Investigation of the Dinuclear Effect of Aluminum Complexes in the Ring-Opening Polymerization of ε-Caporlactone

Chiao-Yin Hsu,[a] Hsi-Ching Tseng,[a] Jaya Kishore Vandavasi,[c] Wei-Yi Lu,[a] Li-Fang Wang,[a] Michael Y. Chiang,[a,b] Yi-Chun Lai,[a] Hsing-Yin Chen,[a]* Hsuan-Ying Chen,[a]*

a Department of Medicinal and Applied Chemistry, Kaohsiung Medical University, Kaohsiung 80708, Taiwan, R.O.C.

b Department of Chemistry, National Chung Hsing University, Taichung 402, Taiwan, R.O.C.

c Department of Chemistry, National Sun Yat-Sen University, Kaohsiung 804, Taiwan, R.O.C.

Electronic supplementary information available: Polymer characterization data, and details of the kinetic study.

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Table S1. The kinetic study of polymerizations of ε-caprolactone using various Al complexes as catalysts

Time/min	L^{N2Bu}-Al_2Me_4	L^{N-NH}-Al_2Me_4	L^{N-NBu}-Al_2Me_4	L^{ClH}-$AlMe_2$	L^{ClBu}-$AlMe_2$	L^{Bu}-$AlMe_2$	L^{Bn}-$AlMe_2$
	Conversion of CL						
10	0.08	0.04		0.04	0.03	0.02	
20	0.33	0.14		0.07	0.05	0.04	
30	0.52	0.23		0.10	0.12	0.07	
40	0.67	0.33		0.12	0.15	0.1	
50	0.76	0.41	0.07	0.18	0.22	0.13	
60	0.80	0.46	0.09	0.22	0.28	0.17	
90	0.88	0.58	-			0.28	
120		0.68	0.20		0.64	0.42	
180		0.77	0.29			0.6	
190					0.82		
205							0.09
210			0.36				
230					0.95		
240			0.41				
270			0.43				
300							0.18
360						0.9	
720				0.99			
1110							0.78
1220							0.81
1330			1.00				
1395		0.95					
1440							0.84
2560							0.97

$k_{obs} \times 10^3$	26.08 (220)	8.54 (49)	2.30 (8)	6.52 (7)	9.79 (43)	6.54 (26)	1.40 (51)
Induction period/min	1.86 (417)	0	20.42 (623)	14.56 (314)	17.96 (377)	25.93 (574)	112 (50)
R^2	0.9827	0.989	0.997	0.999	0.994	0.993	0.997

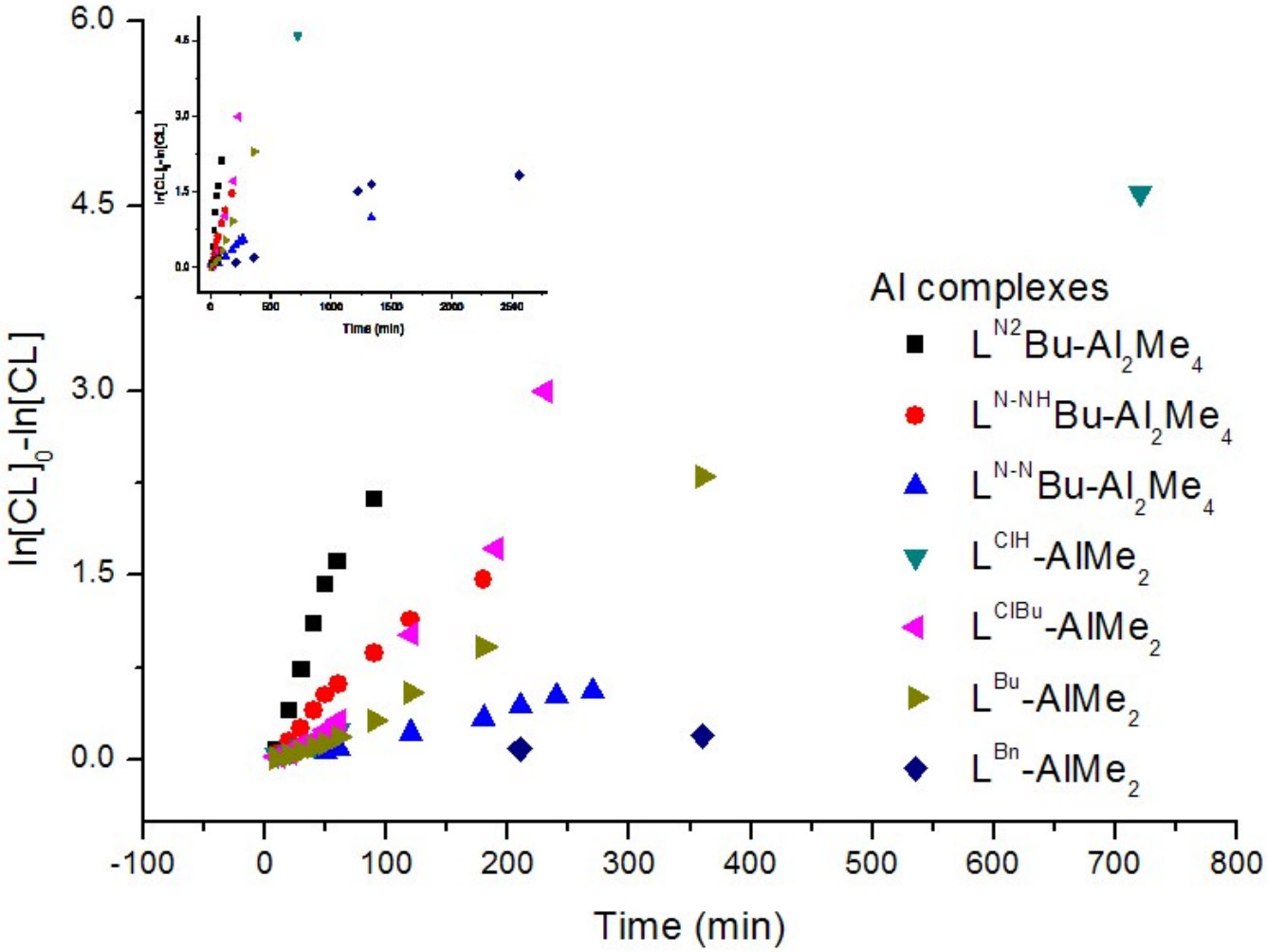

Figure S1. First-order kinetic plots of ε-caprolactone polymerizations with various Al complexes plotted against time (■**L^{N2Bu}-Al_2Me_4,** ●**L^{N-NH}-Al_2Me_4,** ▲**L^{N-NBu}-Al_2Me_4,** ▼**L^{ClH}-$AlMe_2$,** ◄ **L^{ClBu}-$AlMe_2$,** ► **L^{Bu}-$AlMe_2$,** ♦ **L^{Bu}-$AlMe_2$**)

Table S2. The kinetic study of polymerizations of ε-caprolactone using various concentration of **L^{N2Bu}-Al_2Me_4** as a catalyst and BnOH as an initiator

Time (min)	**[L^{N2Bu}-Al_2Me_4]**			
	0.50 M	1.00 M	2.00 M	4.00 M
	Conversion of CL			
1				0.02
3				0.09
4				0.21
5				0.36
6			0.12	0.50
7				0.61
8			0.24	
10		0.08	0.38	0.85
12			0.5	
13				0.9
14			0.61	
16			0.69	0.97
18			0.77	
20	0.05	0.33	0.84	0.99
25			0.88	
30	0.07	0.52	0.97	
40	0.10	0.67		
50	0.12	0.76		

60	0.14	0.80		
90		0.88		
130	0.35			
1000	0.96			
$k_{obs} \times 10^3$	3.24 (2)	26.08 (220)	132.92 (881)	254.14 (1271)
Induction period/min	6.89 (247)	1.86 (417)	6.41 (1.16)	2.70 (52)
R^2	0.999	0.9827	0.983	0.990

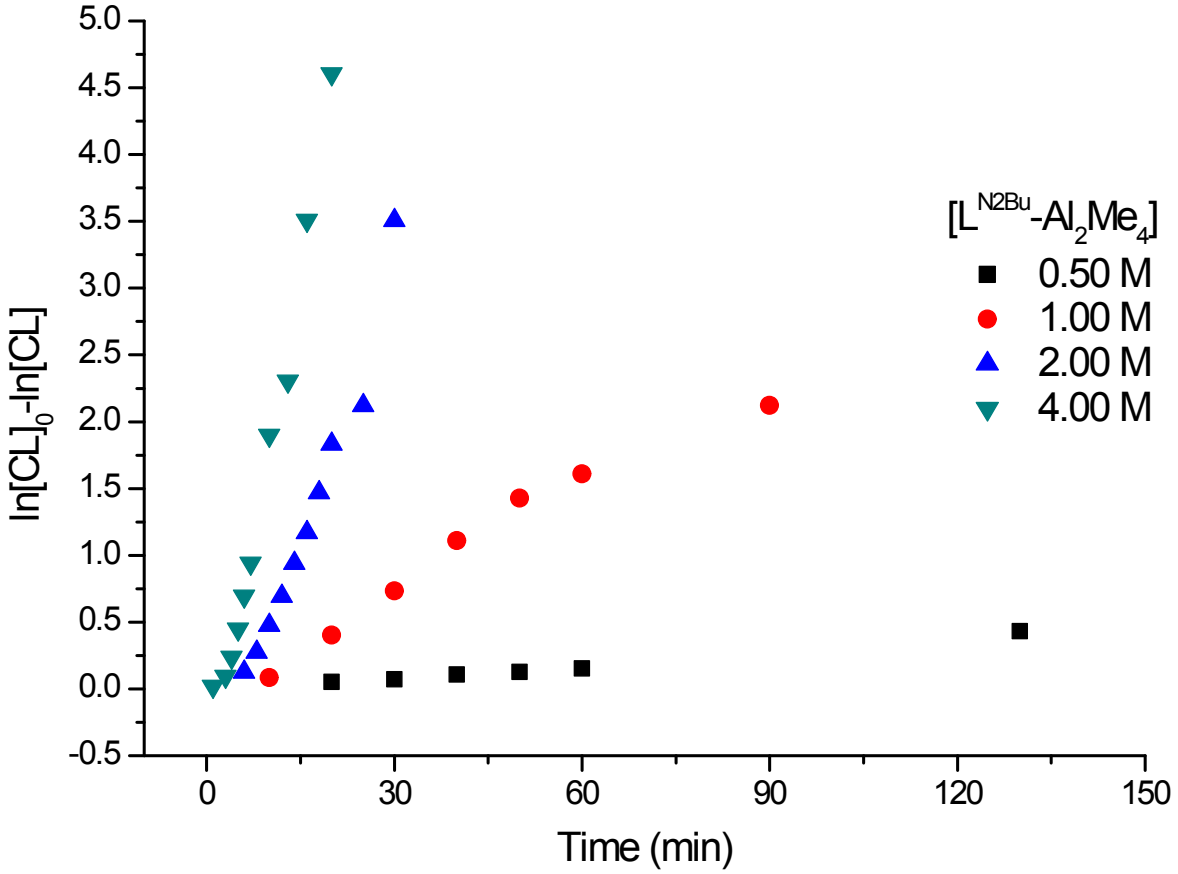

Figure S2. First-order kinetic plots of CL polymerizations with various [$\mathbf{L^{N2Bu}\text{-}Al_2Me_4}$] plotted against time (■ **0.50 M,** ● **1.00 M,** ▲**2.00 M,** ▼**4.00 M**)

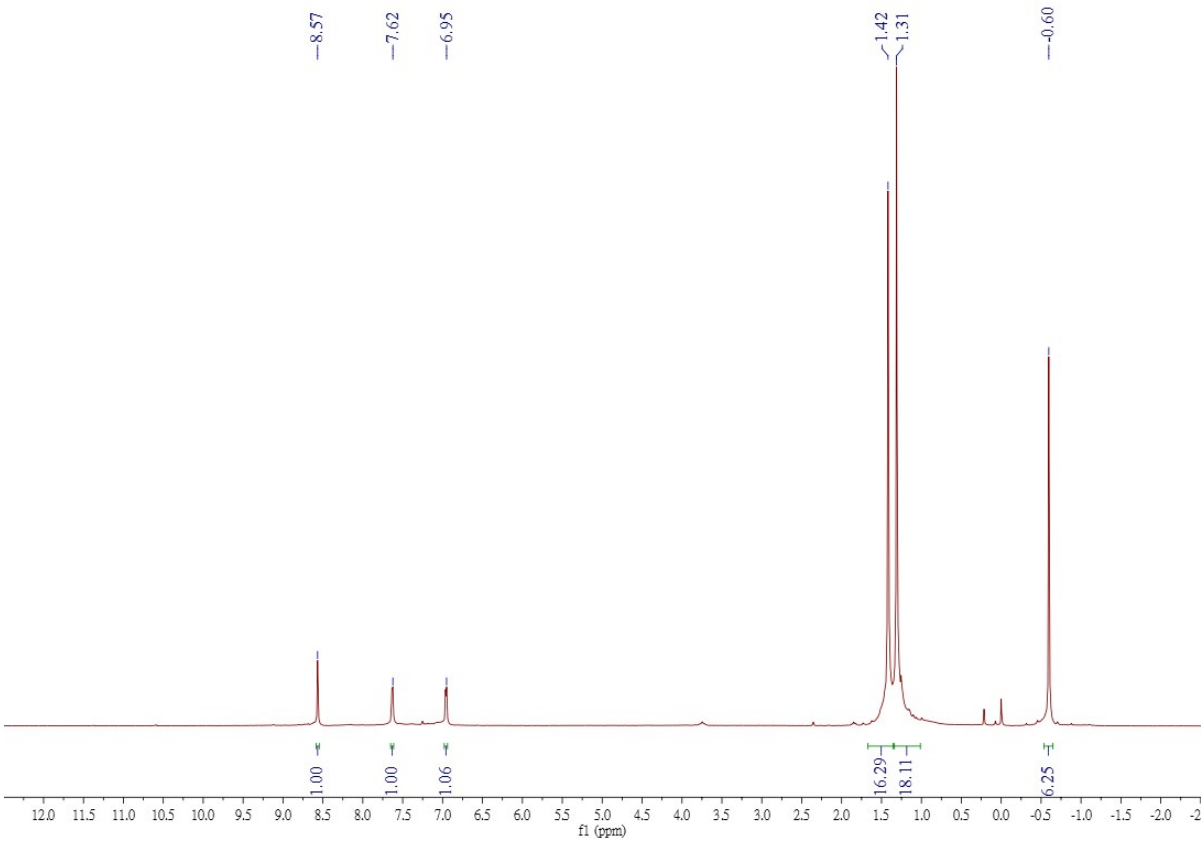

Figure S3. ^{1}H NMR spectrum of $\mathbf{L^{N2Bu}\text{-}Al_2Me_4}$

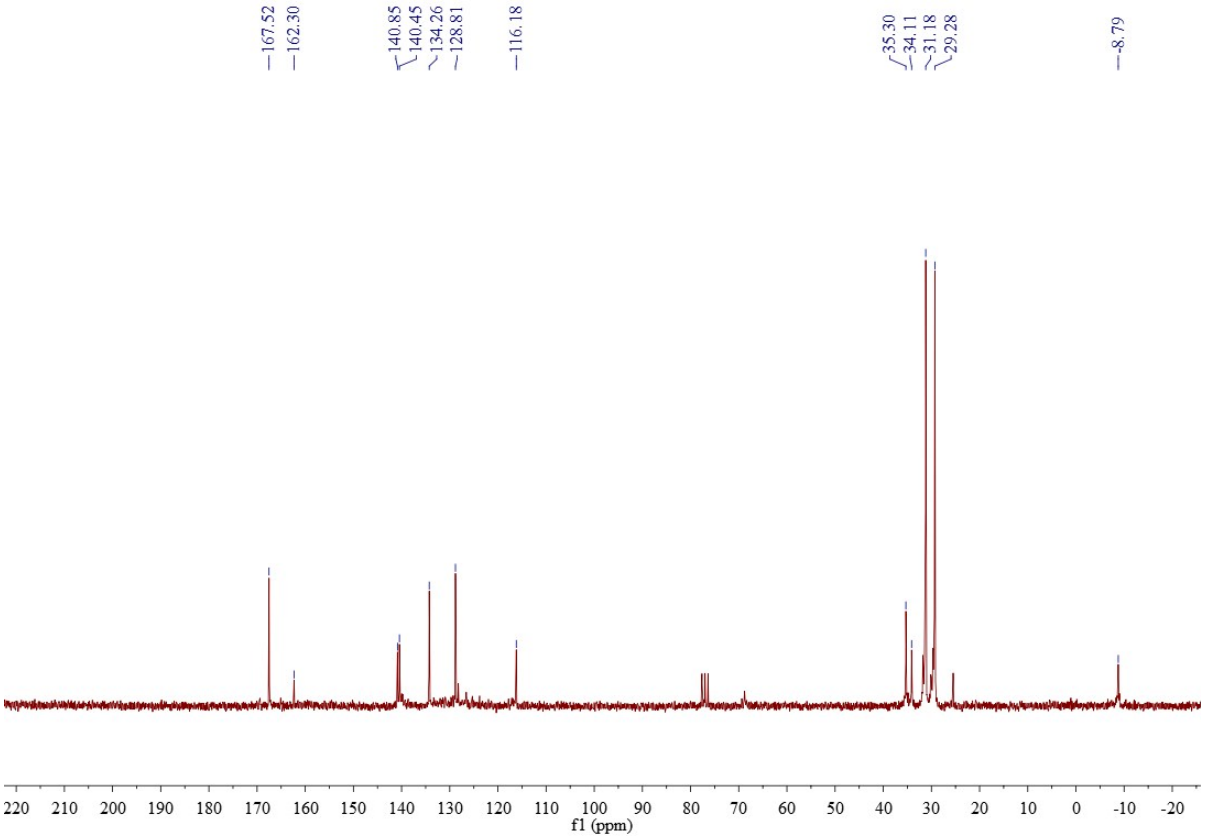

Figure S4. ^{13}C NMR spectrum of $\mathbf{L^{N2Bu}\text{-}Al_2Me_4}$

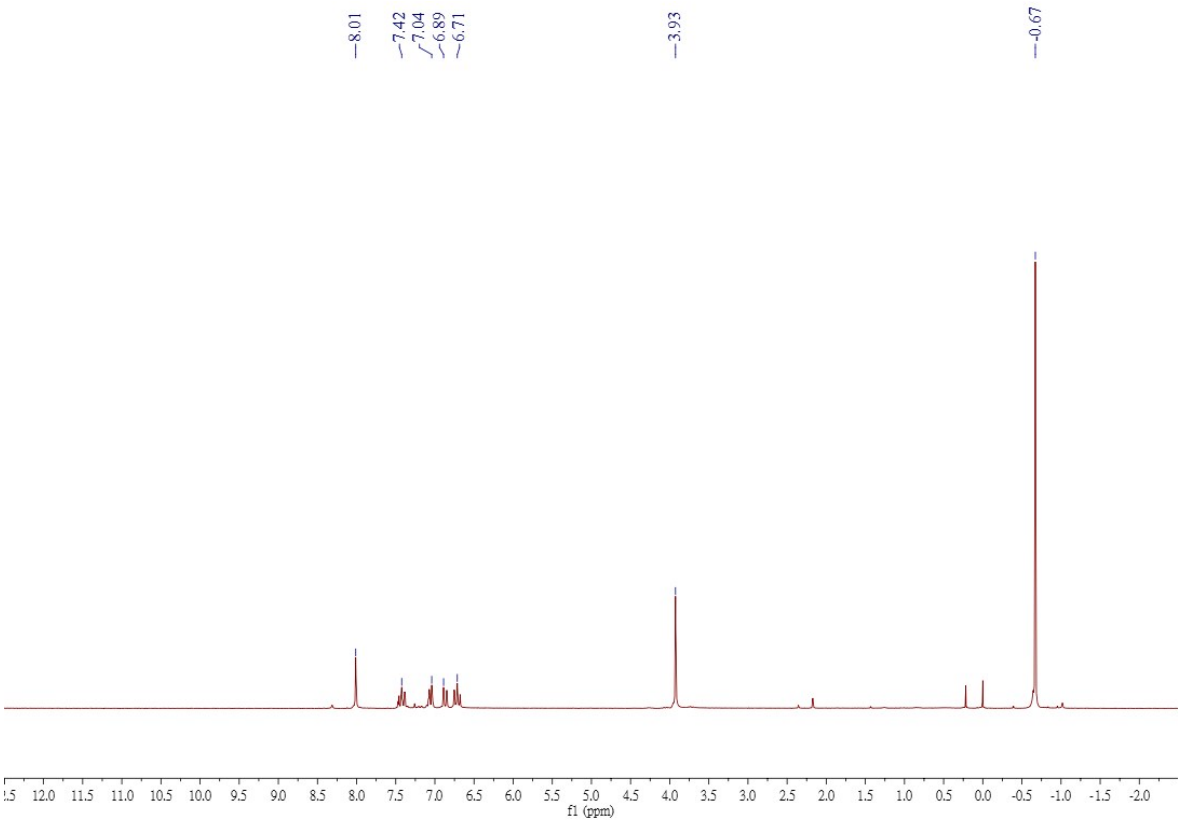

Figure S5. ^{1}H NMR spectrum of $\mathbf{L^{N\text{-}NH}\text{-}Al_2Me_4}$

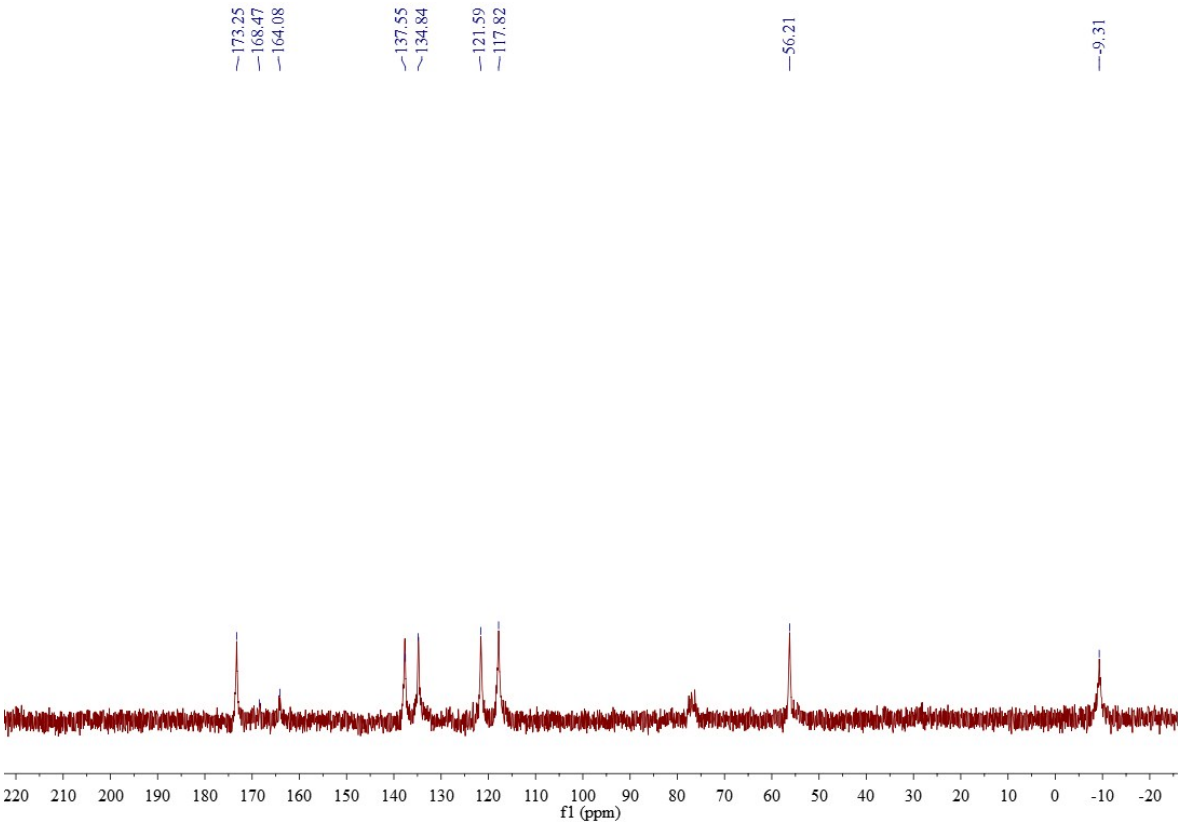

Figure S6. ^{13}C NMR spectrum of $\mathbf{L^{N\text{-}NH}\text{-}Al_2Me_4}$

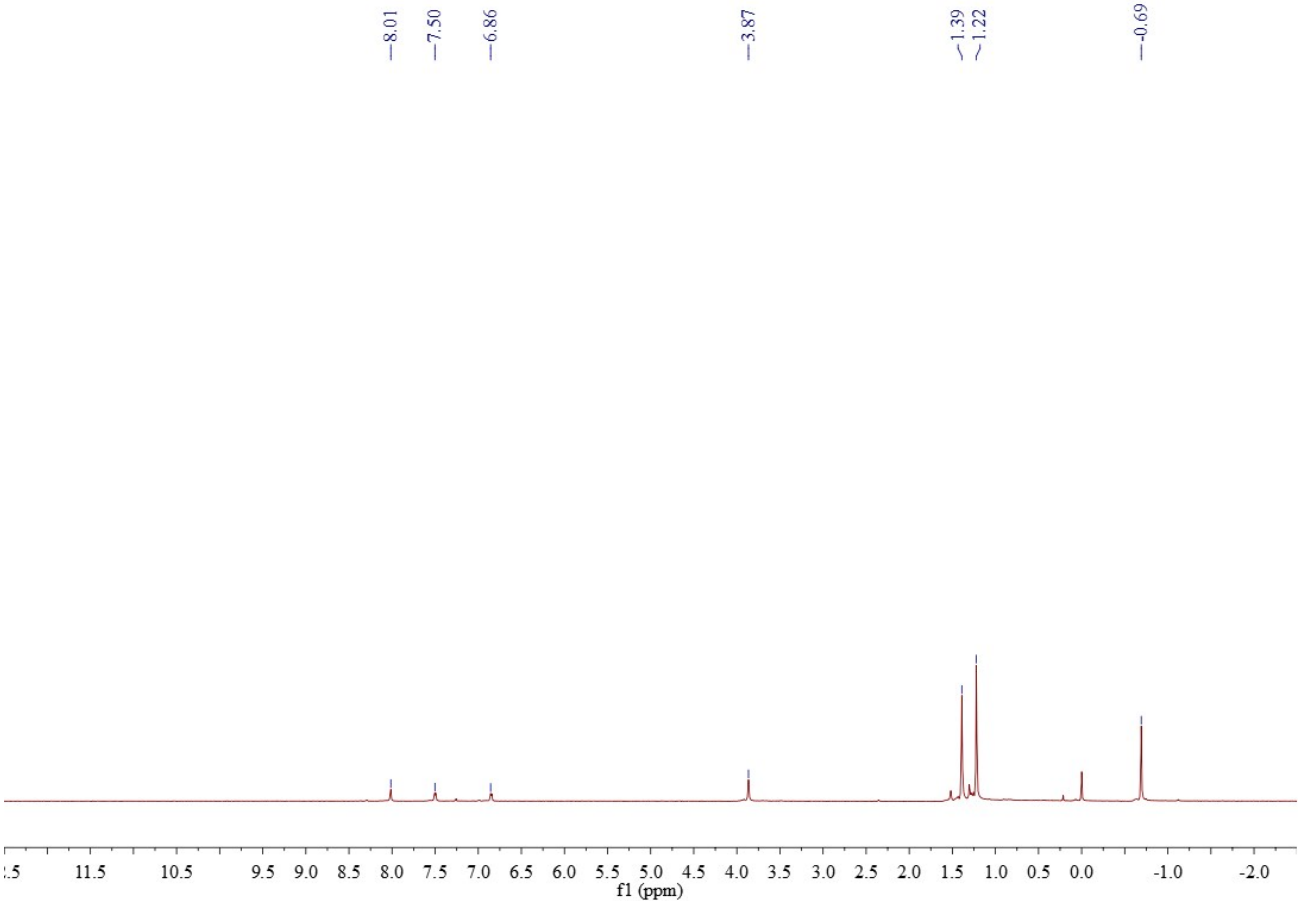

Figure S7. ^{1}H NMR spectrum of $\mathbf{L^{N\text{-}NBu}\text{-}Al_2Me_4}$

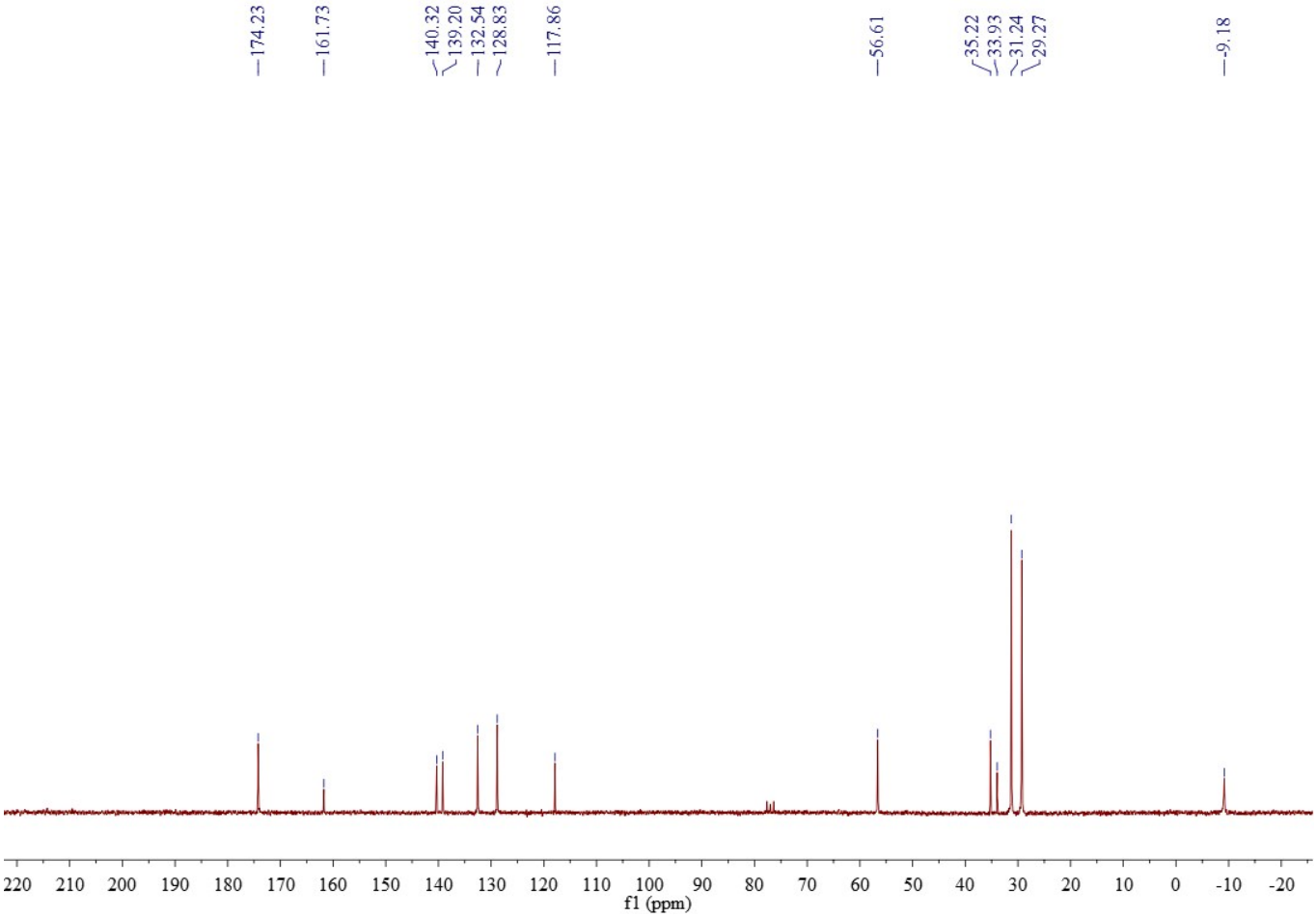

Figure S8. ^{13}C NMR spectrum of $\mathbf{L^{N\text{-}NBu}\text{-}Al_2Me_4}$

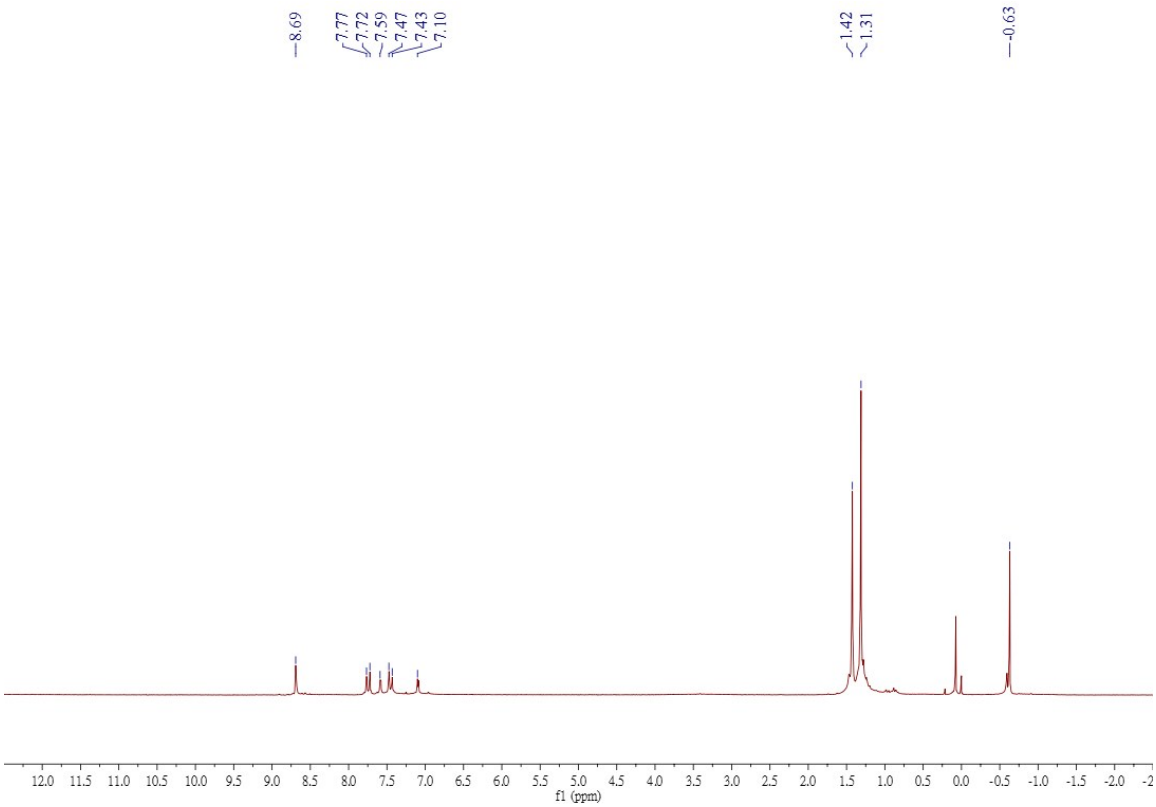

Figure S9. ^{1}H NMR spectrum of $\mathbf{L^{ClH}\text{- }AlMe_2}$

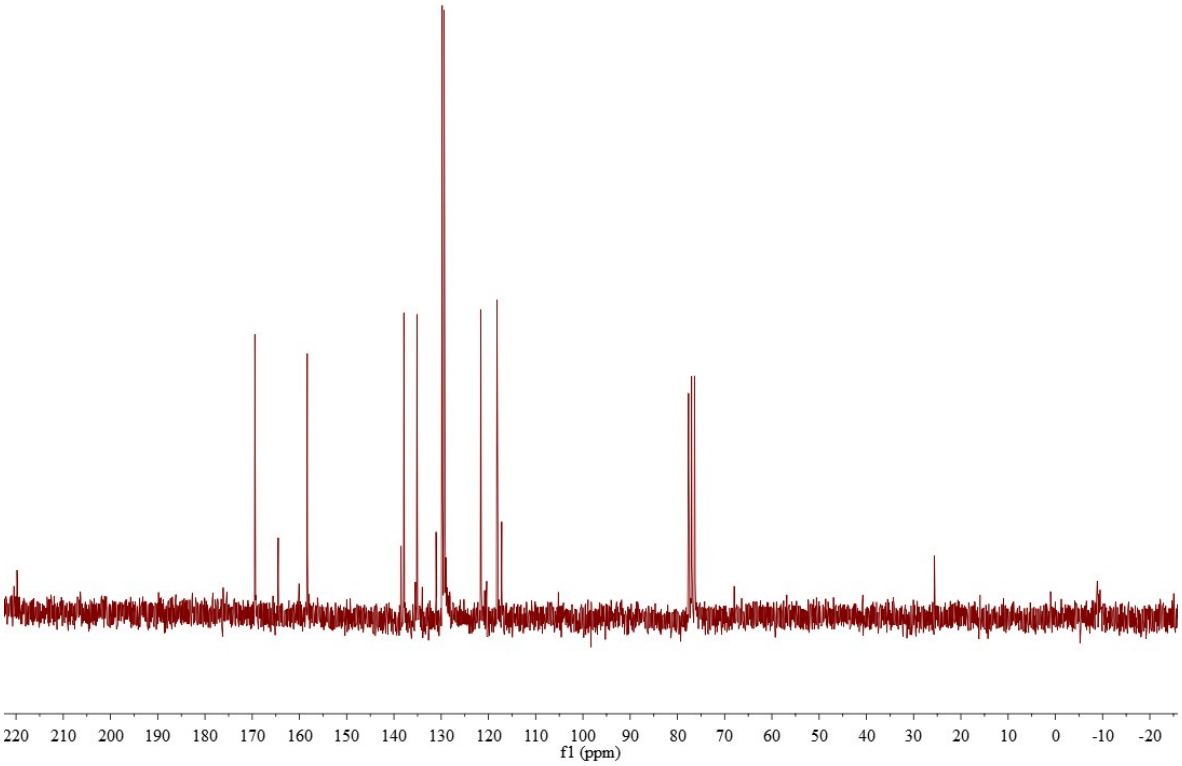

Figure S10. ^{13}C NMR spectrum of $\mathbf{L^{ClH}}$**- AlMe$_2$**

Figure S11. ^{1}H NMR spectrum of $\mathbf{L^{ClBu}}$**- AlMe$_2$**

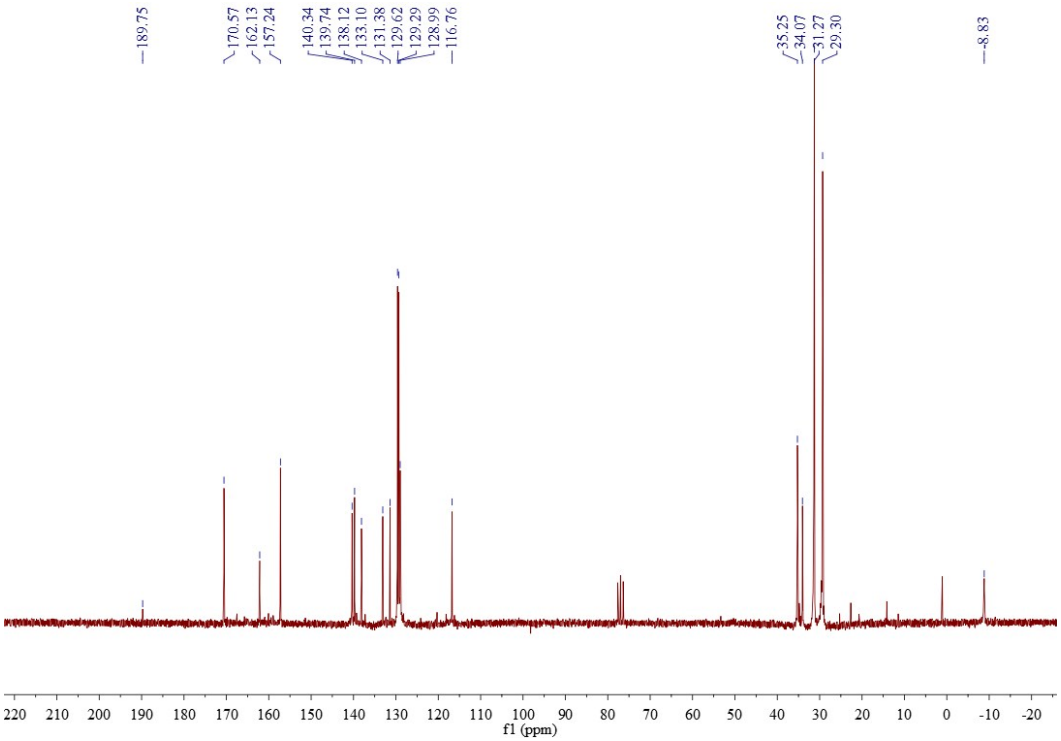

Figure S12. ^{13}C NMR spectrum of $\mathbf{L^{ClBu}}$**- AlMe$_2$**

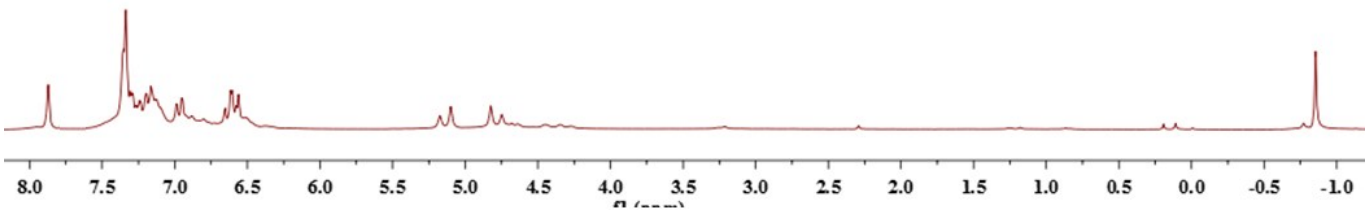

Figure S13. ^{1}H NMR spectrum of $\mathbf{L^{ClBu}}$**- AlMe$_2$**

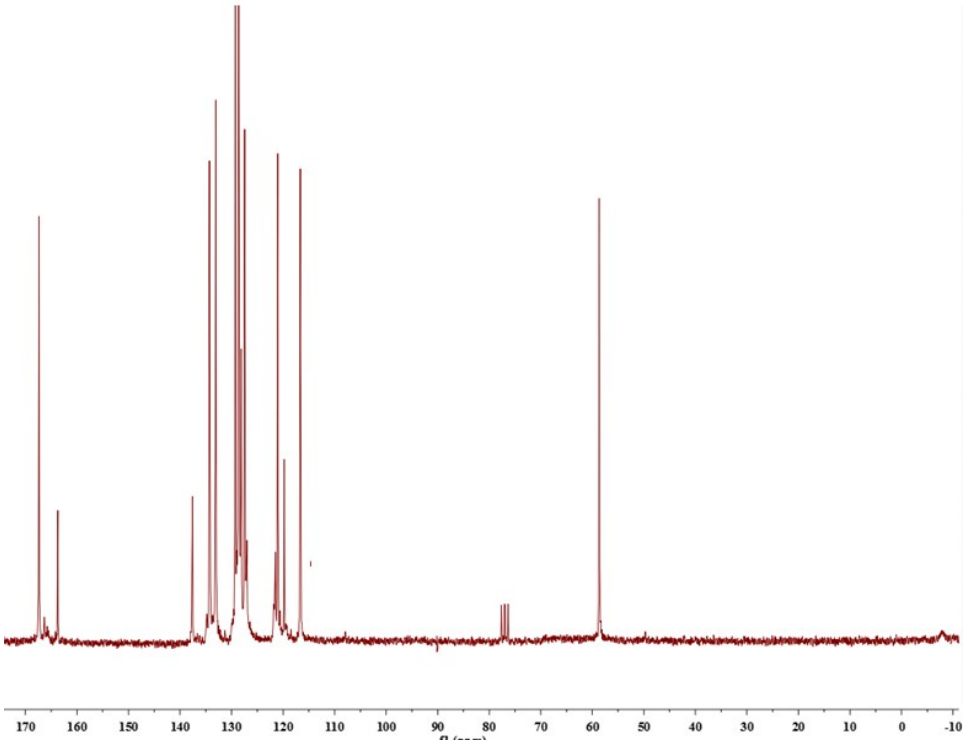

Figure S14. ^{13}C NMR spectrum of $\mathbf{L^{ClBu}}$**- AlMe$_2$**

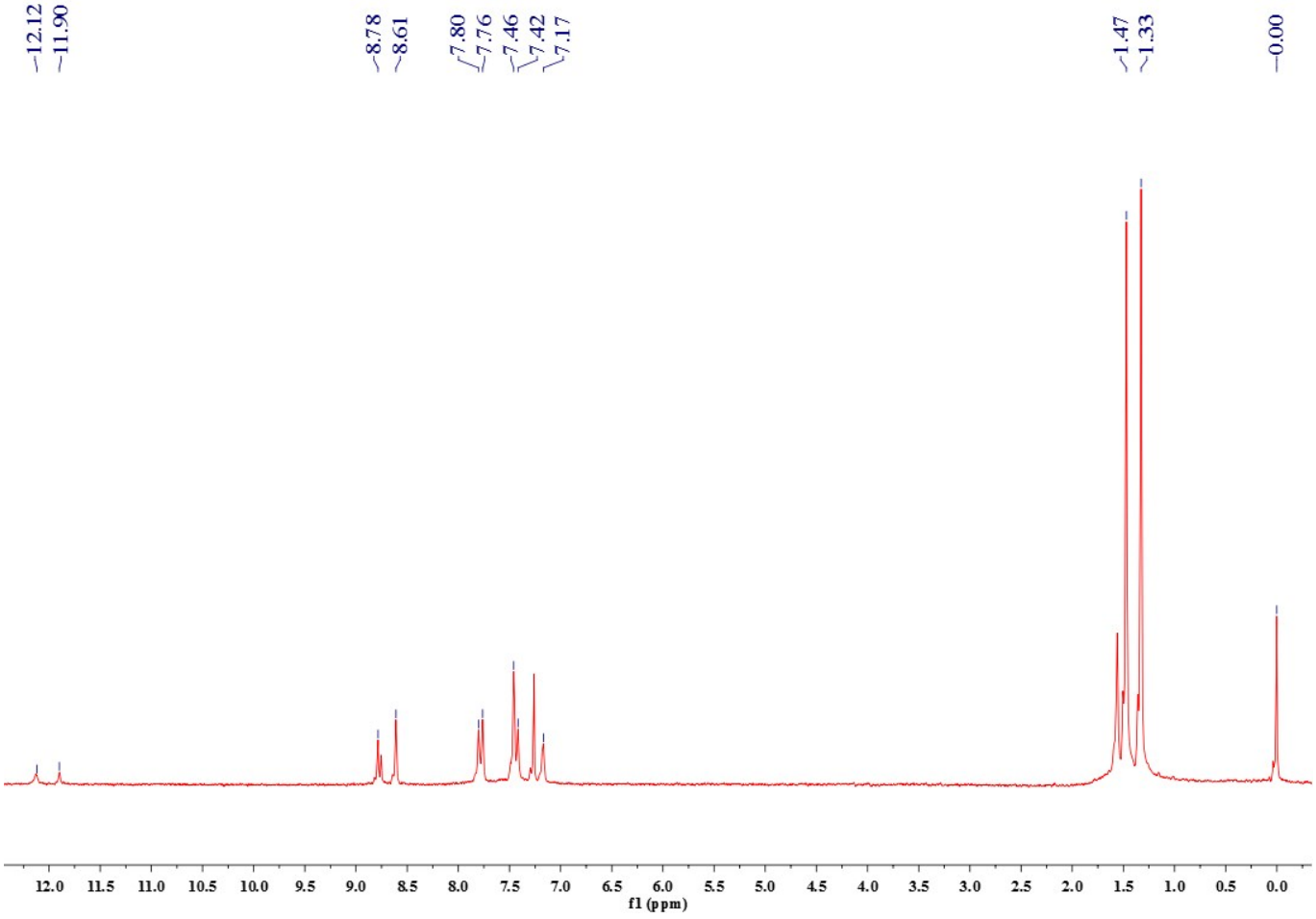

Figure S15. ^{1}H NMR spectrum of $\mathbf{L^{ClBu}}$**- H**

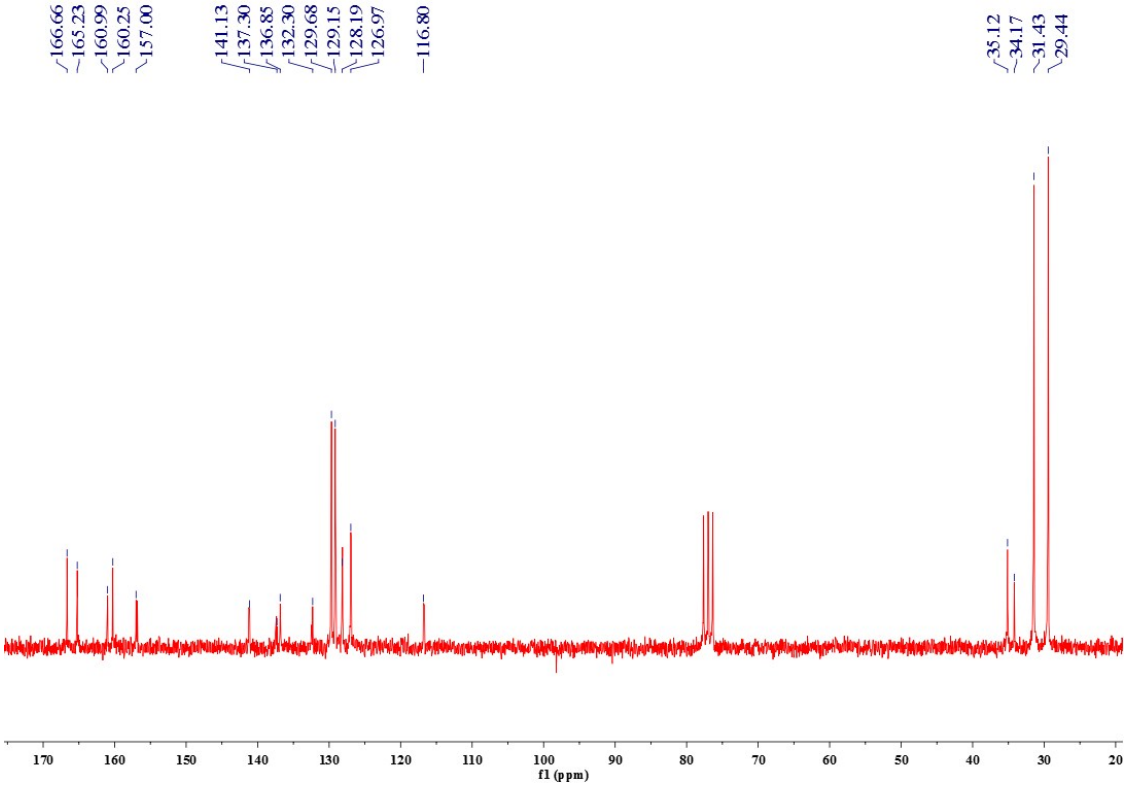

Figure S16. ^{13}C NMR spectrum of $\mathbf{L^{ClBu}\text{-}H}$

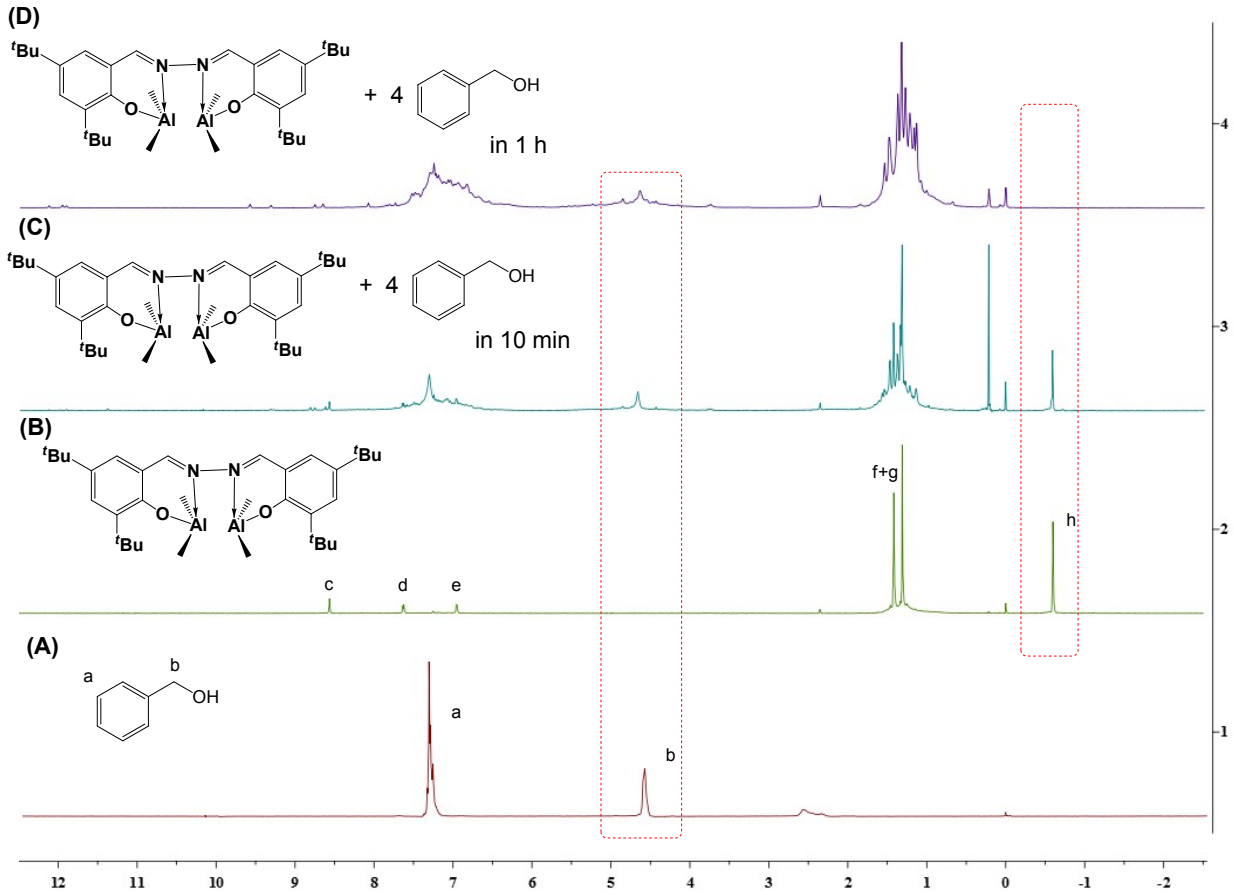

Figure S17. 1H NMR spectra of (A) benzyl alcohol; (B) $\mathbf{L^{N2Bu}\text{-}Al_2Me_4}$; (C) the mixture of benzyl alcohol and $\mathbf{L^{N2Bu}\text{-}Al_2Me_4}$ (4:1) in $CDCl_3$ after 10 min; (D) the mixture of benzyl alcohol and $\mathbf{L^{N2Bu}\text{-}Al_2Me_4}$ (4:1) in $CDCl_3$ after 1 h.