

Supporting Information

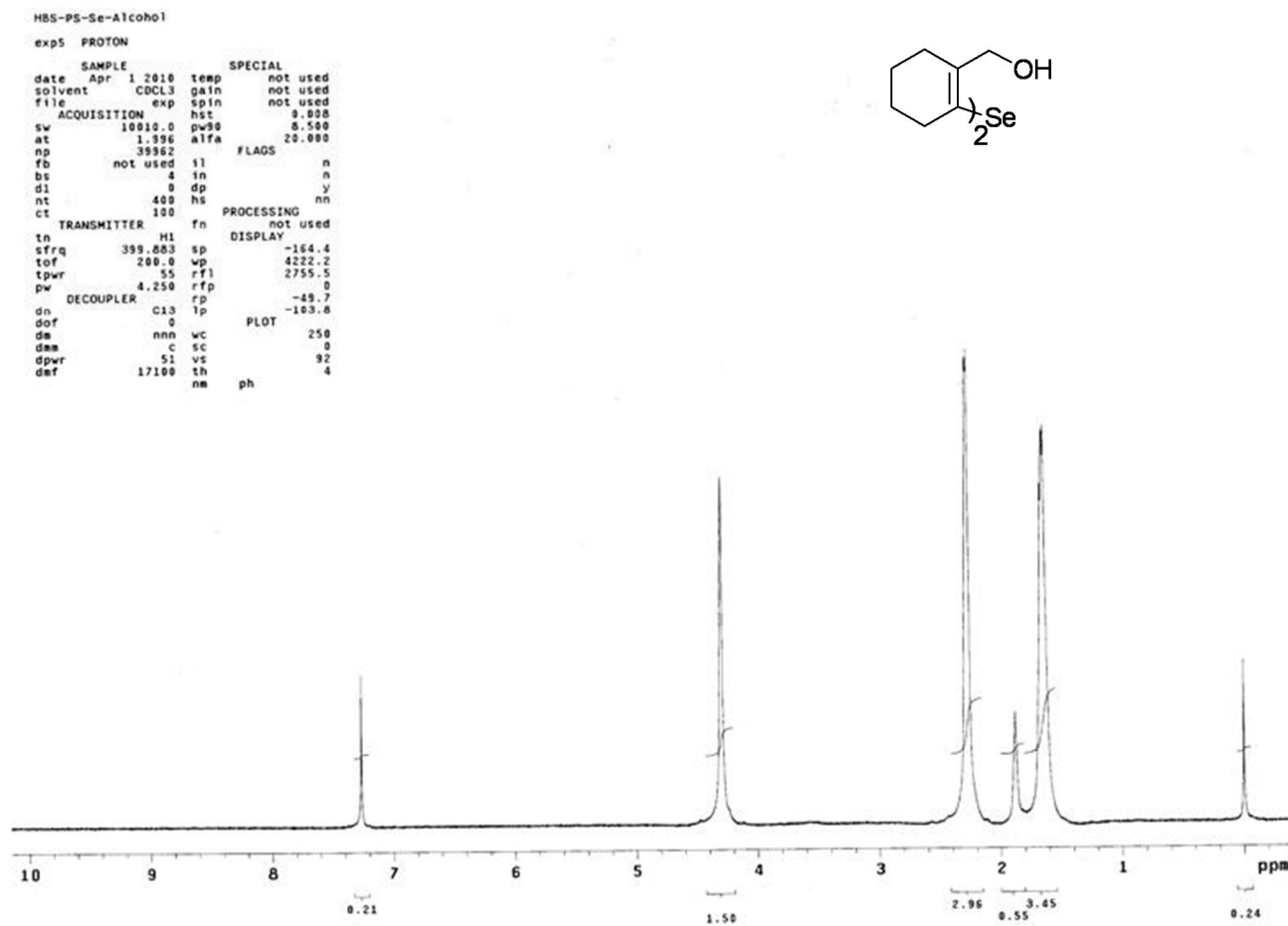
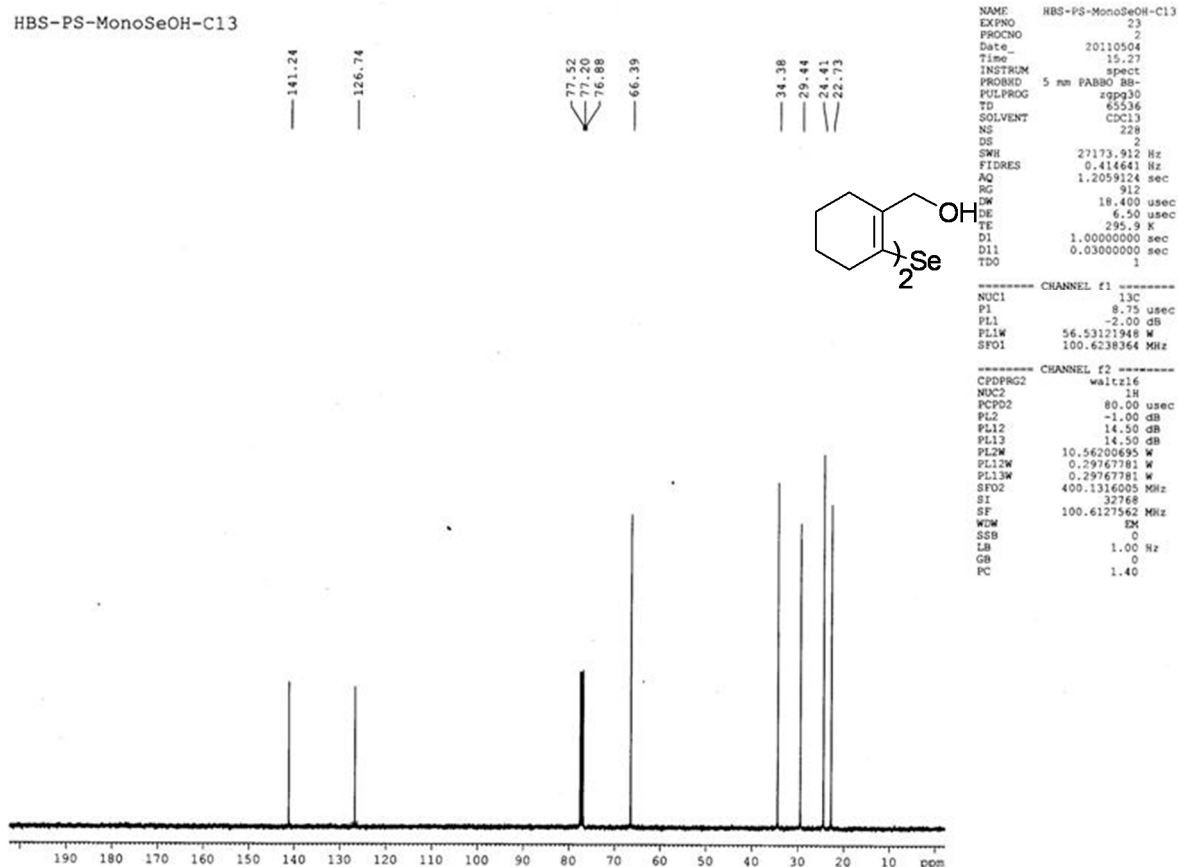
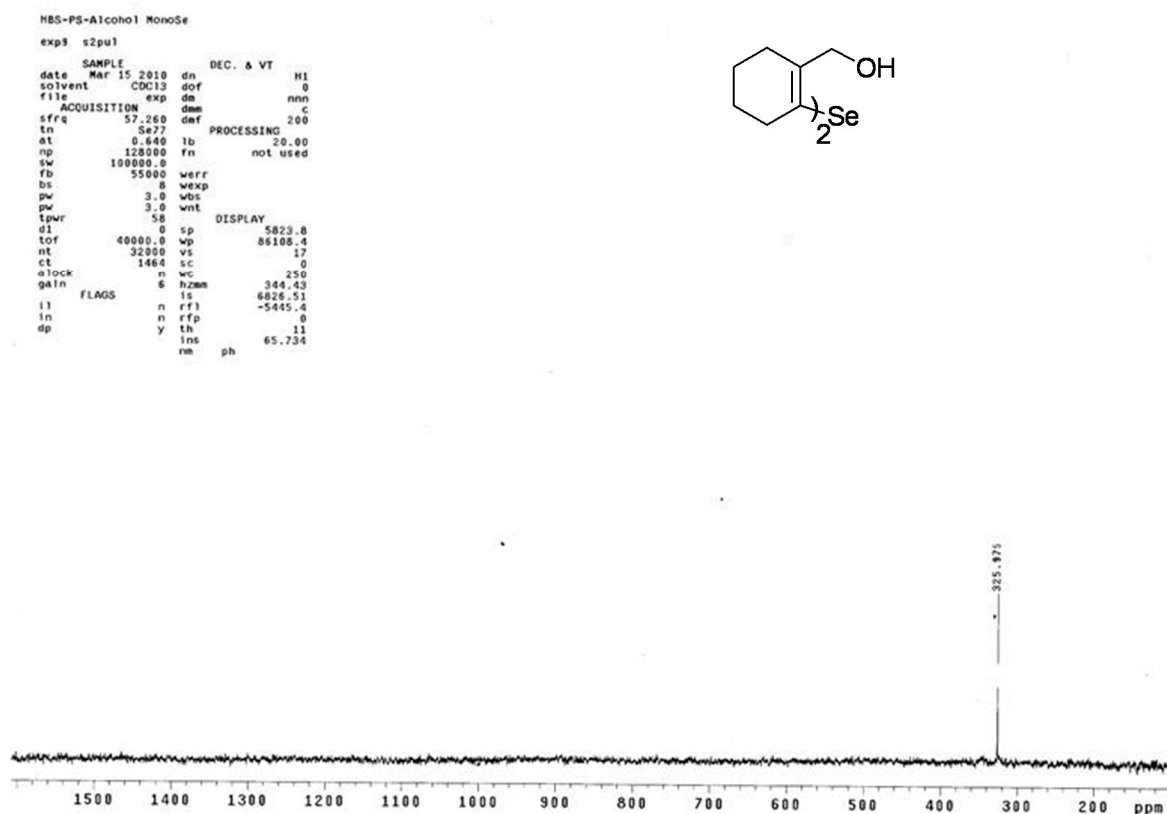


Figure S1. ^1H -NMR spectrum of **19** (CDCl_3).

Figure S2. ^{13}C -NMR spectrum of **19** (CDCl_3).Figure S3. ^{77}Se -NMR spectrum of **19** (CDCl_3).

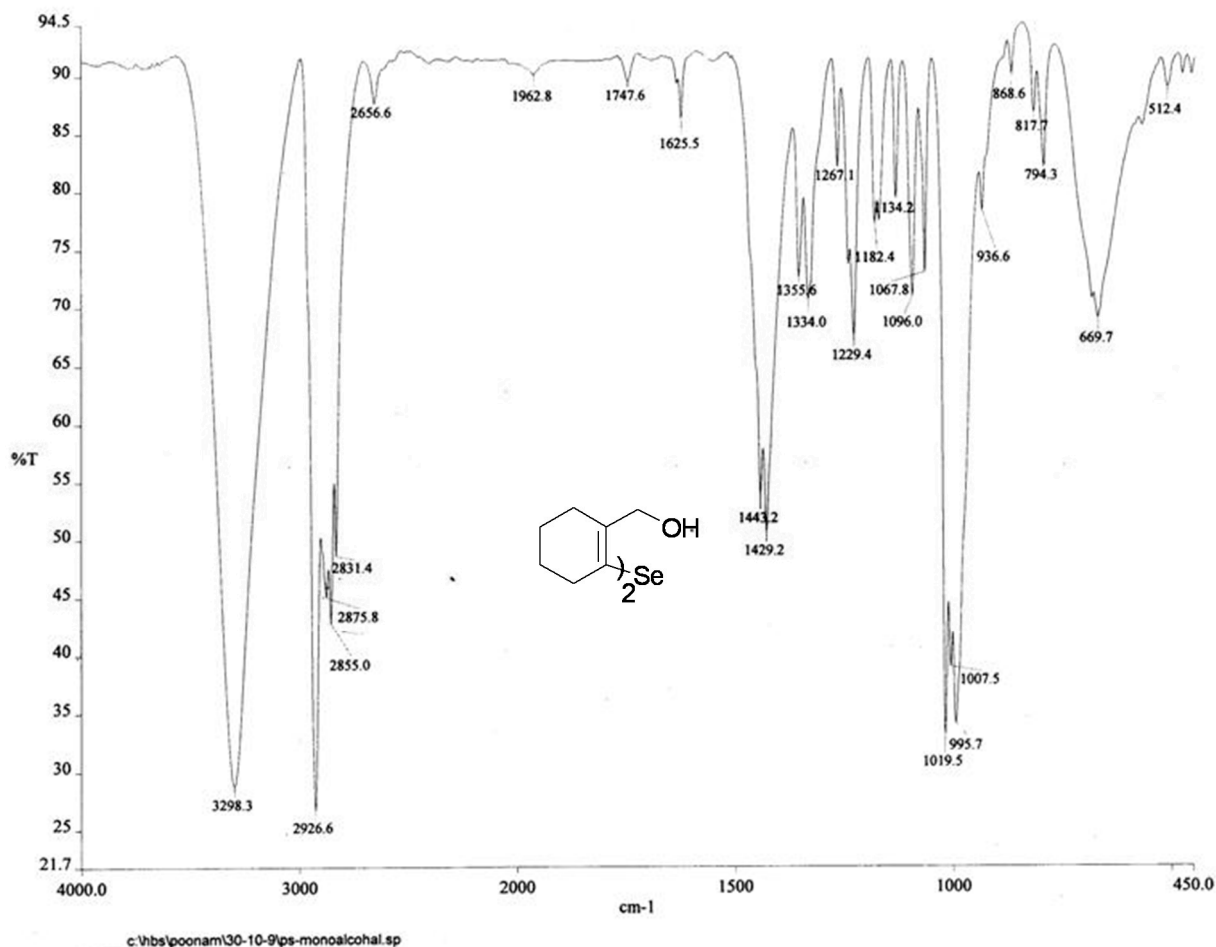


Figure S4. FT-IR spectrum of 19.

Elemental Composition Report

Single Mass Analysis (displaying only valid results)

Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0

Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron Ions

22 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

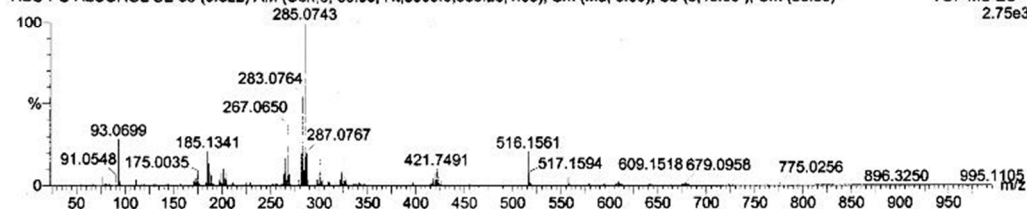
Micromass : Q-ToF micro (YA-105)

Dept. Of Chemistry I.I.T.(B)

27-May-2011 12:12:03

C₁₄H₂₂O₂Se

HBS-PS-ALCOHOL SE 83 (0.822) AM (Cen, 5, 80.00, Ht, 5000.0, 556.28, 1.00); Sm (Md, 6.00); Sb (5, 40.00); Cm (58:83)

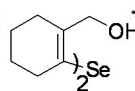
TOF MS ES+
2.75e3

Minimum:						
Maximum:						
Mass	Calc. Mass	mDa	PPM	DBE	Score	Formula
325.0688	325.0683	0.5	1.7	4.5	1	C ₁₄ H ₂₂ O ₂ Se Na

Figure S5. HRMS spectrum of 19.

Eager 300 Report

Page: 1 Sample: PS1 (PS1)



Method Name : SP061109
 Method File : D:\CHNS2008\SP061109.mth
 Chromatogram : PS1
 Operator ID : SP
 Analysed : 11/06/2009 09:03
 Sample ID : PS1 (# 6)
 Analysis Type : UnkNown (Area)

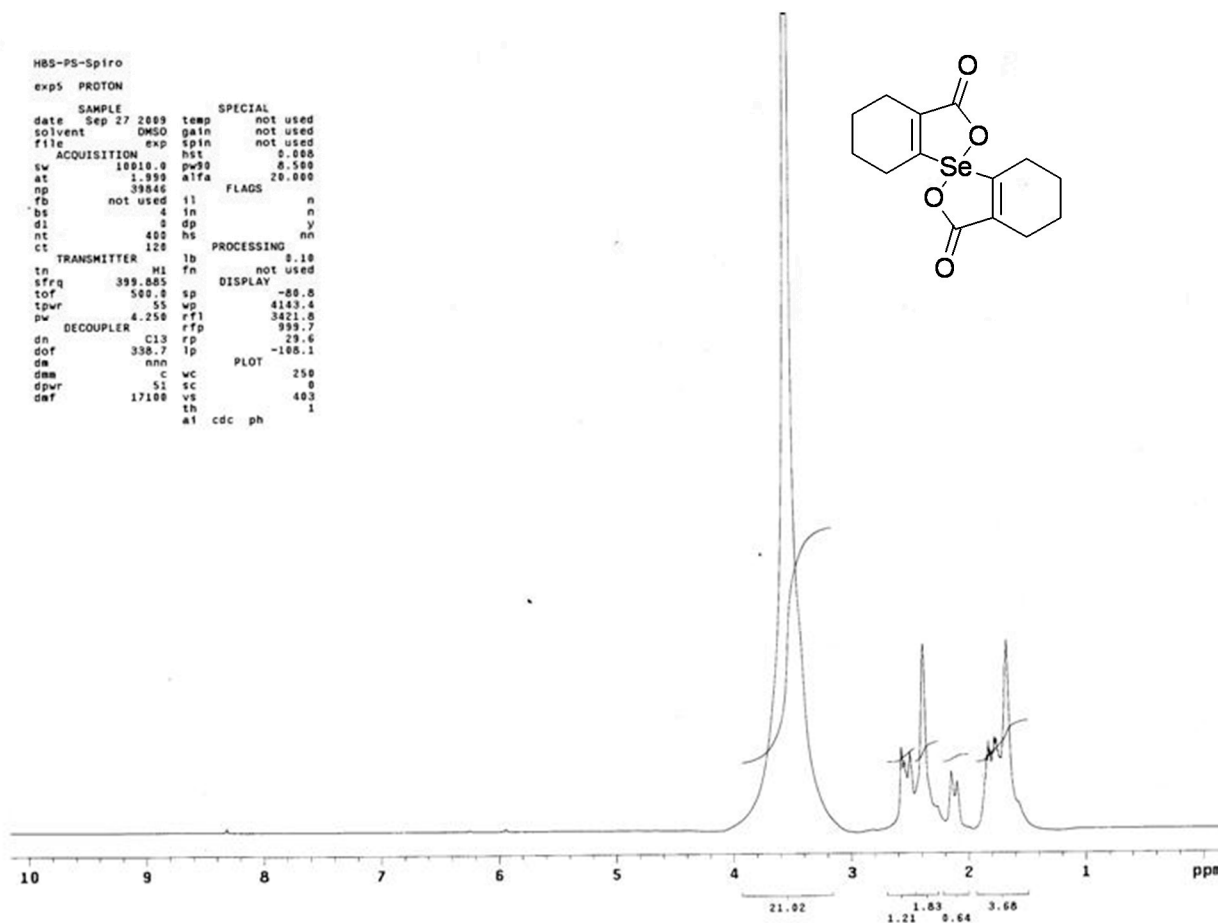
Company Name : C.E. Instruments
 Printed : 11/6/2009 13:10
 Instrument N. : Instrument #1
 Sample weight : .654

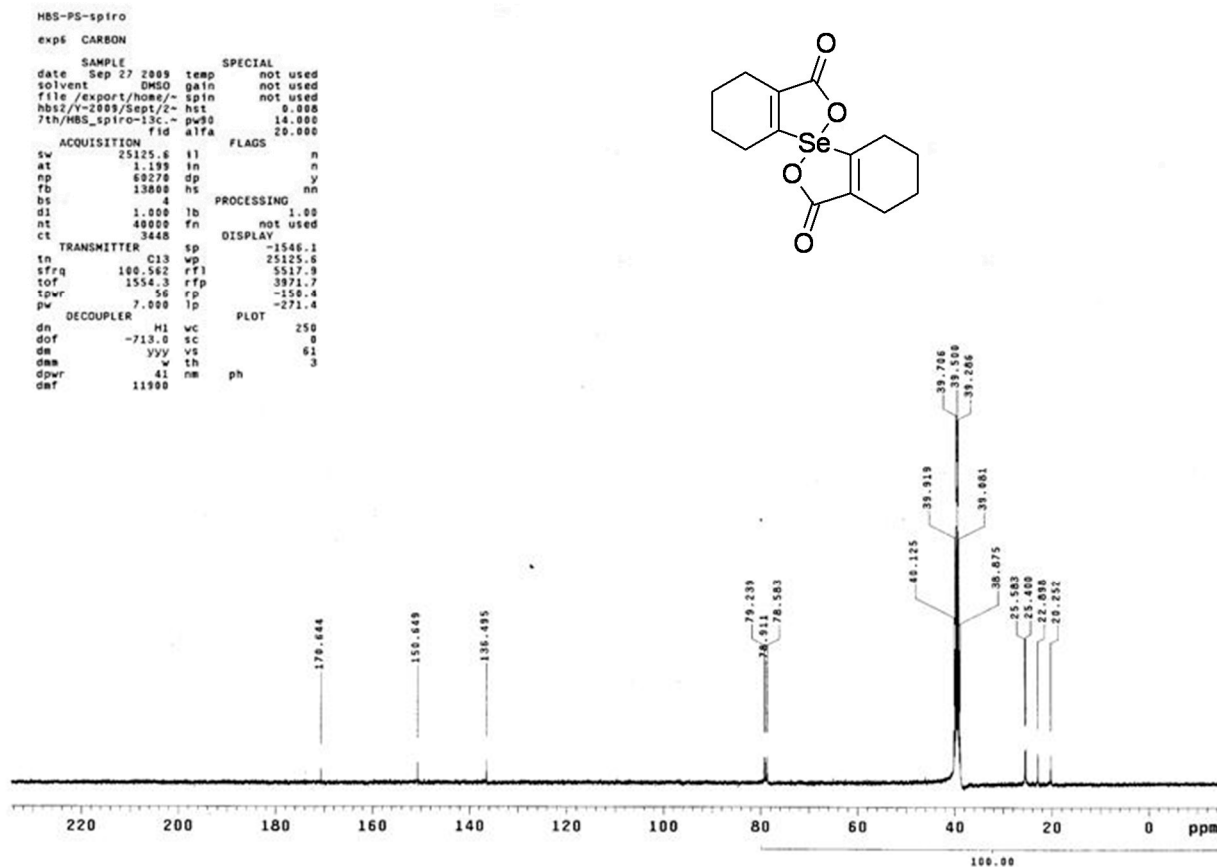
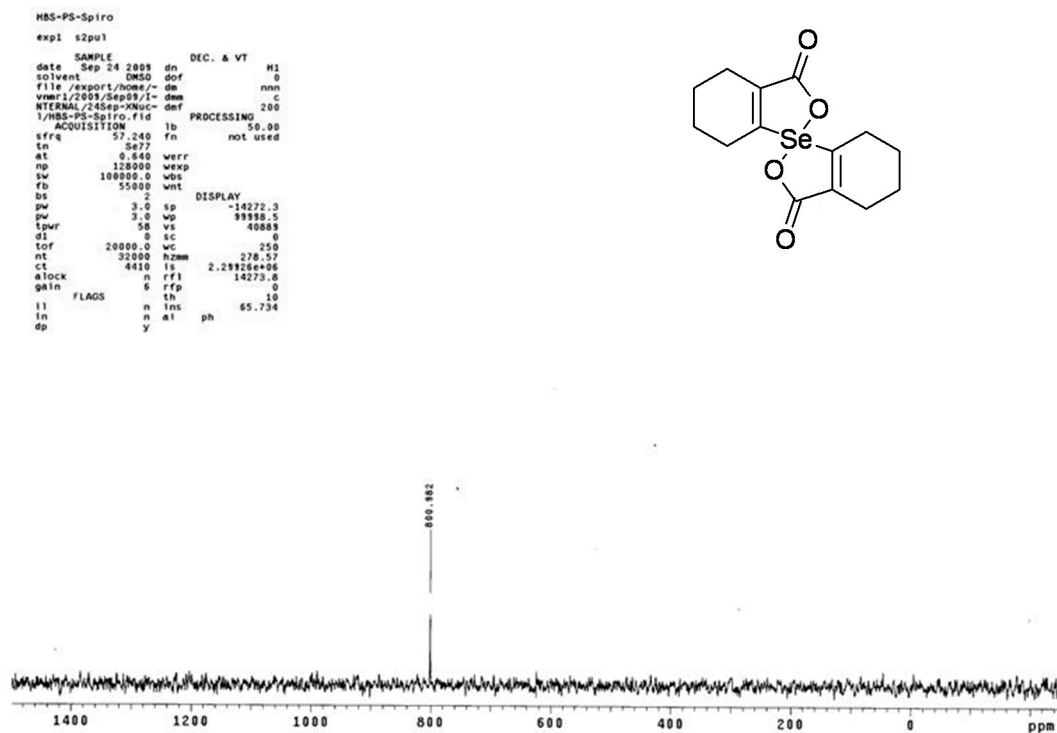
Calib. method : using 'K Factors'

!!! Warning missing one or more peaks.

Element Name	%	Ret.Time	Area	BC	Area ratio	K factor
Carbon	55.81	56.1831	67	909526 RS	1.000000	.246719E+07
Hydrogen	7.36	6.9764	175	247576 RS	3.673724	.525645E+07
Totals		63.1596		1157102		

Figure S6. Elemental analysis (CHN) of 19.

Figure S7. ¹H-NMR spectrum of 20 (CDCl₃).

Figure S8. ¹³C-NMR spectrum of **20** (CDCl₃).Figure S9. ⁷⁷Se-NMR spectrum of **20** (CDCl₃).

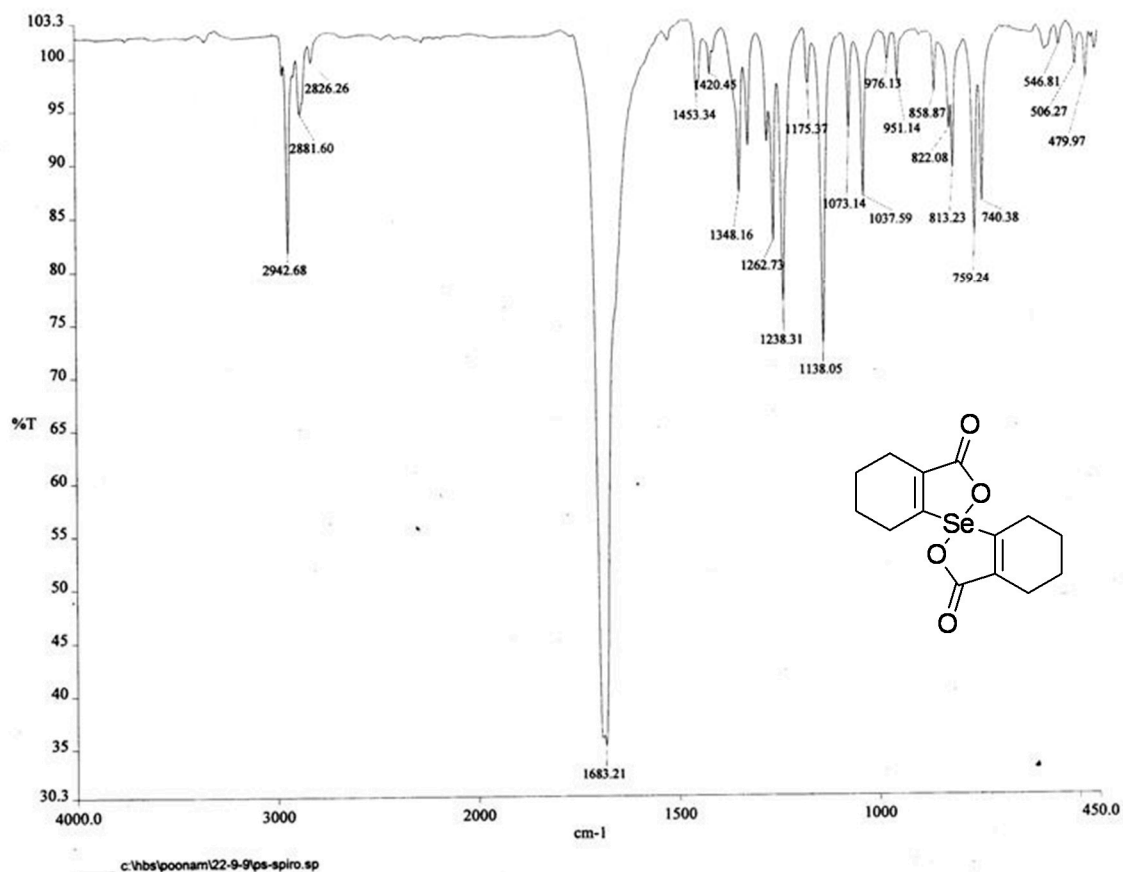


Figure S10. FT-IR spectrum of 20.

Elemental Composition Report

Single Mass Analysis (displaying only valid results)

Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0

Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron Ions

9 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)

Micromass : Q-ToF micro (YA-105)

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05-Aug-2010 15:19:45

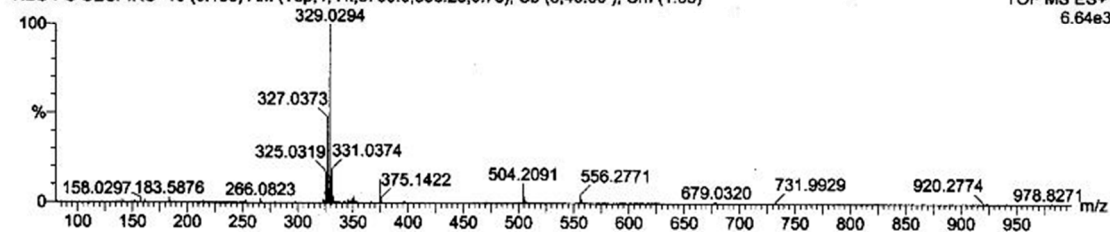
C₁₄H₁₆O₄Se

HBS-PS-SESPIRO 10 (0.186) AM (Top, 4, Ht, 5700.0, 556.28, 0.76); Sb (5, 40.00); Cm (1, 33)

Ionisation Mode

TOF MS ES+

6.64e3



Minimum:

Maximum:

200.0

10.0

-1.5

50.0

Mass

Calc. Mass

mDa

PPM

DBE

Score

Formula

329.0294

329.0292

0.2

0.7

7.5

1

C₁₄ H₁₇ O₄ Se

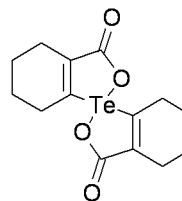
Figure S11. HRMS spectrum of 20.

Eager 300 Report

Page: 1 Sample: TE-SPIRO (TE-SPIRO)

Method Name : SP280110
 Method File : D:\CHNS2008\SP280110.mth
 Chromatogram : TE-SPIRO
 Operator ID : MP
 Analysed : 01/28/2010 12:32
 Sample ID : TE-SPIRO (# 12)
 Analysis Type : UnkNown (Area)

Company Name : C.E. Instruments
 Printed : 1/28/2010 14:59
 Instrument N. : Instrument #1
 Sample weight : 1.078

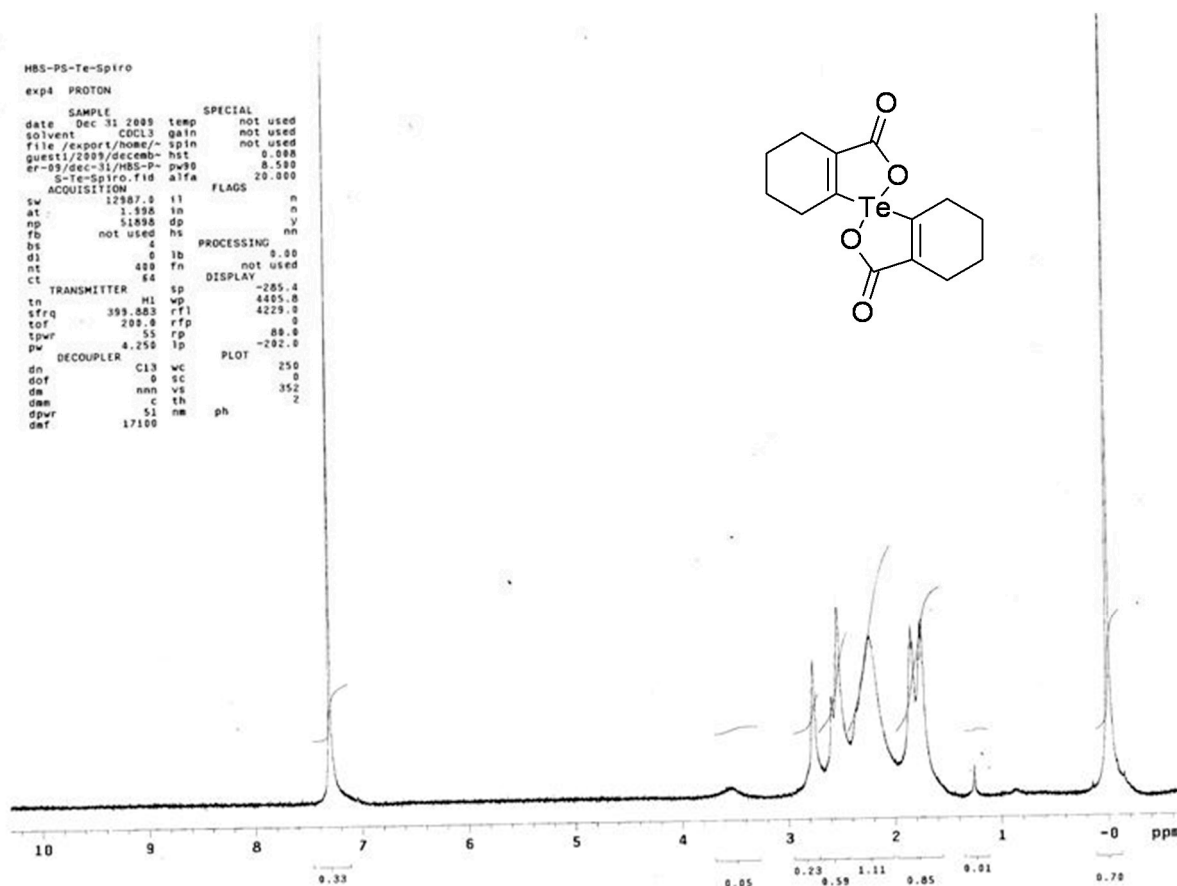


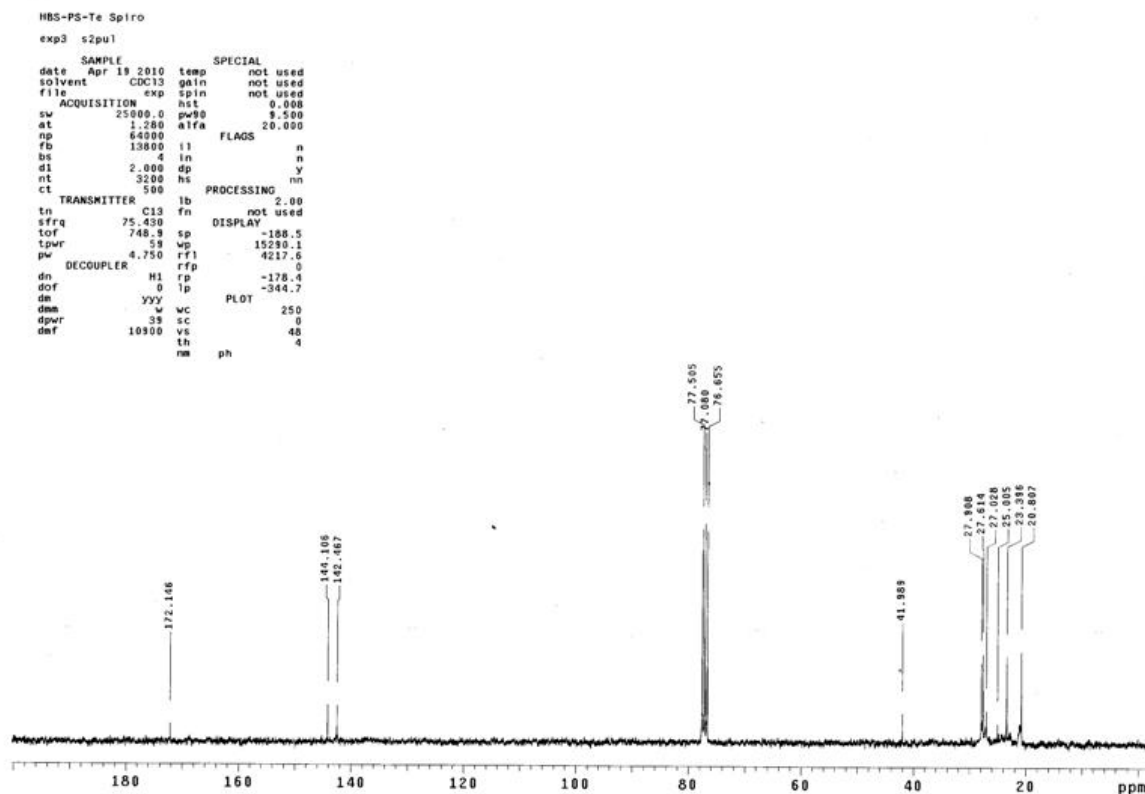
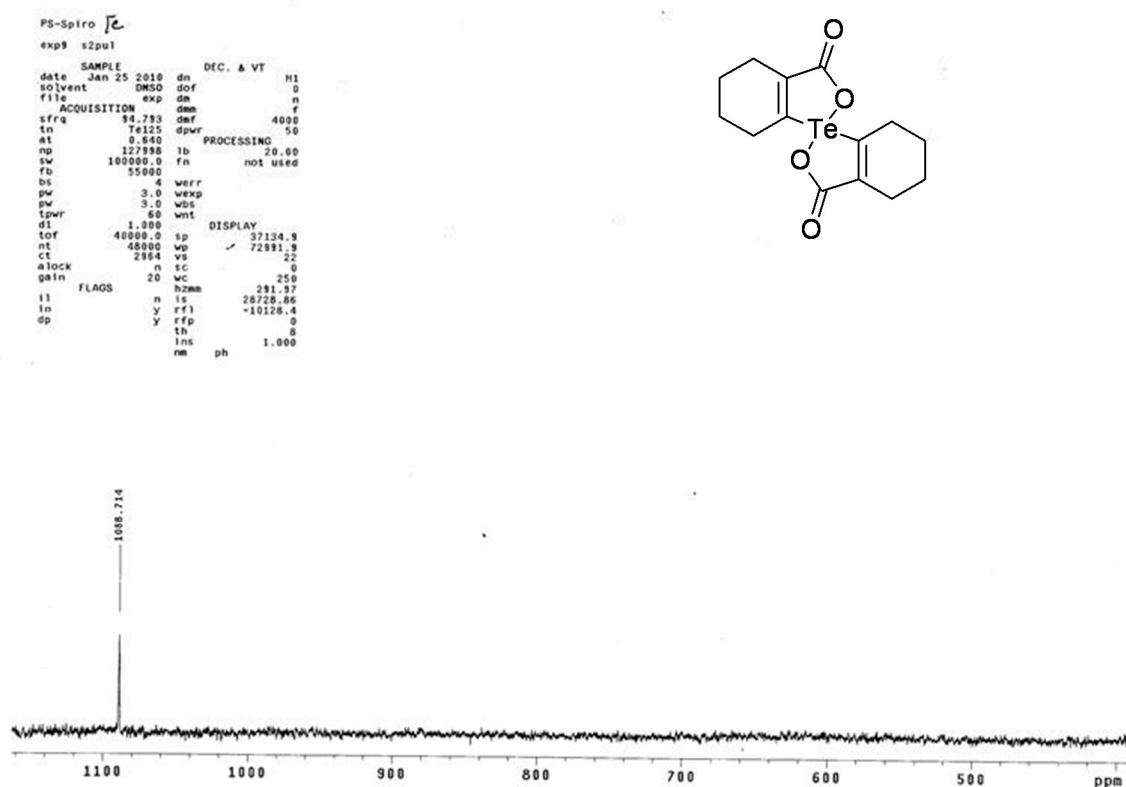
Calib. method : using 'K Factors'

!!! Warning missing one or more peaks.

Element Name	%	Ret.Time	Area	BC	Area ratio	K factor
Carbon	44.74	45.0227	67	1198946 RS	1.000000	.246135E+07
Hydrogen	4.29	5.3807	172	325334 RS	3.685276	.540442E+07
Totals		50.4034		1524280		

Figure S12. Elemental analysis (CHN) of 20.

Figure S13. ¹H-NMR spectrum of 21 (CDCl₃).

Figure S14. ^{13}C -NMR spectrum of **21** (CDCl_3).Figure S15. ^{125}Te -NMR spectrum of **21** (CDCl_3).

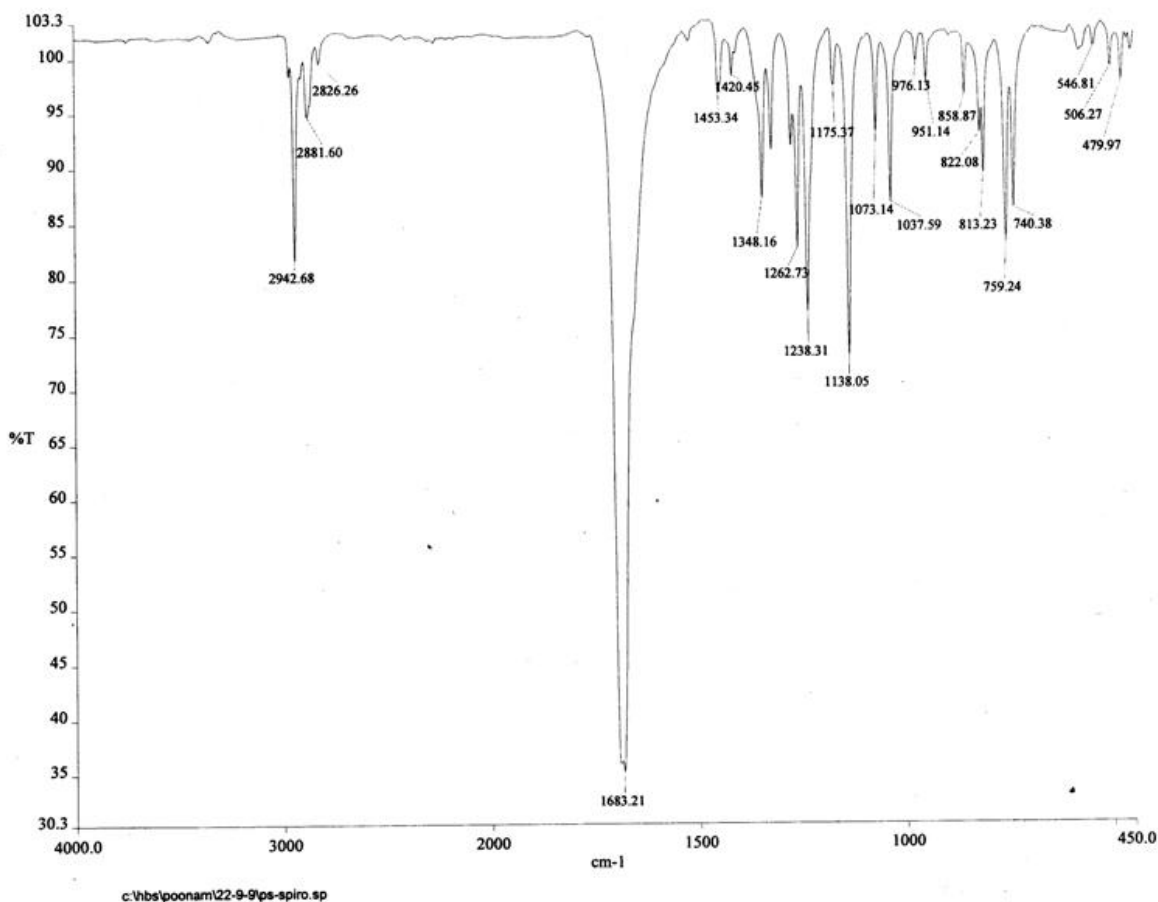


Figure S16. FT-IR spectrum of 21.

Elemental Composition Report

Single Mass Analysis (displaying only valid results)

Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0

Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron Ions

19 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)

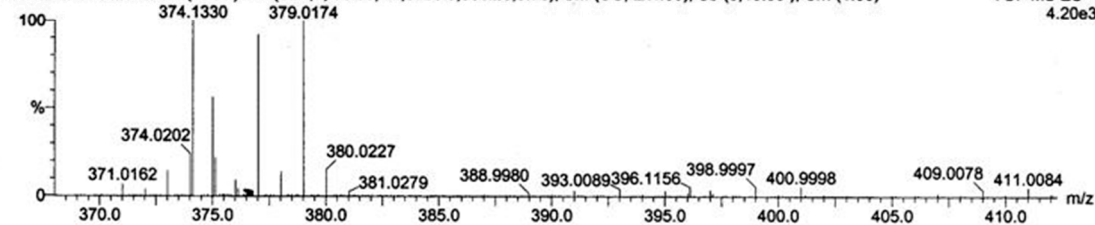
Micromass : Q-ToF micro (YA-105)

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05-Aug-201015:39:39

C₁₄H₁₆O₄Te

HBS-PS-TESPIRO 29 (0.537) AM (Cen,4, 80.00, Ht,5700.0,556.28,0.76); Sm (SG, 2x4.00); Sb (5,40.00); Cm (1:56)

Ionisation Mode
TOF MS ES+
4.20e3

Minimum:

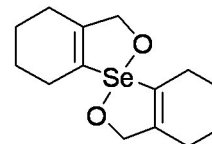
Maximum:

200.0 10.0 -1.5

Mass	Calc. Mass	mDa	PPM	DBE	Score	Formula
379.0174	379.0189	-1.5	-3.9	6.5	1	C ₁₄ H ₁₇ O ₄ Te

Figure S17. HRMS spectrum of 21.

Eager 300 Report

Page: 1 Sample: HBSPSCHALC (HBSPSCHALC) H₂O₂

Method Name : SP040610
 Method File : D:\CHNS2008\SP040610.mth
 Chromatogram : HBSPSCHALC
 Operator ID : SP
 Analysed : 06/04/2010 13:49
 Sample ID : HBSPSCHALC (# 16)
 Analysis Type : UnkNown (Area)

Company Name : C.E. Instruments
 Printed : 6/4/2010 15:45
 Instrument N. : Instrument #1
 Sample weight : .682

Calib. method : using 'K Factors'

!!! Warning missing one or more peaks.

Element Name	%	Ret.Time	Area	BC	Area ratio	K factor
Carbon	54.4053	67	1003864	RS	1.000000	.268468E+07
Hydrogen	7.1917	169	445628	RS	2.252695	.687010E+07
Totals	61.5970		1449492			

Figure S18. Elemental analysis (CHN) of 21.

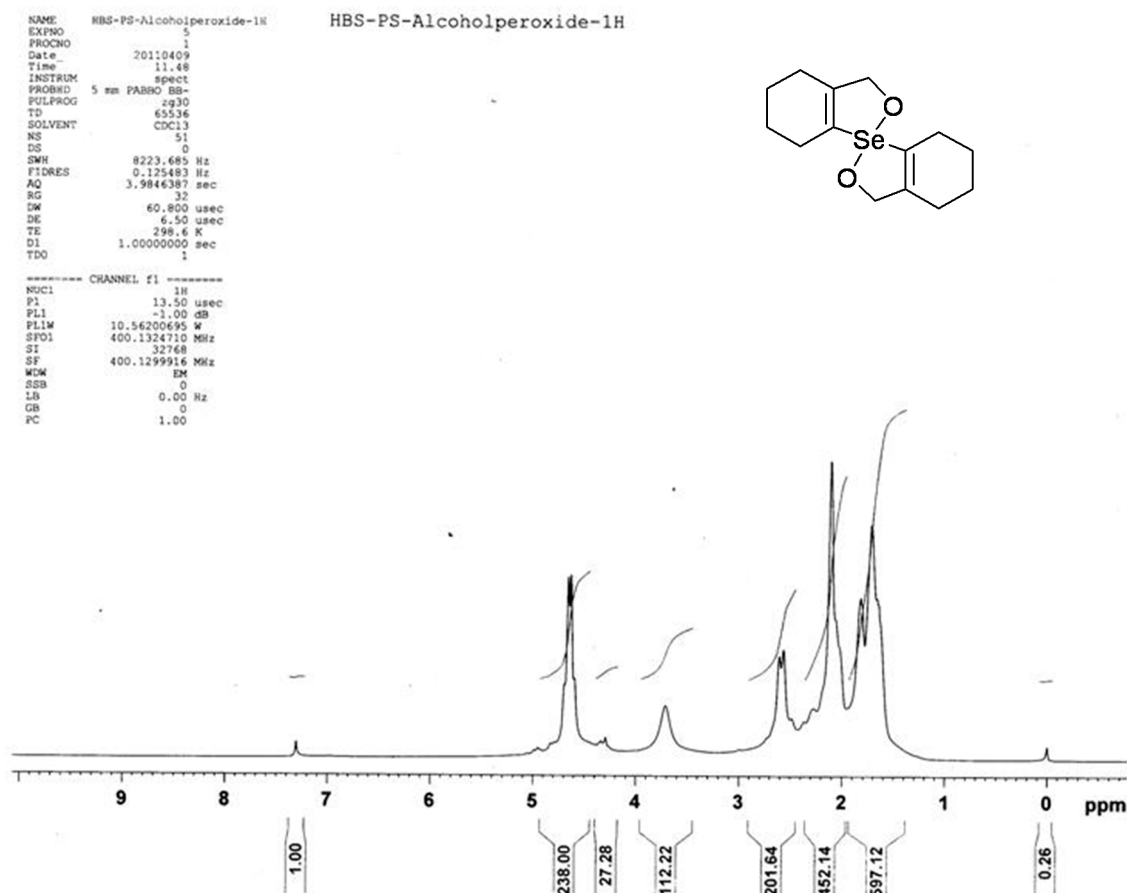


Figure S19. Cont.

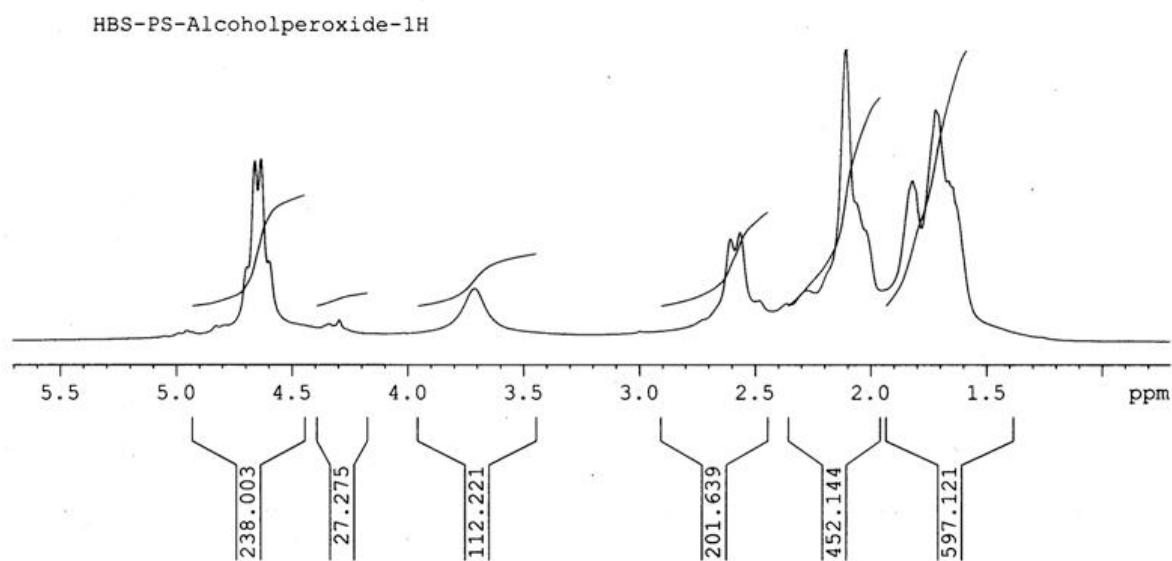


Figure S19. ^1H -NMR spectrum of **22** (CDCl_3).

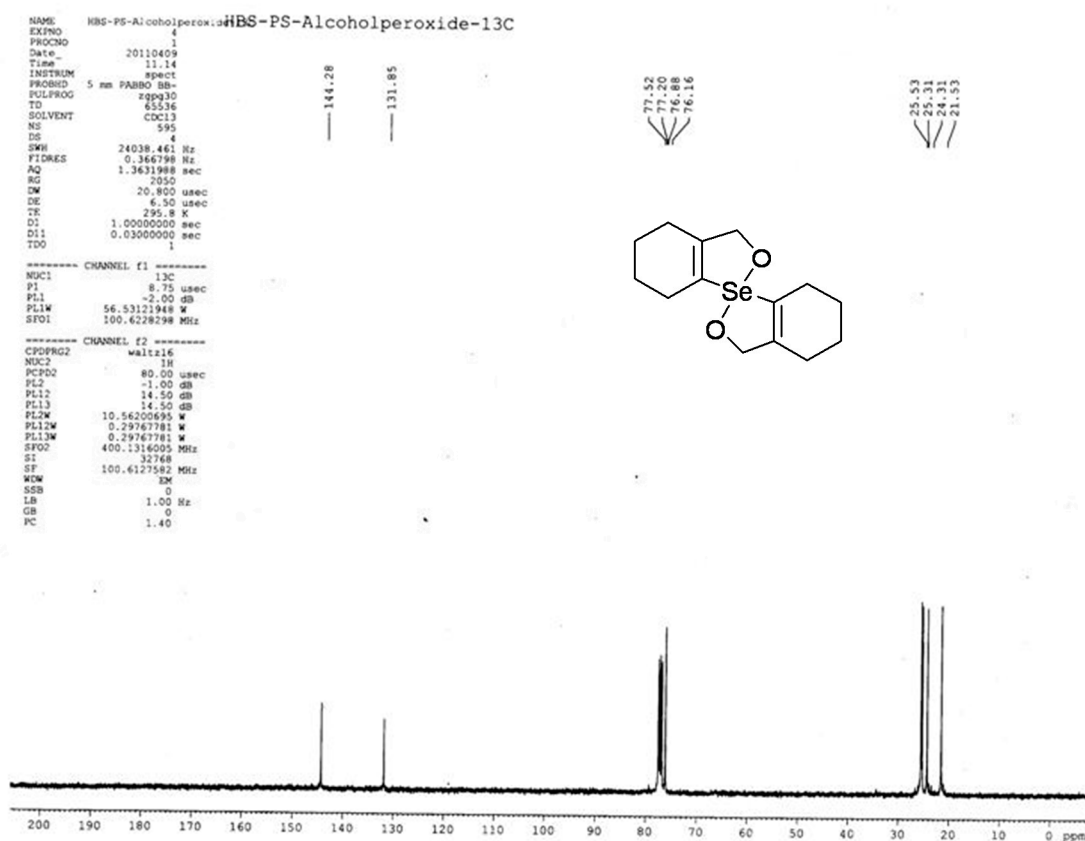
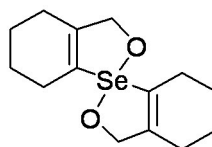


Figure S20. ^{13}C -NMR spectrum of **22** (CDCl_3).

HBS-PS-Alcoholperoxide-Se77



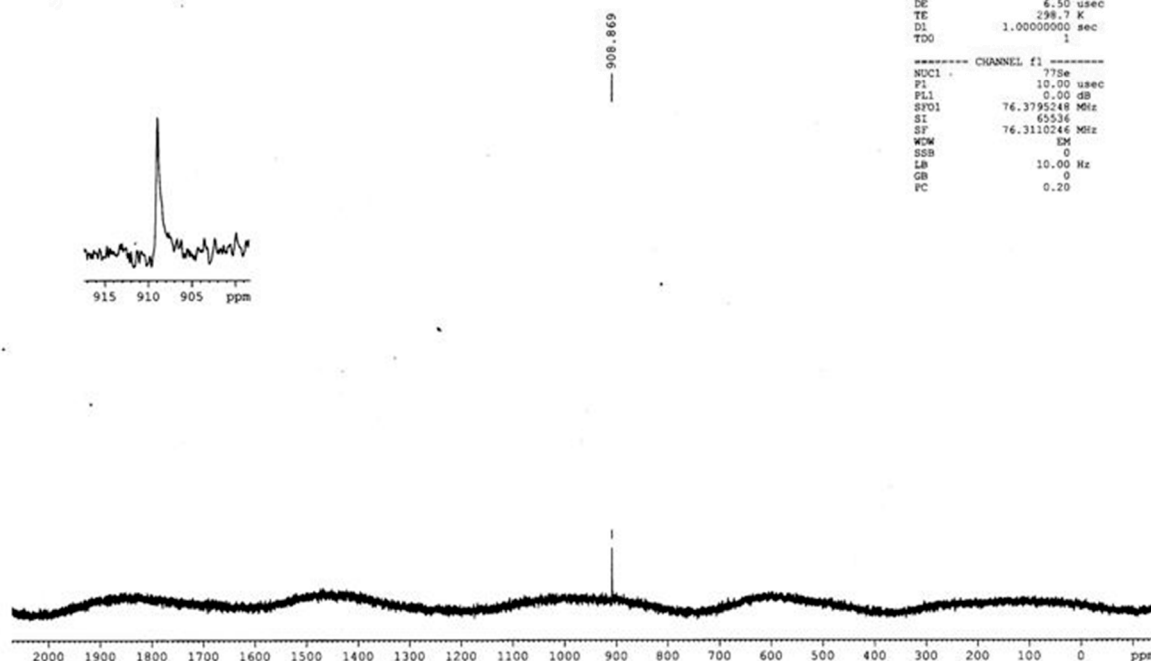
```

NAME      HBS-PS-Alcoholperoxide-Se77
EXPNO     2
PROCNO    2
Date_     20110409
Time      11.52
INSTRUM   spect
PROBHD    5 mm PABBO BB-
PULPROG   zg
TD         66540
SOLVENT   CDCl3
NS         261
DS         4
SWH        288461.531 Hz
FIDRES     4.333857 Hz
AQ         0.1154207 sec
RG         90.5
RW         1.733 usec
DE         6.50 usec
TE         298.7 K
D1         1.00000000 sec
TD0        1
  
```

----- CHANNEL f1 -----

```

NUC1       77Se
P1         10.00 usec
PL1        0.00 dB
SFO1       76.3795248 MHz
SI         65536
SF         76.3110246 MHz
WDW        EM
SSB        0
LB         10.00 Hz
GB         0
PC         0.20
  
```

Figure S21. ^{77}Se -NMR spectrum of **22** (CDCl_3).

Elemental Composition Report

Single Mass Analysis (displaying only valid results)

Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0

Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron Ions

49 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

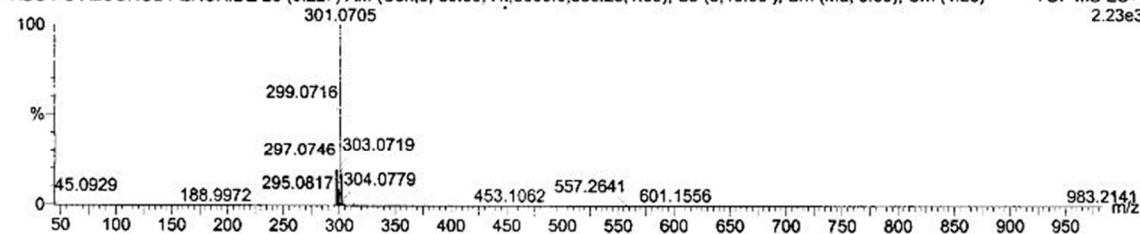
Micromass : Q-ToF micro (YA-105)

Dept. Of Chemistry I.I.T.(B)

27-May-201111:49:37

C₁₄H₂₀O₂Se

HBS-PS-ALCOHOL PEROXIDE 23 (0.227) AM (Cen,5, 80.00, Ht,5000.0,556.28,1.00); Sb (5,40.00); Sm (Md, 6.00); Cm (4:28)

TOF MS ES+
2.23e3

Minimum: -1.5
Maximum: 200.0 10.0 50.0

Mass	Calc. Mass	mDa	PPM	DBE	Score	Formula
301.0705	301.0707	-0.2	-0.7	5.5	1	C ₁₄ H ₂₁ O ₂ Se

Figure S22. HRMS spectrum of **22**.

Catalytic mechanism of di-(2-formylcyclohexenyl)diselenide **16** by ^{77}Se -NMR spectroscopy

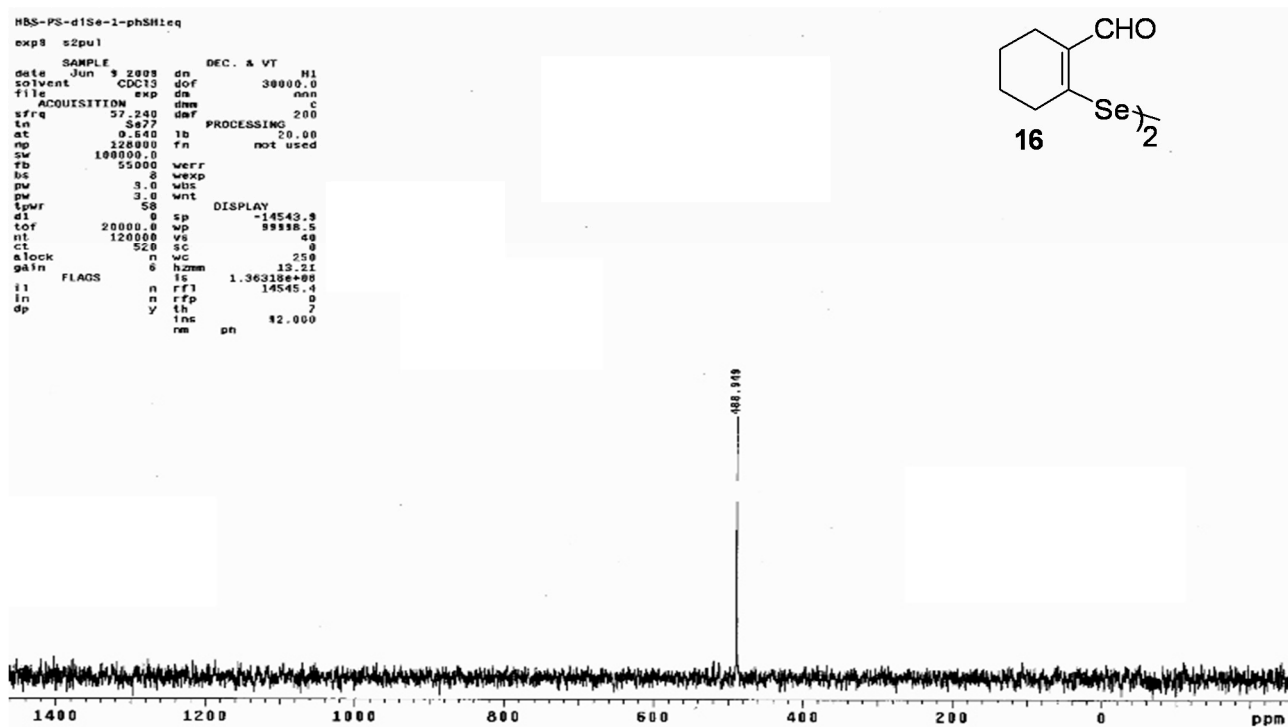


Figure S23. ^{77}Se -NMR spectrum of di-(2-formylcyclohexenyl)diselenide **16** + 1PhSH.

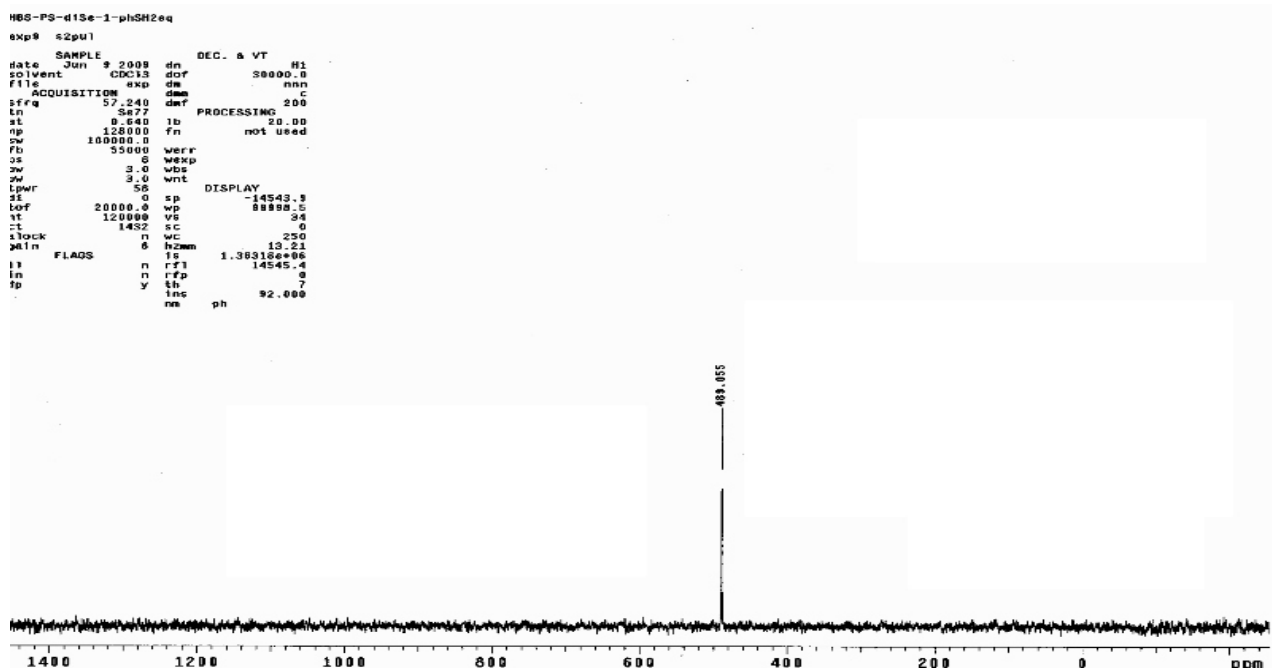


Figure S24. ^{77}Se -NMR spectrum of di-(2-formylcyclohexenyl)diselenide **16** + 2PhSH.

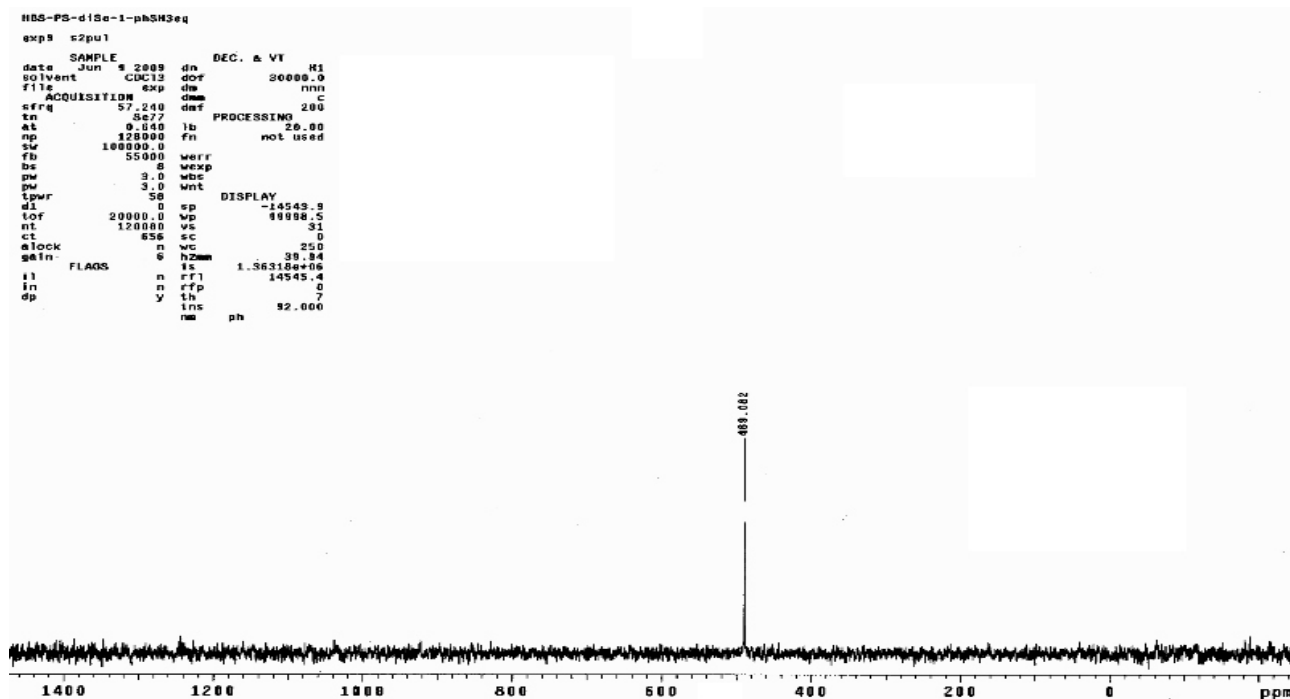


Figure S25. ^{77}Se -NMR spectrum of di-(2-formylcyclohexenyl)diselenide **16** + 3PhSH.

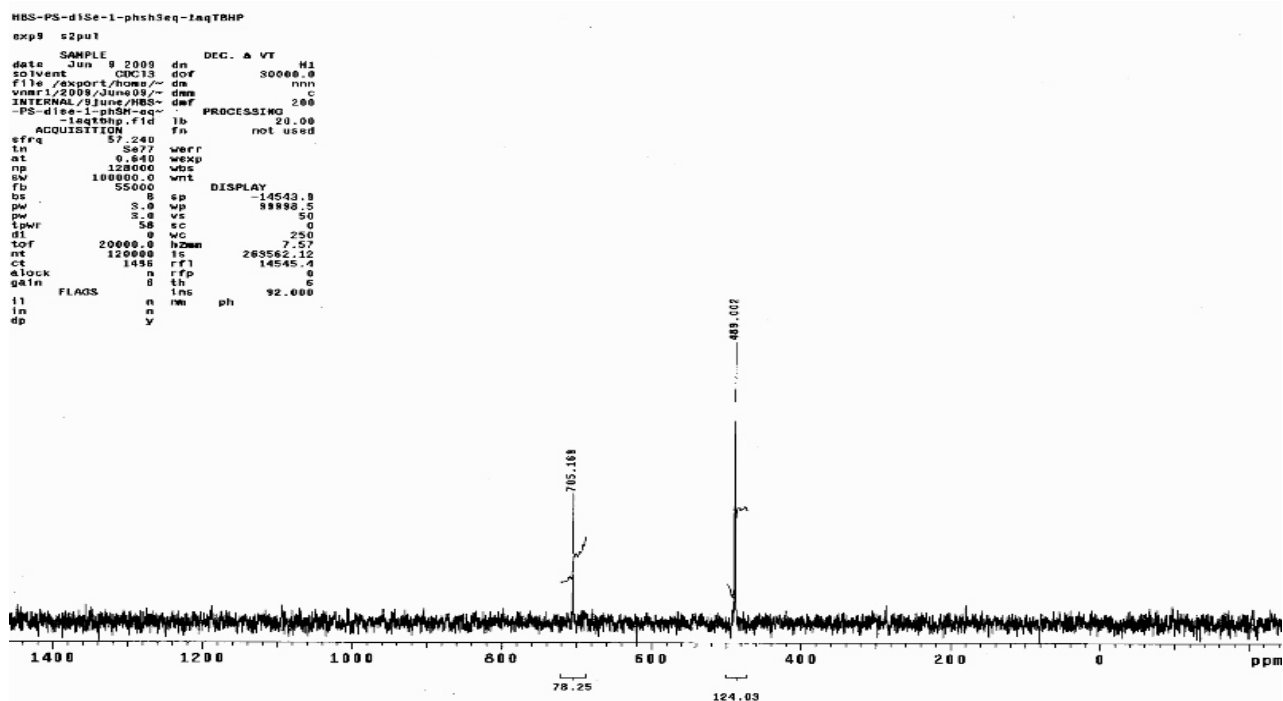


Figure S26. ^{77}Se -NMR spectrum of di-(2-formylcyclohexenyl)diselenide **16** + 2PhSH + 1TBHP.

```

HBS-PS-d1Se-1-phsh12eq-3eqTBHP
exp8 s2pul
SAMPLE          DEC. & VT
date Jun 8 2008 dn H1
solvent CDCl3 dof 30000.0
file exp dm nnn
ACQUISITION    dnm 200
sfrq 57.240
tn Se77 PROCESSING 20.00
at 0.640 lb
np 128000 fn not used
sw 100000.0
fb 55000 werr
bs 8 wexp
pw 3.0 wbs
tpwr 58
d1 0 sp DISPLAY
tor 20000.0 wp -14543.8
nt 128000 vs 99998.5
ct 200 sc 0
atock n wc 250
gain 8 h2mm 8.05
FLAGS n rfl 263562.12
il n rfp 14545.4
in n rfp 0
dp y th 12
ns ins 82.000
ph

```

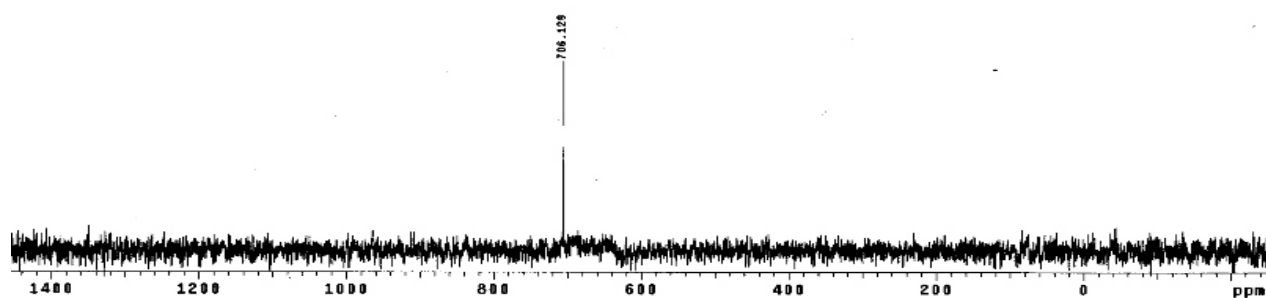


Figure S27. ^{77}Se -NMR spectrum of di-(2-formylcyclohexenyl)diselenide **16** + 2PhSH + 2TBHP.

```

HBS-PS-d1Se-1-phshSeq-3eqTBHP
exp8 s2pul
SAMPLE          DEC. & VT
date Jun 8 2008 dn H1
solvent CDCl3 dof 30000.0
file exp dm nnn
ACQUISITION    dnm 200
sfrq 57.240
tn Se77 PROCESSING 20.00
at 0.640 lb
np 128000 fn not used
sw 100000.0
fb 55000 werr
bs 8 wexp
pw 3.0 wbs
tpwr 58
d1 0 sp DISPLAY
tor 20000.0 wp -14543.8
nt 128000 vs 99998.5
ct 200 sc 0
atock n wc 250
gain 8 h2mm 7.57
FLAGS n rfl 263562.12
il n rfp 14545.4
in n rfp 0
dp y th 12
ns ins 82.000
ph

```

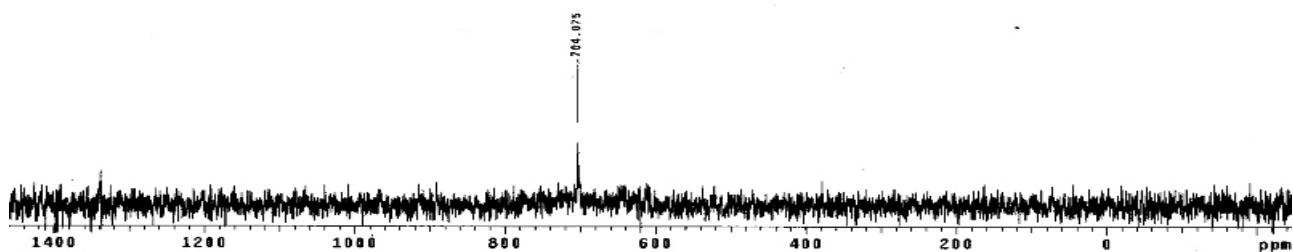
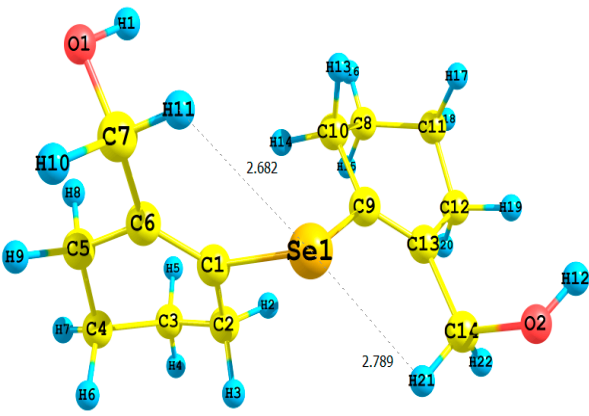


Figure S28. ^{77}Se -NMR spectrum of di-(2-formylcyclohexenyl)diselenide **16** + 2PhSH + 3TBHP.

DFT Calculations and NBO Analysis (in Gas Phase):

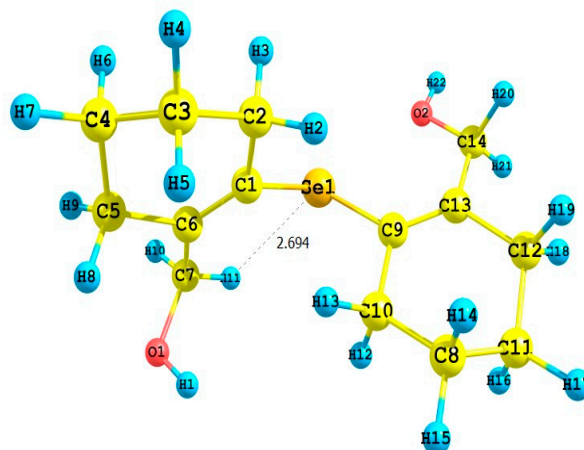
Table S1. Optimized geometries of 19 (19a anti-anti; 19b syn-anti) computed at rb3lyp/6-31+g(d) and NBO at rb3lyp/6-31+g(d).



(19a)

	Electronic Energy = -3096.59172317 a.u.		
34	-0.101100000	-1.150920000	-0.550060000
8	3.387008000	0.785287000	-2.475203000
1	2.742266000	1.510171000	-2.450220000
6	1.444640000	-0.330621000	0.312617000
6	1.266934000	-0.094612000	1.796714000
1	0.316572000	0.428109000	1.970251000
1	1.151520000	-1.070446000	2.292775000
6	2.430693000	0.683191000	2.428217000
1	2.368624000	0.615749000	3.521787000
1	2.347338000	1.749280000	2.170629000
6	3.769387000	0.144086000	1.916149000
1	3.853437000	-0.920794000	2.178155000
1	4.609915000	0.656963000	2.400345000
6	3.863165000	0.308115000	0.394486000
1	4.078572000	1.356119000	0.141493000
1	4.716353000	-0.260613000	-0.001424000
6	2.606392000	-0.132396000	-0.344089000
6	2.799521000	-0.355051000	-1.827333000
1	3.519375000	-1.164339000	-1.997770000
1	1.855817000	-0.630488000	-2.308576000
1	-4.393254000	-1.900314000	-0.438502000
1	-1.035408000	1.595676000	-1.753954000
1	-0.047196000	1.851585000	-0.335227000
6	-2.050123000	2.684989000	-0.166292000
1	-1.860810000	2.903418000	0.894752000
1	-1.878959000	3.618234000	-0.717509000
1	-3.683181000	1.990602000	-1.395693000
1	-4.205688000	2.986960000	-0.036840000
8	-3.580891000	-2.321800000	-0.116466000
6	-1.428436000	0.221387000	-0.168544000

6	-1.069576000	1.608061000	-0.653557000
6	-3.495107000	2.205529000	-0.333877000
6	-3.732565000	0.936838000	0.493816000
1	-4.690781000	0.478047000	0.203859000
1	-3.850632000	1.199220000	1.558145000
6	-2.621803000	-0.097251000	0.371290000
6	-2.979378000	-1.477049000	0.879668000
1	-2.089813000	-2.019915000	1.201572000
1	-3.658069000	-1.381152000	1.741764000



(19b)

Electronic Energy = -3096.58402319 a.u.

34	-0.141084000	-1.157729000	-0.594348000
8	3.195890000	1.101337000	-2.434587000
1	2.516965000	1.782793000	-2.305811000
6	1.399219000	-0.346131000	0.280559000
6	1.261926000	-0.254489000	1.785961000
1	0.303816000	0.221769000	2.035914000
1	1.182628000	-1.275514000	2.188654000
6	2.424125000	0.490559000	2.457965000
1	2.394162000	0.321209000	3.541976000
1	2.310905000	1.573822000	2.302636000
6	3.759733000	0.034268000	1.863618000
1	3.873324000	-1.048264000	2.021917000
1	4.602583000	0.519366000	2.372193000
6	3.806876000	0.341584000	0.361981000
1	3.992248000	1.413908000	0.203975000
1	4.662135000	-0.166299000	-0.106272000
6	2.539763000	-0.058836000	-0.381820000
6	2.694546000	-0.129898000	-1.883856000
1	3.452290000	-0.874920000	-2.153825000
1	1.751023000	-0.411780000	-2.361353000
1	-0.864674000	1.752189000	-1.447885000
1	-0.005287000	1.727395000	0.070109000
6	-1.946287000	2.683580000	0.187753000
1	-1.855454000	2.729125000	1.282945000

1	-1.647177000	3.667183000	-0.196697000
1	-3.488082000	2.329598000	-1.280678000
1	-4.077893000	3.140128000	0.171901000
8	-2.566768000	-2.554805000	0.082843000
6	-1.490564000	0.185206000	-0.145933000
6	-1.004129000	1.607186000	-0.364808000
6	-3.392576000	2.361259000	-0.185787000
6	-3.793738000	1.005370000	0.402603000
1	-4.758386000	0.690142000	-0.021022000
1	-3.970582000	1.114197000	1.485600000
6	-2.764893000	-0.103314000	0.184190000
6	-3.408131000	-1.455632000	0.399141000
1	-3.735752000	-1.514492000	1.452961000
1	-4.323236000	-1.489863000	-0.215895000
1	-3.066882000	-3.375440000	0.211061000

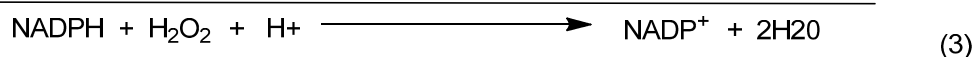
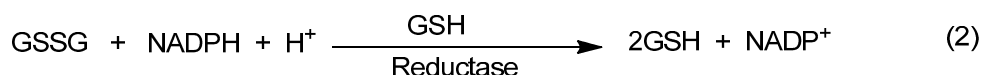
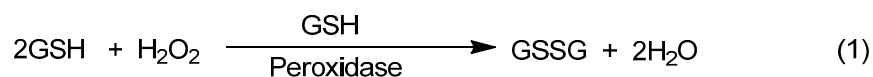
Second Order Perturbation Theory Analysis of Fock Matrix in NBO Basis for 19a

Donor NBO (i) Acceptor NBO (j) kcal/mol a.u. a.u.

74. LP (2)Se 1	/362. BD*(1) C 18 – H 20	2.49	0.65	0.037
74. LP (2)Se 1	/373. BD*(1) C 30 – C 31	2.06	0.62	0.033
74. LP (2)Se 1	/374. BD*(1) C 30 – C 36	2.12	0.87	0.039
74. LP (2)Se 1	/375. BD*(2) C 30 – C 36	5.82	0.26	0.035
74. LP (2)Se 1	/381. BD*(1) C 37 – H 38	1.40	0.65	0.028

Coupled Reductase Assay

The GPx-like activities of 16–20 were measured by JASCO spectrophotometer according to the literature method using ebselen as the standard. The catalytic reaction was carried out at room temperature (25 °C) in 1 mL of the solution containing 100 mM potassium phosphate buffer, pH 7.5, pH 7.48, with EDTA (1 mM), NADPH (0.01 M), GSH (0.05 M), catalysts (0.002 M), H₂O₂ (0.026 M), GR (1.3 unit). The activity was followed by the decrease of NADPH on addition of H₂O₂ and absorption was measured at 340 nm ($\epsilon_{\text{max}} = 6.22 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$) (Equations (1)–(3)). Each of the experiments was carried out in triplicate.



For Control	Volume (μL)	For Sample	Volume (μL)
Buffer solution	940	Buffer solution	930
GSH	20	GSH	20
NADPH	25	NADPH	25
GR	5	GR	5
H ₂ O ₂	10	catalyst	10
		H ₂ O ₂	10

Total volume of the solution was taken 1 mL.

Table S2. Glutathione peroxides like activity of compound **control**.

S.N.	ΔA	Initial Reaction Rates ($\mu\text{M min}^{-1}$)
1	0.01790	8.63
2	0.02369	11.43
3	0.02369	11.43

Table S3. Glutathione peroxides like activity of compound **Ebselen**.

S.N.	ΔA	Initial Reaction Rates ($\mu\text{M min}^{-1}$)
1	0.05516	26.60
2	0.05545	26.74
3	0.6249	30.13

Table S4. Glutathione peroxides like activity of compound bis(*o*-formylphenyl)diselenide.

S.N.	ΔA	Initial Reaction Rates ($\mu\text{M min}^{-1}$)
1	0.6664	32.14
2	0.07385	35.61
3	0.07308	32.24

Table S5. Glutathione peroxides like activity of compound **16**.

S.N.	ΔA	Initial Reaction Rates ($\mu\text{M min}^{-1}$)
1	0.0994	47.94
2	0.1056	50.92
3	0.1047	50.49

Table S6. Glutathione peroxides like activity of compound **17**.

S.N.	ΔA	Initial Reaction Rates ($\mu\text{M min}^{-1}$)
1	0.01902	9.17
2	0.02044	9.95
3	0.01863	8.98

Table S7. Glutathione peroxides like activity of compound **19**.

S.N.	ΔA	Initial Reaction Rates ($\mu\text{M min}^{-1}$)
1	0.01300	6.27
2	0.01339	6.45
3	0.01596	7.69

Table S8. Glutathione peroxides like activity of compound **20**.

S.N.	ΔA	Initial Reaction Rates ($\mu\text{M min}^{-1}$)
1	0.02781	13.41
2	0.03607	17.39
3	0.03792	18.28

Table S9. Glutathione peroxides like activity of compound **22**.

S.N.	ΔA	Initial Reaction Rates ($\mu\text{M min}^{-1}$)
1	0.01804	8.70
2	0.01716	8.27
3	0.01802	8.69