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PAPER

Methylaluminium 8-quinolinolates: synthesis, characterization and use in ring-opening polymerization (ROP) of ε-caprolactone†

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The stoichiometric reactions of 2-(2,6-R-phenylimino)quinolin-8-ol (**L1–L5**, **L1**: R = Me, **L2**: R = Et, **L3**: R = ^{i}Pr, **L4**: R = Cl, **L5**: R = F) with Me_3Al afforded the dimeric aluminium complexes $[Me_2AlL]_2$ (**1–5**) in good yields. By contrast, stoichiometric reactions of 2-(1-(2,6-R-phenylimino)propyl) quinolin-8-ol (**L6–L10**, **L6**: R = Me, **L7**: R = Et, **L8**: R = ^{i}Pr, **L9**: R = Cl, **L10**: R = F)) with Me_3Al gave the mononuclear aluminium complexes Me_2AlL (**6–10**) accompanied with by-products of the form $Me_2AlL{\cdot}Me_3Al$ (**11–15**). All methylaluminium complexes were characterized by NMR spectroscopy, elemental analysis, and the molecular structures of complexes **3**, **6** and **8** were determined by single-crystal X-ray diffraction. Aluminium compounds **1–5** possessed negligible activity towards the ring-opening polymerization of ε-caprolactone either in the presence or absence of BnOH. In contrast, in the presence of BnOH, the mononuclear aluminium compounds **6–10** could efficiently initiate the ring-opening polymerization of ε-caprolactone; the polymerization proceeded in a living manner.

1. Introduction

Recent environmental concerns call for developing environmentally friendly materials.[1] Poly(ε-caprolactone) (PCL) is considered a topical material due to its practical biocompatibility, allowing for its potential applications in the medical, pharmaceutical and tissue engineering arenas.[2] Ring-opening polymerization (ROP) of ε-caprolactone (CL) catalyzed by metal complexes permits excellent controllability over the molecular weight and distribution of the resultant polymer.[2] Thus far, a wide range of metal catalysts or initiators have been developed by combination of various ligands with a range of metals, which include magnesium, calcium, aluminium, titanium, iron, zinc, tin, and rare earth metals.[1–5] Among the reported catalysts, aluminium complexes are promising candidates for industrial application due to their high activity and low toxicity.[3] Although aluminium complexes bearing 8-quinolinolato(Q) derivatives are well known as the emissive and electron transporting material in organic light-emitting devices (OLEDs),[6–8] the catalytic behavior of such species is rather limited. This is primarily because the reaction of 8-quinolinolato(Q) derivatives with R_3Al usually affords either AlQ_3-type complexes or dimeric aluminium complexes $[Al(R)_2Q]_2$, both of which disfavor the initiation of the ROP of ε-CL.[9–11] With this in mind, we have embarked upon a programme to explore the scope of aluminium compounds bearing ligands derived from bulky 2-(arylimino)quinolin-8-ols (**L**). The steric hindrance associated with the 2-(arylimino) quinolin-8-ols (**L**) can be controlled through judicious choice of arylimino groups and can thus be used to prevent the formation of AlL_3 type complexes, instead favoring mononuclear Me_2AlL or dimeric $[Me_2AlL]_2$ complexes. The new mononuclear compounds Me_2AlL are highly active for the ROP of ε-CL acting in a living fashion in the presence of BnOH. Herein, the synthesis and characterization of the title aluminium compounds bearing 2-(arylimino)quinolin-8-olates are reported in detail, as well as the catalytic behavior of the mononuclear aluminium compounds **6–10** in the ROP of ε-CL.

2. Results and discussion

2.1 Synthesis and characterization of aluminium compounds 1–10

The ligands (**L1–L5**) were prepared by the condensation reaction of 8-hydroxyquinoline-2-carbaldehyde with the corresponding substituted anilines (Scheme 1).[12] All organic compounds **L1–L5** were isolated as yellow powders by column chromatography, and fully characterized by IR, ^{1}H NMR, ^{13}C NMR spectroscopy and elemental analysis.

The dimeric aluminium compounds **1–5** were synthesized in good yields by the stoichiometric reaction of Me_3Al with the corresponding ligands **L1–L5** in *n*-heptane (Scheme 1) according to the previous procedure.[9–11] Resultant aluminium compounds were precipitated from the reaction solutions as yellow powders. After being filtered and washed twice with *n*-heptane, they were

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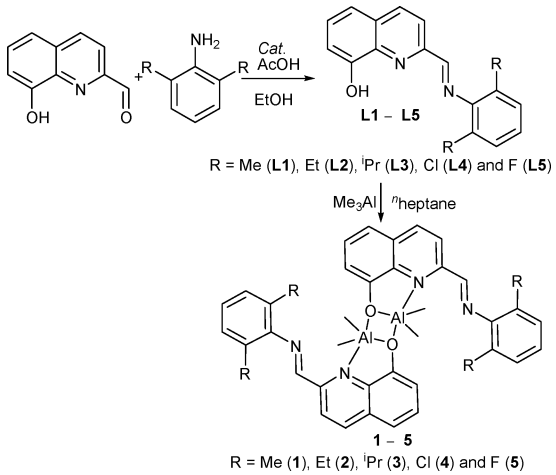


Scheme 1 Synthesis of ligands **L1–L5** and dimeric aluminium compounds **1–5**.

confirmed to be the expected complexes by ^{1}H NMR spectra and elemental analysis. Comparison of the ^{1}H NMR spectra with those of the corresponding ligand **L1–L5**, showed additional resonances in the high field region (–0.60 to –0.40 ppm), which are attributed to the methyl groups attached to the aluminium centers, while the O–*H* signals (broad single peak around 8.17 ppm) of the free ligands had, as expected, disappeared. These aluminium compounds **1–5** are insoluble in *n*-heptane and only slightly soluble in toluene, THF, CH_2Cl_2 and $CHCl_3$.

The molecular structure of aluminium compound **3** was determined by single-crystal X-ray crystallography. The ORTEP diagram is shown in Fig. 1; selected bond lengths and angles are given in the caption. Compound **3** has a dimeric structure with a lozenge plane occupying Al(1), Al(1a), O(1), and O(1a) atoms. The two methyl groups bonded to the same Al center are on the opposite side from the lozenge plane. The Al(1)–O(1) and Al(1a)–O(1) bond lengths are approximately the same as those of Al(1a)–O(1a) and Al(1)–O(1a), respectively. The O(1)–Al(1)–O(1a), O(1)–Al(1a)–O(1a), Al(1)–O(1a)–Al(1a) and Al(1)–O(1)–Al(1a) bond angles are 72.99(15), 73.80(13), 105.97(17) and 107.19(18)°, respectively. The non-ligating imino nitrogen atoms [N(2), N(2a)] adopt an *anti* geometry with respect to the quinoline nitrogen atoms [N(1), N(1a)], placing it in a distal relationship to the aluminium centre. The coordination geometry and bond lengths around the Al centers are similar to the reported dimeric compound $[Et_2Al(quinolin\text{-}8\text{-}olate)]_2$.[9] The Al–O distances for Al(1)–O(1), Al(1a)–O(1a), Al(1a)–O(1) and Al(1)–O(1a) [1.882(3), 1.890(3), 2.001(3) and 2.029(3) Å] are very close to those in previously reported structure $[Et_2Al(quinolin\text{-}8\text{-}olate)]_2$ [1.882(3), 1.868(3), 2.003(4) and 2.009(4) Å, respectively].[9] The Al–N bond distances [Al(1)–N(1) 2.181(3) and Al(1a)–N(1a) 2.208(4) Å] in **3**, however, are somewhat longer than those in the analogue $[Et_2Al(quinolin\text{-}8\text{-}olate)]_2$ [2.132(5) Å], due to the steric repulsion of the arylimino groups.

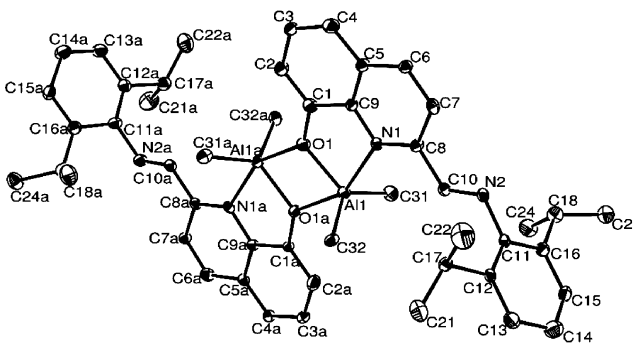
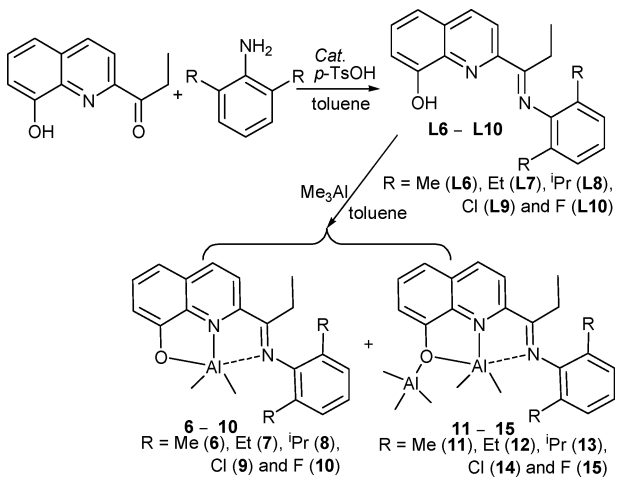


Fig. 1 ORTEP drawing of **3** with thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Al(1)–O(1) 1.882(3), Al(1)–C(32) 1.963(5), Al(1)–C(31) 1.989(6), Al(1)–O(1A) 2.029(3), Al(1)–N(1) 2.181(3), Al(1A)–O(1A) 1.890(3), Al(1A)–C(31A) 1.975(6), Al(1A)–O(1) 2.001(3), Al(1A)–C(32A) 2.065(5), Al(1A)–N(1A) 2.208(4), O(1)–Al(1)–O(1A) 72.99(15), C(31)–Al(1)–O(1A) 96.7(2), C(32)–Al(1)–O(1A) 96.3(2), O(1)–Al(1)–N(1) 79.13(16), C(31)–Al(1)–N(1) 95.9(2), C(32)–Al(1)–N(1) 96.3(2), O(1A)–Al(1)–N(1) 152.12(16), O(1)–Al(1)–C(31) 117.2(3), O(1)–Al(1)–C(32) 116.9(2), C(31)–Al(1)–C(32) 125.8(3), C(1A)–O(1A)–Al(1A) 121.5(3), C(1A)–O(1A)–Al(1) 132.3(3), Al(1A)–O(1A)–Al(1) 105.97(17), O(1A)–Al(1A)–O(1) 73.80(13), C(31A)–Al(1A)–C(32A) 125.5(2), O(1)–Al(1A)–C(32A) 97.96(18), O(1A)–Al(1A)–N(1A) 78.77(14), C(31A)–Al(1A)–N(1A) 96.09(19), O(1)–Al(1A)–N(1A) 152.57(14), C(32A)–Al(1A)–N(1A) 93.85(18).

The ligands (**L6–L10**) were prepared in moderate (acceptable) yields by the condensation reaction of 1-(8-hydroxyquinolin-2-yl)propan-1-one with the corresponding anilines. The stoichiometric reactions of **L6–L10** (for which an ethyl group has been introduced at the imino-carbon) with Me_3Al in toluene gave the mononuclear compounds Me_2AlL (**6–10**) as major products (yields > 90%) and minor by-products $Me_2AlL{\cdot}AlMe_3$ (**11–15**), the structures of which were confirmed by ^{1}H NMR spectroscopy (Scheme 2). The steric hindrance enhanced the bonding between the metal center with the nearby N-atom and reduced further possible aggregation, as reported within alkylaluminium bis(2-methyl-8-quinolinolate)[9] and scandium complexes.[13] In these reactions, the formation of binuclear compounds **11–15** seems unavoidable, and they are obtained as yellow powders precipitated from chilled toluene solutions. Compounds **11–15** were insoluble in saturated hydrocarbons and only slightly soluble in toluene, THF, CH_2Cl_2 and $CHCl_3$. Using saturated hydrocarbons as reaction solvents can increase the yield of the binuclear compounds. Analytically pure samples of **6–10** were collected from the concentrated toluene–*n*-hexane solutions containing the Al complexes cooled in a freezer (–30 °C). Comparing their ^{1}H NMR spectra, there is no signal



Scheme 2 Synthesis of ligands **L6–L10** and aluminium compounds **6–15**.

attributable to the proton of O–*H* in the ligands, whilst at high field one or two sets of signals for the groups $(CH_3)_2$Al and $(CH_3)_3$Al occur in the range δ –0.49 to –0.70 ppm.

Single crystals of compounds **6** and **8** were obtained from toluene/*n*-heptane solutions at –30 °C. Their molecular structures were determined by single-crystal X-ray diffraction. The molecular structure of **6** is shown in Fig. 2, with selected bond lengths and angles given in the caption. The geometry around the Al metal center can be described as a distorted trigonal pyramid. The quinoline nitrogen atom and the two methyl carbon atoms form an equatorial plane. The deviation of the aluminium atom from the equatorial plane is 0.158 Å. The phenyl ring is almost perpendicularly oriented (85.9°) to the coordination plane containing the ligand backbone and the aluminium atom. The Al–C bond distances in **6** [1.971(5) Å, 1.975(5) Å] are typical,[4–9] while the Al(1)–O(1) bond length at 1.891(3) Å is characteristic for an oxygen atom of a σ–bond, which is a little longer than that found in C7 (1.777(2) Å).[14a] The Al(1)–N(1) (nitrogen of quinoline) bond length is 2.010(4) Å, which is longer than that found in C7 (1.987(2)).[14a] It is noted that the Al(1)–N(2)(imino) bond length (2.389(4) Å) is substantially longer than typical Al–N coordination bond distances (about 2.0 Å),[14] which indicates the weak interaction between the Al and imino nitrogen atom in **6**.

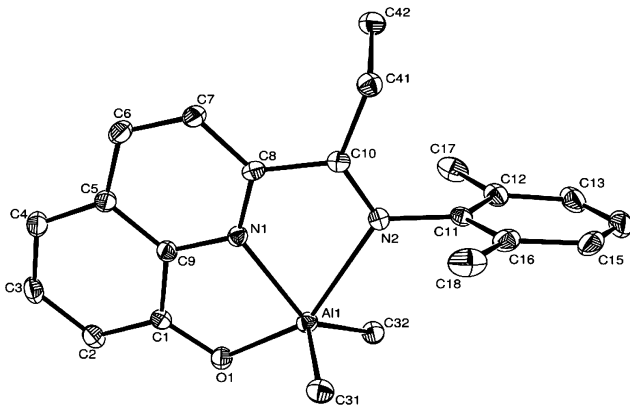


Fig. 2 ORTEP drawing of **6** with thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Al(1)–O(1) 1.891(3), Al(1)–C(32) 1.971(5), Al(1)–C(31) 1.975(5), Al(1)–N(1) 2.010(4), Al(1)–N(2) 2.389(4), N(2)–C(10) 1.282(5), O(1)–Al(1)–C(32) 99.10(17), O(1)–Al(1)–C(31) 103.54(18), C(32)–Al(1)–C(31) 119.2(2), O(1)–Al(1)–N(1) 81.46(14), C(32)–Al(1)–N(1) 129.06(18), C(31)–Al(1)–N(1) 109.87(18), O(1)–Al(1)–N(2) 150.45(14), C(32)–Al(1)–N(2) 92.75(16), C(31)–Al(1)–N(2) 93.90(17), N(1)–Al(1)–N(2) 70.15(13), N(2)–C(10)–C(8) 114.2(4).

The molecular structure of **8** is illustrated in Fig. 3, together with selected bond lengths and angles. The molecular structure of **8** shows the O(1)-quinoline–C(10)–N(2) portion of the ligand to be coplanar to within 0.03 Å, a geometry very similar to **6**. Here, the aluminium atom lies 0.37 Å out of the plane and adopts a severely distorted tetrahedral geometry with angles at aluminium ranging between 82.54(1) and 132.69(14)°. The imino nitrogen N(2) points into the flattened 'basal' face of the tetrahedron; the aluminium atom lies only 0.189 Å out of the N(1)–C(31)–C(32) plane, but lies between 0.658 and 0.994 Å out of the other tetrahedral faces. The distance of N(2)–Al(1) is long at 2.458 Å, but given the potential

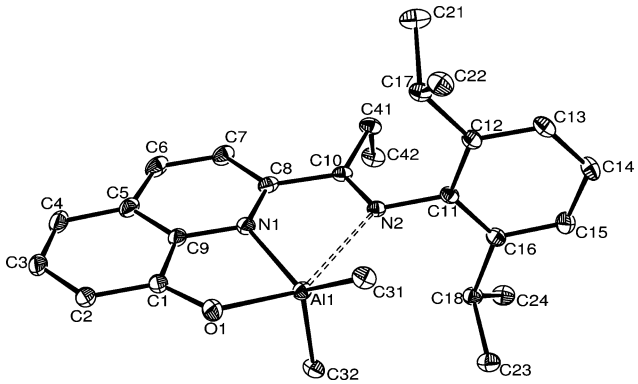


Fig. 3 ORTEP drawing of **8** with thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Al(1)–O(1) 1.881(2), Al(1)–C(31) 1.955(3), Al(1)–C(32) 1.981(3), Al(1)–N(1) 1.991(3), N(2)–C(10) 1.287(4), O(1)–Al(1)–N(1) 82.54(11), O(1)–Al(1)–C(31) 100.55(14), O(1)–Al(1)–C(32) 103.15(13), C(31)–Al(1)–C(32) 122.68(16), C(31)–Al(1)–N(1) 132.69(14), C(32)–Al(1)–N(1) 101.80(14), N(2)–C(10)–C(8) 114.4(3).

for this nitrogen and the quinoline nitrogen to adopt an *anti*-form relationship in **3**, it is believed that a weak interaction is present. Similar to that of **6**, the phenyl ring of the imino group is oriented orthogonally (88.6°) to the coordination rings. The Al–C bond distances in **8** [1.995(3) Å, 1.981(3) Å] are also typical,[4–9] while the Al(1)–O(1) bond length at 1.881(2) Å is characteristic for an oxygen atom of a σ–bond, and the Al(1)–N(1) bond length is 1.991(3) Å, characteristic of a quinoline nitrogen atom with donating coordination.[15]

The ^{1}H NMR resonances of **11–15** corresponding to protons of Al–Me were observed as a combination of $AlMe_3$ (s, *ca.* –0.6 ppm, 9H) and product L–$AlMe_2$ (s, –0.7 ppm, 6H) that was identified by the integration ratios. Combined with the elemental analyses and previous reports,[16] the structure could be identified as Me_2Al**L**·Me_3Al with two Al atoms bridged by O atom. The molecular structure of **12** was also confirmed by single crystal X-ray diffraction,[17] but the *R* value is high due to poor crystal quality.

As the results showed above, the stoichiometric reactions of analogues' (**L1–L10**) with Me_3Al resulted in different types of mononuclear or dimeric methylaluminium compounds. The sterically bulky ethyl group present in the organic ligands **L6–L10** caused congestion and led to the arylimino nitrogen adopting a *syn*-geometry with the quinoline. Meanwhile, the strong interaction between the imino group and the aluminium center results in the formation of mononuclear compounds (**6–10**). The monomeric aluminium compounds **6–10** exhibited high catalytic activity in the ROP of ε-CL.

2.2 Ring-opening polymerization (ROP) of ε-CL by aluminium compounds 6–10

Ring-opening polymerizations (ROP) of ε-caprolactone (CL) using **1–10** were conducted both in the presence and absence of BnOH. The aluminium compounds **1–5** exhibited very low activity in the ROP of ε-CL, and are therefore not discussed further. For the catalytic systems of the aluminium compounds **6–10**, the

Table 1 The ROP of ε-CL by **6–10**/BnOH[a]

Entry	Cat.	CL : Al : BuOH	T/°C	t/min	mg/yield (%)	M_n[b] × 10^{-4}	M_w/M_n[b]	$M_n^{cal.}$ × 10^{-4}
1	**6**	250 : 1 : 1	90	30	503 (87.6)	2.98	1.21	2.51
2	**7**	250 : 1 : 1	90	30	515 (89.7)	3.02	1.26	2.57
3	**8**	250 : 1 : 1	90	30	483(84.1)	2.77	1.13	2.41
4	**9**	250 : 1 : 1	90	30	530 (92.3)	3.60	1.46	2.64
5	**10**	250 : 1 : 1	90	30	537(93.6)	3.52	1.36	2.68
6	**8**	250 : 1 : 1	60	60	528 (92.0)	3.05	1.15	2.64
7	**8**	250 : 1 : 1	90	10	266(46.4)	1.29	1.07	1.33
8	**8**	250 : 1 : 1	90	20	399(69.5)	2.19	1.08	1.99
9	**8**	250 : 1 : 1	90	40	523(91.1)	3.10	1.20	2.61
10	**8**	250 : 1 : 1	90	50	545(94.9)	3.24	1.34	2.71
11	**8**	125 : 1 : 1	90	30	236 (82.3)	1.45	1.14	1.43
12	**8**	500 : 1 : 1	90	30	978 (85.2)	4.93	1.19	4.87
13	**8**	750 : 1 : 1	90	30	1482 (86.1)	7.59	1.29	7.38
14	**8**	1000 : 1 : 1	90	30	1975 (86.0)	10.03	1.32	9.92
15	**8**	250 : 1 : 1	40	360	464(80.8)	2.98	1.21	2.32
16	**8**	250 : 1 : 1	20	720	536(93.4)	3.24	1.31	2.67

[a] Conditions: 20 μmol Al, 1.0 M ε-CL toluene solution. [b] GPC data in THF *vs.* polystyrene standards, using a correcting factor 0.56.[18]

polymerization did not take place without adding BnOH. In the presence of BnOH, the aluminium compounds **6–10** can efficiently initiate the ROP of ε-CL, suggesting the formation of Al–alkoxide species, which can act as the initiator *via* a coordination insertion mechanism,[14–16] which is also in agreement with the ^{1}H NMR of resultant polymer. The high yields are observed within 30 min, results for which are summarized in Table 1.

All the PCLs obtained possessed a narrow distribution [M_w/M_n = 1.07–1.46] with unimodal characteristics (Table 1, entries 1–5), indicating single-site catalysis. Compound **8** was used to investigate the influence of the reaction parameters on the ROP in detail.

According to entries 3, 7–10 in Table 1, the linear relationship between the monomer conversions and M_n values, was observed with narrow molecular weight distributions [1.07–1.34], indicating the classical feature of a living polymerization process (Fig. 4). The molecular weight distributions (M_w/M_n values) of the resultant polymers became a little broader with increased monomer conversions [*e.g.*, PDI: 1.07 (conversion 46.4%), 1.08 (conversion 69.5%), 1.21 (conversion 91.1%), and 1.34 (conversion 94.9%) in Table 1]. The results strongly suggest that a certain degree of transesterification accompanied the propagation in the ROP of ε-CL. The degree of the transesterification seemed to increase in the order with **8** < **7** < **6** < **9**, **10** consistent with a decrease in the bulk of the *ortho*-substituent in the imino groups. It is assumed that the bulkier substituent would be required to prohibit the transesterification process from accompanying the propagation in the ROP, probably *via* a protection effect acting on the active propagating species.[14a]

In addition, the M_n values of the polymers obtained increased linearly along with the molar ratios of CL/Al (Fig. 5), see runs 3, 11–14 in Table 1. Moreover, shown within entries 3, 7–10 in Table 1, the polymerization rate of the ROPs was first-order-dependent upon the monomer concentration (Fig. 6), suggesting no deactivation of active species during the ROP of CL. Taking all results into account, it is clear that the ROP herein proceeds in a living manner.

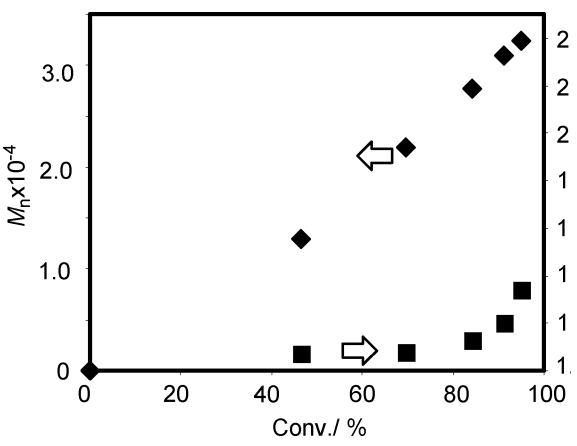


Fig. 4 M_n and M_w/M_n *vs.* monomer conversion in the ROP of ε-CL initiated by **8**/PhCH$_2$OH (entries 3, 7–10, Table 1).

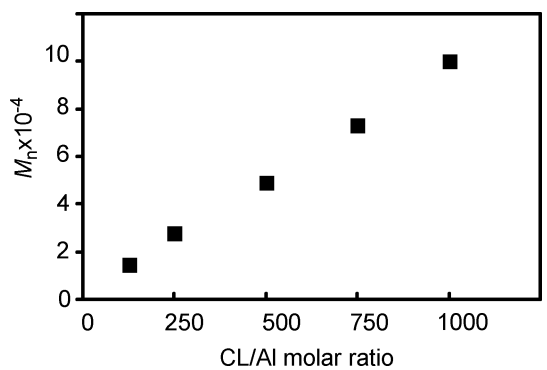


Fig. 5 Plots of M_n values *vs.* CL/Al molar ratio in the ROP of ε-CL initiated by **8**/PhCH$_2$OH (entries 3, 11–14, Table 1).

Reflected by the data in Table 1 (entries 3, 6, 15 and 16), the observed activities decreased upon lowering the polymerization temperature, and conversely, elevating the reaction temperature resulted in higher conversion, which was reflected by the ratio of

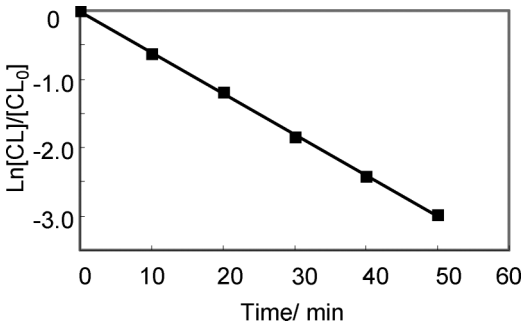


Fig. 6 Plots of Ln[[CL]/[CL]$_0$] *vs.* time in the ROP of *ε*-CL initiated by the catalytic system of **8**/PhCH$_2$OH (entries 3, 7–10, Table 1).

M_n^{cal}/M_n. At higher reaction temperature, the molecular weights are closer to the calculated values.

3. Conclusion

A series of ligands 2-(arylimino)quinolin-8-ols (**L1–L10**) and aluminium compounds (**1–15**) were synthesized and characterized by NMR spectroscopy, and elemental analysis. The molecular structures of compounds **3**, **6** and **8** were confirmed by X-ray crystallography. The introduction of an imino group at the 8-quinolinolato(Q) prevents the formation of common AlQ$_3$-type compounds and allows for the isolation of the monomeric Me$_2$Al**L** or dimeric [Me$_2$Al**L**]$_2$ compounds. Dimeric [Me$_2$Al**L**]$_2$ (**1–5**) showed negligible activity in the ROP of *ε*-CL, whereas mononuclear complexes **6–10** exhibit high activity towards the ROP of *ε*-CL in the presence of BnOH; the polymerization proceeding in a living manner.

4. Experimental

4.1 General procedures

All reactions were performed using standard Schlenk techniques in an atmosphere of high purity nitrogen or glove-box techniques. Toluene, *n*-heptane and THF were dried by refluxing over sodium and benzophenone, distilled under nitrogen and stored over activated molecular sieves (4 Å) for 24 h in a glovebox prior to use. C_6D_6 was dried over activated 4 Å molecular sieves. CH_2Cl_2 and $CDCl_3$ were dried over CaH_2 for 48 h, distilled under nitrogen and stored over activated molecular sieves (4 Å) in a glovebox prior to use. Me_3Al was purchased from Aldrich and used as received. Elemental analyses were performed using a PE2400II Series (Perkin–Elmer Co.). ^{1}H, ^{13}C NMR spectra were recorded on a Bruker DMX-400 (400 MHz for ^{1}H, 100 MHz for ^{13}C) instrument. All spectra were obtained in the solvent indicated at 25 °C unless otherwise noted and chemical shifts are given in ppm and are referenced to $SiMe_4$ (*d* 0.00, ^{1}H, ^{13}C). The GPC measurements were performed on a set of Water-515 HPLC pump, a Waters 2414 refractive index detector, and a combination of Styragel HT-2, HT-3 and HT-4, the effective molar mass ranges of which are 100–10 000, 500–30 000 and 5000–600 000, respectively. THF was used as the eluent (flow rate: 1 mL min^{-1}, at 40 °C). Molecular weights and molecular weight distributions were calculated using polystyrenes as standard.

4.2 Synthesis and characterization of 2-(1-(phenylimino)methyl)quinoline-8-ols (L1–L5) and 2-(1-(phenylimino)propyl)quinoline-8-ols (L6–L10)

Synthesis of 2-((2,6-dimethylphenylimino)methyl)quinolin-8-ol (L1). The starting material 8-hydroxyquinoline-2-carbaldehyde was prepared according to the literature.[12] A mixture of 8-hydroxyquinoline-2-carbaldehyde (0.35 g, 2.0 mmol), 2,6-dimethylaniline (0.24 g, 2.0 mmol) and a few drops of acetic acid was refluxed in ethanol (20 mL) for 4 h. The reaction mixture was concentrated, purified by column chromatography on silica gel and then recrystallized from chilled petrol ether solutions to provide the desired product **L1** (0.42 g, 76% yield) as a yellow powder. ^{1}H NMR ($CDCl_3$): *δ* 8.47 (s, 1H), 8.42 (d, 1H, *J* = 8.5 Hz), 8.27 (d, 1H, *J* = 8.6 Hz), 8.16 (bs, 1H), 7.53 (t, 1H, *J* = 7.9 Hz), 7.40 (d, 1H, *J* = 8.0 Hz), 7.23 (d, 1H, *J* = 7.7 Hz), 7.11 (d, *J* = 7.40 Hz, 2H), 7.00 (t, 1H, *J* = 7.5 Hz), 2.20 (s, 6H). ^{13}C NMR ($CDCl_3$): *δ* 163.3, 152.7, 152.4, 148.6, 137.9, 137.3, 136.9, 129.5, 129.4, 128.3, 127.0, 124.4, 118.9, 118.1, 110.8, 18.5. Mp: 78–80 °C. FT-IR (KBr, cm^{-1}): 3424 (m), 3049 (m), 2952 (m), 2919 (m), 1630 (s), 1593 (m), 1567 (m), 1508 (m), 1466 (s), 1435 (m), 1397 (w), 1371 (m), 1321 (m), 1278 (m), 1249 (m), 1228 (m), 1192 (m), 1165 (m), 1087 (m), 1039 (w), 972 (w), 841 (m), 741 (m), 721 (m). Anal. Calcd for $C_{18}H_{16}N_2O$: C, 78.24; H, 5.84; N, 10.14. Found: C, 78.19; H, 5.77; N, 10.41%.

Synthesis of 2-((2,6-diethylphenylimino)methyl)quinolin-8-ol (L2). The synthesis of **L2** was carried out by the same procedure as that of **L1**, except that 2,6-diethylaniline was used. Yield: 0.49 g (81%). ^{1}H NMR ($CDCl_3$): *δ* 8.47 (s, 1H), 8.40 (d, 1H, *J* = 8.6 Hz), 8.27 (d, 1H, *J* = 8.7 Hz), 8.17 (br, 1H), 7.53 (t, 1H, *J* = 7.8 Hz), 7.40 (d, 1H, *J* = 8.1 Hz), 7.16–7.23 (m, 4H), 2.58–2.53 (m, 4H), 1.17 (t, *J* = 7.2 Hz, 6H). ^{13}C NMR ($CDCl_3$): *δ* 163.0, 152.8, 152.3, 149.7, 137.9, 137.0, 132.9, 129.5, 129.4, 126.6, 126.2, 124.7, 119.0, 118.1, 110.9, 24.9, 14.8. Mp: 56–58 °C. FT-IR (KBr, cm^{-1}): 3409 (m), 3053 (m), 2963 (m), 2930 (m), 2871 (m), 1630 (s), 1590 (m), 1567 (m), 1505 (s), 1469 (s), 1449 (s), 1370 (m), 1327 (m), 1282 (m), 1250 (m), 1234 (m), 1185 (m), 1162 (w), 1084 (m), 1059 (w), 973 (w), 840 (m), 751 (m), 720 (m). Anal. Calcd for $C_{20}H_{20}N_2O$: C, 78.92; H, 6.62; N, 9.20. Found: C, 79.03; H, 6.48; N, 9.39%.

Synthesis of 2-((2,6-diisopropylphenylimino)methyl)quinolin-8-ol (L3). The synthesis of **L3** was carried out by the same procedure as that of **L1**, except that 2,6-diisopropylaniline was used. Yield: 0.58 g (88%). ^{1}H NMR ($CDCl_3$): *δ* 8.45 (s, 1H), 8.42 (d, 1H, *J* = 8.6 Hz), 8.28 (d, 1H, *J* = 8.6 Hz), 8.17 (s, 1H), 7.54 (t, 1H, *J* = 7.9 Hz), 7.40 (d, 1H, *J* = 8.2 Hz), 7.17–7.24 (m, 4H), 3.00 (sept, *J* = 6.8 Hz, 2H), 1.20 (d, *J* = 6.8 Hz, 12H). ^{13}C NMR ($CDCl_3$): *δ* 162.9, 152.3, 148.6, 137.9, 137.3, 137.0, 129.5, 129.4, 124.8, 123.3, 119.0, 118.1, 110.9, 128.2, 28.2, 23.6. Mp: 126–128 °C. FT-IR (KBr, cm^{-1}): 3341 (m), 3069 (w), 2960 (m), 2870 (m), 1640 (s), 1588 (w), 1567 (m), 1504 (s), 1461 (s), 1433 (m), 1381 (m), 1369 (m), 1328 (m), 1280 (w), 1251 (m), 1222 (m), 1183 (m), 1158 (m), 1085 (w), 1045 (m), 934 (w), 848 (m), 755 (m), 723 (m). Anal. Calcd for $C_{22}H_{24}N_2O$: C, 79.48; H, 7.28; N, 8.43. Found: C, 79.12; H, 7.37; N, 8.62%.

Synthesis of 2-((2,6-dichlorophenylimino)methyl)quinolin-8-ol (L4). The synthesis of **L4** was carried out by the same procedure as that of **L1**, except that 2,6-dichloroaniline was used. Yield: 0.29 g (46%). ^{1}H NMR ($CDCl_3$): *δ* 8.63 (s, 1H), 8.44 (d, 1H, *J* = 8.6 Hz), 8.29 (d, 1H, *J* = 8.6 Hz), 8.16 (s, 1H), 7.55 (t, 1H,

J = 8.0 Hz), 7.42–7.39 (m, 3H), 7.25–7.23 (m, 1H), 7.05 (t, 1H, J = 8.1 Hz). ^{13}C NMR ($CDCl_3$): δ 167.1, 152.8, 151.6, 146.6, 137.9, 137.0, 129.8, 129.7, 128.6, 125.8, 125.7, 119.2, 118.1, 110.9. Mp: 128–130 °C. FT-IR (KBr, cm^{-1}): 3386 (m), 3049 (w), 2917 (w), 1640 (s), 1627 (s), 1569 (m), 1558 (m), 1505 (s), 1471 (s), 1432 (s), 1371 (m), 1320 (m), 1285 (m), 1253 (m), 1240 (m), 1195 (m), 1167 (w), 1081 (s), 976 (w), 839 (s), 751 (m), 719 (m). Anal. Calcd for $C_{16}H_{10}Cl_2N_2O$: C, 60.59; H, 3.18; N, 8.83. Found: C, 60.47; H, 3.46; N, 8.58%.

Synthesis of 2-((2,6-difluorophenylimino)methyl)quinolin-8-ol (L5). The synthesis of **L5** was carried out by the same procedure as that of **L1**, except that 2,6-difluoroaniline was used. Yield: 0.38 g (67%). ^{1}H NMR ($CDCl_3$): δ 8.89 (s, 1H), 8.40 (d, 1H, J = 8.6 Hz), 8.24 (d, 1H, J = 8.6 Hz), 8.20–8.16 (m, 1H), 7.53 (t, 1H, J = 7.9 Hz), 7.38 (d, 1H, J = 8.2 Hz), 7.24 (t, 1H, J = 7.6 Hz), 7.18–7.14 (m, 1H), 7.01 (t, 2H, J = 7.9 Hz). ^{13}C NMR ($CDCl_3$): δ 165.8, 156.7, 154.2, 152.8, 152.2, 137.9, 136.8, 129.6, 128.2, 126.5, 119.1, 118.1, 112.2, 110.8. Mp: 128–130 °C. FT-IR (KBr, cm^{-1}): 3435 (s), 3056 (w), 3011 (w), 1621 (s), 1585 (m), 1567 (m), 1508 (s), 1463 (s), 1397 (w), 1373 (m), 1329 (m), 1286 (m), 1237 (m), 1195 (m), 1167 (m), 1087 (m), 1012 (m), 966 (m), 839 (m), 755 (m), 716 (m). Anal. Calcd for $C_{16}H_{10}F_2N_2O$: C, 67.60; H, 3.55; N, 9.85. Found: C, 67.54; H, 3.76; N, 10.03%.

Synthesis of 2-(1-(2,6-dimethylphenylimino)propyl)quinoline-8-ol (L6). A solution of 2,6-dimethylaniline (0.290 g, 2.4 mmol), 1-(8-hydroxyquinoline-2-yl)propan-1-one (0.374 g, 2 mmol), and a catalytic amount of *p*-toluenesulfonic acid (0.1 g) in toluene was refluxed for 24 h, then the solvent was removed *in-vacuo*. The product, 2-(1-(2,6-dimethylphenylimino)propyl), was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 20 : 1), the second part to elute was collected and concentrated to give a yellow green solid in 50% yield (0.308 g). ^{1}H NMR ($CDCl_3$): δ 8.51 (d, 1H, J = 8.6 Hz), 8.26 (d, 1H, J = 8.3 Hz), 8.14 (s, 1H), 7.54 (t, 1H, J = 7.9 Hz), 7.41 (d, 1H, J = 8.2 Hz), 7.24 (d, 1H, J = 7.8 Hz), 7.10 (d, 2H, J = 7.5 Hz), 6.98 (t, 1H, J = 7.5 Hz), 2.83–2.79 (m, 2H), 2.08 (s, 6H), 1.09 (t, 3H, J = 7.4 Hz). ^{13}C NMR ($CDCl_3$): δ 170.9, 153.1, 152.4, 148.4, 137.0, 136.7, 129.0, 128.8, 128.0, 125.2, 123.2, 120.3, 118.0, 110.4, 23.1, 18.2, 11.6. FT-IR (KBr, cm^{-1}): 3394 (w), 2962 (m), 1637.5 (m), 1505 (m), 1467 (m), 1258 (s), 1199 (m), 1028 (m), 1012 (s), 860 (m), 792 (s), 755 (m), 720 (m), 584 (m). Mp: 78–79 °C. Anal. Calcd. for $C_{20}H_{20}N_2O$: C, 78.92; H, 6.62; N, 9.20. Found: C, 79.12; H, 6.73; N, 9.09%.

Synthesis of 2-(1-(2,6-diethylphenylimino)propyl)quinoline-8-ol (L7). Using the above procedure, but 2,6-diethylaniline was used instead of 2,6-dimethylaniline, the 2-(1-(2,6-diethylphenylimino)propyl)quinoline-8-ol was obtained as a yellow green solid in 24% yield. ^{1}H NMR ($CDCl_3$): δ 8.49 (d, 1H, J = 8.6 Hz), 8.26 (d, 1H, J = 8.3 Hz), 8.14 (s, 1H), 7.54 (t, 1H, J = 7.9 Hz), 7.41 (d, 1H, J = 8.2 Hz), 7.22 (d, 1H, J = 7.8 Hz), 7.14 (d, 2H, J = 7.5 Hz), 7.07 (t, 1H, J = 7.5 Hz), 2.82–2.77 (m, 2H), 2.48–2.42 (m, 2H), 2.36–2.32 (m, 2H), 1.20 (t, 6H, J = 7.5 Hz), 1.10 (t, 3H, J = 7.4 Hz). ^{13}C NMR ($CDCl_3$): δ 170.5, 153.3, 152.5, 147.5, 137.1, 136.7, 130.9, 129.0, 128.9, 125.9, 123.5, 120.4, 118.0, 110.4, 24.7, 23.4, 13.6, 11.6. FT-IR (KBr, cm^{-1}): 3443 (m), 3066 (w), 2962 (m), 2929 (m), 2869 (m), 1624 (s), 1566 (s), 1504 (s), 1431 (m), 1333 (s), 1309 (m), 1231 (s), 1191 (s), 1162 (s), 1086 (m), 950 (s), 853 (s). 792 (m), 755 (s), 721 (s), 673 (w), 553 (w). Mp: 83–84 °C. Anal. Calcd. for $C_{22}H_{24}N_2O$: C, 79.48; H, 7.28; N, 8.43. Found: C, 79.24; H, 7.47; N, 8.22%.

Synthesis of 2-(1-(2,6-diisopropylphenylimino)propyl)quinoline-8-ol (L8). Using the same procedure, 2-(1-(2,6-diisopropylphenylimino)propyl)quinoline-8-ol was obtained as a yellow green solid in 25% yield. ^{1}H NMR ($CDCl_3$): δ 8.47 (d, 1H, J = 8.7 Hz), 8.27 (d, 1H, J = 8.3 Hz), 8.16 (s, 1H), 7.52 (t, 1H, J = 7.8 Hz), 7.41 (d, 1H, J = 8.1 Hz), 7.24 (d, 1H, J = 7.4 Hz), 7.19 (d, 2H, J = 7.8 Hz), 7.03 (d, 1H, J = 7.5 Hz), 2.85–2.81 (m, 2H), 2.77–2.72 (m, 2H), 1.23 (d, 6H, J = 7.6 Hz), 1.15 (d, 6H, J = 7.4 Hz), 1.11 (t, 3H, J = 7.1 Hz). ^{13}C NMR ($CDCl_3$): δ 170.3, 153.3, 152.5, 146.2, 137.1, 136.7, 130.8, 129.0, 128.9, 126.7, 123.0, 120.6, 118.0, 110.4, 28.5, 23.6, 13.7, 11.4. FT-IR (KBr, cm^{-1}): 3436 (m), 3066 (m), 2964 (w), 2930 (m), 2865 (s), 1633 (s), 1567 (m), 1505 (m), 1455 (m), 1432 (s), 1333 (m), 1309 (s), 1237 (s), 1188 (s), 1164 (m), 1089 (m), 1060 (m), 951 (m), 873 (s), 789 (m), 761 (w), 749 (m), 721 (m), 678 (w), 551 (w). Mp: 147–148 °C. Anal. Calcd. For $C_{24}H_{28}N_2O$: C, 79.96; H, 7.83; N, 7.77. Found: C, 79.73; H, 7.67; N, 7.91%.

Synthesis of 2-(1-(2,6-dichlorophenylimino)propyl)quinoline-8-ol (L9). Using the same procedure, 2-(1-(2,6-dichlorophenylimino)propyl)quinoline-8-ol was obtained as a yellow green solid in 17% yield. ^{1}H NMR ($CDCl_3$): δ 8.55 (d, 1H, J = 8.4 Hz), 8.31 (d, 1H, J = 8.6 Hz), 8.15 (s, 1H), 7.56 (t, 1H, J = 7.5 Hz), 7.44 (d, 1H, J = 7.5 Hz), 7.25 (d, 1H, J = 7.4 Hz), 7.06 (d, 2H, J = 8.0 Hz), 7.02 (t, 1H, J = 7.6 Hz), 2.94–2.89 (m, 2H), 1.18 (t, 3H, J = 7.4 Hz). ^{13}C NMR ($CDCl_3$): δ 174.9, 152.7, 152.5, 145.6, 137.2, 136.9, 129.3, 128.4, 124.5, 124.4, 120.8, 118.0, 110.6, 112.4, 24.7, 11.5. FT-IR (KBr, cm^{-1}): 3430 (w), 2973 (m), 1638 (s), 1502 (s), 1466 (m), 1224 (m), 1191 (m), 1084 (s), 1023 (w), 844 (s), 794 (m), 755 (s), 729 (m), 573 (w). Mp: 136–137 °C. Anal. Calcd. For $C_{18}H_{14}Cl_2N_2O$: C, 62.62; H, 4.09; N, 8.11. Found: C, 62.18; H, 4.11; N, 7.83%.

Synthesis of 2-(1-((2,6-difluorophenyl)imino)propyl)quinolin-8-ol (L10). Using the same procedure, 2-(1-((2,6-difluorophenyl)imino)propyl)quinolin-8-ol was obtained as a yellow green solid in 15% yield. ^{1}H NMR ($CDCl_3$): δ 8.46 (d, 1H, J = 8.4 Hz), 8.26 (d, 1H, J = 8.6 Hz), 8.11 (s, 1H), 7.53 (t, 1H, J = 7.5 Hz), 7.40 (d, 1H, J = 7.5 Hz), 7.23 (d, 1H, J = 7.4 Hz), 7.07 (d, 2H, J = 8.0 Hz), 6.99 (t, 1H, J = 7.6 Hz), 2.94–2.89 (m, 2H), 1.18 (t, 3H, J = 7.3 Hz). ^{13}C NMR ($CDCl_3$): δ 176.9, 153.7, 152.4, 145.5, 137.7, 136.2, 129.4, 128.1, 124.8, 124.4, 120.8, 118.1, 110.5, 112.7, 24.9, 11.6. FT-IR (KBr, cm^{-1}): 3425 (w), 2965 (m), 1642 (s), 1509 (s), 1464 (m), 1230 (m), 1191 (m), 1085 (s), 1031 (w), 840 (s), 795 (m), 752 (s), 728 (m), 570 (w). Mp: 130–131 °C. Anal. Calcd. For $C_{18}H_{14}F_2N_2O$: C, 69.22; H, 4.52; N, 8.97. Found: C, 69.18; H, 4.41; N, 8.83%.

4.3 Synthesis of aluminium complexes 1–15

Synthesis of 1. Into a stirred solution of 2-((2,6-dimethylphenylimino)methyl)quinolin-8-ol (**L1**) (0.28 g, 1.0 mmol) in toluene (25.0 mL), 1.0 mL (1.0 mmol) $AlMe_3$ solution (1.0 M solution in *n*-hexane) was added dropwise at −30 °C. The solution was allowed to warm slowly to room temperature and was stirred overnight. The mixture was filtered and washed with *n*-heptane. The yellow solid was dried and collected. Yield: 0.29 g (86%). ^{1}H NMR ($CDCl_3$): δ 8.88 (br, 2H),

8.63–8.59 (m, 2H), 8.45 (d, 2H, J = 8.4 Hz), 7.60 (t, 2H, J = 7.8 Hz), 7.41 (d, 2H, J = 7.8 Hz), 7.15–7.28 (m, 8H), 2.07 (s, 12H), –0.59 (s, 12H). Calcd for $C_{40}H_{42}Al_2F_4N_4O_2$: C, 72.27; H, 6.37; N, 8.43. Found: C, 72.08; H, 6.28; N, 8.23%.

Synthesis of 2. The synthesis of **2** was carried out by the same procedure as that of **1**, except that 2-((2,6-diethylphenylimino)methyl)quinolin-8-ol (**L2**) was used. Yield: 0.27 g (78%). ^{1}H NMR ($CDCl_3$): δ 8.89 (br, 2H), 8.61–8.59 (m, 2H), 8.44 (d, 2H, J = 8.1 Hz), 7.60 (t, 2H, J = 7.8 Hz), 7.40 (d, 2H, J = 7.7 Hz), 7.15–7.28 (m, 8H), 2.59–2.51 (m, 8H), 1.17 (t, 12H, J = 7.2 Hz), –0.59 (s, 12H). Calcd for $C_{44}H_{50}Al_2N_4O_2$: C, 73.31; H, 6.99; N, 7.77. Found: C, 73.53; H, 6.72; N, 8.08%.

Synthesis of 3. The synthesis of **3** was carried out by the same procedure as that of **1**, except that 2-((2,6-diisopropylphenylimino)methyl)quinolin-8-ol was used. Yield: 0.29 g (75%). ^{1}H NMR ($CDCl_3$): δ 8.90 (br, 2H), 8.64–8.60 (m, 2H), 8.44 (d, 2H, J = 8.3 Hz), 7.60 (t, 2H, J = 7.8 Hz), 7.41 (d, 2H, J = 7.8 Hz), 7.33 (d, 2H, J = 7.5 Hz), 7.15–7.28 (m, 6H), 3.02–2.98 (m, 4H), 1.21 (d, 12H, J = 6.8 Hz), –0.59 (s, 12H). Calcd for $C_{48}H_{58}Al_2N_4O_2$: C, 74.20; H, 7.52; N, 7.21. Found: C, 74.53; H, 7.62; N, 7.09%.

Synthesis of 4. The synthesis of **4** was carried out by the same procedure as that of **1**, except that 2-((2,6-dichlorophenylimino)methyl)quinolin-8-ol was used. Yield: 0.23 g (66.8%). ^{1}H NMR ($CDCl_3$): δ 8.90 (br, 2H), 8.63–8.58 (m, 2H), 8.44 (d, 2H, J = 8.3 Hz), 7.60 (t, 2H, J = 7.7 Hz), 7.15–7.35 (m, 10H), –0.60 (s, 12H). Calcd for $C_{36}H_{30}Al_2Cl_4N_4O_{22}$: C, 57.93; H, 4.05; N, 7.51. Found: C, 58.03; H, 4.12; N, 7.92%.

Synthesis of 5. The synthesis of **5** was carried out by the same procedure as that of **1**, except that 2-((2,6-difluorophenylimino)methyl)quinolin-8-ol was used. Yield: 0.23 g (66.8%). ^{1}H NMR ($CDCl_3$): δ 8.90 (br, 2H), 8.61–8.58 (m, 2H), 8.44 (d, 2H, J = 8.3 Hz), 7.60 (t, 2H, J = 7.8 Hz), 7.41 (d, 2H, J = 7.8 Hz), 7.33 (d, 2H, J = 7.5 Hz), 7.13–7.28 (m, 6H), –0.53 (s, 12H). Anal. Calcd for $C_{36}H_{30}Al_2F_4N_4O_2$: C, 63.53; H, 4.44; N, 8.23. Found: C, 63.28; H, 4.82; N, 8.49%.

Synthesis of 6 and 11. Into a stirred solution of 2-(1-(2,6-dimethylphenylimino)propyl)quinolin-8-ol (0.30 g, 1.0 mmol) in toluene (10.0 mL), 1.0 mL (1.0 mmol) $AlMe_3$ solution (1.0 M solution in n-hexane) was added dropwise at –30 °C. The solution was allowed to warm slowly to room temperature and was stirred for 3 h. The reaction mixture was filtered and the yellow solid **11** was washed with n-heptane and dried (0.035 g, 8% yield). While the filtrate was concentrated *in vacuo*, the chilled-concentrated toluene–n-hexane solution was placed in the freezer (–30 °C) and afforded the aluminium compound **6** (0.29 g, 81% yield) as red crystals. ^{1}H NMR ($CDCl_3$): δ 8.60 (d, 1H, J = 8.5 Hz), 7.98 (d, 1H, J = 8.5 Hz), 7.67 (t, 1H, J = 8.1 Hz), 7.06–7.18 (m, 5H), 2.70–2.67 (m, 2H), 2.06 (s, 6H), 1.25 (t, 3H, J = 7.6 Hz), –0.79 (s, 6H). ^{13}C NMR ($CDCl_3$): δ 168.3, 160.8, 144.8, 144.0, 141.5, 133.8, 130.2, 128.7, 127.3, 125.3, 119.7, 113.3, 110.5, 23.5, 18.7, 11.4. Anal. Calcd for $C_{22}H_{25}AlN_2O$: C, 73.78; H, 7.46; N, 7.40. Found: C, 73.62; H, 7.81; N, 7.78%. Data for **11**: ^{1}H NMR ($CDCl_3$): δ 8.77 (d, 1H, J = 8.4 Hz), 8.11 (d, 1H, J = 8.5 Hz), 7.86 (t, 1H, J = 7.9 Hz), 7.78 (d, 1H, J = 8.1 Hz), 7.53 (d, 1H, J = 7.9 Hz), 7.16–7.18 (m, 3H), 2.76–2.74 (m, 2H), 2.07 (s, 6H), 1.28 (t, 3H, J = 7.6 Hz), –0.61 (s, 6H), –0.73 (s, 9H). Anal. Calcd for $C_{25}H_{34}Al_2N_2O$: C, 69.42; H, 7.92; N, 6.48. Found: C, 69.29; H, 7.96; N, 6.40%.

Synthesis of 7 and 12. The synthesis of **7** and **12** was carried out by the same procedure as that of **6** and **11**, except that 2-(1-(2,6-diethylphenylimino)propyl)quinolin-8-ol was used. Data for **7**: yield 0.32 g (83%). ^{1}H NMR ($CDCl_3$): δ 8.60 (d, 1H, J = 8.5 Hz), 7.98 (d, 1H, J = 8.5 Hz), 7.67 (t, 1H, J = 8.1 Hz), 7.13–7.28 (m, 5H), 2.71–2.68 (m, 2H), 2.57–2.54 (m, 2H), 2.18–2.14 (m, 2H), 1.18–1.27 (m, 9H), –0.82 (s, 6H). ^{13}C NMR ($CDCl_3$): δ 168.4, 160.8, 144.1, 143.7, 141.5, 140.6, 133.7, 132.8, 130.2, 125.7, 125.6, 119.8, 113.4, 110.6, 23.9, 23.7, 13.9, 11.5, –9.6. Anal. Calcd for $C_{24}H_{29}AlN_2O$: C, 74.20; H, 7.52; N, 7.21. Found: C, 74.28; H, 7.48; N, 7.44%. Data for **12**: 0.028 g (6%). ^{1}H NMR ($CDCl_3$): δ 8.72 (d, 1H, J = 8.5 Hz), 8.10 (d, 1H, J = 8.6 Hz), 7.85 (t, 1H, J = 7.9 Hz), 7.77 (d, 1H, J = 8.1 Hz), 7.52 (d, 1H, J = 7.9 Hz), 7.16–7.28 (m, 3H), 2.72–2.68 (m, 2H), 2.56–2.53 (m, 2H), 2.18–2.15 (m, 2H), 1.18–1.27 (m, 9H), –0.64 (s, 6H), –0.73 (s, 9H). Anal. Calcd for $C_{27}H_{38}Al_2N_2O$: C, 70.41; H, 8.32; N, 6.08. Found: C, 70.75; H, 7.98; N, 6.32%.

Synthesis of 8 and 13. The synthesis of **8** and **13** was carried out by the same procedure as that of **6** and **11**, except that 2-(1-(2,6-diisopropylphenylimino)propyl)quinolin-8-ol was used. Data for **8**: yield 0.31 g (74%). ^{1}H NMR ($CDCl_3$): δ 8.59 (d, 1H, J = 8.5 Hz), 7.98 (d, 1H, J = 8.6 Hz), 7.67 (t, 1H, J = 8.1 Hz), 7.13–7.28 (m, 5H), 2.61–2.78 (m, 4H), 1.35 (t, 3H, J = 7.7 Hz), 1.23 (d, 1H, J = 6.6 Hz), 1.07 (d, 1H, J = 6.8 Hz), –0.78 (s, 6H). ^{13}C NMR ($CDCl_3$): δ 168.7, 160.5, 144.4, 142.6, 141.5, 140.5, 138.6, 133.5, 130.1, 126.0, 124.2, 120.3, 113.5, 111.0, 28.2, 24.9, 24.8, 24.7, 12.3, –9.2. Anal. Calcd for $C_{26}H_{33}AlN_2O$: C, 74.97; H, 7.99; N, 6.73. Found: C, 75.12; H, 7.65; N, 6.88%. Data for **13**: yield: 0.44 g (9%). ^{1}H NMR ($CDCl_3$): δ 8.71 (d, 1H, J = 8.6 Hz), 8.10 (d, 1H, J = 8.5 Hz), 7.84 (t, 1H, J = 7.9 Hz), 7.75 (d, 1H, J = 8.1 Hz), 7.52 (d, 1H, J = 8.0 Hz), 7.15–7.28 (m, 3H), 2.61–2.78 (m, 4H), 1.35 (t, 3H, J = 7.7 Hz), 1.23 (d, 1H, J = 6.7 Hz), 1.07 (d, 1H, J = 6.8), –0.59 (s, 6H),–0.72 (s, 9H). Anal. Calcd for $C_{29}H_{42}Al_2N_2O$: C, 71.28; H, 8.66; N, 5.73. Found: C, 71.43; H, 8.91; N, 5.46%.

Synthesis of 9 and 14. The synthesis of **9** and **14** was carried out by the same procedure as that of **6** and **11**, except that 2-(1-(2,6-dichlorophenylimino)propyl)quinolin-8-ol was used. Data for **9**: yield: 0.28 g (70%). ^{1}H NMR ($CDCl_3$): δ 8.59 (d, 1H, J = 8.5 Hz), 7.97 (d, 1H, J = 8.5 Hz), 7.67 (t, 1H, J = 8.0 Hz), 7.11–7.24 (m, 5H), 2.77–2.75 (m, 2H), 1.28 (t, 3H, J = 7.8 Hz), –0.80 (s, 6H). ^{13}C NMR ($CDCl_3$): δ 172.1, 161.1, 152.0, 143.3, 141.3, 134.3, 130.4, 129.2, 128.4, 126.7, 125.4, 119.5, 113.5, 112.4, 112.2, 110.6, 24.4, 11.6,–10.1. Anal. Calcd for $C_{20}H_{19}AlCl_2N_2O$: C, 59.86; H, 4.77; N, 6.98. Found: C, 60.02; H, 4.49; N, 6.63%. Data for **14**: yield 6%. ^{1}H NMR ($CDCl_3$): δ 8.43 (d, 1H, J = 8.5 Hz), 8.18 (d, 1H, J = 8.4 Hz), 7.51 (t, 1H, J = 8.0 Hz), 7.44 (d, 1H, J = 8.1 Hz), 7.38 (d, 1H, J = 8.0 Hz), 7.15–7.18 (m, 2H), 6.99 (t, 1H, J = 8.1 Hz), 2.68–2.64 (m, 2H), 1.56 (t, 3H, J = 7.5 Hz), –0.32 (s, 6H),–0.72 (s, 9H). Anal. Calcd for $C_{23}H_{28}Al_2Cl_2N_2O$: C, 58.36; H, 5.96; N, 5.92. Found: C, 58.28; H, 6.07; N, 5.67%.

Synthesis of 10 and 15. The synthesis of **10** and **15** was carried out by the same procedure as that of **6** and **11**, except that 2-(1-(2,6-difluorophenylimino)propyl)quinolin-8-ol was used. Data for **10**: yield: 0.30 g (82%). ^{1}H NMR ($CDCl_3$): δ 8.62 (d, 1H, J = 8.5 Hz), 8.03 (d, 1H, J = 8.5 Hz), 7.69 (t, 1H, J = 8.0 Hz), 7.44

Table 2 Crystal data and refinement details for **3**, **6** and **8**

	3	**6**	**8**
Empirical formula	$C_{48}H_{58}N_4Al_2O_2$	$C_{22}H_{25}N_2AlO$	$C_{26}H_{33}N_2AlO$
Formula weight	776.94	360.42	416.52
Crystal color	Yellow	Red	Red
T/K	173(2)	173(2)	173(2)
Wavelength/Å	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1$	$P2_1/n$	$P2_1/n$
a/Å	14.338(3)	14.043(3)	10.237(2)
b/Å	14.612(3)	9.4295(19)	15.701(3)
c/Å	15.122(3)	15.913(3)	14.671(3)
α/°	90.0	90.0	90.0
β/°	103.05(3)	110.56 (3)	95.25(3)
γ/°	90.0	90.0	90.0
Volume/Å^3	3086.6(11)	1972.9(7)	2348.2(8)
Z	2	4	4
D_{calc}/Mg m^{-3}	0.836	1.213	1.178
μ/mm^{-1}	0.077	0.115	0.106
F(000)	832	768	896
Crystal size/mm	0.23 × 0.21 × 0.10	0.16 × 0.13 × 0.05	0.29 × 0.20 × 0.10
θ range/°	1.38–27.33	1.67–25.00	1.90–27.52
Limiting indices	$-18 \le h \le 18$	$-16 \le h \le 16$	$-12 \le h \le 13$
	$-18 \le k \le 17$	$-10 \le k \le 11$	$-19 \le k \le 20$
	$-19 \le l \le 19$	$-18 \le l \le 18$	$-18 \le k \le 19$
No. of rflns collected	24 947	13 031	18 916
No. of unique rflns	13 265	3461	5364
R_{int}	0.0613	0.0670	0.0495
Completeness to θ (%)	99.0 (θ = 27.33)	99.6 (θ = 25.00)	99.1 (θ = 27.52)
Goodness-of-fit on F^2	0.985	1.300	1.274
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0939	R_1 = 0.1086	R_1 = 0.0960
	wR_2 = 0.2407	wR_2 = 0.1950	wR_2 = 0.2285
R indices (all data)	R_1 = 0.1245	R_1 = 0.1225	R_1 = 0.1066
	wR_2 = 0.2638	wR_2 = 0.2022	wR_2 = 0.2351
Largest diff. peak, hole/e Å^{-3}	0.338,–0.349	0.340,–0.255	0.414,–0.494

(d, 2H, J = 8.1 Hz), 7.11–7.24 (m, 3H), 2.77–2.71 (m, 2H), 1.36 (t, 3H, J = 7.8 Hz), –0.73 (s, 6H). ^{13}C NMR ($CDCl_3$): δ 171.3, 160.8, 143.7, 142.5, 141.4, 140.7, 134.1, 130.5, 128.9, 126.6, 126.0, 120.0, 113.7, 111.8, 24.8, 11.6, –9.7. Anal. Calcd for $C_{20}H_{19}AlF_2N_2O$: C, 65.21; H, 5.20; N, 7.60. Found: C, 65.07; H, 5.58; N, 7.68%. Data for **15**: yield 0.031 g (7%). ^{1}H NMR ($CDCl_3$): δ 8.43 (d, 1H, J = 8.5 Hz), 8.18 (d, 1H, J = 8.4 Hz), 7.51 (t, 1H, J = 8.0 Hz), 7.44 (d, 1H, J = 8.1 Hz), 7.38 (d, 1H, J = 8.0 Hz), 7.15–7.18 (m, 2H), 6.99 (t, 1H, J = 8.1 Hz), 2.66–2.62 (m, 2H), 1.56 (t, 3H, J = 7.5 Hz), –0.32 (s, 6H), –0.72 (s, 9H). Anal. Calcd for $C_{23}H_{28}Al_2F_2N_2O$: C, 62.72; H, 6.41; N, 6.36. Found: C, 62.56; H, 6.19; N, 6.78%.

4.4 The ROP of ε-CL

Typical polymerization procedures in the presence of benzyl alcohol (Table 1, run 3) are as follows. A toluene solution of **8** (0.020 mmol, 1.0 mL toluene) and BnOH (0.020 mmol) were added into a Schlenk tube in the glove-box at room temperature. The solution was stirred for 2 min, and then ε-caprolactone (5.0 mmol) along with 3.44 mL toluene was added to the solution. The reaction mixture was then placed into an oil bath preheated at 90 °C, and the solution was stirred for the prescribed time (30 min). The polymerization mixture was then quenched by addition of an excess of glacial acetic acid (0.2 mL) into the solution, and the resultant solution was then poured into methanol (200 mL). The resultant polymer was then collected on filter paper and was dried *in vacuo*.

4.5 Crystal structure determinations†

Single crystals of **3**, **6** and **8** suitable for X-ray diffraction analysis were obtained from chilled toluene/*n*-heptane or dichloromethane/*n*-heptane solutions. With graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å), cell parameters were obtained by global refinement of the positions of all collected reflections. Intensities were corrected for Lorentz and polarization effects and empirical absorption. The structures were solved by direct methods and refined by full-matrix least squares on F^2. All hydrogen atoms were placed in calculated positions. Structure solution and refinement were performed by using the SHELXL-97 package.[19] In solving **3**, the inverted structures is employed for refinement, however, the Flack parameter is even worse, so a racemic twin is concluded. Details of the X-ray structure determinations and refinements are provided in Table 2.

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