Electronic Supplementary Information

Diverse reactivity of an isolable dialkylsilylene toward imines

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Contents

1. X-ray structure determination.

X-ray analysis of 12c'

Molecular structure of **12c** was determined by X-ray structural analysis. There were two independent molecules (**12c** and **12c'**) in an asymmetric unit. Molecular structure of **12c'** is shown in Fig S1.

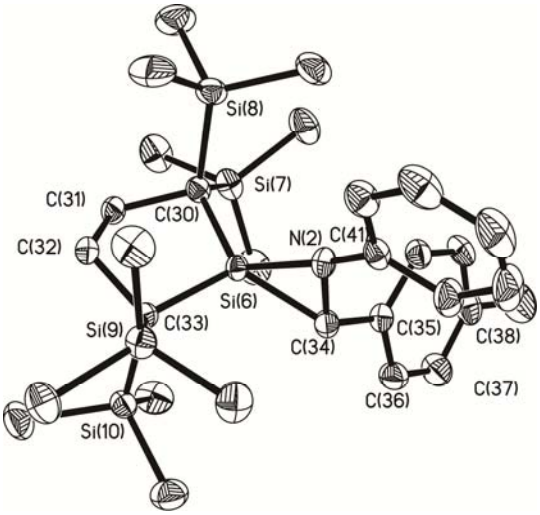


Figure S1. ORTEP drawing of **12c'**. Thermal ellipsoids are shown at the 30% probability level. Hydrogen atoms are omitted for clarity. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at the 30% probability level. Selected bond lengths (Å) and angles (deg): Si6-N2=1.706(2), Si6-C34=1.879(3), C34-N2=1.480(4), C34-C35=1.484(4), C41-N2=1.396(3), Si6-C30=1.884(3), Si6-C33=1.885(3); N2-Si6-C34=48.49(11), C34-N2-Si6=71.86(14), N2-C34-Si6=59.65(13), C30-Si6-C33=101.79(12). Dihedral angles between two planes (deg): 15.25 for C34-Si6-N2/N-aryl planes, 81.31 for C34-Si6-N2/C30-Si6-C33 planes, and 81.76 for C-aryl/N-phenyl planes.

X-ray analysis of 14f

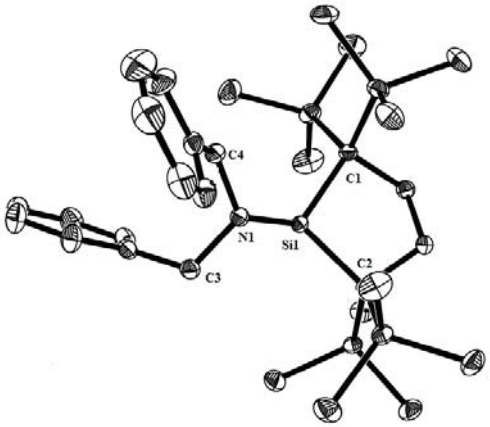


Figure S2. ORTEP drawing of **14f**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at the 30% probability level. Selected bond lengths (Å) and angles (deg):Si1-N1=1.7392(14), Si1-C1=1.8994(17), Si1-C2=1.9135(15), Si1-H1=1.432(18), N1-C3=1.480(2), N1-C4=1.454(2); C1-Si1-C2= 101.23(7).

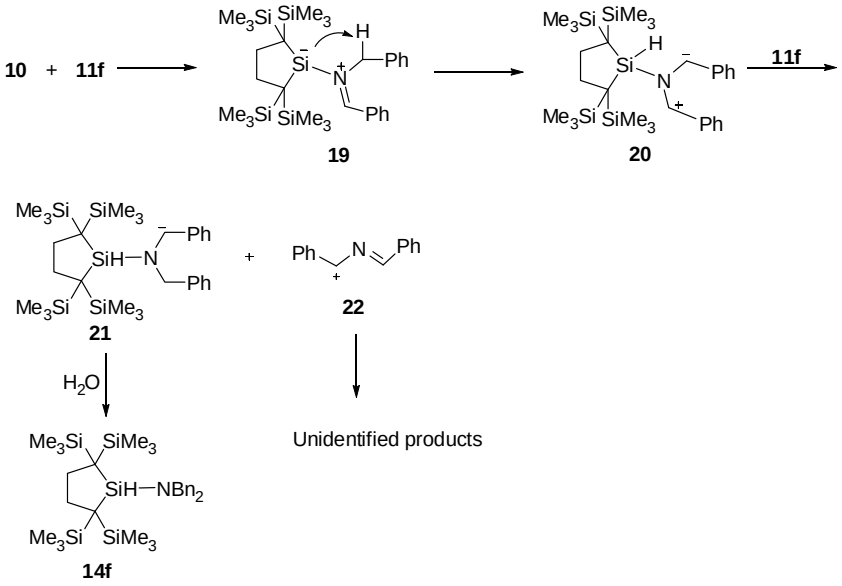
Table S1. Crystal and refinement data for 12a-12c, 13d, 13e, and 14

Table S1. Crystal and refinement data for **12a-c**, **13d-e** and **14f**

Parameters	**12a**	**12b**	**12c**	**13d**	**13e**	**14f**
Empirical formula	$C_{29}H_{51}NSi_5$	$C_{30}H_{53}NOSi_5$	$C_{29}H_{50}ClNSi_5$	$C_{30}H_{50}F_3NSi_5$	$C_{31}H_{49}F_6NSi_5$	$C_{30}H_{55}NSi_5$
Formula weight	554.16	584.18	588.60	622.16	690.16	570.20
Crystal system	Triclinic	Triclinic	Triclinic	Monoclinic	Orthorhombic	Triclinic
Space group	P-1	P-1	P-1	P2(1)/n	Pbca	P-1
a [Å]	9.9889(8)	10.1986(8)	13.1571(11)	11.6872(8)	22.667(4)	11.4647(8)
b [Å]	10.8412(8)	11.4219(9)	15.9991(13)	23.8106(16)	14.110(2)	11.7712(9)
c [Å]	16.4060(13)	16.3207(12)	17.0546(14)	14.0462(10)	23.682(4)	14.2938(11)
α [deg]	81.7450(10)	77.5760(10)	72.259(2)	90	90	74.1470(10)
β [deg]	78.7950(10)	78.1960(10)	84.025(2)	112.988(2)	90	82.1350(10)
γ [deg]	78.6920(10)	71.5880(10)	89.806(2)	90	90	69.5230(10)
V [Å^{-3}]	1698.6(2)	1742.3(2)	3399.2(5)	3598.4(4)	7574(2)	1736.6(2)
Z	2	2	4	4	8	2
D_{calcd} [g cm^{-3}]	1.083	1.114	1.150	1.148	1.210	1.090
μ [mm^{-1}]	0.228	0.227	0.307	0.233	0.239	0.224
F (000)	604	636	1272	1336	2928	624
Reflections collected	23618	24536	36538	26379	25486	23579
Independent Reflections	5936	6091	12553	6332	7395	6067
R(int)	0.0205	0.0245	0.0386	0.0283	0.0505	0.0210
Data/restraints /parameters	5936/6/ 359	6091/ 0/347	12553/0 /673	6332/87/392	7395/17 / 447	6067/0 /341
final R indices [$I>2\sigma(I)$] R_1	0.0411	0.0399	0.0445	0.0391	0.0527	0.0340
R indices (all data) wR_2	0.1554	0.1563	0.1545	0.1456	0.1509	0.1298

2. A plausible mechanism for the reaction of silylene 10 with *N*-benzylbenzaldimine 11f

The reaction would also begin with the formation of the corresponding imine silaylide **19**. The reaction of imine ylide **20**, which is formed by the migration of a benzylic proton of **19**, with starting imine **11f** may give carbanion **21** and 2-azaallyl cation **22**. Carbanion **21** is trapped by water to give the final product **14f**, while **22** gives unidentified products. The fact that the yield of **14f** is lower than 50% is compatible with the proposed mechanism but no other supporting evidence is obtained.


10 + 11f
Me3Si SiMe3
H
Si
N
Ph
Me3Si SiMe3
Ph
19
Me3Si SiMe3
H
Si
N
Ph
Me3Si SiMe3
Ph
20
11f
Me3Si SiMe3
SiH—N
Ph
Ph
Me3Si SiMe3
21
+
Ph N Ph
22
H2O
Unidentified products
Me3Si SiMe3
SiH—NBn2
Me3Si SiMe3
14f

Scheme S1.

4. ^{1}H, ^{13}C, and ^{29}Si NMR spectra of silaaziridines 12a-12c (Figures S1-S9)

Figure S3.

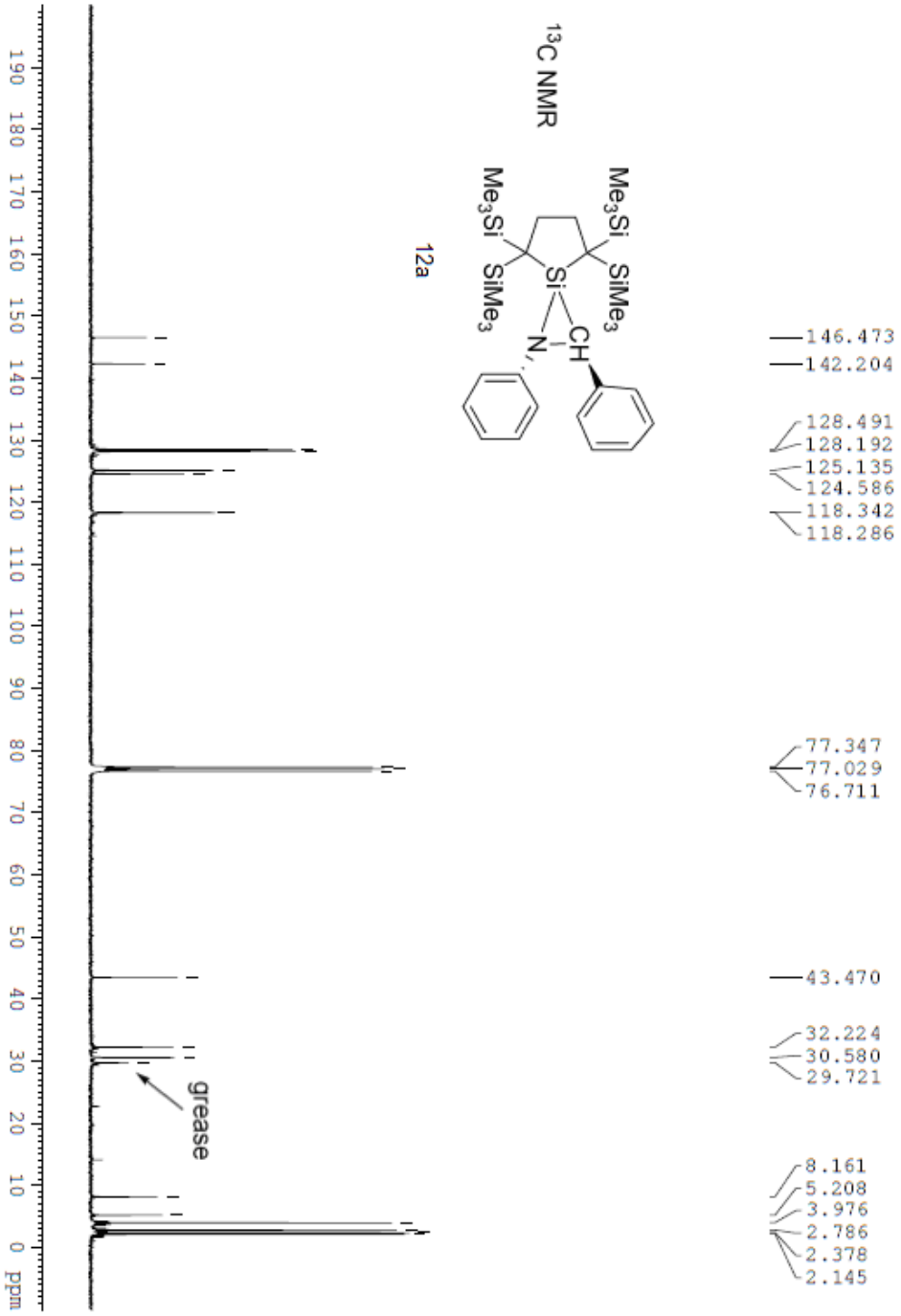

13C NMR
12a
Me3Si
SiMe3
Me3Si
SiMe3
Si
N
CH
146.473
142.204
128.491
128.192
125.135
124.586
118.342
118.286
77.347
77.029
76.711
43.470
32.224
30.580
29.721
8.161
5.208
3.976
2.786
2.378
2.145
grease
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

Figure S4.

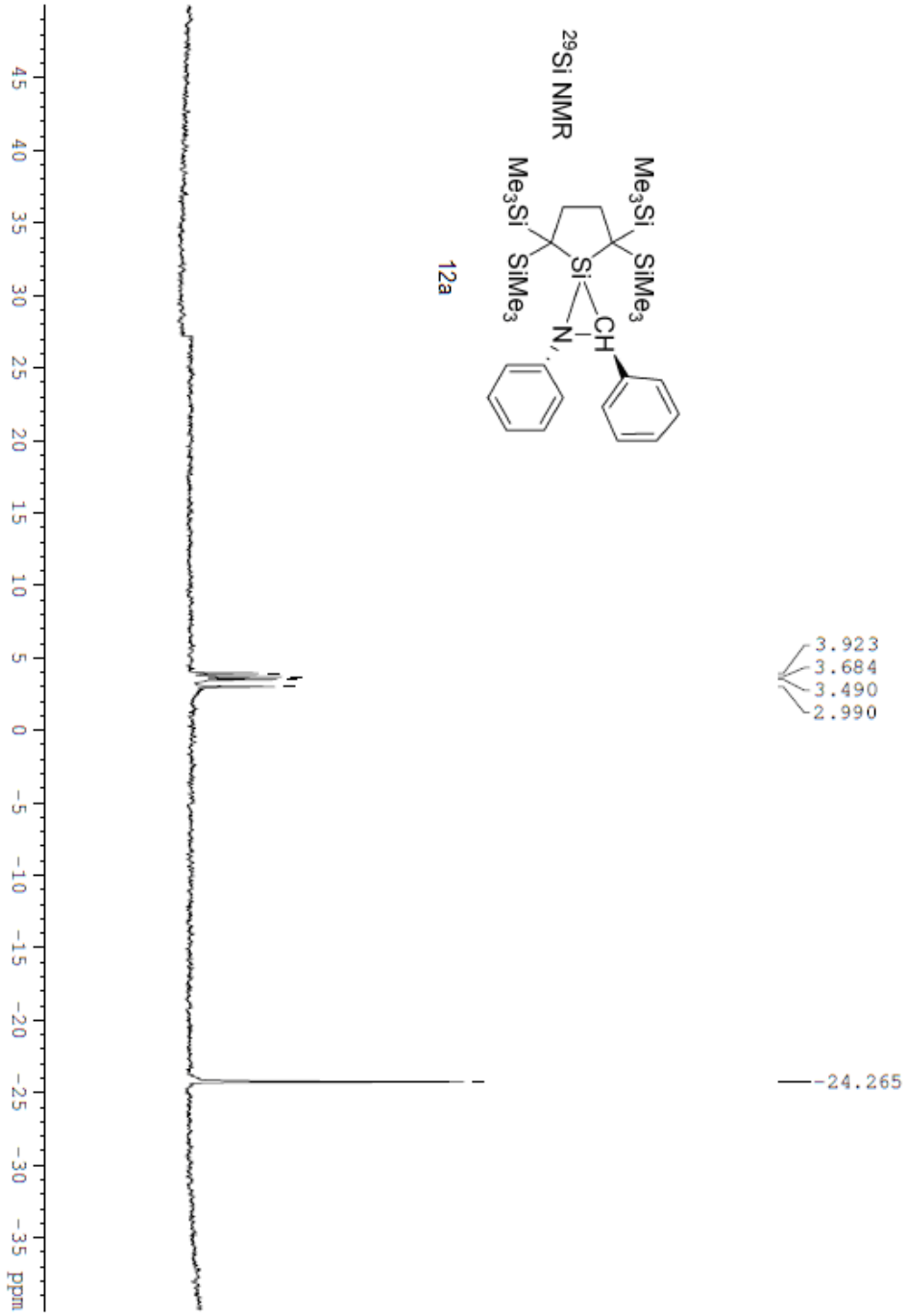


Figure S5.

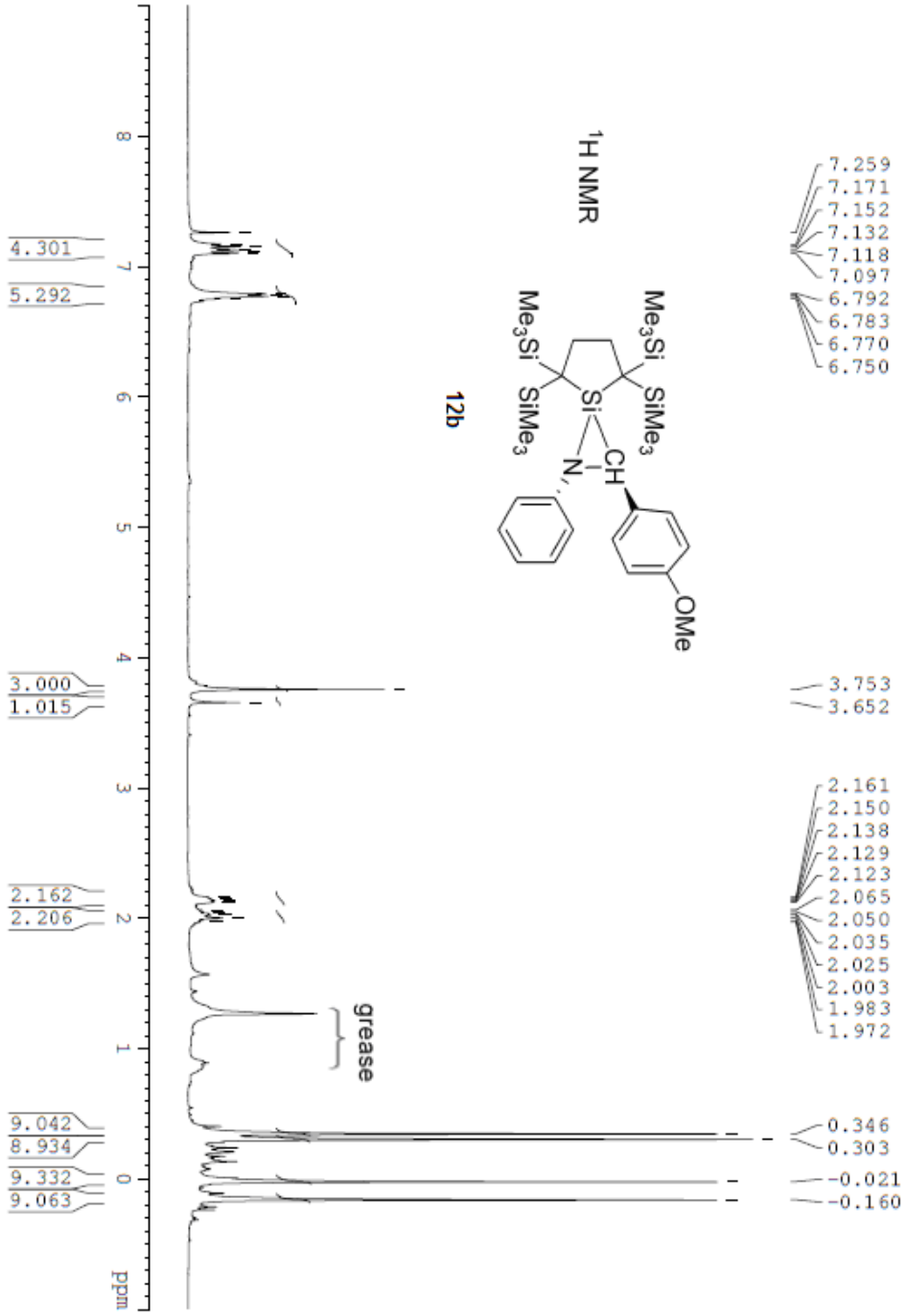

^{1}H NMR
12b
Me$_3$Si
SiMe$_3$
Si
N
CH
OMe
7.259
7.171
7.152
7.132
7.118
7.097
6.792
6.783
6.770
6.750
4.301
5.292
3.000
1.015
3.753
3.652
2.162
2.206
2.161
2.150
2.138
2.129
2.123
2.065
2.050
2.035
2.025
2.003
1.983
1.972
grease
9.042
8.934
9.332
9.063
0.346
0.303
-0.021
-0.160
ppm

Figure S6.

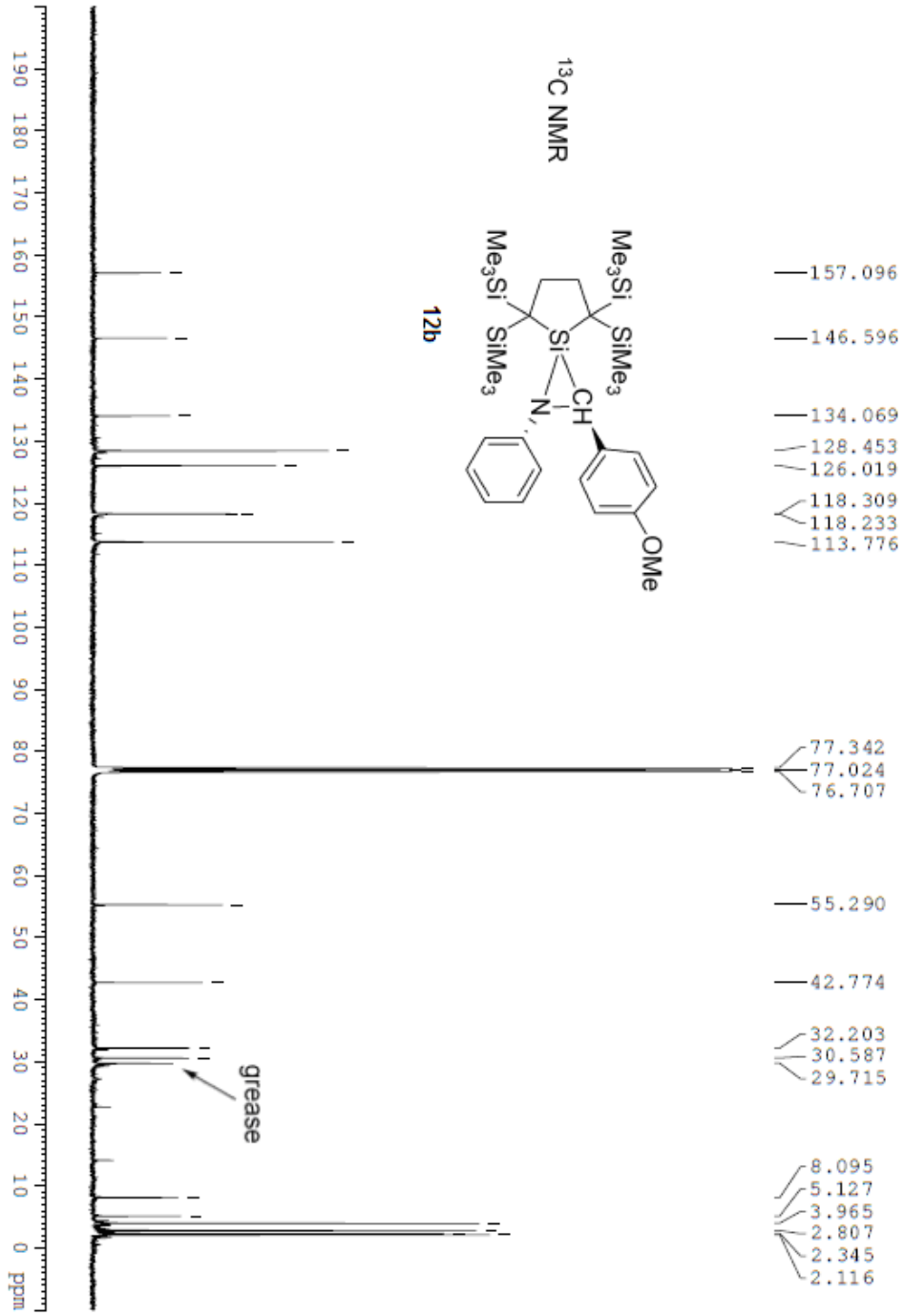

13C NMR
12b
Me3Si
SiMe3
Me3Si
SiMe3
Si
N
CH
OMe
157.096
146.596
134.069
128.453
126.019
118.309
118.233
113.776
77.342
77.024
76.707
55.290
42.774
32.203
30.587
29.715
8.095
5.127
3.965
2.807
2.345
2.116
grease
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

Figure S7.

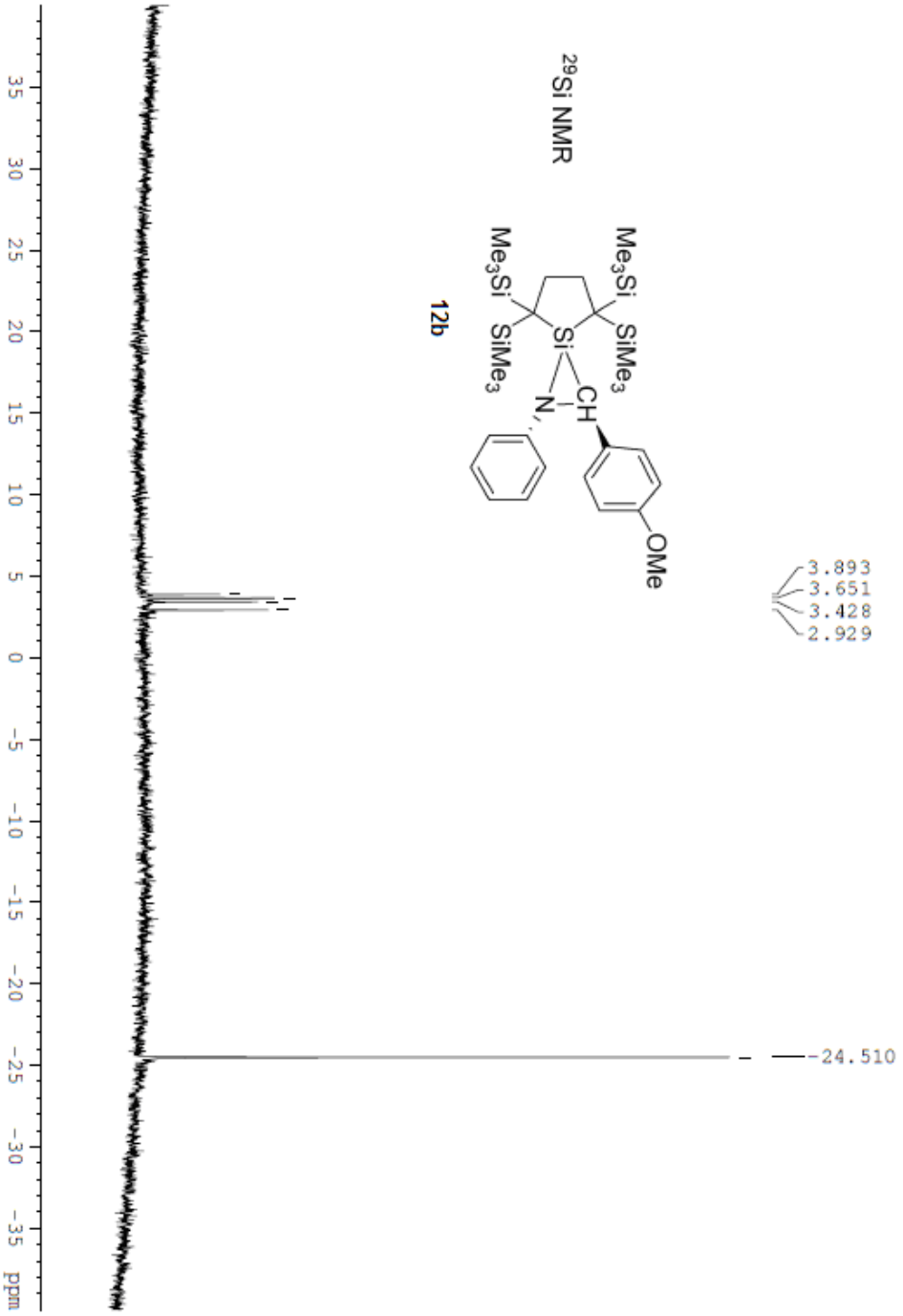

29Si NMR
12b
Me3Si
SiMe3
Me3Si
SiMe3
Si
N
CH
OMe
3.893
3.651
3.428
2.929
-24.510
35
30
25
20
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
ppm

Figure S8.

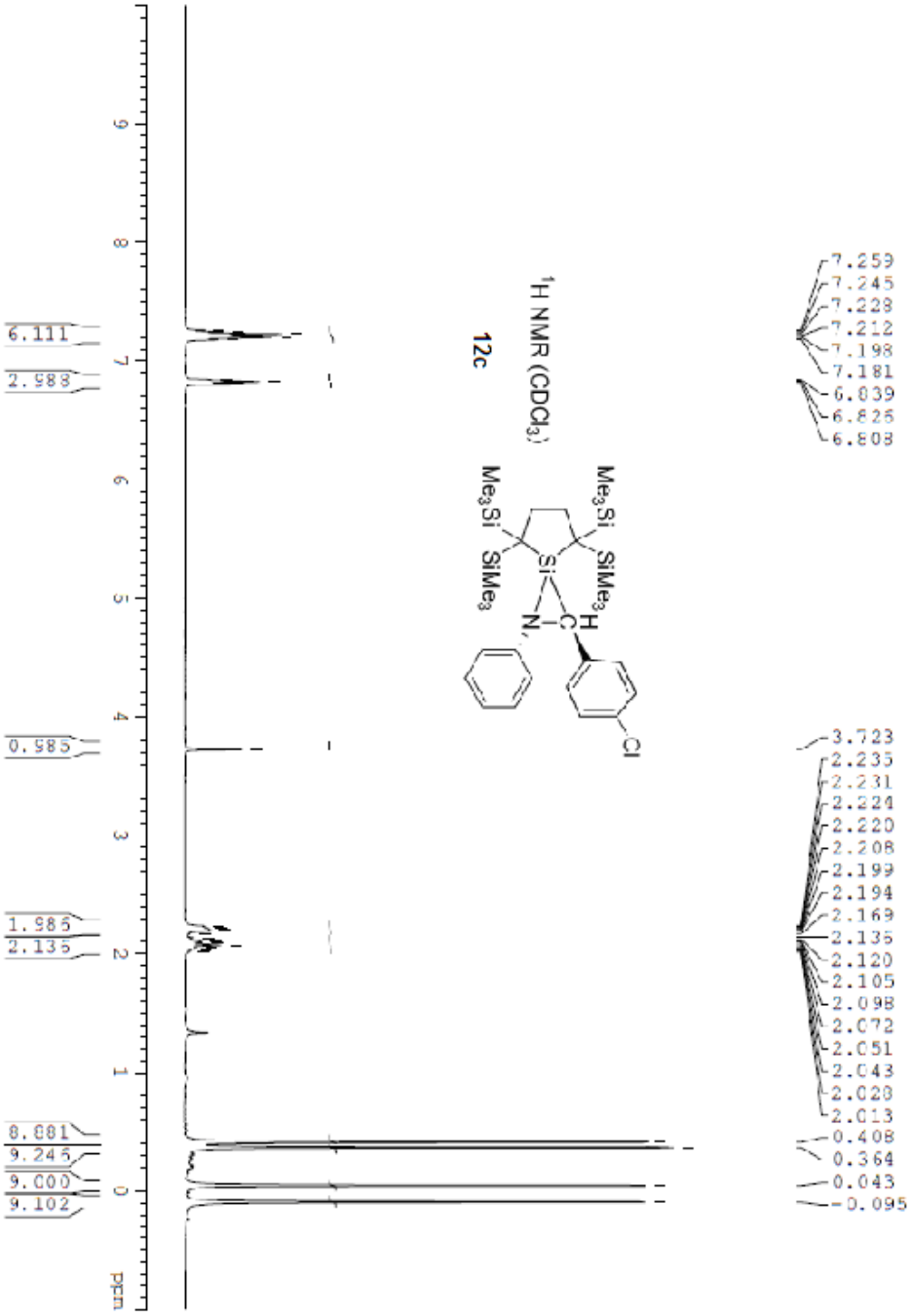

^{1}H NMR (CDCl$_3$)
12c
Me$_3$Si
SiMe$_3$
Si
N
C
H
Cl
6.111
2.988
0.985
1.986
2.135
8.081
9.246
9.000
9.102
7.259
7.245
7.228
7.212
7.198
7.181
6.839
6.825
6.808
3.723
2.235
2.231
2.224
2.220
2.208
2.199
2.194
2.169
2.135
2.120
2.105
2.098
2.072
2.051
2.043
2.020
2.013
0.408
0.364
0.043
-0.095
ppm

Figure S9.

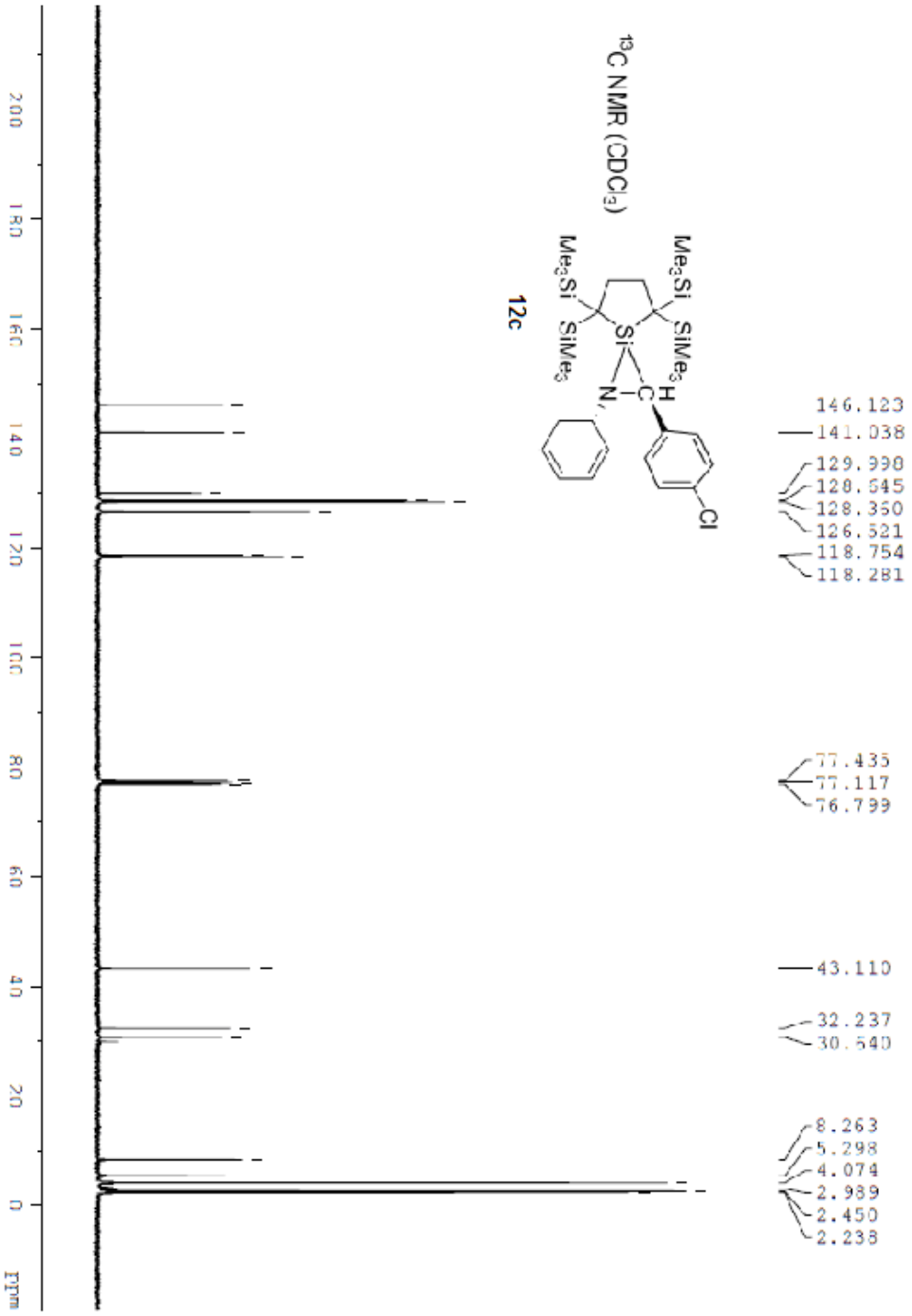

^{13}C NMR ($CDCl_3$)
12c
Me_3Si
$SiMe_3$
Si
N
C
H
Cl
146.123
141.038
129.990
128.545
128.350
126.521
118.754
118.281
77.435
77.117
76.799
43.110
32.237
30.540
8.263
5.298
4.074
2.989
2.450
2.238
200
180
160
140
120
100
80
60
40
20
0
ppm

Figure S10.

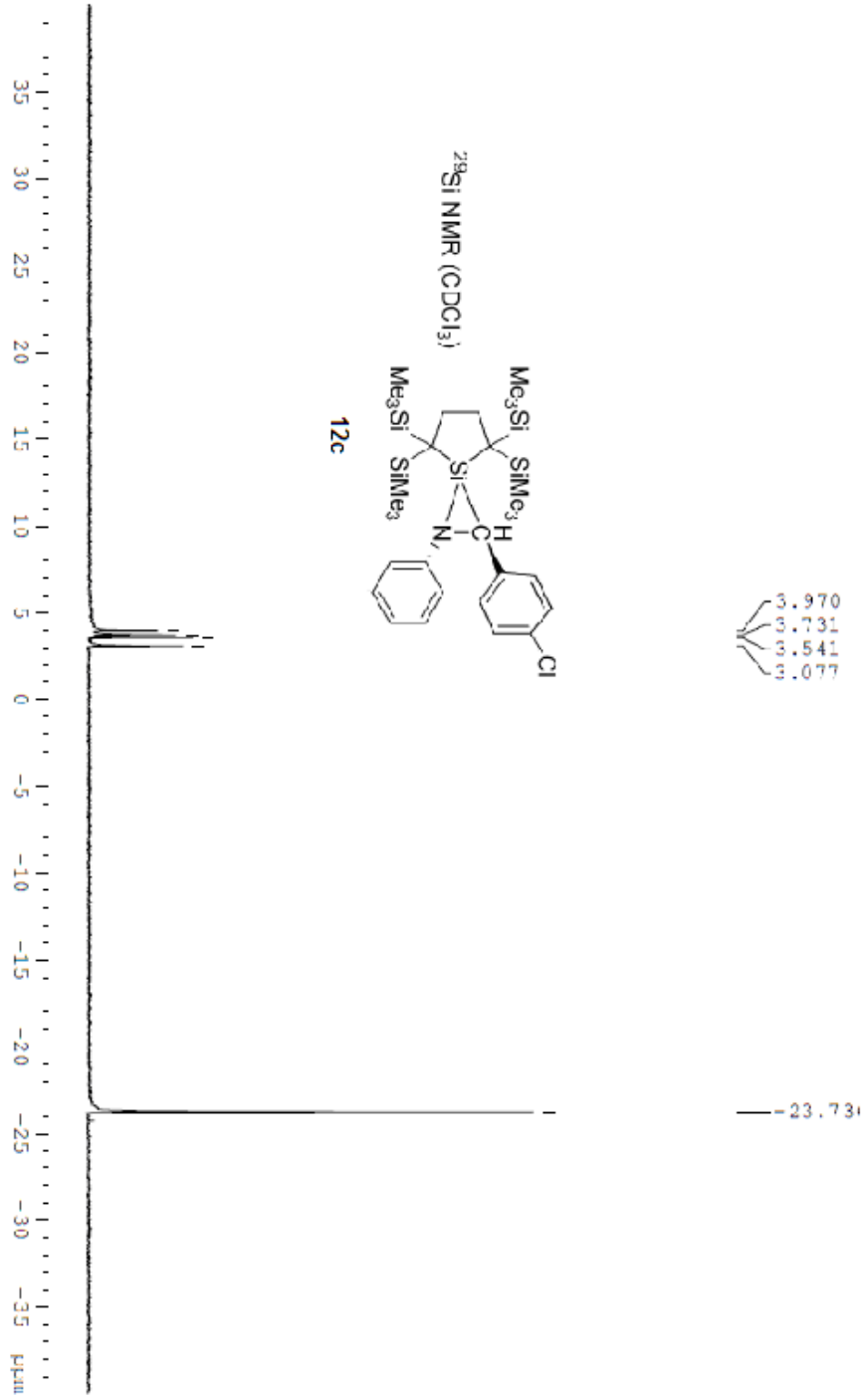


Figure S11.

2. ^{1}H, ^{13}C, ^{19}F, and ^{29}Si NMR spectra of silaazetidines 13d and 13e (Figures S10-S17)

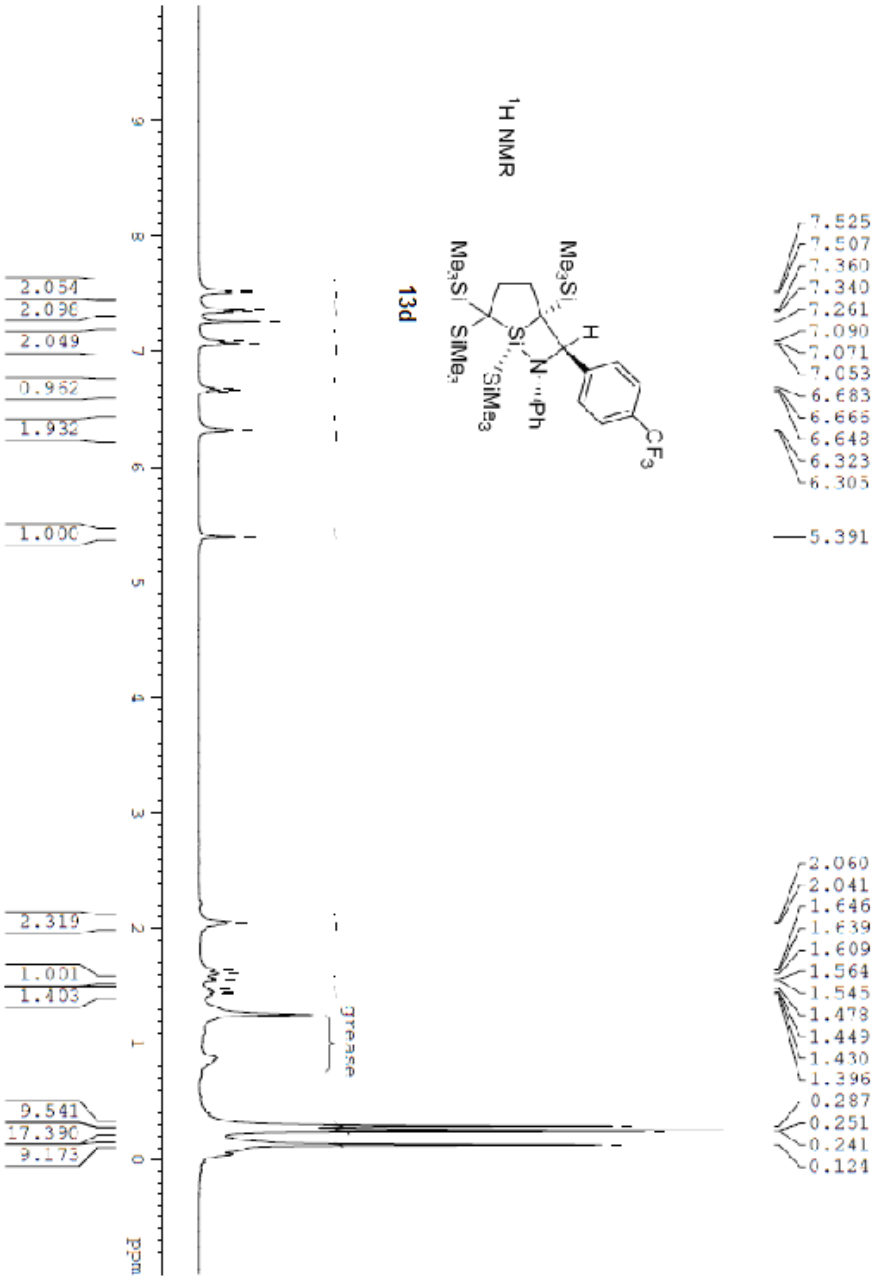


Figure S12.

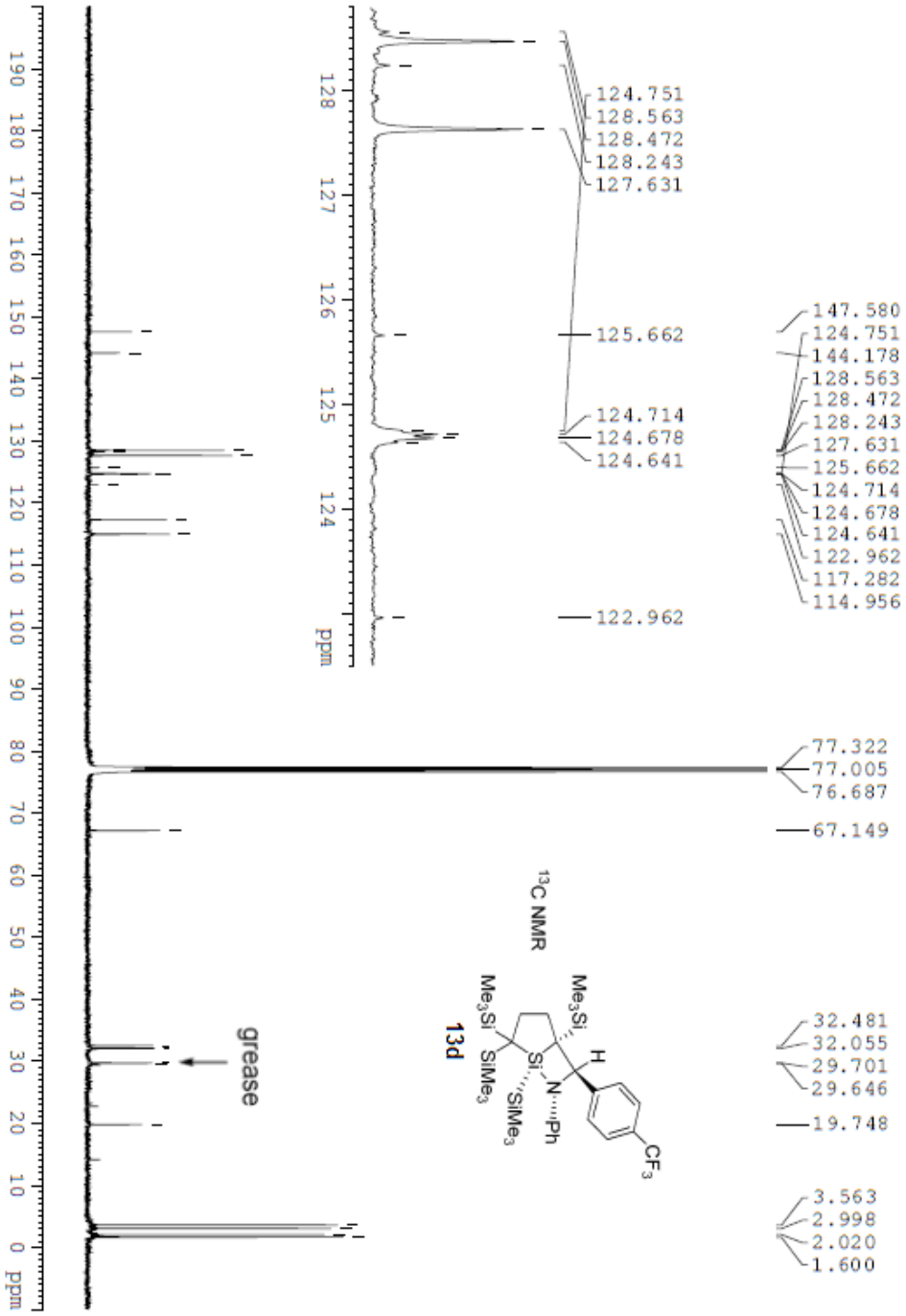

124.751
128.563
128.472
128.243
127.631
125.662
124.714
124.678
124.641
122.962
147.580
124.751
144.178
128.563
128.472
128.243
127.631
125.662
124.714
124.678
124.641
122.962
117.282
114.956
77.322
77.005
76.687
67.149
32.481
32.055
29.701
29.646
19.748
3.563
2.998
2.020
1.600
grease
13C NMR
13d
Me3Si
SiMe3
Me3Si
Si
N
Ph
H
SiMe3
CF3
ppm

Figure S13.

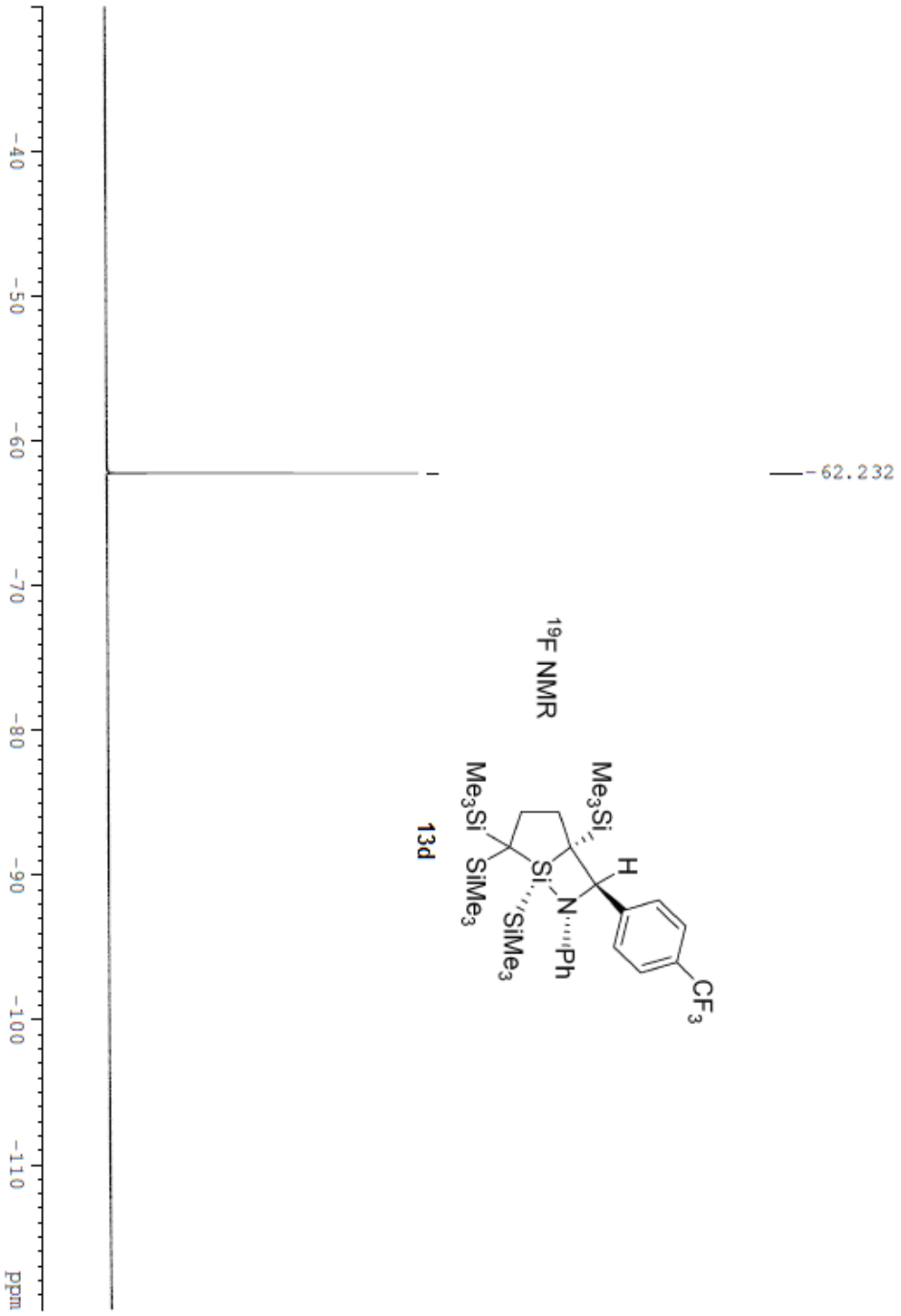

-40
-50
-60
-70
-80
-90
-100
-110
ppm
-62.232
19F NMR
13d
Me3Si
SiMe3
Me3Si
Si
N
Ph
H
CF3

Figure S14.

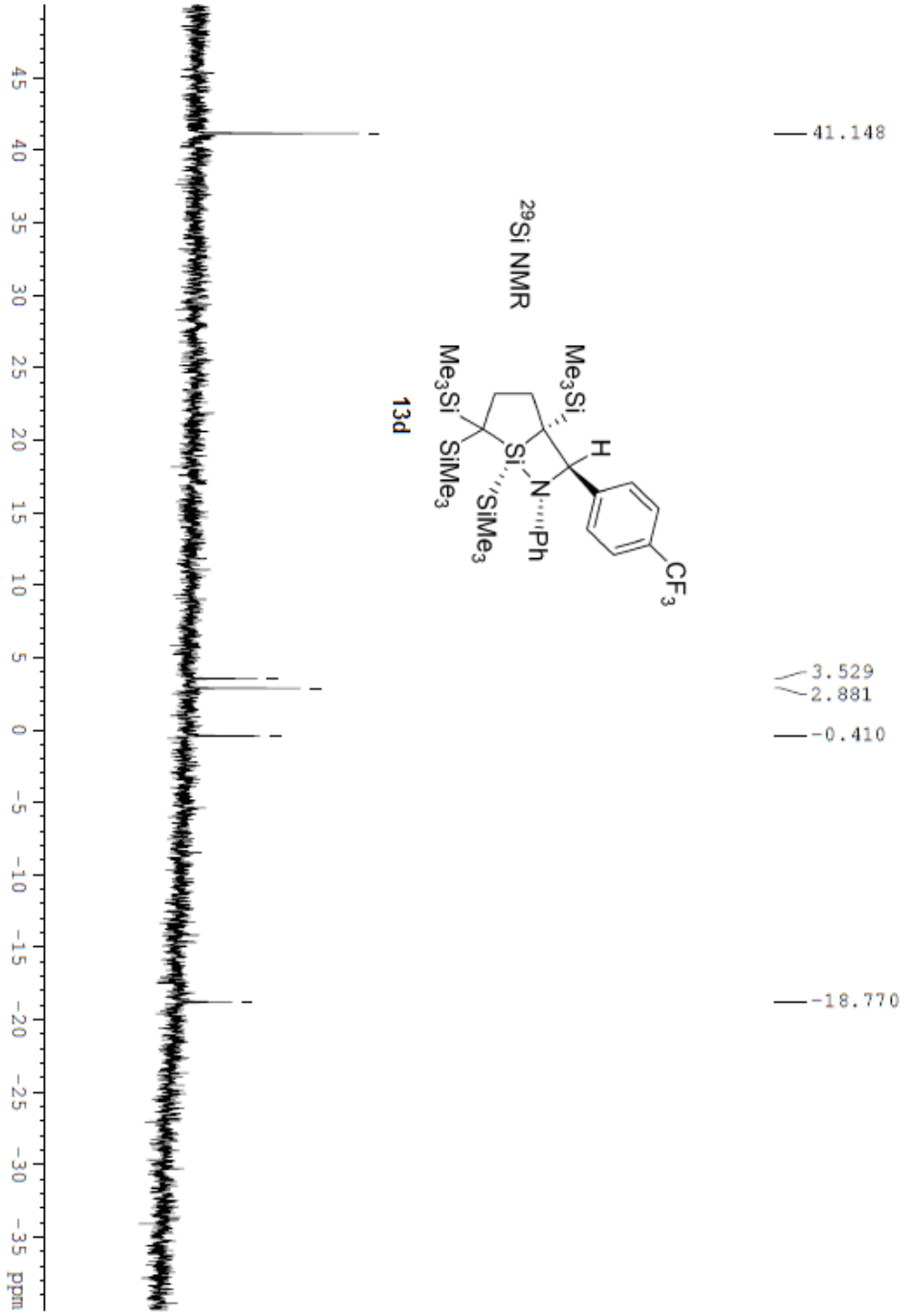

29Si NMR
13d
Me3Si
SiMe3
Me3Si
Si
SiMe3
N
Ph
H
CF3
41.148
3.529
2.881
-0.410
-18.770
45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 -35 ppm

Figure S15.

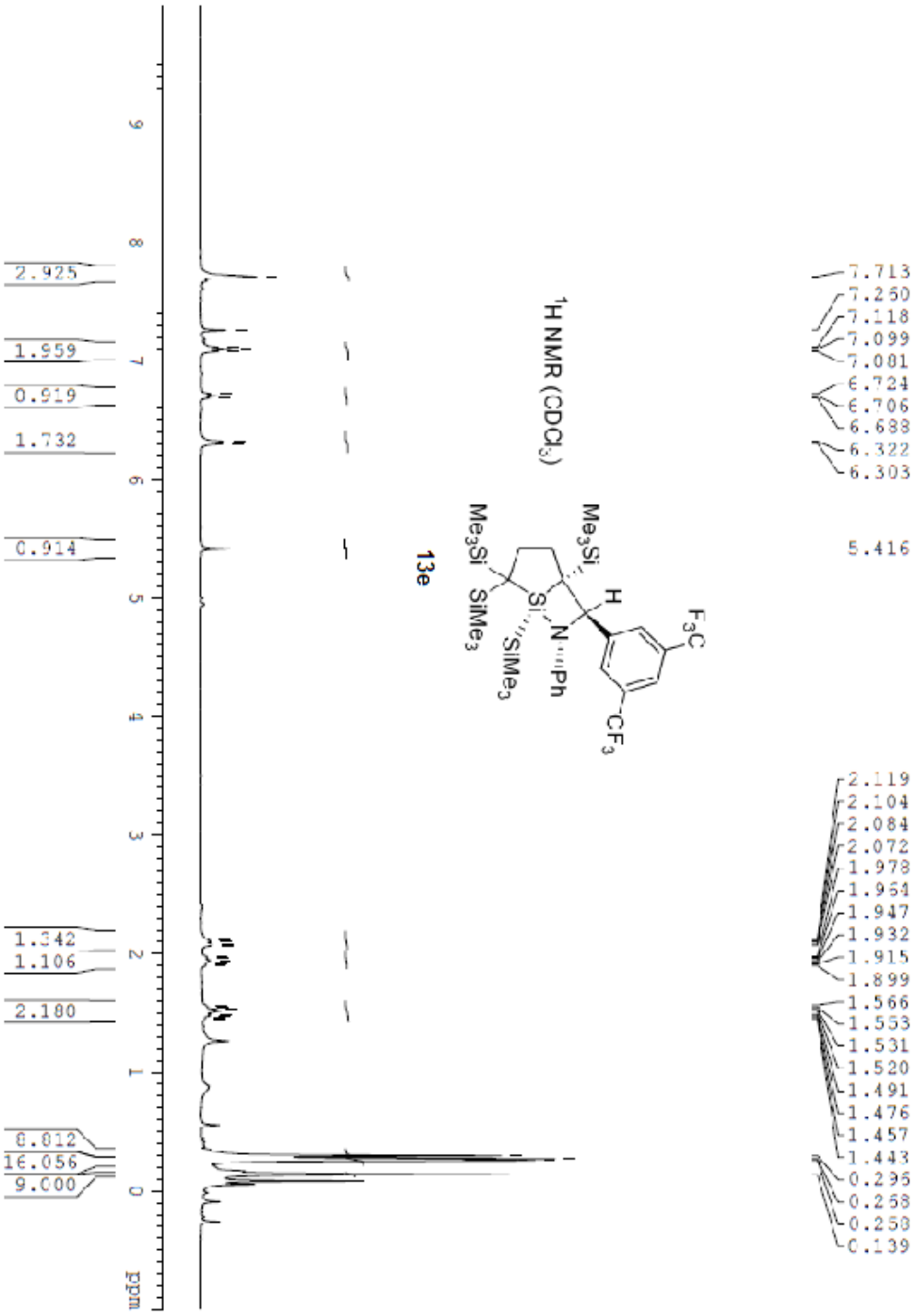

2.925
1.959
0.919
1.732
0.914
1.342
1.106
2.100
8.012
16.056
9.000
ppm
^{1}H NMR ($CDCl_3$)
13e
Me_3Si
$SiMe_3$
Si
N
iPr
Ph
H
F_3C
CF_3
7.713
7.260
7.118
7.099
7.001
6.724
6.706
6.688
6.322
6.303
5.416
2.119
2.104
2.084
2.072
1.978
1.964
1.947
1.932
1.915
1.899
1.566
1.553
1.531
1.520
1.491
1.476
1.457
1.443
0.296
0.258
0.250
0.139

Figure S16.

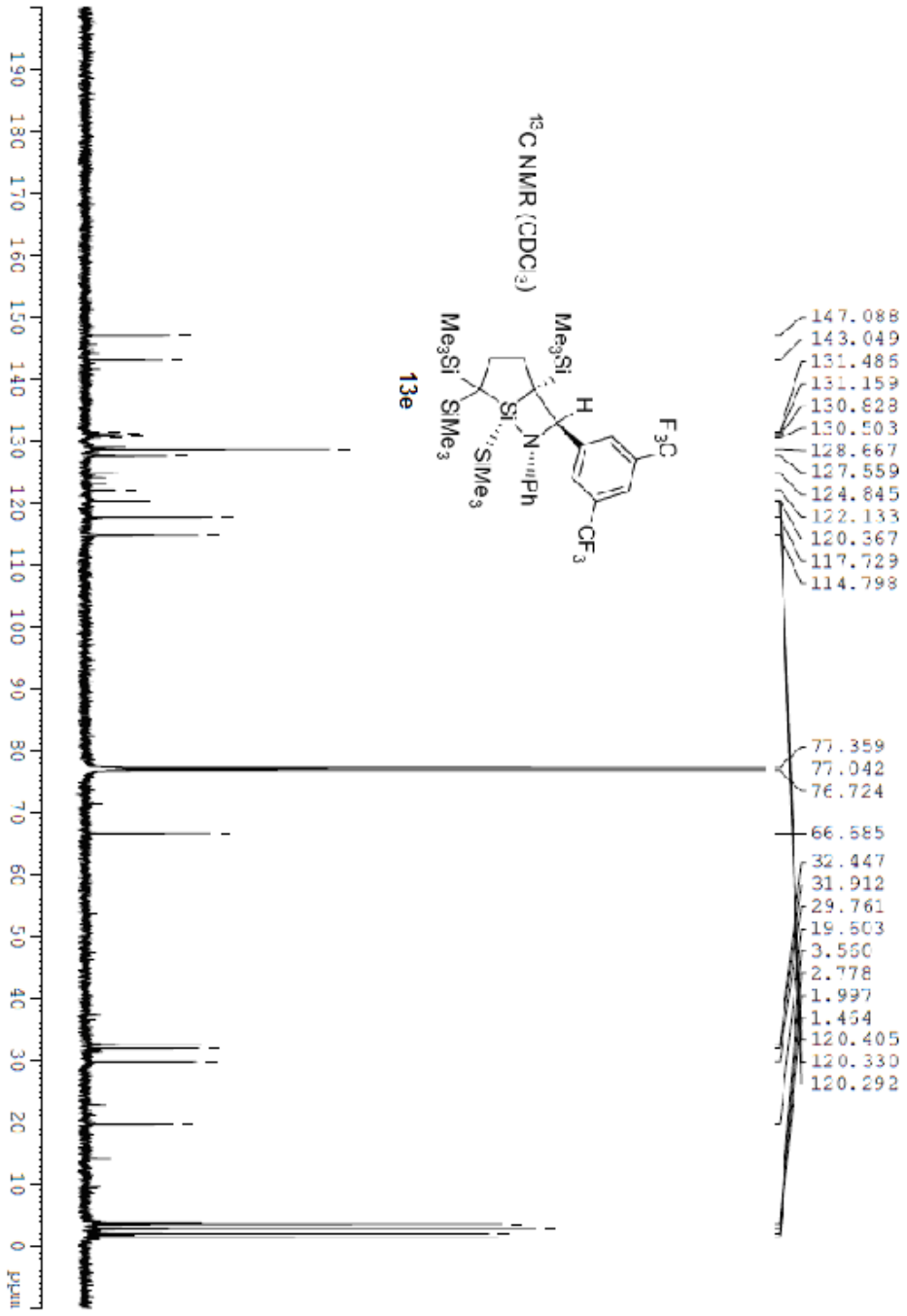

13e
^{13}C NMR (CDCl$_3$)
Me$_3$Si
SiMe$_3$
Si
N
Ph
H
F$_3$C
CF$_3$
147.088
143.049
131.485
131.159
130.828
130.503
128.667
127.559
124.845
122.133
120.367
117.729
114.798
77.359
77.042
76.724
66.585
32.447
31.912
29.761
19.503
3.550
2.778
1.997
1.454
120.405
120.330
120.292
ppm

Figure S17.

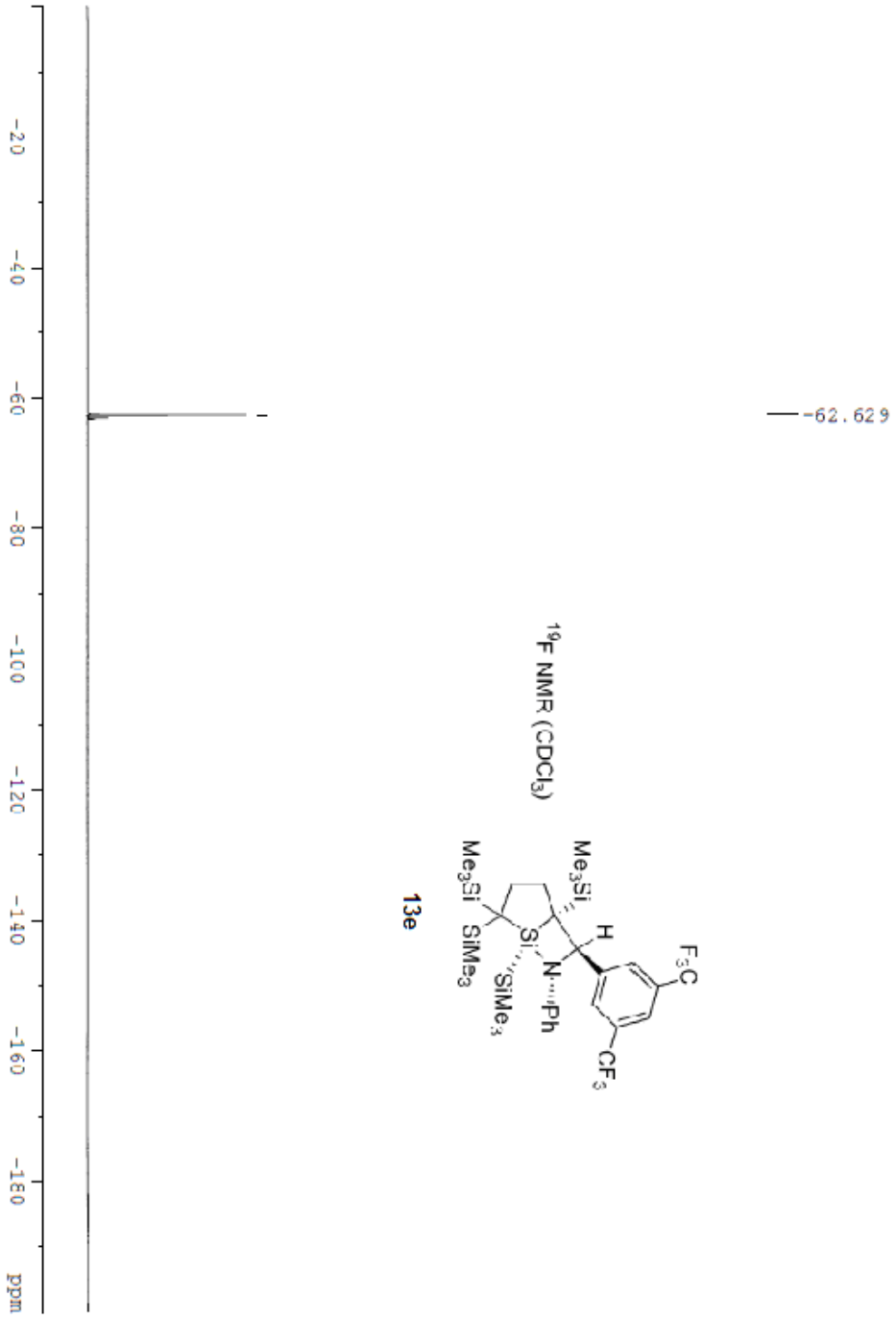


Figure S18.

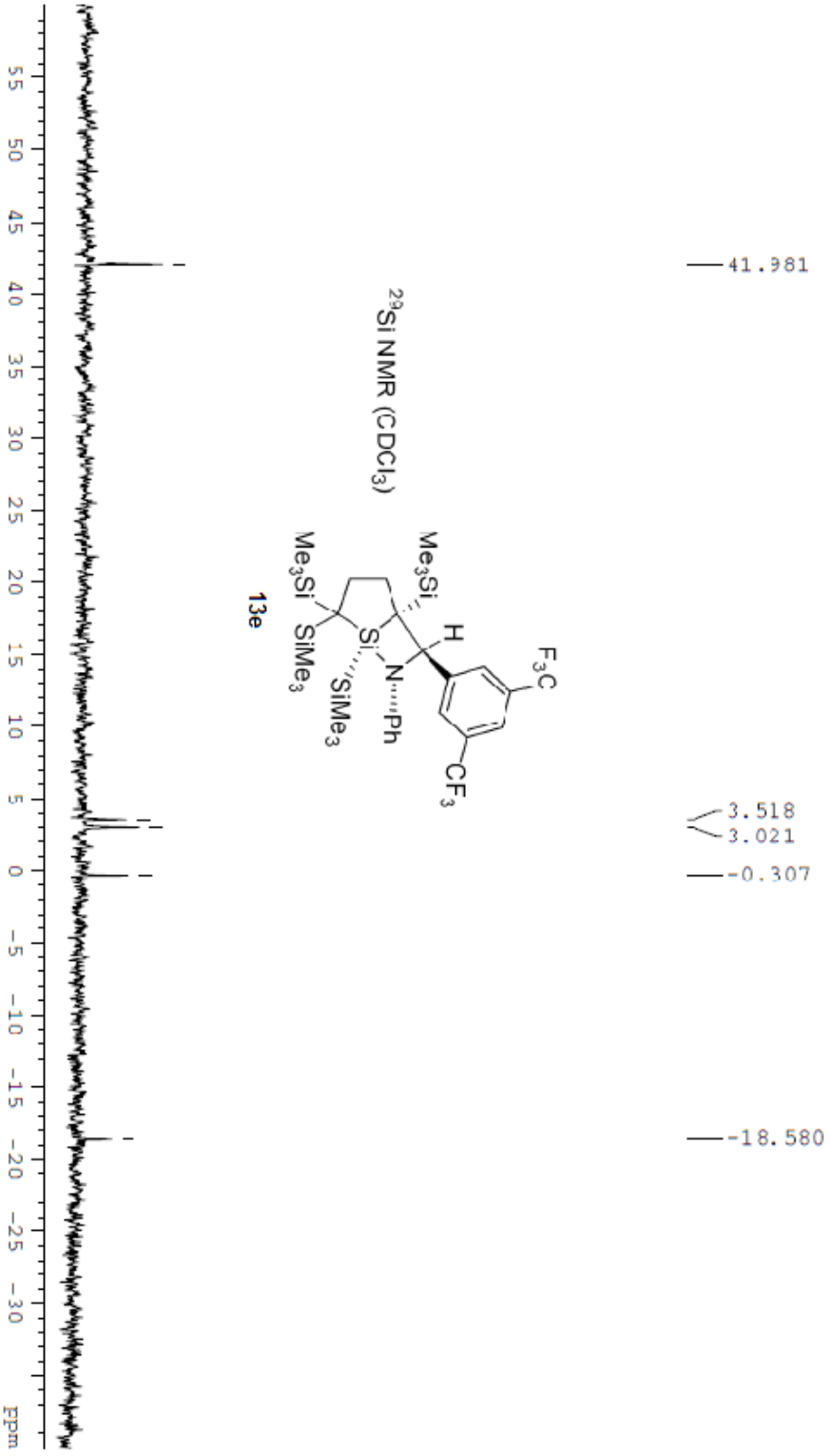


Figure S19.

3. ^{1}H, ^{13}C, and ^{29}Si NMR spectra of aminosilane 14f (Figures 18-20)

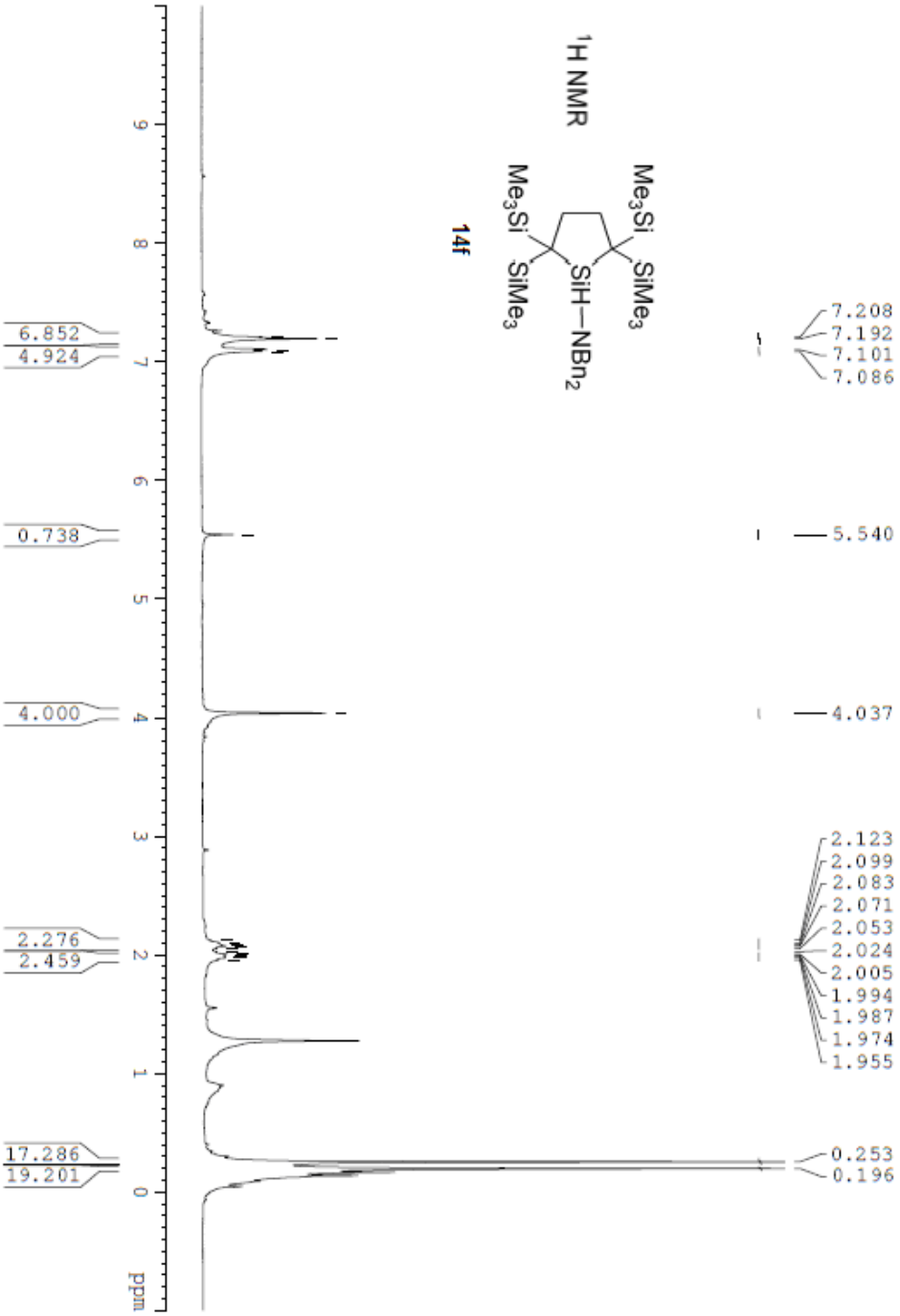


Figure S20.

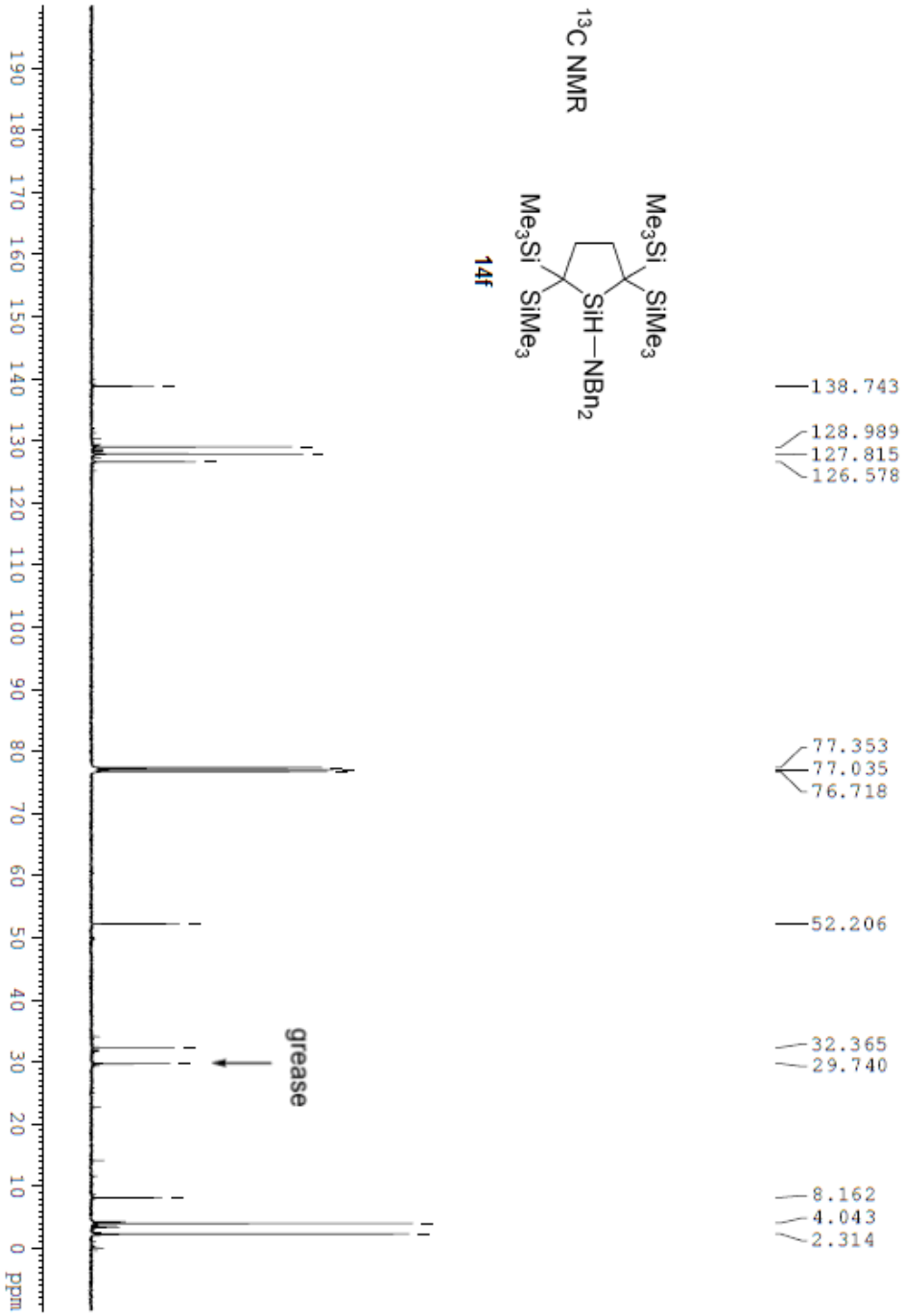

^{13}C NMR
Me$_3$Si
SiMe$_3$
SiH—NBn$_2$
Me$_3$Si
SiMe$_3$
14f
138.743
128.989
127.815
126.578
77.353
77.035
76.718
52.206
32.365
29.740
8.162
4.043
2.314
grease
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

Figure S21.

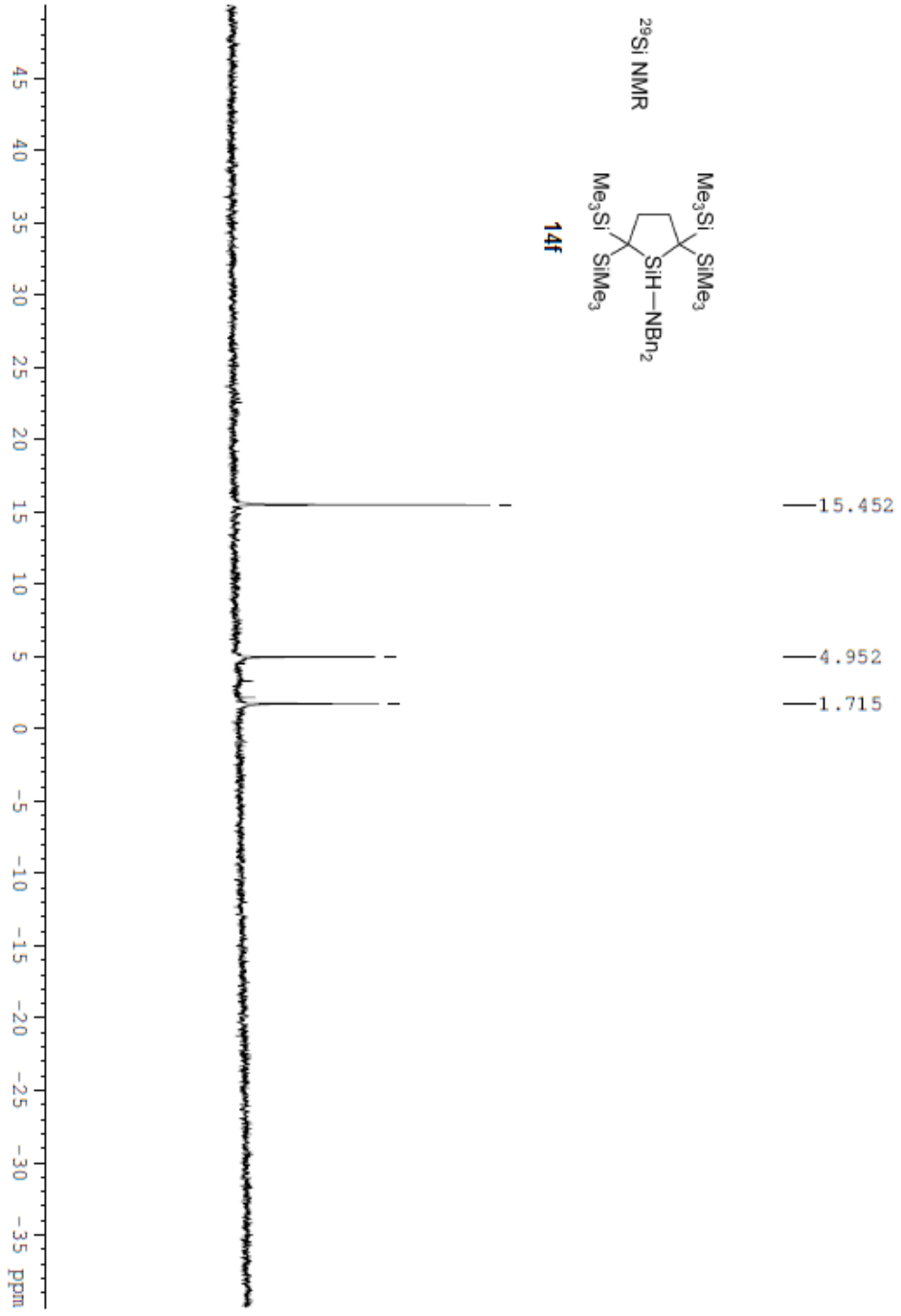


Figure S22.