

Supplementary Information

Isolation and reactivity of an unusually stable organoselenenyl azide

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Experimental

1) **Synthesis of [*o*-(2,6-diisopropylphenyliminomethinyl)phenyl] selenenyl chloride (4):** To a solution of bis[*o*-(2,6-diisopropylphenylimino-methinyl)phenyl]diselenide^{1c} (0.50 g, 0.73 mmol) in dichloromethane (30 mL) was added dropwise a solution of SO₂Cl₂ (0.10 g, 0.74 mmol) in dichloromethane (20 mL) at 0 °C. After the addition was complete the solution was allowed to come slowly at room temperature and the reaction mixture was allowed to stir at room temperature for 4 h. The solvent was removed under vacuum and the sticky solid so obtained was treated with hexane to obtain an off-white solid. The solid thus obtained was crystallized from dichloromethane/hexane. Yield: 0.20 g, 74 %; ¹H NMR (400 MHz, CDCl₃): δ 9.11 (d, *J* = 8.8 Hz, 1H, ArH), 8.94 (s, 1H, =CH-), 8.13 (d, *J* = 8.00, 1H, ArH), 7.80-7.83 (m, 1H, ArH), 7.62-7.79 (m, 1H, ArH), 7.46 (t, *J* = 8 Hz, ArH), 7.31 (s, 1H, ArH), 7.29 (s, 1H, ArH), 2.56-2.63 (m, 2H, -CH-), 1.13 (d, *J* = 7.2 Hz, 6H, -CH₃), 1.25 (d, *J* = 6.8 Hz, 6H, -CH₃). ¹³C NMR (400 MHz, CDCl₃): δ 28.8, 28.9, 67.3, 67.6, 81.1, 82.6, 121.3, 121.3, 124.3, 125.5, 125.7, 127.3, 127.5, 127.6, 131.4, 132.4, 145.6, 149.3, 163.0, 164.6. ⁷⁷Se NMR (500 MHz, CDCl₃): δ 1023. Anal. Calc. for C₁₅H₁₄NSeCl: C, 60.24; H, 5.85; N, 3.70. Found: C, 59.23; H, 5.26; N, 4.00

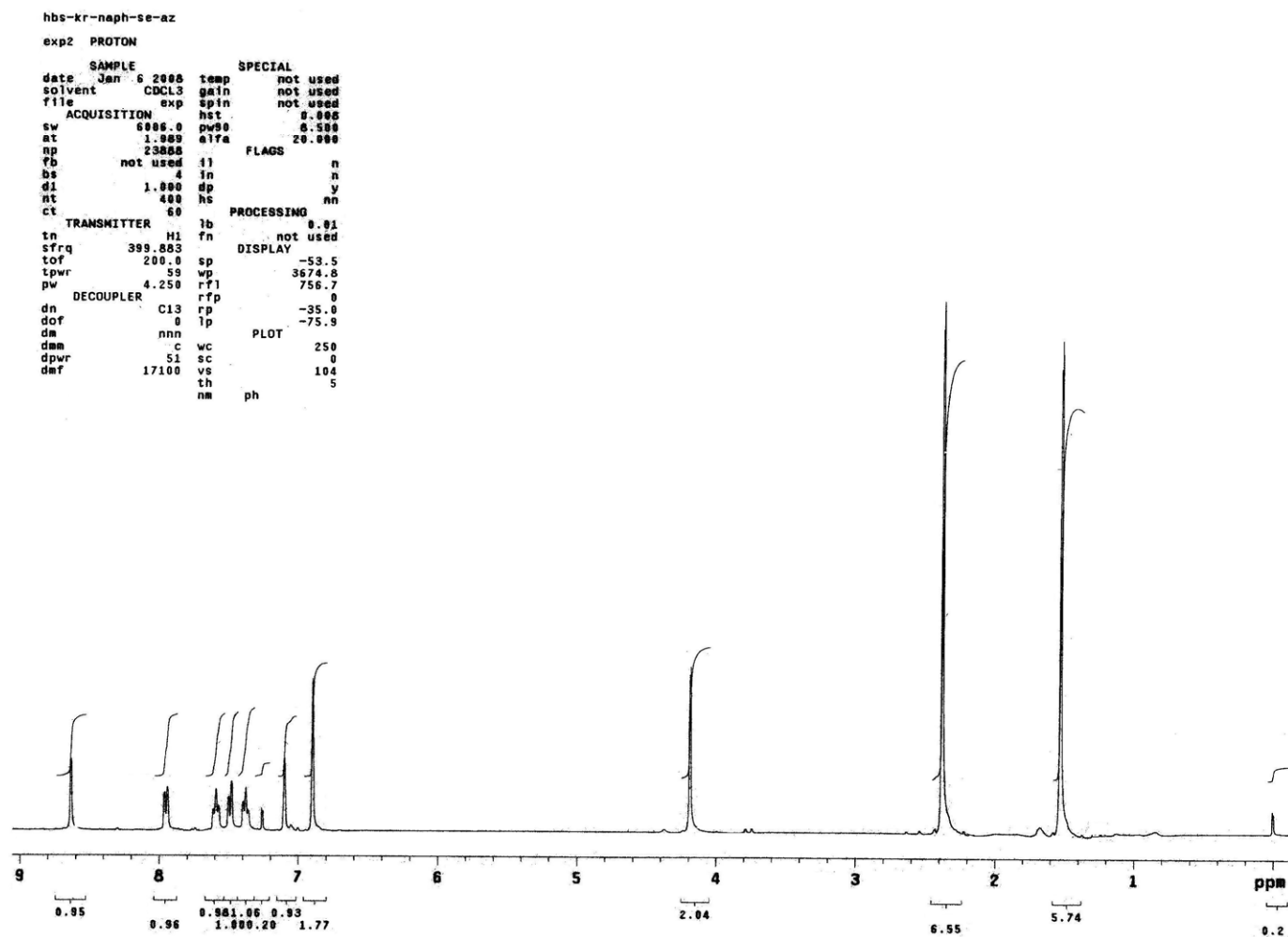


Figure S1: ^1H NMR spectrum of **2a**

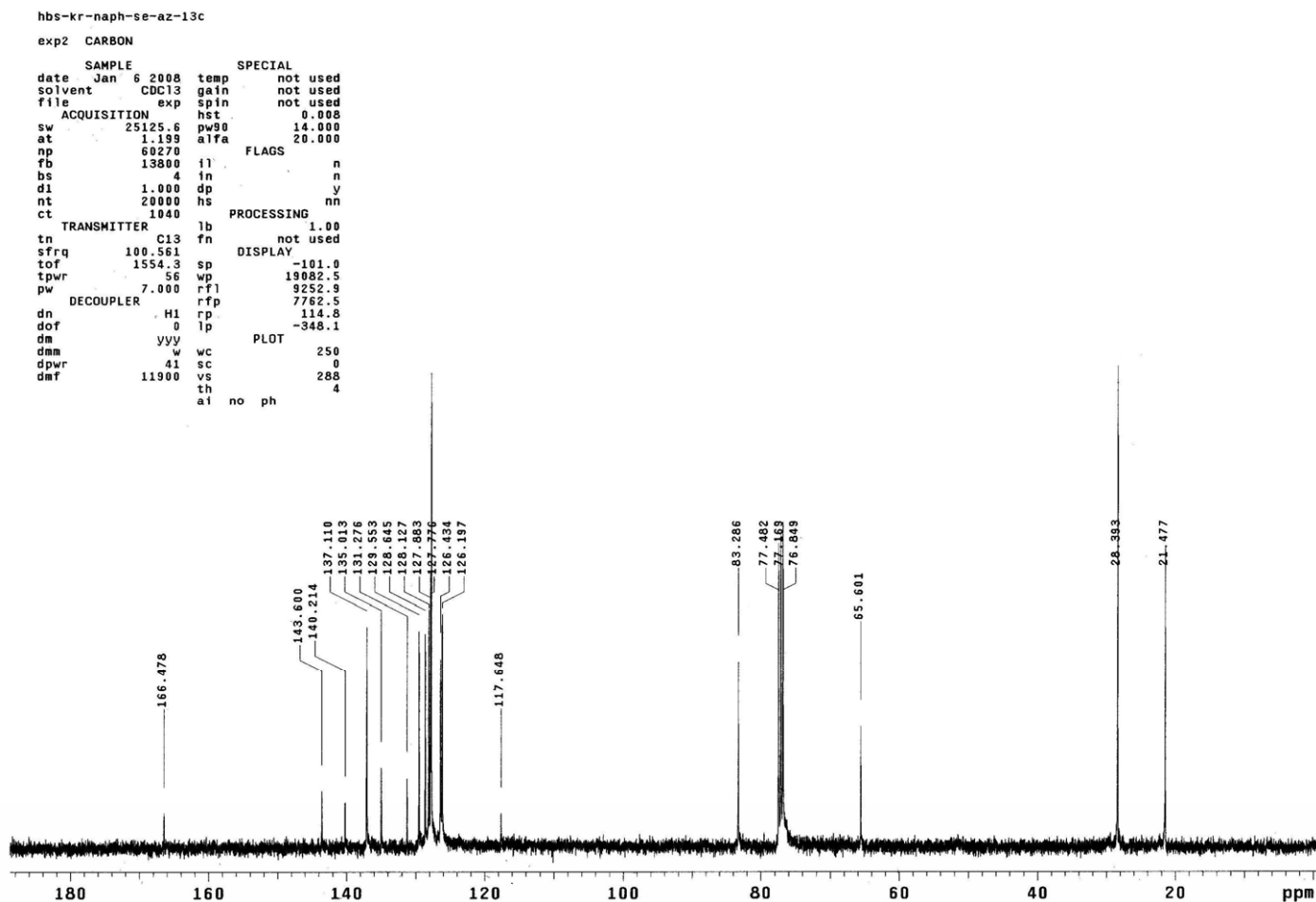


Figure S2: ^{13}C NMR spectrum of 2a

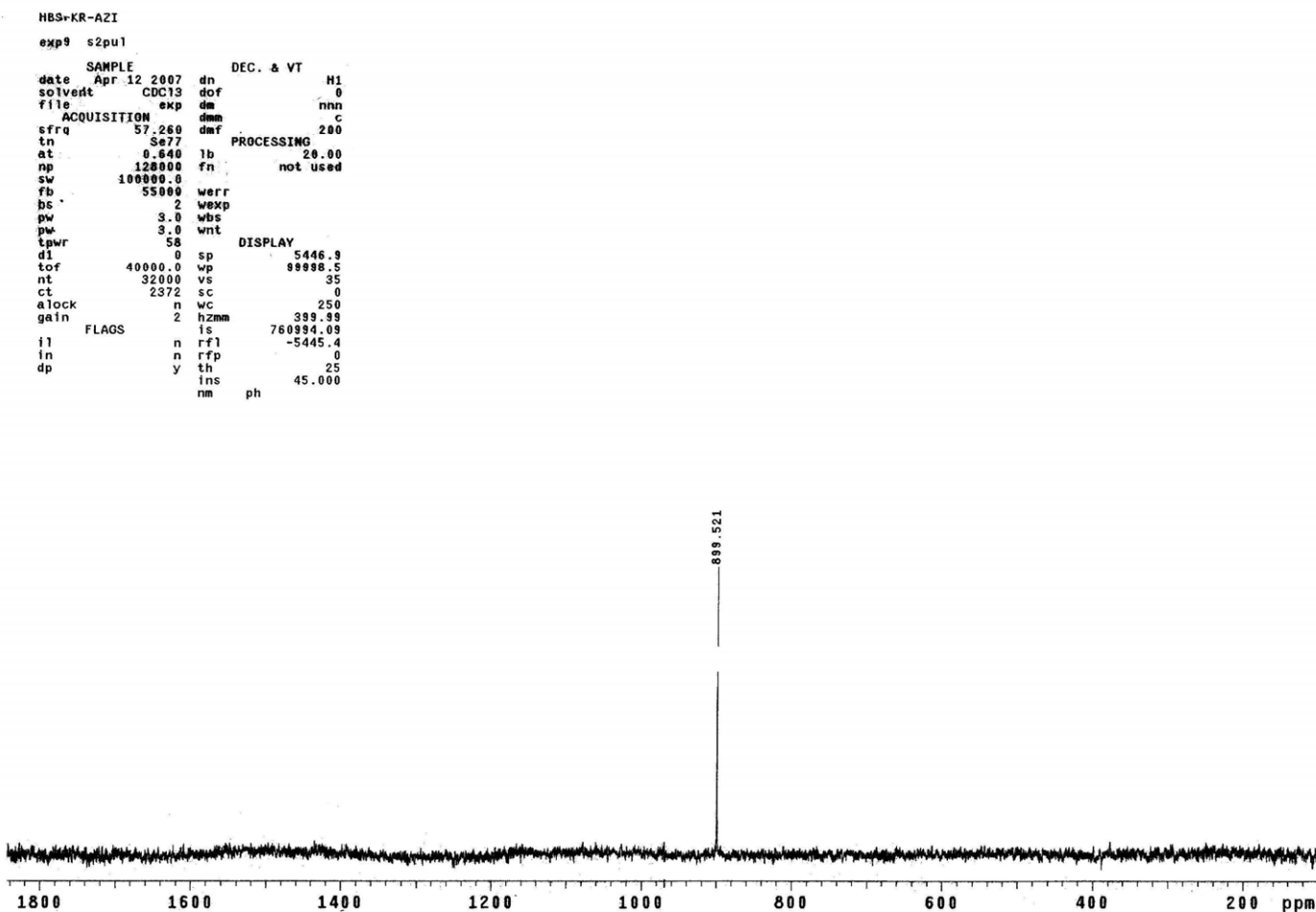
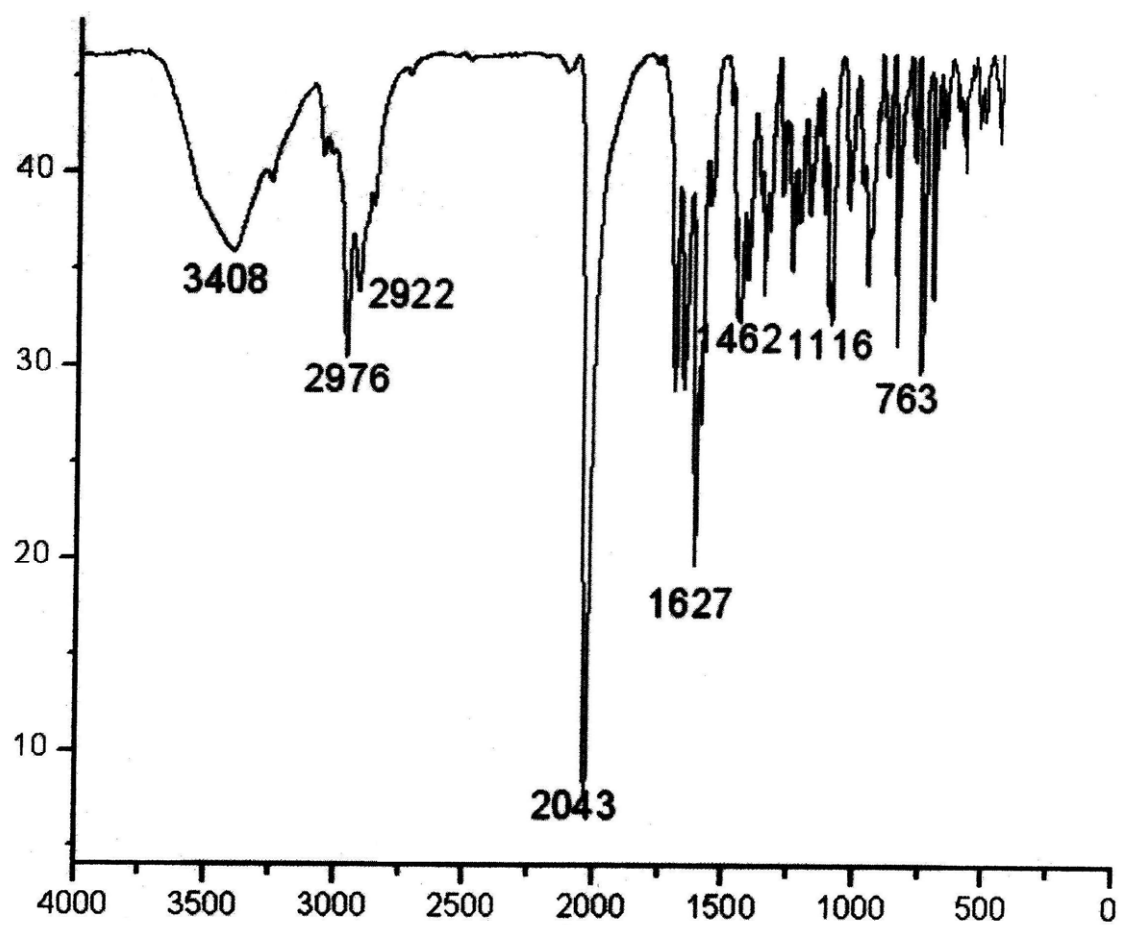


Figure S3: ^{77}Se NMR spectrum of **2a**



FigureS4: FT-IR spectrum of 2a

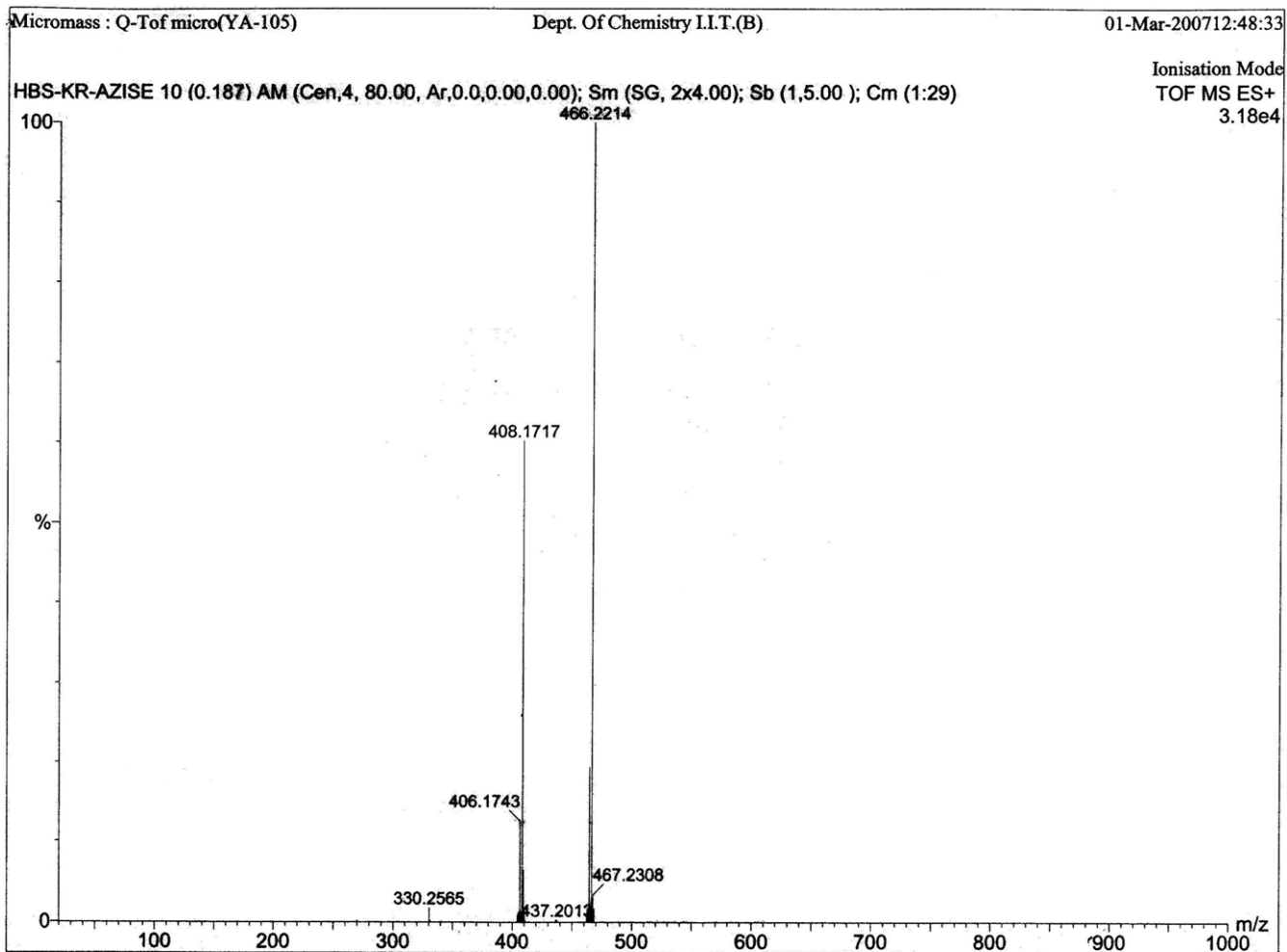


Figure S5: ES-MS spectrum of **2a**

Eager 300 Report

Page: 1 Sample: HBS-KRAZi (HBS-KRAZi)

```

Method Name      : sp300307
Method File      : G:\eager300\Eager 300 EA1112\SP300307.mth
Chromatogram     : HBS-KRAZi
Operator ID      : sp
Analysed         : 03/26/2007 14:34
Sample ID        : HBS-KRAZi (# 21)
Analysis Type    : UnkNown (Area)
Company Name     : C.E. Instruments
Printed          : 3/26/2007 15:43
Instrument N.    : Instrument #1
Sample weight    : 2.213
  
```

Calib. method : using 'K Factors'

!!! Warning missing one or more peaks.

Element Name	%	Ret.Time	Area	BC	Area ratio	K factor
Nitrogen	12.0309	43	275180	RS	12.597270	.103357E+07
Carbon	60.9591	65	3466511	RS	1.000000	.256616E+07
Hydrogen	4.9021	169	647510	RS	5.353602	.596870E+07
Totals	77.8921		4389201			

Figure S6: Elemental analysis (C, H, N) of 2a

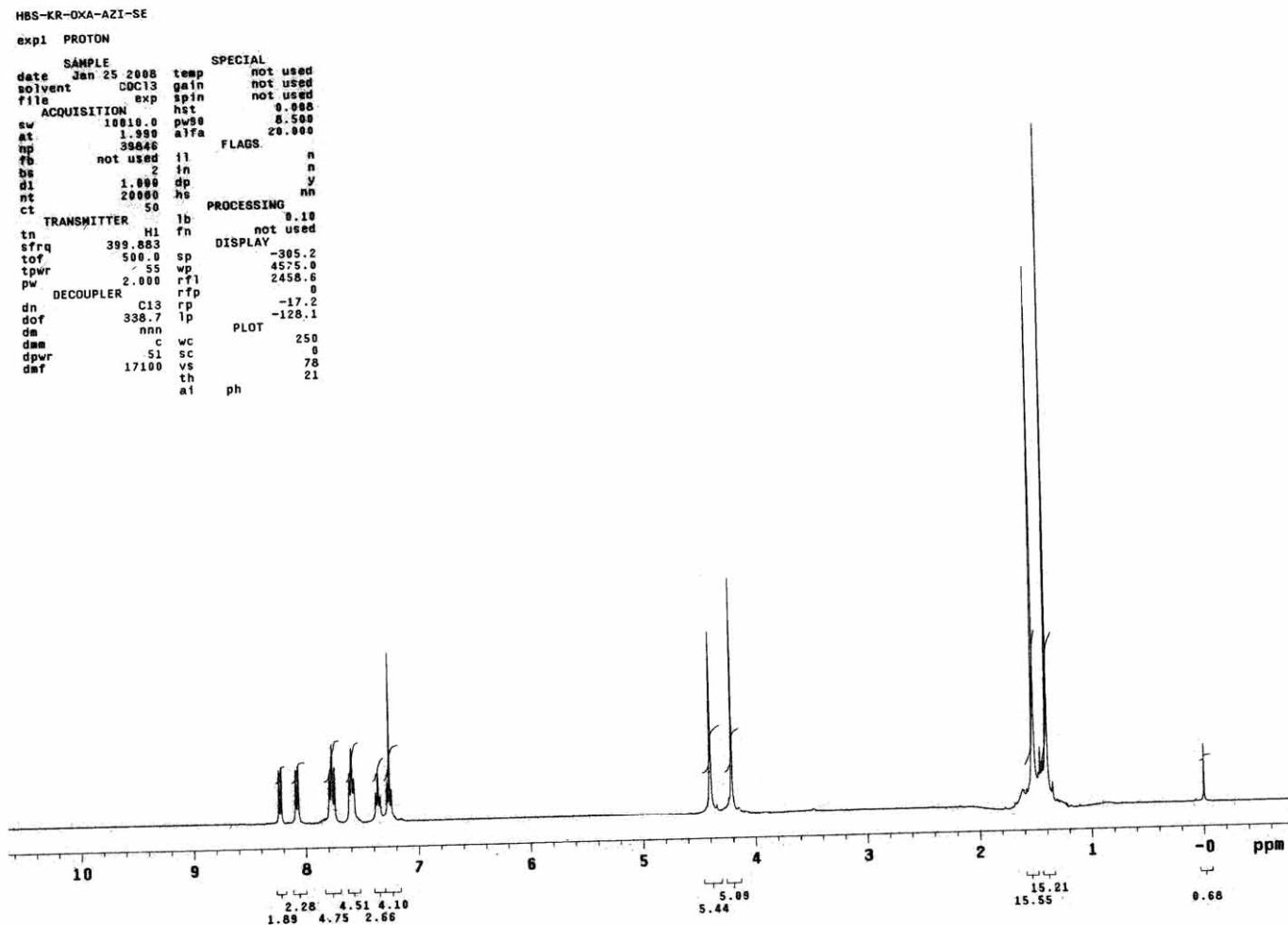
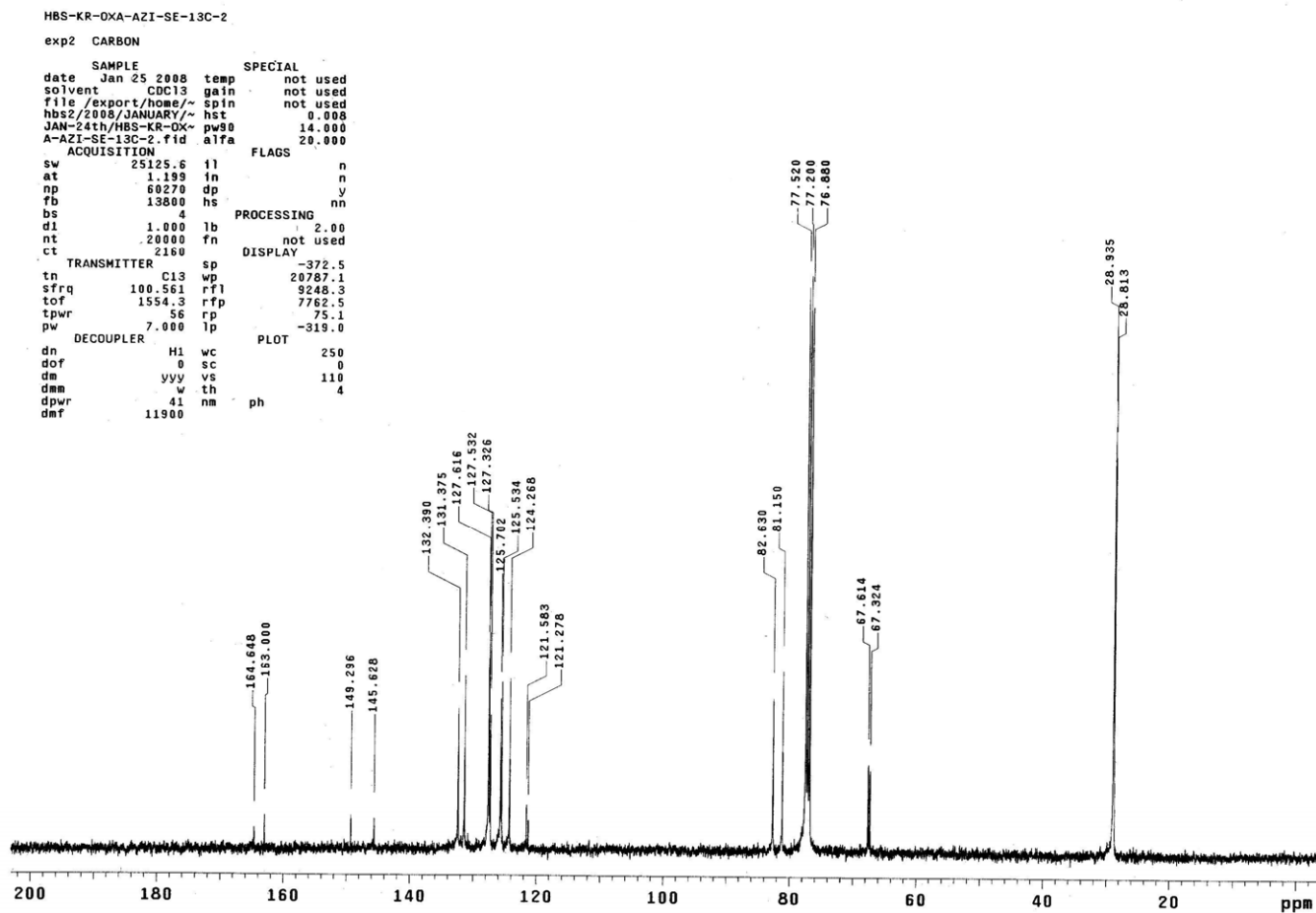


Figure S7: ^1H NMR spectrum of **3a**



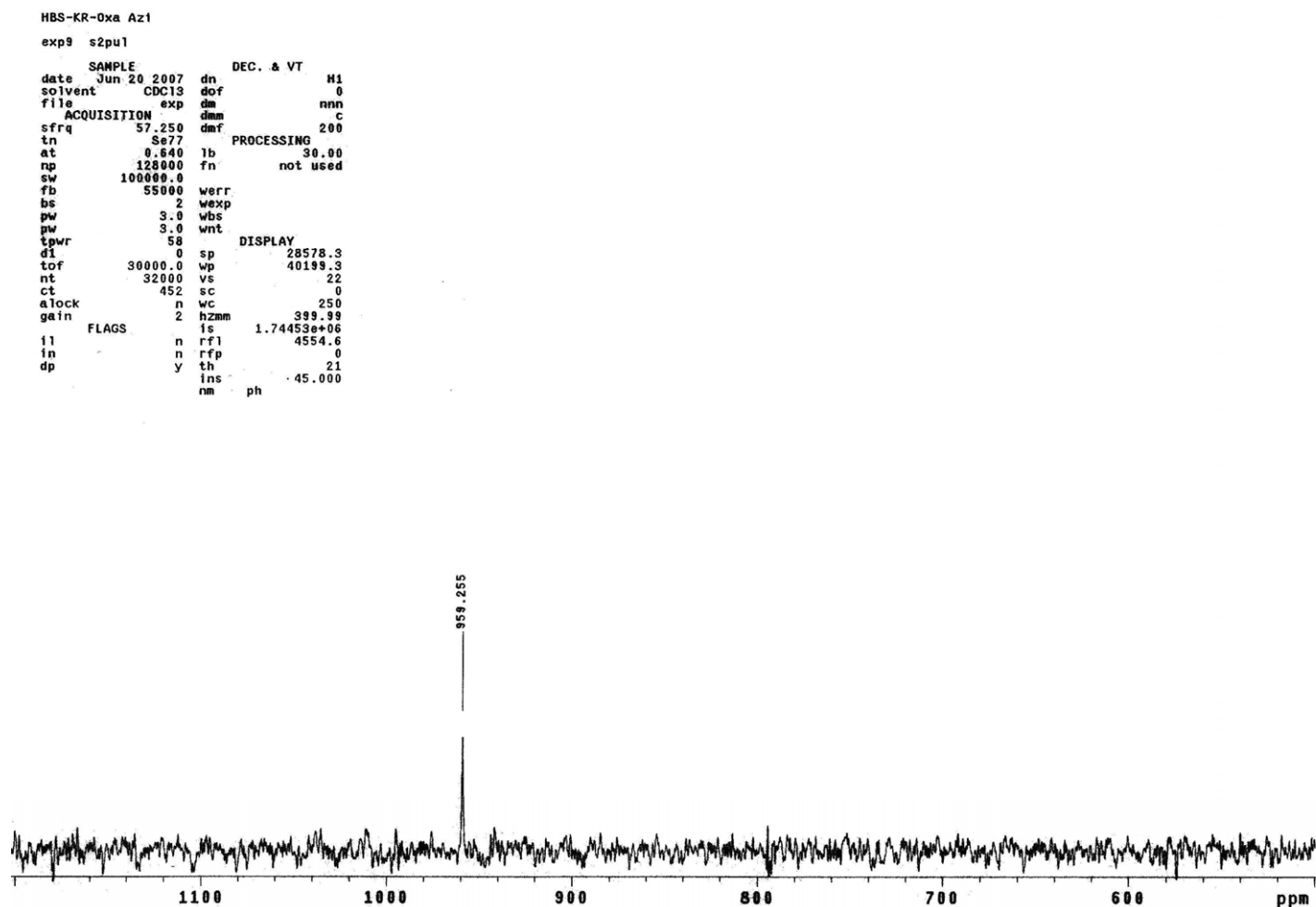


Figure S9: ^{77}Se NMR spectrum of **3a**

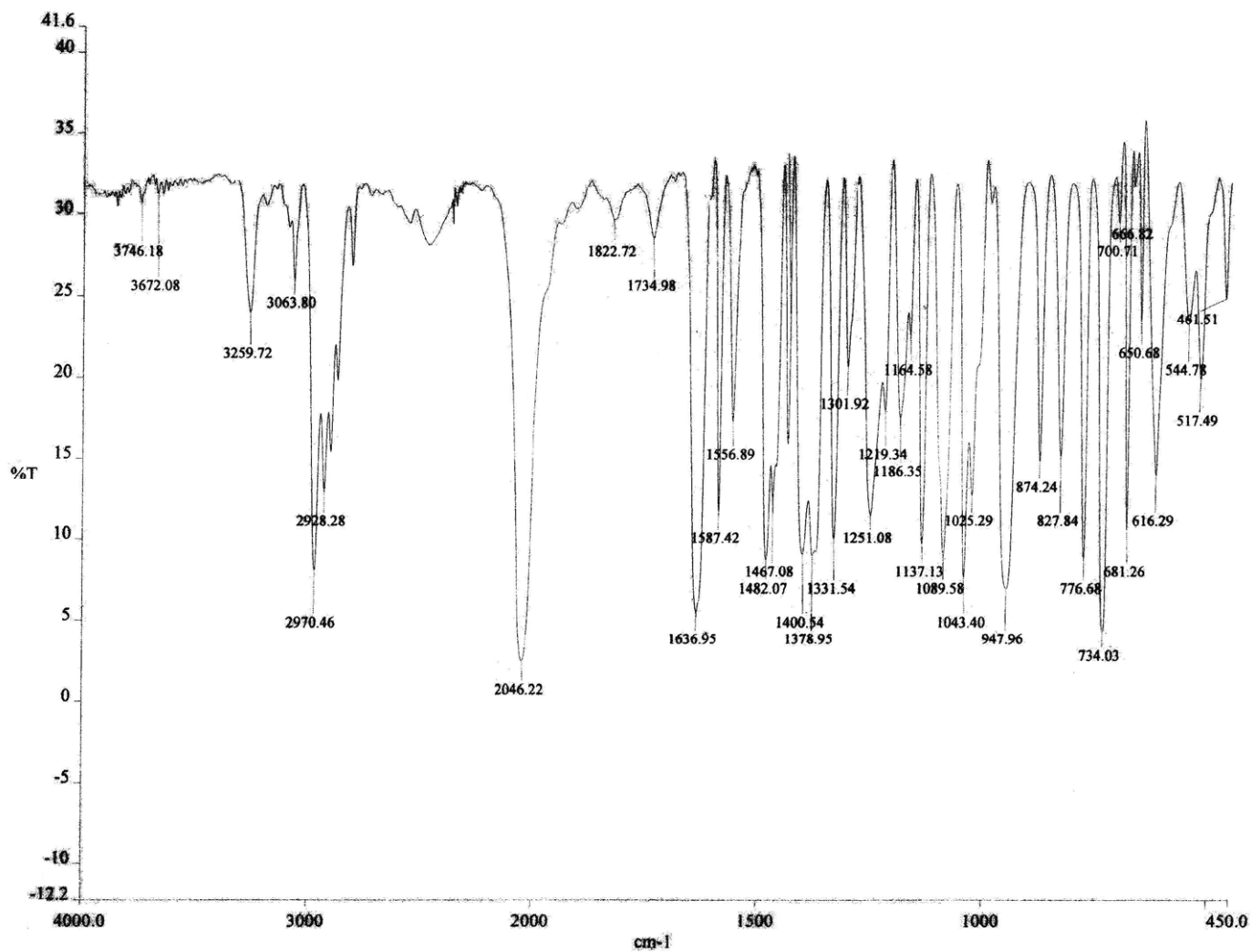


Figure S10: FT-IR spectrum of 3a

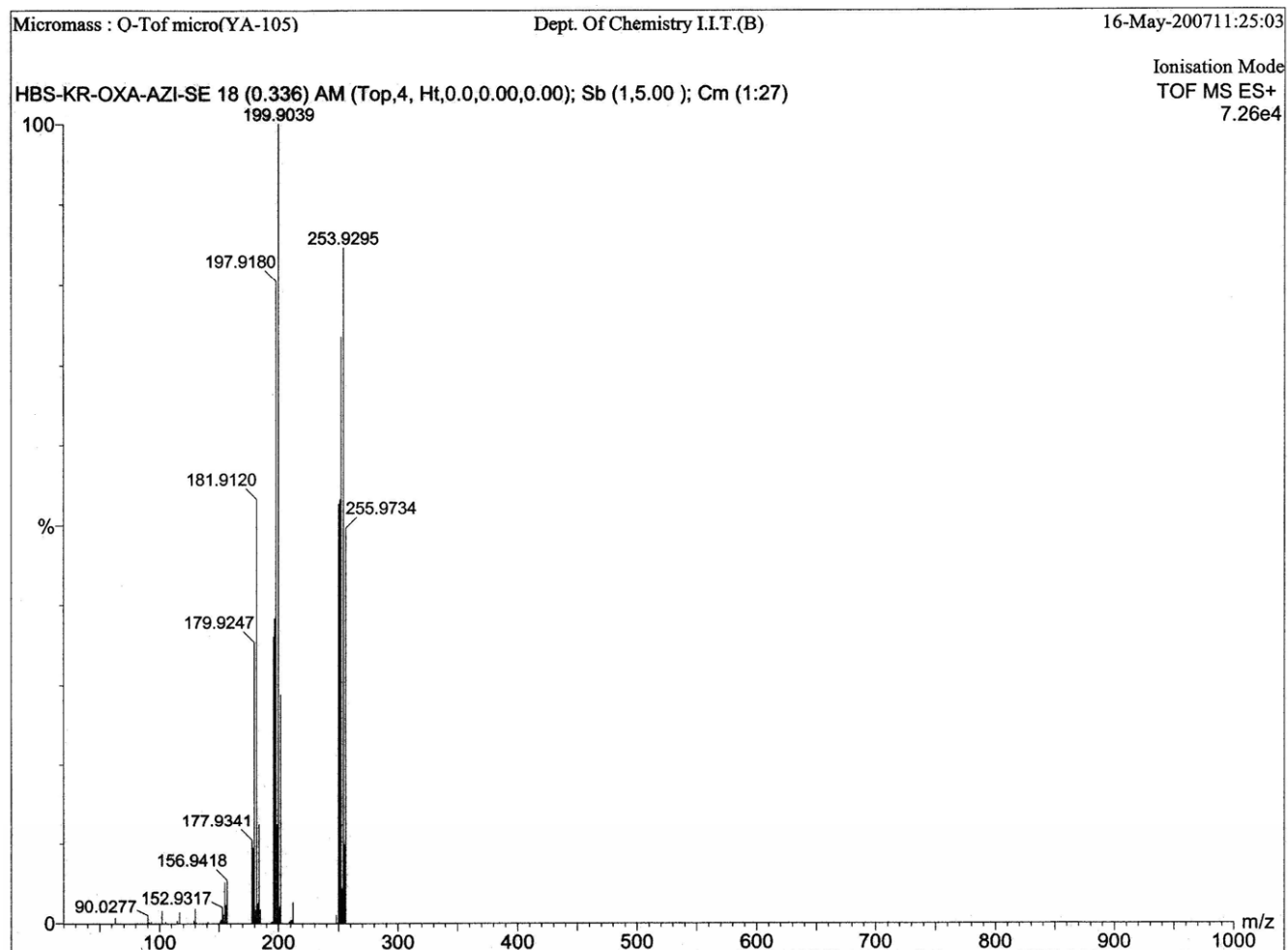


Figure S11: ES-MS spectrum of **3a**

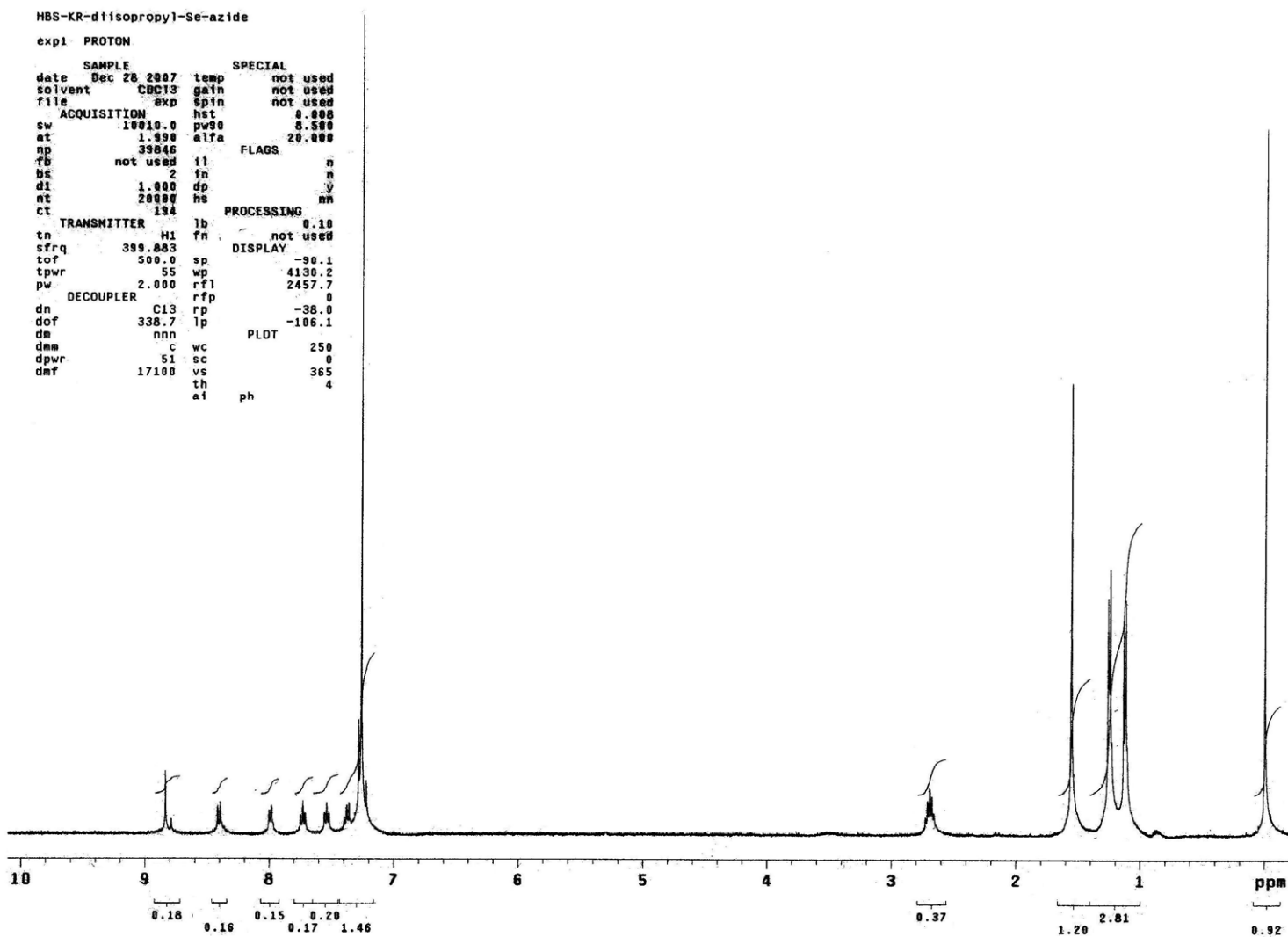


Figure S12: ¹H NMR spectrum of 4a

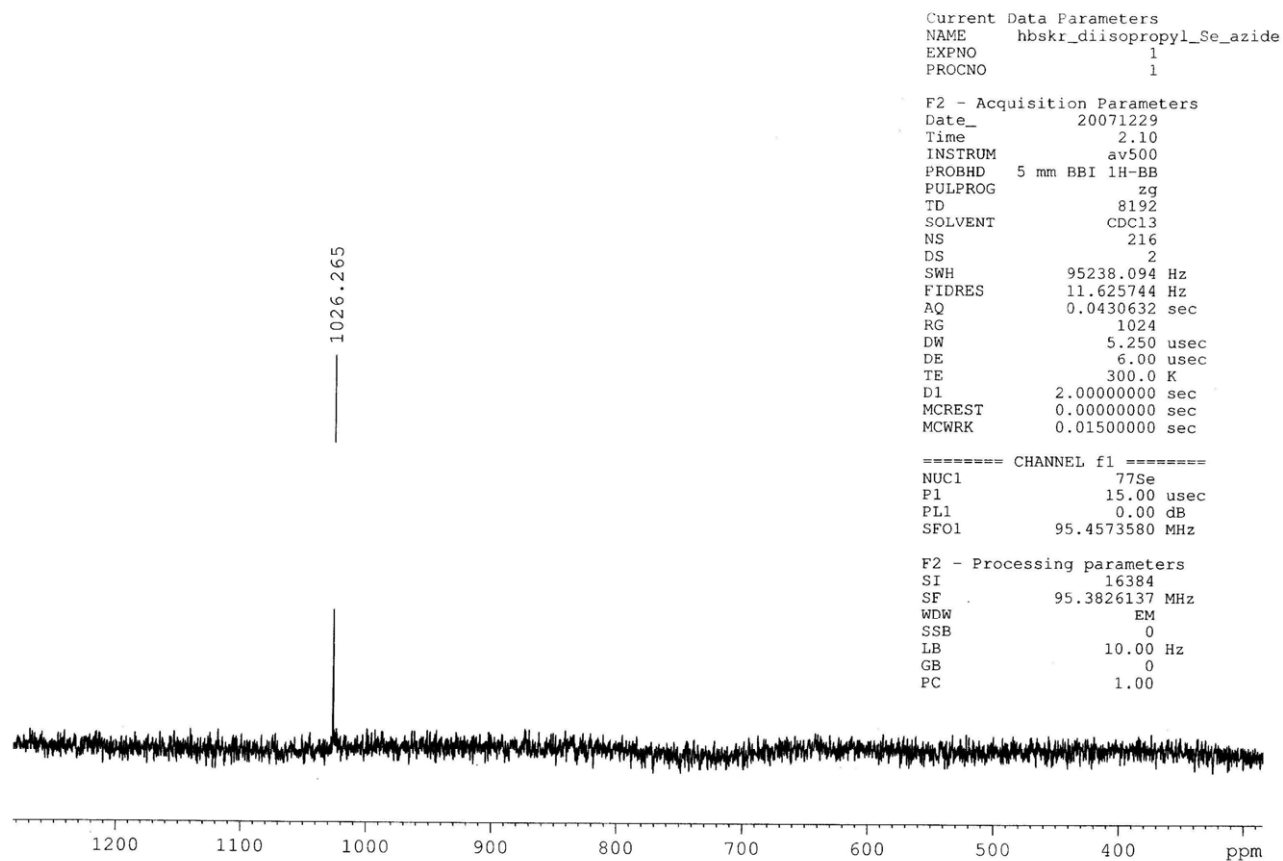


Figure S13: ^{77}Se NMR spectrum of **4a**

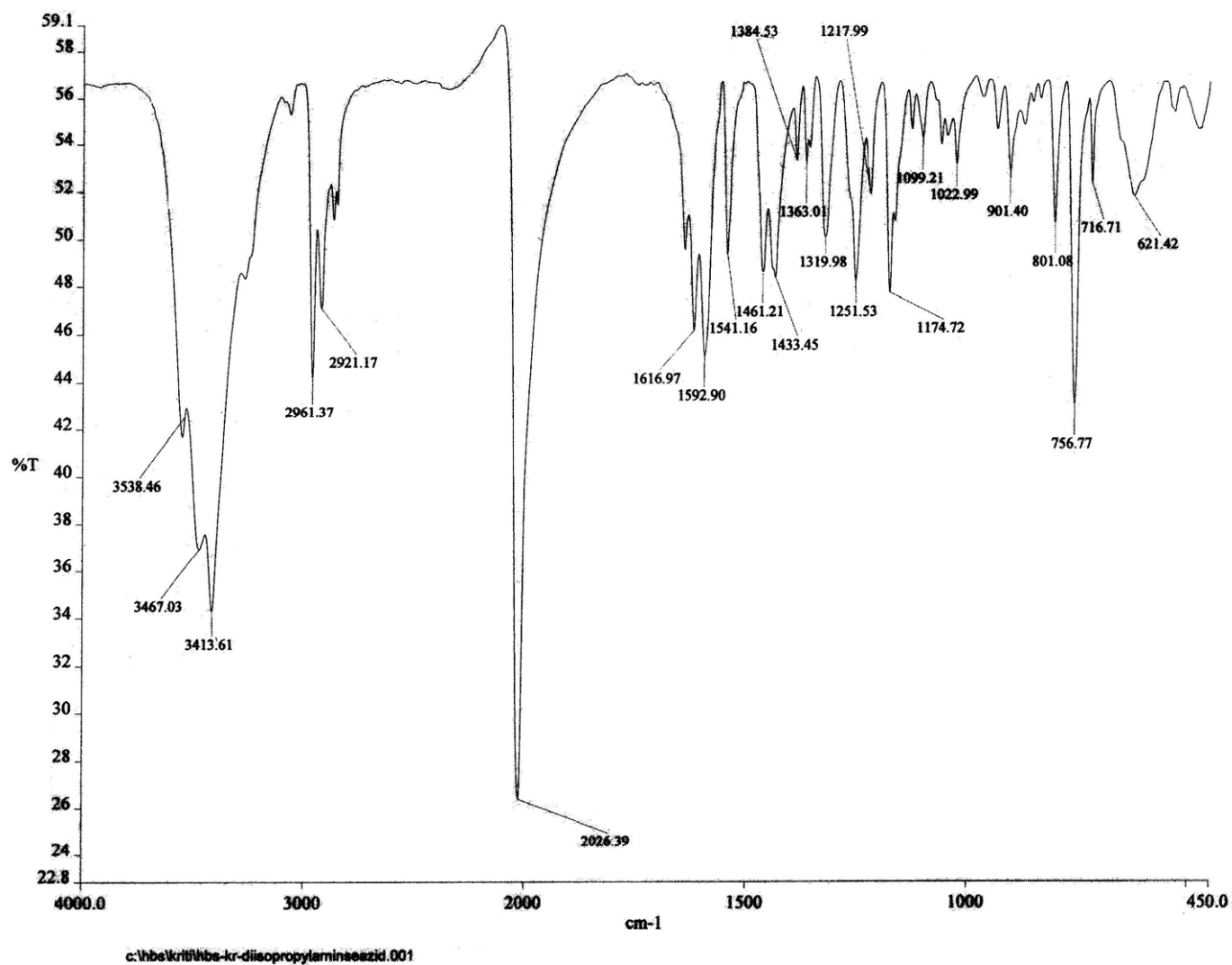


Figure S14: FT-IR spectrum of 4a

Eager 300 Report

Page: 1 Sample: AZI5 (AZI5)

```

Method Name      : sp040108
Method File     : G:\eager300\Eager 300 EA1112\SP040108.mth
Chromatogram    : AZI5
Operator ID     : SP
Analysed        : 01/04/2008 15:06
Sample ID       : AZI5 (# 16)
Analysis Type   : UnkNown (Area)
Company Name    : C.E. Instruments
Printed         : 1/9/2008 16:01
Instrument N.   : Instrument #1
Sample weight   : 1.591
    
```

Calib. method : using 'K Factors'

!!! Warning missing one or more peaks.

Element Name	%	Ret.Time	Area	BC	Area ratio	K factor
Nitrogen	13.5140	43	255852	RS	9.802692	.118997E+07
Carbon	58.9732	65	2508039	RS	1.000000	.267051E+07
Hydrogen	5.3680	169	449747	RS	5.576554	.526610E+07
Totals	77.8551		3213638			

Figure S15: Elemental analysis (C, H, N) of 4a

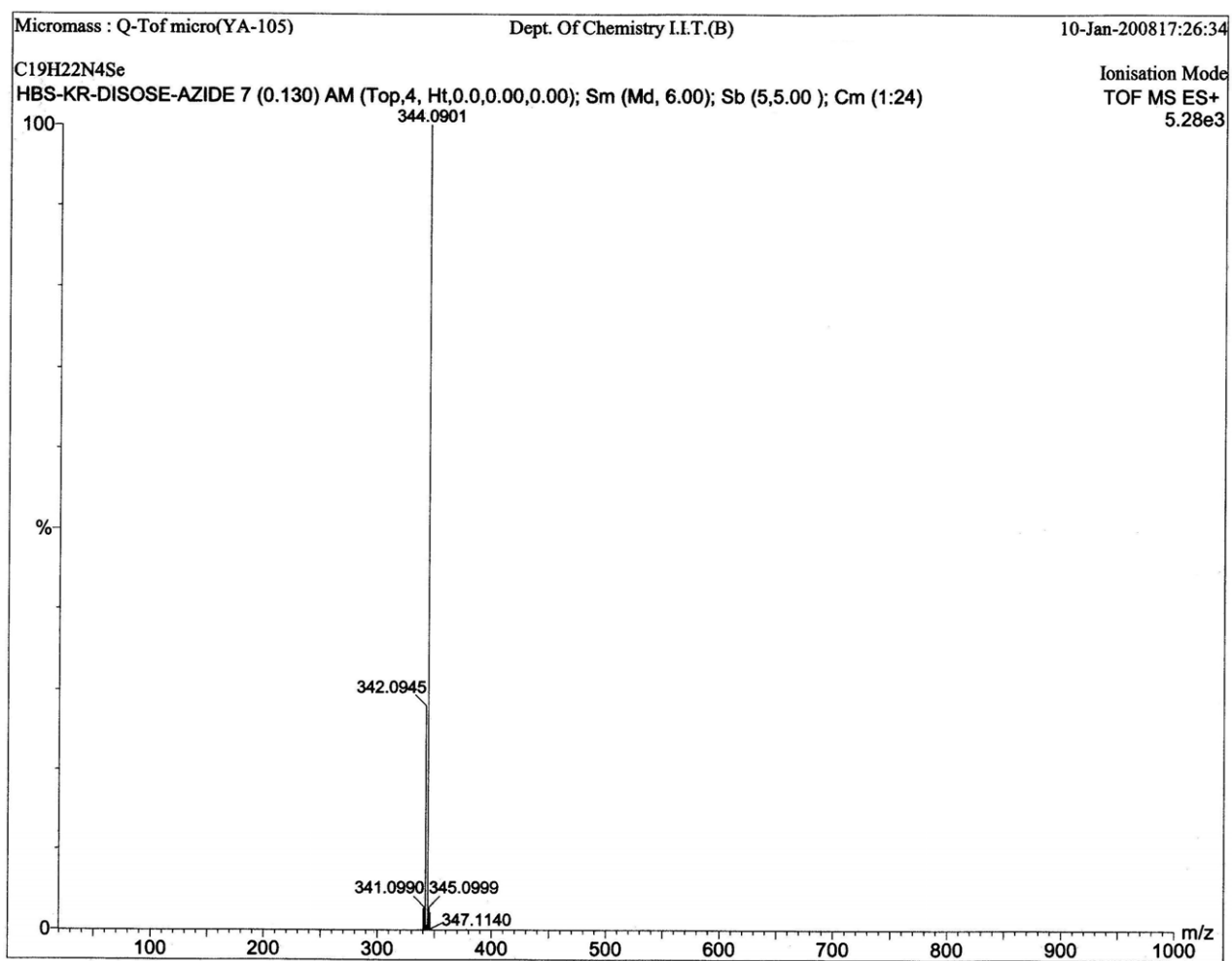


Figure S16: ES-MS spectrum of **4a**

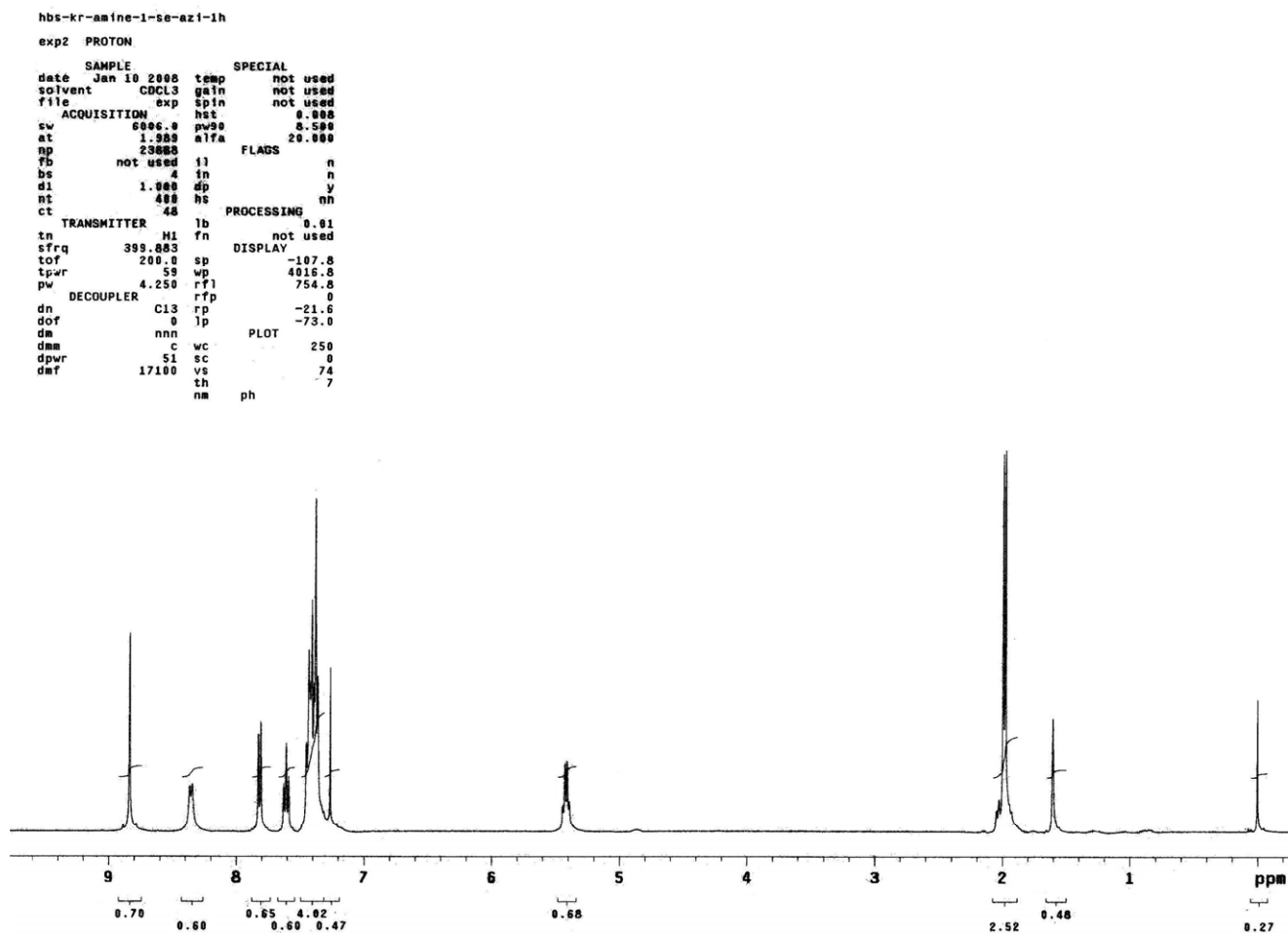


Figure S17: ^1H NMR spectrum of **5a**

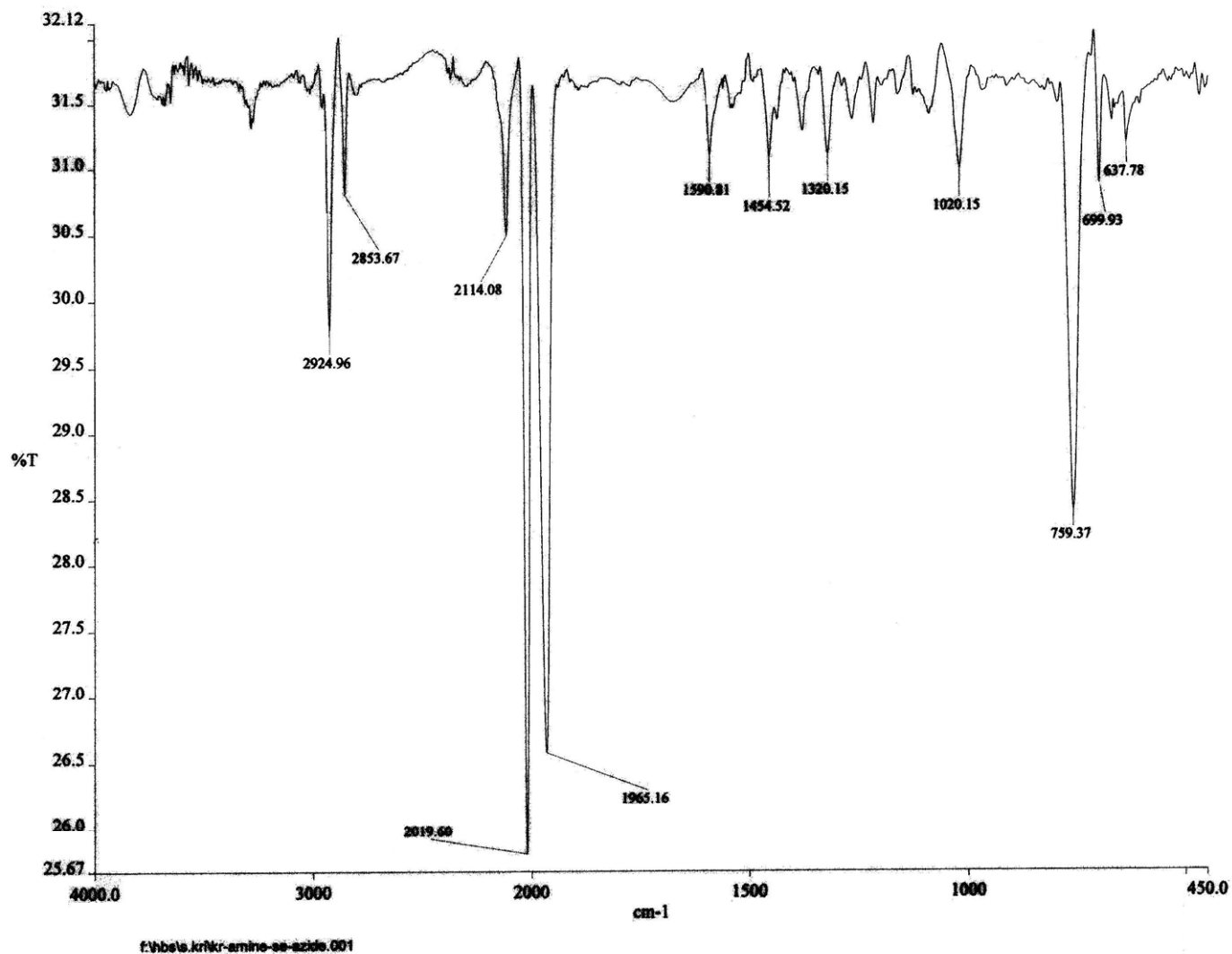
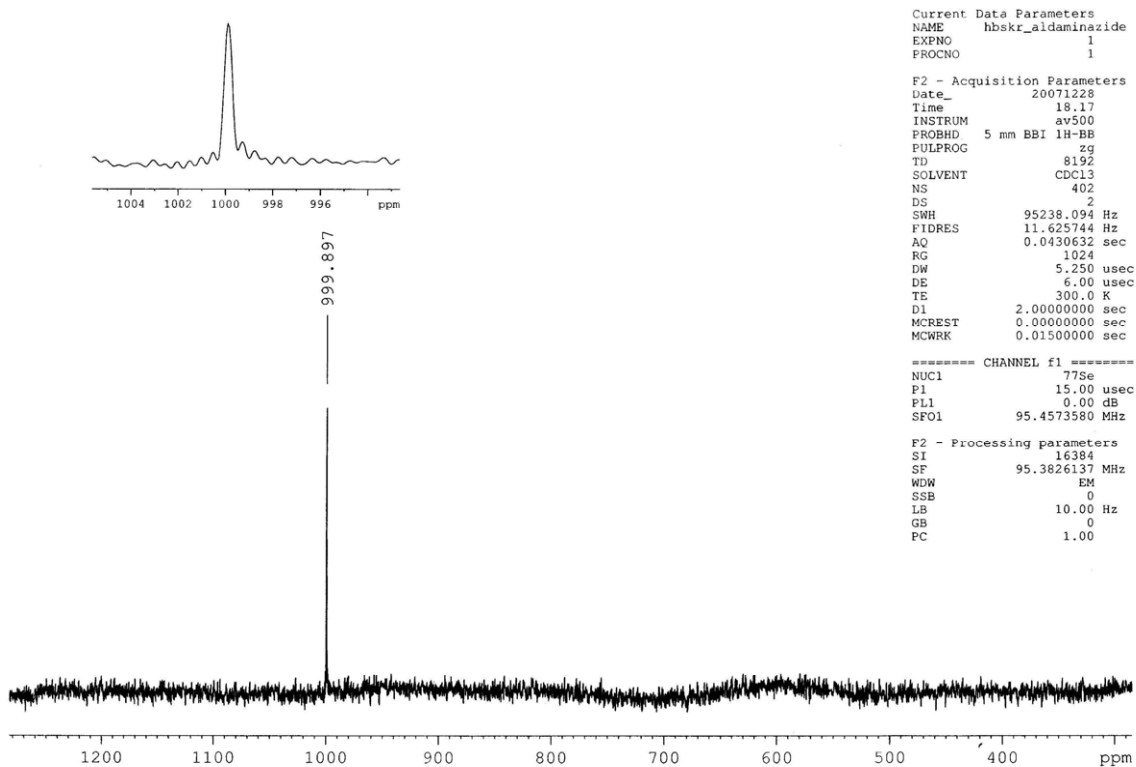


Figure S18: FT-IR spectrum of 5a



FigureS19: ^{77}Se NMR spectrum of **5a**

Eager 300 Report

Page: 1 Sample: KRAMINESEAZI (KRAMINESEAZI)

Method Name : sp090108
Method File : G:\eager300\Eager 300 EA1112\SP090108.mth
Chromatogram : KRAMINESEAZI
Operator ID : SP Company Name : C.E. Instruments
Analysed : 01/09/2008 11:49 Printed : 1/9/2008 15:53
Sample ID : KRAMINESEAZI (# 6) Instrument N. : Instrument #1
Analysis Type : UnkNown (Area) Sample weight : 1.227

Calib. method : using 'K Factors'

!!! Warning missing one or more peaks.

Element Name	%	Ret.Time	Area	BC	Area ratio	K factor
Nitrogen	15.9277	44	243553	RS	7.440680	.124622E+07
Carbon	54.9481	66	1812200	RS	1.000000	.268389E+07
Hydrogen	3.4411	172	255104	RS	7.103769	.579051E+07
Totals	74.3169		2310857			

Figure S20: Elemental analysis (C, H, N) of 5a

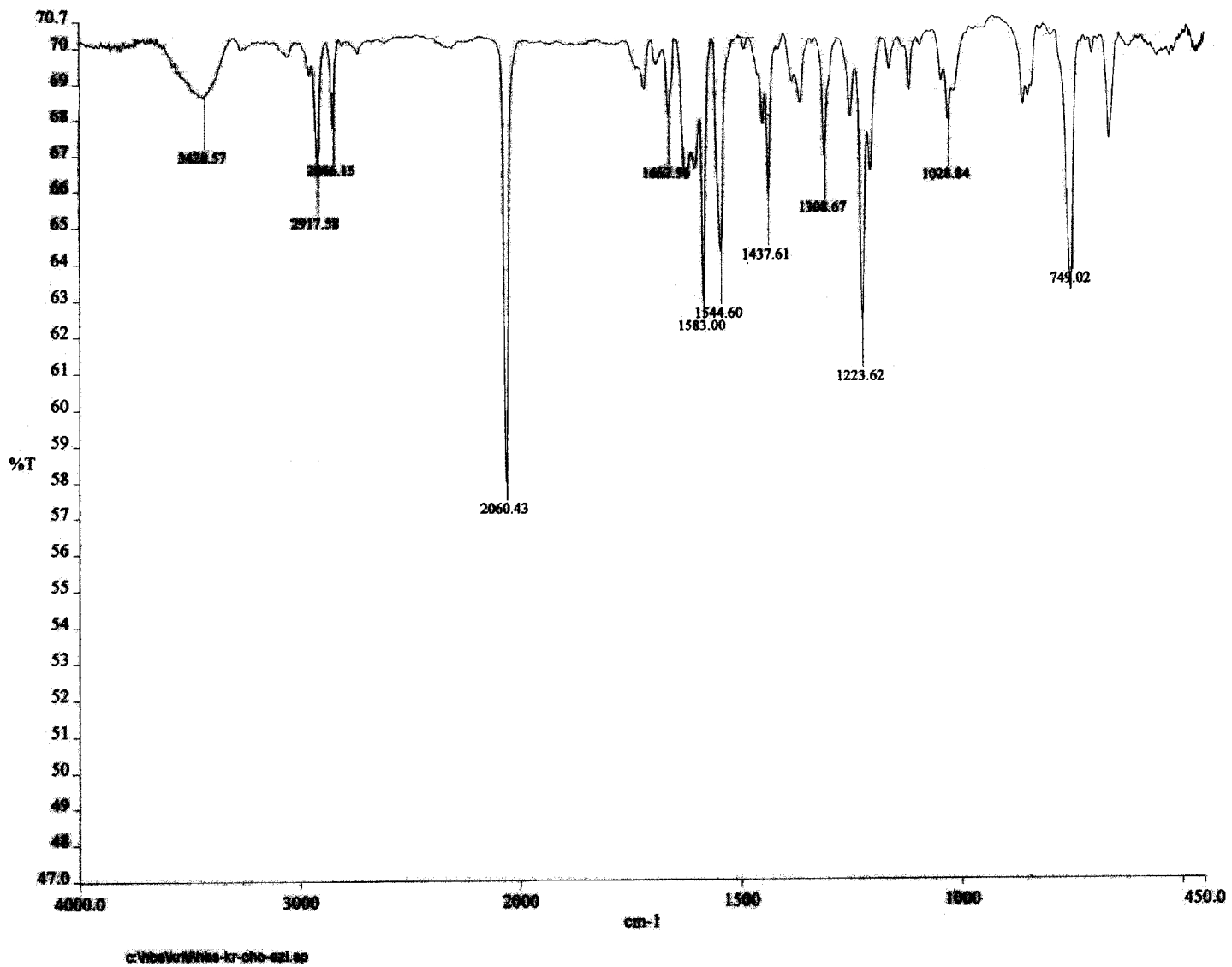
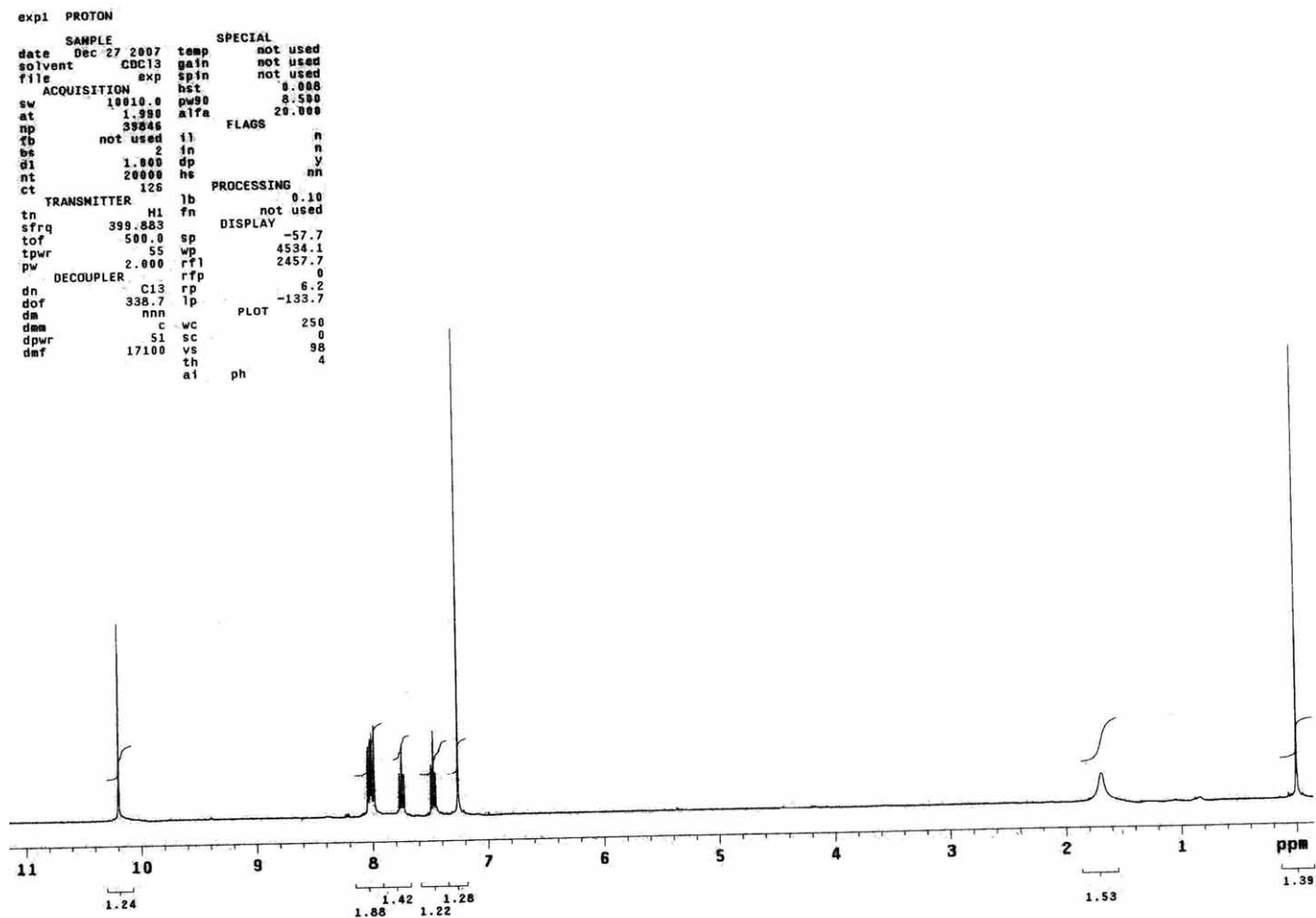


Figure S21: FT-IR spectrum of **6a**



FigureS22: ^1H spectrum of 6a

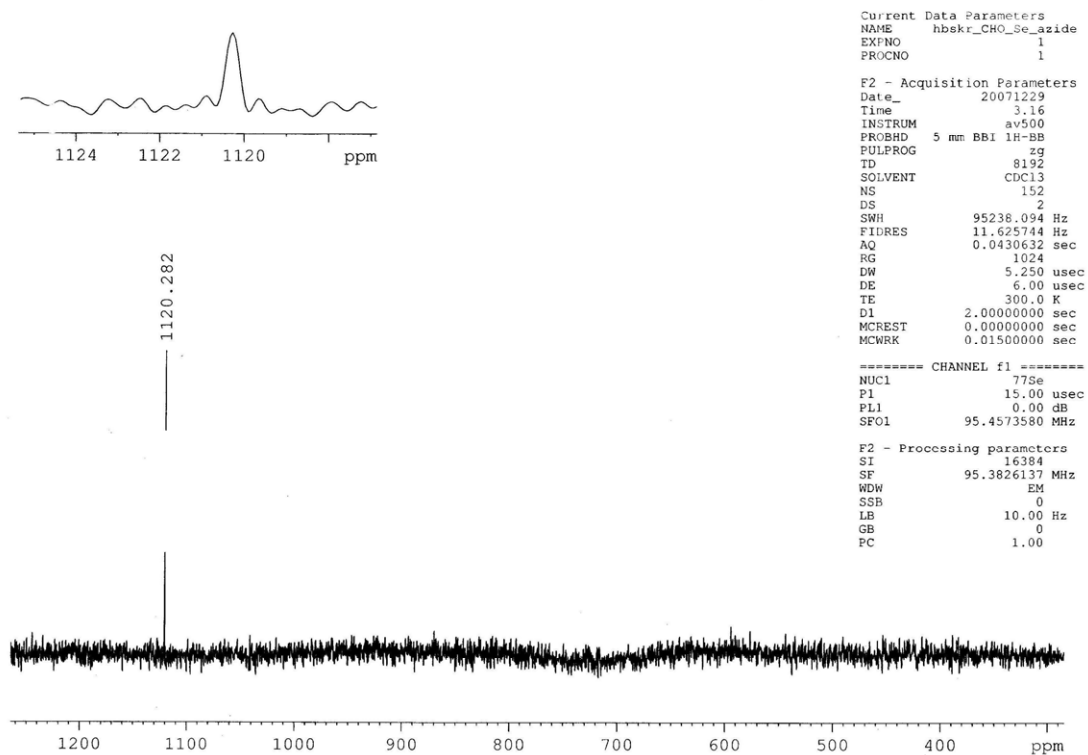


Figure S23: ^{77}Se spectrum of **6a**

Eager 300 Report

Page: 1 Sample: HBS-KR-SECHO (HBS-KR-SECHO)

Method Name : sp230908
Method File : D:\CHMS2008\sp230109.mth
Chromatogram : HBS-KR-SECHO
Operator ID : AGK
Analysed : 09/23/2008 12:43
Sample ID : HBS-KR-SECHO (# 12)
Analysis Type : UnkNown (Area)
Company Name : C.E. Instruments
Printed : 09/23/2008 15:59
Instrument N. : Instrument #1
Sample weight : 1.497

Calib. method : using 'K Factors'

!!! Warning missing one or more peaks.

Element Name	%	Ret.Time	Area	BC	Area ratio	K factor
Nitrogen	15.5570	43	204208	RS	12.463900	.108634E+07
Carbon	36.5559	64	2545221	RS	1.000000	.267233E+07
Hydrogen	2.9552	169	501796	RS	5.072223	.711063E+07
Totals	55.0681		3251225			

Figure S24: Elemental analysis (C, H, N) of 6a

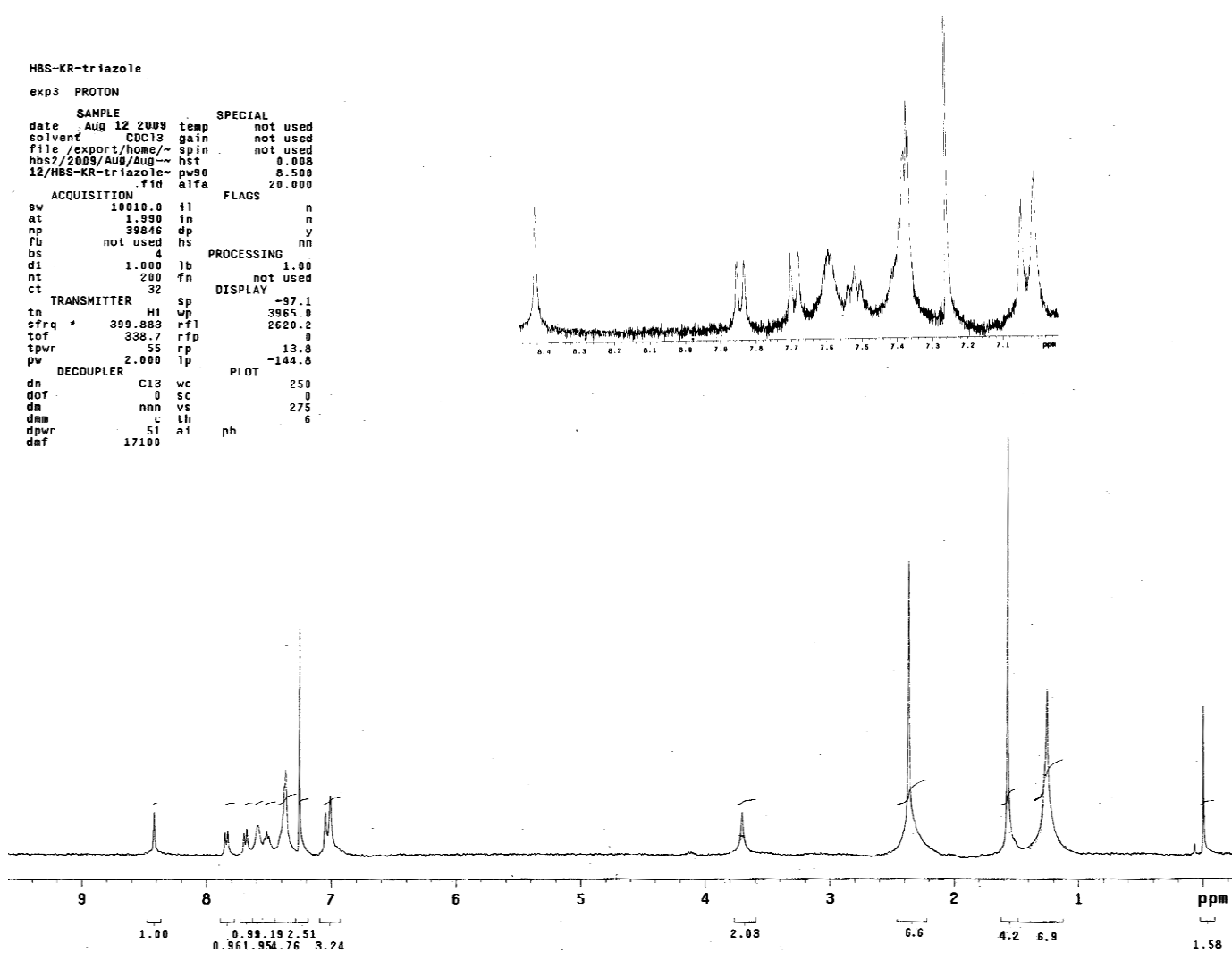


Figure S25: ^1H NMR spectrum of **2b**

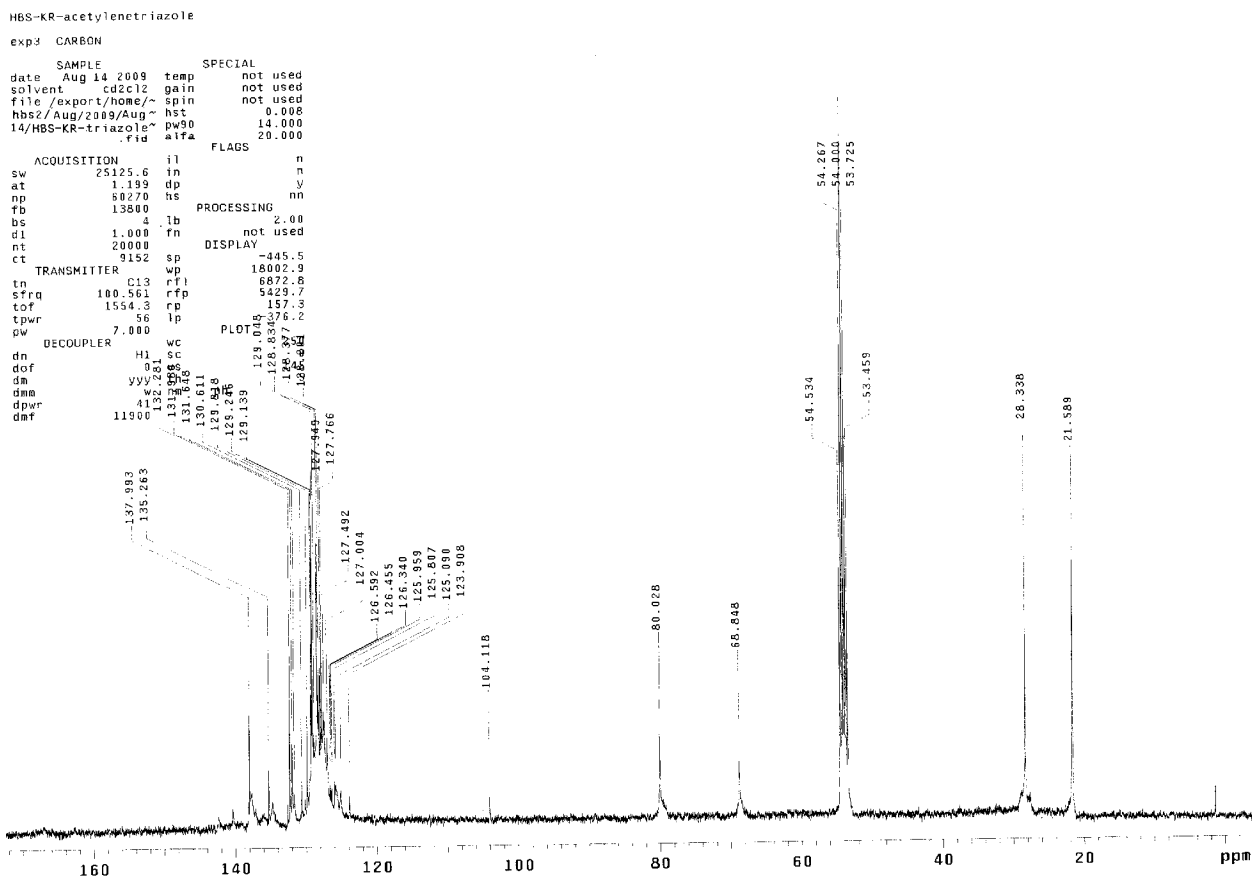


Figure S26: ^{13}C spectrum of **2b**

*Even after scanning for longer time the peak for C=N did not appeared in the ^{13}C spectrum.

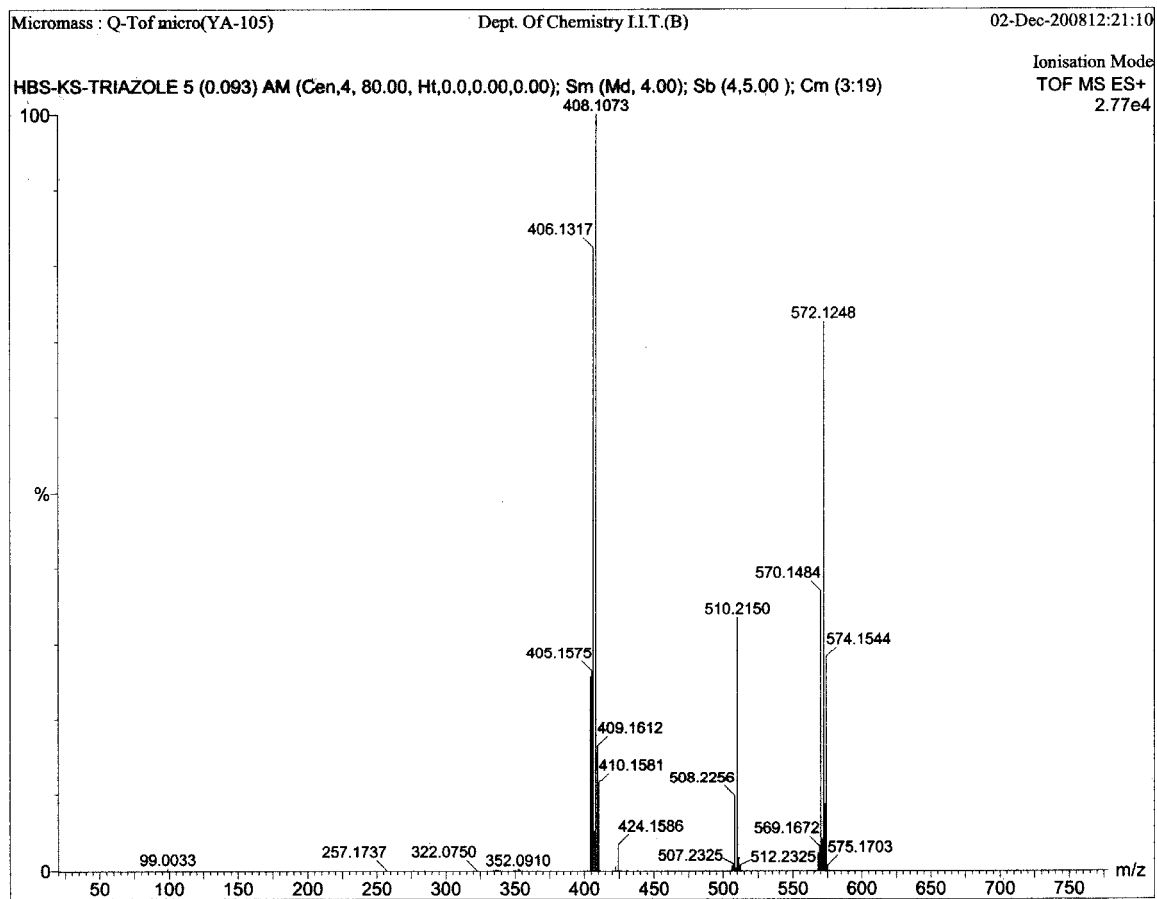


Figure S27: ES-MS spectrum of **2b**

Elemental Composition Report

Page 1

Single Mass Analysis

Tolerance = 100.0 PPM / DBE: min = -1.5, max = 50.0

Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron Ions

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

Micromass : Q-ToF micro(YA-105)

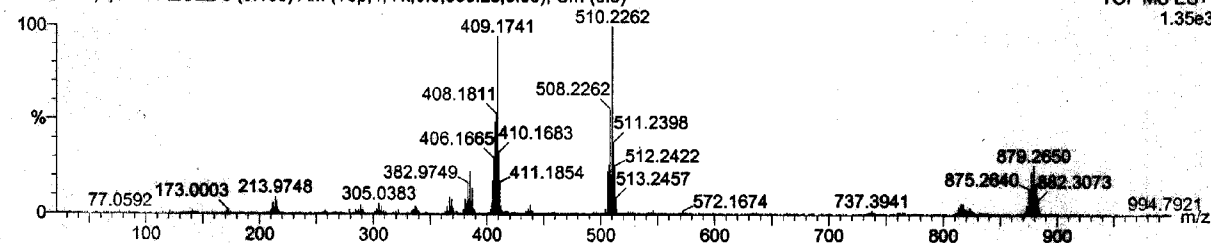
Dept. Of Chemistry I.I.T.(B)

28-May-2009 14:47:07

C₃₁H₂₇N₄OSe

HBS-KS-1,2,3-TRIAZOLE 9 (0.168) AM (Top,4, Ht,0.0,556.28,0.00); Cm (6:9)

Ionisation Mode
TOF MS ES+
1.35e3



Minimum: -1.5
Maximum: 1000.0 100.0 50.0

Mass	Calc. Mass	mDa	PPM	DBE	Score	Formula
575.1342	575.1326	1.6	2.7	20.5	1	C ₃₁ H ₂₈ N ₄ O Na Se

Figure S28: HRMS spectrum of 2b

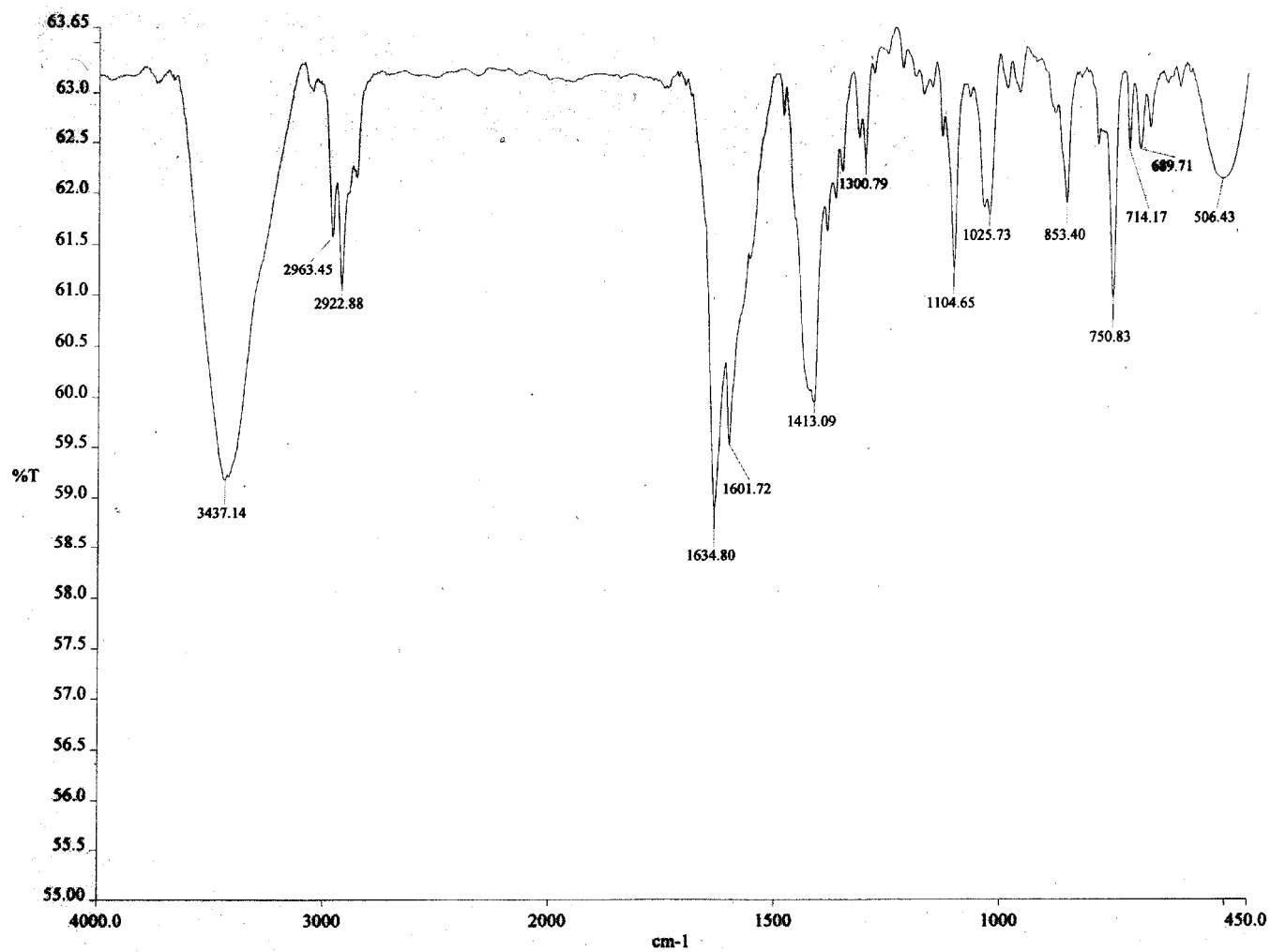
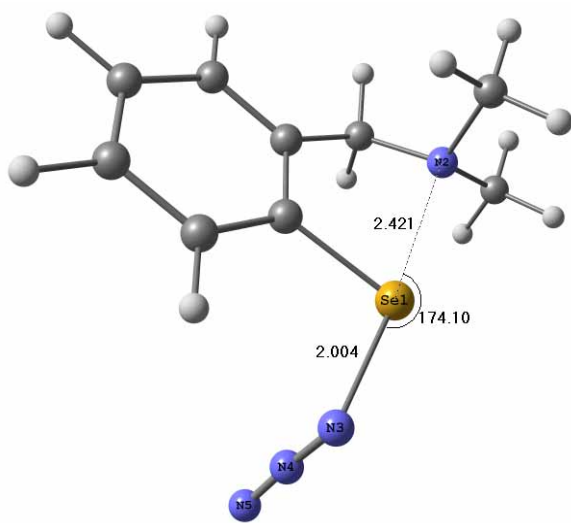
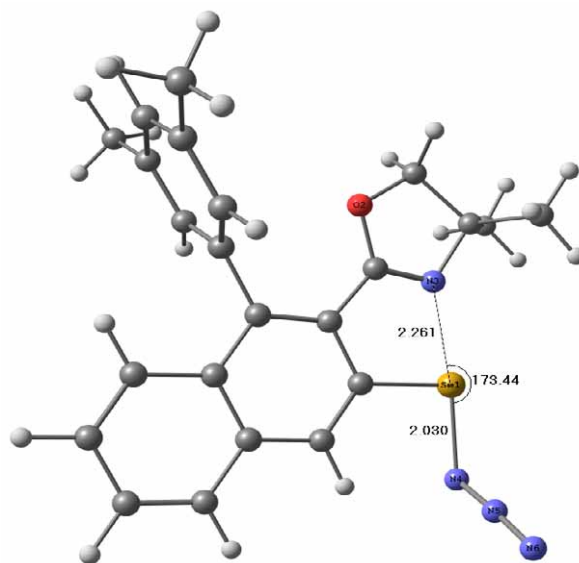


Figure S29: FT-IR spectrum of 2b

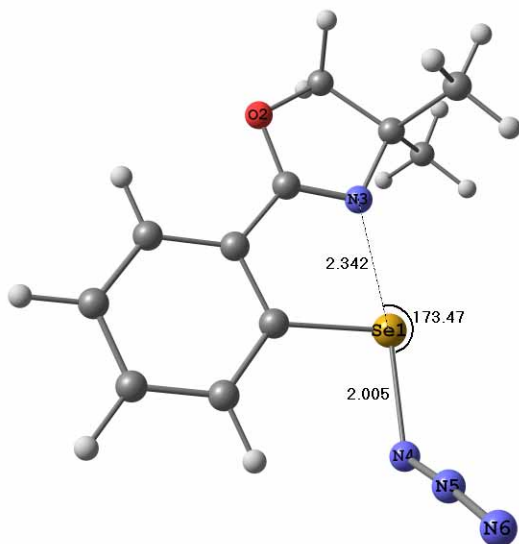
B3LYP/6-31+G(d) optimized geometries of **1**, **2a-6a**



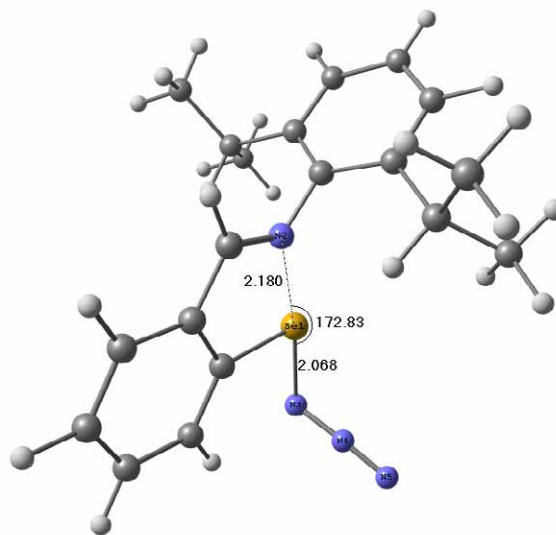
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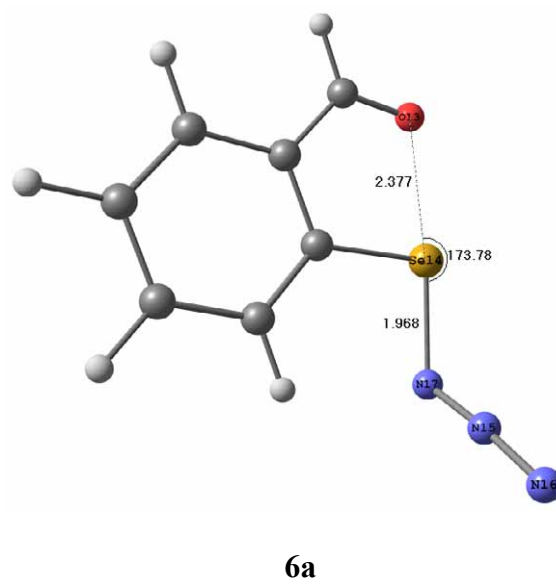
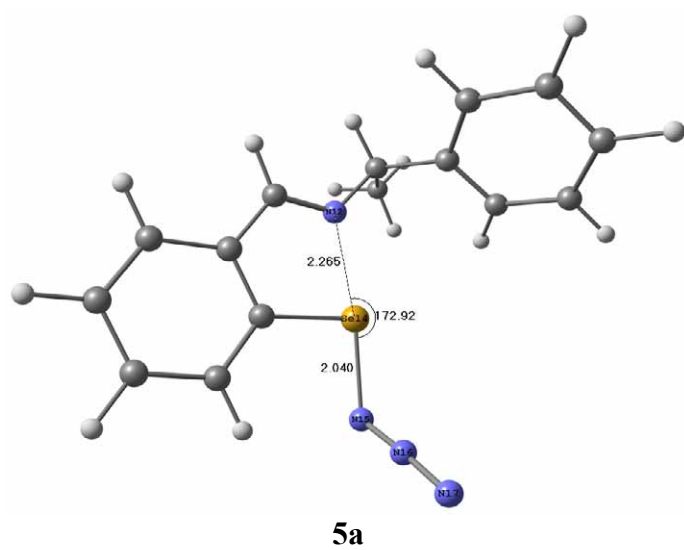
2a



3a



4a



Optimize coordinates and Energy of **1**:

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7	-1.819939000	-1.228348000	0.080721000
7	2.503015000	-0.686560000	-0.663455000
7	3.188286000	-0.560185000	0.351087000
7	3.915036000	-0.431515000	1.229753000
6	0.054068000	0.818695000	-0.139795000
6	0.847454000	1.868697000	-0.608488000
1	1.799229000	1.652543000	-1.082972000
6	0.413139000	3.188210000	-0.455369000
1	1.036126000	4.001066000	-0.819873000
6	-0.816332000	3.463442000	0.148949000
1	-1.156464000	4.489273000	0.261271000
6	-1.611198000	2.408196000	0.604505000
1	-2.573154000	2.614080000	1.070357000
6	-1.184585000	1.085067000	0.467787000
6	-1.989223000	-0.081821000	0.988224000
1	-1.599483000	-0.390699000	1.967367000
1	-3.051534000	0.182346000	1.118862000
6	-2.535458000	-1.071239000	-1.191013000
1	-2.224834000	-1.866379000	-1.874434000
1	-2.275492000	-0.110943000	-1.641944000
1	-3.627795000	-1.119152000	-1.049384000
6	-2.091728000	-2.523271000	0.707106000
1	-1.478023000	-2.627698000	1.606196000
1	-1.818809000	-3.322762000	0.011423000
1	-3.154208000	-2.635525000	0.976647000

Energy (E): -2968.55441

Optimized coordinates and energy of **2a**:

34	-3.047538000	-0.438811000	-0.314871000
8	0.828251000	-2.174200000	0.073437000
7	-1.386024000	-1.967764000	-0.213394000
7	-4.373164000	1.096987000	-0.398873000
7	-4.852408000	1.421013000	0.683851000
7	-5.361425000	1.789334000	1.646387000
6	0.977699000	0.840244000	-0.061930000
6	-0.191277000	0.075810000	-0.125850000
6	-1.482859000	0.697802000	-0.232986000
6	-1.574767000	2.069343000	-0.293617000
1	-2.545198000	2.541671000	-0.402438000
6	-0.414121000	2.875926000	-0.229229000

6	0.879342000	2.265038000	-0.106909000
6	2.026193000	3.111709000	-0.042462000
1	3.008617000	2.661882000	0.051628000
6	1.900055000	4.481675000	-0.096754000
1	2.785819000	5.109378000	-0.044982000
6	0.620227000	5.081614000	-0.220043000
1	0.533600000	6.164344000	-0.261853000
6	-0.507632000	4.295930000	-0.284659000
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6	4.198728000	-0.556527000	1.410292000
6	4.902229000	-0.859559000	0.233370000
1	5.904623000	-1.279354000	0.308677000
6	4.355003000	-0.627265000	-1.032270000
6	3.062890000	-0.085312000	-1.113206000
1	2.620494000	0.107533000	-2.088865000
6	2.335659000	0.215159000	0.041376000
6	2.914216000	-0.017383000	1.298160000
1	2.351953000	0.227910000	2.196634000
6	5.131998000	-0.942399000	-2.291445000
1	5.328349000	-0.034537000	-2.876265000
1	4.578023000	-1.630704000	-2.942131000
1	6.097458000	-1.404542000	-2.060200000
6	-0.246510000	-1.376846000	-0.094687000
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6	-1.208726000	-3.424399000	-0.047397000
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1	-1.678004000	-5.259924000	-1.114895000
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1	5.088141000	-1.868000000	2.889666000
1	4.140118000	-0.538717000	3.576150000
6	-1.786812000	-3.852491000	1.312577000
1	-1.285281000	-3.325946000	2.132329000
1	-1.657090000	-4.931525000	1.461235000
1	-2.855595000	-3.621819000	1.364913000

Energy (E): -3583.34799

Optimized coordinates and energy of **3a**:

34	-0.762416000	-1.086362000	-0.382468000
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7	-2.712683000	-1.489215000	-0.618710000
7	-3.283059000	-1.892521000	0.393642000
7	-3.903294000	-2.287085000	1.275011000
6	0.015556000	3.004561000	0.191424000
6	0.131326000	1.613361000	0.039777000
6	-1.013266000	0.812117000	-0.175245000
6	-2.268243000	1.428600000	-0.242366000
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6	3.601810000	0.548116000	0.146257000
1	4.284524000	0.628810000	0.994943000
1	4.133976000	0.782347000	-0.781800000
6	2.841860000	-0.813902000	0.076960000
6	3.291495000	-1.671988000	-1.110419000
1	2.695078000	-2.588331000	-1.168619000
1	4.345458000	-1.956076000	-1.003068000
1	3.172461000	-1.126216000	-2.052489000
6	2.943477000	-1.591813000	1.399971000
1	2.645183000	-0.961465000	2.245321000
1	3.972718000	-1.932593000	1.566864000
1	2.287440000	-2.467951000	1.380915000
1	0.912215000	3.595118000	0.354672000
1	-1.333579000	4.679796000	0.247134000
1	-3.353266000	3.275295000	-0.145381000

Energy (E): -3120.00878

Optimized coordinates and Energy of **4a**:

6	-4.300305000	-0.709738000	-0.829262000
6	-3.336760000	0.162751000	-0.326641000
6	-2.049924000	-0.311124000	-0.043240000
6	-1.747926000	-1.674530000	-0.275011000
6	-2.732995000	-2.539791000	-0.784795000
6	-4.006285000	-2.062827000	-1.064267000
1	-5.296916000	-0.330600000	-1.040790000
1	-3.576272000	1.202513000	-0.136290000
1	-2.486365000	-3.585568000	-0.956034000
1	-4.768504000	-2.729140000	-1.457562000
6	1.772828000	-1.569114000	0.920133000
7	0.391960000	-1.240169000	0.539132000
6	-0.414188000	-2.115549000	0.049675000
34	-0.641080000	0.771631000	0.670027000
7	-1.786247000	2.458011000	0.747579000
7	-1.581743000	3.260239000	-0.157928000

7	-1.448443000	4.072867000	-0.960369000
1	1.948483000	-2.625488000	0.664087000
1	-0.110964000	-3.155947000	-0.114957000
6	2.749035000	-0.728456000	0.100559000
6	3.083913000	0.584049000	0.460779000
6	3.310404000	-1.269589000	-1.063390000
6	3.958628000	1.336039000	-0.326105000
1	2.667258000	1.027978000	1.360404000
6	4.184427000	-0.519932000	-1.854943000
1	3.062109000	-2.288330000	-1.355917000
6	4.509727000	0.787912000	-1.487860000
1	4.205488000	2.353203000	-0.033129000
1	4.610079000	-0.957842000	-2.754238000
1	5.187686000	1.376026000	-2.100839000
6	1.925870000	-1.411052000	2.440724000
1	1.248380000	-2.097603000	2.959619000
1	2.954090000	-1.639961000	2.740707000
1	1.684762000	-0.395637000	2.766988000

Energy (E): -3198.41453

Optimized coordinates and energy of **5a**:

34	1.128951000	0.229066000	-0.981426000
7	-0.404984000	-0.300857000	0.473748000
7	2.750027000	0.605517000	-2.209068000
7	3.075567000	1.785477000	-2.258389000
7	3.438324000	2.872387000	-2.369787000
6	2.243043000	-1.577939000	2.607839000
6	1.529062000	-0.999008000	1.539174000
6	2.217242000	-0.530716000	0.391311000
6	3.611341000	-0.655950000	0.327228000
1	4.138053000	-0.312903000	-0.555689000
6	4.297870000	-1.234890000	1.391388000
6	3.622508000	-1.695697000	2.535828000
6	0.102020000	-0.842801000	1.530571000
1	5.379088000	-1.330706000	1.332376000
1	4.178352000	-2.141698000	3.355446000
1	1.701561000	-1.930192000	3.483025000
1	-0.520540000	-1.163358000	2.370029000
6	-1.786642000	-0.049319000	0.248051000
6	-2.544883000	-1.017010000	-0.448368000
6	-2.321378000	1.204550000	0.619586000
6	-3.887313000	-0.720724000	-0.715248000
6	-3.669380000	1.446963000	0.326113000
6	-4.448662000	0.496259000	-0.331209000
1	-4.500768000	-1.450429000	-1.237381000

1	-4.113541000	2.397473000	0.609852000
1	-5.492296000	0.706701000	-0.550890000
6	-1.481400000	2.270861000	1.319528000
1	-0.460713000	1.888370000	1.416648000
6	-1.946973000	-2.351645000	-0.889147000
1	-0.888073000	-2.356131000	-0.612776000
6	-1.998948000	2.563889000	2.742185000
1	-3.014156000	2.978763000	2.723634000
1	-2.023385000	1.655172000	3.355683000
1	-1.349178000	3.293725000	3.240426000
6	-1.395430000	3.562813000	0.482385000
1	-0.730804000	4.286497000	0.969458000
1	-0.997199000	3.358933000	-0.517368000
1	-2.377980000	4.036068000	0.365660000
6	-2.011153000	-2.526406000	-2.419483000
1	-1.513226000	-1.696652000	-2.932746000
1	-1.510741000	-3.456326000	-2.715490000
1	-3.046372000	-2.574749000	-2.778434000
6	-2.614740000	-3.539351000	-0.166859000
1	-2.141088000	-4.482388000	-0.465978000
1	-2.529018000	-3.446204000	0.922514000
1	-3.681945000	-3.609148000	-0.410286000

Energy (E): -3355.68219

Optimized coordinates and geometry of **6a**:

6	1.775483000	2.333179000	-0.210921000
6	0.586595000	1.614276000	-0.320126000
6	0.591984000	0.227001000	-0.125995000
6	1.815592000	-0.418127000	0.177888000
6	3.007076000	0.324699000	0.285399000
6	2.991961000	1.697939000	0.093354000
1	1.756398000	3.408813000	-0.367277000
1	-0.340619000	2.118735000	-0.567532000
1	3.935563000	-0.192147000	0.518517000
1	3.906834000	2.277065000	0.174551000
6	1.788585000	-1.849738000	0.356642000
1	2.720747000	-2.383454000	0.603593000
8	0.729242000	-2.481046000	0.235348000
34	-0.958259000	-0.878956000	-0.252414000
7	-2.880974000	0.980514000	0.280012000
7	-3.574945000	1.418569000	1.077836000
7	-2.197752000	0.590701000	-0.672137000

Energy (E): -2908.59419

TableS1: Summary of theoretical data for compounds obtained by geometry optimization (B3LYP/6-31+G(d)) and NBO analysis B3LYP/6-311+G(d,p).

Compounds	$r_{\text{Se}\cdots\text{N/O}}$ (Å)	$\theta_{\text{N/O}\cdots\text{Se-N}}(^{\circ})$	q_{Se} (acceptor)	$q_{\text{N/O}}$ (donor)	$E_{\text{Se}\cdots\text{N/O}}$ (kcal/mol)
1	2.421	174.10	0.559	-0.551	23.66
2a	2.261	173.44	0.638	-0.574	41.58
3a	2.342	173.47	0.654	-0.562	32.15
4a	2.180	172.83	0.697	-0.511	54.41
5a	2.265	172.92	0.672	-0.485	43.16
6a	2.377	173.78	0.697	-0.550	20.64

TableS2: Selected Topographical features of Se $\cdots$ N/O bond computed at B3LYP/6-311+G(d,p) level from B3LYP/6-31+G(d) optimized geometry

Compounds	ρ_{bcp}	$\nabla^2\rho_{\text{bcp}}$	H
1	0.051	-0.025	-0.66
2a	0.063	-0.033	-1.14
3a	0.054	-0.030	-0.72
4a	0.078	-0.034	-1.98
5a	0.065	-0.032	-1.25
6a	0.045	-0.032	-0.25