz, ClC(CHC**H**)$_2$CN), 4.54 (1H, s, β-CH), 4.41 (2H, s, PhC**H$_2$**O) 1.61 (6H, s, C=CNC**H$_3$**) ppm. ^{13}C NMR ($CDCl_3$): δ 167.53 (C=N), 148.50, 144.44, 129.25,128.72, 128.54, 128.46, 127.95, 127.03, 126.49, 125.96 (Ph), 95.64 (β-C), 68.66 (Ph**C**H$_2$O), 23.72 (C=CN**C**H$_3$) ppm. Anal. Calc. (found) for $C_{48}H_{44}Cl_4N_4O_2Zn_2$: C 58.74 (57.67), H 4.52 (4.56), N 5.71 (5.55)%.

4.10. Synthesis of 2-((2-methoxy-5-nitrophenyl)amino)-4-((2-methoxy-5-nitrophenyl)imino)-2-pentene (L^4H) (**2d**)

2-Methoxy-5-nitroaniline (16.8 g, 100 mmol), 2,4-pentanedione (5.0 g, 50 mmol), and p-toluenesulfonic acid (0.30 mL) were refluxed in absolute toluene (30 mL) for 9 days. After being cooled to room temperature, the solution was passed through the silica gel to remove p-toluenesulfonic acid. Volatiles materials were removed under vacuum to give deep yellow powder. The solid was recrystallized from 30 mL ethanol and 15 mL chloroform at 0 °C to get a deep yellow crystal. Yield: 8.01 g (40%). ^{1}H NMR ($CDCl_3$): δ 12.97 (1H, s, N*H*), 7.96 (2H, d, J = 8.8 Hz, MeOCCHC**H**CNO$_2$), 7.93 (2H, s, NO$_2$CC**H**CNC), 6.92 (2H, d, J = 8.8 Hz, MeOCC**H**CHCNO$_2$), 5.07 (1H, s, β-CH), 3.90 (6H, s, CH$_3$O), 2.18

(6H, s, C=CNC**H**$_3$) ppm. ^{13}C NMR ($CDCl_3$): δ 160.32 (C=N),155.63 (MeOCCHCH**C**NO_2), 141.37 (MeO**C**CHCHCNO_2), 135.31 (MeOC**C**N), 119.63, 116.70, 110.02 (Ph), 100.31 (β-C), 56.30 (CH_3O), 21.52 (C=CNCH_3) ppm. Anal. Calc. (found) for $C_{19}H_{20}N_4O_6$: C 57.00 (56.61), H 5.03 (5.49), N 13.99 (14.31)%.

4.11. Synthesis of [(L^4)$_2$Zn] (**4j**)

To a suspension of (L^4H) (2.00 g, 5 mmol) in toluene (15 mL) was added diethyl zinc (6 mL, 6 mmol). After being stirred at 0 °C for 3 h, a deep orange solution was obtained. Volatile materials were removed in vacuo to yield a red powder. From the presence of ethyl group signals in the NMR spectra the formation of L^4ZnEt could be deduced. However, disproportionation to (L^4)$_2$Zn over a period of 2 days at room temperature could be observed. After being added toluene (15 mL), stirred until the solid was redissolved and filtrated, the red crystals appeared from the filtrate at −18 °C for 1 day. Yield: 1.17 g (54%). ^{1}H NMR ($CDCl_3$): δ 7.90 (2H, d, J = 9.2 Hz, MeOCCHC**H**CNO_2), 7.68 (2H, s, NO_2CC**H**CNC), 6.77 (2H, d, J = 9.2 Hz, MeOCC**H**CHCNO_2), 4.57 (1H, s, β-CH), 3.76 (6H, s, CH_3O), 1.70 (6H, s, C=C**NCH**$_3$) ppm. ^{13}C NMR ($CDCl_3$): δ 168.61 (C=N), 157.99 (MeOCCHCH**C**NO_2), 141.51 (MeO**C**CHCHCNO_2), 138.91 (MeOC**C**N), 120.93, 120.74, 110.19 (Ph), 96.70 (β-C), 56.07 (CH_3O), 22.95 (C=CN**C**H_3) ppm. Anal. Calc. (found) for $C_{38}H_{38}N_8O_{12}Zn$: C 52.82 (52.17), H 4.43 (4.57), N 12.97 (13.17)%.

4.12. Synthesis of [(L^4)$_2$Zn$_2$(μ-OBn)$_2$] (**4d**)

To a suspension of L^4ZnEt (0.62 g, 1.25 mmol) was added BnOH (0.16 mL, 1.5 mmol) in toluene (15 mL). After stirring the mixture was for 3 h, the resulting deep yellow powder was collected by filtration. The deep yellow solid was dried in vacuo. Yield: 0.45 g (64%). ^{1}H NMR ($CDCl_3$):δ7.83 (2H, br s, MeOCCHC**H**CNO_2), 7.41, 6.89 (5H, br s, C$_6$**H$_5$**CH_2O), 7.26 (2H, br s, NO_2CC**H**CNC), 6.63 (2H, br s, MeOCC**H**CHCNO_2), 4.74 (2H, s, PhC**H$_2$**O), 4.70 (1H, s, β-CH), 3.82 (6H, s, CH_3O), 1.38 (6H, s, C=C**NCH**$_3$) ppm. ^{13}C NMR ($CDCl_3$): δ 169.34 (C=N), 158.70 (MeOCCHCH**C**NO_2), 140.83 (MeO**C**CHCHCNO_2), 139.60 (MeOC**C**N), 128.69, 127.98, 127.03, 123.05, 121.00, 109.47 (Ph), 95.21 (β-C), 69.69 (Ph**C**H_2O), 56.28 (CH_3O), 23.58 (C=CN**C**H_3) ppm. Anal. Calc. (found) for $C_{52}H_{52}N_8O_{14}Zn_2$: C 54.60 (54.23), H 4.58 (4.50), N 9.80 (9.99)%.

4.13. Synthesis of 2-(2-methoxyphenylimino)-4-(pentafluorophenylamido)-2-pentene.(L^5H) (**2e**)

Pentafluoroaniline (21 g, 110 mmol) was mixed with 2,4-pentanedione (12 g, 120 mmol) in 100 mL toluene containing a catalytic amount (0.1 g) of *p*-toluenesulfonic acid. The solution was refluxed for 24 h with water removed using a Dean–Stark trap. Volatile materials were removed under vacuum and the suspension in toluene (100 mL) was added 2-methoxyaniline (14 mL, 120 mmol). The solution was refluxed for 48 h with water removed using a Dean–Stark trap again. After being cooled to room temperature, the product was purified by column chromatography on silica gel with toluene then removal of volatiles afforded a yellow solid. Yield: 29 g (71%). ^{1}H NMR ($CDCl_3$): δ 12.38 (1H, s, N**H**), 7.15–6.89 (4H, m, Ar**H**), 5.00 (1H, s, β-CH), 3.81 (3H, s, ArOC**H$_3$**), 2.12 (3H, s, C**H$_3$**CNArF$_5$), 1.93 (3H, s, C**H$_3$**CNArOMe). ^{13}C NMR ($CDCl_3$): δ 171.45 (CH_3**C**NArF$_5$), 155.87 (CH_3**C**NHOMe), 152.31 (MeO**C**CN), 140.53, 139.09, 138.92, 137.55, 136.74, 136.46, 128.95, 126.08, 125.36, 124.19, 120.28, 111.22 (Ph), 97.54 (β-C), 55.64 (O**C**H_3), 22.23 (**C**H_3CNArOMe), 20.60 (**C**H_3CNHF$_5$). Anal. Calc. (found) for $C_{18}H_{15}F_5N_2O$: C 58.38 (58.73), H 4.08 (4.12), N 7.56 (7.57)%.

4.14. Synthesis of [(L^5)$_2$Zn$_2$(μ-OBn)$_2$] (**4e**)

To a suspension of L^5H (0.37 g, 1.00 mmol) in hexane (20 mL) was added diethyl zinc (1.2 mL, 1.2 mmol). After being stirred at 0 °C for 8 h, a light yellow solution was obtained. Volatile materials were removed in vacuo to yield yellow oil. To an emulsion of the yellow oil in n-hexane (20 mL) was added BnOH (0.11 mL, 1.0 mmol). After stirring for 8 h, the volatile materials were removed in vacuo to yield a light yellow powder. The solid has been recrystallized from solvent toluene by placing at 0 °C for 10 days and dried in vacuo. Yield: 0.34 g (63%). ^{1}H NMR ($CDCl_3$): δ 7.28–6.51 (9H, m, Ar**H**), 4.75 (1H, s, β-CH), 4.57 (2H, br s, PhC**H$_2$**O), 3.61 (3H, s, ArOC**H$_3$**), 1.61 (3H, s, C**H$_3$**CNArF$_5$), 1.38 (3H, s, C**H$_3$**CNArOMe). ^{13}C NMR ($CDCl_3$): δ 171.93 (CH_3**C**NArF$_5$), 166.72 (CH_3**C**NHOMe), 152.02 (MeO**C**CN), 145.00, 143.29, 140.78, 139.09,138.50, 137.56, 136.65, 136.03, 129.02, 128.21, 127.91, 125.45, 125.29, 119.65 (Ph), 95.90 (β-C), 68.85 (Ph**C**H_2O), 55.03 (O**C**H_3), 23.16 (**C**H_3CNArOMe), 20.56 (**C**H_3CNHF$_5$). Anal. Calc. (found) for $C_{52}H_{48}F_{10}N_4O_4Zn_2$ [(L_6)$_2$Zn$_2$(μ-OBn)$_2$. C_2H_6]: C 56.08 (56.76), H 4.34 (4.98), N 5.03 (5.48)%.

4.15. Synthesis of 4-(2,6-diisopropylphenyl) amino-pent-3-en-2-one

2,6-Diisopropylaniline (20 g, 113 mmol) was mixed with 2,4-pentanedione (14.5 mL, 136 mmol) in 20 mL toluene containing a catalytic amount (0.1 g) of *p*-toluenesulfonic acid. The solution was refluxed for 24 h with continued water removal by a Dean–Stark trap. The product was purified by column chromatography on silica gel with n-hexane. Removal of volatiles afforded an orange oil. This orange oil was recrystallized from n-hexane at −18 °C to yield a white solid. Yield: 21 g (71%). ^{1}H NMR ($CDCl_3$): δ 12.06 (1H, s, N**H**), 7.30–7.12 (3H, m, ArH), 5.21 (1H, s, β-CH), 3.03 (1H, sept, J = 6.8 Hz, C**H**Me_2), 2.12 (1H, s, C**H$_3$**COC), 1.71 (1H, s, C**H$_3$**CNHAr), 1.21 (1H, d, J = 6.8 Hz, CH(C**H$_3$**))$_2$, 1.15 (1H, d, J = 6.8 Hz, CH(C**H$_3$**))$_2$. ^{13}C NMR ($CDCl_3$): δ 195.67 (C=O), 163.02 (HC(**C**NHAr), 146.09, 133.33, 128.10, 123.54 (Ph), 95.43 (β-C), 28.83 (**C**H_3C=O), 28.30 (**C**HMe_2), 24.39, 22.46 (CH(**C**H_3)$_2$), 19.91 (**CH$_3$**CNHAr).

4.16. Synthesis of 2-((4-methoxyphenyl)imino)-4-((2,6-diisopropylphenyl)amido)-2-pentene.(L^6H) (**2f**)

4-Methoxyaniline (3.8 g, 31 mmol), 4-(2,6-diisopropylphenyl)amino-pent-3-en-2-one (7.9 g, 31 mmol), and *p*-toluenesulfonic acid (0.10 g) were refluxed in absolute toluene (5 mL) with water removed using a Dean–Stark trap for 2 days. After being cooled to room temperature, the product was purified by column chromatography on silica gel with n-hexane then removal of volatiles afforded a brown solid. The brown solid was recrystallized from the n-hexane to give yellow a solid. Yield: 4.62 g (41%). ^{1}H NMR ($CDCl_3$): δ 12.61 (1H, s, N**H**), 7.14–7.09 (3H, $^{2,6\text{-iPr}2}$Ar**H**), 6.90 (2H, d, J = 6.8 Hz, MeOC(CHC**H**)$_2$CN), 6.81 (2H, d, J = 6.8 Hz, MeOC(C**H**CH)$_2$CN), 4.84 (1H, s, β-CH), 3.78 (3H, s, ArOC**H$_3$**), 2.98 (2H, sept, J = 6.8 Hz, C**H**Me_2), 2.00 (3H, s, C**H$_3$**CNArOMe), 1.69 (3H, s, C**H$_3$**CNH$^{2,6\text{-iPr}2}$Ar), 1.20, 1.11 (12H, d, J = 6.8 Hz, ArCH(C**H$_3$**)$_2$). ^{13}C NMR ($CDCl_3$): δ 163.52 (CH_3**C**NArOMe), 156.77 (CH_3**C**NH$^{2,6\text{-iPr}2}$Ar), 156.12 (MeO**C**(CHCH)$_2$CN), 143.49 (N**C**CCMe$_2$), 140.18 (NC**C**CMe$_2$), 136.58, 124.71, 123.96, 122.85, 114.03 (Ph), 95.09 (β-C), 55.41 (O**C**H_3), 28.21 (Ar**C**H(CH_3)$_2$), 24.04, 22.65 (ArCH(**C**H_3)$_2$), 21.14 (**C**H_3CNArOMe), 20.42 (**C**H_3CNH$^{2,6\text{-iPr}2}$Ar). Anal. Calc. (found) for $C_{24}H_{32}N_2O$: C 79.08 (78.73), H 8.85 (8.36), N 7.68 (7.08)%.

4.17. Synthesis of L^6ZnEt (**3f**)

To a rapidly stirred solution of L^6H (3.64 g, 10 mmol) in dry n-hexane (15 mL) was added $ZnEt_2$ (12 mL, 12 mmol), and

the mixture was stirred at 0 °C for 1 h. After stirring for 3 h at room temperature the solvent was removed in vacuo to yield an light yellow solids which were redissolved in hexane (15 mL). Recrystallized at −18 °C to yield colorless crystals. Yield: 3.66 g, (80%). ^{1}H NMR ($CDCl_3$): δ 7.14 (3H, m, $^{2,6\text{-iPr2}}$Ar**H**), 6.91 (2H, d, J = 6.4 Hz, MeOC(CHC**H**)$_2$CN), 6.83 (2H, d, J = 6.8 Hz, MeOC(C**H**CH)$_2$CN), 4.91 (1H, s, β-CH), 3.77 (3H, s, OCH_3), 3.00 (2H, sept, J = 6.8 Hz, C**H**Me$_2$), 1.94(3H, s, C**H$_3$**CNArOMe), 1.73 (3H, s, C**H$_3$**CNH$^{2,6\text{-iPr2}}$Ar), 1.20, 1.13 (12H, d, J = 6.8 Hz, ArCH(C**H$_3$**)$_2$), 0.58 (3H, t, J = 8 Hz, ZnCH$_2$C**H$_3$**), −0.14 (2H, q, J = 8 Hz, ZnC**H$_2$**CH$_3$). ^{13}C NMR ($CDCl_3$): δ 167.00 (CH$_3$**C**NArOMe), 166.56 (CH$_3$**C**NH$^{2,6\text{-iPr2}}$Ar), 156.27 (MeO**C**(CHCH)$_2$CN), 144.48 (N**C**CCMe$_2$), 143.24 (NC**C**CMe$_2$), 141.35 (MeOC**C**N), 125.38, 125.19, 123.23, 113.79 (Ph), 95.29 (β-C), 55.29 (OCH_3), 27.86(Ar**C**H(CH$_3$)$_2$), 24.08 (ArCH(**C**H$_3$)$_2$), 23.32 (**C**H$_3$CNArOMe), 23.21 (**C**H$_3$CNH$^{2,6\text{-iPr2}}$Ar), 11.60 (ZnCH$_2$**C**H$_3$), −2.68 (Zn**C**H$_2$CH$_3$). Anal. Calc. (found) for $C_{26}H_{36}N_2OZn$: C 68.19 (68.49), H 7.92 (7.66), N 6.12 (6.32)%.

4.18. Synthesis of $[(L^6)_2Zn_3(\mu\text{-OBn})_4]$ (**4f**)

To a rapidly stirred solution of L^{6}ZnEt (2.28 g, 5 mmol) in dry hexane (30 mL) was slowly added BnOH (0.39 mL, 3.75 mmol) at 0 °C. The mixture was allowed to warm to room temperature and stirred for 12 h. The yellow powder was collected by filtration, and washed with hexane (15 mL, 0 °C) three times. The light yellow powder was dried in vacuo. Yield 1.35 g (40%). ^{1}H NMR ($CDCl_3$): δ 7.08 (3H, m, $^{2,6\text{-iPr2}}$Ar**H**), 7.02, 6.78 (10H, br s, ArH), 6.45 (2H, d, J = 8.8 Hz, MeOC(CHC**H**)$_2$CN), 6.40 (2H, d, J = 8.8 Hz, MeOC(C**H**CH)$_2$CN), 4.63 (1H, s, β-CH), 4.20 (4H, br s, PhC**H$_2$**O), 3.47 (3H, s, OCH_3), 2.95(2H, br s, C**H**Me$_2$), 1.70 (3H, s, C**H$_3$**CNArOMe), 1.56 (3H, s, C**H$_3$**CNH$^{2,6\text{-iPr2}}$Ar), 1.00–0.83 (12H, br m, ArCH(C**H$_3$**)$_2$), 0.77 (6H, s, ArCH(C**H$_3$**)$_2$). ^{13}C NMR ($CDCl_3$): δ 168.12 (CH$_3$**C**NArOMe), 167.04 (CH$_3$**C**NH$^{2,6\text{-iPr2}}$Ar), 155.76 (MeO**C**(CHCH)$_2$CN), 144.88 (N**C**CCMe$_2$), 144.12 (NC**C**CMe$_2$), 142.72 (MeOC(CHCH)$_2$**C**N), 142.27, 127.69, 126.94, 125.88, 125.17, 125.03, 123.43, 113.64 (Ph), 94.86 (β-C), 55.05 (OCH_3), 27.57 (Ar**C**H(CH$_3$)$_2$), 24.05 (ArCH(**C**H$_3$)$_2$), 23.69 (**C**H$_3$CNArOMe), 23.31 (**C**H$_3$CNH$^{2,6\text{-iPr2}}$Ar). Anal. Calc. (found) for $C_{76}H_{90}N_4O_6Zn_3$: C 67.53 (67.25), H 6.71 (6.15), N 4.14 (4.24)%.

4.19. Synthesis of 2-((2-methoxyphenyl)imino)4-((2,6-diisopropylphenyl)amido)-2-pentene(L^7-H) (**2g**).

2-Methoxyaniline (7.6 g, 62 mmol), 4-(2,6-diisopropylphenyl)amino-pent-3-en-2-one (15.8 g, 62 mmol), and p-toluenesulfonic acid (0.10 g) were refluxed in absolute toluene (5 mL) for 2 days with continued water removal by a Dean–Stark trap. After being cooled to room temperature, the product was purified by column chromatography on silica gel with n-hexane then removal of volatiles afforded a brown solid. The brown solid was recrystallized from n-hexane to yield a yellow solid. Yield: 12 g (53%). ^{1}H NMR ($CDCl_3$): δ 12.56 (1H, br s, NH), 7.15–6.97 (3H, $^{2,6\text{-iPr2}}$Ar H), 6.90–6.81 (4H, m, Ar H), 4.89 (1H, s, β-CH), 3.69 (3H, s, ArOCH$_3$), 3.00 (2H, sept, J_{H-H} = 6.8 Hz, CHMe$_2$), 2.12 (3H, s, HC{C(C**H$_3$**)NAr}$_2$), 1.69 (3H, s, HC{C(C**H$_3$**)NAr}$_2$), 1.18 (6H, d, J_{H-H} = 6.8 Hz, ArCH(C**H$_3$**)$_2$), 1.11 (6H, d, J_{H-H} = 6.8 Hz, ArCH(C**H$_3$**)$_2$). ^{13}C NMR ($CDCl_3$): δ 163.21 (HC{**C**(CH$_3$)NAr}), 155.97 (HC{**C**(CH$_3$)NAr}), 151.89 (MeO**C**CN), 143.68 (N**C**CCMe$_2$), 140.11 (NC**C**CMe$_2$), 133.01, 123.81, 123.73, 123.19, 120.37, 111.31(Ph), 96.28 (β-C), 55.53 (OCH_3), 28.44 (Ar**C**H(CH$_3$)$_2$), 23.85 (ArCH(**C**H$_3$)$_2$), 22.70 (ArCH(**C**H$_3$)$_2$), 21.09 (HC{C(**C**H$_3$)NAr}$_2$), 20.90 (HC{C(**C**H$_3$)NAr}$_2$).

4.20. Synthesis of [L^{7}ZnEt] (**3g**)

To a rapidly stirred solution of L^{7}H (4.3 g, 11.8 mmol) in dry n-hexane (30 mL) was added ZnEt$_2$ (14 mL, 1.0 M in hexane, 14mmol), and the mixture was stirred at 0 °C for 1 h. After stirring for 12 h at room temperature the solvent was removed in vacuo to yield a sticky yellow solid which was recrystallized from hexane (15 mL) at −18 °C to yield a white microcystalline solid. Yield 4.7 g, (86%). ^{1}H NMR ($CDCl_3$): δ 7.14 (3H, m, $^{2,6\text{-iPr2}}$Ar H), 6.98–6.87 (4H, m, ArH), 4.94 (1H, s, β-CH), 3.78 (3H, s, OCH_3), 3.05 (2H, sept, J_{H-H} = 7 Hz, CHMe$_2$), 1.94(3H, s, HC{C(C**H$_3$**)NAr}$_2$), 1.74 (s, 3H, HC{C(C**H$_3$**)NAr}$_2$), 1.21 (6H, d, J_{H-H} = 6.8 Hz, ArCH(C**H$_3$**)$_2$), 1.14 (6H, d, J_{H-H} = 6.8 Hz, ArCH(C**H$_3$**)$_2$) 0.50 (3H, t, J_{H-H} = 8.2 Hz, ZnCH$_2$C**H$_3$**), −0.263 (2H, q, J_{H-H} = 8 Hz, ZnC**H$_2$**CH$_3$). ^{13}C NMR ($CDCl_3$): δ 166.96 (HC{**C**(CH$_3$)NAr}), 166.34 (HC{**C**(CH$_3$)NAr}), 152.57 (MeO**C**CN), 144.72 (N**C**CCMe$_2$), 141.46 (NC**C**CMe$_2$), 138.92 (MeOC**C**N), 125.72, 125.07, 125.04, 123.21, 120.44, 111.16 (Ph), 95.17 (β-C), 55.50 (OCH_3), 27.87(Ar**C**H(CH$_3$)$_2$), 24.04 (ArCH(**C**H$_3$)$_2$), 23.36 (ArCH(**C**H$_3$)$_2$), 23.27 (HC{C(**C**H$_3$)NAr}$_2$), 22.96 (HC{C(**C**H$_3$)NAr}$_2$), 11.42 (ZnCH$_2$**C**H$_3$), −2.88 (Zn**C**H$_2$CH$_3$).

4.21. Synthesis of $[(L^7)_2Zn_3(\mu\text{-OBn})_4]$ (**4g**)

To a rapidly stirred solution of L^{7}ZnEt (2 g, 4.37 mmol) in dry hexane (30 mL) was slowly added BnOH (0.55 mL, 5.24 mmol) at 0 °C. The mixture was allowed to warm to room temperature and stirred for 12 h. The resulting white powder was collected by filtration, and washed with hexane (15 mL) three times. The white solid was dried in vacuo. The solid was recrystallized from toluene (15 mL) at −18 °C to yield a white microcystalline solid. Yield 1.2 g (40.7%). ^{1}H NMR ($CDCl_3$): δ 7.10–6.45 (17H, m, ArH), 4.69 (1H, s, β-CH), 4.14(4H, br s, OCH_2Ar), 3.44(3H, s, OCH_3), 2.87(2H, br s, CHMe$_2$), 1.64 (3H, s, HC{C(C**H$_3$**)NAr}$_2$), 1.56 (3H, s, HC{C(C**H$_3$**)NAr}$_2$), 0.94 (6H, d, J_{H-H} = 6.8 Hz, ArCH(C**H$_3$**)$_2$), 0.77 (6H, s, ArCH(C**H$_3$**)$_2$). ^{13}C NMR ($CDCl_3$): δ 168.10 (HC{**C**(CH$_3$)NAr}), 167.92 (HC{**C**(CH$_3$)NAr}), 152.63 (MeO**C**CN), 144.41 (N**C**CCMe$_2$), 142.46 (NC**C**CMe$_2$), 138.77 (MeOC**C**N), 127.74, 127.02, 125.73, 124.86, 124.64, 123.35, 120.74, 111.70 (Ph), 94.51 (β-C), 68.30 (Ph**C**H$_2$O), 55.207 (CH$_3$O), 27.45 (Ar**C**H(CH$_3$)$_2$), 24.14 (ArCH(**C**H$_3$)$_2$), (ArCH(**C**H$_3$)$_2$), 23.71 (HC{C(**C**H$_3$)NAr}$_2$), 22.89 (HC{C(**C**H$_3$)NAr}$_2$). Anal. Calc. (found) for $C_{76}H_{90}N_4O_6Zn_3{\cdot}C_6H_5CH_3$:C, 69.04 (68.82); H, 6.84 (6.71); N, 3.88 (3.81)%.

4.22. Typical polymerization procedure

A typical polymerization procedure was exemplified by the synthesis of PLA (cat.**4e** = $[(L^5)_2Zn_2(\mu\text{-OBn})_2]$) at room temperature. The conversion yield (99%) of PLA was analyzed by ^{1}H NMR spectroscopic studies. A mixture of the catalyst (0.0556 g, 0.05 mmol) and L-lactide (0.72 g, 5 mmol) in toluene (20 mL) was stirred at room temperature for 2 h. Volatile materials were removed in vacuo, and the residue was redissoved in THF (10 mL). The mixture was then quenched by the addition of an aqueous acetic acid solution (0.35 N, 10 mL), and the polymer was precipitated on pouring into n-hexane (40 mL) to give white crystalline solids. Yield: 0.50 g (69%).

4.23. Kinetic studies of polymerization of L-LA by **4e**

L-LA (1.25 mmol) was added to a solution of **4e** (with 2.5, 12.5, 25.0, and 62.5 mM) in toluene (10 mL). The mixture was then stirred at room temperature under N_2. At appropriate time intervals, 0.2 mL aliquots were removed and quenched with methanol (1 drop). The aliquots were then dried to constant weight under vacuum and analyzed by ^{1}H NMR.

4.24. X-ray crystallographic studies

Suitable crystals of zinc complexes were sealed in thin-walled glass capillaries under nitrogen atmosphere and mounted on a Bruker AXS SMART 1000 diffractometer. Intensity data were collected in 1350 frames with increasing (width of 0.3° per frame). The absorption correction was based on the symmetry equivalent reflections using SADABS program. The space group determination was based on a check of the Laue symmetry and systematic absences, and was confirmed using the structure solution. The structure was solved by direct methods using a SHELXTL package. All non-H atoms were located from successive Fourier maps and hydrogen atoms were refined using a riding model. Anisotropic thermal parameters were used for all non-H atoms, and fixed isotropic parameters were used for H atoms.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molcata.2011.02.013.

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