Supporting Information for:

Bis(diphenylphosphino)methane dioxide complexes of lanthanide trichlorides: synthesis, structures and spectroscopy.

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$[Ce(dppmO_2)_4]Cl_3$ –

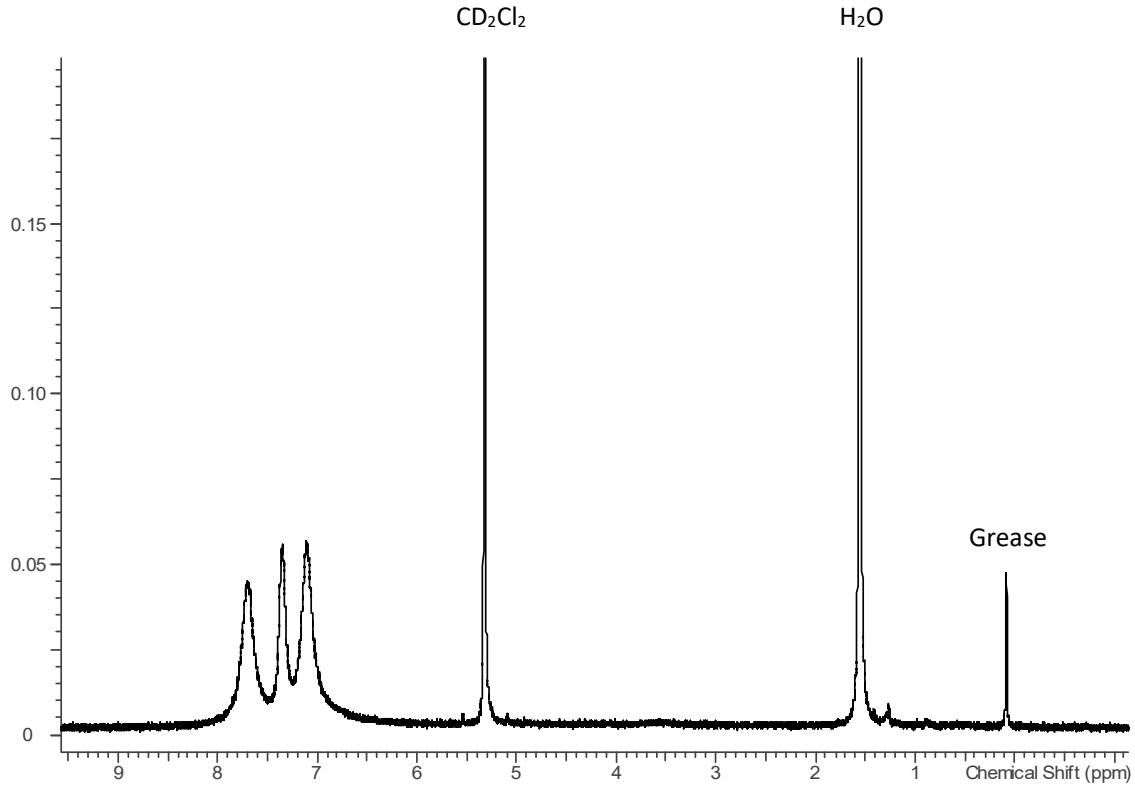

Figure S1 – ^1H NMR spectrum of $[Ce(dppmO_2)_4]Cl_3$ in CD_2Cl_2

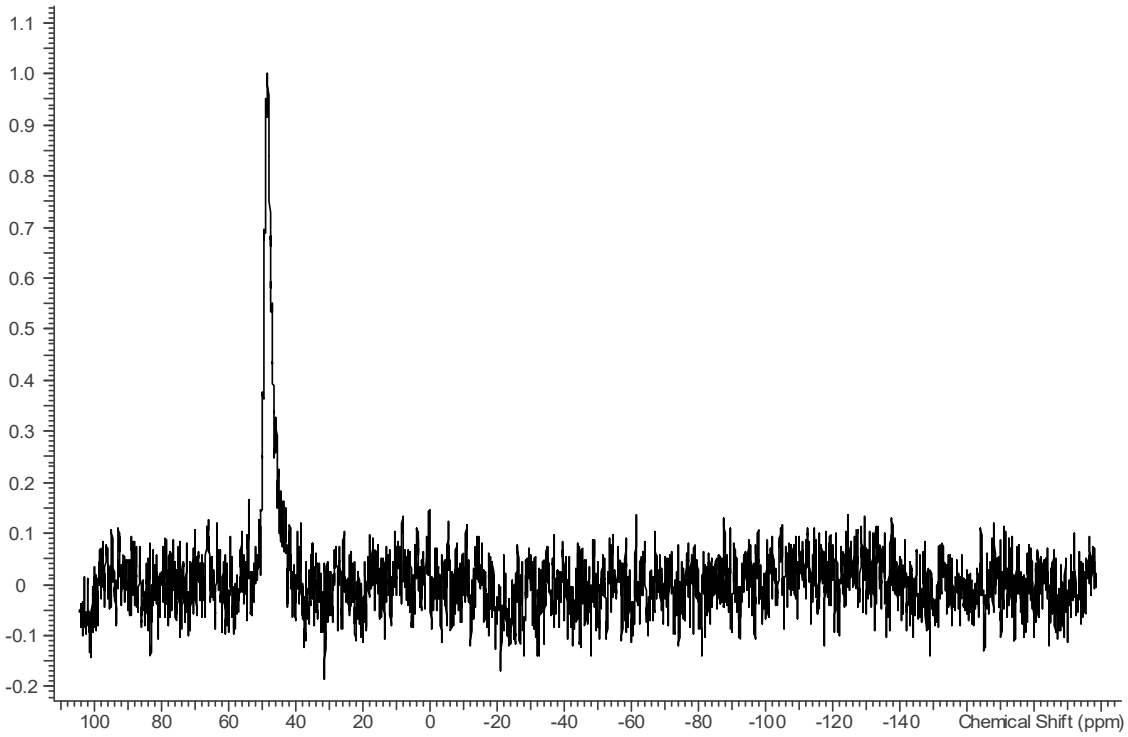

Figure S2 – $^{31}P\{^{1}H\}$ spectrum of $[Ce(dppmO_2)_4]Cl_3$ in CD_2Cl_2

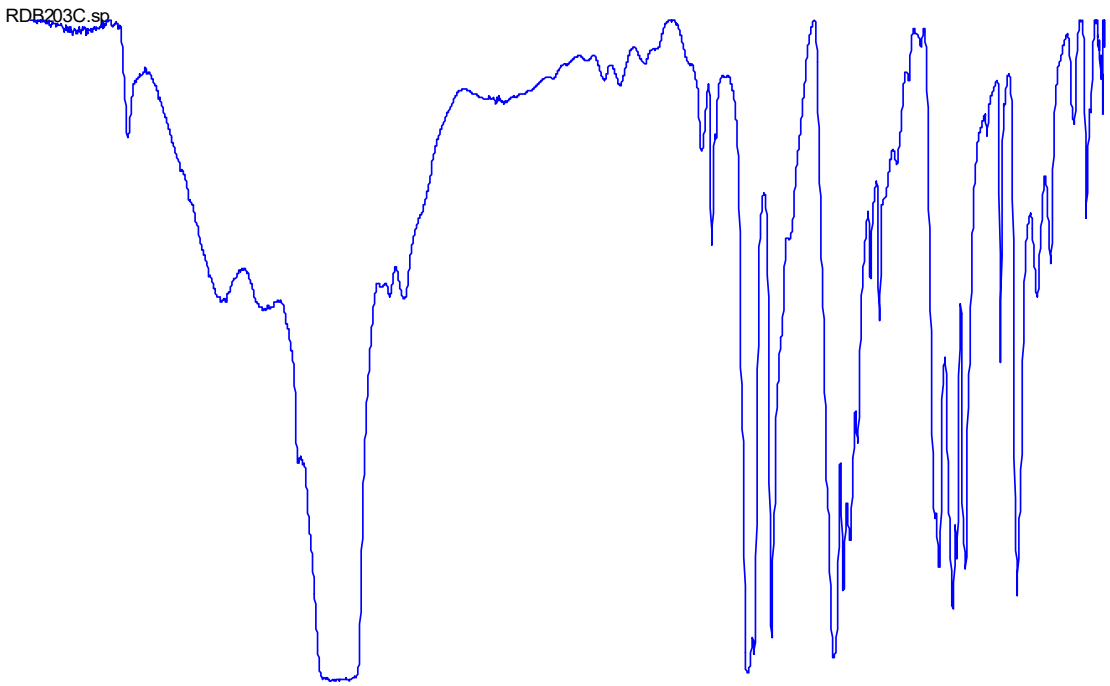

Figure S3 – Infrared spectrum of $[Ce(dppmO_2)_4]Cl_3$ (Nujol mull)

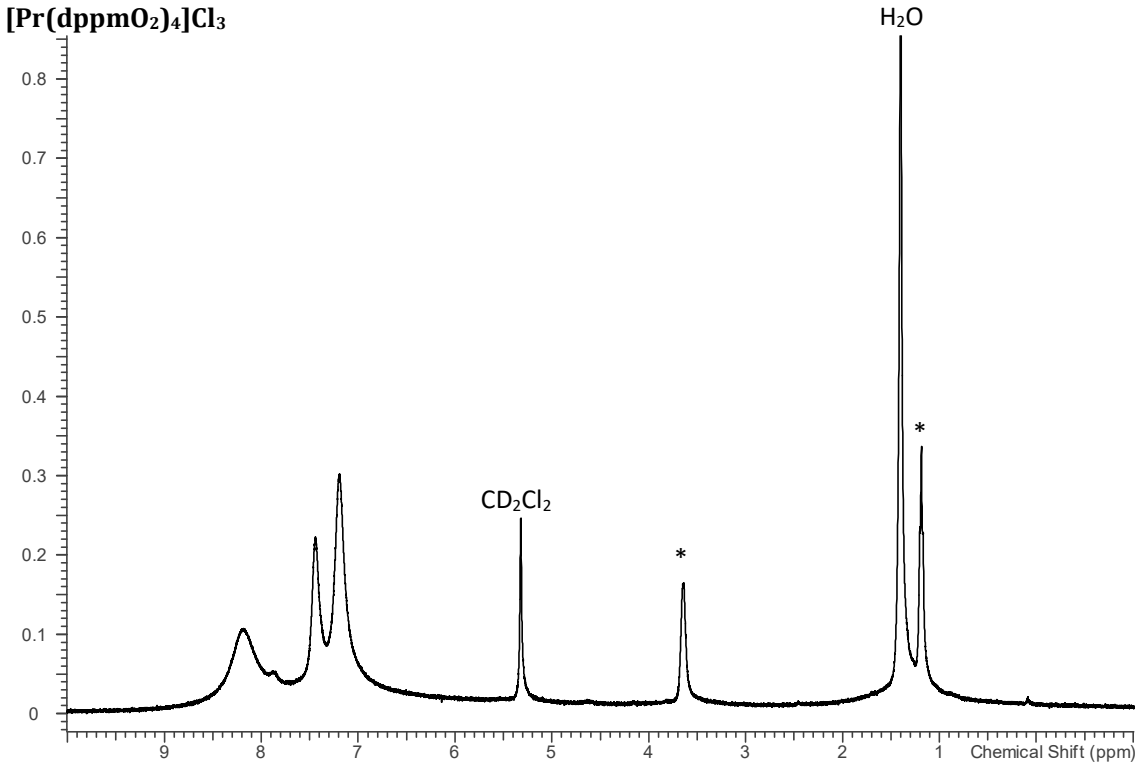

Figure S4 - ^{1}H NMR spectrum of $[Pr(dppmO_2)_4]Cl_3$ in CD_2Cl_2 (* = EtOH)

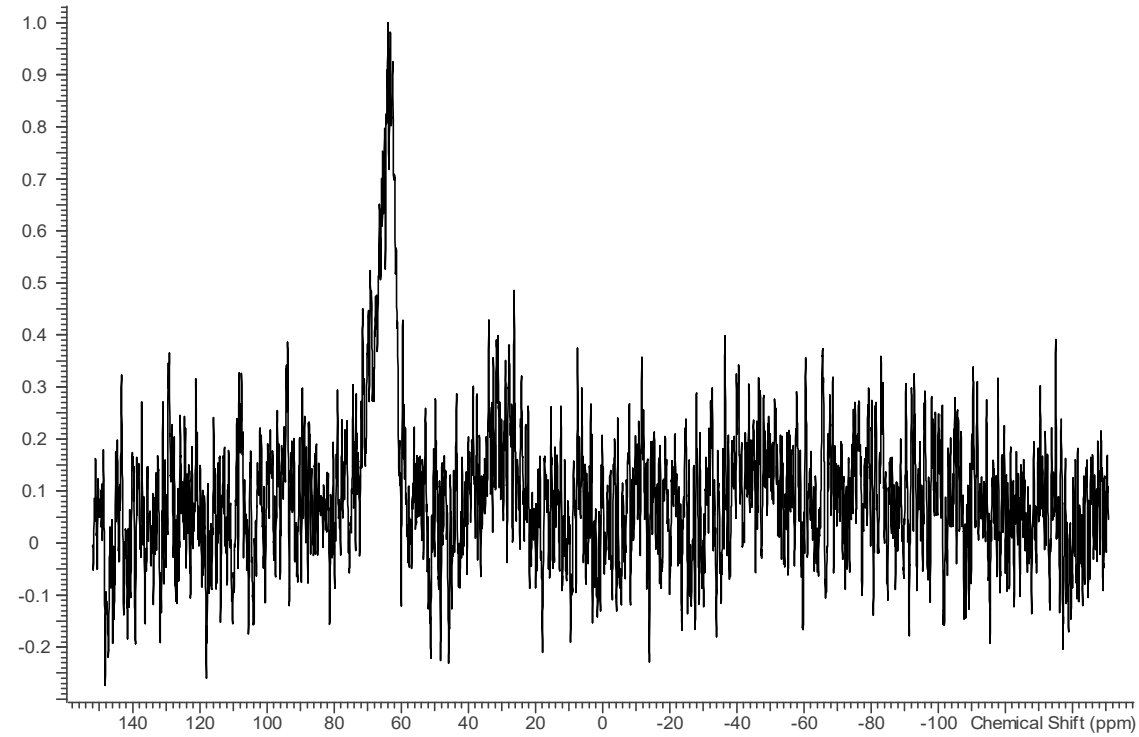

Figure S5 – $^{31}P\{^{1}H\}$ NMR spectrum of $[Pr(dppmO_2)_4]Cl_3$ in CD_2Cl_2

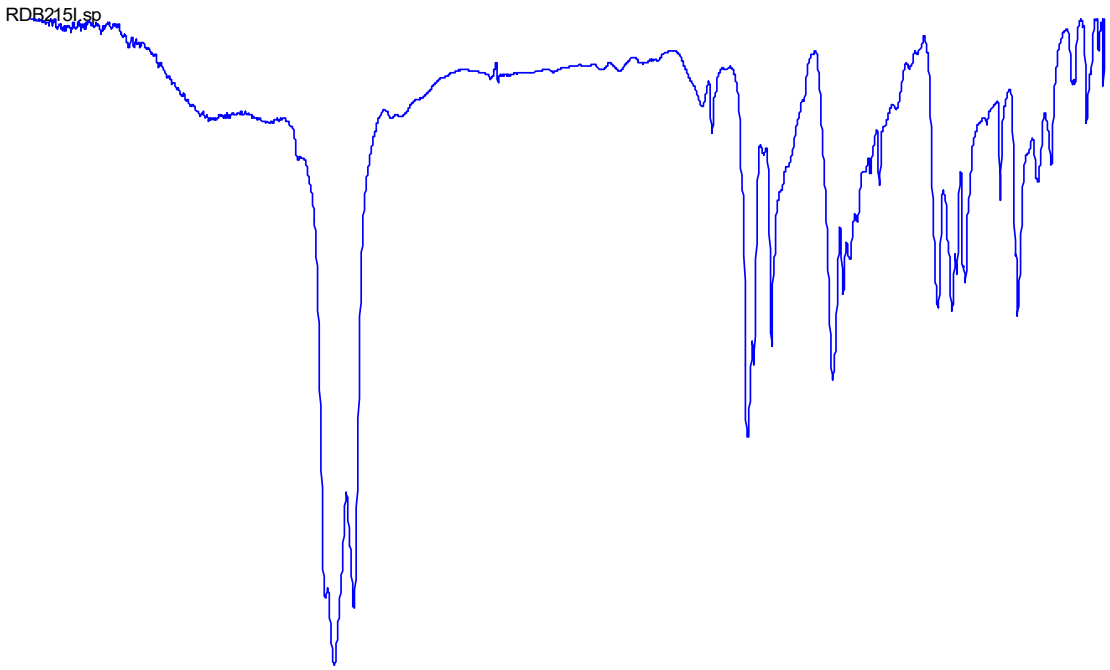

Figure S6 - Infrared spectrum of $[Pr(dppmO_2)_4]Cl_3$ (Nujol mull)

$[Nd(dppmO_2)_4]Cl_3$

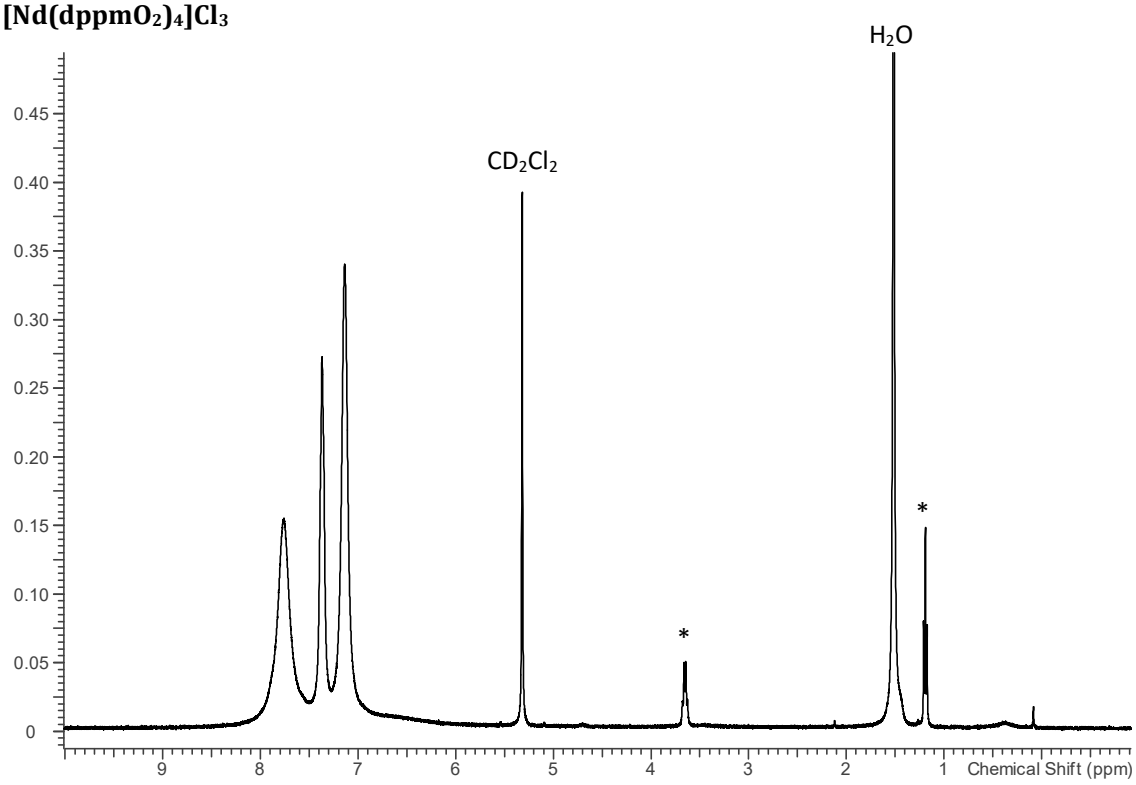

Figure S7 - ^1H NMR spectrum of $[Nd(dppmO_2)_4]Cl_3$ in CD_2Cl_2 (* = EtOH)

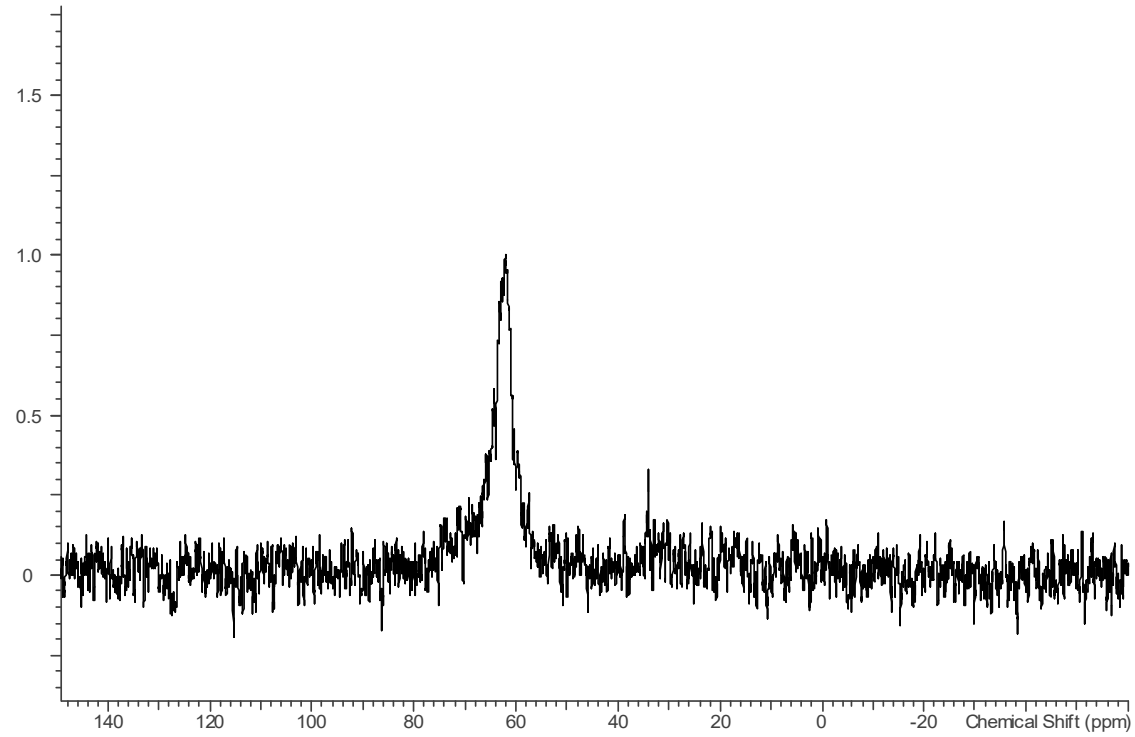

Figure S8 – $^{31}P\{^{1}H\}$ NMR spectrum of $[Nd(dppmO_2)_4]Cl_3$ in CD_2Cl_2

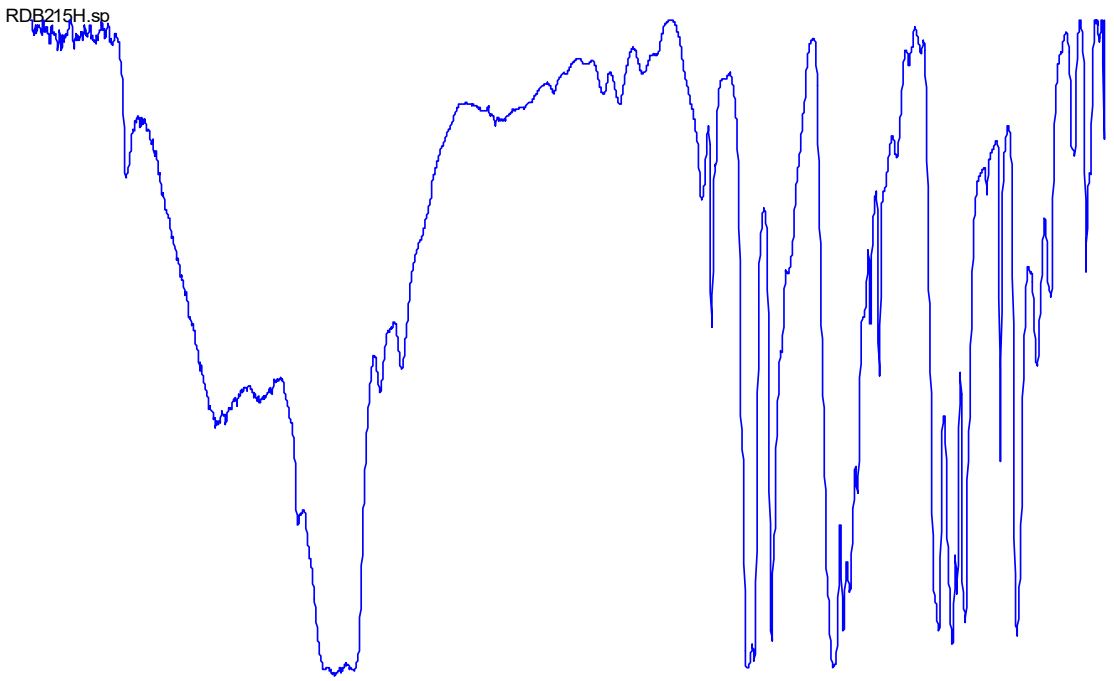

Figure S9 - Infrared spectrum of $[Nd(dppmO_2)_4]Cl_3$ (Nujol mull)

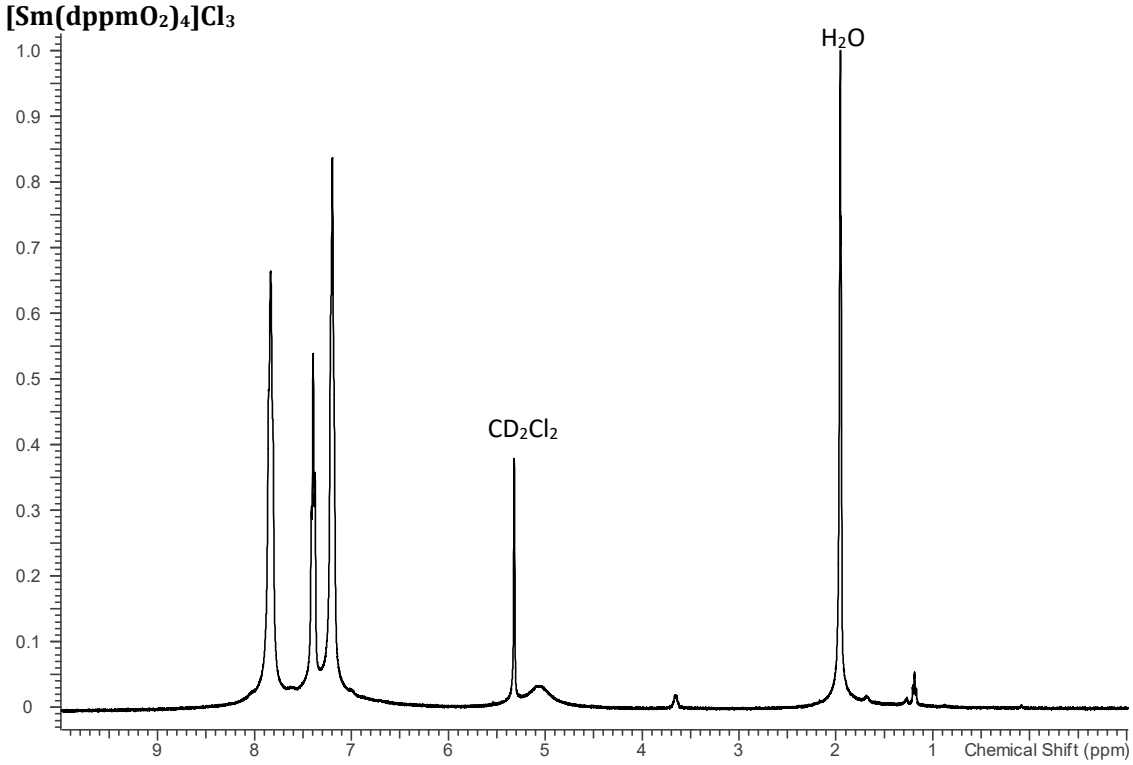

Figure S10 - ^{1}H NMR spectrum of $[Sm(dppmO_2)_4]Cl_3$ in CD_2Cl_2

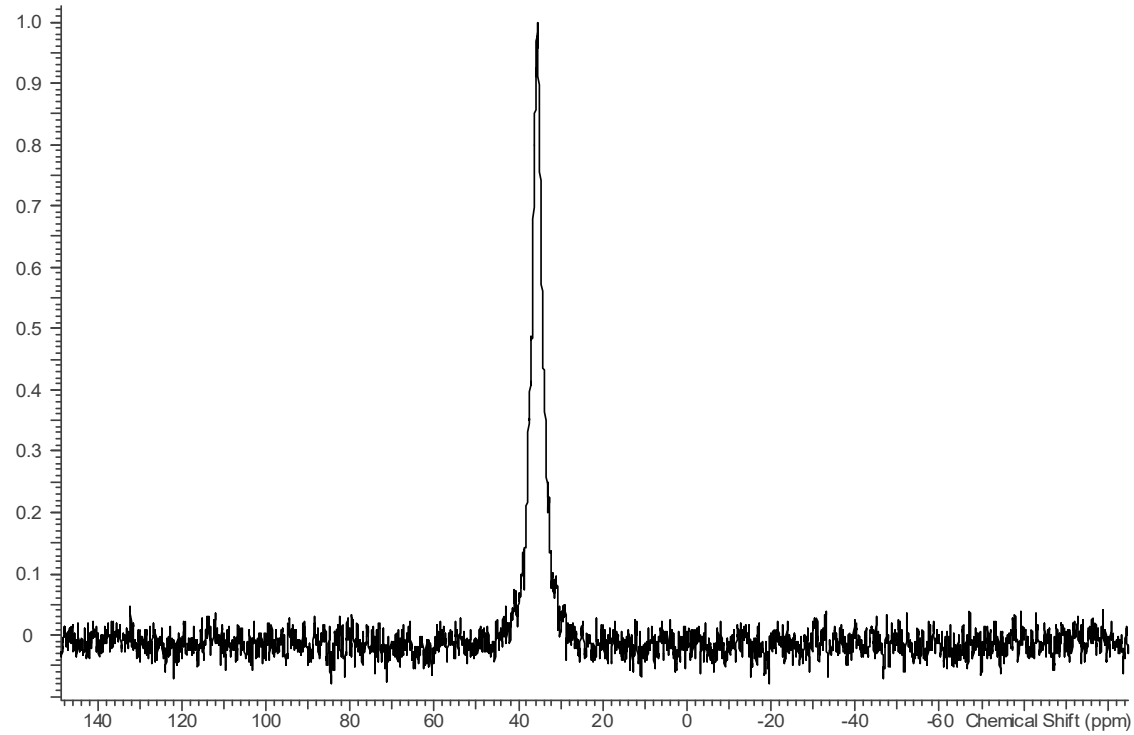

Figure S11 – $^{31}P\{^{1}H\}$ NMR spectrum of $[Sm(dppmO_2)_4]Cl_3$ in CD_2Cl_2

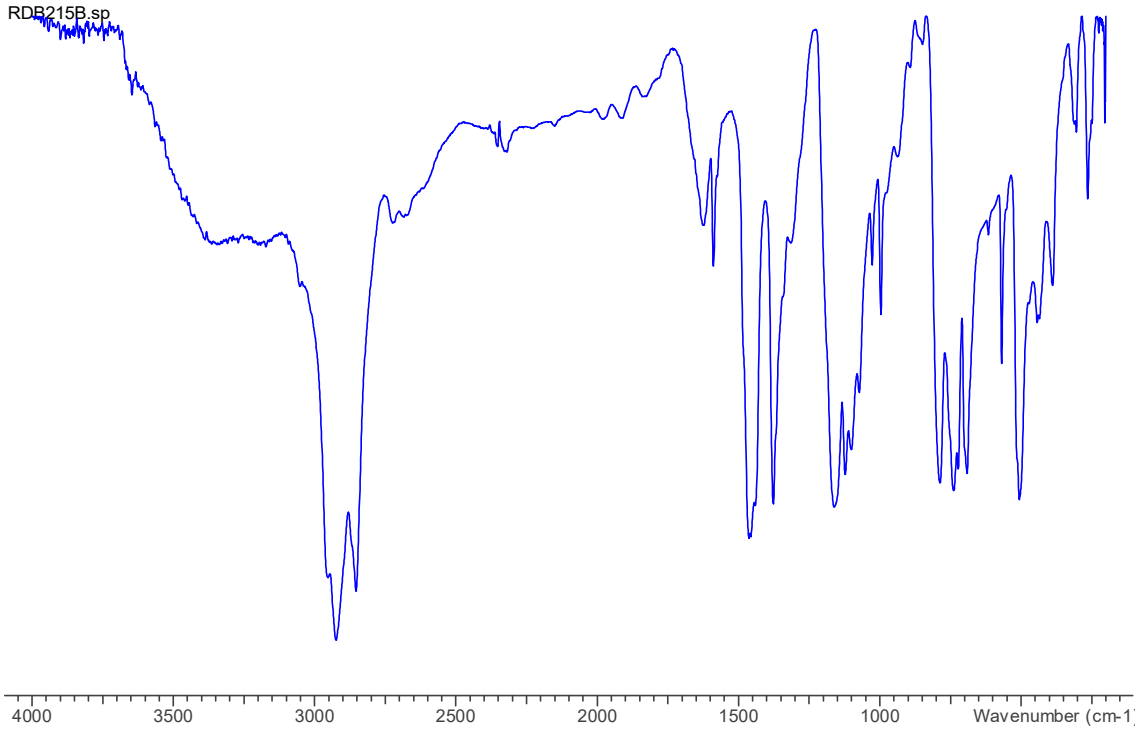

Figure S12 - Infrared spectrum of $[Sm(dppmO_2)_4]Cl_3$ (Nujol mull)

$[Eu(dppmO_2)_4]Cl_3$

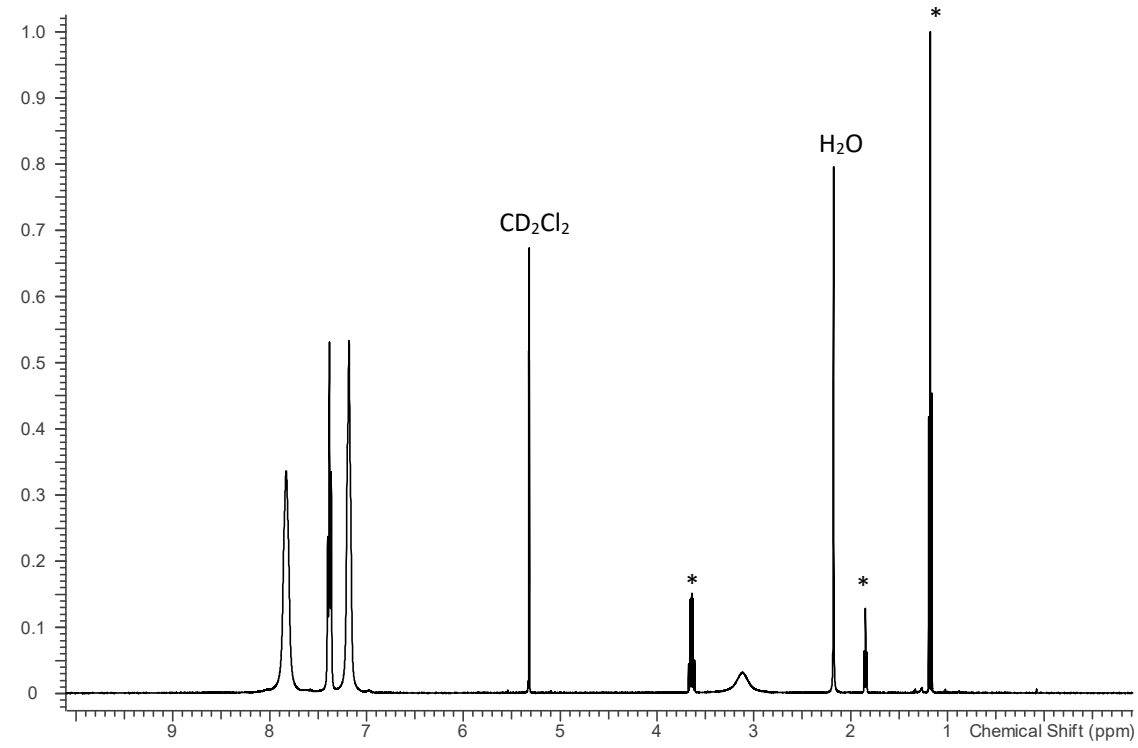

Figure S13 - ^1H NMR spectrum of $[Eu(dppmO_2)_4]Cl_3$ in CD_2Cl_2 (* = EtOH)

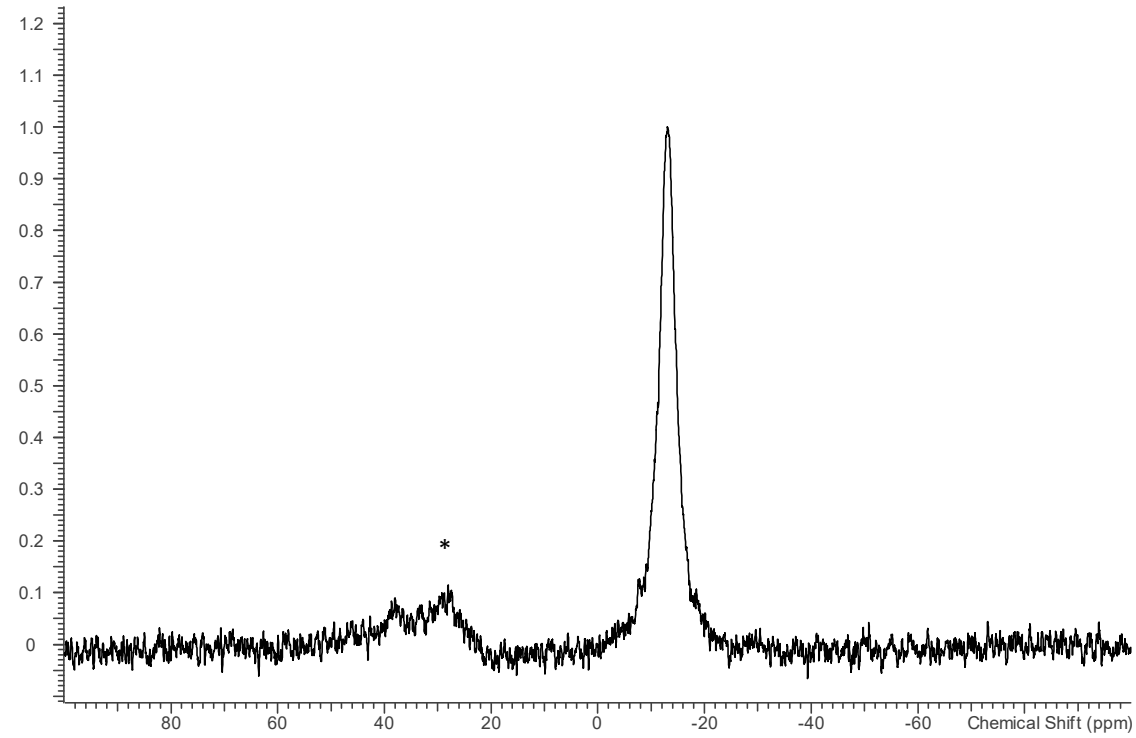

Figure S14 – $^{31}P\{^{1}H\}$ NMR spectrum of $[Eu(dppmO_2)_4]Cl_3$ in CD_2Cl_2 (* = free $dppmO_2$)

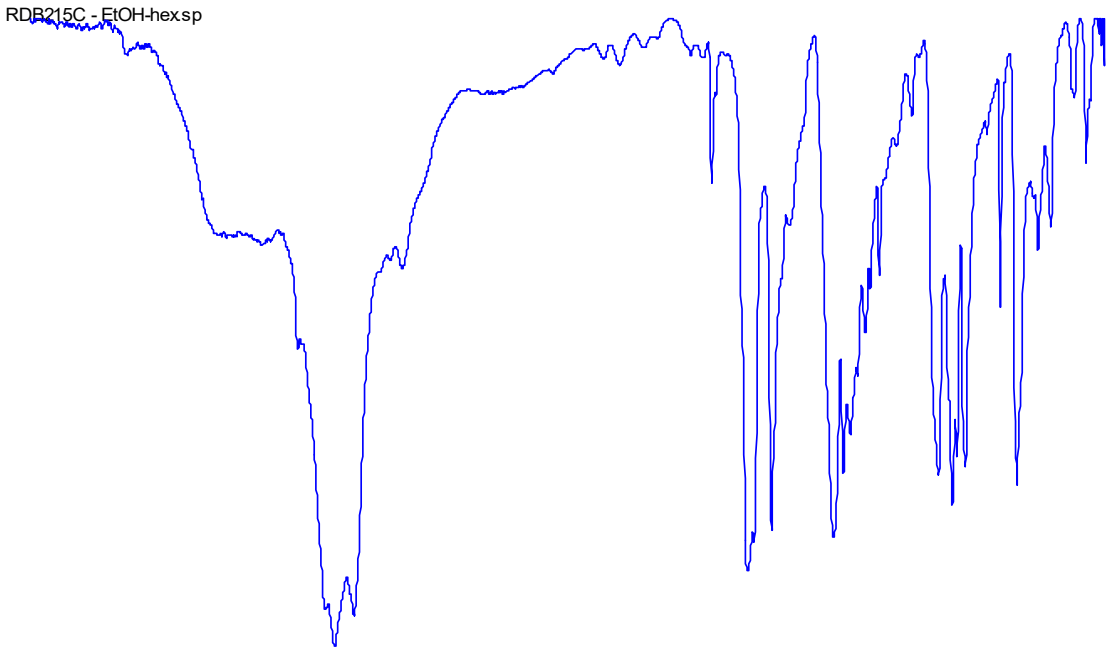

Figure S15 - Infrared spectrum of $[Eu(dppmO_2)_4]Cl_3$ (Nujol mull)

[Gd(dppmO$_2$)$_4$]Cl$_3$

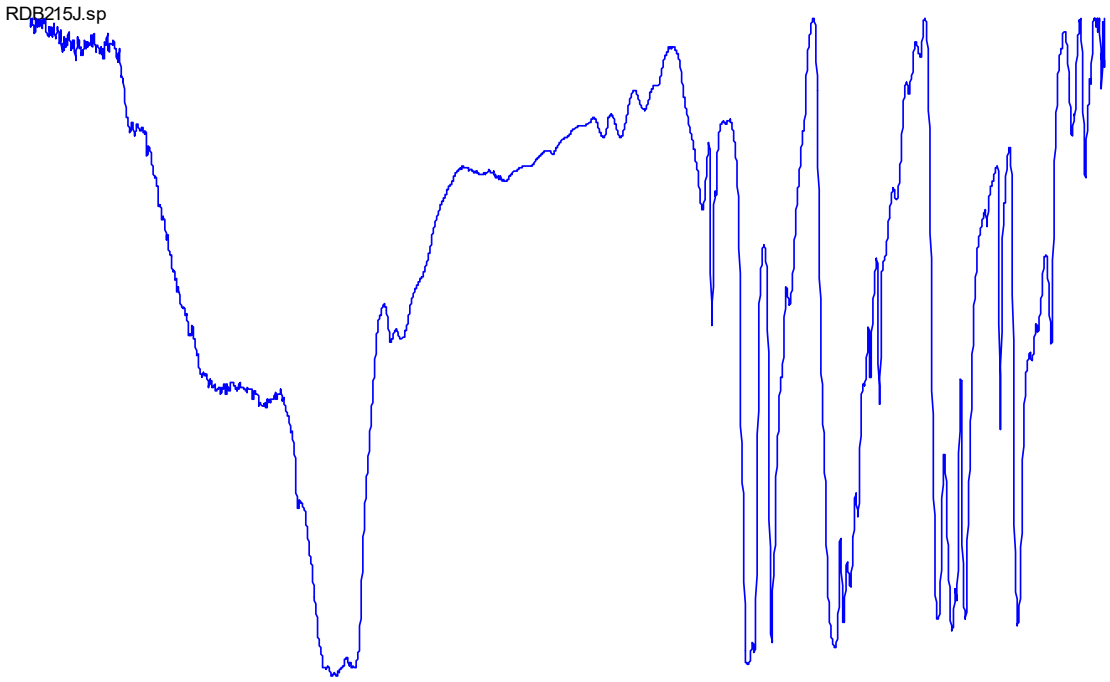

Figure S16 - Infrared spectrum of [Gd(dppmO$_2$)$_4$]Cl$_3$ (Nujol mull)

[SmCl(dppmO$_2$)$_3$]Cl$_2$

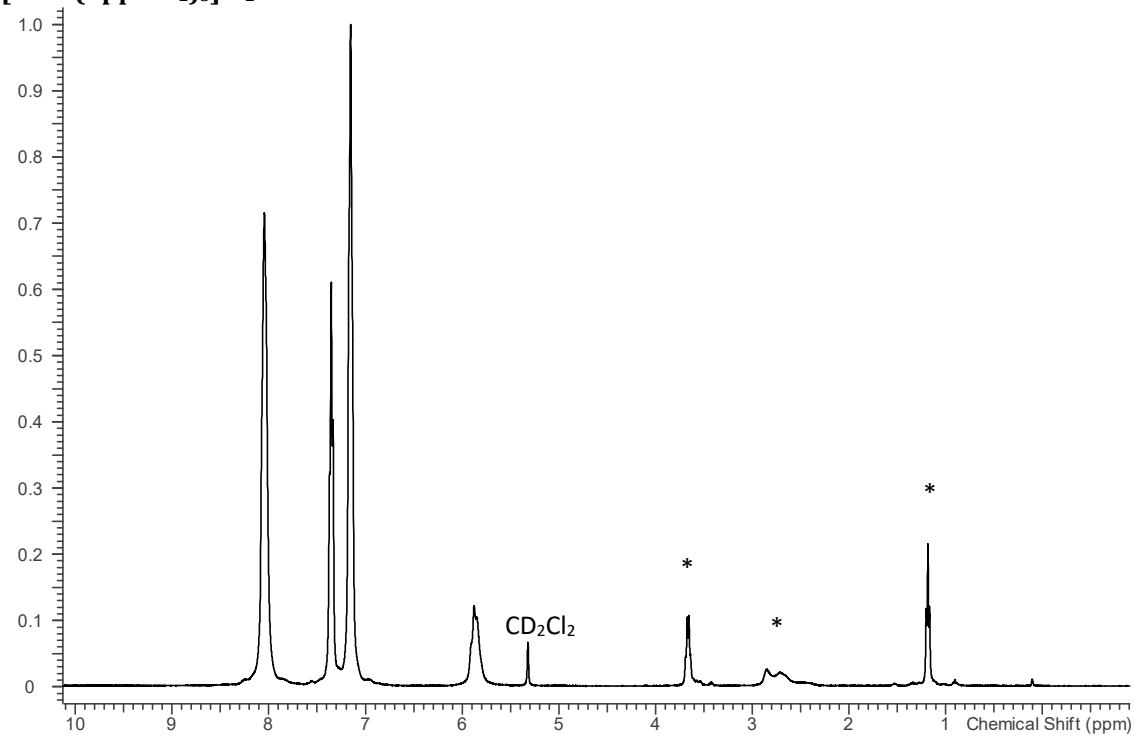

Figure S17 - ^{1}H NMR spectrum of [SmCl(dppmO$_2$)$_3$]Cl$_2$ in CD$_2$Cl$_2$ (* = EtOH)

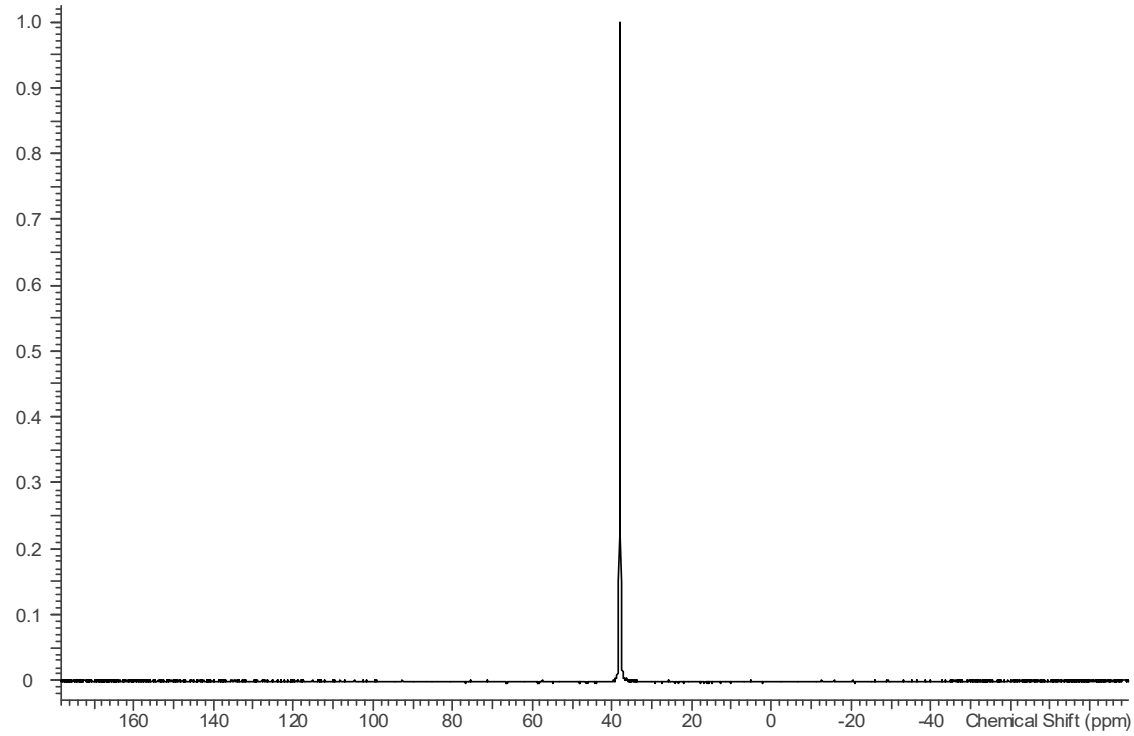

Figure S18 – ^{31}P{^{1}H} NMR spectrum of [SmCl(dppmO$_2$)$_3$]Cl$_2$ in CD$_2$Cl$_2$

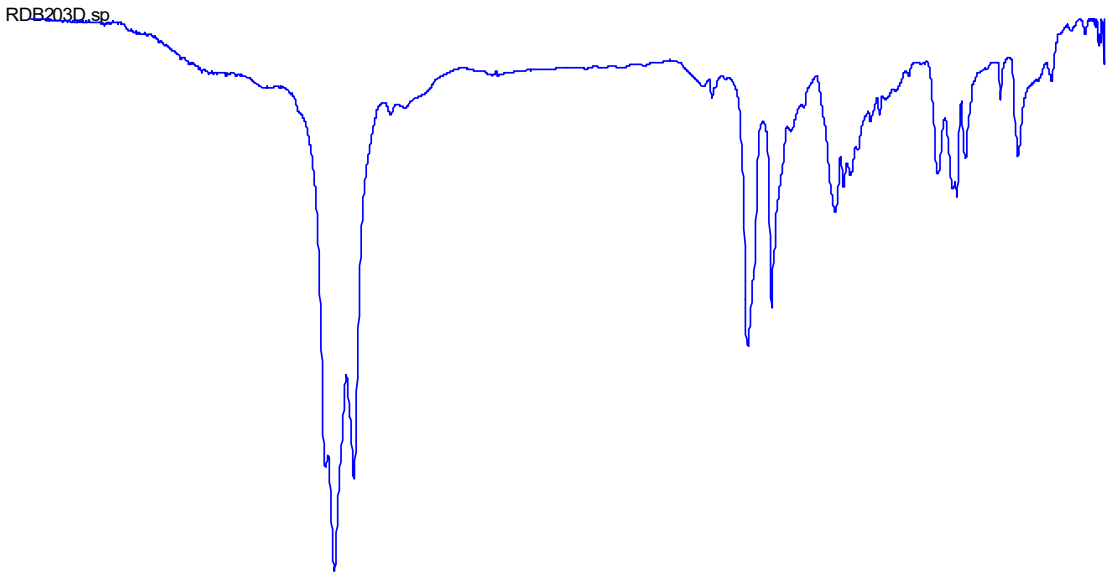

Figure S19 - Infrared spectrum of $[SmCl(dppmO_2)_3]Cl_2$ (Nujol mull)

$[EuCl(dppmO_2)_3]Cl_2$

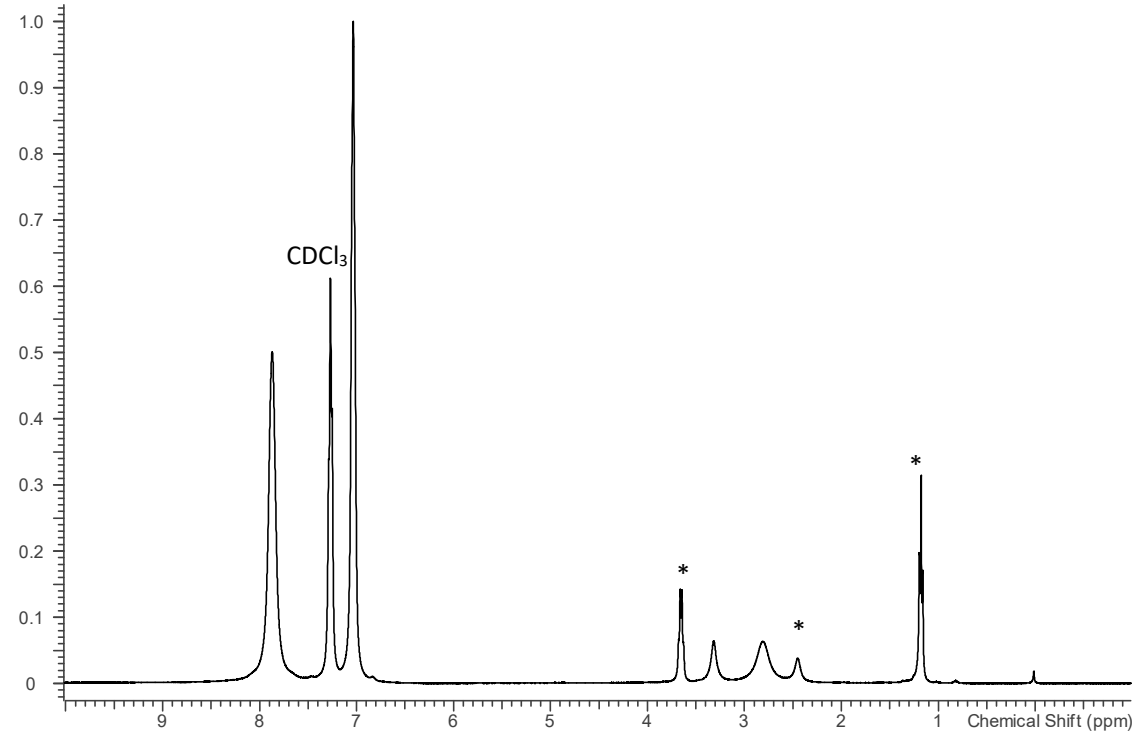

Figure S20 - ^1H NMR spectrum of $[EuCl(dppmO_2)_3]Cl_2$ in $CDCl_3$ (* = EtOH)

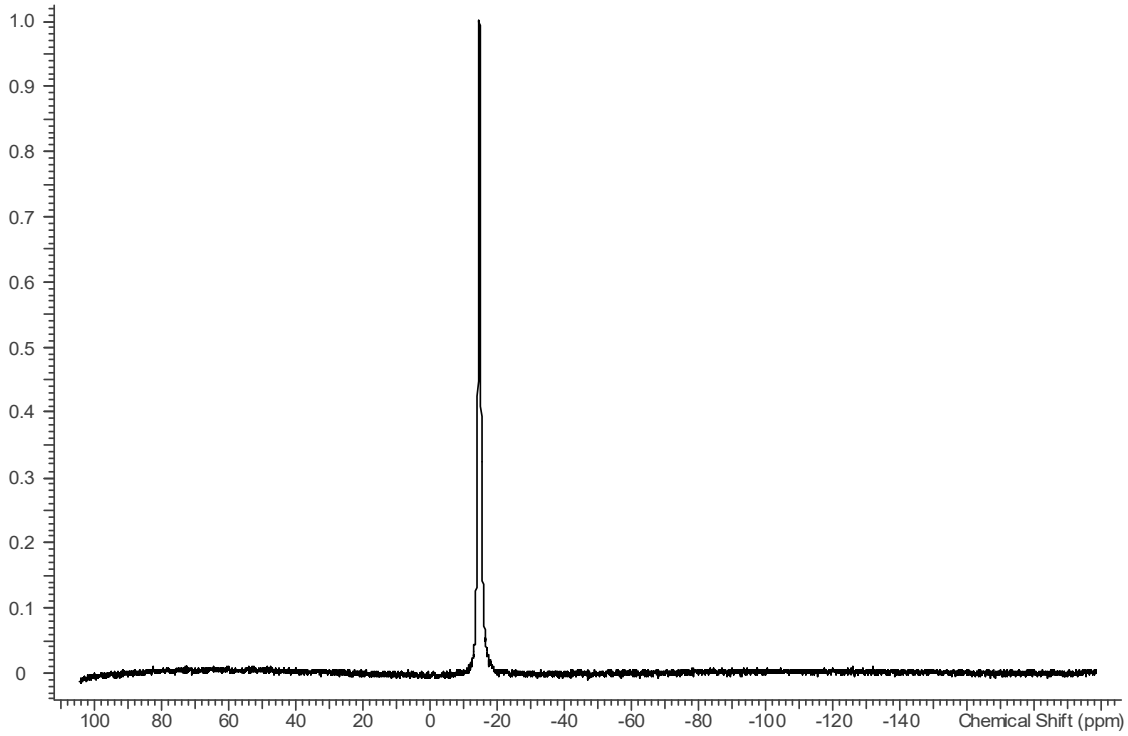

Figure S21 – $^{31}P\{^{1}H\}$ NMR spectrum of $[EuCl(dppmO_2)_3]Cl_2$ in $CDCl_3$

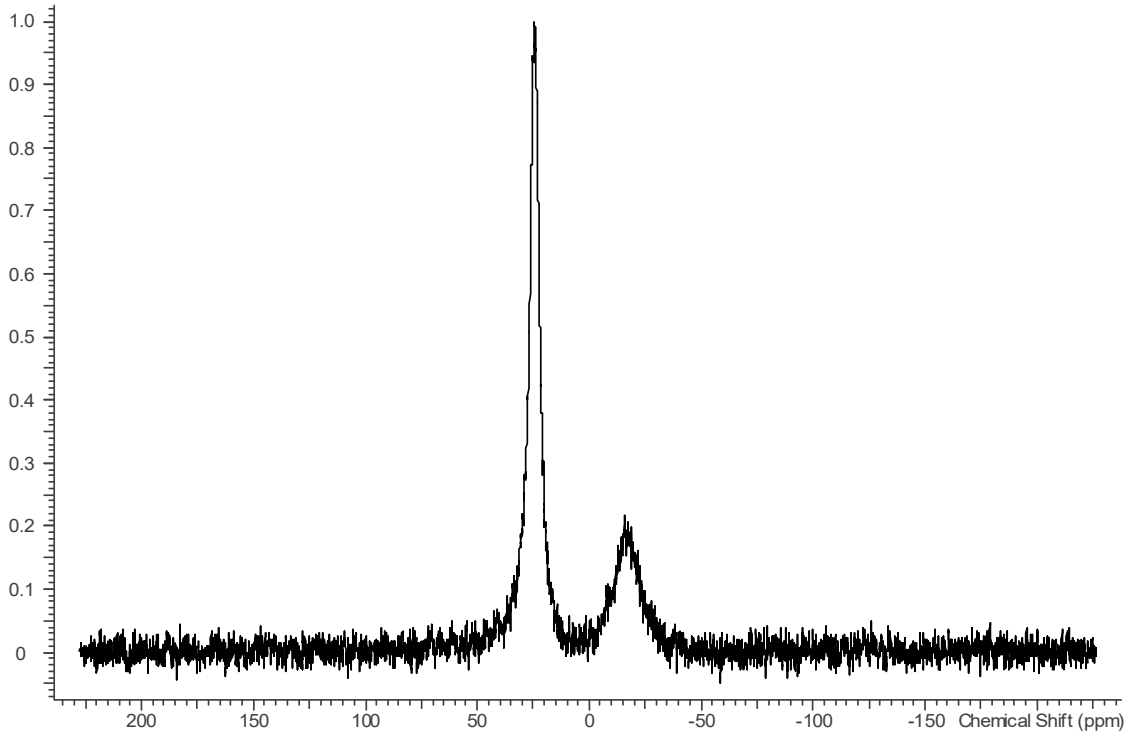

Figure S22 – $^{31}P\{^{1}H\}$ NMR spectrum of $[EuCl(dppmO_2)_3]Cl_2$ + excess $dppmO_2$ in $CDCl_3$

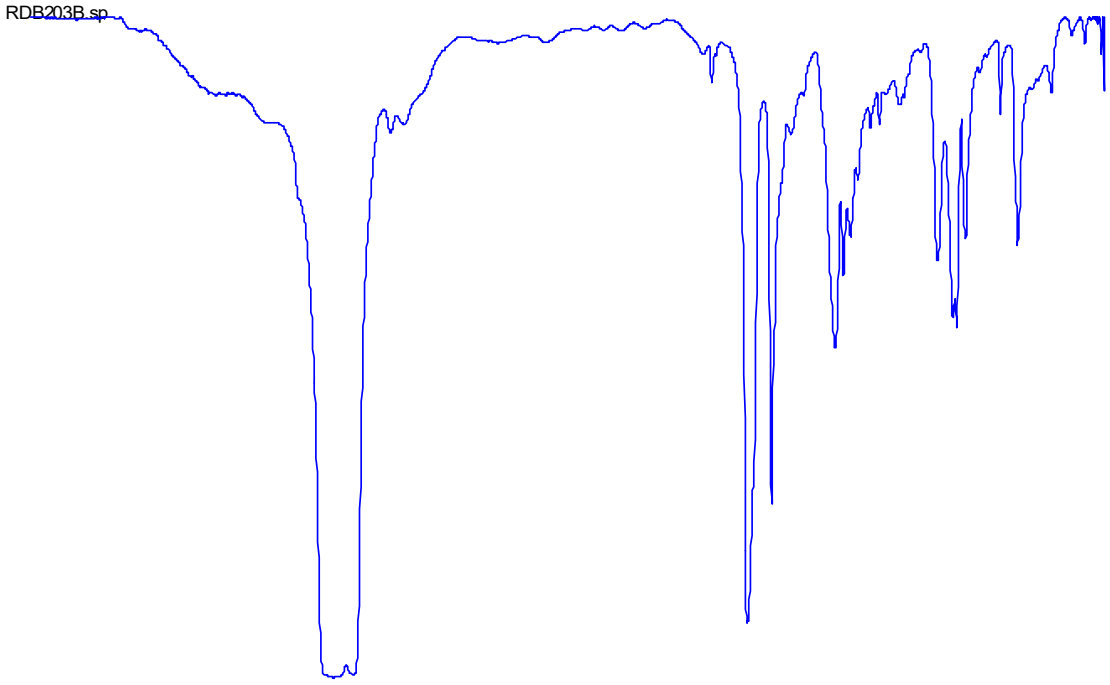

Figure S23 - Infrared spectrum of $[EuCl(dppmO_2)_3]Cl_2$ (Nujol mull)

$[GdCl(dppmO_2)_3]Cl_2$

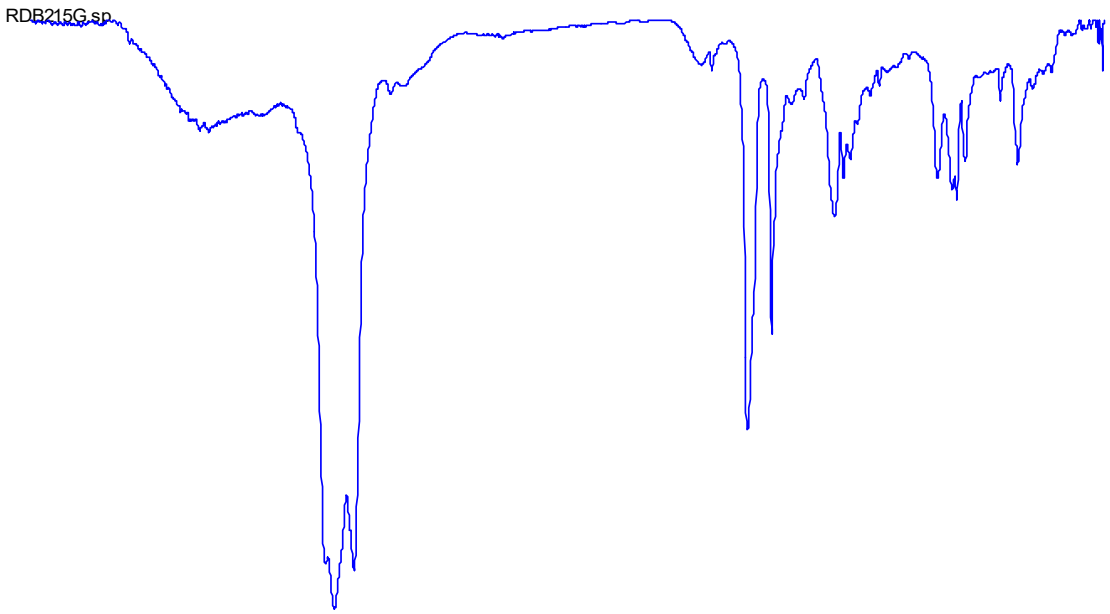

Figure S24 - Infrared spectrum of $[GdCl(dppmO_2)_3]Cl_2$ (Nujol mull)

[TbCl(dppmO$_2$)$_3$]Cl$_2$

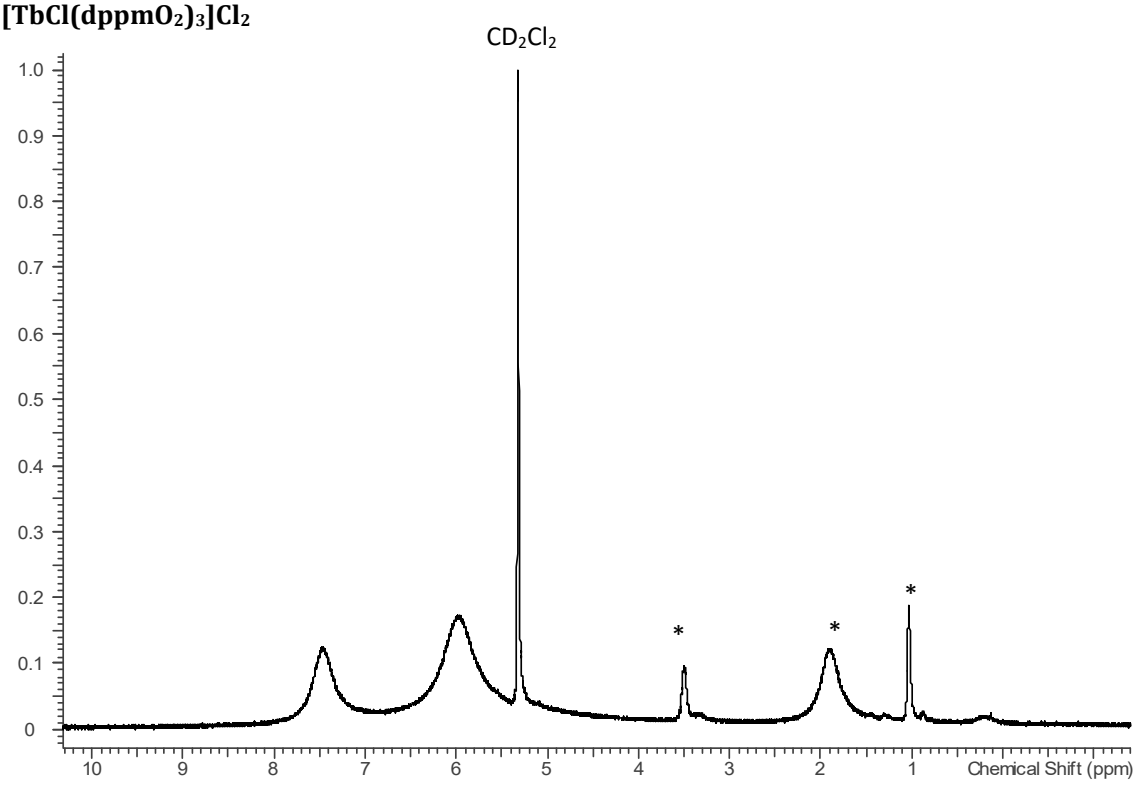

Figure S25 - ^{1}H NMR spectrum of [TbCl(dppmO$_2$)$_3$]Cl$_2$ in CD$_2$Cl$_2$ (* = EtOH)

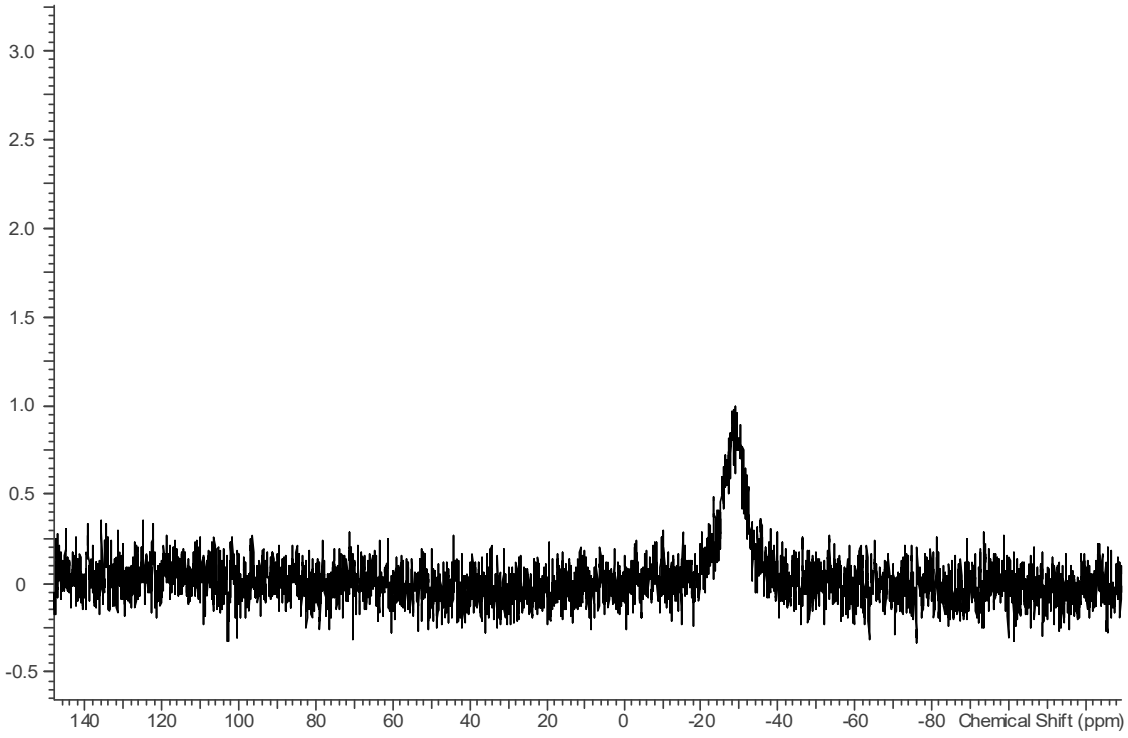

Figure S26 – ^{31}P{^{1}H} NMR spectrum of [TbCl(dppmO$_2$)$_3$]Cl$_2$ in CD$_2$Cl$_2$

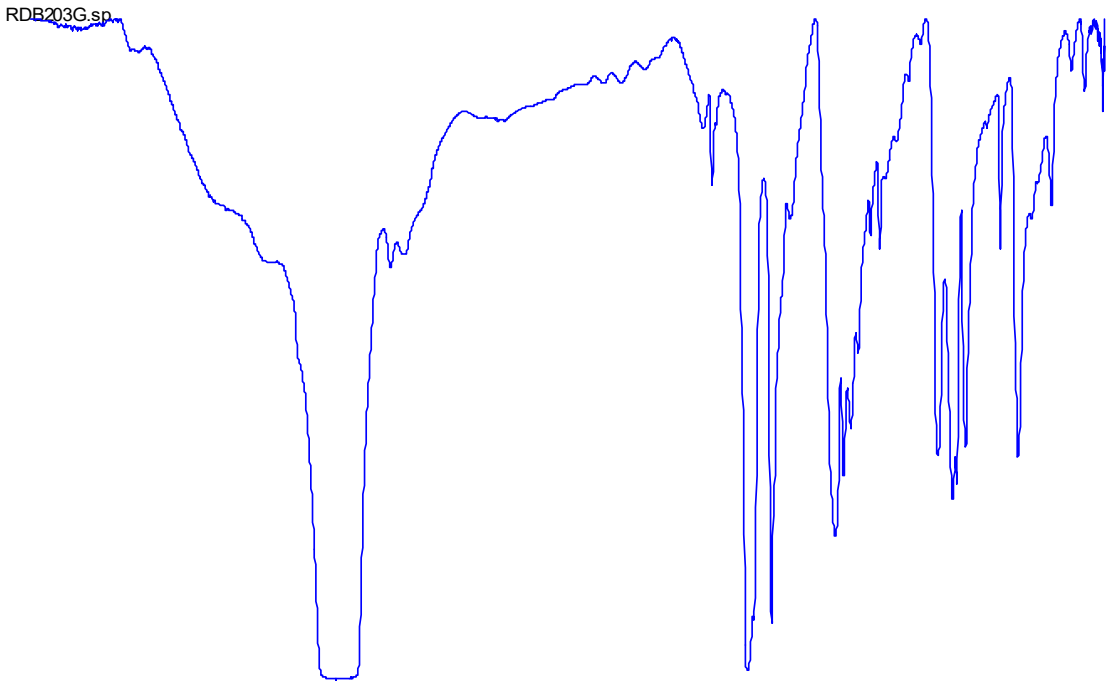

Figure S27 - Infrared spectrum of $[TbCl(dppmO_2)_3]Cl_2$ (Nujol mull)

$[DyCl(dppmO_2)_3]Cl_2$

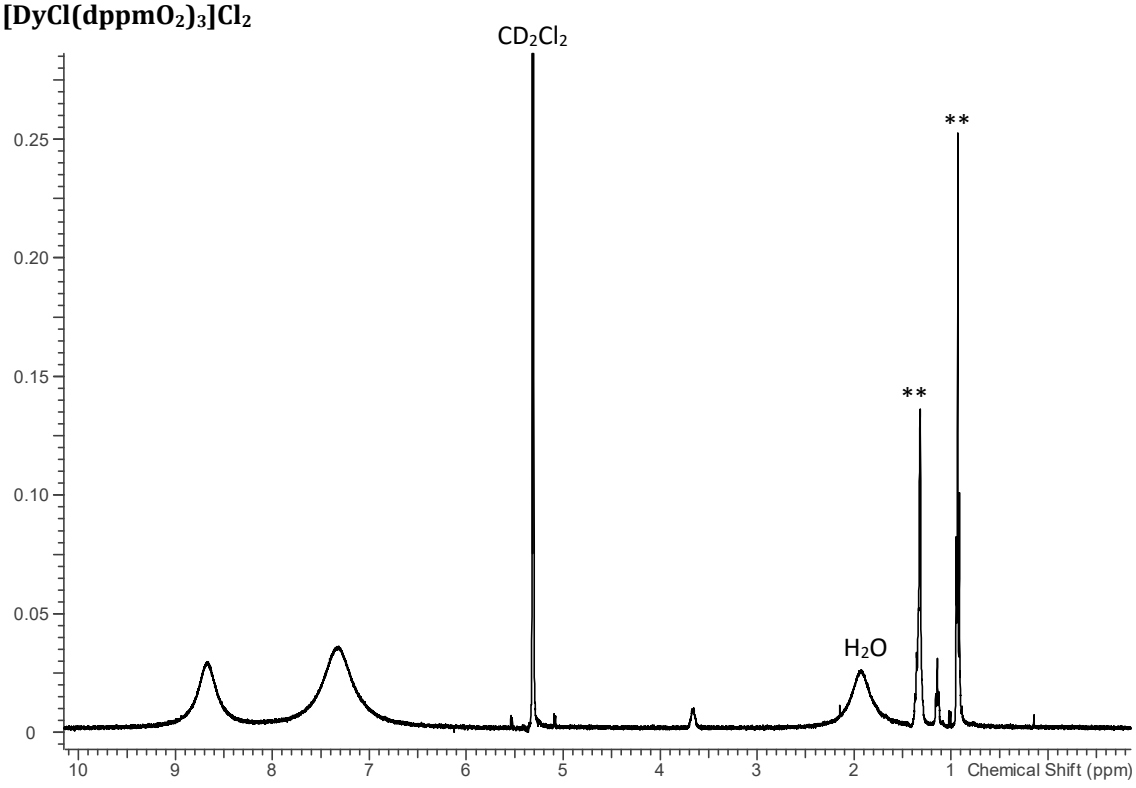

Figure S28 - ^1H NMR spectrum of $[DyCl(dppmO_2)_3]Cl_2$ in CD_2Cl_2 (** = hexane)

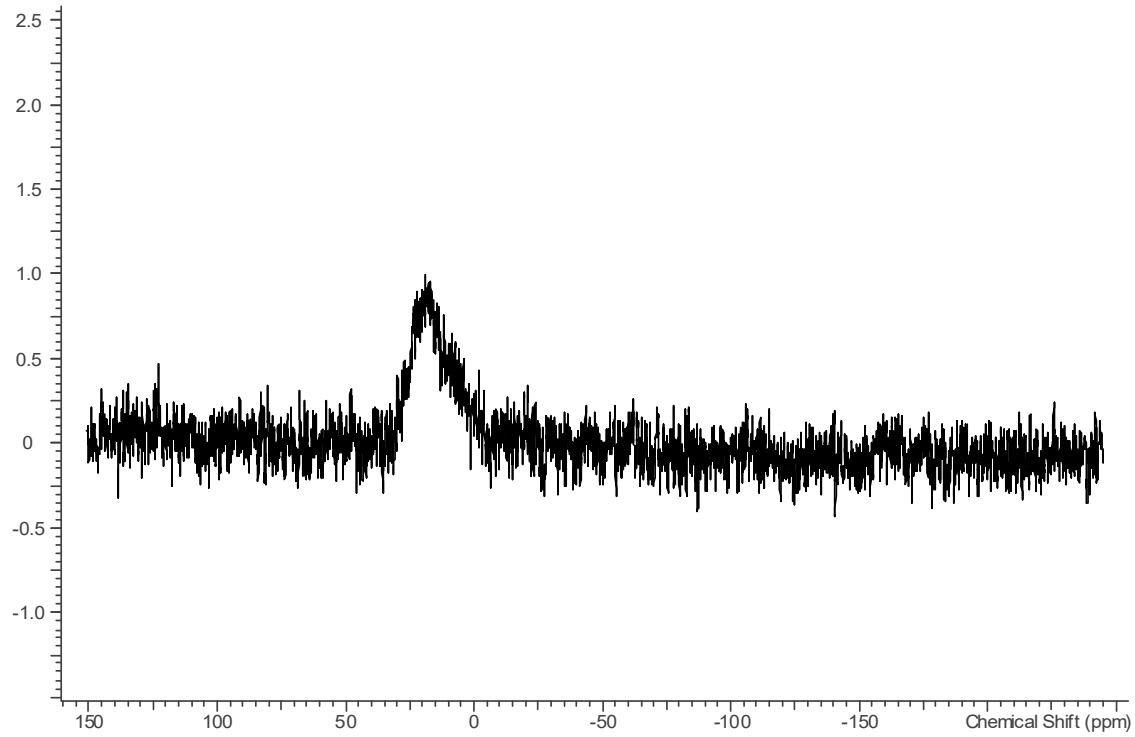

Figure S29 – $^{31}P\{^{1}H\}$ NMR spectrum of $[DyCl(dppmO_2)_3]Cl_2$ in CD_2Cl_2

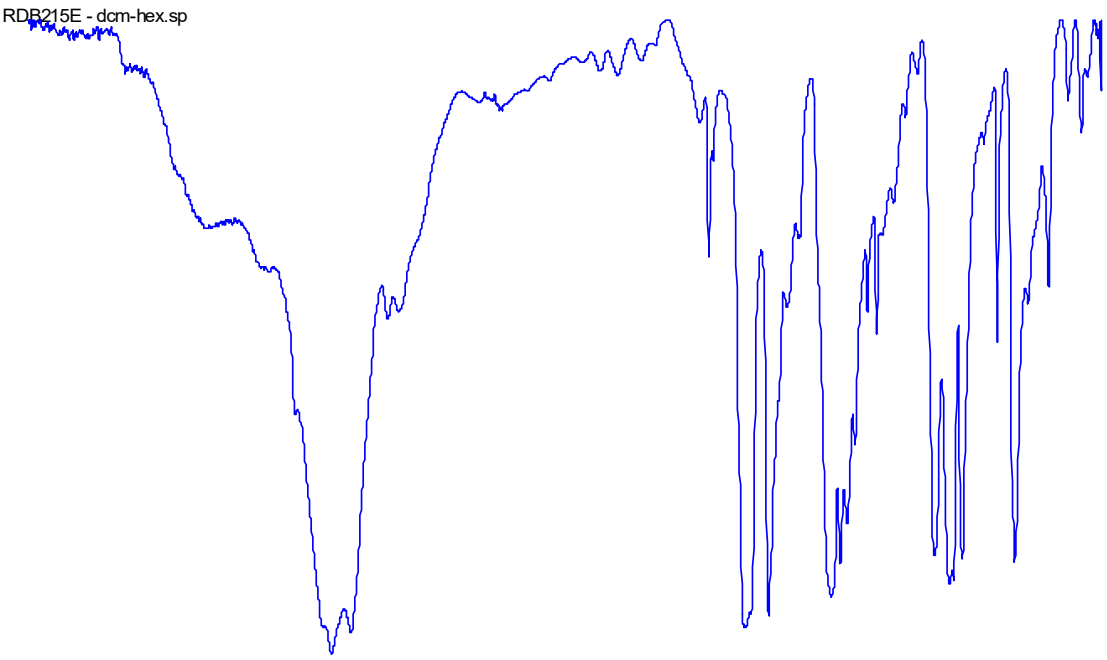

Figure S30 - Infrared spectrum of $[DyCl(dppmO_2)_3]Cl_2$ (Nujol mull)

$[HoCl(dppmO_2)_3]Cl_2$

CD_2Cl_2

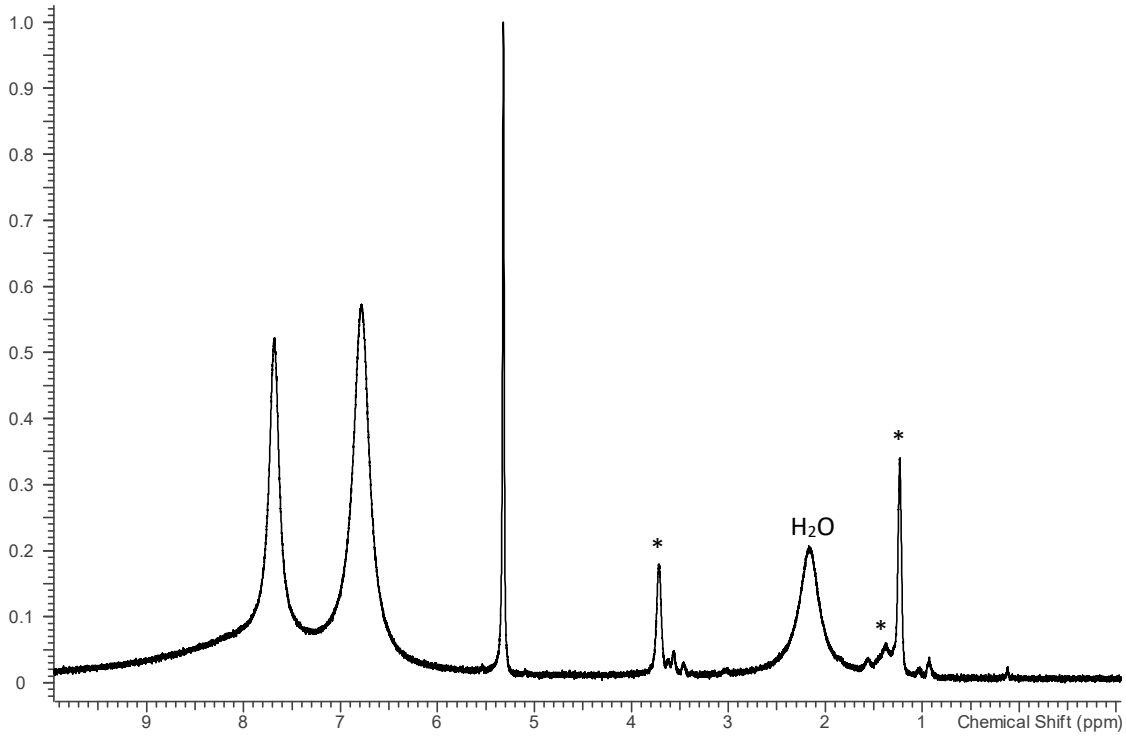

Figure S31 - ^{1}H NMR spectrum of $[HoCl(dppmO_2)_3]Cl_2$ in CD_2Cl_2 (* = EtOH)

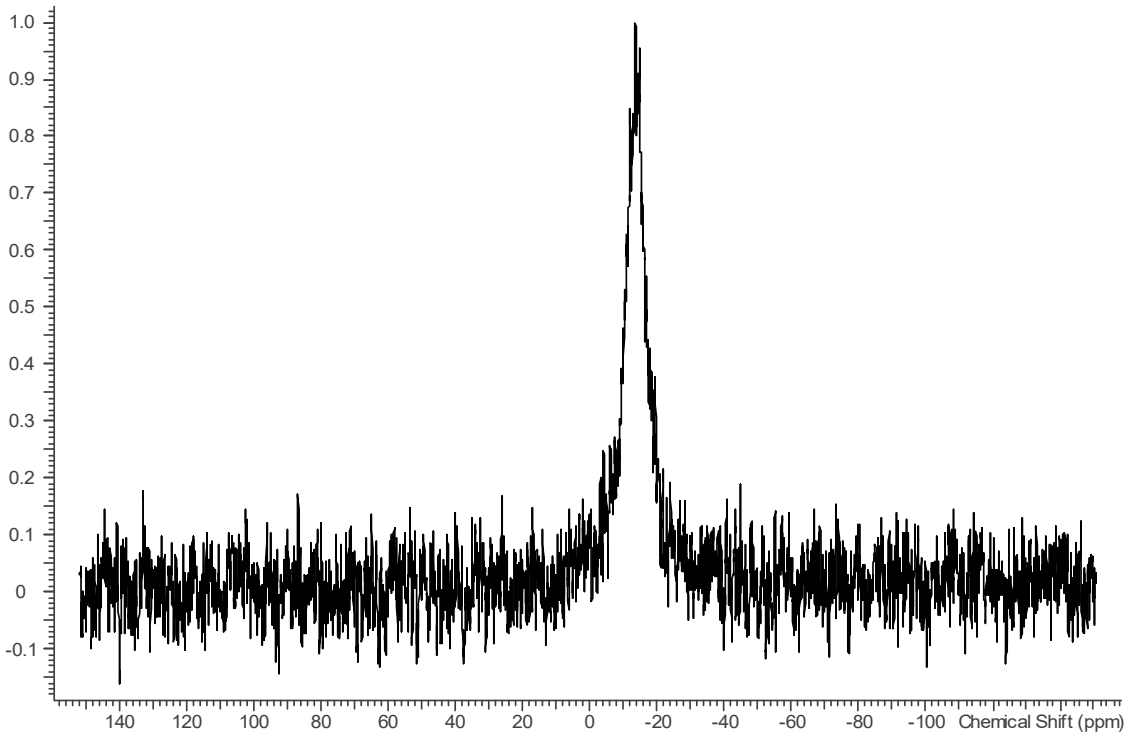

Figure S32 – $^{31}P\{^{1}H\}$ NMR spectrum of $[HoCl(dppmO_2)_3]Cl_2$ in CD_2Cl_2

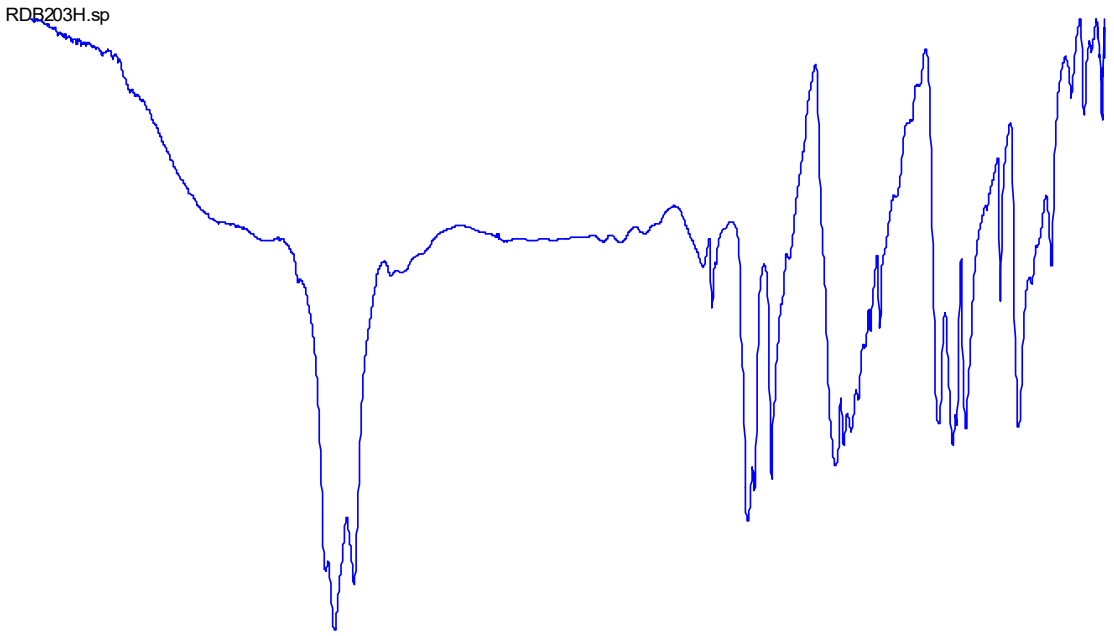

Figure S33 - Infrared spectrum of $[HoCl(dppmO_2)_3]Cl_2$ (Nujol mull)

$[ErCl(dppmO_2)_3]Cl_2$

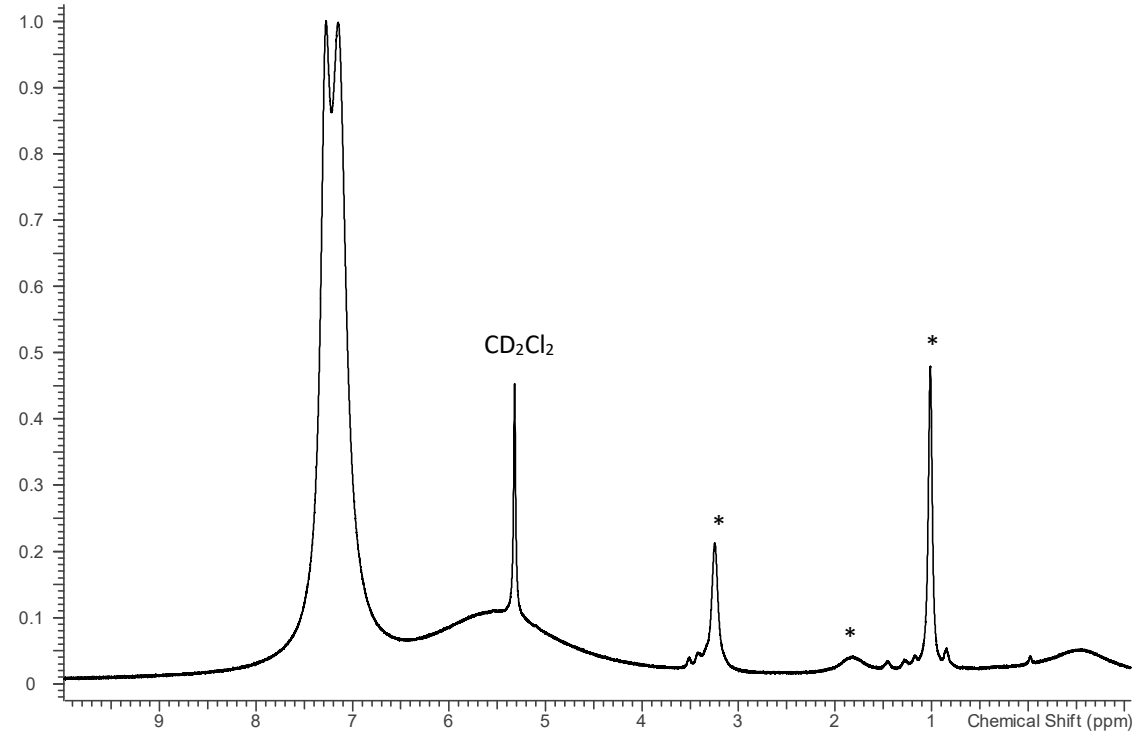

Figure S34 - ^1H NMR spectrum of $[ErCl(dppmO_2)_3]Cl_2$ in CD_2Cl_2 (* = EtOH)

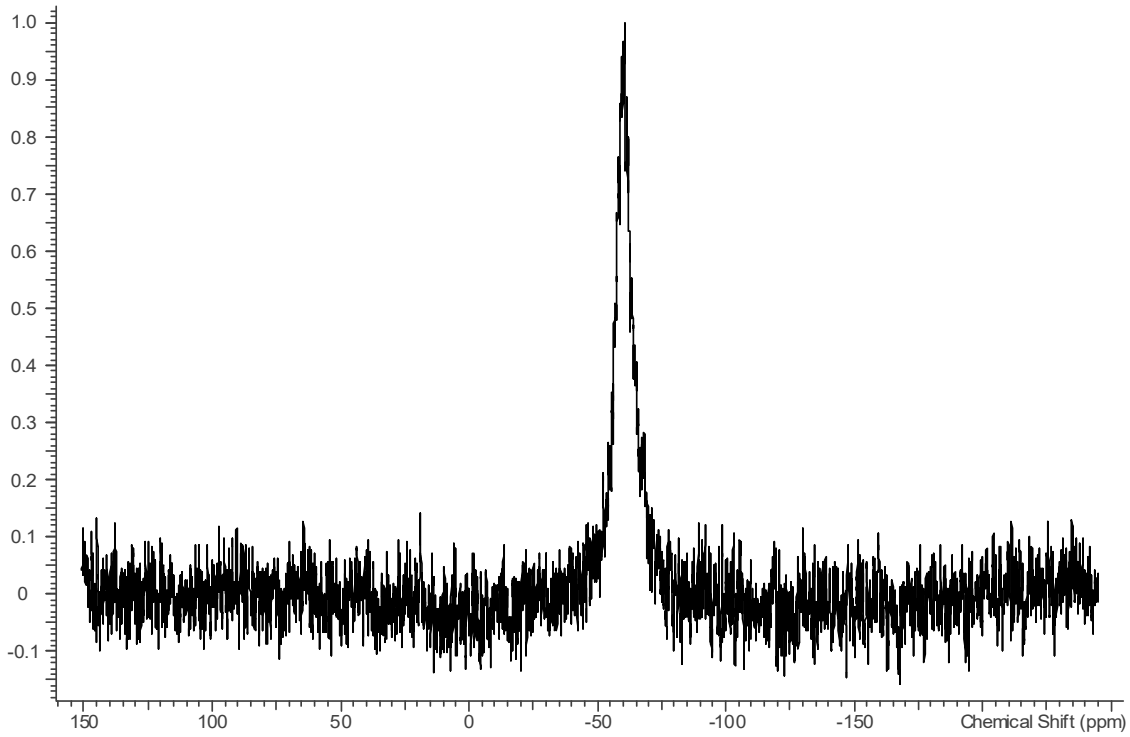

Figure S35 – $^{31}P\{^{1}H\}$ NMR spectrum of $[ErCl(dppmO_2)_3]Cl_2$ in CD_2Cl_2

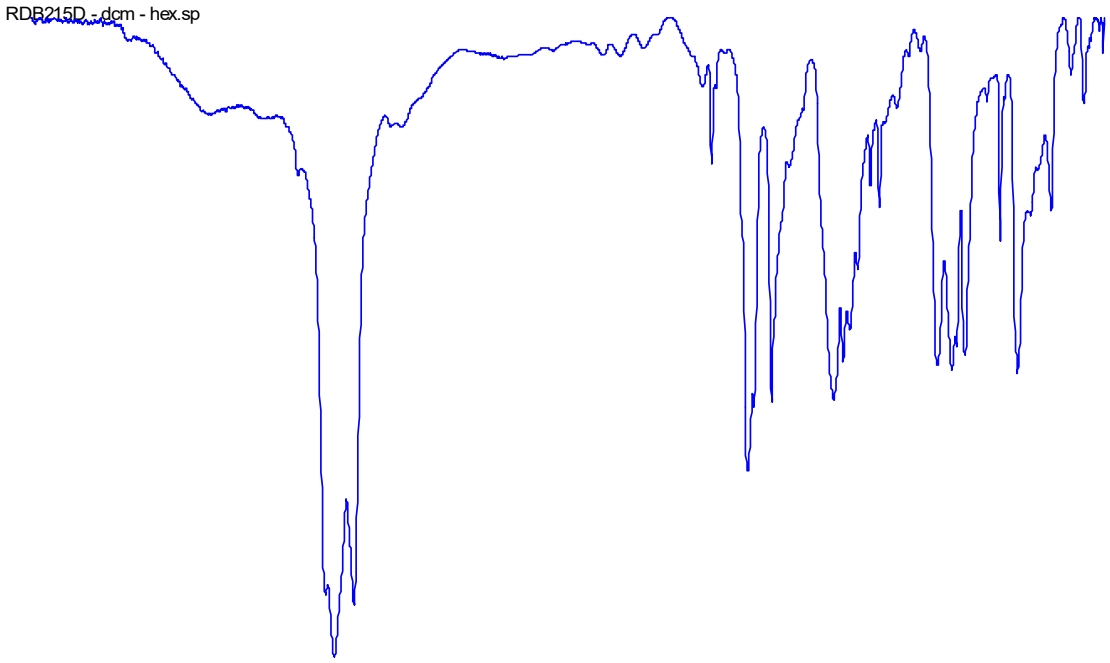

Figure S36 - Infrared spectrum of $[ErCl(dppmO_2)_3]Cl_2$ (Nujol mull)

$[TmCl(dppmO_2)_3]Cl_2$ CD_2Cl_2 *

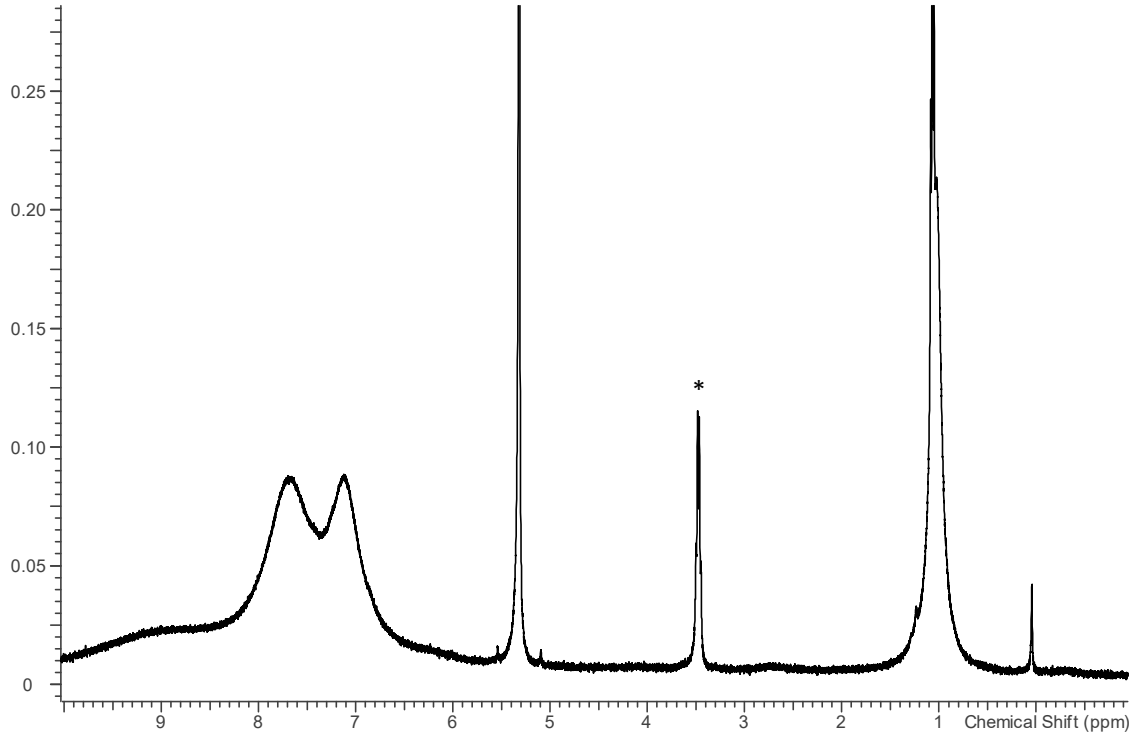

Figure S37 - ^{1}H NMR spectrum of $[TmCl(dppmO_2)_3]Cl_2$ in CD_2Cl_2 (* = EtOH)

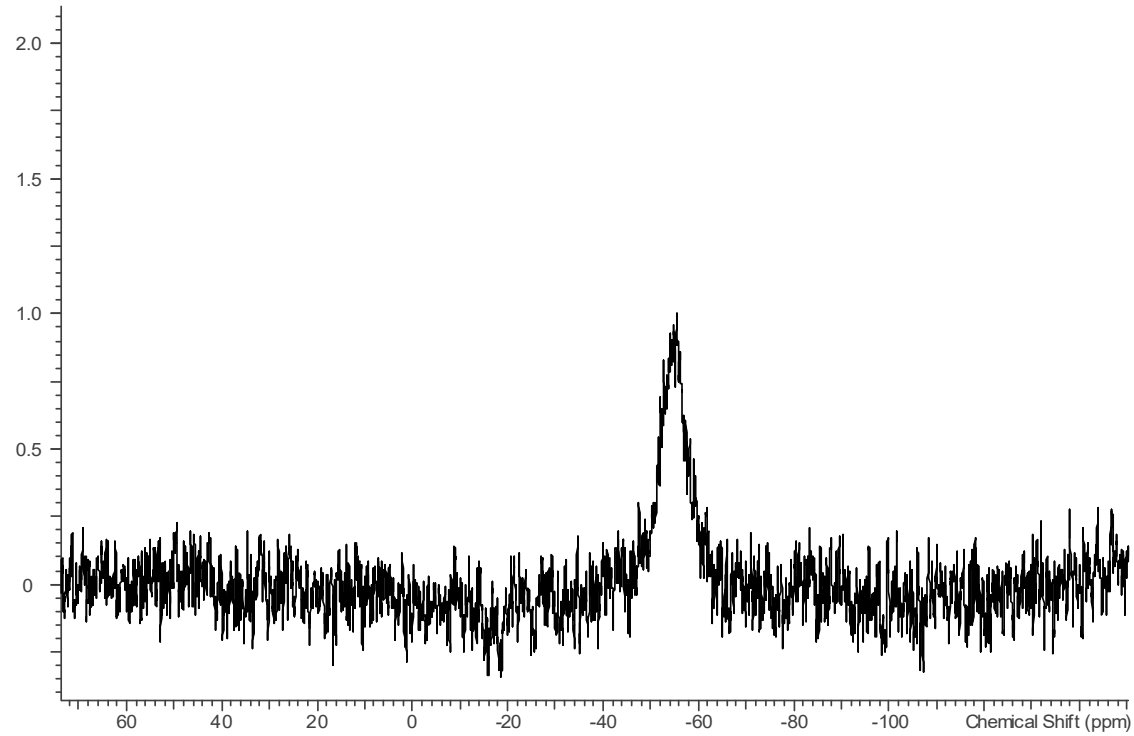

Figure S38 – $^{31}P\{^{1}H\}$ NMR spectrum of $[TmCl(dppmO_2)_3]Cl_2$ in CD_2Cl_2

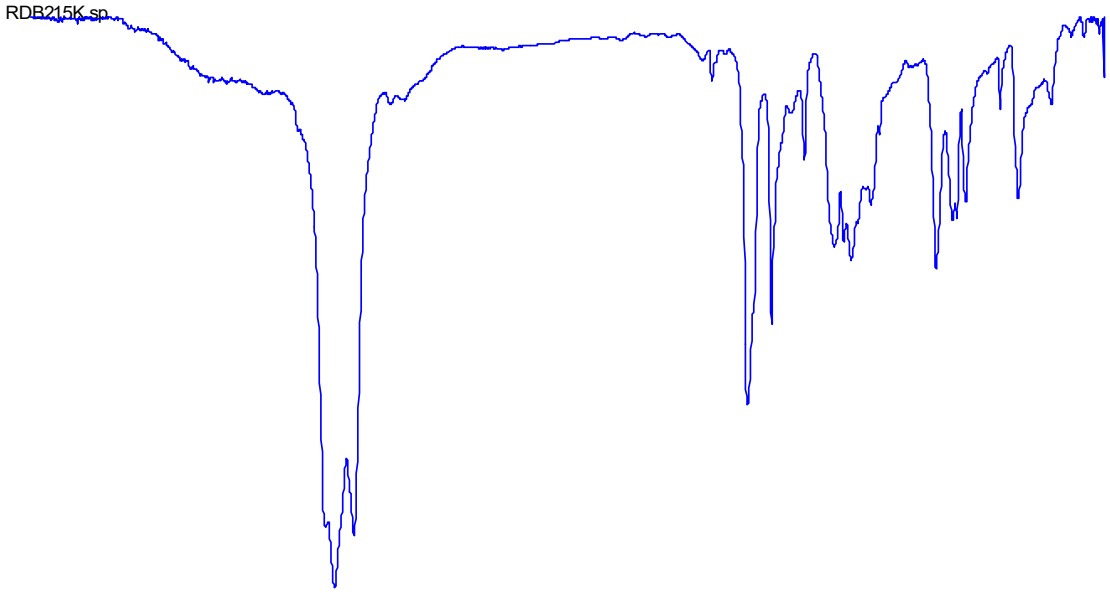

Figure S39 - Infrared spectrum of $[TmCl(dppmO_2)_3]Cl_2$ (Nujol mull)

$[YbCl(dppmO_2)_3]Cl_2$

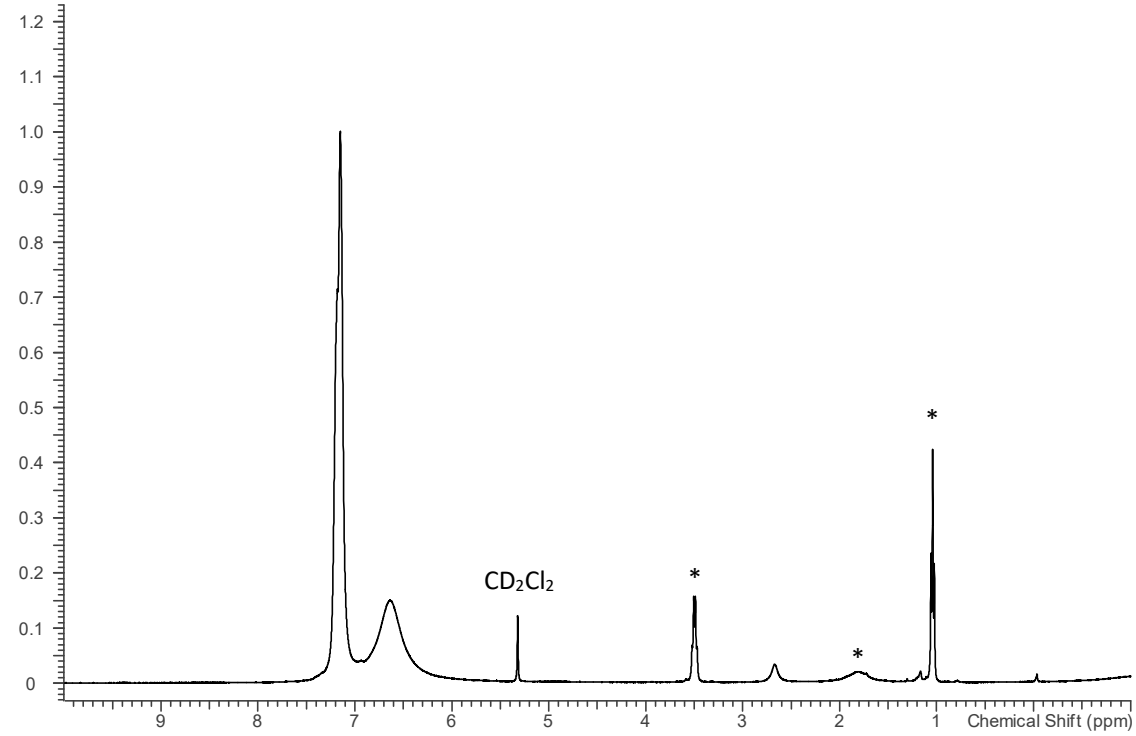

Figure S40 - ^1H NMR spectrum of $[YbCl(dppmO_2)_3]Cl_2$ in CD_2Cl_2 (* = EtOH)

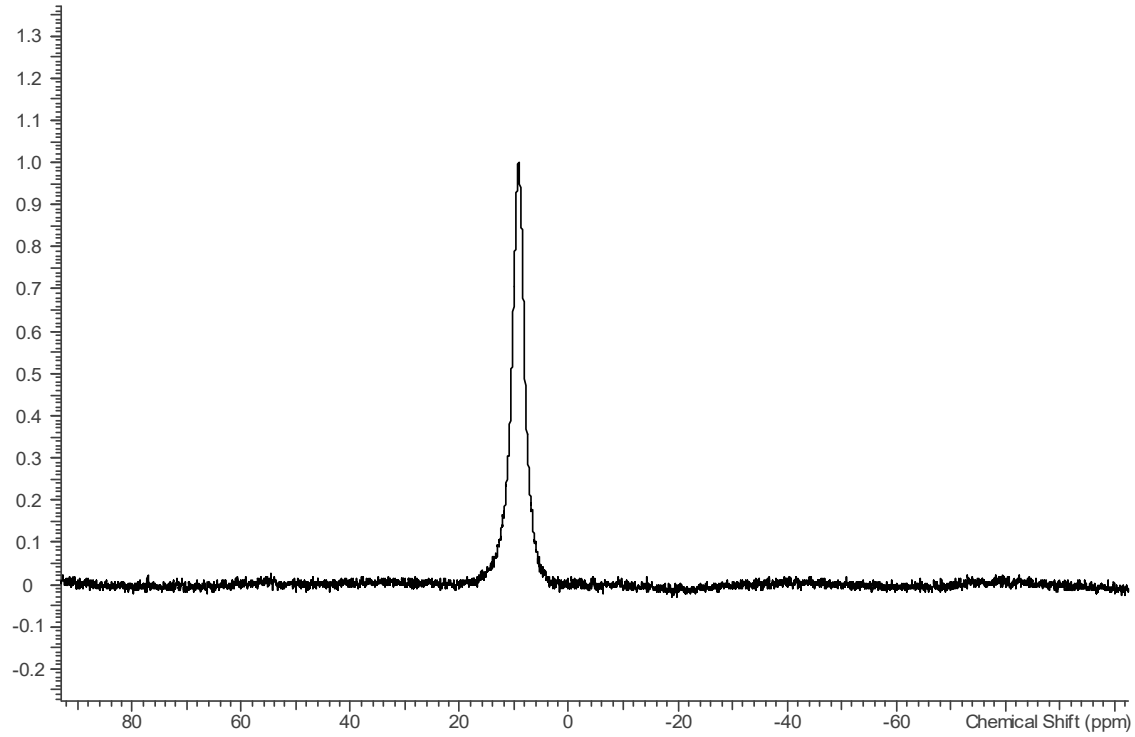

Figure S41 – $^{31}P\{^{1}H\}$ NMR spectrum of $[YbCl(dppmO_2)_3]Cl_2$ in CD_2Cl_2

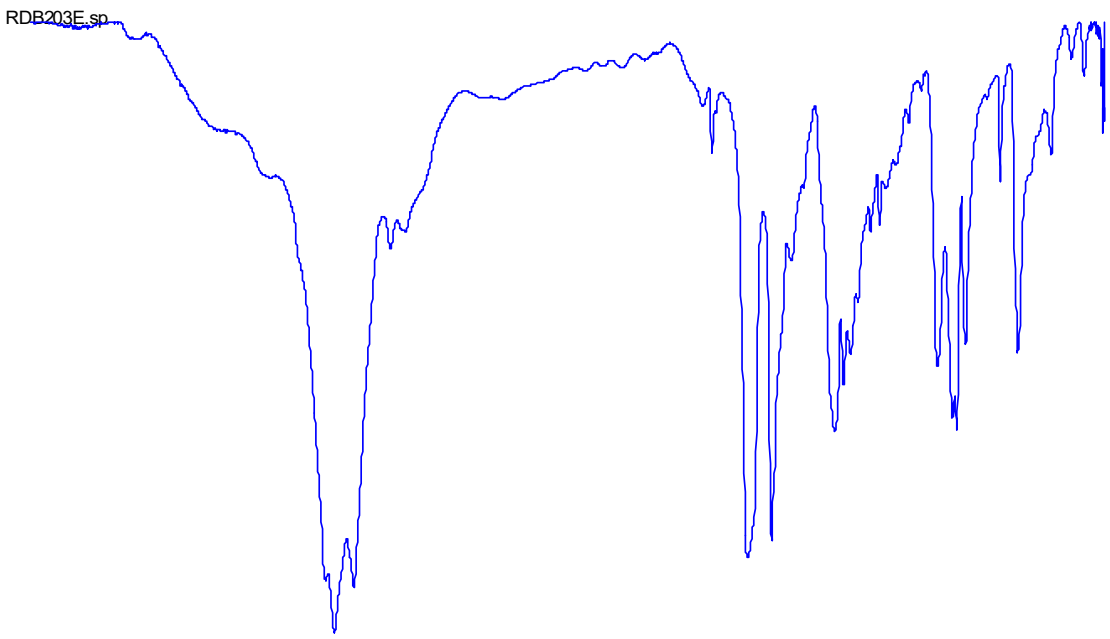

Figure S42 - Infrared spectrum of $[YbCl(dppmO_2)_3]Cl_2$ (Nujol mull)

Additional Crystal Structure Data

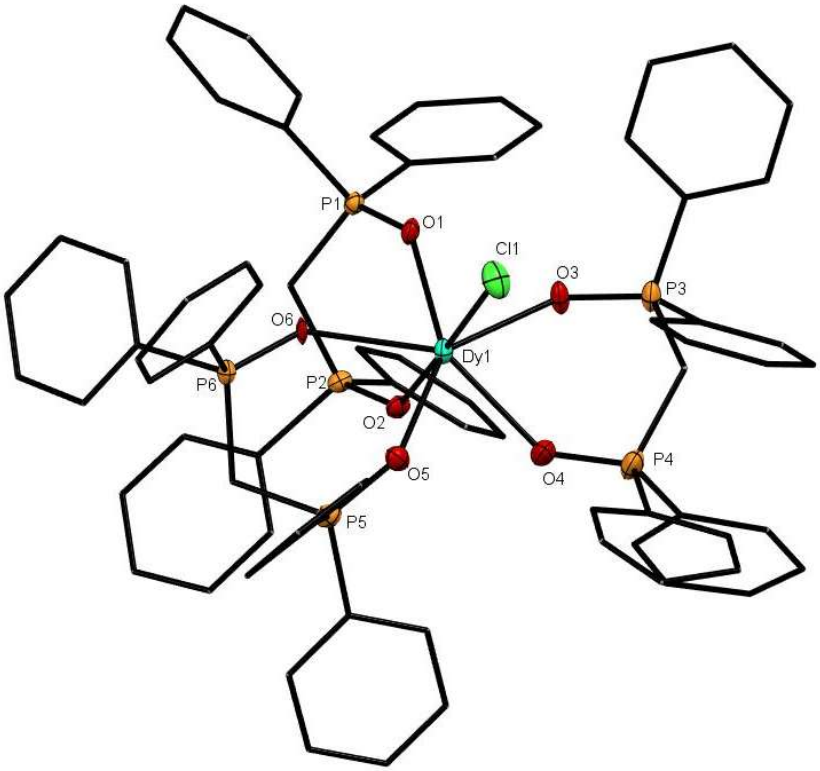

Figure S43 - The cation in $[DyCl(dppmO_2)_3]Cl_2$. The chloride anions and solvate molecules are omitted. Selected bond lengths (Å) and angles (°): Dy1–Cl1 = 2.619(2), Dy1–O1 = 2.289(5), Dy1–O2 = 2.292(6), Dy1–O3 = 2.337(5), Dy1– O4 = 2.328(6), Dy1–O5 = 2.311(5), Dy1–O6 = 2.366(5); chelate angle O–Dy–O = 76.1° (av).

Compound	$[Dy\{Ph_2(O)CH_2P(O)Ph_2\}_3Cl]Cl_2 \cdot 4CH_2Cl_2 \cdot H2O$
Formula	$C_{79}H_{76}Cl_{11}DyO_7P_6$
M	1875.66
Crystal system	Orthorhombic
Space group (no.)	Pcca (54)
a /Å	47.6440(6)
b /Å	12.79230(10)
c /Å	28.4954(3)
α /°	90
β /°	90
γ /°	90
U /Å^3	17367.3(3)
Z	8
μ(Mo-K_α) /mm^{-1}	1.359
F(000)	7592
Total number reflns	236677
R_{int}	0.0631
Unique reflns	22444
No. of params, restraints	882, 82
R_1, wR_2 [I > 2σ(I)] [b]	0.1093, 0.2227
R_1, wR_2 (all data)	0.1140, 0.2245