ESI for

Thioether complexes of $WSCl_4$, $WOCl_4$ and $WSCl_3$ and evaluation of thiochloride complexes as CVD precursors for WS_2 thin films

Danielle E. Smith[a], Victoria K. Greenacre[a], Andrew L. Hector[a], Ruomeng Huang[b], William Levason[a], Gillian Reid[a]*, Fred Robinson[a] and Shibin Thomas[a]

[a] School of Chemistry, University of Southampton, Southampton SO17 1BJ, UK; email: G.Reid@soton.ac.uk

[b] School of Electronics and Computer Science, University of Southampton, Southampton SO17 1BJ, UK

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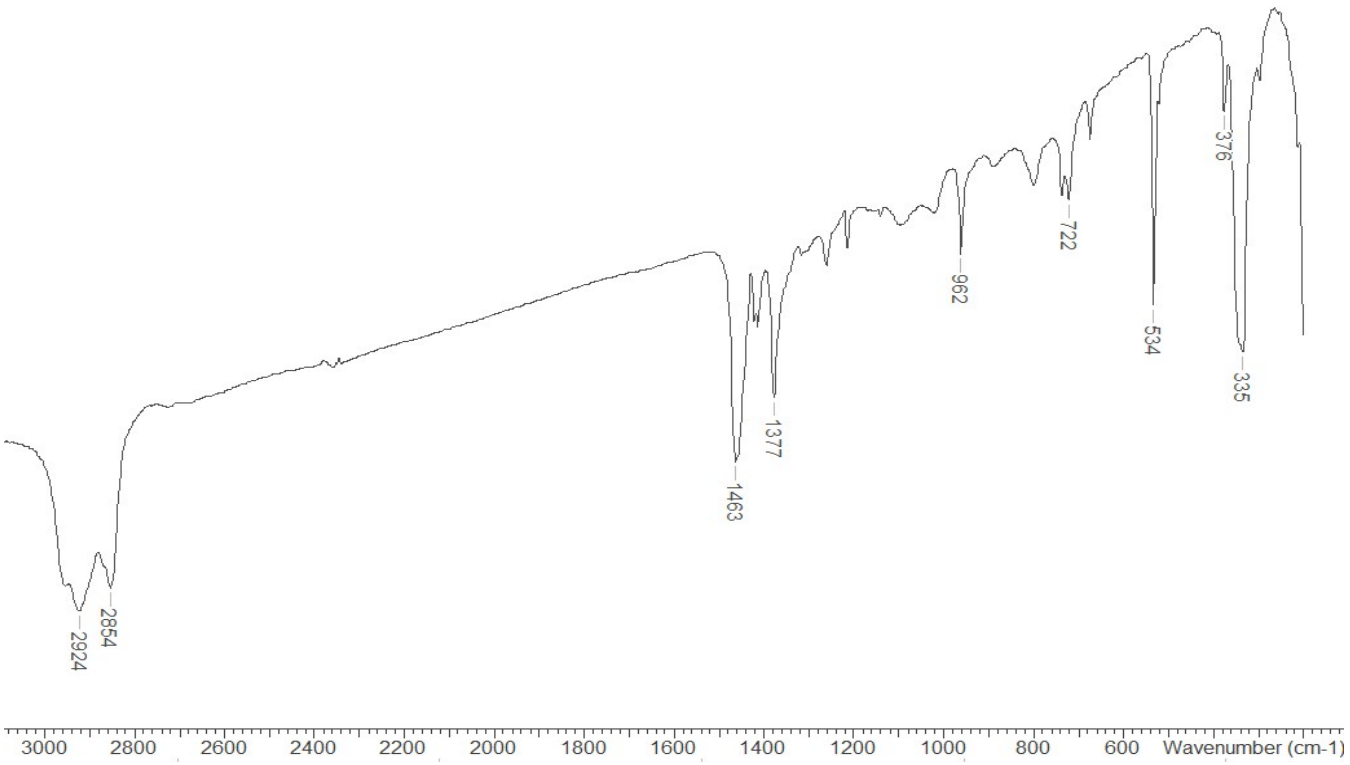


Figure 1: IR spectrum of $[(WSCl_4)_2\{MeS(CH_2)_2SMe\}]$ (Nujol).

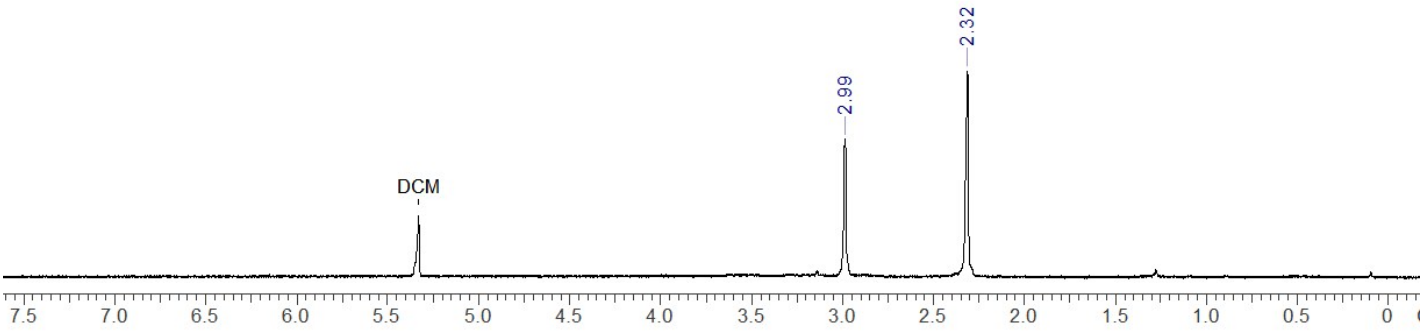


Figure 2: ^1H NMR spectrum of $[(WSCl_4)_2\{MeS(CH_2)_2SMe\}]$ in CD_2Cl_2.

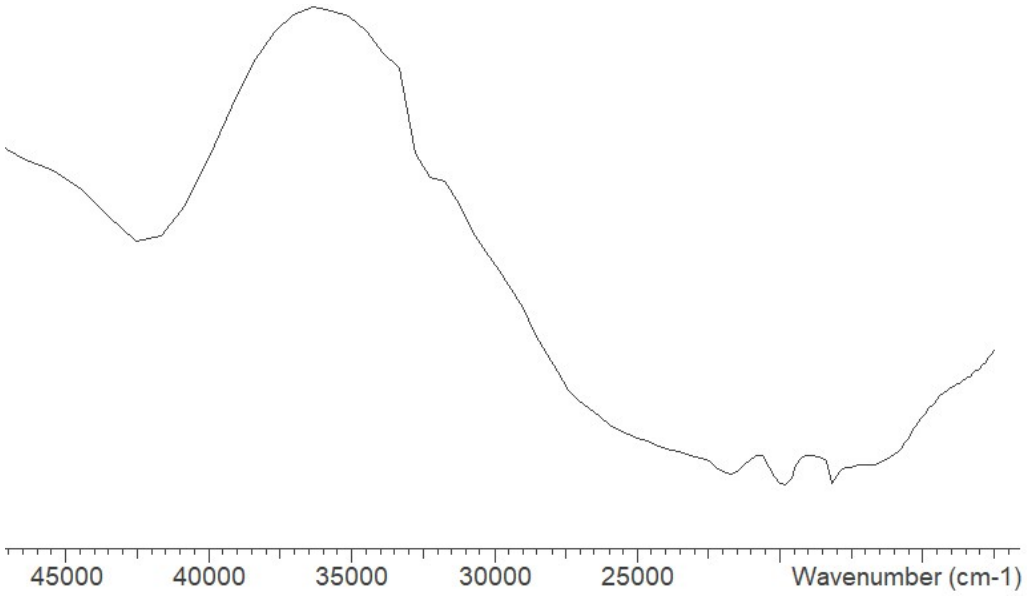


Figure 3: UV/Vis spectrum (diffuse reflectance) for [$(WSCl_4)_2${$MeS(CH_2)_2SMe$}].

Data for [$(WSCl_4)_2(MeS(CH_2)_3SMe)$]

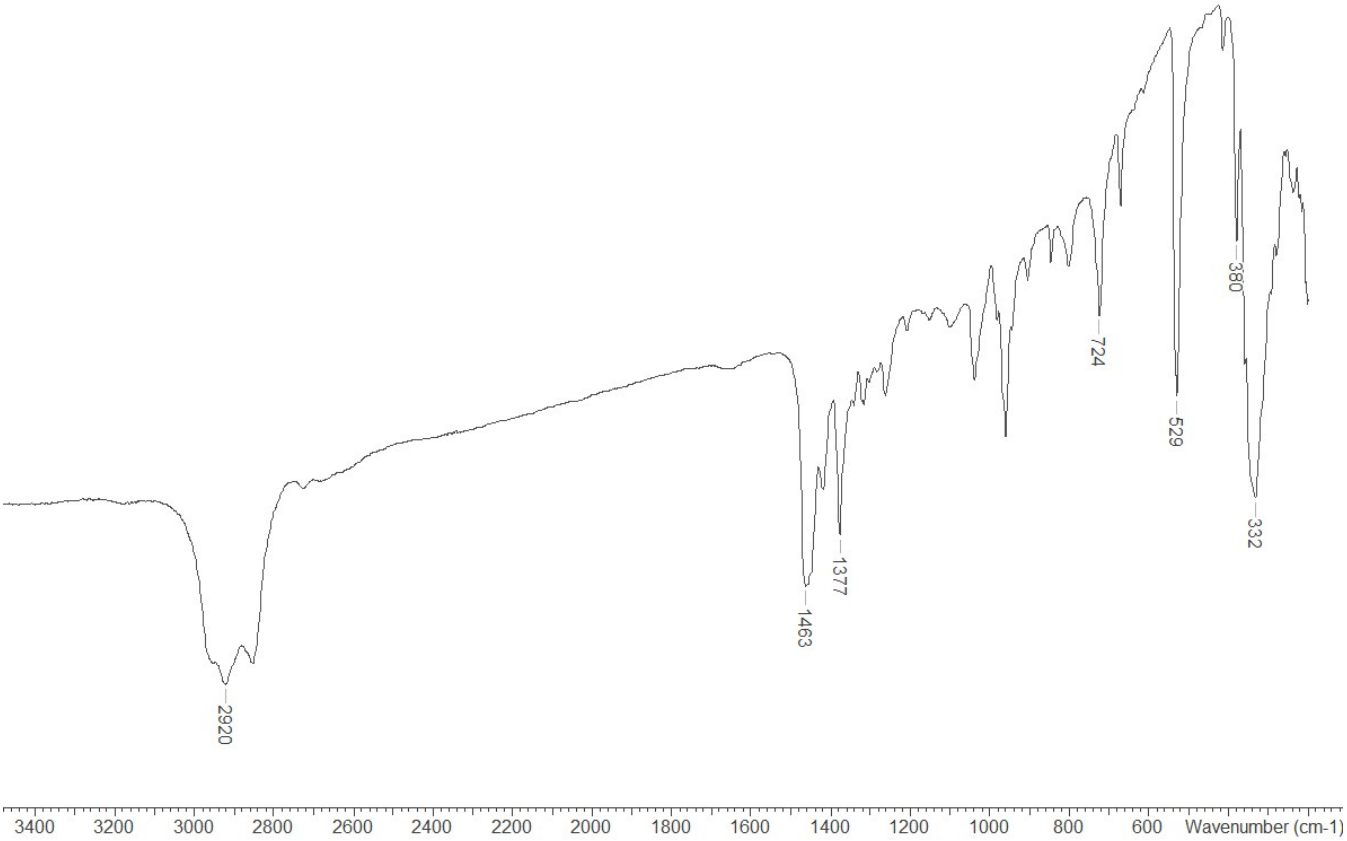


Figure 4: IR spectrum of [$(WSCl_4)_2${$MeS(CH_2)_3SMe$}] (Nujol).

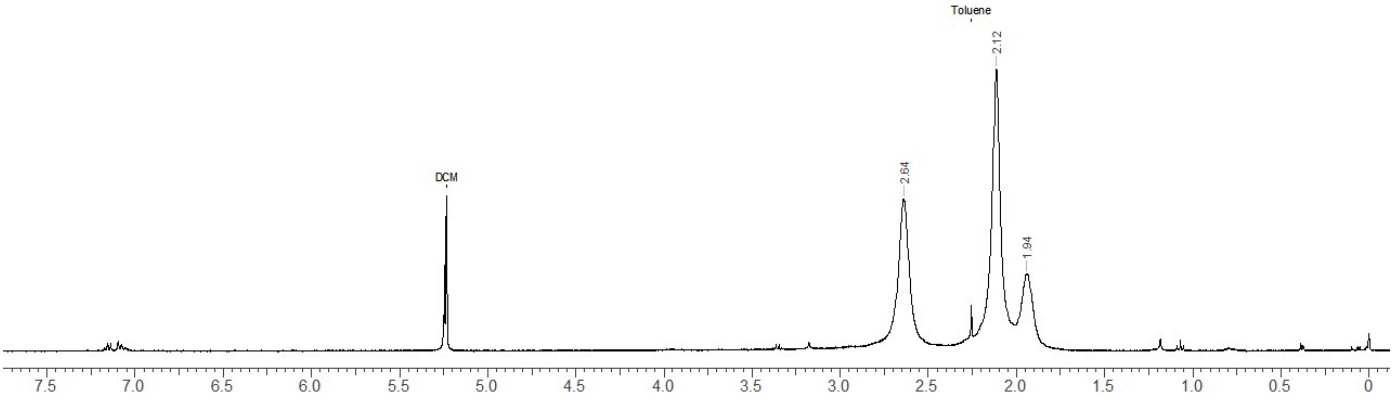


Figure 5: ^{1}H NMR spectrum of $[(WSCl_4)_2\{MeS(CH_2)_3SMe\}]$ in CD_2Cl_2

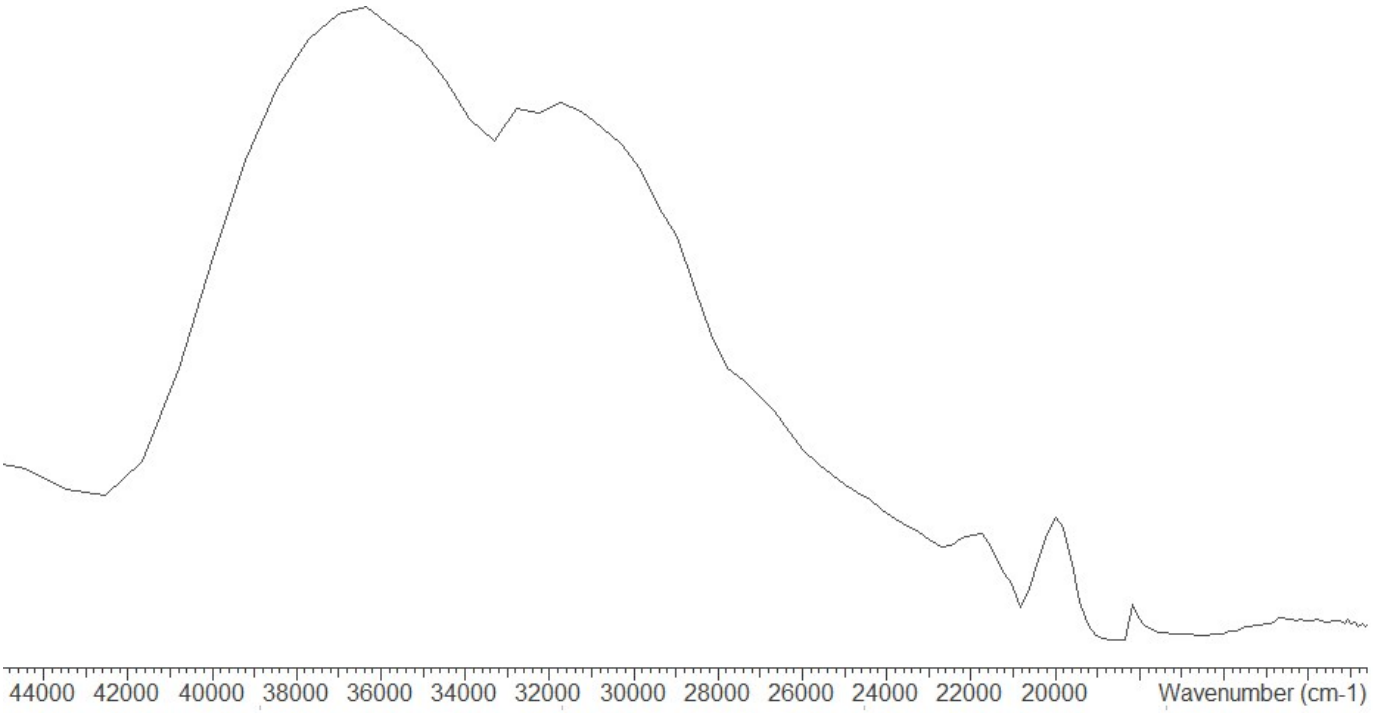


Figure 6: UV/Vis spectrum (diffuse reflectance) for $[(WSCl_4)_2\{MeS(CH_2)_3SMe\}]$.

Data for $[(WSCl_4)_2\{^iPrS(CH_2)_2S^iPr\}]$

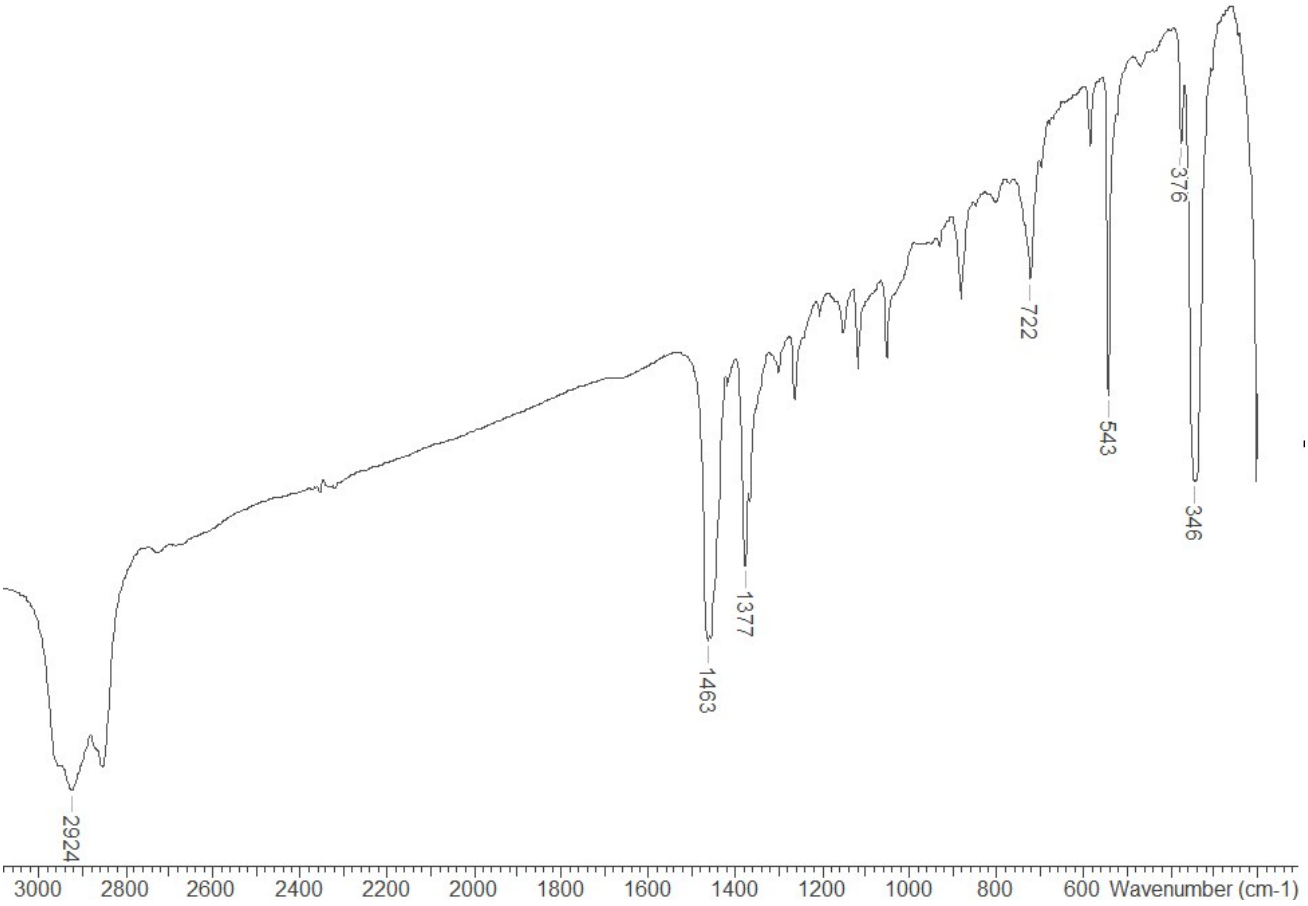


Figure 7: IR spectrum of $[(WSCl_4)_2\{^iPrS(CH_2)_2S^iPr\}]$ (Nujol).

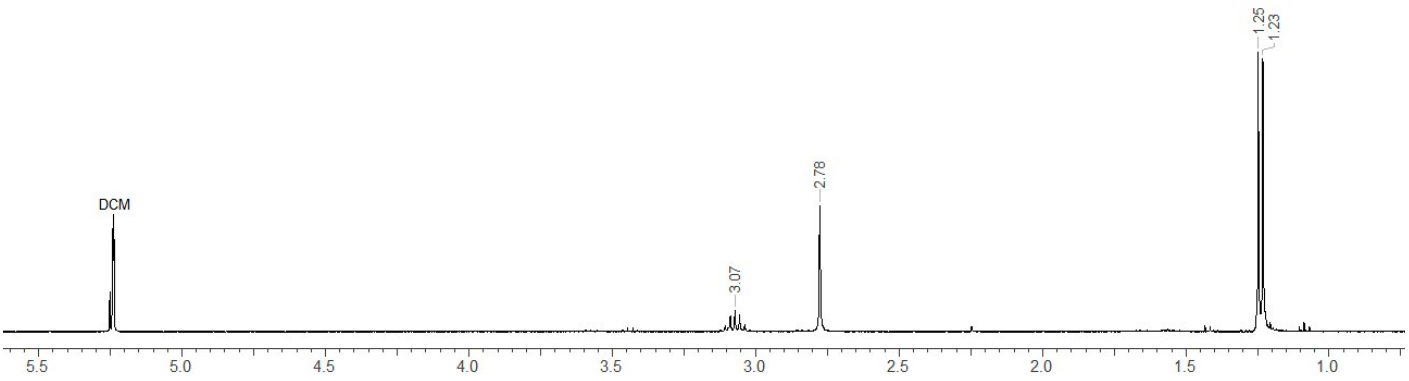


Figure 8: ^1H NMR spectrum of $[(WSCl_4)_2(^iPrS(CH_2)_2S^iPr\}]$ in CD_2Cl_2

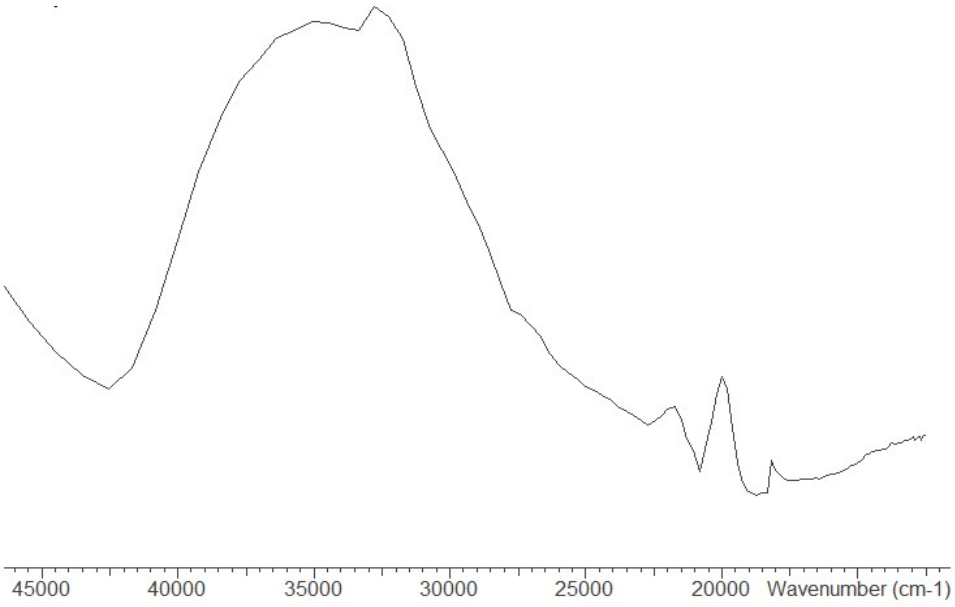


Figure 9: UV/Vis spectrum (diffuse reflectance) for [$(WSCl_4)_2$(^{i}PrS$(CH_2)_2$S^{i}Pr}].

Data for [$(WSCl_4)_2${PhS$(CH_2)_2$SPh}]

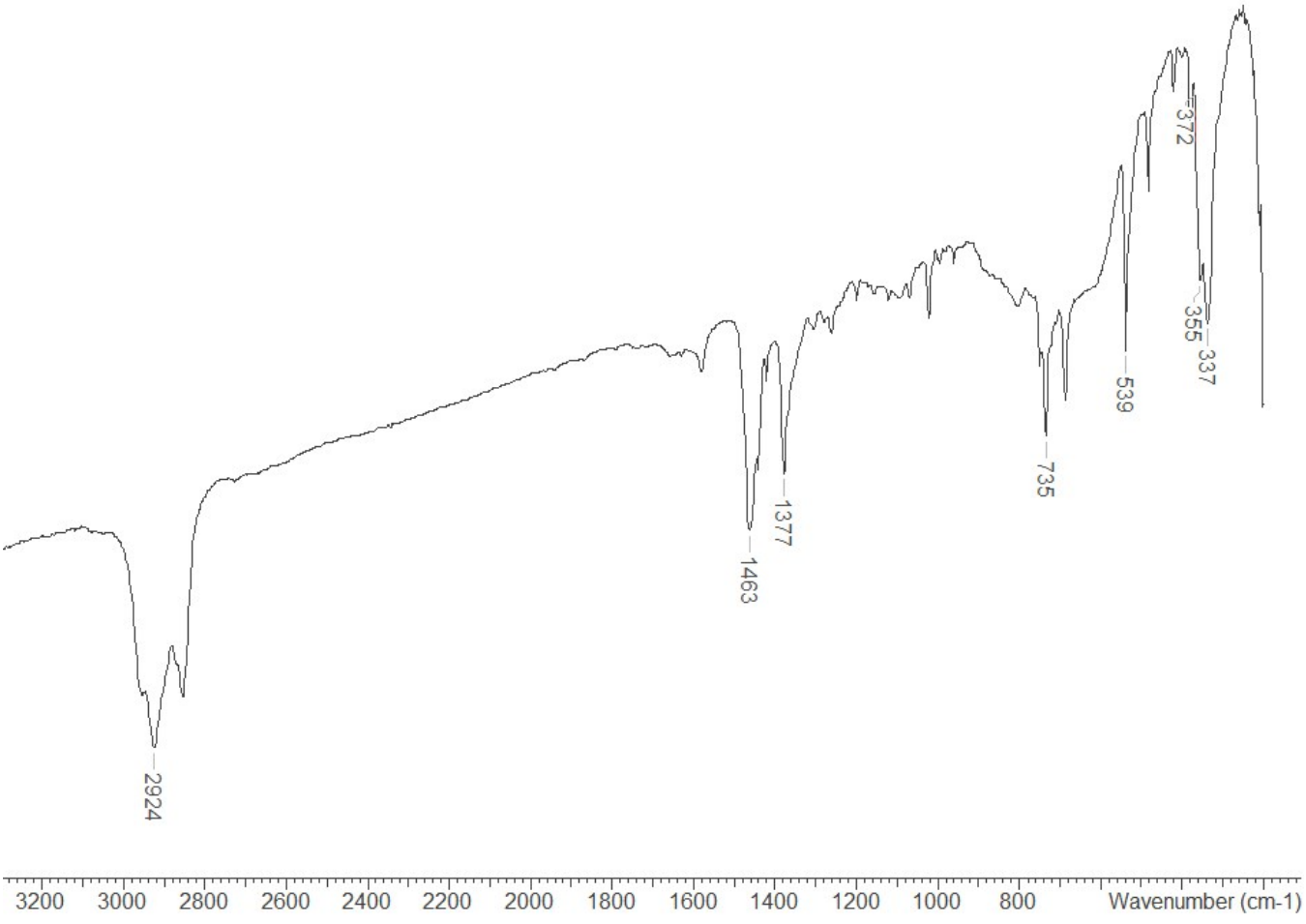


Figure 10: IR spectrum of [$(WSCl_4)_2${PhS$(CH_2)_2$SPh}] (Nujol).

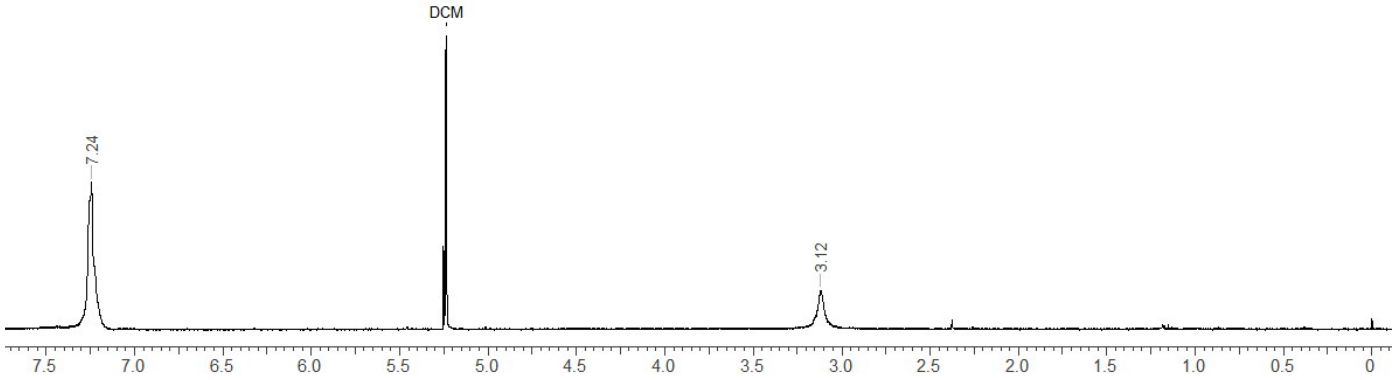


Figure 11: ^{1}H NMR spectrum of $[(WSCl_4)_2\{PhS(CH_2)_3SPh\}]$ in CD_2Cl_2

Data for $[WSCl_4(SMe_2)]$

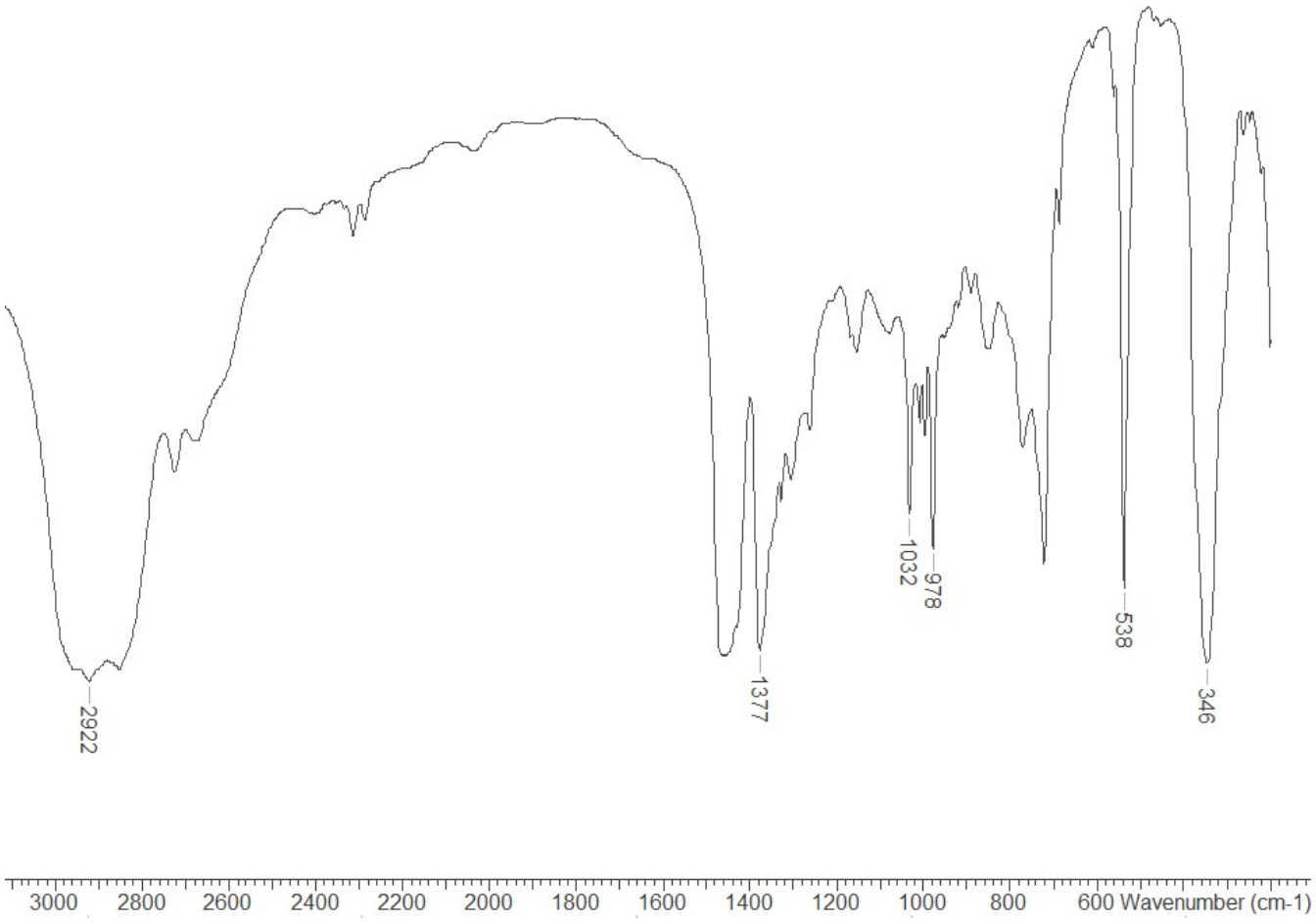


Figure 12: IR spectrum of $[WSCl_4(SMe_2)]$ (Nujol).

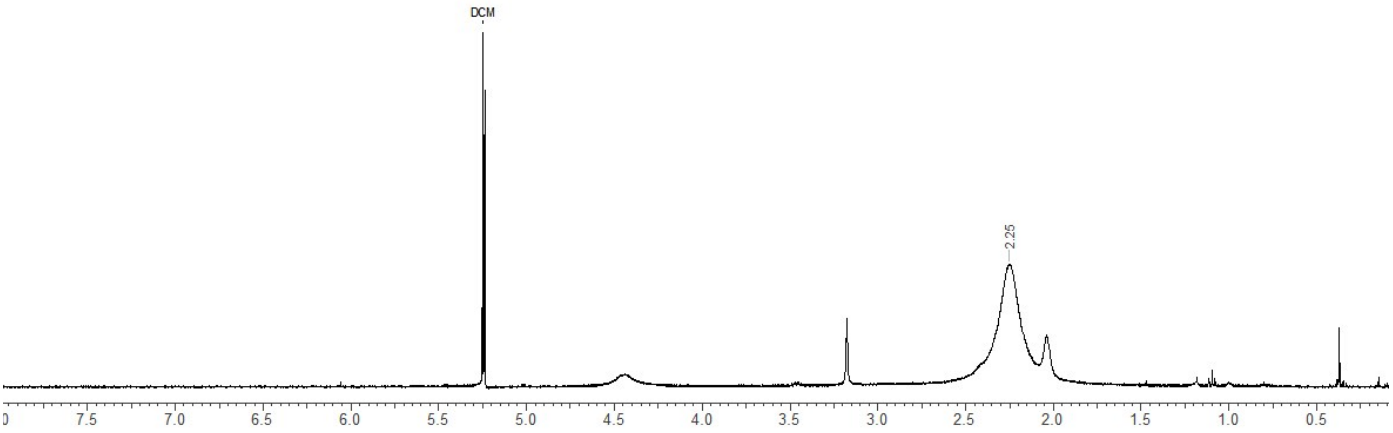


Figure 13: ^{1}H NMR spectrum of $[WSCl_4(SMe_2)]$ in CD_2Cl_2.

Data for $[WSCl_4(SeMe_2)]$

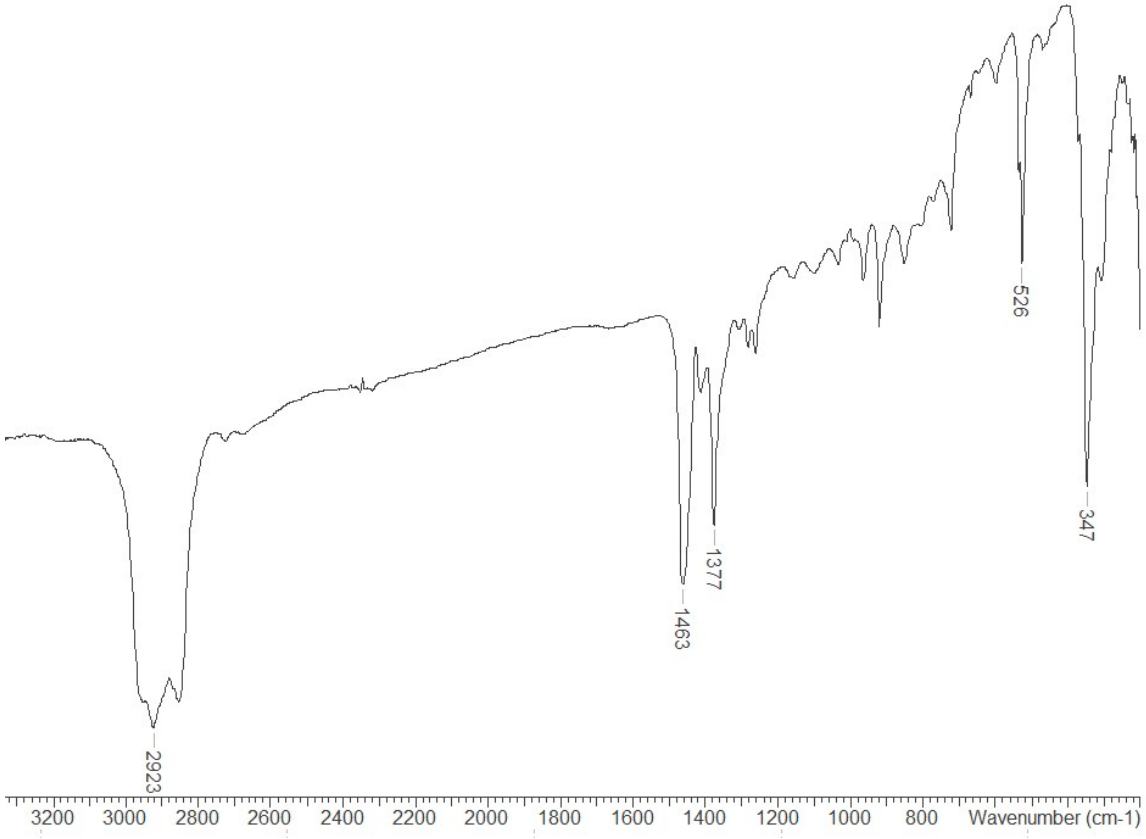
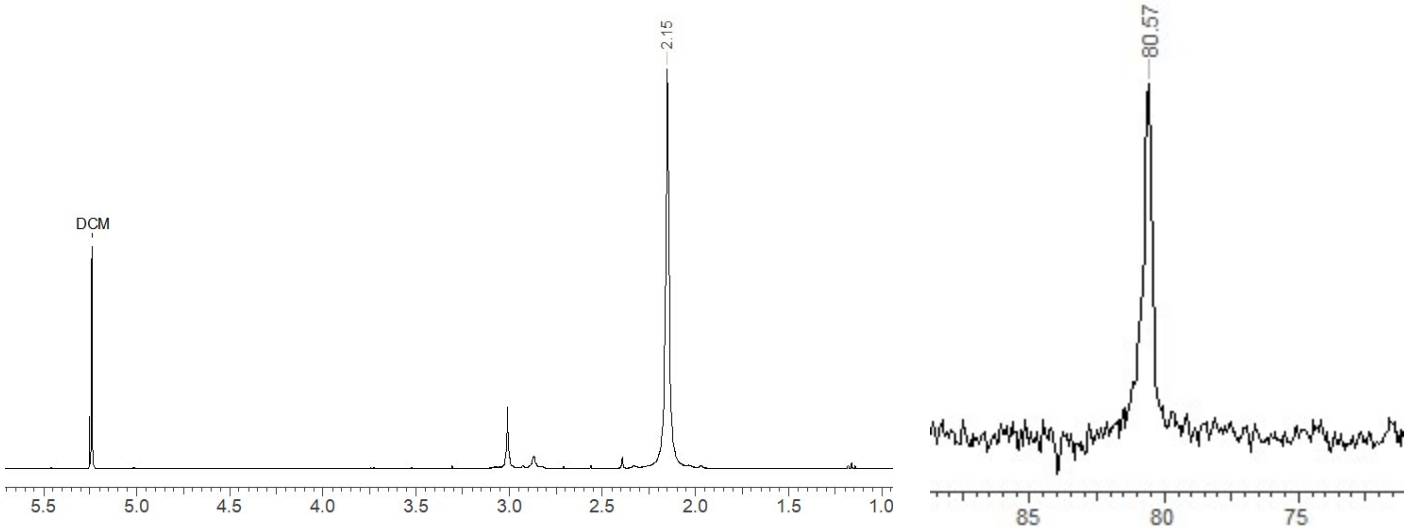


Figure 14: IR spectrum of $[WSCl_4(SeMe_2)]$ (Nujol).



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Data for [$WSCl_3\{MeS(CH_2)_2SMe\}$]

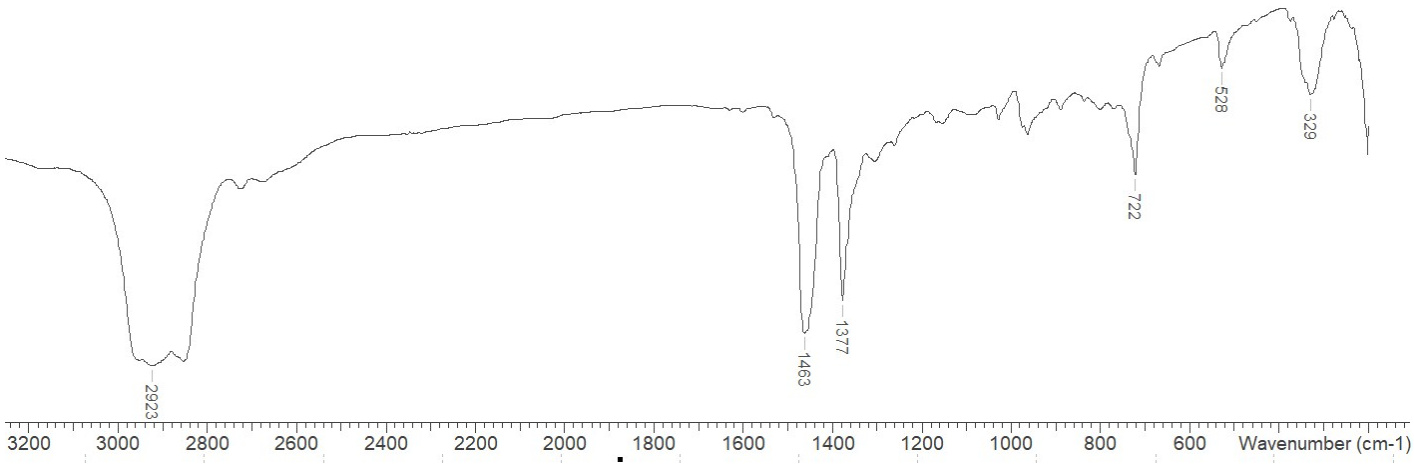

Figure 16: IR spectrum of [$WSCl_3\{MeS(CH_2)_2SMe\}$] (Nujol).

Data for $[WSCl_3\{^iPrS(CH_2)_2S^iPr\}]$

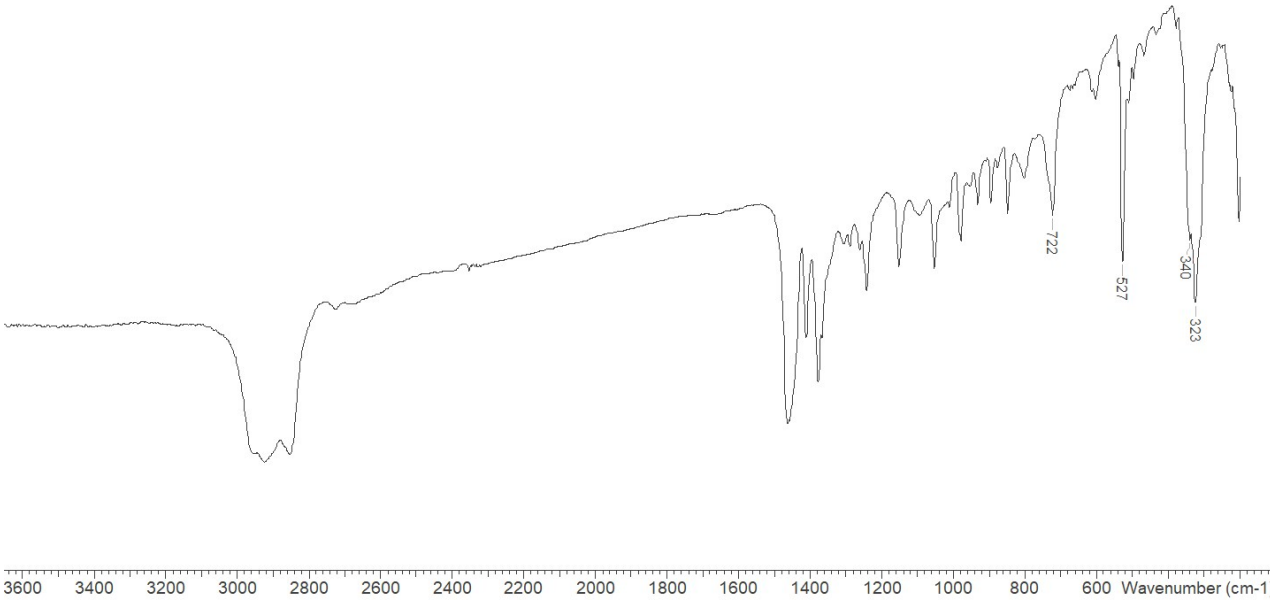

Figure 17: IR spectrum of $[WSCl_3\{^iPrS(CH_2)_2S^iPr\}]$ (Nujol).

Data for $[(WOCl_4)_2\{^iPrS(CH_2)_2S^iPr\}]$

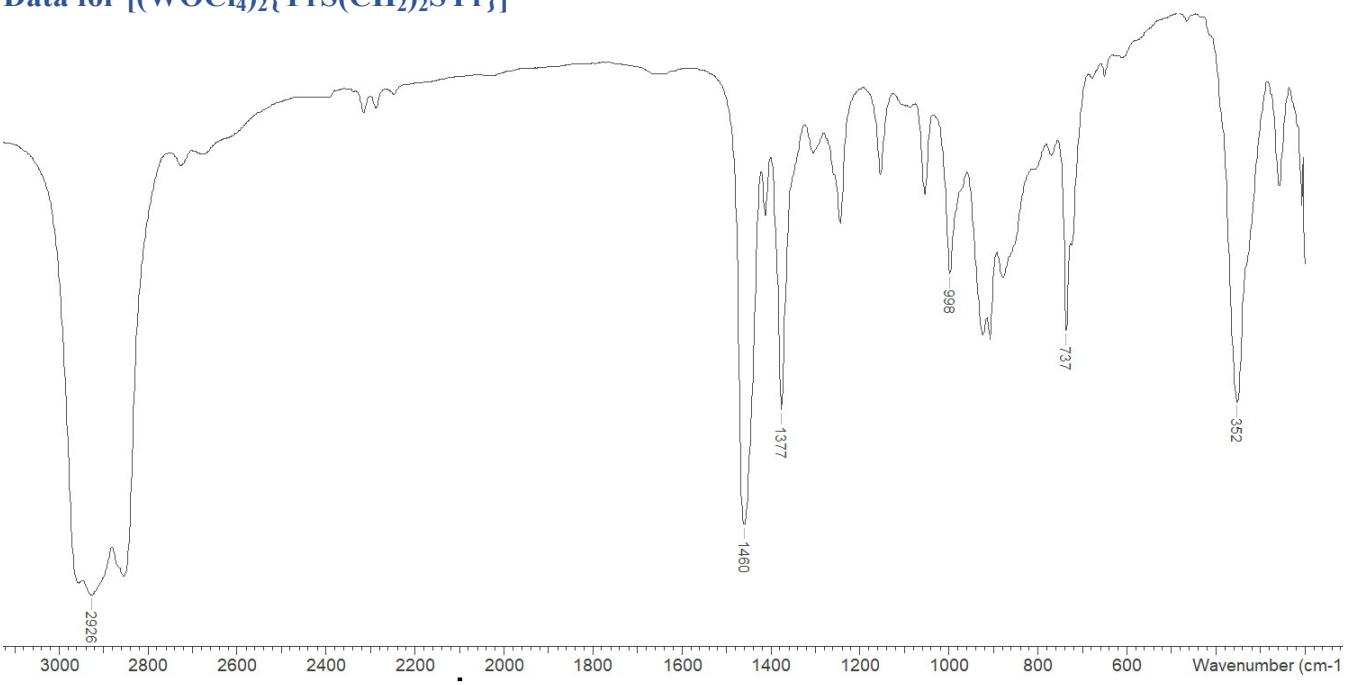

Figure 18: IR spectrum of $[(WOCl_4)_2\{^iPrS(CH_2)_2S^iPr\}]$ (Nujol).

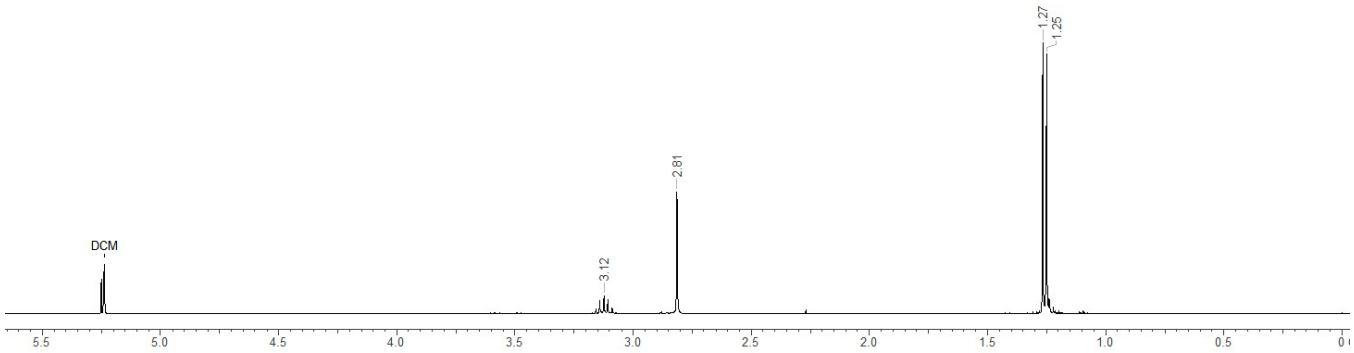

Figure 19: ^1H NMR spectrum of $[(WOCl_4)_2\{^iPrS(CH_2)_2S^iPr\}]$ in CD_2Cl_2

Data for $[(WOCl_4)_2\{PhS(CH_2)_2SPh\}]$

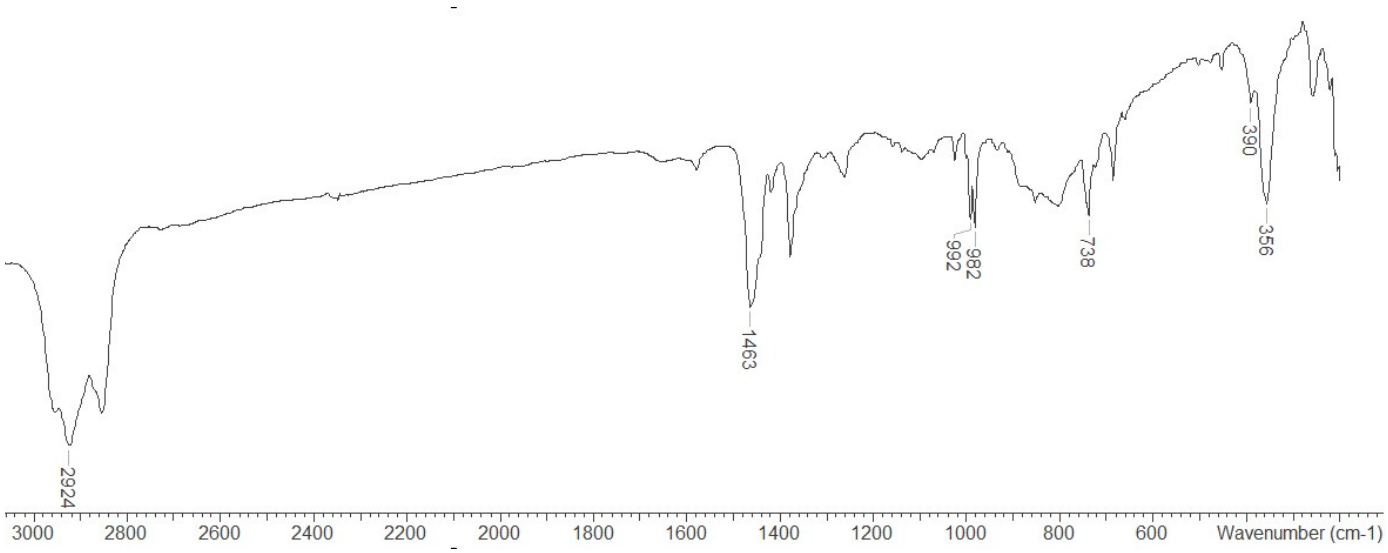

Figure 20: IR spectrum of $[(WOCl_4)_2\{PhS(CH_2)_2SPh\}]$ (Nujol).

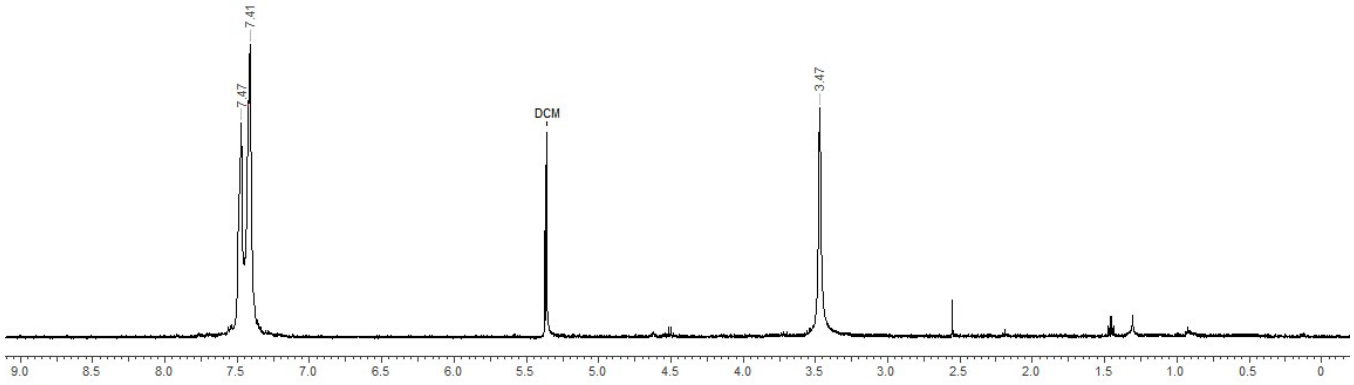

Figure 21: ^1H NMR spectrum of $[(WOCl_4)_2\{PhS(CH_2)_2SPh\}]$ in CD_2Cl_2

Data for $[WOCl_4(SMe_2)]$

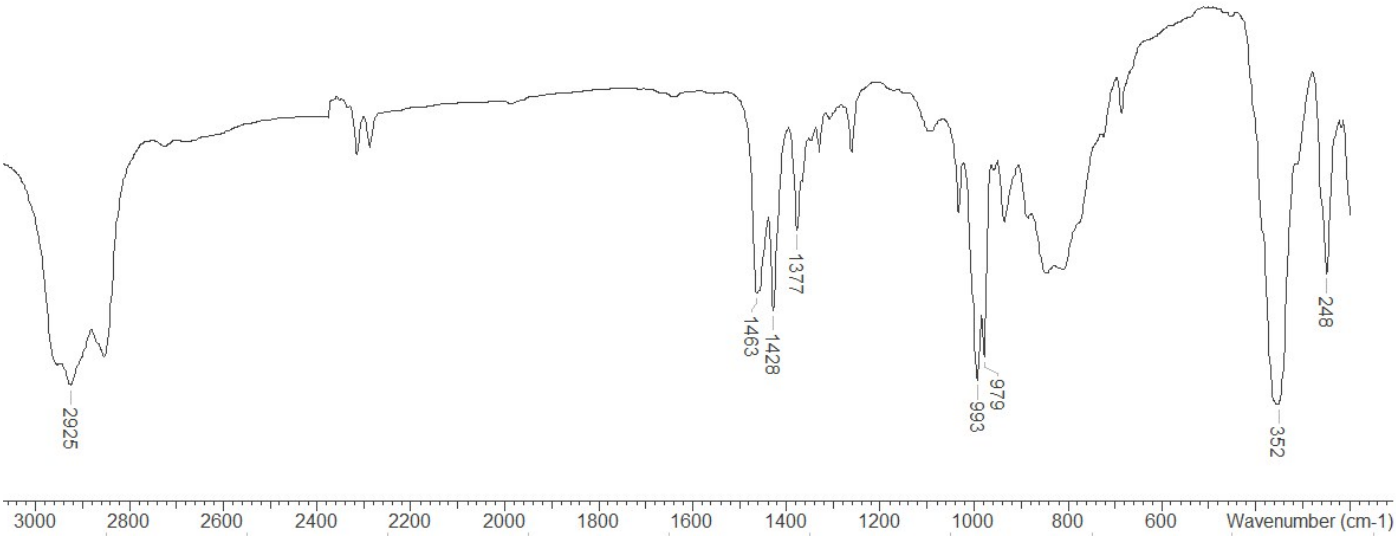

Figure 22: IR spectrum of $[WOCl_4(SMe_2)]$ (Nujol).

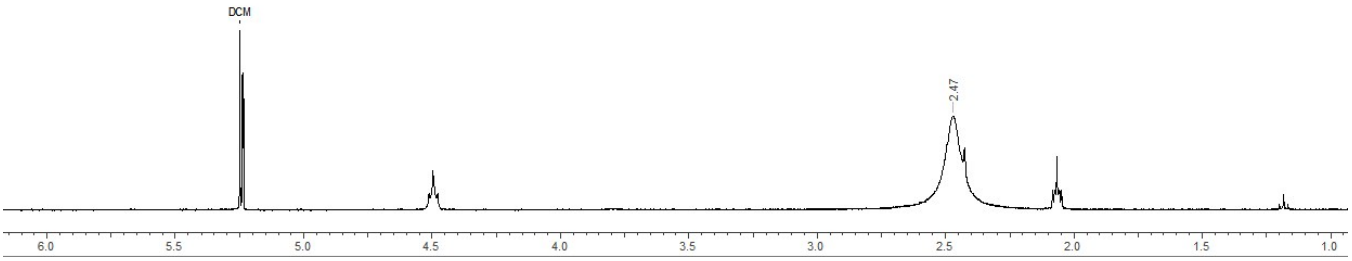

Figure 23: ^1H NMR spectrum of $[WOCl_4(SMe_2)]$ in CD_2Cl_2.

Crystallographic parameters

Table 1: X-ray crystallographic data

Compound	$[(WSCl_4)_2\{PhS(CH_2)_2SPh\}]$	$[(WSCl_4)_2\{MeS(CH_2)_2SMe\}]$	$[(WSCl_4)_2\{^iPrS(CH_2)_2S^iPr\}]$
Formula	$C_{14}H_{14}Cl_8S_2W_2$	$C_4H_{10}Cl_8S_4W_2$	$C_8H_{18}Cl_8S_2W_2$
M	961.79	837.66	893.76
Crystal system	monoclinic	monoclinic	monoclinic
Space group (no)	$P2_1/n$ (14)	$P2_1/c$ (14)	$P2_1/c$ (14)
a/Å	10.5790(2)	7.6849(2)	10.7903(2)
b/Å	13.9272(3)	10.5079(3)	8.89710(10)
c/Å	17.2182(4)	11.8240(4)	12.1898(2)
α/°	90	90	90
β/°	96.368(2)	91.882(3)	106.732(2)
γ/°	90	90	90
U/Å^3	2521.21(9)	954.30(5)	1120.70(3)
Z	4	2	2
μ(Mo-Kα)/mm^{-1}	10.300	13.581	11.574
F(000)	1784	764	828
Total Reflns.	17788	13938	18750
R_{int}	0.070	0.141	0.061
Unique Reflns.	6811	1864	2199
Parameters/restraints	253, 0	83, 0	102, 0
GOF	0.968	1.113	1.180
R_1, $wR_2(I>2\sigma I)$	0.042, 0.071	0.057, 0.148	0.039, 0.087
R1, wR2(all data)	0.063, 0.082	0.060, 0.152	0.041, 0.088

[a] common data: wavelength (Mo-K_α) = 0.71073 Å; θ(max) = 27.5°; [b] $R_1 = \Sigma||Fo|-|Fc||/\Sigma|Fo|$; $wR_2=[\Sigma w(Fo^2-Fc^2)^2/\Sigma wFo^4]^{1/2}$

Compound	**$[(WSCl_4)_2$ $\{MeS(CH_2)_3SMe\}]$**	**$[WOCl_3$ $\{MeS(CH_2)_2SMe\}]$**	**$[WOCl_3$ $\{MeS(CH_2)_3SMe\}]$**	**$[WSCl_3$ $\{MeS(CH_2)_2SMe\}]$**
Formula	$C_5H_{12}Cl_8S_2W_2$	$C_4H_{10}Cl_3OS_2W$	$C_5H_{12}Cl_3OS_2W$	$C_4H_{10}Cl_3S_3W$
M	851.69	428.44	442.47	444.50
Crystal system	triclinic	triclinic	triclinic	monoclinic
Space group (no)	P-1 (2)	P1 (1)	P-1 (2)	$P2_1/n$ (14)
a/Å	6.6665(2)	6.7317(3)	6.7576(4)	6.8758(1)
b/Å	11.1479(2)	6.9581(3)	7.3941(4)	13.2588(2)
c/Å	13.8916(3)	7.1904(3)	12.4200(5)	12.5782(2)
α/°	101.979(2	108.981(4)	78.514(4)	90
β/°	100.011(2)	98.845(4)	81.724(4)	94.541(2)
γ/°	95.717(2)	114.330(4)	72.508(5)	90
U/Å^3	984.61(4)	273.54(2)	577.68(5)	1143.09(3)
Z	2	1	2	4
μ(Mo-Kα)/mm^{-1}	13.166	11.619	11.008	11.296
F(000)	780	199	414	828
Total Reflns.	15275	5239	15495	30189
R_{int}	0.039	0.056	0.069	0.026
Unique Reflns.	5051	2880	3459	3609
Parameters/restraints	174, 0	102, 3	111, 0	111,0
GOF	1.177	1.041	1.097	1.085
R_1, $wR_2(I>2\sigma I)$	0.050, 0.118	0.045, 0.104	0.050, 0.117	0.039, 0.075
R1, wR2(all data)	0.058, 0.128	0.046, 0.105	0.059, 0.121	0.043, 0.176

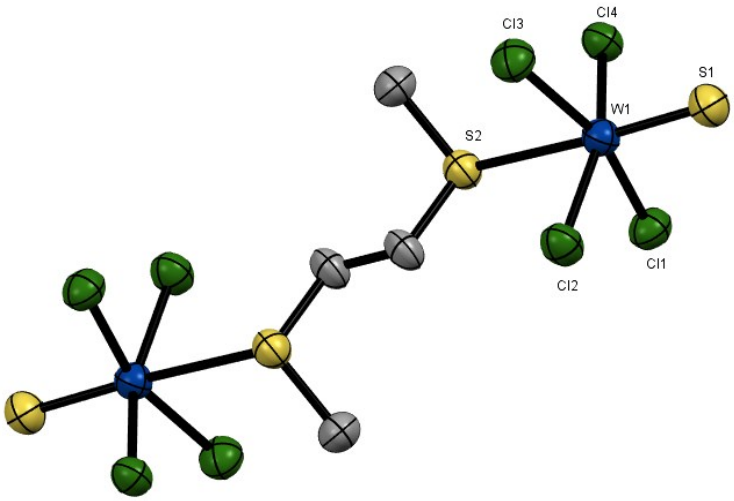

Figure S1 The structure of $[(WSCl_4)_2\{MeS(CH_2)_2SMe\}]$ showing the atom numbering scheme. H atoms are omitted for clarity. Selected bond lengths (Å) and angles (°) are: W1–Cl2 = 2.301(3), W1–Cl1 2.307(2), W1–Cl4 = 2.311(3), W1–Cl3 = 2.295(3)), W1–S1 = 2.095(2), W1–S2 = 2.835(2), S1–W1–Cl(1-4) = 97.84(10) – 101.05(10), S2–W1–Cl(1-4) = 75.01(9) – 86.05(9).

The structure here reported in $P2_1/c$ is very similar to the literature report[16] (in $P2_1/n$), but is of higher precision.