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## Supporting Information

### Living Polymerization of Conjugated Polar Alkenes Catalyzed by *N*-Heterocyclic Olefin-Based Frustrated Lewis Pairs

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## 1. Materials, Reagents, and Methods

All syntheses and manipulations of air- and moisture-sensitive materials were carried out in flamed Schlenk-type glassware on a dual-manifold Schlenk line, or an argon-filled glovebox. Toluene, benzene, diethyl ether, THF and hexane were refluxed over sodium/potassium alloy distilled under nitrogen atmosphere, then stored over molecular sieves 4 Å. Benzene-*d*<sub>6</sub> was dried over molecular sieves 4 Å. NMR spectra were recorded on a Bruker Avance II 500 (500 MHz, <sup>1</sup>H; 126 MHz, <sup>13</sup>C; 471 MHz, <sup>19</sup>F) instrument at room temperature. Chemical shifts for <sup>1</sup>H and <sup>13</sup>C spectra were referenced to internal solvent resonances and are reported as parts per million relative to SiMe<sub>4</sub>, whereas <sup>19</sup>F NMR spectra were referenced to external CFCl<sub>3</sub>. Air sensitive NMR samples were conducted in Teflon-valve sealed J. Young-type NMR tubes.

Methyl methacrylate (MMA) was purchased from J&K and benzyl methacrylate (BnMA) was purchased from Energy Chemical. and then purified through process that MMA was first degassed and dried over CaH<sub>2</sub> overnight, followed by vacuum distillation. Further purification of MMA involved titration with tri(*n*-octyl)aluminum (Strem Chemicals) to a yellow end point,<sup>1</sup> followed by distillation under reduced pressure. All purified monomers were stored in brown bottles inside a glovebox freezer at -30 °C. Trimethylaluminum, triethylaluminum, bromopentafluorobenzene, phenylmagnesium bromide (3.0 M solution in diethyl ether), 4-fluorophenylmagnesium bromide (2.0 M solution in diethyl ether), ammonium acetate, and sodium bicarbonate were purchased from J&K. Ammonium hydroxide, methylglyoxal, potassium bis(trimethylsilyl)amide (KHMDs, 1.0 M solution in THF), boron trichloride (1.0

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M solution in hexanes), and benzil were purchased from Titan. Iodomethane, 2,3-butanedione, 1-phenyl-1,2-propanedione, *n*-BuLi (2.5 M solution in hexanes) and isobutyraldehyde were purchased from Energy Chemical. Potassium hydride (30 wt. % dispersion in mineral oil) was purchased from Alfa Aesar. Tris(pentafluorophenyl)borane, B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>, was prepared according to literature procedures.<sup>2</sup> Al(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>, as a (toluene)<sub>0.5</sub> adduct, or in its unsolvated form, was prepared by ligand exchange reactions between B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> and AlMe<sub>3</sub> or AlEt<sub>3</sub> (for preparation of the unsolvated form)<sup>3</sup> (Extra caution should be exercised when handling these materials, especially the unsolvated Al(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>, due to its thermal and shock sensitivity!). Literature procedures were employed for the preparation of the following compounds: 2-isopropyl-4-methyl-1*H*-imidazole,<sup>4</sup> 2-isopropyl-5-methyl-4-phenyl-1*H*-imidazole,<sup>4,5</sup> 1, 3, 4, 5-tetramethyl-2-(propan-2-ylidene)-2,3-dihydro-1*H*-imidazole (NHO2),<sup>5b</sup> 1,3-Dimethyl- 4,5- diphenyl-2-(propan-2-ylidene)-2,3-dihydro-1*H*-imidazole (NHO4),<sup>6</sup> (Ph)<sub>3</sub>Al·OEt<sub>2</sub><sup>7</sup> and methyl bis(2,6-di-*t*Bu-4-methylphenoxy)aluminum (MeAl(BHT)<sub>2</sub>).<sup>8</sup>

**General Polymerization Procedures.** Polymerizations were performed in 20 mL glass reactors inside the glovebox for ambient temperature (*ca.* 25 °C) runs. For comparable study, two different procedures were employed for polymerization. In procedure A, a predetermined amount of a Lewis acid (LA) (2 equiv.), such as MeAl(BHT)<sub>2</sub>, was first dissolved in 500 μL of MMA and toluene inside a glovebox. The polymerization was started by rapid addition of NHO solution (1 equiv.) via a gastight syringe to the above mixture under vigorous stirring; while for procedure B, a predetermined amount of a Lewis acid (LA), such as MeAl(BHT)<sub>2</sub>, and Lewis base (LB) with a 2:1 ratio, such as NHO, were first dissolved in 4.50 mL toluene

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inside a glovebox. The polymerization was started by rapid addition of 500  $\mu\text{L}$  of MMA via a gastight syringe to the above mixture under vigorous stirring. The amount of the monomer was fixed for all polymerization. After the measured time interval, a 0.1 mL aliquot was taken from the reaction mixture via syringe and quickly quenched into a 4-mL vial containing 0.6 mL of undried “wet”  $\text{CDCl}_3$  stabilized by 250 ppm of BHT-H; the quenched aliquots were later analyzed by  $^1\text{H}$  NMR to obtain the percent monomer conversion data. After the polymerization was stirred for the stated reaction time then the reactor was taken out of the glovebox, and the reaction was quenched by addition of 5 mL of 5% HCl-acidified methanol. The quenched mixture was isolated by filtration and dried in a vacuum oven at room temperature to a constant weight.

**Polymer Characterizations.** Polymer number-average molecular weight ( $M_n$ ) and molecular weight distributions ( $D = M_w/M_n$ ) were measured by gel permeation chromatography (GPC) at 40  $^\circ\text{C}$  and a flow rate of 1 mL/min, with DMF (HPLC grade, containing 50 mmol/L LiBr) as an eluent on a Waters 1515 instrument equipped with Waters 4.6 $\times$ 30 mm guard column and three Waters WAT054466, WAT044226, WAT044223 columns (Polymer Laboratories: linear range of molecular weight = 500 -  $4\times 10^6$ ). The instrument was calibrated with 10 PMMA standards, and chromatograms were processed with Waters Breeze2 software.

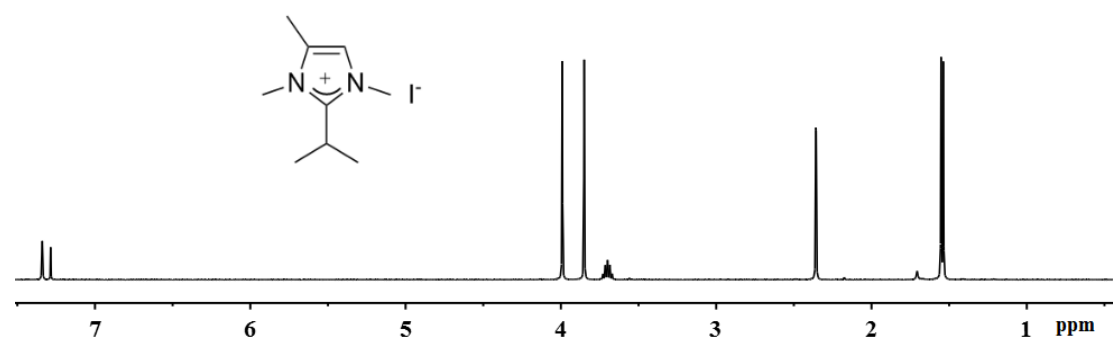
The isolated low-MW polymer samples were analyzed by matrix-assisted laser desorption/ionization time-of-flight mass spectroscopy (MALDI-TOF MS); the experiment was performed on a Bruker Autoflex speed TOF/TOF mass spectrometer in linear, positive

ion, reflector mode using a Nd:YAG laser at 355nm and 25 KV accelerating voltage. A thin layer of 1% CF<sub>3</sub>COONa solution was first deposited on the target plate, followed by 0.6 μL of both sample and matrix (trans-2-[3-(4-tertbutylphenyl)-2-methyl-2-propylidene]malonitrile (DCTB), 20 mg/mL in THF). External calibration was done using a peptide calibration mixture (4-6 peptides) on a spot adjacent to the sample. The raw data were processed in the FlexAnalysis software.

## 2. Synthesis of NHO1 and NHO3

### Synthesis of 2-isopropyl-1,3,4-trimethyl-1H-imidazol-3-ium iodide.

2-Isopropyl-4-methyl-1H-imidazole (12.4 g, 100.0 mmol) and NaHCO<sub>3</sub> (33.6 g, 400.0 mmol) were suspended in dry acetonitrile (600 mL). Methyl iodide (31.1 mL, 500.0 mmol) was added, and the reaction mixture was heated to reflux for 24 h, filtrated while the solution was hot. The resulting mixture was concentrated to half volume under vacuum. Off-white solid was collected by filtration, then washed with THF and dried under vacuum (24.7 g, 88.2%).  
<sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 7.35 (s, 1H, CH=C), 3.99 (s, 3H, NCH<sub>3</sub>), 3.85 (s, 3H, NCH<sub>3</sub>), 3.70 (sept, *J* = 7.3 Hz, 1H, CHMe<sub>2</sub>), 2.35 (s, 3H, C=CMe), 1.54 (d, *J* = 7.3 Hz, 6H, CHMe<sub>2</sub>).

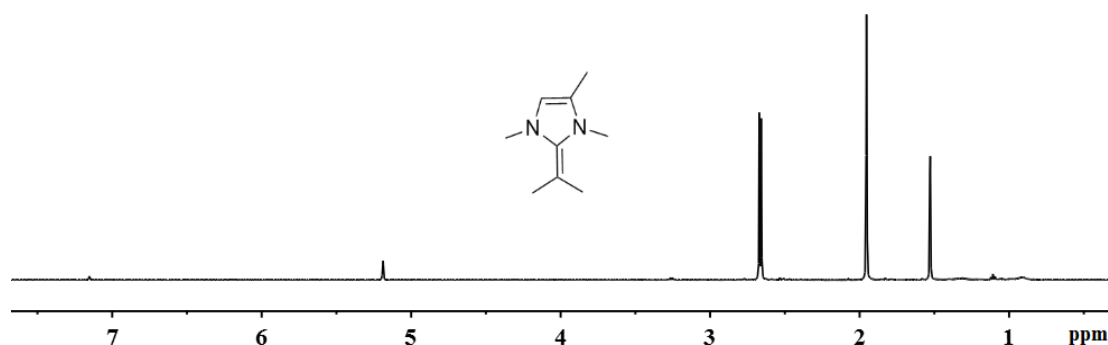


**Figure S1.** <sup>1</sup>H NMR spectrum of 2-isopropyl-1,3,4-trimethyl-1H-imidazol-3-ium iodide (500

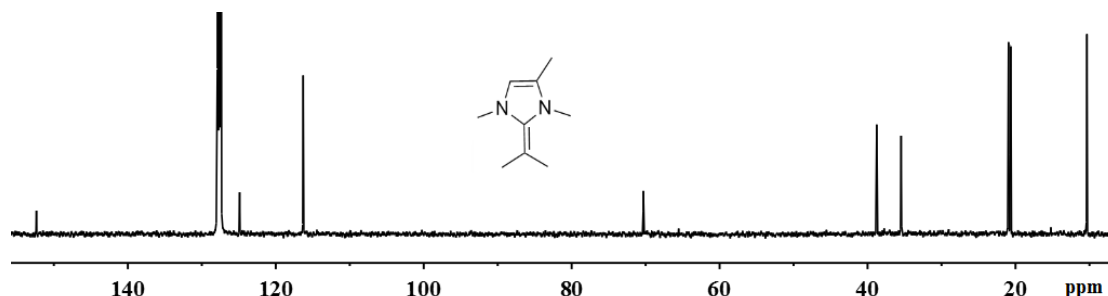
MHz, Chloroform-*d*)

**Synthesis of 1,3,4-trimethyl-2-(propan-2-ylidene)-2,3-dihydro-1H-imidazole (NHO1).**

2-Isopropyl-1,3,4-trimethyl-1H-imidazol-3-ium iodide (5.6 g, 20.0 mmol) was added to a suspension of KH (1.6 g, 40.0 mmol) in THF (100 ml), and the mixture was stirred for 24 h at room temperature in dark place. The solvent was removed under vacuum and the residue was extracted with pentane (50 mL). After filtration through Celite, the solvent was evaporated to yield NHO1 (1.8 g, 59.2%) as a light yellow liquid, which was stored under an atmosphere of argon at  $-35\text{ }^{\circ}\text{C}$ .  $^1\text{H}$  NMR (500 MHz, Benzene-*d*<sub>6</sub>)  $\delta$  5.19 (q,  $J = 1.4\text{ Hz}$ , 1H,  $\text{CH}=\text{C}$ ), 2.67 (s, 3H,  $\text{NCH}_3$ ), 2.66 (s, 3H,  $\text{NCH}_3$ ), 1.95 (s, 6H,  $\text{CMe}_2$ ), 1.53 (d,  $J = 1.4\text{ Hz}$ , 3H,  $\text{C}=\text{CMe}$ ).  $^{13}\text{C}$  NMR (126 MHz, benzene-*d*<sub>6</sub>)  $\delta$  152.4, 124.9, 116.3, 70.3, 38.8, 35.5, 20.9, 20.6, 10.3.



**Figure S2.**  $^1\text{H}$  NMR spectrum of NHO1 (500 MHz, Benzene-*d*<sub>6</sub>)

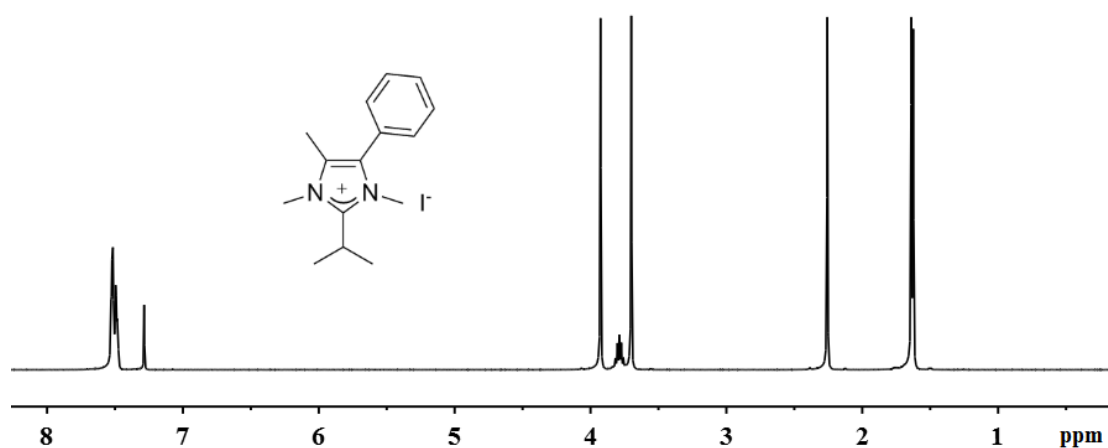


**Figure S3.**  $^{13}\text{C}$  NMR spectrum of NHO1 (126 MHz, Benzene-*d*<sub>6</sub>)

**Synthesis of 2-isopropyl-1,3,5-trimethyl-4-phenyl-1H-imidazol-3-ium iodide.**

2-Isopropyl-5-methyl-4-phenyl-1H-imidazole (20.0 g, 100.0 mmol) and  $\text{NaHCO}_3$  (33.6 g,

400.0 mmol) were suspended in dry acetonitrile (600 mL). Methyl iodide (31.1 mL, 500.0 mmol) was added, and the reaction mixture was heated to reflux for 24 h, filtrated while the solution was hot. The resulting mixture was concentrated to half volume under vacuum. Light yellow solid was collected by filtration, then washed with THF and dried under vacuum (32.5 g, 91.3%).  $^1\text{H}$  NMR (500 MHz, Chloroform-*d*)  $\delta$  7.57 – 7.45 (m, 5H, *Ph*), 3.93 (s, 3H,  $\text{NCH}_3$ ), 3.79 (sept,  $J = 7.3$  Hz, 1H,  $\text{CHMe}_2$ ), 3.70 (s, 1H,  $\text{NCH}_3$ ), 2.26 (s, 3H,  $\text{MeC}=\text{C}$ ), 1.63 (d,  $J = 7.3$  Hz, 6H,  $\text{CHMe}_2$ ).



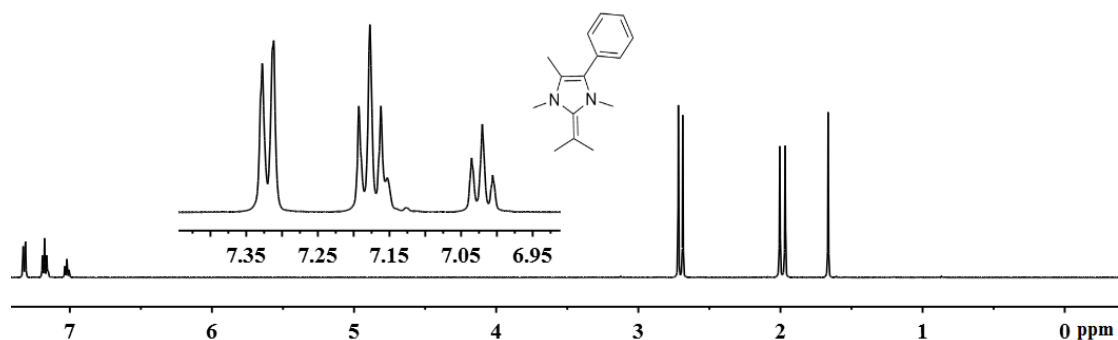
**Figure S4.**  $^1\text{H}$  NMR spectrum of 2-isopropyl-1,3,5-trimethyl-4-phenyl-1H-imidazol-3-ium iodide (500 MHz, Chloroform-*d*)

#### Synthesis of 1,3,4-trimethyl-5-phenyl-2-(propan-2-ylidene)-2,3-dihydro-1H-imidazole

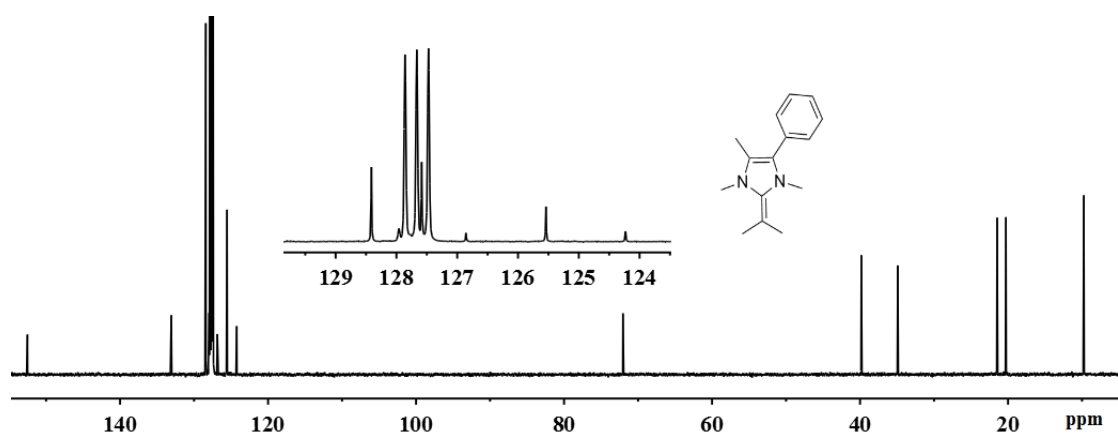
(**NHO3**). 2-Isopropyl-1,3,5-trimethyl-4-phenyl-1H-imidazol-3-ium iodide (3.6 g, 10.1 mmol) and KHMDS (9.2 mL, 9.2 mmol) were dissolved in THF at  $-20$  °C and stirred during 60 minutes. The mixture was then warmed to room temperature and stirred during 12 hours. The solvent was removed under vacuum, and the residue extracted with diethyl ether (2 x 20 mL). After filtration, the solvent was removed under vacuum, affording **NHO3** as a yellow powder (1.6 g, 76.2% yield).  $^1\text{H}$  NMR (500 MHz, Benzene-*d*<sub>6</sub>)  $\delta$  7.32 (dd,  $J = 8.2, 1.4$  Hz, 2H, *Ph*),



7.18 (dd,  $J = 8.4, 7.1$  Hz, 2H, *Ph*), 7.02 (tt,  $J = 7.5, 1.3$  Hz, 1H, *Ph*), 2.72 (s, 3H,  $\text{NCH}_3$ ), 2.69 (s, 3H,  $\text{NCH}_3$ ), 2.00 (s, 3H,  $\text{CMe}_2$ ), 1.97 (s, 3H,  $\text{CMe}_2$ ), 1.66 (s, 3H,  $\text{MeC}=\text{C}$ ).  $^{13}\text{C}$  NMR (126 MHz, Benzene- $d_6$ )  $\delta$  152.5, 133.1, 128.4, 127.6, 126.9, 125.5, 124.2, 72.0, 39.8, 34.9, 21.5, 20.3, 9.8.



**Figure S5.**  $^1\text{H}$  NMR spectrum of **NHO3** (500 MHz, Benzene- $d_6$ )

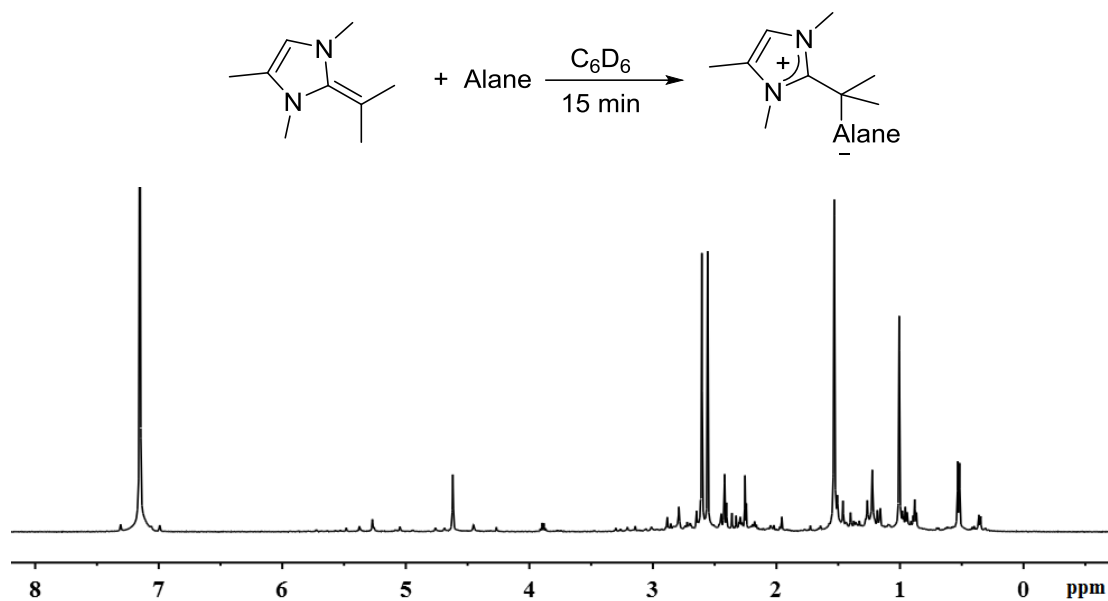


**Figure S6.**  $^{13}\text{C}$  NMR spectrum of **NHO3** (126 MHz, Benzene- $d_6$ )

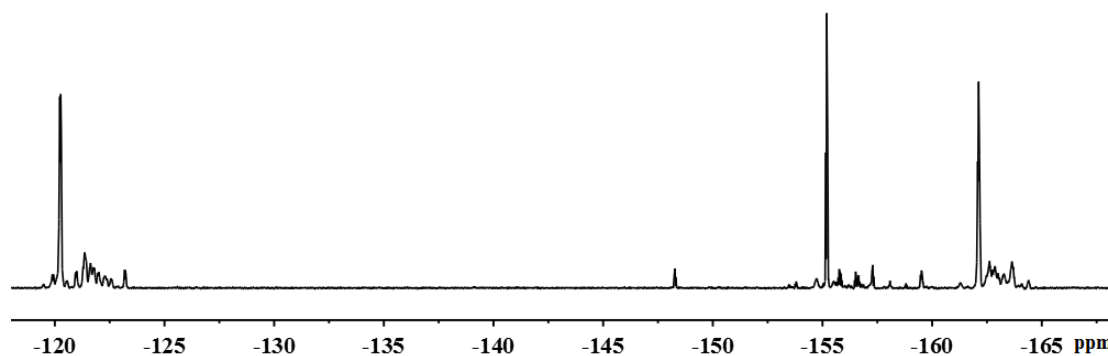
### 3. NMR Reaction of **NHO1** with $\text{Al}(\text{C}_6\text{F}_5)_3$ or $\text{MeAl}(\text{BHT})_2$ in 1:1 Ratio

**NMR reaction of **NHO1** with  $\text{Al}(\text{C}_6\text{F}_5)_3$ :** A Teflon-valve-sealed J. Young-type NMR tube was charged with **NHO1** (3.0 mg, 0.02 mmol) and 0.3 mL of  $\text{C}_6\text{D}_6$ . A solution of alane (10.6 mg, 0.02 mmol, 0.3 mL  $\text{C}_6\text{D}_6$ ) was added to this tube via pipette at ambient temperature, and the mixture was allowed to react for 15 min before analysis by NMR.  $^1\text{H}$  NMR (500 MHz, Benzene- $d_6$ )  $\delta$  4.62 (s, 1H,  $\text{C}=\text{CH}$ ), 2.60 (s, 3H,  $\text{NCH}_3$ ), 2.56 (s, 3H,  $\text{NCH}_3$ ), 1.53 (s, 6H,

$CMe_2$ ), 1.01 (s, 3H, C=CCH<sub>3</sub>). <sup>19</sup>F NMR (471 MHz, Benzene-*d*<sub>6</sub>) δ -120.25 (dd, J = 29.0, 11.0 Hz, 6F, *o*-F), -155.19 (t, J = 20.0 Hz, 3F, *p*-F), -162.05 – -162.18 (m, 6F, *m*-F).

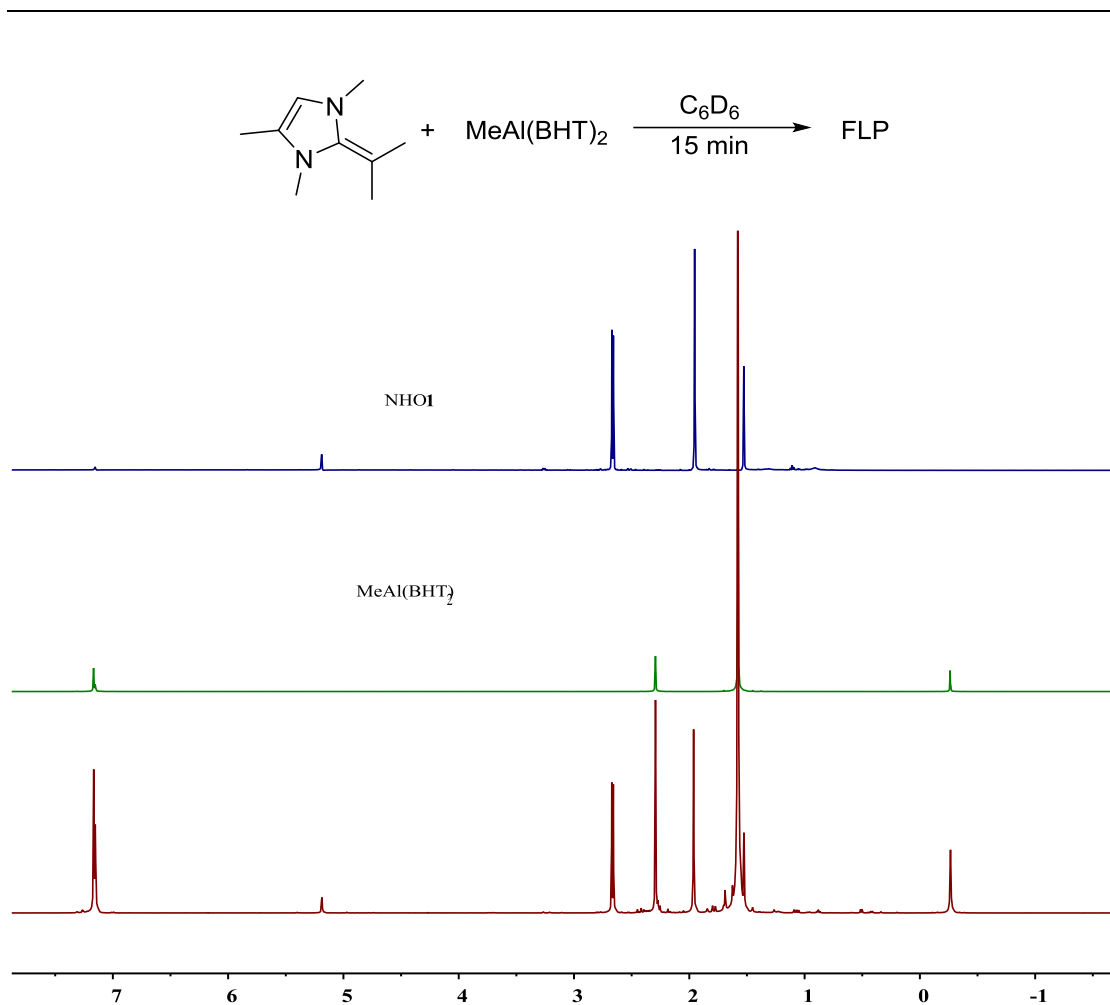


**Figure S7.** <sup>1</sup>H NMR spectrum for reaction of **NHO1** with Al(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (500 MHz, Benzene-*d*<sub>6</sub>)



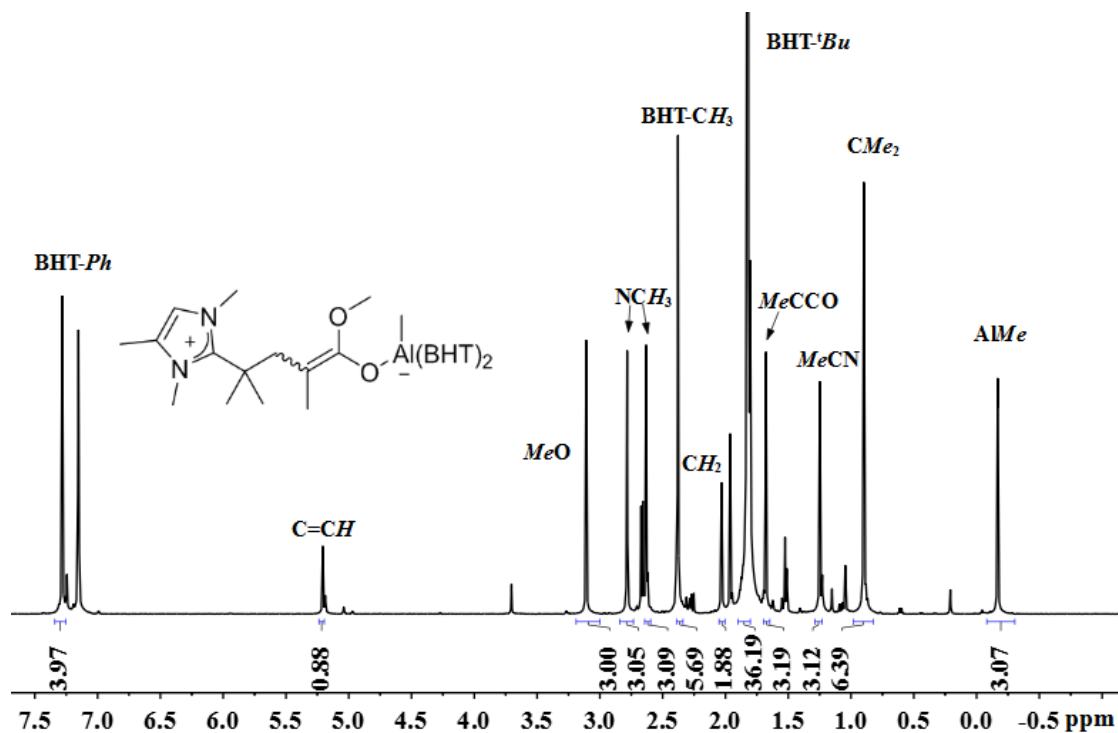
**Figure S8.** <sup>19</sup>F NMR spectrum for reaction of **NHO1** with Al(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (471 MHz, Benzene-*d*<sub>6</sub>)

**NMR reaction of NHO1 with MeAl(BHT)<sub>2</sub>:** A Teflon-valve-sealed J. Young-type NMR tube was charged with **NHO1** (3.0 mg, 0.02 mmol) and 0.3 mL of C<sub>6</sub>D<sub>6</sub>. A solution of MeAl(BHT)<sub>2</sub> (9.6 mg, 0.02 mmol, 0.3 mL C<sub>6</sub>D<sub>6</sub>) was added to this tube via pipette at ambient temperature, and the mixture was allowed to react for 15 min before analysis by NMR, which showed no reaction between Lewis acid and base.

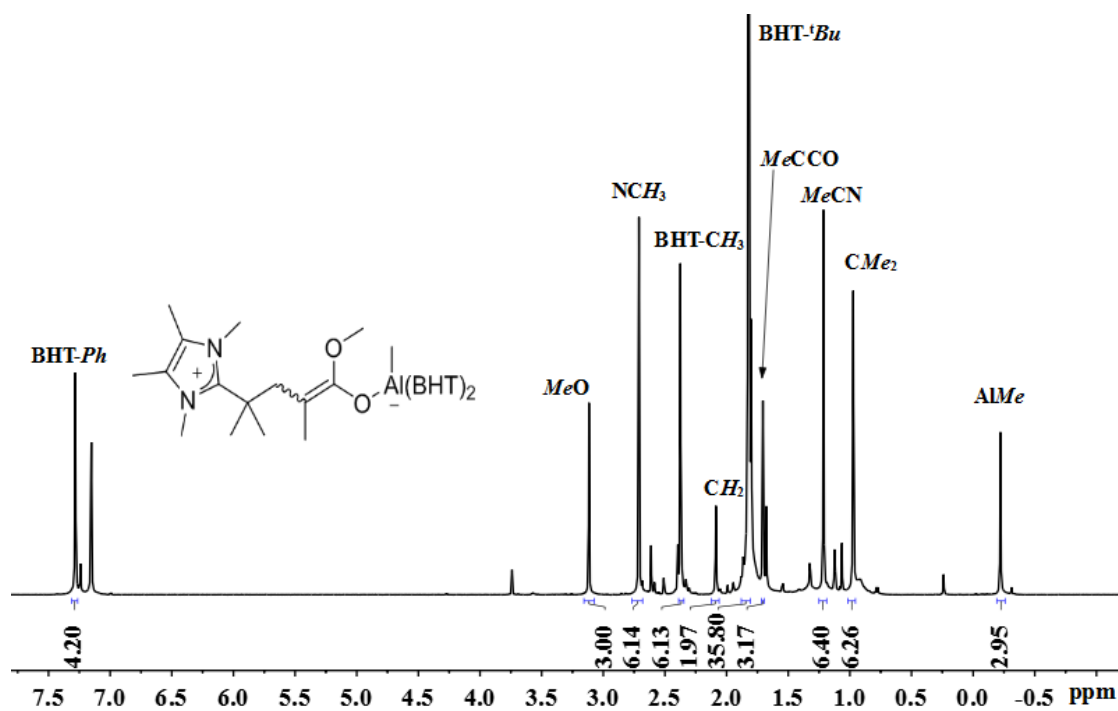


**Figure S9.** Overlay of  $^1\text{H}$  NMR spectra for **NHO1**,  $\text{MeAl(BHT)}_2$  and reaction of **NHO1** with  $\text{MeAl(BHT)}_2$  (500 MHz, Benzene- $d_6$ )

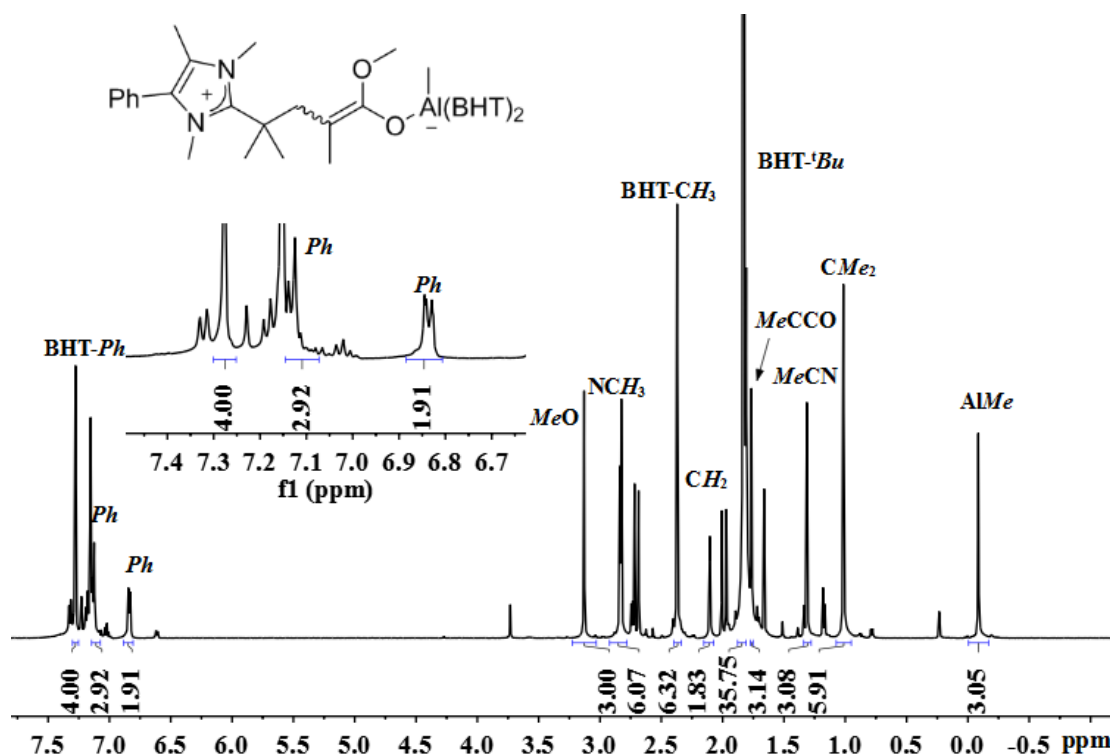
**NMR reaction of NHO with  $\text{MeAl(BHT)}_2 \cdot \text{MMA}$ :** A Teflon-valve-sealed J. Young-type NMR tube was charged with NHO (0.02 mmol) and 0.3 mL of  $\text{C}_6\text{D}_6$ . A solution of  $\text{MeAl(BHT)}_2 \cdot \text{MMA}$  (11.6 mg, 0.02 mmol, 0.3 mL  $\text{C}_6\text{D}_6$ ) was added to this tube via pipette at ambient temperature, and the mixture was allowed to react for 15 min before analysis by  $^1\text{H}$  NMR, which showed generates zwitterionic enolaluminate as two isomers (Z/E = 6-9:1).



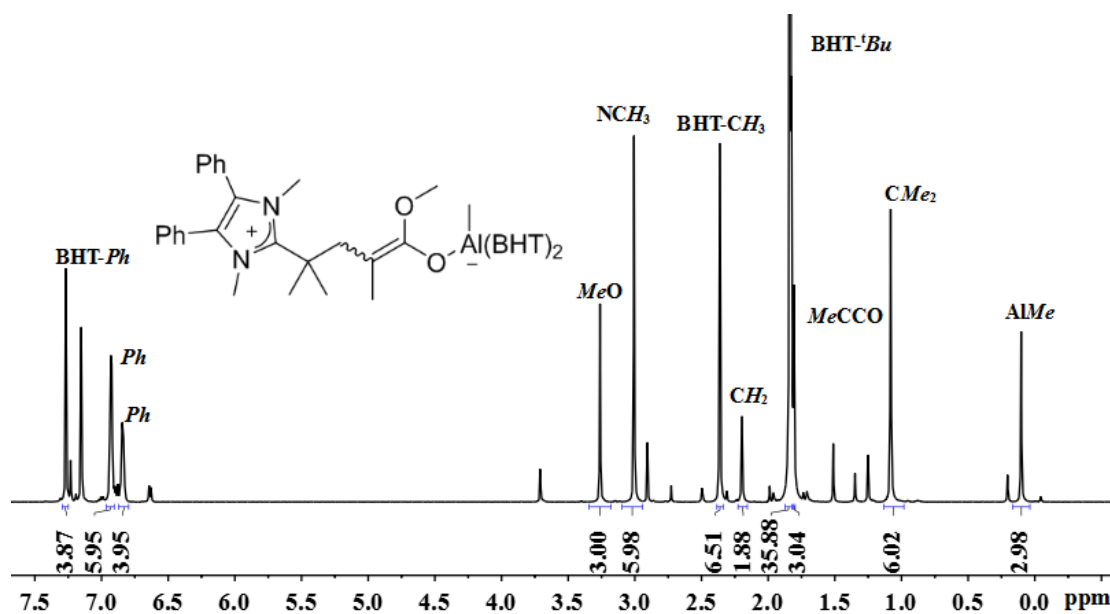
**Figure S10** <sup>1</sup>H NMR spectrum (benzene-*d*<sub>6</sub>, 500 MHz) of the reaction with NHO1/MeAl(BHT)<sub>2</sub>·MMA = 1:1 ratio at RT (9:1 mixture of isomer, only the major isomer was marked for clarity).



**Figure S11** <sup>1</sup>H NMR spectrum (benzene-*d*<sub>6</sub>, 500 MHz) of the reaction with NHO2/MeAl(BHT)<sub>2</sub>·MMA = 1:1 ratio at RT (8:1 mixture of isomer, only the major isomer was marked for clarity).

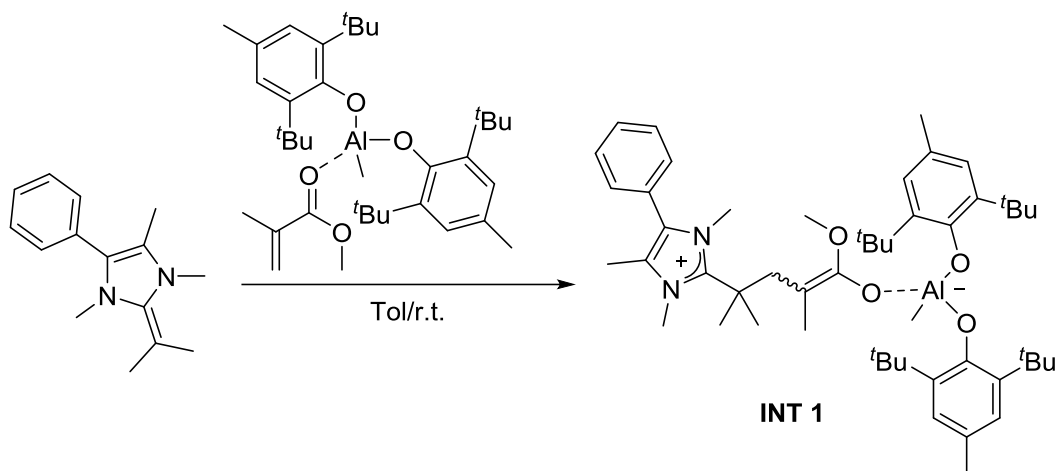


**Figure S12** <sup>1</sup>H NMR spectrum (benzene-*d*<sub>6</sub>, 500 MHz) of the reaction with NHO3/MeAl(BHT)<sub>2</sub>·MMA = 1:1 ratio at RT (8:1 mixture of isomer, only the major isomer was marked for clarity).



**Figure S13** <sup>1</sup>H NMR spectrum (benzene-*d*<sub>6</sub>, 500 MHz) of the reaction with NHO4/MeAl(BHT)<sub>2</sub>·MMA = 1:1 ratio at RT (6:1 mixture of isomer, only the major isomer was marked for clarity).

#### 4. Synthesis and isolation of zwitterionic intermediates



**Scheme S1.** Preparation of zwitterionic intermediate **INT1**

**INT1** could be synthesized in the reaction of **NHO3** with  $\text{MeAl(BHT)}_2\cdot\text{MMA}$  in toluene at RT (Scheme S1). A 20 mL glass vial was charged with **NHO3** (118.0 mg, 0.52 mmol) and 5 mL of toluene, while another vial was charged with  $\text{MeAl(BHT)}_2\cdot\text{MMA}$  (300.0 mg, 0.52 mmol) and 10 mL of hexane. The two vials were mixed via pipet at ambient temperature to give a light yellow suspension. The solid was collected by filtration, then washed with hexane and dried *in vacuo* (291.4 mg, 69.7%). The product as two isomers (Z/E) in 5:1 ratio. Major isomer:  $^1\text{H NMR}$  (500 MHz, Benzene- $d_6$ )  $\delta$  7.29 (s, 4H, BHT-Ph), 7.12–7.10 (m, 3H, ph), 6.83–6.81 (m, 2H, ph), 3.12 (s, 3H, MeO), 2.80 (s, 3H, NCH<sub>3</sub>), 2.79 (s, 3H, NCH<sub>3</sub>), 2.38 (s, 6H, Ar-CH<sub>3</sub>), 2.08 (s, 2H, CH<sub>2</sub>), 1.84 (s, 36H, <sup>t</sup>Bu), 1.78 (s, 3H, MeCCO<sub>2</sub>), 1.29 (s, 3H, MeCN), 0.98 (s, 6H, CMe<sub>2</sub>), -0.08 (s, 3H, AlMe).  $^{13}\text{C NMR}$  (126 MHz, Benzene- $d_6$ )  $\delta$  157.3, 156.9, 151.7, 138.7, 131.4, 130.5, 130.3, 129.3, 129.2, 125.6, 125.5, 122.7, 74.4, 54.6, 44.0, 41.7, 35.9, 35.4, 34.5, 32.2, 29.2, 21.3, 15.6, 9.0. Minor isomer:  $^1\text{H NMR}$  (500 MHz, Benzene- $d_6$ )  $\delta$  7.24 (s, 4H, BHT-Ph), 7.08–6.99 (m, 3H, ph), 6.59–6.57 (m, 2H, ph), 3.75 (s, 3H, MeO), 2.71 (s, 3H, NCH<sub>3</sub>), 2.70 (s, 3H, NCH<sub>3</sub>), 2.38 (s, 6H, Ar-CH<sub>3</sub>), 2.10 (s, 2H, CH<sub>2</sub>),

1.82(s, 36H, *t*Bu), 1.34 (s, 3H, *Me*CCO<sub>2</sub>), 1.15 (s, 6H, *CMe*<sub>2</sub>), 1.12 (s, 3H, *Me*CN), 0.28 (s, 3H, *AlMe*). <sup>13</sup>C NMR (126 MHz, Benzene-*d*<sub>6</sub>) δ 159.5, 157.8, 152.0, 138.7, 131.3, 130.4, 130.3, 129.0, 128.2, 125.4, 125.3, 125.2, 122.3, 76.3, 56.3, 43.3, 40.1, 35.8, 35.3, 34.6, 32.0, 28.7, 21.1, 19.4, 8.6.

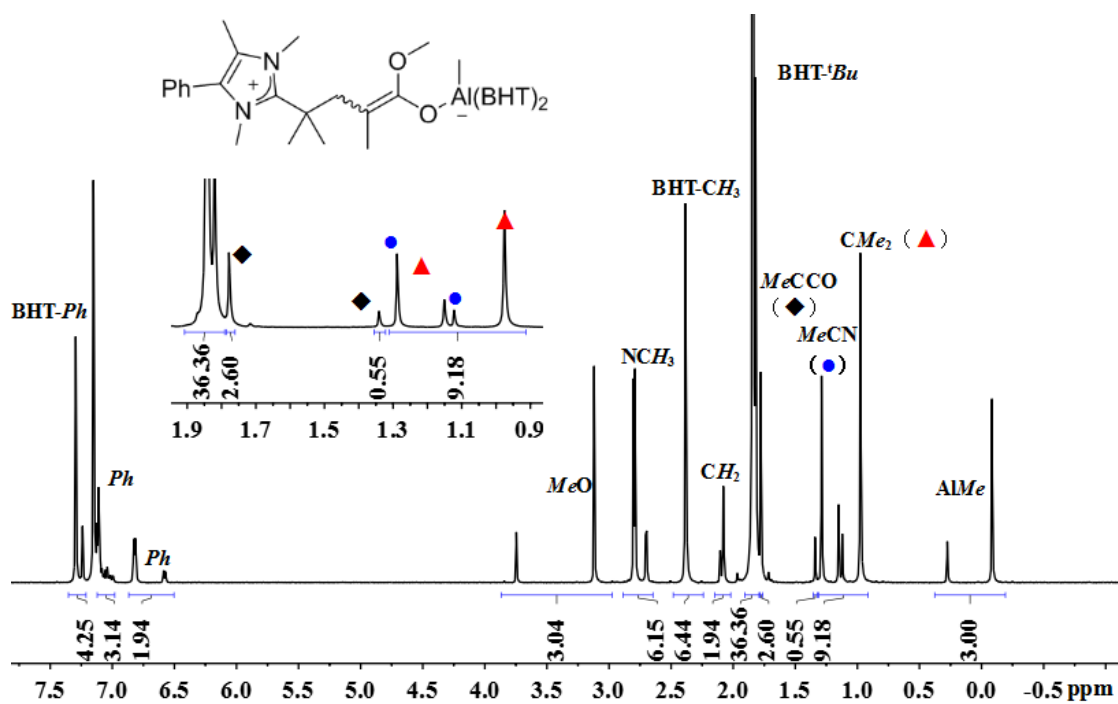


Figure S14 <sup>1</sup>H NMR spectrum (benzene-*d*<sub>6</sub>, 500 MHz) of INT 1.

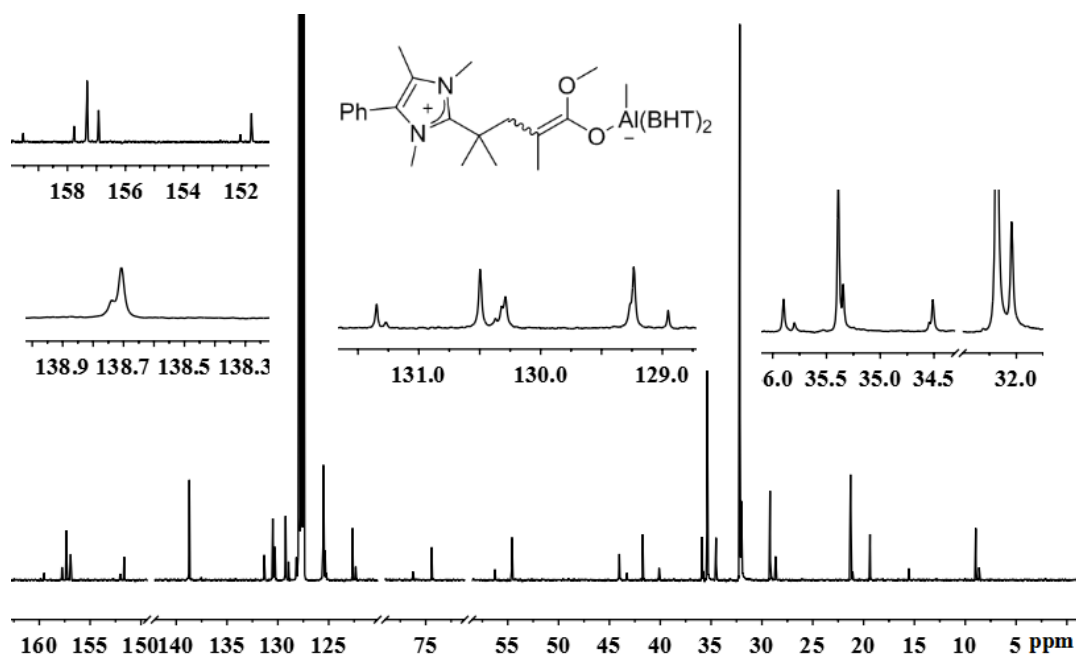
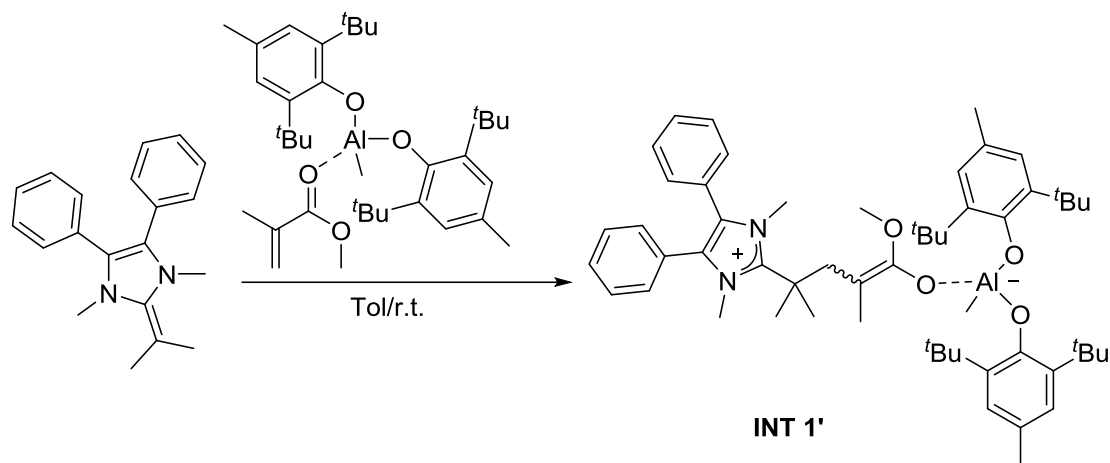


Figure S15 <sup>13</sup>C NMR spectrum (benzene-*d*<sub>6</sub>, 126 MHz) of INT 1.

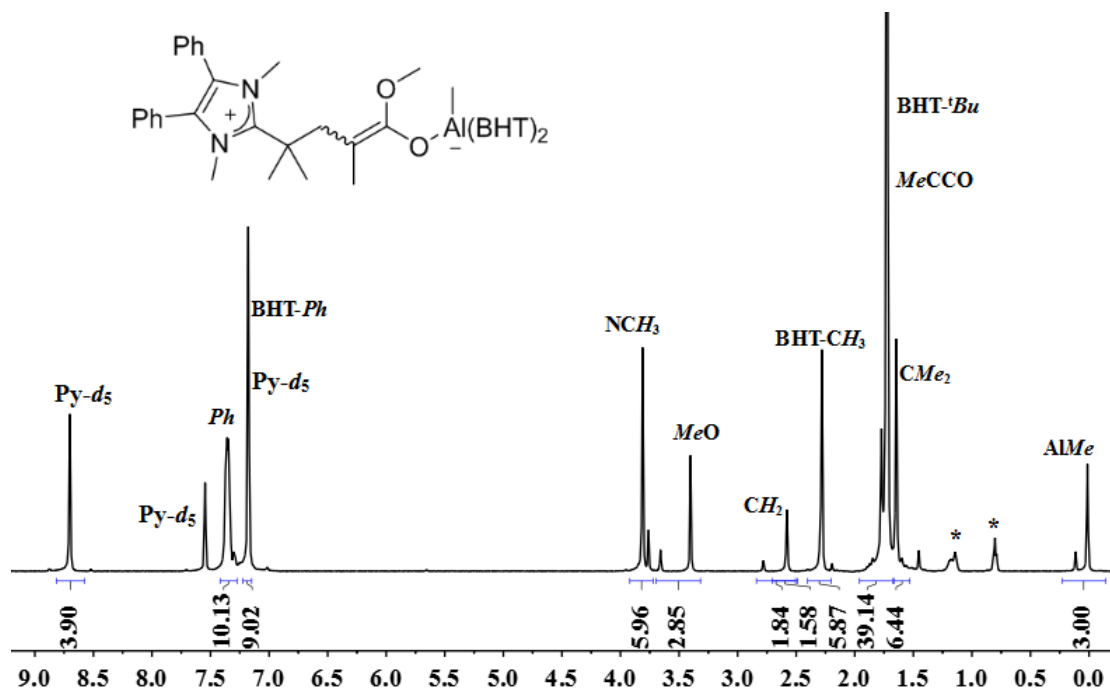


**Scheme S2.** Preparation of zwitterionic intermediate **INT1'**

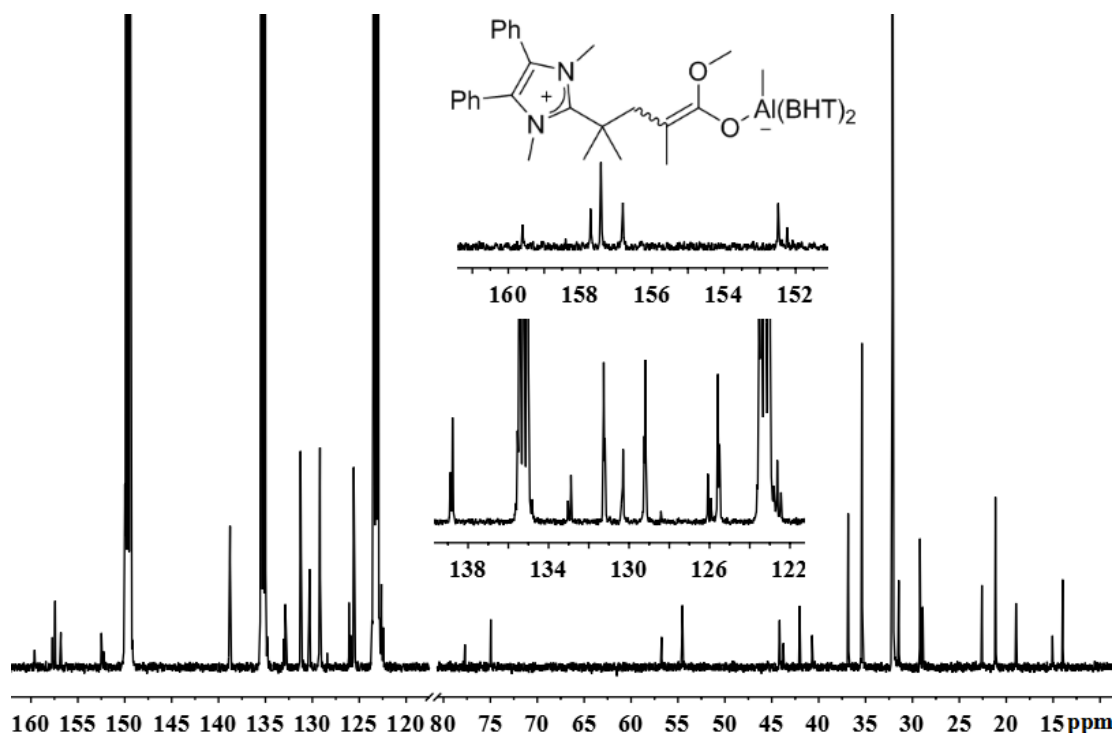
**INT1'** could be synthesized in the reaction of **NHO4** with  $\text{MeAl(BHT)}_2\cdot\text{MMA}$  in toluene at RT (Scheme S2). A 20 mL glass vial was charged with **NHO4** (150.0 mg, 0.52 mmol) and 5 mL of toluene, while another vial was charged with  $\text{MeAl(BHT)}_2\cdot\text{MMA}$  (300.0 mg, 0.52 mmol) and 10 mL of hexane. The two vials were mixed via pipet at ambient temperature to give a light yellow suspension. The solid was collected by filtration, then washed with hexane and dried *in vacuo* (331.7 mg, 73.7%). The product as two isomers (*Z/E*) in 5:1 ratio. Major isomer:  $^1\text{H NMR}$  (500 MHz,  $\text{Py-d}_5$ )  $\delta$  7.16–7.12 (m, 10H, *ph*), 6.96 (s, 4H, *BHT-Ph*), 3.60 (s, 6H,  $\text{NCH}_3$ ), 3.19 (s, 3H, *MeO*), 2.37 (s, 2H,  $\text{CH}_2$ ), 2.07 (s, 6H, *Ar-CH}\_3*), 1.56 (s, 3H,  $\text{MeCCO}_2$ ), 1.51 (s, 36H, *tBu*), 1.44 (s, 6H,  $\text{CMe}_2$ ), -0.20 (s, 3H,  $\text{AlMe}$ ).  $^{13}\text{C NMR}$  (126 MHz,  $\text{Py-d}_5$ )  $\delta$  157.7, 157.4, 152.5, 138.8, 132.9, 131.3, 130.3, 129.2, 126.1, 125.6, 122.6, 75.0, 54.5, 44.2, 42.0, 36.9, 32.1, 31.5, 29.2, 21.2, 14.0. Minor isomer:  $^1\text{H NMR}$  (500 MHz,  $\text{Py-d}_5$ )  $\delta$  7.16–7.12 (m, 6H, *ph*), 7.09–7.08 (m, 4H, *ph*), 6.96 (s, 4H, *BHT-Ph*), 6.59–6.57 (m, 2H, *ph*), 3.55 (s, 6H,  $\text{NCH}_3$ ), 3.45 (s, 3H, *MeO*), 2.57 (s, 2H,  $\text{CH}_2$ ), 2.08 (s, 6H, *Ar-CH}\_3*), 1.56 (s, 3H,  $\text{MeCCO}_2$ ), 1.51 (s, 36H, *tBu*), 1.44 (s, 6H,  $\text{CMe}_2$ ), -0.10 (s, 3H,  $\text{AlMe}$ ).  $^{13}\text{C NMR}$  (126 MHz,  $\text{Py-d}_5$ )  $\delta$  159.6, 156.8, 152.2, 138.9, 133.0, 131.2, 130.4, 129.2, 125.9, 125.5, 122.5, 77.7,



56.8, 43.8, 40.7, 35.4, 32.1, 28.9, 22.6, 19.0, 15.1.



**Figure S16** <sup>1</sup>H NMR spectrum (Py-*d*<sub>5</sub>, 500 MHz) of INT 1'. This spectrum contained a small amount of hexanes (Peaks marked with an \*)



**Figure S17** <sup>13</sup>C NMR spectrum (Py-*d*<sub>5</sub>, 126 MHz) of INT 1'.

## 5. Acidity of Different Lewis Acids Measured through Gutmann–Beckett Method

The relative Lewis acidities were determined by dividing the change in chemical shift of the triethylphosphine oxide resonance upon binding to the electron-deficient aluminum catalyst relative to  $\text{Al}(\text{C}_6\text{F}_5)_3$ , similar to determining the Lewis Acidity of electron-deficient boron catalyst relative to  $\text{B}(\text{C}_6\text{F}_5)_3$  by the Gutmann–Beckett method.<sup>9</sup> In a glove box, aluminum catalyst (0.025mmol) was added to a 0.5 mL  $\text{C}_6\text{D}_6$  solution of  $\text{Et}_3\text{PO}$  (0.025mmol/0.5mL, 0.05M) in a 2-mL NMR tube. The reaction mixture was monitored by  $^{31}\text{P}$  NMR spectroscopy after 30 min at room temperature.

**Table S1. Acidity of different Lewis acids measured through Gutmann–Beckett method**

Aluminum Catalyst	$^{31}\text{P}\{^1\text{H}\}$ NMR ( $\delta/\text{ppm}$ )	$\Delta\delta$ values relative to free $\text{Et}_3\text{PO}$ ( $\delta/\text{ppm}$ )	Relative Lewis Acidity (%)
$\text{Al}(\text{C}_6\text{F}_5)_3$	73.5	28.0	100%
$\text{Ph}_3\text{Al}\cdot\text{OEt}_2$	70.2	24.7	88%
$(\text{BHT})_2\text{AlMe}$	69.5	24.0	86%
$\text{AlMe}_3$ (1.0M in hept)	65.5	20.0	71%
$\text{AlEt}_3$ (1.0M in hex)	65.2	19.7	70%

## 6. Additional Polymerization Data

**Table S2.  $\text{Al}(\text{C}_6\text{F}_5)_3$ -based LP-catalyzed MMA polymerization<sup>a</sup>**

Entry	LB	M: LB:LA	Time	Conv. <sup>b</sup> (%)	$M_n^c$ ( $\text{kg}\cdot\text{mol}^{-1}$ )	$M_n(\text{calcd})$ ( $\text{kg}\cdot\text{mol}^{-1}$ )	$\bar{D}$	$I^*d$ (%)
1	<b>NHO1</b>	200:1:2	30 s	>99	29.9	20.2	1.04	68
2	<b>NHO1</b>	400:1:2	30 s	>99	49.2	40.2	1.03	82
3	<b>NHO1</b>	800:1:2	30 s	>99	88.6	80.2	1.03	91
4	<b>NHO1</b>	1600:1:2	2 min	>99	168	160	1.04	95
5	<b>NHO1</b>	3200:1:2	15 min	>99	300	321	1.08	107
6	<b>NHO2</b>	200:1:2	30 s	>99	30.8	20.2	1.05	66
7	<b>NHO2</b>	400:1:2	30 s	>99	54.8	40.2	1.03	73
8	<b>NHO2</b>	800:1:2	30 s	>99	94.6	80.3	1.04	85
9	<b>NHO2</b>	1600:1:2	2 min	>99	206	160	1.04	78
10	<b>NHO2</b>	3200:1:2	15 min	>99	324	321	1.07	99
11	<b>NHO3</b>	200:1:2	30 s	>99	29.6	20.3	1.07	69

12	<b>NHO3</b>	400:1:2	30 s	>99	45.5	40.3	1.03	89
13	<b>NHO3</b>	800:1:2	30 s	>99	80.6	80.3	1.05	100
14	<b>NHO3</b>	1600:1:2	2 min	>99	154	160	1.03	104
15	<b>NHO3</b>	3200:1:2	15 min	>99	296	321	1.06	108
16	<b>NHO4</b>	200:1:2	30 s	>99	35.2	20.3	1.04	58
17	<b>NHO4</b>	400:1:2	30 s	>99	51.7	40.3	1.05	78
18	<b>NHO4</b>	800:1:2	30 s	>99	85.9	80.3	1.07	93
19	<b>NHO4</b>	1600:1:2	2 min	>99	152	160	1.03	105
20	<b>NHO4</b>	3200:1:2	15 min	>99	270	321	1.08	119

<sup>a</sup> Condition: carried out at RT in 4.5 ml toluene according to procedure A, for a 200/2/1 MMA/LB/LA ratio,  $[MMA]_0 = 0.936$  M,  $[LA]_0 = 2[LB]_0 = 9.36$  mM. <sup>b</sup> Monomer conversions measured by <sup>1</sup>H NMR. <sup>c</sup>  $M_n$  and MWD determined by GPC relative to PMMA standards in DMF. <sup>d</sup> Initiator efficiency ( $I^*$ )% =  $M_n(\text{calcd})/M_n(\text{exptl}) \times 100$ , where  $M_n(\text{calcd}) = [\text{MW}(\text{MMA})]([\text{MMA}]_0/[\text{I}]_0)$  (conversion)+MW of chain-end groups.

**Table S3. MMA polymerization by NHO1-based LPs with different Lewis acid<sup>a</sup>**

Entry	Lewis Acid	Relative Lewis acidity to $\text{Al}(\text{C}_6\text{F}_5)_3$ (%)	Time	Conv. <sup>b</sup> (%)	$M_n^c$ ( $\text{kg}\cdot\text{mol}^{-1}$ )	$\mathcal{D}$	$I^{*d}$ (%)
1	$\text{Al}(\text{C}_6\text{F}_5)_3$	100	1 min	>99	88.6	1.03	91
3	$(\text{Ph})_3\text{Al}\cdot\text{OEt}_2$	88	5 min	96.6	103	1.10	75
4	$\text{MeAl}(\text{BHT})_2$	86	40 min	>99	77.3	1.08	104
5	$\text{AlMe}_3$	71	12 h	38.3	n.d.	n.d.	n.d.
6	$\text{AlEt}_3$	70	12 h	81.9	n.d.	n.d.	n.d.

<sup>a</sup> Condition: carried out with a 800/1/2 MMA/NHO1/ $\text{MeAl}(\text{BHT})_2$  ratio ( $[MMA]_0 = 0.936$  M,  $[\text{MeAl}(\text{BHT})_2]_0 = 2[\text{NHO1}]_0 = 2.34$  mM) in 4.5 ml toluene at RT. n.d.: not determined. <sup>b</sup> Monomer conversions measured by <sup>1</sup>H NMR. <sup>c</sup>  $M_n$  and MWD determined by GPC relative to PMMA standards in DMF. <sup>d</sup> ( $I^*$ )% =  $M_n(\text{calcd})/M_n(\text{exptl}) \times 100$ , where  $M_n(\text{calcd}) = [\text{MW}(\text{MMA})]([\text{MMA}]_0/[\text{I}]_0)$  (conversion)+MW of chain-end groups.

**Table S4. MMA polymerization by NHO1-based LPs using procedure B<sup>a</sup>**

Entry	LA	Time (min)	Conv. <sup>b</sup> (%)	$M_n^c$ ( $\text{kg}\cdot\text{mol}^{-1}$ )	$M_n^c$ ( $\text{kg}\cdot\text{mol}^{-1}$ )	$\mathcal{D}$ ( $M_w/M_n$ )	$I^{*d}$ (%)
1	$\text{Al}(\text{C}_6\text{F}_5)_3$	20	>99	526	80.2	1.20	15
2	$\text{MeAl}(\text{BHT})_2$	40	>99	84.8	80.2	1.09	95

<sup>a</sup> Condition: carried out with a 800/1/2 MMA/NHO1/LA ratio ( $[MMA]_0 = 0.936$  M,  $[LA]_0 = 2[\text{NHO1}]_0 = 2.34$  mM) in 4.5 ml toluene at RT. <sup>b</sup> Monomer conversions measured by <sup>1</sup>H NMR. <sup>c</sup>  $M_n$  and MWD determined by GPC relative to PMMA standards in DMF. <sup>d</sup> Initiator efficiency ( $I^*$ )% =  $M_n(\text{calcd})/M_n(\text{exptl}) \times 100$ , where  $M_n(\text{calcd}) = [\text{MW}(\text{MMA})]([\text{MMA}]_0/[\text{I}]_0)$  (conversion)+MW of chain-end groups.

**Table S5 Control experiments for NHO1/ $\text{MeAl}(\text{BHT})_2$ -catalyzed MMA polymerization<sup>a</sup>**

Entry	LB	LA	M:LB:LA	Time	Conv. <sup>b</sup>
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					(%)
1		MeAl(BHT) <sub>2</sub>	200:2	24 h	0
2	<b>NHO1</b>	MeAl(BHT) <sub>2</sub>	200:1:1	24 h	5.6

<sup>a</sup> Condition: carried out at RT in 4.5 ml toluene according to procedure A, [MMA]<sub>0</sub> = 0.936 M, [LA]<sub>0</sub> = [LB]<sub>0</sub> = 4.68 mM. <sup>b</sup> Monomer conversions measured by <sup>1</sup>H NMR.

**Table S6. BnMA polymerization by MeAl(BHT)<sub>2</sub>-based LPs with different Lewis base<sup>a</sup>**

Entry	LB	M:LB:LA	Time	Conv. <sup>b</sup> (%)	M <sub>n</sub> <sup>c</sup> (kg·mol <sup>-1</sup> )	Đ (M <sub>w</sub> /M <sub>n</sub> )
1	<b>NHO1</b>	800:1:2	60 min	>99	111	1.09
2	<b>NHO2</b>	800:1:2	60 min	>99	92.2	1.09
3	<b>NHO3</b>	800:1:2	60 min	>99	91.3	1.09
4	<b>NHO4</b>	800:1:2	60 min	>99	99.6	1.09

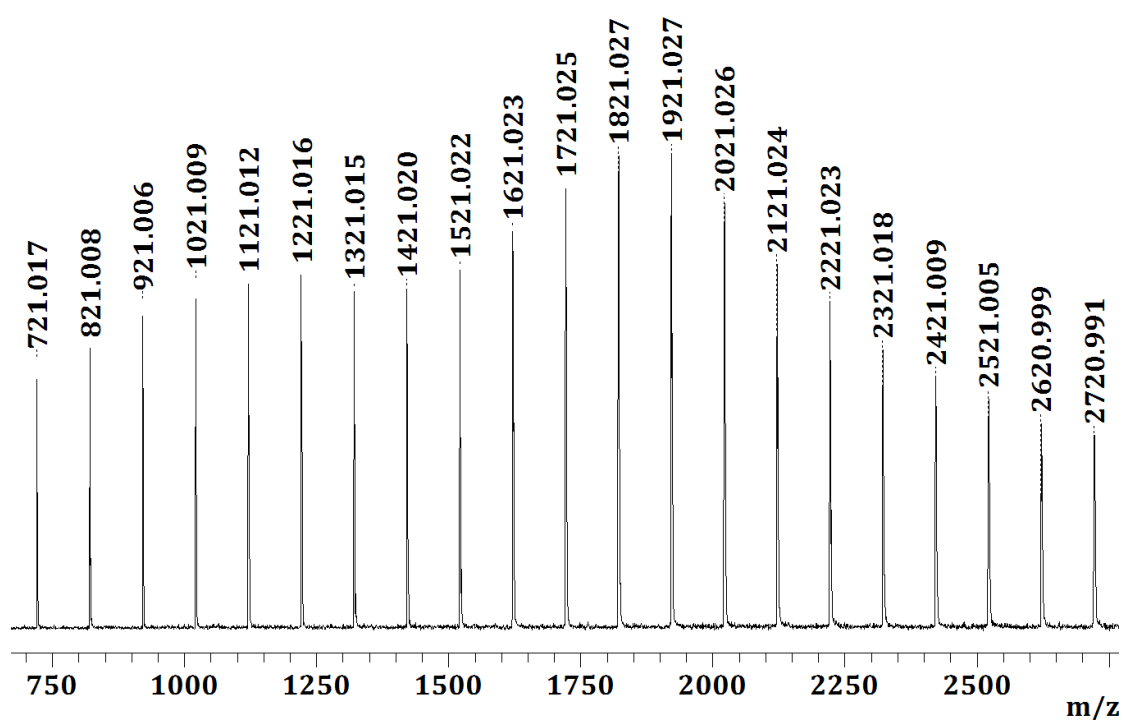
<sup>a</sup> Condition: carried out with a 800/1/2 BnMA/NHO1/MeAl(BHT)<sub>2</sub> ratio ([BnMA]<sub>0</sub> = 0.936 M, [MeAl(BHT)<sub>2</sub>]<sub>0</sub> = 2[NHO]<sub>0</sub> = 2.34 mM) in 4.5 ml toluene at RT. <sup>b</sup> Monomer conversions measured by <sup>1</sup>H NMR. <sup>c</sup> M<sub>n</sub> and MWD determined by GPC relative to PMMA standards in DMF.

**Table S7. Tacticities of PMMA produced by NHO/LA LPs<sup>a</sup>**

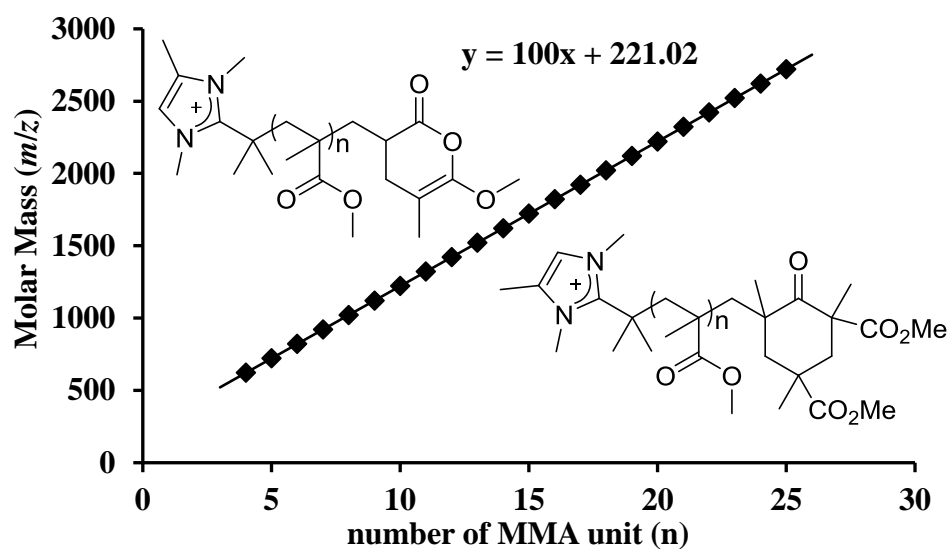
Entry	LB	LA	Conv. <sup>b</sup> (%)	M <sub>n</sub> <sup>c</sup> (kg·mol <sup>-1</sup> )	Đ (M <sub>w</sub> /M <sub>n</sub> )	mm <sup>d</sup> (%)	mr <sup>d</sup> (%)	rr <sup>d</sup> (%)
1	<b>NHO1</b>	Al(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub>	>99	88.6	1.03	1.8	23.0	75.2
2	<b>NHO2</b>	Al(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub>	>99	94.6	1.04	1.9	22.6	75.5
3	<b>NHO3</b>	Al(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub>	>99	80.6	1.05	2.0	23.3	74.7
4	<b>NHO4</b>	Al(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub>	>99	85.9	1.07	1.83	25.5	72.7
5	<b>NHO1</b>	MeAl(BHT) <sub>2</sub>	>99	30.4	1.09	2.1	31.3	66.6
6	<b>NHO2</b>	MeAl(BHT) <sub>2</sub>	>99	27.9	1.14	2.3	30.6	67.1
7	<b>NHO3</b>	MeAl(BHT) <sub>2</sub>	>99	27.2	1.09	2.0	30.5	67.5
8	<b>NHO4</b>	MeAl(BHT) <sub>2</sub>	>99	29.6	1.10	2.10	30.8	67.1

<sup>a</sup> Condition: carried out with a 200/1/2 MMA/NHO/LA ratio ([MMA]<sub>0</sub> = 0.936 M, [LA]<sub>0</sub> = 2[NHO]<sub>0</sub> = 9.36 mM) in 4.5 ml toluene at RT. <sup>b</sup> Monomer conversions measured by <sup>1</sup>H NMR. <sup>c</sup> M<sub>n</sub> and MWD determined by GPC relative to PMMA standards in DMF. <sup>d</sup> rr, mr, mm=polymer methyl triads measured by <sup>1</sup>H (PMMA) spectroscopy.

## 7. MALDI-TOF MS Spectra of Low MW PMMA by $\text{NHO1}/(\text{Ph})_3\text{Al}\cdot\text{OEt}_2$

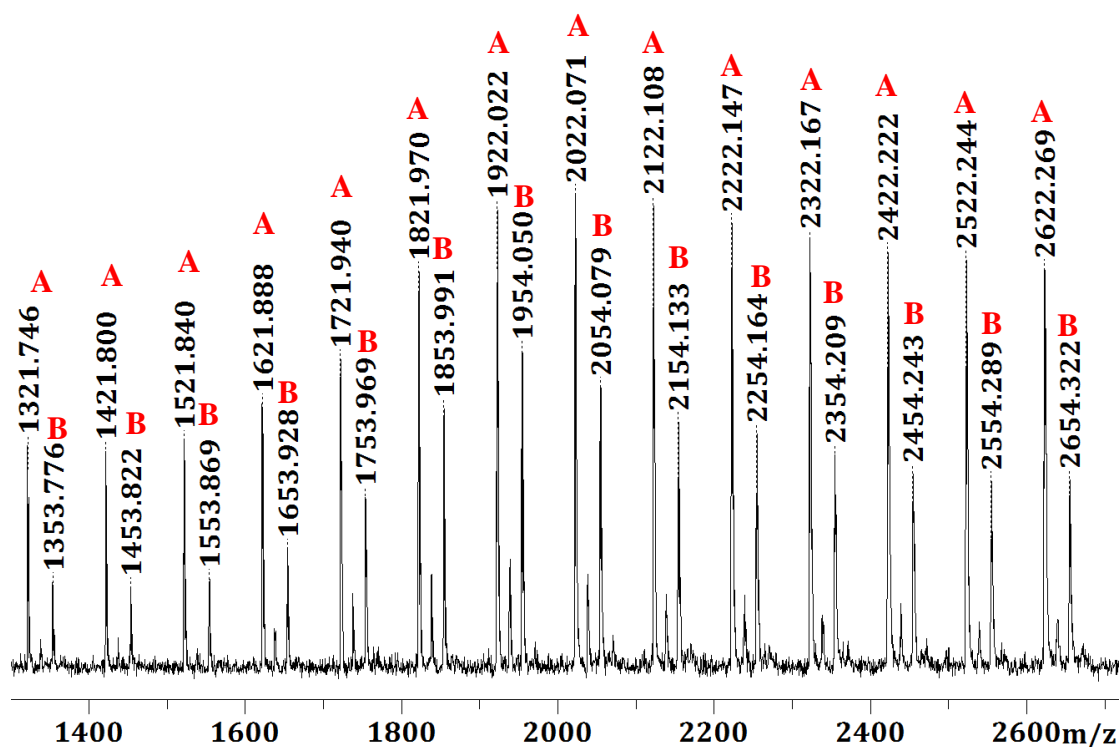


**Figure S18.** MALDI-TOF MS spectrum of the low-MW PMMA sample produced by  $\text{NHO1}/(\text{Ph})_3\text{Al}\cdot\text{OEt}_2$  in toluene at RT

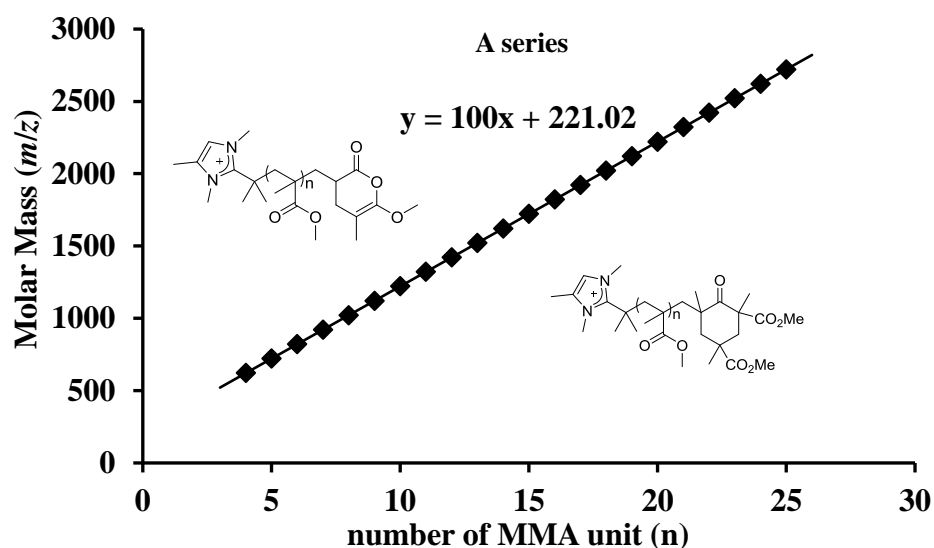


**Figure S19.** Plot of  $m/z$  values taken from Figure S18 vs the number of MMA repeat units ( $n$ ) and the deduced corresponding polymer chain structure produced by  $\text{NHO1}/(\text{Ph})_3\text{Al}\cdot\text{OEt}_2$ .

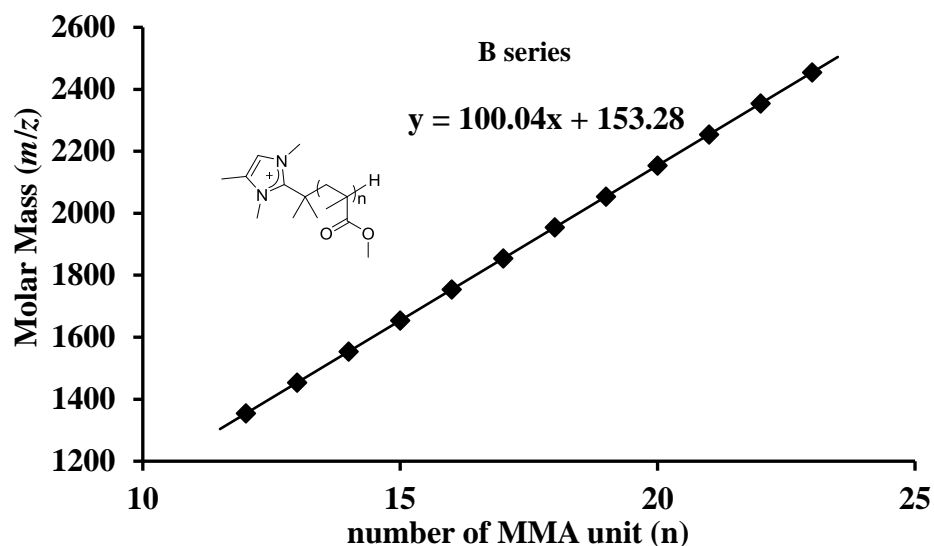
## 8. MALDI-TOF MS Spectra of Low MW PMMA by NHO1/AlEt<sub>3</sub>



**Figure S20.** MALDI-TOF MS spectrum of the low-MW PMMA sample produced by NHO1/AlEt<sub>3</sub> in toluene at RT.



**Figure S21.** Plot of  $m/z$  values taken from Figure S20 vs the number of MMA repeat units ( $n$ ) for A series and the deduced corresponding polymer chain structure produced by NHO1/AlEt<sub>3</sub>



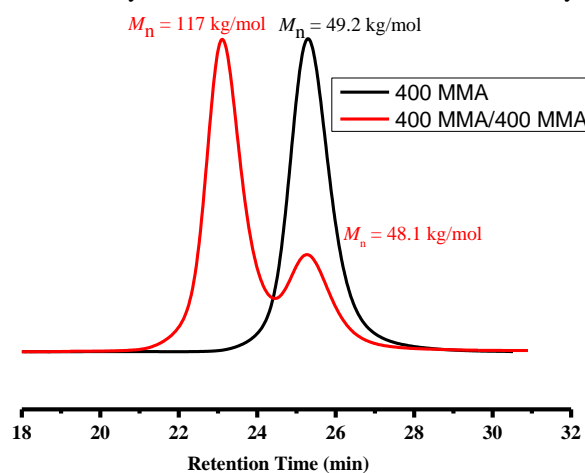
**Figure S22.** Plot of  $m/z$  values taken from Figure S20 vs the number of MMA repeat units ( $n$ ) for B series and the deduced corresponding polymer chain structure produced by **NHO1**/ $\text{AlEt}_3$

### 9. Chain Extension Experiments for MMA Polymerization

**Table S8.** chain-extension polymerization by **NHO1**/ $\text{Al}(\text{C}_6\text{F}_5)_3$  <sup>a</sup>

Entry	M1/M2	Conv. <sup>b</sup> (%)	$M_n^c$ ( $\text{kg}\cdot\text{mol}^{-1}$ )	$\bar{D}$	Area (%)
1	400MMA	>99	49.2	1.03	
2	400/400MMA	>99	117 (48.1)	1.06 (1.04)	74.8 (25.2)

<sup>a</sup> Condition: the first run was carried out with a 400/1/2 MMA/**NHO1**/ $\text{MeAl}(\text{BHT})_2$  ratio ( $[\text{MMA}]_0 = 0.936 \text{ M}$ ,  $[\text{Al}(\text{C}_6\text{F}_5)_3]_0 = 2[\text{NHO1}]_0 = 4.68 \text{ mM}$ ) in 4.50 ml toluene at RT. <sup>b</sup> Monomer conversions measured by  $^1\text{H}$  NMR. <sup>c</sup>  $M_n$  and MWD determined by GPC relative to PMMA standards in DMF.

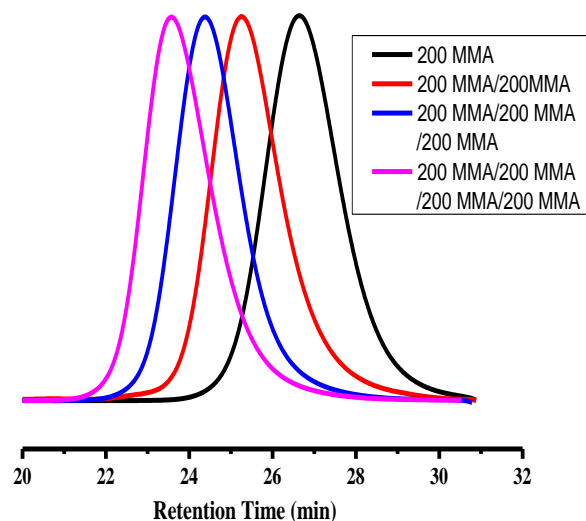


**Figure S23.** The GPC traces of PMMA samples obtained from chain extension experiments by  $\text{Al}(\text{C}_6\text{F}_5)_3$ /**NHO1** in toluene at RT.

**Table S9. chain-extension polymerization by MEAL(BHT)<sub>2</sub>/NHO1<sup>a</sup>**

Entry	M1/M2/M3/M4	Conv. <sup>b</sup> (%)	$M_n^c$ (kg·mol <sup>-1</sup> )	$M_{n\text{ calcd}}$ (kg·mol <sup>-1</sup> )	$\bar{D}$	$I^{*d}$ (%)
1	200MMA	>99	30.4	20.2	1.09	66
2	200/200MMA	>99	48.6	40.2	1.09	83
3	200/200/200MMA	>99	67.5	60.2	1.07	89
4	200/200/200/200MMA	>99	93.5	80.2	1.08	86

<sup>a</sup> Condition: the first run was carried out with a 200/1/2 MMA/NHO1/MeAl(BHT)<sub>2</sub> ratio ([MMA]<sub>0</sub> = 0.936 M, [MeAl(BHT)<sub>2</sub>]<sub>0</sub> = 2[NHO1]<sub>0</sub> = 9.36 mM) in 4.50 ml toluene at RT. <sup>b</sup> Monomer conversions measured by <sup>1</sup>H NMR. <sup>c</sup>  $M_n$  and MWD determined by GPC relative to PMMA standards in DMF. <sup>d</sup> Initiator efficiency ( $I^*$ )% =  $M_n(\text{calcd})/M_n(\text{exptl}) \times 100$ , where  $M_n(\text{calcd}) = [\text{MW}(\text{MMA})]([\text{MMA}]_0/[\text{I}]_0(\text{conversion}) + \text{MW of chain-end groups})$ .



**Figure S24.** The GPC traces of PMMA samples obtained from chain extension experiments in toluene at RT.

## 10. Random and Block Copolymerization

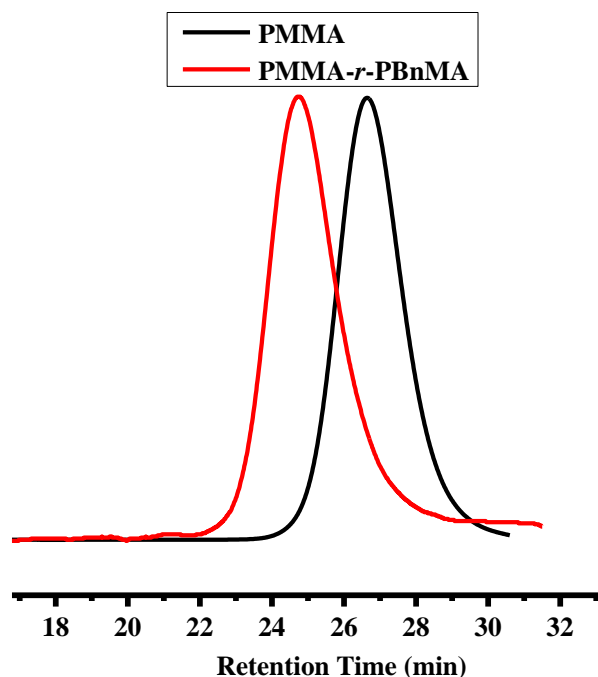
**Table S10 Copolymerization of MMA and BnMA by NHO1/MeAl(BHT)<sub>2</sub> system<sup>a</sup>**

Entry	M1/M2/M3	Conv. <sup>b</sup> (%)	$M_n^c$ (kg·mol <sup>-1</sup> )	$\bar{D}$
1 <sup>d</sup>	200MMA+200BnMA	MMA: > 99 BnMA: > 99	53.2	1.15
2	200MMA/200BnMA	MMA: > 99 BnMA: > 99	49.6	1.13
3	200BnMA /200MMA	MMA: > 99 BnMA: > 99	47.7	1.11
4	200MMA/200BnMA /200MMA	MMA: > 99	65.9	1.10



		BnMA: > 99		
5	200BnMA/200MMA /200BnMA	MMA: > 99	70.7	1.09
		BnMA: > 99		

<sup>a</sup> Carried out in 4.50 ml toluene at RT, where  $[MMA]_0 = [BnMA]_0 = 0.936$  M and  $MeAl(BHT)_2$  was used. <sup>b</sup> Monomer conversions measured by  $^1H$  NMR. <sup>c</sup>  $M_n$  and MWD determined by GPC relative to PMMA standards in DMF. <sup>d</sup> MMA and BnMA was added at the same time.



**Figure S25.** GPC traces of homopolymer PMMA (black) and random copolymer PMMA-*r*-PBnMA (red).

## 11. Kinetics experiments

**Polymerization Kinetics.** Kinetic experiments were carried out in a stirred glass reactor at ambient temperature (*ca.* 25 °C) inside an argon-filled glovebox using the polymerization procedure already described above, with the  $[MMA]_0/[NHO1]_0$  ratio fixed at 800:1,  $[MMA]_0$  was fixed at 0.936 M, where  $NHO1 = 1.17$  mM and  $[MeAl(BHT)_2] = 5.85, 4.68, 3.51, 2.34$  mM in 5 mL mixture solutions. At appropriate time intervals, 0.2 mL aliquots were withdrawn from the reaction mixture using syringe and quickly quenched into 4 mL septum-sealed vials containing 0.6 mL of undried “wet”  $CDCl_3$  mixed with 250 ppm BHT-H.

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The quenched aliquots were analyzed by  $^1\text{H}$  NMR for determining the ratio of  $[\text{MMA}]_t$  at a given time  $t$  to  $[\text{MMA}]_0$ ,  $[\text{MMA}]_t/[\text{MMA}]_0$ . Apparent rate constants ( $k_{\text{app}}$ ) were extracted from the slopes of the best fit lines to the plots of  $[\text{MMA}]_t/[\text{MMA}]_0$  vs time. Another set of kinetic experiments were carried out to determine the kinetic order with respect to **[NHO1]**. In these experiments, with  $[\text{MeAl}(\text{BHT})_2]/[\text{NHO1}]$  ratios of 5:4, 3:2, 2:1, and 1.5:0.5,  $[\text{MMA}]_0$  was fixed at 0.936 M for all polymerization, where  $[\text{NHO1}]_0 = 4.68, 2.34, 1.17, 0.585$  mM and  $[\text{MeAl}(\text{BHT})_2]_0 = 5.85, 3.51, 2.34, 1.755$  mM in 5 mL mixture solutions. The rest of the procedure was same as the described above.

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## 12. References

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