Optimizing Ring-opening Polymerization of ε-Caprolactone by Using Aluminum Complexes Bearing Amide as Catalysts and Their Application in Synthesizing Poly-ε-caprolactone with Special Initiators and Other Polycycloesters

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Table S1 Kinetic study of CL polymerization with various Al complexes in toluene 5

mL, [CL] = 2.0 M at room temperature

time	**TsOMe**	**TsiPr**	**MsOMe**	**MsiPr**	**TcOMe**	**TciPr**	**CbOMe**	**CbiPr**	**MfOMe**
min	Conv.(%)								
5									8
10	4		2				10		23
13		6							
15		9		10				39	39
17		12							
20	24	16	42	22	19		20		50
25				28					59
30	37		60	37.5			43	68	
35									74
40		27	76	52	43		56	78	
45						39		84	83
50	58		82	63			64	88	
58								92	
60	65	42	89	74	6	68	69		91
70	74		92				78		
75						78			95
80	80	52		86	74		83		
90	84					84	86		
100	88	62		92	78	88	89		
110							93		
120		68			86	92			
140		74			90				
160		79							
220		89							
$\mathbf{k_{obs}}$	0.0227 (5)	0.0102 (1)	0.0394 (10)	0.0290 (6)	0.0173 (5)	0.0263 (18)	0.0248 (7)	0.0471 (2)	0.0422 (3)
IP	9.70 (147)	6.27 (96)	5.34 (116)	13.07 (109)	7.12 (280)	20.5 (58)	8.67 (193)	5.6 (18)	3.36 (26)

Table S2 Kinetic study of CL polymerization with various concentration of

MfOMeAlMe2 in toluene 5 mL, [CL] = 2.0 M at room temperature

Time	[CL] : [**MfOMeAlMe2**] : [BnOH]			
	100:0.5: 1	100:1: 2	100:1.5: 3	100:2: 4
min	Conv.(%)			
3				0.37
5		8	0.22	0.53
10		23	0.4	0.73
13				0.82
15		39	0.64	0.87
17				0.89
18			0.72	
20		50	0.78	
25		59		
30			0.93	
35		74		
45		8913		
60		95		
72				
120	0.11			
150	0.17			
230	0.26			
290	0.3			
350	0.36			
kobs	0.0014 (1)	0.0422 (3)	0.0980 (61)	0.1257 (34)
IP	22.91 (1530)	3.36 (26)	4.05 (114)	0

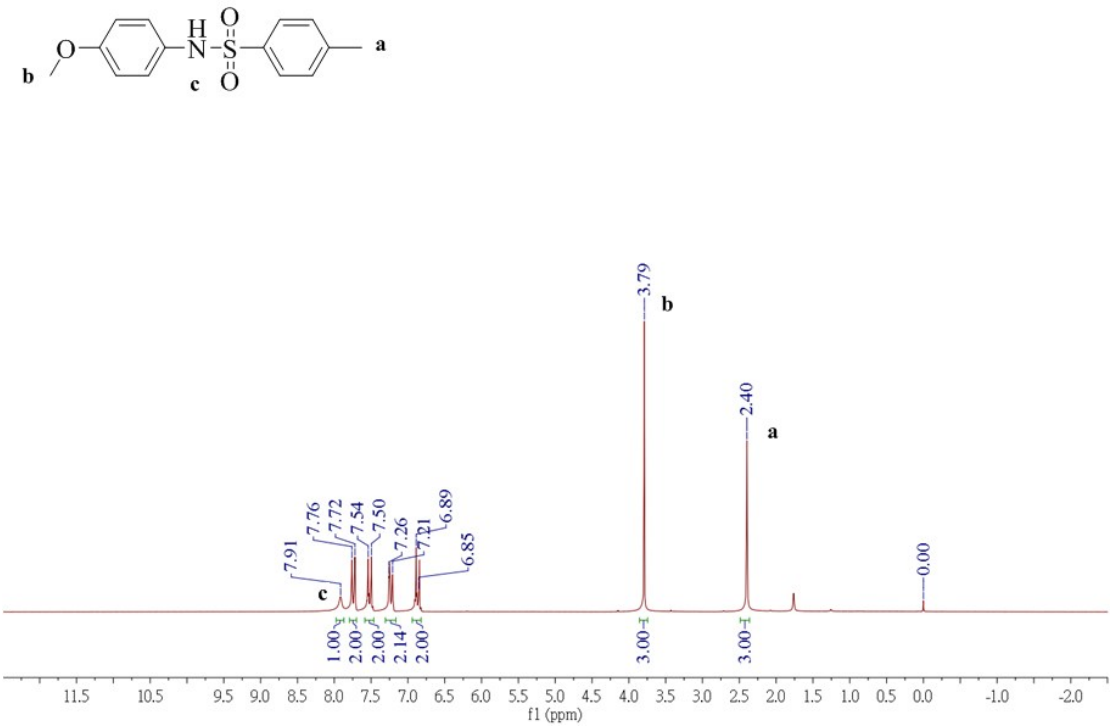


Figure S1 ^{1}H NMR spectrum of TsOMe-H in $CDCl_3$

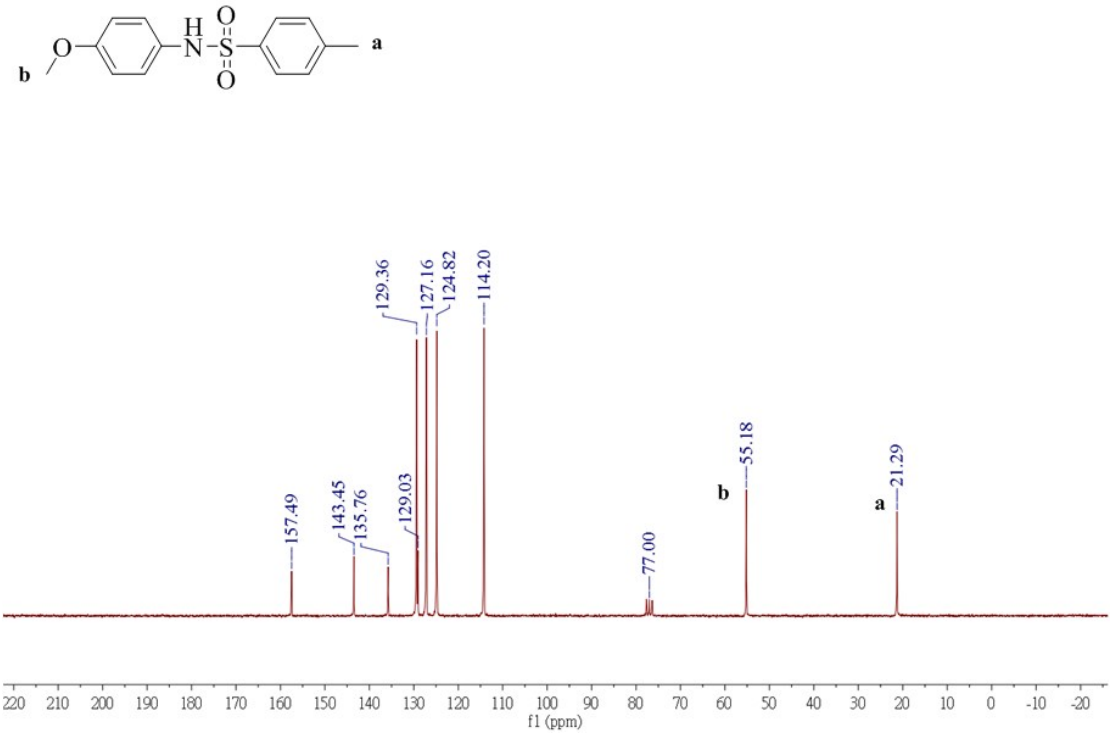


Figure S2 ^{13}C NMR spectrum of TsOMe-H in $CDCl_3$

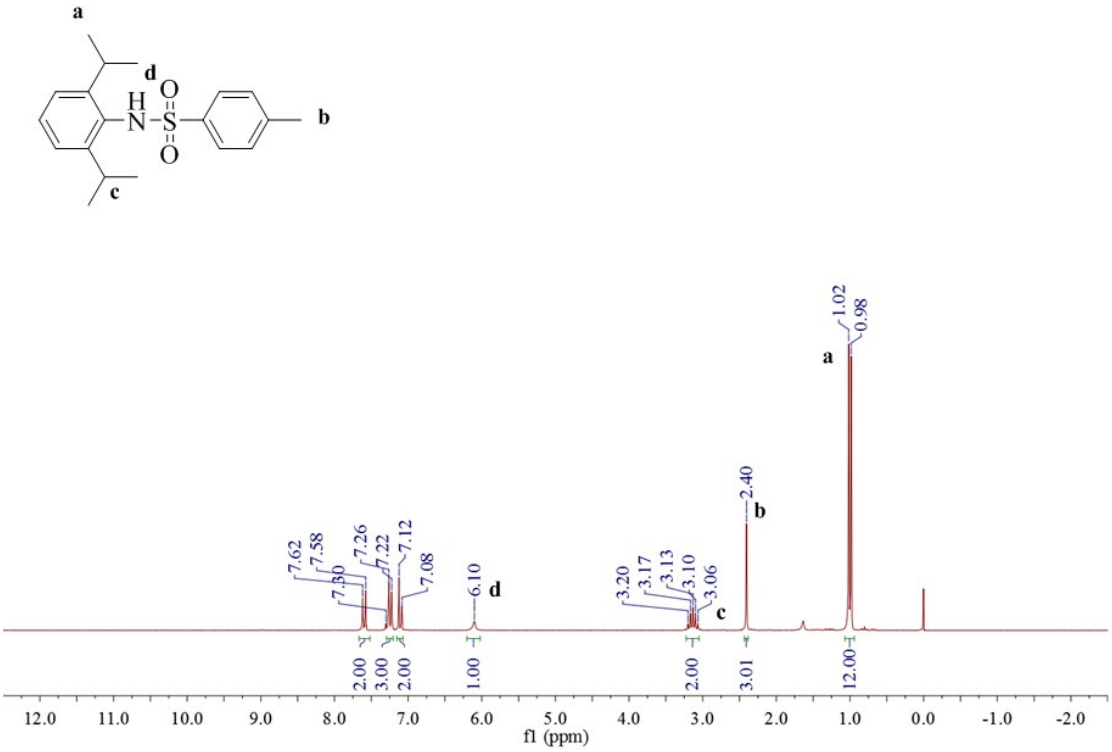


Figure S3 ^{1}H NMR spectrum of TsiPr-H in $CDCl_3$

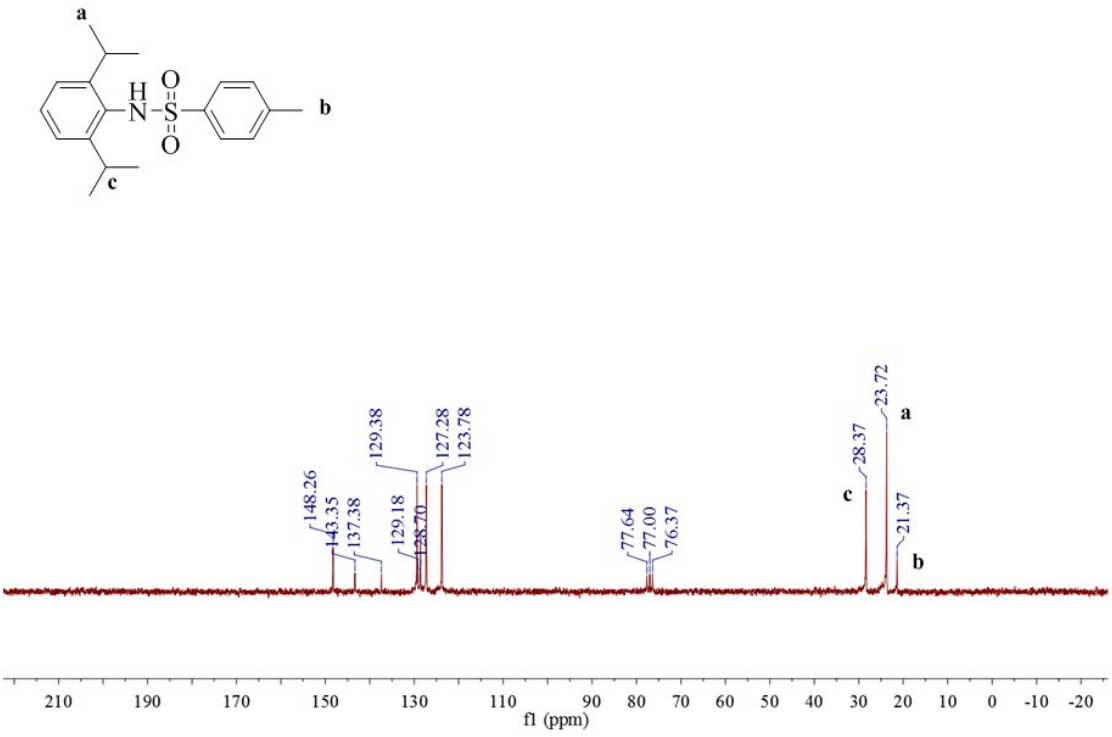


Figure S4 ^{13}C NMR spectrum of TsiPr-H in $CDCl_3$

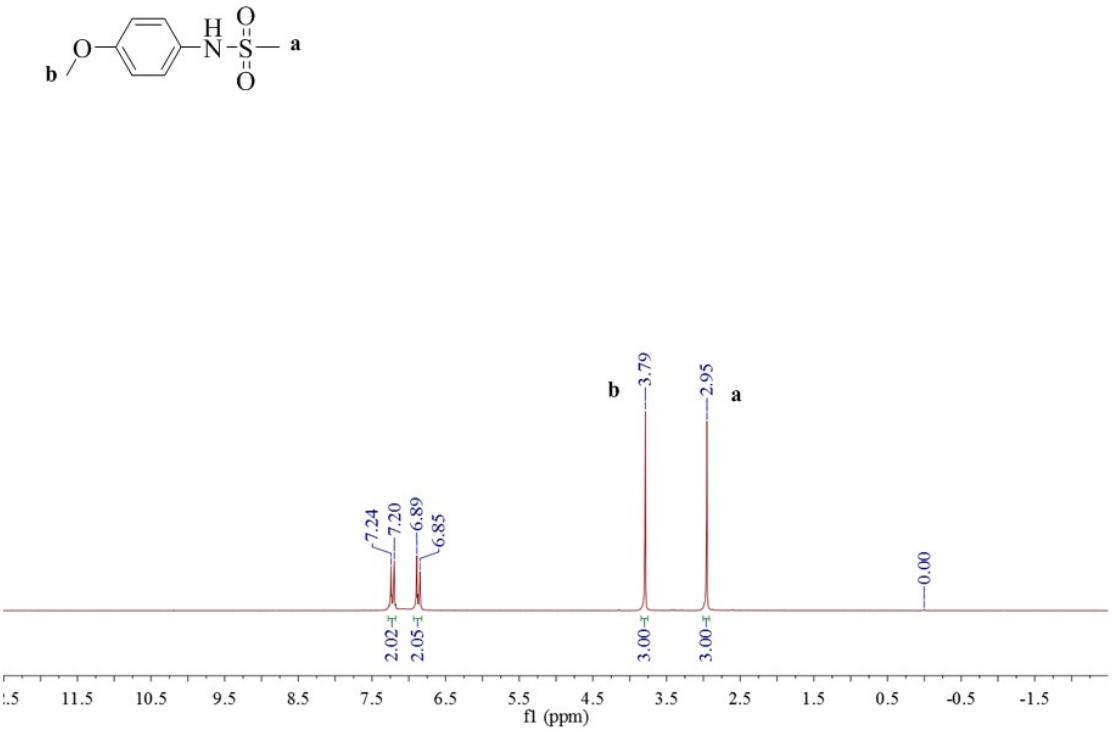


Figure S5 ^{1}H NMR spectrum of MsOMe-H in $CDCl_3$

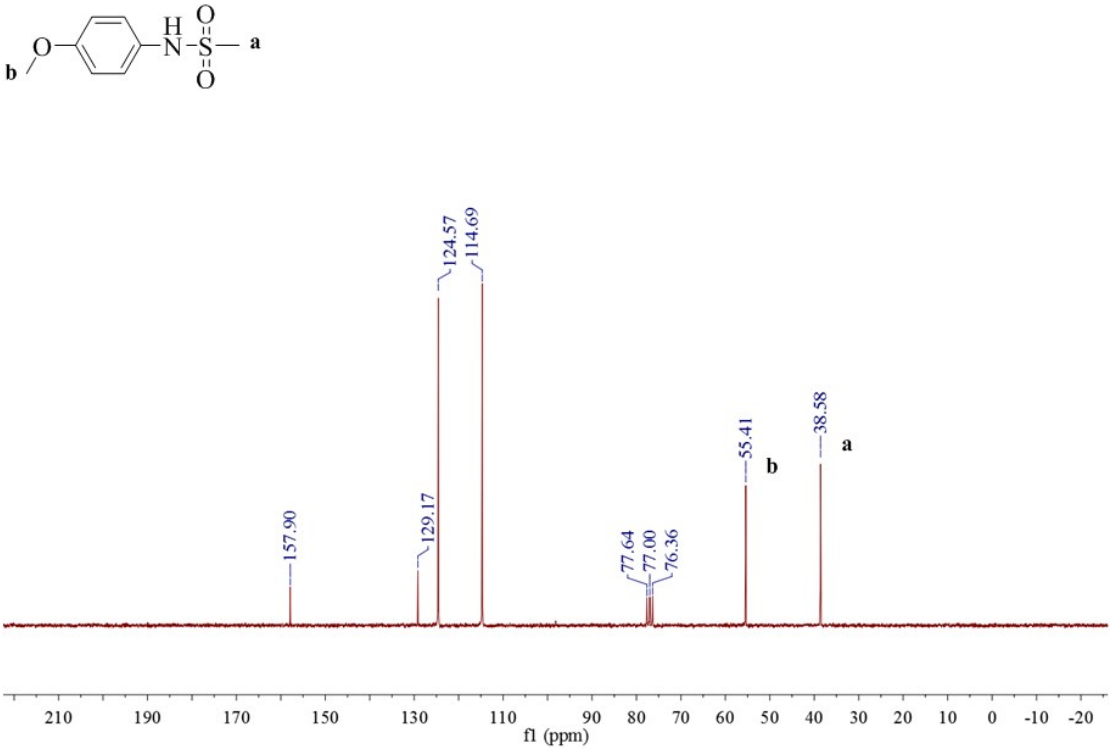


Figure S6 ^{13}C NMR spectrum of MsOMe-H in $CDCl_3$

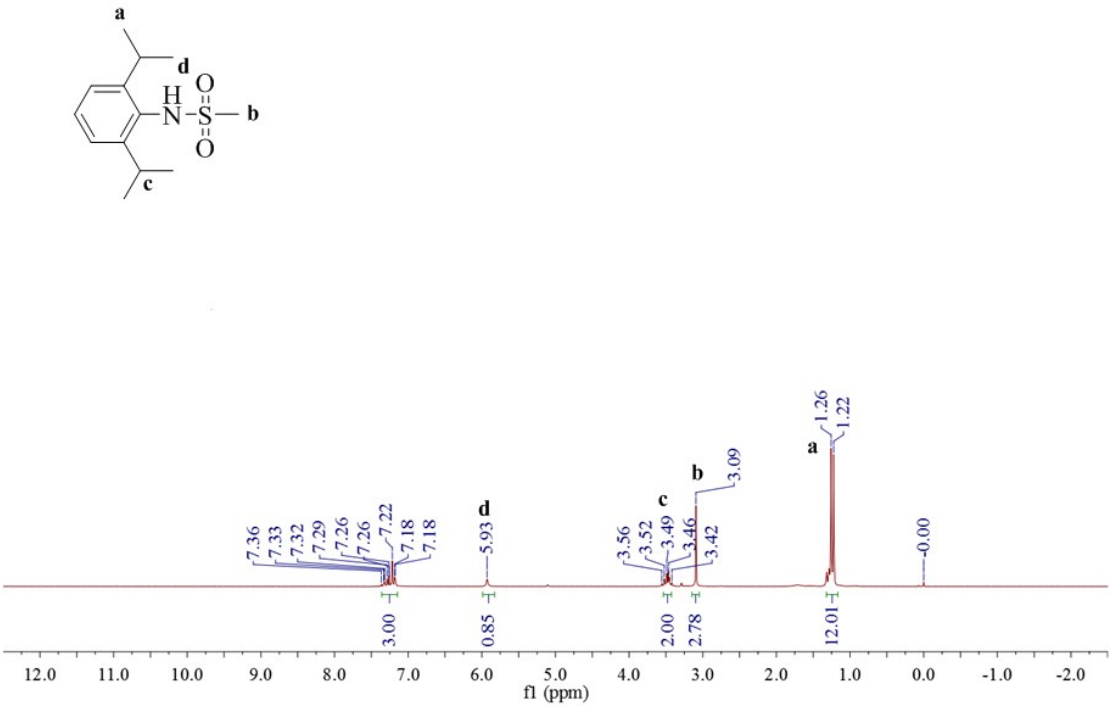


Figure S7 ^{1}H NMR spectrum of MsiPr-H in $CDCl_3$

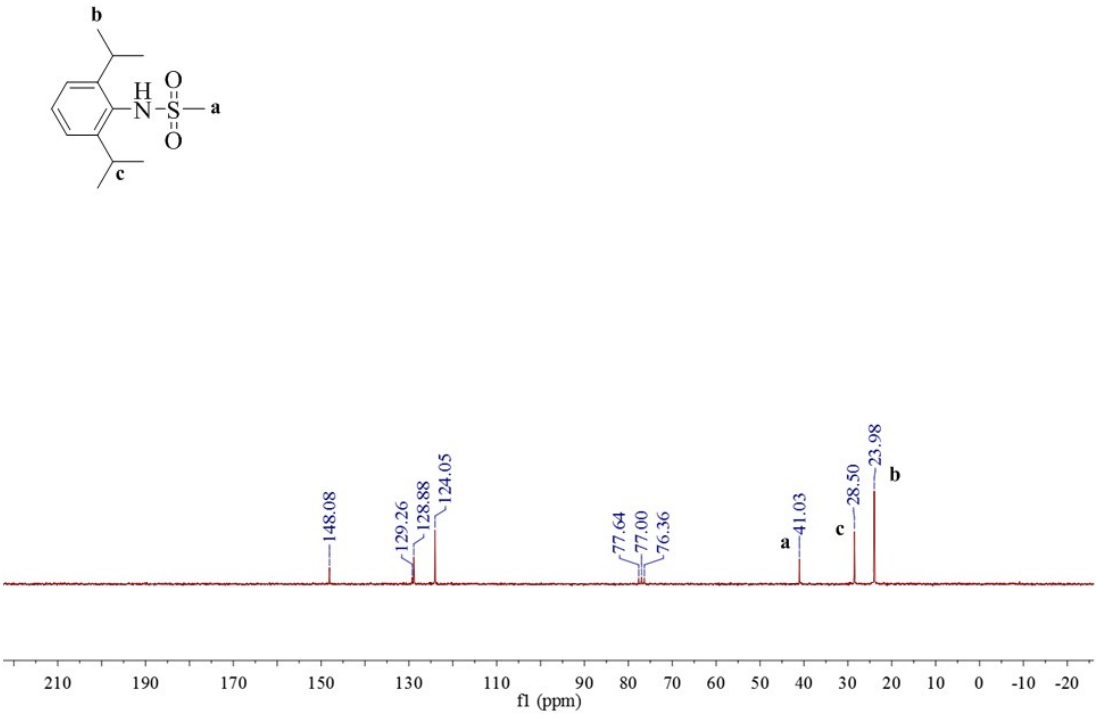


Figure S8 ^{13}C NMR spectrum of MsiPr-H in $CDCl_3$

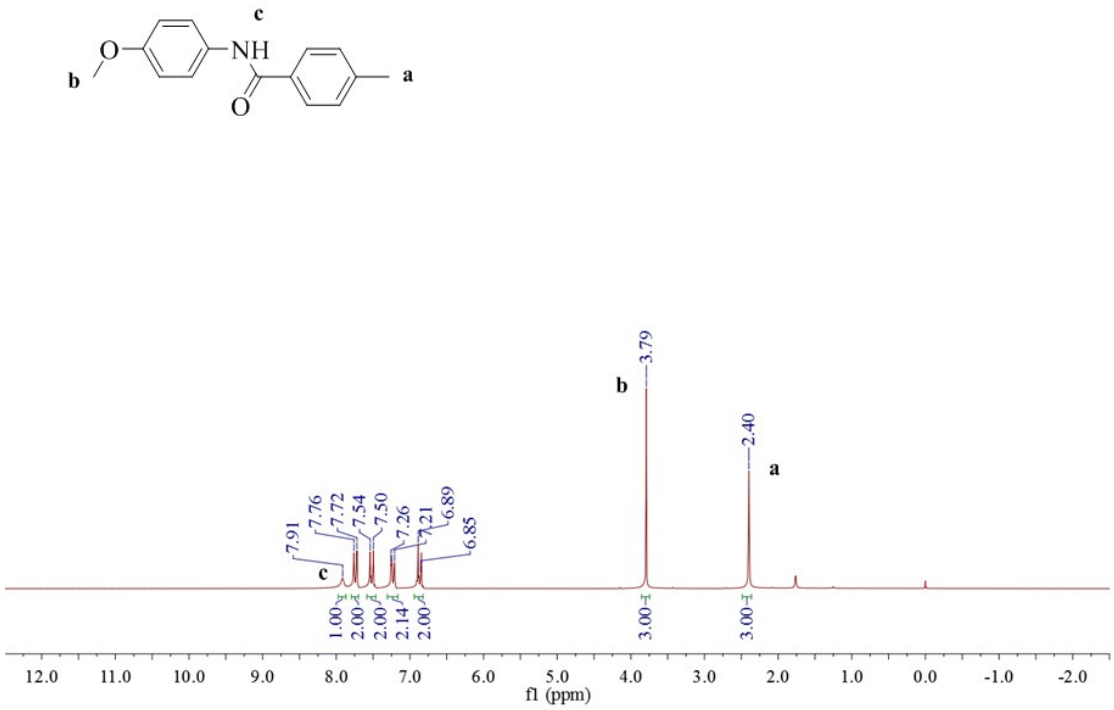


Figure S9 ^{1}H NMR spectrum of TcOMe-H in $CDCl_3$

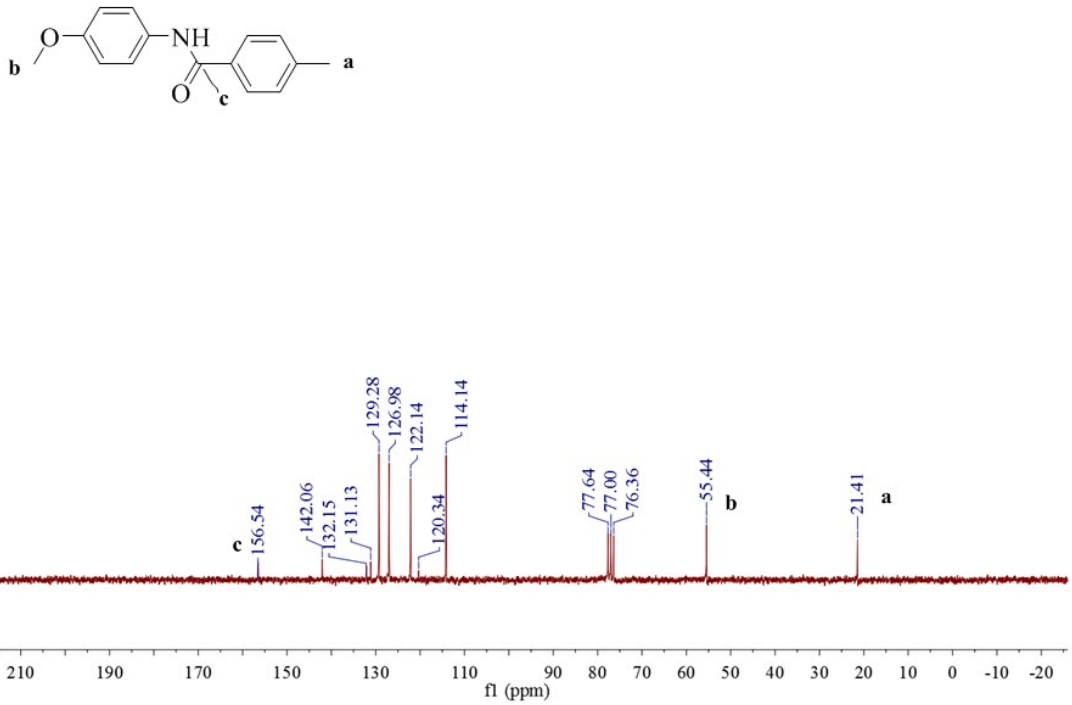


Figure S10 ^{13}C NMR spectrum of TciOMe-H in $CDCl_3$

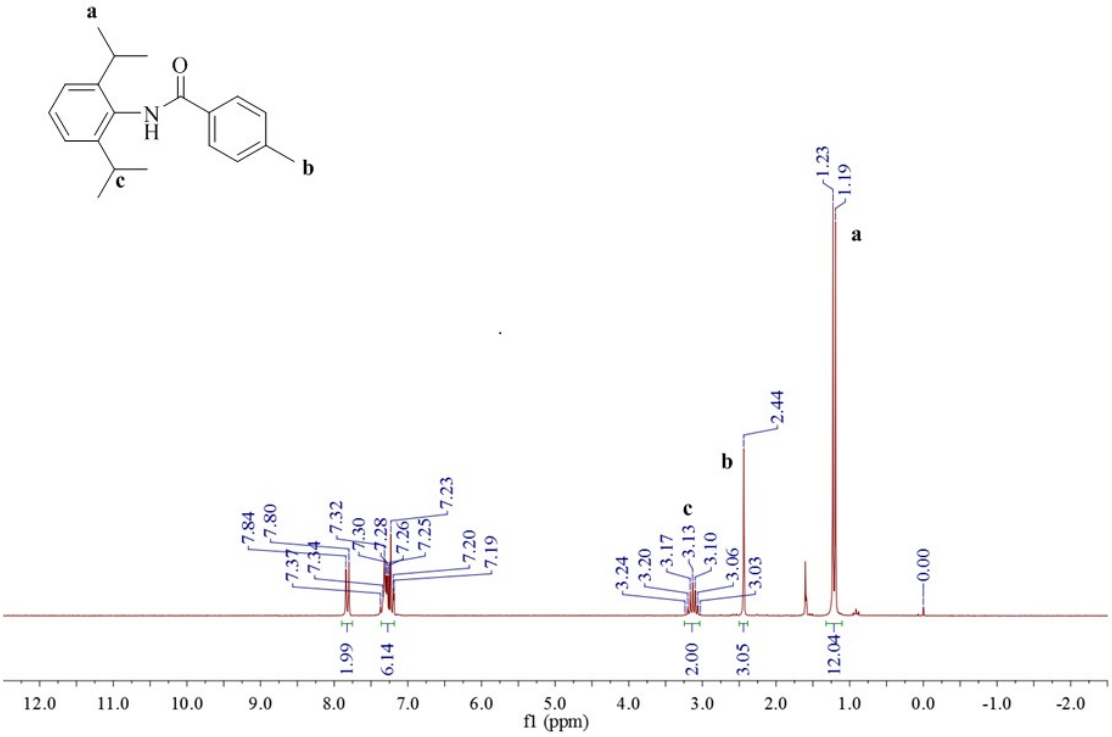


Figure S11 ^{1}H NMR spectrum of TciPr -H in $CDCl_3$

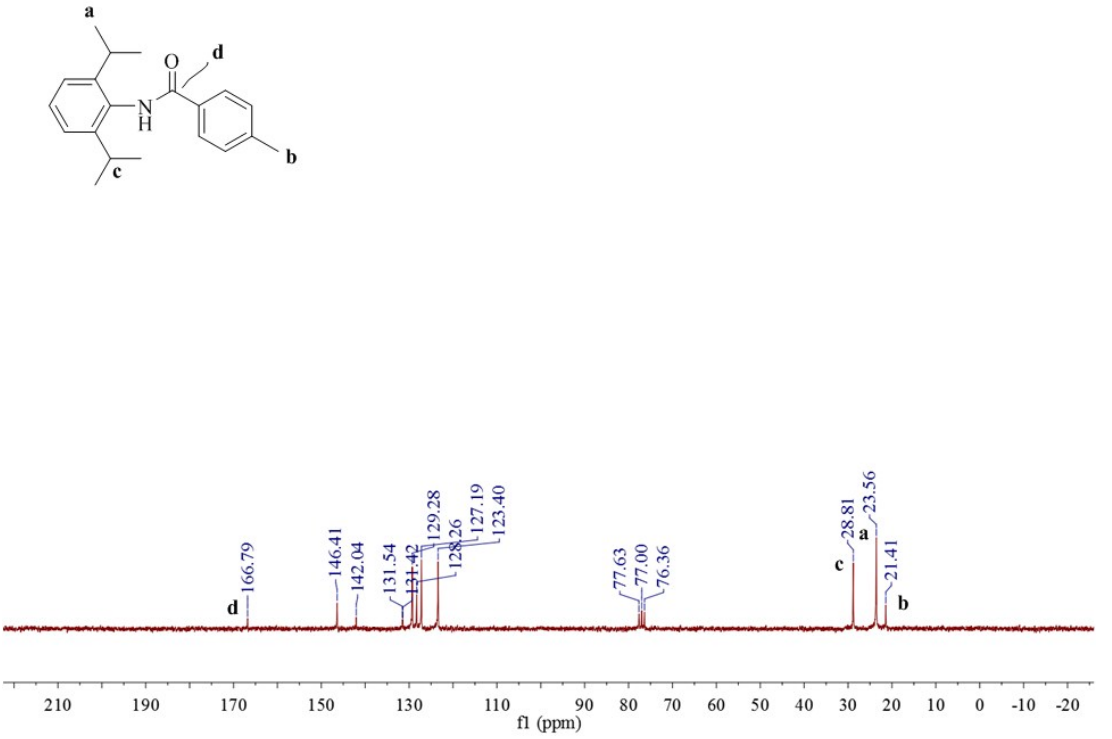


Figure S12 ^{13}C NMR spectrum of TciPr -H in $CDCl_3$

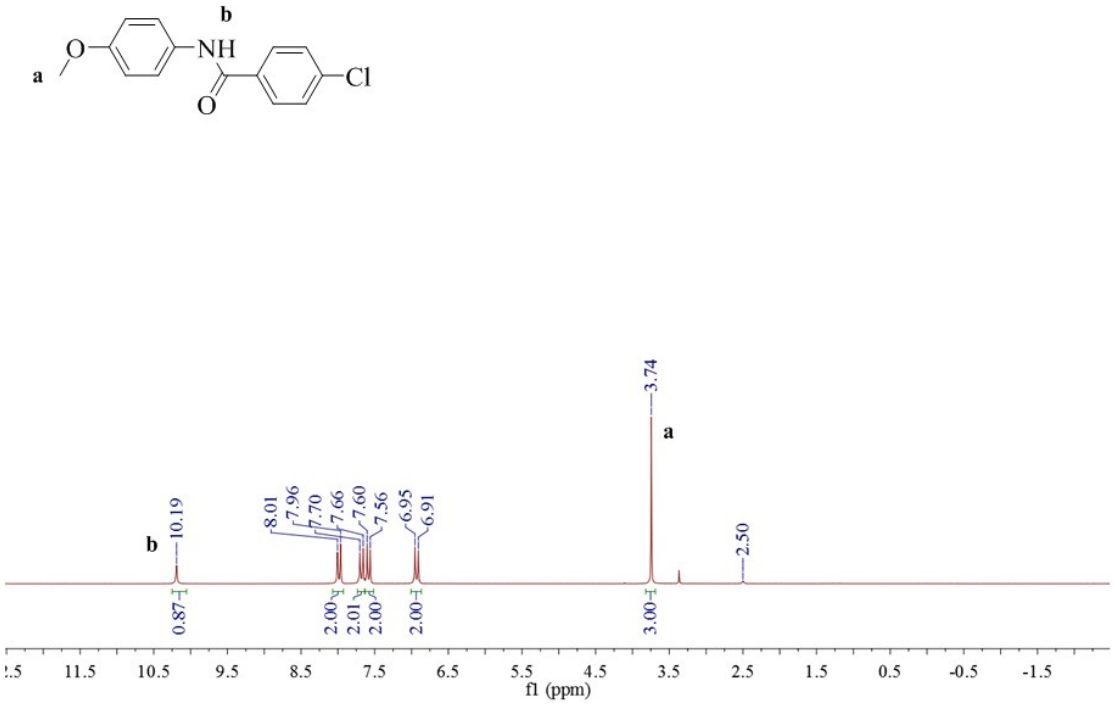


Figure S13 [1]H NMR spectrum of CbOMe-H in d-DMSO

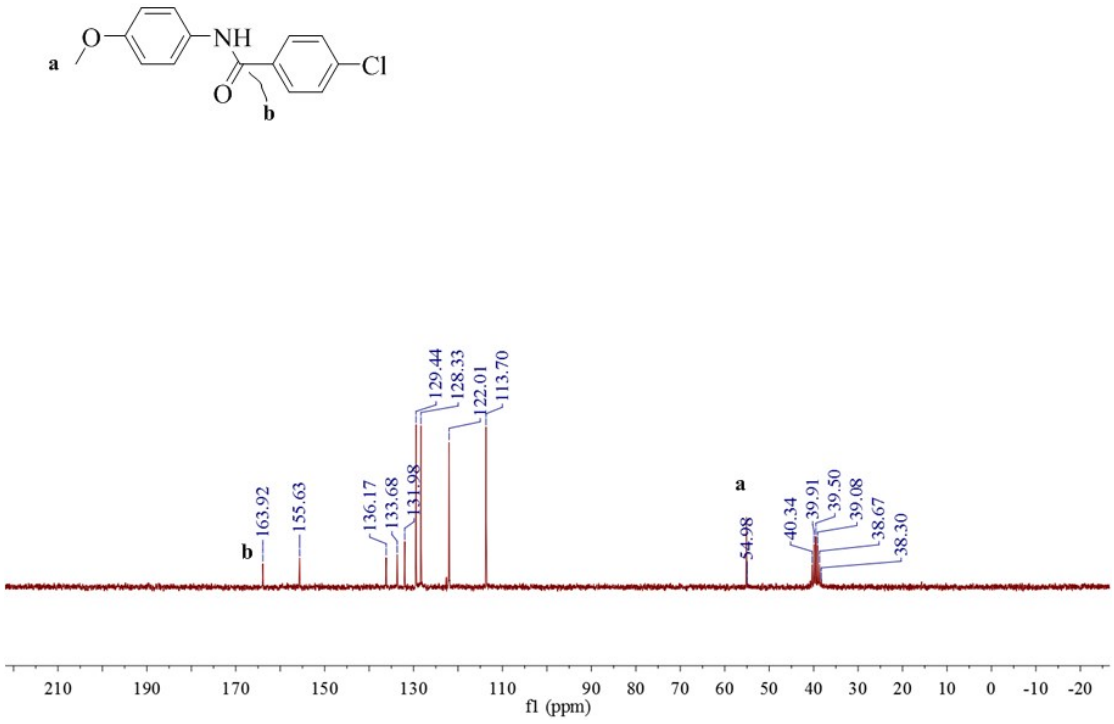


Figure S14 [13]C NMR spectrum of CbOMe-H in d-DMSO

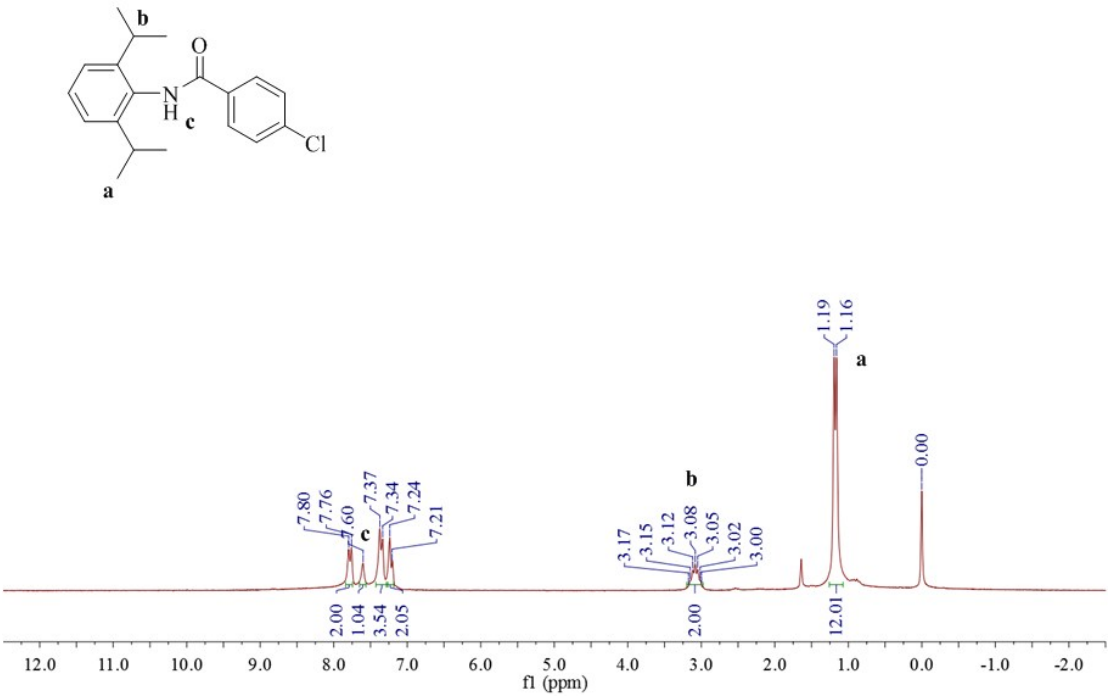


Figure S15 ^{1}H NMR spectrum of CbiPr-H in $CDCl_3$

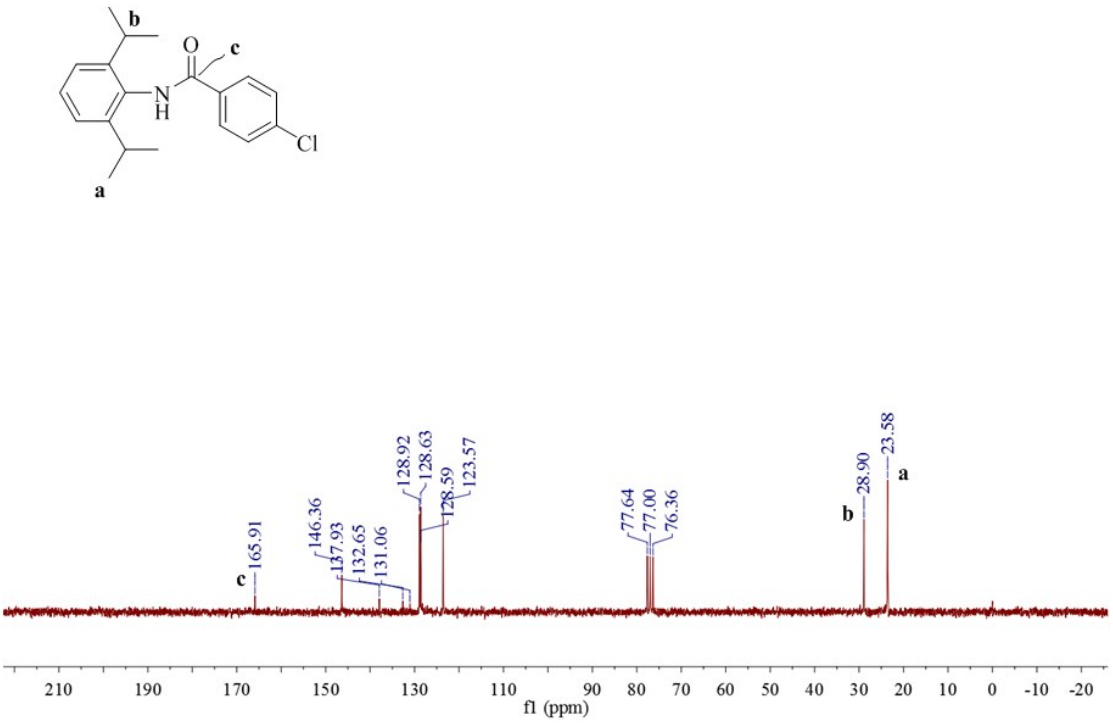


Figure S16 ^{13}C NMR spectrum of CbiPr -H in $CDCl_3$

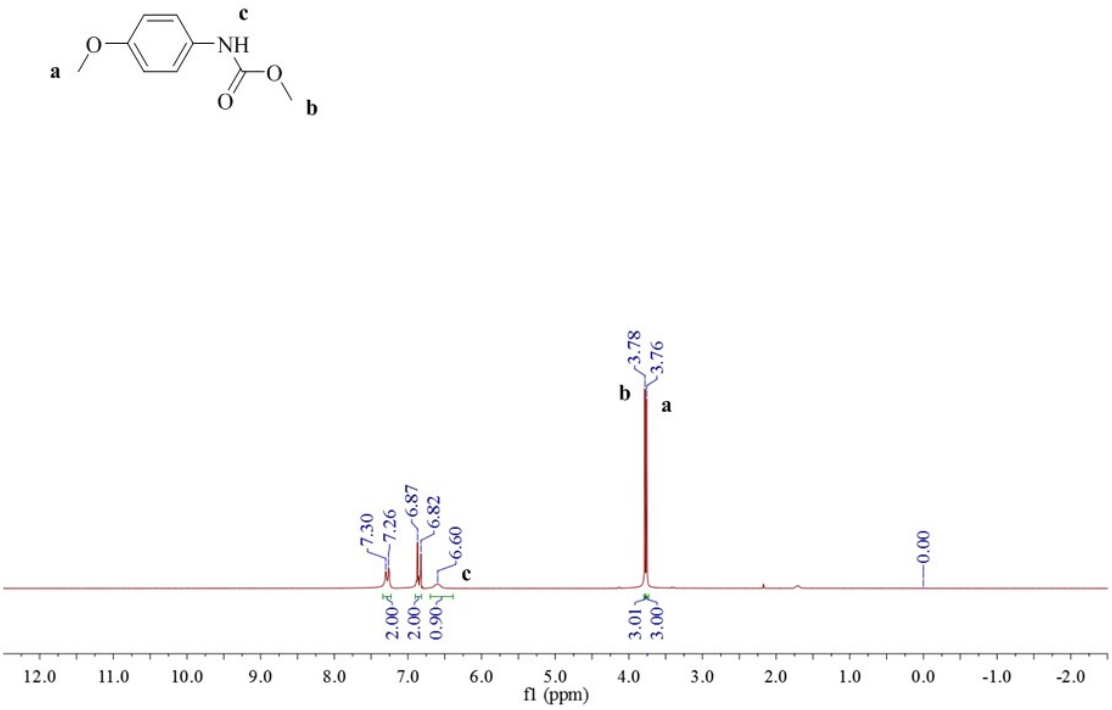


Figure S17 ^{1}H NMR spectrum of MfOMe-H in $CDCl_3$

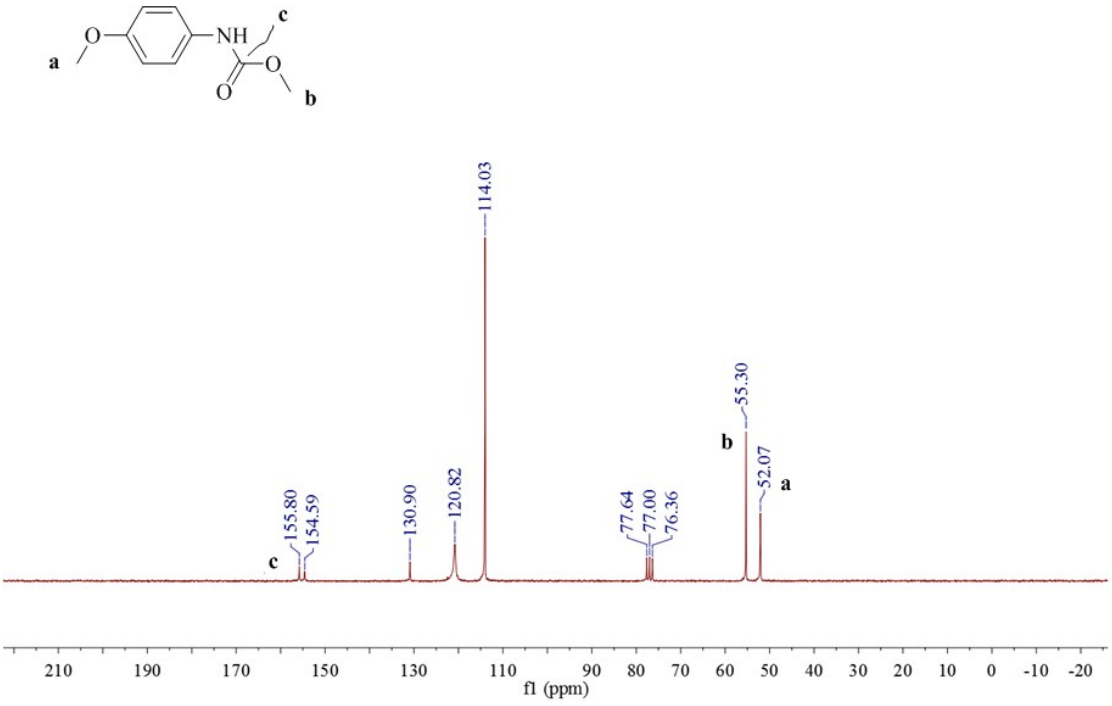


Figure S18 ^{13}C NMR spectrum of MfOMe-H in $CDCl_3$

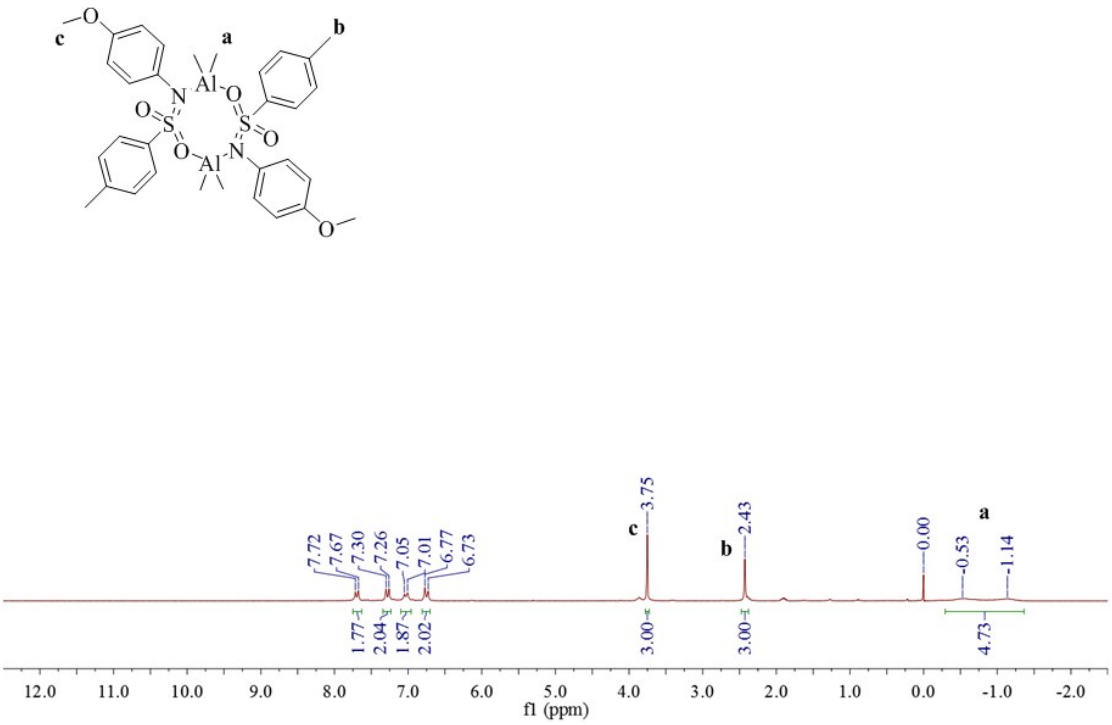


Figure S19 ^{1}H NMR spectrum of $TsOMeAlMe_2$ in $CDCl_3$

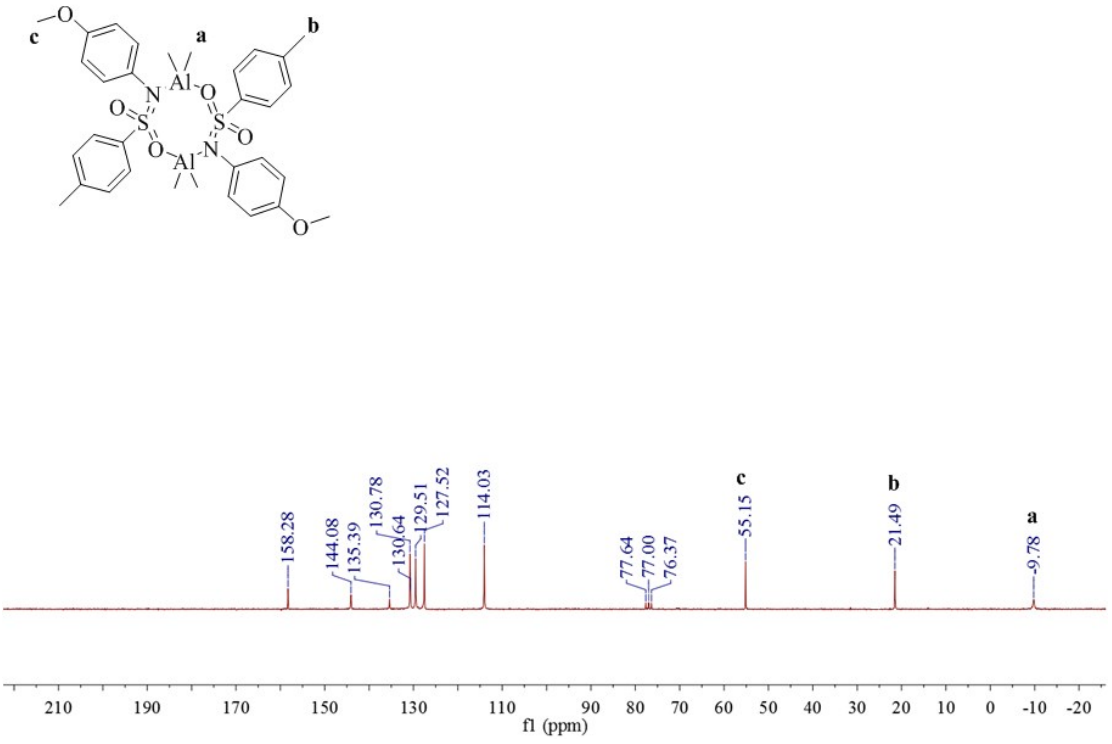


Figure S20 ^{13}C NMR spectrum of $TsOMeAlMe_2$ in $CDCl_3$

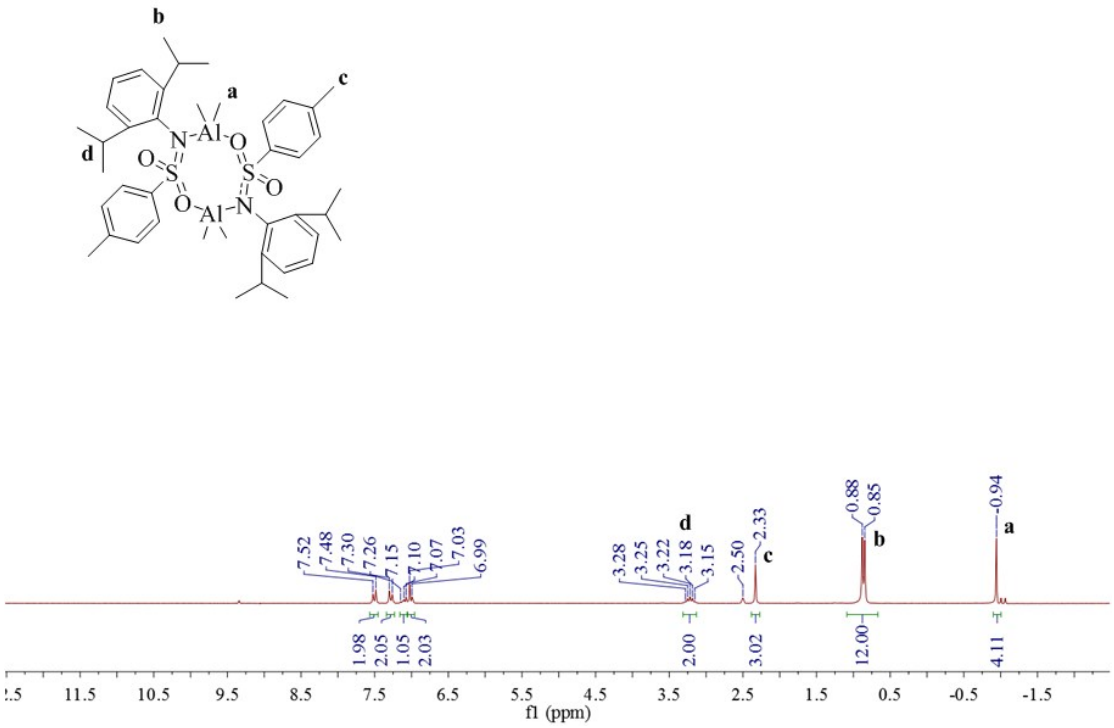


Figure S21 ^{1}H NMR spectrum of TsiPrAlMe$_2$ in d-DMSO

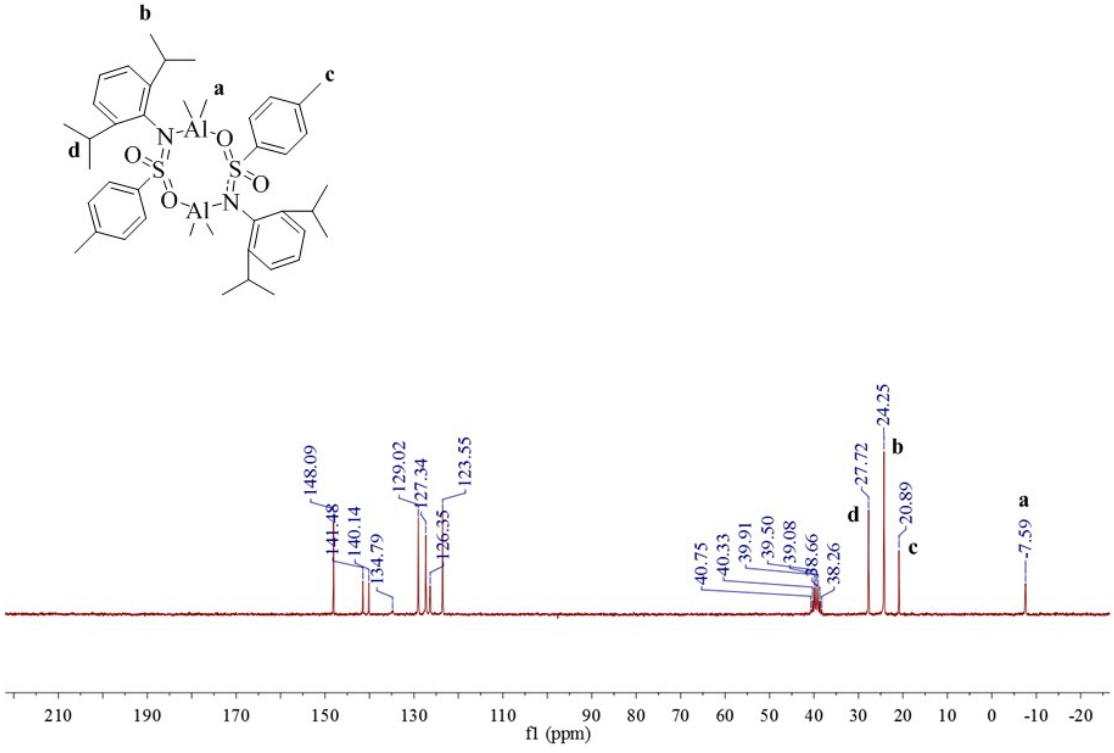


Figure S22 ^{13}C NMR spectrum of TsiPrAlMe$_2$ in d-DMSO

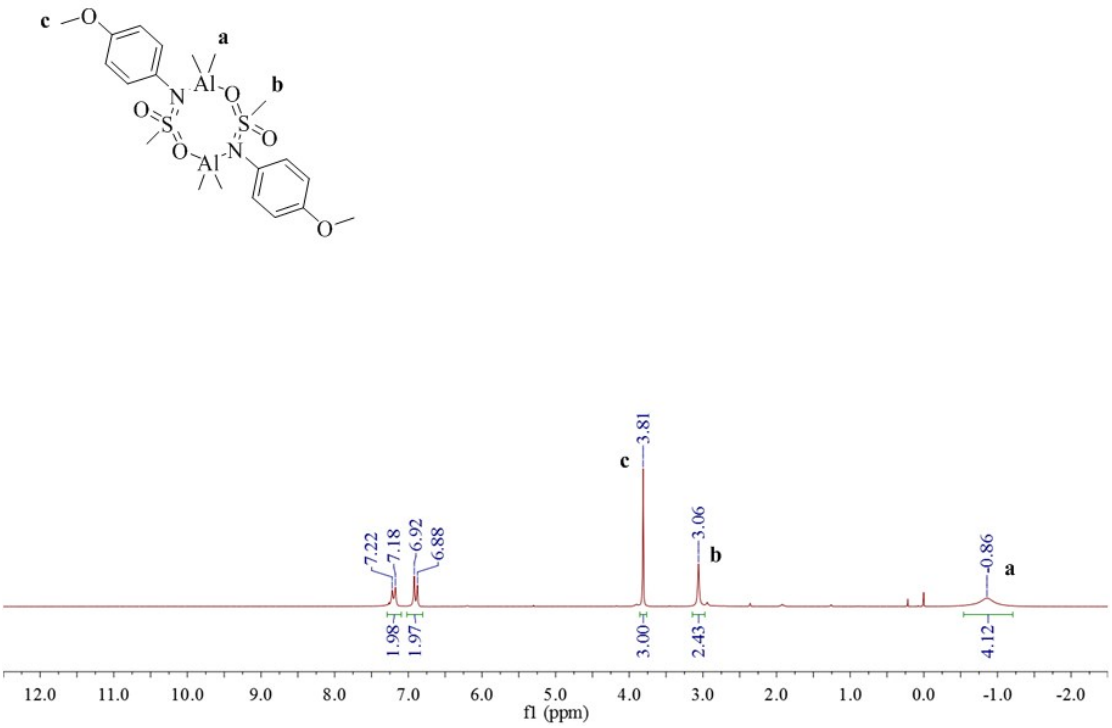


Figure S23 ^{1}H NMR spectrum of $MsOMsAlMe_2$ in $CDCl_3$

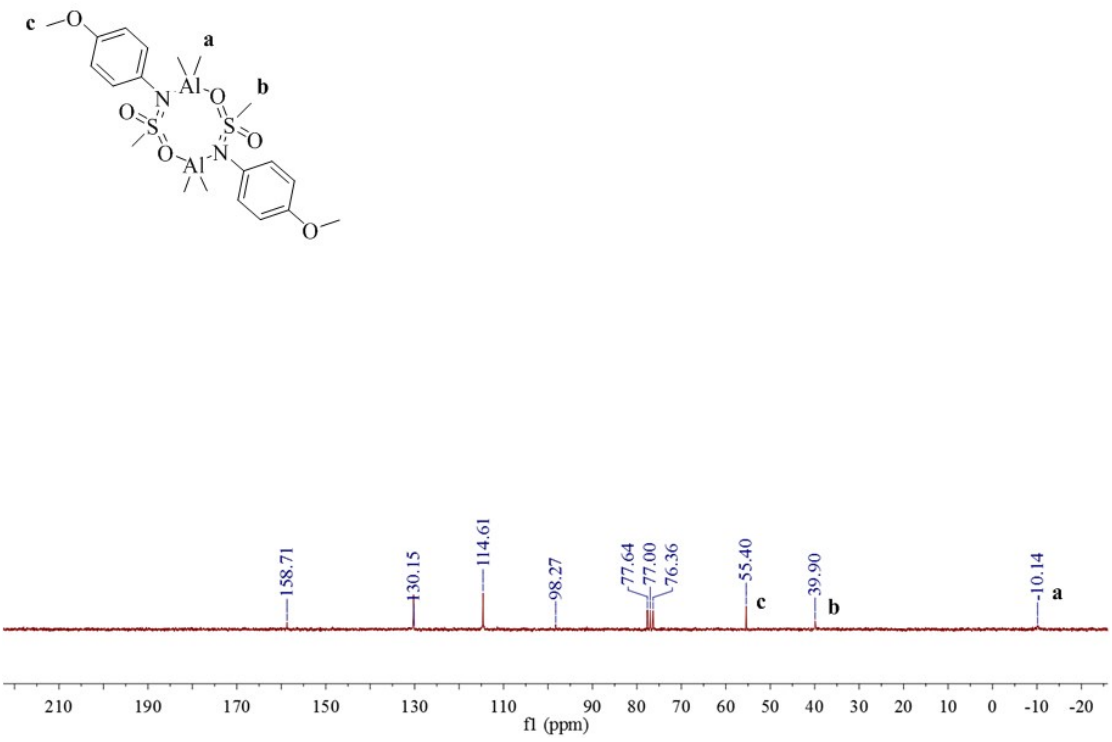


Figure S24 ^{13}C NMR spectrum of $MsOMeAlMe_2$ in $CDCl_3$

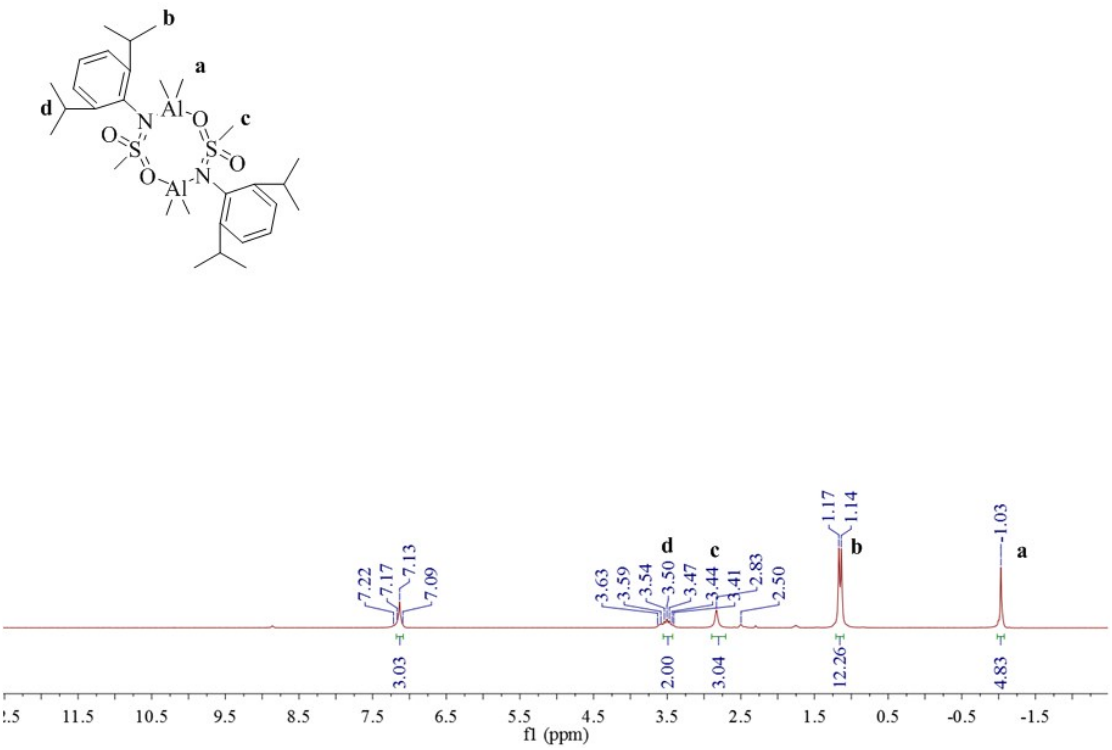


Figure S25 ^{1}H NMR spectrum of $MsiPrAlMe_2$ in d-DMSO

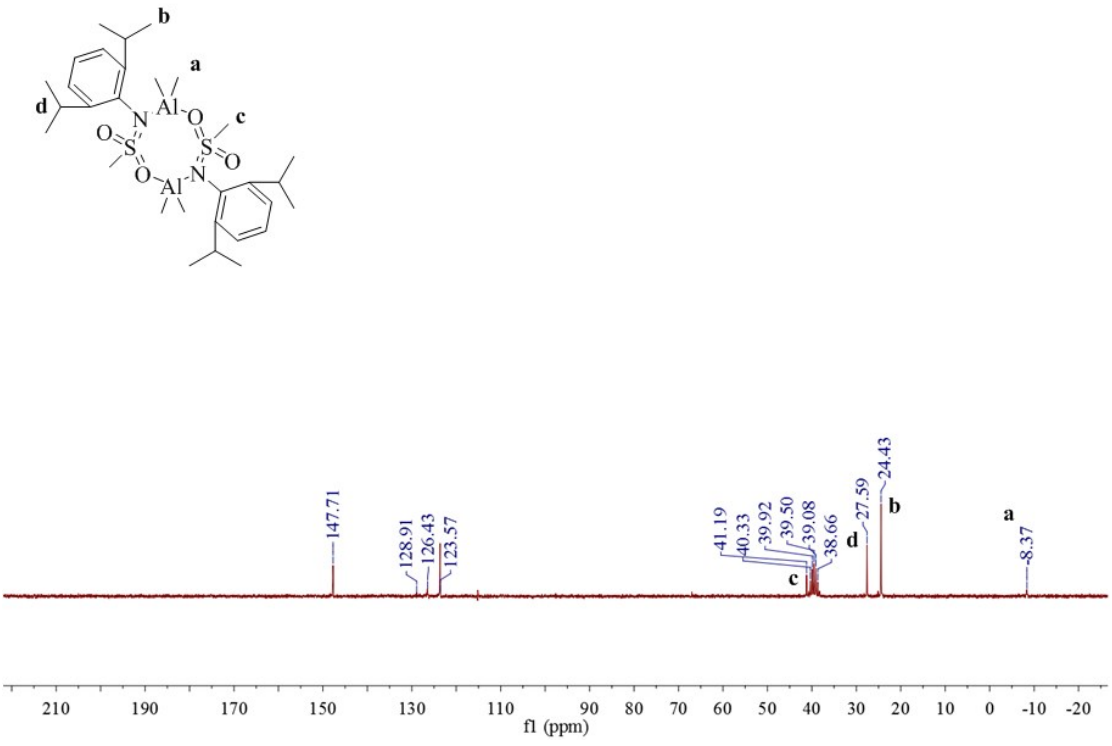


Figure S26 ^{13}C NMR spectrum of $MsiPrAlMe_2$ in d-DMSO

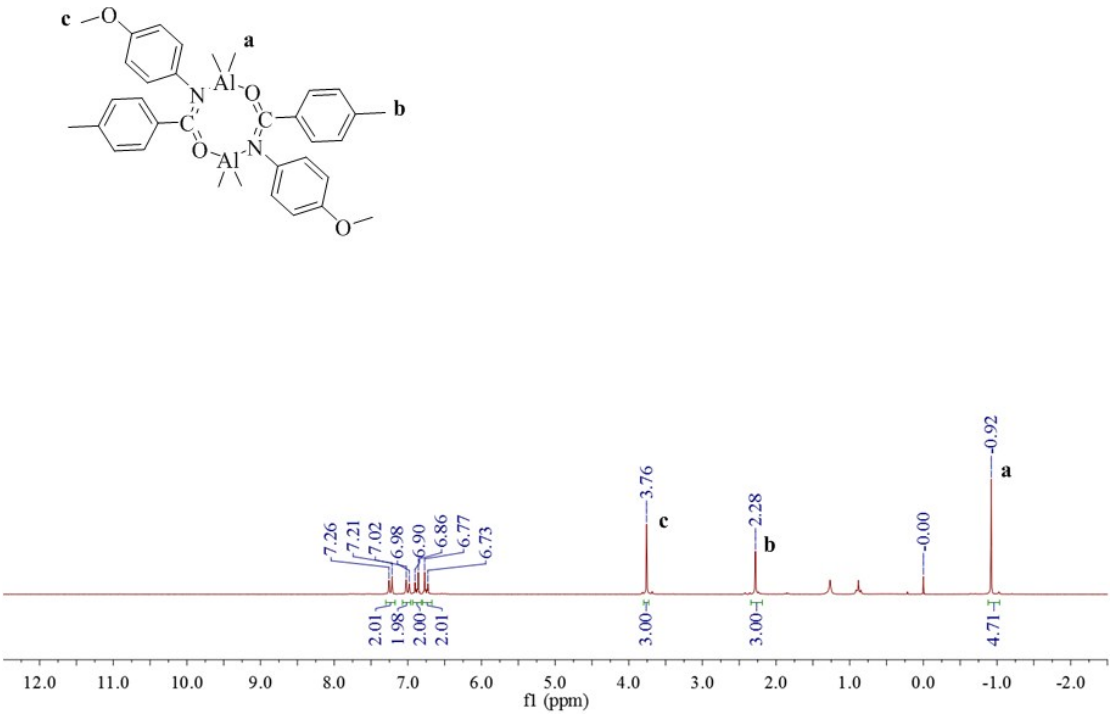


Figure S27 ^{1}H NMR spectrum of TcOMeAlMe$_2$ in $CDCl_3$

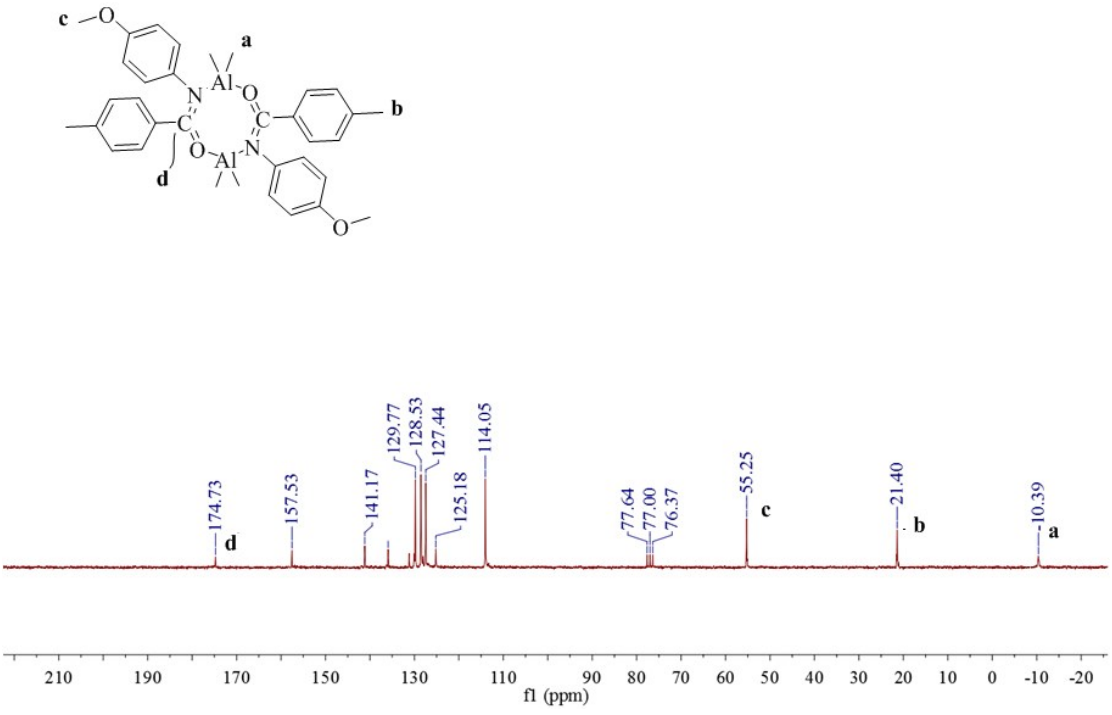
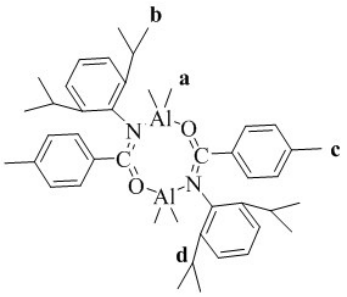


Figure S28 ^{13}C NMR spectrum of TcOMeAlMe$_2$ in $CDCl_3$



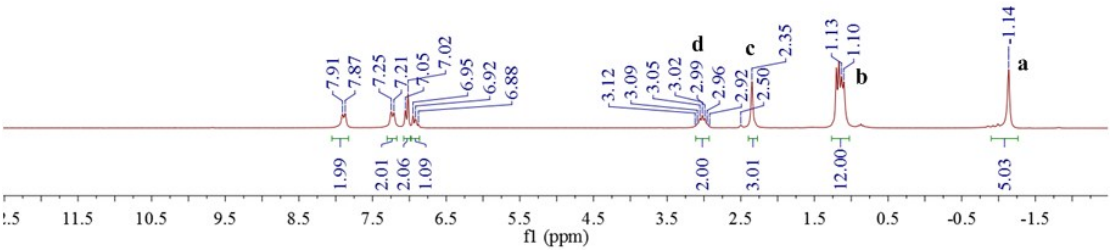
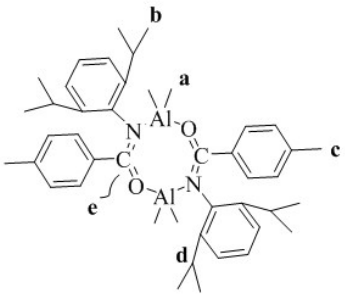


Figure S29 ^{1}H NMR spectrum of TciPrAlMe$_2$ in d-DMSO



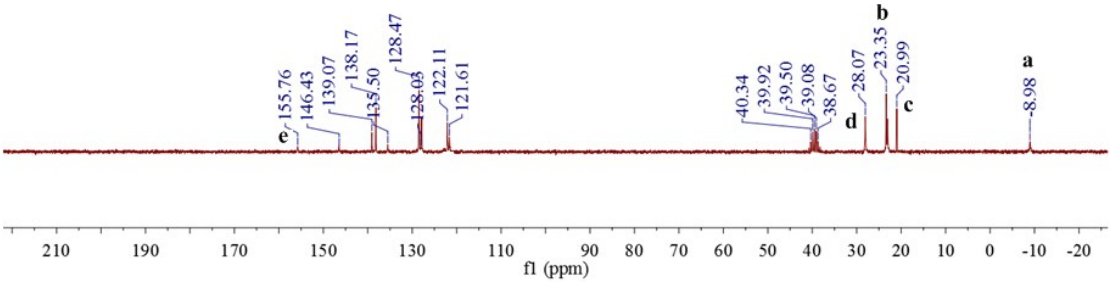


Figure S30 ^{13}C NMR spectrum of TciPrAlMe$_2$ in d-DMSO

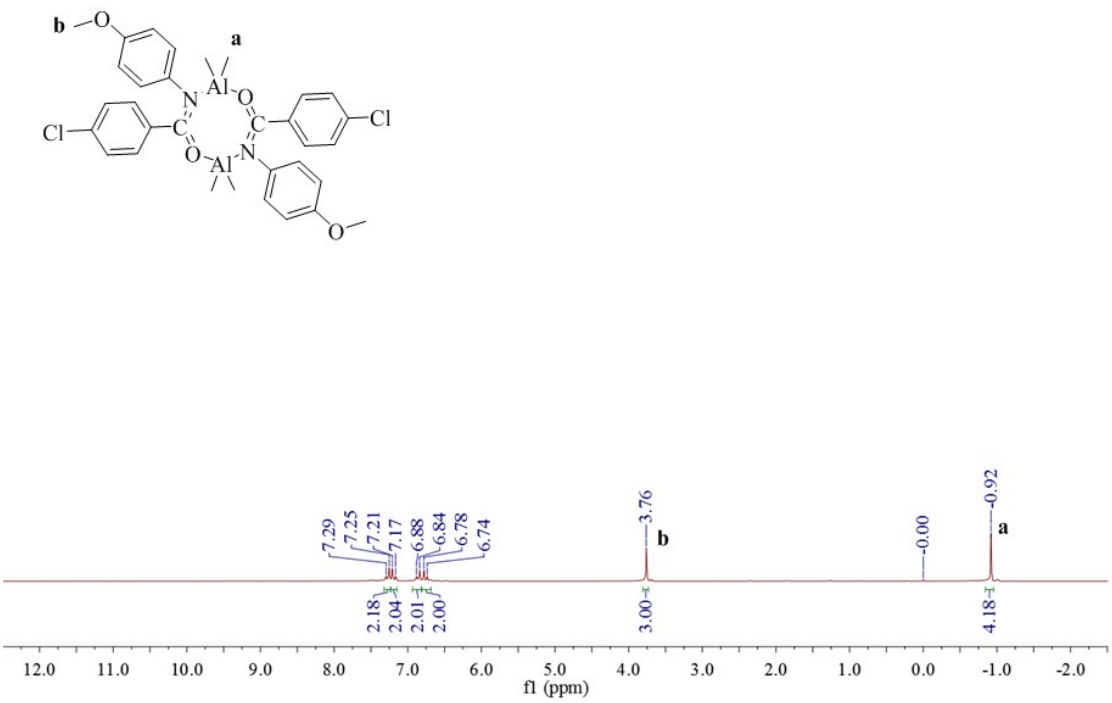


Figure S31 ^{1}H NMR spectrum of CbOMeAlMe$_2$ in CDCl$_3$

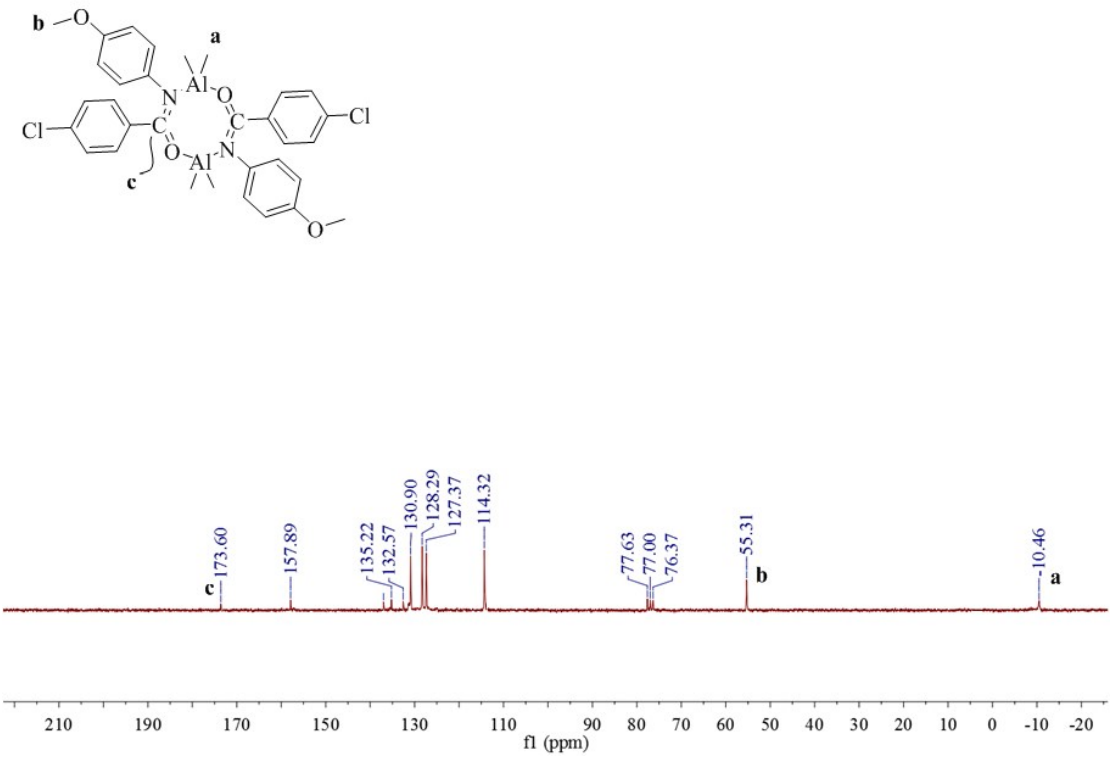


Figure S32 ^{13}C NMR spectrum of CbOMeAlMe$_2$ in CDCl$_3$

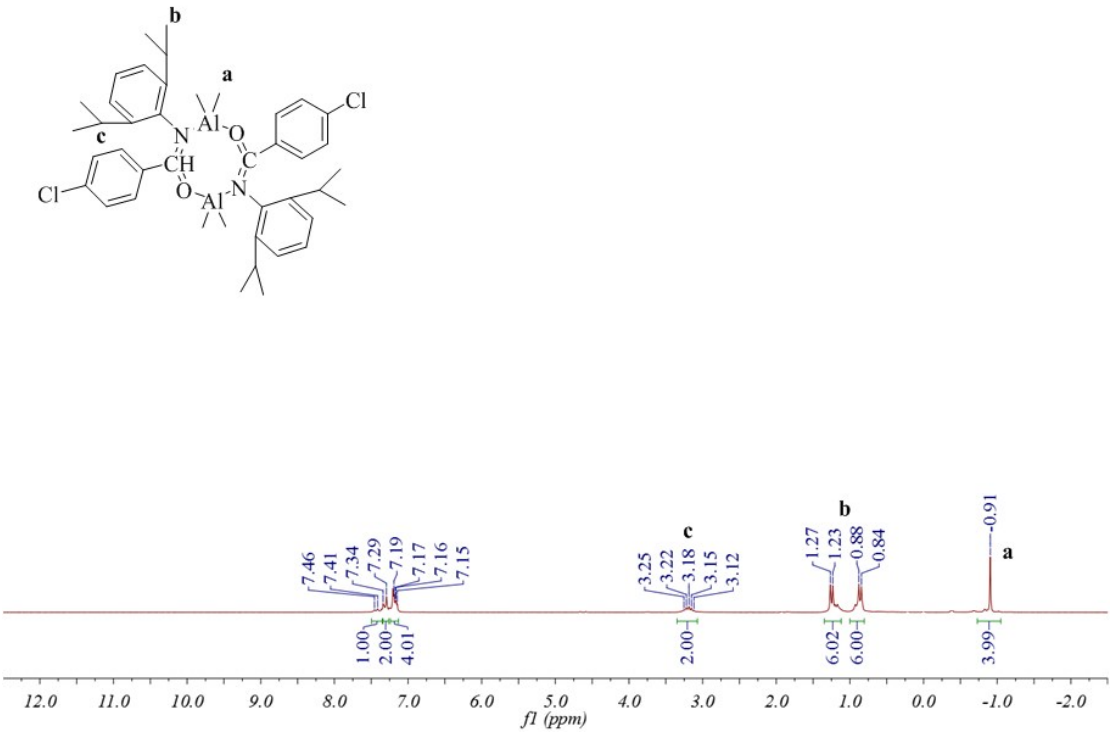


Figure S33 ^{1}H NMR spectrum of CbiPrAlMe$_2$ in CDCl$_3$

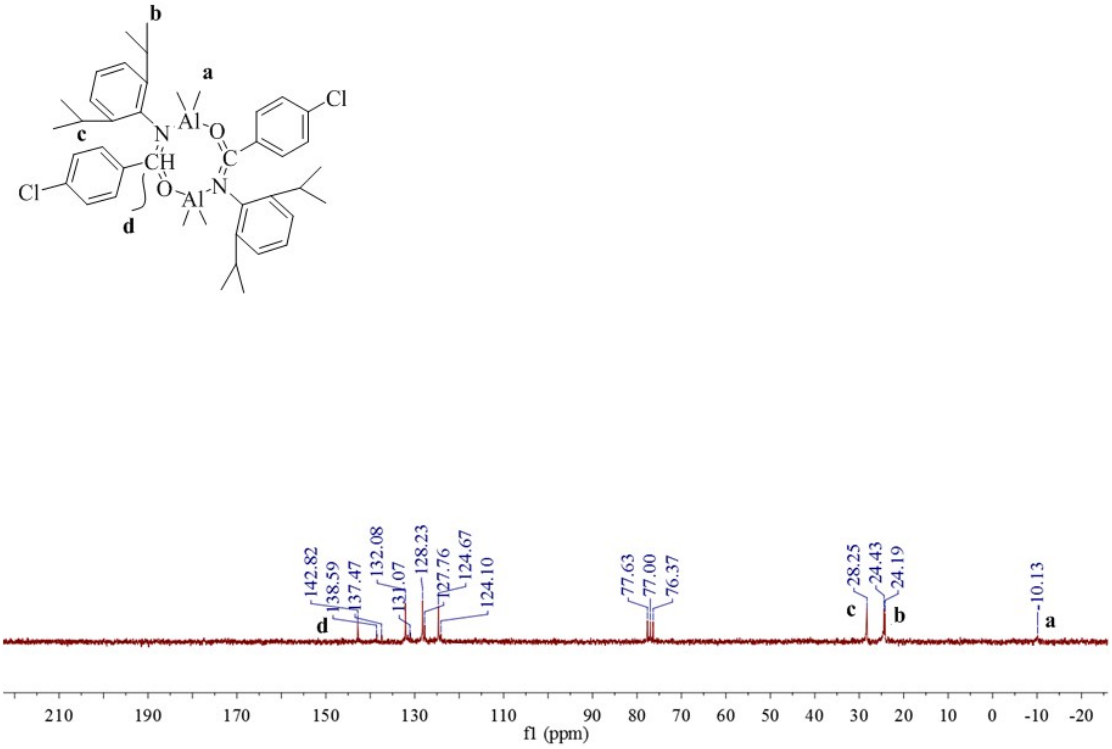


Figure S34 ^{13}C NMR spectrum of CbiPrAlMe$_2$ in CDCl$_3$

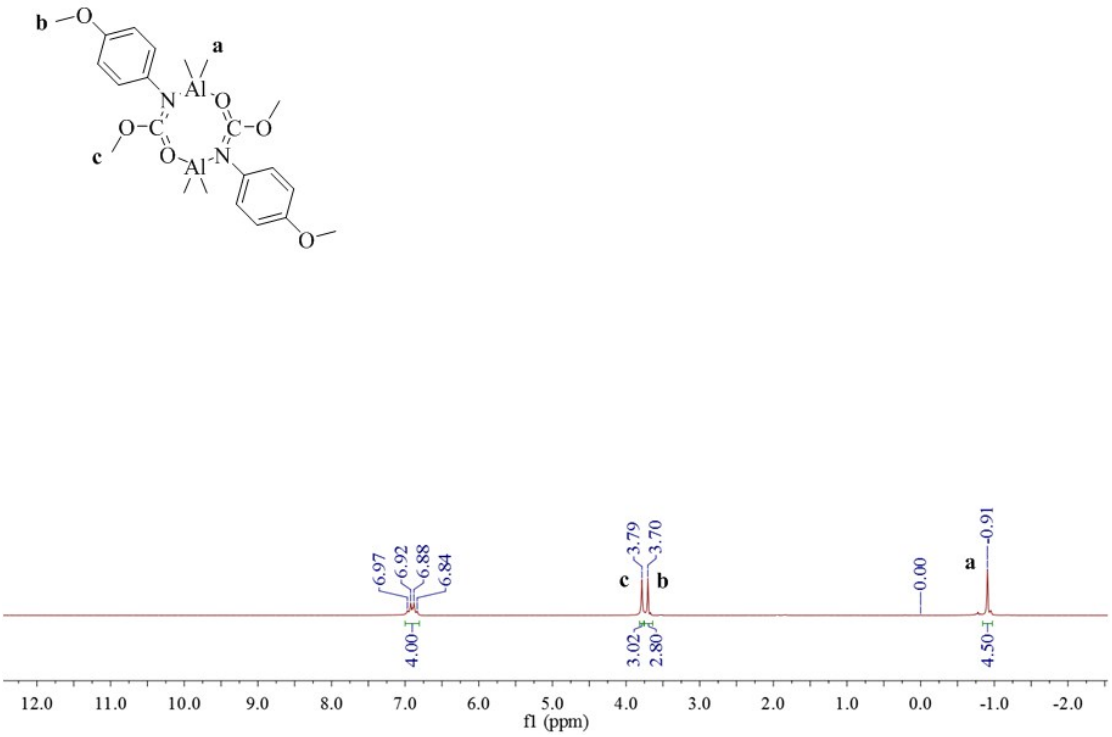


Figure S35 ^{1}H NMR spectrum of $MfOMeAlMe_2$ in $CDCl_3$

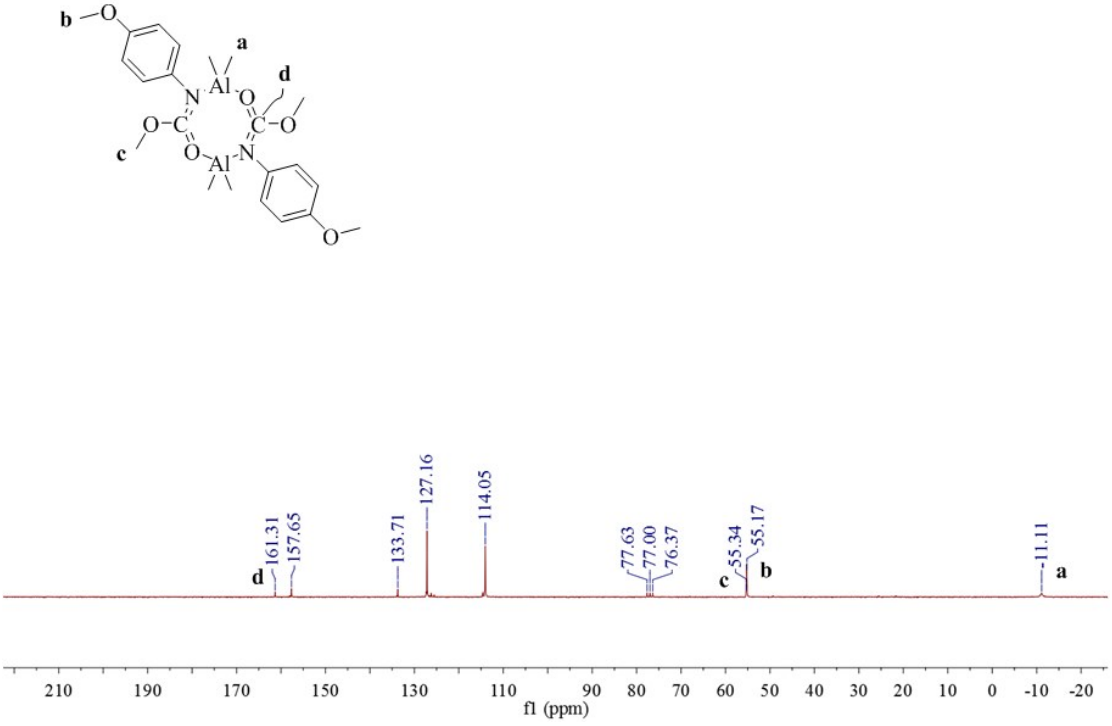


Figure S36 ^{13}C NMR spectrum of $MfOMeAlMe_2$ in $CDCl_3$

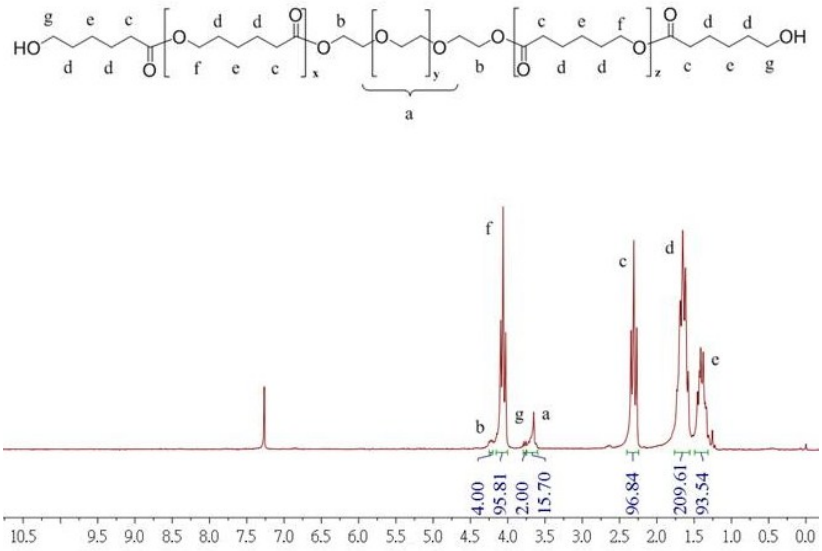


Figure 37. ^{1}H NMR spectrum of PCL in $CDCl_3$ catalyzed by **MfOMeAlMe$_2$** with PEG-200 (**Table 3**, entry 1)

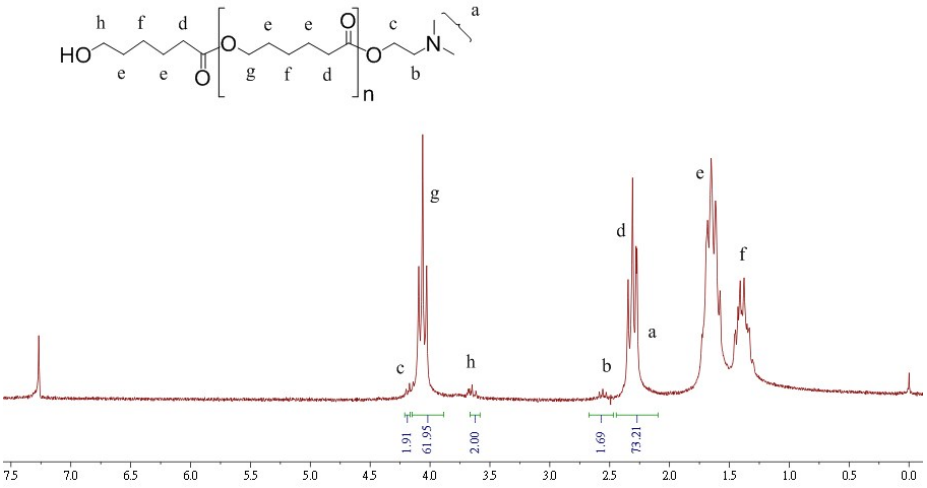


Figure 38. ^{1}H NMR spectrum of PCL in $CDCl_3$ catalyzed by **MfOMeAlMe$_2$** with DMAE (**Table 3**, entry 2)

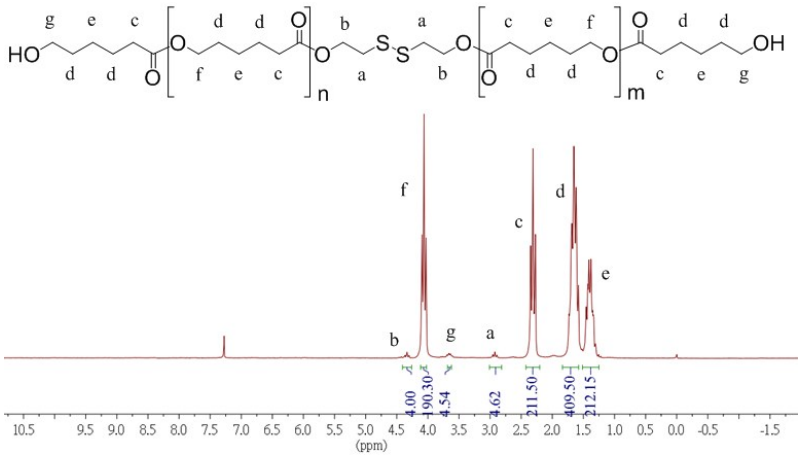


Figure 39. ^{1}H NMR spectrum of PCL in $CDCl_3$ catalyzed by **MfOMeAlMe$_2$** with BHEDS (**Table 3**, entry 3)

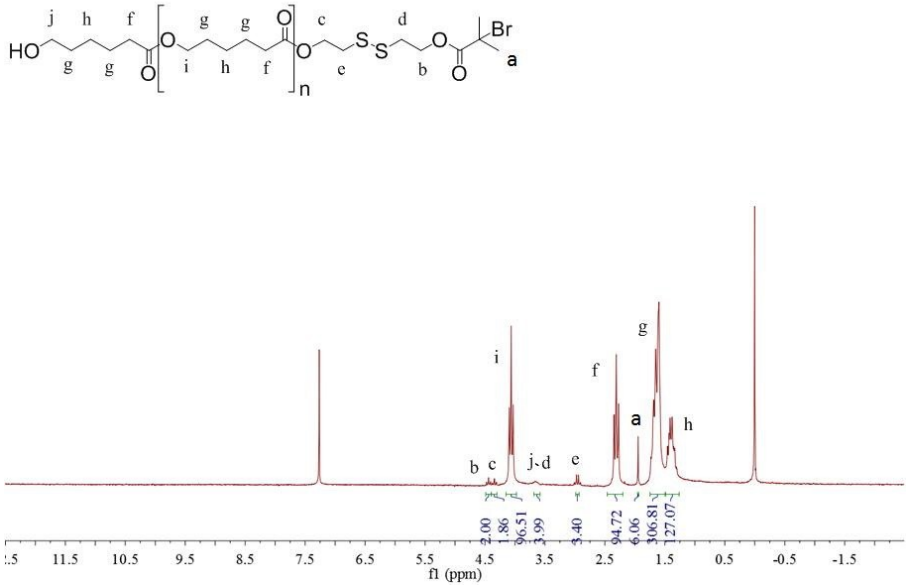


Figure 40. ^{1}H NMR spectrum of PCL in $CDCl_3$ catalyzed by **MfOMeAlMe$_2$** with HOSSBr (**Table 3**, entry 4)

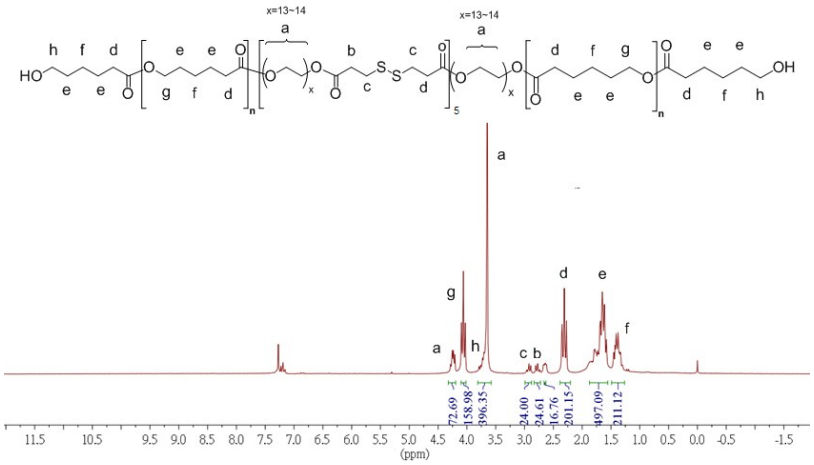


Figure 41. ^{1}H NMR spectrum of PCL in $CDCl_3$ catalyzed by **MfOMeAlMe$_2$** with PEGSS (**Table 3**, entry 5)

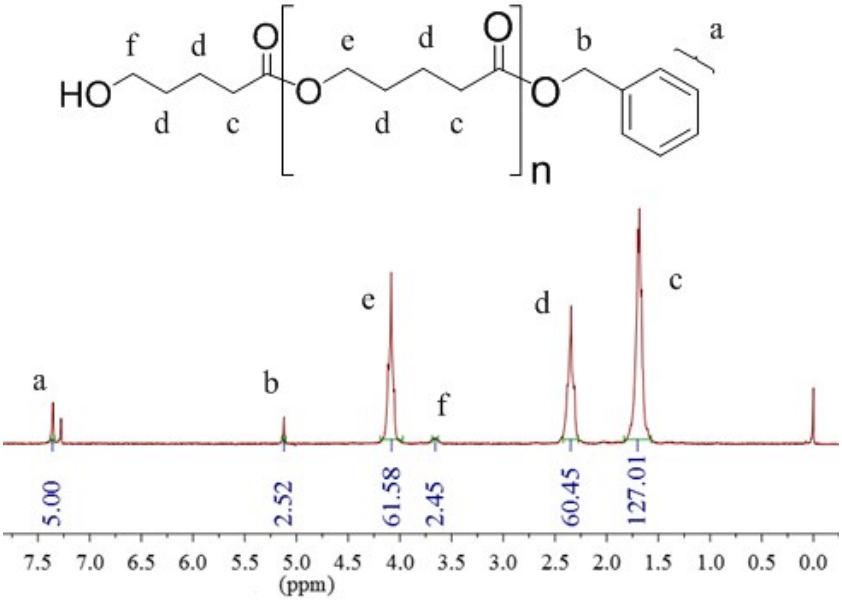


Figure S42. ^{1}H NMR spectrum of PVL in $CDCl_3$ catalyzed by **MfOMeAlMe$_2$** with BnOH (**Table 4**, entry 1)

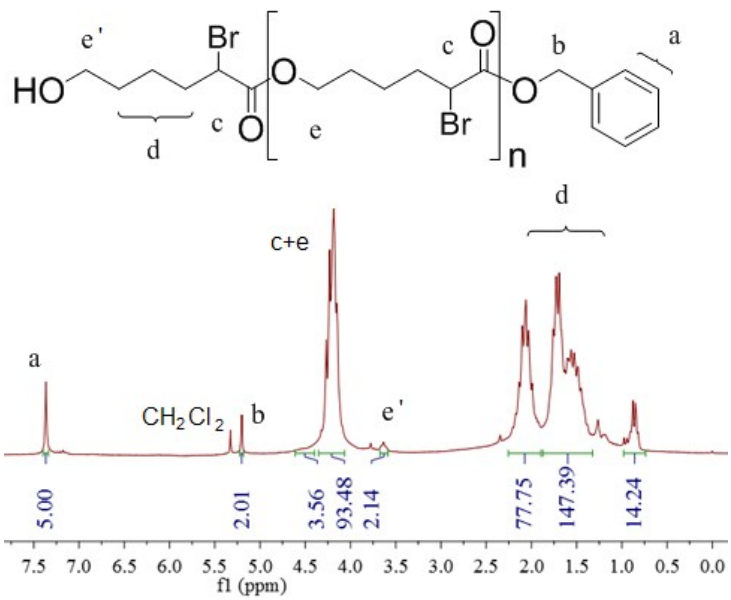


Figure S43. ^{1}H NMR spectrum of PBrCL in $CDCl_3$ catalyzed by **MfOMeAlMe$_2$** with BnOH (**Table 4**, entry 2)