

Supplementary Information

(Experimental details, Tables S1-S3 and Figs. S1-S10)

Oxo-sulfido- and oxo-selenido-molybdenum(VI) complexes possessing dithiolene ligand related to the active sites of hydroxylases of molybdoenzymes: Low temperature preparation and characterisation

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Experimental Section

General. All reagents and solvents were used as received unless otherwise noted. All reactions were carried out under argon in a Schlenk tube or a Miwa DB0-1KP glovebox. $(\text{Et}_4\text{N})[\text{MoO}(\text{OSi}^t\text{BuPh}_2)(\text{S}_2\text{C}_2(\text{COOMe})_2)_2]$ (**2**) was prepared according to the literature.¹ Et_4NSH was synthesised according to the literature² but Et_4NBr and NaSH were used instead of Et_4NOH and H_2S .

Synthesis of tetraethylammonium hydroselenide (Et_4NSeH). Elemental selenium (919 mg, 11.6 mmol) was added to an EtOH solution (30 mL) of Et_4NCl (1.99 g, 12.0 mmol) and NaBH_4 (569 mg, 15.0 mmol). The mixture was stirring at 0 °C in an ice bath. After the color of the resultant mixture changed from brown to almost colorless, the solvent was removed under reduced pressure to provide a pale-green solid. An acetonitrile (20 mL) was added to the green solid to dissolve any impurity. The remaining green powder was collected by filtration and recrystallised from MeCN/ Et_2O , causing pale green block like crystals. Yield; 1.26 g (52 %). ^1H NMR (CD_3CN): δ -6.63 (s, 1H), 1.19 (t, 12H), 3.18 (q, 8H). The spectrum is given in Fig. S10. This compound was highly hygroscopic, and thus, data of the elemental analysis were calculated as three hydrated sample. Anal. Calcd for $\text{C}_8\text{H}_{21}\text{NSe}\cdot 3\text{H}_2\text{O}$: C, 36.36; H, 10.30; N, 5.30. Found: C, 36.65; H, 10.28; N, 5.27.

Synthesis of complexes.

$(\text{Et}_4\text{N})_2[\text{Mo}^{\text{VI}}\text{O}_2(\text{S}_2\text{C}_2(\text{COOMe})_2)_2]$ (**1⁰**). A methanolic solution containing 10% Et_4NOH (30.0 mg, 0.020 mmol) was added to a THF solution (8 mL) of **2** (18.7 mg, 0.021 mmol). After stirring for 5 minutes, a brown microcrystalline powder precipitated from the solution. The resulting powder was collected by filtration, washed with THF and Et_2O , and dried in vacuo. Yield; 13.1 mg (78 %). The ^1H NMR, IR, ESI-mass and UV-visible spectra were identical with those of the authentic sample reported in the literature.³

$(\text{Et}_4\text{N})_2[\text{Mo}^{\text{VI}}\text{O}(\text{S})(\text{S}_2\text{C}_2(\text{COOMe})_2)_2]$ (**1^S**). An acetonitrile solution (0.5 mL) of Et_4NSH (3.2 mg, 0.020 mmol) was added to a THF solution (8 mL) of **2** (18.7 mg, 0.021 mmol). After stirring for 5 minutes, a brown microcrystalline powder

precipitated from the solution. The resulting powder was collected by filtration, washed with THF and Et₂O, and dried in vacuo. Yield; 10.2 mg (60 %). Anal. Calcd for C₂₈H₅₂MoN₂O₉S₅: C, 41.16; H, 6.42; N, 3.43. Found: C, 41.47; H, 6.50; N, 3.69.

(Et₄N)₂[Mo^{VI}O(Se)(S₂C₂(COOMe)₂)] (1^{Se}). An acetonitrile solution (0.5 mL) of Et₄NSeH (3.7 mg, 0.018 mmol) was added to a THF solution (5 mL) of **2** (17.8 mg, 0.020 mmol), providing a dark brown powder. The resulting dark brown powder was collected by filtration, washed with THF and Et₂O, and dried in vacuo. Yield; 4.3 mg (28 %). Anal. Calcd for C₂₈H₅₂MoN₂O₉S₄Se: C, 38.93; H, 6.07; N, 3.24. Found: C, 38.88; H, 6.03; N, 3.28.

Quantification of SPPH₃ after the reaction of 1^S with Triphenylphosphine. An acetonitrile solution (0.1 mL) of triphenylphosphine (14.4 mg, 0.055 mmol) was added to the solution (2 mL) of **1^S** prepared by the reaction of **2** (21.1 mg, 0.023 mmol) and Et₄NSH (5.9 mg, 0.036 mmol) at -40 °C. After stirring for 5 h at -25 °C, volume of the solution was reduced to 0.5 mL in vacuo. Addition of Et₂O of 150 mL to the reduced solution gave a brown powder. The resultant suspension was filtered. The solvent was removed by evaporation to yield triphenylphosphine sulfide in 96 % yield based on **1^S**. ¹H NMR (CDCl₃) δ 7.60-7.80 (m, 6H). EI-MS (CHCl₃): 294.

Quantification of SePPh₃ after the reaction of 1^{Se} with Triphenylphosphine. A propionitrile solution (0.1 mL) of triphenylphosphine (14.9 mg, 0.057 mmol) was added to the propionitrile solution (2 mL) of **1^{Se}** prepared from **2** (25.9 mg, 0.028 mmol) and Et₄NSeH (8.0 mg, 0.038 mmol) at -80 °C. After stirring for 10 h at -80 °C, volume of the solution was reduced to 0.5 mL by evaporator. A brown powder precipitated by adding Et₂O of 150 mL to the reduced solution. The powder was removed by filtration and the resulting filtrate was removed in vacuo to yield triphenylphosphine selenide in 82 % yield based on **1^{Se}**. ¹H NMR (CDCl₃) δ 7.66-7.79 (m, 6H). EI-MS (CHCl₃): 342.

DFT calculation. The molecular geometries of **1^E** (E = O, S, Se), PPh₃, and products of the atom transfer reaction from **1^E** to PPh₃ were fully optimized at the B3LYP level

of theory. The correlation consistent basis set of double- ζ quality augmented with diffuse s and p functions (aug-cc-pVDZ) was adopted for O, S, P, and Se atoms, and the standard cc-pVDZ basis set for C and H atoms. The Stuttgart/Dresden MWB28 effective core potential (ECP) basis set was employed for molybdenum. All DFT calculations were performed using the Gaussian 03 program. The optimized Cartesian coordinates are listed in Tables S1-S3. Bond dissociation energies were calculated as differences in the sum of electronic energy.

Physical measurements. UV-vis spectra were recorded on a Hewlett Packard 8453 photo diode array spectrophotometer equipped with a UNISOK thermo-Statel cell holder. ESI-MS (electrospray ionization mass spectra) measurements were performed on a PE SCIEX API 150EX. NMR spectra were recorded on a JEOL ECP400, a JEOL ECS400 or a Varian UNITY INOVA 600MHz. Resonance Raman scattering was excited at 363.8 nm with a Ar⁺ ion laser (Spectra Physics, BeamLok 2080). Resonance Raman scattering was dispersed by a 75-cm single spectrometer (SPEX750M; Jovin Yvon) and was detected by a liquid nitrogen cooled CCD detector (Spec10:400B/LN; Roper Scientific). The resonance Raman measurements were carried out using a spinning NMR tube at -80 °C by flashing cooled dinitrogen gas. The sample solutions for UV-vis and rR measurements were prepared by adding a solvent solution of Et₄NSH or Et₄NSeH to a cooled solvent solution of **2** at low temperature through a septum cap by using a gas-tight syringe.

Low temperature ESI-mass measurement of 1^S. 1^S was generated *in-situ* in CH₃CN at -40 °C by the reaction of **2** and Et₄NSH in a Schlenk tube under a dry dinitrogen atmosphere. The temperature of the CH₃CN solution was kept with a dry ice-CH₃CN bath. One end of a capillary was connected to the ESI-mass detector and another end was dipped into the complex solution of -40 °C through a septum cap. The CH₃CN solution was sprayed to the detector by pressure with a dinitrogen Bombe instead of pressure using a syringe pump.

Low temperature ^1H NMR measurement of $\mathbf{1}^{\text{S}}$. A ^1H NMR tube containing a CD_3CN solution of $\mathbf{2}$ was cooled and kept at $-40\text{ }^\circ\text{C}$ with a dry ice- CH_3CN bath. To the CD_3CN solution, a CD_3CN solution of Et_4NSH was added through a septum cap by using a gas-tight syringe ($[\mathbf{2}] : [\text{SH}^-] = 1 : 1$). A dummy ^1H NMR tube was injected into a NMR probe and the temperature of the probe was set at $-80\text{ }^\circ\text{C}$. The dummy tube was ejected (by the ejection, the probe temperature was increased once), and the cooled sample ^1H NMR tube was injected quickly and the probe temperature was set at $-40\text{ }^\circ\text{C}$, and, then, a measurement was started. ^1H and ^{77}Se NMR measurements of $\mathbf{1}^{\text{Se}}$ were unsuccessful owing to decomposition of $\mathbf{1}^{\text{Se}}$ to $[\text{Mo}^{\text{IV}}\text{OL}_2]^{2-}$ ($\mathbf{3}$) by an internal redox because the solution temperature was increased over $-80\text{ }^\circ\text{C}$ during the sample tube exchange, sample tube injection and cooling procedures.

References

1. H. Sugimoto, S. Tatemoto, K. Suyama, H. Miyake, R. P. Mtei, S. Itoh and M. L. Kirk, *Inorg. Chem.* 2010, **49**, 5368.
2. G. Heller and W. Eysenbach, *Inorg. Chem.*, 1979, **18**, 380.
3. H. Sugimoto, S. Tatemoto, K. Suyama, H. Miyake, S. Itoh, C. Dong, J. Yang and M. L. Kirk, *Inorg. Chem.* 2009, **48**, 10581.

Table S1. Cartesian coordinates of $\mathbf{1}^{\mathbf{O}}$. SCF energy = -2878.20151483 a.u.

O	-0.235038	0.058485	-0.022475
O	-0.108863	0.006090	2.232776
C	0.474089	0.041020	0.984832
C	-1.530061	-0.023655	2.229617
H	-1.953216	0.870934	1.744579
H	-1.827556	-0.054362	3.287738
H	-1.915264	-0.911896	1.703445
Mo	5.189305	0.353956	2.369524
S	7.495151	0.033657	1.517694
S	5.372380	-2.375303	2.212150
S	2.744847	0.025846	2.618990
S	4.371285	0.109016	-0.233959
O	5.477029	2.034792	2.062744
O	5.227889	0.201354	4.095025
O	9.790479	-3.203218	1.182520
O	10.127154	-0.982292	0.939819
O	7.188322	-4.902857	0.860494
O	7.863776	-4.554865	2.988219
O	1.795066	-0.920224	-2.187219
O	1.672652	1.318923	-1.911905
C	7.947054	-1.692889	1.532378
C	7.019471	-2.675940	1.816074
C	9.320720	-2.064785	1.215997
C	11.472908	-1.305051	0.615046
C	7.376482	-4.137555	1.783575
C	1.931110	0.058489	1.030872
C	2.653280	0.078904	-0.146141
C	1.979355	0.057155	-1.491567
C	0.996398	1.377321	-3.166729
H	11.975826	-1.828268	1.444468
H	11.969091	-0.343205	0.420825
H	11.530938	-1.946826	-0.278797
H	1.620745	0.967177	-3.976163
H	0.794493	2.442704	-3.347538
H	0.053194	0.811539	-3.125371
C	8.259659	-5.925003	3.024664
H	8.652709	-6.095162	4.037110
H	7.404970	-6.592734	2.832692
H	9.039732	-6.123129	2.273874

Table S2. Cartesian coordinates of **1^S**. SCF energy = -3201.18596278 a.u.

O	-0.178870	-0.033344	-0.012989
O	-0.046425	-0.101414	2.241850
C	0.531350	-0.026959	0.993364
C	-1.464807	-0.199441	2.240193
H	-1.930990	0.678614	1.764626
H	-1.758519	-0.254948	3.298284
H	-1.807414	-1.099904	1.705537
Mo	5.231999	0.425657	2.377441
S	7.536799	0.085314	1.539123
S	5.346109	-2.240558	2.190695
S	2.804035	0.066419	2.614822
S	4.417790	0.197266	-0.229837
S	5.628218	2.575337	2.037650
O	5.264802	0.255882	4.091126
O	9.737984	-3.219690	1.172121
O	10.142094	-1.008265	0.951822
O	7.066338	-4.837012	0.837979
O	7.760268	-4.522067	2.964930
O	1.885466	-0.904957	-2.192640
O	1.670142	1.324417	-1.894485
C	7.941042	-1.656799	1.534728
C	6.984940	-2.610148	1.802957
C	9.305195	-2.067572	1.215976
C	11.479714	-1.365286	0.627540
C	7.284654	-4.083596	1.763905
C	1.986031	0.060281	1.035854
C	2.707778	0.110677	-0.144722
C	2.030954	0.073178	-1.489094
C	0.988639	1.368989	-3.147332
H	11.965676	-1.908004	1.454459
H	12.001973	-0.415881	0.441758
H	11.521831	-2.001829	-0.270821
H	1.626807	0.992607	-3.962301
H	0.744267	2.427315	-3.316011
H	0.068825	0.765689	-3.109724
C	8.114037	-5.904412	2.994286
H	8.498234	-6.092223	4.006864
H	7.240135	-6.544425	2.795146
H	8.890460	-6.120764	2.244799

Table S3. Cartesian coordinates of **1^{Se}**. SCF energy = -5204.53962535 a.u.

O	-0.173653	-0.046037	-0.023474
O	-0.031648	-0.051285	2.231850
C	0.540186	-0.012475	0.979514
C	-1.450571	-0.143572	2.239891
H	-1.915293	0.723213	1.742785
H	-1.739024	-0.168732	3.300534
H	-1.799485	-1.056951	1.731940
Mo	5.247705	0.463614	2.325475
S	7.547058	0.094999	1.485382
S	5.343986	-2.182632	2.223011
S	2.820943	0.136935	2.583167
S	4.420557	0.173538	-0.266698
Se	5.697350	2.744322	1.898160
O	5.286924	0.367152	4.042197
O	9.713927	-3.241682	1.188539
O	10.142230	-1.040751	0.918693
O	7.014971	-4.848929	0.960836
O	7.757551	-4.457687	3.058530
O	1.876315	-0.995907	-2.179210
O	1.673894	1.243925	-1.961704
C	7.938151	-1.650435	1.531310
C	6.977479	-2.585277	1.838008
C	9.295935	-2.083829	1.211193
C	11.472309	-1.420550	0.588155
C	7.260772	-4.062145	1.851372
C	1.995556	0.075519	1.012408
C	2.712495	0.089057	-0.173355
C	2.029697	0.006757	-1.512893
C	0.987959	1.247216	-3.213154
H	11.959290	-1.953603	1.420655
H	12.004170	-0.481479	0.379118
H	11.496766	-2.074574	-0.298128
H	1.619758	0.834454	-4.015291
H	0.752345	2.300520	-3.420769
H	0.063115	0.653905	-3.149083
C	8.099738	-5.841276	3.135358
H	8.504983	-5.992186	4.145861
H	7.215933	-6.480135	2.981505
H	8.857186	-6.094852	2.378191

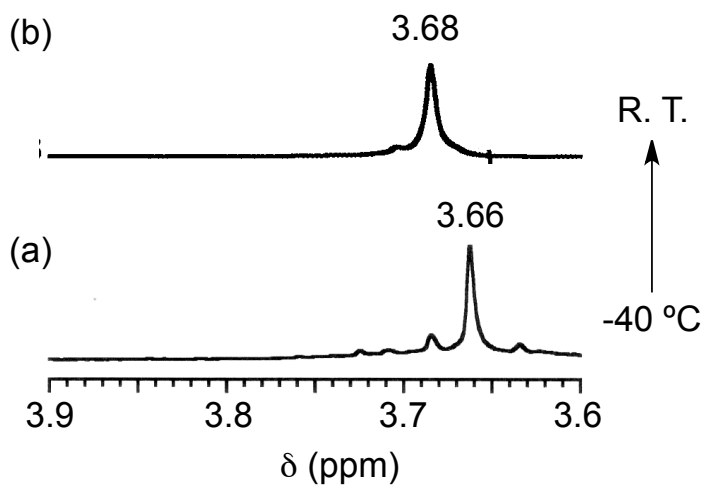


Fig. S1 a) ¹H NMR spectrum reflecting a generation of oxo-sulfido-molybdenum(VI) complex $[\text{Mo}^{\text{VI}}\text{O}(\text{S})\text{L}_2]^{2-}$ ($\mathbf{1}^{\text{S}}$) in CD_3CN at $-40\text{ }^\circ\text{C}$ from $(\text{Et}_4\text{N})[\text{Mo}^{\text{VI}}\text{O}(\text{OSiBuPh}_2)\text{L}_2]$ and Et_4NSH . b) formation of oxo-molybdenum(IV) complex $[\text{Mo}^{\text{IV}}\text{OL}_2]^{2-}$ by decomposition of $\mathbf{1}^{\text{S}}$ at room temperature.

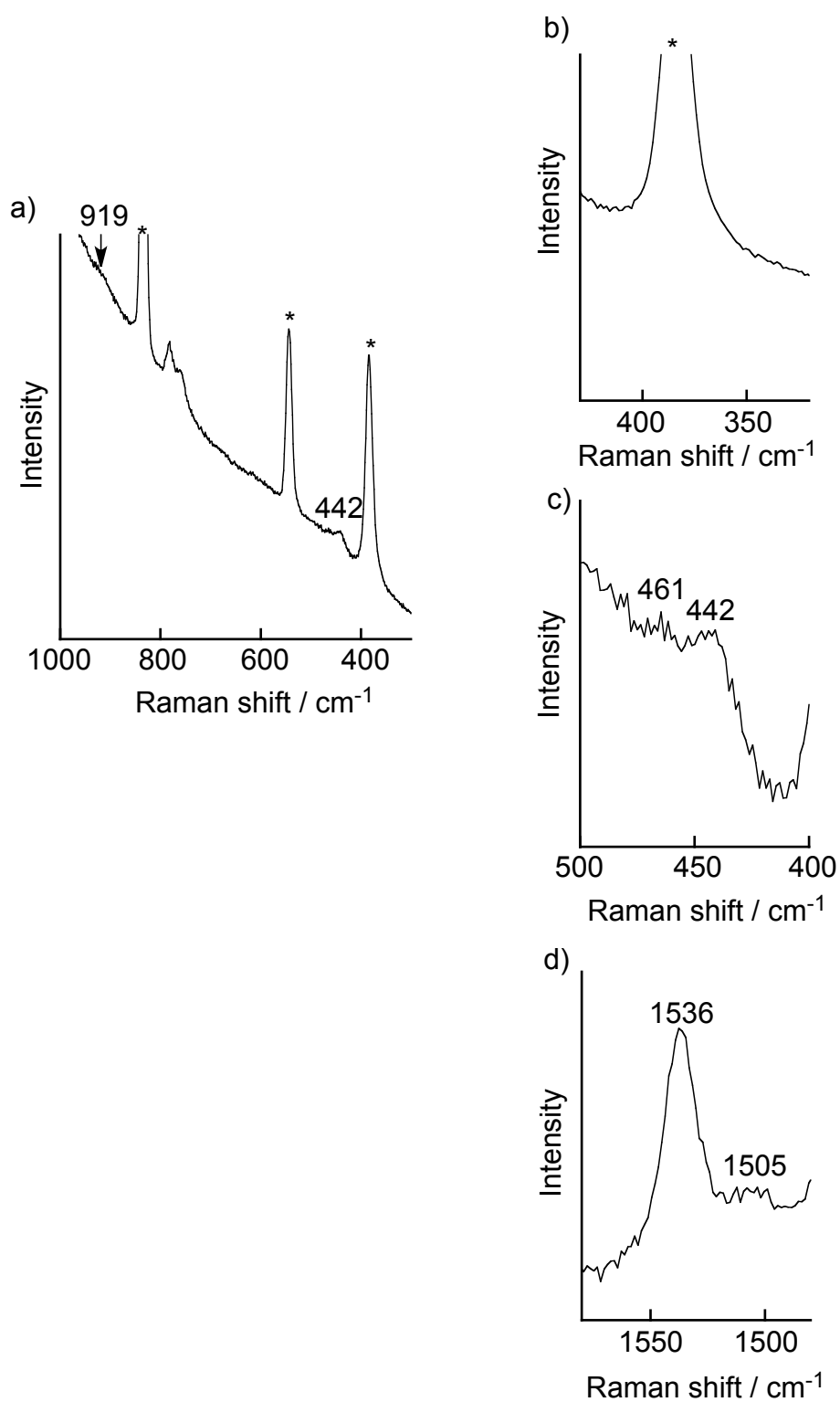


Fig. S2 Resonance Raman spectra (363.8 nm excitation) of 1^{S} generated in the reaction of **2** (0.38 mM) and Et_4NSH (0.40 mM) in $\text{C}_2\text{H}_5\text{CN}$ at $-80\text{ }^\circ\text{C}$: a) 300–1000, b) 430–320, c) 400–500 and d) 1530–1530 cm^{-1} regions. Asterisks indicate solvent peaks.

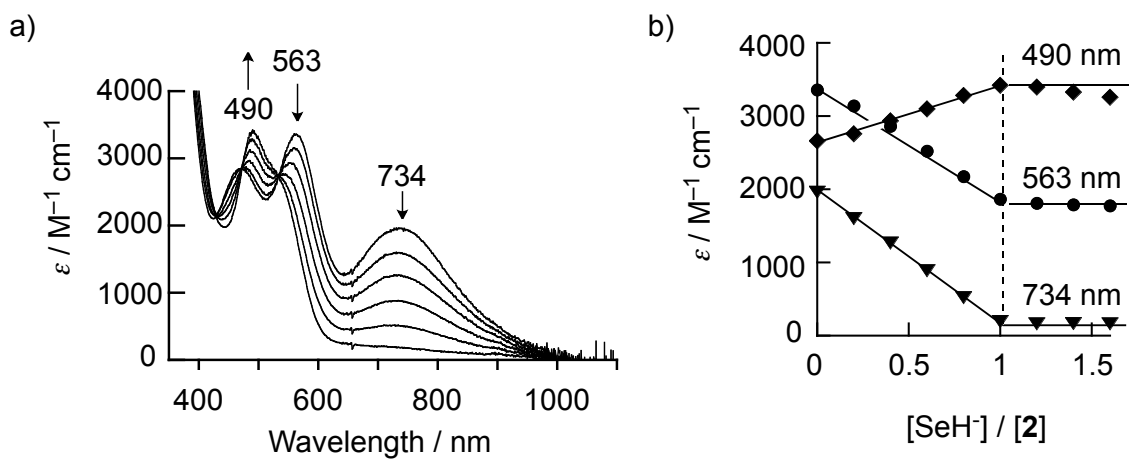


Fig. S3 a) Absorption spectral changes showing the formation of 1^{Se} in the reaction of **2** (0.30 mM) and Et_4NSeH in $\text{C}_2\text{H}_5\text{CN}$ at -80°C . b) plot of $\text{Abs}_{490, 563, 734\text{nm}}$ against the equivalent of Et_4NSeH against **2**.

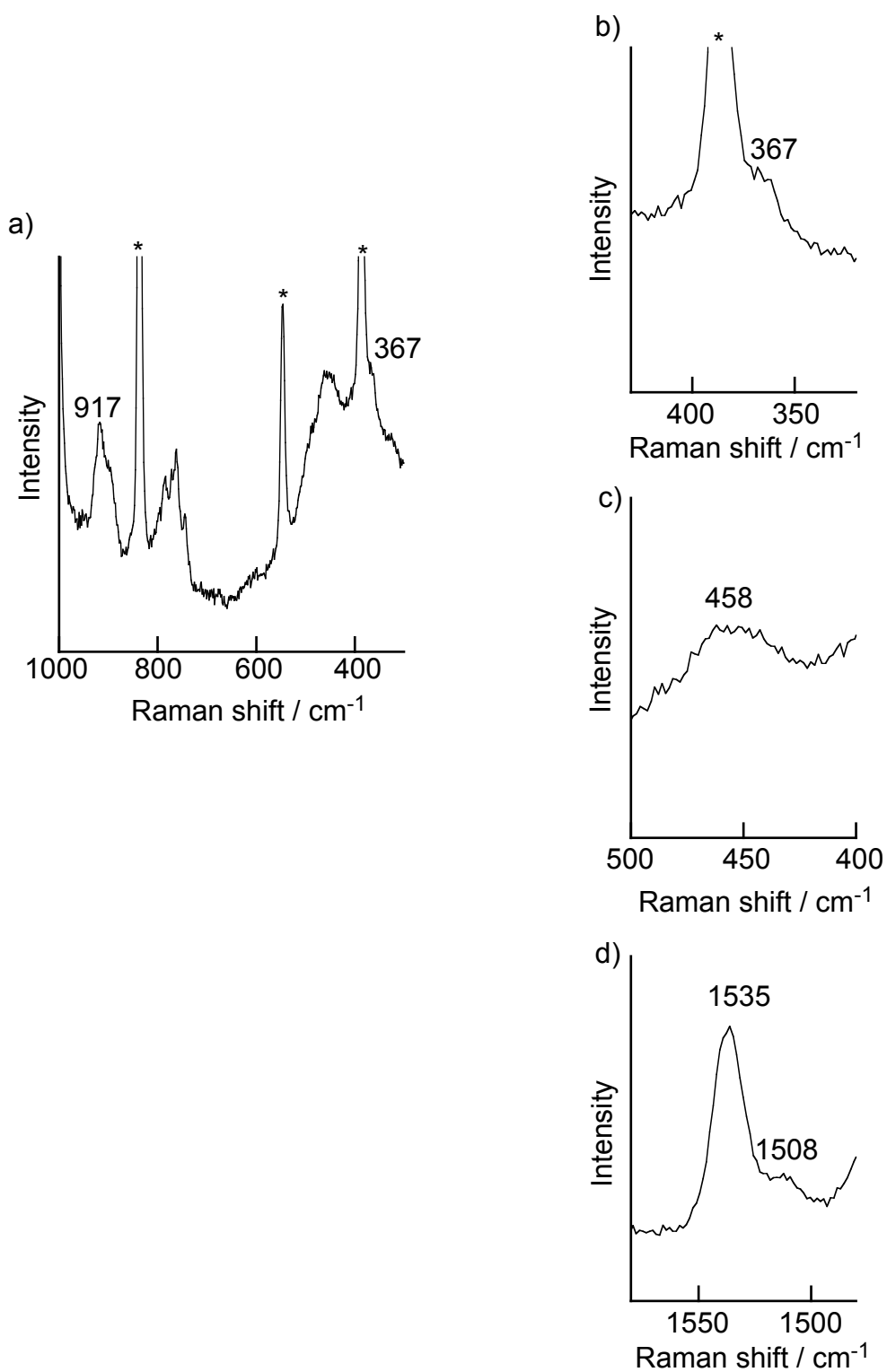


Fig. S4 Resonance Raman spectra (363.8 nm excitation) of 1^{Se} generated in the reaction of **2** (0.38 mM) and Et_4NSeH (0.40 mM) in C_2H_5CN at $-80\text{ }^\circ C$: a) 300–1000, b) 430–320, c) 400–500 and d) 1530–1530 cm^{-1} regions. Asterisks indicate solvent peaks.

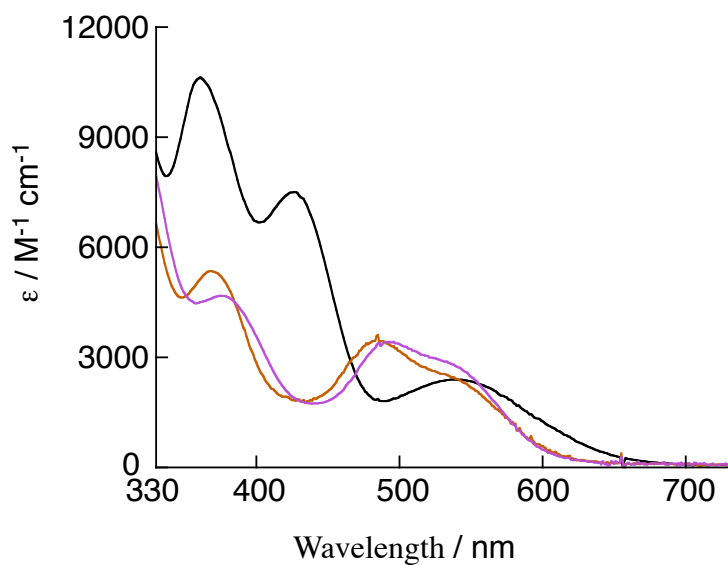


Fig. S5 Overlaid absorption spectra of 1^{O} (black), 1^{S} (brown) and 1^{Se} (magenta).

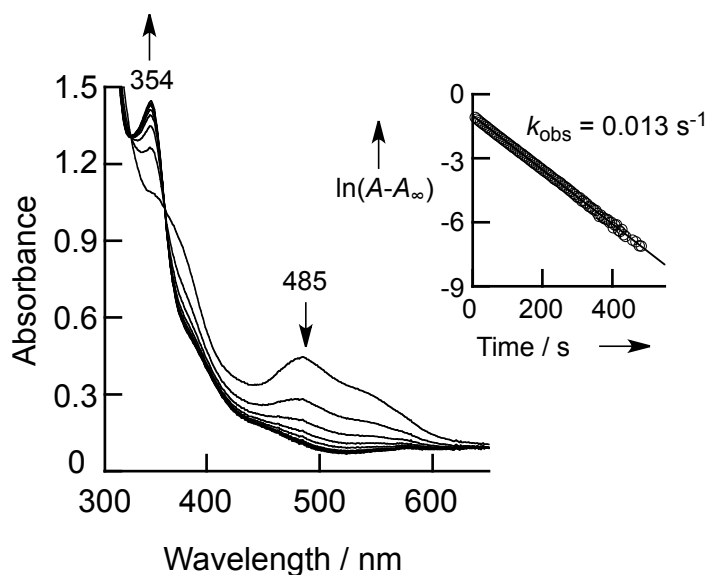


Fig. S6 Time dependent UV-vis spectral changes observed upon addition of Ph_3P (140 equiv.) to 1^{S} (0.10 mM) in CH_3CN at -20°C . Inset shows the first-order plot based on the decay of absorbation at 485 nm.

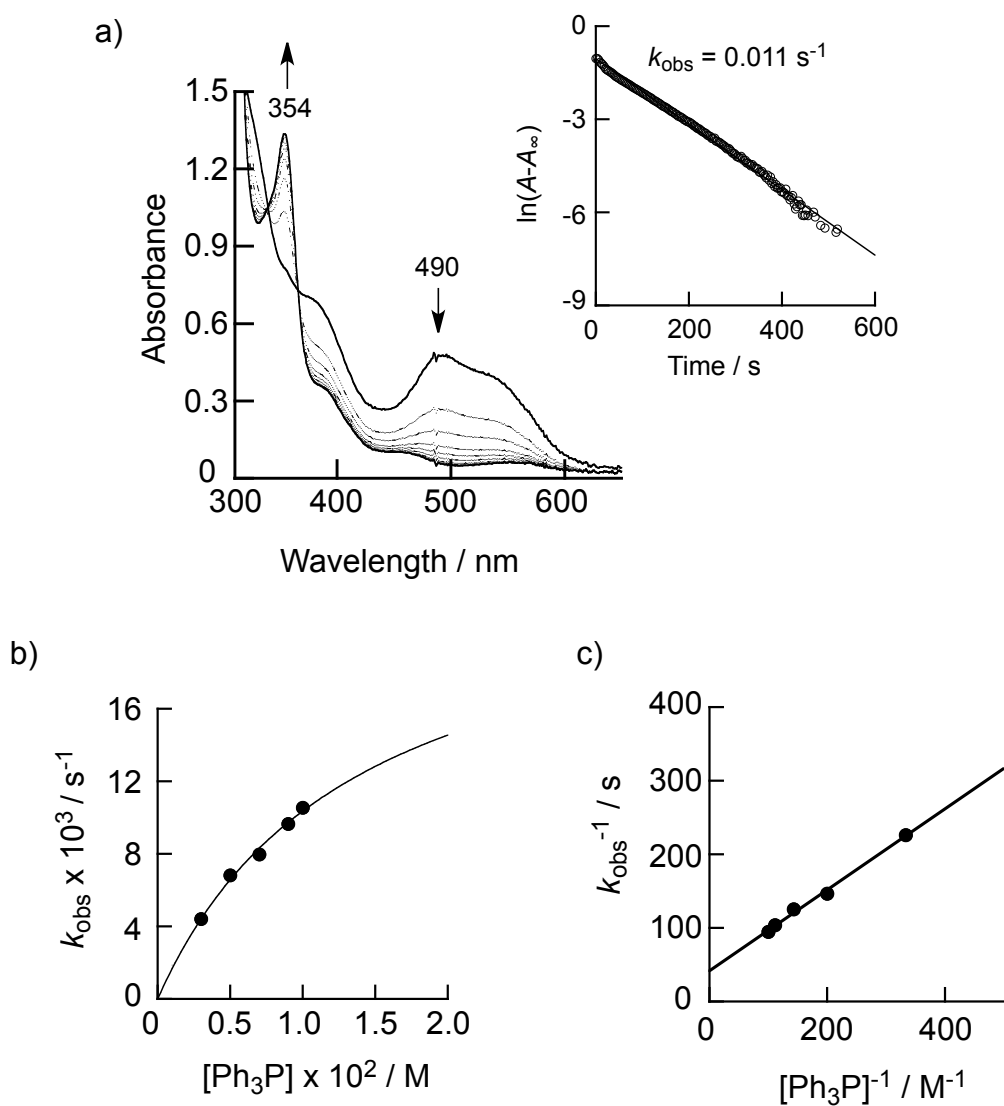


Fig. S7 a) UV-vis spectral changes observed upon addition of Ph_3P (100 equiv.) to 1^{Se} (0.10 mM) in C_2H_5CN at $-80^\circ C$ with 3 s. interval. Inset shows the first-order plot based on the decay of absorption at 490 nm. b) The plot of k_{obs} vs. $[Ph_3P]$. c) The double reciprocal plot of k_{obs}^{-1} against $[Ph_3P]^{-1}$.

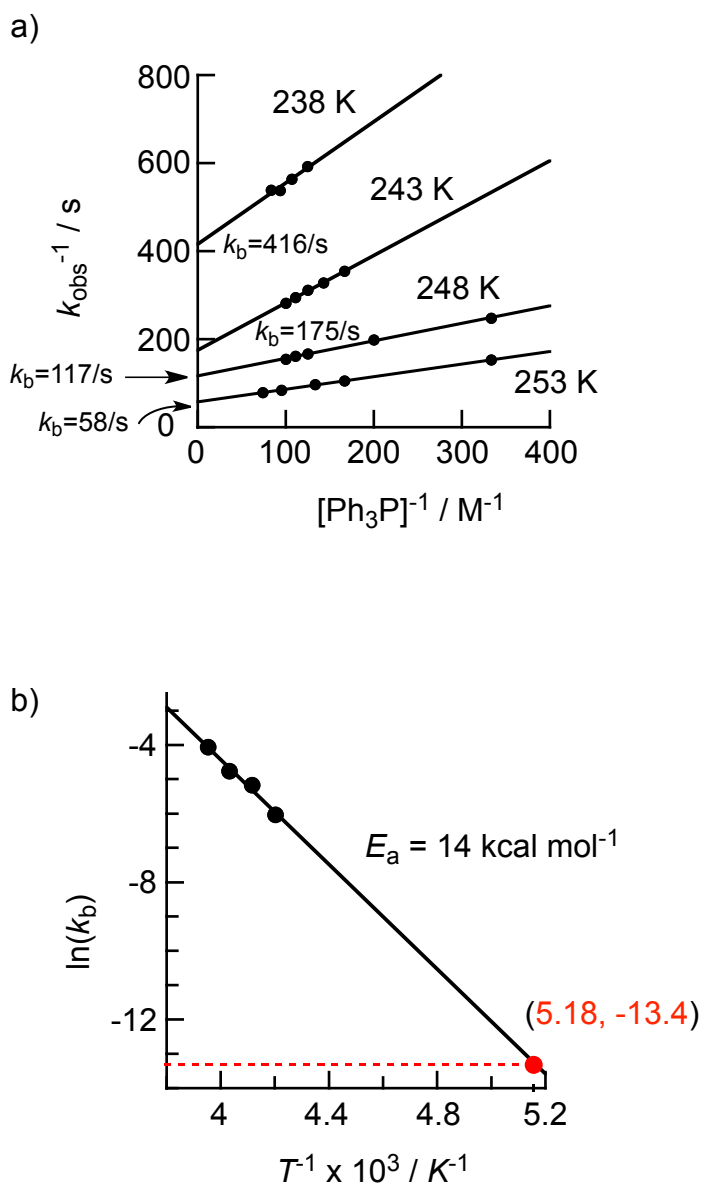


Fig. S8 a) The double reciprocal plots of k_{obs}^{-1} against $[\text{Ph}_3\text{P}]^{-1}$ at -20 (253), -25 (248), -30 (243), and -35 °C (238 K). b) The Arrhenius plot for the sulfur atom transfer of $\mathbf{1}^{\text{S}}$ to Ph_3P .

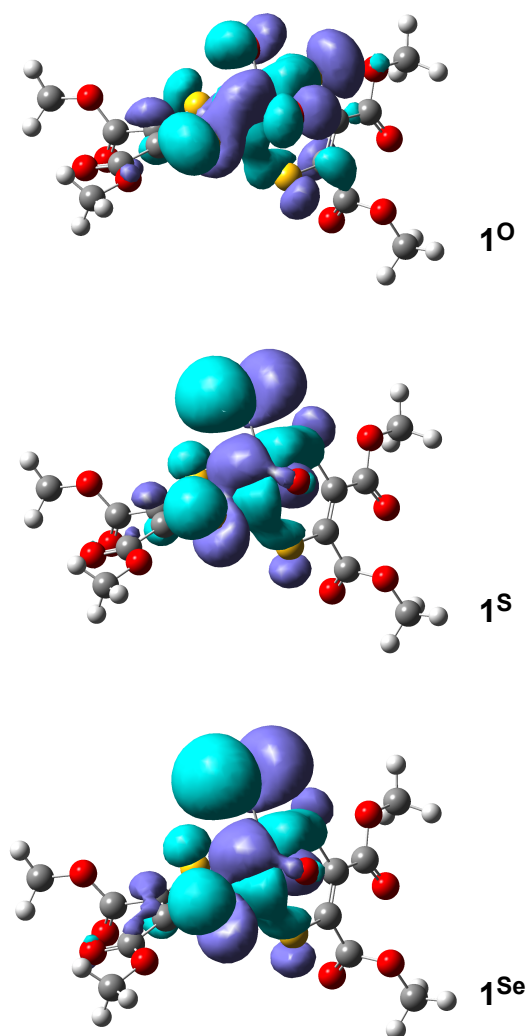


Fig. S9 LUMO Kohn-Sham orbitals for 1^O (top), 1^S (middle) and 1^{Se} (bottom).

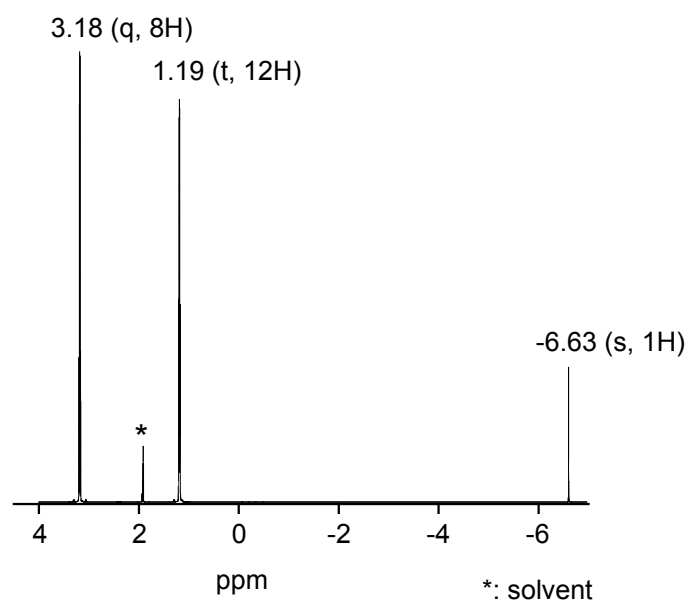


Fig. S10 ^1H NMR spectrum of Et_4NSeH in CD_3CN .