Supporting Information For:

Synthesis of $SiCl_4$ from Gaseous HCl and $Si(OMe)_4$: Reaction Development and Kinetic Studies

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General Information:

All reactions were carried out under a nitrogen atmosphere with magnetic stirring unless otherwise stated. All reagents were purchased from Aldrich and used as received unless otherwise stated. Proton-decoupled ^{13}C-NMR spectra were recorded on a Varian Inova 400 spectrometer with a ^{13}C operational frequency of 100 MHz and are reported in ppm using solvent as an internal standard ($CDCl_3$ at 77.16 ppm and C_6D_6 at 128.6 ppm). ^{29}Si NMR spectra were recorded on Varian Mercury 400, Varian Inova 400 and Agilent DD2 500 NMR spectrometers with a ^{29}Si operational frequencies of 80 and 100 MHz and are reported in ppm using $SiEt_4$ (7.35 ppm) as an internal standard. GCMS work was done on an Agilent 7890A GC with a 5975C MSD attached. An Agilent 190915-433 30 m 250 µm x 0.25 µm LTM column was used. The conditions for the method used were as follows: Oven held constant at 50 ° C, the LTM ran for 1.9 minutes at 50 ° C, then ramped at 140 ° C/min to 200 °C, then held for 4 minutes at 200 ° C for a total run time of 7 minutes.

Experimental Procedures:

General Procedure for Catalyzed Reaction: The reaction was carried out in a 100 mL 2-neck 24/40 round bottom flask. One inlet contained a glass gas sparge tube that was connected to a rotameter, which was in turn connected to an HCl cylinder. The other inlet was connected to a reflux condenser. The condenser was connected to an empty Airfree® bubbler which was cooled to -78 ° C to trap any volatiles that left the reaction mixture. The trap was connected to a manifold under nitrogen, which vented to atmosphere through another bubbler. To a stirred solution of $Si(OMe)_4$ (4 mL, 27.35 mmol, 1 equiv) and acetonitrile (23.4 mL, 437.6 mmol, 16 equiv) was added a catalyst (X g, Y mmol, Z equiv). The reaction mixture was cooled to X' ° C and then HCl gas (X'' sccm) was introduced from the sparge tube. The reaction stirred in this manner for six hours. After six hours the contents of the trap were re-introduced to the flask and an internal standard ($SiEt_4$, 1 mL, 5.29 mmol) was added. An aliquot was taken, diluted with $CDCl_3$, and ^{29}Si and ^{13}C NMR were immediately taken. $SiCl_4$ was not isolated from the reaction mixture.

Optimized Procedure (Table 3, Entry 1): The reaction was carried out in a 100 mL 2-neck 24/40 round bottom flask. One inlet contained a glass gas sparge tube that was connected to a rotameter, which was in turn connected to an HCl cylinder. The other inlet was connected to a reflux condenser. The condenser was connected to an empty Airfree® bubbler which was cooled to -78 ° C to trap any volatiles that left the reaction mixture. The trap was connected to a manifold under nitrogen, which vented to atmosphere through another bubbler. To a stirred solution of $Si(OMe)_4$ (4 mL, 27.35 mmol, 1 equiv) and acetonitrile (23.4 mL, 437.6 mmol, 16 equiv) was added LiCl (0.1 g, 2.735 mmol, 0.1 equiv). The reaction mixture was cooled to 0 ° C and then HCl gas (25 sccm) was introduced from the sparge tube. The reaction stirred in this manner for six hours. After six hours the contents of the trap were re-introduced to the flask and an internal standard ($SiEt_4$, 1 mL, 5.29 mmol) was added. An aliquot was taken, diluted with $CDCl_3$, and ^{29}Si and ^{13}C NMR were immediately taken. Quantitative yield (~99 %) was observed. $SiCl_4$ was not isolated from the reaction mixture.

Kinetics Experiment:

NMR results were integrated directly and exported to excel. It was assumed that tetraethylsilane (TES) did not react and did not significantly volatilize throughout the course of the reactions. Accordingly the integration results were normalized such that the integration value of TES was 1.00. The first measurement (T_1, where 1 indicates hours of reaction time) demonstrated a profile of four out of five of the potential silanes. The molar concentration of the four species was as follows $Si(OZ)_4$ = 0.241, $Si(OZ_3,Cl)$ = 2.462, $Si(OZ_2,Cl_2)$ = 0.220 and $Si(OZ,Cl_3)$ = 0.014 (Cl_0, Cl_1, Cl_2, Cl_3 respectively). Based on the low concentration of $Si(OZ,Cl_3)$ and the progressively slower reaction rate of each additional chlorination, it is assumed that the concentration of SiCl4 is negligible at T_1. While the Time zero sample was not directly measured by NMR, it is assumed that the sum of observed species at T_1(2.937) adequately reflects the concentration of $Si(OZ)_4$ at T_0. Finally it was assumed that later sampling points $SiCl_4$ was not observed due to sample volatility. Accordingly, the concentration of $SiCl_4$ was calculated to be Total Si at T_1 (2.937) minus the current Si concentration for a given time increment. See Table S1.

For formation fitting, the concentration of any given species was taken as the measured concentration plus the concentration of all additional reduction/oxidation products. In other words The $Si(OZ_3, Cl)$ concentration at T_1 is taken as the sum of Cl_1, Cl_2, Cl_3 and Cl_4, and the concentration of Cl_3 was taken as the sum of Cl_3 & Cl_4. See Table S2.

The data was presented to TableCurve2D 5.0 for kinetic modeling. In each case fitting began with the full data set being fitted to first order formation or decay, (Eqn 8101 Form1(a,b,c) and Eqn 8099 Decay1(a,b,c)). The Decay fit of Cl_0 was straight forward requiring no additional adjustments. The formation curve of Cl_1 was also straight forward requiring no additional adjustments. The formation curve of Cl_2 initially produced non-sensical solution due to limited concentration of the first data point resulting from limited concentration of Cl_1 to drive the reaction. Assuming that the reaction rate of $Cl_2 < Cl_1$ this limitation is overcome as more Cl_1 becomes available and the later data points in the formation of Cl_2 become meaningful in the rate determination of the formation of Cl_2. Accordingly the Cl_2 T_1 data point was dropped from the data series and first order formation fitting was allowed to proceed. The resulting fit was exceptional with a correlation of 0.997. The general approach of dropping early data points (up

to T_3) was also successful for Cl_3 and Cl_4. In both Cl_3 and Cl_4 new data points were added to the series. Specifically a maximum concentration of 2.937 was added starting at T_{999}. The resulting fits were visually inspected and the maximum concentration was then reduced in each case to the earliest visual point in the curve profile where maximum intensity was reached, T_{18} and T_{75} respectively. This provided an extra data point for data modeling and minimized the leveraging effect of having a single data point at $T_{infinity}$. See Figures S2-6.

Table S1. ^{29}Si measured molar concentrations plus boundary condition assumptions.

Spectra Data + Boundary Assumptions									
		0	1	2	3	4	5	6	7
		t0	t1	t2	t3	t4	t5	t6	t7
	Cl0	2.937001	2.41E-01	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
	Cl1	0	2.46E+00	1.04E+00	3.02E-01	0.00E+00	0.00E+00	0.00E+00	0.00E+00
	Cl2	0	2.20E-01	1.81E+00	1.79E+00	1.26E+00	8.46E-01	5.31E-01	4.06E-01
	Cl3	0	1.38E-02	0.00E+00	5.94E-01	9.57E-01	1.21E+00	1.39E+00	1.17E+00
	Cl4	0	0.00E+00	8.77E-02	2.50E-01	7.17E-01	8.86E-01	1.02E+00	1.36E+00

Table S2. ^{29}Si NMR observations prepared for formulation curve fitting

formation curves									
		t0	t1	t2	t3	t4	t5	t6	t7
	Cl0	2.937001	2.41E-01	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
	Cl1	0	2.70E+00	2.94E+00	2.94E+00	2.94E+00	2.94E+00	2.94E+00	2.94E+00
	Cl2	0	2.34E-01	1.90E+00	2.63E+00	2.94E+00	2.94E+00	2.94E+00	2.94E+00
	Cl3	0	1.38E-02	8.77E-02	8.44E-01	1.67E+00	2.09E+00	2.41E+00	2.53E+00
	Cl4	0	0.00E+00	8.77E-02	2.50E-01	7.17E-01	8.86E-01	1.02E+00	1.36E+00

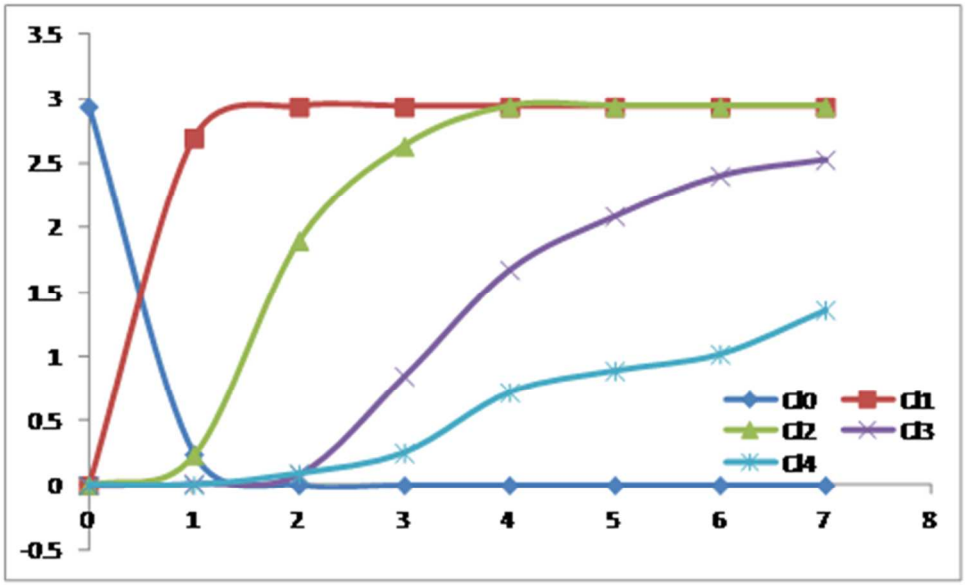


Figure S1. ^{29}Si NMR formation curves for the Kinetics experiment (TMOS = dark blue, $SiCl(OMe)_3$ = red, $SiCl_2(OMe)_2$ = green, $SiCl_3(OMe)$ = purple, $SiCl_4$ = teal).

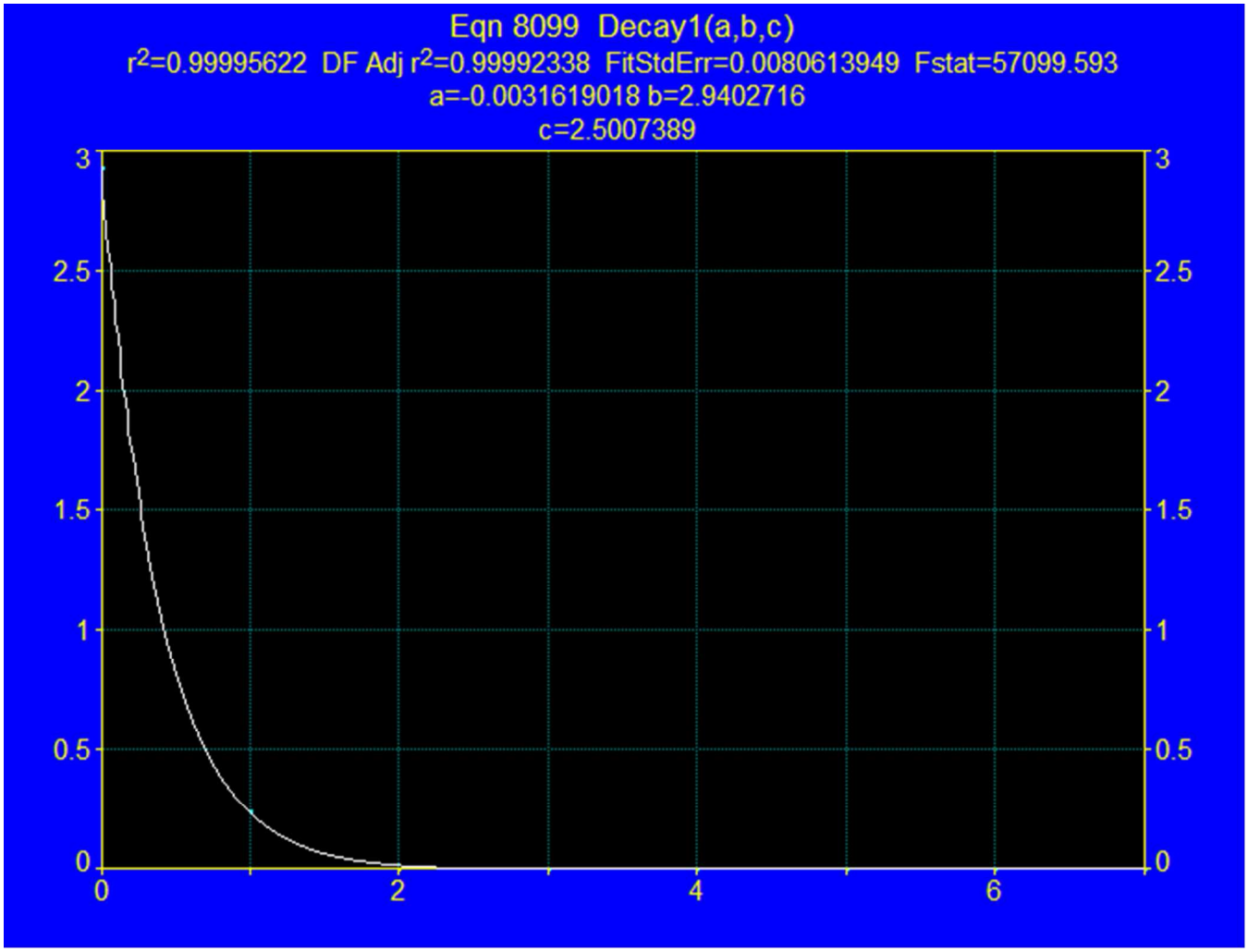


Figure S2. Decay of TMOS in the Kinetics Experiment

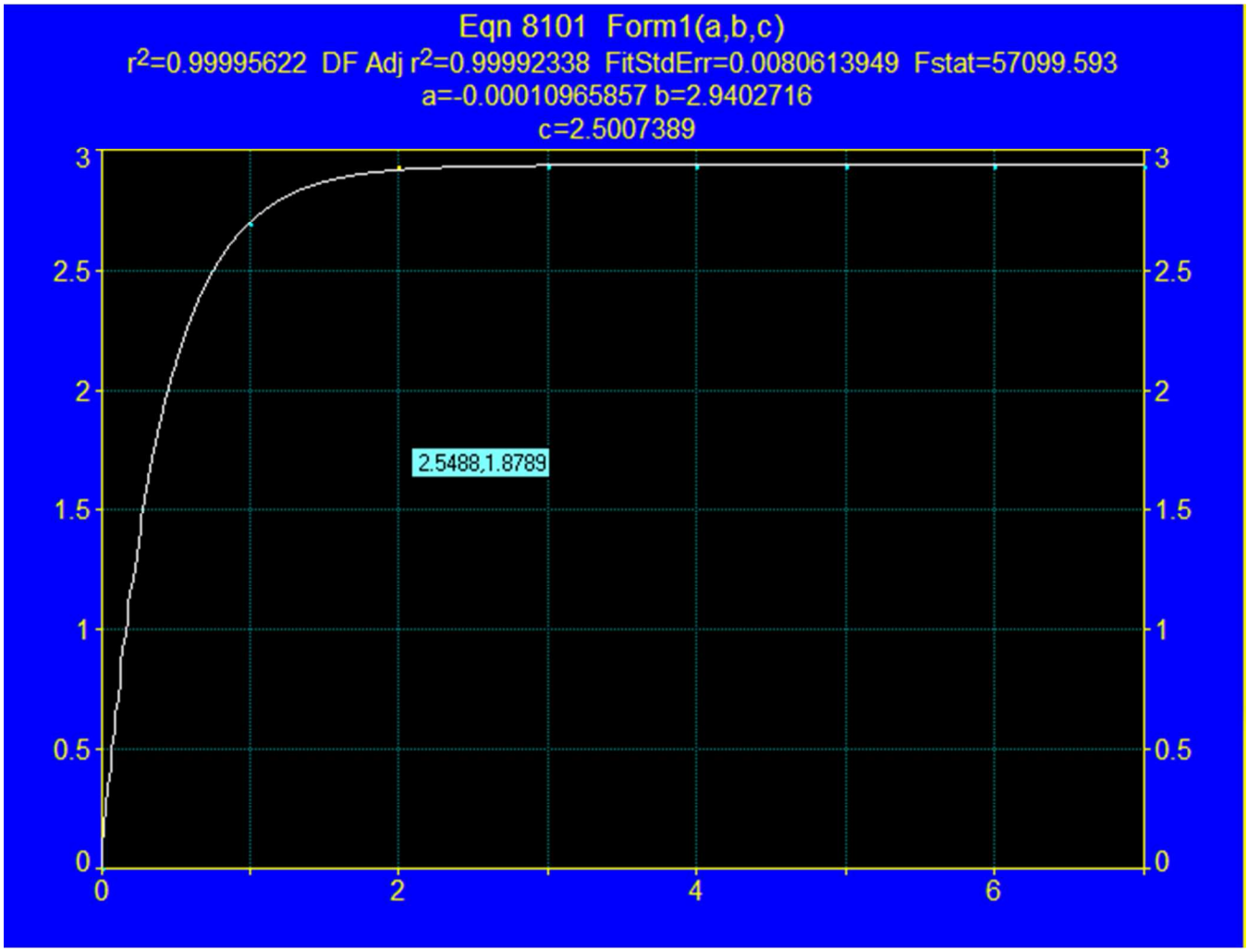


Figure S3. Formation curve of $SiCl(OMe)_3$ in the Kinetics Experiment

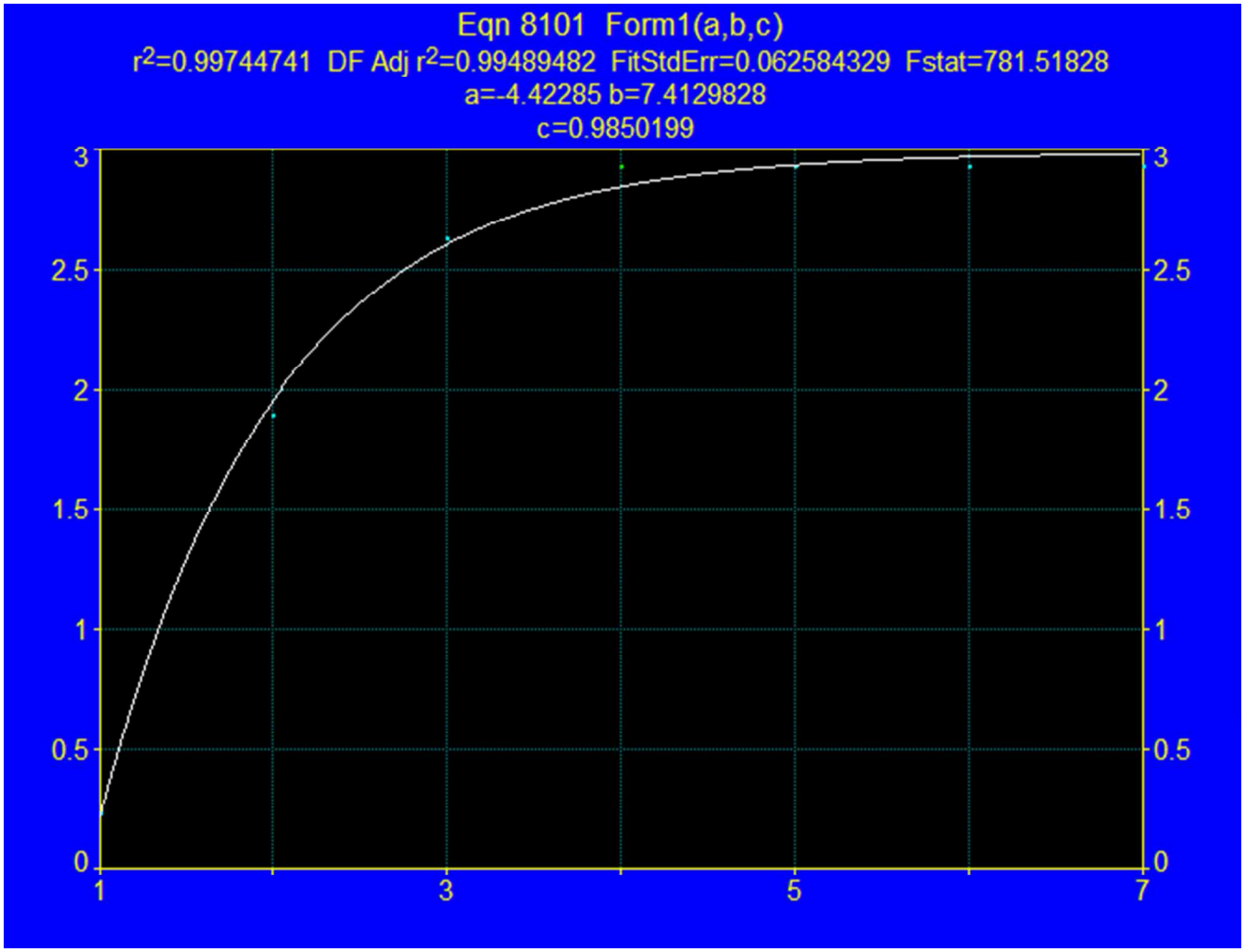


Figure S4. Formation curve of $SiCl_2(OMe)_2$ in the Kinetics Experiment

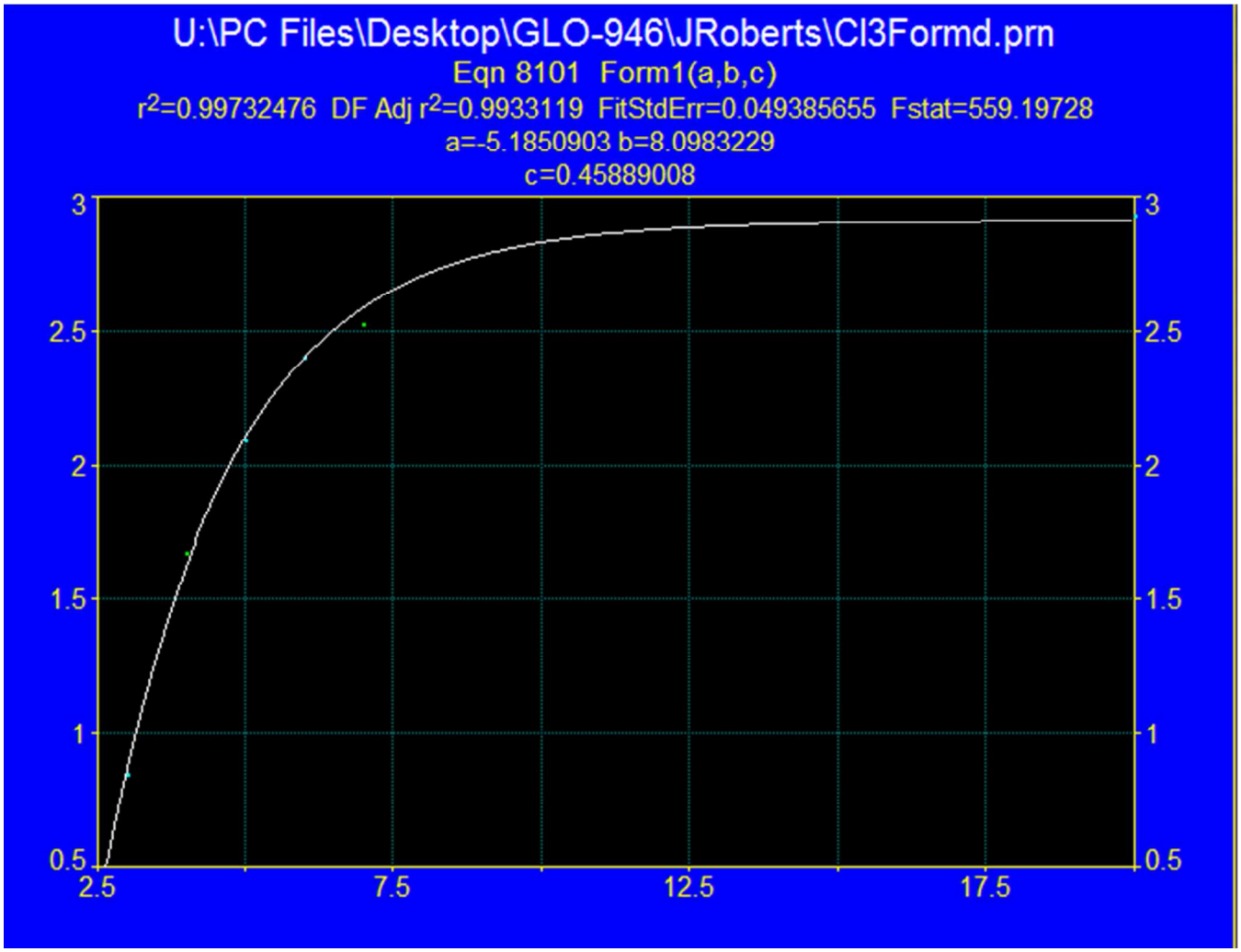


Figure S5. Formation curve of $SiCl_3(OMe)$ in the Kinetics Experiment

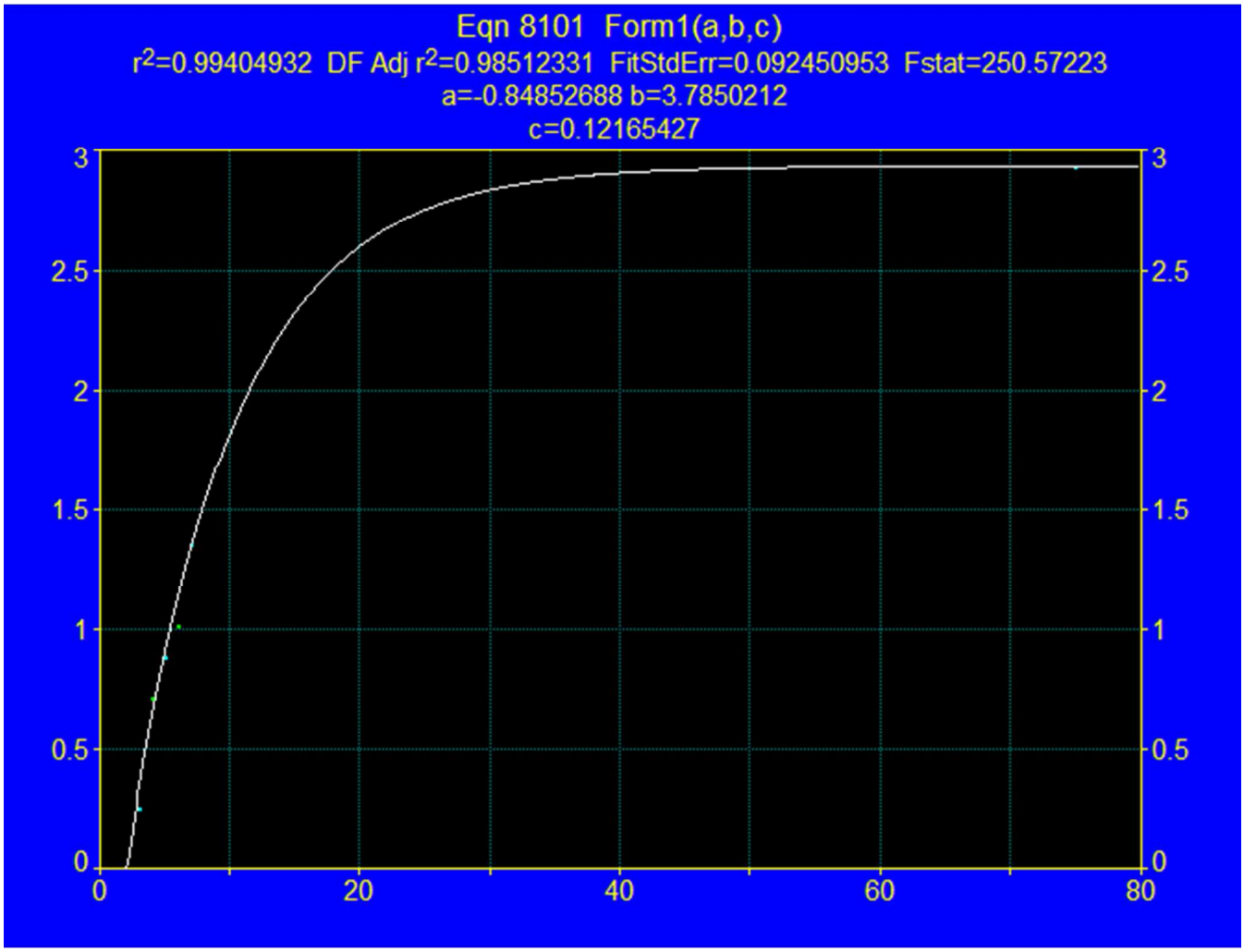


Figure S6. Formation curve of $SiCl_4$ in the Kinetics Experiment

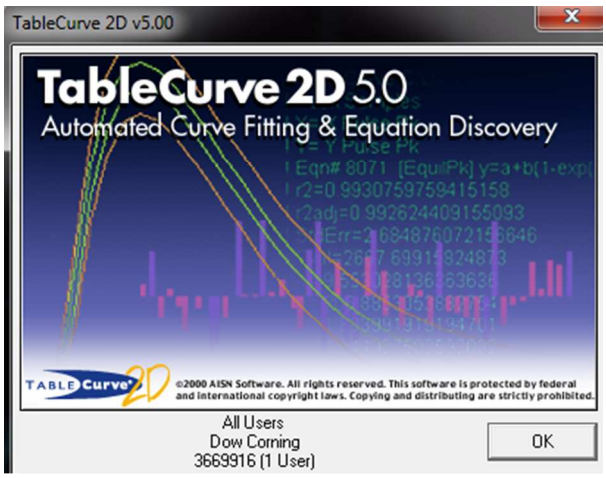


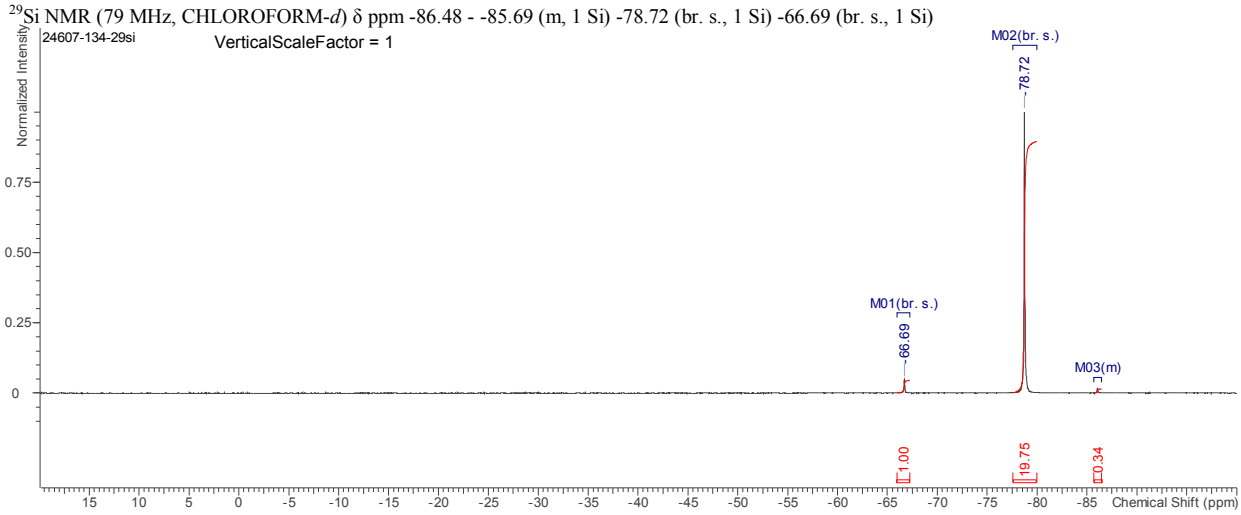
Figure S7. TableCurve program edition used

Selected Spectra:

8/11/2015 2:43:08 PM

Multiplets Integrals Sum 21.09	***Number of Nuclei*** 3 Si's		
Acquisition Time (sec) 1.5996	***Comment*** 24607-134-29si 29Si OBSERVE	***Date*** Dec 12 2012	
Date Stamp Dec 12 2012	***File Name*** \\dw7dkxkdz1\NMRMirrorSite\jmrobert\merc400\jmrfids\24607-134-29si.fid\fid		
Frequency (MHz) 79.49	***Nucleus*** 29Si	***Number of Transients*** 240	***Original Points Count*** 38176
Points Count 65536	***Pulse Sequence*** s2pul	***Receiver Gain*** 30.00	***SW(cyclical) (Hz)*** 23866.35
Solvent CHLOROFORM-d		***Spectrum Offset (Hz)*** -3982.2773	***Spectrum Type*** STANDARD
Sweep Width (Hz) 23865.98	***Temperature (degree C)*** AMBIENT TEMPERATURE		

^{29}Si NMR (79 MHz, CHLOROFORM-*d*) δ ppm -86.48 - -85.69 (m, 1 Si) -78.72 (br. s., 1 Si) -66.69 (br. s., 1 Si)



No.	(ppm)	Value	Absolute Value	Non-Negative Value
1	[-86.48 .. -85.69]	0.336	1.862e+9	0.336
2	[-79.98 .. -77.56]	19.754	1.096e+11	19.754
3	[-67.25 .. -65.98]	1.000	5.546e+9	1.000

No.	Shift1 (ppm)	Si's	Type	Multiplet1	(ppm)
1	-86.08	1	m	M03	[-86.48 .. -85.69]
2	-78.72	1	br. s.	M02	[-79.98 .. -77.56]
3	-66.69	1	br. s.	M01	[-67.25 .. -65.98]

No.	(ppm)	(Hz)	Height
1	-78.72	-6257.4	1.0000
2	-66.69	-5301.1	0.0467

Figure S8. ^{29}Si NMR of Table 1, entry 1($Si(OMe)_3Cl$ (s) -66.7 ppm, ($Si(OMe)_4$ (s) -78.7 ppm)

8/11/2015 2:53:02 PM

Multiplets Integrals Sum	0.00	***Number of Nuclei***	0 Si's				
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Date Stamp	Dec 17 2012	***File Name***	\\dw7dkxkdz1\NMRMirrorSite\jmrobert\merc400\jmrfids\24607-136-29si.fid\fid				
Frequency (MHz)	79.49	***Nucleus***	29Si	***Number of Transients***	240	***Original Points Count***	38176
Points Count	65536	***Pulse Sequence***	s2pul	***Receiver Gain***	24.00	***SW(cyclical) (Hz)***	23866.35
Solvent	CHLOROFORM-d			***Spectrum Offset (Hz)***	-4141.5532	***Spectrum Type***	STANDARD
Sweep Width (Hz)	23865.98	***Temperature (degree C)***	AMBIENT TEMPERATURE				

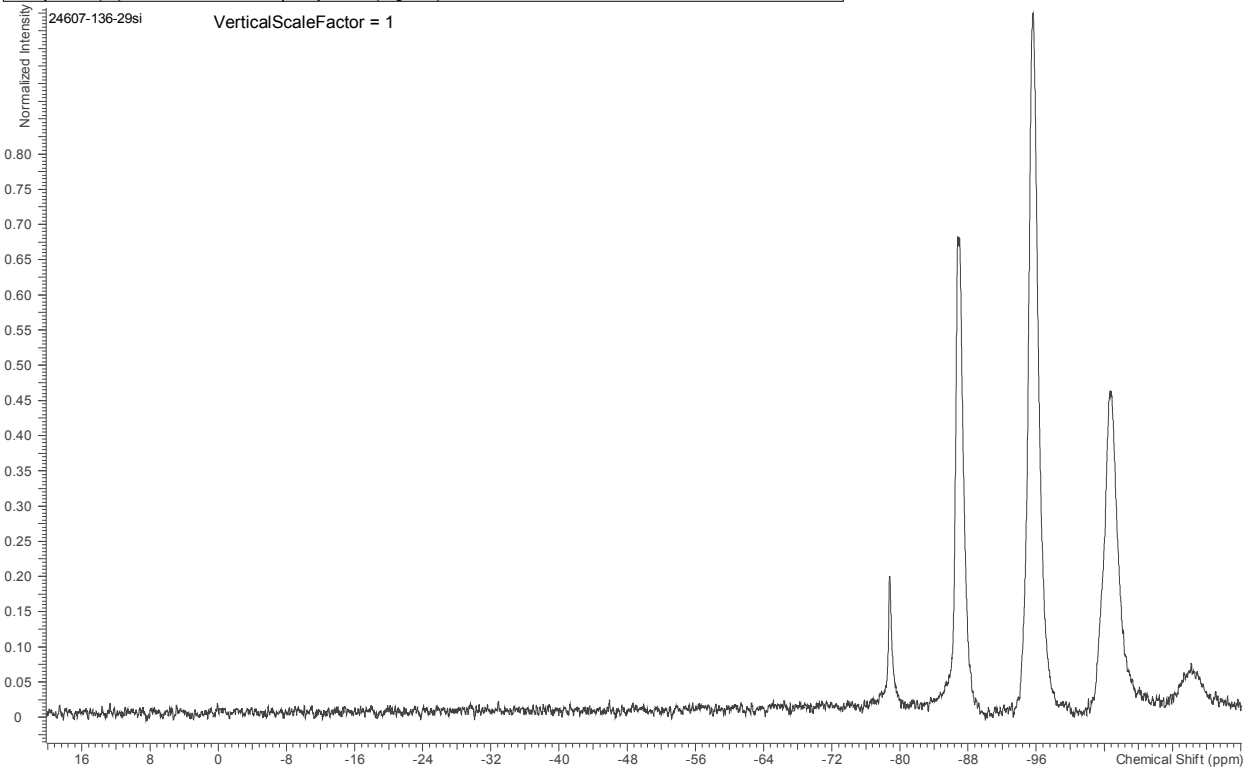

Figure S9. ^{29}Si NMR of Table 1, entry 2 ($Si(OMe)_4$ (s) -78.35 ppm, oligomeric orthosilicates)

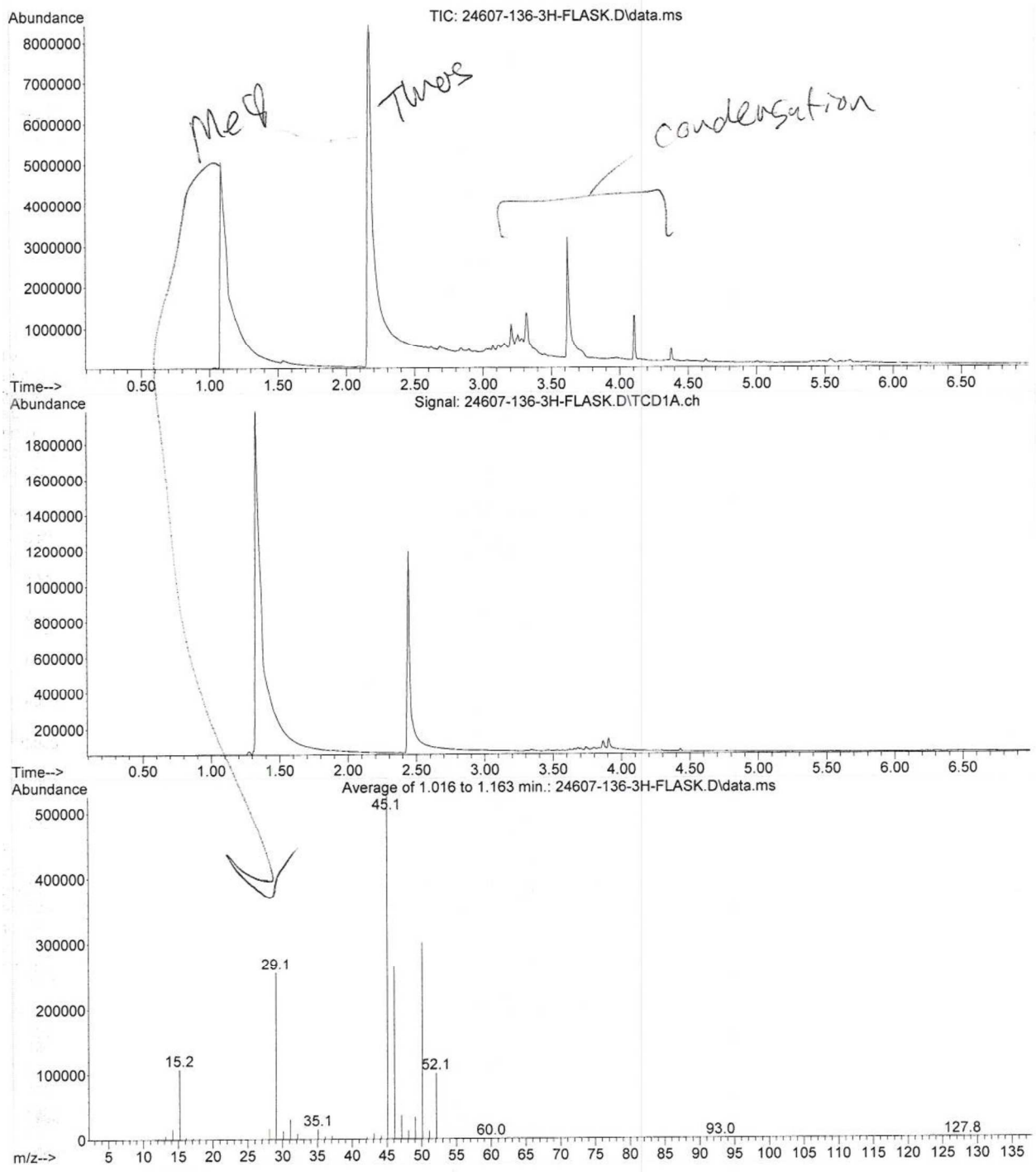

Figure S10. GCMS of Table 1, entry 2

8/11/2015 3:09:48 PM

Multiplets Integrals Sum	0.00	***Number of Nuclei***	0 Si's				
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Date Stamp	Dec 15 2012	***File Name***	\\dw7dkxkdz1\NMRMirrorSite\jmrobert\merc400\jmrfids\24607-135-29si.fid\fid				
Frequency (MHz)	79.49	***Nucleus***	29Si	***Number of Transients***	240	***Original Points Count***	38176
Points Count	65536	***Pulse Sequence***	s2pul	***Receiver Gain***	30.00	***SW(cyclical) (Hz)***	23866.35
Solvent	CHLOROFORM-d			***Spectrum Offset (Hz)***	-3982.2773	***Spectrum Type***	STANDARD
Sweep Width (Hz)	23865.98	***Temperature (degree C)***	AMBIENT TEMPERATURE				

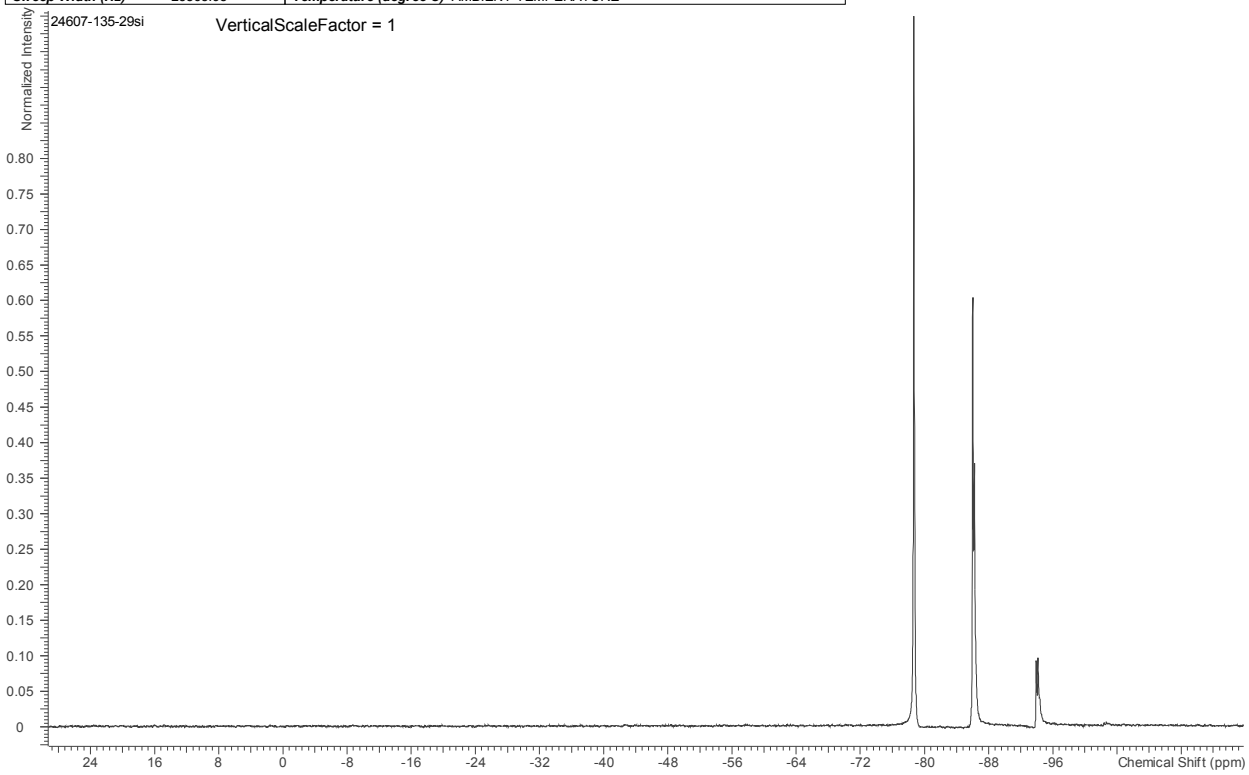

Figure S11. ^{29}Si NMR of Table 1, entry 3 ($Si(OMe)_4$ (s) -78.35 ppm, others condensed species)

1/19/2016 5:21:48 PM

Multiplets Integrals Sum 3.59	***Number of Nuclei*** 2 Si's		
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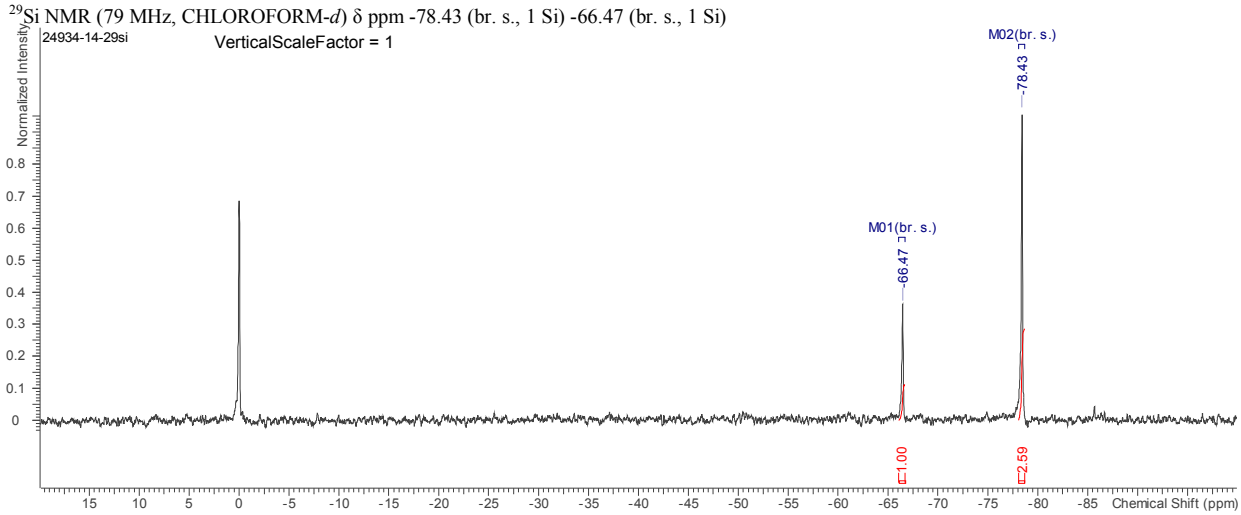
Date Stamp Jan 22 2013	***File Name*** \\dw7dkxkdz1\NMRMirrorSite\jmrobert\merc400\jmrfids\24934-14-29si.fid\fid		
Frequency (MHz) 79.49	***Nucleus*** 29Si	***Number of Transients*** 240	***Original Points Count*** 38176
Points Count 65536	***Pulse Sequence*** s2pul	***Receiver Gain*** 34.00	***SW(cyclical) (Hz)*** 23866.35
Solvent CHLOROFORM-d		***Spectrum Offset (Hz)*** -4008.6187	***Spectrum Type*** STANDARD
Sweep Width (Hz) 23865.98	***Temperature (degree C)*** AMBIENT TEMPERATURE		

^{29}Si NMR (79 MHz, CHLOROFORM-*d*) δ ppm -78.43 (br. s., 1 Si) -66.47 (br. s., 1 Si)



No.	(ppm)	Value	Absolute Value	Non-Negative Value
1	[-78.72 .. -78.08]	2.591	6.964e+9	2.591
2	[-66.69 .. -66.08]	1.000	2.688e+9	1.000

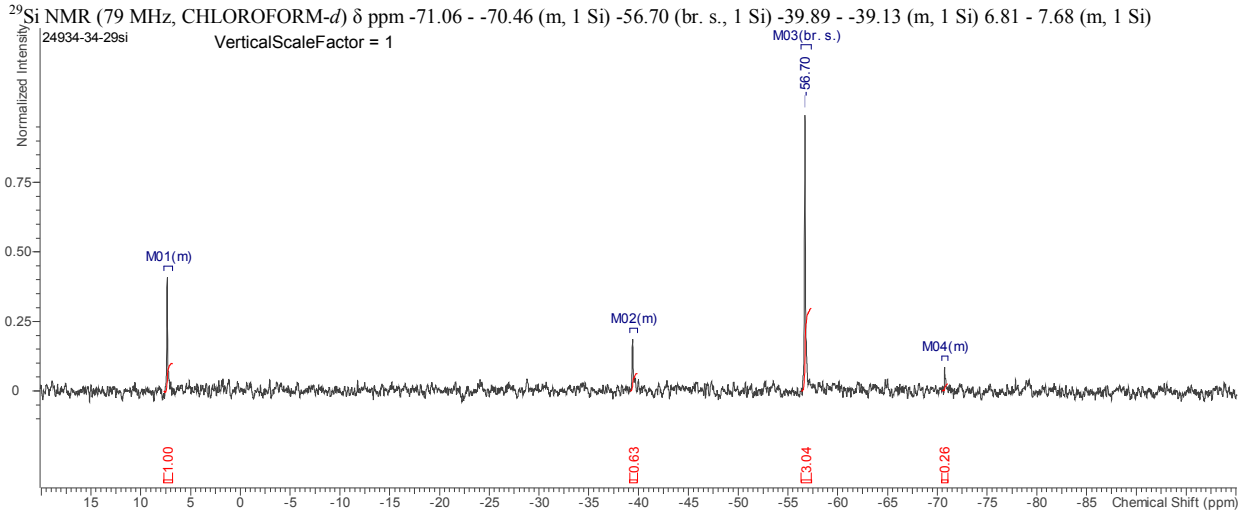
No.	Shift1 (ppm)	Si's	Type	Multiplet1	(ppm)
1	-78.43	1	br. s.	M02	[-78.72 .. -78.08]
2	-66.47	1	br. s.	M01	[-66.69 .. -66.08]

Figure S12. ^{29}Si NMR of Table 1, entry 4 ($SiMe_4$ (s) 0.0 ppm, $(Si(OMe)_3Cl$ (s) -66.4 ppm, $(Si(OMe)_4$ (s) -78.4 ppm)

8/11/2015 3:46:15 PM

Multiplets Integrals Sum 4.93	***Number of Nuclei*** 4 Si's		
Acquisition Time (sec) 1.5996	***Comment*** 24934-34-29si 29Si OBSERVE	***Date*** Feb 26 2013	
Date Stamp Feb 26 2013	***File Name*** \\dw7dkxkdz1\NMRMirrorSite\jmrobert\merc400\jmrfids\24934-34-29si.fid\fid		
Frequency (MHz) 79.49	***Nucleus*** 29Si	***Number of Transients*** 48	***Original Points Count*** 38176
Points Count 65536	***Pulse Sequence*** s2pul	***Receiver Gain*** 36.00	***SW(cyclical) (Hz)*** 23866.35
Solvent CHLOROFORM-d		***Spectrum Offset (Hz)*** -4033.6306	***Spectrum Type*** STANDARD
Sweep Width (Hz) 23865.98	***Temperature (degree C)*** AMBIENT TEMPERATURE		

^{29}Si NMR (79 MHz, CHLOROFORM-*d*) δ ppm -71.06 - -70.46 (m, 1 Si) -56.70 (br. s., 1 Si) -39.89 - -39.13 (m, 1 Si) 6.81 - 7.68 (m, 1 Si)



No.	(ppm)	Value	Absolute Value	Non-Negative Value
1	[-71.06 .. -70.46]	0.258	1.881e+8	0.258
2	[-57.36 .. -56.32]	3.040	2.218e+9	3.040
3	[-39.89 .. -39.13]	0.630	4.595e+8	0.630
4	[6.81 .. 7.68]	1.000	7.299e+8	1.000

No.	Shift1 (ppm)	Si's	Type	Multiplet1	(ppm)
1	-70.76	1	m	M04	[-71.06 .. -70.46]
2	-56.70	1	br. s.	M03	[-57.36 .. -56.32]
3	-39.51	1	m	M02	[-39.89 .. -39.13]
4	7.25	1	m	M01	[6.81 .. 7.68]

No.	(ppm)	(Hz)	Height
1	-56.70	-4506.9	1.0000

Figure S13. ^{29}Si NMR of Table 2, entry 1 ($SiEt_4$ (s) 7.35 ppm, $SiCl_3(OEt)$ (s) -39.5 ppm, $SiCl_2(OEt)_2$ (s) -56.7 ppm, $SiCl(OEt)_3$ (s) -70.8)

8/11/2015 3:49:51 PM

Multiplets Integrals Sum 4.23	***Number of Nuclei*** 4 Si's		
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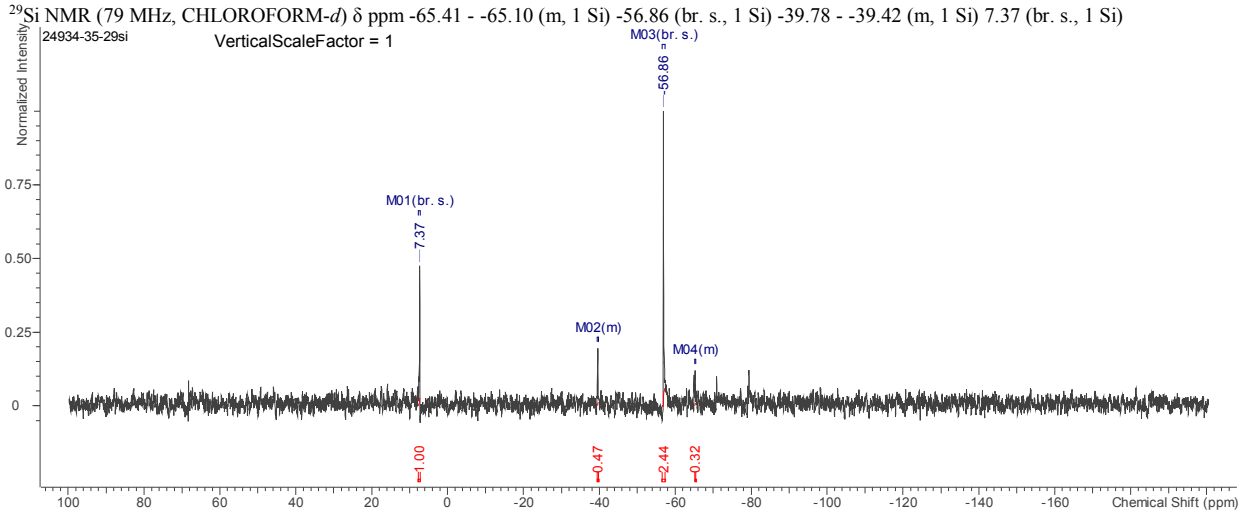
Date Stamp Mar 2 2013	***File Name*** \\dw7dkxkdz1\NMRMirrorSite\jmrobert\merc400\jmrfids\24934-35-29si.fid\fid		
Frequency (MHz) 79.49	***Nucleus*** 29Si	***Number of Transients*** 48	***Original Points Count*** 38176
Points Count 65536	***Pulse Sequence*** s2pul	***Receiver Gain*** 39.00	***SW(cyclical) (Hz)*** 23866.35
Solvent CHLOROFORM-d		***Spectrum Offset (Hz)*** -4000.8552	***Spectrum Type*** STANDARD
Sweep Width (Hz) 23865.98	***Temperature (degree C)*** AMBIENT TEMPERATURE		

^{29}Si NMR (79 MHz, CHLOROFORM-*d*) δ ppm -65.41 - -65.10 (m, 1 Si) -56.86 (br. s., 1 Si) -39.78 - -39.42 (m, 1 Si) 7.37 (br. s., 1 Si)



No.	(ppm)	Value	Absolute Value	Non-Negative Value
1	[-65.41 .. -65.10]	0.318	2.807e+8	0.318
2	[-57.29 .. -56.58]	2.439	2.152e+9	2.439
3	[-39.78 .. -39.42]	0.472	4.168e+8	0.472
4	[7.22 .. 7.74]	1.000	8.822e+8	1.000

No.	Shift1 (ppm)	Si's	Type	Multiplet1	(ppm)
1	-65.26	1	m	M04	[-65.41 .. -65.10]
2	-56.86	1	br. s.	M03	[-57.29 .. -56.58]
3	-39.60	1	m	M02	[-39.78 .. -39.42]
4	7.37	1	br. s.	M01	[7.22 .. 7.74]

No.	(ppm)	(Hz)	Height
1	-56.86	-4519.6	1.0000
2	7.37	585.7	0.4753

Figure S14. ^{29}Si NMR of Table 2, entry 2 ($SiEt_4$ (s) 7.35 ppm, $SiCl_3(OEt)$ (s) -39.6 ppm, $SiCl_2(OEt)_2$ (s) -56.9 ppm), $SiCl(OEt)_3$ (s) -65.2)

8/11/2015 3:53:17 PM

Multiplets Integrals Sum 5.46	***Number of Nuclei*** 3 Si's		
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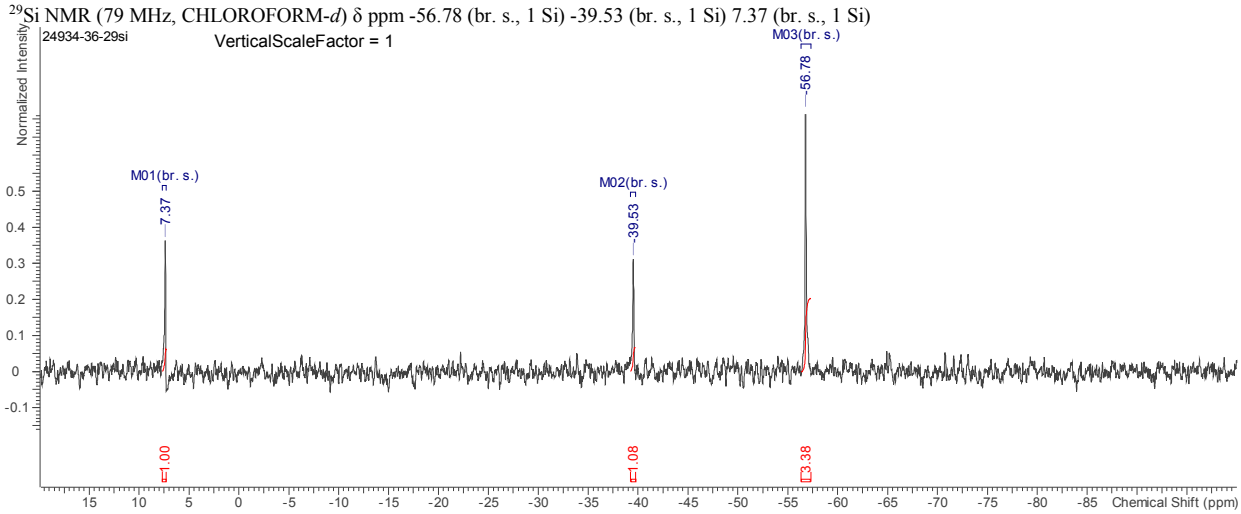
Date Stamp Mar 5 2013	***File Name*** \\dw7dkxkdz1\NMRMirrorSite\jmrobert\merc400\jmrfids\24934-36-29si.fid\fid		
Frequency (MHz) 79.49	***Nucleus*** 29Si	***Number of Transients*** 48	***Original Points Count*** 38176
Points Count 65536	***Pulse Sequence*** s2pul	***Receiver Gain*** 39.00	***SW(cyclical) (Hz)*** 23866.35
Solvent CHLOROFORM-d		***Spectrum Offset (Hz)*** -4004.4971	***Spectrum Type*** STANDARD
Sweep Width (Hz) 23865.98	***Temperature (degree C)*** AMBIENT TEMPERATURE		

^{29}Si NMR (79 MHz, CHLOROFORM-*d*) δ ppm -56.78 (br. s., 1 Si) -39.53 (br. s., 1 Si) 7.37 (br. s., 1 Si)



No.	(ppm)	Value	Absolute Value	Non-Negative Value
1	[-57.31 .. -56.33]	3.375	2.370e+9	3.375
2	[-39.77 .. -39.24]	1.082	7.599e+8	1.082
3	[7.28 .. 7.66]	1.000	7.023e+8	1.000

No.	Shift1 (ppm)	Si's	Type	Multiplet1	(ppm)
1	-56.78	1	br. s.	M03	[-57.31 .. -56.33]
2	-39.53	1	br. s.	M02	[-39.77 .. -39.24]
3	7.37	1	br. s.	M01	[7.28 .. 7.66]

No.	(ppm)	(Hz)	Height
1	-56.78	-4513.4	1.0000
2	-39.53	-3142.3	0.3121
3	7.37	586.1	0.3633

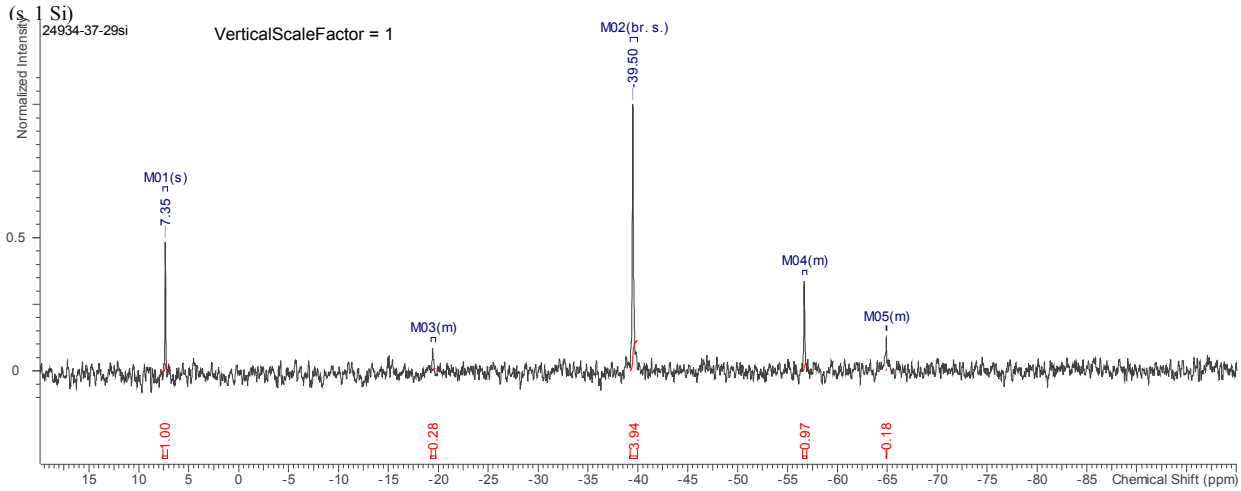
Figure S15. ^{29}Si NMR of Table 2, entry 3 ($SiEt_4$ (s) 7.35 ppm, $SiCl_3(OEt)$ (s) -39.6 ppm, $SiCl_2(OEt)_2$ (s) -56.8 ppm)

8/11/2015 3:57:29 PM

Multiplets Integrals Sum 6.37	***Number of Nuclei*** 5 Si's		

Acquisition Time (sec)	1.5996	***Comment***	24934-37-29si 29Si OBSERVE			***Date***	Mar 5 2013
Date Stamp	Mar 5 2013	***File Name***	\\dw7dkxkdz1\NMRMirrorSite\jmrobert\merc400\jmrfids\24934-37-29si.fid\fid				
Frequency (MHz)	79.49	***Nucleus***	29Si	***Number of Transients***	48	***Original Points Count***	38176
Points Count	65536	***Pulse Sequence***	s2pul	***Receiver Gain***	39.00	***SW(cyclical) (Hz)***	23866.35
Solvent	CHLOROFORM-d			***Spectrum Offset (Hz)***	-4006.3179	***Spectrum Type***	STANDARD
Sweep Width (Hz)	23865.98	***Temperature (degree C)***	AMBIENT TEMPERATURE				

^{29}Si NMR (79 MHz, CHLOROFORM-*d*) δ ppm -64.95 - -64.88 (m, 1 Si) -56.93 - -56.51 (m, 1 Si) -39.50 (br. s., 1 Si) -19.72 - -19.26 (m, 1 Si) 7.35 (s, 1 Si)



No.	(ppm)	Value	Absolute Value	Non-Negative Value
1	[-64.95 .. -64.88]	0.175	9.212e+7	0.175
2	[-56.93 .. -56.51]	0.965	5.081e+8	0.965
3	[-39.98 .. -39.23]	3.942	2.074e+9	3.942
4	[-19.72 .. -19.26]	0.285	1.499e+8	0.285
5	[7.16 .. 7.61]	1.000	5.263e+8	1.000

No.	Shift1 (ppm)	Si's	Type	Multiplet1	(ppm)
1	-64.91	1	m	M05	[-64.95 .. -64.88]
2	-56.72	1	m	M04	[-56.93 .. -56.51]
3	-39.50	1	br. s.	M02	[-39.98 .. -39.23]
4	-19.49	1	m	M03	[-19.72 .. -19.26]
5	7.35	1	s	M01	[7.16 .. 7.61]

No.	(ppm)	(Hz)	Height
1	-39.50	-3140.1	1.0000
2	7.35	584.2	0.4846

Figure S16. ^{29}Si NMR of Table 2, entry 4 ($SiEt_4$ (s) 7.35 ppm, $SiCl_4$ (s) -19.5 ppm, $SiCl_3(OEt)$ (s) -39.5 ppm, $SiCl_2(OEt)_2$ (s) -56.7 ppm, $SiCl(OEt)_3$ (s) -64.9 ppm)

8/12/2015 3:33:20 PM

Multiplets Integrals Sum	0.00	***Number of Nuclei***	0 Si's				
Acquisition Time (sec)	1.5996	***Comment***	24934-59-29si 29Si OBSERVE			***Date***	Apr 5 2013
Date Stamp	Apr 5 2013	***File Name***	\\dw7dkxkdz1\NMRMirrorSite\jmrobert\merc400\jmrfids\24934-59-29si.fid\fid				
Frequency (MHz)	79.49	***Nucleus***	29Si	***Number of Transients***	48	***Original Points Count***	38176
Points Count	65536	***Pulse Sequence***	s2pul	***Receiver Gain***	39.00	***SW(cyclical) (Hz)***	23866.35
Solvent	CHLOROFORM-d			***Spectrum Offset (Hz)***	-4005.9539	***Spectrum Type***	STANDARD
Sweep Width (Hz)	23865.98	***Temperature (degree C)***	AMBIENT TEMPERATURE				

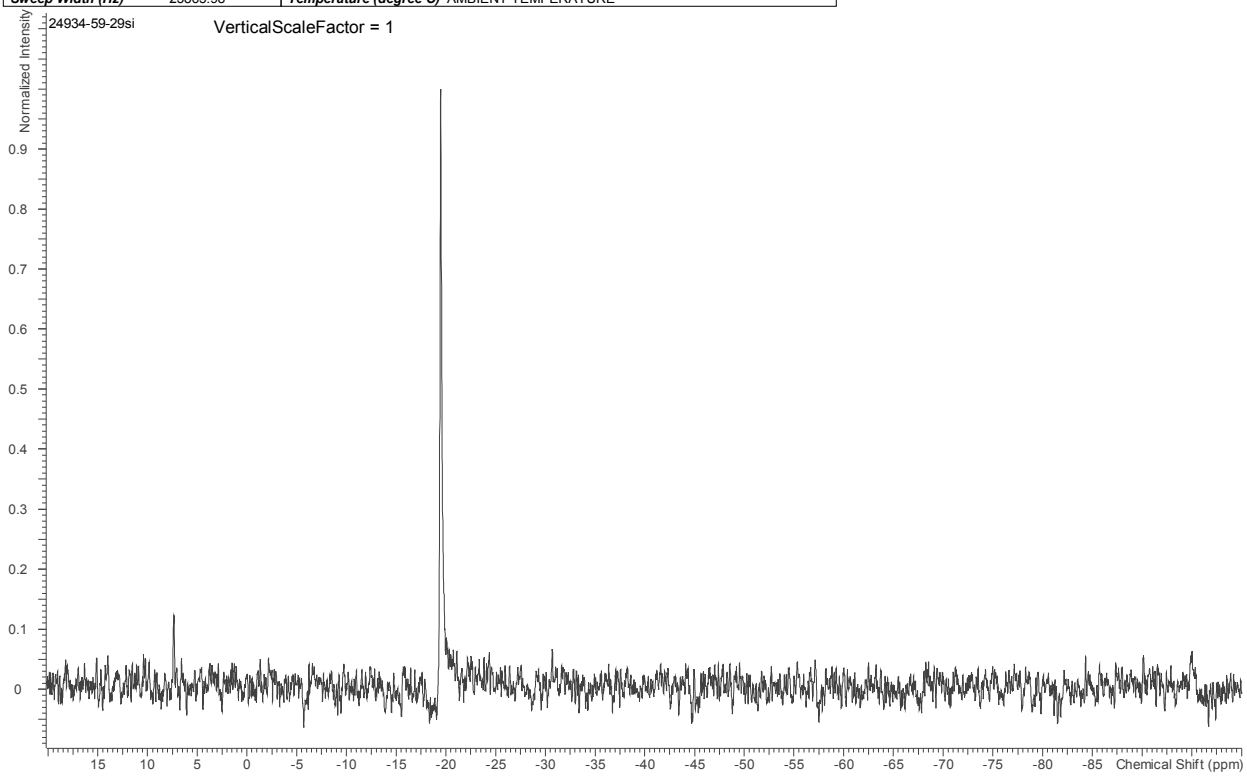
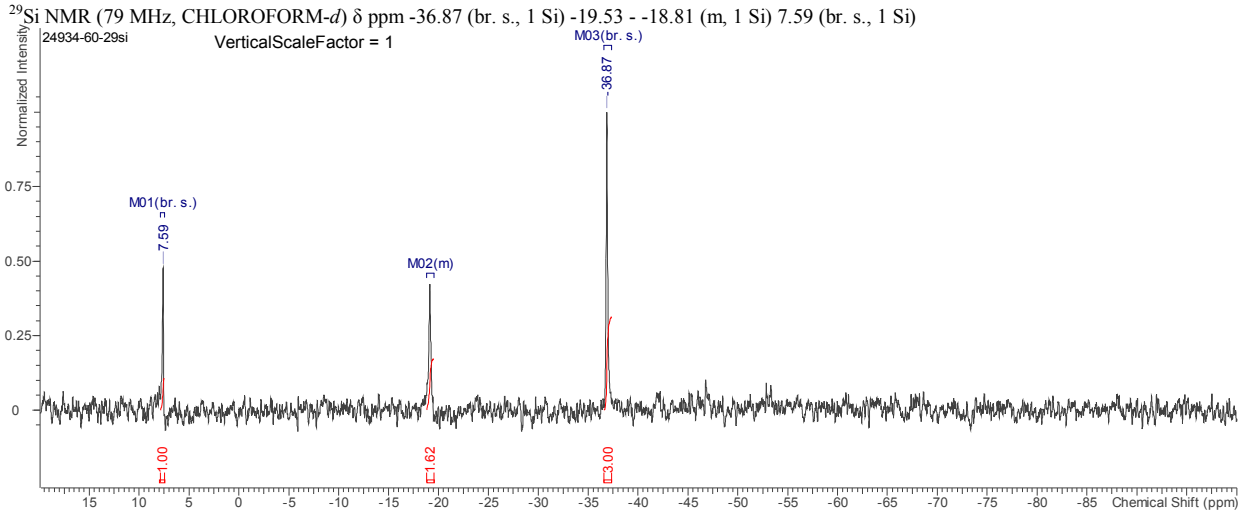


Figure S17. ^{29}Si NMR of Table 3, entry 1 ($SiEt_4$ (s) 7.35 ppm, $SiCl_4$ (s) -19.65 ppm)

8/12/2015 2:03:13 PM

Multiplets Integrals Sum 5.62	***Number of Nuclei*** 3 Si's		
Acquisition Time (sec) 1.5996	***Comment*** 24934-60-29si 29Si OBSERVE	***Date*** Apr 10 2013	
Date Stamp Apr 10 2013	***File Name*** \\dw7dkxkdz1\NMRMirrorSite\jmrobert\merc400\jmrfids\24934-60-29si.fid\fid		
Frequency (MHz) 79.49	***Nucleus*** 29Si	***Number of Transients*** 48	***Original Points Count*** 38176
Points Count 65536	***Pulse Sequence*** s2pul	***Receiver Gain*** 39.00	***SW(cyclical) (Hz)*** 23866.35
Solvent CHLOROFORM-d		***Spectrum Offset (Hz)*** -3982.2773	***Spectrum Type*** STANDARD
Sweep Width (Hz) 23865.98	***Temperature (degree C)*** AMBIENT TEMPERATURE		

^{29}Si NMR (79 MHz, CHLOROFORM-*d*) δ ppm -36.87 (br. s., 1 Si) -19.53 - -18.81 (m, 1 Si) 7.59 (br. s., 1 Si)



No.	(ppm)	Value	Absolute Value	Non-Negative Value
1	[-37.35 .. -36.60]	3.001	2.458e+9	3.001
2	[-19.53 .. -18.81]	1.620	1.327e+9	1.620
3	[7.46 .. 7.86]	1.000	8.191e+8	1.000

No.	Shift1 (ppm)	Si's	Type	Multiplet1	(ppm)
1	-36.87	1	br. s.	M03	[-37.35 .. -36.60]
2	-19.17	1	m	M02	[-19.53 .. -18.81]
3	7.59	1	br. s.	M01	[7.46 .. 7.86]

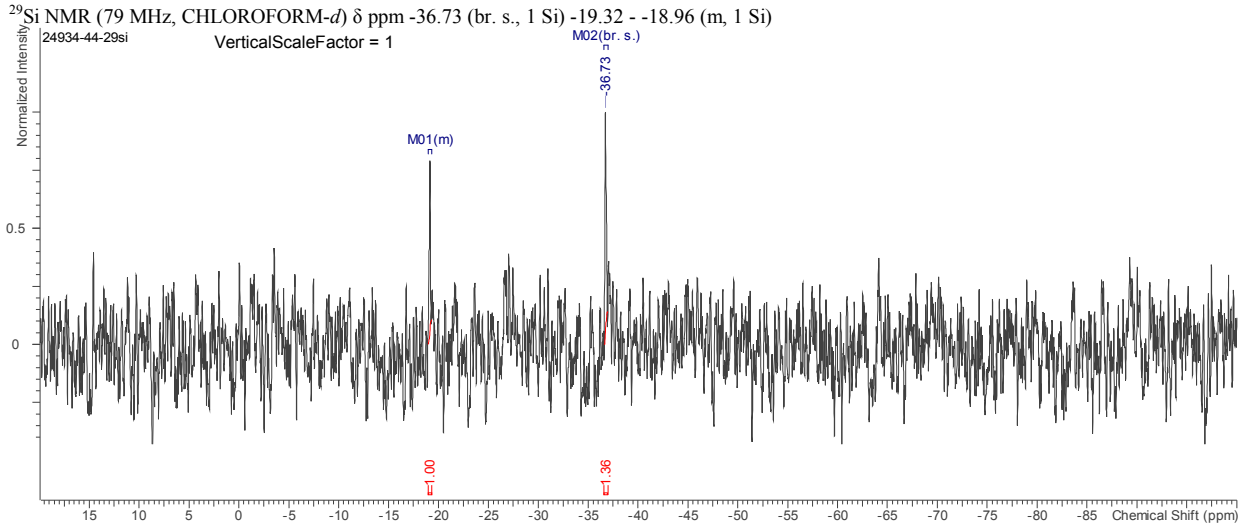
No.	(ppm)	(Hz)	Height
1	-36.87	-2931.1	1.0000
2	7.59	603.6	0.4780

Figure S18. ^{29}Si NMR of Table 3, entry 2 ($SiEt_4$ (s) 7.35 ppm, $SiCl_4$ (s) -19.2 ppm, $SiCl_3(OMe)$ (s) -36.8 ppm)

8/12/2015 1:24:15 PM

Multiplets Integrals Sum 2.36	***Number of Nuclei*** 2 Si's		
Acquisition Time (sec) 1.5996	***Comment*** 24934-44-29si 29Si OBSERVE		***Date*** Mar 13 2013
Date Stamp Mar 13 2013	***File Name*** \\dw7dkxkdz1\NMRMirrorSite\jmrobert\merc400\jmrfids\24934-44-29si.fid\fid		
Frequency (MHz) 79.49	***Nucleus*** 29Si	***Original Points Count*** 38176	***Points Count*** 65536
Pulse Sequence s2pul	***Receiver Gain*** 39.00	***SW(cyclical) (Hz)*** 23866.35	***Solvent*** CHLOROFORM-d
Spectrum Offset (Hz) -3982.2773	***Spectrum Type*** STANDARD	***Sweep Width (Hz)*** 23865.98	***Temperature (degree C)*** AMBIENT TEMPERATURE

^{29}Si NMR (79 MHz, CHLOROFORM-*d*) δ ppm -36.73 (br. s., 1 Si) -19.32 - -18.96 (m, 1 Si)



No.	(ppm)	Value	Absolute Value	Non-Negative Value
1	[-36.99 .. -36.60]	1.356	4.415e+7	1.356
2	[-19.32 .. -18.96]	1.000	3.257e+7	1.000

No.	Shift1 (ppm)	Si's	Type	Multiplet1	(ppm)
1	-36.73	1	br. s.	M02	[-36.99 .. -36.60]
2	-19.14	1	m	M01	[-19.32 .. -18.96]

No.	(ppm)	(Hz)	Height
1	-36.73	-2919.8	1.0000

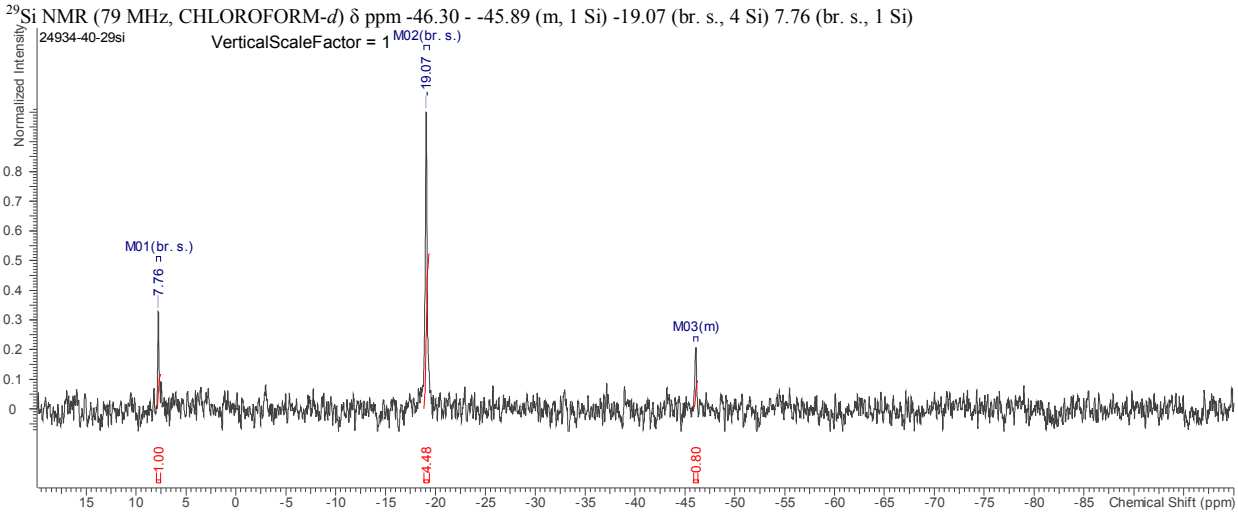
Figure S19. ^{29}Si NMR of Table 3, entry 3 ($SiEt_4$ (s) 7.35 ppm, $SiCl_4$ (s) -19.2 ppm, $SiCl_3$(O<u>Me</u>) (s) -36.7)

8/12/2015 1:17:49 PM

Multiplets Integrals Sum 6.28	***Number of Nuclei*** 6 Si's		

Acquisition Time (sec)	1.5996	***Comment***	24934-40-29si 29Si OBSERVE			***Date***	Mar 10 2013
Date Stamp	Mar 10 2013	***File Name***	\\dw7dkxkdz1\NMRMirrorSite\jmrobert\merc400\jmrfids\24934-40-29si.fid\fid				
Frequency (MHz)	79.49	***Nucleus***	29Si	***Number of Transients***	48	***Original Points Count***	38176
Points Count	65536	***Pulse Sequence***	s2pul	***Receiver Gain***	39.00	***SW(cyclical) (Hz)***	23866.35
Solvent	CHLOROFORM-d			***Spectrum Offset (Hz)***	-3982.2773	***Spectrum Type***	STANDARD
Sweep Width (Hz)	23865.98	***Temperature (degree C)***	AMBIENT TEMPERATURE				

^{29}Si NMR (79 MHz, CHLOROFORM-*d*) δ ppm -46.30 - -45.89 (m, 1 Si) -19.07 (br. s., 4 Si) 7.76 (br. s., 1 Si)



No.	(ppm)	Value	Absolute Value	Non-Negative Value
1	[-46.30 .. -45.89]	0.797	4.097e+8	0.797
2	[-19.38 .. -18.85]	4.483	2.305e+9	4.483
3	[7.54 .. 7.95]	1.000	5.142e+8	1.000

No.	Shift1 (ppm)	Si's	Type	Multiplet1	(ppm)
1	-46.09	1	m	M03	[-46.30 .. -45.89]
2	-19.07	4	br. s.	M02	[-19.38 .. -18.85]
3	7.76	1	br. s.	M01	[7.54 .. 7.95]

No.	(ppm)	(Hz)	Height
1	-19.07	-1515.9	1.0000
2	7.76	617.0	0.3277

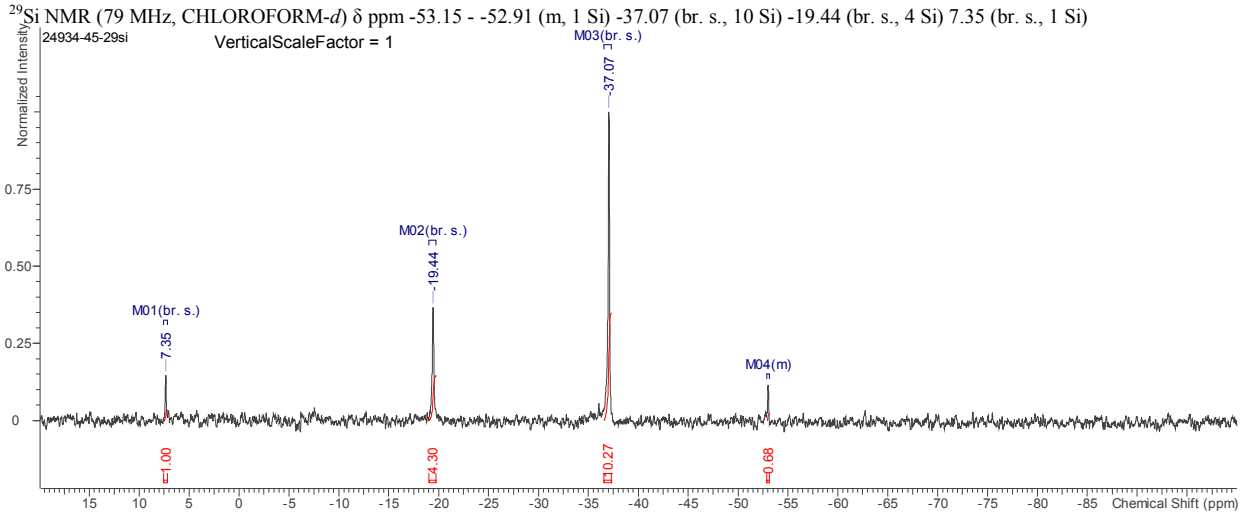
Figure S20. ^{29}Si NMR of Table 3, entry 4 ($SiEt_4$ (s) 7.35 ppm, $SiCl_4$ (s) -19.1 ppm, $SiCl_3(OMe)$ (s) -46.1 ppm)

8/12/2015 1:32:38 PM

Multiplets Integrals Sum 16.25	***Number of Nuclei*** 16 Si's		

Acquisition Time (sec)	1.5996	***Comment***	24934-45-29si 29Si OBSERVE			***Date***	Mar 15 2013
Date Stamp	Mar 15 2013	***File Name***	\\dw7dkxkdz1\NMRMirrorSite\jmrobert\merc400\jmrfids\24934-45-29si.fid\fid				
Frequency (MHz)	79.49	***Nucleus***	29Si	***Number of Transients***	48	***Original Points Count***	38176
Points Count	65536	***Pulse Sequence***	s2pul	***Receiver Gain***	39.00	***SW(cyclical) (Hz)***	23866.35
Solvent	CHLOROFORM-d			***Spectrum Offset (Hz)***	-4003.0403	***Spectrum Type***	STANDARD
Sweep Width (Hz)	23865.98	***Temperature (degree C)***	AMBIENT TEMPERATURE				

^{29}Si NMR (79 MHz, CHLOROFORM-*d*) δ ppm -53.15 - -52.91 (m, 1 Si) -37.07 (br. s., 10 Si) -19.44 (br. s., 4 Si) 7.35 (br. s., 1 Si)



No.	(ppm)	Value	Absolute Value	Non-Negative Value
1	[-53.15 .. -52.91]	0.679	3.281e+8	0.679
2	[-37.31 .. -36.57]	10.267	4.960e+9	10.267
3	[-19.74 .. -19.02]	4.303	2.079e+9	4.303
4	[7.18 .. 7.55]	1.000	4.831e+8	1.000

No.	Shift1 (ppm)	Si's	Type	Multiplet1	(ppm)
1	-53.03	1	m	M04	[-53.15 .. -52.91]
2	-37.07	10	br. s.	M03	[-37.31 .. -36.57]
3	-19.44	4	br. s.	M02	[-19.74 .. -19.02]
4	7.35	1	br. s.	M01	[7.18 .. 7.55]

No.	(ppm)	(Hz)	Height
1	-37.07	-2946.8	1.0000
2	-19.44	-1545.4	0.3659
3	7.35	583.9	0.1471

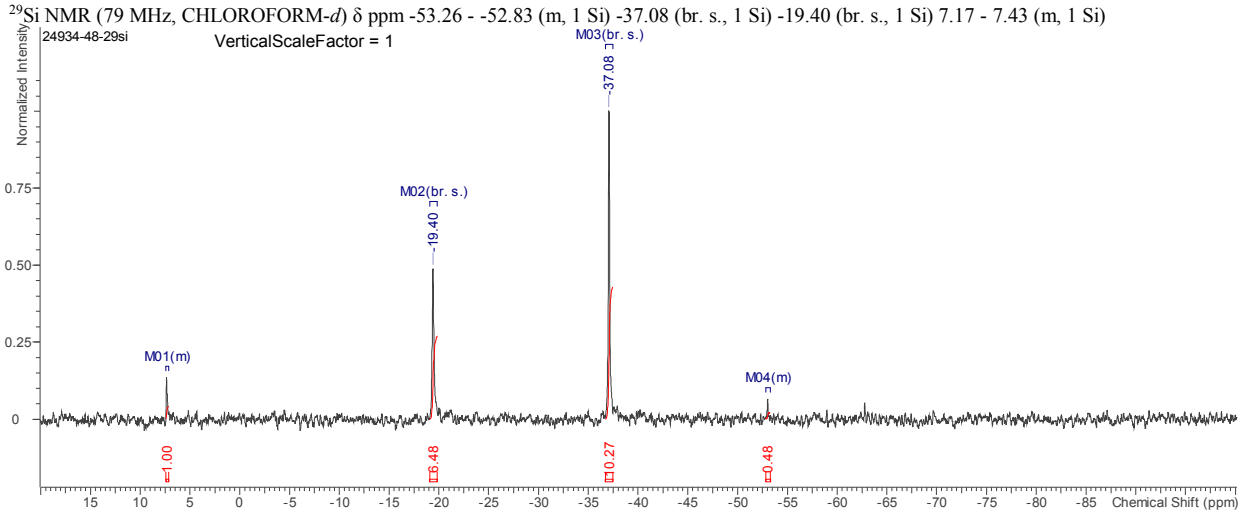
Figure S21. ^{29}Si NMR of Table 3, entry 5 ($SiEt_4$ (s) 7.35 ppm, $SiCl_4$ (s) -19.4 ppm, $SiCl_3(OMe)$ (s) -37.1 ppm, $SiCl_2(OMe)_2$ (s) -53 ppm)

8/12/2015 1:45:28 PM

Multiplets Integrals Sum 18.23	***Number of Nuclei*** 4 Si's		

Acquisition Time (sec)	1.5996	***Comment***	24934-48-29si 29Si OBSERVE			***Date***	Mar 20 2013
Date Stamp	Mar 20 2013	***File Name***	\\dw7dkxkdz1\NMRMirrorSite\jmrobert\merc400\jmrfids\24934-48-29si.fid\fid				
Frequency (MHz)	79.49	***Nucleus***	29Si	***Number of Transients***	48	***Original Points Count***	38176
Points Count	65536	***Pulse Sequence***	s2pul	***Receiver Gain***	39.00	***SW(cyclical) (Hz)***	23866.35
Solvent	CHLOROFORM-d			***Spectrum Offset (Hz)***	-3993.2078	***Spectrum Type***	STANDARD
Sweep Width (Hz)	23865.98	***Temperature (degree C)***	AMBIENT TEMPERATURE				

^{29}Si NMR (79 MHz, CHLOROFORM-*d*) δ ppm -53.26 - -52.83 (m, 1 Si) -37.08 (br. s., 1 Si) -19.40 (br. s., 1 Si) 7.17 - 7.43 (m, 1 Si)



No.	(ppm)	Value	Absolute Value	Non-Negative Value
1	[-53.26 .. -52.83]	0.477	1.966e+8	0.477
2	[-37.46 .. -36.74]	10.274	4.234e+9	10.274
3	[-19.84 .. -19.10]	6.478	2.670e+9	6.478
4	[7.17 .. 7.43]	1.000	4.121e+8	1.000

No.	Shift1 (ppm)	Si's	Type	Multiplet1	(ppm)
1	-53.04	1	m	M04	[-53.26 .. -52.83]
2	-37.08	1	br. s.	M03	[-37.46 .. -36.74]
3	-19.40	1	br. s.	M02	[-19.84 .. -19.10]
4	7.30	1	m	M01	[7.17 .. 7.43]

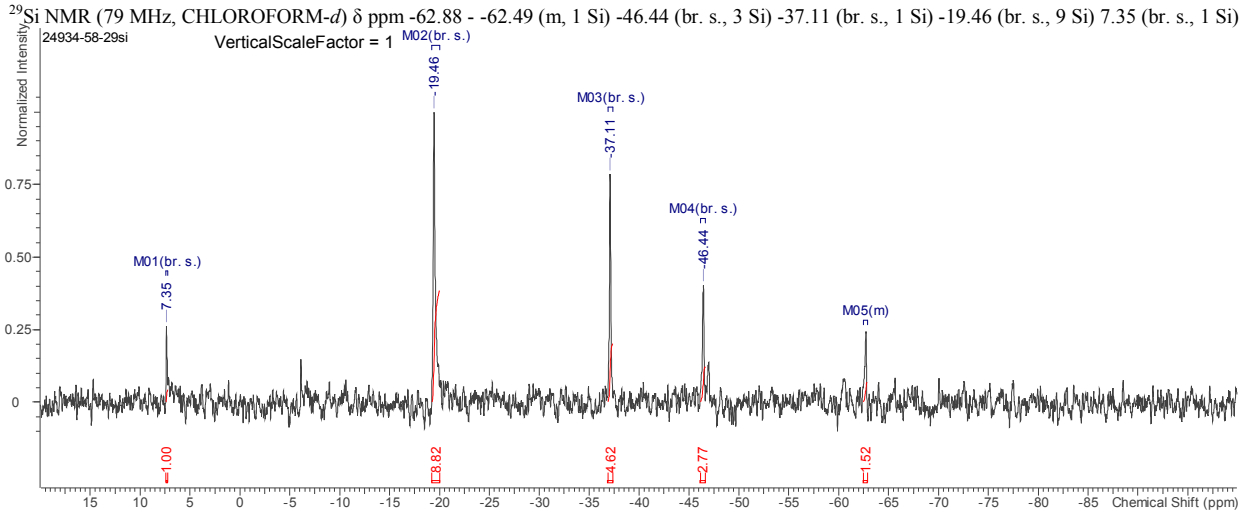
No.	(ppm)	(Hz)	Height
1	-37.08	-2947.9	1.0000
2	-19.40	-1542.2	0.4889

Figure S22. ^{29}Si NMR of Table 3, entry 6 ($SiEt_4$ (s) 7.35 ppm, $SiCl_4$ (s) -19.4 ppm, $SiCl_3(OMe)$ (s) -37.1 ppm, $SiCl_2(OMe)_2$ (s) -53 ppm)

8/12/2015 1:53:41 PM

Multiplets Integrals Sum 18.73	***Number of Nuclei*** 15 Si's		
Acquisition Time (sec) 1.5996	***Comment*** 24934-58-29si 29Si OBSERVE	***Date*** Apr 5 2013	
Date Stamp Apr 5 2013	***File Name*** \\dw7dkxkdz1\NMRMirrorSite\jmrobert\merc400\jmrfids\24934-58-29si.fid\fid		
Frequency (MHz) 79.49	***Nucleus*** 29Si	***Number of Transients*** 48	***Original Points Count*** 38176
Points Count 65536	***Pulse Sequence*** s2pul	***Receiver Gain*** 39.00	***SW(cyclical) (Hz)*** 23866.35
Solvent CHLOROFORM-d		***Spectrum Offset (Hz)*** -3996.4854	***Spectrum Type*** STANDARD
Sweep Width (Hz) 23865.98	***Temperature (degree C)*** AMBIENT TEMPERATURE		

^{29}Si NMR (79 MHz, CHLOROFORM-*d*) δ ppm -62.88 - -62.49 (m, 1 Si) -46.44 (br. s., 3 Si) -37.11 (br. s., 1 Si) -19.46 (br. s., 9 Si) 7.35 (br. s., 1 Si)



No.	(ppm)	Value	Absolute Value	Non-Negative Value
1	[-62.88 .. -62.49]	1.518	4.464e+8	1.518
2	[-46.63 .. -46.15]	2.768	8.143e+8	2.768
3	[-37.37 .. -36.87]	4.622	1.360e+9	4.622
4	[-20.01 .. -19.25]	8.823	2.595e+9	8.823
5	[7.22 .. 7.44]	1.000	2.942e+8	1.000

No.	Shift1 (ppm)	Si's	Type	Multiplet1	(ppm)
1	-62.68	1	m	M05	[-62.88 .. -62.49]
2	-46.44	3	br. s.	M04	[-46.63 .. -46.15]
3	-37.11	1	br. s.	M03	[-37.37 .. -36.87]
4	-19.46	9	br. s.	M02	[-20.01 .. -19.25]
5	7.35	1	br. s.	M01	[7.22 .. 7.44]

No.	(ppm)	(Hz)	Height
1	-46.44	-3691.9	0.4029
2	-37.11	-2949.7	0.7856
3	-19.46	-1546.9	1.0000
4	7.35	584.2	0.2616

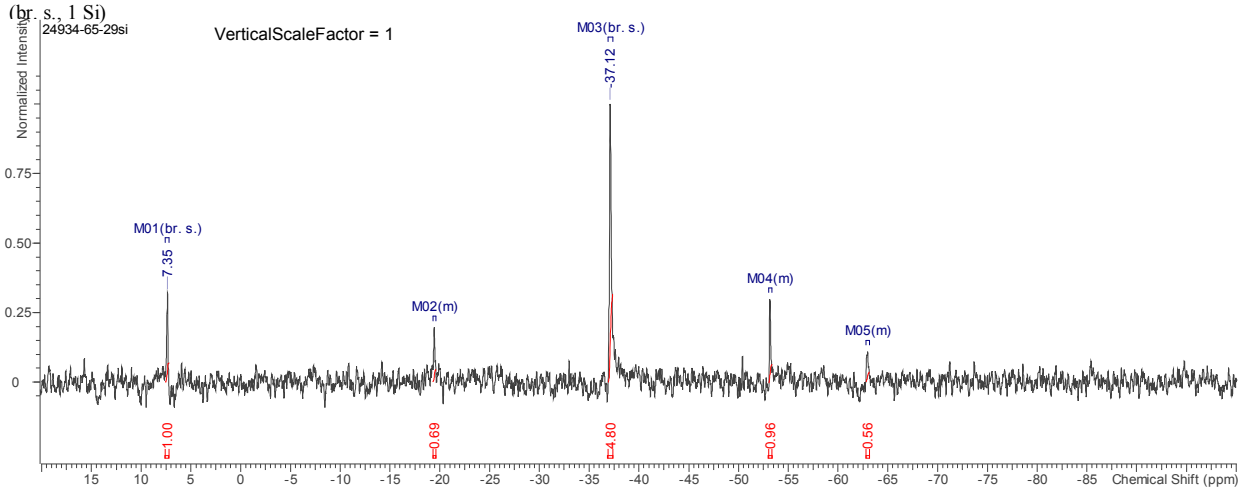
Figure S23. ^{29}Si NMR of Table 3, entry 7 ($SiEt_4$ (s) 7.35 ppm, $SiCl_4$ (s) -19.5 ppm, $SiCl_3(OMe)$ (s) -37.1 ppm, $SiCl_2(OMe)_2$ (s) -46.4 ppm, $SiCl(OMe)_3$ (s) -62.7 ppm)

8/12/2015 2:09:10 PM

Multiplets Integrals Sum 8.02	***Number of Nuclei*** 5 Si's		

Acquisition Time (sec)	1.5996	***Comment***	24934-65-29si 29Si OBSERVE			***Date***	Apr 17 2013
Date Stamp	Apr 17 2013	***File Name***	\\dw7dkxkdz1\NMRMirrorSite\jmrobert\merc400\jmrfids\24934-65-29si.fid\fid				
Frequency (MHz)	79.49	***Nucleus***	29Si	***Number of Transients***	48	***Original Points Count***	38176
Points Count	65536	***Pulse Sequence***	s2pul	***Receiver Gain***	36.00	***SW(cyclical) (Hz)***	23866.35
Solvent	CHLOROFORM-d			***Spectrum Offset (Hz)***	-4008.5029	***Spectrum Type***	STANDARD
Sweep Width (Hz)	23865.98	***Temperature (degree C)***	AMBIENT TEMPERATURE				

^{29}Si NMR (79 MHz, CHLOROFORM-*d*) δ ppm -63.19 - -62.78 (m, 1 Si) -53.37 - -53.03 (m, 1 Si) -37.12 (br. s., 1 Si) -19.60 - -19.32 (m, 1 Si) 7.35 (br. s., 1 Si)



No.	(ppm)	Value	Absolute Value	Non-Negative Value
1	[-63.19 .. -62.78]	0.563	1.851e+8	0.563
2	[-53.37 .. -53.03]	0.961	3.156e+8	0.961
3	[-37.38 .. -36.91]	4.801	1.577e+9	4.801
4	[-19.60 .. -19.32]	0.693	2.276e+8	0.693
5	[7.19 .. 7.56]	1.000	3.285e+8	1.000

No.	Shift1 (ppm	Si's	Type	Multiplet1	(ppm)
1	-62.98	1	m	M05	[-63.19 .. -62.78]
2	-53.20	1	m	M04	[-53.37 .. -53.03]
3	-37.12	1	br. s.	M03	[-37.38 .. -36.91]
4	-19.46	1	m	M02	[-19.60 .. -19.32]
5	7.35	1	br. s.	M01	[7.19 .. 7.56]

No.	(ppm)	(Hz)	Height
1	-37.12	-2950.4	1.0000
2	7.35	584.2	0.3214

Figure S24. ^{29}Si NMR of Table 3, entry 8 ($SiEt_4$ (s) 7.35 ppm, $SiCl_4$ (s) -19.5 ppm, $SiCl_3(OMe)$ (s) -37.1 ppm, $SiCl_2(OMe)_2$ (s) -53.2 ppm, $SiCl(OMe)_3$ (s) -63 ppm)

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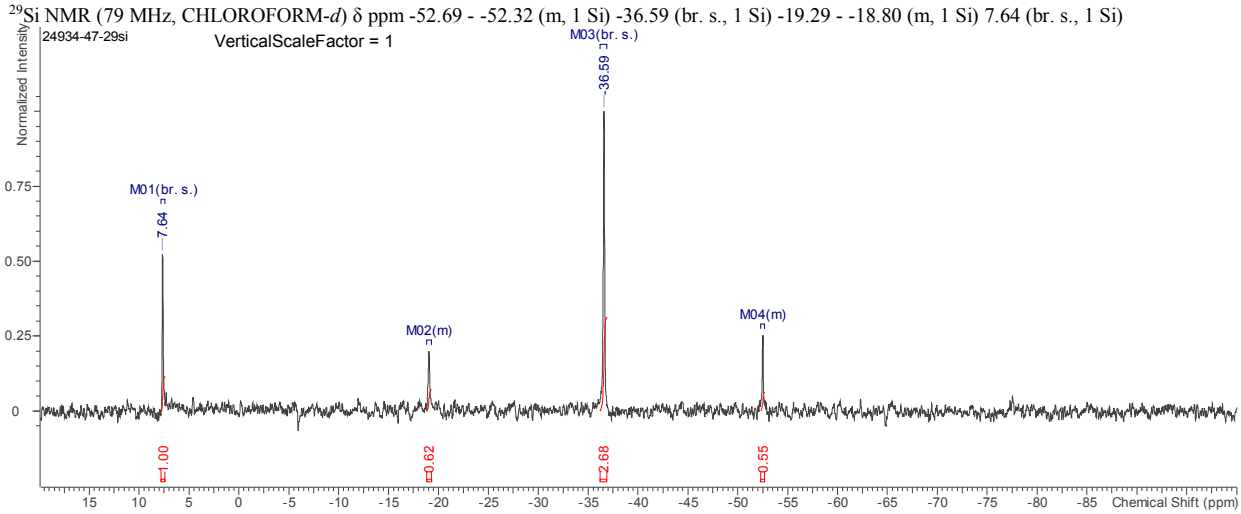
Multiplets Integrals Sum 4.84	***Number of Nuclei*** 4 Si's		

Acquisition Time (sec)	1.5996	***Comment***	24934-47-29si 29Si OBSERVE			***Date***	Mar 19 2013
Date Stamp	Mar 19 2013	***File Name***	\\dw7dkxkdz1\NMRMirrorSite\jmrobert\merc400\jmrfids\24934-47-29si.fid\fid				
Frequency (MHz)	79.49	***Nucleus***	29Si	***Number of Transients***	48	***Original Points Count***	38176
Points Count	65536	***Pulse Sequence***	s2pul	***Receiver Gain***	36.00	***SW(cyclical) (Hz)***	23866.35
Solvent	CHLOROFORM-d			***Spectrum Offset (Hz)***	-3982.2773	***Spectrum Type***	STANDARD
Sweep Width (Hz)	23865.98	***Temperature (degree C)***	AMBIENT TEMPERATURE				

^{29}Si NMR (79 MHz, CHLOROFORM-*d*) δ ppm -52.69 - -52.32 (m, 1 Si) -36.59 (br. s., 1 Si) -19.29 - -18.80 (m, 1 Si) 7.64 (br. s., 1 Si)



No.	(ppm)	Value	Absolute Value	Non-Negative Value
1	[-52.69 .. -52.32]	0.548	5.049e+8	0.548
2	[-36.89 .. -36.21]	2.675	2.466e+9	2.675
3	[-19.29 .. -18.80]	0.621	5.725e+8	0.621
4	[7.40 .. 7.78]	1.000	9.217e+8	1.000

No.	Shift1 (ppm)	Si's	Type	Multiplet1	(ppm)
1	-52.50	1	m	M04	[-52.69 .. -52.32]
2	-36.59	1	br. s.	M03	[-36.89 .. -36.21]
3	-19.05	1	m	M02	[-19.29 .. -18.80]
4	7.64	1	br. s.	M01	[7.40 .. 7.78]

No.	(ppm)	(Hz)	Height
1	-36.59	-2908.9	1.0000
2	7.64	607.2	0.5237

Figure S25. ^{29}Si NMR of reaction with ethylisocyanate ($SiEt_4$ (s) 7.35 ppm, $SiCl_4$ (s) -19.1 ppm, $SiCl_3(OEt)$ (s) -36.6 ppm, $SiCl_2(OEt)_2$ (s) -52.5 ppm)

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Multiplets Integrals Sum	0.00	***Number of Nuclei***	0 C's				
Acquisition Time (sec)	1.6004	***Comment***	24934-40-13c 13C OBSERVE			***Date***	Mar 10 2013
Date Stamp	Mar 10 2013	***File Name***	\\dw7dkxkdz1\NMRMirrorSite\jmrobert\merc400\jmrfids\24934-40-13c.fid\fid				
Frequency (MHz)	100.62	***Nucleus***	13C	***Number of Transients***	112	***Original Points Count***	38656
Points Count	65536	***Pulse Sequence***	s2pul	***Receiver Gain***	22.00	***SW(cyclical) (Hz)***	24154.59
Solvent	CHLOROFORM-d			***Spectrum Offset (Hz)***	10035.7373	***Spectrum Type***	STANDARD
Sweep Width (Hz)	24154.22	***Temperature (degree C)***	AMBIENT TEMPERATURE				

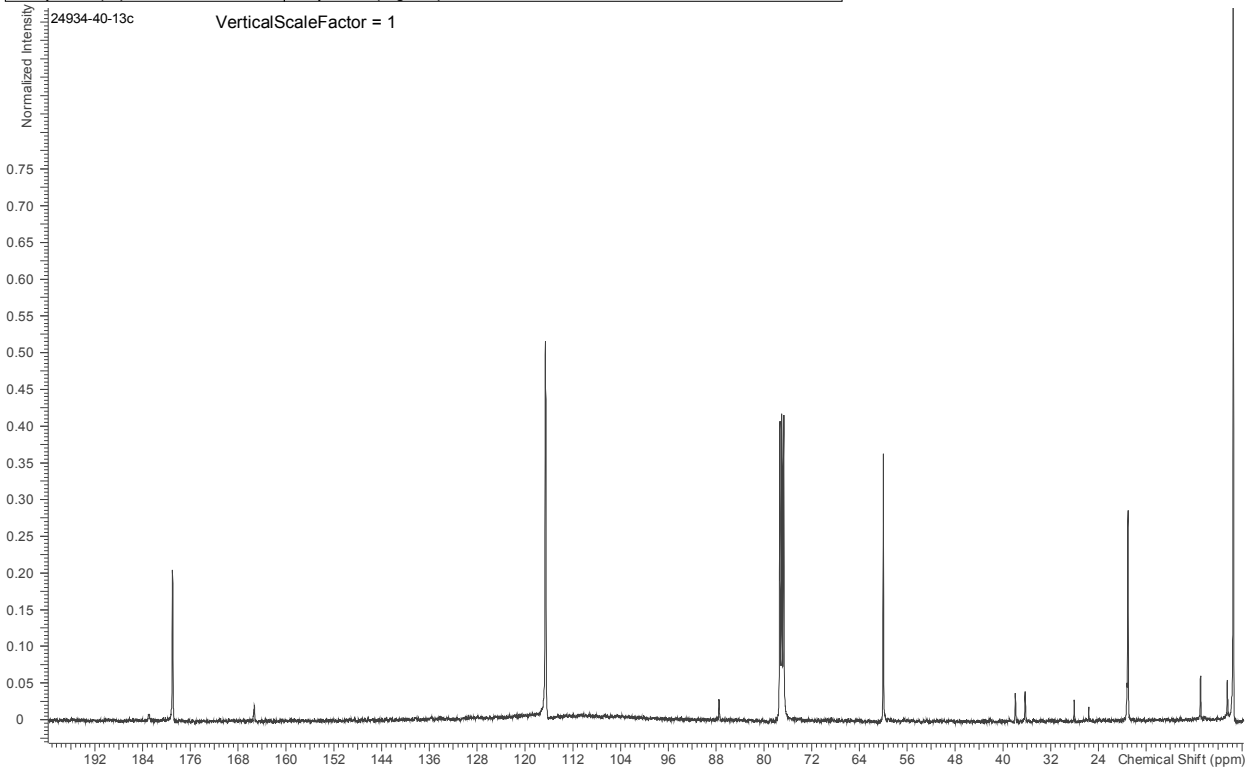

Figure S26. ^{13}C NMR of Table 2, entry 1

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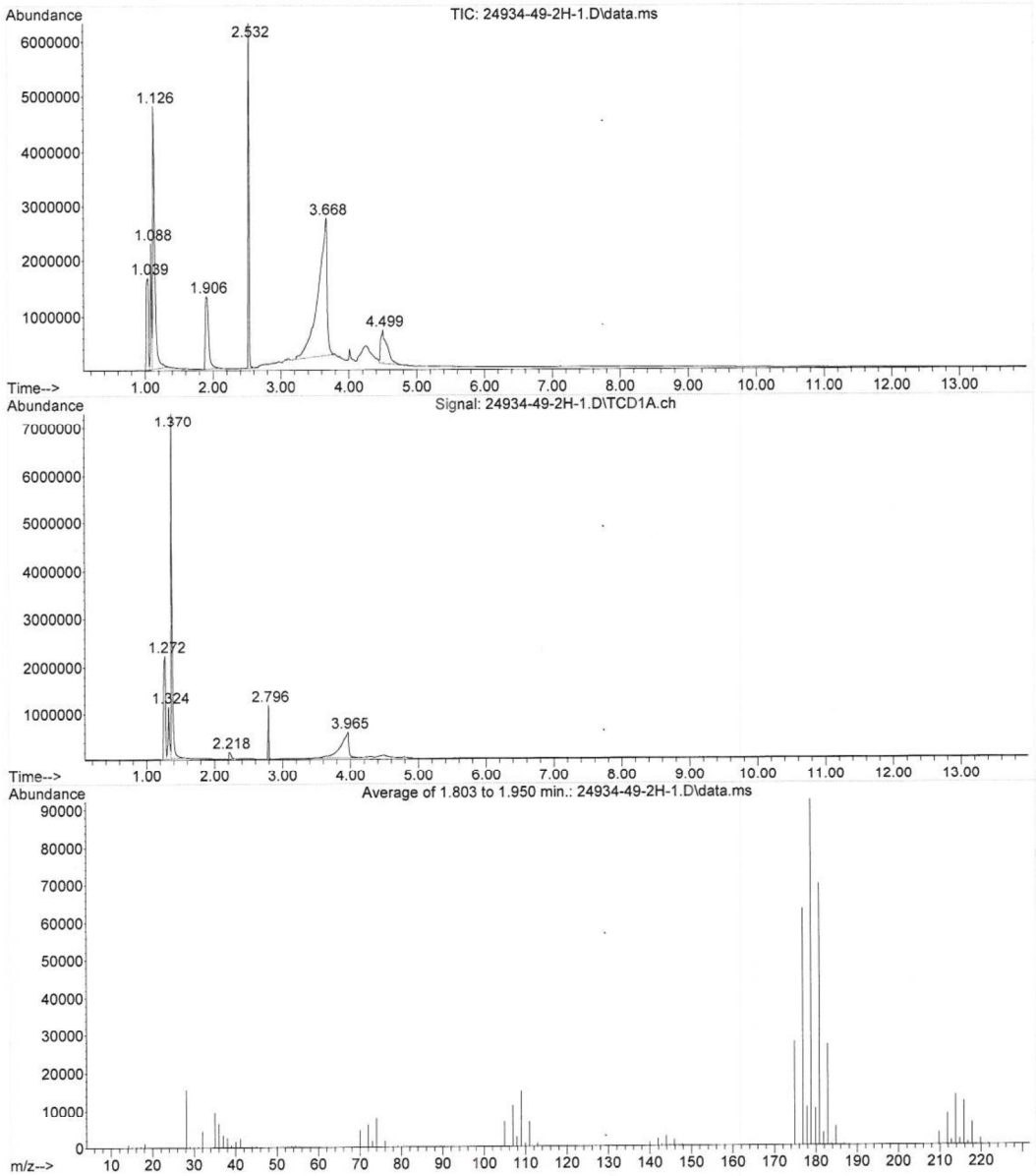

Figure S27. GCMS of $GeCl_4$

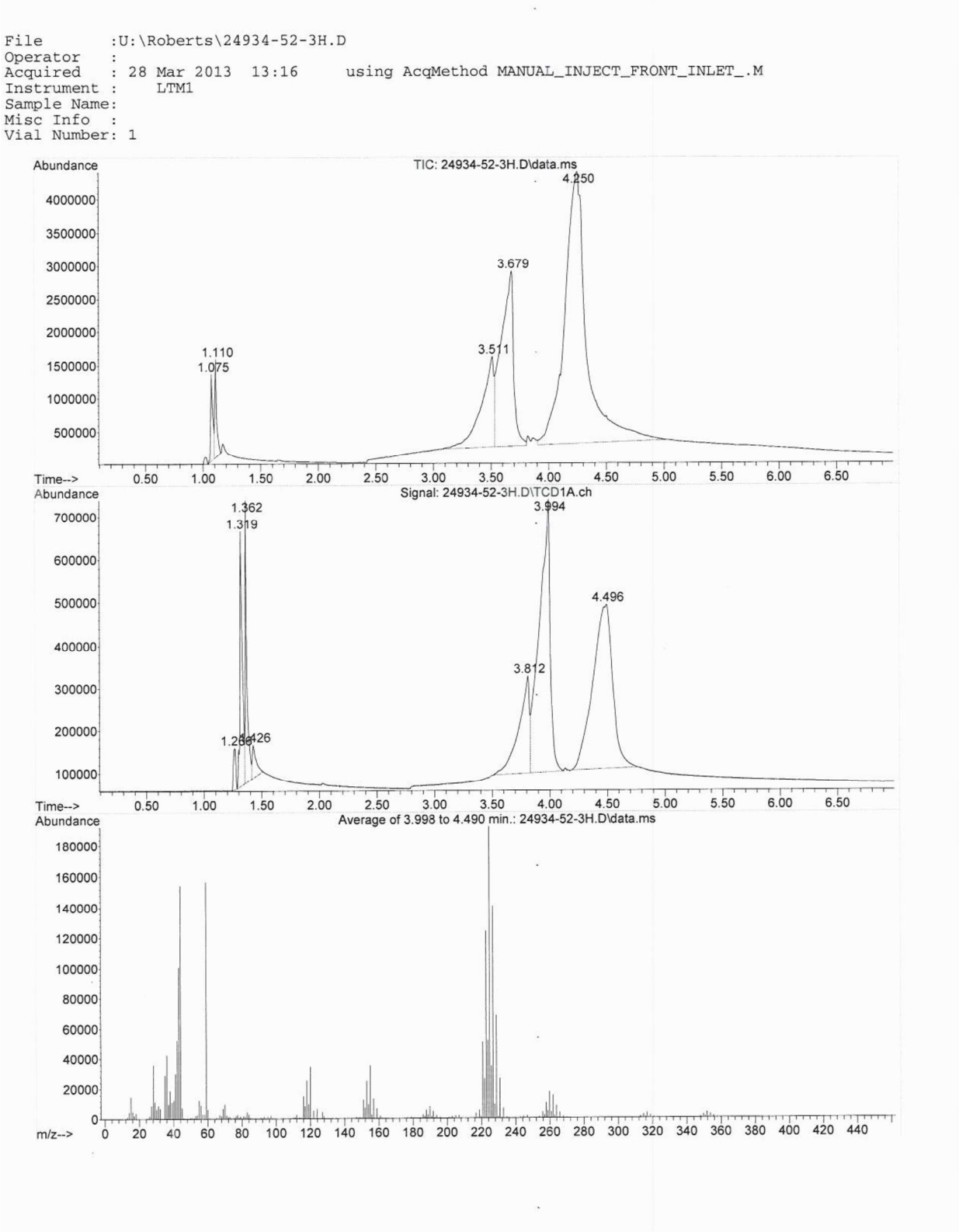

Figure S28. GCMS of $SnCl_4$