Borohydrides Catalyzed Redistribution Reaction of Hydrosilane and Chlorosilane: A Potential System for Facile Preparation of Hydrochlorosilanes

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Supporting Information

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Ⅰ. General information

All the reactions were carried out under nitrogen atmosphere. The chlorosilanes Et_2SiCl_2, $PhSiCl_3$, $PhMeSiCl_2$, Ph_2SiCl_2, as well as hydrosilane Et_2SiH_2, $PhSiH_3$, $PhMeSiH_2$, and Ph_2SiH_2 were purchased from Shanghai Aladdin Bio-Chem Technology Co., Ltd and used without further purification. The chlorosilanes, $ClCH_2SiCl_3$, $ClCH_2SiMeCl_2$, and $Cl_2CHSiMeCl_2$ were purchased from Hebei Taifeng Chemicals Co., Ltd and used as received. The hydrosilanes $ClCH_2SiH_3$, $ClCH_2SiMeH_2$, $Cl_2CHSiMeH_2$ were prepared by referring literature[1,2]. The borohydrides $LiBH_4$, $NaBH_4$, KBH_4, $LiBEt_3H$, BH_3/THF solution and the solvents tetrahydrofuran (THF), diethylene glycol dimethyl ether (diglyme), Et_2O, toluene, CH_3CN, 1,3-dimethyl-2-imidazolidinone (DMI), hexamethylphosphoric triamide (HMPA) were purchased from Shanghai Aladdin Bio-Chem Technology Co., Ltd. n-Butyl ether (Bu_2O) was purchased from Beijing J&K Technology Co., Ltd. All reactions were monitored by ^1H NMR using a Bruker AvanceIII-400 MHz spectrometer or a Fourier 300 MHz spectrometer, with the solvent resonance ($CDCl_3$:7.26) as the internal standard. Data for ^1H NMR are expressed as follows: chemical shift (δ ppm) values, multiplicity (s=singlet, d=doublet, t=triplet, q=quartet, quin=quintet, m=multiplet, b=broad), coupling constants (Hz), integration. $Cl_2CHSiMeHCl$ was verified by GC-MS equipped with MS detector (EI), DB-5MS (30m×0.25mm), and using the following temperature program: Injector 250℃, oven $T_{initial}$ = 50 °C (2 min), rate 20 °C /min, T_{final} = 300 °C, hold 20 min.

Ⅱ. Synthesis of hydrosilanes

General Procedure for Synthesis of $ClCH_2SiH_3$

To a mixture of $LiAlH_4$ (7.84 g, 0.21mol), 50 mL Bu_2O in a 250 mL four-necked flask was added $ClCH_2SiCl_3$ (46.0 g, 0.25 mol) dropwise. After finishing the addition of chlorosilane, the reaction mixture was further stirred mechanically at 25 ℃ for 6 h. The final mixture solution was distilled to give 9.6 g (0.12 mol) of $ClCH_2SiH_3$（bp. 31℃）in 48% yield as a colorless, volatile liquid. ^1H NMR (400M, $CDCl_3$): δ 3.82 (t, J = 3.5 Hz, 3H, -SiH_3), 2.98 (q, J = 3.6 Hz, 2H, ClCH_2-). ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.78. ^{29}Si NMR ($CDCl_3$, 79 MHz, 25 ℃): δ -55.73 (see in Figure 1)

Synthesis of $ClCH_2SiMeH_2$

This compound was prepared in the same manner as described for $ClCH_2SiH_3$, and was obtained in 70% yield as a colorless, volatile liquid. （bp. 59℃） ^1H NMR (400M, $CDCl_3$): δ 3.95 (dtd, J = 7.1, 4.0, 2.9 Hz, 2H, -SiH_2-), 2.93 (t, J = 3.0 Hz, 2H, ClCH_2-), 0.29 (t, J = 4.1 Hz, 3H, CH_3-). ^{13}C NMR (75 MHz, $CDCl_3$) δ 25.86, -9.61. ^{29}Si NMR ($CDCl_3$, 79 MHz, 25 ℃): δ -31.84. (see in Figure 2)

Synthesis of $Cl_2CHSiMeH_2$

This compound was prepared in the same manner as described for $ClCH_2SiH_3$. The solvent used herein is Et_2O, and after the reduction completed, all the volatiles were distilled into a -196℃ trap (liquid nitrogen) under vacuum. Then the mixture was distilled to remove the Et_2O solvent to obtain a pure $Cl_2CHSiMeH_2$ in 65% yield as a colorless, volatile liquid. ^{1}H NMR (400M, $CDCl_3$): δ 5.44 (t, J = 2.0 Hz, 1H, Cl_2CH-), 4.13 (dt, J = 3.9, 2.0 Hz, 2H, -SiH_2-), 0.41 (t, J = 4.0 Hz, 3H, CH_3-) ^{13}C NMR (75 MHz, $CDCl_3$) δ 58.30, -10.03. ^{29}Si NMR ($CDCl_3$, 79 MHz, 25 ℃): δ -21.10. (see in Figure 3)

Ⅲ. Redistribution of hydrosilane and chlorosilane

General Procedure for redistribution of hydrosilane and chlorosilane:

To a mixture of catalyst (e.g. $LiBH_4$), solvent (or neat) in a 25 mL two-necked flask was added hydrosilane and chlorosilane in sequence. The reaction mixture was stirred at room temperature and monitored by ^{1}H-NMR.

Hydrochlorosilane products

$ClCH_2SiHCl_2$: ^{1}H NMR (400 MHz, Chloroform-d) δ 5.57 (t, J = 2.3 Hz, 1H, -$SiHCl_2$), 3.18 (d, J = 2.3 Hz, 2H, $ClCH_2$-). The ^{1}H NMR data was consistent with previously reported[3].

$ClCH_2SiH_2Cl$: ^{1}H NMR (400 MHz, Chloroform-d) δ 4.82 (t, J = 3.4 Hz, 2H, -SiH_2Cl), 3.15 (t, J = 3.4 Hz, 2H, $ClCH_2$-). The ^{1}H NMR data was consistent with previously reported[3].

$ClCH_2SiMeHCl$: All volatiles were distilled into a cold trap under vacuum at room temperature and then fractionally distilled with packed fractional column. Unreacted starting $ClCH_2SiMeH_2$ (5.5 g) was separated at 59 °C, while the desired product $ClCH_2SiMeHCl$ distilled at 94°C as a colorless liquid in 62% yield. ^{1}H NMR (400 MHz, Chloroform-d) δ 4.86 (dqd, J = 4.4, 3.0, 1.3 Hz, 1H, -Si*H*Cl), 3.03 (m, 2H, $ClCH_2$-), 0.63 (d, J = 3.0 Hz, 3H, CH_3-Si-). ^{13}C NMR (101 MHz, Chloroform-d) δ 30.56, 0.00. ^{29}Si NMR (79 MHz, 25°C) δ 4.90. COSY ^{1}H-^{1}H NMR (Figure 15d) The ^{1}H NMR data was consistent with previously reported[4]. (see in Figure 15)

$Cl_2CHSiMeHCl$: All volatiles were distilled into a cold trap under vacuum and then fractionally distilled with packed fractional column. Unreacted starting $Cl_2CHSiMeH_2$ was separated at 86 °C, while the desired product $Cl_2CHSiMeHCl$ distilled at 121°C as a colorless liquid in 72% yield. ^{1}H NMR (400 MHz, Chloroform-d) δ 5.43 (d, J = 1.6 Hz, -$CHCl_2$), 4.92 (dd, J = 2.9, 1.6 Hz, -SiHCl-), 0.73 (d, J = 2.9 Hz, -$SiCH_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 58.90, -3.73. ^{29}Si NMR (79 MHz, 25°C) δ 3.89. (Figure 16a-c) COSY ^{1}H-^{1}H NMR (Figure 16d) EI-MS (Figure 16e).

Et_2SiHCl: ^{1}H NMR (400 MHz, Chloroform-d) δ 4.63 (q, J = 2.6 Hz, -SiH_2-), 1.14 – 1.02 (m, -CH_3), 0.94 – 0.85 (m, -$SiCH_2$-). The ^{1}H NMR data was consistent with previously reported[5].

Ph_2SiHCl: ^{1}H NMR (400 MHz, Chloroform-d): d 5.74 (s,1H, -SiHCl-), 7.47-7.76 (m, 10H, $Si(C_6H_5)$)). The ^{1}H NMR data was consistent with previously reported[6].

PhMeSiHCl: ^{1}H NMR (400 MHz, Chloroform-d) δ 7.65 – 7.40 [m, 5H, -Si($C_6\mathit{H}_5$)-], 5.30 (q, J = 3.1 Hz, 3H, -Si*H*Cl-), 0.76 (d, J = 3.2 Hz, 3H, -SiCH_3). The ^{1}H NMR data was consistent with previously reported[6].

PhSiHCl$_2$: ^{1}H NMR (400 MHz, Chloroform-d) δ 5.98 [s, 1H, -Si*H*Cl_2], 7.45 – 7.75 [m, 5H, -Si($C_6\mathit{H}_5$)-]. The ^{1}H NMR data was consistent with previously reported[6].

PhSiH$_2$Cl: ^{1}H NMR (400 MHz, Chloroform-d) δ 5.24 [s, 2H, -SiH_2Cl], 7.55 – 7.74 [m, 5H, -Si($C_6\mathit{H}_5$)]. The ^{1}H NMR data was consistent with previously reported[6].

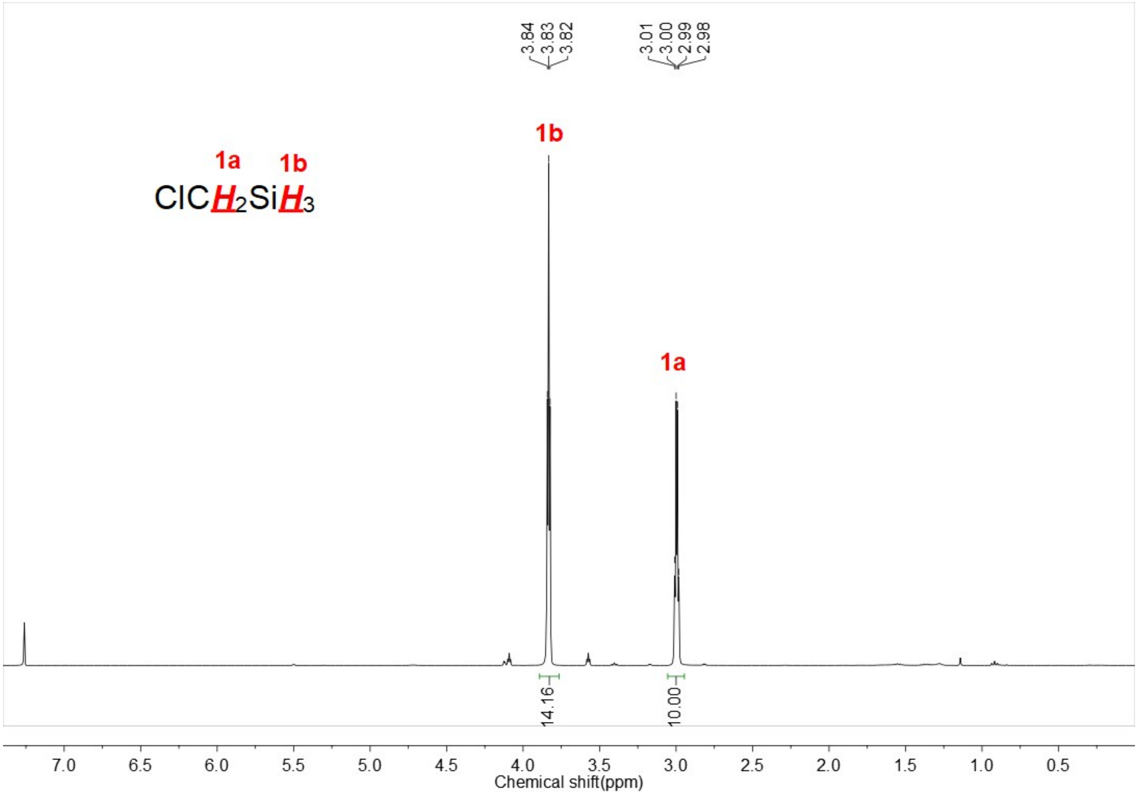


Figure 1a. ^{1}H NMR of $ClCH_2SiH_3$

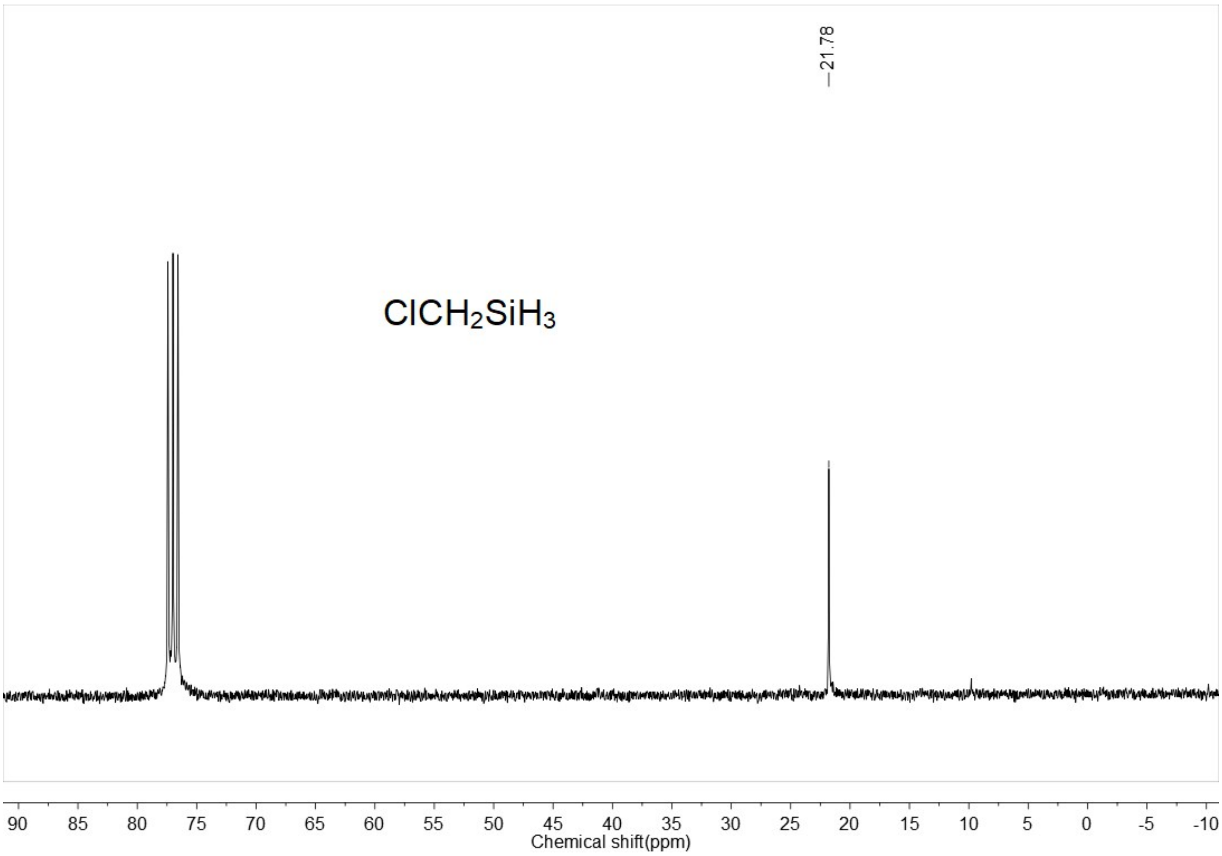


Figure 1b. ^{13}C NMR of $ClCH_2SiH_3$

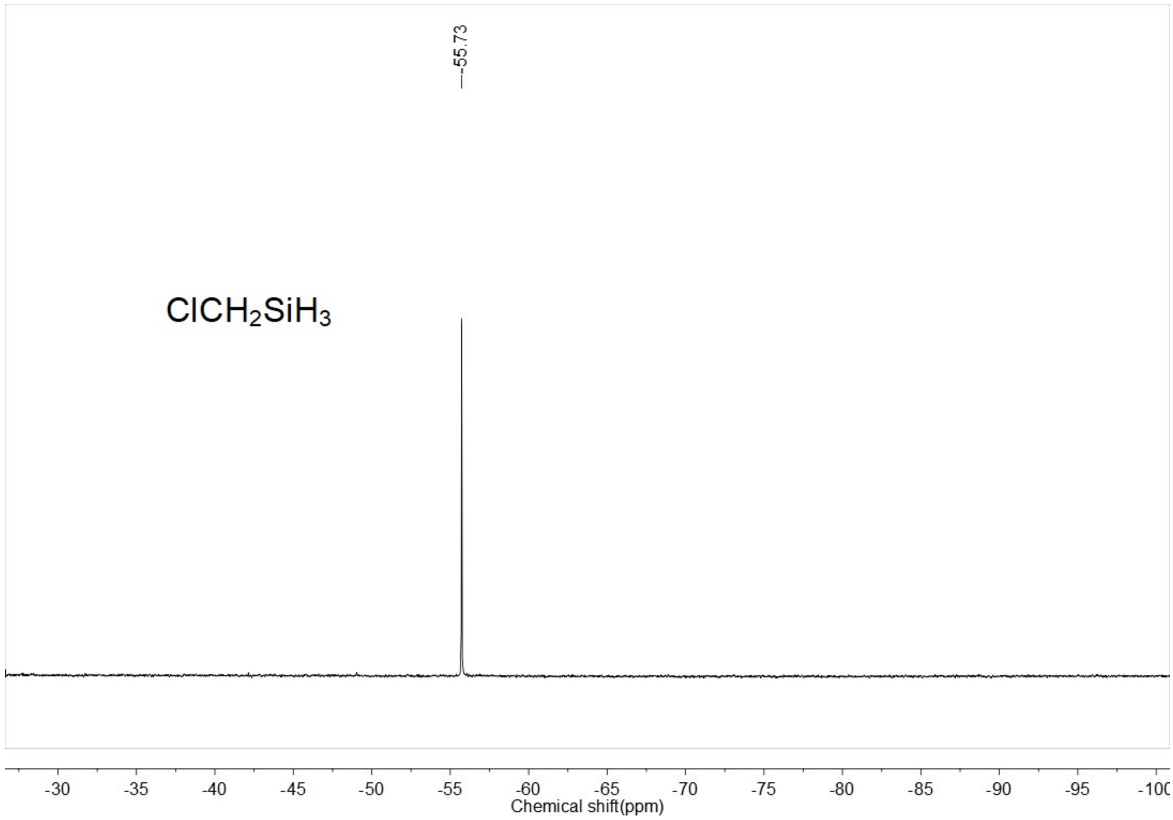


Figure 1c. ^{29}Si NMR of $ClCH_2SiH_3$

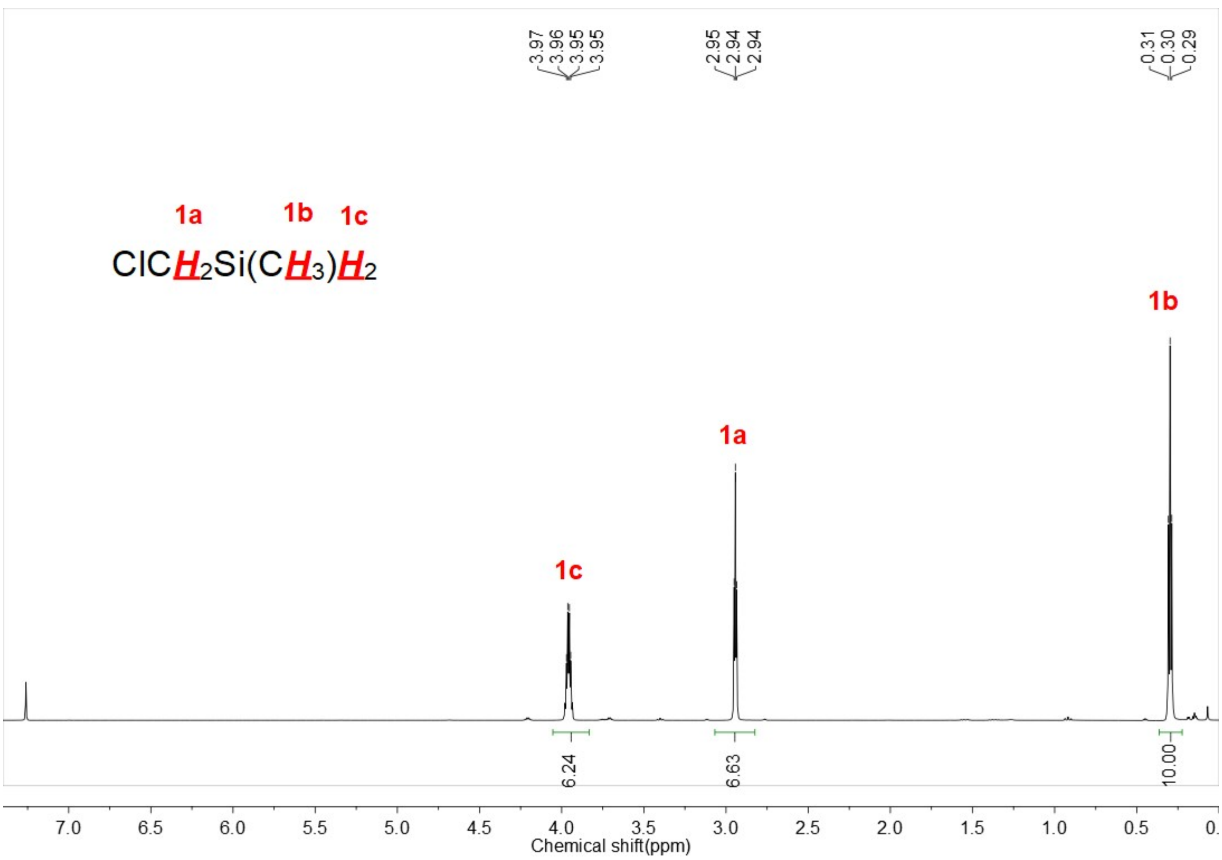


Figure 2a. ^{1}H NMR of $ClCH_2SiMeH_2$

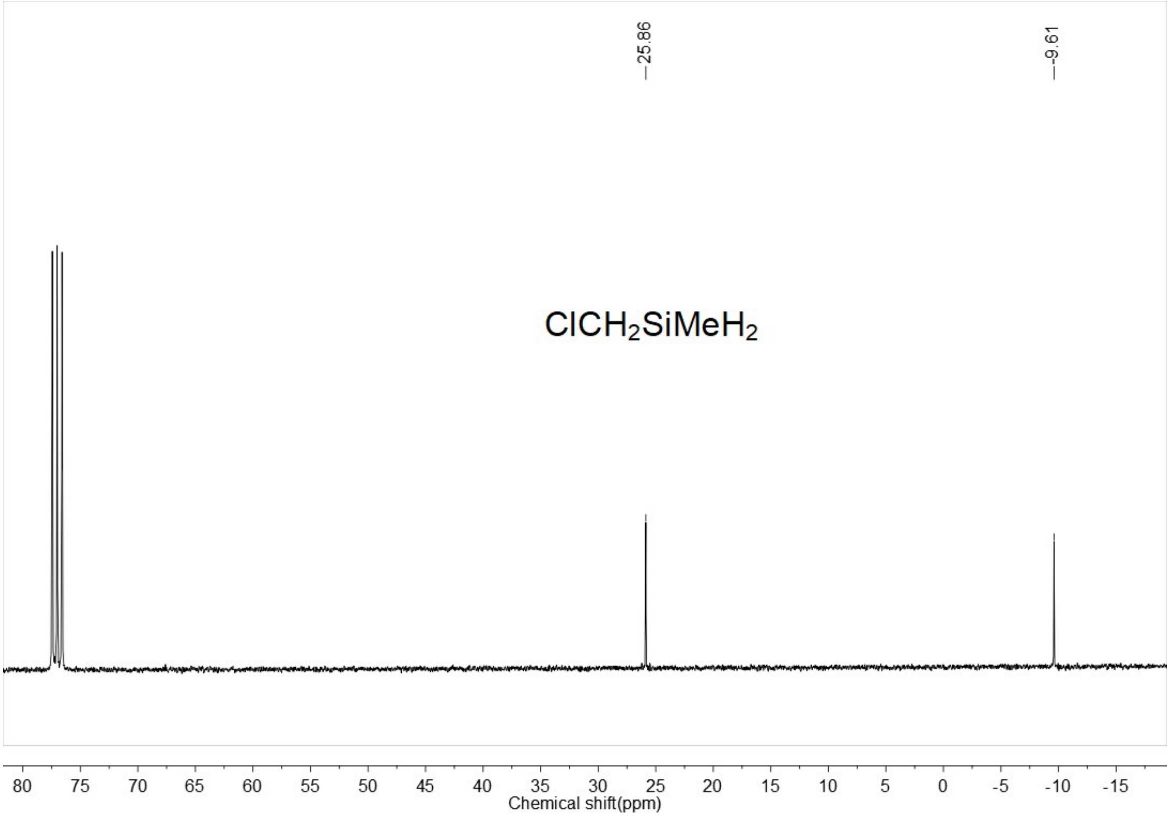


Figure 2b. ${}^{13}C$ NMR of $ClCH_2SiMeH_2$

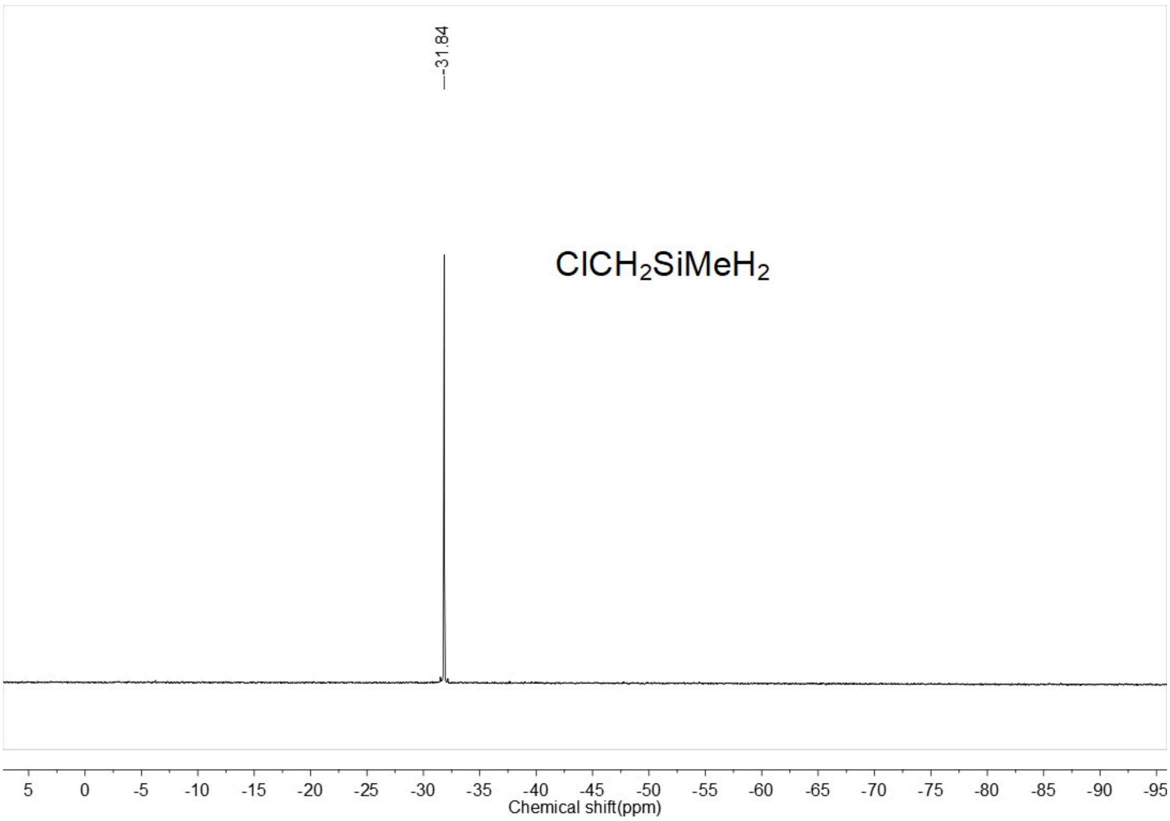


Figure 2c. ${}^{29}Si$ NMR of $ClCH_2SiMeH_2$

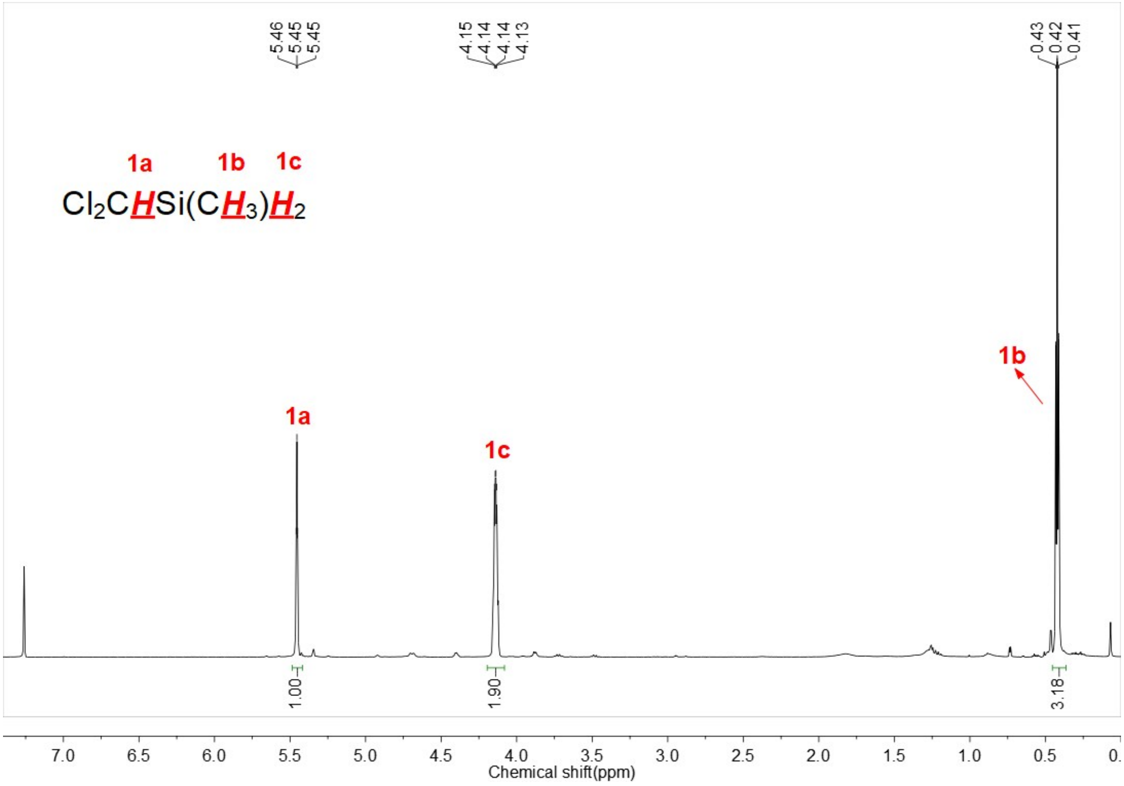


Figure 3a. ^{1}H NMR of $Cl_2CHSiMeH_2$

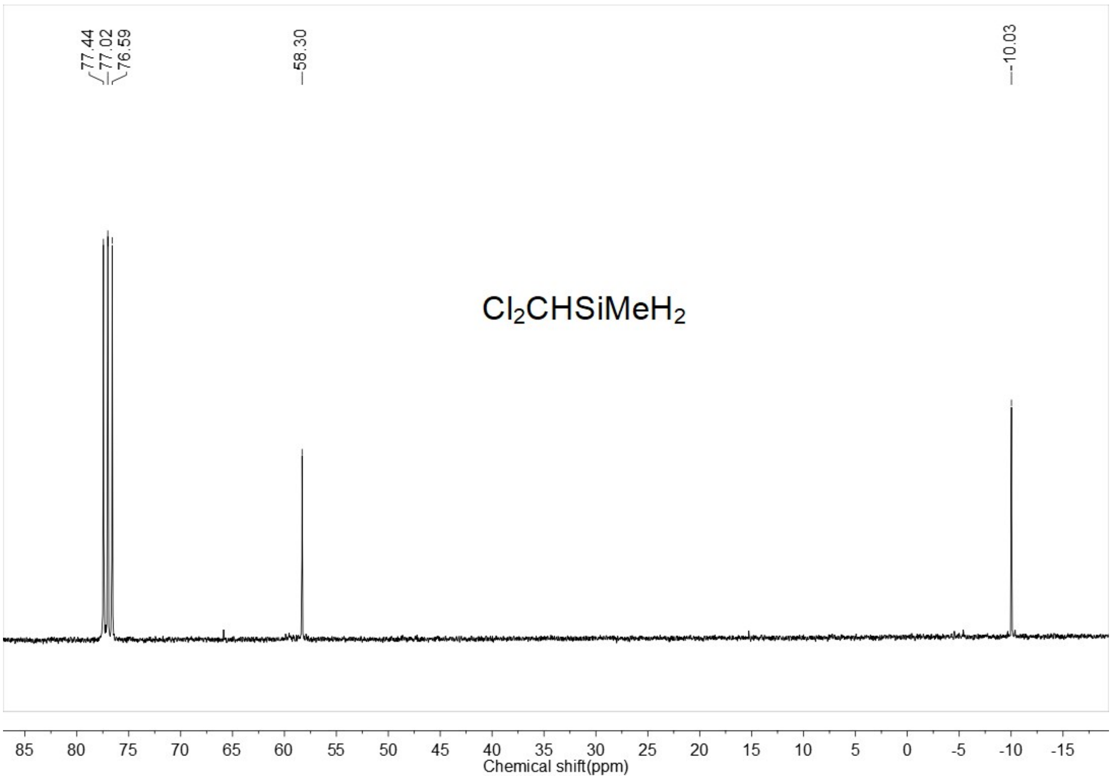


Figure 3b. ^{13}C NMR of $Cl_2CHSiMeH_2$

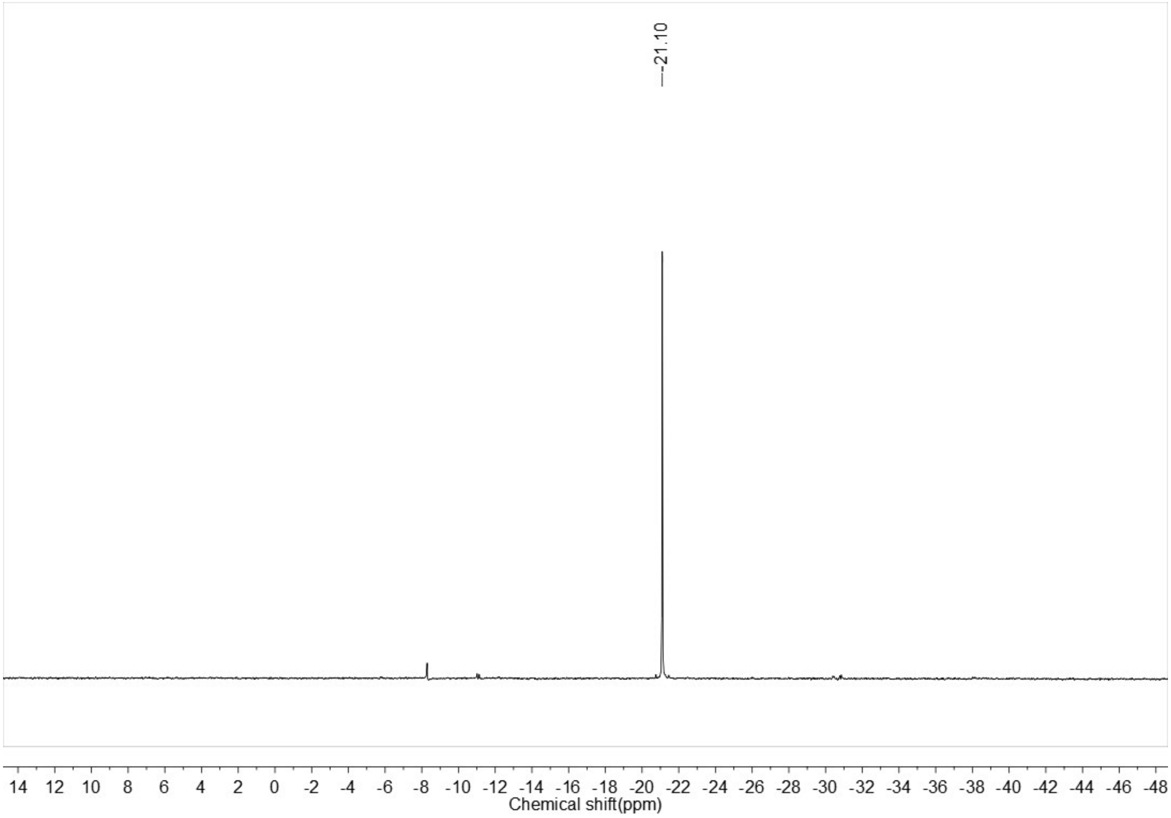


Figure 3c. ^{29}Si NMR of $Cl_2CHSiMeH_2$

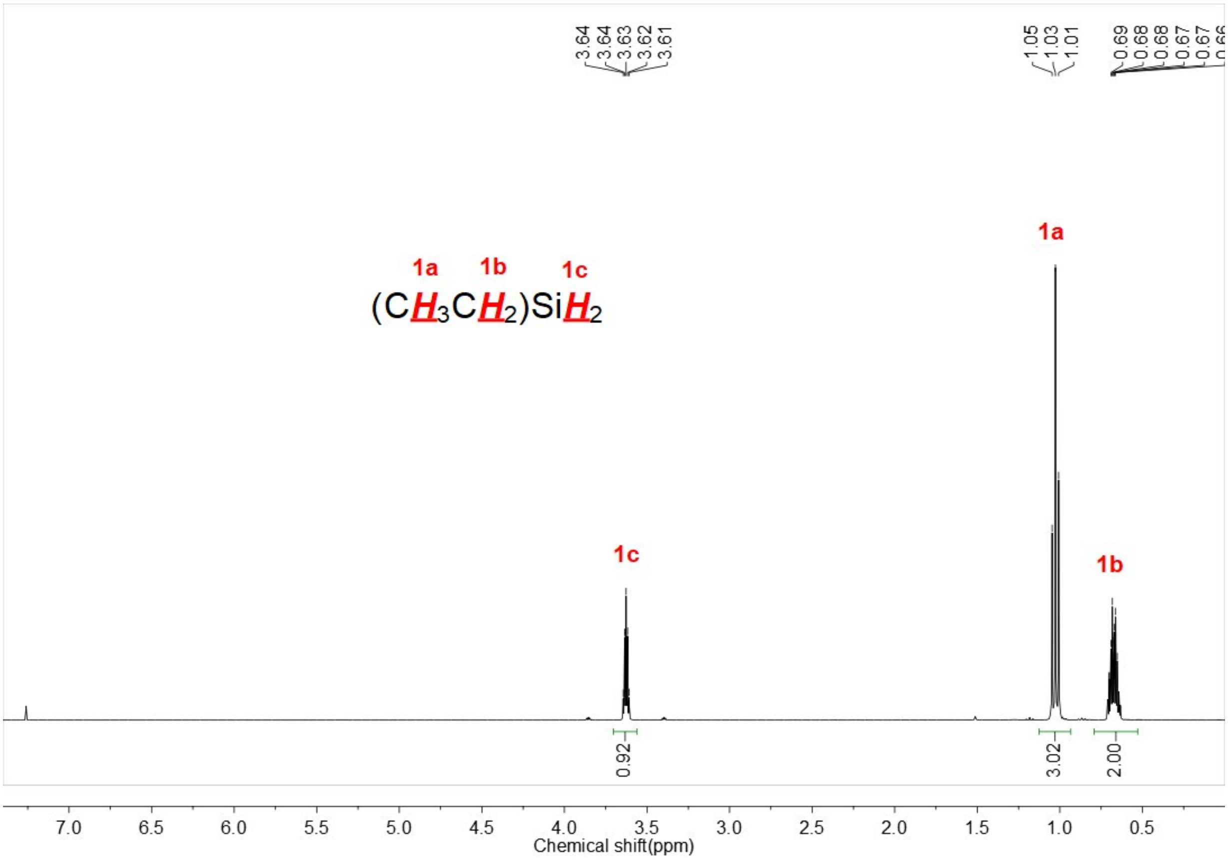


Figure 4. ^{1}H NMR of Et_2SiH_2

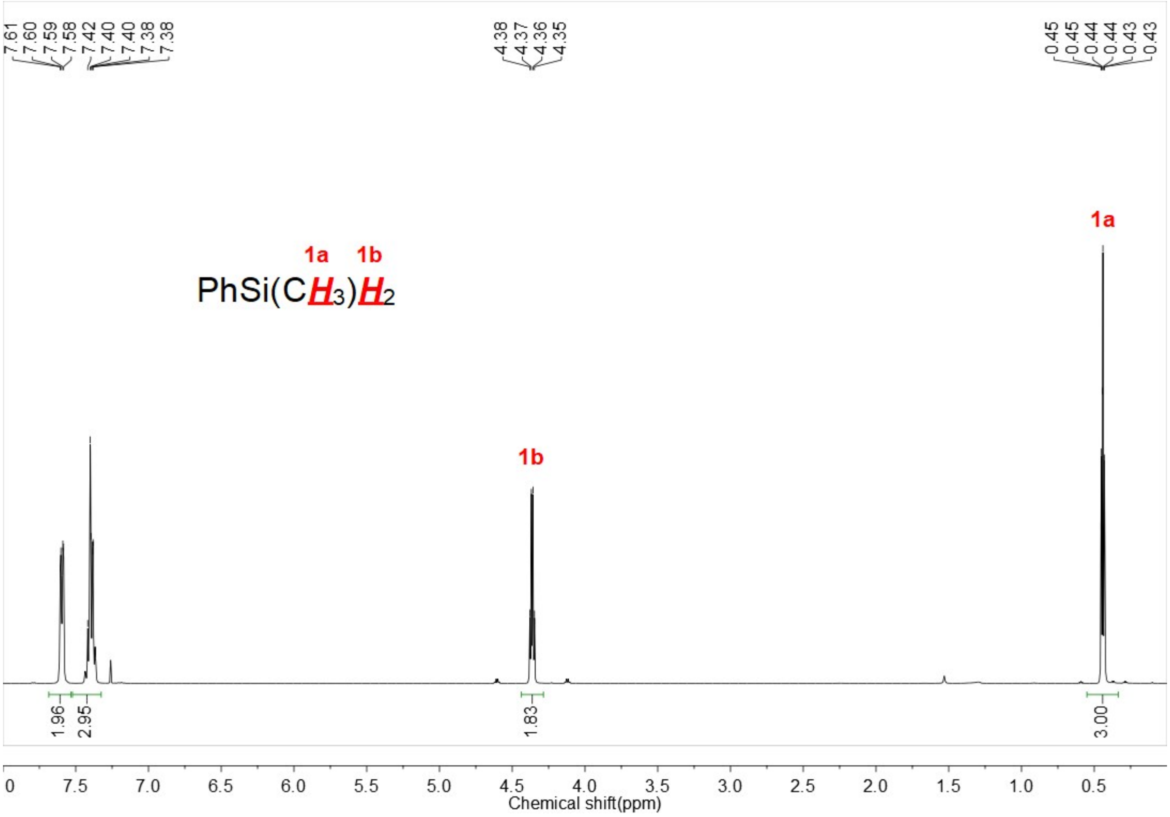


Figure 5. ^{1}H NMR of $PhSiMeH_2$

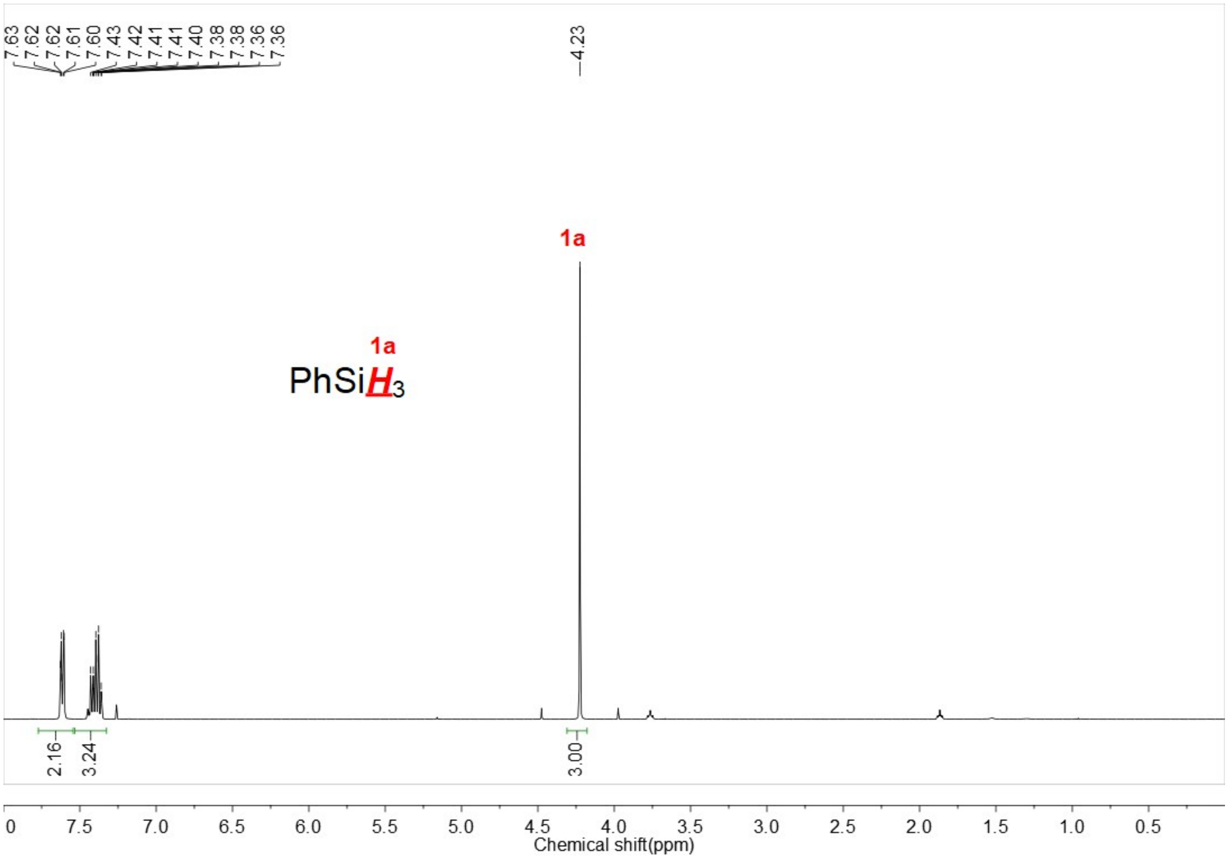


Figure 6. ^{1}H-NMR of $PhSiH_3$

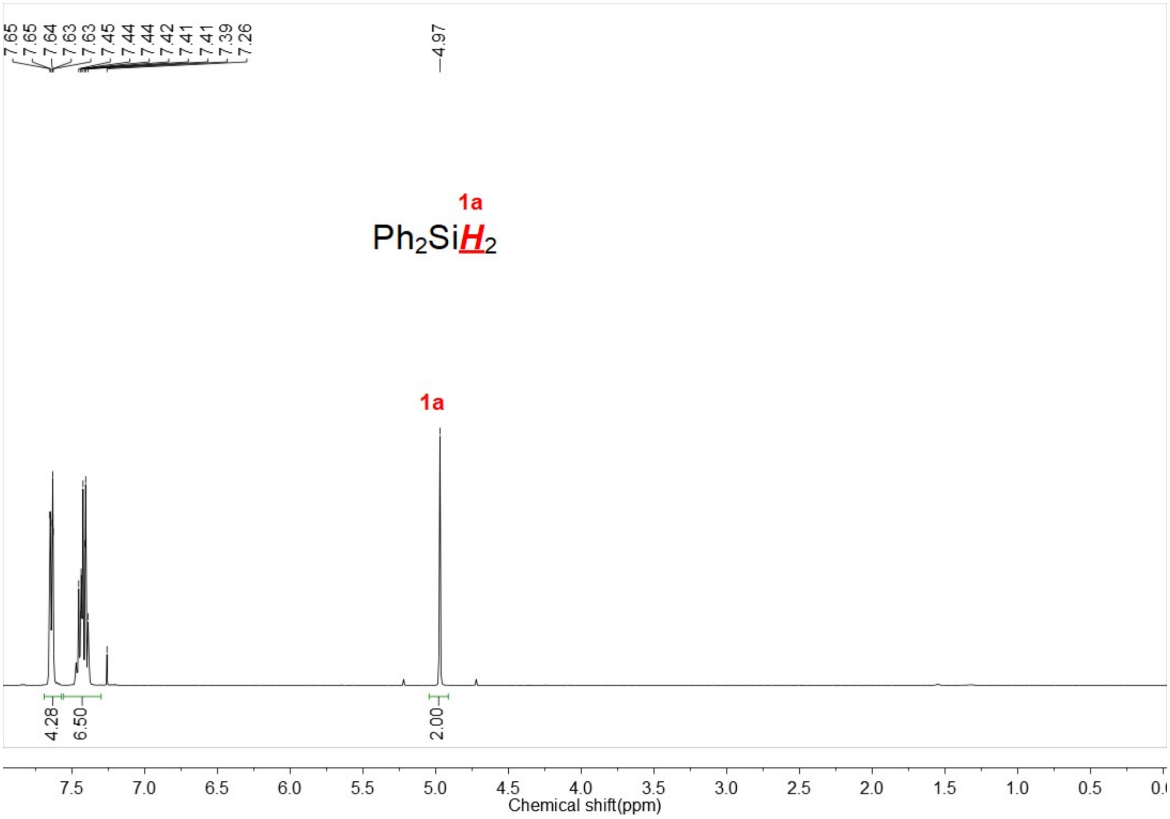


Figure 7. [1]H NMR of Ph_2SiH_2

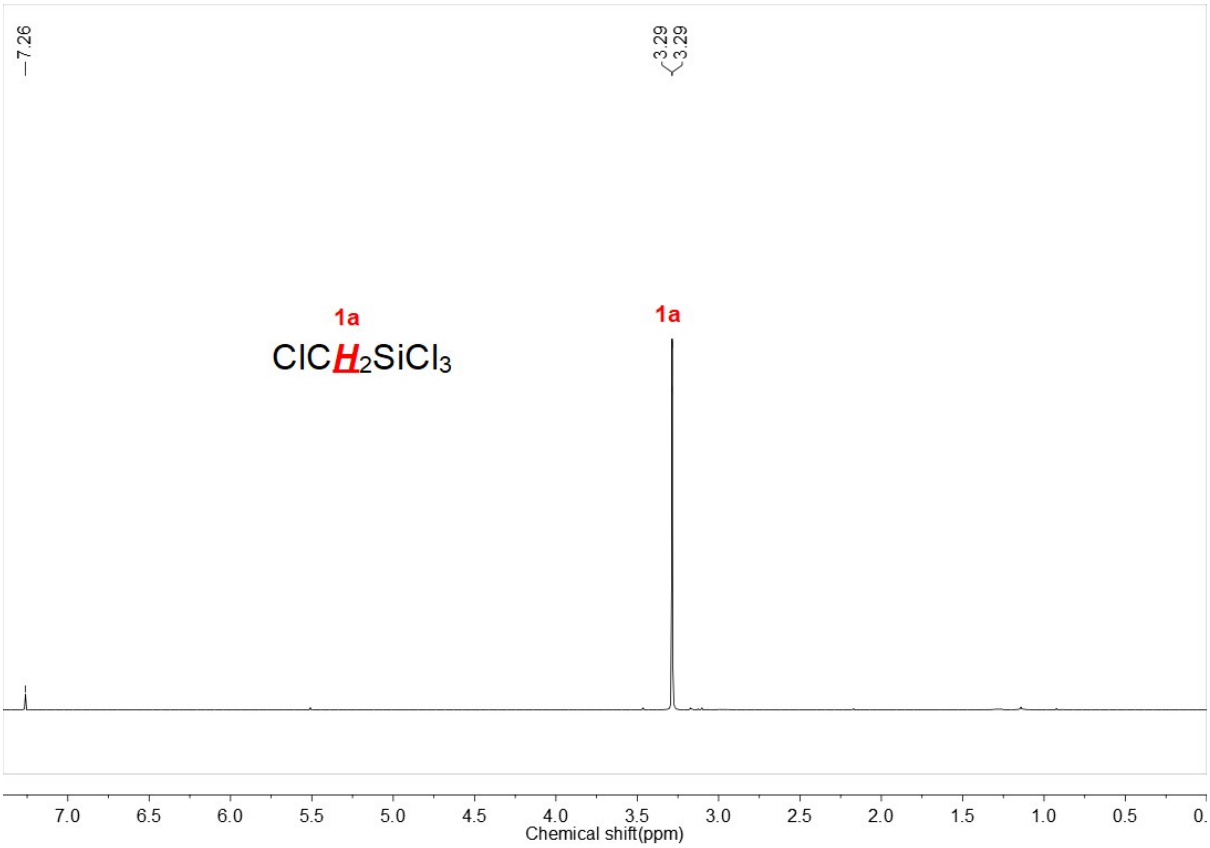


Figure 8. [1]H-NMR of $ClCH_2SiCl_3$

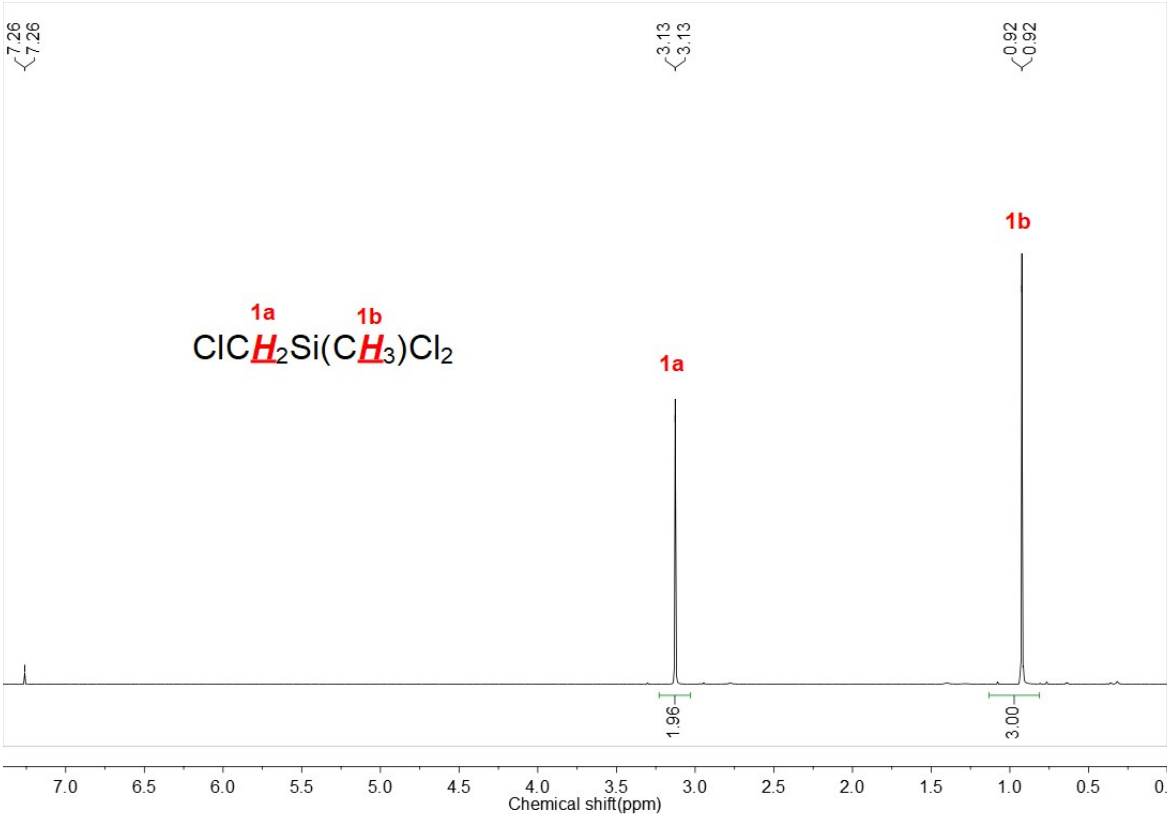


Figure 9. ^{1}H-NMR of $ClCH_2SiMeCl_2$

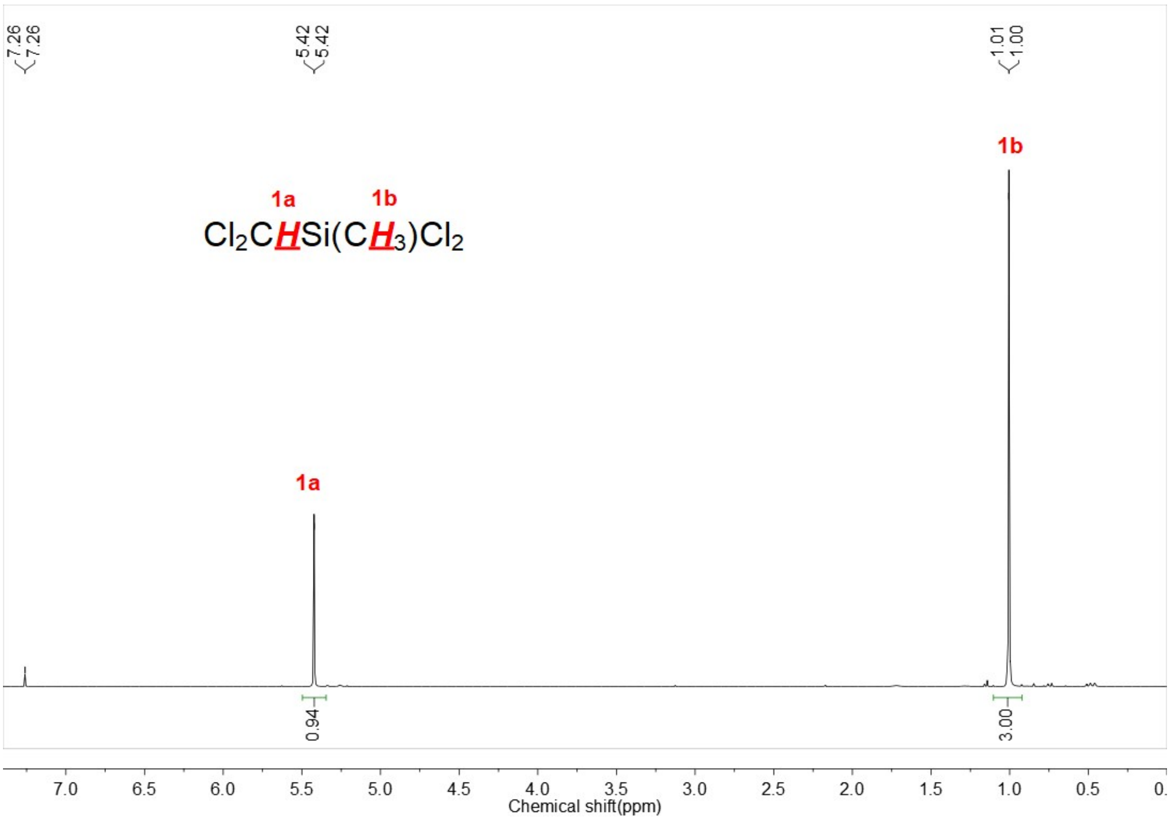


Figure 10. ^{1}H NMR of $Cl_2CHSiMeCl_2$

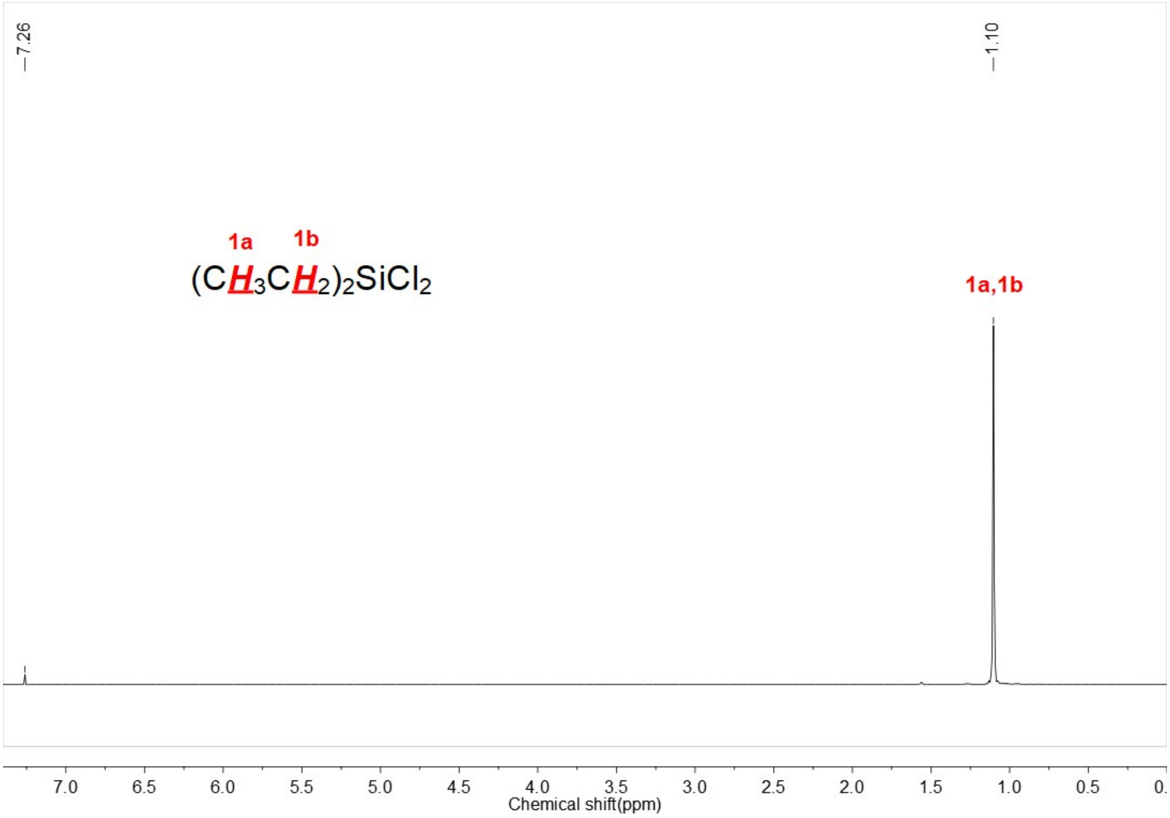


Figure 11. [1]H-NMR of Et_2SiCl_2

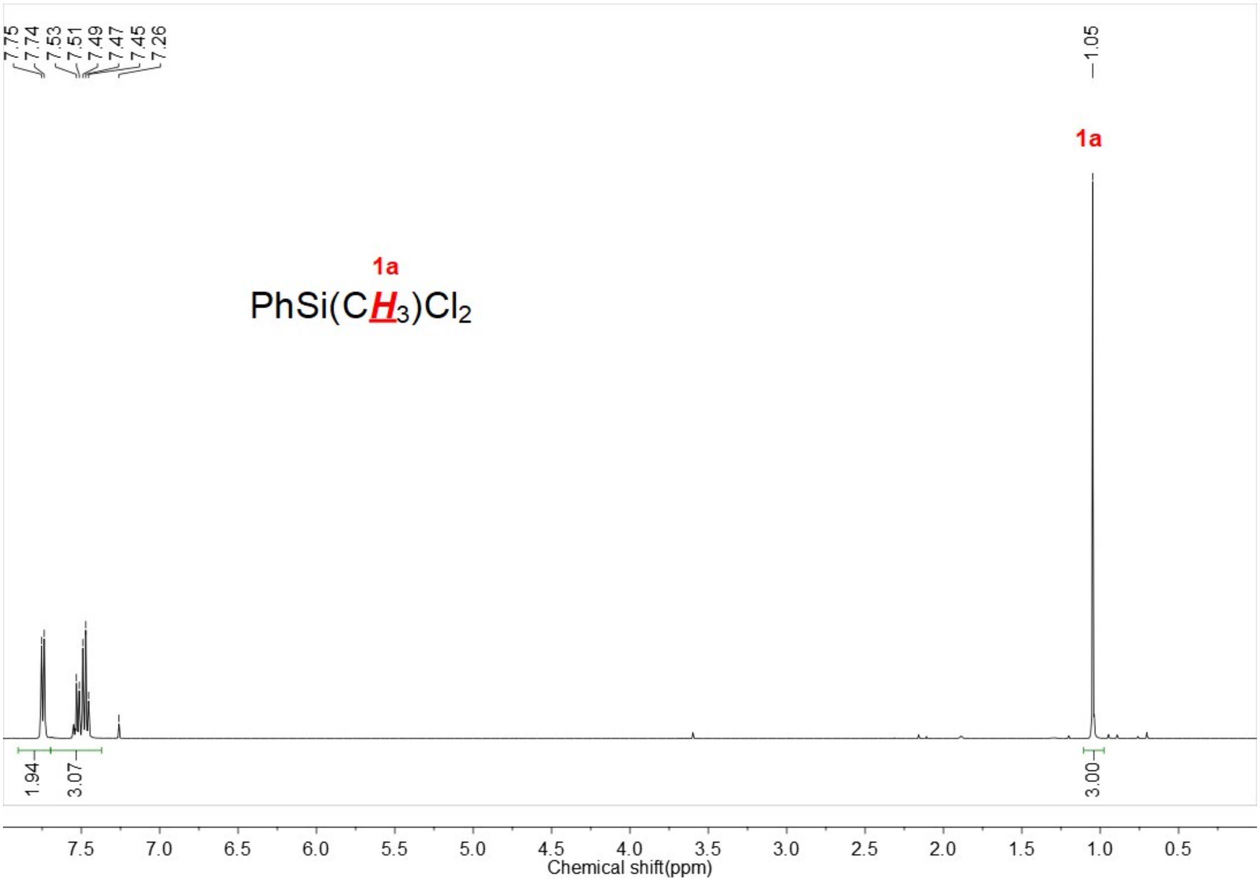


Figure 12. [1]H-NMR of $PhSiMeCl_2$

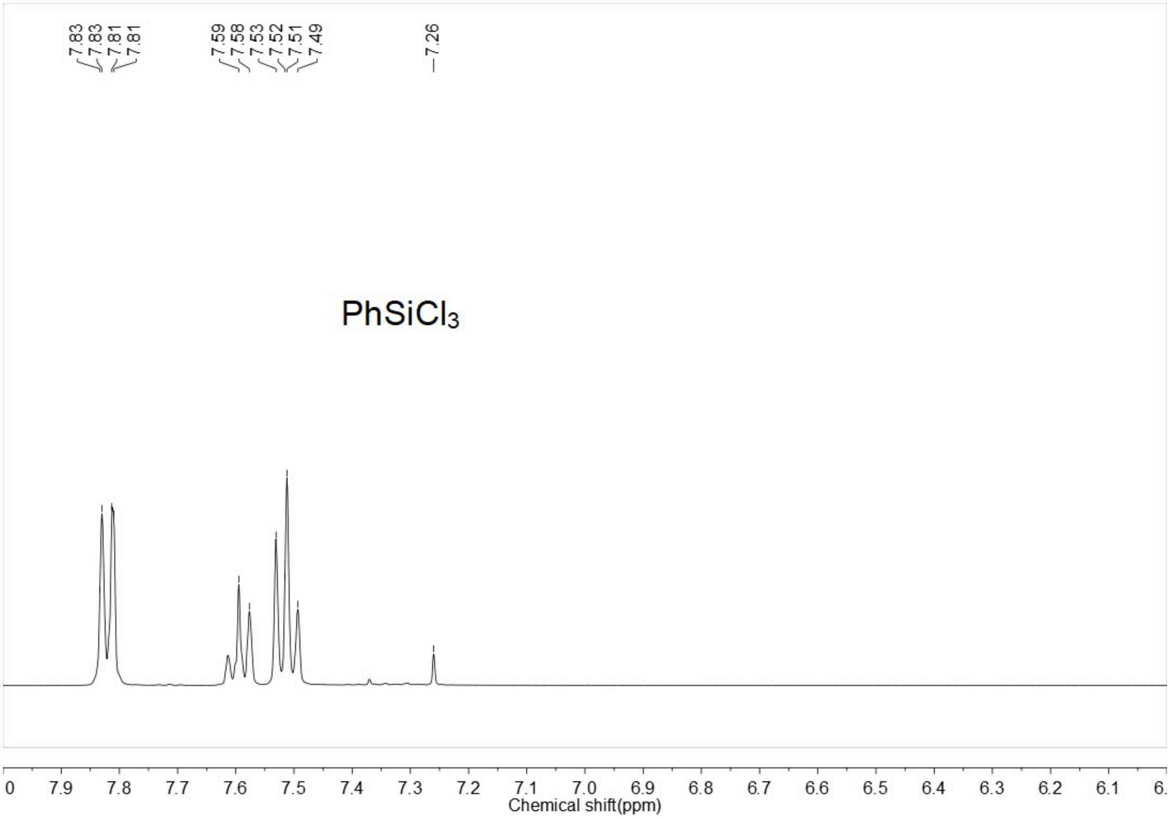


Figure 13. [1]H-NMR of $PhSiCl_3$

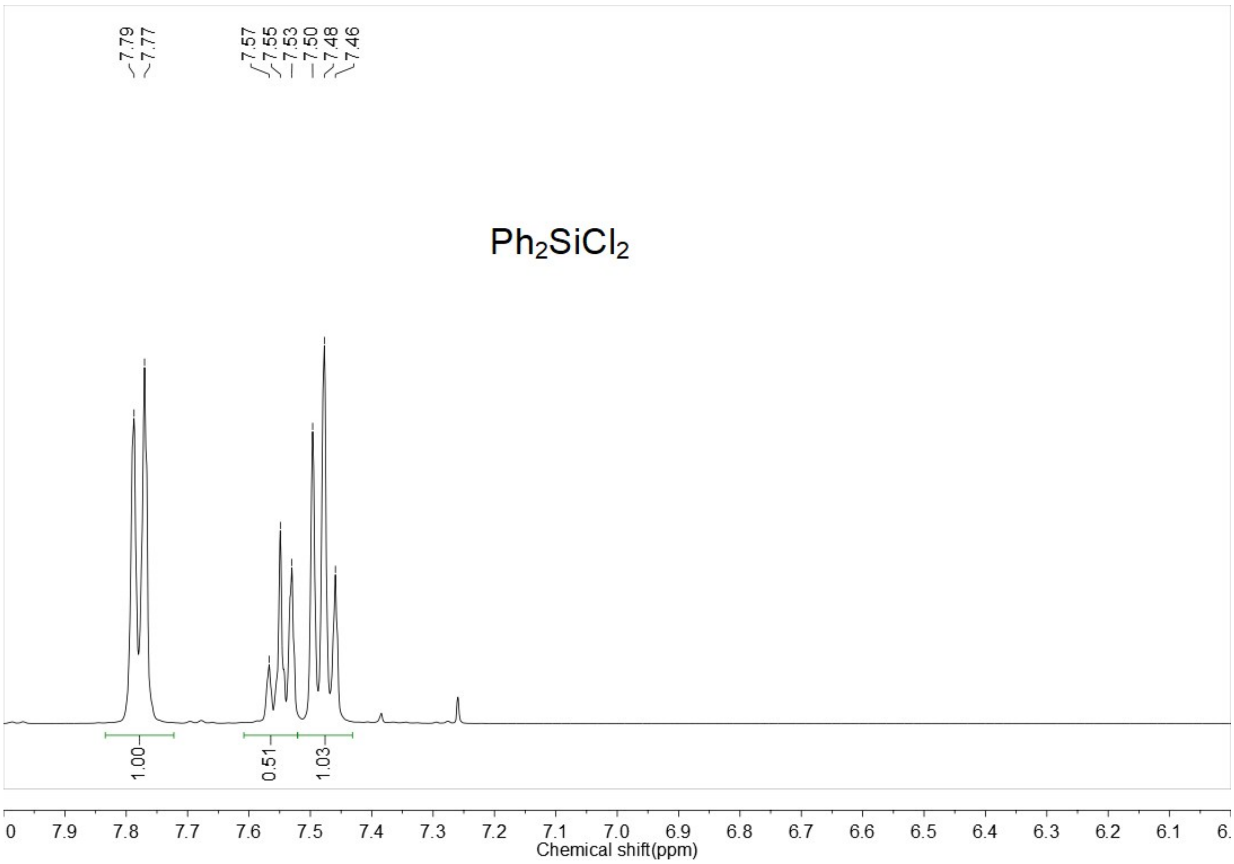


Figure 14. [1]H-NMR of Ph_2SiCl_2

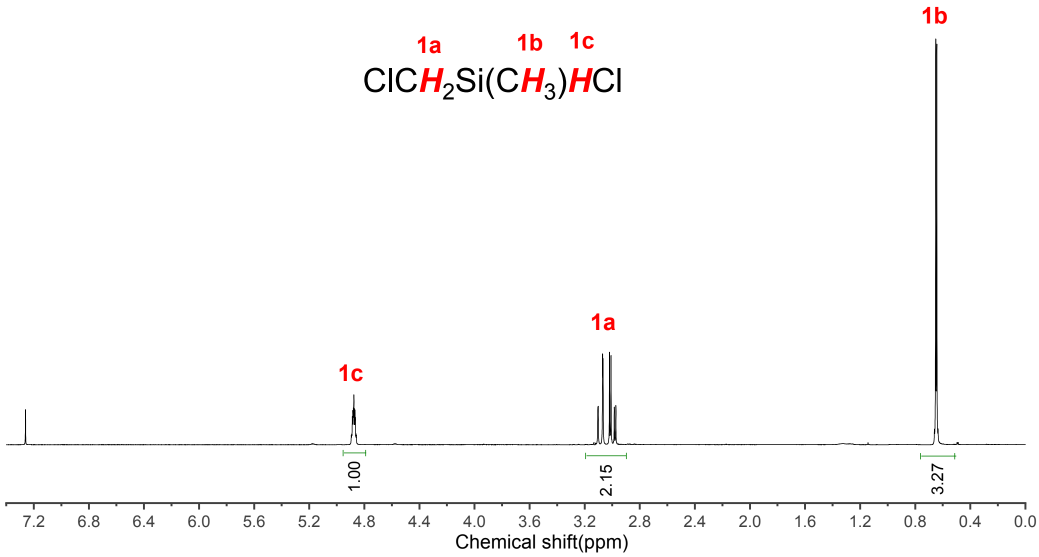


Figure 15. ^{1}H-NMR of $ClCH_2SiMeHCl$

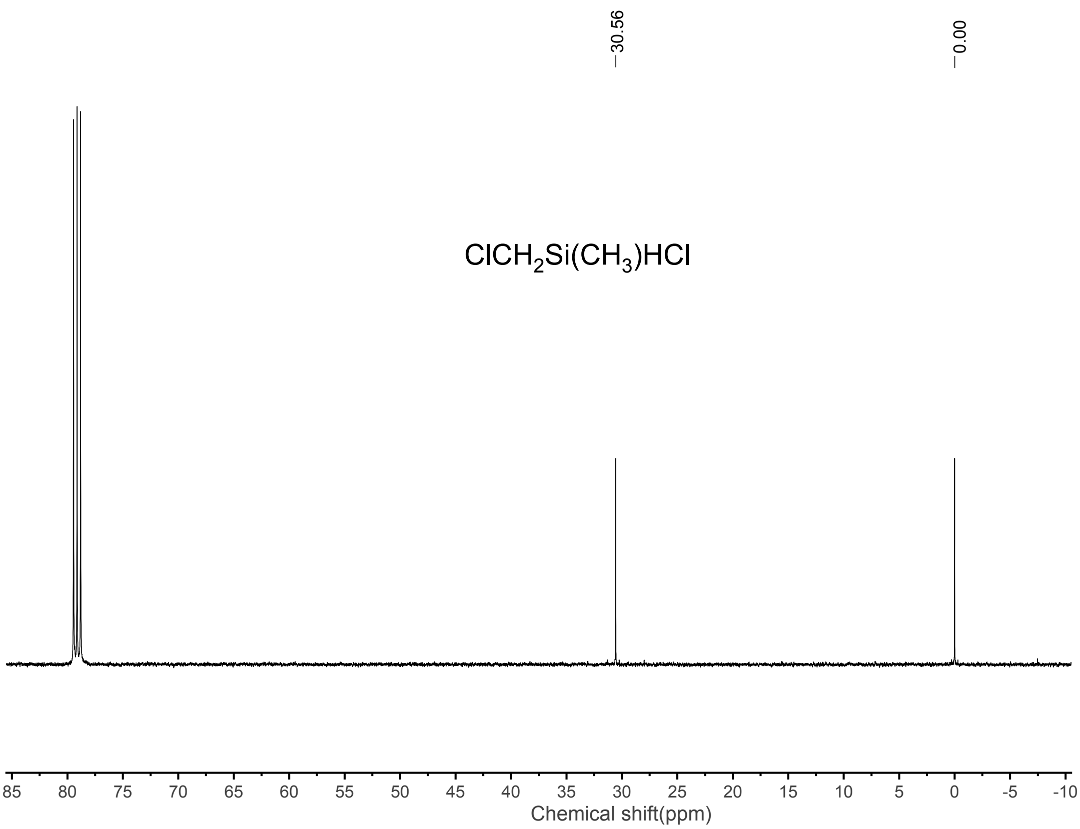


Figure 15b. ^{13}C-NMR of $ClCH_2SiMeHCl$

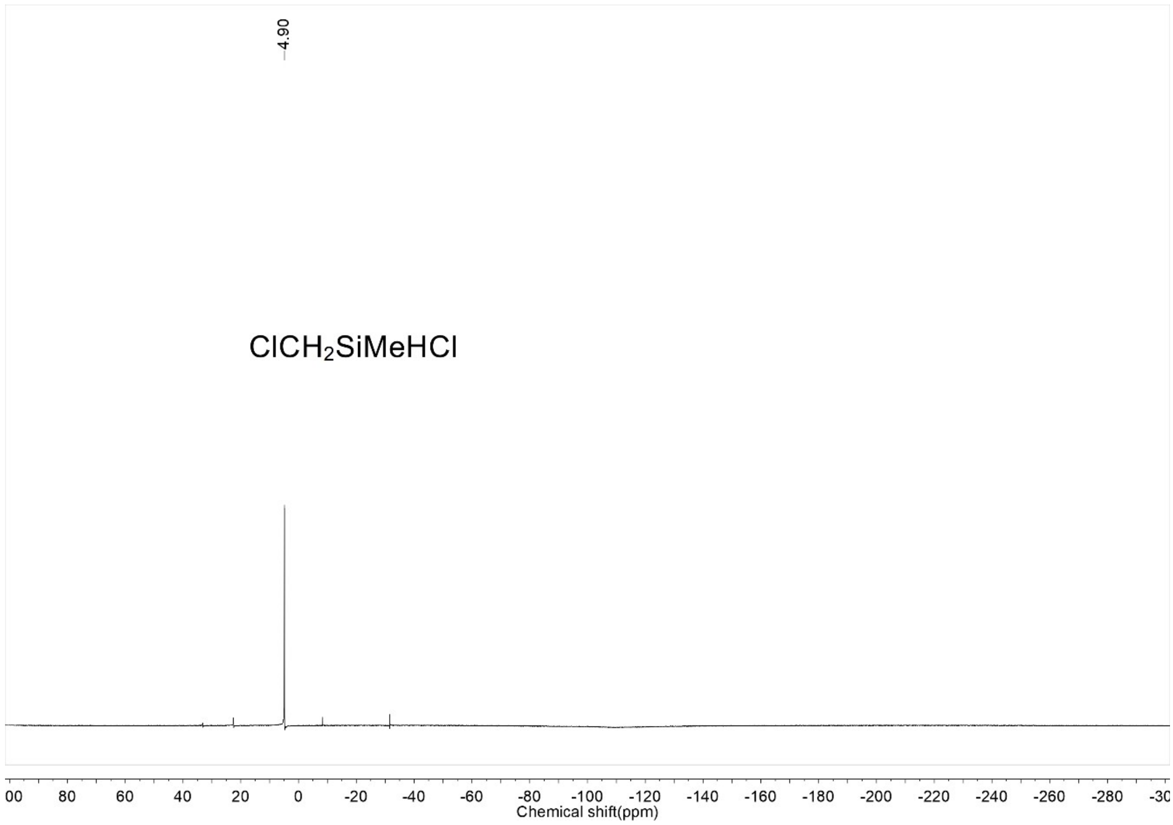


Figure 15c. ^{29}Si-NMR of $ClCH_2SiMeHCl$

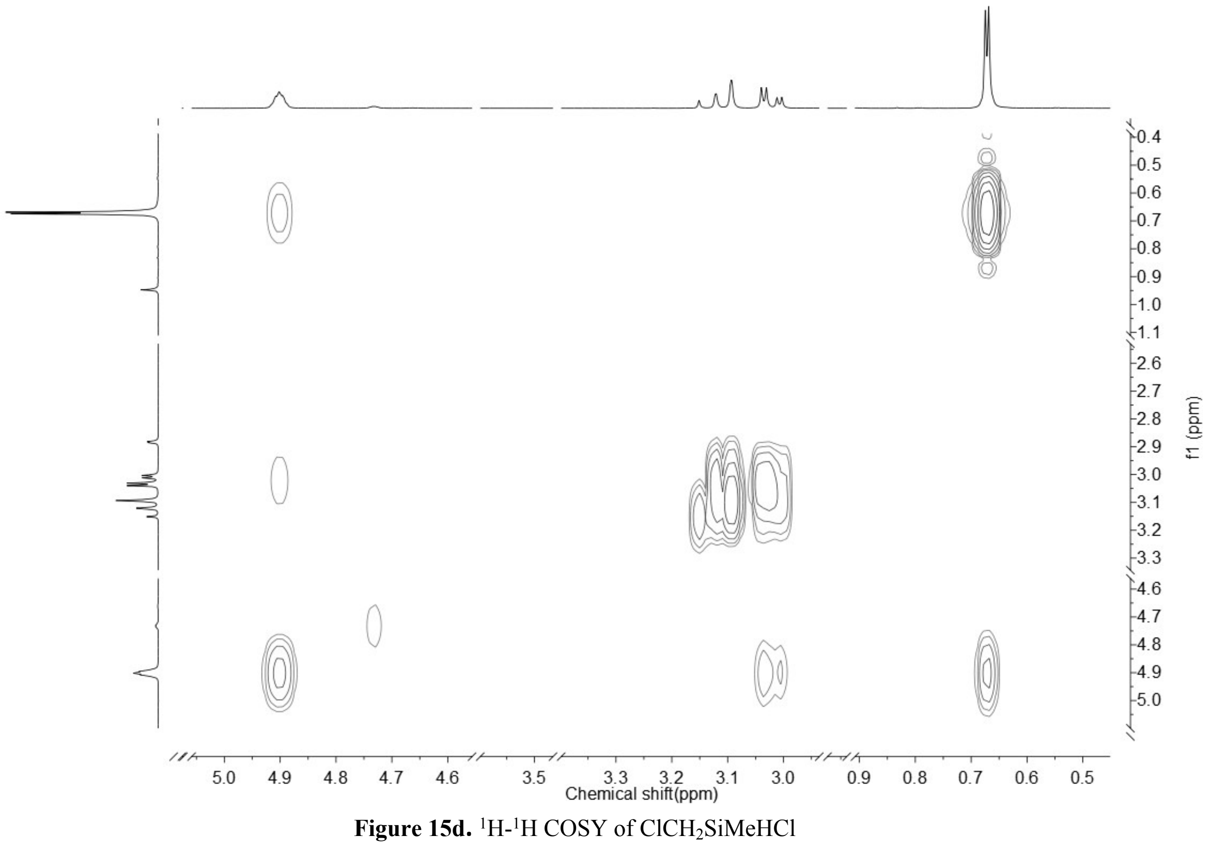


Figure 15d. ^{1}H-^{1}H COSY of $ClCH_2SiMeHCl$

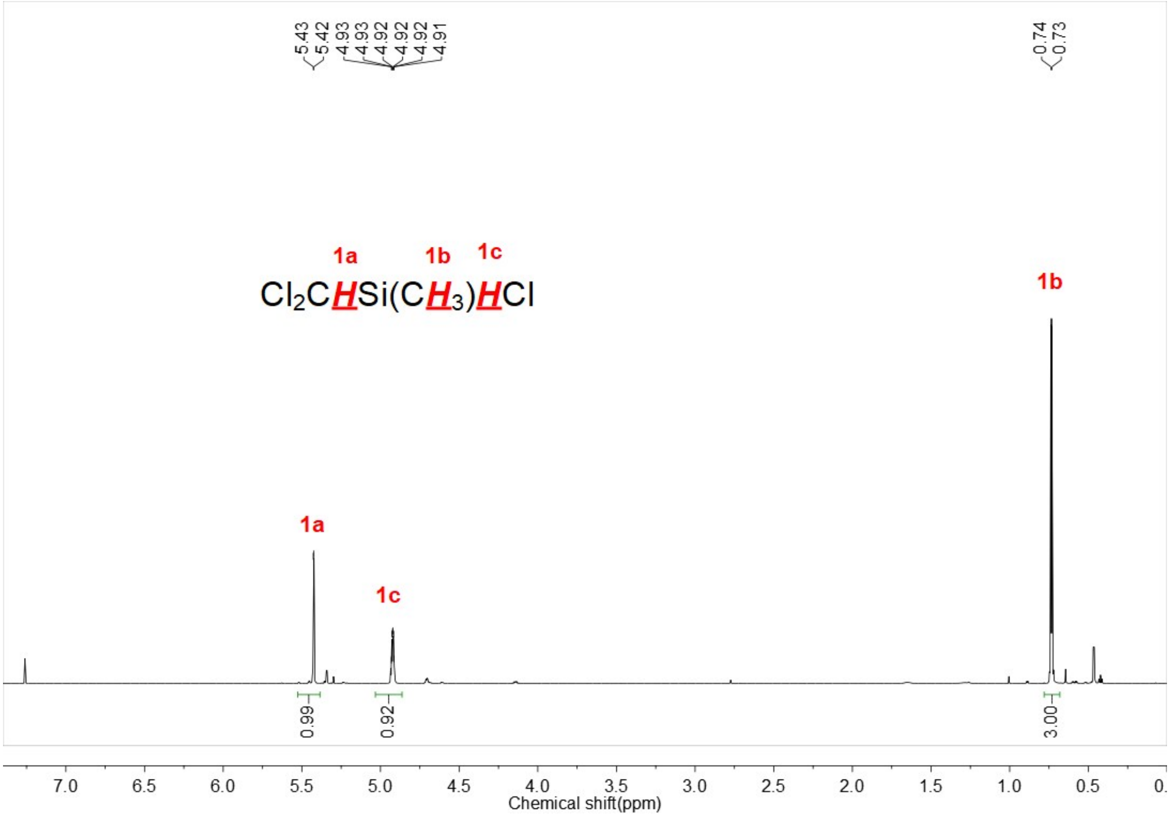


Figure 16a. ^{1}H-NMR of $Cl_2CHSiMeHCl$

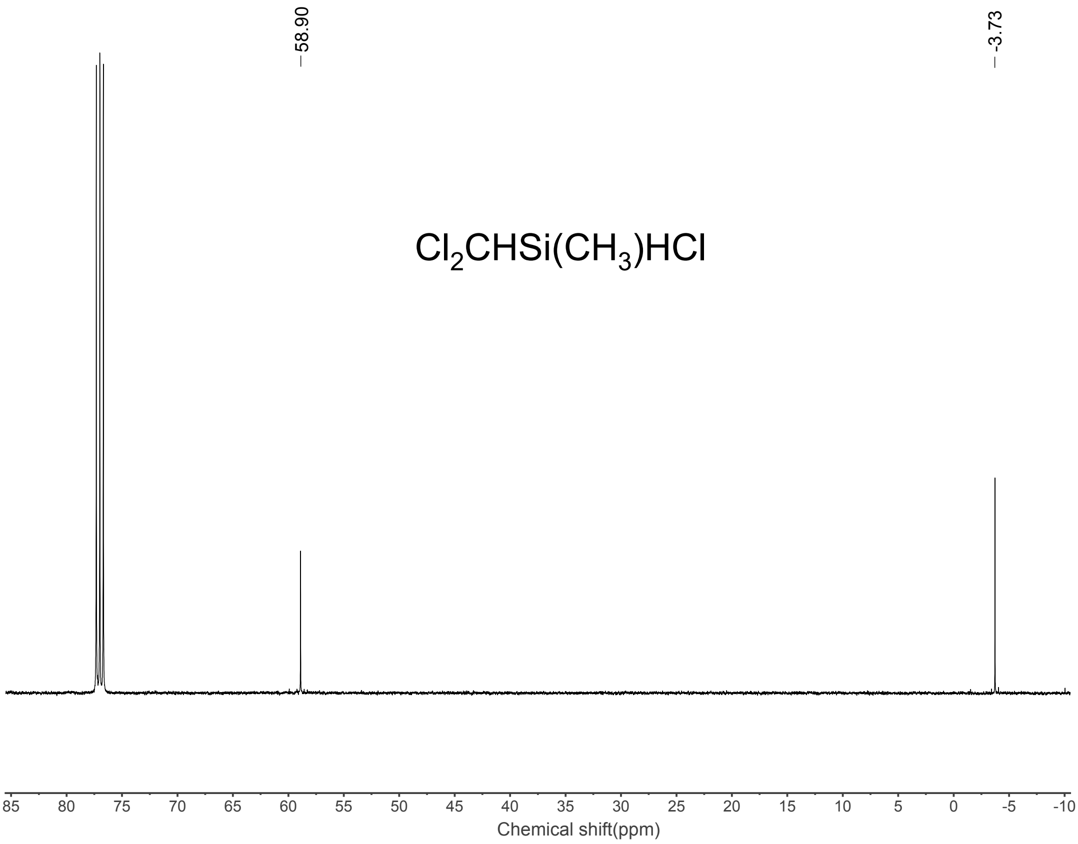


Figure 16b. ^{13}C-NMR of $Cl_2CHSiMeHCl$

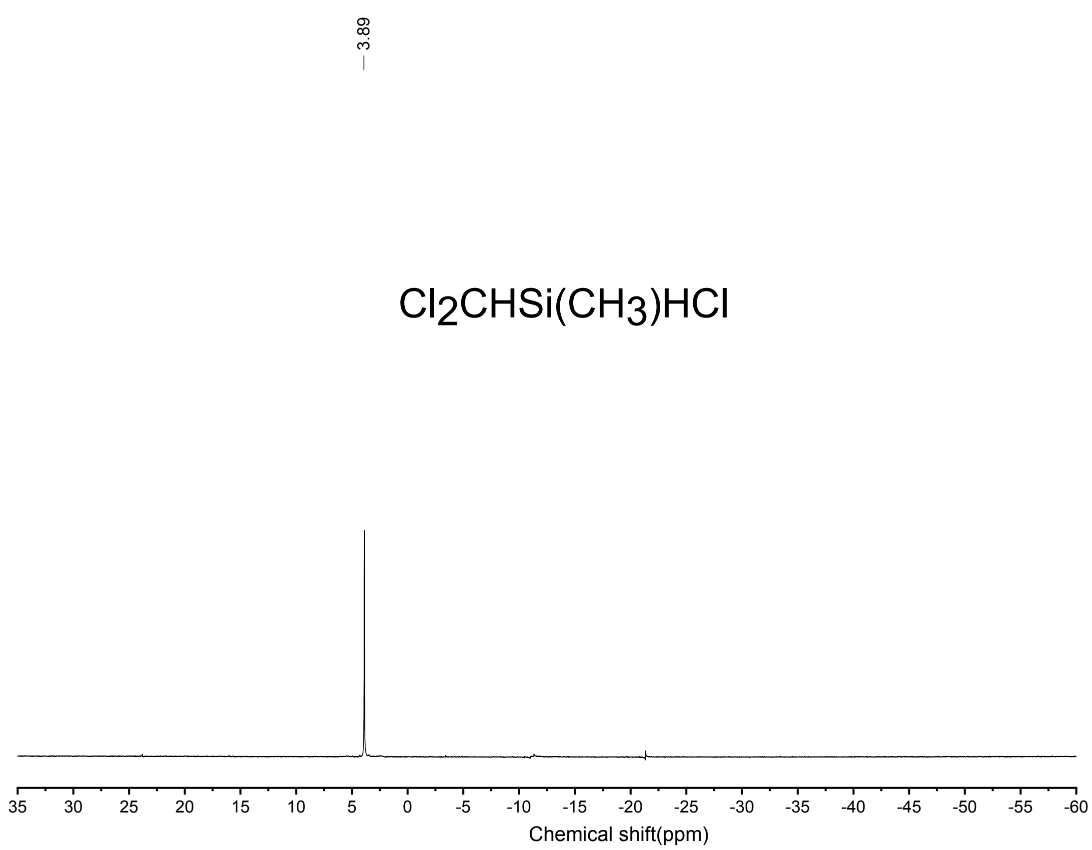


Figure 16c. ^{29}Si NMR of $Cl_2CHSiMeHCl$

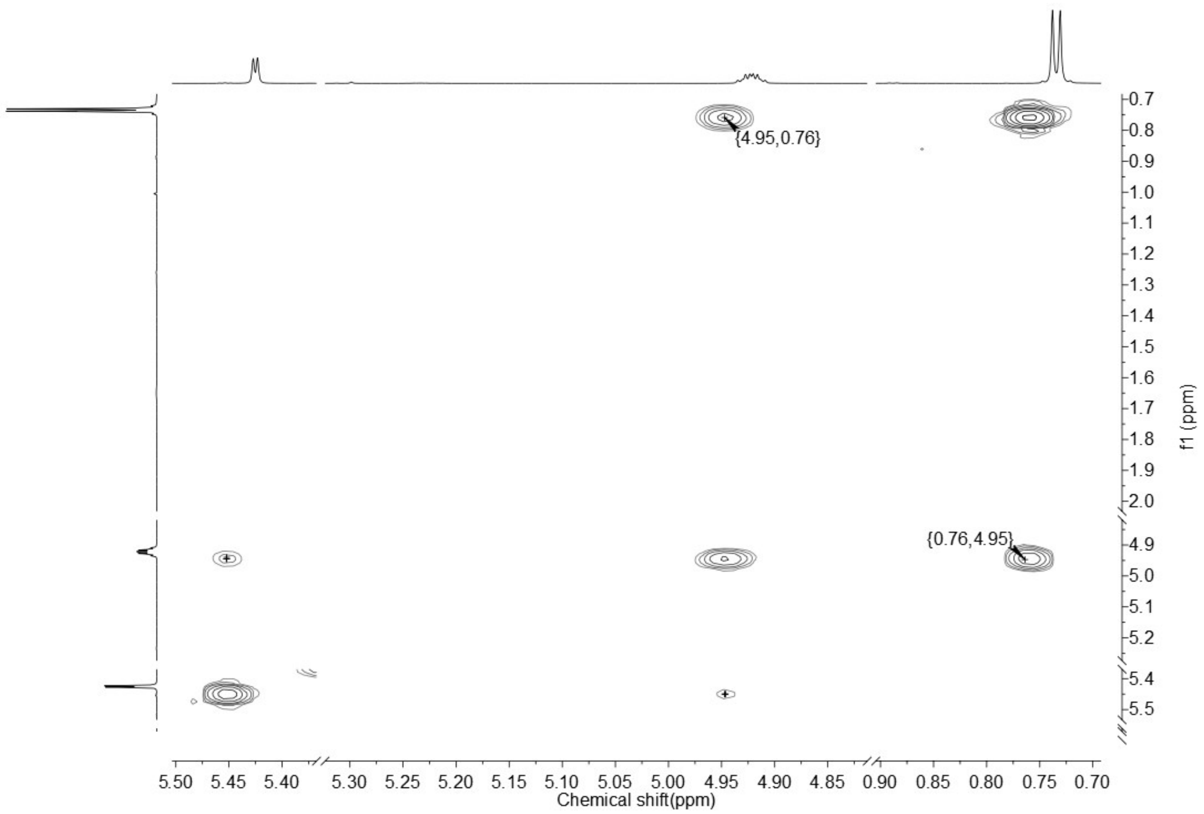


Figure 16d. COSY ^{1}H-^{1}H NMR of $Cl_2CHSiMeHCl$

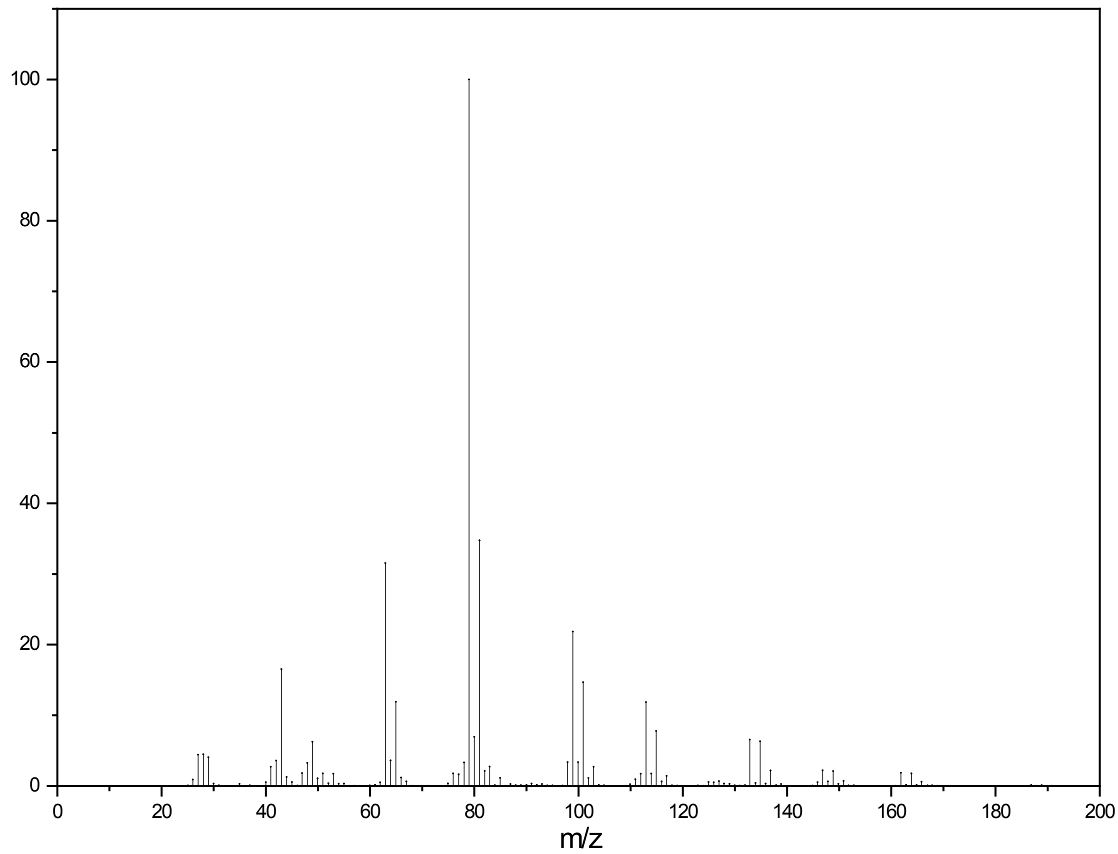


Figure 16e. MS of $Cl_2CHSiMeHCl$ (EI-MS)

Ⅳ. Solvent optimization with $ClCH_2SiH_3$ and $ClCH_2SiCl_3$ (Table 1)

Procedure for the redistribution reaction of $ClCH_2SiH_3$ and $ClCH_2SiCl_3$ (molar ratio = 1:2) catalyzed by $LiBH_4$ (Table 1)

To a mixture of $LiBH_4$ (0.018 g, 0.8 mmol), 5 mL solvent (or no solvent, **entry 1**) in a 25 mL two-necked flask was added $ClCH_2SiH_3$ (0.80 g, 0.01 mol) and $ClCH_2SiCl_3$ (3.68 g, 0.02 mol) in sequence. The reaction mixture was stirred by magneton at room temperature for 16 h and measured by ^{1}H-NMR.

Table 1 Solvent optimization of redistribution reaction of $ClCH_2SiH_3/ClCH_2SiCl_3$[a]

$$ClCH_2SiH_3 + ClCH_2SiCl_3 \xrightarrow[\text{RT, 16h}]{LiBH_4\text{(cat.)}} ClCH_2SiH_2Cl + ClCH_2SiHCl_2$$

Entry	Solvent	Product (yield)[b]
1	none	No reaction
2	diglyme	CH_3SiHCl_2: 6%, $ClCH_2SiHCl_2$: 63%, $ClCH_2SiH_2Cl$: 12%
3	THF	$ClCH_2SiHCl_2$: 63%, $ClCH_2SiH_2Cl$: 16%
4	CH_3CN	$ClCH_2SiHCl_2$: 71%, $ClCH_2SiH_2Cl$: 11%
5	DMI	$ClCH_2SiHCl_2$: 71%, $ClCH_2SiH_2Cl$: 14%
6	HMPA	$ClCH_2SiHCl_2$: 72%, $ClCH_2SiH_2Cl$: 9%
7	Bu_2O	No reaction
8	Et_2O	No reaction
9	Toluene	No reaction

[a] Reaction conditions: $ClCH_2SiH_3$ (0.01 mol), $ClCH_2SiCl_3$ (0.02 mol), $LiBH_4$ (3.0 mol/%), THF (5 mL), room temperature; [b] yields were determined by ^{1}H NMR.

Redistribution results of $ClCH_2SiCl_3$ and $ClCH_2SiH_3$ (molar ratio = 2:1) without solvent (Table 1, entry 1)

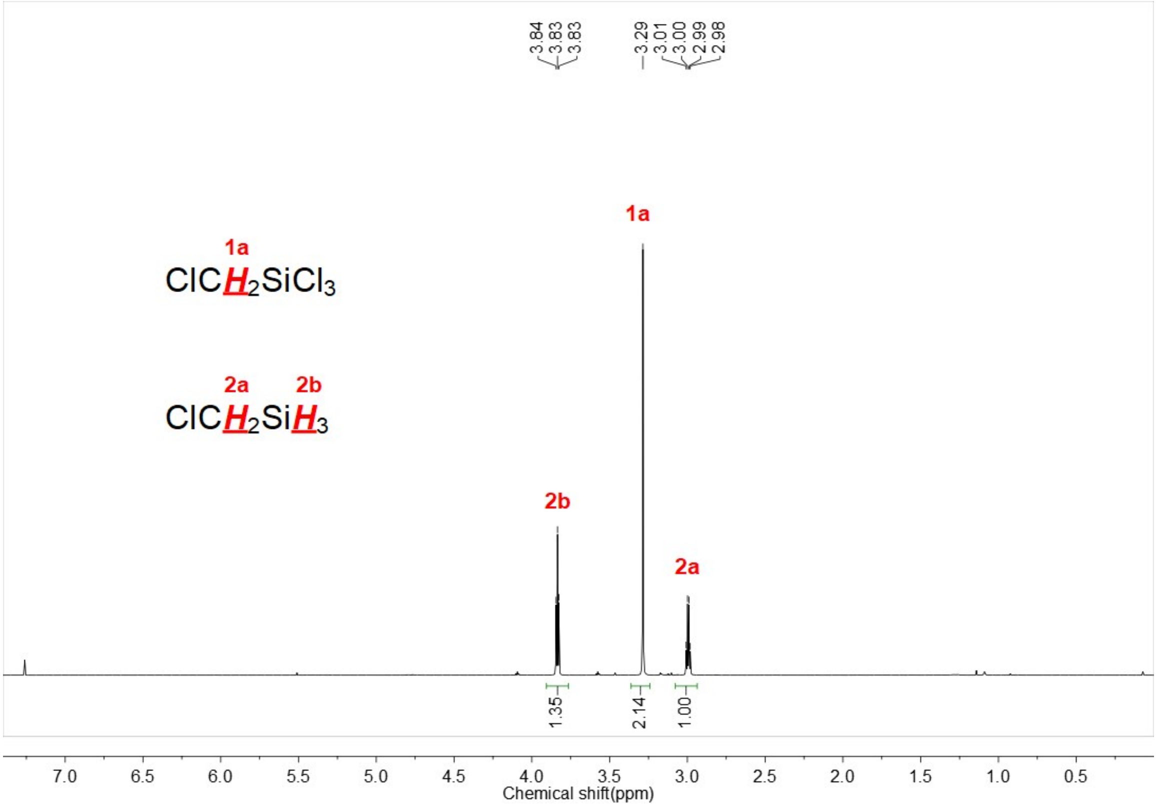


Figure 17a. Redistribution results of $ClCH_2SiCl_3$ and $ClCH_2SiH_3$ without solvent (**entry 1**)

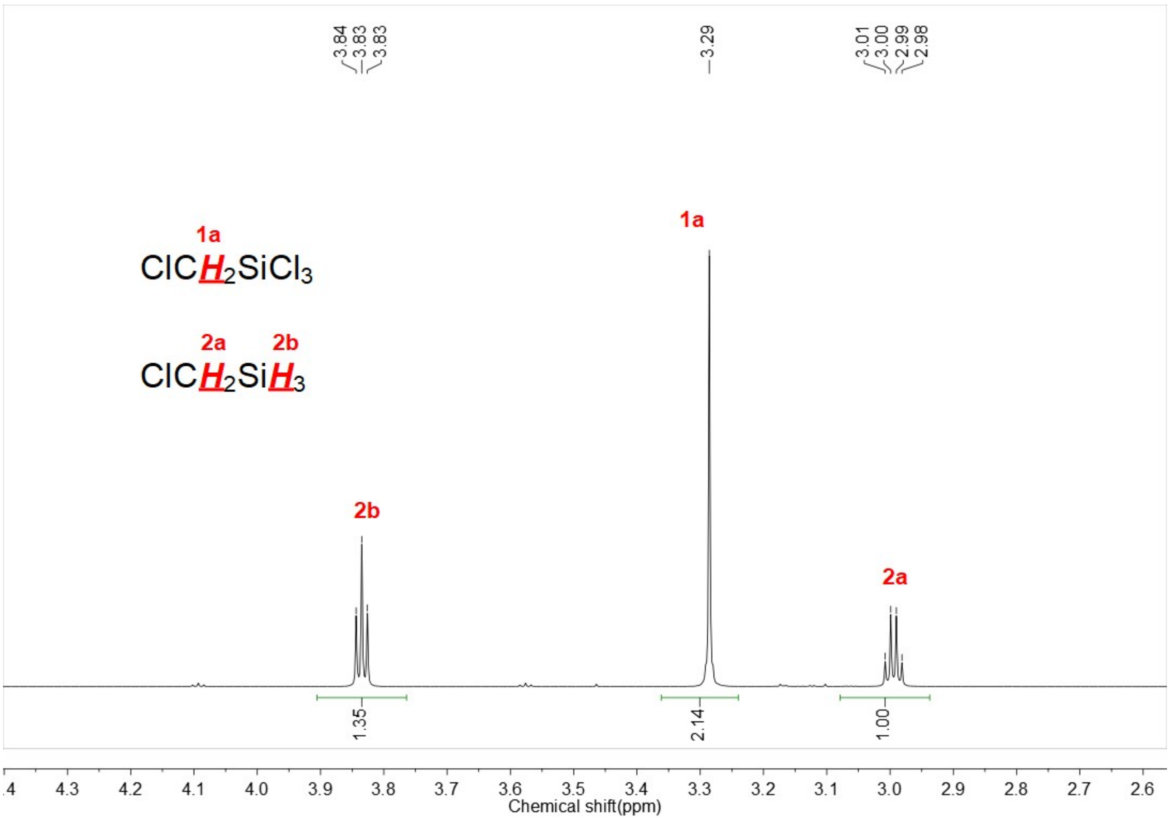


Figure 17b. Redistribution results of $ClCH_2SiCl_3$ and $ClCH_2SiH_3$ without solvent (**entry 1, zoom in**)

Redistribution results of $ClCH_2SiCl_3$ and $ClCH_2SiH_3$ (molar ratio = 2:1) in diglyme (Table 1, entry 2)

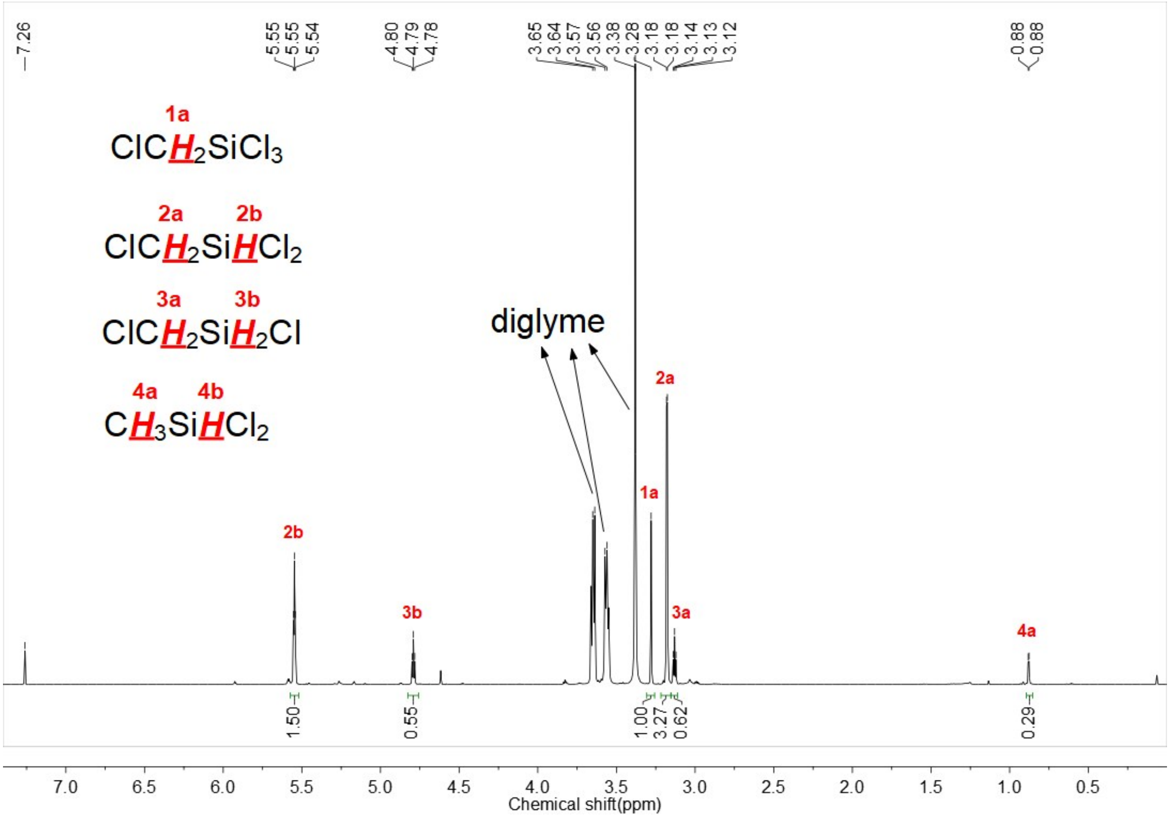


Figure 18a. Redistribution results of $ClCH_2SiCl_3$ and $ClCH_2SiH_3$ in diglyme (**entry 2**)

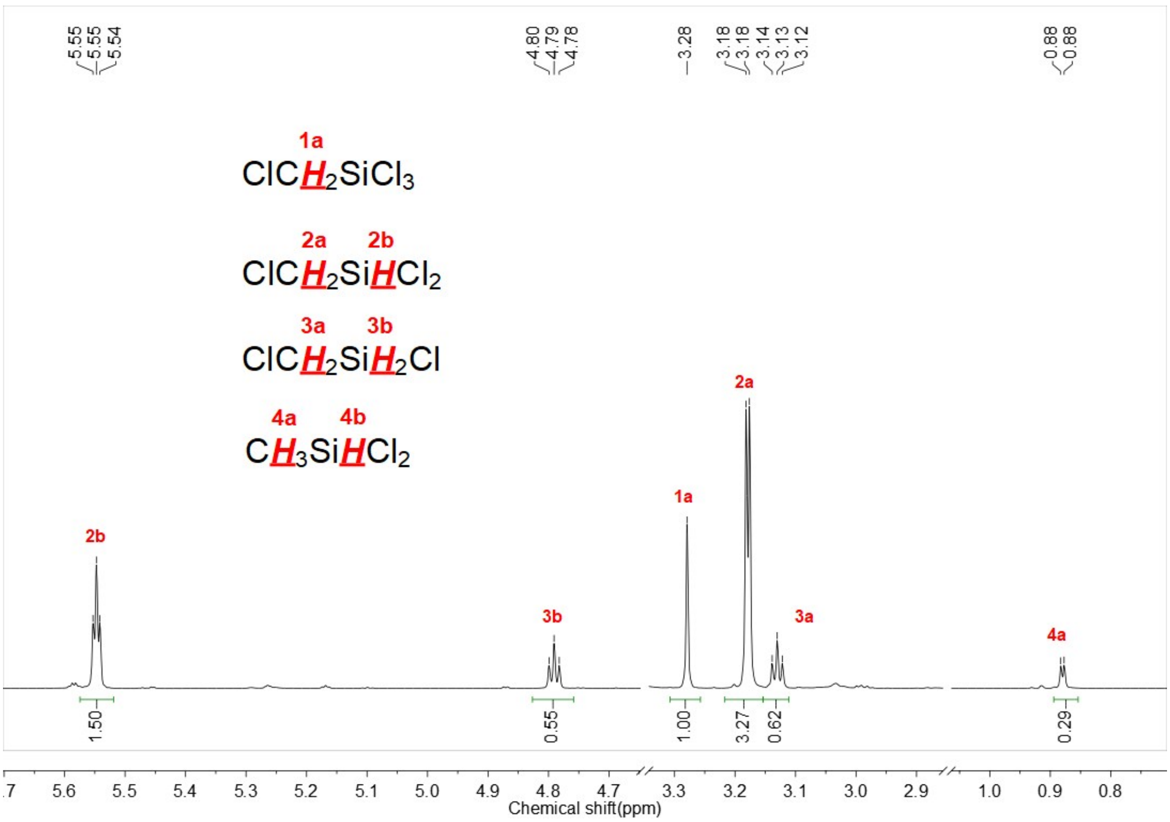


Figure 18b. Redistribution results of $ClCH_2SiCl_3$ and $ClCH_2SiH_3$ in diglyme **(entry 2, zoom in)**

Redistribution results of $ClCH_2SiCl_3$ and $ClCH_2SiH_3$ (molar ratio = 2:1) in THF (Table 1, entry 3)

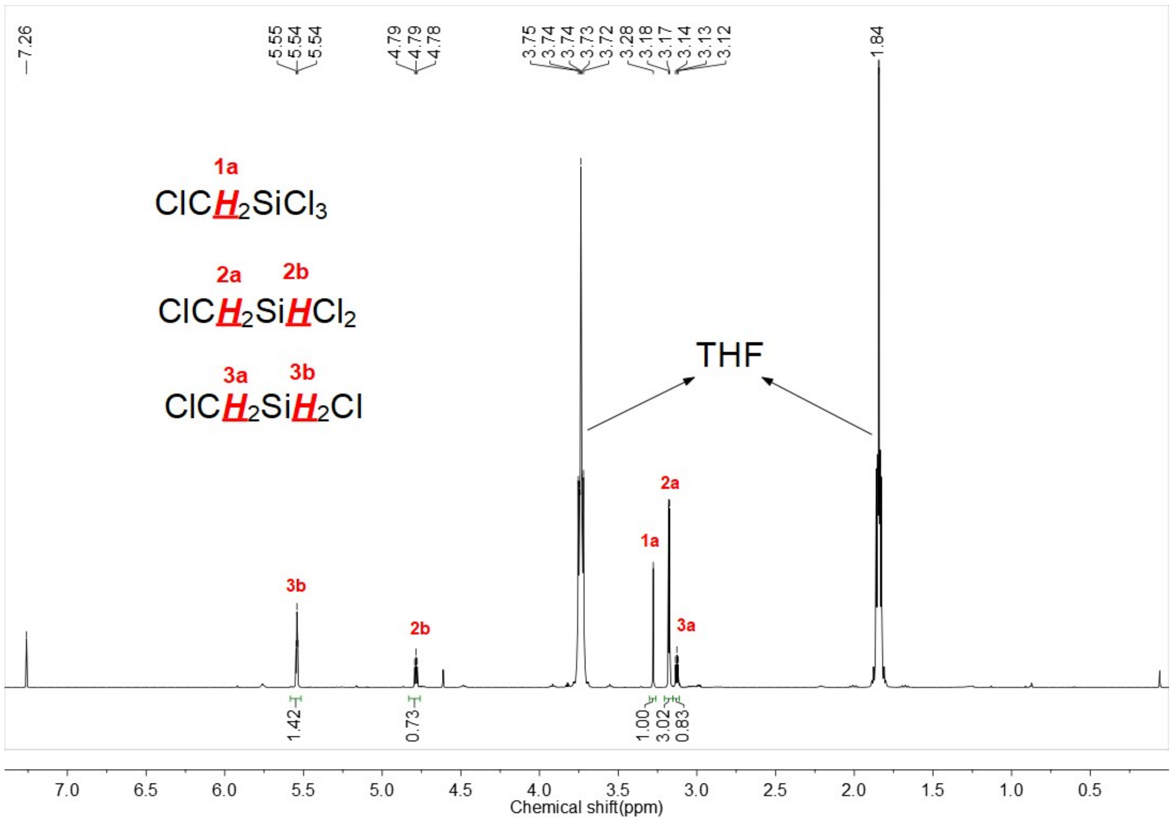


Figure 19a. Redistribution results of $ClCH_2SiCl_3$ and $ClCH_2SiH_3$ in THF (**entry 3**)

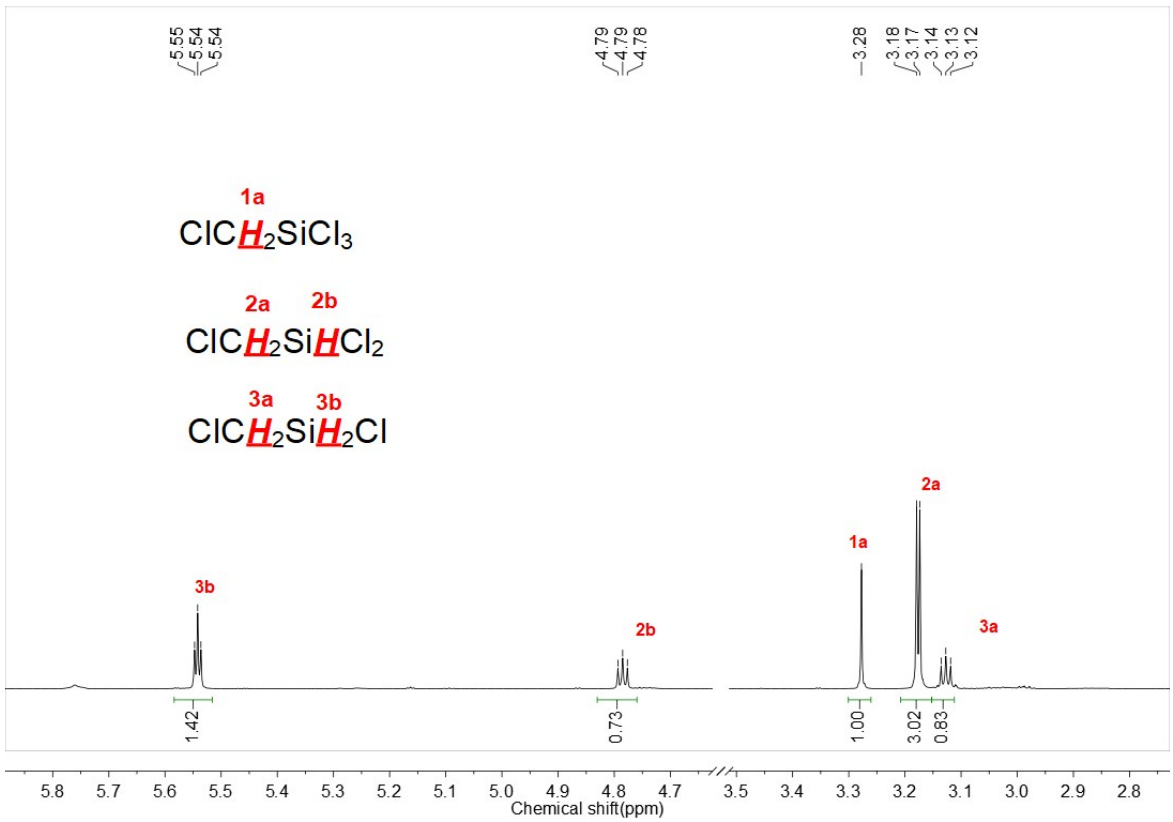


Figure 19b. Redistribution results of $ClCH_2SiCl_3$ and $ClCH_2SiH_3$ in THF (**entry 3, zoom in**)

Redistribution results of $ClCH_2SiCl_3$ and $ClCH_2SiH_3$ (molar ratio = 2:1) in CH_3CN (Table 1, entry 4)

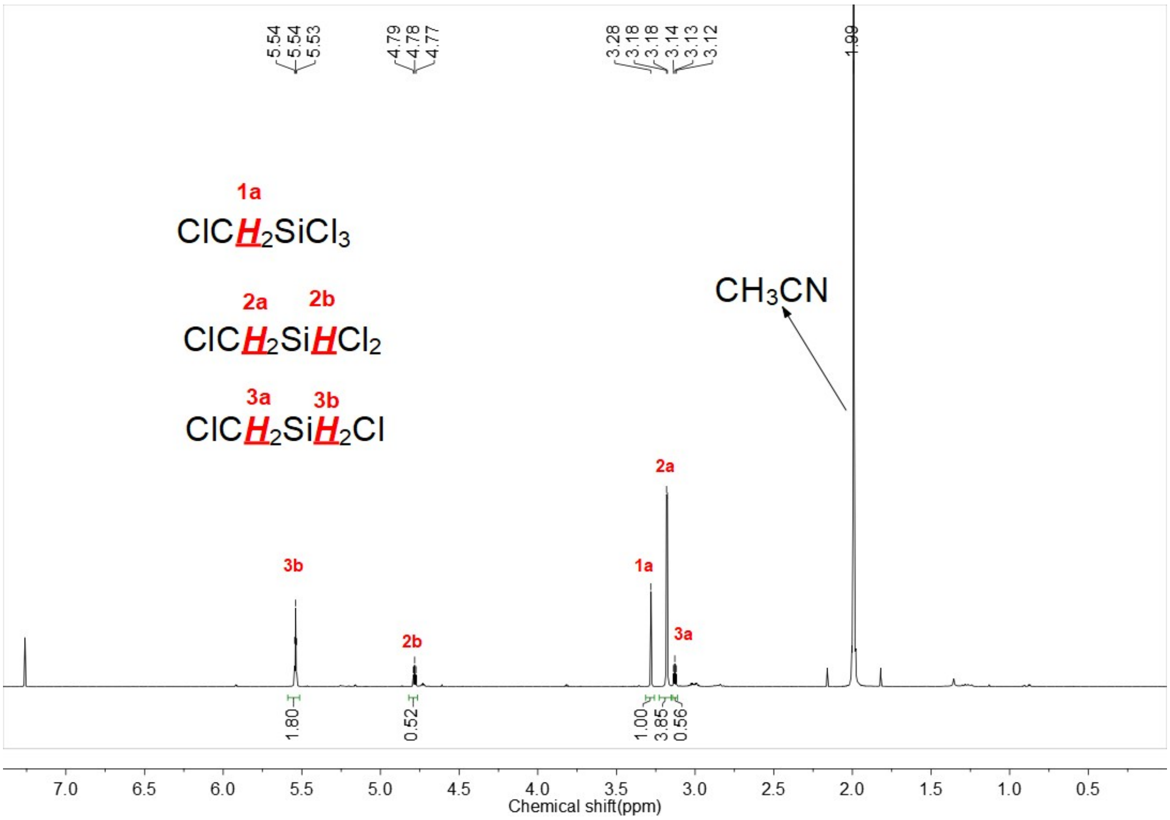


Figure 20a. Redistribution results of $ClCH_2SiCl_3$ and $ClCH_2SiH_3$ in CH_3CN (**entry 4**)

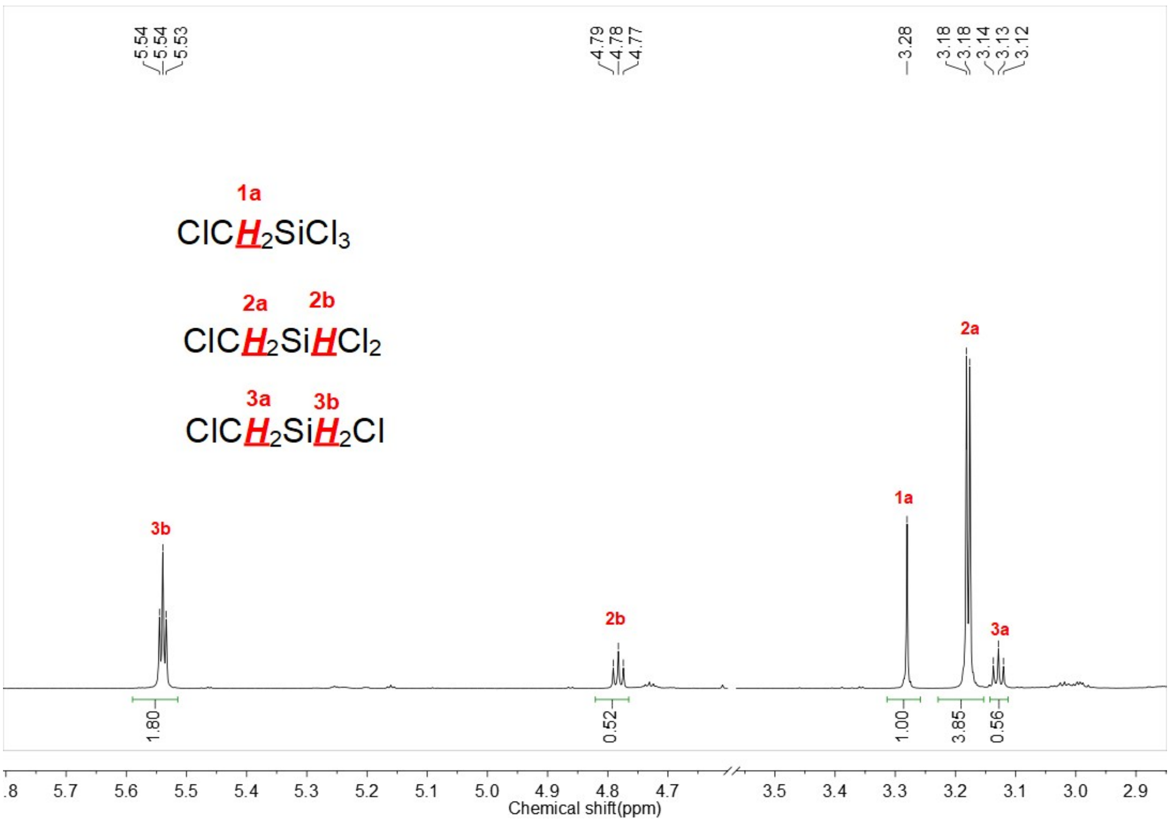


Figure 20b. Redistribution results of $ClCH_2SiCl_3$ and $ClCH_2SiH_3$ in CH_3CN (**entry 4, zoom in**)

Redistribution results of $ClCH_2SiCl_3$ and $ClCH_2SiH_3$ (molar ratio = 2:1) in DMI (Table 1, entry 5)

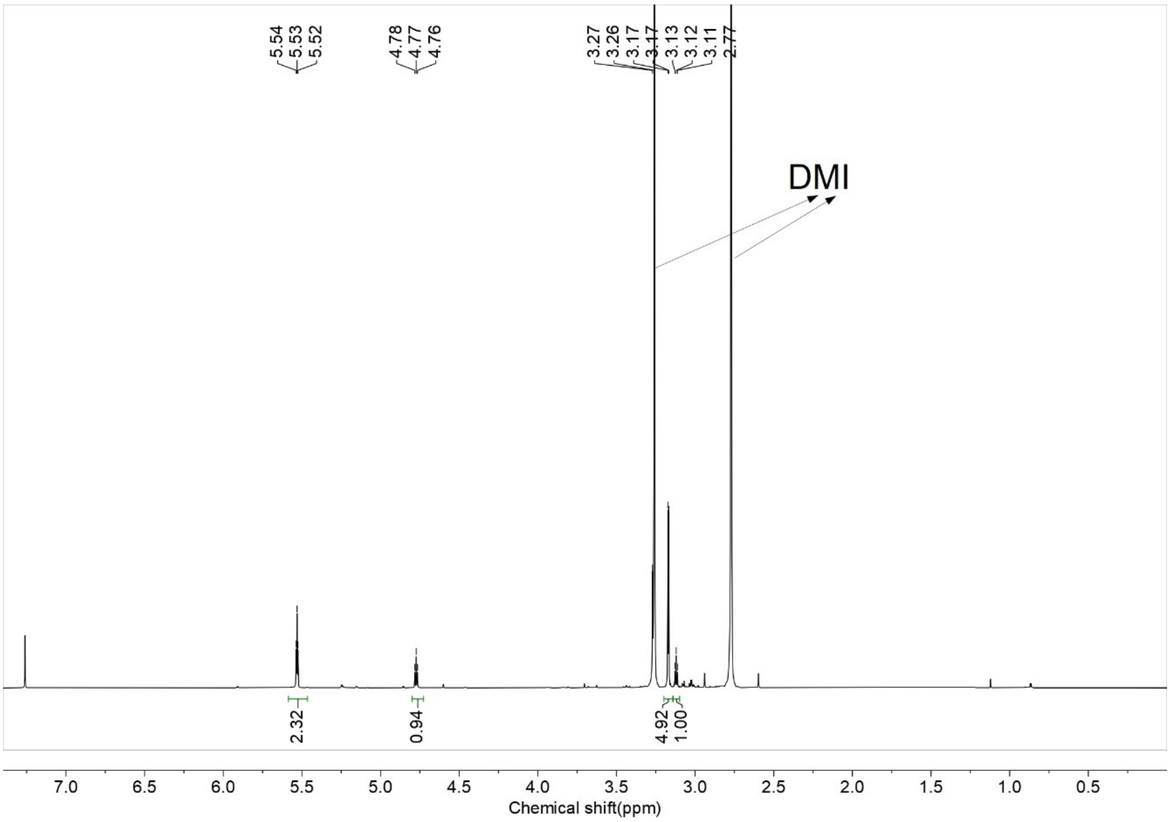


Figure 21a. Redistribution results of $ClCH_2SiCl_3$ and $ClCH_2SiH_3$ in DMI (**entry 5**)

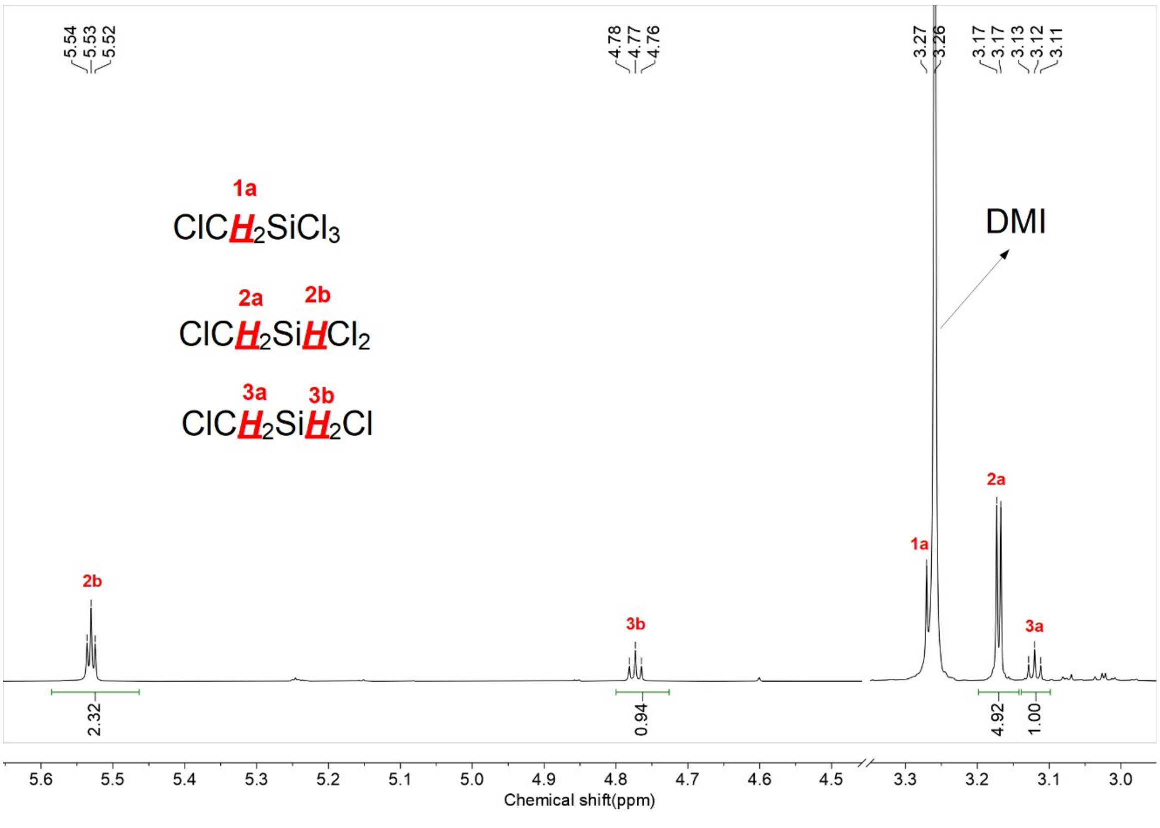


Figure 21b. Redistribution results of $ClCH_2SiCl_3$ and $ClCH_2SiH_3$ in DMI (**entry 5, zoom in**)

Redistribution results of $ClCH_2SiCl_3$ and $ClCH_2SiH_3$ (molar ratio = 2:1) in HMPA (Table 1, entry 6)

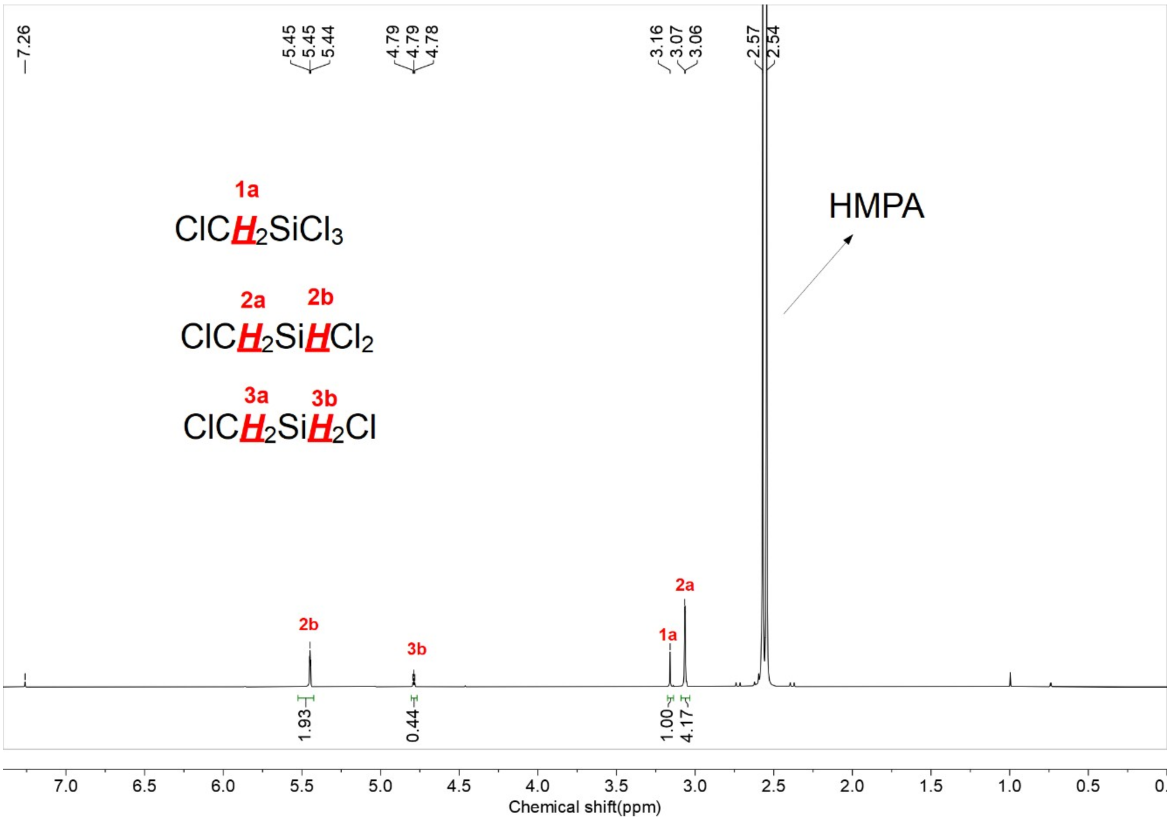


Figure 22a. Redistribution results of $ClCH_2SiCl_3$ and $ClCH_2SiH_3$ in HMPA (**entry 6**)

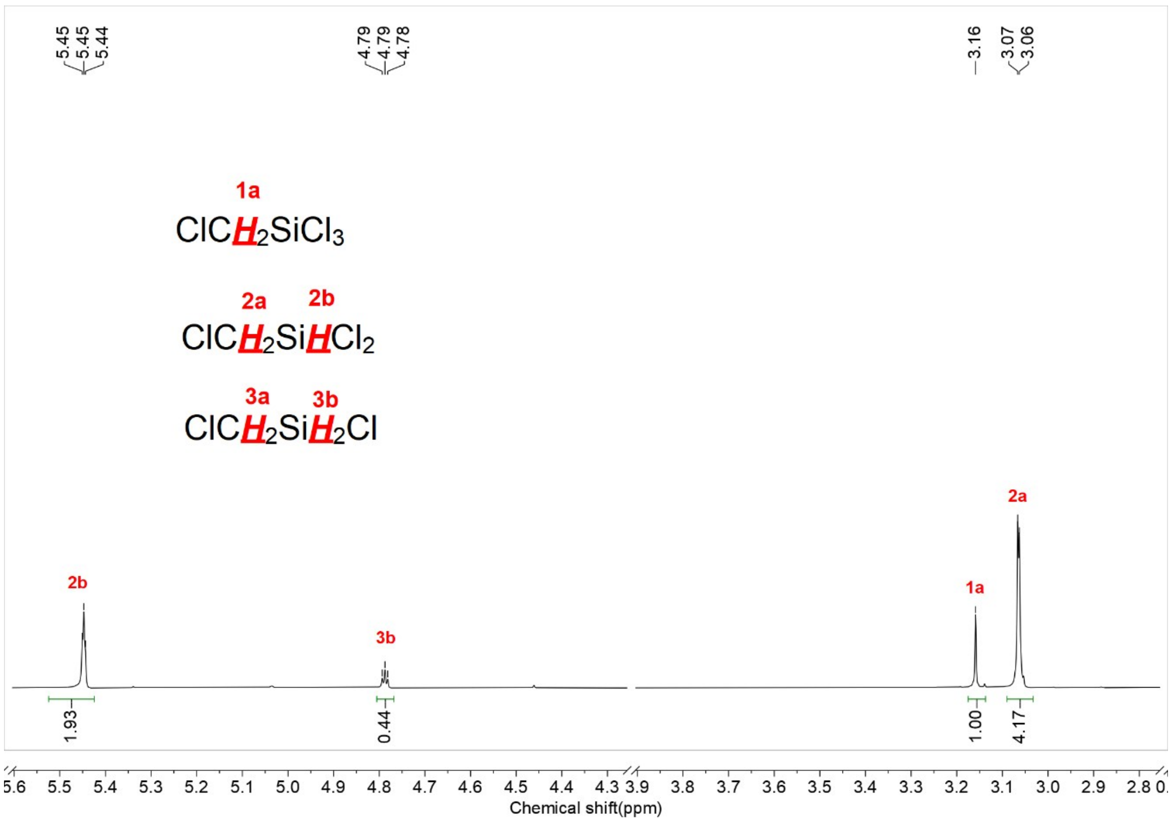


Figure 22b. Redistribution results of $ClCH_2SiCl_3$ and $ClCH_2SiH_3$ in HMPA (**entry 6, zoom in**)

Redistribution results of $ClCH_2SiCl_3$ and $ClCH_2SiH_3$ (molar ratio = 2:1) in Bu_2O (Table 1, entry 7)

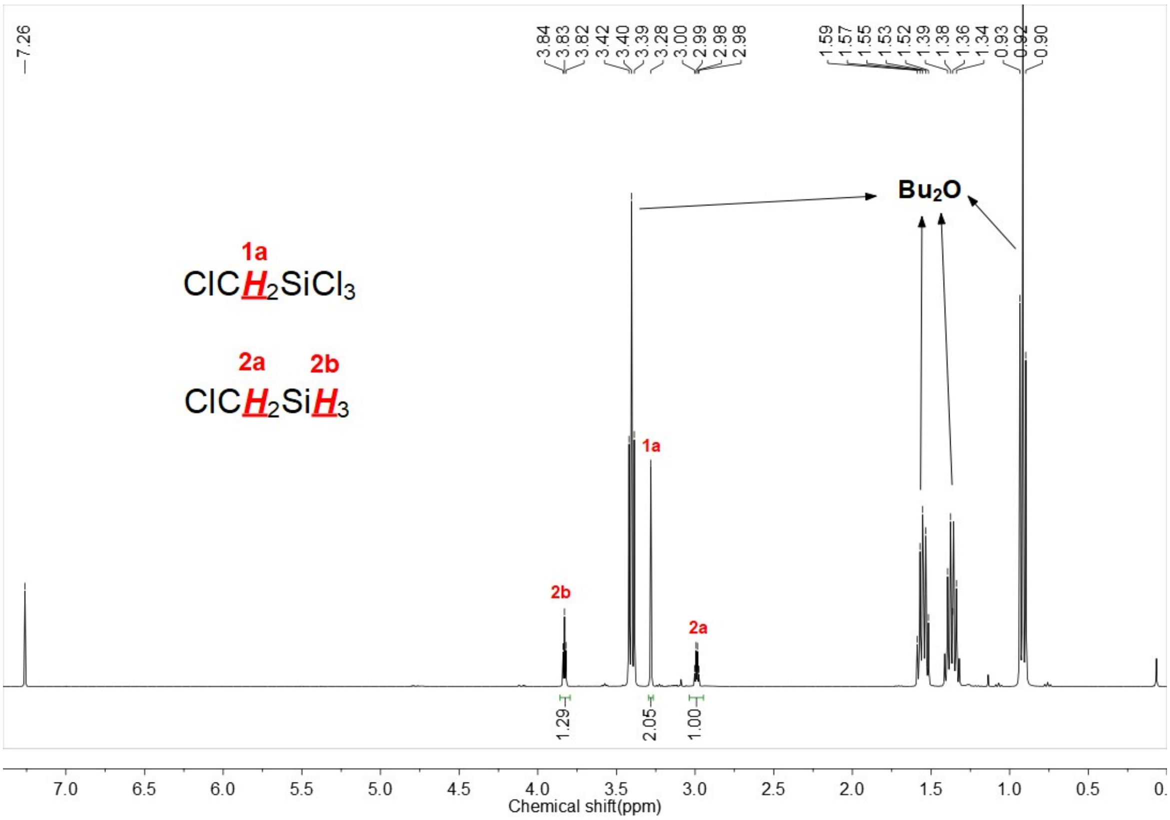


Figure 23a. Redistribution results of $ClCH_2SiCl_3$ and $ClCH_2SiH_3$ in Bu_2O (**entry 7**)

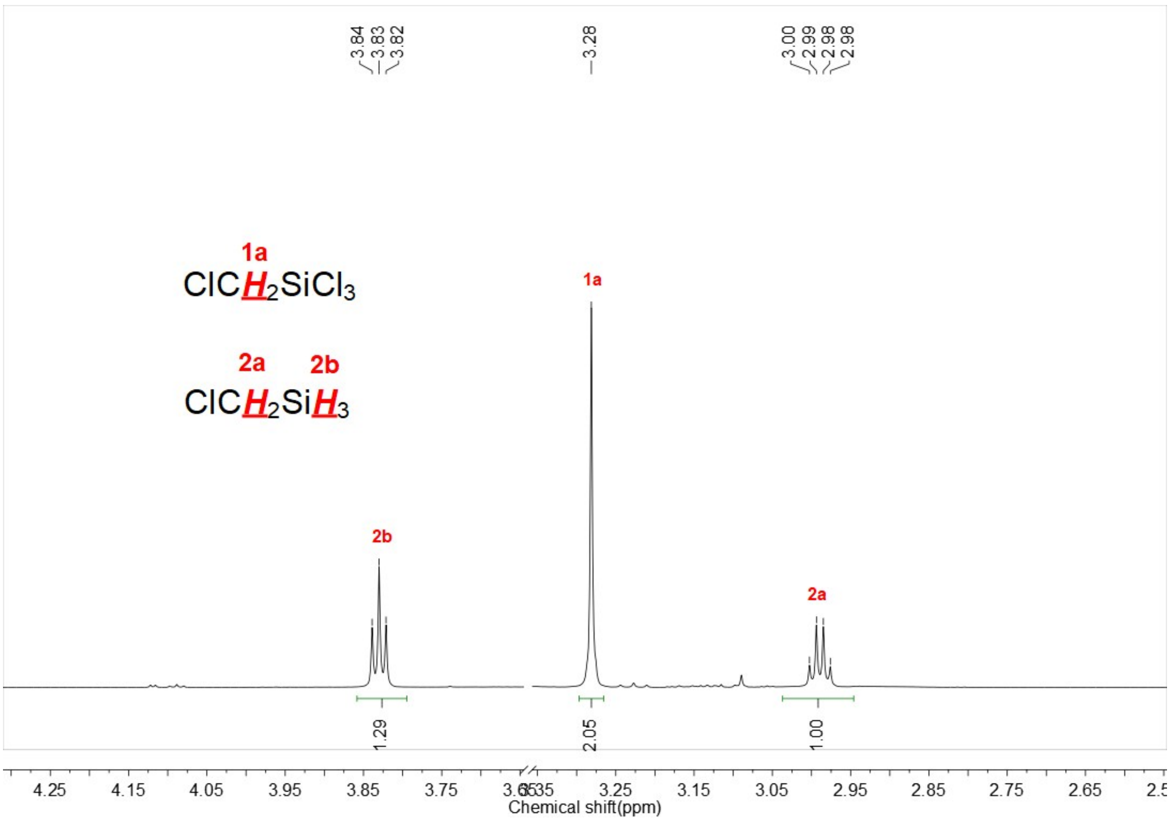


Figure 23b. Redistribution results of $ClCH_2SiCl_3$ and $ClCH_2SiH_3$ in Bu_2O (**entry 7, zoom in**)

Redistribution results of $ClCH_2SiCl_3$ and $ClCH_2SiH_3$ (molar ratio = 2:1) in Et_2O (Table 1, entry 8)

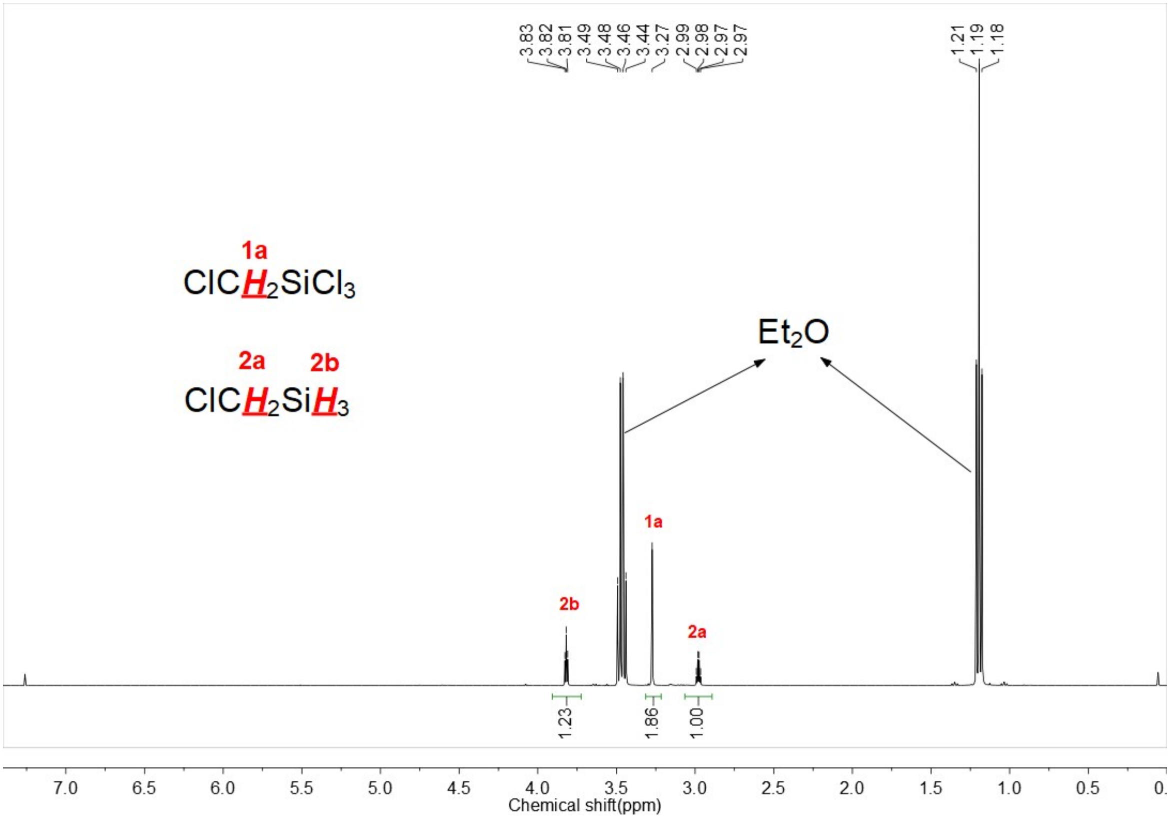


Figure 24a. Redistribution results of $ClCH_2SiCl_3$ and $ClCH_2SiH_3$ in Et_2O (**entry 8**)

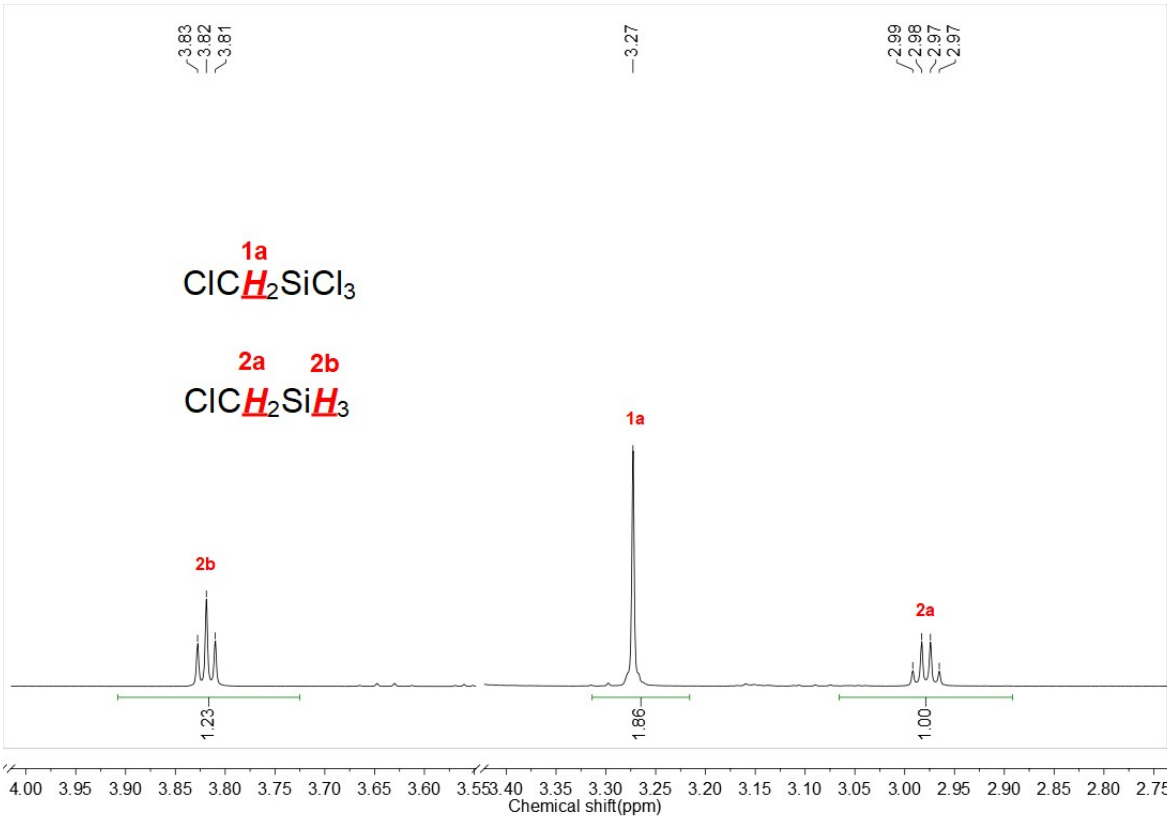


Figure 24b. Redistribution results of $ClCH_2SiCl_3$ and $ClCH_2SiH_3$ in Et_2O (**entry 8, zoom in**)

Redistribution results of $ClCH_2SiCl_3$ and $ClCH_2SiH_3$ (molar ratio = 2:1) in toluene (Table 1, entry 9)

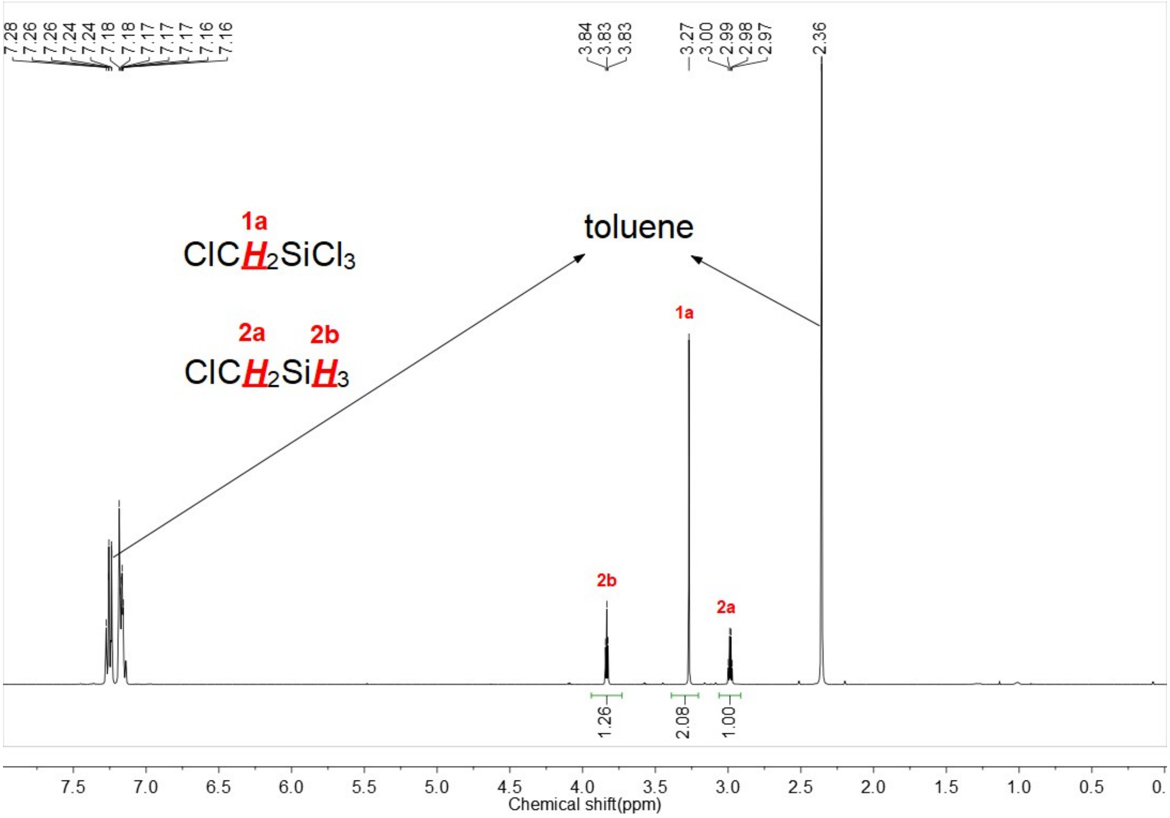


Figure 25a. Redistribution results of $ClCH_2SiCl_3$ and $ClCH_2SiH_3$ in toluene (**entry 9**)

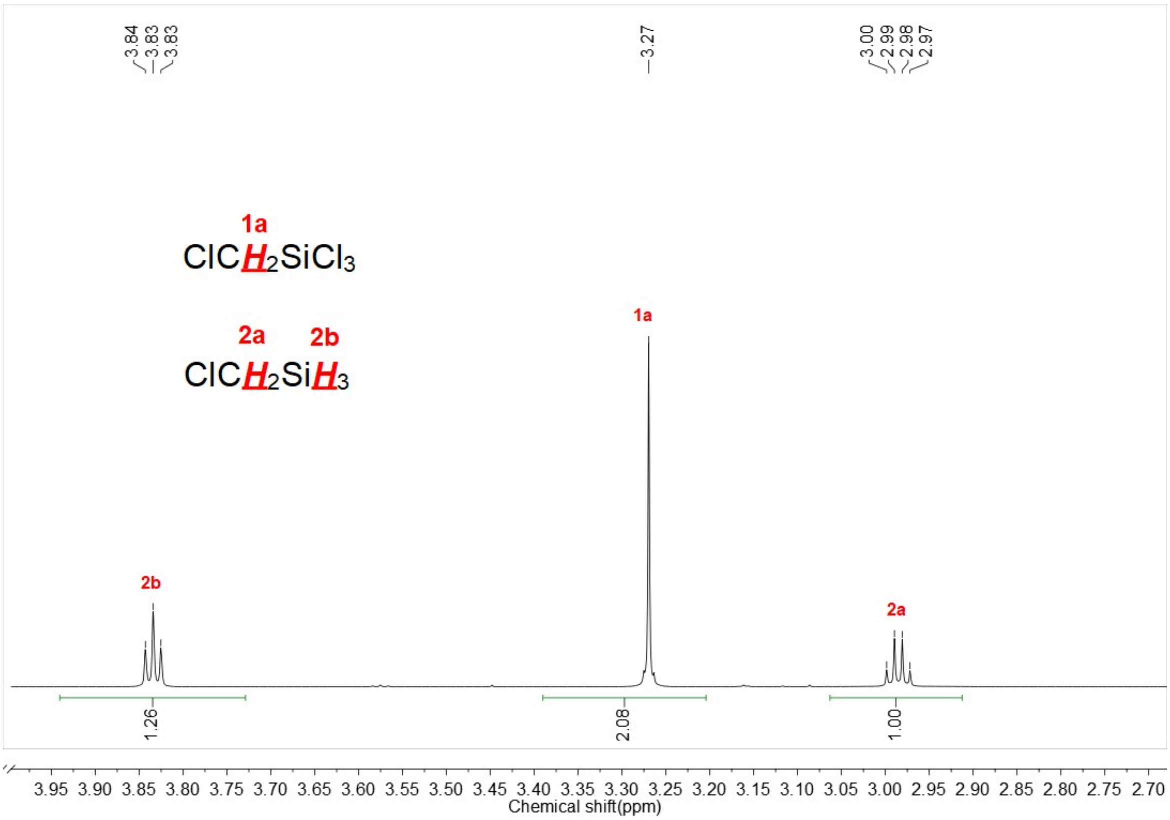


Figure 25b. Redistribution results of $ClCH_2SiCl_3$ and $ClCH_2SiH_3$ in toluene (**entry 9, zoom in**)

Ⅴ. Catalyst optimization with $ClCH_2SiH_3$ and $ClCH_2SiCl_3$ in THF (Table 2)

Procedure for the redistribution reaction of $ClCH_2SiH_3$ and $ClCH_2SiCl_3$ (molar ratio = 1 : 2) in THF catalyzed by different catalysts (Table 2)

To a mixture of catalysts, 5 mL THF in a 25 mL two-necked flask was added $ClCH_2SiH_3$ (0.80 g, 0.01 mol) and $ClCH_2SiCl_3$ (1.84 g, 0.01 mol) in sequence. The reaction mixture was stirred by magneton at room temperature and measured by ^{1}H-NMR.

Table 2 Catalyst optimization of redistribution reaction of $ClCH_2SiH_3$/$ClCH_2SiCl_3$[a]

$$ClCH_2SiH_3 + ClCH_2SiCl_3 \xrightarrow[\text{THF,RT, 20h}]{\text{catalyst}} ClCH_2SiH_2Cl + ClCH_2SiHCl_2$$

Entry	Cat.	Cat. (mol%)	Product (yield)[b]
1	$LiBH_4$	0.4	$ClCH_2SiHCl_2$: 10%, $ClCH_2SiH_2Cl$: 20%
2	$LiBH_4$	0.8	$ClCH_2SiHCl_2$: 32%, $ClCH_2SiH_2Cl$: 27%
3	$LiBH_4$	1.5	$ClCH_2SiHCl_2$: 55%, $ClCH_2SiH_2Cl$: 18%
4	$LiBH_4$	3.0	$ClCH_2SiHCl_2$: 63%, $ClCH_2SiH_2Cl$: 16%
5	$LiBEt_3H$	3.0	$ClCH_2SiHCl_2$: 68%, $ClCH_2SiH_2Cl$: 12%
6	$NaBH_4$	3.0	No reaction
7	KBH_4	3.0	No reaction
8	$LiAlH_4$	3.0	$ClCH_2SiHCl_2$: 18%, $ClCH_2SiH_2Cl$: 21%

[a] Reaction conditions: $ClCH_2SiH_3$ (0.01 mol), $ClCH_2SiCl_3$ (0.02 mol), THF (5 mL), room temperature; [b] yields were determined by ^{1}H NMR.

Redistribution results of $ClCH_2SiH_3$ and $ClCH_2SiCl_3$ (molar ratio = 1:2) in THF catalyzed by $LiBH_4$ (0.4 mol%) (Table 2, entry 1)

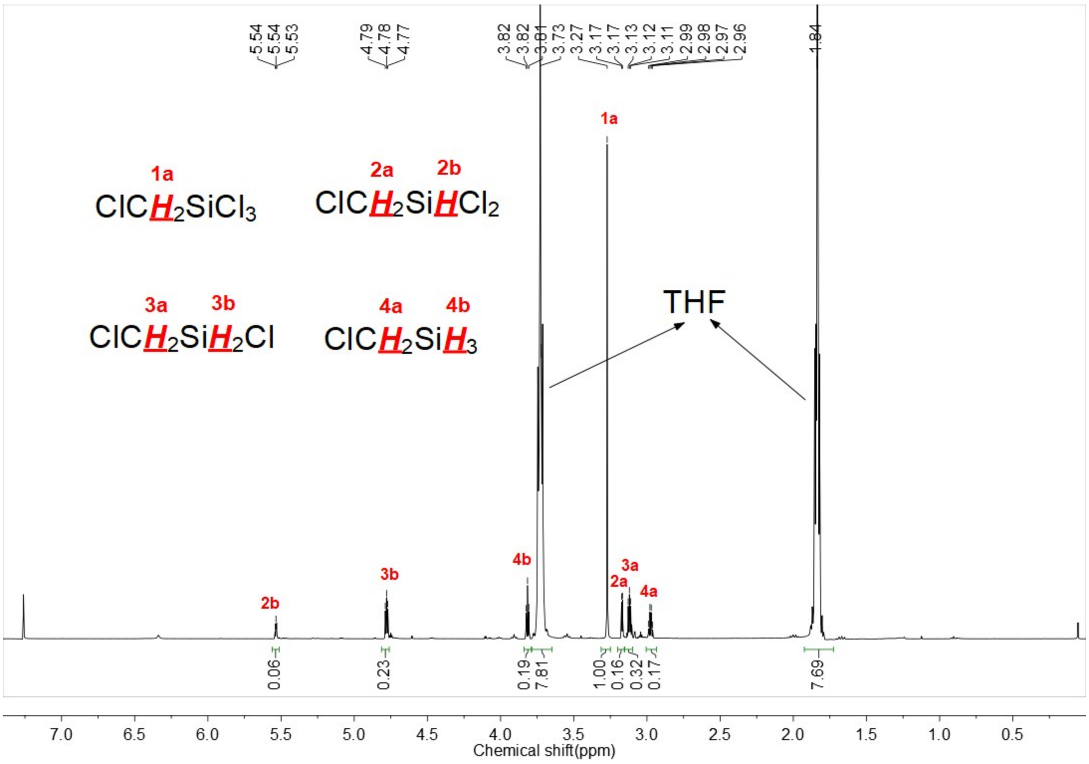


Figure 26a. Redistribution results of $ClCH_2SiH_3$ and $ClCH_2SiCl_3$ (1:2) in THF (**entry 1**)

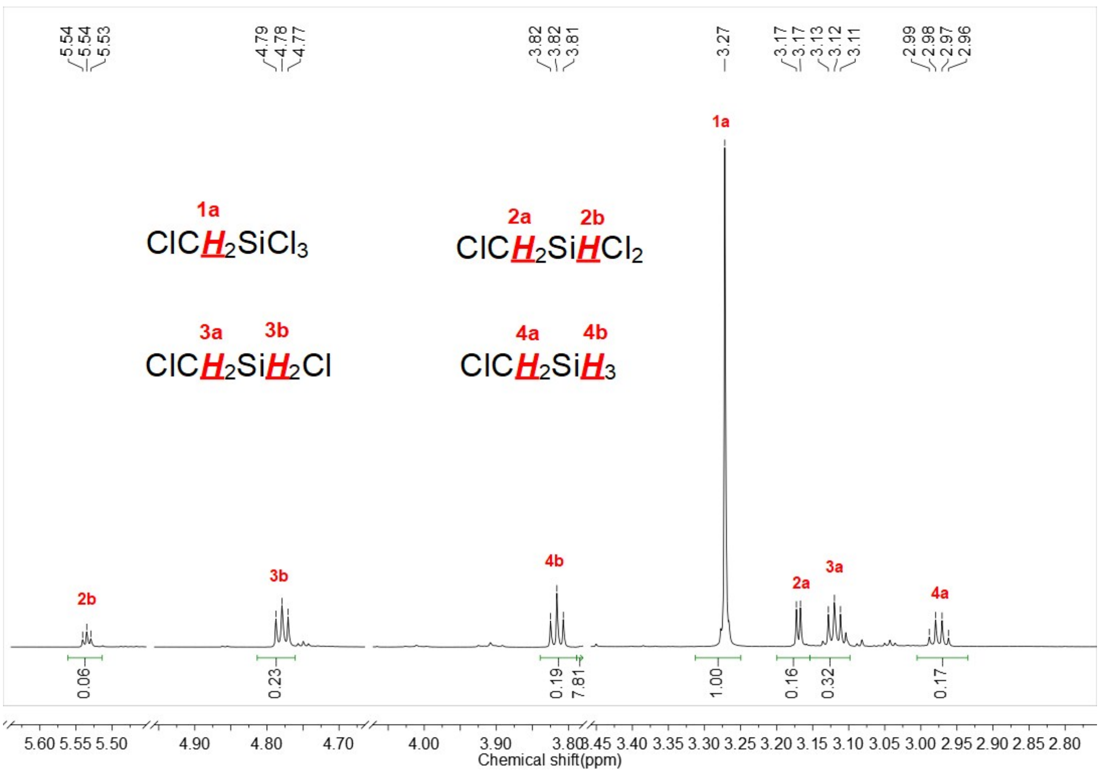


Figure 26b. Redistribution results of $ClCH_2SiH_3$ and $ClCH_2SiCl_3$ (1:2) in THF (**entry 1, zoom in**)

Redistribution results of $ClCH_2SiH_3$ and $ClCH_2SiCl_3$ (molar ratio = 1:2) in THF catalyzed by $LiBH_4$ (0.8 mol%) (Table 2, entry 2)

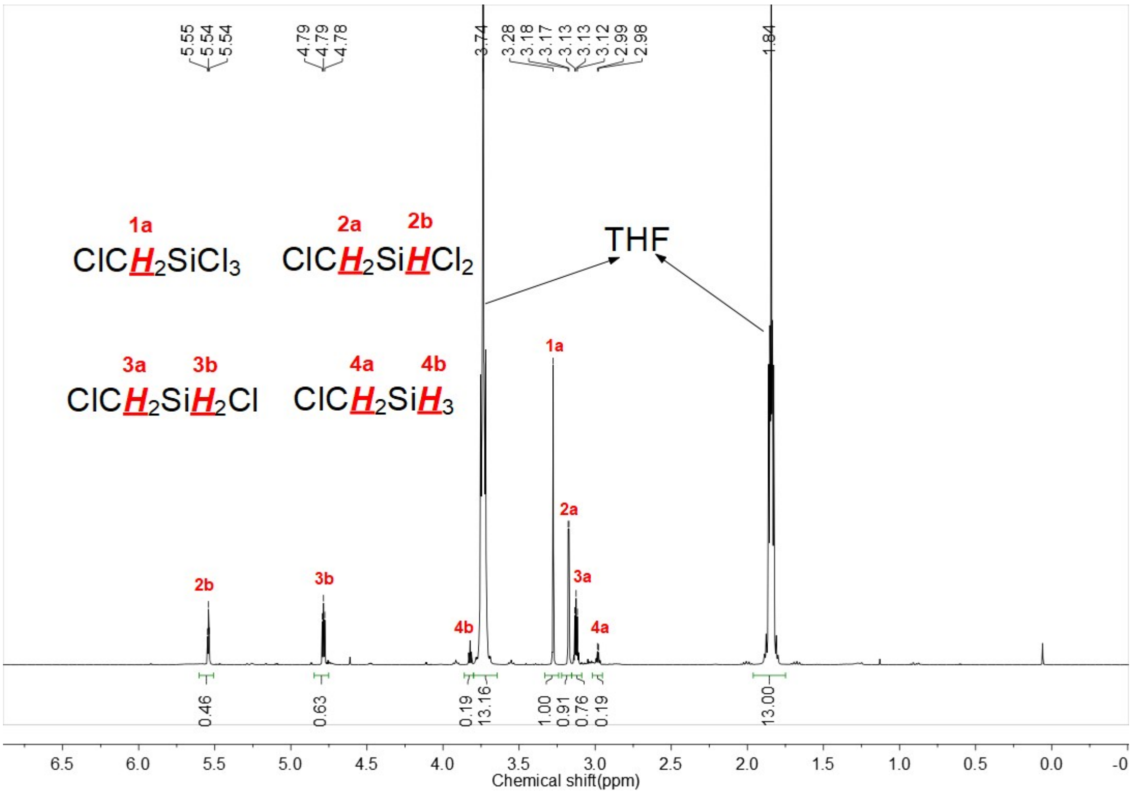


Figure 27a. Redistribution results of $ClCH_2SiH_3$ and $ClCH_2SiCl_3$ (1:2) in THF (**entry 2**)

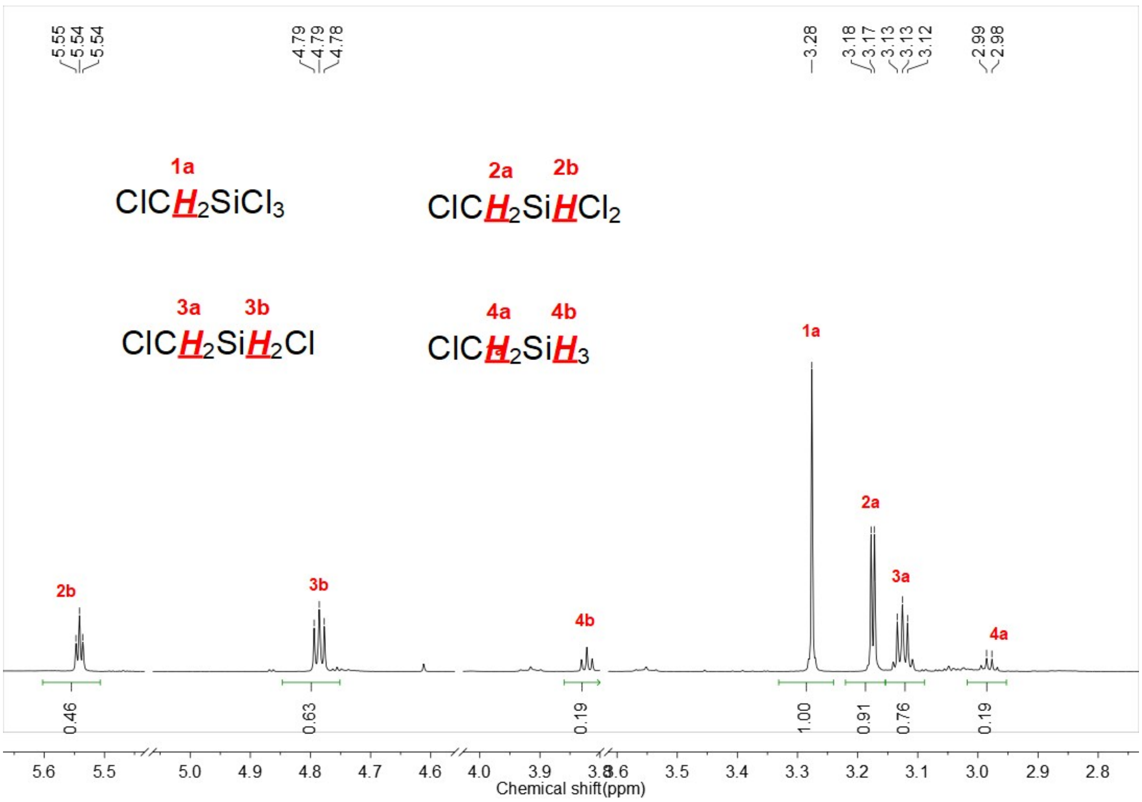


Figure 27b. Redistribution results of $ClCH_2SiH_3$ and $ClCH_2SiCl_3$ (1:2) in THF (**entry 2, zoom in**)

Redistribution results of $ClCH_2SiH_3$ and $ClCH_2SiCl_3$ (molar ratio = 1:2) in THF catalyzed by $LiBH_4$ (1.5 mol%) (Table 2, entry 3)

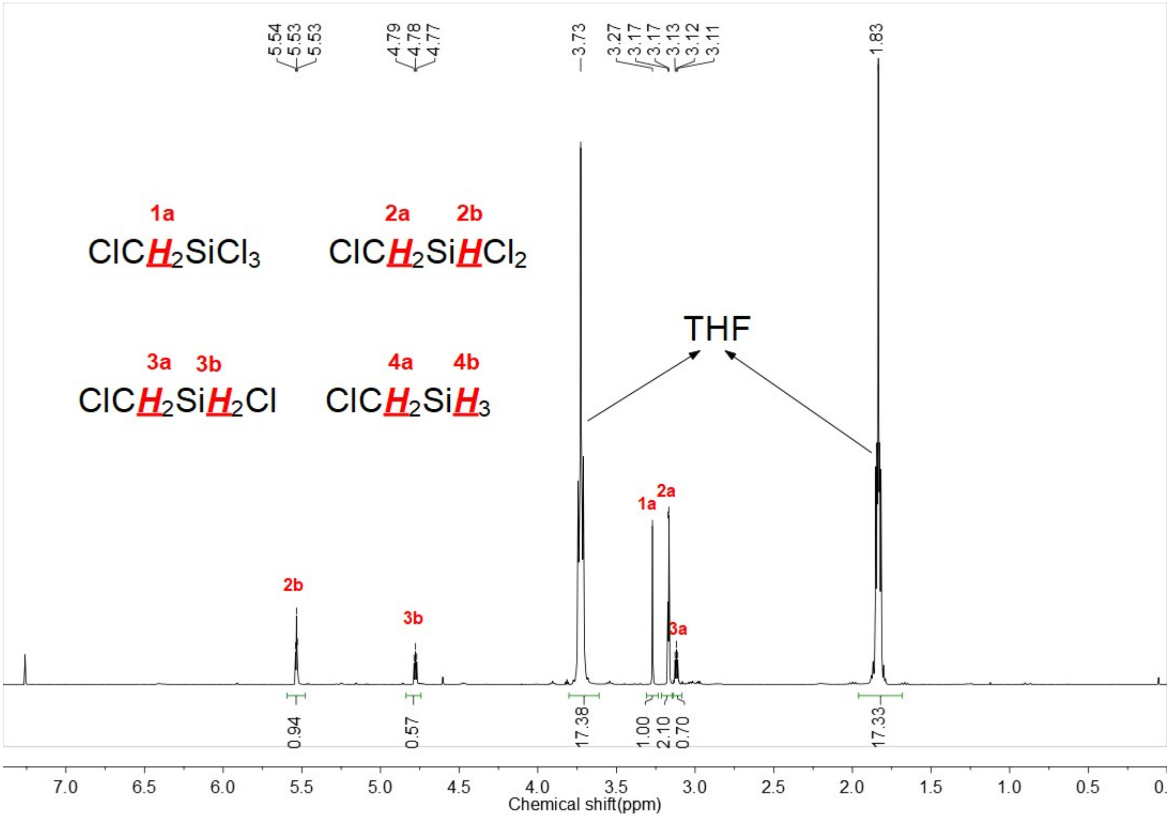


Figure 28a. Redistribution results of $ClCH_2SiH_3$ and $ClCH_2SiCl_3$ (1:2) in THF (**entry 3**)

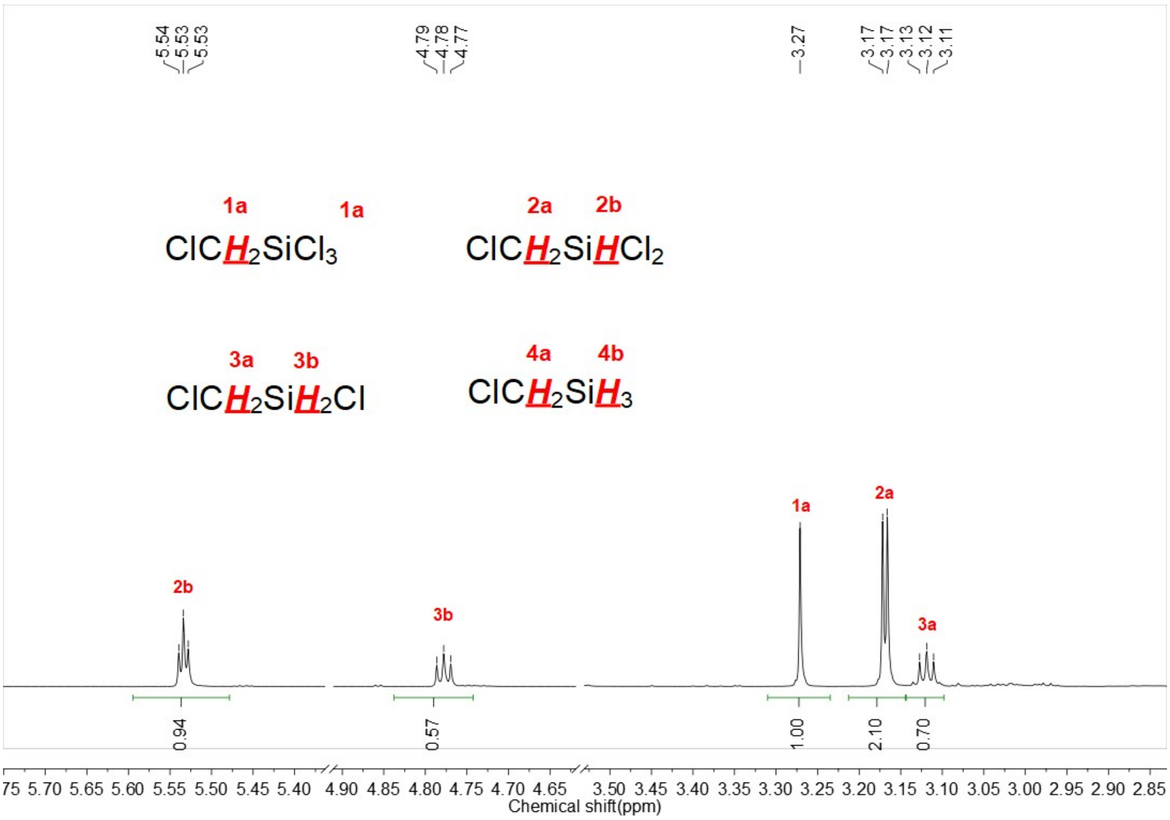


Figure 28b. Redistribution results of $ClCH_2SiH_3$ and $ClCH_2SiCl_3$ (1:2) in THF (**entry 3, zoom in**)

Redistribution results of $ClCH_2SiH_3$ and $ClCH_2SiCl_3$ (molar ratio = 1:2) in THF catalyzed by $LiBH_4$ (3.0 mol%) (Table 2, entry 4)

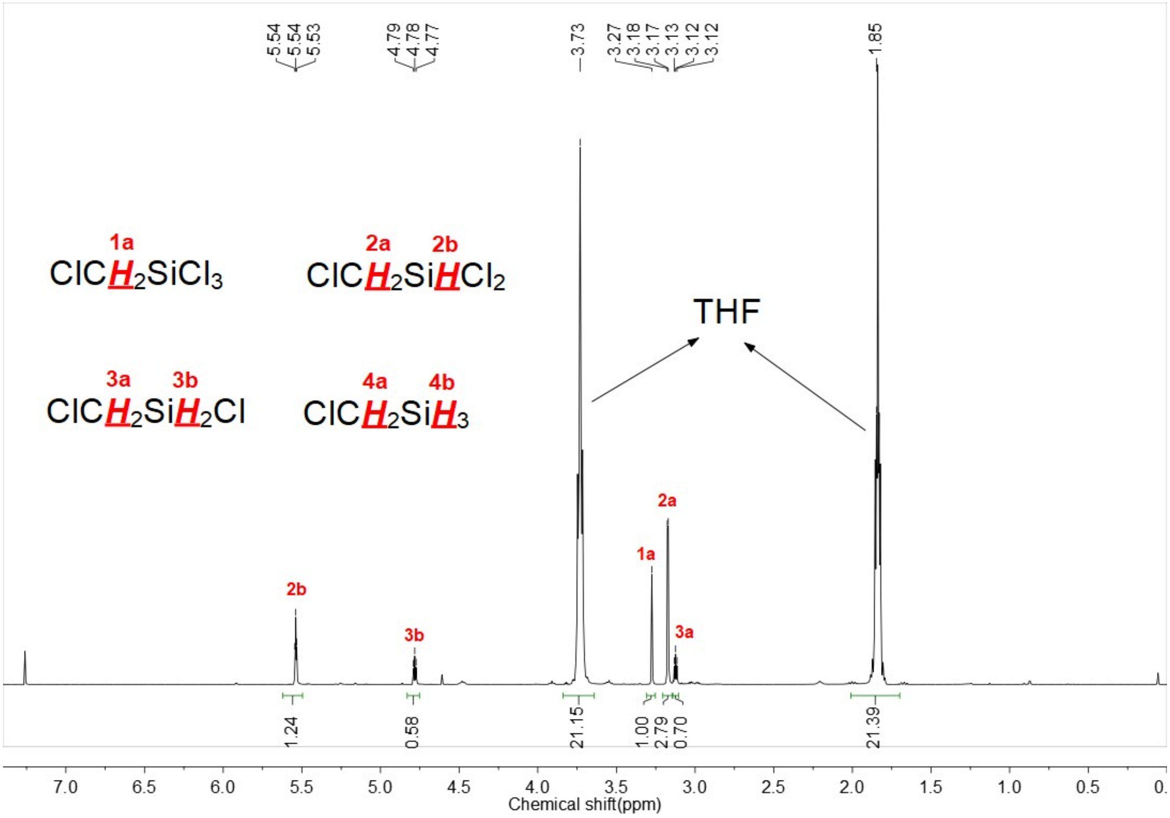


Figure 29a. Redistribution results of $ClCH_2SiH_3$ and $ClCH_2SiCl_3$ (1:2) in THF (**entry 4**)

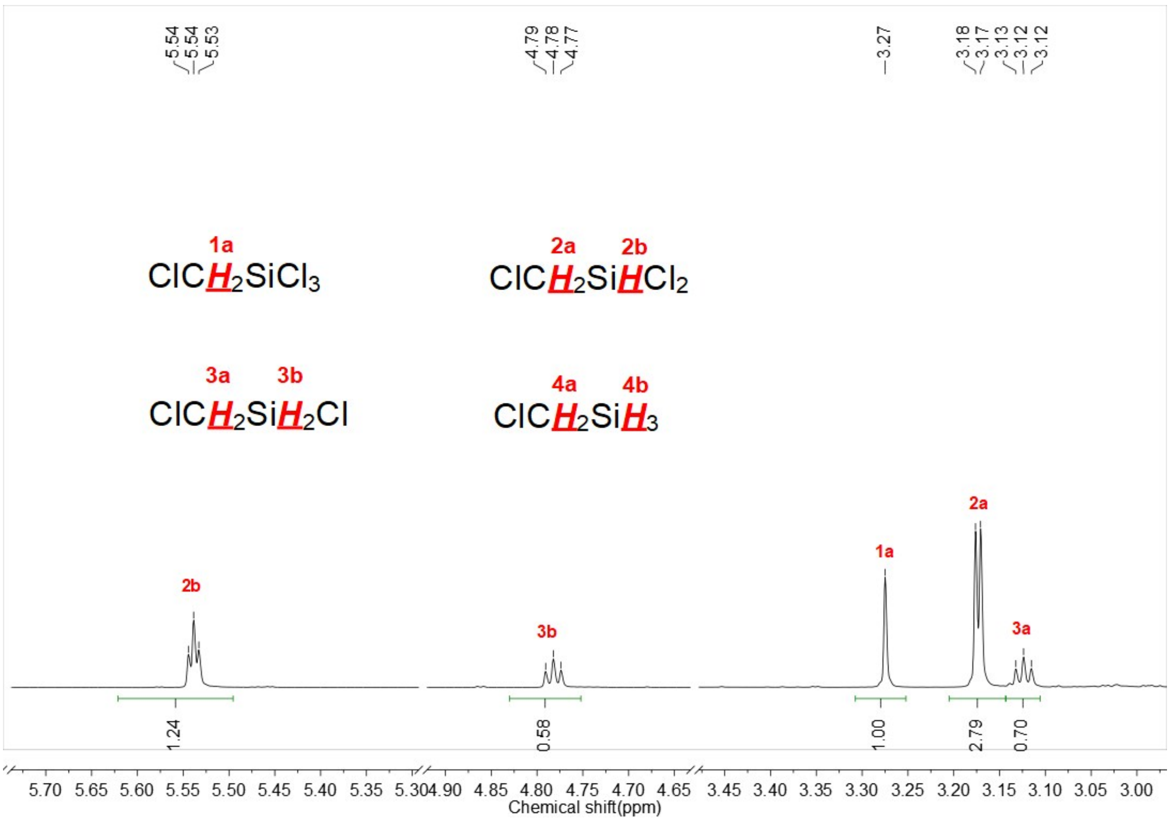


Figure 29b. Redistribution results of $ClCH_2SiH_3$ and $ClCH_2SiCl_3$ (1:2) in THF (**entry 4, zoom in**)

Redistribution results of $ClCH_2SiH_3$ and $ClCH_2SiCl_3$ (molar ratio = 1:2) in THF catalyzed by $LiBEt_3H$ (3.0 mol%) (Table 2, entry 5)

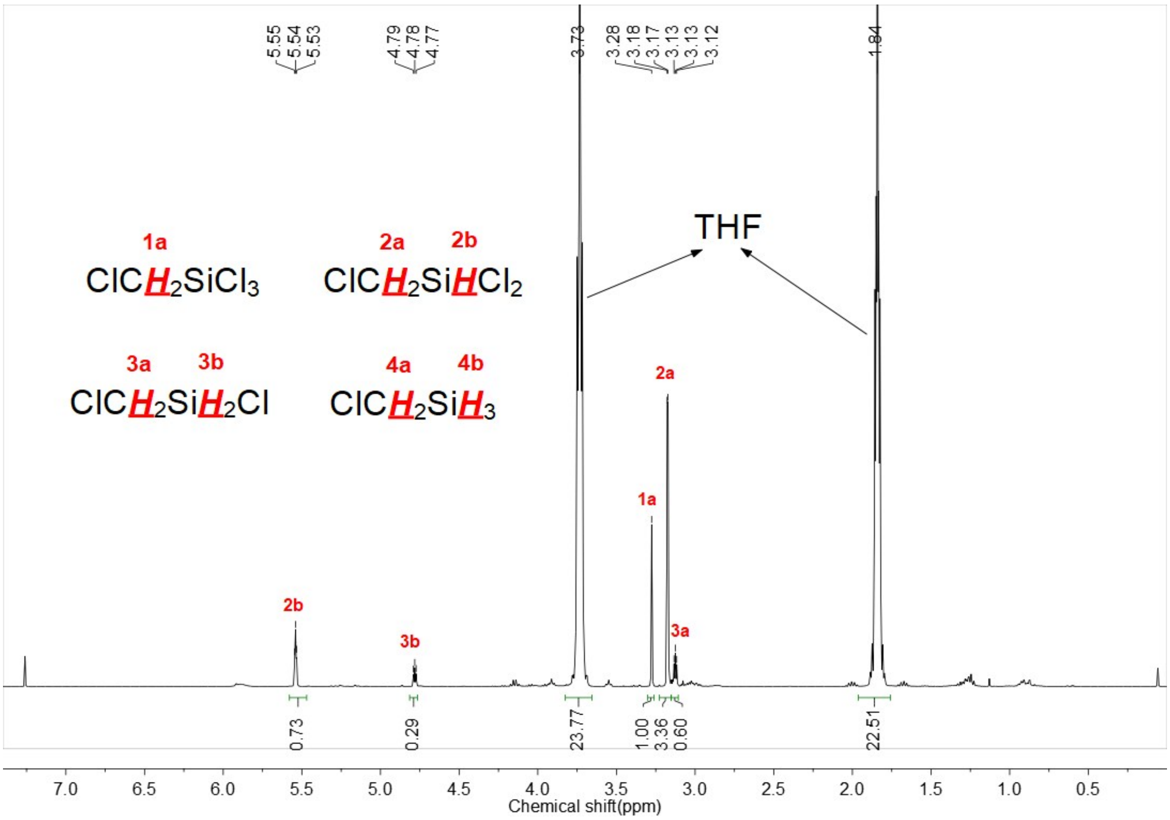


Figure 30a. Redistribution results of $ClCH_2SiH_3$ and $ClCH_2SiCl_3$ (1:2) in THF (**entry 5**)

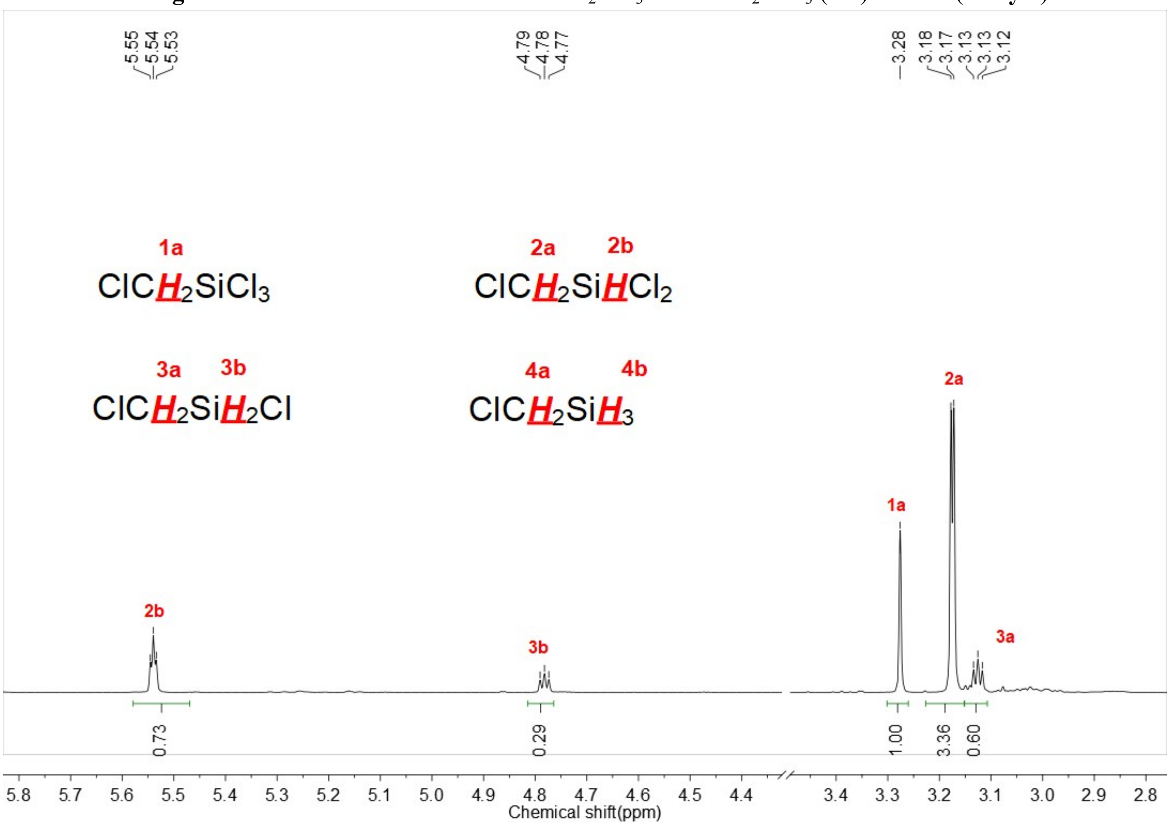


Figure 30b. Redistribution results of $ClCH_2SiH_3$ and $ClCH_2SiCl_3$ (1:2) in THF (**entry 5, zoom in**)

Redistribution results of $ClCH_2SiH_3$ and $ClCH_2SiCl_3$ (molar ratio = 1:2) in THF catalyzed by $NaBH_4$ (3.0 mol%) (Table 2, entry 6)

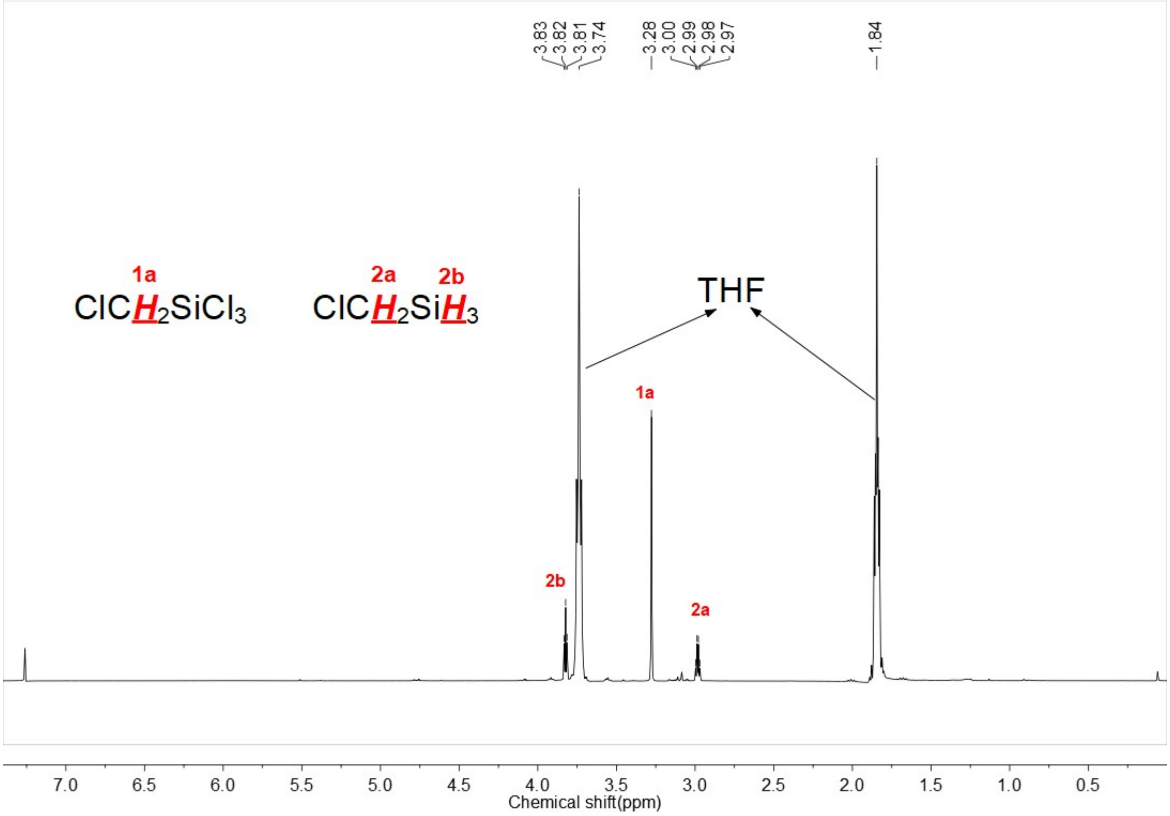


Figure 31a. Redistribution results of $ClCH_2SiH_3$ and $ClCH_2SiCl_3$ (1:2) in THF (**entry 6**)

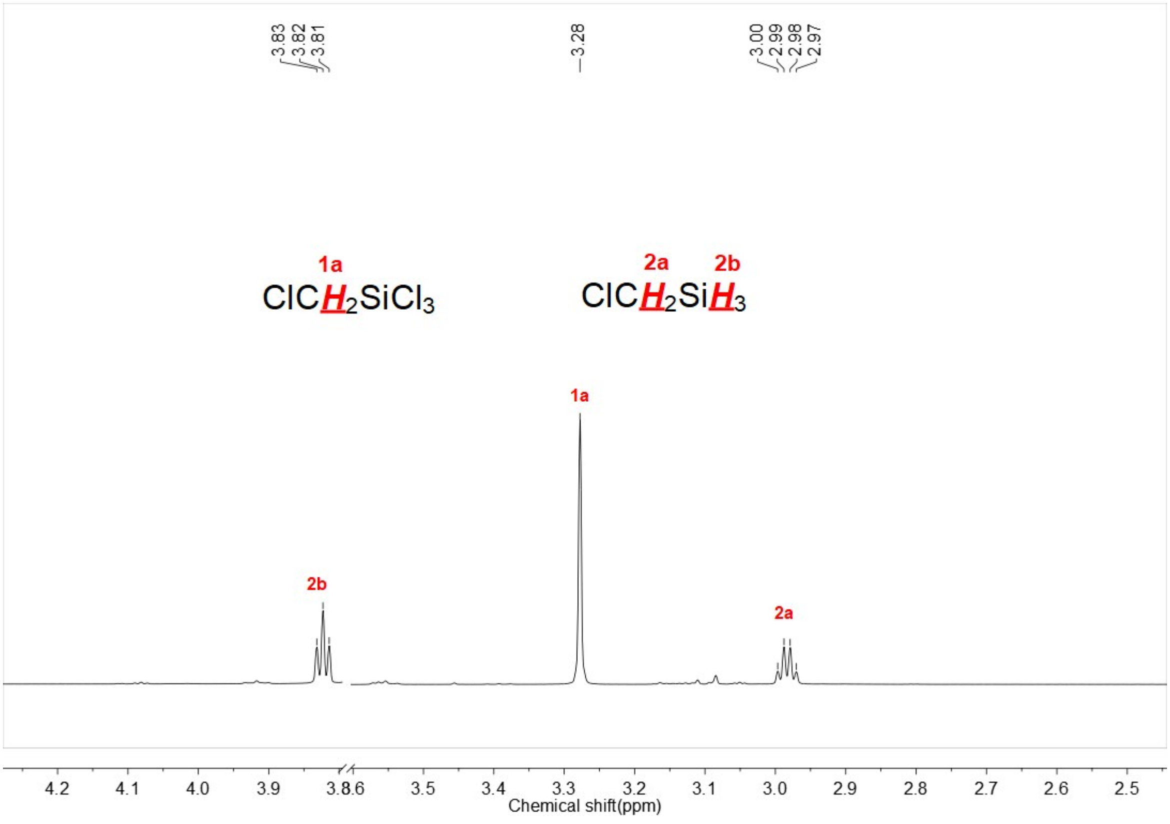


Figure 31b. Redistribution results of $ClCH_2SiH_3$ and $ClCH_2SiCl_3$ (1:2) in THF (**entry 6, zoom in**)

Redistribution results of $ClCH_2SiH_3$ and $ClCH_2SiCl_3$ (molar ratio = 1:2) in THF catalyzed by KBH_4 (3.0 mol%) (Table 2, entry 7)

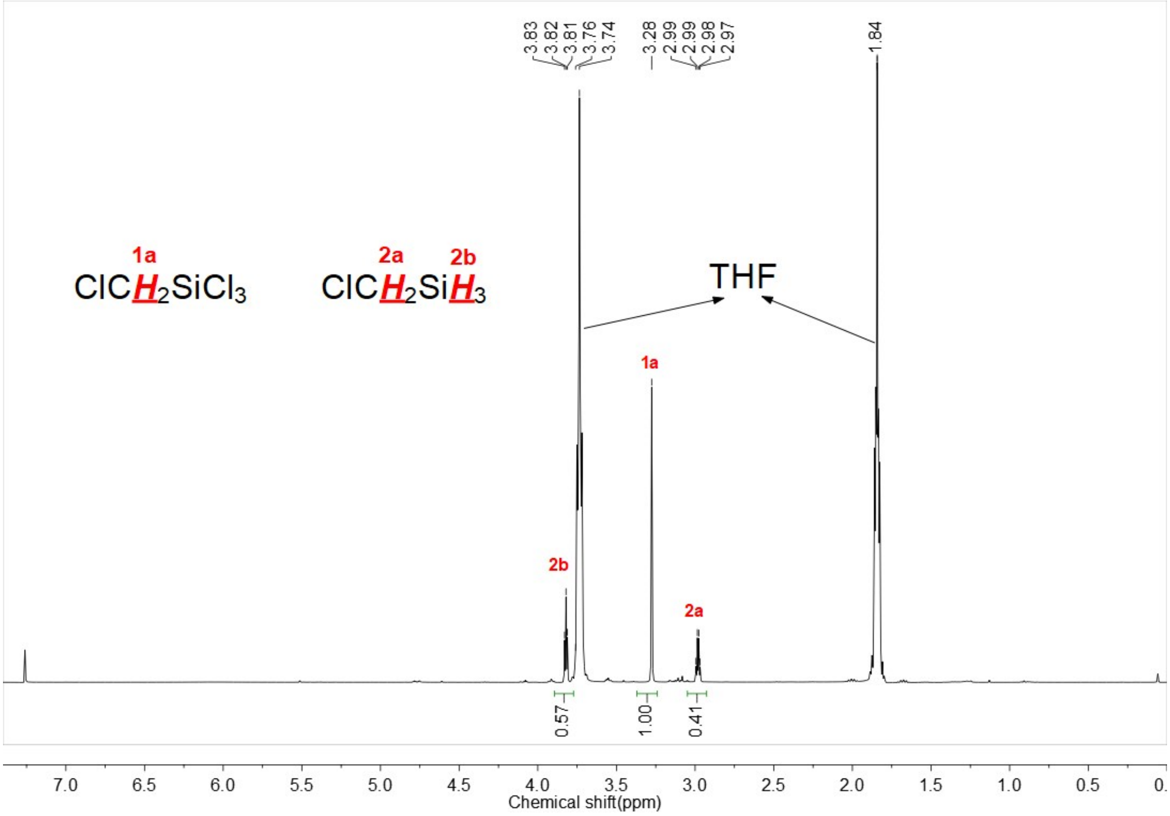


Figure 32a. Redistribution results of $ClCH_2SiH_3$ and $ClCH_2SiCl_3$ (1:2) in THF (**entry 7**)

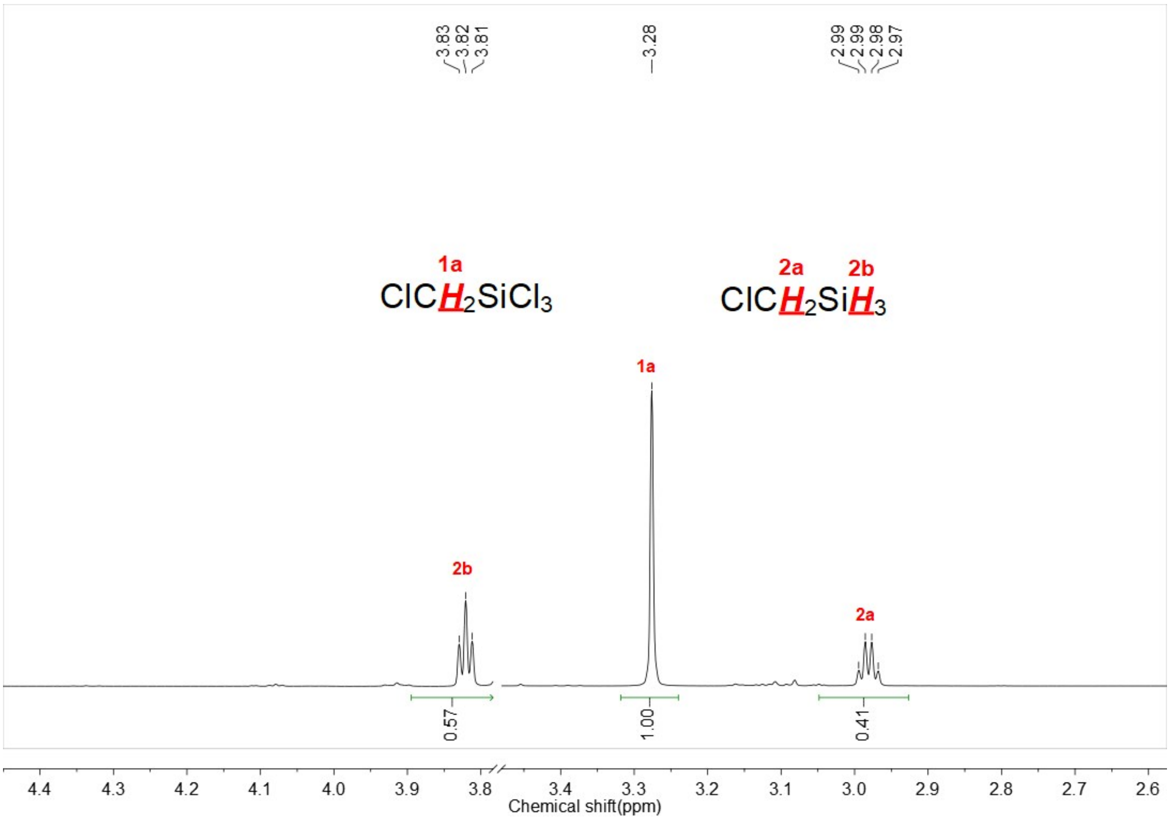


Figure 32b. Redistribution results of $ClCH_2SiH_3$ and $ClCH_2SiCl_3$ (1:2) in THF (**entry 7, zoom in**)

Redistribution results of $ClCH_2SiH_3$ and $ClCH_2SiCl_3$ (molar ratio = 1:2) in THF catalyzed by $LiAlH_4$ (3.0 mol%) (Table 2, entry 8)

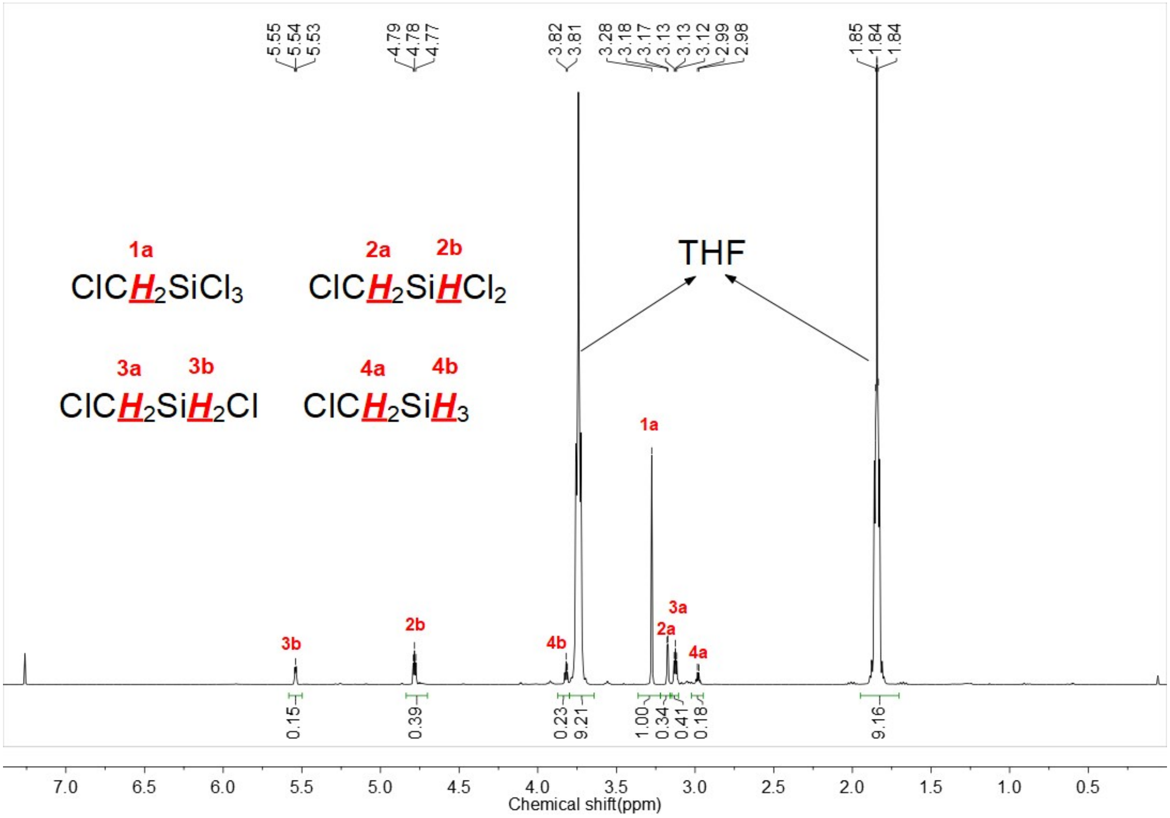


Figure 33a. Redistribution results of $ClCH_2SiH_3$ and $ClCH_2SiCl_3$ (1:2) in THF (**entry 8**)

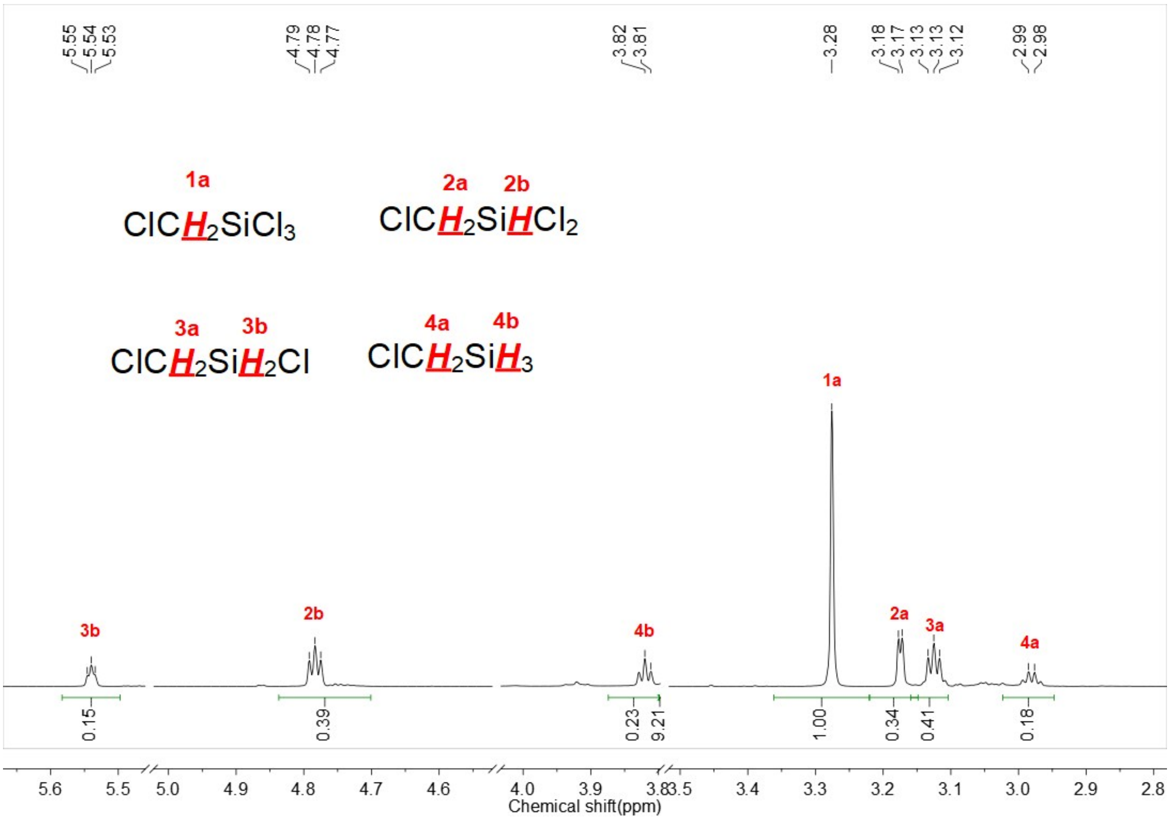


Figure 33b. Redistribution results of $ClCH_2SiH_3$ and $ClCH_2SiCl_3$ (1:2) in THF (**entry 8, zoom in**)

Redistribution results of $ClCH_2SiH_3$ and $ClCH_2SiCl_3$ (molar ratio = 1:2) in catalyzed by $NaBH_4$ in diglyme (3.0 mol%)-20 h

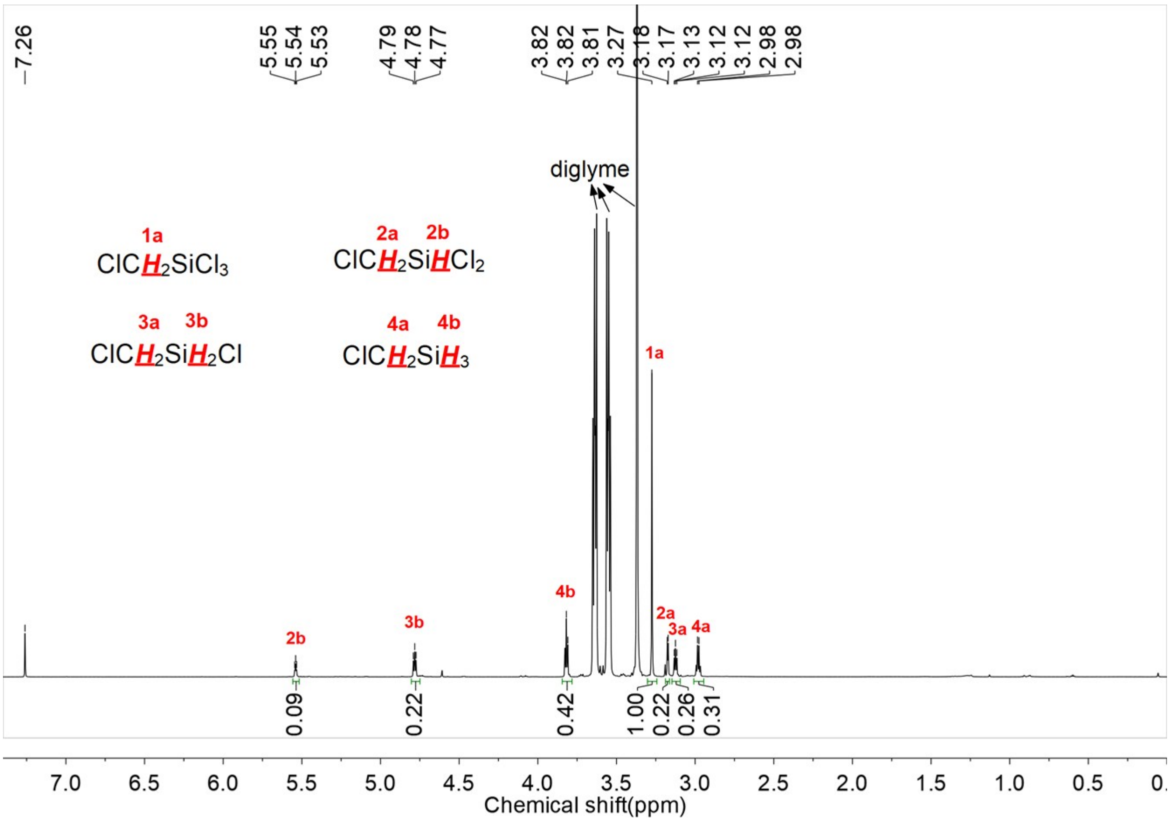


Figure 34a. Redistribution results of $ClCH_2SiH_3$ and $ClCH_2SiCl_3$ (1:2) in diglyme catalyzed by $NaBH_4$

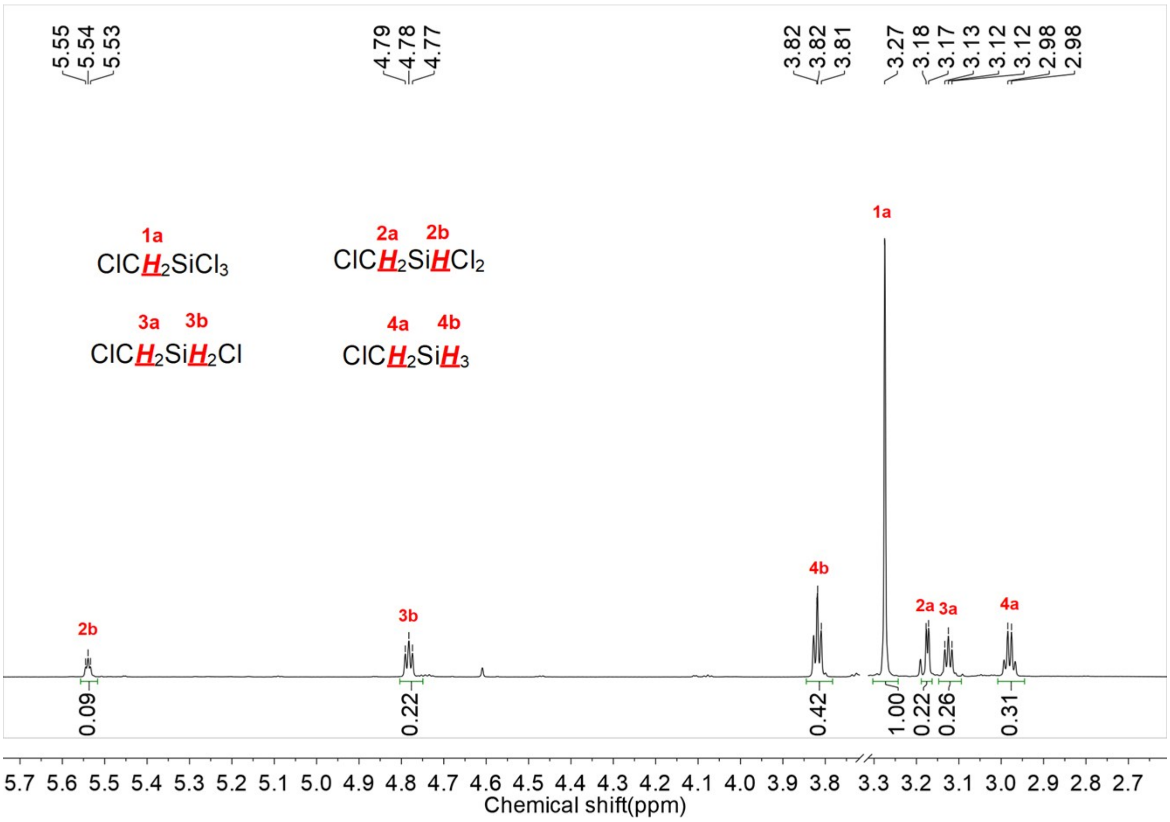


Figure 34b. Redistribution results of $ClCH_2SiH_3$ and $ClCH_2SiCl_3$ (1:2) catalyzed by $NaBH_4$ (**zoom in**)

Redistribution results of $ClCH_2SiH_3$ and $ClCH_2SiCl_3$ (molar ratio = 1:2) in catalyzed by KBH_4 in diglyme (3.0 mol%)-20 h

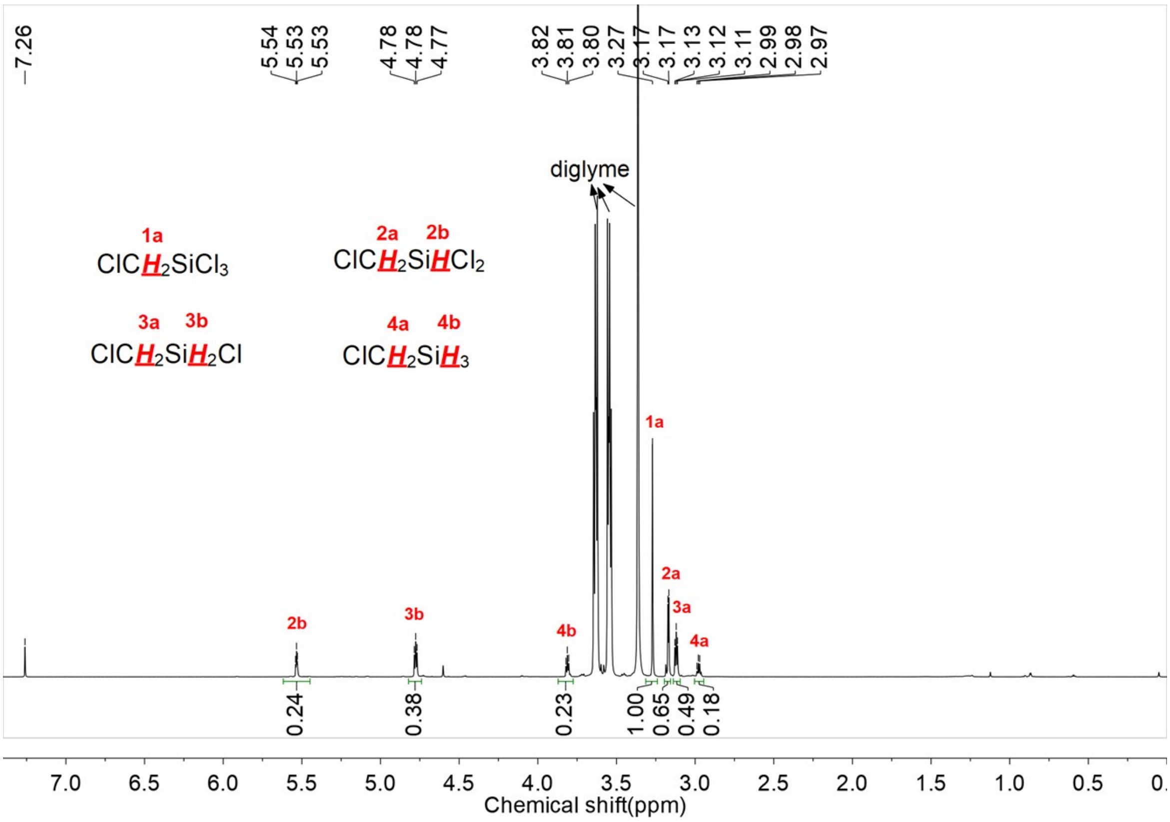


Figure 35a. Redistribution results of $ClCH_2SiH_3$ and $ClCH_2SiCl_3$ (1:2) in diglyme catalyzed by KBH_4

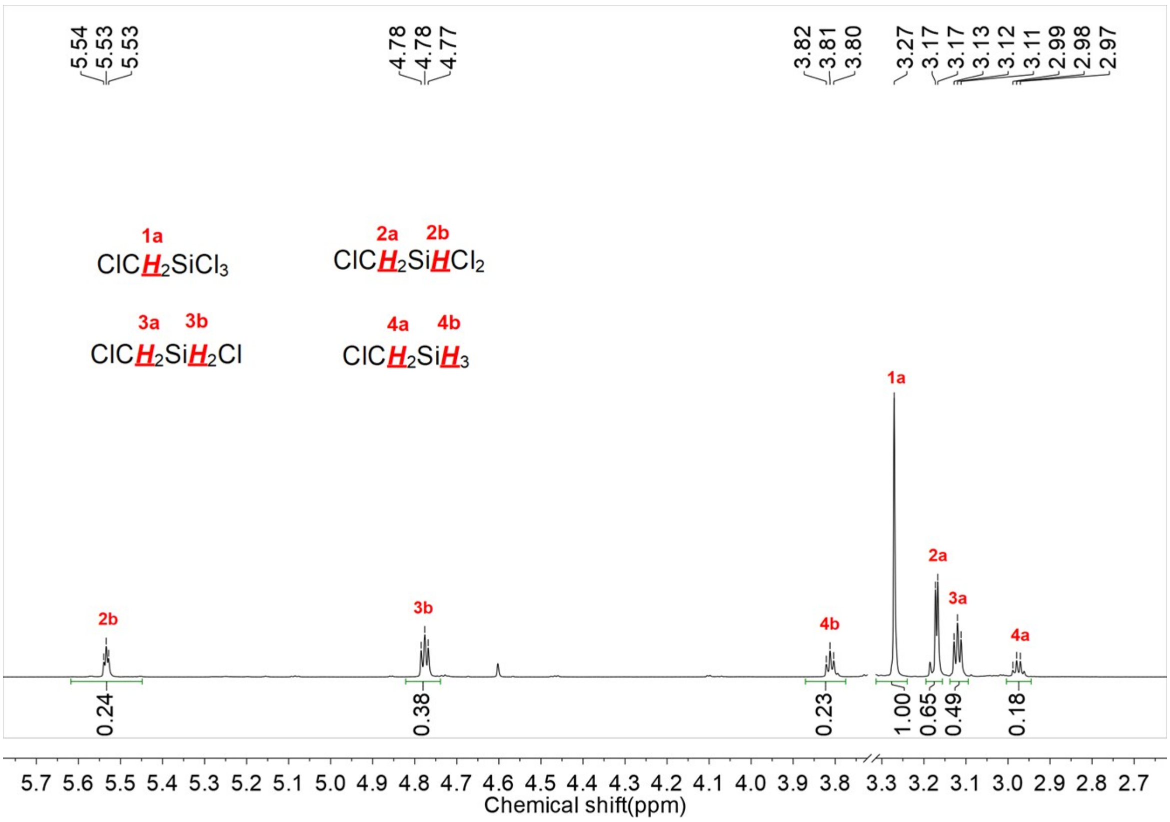


Figure 35b. Redistribution results of $ClCH_2SiH_3$ and $ClCH_2SiCl_3$ (1:2) catalyzed by KBH_4 (**zoom in**)

Redistribution results of $Cl_2CHSiMeH_2$ and $Cl_2CHSiMeCl_2$ (molar ratio = 1:1) in diglyme catalyzed by $LiBH_4$ (4.0 mol%)-11 h

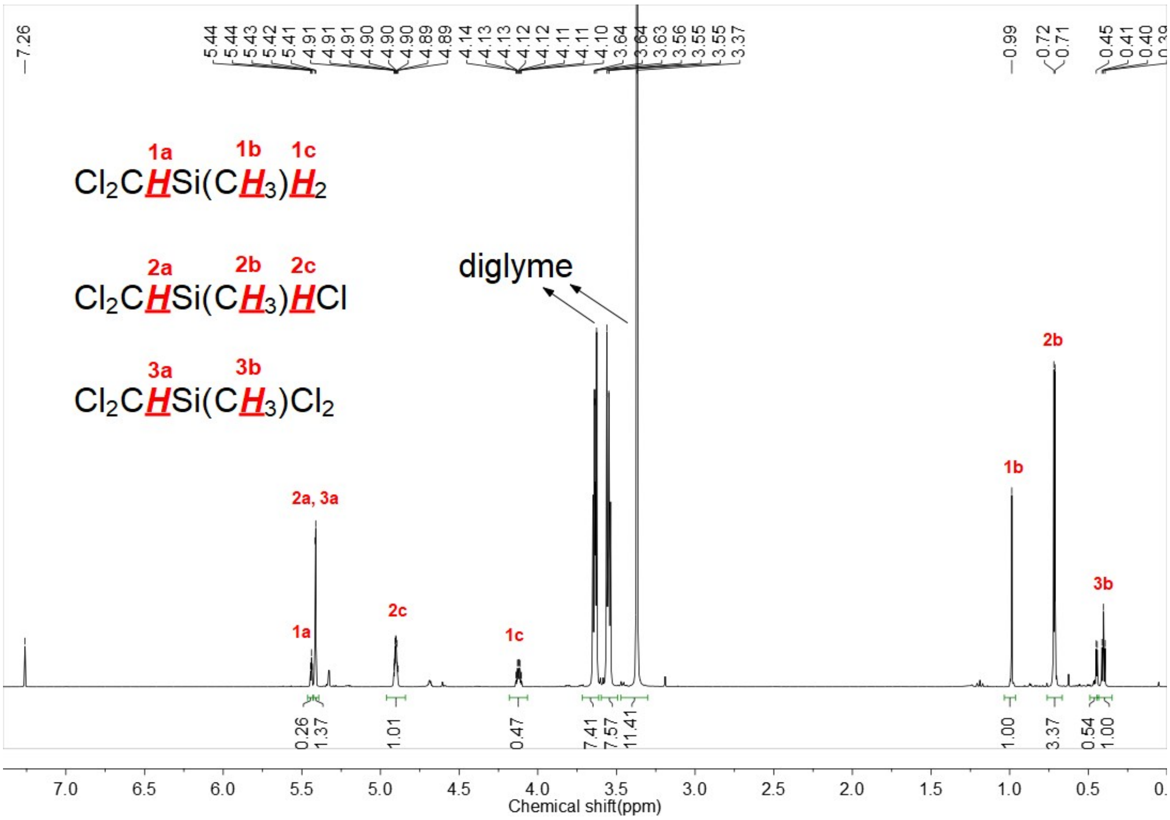


Figure 36a. Redistribution results of $Cl_2CHSiMeH_2$ and $Cl_2CHSiMeCl_2$ (1:1) in diglyme catalyzed by $LiBH_4$

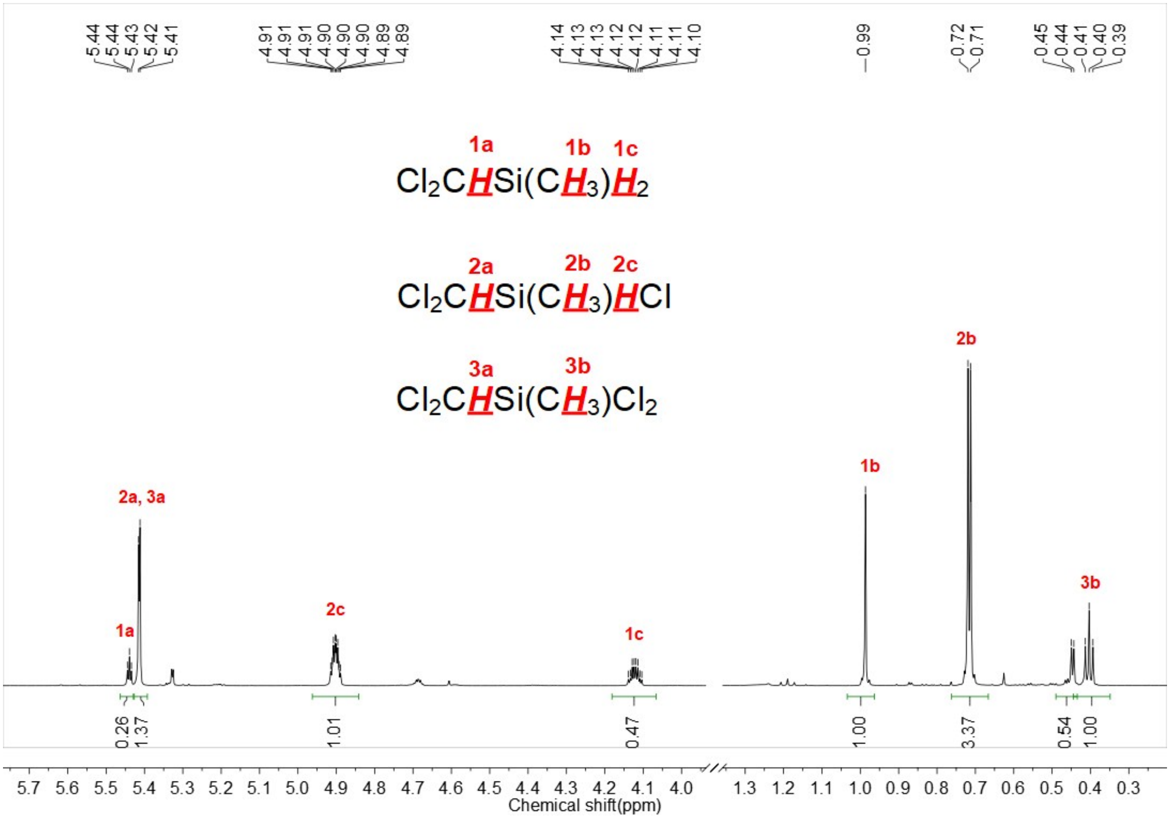


Figure 36b. Redistribution results of $Cl_2CHSiMeH_2$ and $Cl_2CHSiMeCl_2$ (1:1) (**zoom in**)

Redistribution results of $Cl_2CHSiMeH_2$ and $Cl_2CHSiMeCl_2$ (molar ratio = 1:1) in diglyme catalyzed by $NaBH_4$ (4.0 mol%)-11 h

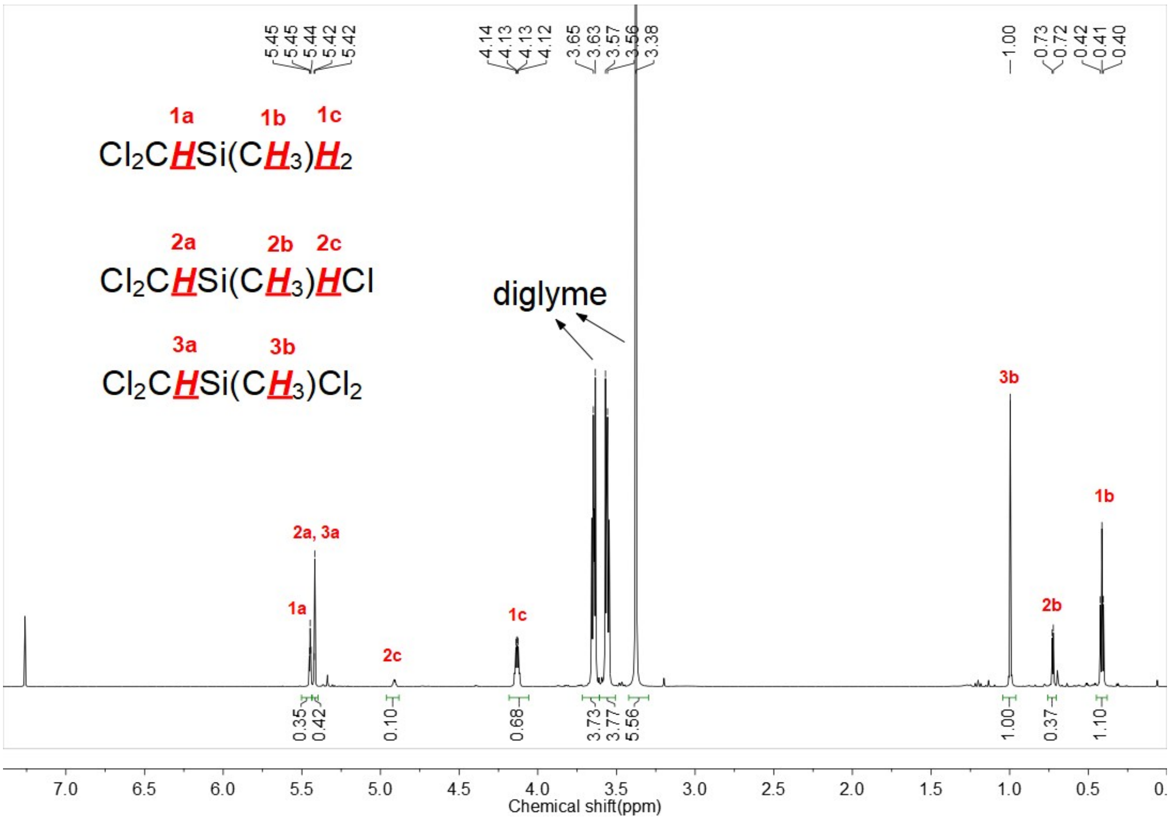


Figure 37a. Redistribution results of $Cl_2CHSiMeH_2$ and $Cl_2CHSiMeCl_2$ (1:1) catalyzed by $NaBH_4$

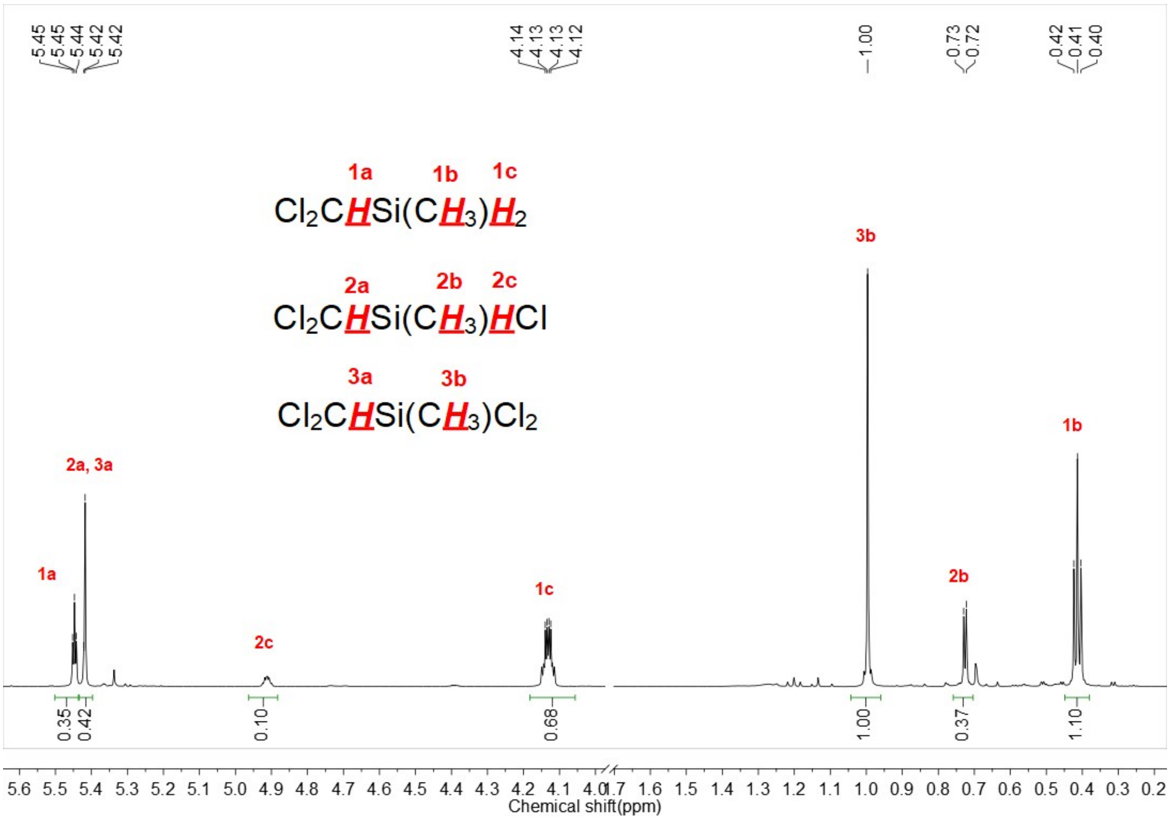


Figure 37b. Redistribution results of $Cl_2CHSiMeH_2$ and $Cl_2CHSiMeCl_2$ (1:1) (**zoom in**)

Ⅵ. Substrate scope study with $LiBH_4$/HMPA system (Table 3)

Procedure for the redistribution reaction of hydrosilane and chlorosilane in HMPA catalyzed by $LiBH_4$ (Table 3)

To a mixture of $LiBH_4$, 5 mL HMPA in a 25 mL two-necked flask was added hydrosilane and chlorosilane in sequence. The reaction mixture was stirred by magneton at room temperature and measured by ^{1}H-NMR.

Table 3 Redistribution reaction between hydrosilane and chlorosilane in HMPA catalyzed by $LiBH_4$[a]

$$R_{4-x}SiH_x + R_{4-x}SiCl_x \xrightarrow[\text{HMPA}]{LiBH_4\text{(cat.)}} R_{4-x}SiH_{x-y}Cl_y$$

Entry	$R_{4-x}SiH_x$/ $R_{4-x}SiCl_x$	Ratio	cat. (mol%)	t (h)	Product (yield)[b]
1	$ClCH_2SiH_3$/ $ClCH_2SiCl_3$	1:2	3	0.5	$ClCH_2SiHCl_2$: 75%, $ClCH_2SiH_2Cl$: 9%
2	$ClCH_2SiH_3$/ $ClCH_2SiCl_3$	2:1	3	0.5	$ClCH_2SiHCl_2$: 23% $ClCH_2SiH_2Cl$: 56%
3	$ClCH_2SiMeH_2$/ $ClCH_2SiMeCl_2$	1:1	2	0.5	$ClCH_2SiMeHCl$: 74% (62%[c])
4	$Cl_2CHSiMeH_2$/ $Cl_2CHSiMeCl_2$	1:1	4	0.5	$Cl_2CHSiMeHCl$: 85% (72%[c])
5	Et_2SiH_2/ Et_2SiCl_2	1:1	4	8	Et_2SiHCl:72%
6	$PhSiH_3$/ $PhSiCl_3$	1:2	3	2	$PhSiHCl_2$: 61% $PhSiH_2Cl$: 10%
7	$PhSiH_3$/ $PhSiCl_3$	2:1	3	2	$PhSiHCl_2$:12% $PhSiH_2Cl$: 61%
8	$PhMeSiH_2$/ $PhMeSiCl_2$	1:1	4	2	PhMeSiHCl: 66%
9	Ph_2SiH_2/ Ph_2SiCl_2	1:1	4	8	Ph_2SiHCl: 63%

[a] Reaction conditions: [entry 3-5, 8, 9] hydrosilane (0.01 mol), chlorosilane (0.01 mol); [entry 1, 6] hydrosilane (0.01 mol), chlorosilane (0.02 mol); [entry 2, 7] hydrosilane (0.02 mol), chlorosilane (0.01 mol); HMPA (5 mL), room temperature; [b] yields determined by ^{1}H NMR; [c] Isolated yield in a larger scale reaction. Reaction conditions: hydrosilane (0.2 mol), chlorosilane (0.2 mol), HMPA (10 mL), $LiBH_4$ (2 mol %), room temperature.

Redistribution results of $ClCH_2SiH_3$ and $ClCH_2SiCl_3$ (molar ratio = 1:2) in HMPA catalyzed by $LiBH_4$ (3.0 mol%) (Table 3, entry 1)

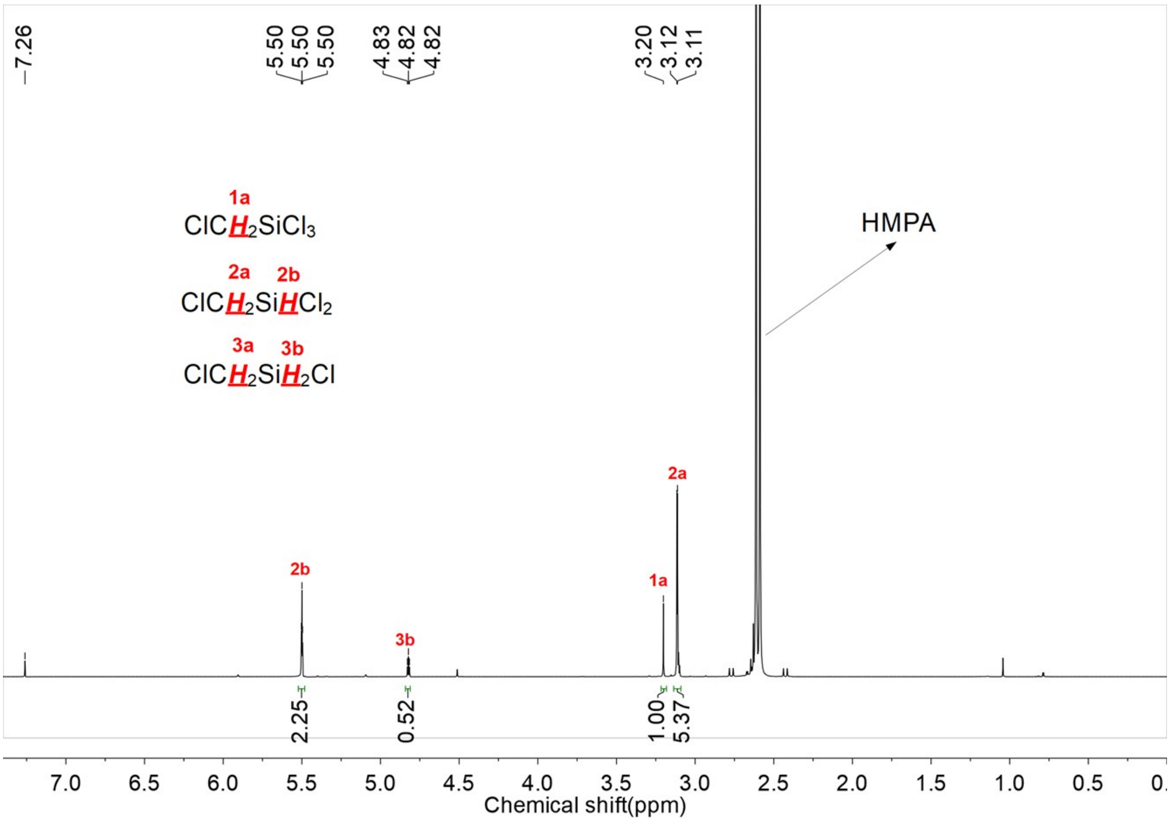


Figure 38a. Redistribution results of $ClCH_2SiH_3$ and $ClCH_2SiCl_3$ (1:2) in HMPA (**Table 3, entry 1**)

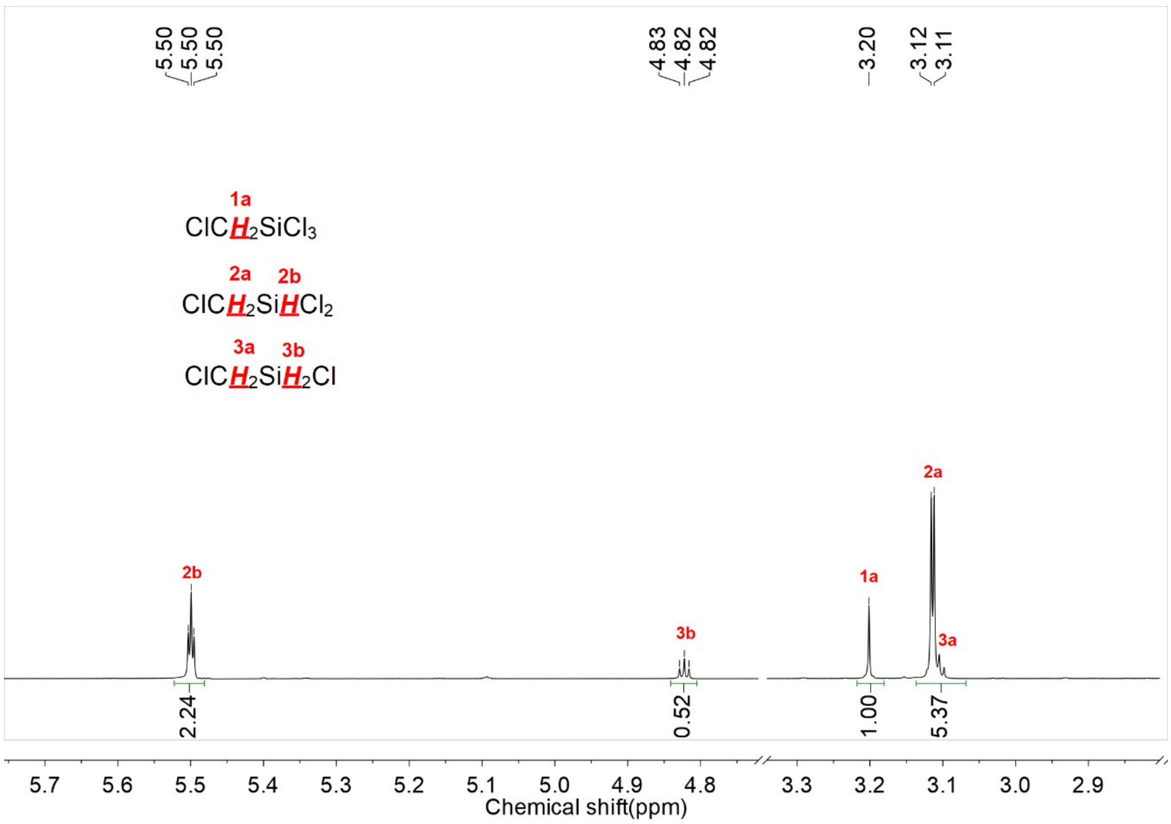


Figure 38b. Redistribution results of $ClCH_2SiH_3$ and $ClCH_2SiCl_3$ (1:2) in THF (**entry 1, zoom in**)

Redistribution results of $ClCH_2SiH_3$ and $ClCH_2SiCl_3$ (molar ratio = 2:1) in HMPA catalyzed by $LiBH_4$ (3.0 mol%) (Table 3, entry 2)

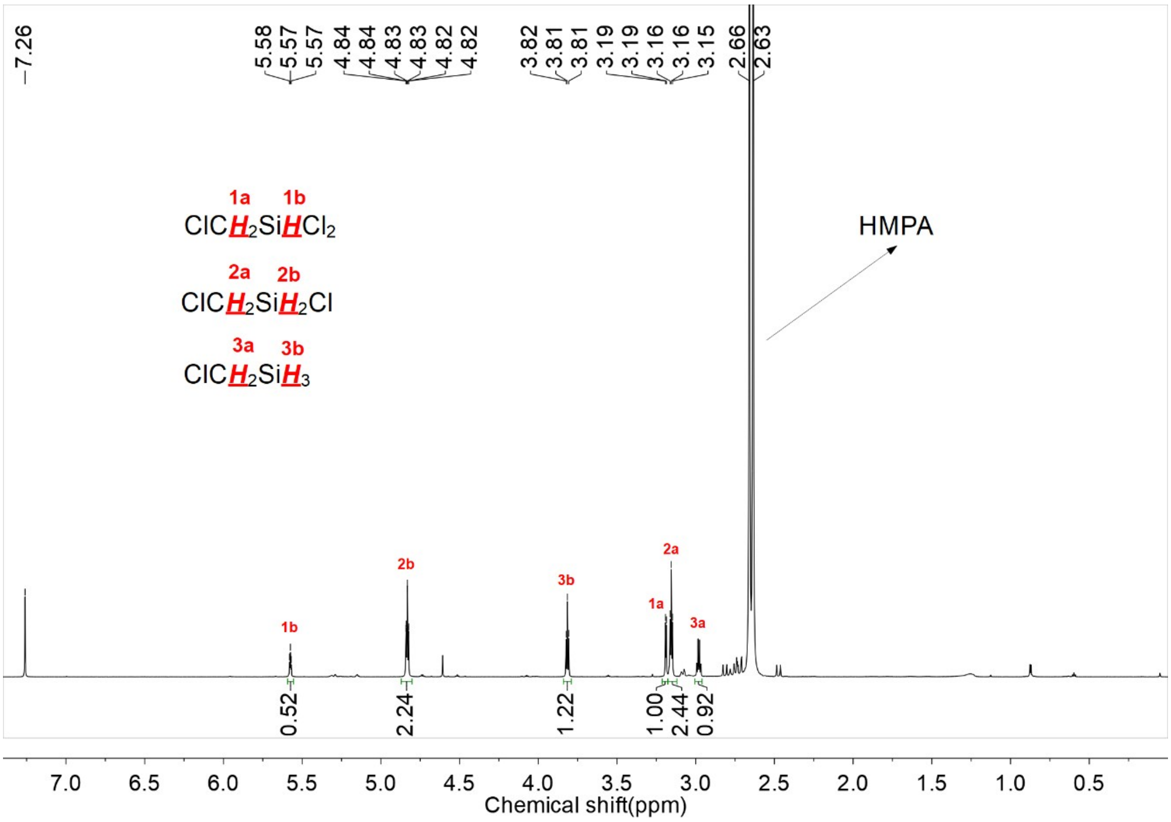


Figure 39a. Redistribution results of $ClCH_2SiH_3$ and $ClCH_2SiCl_3$ (2:1) in HMPA (**Table 3, entry 2**)

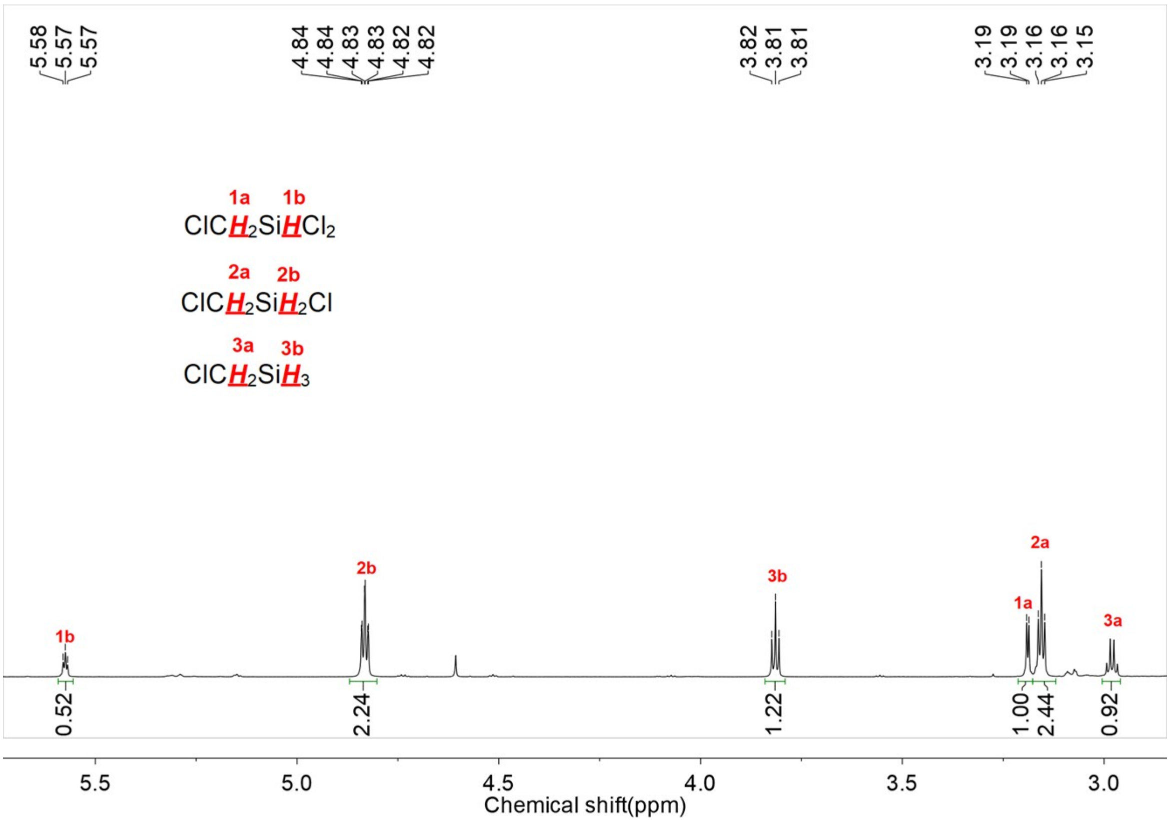


Figure 39b. Redistribution results of $ClCH_2SiH_3$ and $ClCH_2SiCl_3$ (2:1) in HMPA (**entry 2, zoom in**)

Redistribution results of $ClCH_2SiMeH_2$ and $ClCH_2SiMeCl_2$ (molar ratio = 1:1) in HMPA catalyzed by $LiBH_4$ (2.0 mol%) (Table 3, entry 3)

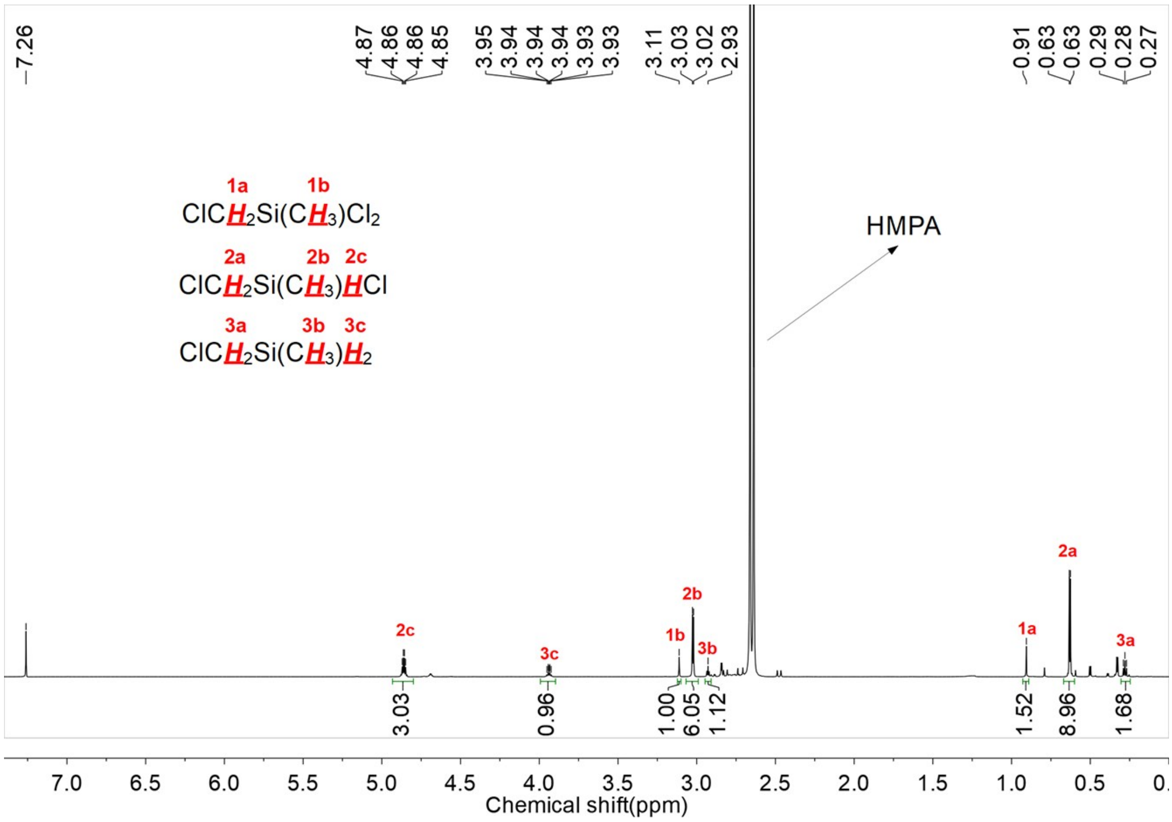


Figure 40a. Redistribution results of $ClCH_2SiMeH_2$ and $ClCH_2SiMeCl_2$ (1:1) in HMPA (**Table 3, entry 3**)

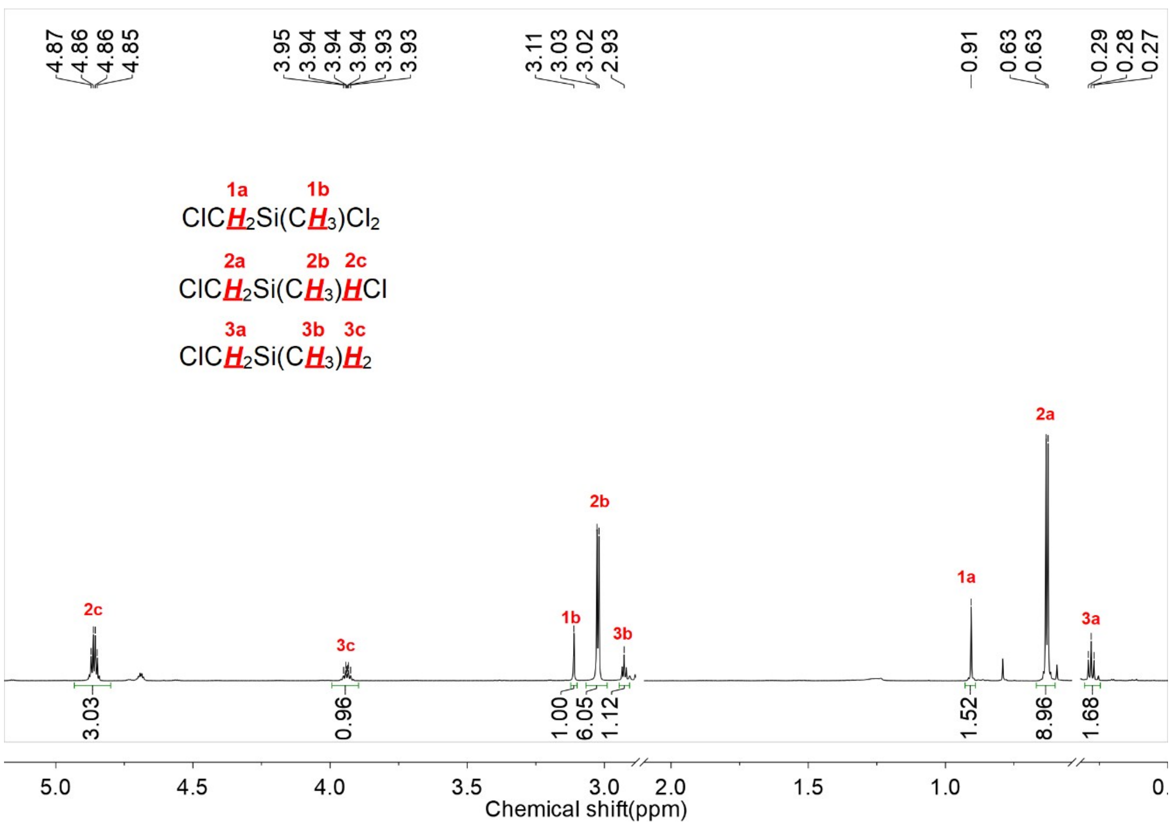


Figure 40b. Redistribution results of $ClCH_2SiMeH_2$ and $ClCH_2SiMeCl_2$ (1:1) in HMPA (**entry 3, zoom in**)

Redistribution results of $Cl_2CHSiMeH_2$ and $Cl_2CHSiMeCl_2$ (molar ratio = 1:1) in HMPA catalyzed by $LiBH_4$ (4.0 mol%) (Table 3, entry 4)

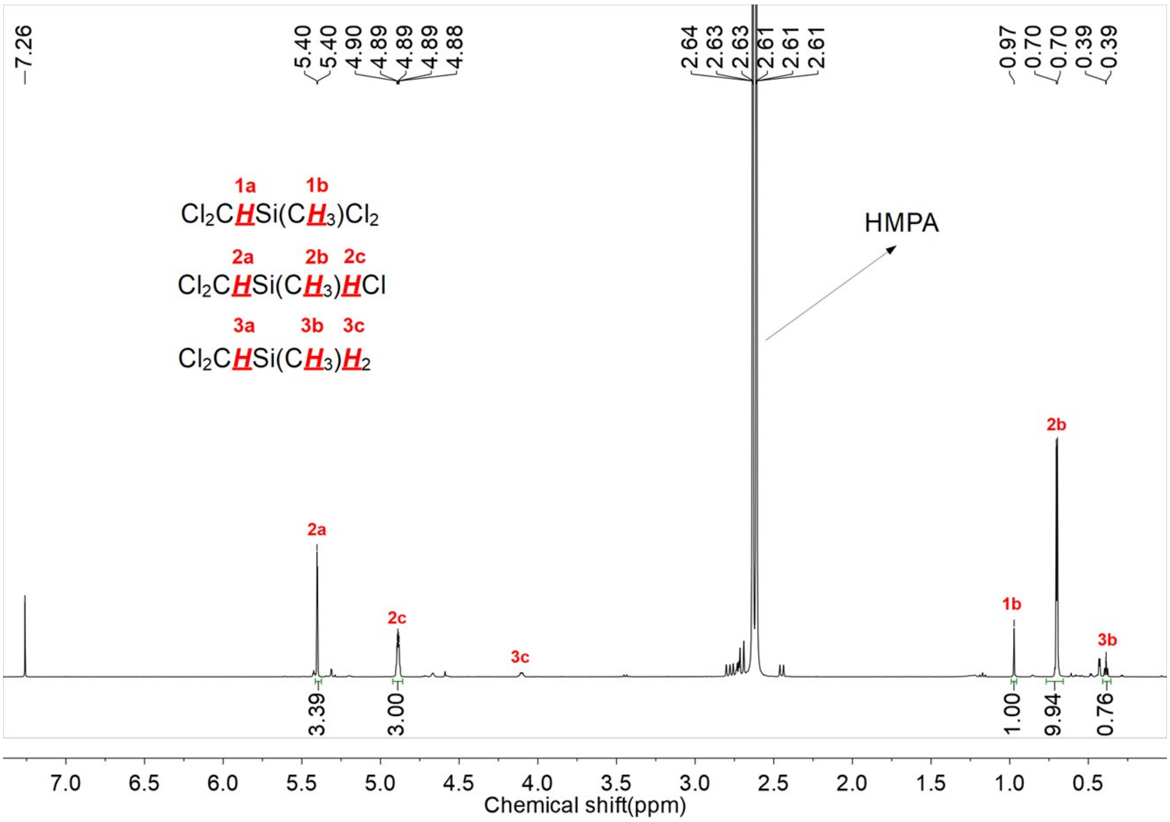


Figure 41a. Redistribution results of $Cl_2CHSiMeH_2$ and $Cl_2CHSiMeCl_2$ (1:1) in HMPA (**Table 3, entry 4**)

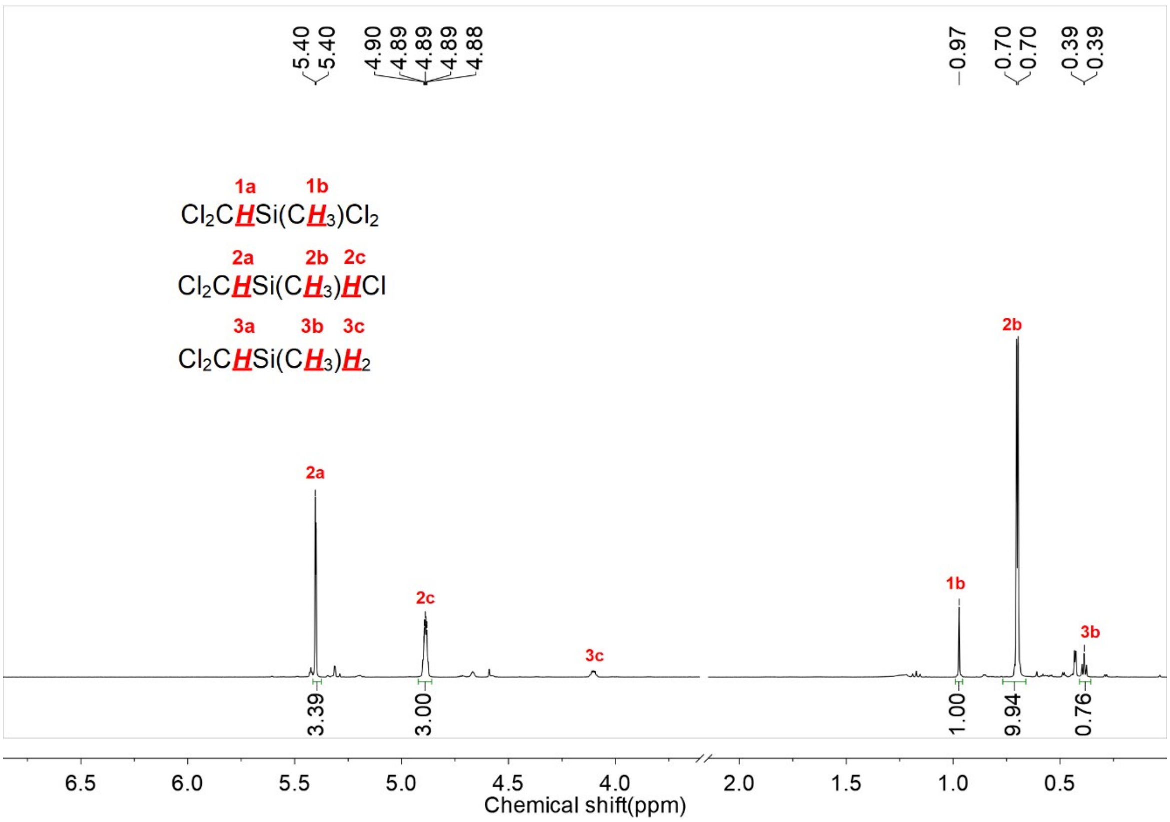


Figure 41b. Redistribution results of $Cl_2CHSiMeH_2$ and $Cl_2CHSiMeCl_2$ (1:1) in HMPA (**entry 4, zoom in**)

Redistribution results of Et_2SiH_2 and Et_2SiCl_2 (molar ratio = 1:1) in HMPA catalyzed by $LiBH_4$ (4.0 mol%) (Table 3, entry 5)

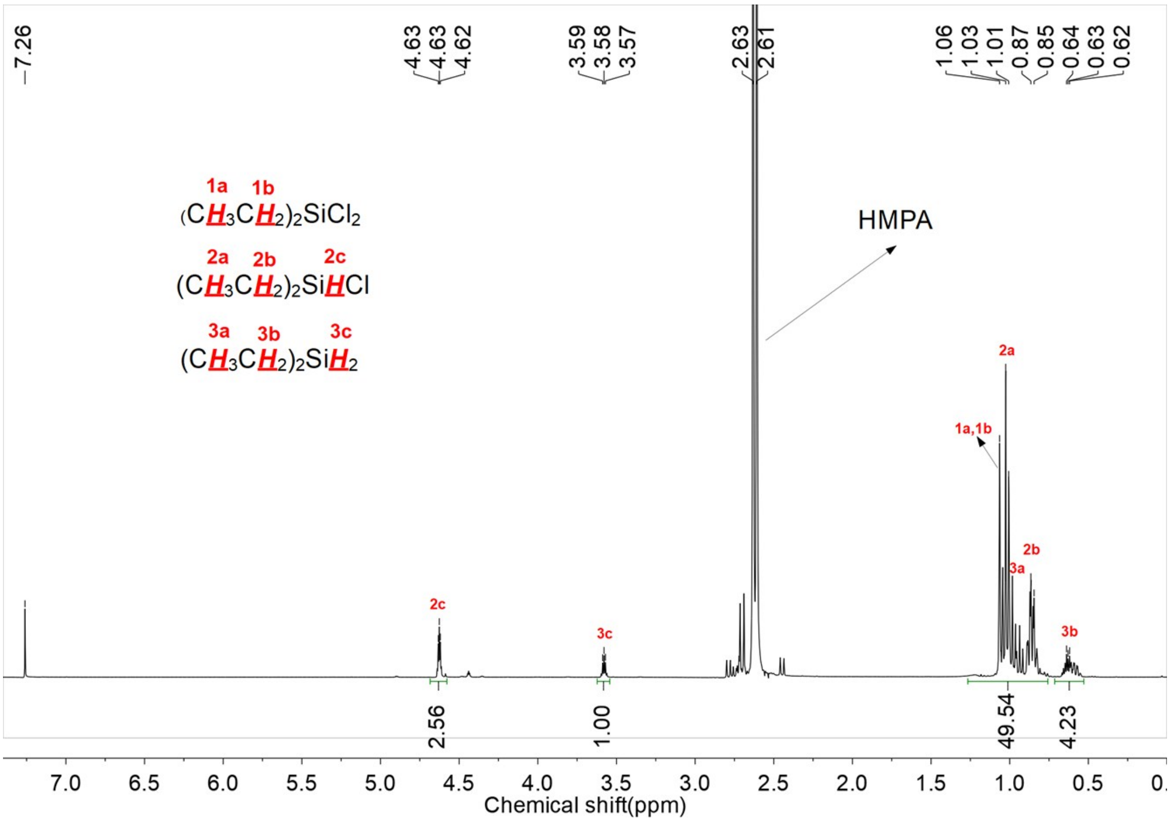


Figure 42a. Redistribution results of Et_2SiH_2 and Et_2SiCl_2 (1:1) in HMPA (**Table 3, entry 5**)

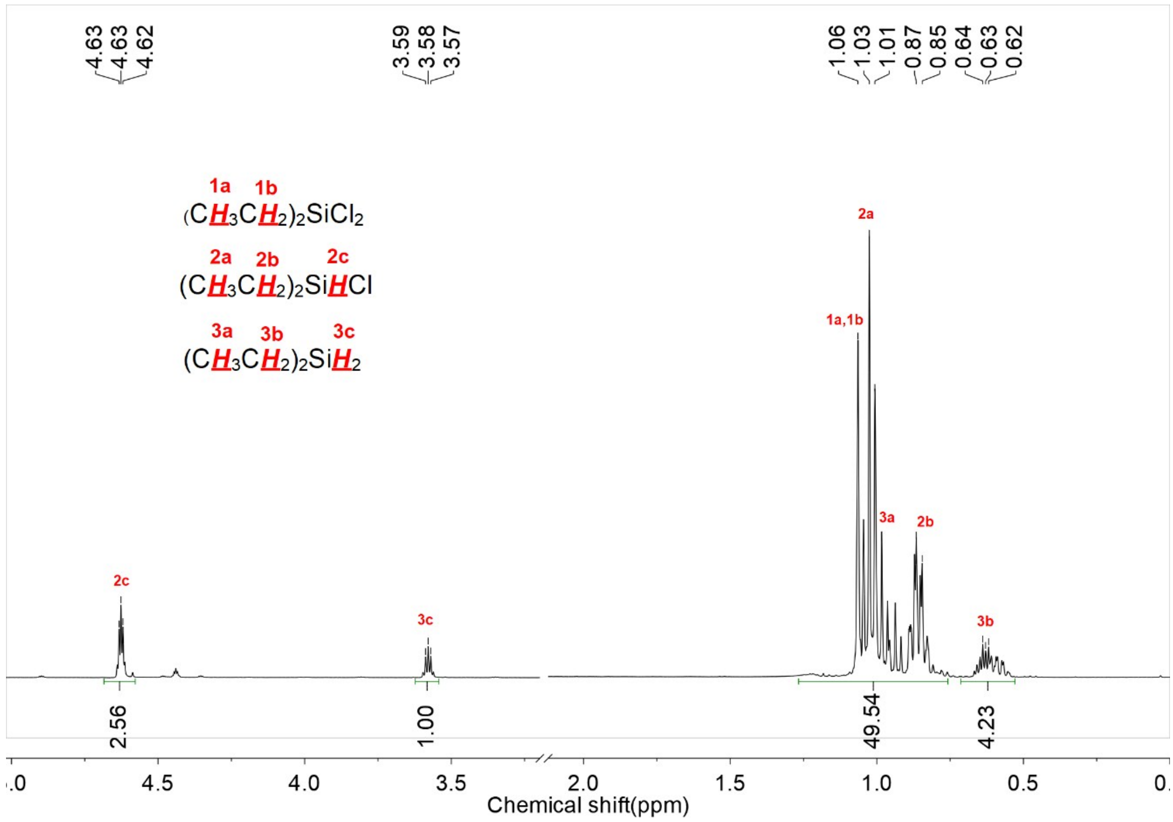


Figure 42b. Redistribution results of Et_2SiH_2 and Et_2SiCl_2 (1:1) in HMPA (**entry 5, zoom in**)

Redistribution results of $PhSiH_3$ and $PhSiCl_3$ (molar ratio = 1:2) in HMPA catalyzed by $LiBH_4$ (3.0 mol%) (Table 3, entry 6)

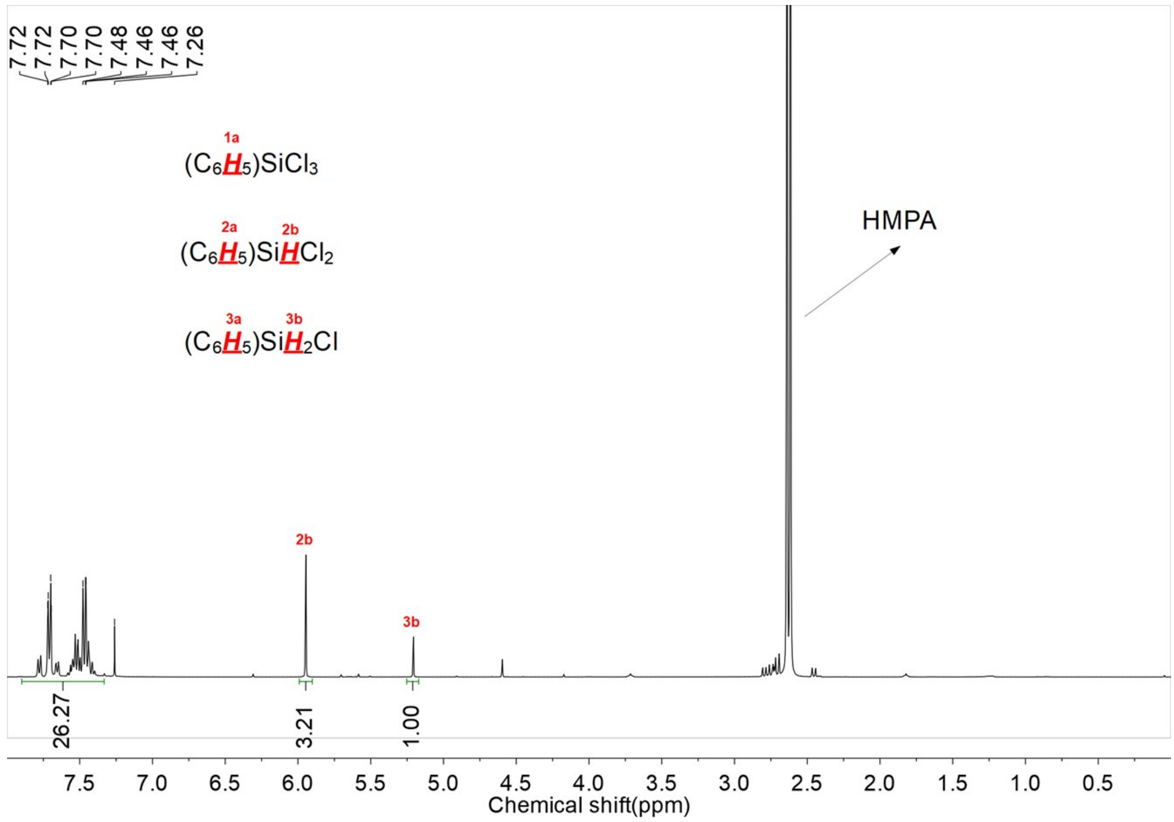


Figure 43a. Redistribution results of $PhSiH_3$ and $PhSiCl_3$ (1:2) in HMPA (**Table 3, entry 6**)

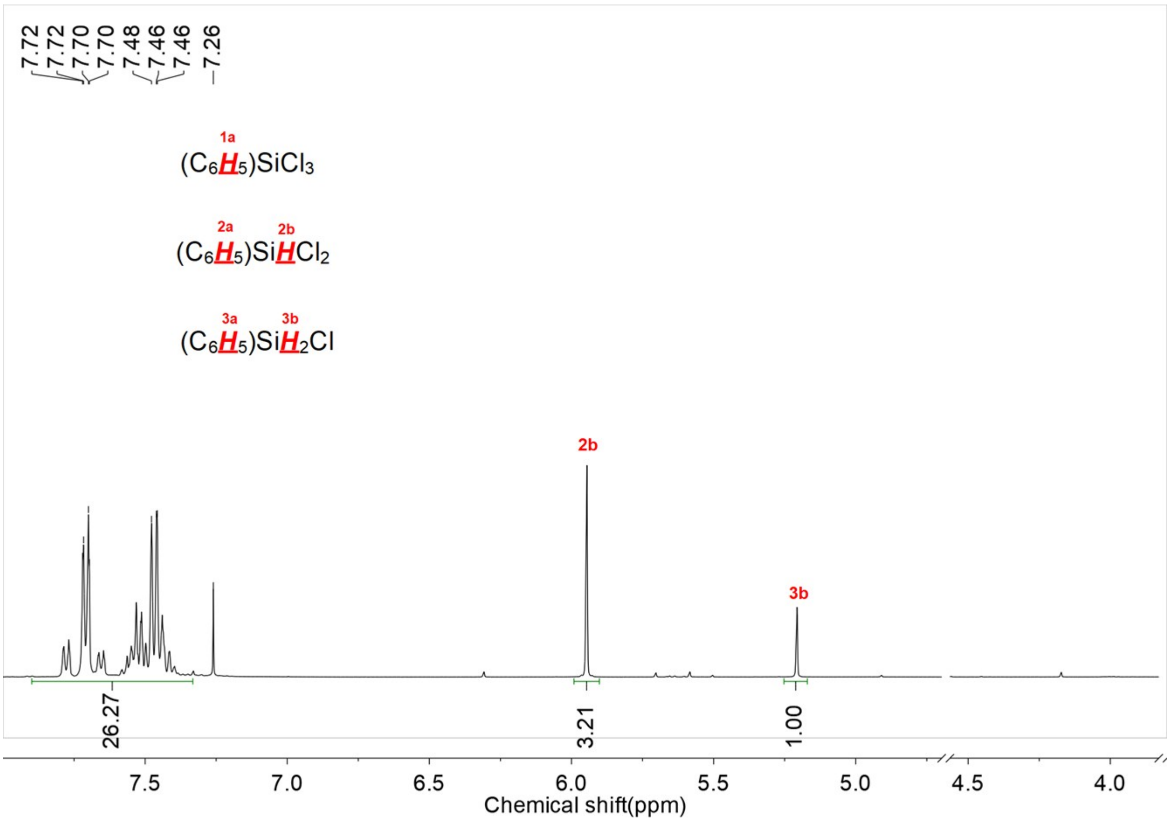


Figure 43b. Redistribution results of $PhSiH_3$ and $PhSiCl_3$ (1:2) in HMPA (**entry 6, zoom in**)

Redistribution results of $PhSiH_3$ and $PhSiCl_3$ (molar ratio = 2:1) in HMPA catalyzed by $LiBH_4$ (3.0 mol%) (Table 3, entry 7)

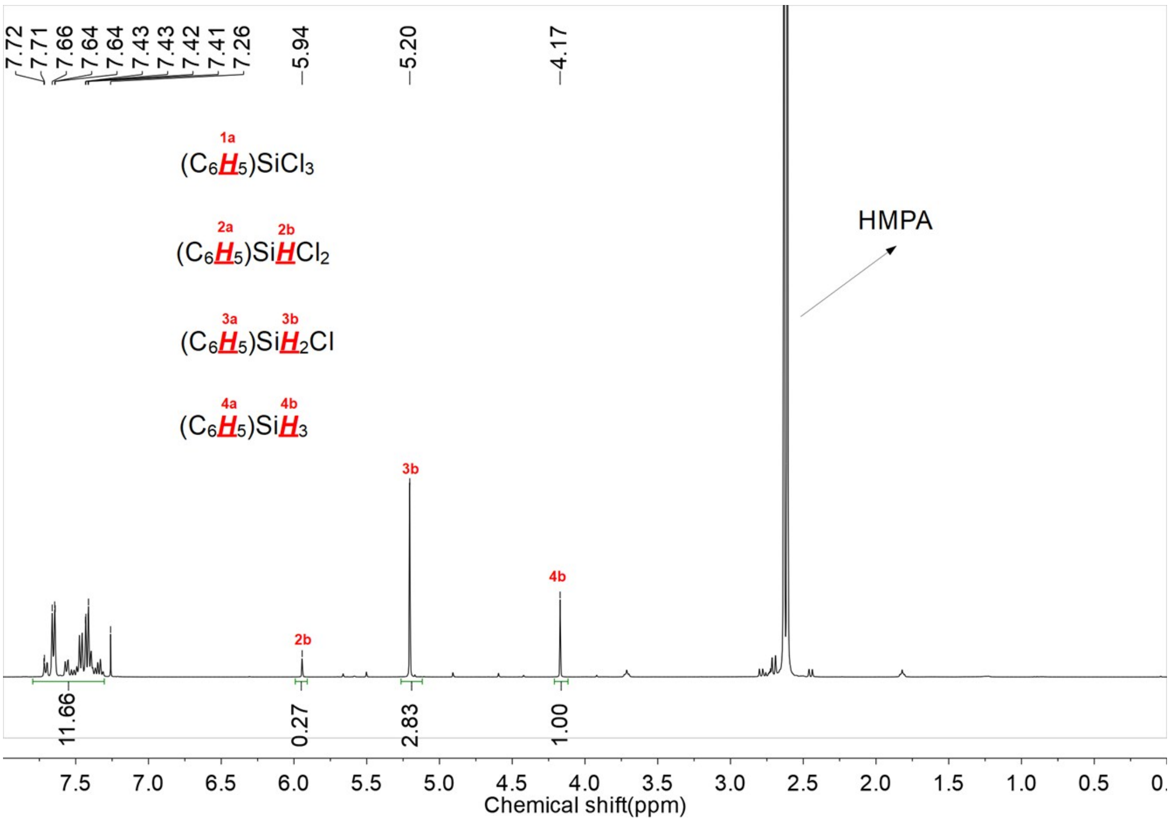


Figure 44a. Redistribution results of $PhSiH_3$ and $PhSiCl_3$ (2:1) in HMPA (**Table 3, entry 7**)

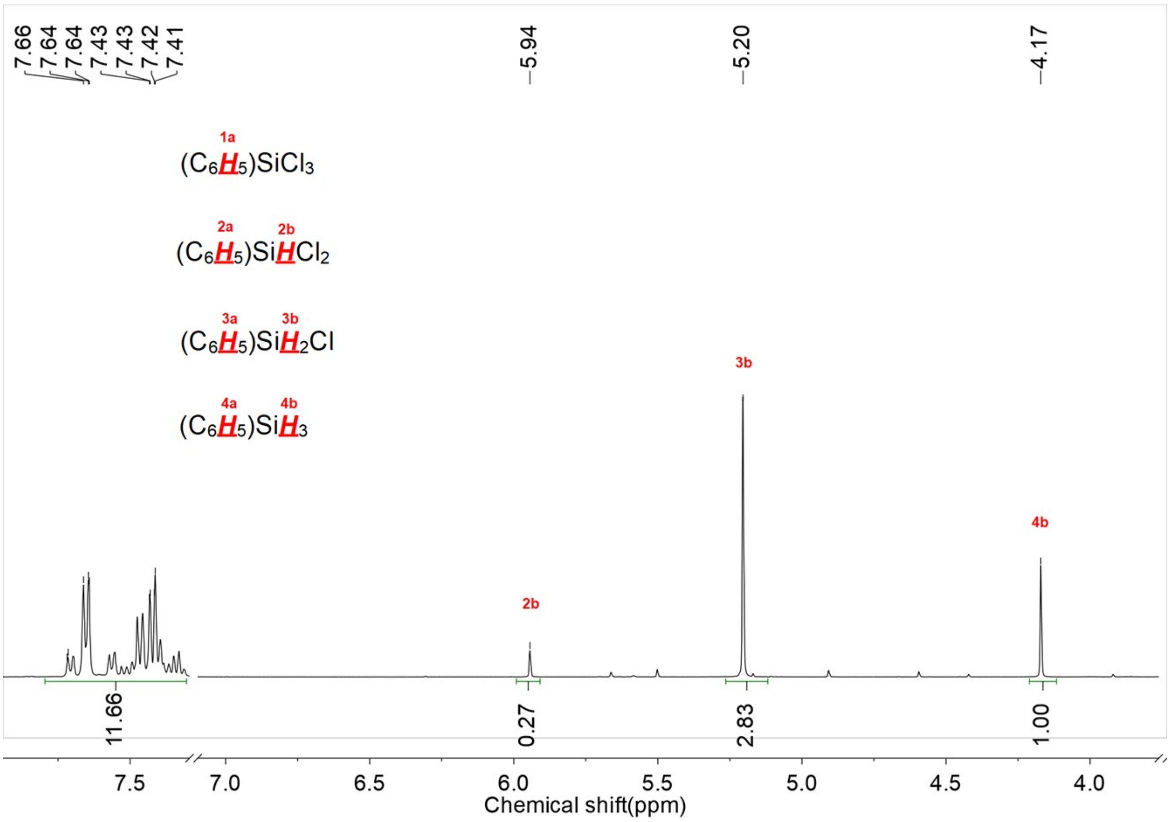


Figure 44b. Redistribution results of $PhSiH_3$ and $PhSiCl_3$ (2:1) in HMPA (**entry 7, zoom in**)

Redistribution results of $PhMeSiH_2$ and $PhMeSiCl_2$ (molar ratio = 1:1) in HMPA catalyzed by $LiBH_4$ (4.0 mol%) (Table 3, entry 8)

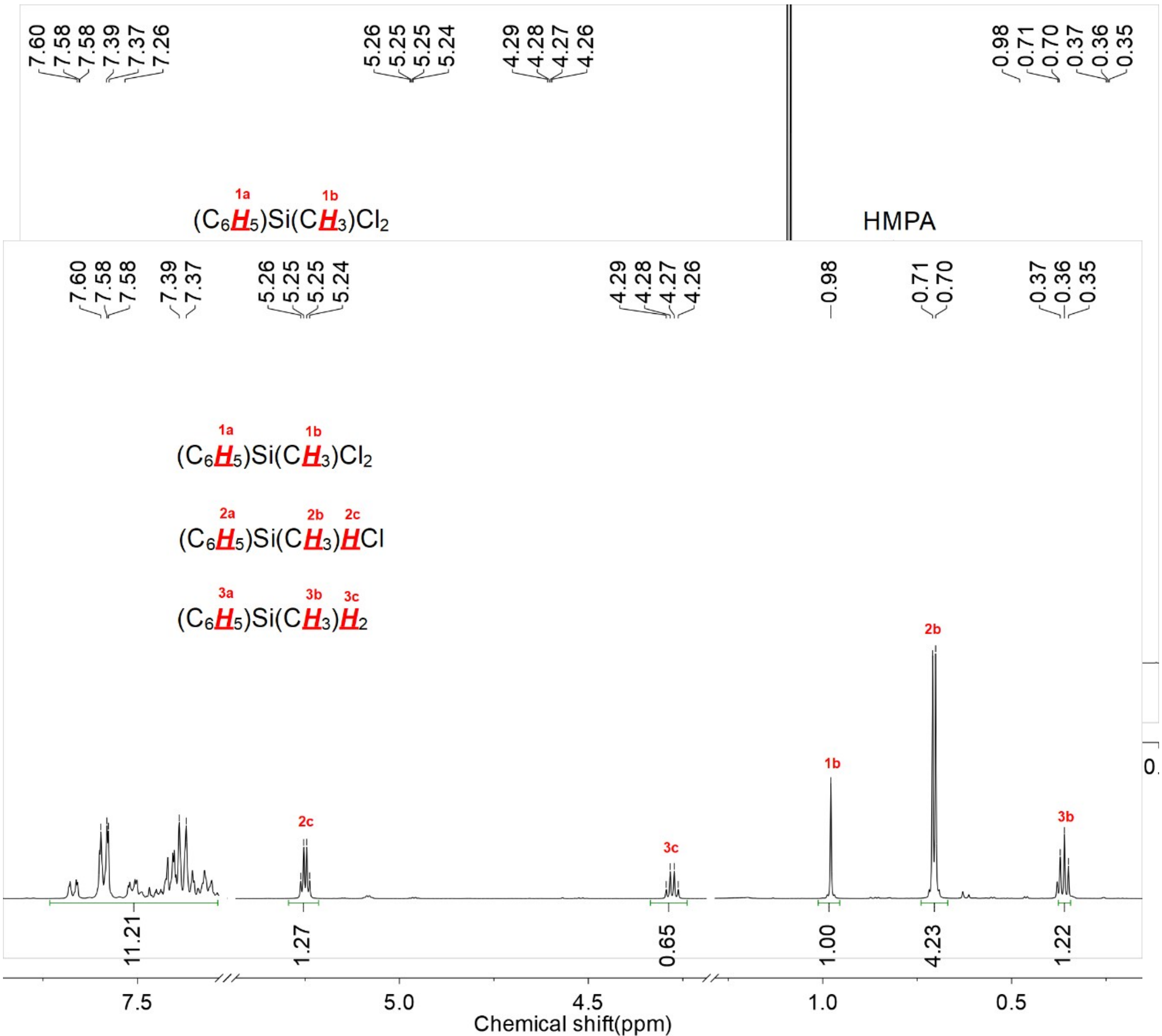


Figure 45a. Redistribution results of $PhSiMeH_2$ and $PhSiMeCl_2$ (1:1) in HMPA (**Table 3, entry 8**)

Figure 45b. Redistribution results of $PhSiMeH_2$ and $PhSiMeCl_2$ (1:1) in HMPA (**entry 8, zoom in**)

Redistribution results of Ph_2SiH_2 and Ph_2SiCl_2 (molar ratio = 1:1) in HMPA catalyzed by $LiBH_4$ (4.0 mol%) (Table 3, entry 9)

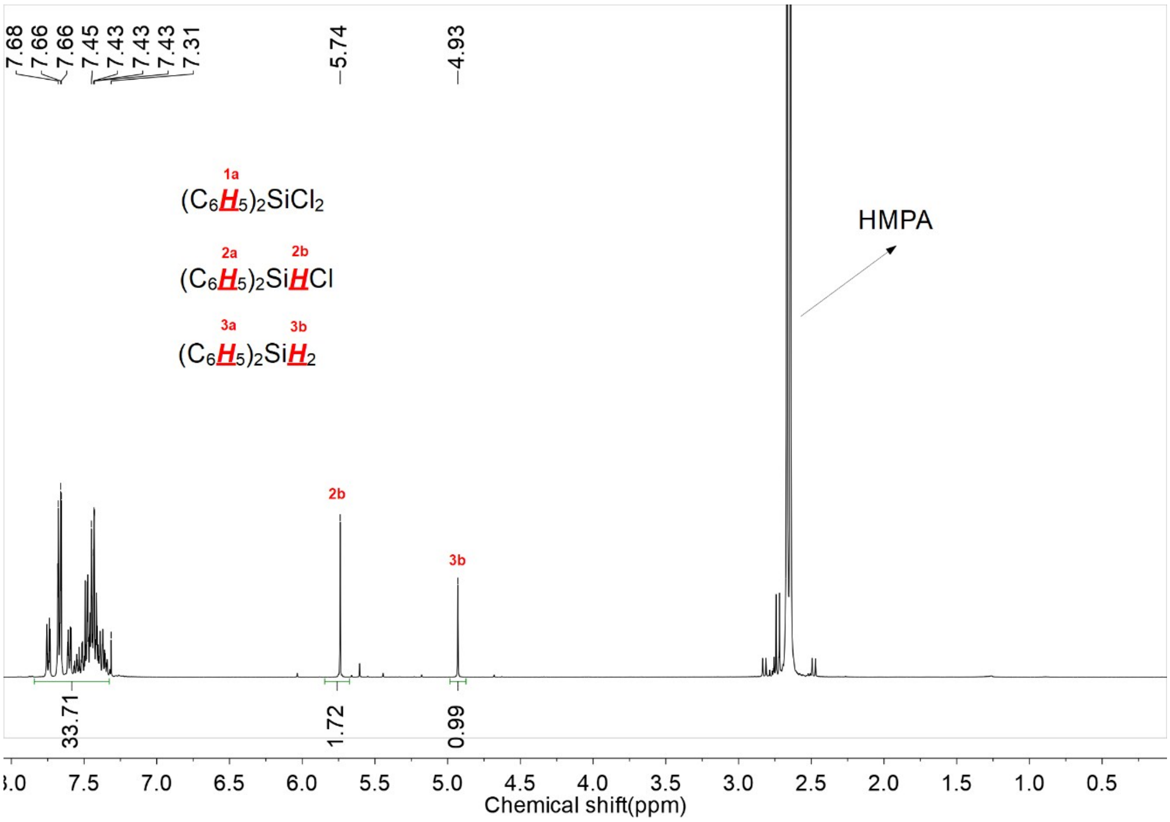


Figure 46a. Redistribution results of Ph_2SiH_2 and Ph_2SiCl_2 (1:1) in HMPA (**Table 3, entry 9**)

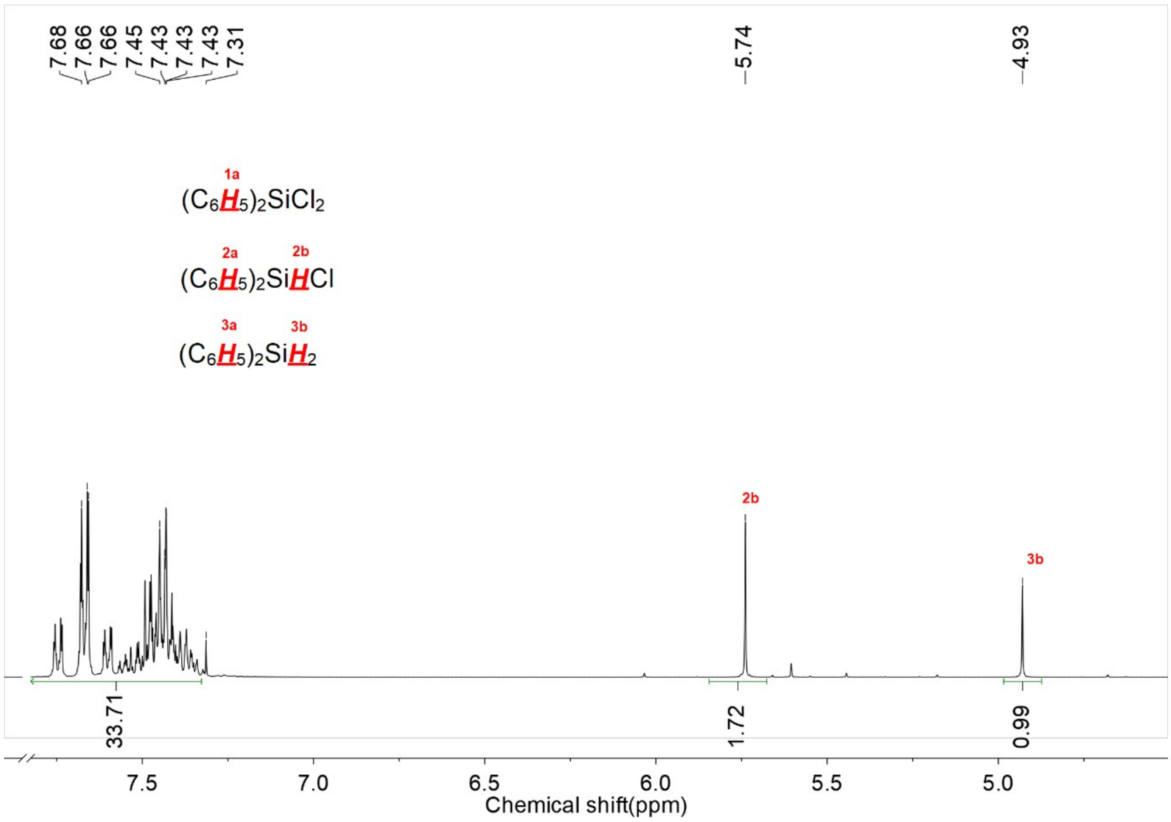


Figure 46b. Redistribution results of Ph_2SiH_2 and Ph_2SiCl_2 (1:1) in HMPA (**entry 9, zoom in**)

Ⅶ. Control experiments of redistribution reaction of $ClCH_2SiH_3$/ $ClCH_2SiCl_3$ (Table 4)

Procedure for the redistribution reaction of hydrosilane and chlorosilane in THF catalyzed by different catalysts (Table 4)

To a mixture of catalyst, 5 mL THF in a 25 mL two-necked flask was added hydrosilane and chlorosilane in sequence. The reaction mixture was stirred by magneton at room temperature and measured by ^{1}H-NMR.

Procedure for the reduction reaction of $ClCH_2SiCl_3$ in THF catalyzed by $LiBH_4$

In a 25 mL two-necked flask was added 5 mL THF, 0.03 mol $LiBH_4$, and the solution was measured by ^{11}B NMR in d8-THF (Figure 51a). Then 0.01 mol $ClCH_2SiCl_3$ was added to the solution dropwise. The reaction mixture was stirred by magneton for 1 hour at room temperature and measured by ^{11}B-NMR in d8-THF (Figure 51b). The peak of BH_3·THF [^{11}B NMR (128 MHz) δ -0.40 (q, J = 105.8 Hz)] was found according to NMR data previously reported[7].

Table 4 Control experiments of redistribution reaction of $ClCH_2SiH_3$/$ClCH_2SiCl_3$[a]

$$ClCH_2SiH_3 + ClCH_2SiCl_3 \xrightarrow[\text{RT,THF}]{\text{catalyst}} ClCH_2SiH_2Cl + ClCH_2SiHCl_2$$

Entry	Catalyst	t(h)	Product (yield)[b]
1	BH_3	20	No reaction
2	LiCl	5	$ClCH_2SiHCl_2$: 40%, $ClCH_2SiH_2Cl$: 23%
3	BH_3, LiCl	5	$ClCH_2SiHCl_2$: 62%, $ClCH_2SiH_2Cl$: 18%
4	$LiBH_4$	5	$ClCH_2SiHCl_2$: 62%, $ClCH_2SiH_2Cl$: 18%

[a] Reaction conditions: $ClCH_2SiH_3$ (0.01 mol), $ClCH_2SiCl_3$ (0.02 mol), catalyst (3.0 mol/%), THF (5 mL), room temperature; [b] yields were determined by ^{1}H NMR.

Redistribution results of $ClCH_2SiH_3$ and $ClCH_2SiCl_3$ (molar ratio = 1:2) in THF catalyzed by BH_3 (3.0 mol%)-20 h (Table 4, entry 1)

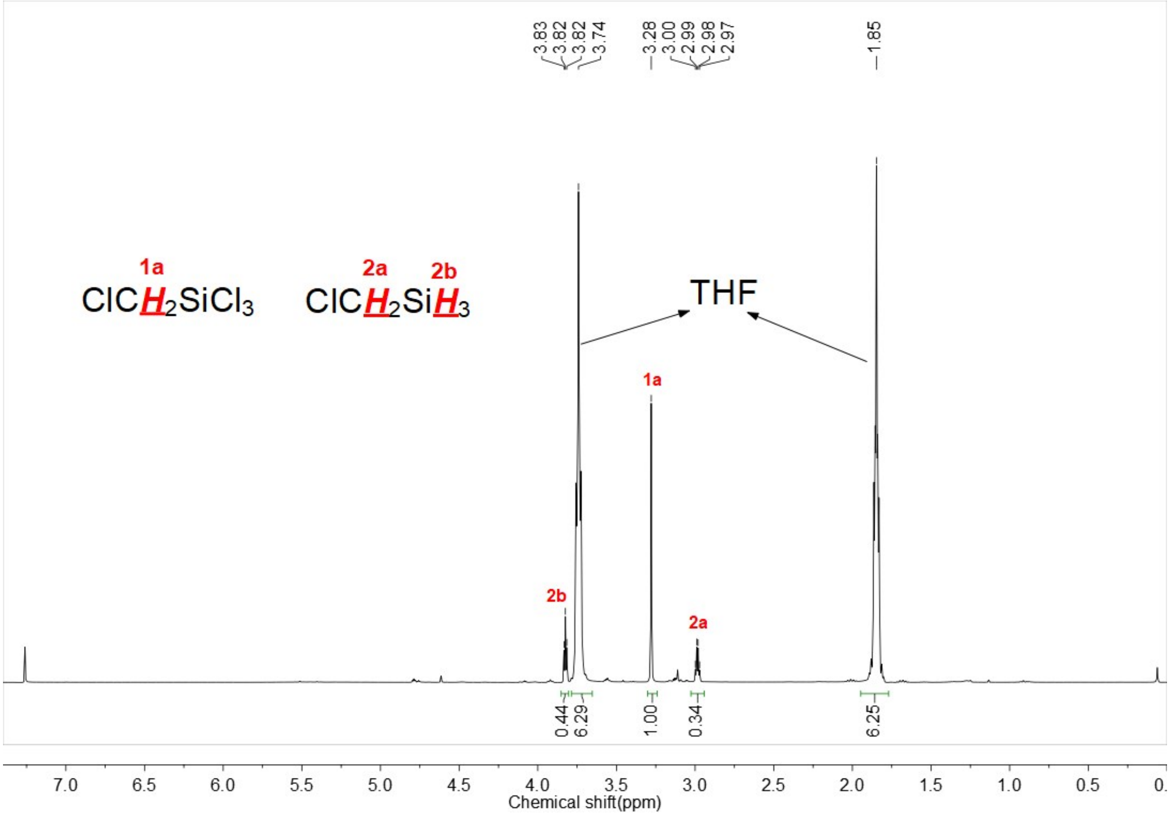


Figure 47a. Redistribution results of $ClCH_2SiH_3$ and $ClCH_2SiCl_3$ (1:2) in THF-20 h (**entry 1**)

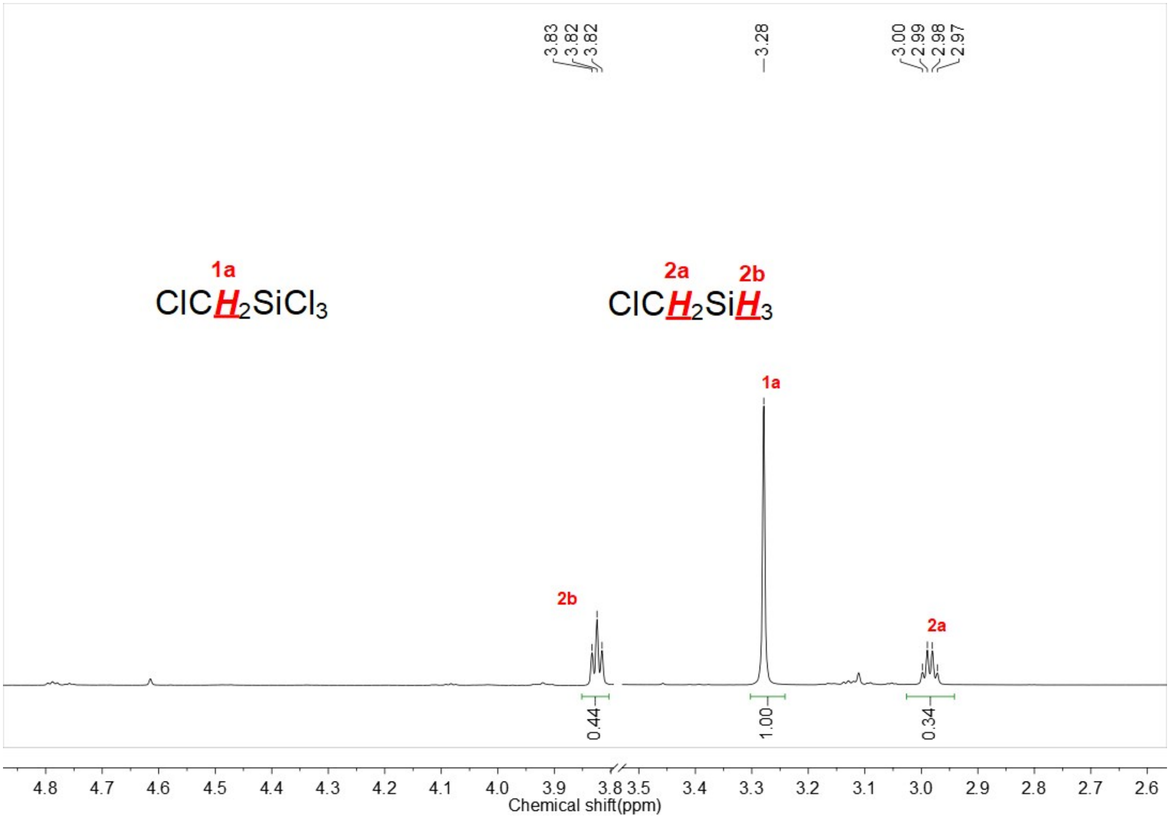


Figure 47b. Redistribution results of $ClCH_2SiH_3$ and $ClCH_2SiCl_3$ (1:2) in THF-20 h (**entry 1, zoom in**)

Redistribution results of $ClCH_2SiH_3$/$ClCH_2SiCl_3$ (molar ratio = 1:2) catalyzed by LiCl (3 mol%)-5 h (Table 4, entry 2)

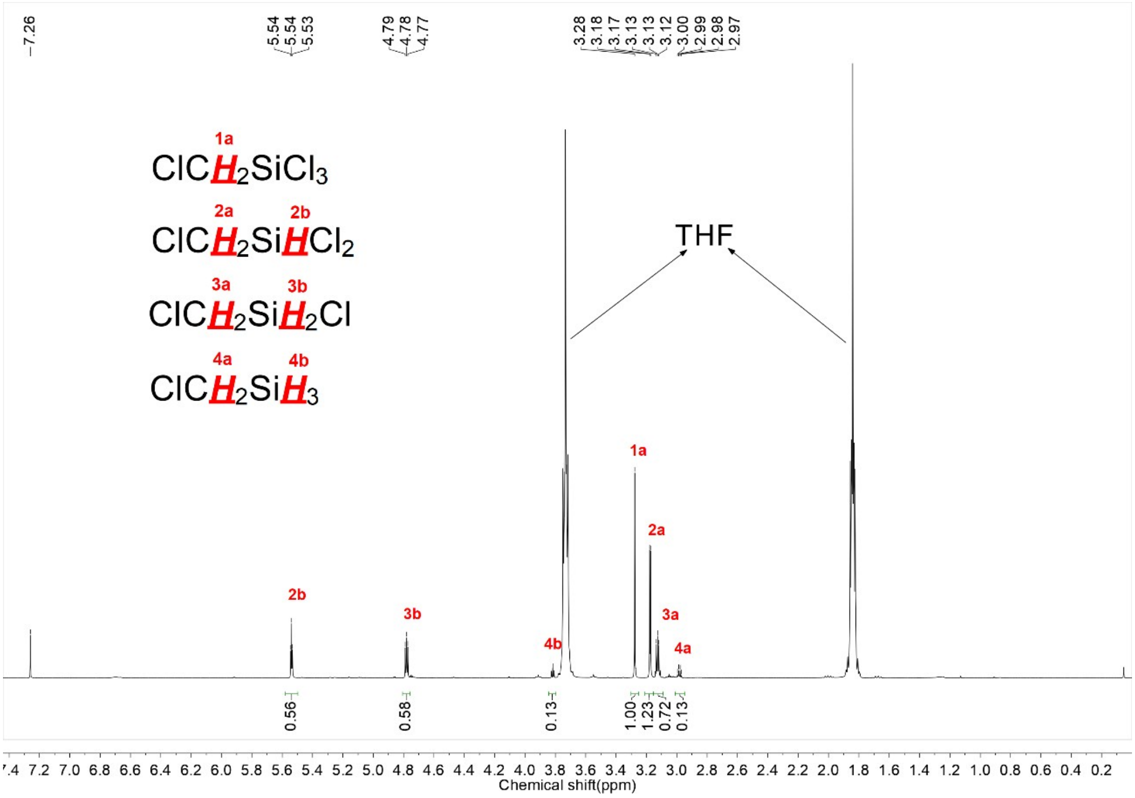


Figure 48a. Redistribution results of $ClCH_2SiH_3$/$ClCH_2SiCl_3$ catalyzed by LiCl (3 mol%)-5 h (**entry 2**)

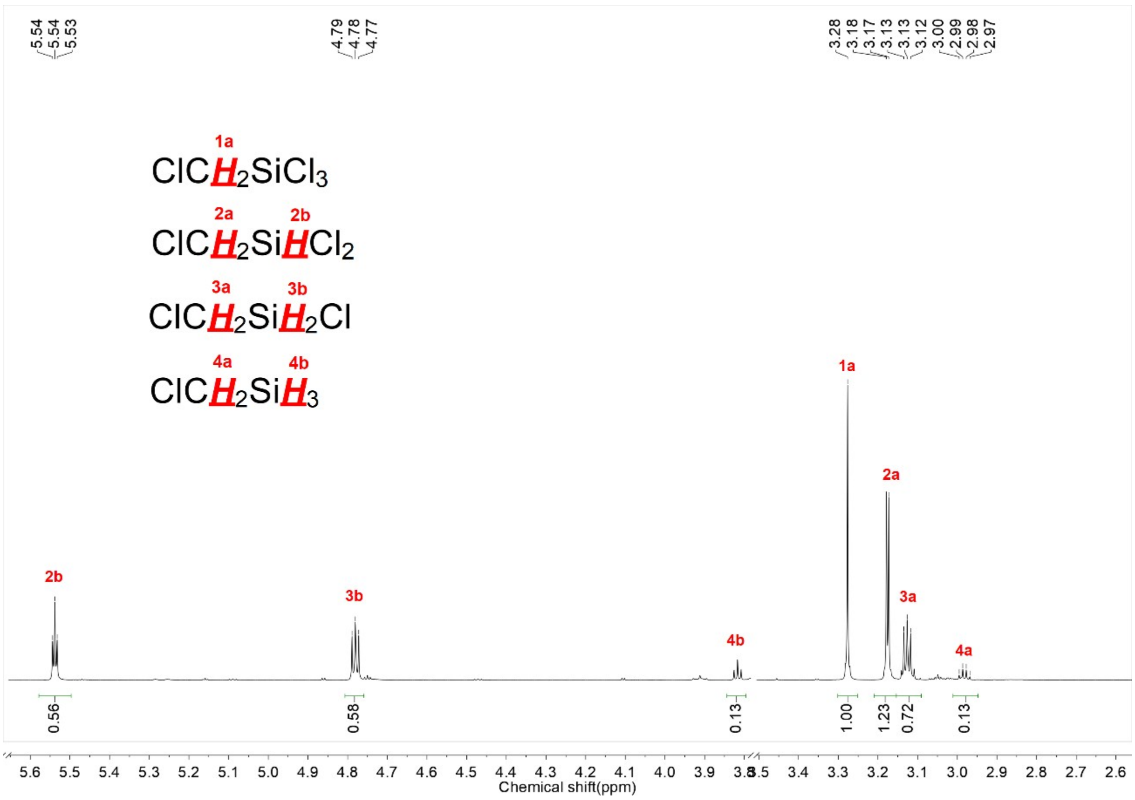


Figure 48b. Redistribution results of $ClCH_2SiH_3$/$ClCH_2SiCl_3$ catalyzed by LiCl (3 mol%)-5 h (**entry 2, zoom in**)

Redistribution results of $ClCH_2SiH_3$/$ClCH_2SiCl_3$ (molar ratio = 1:2) catalyzed by BH_3/LiCl (3 mol%)-5 h (Table 4, entry 3)

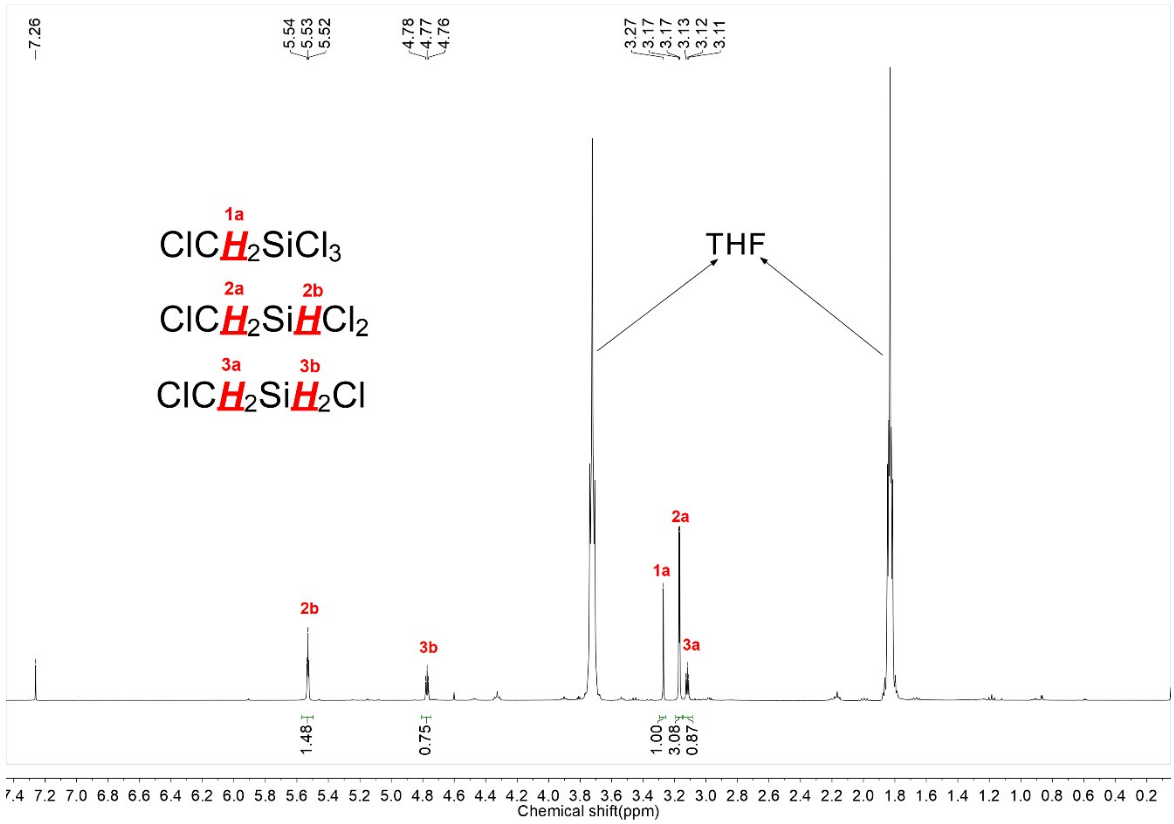


Figure 49a. Redistribution results of $ClCH_2SiH_3$/$ClCH_2SiCl_3$ catalyzed by BH_3/LiCl (3 mol%)-5 h (**entry 3**)

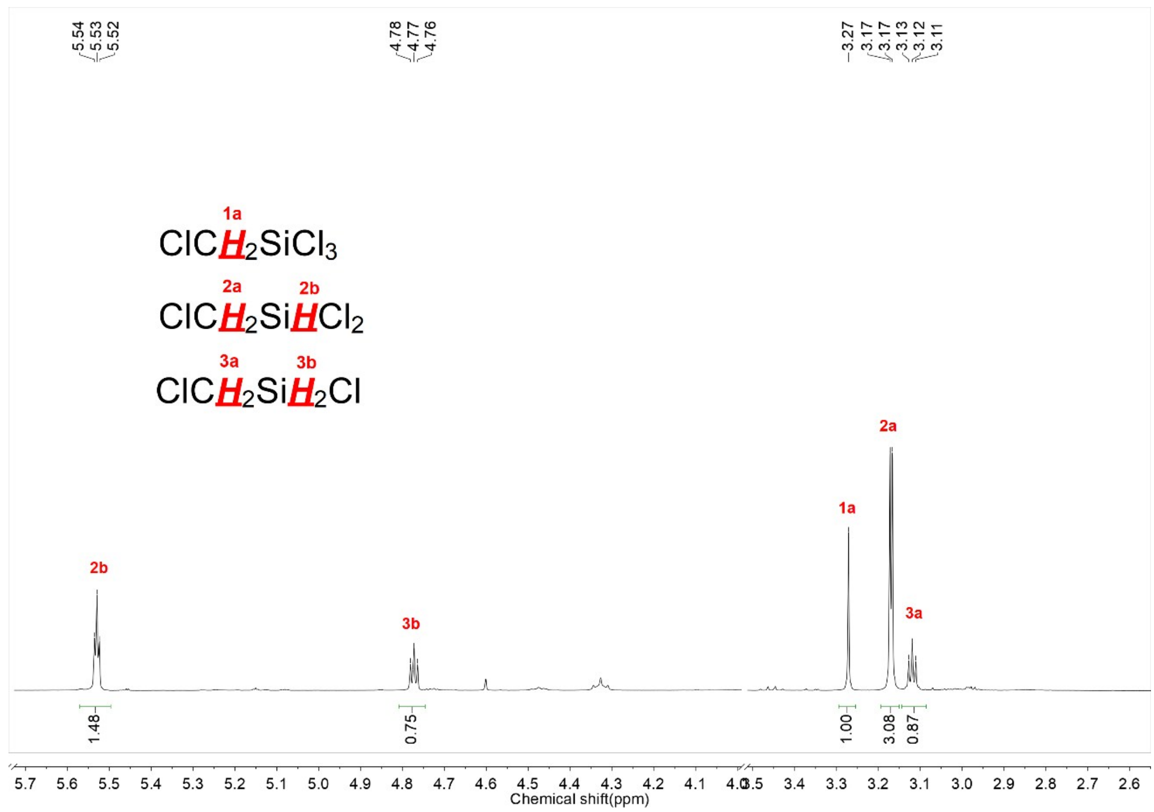


Figure 49b. Redistribution results of $ClCH_2SiH_3$/$ClCH_2SiCl_3$ catalyzed by BH_3/LiCl (3 mol%)-5h (**entry 3, zoom in**)

Redistribution results of $ClCH_2SiH_3$/$ClCH_2SiCl_3$ (molar ratio = 1:2) catalyzed by $LiBH_4$ (3 mol%)-5 h (Table 4, entry 4)

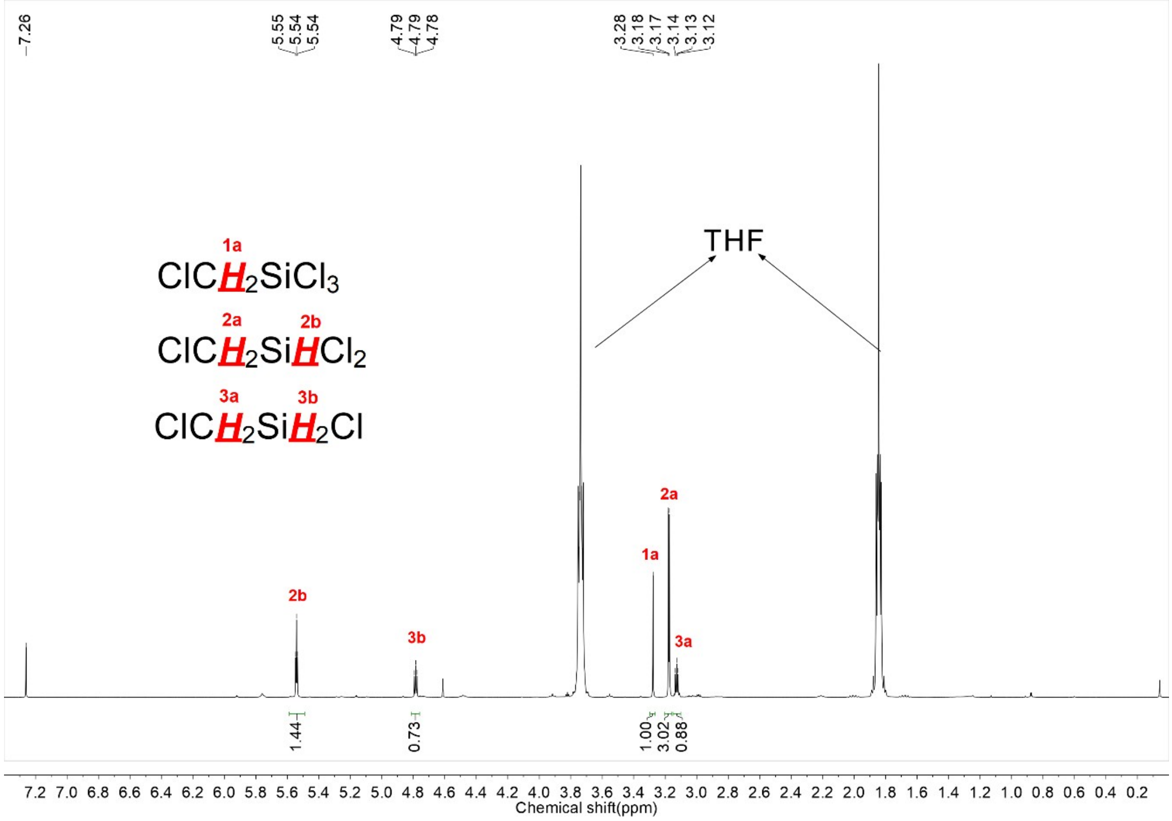


Figure 50a. Redistribution results of $ClCH_2SiH_3$/$ClCH_2SiCl_3$ catalyzed by $LiBH_4$ (3 mol%)-5 h (**entry 4**)

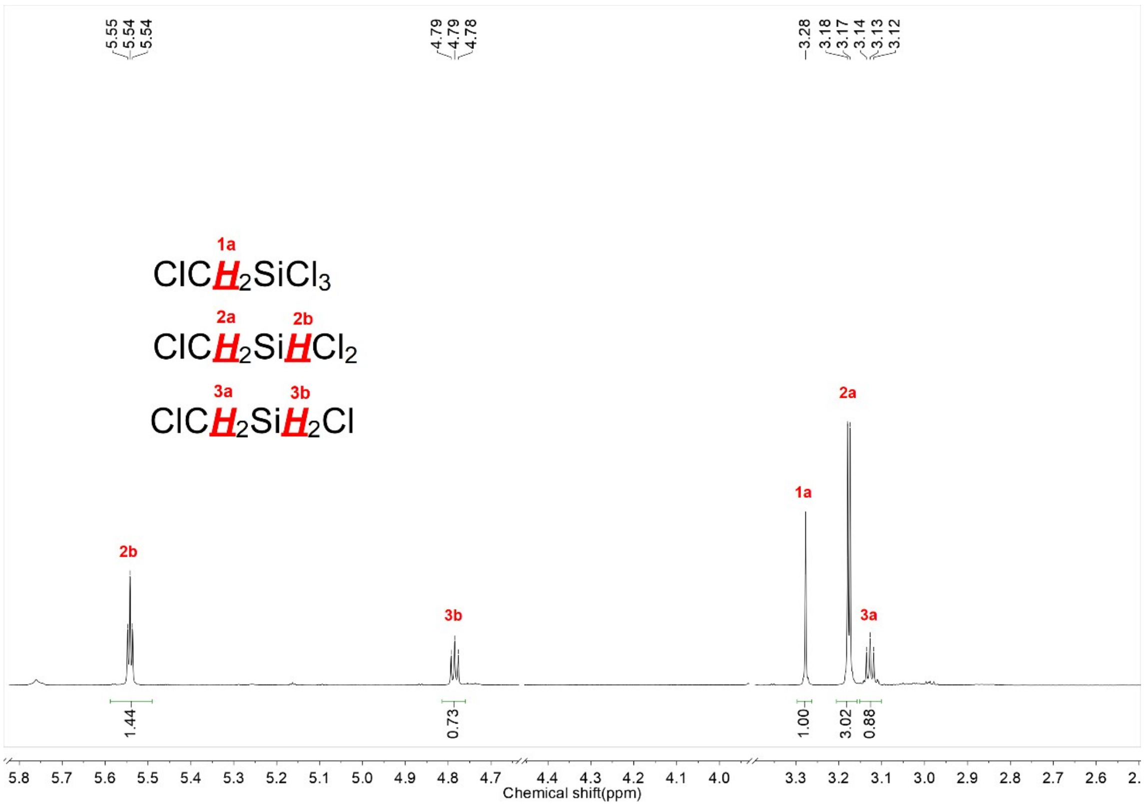


Figure 50b. Redistribution results of $ClCH_2SiH_3$/$ClCH_2SiCl_3$ catalyzed by $LiBH_4$ (3 mol%)-5 h (**entry 4, zoom in**)

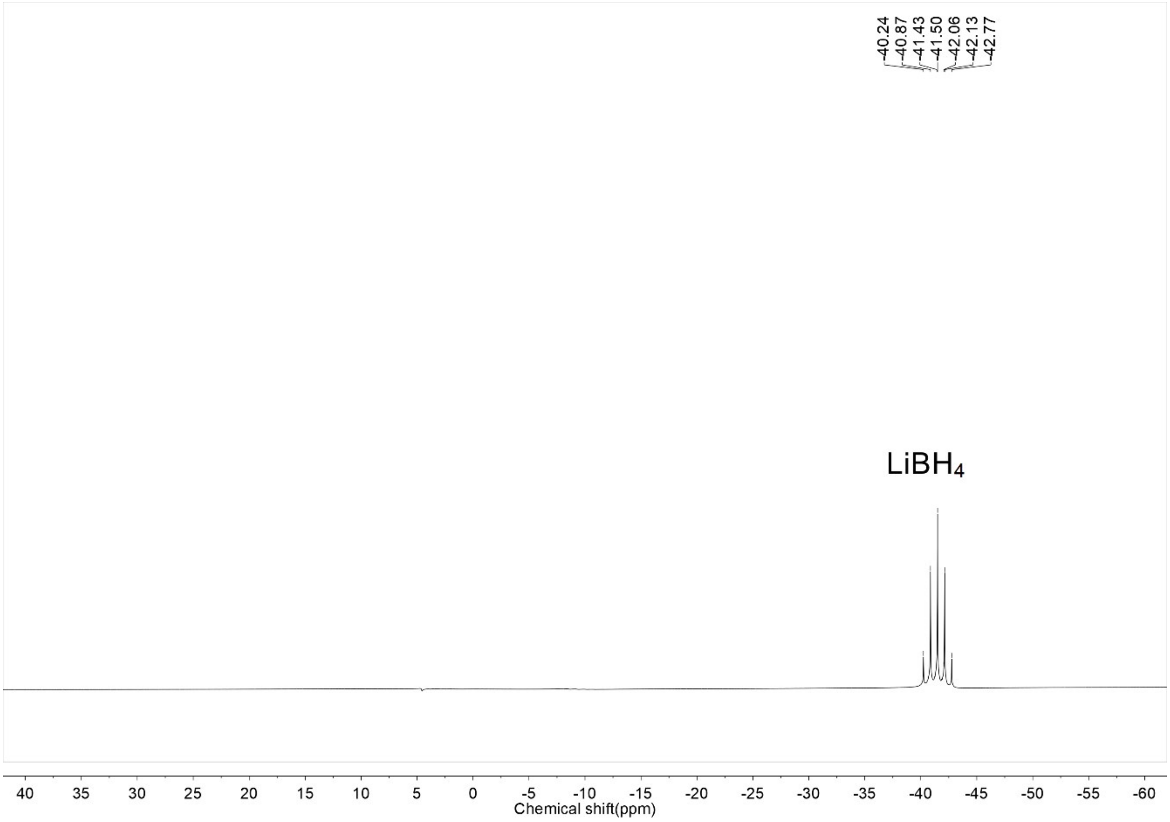


Figure 51a. ^{11}B NMR of $LiBH_4$ THF solution (d8-THF)

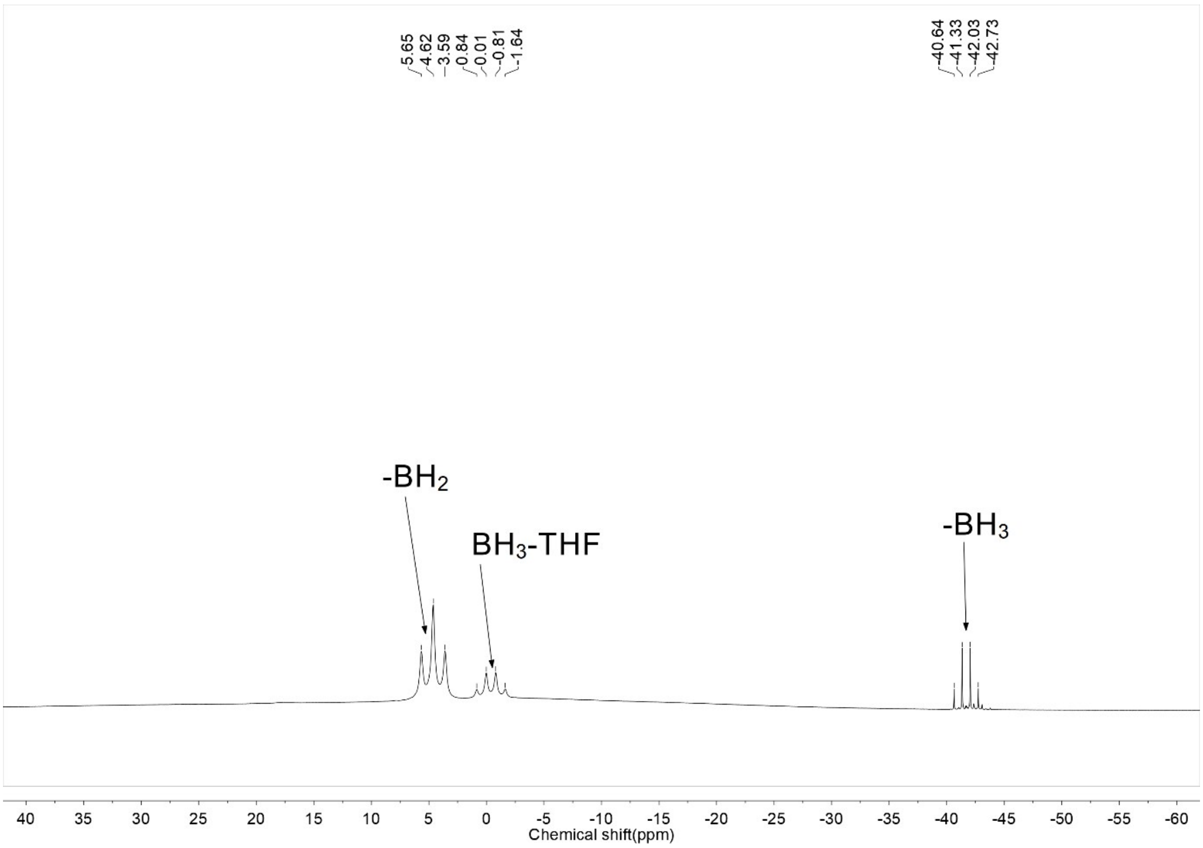
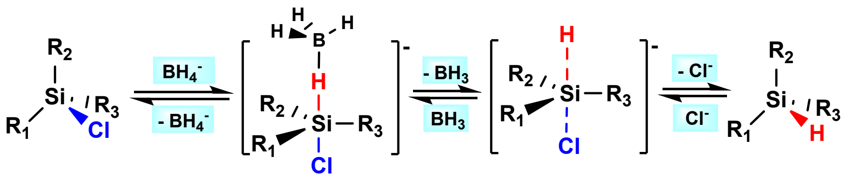


Figure 51b. ^{11}B NMR of the reaction mixture between $LiBH_4$ and $ClCH_2SiCl_3$ after 1 hour (d8-THF)

Ⅷ. DFT calculations

DFT calculations were performed using Gaussian 09, and geometry optimizations of all molecules and intermediates were carried out using B3LYP/6-311G (d, p) basis sets implemented in the Gaussian 09 software. The solvation effect of THF is also considered with SMD model. Frequency analysis of all the molecules and intermediates contained no imaginary frequency showing that they are energy minima. Pictures of molecular structures were generated with the Cylview[8] program.

Scheme 1 The possible mechanism of borohydrides catalyzed Si-H/Si-Cl redistribution reaction



Scheme 2 The possible redistribution process of borohydrides catalyzed Si-H/Si-Cl redistribution reaction of $ClCH_2SiH_3$/$ClCH_2SiCl_3$ in THF.

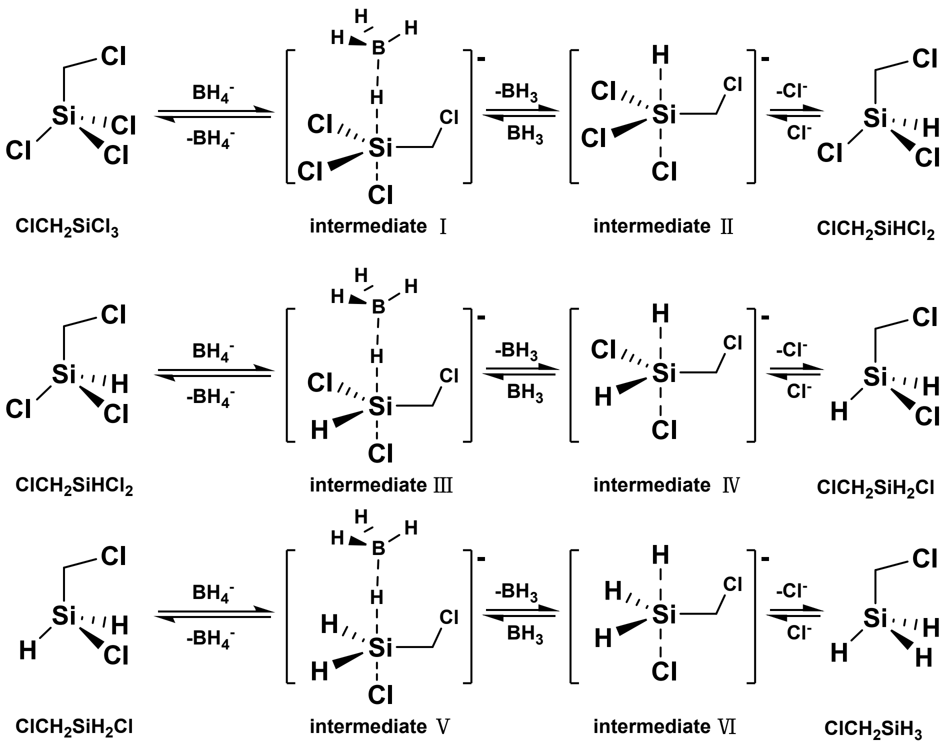


Table 5 Calculation results of Si-H bond length at the B3LYP/6-311G (d, p) level of theory

	Si-H bond length/Å (in THF)
$ClCH_2SiHCl_2$	1.46858
$ClCH_2SiH_2Cl$	1.47511
$ClCH_2SiH_3$	1.48505
Intermediate Ⅰ	1.64904*
Intermediate Ⅱ	1.49092*
Intermediate Ⅲ	1.72186*
Intermediate Ⅳ	1.47912*
Intermediate Ⅴ	1.75757*
Intermediate Ⅵ	1.49159*

* Apical Si-H bond length.

$ClCH_2SiCl_3$:

Cl	0	-2.674053	0.000001	0.362646
C	0	-1.081923	0.000029	1.231899
H	0	-1.054540	0.886752	1.866081
H	0	-1.054541	-0.886633	1.866163
Si	0	0.380716	-0.000003	0.063371
Cl	0	2.095008	-0.000308	1.207626
Cl	0	0.385883	1.668727	-1.138191
Cl	0	0.385551	-1.668435	-1.138600

Sum of electronic and zero-point Energies= -2169.868124 Hartree

Sum of electronic and thermal Energies= -2169.859931 Hartree

Sum of electronic and thermal Enthalpies= -2169.858987 Hartree

Sum of electronic and thermal Free Energies= -2169.903358 Hartree

BH_4^-:

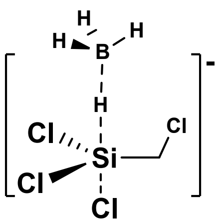
B	0	0.000183	0.000074	-0.000071
H	0	-0.463721	0.135245	1.127321
H	0	1.189816	0.302066	0.007240
H	0	-0.123464	-1.168232	-0.354935
H	0	-0.603547	0.730551	-0.779271

Sum of electronic and zero-point Energies=-27.331697 Hartree

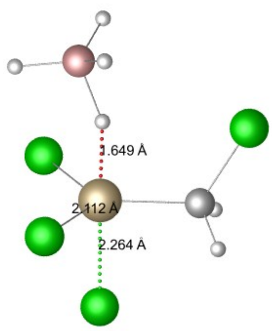
Sum of electronic and thermal Energies=-27.328758 Hartree

Sum of electronic and thermal Enthalpies=-27.327814 Hartree

Sum of electronic and thermal Free Energies=-27.351618 Hartree



intermediate I



Si	0	-0.278288	0.061820	0.000039
C	0	1.052105	-1.304459	-0.000218
Cl	0	2.798754	-0.810230	0.000160
H	0	0.890174	1.225444	0.000838
H	0	0.903040	-1.925229	-0.882625
H	0	0.902806	-1.925830	0.881723
Cl	0	-1.844966	-1.572190	-0.000449
B	0	1.432813	2.443616	0.000184
H	0	2.075515	2.430562	1.019825
H	0	2.075296	2.429977	-1.019571
H	0	0.489974	3.191315	0.000029
Cl	0	-0.974750	0.876659	1.819968
Cl	0	-0.974183	0.877347	-1.819701

Sum of electronic and zero-point Energies= -2197.190834 Hartree

Sum of electronic and thermal Energies=-2197.179449 Hartree

Sum of electronic and thermal Enthalpies= -2197.178504 Hartree

Sum of electronic and thermal Free Energies=-2197.229341 Hartree

BH_3:

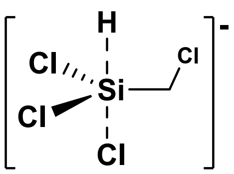
B	0	0.000000	0.000000	0.000000
H	0	0.000000	1.189458	0.000000
H	0	1.030101	-0.594729	0.000000
H	0	-1.030101	-0.594729	0.000000

Sum of electronic and zero-point Energies= -26.595228 Hartree

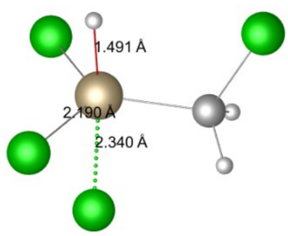
Sum of electronic and thermal Energies=-26.592337 Hartree

Sum of electronic and thermal Enthalpies=-26.591393 Hartree

Sum of electronic and thermal Free Energies=-26.612774 Hartree



intermediate Ⅱ



Si	0	-0.148934	-0.000001	-0.328768
C	0	1.352122	-0.000008	0.856236
Cl	0	2.970345	-0.000006	-0.006780
H	0	0.568022	-0.000004	-1.635986
H	0	1.348231	-0.882076	1.494353
H	0	1.348233	0.882055	1.494361
Cl	0	-1.471035	0.000004	1.601937
Cl	0	-1.022944	1.938093	-0.853090
Cl	0	-1.022963	-1.938087	-0.853090

Sum of electronic and zero-point Energies= -2170.575375 Hartree

Sum of electronic and thermal Energies= -2170.566271 Hartree

Sum of electronic and thermal Enthalpies= -2170.565327 Hartree

Sum of electronic and thermal Free Energies= -2170.612538 Hartree

Cl^-:

Cl	0	0.000000	0.000000	0.000000

Sum of electronic and zero-point Energies= -460.395968 Hartree

Sum of electronic and thermal Energies= -460.394552 Hartree

Sum of electronic and thermal Enthalpies= -460.393607 Hartree

Sum of electronic and thermal Free Energies= -460.410991 Hartree

$ClCH_2SiHCl_2$:

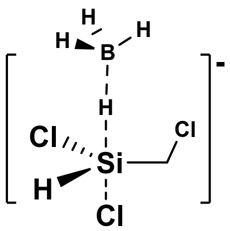
Cl	0	2.596074	-0.305807	0.059117
C	0	0.979350	-0.953269	-0.477761
H	0	0.914334	-0.817224	-1.556755
H	0	0.972350	-2.020849	-0.255608
Si	0	-0.409907	-0.080982	0.433915
H	0	-0.274087	-0.116215	1.895774
Cl	0	-2.185775	-1.020473	-0.094072
Cl	0	-0.513240	1.903200	-0.158672

Sum of electronic and zero-point Energies= -1710.188479 Hartree

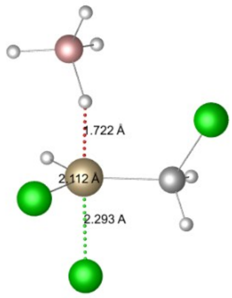
Sum of electronic and thermal Energies= -1710.181472 Hartree

Sum of electronic and thermal Enthalpies= -1710.180528 Hartree

Sum of electronic and thermal Free Energies= -1710.222018 Hartree



intermediate Ⅲ



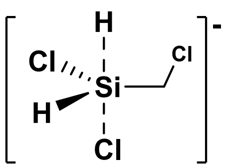
Si	0	0.397959	0.233042	0.478925
C	0	-0.713502	-1.242501	0.013764
Cl	0	-2.415563	-0.893170	-0.531680
H	0	0.810535	0.673285	1.813471
H	0	-1.007645	1.221468	0.588858
H	0	-0.791750	-1.905390	0.876403
H	0	-0.248138	-1.795877	-0.798581
Cl	0	2.226014	-1.147470	0.368336
B	0	-1.574283	1.895131	1.527975
H	0	-2.573304	2.295304	0.974645
H	0	-1.789256	1.109697	2.424312
H	0	-0.791049	2.765851	1.829771
Cl	0	0.952584	1.473136	-1.138790

Sum of electronic and zero-point Energies= -1737.514216 Hartree

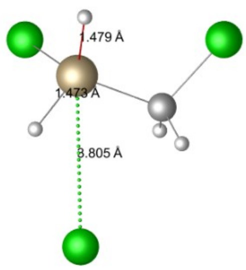
Sum of electronic and thermal Energies= -1737.503866 Hartree

Sum of electronic and thermal Enthalpies= -1737.502922 Hartree

Sum of electronic and thermal Free Energies= -1737.551321 Hartree



intermediate Ⅳ



Si	0	0.351566	0.710843	0.940341

C	0	0.526713	-1.005806	0.181276
Cl	0	2.255085	-1.357722	-0.336384
H	0	-0.101606	-1.125704	-0.696652
H	0	0.258050	-1.771813	0.907310
H	0	-0.812659	0.811039	1.836725
Cl	0	0.101013	2.150245	-0.571327
Cl	0	-2.887127	-0.963847	-0.147492
H	0	1.601513	1.082029	1.638651

Sum of electronic and zero-point Energies= -1710.901045 Hartree

Sum of electronic and thermal Energies= -1710.892804 Hartree

Sum of electronic and thermal Enthalpies= -1710.891859 Hartree

Sum of electronic and thermal Free Energies= -1710.938708 Hartree

$ClCH_2SiH_2Cl$:

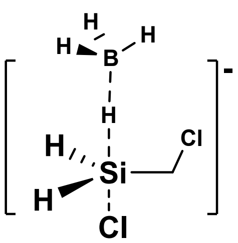
Si	0	0.482934	0.629043	0.000133
C	0	-0.794220	-0.757331	0.000292
Cl	0	-2.458899	0.006747	-0.000153
H	0	0.378205	1.444180	1.225061
H	0	0.377740	1.444375	-1.224657
H	0	-0.734544	-1.386126	0.887776
H	0	-0.734616	-1.386835	-0.886723
Cl	0	2.383456	-0.264289	-0.000146

Sum of electronic and zero-point Energies= -1250.505460 Hartree

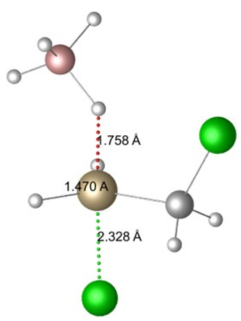
Sum of electronic and thermal Energies= -1250.499547 Hartree

Sum of electronic and thermal Enthalpies= -1250.498603 Hartree

Sum of electronic and thermal Free Energies= -1250.536334 Hartree



intermediate V



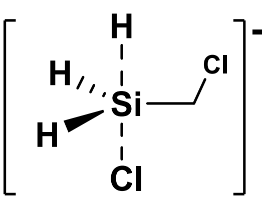
Si	0	-0.496631	0.680355	-0.000001
C	0	0.318418	-1.050383	0.000523
Cl	0	2.144817	-1.156607	-0.000187
H	0	-0.753003	1.343966	-1.286488
H	0	1.113858	1.384185	0.000431
H	0	-0.753599	1.344486	1.286107
H	0	-0.010371	-1.599642	-0.880089
H	0	-0.009668	-1.598740	0.881968
Cl	0	-2.584353	-0.348610	-0.000114
B	0	1.567769	2.575756	0.000021
H	0	2.228801	2.634711	1.015212
H	0	2.228192	2.634616	-1.015551
H	0	0.631389	3.343672	0.000283

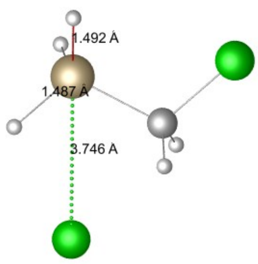
Sum of electronic and zero-point Energies = -1277.833146 Hartree

Sum of electronic and thermal Energies = -1277.823808 Hartree

Sum of electronic and thermal Enthalpies = -1277.822864 Hartree

Sum of electronic and thermal Free Energies = -1277.868448 Hartree





intermediate Ⅵ

Si	0	-0.266256	1.475332	0.017671
C	0	-0.630191	-0.364546	-0.311748
Cl	0	-2.382136	-0.793141	0.095272
H	0	0.788572	1.980184	-0.900769
H	0	0.130013	1.690919	1.436504
H	0	-0.008514	-1.018926	0.296569

H	0	-0.490267	-0.633725	-1.358616
Cl	0	2.888578	-0.543611	0.045505
H	0	-1.520589	2.238953	-0.243810

Sum of electronic and zero-point Energies= -1251.215801 Hartree

Sum of electronic and thermal Energies= -1251.208563 Hartree

Sum of electronic and thermal Enthalpies= -1251.207619 Hartree

Sum of electronic and thermal Free Energies= -1251.250114 Hartree

$ClCH_2SiH_3$:

Si	0	1.523527	-0.191844	-0.000007
C	0	-0.068002	0.839699	0.000006
Cl	0	-1.555237	-0.232492	-0.000002
H	0	1.568123	-1.043770	1.212356
H	0	2.675603	0.745226	0.000106
H	0	1.568208	-1.043628	-1.212390
H	0	-0.147118	1.471108	-0.884355
H	0	-0.147155	1.471051	0.884387

Sum of electronic and zero-point Energies= -790.820445 Hartree

Sum of electronic and thermal Energies= -790.815480 Hartree

Sum of electronic and thermal Enthalpies= -790.814536 Hartree

Sum of electronic and thermal Free Energies= -790.848518 Hartree

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