Supplementary Material

Cu(II) complexes with tridentate sulfur and selenium ligands: catecholase and hydrolysis activity

by

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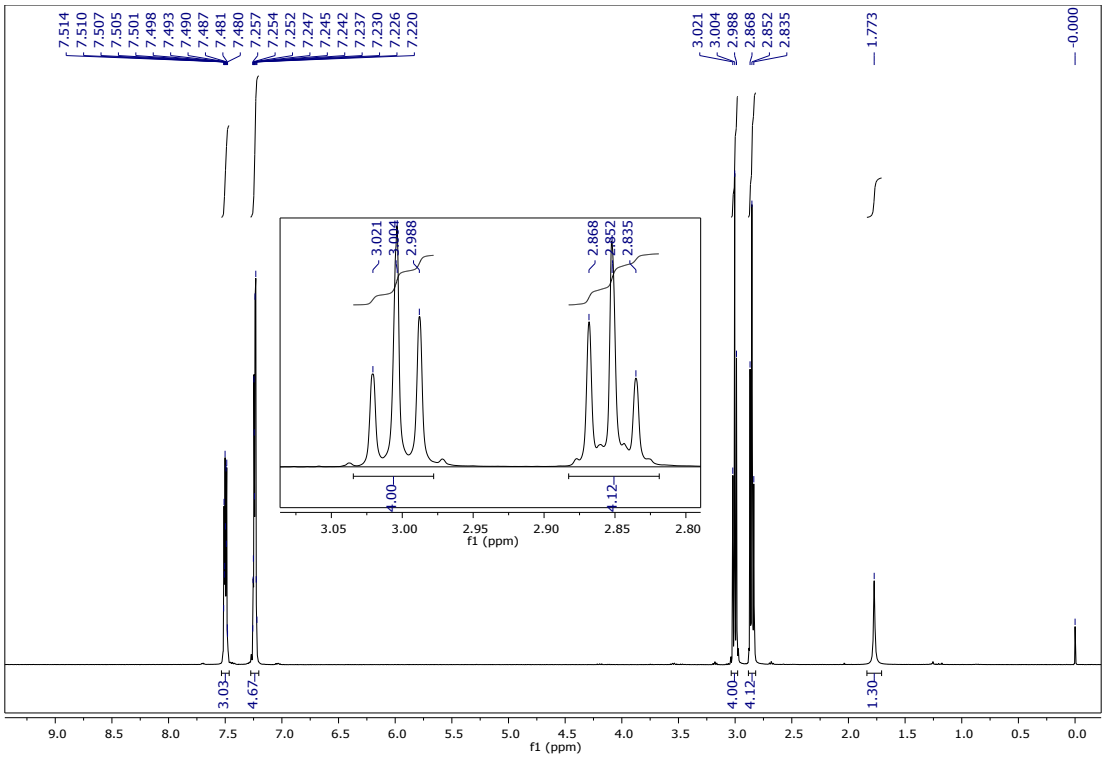


Figure S1 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of $\mathbf{L_{Se}}$.

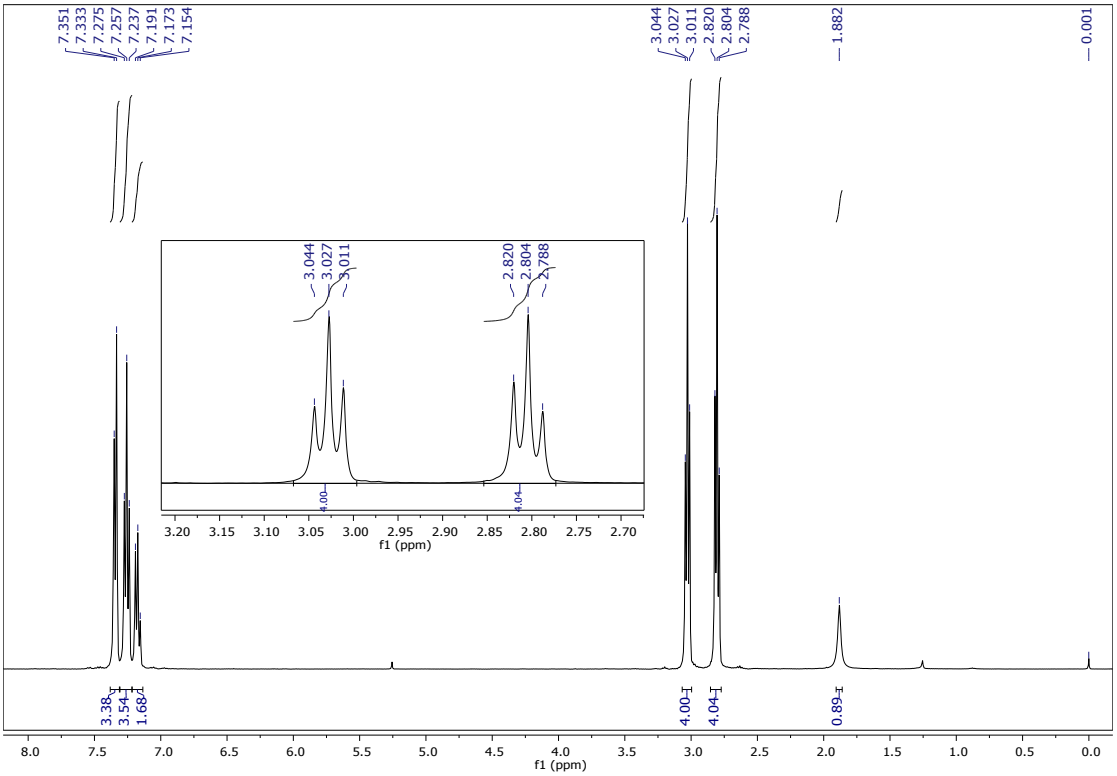


Figure S2 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of $\mathbf{L_S}$.

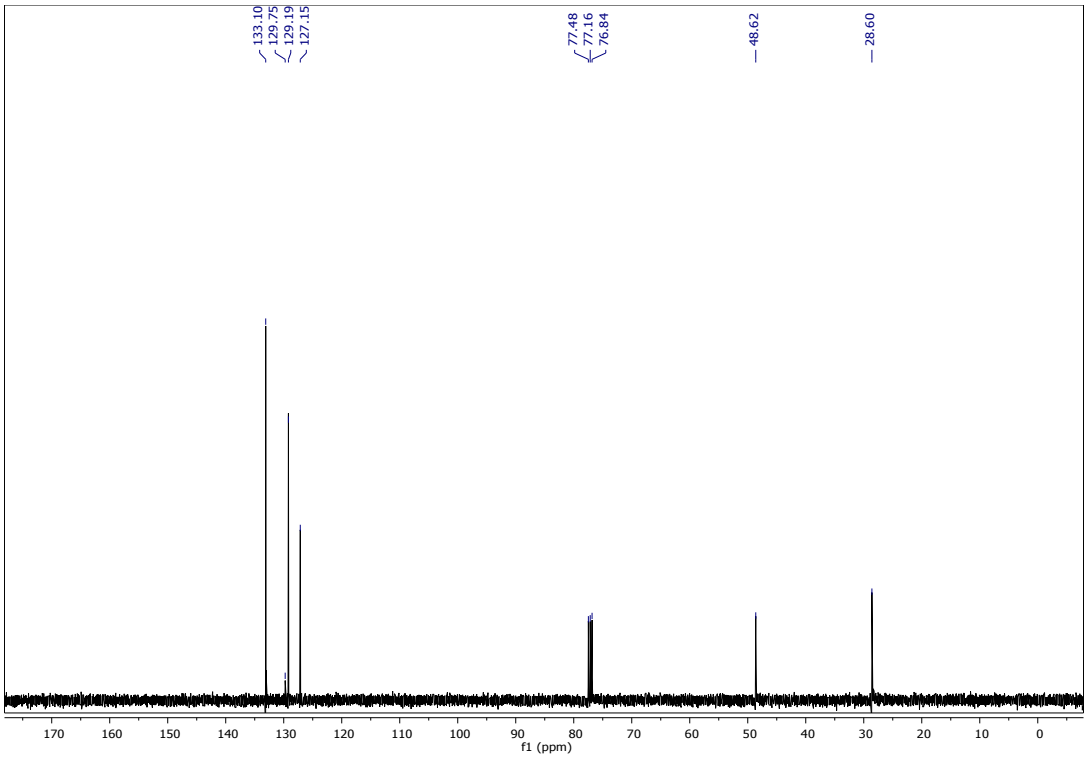


Figure S3 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of $\mathbf{L_{Se}}$.

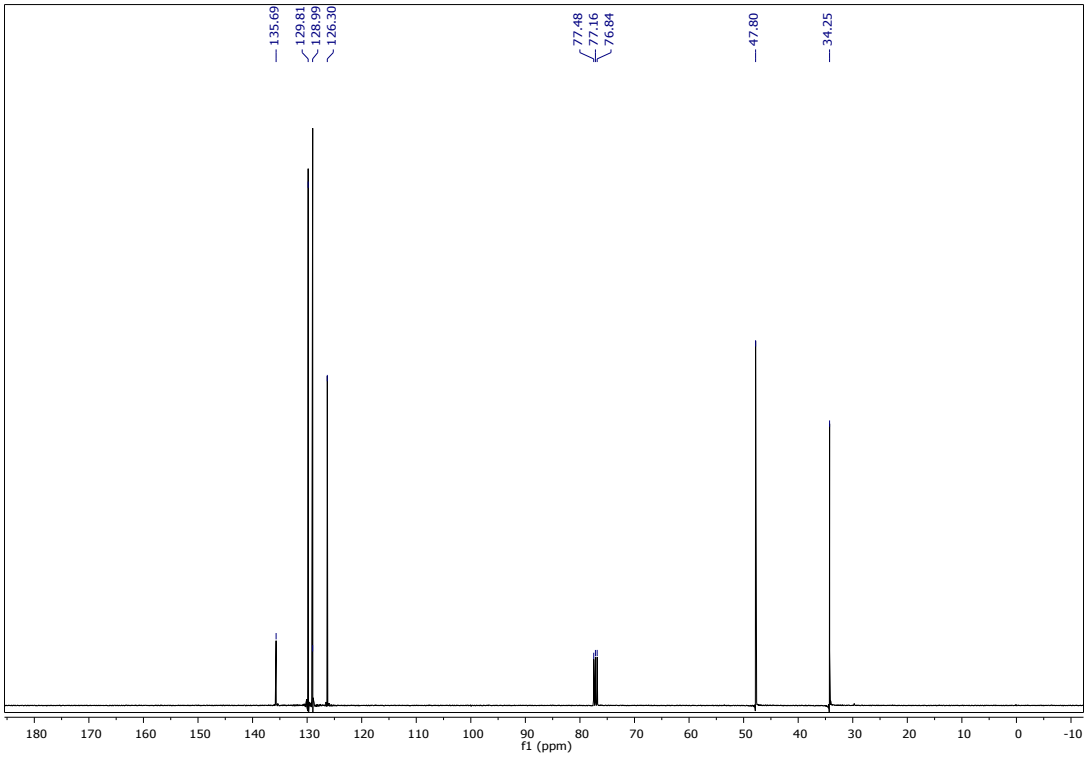


Figure S4 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of $\mathbf{L_S}$.

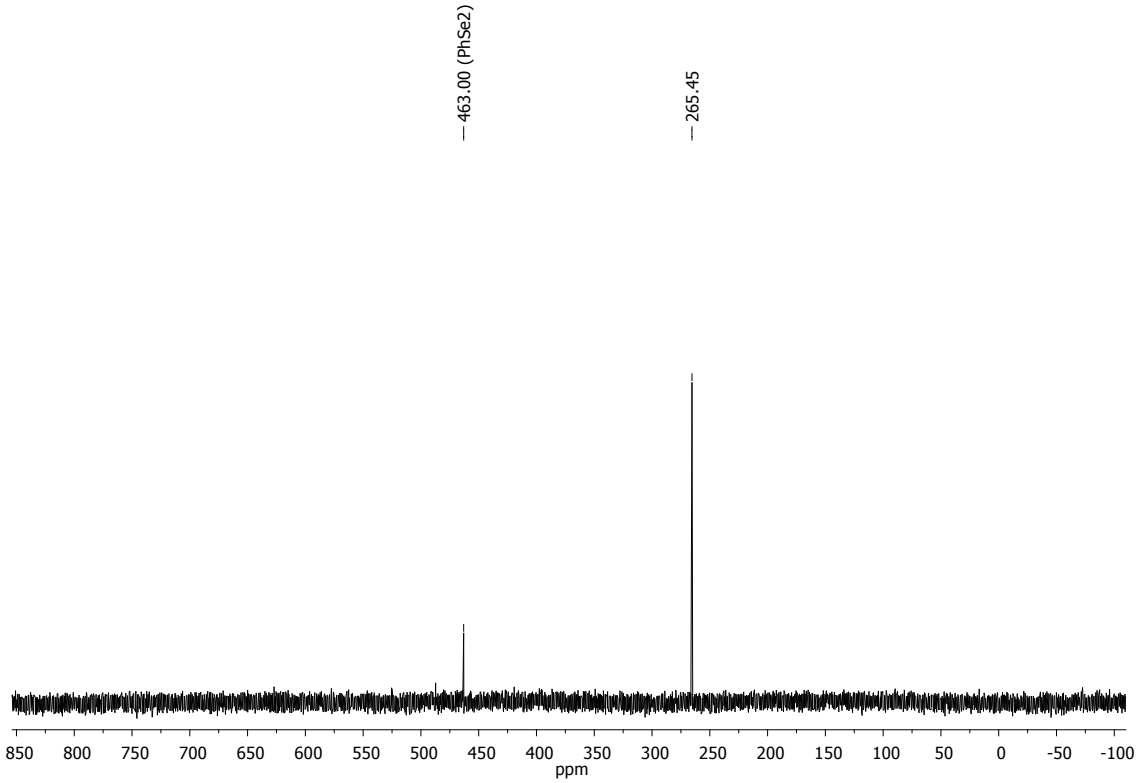


Figure S5 ^{77}Se NMR (76 MHz, $CDCl_3$) spectrum of $\mathbf{L_{Se}}$.

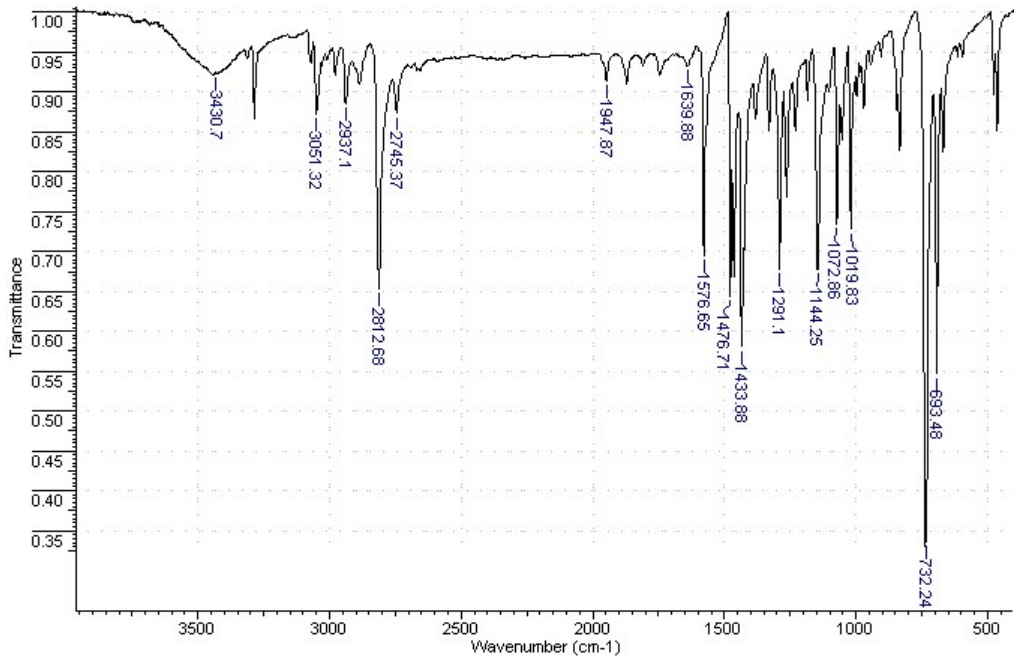


Figure S6 IR (KBr, cm^{-1}) of $\mathbf{L_{Se}}$.

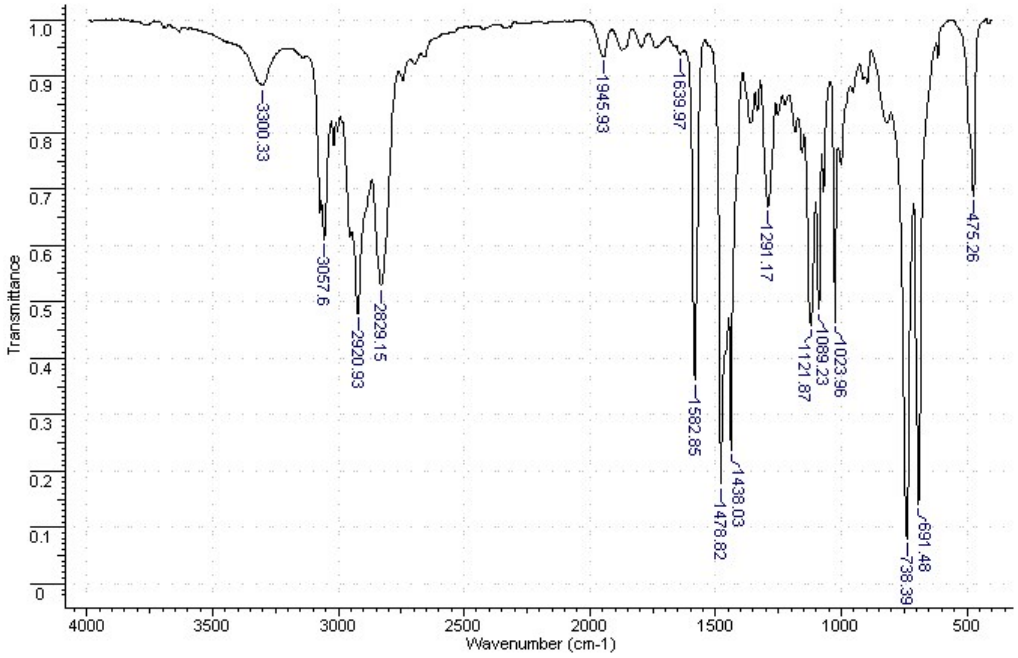


Figure S7 IR (KBr, cm^{-1}) of $\mathbf{L_S}$.

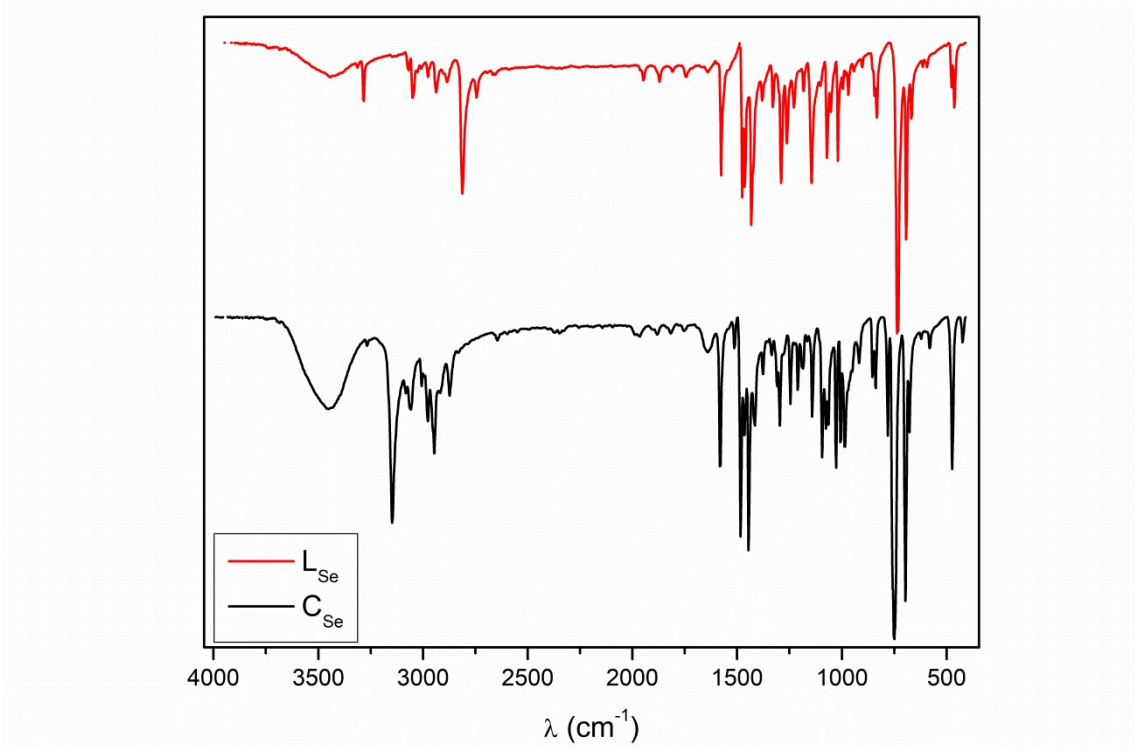


Figure S8 IR spectra overlay of the $\mathbf{L_{Se}}$ (red) and $\mathbf{C_{Se}}$ (black).

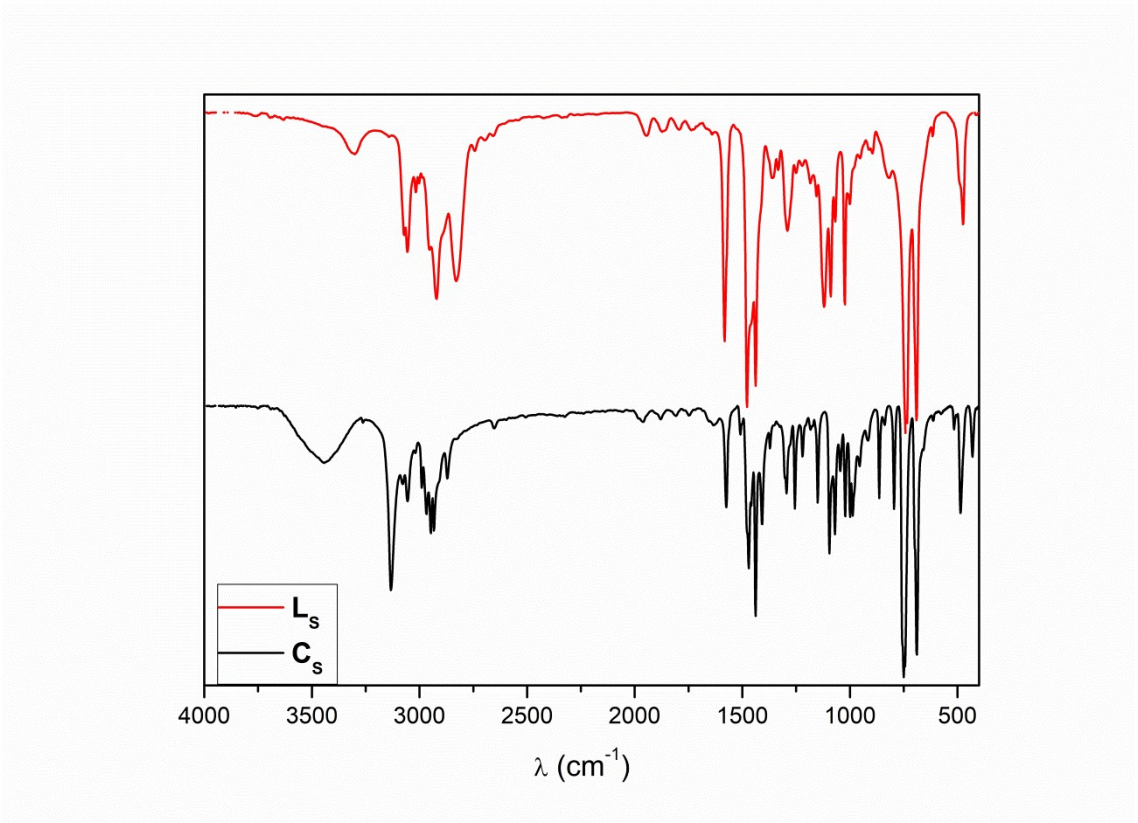


Figure S9 IR spectra overlay of the $\mathbf{L_S}$ (red) and $\mathbf{C_S}$ (black).

Crystallographic Data

Table S1 Bond lengths (Å) and angles (°) for $\mathbf{C_{Se}}$.

Cu1-N1	2.036(3)	C1-C2	1.516(3)
Cu1-Cl1	2.2411(9	C1-H1A	0.9900
Cu1-Cl2	2.4076(8)	C1-H1B	0.9900
Cu1-Se1	2.5196(3)	C2-Se1	1.968(2)
Cu1-Se1^{i}	2.5196(3)	C2-H2A	0.9900
N1-C1^{i}	1.472(3)	C2-H2B	0.9900
N1-C1	1.473(3)	Se1-C3	1.925(2)
N1-H1	0.8718	C3-C4	1.384(3)
C3-C8	1.385(3)	C7-H7	0.9500
C4-C5	1.385(3)	C8-H8	0.9500
C4-H4	0.9500	N1-Cu1-Cl1	164.62(8)
C5-C6	1.385(4)	N1-Cu1-Cl2	96.72(8)
C5-H5	0.9500	Cl1-Cu1-Cl2	98.66(3)

C6-C7	1.382(4)	N1-Cu1-Se1	82.36(3)
C6-H6	0.9500	Cl1-Cu1-Se1	92.312(13)
C7-C8	1.389(4)	Cl2-Cu1-Se1	110.164(10)
N1-Cu1-Se1^{i}	82.36(3)	Cu1-N1-H1	105.3
Cl1-Cu1-Se1^{i}	92.312(13)	N1-C1-C2	108.31(19
Cl2-Cu1-Se1^{i}	110.164(10)	N1-C1-H1A	110.0
Se1-Cu1-Se1^{i}	138.154(19)	C2-C1-H1A	110.
C1^{i}-N1-C1	114.2(2)	N1-C1-H1B	110.0
C1^{i}-N1-Cu1	111.67(14)	C2-C1-H1B	110.0
C1-N1-Cu1	111.67(14)	H1A-C1-H1B	108.4
C1^{i}-N1-H1	106.7	C1-C2-Se1	111.00(15)
C1-N1-H1	106.7	C1-C2-H2A	109.4
Se1-C2-H2A	109.4	C3-Se1-C2	99.13(10)
C1-C2-H2B	109.4	C3-Se1-Cu1	113.30(7)
Se1-C2-H2B	109.4	C2-Se1-Cu1	93.56(7)
H2A-C2-H2B	108.0	C4-C3-C8	120.2(2)
C4-C3-Se1	123.16(17)	C6-C5-H5	119.7
C8-C3-Se1	116.59(19)	C7-C6-C5	119.6(3)
C3-C4-C5	119.6(2)	C7-C6-H6	120.2
C3-C4-H4	120.2	C5-C6-H6	120.2
C5-C4-H4	120.2	C6-C7-C8	120.2(3)
C4-C5-C6	120.6(3)	C6-C7-H7	119.
C4-C5-H5	119.7	C8-C7-H7	119.9
C3-C8-C7	119.8(3)	C7-C8-H8	120.1
C3-C8-H8	120.1		

Symmetry transformations used to generate equivalent atoms: (i) X,-Y+1.5, Z.

Table S2 Bond lengths (Å) and angles (°) for $\mathbf{C_S}$

Cu1-N1	2.0141(18)	C3-C8	1.393(2)
Cu1-Cl1	2.2284(6)	C4-C5	1.391(2)
Cu1-Cl2	2.4100(6)	C4-H4	0.9500
Cu1-S1	2.4500(4)	C5-C6	1.382(3)
Cu1-S1^{i}	2.4501(4)	C5-H5	0.9500
N1-C1	1.4769(18)	C6-C7	1.382(3)

N1-C1^{i}	1.4770(18)	C6-H6	0.9500
N1-H1	0.8722	C7-C8	1.393(3)
C1-C2	1.515(2)	C7-H7	0.9500
C1-H1A	0.9900	C8-H8	0.9500
C1-H1B	0.9900	C1-C2-S1	111.60(11)
C2-S1	1.8303(17)	C1-C2-H2A	109.3
C2-H2A	0.9900	S1-C2-H2A	109.3
C2-H2B	0.9900	C1-C2-H2B	109.3
S1-C3	1.7797(17)	S1-C2-H2B	109.3
C3-C4	1.393(2)	H2A-C2-H2B	108.0
N1-Cu1-Cl1	164.92(6)	C3-S1-C2	102.00(7)
N1-Cu1-Cl2	96.60(6)	C3-S1-Cu1	115.06(5)
Cl1-Cu1-Cl2	98.48(2)	C2-S1-Cu1	96.47(5)
N1-Cu1-S1	81.774(19)	C4-C3-C8	119.96(16)
Cl1-Cu1-S1	93.720(12)	C4-C3-S1	123.06(12)
Cl2-Cu1-S1	107.228(11)	C8-C3-S1	116.95(13)
N1-Cu1-S1^{i}	81.774(19)	C5-C4-C3	119.46(16)
Cl1-Cu1-S1^{i}	93.720(12)	C5-C4-H4	120.3
Cl2-Cu1-S1^{i}	107.228(11)	C3-C4-H4	120.3
S1-Cu1-S1^{i}	143.18(2)	C6-C5-C4	120.58(17)
C1-N1-C1^{i}	114.10(17)	C6-C5-H5	119.7
C1-N1-Cu1	111.51(10)	C4-C5-H5	119.7
C1^{i} -N1-Cu1	111.51(10)	C7-C6-C5	119.99(18)
C1-N1-H1	106.9	C7-C6-H6	120.0
C1^{i} -N1-H1	106.9	C5-C6-H6	120.0
Cu1-N1-H1	105.3	C6-C7-C8	120.17(18)
N1-C1-C2	107.26(13)	C6-C7-H7	119.9
N1-C1-H1A	110.3	C8-C7-H7	119.9
C2-C1-H1A	110.3	C7-C8-C3	119.78(17)
N1-C1-H1B	110.3	C7-C8-H8	120.1
C2-C1-H1B	110.3	C3-C8-H8	120.1
H1A-C1-H1B	108.5		

Symmetry transformations used to generate equivalent atoms: (i) X, -Y+1.5, Z

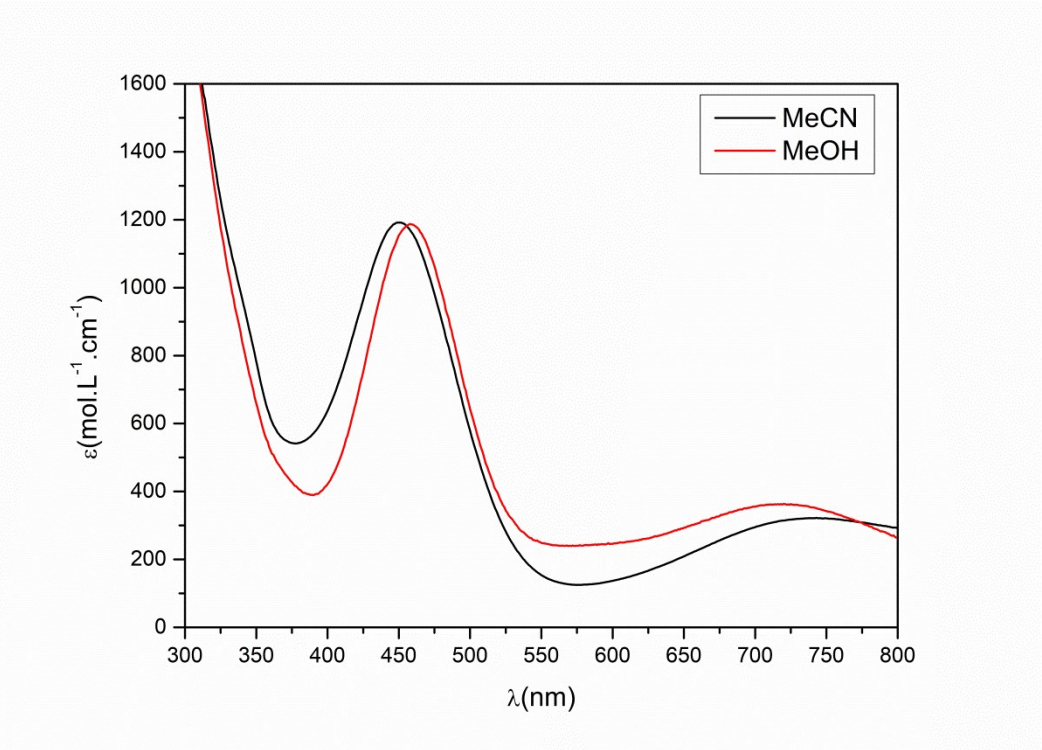


Figure S10 Electronic spectrum of C_{Se} complex in acetonitrile solution in black and in methanol solution in red.

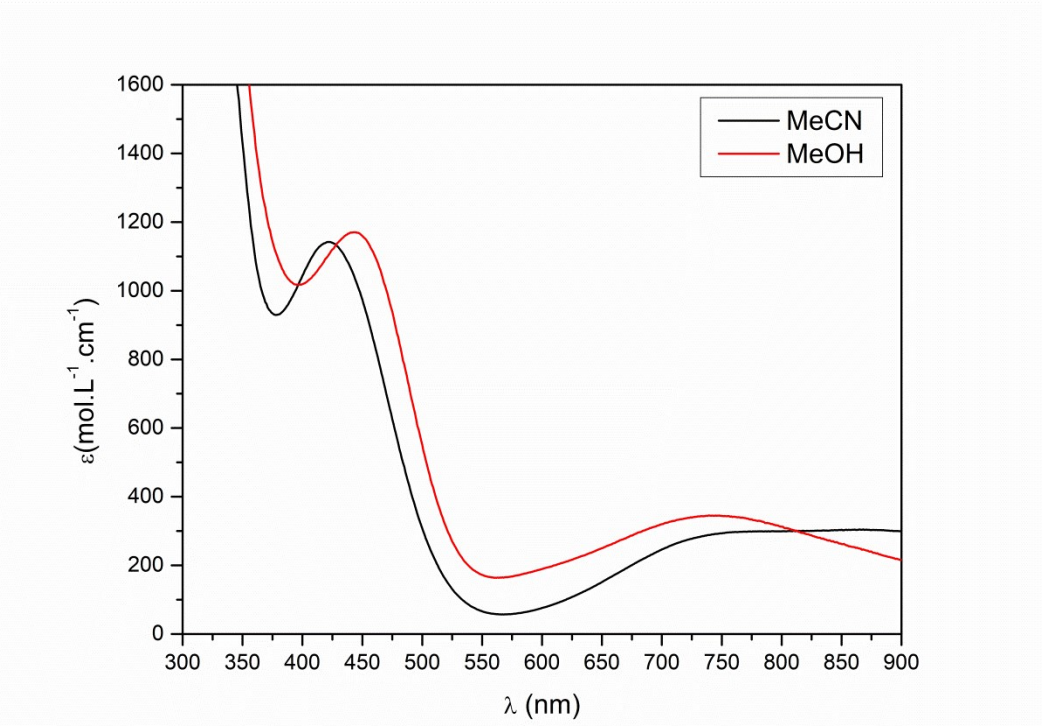


Figure S11 Electronic spectrum of C_S complex in acetonitrile solution in black and in methanol solution in red.

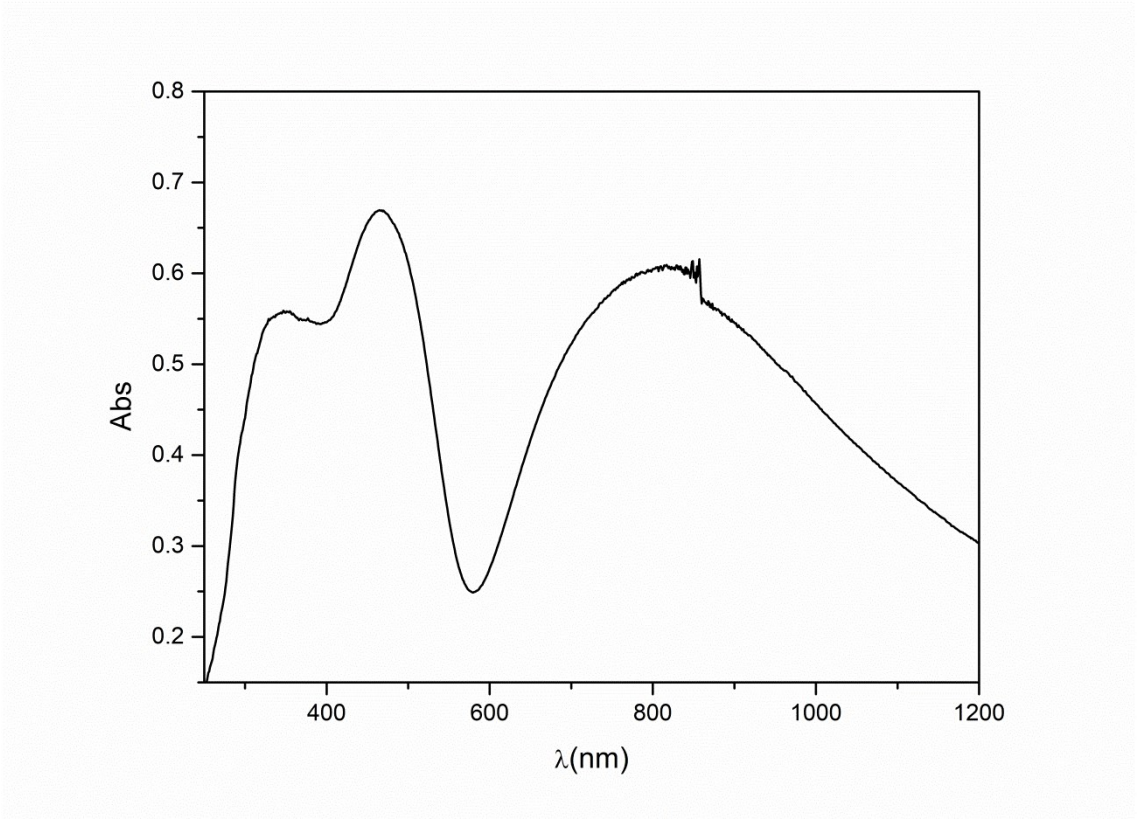


Figure S12 Electronic spectrum of $\mathbf{C_{Se}}$ in KBr pellet.

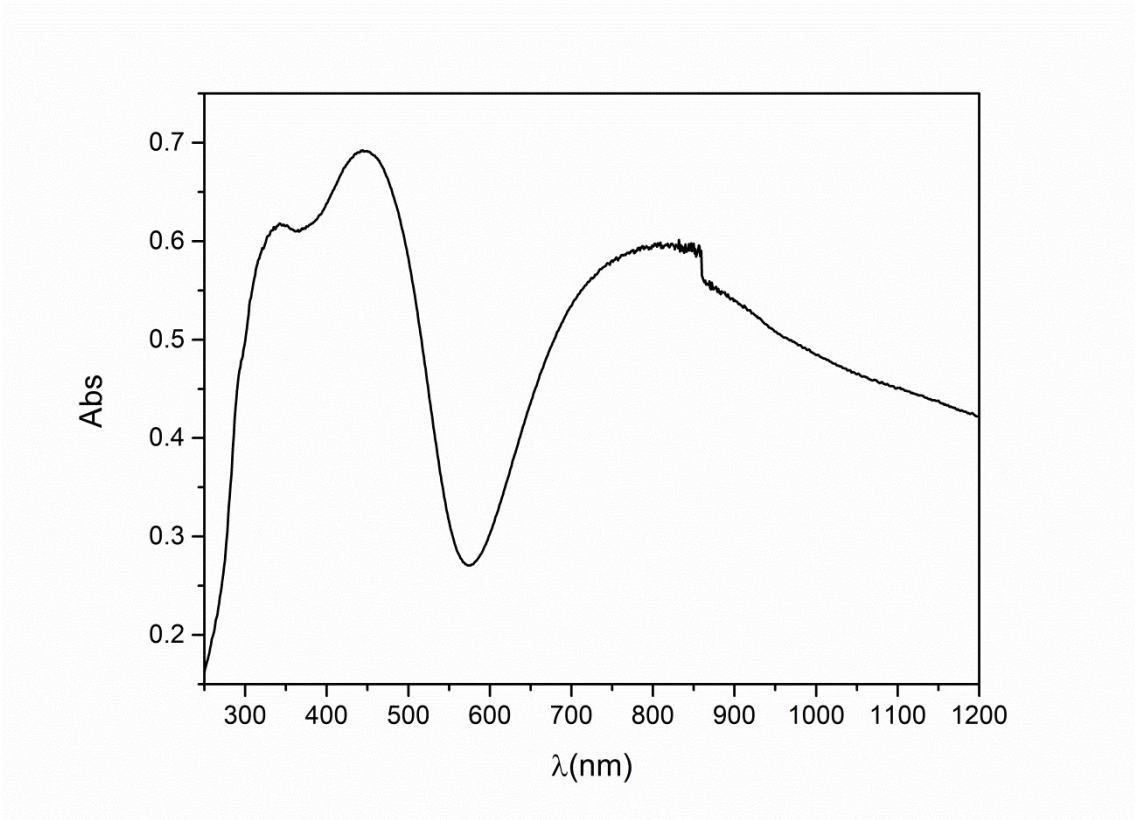
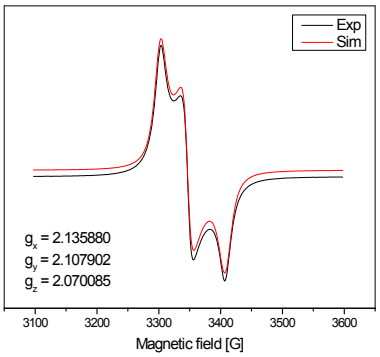
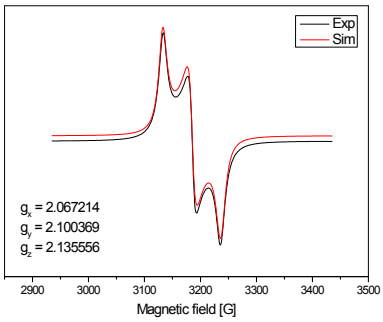


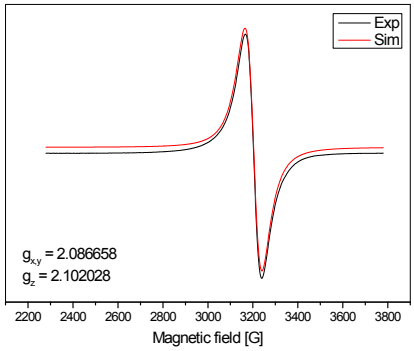
Figure S13 Electronic spectrum of $\mathbf{C_S}$ in KBr pellet.



C_{Se} Solid (r.t.)

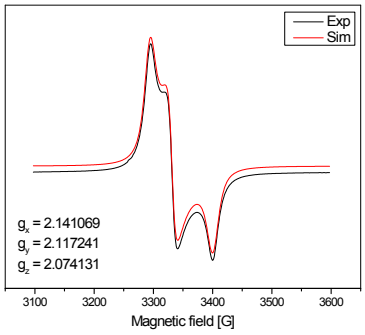


C_{Se} Solid(77 K)

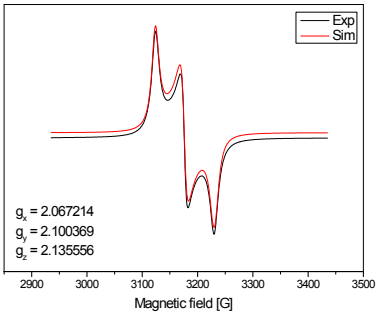


C_{Se} DCM solution 77 K

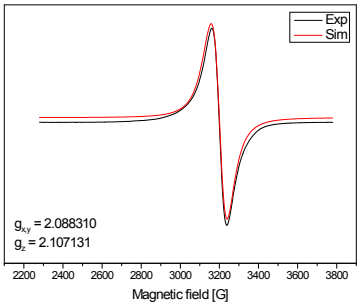
Figure S14 EPR Spectra of **C_{Se}** complex.



C_S solid (r.t.)



C_S solid (77 K)



C_S DCM solution 77 K

Figure S15 EPR Spectra of **C_S** complex.

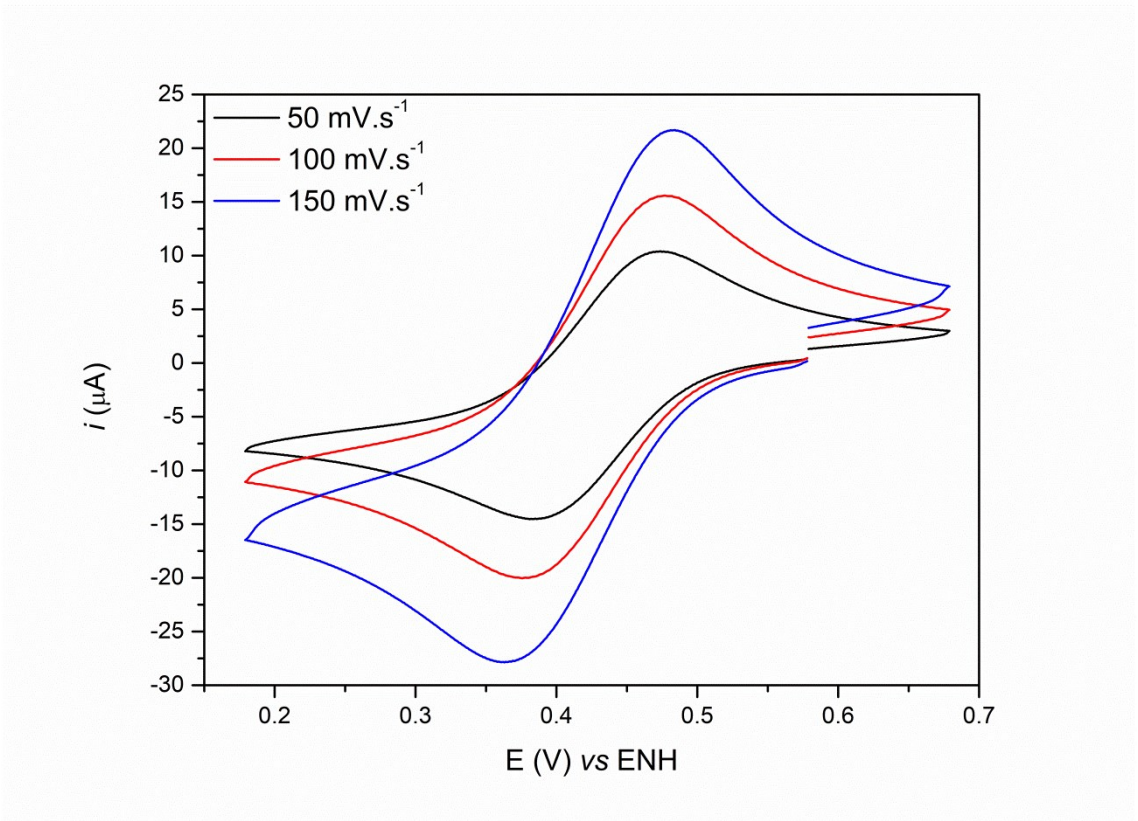


Figure S16 Cyclic voltammetry of complex $\mathbf{C_{Se}}$ in methanol. Conditions: working electrode (carbon); reference electrode (Ag/Ag^{+}); auxiliary electrode (Pt); supporting electrolyte $TBAPF_6$ 0.1 mol L^{-1}.

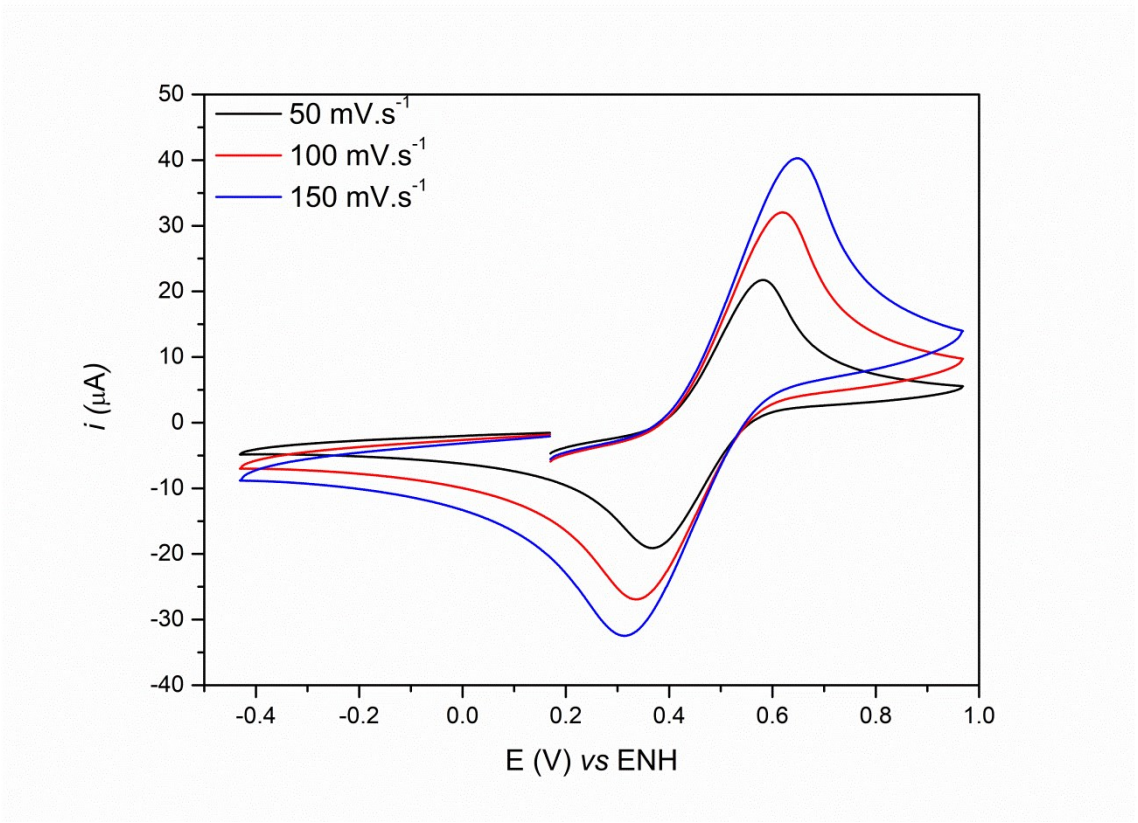
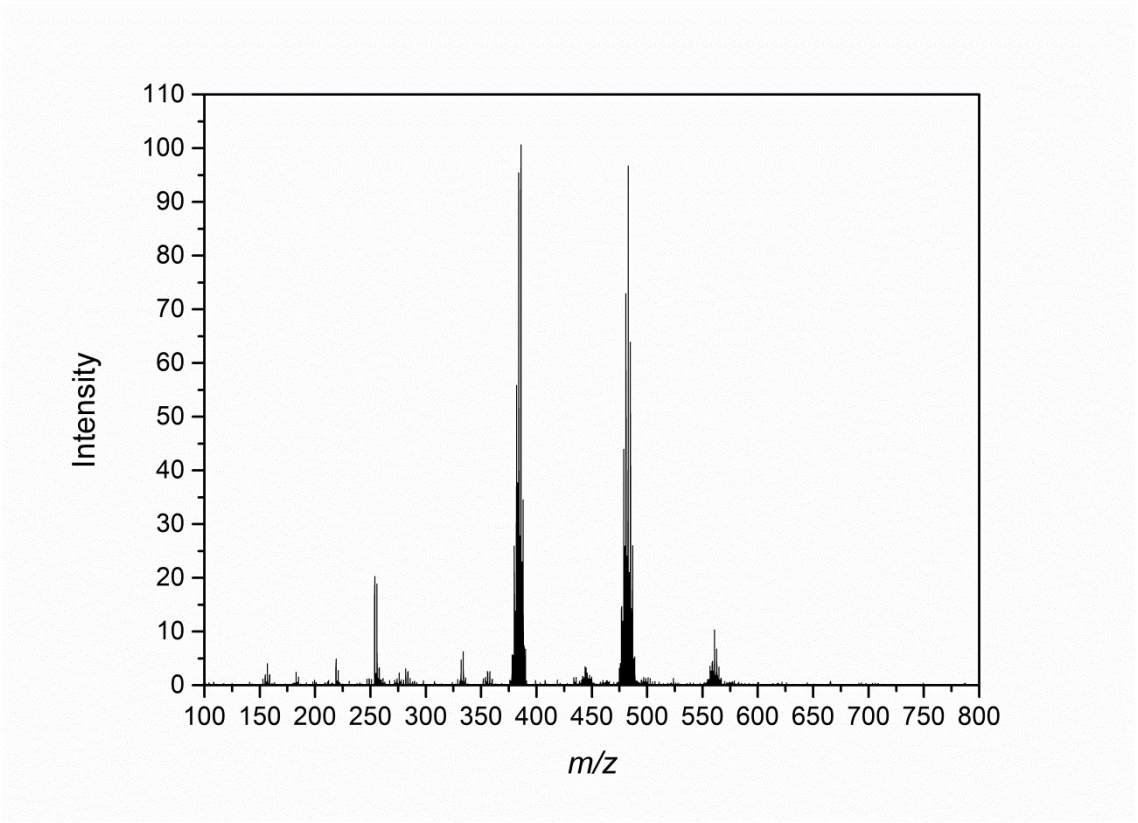


Figure S17 Cyclic voltammetry of complex $\mathbf{C_S}$ in methanol. Conditions: working electrode (carbon); reference electrode (Ag/Ag^+); auxiliary electrode (Pt); supporting electrolyte $TBAPF_6$ 0.1 mol L^{-1}.



F**igure S18** ESI-MS spectrum (positive mode) in methanol of $\mathbf{C_{Se}}$.

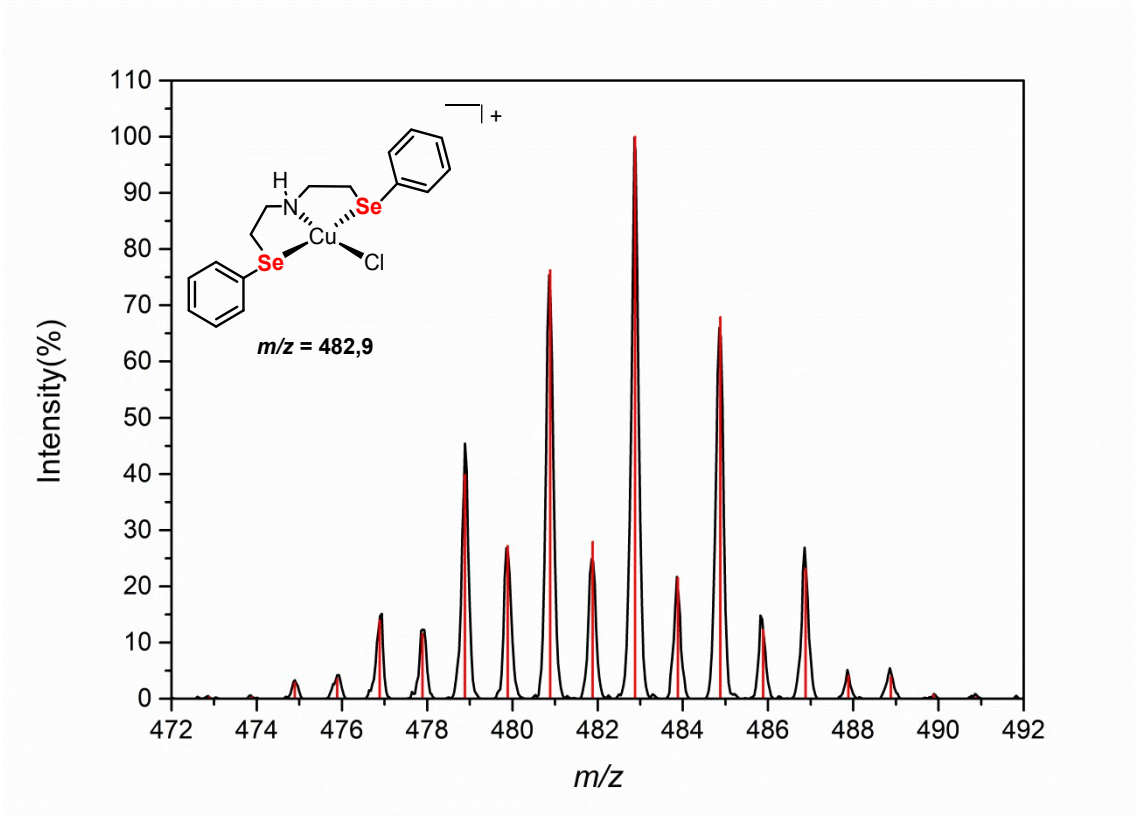


Figure S19 Calculated (red) and experimental (black) isotopic distributions for the species present in the electrospray of $\mathbf{C_{Se}}$.

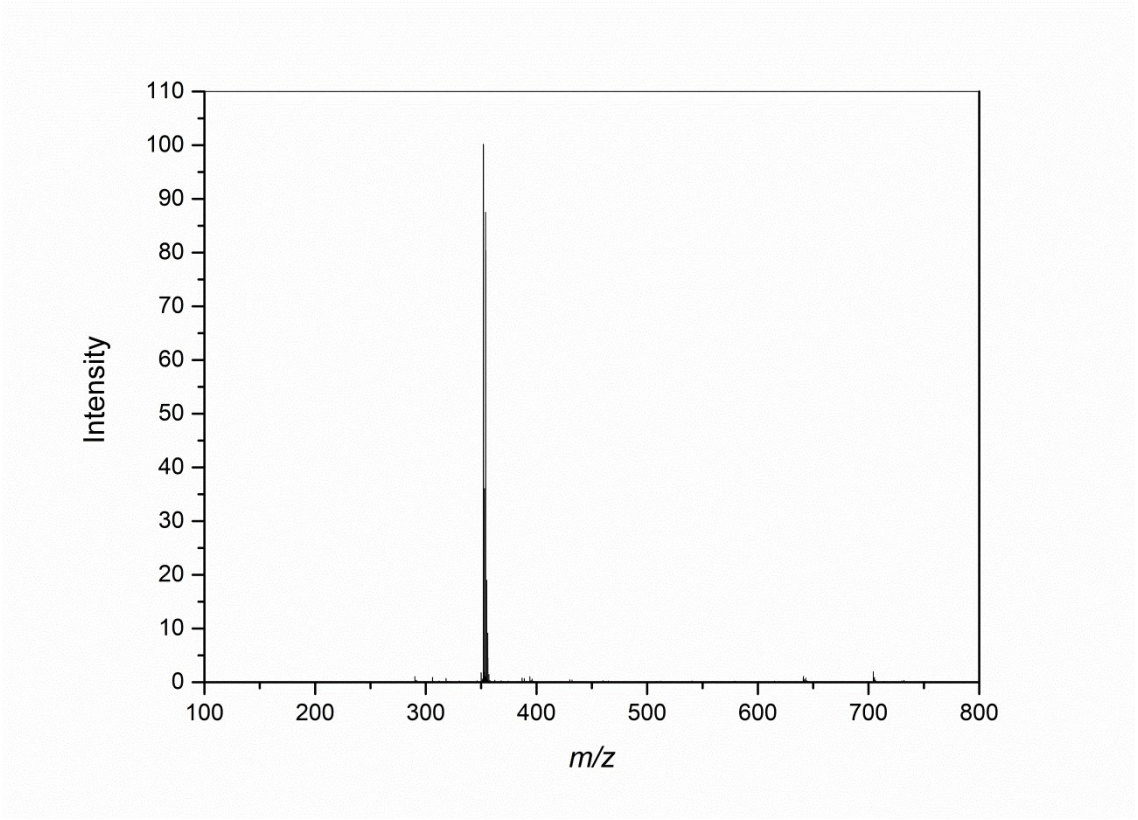
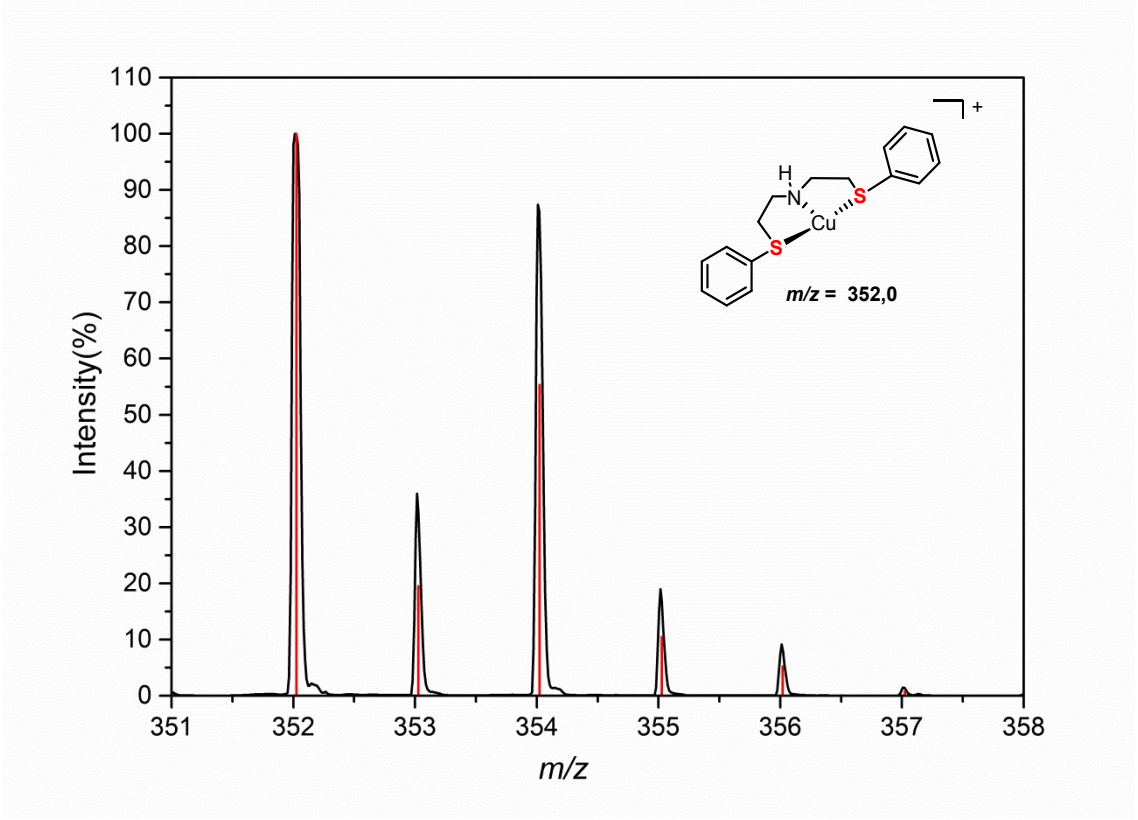


Figure S20 ESI-MS spectrum (positive mode) in methanol of $\mathbf{C_S}$.



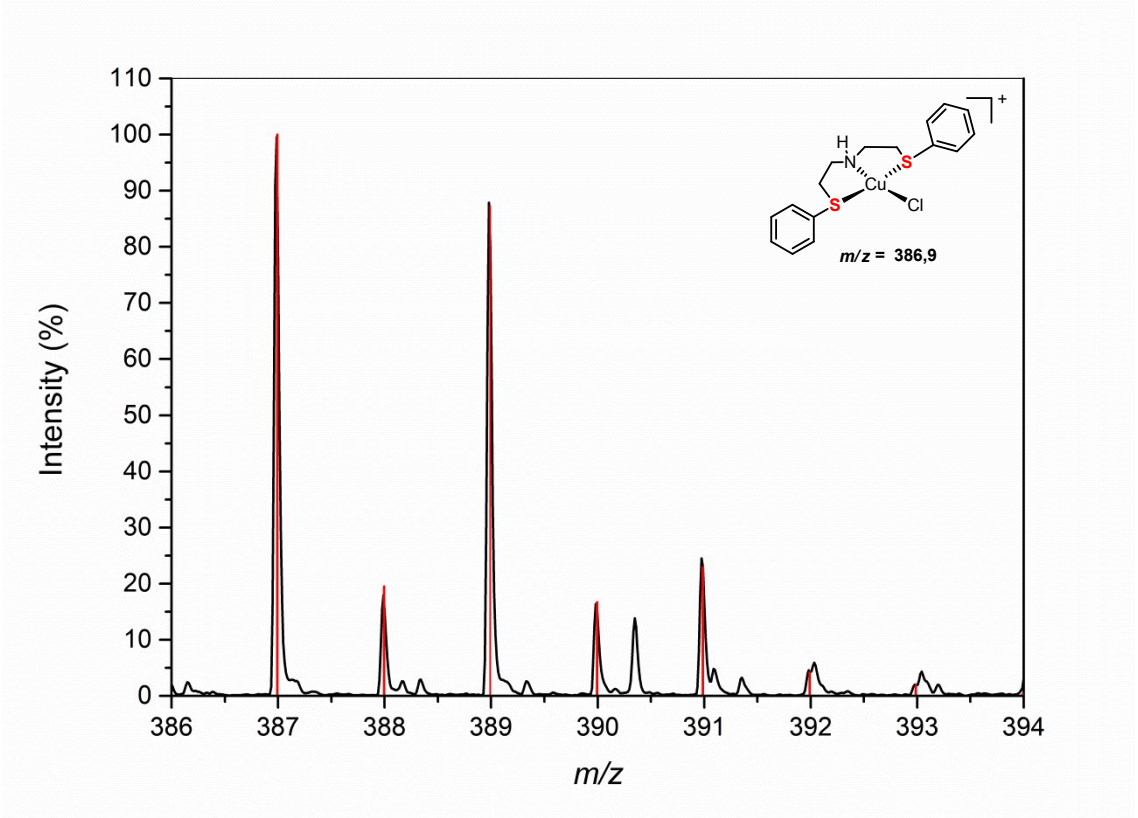


Figure S21 Calculated (red) and experimental (black) isotopic distributions for the species present in the electrospray of $\mathbf{C_S}$.

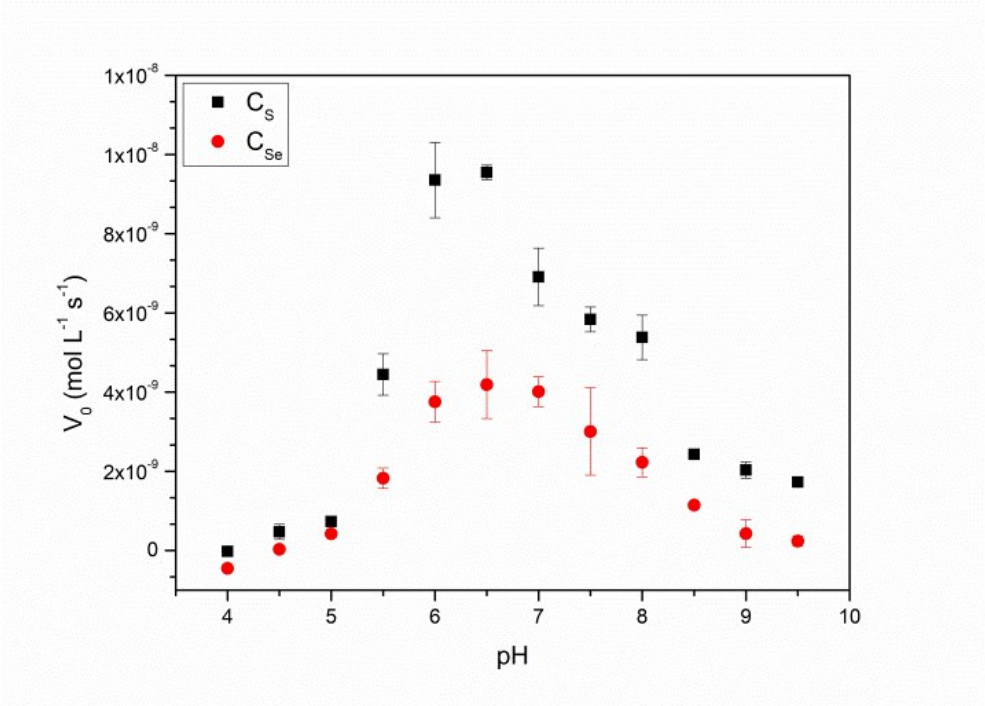


Figure S 22 Graph showing the pH dependence in the hydrolysis of 2,4- BDNPP by complexes $\mathbf{C_{Se}}$ and $\mathbf{C_S}$.

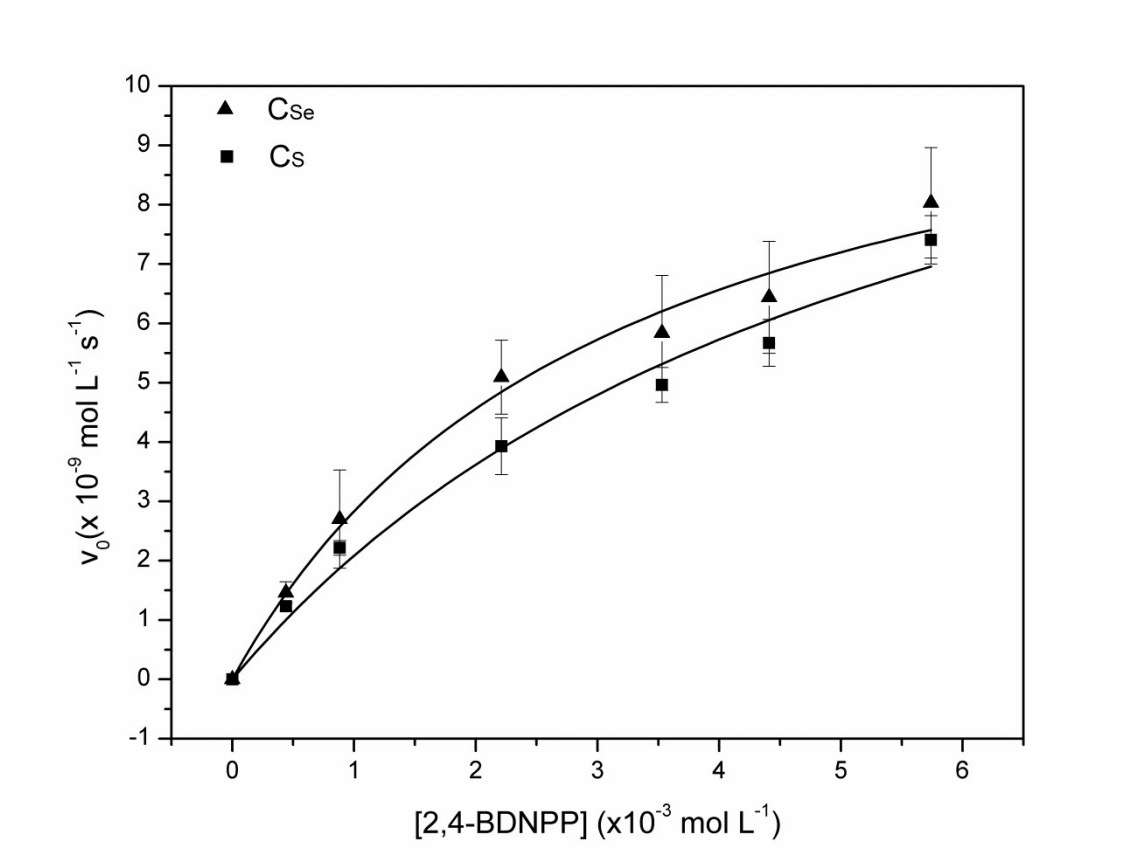


Figure S 23 Dependence of substrate 2,4-BDNPP concentration for $\mathbf{C_S}$ and $\mathbf{C_{Se}}$ complexes at 25 ° C and pH 6.5. MeCN/H_2O solution 50:50% v/v; [complex] = 7.0 x 10^{-5} mol L^{-1}; [substrate] = 4.0 × 10^{-4} to 6.0 × 10^{-3} and [Buffer]= 0.05 mol L^{-1}.

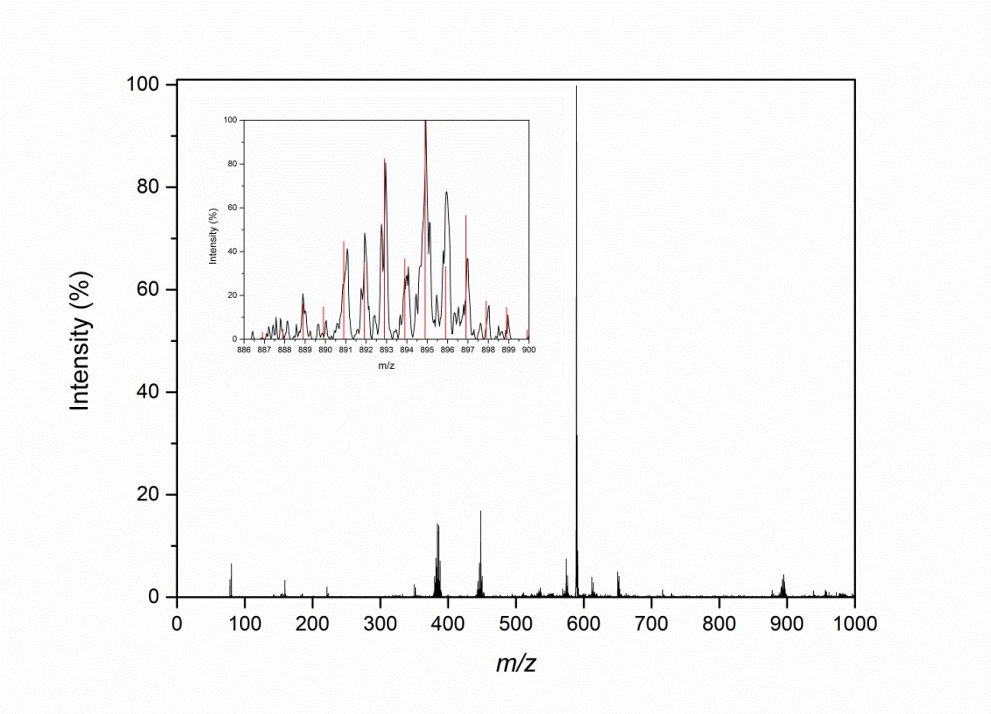


Figure S24 ESI-MS analysis of the $\mathbf{C_{Se}}$ in the presence of the substrate 2,4-BDNPP an acetonitrile/water (1:1, v/v), the expanding spectrum refers to the species: $[Cu(L_{Se})(OH)(2,4\text{-}BDNPP)] + H^+]$

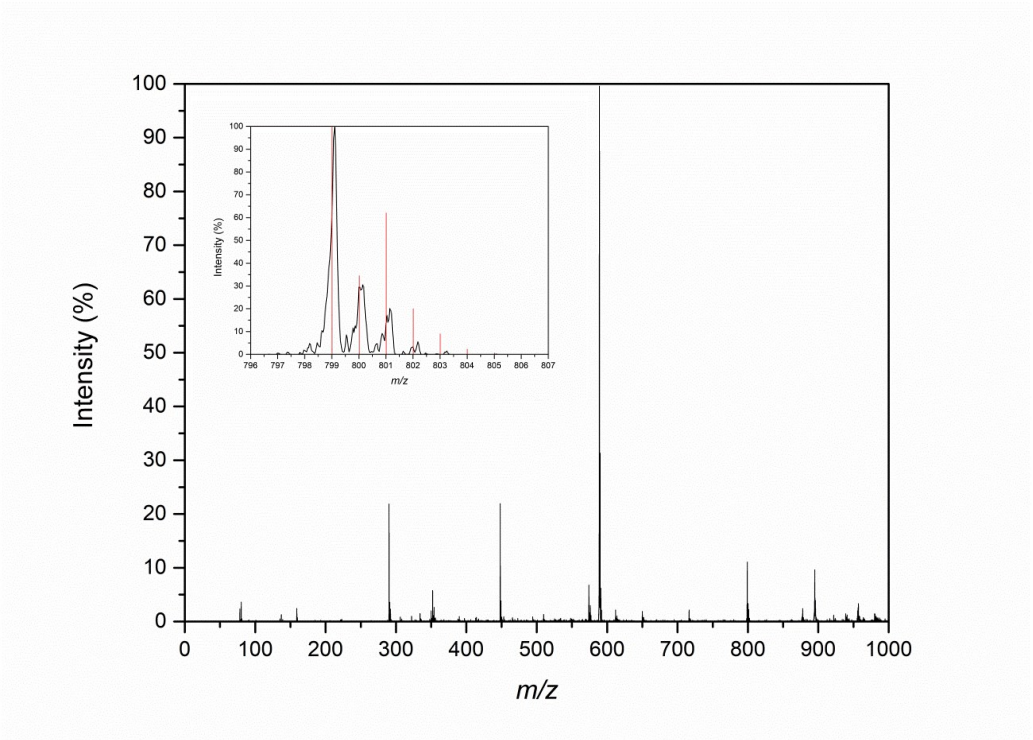


Figure S25 ESI-MS analysis of the $\mathbf{C_S}$ in the presence of the substrate 2,4-BDNPP an acetonitrile/water (1:1, v/v), the expanding spectrum refers to the species: $[Cu(L_S)(OH)(2,4\text{-}BDNPP)] + H^+]$.

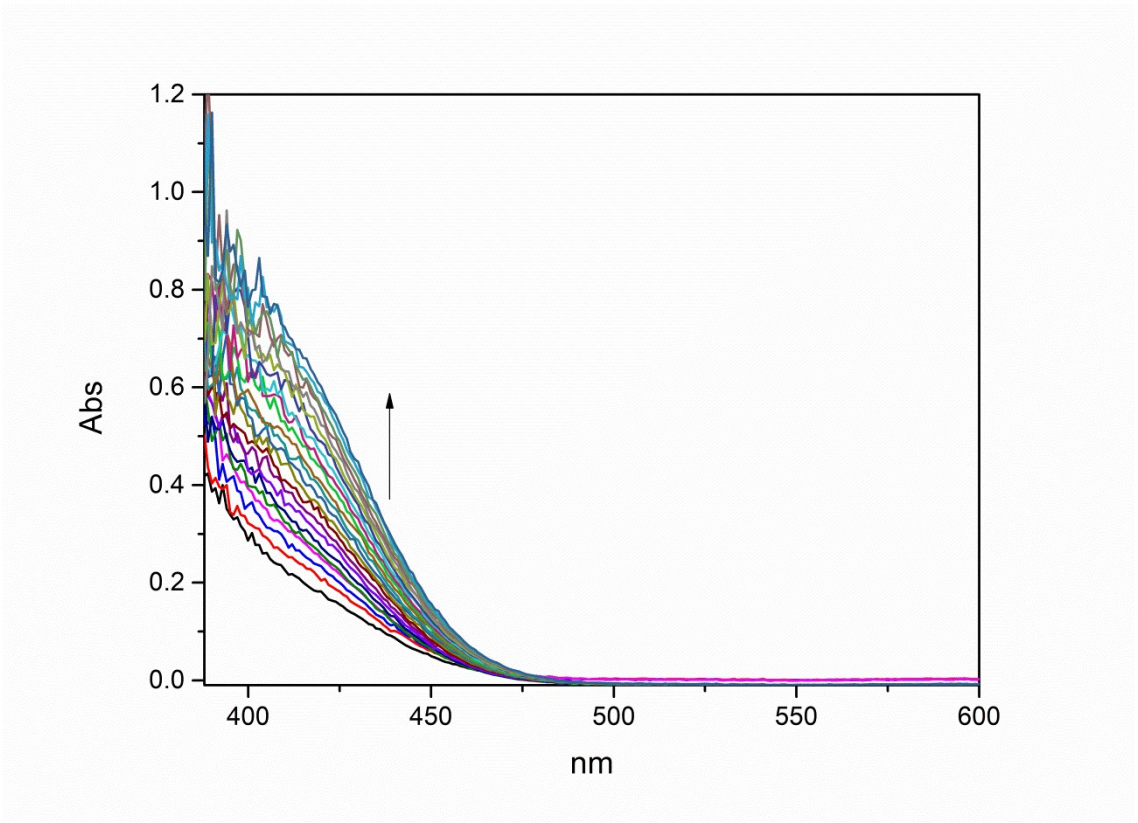


Figure S26 Spectral variation observed during the hydrolysis of the substrate 2,4-BDNPP promoted by the $\mathbf{C_S}$ complex. Conditions: pH 6.5; 25 °C; MeCN / H_2O solution (1: 1 v / v); [complex] = 8.0×10^{-5} mol L^{-1}; [substrate] = 8.0×10^{-3} mol L^{-1}; [buffer] = 0.05 mol L^{-1}. The duration of the spectral variation experiment was 4 hours with an interval of 10 minutes between two spectral scans.

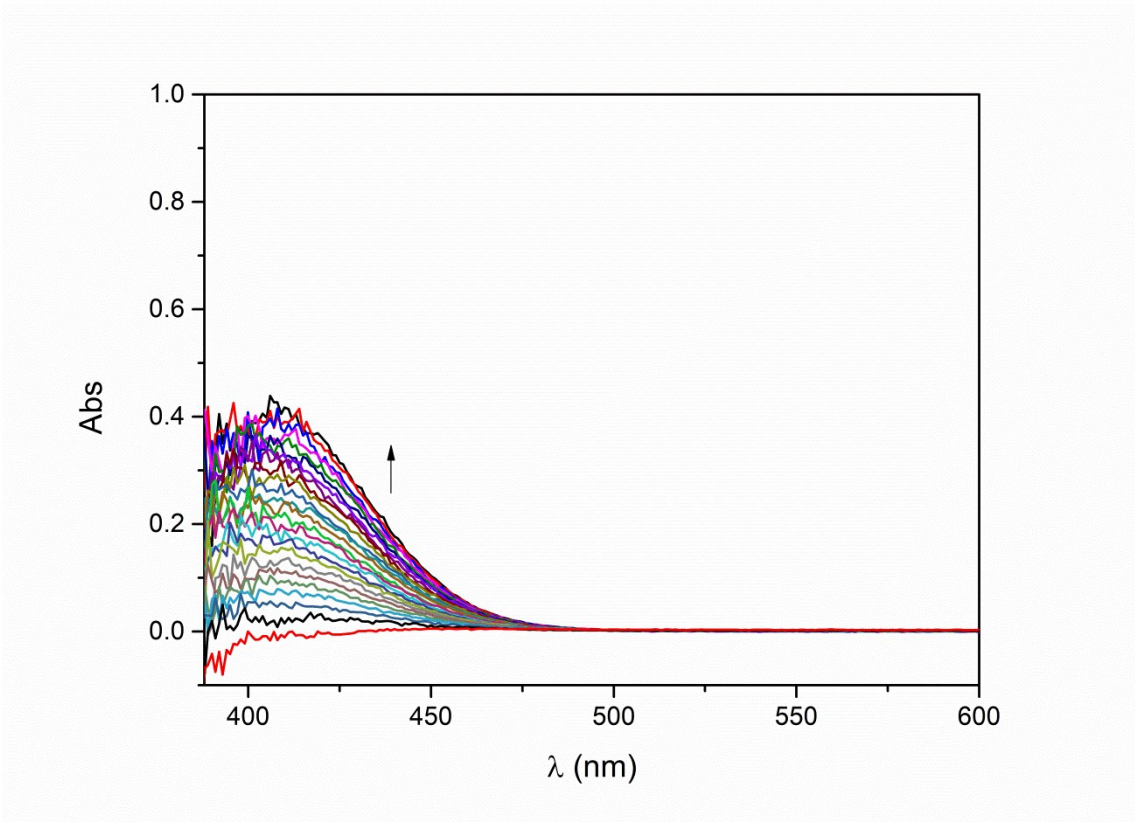


Figure S27 Spectral variation observed during the hydrolysis of the substrate 2,4-BDNPP promoted by the $\mathbf{C_{Se}}$ complex. Conditions: pH 6.5; 25 °C; MeCN / H_2O solution (1: 1 v / v); [complex] = 8.0×10^{-5} mol L^{-1}; [substrate] = 8.0×10^{-3} mol L^{-1}; [buffer] = 0.05 mol L^{-1}. The duration of the spectral variation experiment was 4 hours with an interval of 10 minutes between two spectral scans.

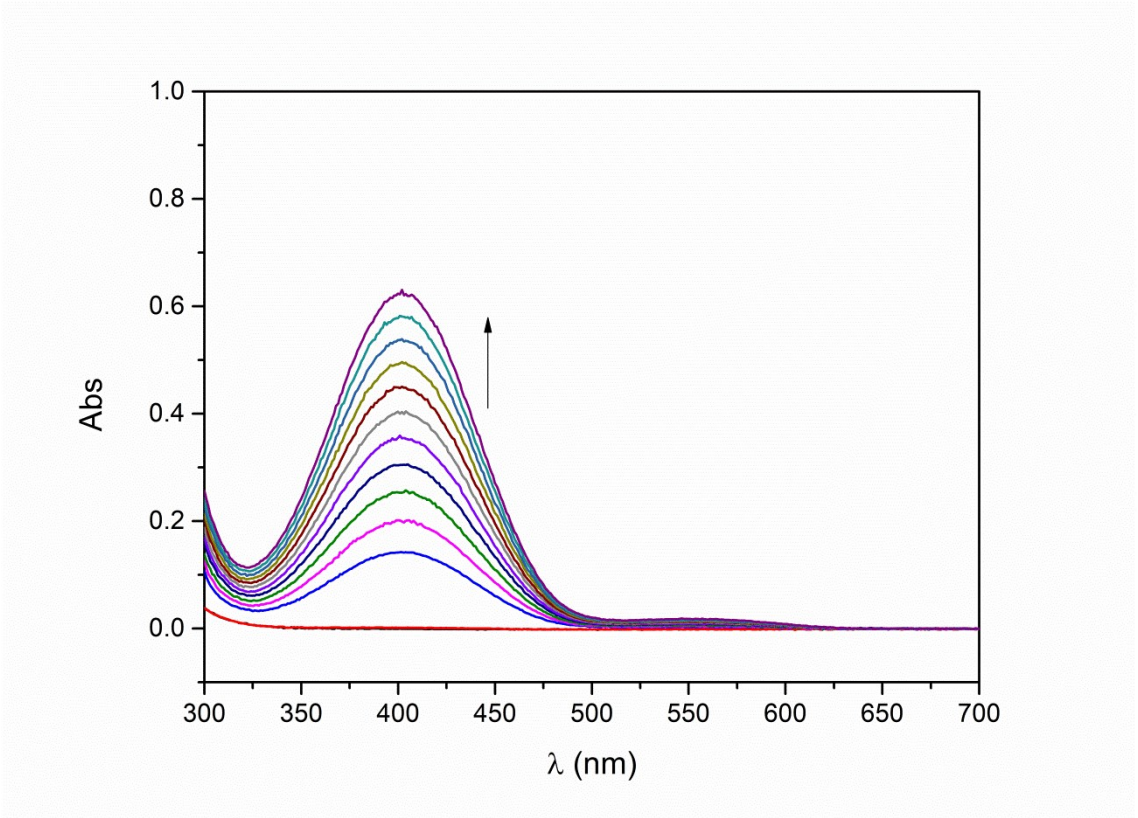


Figure S28 Spectral variation observed during the oxidation of the substrate 3,5-DTBC promoted by the $\mathbf{C_{Se}}$ complex. Conditions: pH 7; 25 ° C; MeOH / H_2O solution (97: 3% v / v); [complex] = 3.0×10^{-5} mol L^{-1}; [substrate] = 3.0×10^{-3} mol L^{-1}; [buffer] = 0.03 mol L^{-1}. The duration of the spectral variation experiment was 1 hour with an interval of 5 minutes between two spectral scans.

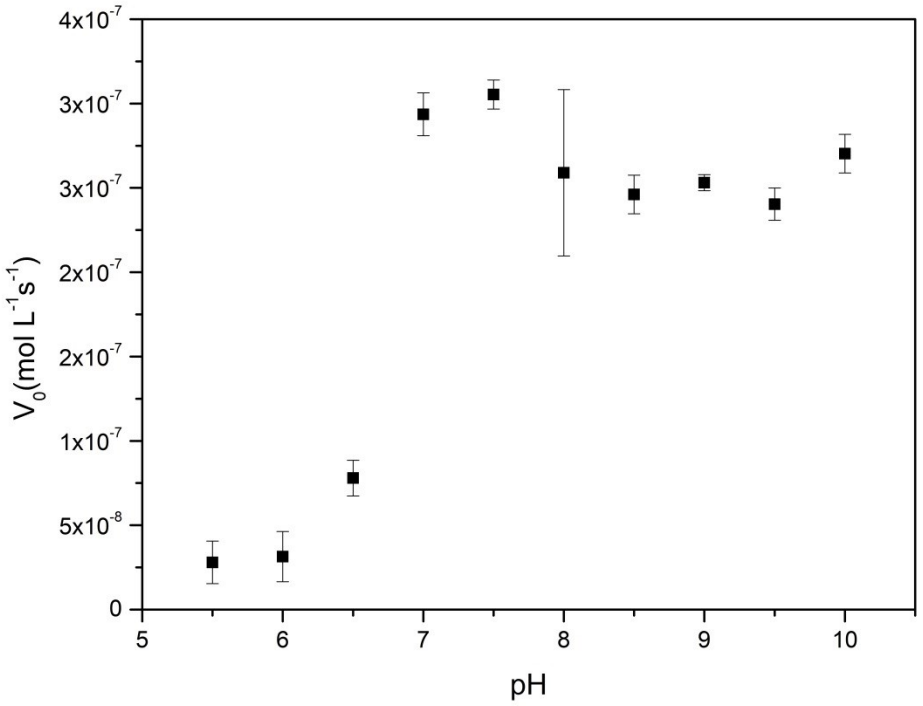


Figure S29 Plots of v_0 *versus* pH of $\mathbf{C_{Se}}$ complex for 3,5-DTBC substrate oxidation reaction at 25 ° C. MeOH / H_2O solution: 97: 3% v / v; [complex] = 2.0 x 10^{-5} mol L^{-1}; [substrate] = 2.4 x 10^{-3} mol L^{-1}; [buffer] = 0.03 mol L^{-1}. (MES - pH 5.5 at 6.5, TRIS - pH 7.0 at 10.0).

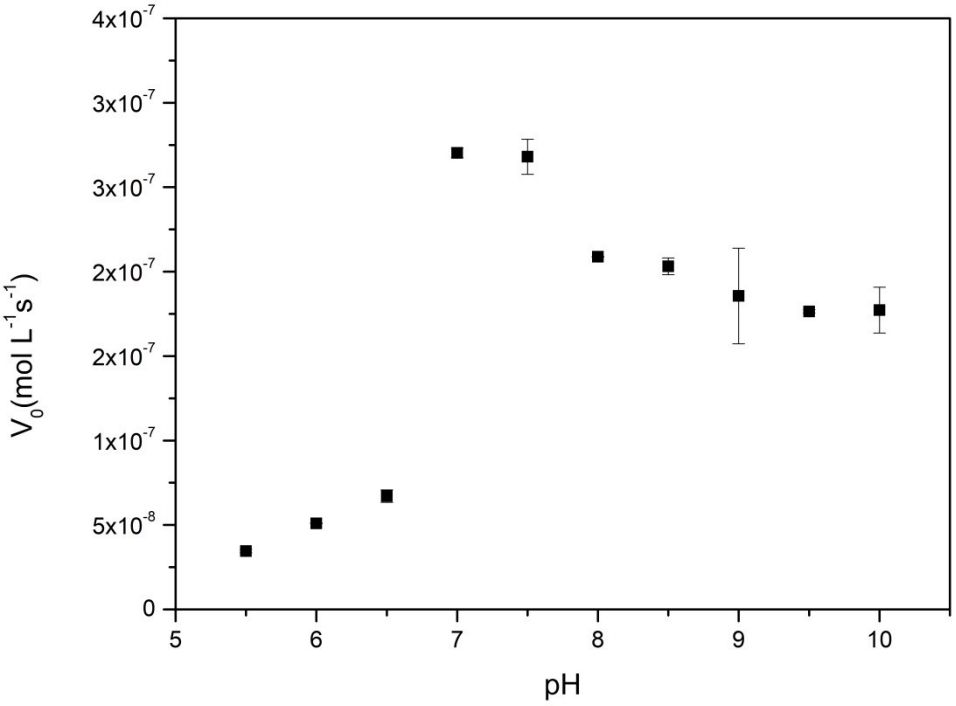


Figure S30 Plots of v_0 versus pH of C_S complex for 3,5-DTBC substrate oxidation reaction at 25 ° C. MeOH / H_2O solution 97: 3% v / v; [complex] = 2.0 x 10^{-5} mol L^{-1}; [substrate] = 2.4 x 10^{-3} mol L^{-1}; [buffer] = 0.03 mol L^{-1}. (MES - pH 5.5 at 6.5, TRIS - pH 7.0 at 10.0).

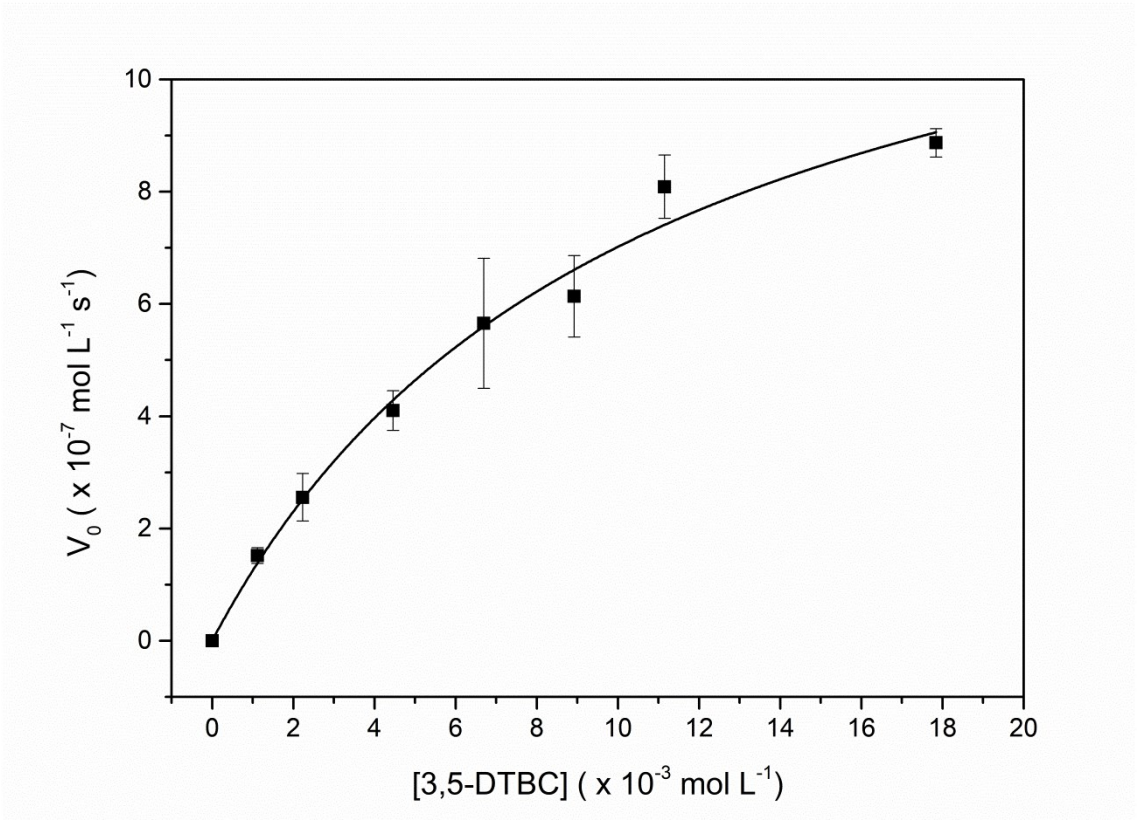


Figure S31 Dependence on oxidation reaction rate of 3,5 - DTBC with substrate concentration for **C_S** complex at 25 °C and pH 7. MeOH / H_2O solution 97:3% v / v; [complex] = 3.3 x 10^{-5} mol L^{-1}; [substrate] = 11.15 x 10^{-4} to 17.84 x 10^{-3} mol L^{-1}; [buffer] = 0.03 mol L^{-1}.

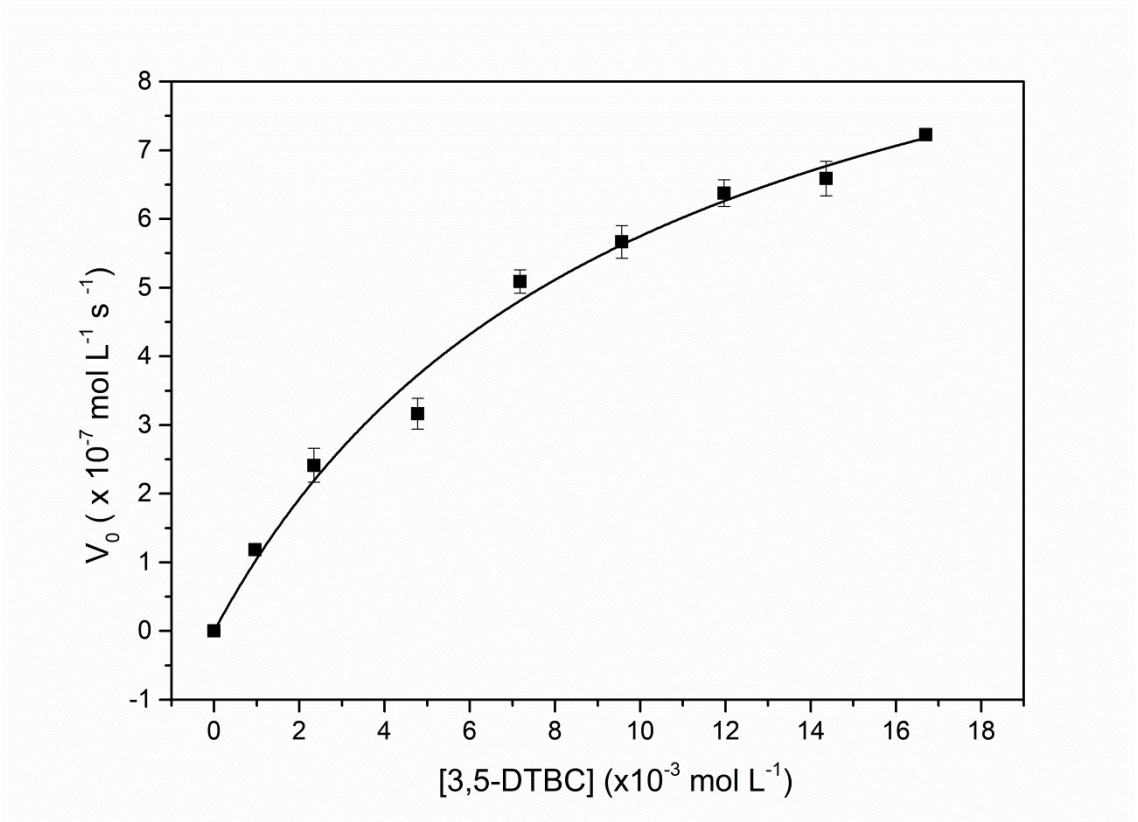


Figure S32 Dependence on oxidation reaction rate of 3,5 - DTBC with substrate concentration for $\mathbf{C_{Se}}$ complex at 25 ° C and pH 7. MeOH / H_2O solution 97: 3% v / v; [complex] = 2.0 x 10^{-5} mol L^{-1}; [substrate] = 9.57 x 10^{-4} to 16.7 x 10^{-3} mol L^{-1}; [buffer] = 0.03 mol L^{-1}.

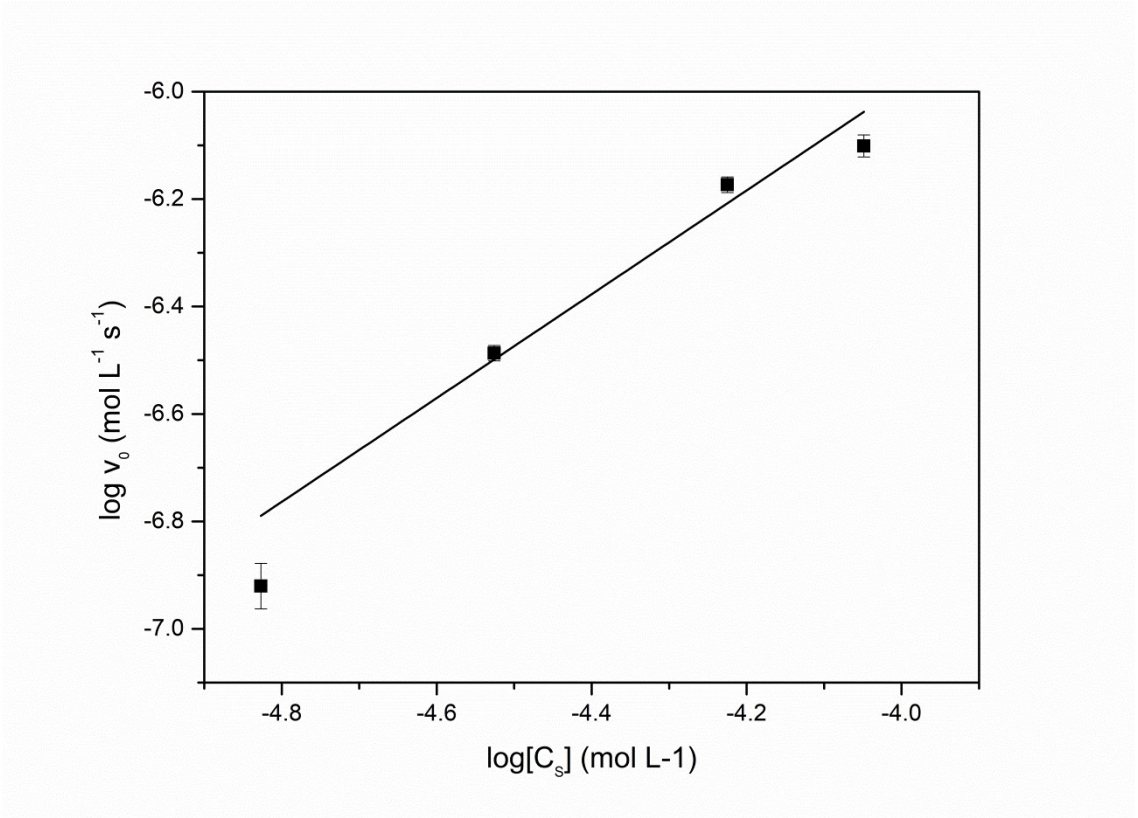


Figure S33 Dependence on oxidation reaction rate of 3,5 - DTBC with substrate concentration for $\mathbf{C_S}$ complex at 25 °C and pH 7. MeOH / H_2O solution 97: 3% v / v; [complex] = 2.0 x 10^{-5} mol L^{-1}; [substrate] = 9.0 x 10^{-4} to 1.6 x 10^{-3} mol L^{-1}; [buffer] = 0.03 mol L^{-1}.

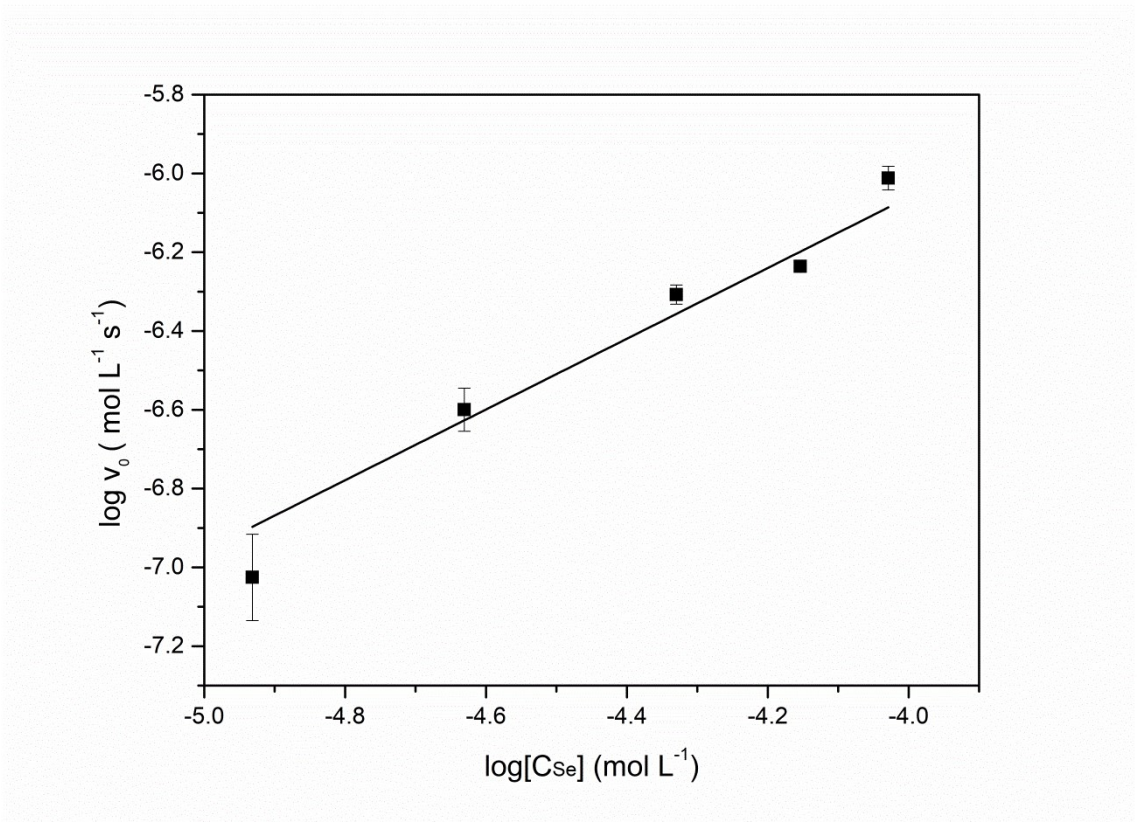


Figure S34 Dependence on oxidation reaction rate of 3,5-DTBC with substrate concentration for $\mathbf{C_{Se}}$ complex at 25 °C and pH 7. MeOH / H_2O solution 97: 3% v / v; [complex] = 2.0 x 10^{-5} mol L^{-1}; [substrate] = 9.0 x 10^{-4} to 1.6 x 10^{-3} mol L-1; [buffer] = 0.03 mol L^{-1}.