

Binuclear Aluminium Lewis Acid and Its Behavior in the Polymerization of Methyl Methacrylate and n-Butyl acrylate

Wang Zhe^a, Zhang Xianhui^{a,c}, Liang Hongwen^b, Xian Mo^{*a} and Wang Xiaowu^{*a}

a. Key Laboratory of Biobased Materials, Qingdao Institute of Biomass Energy and Bioprocess Technology, Chinese Academy of Sciences, Qingdao, 266101, China;

*b. China Petroleum and Chemical Corporation Baling Branch, Yueyang, 414014, China;
lianghw.blsh@sinopec.com*

c. University of Chinese Academy of Sciences, Beijing, 100049, China.

*CORRESPONDING AUTHOR FOOTNOTE Tel: +86-532-58782991. E-mail: wangxw@qibebt.ac.cn and
xianmo@qibebt.ac.cn*

Experimental Section

Materials

All syntheses and manipulations of air- and moisture sensitive materials were carried out in flame-dried Schlenk-type glassware on a dual-manifold Schlenk line or in an inert Ar-filled glovebox. Toluene (AR, Sinopharm Chemical Reagent Co., Ltd) were dried over sodium with benzophenone as indicator and then fractionally distilled under nitrogen atmosphere prior to use. Methyl methacrylate (MMA) and Butyl acrylate (nBA) were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd., then dried over CaH₂ overnight, followed by vacuum distillation. Further purification of MMA and nBA involved titration with tri(n-octyl)aluminum to a yellow end point, followed by distillation under reduced pressure. All purified monomers were stored in cap-tight bottles inside a refrigerator at -30°C. Tri(n-octyl)aluminium, acetoin, cyanogen bromide, 1,3-diisopropyl-2-thiourea and PCy₃ were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. and PEt₃ and 2,6-Di-tert-butyl-4-methylphenol (BHT) were purchased from Shanghai Macklin Biochemical Co., Ltd.. Celite was purchased from Qingdao Purell Biological Technology Co., Ltd.. Deuterium solvents were purchased from Cambridge Isotope Laboratories. 6,6'-methylenebis(2-(tert-butyl)-4-methylphenol) was purchased from SAIN Chemical Technology (Shanghai) Co., Ltd. and other phosphines were purchased from Alfa Aesar (China) Chemicals Co., Ltd.. Literature procedures were employed for the preparation of the following compounds: Al(C₆F₅), [Al(mbmp)Me]₂, MeAl(BHT)₂, ⁱBuAl(BHT)₂ and ⁱBu₂Al(BHT)₂^[1]. NHO-1, NHO-2, IAP-3 were synthesized according to the literature^[2]. Other commercially available reagents were used as received without further purification unless otherwise noted.

Instruments

Nuclear magnetic resonance (NMR) spectra including ¹H NMR and ³¹P NMR were recorded on a Bruker Avance III 400 MHz spectrometer using the residual proton of the deuterated solvent for reference. The molecular weight and polydispersity of polymerizations were calculated using polystyrene standards with narrow molecular weight distribution as references and determined by gel permeation chromatograph (GPC, Viscotek VE2001 GPC, Viscotek Corporation, USA). X-ray diffraction (XRD) was carried out to measure the structure of single crystals. The data of Co1 and Fe1 was collected on Super Nova diffractometer with Mo K-alpha X-ray source ($\lambda = 0.71073 \text{ \AA}$) at

150 K. The collected data were solved using the SUPERFLIP72 program and refined by the SHELX-97 and OLEX274 programs.

Characterization of Polymer

Polymer number-average molecular weight (M_n) and molecular weight distributions ($\mathcal{D} = M_w/M_n$) were measured by gel permeation chromatography (GPC) at 35°C and a flow rate of 1 mL/min, with THF (HPLC grade) as an eluent on an Agilent Technologies 1260 Infinity instrument equipped with PL gel 5 μ m MIXED-C 300 \times 7.5 mm columns. The flow rate is 1.0 mL/min with injection volume 50 μ L and RI detector. The instrument was calibrated with polystyrene standards, and chromatograms were processed with Agilent software. Matrix-assisted laser desorption/ionization time-of-flight mass spectroscopy (MALDI-TOF MS) analyses were conducted on a Bruker Microflex LRF MS spectrometer equipped with a 337 nm nitrogen laser operating in a positive ion, linear mode. The sample solutions (10 mg/mL in THF), trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene] malononitrile (DCTB) solution (10 mg/mL in THF) and sodium trifluoroacetate solution (5 mg/mL) were mixed in a volume ratio of 5:1:1, 2 μ L of which was then deposited on the target plate and dried before measurement.

General Polymerization Procedures.

Polymerizations were performed in 10 mL Schlenk glass tubes inside the glovebox at ambient temperature (ca. 25°C). A predetermined amount of a Lewis acid (LA) (1 equiv. for bimetallic organoaluminum; 2 equiv. for monomeric organoaluminum) was first dissolved in 500 μ L (equiv.) of MMA or 680 μ L (equiv.) of nBA. The solution changed from colorless to yellow and 2 mL of toluene was injected. The polymerization was initiated by rapid addition of LB solution (1 equiv.) via a syringe to the above mixture under vigorous stirring. The solution immediately became colorless and bubbles were generated, in which the solution became sticky and exothermic. After 2 h, 0.1 mL methanol solution containing 5% BHT and 0.24 M HCl was injected to the reaction mixture. 0.2 mL aliquot was taken from the reaction mixture via syringe and mixed with 0.4 mL CDCl_3 . The mixed aliquot was analyzed by ^1H NMR to obtain the monomer conversion. The quenched mixture was precipitated by a large amount of methanol and the isolated polymer was filtered and vacuum dried overnight at room temperature.

Synthesis of $[\text{Al}(\text{mbmp})\text{Me}]_2$

To a suspension of 6,6'-methylenebis(2-(tert-butyl)-4-methylphenol) (10.0 g, 29.5 mmol) in 40 mL of hexane was slowly added a 2.0 M solution of trimethylaluminum in hexane (14.75 mL, 29.5 mmol). Instantaneous and vigorous evolution of methane and heat were observed. Upon cooling the reaction

mixture, colorless precipitates formed and then it was filtered, washed with cold hexane (2×10 mL) and dried in *vacuo* to give colorless microcrystals in 94% yield (11.225 g).

^1H NMR (400 MHz, CDCl_3 , 298 K): δ : 6.94-7.07 (m, Ar-H, 4 H), 4.33 (d, $^2J = 13.7$ Hz, CH_2 , 1 H), 3.52 (d, $^2J = 13.8$ Hz, CH_2 , 1 H), 2.31 (s, CH_3 , 3H), 2.23 (s, CH_3 , 3H), 1.37 (s, ^tBu , 9H), 1.21 (s, ^tBu , 9H), -0.32 (s, 3H, Me).

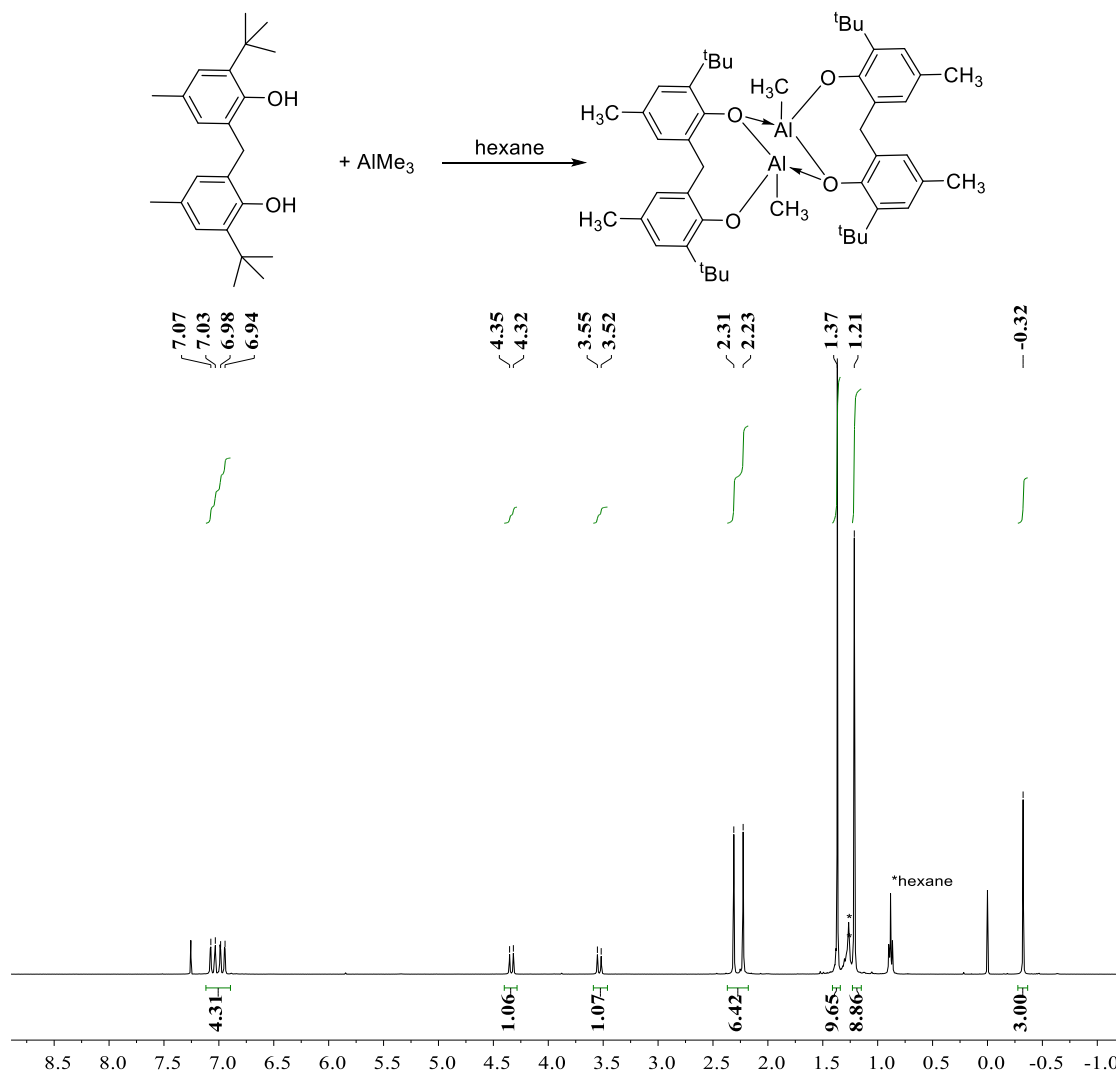


Figure S1. ^1H NMR spectrum of $[\text{Al}(\text{mbmp})\text{Me}]_2$ (400 MHz, CDCl_3 , 298 K)

Mechanistic study---- ^1H NMR spectra

NMR Reaction of phosphines with $[\text{Al}(\text{mbmp})\text{Me}]_2$ in 2:1 Ratio

In the glovebox, a glass vial was charged with $[\text{Al}(\text{mbmp})\text{Me}]_2$ (0.024 mmol, 18.3 mg) and 0.3 mL of CDCl_3 , then a solution of phosphines (0.048 mmol) in 0.2 mL CDCl_3 was added to the glass bottle via pipette at ambient temperature. The reaction mixture was transferred to a NMR tube and sealed. The sealed

NMR tube was immediately recorded by NMR spectroscopy.

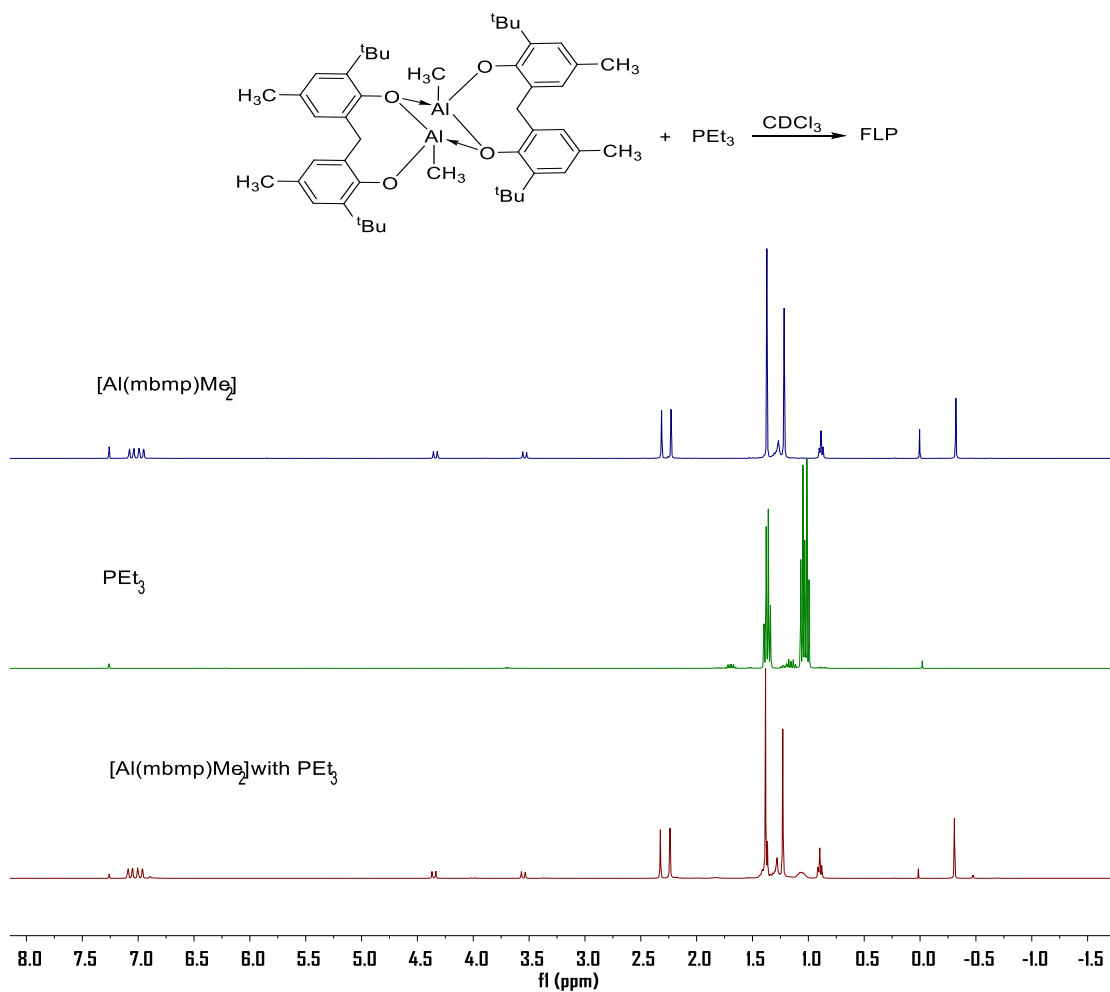


Figure S2. ^1H NMR (400 MHz, CDCl_3 , 298 K) spectra of reaction of $[\text{Al}(\text{mbmp})\text{Me}]_2$ with PEt_3

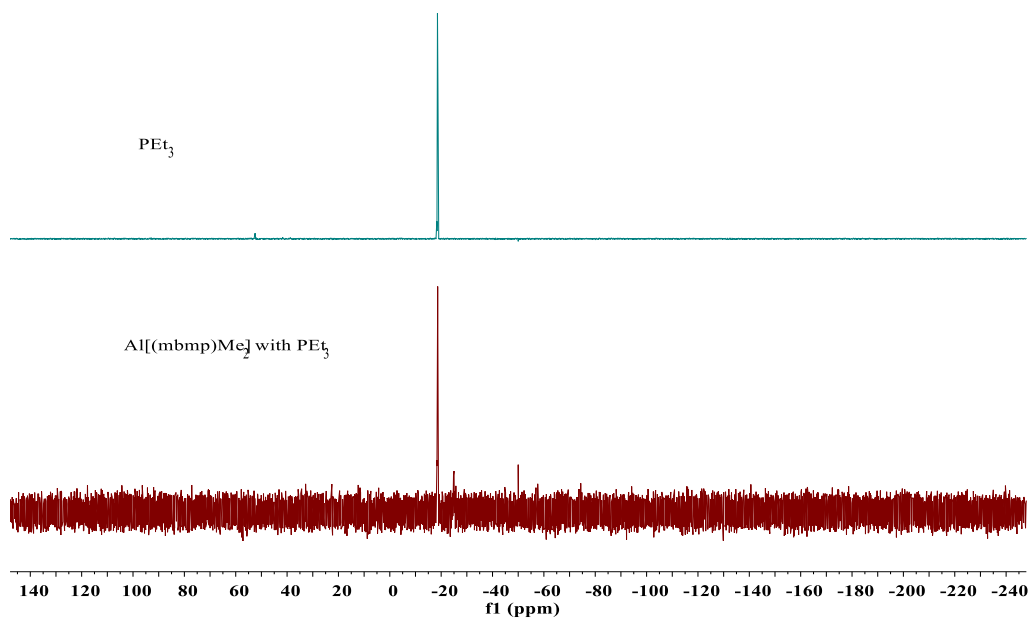


Figure S3. ^{31}P $\{^1\text{H}\}$ (162 MHz, CDCl_3 , 298 K) spectra of reaction of $[\text{Al}(\text{mbmp})\text{Me}]_2$ with PEt_3

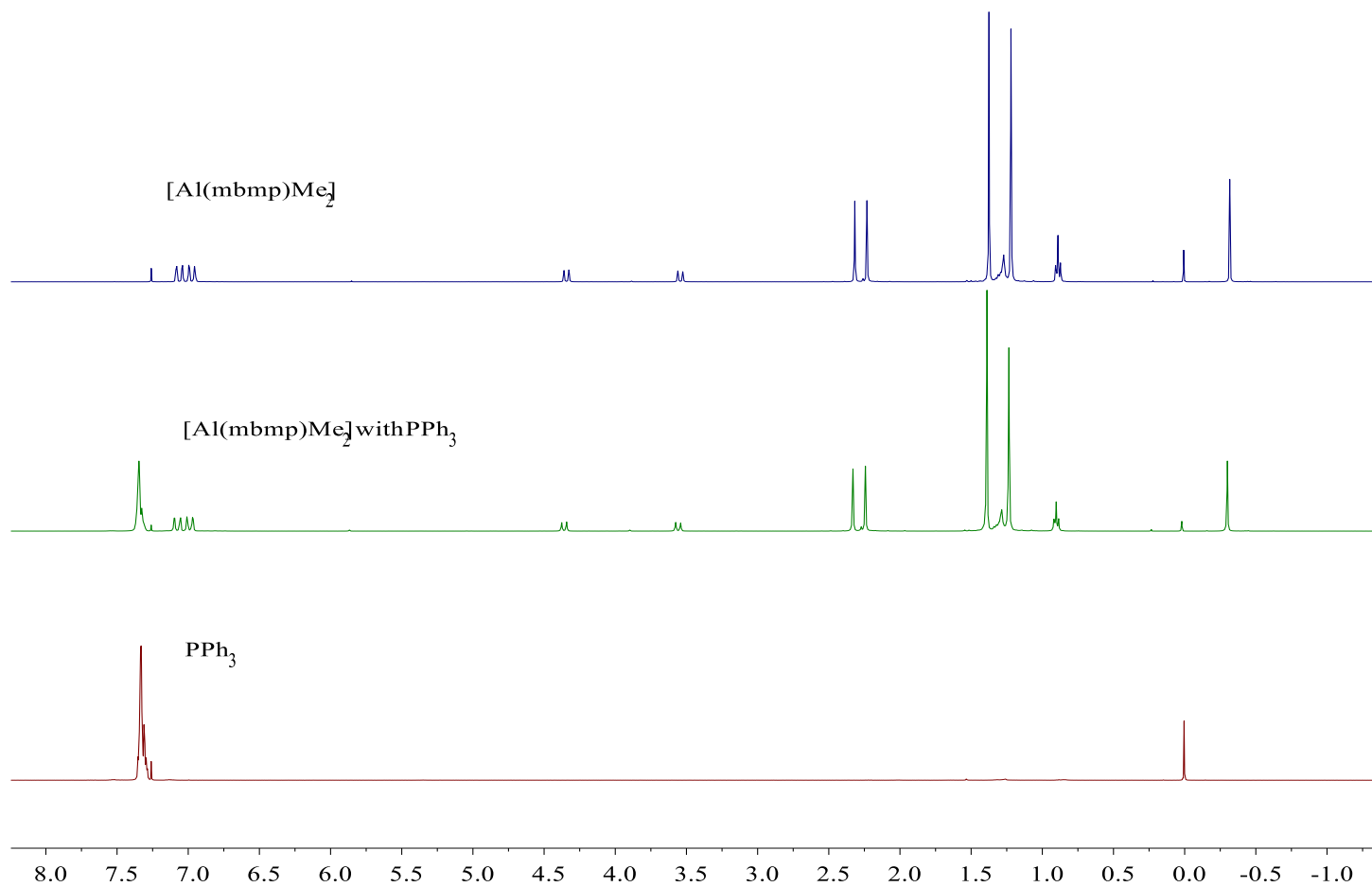
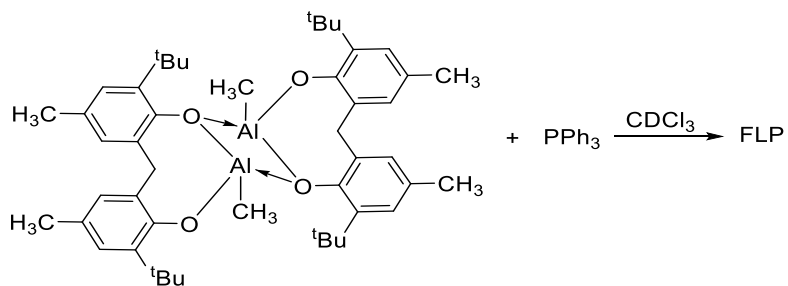


Figure S4. ¹H NMR (400 MHz, CDCl₃, 298 K) spectra of reaction of [Al(mbmp)Me₂] with PPh₃

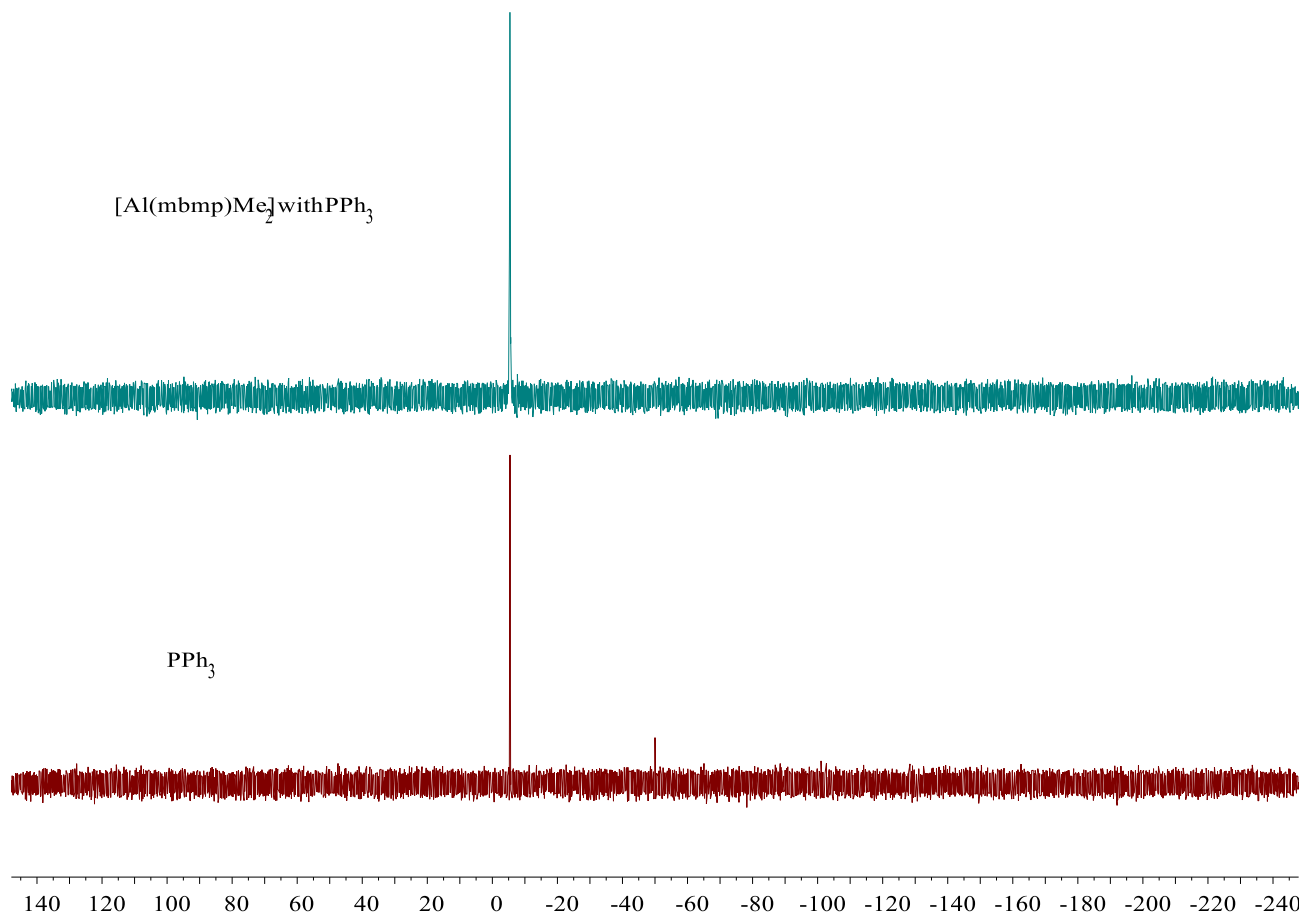
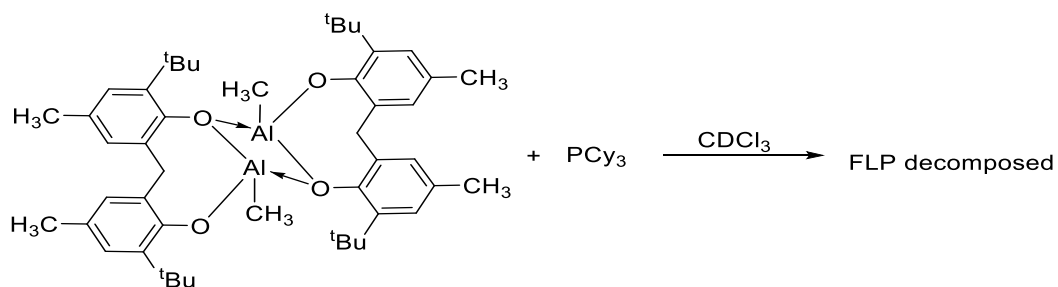


Figure S5. ^{31}P $\{^1\text{H}\}$ (162 MHz, CDCl_3 , 298 K) spectra of reaction of $[\text{Al}(\text{mbmp})\text{Me}]_2$ with PPh_3



Combination of $[\text{Al}(\text{mbmp})\text{Me}]_2$ with PCy_3 formed FLP. However, it decomposed in CDCl_3 , probably due to the higher basicity of PCy_3 .

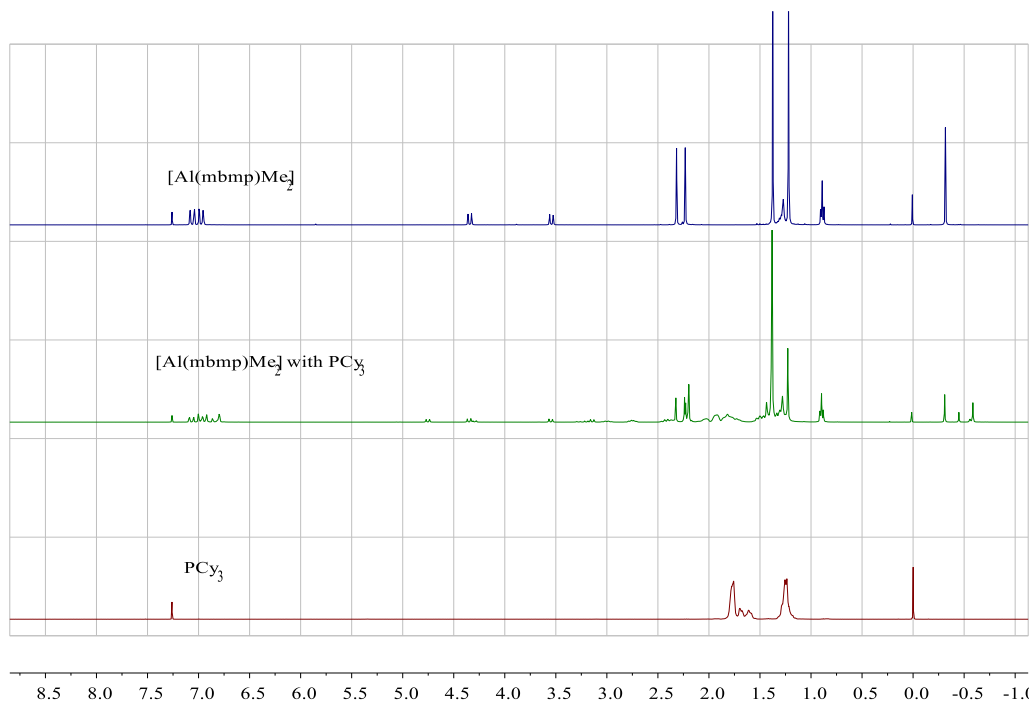


Figure S6. ^1H NMR (400 MHz, CDCl_3 , 298 K) spectra of reaction of $[\text{Al}(\text{mbmp})\text{Me}]_2$ with PCy_3

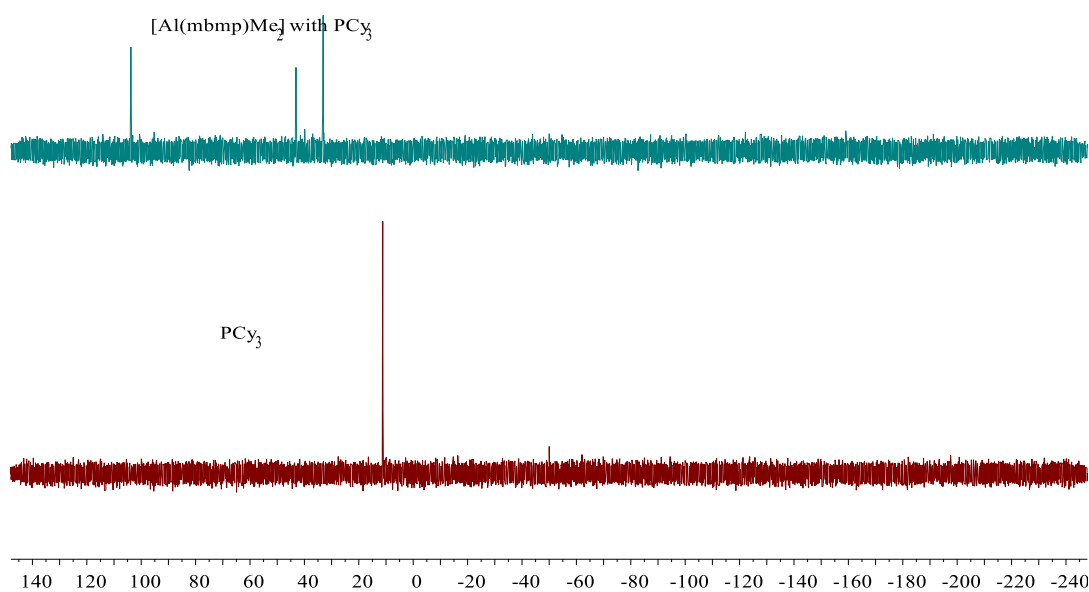
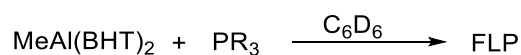


Figure S7. ^{31}P $\{^1\text{H}\}$ (162 MHz, CDCl_3 , 298 K) spectra of reaction of $[\text{Al}(\text{mbmp})\text{Me}]_2$ with PCy_3

NMR Reaction of phosphines with $\text{MeAl}(\text{BHT})_2$ in 1:1 Ratio



In the glovebox, a glass vial was charged with $\text{MeAl}(\text{BHT})_2$ (0.043 mmol, 20 mg) and 0.3 mL of C_6D_6 , then a solution of phosphines (0.043 mmol) in 0.2 mL of C_6D_6 was added to the vial via pipette at ambient temperature. The reaction mixture was transferred to a NMR tube and sealed. The sealed NMR tube was immediately recorded by NMR spectroscopy. In general, there is almost no chemical shift in ^{31}P $\{^1\text{H}\}$

NMR compared to the free phosphine, indicating non-interacting behavior of LA and LB.

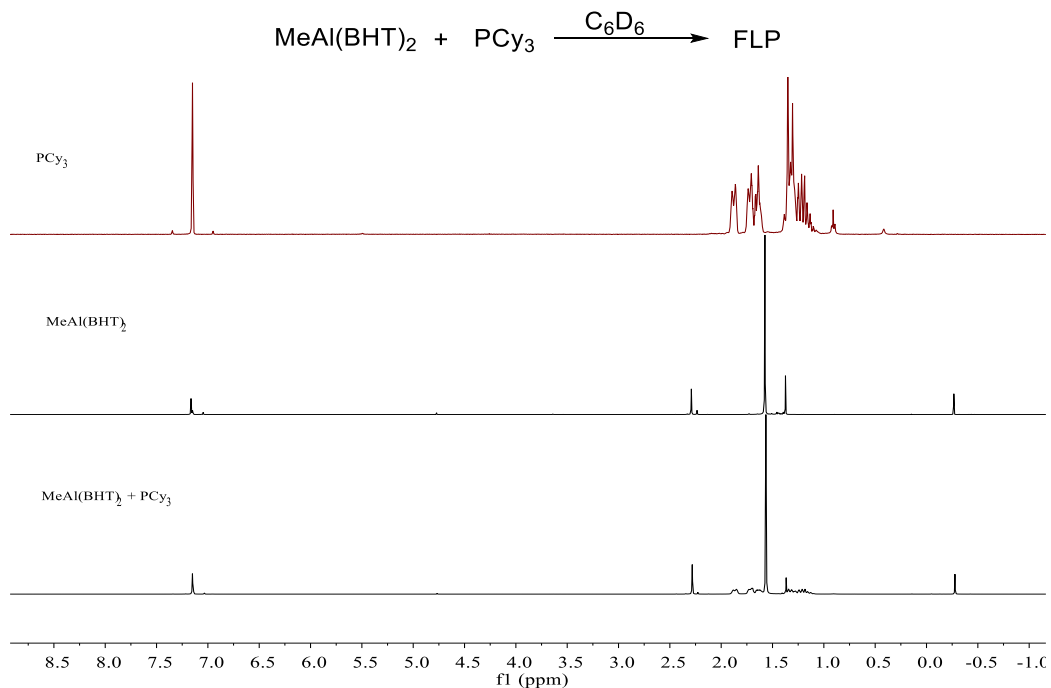


Figure S8. ¹H NMR (400 MHz, C₆D₆, 298 K) spectra of reaction of MeAl(BHT)₂ with PCy₃

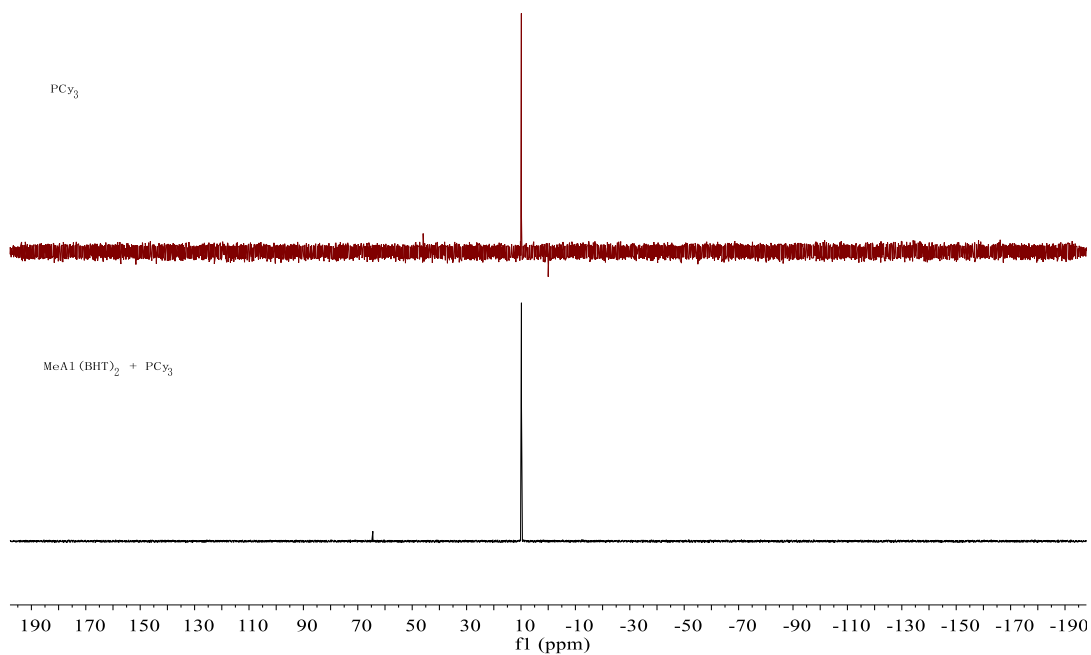
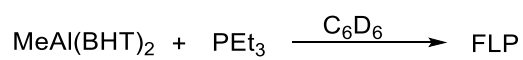


Figure S9. ³¹P {¹H} (162 MHz, C₆D₆, 298 K) spectra of reaction of MeAl(BHT)₂ with PCy₃



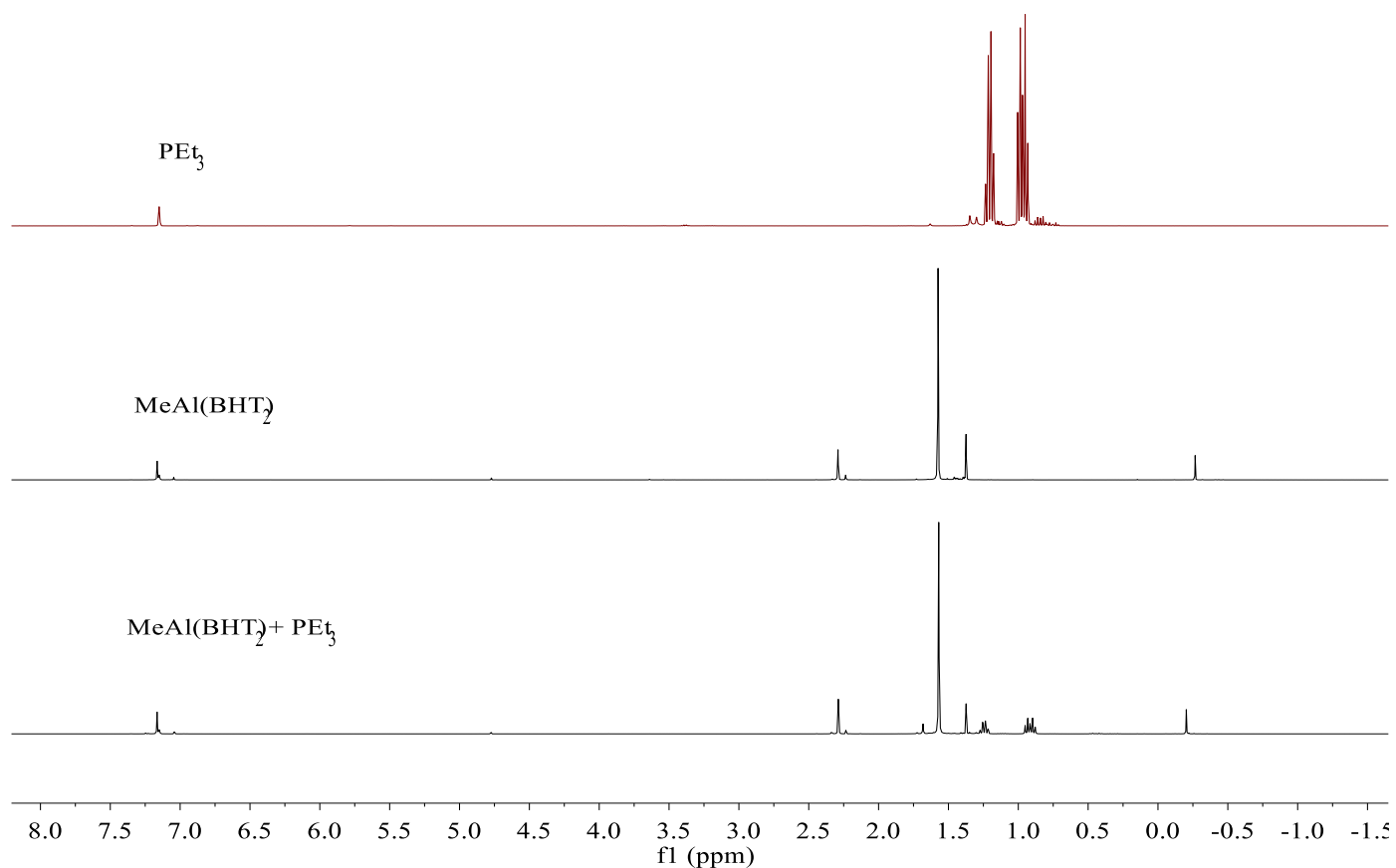


Figure S10. ^1H NMR (400 MHz, C_6D_6 , 298 K) spectra of reaction of $\text{MeAl}(\text{BHT})_2$ with PEt_3

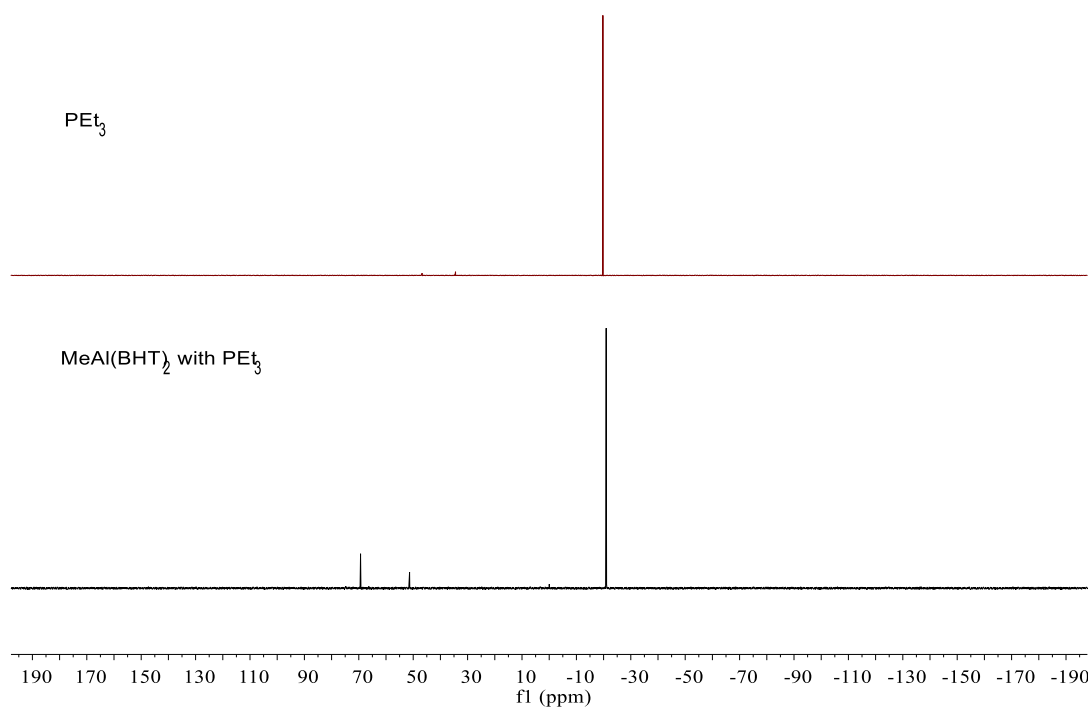
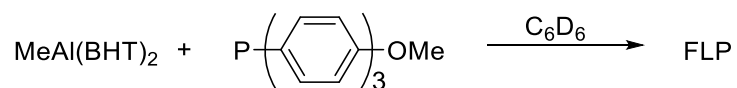


Figure S11. ^{31}P $\{^1\text{H}\}$ (162 MHz, C_6D_6 , 298 K) spectra of reaction of $\text{MeAl}(\text{BHT})_2$ with PEt_3



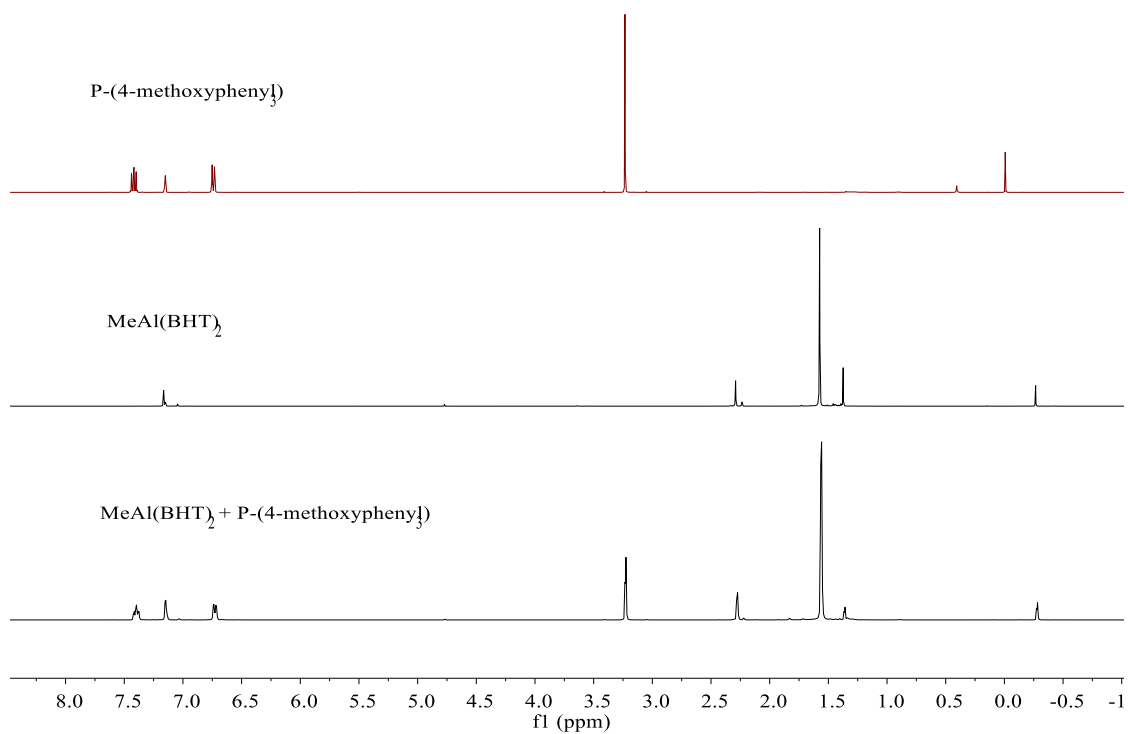


Figure S12. ^1H NMR (400 MHz, C_6D_6 , 298 K) spectra of reaction of $\text{MeAl}(\text{BHT})_2$ with $\text{P}(\text{4-methoxyphenyl})_3$

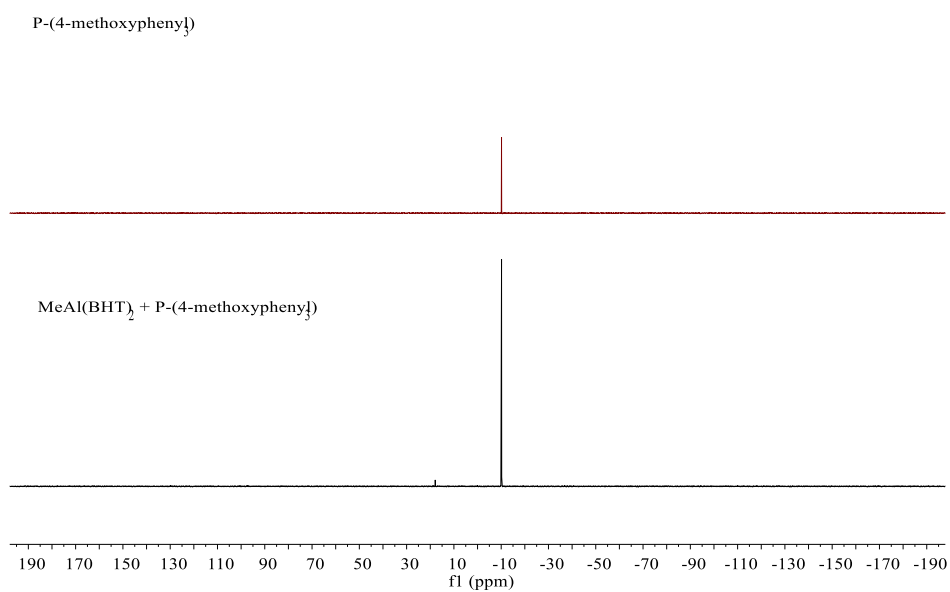
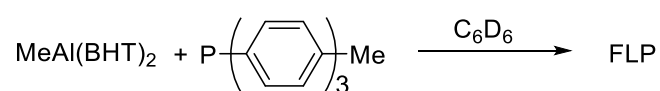


Figure S13. ^{31}P $\{^1\text{H}\}$ (162 MHz, C_6D_6 , 298 K) spectra of reaction of $\text{MeAl}(\text{BHT})_2$ with $\text{P}(\text{4-methoxyphenyl})_3$



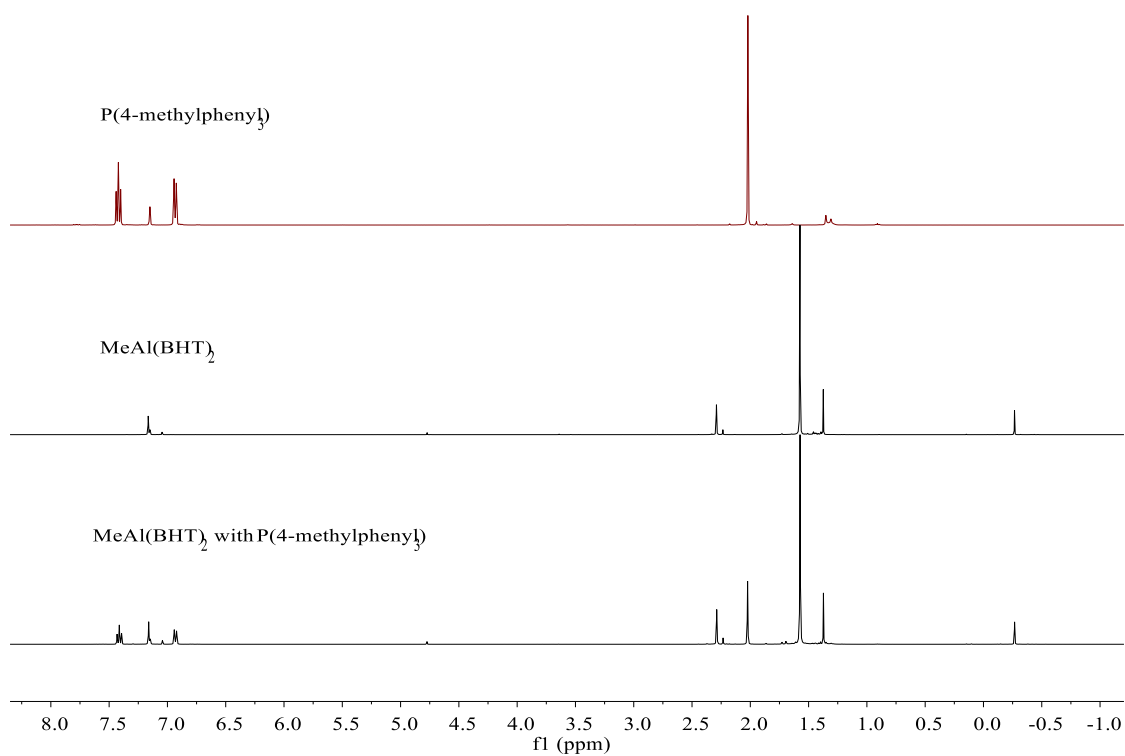


Figure S14. ^1H NMR (400 MHz, C_6D_6 , 298 K) spectra of reaction of $\text{MeAl}(\text{BHT})_2$ with $\text{P}(\text{4-methylphenyl})_3$

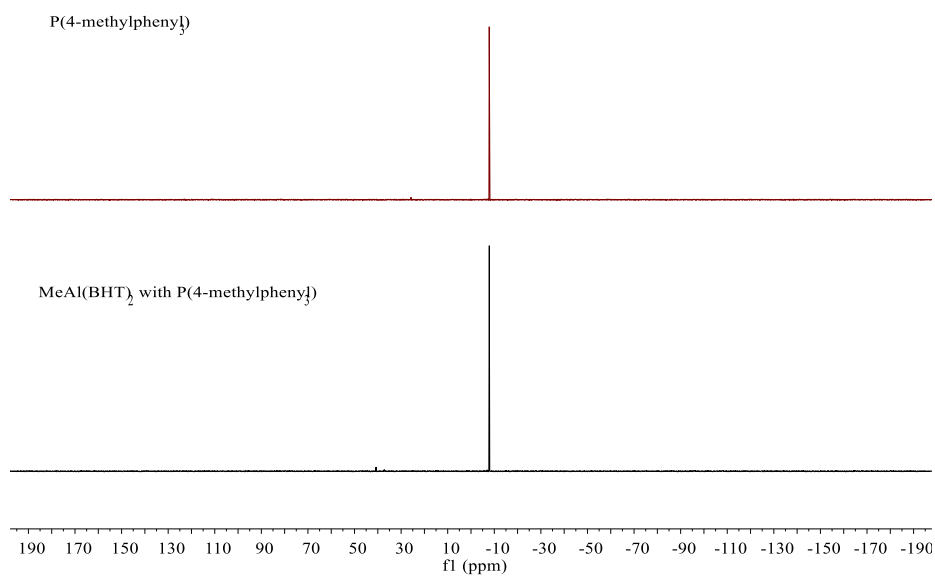
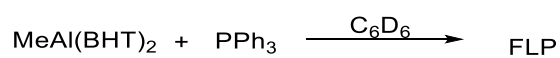


Figure S15. ^{31}P $\{^1\text{H}\}$ (162 MHz, C_6D_6 , 298 K) spectra of reaction of $\text{MeAl}(\text{BHT})_2$ with $\text{P}(\text{4-methylphenyl})_3$



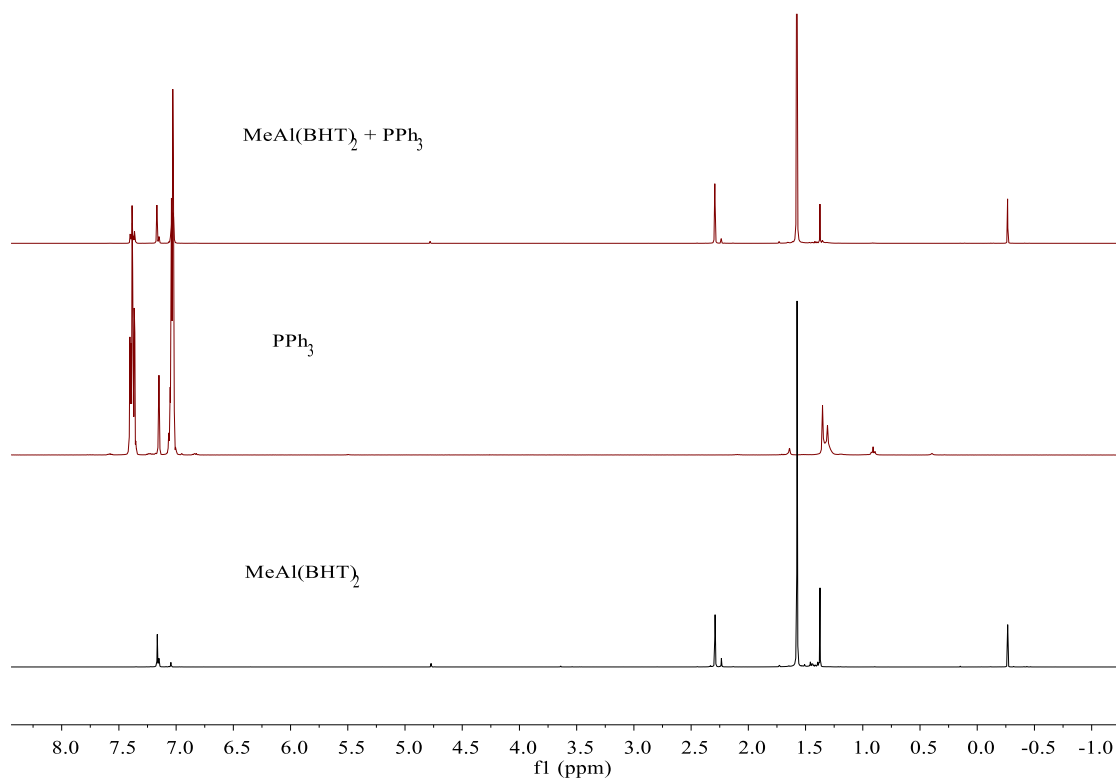


Figure S16. ^1H NMR (400 MHz, C_6D_6 , 298 K) spectra of reaction of $\text{MeAl}(\text{BHT})_2$ with PPh_3

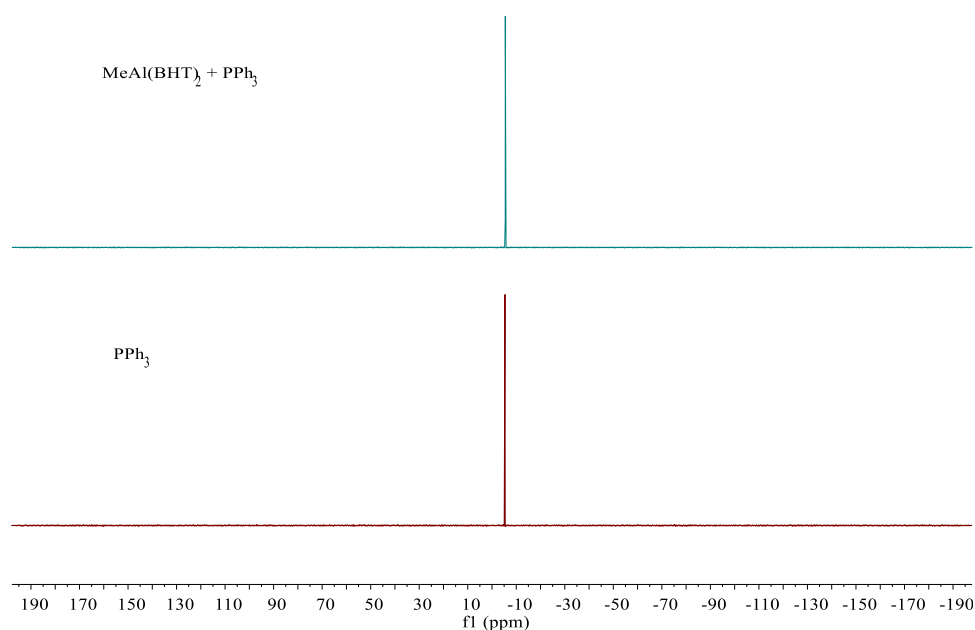


Figure S17. ^{31}P $\{^1\text{H}\}$ (162 MHz, C_6D_6 , 298 K) spectra of reaction of $\text{MeAl}(\text{BHT})_2$ with PPh_3

NMR Reaction of $\text{MeAl}(\text{BHT})_2$ with MMA and nBA in 1:1 Ratio

In the glovebox, a glass vial was charged with $\text{MeAl}(\text{BHT})_2$ (0.043 mmol, 20 mg) and 0.5 mL of CDCl_3 or C_6D_6 , then MMA or nBA (0.043 mmol) was injected via a micro-syringe at ambient temperature. The reaction mixture was transferred to a NMR tube and sealed. The sealed NMR tube was immediately

recorded by NMR spectroscopy.

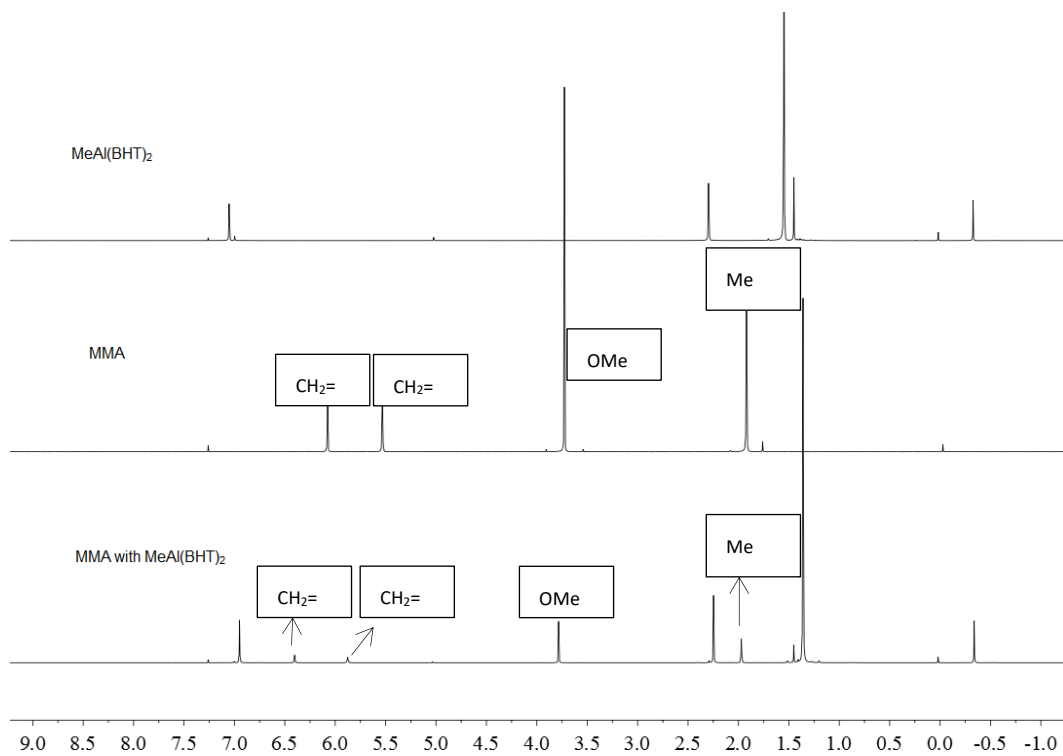


Figure S18. ^1H NMR spectra for reaction of MeAl(BHT)_2 with MMA (400 MHz, CDCl_3 , 298 K)

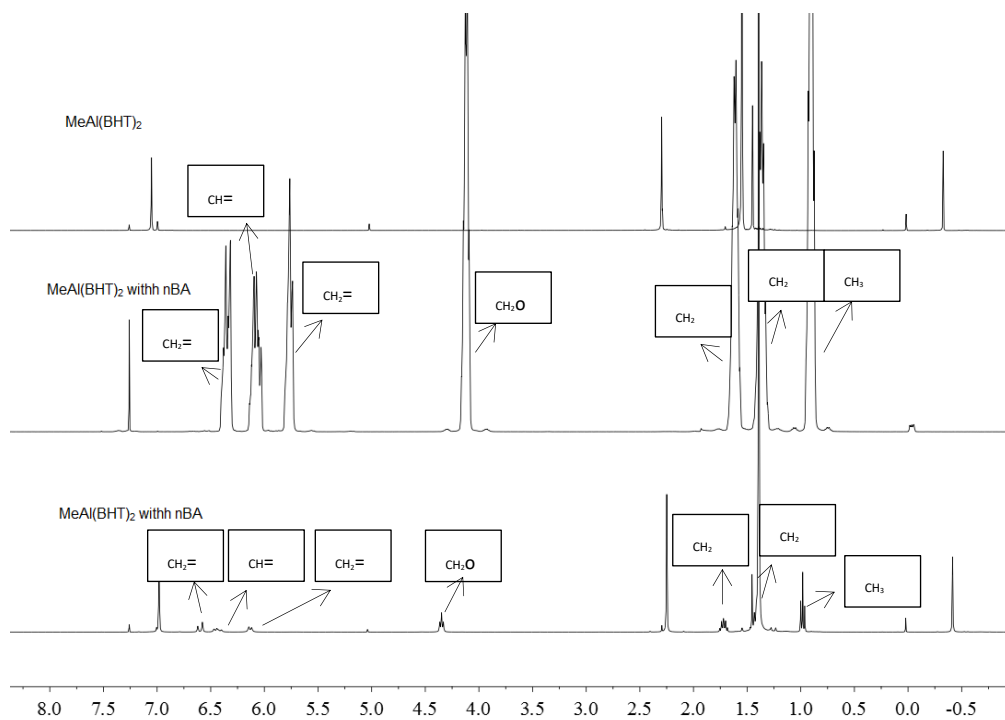


Figure S19. ^1H NMR spectra for reaction of MeAl(BHT)_2 with nBA (400 MHz, CDCl_3 , 298 K)

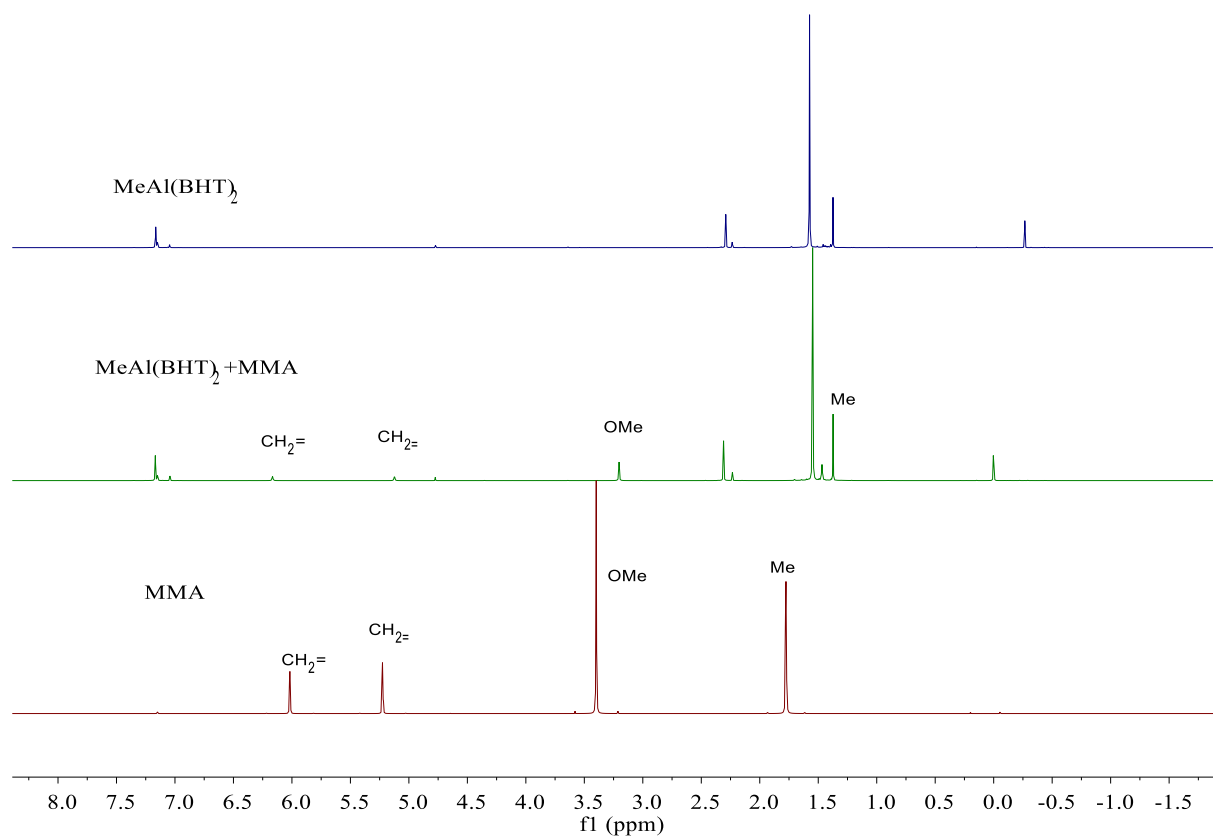


Figure S20. ^1H NMR spectra for reaction of $\text{MeAl}(\text{BHT})_2$ with MMA (400 MHz, C_6D_6 , 298 K)

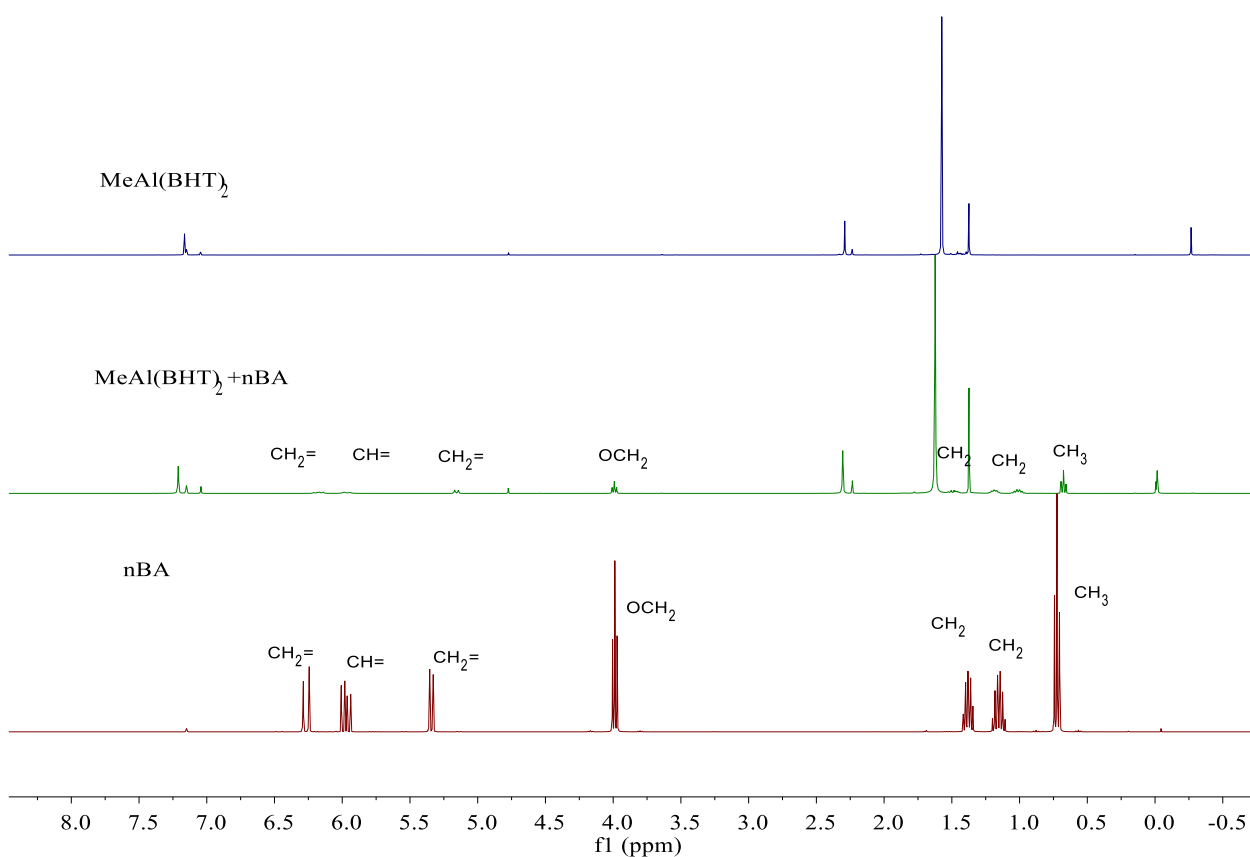


Figure S21. ^1H NMR spectrum for reaction of $\text{MeAl}(\text{BHT})_2$ with nBA (400 MHz, C_6D_6 , 298 K)

NMR Reaction of $[\text{Al}(\text{mbmp})\text{Me}]_2$ with MMA and nBA in 1:2 Ratio

In the glovebox, a glass vial was charged with $[\text{Al}(\text{mbmp})\text{Me}]_2$ (0.0215 mmol, 16.4 mg) and 0.5 mL of CDCl_3 , then MMA or nBA (0.043 mmol) was injected *via* a micro-syringe at ambient temperature. The reaction mixture was transferred to a NMR tube and sealed. The sealed NMR tube was immediately recorded by NMR spectroscopy.

NMR Reaction of $[\text{Al}(\text{mbmp})\text{Me}]_2$ with MMA in 1:2 and 1:10 Ratio

In the glovebox, a glass vial was charged with $[\text{Al}(\text{mbmp})\text{Me}]_2$ (0.0215 mmol, 16.4 mg) and 0.5 mL of CDCl_3 , then required amount of MMA was injected *via* a micro-syringe at ambient temperature. The reaction mixture was transferred to a NMR tube and sealed. The sealed NMR tube was immediately recorded by NMR spectroscopy.

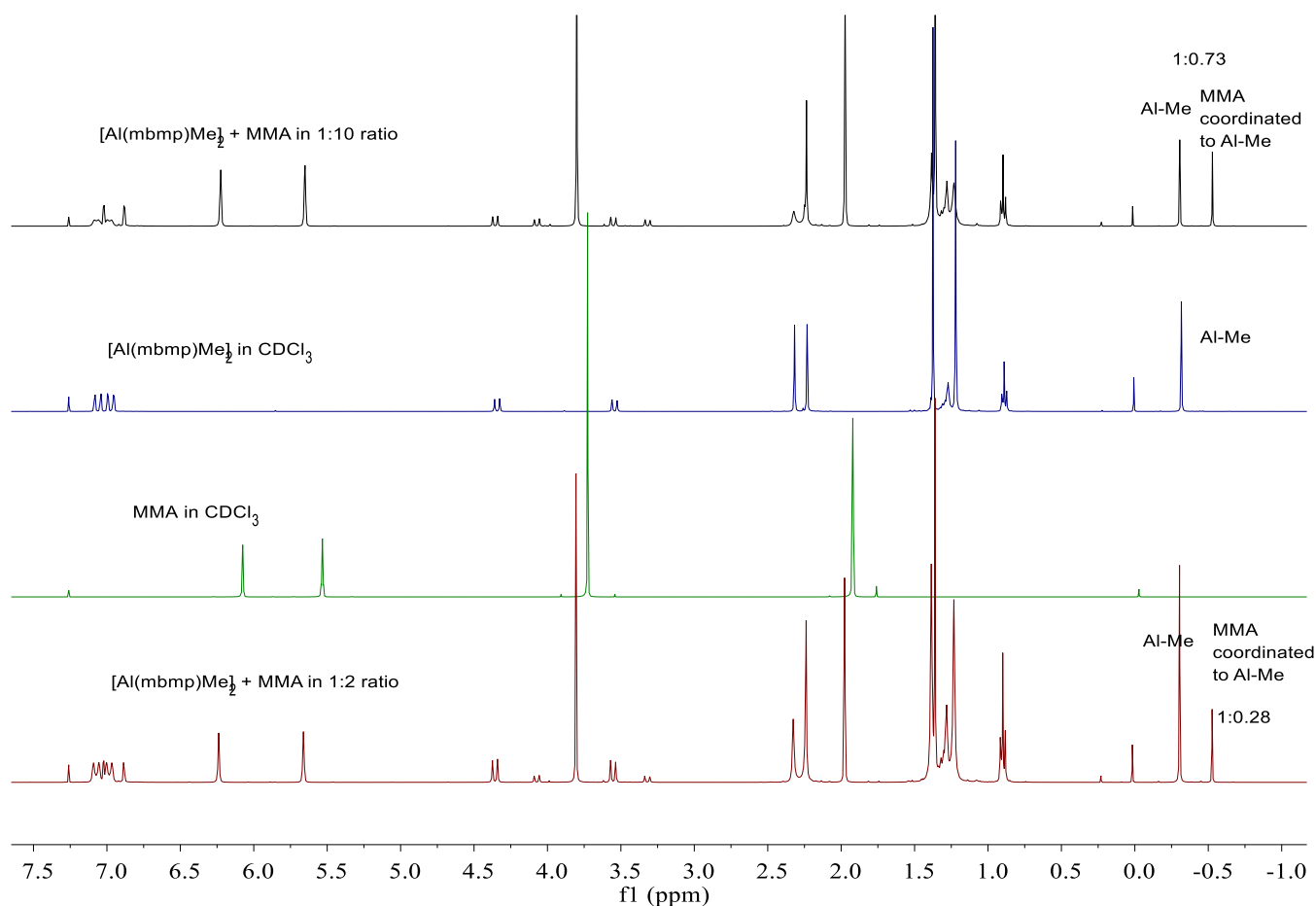


Figure S22. ^1H NMR spectra for reaction of $[\text{Al}(\text{mbmp})\text{Me}]_2$ with MMA (400 MHz, CDCl_3 , 298 K)

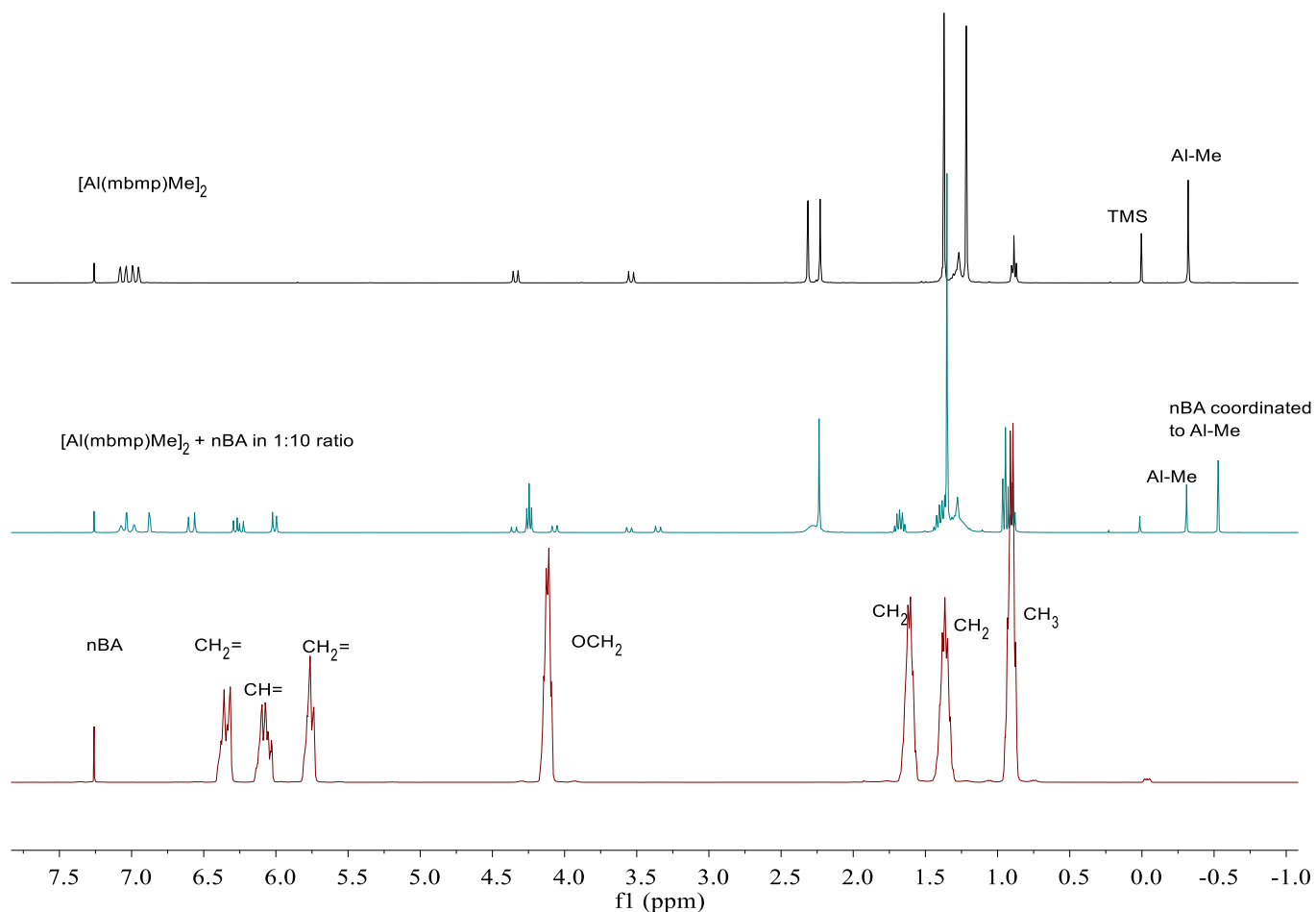
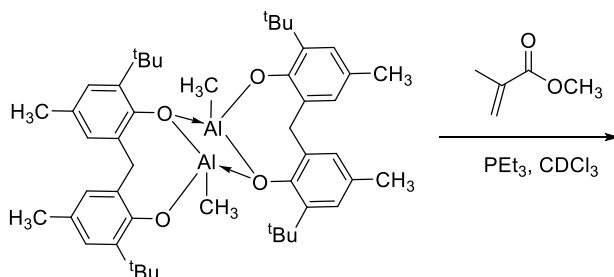


Figure S23. ^1H NMR spectra for reaction of $[\text{Al}(\text{mbmp})\text{Me}]_2$ with nBA (400 MHz, CDCl_3 , 298 K)

NMR Reaction of PEt_3 with $[\text{Al}(\text{mbmp})\text{Me}]_2 \cdot \text{MMA}$ or nBA in 2:1:2 Ratio

In the glovebox, a 5 mL glass vial was charged with PEt_3 (0.043 mmol, 5.0 mg) and 0.2 mL of CDCl_3 , while another vial was added to $[\text{Al}(\text{mbmp})\text{Me}]_2$ (0.0215 mmol, 16.4mg), 0.3 mL of CDCl_3 and MMA or nBA (0.043mmol). The two vials were mixed *via* a syringe at ambient temperature. The reaction mixture was sealed and recorded immediately by NMR spectroscopy.



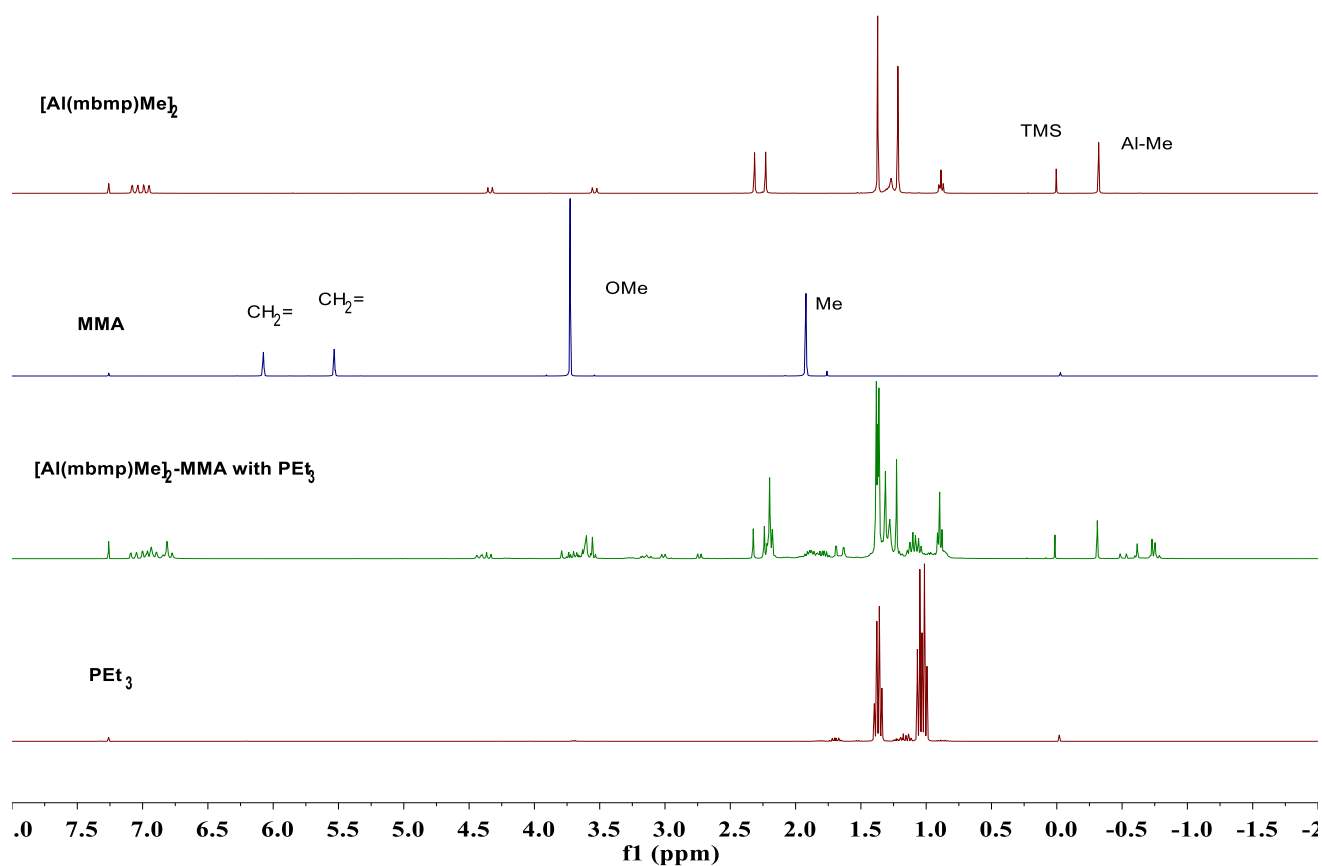


Figure S24. ^1H NMR spectra for reaction of PEt₃ with [Al(mbmp)Me]₂·MMA (400 MHz, CDCl₃, 298 K)

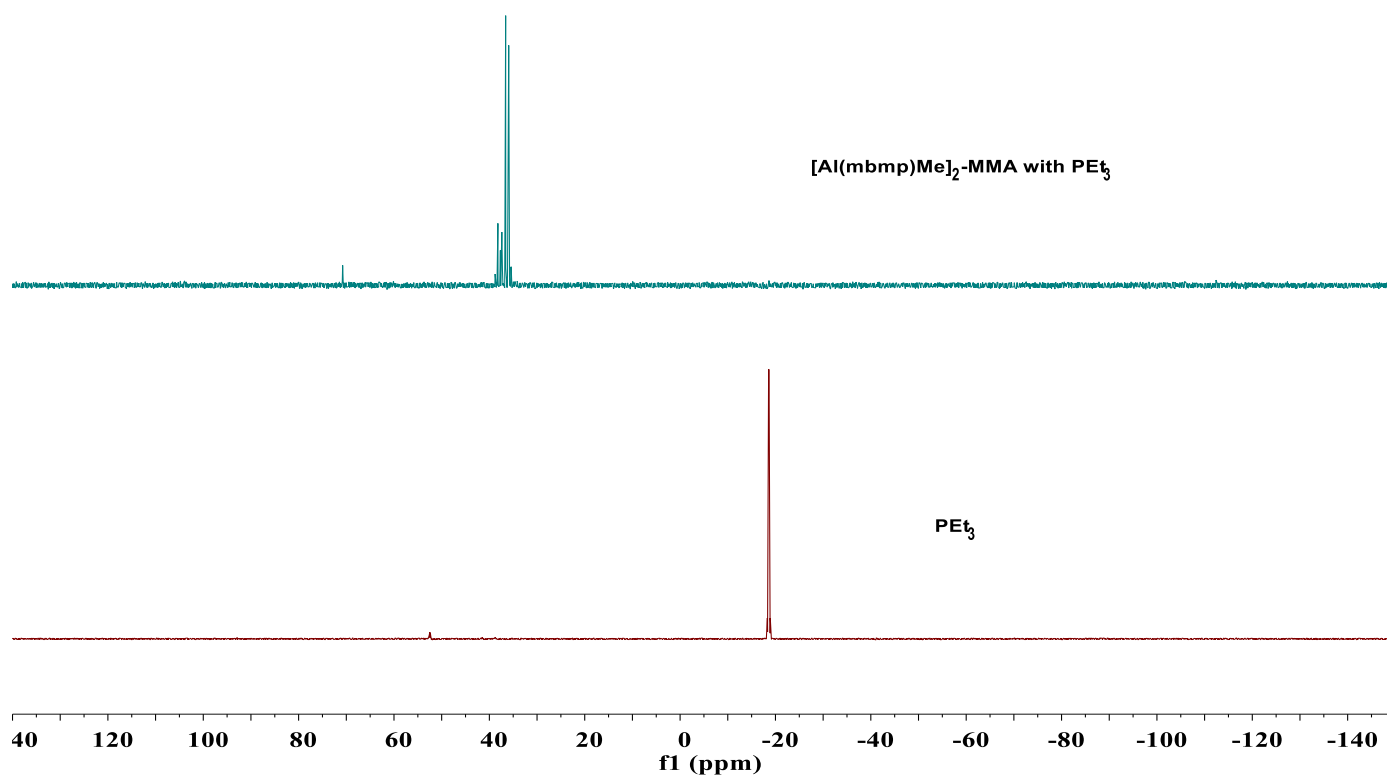


Figure S25. ^{31}P { ^1H } (162 MHz, CDCl₃, 298 K) spectra for reaction of PEt₃ with [Al(mbmp)Me]₂·MMA

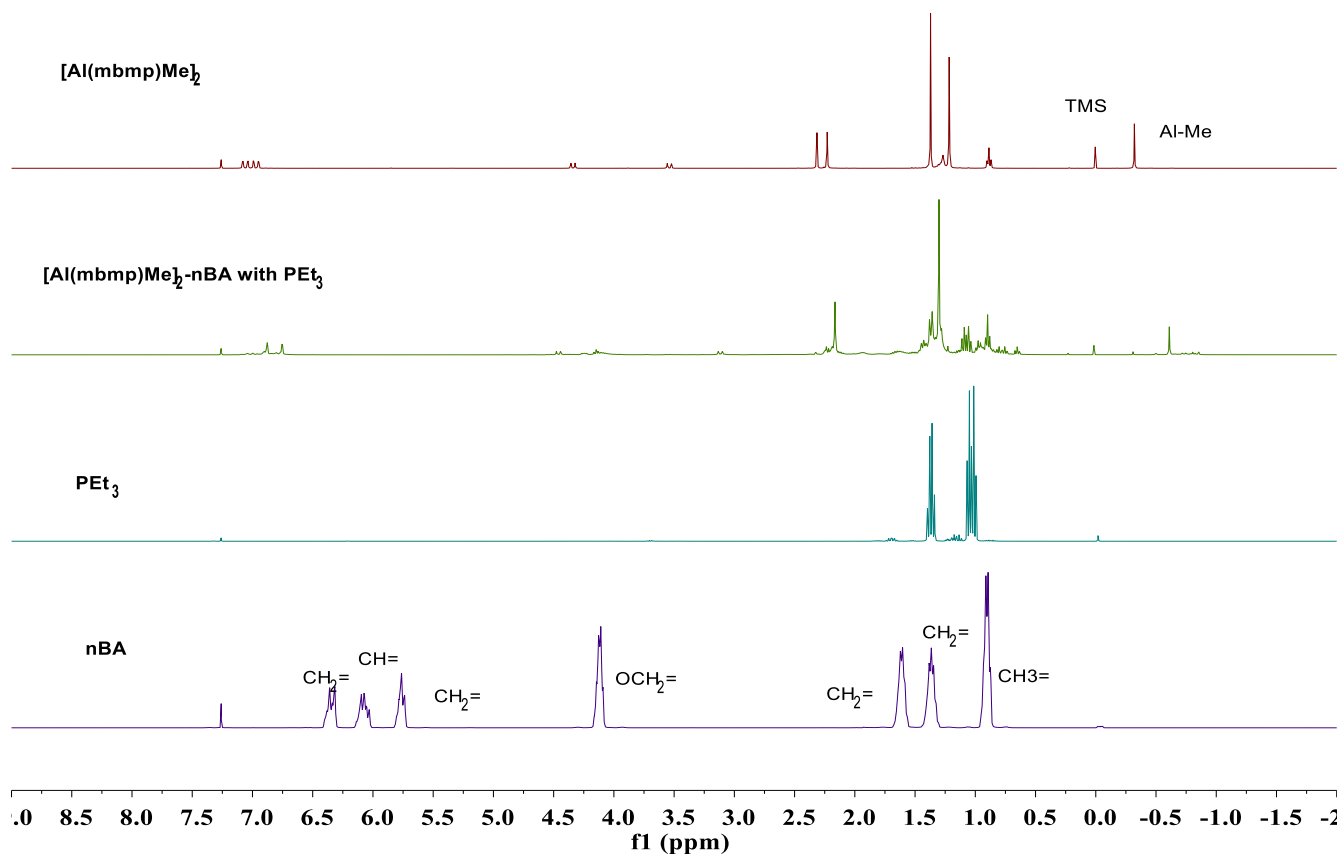
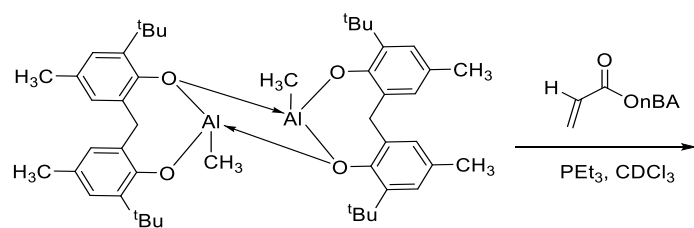


Figure S26. ^1H NMR spectra for reaction of PEt_3 with $[\text{Al}(\text{mbmp})\text{Me}]_2 \cdot \text{nBA}$ (400 MHz, CDCl_3 , 298 K)

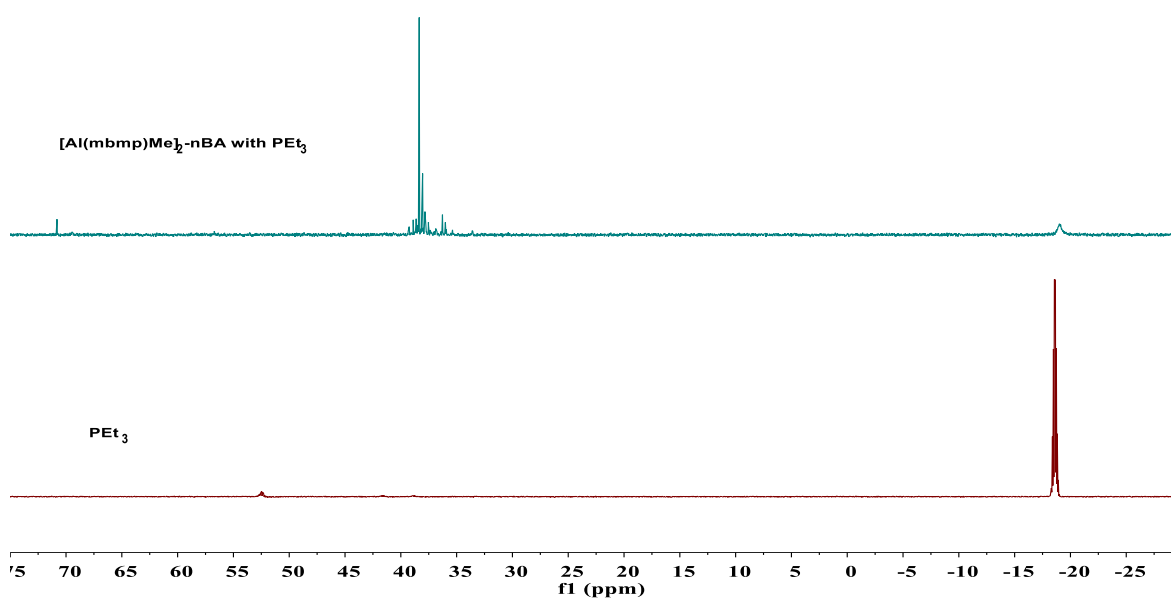
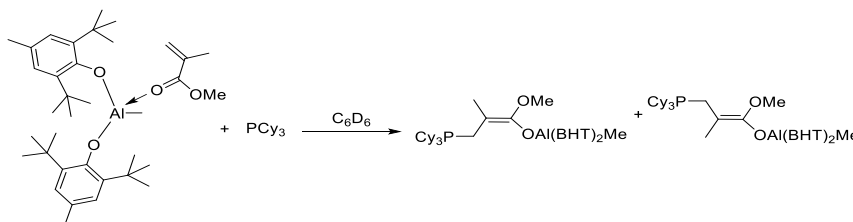


Figure S27. ^{31}P { ^1H } (162 MHz, CDCl_3 , 298 K) spectra for reaction of PEt_3 with $[\text{Al}(\text{mbmp})\text{Me}]_2 \cdot \text{nBA}$
NMR Reaction of phosphines with $\text{MeAl}(\text{BHT})_2 \cdot \text{MMA}$ or nBA in 1:1:1 Ratio

In the glovebox, a 5 mL glass vial was charged with phosphines (0.043 mmol) and 0.2 mL of C_6D_6 , while another vial was added to $\text{MeAl}(\text{BHT})_2$ (0.043 mmol, 20 mg, 0.3 mL of C_6D_6 and MMA or nBA (0.043 mmol). The two vials were mixed via a syringe at ambient temperature. The reaction mixture was sealed and allowed immediately recorded by NMR. Further purification of the sample led to decomposition and reappearance of monomer.



^1H NMR (400 MHz, C_6D_6 , 298 K): δ : 7.31 (s, BHT-Ar-H, 4H), 3.47 (s, OMe, 3H), 2.41 (s, BHT-Me, 6H), 2.32 (d, $^2J_{\text{PH}} = 10.2$ Hz, $\text{Cy}_2\text{P-CH}_2$, 2H), 1.88 (s, ^tBu , 36H), 1.81 (s, Me, 3H), 0.89-1.66 (m, Cy, 33H), 0.17 (s, Al-Me, 3H).

The molar ratio of major species to the minor species is 1:0.08 based on the ^{31}P { ^1H } NMR spectrum

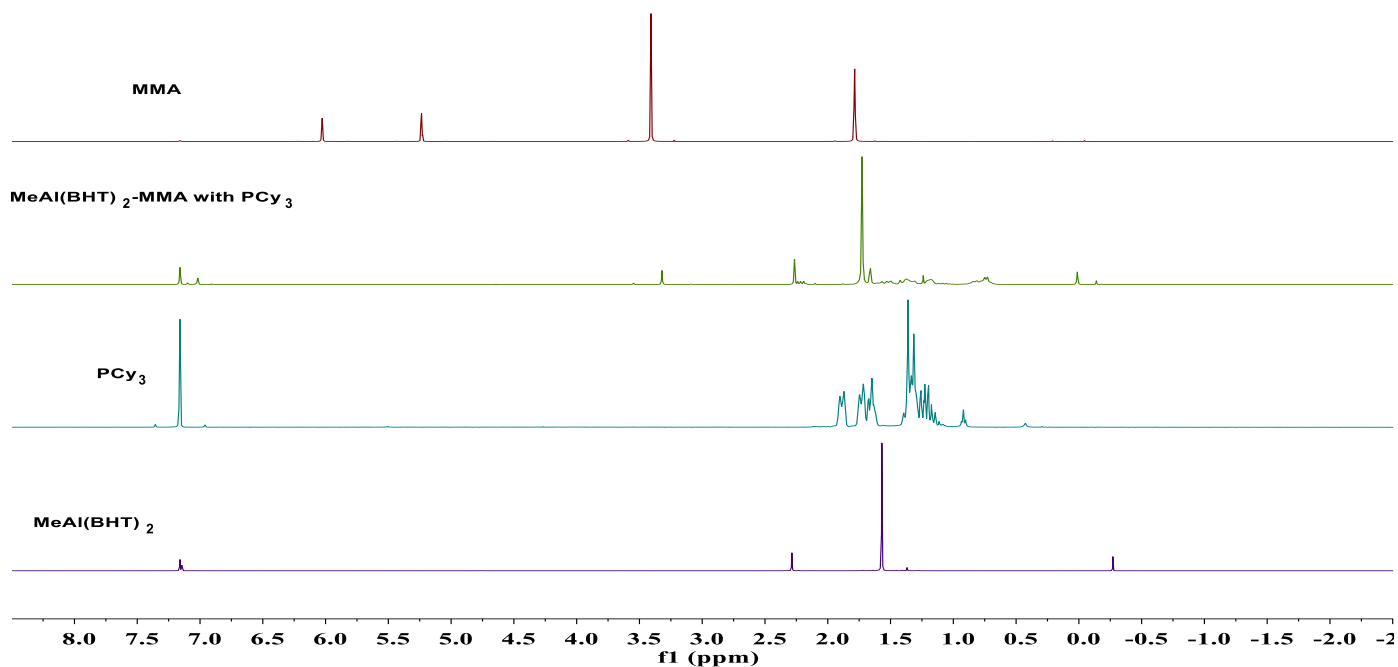
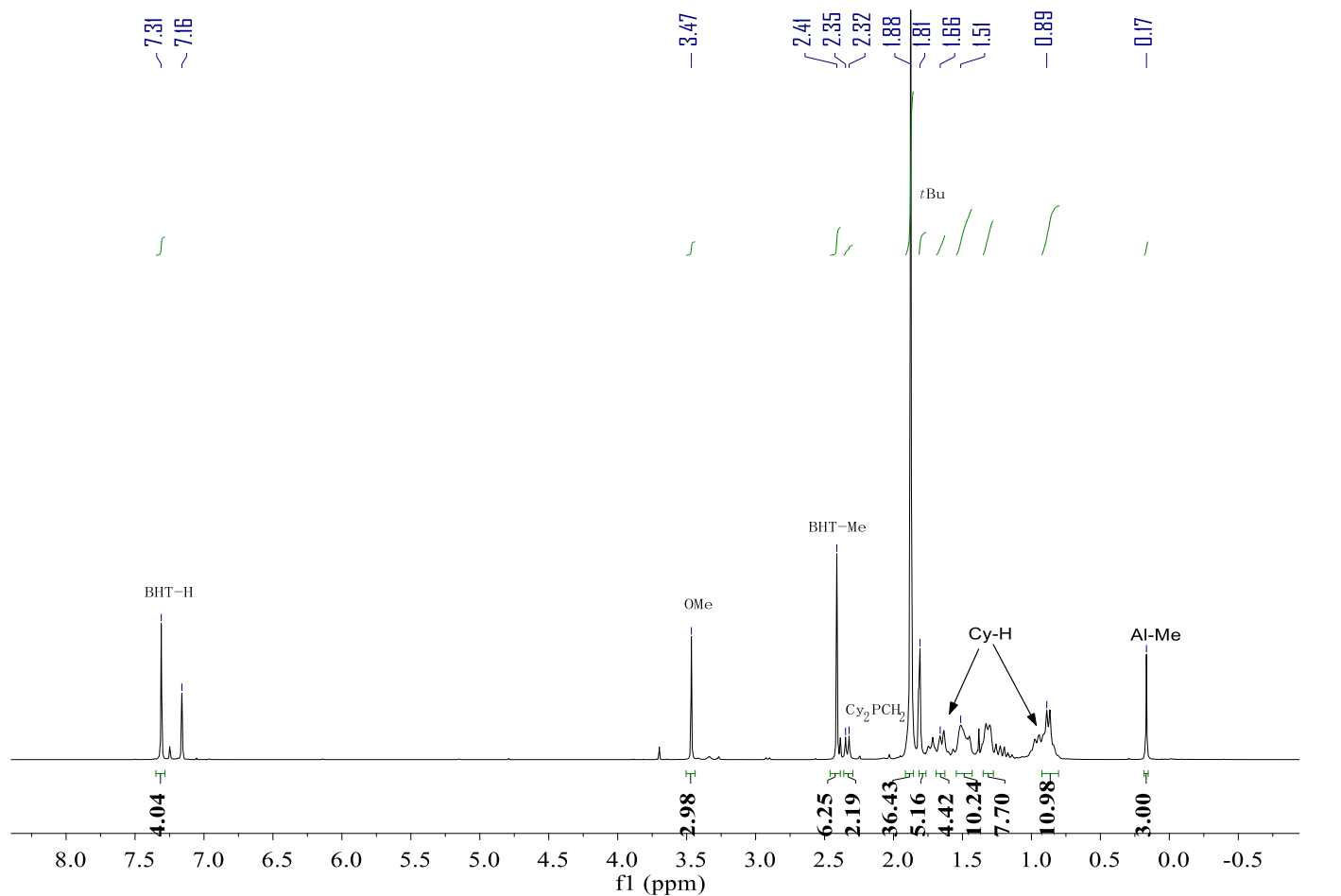


Figure S28. ^1H NMR spectra for reaction of $\text{MeAl}(\text{BHT})_2\cdot\text{MMA}$ with PCy_3 (400 MHz, C_6D_6 , 298 K), upper: separated spectrum; bottom: stacked spectra

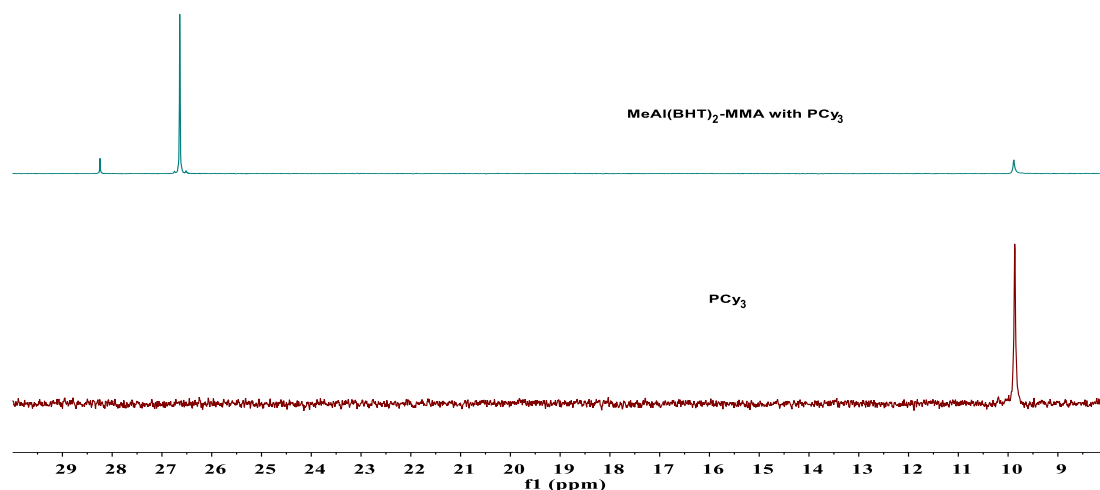


Figure S29. ^{31}P $\{^1\text{H}\}$ (162 MHz, C_6D_6 , 298 K) spectra for reaction of $\text{MeAl}(\text{BHT})_2\cdot\text{MMA}$ with PCy_3

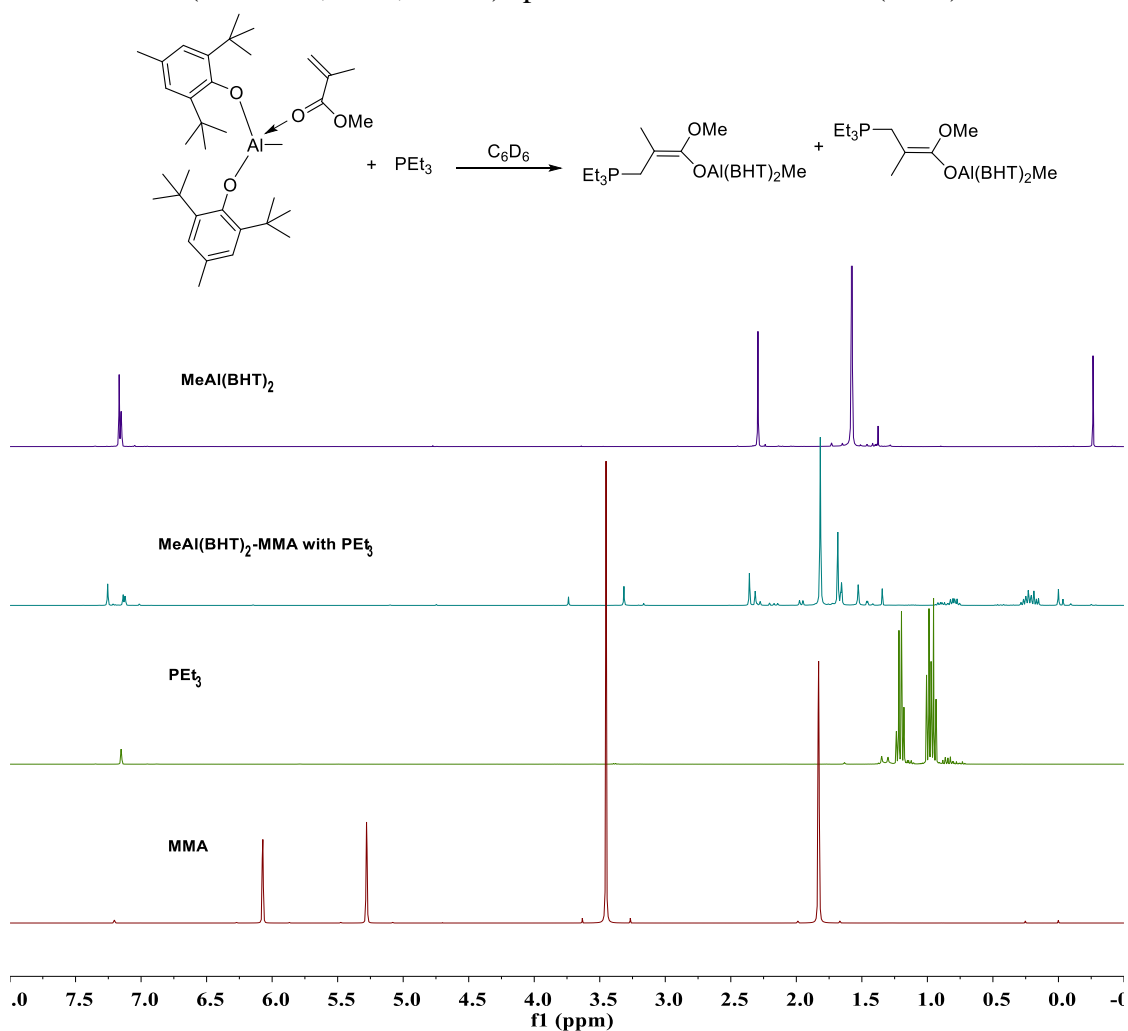


Figure S30. ^1H NMR spectra for reaction of $\text{MeAl}(\text{BHT})_2\cdot\text{MMA}$ with PEt_3 (400 MHz, C_6D_6 , 298 K)

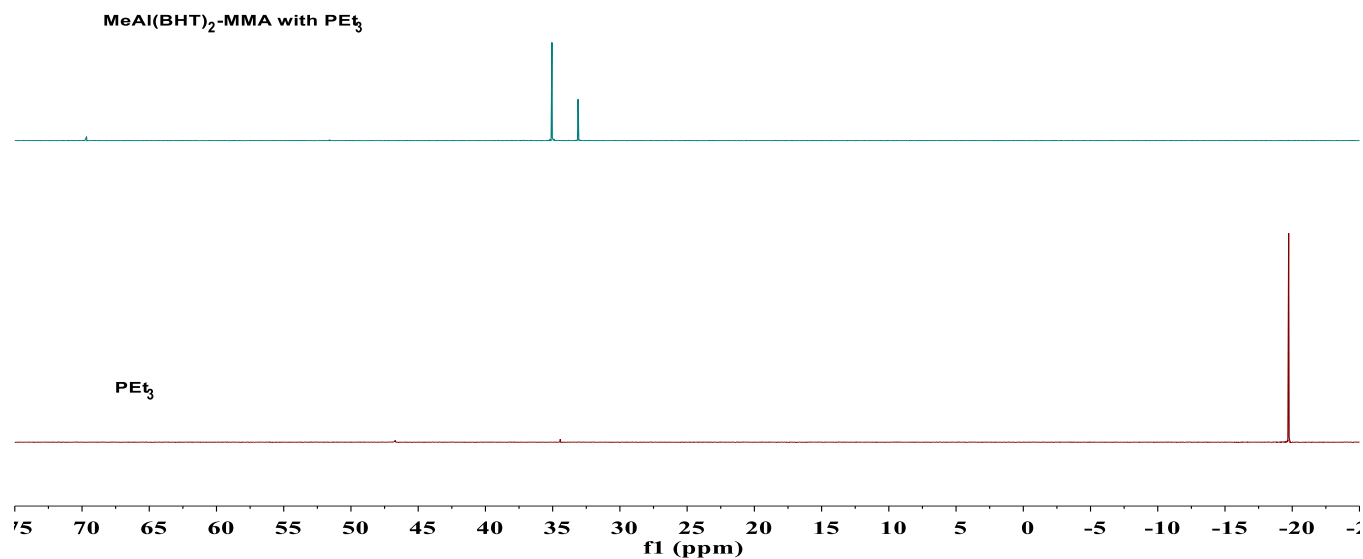
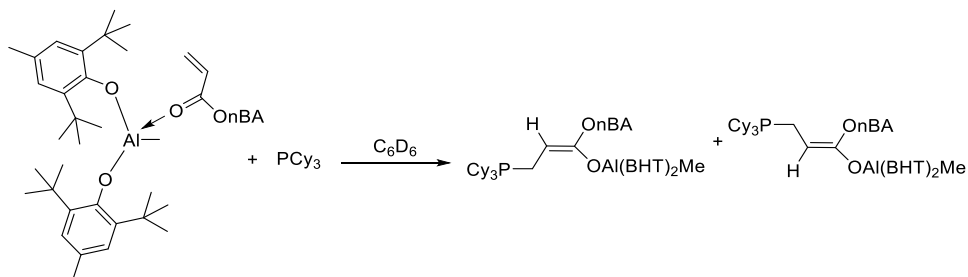


Figure S31. ^{31}P { ^1H } (162 MHz, C_6D_6 , 298 K) spectra for reaction of $\text{MeAl}(\text{BHT})_2\cdot\text{MMA}$ with PEt_3



The molar ratio of major species to the minor species is 1:0.17 based on the ^1H NMR and ^{31}P { ^1H } NMR spectra

Tentative assignment of the major species : ^1H NMR (400 MHz, C_6D_6 , 298 K): δ : 7.29 (s, BHT-Ar-H, 4H), 4.25 (t, $^3J_{\text{HH}} = 6.9$ Hz, OCH_2 , 2H), 2.52 (d, $^2J_{\text{PH}} = 10.2$ Hz, $\text{Cy}_2\text{P-CH}_2$, 2H), 2.38 (s, BHT-Me, 6H), 1.87 (s, ^tBu , 36H), 0.89-1.81 (m, Cy and Me, 36H), 0.09 (s, Al-Me, 3H).

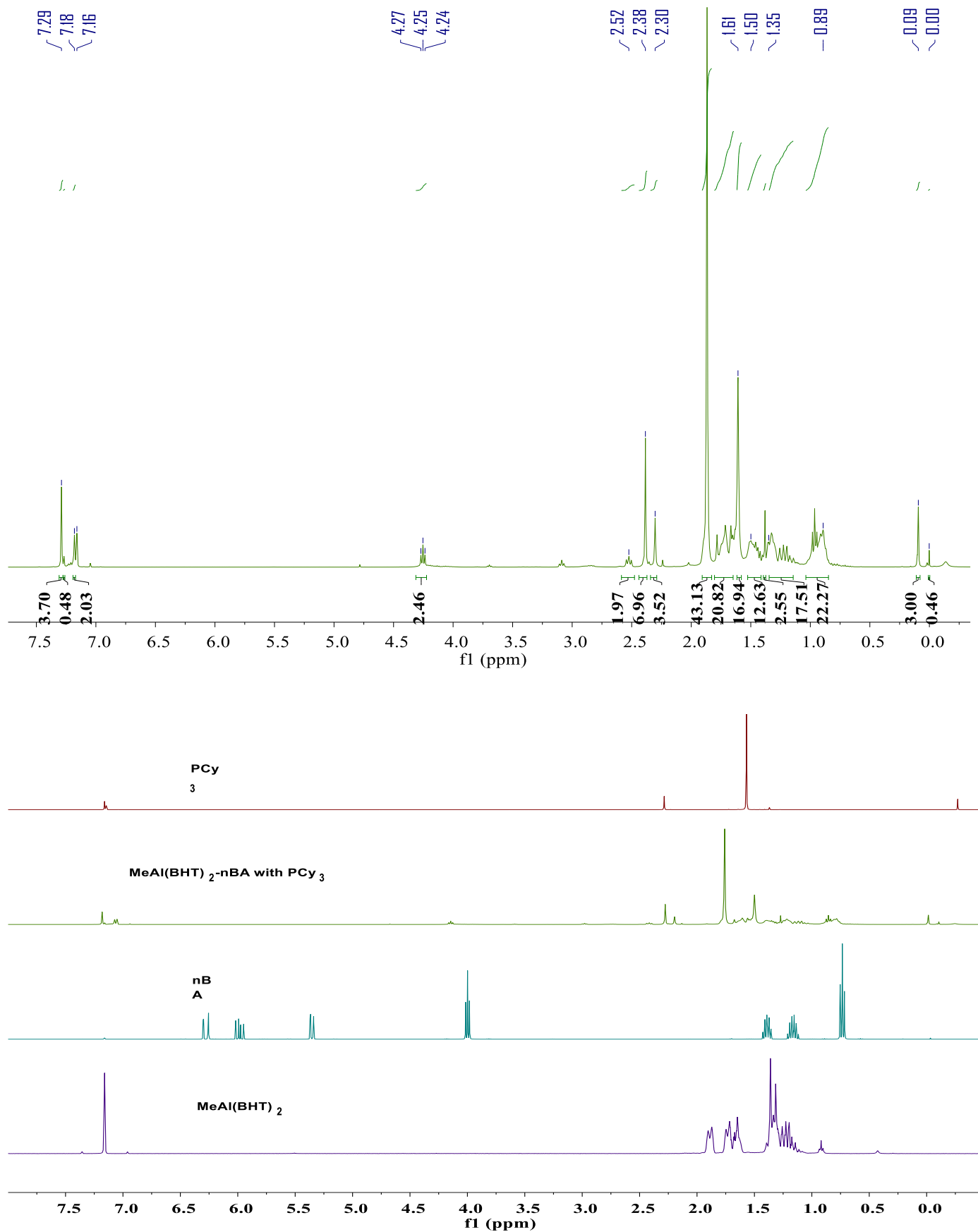


Figure S32. ^1H NMR spectra for reaction of $\text{MeAl}(\text{BHT})_2 \cdot \text{nBA}$ with PCy_3 (400 MHz, C_6D_6 , 298 K) upper: separated spectrum; bottom: stacked spectra

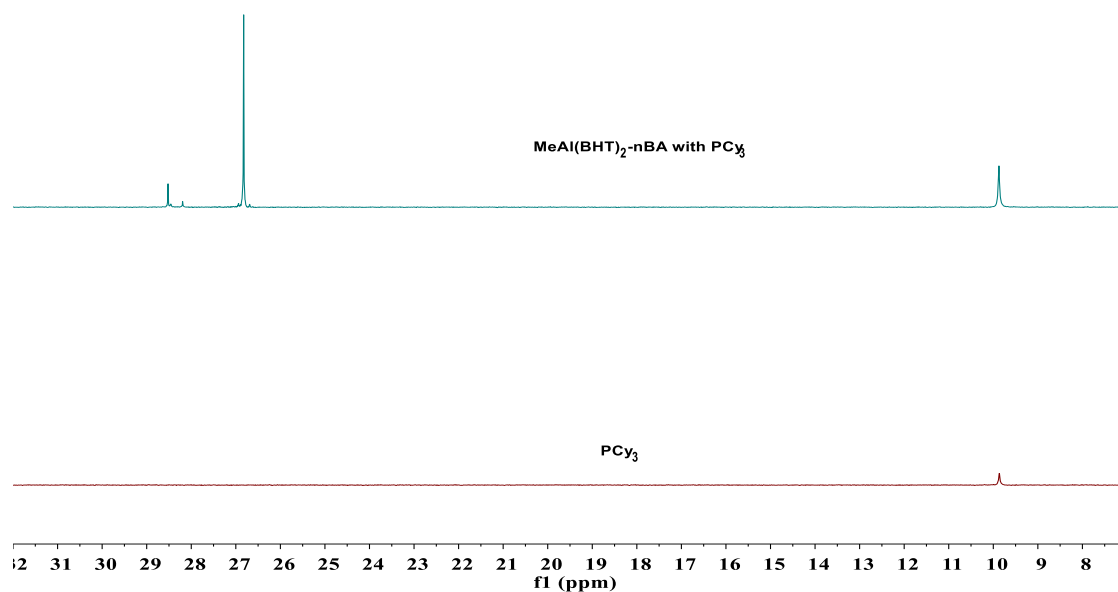


Figure S33. ^{31}P { ^1H } (162 MHz, C_6D_6 , 298 K) spectra for reaction of $\text{MeAl}(\text{BHT})_2\cdot\text{nBA}$ with PCy_3

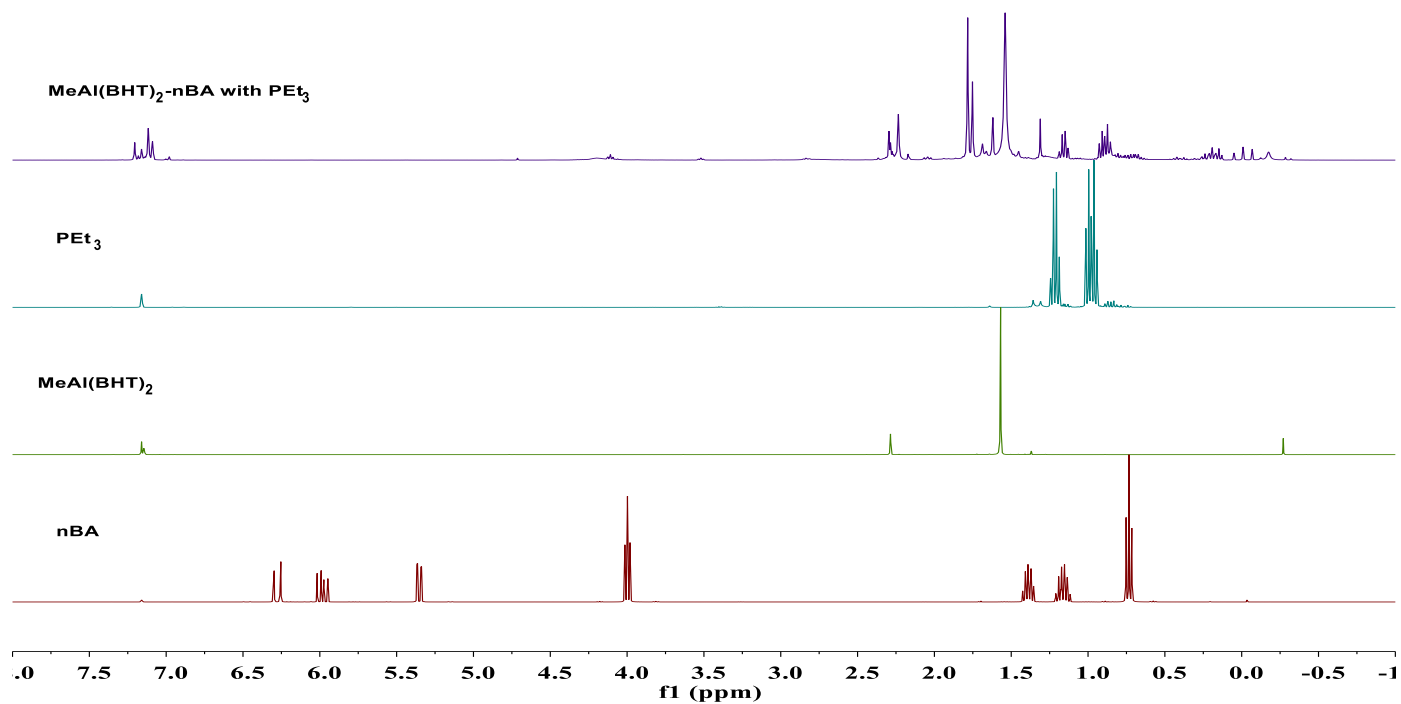
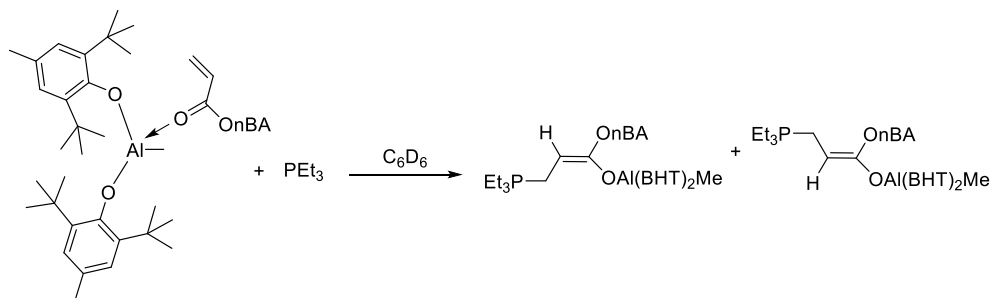


Figure S34. ^1H NMR spectra for reaction of $\text{MeAl}(\text{BHT})_2\cdot\text{nBA}$ with PEt_3 (400 MHz, C_6D_6 , 298 K)

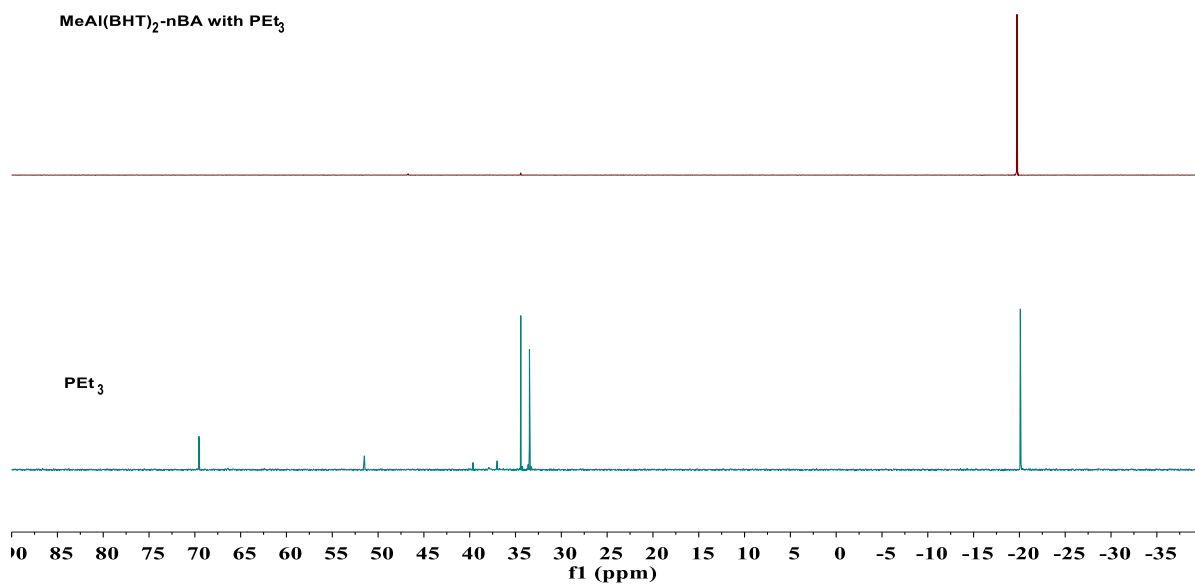


Figure S35. ^{31}P { ^1H } (162 MHz, C_6D_6 , 298 K) spectra for reaction of $\text{MeAl}(\text{BHT})_2 \cdot \text{nBA}$ with PEt_3

Oct08-2018wxx-2018-09-26-toluene.1.fid

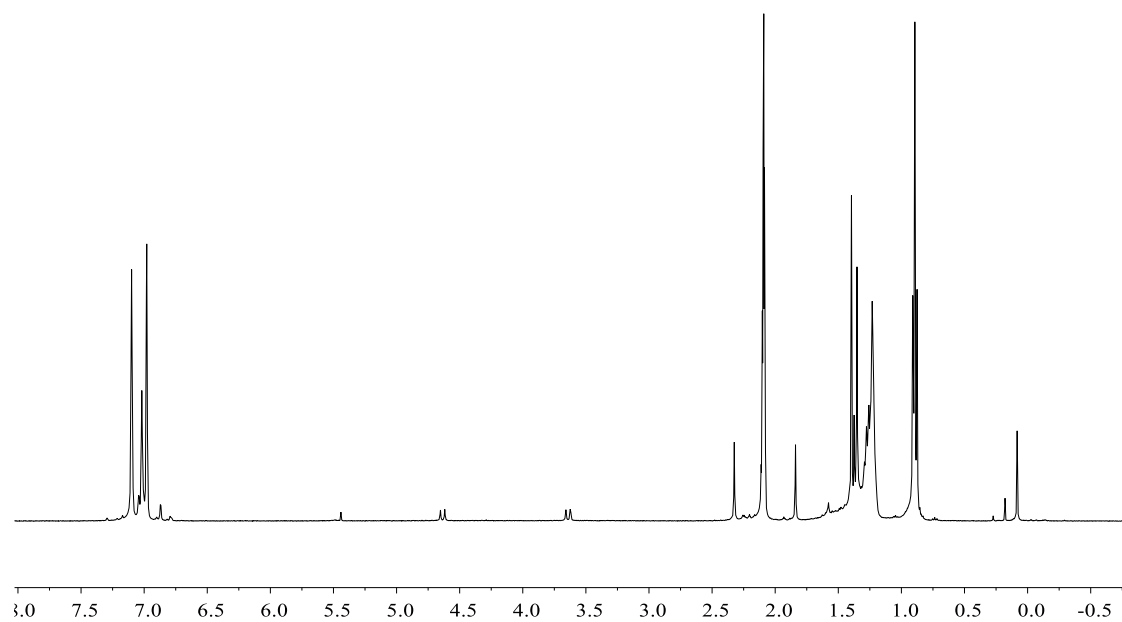


Figure S36. ^1H NMR spectrum of $[\text{Al}(\text{mbmp})\text{Me}]_2$ in toluene-d_8 (400 MHz, toluene-d_8 , 298 K)

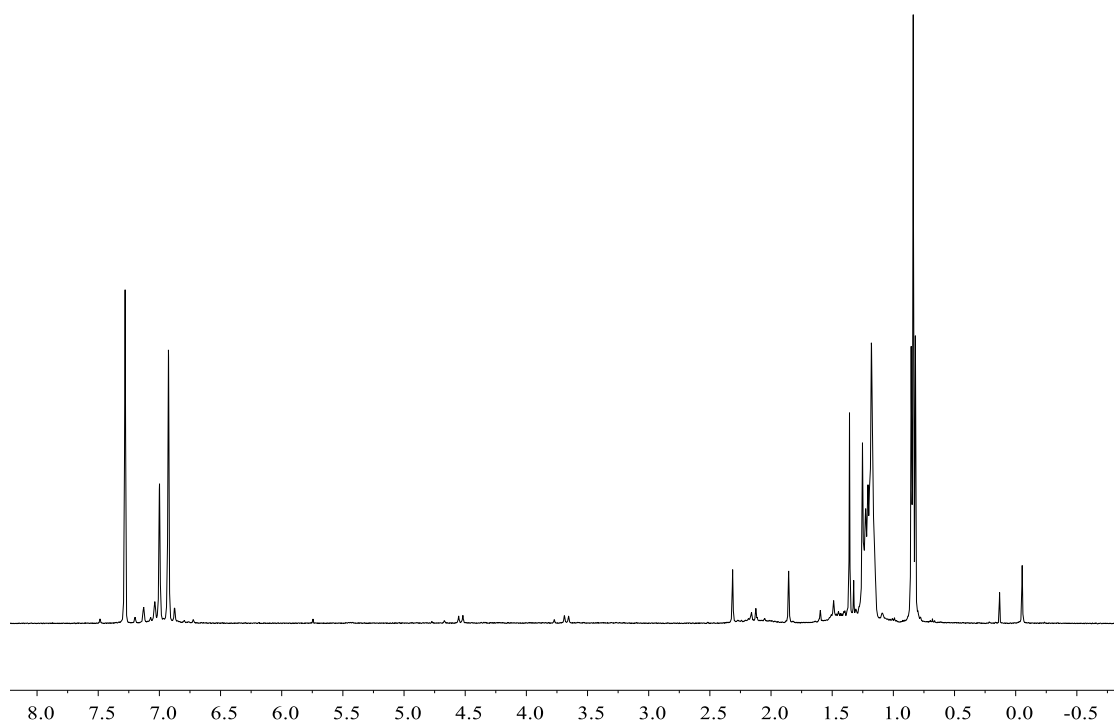
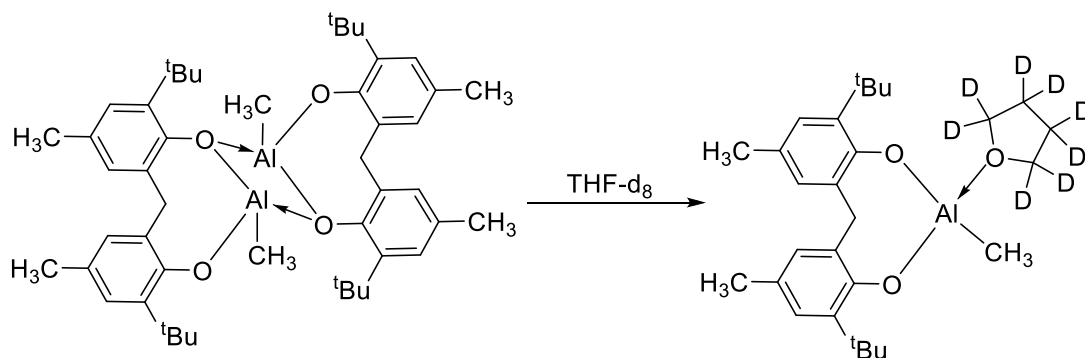


Figure S37. ^1H NMR Spectrum of $[\text{Al}(\text{mbmp})\text{Me}]_2$ in $\text{C}_6\text{D}_5\text{Br}$ (400 MHz, $\text{C}_6\text{D}_5\text{Br}$, 298 K)



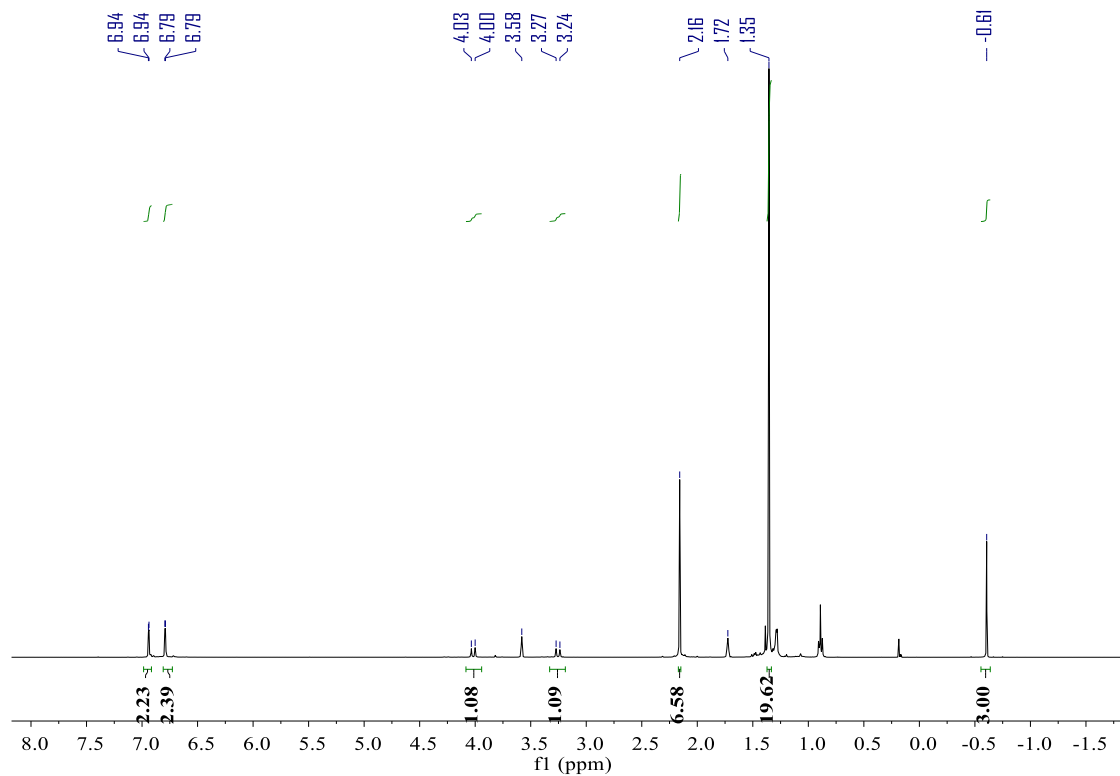


Figure S38. ^1H NMR spectrum of $[\text{Al}(\text{mbmp})\text{Me}]_2$ in THF-d_8 (400 MHz, THF-d_8 , 298 K)

^1H NMR of PnBA obtained by $\text{MeAl}(\text{BHT})_2/\text{P}[2,4,6-(\text{MeO})\text{C}_6\text{H}_2]_3$

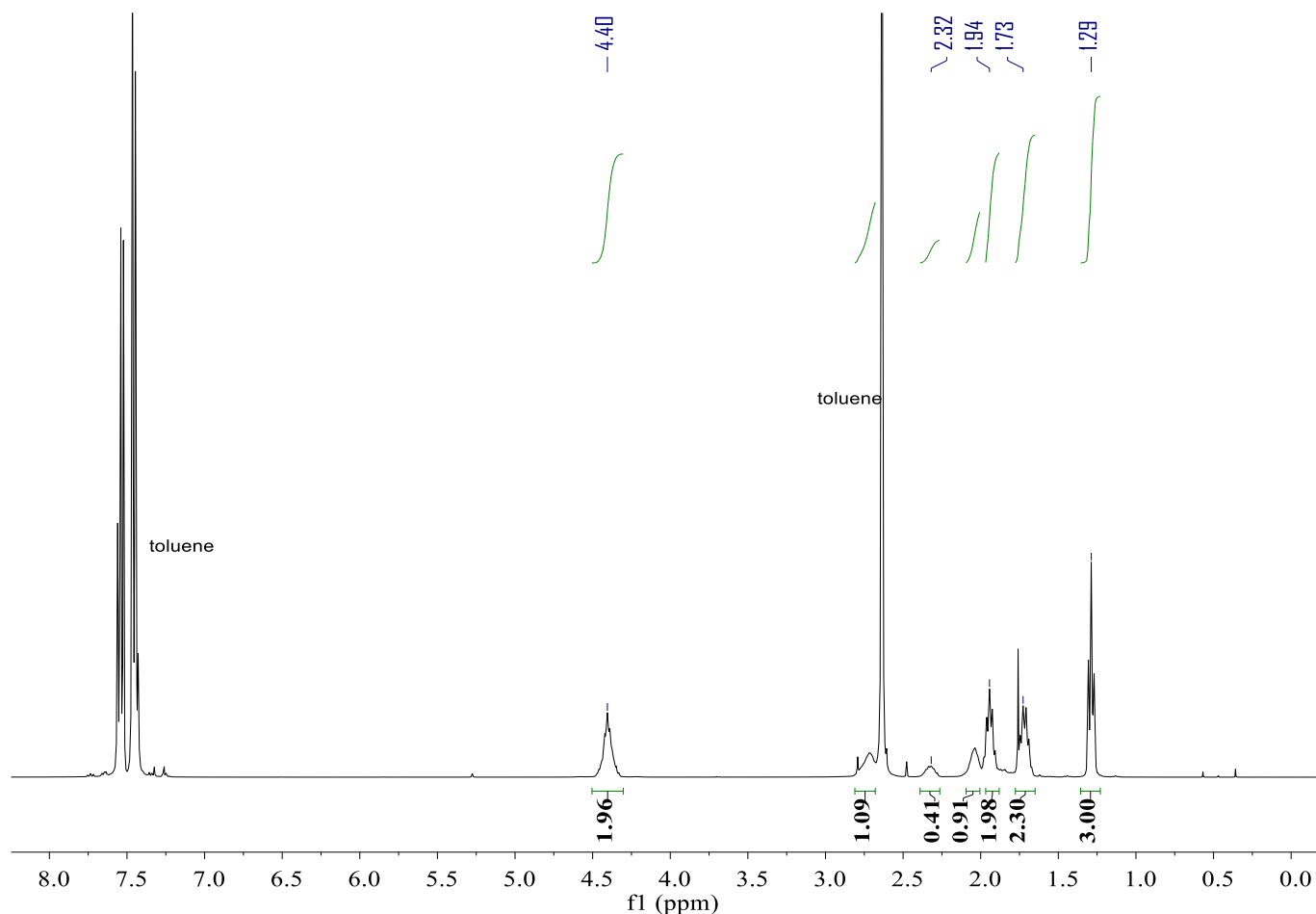


Figure S39. ^1H NMR spectrum of PnBA (400 MHz, CDCl_3 , 298 K)

Acidity of Different Lewis Acids Measured through Gutmann–Beckett Method^[3]

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 method². In a glove box, aluminum catalyst (0.012 mmol) was added to a 0.5 mL CDCl_3 solution of Et_3PO (0.012 mmol/0.5 mL, 0.05 M) in a 2 mL NMR tube. The reaction mixture was monitored by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy after 30 min at room temperature. The $^{31}\text{P}\{^1\text{H}\}$ chemical shift of Et_3PO in CDCl_3 is 52.5 ppm.

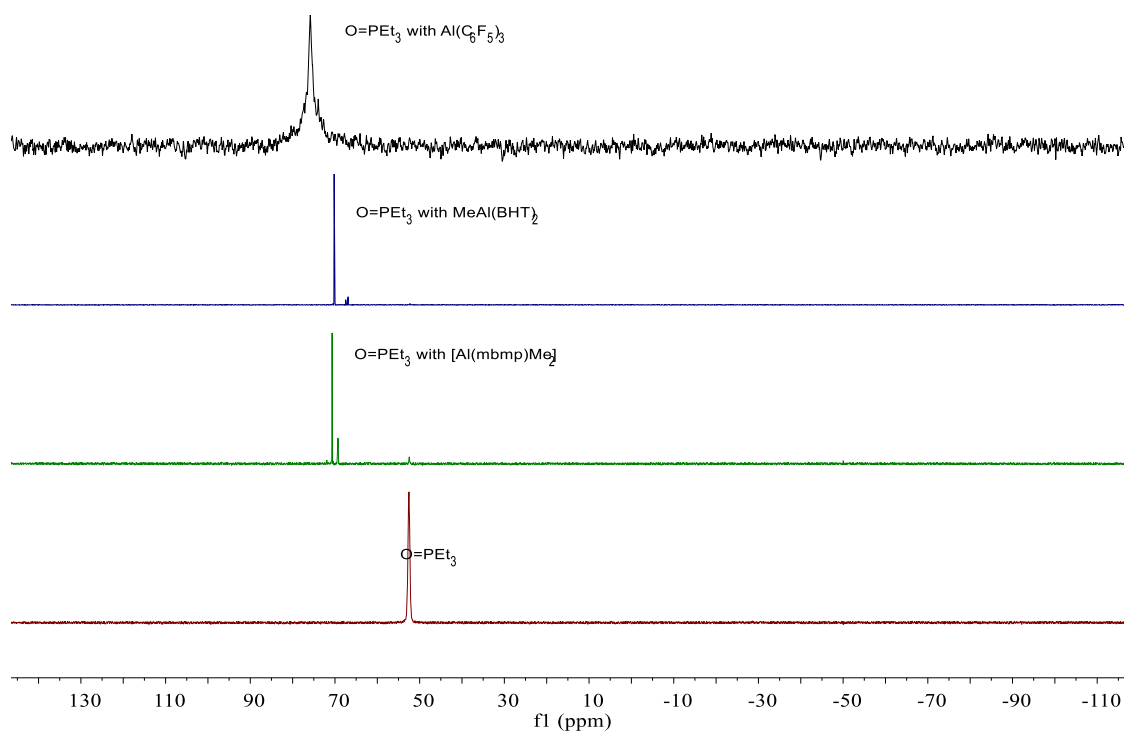


Figure S40. $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3 , 298 K)

Table S1 Acidity of Different Lewis Acids Measured through Gutmann–Beckett Method

Aluminum Catalyst	$^{31}\text{P}\{^1\text{H}\}$ NMR (δ/ppm)	$\Delta\delta$ values relative to free Et_3PO (δ/ppm)	Relative Lewis Acidity (%)
$\text{Al}(\text{C}_6\text{F}_5)_3$	75.8	23.3	100
$\text{MeAl}(\text{BHT})_2$	70.2	17.7	76
$[\text{Al}(\text{mbmp})\text{Me}]_2$	70.7	18.2	78

Polymerization Data

Table S2 Only Lewis acid and Lewis base effect in MMA polymerization

Run ^a	Acid : base : monomer	Conv. ^b (%)	$M_n^c(\text{kg}\cdot\text{mol}^{-1})$	$\text{Đ} (M_w/M_n)$	I^{*d} (%)
1	$\text{MeAl}(\text{BHT})_2$:base:monomer = 2:0:200	no			
2	$[\text{Al}(\text{mbmp})\text{Me}]_2$:base:monomer = 1:0:200	no			
3	$t\text{BuAl}(\text{BHT})_2$:base:monomer = 1:0:200	no			

	ⁱ Bu ₂ Al(BHT):base:monomer = 1:0:200	
4		no
5 ^e	0:1:200	no
6 ^f	0:1:200	no
7 ^g	0:1:200	no
8 ^h	0:1:200	no
9 ⁱ	0:1:200	no
10 ^j	0:1:200	no

^aCondition: The polymerization was carried out at RT for 2 h in 2 mL of toluene using the following procedure: for a 200 MMA/1 LB/1 LA ratio, [MMA]₀ = 1.92 M (4.8 mmol) and [LA]₀ = [LB]₀ = 9.6 mM (0.024 mmol). n.d.: not determined. ^bMonomer conversions measured by ¹H NMR spectra. ^cM_n and Đ determined by GPC relative to PS standards in THF. ^dInitiation efficiency (I*)% = M_n(calcd)/M_n(exptl) × 100, where M_n(calcd) = [M_w(MMA)]([MMA]₀/[I]₀)(conversion) + M_w of chain end groups. ^e base P(Ph)₃(OMe); ^f base PCy₃; ^g base PEt₃; ^h base P(4-OCH₃C₆H₅)₃; ⁱ base P(4-CH₃C₆H₅)₃; ^j base PPh₃.

Table S3 Solvent and LA:LB ratio effect on [Al(mbmp)Me]₂/PPh₃ in MMA polymerization

Run ^a	Solvent	LA:LB:M	Conv. ^b (%)	Selectivity			M _n ^c (kg·mol ⁻¹)	M _n (calcd) (kg·mol ⁻¹)	Đ (M _w /M _n)	I* ^d (%)
				rr	mr	mm				
1	CH ₂ Cl ₂	1:1:200	>99	66.2	31.1	2.7	2100	20286	7.0	980
2	toluene	1:1:200	>99	65.8	29.6	4.6	20300	20286	4.7	100
3	no	1:1:200	95	-	-	-	n.d.	20286	n.d.	
4	toluene	2:1:200	>99	67.5	30.4	2.1	2100	20286	15.6	973
5 ^e	toluene	0.5:1:200	>99	-	-	-	35800	20300	1.7	56.7

^aCondition: The polymerization was carried out at RT for 2 h in 2 mL of solvent using the following procedure: for a 200 MMA/1 LB/1 LA ratio, [MMA]₀ = 1.92 M (4.8 mmol) and [LA]₀ = [LB]₀ = 9.6 mM (0.024 mmol), [LA]₀ = 2[LB]₀ = 19.2 mM (0.048 mmol, run 4). n.d.: not determined. ^bMonomer conversions measured by ¹H NMR. ^cM_n and Đ determined by GPC relative to PMMA standards in THF. ^dInitiation efficiency (I*)% = M_n(calcd)/M_n(exptl) × 100, where M_n(calcd) = [M_w(MMA)]([MMA]₀/[I]₀)(conversion) + M_w of chain end groups. ^e using PCy₃ instead of PPh₃ as Lewis base, reaction time, 5 min.

Table S4 MMA polymerization catalyzed by different phosphines/organoaluminum

Run ^a	LP	Conv. ^b (%)	Selectivity			M _n ^c (g·mol ⁻¹)	M _n (calcd) (g·mol ⁻¹)	Đ (M _w /M _n)	I* ^d (%)
			rr	mr	mm				

1	PCy ₃ / MeAl(BHT) ₂	>99	70	26.9	4.1	40400	20304	2.5	50.3
2	PEt ₃ / MeAl(BHT) ₂	>99	71.5	24.4	2.1	8500	20142	1.3	29.4
3	P (4-OCH ₃ C ₆ H ₅) ₃ / MeAl(BHT) ₂	>99	71.9	25.9	2.2	102000	20376	2.2	20
4	P(4-CH ₃ C ₆ H ₅) ₃ / MeAl(BHT) ₂	no							
5	PPh ₃ / MeAl(BHT) ₂	no							
6	PCy ₃ / ⁱ BuAl(BHT) ₂	>99	78.1	18.8	3.1	76100	20304	1.3	26.7
7	PEt ₃ / ⁱ BuAl(BHT) ₂	>99	80	19.2	0.8	103000	20142	1.6	19.6
8	P (4-OCH ₃ C ₆ H ₅) ₃ / ⁱ BuAl(BHT) ₂	no							
9	P(4-CH ₃ C ₆ H ₅) ₃ / ⁱ BuAl(BHT) ₂	no							
10	PPh ₃ / ⁱ BuAl(BHT) ₂	no							
11	PCy ₃ / ⁱ Bu ₂ AlBHT	42	65.4	27.5	7.1	93000	20304	1.5	21.8
12	PEt ₃ / ⁱ Bu ₂ AlBHT	no							
13	P (4-OCH ₃ C ₆ H ₅) ₃ / ⁱ Bu ₂ AlBHT	no							
14	P(4-CH ₃ C ₆ H ₅) ₃ / ⁱ Bu ₂ AlBHT	no							
15	PPh ₃ / ⁱ Bu ₂ AlBHT	no							

^aCondition: The polymerization was carried out at RT for 2 h in 2 mL of toluene using the following procedure: for a 200 MMA/1 LB/1 LA ratio, [MMA]₀ = 1.92 M (4.8 mmol) and [LA]₀ = 2[LB]₀ = 19.2 mM (0.048 mmol). n.d.: not determined. ^bMonomer conversions measured by ¹H NMR. ^cM_n and Đ determined by GPC relative to PMMA standards in THF. ^dInitiation efficiency (I*)% = M_n(calcd)/M_n(exptl) × 100, where M_n(calcd) = [M_w(MMA)]/[MMA]₀/[I]₀(conversion) + M_w of chain end groups.

Table S5 MMA polymerization catalyzed by different NHOs/[Al(mbmp)Me]₂

Run ^a	LP	Conv. ^b (%)	Selectivity			M _n ^c (g·mol ⁻¹)	Đ (M _w /M _n)
			rr	mr	mm		
1	NHO-	>99	65.3	33.1	1.6	58100	1.2

	1/[Al(mbmp)Me] ₂						
2	NHO-2/ [Al(mbmp)Me] ₂	>99	64.5	32.9	2.6	65700	1.2
3	NHO-1/MeAl(BHT) ₂	>99	66.7	30.7	2.7	33900	1.2
4	NHO-2/MeAl(BHT) ₂	>99	67.1	30.2	2.7	27500	1.5
5 ^d	NHO-1/MeAl(BHT) ₂	>99	67.1	30.6	2.3	27900	1.1
6 ^d	NHO-2/MeAl(BHT) ₂	>99	66.6	31.3	2.1	30400	1.1
7 ^e	IAP-3/[Al(mbmp)Me] ₂	>99	65.2	32.5	2.3	11127	1.3

^aCondition: The polymerization was carried out at RT for 2 min in 2 mL of toluene using the following procedure: for a 200 MMA/1 LB/1 LA ratio, [MMA]₀ = 1.92 M (4.8 mmol) and [LA]₀ = 2[LB]₀ = 19.2 mM (0.048 mmol). n.d.: not determined. ^bMonomer conversions measured by ¹H NMR. ^cM_n and Đ determined by GPC relative to PMMA standards in THF. ^dData obtained from reference *ACS Catalysis*, **2018**, *8*, 3571-3578.

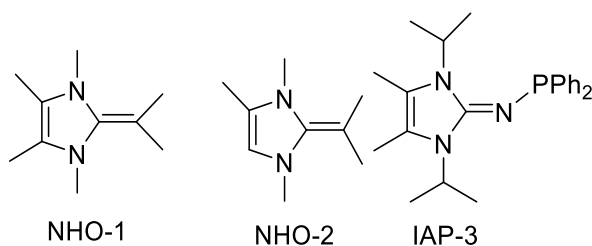


Table S6 MMA polymerization catalyzed by different phosphines/[Al(mbmp)Me]₂ in a molar ratio of 1:0.5

Run ^a	LP	Conv. ^b (%)	Selectivity			M _n ^c (g·mol ⁻¹)	Đ (M _w /M _n)
			rr	mr	mm		
1	P(Ph) ₃ (OMe) ₉ /[Al(mbmp)Me] ₂	46.3	65.0	33.1	1.9	7700	1.5
2	PCy ₃ /[Al(mbmp)Me] ₂	>99	64.8	32.9	2.3	51000	1.4
3	PEt ₃ /[Al(mbmp)Me] ₂	93.7	66.5	30.7	2.9	35100	1.7
4	P(4-OCH ₃ C ₆ H ₅) ₃ /[Al(mbmp)Me] ₂	90.6	67.4	30.2	2.4	28580	1.5
5	P(4-CH ₃ C ₆ H ₅) ₃ /[Al(mbmp)Me] ₂	no	-	-	-	-	-
6	PPh ₃ /[Al(mbmp)Me] ₂	96.5	67.4	30.6	2.0	87600	2.7

^aCondition: The polymerization was carried out at RT for 2 min in 2 mL of toluene using the following procedure: for a 200 MMA/1 LB/0.5 LA ratio, [MMA]₀ = 1.92 M (4.8 mmol) and [LA]₀ = 0.5[LB]₀ = 9.6 mM (0.024 mmol).

X-ray data of [Al(mbmp)OH]₂

CCDC numbers of binuclear [Al(mbmp)OH]₂ is 1961188. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table S7 Crystal data and structure refinement for 1961188.

Identification Code	1961188
Empirical formula	C ₄₆ H ₆₂ Al ₂ O ₆
Formula weight	764.92
Temperature	298(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, C2/c
Unit cell dimensions	a = 16.1738(14) Å alpha = 90 deg. b = 11.4534(9) Å beta = 96.754(2) deg. c = 27.691(2) Å gamma = 90 deg.
Volume	5093.9(7) Å ³
Z, Calculated density	4, 0.997 Mg/m ³
Absorption coefficient	0.096 mm ⁻¹
F(000)	1648
Crystal Size	0.43 x 0.33 x 0.30 mm
Theta range for data collection	2.54 to 25.02 deg.
Limiting indices	-18 ≤ h ≤ 19, 12 ≤ k ≤ 13, -29 ≤ l ≤ 32
Reflections collected / unique	12396 / 4488 [R(int) = 0.0861]
Completeness to theta = 25.02	99.7 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9718 and 0.9599
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	4488 / 0 / 253
Goodness-of-fit on F ²	1.034

Final R indices [$I > 2\sigma(I)$]	R1 = 0.0729, wR2 = 0.2024
R indices (all data)	R1 = 0.1187, wR2 = 0.2252
Largest diff. peak and hole	0.293 and -0.566 e.Å ⁻³ e.Å ⁻³

Table S8 Bond lengths [Å] and angles [deg] for 1961188.

Atom	length /Å
Al(1)-O(2)	1.693(2)
Al(1)-O(1)	1.858(2) 1.865(2)
Al(1)-O(1)#1	1.927(4)
Al(1)-O(3)	2.858(2)
Al(1)-Al(1)#1	1.422(4)
sO(1)-C(3)	1.865(2) 1.364(4)
O(1)-Al(1)#1	0.8200
O(2)-C(14)	1.513(5)
O(3)-H(3)	1.525(5)
C(1)-C(13)	0.9700
C(1)-C(2)	0.9700
C(1)-H(1A)	1.374(5)
C(1)-H(1B)	1.391(4)
C(2)-C(7)	1.412(5)
C(2)-C(3)	1.380(5)
C(3)-C(4)	1.545(5)
C(4)-C(5)	1.391(5)
C(4)-C(8)	0.9300
C(5)-C(6)	1.380(5)
C(5)-H(5)	1.502(6)
C(6)-C(7)	0.9300
C(6)-C(12)	1.512(6)
C(7)-H(7)	1.528(6)

C(8)-C(11)	1.529(6)
C(8)-C(10)	0.9600
C(8)-C(9)	0.9600
C(9)-H(9A)	0.9600
C(9)-H(9B)	0.9600
C(9)-H(9C)	0.9600
C(10)-H(10A)	0.9600
C(10)-H(10B)	0.9600
C(10)-H(10C)	0.9600
C(11)-H(11A)	0.9600
C(11)-H(11B)	0.9600
C(11)-H(11C)	0.9600
C(12)-H(12A)	0.9600
C(12)-H(12B)	1.385(5)
C(12)-H(12C)	1.394(5)
C(13)-C(14)	1.411(5)
C(13)-C(18)	1.385(5)
C(14)-C(15)	1.548(5)
C(15)-C(16)	1.384(6)
C(15)-C(19)	0.9300
C(16)-C(17)	1.369(5)
C(16)-H(16)	1.511(5)
C(17)-C(18)	0.9300
C(17)-C(23)	1.530(7)
C(18)-H(18)	1.537(6)
C(19)-C(21)	1.547(5)
C(19)-C(20)	0.9600
C(19)-C(22)	0.9600
C(20)-H(20A)	0.9600
C(20)-H(20B)	0.9600

C(20)-H(20C)	0.9600
C(21)-H(21A)	0.9600
C(21)-H(21B)	0.9600
C(21)-H(21C)	0.9600
C(22)-H(22A)	0.9600
C(22)-H(22B)	0.9600
C(22)-H(22C)	0.9600
C(23)-H(23A)	0.9600
C(23)-H(23B)	
C(23)-H(23C)	

Atom	Angle/°
O(2)-Al(1)-O(1)	111.51(12)
O(2)-Al(1)-O(1)#1	120.56(12)
O(1)-Al(1)-O(1)#1	79.72(11)
O(2)-Al(1)-O(3)	107.61(16)
O(1)-Al(1)-O(3)	123.14(16)
O(1)#1-Al(1)-O(3)	112.99(18)
O(2)-Al(1)-Al(1)#1	124.77(10)
O(1)-Al(1)-Al(1)#1	39.95(7)
O(1)#1-Al(1)-Al(1)#1	39.77(7)
O(3)-Al(1)-Al(1)#1	127.61(14)
C(3)-O(1)-Al(1)	123.0(2)
C(3)-O(1)-Al(1)#1	126.0(2)
Al(1)-O(1)-Al(1)#1	100.28(11)
C(14)-O(2)-Al(1)	156.7(2)
Al(1)-O(3)-H(3)	109.5
C(13)-C(1)-C(2)	112.9(3)
C(13)-C(1)-H(1A)	109.0

C(2)-C(1)-H(1A)	109.0
C(13)-C(1)-H(1B)	109.0
C(2)-C(1)-H(1B)	109.0
H(1A)-C(1)-H(1B)	107.8
C(7)-C(2)-C(3)	119.0(3)
C(7)-C(2)-C(1)	116.9(3)
C(3)-C(2)-C(1)	124.1(3)
C(2)-C(3)-C(4)	121.7(3)
C(2)-C(3)-O(1)	117.7(3)
C(4)-C(3)-O(1)	120.5(3)
C(5)-C(4)-C(3)	115.9(3)
C(5)-C(4)-C(8)	119.9(3)
C(3)-C(4)-C(8)	124.2(3)
C(4)-C(5)-C(6)	124.0(4)
C(4)-C(5)-H(5)	118.0
C(6)-C(5)-H(5)	118.0
C(7)-C(6)-C(5)	117.3(4)
C(7)-C(6)-C(12)	122.3(4)
C(5)-C(6)-C(12)	120.3(4)
C(2)-C(7)-C(6)	122.0(3)
C(2)-C(7)-H(7)	119.0
C(6)-C(7)-H(7)	119.0
C(11)-C(8)-C(10)	106.4(4)
C(11)-C(8)-C(9)	110.1(4)
C(10)-C(8)-C(9)	106.4(4)
C(11)-C(8)-C(4)	112.1(3)
C(10)-C(8)-C(4)	111.7(3)
C(9)-C(8)-C(4)	110.0(3)
C(8)-C(9)-H(9A)	109.5
C(8)-C(9)-H(9B)	109.5

H(9A)-C(9)-H(9B)	109.5
C(8)-C(9)-H(9C)	109.5
H(9A)-C(9)-H(9C)	109.5
H(9B)-C(9)-H(9C)	109.5
C(8)-C(10)-H(10A)	109.5
C(8)-C(10)-H(10B)	109.5
H(10A)-C(10)-H(10B)	109.5
C(8)-C(10)-H(10C)	109.5
H(10A)-C(10)-H(10C)	109.5
H(10B)-C(10)-H(10C)	109.5
C(8)-C(11)-H(11A)	109.5
C(8)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11B)	109.5
C(8)-C(11)-H(11C)	109.5
H(11A)-C(11)-H(11C)	109.5
H(11B)-C(11)-H(11C)	109.5
C(6)-C(12)-H(12A)	109.5
C(6)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12B)	109.5
C(6)-C(12)-H(12C)	109.5
H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5
C(14)-C(13)-C(18)	119.7(3)
C(14)-C(13)-C(1)	119.8(3)
C(18)-C(13)-C(1)	120.5(3)
O(2)-C(14)-C(13)	118.4(3)
O(2)-C(14)-C(15)	121.1(3)
C(13)-C(14)-C(15)	120.6(3)
C(16)-C(15)-C(14)	116.9(4)
C(16)-C(15)-C(19)	121.1(3)

C(14)-C(15)-C(19)	121.9(3)
C(17)-C(16)-C(15)	123.6(4)
C(17)-C(16)-H(16)	118.2
C(15)-C(16)-H(16)	118.2
C(18)-C(17)-C(16)	118.0(4)
C(18)-C(17)-C(23)	121.4(4)
C(16)-C(17)-C(23)	120.7(4)
C(17)-C(18)-C(13)	121.3(4)
C(17)-C(18)-H(18)	119.4
C(13)-C(18)-H(18)	119.4
C(21)-C(19)-C(20)	110.6(4)
C(21)-C(19)-C(22)	106.3(4)
C(20)-C(19)-C(22)	107.8(4)
C(21)-C(19)-C(15)	110.5(4)
C(20)-C(19)-C(15)	109.7(3)
C(22)-C(19)-C(15)	111.9(4)
C(19)-C(20)-H(20A)	109.5
C(19)-C(20)-H(20B)	109.5
H(20A)-C(20)-H(20B)	109.5
C(19)-C(20)-H(20C)	109.5
H(20A)-C(20)-H(20C)	109.5
H(20B)-C(20)-H(20C)	109.5
C(19)-C(21)-H(21A)	109.5
C(19)-C(21)-H(21B)	109.5
H(21A)-C(21)-H(21B)	109.5
C(19)-C(21)-H(21C)	109.5
H(21A)-C(21)-H(21C)	109.5
H(21B)-C(21)-H(21C)	109.5
C(19)-C(22)-H(22A)	109.5
C(19)-C(22)-H(22B)	109.5

H(22A)-C(22)-H(22B)	109.5
C(19)-C(22)-H(22C)	109.5
H(22A)-C(22)-H(22C)	109.5
H(22B)-C(22)-H(22C)	109.5
C(17)-C(23)-H(23A)	109.5
C(17)-C(23)-H(23B)	109.5
H(23A)-C(23)-H(23B)	109.5
C(17)-C(23)-H(23C)	109.5
H(23A)-C(23)-H(23C)	109.5
H(23B)-C(23)-H(23C)	109.5

MALDI-TOF MS spectra of low-MW PMMA by PCy₃/[Al(mbmp)Me]₂

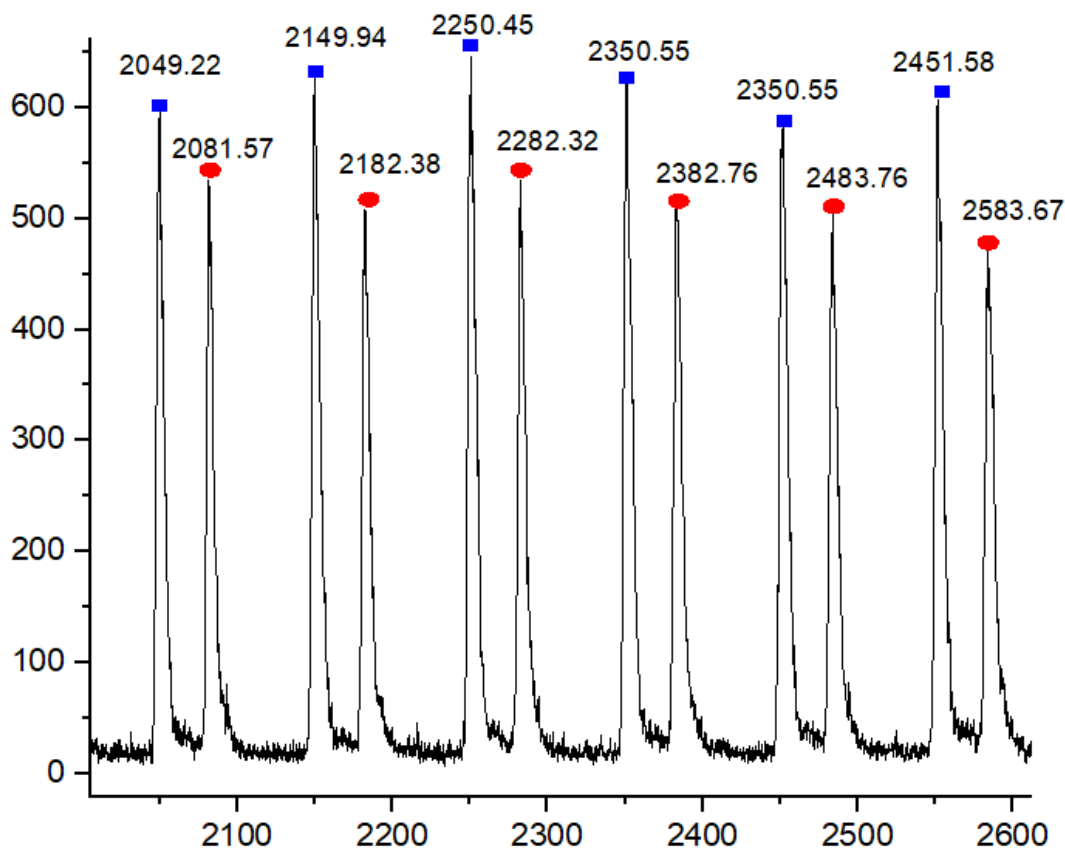


Figure S41. MALDI-TOF mass spectrum of the low-MW PMMA sample produced by PCy₃/[Al(mbmp)Me]₂ in toluene at RT.

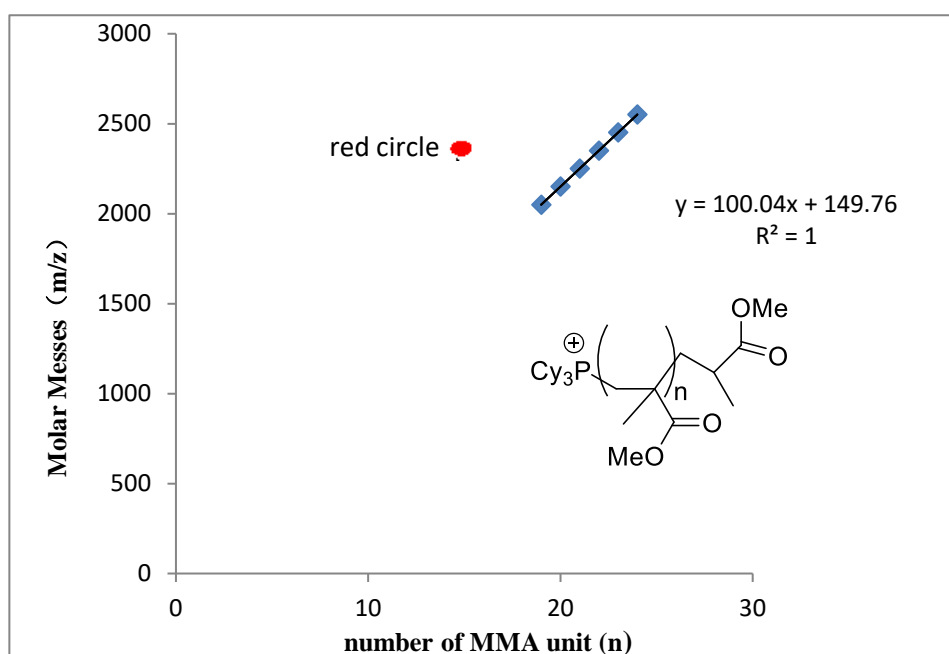
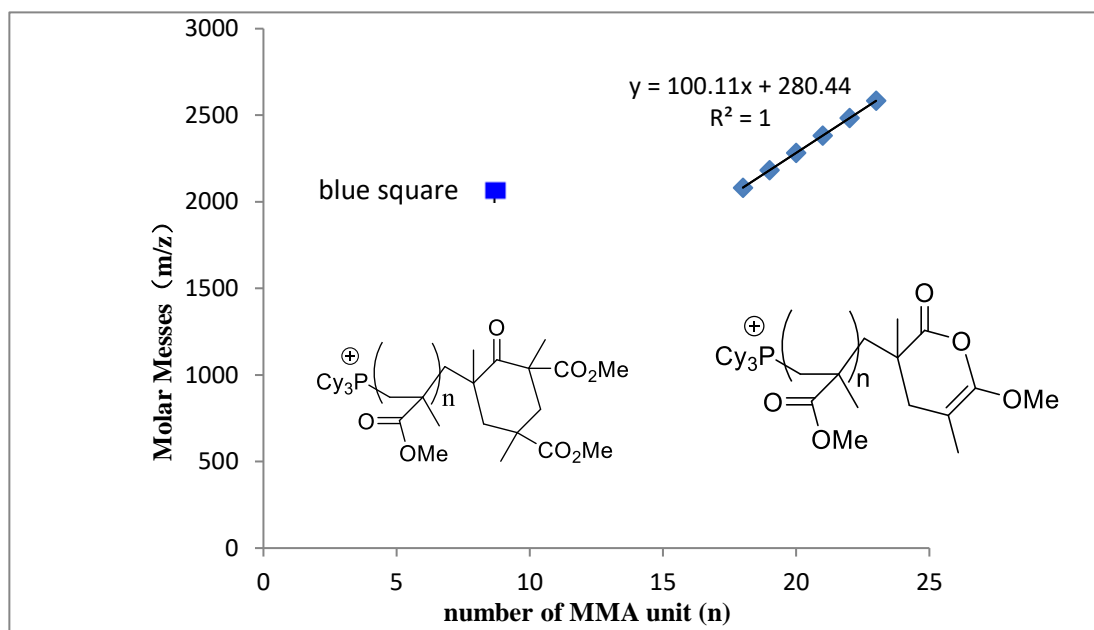


Figure S42. Plot of m/z values from Figure S38 vs the number of MMA repeat units (n).

Selected GPC Traces of Polymer Products

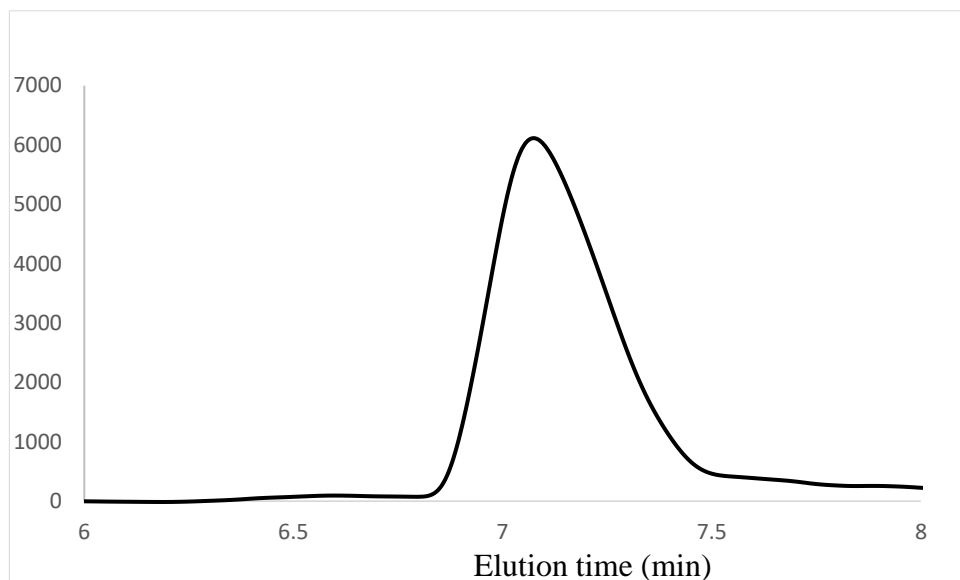


Figure S43. GPC (dRI) trace of PMMA synthesized by MMA/PCy₃/[Al(mbmp)Me]₂ = 200/1/1 (Table 2, run 3; M_n = 14.5 kg/mol, Đ = 1.1).

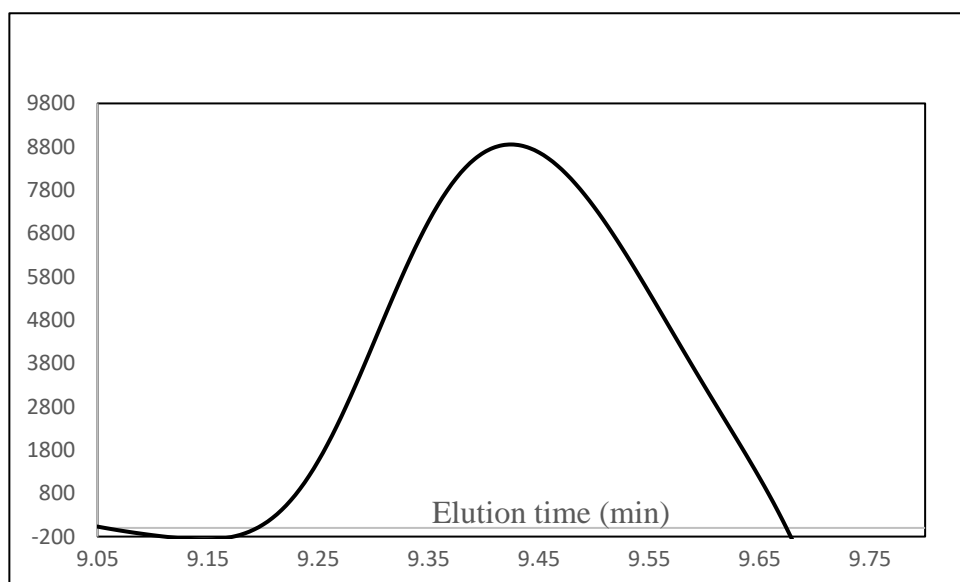


Figure S44. GPC (dRI) trace of PMMA synthesized by MMA/P(Ph)₃(OMe)₉/[Al(mbmp)Me]₂ = 200/1/1 (Table 2, run 2; M_n = 0.46 kg/mol, Đ = 1.1).

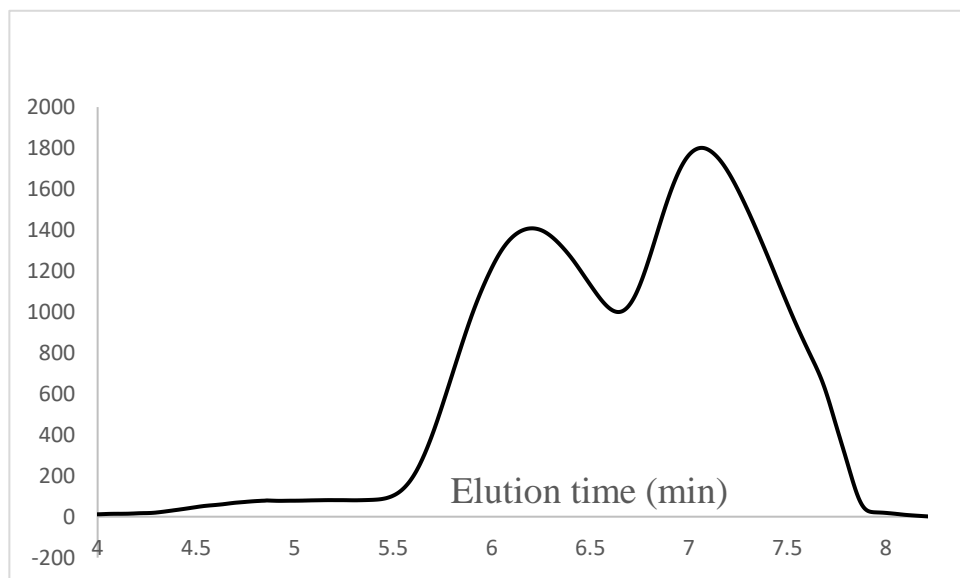


Figure S45. GPC (dRI) trace of PMMA synthesized by MMA/PEt₃/[Al(mbmp)Me]₂ = 200/1/1 (Table 2, run 4; M_n = 19.1 kg/mol, Đ = 3.7).

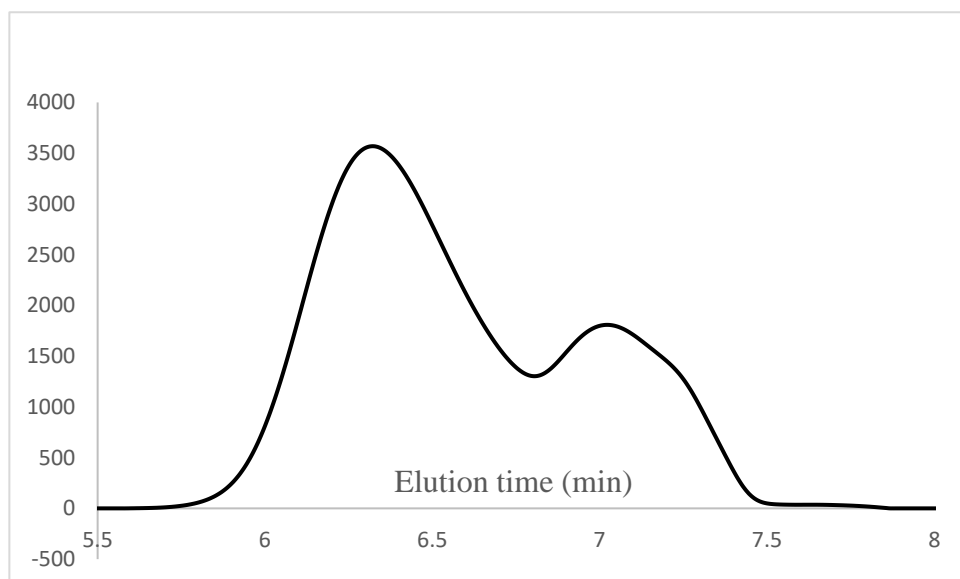


Figure S46. GPC (dRI) trace of PMMA synthesized by MMA/P(4-OCH₃C₆H₅)₃/[Al(mbmp)Me]₂ = 200/1/1 (Table 2, run 5; M_n = 36.8 kg/mol, Đ = 1.9).

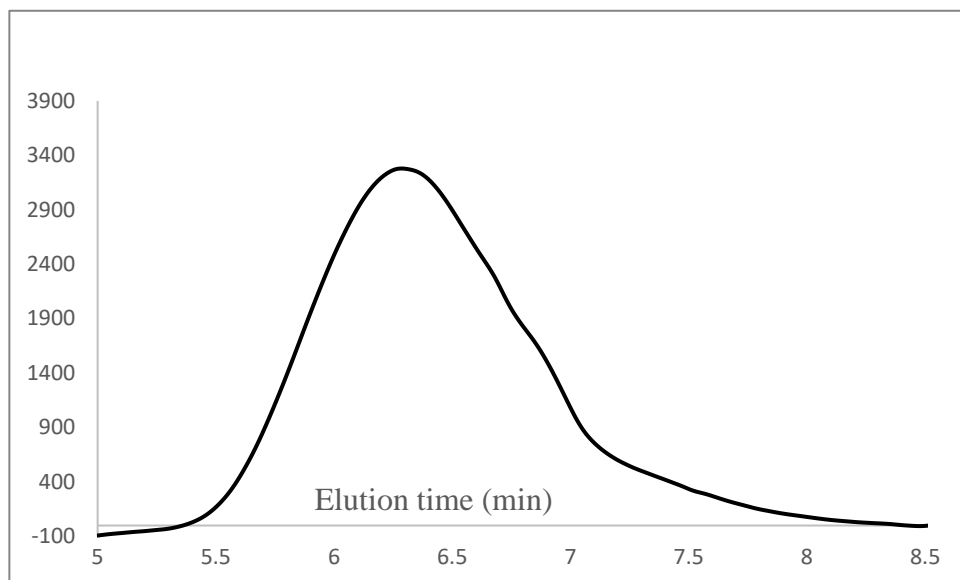


Figure S47. GPC (dRI) trace of PMMA synthesized by MMA/PPh₃/[Al(mbmp)Me]₂ = 200/1/1 (Table 2, run 7; M_n = 45.7 kg/mol, Đ = 2.5).

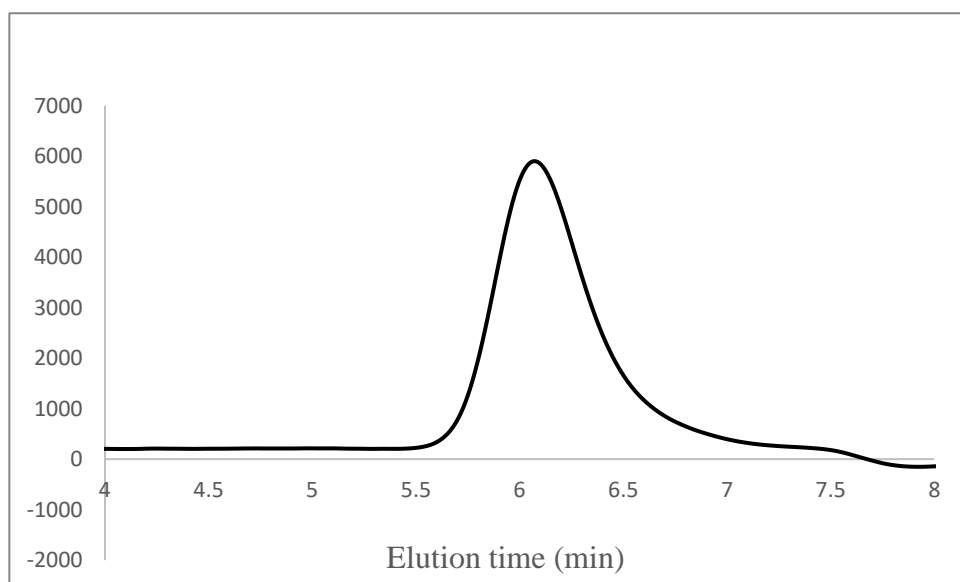


Figure S48. GPC (dRI) trace of PMMA synthesized by MMA/^tBuNHC/[Al(mbmp)Me]₂ = 200/1/1 (Table 2, run 8; M_n = 146 kg/mol, Đ = 1.4).

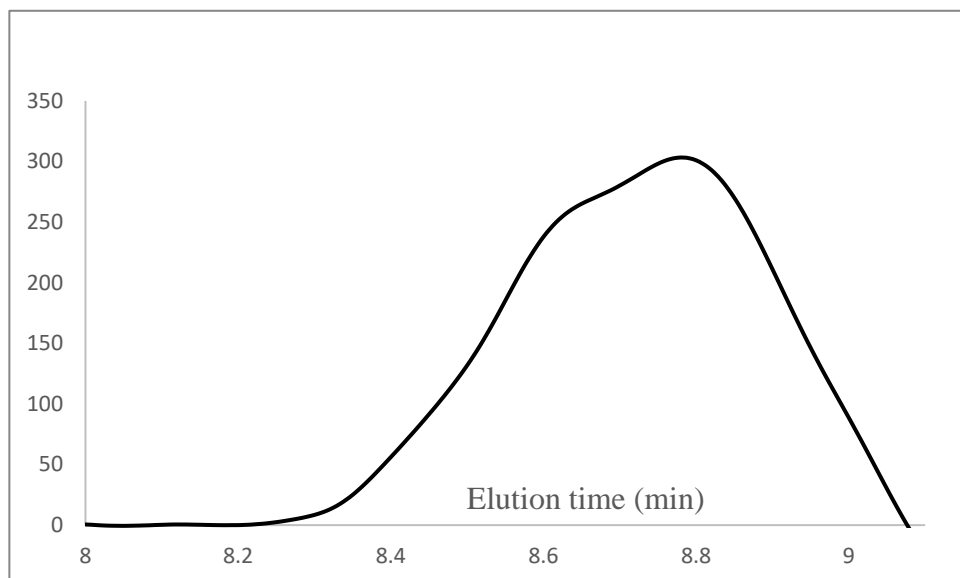


Figure S49. GPC (dRI) trace of PMMA synthesized by MMA/ MesNHC / $[\text{Al}(\text{mbmp})\text{Me}]_2 = 200/1/1$ (Table 2, run 9; $M_n = 0.53$ kg/mol, $\text{Đ} = 1.2$).

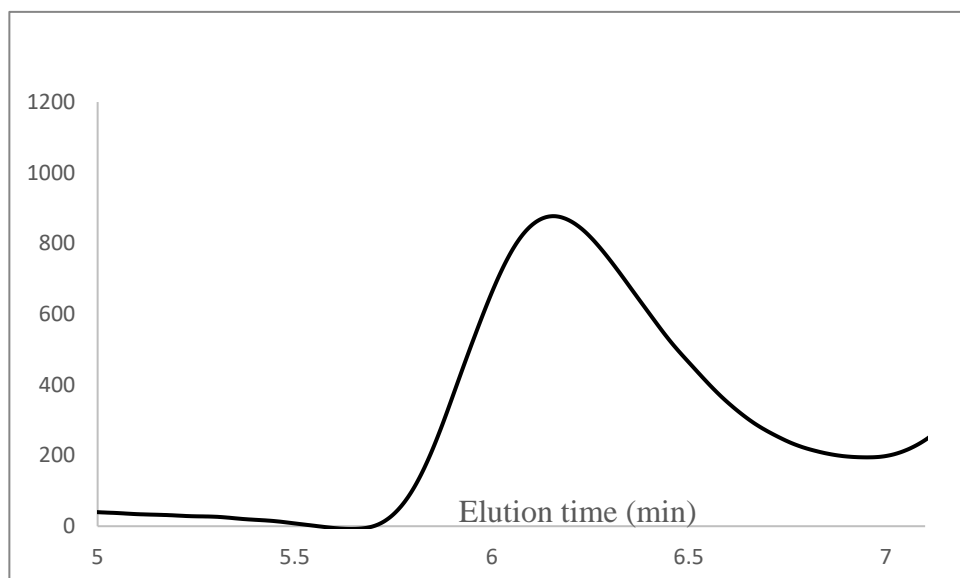


Figure S50. GPC (dRI) trace of PMMA synthesized by MMA/ $\text{PCy}_3/\text{MeAl}(\text{BHT})_2 = 200/1/1$ (SI, Table S4, run 1; $M_n = 40.4$ kg/mol, $\text{Đ} = 2.5$).

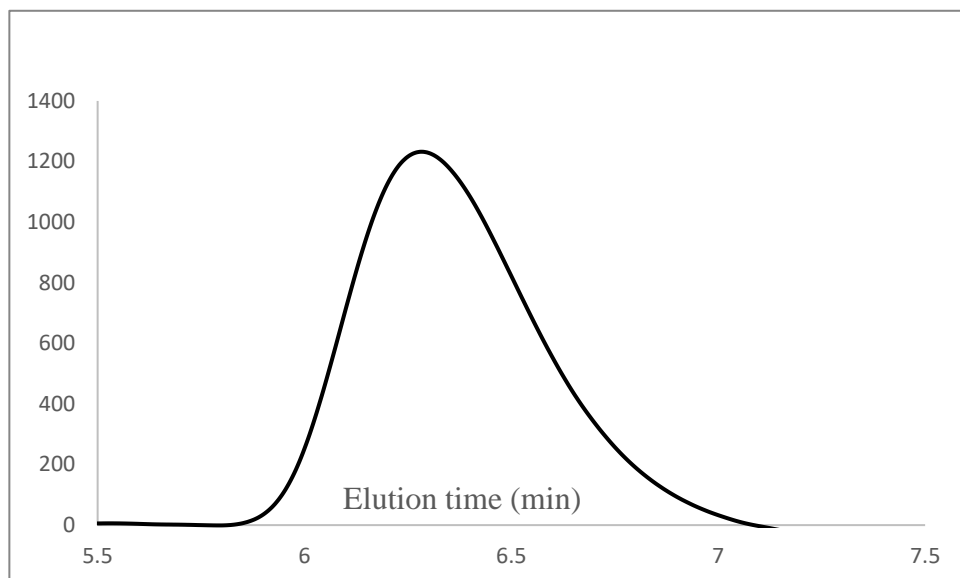


Figure S51. GPC (dRI) trace of PMMA synthesized by MMA/PEt₃/MeAl(BHT)₂ = 200/1/1 (SI, Table S4, run 2; M_n = 68.5 kg/mol, Đ = 1.3).

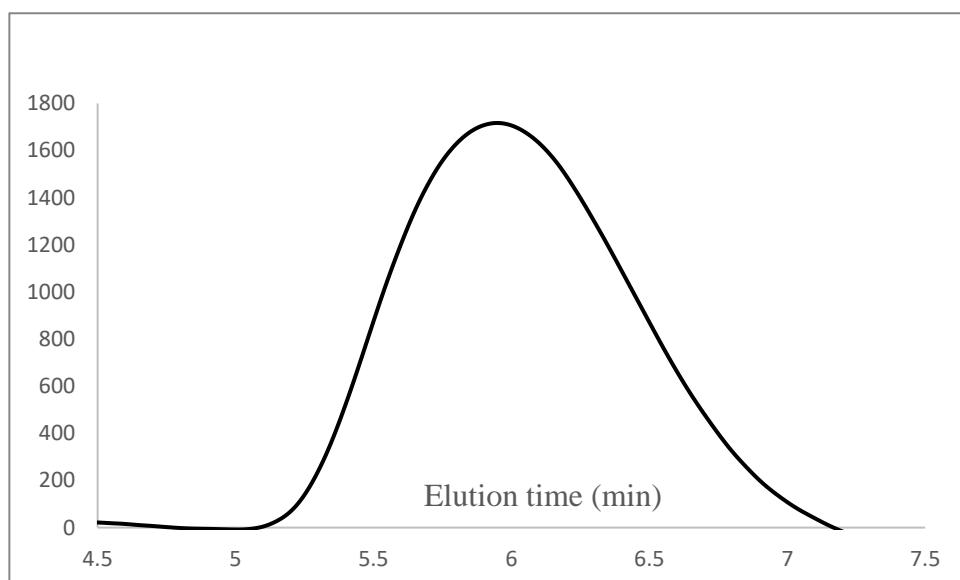


Figure S52. GPC (dRI) trace of PMMA synthesized by MMA/P(4-OCH₃C₆H₅)₃/MeAl(BHT)₂ = 200/1/1 (SI, Table S4, run 3; M_n = 102 kg/mol, Đ = 2.2).

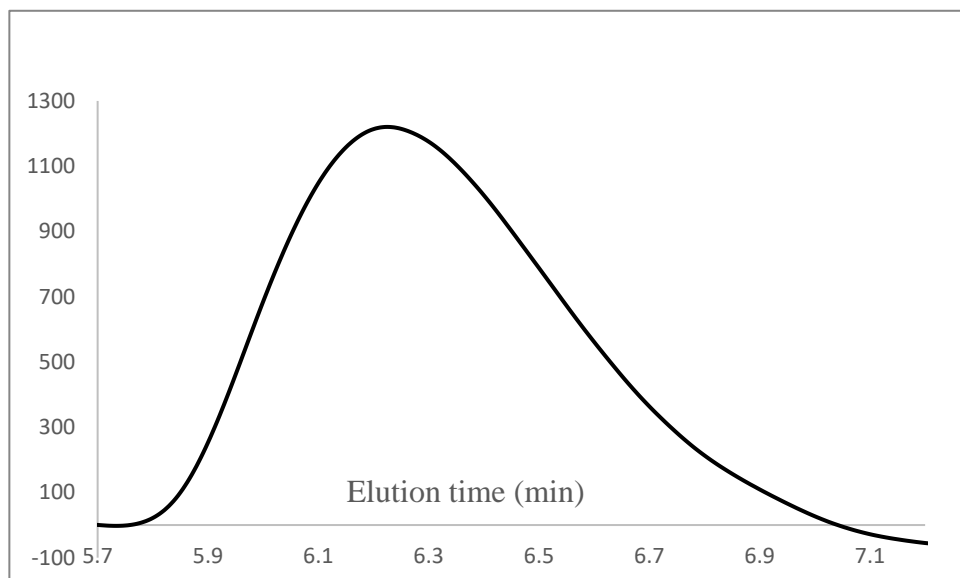


Figure S53. GPC (dRI) trace of PMMA synthesized by MMA/PCy₃/*i*BuAl(BHT)₂ = 200/1/1 (SI, Table S4, run 6; M_n = 76 kg/mol, Đ = 1.3).

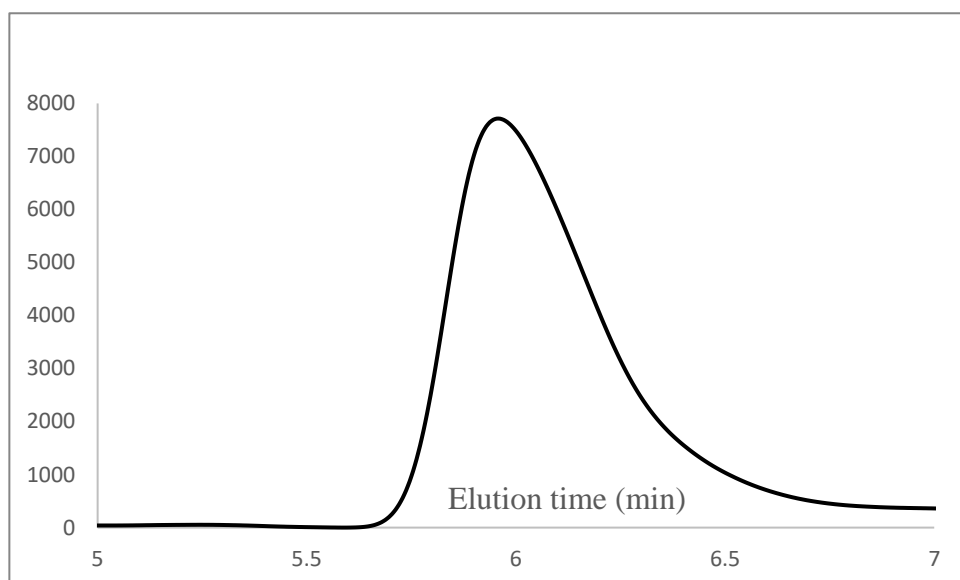


Figure S54. GPC (dRI) trace of PMMA synthesized by MMA/PEt₃/*i*BuAl(BHT)₂ = 200/1/1 (SI, Table S4, run 7; M_n = 103 kg/mol, Đ = 1.6).

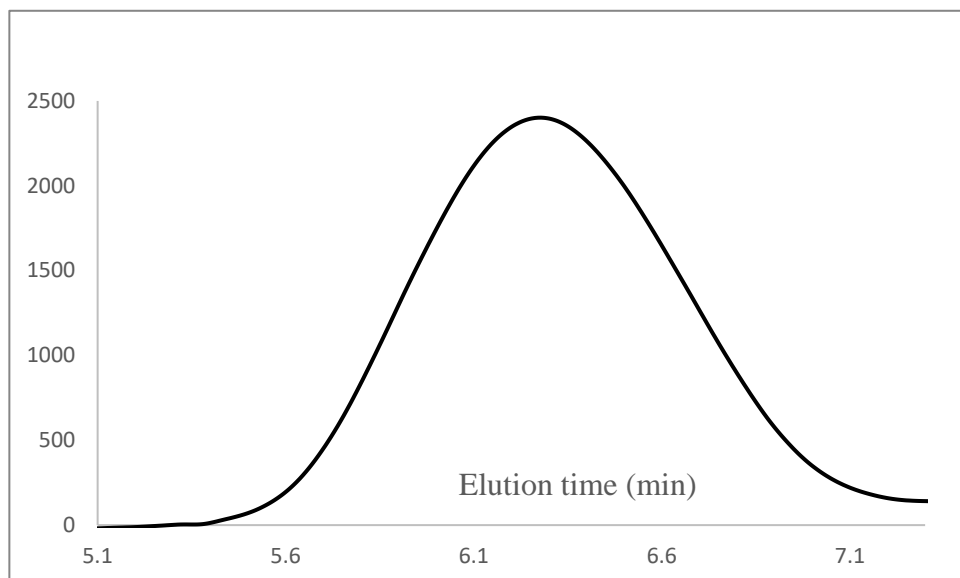


Figure S55. GPC (dRI) trace of PMMA synthesized by MMA/PCy₃^{*i*}Bu₂Al(BHT) = 200/1/1 (SI, Table S4, run 11; M_n = 93 kg/mol, Đ = 1.5).

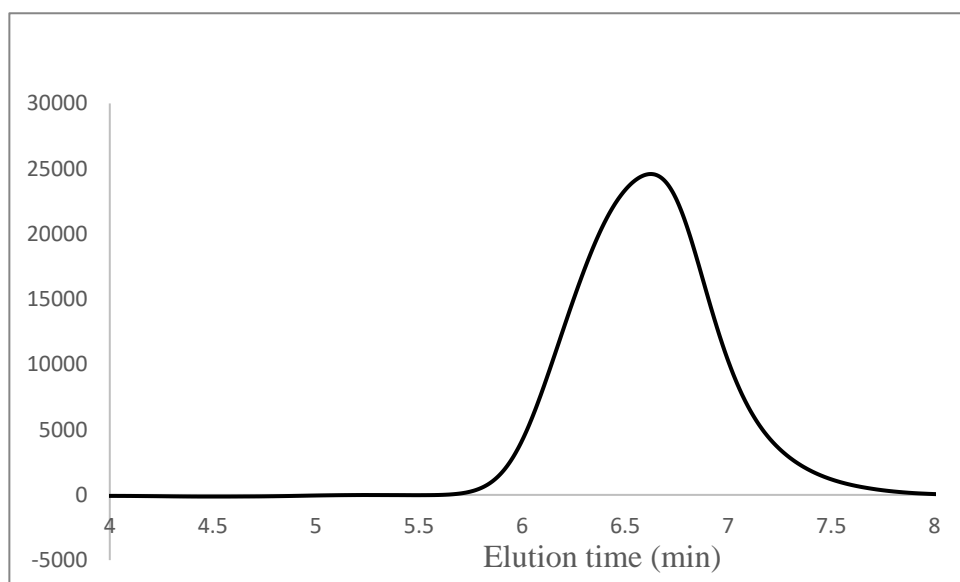


Figure S56. GPC (dRI) trace of PnBA synthesized by nBA/PEt₃/MeAl(BHT)₂ = 200/1/1 (Table 3, run 8; M_n = 93 kg/mol, Đ = 1.7).

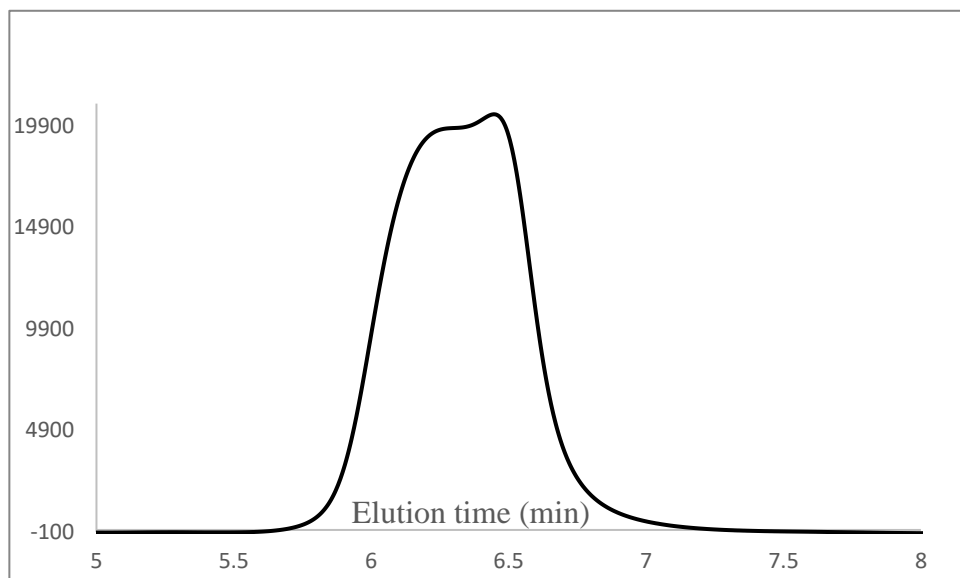


Figure S57. GPC (dRI) trace of PnBA synthesized by nBA/P(4-OCH₃C₆H₅)₃/MeAl(BHT)₂ = 200/1/1 (Table 3, run 9; M_n = 79 kg/mol, Đ = 1.3).

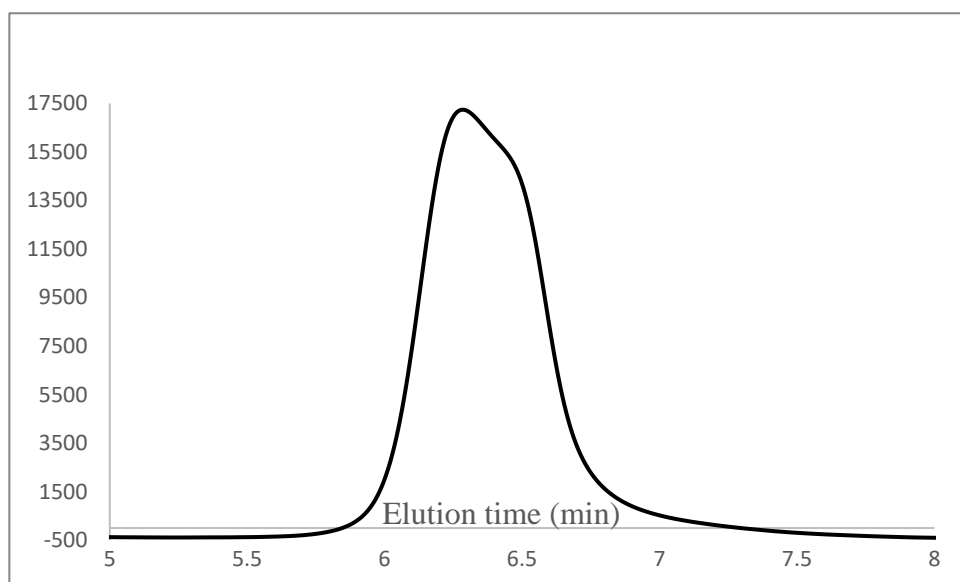


Figure S58. GPC (dRI) trace of PnBA synthesized by nBA/P(4-CH₃C₆H₅)₃/MeAl(BHT)₂ = 200/1/1 (Table 3, run10; M_n = 64 kg/mol, Đ = 1.4).

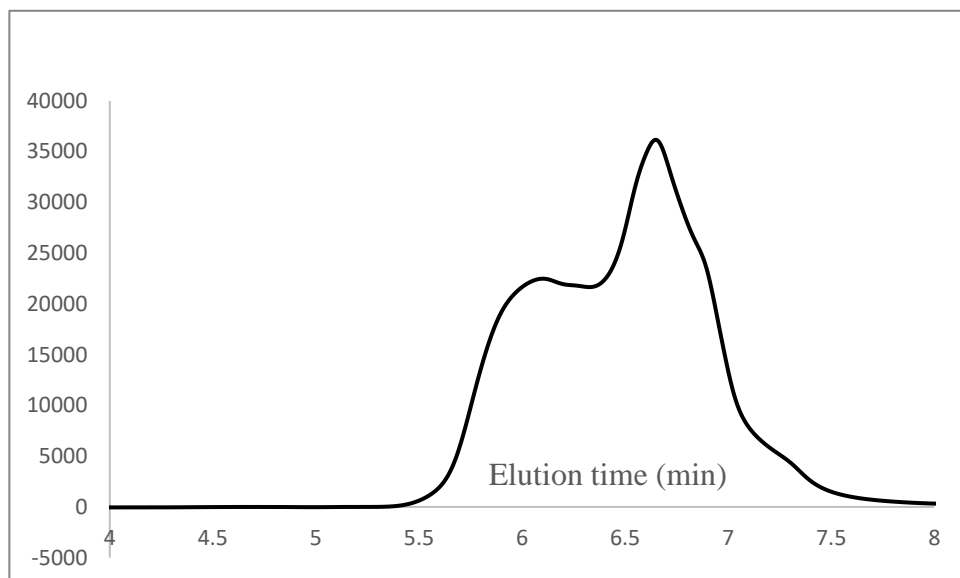


Figure S59. GPC (dRI) trace of PnBA synthesized by nBA/ PPh_3 / $\text{MeAl}(\text{BHT})_2 = 200/1/1$ (Table 3, run11; $M_n = 44 \text{ kg/mol}$, $\text{Đ} = 2.2$).

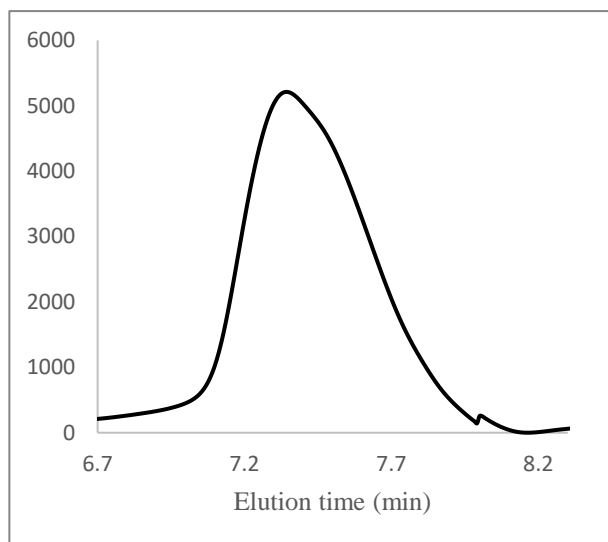


Figure S60. GPC (dRI) trace of PMMA synthesized by MMA/ $\text{P}(\text{Ph})_3(\text{OMe})_9$ / $[\text{Al}(\text{mbmp})\text{Me}]_2 = 200/1/0.5$ (SI, Table S6, run1; $M_n = 7.7 \text{ kg/mol}$, $\text{Đ} = 1.5$).

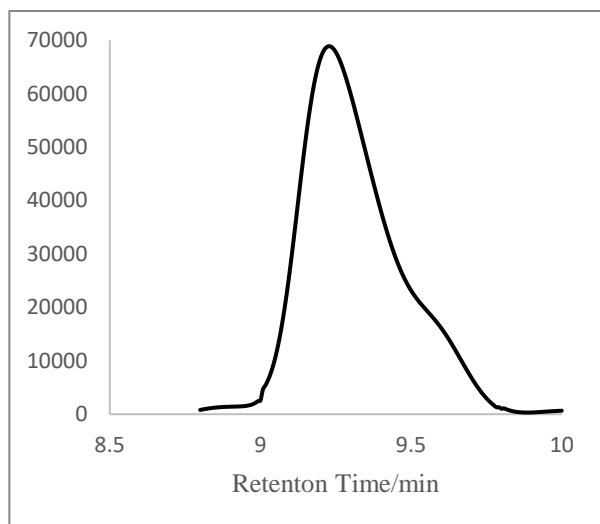


Figure S61. GPC (dRI) trace of PMMA synthesized by MMA/PCy₃/[Al(mbmp)Me]₂ = 200/1/0.5 (SI, Table S6, run2; M_n = 51 kg/mol, Đ = 1.4).

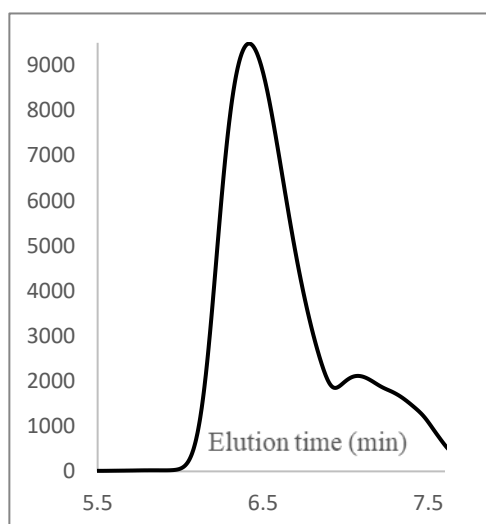


Figure S62. GPC (dRI) trace of PMMA synthesized by MMA/PEt₃/[Al(mbmp)Me]₂ = 200/1/0.5 (SI, Table S6, run3; M_n = 35 kg/mol, Đ = 1.7).

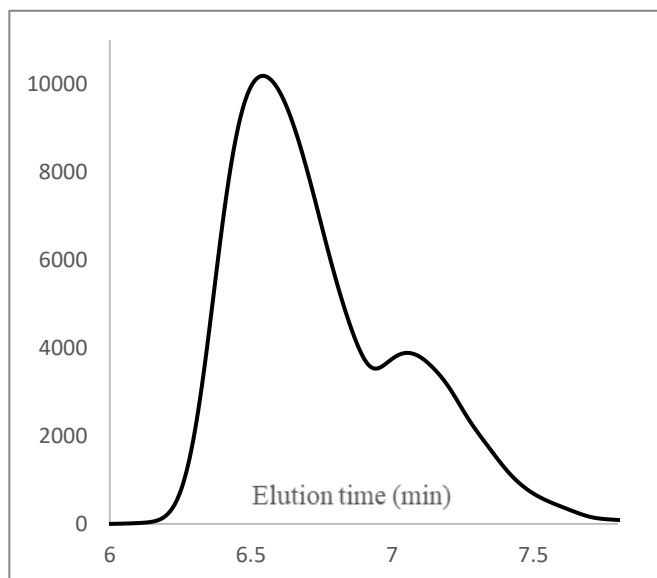


Figure S63. GPC (dRI) trace of PMMA synthesized by MMA/ P (4-OCH₃C₆H₅)₃/[Al(mbmp)Me]₂ = 200/1/0.5 (SI, Table S6, run4; M_n = 28.6 kg/mol, Đ = 1.5).

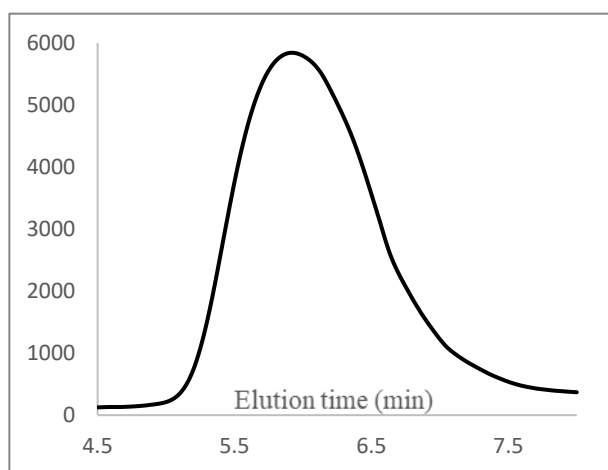


Figure S64. GPC (dRI) trace of PMMA synthesized by MMA/ PPh₃/[Al(mbmp)Me]₂ = 200/1/0.5 (SI, Table S6, run6; M_n = 87.6 kg/mol, Đ = 2.7).

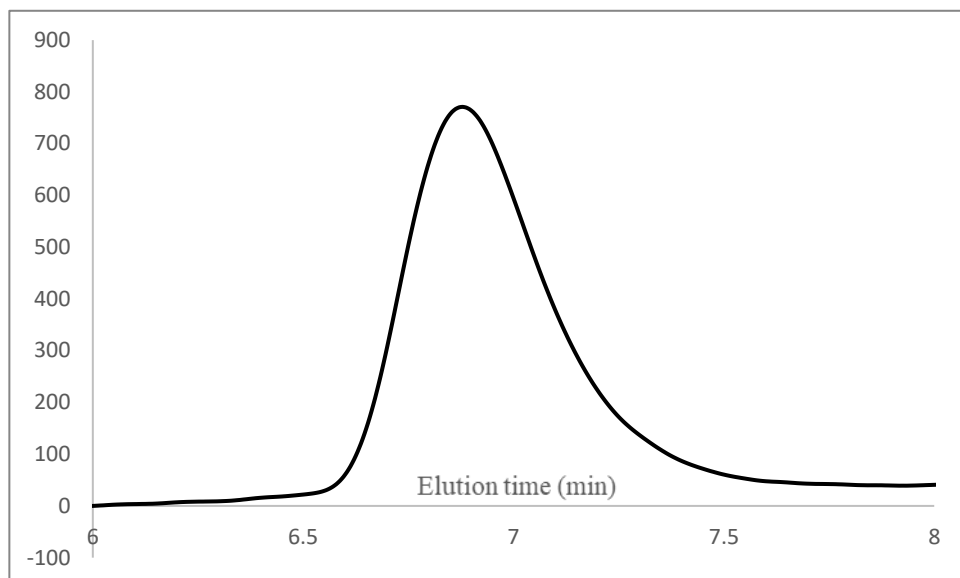


Figure S65. GPC (dRI) trace of PMMA synthesized by MMA/NHO-1/[Al(mbmp)Me]₂ = 200/1/1 (SI, Table S5, run1; M_n = 58 kg/mol, Đ = 1.2).

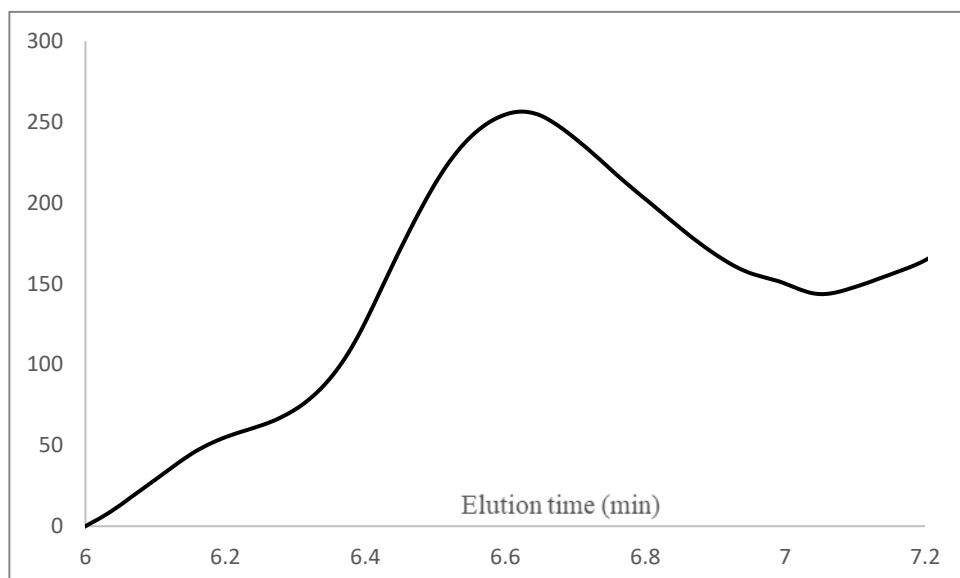


Figure S66. GPC (dRI) trace of PMMA synthesized by MMA/NHO-2/[Al(mbmp)Me]₂ = 200/1/1 (SI, Table S5, run2; M_n = 58 kg/mol, Đ = 1.2).

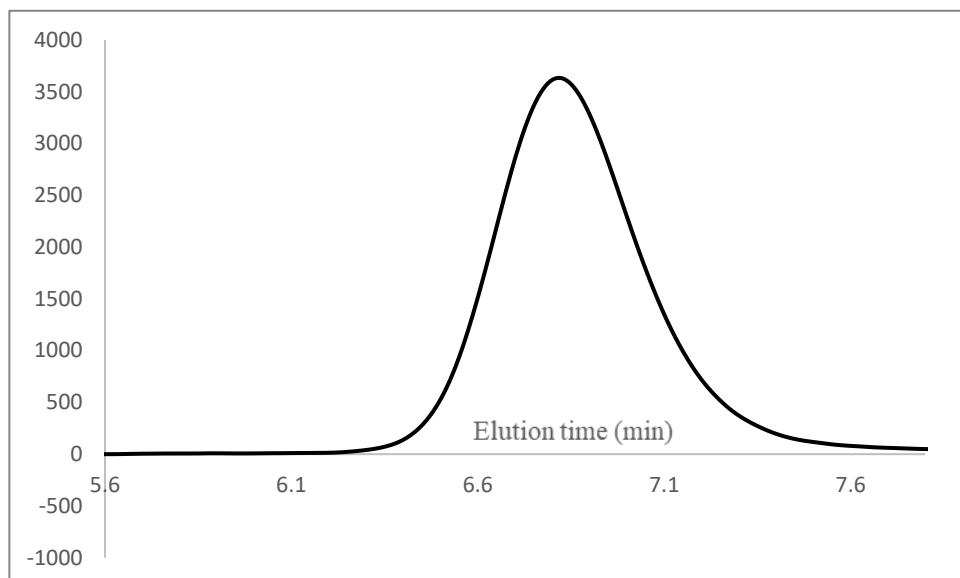


Figure S67. GPC (dRI) trace of PMMA synthesized by MMA/ NHO-1/Al(BHT)₂Me = 200/1/1 (SI, Table S5, run3; $M_n = 33.9$ kg/mol, $\bar{D} = 1.2$).

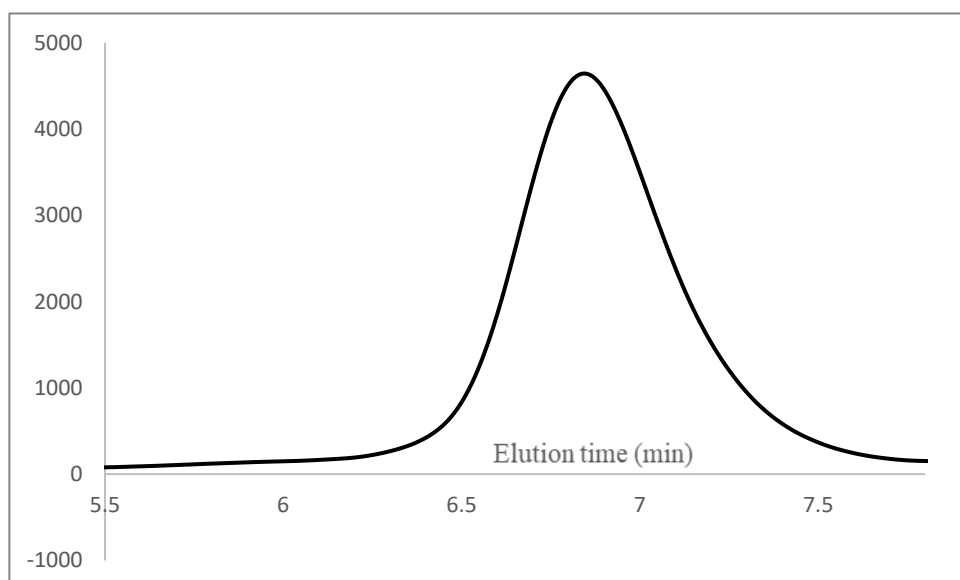


Figure S68. GPC (dRI) trace of PMMA synthesized by MMA/ NHO-2/Al(BHT)₂Me = 200/1/1 (SI, Table S5, run4; $M_n = 27.5$ kg/mol, $\bar{D} = 1.5$).

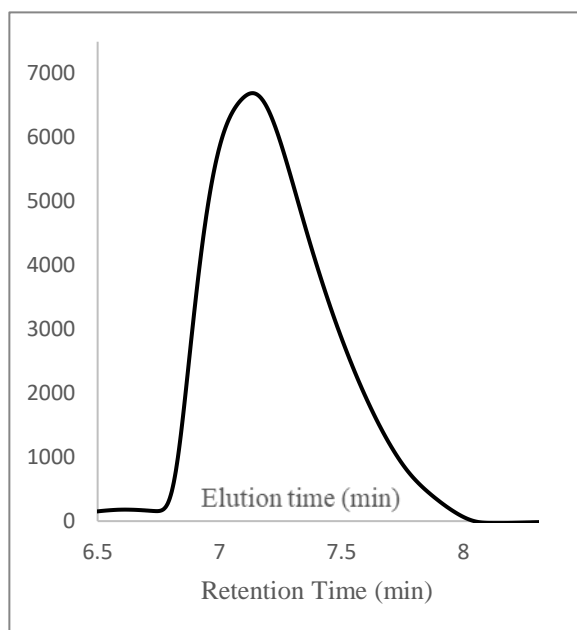


Figure S69. GPC (dRI) trace of PMMA synthesized by MMA/ IAP-3/[Al(mbmp)Me]₂ = 200/1/1 (SI, Table S5, run7; M_n = 11 kg/mol, Đ = 1.3).

References

- [1] (a) E. E. Faingol'd, N. M. Bravaya, A. N. Panin, O. N. Babkina, S. L. Saratovskikh and V. I. Privalov, *J. Appl. Polym. Sci.*, 2016, **133**, 43276-43284. (b) R. A. Stapleton, A. Al-Humydi, J. Chai, B. R. Galan and S. Collins, *Organometallics*, 2006, **25**, 5083-5092.
- [2] (a) S. Naumann, W. Thomas Anthony and P. Dove Andrew, *Angew. Chem. Int. Ed.*, 2015, **54**, 9550-9554. (b) M. A. Wünsche, P. Mehlmann, T. Witteler, F. Buß, P. Rathmann and F. Dielmann, *Angew. Chem. Int. Ed.*, 2015, **54**, 11857-11860.
- [3] (a) Beckett, M. A.; Brassington, D. S.; Coles, S. J.; Hursthouse, M. B. *Inorg. Chem. Commun.* 2000, **3**, 530-533. (b) Heiden, Z. M.; Lathem, A. P. *Organometallics* 2015, **34**, 1818-1827.