Supporting Information for:

Constrained Phosphine Chalcogenide Selenoethers Supported by *peri*-Substitution

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Additional NMR Spectra

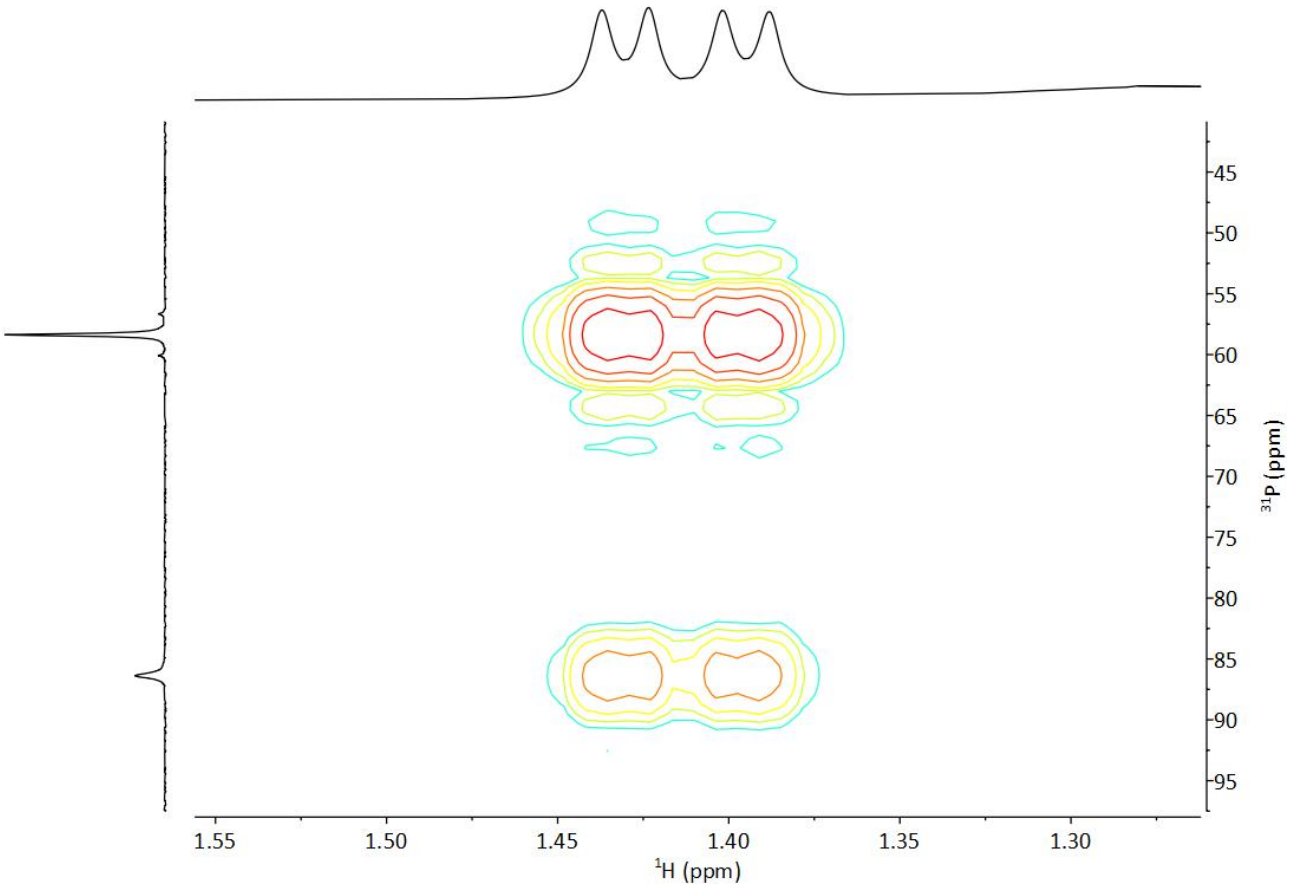

Figure S1. $^{1}H–^{31}P$ HMBC NMR spectrum of **1-Se**.

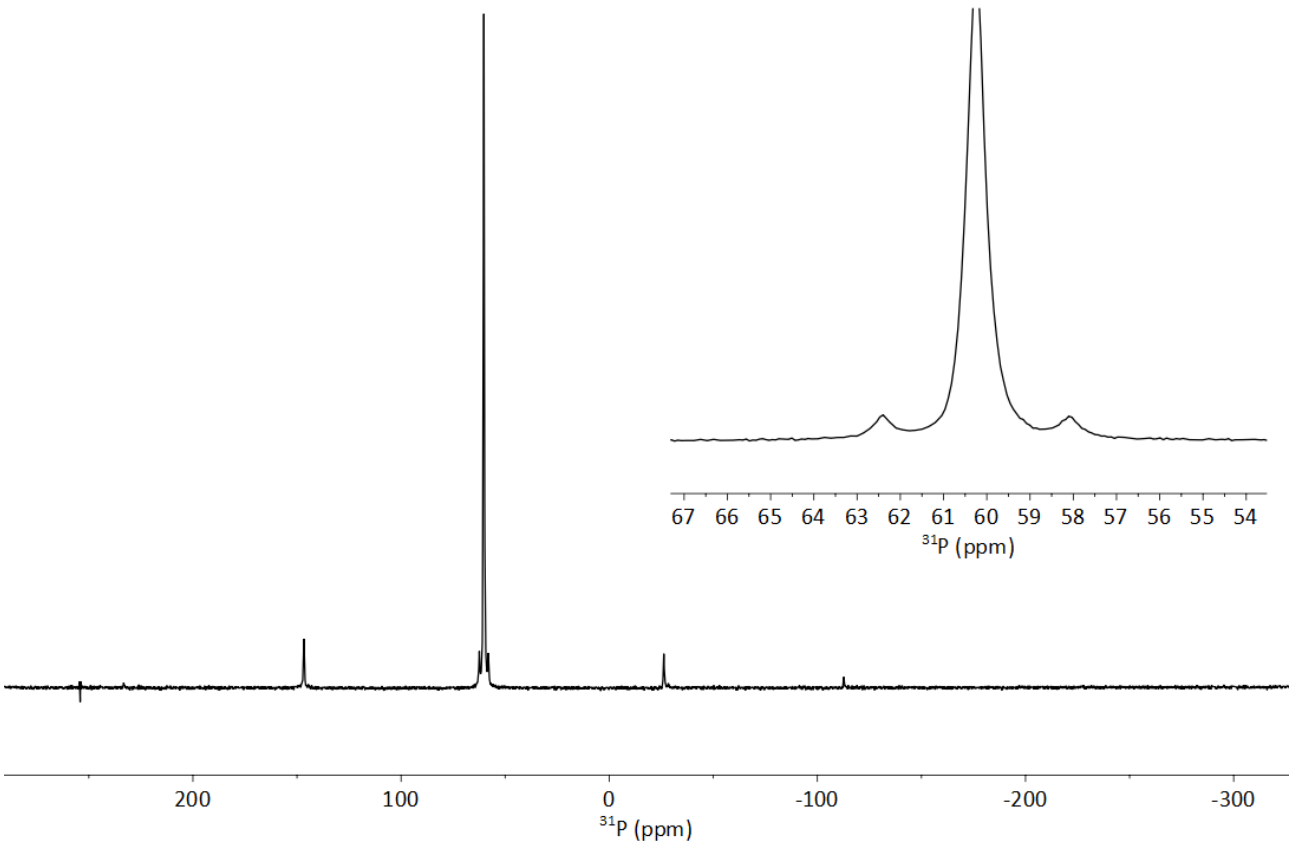

Figure S2. The $^{31}P\{^{1}H\}$ SS-MAS NMR spectrum of 1-Se recorded at 162.0 MHz with expansion of the isotropic peak showing the ^{77}Se satellites.

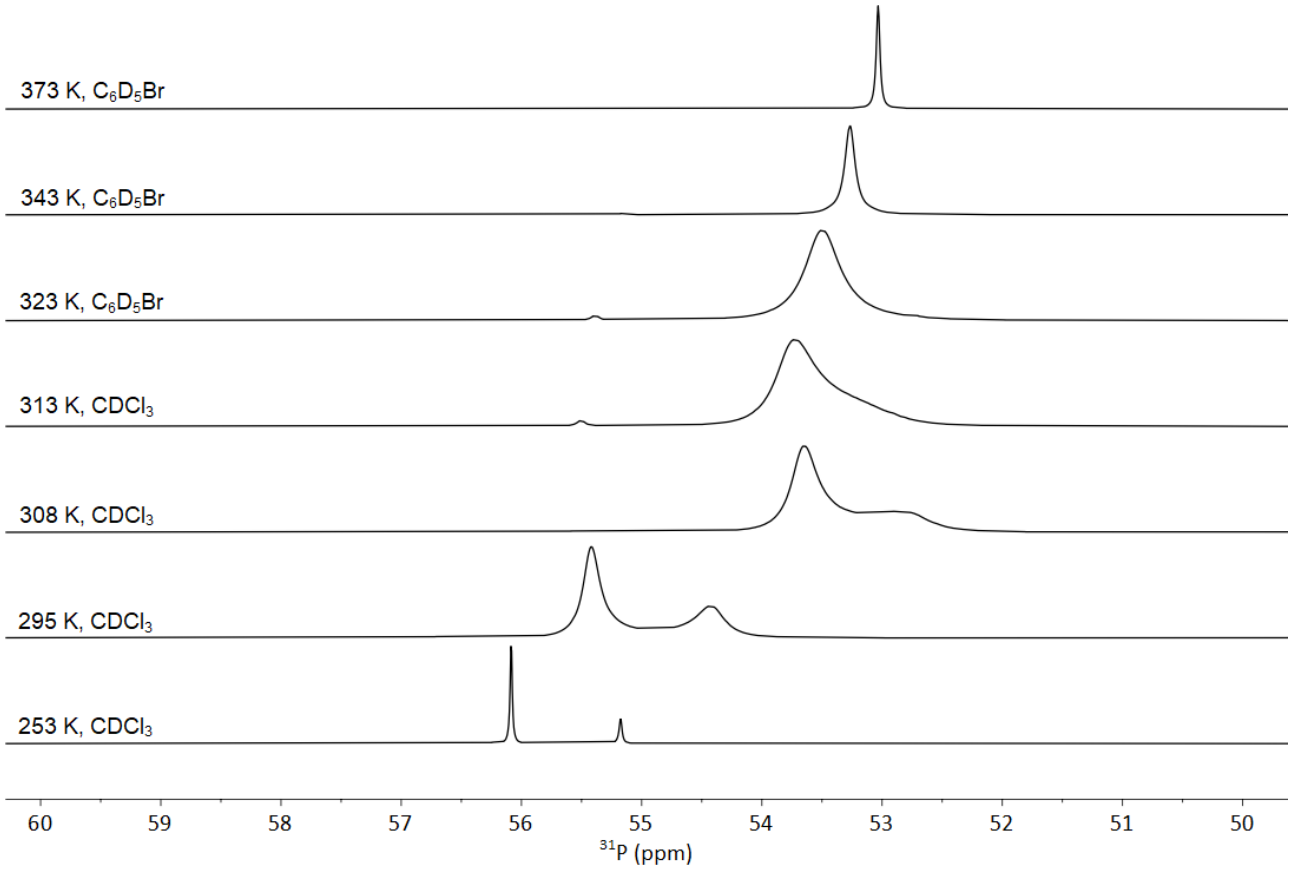

Figure S3. The $^{31}P\{^{1}H\}$ VT NMR spectra of **1-O** with solvent and temperatures indicated (acquired at 202.5 MHz).

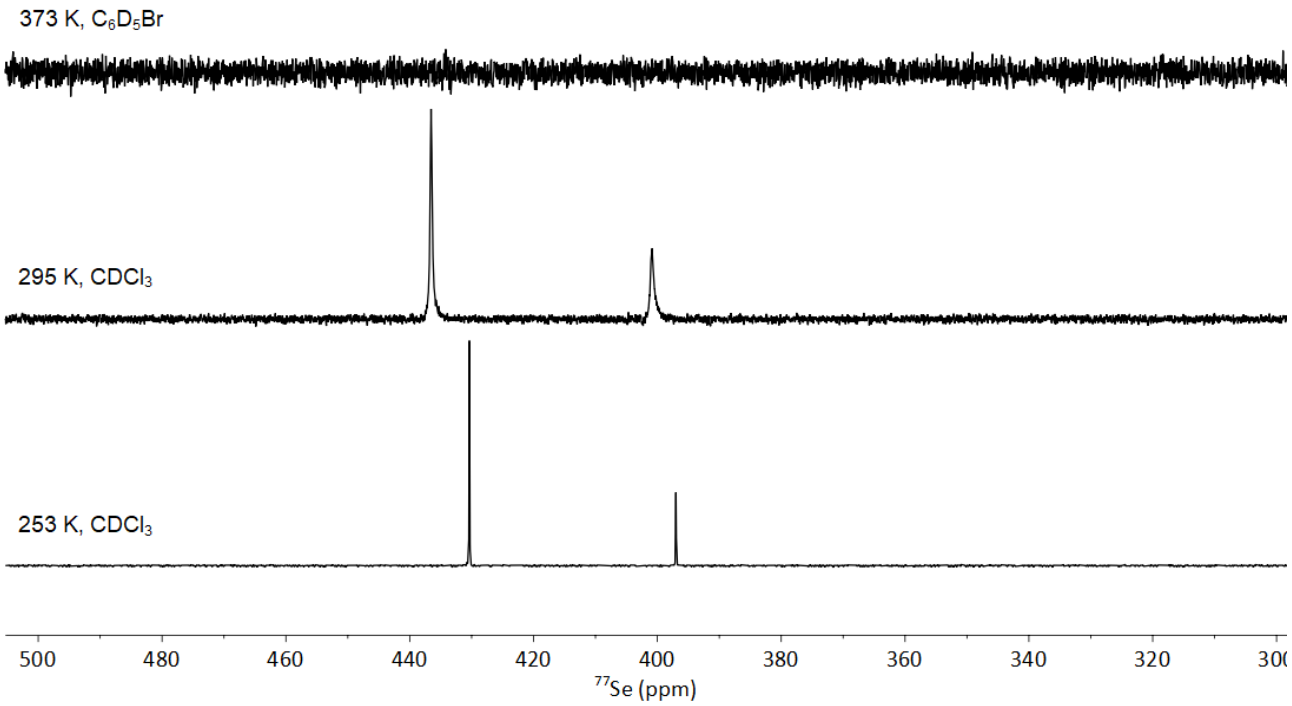

Figure S4. The $^{77}Se\{^{1}H\}$ VT NMR spectra of **1-Se** with solvent and temperatures indicated (acquired at 95.4 MHz)

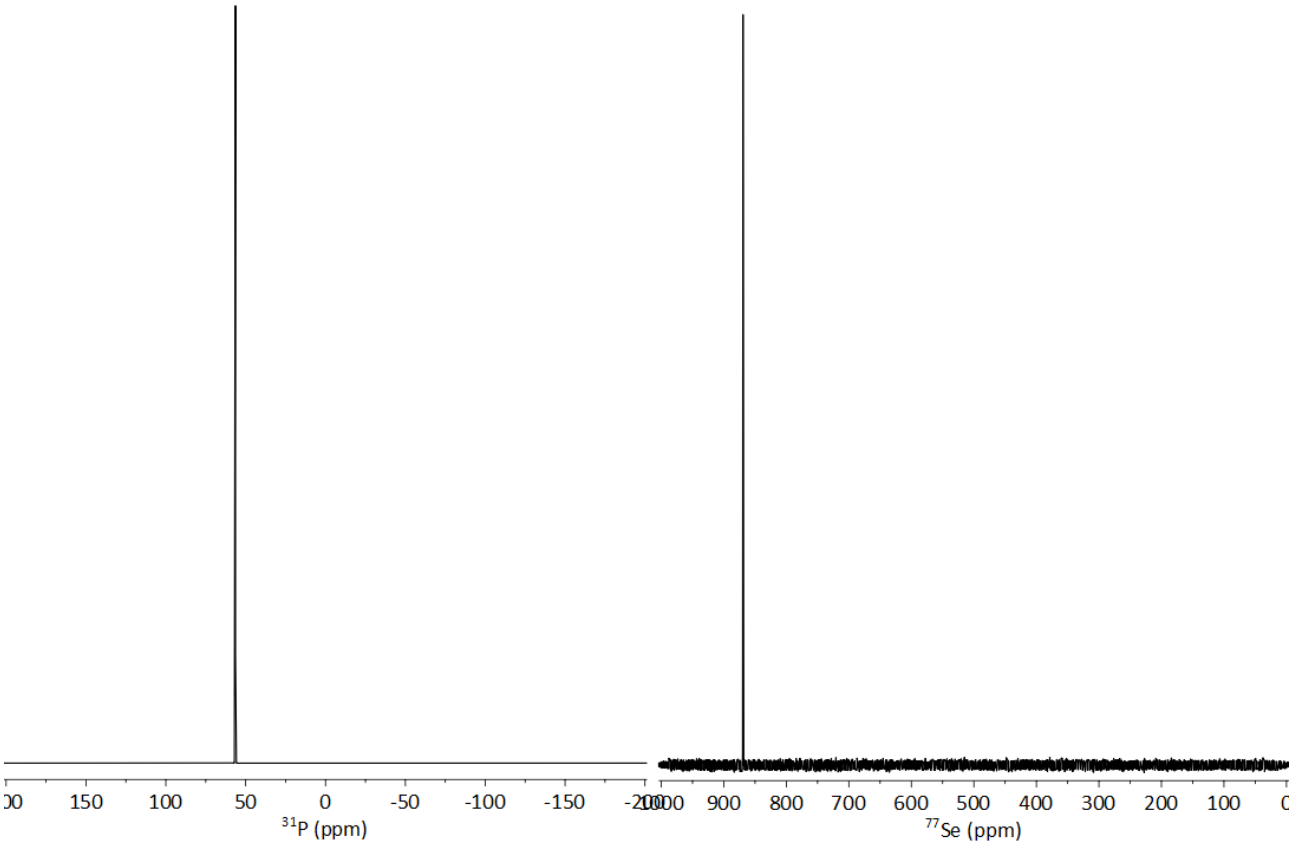

Figure S5. The $^{31}P\{^{1}H\}$ NMR (left) and 77Se{1H} NMR (right) spectra of **1-O2** (acquired at 202.5 and 95.4 MHz, respectively)

Infrared Spectra

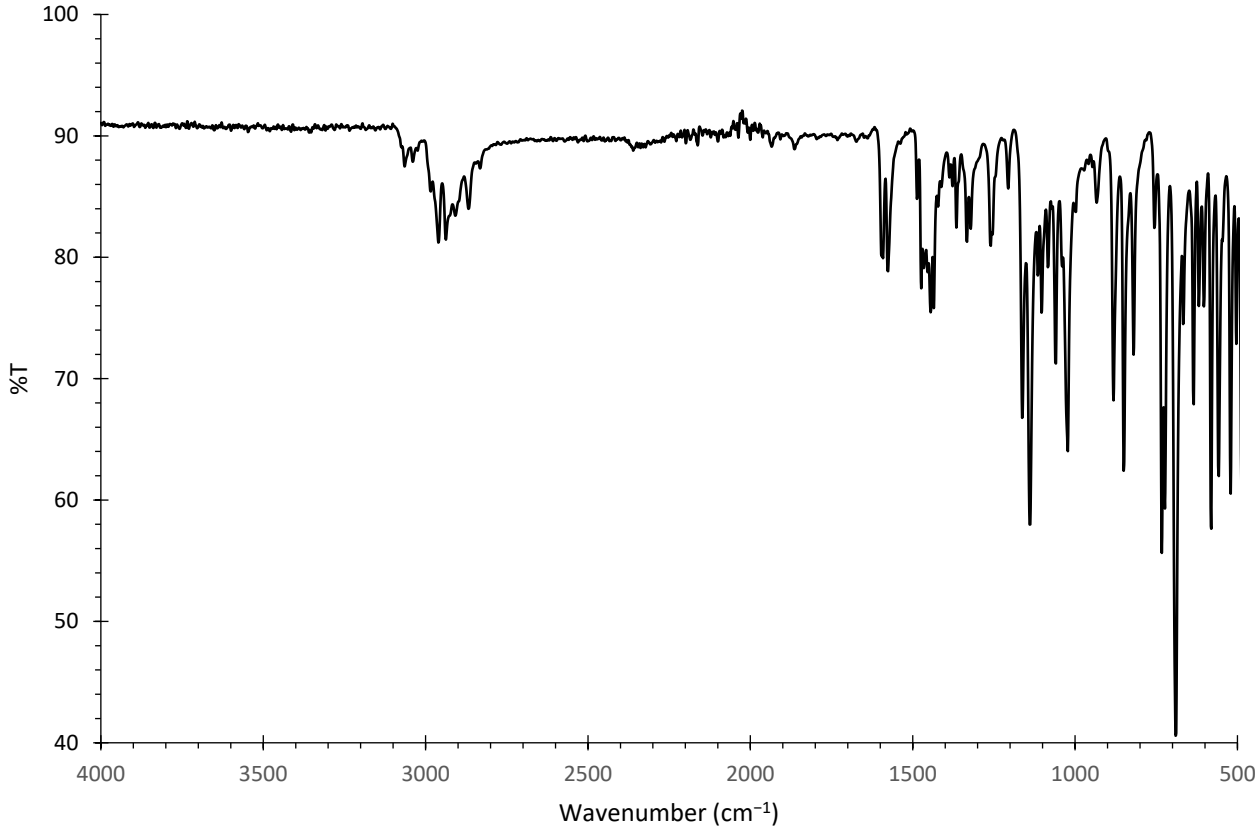

Figure S6. Infrared spectrum of **1-O**.

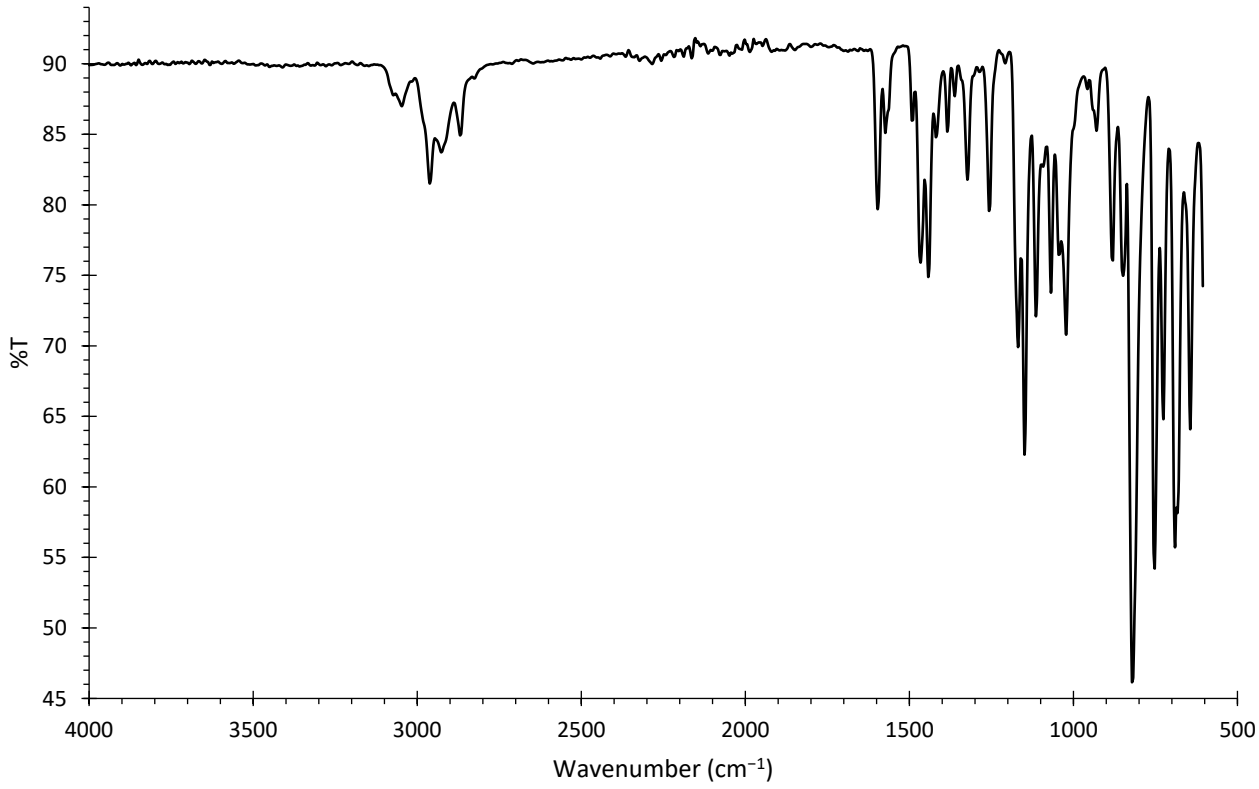

Figure S7. Infrared Spectrum of **1-O2**.

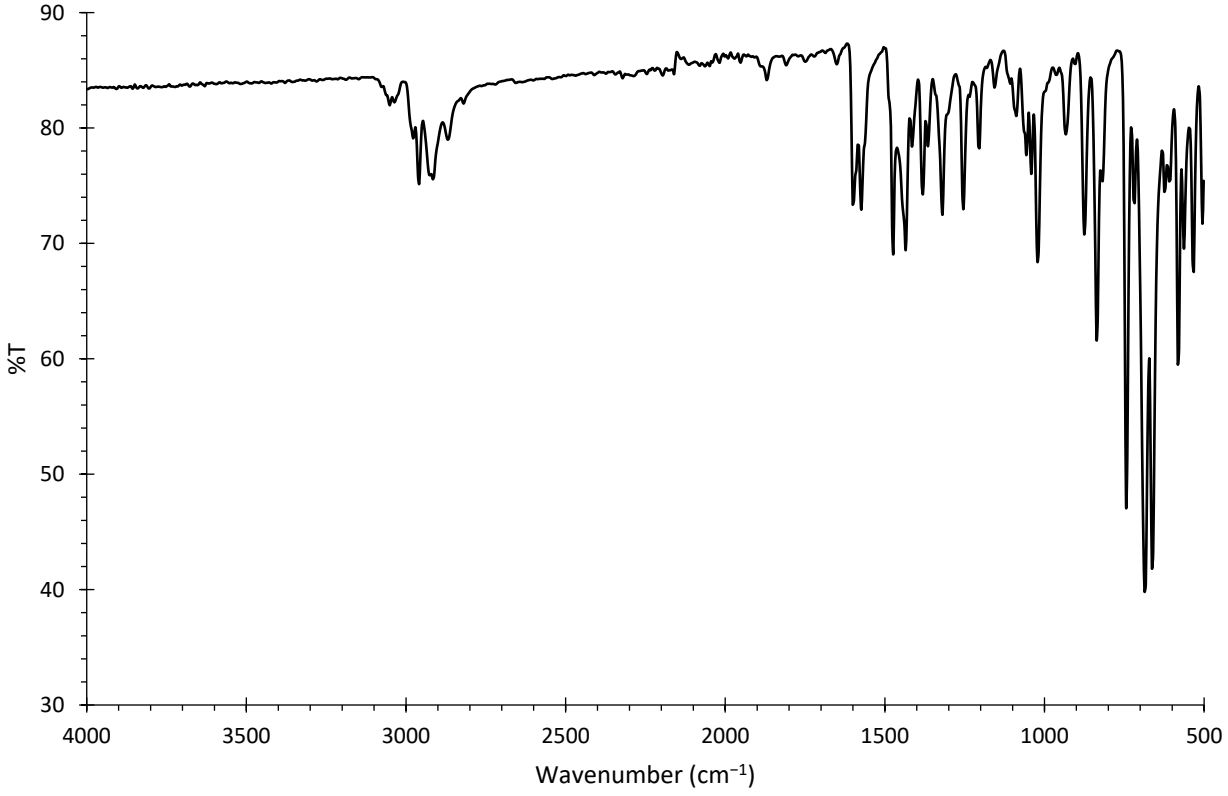

Figure S8. Infrared Spectrum of 1-S.

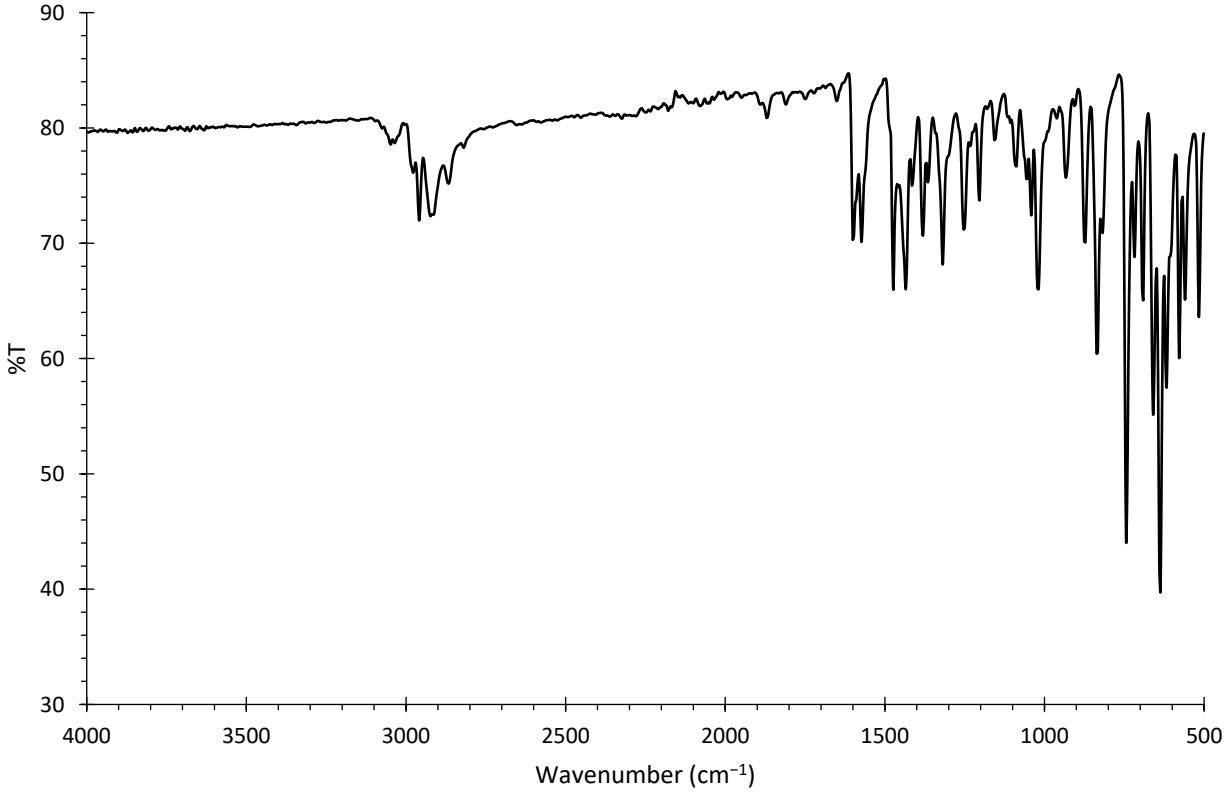

Figure S9. Infrared Spectrum of **1-Se**.

X-ray Diffraction

Table S1 lists details of data collections and refinements.

Table S1. Crystal and Structure Refinement Data.

	1-O	1-O2	1-S	1-Se
Formula	$C_{24}H_{27}OPSe$	$C_{24}H_{27}O_2PSe$	$C_{24}H_{27}SPSe$	$C_{24}H_{27}PSe_2$
M_r	441.41	457.41	457.47	504.37
Colour/Habit	Colourless prism	Colourless prism	Colourless prism	Colourless prism
Crystal Dimensions [mm]	0.200×0.200×0.200	0.290×0.120×0.100	0.120×0.090×0.030	0.210×0.110×0.060
Crystal System	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space Group	$P2_1/n$ (#14)	$P2_1/n$ (#14)	$P2_1/n$ (#14)	$P2_1/n$ (#14)
***a* [Å]**	8.886(2)	8.2723(3)	9.20428(9)	9.2477(6)
***b* [Å]**	11.950(2)	16.1425(6)	12.20590(11)	12.1871(8)
***c* [Å]**	19.754(4)	32.4731(10)	19.15860(18)	19.0466(13)
α [°]	90	90	90	90
β [°]	96.223(6)	93.484(3)	97.3870(9)	97.689(5)
γ [°]	90	90	90	90
V [Å^3]	2085.3(7)	4329.0(3)	2134.54(4)	2127.3(2)
Z	4	8	4	4
$\rho_{calcd.}$ [g cm^{-1}]	1.406	1.404	1.423	1.575
μ [cm^{-1}]	18.888	18.257	40.317	35.587
$2\theta_{max}$	50.8	63.7	136.6	50.8
F_{000}	912.00	1888.00	944.00	1016.00
Measured refln.	24111	53402	21590	18325
Unique refln.	3760	14265	3873	3900
R [I>2σ(I)]	0.0713	0.0833	0.0233	0.0248
wR	0.2117	0.1917	0.0728	0.0563
Goodness of Fit	1.252	0.967	1.021	1.006
Largest peak/hole [e Å^{-3}]	2.42/−0.79	3.82/−0.98	0.27/−0.40	0.40/−0.29

Computational Details

Cartesian coordinates in Å, B3LYP/6-31+G(d,p) optimised (xyz format)

Compound 1-Se(A)

Se 6.7046103247 2.0185304845 10.6286318189
Se 7.8904596585 1.6533181066 7.5307122048
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Compound 1-Se(C)

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Compound 1-Se(D)

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