A Closer Look on ε-Captolactone Polymerization Catalyzed by Alkyl Aluminum Complexes: The Effect of Induction Period on Overall Catalytic Activity

Hsi-Ching Tseng,[a] Michael Y. Chiang,[a,b] Wei-Yi Lu,[a] Yen-Jen Chen,[a] Cheng-Jie Lian,[a] Yu-Hsieh Chen,[a] Hsin-Yi Tsai,[a] Yi-Chun Lai,[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 Sun Yat-sen University, Kaohsiung, Taiwan, 80424, R.O.C.*

Electronic Supplementary Information Available: Polymer characterization data, and details of the kinetic study.

Table of Contents

$L^{H5}AlMe_2$		$L^{F5}AlMe_2$		$L^{o\text{-}F}AlMe_2$		$L^{p\text{-}F}AlMe_2$		$L^{Cl3}AlMe_2$		$L^{Br3}AlMe_2$	
Time (min)	Conv. (%)	Time (min)	Conv. (%)	Time (min)	Conv. (%)	Time (min)	Conv. (%)	Time (min)	Conv. (%)	Time (min)	Conv. (%)
40	20	20	18	70	22	20	10	20	18	25	26
65	30	32	42	100	29	40	20	35	40	35	50
80	35	40	56	120	39	61	34	40	60	40	61
120	47	80	80	170	55	80	42	58	72	50	72
180	59			200	60	108	51	68	82	70	88
200	64			240	70	150	68	88	89		
240	68					180	74				
k_{obs} = 0.005		k_{obs} = 0.023		k_{obs} = 0.006		k_{obs} = 0.008		k_{obs} = 0.031		k_{obs} = 0.037	
R = 0.998		R = 0.993		R = 0.996		R = 0.998		R = 0.992		R = 0.974	
SD = 0.025		SD = 0.086		SD = 0.036		SD = 0.034		SD = 0.104		SD = 0.177	

$L^{p\text{-}Cl}AlMe_2$		$L^{p\text{-}NO2}AlMe_2$		$L^{p\text{-}OMe}AlMe_2$		$L^{Me3}AlMe_2$		$L^{iPr}AlMe_2$		$L^{Bn}AlMe_2$	
Time (min)	Conv. (%)	Time (min)	Conv. (%)	Time (min)	Conv. (%)	Time (min)	Conv. (%)	Time (min)	Conv. (%)	Time (min)	Conv. (%)
20	7	40	29	40	15	10	10	10	11	40	7
40	14	60	40	65	24	15	26	15	21	70	25
60	23	95	60	80	27	20	40	20	42	100	48
80	34	150	75	120	37	26	55	26	53	170	77
120	48			200	51	35	71	35	72	210	81
180	66					40	75	40	75		
						55	88	55	87		
k_{obs} = 0.06		k_{obs} = 0.010		k_{obs} = 0.003		k_{obs} = 0.045		k_{obs} = 0.044		k_{obs} = 0.010	
R = 0.998		R = 0.998		R = 0.998		R = 0.999		R = 0.997		R = 0.993	
SD = 0.029		SD = 0.372		SD = 0.014		SD = 0.029		SD = 0.057		SD = 0.094	

$L^{THF}AlMe_2$		$L^{Py}AlMe_2$		$L^{NMe2}AlMe_2$		$L^{iPr2}AlMe_2$	
Time (min)	Conv. (%)	Time (min)	Conv. (%)	Time (min)	Conv. (%)	Time (min)	Conv. (%)
10	5	40	11	40	11	10	14
25	9	70	19	70	21	11	19
45	13	100	26	140	34	13	30
75	22	140	33	170	38	16	43
120	27	210	46	210	44	19	54
240	46	330	62	330	57	22	65
300	58					30	78
$k_{obs} = 0.003$		$k_{obs} = 0.003$		$k_{obs} = 0.002$		$k_{obs} = 0.067$	
R = 0.994		R = 0.999		R = 0.997		R = 0.998	
SD = 0.034		SD = 0.068		SD = 0.023		SD = 0.032	

Table 1 Kinetic study of CL polymerization with various Al complexes in toluene 5 mL, [CL] = 2.0 M at room temperature

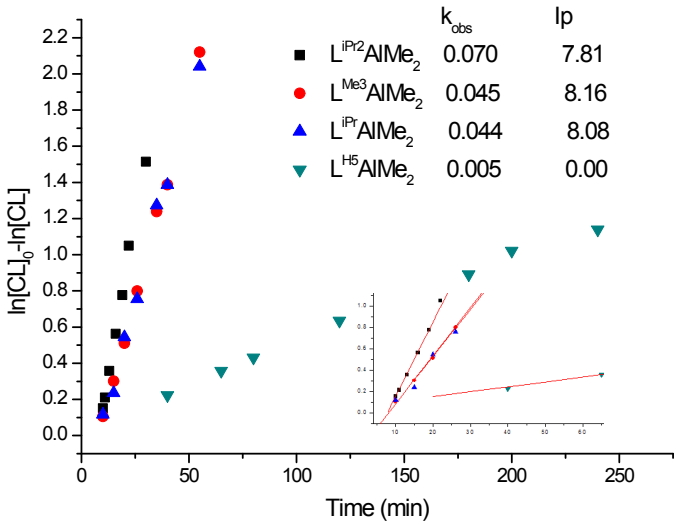


Figure S1 First-order kinetic plots for CL polymerizations with time with various Al complexes (steric effect)

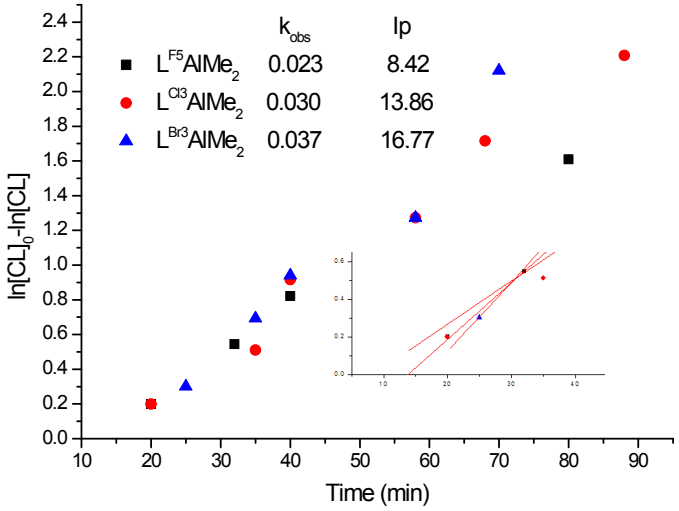


Figure S2 First-order kinetic plots for CL polymerizations with time with various Al complexes (steric and electronic effect)

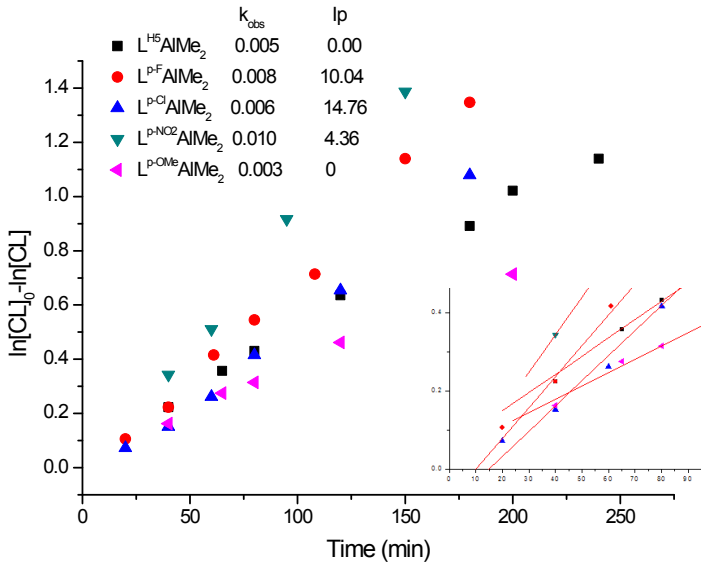


Figure S3 First-order kinetic plots for CL polymerizations with time with various Al complexes (electronic effect)

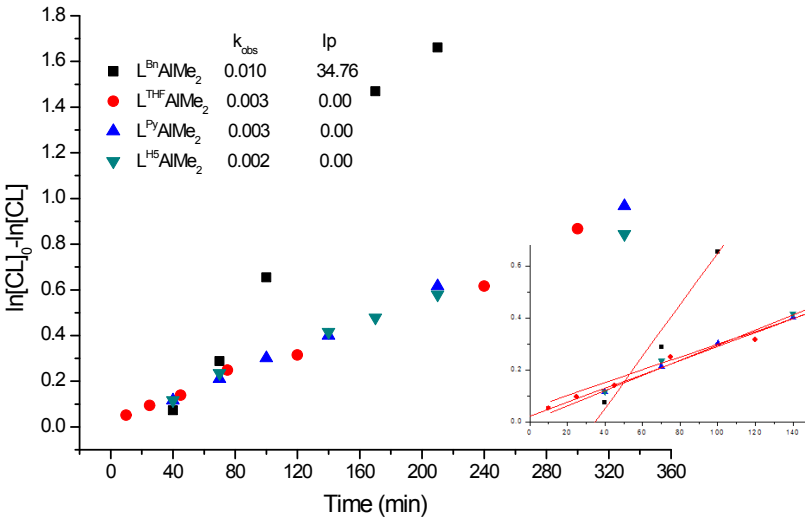


Figure S4 First-order kinetic plots for CL polymerizations with time with various Al complexes (chelating effect)

Table S2 The variations of [CL][a] in ROP process with a wide range of LiPr2AlMe$_2$ + 2 BnOH in toluene 5 mL, [CL] = 2.0 M atroom temperature.

[Al]/[BnOH]/[CL]							
0.5:1:100		**1:2:100**		**1.25:2.5:100**		**1.75:3.5:100**	
Time (min)	Conv. (%)	Time (min)	Conv. (%)	Time (min)	Conv. (%)	Time (min)	Conv. (%)
19	0.22	10	0.14	10	0.21	8	0.24
25	0.37	11	0.19	12	0.32	11	0.51
35	0.54	13	0.3	16	0.49	16	0.74
45	0.65	16	0.43	20	0.69	20	0.85
60	0.75	19	0.54				
		22	0.65				
		30	0.78				
		40	0.88				
k_{obs}							
0.0277		0.0664		0.0920		0.1339	
R and SD							
0.996, 0.047		0.998, 0.041		0.990, 0.071		0.999, 0.021	

[a] Obtained from ^{1}H NMR analysis.

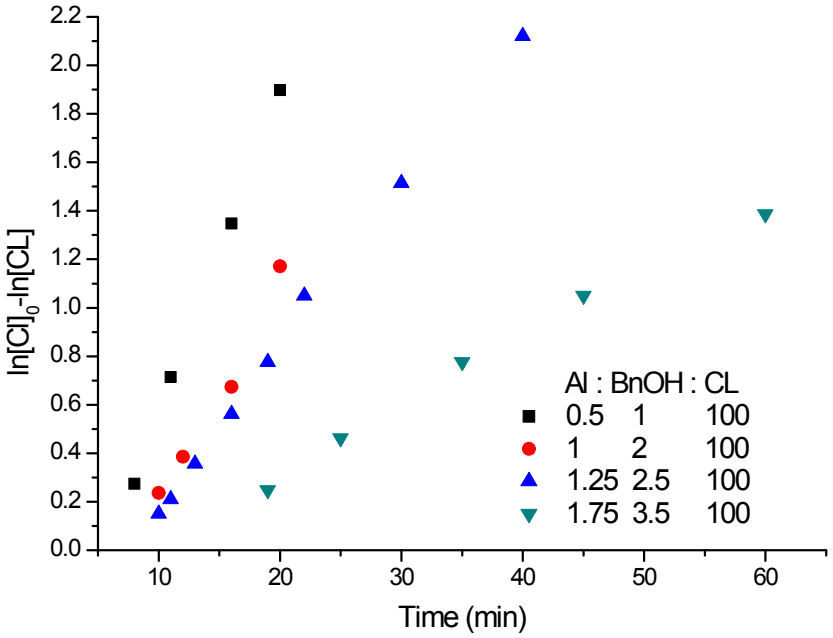


Figure S5 First-order kinetic plots for CL polymerizations with time in toluene (5 mL) with different concentration of [$L^{iPr2}AlMe_2$ + 2 BnOH]

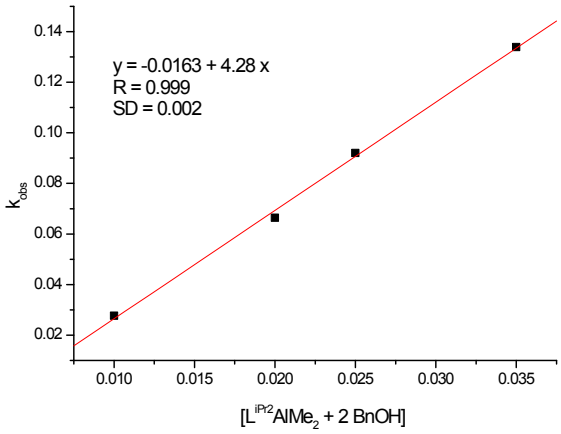


Figure S6 Linear plot of k_{obs} vs [$L^{iPr2}AlMe_2$ + 2 BnOH] for the polymerization of CL with [CL] = 2.0 M in toluene (5 mL) at room temperature.

Figure S7 ^{1}H and ^{13}C NMR spectrum of $L^{H5}AlMe_2$

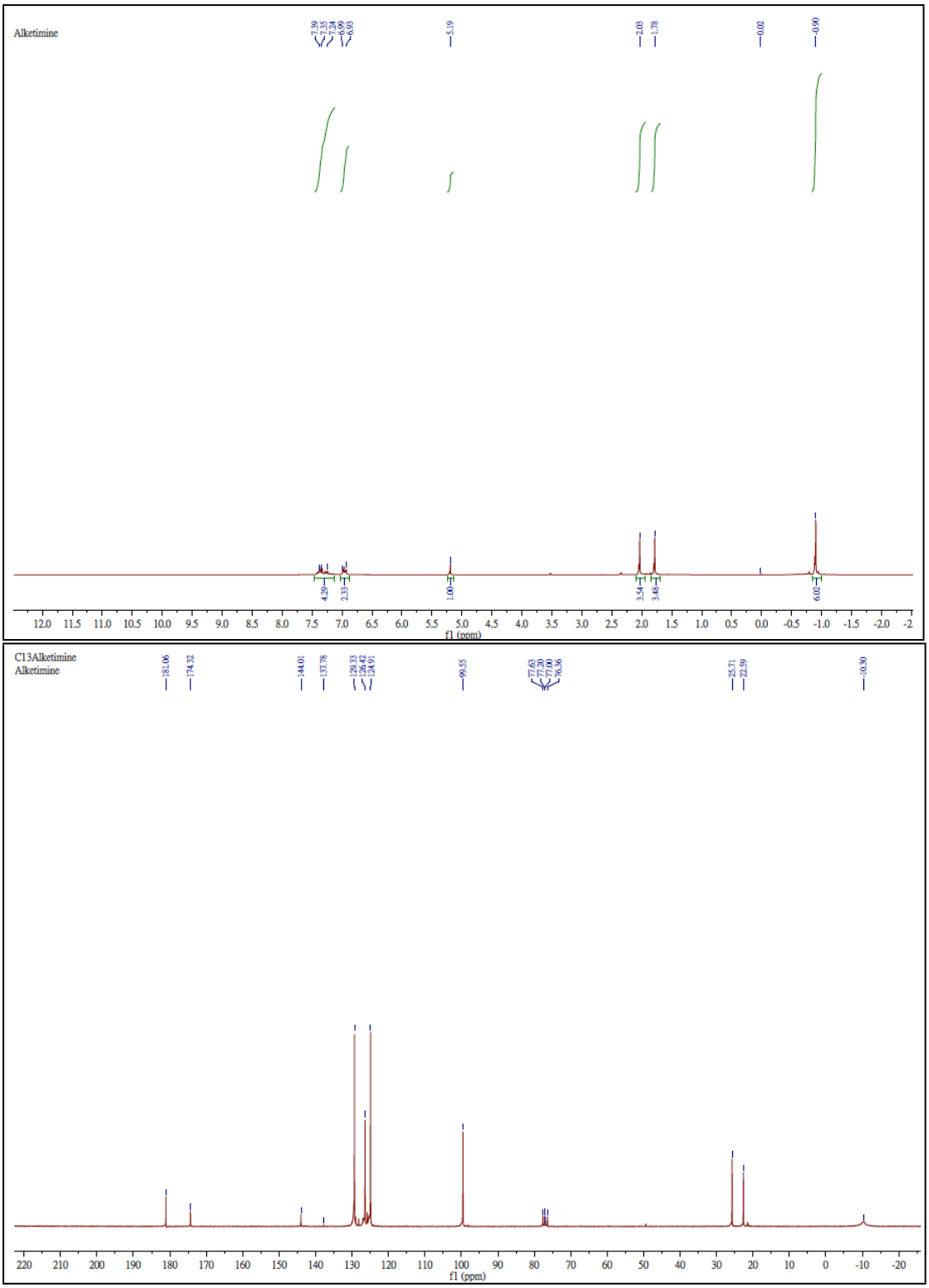


Figure S8 ^{1}H and ^{13}C NMR spectrum of $L^{F5}AlMe_2$

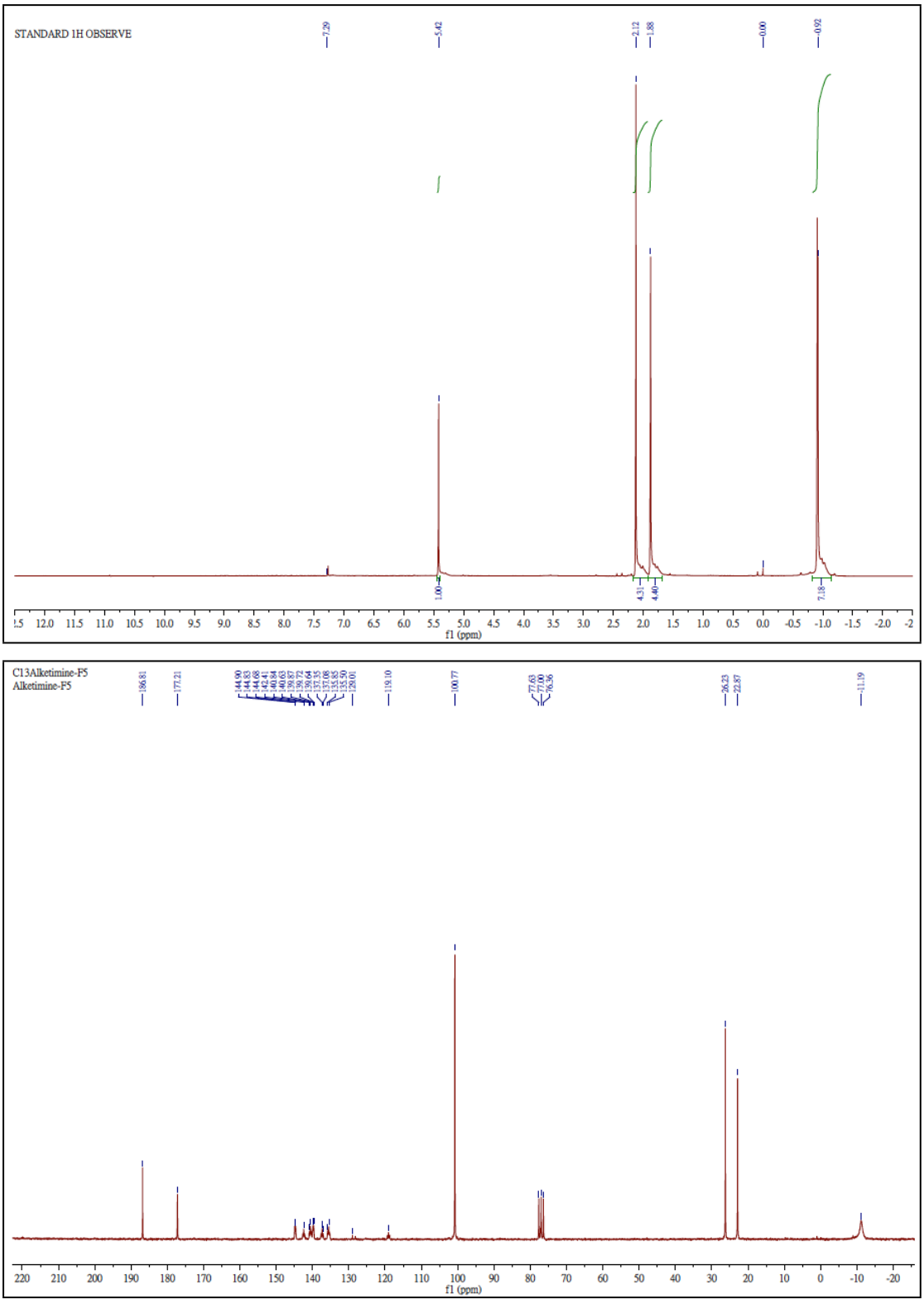


Figure S9 ^{1}H and ^{13}C NMR spectrum of $L^{o\text{-}F}AlMe_2$

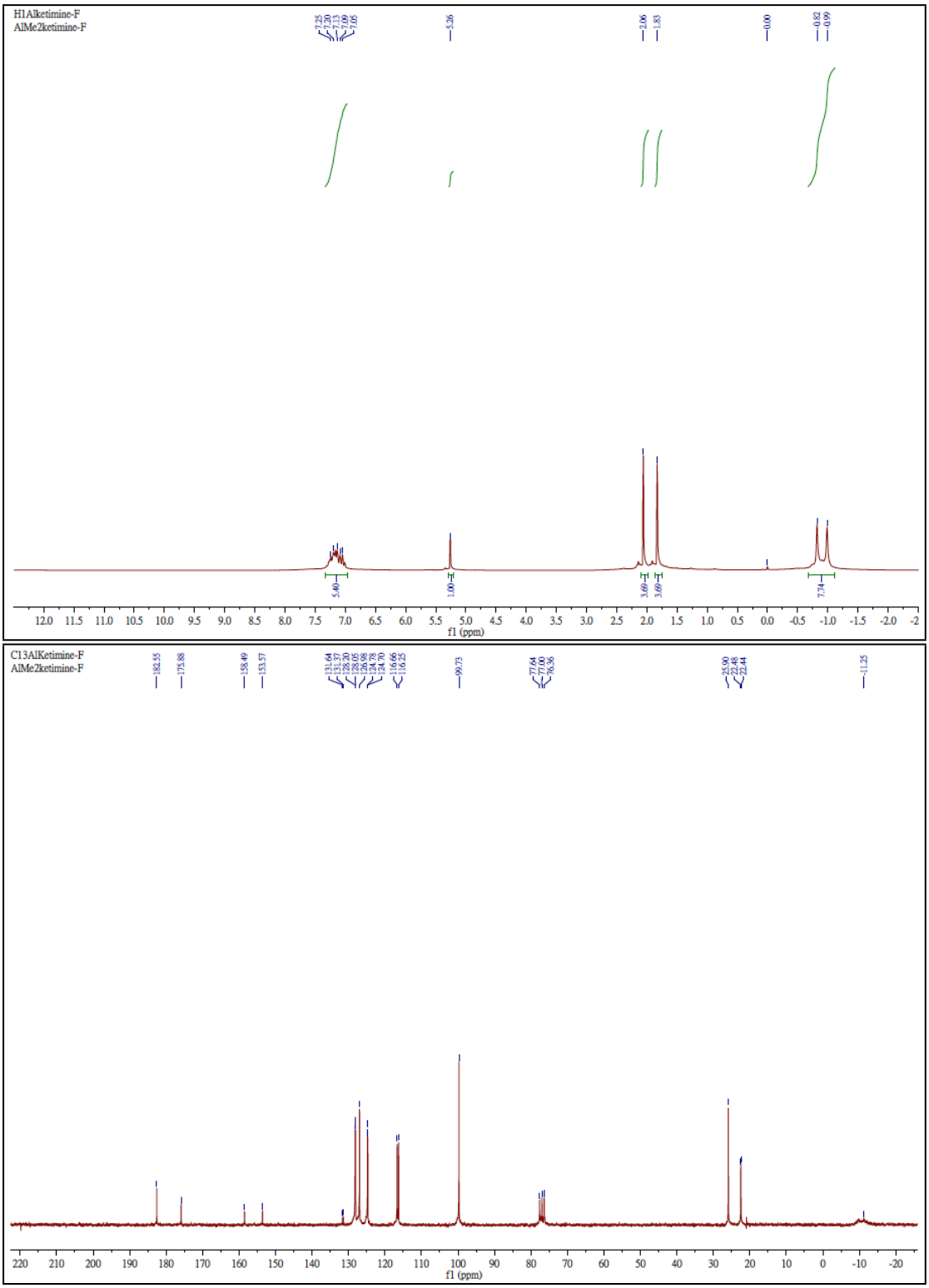
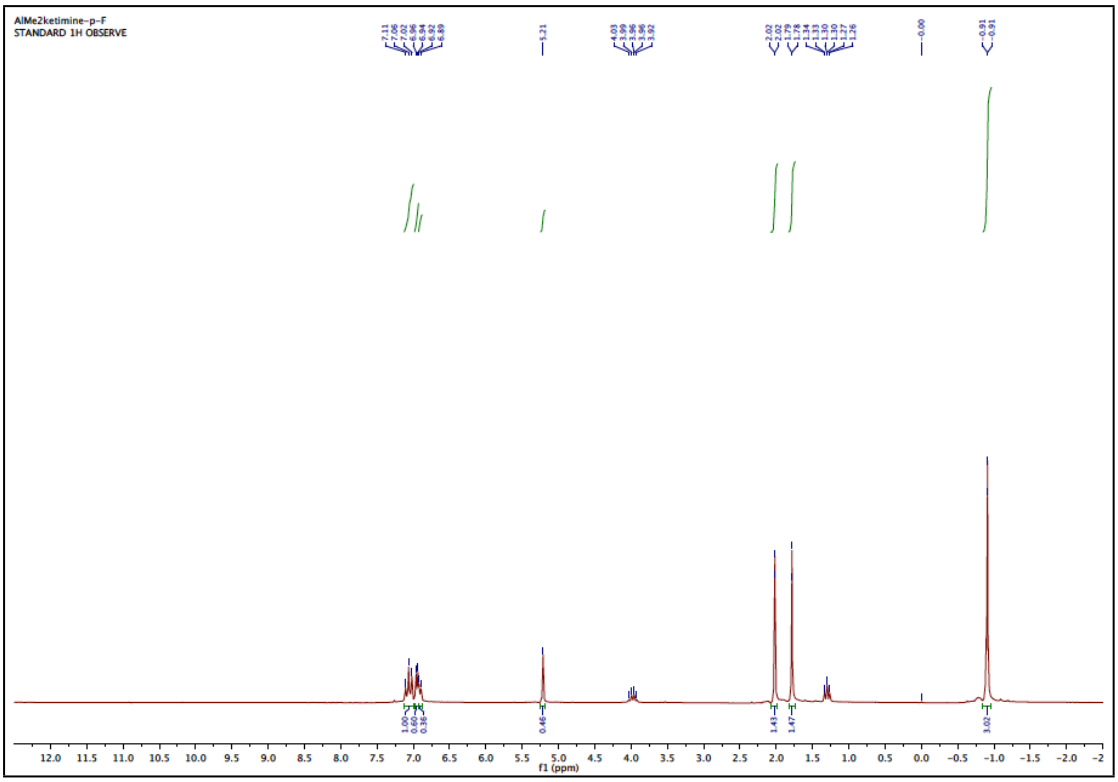


Figure S10 ^{1}H and ^{13}C NMR spectrum of $L^{p\text{-}F}AlMe_2$



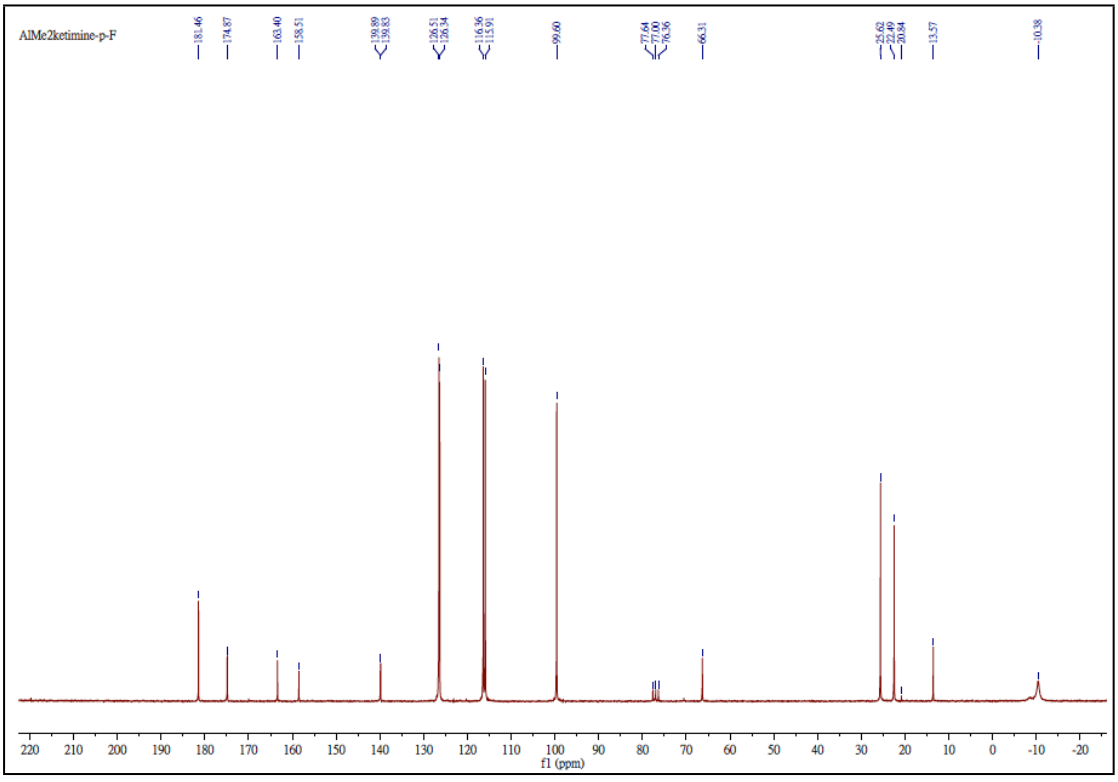
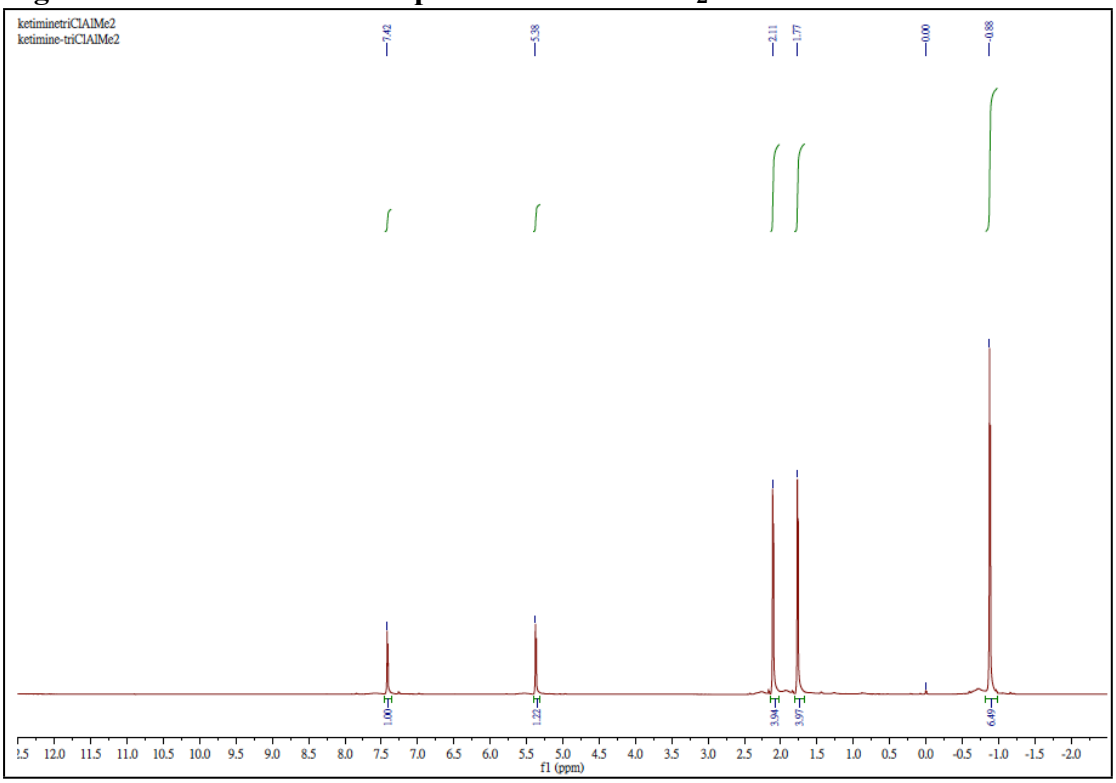


Figure S11 ^{1}H and ^{13}C NMR spectrum of $L^{Cl3}AlMe_2$



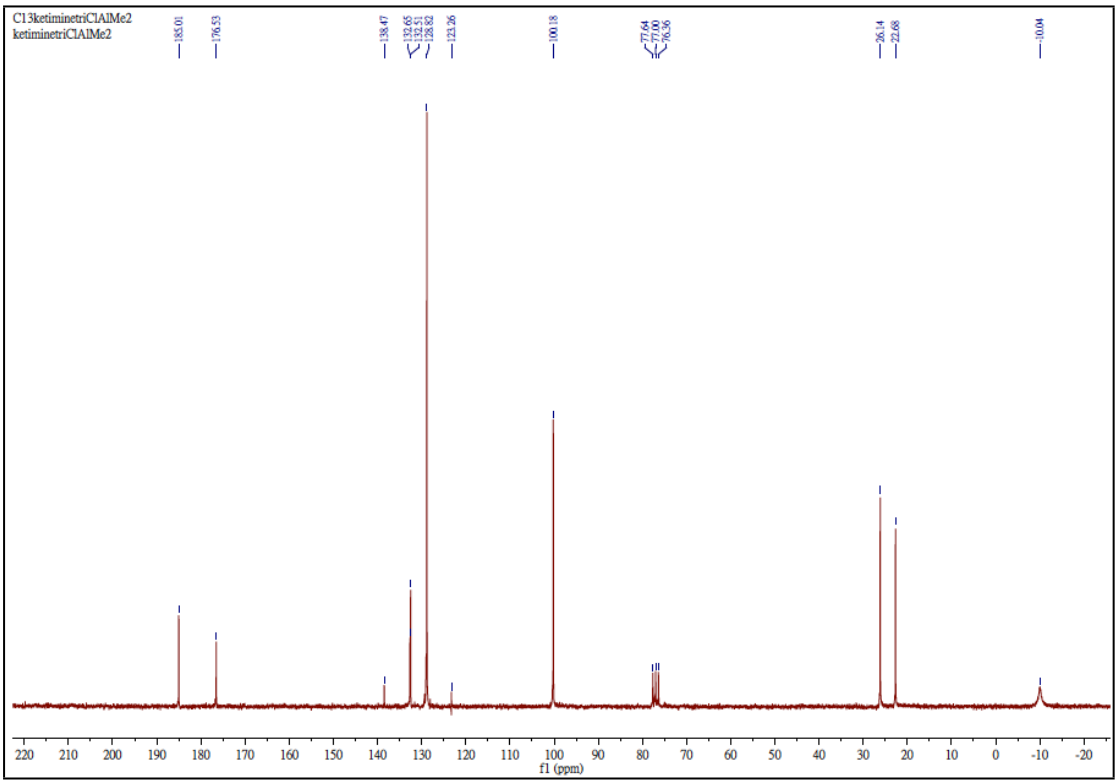
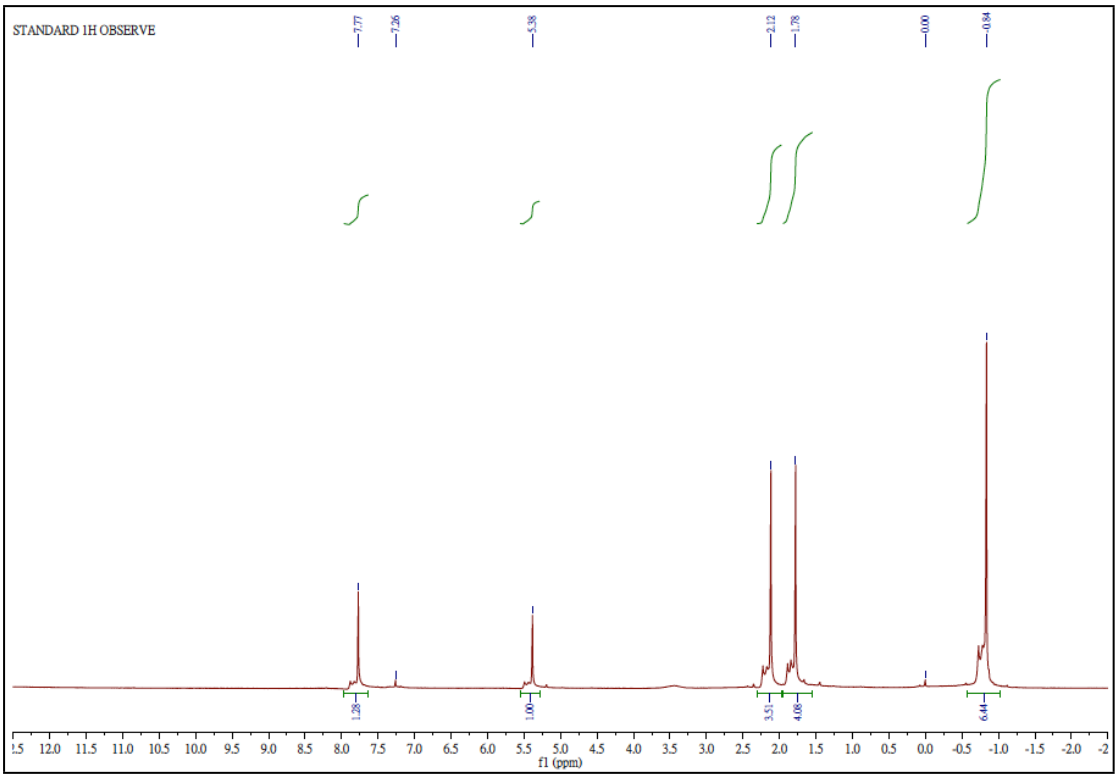


Figure S12 ^{1}H and ^{13}C NMR spectrum of $L^{Br3}AlMe_2$



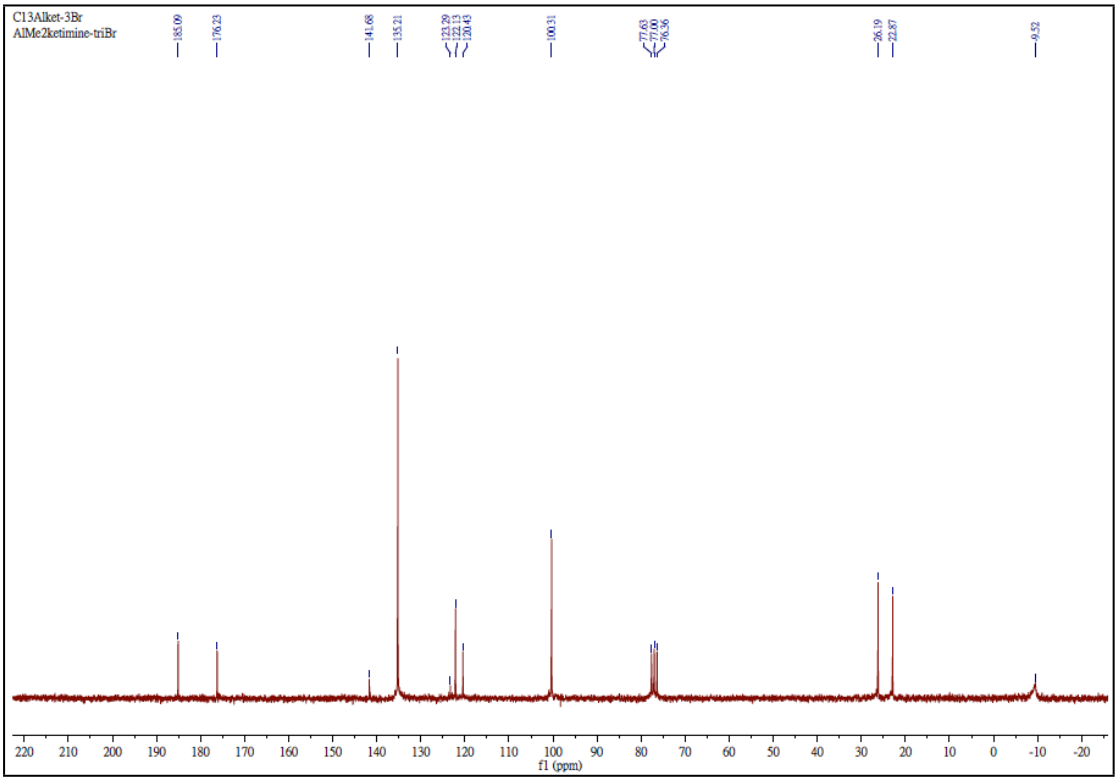


Figure S13 ^{1}H and ^{13}C NMR spectrum of $L^{p\text{-}Cl}AlMe_2$

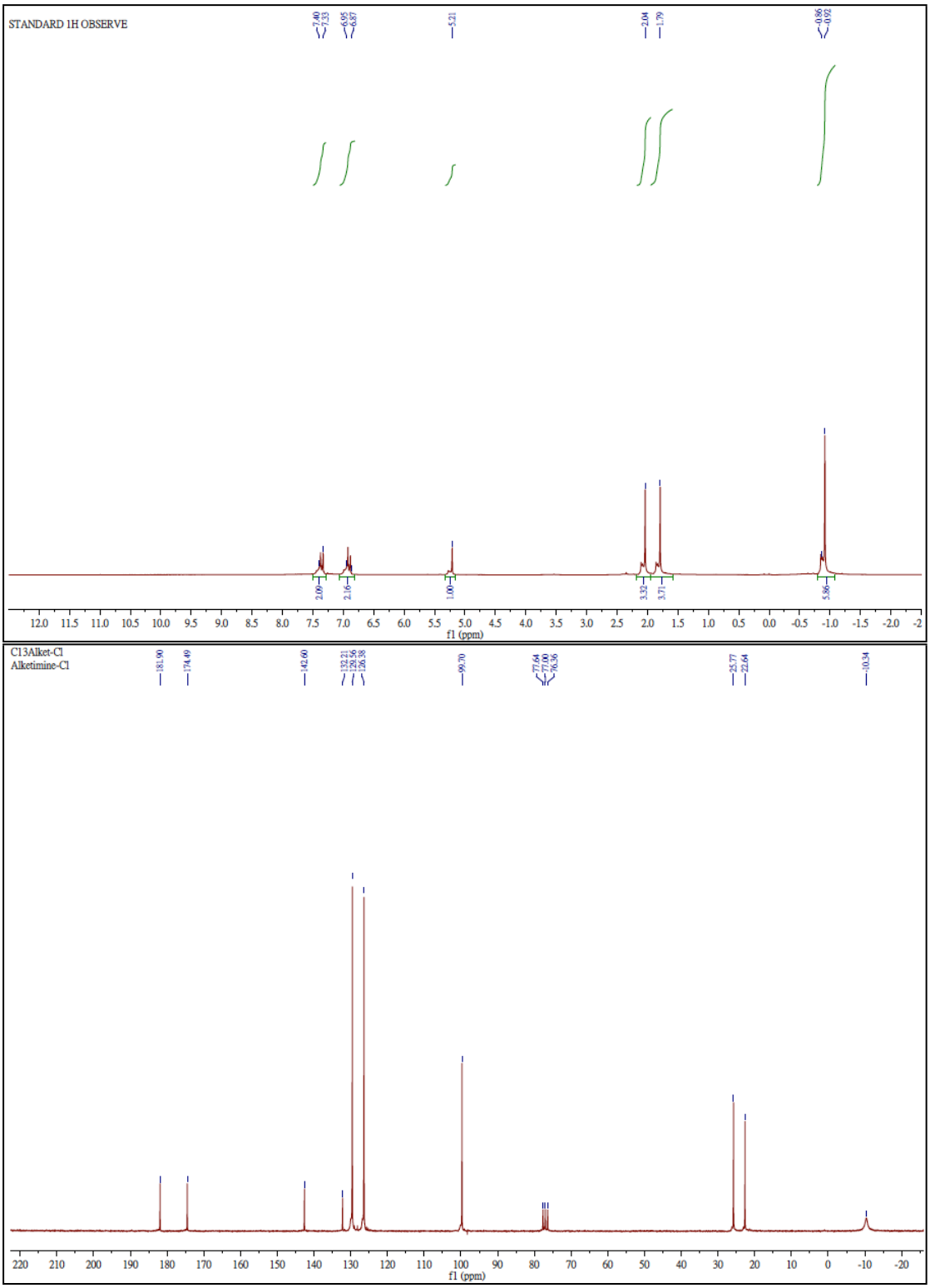
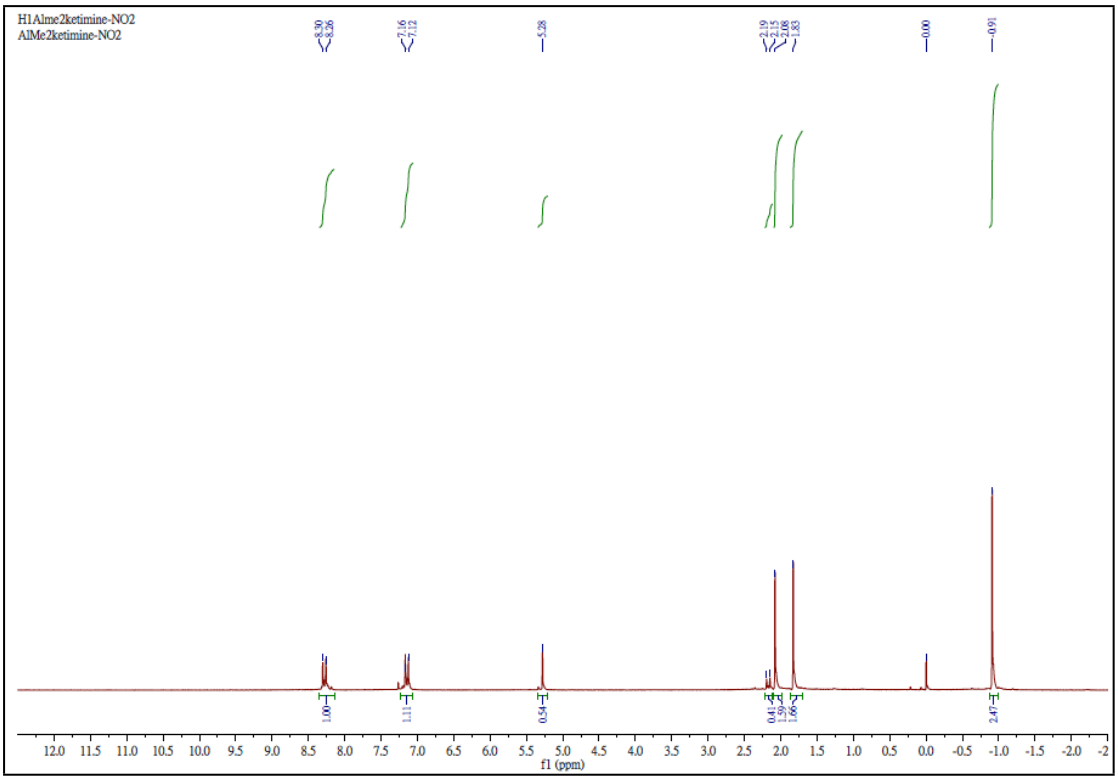


Figure S14 ^{1}H and ^{13}C NMR spectrum of $L^{NO2}AlMe_2$



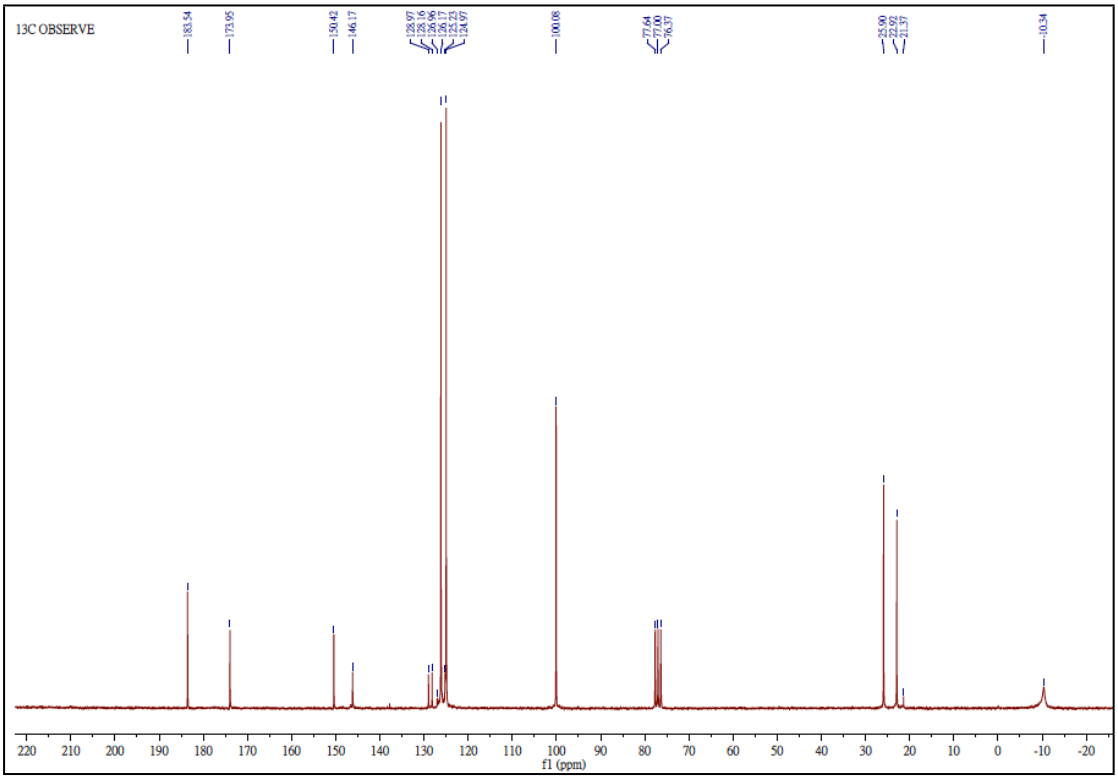
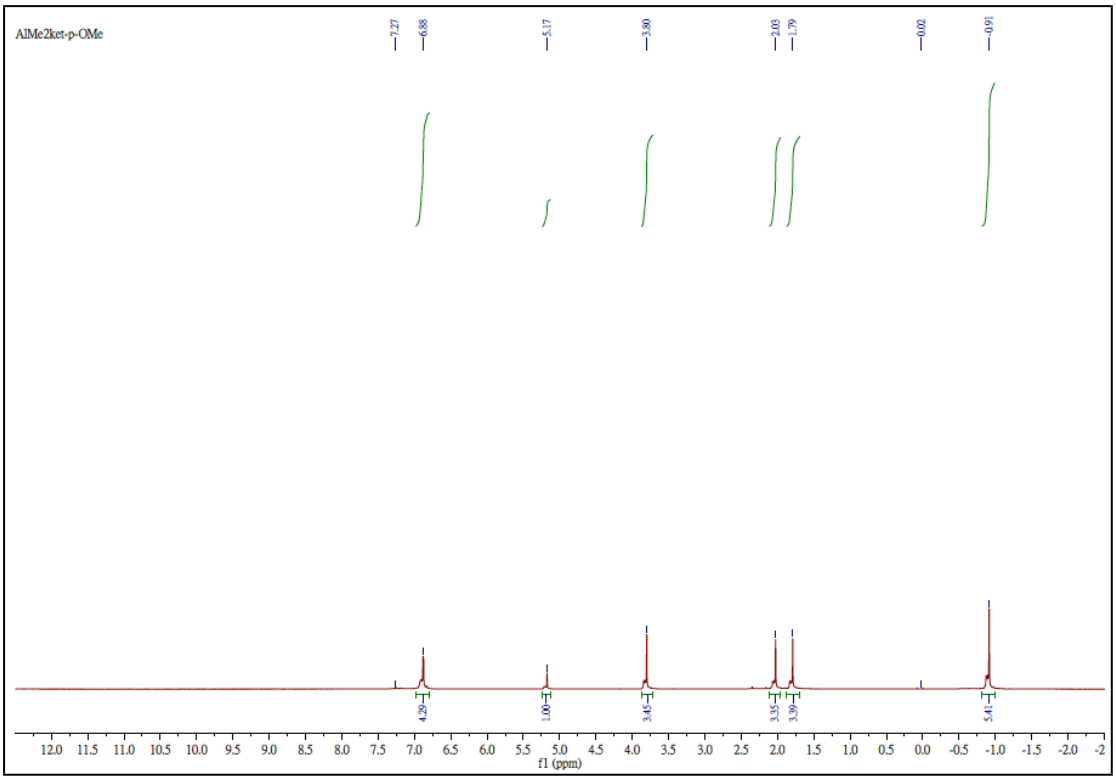


Figure S15 ^{1}H and ^{13}C NMR spectrum of $L^{p\text{-}OMe}AlMe_2$



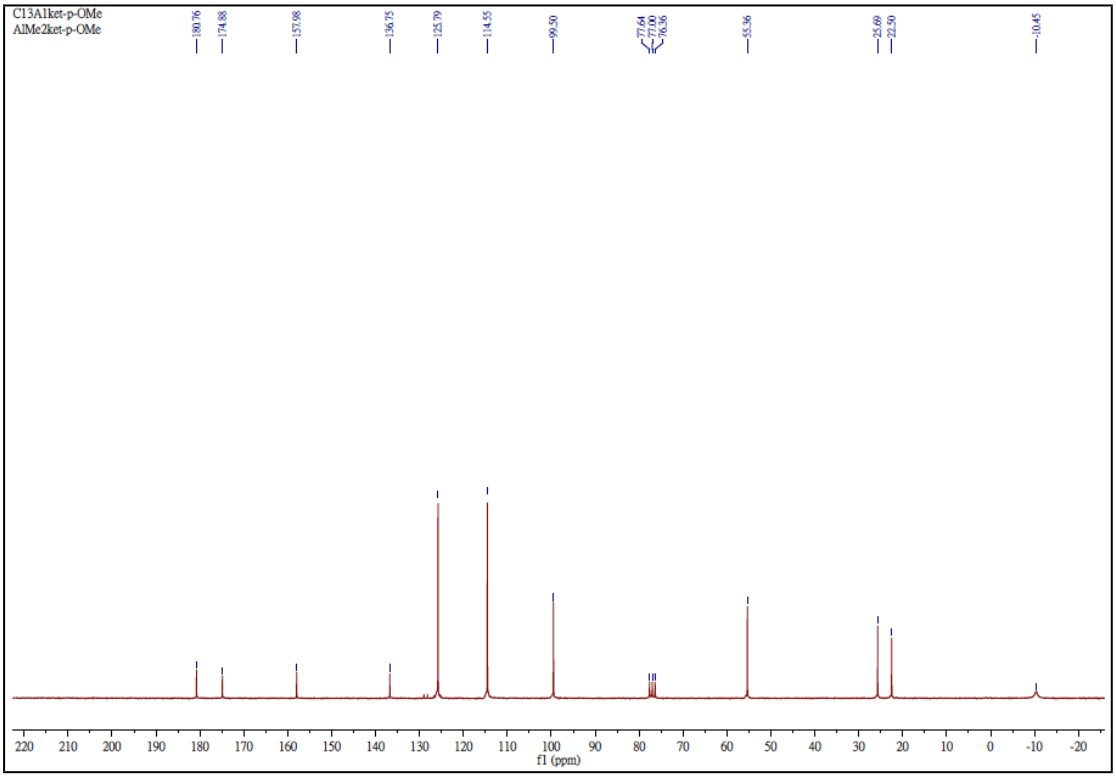
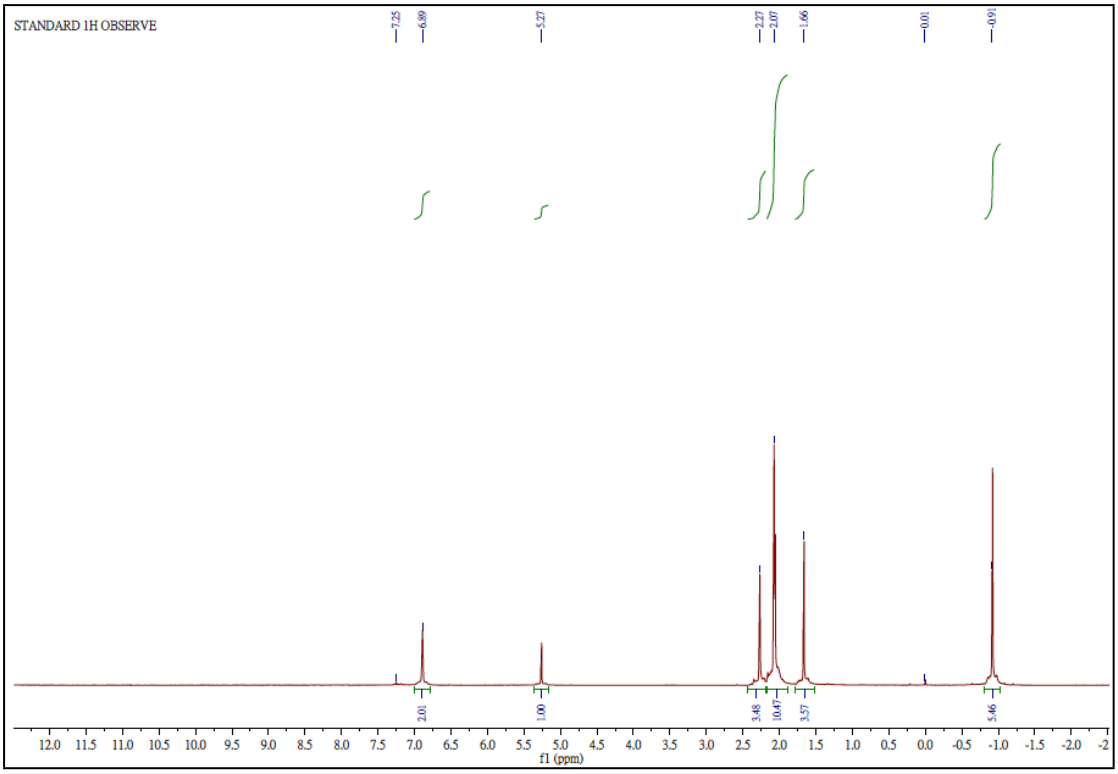


Figure S16 ^{1}H and ^{13}C NMR spectrum of $L^{Me3}AlMe_2$



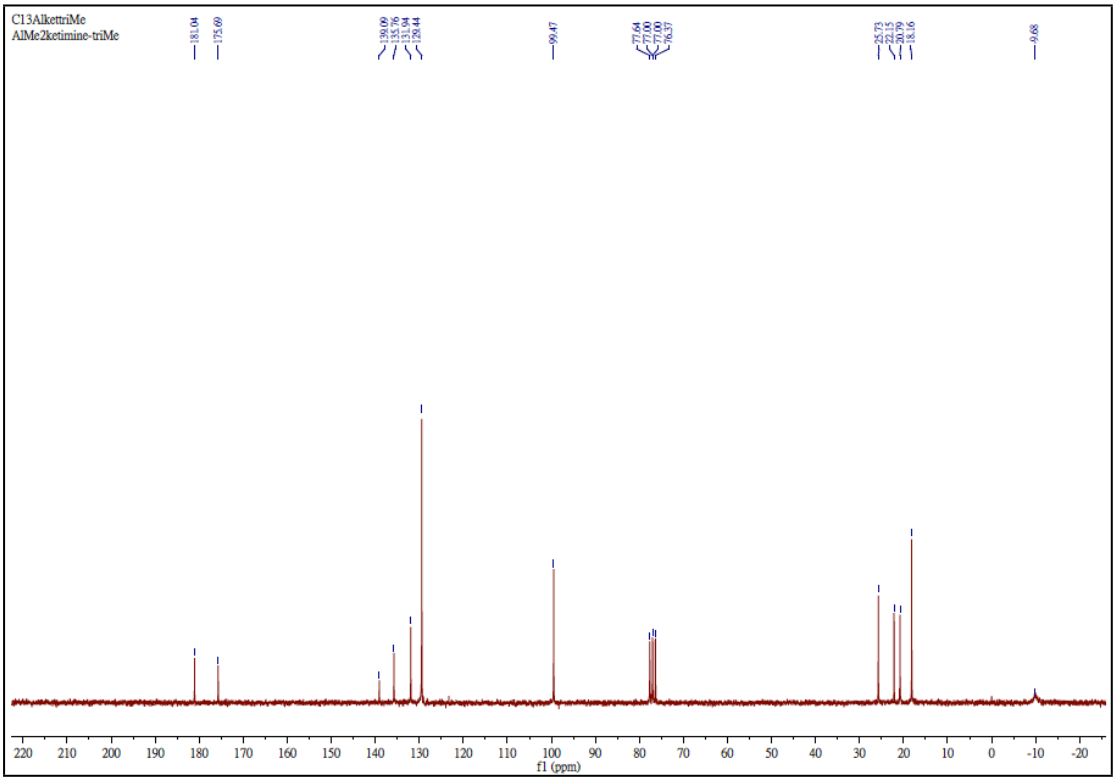
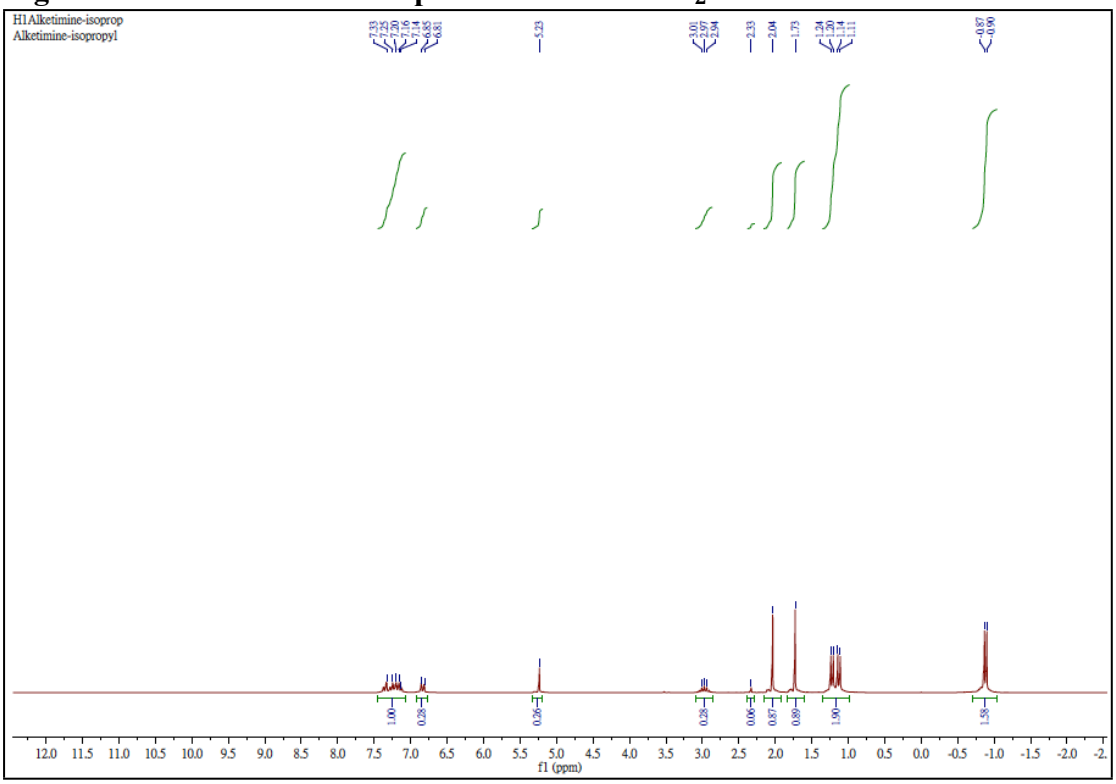


Figure S17 ^{1}H and ^{13}C NMR spectrum of $L^{iPr}AlMe_2$



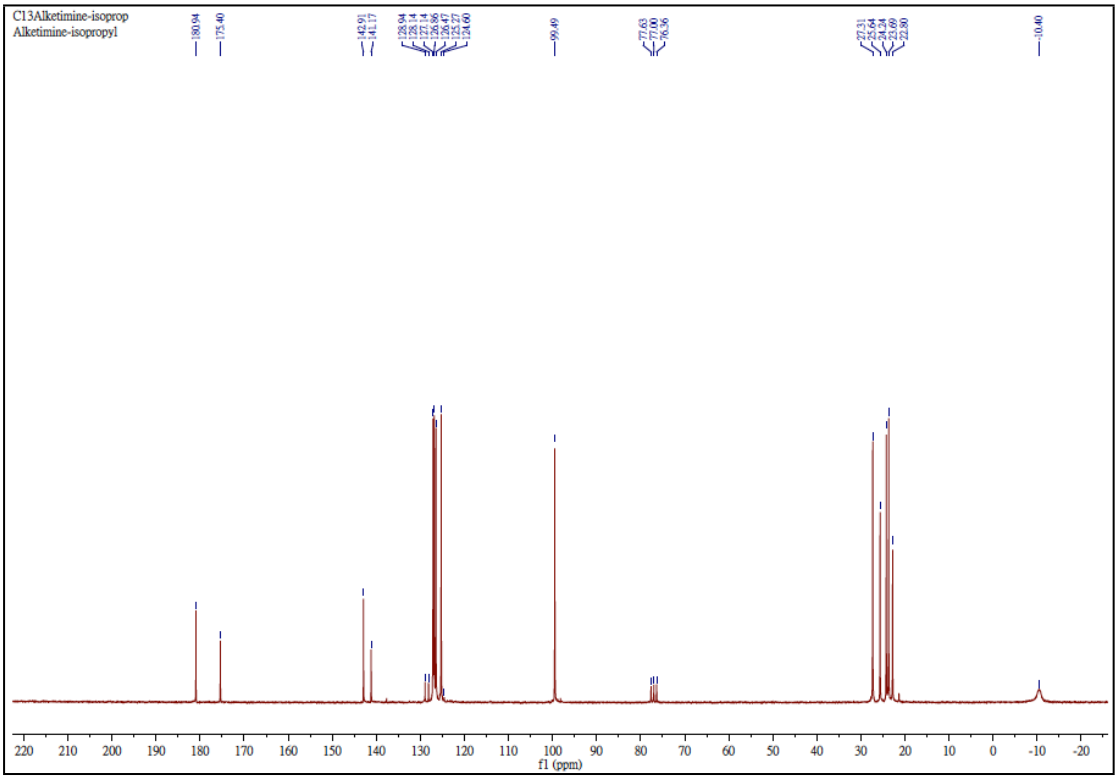
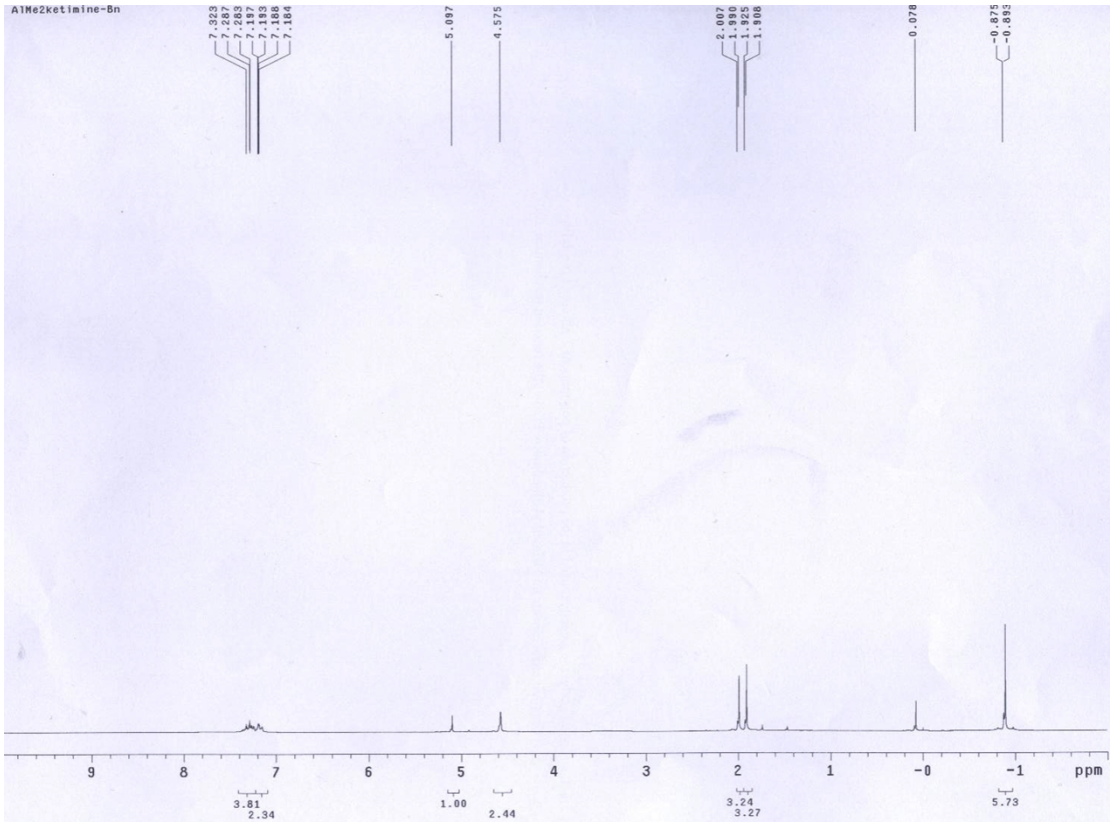


Figure S18 ^{1}H and ^{13}C NMR spectrum of $L^{Bn}AlMe_2$



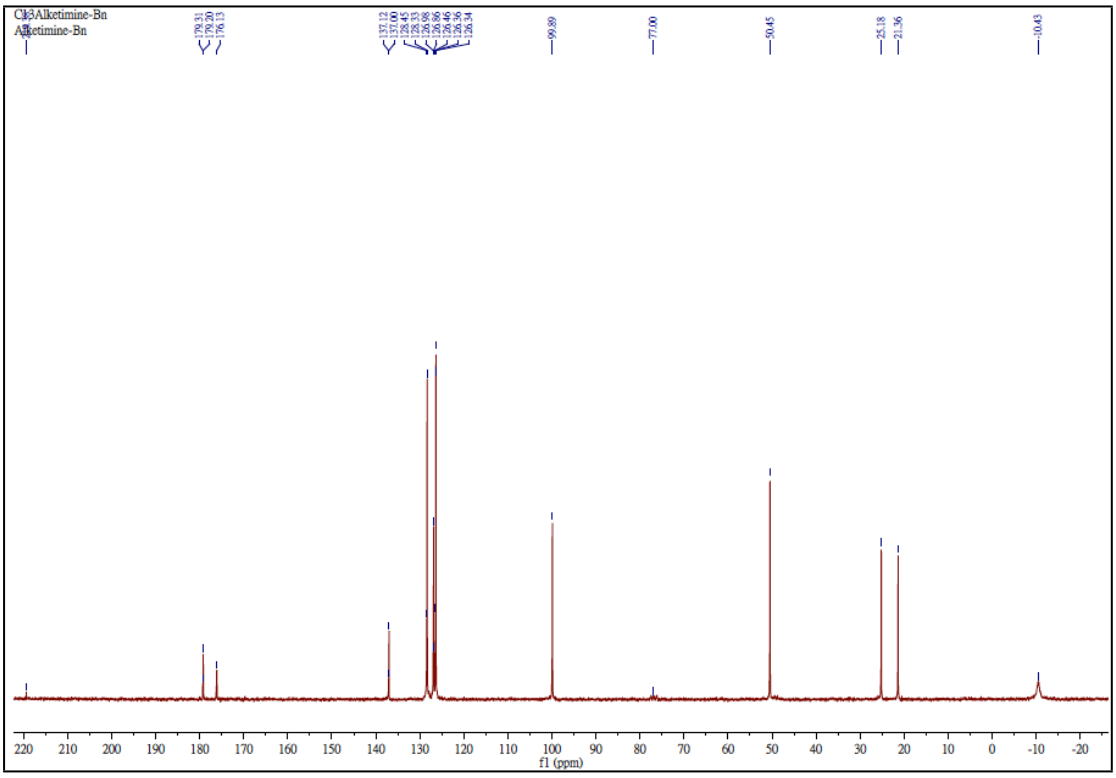
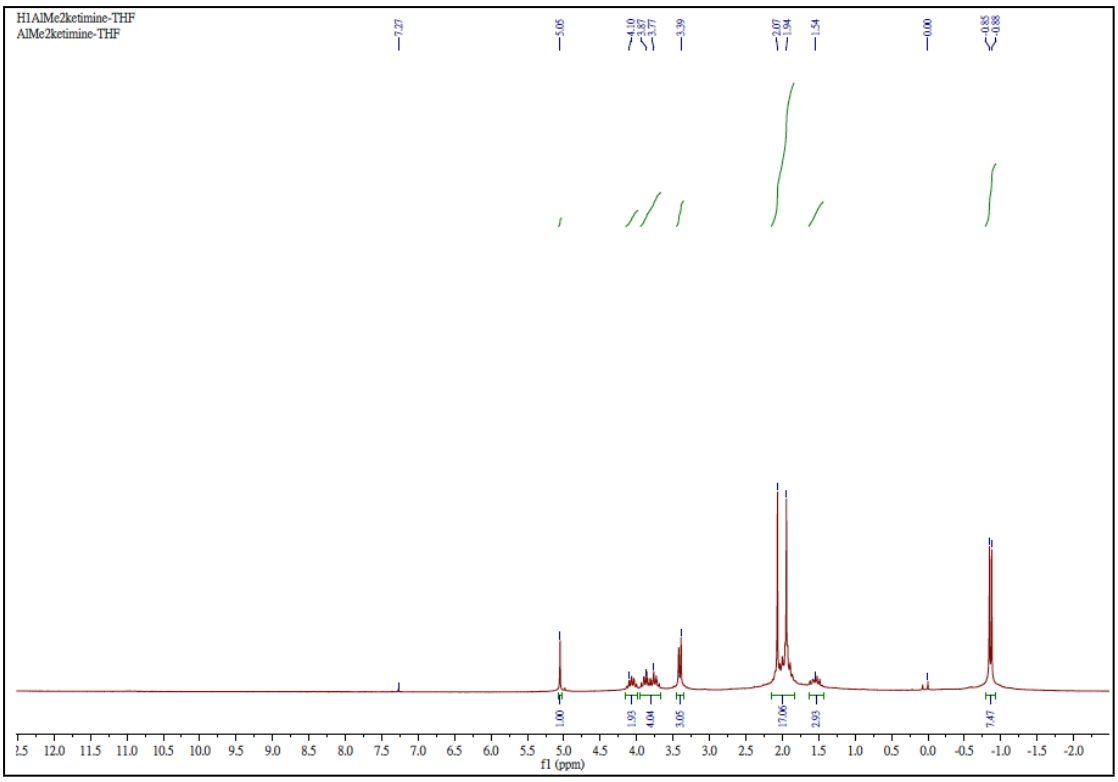


Figure S19 ^{1}H and ^{13}C NMR spectrum of $L^{THF}AlMe_2$



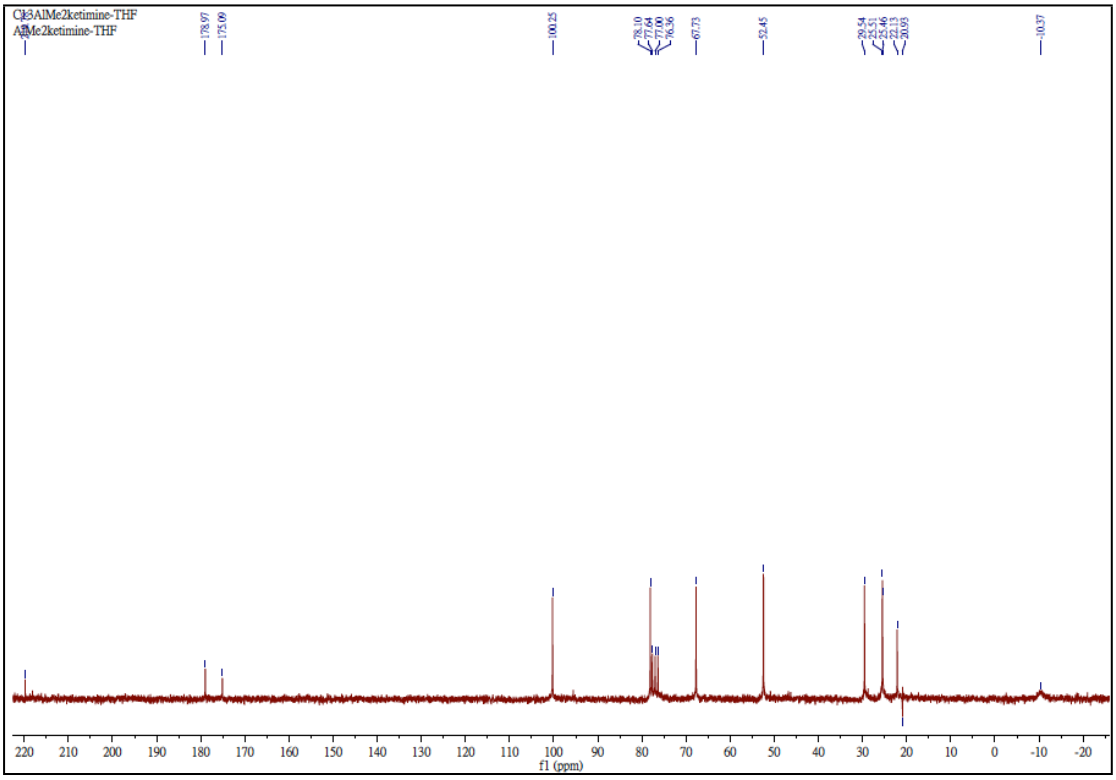


Figure S20 ^{1}H and ^{13}C NMR spectrum of $L^{Py}AlMe_2$

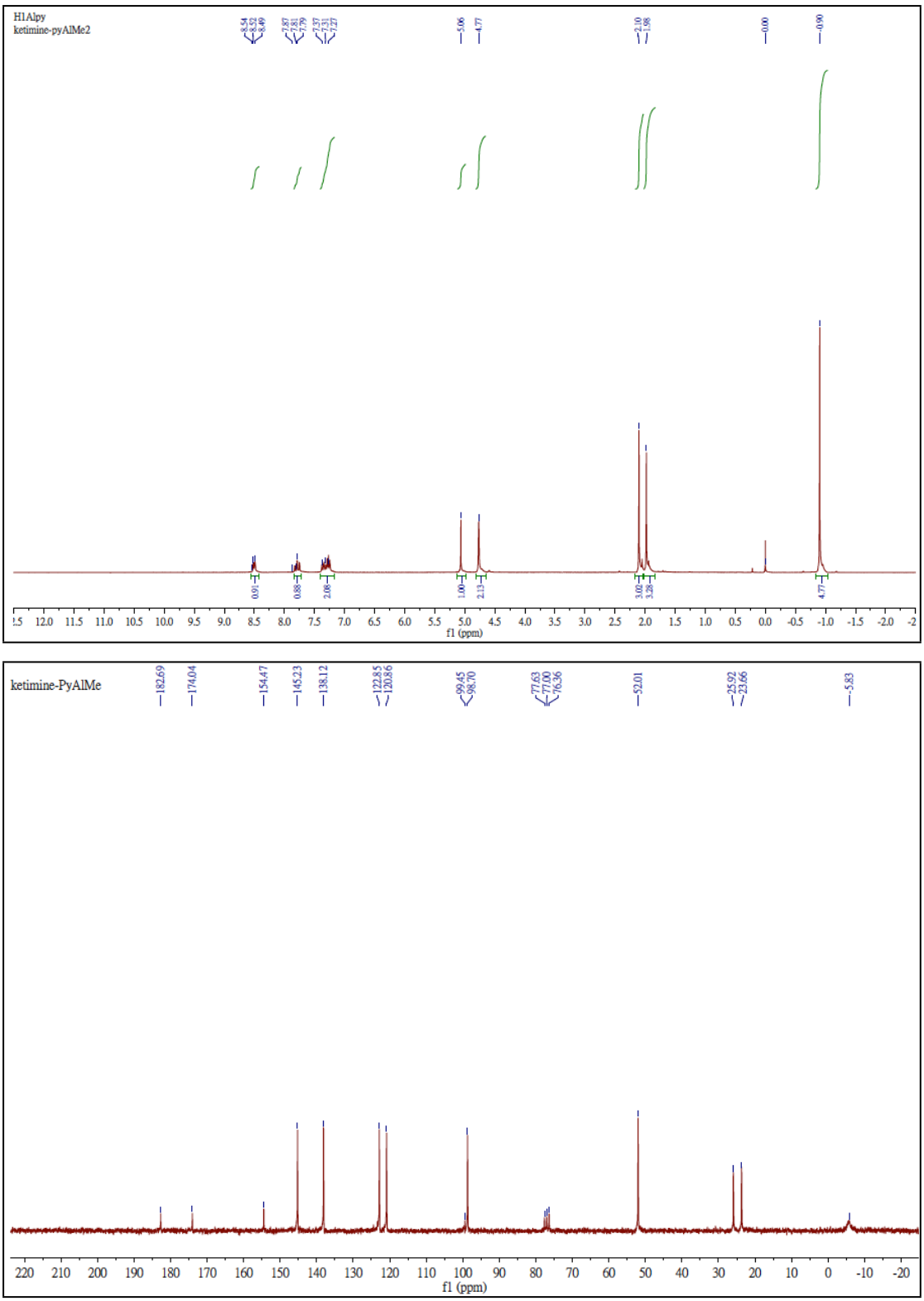


Figure S21 ^{1}H and ^{13}C NMR spectrum of $L^{NMe2}AlMe_2$

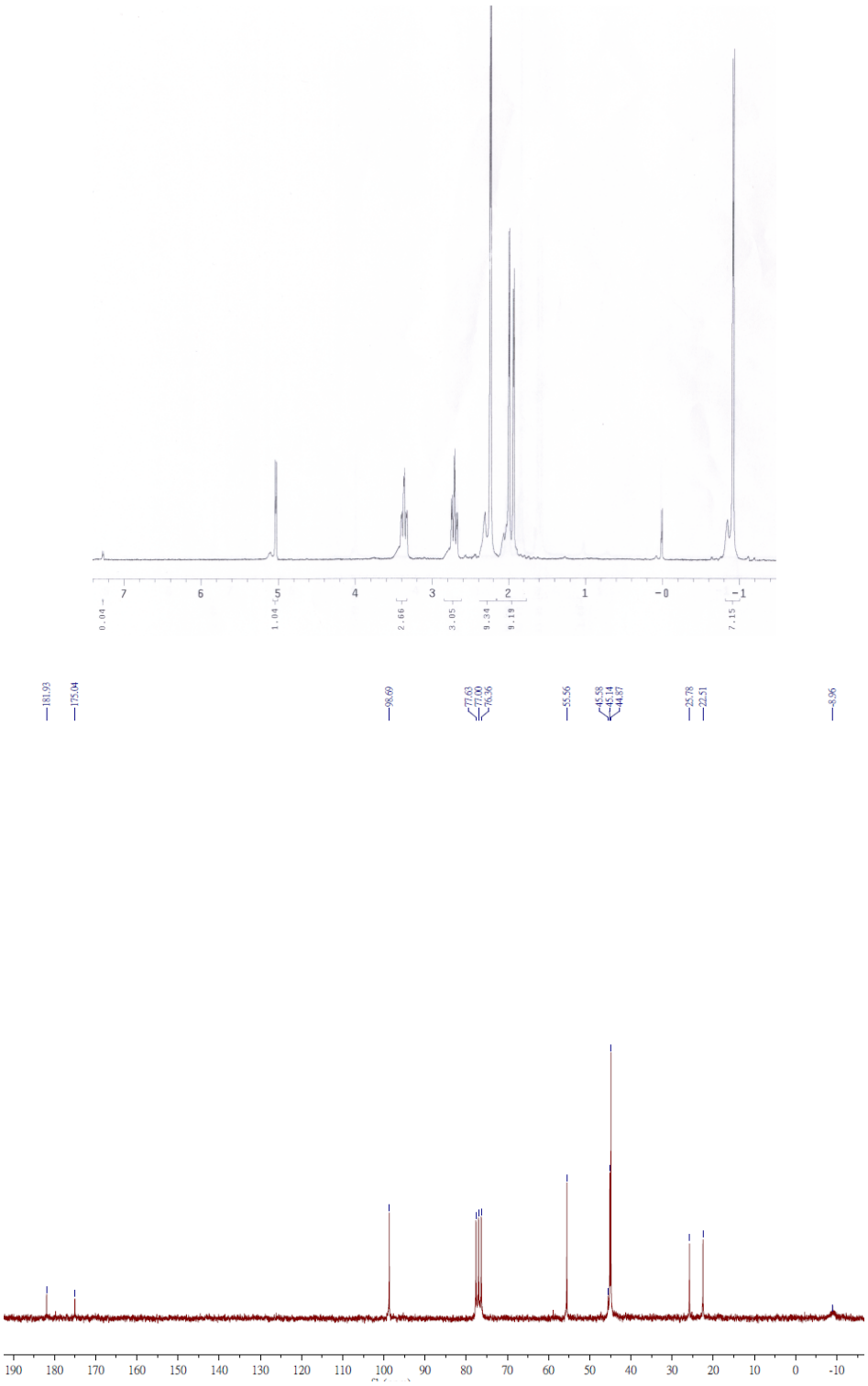
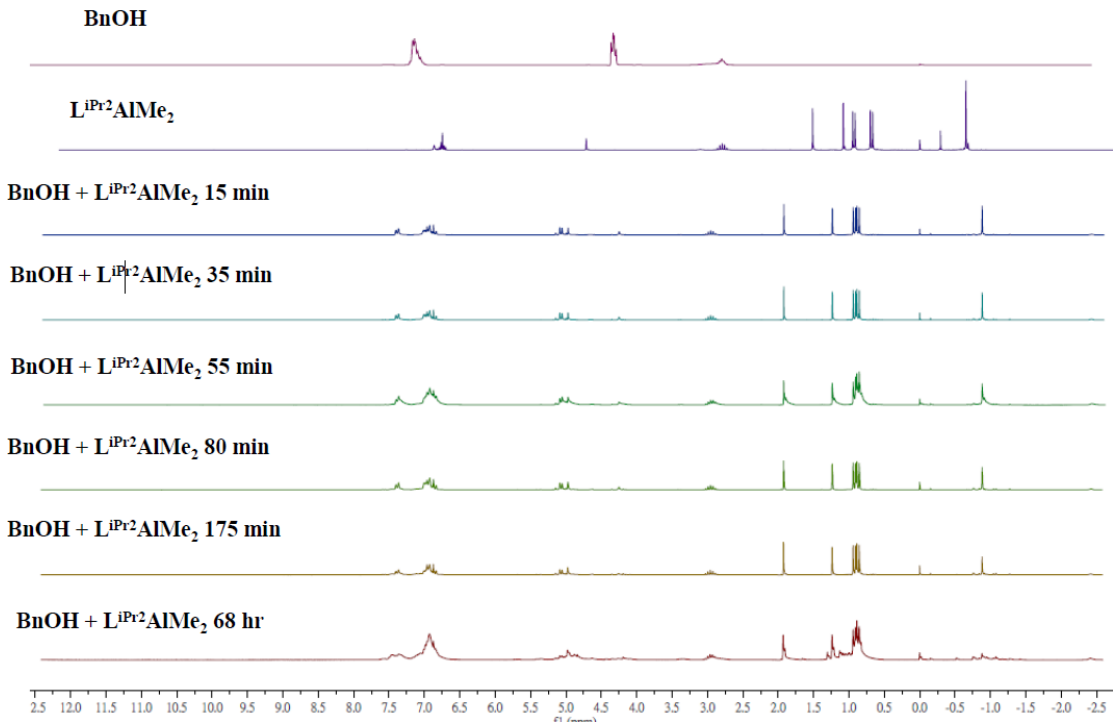


Figure S22 ^{1}H NMR spectrum of the mixture of $L^{iPr2}AlMe_2$ and 2 equ. BnOH


BnOH
L^iPr2AlMe2
BnOH + L^iPr2AlMe2 15 min
BnOH + L^iPr2AlMe2 35 min
BnOH + L^iPr2AlMe2 55 min
BnOH + L^iPr2AlMe2 80 min
BnOH + L^iPr2AlMe2 175 min
BnOH + L^iPr2AlMe2 68 hr
2.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5 -2.0 -2.5