# Supporting information for

# Pt(0)-Catalysed Synthesis of New Bifunctional Silanes

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## 1. Materials and methods

Karstedt's catalyst, hexamethyldisilazane, dime-thylchlorosilane, sodium hydride, allyl glycidyl ether, allyl methacrylate, allyl chloride, 5-allyloxy-1,1,2,2,3,3,4,4-oktafluropentl ether were purchased from Sigma-Aldrich, NaOH was obtained from POCH. All chemicals were used without any further purification. The $^{1}H$ NMR and $^{13}C$ NMR spectra were recorded on a Bruker Ultrashield 300 MHz spectrometer using $CDCl_3$ as solvent. The $^{29}Si$ NMR spectra were recorded using Bruker Ascend 400 spectrometer. The mass spectra were obtained by GCMS analysis (Bruker MS320 Triple quad, equipped with a VF-5 Factor four capillary column (30 m) and a quadrupole detector). 5-allyloxy-1,1,2,2,3,3,4,4-oktafluropentl ether[1] and 3-chloropropyldimethylsilane[2] were prepared according to the published methods.

[1] R. Januszewski, I. Kownacki, H. Maciejewski, B. Marciniec, *Journal of Organometallic Chemistry* **2017**, *846*, 263-268.

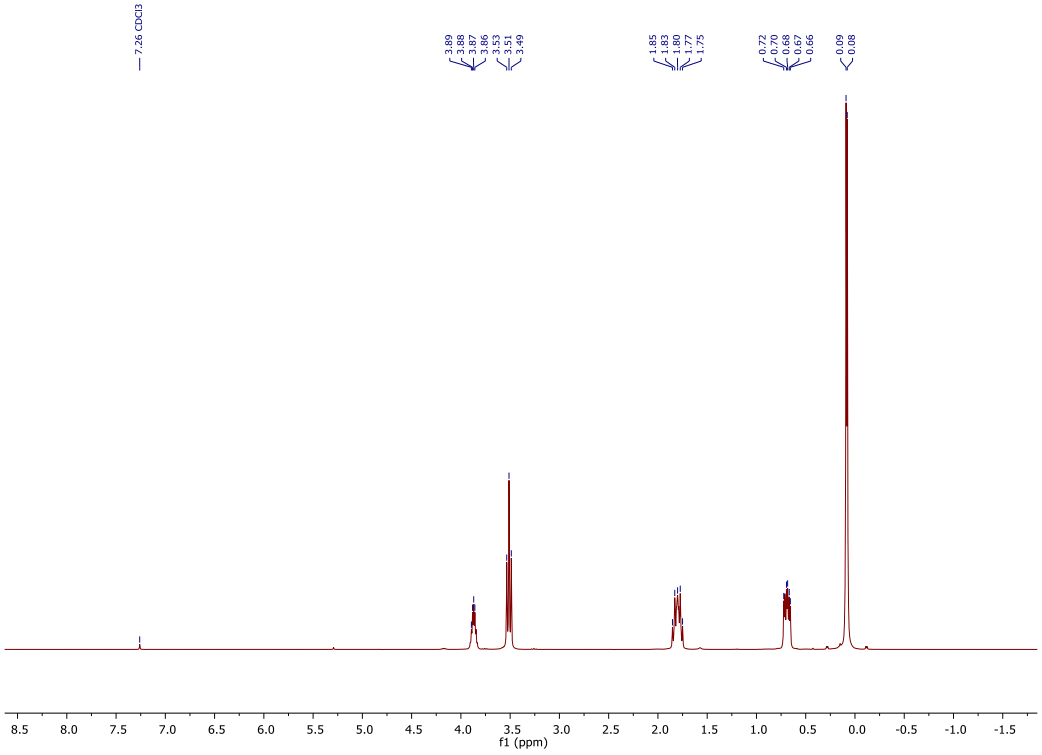
[2] J.O. Daiss, S. Duda-Johner, C. Burschka, U. Holzgrabe, K. Mohr, R. Tacke, *Organometallics* **2002**, 21, 803-811.

## 2. Synthesis of hydrosilanes

### 2.1. Synthesis of 3-chloropropylsilane (**1**)

Product was obtained by method published by J.O Daiss et al. (Yield 93%). **$^{1}$H NMR** ($CDCl_3$, 298K, δ): 3.87 (m, 1H SiH), 3.51 (t, 2H $CH_2Cl$), 1.80, (m, 2H $CH_2$), 0.70 (m, 2H $SiCH_2$), 0.09 (d, 6H $SiCH_3$). **$^{13}$C NMR** ($CDCl_3$, 298K, δ): 47.49 ($CH_2Cl$), 28.15 ($CH_2$), 11.91 ($SiCH_2$), -4.46 ($SiCH_3$). **MS (EI, m/z):** 96.0 (23.0), 93.1 (85.1), 81.0 (23.2), 80.1 (5.3), 79.1 (59.5), 67.2 (5.3), 65.1 (11.4), 63.1 (11.6), 59.1 (100) 58.0 (8.4), 57.1 (5.3), 56.2 (7.1).

**$^{1}$H NMR:**



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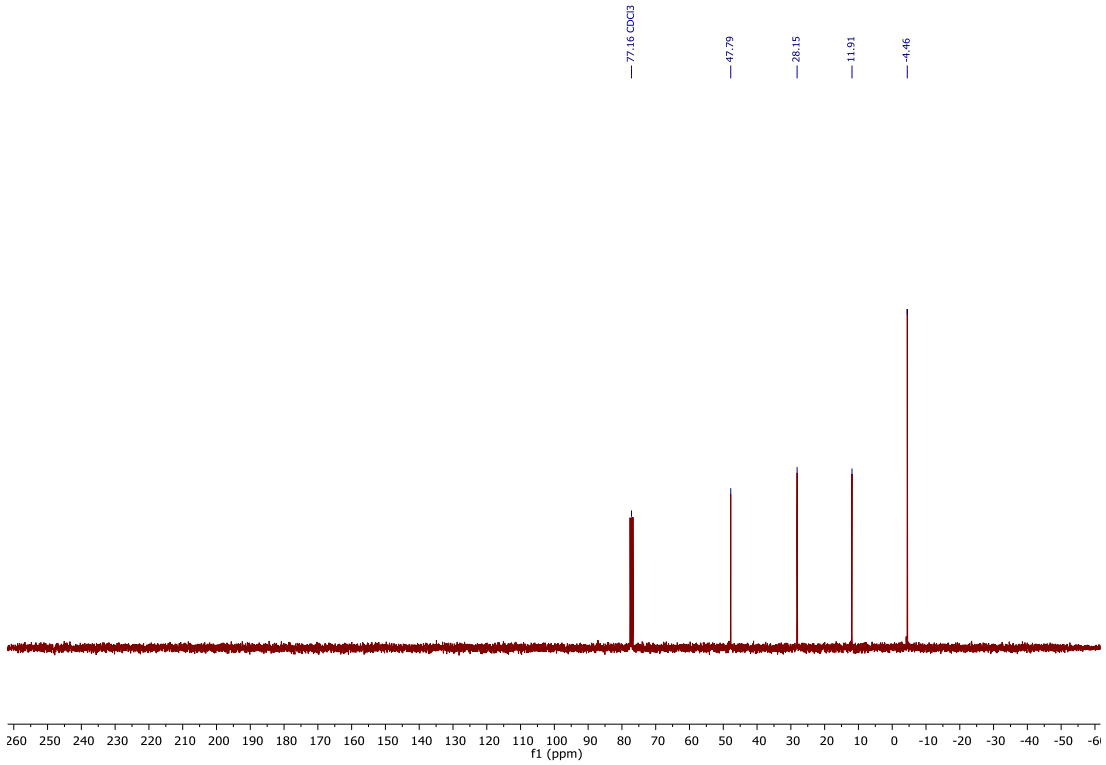
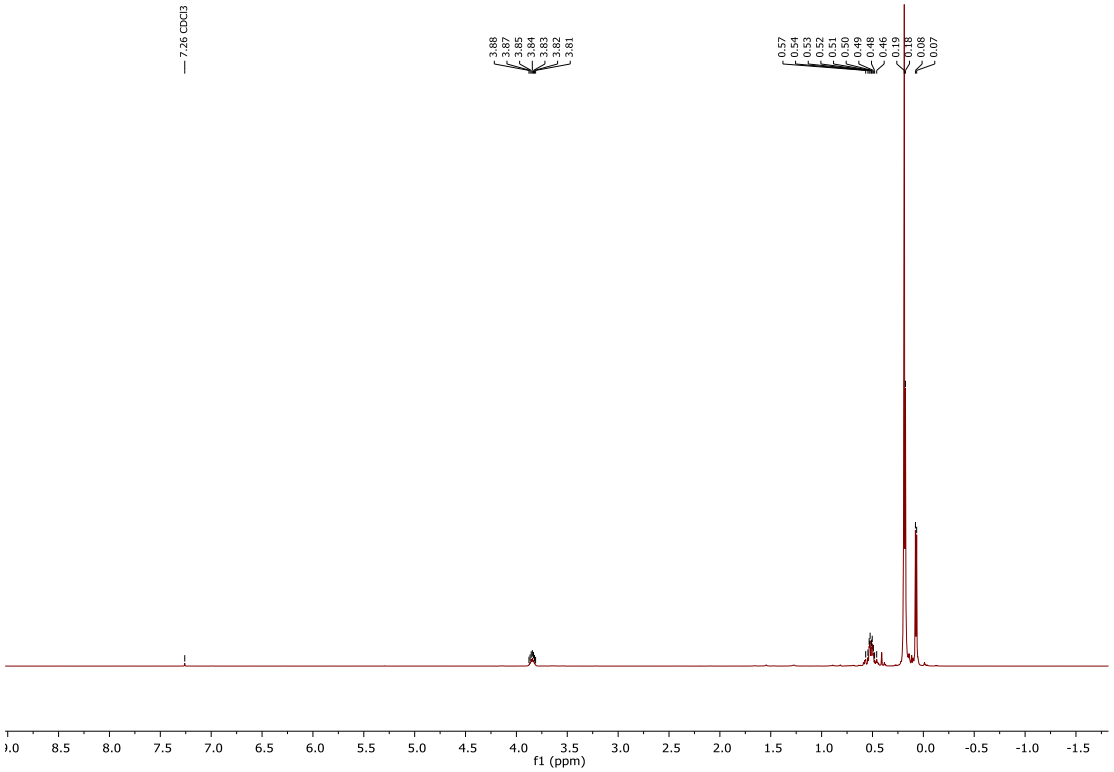



2.2. Synthesis of Synthesis of dimethyl{ethyl[dimethysilylbis(trimethylsilyl)amine]}silane (**2**)

To a mixture prepared from 20 g (81.40 mmol) of dimethylvinylsilylbis(trimethylsilyl)amine, 90 mmol of chlorodimethylsilane and 100 mL of anhydrous THF Karstedt catalyst was added ($10^{-4}$mol Pt/mol C=C bond). Then mixture was refluxed and controlled by gas chromatography. After total conversion of silylamine mixture was cooled to room temperature and 3.54 (93.61 mmol) of sodium borohydride was added. Reaction was stirred at room temperature for one hour and refluxed overnight. After filtration and evaporation of the solvent obtained oil was purified by trap to trap distillation to give pure product with a yield 83%. **$^{1}$H NMR** ($CDCl_3$, 298K, δ): 3.84 (m, 1H Si-H), 0.53 (m, 4H $SiCH_2$), 0.19, 0.07 (24H Si-$CH_3$). **$^{13}$C NMR** ($CDCl_3$, 298K, δ): 13.20, 6.58 (Si-$CH_2$), 5.58 [$N(SiMe_3)_2$], 3.11 $NSiMe_2$, -4.81 $HSiMe_2$. **$^{29}$Si NMR** ($CDCl_3$, 298K, δ): 4.78, 2.31, -10.02. **MS (EI, m/z):** 220.3 (11.9), 219.3 (23.7), 118.3 (100), 217.4 (12.4), 116.3 (21.1), 203.3 (7.0), 202.3 (30.7), 188.2 (5.3), 130.2 (22.9), 100.1 (8.7), 73.2 (22.5), 59.1 (17.8).

**$^{1}$H NMR:**

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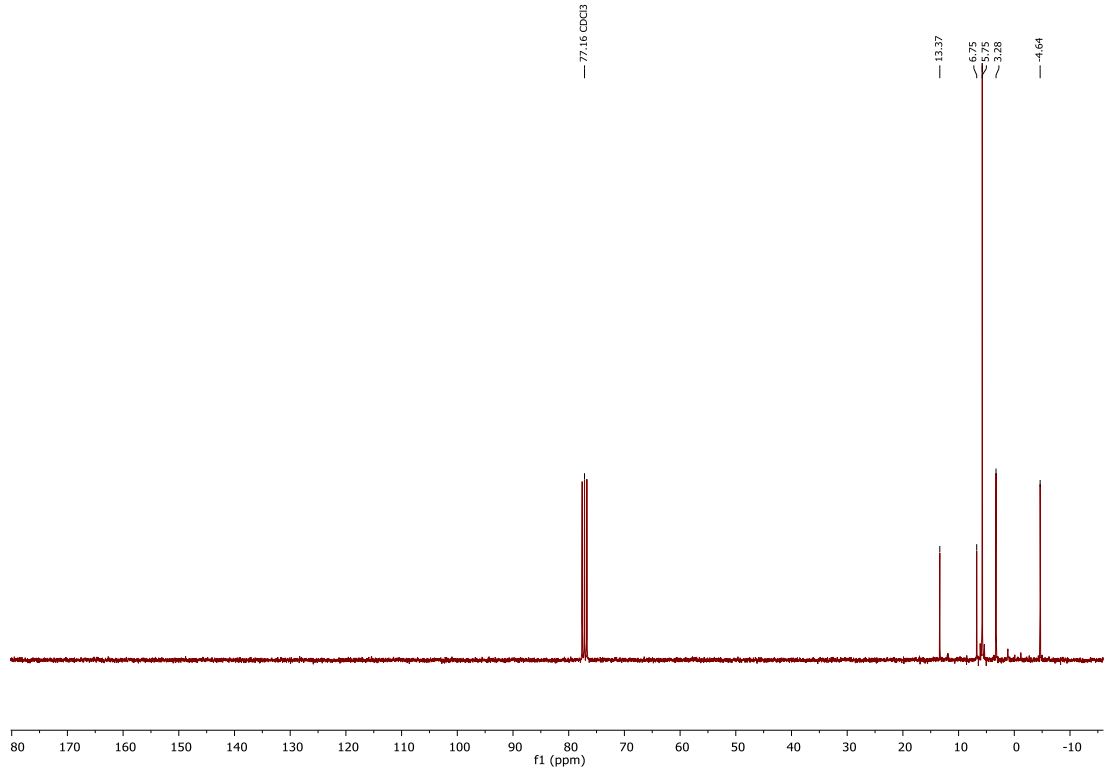

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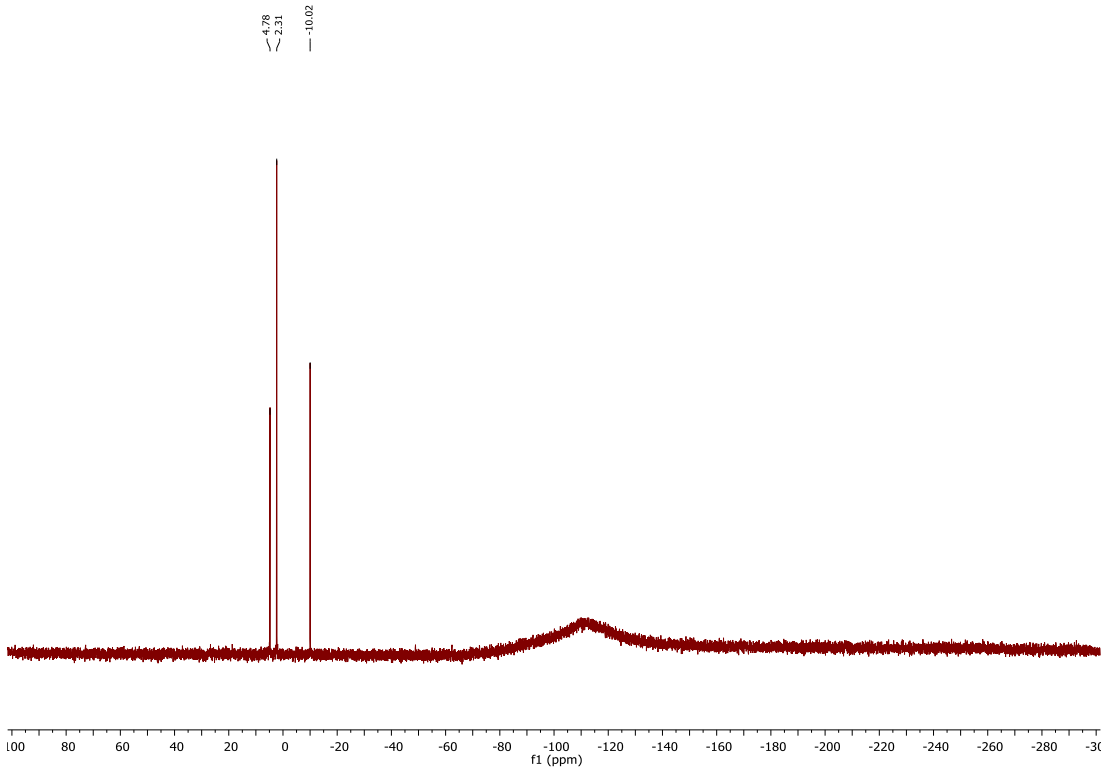
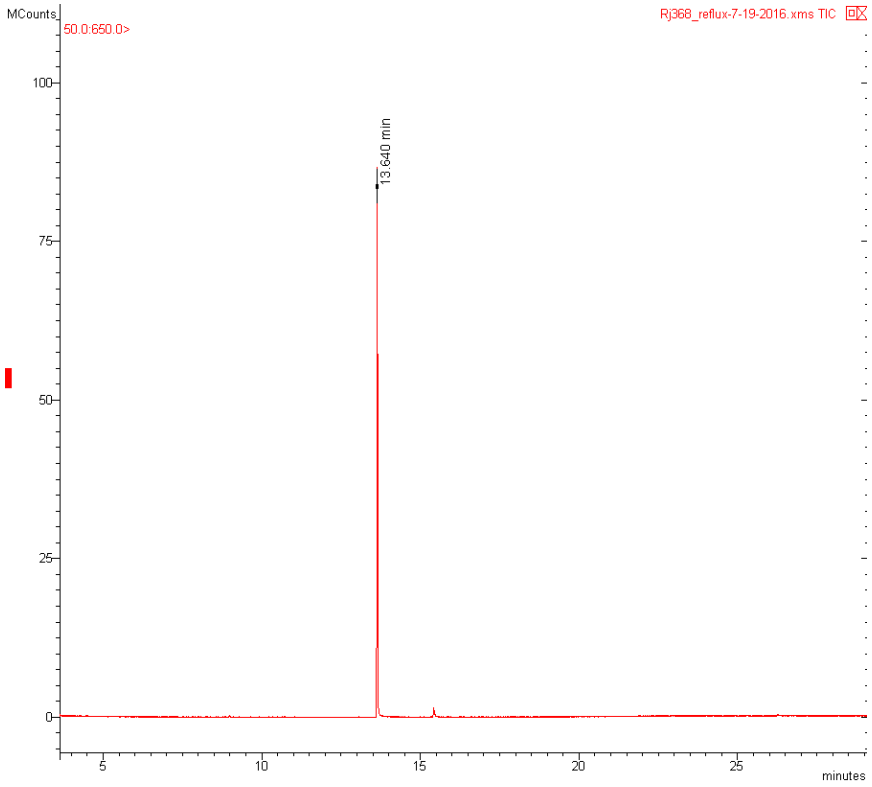


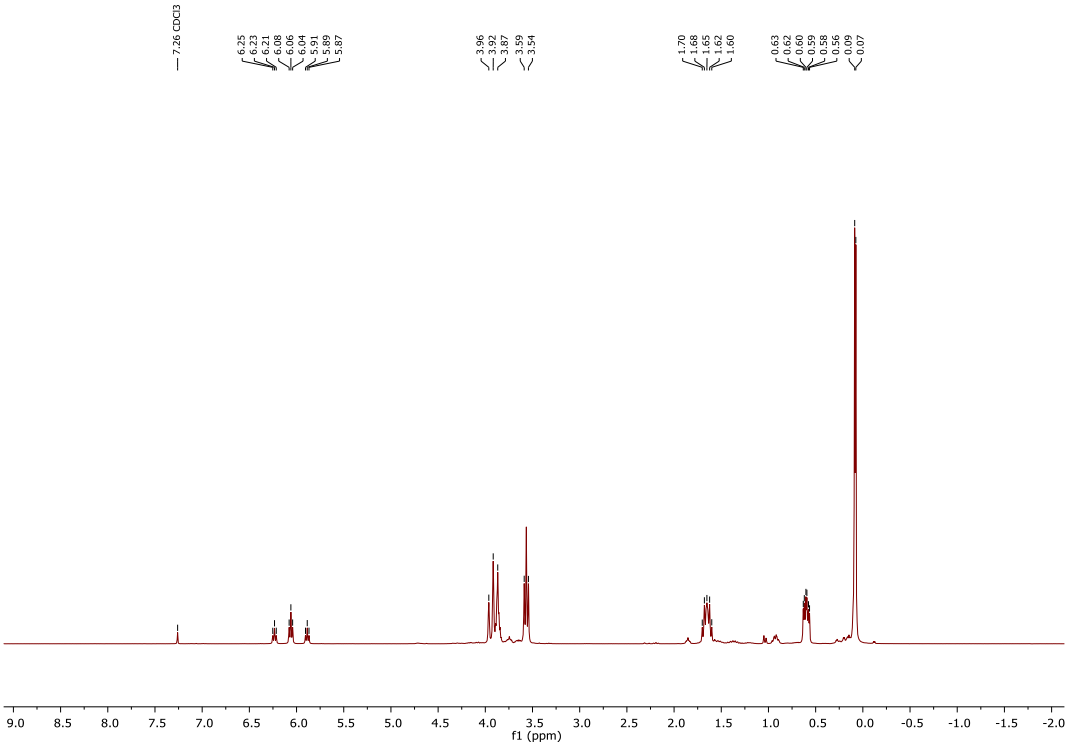

## GC Analysis:



2.3. Synthesis of dimethyl(3-oktafluoropentyloxy)propylsilane (**3**)

To a mixture made of 21.45 g (78.8 mmol) of 5-allyloxy-1,1,2,2,3,3,4,4-oktafluropentl ether, 8.95 g (94.5 mmol) of dimethylchlorosilane, 50 mL of anhydrous THF, Karstedt catalyst was added ($10^{-4}$mol Pt/mol C=C bond). Then the mixture was refluxed and controlled by gas chromatography. After complete conversion of alkene, the mixture was cooled to room temperature and was diluted by 50 mL of THF and then 5 g (0.132 mol) of sodium borohydride. The reaction mixture was stirred at room temperature for one hour and refluxed overnight. After filtration and evaporation of the solvent, the oil obtained was purified by trap to trap distillation to give pure product with a yield (81%). **$^{1}$H NMR** ($CDCl_3$, 298K, δ): 6.06 (tt, 1H $F_2CH$), 3.92 (t, 2H $OCH_2$), 3.87 (1H, SiH), 3.56 (t, 2H $CH_2O$), 1.56 (m, 2H $CH_2$), 0.60 (m, 2H $SiCH_2$), 0.09 (d, 6H Si-$CH_3$). **$^{13}$C NMR** ($CDCl_3$, 298K, δ): 115.71, 111.81, 108.82, 104.45 ($CF_2$, $HCF_2$), 75.70 ($CH_2O$), 67.66 ($OCH_2$), 24.52 ($CH_2$), 10.08 ($SiCH_2$), 4.50 ($SiCH_3$), **$^{29}$Si NMR** ($CDCl_3$, 298K, δ): -12.58, **MS (EI, m/z):** 317.2 (4.9) [$M^+$-15], 193.1 (9.0), 145.1 (53.7), 125.1 (7.6), 113.0 (5.8), 101.0 (5.7), 97.1 (11.7), 95.1 (37.9), 93.0 (5.3), 87.1 (7.1), 83.1 (14.3), 81.1 (9.3), 77.1 (54.0), 73.3 (6.0), 69.1 (5.4), 63.1 (23.9), 61.1 (7.7), 60.2 (7.2), 59.1 (100), 58.0 (6.5), 57.1 (5.6), 51.1 (21.2).

**$^{1}$H NMR:**



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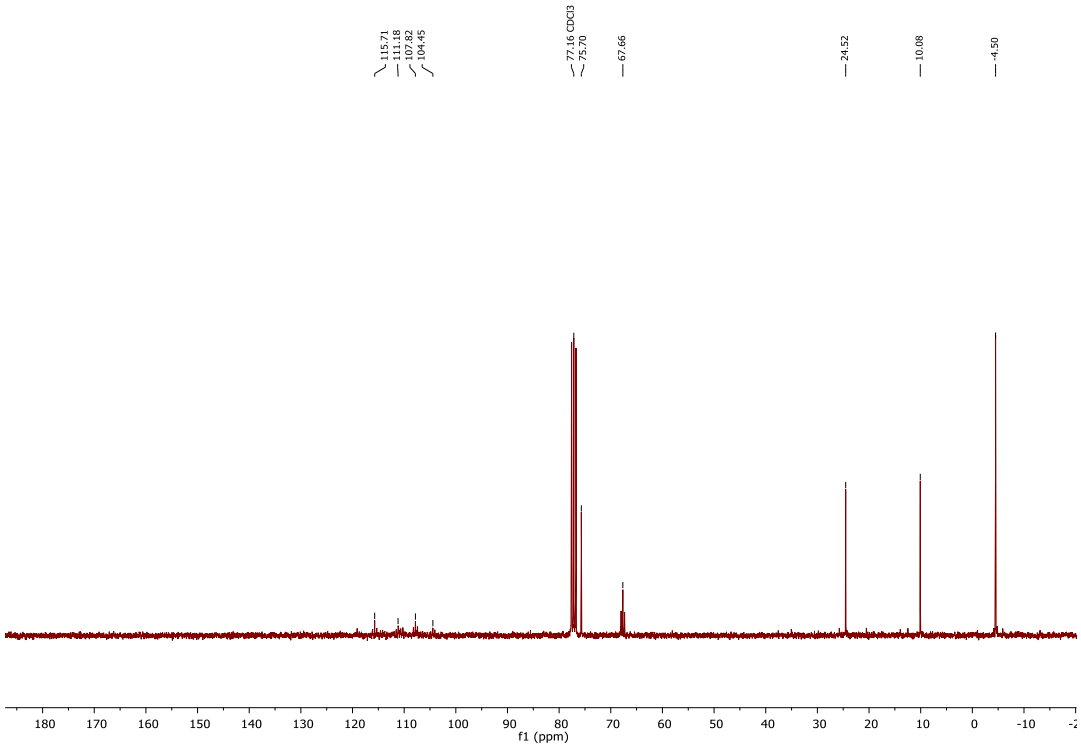


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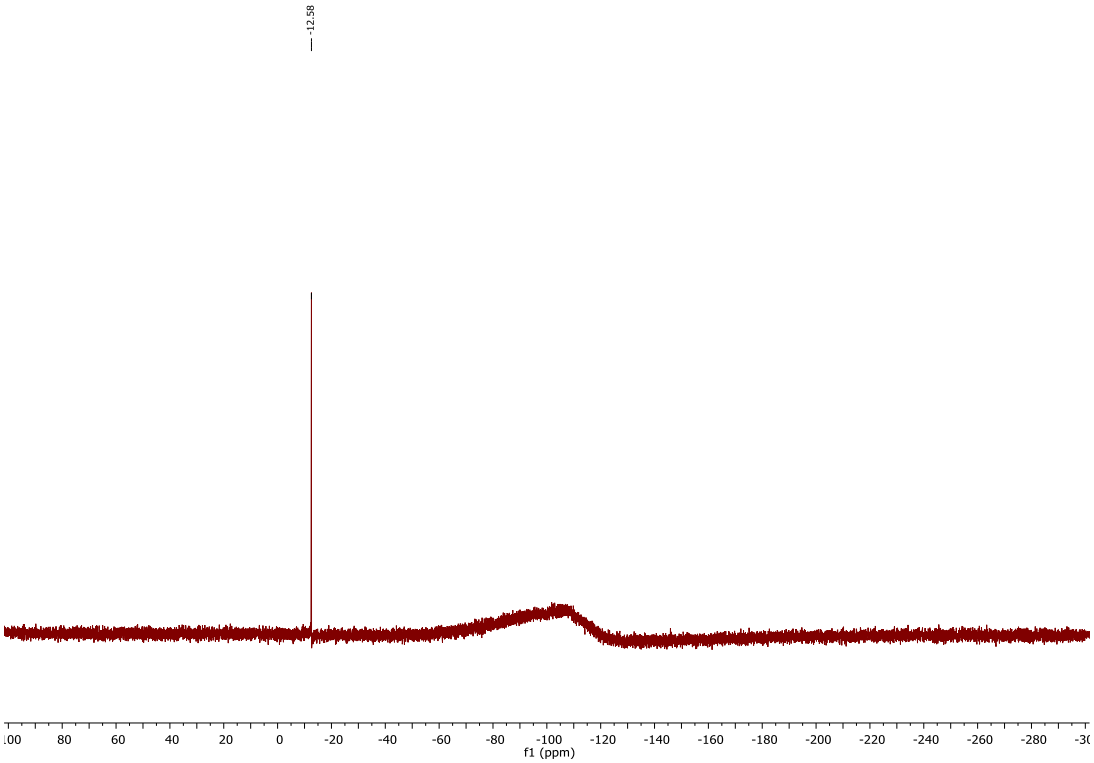
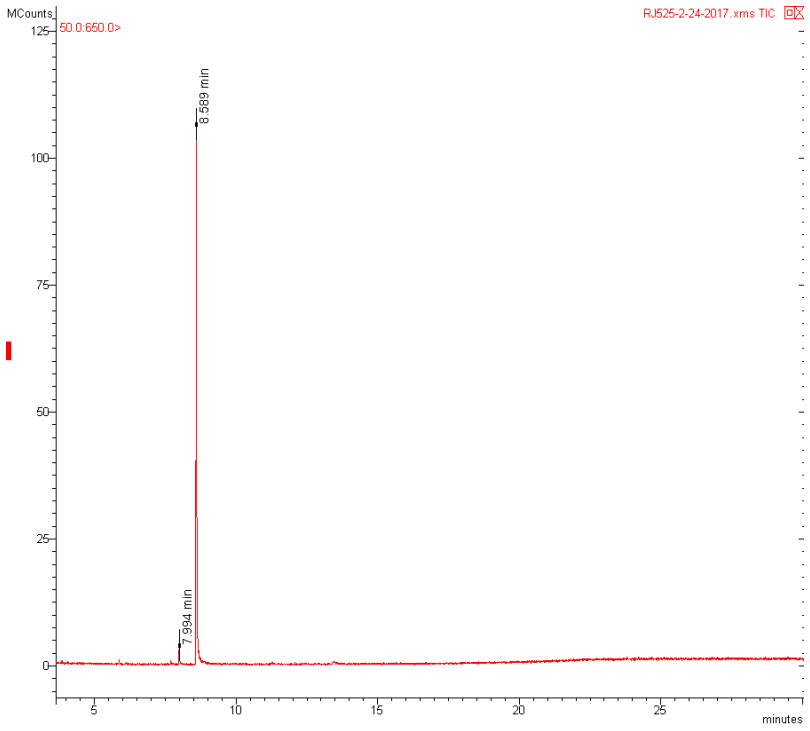


**GC Analysis:**




## 3. General procedure for synthesis of bifunctional silanes

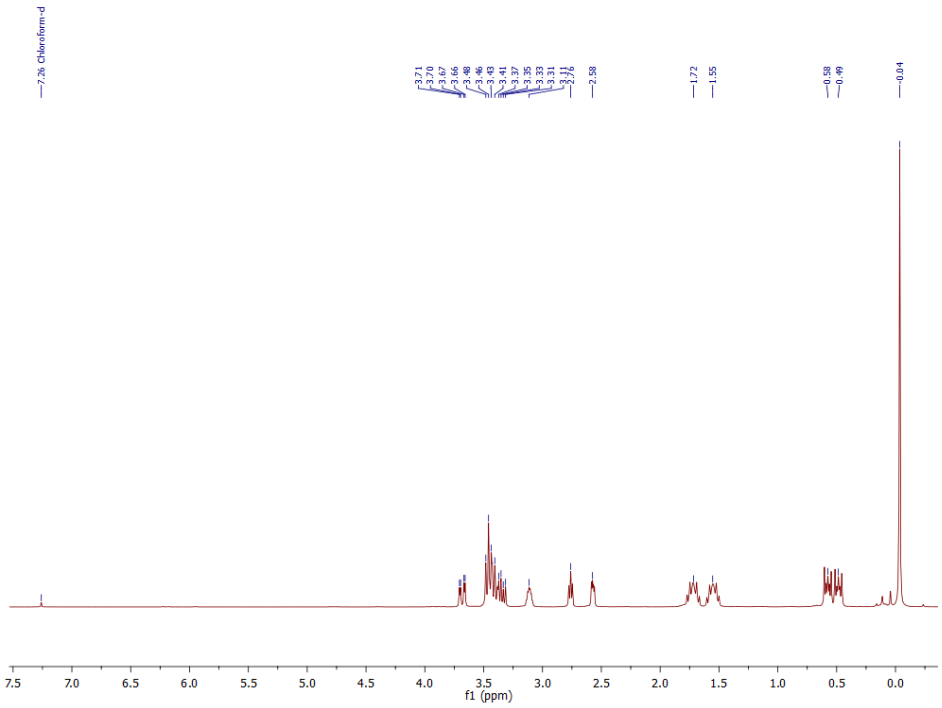
To a mixture containing 1.8 mmol of silane (**1-3**) and 2 mL of toluene and appropriate amount of alkene was added and mixture was heated at 90$^{o}$C, then catalyst was added. Reaction was monitored by *in-situ* FTIR spectroscopy by following the band assigned to the H-Si group (~ 880 $cm^{-1}$) After total disappearance of the H-Si peak GC analysis was performed in order to confirm total consumption of reagents. Then, the reaction mixture was cooled to room temperature and excess of alkene and toluene were evaporated in vacuum. Then obtained liquids were dissolved in methylene chloride and filtered through silica to separate the catalyst. Evaporation of solvent gave pure products with yield in the range from 91% to 97%. For catalytic tests with allyl methacrylate reactions were performed at 40$^{o}$C in THF. Distributions of the products were calculated on the basis of GC-MS analysis.

### 3.1. Analytical data for silane **4**

Yield (93%) **$^{1}$H NMR** ($CDCl_3$, 298K, δ): 3.68 (dd, 1H CHO), 3.48-3.31 (m, 5H), 3.11 (m, 1H), 2.76 (t, 1H CH), 2.58 (m, 1H CH), 1.72, 1.56 (m, 4H $CH_2$), 0.58, 0.49 ($SiCH_2$), -0.04 ($SiCH_3$). **$^{13}$C NMR** ($CDCl_3$, 298K, δ): 74.41, 71.54 ($CH_2O$), 50.92, 44.35 ($C_{oxirane}$), 48.14 ($CH_2Cl$), 27.69,

24.07 ($CH_2$), 12.87, 11.02 ($SiCH_2$), -3.53 ($SiCH_3$), **$^{29}$Si NMR** ($CDCl_3$, 298K, δ): 3.28, **MS (EI, m/z):** 143.1 (7.9), 135.1 (10.8), 131.1 (9.3), 123.1 (6.9), 121.0 (19.3), 115.1 (5.3), 102.2 (7.5), 101.1 (80.2), 95.1 (37.3), 94.1 (8.0), 93.0 (100), 75.1 (10.2), 59.1 (15.5), 57.2 (5.6).

**$^{1}$H NMR:**

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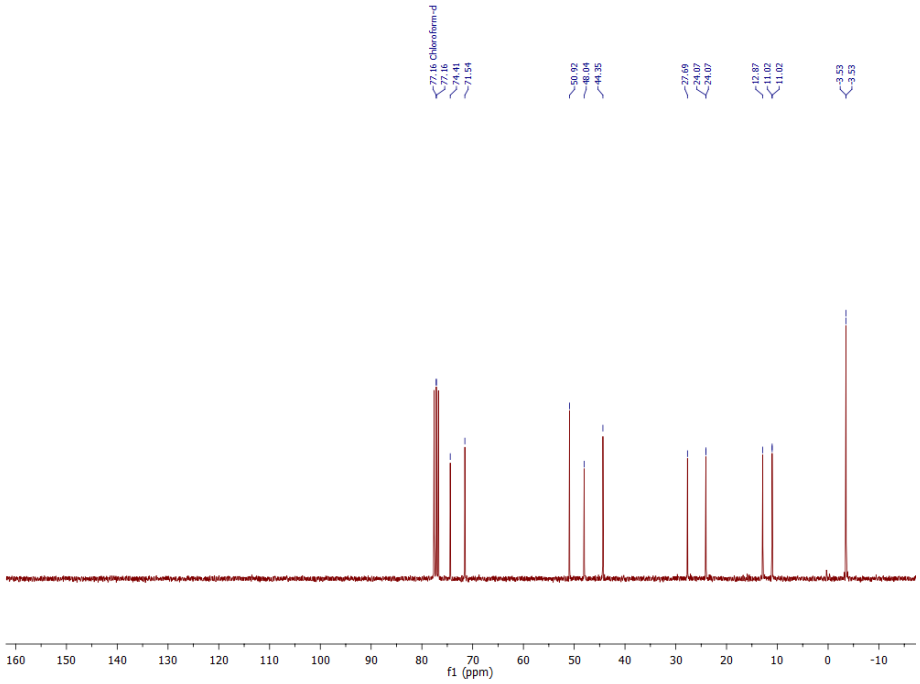
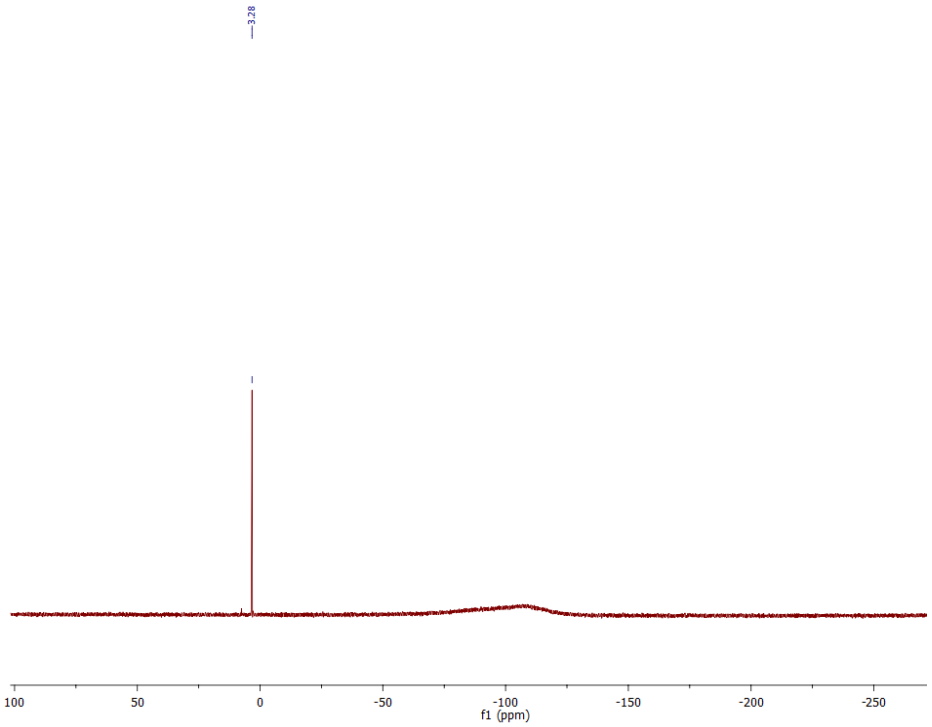
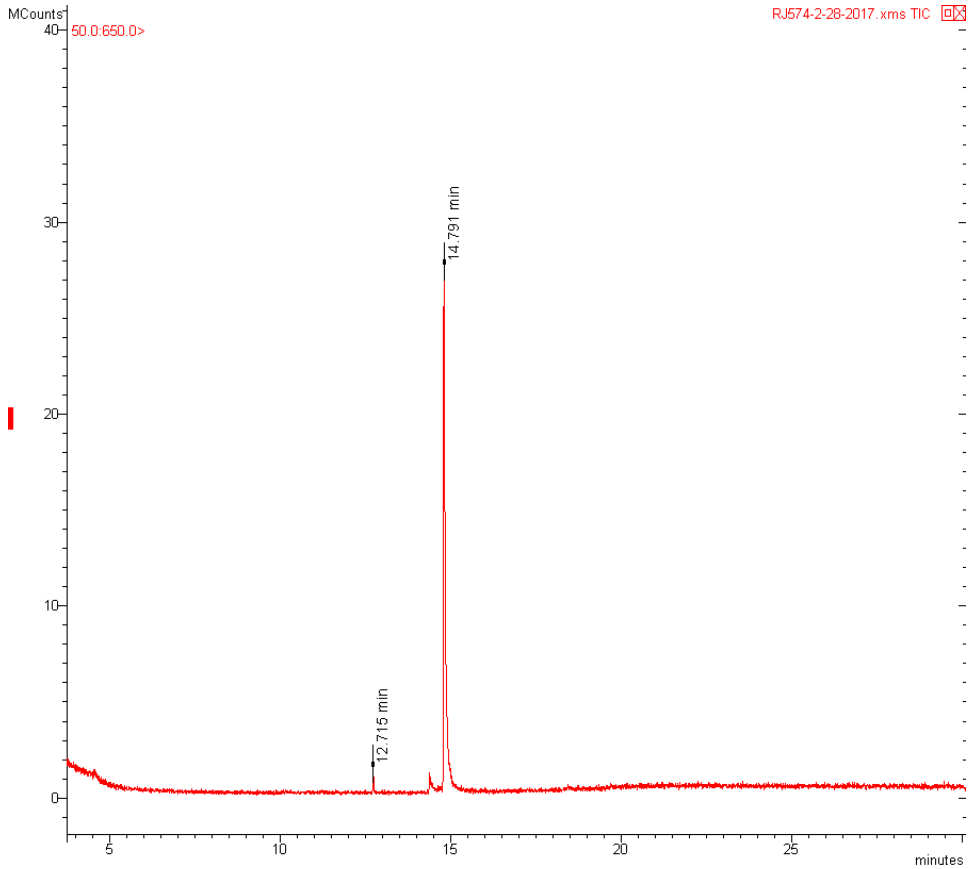


## $^{29}$Si NMR:



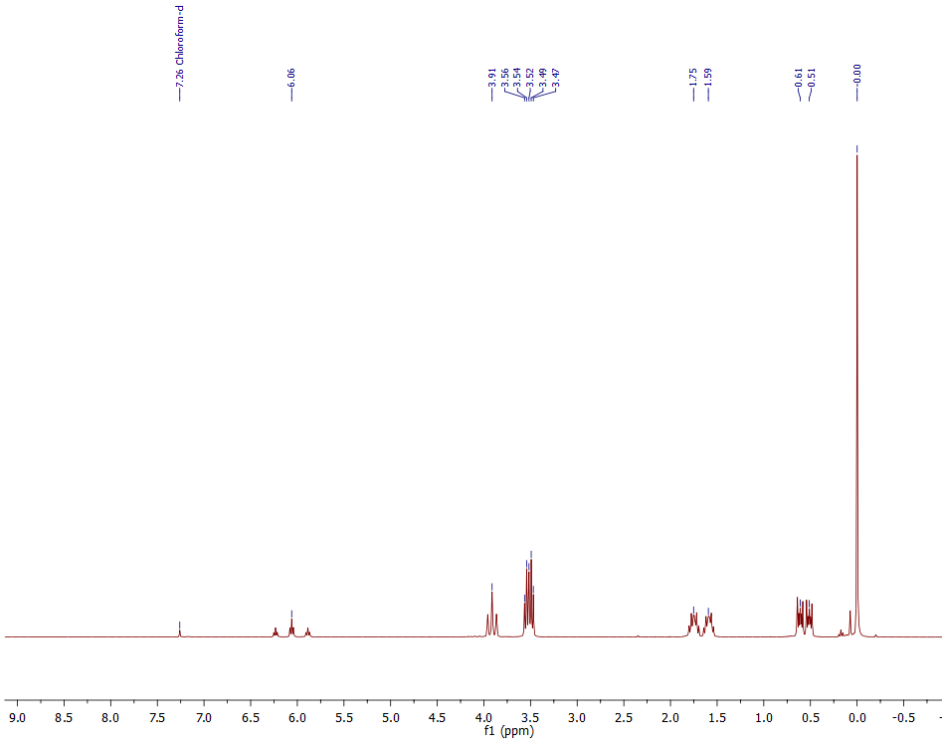

## GC analysis:



3.2. Analytical data for silane **5**

Yield 95%. **$^{1}$H NMR** ($CDCl_3$, 298K, δ): 6.06 (tt, 1H $HCF_2$), 3.91 (t, 2H $CH_2O$), 3.56-3.45 (m, 4H, $CH_2O$, $CH_2Cl$), 1.75, 1.58 ($CH_2$), 0.61, 0.51 (m, 4H $SiCH_2$), 0.00 (s, 6H $SiCH_3$). **$^{13}$C NMR** ($CDCl_3$, 298K, δ): 115.80-104.43 ($CF_2$, $HCF_2$), 76.01 ($CH_2O$), 67.67 ($CH_2O$), 47.95 ($CH_2Cl$), 27.73, 23.97 ($CH_2$), 12.87, 10.84 ($SiCH_2$), -3.58 ($SiCH_3$). **$^{29}$Si NMR** ($CDCl_3$, 298K, δ): 3.34, **MS** (EI, m/z): 193.1 (6.5), 145.1 (30.6), 137.1 (10.0), 135.1 (30.1), 97.1 (25.9), 95.1 (48.5), 94.1 (7.1), 93.0 (100), 77.1 (45.7), 51.1 (12.2).

**$^{1}$H NMR:**



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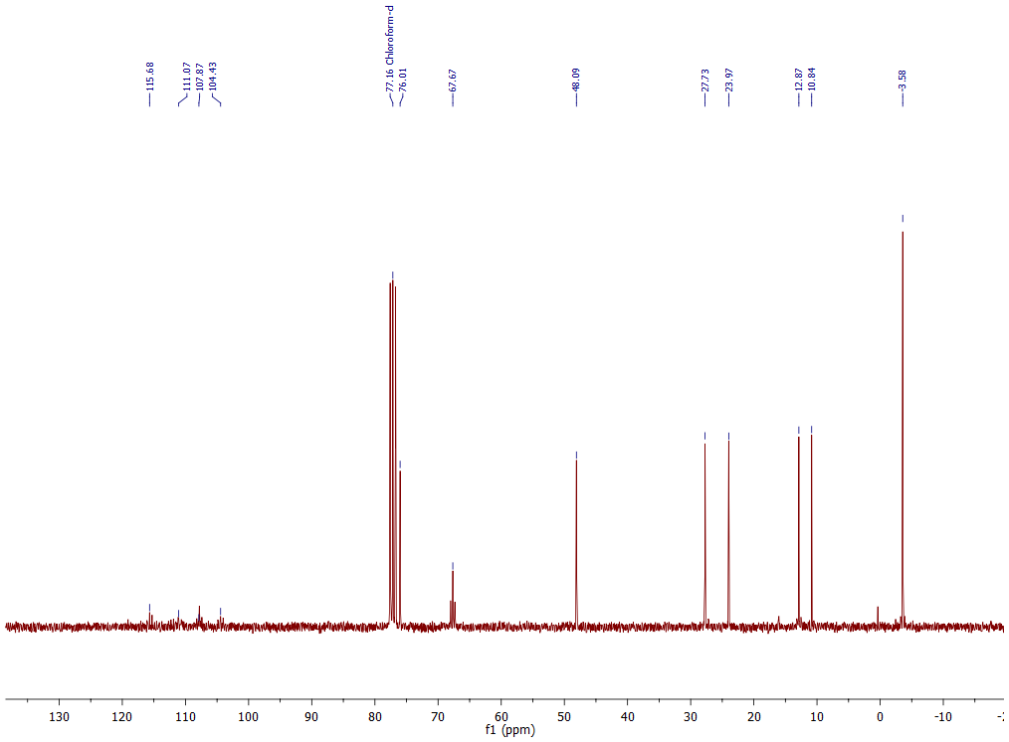


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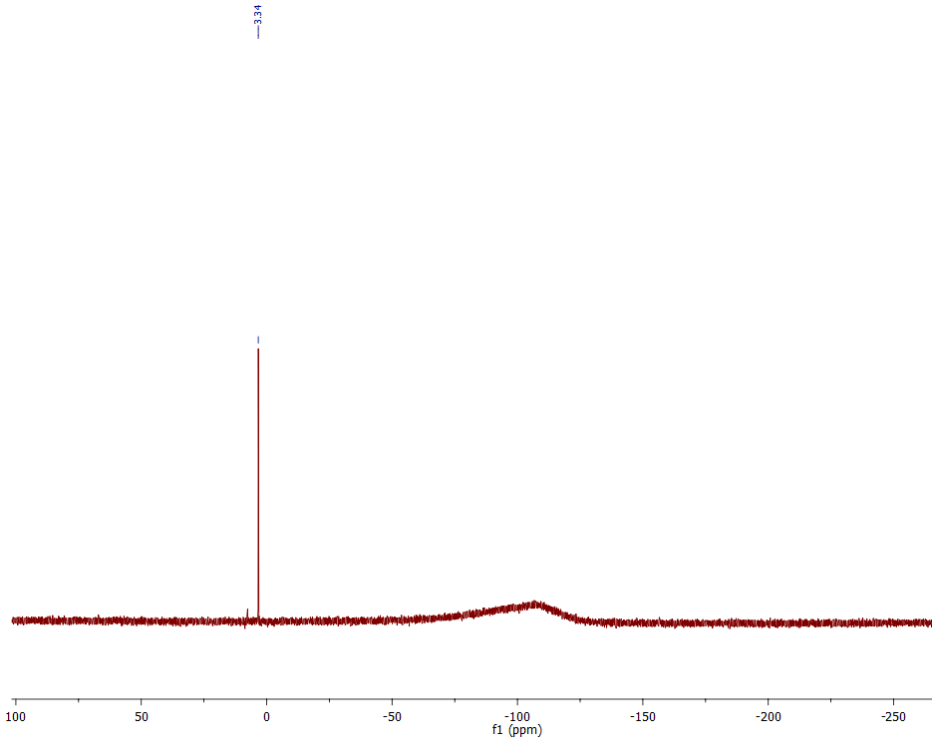
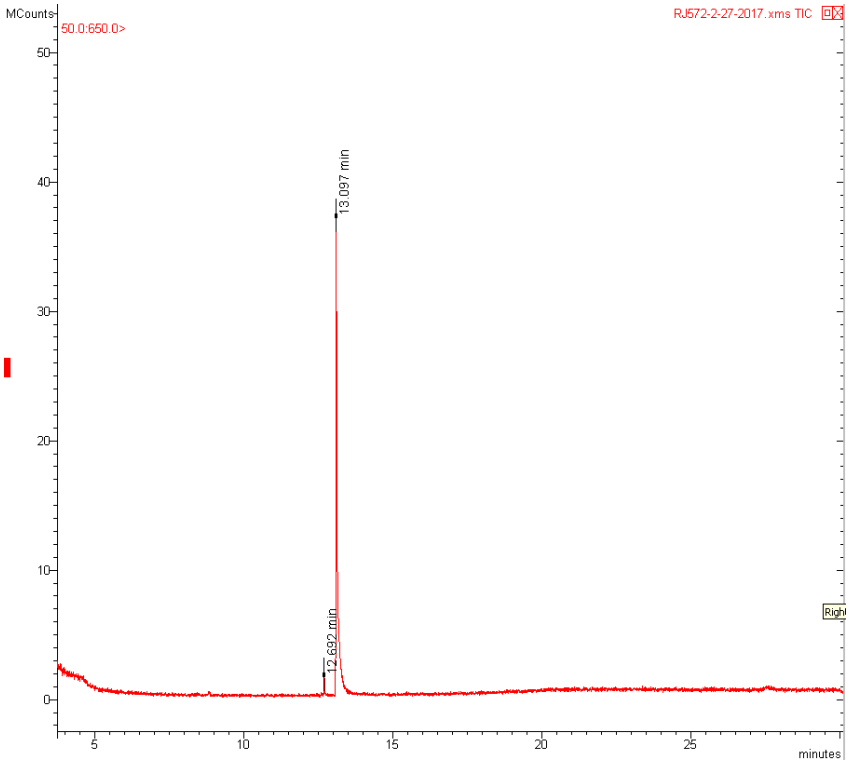


## GC analysis: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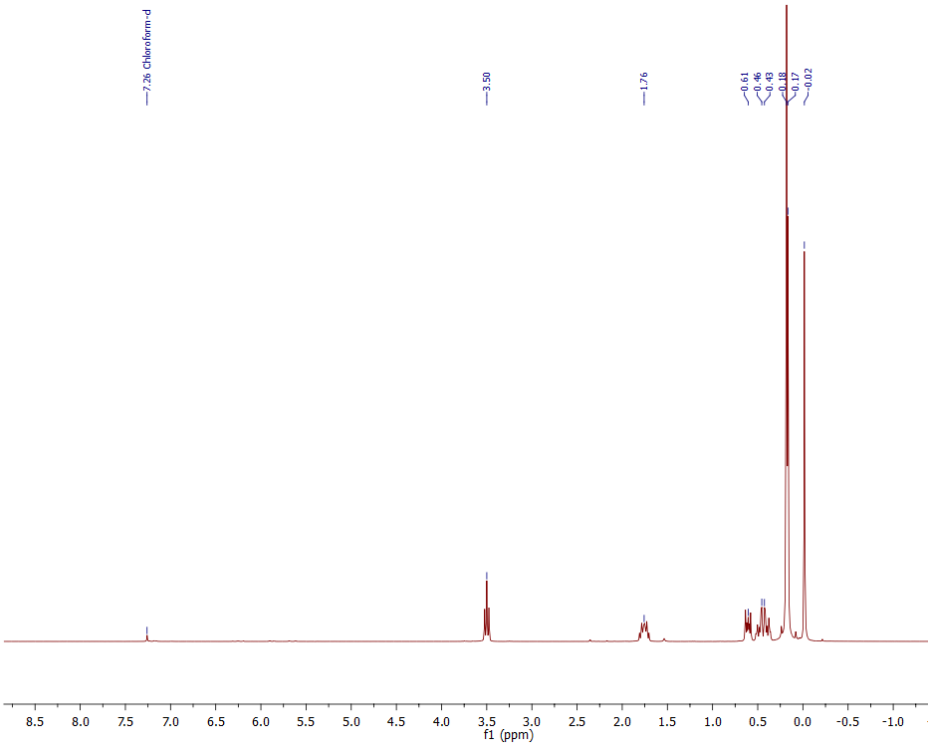
minutes

3.3. Analytical data for silane **6**

Yield 93%. **$^{1}$H NMR** ($CDCl_3$, 298K, δ): 3.50 (t, 2H $CH_2Cl$, 1.76 (m, 2H $CH_2$), 0.61, 0.50-0.38 (m, 6H $SiCH_2$), 0.18, 0.17, -0.02 (30H $SiCH_3$). **$^{13}$C NMR** ($CDCl_3$, 298K, δ): 48.19 ($CH_2Cl$), 27.91 ($CH_2$), 12.67, 12.62, 7.50 ($SiCH_2$), 5.75, 3.21, -3.83 ($SiCH_3$). **$^{29}$Si NMR** ($CDCl_3$, 298K, δ): 4.85, 4.39, 2.29 **MS (EI, m/z):** 220.3 (11.0), 219.3 (21.3), 218.3 (100), 216.2 (5.5), 202.2 (7.6), 135.1 (10.1), 130.1 (12.9), 95.1 (9.6), 93.1 (26.2), 73.2 (5.8).

**$^{1}$H NMR:**



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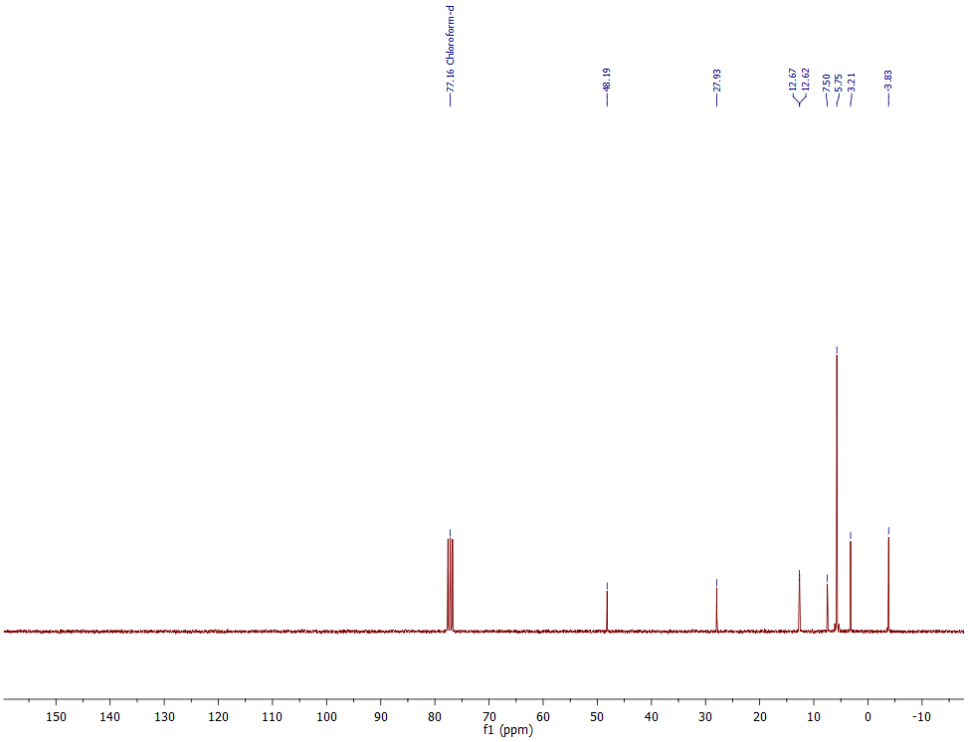


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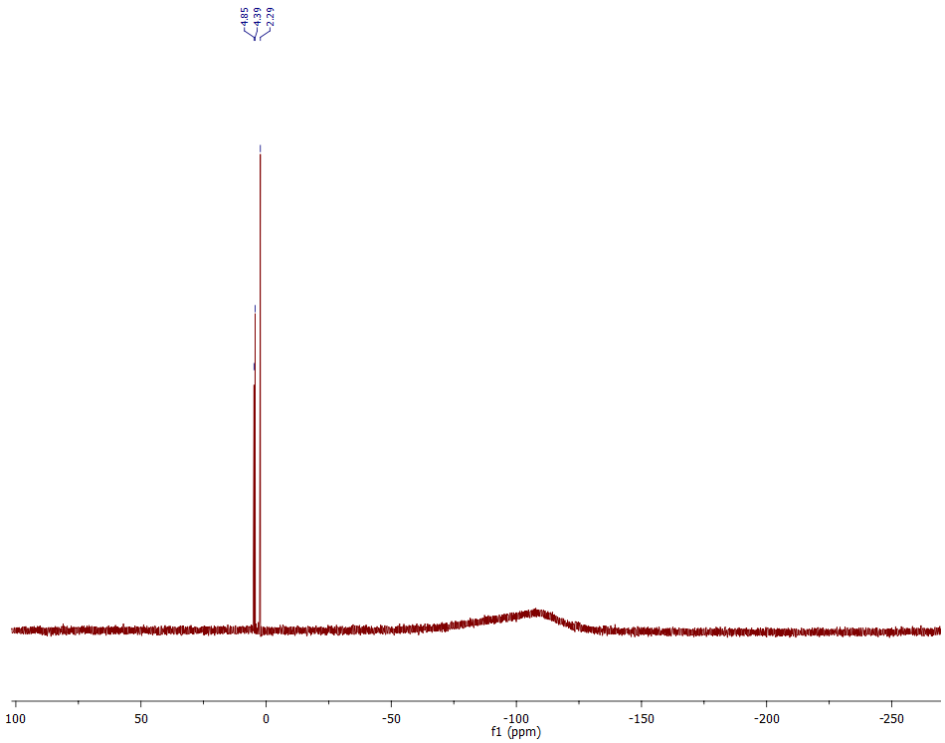

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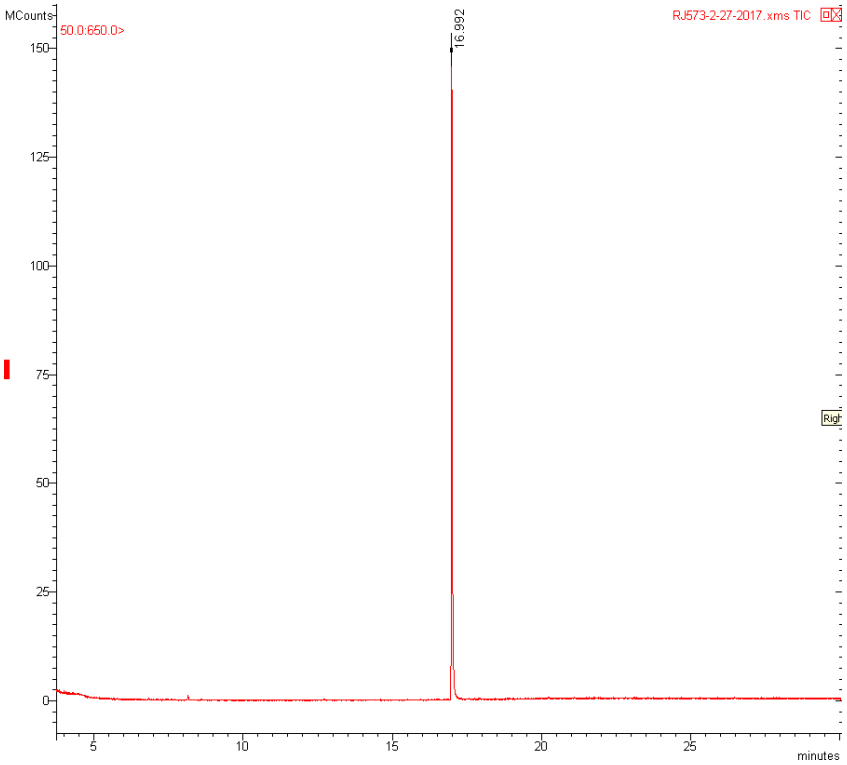
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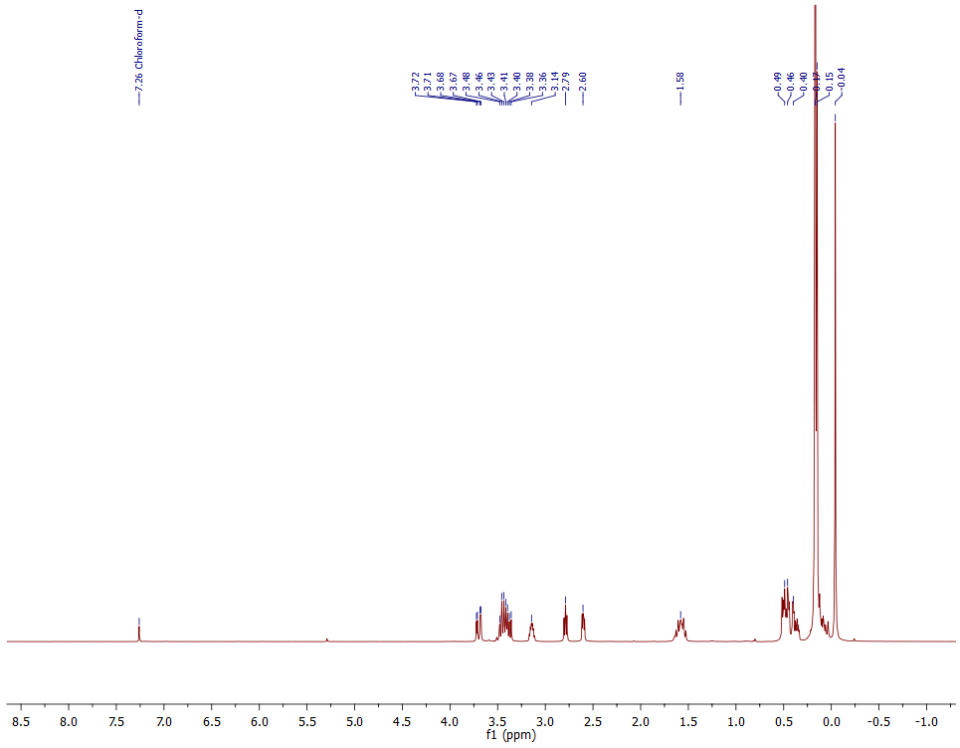
minutes

3.4. Analytical data for silane **7**

Yield 91%. **$^{1}$H NMR** ($CDCl_3$, 298K, δ): 3.91 3.70 (1H, dd CHO), 3.51-3.36 (m, 3H CHO), 3.13 (m, 1H CHO), 2.79 (t, 1H CH), 2.60 (m, 1H CH), 1.58 (m, 2H $CH_2$), 0.52-0.39 (m, 6H $SiCH_2$), 0.17, 0.15, -0.04 (30H Si-$CH_3$). **$^{13}$C NMR** ($CDCl_3$, 298K, δ): 74.73 ($CH_2O$), 71.57 ($CH_2O$), 51.02, 44.49 (C-$O_{oxirane}$), 24.26 ($CH_2$), 12.69, 10.76, 7.53 (Si-$CH_2$), 5.72, 3.18, -3.84 (Si-$CH_3$); **$^{29}$Si NMR** ($CDCl_3$, 298K, δ): 4.88, 4.52, 2.23, **MS** (EI, m/z): 220.3 (10.0), 219.3 (16.7), 218.3 (73.1), 216.2 (15.7), 202.2 (15.7), 188.1 (6.3), 174.2 (9.2), 173.2 (59.3), 146.2 (5.0), 144.2 (8.6), 143.2 (59.4), 131.1 (61.8), 130.1 (26.6), 115.1 (6.5), 102.2 (9.2), 101.1 (100), 100.0 (7.9), 75.2 (14.2), 73.2 (15.9), 59.1 (18.8).

**$^{1}$H NMR:**



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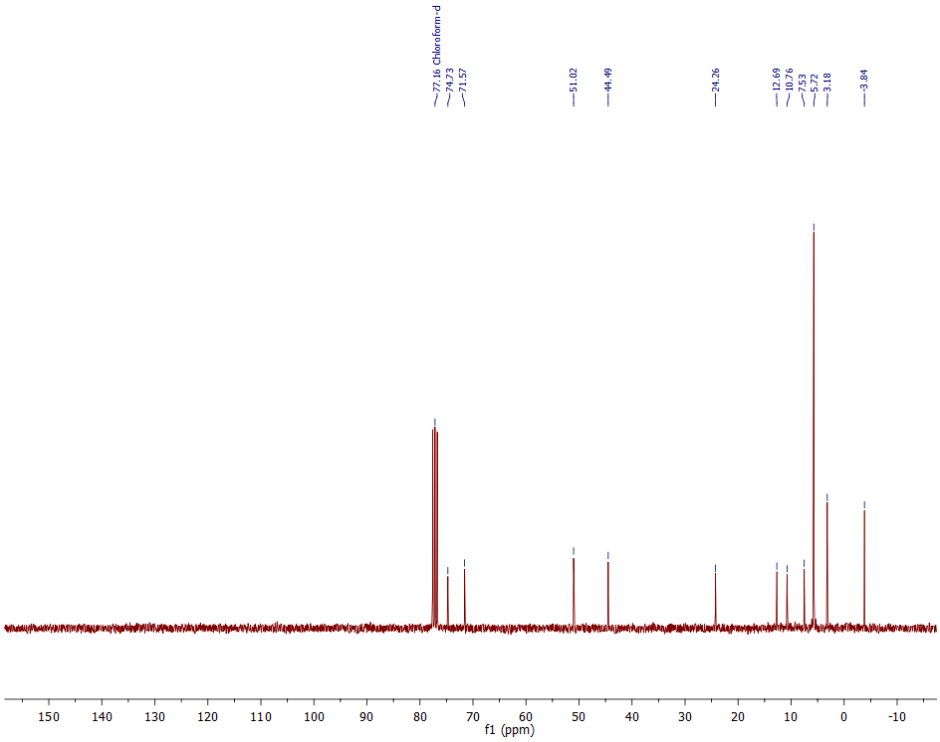


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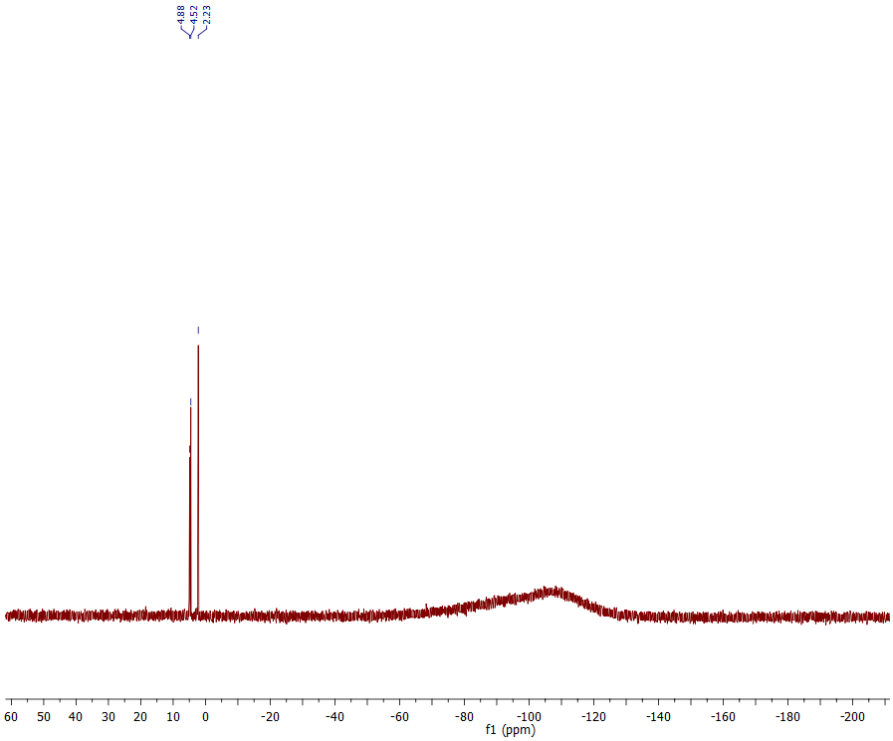

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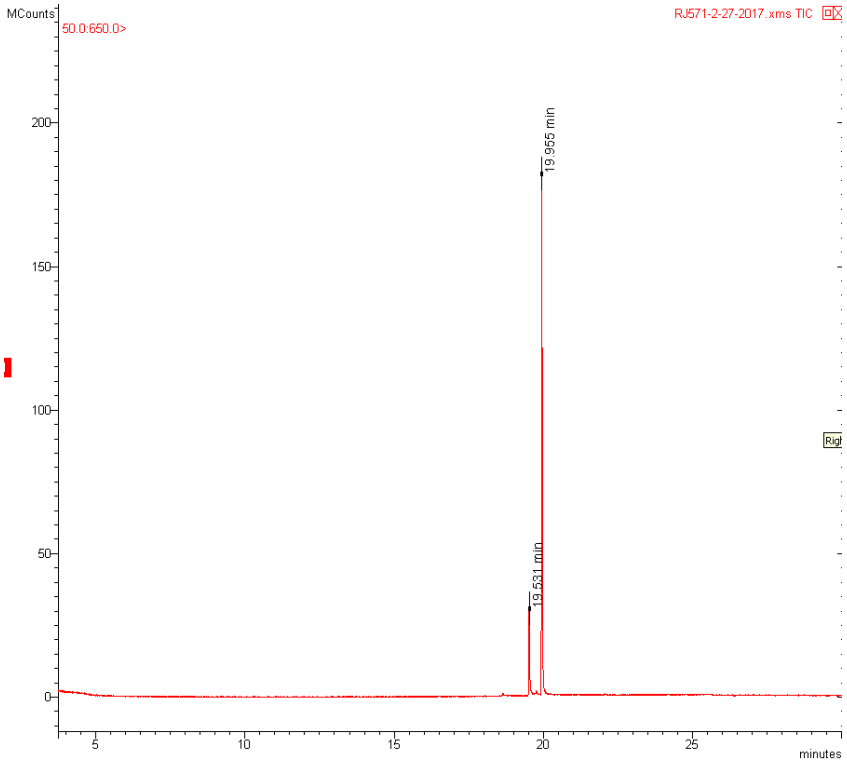
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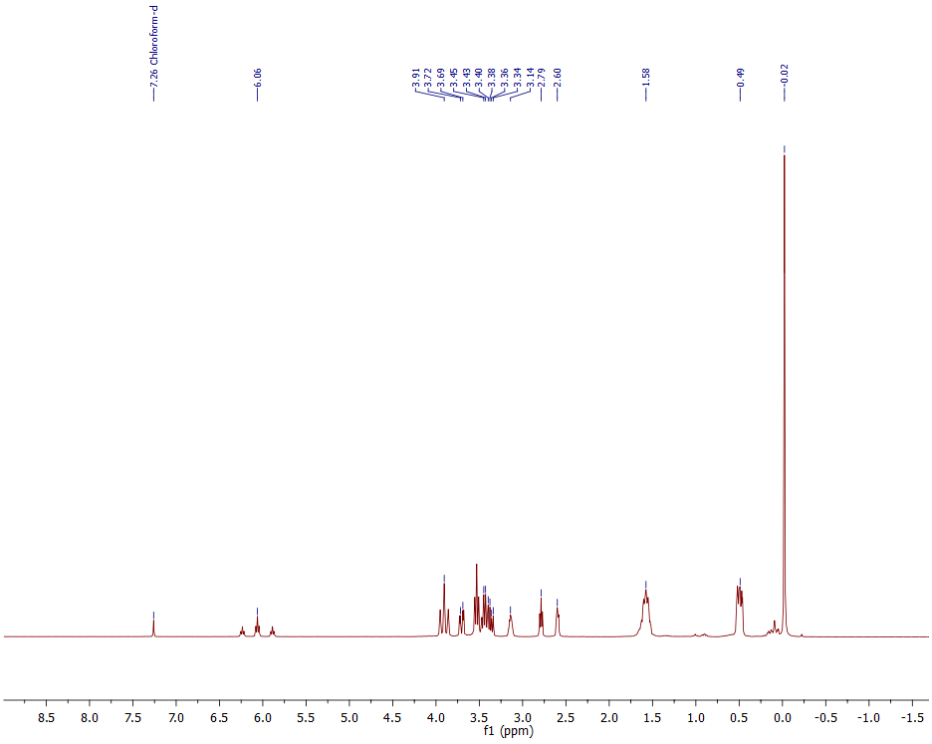
minutes

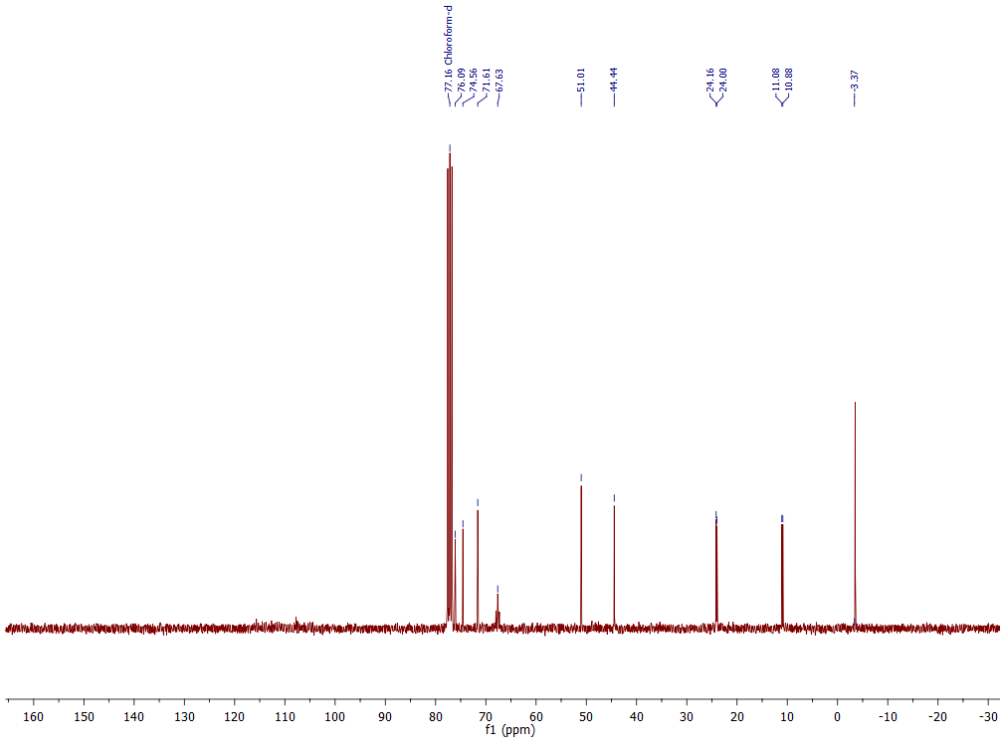
3.5. Analytical data for silane **8**

Yield 97%.**$^{1}$H NMR** ($CDCl_3$, 298K, δ): 6.06 (tt, 1H $F_2CH$), 3.91 (t, 2H $OCH_2$), 3.70 (1H, dd CHO), 3.53 (t, 2H $CH_2O$), 3.47-3.34 (m, 3H CHO), 3.14 (m, 1H CHO), 2.97 (t, 1H CH), 2.60 (m, 1H CH), 1.98 (m, 4H $CH_2$), 0.49 (m, 4H $SiCH_2$), 0.02 (s, 6H Si-$CH_3$). **$^{13}$C NMR** ($CDCl_3$, 298K, δ): 115.67, 112.66, 107.78, 104.43 ($CF_2$, $HCF_2$), 76.09, 74.56, 71.61, 67.63 ($CH_2O$), 51.01, 44.44 (C-$O_{oxirane}$), 24.16, 24.00 ($CH_2$), 11.08, 10.88 ($SiCH_2$), 3.51 ($SiCH_3$), **$^{29}$Si NMR** ($CDCl_3$, 298K, δ): 3.43, **MS (EI, m/z):** 331.2 (12.9), 193.1 (10.9), 145.1 (33.8), 143.1 (19.3), 131.1 (19.5), 115.2 (6.1), 105.0 (10.7), 103.1 (6.1), 102.1 (9.6), 101.1 (100), 99.1 (5.8), 97.1 (23.4), 95.1 (11.7), 77.1 (59.2), 75.2 (11.0), 59.1 (15.9), 57.2 (6.3), 51.0 (5.0).

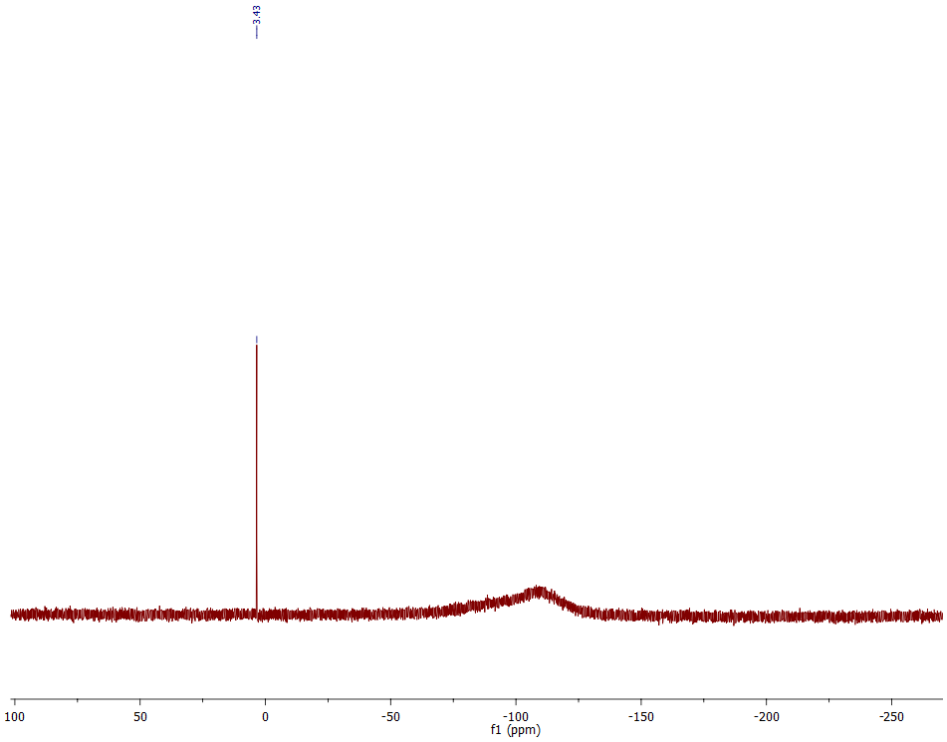
**$^{1}$H NMR:**



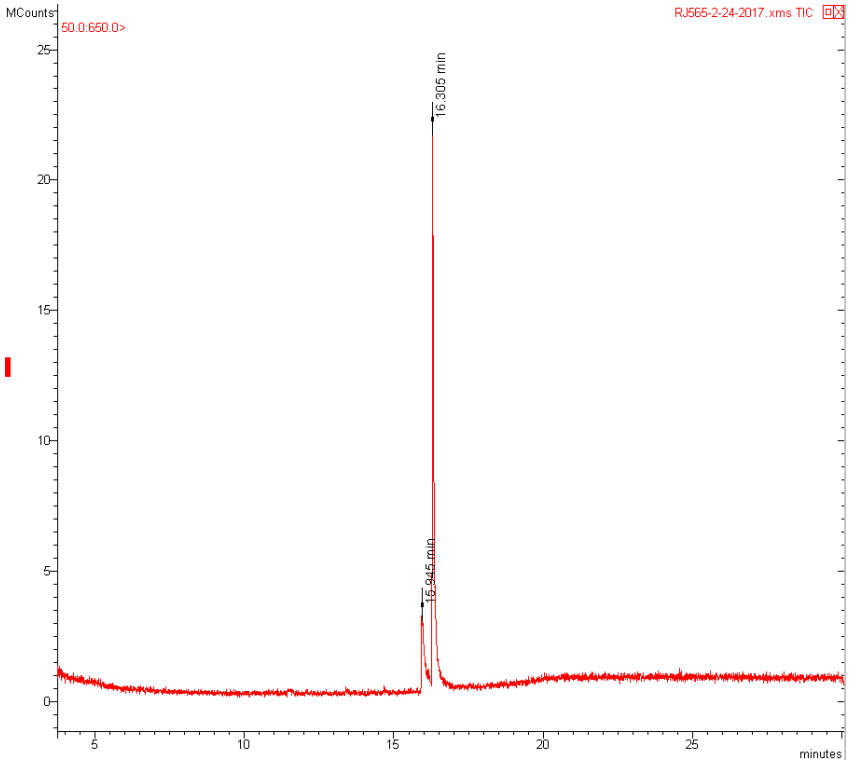
**$^{13}$C NMR:**




**$^{29}$Si NMR:**



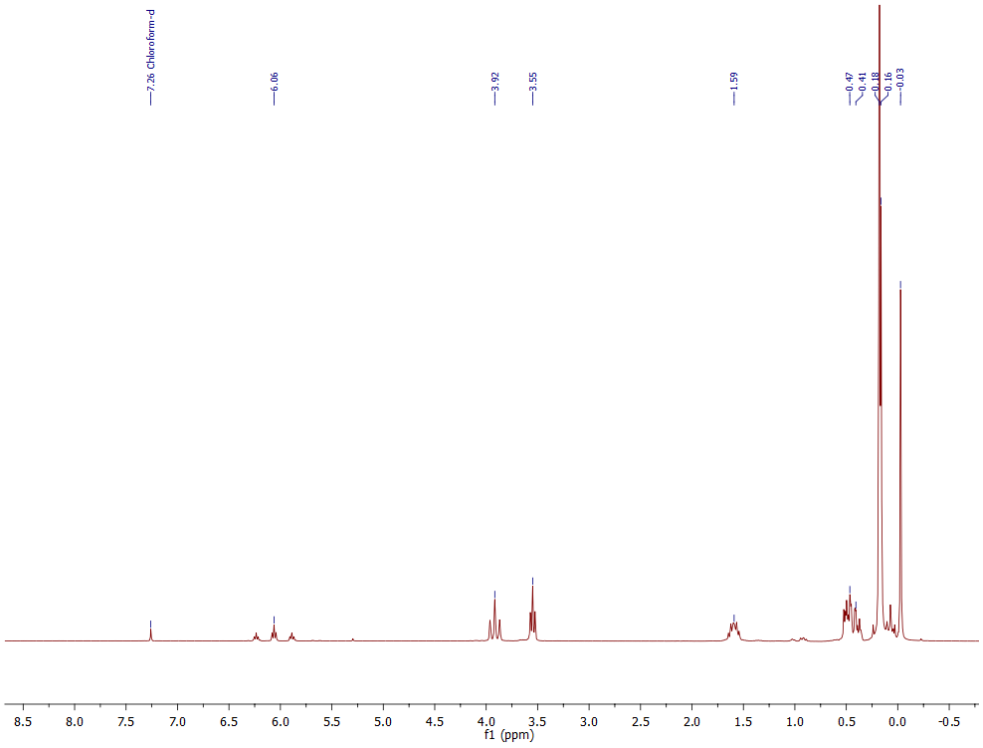
## GC analysis:


MCounts
50.0:650.0>
RJ565-2-24-2017.xms TIC
16.305 min
15.945 min
25
20
15
10
5
0
5
10
15
20
25
minutes

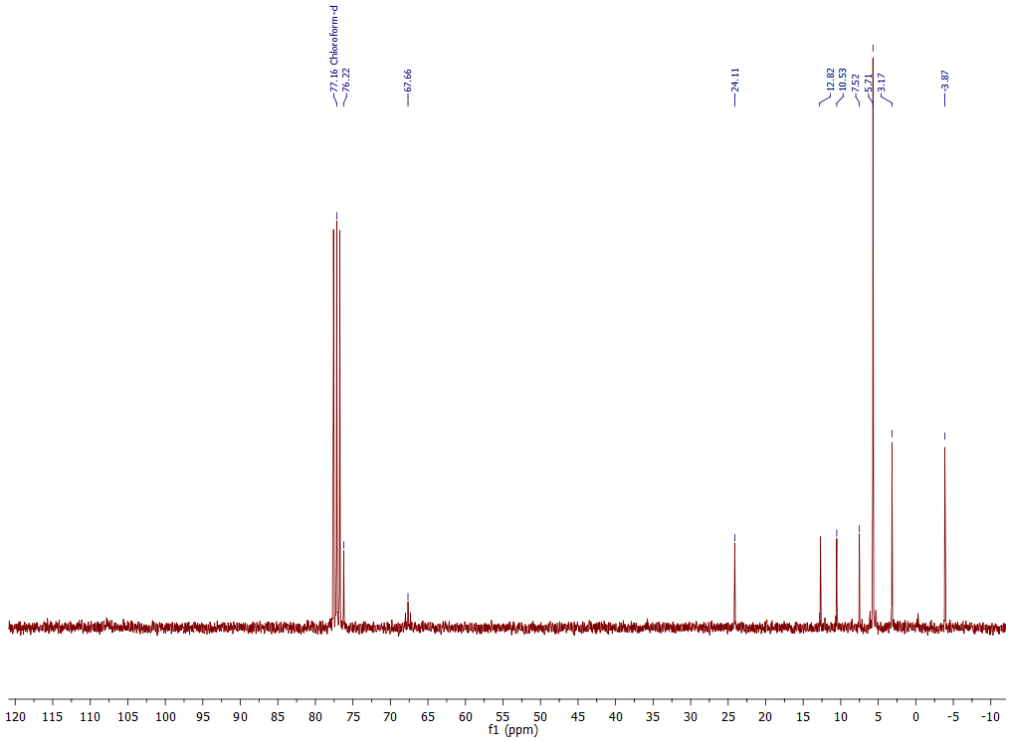
3.6. Analytical data for silane **9**

Yield 92%. **$^{1}$H NMR** ($CDCl_3$, 298K, δ): 6.06 (tt, 1H $HCF_2$), 3.92 (t, 2H $CH_2O$), 3.55 (t, 2H, $CH_2O$), 1.60 (m, 2H $CH_2$), 0.52-0.37 (m, 6H $SiCH_2$), 0.18, 0.16, -0.03 (30H $SiCH_3$), **$^{13}$C NMR** ($CDCl_3$, 298K, δ): 115.76-104 ($CF_2$, $HCF_2$), 76.22 ($CH_2O$), 67.66 ($CH_2O$), 24.11 ($CH_2$), 12.70, 10.53, 7.52 ($SiCH_2$), 5.71, 3.17, -3.87 ($SiCH_3$), **$^{29}$Si NMR** ($CDCl_3$, 298K, δ): 4.87, 4.52, 2.27, **MS (EI, m/z)**: 322.3 (5.8), 331.2 (37.3), 220.3 (12.6), 219.3 (22.3), 218.2 (100), 216.2 (12.7), 202.2 (12.2), 193.1 (9.9), 145.1 (29.3), 130.1 (16.6), 100.1 (5.9), 97.1 (24.9), 95.1 (5.6), 77.1 (42.9), 73.2 (10.5).

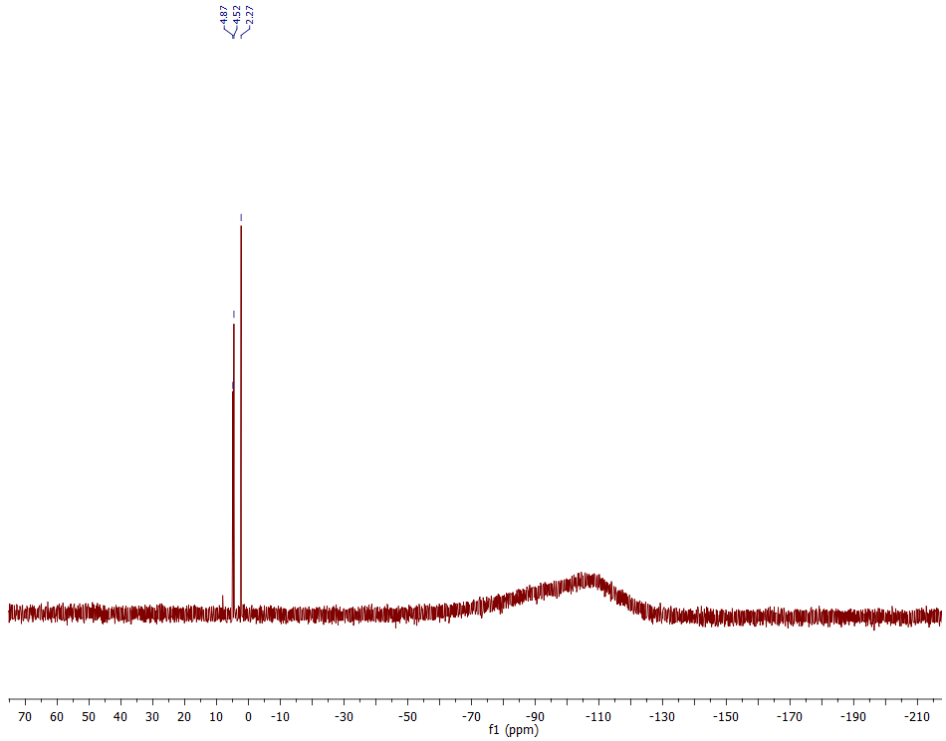
**$^{1}$H NMR:**



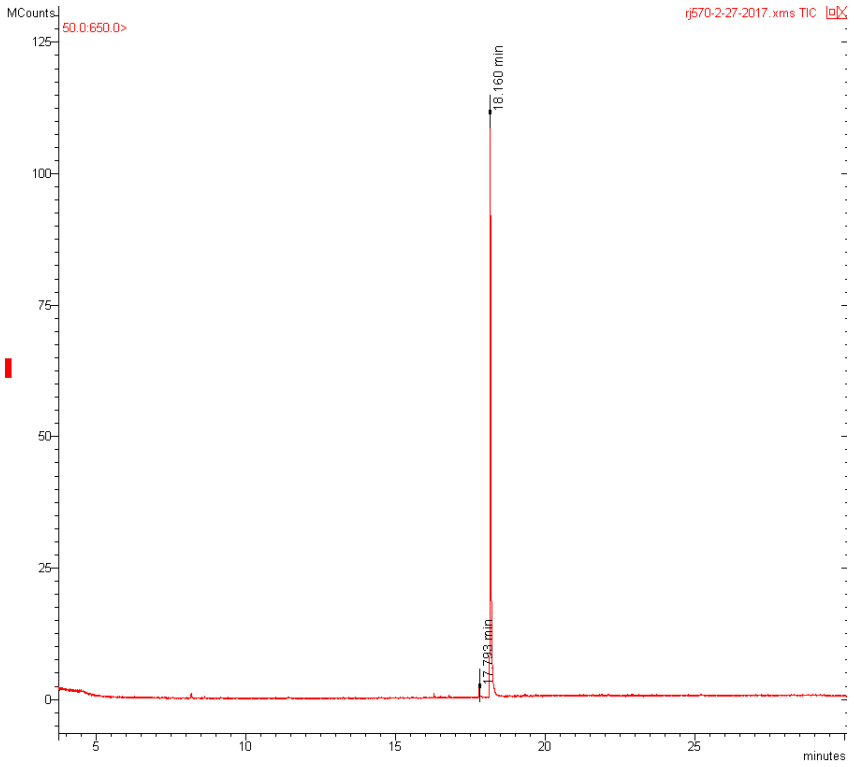
**$^{13}$C NMR:**




**$^{29}$Si NMR:**



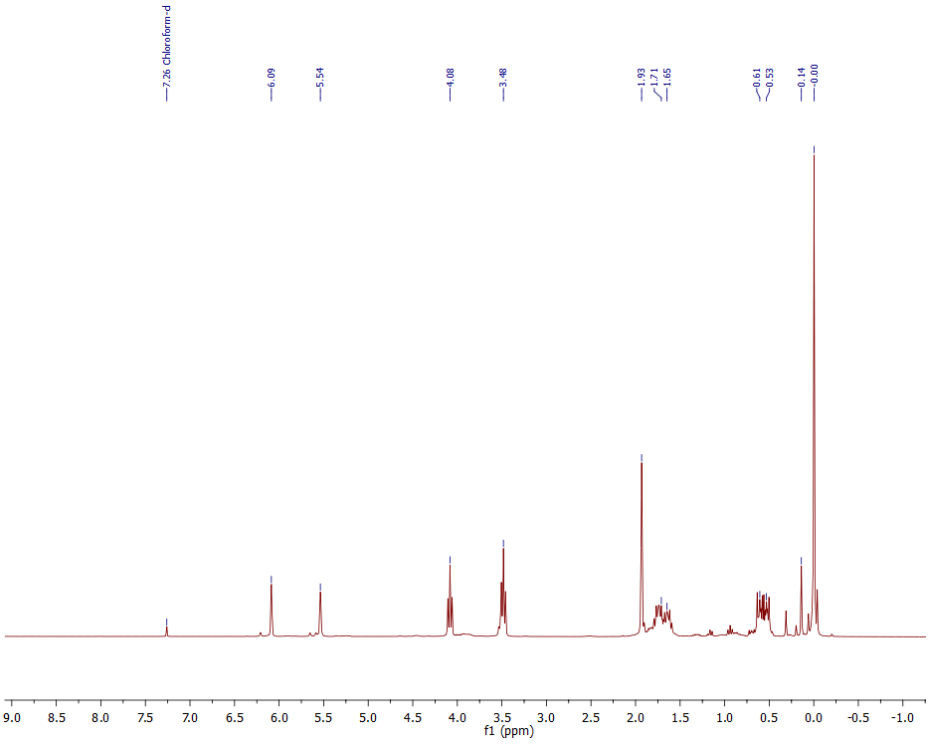
## GC analysis:


MCounts
50.0:650.0>
rj570-2-27-2017.xms TIC
125
100
75
50
25
0
18.160 min
17.793 min
5
10
15
20
25
minutes

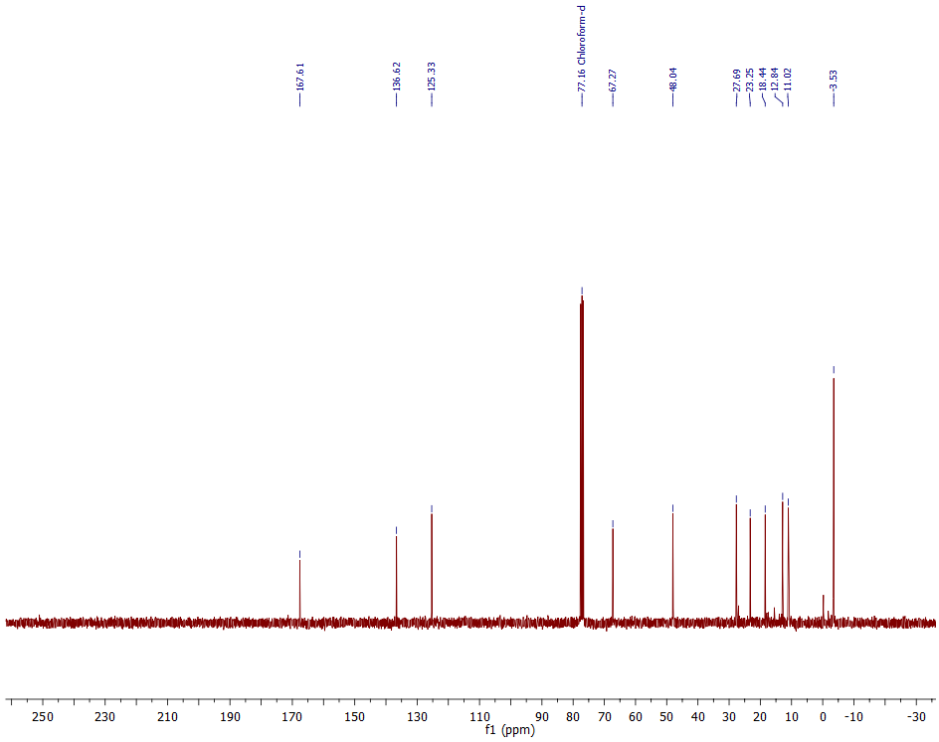
3.7. Analytical data for silane **10** (**A** + **B**)

Yield 92%. **$^{1}$H NMR** ($CDCl_3$, 298K, δ): 6.09, 5.54 (s, 2H $CH_2$=C), 4.08 (t, 2H $CH_2O$), 3.48 ($CH_2Cl$), 1.93 (s, 3H $CH_3$), 1.74, 1.65 (m, 4H $CH_2$), 0.61, 0.53 (m, 4H $SiCH_2$), 0.00 (s, 6H $SiCH_3$). **$^{13}$C NMR** ($CDCl_3$, 298K, δ): 167.61 (C=O), 136.62, 125.33 (C=C), 67.77 ($CH_2O$), 48.04 ($CH_2Cl$), 27.69, 23.25 ($CH_2$), 18.44 ($CH_3$), 12.84, 11.02 ($SiCH_2$), -3.53 ($SiCH_3$), **$^{29}$Si NMR** ($CDCl_3$, 298K, δ): 3.31 (**A**), 17.25 (**B**) **MS (EI, m/z):** 185.1 (7.5), 163.1 (7.7), 144.2 (5.2), 143.1 (46.7), 137.1 (5.2), 135.1 (14.8), 95.0 (35.1), 94.0 (8.1), 93.1 (100), 69.2 (69.7).

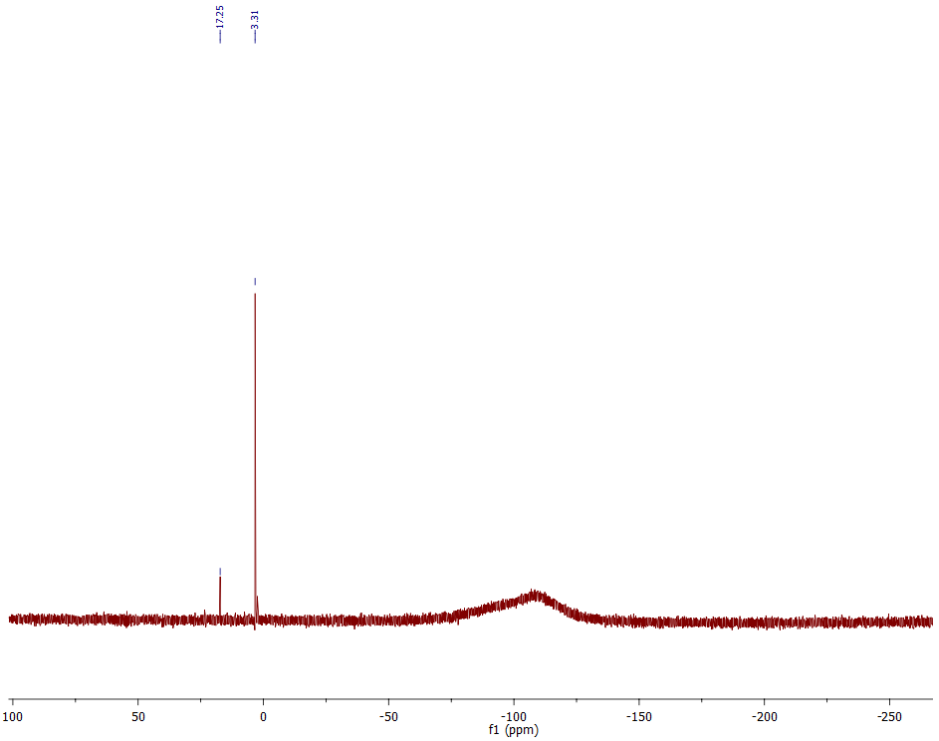
**$^{1}$H NMR:**



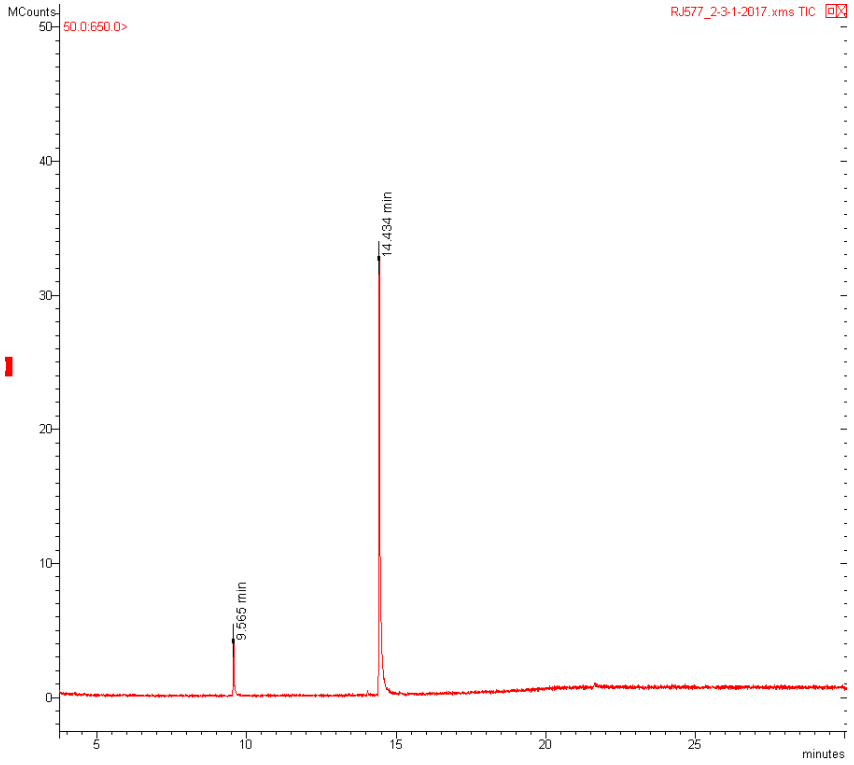
**$^{13}$C NMR:**




**$^{29}$Si NMR:**



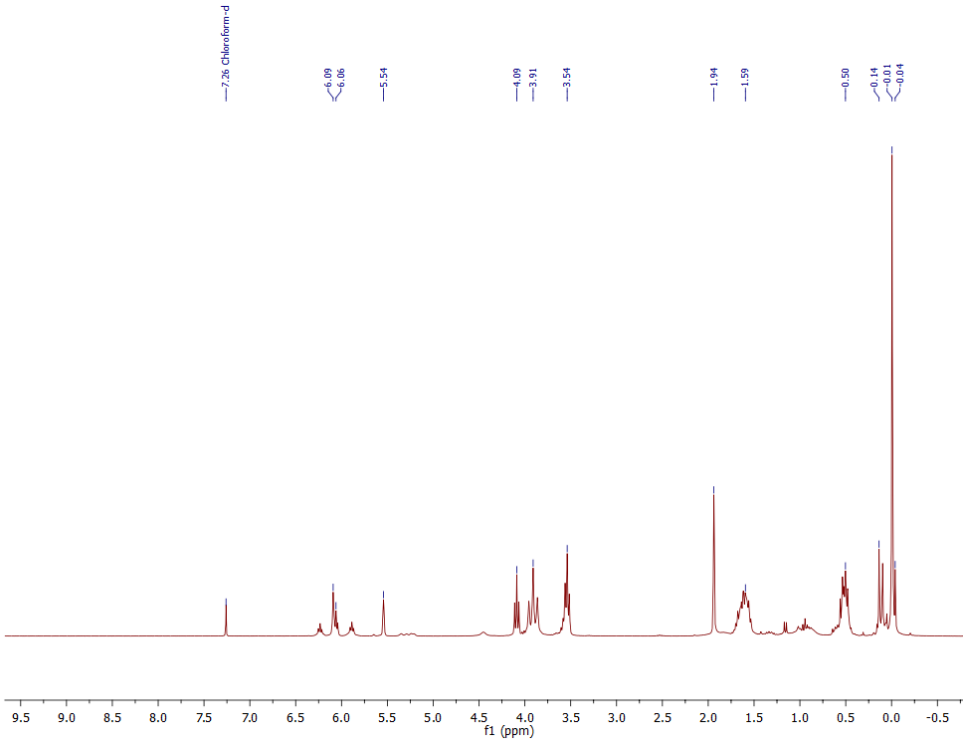
## GC analysis:


MCounts
50.0:650.0>
RJ577_2-3-1-2017.xms TIC
50
40
30
20
10
0
9.565 min
14.434 min
5
10
15
20
25
minutes

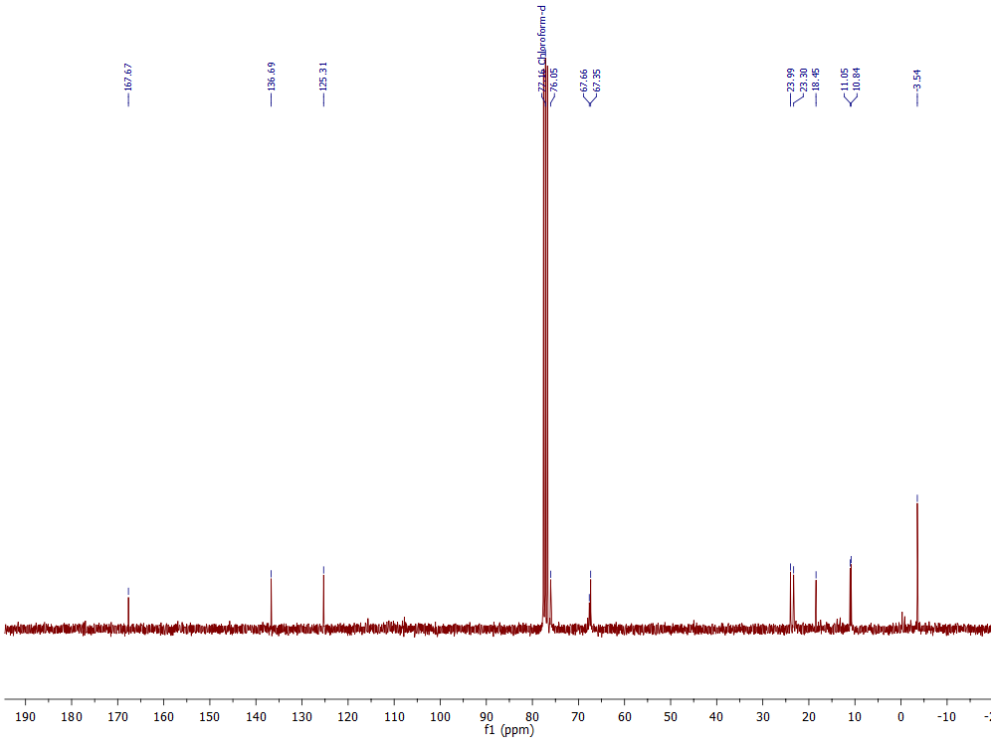
3.8. Analytical data for silane **11** (**A** + **B**)

Yield 93%. **$^{1}$H NMR** ($CDCl_3$, 298K, δ): 6.09, 5.54 (s, 2H $CH_2$=C), 6.06 (tt, 1H $HCF_2$), 4.09, 3.91, 3.54 (t, 6H $CH_2O$), 1.94 (s, 3H $CH_3$), 1.62 (m, 4H –$CH_2$-), 0.5 (m, 4H $SiCH_2$), 0.01 (s, 6H $SiCH_3$), **$^{13}$C NMR** ($CDCl_3$, 298K, δ): 167.67 (C=O), 136.69, 125.31 ($CH_2$=C), 76.05, 67.66, 67.35 ($CH_2O$), 23.99, 23.30 (-$CH_2$-), 18.45 ($CH_3$), 11.05, 10.84 (Si-$CH_2$), -3.54. **$^{29}$Si NMR** ($CDCl_3$, 298K, δ): 3.44 (**A**) , 17.73 (**B**) **MS (EI, m/z):** 331.2 (15.3), 193.1 (11.0), 185.2 (27.5), 147.0 (15.0), 145.1 (34.6), 144.1 (9.1), 143.1 (83.7), 101.2 (5.7), 99.1 (7.2), 97.1 (28.4), 95.1 (11.1), 78.2 (8.8), 77.1 (84.3), 69.2 (100), 61.2 (7.1), 59.1 (5.2).

**$^{1}$H NMR:**



**$^{13}$C NMR:**




**$^{29}$Si NMR:**