

Supporting Information

Synthesis, Structure and Bonding of 1-Oxa-6,6a λ^4 -Chalcogenopentalenes and Related Derivatives; Role of Intramolecular Coordination

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Dedicated to Professor Vladimir I. Minkin on the occasion of his 80th birthday

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S1. Spectral data for compounds 33-39

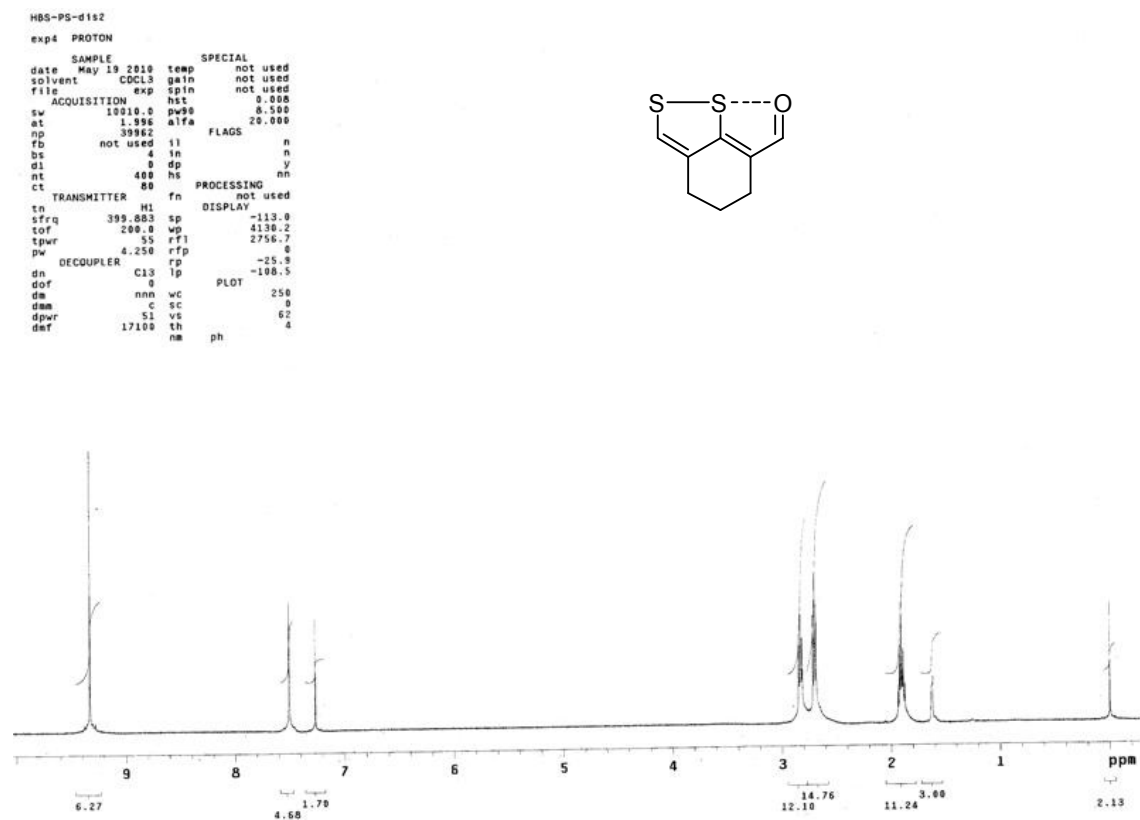


Figure S1. ^1H NMR spectrum of **33** (CDCl_3)

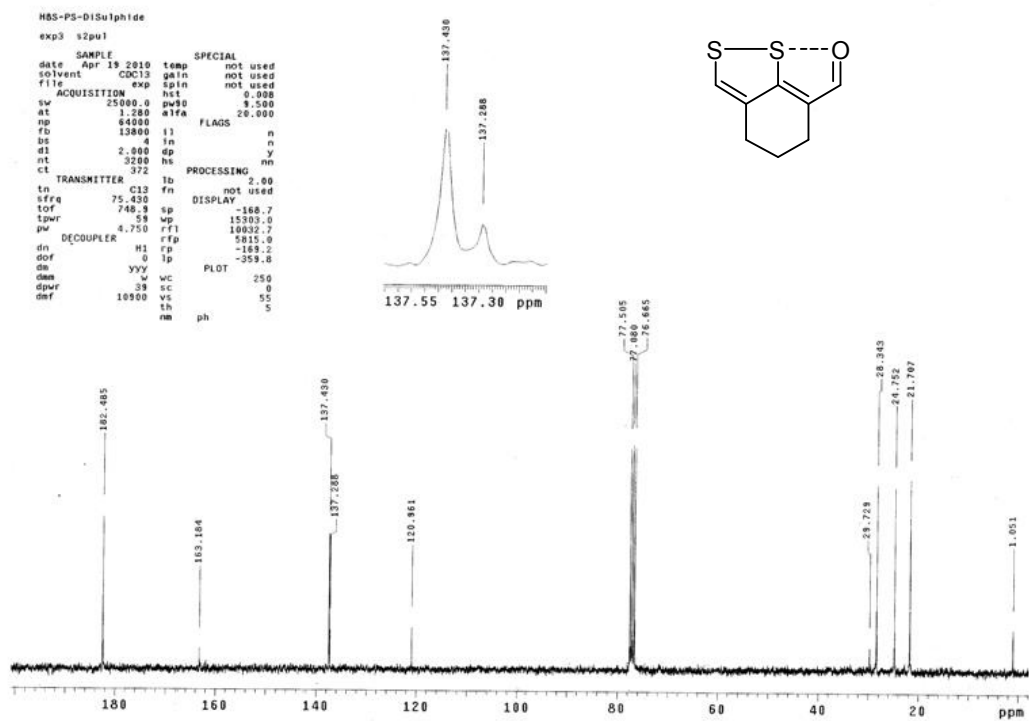


Figure S2. ^{13}C NMR spectrum of **33** (CDCl_3)

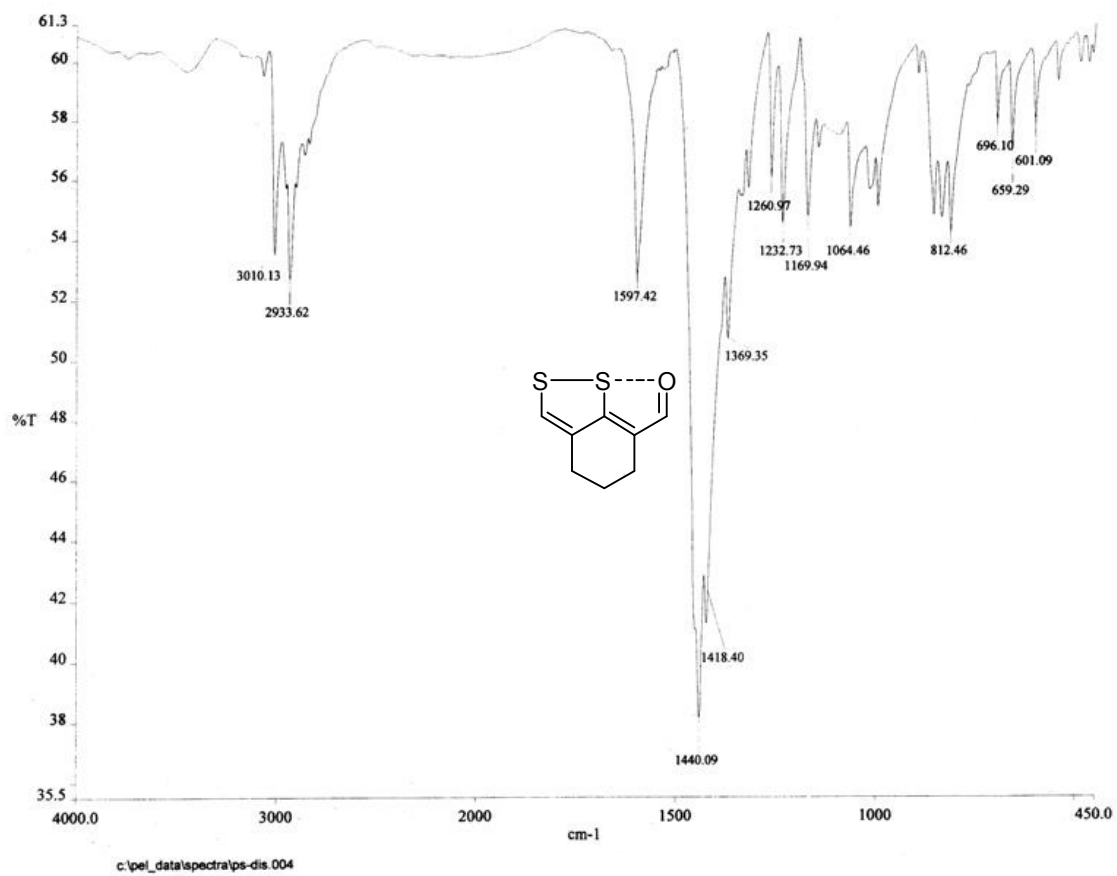


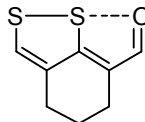
Figure S3. FT-IR spectrum of **33**

Elemental Composition Report

Single Mass Analysis

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

Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%



Page 1

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)

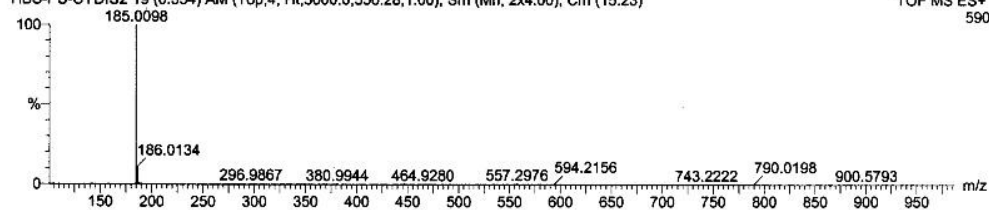
Department Of Chemistry I.I.T. (B)

27-Sep-2010 12:43:16

C8H8OS2

HBS-PS-CYDIS2 19 (0.354) AM (Top,4, Ht,5000.0,556.28,1.00); Sm (Mn, 2x4.00); Cm (15:23)

Ionisation Mode
TOF MS ES+
590



Minimum:

Maximum:

80.0

10.0

-1.5

50.0

Mass	Calc. Mass	mDa	PPM	DBE	Score	Formula
185.0098	185.0095	0.3	1.8	4.5	1	C8 H9 O S2

Figure S4. HRMS-ESI spectrum of 33

HBS-PS-CYDISE-1H

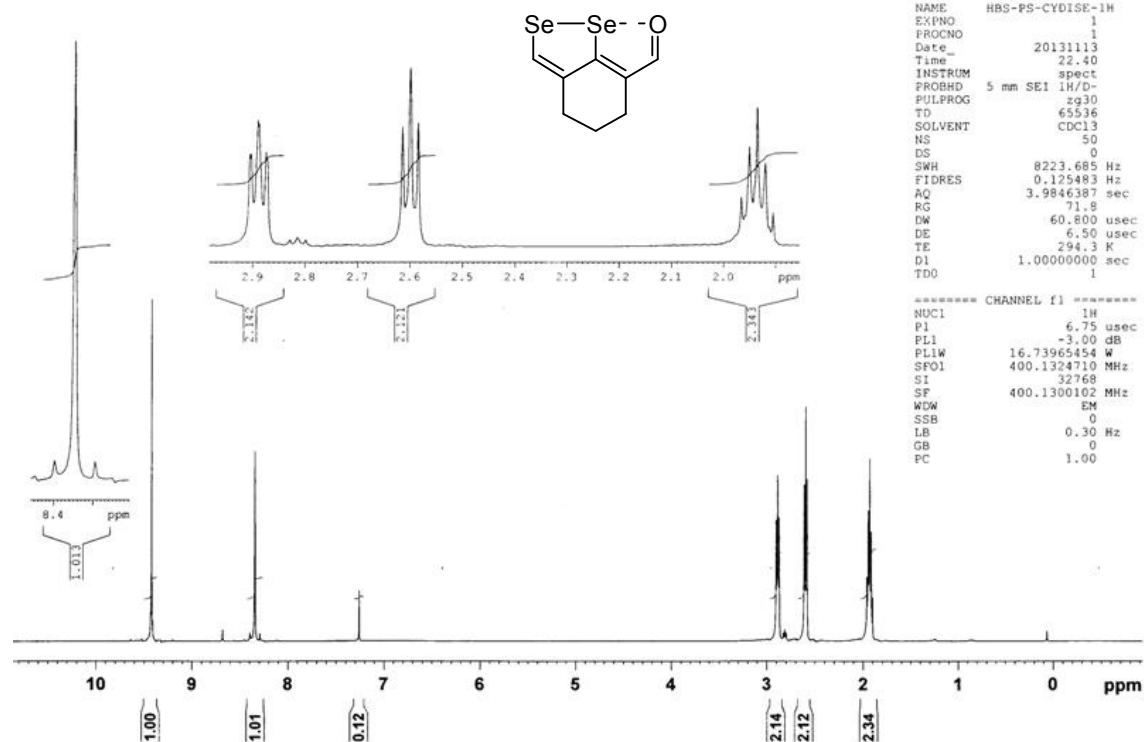


Figure S5. ¹H NMR spectrum of **34** (CDCl₃)

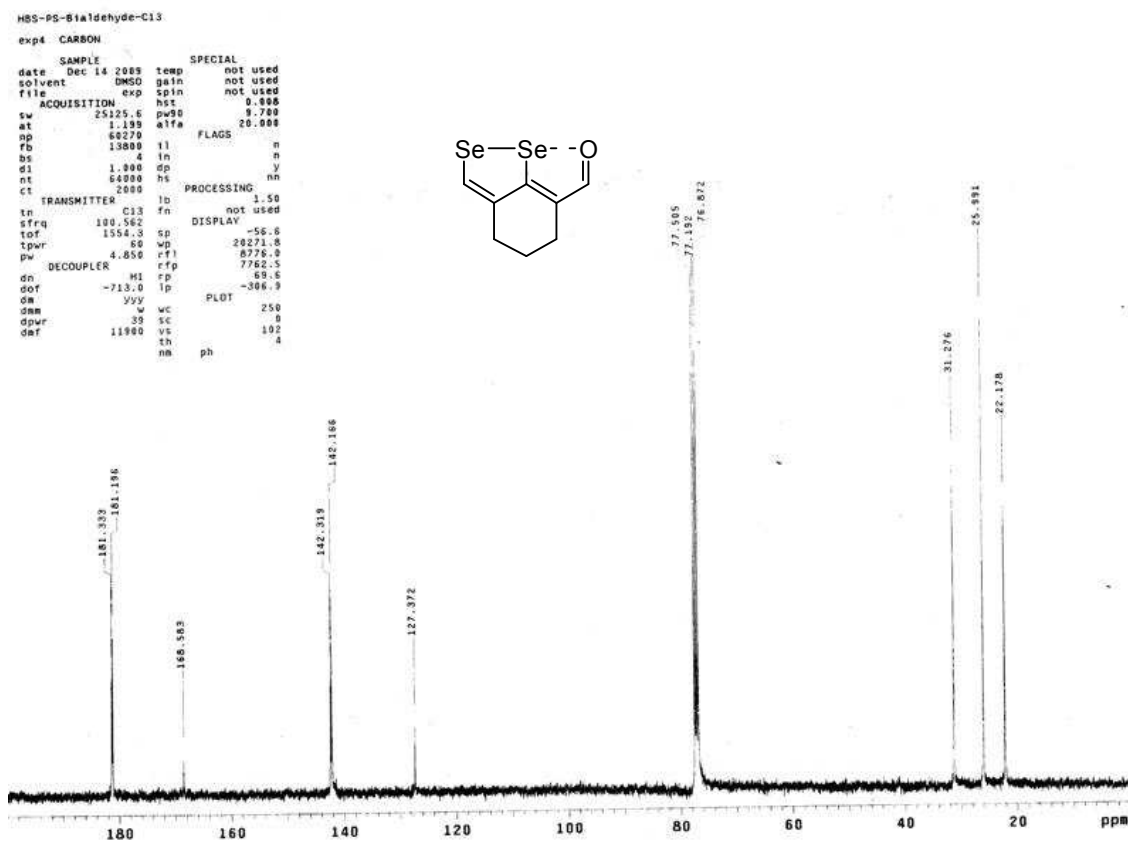


Figure S6. ^{13}C NMR spectrum of **34** (CDCl_3)

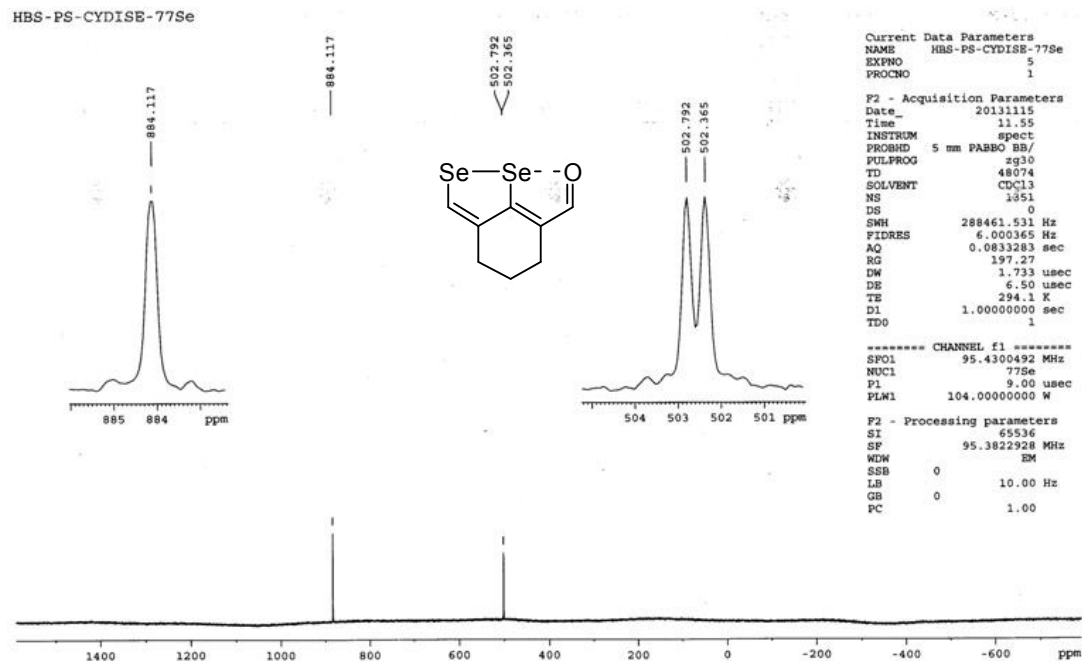


Figure S7. ^{77}Se NMR (coupled Se-H) spectrum of **34** (CDCl_3)

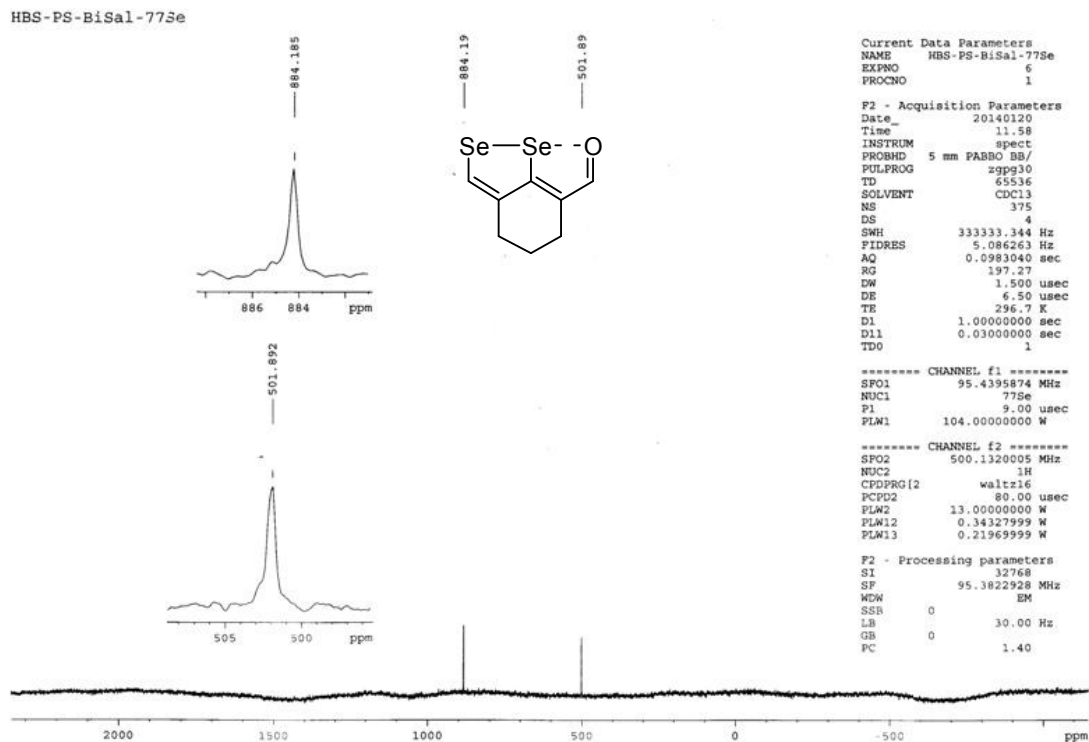


Figure S8. ^{77}Se NMR (decoupled Se-H) spectrum of **34** (CDCl_3)

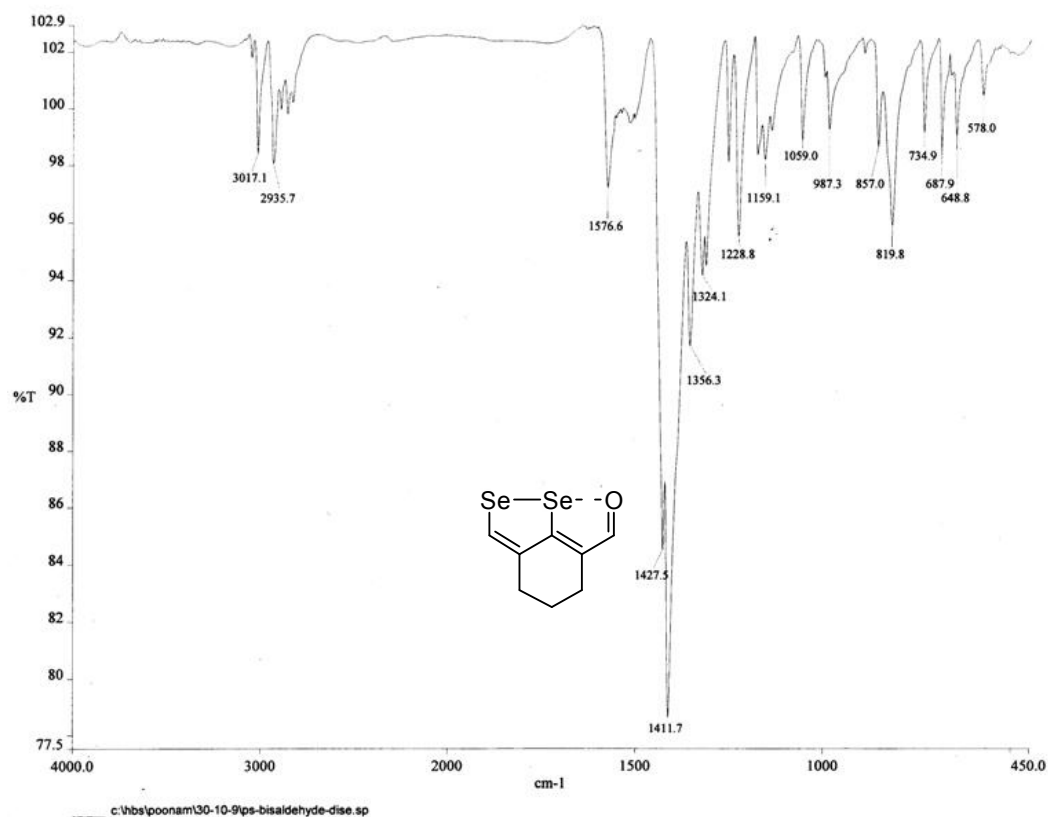
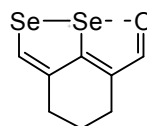


Figure S9. FT-IR spectrum of **34**

Elemental Composition Report



Page 1

Single Mass Analysis

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

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

Micromass :Q-Tof Micro (YA-105)

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

27-Sep-2010 12:19:22

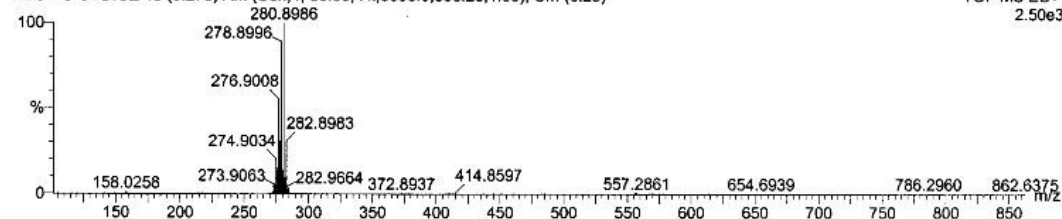
C8H8OSe2

HBS-PS-CYDISE 15 (0.278) AM (Cen,4, 80.00, Ht,5000.0,556.28,1.00); Cm (6:23)

Ionisation Mode

TOF MS ES+

2.50e3



Minimum:

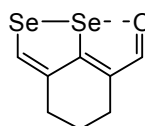
Maximum:

80.0 10.0 -1.5
50.0

Mass	Calc. Mass	mDa	PPM	DBE	Score	Formula
280.8986	280.8984	0.2	0.6	6.5	1	C8 H9 O Se2

Figure S10. HRMS-ESI spectrum of 34

Eager 300 Report



Page: 1 Sample: PS-1 (PS-1)

bisaldehyde diSe

Method Name : SP291009

Method File : D:\CHNS2008\SP291009.mth

Chromatogram : PS-1

Operator ID : MP

Analysed : 10/29/2009 14:31

Sample ID : PS-1 (# 24)

Analysis Type : UnkNown (Area)

Company Name : C.E. Instruments

Printed : 10/29/2009 16:35

Instrument N. : Instrument #1

Sample weight : 1.324

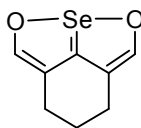
Calib. method : using 'K Factors'

!!! Warning missing one or more peaks.

Element Name	%	Ret.Time	Area	BC	Area ratio	K factor
Carbon	34.5589	67	1133451	RS	1.000000	.247095E+07
Hydrogen	2.7546	175	211915	RS	5.348611	.552060E+07
Totals	37.3135		1345366			

Figure S11. Elemental analysis (CHN) of 34

HBS-PS-CydiseN-1H



```

NAME      HBS-PS-CydiseN
EXPNO     25
PROCNO    1
Date_     20101019
Time      17.05
INSTRUM   spect
PROBHD    5 mm PABBO BB-
PULPROG   zg30
TD         65536
SOLVENT   CDCl3
NS         21
DS         0
SWH        8223.685 Hz
FIDRES     0.125483 Hz
AQ         3.9846367 sec
RG         32
DW         60.800 usec
DE         6.50 usec
TE         294.2 K
D1         1.00000000 sec
TD0        1

===== CHANNEL f1 =====
NUC1       1H
P1         13.50 usec
PL1        -1.00 dB
PL1W       10.56200695 W
SFO1       400.1324710 MHz
SI         32768
SF         400.1300001 MHz
WDW        EM
SSB        0
LB         0.00 Hz
GB         0
PC         1.00

```

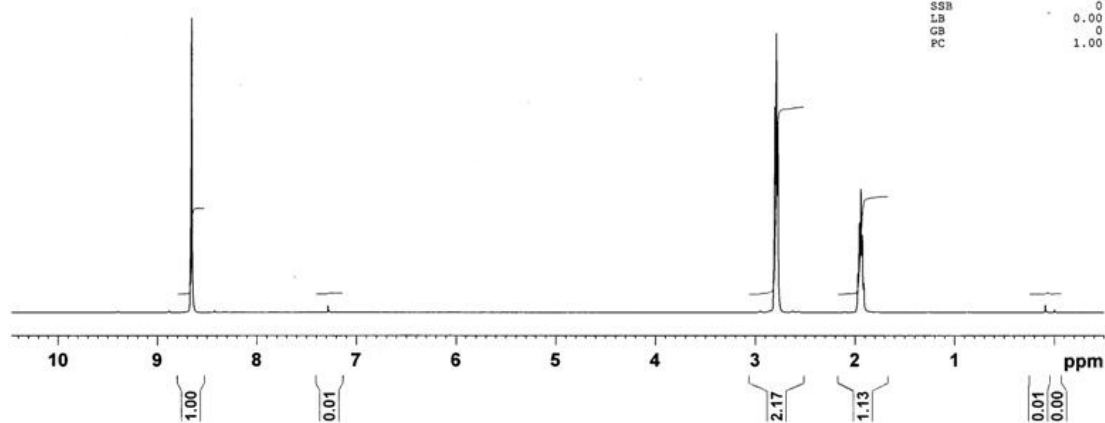


Figure S12. ^1H NMR spectrum of **35** (CDCl_3)

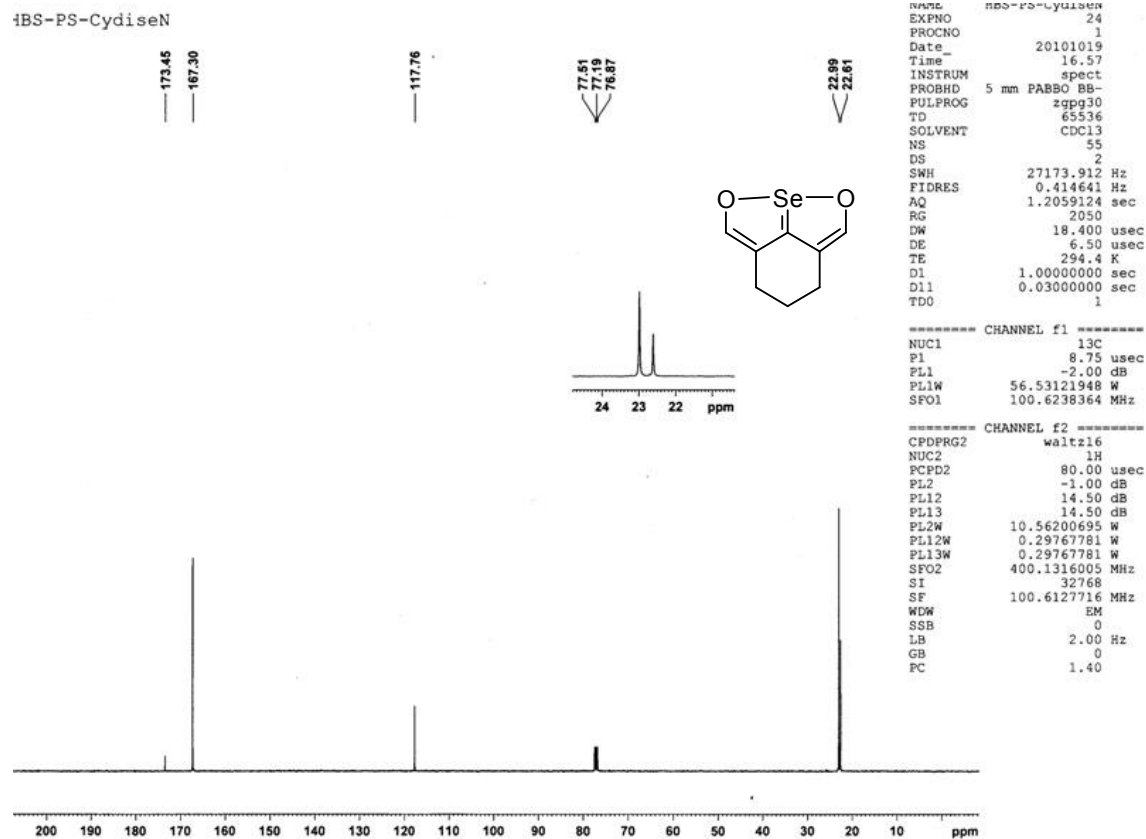


Figure S13. ¹³C NMR spectrum of **35** (CDCl₃)

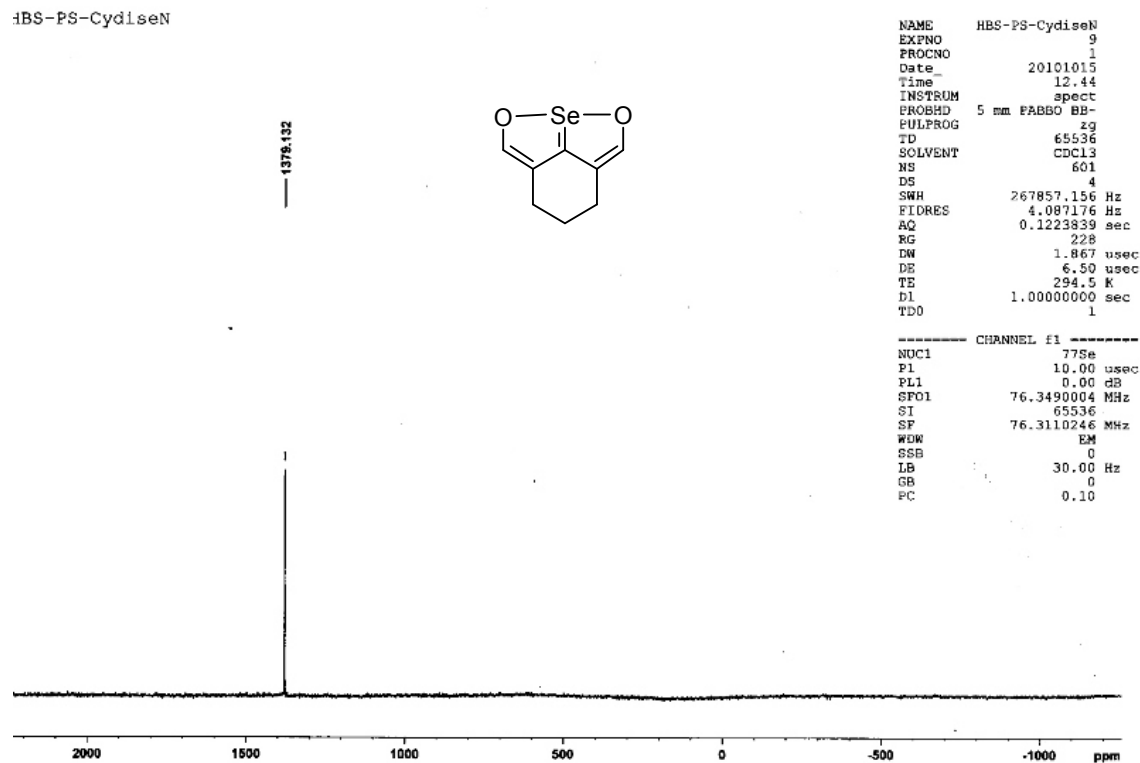


Figure S14. ⁷⁷Se NMR spectrum of **35** (CDCl₃)

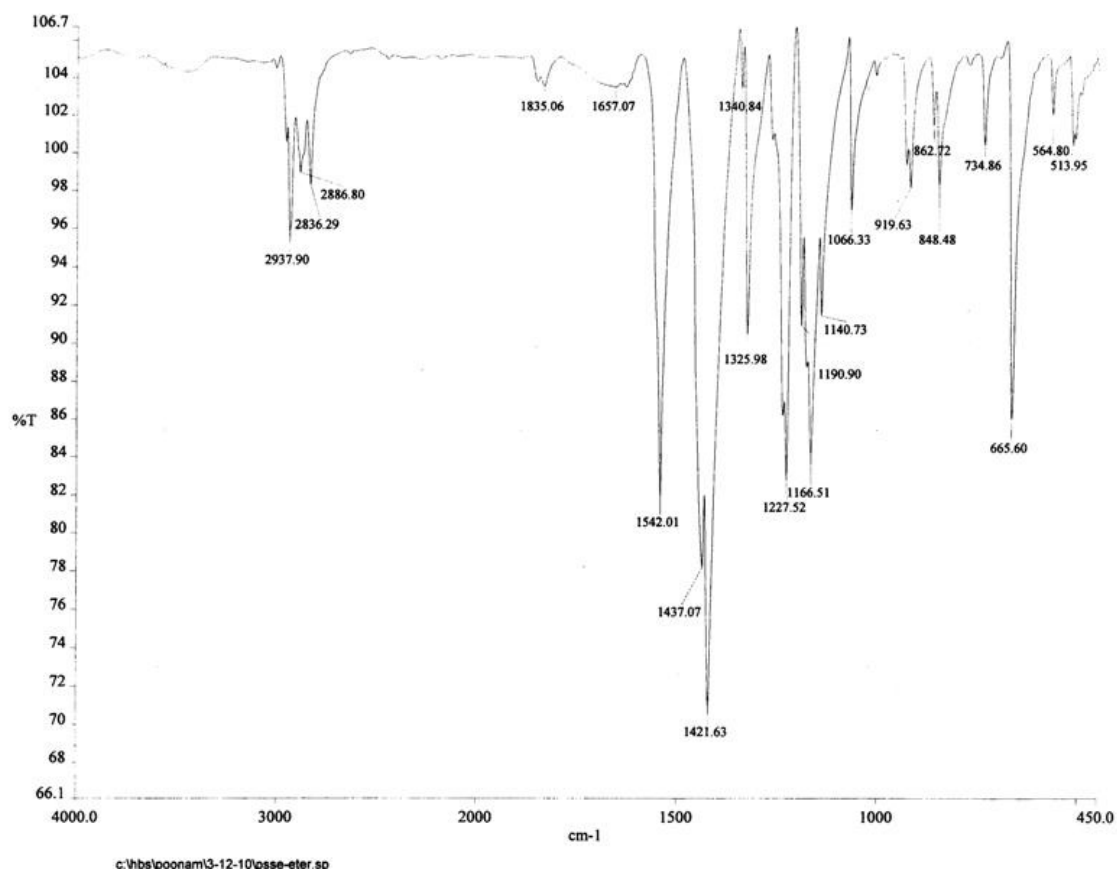


Figure S15. FT-IR spectrum of **35**

Elemental Composition Report

Page 1

Single Mass Analysis

Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0

Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron Ions

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

Micromass : Q-ToF Micro (YA-105)

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

28-Oct-2010 15:16:05

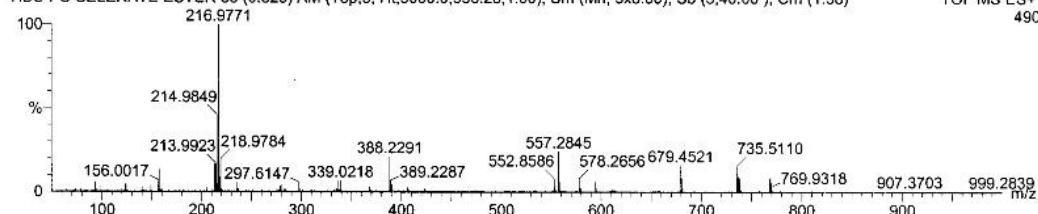
C8H8O2Se

HBS-PS-SELENATE ESTER 33 (0.325) AM (Top,5, Ht,5000.0,556.28,1.00); Sm (Mn, 3x6.00); Sb (5,40.00); Cm (1:38)

Ionisation Mode

TOF MS ES+

490



Minimum: -1.5
Maximum: 80.0 5.0 50.0

Mass	Calc. Mass	mDa	PPM	DBE	Score	Formula
216.9771	216.9768	0.3	1.3	5.5	1	C8 H9 O2 Se

Figure S16. HRMS-ESI spectrum of 35

Eager 300 Report

Page: 1 Sample: PS-SEEST (PS-SEEST)

Se-ester

Method Name : SP131210

Method File : D:\CHNS2008\SP131210.mth

Chromatogram : PS-SEEST

Operator ID : SD

Company Name : C.E. Instruments

Analysed : 12/13/2010 12:37

Printed : 12/13/2010 17:00

Sample ID : PS-SEEST (# 8)

Instrument N. : Instrument #1

Analysis Type : UnkNown (Area)

Sample weight : .716

Calib. method : using 'K Factors'

!!! Warning missing one or more peaks.

Element Name	%	Ret.Time	Area	BC	Area ratio	K factor
Carbon	44.67	44.5440	66	829241 RS	1.000000	.260003E+07
Hydrogen	3.45	3.4148	175	146899 RS	5.644974	.600812E+07
Totals		47.9589		976140		

Figure S17. Elemental analysis (CHN) of 35

HBS-PS-CydiTe

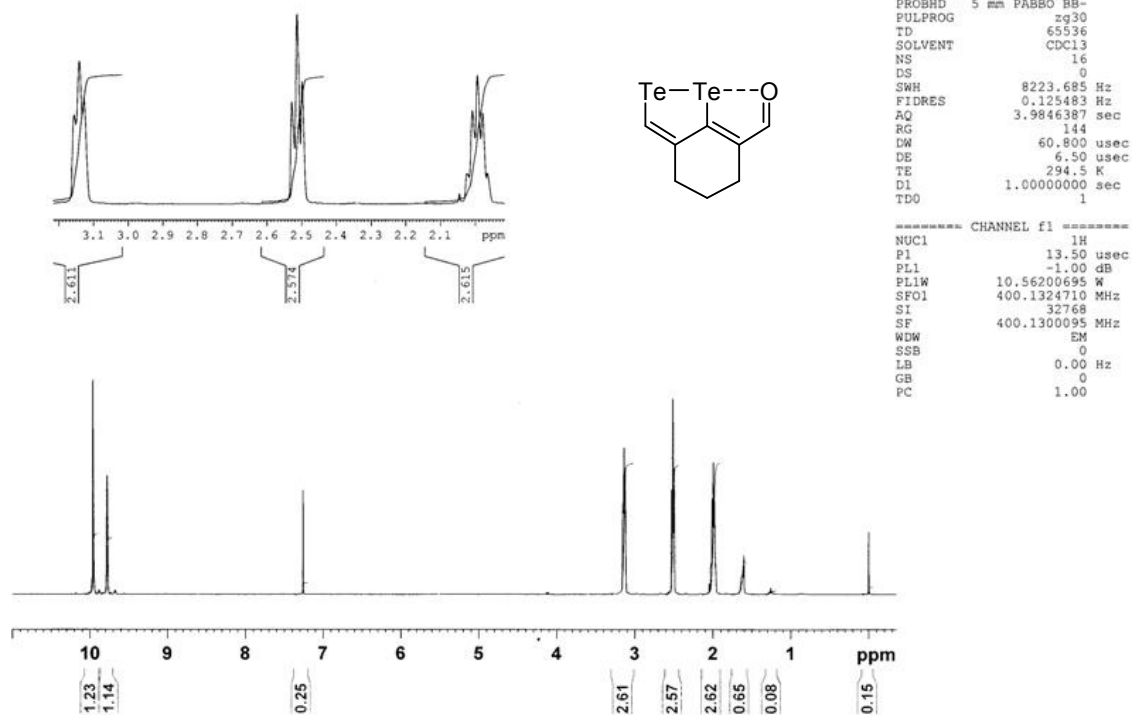


Figure S18. ¹H NMR spectrum of 36 (CDCl₃)

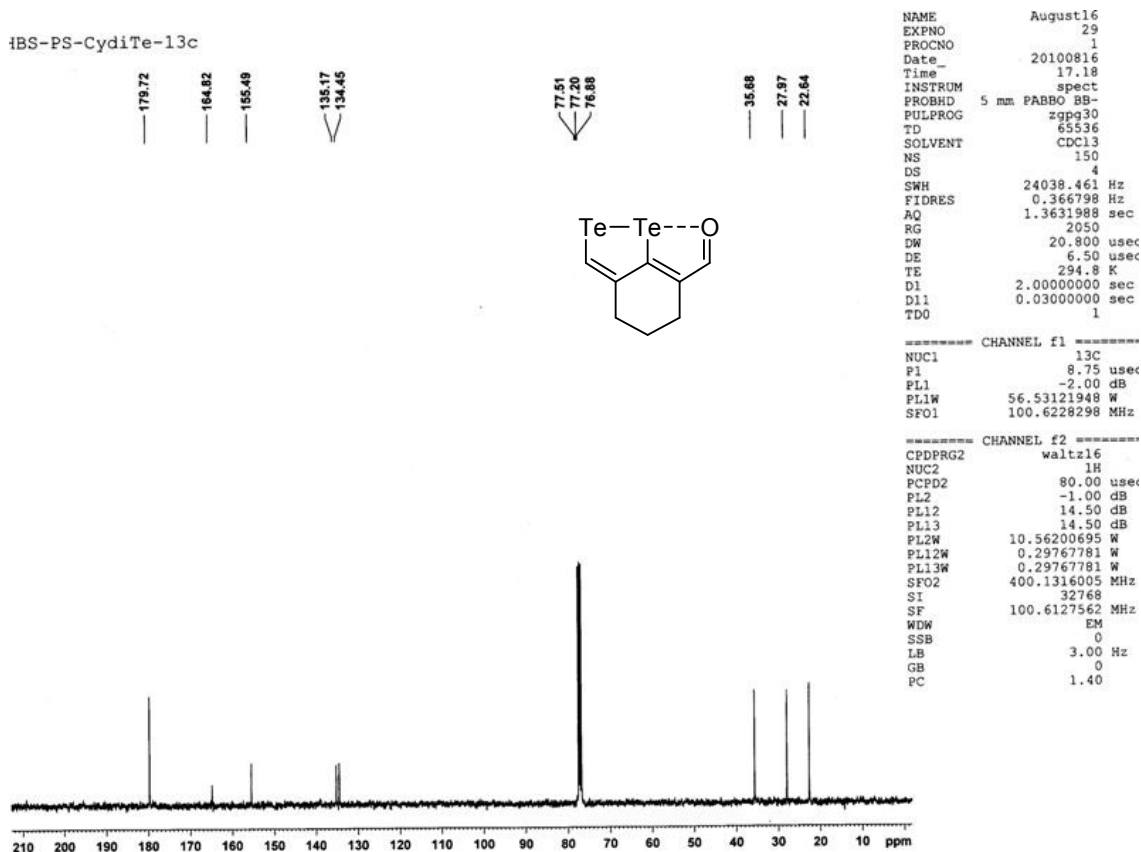


Figure S19. ^{13}C NMR spectrum of **36** (CDCl_3)

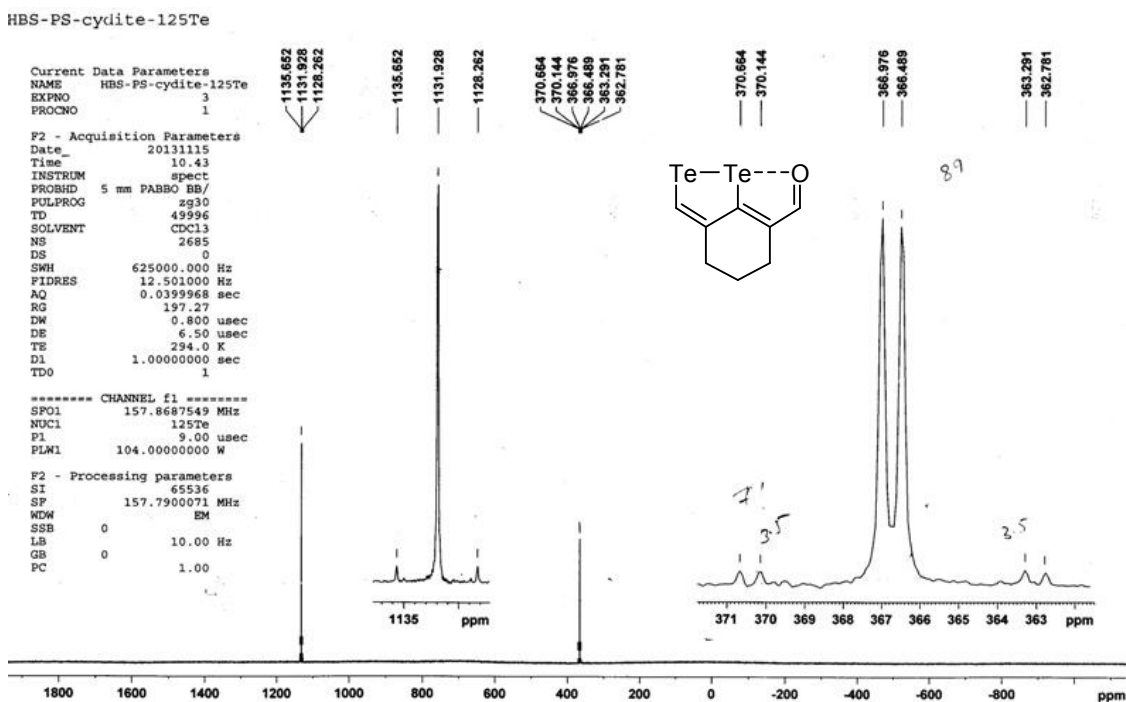


Figure S20. ^{125}Te NMR (Te-H Coupled) spectrum of **36** (CDCl_3)

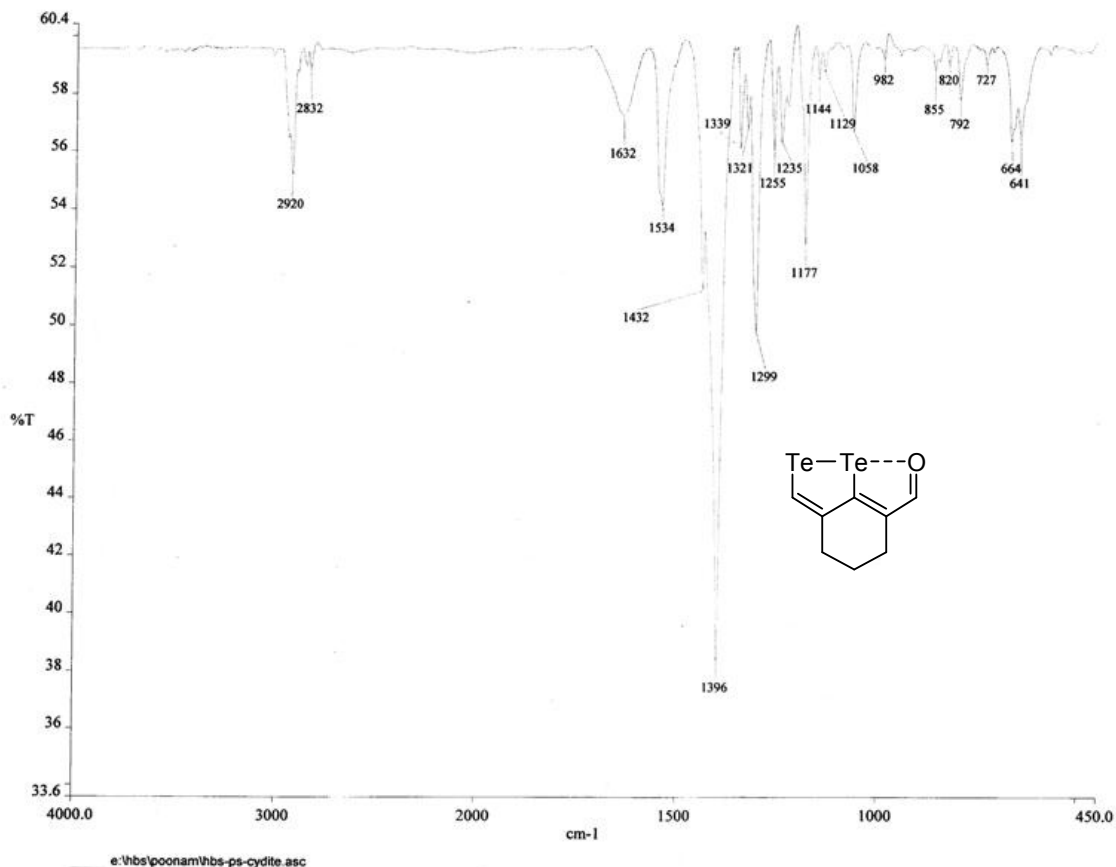


Figure S21. FT-IR spectrum of 36

Elemental Composition Report

Single Mass Analysis

Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0

Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron Ions

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

Micromass :Q-ToF Micro (YA-105)

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

27-Sep-201012:10:03

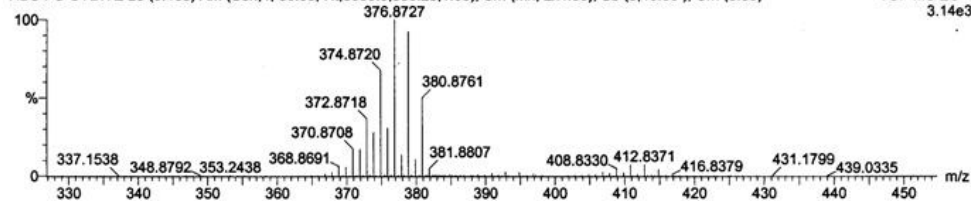
C16H16O4Te2

HBS-PS-CYDITE 25 (0.465) AM (Cen,4, 80.00, Ht,5000.0,556.28,1.00); Sm (Mn, 2x4.00); Sb (5,40.00); Cm (8:53)

Ionisation Mode

TOF MS ES+

3.14e3



Minimum:

Maximum:

Mass

Calc. Mass

mDa

PPM

DBE

Score

Formula

380.8761

380.8778

-1.7

-4.4

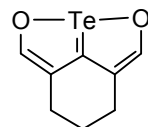
4.5

1

C8 H9 O Te2

Figure S22. HRMS-ESI spectrum of 36

HBS-PS-Te-ester



```

NAME      HBS-PS-Te-ester
EXPNO     12
PROCNO    2
Date_     20101115
Time_     10.04
INSTRUM    spect
PROBHD     5 mm PABBO BB-
PULPROG    zg30
TD         65536
SOLVENT     CDCl3
NS         40
DS         0
SWH        8223.685 Hz
FIDRES     0.125483 Hz
AQ         3.9846387 sec
RG         128
DW         60.800 usec
DE         6.50 usec
TE         296.8 K
D1         1.00000000 sec
TD0        1
  
```

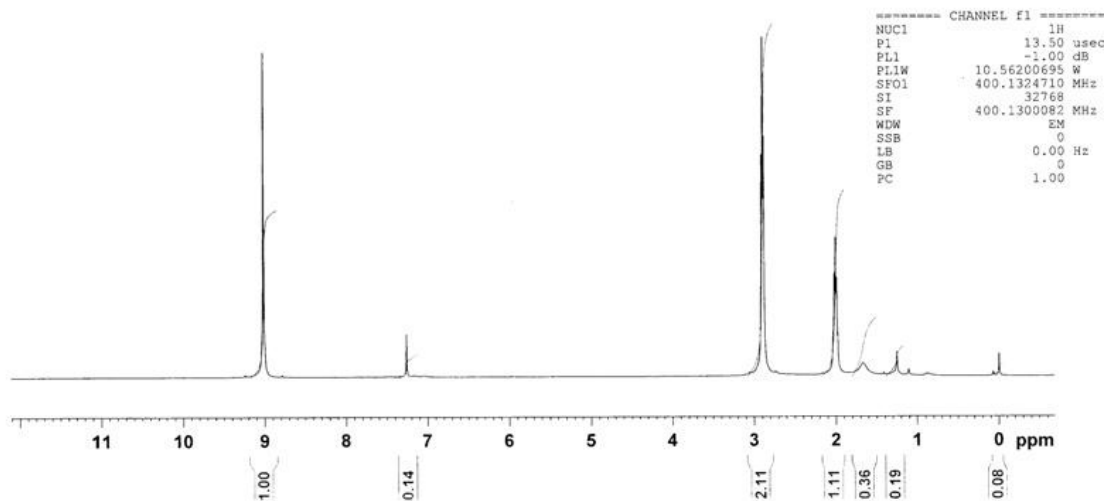


Figure S23. ^1H NMR spectrum of **37** (CDCl_3)

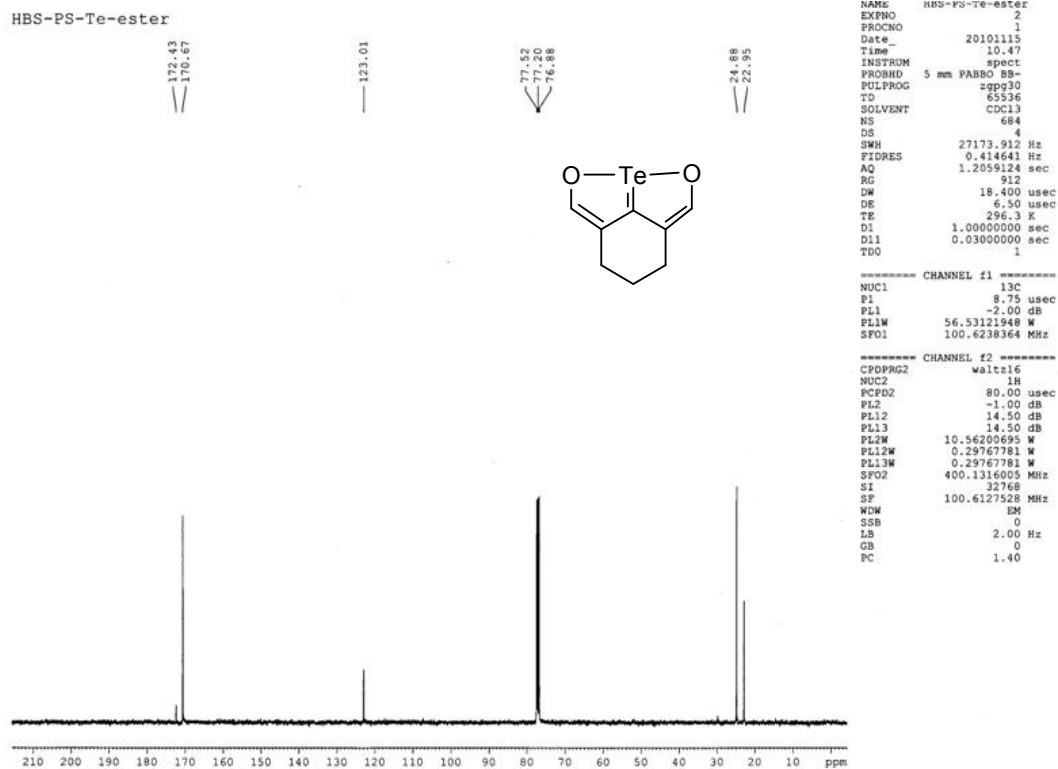


Figure S24. ^{13}C NMR spectrum of 37 (CDCl_3)

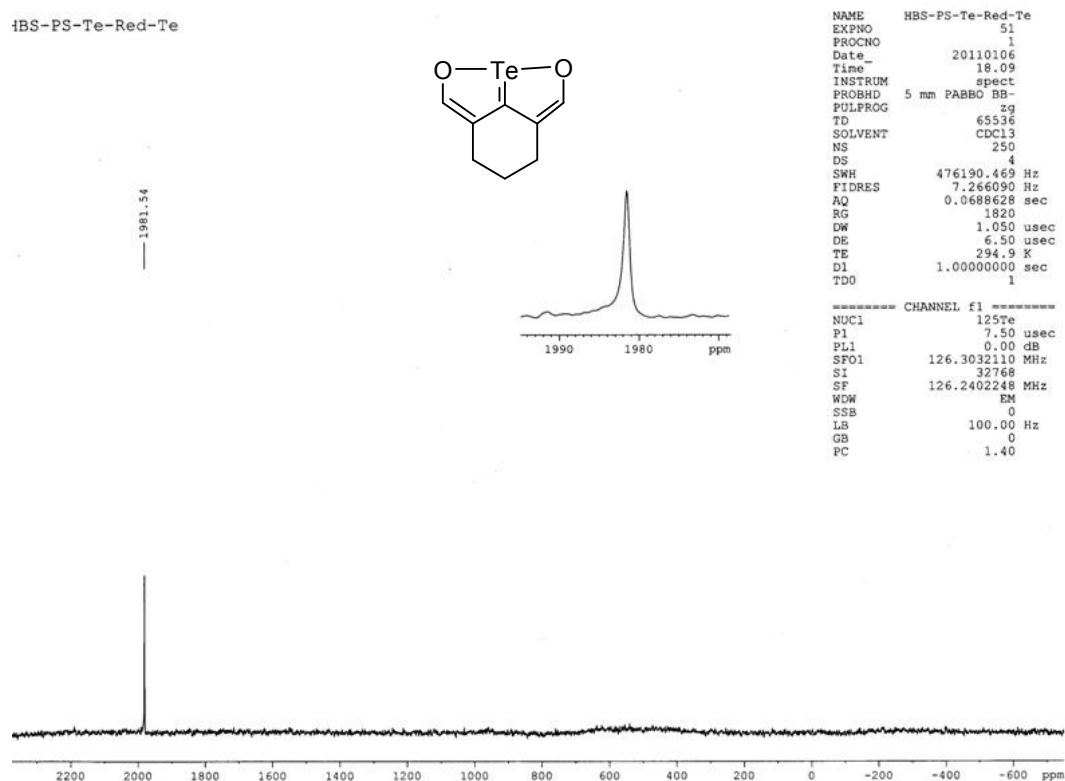


Figure S25. ^{125}Te NMR spectrum of 37 (CDCl_3)

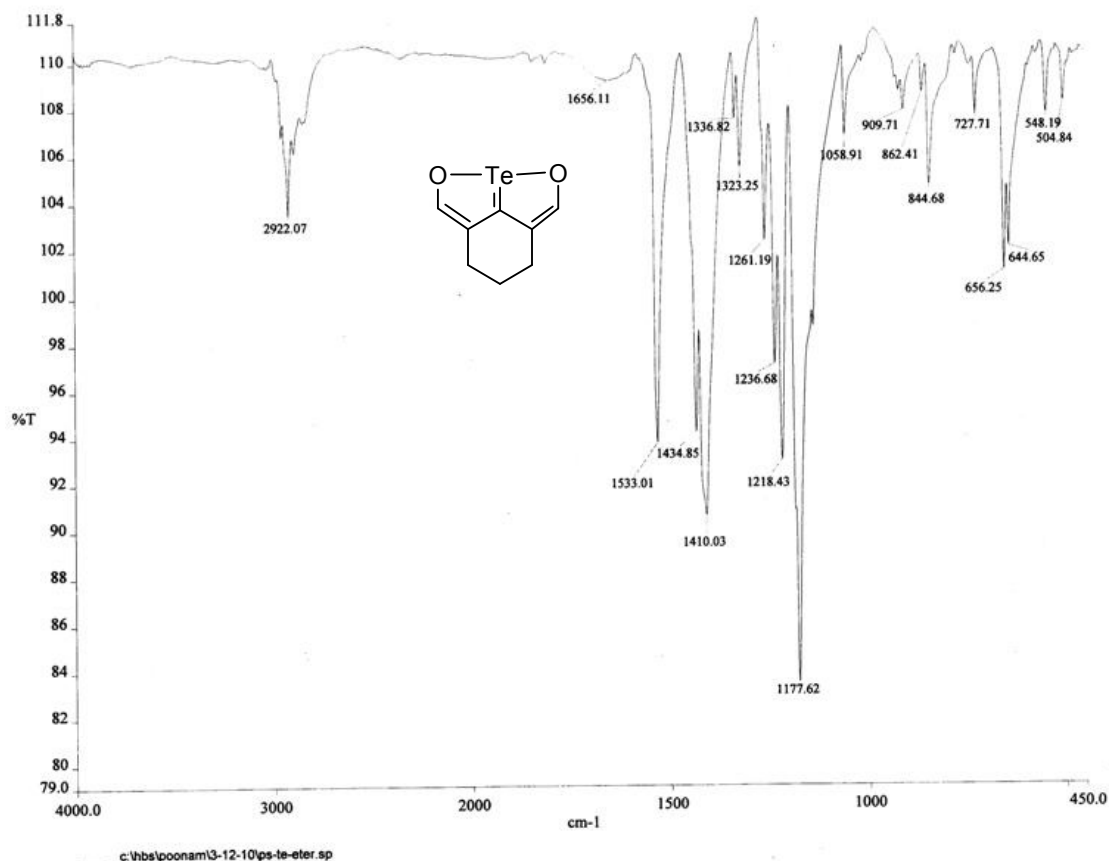
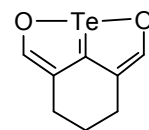


Figure S26. FT-IR spectrum of 37

Elemental Composition Report



Page 1

Single Mass Analysis (displaying only valid results)

Tolerance = 10.0 PPM / DBE: min = -1.5, max = 200.0

Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron Ions

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

Micromass : Q-ToF micro (YA-105)

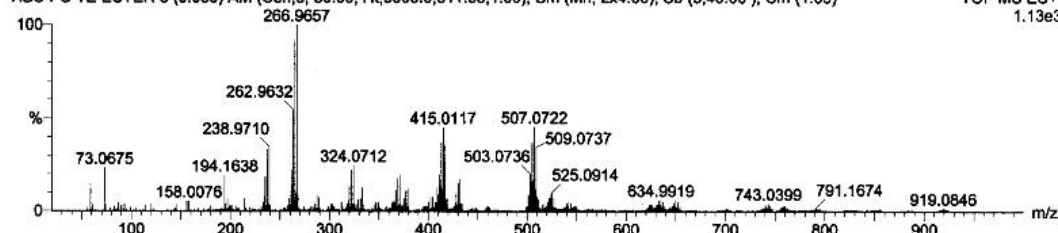
Dept. Of Chemistry I.I.T.(B)

27-Jun-2012 15:45:56

C10H12O2Te

HBS-PS-TE ESTER 8 (0.080) AM (Cen,5, 80.00, Ht,5000.0,311.08,1.00); Sm (Mn, 2x4.00); Sb (5,40.00); Cm (1:63)

TOF MS ES+
1.13e3



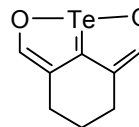
Minimum: -1.5
Maximum: 200.0 10.0 200.0

Mass	Calc. Mass	mDa	PPM	DBE	Score	Formula
266.9657	266.9655	-0.8	-3.1	4.5	1	C8 H9 O2 Te

Figure S27. HRMS-ESI spectrum of 37

Eager 300 Report

Page: 1 Sample: PS-TEEST2 (PS-TEEST2)



Method Name : SP21012011
 Method File : D:\CHNS2011\SP21012011.mth
 Chromatogram : PS-TEEST2
 Operator ID : SD
 Analysed : 01/21/2011 11:48
 Sample ID : PS-TEEST2 (# 7)
 Analysis Type : UnkNown (Area)

Company Name : C.E. Instruments
 Printed : 1/21/2011 14:51
 Instrument N. : Instrument #1
 Sample weight : .792

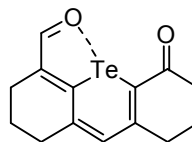
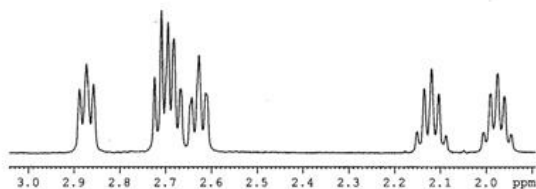
Calib. method : using 'K Factors'

!!! Warning missing one or more peaks.

Element Name	%	Ret.Time	Area	BC	Area ratio	K factor
Carbon	36.43	36.5909	67	769052 RS	1.000000	.265374E+07
Hydrogen	H = 3.86	2.9127	178	135263 RS	5.685605	.586343E+07
Totals		39.5036		904315		

Figure S28. Elemental analysis (CHN) of 37

HBS-PS-CyMonote-1H



NAME HBS-PS-CyMonote
 EXPNO 43
 PROCNO 1
 Date_ 20101021
 Time 15.20
 INSTRUM spect
 PROBD 5 mm FASBO BB-
 PULPROG zg30
 TD 65536
 SOLVENT CDCl3
 NS 8
 DS 0
 SWH 8223.685 Hz
 FIDRES 0.125483 Hz
 AQ 3.9846387 sec
 RG 161
 DW 60.800 usec
 DE 6.50 usec
 TE 293.9 K
 D1 1.00000000 sec
 TDO 1
 ===== CHANNEL f1 =====
 NUC1 1H
 P1 13.50 usec
 PL1 -1.00 dB
 PL1W 10.5620695 W
 SFO1 400.1324710 MHz
 SI 32768
 SF 400.1300063 MHz
 WDW EM
 SSB 0
 LB 0.00 Hz
 GB 0
 PC 1.00

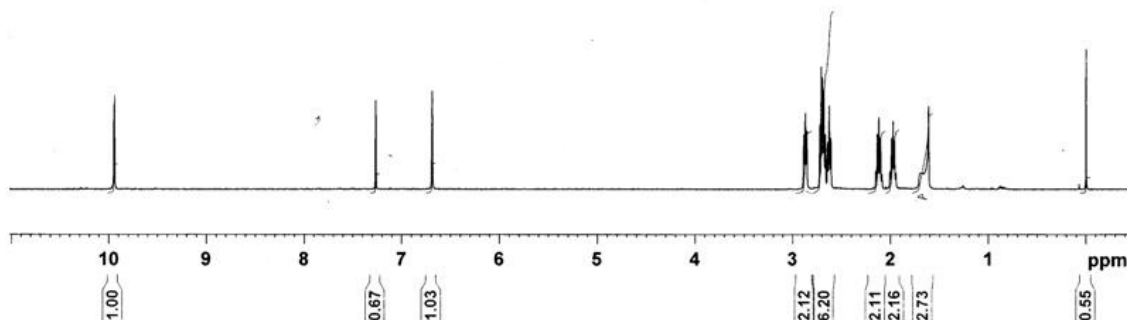


Figure S29. ¹H NMR spectrum of 38 (CDCl₃)

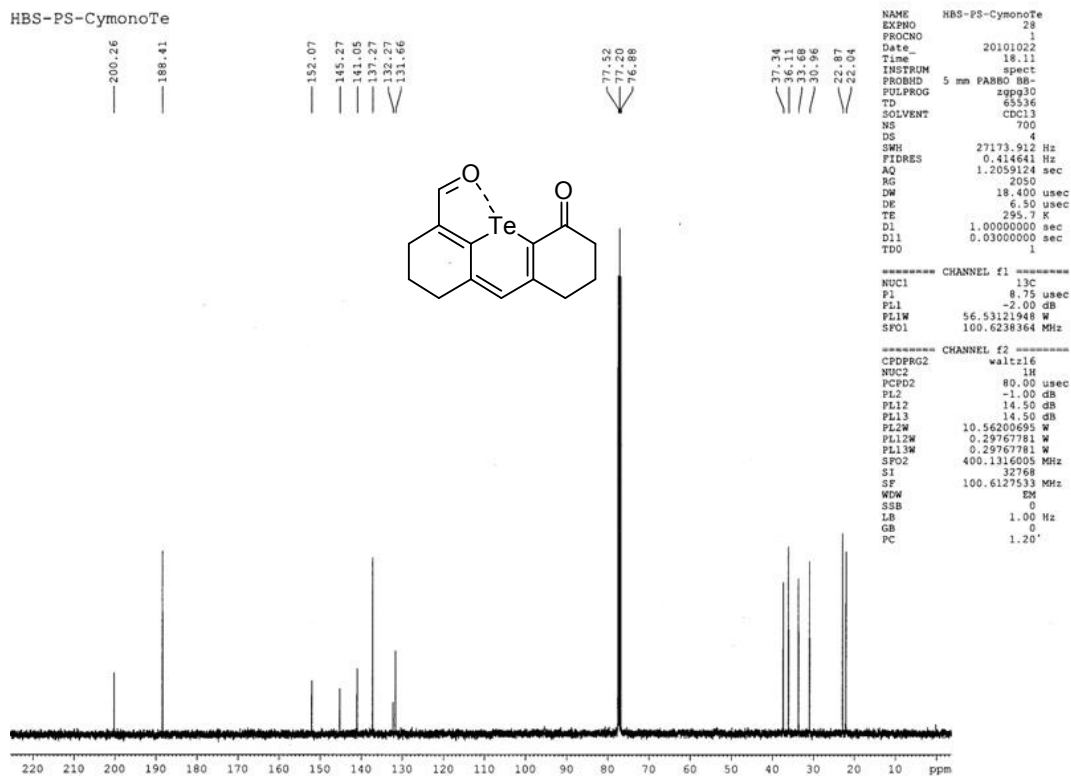


Figure S30. ^{13}C NMR spectrum of **38** (CDCl_3)

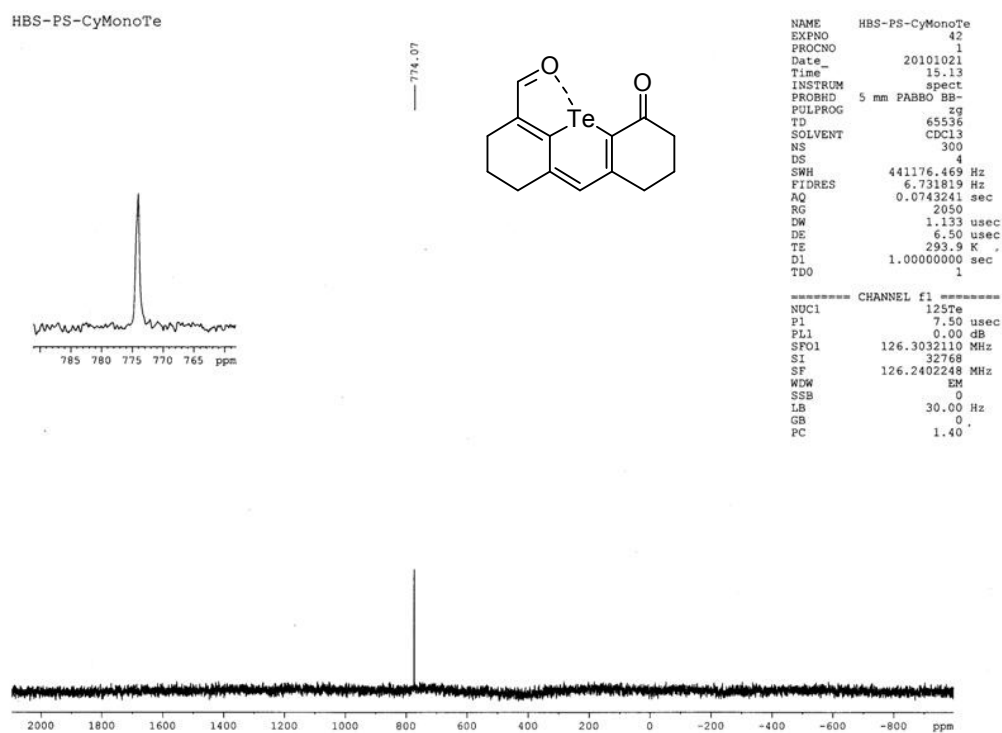


Figure S31. ^{125}Te NMR spectrum of **38** (CDCl_3)

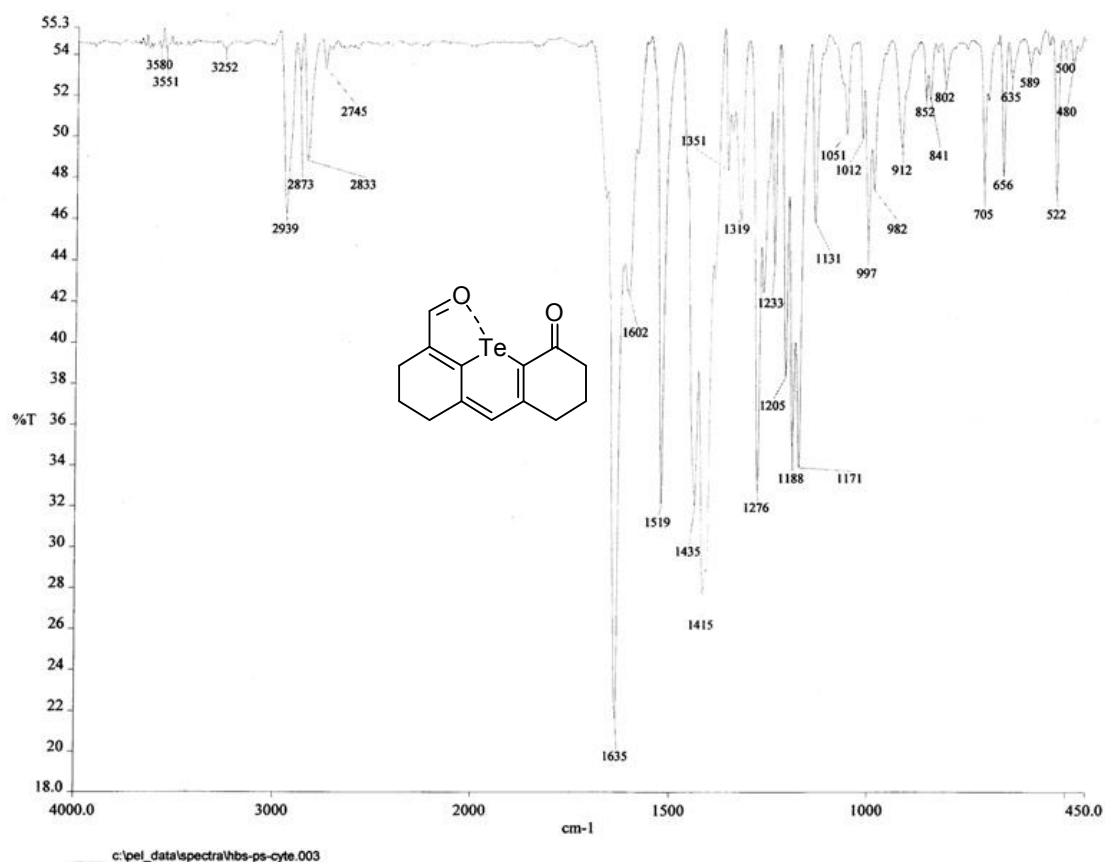


Figure S32. FT-IR spectrum of **38**

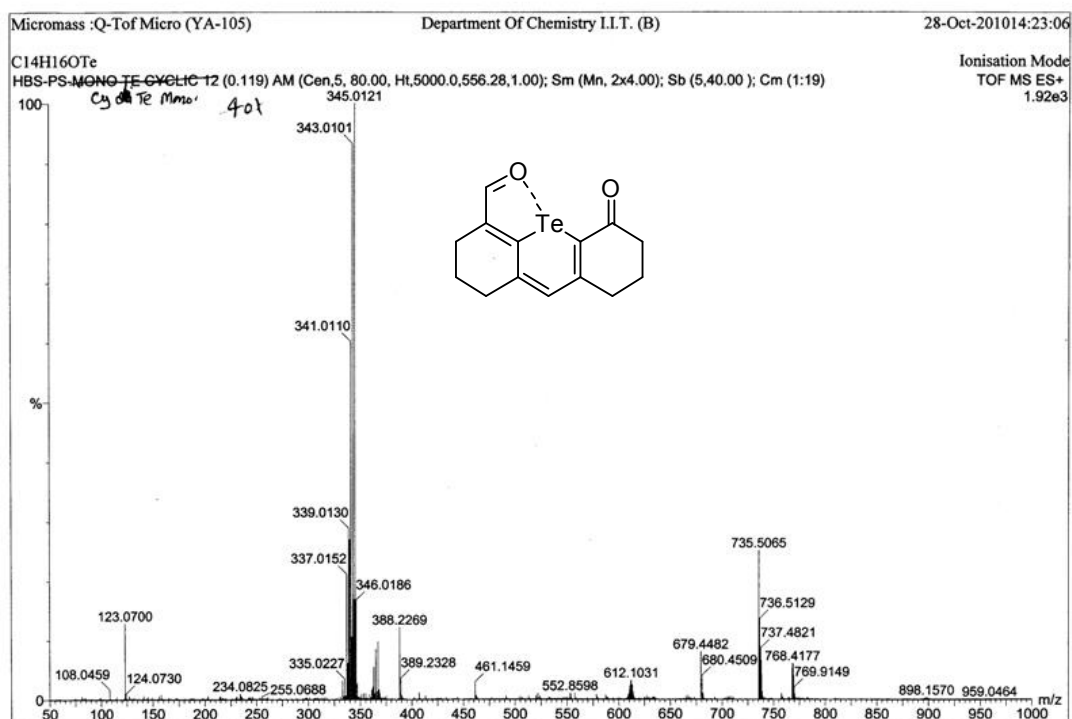
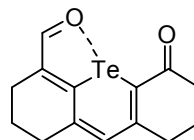


Figure S33. MS-ESI spectrum of **38**

Eager 300 Report

Page: 1 Sample: DITE-2 (DITE-2)

Method Name : SP110310
Method File : D:\CHNS2008\SP110310.mth
Chromatogram : DITE-2
Operator ID : MP
Analysed : 03/11/2010 13:35
Sample ID : DITE-2 (# 19)
Analysis Type : UnkNown (Area)



Company Name : C.E. Instruments
Printed : 3/11/2010 15:37
Instrument N. : Instrument #1
Sample weight : 1.201

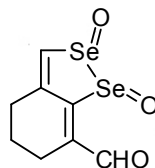
Calib. method : using 'K Factors'

!!! Warning missing one or more peaks.

Element Name	%	Ret.Time	Area	BC	Area ratio	K factor
Carbon	49.6372	66	1600521	RS	1.000000	.267627E+07
Hydrogen	4.4106	169	422465	RS	3.788529	.684543E+07
Totals	54.0478		2022986			

Figure S34. Elemental analysis (CHN) of 38

HBS-PS-MCpba-proton



NAME july26
EXPNO 5
PROCNO 1
Date_ 20100726
Time 12.24
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 35
DS 0
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 203
OW 60.800 usec
DE 6.50 usec
TE 300.0 K
D1 1.00000000 sec
TD0 1
----- CHANNEL f1 -----
NUC1 1H
P1 13.50 usec
PL1 -1.00 dB
PL1W 10.56200635 W
SF01 400.1324710 MHz
SI 32768
SF 400.1300095 MHz
WDW EM
SSB 0
LB 0.00 Hz
GB 0
PC 1.00

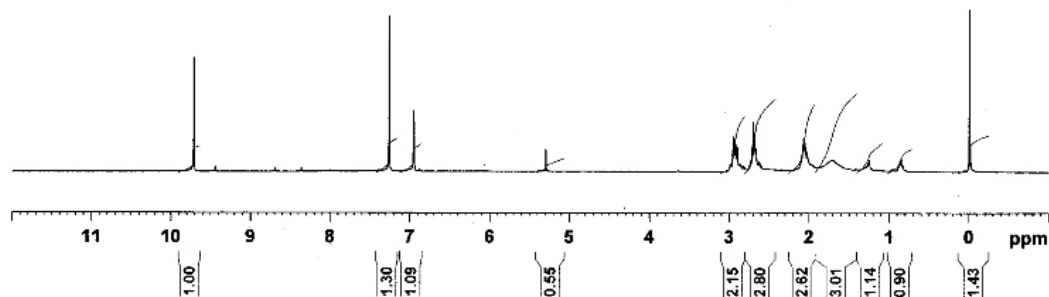
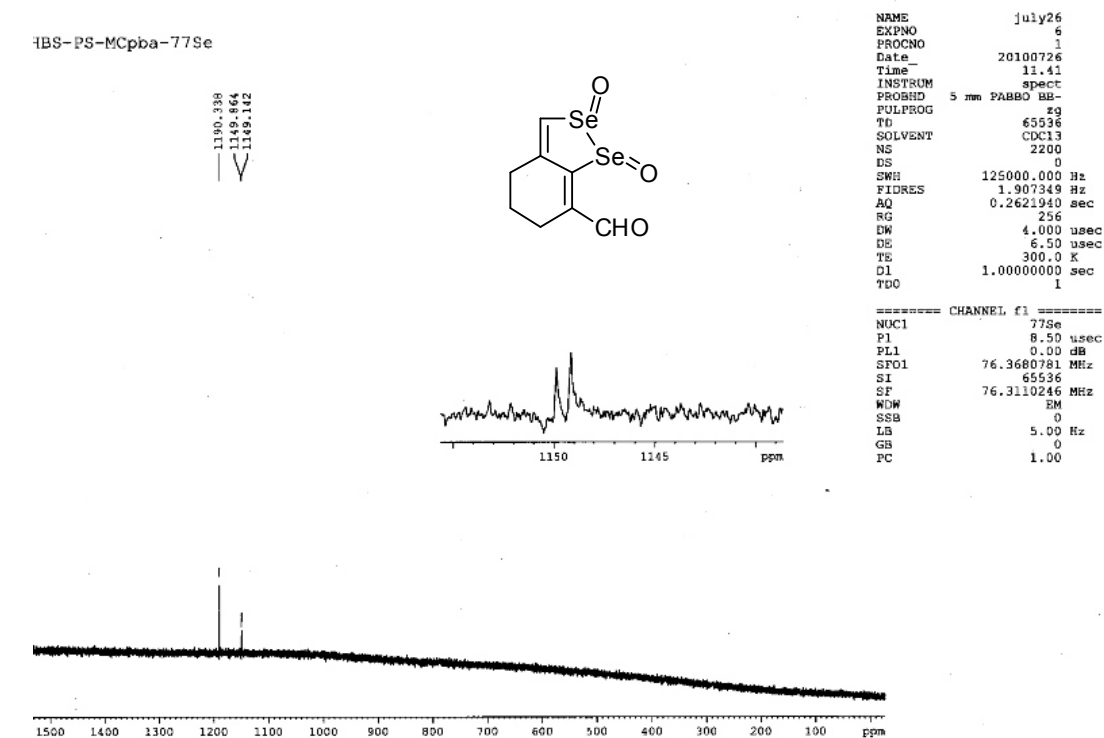
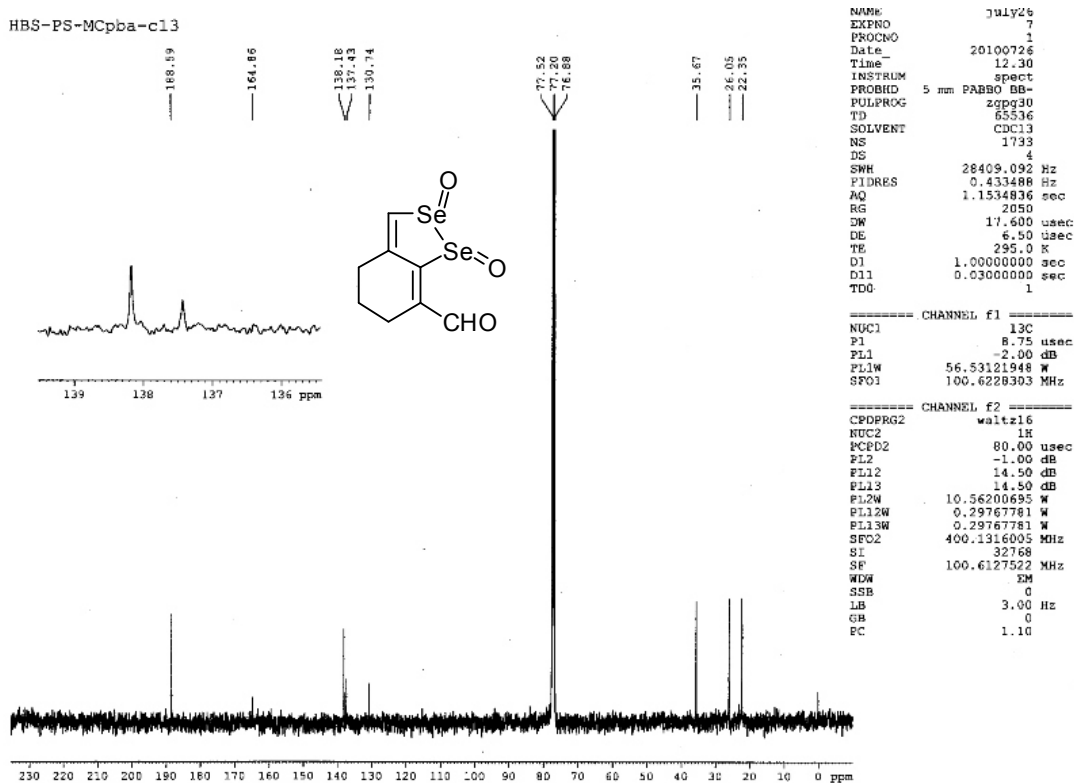


Figure S35. ¹H NMR spectrum of 39 (CDCl₃)



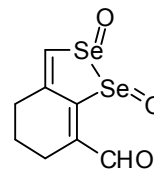
Elemental Composition Report

Page 1

Single Mass Analysis

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

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

Micromass : Q-ToF micro (YA-105)

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

06-Aug-2010 20:15:08

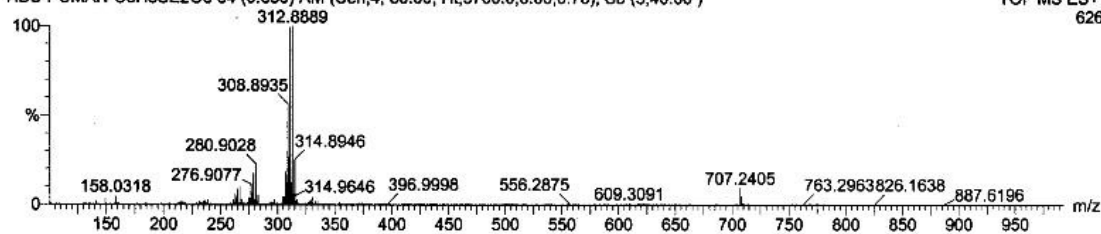
C8H8Se2O3

HBS-PUMAN-C8H8SE2O3 34 (0.630) AM (Cen,4, 80.00, Ht,5700.0,0.00,0.76); Sb (5.40.00)

Ionisation Mode

TOF MS ES+

626



Minimum:

Maximum: 200.0 10.0 -1.5

Mass	Calc. Mass	mDa	PPM	DBE	Score	Formula
312.8889	312.8882	0.6	2.1	6.5	1	C8 H9 O3 Se2

Figure S38. HRMS-ESI spectrum of **39**

S2. Single crystal X-Ray data, packing diagrams with weak secondary interactions, thermal ellipsoids and unit cell packing diagrams

Table S1. Crystal data and structure refinement for **33**, **34**, **35** and **36**.

Compound	33	34	35	36
Empirical formula	C ₈ H ₈ OS ₂	C ₈ H ₈ OSe ₂	C ₈ H ₈ O ₂ Se	C ₈ H ₈ OTe ₂
Formula weight	184.26	278.06	215.10	374.34
Crystal system	Triclinic	Monoclinic	Triclinic	Orthorhombic
Space group	<i>P</i> -1	<i>C</i> 2/ <i>m</i>	<i>P</i> -1	<i>P</i> na21
<i>a</i> (Å)	6.8851(9)	14.8825(13)	7.8765(4)	11.4121(3)
<i>b</i> (Å)	7.9251(12)	7.0999(7)	8.1219(5)	16.6843(5)
<i>c</i> (Å)	8.1801(7)	8.2818(8)	13.0249(7)	4.8996(2)
α (deg)	85.683(9)	90	74.478(5)	90
β (deg)	89.920(9)	95.735(10)	76.975(4)	90
γ (deg)	64.419(14)	90	89.917(4)	90
<i>V</i> (Å ³)	401.21(9)	870.71(14)	780.65(8)	932.90(5)
<i>Z</i>	2	4	4	4
<i>D</i> (calcd) (Mg/m ³)	1.525	2.121	1.830	2.665
Absorption coefficient (mm ⁻¹)	0.595	8.430	4.751	48.892
Reflections collected	3850	2809	11939	1868
Final <i>R</i> (<i>F</i>) [<i>I</i> >2σ(<i>I</i>)] ^[a]	0.0483	0.0479	0.0552	0.0917
<i>wR</i> (<i>F</i> ²) indices [<i>I</i> >2σ(<i>I</i>)]	0.1311	0.0930	0.0874	0.2452
Data / restraints / parameters	1889 / 0 / 101	1536 / 0 / 71	6307 / 0 / 200	1139 / 61 / 100
Goodness-of-fit on <i>F</i> ²	1.050	0.862	1.038	1.141

$$^{[a]}R(F_o) = \Sigma||F_o| - |F_c||/\Sigma|F_o| \text{ and } wR(F_o^2) = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_c^2)^2]\}^{1/2}$$

Table S2. Crystal data and structure refinement for **37**, **38** and **40**.

Compound	37	38	40
Empirical formula	C ₈ H ₈ O ₂ Te	C ₁₄ H ₁₄ O ₂ Te	C ₁₆ H ₂₀ O ₄ Te
Formula weight	263.74	341.85	403.92
Crystal system	Orthorhombic	Monoclinic	Orthorhombic
Space group	<i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> nma
<i>a</i> (Å)	5.0492(11)	9.2886(4)	11.0465(6)
<i>b</i> (Å)	6.5696(14)	14.6360(5)	7.3367(5)
<i>c</i> (Å)	24.078(4)	9.5487(4)	20.3405(13)
α (deg)	90	90	90
β (deg)	90	103.428(4)	90
γ (deg)	90	90	90
<i>V</i> (Å ³)	798.7(3)	1262.64(9)	1648.49(18)
<i>Z</i>	4	4	4
<i>D</i> (calcd) (Mg/m ³)	2.193	1.798	1.627
Absorption coefficient (mm ⁻¹)	3.667	18.493	1.817
Reflections collected	13483	8138	14641
Final <i>R</i> (<i>F</i>) [<i>I</i> > 2σ(<i>I</i>)] ^[a]	0.0672	0.0587	0.0318
<i>wR</i> (<i>F</i> ²) indices [<i>I</i> > 2σ(<i>I</i>)]	0.1506	0.1449	0.0805
Data / restraints / parameters	4112 / 0 / 100	2564 / 0 / 154	2282 / 0 / 126
Goodness-of-fit on <i>F</i> ²	1.133	1.094	1.099

$$^{[a]}R(F_o) = \Sigma ||F_o| - |F_c| / \Sigma |F_o| \text{ and } wR(F_o^2) = \{ \Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_c^2)^2] \}^{1/2}$$

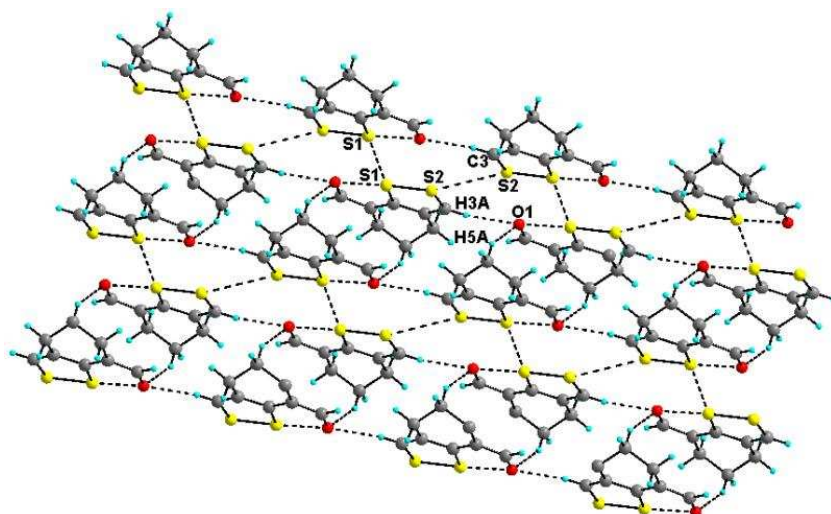


Figure S39. Two-dimensional packing diagram showing intermolecular S...S and O...H bonding interactions in **33**

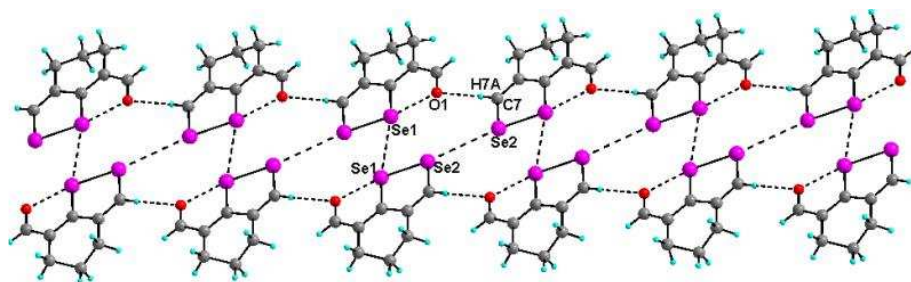


Figure S40. Packing diagram of **34** showing weak Se...Se and O...H interactions

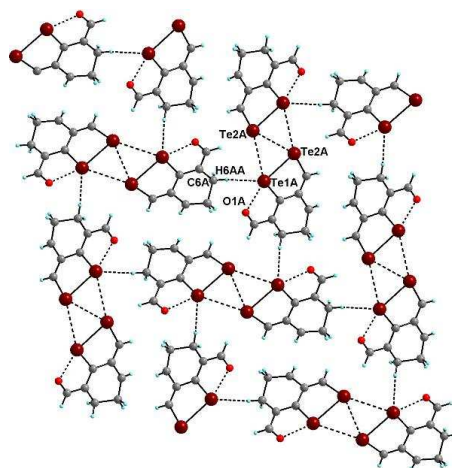


Figure S41. 2-D Packing diagram of **36** showing Te...Te interactions

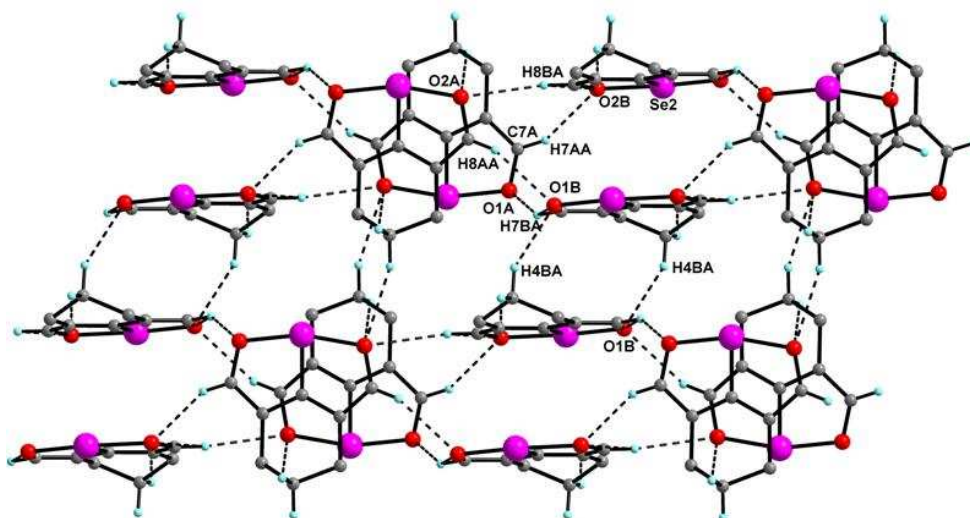


Figure S42. Intermolecular weak hydrogen bonding interaction in **35**.

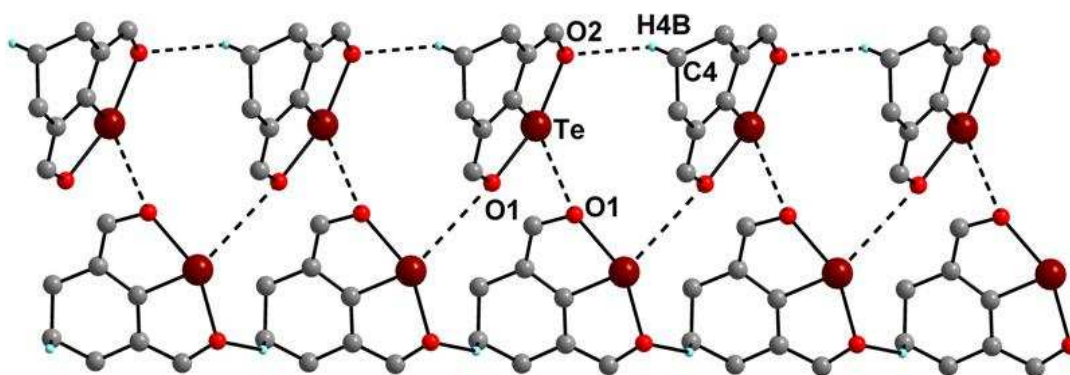


Figure S43. Intermolecular hydrogen bonding and Te...O interactions in **37**

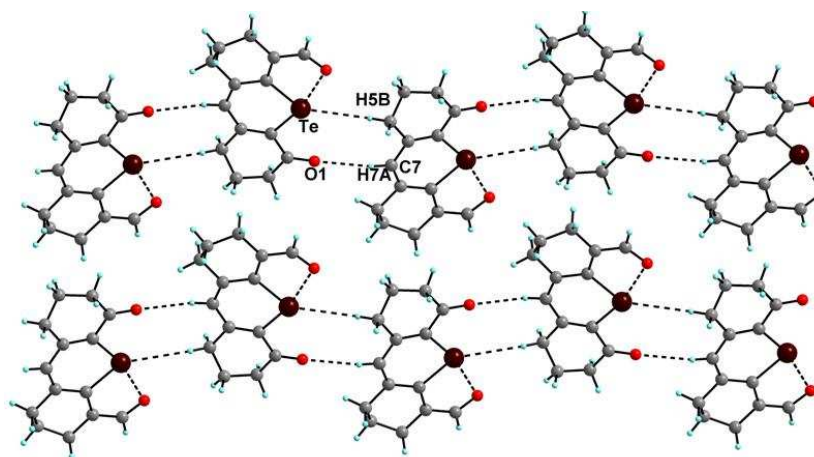


Figure S44. Chain structure of **38** showing intermolecular Te...O and O...H-C interaction

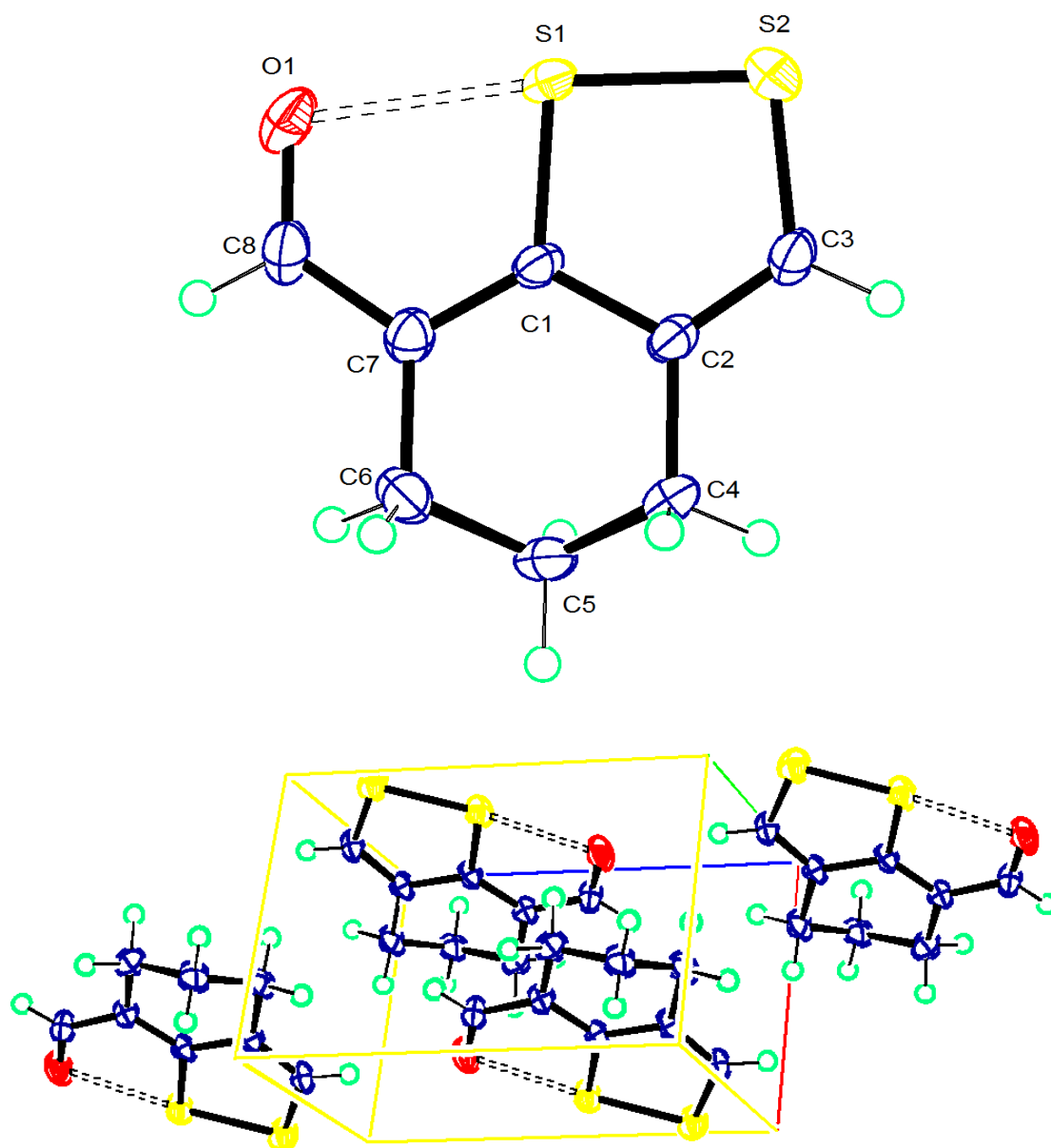


Figure S45. ORTEP diagram of compound **33** and its unit cell packing, thermal ellipsoids are drawn at 50% probability.

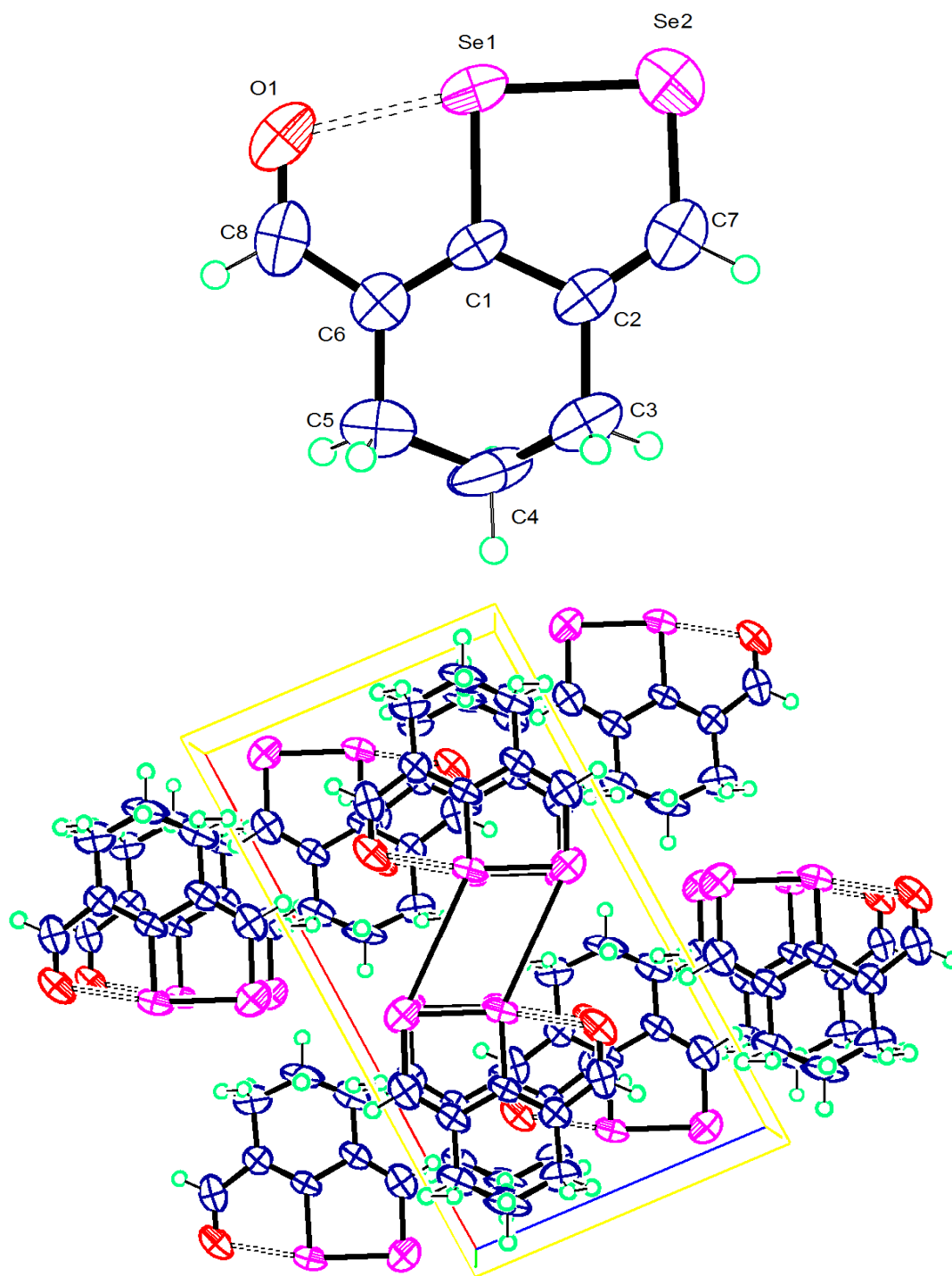


Figure S46. ORTEP diagram of compound **34** and its unit cell packing, thermal ellipsoids are drawn at 50% probability.

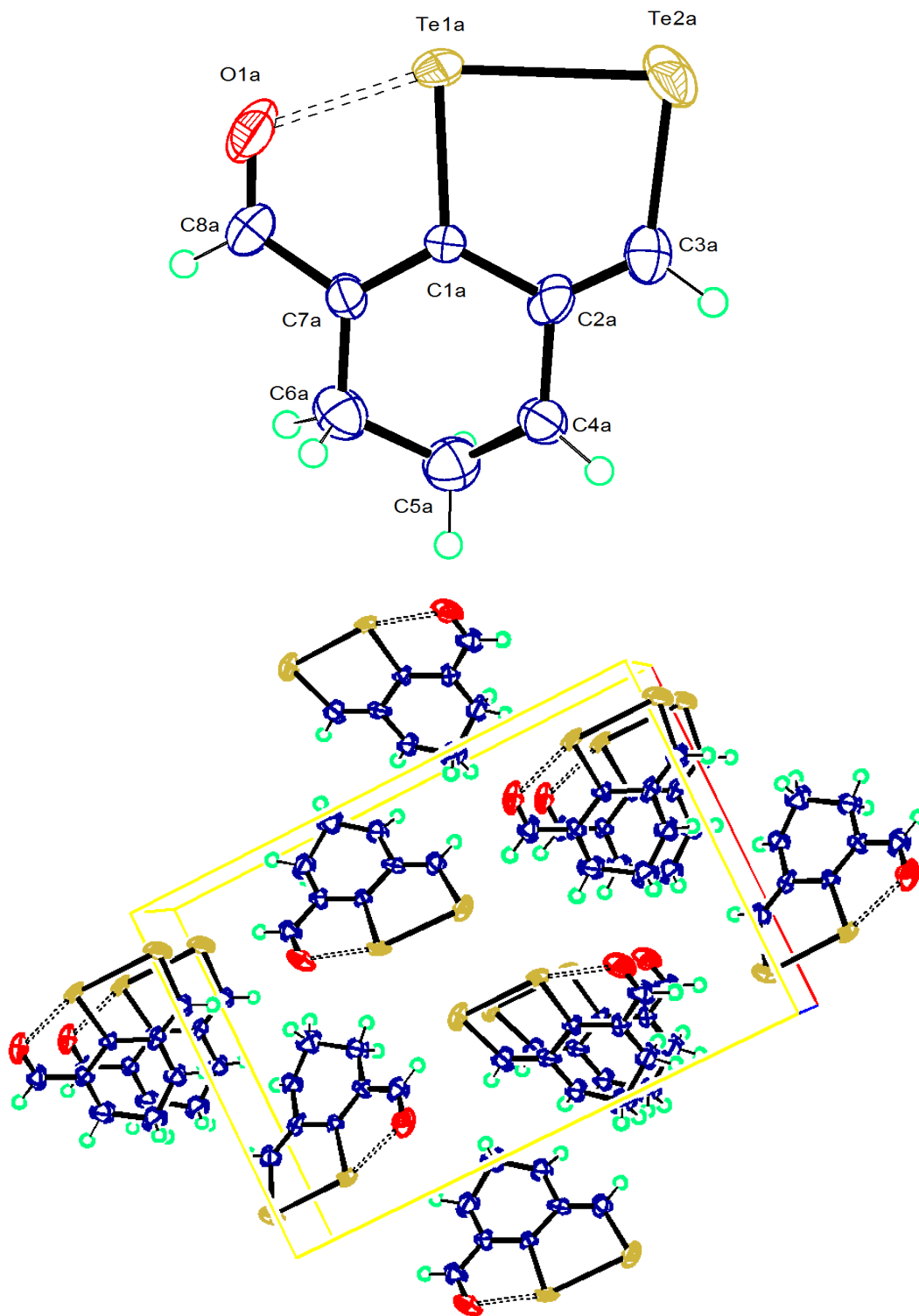


Figure S47. ORTEP diagram of compound **36** and its unit cell packing, thermal ellipsoids are drawn at 50% probability.

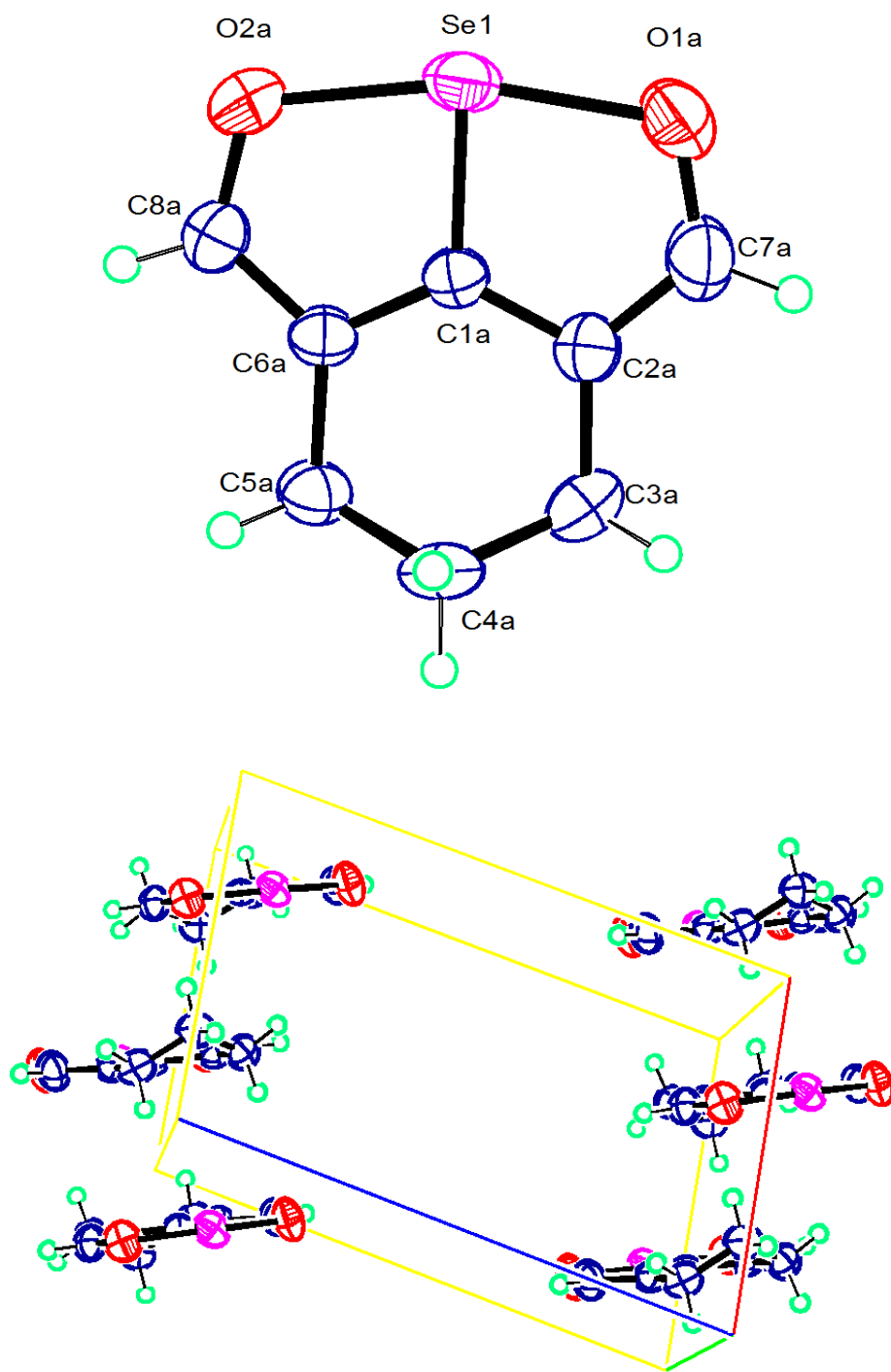


Figure S48. ORTEP diagram of compound **35** and its unit cell packing, thermal ellipsoids are drawn at 50% probability.

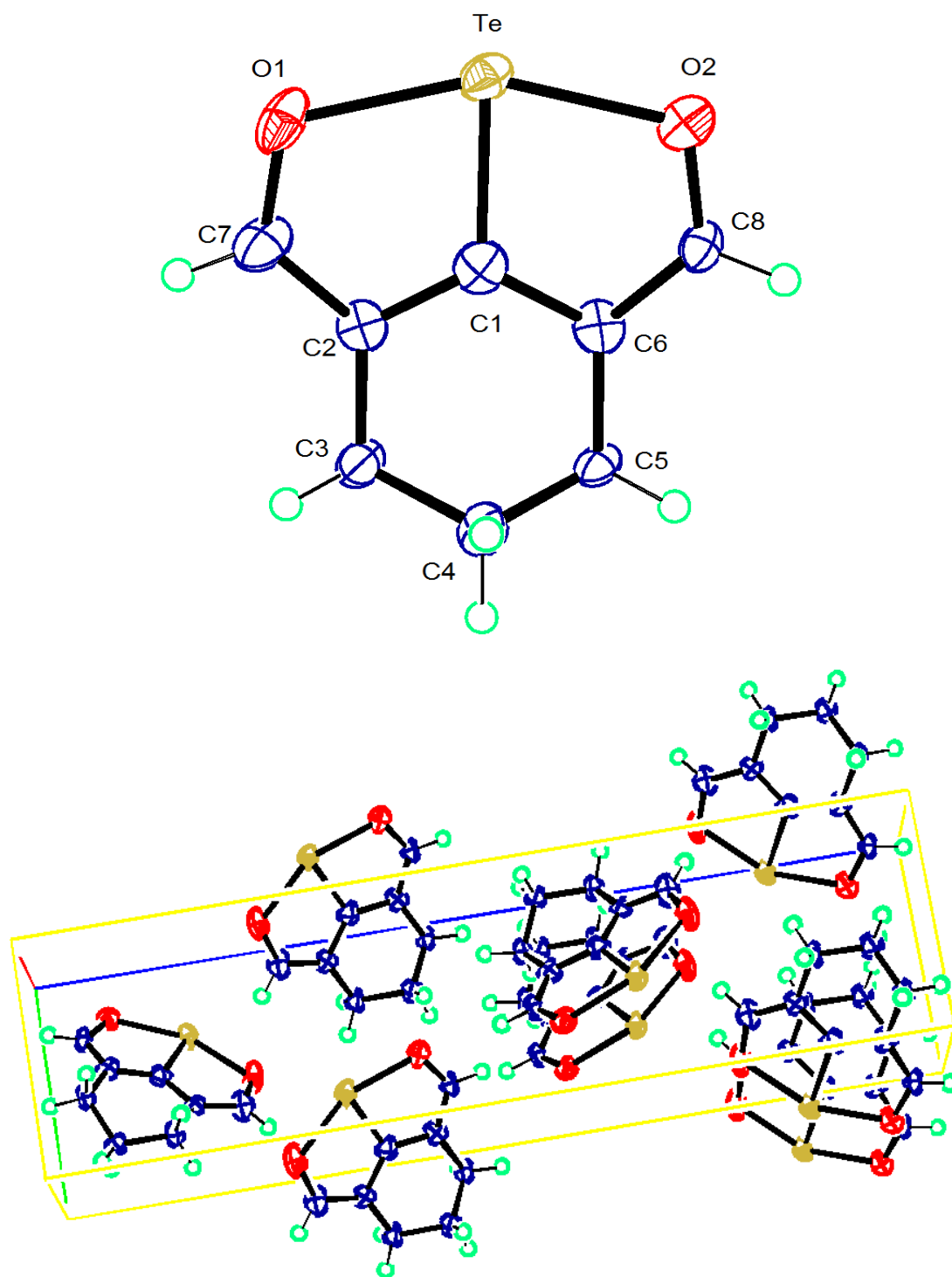


Figure S49. ORTEP diagram of compound **37** and its unit cell packing, thermal ellipsoids are drawn at 50% probability.

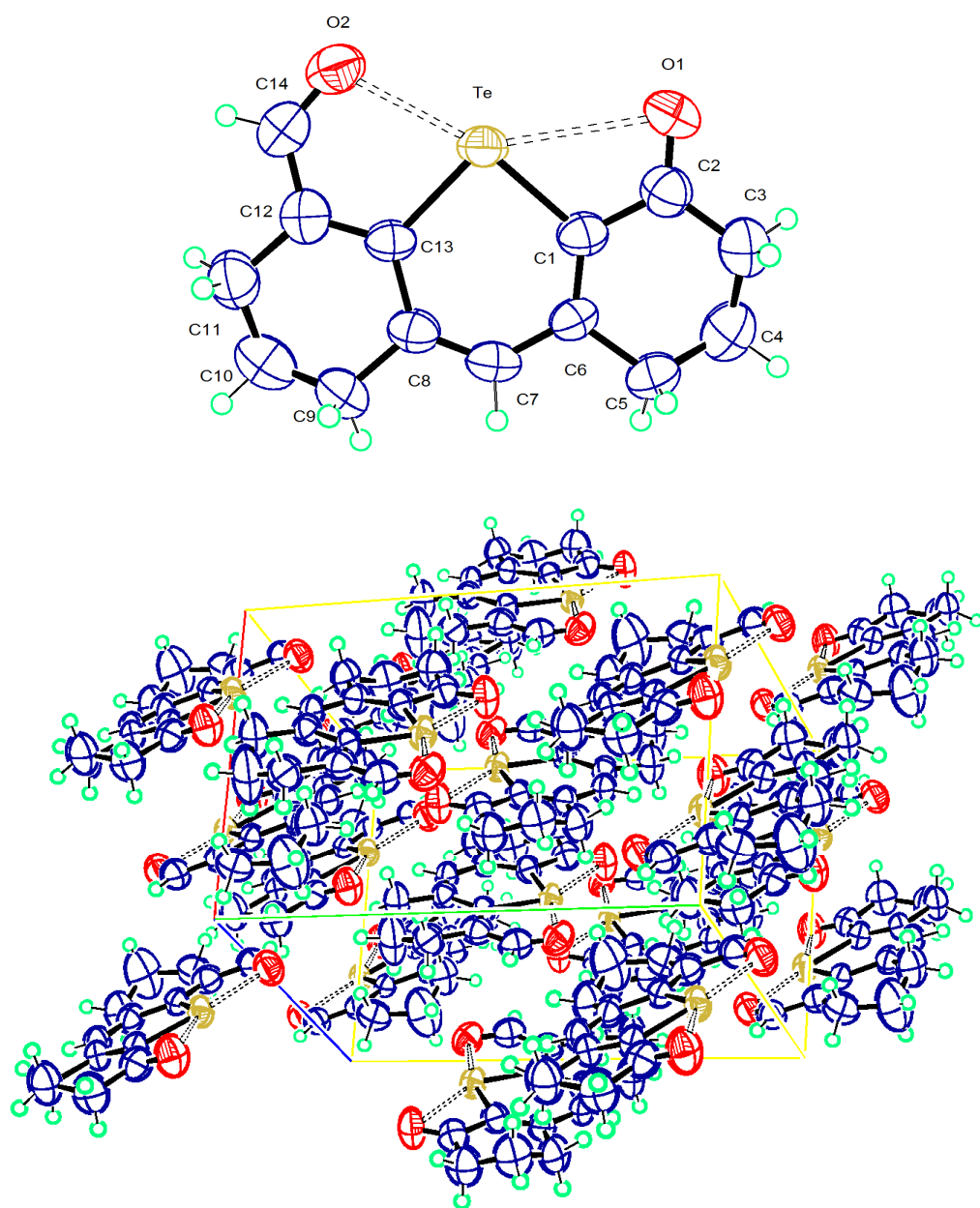


Figure S50. ORTEP diagram of compound **38** and its unit cell packing, thermal ellipsoids are drawn at 50% probability.

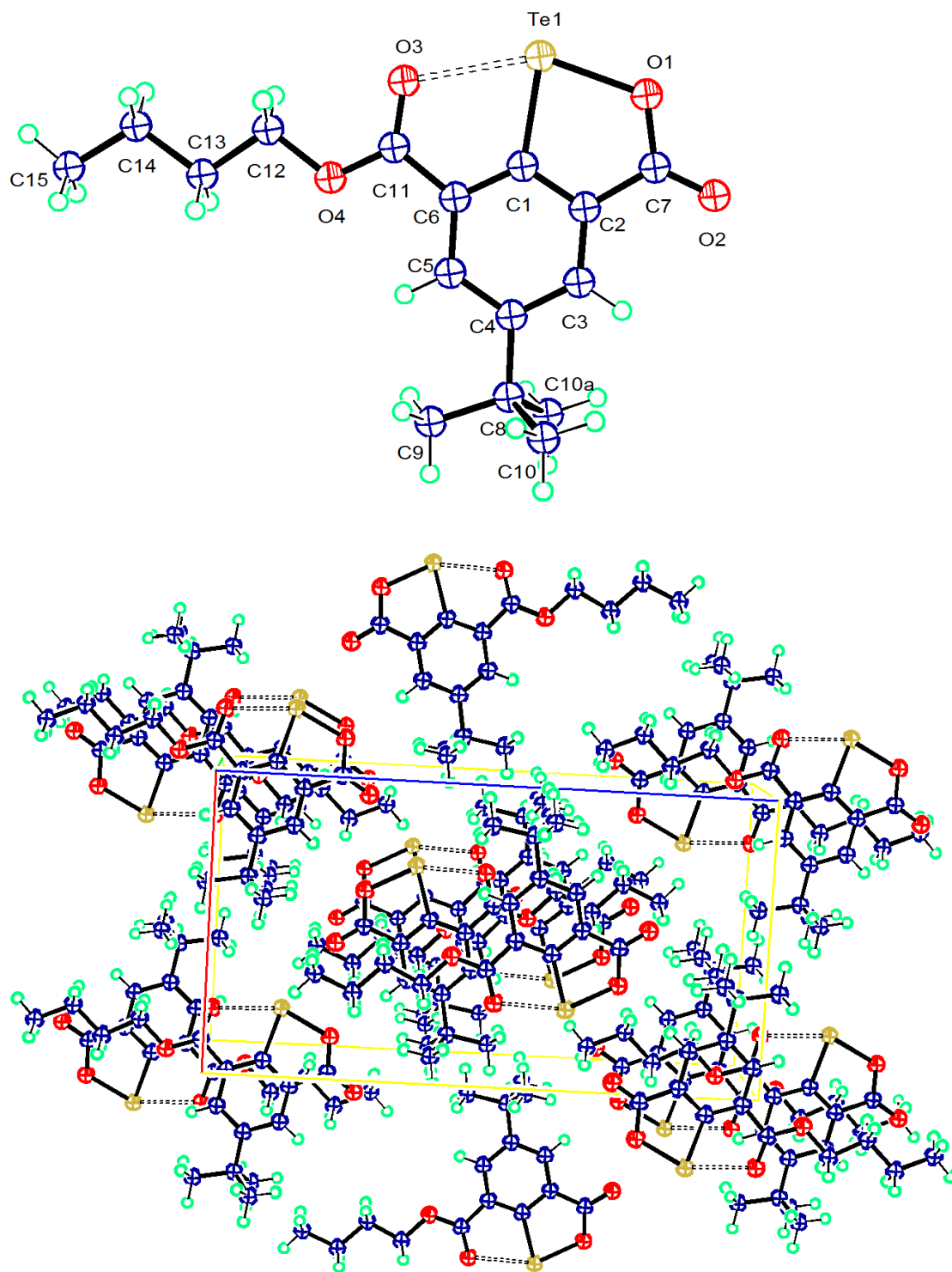
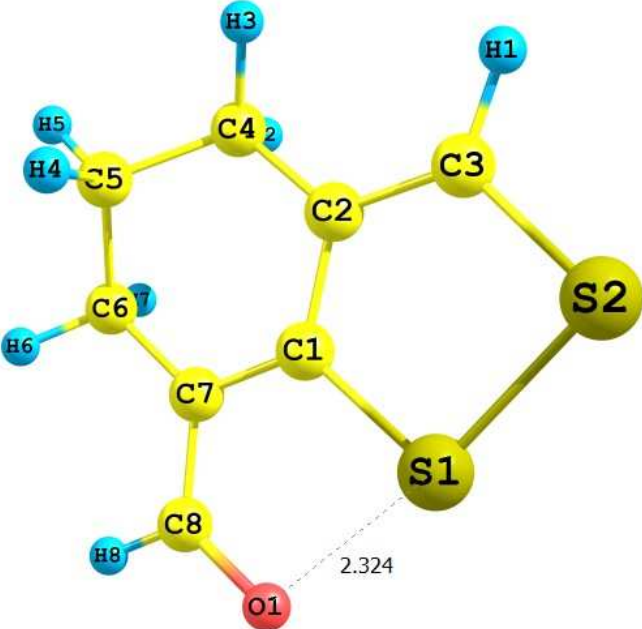
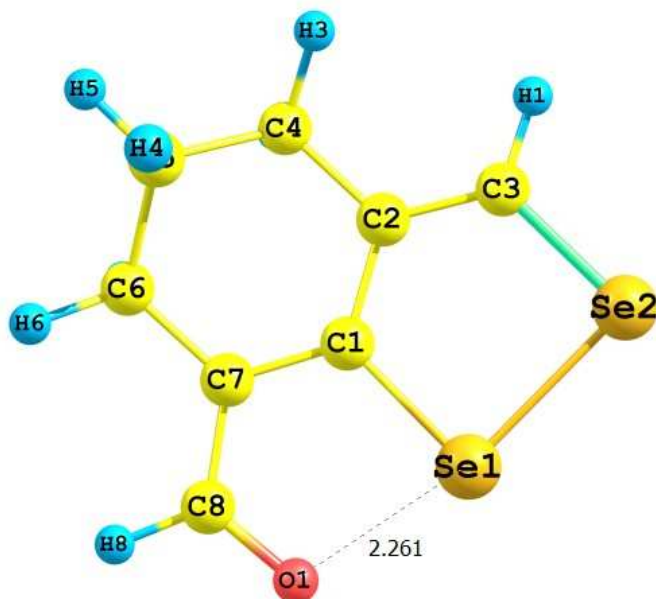


Figure S51. ORTEP diagram of compound **40** and its unit cell packing, thermal ellipsoids are drawn at 50% probability.

S3. Optimized structures of 33-40

Table S3. Optimized structures of **33-40** using at mpw1pw91 level of theory

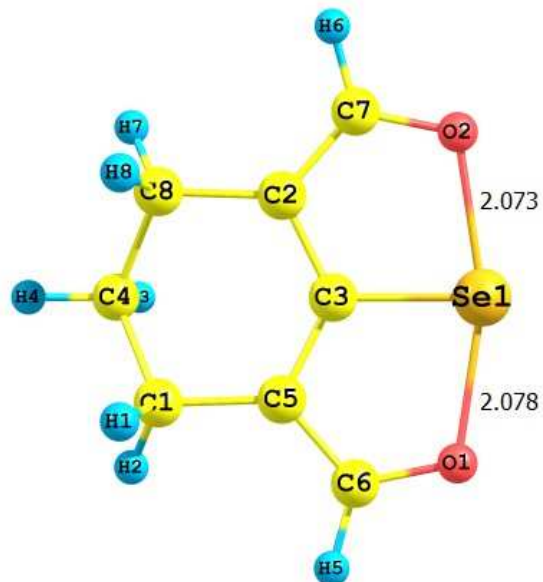
 <p style="text-align: center;">33</p>			
Electronic Energy = -405.158344754 a.u.			
16	-1.273687000	1.185256000	0.029289000
16	-2.643738000	-0.477747000	0.050249000
8	0.418527000	2.777483000	0.023256000
6	0.132100000	0.138535000	-0.065227000
6	-0.112268000	-1.273035000	-0.102653000
6	-1.403161000	-1.672451000	-0.039049000
1	-1.717633000	-2.708800000	-0.043699000
6	1.072962000	-2.194700000	-0.218761000
1	1.282591000	-2.372450000	-1.280393000
1	0.834687000	-3.164823000	0.222803000
6	2.310360000	-1.585775000	0.440392000
1	2.137238000	-1.494038000	1.517180000
1	3.166798000	-2.250282000	0.305030000
6	2.612544000	-0.206166000	-0.141255000
1	3.437084000	0.260670000	0.405453000
1	2.955212000	-0.317953000	-1.178000000
6	1.400777000	0.683484000	-0.083641000
6	1.453377000	2.095463000	-0.022844000
1	2.434455000	2.595550000	-0.008797000



34

Electronic Energy = -403.396311371 a.u.

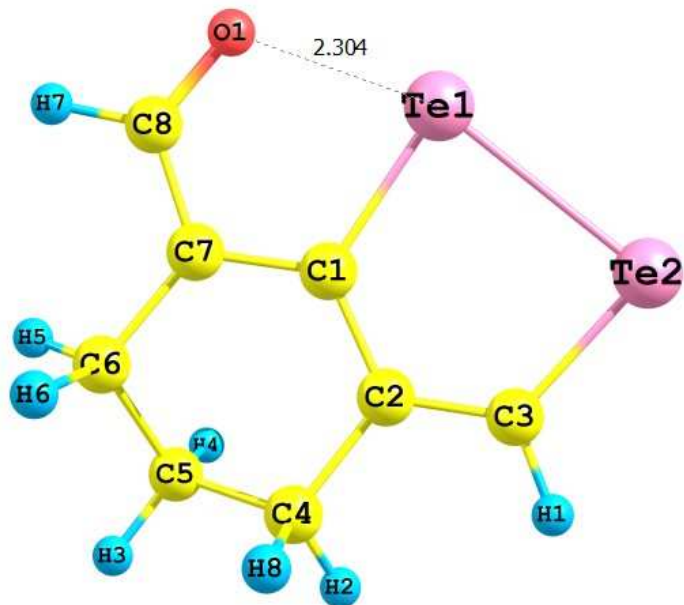
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6	0.728159000	-0.000852000	-0.073894000
6	0.416202000	-1.395953000	-0.110785000
6	-0.875436000	-1.804454000	-0.057988000
1	-1.146427000	-2.853609000	-0.067847000
6	1.572819000	-2.362459000	-0.223375000
1	1.784977000	-2.539130000	-1.284903000
1	1.289959000	-3.326091000	0.205987000
6	2.829014000	-1.816157000	0.451830000
1	2.647843000	-1.715518000	1.526593000
1	3.655106000	-2.520117000	0.326348000
6	3.201478000	-0.454233000	-0.128026000
1	4.040652000	-0.021308000	0.424084000
1	3.544544000	-0.583367000	-1.162343000
6	2.026547000	0.484596000	-0.083687000
6	2.143822000	1.883905000	-0.025470000
1	3.136122000	2.352461000	-0.006078000
34	-0.675601000	1.260262000	0.015301000
34	-2.273358000	-0.582647000	0.027050000



35

Electronic Energy = -469.354871183 a.u.

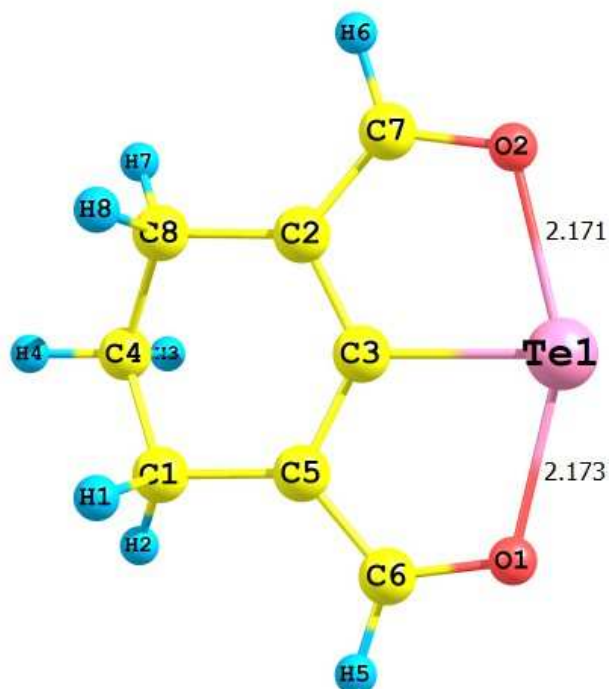
34	1.606369000	-0.000042000	0.030965000
8	1.309765000	2.012290000	0.027025000
6	-2.367578000	1.281864000	-0.175902000
1	-2.685706000	1.370683000	-1.221609000
1	-2.763991000	2.156636000	0.346213000
8	1.310789000	-2.010948000	0.026827000
6	-0.865649000	-1.247379000	-0.095961000
6	-0.240869000	0.000160000	-0.072063000
6	-2.962290000	-0.000452000	0.428471000
1	-2.773225000	-0.000171000	1.506570000
1	-4.046273000	-0.000745000	0.292759000
6	-0.866162000	1.247228000	-0.095948000
6	0.049709000	2.277789000	-0.030818000
1	-0.224602000	3.332319000	-0.021427000
6	0.050564000	-2.277353000	-0.031038000
1	-0.222616000	-3.332095000	-0.021729000
6	-2.367086000	-1.282825000	-0.175314000
1	-2.762745000	-2.157361000	0.347804000
1	-2.685665000	-1.372760000	-1.220758000



36

Electronic Energy = -401.044231794 a.u.

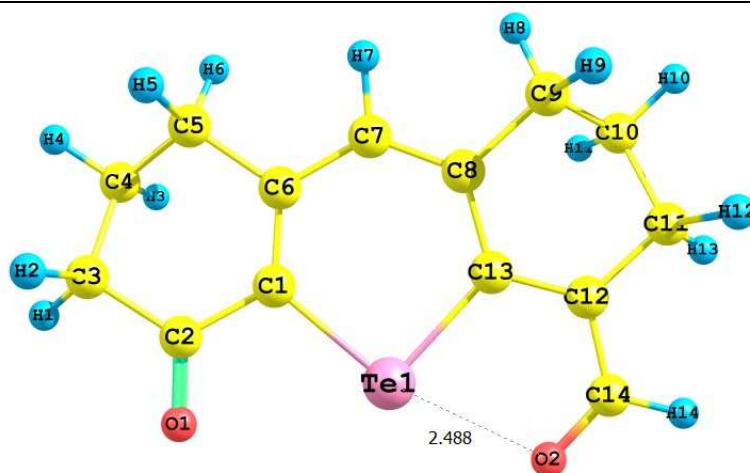
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52	2.194774000	0.572529000	0.015907000
8	-1.881173000	-2.378705000	0.008432000
6	-1.127427000	0.211177000	-0.075563000
6	-0.671408000	1.567395000	-0.109484000
6	0.641866000	1.913475000	-0.064384000
1	0.923202000	2.960607000	-0.077529000
6	-1.734768000	2.645290000	-0.218941000
1	-1.351614000	3.576785000	0.203110000
6	-3.037770000	2.237780000	0.461064000
1	-3.784233000	3.026670000	0.340710000
1	-2.865790000	2.112844000	1.534807000
6	-3.548640000	0.928777000	-0.127963000
1	-4.432472000	0.579722000	0.413769000
1	-3.866170000	1.099616000	-1.164309000
6	-2.476427000	-0.127207000	-0.084567000
6	-2.779267000	-1.495016000	-0.028743000
1	-3.823539000	-1.825319000	-0.009413000
1	-1.931448000	2.837523000	-1.280937000



37

Electronic Energy = -468.190151591 a.u.

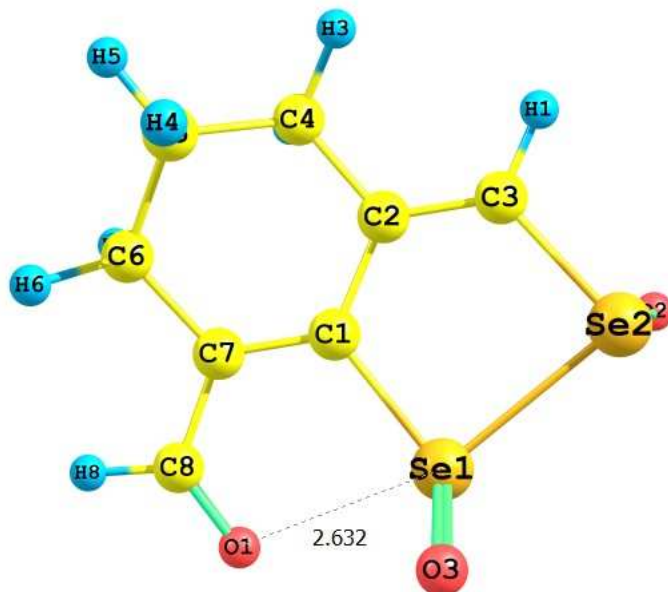
8	0.994452000	2.117647000	0.014237000
6	-2.671742000	1.281057000	-0.170928000
1	-2.994605000	1.368487000	-1.215484000
1	-3.066686000	2.156569000	0.351822000
8	0.996447000	-2.115702000	0.014376000
6	-1.167084000	-1.247640000	-0.098258000
6	-0.544953000	0.000200000	-0.077669000
6	-3.263136000	-0.001104000	0.436474000
1	-3.067965000	-0.001204000	1.513621000
1	-4.348099000	-0.001575000	0.307121000
6	-1.168125000	1.247124000	-0.098236000
6	-0.280068000	2.307760000	-0.038203000
1	-0.609022000	3.347501000	-0.029196000
6	-0.278368000	-2.307249000	-0.038061000
1	-0.605675000	-3.347381000	-0.029166000
6	-2.670663000	-1.282543000	-0.171400000
1	-3.065181000	-2.158584000	0.350751000
1	-2.993078000	-1.369631000	-1.216129000
52	1.482461000	0.000089000	0.024528000



38

Electronic Energy = -700.431355962 a.u.

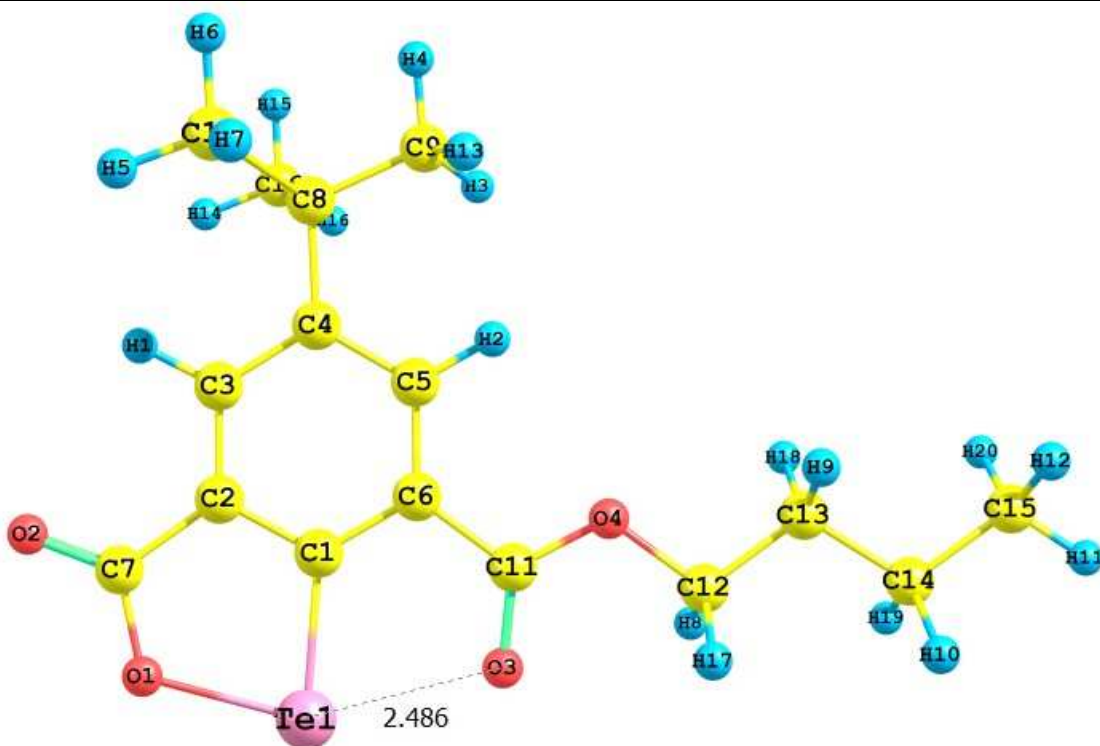
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8	2.920033000	-1.867815000	-0.006235000
8	-2.250749000	-2.386978000	0.060298000
6	1.586505000	0.051457000	-0.039384000
6	2.881041000	-0.651829000	-0.046784000
6	4.134466000	0.183991000	-0.143383000
1	4.956643000	-0.388702000	0.287609000
1	4.353300000	0.306508000	-1.212285000
6	3.952937000	1.546941000	0.509915000
1	3.800879000	1.415314000	1.586268000
1	4.853614000	2.152875000	0.387272000
6	2.748233000	2.264731000	-0.080594000
1	2.963088000	2.560459000	-1.116607000
1	2.549909000	3.191992000	0.464141000
6	1.498625000	1.410951000	-0.075665000
6	0.253302000	2.107624000	-0.142025000
1	0.342405000	3.189872000	-0.193980000
6	-1.025042000	1.628428000	-0.161515000
6	-2.137268000	2.645623000	-0.310664000
1	-1.770829000	3.628997000	-0.009188000
1	-2.394533000	2.718685000	-1.375577000
6	-3.386386000	2.260496000	0.467632000
1	-4.159359000	3.022820000	0.344980000
1	-3.150395000	2.203199000	1.535048000
6	-3.878044000	0.910102000	-0.023773000
1	-4.285828000	1.021350000	-1.037306000
1	-4.701857000	0.546166000	0.597758000
6	-2.765121000	-0.104454000	-0.023740000
6	-1.424665000	0.242569000	-0.068622000
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1	-4.166893000	-1.751376000	0.113876000



39

Electronic Energy = -553.693419598 a.u.

8	-1.944649000	-2.477916000	-0.517849000
6	-0.953946000	0.150003000	-0.118843000
6	-0.476767000	1.520997000	-0.062370000
6	0.828002000	1.806985000	0.070857000
1	1.199358000	2.825684000	0.052653000
6	-1.525408000	2.595822000	-0.203214000
1	-1.745320000	2.723487000	-1.270080000
1	-1.134993000	3.547153000	0.160457000
6	-2.800920000	2.199567000	0.534883000
1	-2.580104000	2.085540000	1.600470000
1	-3.551427000	2.987109000	0.443845000
6	-3.343873000	0.887768000	-0.013572000
1	-4.137763000	0.498649000	0.632693000
1	-3.809195000	1.052986000	-0.994306000
6	-2.270372000	-0.156211000	-0.154353000
6	-2.702202000	-1.542270000	-0.393930000
1	-3.793923000	-1.692415000	-0.484356000
34	0.378303000	-1.311191000	-0.102428000
34	2.203292000	0.470995000	0.223676000
8	3.076610000	0.649455000	-1.171689000
8	0.274546000	-1.951227000	1.411970000



40

Electronic Energy = -930.776916212

52	0.955587000	-2.577607000	0.000000000
8	3.000152000	-2.238895000	0.000000000
8	4.558620000	-0.639029000	0.000000000
8	-1.381768000	-1.723628000	0.000003000
8	-2.502928000	0.215079000	0.000005000
6	0.990659000	-0.536750000	0.000000000
6	2.262475000	0.006758000	-0.000004000
6	2.399660000	1.384247000	-0.000003000
1	3.406433000	1.785731000	-0.000007000
6	1.278767000	2.233103000	0.000002000
6	0.010452000	1.652979000	0.000004000
1	-0.879214000	2.267012000	0.000007000
6	-0.139999000	0.262631000	0.000003000
6	3.399641000	-0.964985000	-0.000011000
6	1.491178000	3.747995000	0.000001000
6	0.168633000	4.517191000	0.000007000
1	-0.430995000	4.297252000	0.886914000
1	0.371095000	5.590432000	0.000011000
6	2.284356000	4.146301000	-1.254691000
1	3.261459000	3.660895000	-1.288157000
1	2.448976000	5.226827000	-1.268533000
1	1.742726000	3.872547000	-2.163042000
6	-1.390015000	-0.489905000	0.000005000
6	-3.744137000	-0.521856000	0.000004000
1	-3.765262000	-1.164351000	0.882881000

6	-4.873251000	0.480232000	-0.000001000
1	-4.776953000	1.125693000	-0.878631000
6	-6.238980000	-0.198851000	-0.000003000
1	-6.320726000	-0.852269000	-0.875492000
6	-7.389780000	0.797650000	-0.000006000
1	-8.355004000	0.288153000	-0.000009000
1	-7.354558000	1.442268000	-0.881978000
1	-0.430999000	4.297260000	-0.886900000
6	2.284368000	4.146304000	1.254684000
1	3.261470000	3.660896000	1.288145000
1	2.448993000	5.226829000	1.268519000
1	1.742745000	3.872557000	2.163041000
1	-3.765258000	-1.164356000	-0.882871000
1	-4.776958000	1.125697000	0.878627000
1	-6.320729000	-0.852268000	0.875486000
1	-7.354563000	1.442267000	0.881968000

S4. Molecular graphs of 33-40 obtained from AIM

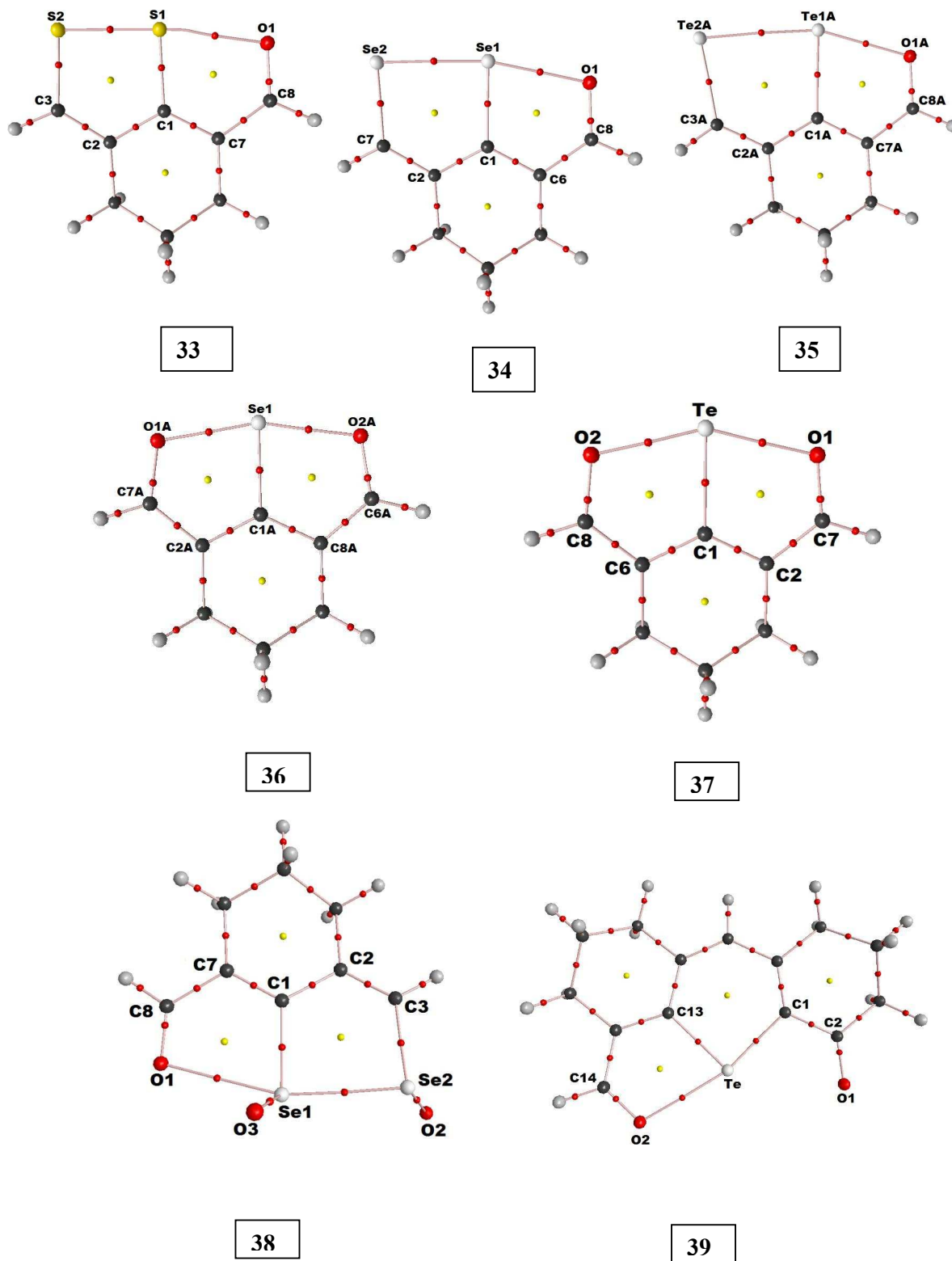


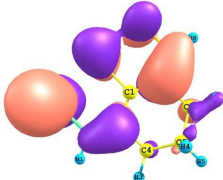
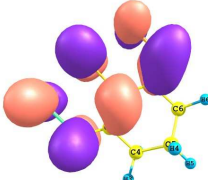
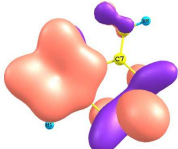
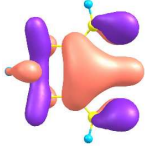
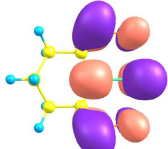
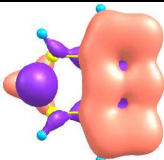
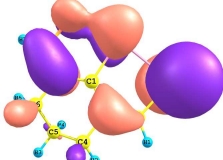
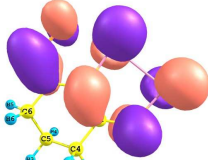
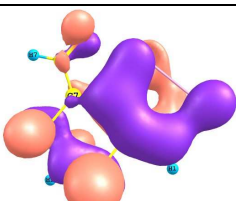
Figure S52. The molecular graphs for the compounds 33-39 (Obtained from AIM calculations)

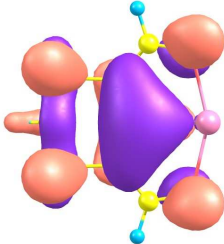
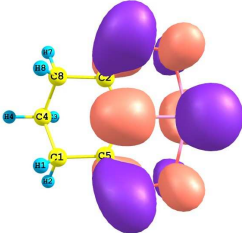
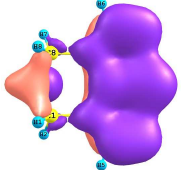
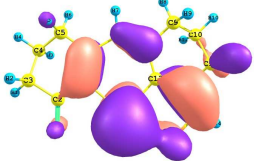
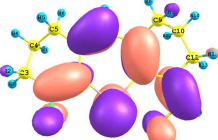

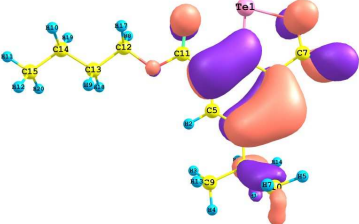
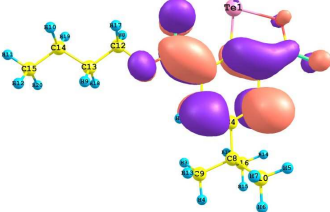


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S5. Representative molecular orbitals for 33-40

Table S4. Pictorial representation of molecular orbital

Compound	HOMO	LUMO
34	 HOMO	 LUMO
	 HOMO-6	
35	 HOMO-3	 LUMO
	 HOMO-11	
36	 HOMO	 LUMO
	 HOMO-6	

37	 <p>HOMO</p>	 <p>LUMO</p>
	 <p>HOMO-3</p>	
38	 <p>HOMO</p>	 <p>LUMO</p>
	 <p>HOMO-7</p>	
40	 <p>HOMO</p>	 <p>LUMO</p>

S6. Interpretation of O···Se bond strengths calculated for compound **34** and **39** using NBO analysis

Within NBO method, second order perturbation theory can be used to estimate the stabilization energy associated with delocalization of electron density from an i^{th} donor orbital to a j^{th} acceptor orbital as $E(2)$ or $\Delta E_{ij} = q_i \times F(i,j)^2 / (\epsilon_j - \epsilon_i)$. Where, q_i is the donor orbital occupancy, ϵ_i and ϵ_j are the respective orbital energies, and $F(i,j)$ is the off-diagonal Fock matrix element expressed in the NBO basis. $F(i,j)$ is resonance integral which is a measure of strength of bonding interaction arising out of the orbital overlap ($i \rightarrow j$). The $F(i,j)$ value computed for O···Se interaction in **39** is two times lower than the corresponding $F(i,j)$ value computed for compound **34** (Table S5). The weaker orbital overlap in the former could be attributed to the increase of ionic character in the O···Se bonding. It is further supported by the results obtained in AIM analysis (Table 4).

Table S5. Computed q_i , $\epsilon_j - \epsilon_i$, and $F(i,j)$ for **34** and **39**

Entry	q_i	$\epsilon_j - \epsilon_i$	$F(i,j)$
34	1.764	0.33	0.100
39	1.897	0.20	0.042

S7. Correlation of $\pi_{C=C} \rightarrow \pi^*_{C=O}$ stabilization energy with C=O IR stretching frequencies of compound **33**, **34** and **36**

As we can observe from the data shown for **33**, **34** and **36** (Table S6), higher the $\pi_{C=C} \rightarrow \pi^*_{C=O}$ stabilization energy lower will be the $\nu_{C=O}$. In other words, stronger the $E \cdots O$ interaction lower will be the $\nu_{C=O}$. Stronger $E \cdots O$ interaction increases (e. g. **36**) the electron density of the $\pi^*_{C=O}$ orbital. Hence, it reduces the double bond character and concomitantly the $\nu_{C=O}$ stretching frequencies.

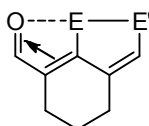


Table S6. Computed $E(\pi_{C=C} \rightarrow \pi^*_{C=O})$ and experimental IR $\nu_{C=O}$ stretching frequencies

Entry	$E(\pi_{C=C} \rightarrow \pi^*_{C=O})^{\#}$ kcal/mol	$\nu_{C=O}$ cm ⁻¹
33	33.25	1597
34	36.02	1577
36	37.88	1534

[#] $E = E(2)$ or ΔE Stabilization energy resulting from $\pi_{C=C}$ to $\pi^*_{C=O}$ electron delocalization, obtained from NBO analysis.