Supporting Information

Aryl(silyl)amino group stabilized hydridosilanediols: synthesis and characterization and the use for preparation of alumino(hydrido)siloxanes

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Content:

I. X-ray crystallographic data of **6** and **8**–**11** and crystal structures of **6** and **11**

Table S1 Crystal data and refinements for compounds **6** and **8**–**11**

	6	**8**	**9**
Empirical formula	$C_{17}H_{25}NO_2Si_2$	$C_{40}H_{76}Al_2N_2O_6Si_4$	$C_{56}H_{92}Al_2N_2O_6Si_4$
formula weight	331.56	847.35	1055.64
crystal system	Triclinic	Triclinic	Monoclinic
space group	*P*–1	*P*–1	*Cc*
CCDC	1442616	1442617	1442618
a/Å	10.4955(7)	10.0975(9)	27.6137(17)
b/Å	12.9201(11)	10.2652(7)	9.4580(7)
c/Å	16.0791(11)	14.3031(10)	23.5911(17)
α/deg	109.295(7)	73.704(6)	
β/deg	106.762(6)	70.848(7)	98.582(7)
γ/deg	97.856(6)	63.167(8)	
V/Å^3	1904.4(2)	1234.17(16)	6092.3(7)
Z	4	1	4
ρ_{calcd}/g·cm^{-3}	1.156	1.140	1.151
μ/mm^{-1}	0.192	1.794	0.173
F(000)	712	460	2288
crystal size/mm^3	0.40 x 0.30 x 0.20	0.40 x 0.40 x 0.40	0.30 x 0.20 x 0.10
θ range/deg	3.04–26.00	3.31–62.13	2.94–26.00
index ranges	$-12 \le h \le 12$	$-11 \le h \le 11$	$-34 \le h \le 18$
	$-8 \le k \le 15$	$-11 \le k \le 11$	$-11 \le k \le 11$
	$-19 \le l \le 19$	$-13 \le l \le 16$	$-29 \le l \le 29$
collected data	11293	7741	12847
unique data	7416	3864	7358
	(R_{int} = 0.0250)	(R_{int} = 0.0247)	(R_{int} = 0.0632)
completeness to *θ*	99.3%	99.2%	99.9%
data/restraints/parameters	7416/0/446	3864/0/256	7358/242/604
GOF on F^2	1.024	1.045	1.019
final *R* indices [$I > 2$ (*I*)]	R_1 = 0.0512	R_1 = 0.0373	R_1 = 0.0873
	wR_2 = 0.1120	wR_2 = 0.0948	wR_2 = 0.1988
R indices (all data)	R_1 = 0.0716	R_1 = 0.0439	R_1 = 0.1296
	wR_2 = 0.1214	wR_2 = 0.1008	wR_2 = 0.2265
Largest diff peak/hole (e·Å^{-3})	0.357/–0.287	0.474/–0.277	0.653/–0.394

[a] The data were collected at 173(2) K by using Mo K_α (λ = 0.71073 Å) radiation for compounds **6** and **9** and Cu K_α (λ = 1.54178 Å) radiation for compound **8**. $R_1 = \sum(||F_o| - |F_c||)/\sum|F_o|$, $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)]^{1/2}$, GOF = $[\sum w(F_o^2 - F_c^2)^2/(N_o - N_p)]^{1/2}$.

	10	**11**
Empirical formula	$C_{68}H_{103}Al_2N_3O_8Si_6$	$C_{46.70}H_{77.30}Al_2N_{3.30}O_{4.70}Si_4$
formula weight	1313.03	926.54
crystal system	Monoclinic	Monoclinic
space group	*P*2(1)/*n*	*P*2(1)/*c*
CCDC	1442619	1442615
a/Å	12.6280(9)	15.2140(5)
b/Å	25.7705(17)	10.4426(3)
c/Å	23.4218(12)	17.3308(5)
α/deg		
β/deg	101.117(6)	103.941(3)
γ/deg		
V/Å^3	7479.1(8)	2672.30(14)
Z	4	2
ρ_{calcd}/g·cm^{-3}	1.166	1.151
μ/mm^{-1}	0.186	1.689
F(000)	2824	1000
crystal size/mm^3	0.40 x 0.40 x 0.40	0.40 x 0.20 x 0.20
θ range/deg	2.89–26.00	4.98– 62.11
index ranges	$-15 \le h \le 15$	$-15 \le h \le 17$,
	$-31 \le k \le 31$	$-11 \le k \le 11$,
	$-28 \le l \le 28$	$-17 \le l \le 19$
collected data	40158	16109
unique data	14677	4179
	(R_{int} = 0.0838)	(R_{int} = 0.0321)
completeness to *θ*	99.7%	99.5%
data/restraints/parameters	14677/600/906	4179/112/334
GOF on F^2	1.044	1.044
final *R* indices [$I > 2$ (*I*)]	R_1 = 0.0879	R_1 = 0.0364
	wR_2 = 0.2013	wR_2 = 0.0990
R indices (all data)	R_1 = 0.1164	R_1 = 0.0420
	wR_2 = 0.2180	wR_2 = 0.1040
Largest diff peak/hole (e·Å^{-3})	1.084/–0.488	0.379/–0.304

[a] The data were collected at 173(2) K by using Mo K_α (λ = 0.71073 Å) radiation for compound **10** and Cu K_α (λ = 1.54178 Å) radiation for compound **11**. $R_1 = \sum(||F_o| - |F_c||)/\sum|F_o|$, $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)]^{1/2}$, GOF = $[\sum w(F_o^2 - F_c^2)^2/(N_o - N_p)]^{1/2}$.

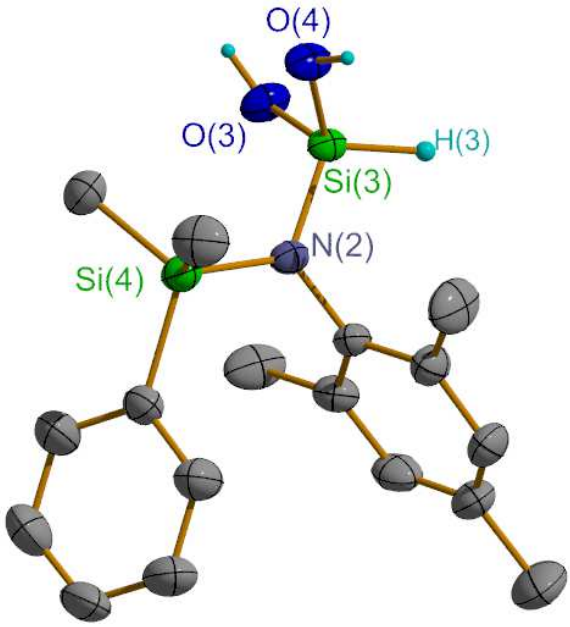


Figure S1 X-ray crystal structure of another independent molecule of **6** with thermal ellipsoids at 50% probability level. H atoms except for those of SiH and OH are omitted for clarity.

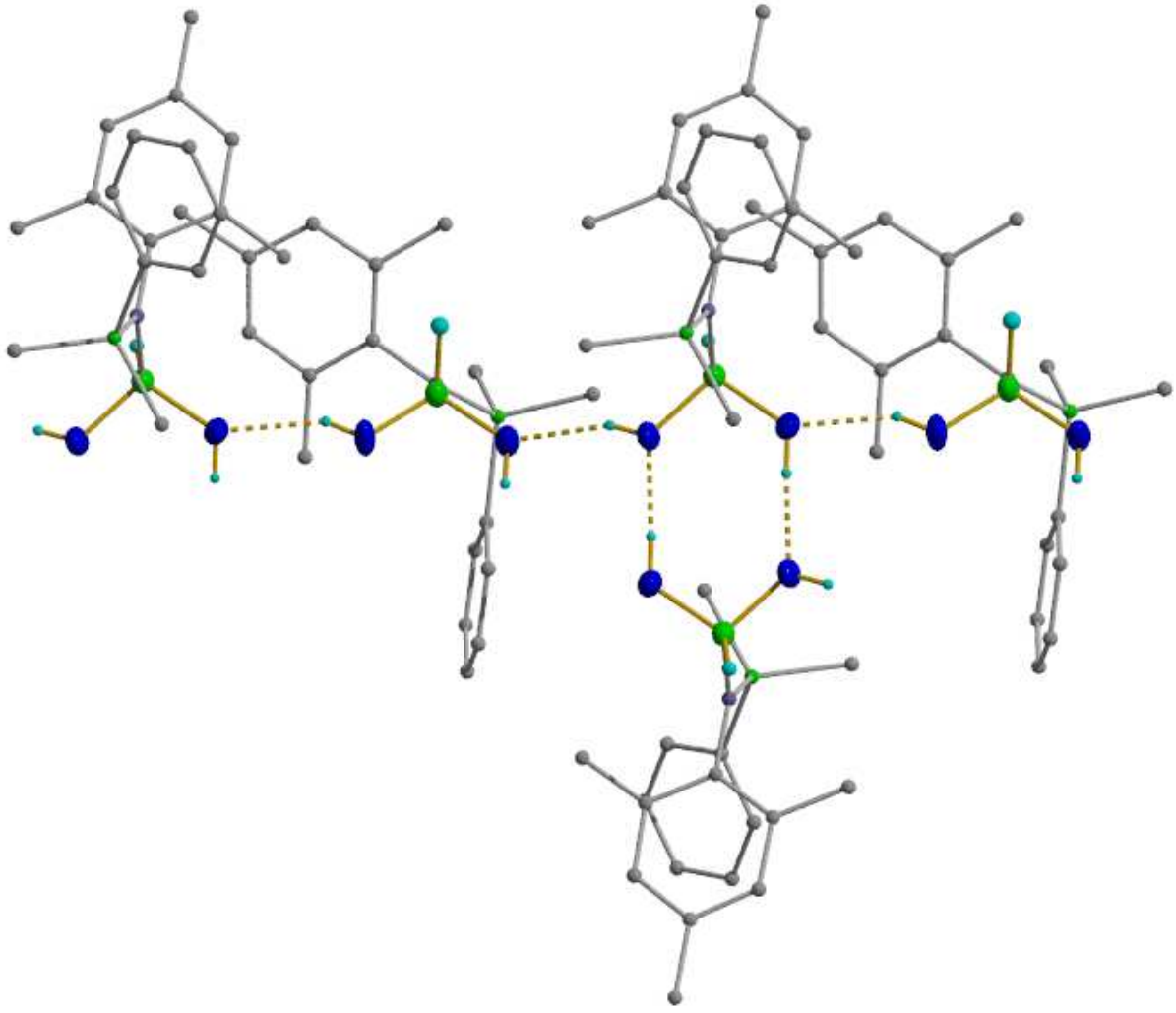


Figure S2 X-ray crystal structure of **6** with intermolecular SiO−H···O(H)Si hydrogen bonding network (the separations of SiO−H···O(H)Si, 1.8519(2), 1.9688(1), and 2.0097(1) Å). H atoms except for those of SiH and OH are omitted for clarity.

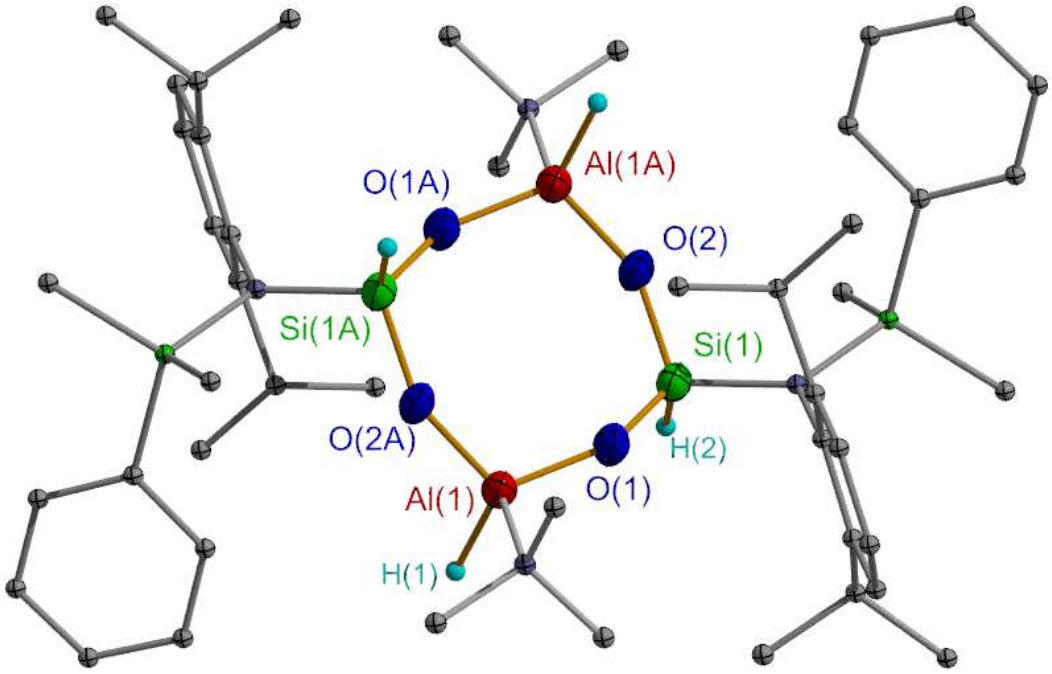


Figure S3 X-ray crystal structure of **11** with NMe_3 bonded at the Al atom in thermal ellipsoids at 50% probability level. H atoms except for those of SiH and AlH are omitted for clarity. Selected bond lengths (Å): Al–N_{NMe3} 2.038(5). Symmetry code for A: –x, –y+2, –z.

II. Table of selected bond lengths and angles of **8**–**11**

Table S2 Important bond lengths (Å) and angles (°) of **8**–**11**

Compound	**8**	**9**	**10**	**11**
Si–H (Å)	1.44(2)	1.44(3)–1.45(3)	1.35(4)–1.42(4)	1.39(2)
Si–O (Å)	1.597(1)–1.598(2)	1.572(7)–1.631(8)	1.599(3)–1.618(3)	1.601(2)–1.606(1)
Al–O (Å)	1.712(1)–1.714(2)	1.668(8)–1.769(8)	1.707(3)–1.718(3)	1.709(1)–1.714(1)
O–Si–O (°)	113.3(8)	112.1(4)–113.2(4)	111.9(1)–113.8(1)	112.6(8)
O–Al–O (°)	115.7(5)	114.6(4)–114.8(4)	112.0(1)–115.4(1)	115.4(7)
Si–O–Al (°)	149.3(1)–151.0(1)	145.9(5)–158.3(5)	128.9(2)–145.3(2)	145.7(1)–147.7(1)

III. The ^{1}H, ^{13}C, and ^{29}Si NMR Spectra of **1**–**11**

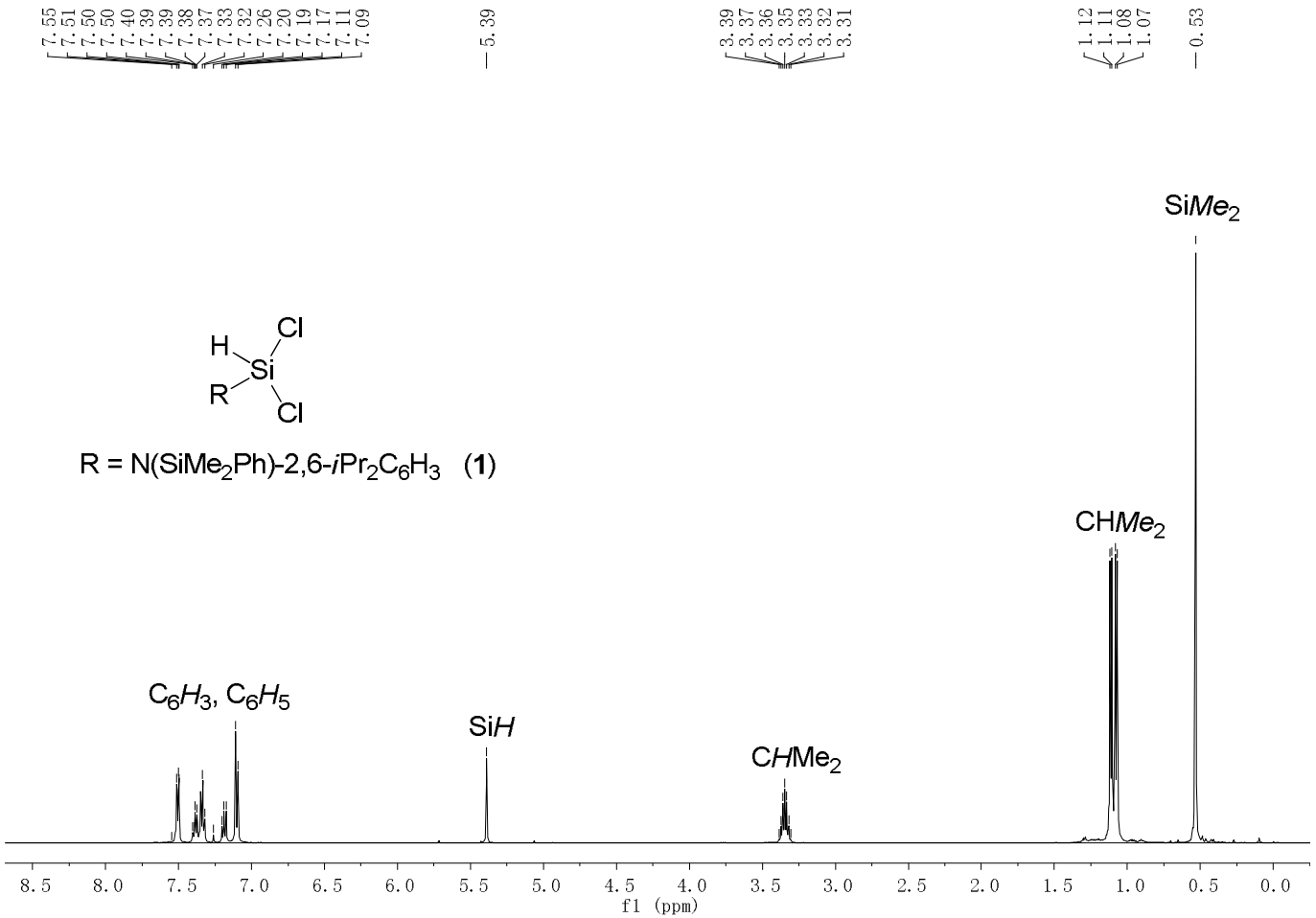


Figure S4-1 ^{1}H NMR spectrum of **1** in $CDCl_3$

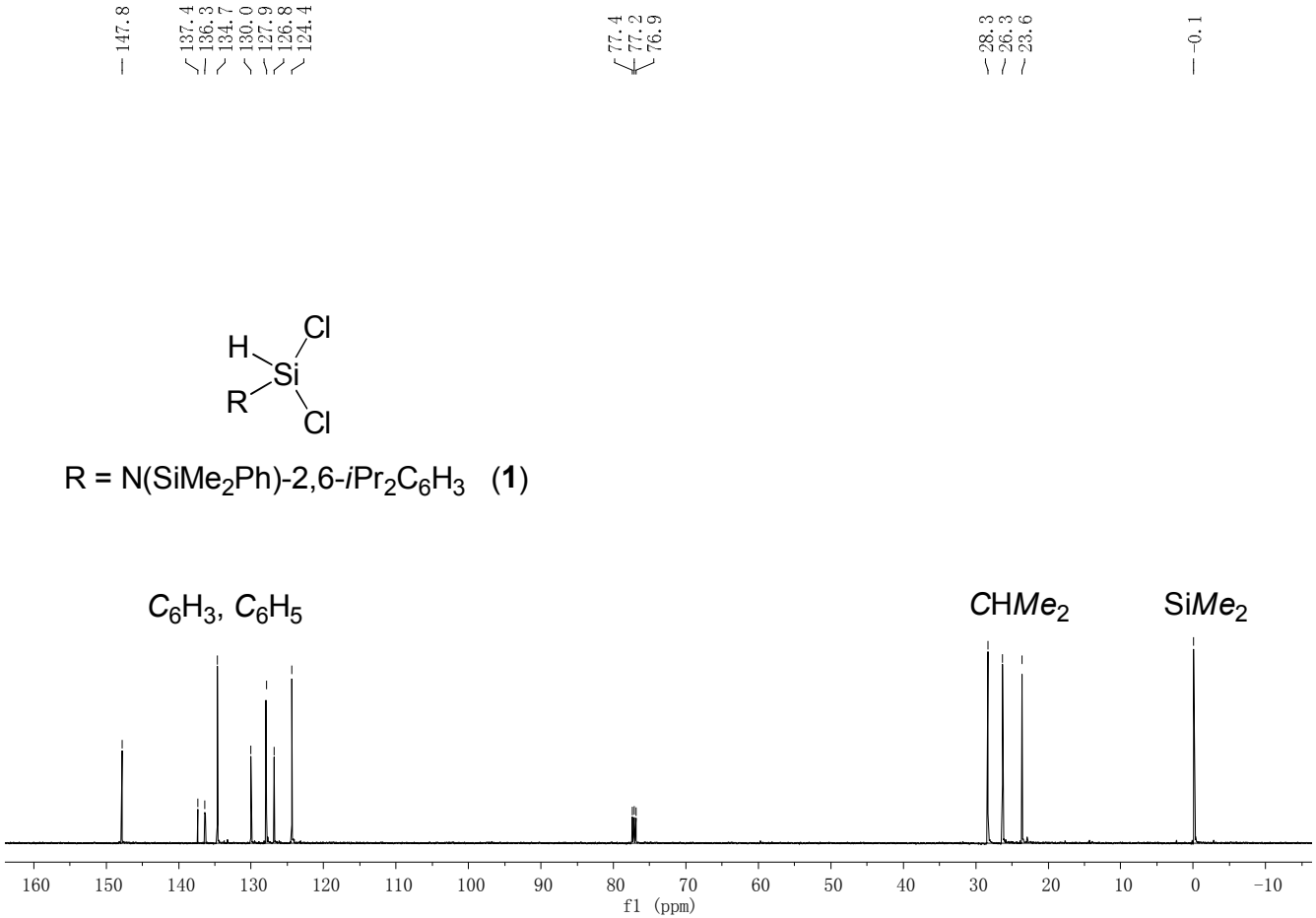


Figure S4-2 ^{13}C NMR spectrum of **1** in $CDCl_3$

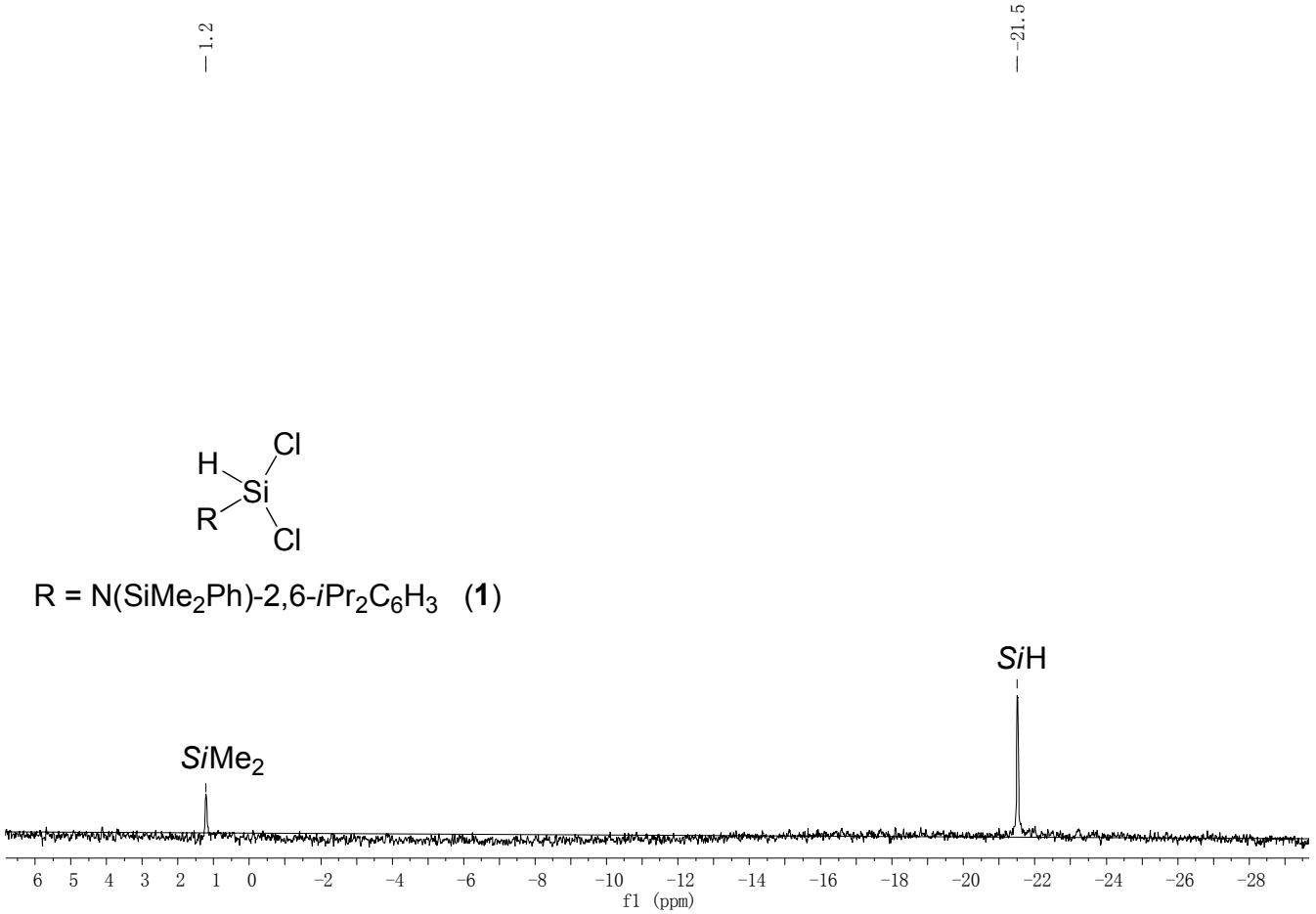


Figure S4-3 ^{29}Si NMR spectrum of **1** in $CDCl_3$

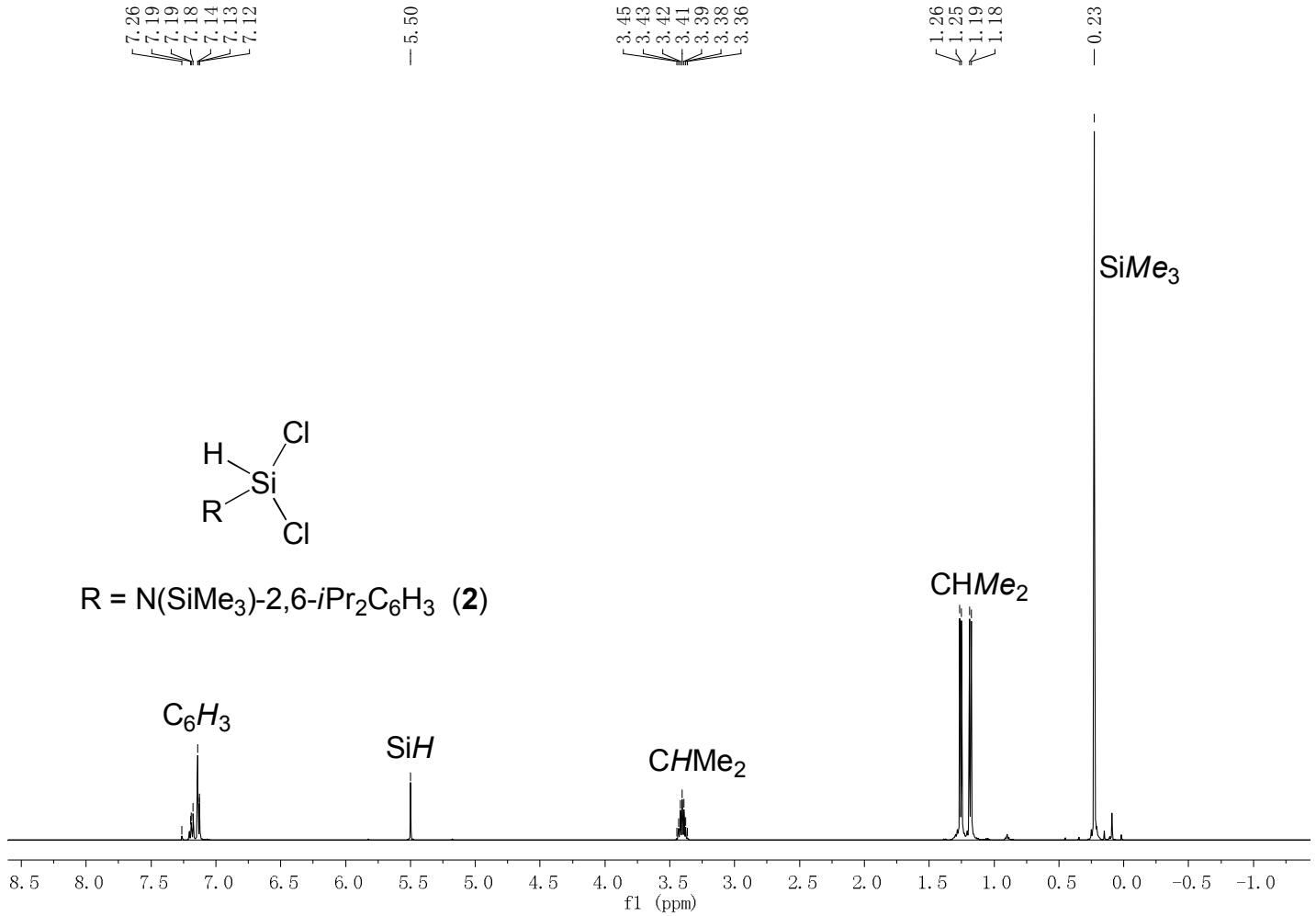


Figure S5-1 ^{1}H NMR spectrum of **2** in $CDCl_3$

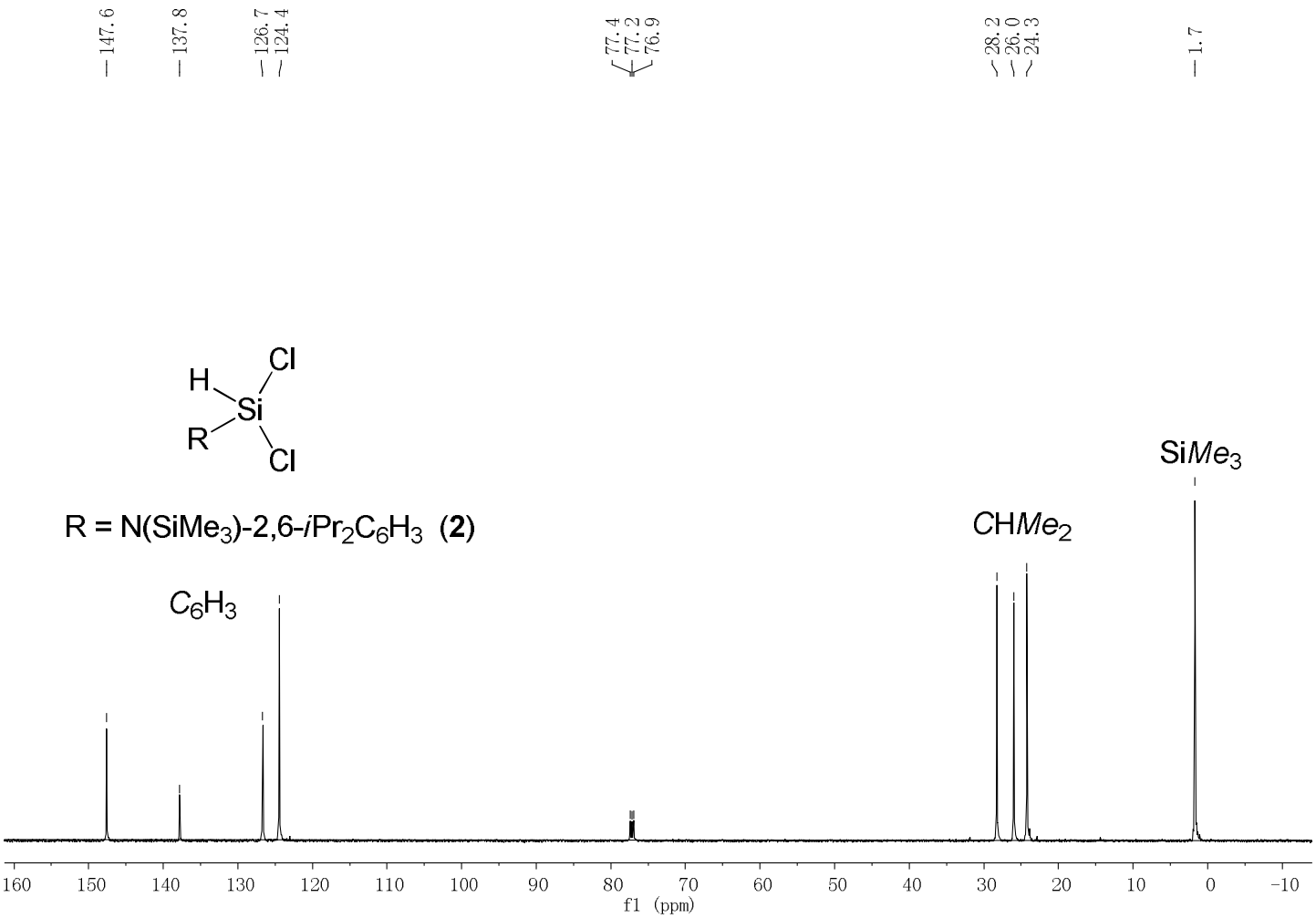


Figure S5-2 ^{13}C NMR spectrum of **2** in $CDCl_3$

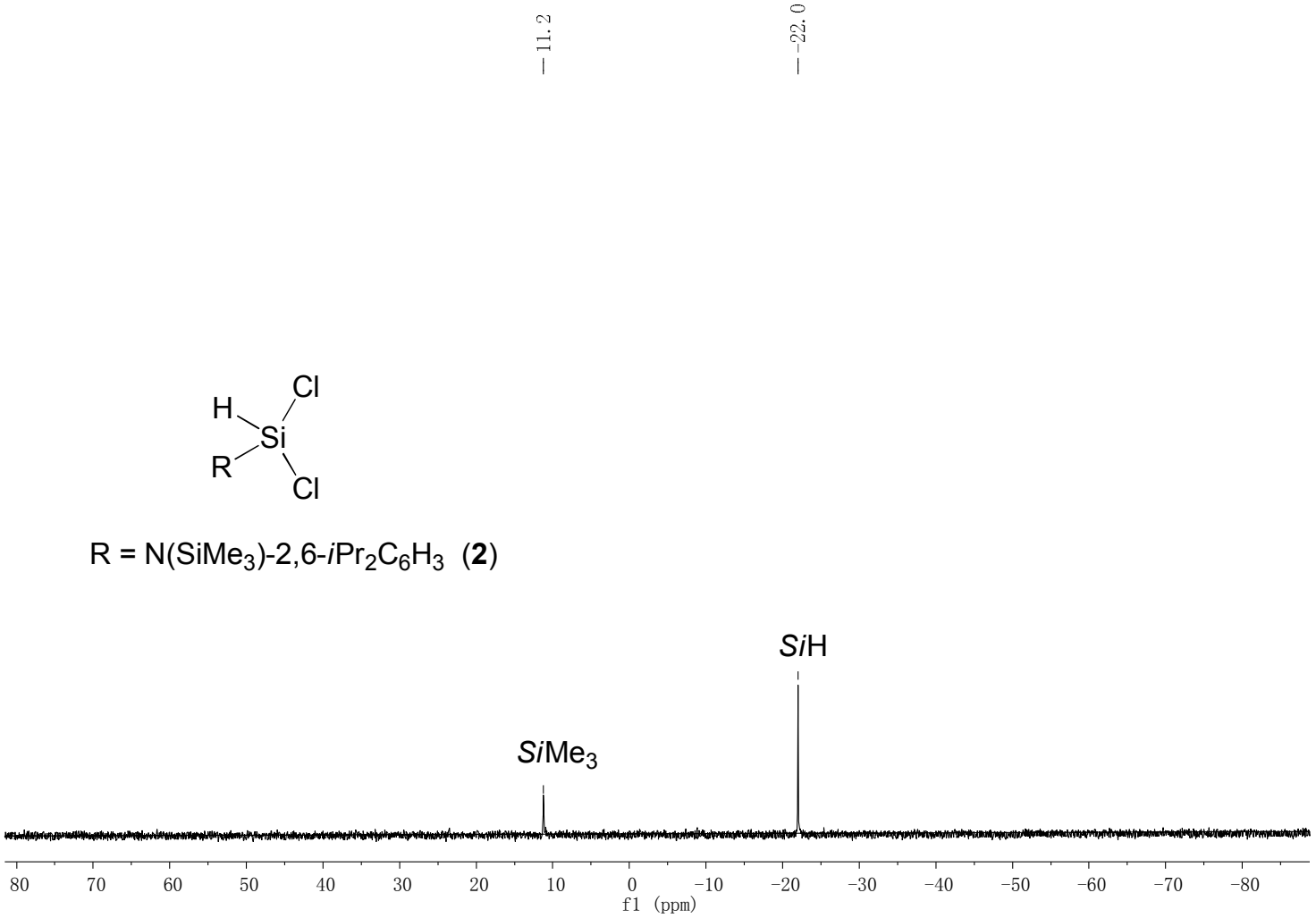


Figure S5-3 ^{29}Si NMR spectrum of **2** in $CDCl_3$

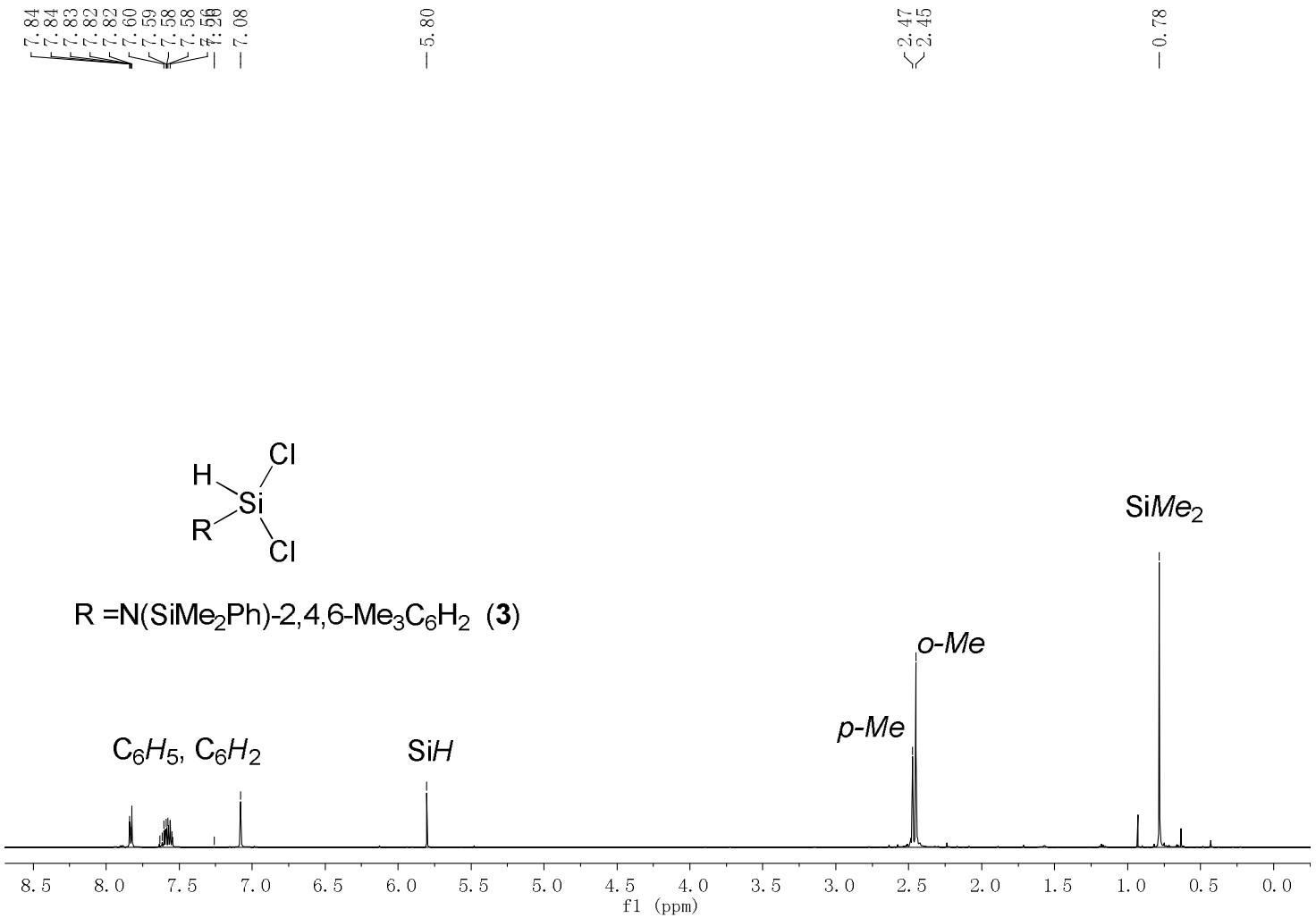


Figure S6-1 ^{1}H NMR spectrum of **3** in $CDCl_3$

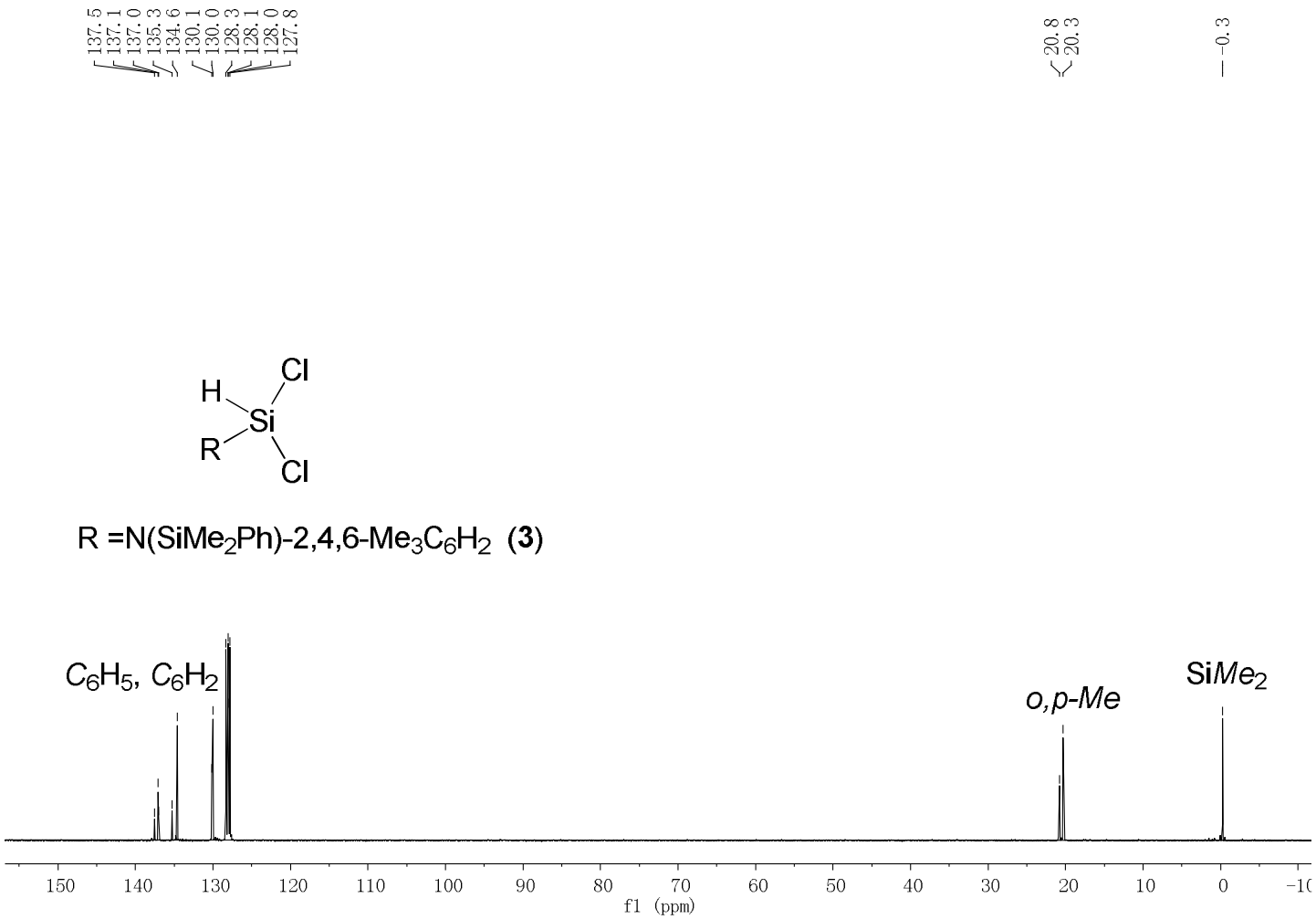


Figure S6-2 ^{13}C NMR spectrum of **3** in C_6D_6

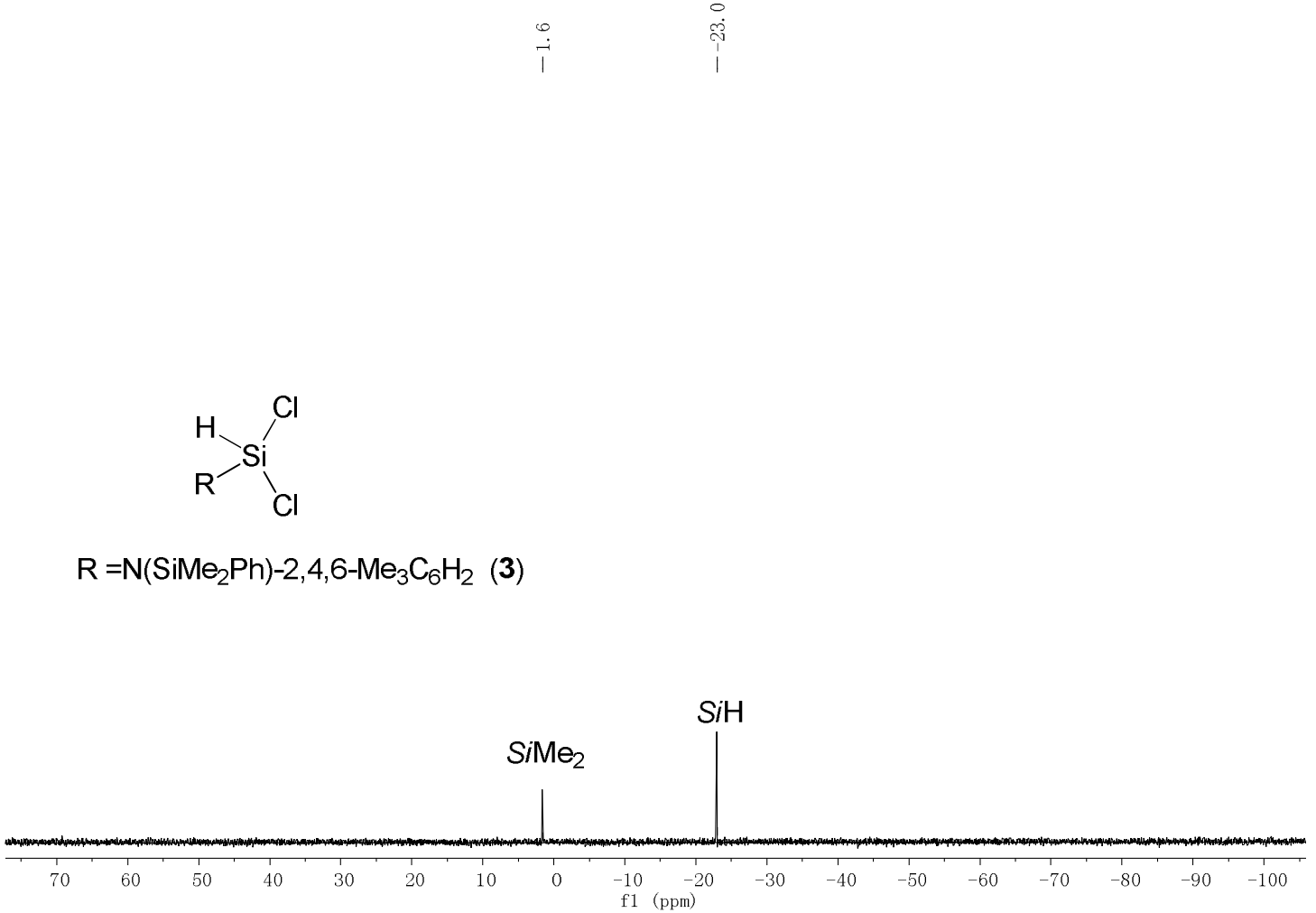


Figure S6-3 ^{29}Si NMR spectrum of **3** in $CDCl_3$

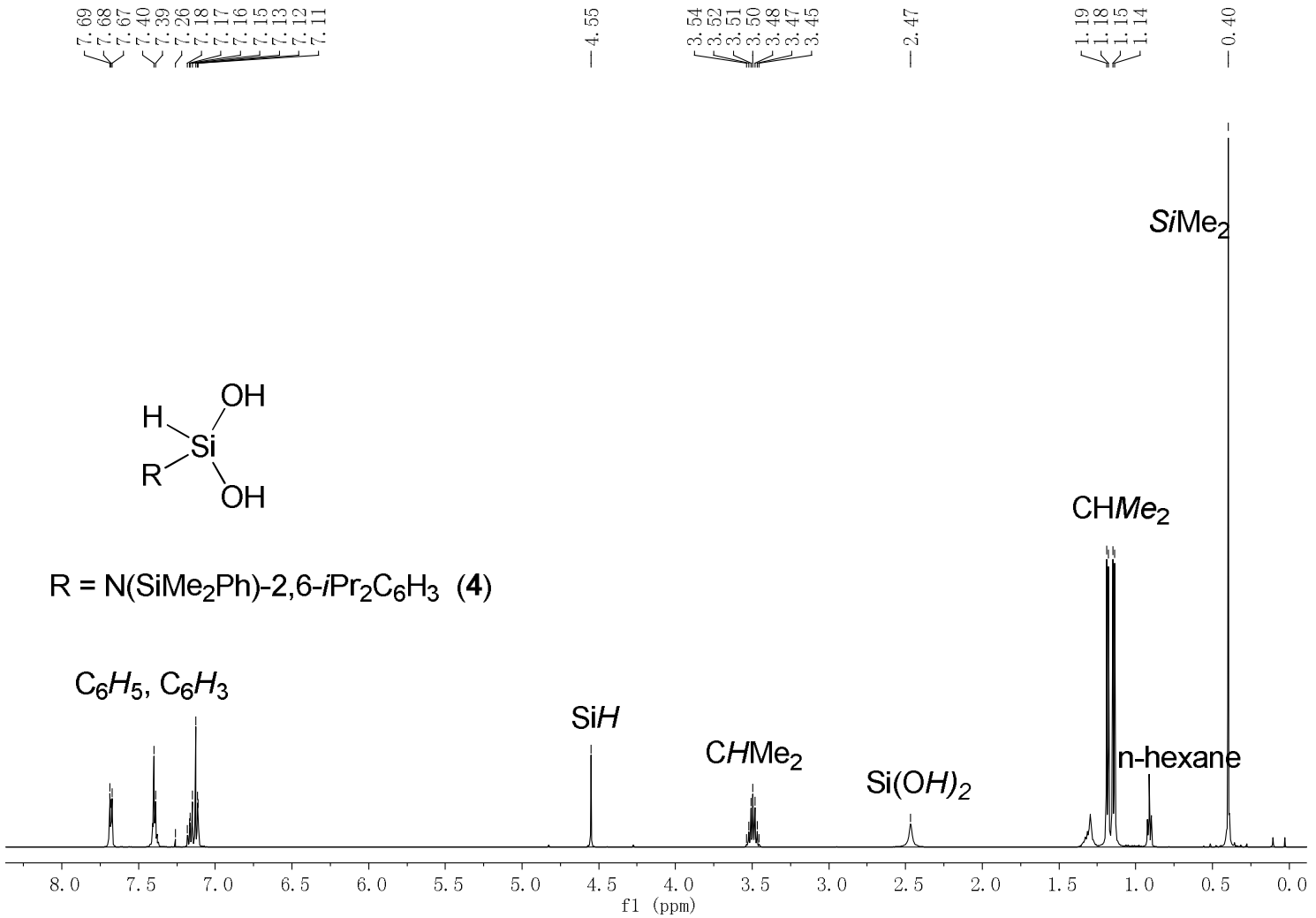


Figure S7-1 ^{1}H NMR spectrum of **4** in $CDCl_3$

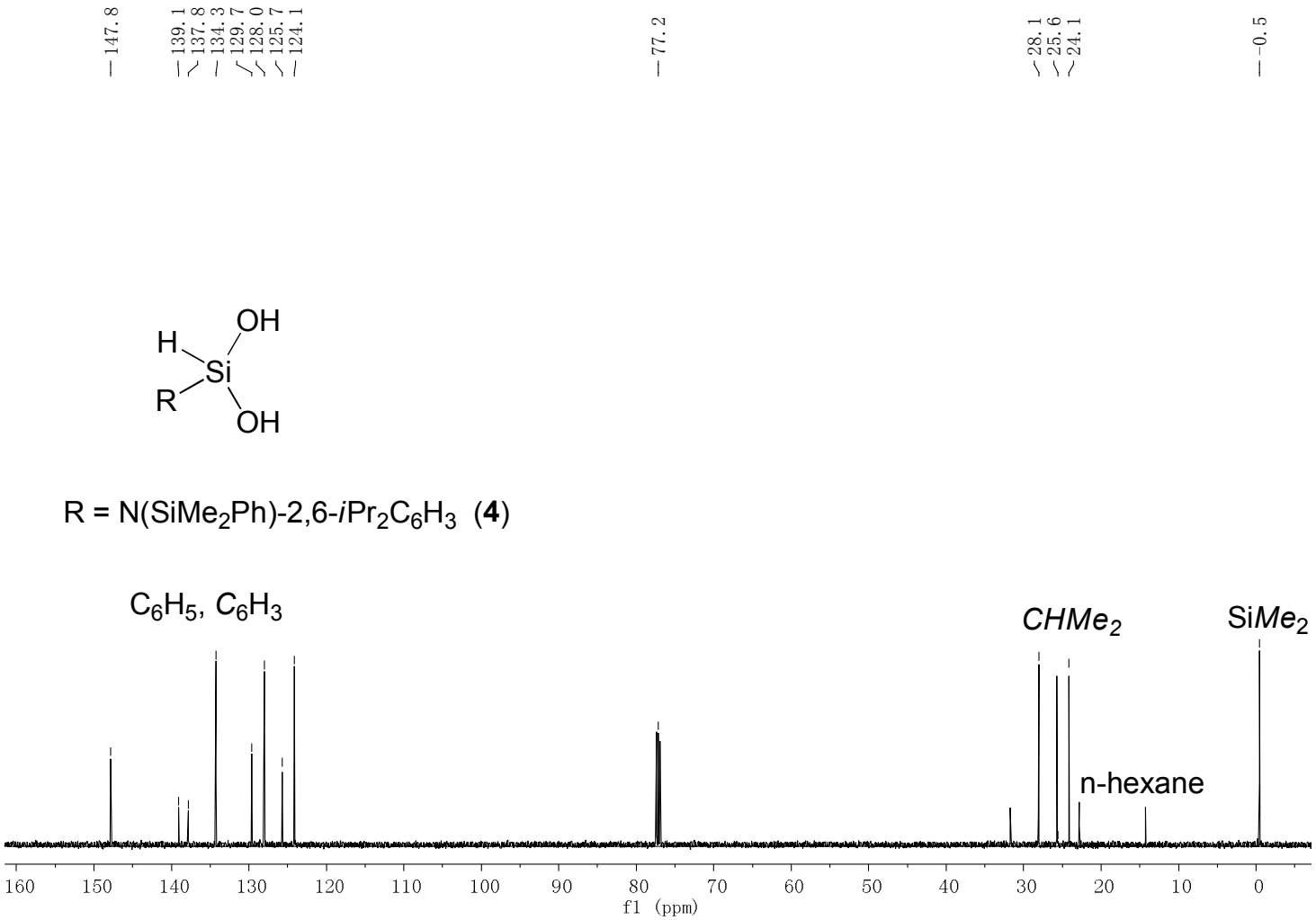


Figure S7-2 ^{13}C NMR spectrum of **4** in $CDCl_3$

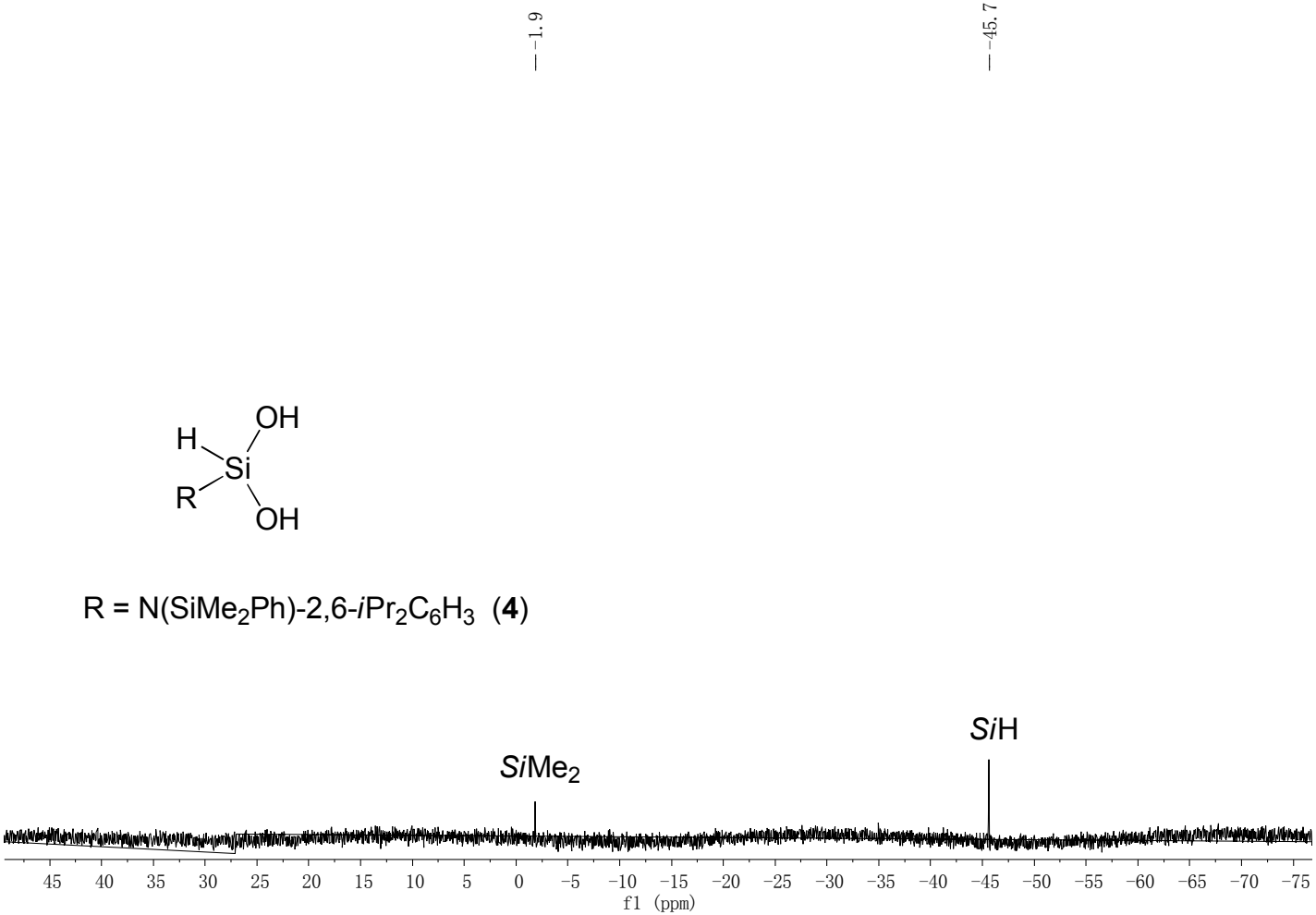


Figure S7-3 ^{29}Si NMR spectrum of **4** in $CDCl_3$

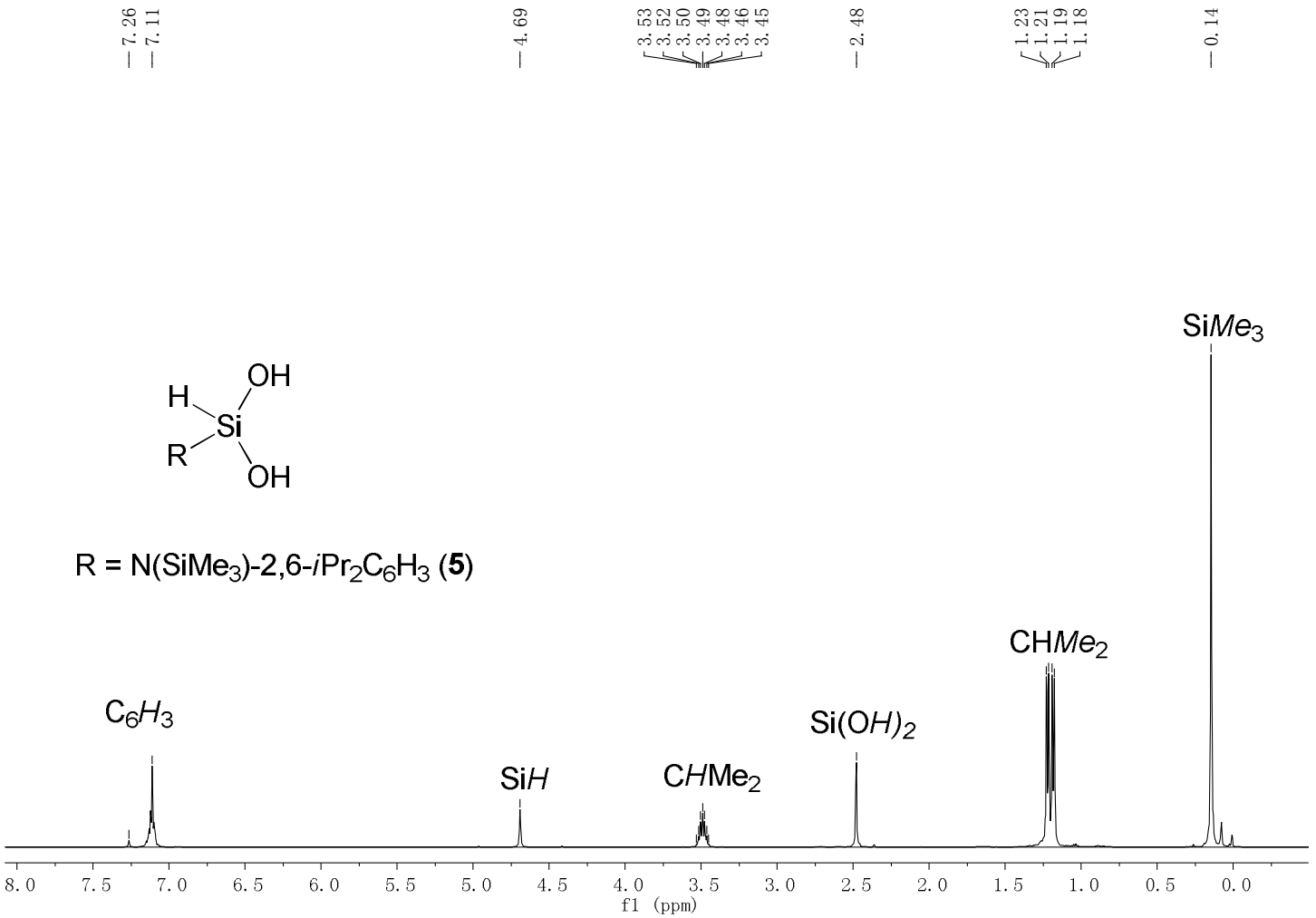


Figure S8-1 ^{1}H NMR spectrum of **5** in $CDCl_3$

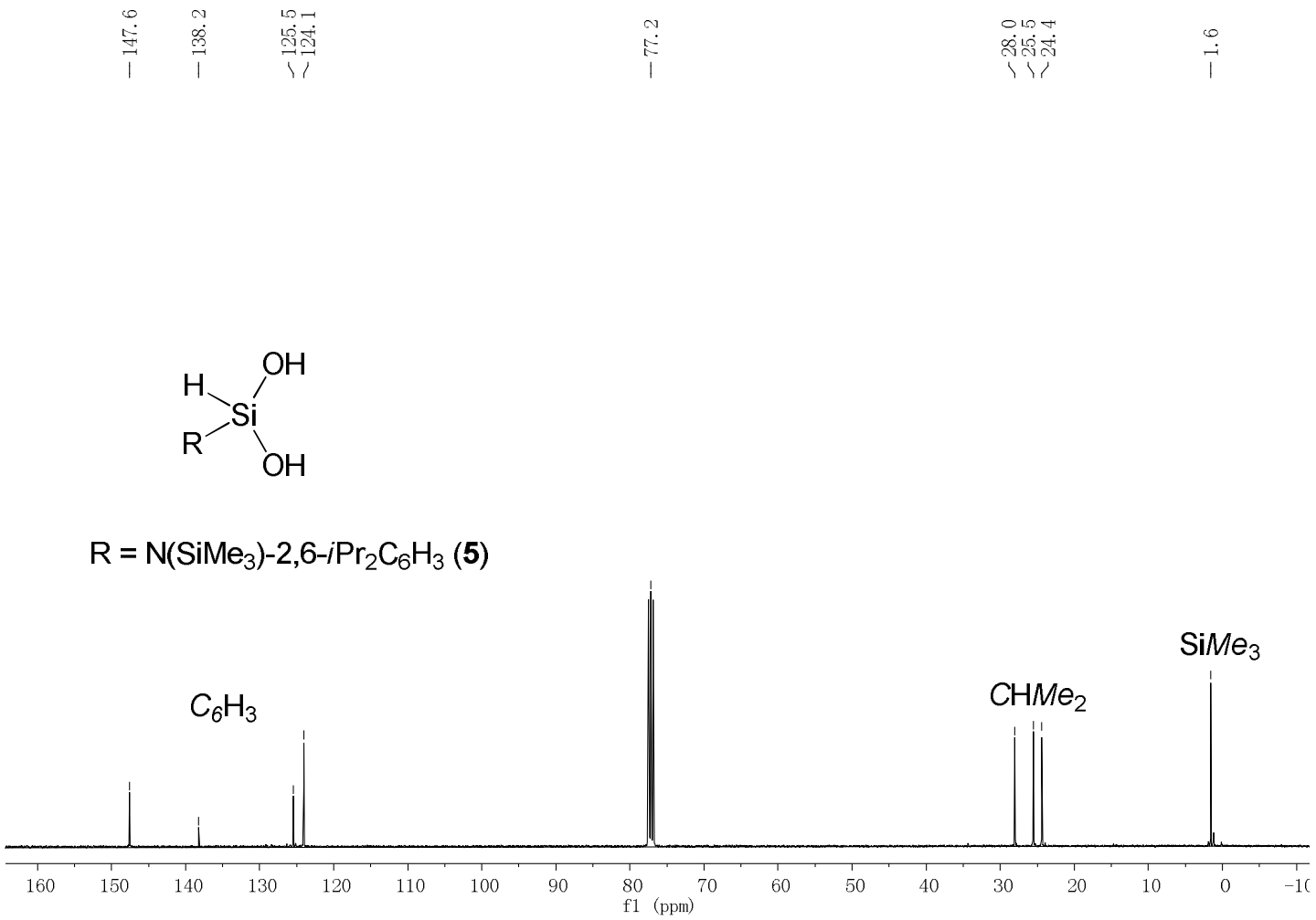


Figure S8-2 ^{13}C NMR spectrum of **5** in $CDCl_3$

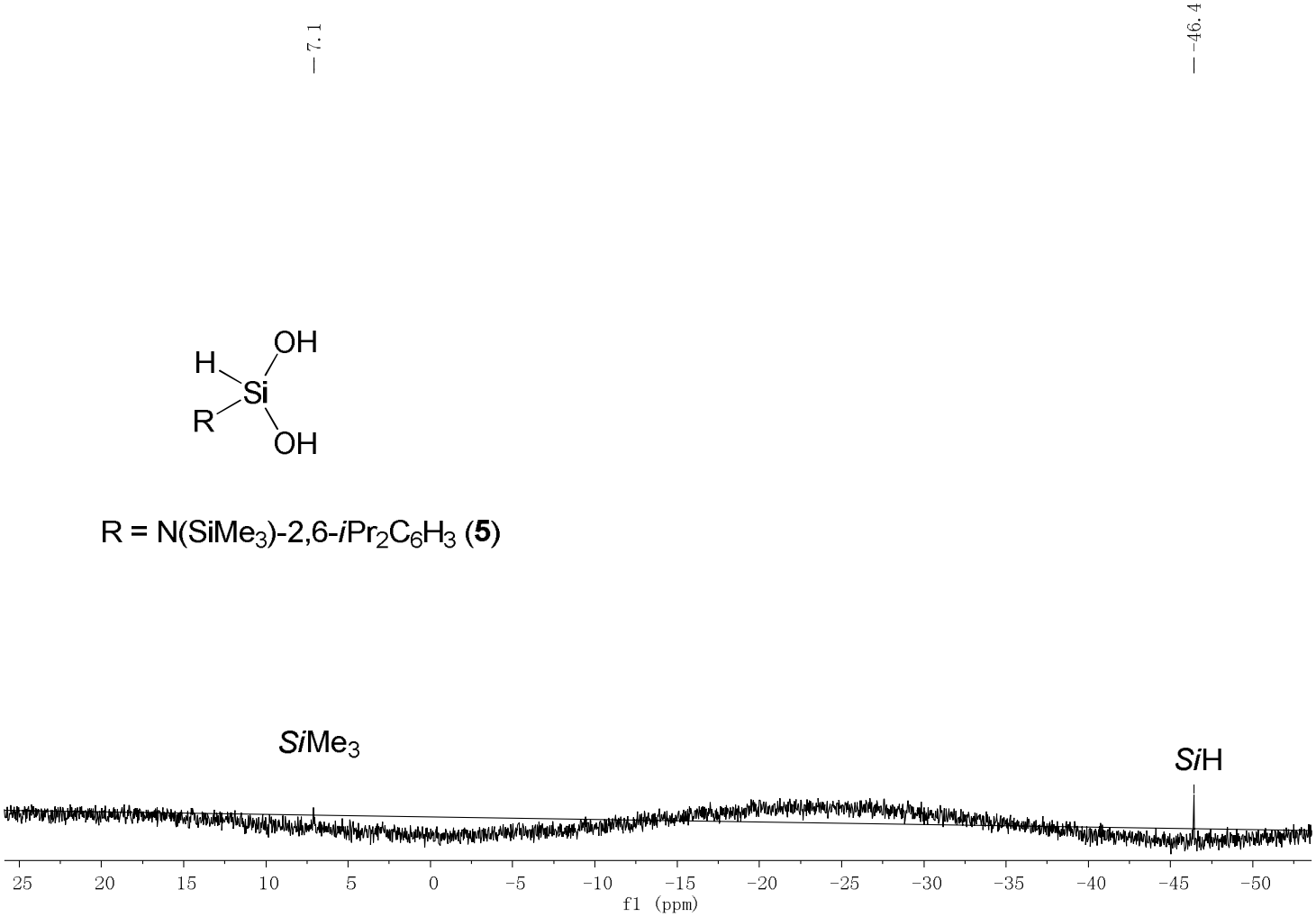


Figure S8-3 ^{29}Si NMR spectrum of **5** in $CDCl_3$

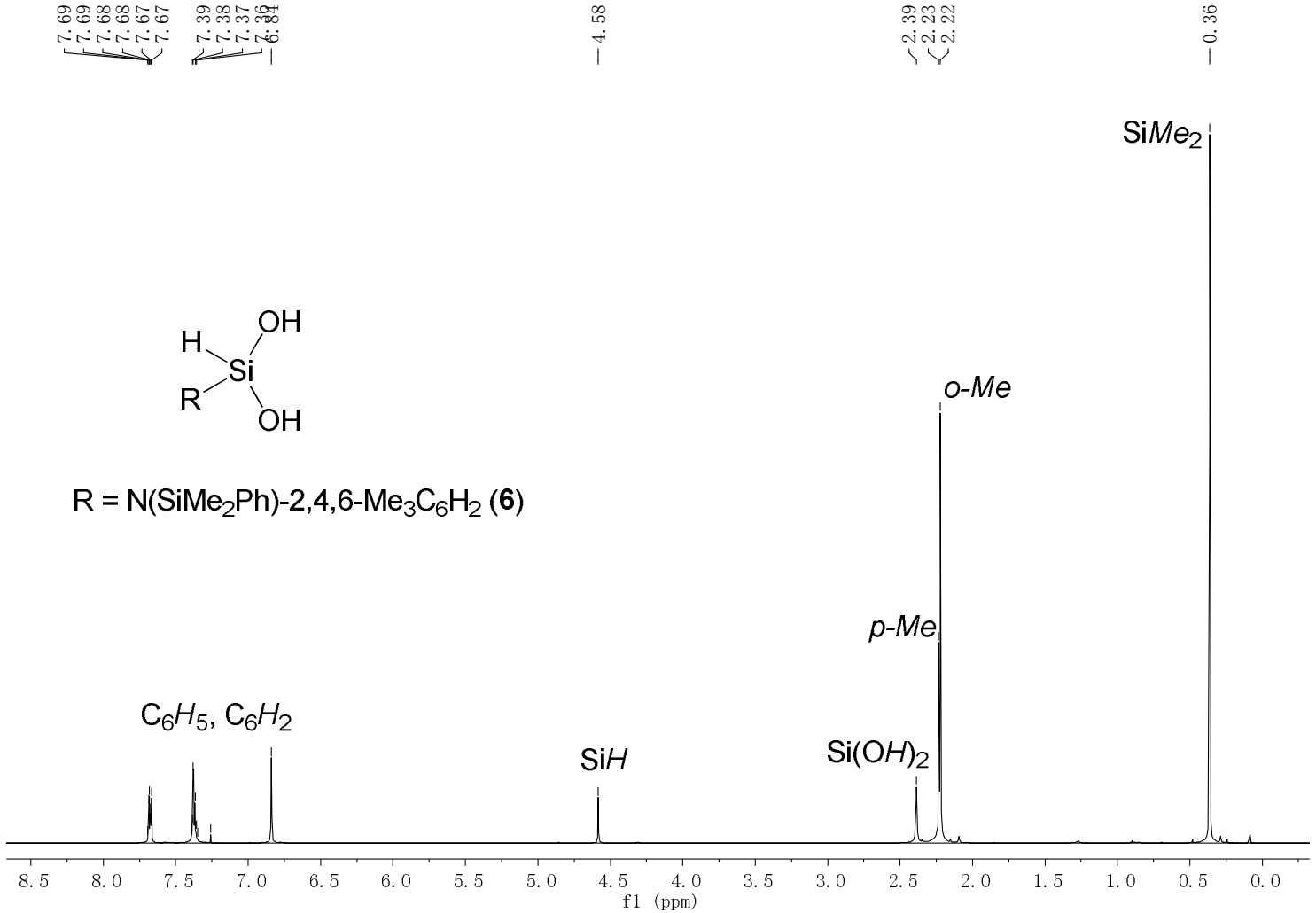


Figure S9-1 ^{1}H NMR spectrum of **6** in $CDCl_3$

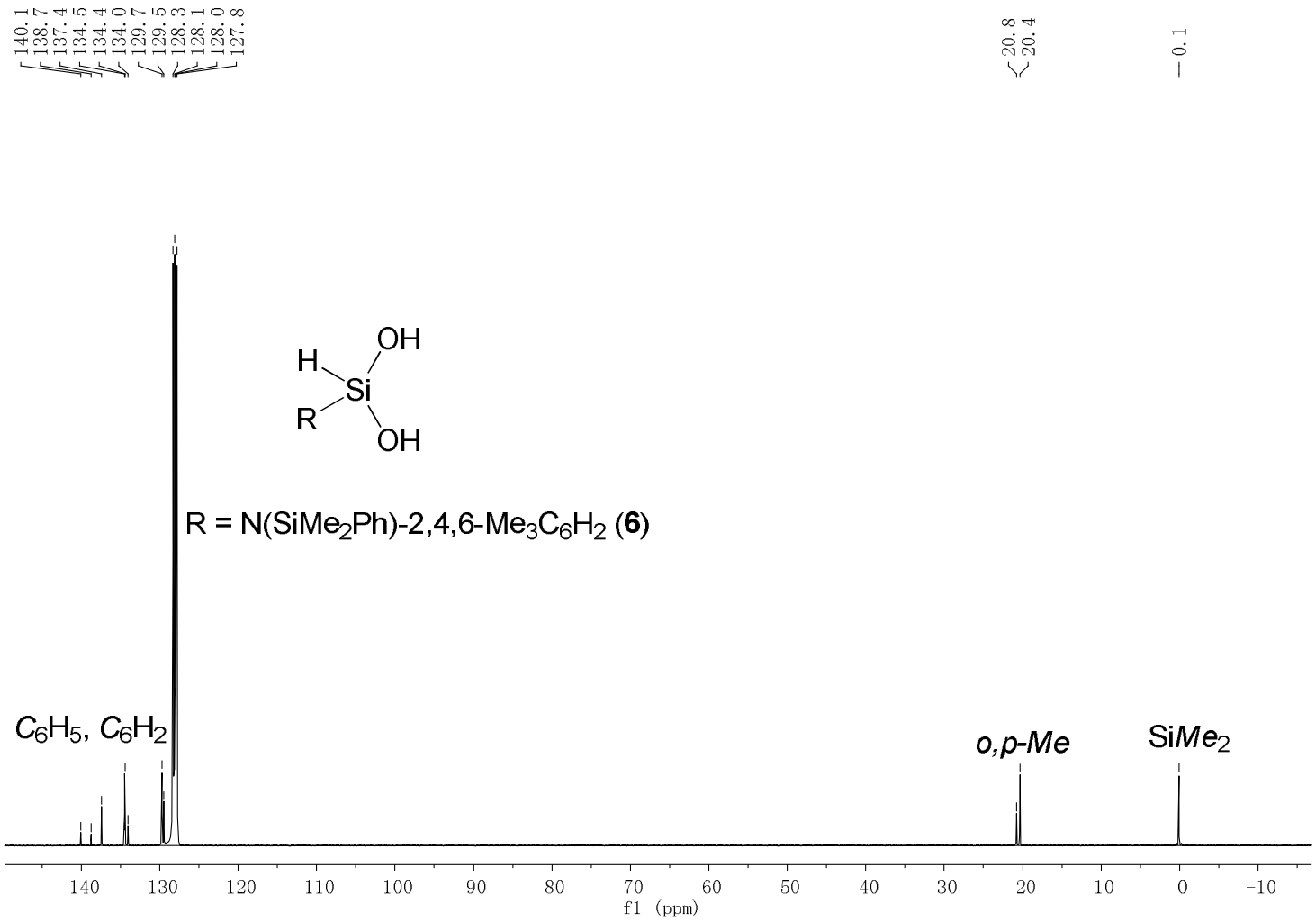


Figure S9-2 ^{13}C NMR spectrum of **6** in C_6D_6

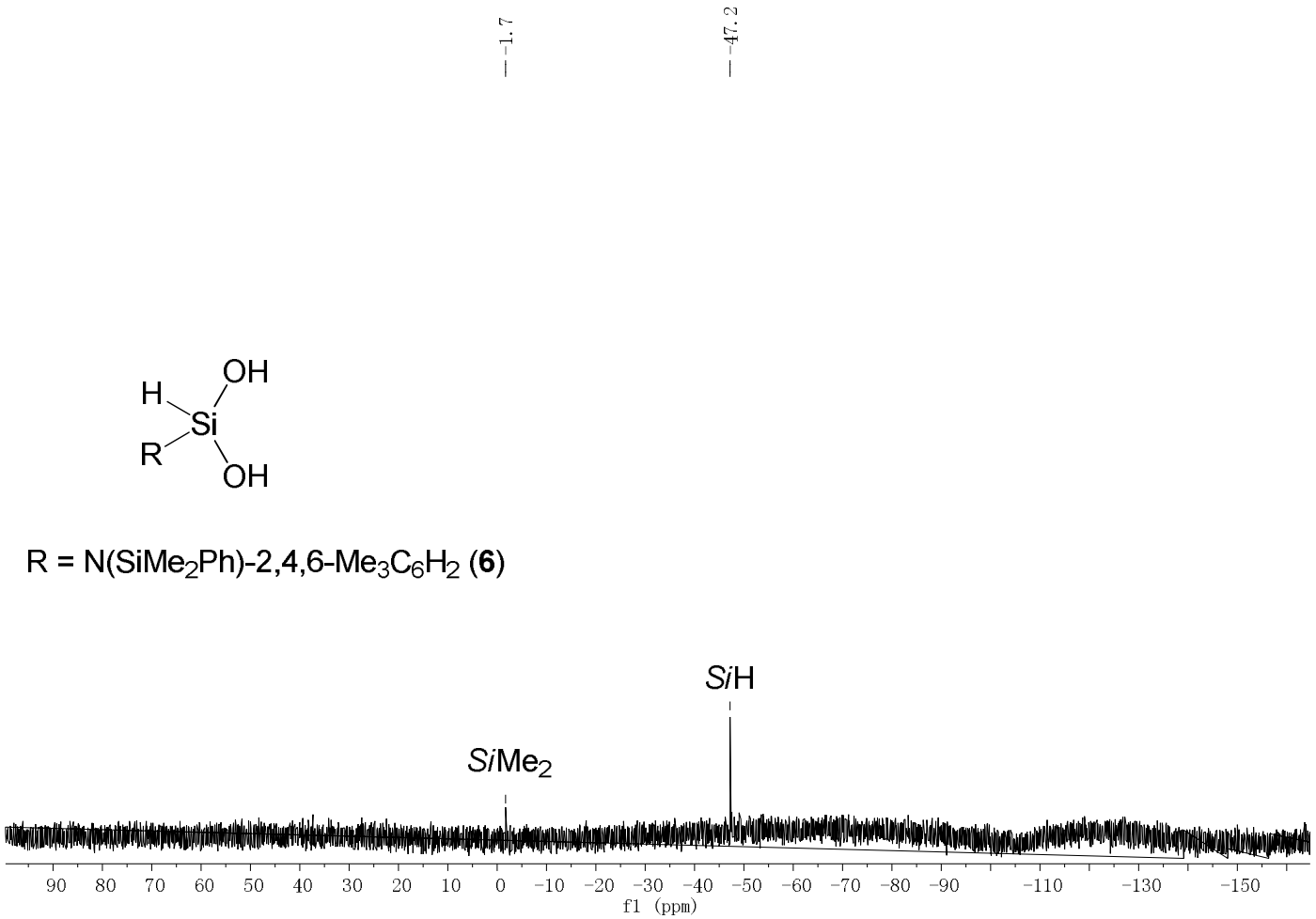


Figure S9-3 ^{29}Si NMR spectrum of **6** in $CDCl_3$

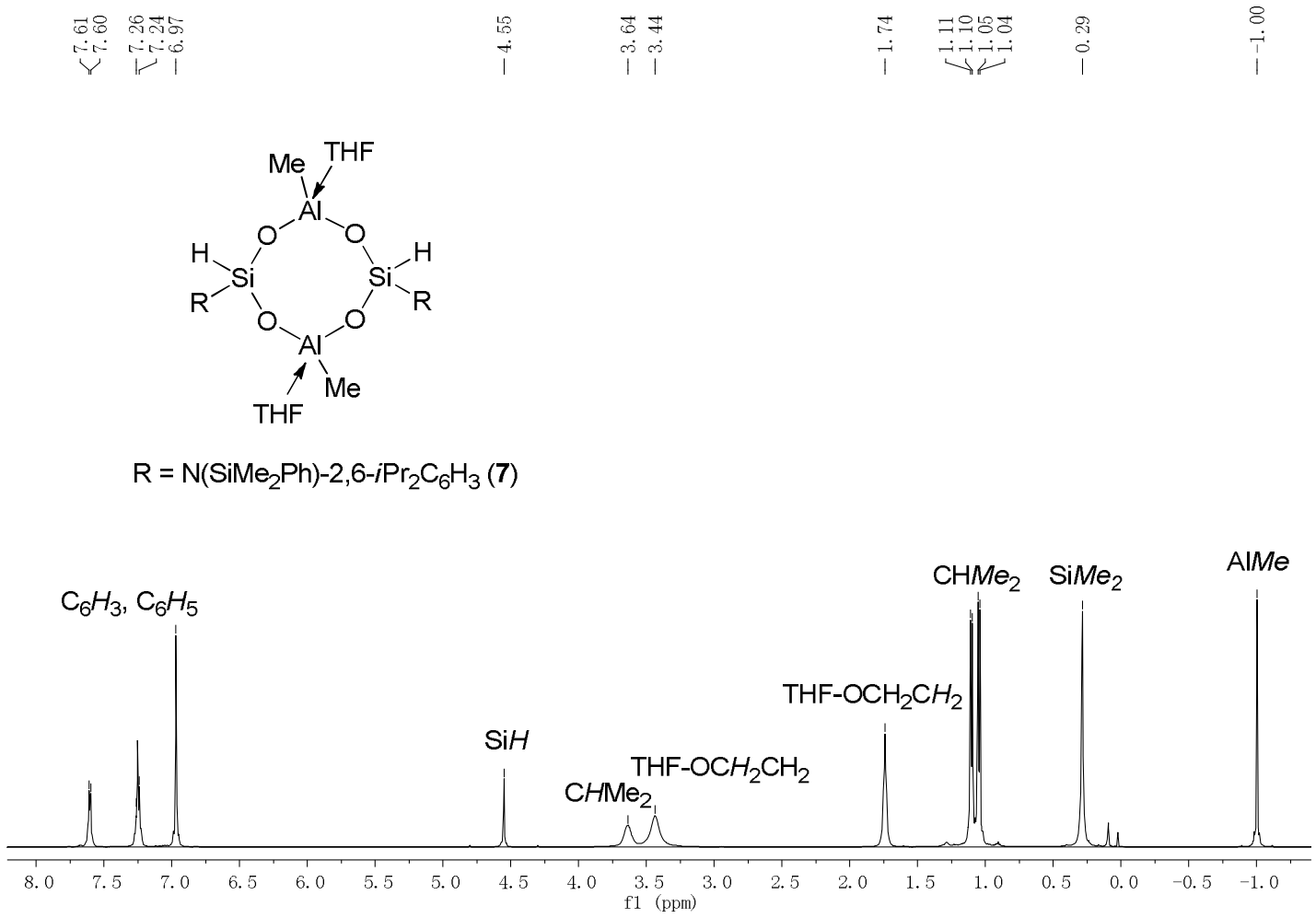
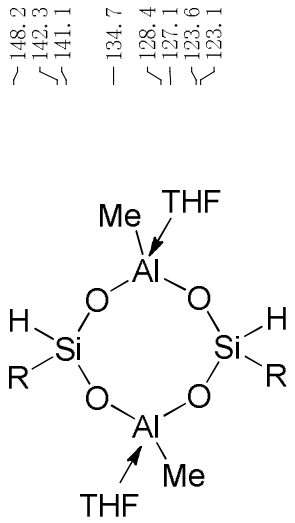


Figure S10-1 ^{1}H NMR spectrum of **7** in $CDCl_3$



R = N(SiMe$_2$Ph)-2,6-*i*Pr$_2$C$_6$H$_3$ (**7**)

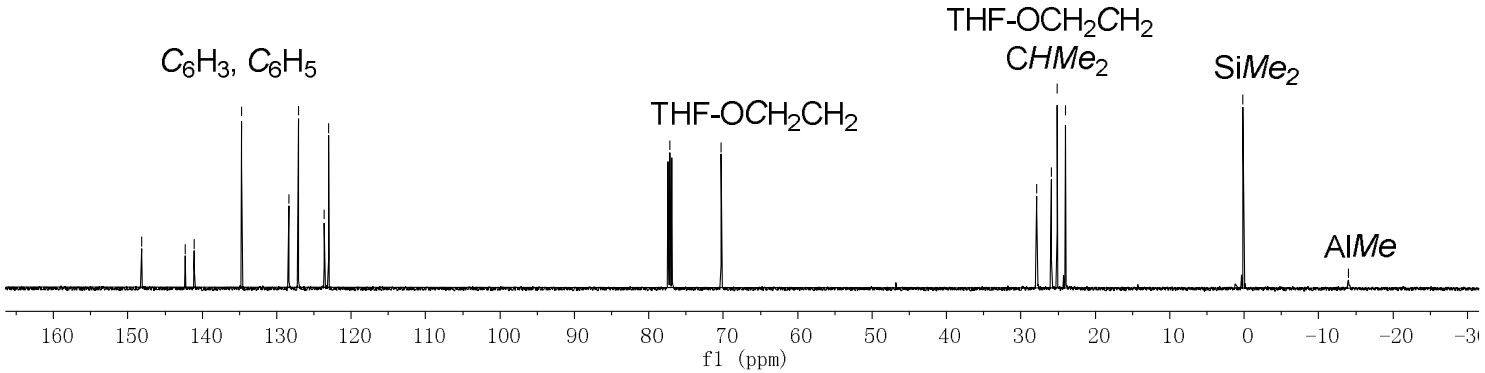


Figure S10-2 ^{13}C NMR spectrum of **7** in $CDCl_3$

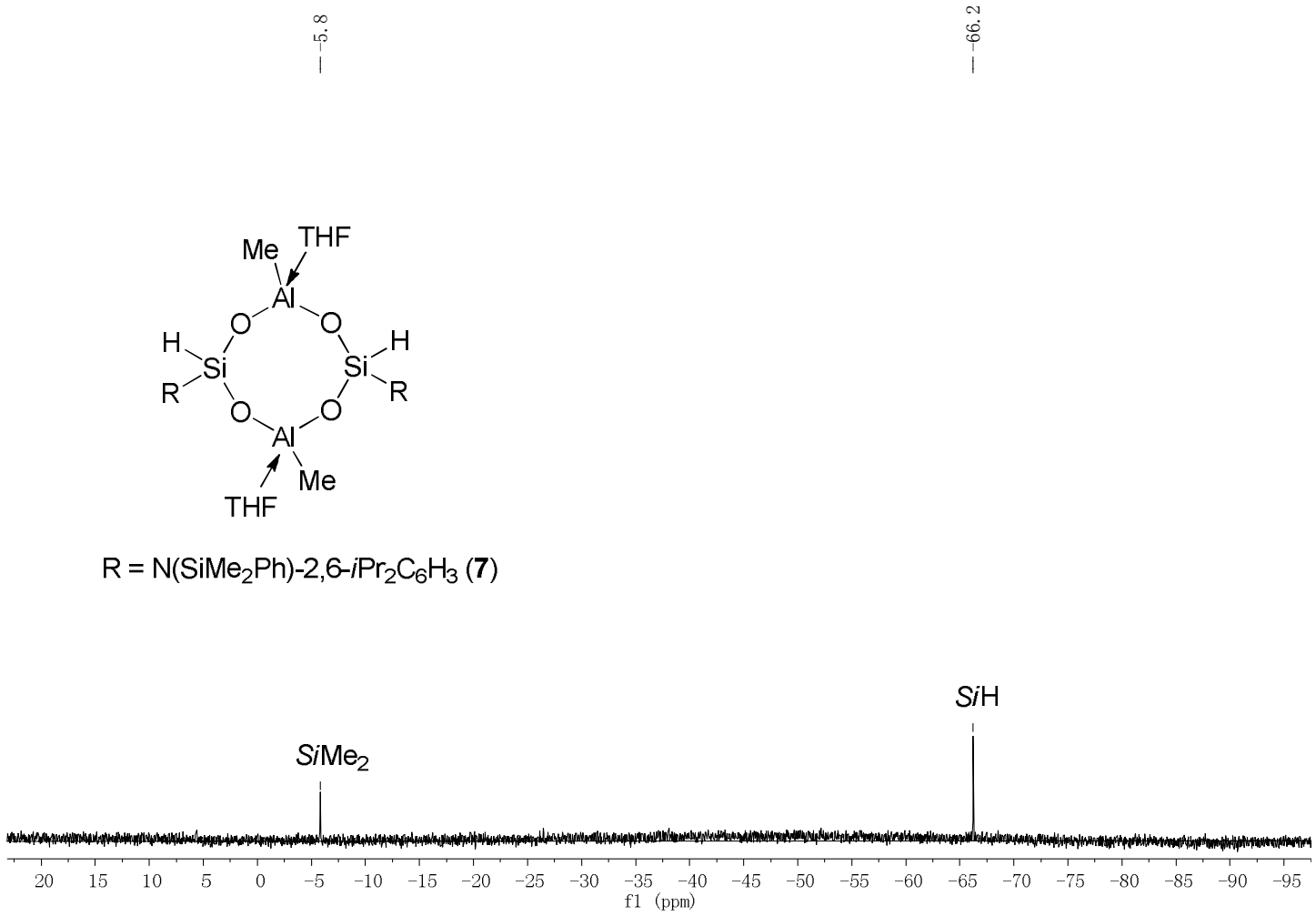


Figure S10-3 ^{29}Si NMR spectrum of **7** in $CDCl_3$

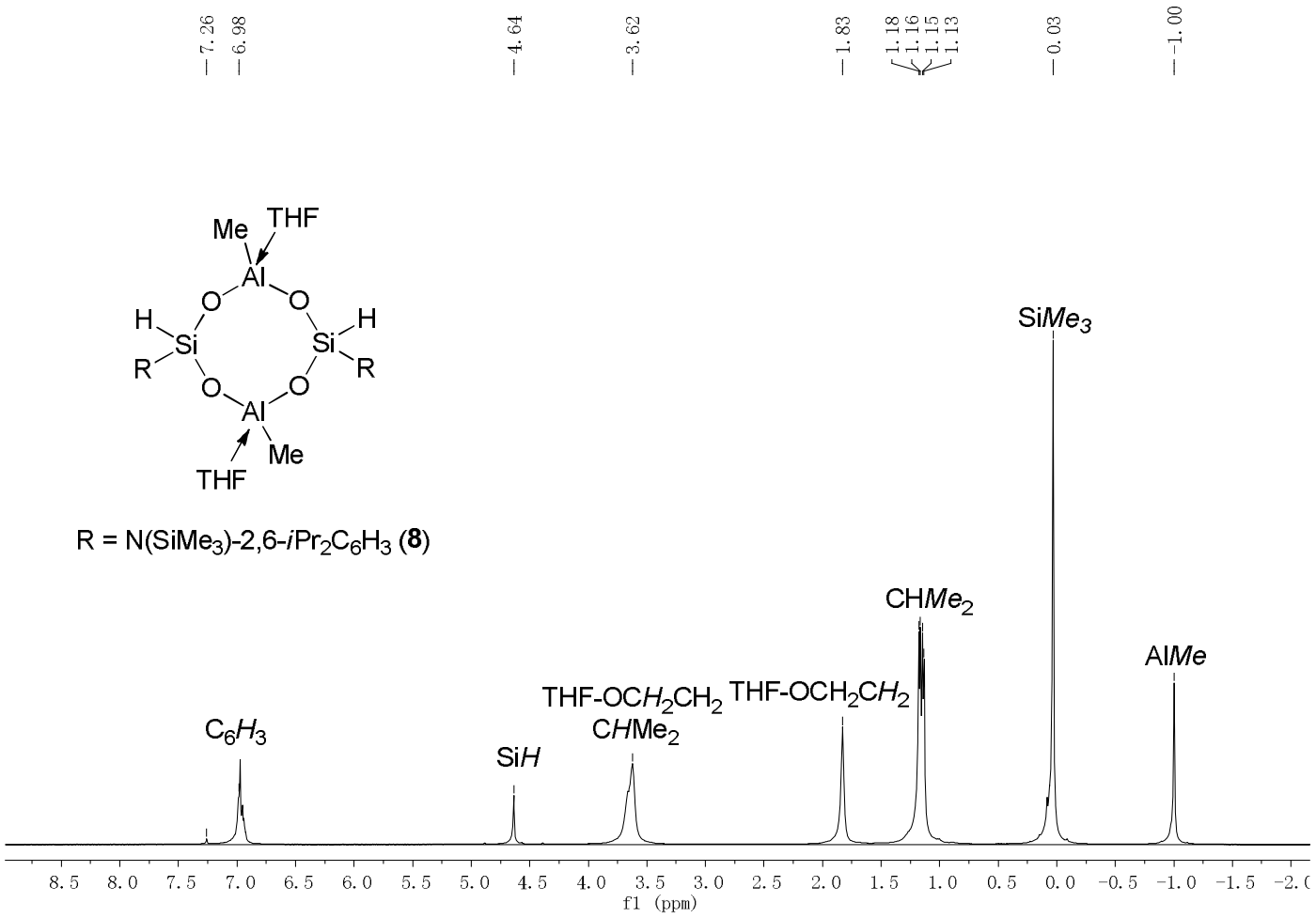


Figure S11-1 ^{1}H NMR spectrum of **8** in $CDCl_3$

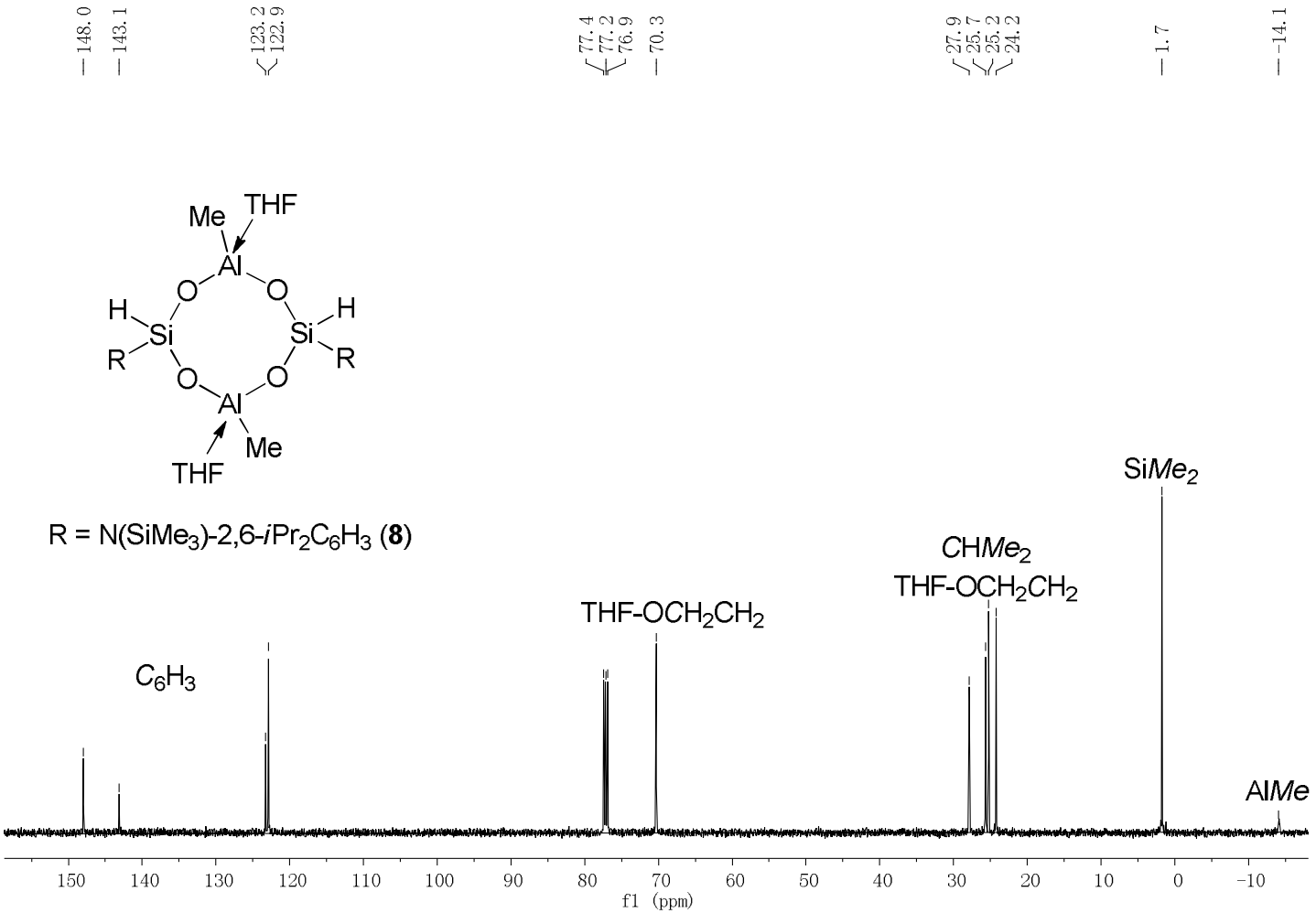


Figure S11-2 ^{13}C NMR spectrum of **8** in $CDCl_3$

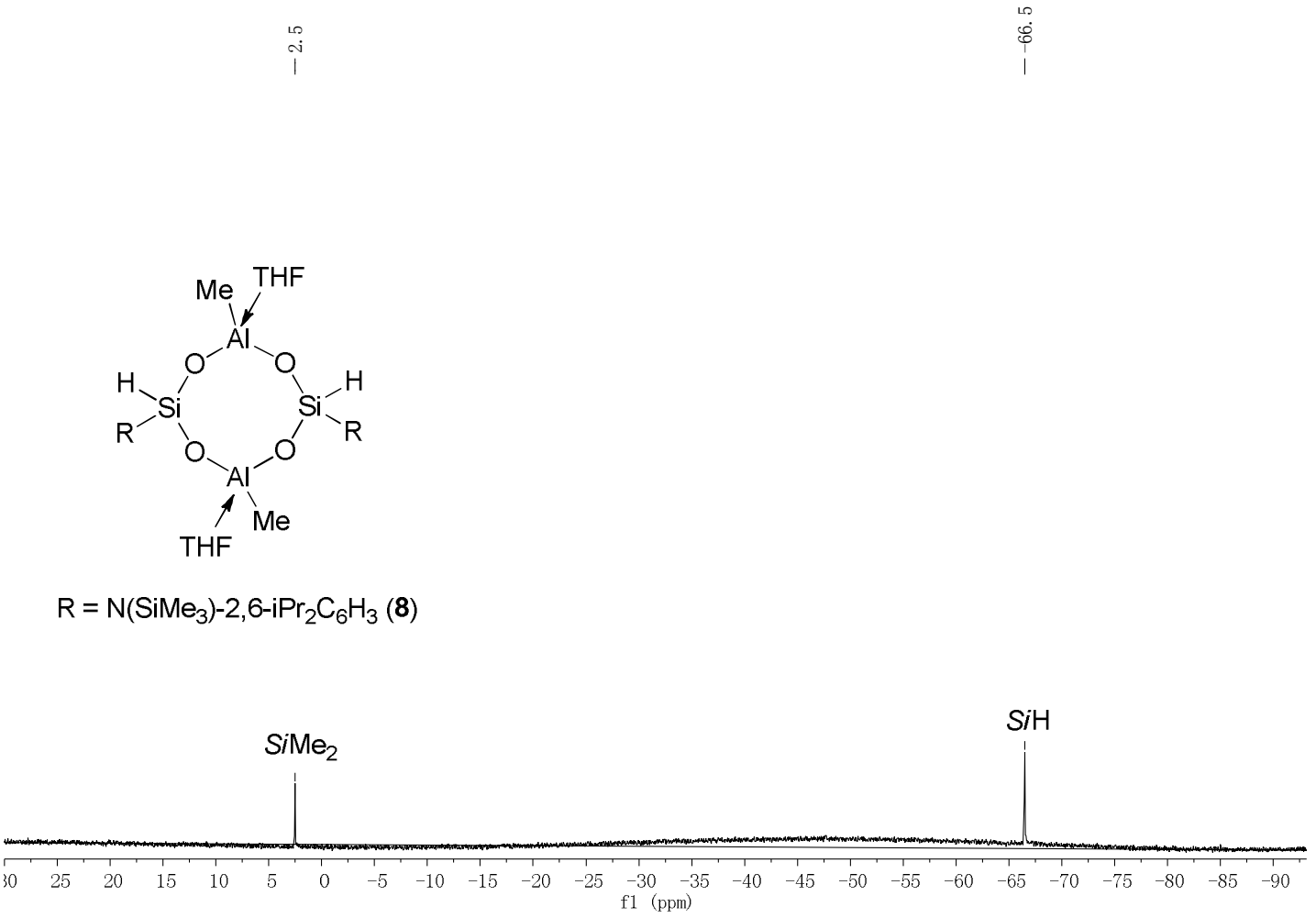


Figure S11-3 ^{29}Si NMR spectrum of **8** in $CDCl_3$

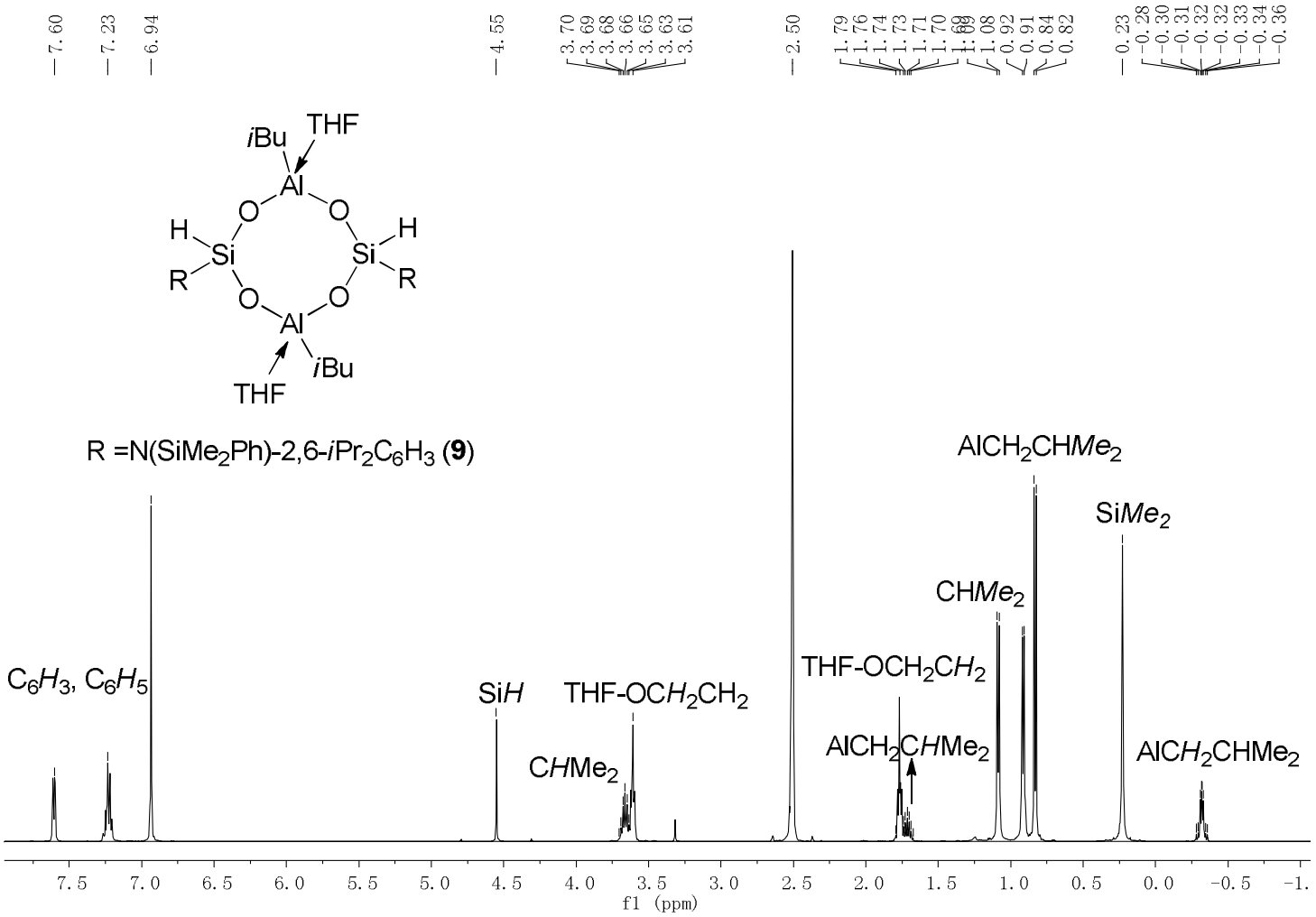


Figure S12-1 ^{1}H NMR spectrum of **9** in d^{6}-DMSO

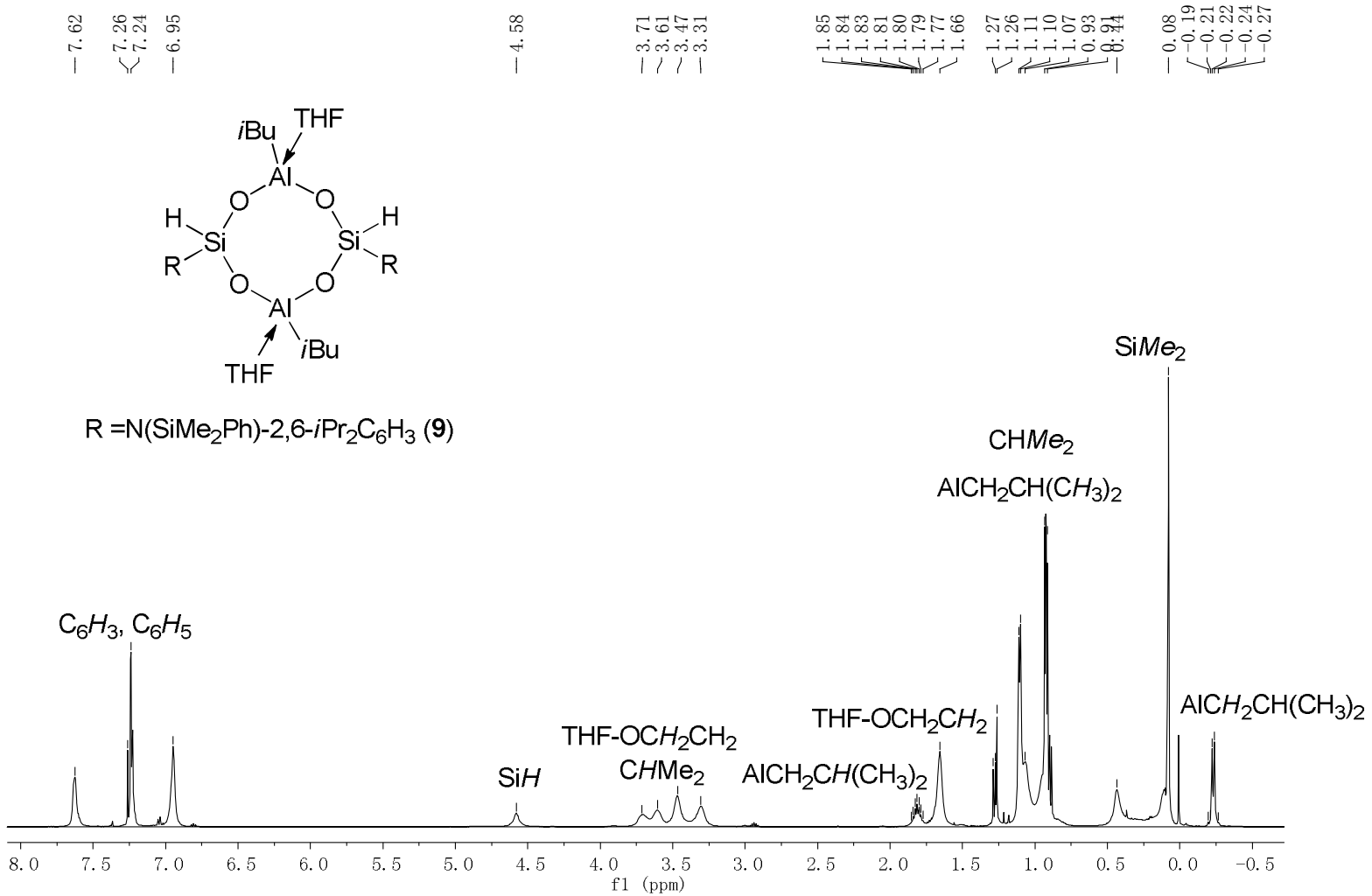


Figure S12-2 ^{1}H NMR spectrum of **9** in $CDCl_3$

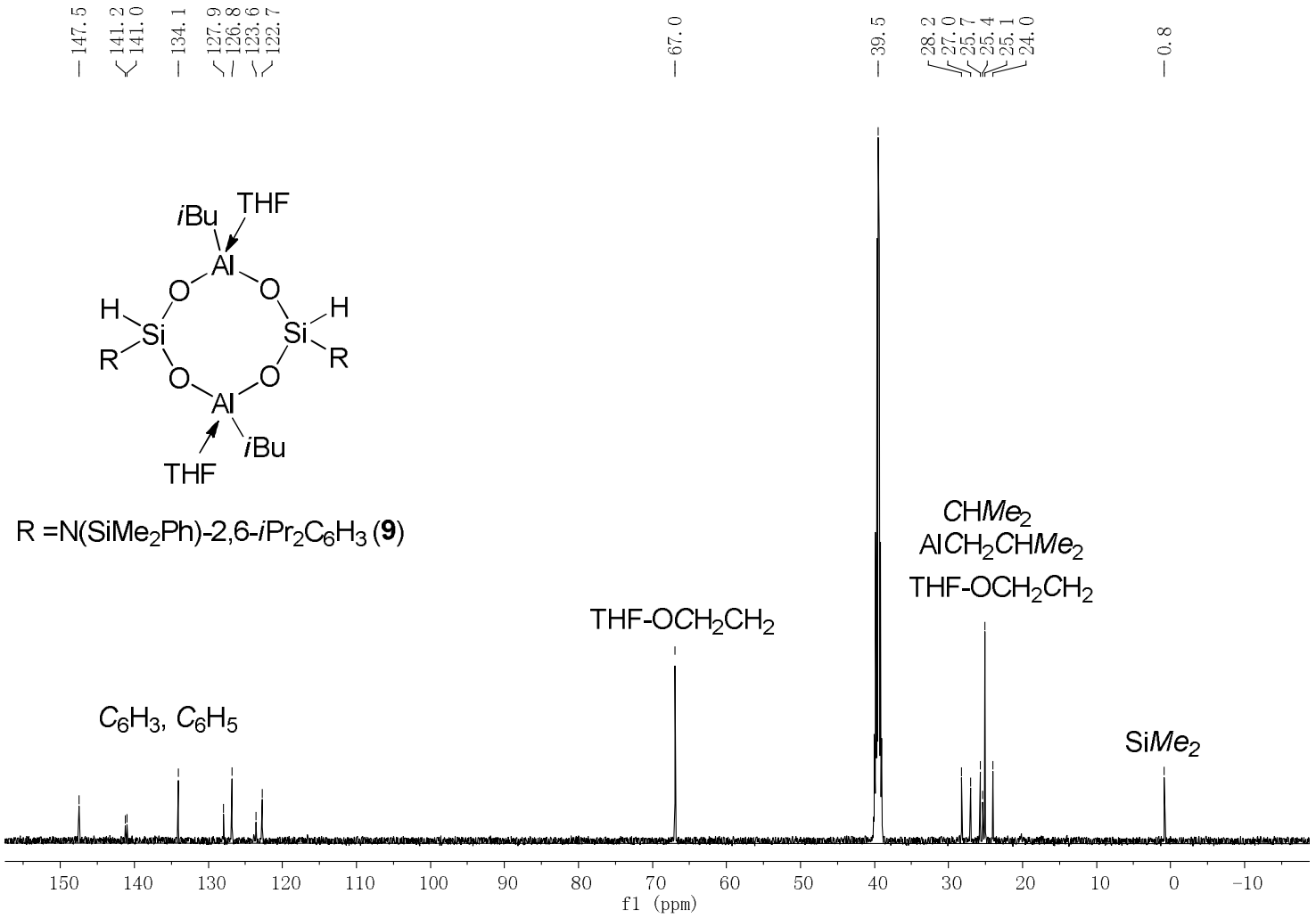


Figure S12-3 ^{13}C NMR spectrum of **9** in d^6-DMSO

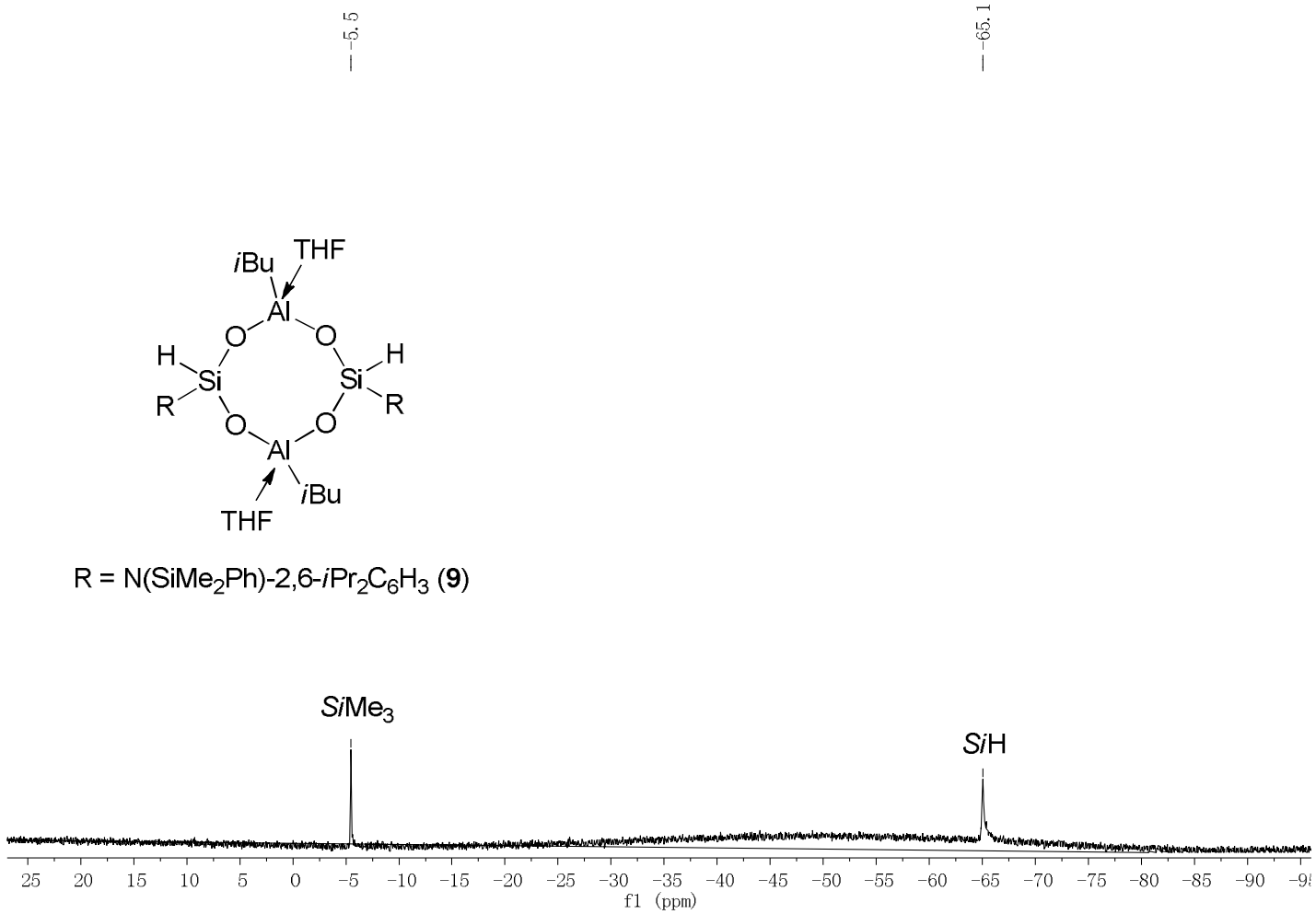


Figure S12-4 ^{29}Si NMR spectrum of **9** in $CDCl_3$

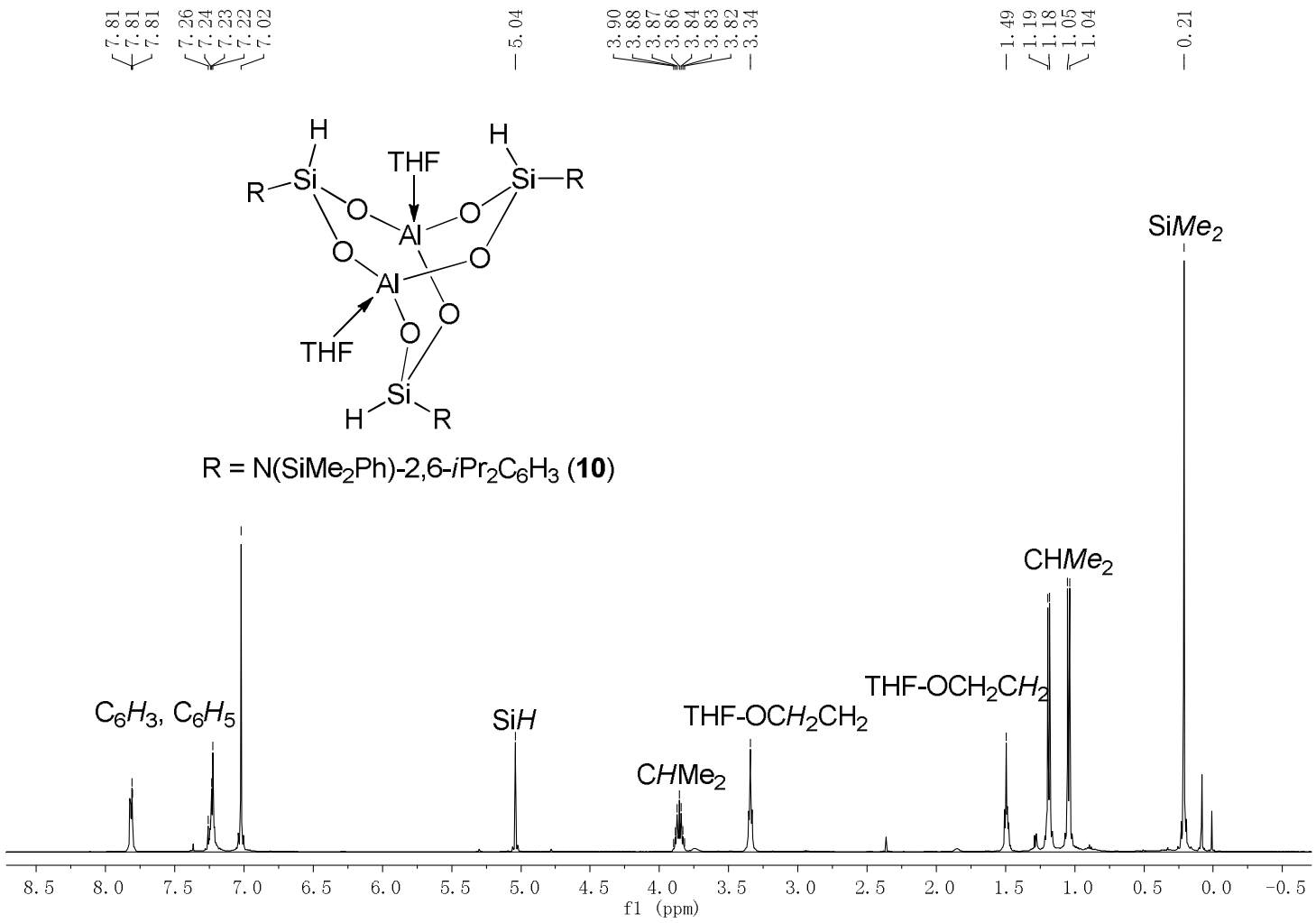


Figure S13-1 ^{1}H NMR spectrum of **10** in $CDCl_3$

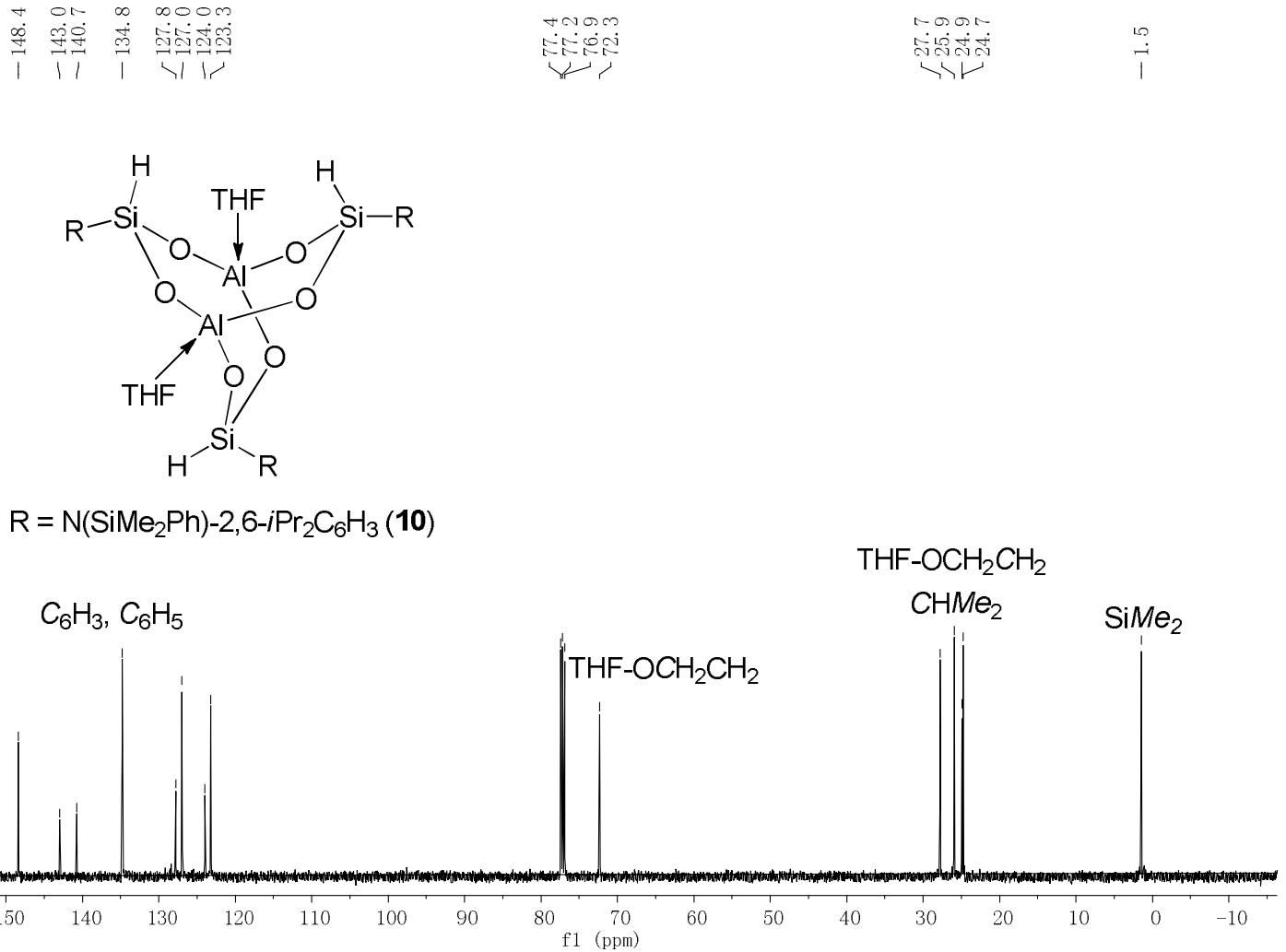
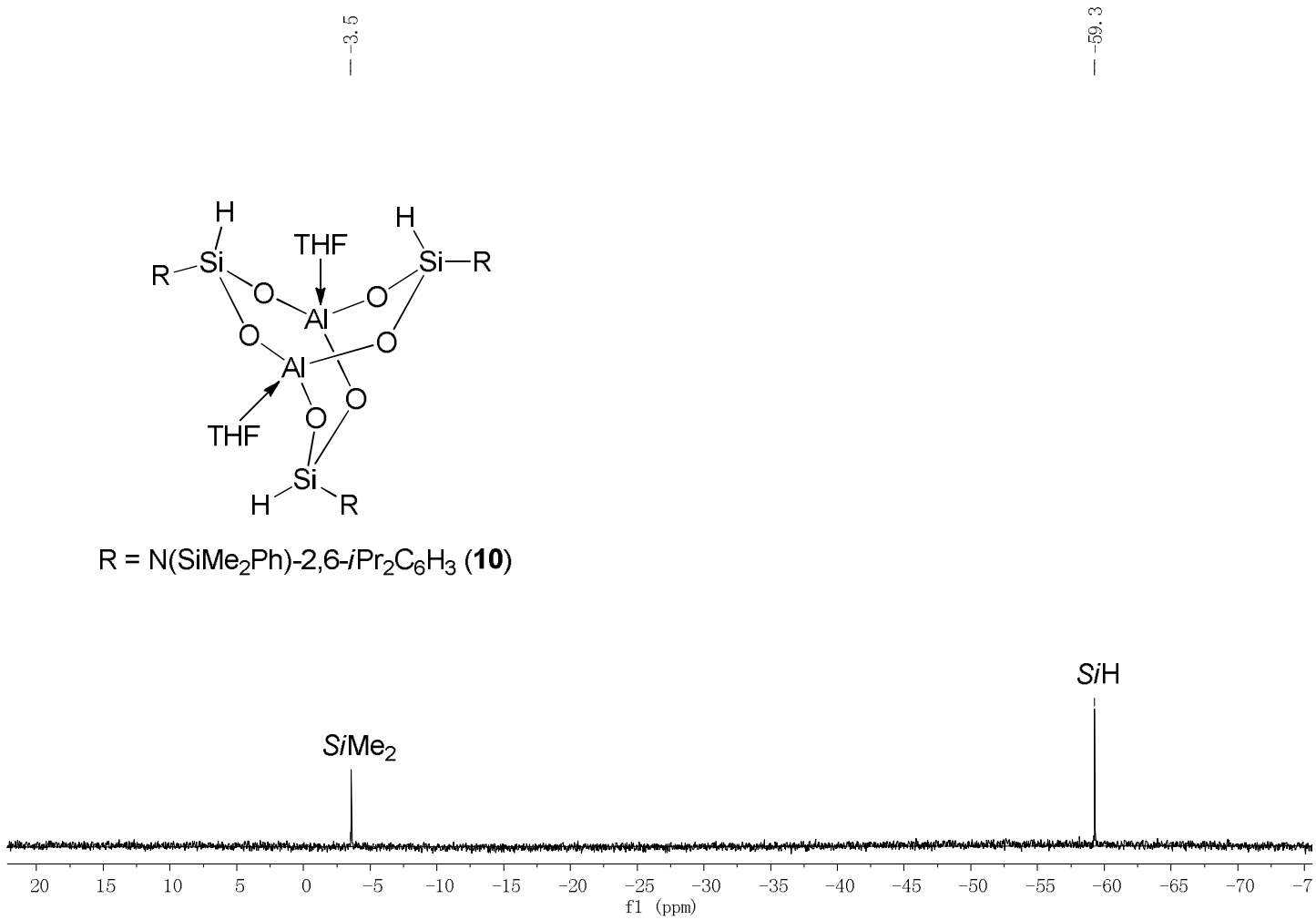


Figure S13-2 ^{13}C NMR spectrum of **10** in $CDCl_3$



R = N(SiMe$_2$Ph)-2,6-*i*Pr$_2$C$_6$H$_3$ (**10**)

Figure S13-3 ^{29}Si NMR spectrum of **10** in $CDCl_3$

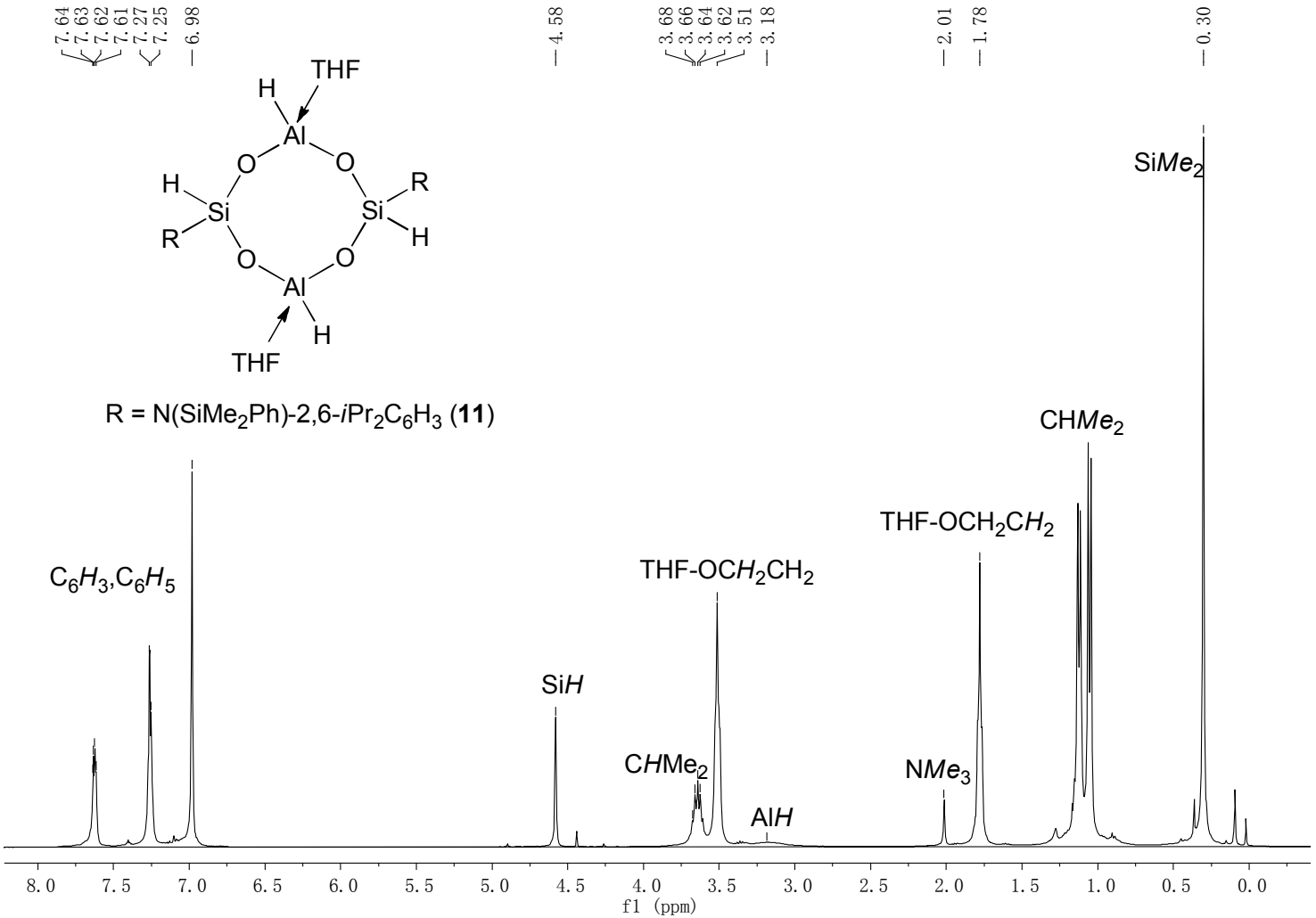


Figure S14-1 ^{1}H NMR spectrum of **11** in $CDCl_3$

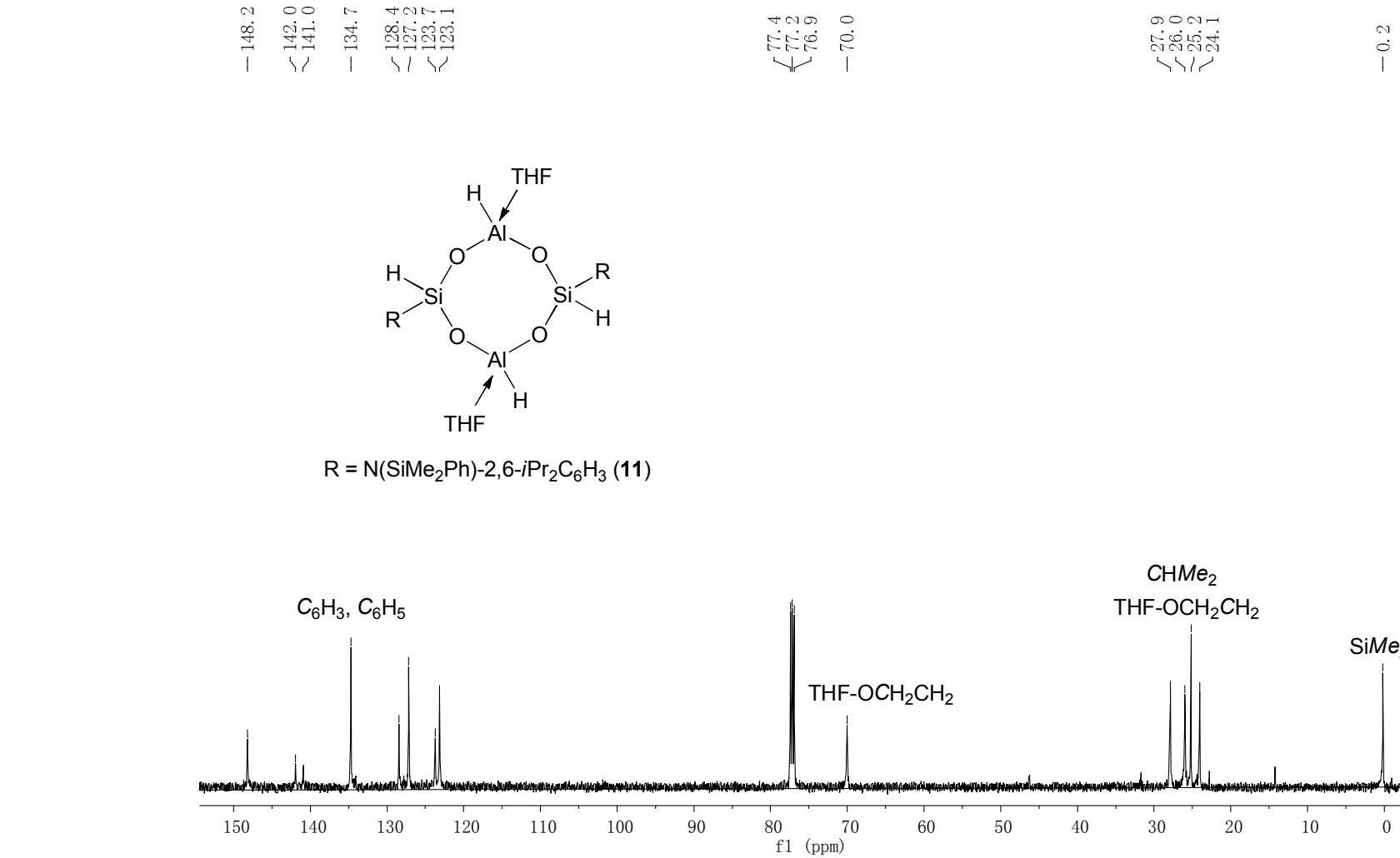
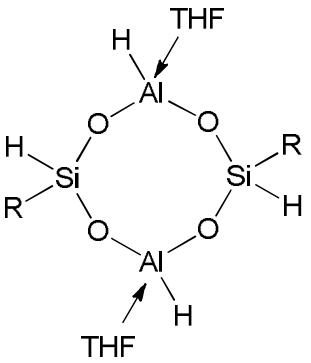


Figure S14-2 ^{13}C NMR spectrum of **11** in $CDCl_3$



R = N(SiMe$_2$Ph)-2,6-*i*Pr$_2$C$_6$H$_3$ (**11**)

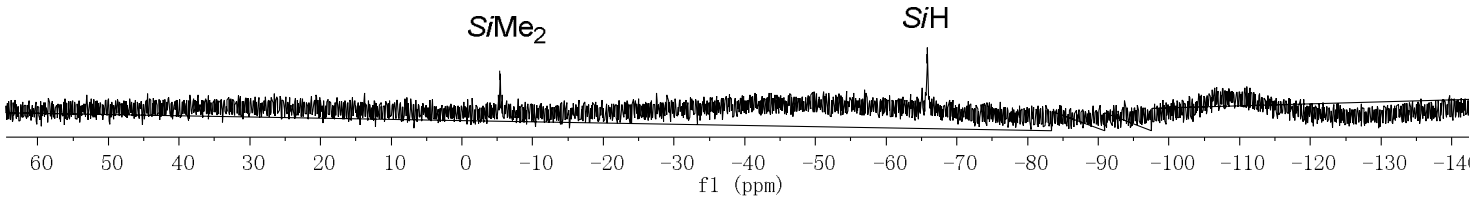


Figure S14-3 ^{29}Si NMR spectrum of **11** in $CDCl_3$