Supporting Information for the Paper

Effect of a Bromo Substituent on the Glutathione Peroxidase Activity of a Pyridoxine-like Diselenide

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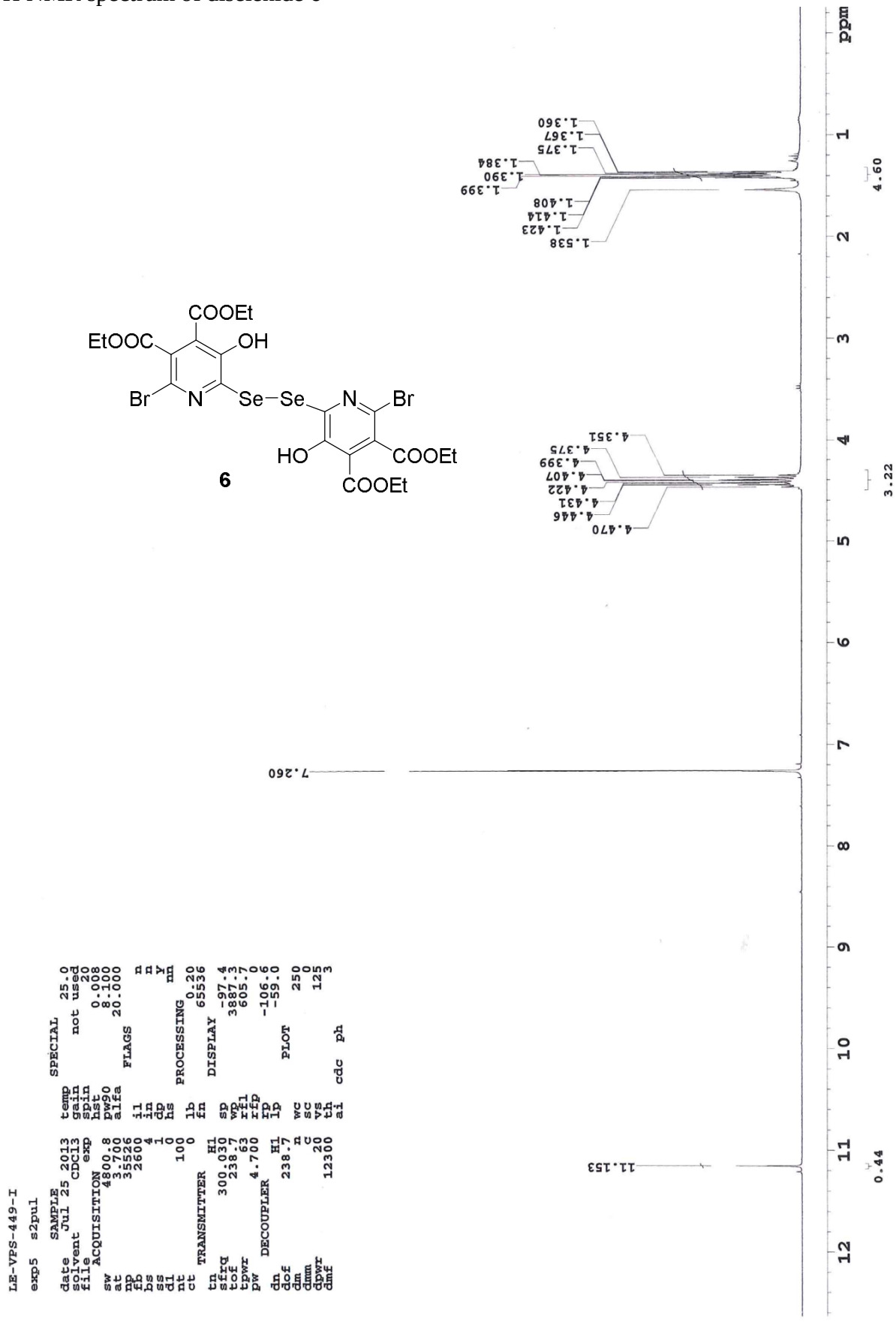
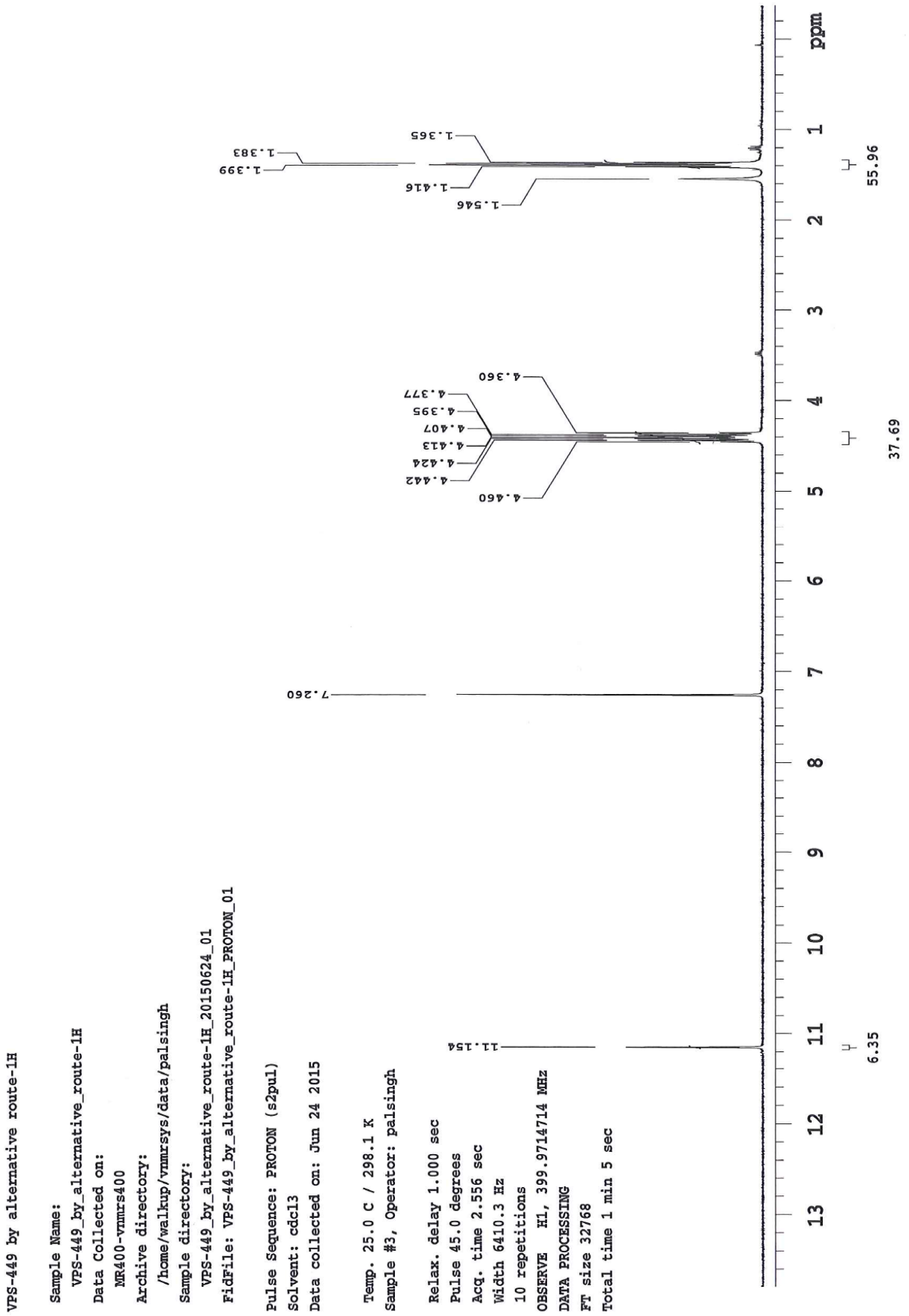
---Table of Contents---

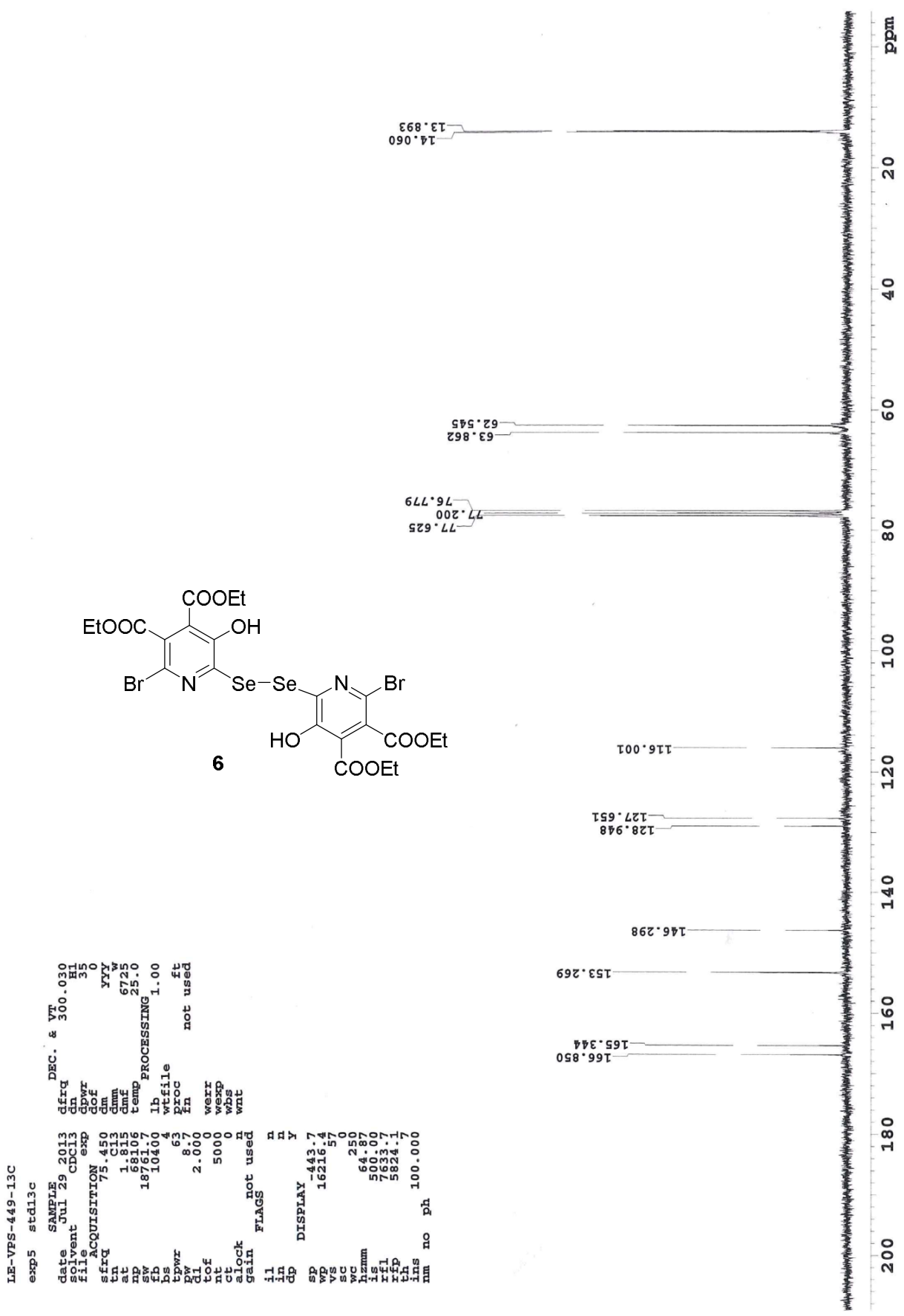
^{1}H NMR spectrum of diselenide **6**



^{1}H NMR spectrum of diselenide **6** via oxidation of selenide **8**

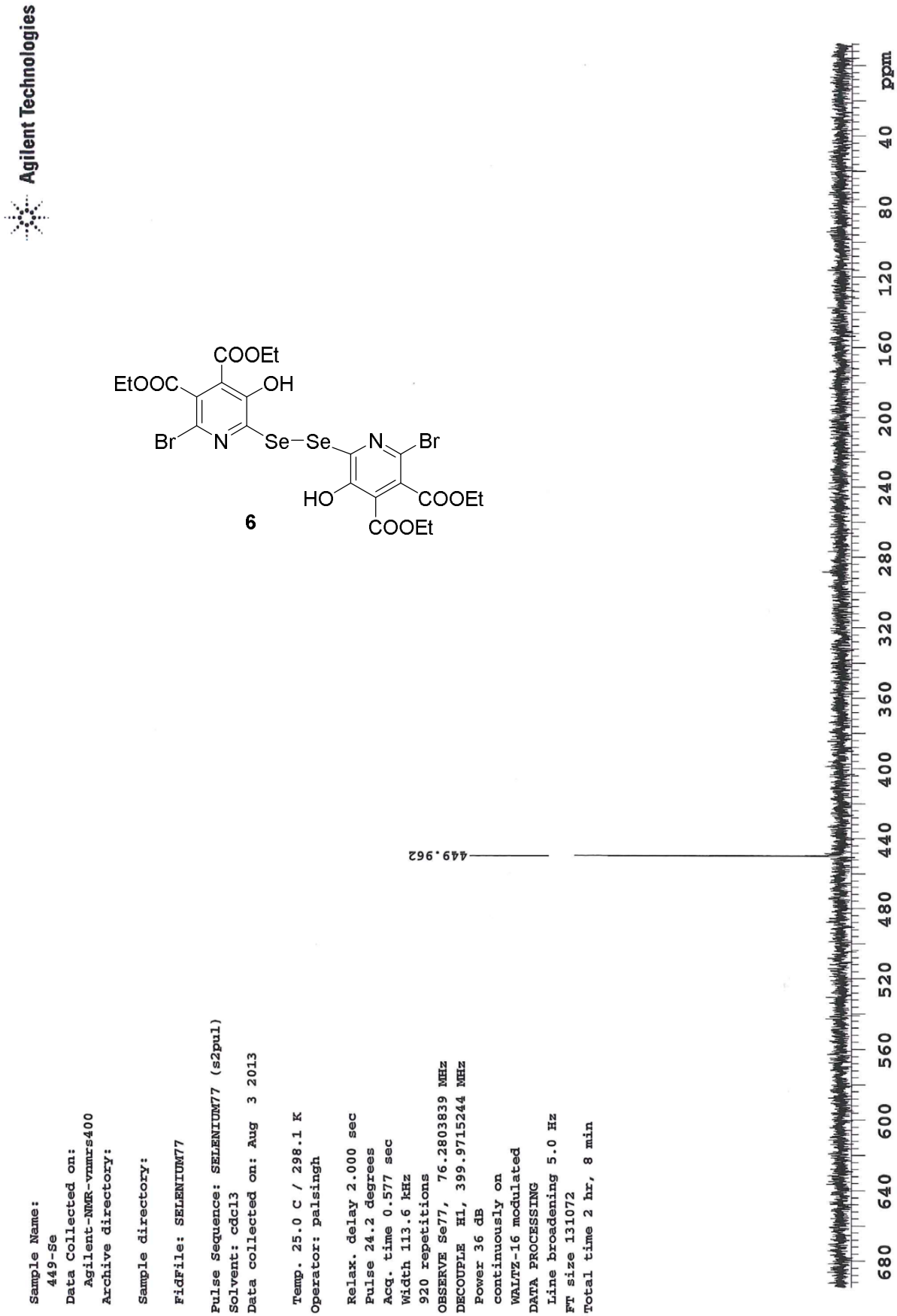


^{13}C NMR spectrum of diselenide **6**

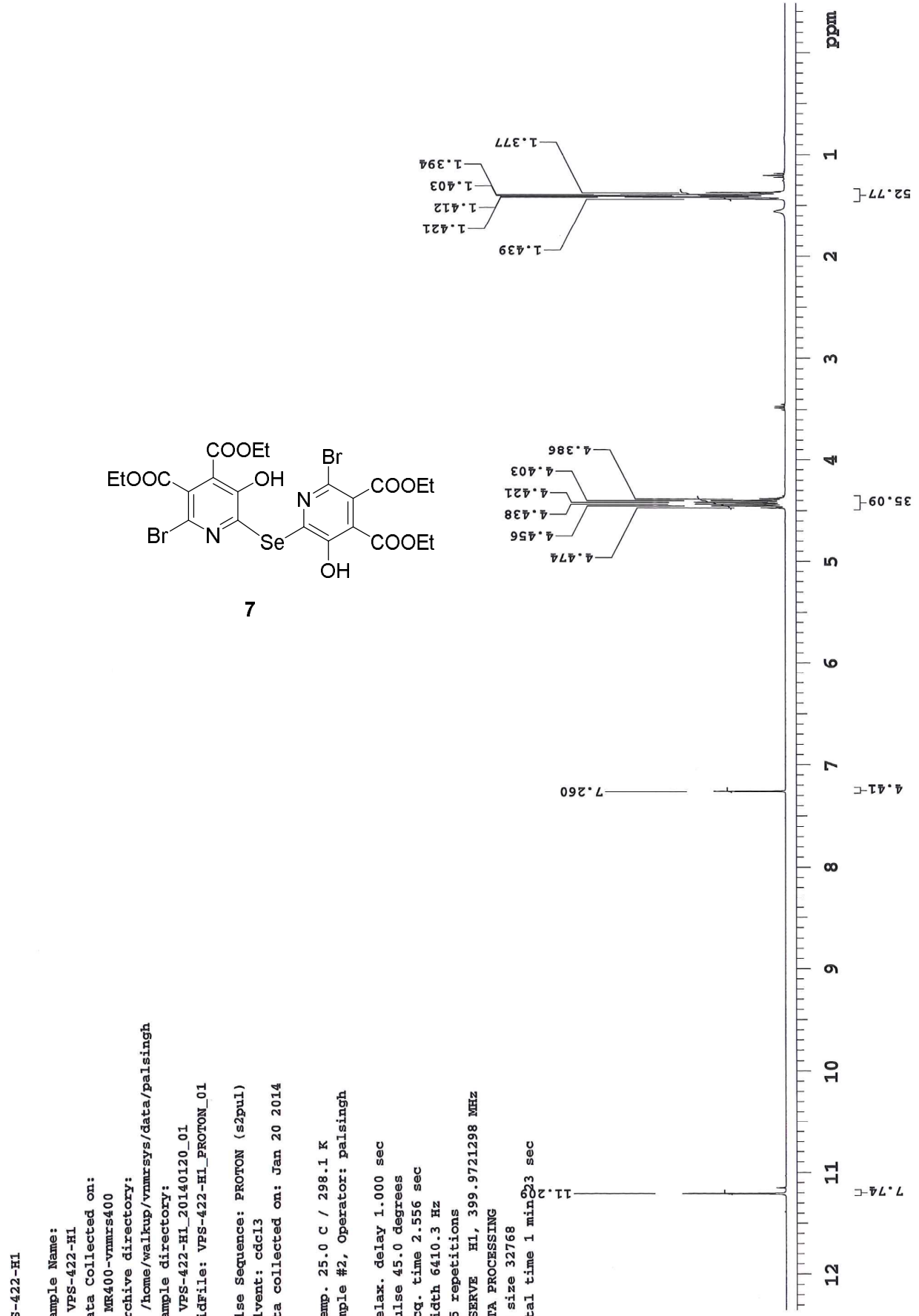


6

^{77}Se NMR spectrum of diselenide **6**



^{1}H NMR spectrum of **7**



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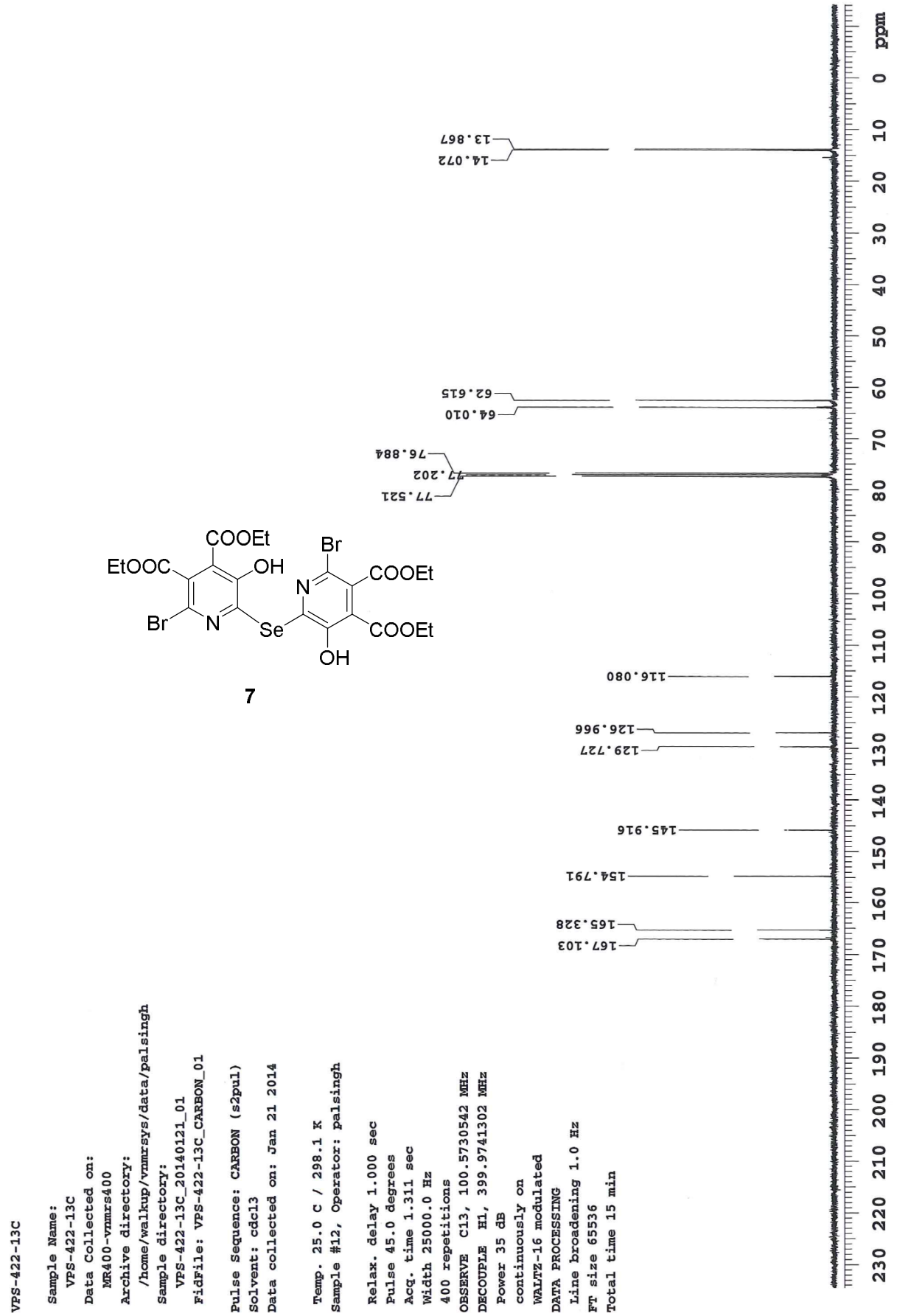

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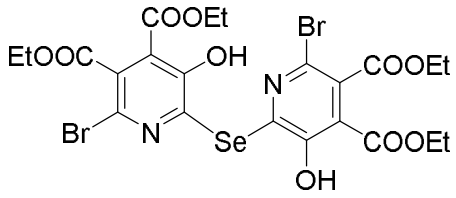

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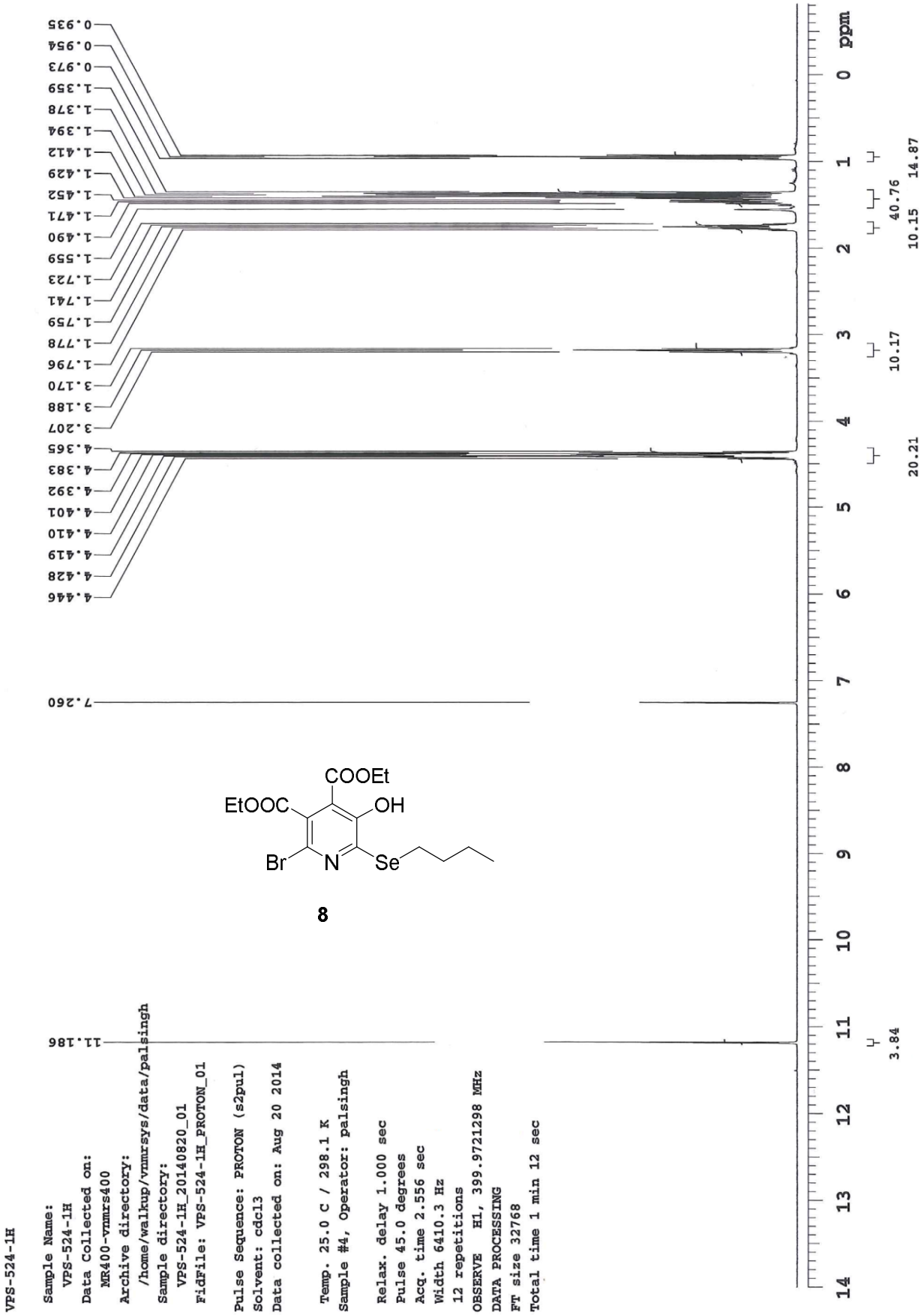

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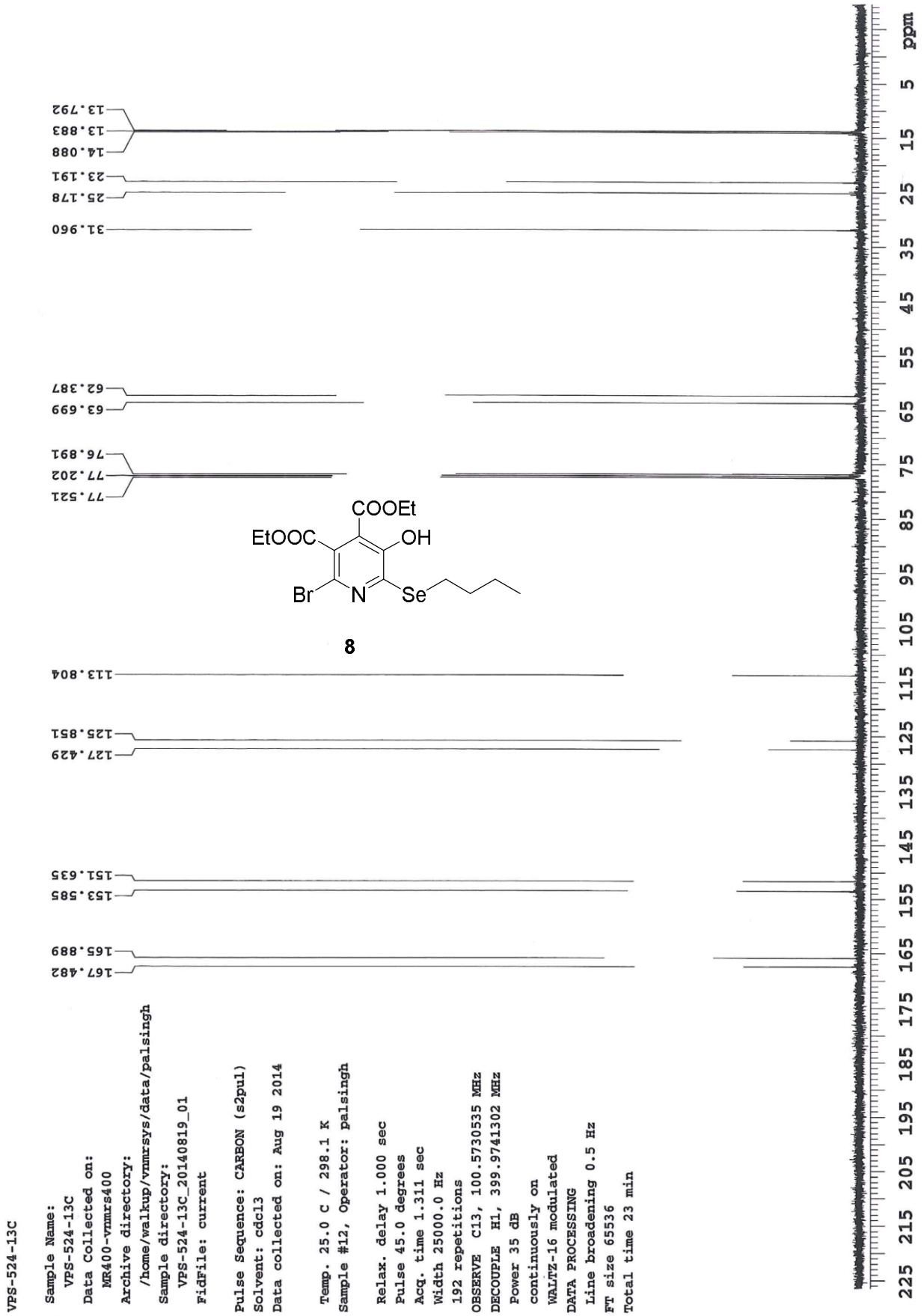

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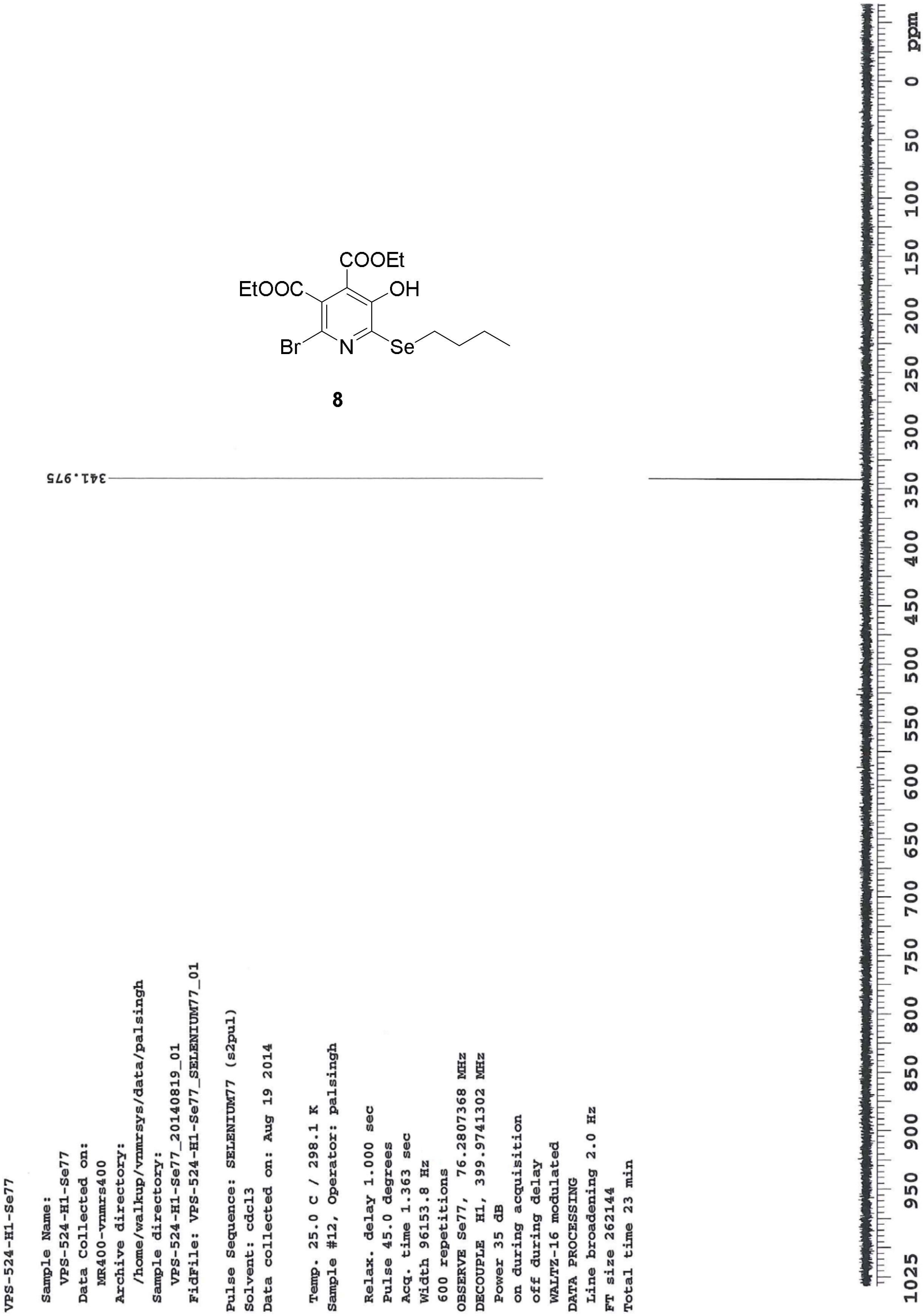

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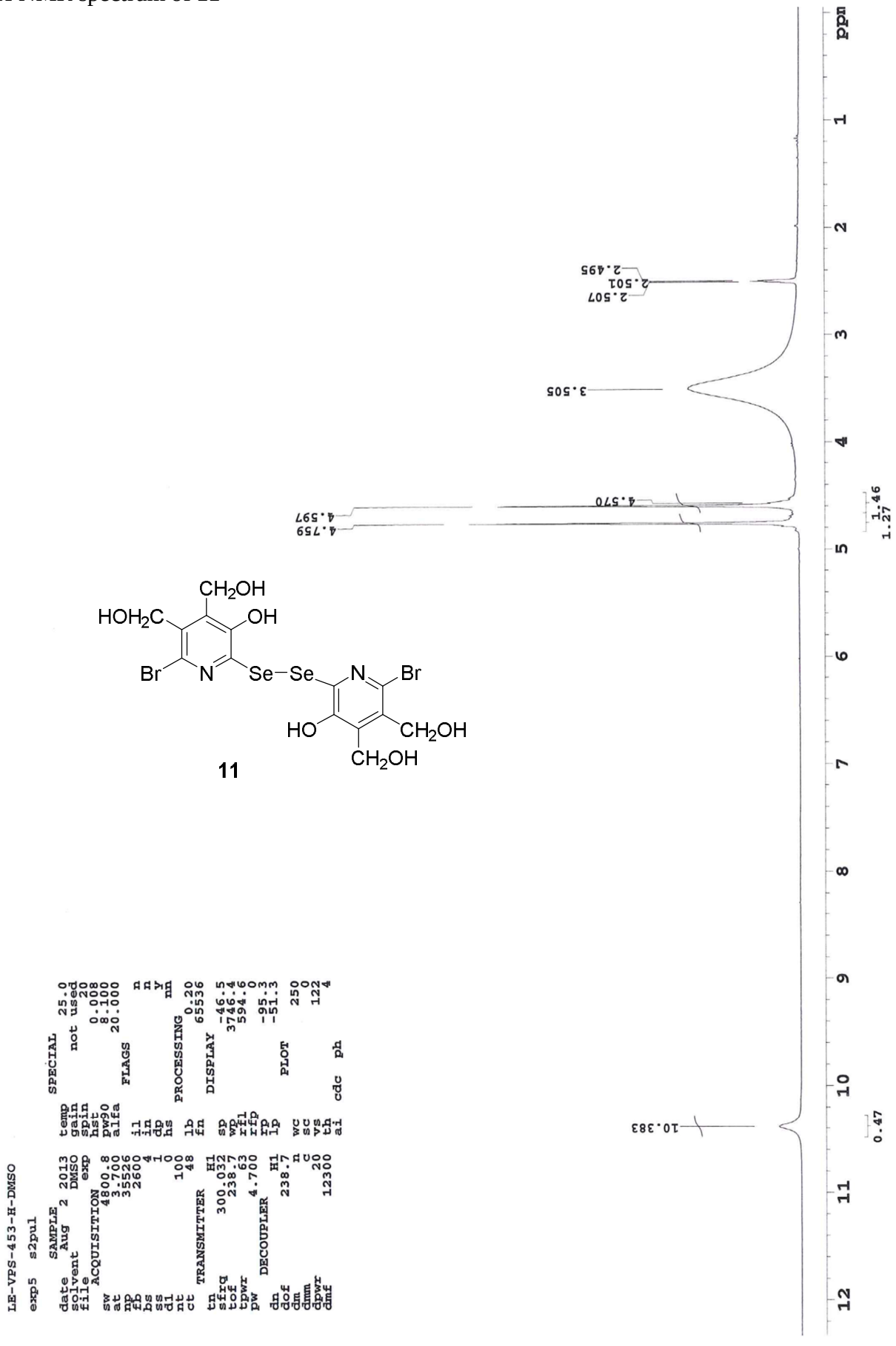

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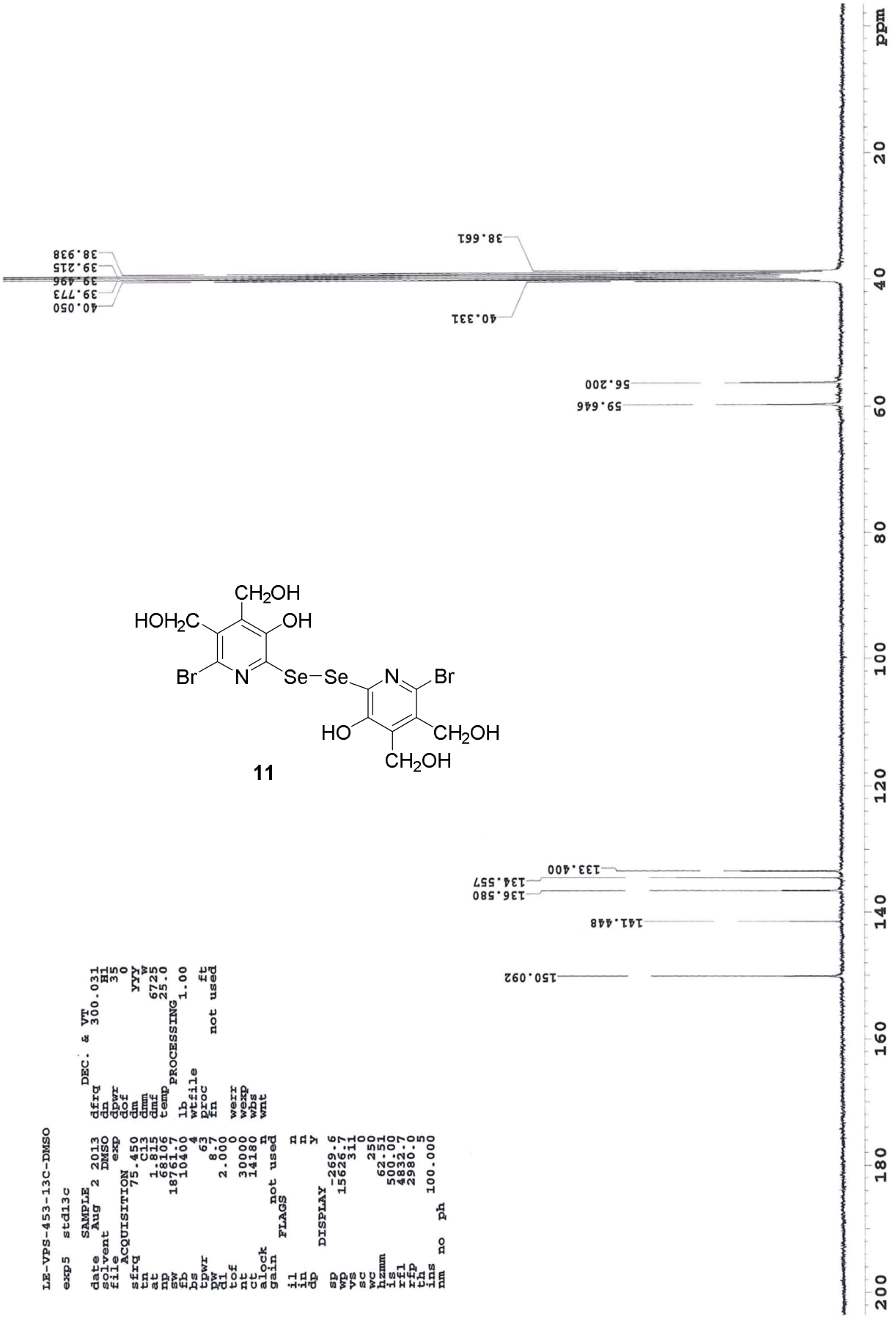
^{13}C NMR spectrum of **11**



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date Aug 2 2013
solvent DMSO
file exp
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sw 18761.7
fb 10400
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tpwr 63
pw 8.7
d1 2.000
tof 0
nt 30000
ct 14180
alock n
gain not used
FLAGS
il n
in n
dp y
DISPLAY
sp -269.6
wp 15626.7
vs 317
sc 0
wc 250
hzmm 62.51
is 500.00
rf1 4832.7
rfp 2980.0
th 5
ins 100.000
nm no ph
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dn H1
dpwr 35
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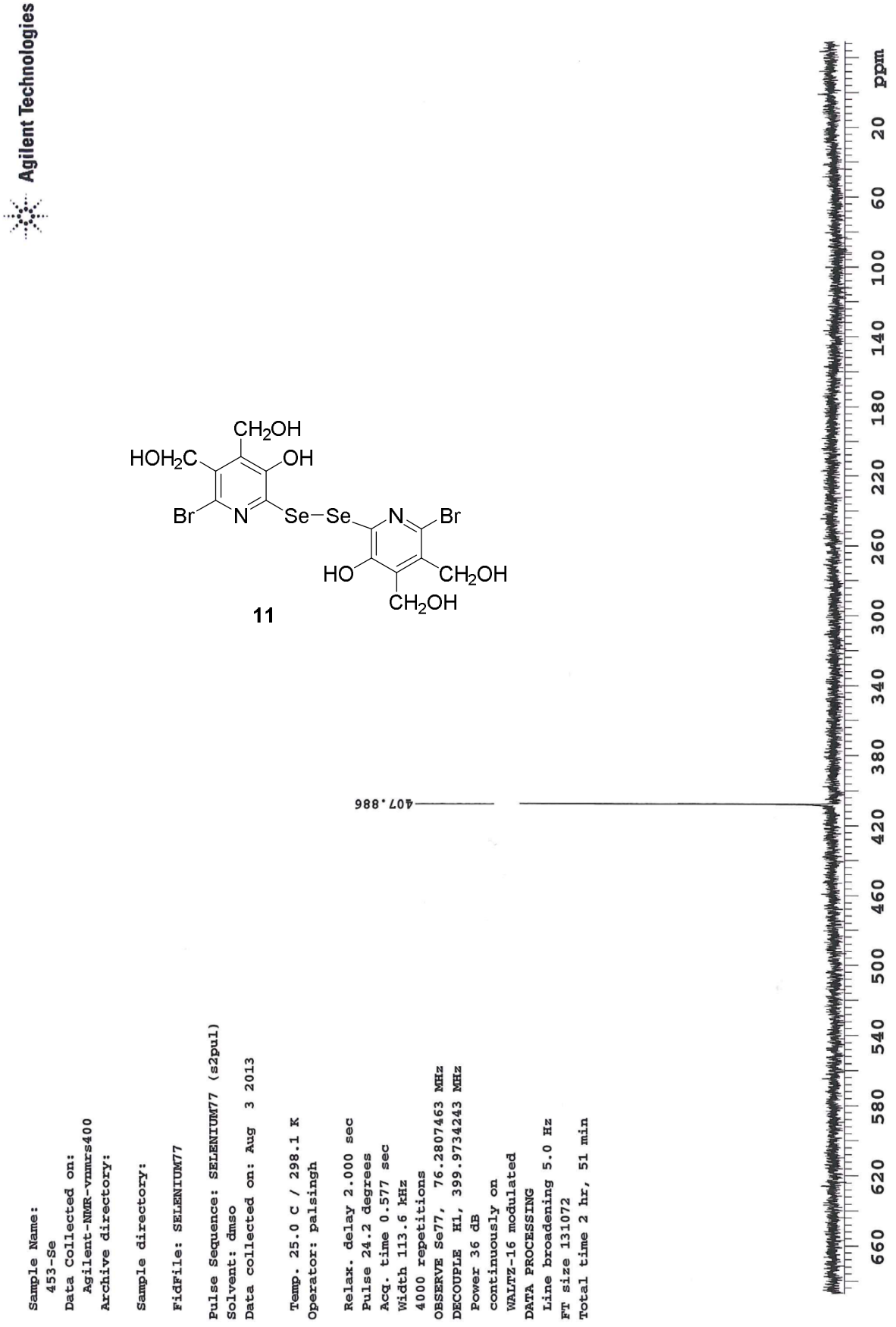
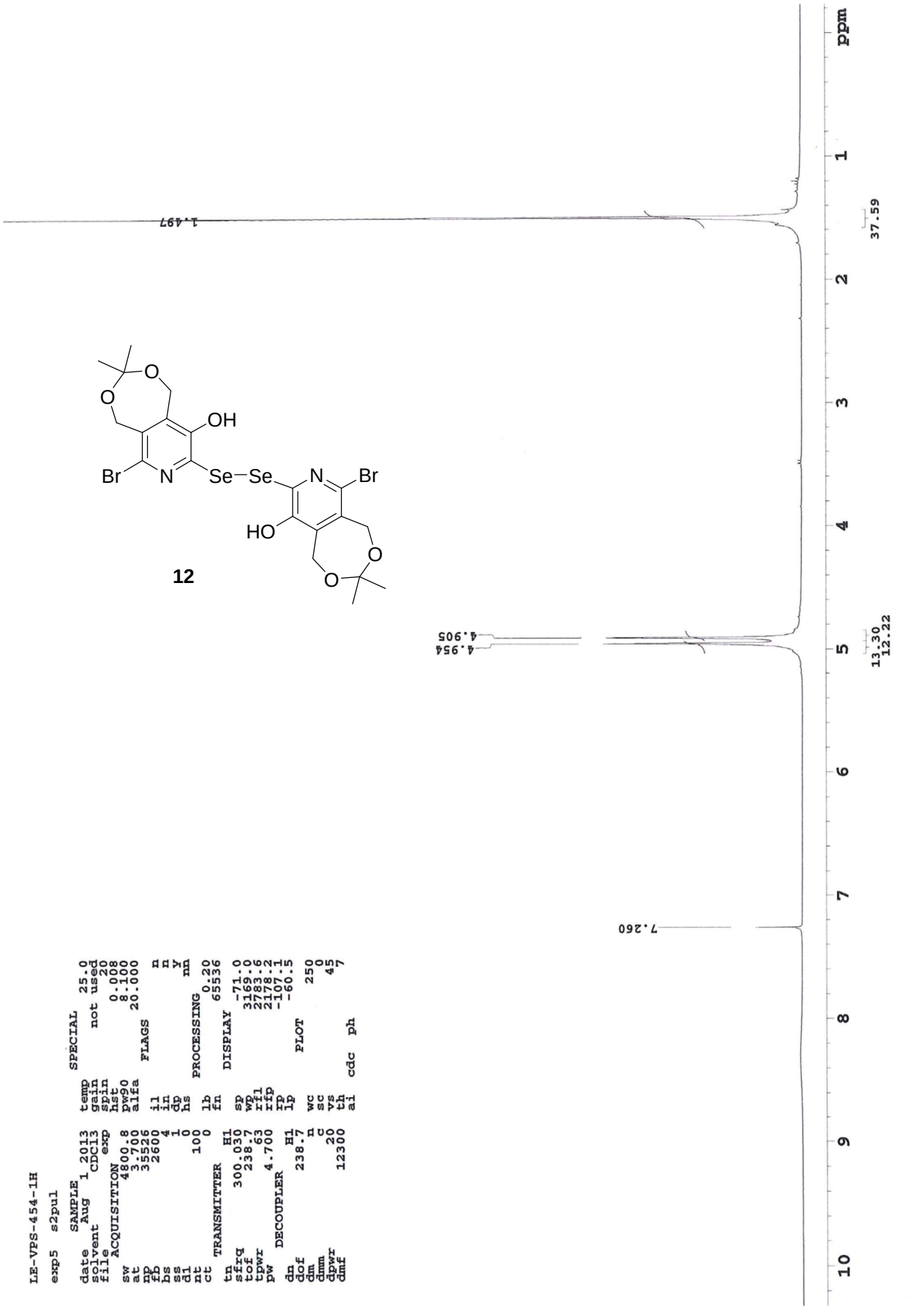
wnt

^{77}Se NMR spectrum of **11**



11

^{1}H NMR spectrum of **12**



12

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  ACQUISITION       hst       20.000
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np           35526   FLAGS       n
fb            2600   il          y
bs               4   in         nn
ss               1   dp
d1               0   hs
nt             100   PROCESSING    0.20
ct               0   lb        65536
                     fn
  TRANSMITTER       DISPLAY
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sfrq        300.030   wp       3169.0
tof         238.7     rfl      2783.6
tpwr           63     rfp      2178.2
pw          4.700     rp       -107.1
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dn              H1        PLOT
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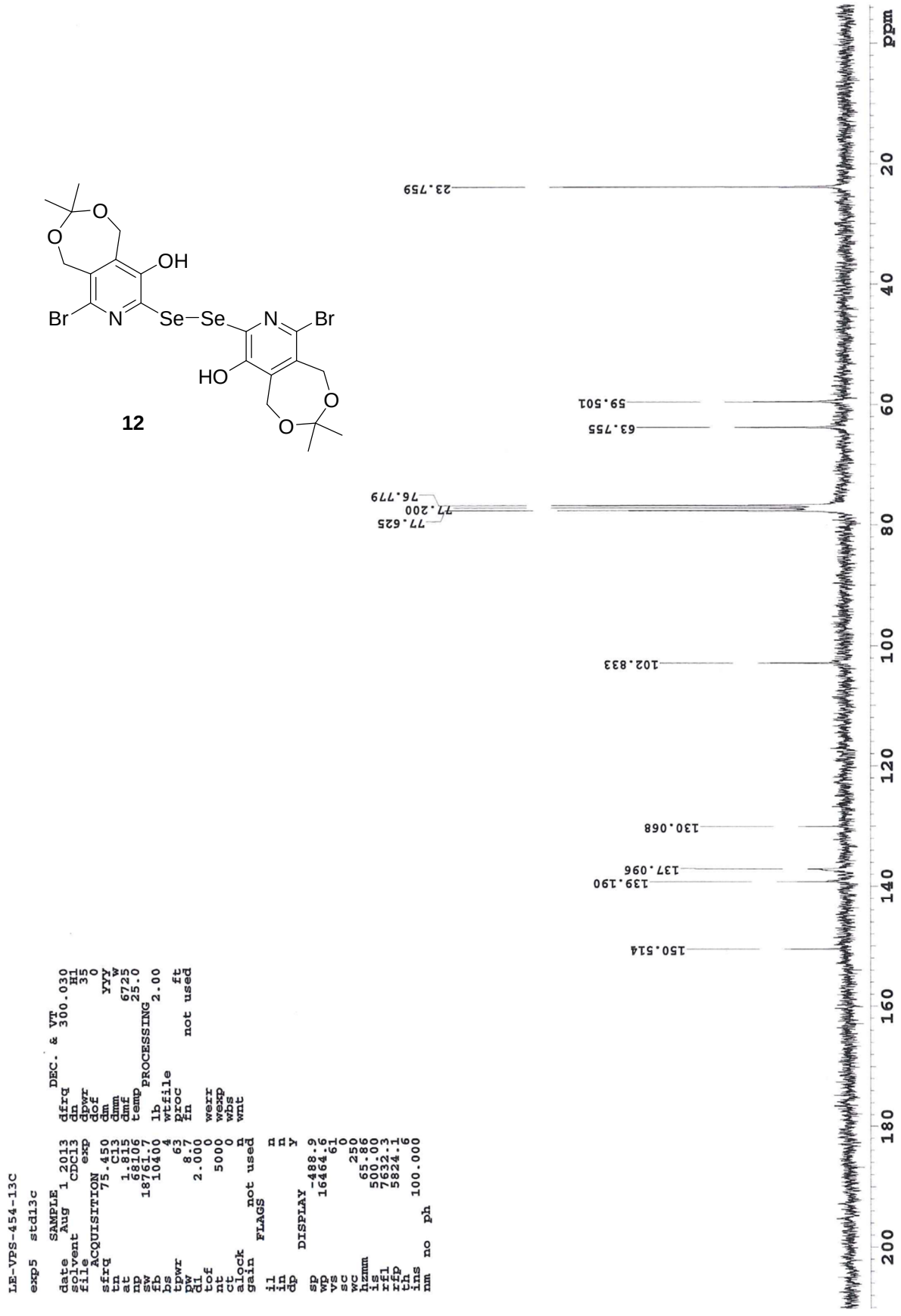
dpwr           20     th          7
dmf         12300     ai
                      cdc  ph
```

^{13}C NMR spectrum of **12**



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date Aug 1 2013
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at 1.815
np 68106
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fb 10400
bs 4
tpwr 63
pw 8.7
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ct 0
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gain not used
FLAGS
il n
in n
dp y
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wp 16464.6
vs 61
sc 0
wc 250
hzmm 65.86
is 500.00
rfl 7632.3
rfp 5824.1
th 100.000
ins
nm no ph
DEC. & VT
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dpwr 35
dof 0
dm yyy
dmm w
dmf 6725
temp 25.0
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proc ft
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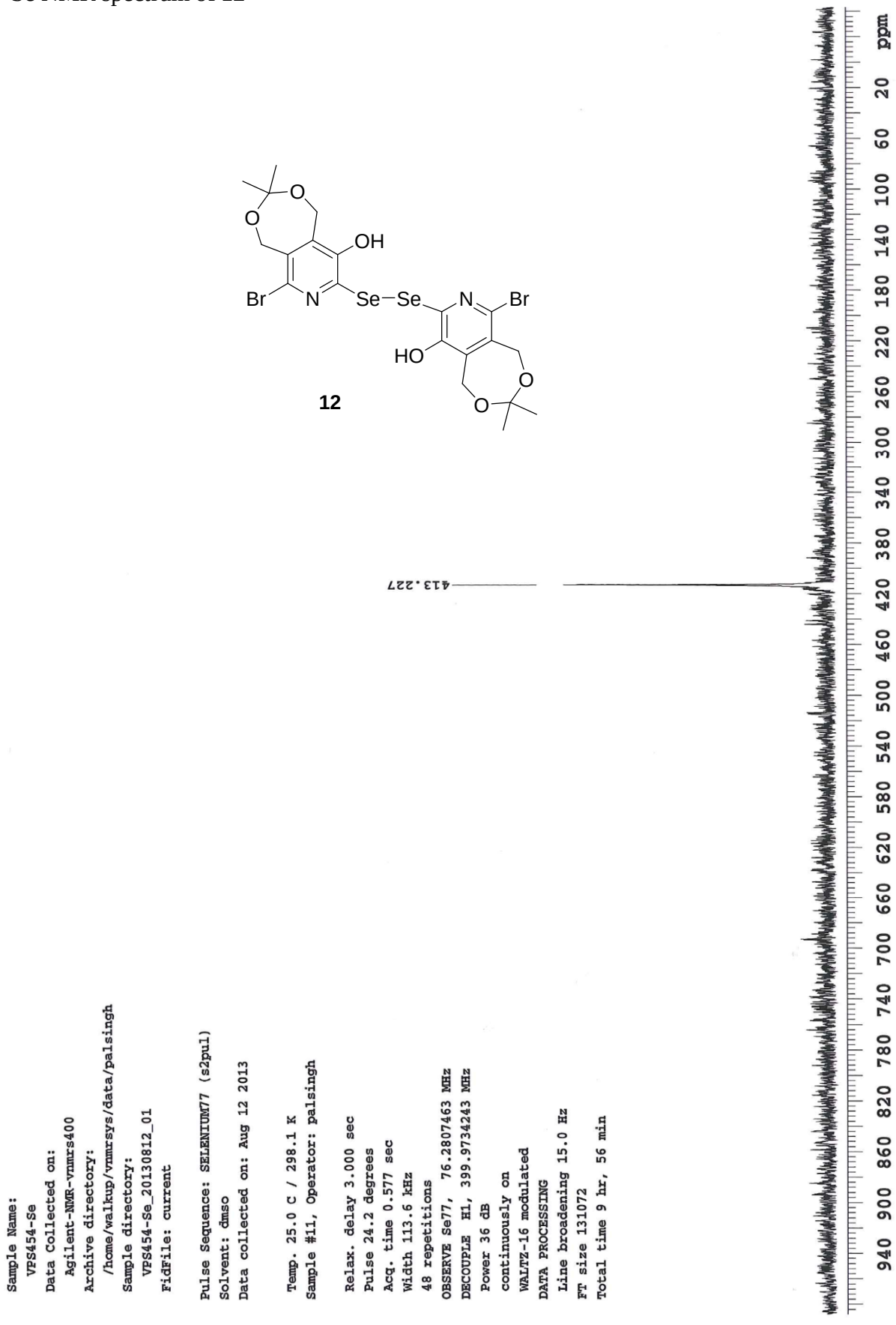
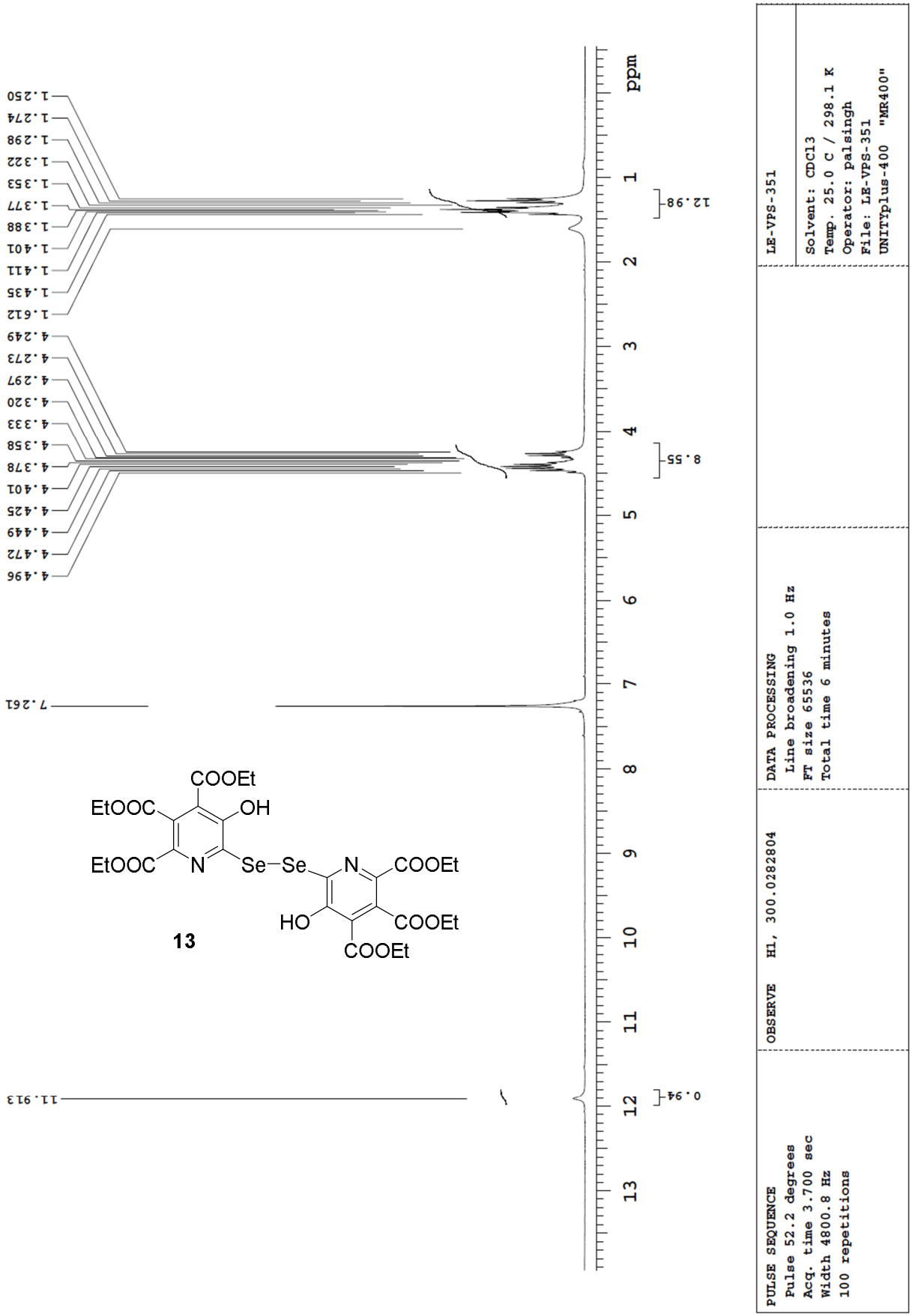
werr
wexp
wbs
wnt

^{77}Se NMR spectrum of **12**

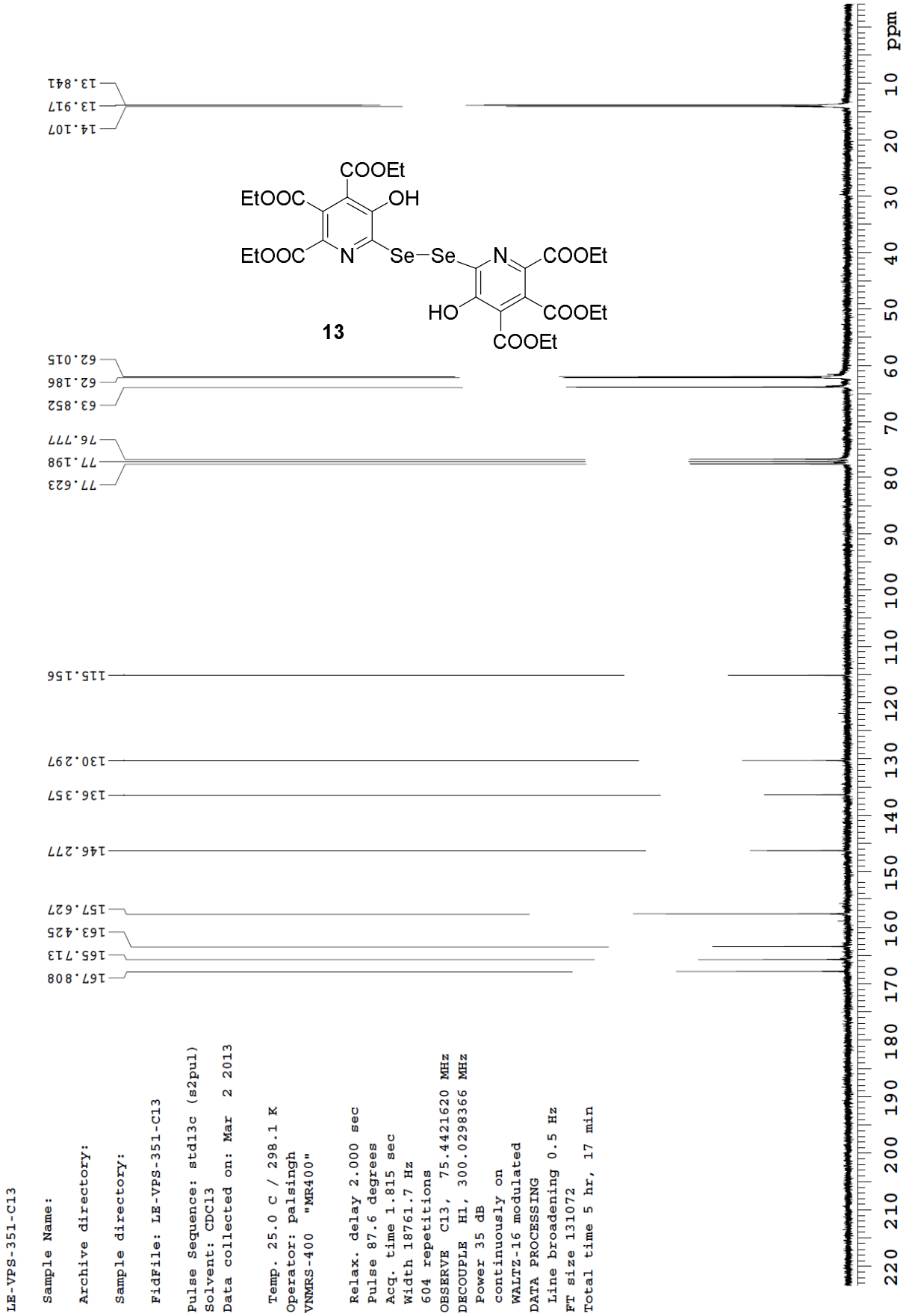


12

^{1}H NMR spectrum of **13**



^{13}C NMR spectrum of **13**



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Archive directory:
Sample directory:
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Solvent: CDCl3
Data collected on: Mar 2 2013
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Operator: palsingh
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Pulse 87.6 degrees
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DECOUPLE H1, 300.0298366 MHz
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continuously on
WALTZ-16 modulated
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Line broadening 0.5 Hz
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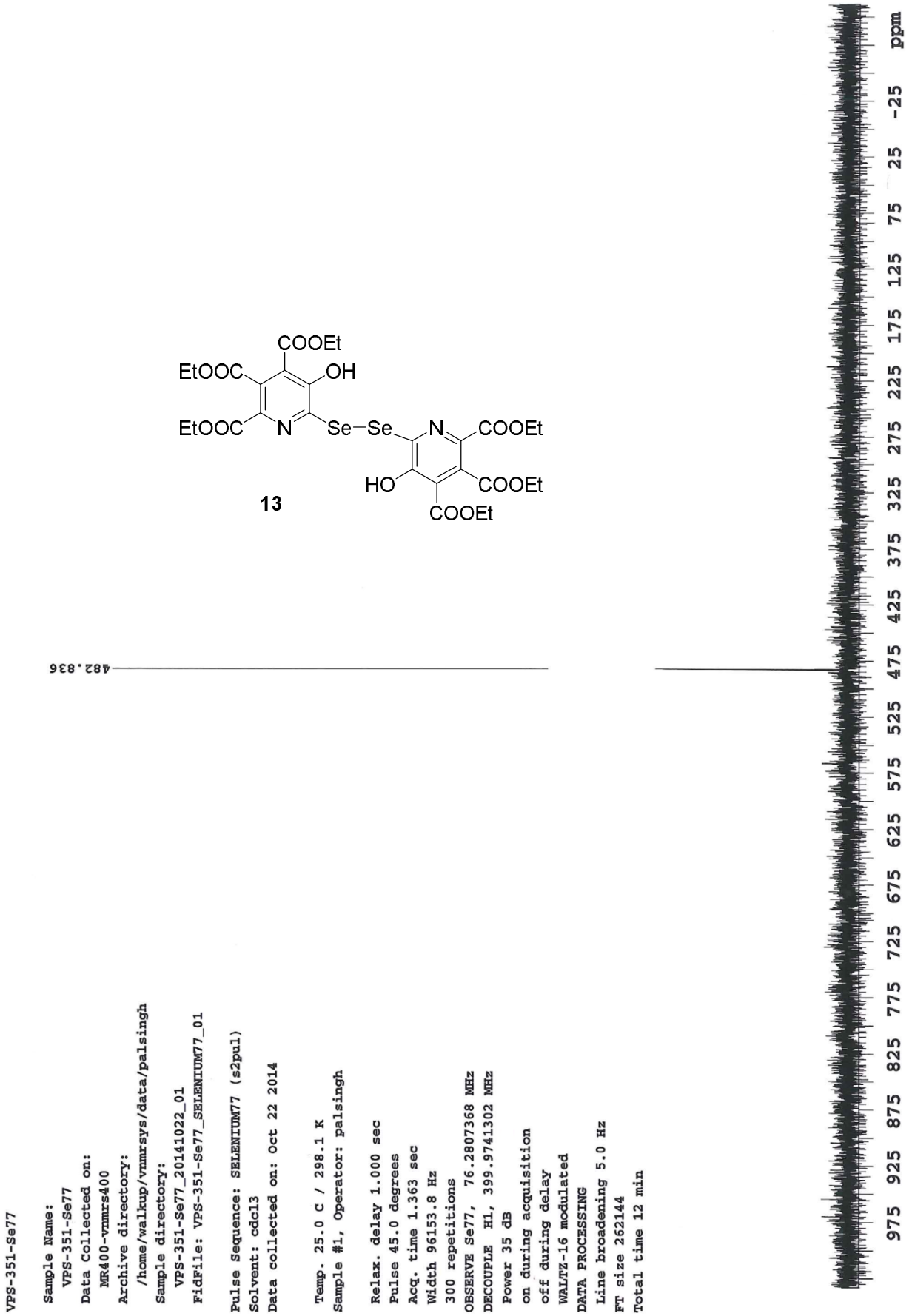
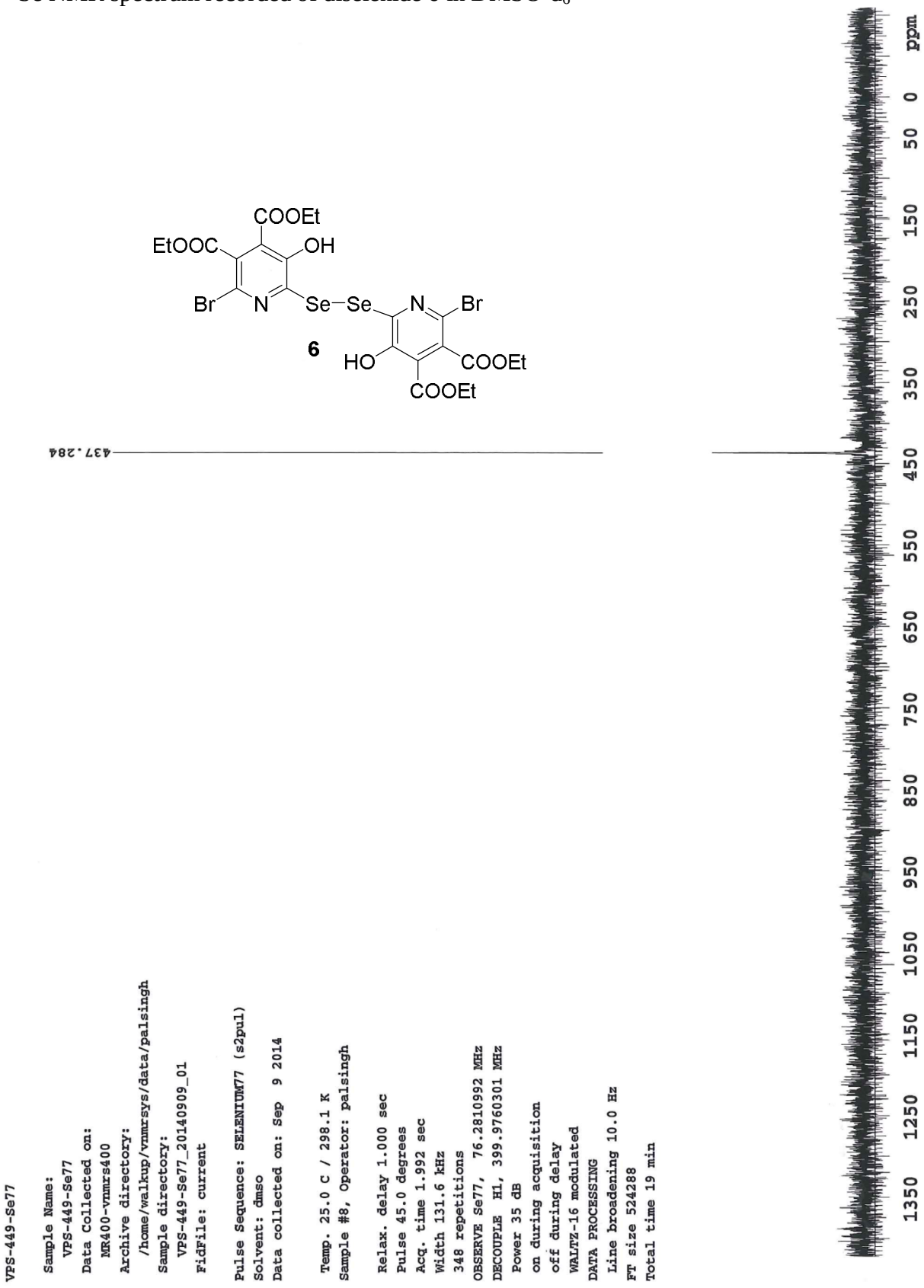
^{77}Se NMR spectrum of **13**



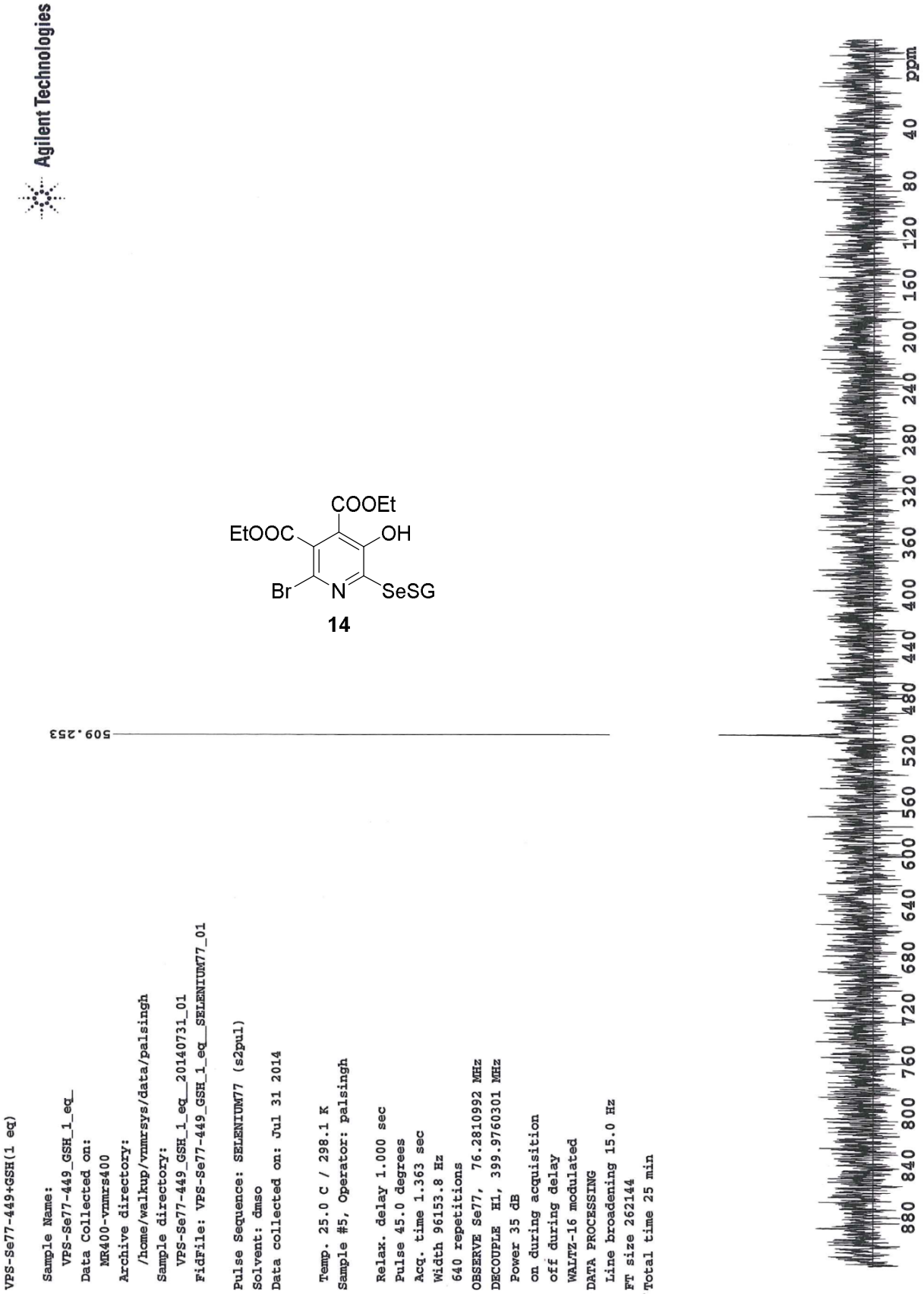
13

^{77}Se NMR Experimental Data for the Mechanistic Studies with Diselenide 6

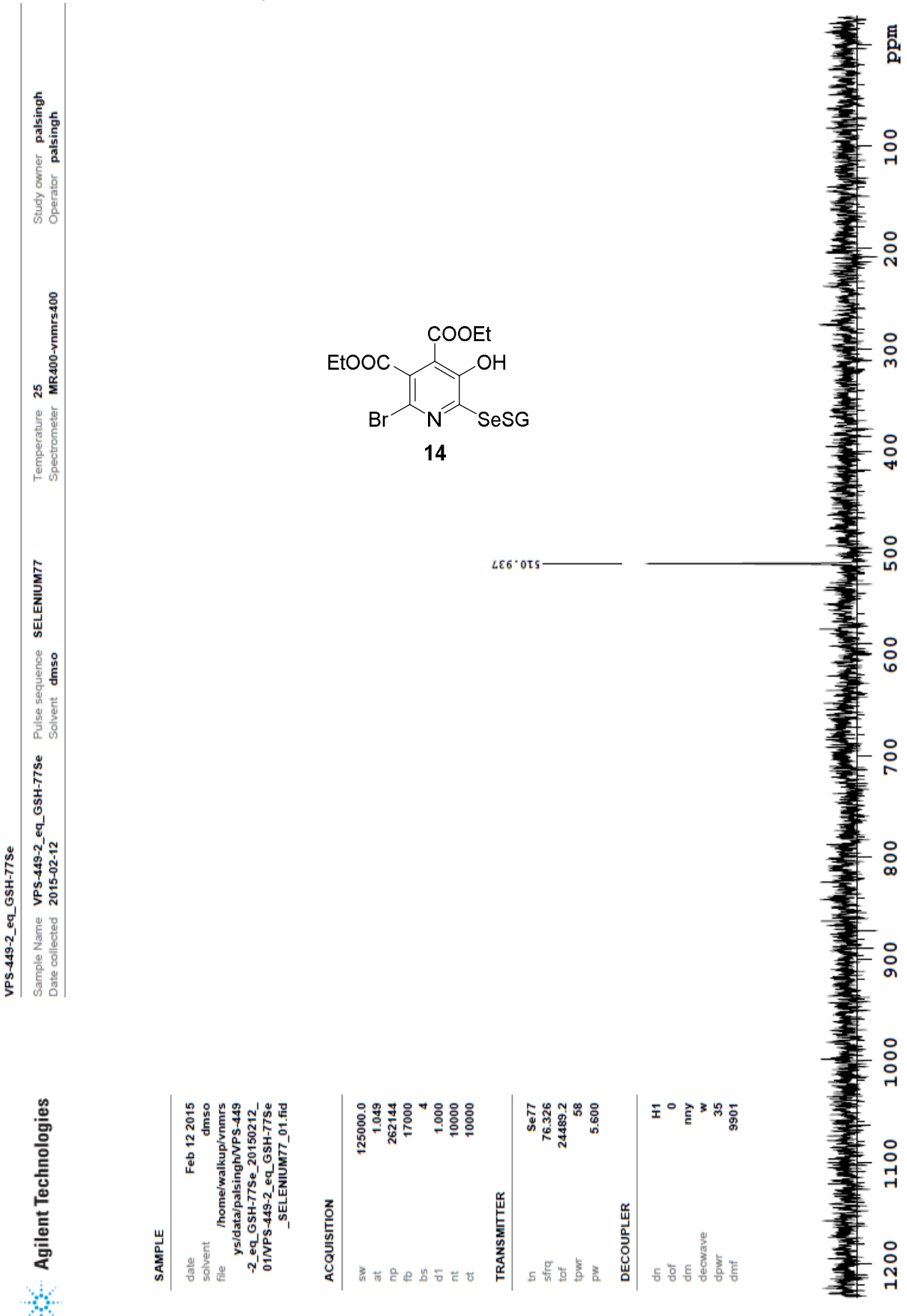
^{77}Se NMR spectrum recorded of diselenide **6** in DMSO-d_6



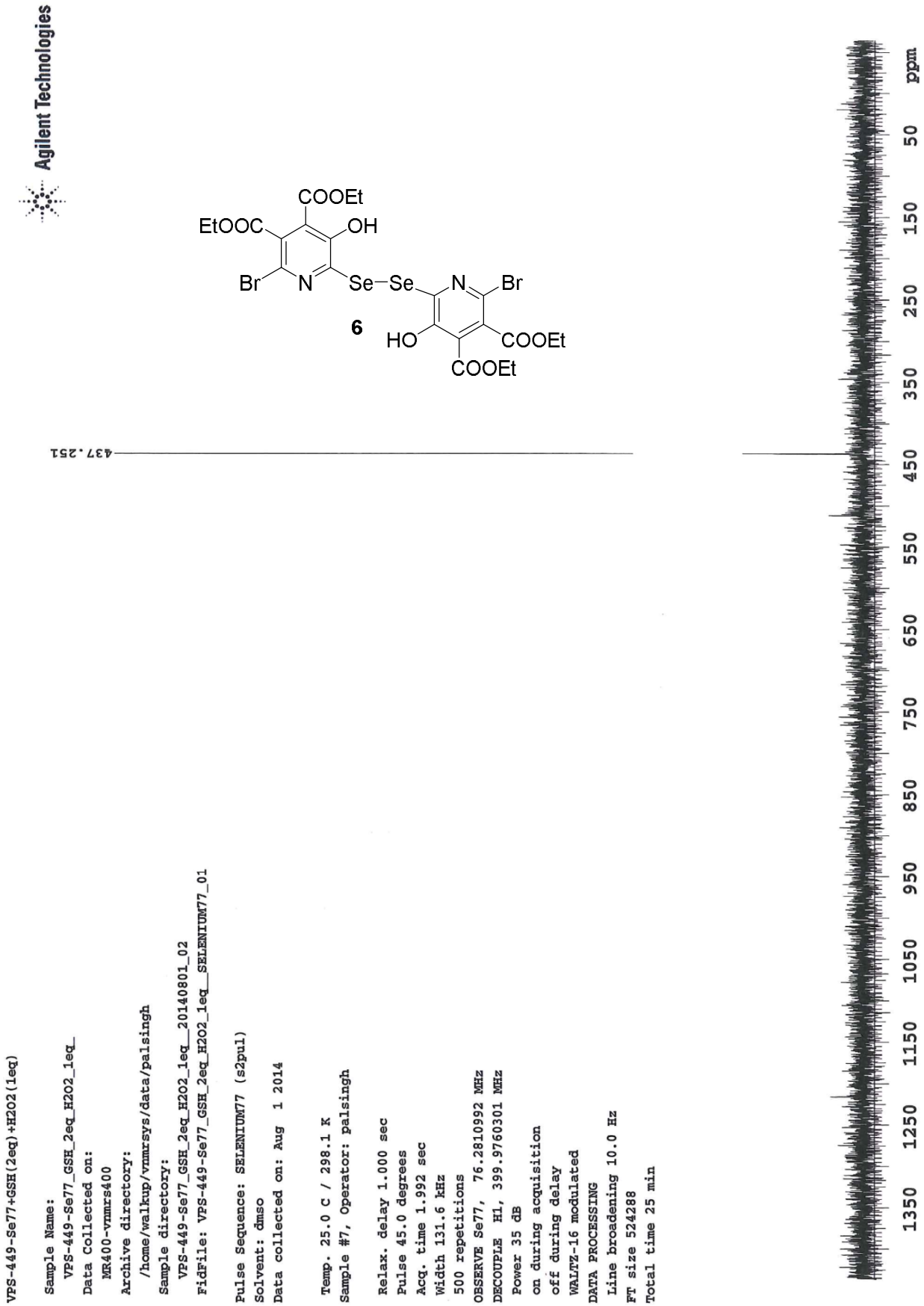
^{77}Se NMR spectrum recorded after the addition of 1 equiv of GSH (dissolved in 200 µL H_2O) to a solution of diselenide **6** in DMSO-d_6.



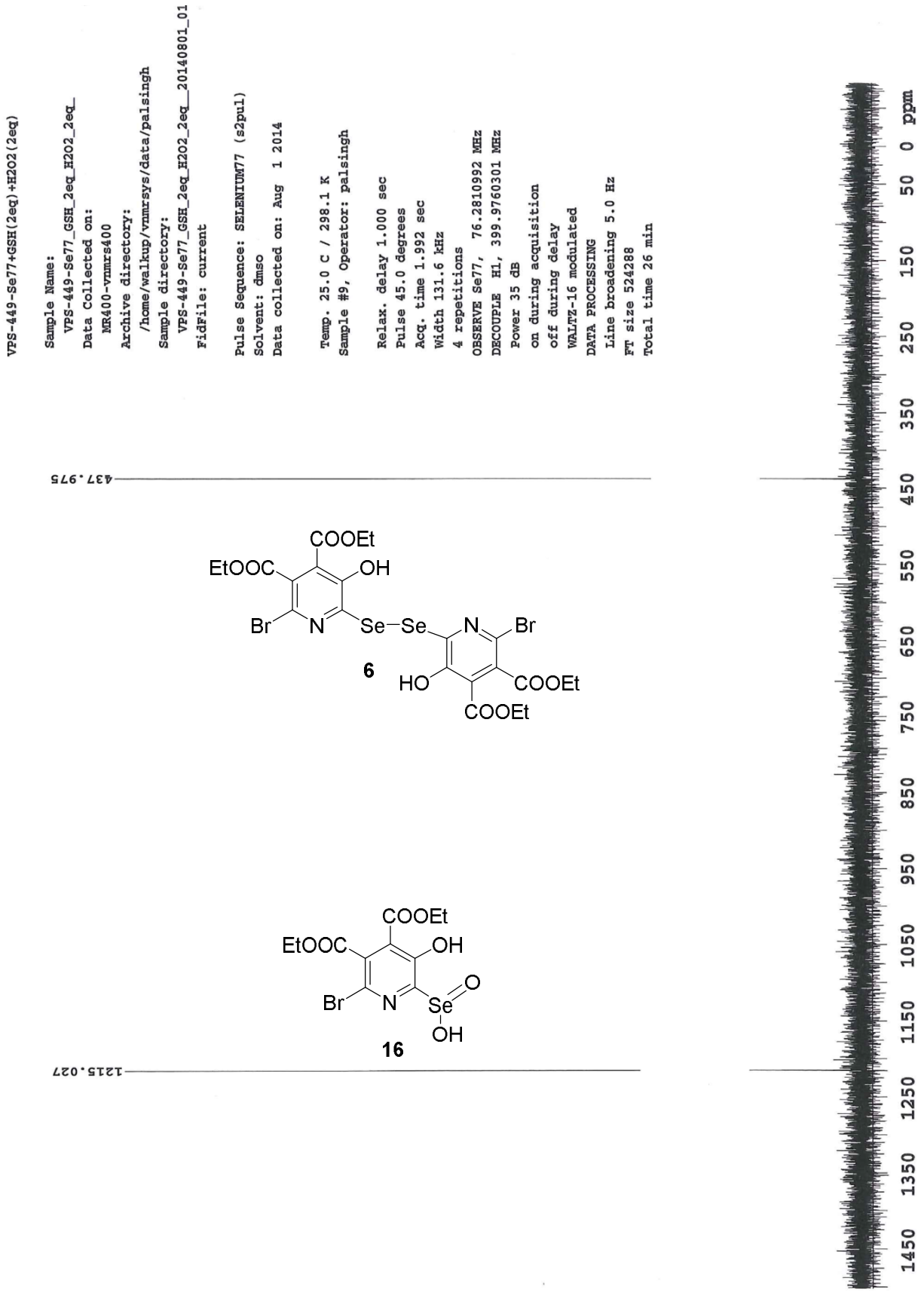
^{77}Se NMR spectrum recorded after the addition of 1 more equiv of GSH (2 equiv) to the above mixture in DMSO-d_6.



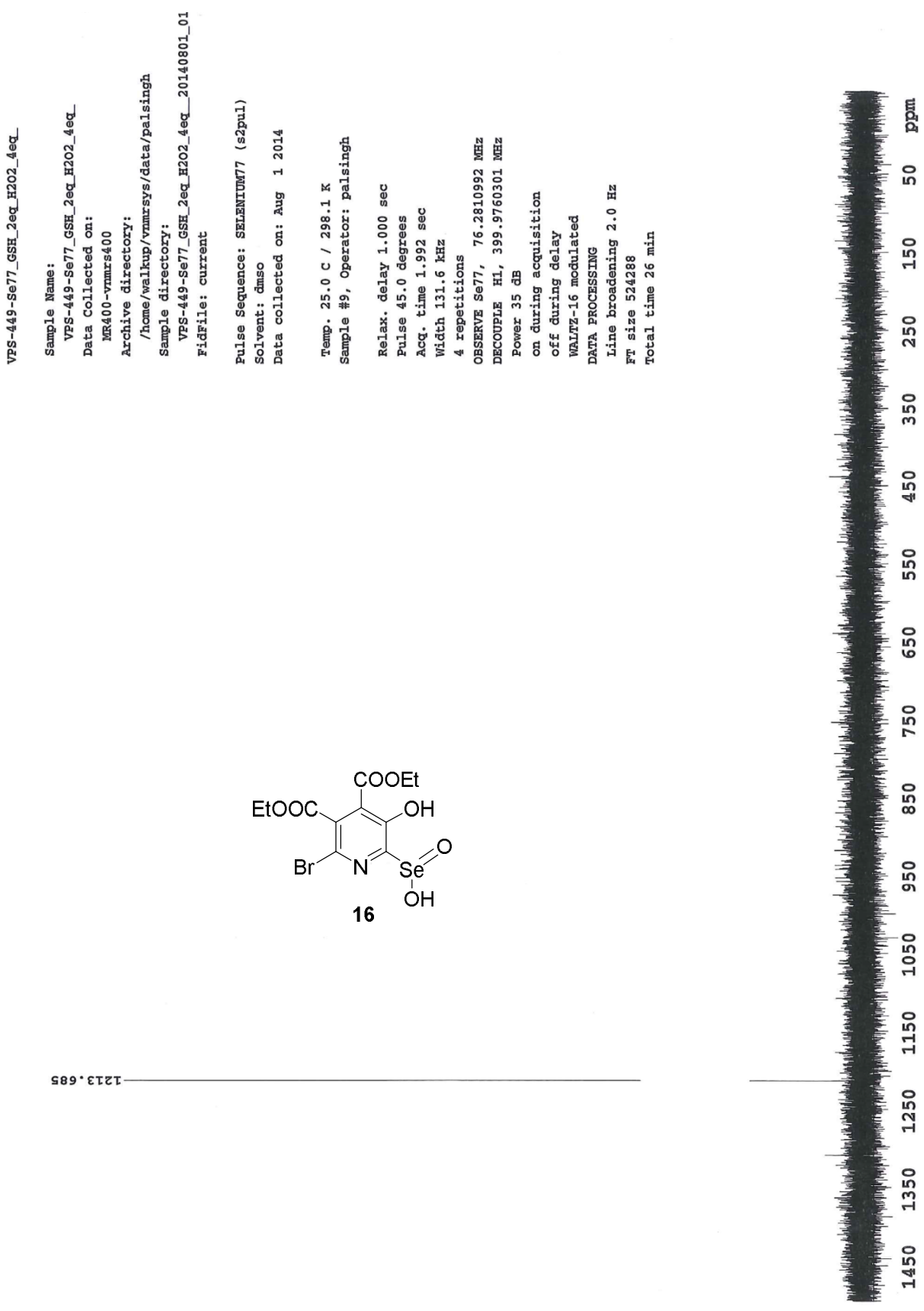
^{77}Se NMR spectrum recorded after the addition of 1 equiv of H_2O_2 to the above mixture of diselenide **6** containing GSH (2 equiv) in DMSO-d_6.



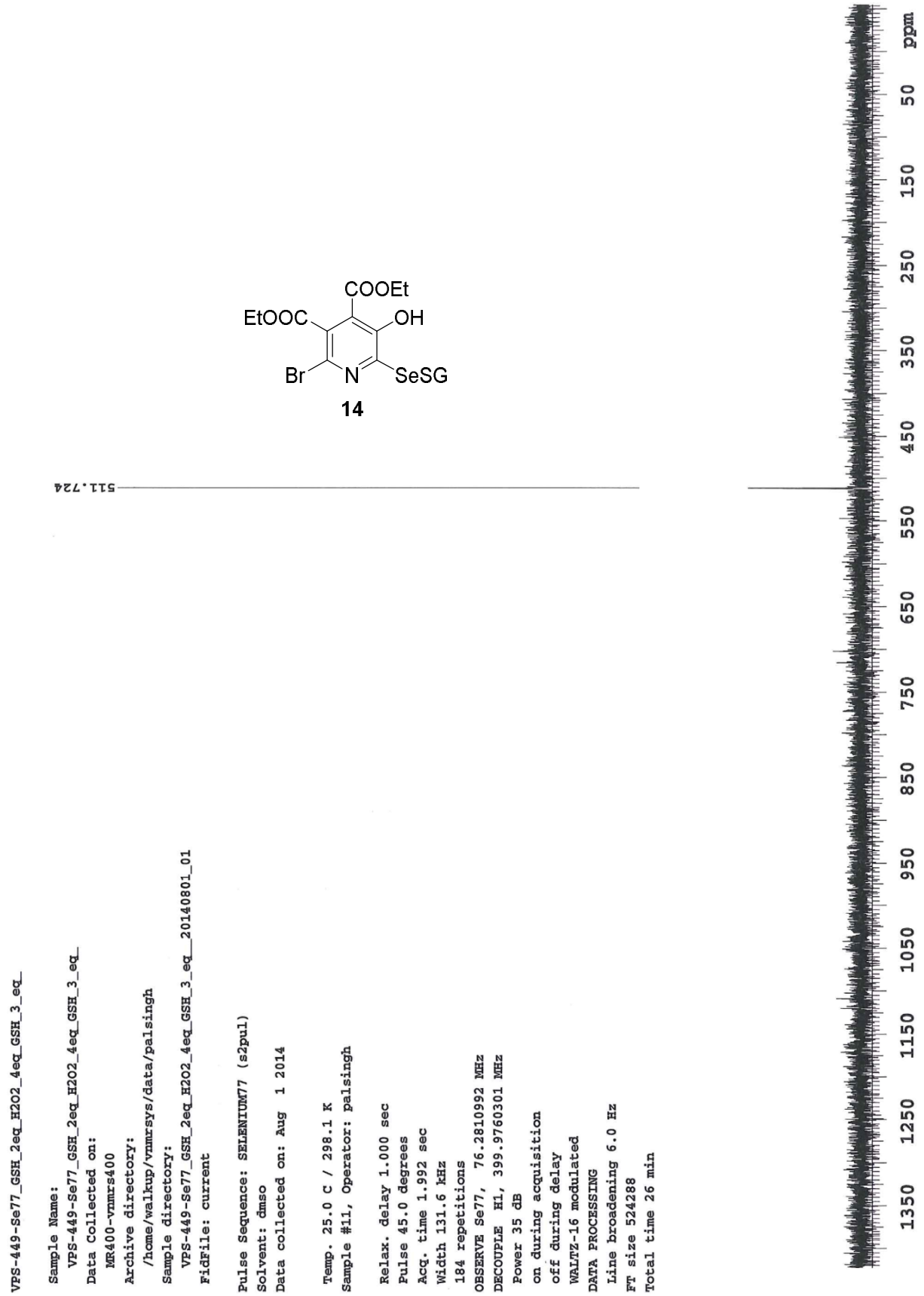
^{77}Se NMR spectrum recorded after the addition of 1 more equiv of H_2O_2 (2 equiv) to the above mixture of diselenide **6** in DMSO-d_6.



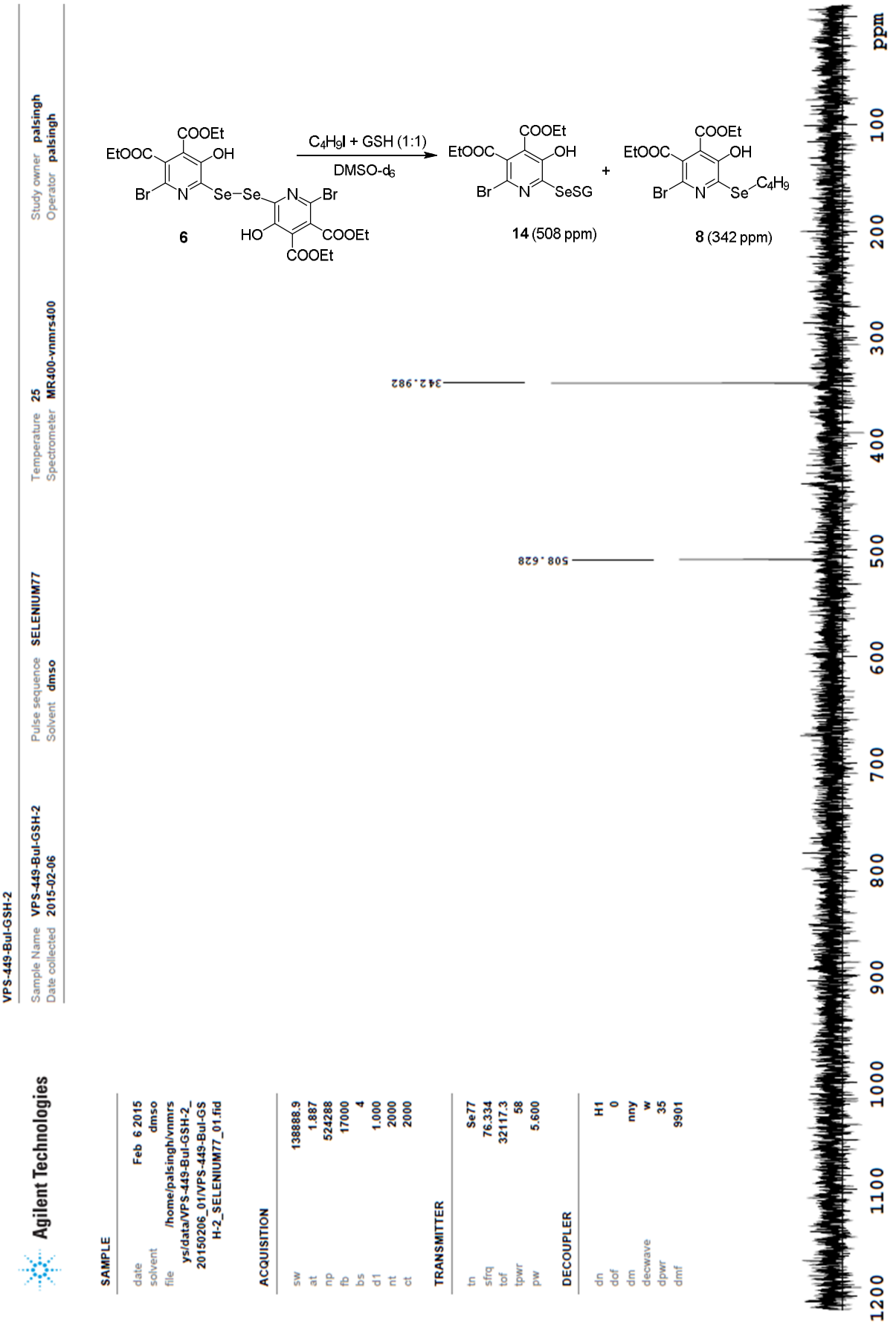
^{77}Se NMR spectrum recorded after the addition of 2 more equiv of H_2O_2 (4 equiv) to the above mixture of diselenide **6** in DMSO-d_6.



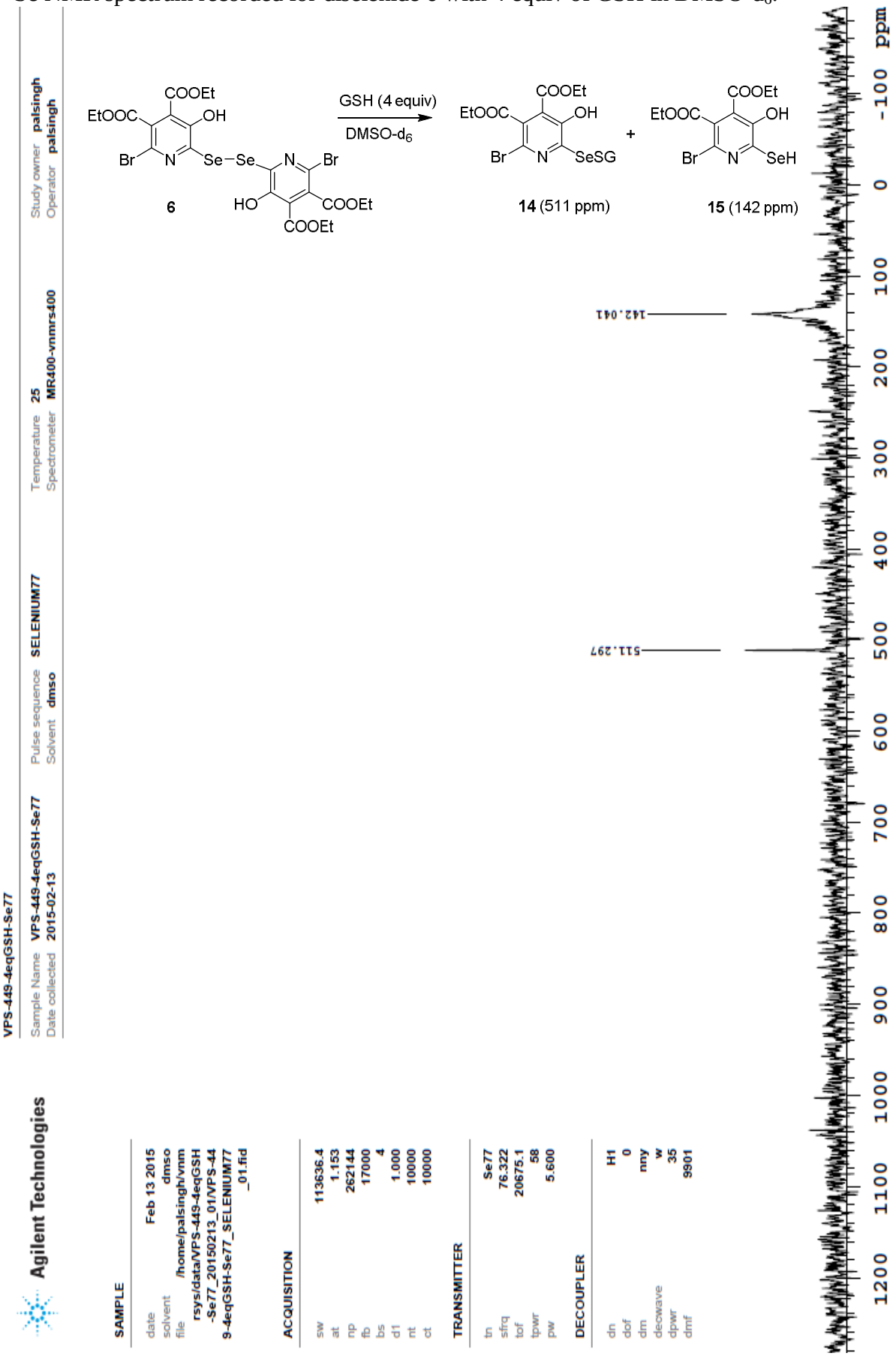
^{77}Se NMR spectrum recorded after the addition of 3 equiv of GSH to the above mixture of diselenide **6** in DMSO-d_6.



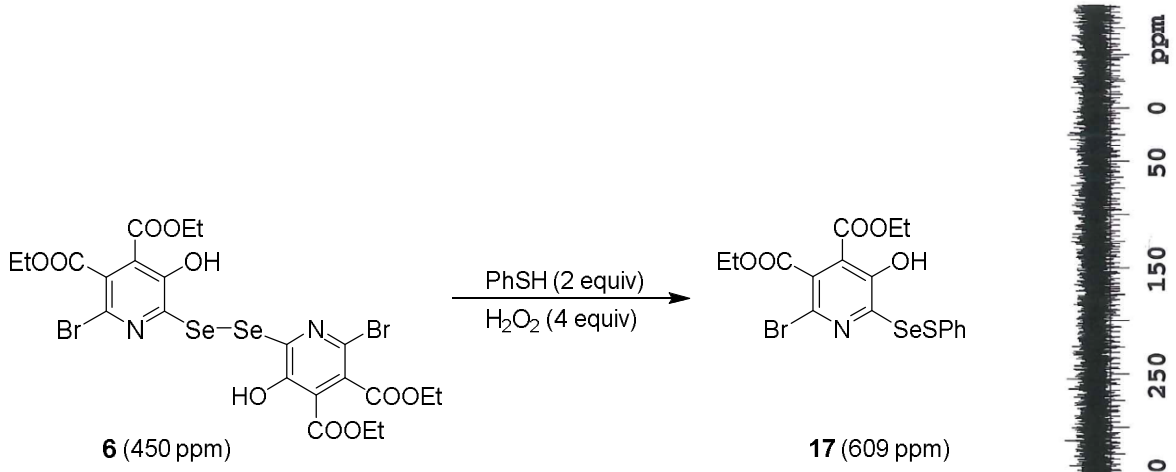
^{77}Se NMR spectrum of diselenide **6** with a mixture of iodobutane and GSH in DMSO-d6



^{77}Se NMR spectrum recorded for diselenide **6** with 4 equiv of GSH in DMSO-d_6.



^{77}Se NMR spectrum of diselenide **6** with PhSH (2 equiv) and H_2O_2 (4 equiv) in $CDCl_3$



6 (450 ppm) **17** (609 ppm)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    /home/walkup/vnmrsys/data/palsingh
  Sample directory:
    VPS-449_PhSH_2eq_H2O2_4_eq_20141023_01
  FidFile: VPS-449_PhSH_2eq_H2O2_4_eq_SELENIUM77_01

  Pulse Sequence: SELENIUM77 (s2pul)
  Solvent: cdcl3
  Data collected on: Oct 23 2014

  Temp. 25.0 C / 298.1 K
  Sample #1, Operator: palsingh

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  DECOUPLE H1, 399.9741302 MHz
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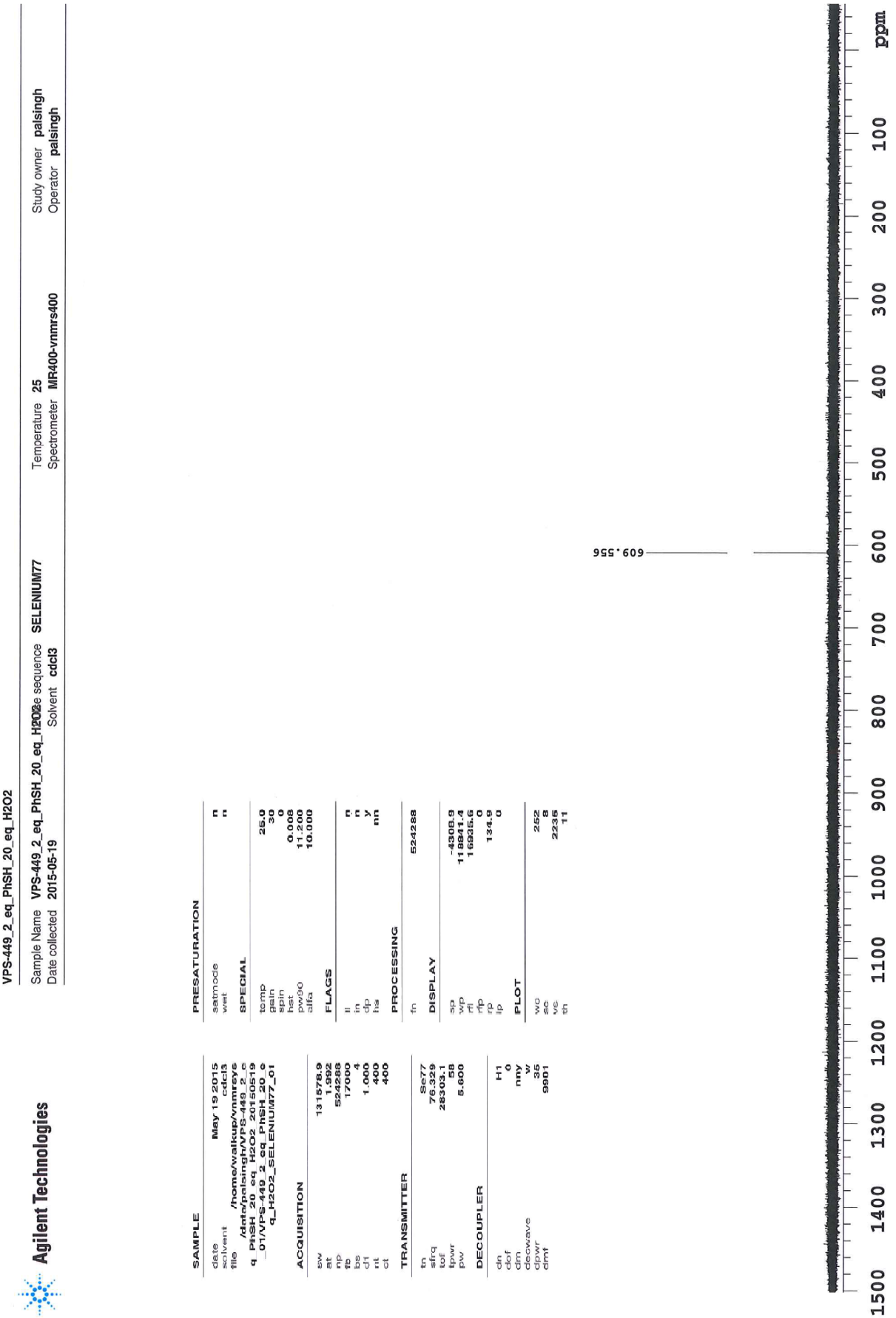
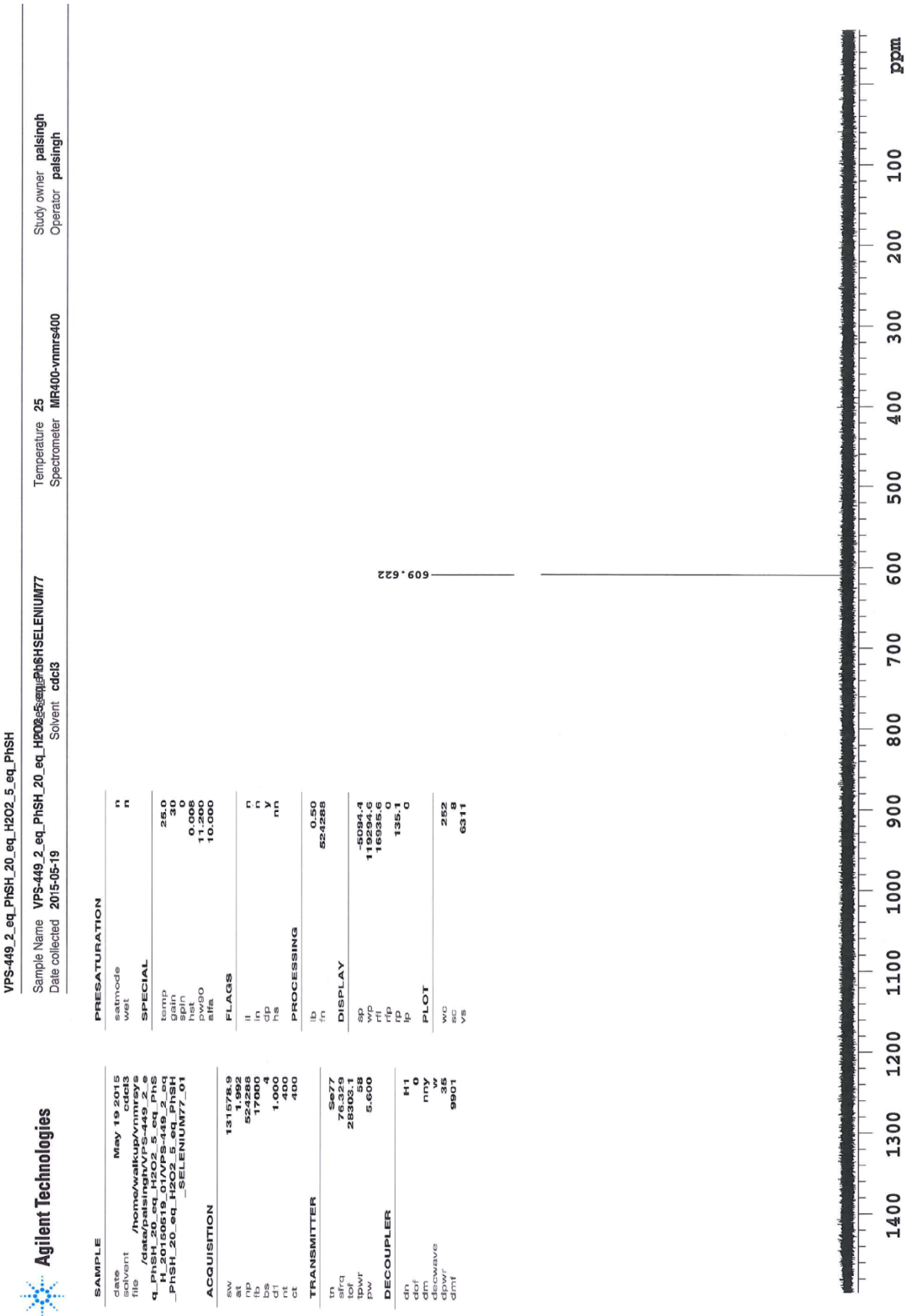
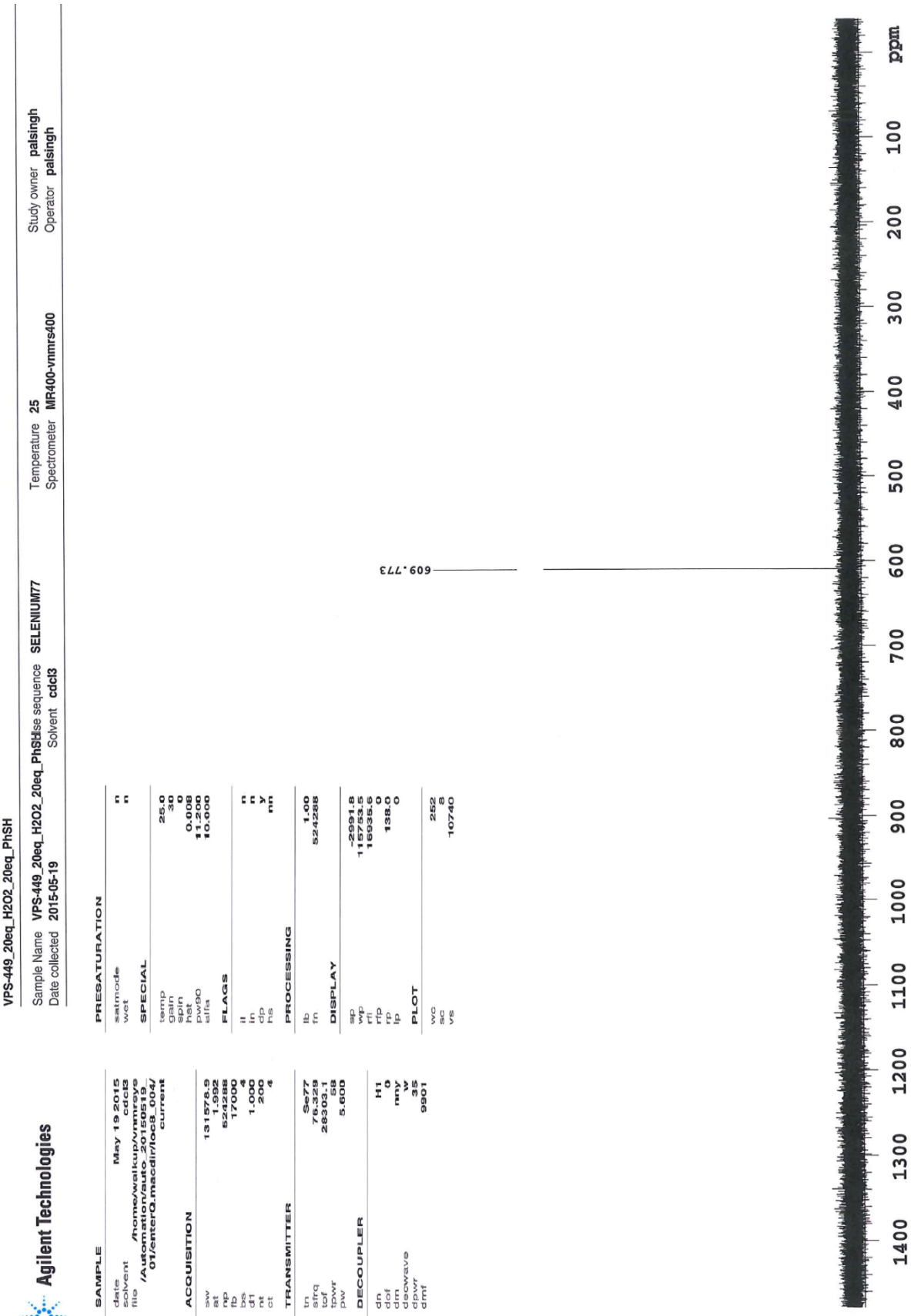
^{77}Se NMR spectrum of diselenide **6** with PhSH (2 equiv) and H_2O_2 (20 equiv) in $CDCl_3$



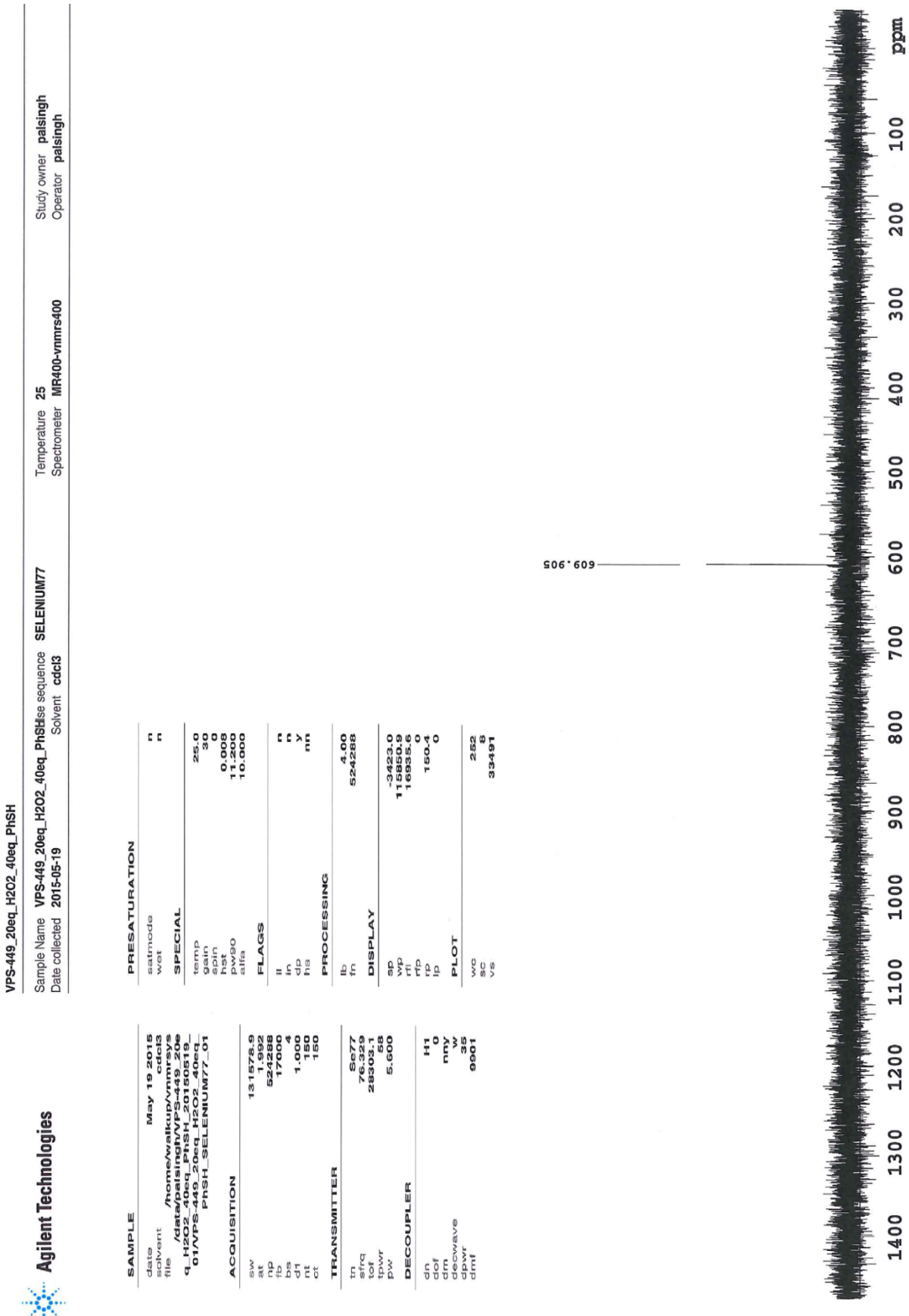
^{77}Se NMR spectrum of diselenide **6** after the addition of PhSH (3 equiv) to the above [total PhSH (5 equiv) and H_2O_2 (20 equiv)]



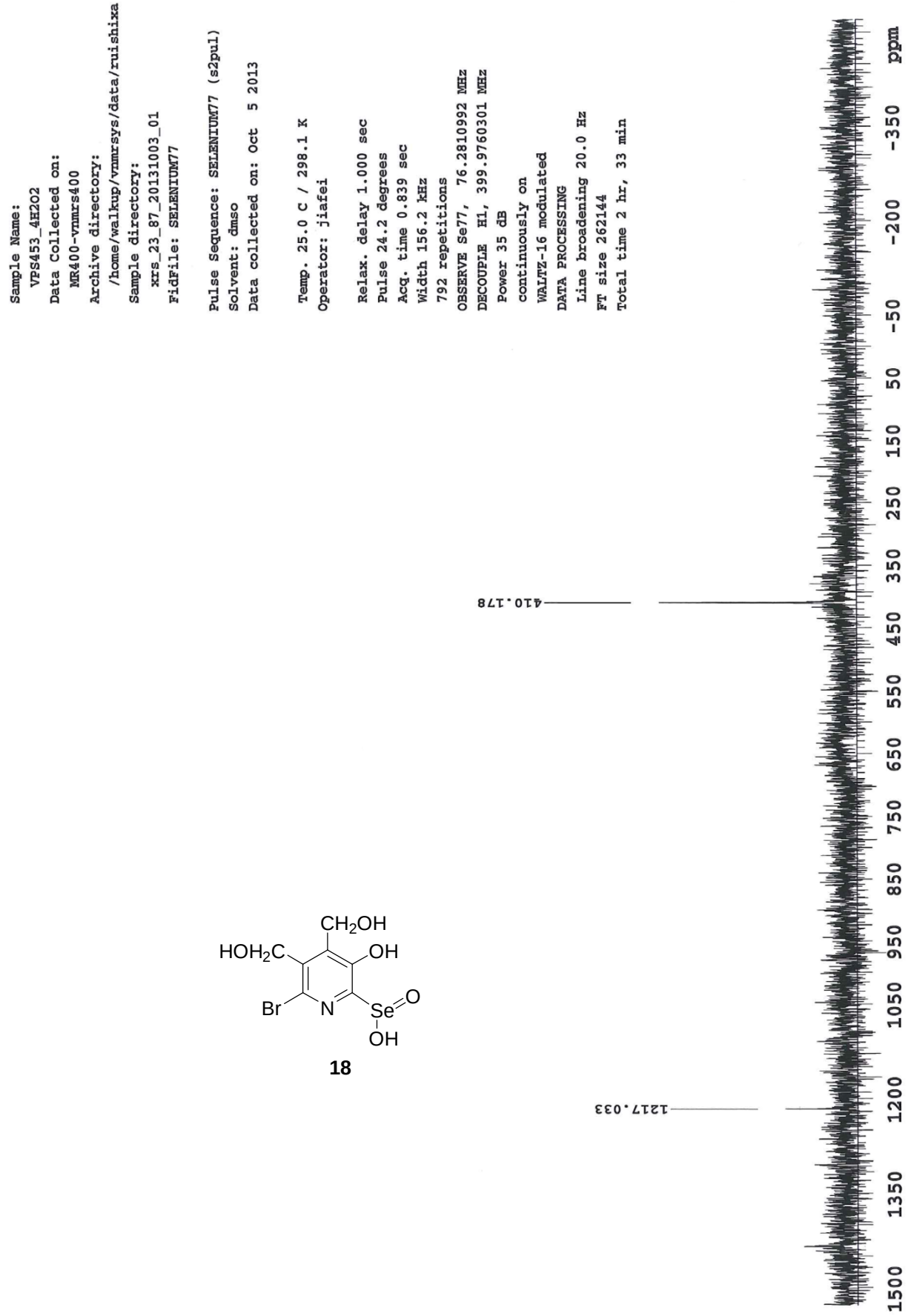
^{77}Se NMR spectrum of diselenide **6** after the addition of PhSH (15 equiv) to the above [total PhSH (20 equiv) and H_2O_2 (20 equiv)]



^{77}Se NMR spectrum of diselenide **6** after the addition of PhSH (20 equiv) to the above [total PhSH (40 equiv) and H_2O_2 (20 equiv)]

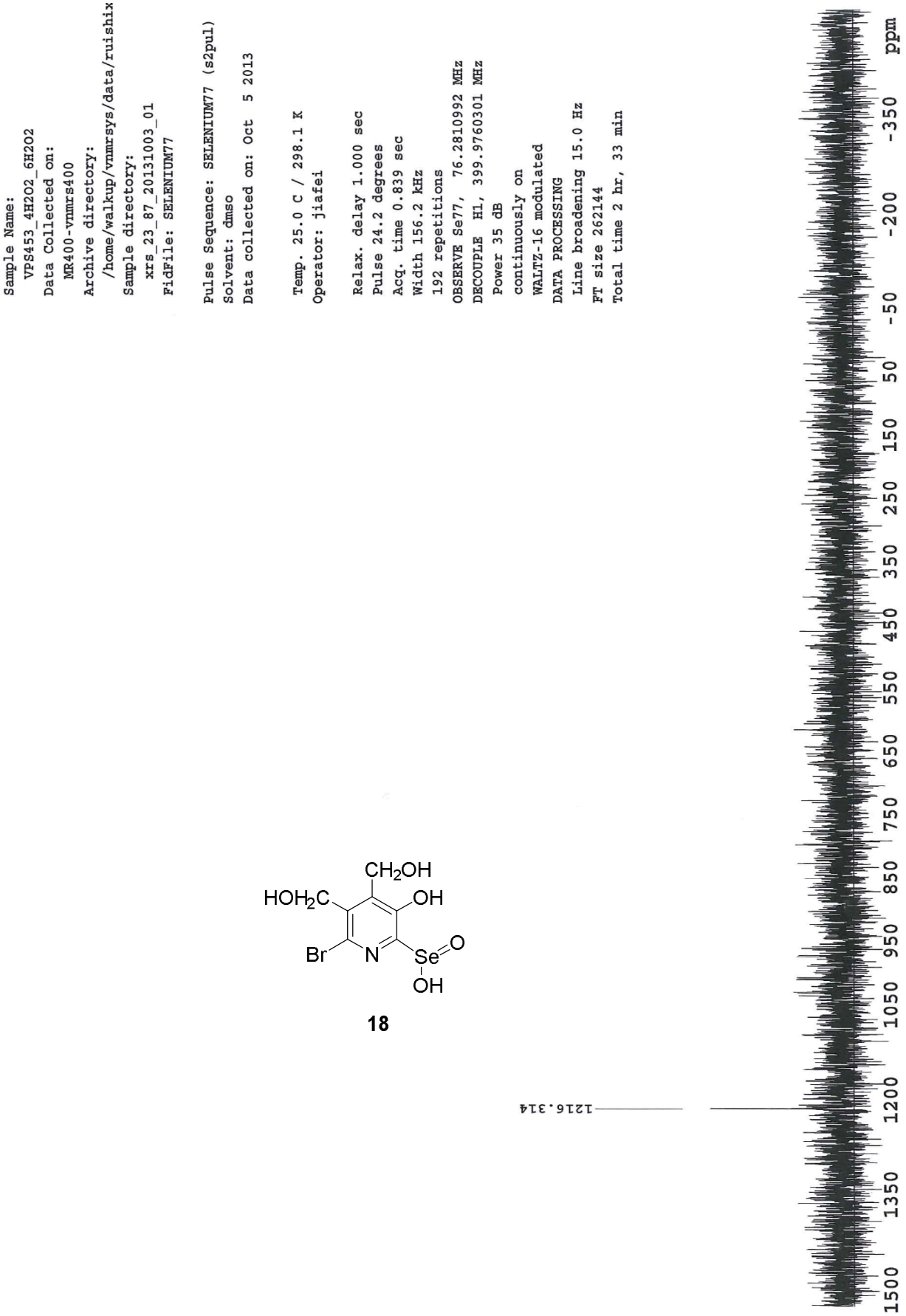


^{77}Se NMR spectrum of **11** with H_2O_2 (4 equiv)



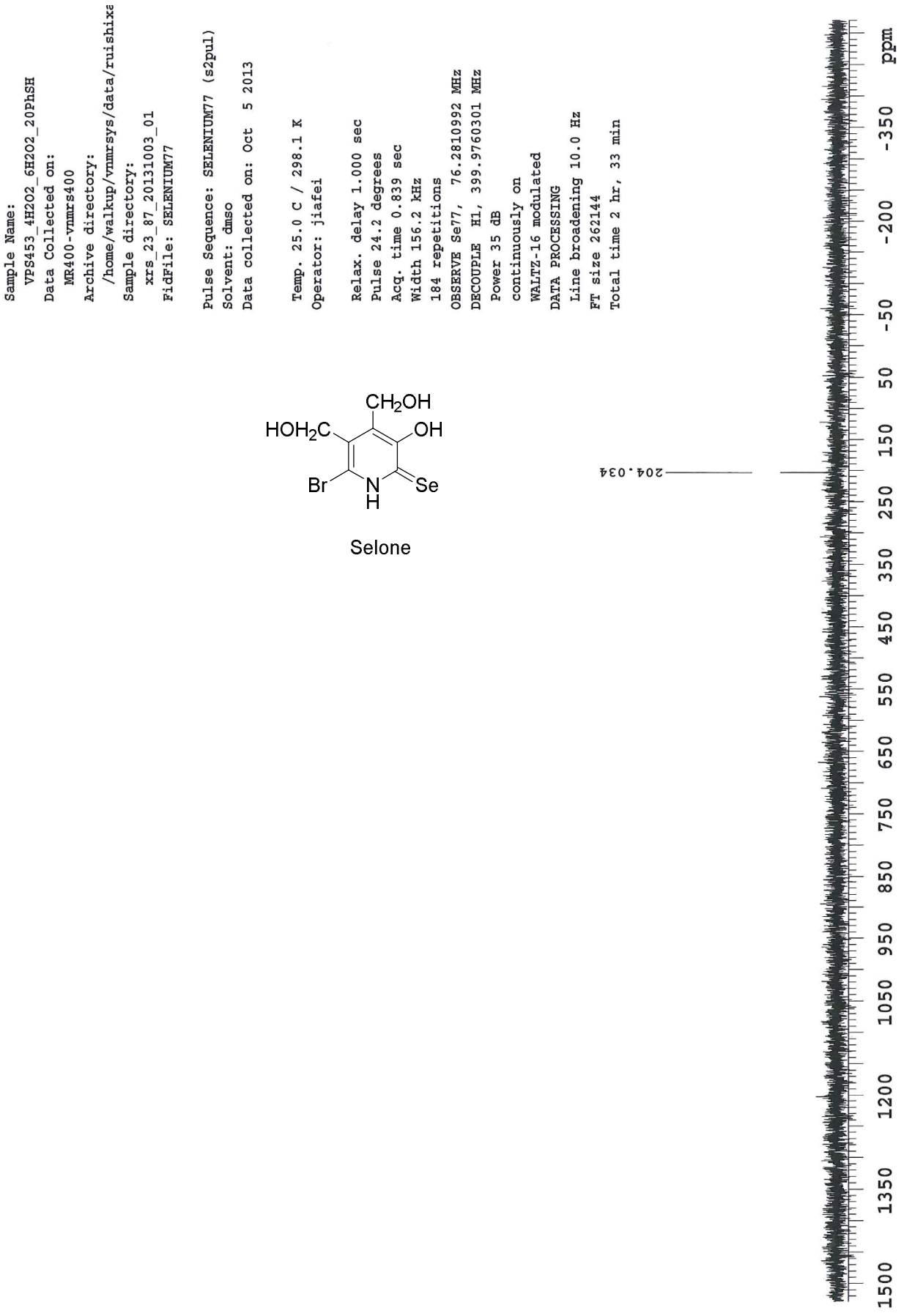
18

^{77}Se NMR spectrum of **11** with H_2O_2 (10 equiv)

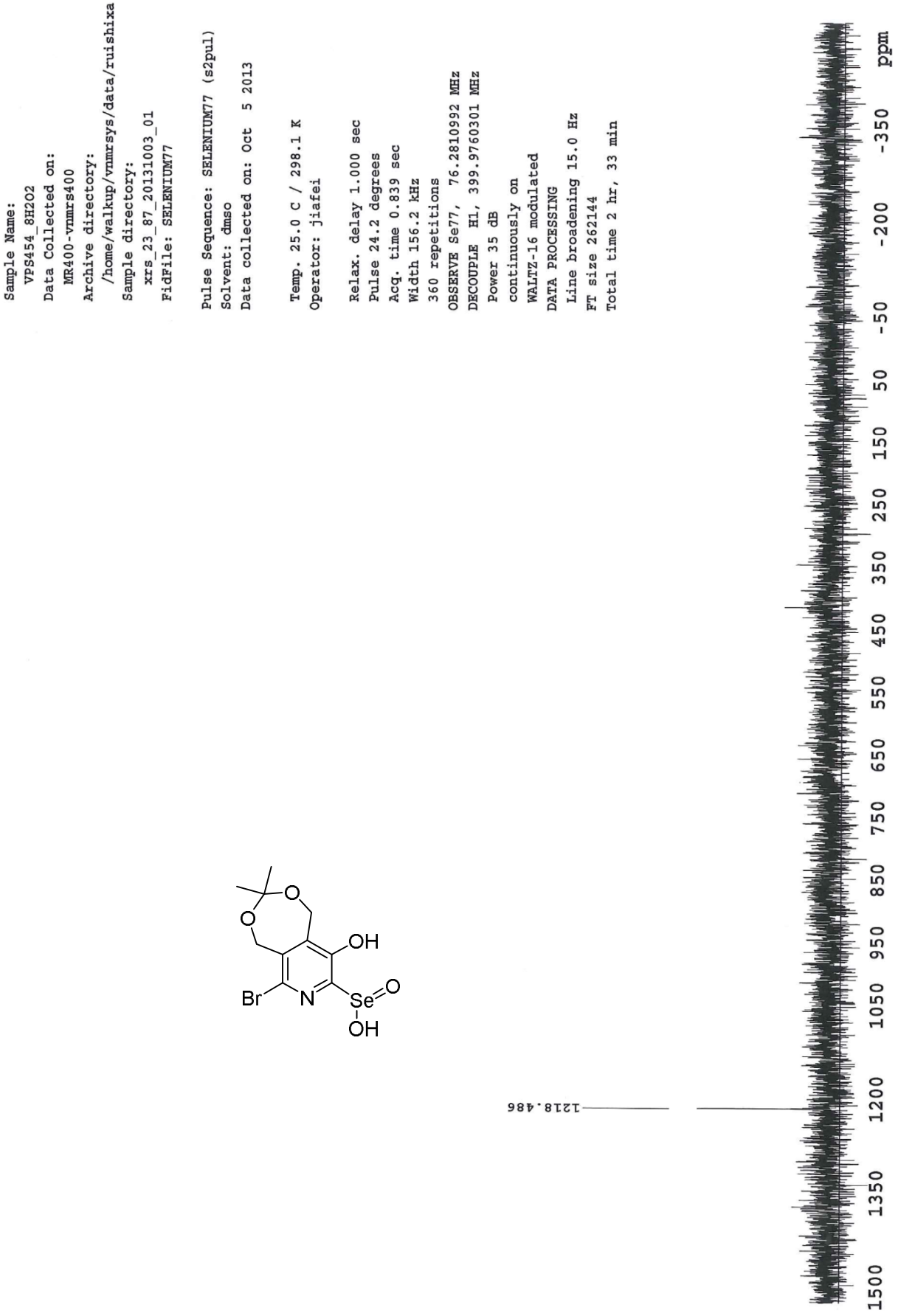


18

^{77}Se NMR spectrum of **11** with H_2O_2 (10 equiv) and PhSH (20 equiv)



^{77}Se NMR spectrum of **12** with H_2O_2 (8 equiv)



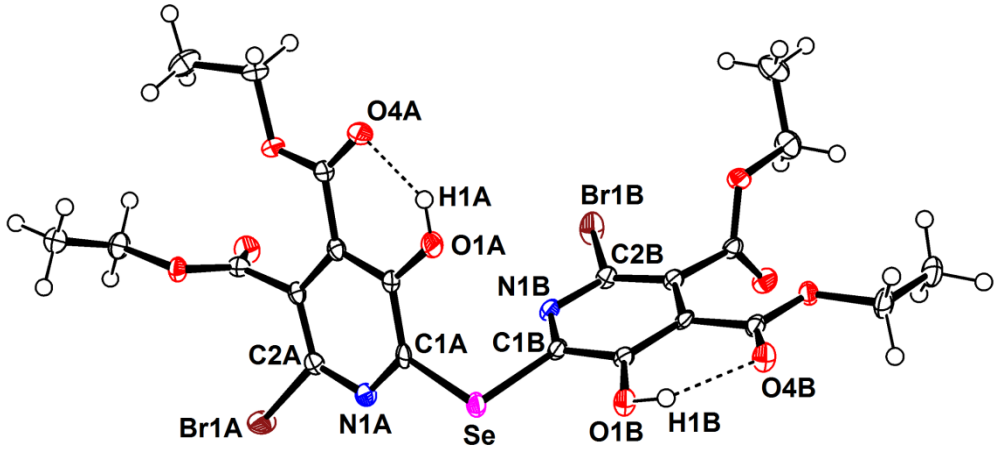
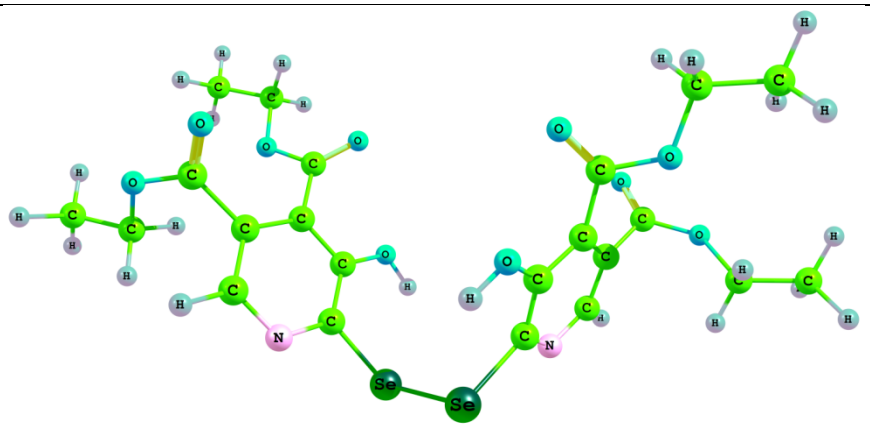


Figure S1. Molecular structure of momoselenide **7**. Thermal ellipsoids are set at 50% probability. Significant bond lengths [Å] Se-C1A 1.922(4), Se-C1B 1.920(4), H1A···O4A 1.813, H1B···O4B 1.897, C1-N1 1.352(17), C1-C2 1.420(18), and angles [^{o}] C1A-Se-C1B 97.46(15).

The molecular structure of monoselenide **7** showed a bent geometry around the Se atom with a C1A-Se-C1B bond angle of 97.46(15)^{o}. The pyridinolic OH groups were intramolecularly H-bonded to the oxygen atom neighbouring ester groups. The H···O distances (H1A···O4A 1.813 Å, H1B···O4B 1.897 Å) are significantly shorter than the sum of the van der Waals radii of these two atoms.

Table S1. Optimized geometries and coordinates of **3a**



3a

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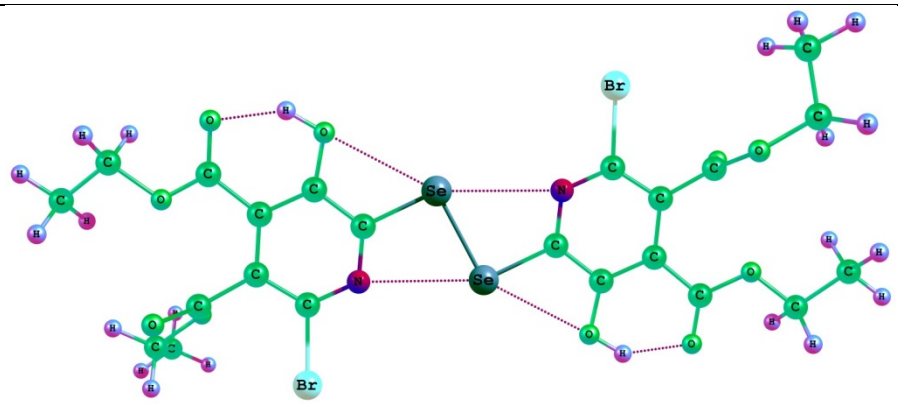
6	2.132218	-0.475884	0.709536	6	-8.139348	-0.061233	0.657924
6	3.068047	0.471058	0.255234	6	-6.631298	-0.163582	0.564889
6	3.938229	0.097999	-0.772104	1	4.457307	-1.484731	-2.156860
6	3.822249	-1.179866	-1.330560	1	0.725636	-0.903390	1.912428
8	1.310944	-0.149062	1.718289	1	-4.089013	-1.309233	2.377331
6	-2.036497	-1.699335	-0.109782	1	-0.854112	-0.951853	-2.122949
6	-2.168789	-0.492108	-0.829401	1	6.182316	4.896426	2.017742
6	-3.091716	0.456841	-0.353524	1	6.449133	3.202053	2.445674
6	-3.818329	0.150613	0.799858	1	6.551149	3.719744	0.750023
6	-3.572937	-1.061413	1.454577	1	4.090481	4.273775	0.771589
7	-2.706756	-1.962776	1.000674	1	3.982075	3.750668	2.455376
8	-1.482616	-0.228010	-1.951907	1	8.621467	-0.529931	0.667273
6	3.091178	1.856324	0.840391	1	8.715751	-0.021417	-1.026634
8	2.118766	2.528894	1.046976	1	8.419615	1.178239	0.241352
8	4.360231	2.243964	1.081552	1	6.196547	0.126112	0.731265
6	6.018207	3.865754	1.691970	1	6.499130	-1.096348	-0.521073
6	4.535018	3.619288	1.523393	1	-6.599295	4.585307	-2.096862
6	4.911489	1.072877	-1.393941	1	-6.828169	2.849973	-2.344808
8	4.534007	1.979237	-2.087135	1	-6.765769	3.514413	-0.699260
8	6.228100	0.850088	-1.218897	1	-4.353335	4.157339	-1.048878
6	8.206925	0.155750	-0.076853	1	-4.407659	3.497099	-2.686735
6	6.715564	-0.072038	-0.208495	1	-8.601441	-0.8191960	0.019470
6	-3.248950	1.779855	-1.051302	1	-8.480295	-0.222718	1.682682
8	-2.342010	2.463610	-1.439161	1	-8.486248	0.921178	0.331530
8	-4.554882	2.100053	-1.161082	1	-6.279591	0.016568	-0.452991
6	-6.349117	3.595599	-1.705424	1	-6.282290	-1.146829	0.888571
6	-4.846000	3.423880	-1.689697	34	0.914660	-3.110281	0.780970
6	-4.761400	1.140995	1.443707	34	-0.851283	-3.079084	-0.823065

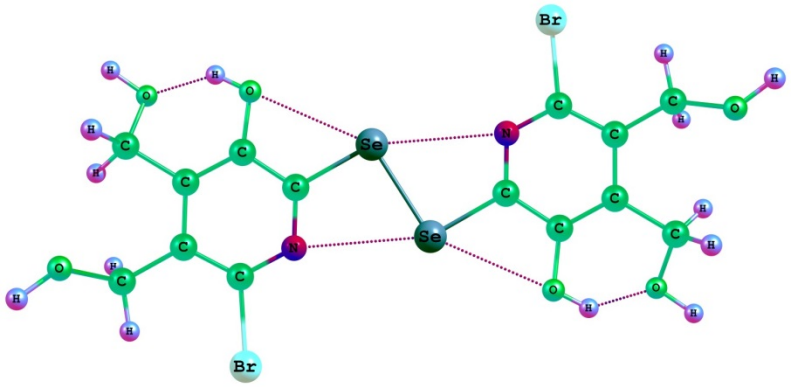
Table S2. Optimized geometries and coordinates of **6**



6

35	-4.175135	2.901887	0.336984	1	-8.572064	1.229940	-1.810897
35	4.152203	-2.925661	-0.436161	1	-8.770641	0.969375	-0.062836
34	-0.394868	-1.140485	-0.067940	6	-8.195062	2.991895	-0.601602
34	0.387132	1.127966	-0.004564	1	-9.219489	3.367593	-0.683673
8	-2.745045	-2.883890	-0.030479	1	-7.584646	3.501947	-1.349768
8	-5.238870	-3.554940	0.082333	1	-7.818333	3.246823	0.389861
8	-6.827232	-1.978081	0.043215	6	2.227044	0.585064	-0.116731
8	-6.866203	0.700224	1.426177	6	3.202876	1.609157	-0.112133
8	-6.838958	0.951521	-0.822740	6	4.558319	1.241676	-0.176038
8	5.251574	3.521528	-0.158472	6	4.885473	-0.135215	-0.271431
8	6.821454	1.929575	-0.027921	6	3.829254	-1.036870	-0.276802
8	6.808511	-1.082324	0.693605	6	5.562760	2.336679	-0.126338
8	6.850970	-0.679378	-1.528238	6	7.851565	2.960609	-0.023475
7	-2.566489	0.673157	0.1199320	1	7.671309	3.615392	0.830784
7	2.552161	-0.691241	-0.195925	1	7.739580	3.552183	-0.933392
6	-2.236039	-0.601561	0.044227	6	9.194430	2.269220	0.050483
6	-3.207345	-1.629911	0.042106	1	9.988867	3.020249	0.047046
6	-4.564826	-1.269265	0.108600	1	9.346286	1.609228	-0.805761
6	-4.897994	0.107664	0.195965	1	9.288895	1.683280	0.967411
6	-3.845554	1.013417	0.198126	6	6.295345	-0.640729	-0.460332
6	-5.561470	-2.372443	0.079770	6	8.113441	-1.713262	0.622827
6	-7.845155	-3.021276	0.062522	1	8.828075	-0.984391	0.234787
1	-7.679912	-3.636357	0.948359	1	8.054535	-2.538037	-0.090295
1	-7.701660	-3.650121	-0.817826	6	8.470483	-2.183594	2.016363
6	-9.197765	-2.345329	0.076565	1	9.450924	-2.667553	2.002568
1	-9.981977	-3.106623	0.102704	1	7.739707	-2.905180	2.387371
1	-9.347756	-1.737691	-0.818397	1	8.513525	-1.347598	2.718303
1	-9.311876	-1.708404	0.955780	1	-3.504181	-3.507018	0.004603
6	-6.314695	0.605461	0.359851	8	2.747965	2.865926	-0.037151
6	-8.189433	1.490455	-0.823810	1	3.509513	3.484938	-0.083367

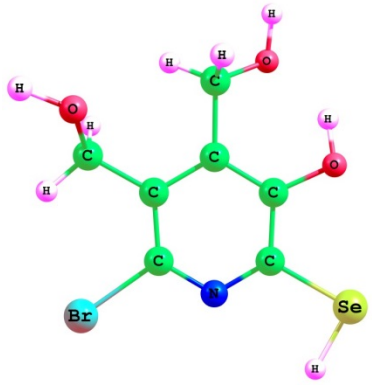
Table S3. Optimized geometries and coordinates of **11**



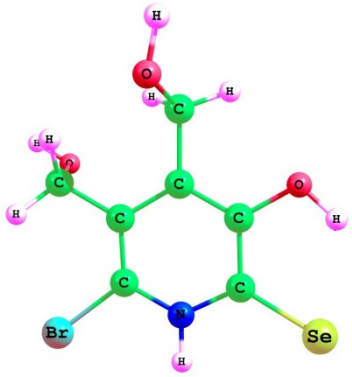
11

35	-0.274694	-0.227880	-0.009656	6	4.952724	0.138314	1.528016
35	0.280670	-0.111412	10.151738	1	5.167513	-0.281898	0.545419
34	1.172632	-0.112976	5.338690	1	5.210204	1.202791	1.494005
34	-1.166622	-0.226978	4.803368	6	2.926103	-0.040980	-0.593207
8	3.902468	0.0450060	4.278896	1	2.047414	-0.109180	-1.233102
7	0.786364	-0.150421	2.526077	1	3.571045	-0.902815	-0.819409
7	-0.780924	-0.178035	7.615900	8	5.758135	-0.533202	2.520374
6	1.696204	-0.100816	3.487469	1	6.687973	-0.329711	2.370857
6	3.073245	-0.028970	3.209657	8	3.640000	1.180775	-0.839496
6	3.488714	-0.014758	1.876180	1	3.763650	1.287361	-1.790407
6	2.512527	-0.072347	0.852962	6	-4.956902	-0.259873	8.611969
6	1.181196	-0.134275	1.268050	1	-5.132675	-0.679817	9.602376
6	-1.690639	-0.230426	6.654506	1	-5.312397	0.776457	8.626191
6	-3.068595	-0.281932	6.932163	6	-2.924053	-0.211949	10.734558
6	-3.484674	-0.282464	8.265555	1	-2.043313	-0.186984	11.374787
6	-2.508241	-0.230793	9.288819	1	-3.486606	-1.125578	10.976812
6	-1.176567	-0.176186	8.873743	8	-5.695328	-1.021815	7.632824
1	4.811696	-0.157790	3.989122	1	-6.640227	-0.903968	7.779936
8	-3.900263	-0.304564	5.862521	8	-3.748100	0.942774	10.959482
1	-4.786841	-0.586083	6.156650	1	-3.883114	1.053620	11.908369

Table S4. Optimized geometries and coordinates of **9** and **10**



Selenol **9**



Selone **10**

34	-0.071748000	-0.199011000	0.122877000	6	-0.027562000	-0.005076000	-0.009218000
8	0.156760000	-0.034512000	3.059001000	6	-0.013450000	-0.029745000	1.359995000
7	2.720989000	-0.250531000	0.569261000	7	1.164767000	-0.026190000	2.047763000
6	1.544212000	-0.192657000	1.169719000	6	2.404655000	-0.008466000	1.474408000
6	1.415787000	-0.115479000	2.565947000	6	2.412168000	0.009331000	0.041892000
6	2.578194000	-0.102764000	3.344384000	6	1.235074000	0.003049000	-0.682551000
6	3.834392000	-0.168159000	2.700731000	8	3.599014000	0.026334000	-0.585352000
6	3.813302000	-0.237270000	1.304884000	6	1.292158000	0.018652000	-2.189989000
1	0.178301000	-0.234358000	4.013892000	6	-1.307999000	-0.027823000	-0.800343000
6	2.493834000	0.056885000	4.846302000	1	1.143087000	-0.040218000	3.060071000
1	3.374520000	-0.359990000	5.334576000	1	4.296186000	0.023149000	0.108710000
1	2.451625000	1.122563000	5.097456000	1	0.624602000	-0.752693000	-2.588743000
6	5.104536000	-0.137608000	3.507502000	1	2.311254000	-0.195839000	-2.513275000
1	5.136742000	-0.998948000	4.190809000	1	-1.208434000	0.634194000	-1.663981000
1	5.967530000	-0.208210000	2.846828000	1	-2.137082000	0.331825000	-0.185741000
8	5.139505000	1.085134000	4.259348000	8	0.879174000	1.319575000	-2.642510000
1	6.016120000	1.191659000	4.648022000	8	-1.543807000	-1.380770000	-1.219608000
8	1.313037000	-0.613411000	5.336341000	1	1.107755000	1.412392000	-3.575053000
1	1.194034000	-0.413639000	6.271407000	1	-2.350127000	-1.407047000	-1.749715000
1	0.702268000	-0.281688000	-1.137076000	34	3.949360000	-0.003390000	2.475107000
35	5.452420000	-0.345411000	0.272927000	35	-1.556401000	-0.078866000	2.471924000

Table S5. Second Order Perturbation Theory Analysis of Fock Matrix in NBO Basis for **6**

Donor NBO (i)	Acceptor NBO (j)	E(2)	E(j)-E(i)	F(i,j)
		kcal/mol	a.u.	a.u.
172. LP (1) O5	/996. BD*(1) Se3-Se4	1.11	0.58	0.023
172. LP (1) O5	/997. BD*(1) Se3-C16	0.61	0.72	0.019
190. LP (1) N14	/996. BD*(1) Se3-Se4	0.69	0.34	0.014
190. LP (1) N14	/997. BD*(1) Se3-C16	3.87	0.47	0.039
190. LP (1) N14	/998. BD*(1) Se4-C37	2.50	0.47	0.031
191. LP (1) N15	/997. BD*(1) Se3-C16	2.49	0.63	0.036
191. LP (1) N15	/998. BD*(1) Se4-C37	2.48	0.63	0.036
174. LP (1) O6	/***. BD*(1) O5 - H58	3.74	1.12	0.058

Table S6. Second Order Perturbation Theory Analysis of Fock Matrix in NBO Basis for **11**

Donor NBO (i)	Acceptor NBO (j)	E(2)	E(j)-E(i)	F(i,j)
		kcal/mol	a.u.	a.u.
135. LP (1) O5	/717. BD*(1) Se3-Se4	1.11	0.58	0.023
135. LP (1) O5	/718. BD*(1) Se3-C8	0.61	0.72	0.019
141. LP (1) O19	/717. BD*(1) Se3-Se4	1.11	0.58	0.023
141. LP (1) O19	/719. BD*(1) Se4-C13	0.61	0.72	0.019
137. LP (1) N6	/717. BD*(1) Se3-Se4	0.61	0.33	0.013
137. LP (1) N6	/718. BD*(1) Se3-C8	3.50	0.47	0.037
137. LP (1) N6	/719. BD*(1) Se4-C13	2.49	0.47	0.031
138. LP (1) N7	/717. BD*(1) Se3-Se4	0.61	0.33	0.013
138. LP (1) N7	/718. BD*(1) Se3-C8	2.49	0.47	0.031
138. LP (1) N7	/719. BD*(1) Se4-C13	3.50	0.47	0.037

Figure S2. Molecular graphs of **6**, **10** and **11**

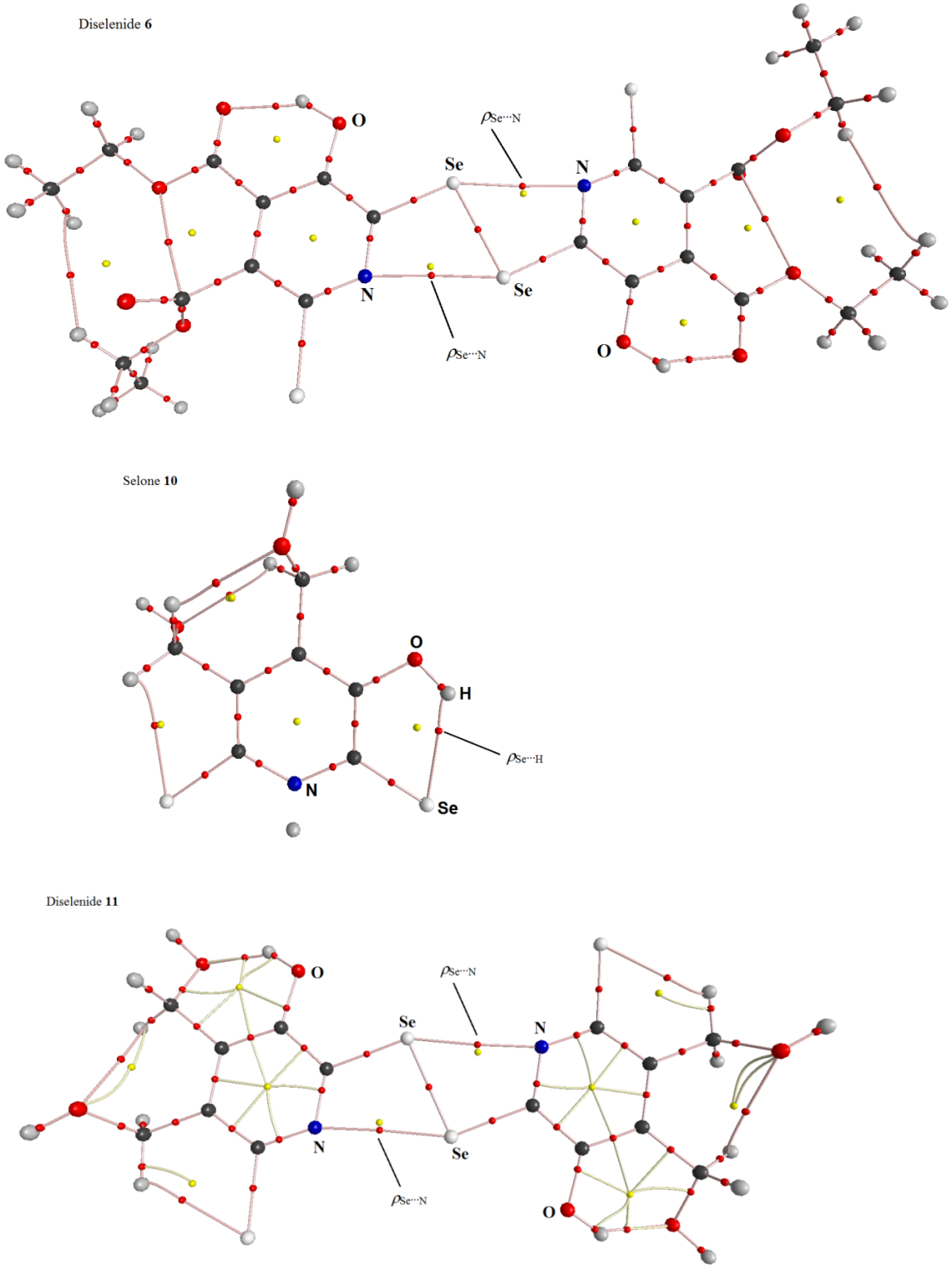


Table S7. Summary of properties of electron density at the bond critical point. AIM calculations were carried out by using the wave functions obtained at the B3LYP/6–311+G(d)//B3LYP/6–311+G(d,p).

Compound	$\rho_{Se\cdots N}$ (ea_0^{-3})[a]	$\nabla^2\rho_{Se\cdots N}$ (ea_0^{-5}) [b]	$H_{Se\cdots N}$ (ea_0^{-4}) [c]	$\rho_{Se\cdots H}$ (ea_0^{-3})[a]	$\nabla^2\rho_{Se\cdots H}$ (ea_0^{-5}) [b]	$H_{Se\cdots H}$ (ea_0^{-4}) [c]
6	0.0146	0.0526	+0.00176			
11	0.0144	0.0514	+0.00175			
10				0.0247	0.0525	-0.00098

[a] The electron density at the bond critical point. [b] The Laplacian of the electron density at the bond critical point. [c] The total energy density at the bond critical point.

Table S8. Effect of substrate (GSH) concentration on the initial rate of NADPH-consumption for catalyst **6**.

[GSH] (mM)	ν_0 ($\mu M.min^{-1}$)	Mean ν_0 ($\mu M.min^{-1}$)	1/ [GSH] (mM^{-1})	$1/\nu_0$ ($\mu M^{-1}.min$)
0.125	209.40 216.27 217.52	214.4 ± 4.4	8.0	0.00466
0.25	221.19 217.04 216.46	218.2 ± 2.6	4.0	0.00458
0.50	221.29 225.62 229.10	225.3 ± 3.9	2.0	0.00443
1.0	242.60 245.11 238.98	242.2 ± 3.1	1.0	0.00413
2.0	244.92 247.23 245.11	245.8 ± 1.3	0.5	0.00407
3.0	263.34 264.40 265.47	264.4 ± 1.1	0.33	0.00378

Assay conditions: phosphate buffer (100 mM), pH 7.5, with EDTA (1 mM), GSH (variable), NADPH (0.20 mM), glutathione reductase (1.3 unit/mL), and H_2O_2 (0.8 mM) catalyst **6** (20 μM).

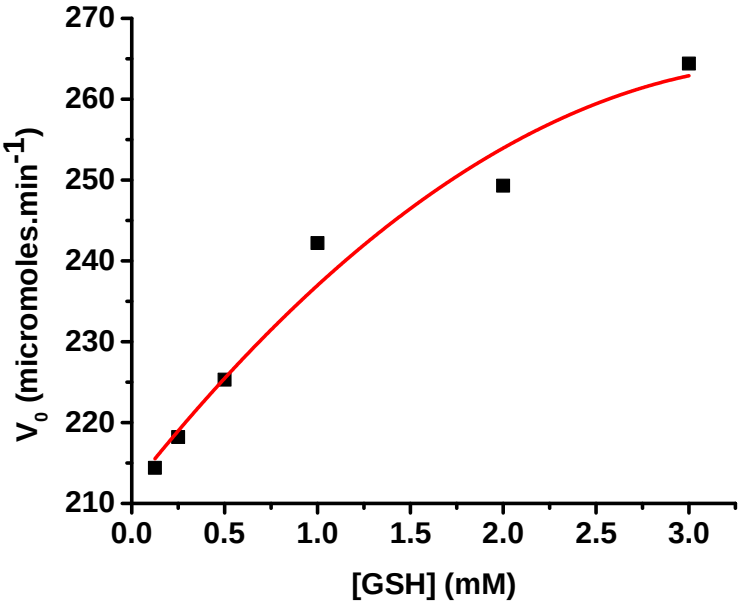


Figure S3. Effect of thiol concentration on initial rate of NADPH consumption for reduction of H_2O_2 in the presence of catalyst **6**.

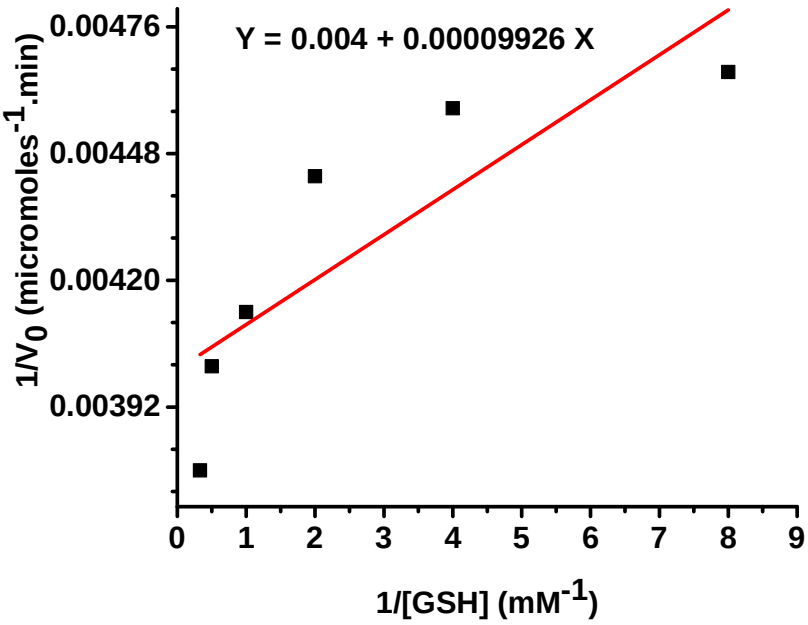


Figure S4. Lineweaver-Burk (double-reciprocal) plot obtained for catalyst **6** with GSH (variable) at a fixed concentration of H_2O_2.

Table S9. Effect of substrate (H_2O_2) concentration on the initial rate of NADPH-consumption for catalyst **6**.

$[H_2O_2]$ (mM)	ν_0 ($\mu M \cdot min^{-1}$)	Mean ν_0 ($\mu M \cdot min^{-1}$)	$1/[H_2O_2]$ (mM^{-1})	$1/\nu_0$ ($\mu M^{-1} \cdot min$)
0.20	74.28 78.14 77.94	76.8 ± 2.2	5.0	0.01302
0.40	144.41 141.90 136.78	141.0 ± 3.9	2.5	0.00709
0.60	194.86 194.28 195.14	194.8 ± 0.4	1.66	0.00513
0.80	242.60 245.11 238.98	242.2 ± 3.1	1.0	0.00413
1.0	285.28 279.83 285.63	283.6 ± 3.3	1.0	0.00353
1.2	310.99 309.55 306.95	309.2 ± 2.0	0.833	0.00323

Assay conditions: phosphate buffer (100 mM), pH 7.5, with EDTA (1 mM), H_2O_2 (variable), NADPH (0.20 mM), glutathione reductase (1.3 unit$\cdot mL^{-1}$), and GSH (1 mM) catalyst **6** (20 μM).

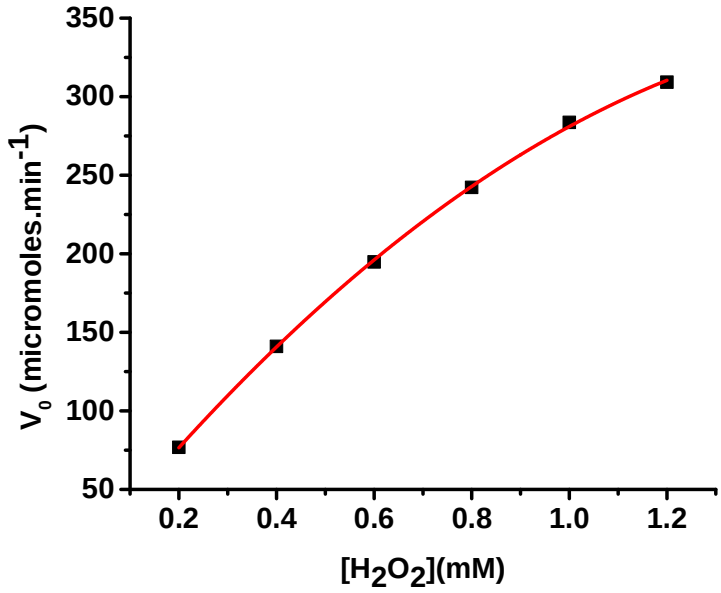


Figure S5. Effect of hydrogen peroxide concentration on initial rate of NADPH consumption for reduction of H_2O_2 in the presence of catalyst **6**.

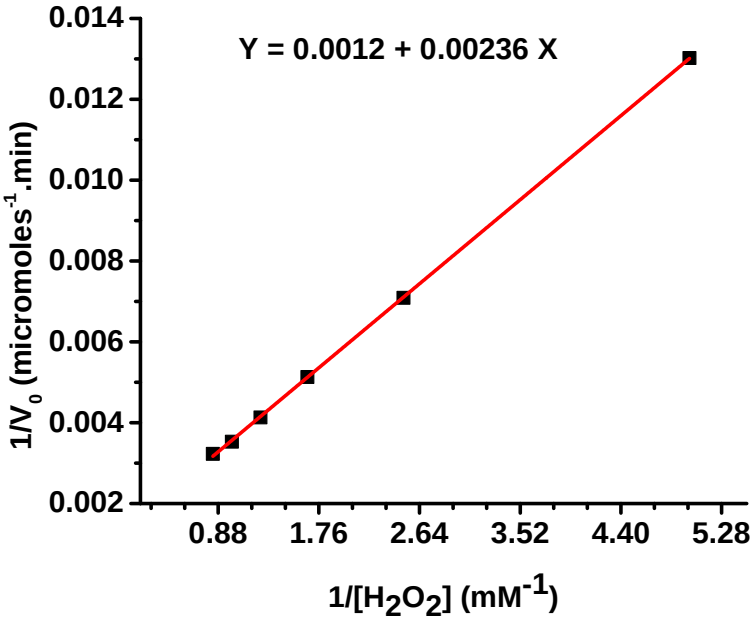


Figure S6. Lineweaver-Burk (double-reciprocal) plot obtained for catalyst **6** with hydrogen peroxide (variable) at a fixed concentration of GSH.

Table S10. Effect of substrate (GSH) concentration on the initial rate of NADPH-consumption for catalyst **11**.

[GSH] (mM)	ν_0 ($\mu M \cdot min^{-1}$)	Mean ν_0 ($\mu M \cdot min^{-1}$)	1/ [GSH] (mM^{-1})	$1/\nu_0$ ($\mu M^{-1} \cdot min$)
0.125	95.02 92.12 97.52	94.9 ± 2.7	8.0	0.01054
0.25	102.06 106.40 106.50	105.0 ± 2.5	4.0	0.00952
0.50	122.12 126.75 123.57	124.1 ± 2.4	2.0	0.00806
1.0	171.80 166.39 167.27	168.5 ± 2.9	1.0	0.00593
2.0	215.11 211.93 212.60	213.2 ± 1.7	0.5	0.00469
3.0	245.11 243.67 247.33	245.4 ± 1.8	0.33	0.00407

Assay conditions: phosphate buffer (100 mM), pH 7.5, with EDTA (1 mM), GSH (variable), NADPH (0.20 mM), glutathione reductase (1.3 $unit \cdot mL^{-1}$), and H_2O_2 (0.8 mM) catalyst **11** (20 μM).

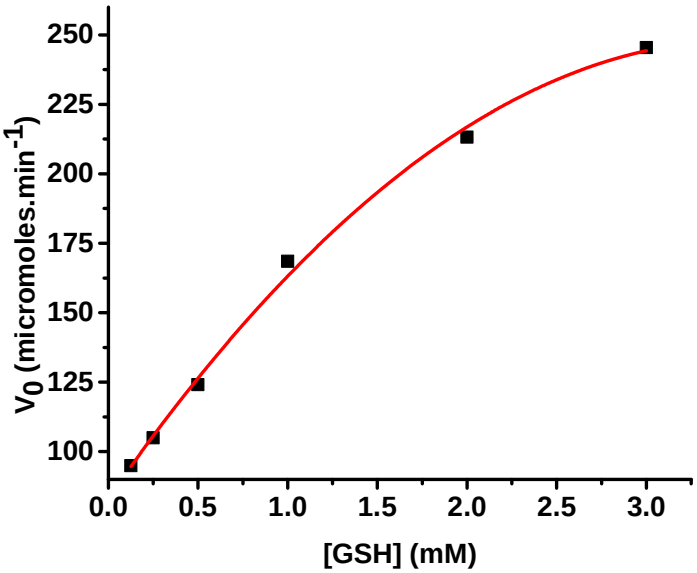


Figure S7. Effect of thiol concentration on initial rate of NADPH consumption for reduction of H_2O_2 in the presence of catalyst **11**.

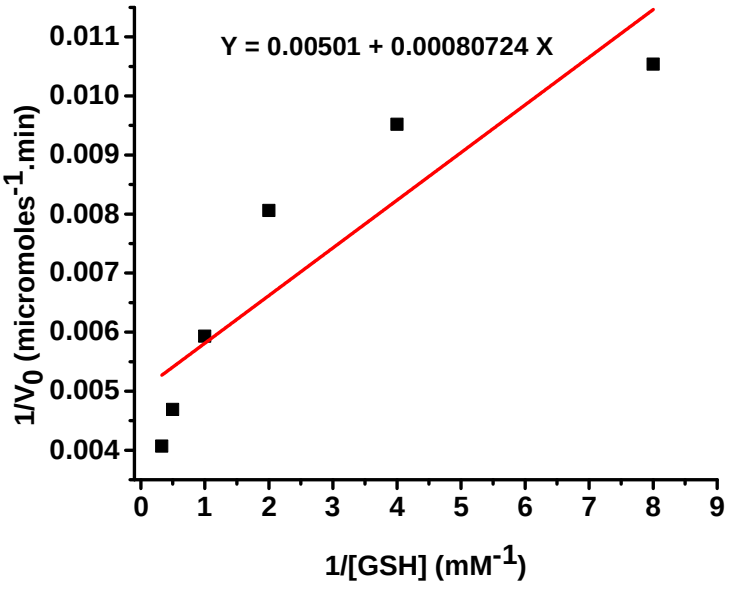


Figure S8. Lineweaver-Burk (double-reciprocal) plot obtained for catalyst **11** with GSH (variable) at a fixed concentration of H_2O_2.

Table S11. Effect of substrate (H_2O_2) concentration on the initial rate of NADPH-consumption for catalyst **11**.

$[H_2O_2]$ (mM)	ν_0 ($\mu M \cdot min^{-1}$)	Mean ν_0 ($\mu M \cdot min^{-1}$)	$1/[H_2O_2]$ (mM^{-1})	$1/\nu_0$ ($\mu M^{-1} \cdot min$)
0.20	59.04 65.69 63.76	62.8 ± 3.4	5.0	0.01591
0.40	108.14 102.93 103.70	104.9 ± 2.8	2.5	0.00953
0.60	145.76 144.02 139.00	142.9 ± 3.5	1.66	0.00699
0.80	171.80 166.39 167.27	168.5 ± 2.9	1.25	0.00593
1.0	194.76 195.43 197.46	195.9 ± 1.4	1.0	0.00510
1.2	238.17 234.89 231.03	234.7 ± 3.6	0.833	0.00426

Assay conditions: phosphate buffer (100 mM), pH 7.5, with EDTA (1 mM), H_2O_2 (variable), NADPH (0.20 mM), glutathione reductase (1.3 unit$\cdot mL^{-1}$), and GSH (1 mM) catalyst **11** (20 μM).

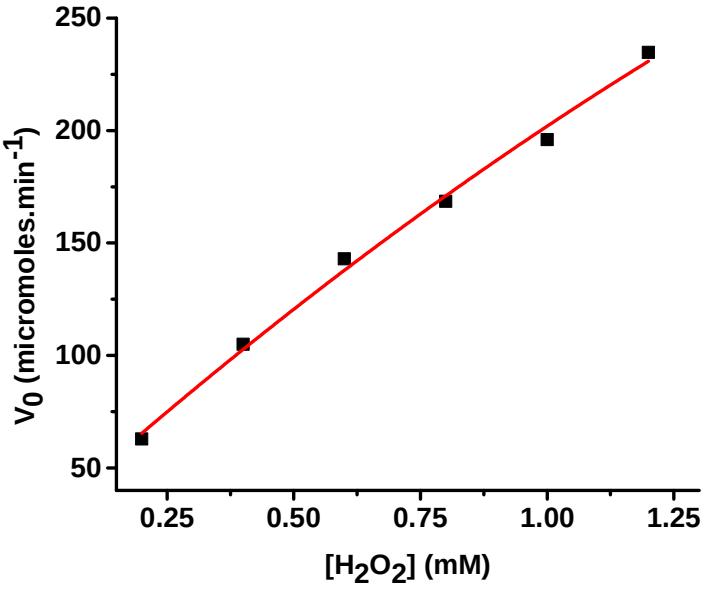


Figure S9. Effect of hydrogen peroxide concentration on initial rate of NADPH consumption for reduction of H_2O_2 in the presence of catalyst **11**.

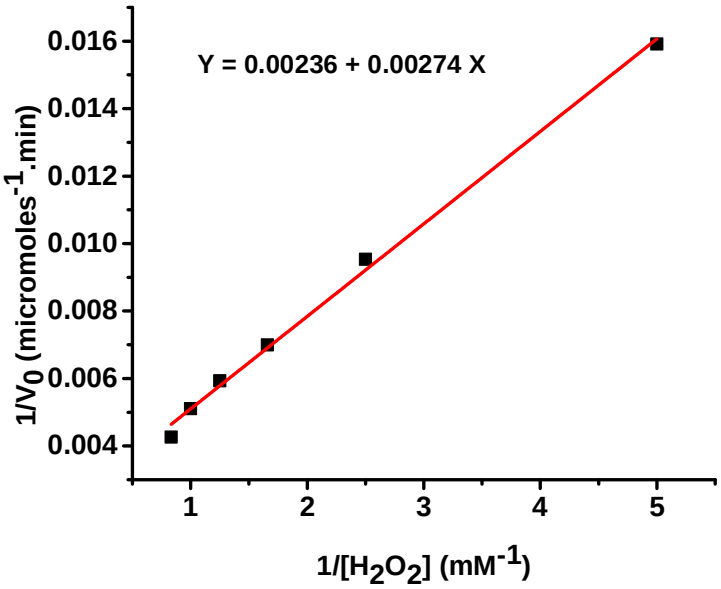


Figure S10. Lineweaver-Burk (double-reciprocal) plot obtained for catalyst **11** with hydrogen peroxide (variable) at a fixed concentration of GSH.

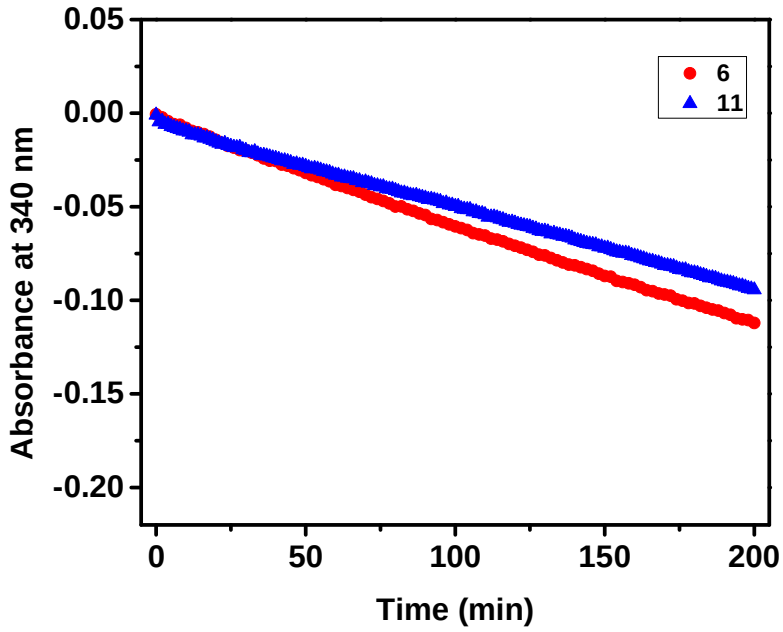


Figure S11. Consumption of NADPH with time in the absence of H_2O_2 (catalyst and GSH) for catalysts **6** and **11**. Assay conditions: reactions were carried out with phosphate buffer (100 mM), pH 7.5, with EDTA (1 mM), GSH (0.10 mM), NADPH (0.20 mM), GR (1.3 unit·mL^{-1}), and selenium catalyst (2 μM).

Table S12. Crystal Data and Structure Refinement for compounds **6** and **7**.

Compound	**6**	**7**
Empirical formula	$C_{22}H_{22}Br_2N_2O_{10}Se_2$	$C_{22}H_{22}Br_2N_2O_{10}Se$
Formula weight	792.15	713.19
Crystal system	Monoclinic	Monoclinic
Space group	P *c*	P $2_1/c$
a(Å)	20.039(15)	18.527(6)
b(Å)	5.315(4)	8.443(4)
c(Å)	25.268(2)	16.977(7)
α(deg)	90	90
β(deg)	90.05(3)	102.39(2)^o
γ(deg)	90	90
V(Å^3)	2691.2(4)	2593.85(18)
Z	4	4
T	100(2)K	120(2)
ρ_{calcd} (Mg/m^3)	1.955	1.806
Abs coeff(mm^{-1})	5.774	4.586
Reflections collected	48954	15892
Final R(F) indices [I<2σ(I)][a]	R1 = 0.0492 wR2 = 0.1261	R1 = 0.0489 wR2 = 0.1056
wR(F^2) indices	R1 = 0.0536 wR2 = 0.1309 (all data)	R1 = 0.0759 wR2 = 0.01163 (all data)
Data/restrain/parameters	13011 / 896 / 700	7379 / 0 / 340
Goodness of fit on F^2	1.085	1.038

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

CheckCIF/PLATON (standard) report for compound 6

Datablock: shelx

```
Bond precision:      C-C = 0.0253 A              Wavelength=0.71073
Cell:          a=20.0390(15)  b=5.3151(4)    c=25.268(2)
               alpha=90       beta=90.051(3) gamma=90
Temperature:100 K
                    Calculated                    Reported
Volume              2691.3(4)                     2691.2(4)
Space group         P c                           P c
Hall group          P -2yc                        P -2yc
Moiety formula      C22 H22 Br2 N2 O10 Se2        C22 H22 Br2 N2 O10 Se2
Sum formula         C22 H22 Br2 N2 O10 Se2        C22 H22 Br2 N2 O10 Se2
Mr                  792.14                        792.15
Dx,g cm-3           1.955                         1.955
Z                   4                             4
Mu (mm-1)           5.774                         5.774
F000                1544.0                        1544.0
F000'               1541.88
h,k,lmax            26,7,33                       26,7,33
Nref                13381[ 6694]                  13011
Tmin,Tmax           0.299,0.630                   0.445,0.746
Tmin'               0.227
Correction method= # Reported T Limits: Tmin=0.445
Tmax=0.746 AbsCorr = MULTI-SCAN
Data completeness= 1.94/0.97   Theta(max)= 28.333
R(reflections)= 0.0492( 12389)    wR2(reflections)= 0.1309( 13011)
S = 1.085             Npar= 700
```

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level B

PLAT341_ALERT_3_B Low Bond Precision on C-C Bonds ..... 0.0253 Ang.
PLAT369_ALERT_2_B Long C(sp2)-C(sp2) Bond C3A - C6A ... 1.58 Ang.

Alert level C

DIFMX01_ALERT_2_C The maximum difference density is > 0.1*ZMAX*0.75
_refine_diff_density_max given = 2.925
Test value = 2.625
DIFMX02_ALERT_1_C The maximum difference density is > 0.1*ZMAX*0.75
The relevant atom site should be identified.
PLAT034_ALERT_1_C No Flack Parameter Given. Z > Si, NonCentro .... Please Do !
PLAT090_ALERT_3_C Poor Data / Parameter Ratio (Zmax > 18) ..... 9.50 Note
PLAT094_ALERT_2_C Ratio of Maximum / Minimum Residual Density .... 2.57 Report
PLAT097_ALERT_2_C Large Reported Max. (Positive) Residual Density 2.92 eA-3
PLAT213_ALERT_2_C Atom Br2A has ADP max/min Ratio ..... 3.7 oblate
PLAT220_ALERT_2_C Large Non-Solvent C Ueq(max)/Ueq(min) Range 4.0 Ratio
And 3 other PLAT220 Alerts

More ...
PLAT222_ALERT_3_C Large Non-Solvent H Uiso(max)/Uiso(min) ... 4.3 Ratio
PLAT360_ALERT_2_C Short C(sp3)-C(sp3) Bond C10B - C11B ... 1.42 Ang.
PLAT369_ALERT_2_C Long C(sp2)-C(sp2) Bond C3B - C6B ... 1.53 Ang.
PLAT480_ALERT_4_C Long H...A H-Bond Reported H11A .. BR1B .. 2.98 Ang.
And 6 other PLAT480 Alerts
More ...
PLAT910_ALERT_3_C Missing # of FCF Reflection(s) Below Th(Min) ... 5 Report
PLAT911_ALERT_3_C Missing # FCF Refl Between THmin & STh/L= 0.600 26 Report

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Alert level G

PLAT003_ALERT_2_G Number of Uiso or Uij Restrained non-H Atoms ... 71 Report
PLAT007_ALERT_5_G Number of Unrefined Donor-H Atoms ..... 4 Report
PLAT083_ALERT_2_G SHELXL Second Parameter in WGHT Unusually Large. 16.57 Why ?
PLAT112_ALERT_2_G ADDSYM Detects Additional (Pseudo) Symm. Elem... 21 Check
PLAT112_ALERT_2_G ADDSYM Detects Additional (Pseudo) Symm. Elem... 21 Check
PLAT720_ALERT_4_G Number of Unusual/Non-Standard Labels ..... 10 Note
PLAT860_ALERT_3_G Number of Least-Squares Restraints ..... 896 Note
PLAT870_ALERT_4_G ALERTS Related to Twinning Effects Suppressed .. ! Info
PLAT912_ALERT_4_G Missing # of FCF Reflections Above STh/L= 0.600 15 Note
PLAT931_ALERT_5_G Found Twin Law (0 0 1)[ ] Estimated BASF 0.52 Check

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0 **ALERT level A** = Most likely a serious problem - resolve or explain
2 **ALERT level B** = A potentially serious problem, consider carefully
23 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
10 **ALERT level G** = General information/check it is not something unexpected

2 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
15 ALERT type 2 Indicator that the structure model may be wrong or deficient
6 ALERT type 3 Indicator that the structure quality may be low
10 ALERT type 4 Improvement, methodology, query or suggestion
2 ALERT type 5 Informative message, check

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

Publication of your CIF in IUCr journals

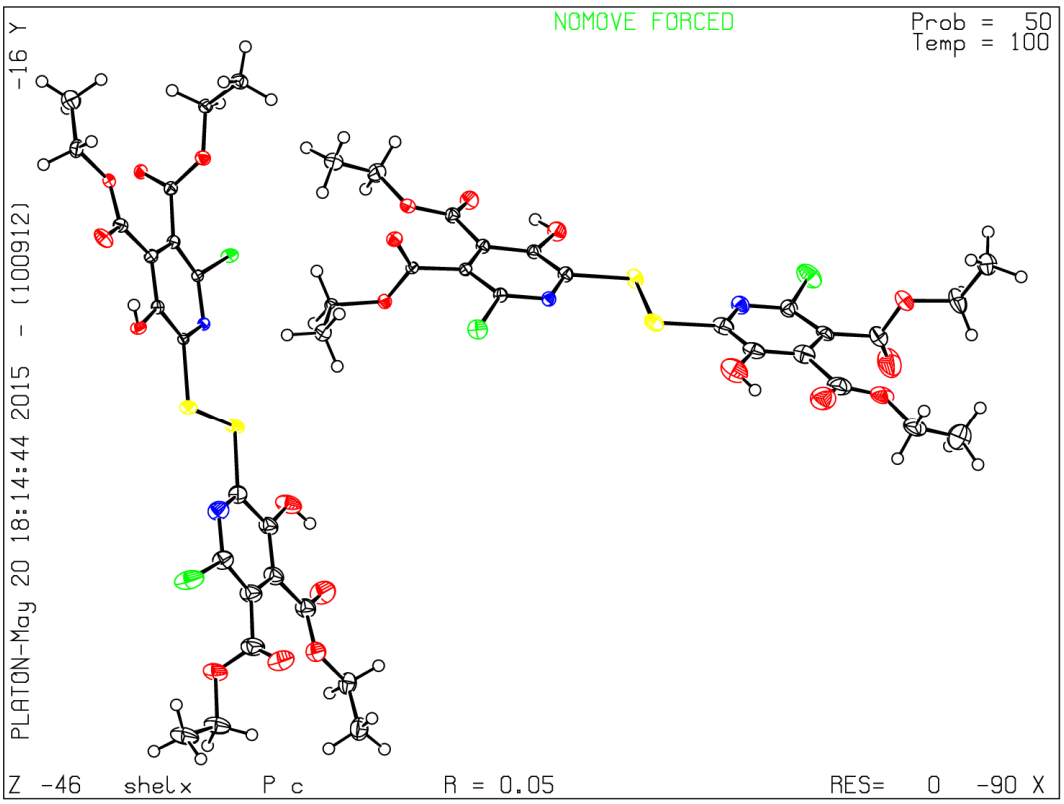
A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

Publication of your CIF in other journals

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 21/04/2015; check.def file version of 09/03/2015

Datablock shelx - ellipsoid plot



CheckCIF/PLATON (standard) report for compound 7

Datablock: shelx

```
Bond precision:      C-C = 0.0052 A              Wavelength=0.71073
Cell:        a=18.5268(6)    b=8.4433(4)     c=16.9773(7)
             alpha=90        beta=102.391(2) gamma=90
Temperature: 120 K
                    Calculated                      Reported
Volume              2593.85(18)                     2593.85(18)
Space group         P 21/c                          P 21/c
Hall group          -P 2ybc                         -P 2ybc
Moiety formula      C22 H22 Br2 N2 O10 Se           C22 H22 Br2 N2 O10 Se
Sum formula         C22 H22 Br2 N2 O10 Se           C22 H22 Br2 N2 O10 Se
Mr                  713.18                          713.19
Dx,g cm-3           1.826                           1.826
Z                   4                               4
Mu (mm-1)           4.586                           4.586
F000                1408.0                          1408.0
F000'               1406.13
h,k,lmax            26,12,24                        24,11,24
Nref                8291                            7379
Tmin,Tmax           0.397,0.577                     0.513,0.746
Tmin'               0.367
Correction method= # Reported T Limits: Tmin=0.513
Tmax=0.746 AbsCorr = MULTI-SCAN
Data completeness= 0.890        Theta(max)= 31.017
R(reflections)= 0.0489( 5533)     wR2(reflections)= 0.1163( 7379)
S = 1.038             Npar= 340
```

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

PLAT094_ALERT_2_C Ratio of Maximum / Minimum Residual Density .... 2.45 Report
PLAT480_ALERT_4_C Long H...A H-Bond Reported H1B .. O4B .. 2.62 Ang.
And 2 other PLAT480 Alerts
More ...
PLAT906_ALERT_3_C Large K value in the Analysis of Variance ..... 3.253 Check
PLAT911_ALERT_3_C Missing # FCF Refl Between THmin & STh/L= 0.600 79 Report
PLAT971_ALERT_2_C Check Calcd Residual Density 0.90A From Se1 2.05 eA-3
PLAT971_ALERT_2_C Check Calcd Residual Density 0.69A From Br1B 1.66 eA-3

Alert level G

PLAT007_ALERT_5_G Number of Unrefined Donor-H Atoms ..... 2 Report
PLAT083_ALERT_2_G SHELXL Second Parameter in WGHT Unusually Large. 7.28 Why ?
PLAT432_ALERT_2_G Short Inter X...Y Contact O2B .. C9B .. 2.75 Ang.
PLAT720_ALERT_4_G Number of Unusual/Non-Standard Labels ..... 10 Note

PLAT910_ALERT_3_G Missing # of FCF Reflection(s) Below Th(Min) ... 1 Report
PLAT912_ALERT_4_G Missing # of FCF Reflections Above STh/L= 0.600 703 Note
PLAT950_ALERT_5_G Calculated (ThMax) and CIF-Reported Hmax Differ 2 Units
PLAT956_ALERT_1_G Calculated (ThMax) and Actual (FCF) Hmax Differ 2 Units

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PLATON version of 21/04/2015; check.def file version of 09/03/2015

Datablock shelx - ellipsoid plot