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Aluminium complexes containing pyrazolyl–phenolate ligands as catalysts for ring opening polymerization of ε-caprolactone

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ABSTRACT

A series of pyrazolyl–phenolate ligand precursors has been described. Reactions of five pyrazolyl-phenolate ligand precursors, **HOPh^{Me}Pz^{Me}**, **HOPh^{Me}Pz^{tBu}**, **HOPh^{Me}Pz^{Ph}**, **HOPh^{Me}Pz$^{F\text{-}Ph}$** or **HOPh^{H}Pz^{tBu}**, with one molar equivalent of $AlMe_3$ in THF gave the aluminium dimethyl complexes, $Me_2Al(OPh^{R1}Pz^{R2})$ [R1 = methyl, R2 = methyl, $Me_2Al(OPh^{Me}Pz^{Me})$ (**1**); R1 = methyl, R2 = *tert*-butyl, $Me_2Al(OPh^{Me}Pz^{tBu})$ (**2**); R1 = methyl, R2 = phenyl, $Me_2Al(OPh^{Me}Pz^{Ph})$ (**3**); R1 = methyl, R2 = 4-fluorophenyl, $Me_2Al(OPh^{Me}Pz^{F\text{-}Ph})$ (**4**); R1 = H, R2 = *tert*-butyl, $Me_2Al(OPh^{H}Pz^{tBu})$ (**5**)], respectively. The molecular structures are reported for compounds **3** and **5**. Their catalytic activities towards the ring opening polymerization reaction of ε-caprolactone in the presence of benzyl alcohol are also under investigation.

1. Introduction

Environmentally friendly polyesters such as poly(caprolactone) and polylactide as well as their co-polymers have been leading candidates in biomedical and pharmaceutical industries due to their biocompatible and biodegradable properties [1]. Up to date, a diversity of main group and transition metal complexes worked as initiators/catalysts for ring opening polymerization to produce well-controlled polymers has been reported and reviewed [2–10]. In those reports, introduction of suitable auxiliary ligands could prevent polymers from trans-esterifications which always occur as side reactions during the ring opening polymerization. Aluminium-catalyzed polymerization of cyclic esters demonstrated by using complexes containing ligands with *N,O*-coordination modes has been a focus of interest, mainly due to the great success of those complexes bearing salen or salan [11–24], imino-phenolate [25–37] or ketiminate [38–43] ligands in ring opening polymerization. Some of them exhibit significant advances in stereo-controlled polymerization. Pyrazole-containing metal complexes seem to be another attractive focus since Chisholm reported tris(pyrazolyl) hydroborate metal complexes exhibited efficient activities and controlled characters [44–46]. Several aluminium complexes bearing ligands with pendant pyrazolyl functionalities have been reported and applied in catalyzing ring opening polymerization of cyclic esters recently [47–52]. These achievements encouraged us to prepare metal complexes bearing ligands with combination of chelating systems with pyrazolyl and phenolate features for examination of their catalytic activities in ring opening polymerization. In this paper, several phenolate ligand precursors bearing pyrazolyl functionalities and their aluminium dimethyl complexes have been synthesized. Their catalytic activities in ring opening polymerization are also investigated.

2. Results and discussion

2.1. Syntheses and characterization of aluminium complexes

Ligand precursor, **HOPh^{Me}Pz^{Me}**, was prepared by methylation of 3-(2-hydroxy-5-methyl-phenyl)(5-phenyl)pyrazole using NaH and methyl iodide in tetrahydrofuran. Preparation of ligand precursors, **HOPh^{Me}Pz^{tBu}**, **HOPh^{Me}Pz^{Ph}** or **HOPh^{Me}Pz$^{F\text{-}Ph}$**, was straightforward via the condensation reaction of related diketone with *tert*-butyl hydrazine (for **HOPh^{Me}Pz^{tBu}**), phenylhydrazine (for **HOPh^{Me}Pz^{Ph}**) or para-flurophenylhydrazine (for **HOPh^{Me}Pz$^{F\text{-}Ph}$**). Ligand precursor, **HOPh^{H}Pz^{tBu}**, was prepared from condensation of related diketone with *tert*-butyl hydrazine, as shown in (Scheme 1). All of the compounds were characterized by NMR spectroscopy as well as elemental analyses.

Complexes **1**–**5** were synthesized by alkane elimination reactions in moderate to high yields. Treatment of ligand precursors, **HOPh^{Me}Pz^{Me}**, **HOPh^{Me}Pz^{tBu}**, **HOPh^{Me}Pz^{Ph}**, **HOPh^{Me}Pz$^{F\text{-}Ph}$** or **HOPh^{H}Pz^{tBu}**, with one equivalent of $AlMe_3$ in tetrahydrofuran

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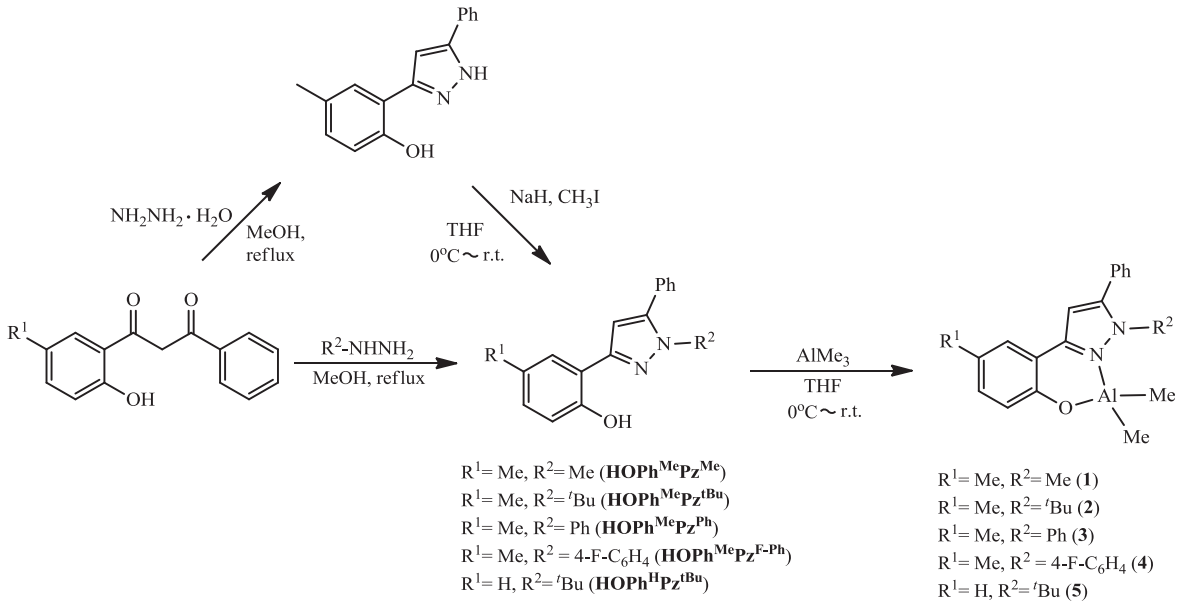

Scheme 1. Synthesis of aluminium pyrazolyl–phenolate complexes **1**–**5**.

yielded the desired aluminium dimethyl complexes **1**–**5**. Complexes **1**–**5** were all characterized by NMR spectroscopy and elemental analyses. The disappearance of the O–H signal of the ligand precursors and the appearance of the resonance for protons of methyl groups in the high field region are consistent with the structures proposed in (Scheme 1). Singlets corresponding to two methyl groups on metal centre, methyl or *tert*-butyl groups on nitrogen atom of pyrazolyl group, proton on pyrazolyl ring, or methyl on phenyl ring might result from the symmetric environment around the metal centre.

Suitable crystals for structural determination of **3** or **5** were obtained from concentrated hexane solutions. Their molecular structures are depicted in Figs. 1 and 2 The structures of **3** or **5** reveal that the aluminium centres adopt a distorted tetrahedral geometry with the metal centres chelated by one nitrogen donor atom of pyrazolyl ring, one oxygen donor atom of phenolate group and two methyl groups. Basically, compounds **3** and **5** are quite similar with different substituents on the phenolate and pyrazolyl groups. The bond distances of Al–$N_{pyrazole}$ 1.9697(12) Å for **3**; 2.0049(13) Å for **5** are in the normal range 1.890(2)–2.037(18) Å found in aluminium pyrazolyl-containing complexes [47,48,50–55]. The bond distances of Al–$O_{phenoxide}$ 1.7737(11) Å for **3**; 1.7814(12) Å for **5** are slightly longer than those found in the literature 1.748(3)–1.7673(15) Å [47,51]. The bond distances of Al–C_{methyl} 1.9584(16) and 1.9595(15) Å for **3**; 1.9521(17) and 1.9637(16) Å for **5** are between those found in the literature 1.933(4)–1.98(1) Å [47,48,50–55].

2.2. Polymerization studies

Due to the successful application of aluminium complexes bearing *N*,*O*-coordination modes ligands in the ring opening polymerization (ROP) [11–43,47–52], the structurally-related aluminium complexes **1**–**5** were expected to work as catalysts

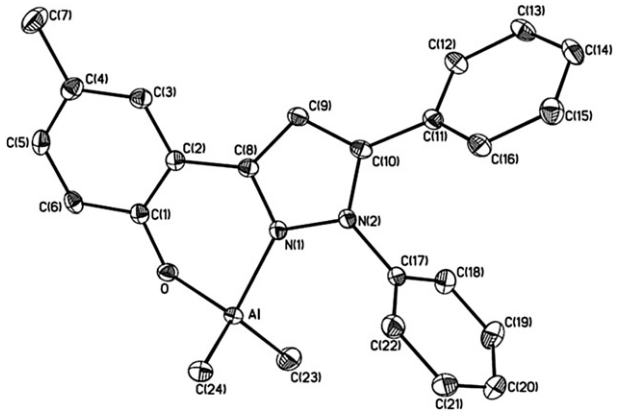

Fig. 1. Molecular structure of **3**. Select bond lengths (Å) and bond angles (°): Al–N(1) 1.9697(12), Al–O 1.7737(11), Al–C(23) 1.9584(16), Al–C(24) 1.9595(15), N(1)–N(2) 1.3691(16), O–C(1) 1.3328(17); O–Al–C(23) 111.17(7), C(23)–Al–C(24) 117.79(7), O–Al–N(1) 91.96(5), C(23)–Al–N(1) 110.95(6), C(24)–Al–N(1) 108.83(6), C(1)–O–Al 129.64(9). Hydrogen atoms on carbon atoms omitted for clarity.

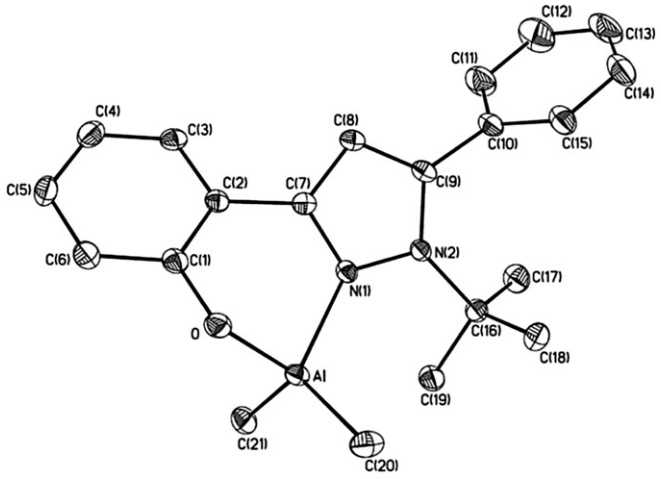

Fig. 2. Molecular structure of **5**. Select bond lengths (Å) and bond angles (°): Al–N(1) 2.0049(13), Al–O 1.7814(12), Al–C(20) 1.9521(17), Al–C(21) 1.9637(16), N(1)–N(2) 1.3778(17), O–C(1) 1.3397(18); O–Al–C(20) 105.03(7), C(20)–Al–C(21) 122.46(7), O–Al–N(1) 94.66(5), C(20)–Al–N(1) 115.12(7), C(21)–Al–N(1) 108.12(7), C(1)–O–Al 121.62(10). Hydrogen atoms on carbon atoms omitted for clarity.

Table 1
Polymerization of ε-Caprolactone using compounds **1**–**5** as catalysts in toluene if not otherwise stated.[a]

Entry	Catalyst	$[M]_0$:$[Al]_0$:[BnOH]	T (°C)	t (min)	M_n (obsd)[b]	M_n (calcd)[c]	Conv. (%)[d]	Yield (%)[e]	M_w/M_n[b]
1[f]	**2**	100:1:2	25	60	–	–	27	–	–
2	**2**	100:1:2	25	60	5000	5400	93	73	1.10
3[g]	**2**	100:1:2	50	20	–	–	49	–	–
4	**2**	100:1:2	50	20	6200	5500	95	79	1.11
5	**1**	100:1:2	50	60	4800	5500	95	37	1.20
6	**3**	100:1:2	50	60	4600	5300	91	70	1.21
7	**4**	100:1:2	50	60	4500	5300	91	73	1.17
8	**5**	100:1:2	50	20	7100	5500	97	81	1.11
9	**2**	200:1:2	50	40	11,500	11,100	96	84	1.21
10	**2**	300:1:2	50	60	15,500	16,700	97	93	1.27
11	**2**	400:1:2	50	80	18,500	22,300	97	96	1.30
12	**2**	200:1:2	25	120	11,100	10,400	90	91	1.14
13	**2**	300:1:2	25	420	16,300	16,700	97	98	1.16
14	**2**	400:1:2	25	540	18,700	21,300	93	90	1.21
15	**2**	200:1:4	25	240	5100	5400	93	90	1.07

[a] In 15 mL.
[b] Obtained from GPC analysis times 0.56.
[c] Calculated from $[M(\text{monomer}) \times [M]_0/[Al]_0 \times \text{conversion yield}/([BnOH]_{eq})] + M(BnOH)$.
[d] Obtained from ^{1}H NMR analysis.
[e] Isolated yield.
[f] In 15 mL CH_2Cl_2.
[g] In 15 mL THF.

towards the ROP of cyclic esters. The ring opening polymerization of ε-caprolactone employing **1**–**5** as catalysts in the presence of benzyl alcohol has been systematically investigated under a dry nitrogen atmosphere. Representative results are shown in Table 1. Experimental conditions were found to be 15 mL toluene at 50 °C in the presence of benzyl alcohol after several trials on running the polymerization with dichloromethane, tetrahydrofuran or toluene at 25 °C or 50 °C using **2** as pre-catalyst (entries 1–4). The optimized conditions were applied to examine the catalytic activities of **1**, **3**, **4** and **5** (entries 5–8). Catalytic results show compounds **2** and **5** can reach similar activities within the same period (entries 4 and 8), whereas compounds **1**, **3** and **4** exhibit poor catalytic activities with time up to 1 h. The catalytic results exhibited by compounds **1** and **2** show the steric effect caused by *tert*-butyl group on the nitrogen atom of the pyrazolyl ring might enhance the catalytic activity of the ROP of ε-caprolactone. Poor conversions demonstrated by **3** and **4** might result from the presence of phenyl rings interfering with the coordination of monomer to the aluminium centre during ROP. Based on those results, electron-donating groups on the nitrogen atom of the pyrazolyl ring could enhance the catalytic activities; however, the electron-withdrawing phenyl substituents in **3** and **4** showed diminished ROP activity resulting from steric and electronic effects. No significant differences of catalytic activities were observed upon changing the substituents on phenolate-part (entries 2 and 8). The linear relationship between the number-average molecular weight (M_n) and the monomer-to-initiator ratio ($[M]_0/[I]_0$) exhibited by **2** at different temperatures implies the "living" character of the polymerization process. Representative results are demonstrated in Fig. 3 (at 50 °C; entries 4, 9–11) and Fig. 4 (at 25 °C; entries 2, 12–14). The "immortal" character was examined using four equiv. ratios (on $[M]_0/[Al]_0$) of benzyl alcohol as the chain transfer agent (entry 15). The M_n of the polymer created from this polymerization reaction became half of those found in the reactions with the addition of two equiv. ratios of benzyl alcohol (entries 9 and 12). The end group analysis is demonstrated by the ^{1}H NMR spectrum of the polymer produced from ε-caprolactone and **2** ($[M]_0/[BnOH] = 50$; Table 1, entry 2), as shown in Fig. 5. Peaks are assignable to the corresponding protons in the proposed structure, indicating the ROP might be initiated with metal benzyl oxide complex first, followed by the ring cleavage of the acyl–oxygen bond to form a metal alkoxide intermediate, which further reacts with excess lactones to yield polyesters [30].

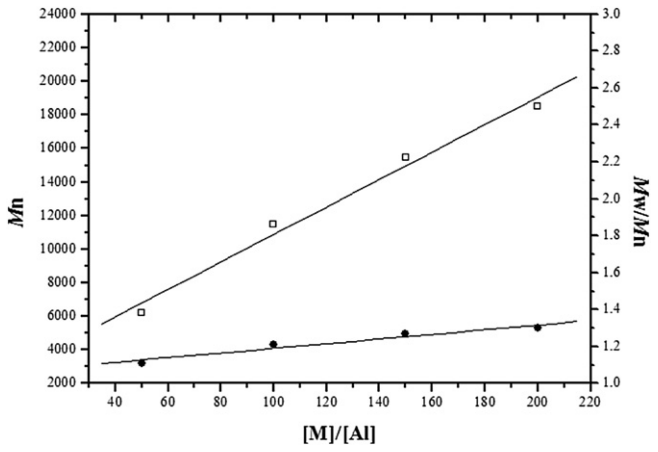

Fig. 3. Polymerization of ε-caprolactone initiated by **2** in toluene at 50 °C.

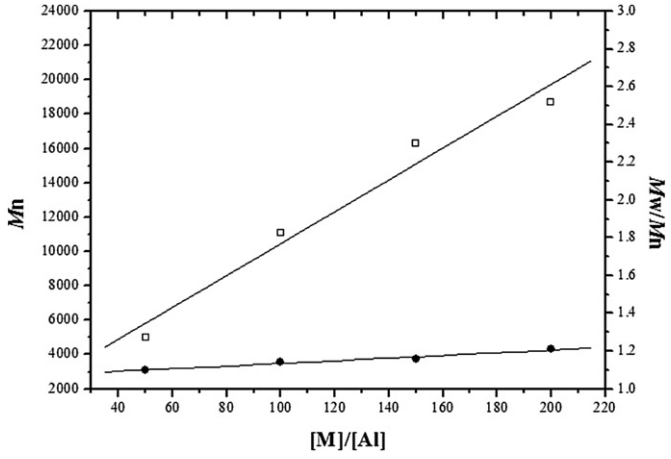

Fig. 4. Polymerization of ε-caprolactone initiated by **2** in toluene at 25 °C.

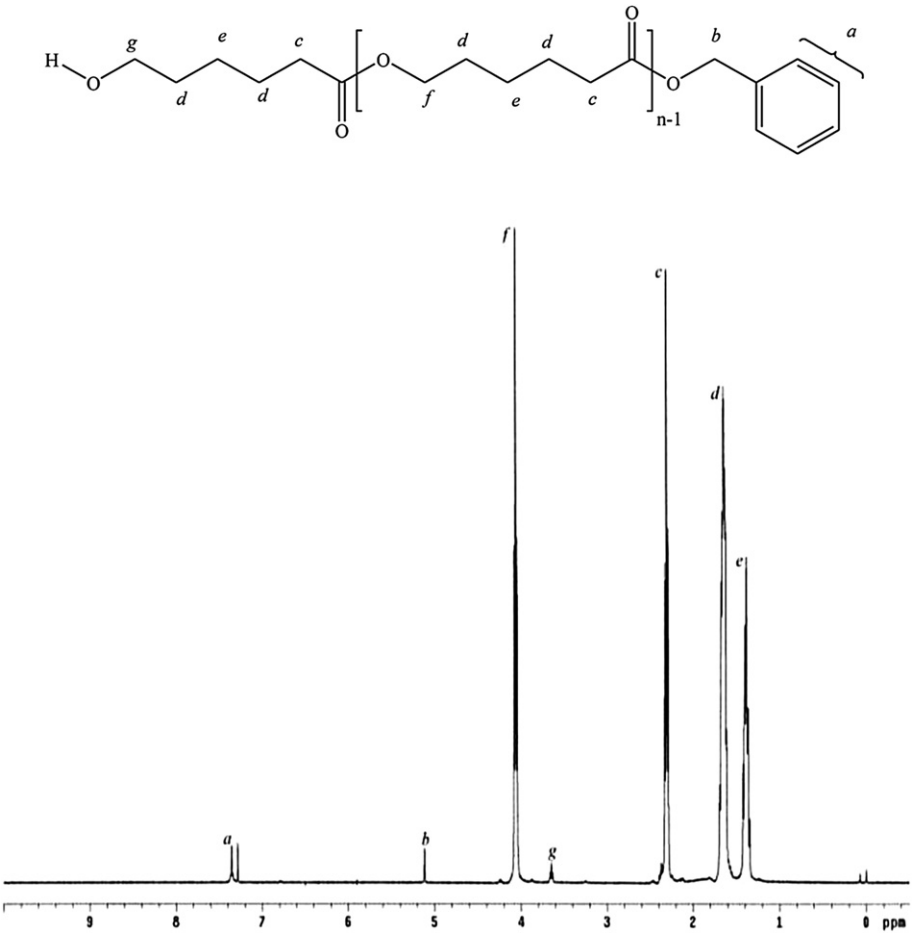

Fig. 5. ^{1}H NMR spectrum of PCL-50 initiated by **2** in toluene at 25 °C (Table 1, entry 2).

3. Conclusion

In conclusion, a family of aluminium dimethyl complexes containing pyrazolyl–phenolate ligands has been prepared and fully characterized. They all show catalytic activities in the ring opening polymerization of ε-caprolactone in the presence of benzyl alcohol. Under optimized conditions, compound **2** demonstrates efficient activities for the controlled polymerization of ε-caprolactone with both living and immortal characters. According to the catalytic results, bulkier aliphatic substituent on the nitrogen atom of pyrazolyl ring seems suitable for the enhancement of catalytic activities. Poor activities demonstrated by complexes bearing ligands with phenyl groups on the nitrogen atom of pyrazolyl ring might result from the electronic effect of aromaticity leading to affect the Lewis acidity of metal centre.

4. Experimental

4.1. General

All manipulations were carried out under an atmosphere of dinitrogen using standard Schlenk-line or dry box techniques. Solvents were refluxed over the appropriate drying agent and distilled prior to use. Deuterated solvents were dried over molecular sieves. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded either on Varian Mercury-400 (400 MHz) or Varian Inova-600 (600 MHz) spectrometers in chloroform-*d* at ambient temperature unless stated otherwise and referenced internally to the residual solvent peak and reported as parts per million relative to tetramethylsilane. Elemental analyses were performed using an Elementar Vario ELIV instrument. The GPC measurements were performed in THF at 35 °C with a Waters 1515 isocratic HPLC pump, a Waters 2414 refractive index detector, and Waters styragel column (HR4E). Molecular weights and molecular weight distributions were calculated using polystyrene as standard. High-resolution mass spectra (EI-HRMS) were recorded with a Finnigan/Thermo Quest MAT 95XL spectrometer.

Methyl iodide (Showa), NaH (Fluka, 55–65% gas-volumetric), hydrazine monohydrate (Alfa), *tert*-butyl hydrazine hydrochloride (TCI), phenylhydrazine (Alfa), 4-flurophenylhydrazine hydrochloride (Acros), 1-(2-hydroxy-5-methylphenyl)-3-phenyl-1,3-propanedione (Acros), 1-(2-hydroxyphenyl)-3-phenyl-1,3-propanedione (Alfa) and $AlMe_3$ (Aldrich, 2.0 M in toluene) were used as supplied. 4-Methyl-2-(5-phenyl-1*H*-pyrazol-3-yl)phenol [56], 3-(2-hydroxy-5-methyl-phenyl)(5-phenyl)(1-methyl)pyrazole [57] were prepared by the literature's method. Benzyl alcohol was dried over magnesium sulphate and distilled before use. NEt_3 was dried with CaH_2 and distilled before use. ε-Caprolactone was dried over magnesium sulphate and distilled under reduced pressure.

4.2. Synthesis of $HOPh^{Me}Pz^{Me}$

A solution of $HOPh^{Me}Pz$ (1.45 g, 5.8 mmol) in 25 mL dry THF was added slowly with NaH (0.46 g of 55–65%, 11.6 mmol) at 0 °C. The reaction mixture was warmed up to room temperature and stirred for a further 3 h until hydrogen evolution ceased. To this solution,

0.36 mL of methyl iodide (5.8 mmol) was added dropwise and resulting mixture was stirred for 12 h at room temperature. The solvent was removed in vacuum and 25 mL of a 1 M solution of $NaHCO_3$ were added to the residue. The aqueous solution was extracted three times with 20 mL diethylether, the organic layer was dried over Na_2SO_4 and filtered. All volatiles were removed under reduced pressure to yield a white solid. The crude product was purified by flash column chromatography on silica gel (ethyl acetate:hexane = 1:5) afforded a white solid (0.69 g, 45%). Anal. Calc. for $C_{17}H_{16}N_2O$: C, 77.25; H, 6.10; N, 10.60. Found: C, 77.25; H, 6.47; N, 10.23. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 10.69 (s, 1H, O*H*), 7.33–7.50 (br, 6H, Ar*H*), 7.02 (d, $^3J_{HH}$ = 8 Hz, 1H, Ar*H*), 6.93 (d, $^3J_{HH}$ = 8.4 Hz, 1H, Ar*H*), 6.65 (s, 1H, Pz*H*), 3.90 (s, 3H, PzCH_3), 2.32 (s, 3H, ArCH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 153.6, 150.2, 144.4, 129.7, 128.0, 116.0 (*C*), 129.6, 128.7, 128.63, 128.60, 126.4, 116.6, 102.2 (ArCH or PzCH), 37.2 (PzCH_3), 20.4 (ArCH_3).

4.3. Synthesis of **HOPh^{Me}Pz^{tBu}**

To a flask containing 1-(2-hydroxy-5-methylphenyl)-3-phenyl-1,3-propanedione (1.52 g, 6.0 mmol), *tert*-butyl hydrazine hydrochloride (0.90 g, 7.2 mmol) and triethylamine (1.25 mL, 9.0 mmol), 30 mL methanol was added. The reaction mixture was refluxed for 12 h and cooled to room temperature. All volatiles were removed under reduced pressure and the residue was extracted with 20 mL toluene to afford brown solid. The crude product was purified by flash column chromatography on silica gel (ethyl acetate:hexane = 1:10) afforded a brown solid (0.82 g, 45%). Anal. Calc. for $C_{20}H_{22}N_2O$: C, 78.40; H, 7.24; N, 9.14. Found: C, 78.22; H, 7.44; N, 8.99. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 11.03 (s, 1H, O*H*), 7.37–7.46 (m, 5H, Ar*H*), 7.31 (d, $^3J_{HH}$ = 0.8 Hz, 1H, Ar*H*), 7.00 (dd, $^3J_{1HH}$ = 8.4 Hz, $^3J_{2HH}$ = 2 Hz, 1H, Ar*H*), 6.92 (d, $^3J_{HH}$ = 8.4 Hz, 1H, Ar*H*), 6.53 (s, 1H, Pz*H*), 2.29 (s, 3H, ArCH_3), 1.50 (s, 9H, PzC(CH_3)$_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 153.7, 148.1, 143.8, 133.2, 128.0, 116.2 (*C*), 130.3, 129.5, 128.7, 127.9, 126.3, 116.5, 105.8 (ArCH or PzCH), 61.5 (PzC(CH$_3$)$_3$), 30.8 (PzC(CH$_3$)$_3$), 20.5 (ArCH$_3$).

4.4. Synthesis of **HOPh^{Me}Pz^{Ph}**

To a flask containing 1-(2-hydroxy-5-methylphenyl)-3-phenyl-1,3-propanedione (1.52 g, 6.0 mmol) and phenylhydrazine (0.708 mL, 7.2 mmol), 40 mL methanol was added. The reaction mixture was refluxed for 12 h and cooled to room temperature. The formed precipitates were successively collected and dried under reduced pressure to yield pink solid. The crude product was purified by flash column chromatography on silica gel (ethyl acetate:hexane = 1:15) afforded a pink solid (1.50 g, 71%). Anal. Calc. for $C_{22}H_{18}N_2O$: C, 80.96; H, 5.56; N, 8.58. Found: C, 81.19; H, 5.89; N, 8.35. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 10.66 (s, 1H, O*H*), 7.44 (dd, $^3J_{1HH}$ = 1.6 Hz, $^3J_{2HH}$ = 0.4 Hz, 1H, Ar*H*), 7.27–7.38 (m, 10H, Ar*H*), 7.06 (dd, $^3J_{1HH}$ = 8 Hz, $^3J_{2HH}$ = 2.4 Hz, 1H, Ar*H*), 6.95 (d, $^3J_{HH}$ = 8.4 Hz, 1H, Ar*H*), 6.88 (s, 1H, Pz*H*), 2.34 (s, 3H, ArCH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 153.9, 151.9, 143.8, 139.3, 129.8, 128.2, 115.7 (*C*), 130.2, 128.89, 128.77, 128.7, 128.5, 127.6, 126.7, 124.8, 116.9, 104.6 (ArCH or PzCH), 20.57 (ArCH_3).

4.5. Synthesis of **HOPh^{Me}Pz$^{F\text{-}Ph}$**

To a flask containing 1-(2-hydroxy-5-methylphenyl)-3-phenyl-1,3-propanedione (1.52 g, 6.0 mmol), 4-fluorophenylhydrazine hydrochloride (1.17 g, 7.2 mmol) and triethylamine (1.25 mL, 9.0 mmol), 40 mL methanol was added. The reaction mixture was refluxed for 12 h and cooled to room temperature. All volatiles were removed under reduced pressure and the residue was washed with 20 mL toluene to afford brown solid. The crude product was purified by flash column chromatography on silica gel (ethyl acetate:hexane = 1:5) afforded a brown solid (0.92 g, 45%). Anal. Calc. for $C_{22}H_{17}FN_2O$: C, 76.73; H, 4.98; N, 8.13. Found: C, 76.73; H, 5.18; N, 7.86. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 10.54 (s, 1H, O*H*), 7.43 (d, $^3J_{HH}$ = 1.6 Hz, 1H, Ar*H*), 7.26–7.37 (m, 7H, Ar*H*), 7.01–7.07 (m, 3H, Ar*H*), 6.95 (d, $^3J_{HH}$ = 1.6 Hz, 1H, Ar*H*), 6.87 (s, 1H, Pz*H*), 2.34 (s, 3H, ArCH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 153.8, 152.0, 143.9, 135.5, 129.6, 128.8, 128.2, 115.6 (*C*), 130.3, 128.8, 128.6, 126.7, 126.6, 116.9, 116.0, 115.7, 104.5 (ArCH or PzCH), 20.5 (ArCH_3).

4.6. Synthesis of **HOPh^{H}Pz^{tBu}**

To a flask containing benzoyl(2-hydroxybenzoyl) methane (1.44 g, 6.0 mmol), *tert*-butyl hydrazine hydrochloride (0.90 g, 7.2 mmol) and triethylamine (1.25 mL, 9.0 mmol), 40 mL methanol was added. The reaction mixture was refluxed for 12 h and cooled to room temperature. All volatiles were removed under reduced pressure and the residue was extracted with 20 mL toluene to afford brown solid. The crude product was purified by flash column chromatography on silica gel (ethyl acetate:hexane = 1:10) afforded a yellow solid (1.00 g, 57%). Anal. Calc. for $C_{19}H_{20}N_2O$: C, 78.05; H, 6.89; N, 9.58. Found: C, 78.30; H, 7.08; N, 9.35. ^{1}H NMR (400 MHz, CDCl3): δ (ppm) 11.23 (s, 1H, O*H*), 7.52 (dd, $^3J_{1HH}$ = 7.8 Hz, $^3J_{2HH}$ = 2 Hz, 1H, Ar*H*), 7.38–7.47 (m, 5H, Ar*H*), 7.19 (t, $^3J_{HH}$ = 7.6 Hz, 1H, Ar*H*), 7.02 (dd, $^3J_{1HH}$ = 8.4 Hz, $^3J_{2HH}$ = 1.2 Hz, 1H, Ar*H*), 6.88 (t, $^3J_{HH}$ = 7.6 Hz, 1H, Ar*H*), 6.53 (s, 1H, Pz*H*), 1.50 (s, 9H, PzC(CH_3)$_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 155.9, 148.0, 143.8, 143.8, 133.1, 116.6 (*C*), 133.1, 130.3, 128.7, 127.9, 125.9, 119.1, 116.7, 105.8 (ArCH or PzCH), 61.5 (PzC(CH$_3$)$_3$), 30.8 (PzC(CH$_3$)$_3$).

4.7. Synthesis of ($Me_2AlOPh^{Me}Pz^{Me}$) (**1**)

To a flask containing **HOPh^{Me}Pz^{Me}** (0.36 g, 1.3 mmol) and 25 mL THF, 0.66 mL $AlMe_3$ (2.0 M in toluene, 1.32 mmol) was added at 0 °C. The reaction mixture was allowed to warm to room temperature and reacted overnight. After 12 h of stirring, the volatiles were removed under reduced pressure. The residue was washed with 15 mL hexane to afford white solid (0.25 g, 57%). Suitable crystals of **1** for structural determination were recrystallized from concentrated hexane solution. Anal. Calc. for $C_{19}H_{21}N_2OAl$: C, 71.23; H, 6.61; N, 8.74. Found: C, 71.03; H, 6.77; N, 8.70. ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.54 (m, 3H, Ar*H*), 7.48 (m, 2H, Ar*H*), 7.36 (d, $^3J_{HH}$ = 2.4 Hz, 1H, Ar*H*), 7.06 (dd, $^3J_{1HH}$ = 8.1 Hz, $^3J_{2HH}$ = 2.4 Hz, 1H, Ar*H*), 6.86 (d, $^3J_{HH}$ = 8.4 Hz, 1H, Ar*H*), 6.75 (s, 1H, Pz*H*), 3.94 (s, 3H, PzCH_3), 2.28 (s, 3H, ArCH_3), -0.65 (s, 6H, AlCH_3). ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 156.3, 151.0, 147.5, 128.7, 126.2, 115.2 (*C*), 132.5, 130.2, 129.1, 129.0, 127.0, 121.1, 103.1 (ArCH or PzCH), 36.1 (PzCH_3), 20.4 (ArCH_3), −8.7 (AlCH_3).

4.8. Synthesis of ($Me_2AlOPh^{Me}Pz^{tBu}$) (**2**)

To a flask containing HOPh^{Me}Pz^{tBu} (0.46 g, 1.5 mmol) and 25 mL THF, 0.75 mL $AlMe_3$ (2.0 M in toluene, 1.5 mmol) was added at 0 °C. The reaction mixture was allowed to warm to room temperature and reacted overnight. After 12 h of stirring, the volatiles were removed under reduced pressure. The residue was washed with 15 mL hexane to afford white solid (0.35 g, 73%). Anal. Calc. for $C_{22}H_{27}AlN_2O$: C, 72.90; H, 7.51; N, 7.73. Found: C, 73.33; H, 7.41; N, 7.32. ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.45–7.49 (m, 4H, Ar*H*), 7.40 (m, 2H, Ar*H*), 7.08 (d, $^3J_{HH}$ = 8.4 Hz, 1H, Ar*H*), 6.88 (d, $^3J_{HH}$ = 7.8 Hz, 1H, Ar*H*), 6.56 (s, 1H, Pz*H*), 2.27 (s, 3H, ArCH_3), 1.62 (s, 9H, PzC(CH_3)$_3$), -0.59 (s, 6H, AlCH_3). ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 156.1, 152.2, 148.7, 132.5, 129.5, 126.5, 116.7 (*C*), 132.6, 129.4, 128.4, 127.7, 120.4, 109.0 (ArCH or PzCH), 63.9 (PzC(CH$_3$)$_3$), 32.3, (PzC(CH$_3$)$_3$), 20.5 (ArCH_3), −7.3 (AlCH_3).

4.9. Synthesis of ($Me_2AlOPh^{Me}Pz^{Ph}$) (**3**)

To a flask containing $HOPh^{Me}Pz^{Ph}$ (0.37 g, 1.1 mmol) and 25 mL THF, 0.57 mL $AlMe_3$ (2.0 M in toluene, 1.1 mmol) was added at 0 °C. The reaction mixture was allowed to warm to room temperature and reacted overnight. After 12 h of stirring, the volatiles were removed under reduced pressure. The residue was washed with 15 mL hexane to afford white solid (0.32 g, 74%). Anal. Calc. for $C_{24}H_{23}N_2OAl$: C, 75.37; H, 6.06; N, 7.33. Found: C, 74.96; H, 6.35; N, 6.93. ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.51 (t, $^3J_{HH} = 7.2$ Hz, 1H, Ar*H*), 7.46 (t, $^3J_{HH} = 7.8$ Hz, 2H, Ar*H*), 7.42 (s, 1H, Ar*H*), 7.36 (m, 3H, Ar*H*), 7.31 (t, $^3J_{HH} = 7.2$ Hz, 2H, Ar*H*), 7.25 (d, $^3J_{HH} = 7.8$ Hz, 2H, Ar*H*), 7.09 (dd, $^3J_{1HH} = 8.4$ Hz, $^3J_{2HH} = 1.8$ Hz, 1H, Ar*H*), 6.99 (s, 1H, Pz*H*), 6.87 (d, $^3J_{HH} = 8.4$ Hz, 1H, Ar*H*), 2.32 (s, 3H, $ArCH_3$), −1.07 (s, 6H, $AlCH_3$). ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 156.8, 152.2, 147.3, 132.9, 127.6, 126.2, 115.2 (*C*), 136.4, 130.7, 129.7, 129.6, 128.7, 128.4, 127.2, 121.2, 103.7 (Ar*C*H or Pz*C*H), 20.5 ($ArCH_3$), −9.3 ($AlCH_3$).

4.10. Synthesis of ($Me_2AlOPh^{Me}Pz^{F\text{-}Ph}$) (**4**)

To a flask containing $HOPh^{Me}Pz^{F\text{-}Ph}$ (0.51 g, 1.5 mmol) and 25 mL THF, 0.75 mL $AlMe_3$ (2.0 M in toluene, 1.5 mmol) was added at 0 °C. The reaction mixture was allowed to warm to room temperature and reacted overnight. After 12 h of stirring, the volatiles were removed under reduced pressure. The residue was washed with 15 mL hexane to afford brown solid (0.29 g, 48%). Anal. Calc. for $C_{24}H_{22}FN_2OAl$: C, 71.99; H, 5.54; N, 7.00. Found: C, 71.48; H, 6.03; N, 6.65. ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.33–7.42 (m, 6H, Ar*H*), 7.26 (d, $^3J_{HH} = 7.2$ Hz, 2H, Ar*H*), 7.15 (t, $^3J_{HH} = 7.8$ Hz, 2H, Ar*H*), 7.11 (d, $3J_{HH} = 7.8$ Hz, 1H, Ar*H*), 6.99 (s, 1H, Pz*H*), 6.87 (d, $^3J_{HH} = 7.8$ Hz, 1H, Ar*H*), 2.32 (s, 3H, $ArCH_3$), −1.06 (s, 6H, $AlCH_3$). ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 162.6, 156.8, 152.3, 147.6, 132.4, 127.4, 126.3, 115.0 (*C*), 133.1, 130.6, 130.5, 129.9, 128.9, 128.7, 127.2, 121.2, 116.9, 116.7, 103.8 (Ar*C*H or Pz*C*H), 20.5 ($ArCH_3$), −9.2 ($AlCH_3$).

4.11. Synthesis of ($Me_2AlOPh^{H}Pz^{tBu}$) (**5**)

To a flask containing $HOPh^{H}Pz^{tBu}$ (0.29 g, 1 mmol) and 25 mL THF, 0.50 mL $AlMe_3$ (2.0 M in toluene, 1.0 mmol) was added at 0 °C. The reaction mixture was allowed to warm to room temperature and reacted overnight. After 12 h of stirring, the volatiles were removed under reduced pressure. The residue was washed with 15 mL hexane to afford white solid (0.19 g, 55%). Anal. Calc. for $C_{21}H_{25}AlN_2O$: C, 72.39; H, 7.23; N, 8.04. Found: C, 71.92; H, 7.12; N, 8.04. ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.45–7.49 (m, 4H, Ar*H*), 7.39–7.40 (m, 2H, Ar*H*), 7.26 (t, $^3J_{HH} = 7.2$ Hz, 1H, Ar*H*), 6.97 (d, $^3J_{HH} = 8.4$ Hz, 1H, Ar*H*), 6.78 (t, $^3J_{HH} = 7.2$ Hz, 1H, Ar*H*), 6.56 (s, 1H, Pz*H*), 1.63 (s, 9H, $PzC(CH_3)_3$), −0.58 (s, 6H, $AlCH_3$). ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 158.4, 152.2, 148.8, 132.4, 117.2 (*C*), 131.7, 129.5, 129.4, 128.4, 127.6, 120.7, 117.7, 109.1 (Ar*C*H or Pz*C*H), 64.0 ($PzC(CH_3)_3$), 32.3 ($PzC(CH_3)_3$), −7.2 ($AlCH_3$).

4.12. General procedure for ε-caprolactone polymerization

Typically, to a flask containing prescribed amount of catalysts (0.125 mmol) was added 15 mL toluene (containing 0.25 mmol benzyl alcohol). After 5 min of stirring, prescribed amount of monomers (ε-caprolactone) was added. The reaction mixture was stirred at prescribed temperature for prescribed time. After the reaction was quenched by the addition of 10 mL acetic acid solution (0.35 N), the resulting mixture was poured into 50 mL *n*-heptane to precipitate polymers. Crude products were recrystallized from THF/hexane and dried *in vacuo* up to a constant weight.

Table 2
Summary of crystal data for compounds **3** and **5**.

	3	**5**
Empirical formula	$AlC_{24}H_{23}N_2O$	$AlC_{21}H_{25}N_2O$
Formula mass	382.42	348.41
T, K	100(2)	100(2)
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$C2/c$
a, [Å]	10.7074(3)	22.8072(7)
b, [Å]	9.0691(2)	9.2707(3)
c, [Å]	21.3827(5)	18.2968(6)
α [°]	90	90
β [°]	95.887(2)	96.984(3)
γ [°]	90	90
V, [Å^3]	2065.45(9)	3839.9(2)
Z	4	8
ρ_{calc}, [Mg/m^3]	1.230	1.205
μ(Mo K$_\alpha$), [mm^{-1}]	0.114	0.116
Reflections collected	9303	9954
No. of parameters	253	226
R_1[a]	0.0403	0.0425
wR_2[a]	0.1350	0.1177
GoF[b]	1.006	1.001

[a] $R_1 = [\Sigma|F_0| - |F_c|]/\Sigma|F_0|]$; $wR_2 = [\Sigma w(F_0^2 - F_c^2)^2/\Sigma w(F_0^2)^2]^{1/2}$, $w = 0.10$.
[b] $GoF = [\Sigma w(F_0^2 - F_c^2)^2/(N_{rflns} - N_{params})]^{1/2}$.

4.13. X-ray crystallography

Crystals **3** and **5** were grown from concentrated hexane solutions and isolated by filtration. Suitable crystals of **3** or **5** were mounted onto a glass fibre using perfluoropolyether oil and cooled rapidly in a stream of cold nitrogen gas using an Oxford Cryosystems Cryostream unit. Diffraction data were collected at 100 K using Oxford Gemini S diffractometer. The absorption correction was based on the symmetry equivalent reflections using the SADABS program [58]. 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 [59]. 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. Some details of the data collection and refinement are given in Table 2.

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Appendix A. Supplementary material

CCDC-875010 (for **3**) and 875011 (for **5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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