

## Ring-opening Polymerization of $\epsilon$ -Caprolactone and L-Lactide by Using Aluminum Complexes Bearing Benzothiazole Ligands as Catalysts

Yen-Tzu Huang,<sup>a</sup> Wei-Chu Wang,<sup>a</sup> Chun-Pin Hsu,<sup>a</sup> Wei-Yi Lu,<sup>a</sup> Wan-Jung Chuang,<sup>a</sup>  
Michael Y. Chiang,<sup>ab</sup> Yi-Chun Lai,<sup>a</sup> Hsuan-Ying Chen\*<sup>a</sup>

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

<sup>b</sup> Department of Chemistry, National Sun Yat-sen University, Kaohsiung, Taiwan, 80424, R.O.C.

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**Table S1** Kinetic study of CL polymerization with various Al complexes in toluene

10 mL, [CL] = 1.0 M at room temperature ([CL]:[Cat]:[BnOH]=100:1:3)

	LAlMe <sub>3</sub> L =							
time	HPh	Hfur	HBr	HTh	HMe	H2OMe	O	S
min	Conv.(%)							
5			0.08					
10			0.2		0.39		0.28	
15	0.3	0.14	0.3		0.45	0.03		0.3
20				0.27	0.5		0.51	
25					0.55			
30	0.54	0.32	0.58			0.14	0.66	0.47
40				0.53	0.7	0.2	0.74	
45	0.69	0.44						0.57
50			0.81				0.85	
55				0.7		0.27		
60	0.8	0.53						
65				0.78				
70	0.85					0.42		
75		0.64		0.84				0.82
90		0.72		0.89				
100				0.93				
120								0.90
k <sub>obs</sub> × 10 <sup>-2</sup> / min <sup>-1</sup> (error)	2.79 (2)	4.51 (13)	3.52 (13)	2.91 (10)	2.37 (11)	0.67 (3)	1.85 (4)	3.77 (23)
I.P/ min	2.40 (49)	2.9 (48)	3.88 (05)	12.13	9.95	10.18 (243)	0 (0)	1.54

(error)				(252)	(117)			(202)
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	LAlMe <sub>3</sub> L =				
time	H <sup>NO2</sup>	HNO <sub>2</sub> <sup>a</sup>	HNO <sub>2</sub> <sup>b</sup>	HNO <sub>2</sub> <sup>c</sup>	CINO <sub>2</sub>
min	Conv.(%)				
3			0.23	0.29	
5		0.19			
6			0.42	0.48	
9			0.60	0.65	
10	0.26	0.40			0.38
12			0.7	0.76	
15		0.57	0.78	0.85	
20	0.51	0.74	0.86		0.71
25		0.80			
30	0.7	0.85			0.86
35					0.90
40					0.92
45	0.85				
50	0.9				
k <sub>obs</sub> ×10 <sup>-2</sup> /min <sup>-1</sup>	4.90	6.99	10.15	12.43	6.95
(error)	(22)	(31)	(24)	(46)	(28)
I.P/ min	4.83	2.19	0	1.43	3.86
(error)	(158)	(87)		(36)	(117)

<sup>a</sup>[CL]:[Cat]:[BnOH]=100:2:6, [CL]=1.0 M, toluene 10 mL

<sup>b</sup>[CL]:[Cat]:[BnOH]=100:3:9, [CL]=1.0 M, toluene 10 mL

<sup>c</sup>[CL]:[Cat]:[BnOH]=100:4:12, [CL]=1.0 M, toluene 10 mL

time	<b>L<sup>4-OMe</sup> AlMe<sub>3</sub></b>	<b>L<sup>4-OMe</sup> AlEt<sub>3</sub></b>	<b>L<sup>4-OMe</sup> AlBu<sub>3</sub></b>
min	Conv.(%)		
3		0.08	
6		0.22	
9		0.35	
10			0.58
12		0.49	
15	0.18	0.60	
20			0.72
30	0.37		0.9
40	0.51		0.95
55	0.61		
70	0.75		
<b>k<sub>obs</sub>×10<sup>-2</sup>/min<sup>-1</sup></b>	<b>2.12</b>	<b>6.97</b>	<b>7.41</b>
<b>(error)</b>	<b>(14)</b>	<b>(36)</b>	<b>(81)</b>
<b>I.P/ min</b>	<b>7.07(299)</b>	<b>2.20</b>	<b>0</b>
<b>(error)</b>		<b>(51)</b>	

**Table S2** Kinetic study of LA polymerization with various Al complexes in toluene  
 10 mL, [LA] = 1.0 M at 80 °C ([LA]:[Cat]:[BnOH]=100:1:3)

	LAlMe <sub>3</sub> L =							
time	HPh	Hfur	HBr	HTh	HMe	H2OMe	O	S
min	Conv.(%)							
10							0.18	0.26
15	0.4	0.30	0.27	0.50	0.26	0.20		
20							0.36	0.51
30	0.57	0.64	0.54	0.70	0.58	0.49	0.47	0.72
40	0.69		0.71	0.81	0.7		0.67	0.85
45		0.78				0.64		
50	0.78		0.81	0.86	0.75		0.78	0.91
60	0.85	0.88	0.86	0.91		0.76		
65					0.86			
70	0.88					0.81		
75					0.90			
80	0.92	0.93						
k <sub>obs</sub> × 10 <sup>-2</sup> / min <sup>-1</sup> (error)	3.41 (7)	3.55 (17)	3.79 (16)	3.80 (12)	3.26 (11)	2.42 (13)	3.53 (31)	5.39 (19)
I.P/ min (error)	5.89 (119)	2.74 (254)	7.58 (181)	3.21 (35)	4.81 (183)	3.84 (276)	5.63 (297)	5.57 (121)

	LAlMe <sub>3</sub> L =				
time	HNO <sub>2</sub>	HNO <sub>2</sub> <sup>a</sup>	HNO <sub>2</sub> <sup>b</sup>	HNO <sub>2</sub> <sup>c</sup>	CINO <sub>2</sub>
min	Conv.(%)				
3			0.20	0.24	
6				0.39	
9		0.20		0.49	
10					0.13
12		0.30	0.49	0.56	
15	0.42	0.37	0.56	0.65	
20		0.46	0.68		0.32
25		0.80			
30	0.65	0.64	0.82		0.47
35					
40	0.71	0.75	0.89		0.67
45					
50	0.78	0.86			0.78
60	0.83				
65					
70					
75					
80					
k <sub>obs</sub> ×10 <sup>-2</sup> /min <sup>-1</sup> (error)	3.02 (11)	3.73 (11)	5.47 (10)	6.26 (24)	3.47 (29)
I.P/ min (error)	0	2.83 (55)	0	0	8.21 (277)

<sup>a</sup>[CL]:[Cat]:[BnOH]=100:2:6, [LA]=1.0 M, toluene 10 mL

<sup>b</sup>[CL]:[Cat]:[BnOH]=100:3:9, [LA]=1.0 M, toluene 10 mL

<sup>c</sup>[CL]:[Cat]:[BnOH]=100:4:12, [LA]=1.0 M, toluene 10 mL

time	<b>L<sup>4-OMe</sup> AlMe<sub>3</sub></b>	<b>L<sup>4-OMe</sup> AlEt<sub>3</sub></b>	<b>L<sup>4-OMe</sup> AlBu<sub>3</sub></b>
min	Conv.(%)		
10			0.05
15	0.19	0.30	
20			0.16
30	0.43	0.64	0.26
40		0.78	0.32
45	0.65		
50		0.87	0.41
55			
60	0.77		
70	0.82	0.93	
80			0.65
110			0.77
$k_{\text{obs}} \times 10^{-2} / \text{min}^{-1}$	2.80	4.15	1.44
(error)	(7)	(13)	(5)
I.P/ min	8.24	5.47	9.67
(error)	(1.36)	(139)	(210)

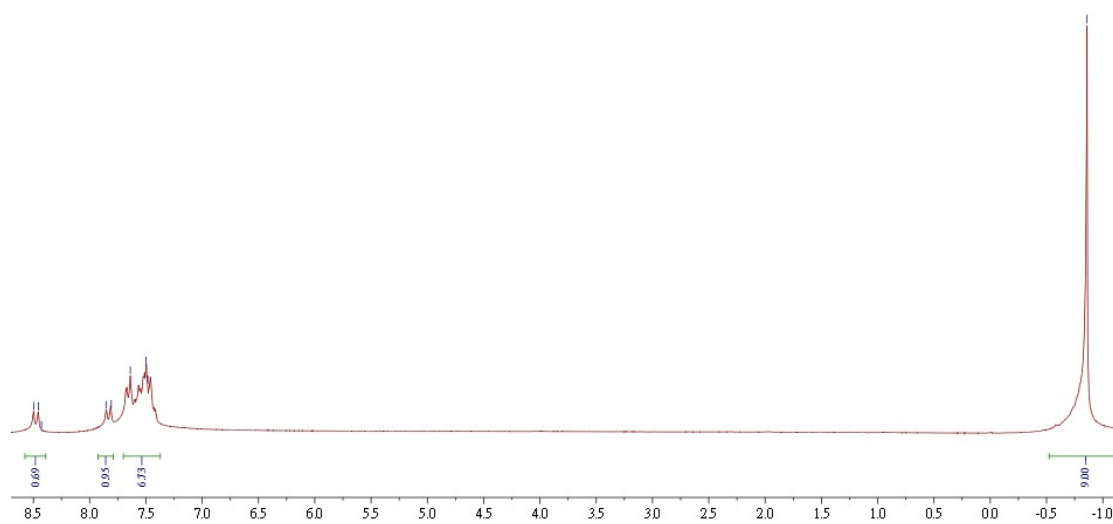


Figure S1  $^1\text{H}$  NMR spectrum of  $\text{L}^{\text{HPh}}\text{AlMe}_3$  in  $\text{CDCl}_3$

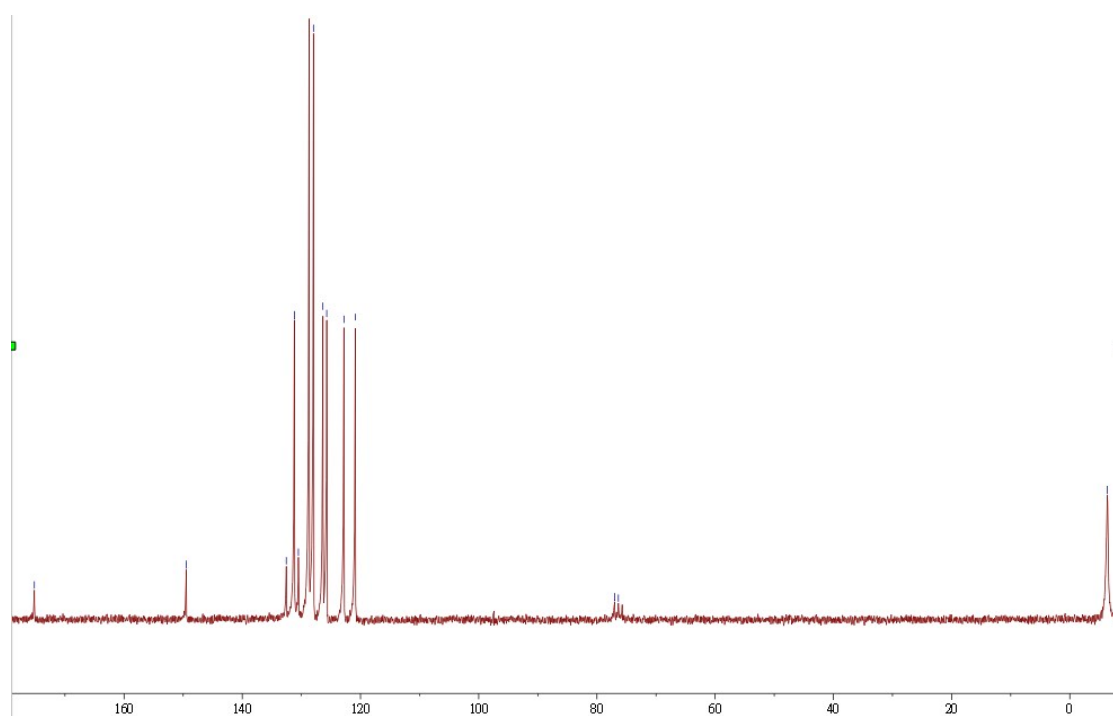


Figure S2  $^{13}\text{C}$  NMR spectrum of  $\text{L}^{\text{HPh}}\text{AlMe}_3$  in  $\text{CDCl}_3$



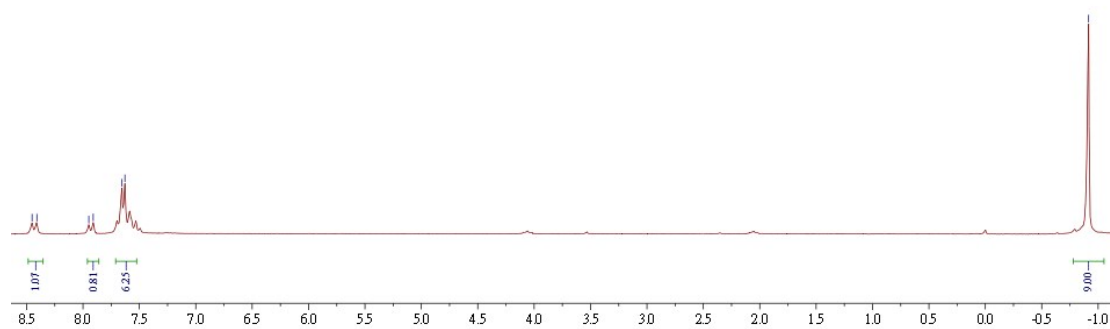


Figure S3  $^1\text{H}$  NMR spectrum of  $\text{L}^{\text{HBr}}\text{AlMe}_3$  in  $\text{CDCl}_3$

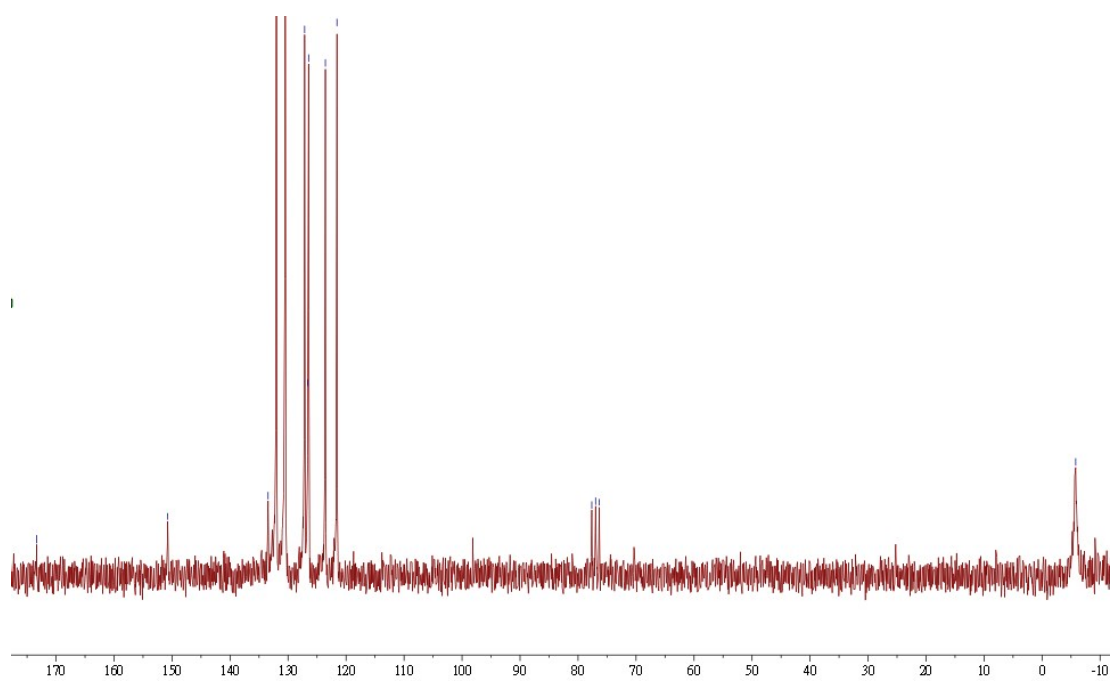


Figure S4  $^{13}\text{C}$  NMR spectrum of  $\text{L}^{\text{HBr}}\text{AlMe}_3$  in  $\text{CDCl}_3$

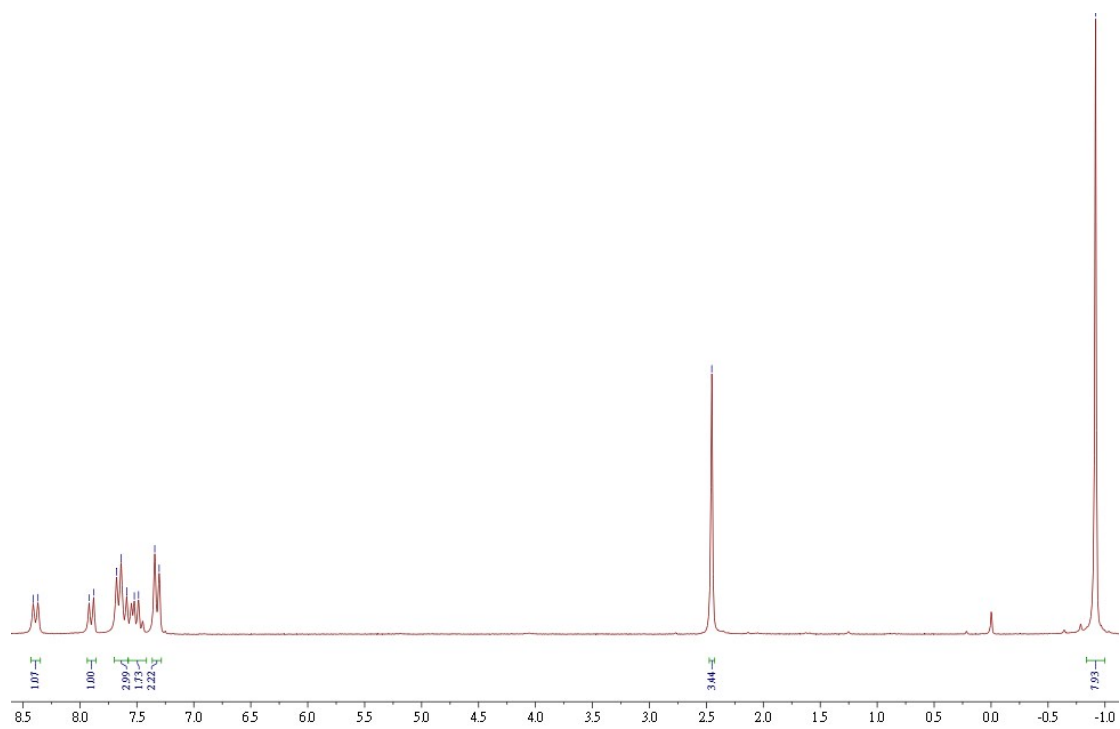


Figure S5  $^1\text{H}$  NMR spectrum of  $\text{L}^{\text{HMe}}\text{AlMe}_3$  in  $\text{CDCl}_3$

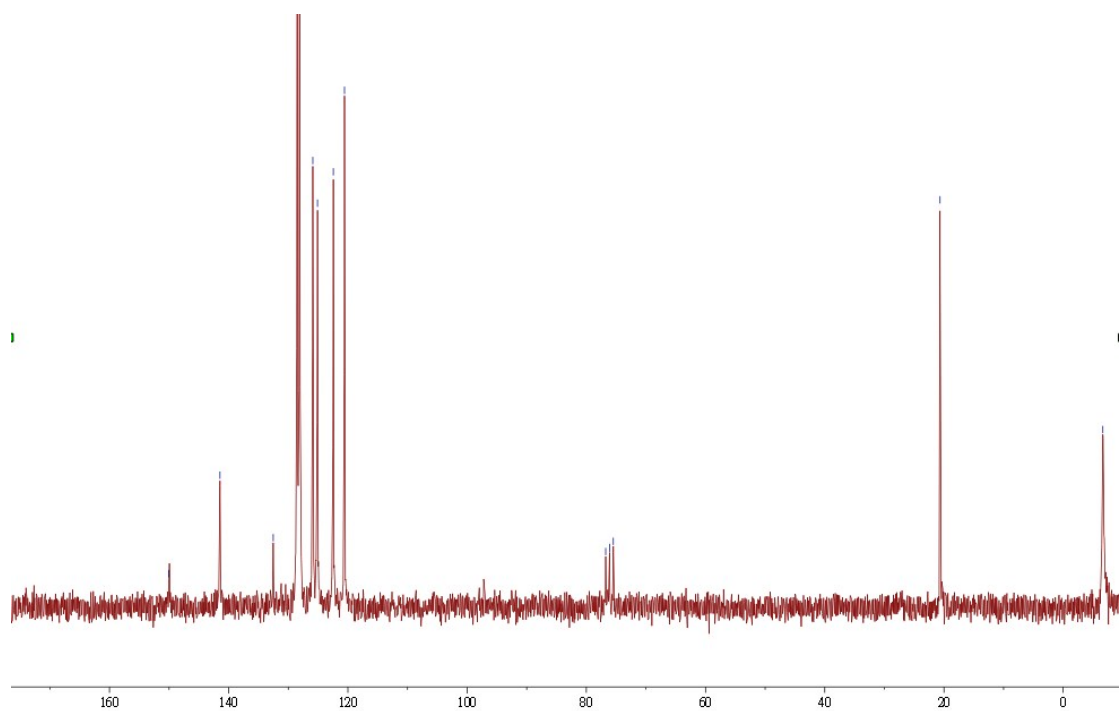


Figure S6  $^{13}\text{C}$  NMR spectrum of  $\text{L}^{\text{HMe}}\text{AlMe}_3$  in  $\text{CDCl}_3$

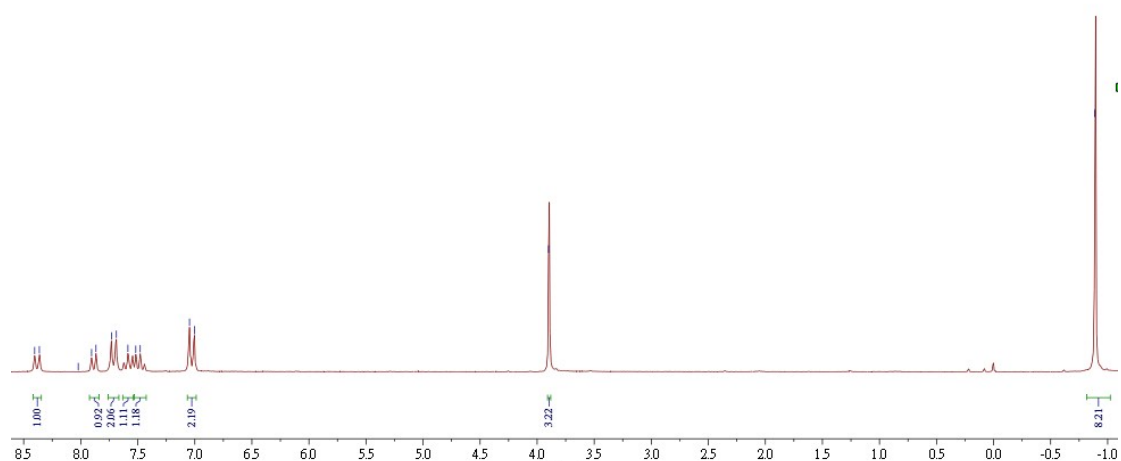


Figure S7  $^1\text{H}$  NMR spectrum of  $\text{L}^{\text{H4OMeAlMe}_3}$  in  $\text{CDCl}_3$

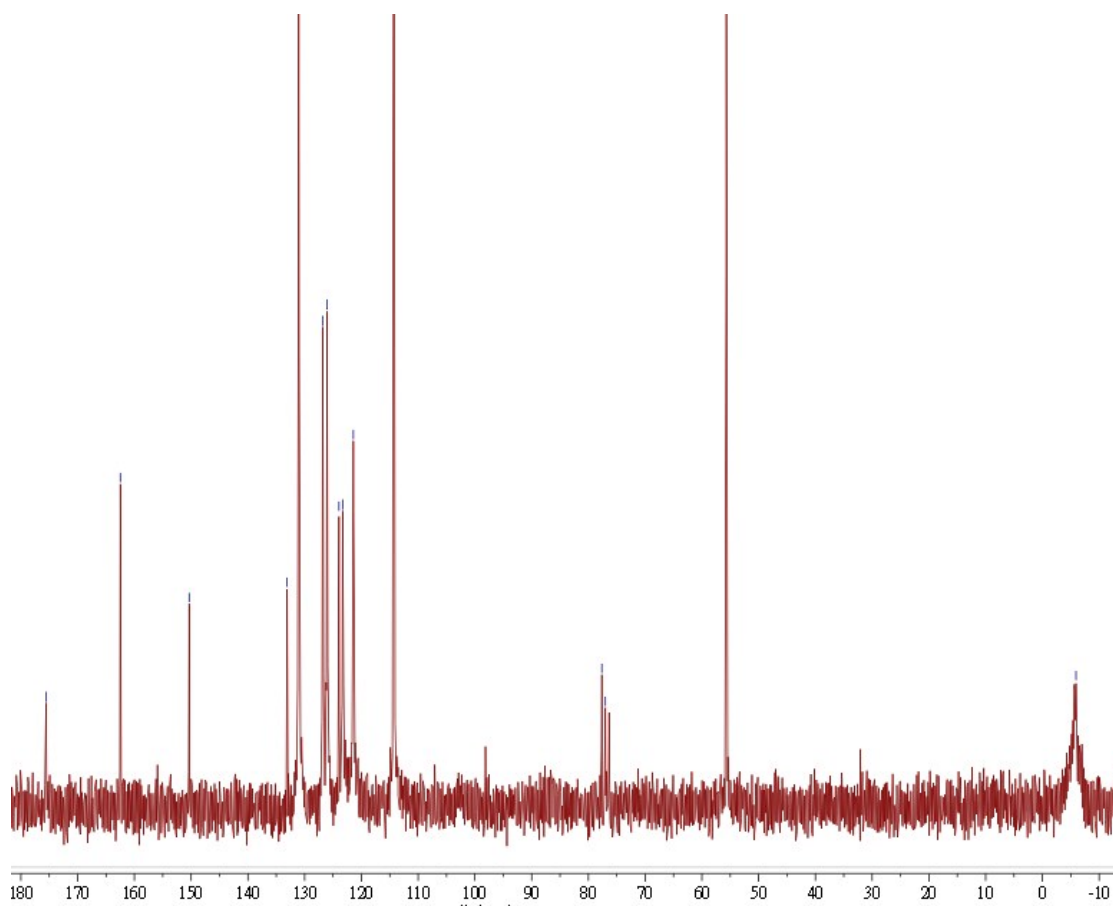


Figure S8  $^{13}\text{C}$  NMR spectrum of  $\text{L}^{\text{H4OMeAlMe}_3}$  in  $\text{CDCl}_3$

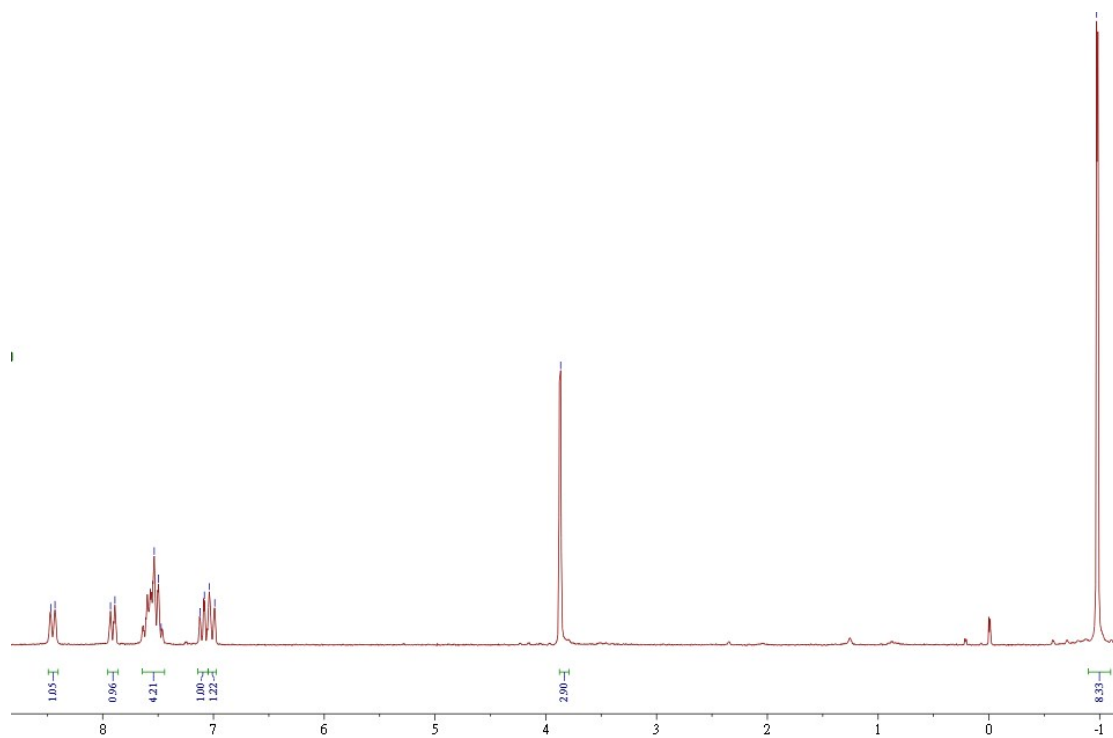


Figure S9  $^1\text{H}$  NMR spectrum of  $\text{L}^{\text{H2OMeAlMe}_3}$  in  $\text{CDCl}_3$

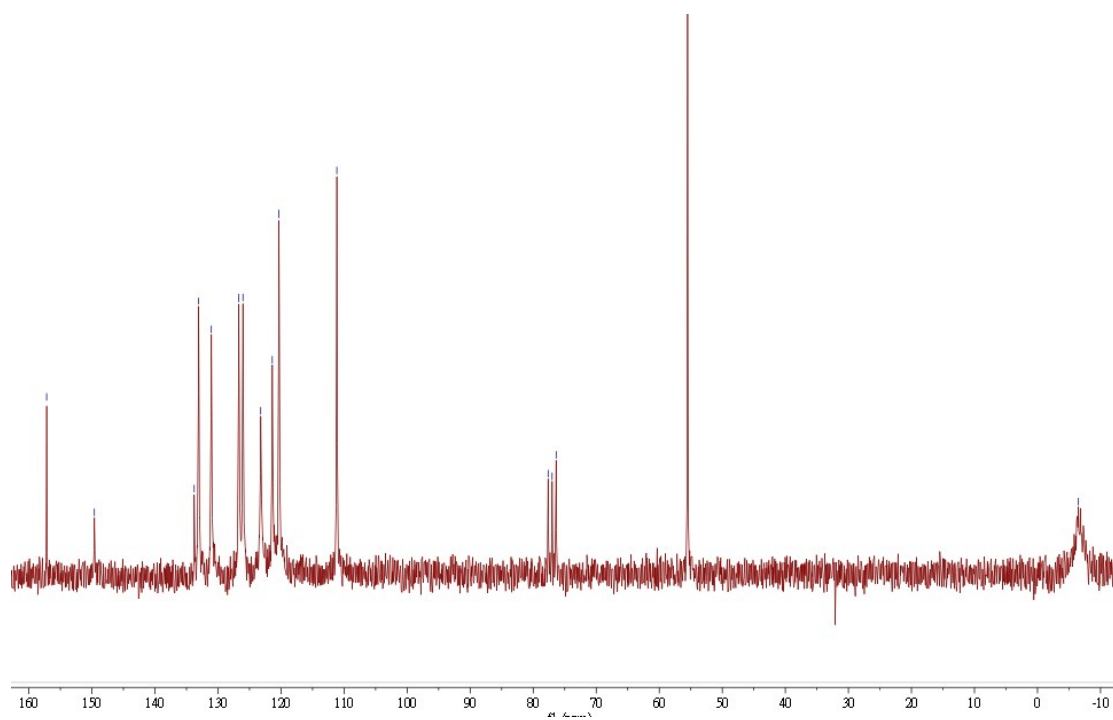


Figure S10  $^{13}\text{C}$  NMR spectrum of  $\text{L}^{\text{H2OMeAlMe}_3}$  in  $\text{CDCl}_3$

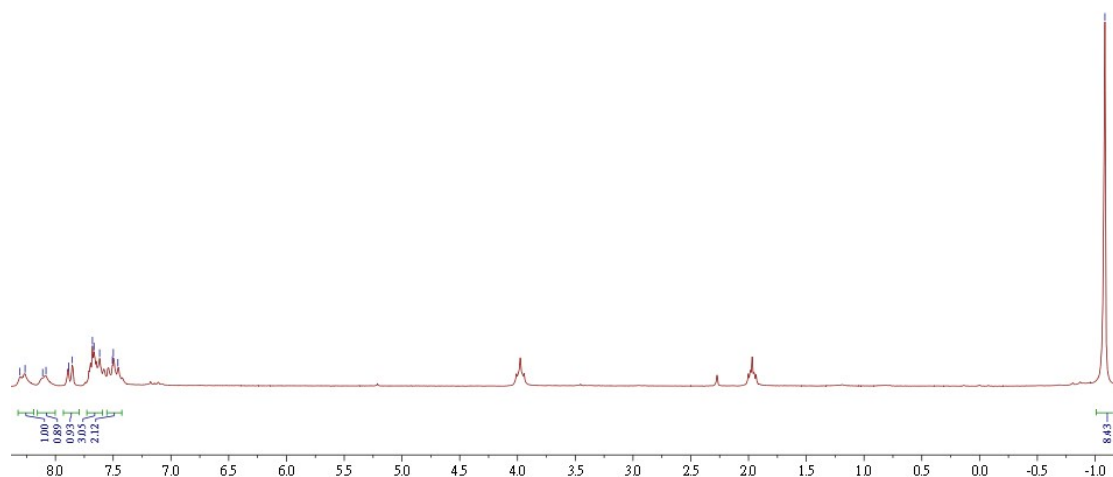


Figure S11  $^1\text{H}$  NMR spectrum of  $\text{L}^{\text{HNO}_2}\text{AlMe}_3$  in  $\text{CDCl}_3$

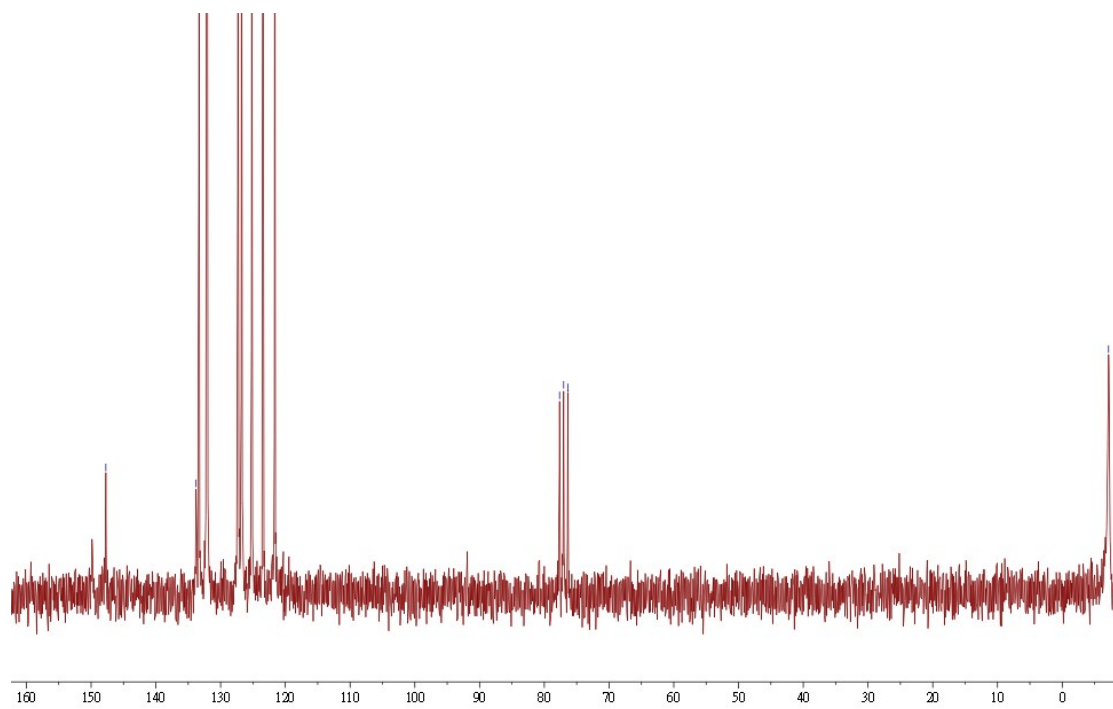


Figure S12  $^{13}\text{C}$  NMR spectrum of  $\text{L}^{\text{HNO}_2}\text{AlMe}_3$  in  $\text{CDCl}_3$

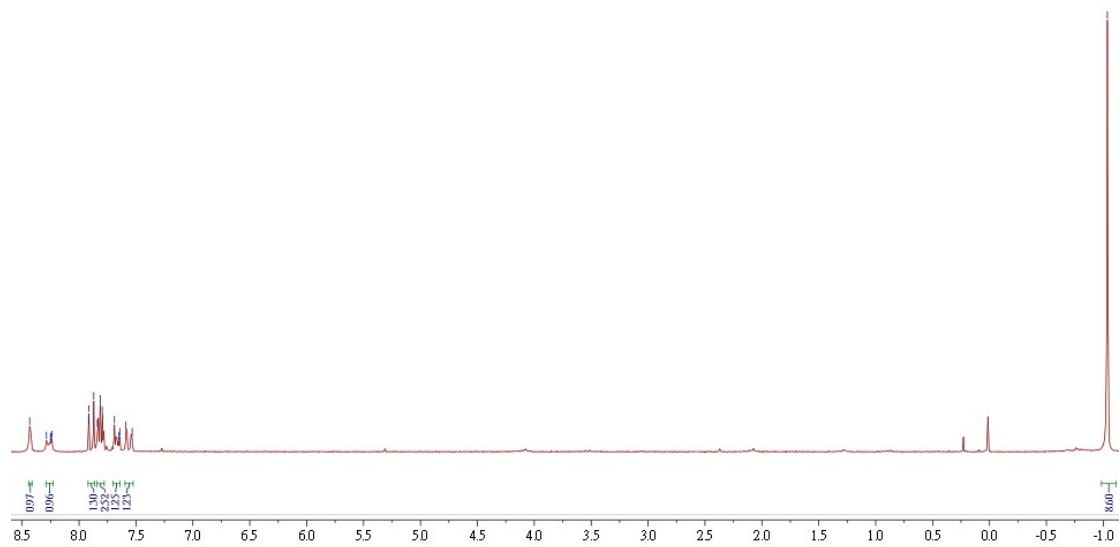


Figure S13  $^1\text{H}$  NMR spectrum of  $\text{L}^{\text{CINO}_2}\text{AlMe}_3$  in  $\text{CDCl}_3$

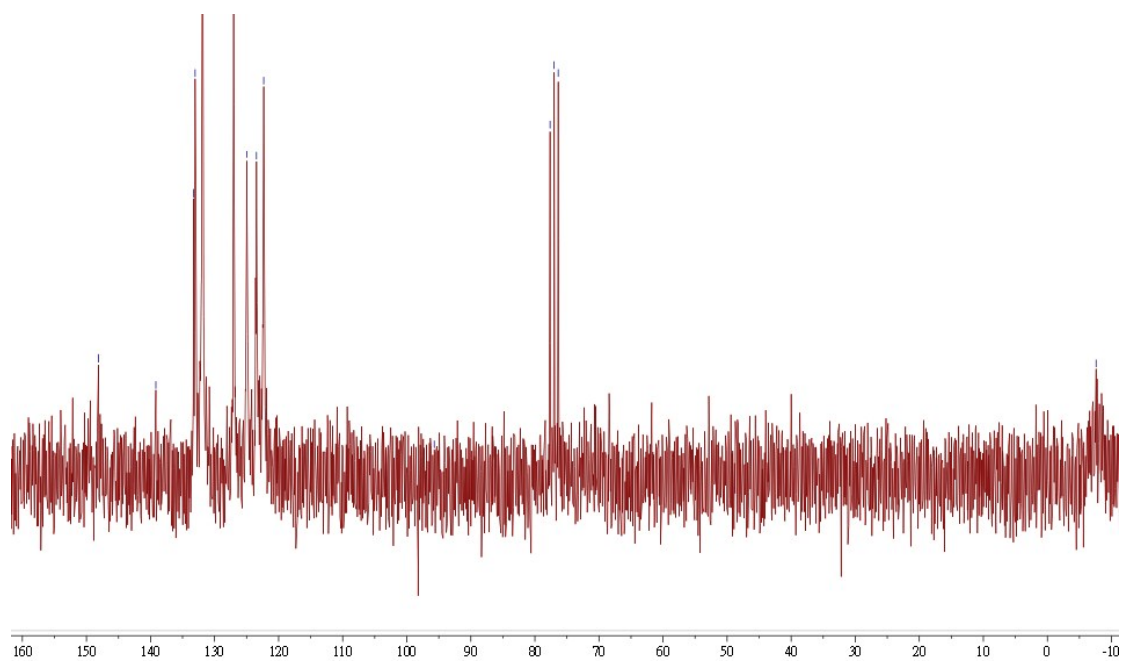


Figure S14  $^{13}\text{C}$  NMR spectrum of  $\text{L}^{\text{CINO}_2}\text{AlMe}_3$  in  $\text{CDCl}_3$

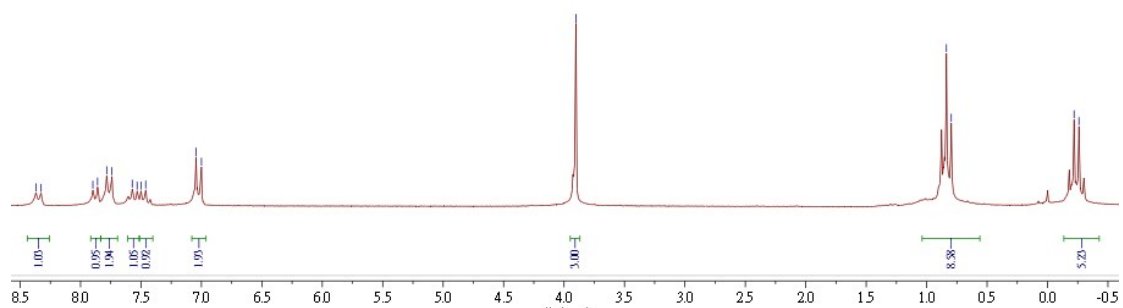


Figure S15  $^1\text{H}$  NMR spectrum of  $\text{L}^{\text{H4OMe}}\text{AlEt}_3$  in  $\text{CDCl}_3$

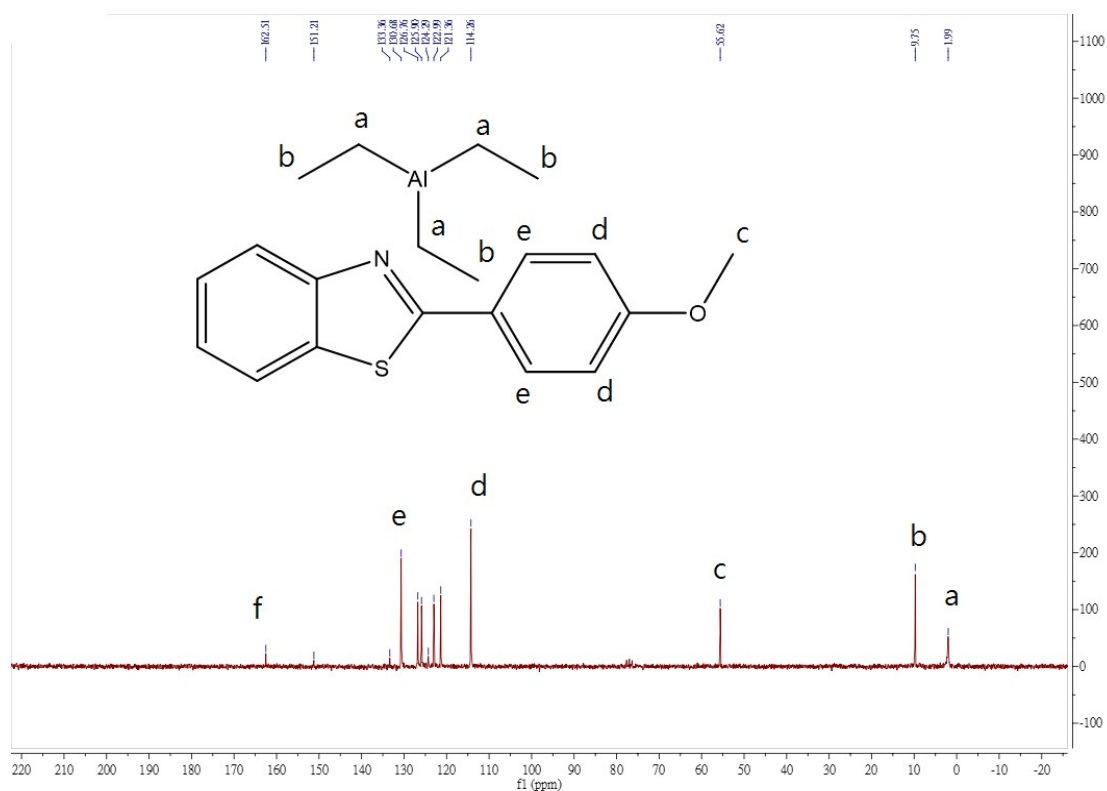


Figure S16  $^{13}\text{C}$  NMR spectrum of  $\text{L}^{\text{H4OMe}}\text{AlEt}_3$  in  $\text{CDCl}_3$

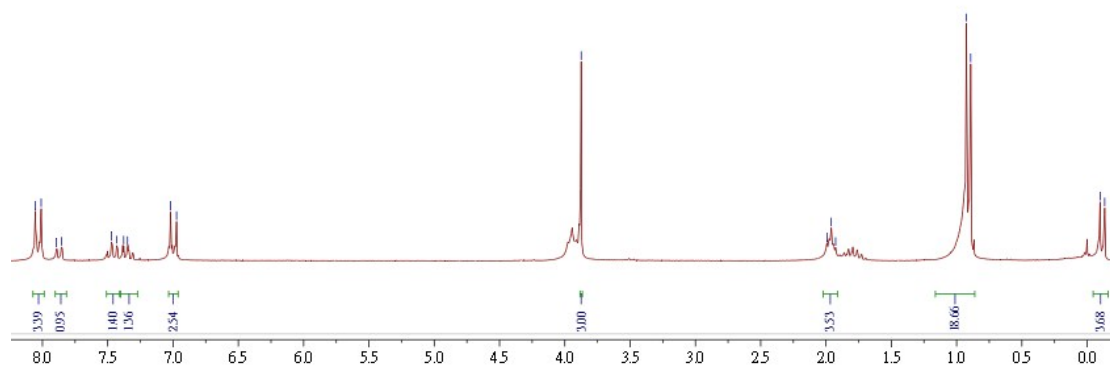


Figure S17  $^1\text{H}$  NMR spectrum of  $\text{L}^{\text{H4OMe}}\text{AlBu}_3$  in  $\text{CDCl}_3$

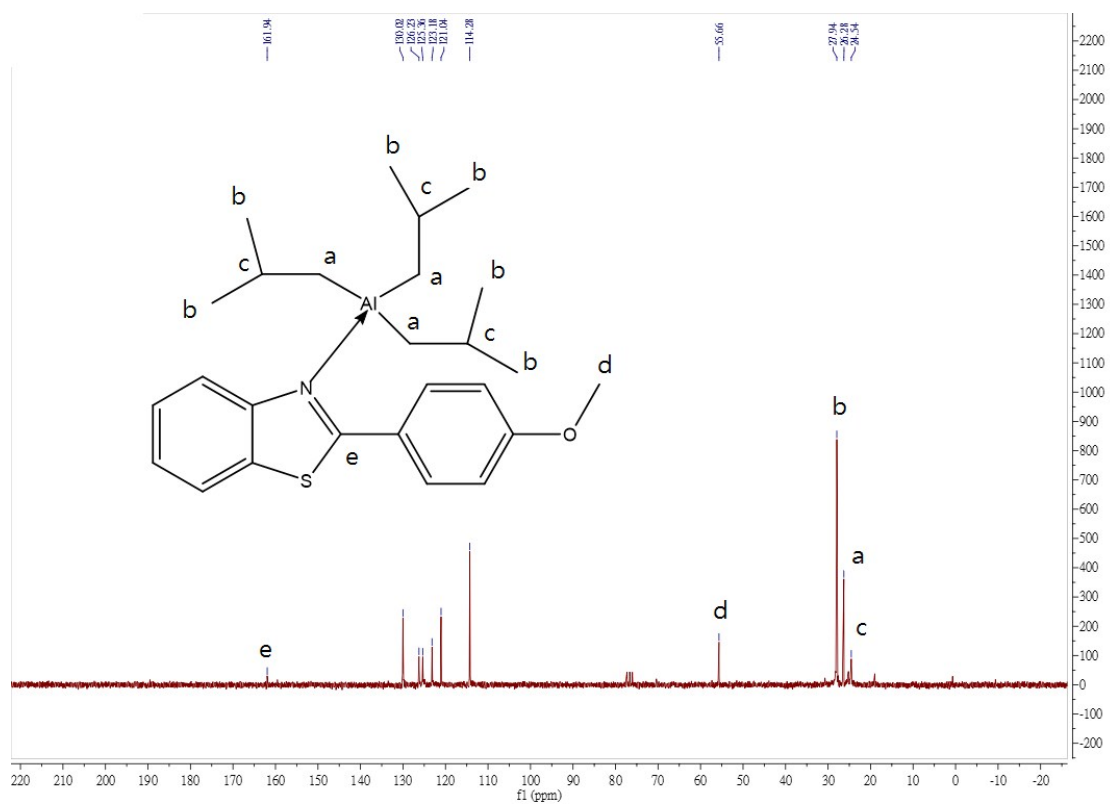


Figure S18  $^{13}\text{C}$  NMR spectrum of  $\text{L}^{\text{H4OMe}}\text{AlBu}_3$  in  $\text{CDCl}_3$



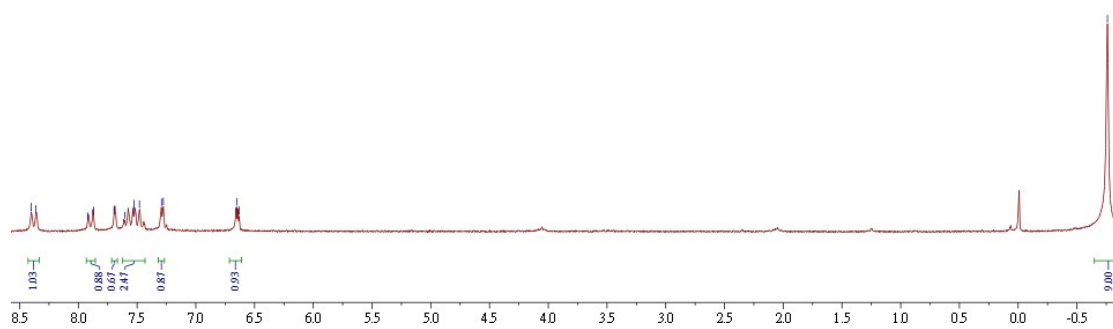


Figure S19  $^1\text{H}$  NMR spectrum of  $\text{L}^{\text{HFu}}\text{AlMe}_3$  in  $\text{CDCl}_3$

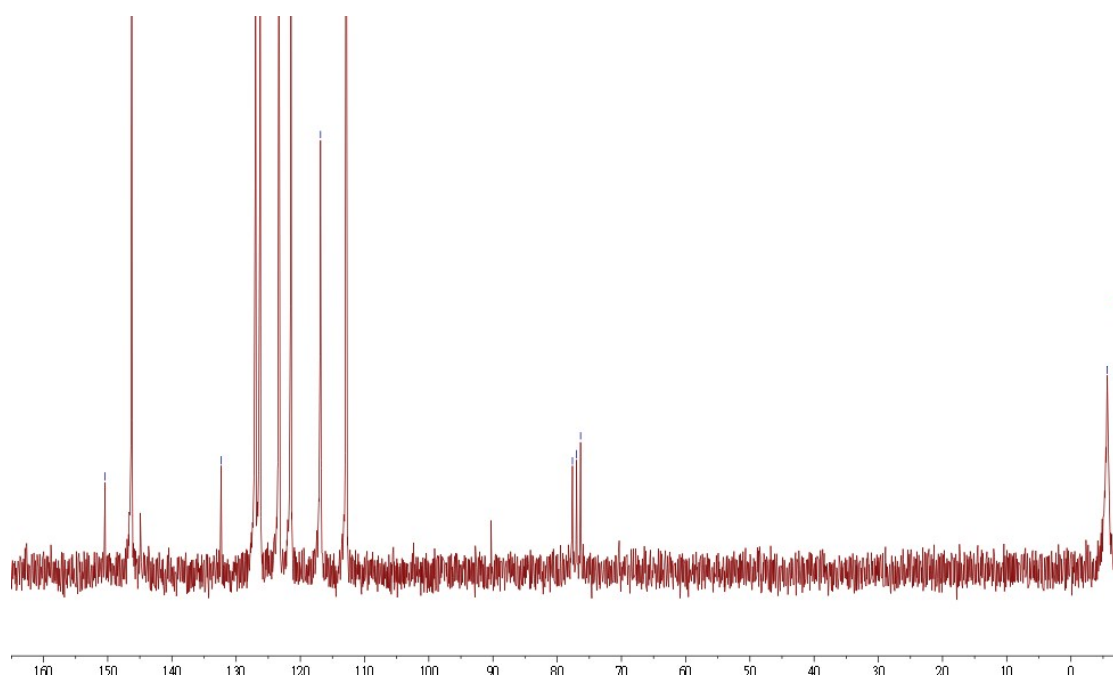


Figure S20  $^{13}\text{C}$  NMR spectrum of  $\text{L}^{\text{HFu}}\text{AlMe}_3$  in  $\text{CDCl}_3$

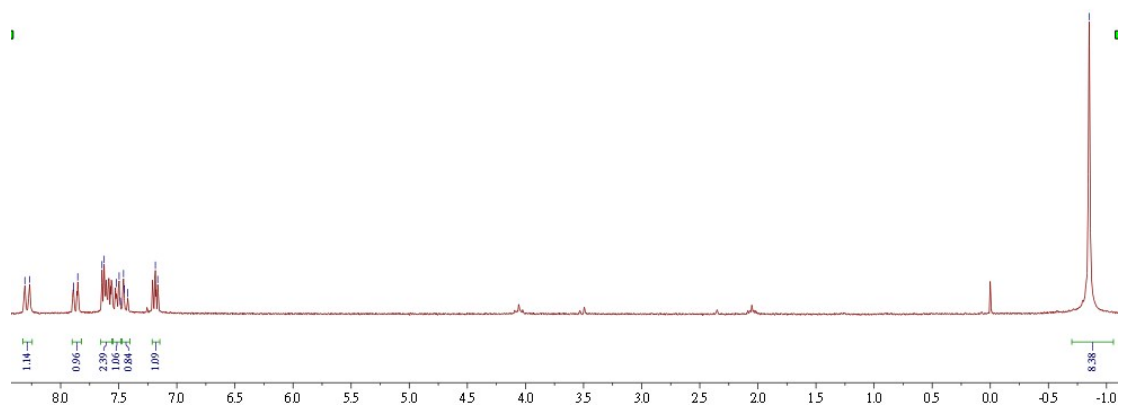


Figure S21  $^1\text{H}$  NMR spectrum of  $\text{L}^{\text{HTh}}\text{AlMe}_3$  in  $\text{CDCl}_3$

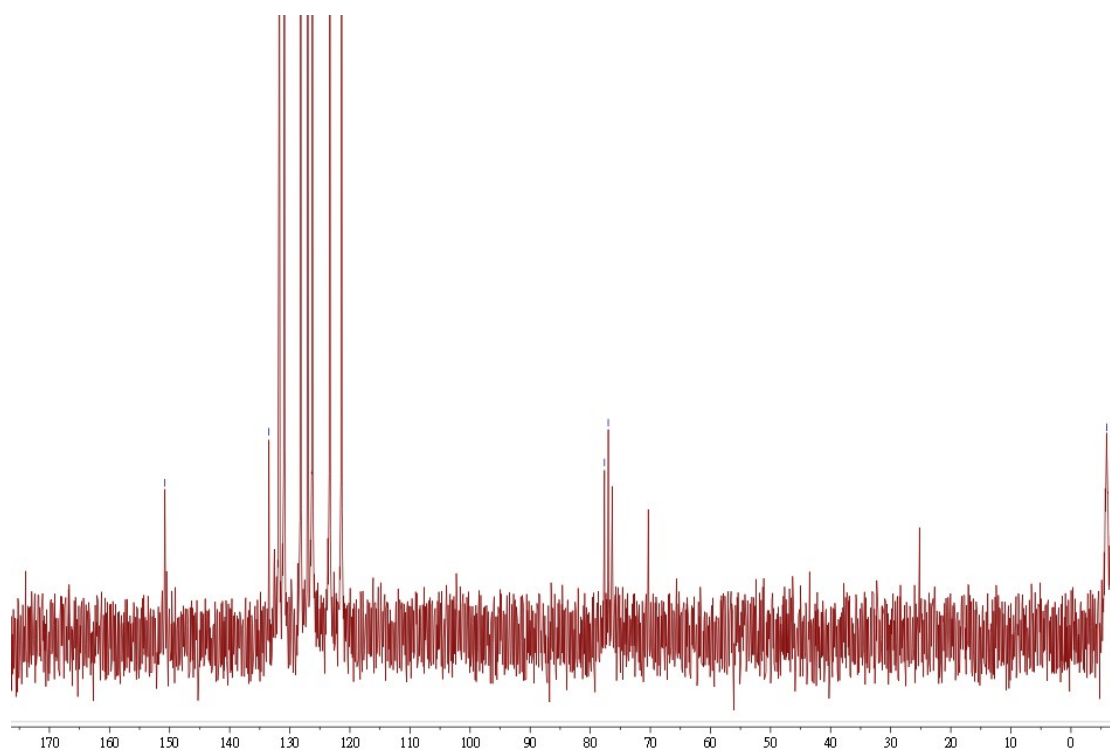


Figure S22  $^{13}\text{C}$  NMR spectrum of  $\text{L}^{\text{HTh}}\text{AlMe}_3$  in  $\text{CDCl}_3$

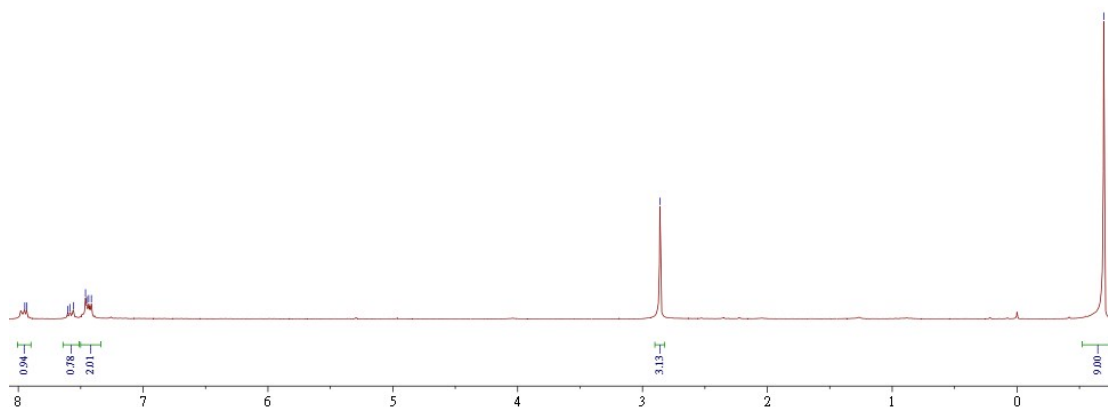


Figure S23  $^1\text{H}$  NMR spectrum of  $\text{L}^0\text{AlMe}_3$  in  $\text{CDCl}_3$

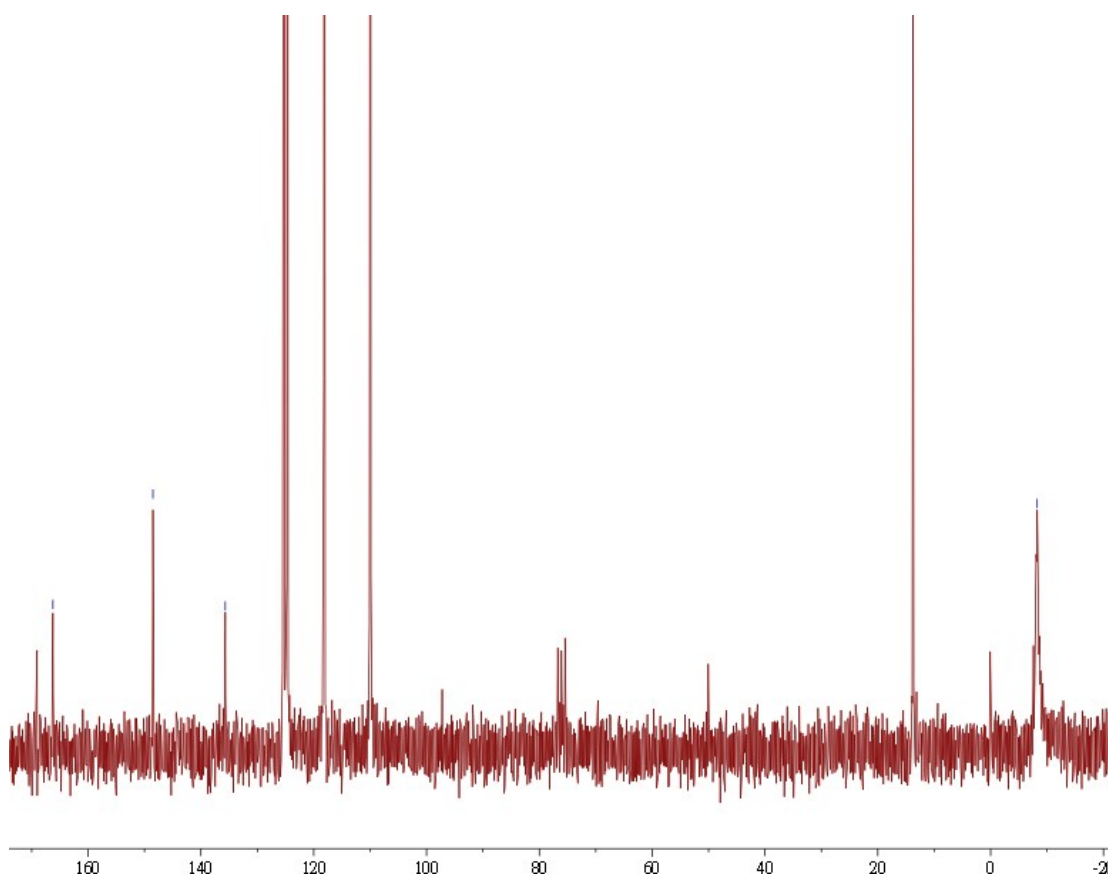


Figure S24  $^{13}\text{C}$  NMR spectrum of  $\text{L}^0\text{AlMe}_3$  in  $\text{CDCl}_3$

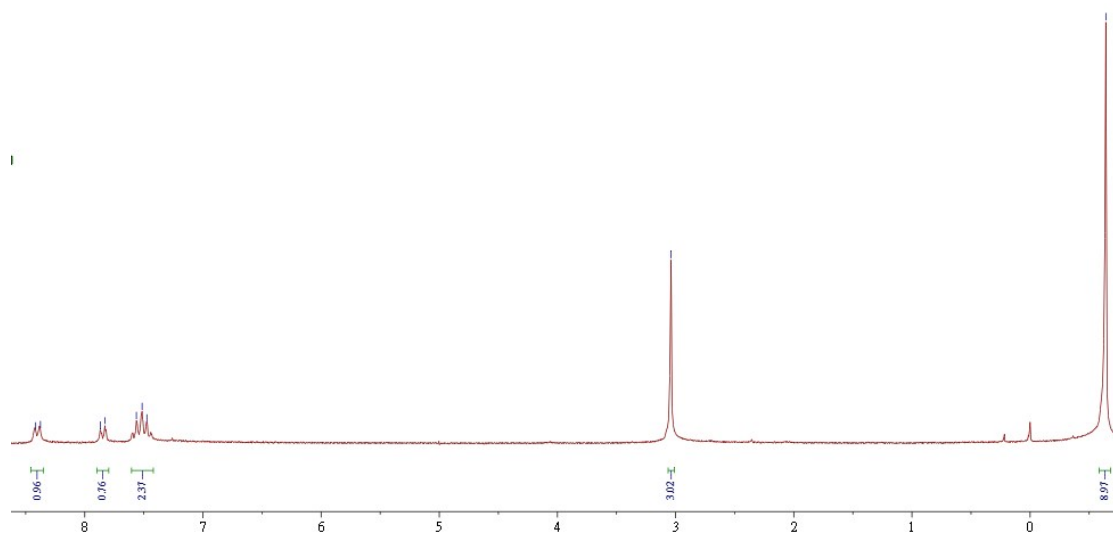


Figure S25  $^1\text{H}$  NMR spectrum of  $\text{L}^{\text{S}}\text{AlMe}_3$  in  $\text{CDCl}_3$

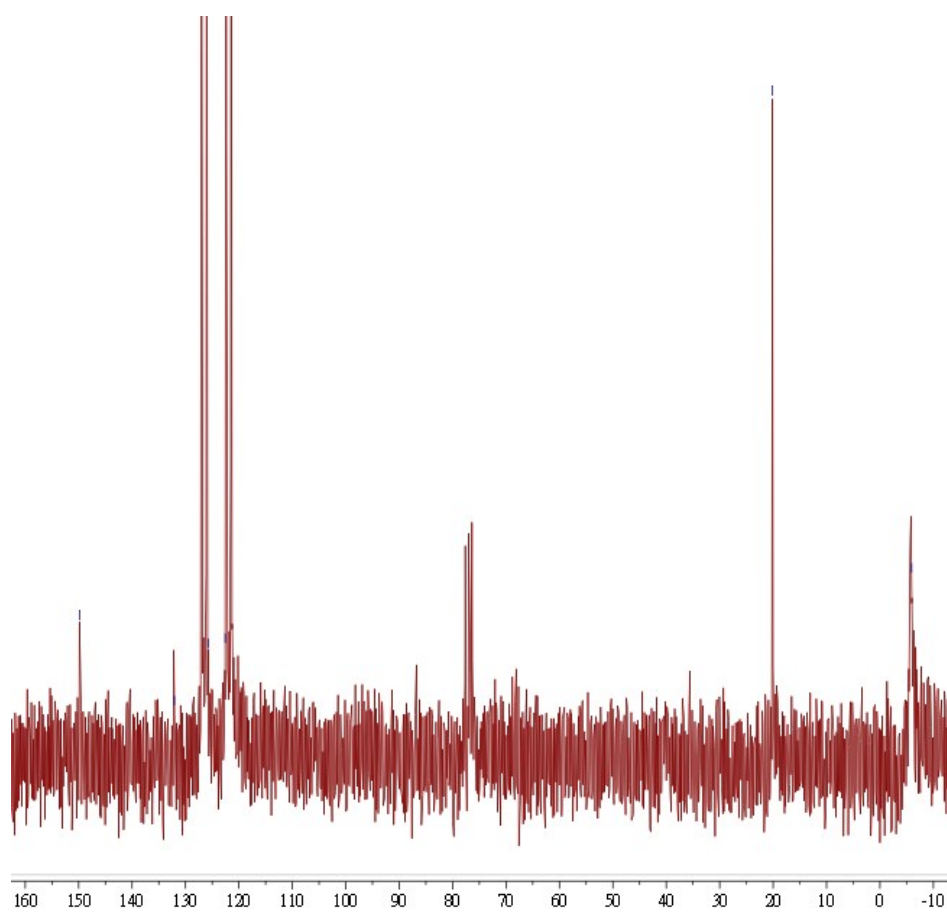
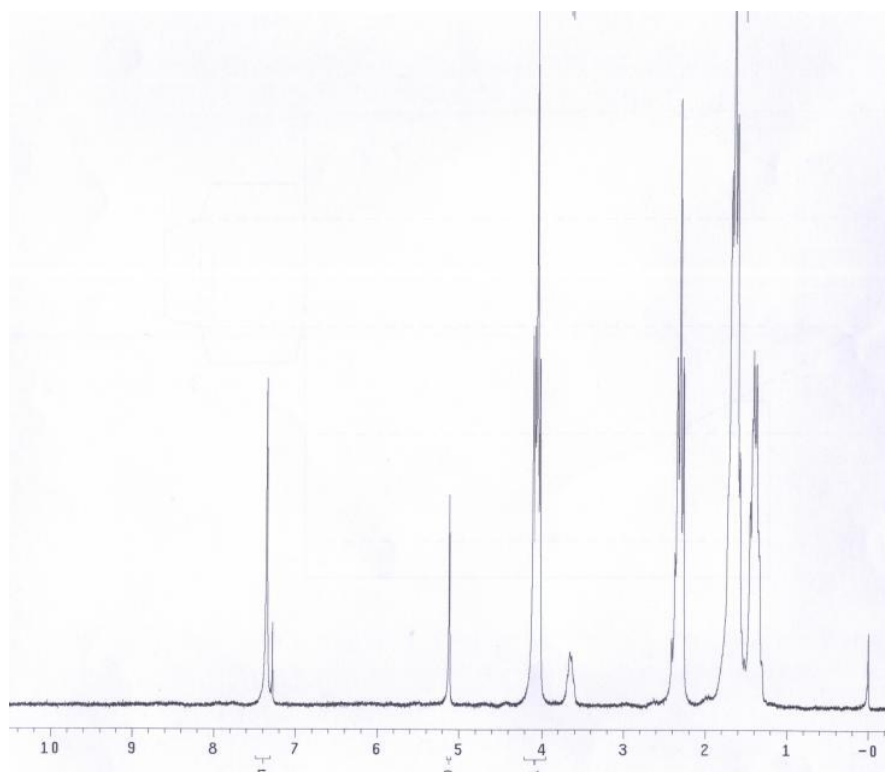
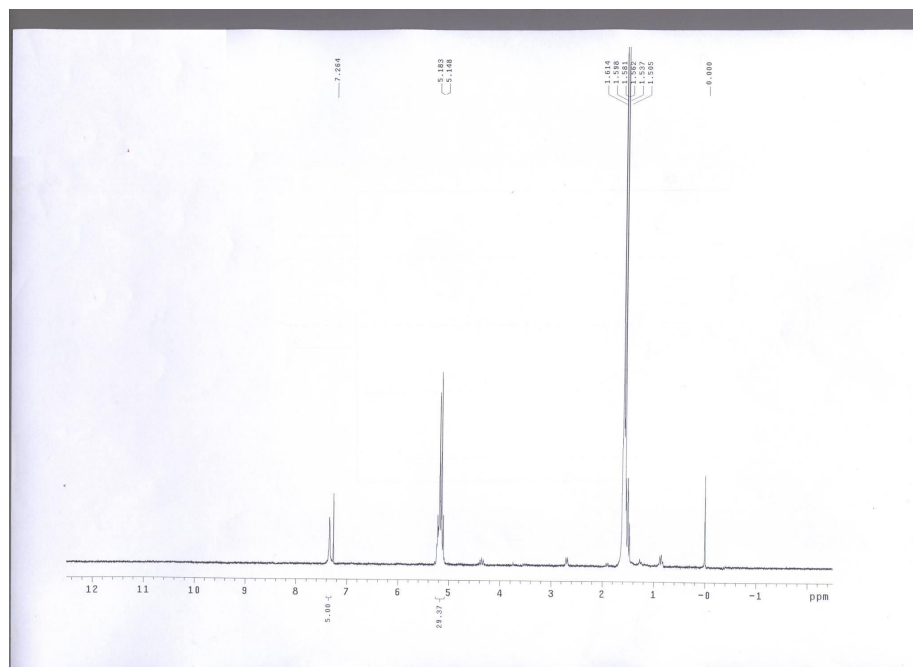


Figure S26  $^{13}\text{C}$  NMR spectrum of  $\text{L}^{\text{S}}\text{AlMe}_3$  in  $\text{CDCl}_3$



**Figure S27** <sup>1</sup>H NMR spectrum of PCL (Table 1, entry 18)



**Figure S28** <sup>1</sup>H NMR spectrum of PLA (Table 2, entry 18)