ESI

Tungsten(VI) selenide tetrachloride, $WSeCl_4$ – synthesis, properties, coordination complexes and application for CVD growth of WSe_2 thin films

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Table S1 Crystallographic parameters.

Compound	$WSeCl_4$	$[WSeCl_4(OPPh_3)]$	$[WSeCl_4(DMF)]$	$[(WSeCl_4)_2(4,4'\text{-bipy})]\cdot 3C_6H_6$
Formula	Cl_4SeW	$C_{18}H_{15}Cl_4OPSeW$	$C_9H_{13}Cl_4NOSeW$	$C_{28}H_{26}Cl_8N_2Se_2W_2$
M	404.61	682.88	555.81	1199.73
Crystal system	monoclinic	monoclinic	monoclinic	triclinic
Space group (no)	$P2_1/n$ (14)	$P2_1/n$ (14)	C2/c (15)	P-1 (2)
a /Å	8.8639(2)	12.59105(17)	18.8765(10)	6.03153(11)
b /Å	12.4149(2	11.06907(14)	7.3681(3)	15.4384(4)
c /Å	12.1003(3)	15.00109(19)	22.8710(13)	20.1476(5)
α /°	90	90	90	103.815(2)
β /°	111.125(2)	96.3449(12)	104.559(6)	94.9132(17)
γ /°	90	90	90	98.3755(17)
U /Å^3	1242.08(5)	2077.91(5)	3078.8(3)	1788.18(7)
Z	8	4	8	2
μ(Mo-K$_\alpha$)/mm^{-1}	55.880	7.908	10.546	9.084
F(000)	1408	1288	2064	1120
Total number reflns	18376	56394	20205	52666
R_{int}	0.055	0.041	0.075	0.082
Unique reflns	2207	6896	3969	8594
No. of params, restraints	109, 0	235, 0	180, 55	379, 0
GOF	1.017	1.019	1.053	1.058
R_1, wR_2 [$I > 2\sigma(I)$] [b]	0.016, 0.039	0.021, 0.037	0.040, 0.089	0.041, 0.096
R_1, wR_2 (all data) [b]	0.018, 0.040	0.027, 0.038	0.052, 0.093	0.050, 0.100

[a] common data: T = 100 K; wavelength (Mo-K$_\alpha$) = 0.71073 Å; θ(max) = 27.5°; [b] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4]^{1/2}$.

Table S1 Cont.

Compound	$[WSeCl_4(MeCN)]$	$[(WSeCl_4)_2(dioxane)]$	$[(WSeCl_4)_2(SeMe_2)]$	$[\{WCl_3(SMe_2)\}_2(\mu\text{-Se})(\mu\text{-Se}_2)]$
Formula	$C_2H_3Cl_4NSeW$	$C_4H_8Cl_8O_2SeW_2$	$C_2H_6Cl_8Se_3W_2$	$C_4H_{12}Cl_6S_2Se_3W_2$
M	445.66	897.32	918.25	941.54
Crystal system	monoclinic	monoclinic	triclinic	orthorhombic
Space group (no)	$P2_1/m$ (11)	C_1/c (15)	P-1 (2)	Pnma (62)
a /Å	5.8784(2)	22.1170(4)	6.6025(2)	13.58820(13)
b /Å	7.8378(4)	6.51400(10)	10.2899(5)	19.5279(2)
c /Å	14.8140(6)	11.5767(2)	12.2583(6)	6.69716(7)
α /°	90	90	89.211(4)	90
β /°	88.834(3)	90.841(2)	85.388(3)	90
γ /°	90	90	81.076(3)	90
U /$Å^3$	682.39(5)	1667.68(5)	820.07(6)	1777.09(3)
Z	2	4	2	4
$\mu(Mo\text{-}K_\alpha)/mm^{-1}$	11.860	19.419	21.945	40.932
F(000)	396	1600	808	1680
Total number reflns	17488	17262	9411	30236
R_{int}	0.062	0.073	0.035	0.038
Unique reflns	1882	2152	4223	1743
No. of params, restraints	50, 0	82, 0	138, 0	84, 0
GOF	1.059	1.071	1.012	1.188
R_1, wR_2 [$I > 2\sigma(I)$][b]	0.039, 0.103	0.021, 0.049	0.036, 0.072	0.030, 0.071
R_1, wR_2 (all data) [b]	0.046, 0.109	0.023, 0.050	0.046, 0.078	0.030, 0.071

Fig. S1. Rietveld fit to the PXRD pattern of $WSeCl_4$. Blue crosses mark the data points, green continuous line the fit, cyan line the difference and blue tick marks the allowed reflecton positions. Strong peaks from the Al sample holder at 38.2 and 44.5 ° were excluded. The fit used the crystal structure described in Table S1 ($P2_1/n$) with a = 8.9371(5), b = 12.5479(12), c = 12.2271(9) Å and β = 111.2098(17) °.

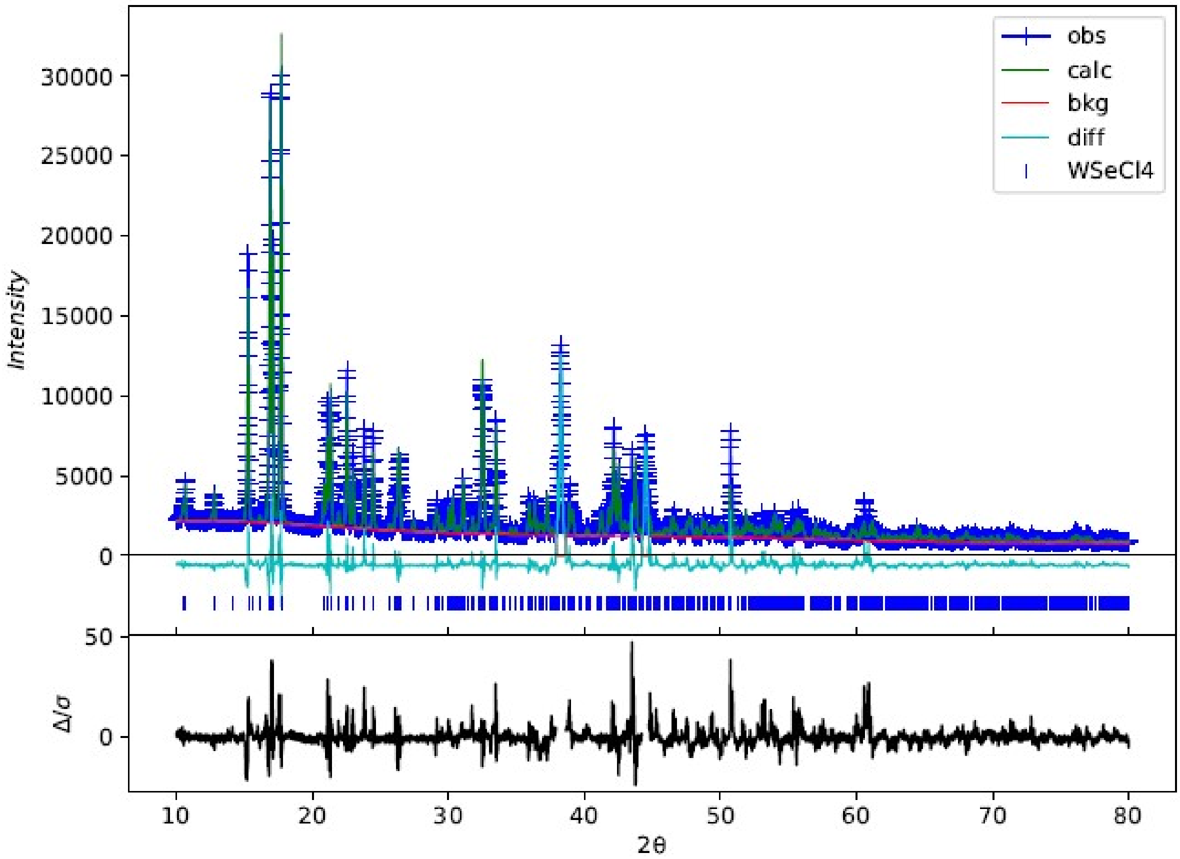


Fig. S2. IR Spectrum of $WSeCl_4$ (Nujol)

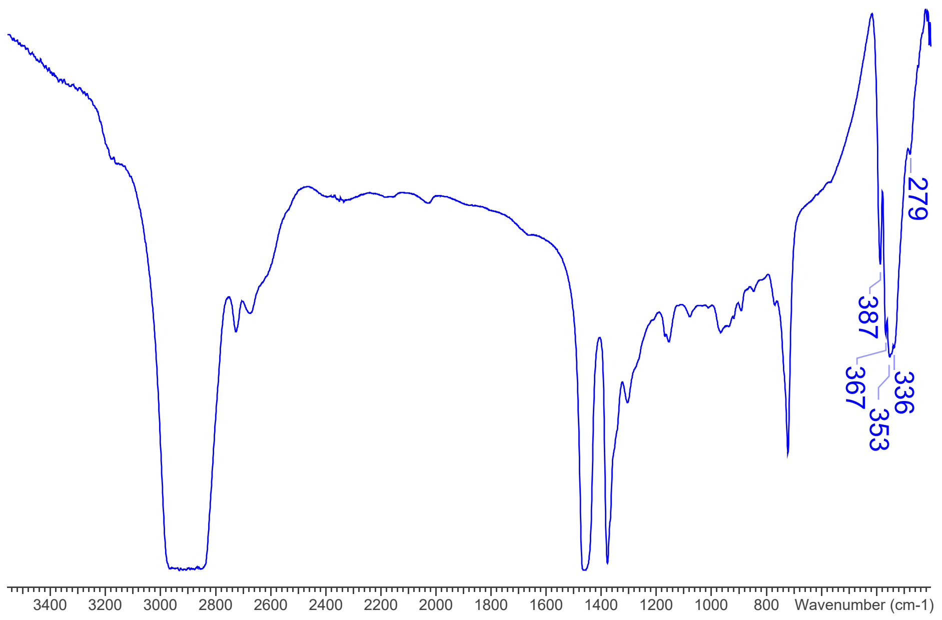


Fig. S3. [1]H NMR spectrum of $[WSeCl_4(MeCN)]$ (CD_2Cl_2)

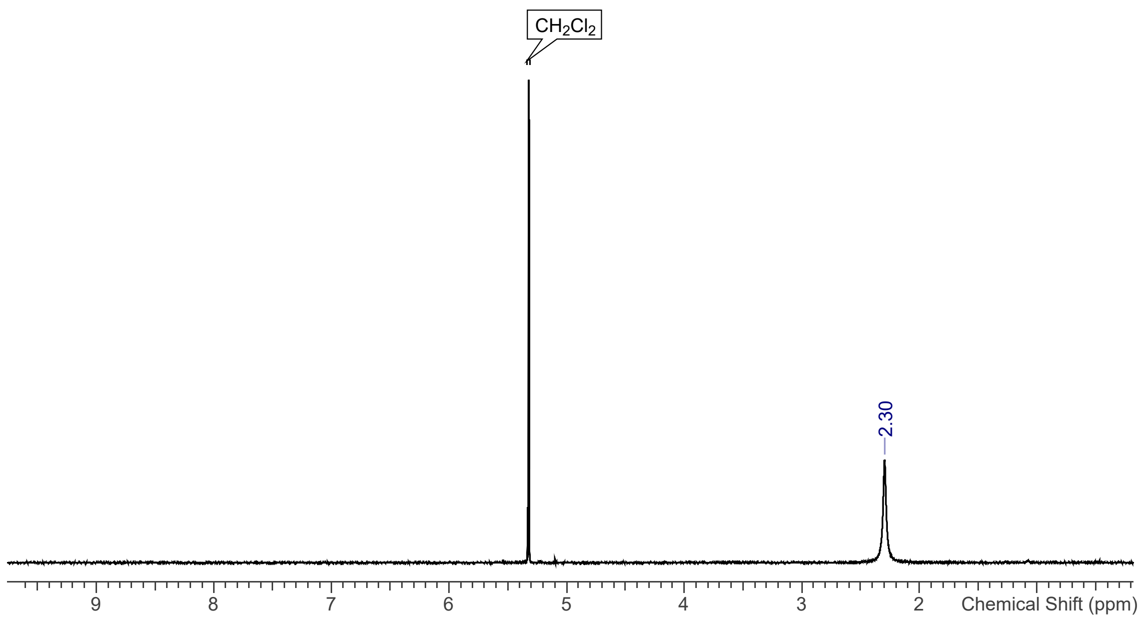


Fig. S4. IR Spectrum of [$WSeCl_4(MeCN)$] (Nujol)

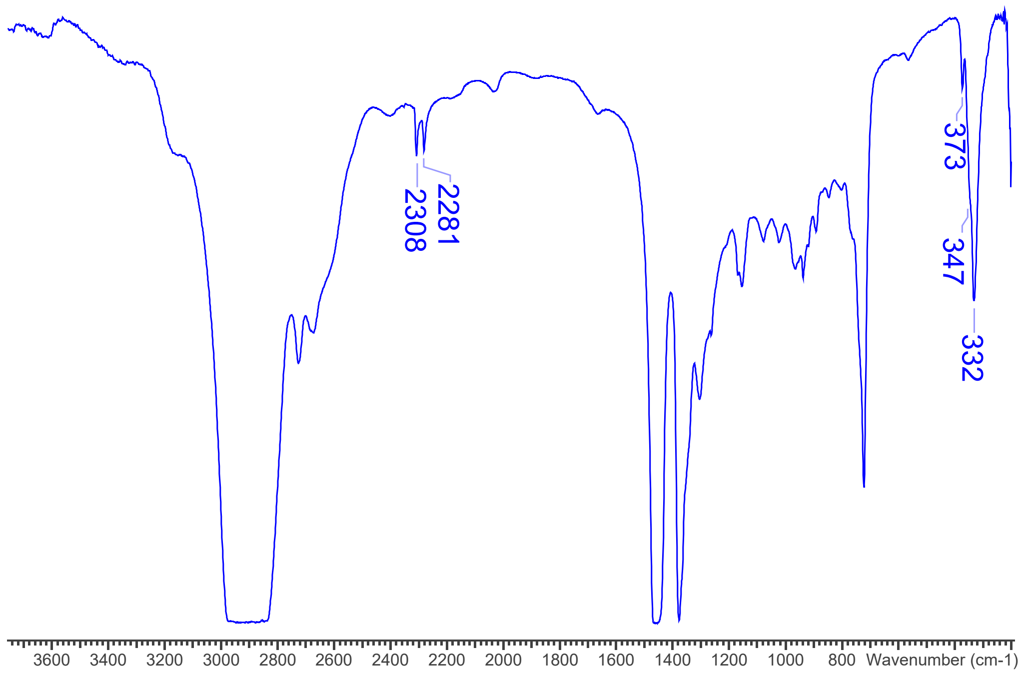


Fig. S5. ^{1}H NMR spectrum of [$WSeCl_4(thf)$] (CD_2Cl_2)

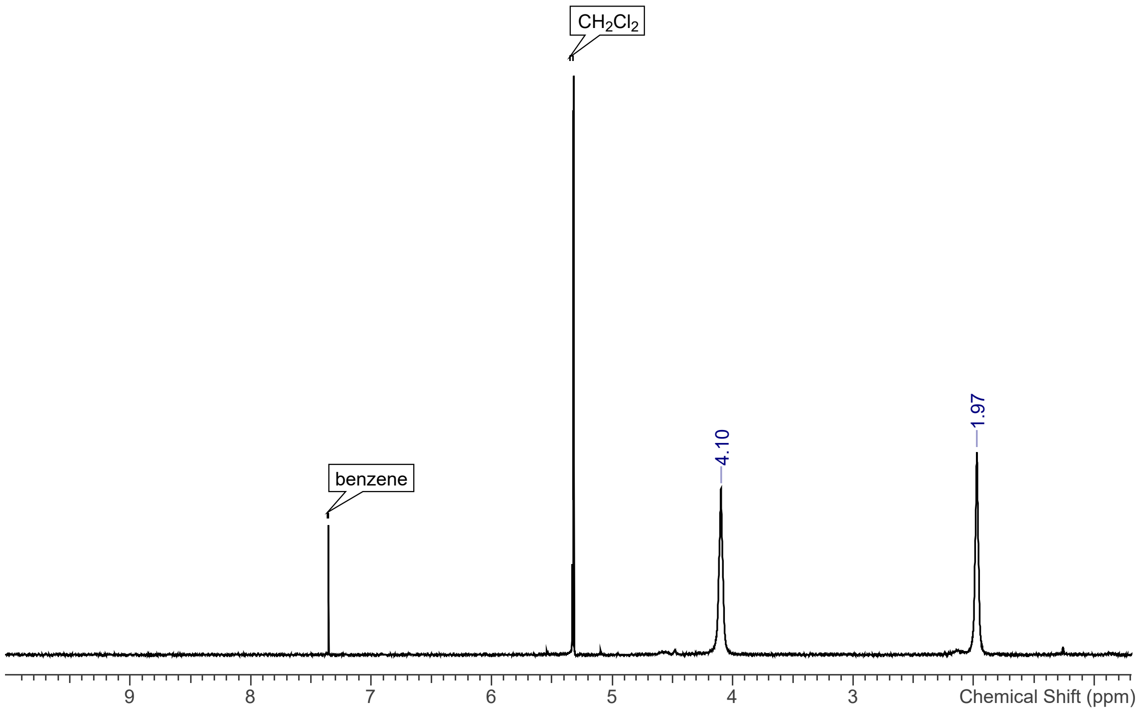


Fig. S6. IR Spectrum of [$WSeCl_4$(thf)] (Nujol)

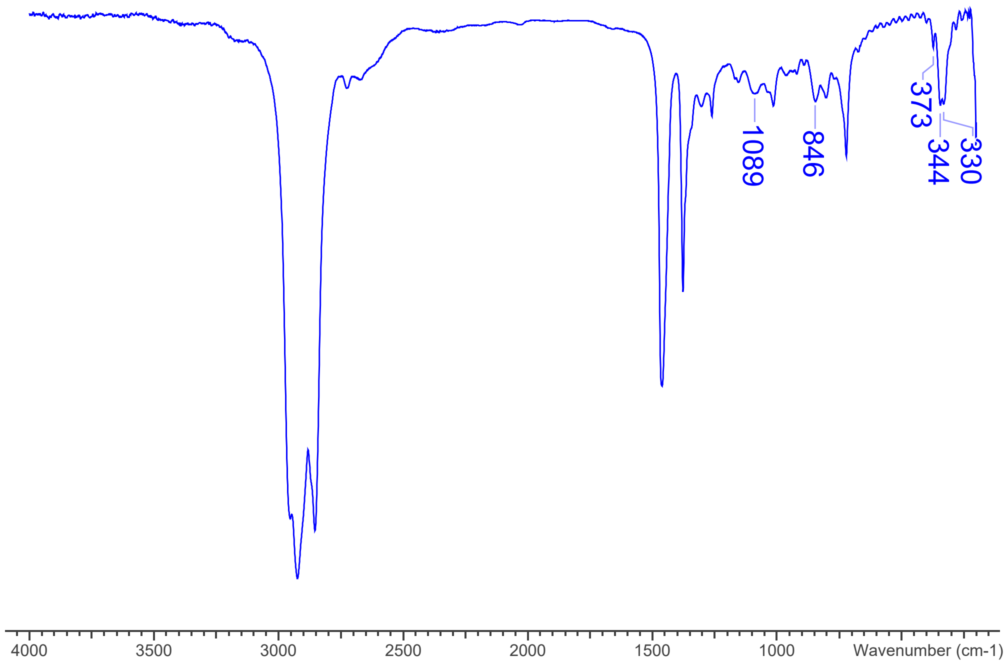


Fig. S7. ^{1}H NMR spectrum of [$WSeCl_4(OPPh_3)$] (CD_2Cl_2)

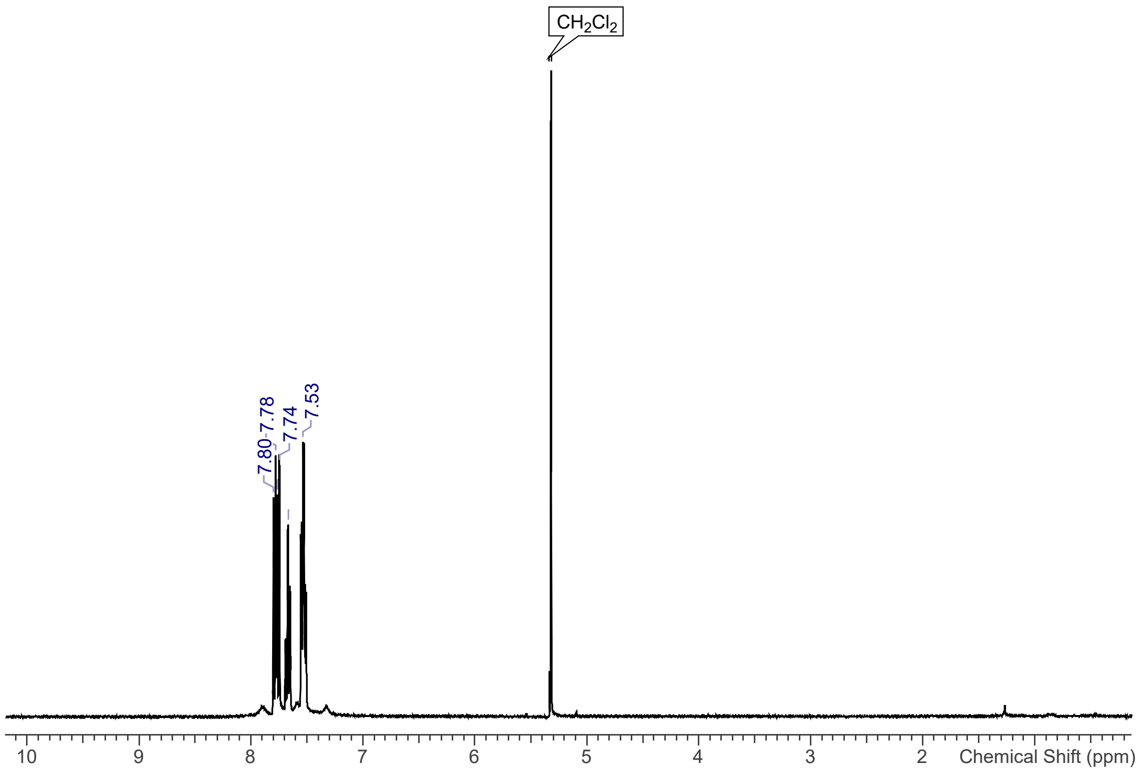


Fig. S8. $^{31}P\{^1H\}$ NMR spectrum of $[WSeCl_4(OPPh_3)]$ (CD_2Cl_2)

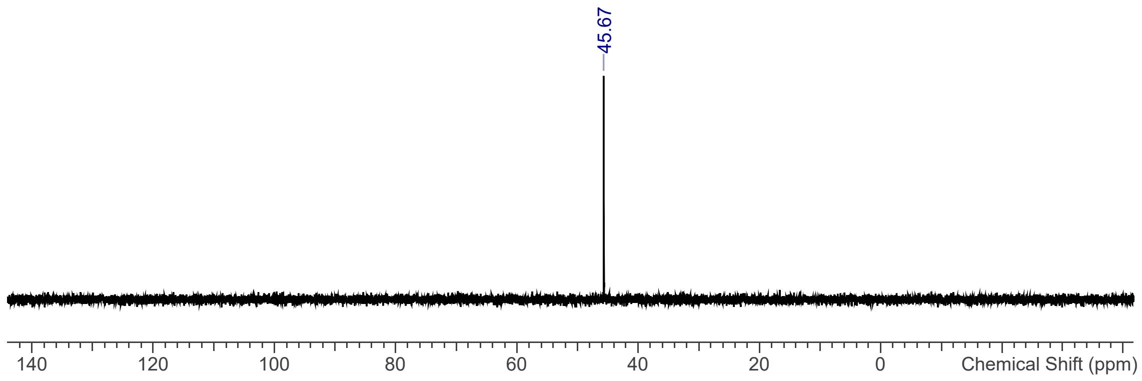


Fig. S9. IR Spectrum of $[WSeCl_4(OPPh_3)]$ (Nujol)

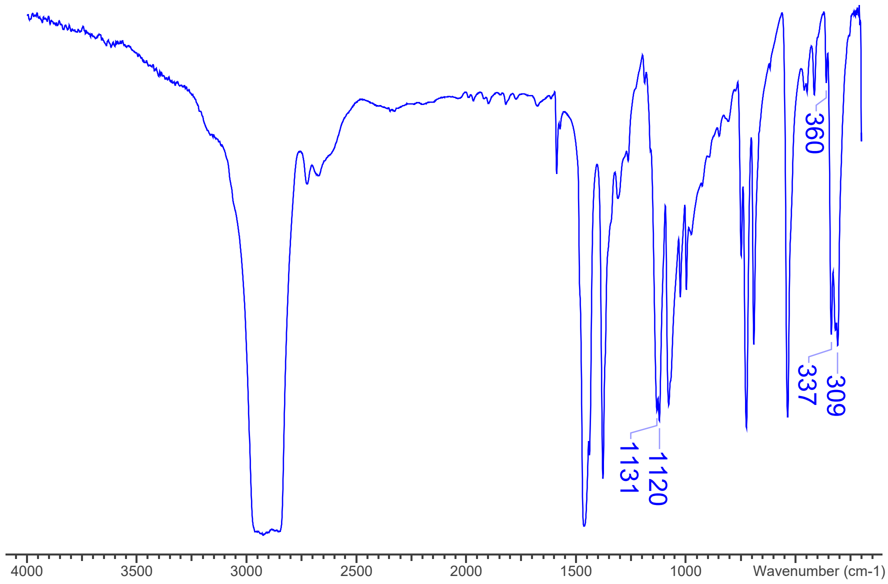


Fig. S10. ^1H NMR spectrum of $[WSeCl_4(DMF)]$ (C_6D_6)

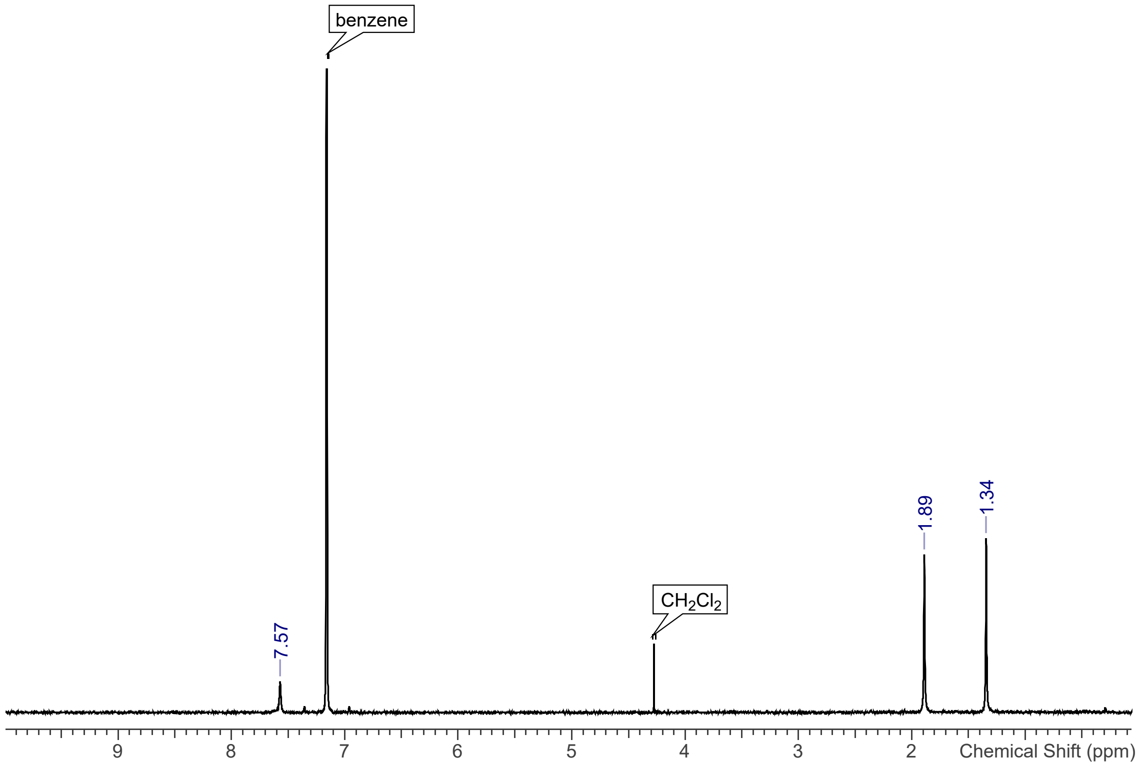


Fig. S11. IR Spectrum of [$WSeCl_4$(DMF)] (Nujol)

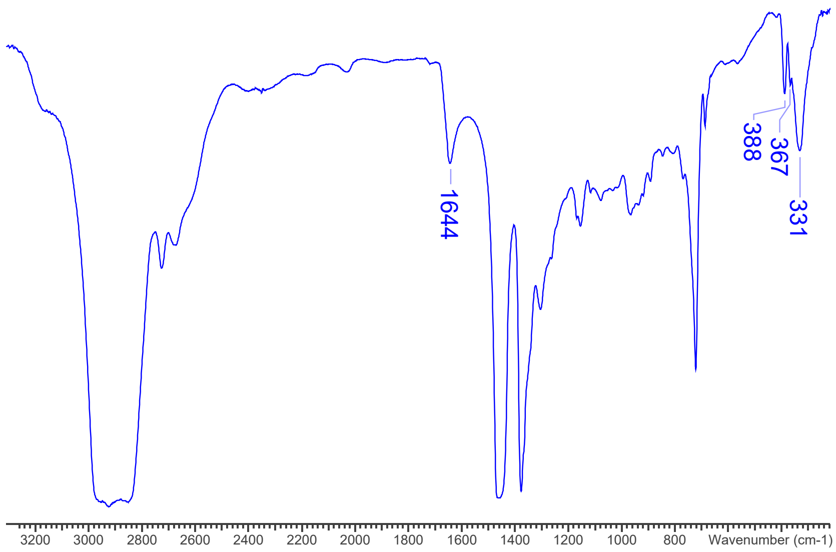


Fig. S12. ^1H NMR Spectrum of [$(WSeCl_4)_2$(4,4'-bipy)] (CD_2Cl_2)

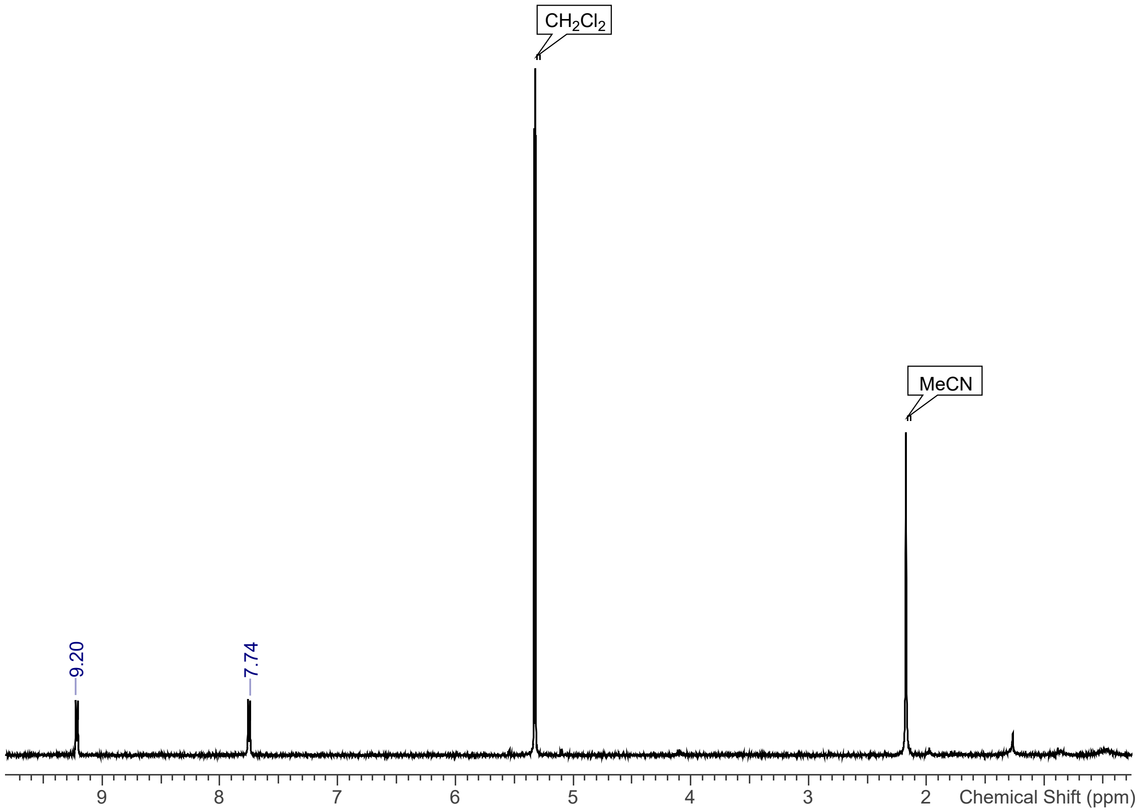


Fig. S13. IR Spectrum of [$(WSeCl_4)_2$(4,4'-bipy)] (Nujol)

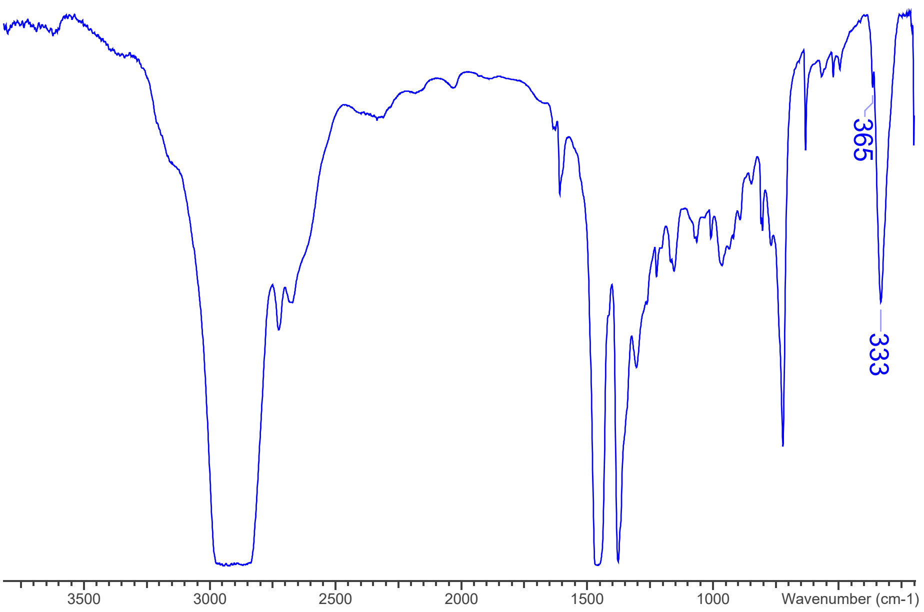


Fig. S14. IR Spectrum of [$WSeCl_4$(py)] (Nujol)

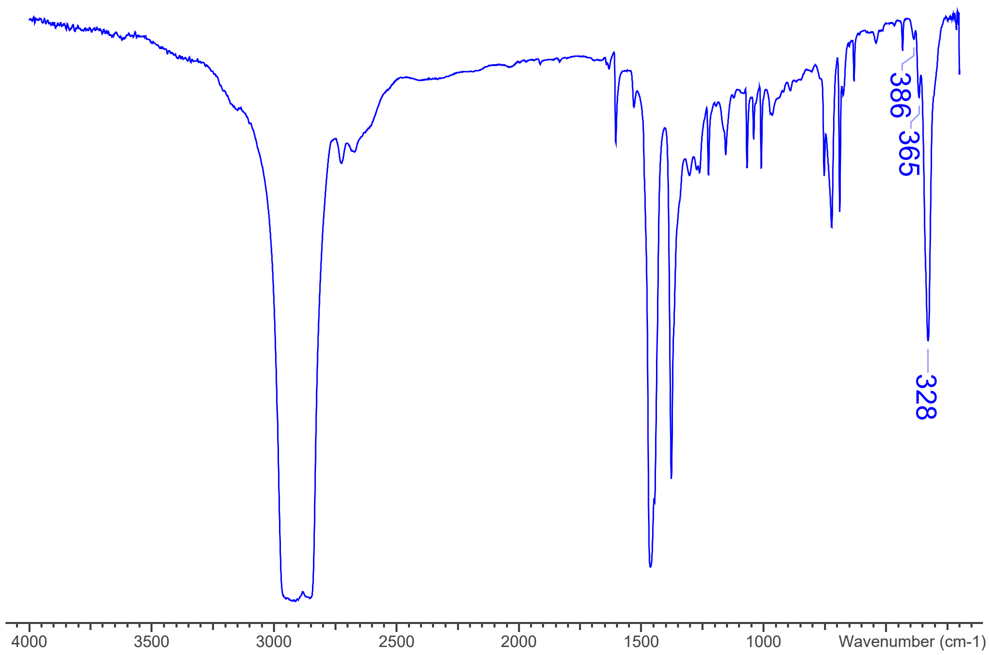


Fig. S15. [1]H NMR Spectrum of [$WSeCl_4$(py)] (CD_2Cl_2)

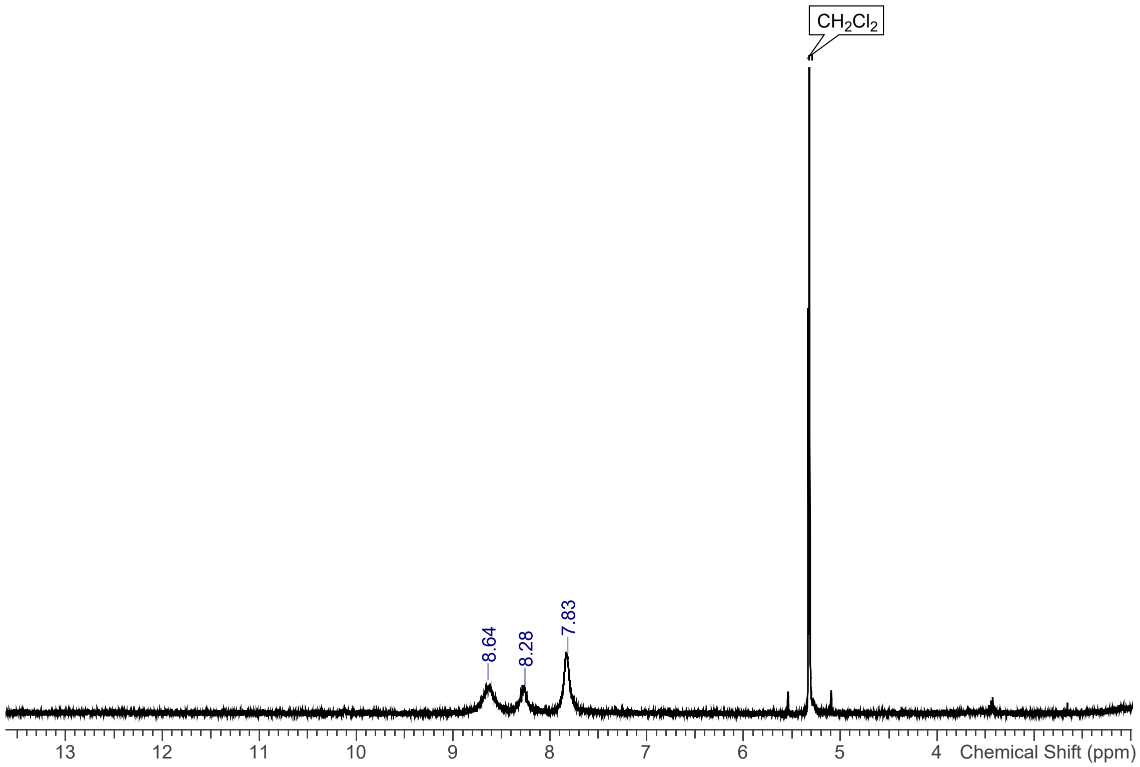


Fig. S16. IR spectrum of [$WSeCl_4$(2,2'-bipy)] (Nujol)

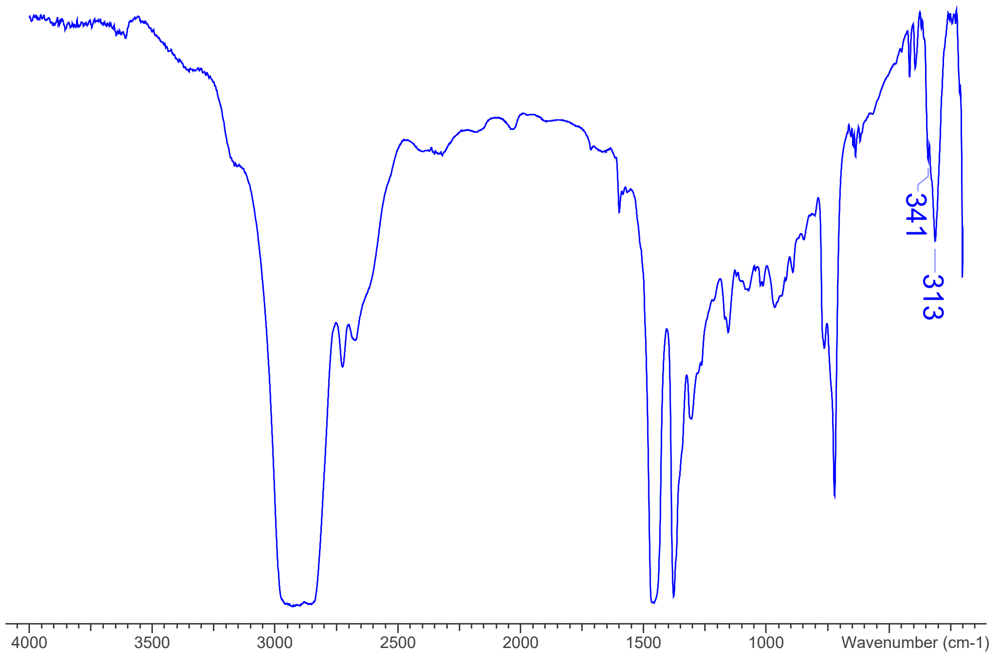


Fig. S17. ^1H NMR spectrum of [$WSeCl_4$(2,2'-bipy)] (CD_2Cl_2)

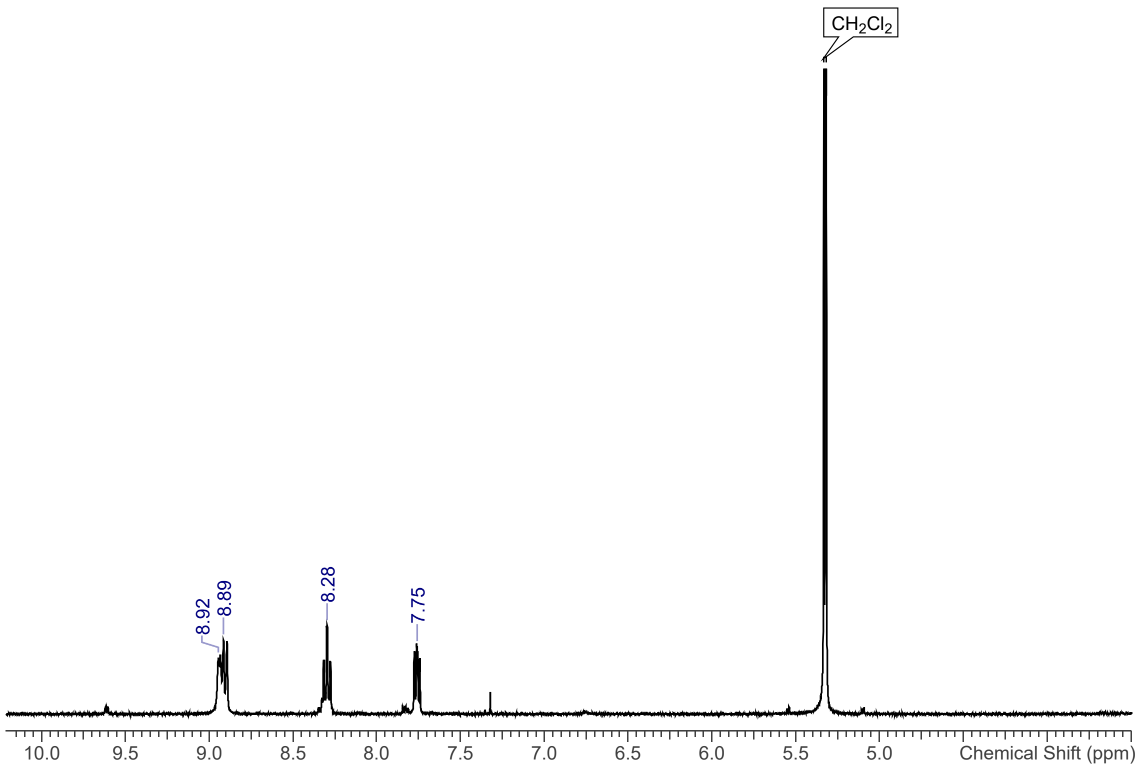


Fig. S18. IR spectrum of [$(WSeCl_4)(\mu\text{-dppmO}_2)$] (Nujol)

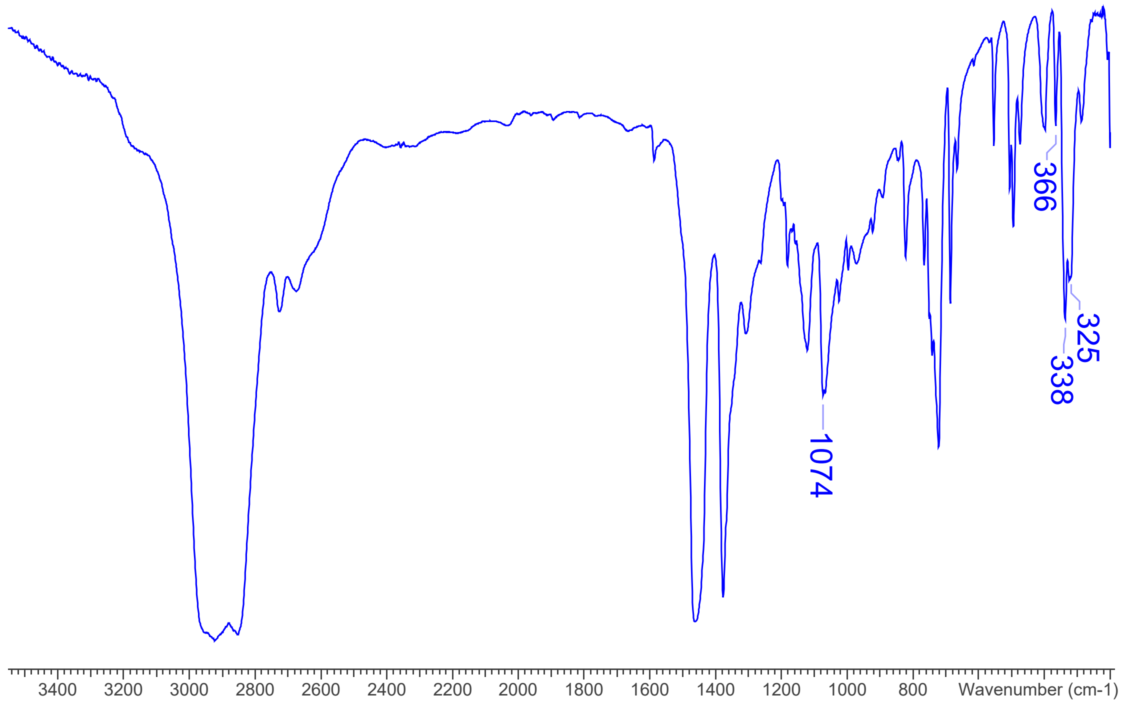


Fig. S19. ^{1}H NMR spectrum of [$(WSeCl_4)(\mu\text{-dppmO}_2)$] recorded *in situ* in C_6D_6

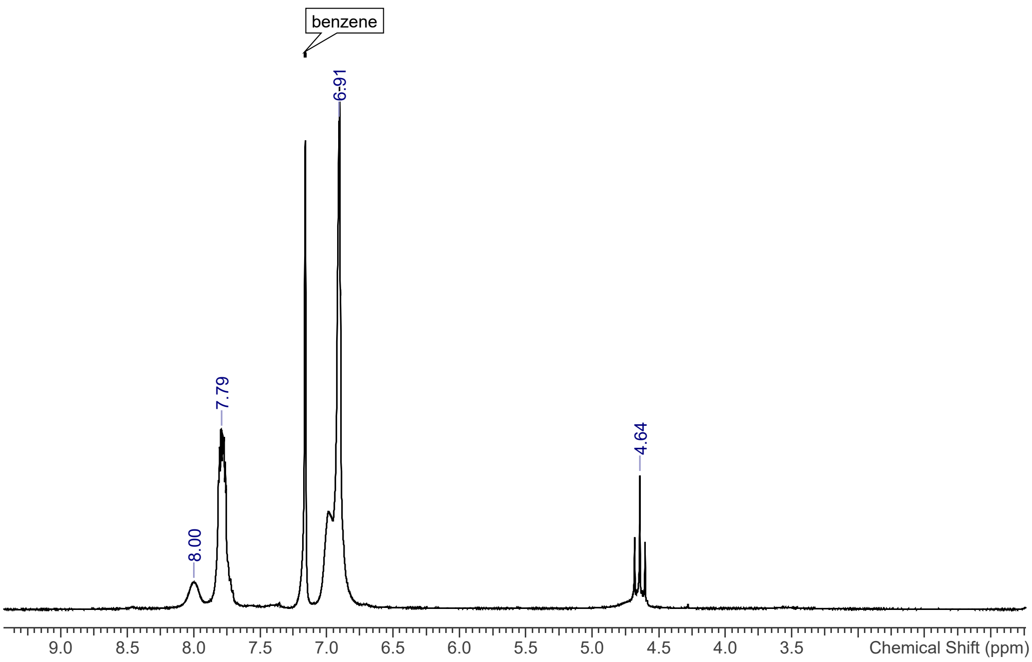


Fig. S20. $^{31}P\{^{1}H\}$ NMR spectrum of [($WSeCl_4$)(μ-dppmO_2)] (C_6D_6)

* Decomposition product

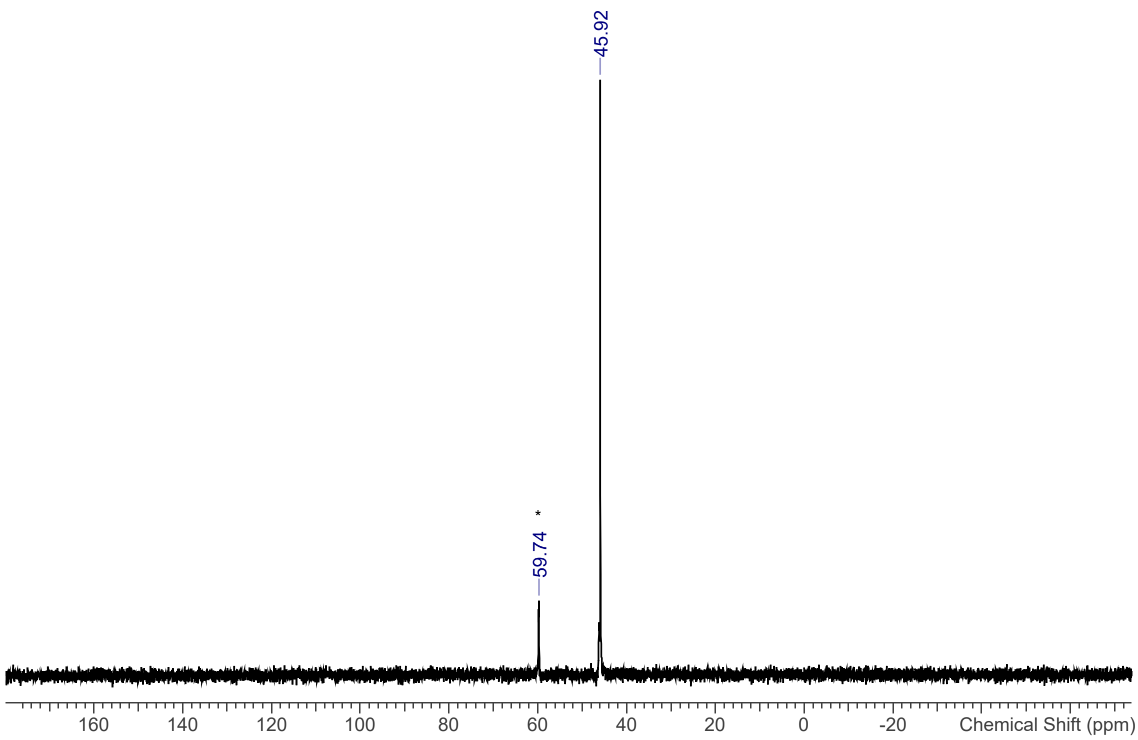


Fig. S21. IR spectrum of [$(WSeCl_4)_2$(1,4 dioxane)] (Nujol)

Fig. S22. [1]H NMR spectrum of [$(WSeCl_4)_2$(1,4 dioxane)] (C_6D_6)

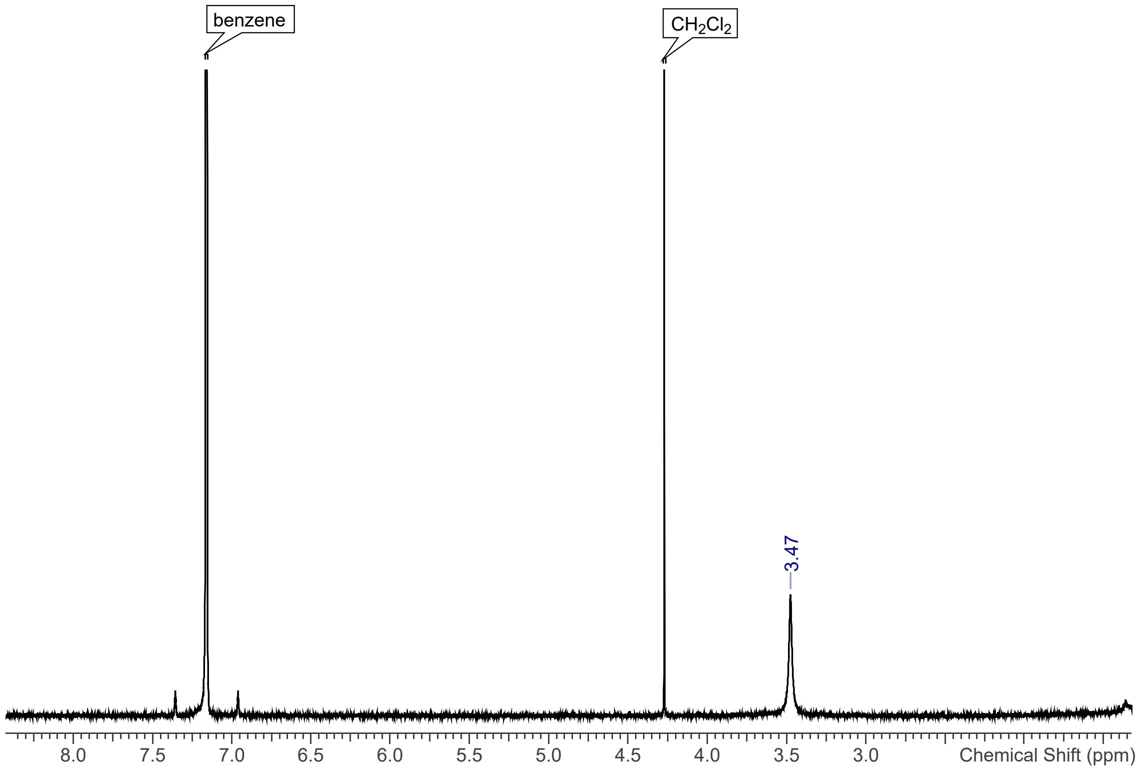


Fig. S23. IR spectrum of [$WSeCl_4(SeMe_2)$] (Nujol)

Fig. S24. ^{1}H NMR spectrum of [$WSeCl_4(SeMe_2)$] (C_6D_6)

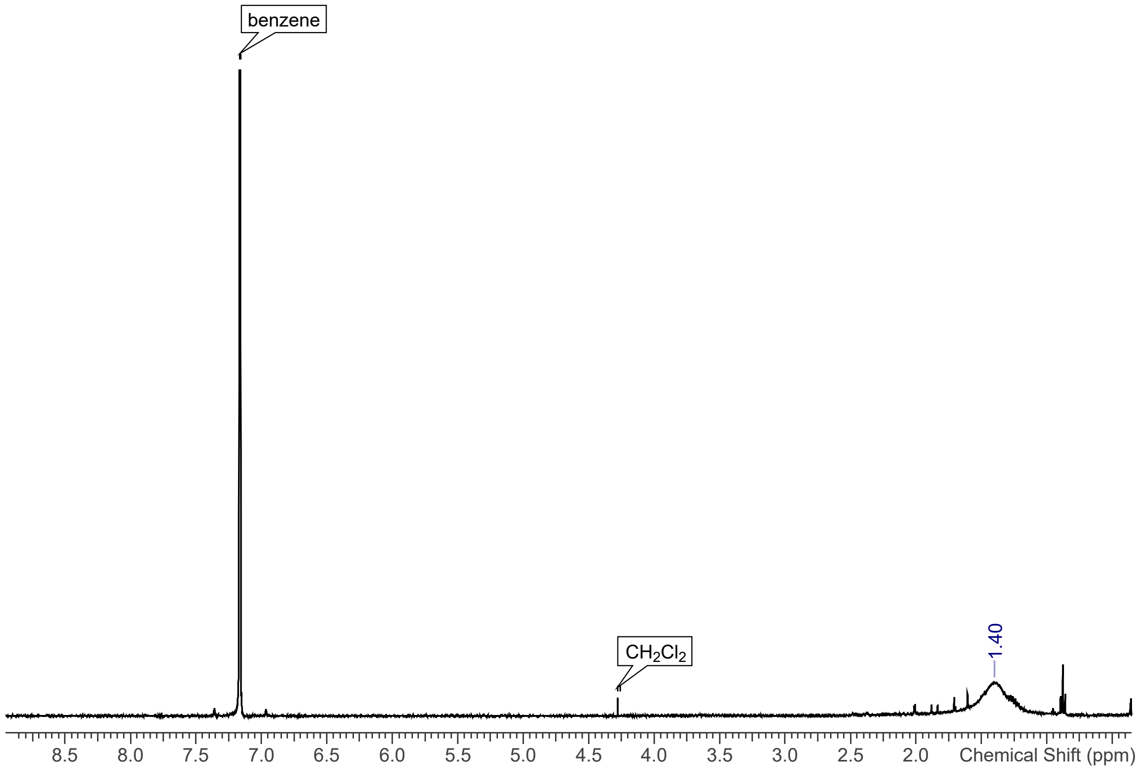


Fig. S25. ^{77}Se{^{1}H} NMR spectrum of [$WSeCl_4(SeBu_2)$] (298 K)

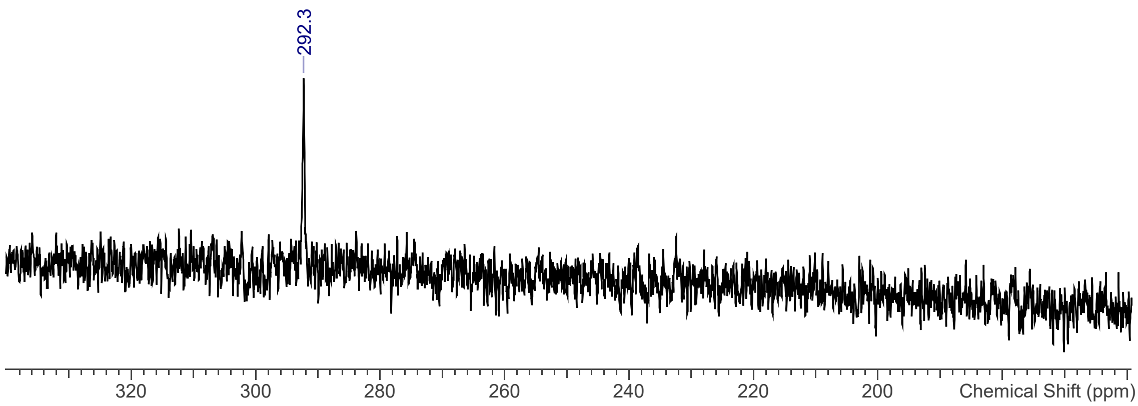


Fig. S26. $^{77}Se\{^1H\}$ NMR spectrum of $[WSeCl_4(SeBu_2)]$ (183 K)

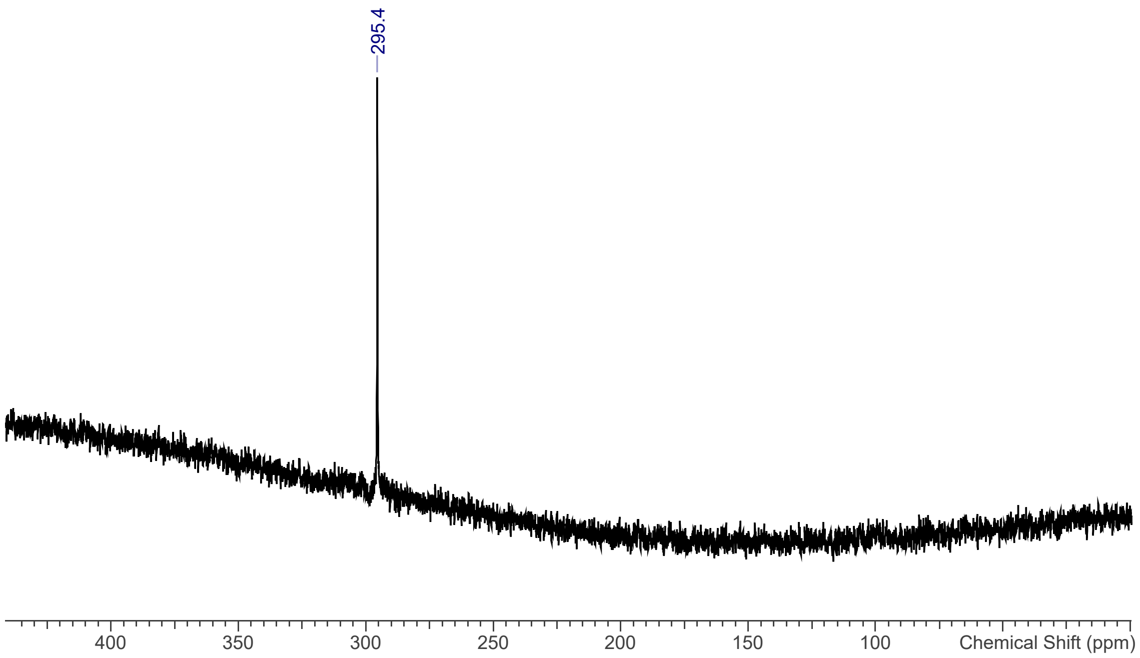


Fig. S27. IR spectrum of $[WSeCl_4(SeBu_2)]$ (Nujol)

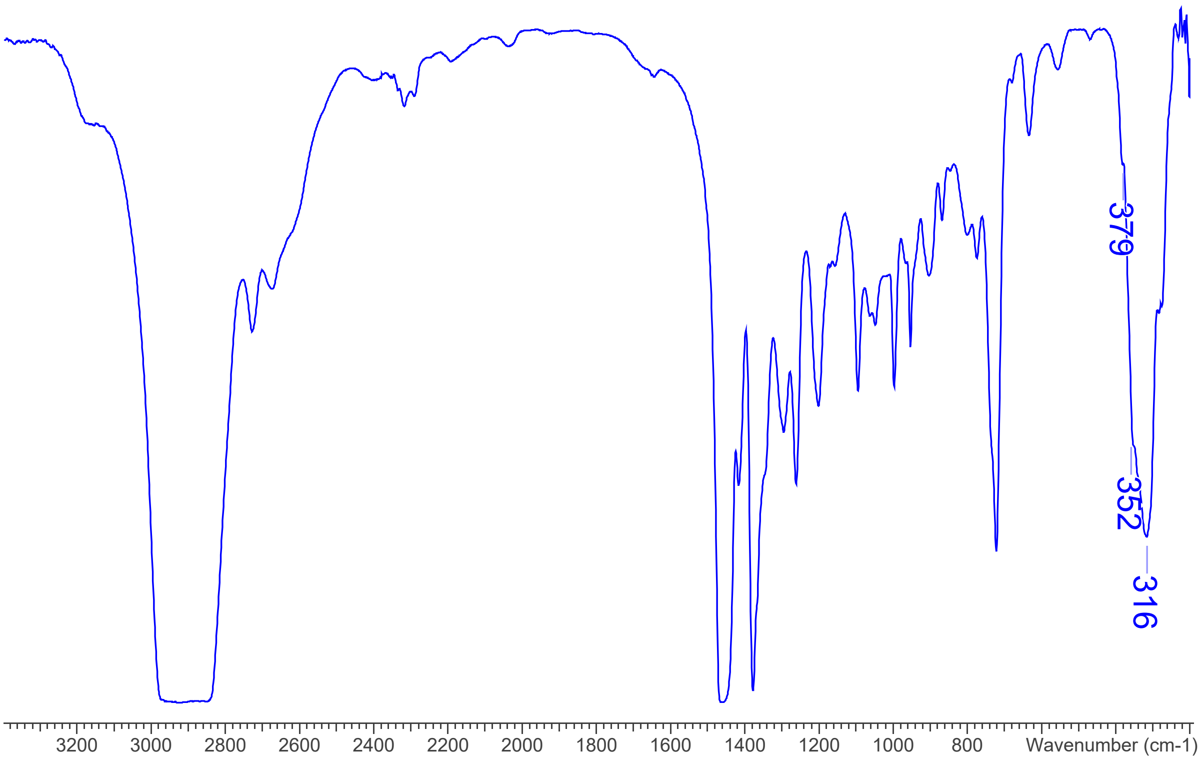


Fig. S28. ^{1}H NMR spectrum of [$WSeCl_4(SeBu_2)$] (C_6D_6)

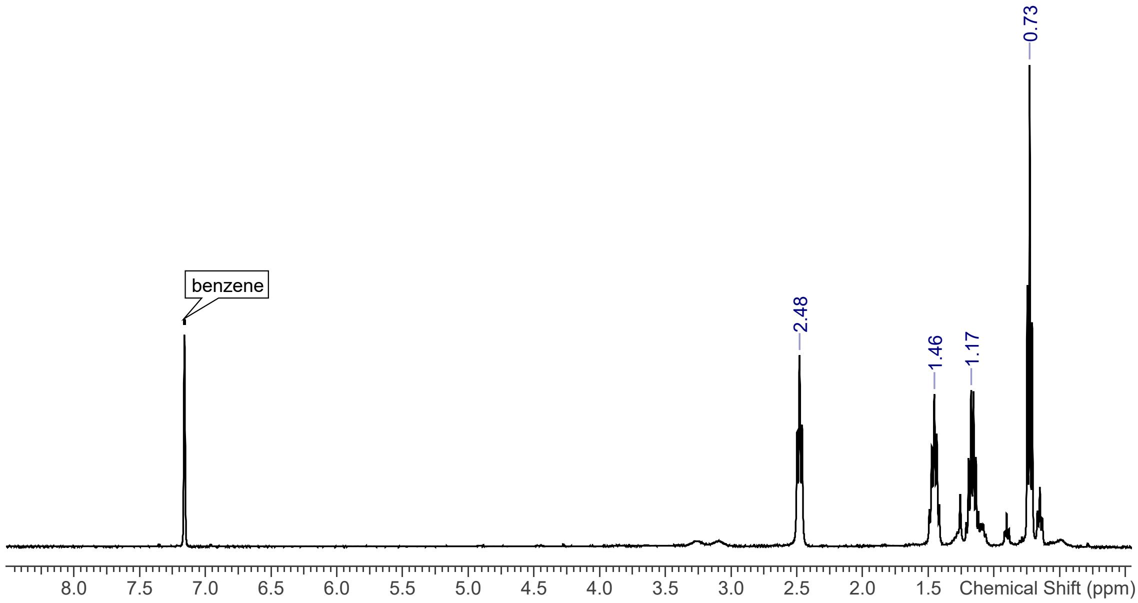
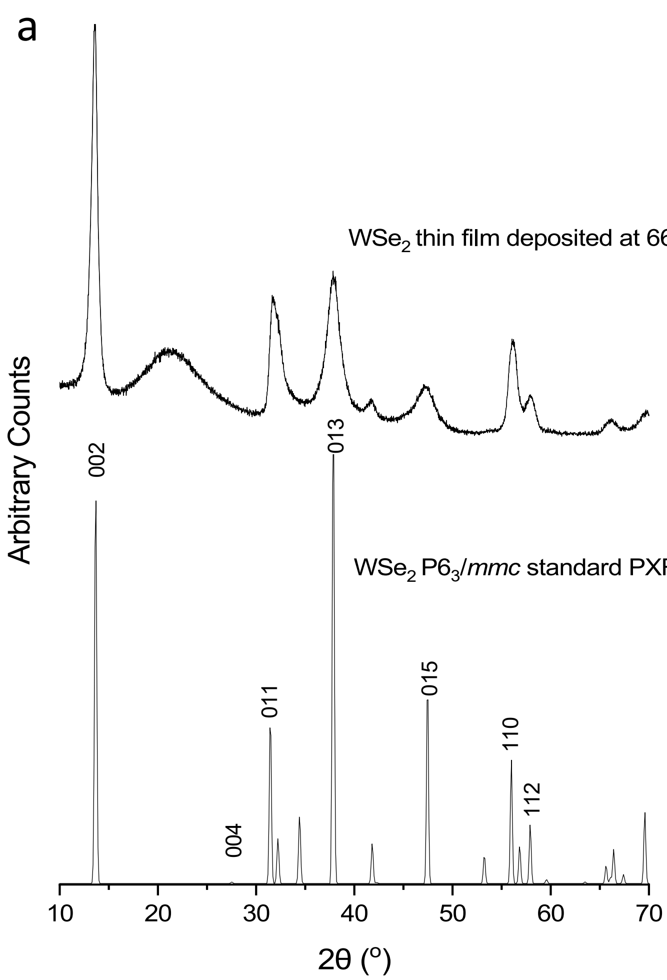
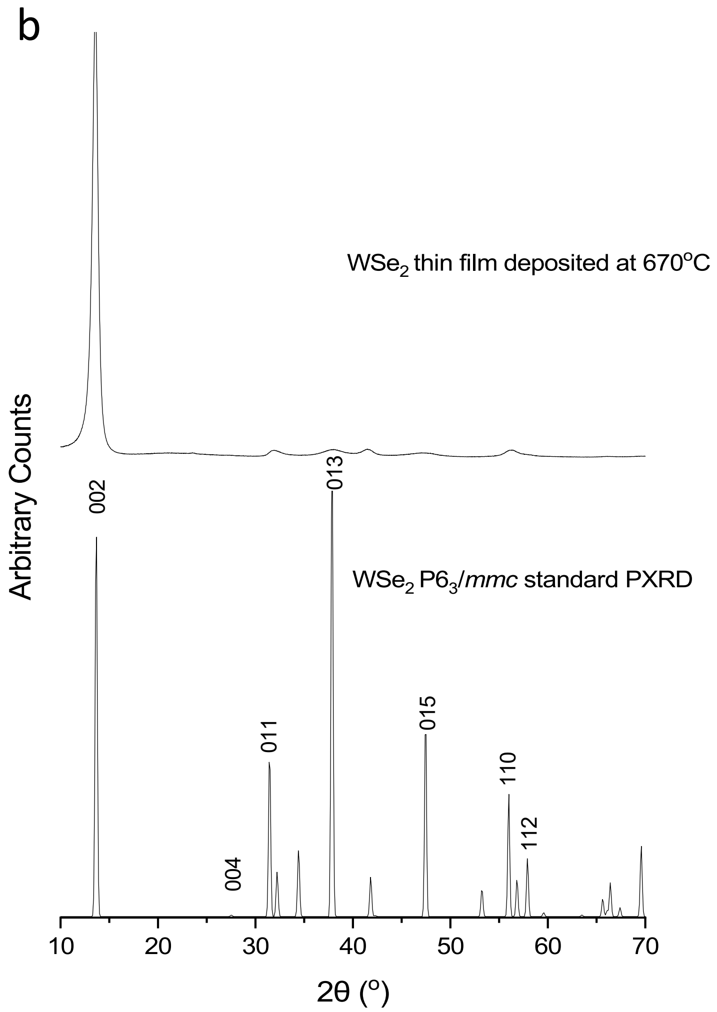


Fig. S29 Grazing incidence XRD patterns from WSe_2 thin films deposited at different temperatures in this work.




b
WSe2 thin film deposited at 670°C
WSe2 P63/mmc standard PXRD
Arbitrary Counts
002
004
011
013
015
110
112
10
20
30
40
50
60
70
2θ (°)

Density Functional Theory (DFT) calculations:

Table S2: Comparative structural data for $WSeCl_4$

$WSeCl_4$	**X-ray**		**E-diffraction***	**DFT****	**Literature calculations**	
W=Se (Å)	2.2099(4)	2.2128(4)	2.203 (4)	2.24460	2.17[a]	2.260[b]
W-Cl (Å)	2.2944(9) 2.3048(8) 2.3045(8) 2.3038(9)	2.2689(8) 2.2762(9) 2.3419(8) 2.3949(8)	2.284 (3)	2.37178 2.38413 2.36433 2.36069	2.33[a]	2.363[b]
Se…Cl (Å)	3.488 3.500 3.508 3.488	3.471 3.445 3.468 3.470	3.545 (9)	3.58184 3.58279 3.58233 3.58269		
Cl…Cl (Å)	3.181 3.203 3.185 3.187	3.220 3.254 3.205 3.255	3.129 (6)	3.18320 3.18395 3.18327 3.18379		
Cl…Cl (Å)	4.516 4.505	4.597 4.549	4.425 (9)	4.50179 4.50266		
Se-W-Cl (°)	101.46 101.45 101.98 101.66	101.49 101.18 98.24 97.65	104.4 (3)	104.13557 104.18248 104.15197 104.16753	105[a]	103.6[b]
Cl-W-Cl (°)	87.68 87.75 87.30 88.06	88.58 91.45 88.32 85.15	86.5 (2)	86.55511 86.58812 86.56221 86.57228		

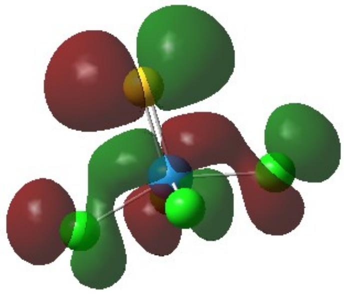
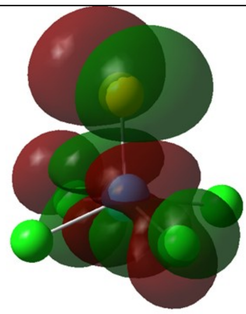
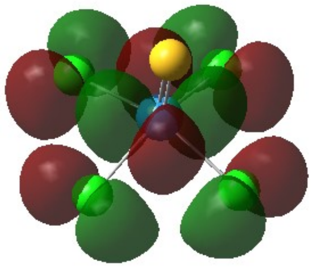
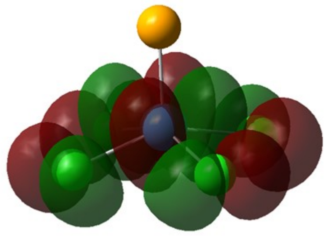
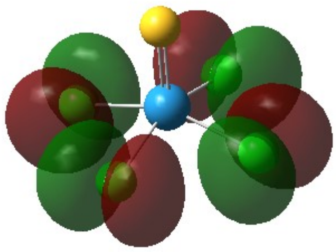
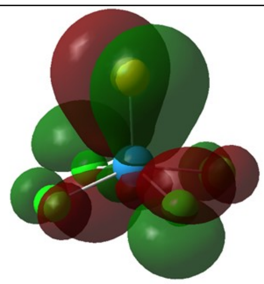
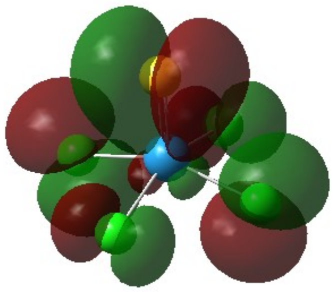
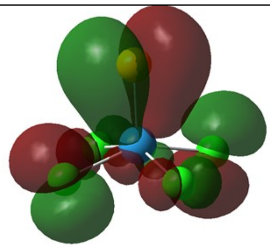
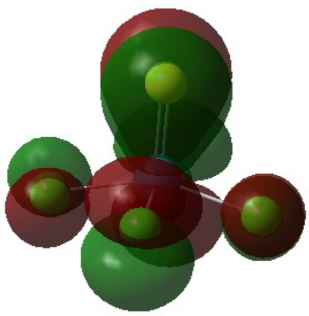
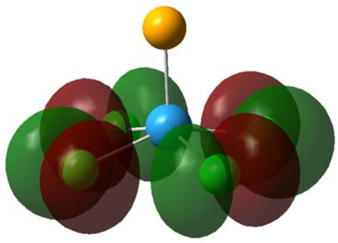
* Diffraction data: https://pubs.acs.org/doi/pdf/10.1021/ic00139a006

** DFT (6-311G* on Se, Cl and LanL2dz on W)

[a] *ab initio* molecular quantum chemistry calculations using GAMESS (Ref. 1)

[b] DFT calculations using ADF program (Ref. 2)

Fig. S30: Frontier molecular orbitals of $WSCl_4$ and $WSeCl_4$

eV	$WSCl_4$	eV	$WSeCl_4$
LUMO+1 -4.50		LUMO+1 -4.50	
LUMO -5.49		LUMO -5.34	
HOMO -8.74		HOMO -8.54	
HOMO-1 -8.93		HOMO-1 -8.55	
HOMO-2 -8.93		HOMO-2 -8.65	

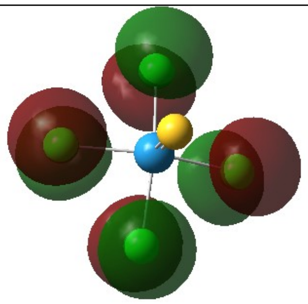
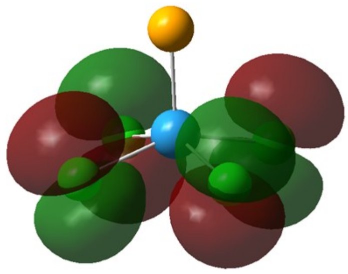
HOMO-3 -9.39		HOMO-3 -9.29	

Table S3: Comparative structural data for $WECl_4(OPPh_3)$ (E = S, Se) bond distances (Å)

	[$WSCl_4(OPPh_3)$]		**[$WSeCl_4(OPPh_3)$]**	
	X-ray*	**DFT**	**X-ray**	**DFT**
W-E	2.0938(6)	2.11048	2.2321(2)	2.24460
W-Cl	2.3196(6) 2.3141(6) 2.23488(5) 2.3447(7)	2.36959 2.36256 2.35912 2.38193	2.3514(5) 2.3577(5) 2.3217(5) 2.3218(5)	2.37178 2.38413 2.36433 2.36069
W-O	2.163(2)	2.14443	2.1669(14)	2.14717

*data from Ref. 3

Table S4: Energies of monomers and dimers of $WECl_4$ (E = S, Se)

	au
$WSCl_4$	-2307.141894
WS dimer	-4614.313648
$WSeCl_4$	-4310.482002
WSe dimer	-8620.993048

Table S5: Energies of [$WECl_4(OPPh_3)$] (E = S, Se)

	au
$OPPh_3$	-1111.827444
$WSCl_4$	-2307.141894
$WSeCl_4$	-4310.482002
[$WSCl_4(OPPh_3)$]	-3419.030719
[$WSeCl_4(OPPh_3)$]	-5422.369043

References

1. M. T. Benson, T. R. Cundari, S. J. Lim, H. D. Nguyen and K. Pierce-Beaver, *J. Am. Chem. Soc.*, 1994, **116**, 3955.
2. Ò. González-Blanco, V. Branchadell, K. Monteyne and T. Ziegler, *Inorg. Chem.*, 1998, **37**, 1744.
3. V. K. Greenacre, A. L. Hector, W. Levason, G. Reid, D. E. Smith and L. Sutcliffe, *Polyhedron,* 2019*,* **162,** 14.