Electronic Supplementary Material (ESI) for Polymer Chemistry.


# Supporting Information

# Living Polymerization of Naturally Renewable Butyrolactone-based vinylidenes Mediated by Frustrated Lewis Pair

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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, a high-vacuum, or an argon-filled glovebox. Toluene, benzene and THF were refluxed over sodium/potassium alloy distilled under nitrogen atmosphere; hexane and $CH_2Cl_2$ were refluxed over $CaH_2$ distilled under nitrogen atmosphere. All solvents were stored over molecular sieves 4 Å. Benzene-$d_6$ and $CD_2Cl_2$ was dried over molecular sieves 4 Å. NMR spectra were recorded on a Bruker Avance II 500 (500 MHz, $^1$H; 125 MHz, $^{13}$C; 471 MHz, $^{19}$F; 202 MHz, $^{31}$P) instrument at room temperature. Chemical shifts for $^1$H and $^{13}$C spectra were referenced to internal solvent resonances and are reported as parts per million relative to $SiMe_4$, whereas $^{19}$F NMR spectra were referenced to external $CFCl_3$. Air sensitive NMR samples were conducted in Teflon-valve sealed J. Young-type NMR tubes.

Methyl methacrylate (MMA) was purchased from J&K and purified through process that MMA was first degassed and dried over $CaH_2$ overnight, followed by vacuum distillation. Further purification of MMA involved titration with tri(*n*-octyl)aluminum (Strem Chemicals) to a yellow end point,[1] followed by distillation under reduced pressure. *γ*-methyl-*α*-methylene-*γ*-butyrolactone (MMBL) and *α*-methylene-*γ*-butyrolactone (MBL) and 2-Ethoxyethyl methacrylate (EEMA) was purchased from TCI and dried over $CaH_2$ overnight, followed by vacuum distillation. All purified monomers were stored in brown bottles inside a glovebox freezer at -30 °C. Boron trichloride (1.0 M solution in hexanes) were purchased from Titan. *n*-BuLi (2.5 M solution in hexanes), chlorodiisopropylphosphine, chlorodiphenylphosphine, chlorodi-tert-butyl phosphine, 2-bromomesitylene, bromopentafluorobenzene, phosphorus trichloride, 3-hydroxy-2-butanone, 1,3-diisopropylthiourea and azidotrimethylsilane were purchased from Energy Chemical. Trimethylaluminum, triethylaluminum, triisobutylaluminium and 2,6-di-tert-butyl-4-methylphenol was purchased from J&K. Tris(pentafluorophenyl)borane, $B(C_6F_5)_3$, was prepared according to literature procedures.[2-3] $Al(C_6F_5)_3$, as a $(toluene)_{0.5}$ adduct, or in its unsolvated form, was prepared by ligand exchange reactions between $B(C_6F_5)_3$ and $AlMe_3$ or $AlEt_3$ (for preparation of the unsolvated form)[4-6] (Extra caution should be exercised when handling these materials, especially the unsolvated $Al(C_6F_5)_3$, due to its thermal and shock sensitivity!). Literature procedures were employed for the preparation of the following

compounds: N,N'-diisopropylimidazolin-2-imine (NI$^i$Pr)H, [7-8] N-(diisopropylphosphanyl)-1,3-diisopropyl-4,5-dimethyl-1,3-dihydro-2*H*-imidazol-2-imine (P(NI$^i$Pr)$^i$Pr$_2$),[9] methyl bis(2,6-di-$^t$Bu-4-methylphenoxy)aluminum ((BHT)$_2$AlMe),[10] isobutyl bis(2,6-di-$^t$Bu-4-methylphenoxy)aluminum ((BHT)$_2$Al$^i$Bu), [11] diisobutyl (2,6-di-$^t$Bu-4-methylphenoxy)aluminum ((BHT)Al$^i$Bu$_2$)[11] and Al(C$_6$F$_5$)$_3$·MMBL.[12] The P(NI$^i$Pr)$^t$Bu$_2$, P(NI$^i$Pr)Ph$_2$, P(NI$^i$Pr)Mes$_2$ and P(NI$^i$Pr)(C$_6$F$_5$)$_2$ were synthesized based on the previous literature.[13]

**General Polymerization Procedures.** Polymerizations were performed in 20 mL glass reactors inside the glovebox for ambient temperature (ca. 25 °C) runs. In a typical polymerization procedure, a predetermined amount of a Lewis acid (LA) (2 equiv.), such as (BHT)$_2$Al$^i$Bu·MMBL, was first dissolved in 250 $\mu$L of MMBL and $CH_2Cl_2$ inside a glovebox. The polymerization was started by rapid addition of P(NI$^i$Pr)R$_2$ solution (1 equiv.) via a gastight syringe to the above mixture under vigorous stirring, After the measured time interval, a 0.2 mL aliquot was taken from the reaction mixture via pipet and quickly quenched into a 4-mL vial containing 0.6 mL of undried "wet" $CDCl_3$ stabilized by 250 ppm of BHT-H; the quenched aliquots were later analyzed by $^1$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 50 °C to a constant weight.

**Polymer Characterizations.** For P(M)MBL and copolymers, polymer weight-average molecular weight ($M_w$) and molecular weight distributions ($Đ = M_w/M_n$) were measured by gel permeation chromatography (GPC) coupled with a Wyatt DAWAN 8+ light scattering (LS) detector at 35 °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 4.6×30 mm guard column and three Waters WAT054466, WAT044226, WAT044223 columns (Polymer Laboratories: linear range of molecular weight = 500 - 4×10$^6$), or gel permeation chromatography (GPC) analyses were performed on a Waters 1515 instrument equipped with a guard column MIXED 7.5×50 mm PL column and two MIXED-C 7.5X300 columns and a differential refractive index detector using DMF (HPLC grade, containing 50 mmol/L LiBr) as

the eluent at 35 °C and a flow rate of 1 mL/min. The differential refractive index (DRI) increment (d*n*/d*c*) value of 0.0844 mL/g was used for PMMBL and 0.0981 for PMBL. For PMMA, number-average molecular weight ($M_n$) and $Đ = M_w/M_n$ were measured by the GPC instrument calibrated with 10 PMMA standards, and chromatograms were processed with Waters Breeze 2 software.

Glass transition temperatures ($T_g$) of the polymers were measured by differential scanning calorimetry (DSC) on a Q20, TA Instruments. Polymer samples were first heated to 240 °C at 20 °C/min, equilibrated at this temperature for 2 min, then cooled to -60 °C at 20 °C/min, held at this temperature for 2 min, and then reheated to 240 °C at 20 °C/min. All $T_g$ values were obtained from the second scan, after the removal of the thermal history.

The isolated low-MW polymer samples were analyzed by matrix-assissted 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% $CF_3COONa$ 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. Isolation of adduct.**

**Isolation of $(BHT)_2AlMe·MMBL$** $(BHT)_2AlMe·MMBL$ Adduct was prepared and isolated as a white powder in 85% yield (504mg) using the same procedure as described for the preparation of $Al(C_6F_5)_3·MMBL$.[12] $^1H$ NMR (500 MHz, Benzene-$d_6$) δ 7.24 (s, 4H, Ar-H), 6.33 (t, *J* = 3Hz, 1H, =C*H*), 5.00 (t, *J* = 2.5Hz, 1H, =CH ), 3.77 (m, 1H, OC*H*), 2.33 (s, 6H, 2*Me*Ar), 1.69 (s, 36H, 2$^t$*Bu*Ar), 0.55 (d, *J* = 6.5 Hz, 3H, C$H_3$), 0.07 (s, 3H, Al*Me*). $^{13}C$ NMR (126 MHz, Benzene-

$d_6$) δ 177.3, 155.2, 139.0, 138.9, 133.8, 130.2, 126.3, 125.3, 82.5, 35.5, 33.1, 32.1, 21.5, 20.6 ppm.

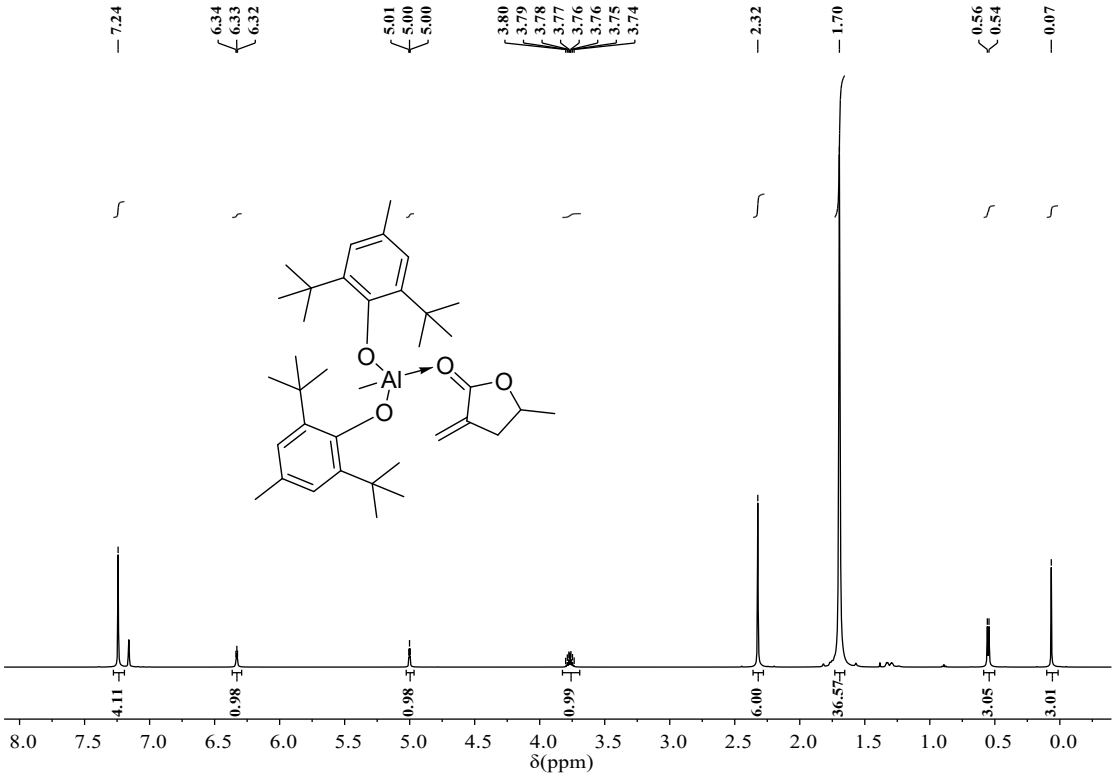



Figure S1. $^1$H NMR spectrum of (BHT)$_2$AlMe·MMBL (Benzene-$d_6$, 500 MHz).

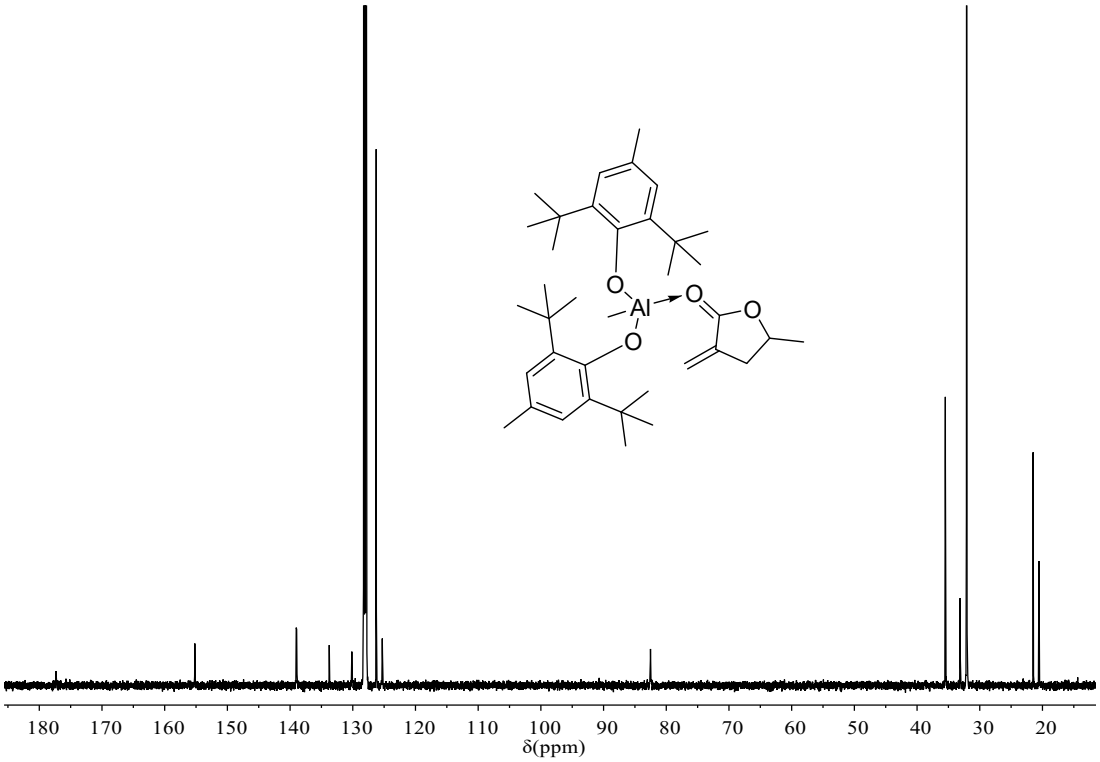



Figure S2. $^{13}C$ NMR spectrum of $(BHT)_2AlMe{\cdot}MMBL$ (Benzene-$d_6$, 125 MHz).

**Isolation of $(BHT)_2Al^iBu{\cdot}MMBL$** $(BHT)_2Al^iBu{\cdot}MMBL$ Adduct was prepared and isolated as a white powder in 85% yield (540mg) using the same procedure as described for the preparation of $Al(C_6F_5)_3{\cdot}MMBL$. $^1H$ NMR (500 MHz, Benzene-$d_6$) δ 7.25 (s, 4H, Ar-H), 6.46 (s, 1H, =C*H*), 5.04 (s, 1H, =CH), 3.81 (m, 1H, OC*H*), 2.31 (s, 6H, 2*Me*Ar), 2.13 (m, 1H, $CH_2CH(CH_3)_2$), 1.68 (s, 36H, 2$^t$*Bu*Ar), 1.15 (d, *J* = 6.0Hz, 6H, $CH_2CH(CH_3)_2$), 0.76 (m, 2H, $CH_2CH(CH_3)_2$), 0.58 (d, *J* = 6.5 Hz, 3H, $CH_3$). $^{13}C$ NMR (126 MHz, Benzene-$d_6$) δ 177.0, 154.8, 138.4, 133.5, 129.7, 126.0, 125.0, 82.0, 35.2, 32.9, 31.8, 28.6, 28.4, 25.7, 25.2, 21.1, 20.2, 14.0 ppm.

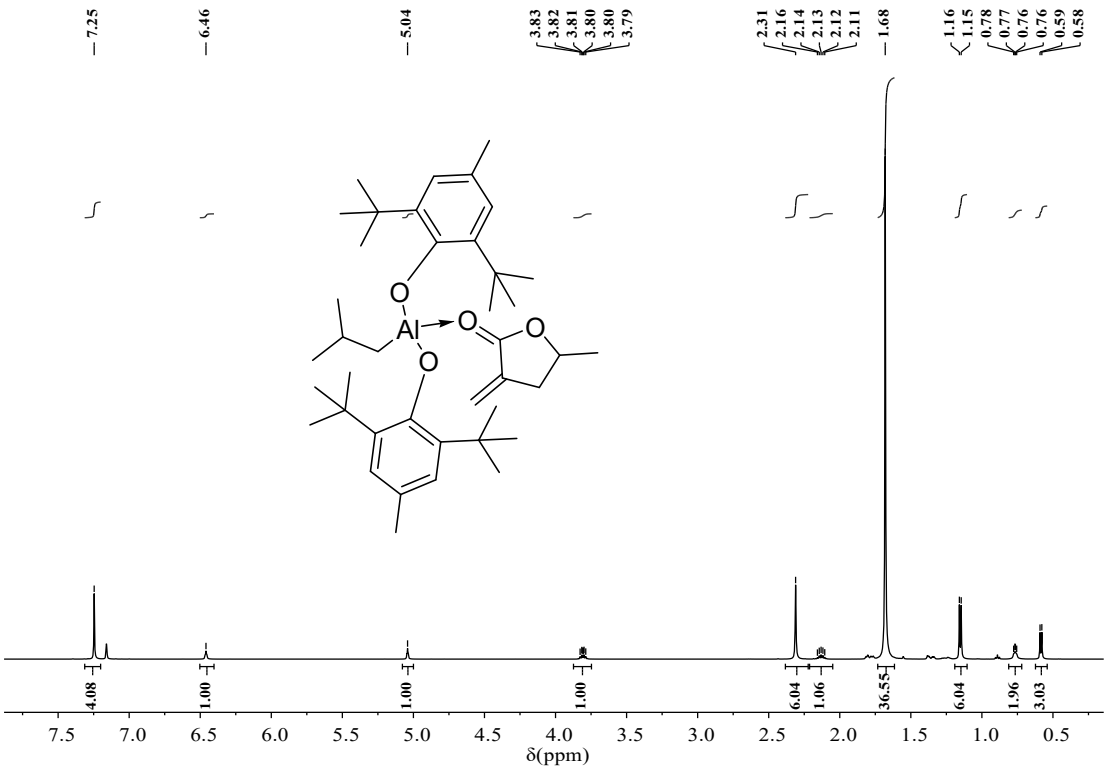



Figure S3. $^{1}$H NMR spectrum of (BHT)$_2$Al$^{i}$Bu·MMBL (Benzene-$d_6$, 500 MHz).

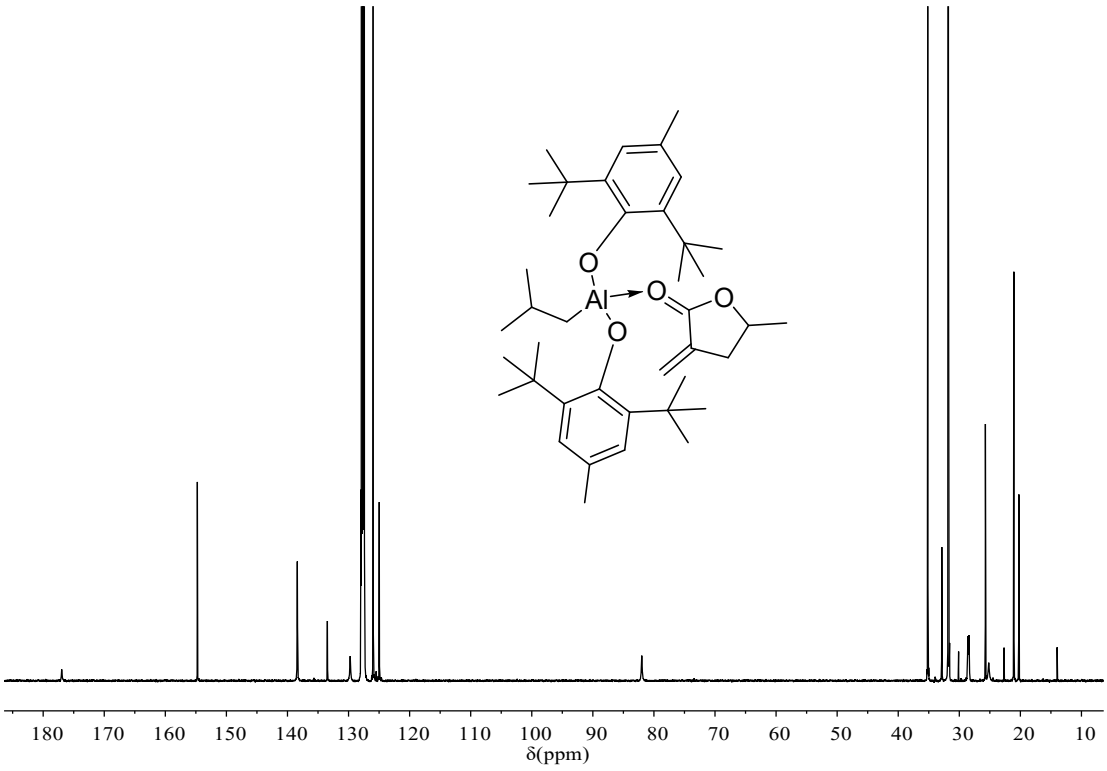



Figure S4. $^{13}$C NMR spectrum of (BHT)$_2$Al$^{i}$Bu·MMBL (Benzene-$d_6$, 125 MHz).

## 3. Stoichiometric NMR Reaction

### NMR Reaction of P(NI$^i$Pr)$^i$Pr$_2$ with (BHT)$_2$Al$^i$Bu·MMBL in a 1:1 ratio

In an argon-filled glovebox, a Teflon-valve-sealed J. Young-type NMR tube was charged with 3.11 mg (0.01 mmol) of P(NI$^i$Pr)$^i$Pr$_2$ and 0.3 mL of $C_6D_6$. A 0.3 mL $C_6D_6$ solution of (BHT)$_2$Al$^i$Bu·MMBL (6.40 mg, 0.01 mmol) was slowly added to this tube via pipet at room temperature. The mixture was allowed to react for 15 min at room temperature before the NMR spectra were recorded, which showed the clean formation of the zwitterion **1**. $^1$H NMR (500 MHz, Benzene-$d_6$) δ 7.29 (s, 4H, Ar-H), 4.36 (m, 1H, OC*H*), 4.31 (m, 2H, 2NC*H*(CH$_3$)$_2$), 2.99 (dd, *J* = 15.5Hz, 11Hz, 1H, PC*H*$_2$), 2.88 (dd, *J* = 15.5Hz, 11Hz, 1H, PC*H*$_2$), 2.53 (m, 1H, CH$_2$C*H*(CH$_3$)$_2$), 2.39 (s, 6H, 2*Me*Ar), 2.37 (dd, *J* = 11.5Hz, 8Hz, 1H, C*H*$_2$), 2.01 (dd, *J* = 11.5Hz, 8Hz, 1H, C*H*$_2$), 1.83 (s, 36H, 2$^t$*Bu*Ar), 3.20(d, *J* = 10Hz, 2H, P*CH*$_2$), 1.57 (s, 6H, *Me*C=C*Me*), 1.41 (d, *J* = 6.5Hz, 6H, CH$_2$CH(C*H*$_3$)$_2$), 1.27 (d, *J* = 6.5 Hz, 3H, OCHC*H*$_3$), 0.92-1.02 (m, 2H, C*H*$_2$CH(CH$_3$)$_2$), 0.92-1.02 (m, 12H, PCH(CH$_3$)$_2$), 0.92-1.02 (m, 12H, NCH(*CH*$_3$)$_2$). $^{31}$P NMR (202Hz, Benzene-$d_6$) δ 37.2 ppm (m).

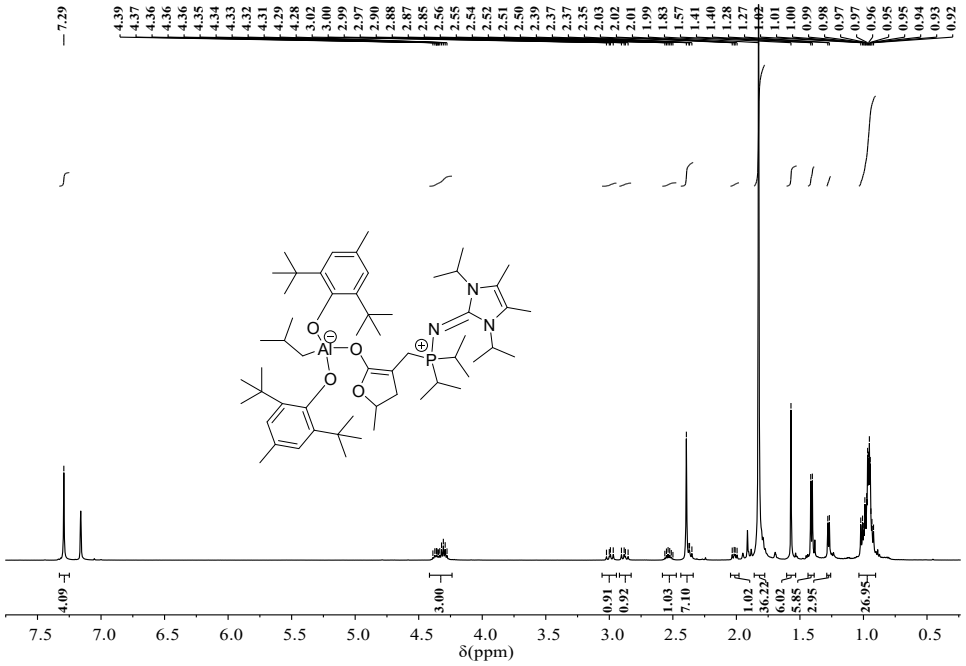



Figure S5. $^1$H NMR spectrum for the reaction of P(NI$^i$Pr)$^i$Pr$_2$ with (BHT)$_2$Al$^i$Bu·MMBL. (500 MHz, Benzene-$d_6$).

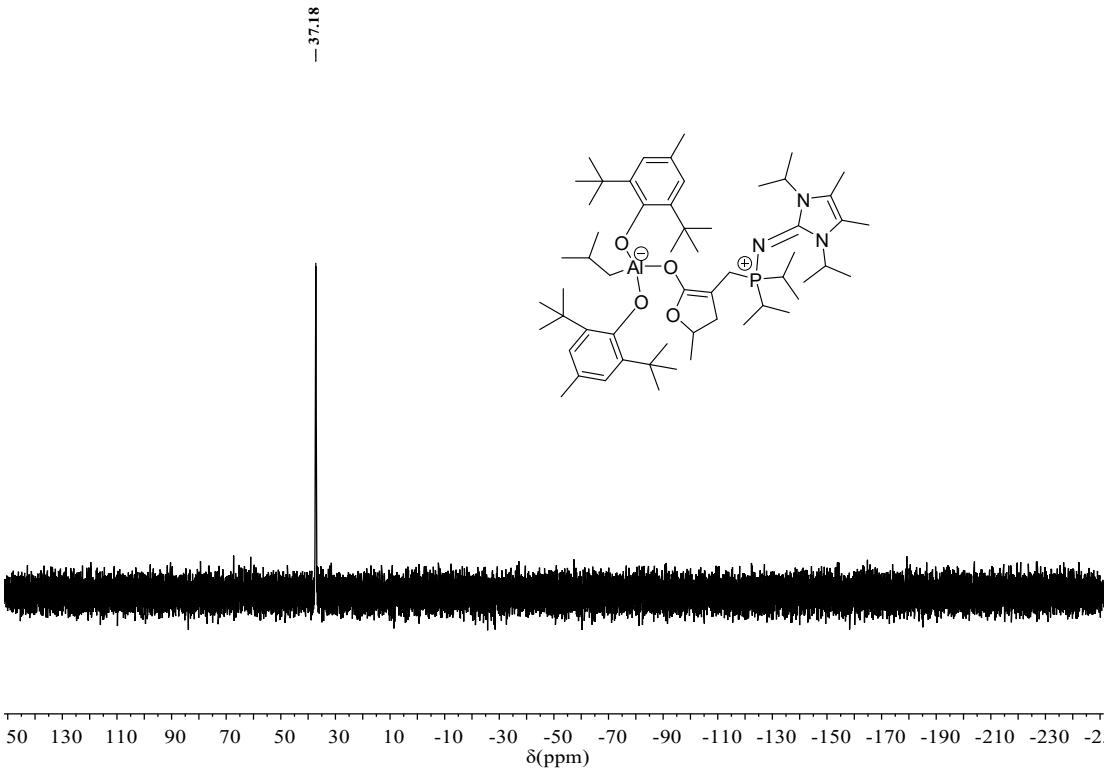



Figure S6. $^{31}$P NMR spectrum for the reaction of P(NI$^{i}$Pr)$^{i}$Pr$_2$ with (BHT)$_2$Al$^{i}$Bu·MMBL. (202 MHz, Benzene-$d_6$).

**NMR Reaction of P(NI$^{i}$Pr)Ph$_2$ with (BHT)$_2$Al$^{i}$Bu·MMBL in a 1:1 ratio**

In an argon- filled glovebox, a Teflon-valve-sealed J. Young-type NMR tube was charged with 3.79 mg (0.01 mmol) of P(NI$^{i}$Pr)Ph$_2$ and 0.3 mL of $C_6D_6$. A 0.3 mL $C_6D_6$ solution of (BHT)$_2$Al$^{i}$Bu·MMBL (6.40 mg, 0.01 mmol) was slowly added to this tube via pipet at room temperature. The mixture was allowed to react for 15 min at room temperature before the NMR spectra were recorded, which showed the clean formation of the zwitterion **2**. $^{1}$H NMR (500 MHz, Benzene-$d_6$) δ 7.53-7.56 (m, 2H, P-Ph), 7.46-7.50 (m, 2H, P-Ph), 7.31 (s, 4H, Ar-H), 7.07-7.10 (m, 6H, P-Ph), 4.30 (m, 1H, OC*H*), 4.30 (m, 2H, 2NC*H*(CH$_3$)$_2$), 3.95 (dd, *J* = 16Hz, 12Hz, 1H, PC$H_2$), 3.67 (dd, *J* = 16Hz, 12Hz, 1H, PC$H_2$), 2.58 (m, 1H, CH$_2$C*H*(CH$_3$)$_2$), 2.38 (s, 6H, 2*Me*Ar), 2.12 (dd, *J* = 12.5Hz, 9.5Hz, 1H, C$H_2$), 1.84 (dd, *J* = 12.5Hz, 9.5Hz, 1H, C$H_2$), 1.84 (s, 36H, 2$^{t}$*Bu*Ar), 1.50 (s, 6H, *Me*C=C*Me*), 1.42 (d, *J* = 6.5Hz, 6H, CH$_2$CH(C$H_3$)$_2$), 1.12 (d, *J* = 6.0 Hz, 3H, OCHC$H_3$), 0.85 (d, *J* = 7Hz, 6H, NCH(*CH*$_3$)$_2$), 0.81 (d, *J* = 7Hz, 6H, NCH(*CH*$_3$)$_2$). $^{31}$P NMR (202Hz, Benzene-$d_6$) δ 9.9 ppm (m).

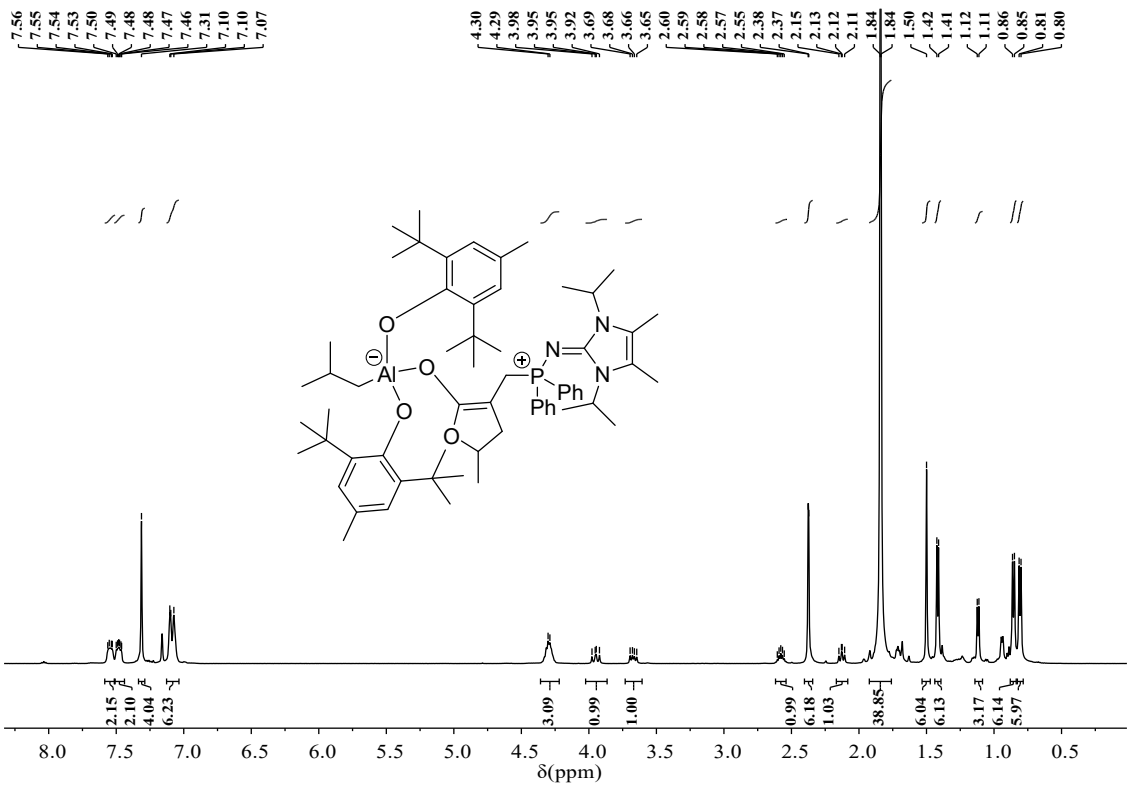



Figure S7. $^{1}$H NMR spectrum for the reaction of P(NI$^{i}$Pr)Ph$_2$ with (BHT)$_2$Al$^{i}$Bu·MMBL. (500 MHz, Benzene-$d_6$).

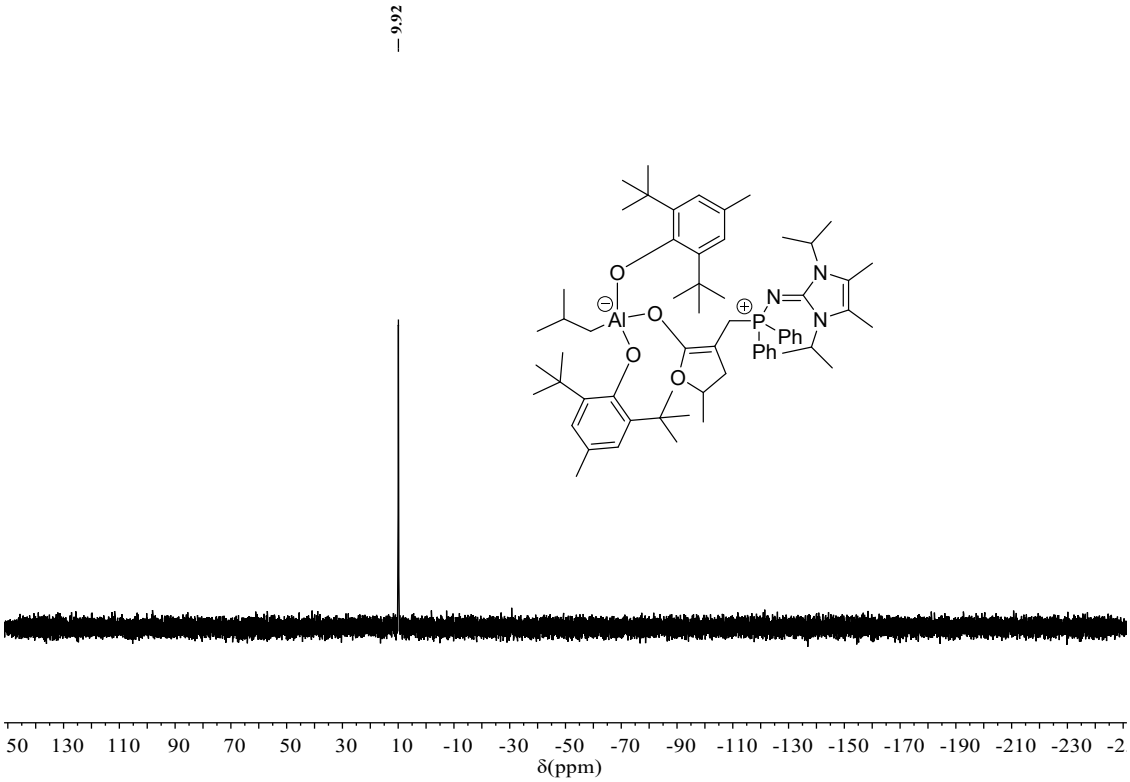



Figure S8. $^{31}$P NMR spectrum for the reaction of P(NI$^{i}$Pr)Ph$_2$ with (BHT)$_2$Al$^{i}$Bu·MMBL. (202 MHz, Benzene-$d_6$).

## 4. 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 triethylphsophine oxide resonance upon binding to the electron–deficient aluminum catalyst relative to $Al(C_6F_5)_3$, similar to determining the Lewis Acidity of electron–deficient boron catalyst relative to $B(C_6F_5)_3$ by the Gutmann−Beckett method [14,15]. In a glove box, aluminum catalyst (0.025 mmol) was added to a 0.5 mL $C_6D_6$ solution of $Et_3PO$ (0.025 mmol/0.5 mL, 0.05 M) in a 4-mL NMR tube. The reaction mixture was monitored by $^{31}P$ NMR spectroscopy after 30 min at room temperature.

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

| Aluminum Catalyst | $^{31}P\{^1H\}$ NMR (δ/ppm) | △δ values relative to free $Et_3PO$ (δ/ppm) | Relative Lewis Acidity (%) |
|---|---|---|---|
| $Al(C_6F_5)_3$ | 73.5 | 28.0 | 100% |
| $(BHT)_2AlMe$ | 69.5 | 24.0 | 86% |
| $(BHT)_2Al^iBu$ | 69.4 | 23.9 | 85% |
| $(BHT)Al^iBu_2$ | 66.3 | 20.8 | 74% |

## 5. Selected polymerization results

**Table S2. (M)MBL Polymerization by $P(NI^iPr)R_2$-based LPs.**[a]

| Run | LB | LA | M | [M]:[LA]:[LB] | T (min) | conv.[b] (%) | $M_n$[c] (kg·mol$^{-1}$) | $M_w$[c] (kg·mol$^{-1}$) | $Đ$[c] |
|---|---|---|---|---|---|---|---|---|---|
| 1 | $P(NI^iPr)^iPr_2$ | $(BHT)_2Al^iBu$·MMBL | MMBL | 400:2:1 | 90 | 100 | 105 | 112 | 1.07 |
| 2 | $P(NI^iPr)^tBu_2$ | $(BHT)_2Al^iBu$·MMBL | MMBL | 400:2:1 | 720 | 100 | 234.6 | 338 | 1.44 |
| 3 | $P(NI^iPr)Mes_2$ | $(BHT)_2Al^iBu$·MMBL | MMBL | 400:2:1 | 1440 | 100 | 208 | 300 | 1.44 |
| 4 | $P(NI^iPr)(C_6F_5)_2$ | $(BHT)_2Al^iBu$·MMBL | MMBL | 400:2:1 | 1440 | 0 | | | |
| 5 | $P(NI^iPr)Ph_2$ | $(BHT)Al^iBu_2$·MMA | MMBL | 200:2:1 | 1 | 100 | 32.1 | 33.4 | 1.04 |
| 6 | $P(NI^iPr)Ph_2$ | $(BHT)Al^iBu_2$·MMA | MMBL | 200:2:1 | 1 | | | | |
| | | | MMBL | 200:2:1 | 1 | 100 | 54.9 | 60 | 1.09 |
| 7 | $P(NI^iPr)Ph_2$ | $Al(C_6F_5)_3$·MMBL | MMBL | 200:2:1 | 1 | 100 | 36.5 | 43.8 | 1.2 |
| 8 | $P(NI^iPr)Ph_2$ | $Al(C_6F_5)_3$·MMBL | MMBL | 200:2:1 | 1 | | | | |
| | | | MMBL | 200:2:1 | 1 | 100 | 267/16.9[d] | 371/25 | 1.39/1.47 |
| 9 | $P(NI^iPr)Ph_2$ | $(BHT)_2AlMe$·MMBL | MMBL | 200:2:1 | 2 | 100 | 24.2 | 24.9 | 1.03 |
| 10 | $P(NI^iPr)Ph_2$ | $(BHT)_2AlMe$·MMBL | MMBL | 200:2:1 | 2 | | | | |
| | | | MMBL | 200:2:1 | 2 | 100 | 39.1 | 40.7 | 1.04 |
| 11 | $P(NI^iPr)Ph_2$ | $(BHT)_2AlMe$·MMBL | MMBL | 200:2:1 | 2 | | | | |
| | | | MBL | 200:2:1 | 2 | 100 | 48.5 | 52.8 | 1.09 |

[a] Conditions: carried out in dichloromethane at RT; $[M]_0$ = 0.936 M. [b] Monomer conversions measured by $^1H$ NMR. [c] Absolute molecular weight ($M_w$) measured by GPC using a light scattering detector. Number-average molecular weight ($M_n$) is calculated from $M_w/Đ$. [d] Bimodal distribution.

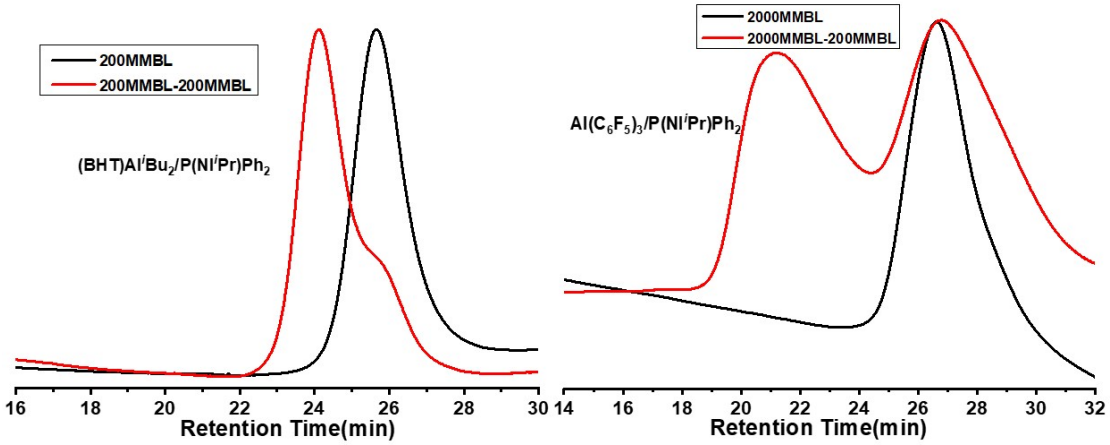



Figure S9. GPC traces for PMMBL samples obtained from chain extension experiments by P(NI$^{i}$Pr)Ph$_2$/(BHT)Al$^{i}$Bu$_2$ (left) and P(NI$^{i}$Pr)Ph$_2$/Al(C$_6$F$_5$)$_3$ LPs (right).

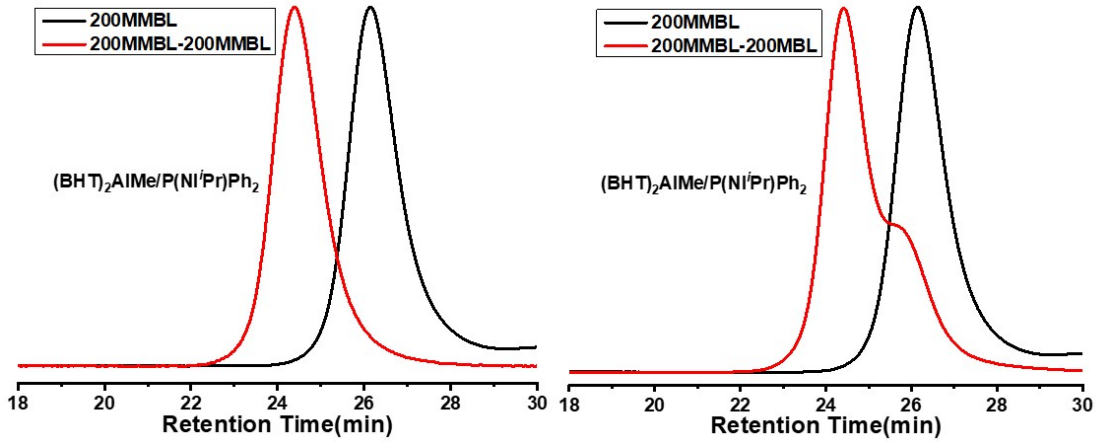



Figure S10. GPC traces for (left) PMMBL samples obtained from chain extension experiments by P(NI$^{i}$Pr)Ph$_2$/(BHT)$_2$AlMe and (right) diblock copolymer produced from the sequential block copolymerization of MMBL and MBL by P(NI$^{i}$Pr)Ph$_2$/(BHT)$_2$AlMe.

**Table S3. MMBL polymerization by different activation procedures**[a]

| run | LA | M:LA: P(NI$^{i}$Pr)Ph$_2$ | Time (min) | conv.[b] (%) | $M_n$[c] (kg/mol) | $M_w$[c] (kg·mol$^{-1}$) | MWD[c] | $I$*[d] (%) |
|---|---|---|---|---|---|---|---|---|
| 1[A] | (BHT)$_2$Al$^{i}$Bu | 400:2:1 | 90 | 100 | 47.5 | 54.7 | 1.15 | 94 |
| 2[B] | (BHT)$_2$Al$^{i}$Bu | 400:2:1 | 90 | 100 | 47.4 | 54.3 | 1.15 | 94 |

[a]Condition: carried out in dichloromethane at RT; [M]$_0$ = 0.936 M. [b]Monomer conversions measured by $^1$H NMR. [c] Absolute molecular weight ($M_w$) measured by GPC using a light scattering detector. Number-average molecular weight ($M_n$) is calculated from $M_w/Đ$. [d] Initiator efficiency ($I$*)% = $M_n$(calcd)/$M_n$(exptl) × 100, where $M_n$(calcd) = [MW(MMBL)] × ([MMBL]$_0$/[I]$_0$) (conversion) + MW of chain-end groups, A: premixed LA and monomer to preactivate monomer first; B: the premixed LA and LB first, followed by the addition of monomer.

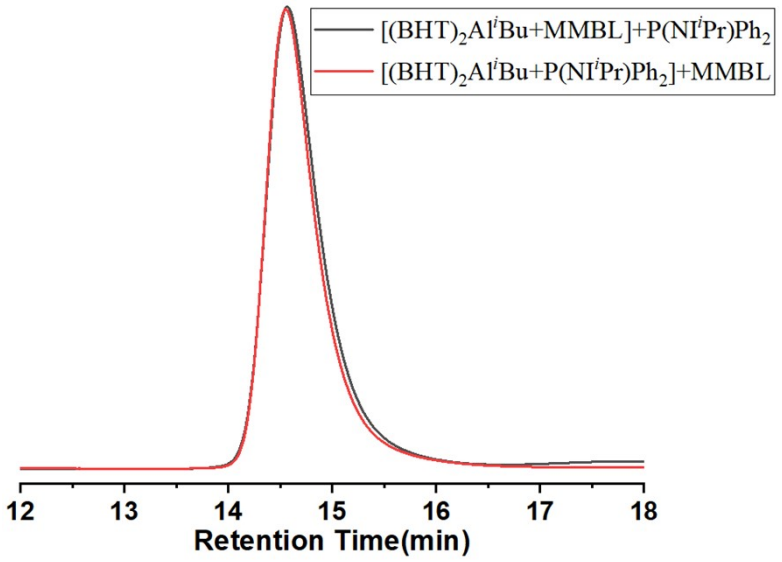



Figure S11. GPC traces of PMMBL obtained from the polymerization performed using different activation procedures.

**6. MALDI-TOF MS spectra of low MW PMMBL sample**

**MALDI-TOF MS spectra of low MW PMMBL sample produced by P(NI$^i$Pr)Ph$_2$/(BHT)Al$^i$Bu$_2$**

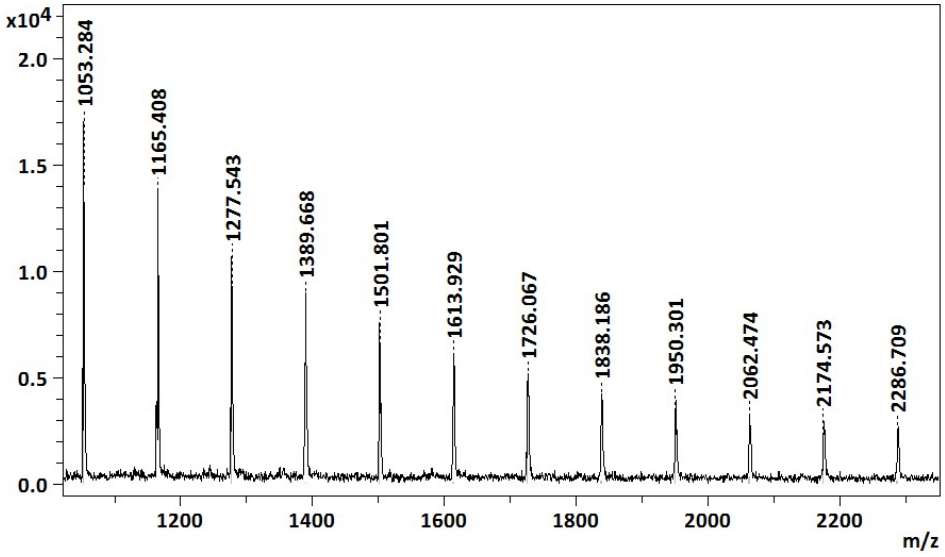



Figure S12. MALDI-TOF MS spectrum of the low-MW PMMBL sample produced by P(NI$^i$Pr)Ph$_2$/(BHT)Al$^i$Bu$_2$ in dichloromethane at RT.

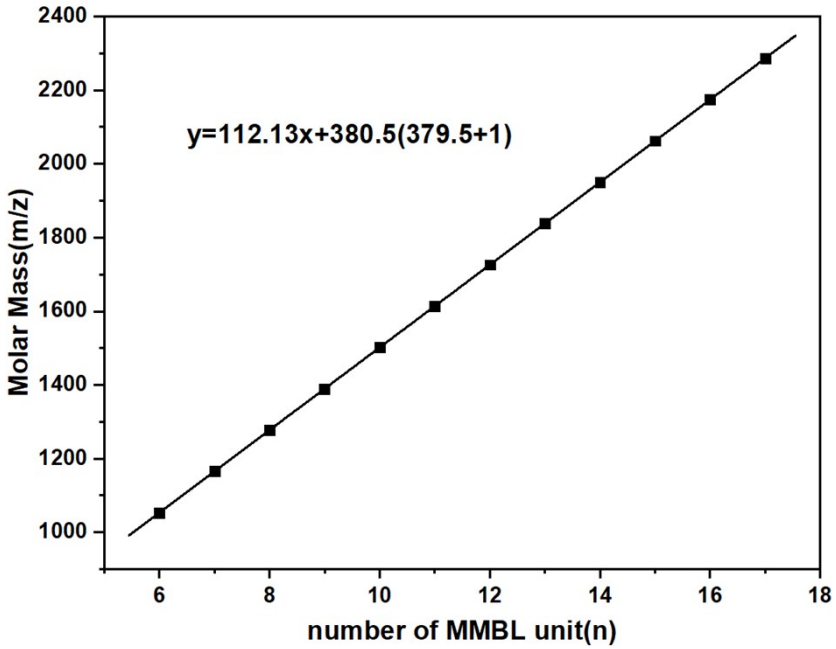



Figure S13. Plot of *m*/*z* values from Figure S12 vs the number of MMBL repeat units (*n*).

**MALDI-TOF MS spectra of low MW PMMBL sample produced by P(NI$^i$Pr)Ph$_2$/Al(C$_6$F$_5$)$_3$**

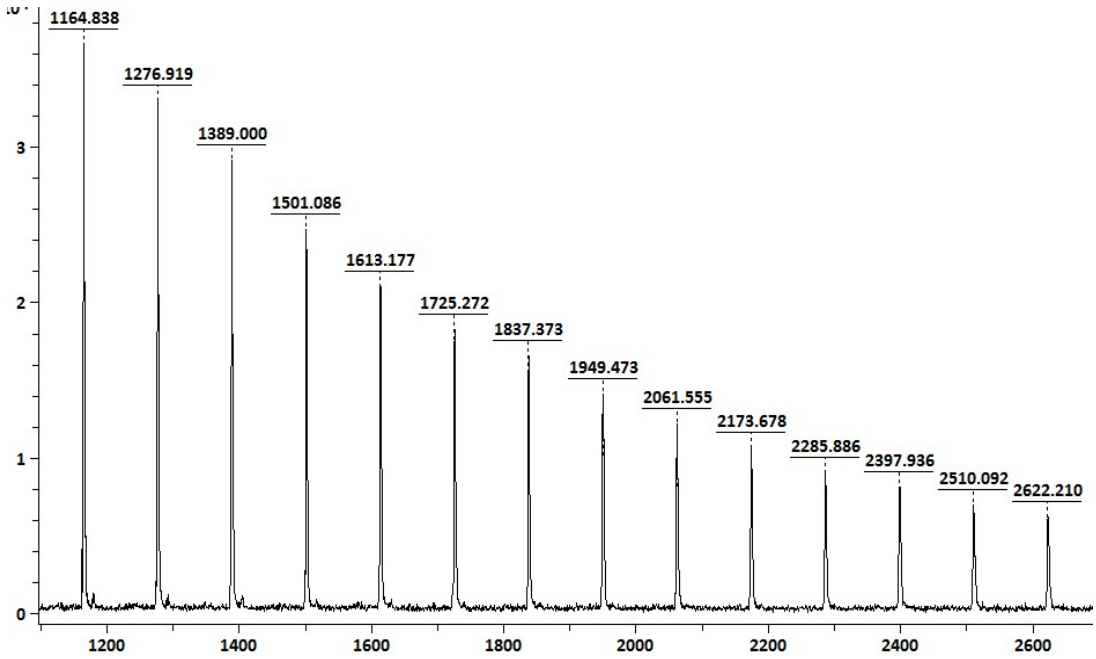



Figure S14. MALDI-TOF mass spectrum of the low-MW PMMBL sample produced by P(NI$^i$Pr)Ph$_2$/Al(C$_6$F$_5$)$_3$ in dichloromethane at RT.

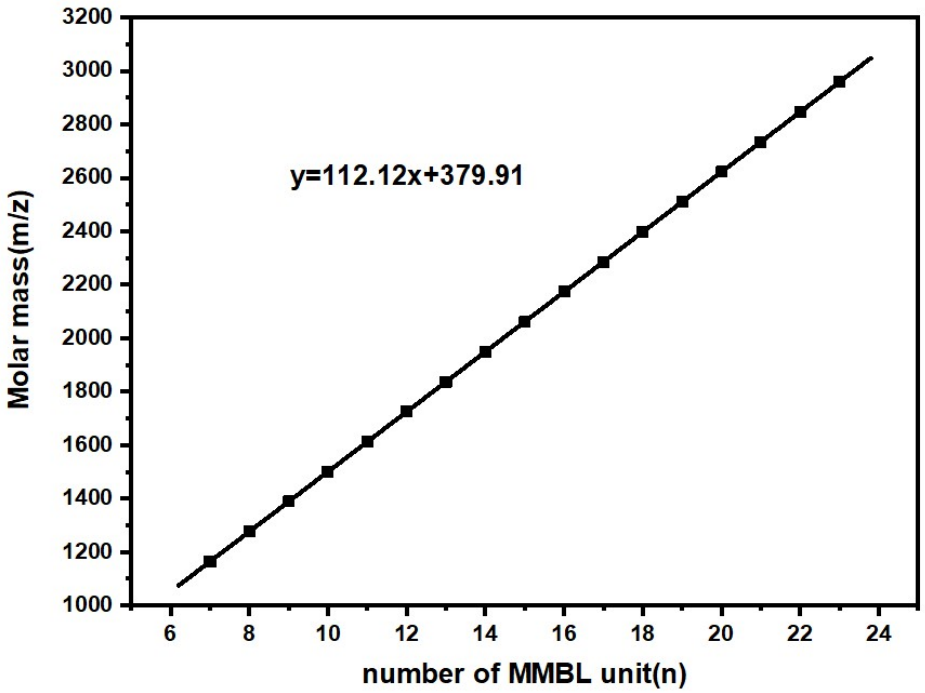



Figure S15. Plot of *m*/*z* values from Figure S14 vs the number of MMBL repeat units (*n*).

**MALDI-TOF MS spectra of low MW PMMBL sample produced by P(NI$^i$Pr)Ph$_2$/(BHT)$_2$AlMe**

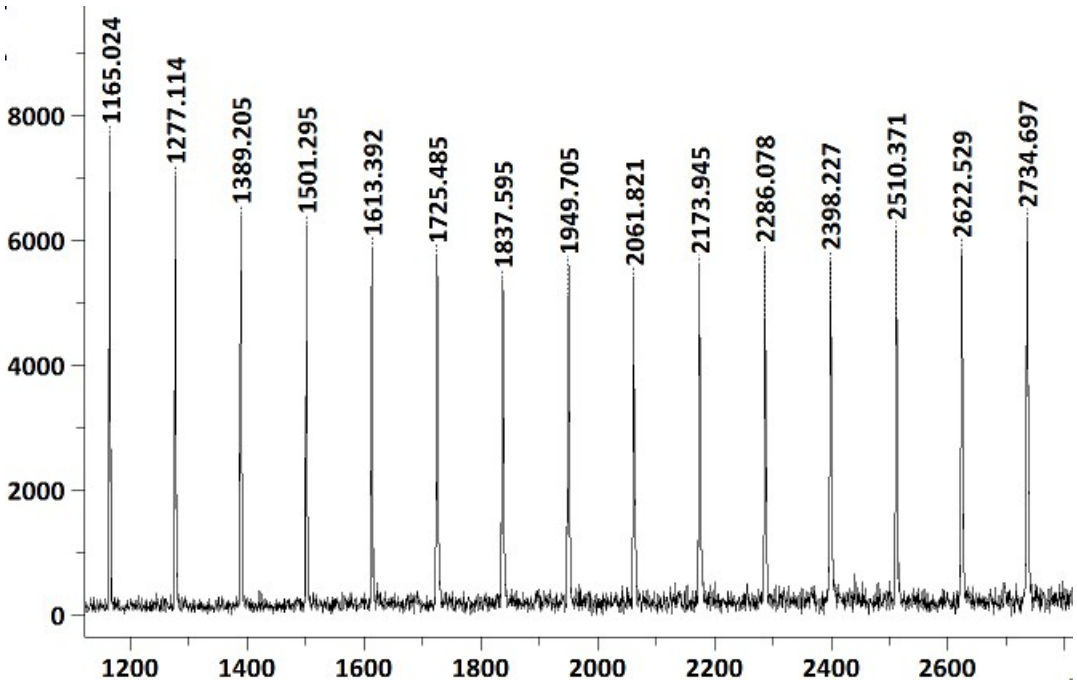



Figure S16. MALDI-TOF mass spectrum of the low-MW PMMBL sample produced by P(NI$^i$Pr)Ph$_2$/(BHT)$_2$AlMe in dichloromethane at RT.

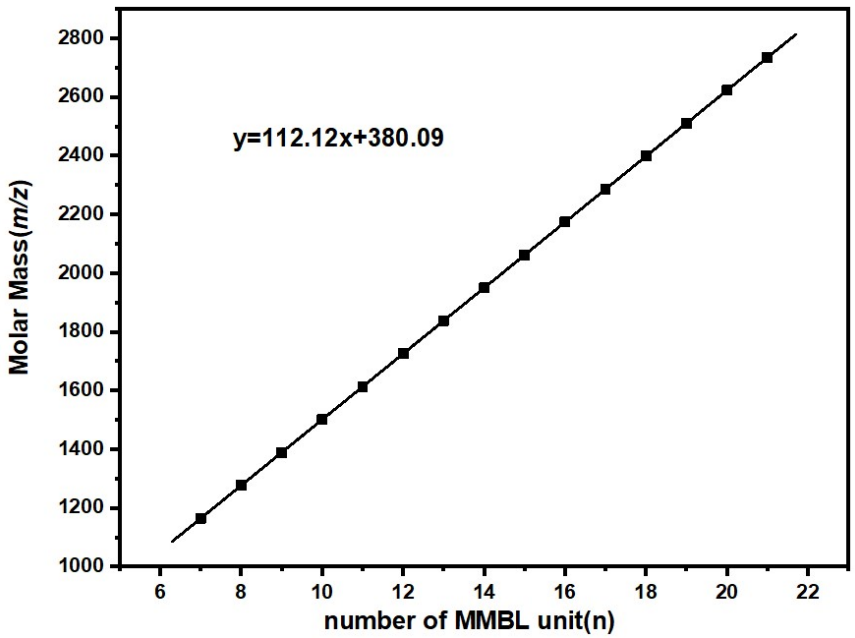



Figure S17. Plot of *m*/*z* values from Figure S16 vs the number of MMBL repeat units (*n*).

**MALDI-TOF MS spectra of low MW PMMBL sample produced by P(NI$^i$Pr)Ph$_2$/(BHT)$_2$Al$^i$Bu**

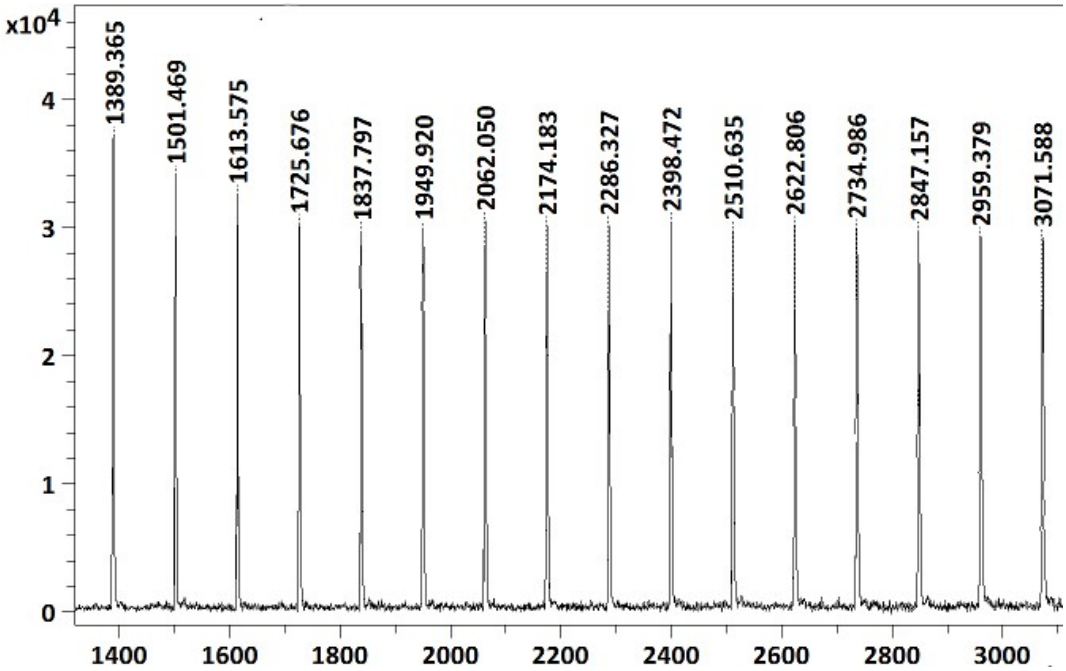



Figure S18. MALDI-TOF mass spectrum of the low-MW PMMBL sample produced by P(NI$^i$Pr)Ph$_2$/(BHT)$_2$Al$^i$Bu in dichloromethane at RT.

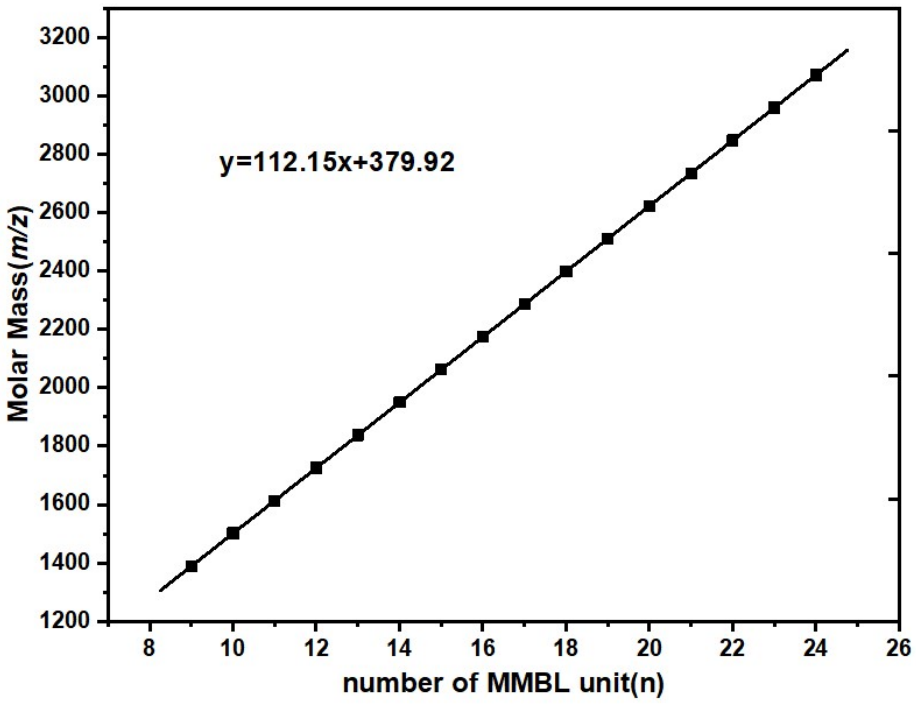
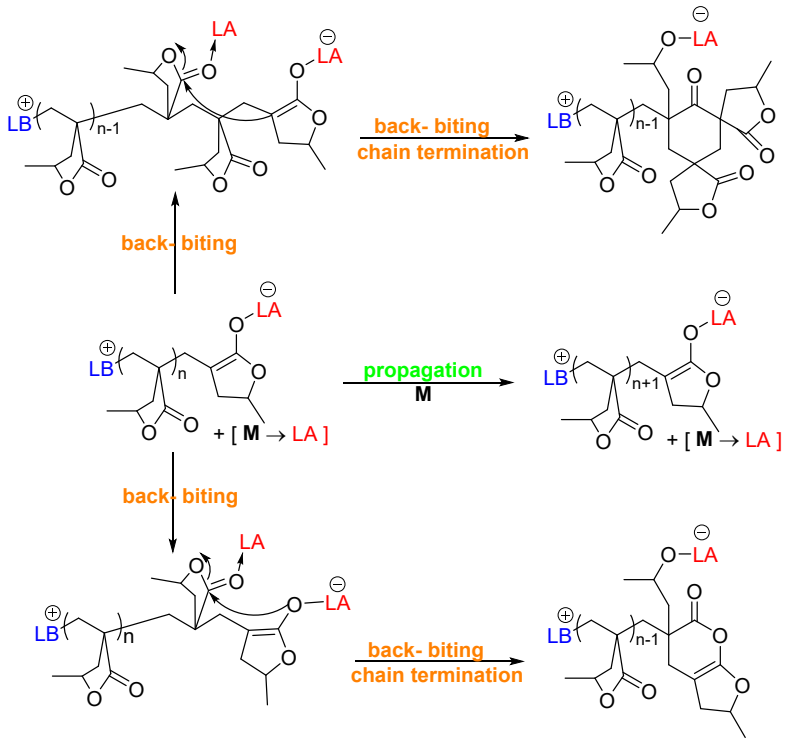



Figure S19. Plot of *m*/*z* values from Figure S18 vs the number of MMBL repeat units (*n*).




Scheme S1. Possible backbiting chain-termination pathways that compete with chain propagation in the polymerization of MMBL by the P(NI$^i$Pr)$R_2$-based Lewis pair.

## 7. Chain extension experiments by P(NI$^i$Pr)Ph$_2$/(BHT)$_2$Al$^i$Bu

**Table S4 chain-extension experiments by P(NI$^i$Pr)Ph$_2$/(BHT)$_2$Al$^i$Bu** [a]

| run | M1/M2/M3 | Conv.[b] (%) | $M_n$[c] (kg·mol$^{-1}$) | $M_w$[c] (kg·mol$^{-1}$) | $Đ$[c] | $I$*[d] (%) |
|---|---|---|---|---|---|---|
| 1 | 200MMBL | >99 | 26.2 | 27.5 | 1.05 | 85 |
| 2 | 200/200MMBL | >99 | 45.3 | 48.5 | 1.07 | 99 |
| 3 | 200/200/200MMBL | >99 | 73.2 | 79.1 | 1.08 | 92 |

[a] Conditions: carried out in dichloromethane at RT; $[M]_0$ = 0.936 M. [b] Monomer conversions measured by $^1$H NMR [c] Absolute molecular weight ($M_w$) measured by GPC using a light scattering detector. Number-average molecular weight ($M_n$) is calculated from $M_w/Đ$. [d] Initiator efficiency ($I$*)% = $M_n$(calcd)/$M_n$(exptl) × 100, where $M_n$(calcd) = [MW(MMBL)] × ($[MMBL]_0/[I]_0$) (conversion) + MW of chain-end groups.

## 8. Copolymerization catalyzed by P(NI$^i$Pr)Ph$_2$/(BHT)$_2$Al$^i$Bu FLP

**Table S5. Copolymerization of MMBL and MBL by P(NI$^i$Pr)Ph$_2$/(BHT)$_2$Al$^i$Bu FLP.**[a]

| Run | M1/M2 | Conv.[b] (%) | $M_n$[c] (kg·mol$^{-1}$) | $M_w$[c] (kg·mol$^{-1}$) | $Đ$[c] |
|---|---|---|---|---|---|
| 1 | 200MMBL | >99 | 26.2 | 27.5 | 1.05 |
| 2[d] | 200MMBL+200MBL | MMBL:100 | | | |
| | | MBL:100 | 50.9 | 52.5 | 1.03 |
| 3 | 200MMBL/200MBL | MMBL:100 | | | |
| | | MBL:100 | 45.8 | 48.1 | 1.05 |
| 4 | 200MMBL/200MBL/200MMBL | MMBL:100 | | | |
| | | MBL:100 | | | |
| | | MMBL:100 | 65.7 | 69.7 | 1.06 |

[a] Conditions: carried out in dichloromethane at RT; $[M]_0$ = 0.936 M. [b] Monomer conversions measured by $^1$H NMR [c] Absolute molecular weight ($M_w$) measured by GPC using a light scattering detector. Number-average molecular weight ($M_n$) is calculated from $M_w/Đ$. [d] MMBL and MBL was added at the same time.

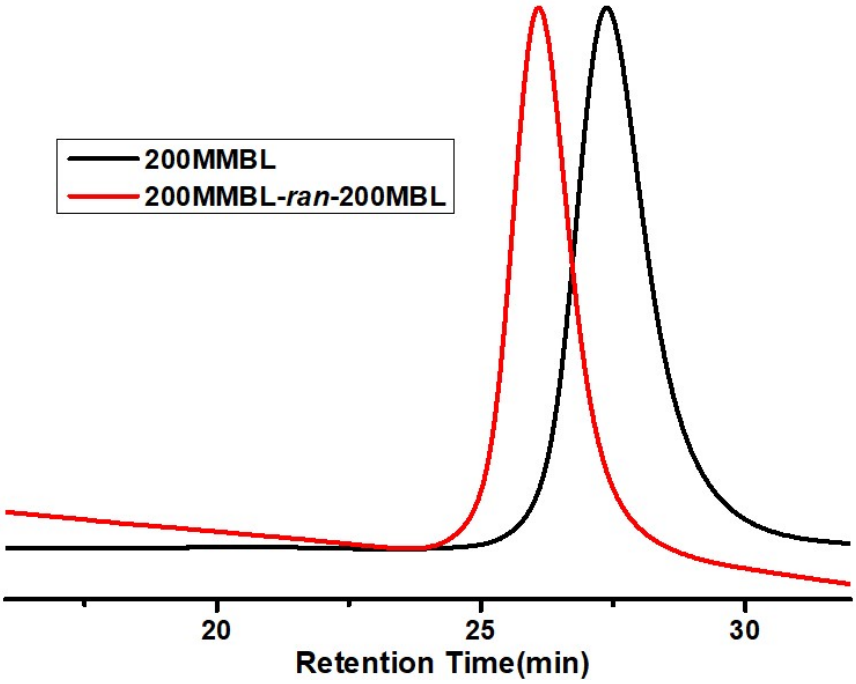



Figure S20. GPC traces of homopolymer (black), random copolymer (red) by $(BHT)_2Al^iBu$/ $P(NI^iPr)Ph_2$ in dichloromethane, where $[MMA]_0 = 0.936$ M.

**Table S6. Copolymerization of MMA, EEMA and MMBL by $P(NI^iPr)Ph_2/(BHT)_2Al^iBu$ FLP.**[a]

| run | M1/M2/M3 | Solvent | Conv.[b] (%) | $M_n$[c] (kg·mol$^{-1}$) | $Đ$[c] |
|---|---|---|---|---|---|
| 1 | 200MMA | TOL | 100 | 31.8 | 1.09 |
| 2 | 200/200MMA | TOL | 100 | 54.6 | 1.07 |
| 3 | 200/200/200MMA | TOL | 100 | 76.4 | 1.07 |
| 4 | 100MMA | DCM | 100 | 13.0 | 1.25 |
| 5 | 100MMA/100MMBL | DCM | MMA:100 MMBL:100 | 26.0 | 1.17 |
| 6 | 100MMBL | DCM | 100 | 18.3 | 1.05 |
| 7 | 100MMBL/100MMA | DCM | MMBL:100 MMA:0 | n.d | n.d |
| 8[d] | 200MMA+200MBL | DCM | MMBL:100 MMA:0 | n.d | n.d |
| 9 | 100EEMA | TOL | 100 | 16.2 | 1.18 |
| 10 | 100EEMA/100MMBL | TOL | EEMA:100 MMBL:100 | 28.0 | 1.15 |

[a] Conditions: carried out in dichloromethane or toluene at RT; $[M]_0 = 0.936$ M. [b] Monomer conversions measured by $^1$H NMR [c] $M_n$ and $Đ$ determined by GPC relative to PMMA standards in DMF. n.d.=not determined. [d] MMA and MMBL was added at the same time.

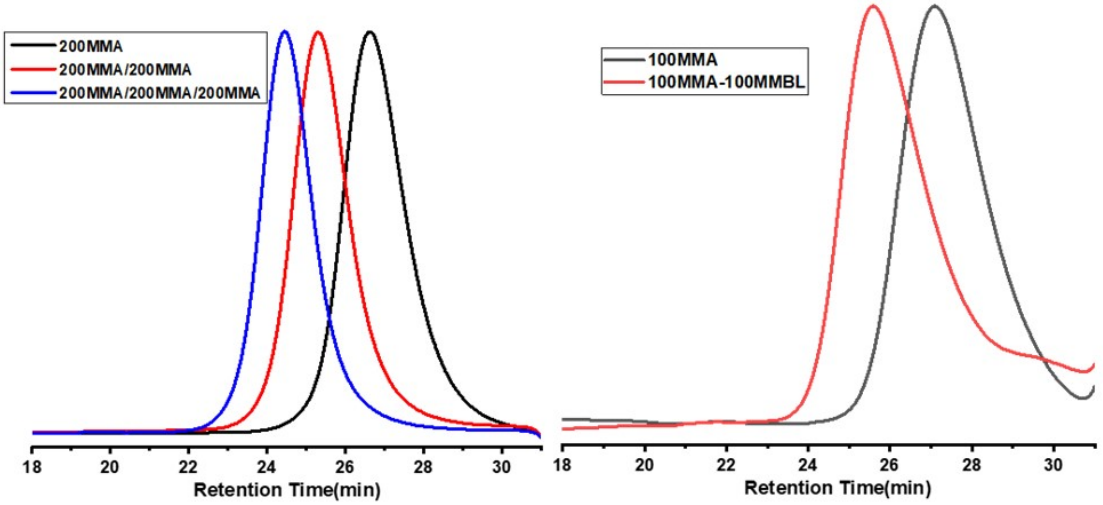



Figure S21. GPC traces for PMMA samples obtained from chain extension experiments by $P(NI^iPr)Ph_2/(BHT)_2Al^iBu$ in toluene, where $[MMA]_0$ = 0.936 M (Left) and homopolymer, diblock copolymer produced from the sequential block copolymerization of MMA and MMBL by $P(NI^iPr)Ph_2/(BHT)_2Al^iBu$ in dichloromethane at RT (Right).

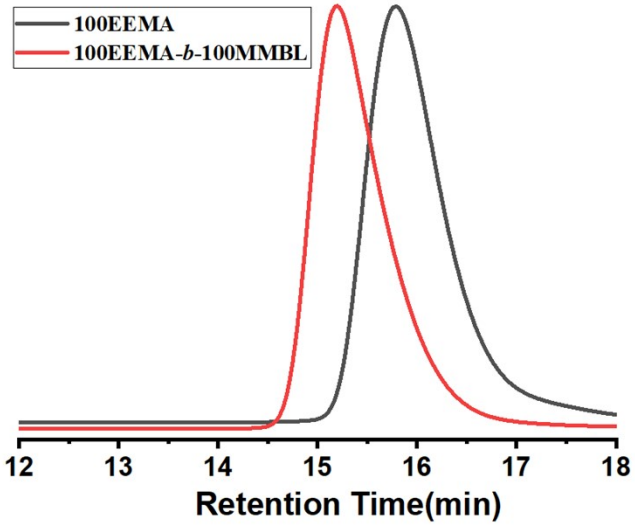



Figure S22. GPC traces of homopolymer, diblock copolymer produced from the sequential block copolymerization of EEMA and MMBL by $P(NI^iPr)Ph_2/(BHT)_2Al^iBu$ in toluene at RT.

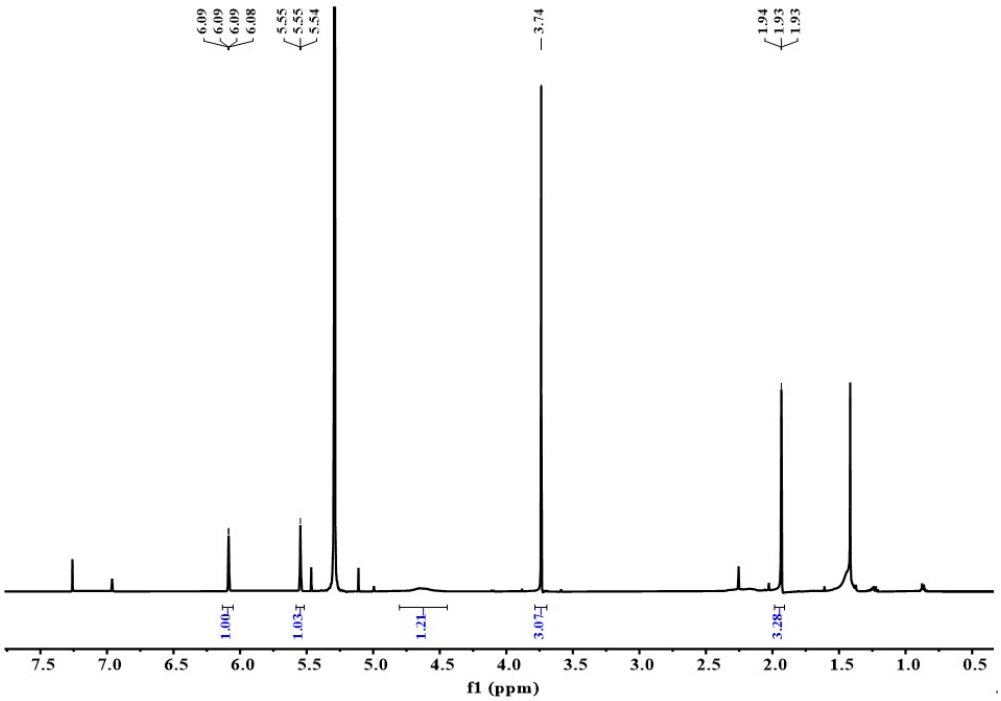



Figure S23. The aliquot of the polymerization for run7 in Table S6. (500 MHz, Chloroform-*d*).

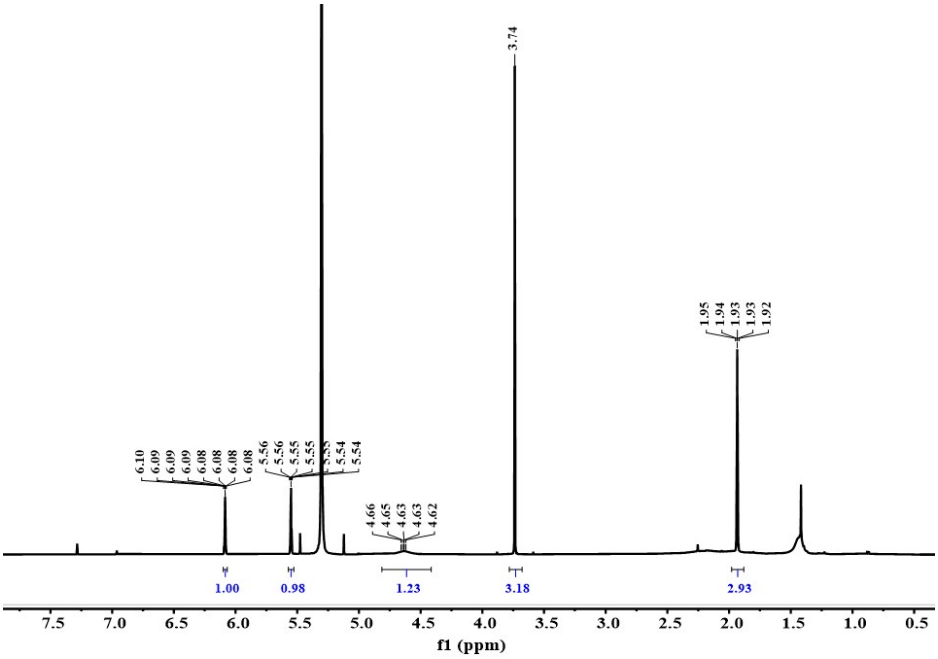



Figure S24. The aliquot of the polymerization for run8 in Table S6. (500 MHz, Chloroform-*d*).

**9. DSC of polymer samples obtained with P(NI$^i$Pr)Ph$_2$/(BHT)$_2$Al$^i$Bu FLP**

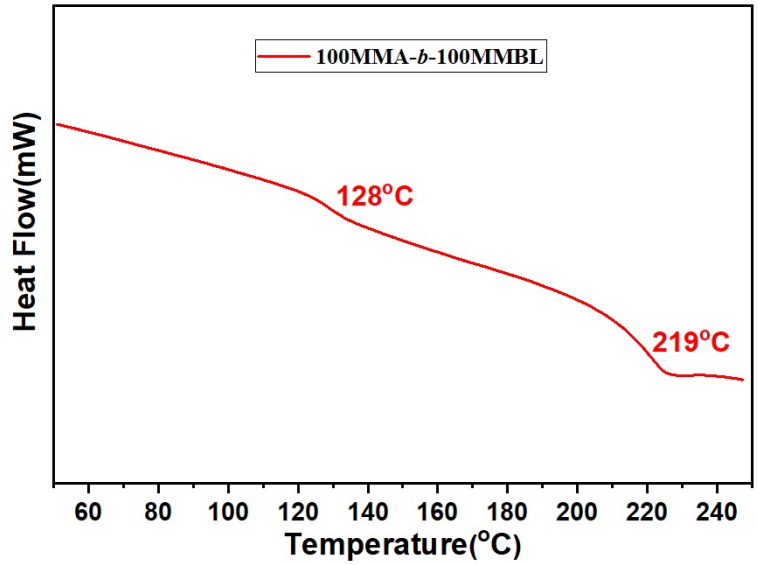



Figure S25. DSC of diblock PMMA-*b*-PMMBL copolymer produced by P(NI$^i$Pr)Ph$_2$/(BHT)$_2$Al$^i$Bu

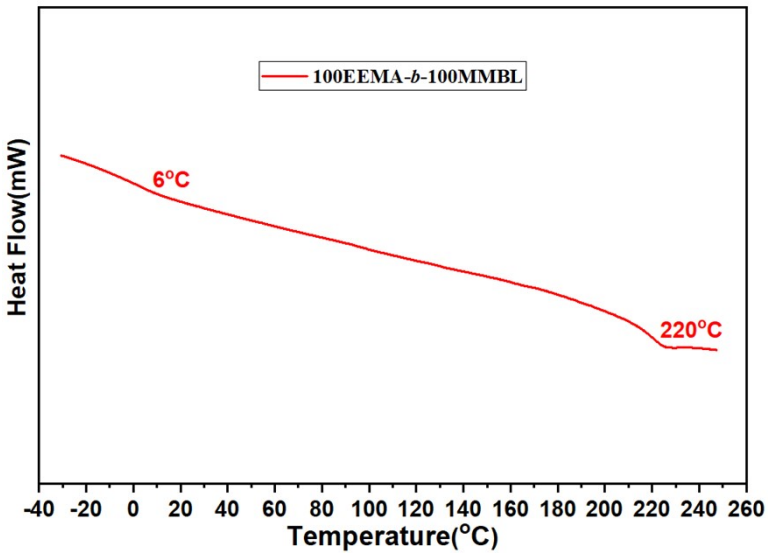



Figure S26. DSC of diblock PEEMA-*b*-PMMBL copolymer produced by P(NI$^i$Pr)Ph$_2$/(BHT)$_2$Al$^i$Bu

**10. 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 fixed 1:2 [P(NI$^i$Pr)Ph$_2$]$_0$/[(BHT)$_2$Al$^i$Bu]$_0$ ratio and

$[MMBL]_0$ at 0.936 M, where $[P(NI^iPr)Ph_2]_0$ = 1.17, 2.34, 4.68, and 9.36 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. The quenched aliquots were analyzed by $^1H$ NMR for determining the ratio of $[MMBL]_t$ at a given time *t* to $[MMBL]_0$, $[MMBL]_t/[MMBL]_0$. apparent rate constants ($K_{app}$) were extracted from the slopes of the best fit lines to the plots of $[MMBL]_t/[MMBL]_0$ vs time. In the second set of kinetic experiments, with a fixed $[MMBL]_0/[P(NI^iPr)Ph_2]_0$ ratio of 400:1 but varied $[(BHT)_2Al^iBu]_0$ concentration: $[MMBL]_0/[P(NI^iPr)Ph_2]_0/[(BHT)_2Al^iBu]_0$ = 400:1:2, 400:1:3, 400:1:4 and 400:1:5. $[MMBL]_0$ was fixed at 0.936 M for all polymerization, where $[P(NI^iPr)Ph_2]_0$= 2.34mM and $[(BHT)_2Al^iBu]_0$ = 4.68, 7.02, 9.36, 11.7 mM in 5 mL mixture solutions. The rest of the procedure was same as the described above.

**11. X-ray diffraction data**

Single crystals were quickly covered with a layer of Paratone-N oil (Exxon, dried and degassed at 120°C/$10^{-6}$ Torr for 24 h) after decanting the mother liquor. A crystal was then mounted on a thin glass fiber and transferred into the cold nitrogen stream of a Bruker APEX-II CCD diffractometer. The structures were solved by direct methods and refined using the Bruker SHELXTL program library by full-matrix least squares on *F2* for all reflections (*SHELXTL*, Version 6.12; Bruker Analytical X-ray Solutions: Madison, WI, 2001). The structure was refined by full-matrix least-squares on *F*2 for all reflections. All non-hydrogen atoms were refined with anisotropic displacement parameters, whereas hydrogen atoms were included in the structure factor calculations at idealized positions (Sheldrick, G. M. *Acta Crystallogr., Sect. A.* **1990**, *46*, 467–473 & **2008**, *64*, 112–122.).

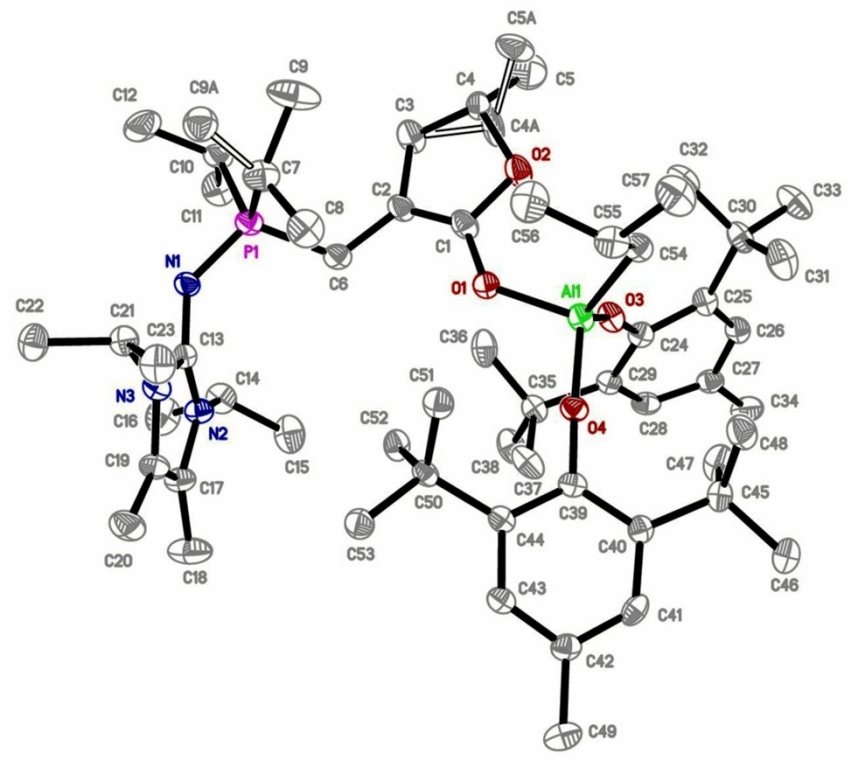



Figure S27. X-ray crystal structure of P(NI$^i$Pr)$^i$Pr$_2$-MMBL-(BHT)$_2$Al$^i$Bu. Hydrogen atoms are omitted for clarity and ellipsoids drawn at 30% probability.

**Table S7. Crystal Data and Structure Refinement for P(NI$^i$Pr)$^i$Pr$_2$-MMBL-(BHT)$_2$Al$^i$Bu**

| Compound | P(NI$^i$Pr)$^i$Pr$_2$-MMBL-(BHT)$_2$Al$^i$Bu |
|---|---|
| empirical formula | $C_{60}H_{100}AlN_3O_4P$ |
| MW | 985.37 |
| wavelength, Å | 0.71073 |
| crystal system | Monoclinic |
| space group | P2(1)/n |
| *a*, Å | 19.437(2) |
| *b*, Å | 15.0322(18) |
| *c*, Å | 20.796(2) |
| *α*, deg | 90 |
| *β*, deg | 91.599(3) |
| *γ*, deg | 90 |
| V, Å$^3$ | 6073.8(11) |
| Z | 4 |
| $D_{calc}$, g cm$^{-3}$ | 1.078 |
| μ, mm$^{-1}$ | 0.104 |
| F(000) | 2164 |
| crystal size, mm | 0.08 x 0.07 x 0.06 |
| *ϑ* range, deg | 1.414 - 26.371 |
| limiting indices | -24≤*h*≤20, |

| | |
|---|---|
| | -18≤*k*≤17, |
| | -25≤*l*≤16 |
| reflns collected | 34143 |
| independent reflns | 12334 |
| | [*R*(int) = 0.1361] |
| absorption correction | None |
| data/restraints/para's | 12334 / 45 / 680 |
| goodness-of-fit on $F^2$ | 0.946 |
| final R indices | *R*1 = 0.0794 |
| [ I >2σ(I) ] [a] | w*R*2 = 0.1690 |
| R indices (all data) [a] | *R*1 = 0.2091 |
| | w*R*2 = 0.2213 |
| $peak_{max}/hole_{min}$ (e $Å^{-3}$) | 0.373 / -0.318 |

[a] $R1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$; $wR2 = \{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$

**Table S8. Bond Lengths [Å] and Angles [º] for P(NI$^i$Pr)$^i$Pr$_2$-MMBL-(BHT)$_2$Al$^i$Bu.**

| | | | |
|---|---|---|---|
| P(1)-N(1) | 1.588(3) | C(28)-H(28) | 0.9300 |
| P(1)-C(6) | 1.816(4) | C(28)-C(29) | 1.392(6) |
| P(1)-C(7) | 1.797(4) | C(29)-C(35) | 1.539(6) |
| P(1)-C(10) | 1.816(4) | C(30)-C(31) | 1.519(6) |
| Al(1)-O(1) | 1.801(3) | C(30)-C(32) | 1.540(6) |
| Al(1)-O(3) | 1.754(3) | C(30)-C(33) | 1.540(6) |
| Al(1)-O(4) | 1.747(3) | C(31)-H(31A) | 0.9600 |
| Al(1)-C(54) | 1.990(4) | C(31)-H(31B) | 0.9600 |
| O(1)-C(1) | 1.323(5) | C(31)-H(31C) | 0.9600 |
| O(2)-C(1) | 1.386(5) | C(32)-H(32A) | 0.9600 |
| O(2)-C(4) | 1.466(5) | C(32)-H(32B) | 0.9600 |
| O(2)-C(4A) | 1.463(4) | C(32)-H(32C) | 0.9600 |
| O(3)-C(24) | 1.347(5) | C(33)-H(33A) | 0.9600 |
| O(4)-C(39) | 1.360(4) | C(33)-H(33B) | 0.9600 |
| N(1)-C(13) | 1.332(5) | C(33)-H(33C) | 0.9600 |
| N(2)-C(13) | 1.338(5) | C(34)-H(34A) | 0.9600 |
| N(2)-C(14) | 1.473(5) | C(34)-H(34B) | 0.9600 |
| N(2)-C(17) | 1.419(5) | C(34)-H(34C) | 0.9600 |
| N(3)-C(13) | 1.368(5) | C(35)-C(36) | 1.527(6) |
| N(3)-C(19) | 1.403(5) | C(35)-C(37) | 1.521(6) |
| N(3)-C(21) | 1.472(5) | C(35)-C(38) | 1.534(6) |
| C(1)-C(2) | 1.329(6) | C(36)-H(36A) | 0.9600 |
| C(2)-C(3) | 1.518(5) | C(36)-H(36B) | 0.9600 |
| C(2)-C(6) | 1.479(6) | C(36)-H(36C) | 0.9600 |
| C(3)-H(3AA) | 0.9700 | C(37)-H(37A) | 0.9600 |
| C(3)-H(3AB) | 0.9700 | C(37)-H(37B) | 0.9600 |
| C(3)-H(3BC) | 0.9700 | C(37)-H(37C) | 0.9600 |
| C(3)-H(3BD) | 0.9700 | C(38)-H(38A) | 0.9600 |

| | | | |
|---|---|---|---|
| C(3)-C(4) | 1.538(5) | C(38)-H(38B) | 0.9600 |
| C(3)-C(4A) | 1.532(5) | C(38)-H(38C) | 0.9600 |
| C(4)-H(4) | 0.9800 | C(39)-C(40) | 1.415(5) |
| C(4)-C(5) | 1.538(5) | C(39)-C(44) | 1.425(5) |
| C(5A)-H(5AA) | 0.9600 | C(40)-C(41) | 1.405(5) |
| C(5A)-H(5AB) | 0.9600 | C(40)-C(45) | 1.527(6) |
| C(5A)-H(5AC) | 0.9600 | C(41)-H(41) | 0.9300 |
| C(5A)-C(4A) | 1.534(5) | C(41)-C(42) | 1.381(6) |
| C(6)-H(6A) | 0.9700 | C(42)-C(43) | 1.382(6) |
| C(6)-H(6B) | 0.9700 | C(42)-C(49) | 1.512(6) |
| C(7)-H(7A) | 0.9800 | C(43)-H(43) | 0.9300 |
| C(7)-H(7B) | 0.9800 | C(43)-C(44) | 1.397(5) |
| C(7)-C(8) | 1.536(4) | C(44)-C(50) | 1.544(6) |
| C(7)-C(9) | 1.517(4) | C(45)-C(46) | 1.546(6) |
| C(7)-C(9A) | 1.526(5) | C(45)-C(47) | 1.545(6) |
| C(8)-H(8A) | 0.9600 | C(45)-C(48) | 1.526(6) |
| C(8)-H(8B) | 0.9600 | C(46)-H(46A) | 0.9600 |
| C(8)-H(8C) | 0.9600 | C(46)-H(46B) | 0.9600 |
| C(9)-H(9A) | 0.9600 | C(46)-H(46C) | 0.9600 |
| C(9)-H(9B) | 0.9600 | C(47)-H(47A) | 0.9600 |
| C(9)-H(9C) | 0.9600 | C(47)-H(47B) | 0.9600 |
| C(10)-H(10) | 0.9800 | C(47)-H(47C) | 0.9600 |
| C(10)-C(11) | 1.527(6) | C(48)-H(48A) | 0.9600 |
| C(10)-C(12) | 1.527(6) | C(48)-H(48B) | 0.9600 |
| C(11)-H(11A) | 0.9600 | C(48)-H(48C) | 0.9600 |
| C(11)-H(11B) | 0.9600 | C(49)-H(49A) | 0.9600 |
| C(11)-H(11C) | 0.9600 | C(49)-H(49B) | 0.9600 |
| C(12)-H(12A) | 0.9600 | C(49)-H(49C) | 0.9600 |
| C(12)-H(12B) | 0.9600 | C(50)-C(51) | 1.537(5) |
| C(12)-H(12C) | 0.9600 | C(50)-C(52) | 1.535(5) |
| C(14)-H(14) | 0.9800 | C(50)-C(53) | 1.525(5) |
| C(14)-C(15) | 1.517(6) | C(51)-H(51A) | 0.9600 |
| C(14)-C(16) | 1.520(6) | C(51)-H(51B) | 0.9600 |
| C(15)-H(15A) | 0.9600 | C(51)-H(51C) | 0.9600 |
| C(15)-H(15B) | 0.9600 | C(52)-H(52A) | 0.9600 |
| C(15)-H(15C) | 0.9600 | C(52)-H(52B) | 0.9600 |
| C(16)-H(16A) | 0.9600 | C(52)-H(52C) | 0.9600 |
| C(16)-H(16B) | 0.9600 | C(53)-H(53A) | 0.9600 |
| C(16)-H(16C) | 0.9600 | C(53)-H(53B) | 0.9600 |
| C(17)-C(18) | 1.494(6) | C(53)-H(53C) | 0.9600 |
| C(17)-C(19) | 1.335(6) | C(54)-H(54A) | 0.9700 |
| C(18)-H(18A) | 0.9600 | C(54)-H(54B) | 0.9700 |
| C(18)-H(18B) | 0.9600 | C(54)-C(55) | 1.541(6) |
| C(18)-H(18C) | 0.9600 | C(55)-H(55) | 0.9800 |

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| C(19)-C(20) | 1.508(6) | C(55)-C(56) | 1.528(6) |
| C(20)-H(20A) | 0.9600 | C(55)-C(57) | 1.528(6) |
| C(20)-H(20B) | 0.9600 | C(56)-H(56A) | 0.9600 |
| C(20)-H(20C) | 0.9600 | C(56)-H(56B) | 0.9600 |
| C(21)-H(21) | 0.9800 | C(56)-H(56C) | 0.9600 |
| C(21)-C(22) | 1.520(6) | C(57)-H(57A) | 0.9600 |
| C(21)-C(23) | 1.533(6) | C(57)-H(57B) | 0.9600 |
| C(22)-H(22A) | 0.9600 | C(57)-H(57C) | 0.9600 |
| C(22)-H(22B) | 0.9600 | C(58)-H(58) | 0.9300 |
| C(22)-H(22C) | 0.9600 | C(58)-C(59) | 1.359(4) |
| C(23)-H(23A) | 0.9600 | C(58)-C(60)#1 | 1.324(8) |
| C(23)-H(23B) | 0.9600 | C(59)-H(59) | 0.9300 |
| C(23)-H(23C) | 0.9600 | C(59)-C(60) | 1.374(5) |
| C(24)-C(25) | 1.436(6) | C(60)-H(60) | 0.9300 |
| C(24)-C(29) | 1.413(6) | C(5)-H(5A) | 0.9600 |
| C(25)-C(26) | 1.392(6) | C(5)-H(5B) | 0.9600 |
| C(25)-C(30) | 1.541(6) | C(5)-H(5C) | 0.9600 |
| C(26)-H(26) | 0.9300 | C(4A)-H(4A) | 0.9800 |
| C(26)-C(27) | 1.382(6) | C(9A)-H(9AA) | 0.9600 |
| C(27)-C(28) | 1.380(6) | C(9A)-H(9AB) | 0.9600 |
| C(27)-C(34) | 1.502(6) | C(9A)-H(9AC) | 0.9600 |
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| N(1)-P(1)-C(6) | 113.51(19) | C(31)-C(30)-C(32) | 111.5(4) |
| N(1)-P(1)-C(7) | 112.2(2) | C(31)-C(30)-C(33) | 107.1(4) |
| N(1)-P(1)-C(10) | 105.7(2) | C(32)-C(30)-C(25) | 110.0(4) |
| C(6)-P(1)-C(10) | 108.8(2) | C(33)-C(30)-C(25) | 111.4(4) |
| C(7)-P(1)-C(6) | 107.8(2) | C(33)-C(30)-C(32) | 106.1(4) |
| C(7)-P(1)-C(10) | 108.7(2) | C(30)-C(31)-H(31A) | 109.5 |
| O(1)-Al(1)-C(54) | 107.88(17) | C(30)-C(31)-H(31B) | 109.5 |
| O(3)-Al(1)-O(1) | 103.40(14) | C(30)-C(31)-H(31C) | 109.5 |
| O(3)-Al(1)-C(54) | 115.84(17) | H(31A)-C(31)-H(31B) | 109.5 |
| O(4)-Al(1)-O(1) | 105.17(14) | H(31A)-C(31)-H(31C) | 109.5 |
| O(4)-Al(1)-O(3) | 114.06(15) | H(31B)-C(31)-H(31C) | 109.5 |
| O(4)-Al(1)-C(54) | 109.57(16) | C(30)-C(32)-H(32A) | 109.5 |
| C(1)-O(1)-Al(1) | 126.9(3) | C(30)-C(32)-H(32B) | 109.5 |
| C(1)-O(2)-C(4) | 104.5(4) | C(30)-C(32)-H(32C) | 109.5 |
| C(1)-O(2)-C(4A) | 105.4(4) | H(32A)-C(32)-H(32B) | 109.5 |
| C(24)-O(3)-Al(1) | 163.4(3) | H(32A)-C(32)-H(32C) | 109.5 |
| C(39)-O(4)-Al(1) | 172.1(3) | H(32B)-C(32)-H(32C) | 109.5 |
| C(13)-N(1)-P(1) | 135.0(3) | C(30)-C(33)-H(33A) | 109.5 |
| C(13)-N(2)-C(14) | 123.1(3) | C(30)-C(33)-H(33B) | 109.5 |
| C(13)-N(2)-C(17) | 109.4(3) | C(30)-C(33)-H(33C) | 109.5 |
| C(17)-N(2)-C(14) | 127.1(4) | H(33A)-C(33)-H(33B) | 109.5 |
| C(13)-N(3)-C(19) | 108.4(4) | H(33A)-C(33)-H(33C) | 109.5 |

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| C(13)-N(3)-C(21) | 123.0(3) | H(33B)-C(33)-H(33C) | 109.5 |
| C(19)-N(3)-C(21) | 128.1(4) | C(27)-C(34)-H(34A) | 109.5 |
| O(1)-C(1)-O(2) | 114.5(4) | C(27)-C(34)-H(34B) | 109.5 |
| O(1)-C(1)-C(2) | 130.9(4) | C(27)-C(34)-H(34C) | 109.5 |
| C(2)-C(1)-O(2) | 114.6(4) | H(34A)-C(34)-H(34B) | 109.5 |
| C(1)-C(2)-C(3) | 107.4(4) | H(34A)-C(34)-H(34C) | 109.5 |
| C(1)-C(2)-C(6) | 124.9(4) | H(34B)-C(34)-H(34C) | 109.5 |
| C(6)-C(2)-C(3) | 127.2(4) | C(36)-C(35)-C(29) | 110.6(4) |
| C(2)-C(3)-H(3AA) | 111.7 | C(36)-C(35)-C(38) | 106.1(4) |
| C(2)-C(3)-H(3AB) | 111.7 | C(37)-C(35)-C(29) | 111.0(4) |
| C(2)-C(3)-H(3BC) | 111.4 | C(37)-C(35)-C(36) | 111.4(4) |
| C(2)-C(3)-H(3BD) | 111.4 | C(37)-C(35)-C(38) | 105.3(4) |
| C(2)-C(3)-C(4) | 100.3(4) | C(38)-C(35)-C(29) | 112.2(4) |
| C(2)-C(3)-C(4A) | 102.1(4) | C(35)-C(36)-H(36A) | 109.5 |
| H(3AA)-C(3)-H(3AB) | 109.5 | C(35)-C(36)-H(36B) | 109.5 |
| H(3BC)-C(3)-H(3BD) | 109.2 | C(35)-C(36)-H(36C) | 109.5 |
| C(4)-C(3)-H(3AA) | 111.7 | H(36A)-C(36)-H(36B) | 109.5 |
| C(4)-C(3)-H(3AB) | 111.7 | H(36A)-C(36)-H(36C) | 109.5 |
| C(4A)-C(3)-H(3BC) | 111.4 | H(36B)-C(36)-H(36C) | 109.5 |
| C(4A)-C(3)-H(3BD) | 111.4 | C(35)-C(37)-H(37A) | 109.5 |
| O(2)-C(4)-C(3) | 104.1(4) | C(35)-C(37)-H(37B) | 109.5 |
| O(2)-C(4)-H(4) | 112.7 | C(35)-C(37)-H(37C) | 109.5 |
| O(2)-C(4)-C(5) | 103.7(10) | H(37A)-C(37)-H(37B) | 109.5 |
| C(3)-C(4)-H(4) | 112.7 | H(37A)-C(37)-H(37C) | 109.5 |
| C(3)-C(4)-C(5) | 110.3(5) | H(37B)-C(37)-H(37C) | 109.5 |
| C(5)-C(4)-H(4) | 112.7 | C(35)-C(38)-H(38A) | 109.5 |
| H(5AA)-C(5A)-H(5AB) | 109.5 | C(35)-C(38)-H(38B) | 109.5 |
| H(5AA)-C(5A)-H(5AC) | 109.5 | C(35)-C(38)-H(38C) | 109.5 |
| H(5AB)-C(5A)-H(5AC) | 109.5 | H(38A)-C(38)-H(38B) | 109.5 |
| C(4A)-C(5A)-H(5AA) | 109.5 | H(38A)-C(38)-H(38C) | 109.5 |
| C(4A)-C(5A)-H(5AB) | 109.5 | H(38B)-C(38)-H(38C) | 109.5 |
| C(4A)-C(5A)-H(5AC) | 109.5 | O(4)-C(39)-C(40) | 120.2(4) |
| P(1)-C(6)-H(6A) | 107.9 | O(4)-C(39)-C(44) | 119.6(4) |
| P(1)-C(6)-H(6B) | 107.9 | C(40)-C(39)-C(44) | 120.2(4) |
| C(2)-C(6)-P(1) | 117.6(3) | C(39)-C(40)-C(45) | 124.0(4) |
| C(2)-C(6)-H(6A) | 107.9 | C(41)-C(40)-C(39) | 117.5(4) |
| C(2)-C(6)-H(6B) | 107.9 | C(41)-C(40)-C(45) | 118.4(4) |
| H(6A)-C(6)-H(6B) | 107.2 | C(40)-C(41)-H(41) | 118.2 |
| P(1)-C(7)-H(7A) | 105.1 | C(42)-C(41)-C(40) | 123.6(4) |
| P(1)-C(7)-H(7B) | 101.4 | C(42)-C(41)-H(41) | 118.2 |
| C(8)-C(7)-P(1) | 110.8(3) | C(41)-C(42)-C(43) | 117.0(4) |
| C(8)-C(7)-H(7A) | 105.1 | C(41)-C(42)-C(49) | 121.2(4) |
| C(8)-C(7)-H(7B) | 101.4 | C(43)-C(42)-C(49) | 121.7(4) |
| C(9)-C(7)-P(1) | 119.0(4) | C(42)-C(43)-H(43) | 118.1 |

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| C(9)-C(7)-H(7A) | 105.1 | C(42)-C(43)-C(44) | 123.7(4) |
| C(9)-C(7)-C(8) | 110.7(3) | C(44)-C(43)-H(43) | 118.1 |
| C(9A)-C(7)-P(1) | 126.0(8) | C(39)-C(44)-C(50) | 124.0(3) |
| C(9A)-C(7)-H(7B) | 101.4 | C(43)-C(44)-C(39) | 117.6(4) |
| C(9A)-C(7)-C(8) | 111.6(4) | C(43)-C(44)-C(50) | 118.4(4) |
| C(7)-C(8)-H(8A) | 109.5 | C(40)-C(45)-C(46) | 113.4(4) |
| C(7)-C(8)-H(8B) | 109.5 | C(40)-C(45)-C(47) | 110.3(4) |
| C(7)-C(8)-H(8C) | 109.5 | C(47)-C(45)-C(46) | 106.0(4) |
| H(8A)-C(8)-H(8B) | 109.5 | C(48)-C(45)-C(40) | 110.0(4) |
| H(8A)-C(8)-H(8C) | 109.5 | C(48)-C(45)-C(46) | 106.6(4) |
| H(8B)-C(8)-H(8C) | 109.5 | C(48)-C(45)-C(47) | 110.3(4) |
| C(7)-C(9)-H(9A) | 109.5 | C(45)-C(46)-H(46A) | 109.5 |
| C(7)-C(9)-H(9B) | 109.5 | C(45)-C(46)-H(46B) | 109.5 |
| C(7)-C(9)-H(9C) | 109.5 | C(45)-C(46)-H(46C) | 109.5 |
| H(9A)-C(9)-H(9B) | 109.5 | H(46A)-C(46)-H(46B) | 109.5 |
| H(9A)-C(9)-H(9C) | 109.5 | H(46A)-C(46)-H(46C) | 109.5 |
| H(9B)-C(9)-H(9C) | 109.5 | H(46B)-C(46)-H(46C) | 109.5 |
| P(1)-C(10)-H(10) | 107.7 | C(45)-C(47)-H(47A) | 109.5 |
| C(11)-C(10)-P(1) | 111.4(3) | C(45)-C(47)-H(47B) | 109.5 |
| C(11)-C(10)-H(10) | 107.7 | C(45)-C(47)-H(47C) | 109.5 |
| C(12)-C(10)-P(1) | 111.2(3) | H(47A)-C(47)-H(47B) | 109.5 |
| C(12)-C(10)-H(10) | 107.7 | H(47A)-C(47)-H(47C) | 109.5 |
| C(12)-C(10)-C(11) | 110.9(4) | H(47B)-C(47)-H(47C) | 109.5 |
| C(10)-C(11)-H(11A) | 109.5 | C(45)-C(48)-H(48A) | 109.5 |
| C(10)-C(11)-H(11B) | 109.5 | C(45)-C(48)-H(48B) | 109.5 |
| C(10)-C(11)-H(11C) | 109.5 | C(45)-C(48)-H(48C) | 109.5 |
| H(11A)-C(11)-H(11B) | 109.5 | H(48A)-C(48)-H(48B) | 109.5 |
| H(11A)-C(11)-H(11C) | 109.5 | H(48A)-C(48)-H(48C) | 109.5 |
| H(11B)-C(11)-H(11C) | 109.5 | H(48B)-C(48)-H(48C) | 109.5 |
| C(10)-C(12)-H(12A) | 109.5 | C(42)-C(49)-H(49A) | 109.5 |
| C(10)-C(12)-H(12B) | 109.5 | C(42)-C(49)-H(49B) | 109.5 |
| C(10)-C(12)-H(12C) | 109.5 | C(42)-C(49)-H(49C) | 109.5 |
| H(12A)-C(12)-H(12B) | 109.5 | H(49A)-C(49)-H(49B) | 109.5 |
| H(12A)-C(12)-H(12C) | 109.5 | H(49A)-C(49)-H(49C) | 109.5 |
| H(12B)-C(12)-H(12C) | 109.5 | H(49B)-C(49)-H(49C) | 109.5 |
| N(1)-C(13)-N(2) | 126.9(4) | C(51)-C(50)-C(44) | 110.2(3) |
| N(1)-C(13)-N(3) | 125.3(4) | C(52)-C(50)-C(44) | 110.2(3) |
| N(2)-C(13)-N(3) | 107.3(3) | C(52)-C(50)-C(51) | 111.0(3) |
| N(2)-C(14)-H(14) | 106.5 | C(53)-C(50)-C(44) | 112.5(3) |
| N(2)-C(14)-C(15) | 112.5(4) | C(53)-C(50)-C(51) | 106.2(4) |
| N(2)-C(14)-C(16) | 111.5(4) | C(53)-C(50)-C(52) | 106.7(3) |
| C(15)-C(14)-H(14) | 106.5 | C(50)-C(51)-H(51A) | 109.5 |
| C(15)-C(14)-C(16) | 112.8(4) | C(50)-C(51)-H(51B) | 109.5 |
| C(16)-C(14)-H(14) | 106.5 | C(50)-C(51)-H(51C) | 109.5 |

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| C(14)-C(15)-H(15A) | 109.5 | H(51A)-C(51)-H(51B) | 109.5 |
| C(14)-C(15)-H(15B) | 109.5 | H(51A)-C(51)-H(51C) | 109.5 |
| C(14)-C(15)-H(15C) | 109.5 | H(51B)-C(51)-H(51C) | 109.5 |
| H(15A)-C(15)-H(15B) | 109.5 | C(50)-C(52)-H(52A) | 109.5 |
| H(15A)-C(15)-H(15C) | 109.5 | C(50)-C(52)-H(52B) | 109.5 |
| H(15B)-C(15)-H(15C) | 109.5 | C(50)-C(52)-H(52C) | 109.5 |
| C(14)-C(16)-H(16A) | 109.5 | H(52A)-C(52)-H(52B) | 109.5 |
| C(14)-C(16)-H(16B) | 109.5 | H(52A)-C(52)-H(52C) | 109.5 |
| C(14)-C(16)-H(16C) | 109.5 | H(52B)-C(52)-H(52C) | 109.5 |
| H(16A)-C(16)-H(16B) | 109.5 | C(50)-C(53)-H(53A) | 109.5 |
| H(16A)-C(16)-H(16C) | 109.5 | C(50)-C(53)-H(53B) | 109.5 |
| H(16B)-C(16)-H(16C) | 109.5 | C(50)-C(53)-H(53C) | 109.5 |
| N(2)-C(17)-C(18) | 124.4(4) | H(53A)-C(53)-H(53B) | 109.5 |
| C(19)-C(17)-N(2) | 106.7(4) | H(53A)-C(53)-H(53C) | 109.5 |
| C(19)-C(17)-C(18) | 128.8(4) | H(53B)-C(53)-H(53C) | 109.5 |
| C(17)-C(18)-H(18A) | 109.5 | Al(1)-C(54)-H(54A) | 107.7 |
| C(17)-C(18)-H(18B) | 109.5 | Al(1)-C(54)-H(54B) | 107.7 |
| C(17)-C(18)-H(18C) | 109.5 | H(54A)-C(54)-H(54B) | 107.1 |
| H(18A)-C(18)-H(18B) | 109.5 | C(55)-C(54)-Al(1) | 118.3(3) |
| H(18A)-C(18)-H(18C) | 109.5 | C(55)-C(54)-H(54A) | 107.7 |
| H(18B)-C(18)-H(18C) | 109.5 | C(55)-C(54)-H(54B) | 107.7 |
| N(3)-C(19)-C(20) | 124.0(4) | C(54)-C(55)-H(55) | 107.8 |
| C(17)-C(19)-N(3) | 108.1(4) | C(56)-C(55)-C(54) | 111.6(4) |
| C(17)-C(19)-C(20) | 127.8(4) | C(56)-C(55)-H(55) | 107.8 |
| C(19)-C(20)-H(20A) | 109.5 | C(56)-C(55)-C(57) | 109.3(4) |
| C(19)-C(20)-H(20B) | 109.5 | C(57)-C(55)-C(54) | 112.4(4) |
| C(19)-C(20)-H(20C) | 109.5 | C(57)-C(55)-H(55) | 107.8 |
| H(20A)-C(20)-H(20B) | 109.5 | C(55)-C(56)-H(56A) | 109.5 |
| H(20A)-C(20)-H(20C) | 109.5 | C(55)-C(56)-H(56B) | 109.5 |
| H(20B)-C(20)-H(20C) | 109.5 | C(55)-C(56)-H(56C) | 109.5 |
| N(3)-C(21)-H(21) | 106.9 | H(56A)-C(56)-H(56B) | 109.5 |
| N(3)-C(21)-C(22) | 110.8(4) | H(56A)-C(56)-H(56C) | 109.5 |
| N(3)-C(21)-C(23) | 112.8(3) | H(56B)-C(56)-H(56C) | 109.5 |
| C(22)-C(21)-H(21) | 106.9 | C(55)-C(57)-H(57A) | 109.5 |
| C(22)-C(21)-C(23) | 112.1(4) | C(55)-C(57)-H(57B) | 109.5 |
| C(23)-C(21)-H(21) | 106.9 | C(55)-C(57)-H(57C) | 109.5 |
| C(21)-C(22)-H(22A) | 109.5 | H(57A)-C(57)-H(57B) | 109.5 |
| C(21)-C(22)-H(22B) | 109.5 | H(57A)-C(57)-H(57C) | 109.5 |
| C(21)-C(22)-H(22C) | 109.5 | H(57B)-C(57)-H(57C) | 109.5 |
| H(22A)-C(22)-H(22B) | 109.5 | C(59)-C(58)-H(58) | 119.5 |
| H(22A)-C(22)-H(22C) | 109.5 | C(59)-C(58)-C(60)#1 | 121.0(7) |
| H(22B)-C(22)-H(22C) | 109.5 | C(60)#1-C(58)-H(58) | 119.5 |
| C(21)-C(23)-H(23A) | 109.5 | C(58)-C(59)-H(59) | 122.7 |
| C(21)-C(23)-H(23B) | 109.5 | C(58)-C(59)-C(60) | 114.6(7) |

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| C(21)-C(23)-H(23C) | 109.5 | C(60)-C(59)-H(59) | 122.7 |
| H(23A)-C(23)-H(23B) | 109.5 | C(58)#1-C(60)-H(60) | 117.9 |
| H(23A)-C(23)-H(23C) | 109.5 | C(59)-C(60)-C(58)#1 | 124.1(7) |
| H(23B)-C(23)-H(23C) | 109.5 | C(59)-C(60)-H(60) | 117.9 |
| O(3)-C(24)-C(25) | 119.5(4) | C(4)-C(5)-H(5A) | 109.5 |
| O(3)-C(24)-C(29) | 121.6(4) | C(4)-C(5)-H(5B) | 109.5 |
| C(29)-C(24)-C(25) | 118.9(4) | C(4)-C(5)-H(5C) | 109.5 |
| C(24)-C(25)-C(30) | 123.7(4) | H(5A)-C(5)-H(5B) | 109.5 |
| C(26)-C(25)-C(24) | 117.2(4) | H(5A)-C(5)-H(5C) | 109.5 |
| C(26)-C(25)-C(30) | 119.0(4) | H(5B)-C(5)-H(5C) | 109.5 |
| C(25)-C(26)-H(26) | 117.9 | O(2)-C(4A)-C(3) | 104.5(4) |
| C(27)-C(26)-C(25) | 124.2(4) | O(2)-C(4A)-C(5A) | 105.8(6) |
| C(27)-C(26)-H(26) | 117.9 | O(2)-C(4A)-H(4A) | 111.4 |
| C(26)-C(27)-C(34) | 122.0(4) | C(3)-C(4A)-C(5A) | 111.8(5) |
| C(28)-C(27)-C(26) | 116.3(4) | C(3)-C(4A)-H(4A) | 111.4 |
| C(28)-C(27)-C(34) | 121.7(4) | C(5A)-C(4A)-H(4A) | 111.4 |
| C(27)-C(28)-H(28) | 118.1 | C(7)-C(9A)-H(9AA) | 109.5 |
| C(27)-C(28)-C(29) | 123.8(4) | C(7)-C(9A)-H(9AB) | 109.5 |
| C(29)-C(28)-H(28) | 118.1 | C(7)-C(9A)-H(9AC) | 109.5 |
| C(24)-C(29)-C(35) | 122.6(4) | H(9AA)-C(9A)-H(9AB) | 109.5 |
| C(28)-C(29)-C(24) | 118.3(4) | H(9AA)-C(9A)-H(9AC) | 109.5 |
| C(28)-C(29)-C(35) | 119.1(4) | H(9AB)-C(9A)-H(9AC) | 109.5 |
| C(31)-C(30)-C(25) | 110.6(4) | | |

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