ELECTRONIC SUPPLEMENTARY INFORMATION FOR

Formation of a Spirodiazaselenurane and its Corresponding Azaselenonium Derivatives from the Oxidation of 2,2'-Selenobis(benzamide). Structure, Properties and Glutathione Peroxidase Activity.

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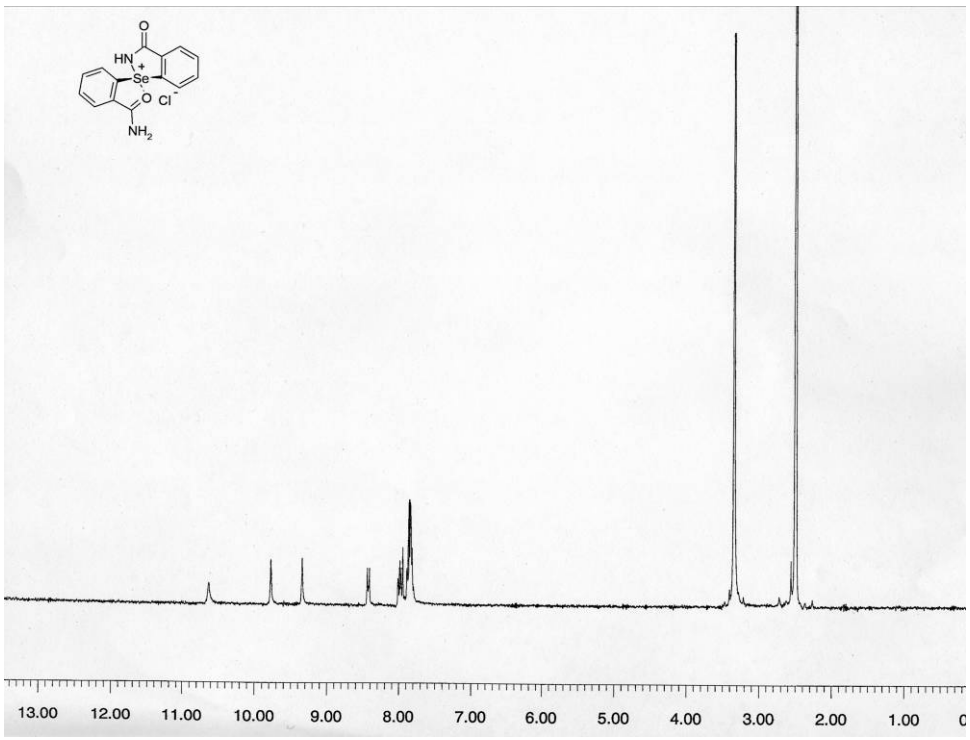
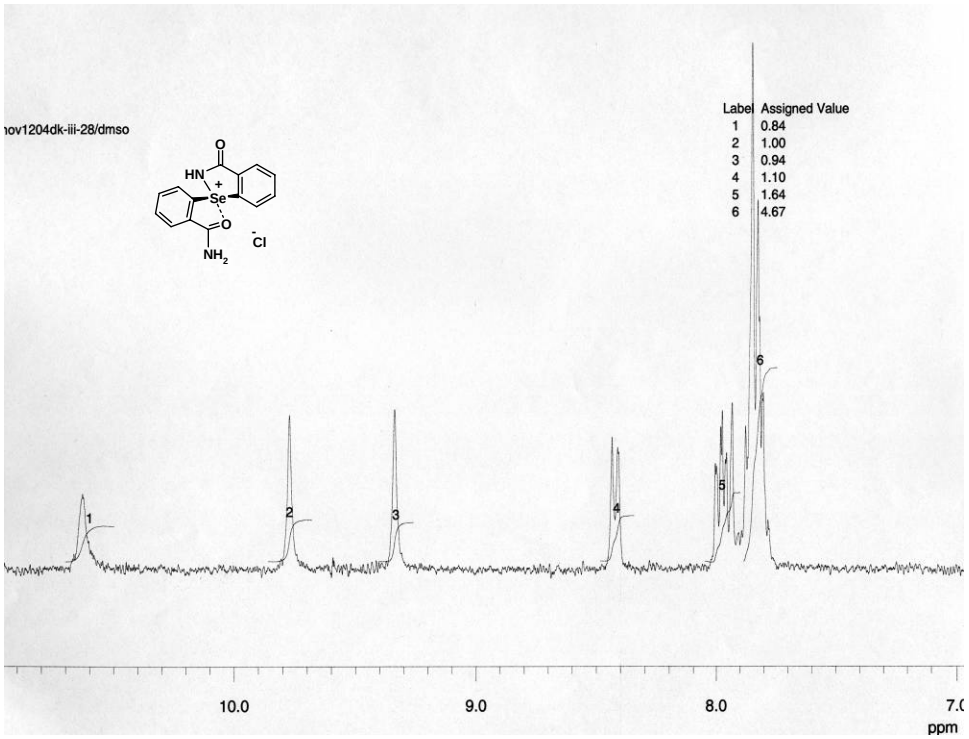
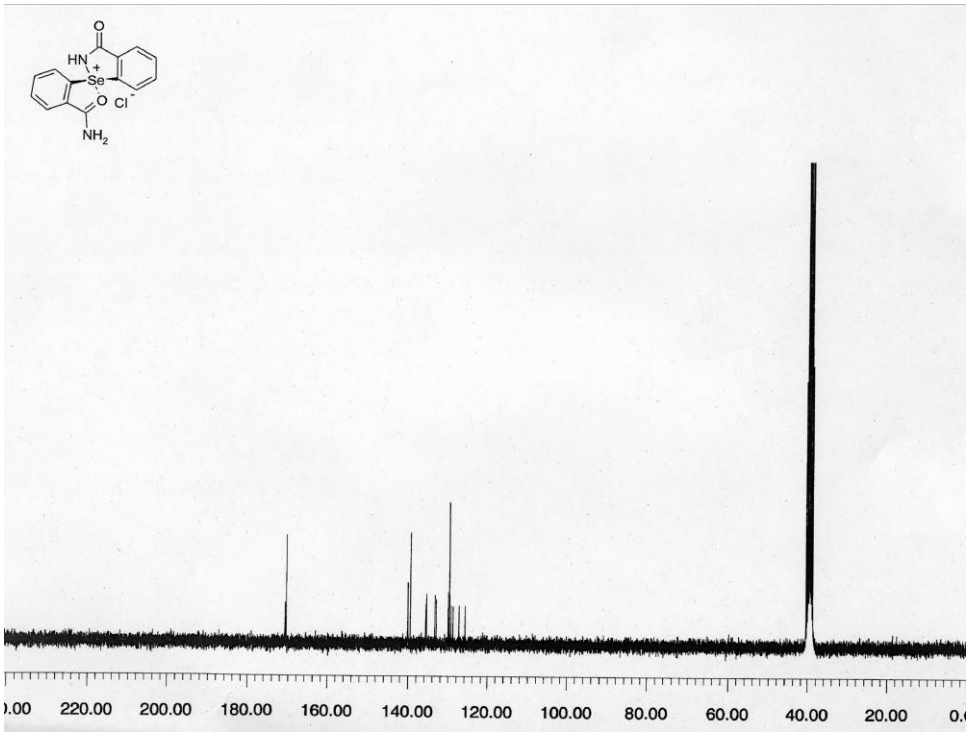
Contents:

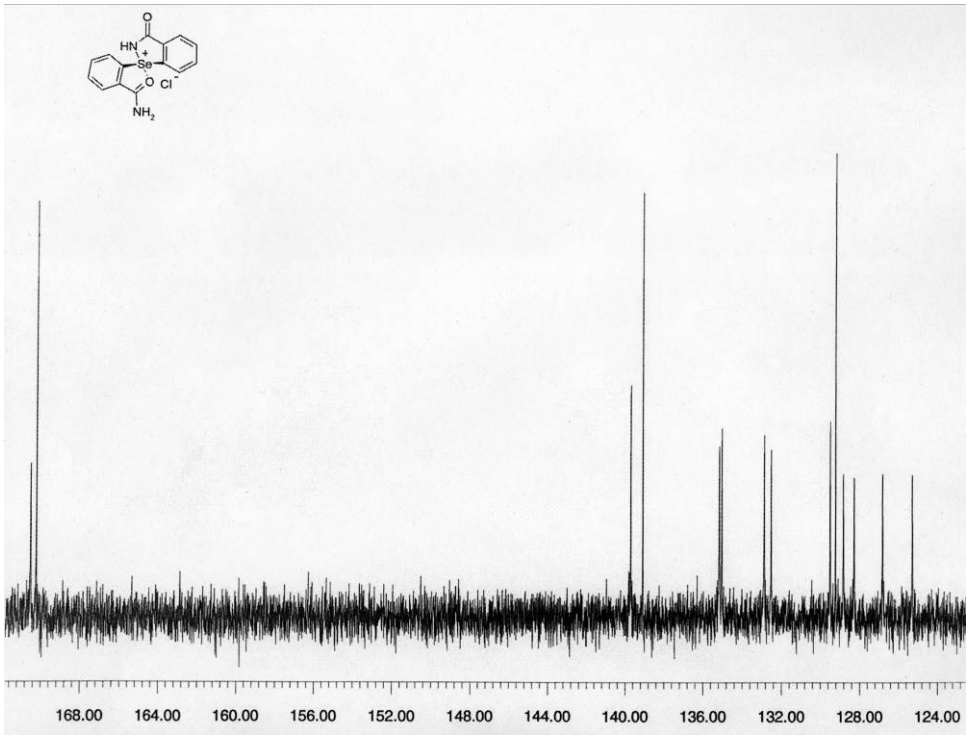
^{1}H NMR Spectrum of **15** in DMSO-d_6



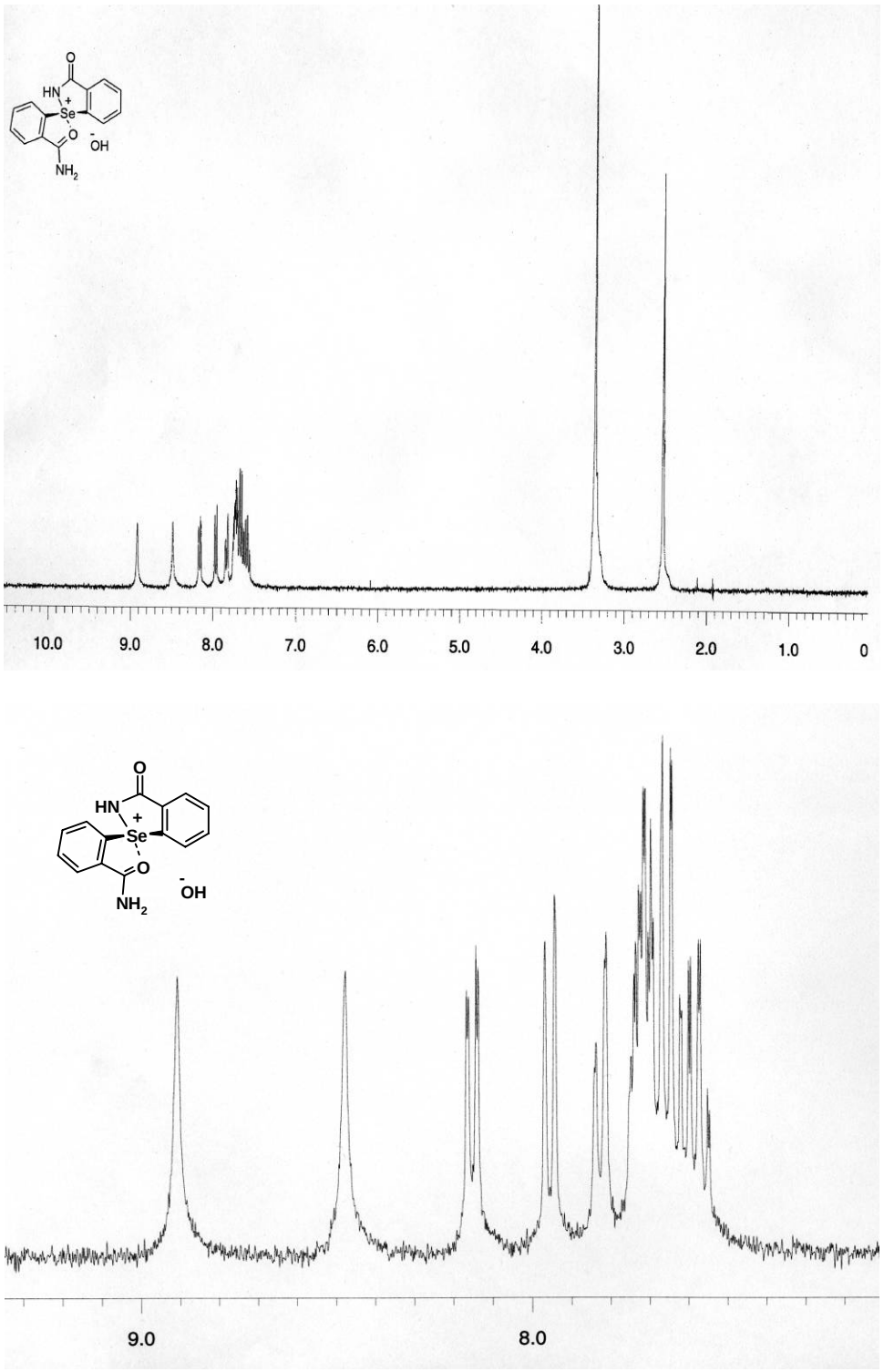


^{13}C NMR Spectrum of **15** in DMSO-d_6

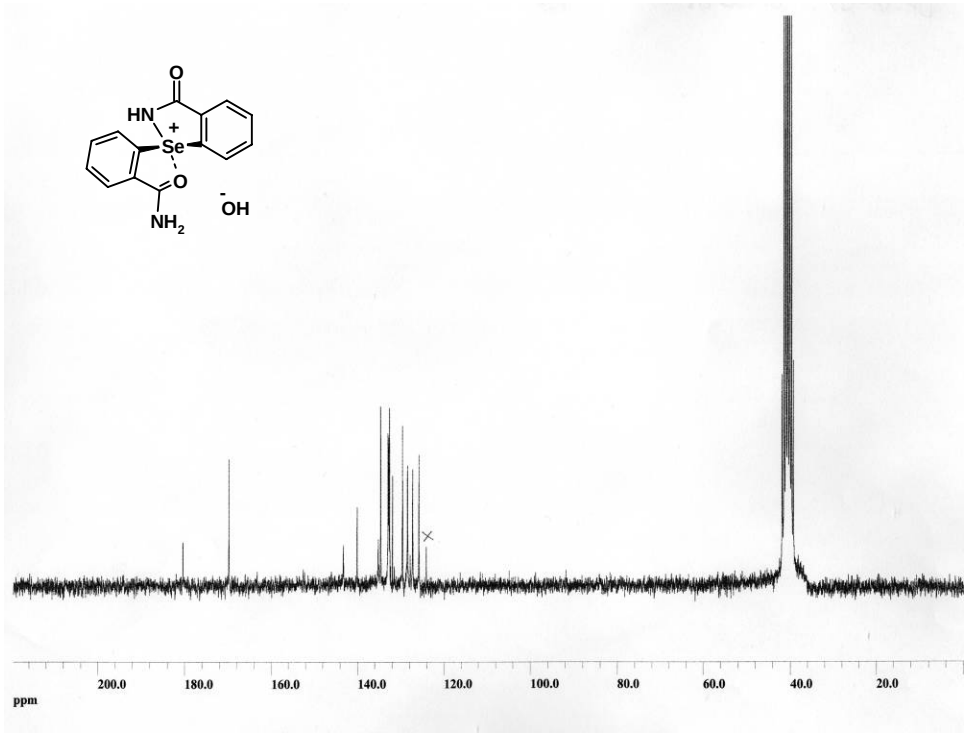


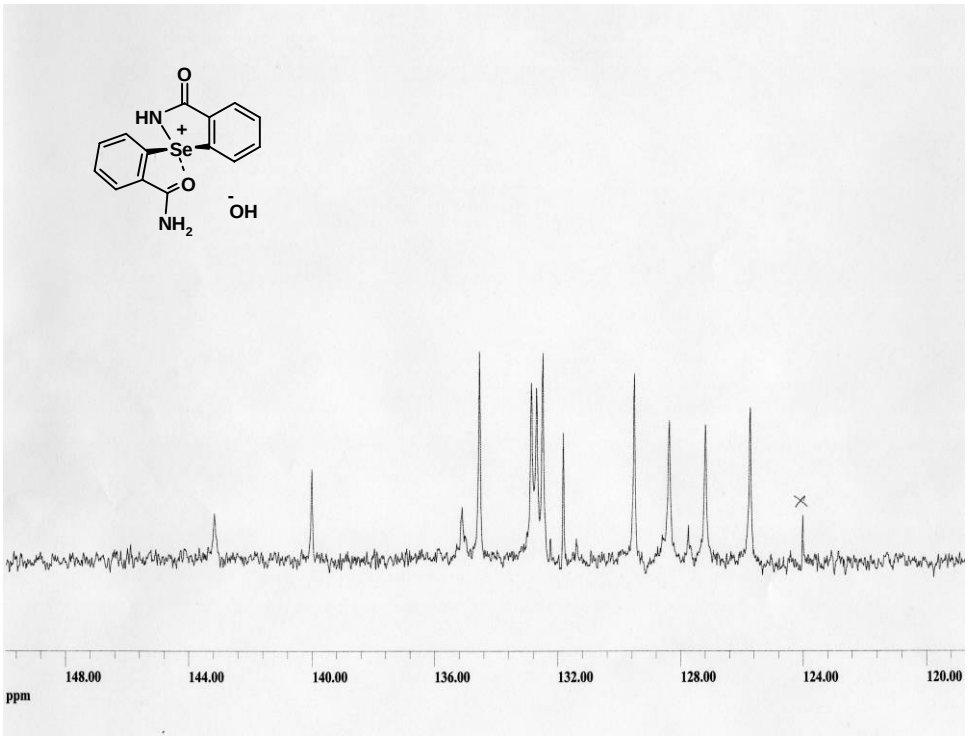


^{1}H NMR Spectrum of **16** in DMSO-d_6

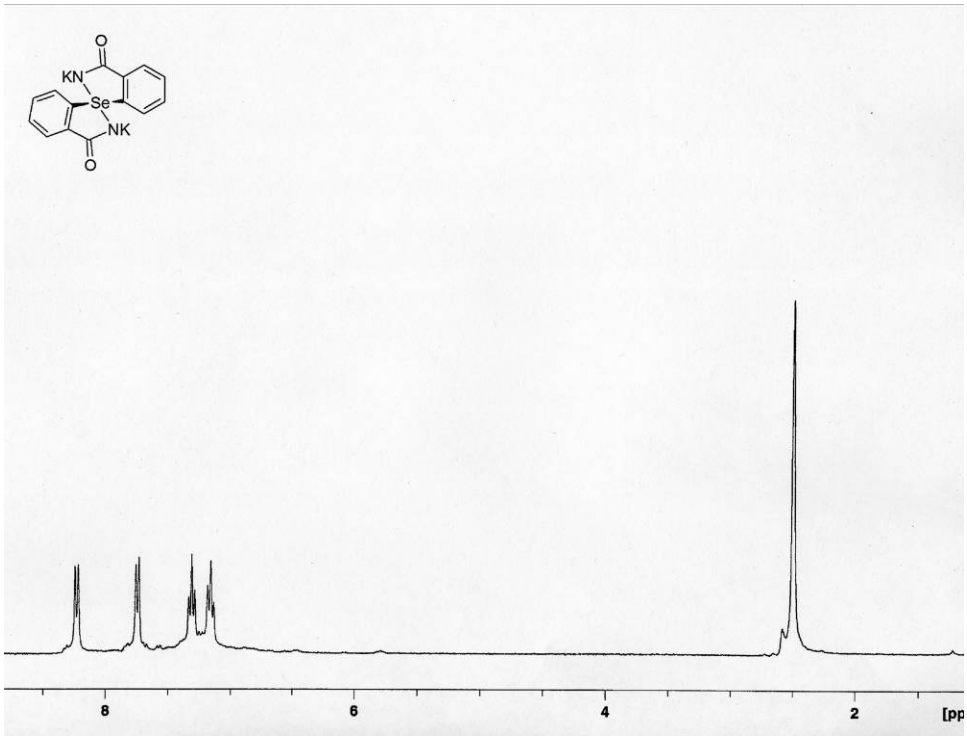


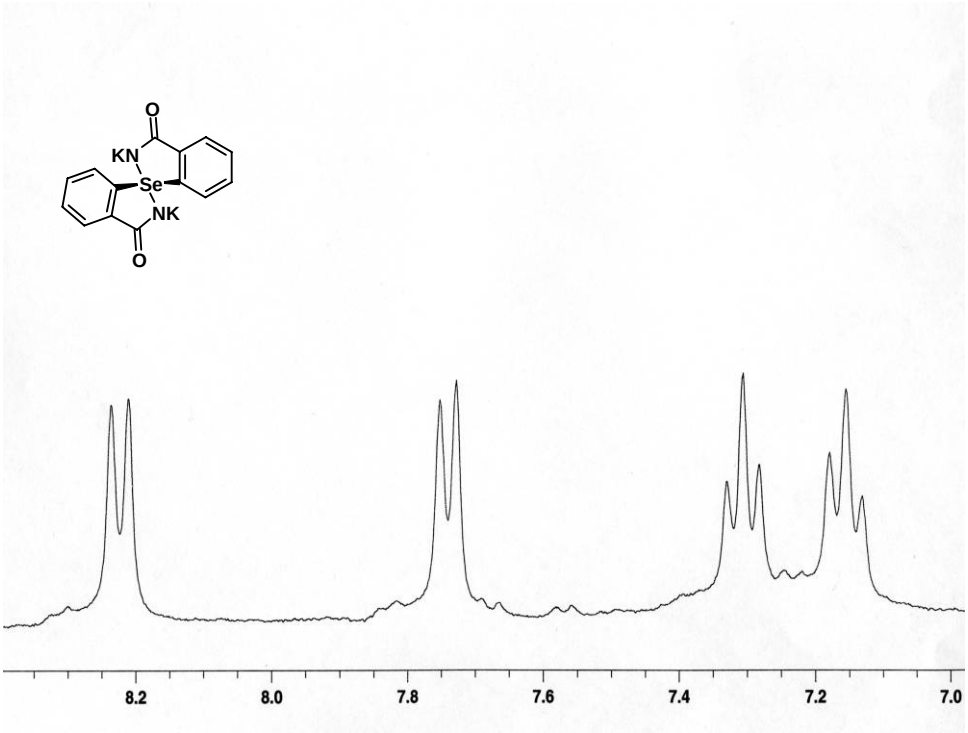
^{13}C NMR Spectrum of **16** in DMSO-d_6



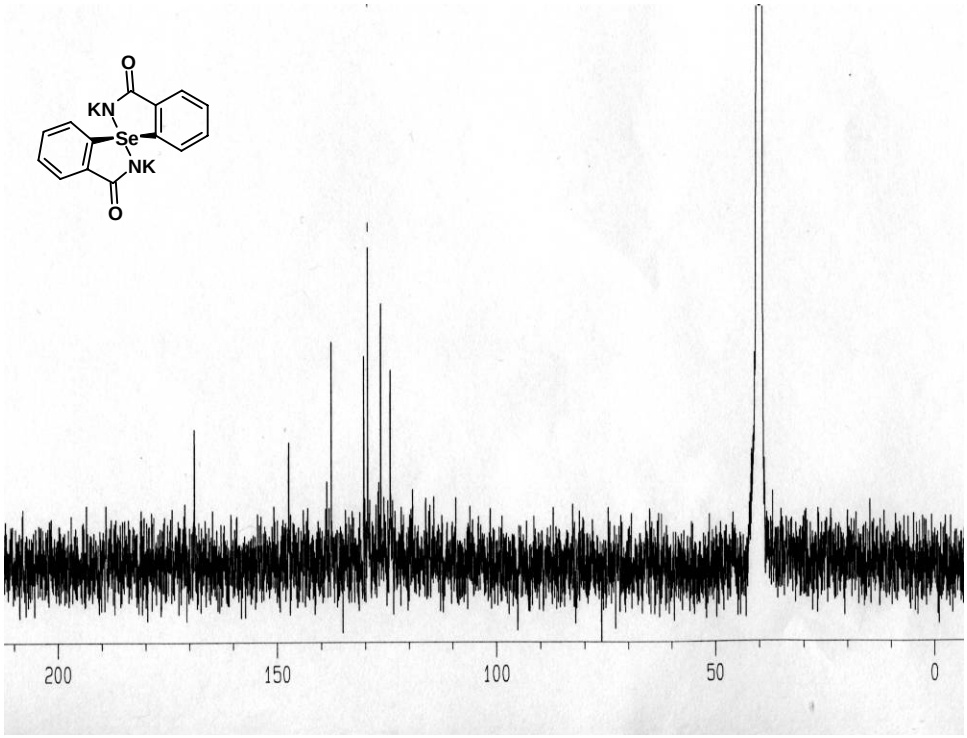


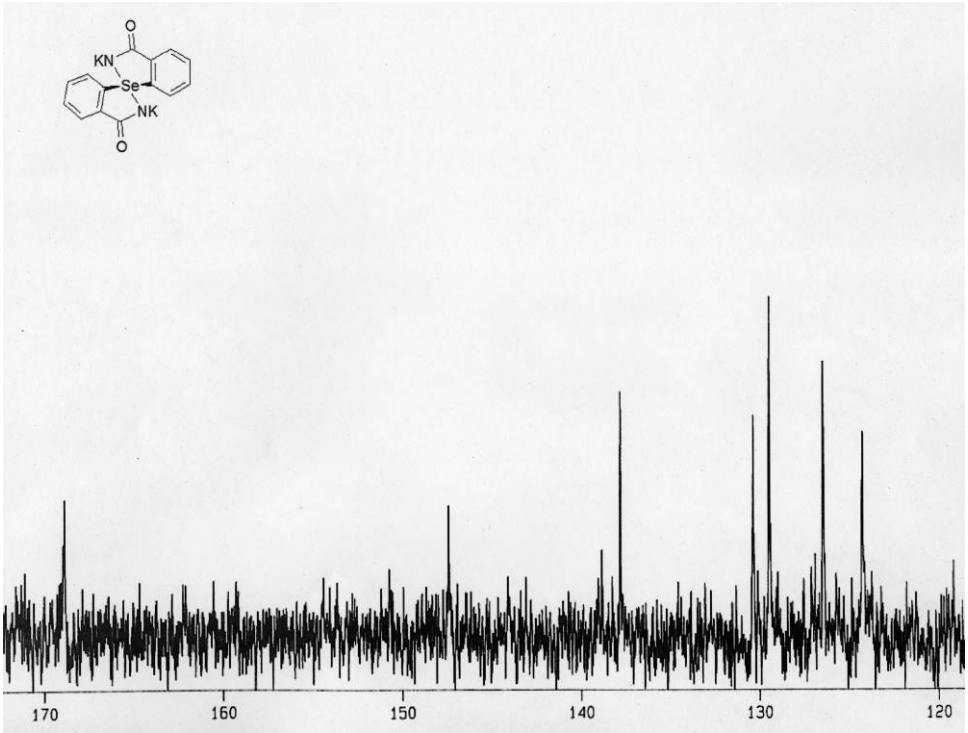
^{1}H NMR Spectrum of **21** in DMSO-d_6



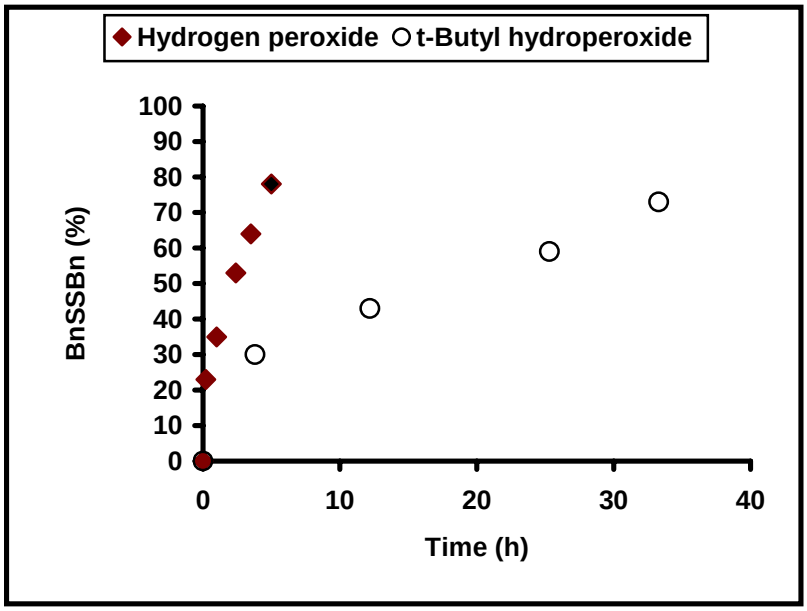


^{13}C NMR Spectrum of **21** in DMSO-d_6





Catalytic Activity of 15 in the Oxidation of BnSH to BnSSBn with *tert*-Butyl Hydroperoxide and Hydrogen Peroxide



Reactions were performed with BnSH (0.031 M), **15** (0.0031 M), and either *tert*-butyl hydroperoxide (0.038 M) or H_2O_2 (0.040 M) in CH_2Cl_2-MeOH (4:1) at 18 °C. Analyses were performed by HPLC on a Novapak C18 column (3.9 x 150 mm) with water-acetonitrile (20:80) as the solvent.

X-Ray Crystallographic Data for 15

A colorless prismatic crystal of C_{14} H_{11} Cl N_2 O_2 Se · 0.5 H_2 O was coated with Paratone 8277 oil (Exxon) and mounted on a glass fiber. All measurements were made on a Nonius KappaCCD diffractometer with graphite monochromated Mo-Kα radiation. The details[1,2] of crystal data and structure refinement have been provided in Table 1. The structure was solved by the direct methods[3] and expanded using Fourier techniques[4]. The non-hydrogen atoms were refined anisotropically. A difference map showed electron density region consistent with a disordered water molecule lying over two sites across an inversion center with 0.25 site occupancy factor each. Hydrogen atoms were located from a difference map. H-atoms bonded to C-atoms were included at geometrically idealized positions and were not refined while those bonded to N-atoms were allowed to refine; H-atoms of the disordered water of solvation were ignored. The final cycle of full-matrix least-squares refinement using SHELXL97[5] converged with unweighted and weighted agreement factors, R = 0.035 and wR = 0.081 (all data), respectively, and goodness of fit, S = 1.04. The weighting scheme was based on counting statistics and the final difference map was free of any chemically significant features. The figure was plotted with the aid of ORTEPII[6].

Crystal data and structure refinement for C_{14} H_{11} Cl N_2 O_2 Se · 0.5 H_2 O.

Empirical formula	C_{14} H_{11} Cl N_2 O_2 Se · 0.5 H_2 O	
Formula weight	362.67	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 7.944(3) Å	α= 81.649(3)°.
	b = 9.700(4) Å	β= 74.131(3)°.
	c = 11.001(3) Å	γ = 67.241(2)°.
Volume	751.2(5) $Å^3$	
Z	2	
Density (calculated)	1.603 Mg/m^3	
Absorption coefficient	2.68 mm^{-1}	
F(000)	362	
Crystal size	0.06 x 0.05 x 0.04 mm^3	
Theta range for data collection	3.8 to 27.4°.	
Index ranges	-10<=h<=10, -12<=k<=12, -14<=l<=14	
Reflections collected	6428	
Independent reflections	3416 [R(int) = 0.032]	

Completeness to theta = 27.4°	99.3 %
Absorption correction	Multi-scan method
Max. and min. transmission	0.900 and 0.855
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3416 / 0 / 208
Goodness-of-fit on F^2	1.04
Final R indices [I>2sigma(I)]	R1 = 0.035, wR2 = 0.076
R indices (all data)	R1 = 0.050, wR2 = 0.081
Largest diff. peak and hole	0.53 and -0.52 e.$Å^{-3}$

X-Ray Crystallographic Data for 16

A colorless prismatic crystal of $C_{14}\ H_{12}\ N_2\ O_3\ Se \cdot 3\ H_2\ O$ was coated with Paratone 8277 oil (Exxon) and mounted on a glass fiber. All measurements were made on a Nonius KappaCCD diffractometer with graphite monochromated Mo-Kα radiation. The details[1,2] of crystal data and structure refinement have been provided in Table 1. The structure was solved by the direct methods[3] and expanded using Fourier techniques[4]. The non-hydrogen atoms were refined anisotropically. Se atom was disordered with a small fraction with s.o.f. 0.046(8) lying close to the major component. H-atoms were included at geometrically idealized positions and were not refined; H-atoms of the water of solvation and OH^- group were constrained. The final cycle of full-matrix least-squares refinement using SHELXL97[5] converged with unweighted and weighted agreement factors, R = 0.075 and wR = 0.159 (all data), respectively, and goodness of fit, S = 1.21. The weighting scheme was based on counting statistics and the final difference map was free of any chemically significant features. Due to the poor quality of data, an absolute structure could not be established. The figure was plotted with the aid of ORTEPII[6].

Crystal data and structure refinement for $C_{14}\ H_{12}\ N_2\ O_3\ Se \cdot 3\ H_2\ O$.

Empirical formula	$C_{14}\ H_{12}\ N_2\ O_3\ Se \cdot 3\ H_2\ O$	
Formula weight	389.26	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1$	
Unit cell dimensions	a = 4.554(2) Å	α= 90°.
	b = 18.386(4) Å	β= 102.57(2)°.
	c = 9.912(7) Å	γ = 90°.
Volume	810.0(7) $Å^3$	
Z	2	
Density (calculated)	1.596 Mg/m^3	
Absorption coefficient	2.350 mm^{-1}	
F(000)	396	
Crystal size	0.06 x 0.05 x 0.04 mm^3	
Theta range for data collection	3.9 to 25.0°.	
Index ranges	-5<=h<=5, -21<=k<=21, -11<=l<=11	
Reflections collected	4116	
Independent reflections	1397 [R(int) = 0.12]	
Completeness to theta = 25.0°	95.3 %	

Absorption correction	Multi-scan method
Max. and min. transmission	0.912 and 0.872
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1397 / 12 / 236
Goodness-of-fit on F^2	1.21
Final R indices [I>2sigma(I)]	R1 = 0.075, wR2 = 0.137
R indices (all data)	R1 = 0.120, wR2 = 0.159
Largest diff. peak and hole	0.67 and -0.85 e.$Å^{-3}$

References for X-ray Structure Determinations:

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3. A. Altomare, M. Cascarano, C. Giacovazzo and A. Guagliardi. Completion and Refinement of Crystal Structures with *SIR92*. *J. Appl. Cryst.*, 1993, **26**, 343-350.

4. P. T. Beurskens, G. Admiraal, G. Beurskens, W. P Bosman, R. de Gelder, R. Israel and J. M. M. Smits, The *DIRDIF-94* program system, Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands, 1994.

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6. C. K. Johnson, *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA, 1976.