Electronic Supporting Information

The effect of leaving radical on the formation of tetrahydroselenophene by S_Hi ring closure: an experimental and computational study.

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Figures S1 – S3: Dependance of [**14**]/[**15**] on thiol concentration for the cyclization of **10** (R = *n*-Oct, 2-Oct, *tert*-Bu); general procedures for the preparation of **13** and **17** (R ≠ Bn); ^{1}H, ^{13}C and ^{77}Se NMR spectra of compounds **13**, **15** and **17**; Gaussian Archive Entries of all structures calculated in this work (Table S1), total electronic energies (E) at G3(MP2)-RAD (Table S2), Gibb's Free Energies of Solvation (ΔG_{solv}, kJ mol^{-1}) (Table S3), (49 pages).

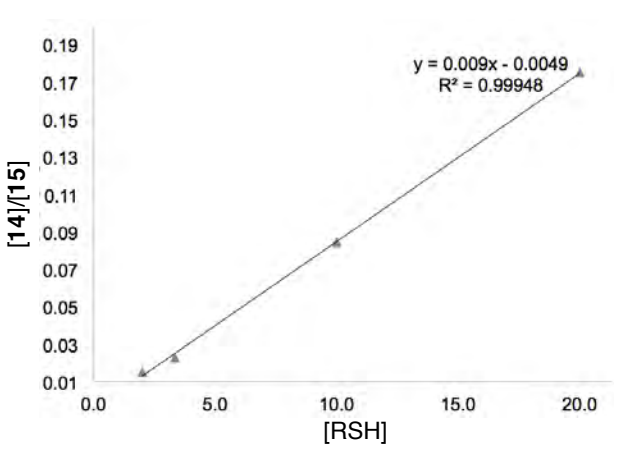


Figure S1. Dependence of [14]/[15] on RSH concentration at 80° for the cyclization of 1 (R = *n*-Oct) in benzene.

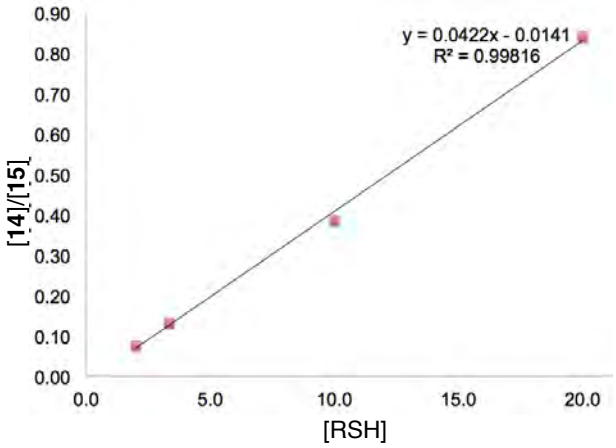


Figure S2. Dependence of [14]/[15] on RSH concentration at 80° for the cyclization of 1 (R = 2-Oct) in benzene.

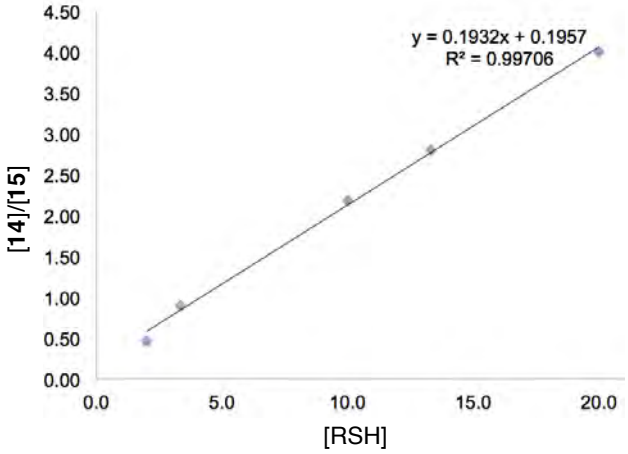


Figure S3. Dependence of [14]/[15] on RSH concentration at 80° for the cyclization of 1 (R = *tert*-Bu) in benzene.

Materials. Chemicals and HPLC grade solvents were used as received and reactions were performed under argon or dry nitrogen unless otherwise stated. Ethanol was distilled over magnesium and dichloromethane, diethyl ether and tetrahydrofuran were dried using Glass Contour© solvent system.

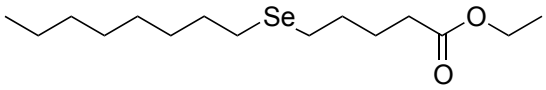
General Apparatus. ^{1}H NMR spectra were collected using a Varian INOVA 400 or 500 MHz NMR; ^{13}C and ^{77}Se NMR spectra were recorded on a Varian INOVA 500 mHz NMR. ^{1}H and ^{13}C NMR chemical shifts are given in ppm relative to internally referenced $CHCl_3$. ^{77}Se NMR chemical shifts are given in ppm relative to externally referenced diphenyl diselenide (δ 464). High resolution mass spectra were collected on a Finnigan LTQ FT by Thermo Electron Corporation. Infrared spectra were obtained using a Perkin Elmer Spectrum One FTIR spectrometer. Gas chromatography analysis was performed using Schimadzu GC-17A (column: CYDEX-B, 50m × 0.220mm, film thickness 0.25μm.

Laser Flash Photolysis studies were conducted on an Edinburgh Instruments LP920 spectrometer using the third harmonic of a Quantel Brilliant B Nd:YAG LASER (6 ns pulse, 355 nm). All experiments were performed with the laser operating at a nominal power rating of 20-30 mJ to eliminate any laser power dependency thereby minimizing the contributions of radical-radical reactions to the observed rate constant. The detection system employs a Hammamatsu R2856 photomultiplier tube interfaced with a Tektroniz TDS 3012C Digital Phosphor oscilloscope for transient absorption spectra; wavelength resolved spectra were collected using an ANDOR DH720 ICCD camera**.** Each individual transient represents 5-25 averages.

General Synthetic Procedures:

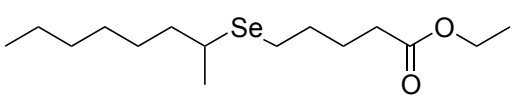
A. General procedure for the preparation of ethyl 5-(alkylseleno)pentanoates 17 and alkyl, butyl selenides 15. Sodium borohydride was added portion-wise to a solution of the dialkyl diselenide (0.55 equiv) in anhydrous ethanol (5 mL per mmol diselenide) at 0° until a colorless solution was achieved. Ethyl 5-bromovalerate or 1-bromopentane (1.0 equiv) was added and the solution was stirred at RT overnight. The solvent was removed *in vacuo* and residue taken up in water. The resultant mixture was extracted with ether (3x), the combined organic phases were dried ($MgSO_4$ or Na_2SO_4) and concentrated *in vacuo*. The crude oil was purified by short path distillation or separated by flash chromatography (petroleum spirits : ethyl acetate) to yield the required products as pure oils.

Ethyl 5-(*n*-octylseleno)pentanoate (17, R = *n*-Oct)



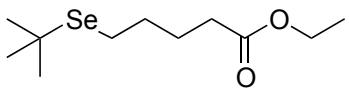
The desired selenide was synthesized according the general procedure A and was obtained as a yellow oil; δ_H (500 MHz, $CDCl_3$) 4.08 (q, J = 7.1 Hz, 2H), 2.51 (td, J = 7.4, 3.4 Hz, 4H), 2.28 (t, J = 7.1 Hz, 2H), 1.75 – 1.56 (m, 6H), 1.38 – 1.15 (m, 13H) and 0.84 (t, J = 7.0 Hz, 3H) ppm; δ_C (125 MHz, $CDCl_3$) 173.32, 60.23, 33.81, 31.85, 30.66, 30.10, 30.00, 29.22, 29.15, 25.26, 24.04, 23.23, 22.67, 14.27 and 14.10 ppm; δ_{Se} (95 MHz, $CDCl_3$) 166.15 ppm; ν_{max} (neat) 2924, 2854, 1735, 1457, 1373, 1252, 1190 and 1038 cm^{-1}; HRMS $C_{15}H_{30}O_2SeNa$ requires 345.13032; found 345.13039.

Ethyl 5-((2-octyl)seleno)pentanoate (17, R = 2-Oct)



The desired selenide was synthesized according the general procedure A and was obtained as a yellow oil; δ_H (500 MHz, $CDCl_3$) 3.99 (q, *J* = 7.1 Hz, 2H), 2.80 (h, *J* = 6.8 Hz, 1H), 2.43 (td, *J* = 7.2, 1.9 Hz, 2H), 2.19 (t, *J* = 7.1 Hz, 2H), 1.68 – 1.07 (m, 21H) and 0.76 (t, *J* = 6.9 Hz, 3H) ppm; δ_C (125 MHz, $CDCl_3$) 14.17, 14.37, 21.99, 22.60, 22.74, 25.48, 27.92, 29.26, 30.38, 31.90, 33.89, 34.97, 38.23, 60.25 and 173.40 ppm; δ_{Se} (95 MHz, $CDCl_3$) 267.22 ppm; ν_{max} (neat) 2957, 2928, 2857, 1737, 1457, 1375, 1184, 1039 cm^{-1}; HRMS $C_{15}H_{30}O_2SeNa$ requires 345.13032; found 345.13034.

Ethyl 5-(*t*-butylseleno)pentanoate (17, R = *tert*-Bu)

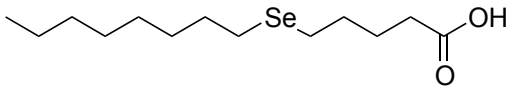


The desired selenide was synthesized according the general procedure A and was obtained as a yellow oil; δ_H (500 MHz, $CDCl_3$) 4.10 (q, *J* = 7.1 Hz, 2H), 2.57 (t, *J* = 7.2 Hz, 2H), 2.29 (t, *J* = 7.1 Hz, 2H), 1.76 – 1.63 (m, 4H), 1.42 (s, 9H) and 1.23 (t, *J* = 7.1 Hz, 3H) ppm; δ_C (125 MHz, $CDCl_3$) 173.36, 60.23, 38.54, 33.84, 32.51, 30.18, 25.55, 21.31 and 14.23 ppm; δ_{Se} (95 MHz, $CDCl_3$) 377.61 ppm; ν_{max} (neat) 2948, 2931, 2855, 1731, 1451, 1366, 1268, 1247, 1182, 1156, 1116 and 1030 cm^{-1}; HRMS $C_{11}H_{22}O_2SeAg$ requires 372.98305; found 372.98301.

B. General procedure for the hydrolysis of esters 17. Aqueous sodium hydroxide (ca. 1.0 equiv) was added to a solution of the required ester **17** (1.0 equiv) in ethanol (3.0 mL per mmol ester) and the resultant solution refluxed for 1 h. After cooling to RT, the ethanol was removed *in vacuo*, the residue dissolved in water and the aqueous solution washed with ether (3 x). After acidifying with 10% hydrochloric acid, the solution was extracted with ether (3 x), the combined organic phases dried (Na_2SO_4) and the solvent removed *in vacuo* to afford the required 5-(alkylseleno)pentanoic acid as pale solids which was converted to the corresponding

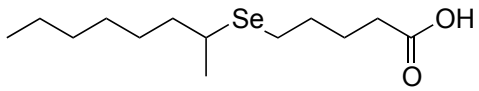
Kim ester **5** without further purification.

5-(Octylseleno)pentanoic acid



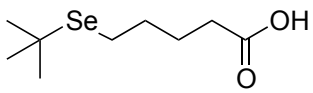
The desired selenovaleric acid was synthesized according the general procedure B and was obtained as a solid in quantitative yield; m.p. = 38-39 °C; δ_H (500 MHz, $CDCl_3$) 2.58 (dd, *J* = 12.0, 7.0 Hz, 4H), 2.41 (t, *J* = 6.8 Hz, 2H), 1.82 – 1.60 (m, 6H), 1.45 – 1.22 (m, 10H) and 0.91 (t, *J* = 6.7 Hz, 3H) ppm; δ_C (125 MHz, $CDCl_3$) 179.60, 33.32, 31.83, 30.64, 29.98, 29.95, 29.20, 29.13, 24.91, 24.14, 23.17, 22.67 and 14.09 ppm; δ_{Se} (95 MHz, $CDCl_3$) 165.65 ppm; ν_{max} (neat) 2955, 2918, 2848, 1689, 1458, 1432, 1409, 1288, 1233, 1175, 1065, 925 and 719 cm^{-1}; HRMS $C_{13}H_{26}O_2SeNa$ requires 317.09902; found 317.09910.

5-((2-octyl)seleno)pentanoic acid



The desired selenovaleric acid was synthesized according the general procedure B and was obtained as a solid; δ_H (500 MHz, $CDCl_3$) 2.92 (h, *J* = 6.8 Hz, 1H), 2.55 (t, *J* = 6.2 Hz, 2H), 2.36 (t, *J* = 7.1 Hz, 2H), 1.78 – 1.46 (m, 6H), 1.42 – 1.20 (m, 11H) and 0.86 (t, *J* = 6.9 Hz, 3H) ppm; δ_C (125 MHz, $CDCl_3$) 179.83, 38.31, 35.25, 33.74, 31.98, 30.32, 29.33, 28.00, 25.25, 22.83, 22.66, 22.07 and 14.27 ppm; δ_{Se} (95 MHz, $CDCl_3$) 266.67 ppm; ν_{max} (neat) 2951, 2920, 2850, 1735, 1708, 1434, 1350, 1269, 1215, 1175, 1032, 913 and 720 cm^{-1}; HRMS $C_{13}H_{26}O_2SeNa$ requires 317.09902; found 317.09910.

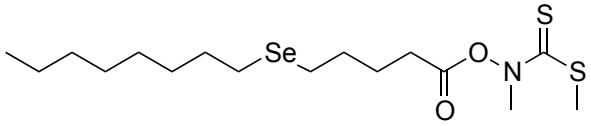
5-((*t*-butyl)sele dno)pentanoic acid



The desired selenovaleric acid was synthesized according the general procedure B and was obtained as a solid; δ_H (500 MHz, $CDCl_3$) 2.61 (t, J = 6.0 Hz, 2H), 2.39 (t, J = 5.9 Hz, 2H), 1.75 (d, J = 2.7 Hz, 4H) and 1.50 – 1.39 (s, 9H) ppm; δ_C (125 MHz, $CDCl_3$) 179.89, 38.88, 33.56, 32.51, 30.01, 25.20 and 21.24 ppm; δ_{Se} (95 MHz, $CDCl_3$) 376.11 ppm; ν_{max} (neat) 2935, 1702, 1454, 1410, 1365, 1279, 1212, 1155, 924, 754 and 669 cm^{-1}; HRMS $C_9H_{18}O_2SeAg$ requires 344.9517; found 344.95183.

C. General procedure for the preparation of Kim esters 13. A solution of *N,S*-dimethyl-*N*-hydroxydithiocarbamate (1.5 equiv) in dichloromethane (1.0 mL per 1.5 mmol carbamate) was added dropwise to a solution of *N,N'*-dicyclohexylcarbodiimide (1.0 equiv) and the required 5-(alkylseleno)pentanoic acid (1.0 equiv) in dichloromethane (2.0 mL per mmol acid). The reaction mixture was stirred at RT overnight and then filtered through celite. The filtrate was washed with $NaHCO_3$ and saturated NaCl. The organic phase was dried (Na_2SO_4) and concentrated *in vacuo* to afford a grey-green oil that was separated by flash chromatography (petroleum spirts : ethyl acetate) to yield the required product as a yellow/green oil.

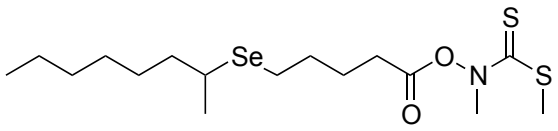
Kim ester 13 (R = *n*-Oct)



The title compound was synthesized according to procedure C and obtained as an oil in 49% yield; δ_H (500 MHz, $CDCl_3$) 3.76 (s, 3H), 2.59 – 2.49 (m, 9H), 1.89 – 1.80 (m, 2H), 1.80 – 1.71 (m, 2H), 1.68 – 1.58 (m, 2H), 1.41 – 1.19 (m, 10H) and 0.86 (t, J = 7.0 Hz, 3H) ppm; δ_C (125 MHz, $CDCl_3$) 196.69, 169.59, 42.66, 31.80, 30.95, 30.60, 29.95, 29.81, 29.17, 29.11, 24.60, 24.21, 22.92, 22.63 and 18.65, 14.07 ppm; δ_{Se} (95 MHz, $CDCl_3$) 161.45 ppm; ν_{max} (neat) 3677,

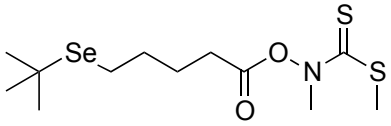
2955, 2922, 2853, 1797, 1456, 1421, 1359, 1190, 1065, 1011, 962, 870 and 722 cm^{-1}; HRMS $C_{16}H_{31}NO_2S_2SeNa$ requires 436.08536; found 436.08549.

Kim ester 13 (R = 2-Oct)

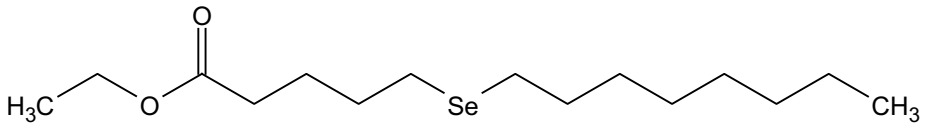


The title compound was synthesized according to procedure C and obtained as an oil in 57% yield; δ_H (500 MHz, $CDCl_3$) 3.79 (s, 3H), 2.56 (s, 5H), 1.88 – 1.16 (m, 23H) and 0.88 (t, J = 6.9 Hz, 3H) ppm; δ_C (125 MHz, $CDCl_3$) 196.95, 170.00, 42.91, 38.34, 35.31, 31.99, 31.57, 30.48, 29.60, 29.36, 28.03, 24.23, 22.85 22.72, 22.35 and 14.30 ppm; δ_{Se} (95 MHz, $CDCl_3$) δ 266.45 ppm; ν_{max} (neat) I2954, 2921, 2852, 1798, 1739, 1455, 1358, 1230, 1197, 1063, 1012, 960, 873 and 722 cm^{-1}; HRMS $C_{16}H_{31}NO_2S_2SeNa$ requires 436.08536; found 436.08552.

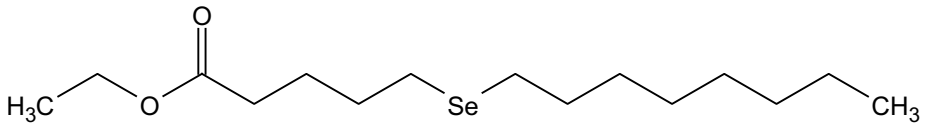
Kim ester 13 (R = *t*-Bu)



The title compound was synthesized according to procedure C and obtained as an oil in 66% yield; δ_H (500 MHz, $CDCl_3$) 3.71 (s, 3H), 2.20-2.67 (m, J = 5.9 Hz, 4H), 1.94 – 1.56 (m, 4H), 1.41 (s, 9H) and 0.89 (t, J = 7.3 Hz, 3H) ppm; δ_C (125 MHz, $CDCl_3$) 196.77, 169.60, 42.67, 38.82, 32.52, 30.99, 29.96, 24.93, 21.00 and 18.66 ppm; δ_{Se} (95 MHz, $CDCl_3$) δ 376.36 ppm; ν_{max} (neat) 3449, 3015, 2970, 2940, 1737, 1434, 1366, 1228, 1217, 1203, 1092, 895 and 776 cm^{-1}; HRMS $C_{12}H_{23}NO_2S_2SeAg$ requires 463.93809; found 463.93836.


O
H3C
O
Se
CH3

1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
0.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


O
H3C
O
Se
CH3

2400
2300
2200
2100
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
-200
00
190
180
170
160
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140
130
120
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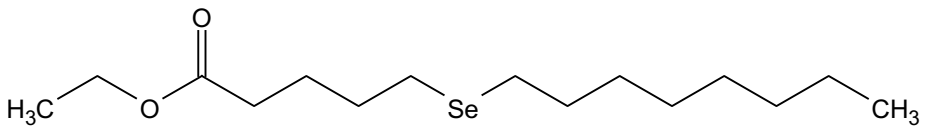
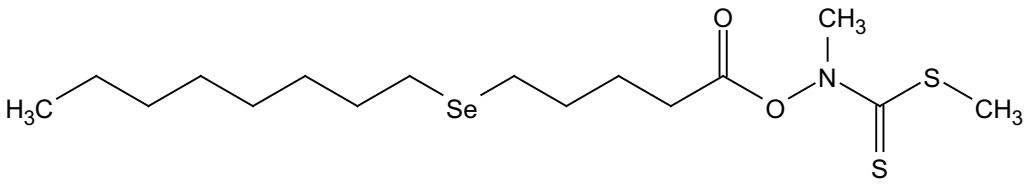
100
90
80
70
60
50
40
30
20
10
f1 (ppm)



NMR (95 MHz, $CDCl_3$) δ 166.00.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CH3
H3C
Se
O
N
S
CH3
S

1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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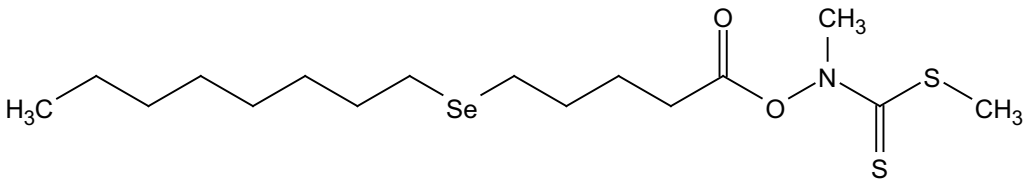
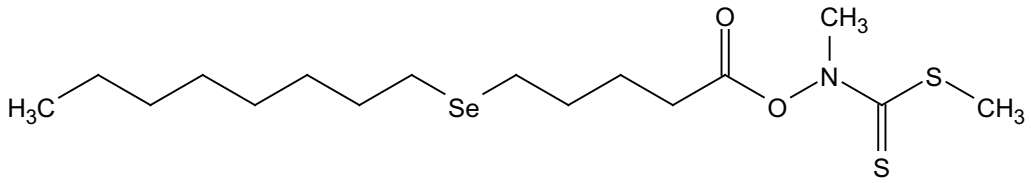
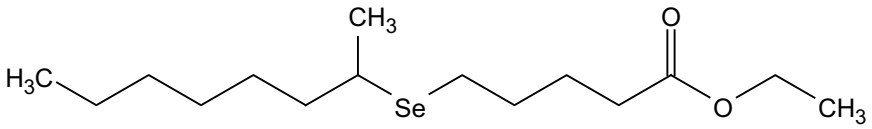
2.5
2.0
1.5
1.0
f1 (ppm)


O
CH3
N
S
CH3
H3C
Se
O
S

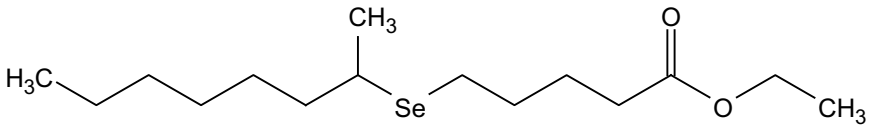
6E+06
6E+06
6E+06
5E+06
4E+06
4E+06
4E+06
3E+06
2E+06
2E+06
2E+06
1E+06
5E+05
0
-5E+05
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


O
CH3
H3C
Se
O
N
S
CH3
S

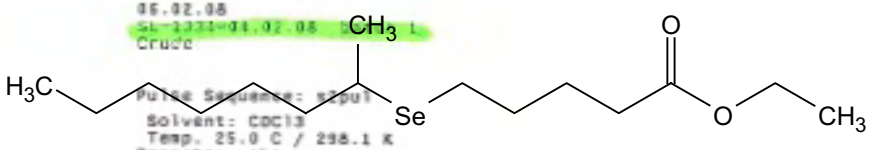
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
−100
400 390 380 370 360 350 340 330 320 310 300 290 280 270 260 250 240 230 220 210 200 190 180 170 160
f1 (ppm)


CH3
O
H3C
Se
O
CH3

750
700
650
600
550
500
450
400
350
300
250
200
150
100
50
0
-50
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


CH3
O
H3C
Se
O
CH3

70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
-5
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

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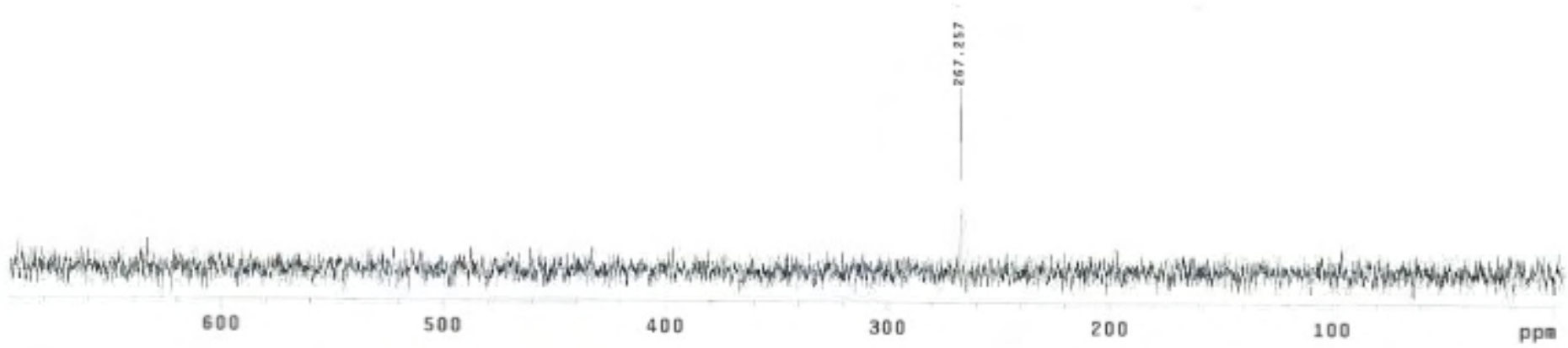
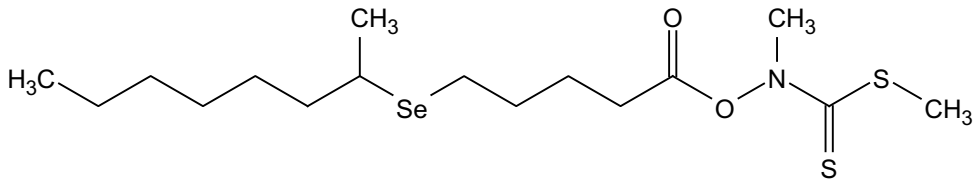
05.02.08
SL-1221-04.02.08  CH3 L
Crude

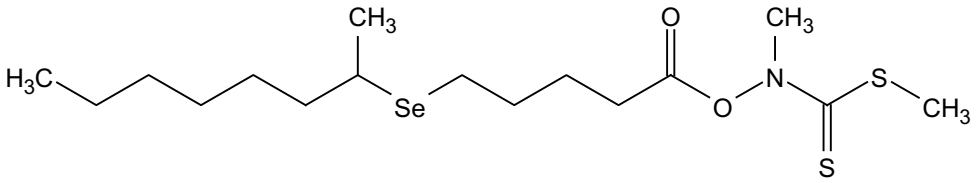
Pulse Sequence: s2pul
 Solvent: CDCl3
 Temp. 25.0 C / 298.1 K
Operator: chs
INOVA-500  "bio500"

 Relax. delay 2.000 sec
 Pulse 54.0 degrees
 Acq. time 2.621 sec
 Width 56778.8 Hz
 48 repetitions
OBSERVE Se77,  95.3377759 MHz
DECOUPLE  H1, 500.2135889 MHz
 Power 38 dB
 continuously on
 single frequency
DATA PROCESSING
 Line broadening 10.0 Hz
FT size 524288
Total time 19 min, 45 sec
```

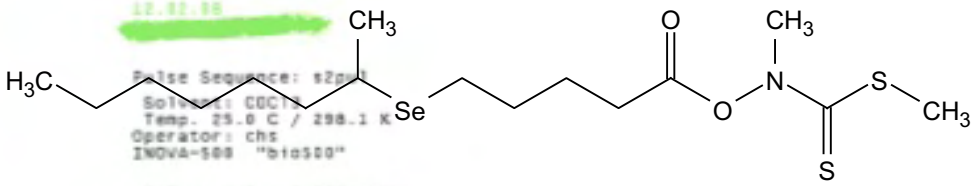



CH3
O
CH3
H3C
Se
O
N
S
CH3
S

450
400
350
300
250
200
150
100
50
0
4
13
12
11
10
9
8
7
6
5
4
3
2
1
0
−1
−2
f1 (ppm)


CH3
O
CH3
H3C
N
S
CH3
Se
O
S

130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

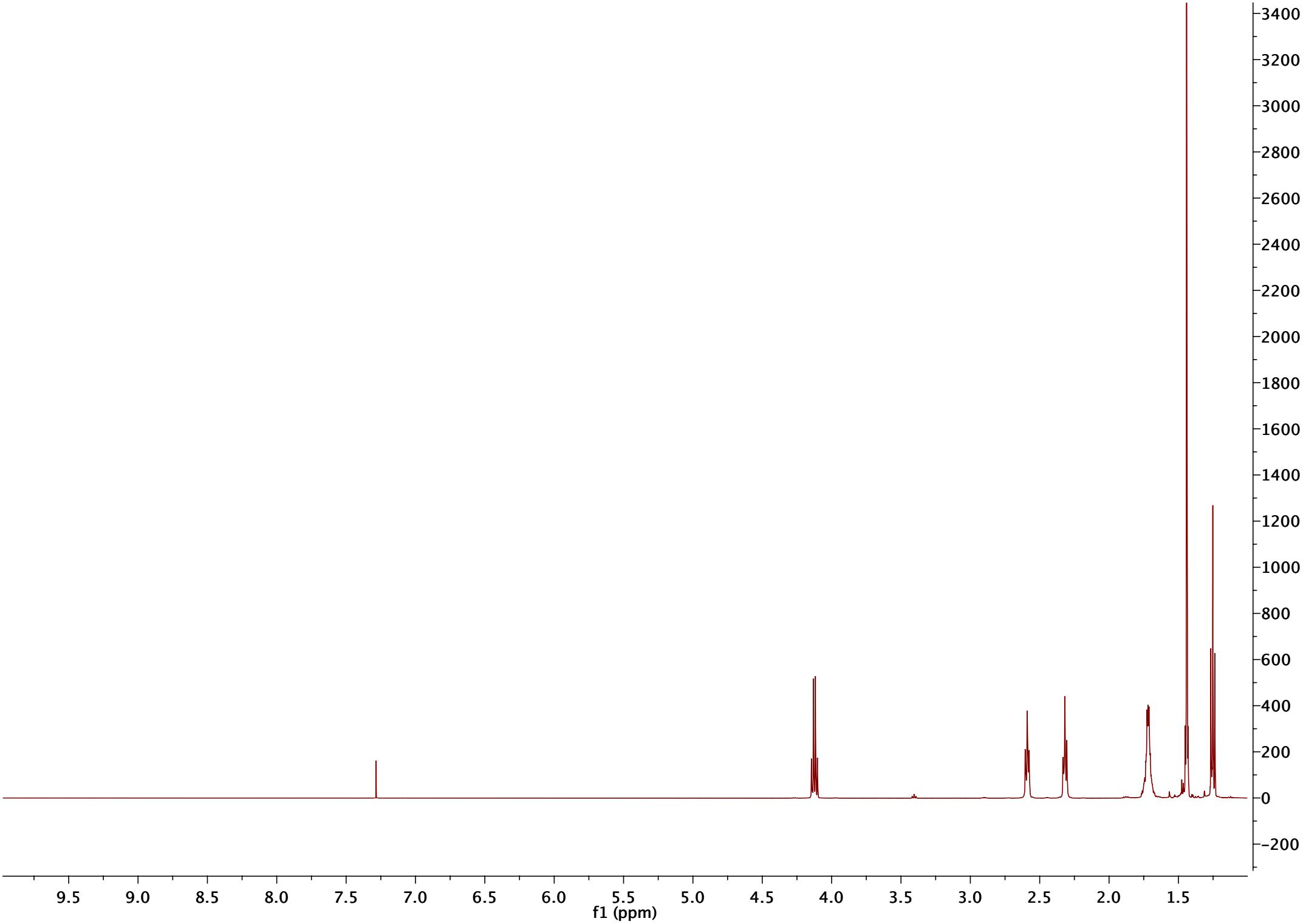


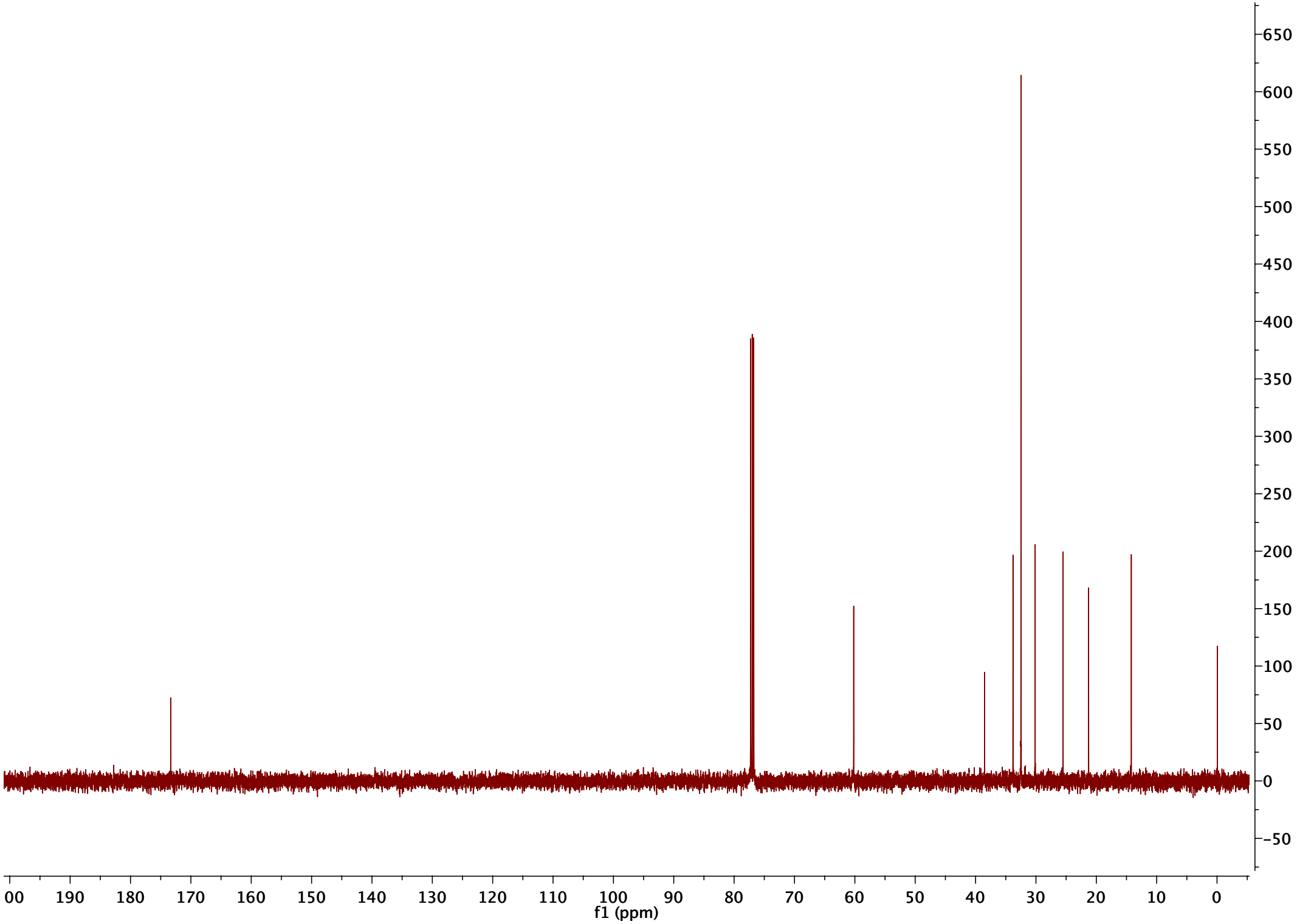
[redacted]

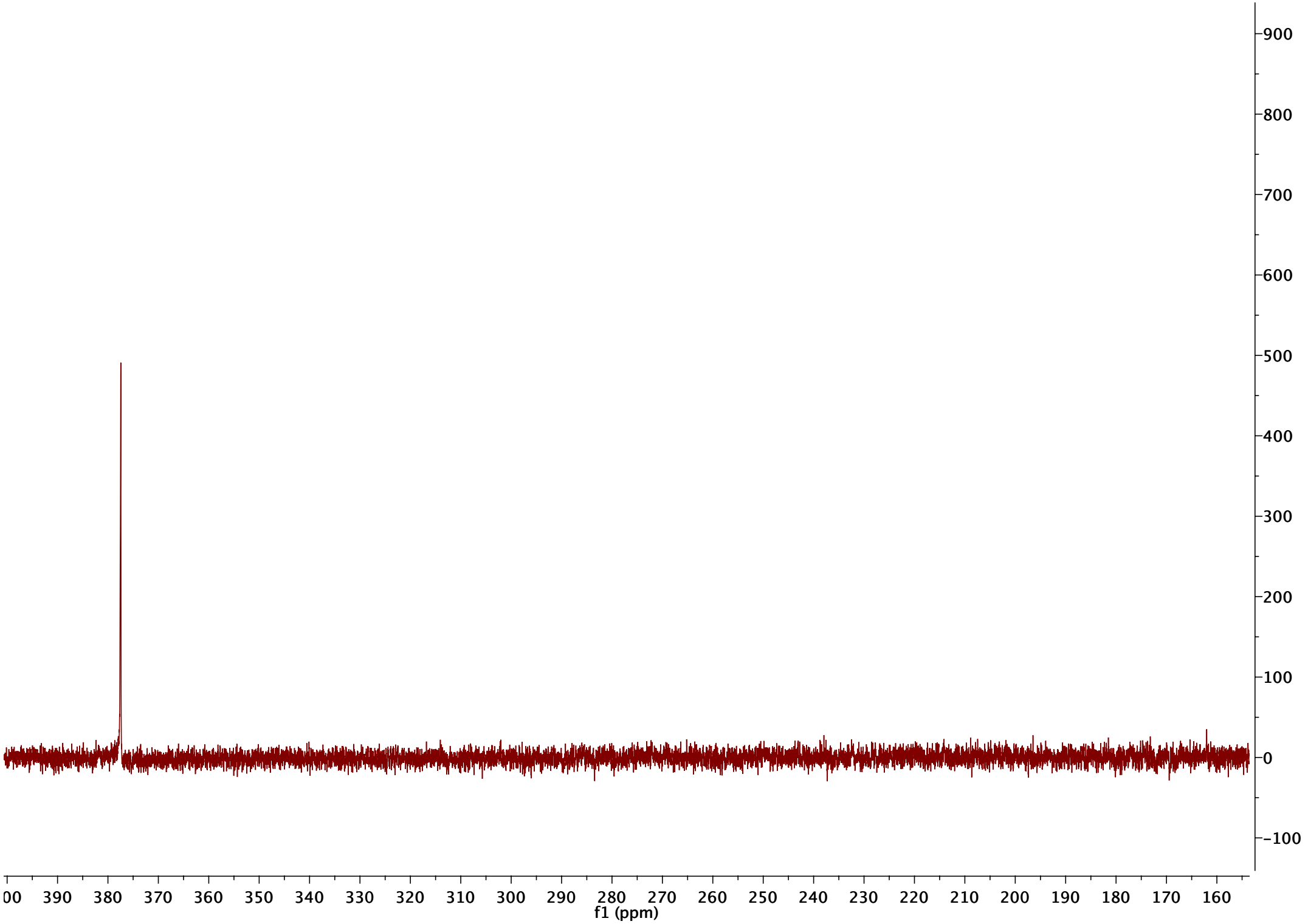
Pulse Sequence: s2pul
Solvent: CDCl3
Temp. 25.0 C / 298.1 K
Operator: chs
INOVA-500 "bio500"

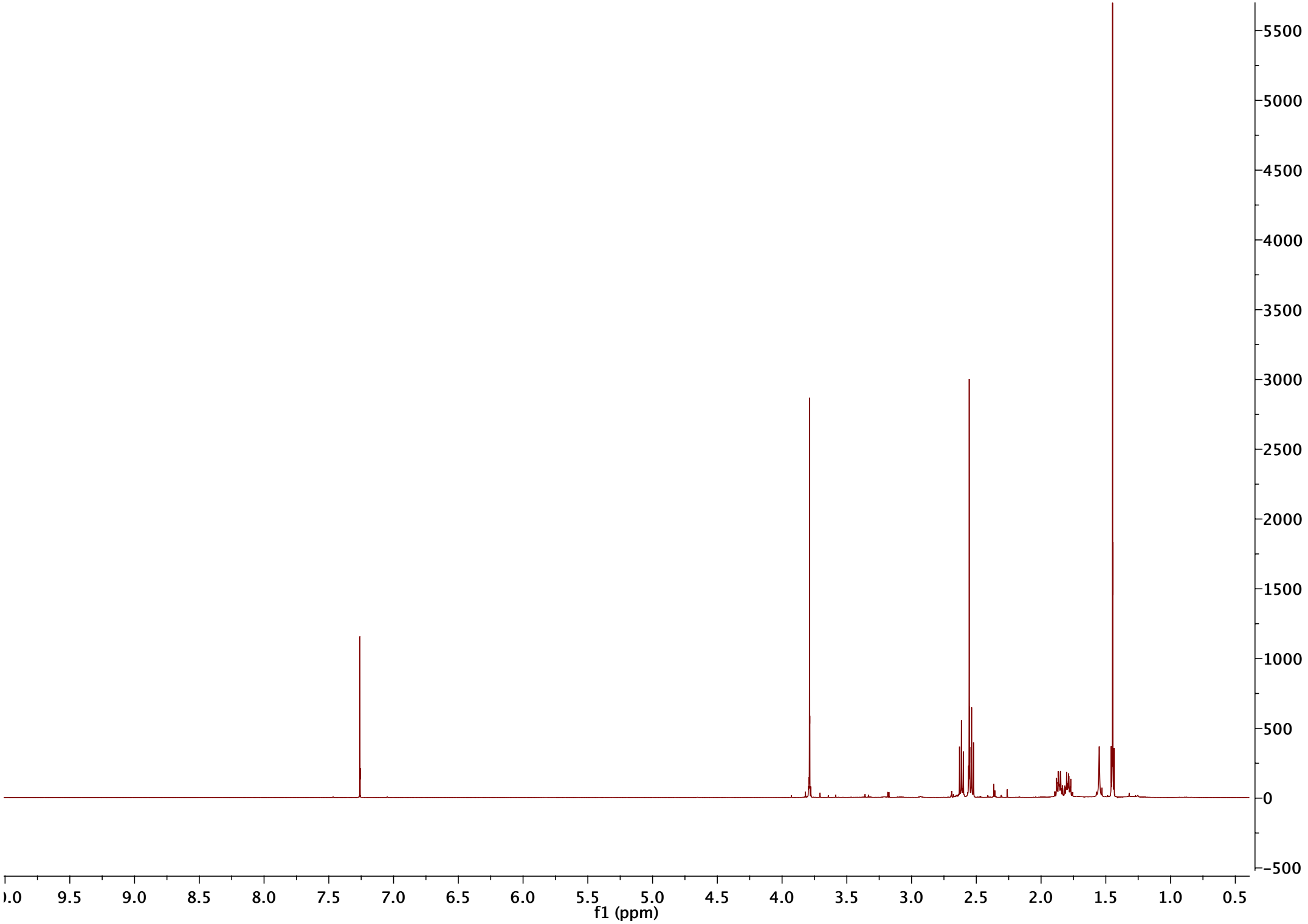
Relax. delay 2.000 sec
Pulse 54.0 degrees
Acq. time 2.621 sec
Width 76335.9 Hz
1048 repetitions
OBSERVE Se77, 95.3877924 MHz
DECOUPLE H1, 500.2135809 MHz
Power 38 dB
continuously on
single frequency
DATA PROCESSING
Line broadening 10.0 Hz
FT size 524288
Total time 2 hr, 34 min, 20 sec

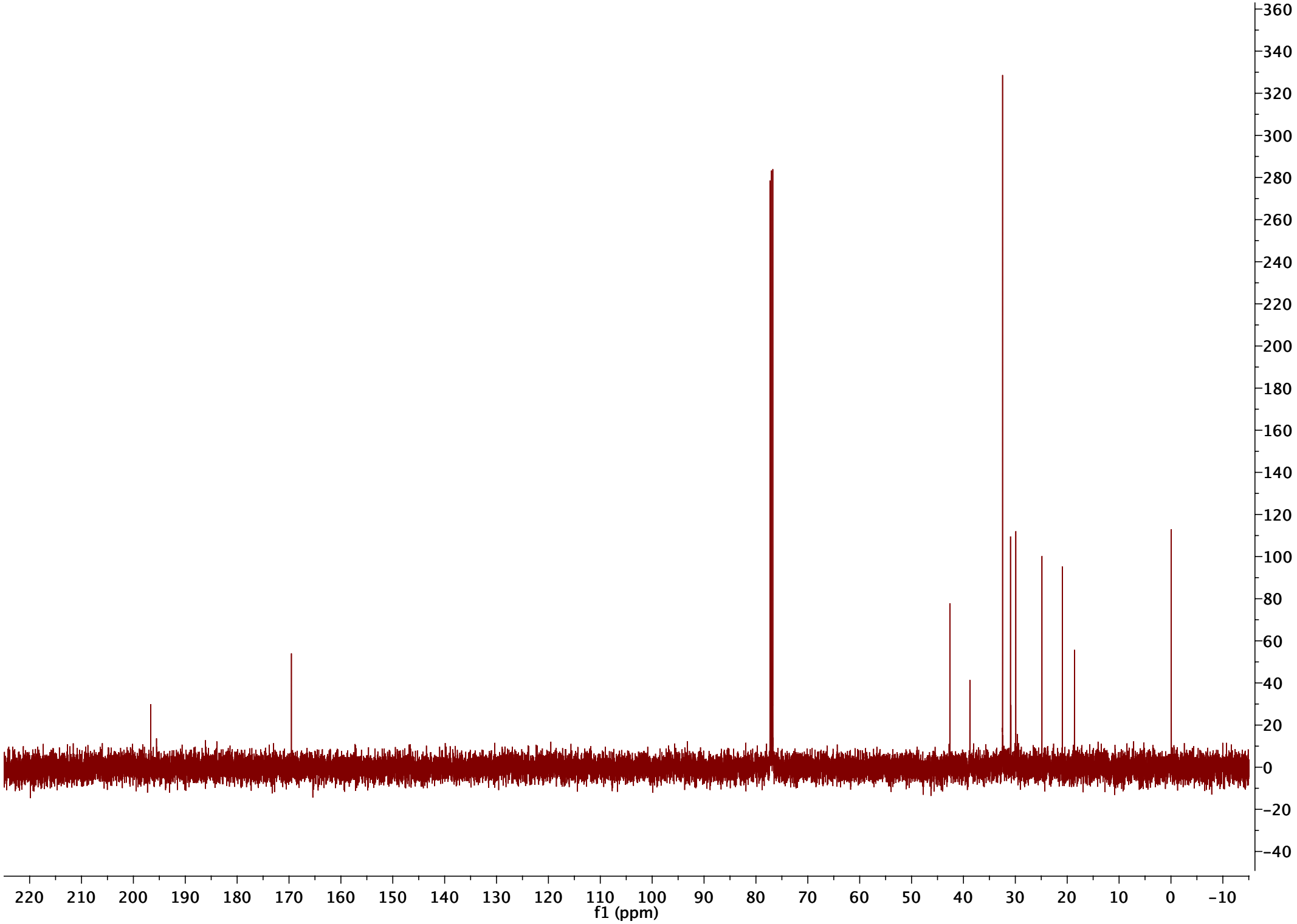
266.23

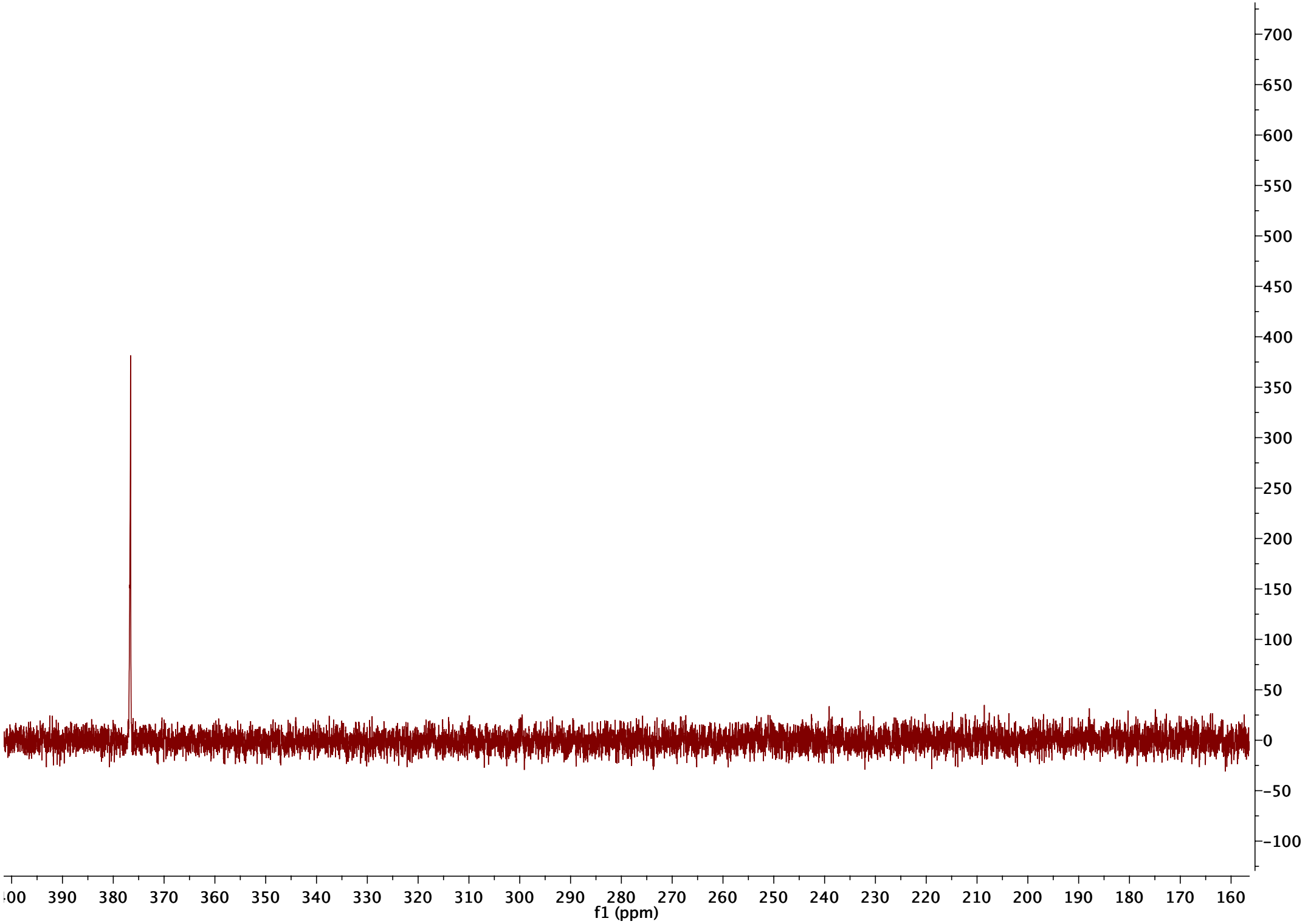

3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f1 (ppm)

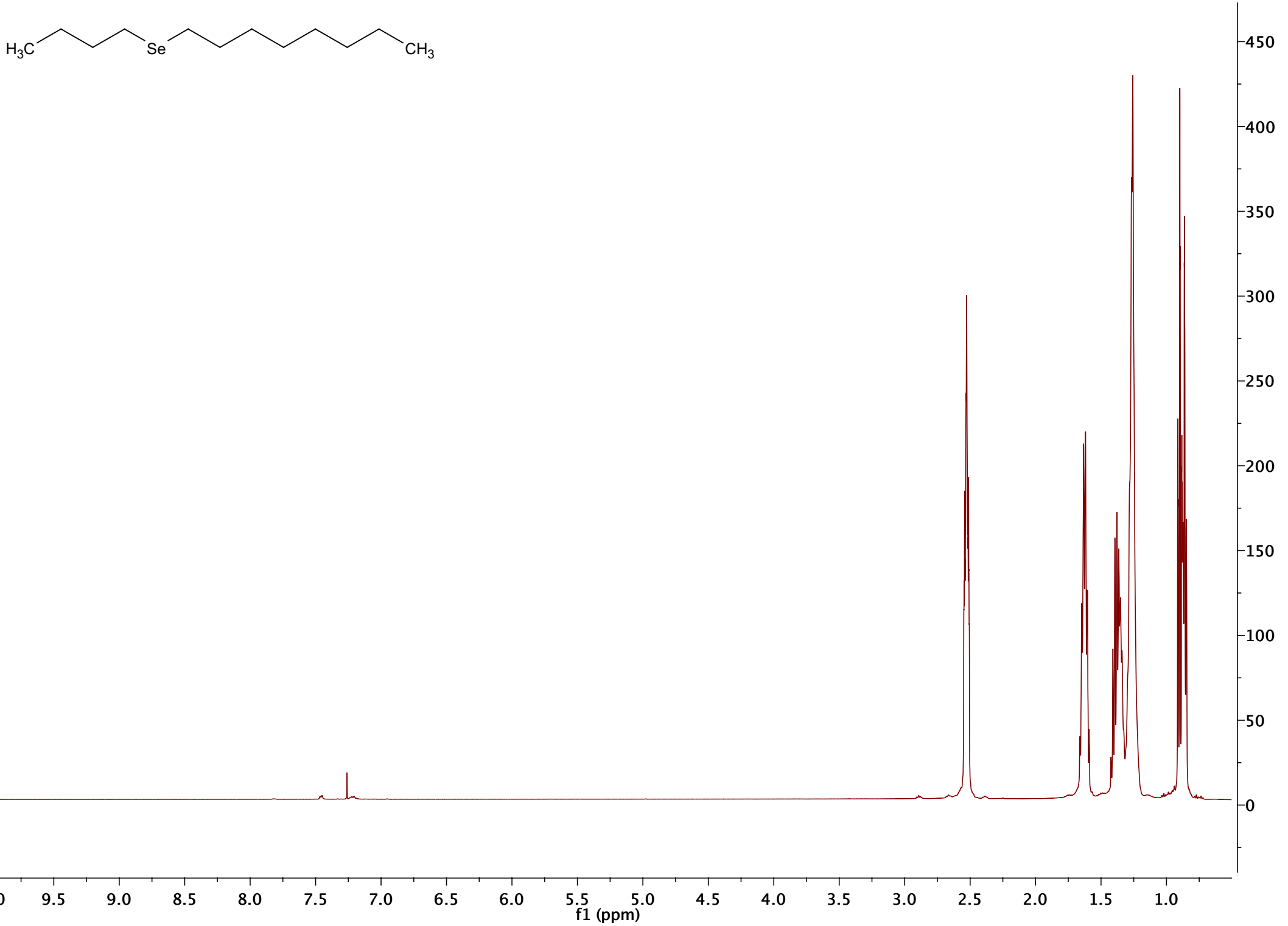

650
600
550
500
450
400
350
300
250
200
150
100
50
0
-50
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

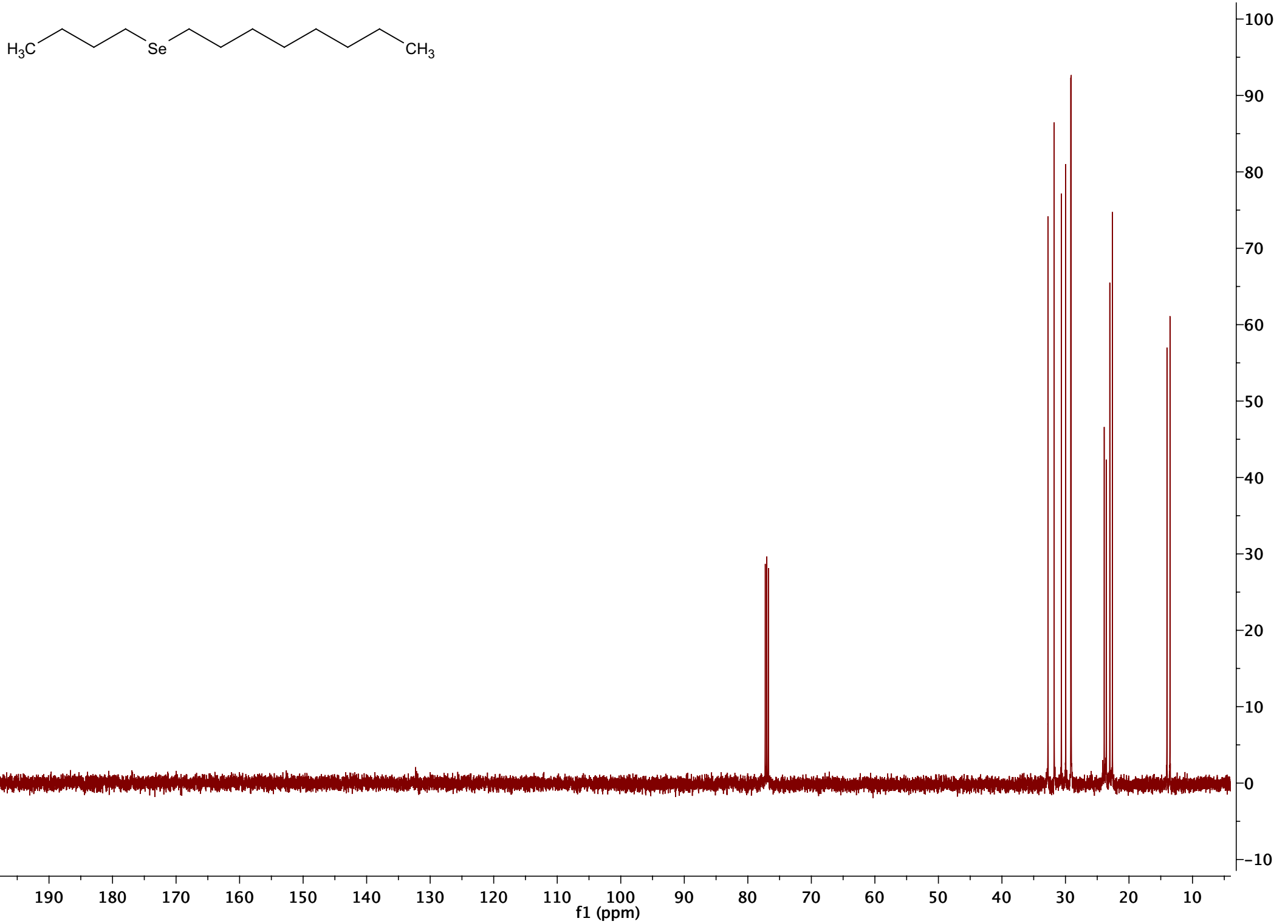

900
800
700
600
500
400
300
200
100
0
-100
00 390 380 370 360 350 340 330 320 310 300 290 280 270 260 250 240 230 220 210 200 190 180 170 160
f1 (ppm)

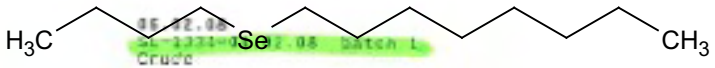

5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


360
340
320
300
280
260
240
220
200
180
160
140
120
100
80
60
40
20
0
−20
−40
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)


700
650
600
550
500
450
400
350
300
250
200
150
100
50
0
-50
-100
390
380
370
360
350
340
330
320
310
300
290
280
270
260
250
240
230
220
210
200
190
180
170
160
f1 (ppm)


H3C
Se
CH3
450
400
350
300
250
200
150
100
50
0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)


H3C
Se
CH3
100
90
80
70
60
50
40
30
20
10
0
−10
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

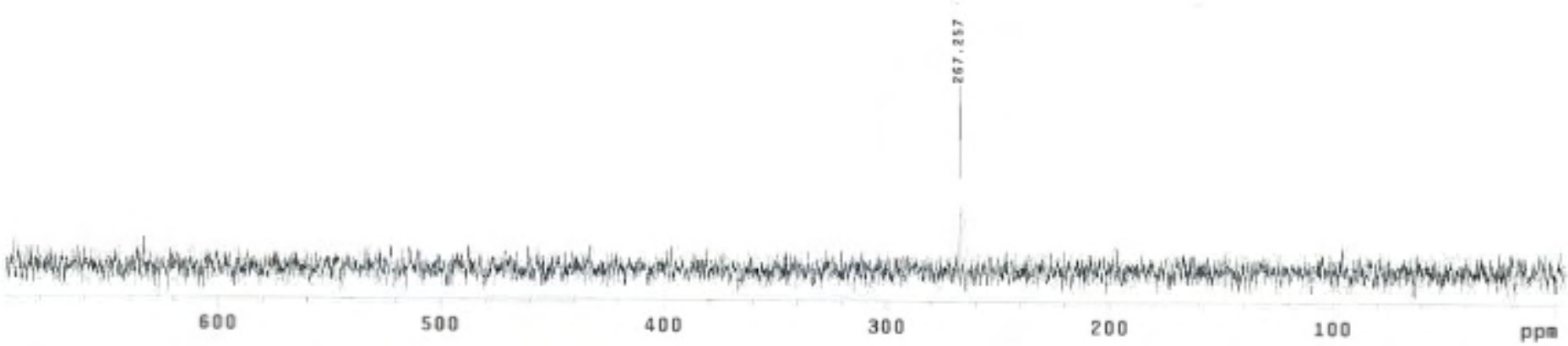


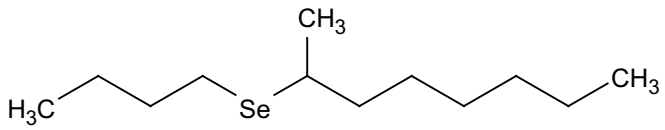
Crude

Pulse Sequence: s2pul

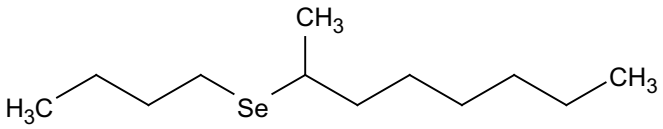
Solvent: CDCl3
Temp. 25.0 C / 298.1 K
Operator: chs
INOVA-500 "bio500"

Relax. delay 2.000 sec
Pulse 54.0 degrees
Acq. time 2.621 sec
Width 66778.8 Hz
48 repetitions
OBSERVE Se77, 95.3377759 MHz
DECOUPLE H1, 500.2135899 MHz
Power 38 dB
continuously on
single frequency
DATA PROCESSING
Line broadening 10.0 Hz
FT size 524288
Total time 19 min, 45 sec

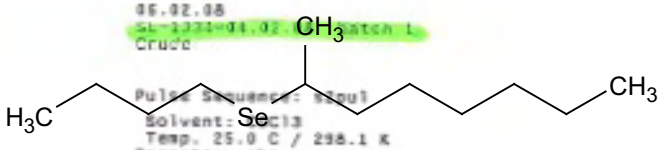



CH3
H3C
Se
CH3

450
400
350
300
250
200
150
100
50
0
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)


CH3
H3C
Se
CH3

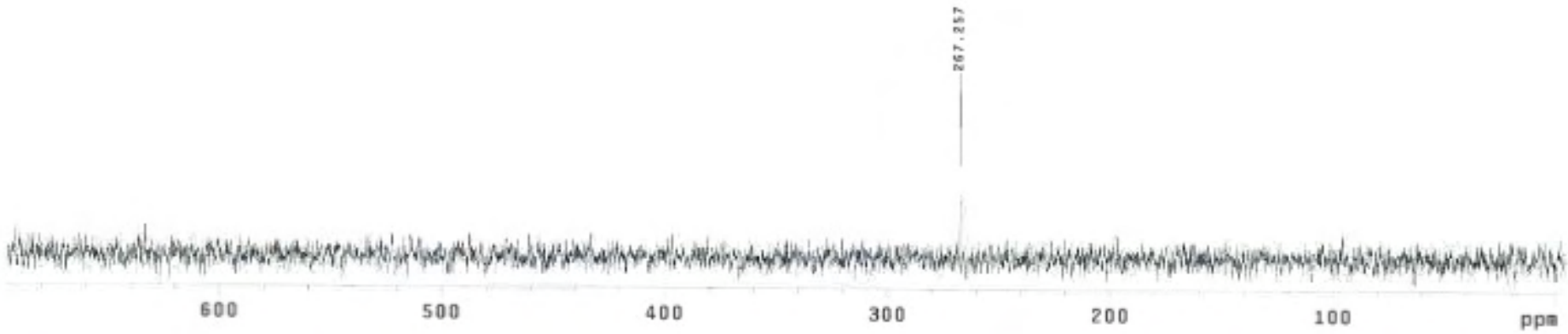
400
350
300
250
200
150
100
50
0
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

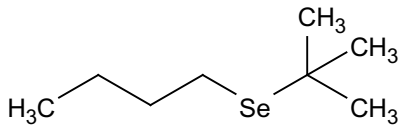



```
06.02.08
SL-1224-04.02.08 batch 1
Crude

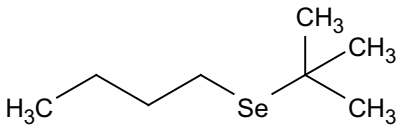
Pulse Sequence: s2pul
 Solvent: CDCl3
 Temp. 25.0 C / 298.1 K
Operator: chs
INOVA-500  "bio500"

 Relax. delay 2.000 sec
 Pulse 54.0 degrees
 Acq. time 2.621 sec
 Width 66778.8 Hz
 48 repetitions
OBSERVE Se77,  95.3377759 MHz
DECOUPLE  H1, 500.2135889 MHz
 Power 38 dB
 continuously on
 single frequency
DATA PROCESSING
 Line broadening 10.0 Hz
FT size 524288
Total time 19 min, 45 sec
```

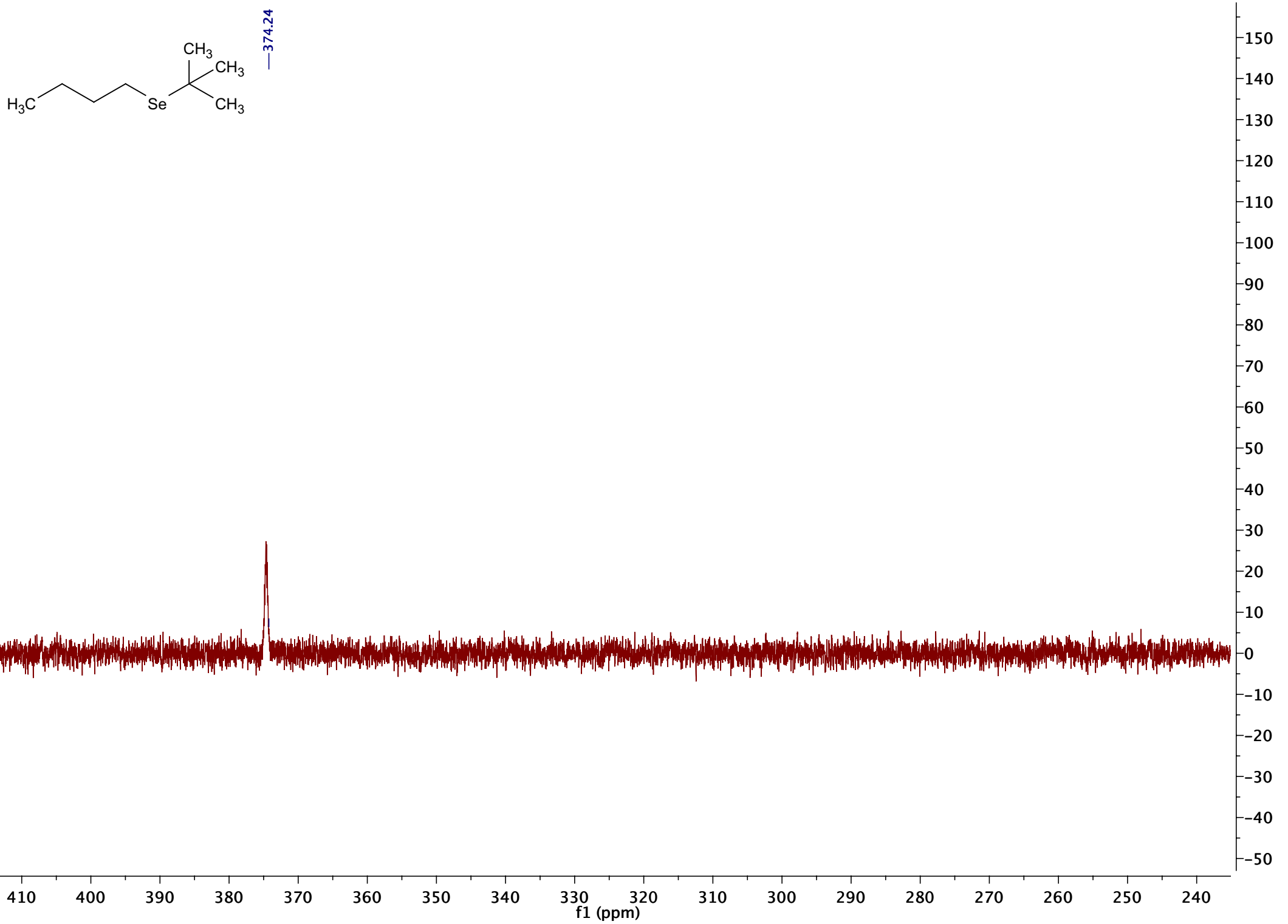


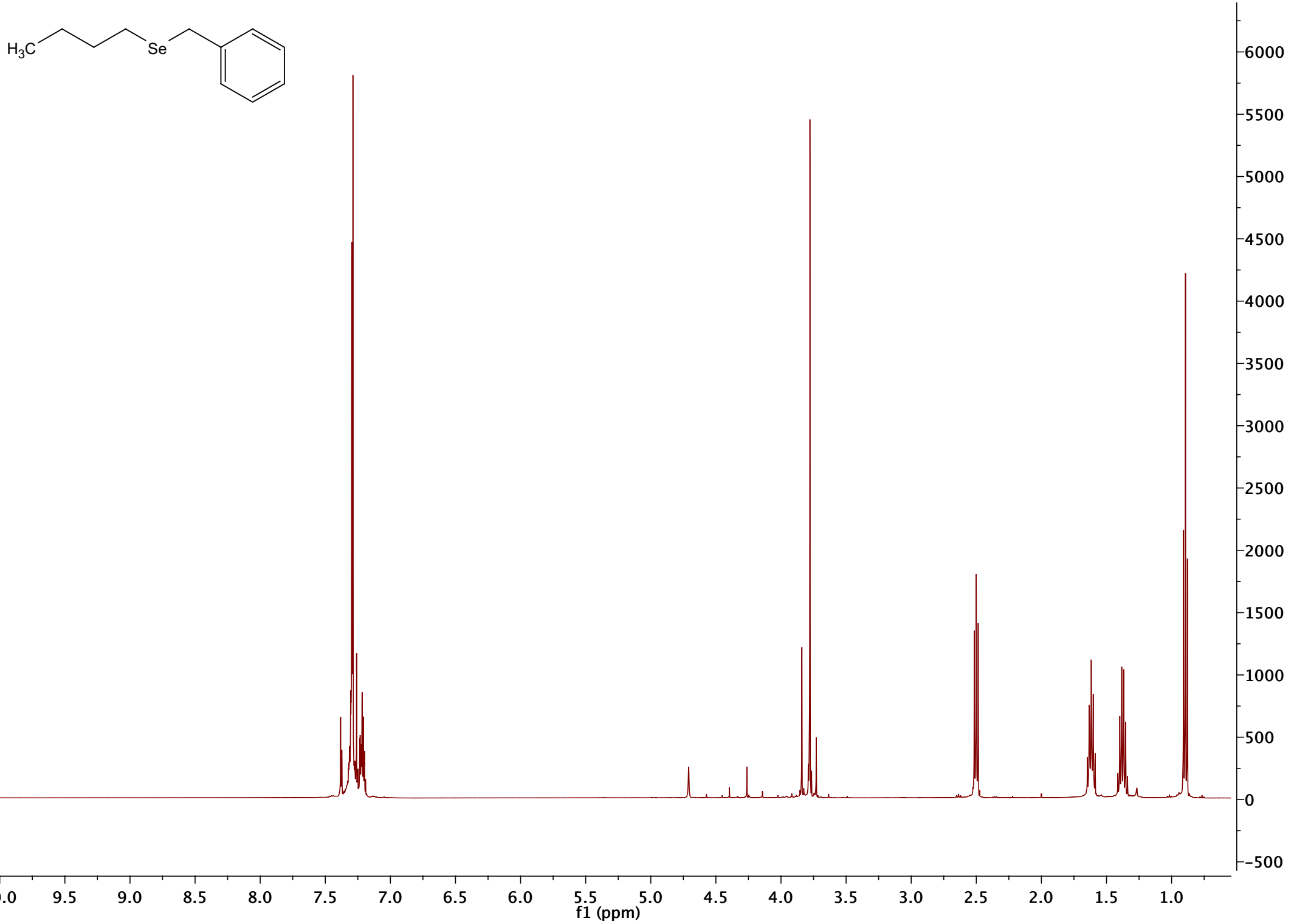

CH3
CH3
H3C
Se
CH3

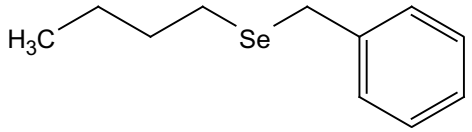
20000
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
0.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


CH3
CH3
H3C
Se
CH3

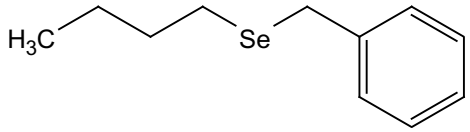
700
650
600
550
500
450
400
350
300
250
200
150
100
50
0
-50
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


374.24
CH3
CH3
H3C
Se
CH3
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
410
400
390
380
370
360
350
340
330
320
310
300
290
280
270
260
250
240
f1 (ppm)

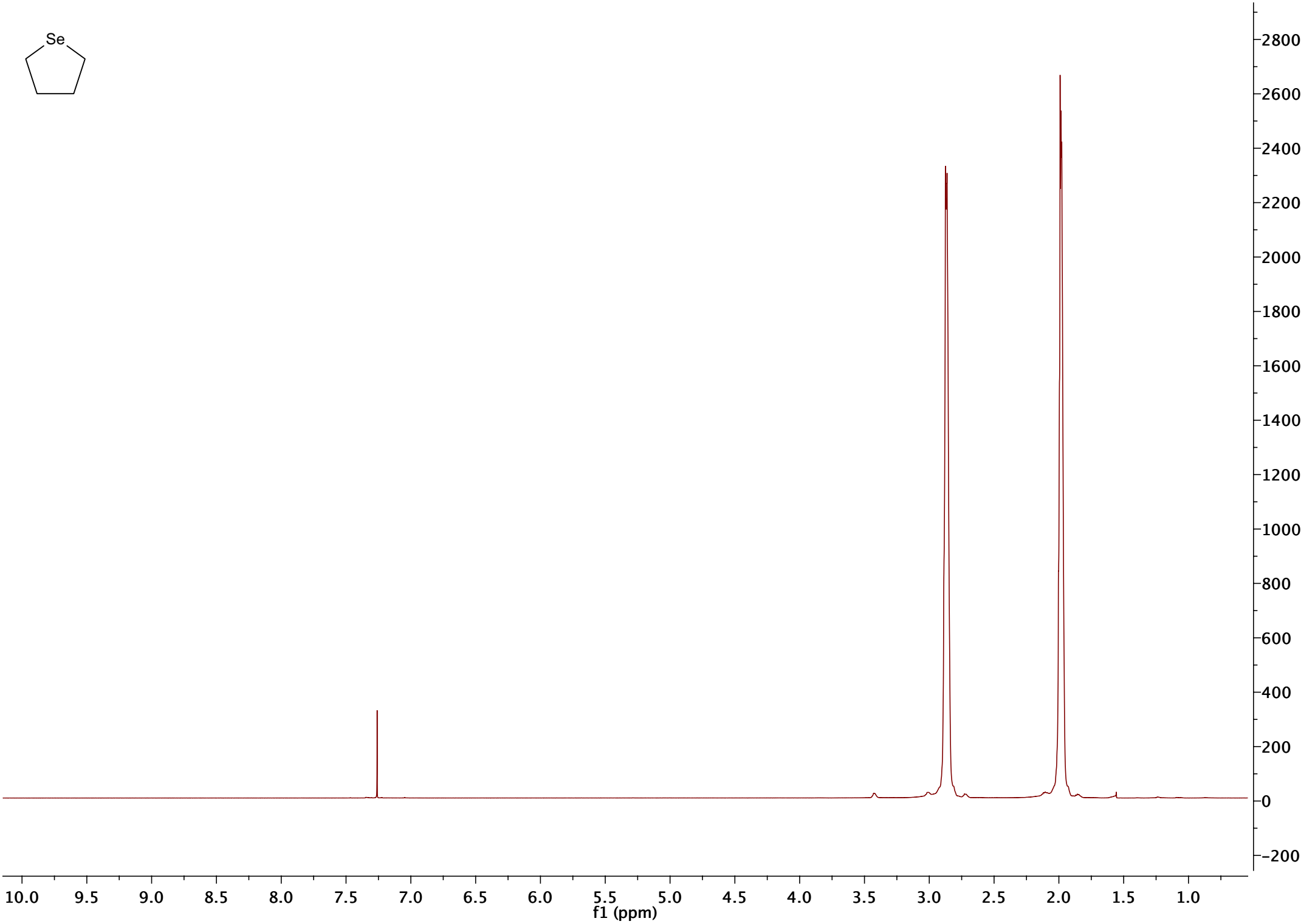

H3C
Se
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)

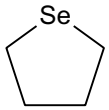

H3C
Se

240
220
200
180
160
140
120
100
80
60
40
20
0
-20
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

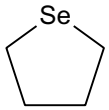

H3C
Se

160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
400
390
380
370
360
350
340
330
320
310
300
290
280
270
260
250
240
230
220
210
200
190
180
170
f1 (ppm)


Se
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)


Se

75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
-5
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


Se

100
90
80
70
60
50
40
30
20
10
0
-10
-20
390
370
350
330
310
290
270
250
230
210
190
170
150
130
110
f1 (ppm)

Table S1. B3LYP/6-31G(d) Optimized Geometries

R = Me - *Global minimum of reactant*

1\1\GINC-R139\FOpt\UB3LYP\Gen\C5H11Se1(2)\ROOT\27-Oct-2014\0\\#B3LYP/gen 6D OPT INT(grid=ultrafine) SCF=tight Freq=(noraman) maxdisk=536870912\\BuSeMe.freq\\0,2\C,-2.7179058027,0.6734599724,0.3408913492\Se,-1.0718172159,-0.414724587,0.3353261909\C,0.1024524815,0.9567813273,-0.5080865845\C,1.4923173196,0.4074332201,-0.833262843\C,2.334401436,0.0205347436,0.395360665\C,3.7249383441,-0.3920703122,0.0486941269\H,4.2388596724,0.0466684692,-0.8023059709\H,4.3066124221,-1.0166987601,0.7189839214\H,1.8355325627,-0.7805494145,0.9583007852\H,2.3515556798,0.8842037656,1.0888014727\H,1.4032158594,-0.4561339417,-1.5041549766\H,2.0318022203,1.1820797117,-1.3983648613\H,0.1685783728,1.8081829329,0.1773169632\H,-0.4026583148,1.2839500633,-1.4214700713\H,-2.5831640591,1.5673055479,0.9536783688\H,-2.9950578211,0.9502423365,-0.678713841\H,-3.5052233266,0.0532483593,0.7746941691\\Version=ES64L-G09RevD.01\State=2-A\HF=-2598.3857414\S2=0.753887\S2-1=0.\S2A=0.75001\RMSD=8.989e-09\RMSF=1.083e-05\Dipole=-0.0924931,0.6602713,-0.1750615\Quadrupole=2.0206645,-0.6734421,-1.3472225,-1.0637844,-0.3938768,-0.990316\PG=C01 [X(C5H11Se1)]\\@

R = Me - *Cyclization transition state*

1\1\GINC-R194\FTS\UB3LYP\Gen\C5H11Se1(2)\ROOT\27-Oct-2014\0\\#B3LYP/gen 6D OPT(TS,Calcfc) INT(grid=ultrafine) SCF=tight Freq=(noraman) maxdisk=536870912\\BuSeMe-TS.freq\\0,2\C,-1.6302872254,-0.830252956,-0.2174667482\C,-1.6756733888,-0.7637612274,1.2996548467\C,-0.2552946653,-0.9749126334,1.8470824671\C,0.6815803061,0.0346899685,1.1892697913\Se,0.2216284395,0.11666415,-0.7533340787\C,1.730457421,1.8604655516,-1.0126581751\H,-1.5416782188,-1.8465932782,-0.6094387086\H,-2.4325131609,-0.2932742044,-0.7240496839\H,-2.045792907,0.2195088867,1.6182058866\H,-2.365492346,-1.5153331293,1.7099878311\H,0.0773399579,-1.9951218562,1.6159694534\H,-0.2291371028,-0.8640945528,2.9392161652\H,0.549228716,1.0383633785,1.6037836174\H,1.7339492895,-0.2444117749,1.2740203497\H,1.3883904982,2.6725959196,-0.3740517004\H,2.6854131537,1.4295065905,-0.7123886215\H,1.6687267585,2.086697134,-2.075166217\\Version=ES64L-G09RevD.01\State=2-A\HF=-2598.3721798\S2=0.763417\S2-1=0.\S2A=0.750062\RMSD=5.875e-09\RMSF=3.251e-06\Dipole=-0.1479137,-0.0503191,0.6077581\Quadrupole=0.4372968,-0.5002978,0.063001,0.9764753,0.5673651,-0.4315044\PG=C01 [X(C5H11Se1)]\\@

R = n-Bu - *Global minimum of reactant*

1\1\GINC-R139\FOpt\UB3LYP\Gen\C8H17Se1(2)\ROOT\27-Oct-2014\0\\#B3LYP/gen 6D OPT INT(grid=ultrafine) SCF=tight Freq=(noraman) maxdisk=1073741824\\BuSenBu.freq\\0,2\C,-0.2431154542,-0.1572068398,-1.536713969\Se,-0.2691992607,0.0720747659,0.4374912505\C,1.704123931,-0.0142519703,0.7044068557\C,2.0864905397,-0.058832049,2.1848629036\C,1.7388172052,1.2139683583,2.977095741\C,2.2365391614,1.1862292666,4.3826104328\H,3.1605302916,0.6727505736,4.6345222891\H,1.7779311965,1.8001808131,5.151083807\H,0.652608416,1.3793769985,2.9674584057\H,2.1620193052,2.0835747161,2.4368601646\H,1.6189209537,-0.9282660492,2.663462644\H,3.1731056356,-0.2217927077,2.2427441232\H,2.1489886739,0.8567742162,0.2121441684\H,2.0517729708,-0.9169477852,0.193754418\H,0.3507917636,0.658371553,-1.9614109787\C,-1.6624789105,-0.1503668756,-2.1049914691\H,0.2611701351,-1.1038836606,-1.7562148128\C,-1.6838540306,-0.3282168318,-3.6314015744\H,-2.249724956,-0.9523420616,-1.6375855133\H,-2.1593275137,0.7933226987,-1.8422885923\C,-3.102253969,-0.3230108183,-4.2110477179\H,-1.0934894949,0.4725729444,-4.0984510753\H,-1.1835146942,-1.2708655979,-3.8940598256\H,-3.0880961868,-0.4513153014,-5.2992497761\H,-3.7065027057,-1.

1342520174,-3.7871360568\H,-3.6160210315,0.6211318857,-3.9929244364\\V
ersion=ES64L-G09RevD.01\State=2-A\HF=-2716.3273096\S2=0.753887\S2-1=0.
\S2A=0.75001\RMSD=3.558e-09\RMSF=6.288e-07\Dipole=0.4609722,-0.0374061
,-0.536964\Quadrupole=1.1120411,-1.6942304,0.5821893,-0.3211633,1.5235
455,0.8255202\PG=C01 [X(C8H17Se1)]\\@

R = n-Bu - *Cyclization transition state*

1\1\GINC-R195\FTS\UB3LYP\Gen\C8H17Se1(2)\ROOT\27-Oct-2014\0\\#B3LYP/ge
n 6D OPT(TS,Calcfc) INT(grid=ultrafine) SCF=tight Freq=(noraman) maxdi
sk=1073741824\\BuSenBu-TS.freq\\0,2\C,-0.0751266764,0.0725774758,-1.52
73768187\Se,0.0139259681,-0.2224931197,0.7057823119\C,2.0102741818,-0.
1525410839,0.6447516995\C,2.5371896295,-0.2445943739,2.0739687392\C,1.
6939555186,0.6627929575,2.9846709546\C,0.2340064738,0.2821525742,2.849
3241002\H,-0.0391715236,-0.6466012692,3.354943372\H,-0.4822559252,1.07
50861268,3.0615876051\H,1.8358657314,1.7099005992,2.686590244\H,2.0329
103993,0.5784528273,4.0281852154\H,2.4678007981,-1.2813158171,2.428171
6912\H,3.597835099,0.0384184951,2.1057613235\H,2.2950045763,0.79269051
49,0.1724061357\H,2.3563854002,-0.9760714202,0.0163056268\H,0.43689827
5,1.0205336619,-1.7057538178\H,0.5130613814,-0.7716230844,-1.897835077
5\C,-1.5238253289,0.0581322362,-1.9602803164\C,-1.7007491554,0.2098476
16,-3.4843469784\H,-1.998520295,-0.8797137898,-1.6388031394\H,-2.06770
0108,0.8687917954,-1.4554921655\C,-3.1712490179,0.1963224184,-3.916806
0368\H,-1.2290429225,1.146739792,-3.8116418063\H,-1.1597553407,-0.5994
176522,-3.9940490614\H,-3.2690628098,0.3057861703,-5.0030335809\H,-3.6
594918086,-0.7433291592,-3.6306487651\H,-3.7296867085,1.0153013939,-3.
4470652615\\Version=ES64L-G09RevD.01\State=2-A\HF=-2716.3160958\S2=0.7
64272\S2-1=0.\S2A=0.750068\RMSD=7.411e-09\RMSF=3.387e-06\Dipole=0.4975
645,0.1745324,0.0216831\Quadrupole=0.7607091,-1.8629004,1.1021913,-0.2
092137,1.2097235,0.4150966\PG=C01 [X(C8H17Se1)]\\@

R = s-Bu - *Global minimum of reactant*

1\1\GINC-R92\FOpt\UB3LYP\Gen\C8H17Se1(2)\ROOT\31-Oct-2014\0\\#B3LYP/ge
n OPT 6D INT(grid=ultrafine) SCF=tight Freq=(noraman) maxdisk=10737418
24\\BuSesBu.freq\\0,2\C,1.0031981384,-0.0631985814,0.8661591844\C,0.98
35631412,-0.189314128,2.3899400877\C,2.4013354477,-0.3074885235,2.9845
257632\C,2.4077718472,-0.4763632206,4.4667160914\Se,-0.847206012,0.096
9794907,0.157486013\C,-0.4353332485,-0.0202502544,-1.803190376\C,-1.77
2853494,-0.2187570559,-2.534475787\C,-1.6202689186,-0.5060956666,-4.03
51935063\H,0.1703286208,-0.9275526769,-1.9149007955\H,1.6314393138,-1.
0543761387,4.9601261956\H,3.2591285482,-0.1647158731,5.0632524639\H,2.
9954857222,0.5746472897,2.704897893\H,2.9103840639,-1.1635962754,2.500
219823\H,0.4812792505,0.680992066,2.8304806431\H,0.3963964749,-1.07045
52689,2.6795601246\H,1.5718566672,0.8197819211,0.5599299872\H,1.459571
4502,-0.9469774195,0.4081655094\C,0.3539717479,1.1960219515,-2.2871454
158\H,-2.3125498289,-1.0513263279,-2.0669498105\H,-2.3964061833,0.6751
062989,-2.3949196856\H,-2.5983644023,-0.7050007005,-4.487353571\H,-1.1
746916892,0.3367421719,-4.5741792405\H,-0.9894603489,-1.386791429,-4.2
082755558\H,0.6297049291,1.0859935229,-3.3439710809\H,-0.2375479927,2.
1121706099,-2.1809537496\H,1.2825099607,1.3280208341,-1.7230046647\\Ve
rsion=ES64L-G09RevD.01\State=2-A\HF=-2716.3274337\S2=0.753887\S2-1=0.\
S2A=0.75001\RMSD=4.279e-09\RMSF=4.547e-06\Dipole=0.580196,-0.1114567,-
0.4167376\Quadrupole=0.038544,-1.7348312,1.6962873,0.2535143,1.9029196
,-0.3284846\PG=C01 [X(C8H17Se1)]\\@

R = s-Bu - *Cyclization transition state*

1\1\GINC-R139\FTS\UB3LYP\Gen\C8H17Se1(2)\ROOT\27-Oct-2014\0\\#B3LYP/ge
n 6D OPT(TS,Calcfc) INT(grid=ultrafine) SCF=tight Freq=(noraman) maxdi
sk=1073741824\\BuSesBu-TS.freq\\0,2\C,-0.3260748639,0.0281369338,-1.73

11059088\Se,-0.2952554469,-0.179095201,0.4851854845\C,1.6860537062,-0.
4257511994,0.5388731072\C,2.1089506774,-0.6702780218,1.9848519125\C,1.
4107631914,0.3429094661,2.9076126964\C,-0.0858989698,0.2417436221,2.73
1213846\H,-0.5487022118,-0.6440582889,3.1686595409\H,-0.6617821541,1.1
459965517,2.9193871797\H,1.749692482,1.3565268643,2.6563876004\H,1.700
901457,0.1605339697,3.9542733558\H,1.8290713273,-1.68844777,2.28489641
91\H,3.2011711291,-0.5949329499,2.0745378993\H,2.1539463236,0.47956485
13,0.140597891\H,1.9367758715,-1.2658678225,-0.1129377976\C,0.28149938
9,1.3548137156,-2.1411710274\H,0.2991628941,-0.8239402952,-2.020389521
5\C,-1.7799474565,-0.1838804609,-2.1272664604\C,-1.9961954439,-0.28478
39544,-3.6479243144\H,-2.1537843031,-1.101111188,-1.6552966901\H,-2.38
7918502,0.6408505763,-1.7293514897\H,-3.0514665942,-0.4754620374,-3.87
6061002\H,-1.7078714298,0.6378124045,-4.1636018615\H,-1.4090741544,-1.
1057631648,-4.0774016401\H,0.3294116738,1.44889332,-3.2367053424\H,-0.
314084579,2.1932313235,-1.761559227\H,1.3038112309,1.4715732524,-1.766
4599365\\Version=ES64L-G09RevD.01\State=2-A\HF=-2716.317198\S2=0.76665
5\S2-1=0.\S2A=0.750081\RMSD=7.070e-09\RMSF=1.122e-06\Dipole=0.484383,0
.0645319,-0.0569668\Quadrupole=0.5629101,-1.8155952,1.2526851,-0.65092
96,1.2150538,0.101471\PG=C01 [X(C8H17Se1)]\\@

R = t-Bu - *Global minimum of reactant*

1\1\GINC-R90\FOpt\UB3LYP\Gen\C8H17Se1(2)\ROOT\31-Oct-2014\0\\#B3LYP/ge
n 6D OPT INT(grid=ultrafine) SCF=tight Freq=(noraman) maxdisk=10737418
24\\BuSetBu.freq\\0,2\C,-1.0361145586,0.0070229101,-1.8318770209\Se,-0
.9563874005,0.0064892623,0.1934477973\C,1.0068891442,0.0065808432,0.50
52208061\C,1.2951772304,0.0038581566,2.0078027873\C,2.8068663026,-0.00
41129952,2.3118807428\C,3.1150888882,-0.0498634882,3.7707719445\H,2.48
66435498,-0.6184989886,4.4504519506\H,4.0470104646,0.3471819597,4.1602
146859\H,3.2814799489,0.8767887173,1.855627533\H,3.2597096978,-0.87450
33197,1.7981810448\H,0.8378898169,0.8833483628,2.4773837641\H,0.831313
4708,-0.8766127761,2.4717140634\H,1.4339317971,0.896284553,0.033231839
3\H,1.4350832828,-0.8810048247,0.0301284765\C,-0.3716208904,1.27093812
71,-2.3888578794\C,-0.3700040971,-1.2556083472,-2.3897727013\C,-2.5374
388966,0.0061844633,-2.1517798132\H,-2.6819108673,0.0066557169,-3.2406
410485\H,-3.0350363058,-0.882503587,-1.748376712\H,-3.0362239893,0.893
7817471,-1.7474505475\H,-0.4633422734,-1.2714377451,-3.485272093\H,0.6
98893274,-1.2925582298,-2.1538918685\H,-0.8386165741,-2.1620708288,-1.
9946306447\H,-0.4649201777,1.2874736817,-3.4843525147\H,-0.8414334217,
2.1764751563,-1.9930334954\H,0.6972102785,1.3091074706,-2.1528608089\\
Version=ES64L-G09RevD.01\State=2-A\HF=-2716.3283229\S2=0.753888\S2-1=0
.\S2A=0.75001\RMSD=7.015e-09\RMSF=4.294e-06\Dipole=0.4812817,-0.029885
2,-0.5267712\Quadrupole=0.4052105,-1.669052,1.2638415,0.2451136,2.0264
407,-0.4038422\PG=C01 [X(C8H17Se1)]\\@

R = t-Bu - *Cyclization transition state*

1\1\GINC-R3398\FTS\UB3LYP\Gen\C8H17Se1(2)\ROOT\27-Oct-2014\0\\#B3LYP/g
en 6D OPT(TS,Calcfc) INT(grid=ultrafine) SCF=tight Freq=(noraman) maxd
isk=1073741824\\BuSetBu-TS.freq\\0,2\C,-0.570123525,-0.0211034505,-1.8
82711942\Se,-0.4488302468,-0.1329624584,0.3431449669\C,1.5413088544,-0
.0474868661,0.4714318266\C,1.9506745085,-0.2724014991,1.9253072122\C,1
.0901507129,0.5966990111,2.8581631559\C,-0.3692279511,0.2746651841,2.6
615878199\H,-0.7029538432,-0.6870146994,3.0512170949\H,-1.0851321732,1
.0759501461,2.8309402559\H,1.2736762484,1.6566523304,2.638987809\H,1.3
937015081,0.4317083873,3.9045598656\H,1.8162163163,-1.3298598871,2.187
3734195\H,3.0172883561,-0.0407614549,2.0513762219\H,1.864896232,0.9373
765581,0.1224046634\H,1.9606315655,-0.8096945911,-0.1886789093\C,0.145
7468262,1.2359534214,-2.3507989313\C,0.0430110505,-1.2985834973,-2.437
229347\C,-2.0724989368,0.0459106727,-2.1167260504\H,-2.2845264272,0.07

52825015,-3.1968118725\H,-2.5858149991,-0.8302600879,-1.7043662497\H,-2.5112678832,0.9434891522,-1.6674231847\H,-0.063182752,-1.318566111,-3.5347669028\H,1.113943884,-1.3741001125,-2.2190498239\H,-0.4515138885,-2.1902843284,-2.0390302198\H,0.0362210566,1.3462241432,-3.4421411377\H,-0.2700542209,2.1337945011,-1.8820521333\H,1.2199655396,1.2034303358,-2.1386673989\\Version=ES64L-G09RevD.01\State=2-A\HF=-2716.3194709\S2=0.76869\S2-1=0.\S2A=0.750093\RMSD=4.943e-09\RMSF=1.841e-06\Dipole=0.4534883,0.1166089,-0.0812586\Quadrupole=0.2143883,-1.9385996,1.7242113,-0.1338203,1.1604785,0.2547713\PG=C01 [X(C8H17Se1)]\\@

R = Bn - *Global minimum of reactant*

1\1\GINC-R3580\FOpt\UB3LYP\Gen\C11H15Se1(2)\ROOT\19-Sep-2014\0\\# B3LYP/Gen SCF=Tight INT(grid=ultrafine) OPT IOP(2/17=4) maxdisk=1610612736\\BuSeBn.B3LYP\\0,2\C,-1.6388396668,0.306513676,-1.0326145798\Se,-1.3856937932,0.5478712056,0.9398609331\C,0.5263041755,1.0827685606,0.9099263926\C,1.0671101613,1.2235467999,2.3331192414\C,2.5526453227,1.6382441366,2.3520518939\C,3.1192451592,1.7396931054,3.728632574\H,2.8094034507,1.0463215211,4.5055220935\H,3.9569659622,2.395231556,3.9438386229\H,2.677235964,2.5944871905,1.8234912251\H,3.1251711913,0.9012781546,1.7560283357\H,0.4801589288,1.9665645525,2.8873772199\H,0.9530354814,0.2706491017,2.8663501138\H,0.6030141695,2.0302623729,0.366702491\H,1.0735079572,0.3158577935,0.3541334155\H,-1.4657322803,1.2763377074,-1.5053067912\C,-0.7863073447,-0.767234576,-1.6477543293\H,-2.7046355126,0.0746589384,-1.1155428218\C,0.3262424927,-0.4317270683,-2.4320142427\C,1.1197031975,-1.4239694267,-3.0136305234\C,0.8092426864,-2.769902532,-2.8203972788\C,-0.2988245596,-3.1172181978,-2.0411018704\C,-1.0859373158,-2.125779916,-1.4595080264\H,0.5669090557,0.6164213575,-2.5965022828\H,1.9766815685,-1.1425539584,-3.620095824\H,1.4226914832,-3.5438011229,-3.2738053389\H,-0.5496796288,-4.1636234477,-1.8879803139\H,-1.9399876405,-2.4022685757,-0.8458674033\\Version=ES64L-G09RevD.01\State=2-A\HF=-2829.4222325\S2=0.753882\S2-1=0.\S2A=0.75001\RMSD=4.649e-09\RMSF=3.963e-06\Dipole=0.4752634,-0.007559,-0.4917473\Quadrupole=0.2365131,1.3842175,-1.6207307,1.8039674,0.3566989,-0.3770439\PG=C01 [X(C11H15Se1)]\\@

R = Bn - *Cyclization transition state*

1\1\GINC-R89\FTS\UB3LYP\Gen\C11H15Se1(2)\ROOT\19-Sep-2014\0\\# B3LYP/Gen SCF=Tight INT(grid=ultrafine) OPT=(TS,calcfc,noeigentest,maxcyc=200) IOP(2/17=4) maxdisk=1610612736\\BuSeBn-TS.B3LYP\\0,2\C,-3.1360980551,-0.6462073658,0.6908922526\C,-3.4000283776,-0.2043971308,2.1062738248\C,-2.2407387833,-0.6390919538,3.020461555\C,-0.9235109073,-0.055850089,2.5158344776\Se,-0.7784175368,-0.3523076088,0.5468419513\C,1.1641123896,0.6206485304,0.4770223411\H,-3.1976298052,-1.7176600793,0.4993161506\H,-3.5445634179,-0.0390436362,-0.1132548922\H,-3.5048942716,0.8877142183,2.1451394962\H,-4.3459531513,-0.6271561491,2.4820922407\H,-2.1790494729,-1.7350756176,3.0319580878\H,-2.4184293402,-0.3152720985,4.0550428224\H,-0.8747308708,1.0236168896,2.6929669927\H,-0.05883275,-0.5265958408,2.990288296\H,1.7334806548,0.0654911952,1.2248260461\C,1.7272721976,0.5313925406,-0.8869758876\H,0.9682309758,1.6407828599,0.8086828365\C,1.4788237443,1.5372676743,-1.8385312095\C,1.9942725408,1.445402159,-3.1301911488\C,2.7671225059,0.3422722627,-3.5022135148\C,3.0177363608,-0.6684997012,-2.5702970357\C,2.5012110367,-0.576028457,-1.2792831301\H,0.877264869,2.3979826711,-1.5552534188\H,1.7945704422,2.2370444936,-3.8479122466\H,3.170969814,0.2712913316,-4.5085658914\H,3.6183829327,-1.5302203112,-2.8500923113\H,2.6976204262,-1.3673447138,-0.559470051\\Version=ES64L-G09RevD.01\State=2-A\HF=-2829.4151114\S2=0.766662\S2-1=0.\S2A=0.750125\RMSD=7.142e-09\RMSF=2.843e-06\Dipole=-0.1966592,0.169946,0.5795185\Quadrupole=-0.9952518,-1.690263,2.6855148,-1.413513,-2

.5846915,-0.5837103\PG=C01 [X(C11H15Se1)]\\@

R = CHPh$_2$ - *Global minimum of reactant*

1\1\GINC-R199\FOpt\UB3LYP\Gen\C17H19Se1(2)\ROOT\27-Oct-2014\0\\#B3LYP/
gen 6D OPT INT(grid=ultrafine) SCF=tight Freq=(noraman) maxdisk=214748
3648\\BuSePh2.freq\\0,2\C,-0.284419177,0.3500603395,-0.7594766393\Se,-
0.1950753794,0.785674818,1.2115073916\C,1.7807709783,0.7187769197,1.43
0839882\C,2.1688314405,1.0327013839,2.8761074727\C,3.6953161292,0.9858
12007,3.0920980999\C,4.0996363083,1.2449106005,4.5044428694\H,3.493650
0019,0.8784903155,5.3283690819\H,5.0728822413,1.6619453118,4.742374751
6\H,4.186148562,1.7069813227,2.4227212222\H,4.0607254255,-0.0069832133
,2.765204215\H,1.7960973045,2.0250093634,3.1585648873\H,1.6894668779,0
.3127206235,3.5527617576\H,2.2197572939,1.4469564811,0.7412127652\H,2.
1154835624,-0.2810680947,1.1402081475\H,0.2842537259,1.1539135108,-1.2
349937201\C,0.3648327056,-0.9713320616,-1.131735994\C,-1.7390657802,0.
5048799064,-1.1721554359\C,-2.2024119798,1.7664574166,-1.5759533295\C,
-3.5315415657,1.9566983755,-1.9498086405\C,-4.4257099163,0.8845084565,
-1.9248224079\C,-3.9770265484,-0.3743342862,-1.5240410572\C,-2.6455536
502,-0.5634926857,-1.1509094782\H,-1.511942513,2.6067029128,-1.5916007
771\H,-3.8677499299,2.9417397798,-2.2627690408\H,-5.4621326288,1.02899
40239,-2.2178891014\H,-4.6636055779,-1.2167107577,-1.5043853741\H,-2.3
071795636,-1.5512943938,-0.8553141294\C,1.0936634926,-1.0400882021,-2.
3283585349\C,1.678614772,-2.2352039649,-2.747737176\C,1.5471408662,-3.
3880834227,-1.9724174915\C,0.8312205285,-3.3316519755,-0.7754048021\C,
0.2490880346,-2.1341658476,-0.3567371405\H,1.1982337659,-0.1471887814,
-2.9410392925\H,2.2397453456,-2.2631328137,-3.6781964723\H,2.004744739
5,-4.3198458049,-2.2938863692\H,0.7301076284,-4.2212075923,-0.15894768
67\H,-0.283914385,-2.0907716449,0.58872281\\Version=ES64L-G09RevD.01\S
tate=2-A\HF=-3060.4845674\S2=0.753887\S2-1=0.\S2A=0.75001\RMSD=7.567e-
09\RMSF=2.868e-06\Dipole=0.51034,-0.2192546,-0.4182158\Quadrupole=1.81
06984,0.9849712,-2.7956695,0.0711786,1.0428007,-2.3477231\PG=C01 [X(C1
7H19Se1)]\\@

R = CHPh$_2$ - *Cyclization transition state*

1\1\GINC-R2217\FTS\UB3LYP\Gen\C17H19Se1(2)\ROOT\28-Oct-2014\0\\#B3LYP/
gen 6D OPT(TS,Calcfc) INT(grid=ultrafine) SCF=tight Freq=(noraman) max
disk=2147483648\\BuSePh2-TS.freq\\0,2\C,-2.669959115,-1.4340106584,2.5
407451418\C,-1.7605261428,-2.3597339548,3.295255539\C,-0.7032973722,-2
.9732008385,2.3588781165\C,0.1613824402,-1.8900083329,1.7185101698\Se,
-1.005122117,-0.4703668375,0.9432241436\C,0.6307832297,0.6440906734,0.
0389222718\H,-3.336677175,-1.8761622509,1.8023389128\H,-3.0703619782,-
0.5607364663,3.0476034989\H,-1.2584945084,-1.8158973628,4.1058690759\H
,-2.3382136991,-3.1704257806,3.7705811221\H,-1.2065784838,-3.553979727
3,1.5749922801\H,-0.0613812903,-3.6717703356,2.9132396477\H,0.81369376
06,-1.4180309639,2.4605987068\H,0.7793455339,-2.2885251616,0.911777153
5\H,1.2272636428,0.8879283799,0.9207625133\C,1.4109383845,-0.251041393
7,-0.8735522103\C,0.0127302507,1.89979058,-0.5095133546\C,2.7840323021
,-0.4382562314,-0.6415568831\C,3.5520667856,-1.2604784915,-1.467239638
5\C,2.959609114,-1.9210615329,-2.5436363433\C,1.5917783507,-1.75776733
63,-2.7799319052\C,0.8254908698,-0.9389239614,-1.9527934754\H,3.256233
0898,0.0769019402,0.1920485335\H,4.6134070689,-1.3836762223,-1.2673283
563\H,3.5540108913,-2.5635400501,-3.1876748279\H,1.1170217881,-2.27848
42564,-3.6076164246\H,-0.2428516021,-0.847414935,-2.1236904516\C,-0.44
69870774,2.8742201662,0.3969530532\C,-1.0206178445,4.0616311966,-0.048
3034578\C,-1.1499860048,4.3091622146,-1.4176677102\C,-0.6936568937,3.3
571225224,-2.3282564649\C,-0.1186122308,2.1658704996,-1.8810521027\H,-
0.3544263726,2.6872701167,1.4640301313\H,-1.3653950669,4.7968853001,0.
6743551201\H,-1.5967554967,5.2356652815,-1.7683211921\H,-0.7782109588,

3.5403866283,-3.3964650411\H,0.24951271,1.4500961953,-2.6075745832\\Version=ES64L-G09RevD.01\State=2-A\HF=-3060.4803009\S2=0.767379\S2-1=0.\S2A=0.750129\RMSD=9.478e-09\RMSF=2.560e-06\Dipole=0.2862464,-0.4546229,0.3397522\Quadrupole=-2.0222172,0.062895,1.9593221,-2.1276782,-0.084269,-0.2313821\PG=C01 [X(C17H19Se1)]\\@

Table S2. Total Electronic Energies (E) at G3(MP2)-RAD and Component Levels of Theory and Corresponding Zero-Point Vibrational Energies (ZPVE), Thermal Corrections (TC), Entropies (S), Gas-phase Enthalpies (H_{gas}) and Gas-phase Gibb's Free Energies (G_{gas}) at 294.15 K (Hartrees or Hartrees / K)[a].

Species	E(ROMP2/ 6-31G*)	E(ROMP2/ GTMP2Large)	E(ROCCSD(T)/ 6-31G*)	HLC	E(G3MP2-RAD)	ZPVE	TC	S x 10^3	H_{gas}	G_{gas}
BuSe-Me	-2596.12861	-2596.80899	-2596.21883	-0.17340	-2597.07262	0.14298	0.01028	0.15777	-2596.91936	-2596.96577
BuSe-Me-TS	-2596.11077	-2596.79499	-2596.20103	-0.17340	-2597.05866	0.14406	0.00875	0.14276	-2596.90585	-2596.94784
BuSe-nBu	-2713.62717	-2714.46262	-2713.76528	-0.25812	-2714.85885	0.22746	0.01427	0.19474	-2714.61712	-2714.67440
BuSe-nBu-TS	-2713.61565	-2714.45529	-2713.74939	-0.25812	-2714.84714	0.22887	0.01264	0.17898	-2714.60562	-2714.65827
BuSe-sBu	-2713.62985	-2714.46574	-2713.76724	-0.25812	-2714.86125	0.22717	0.01434	0.19237	-2714.61974	-2714.67633
BuSe-sBu-TS	-2713.61619	-2714.45594	-2713.75254	-0.25812	-2714.85042	0.22851	0.01274	0.17737	-2714.60917	-2714.66135
BuSe-tBu	-2713.63483	-2714.47132	-2713.77124	-0.25812	-2714.86586	0.22642	0.01428	0.18961	-2714.62515	-2714.68093
BuSe-tBu-TS	-2713.61970	-2714.45945	-2713.75777	-0.25812	-2714.85564	0.22769	0.01278	0.17473	-2714.61517	-2714.66657
BuSe-Bn	-2826.43377	-2827.35020	-2826.58663	-0.30519	-2827.80824	0.22339	0.01452	0.19834	-2827.57033	-2827.62867
BuSe-Bn-TS	-2826.41864	-2827.33817	-2826.57351	-0.30519	-2827.79822	0.22467	0.01292	0.18410	-2827.56062	-2827.61477
BuSe-$CHPh_2$	-3056.73962	-3057.89277	-3056.95306	-0.43697	-3058.54318	0.30272	0.01917	0.23844	-3058.22128	-3058.29142
BuSe-$CHPh_2$-TS	-3056.72956	-3057.88519	-3056.94445	-0.43697	-3058.53706	0.30414	0.01754	0.22178	-3058.21537	-3058.28061

Table S3. Gibb's Free Energies of Solvation (ΔG_{solv}, kJ mol^{-1}) in Benzene and Acetonitrile Calculated using the COSMO-RS and SMD solvent models. Gibb's Free Energies in Solution should be Calculated as: $G_{soln} = G_{gas} + \Delta G_{solv} + RTln(R'T)$ where R and R' are the Gas Constant in Units of J mol^{-1} K^{-1} and L atm mol^{-1} K^{-1}, Respectively (R = 8.31446 J mol^{-1} K^{-1}, R' = 0.0820575 L atm mol^{-1} K^{-1}) and T is the Temperature.

	COSMO-RS						SMD	
	294.15 K		298.15 K		323.15 K			
	benzene	acetonitrile	benzene	acetonitrile	benzene	acetonitrile	benzene	acetonitrile
BuSe-Me	-17.4	-14.3	-17.4	-14.2	-16.8	-13.7	-15.4	-21.2
BuSe-Me-TS	-15.3	-11.6	-15.2	-11.5	-14.7	-11.0	-14.7	-18.2
BuSe-nBu	-26.3	-20.2	-26.2	-20.1	-25.7	-19.5	-25.5	-28.9
BuSe-nBu-TS	-24.0	-17.3	-23.9	-17.2	-23.5	-16.7	-26.2	-27.3
BuSe-sBu	-26.0	-20.1	-25.9	-20.0	-25.4	-19.4	-24.0	-28.1
BuSe-sBu-TS	-24.0	-17.7	-23.9	-17.6	-23.5	-17.1	-24.9	-27.6
BuSe-tBu	-25.3	-19.8	-25.2	-19.7	-24.7	-19.2	-22.9	-27.4
BuSe-tBu-TS	-23.6	-17.8	-23.5	-17.7	-23.0	-17.2	-24.4	-28.1
BuSe-Bn	-36.7	-32.7	-36.6	-32.6	-35.9	-31.9	-35.4	-43.6
BuSe-Bn-TS	-37.1	-32.7	-37.0	-32.5	-36.4	-31.9	-37.4	-46.0
BuSe-$CHPh_2$	-55.7	-50.1	-55.5	-49.9	-54.9	-49.1	-50.3	-60.0
BuSe-$CHPh_2$-TS	-54.5	-48.9	-54.4	-48.7	-53.8	-48.0	-51.9	-61.8