Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry

Supporting Information

Stable selones in glutathione peroxidase catalytic cycle of selenonicotinamide derivative

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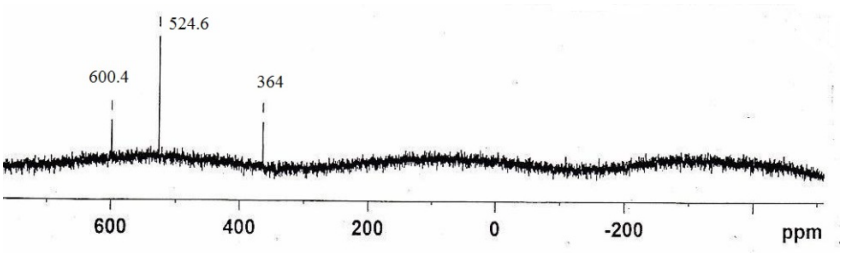
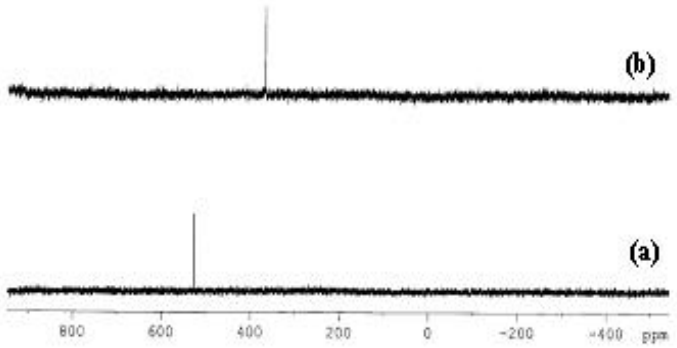
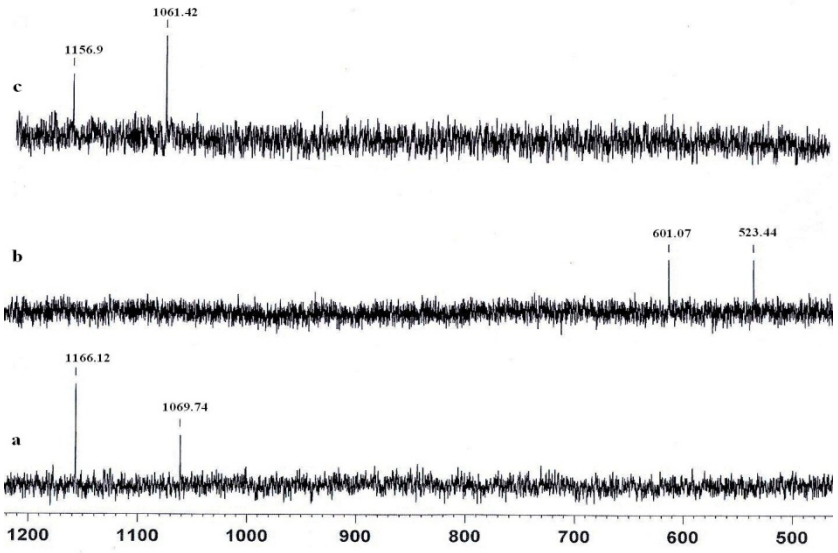


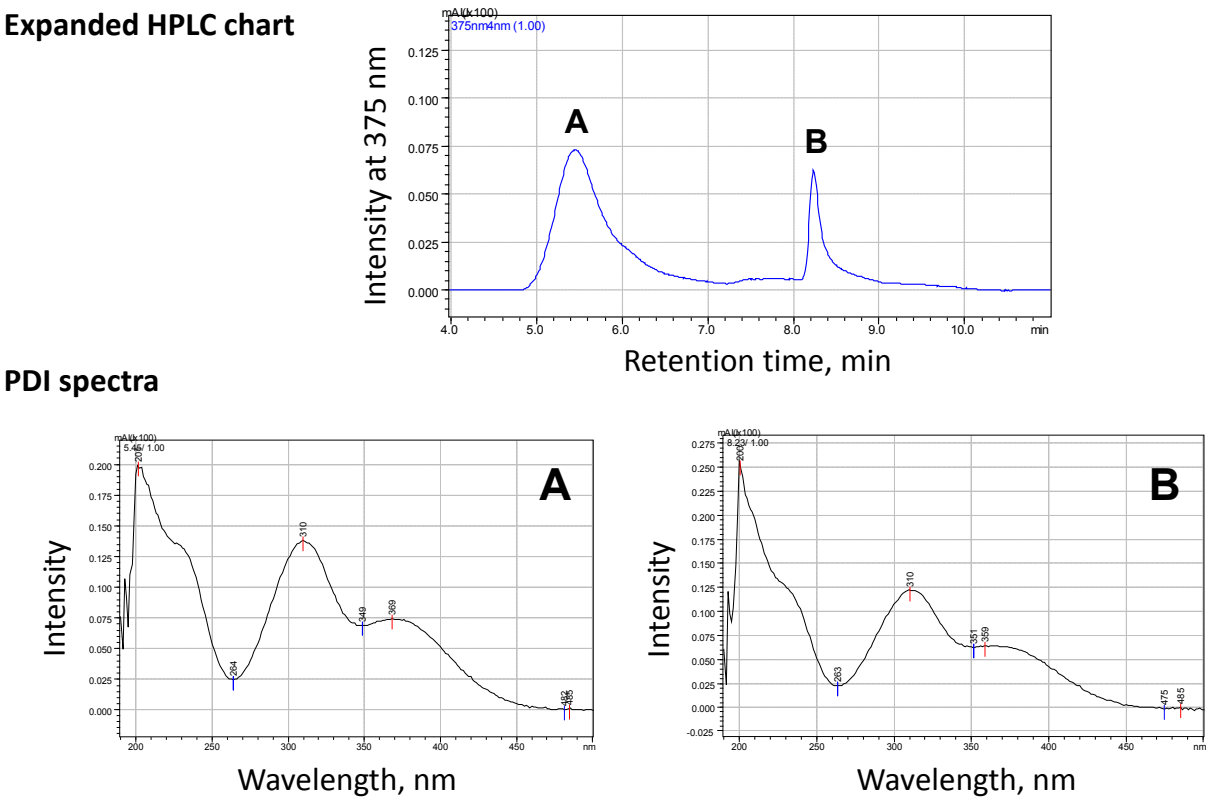
SI Figure 1.^{77}Se NMR spectra in dmso(d_6) solvent for thereaction between NictSeSeNict and GSH in 1 : 3 ratio under areated condition.



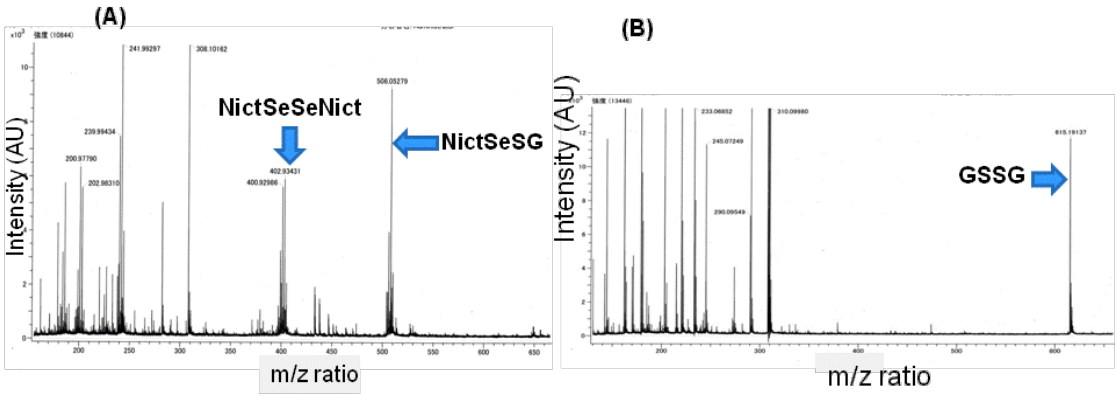
SI Figure 2. ^{77}Se NMR spectra in dmso(d_6) solvent showing (**a**) NictSeSeNict; (**b**) reaction of NictSeSeNict with $NaBH_4$, further acidified with TFA



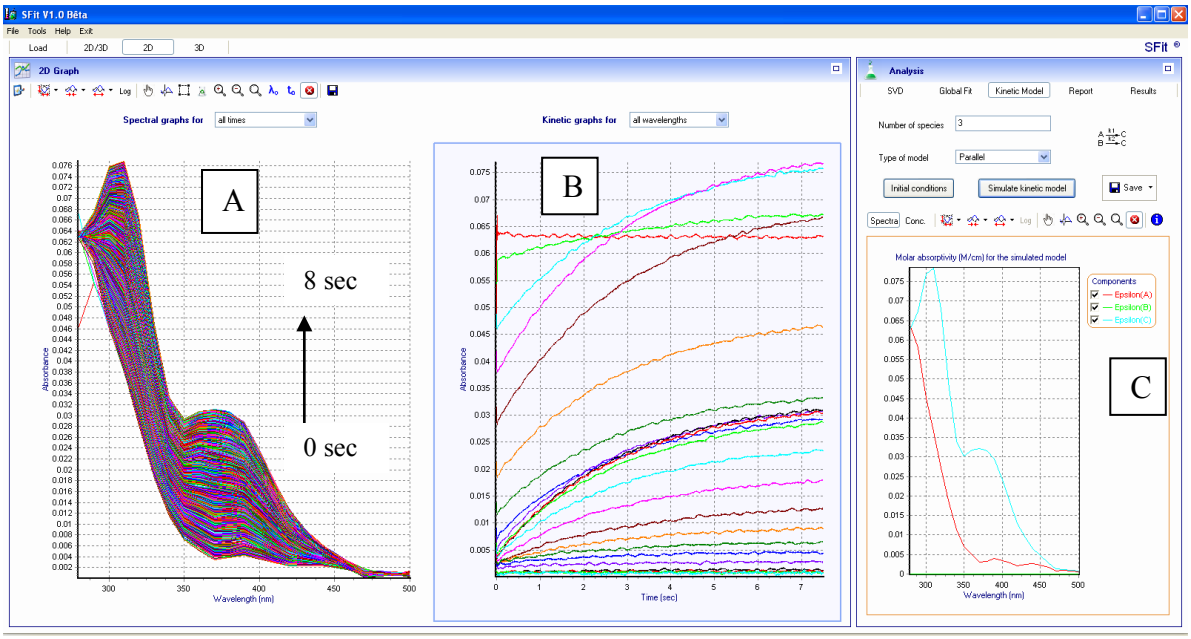
SI Figure 3 . ^{77}Se NMR spectra in dmso(d_6) solventshowing (**a**) reaction between NictSeSeNict and hydrogen peroxide (1:4); (**b**) reaction mixture containing NictSeSeNict, hydrogen peroxide (4 equivalents) and GSH (3equivalents); (**c**):reaction of **b** and hydrogen peroxide(4 equivalent) at 20th min.



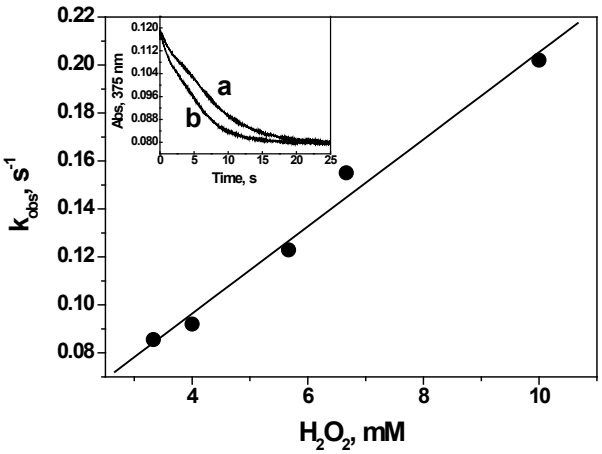
SI Figure 4:Photodiode array (PDI) UV spectra of Nict=Se on the HPLC chromatogram shown in Fig. 4B



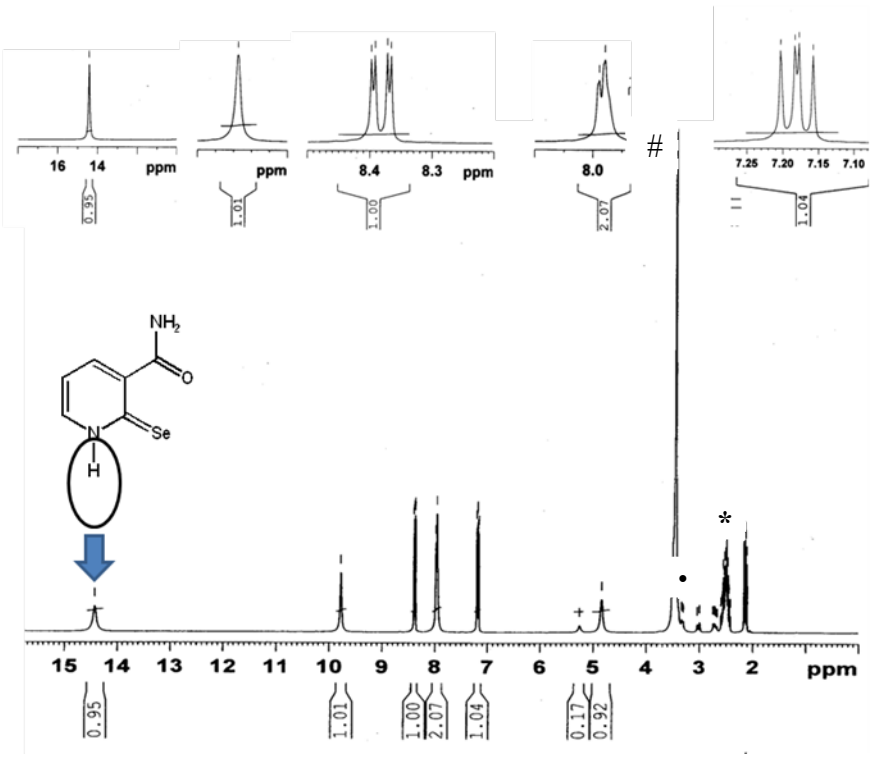
SI Figure 5: Mass spectrum obtained on mixing NictSeSeNict with (A) 1.2 equivalent of GSH_{red}, (B) 240 equivalent of GSH_{red}.The reagents were dissolved in70 % acetonitrile – 30 % water mixture.



SI Figure 6: Plot (A) shows the time resolved spectra obtained on mixing NictSeSeNict (50 µM) with GSH (2 mM) in a stopped flow spectrometer. Plot (B) shows the absorbance-time plot obtained at different wavelength. Plot (C) shows the spectra obtained from stimulation using parallel consecutive reaction (A→C and B→ C, where A, B and C corresponds to NictSeSeNict, NictSeSG and NictC=Se, respectively) by performing the global kinetic trace analysis of absorption-time plots as seen in (B) with S-Fit software.

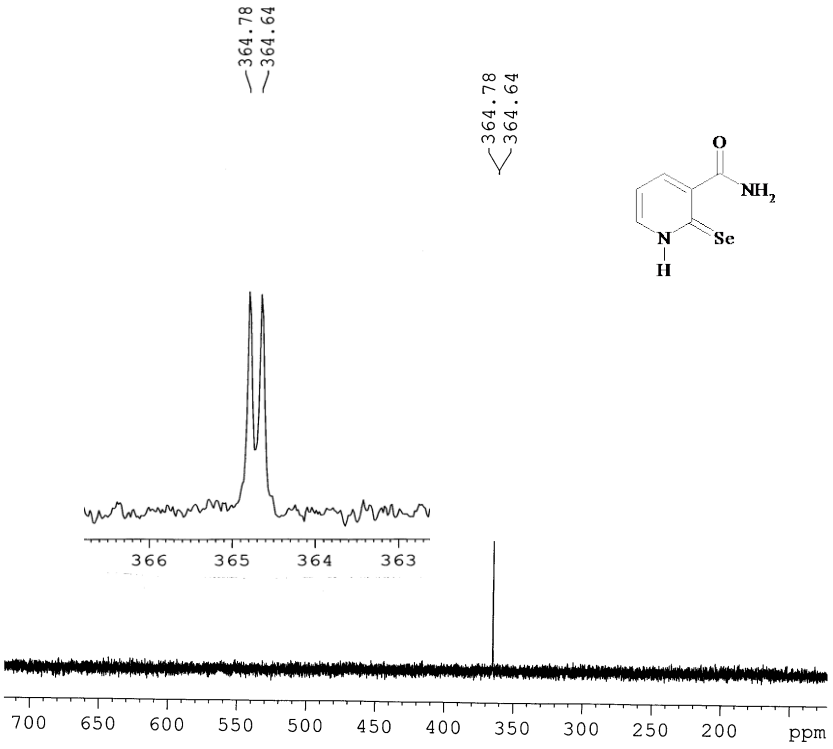


SI Figure 7: Linear plot of observed rate constant at 375 nm as a function of H_2O_2 concentration. Inset shows absorption-time plot obtained at 375 nm on treating different concentration of H_2O_2(a = 6.6 mM; b = 10 mM) to a solution containing 50 µM NictSeSeNict and 50 µM DTT_{red} in 1% DMSO aqueous solution.



SI Figure 8: ^{1}H NMR spectrum in dmso (d_6) solvent obtained on mixing NictSeSeNict with dithiothreitol in 1: 1 ratio

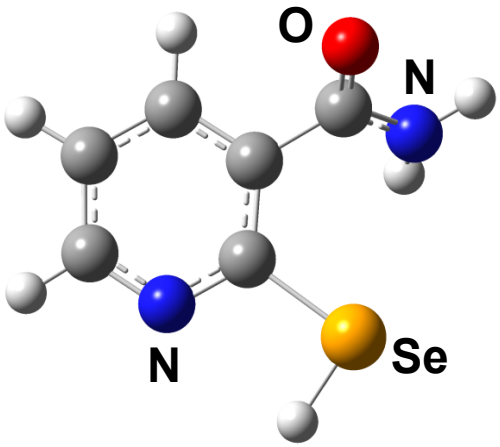
* 1H NMR peak for DMSO-d_6 at δ 2.50 ppm; # for H_2O in DMSO-d_6 δ 3.3 ppm; and ● for DTT_{ox} at δ 2.87, 3.03, 3.49 ppm.



SI Figure 9: ^{1}H coupled ^{77}Se NMR spectrum of selone in dmso (d_6) solvent (^{2}J (Se-H) = 10.7 Hz)

SI Summary of quantum chemical calculation.

pyridineSeH1w



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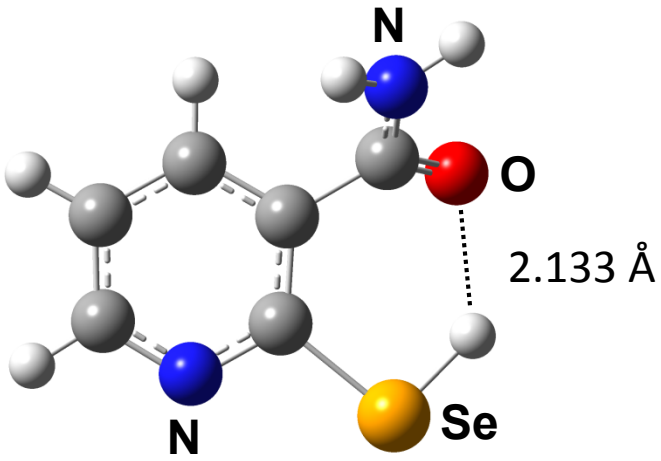
Frequencies -- 52.2953
Se Isotropic = 1776.2854

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z	Mulliken atomic charges
1	6	0	-0.118670	0.039306	0.048092	-0.827318
2	6	0	-0.129902	0.095432	1.455388	0.639616
3	6	0	1.096539	-0.011074	2.119852	-0.025515
4	6	0	2.267485	-0.199815	1.388808	0.309006
5	6	0	2.165655	-0.250428	-0.001345	-0.354630
6	1	0	1.120166	0.047465	3.207451	0.180811
7	1	0	3.233315	-0.298163	1.880143	0.194663
8	1	0	3.052480	-0.394297	-0.619453	0.187191
9	1	0	-1.002685	0.249592	-2.242760	0.137766
10	34	0	-1.732551	0.242953	-0.976108	0.007686
11	6	0	-1.370268	0.329028	2.274441	0.094685
12	8	0	-1.414241	1.248548	3.104869	-0.608295
13	7	0	-2.412823	-0.495021	2.037394	-0.553295
14	1	0	-3.261134	-0.382397	2.593471	0.397800
15	1	0	-2.301812	-1.362196	1.513532	0.379535
16	7	0	1.004188	-0.126271	-0.659897	-0.159706

pyridineSeH2w



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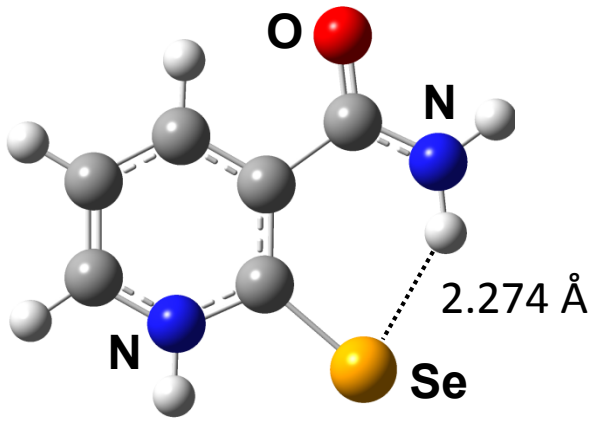
Frequencies -- 49.3453
Se Isotropic = 1920.3661

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z	Mulliken atomic charges
1	6	0	-0.104148	-0.634497	0.003158	-0.399853
2	6	0	0.956603	0.296244	0.069008	0.370089
3	6	0	2.257722	-0.222323	0.124785	-0.184535
4	6	0	2.469498	-1.599759	0.110697	0.195042
5	6	0	1.351798	-2.427232	0.024676	-0.352853
6	1	0	3.107106	0.456370	0.197995	0.186919
7	1	0	3.472270	-2.018337	0.164086	0.193431
8	1	0	1.458663	-3.512221	0.001399	0.184992
9	1	0	-1.818920	1.212221	0.163544	0.177745
10	34	0	-1.969312	-0.217066	-0.096574	0.006959
11	6	0	0.754024	1.786257	0.117291	0.142701
12	7	0	1.591428	2.520556	-0.640768	-0.545581
13	1	0	2.230849	2.105247	-1.314402	0.377330
14	1	0	1.507364	3.536599	-0.622423	0.396777
15	8	0	-0.117080	2.307913	0.835679	-0.615995
16	7	0	0.097561	-1.956995	-0.029202	-0.133168

pyridineSeone1w



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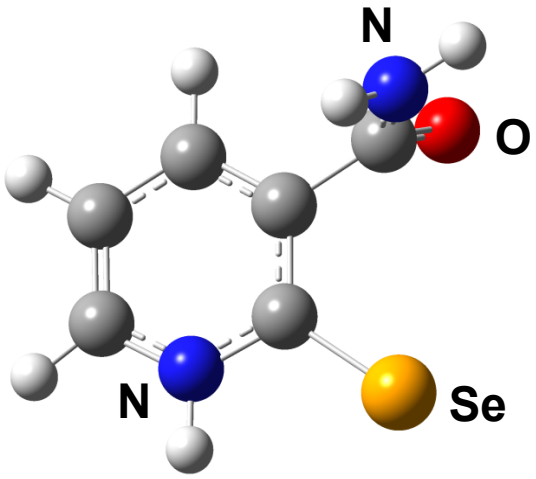
Frequencies -- 61.6070
Se Isotropic = 1727.1787

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z	Mulliken atomic charges
1	6	0	0.152845	0.598331	0.487568	-0.292983
2	6	0	0.298796	-0.017444	1.769543	0.206277
3	6	0	1.507661	-0.642127	2.082835	0.225484
4	6	0	2.587704	-0.693789	1.193533	-0.081818
5	6	0	2.424585	-0.096210	-0.035526	-0.280055
6	1	0	1.594124	-1.102047	3.063671	0.217714
7	1	0	3.521625	-1.184380	1.454290	0.210936
8	1	0	3.185548	-0.068104	-0.813619	0.222954
9	34	0	-1.295064	1.504694	-0.245860	-0.315636
10	6	0	-0.739873	-0.077489	2.874207	-0.017051
11	1	0	1.164697	0.944105	-1.262443	0.453300
12	7	0	1.253892	0.505722	-0.330605	-0.054712
13	8	0	-0.463237	-0.658166	3.941680	-0.665845
14	7	0	-1.933742	0.499822	2.672436	-0.503671
15	1	0	-2.150897	0.971550	1.792586	0.272074
16	1	0	-2.625516	0.455942	3.419350	0.403030

pyridineSeone2w



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Frequencies -- 44.6804
Se Isotropic = 1792.8870

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z	Mulliken atomic charges
1	6	0	0.039379	0.221357	0.237711	-0.673409
2	6	0	0.172588	-0.157870	1.599843	0.084069
3	6	0	1.420543	-0.437094	2.137535	0.458858
4	6	0	2.584655	-0.354963	1.348595	0.022128
5	6	0	2.443311	0.009096	0.030452	-0.305030
6	1	0	1.501556	-0.727378	3.185846	0.198536
7	1	0	3.567524	-0.570452	1.759369	0.210108
8	1	0	3.271591	0.102383	-0.669067	0.219775
9	34	0	-1.548472	0.618626	-0.623413	-0.312834
10	6	0	-1.055043	-0.322192	2.468195	-0.096991
11	1	0	1.142001	0.549953	-1.462199	0.462615
12	7	0	1.212042	0.278153	-0.467350	-0.046726
13	8	0	-1.629480	-1.417449	2.548245	-0.561315
14	7	0	-1.417175	0.760751	3.177575	-0.434308
15	1	0	-0.963328	1.662073	3.038497	0.379189
16	1	0	-2.258544	0.725416	3.753811	0.395334