Electronic Supplementary Material (ESI) for Dalton Transactions.

Three derivatives of phenacyldiphenylphosphine oxide: Influence of aromatic and alkyl substituents on the luminescence sensitization of four $Ln(NO_3)_3$ salts

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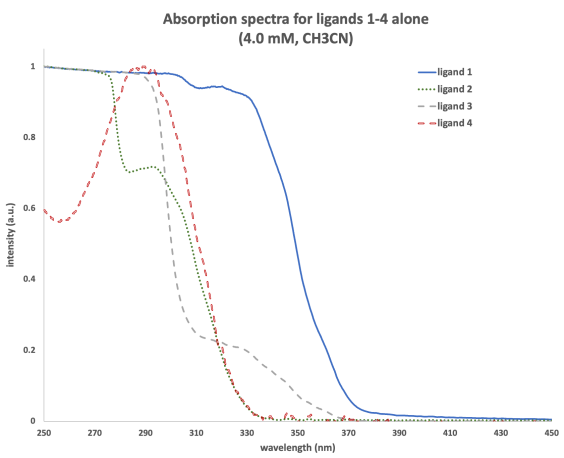
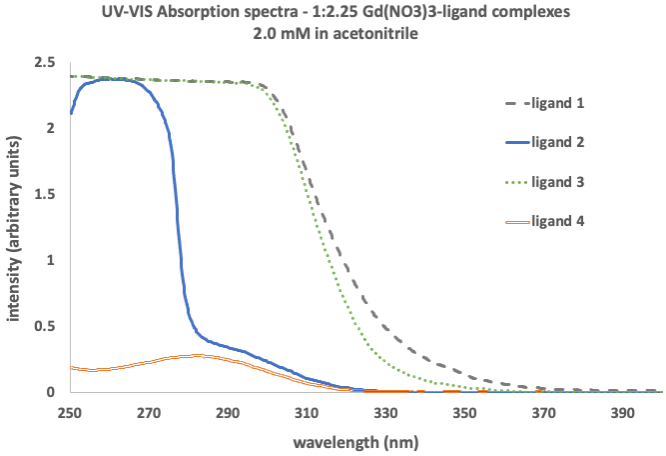
General considerations

All chemicals (including deuterated solvents) were purchased from Sigma-Aldrich or Strem Chemical and used without further purification. NMR spectral data (^{1}H, ^{13}C, ^{31}P) were recorded on either a JEOL Eclipse 300, Varian Inova 400, JEOL ECZS 400 or JEOL 500 NMR spectrophotometer, as stated. For NMR spectra, chemical shifts are expressed as parts per million (δ) relative to $SiMe_4$ (TMS, $\delta = 0$) for ^{1}H and ^{13}C data, and H_3PO_4 ($\delta = 0$) for ^{31}P data. ^{31}P NMR spectra were obtained as proton-decoupled data. IR spectra were acquired neat on either a Jasco 4100 or ThermoScientific Nicolet iS10 FTIR. Elemental (CHN) analyses were performed by Atlantic Microlab Inc., Norcross, GA; all CHN percentages calculated for lanthanide complexes assume two phosphine oxide ligands + $Ln(NO_3)_3$ + residual water/solvents as indicated. Low resolution mass spectrometry data were acquired on an Advion Expression-L Compact Mass Spectrometer in ESI mode (direct introduction). Luminescence data were recorded on a Horiba Fluoromax 4 fluorimeter, and absorption spectra were collected using a Shimadzu UV-2450 spectrophotomer. All photophysical data were acquired at ambient temperature.

A. Absorption, excitation and emission spectra

1. Absorption spectra for each ligand (alone) and the 1:2.25 $Gd(NO_3)_3$ complexes





2. Spectra for each Ln-ligand complex

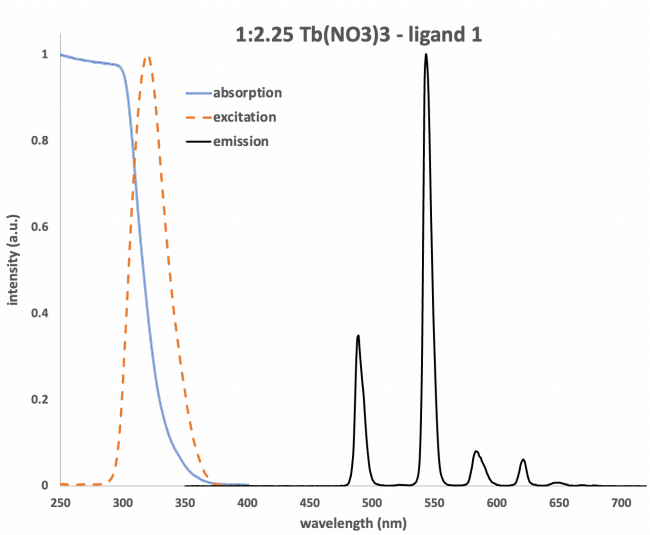
General conditions. For each sample, the ratio between the ligand and $Ln(NO_3)_3$ is 2.25:1 with a 2.0 mM complex concentration in CH_3CN. For all spectra shown in this section, the intensity values have been normalized for ease of comparison.

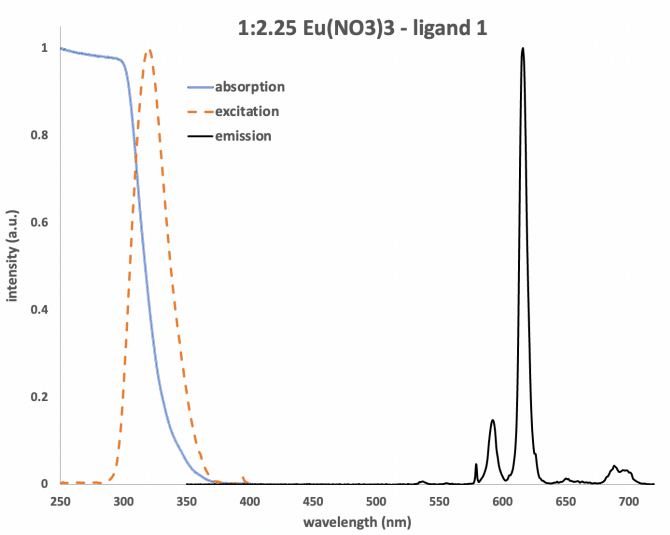
Absorption spectra details:

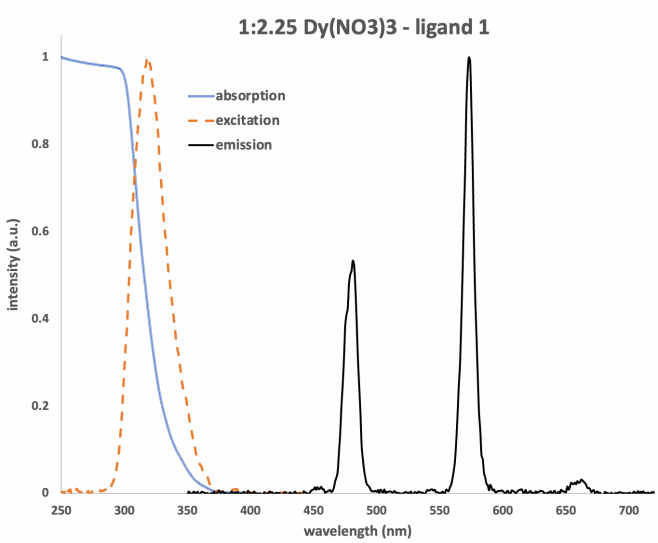
Excitation spectra details:
$Tb(NO_3)_3$ complexes: monitored emission at 543 nm, both slit widths = 1.0 nm
$Eu(NO_3)_3$ complexes: monitored emission at 616 nm, both slit widths = 1.0 nm
$Sm(NO_3)_3$ complexes: monitored emission at 642 nm, both slit widths = 1.5 nm
$Dy(NO_3)_3$ complexes: monitored emission at 573 nm, both slit widths = 1.5 nm

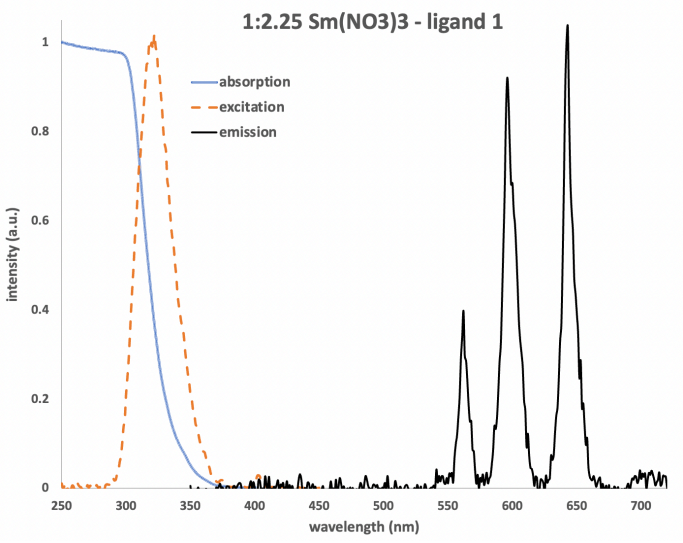
Emission spectra details:
Solutions of all complexes were excited at 300 nm.
$Tb(NO_3)_3$ complexes: both slit widths = 1.0 nm
$Eu(NO_3)_3$ complexes: both slit widths = 1.0 nm
$Sm(NO_3)_3$ complexes: both slit widths = 1.5 nm
$Dy(NO_3)_3$ complexes: both slit widths = 1.5 nm

Ligand 1 complexes

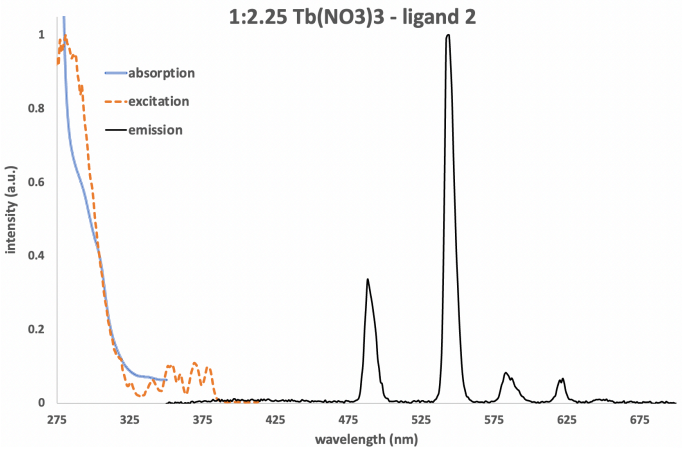


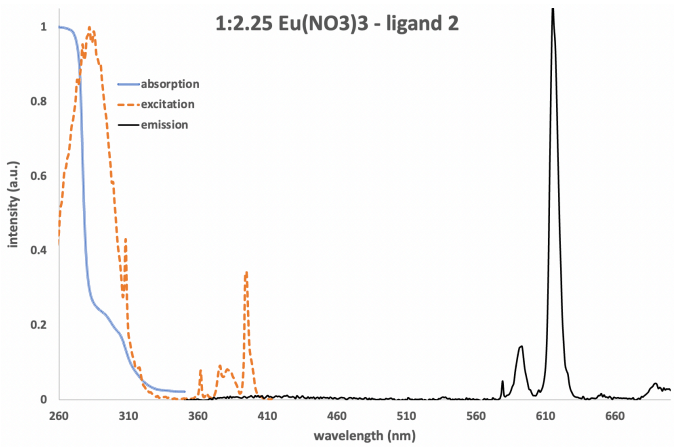


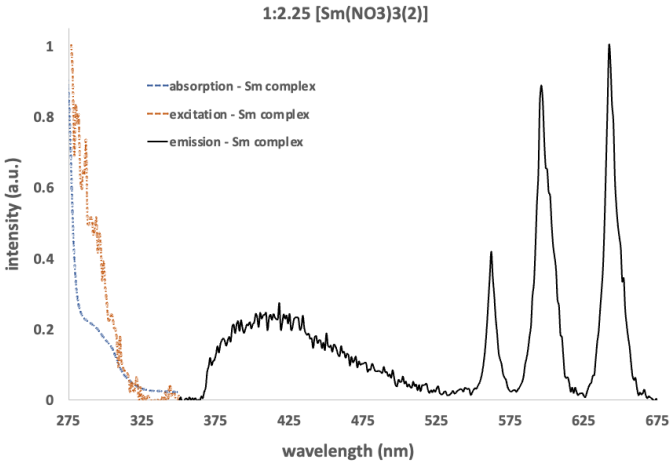


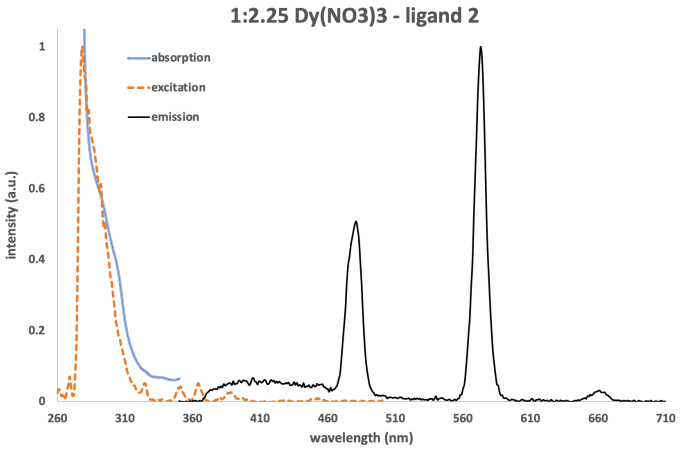


Ligand 2 complexes

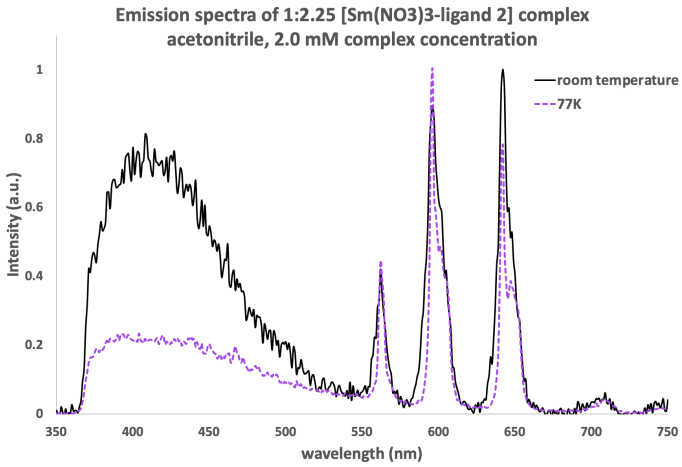




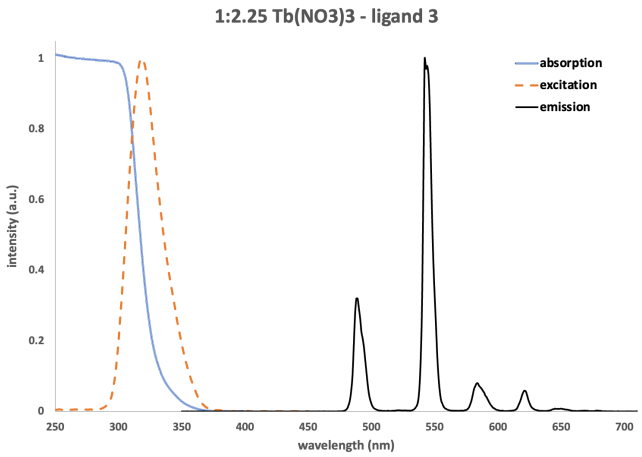


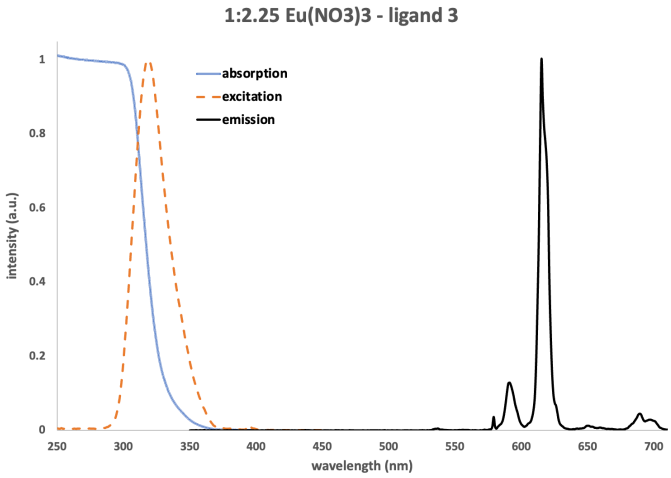


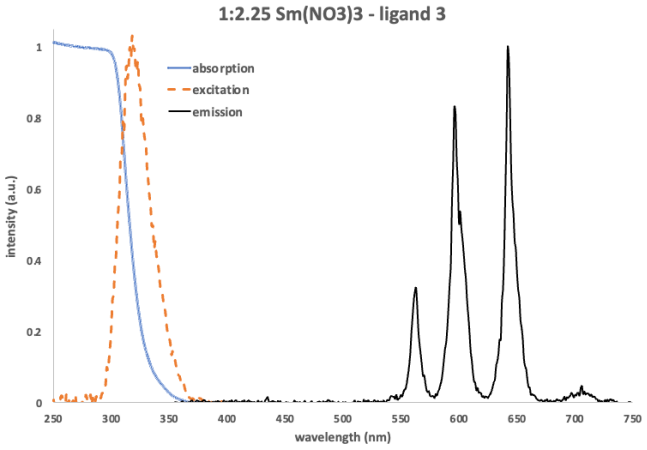
Emission spectra of $Sm(2)_{2.25}(NO_3)_3$ complex at room temperature vs. 77 K

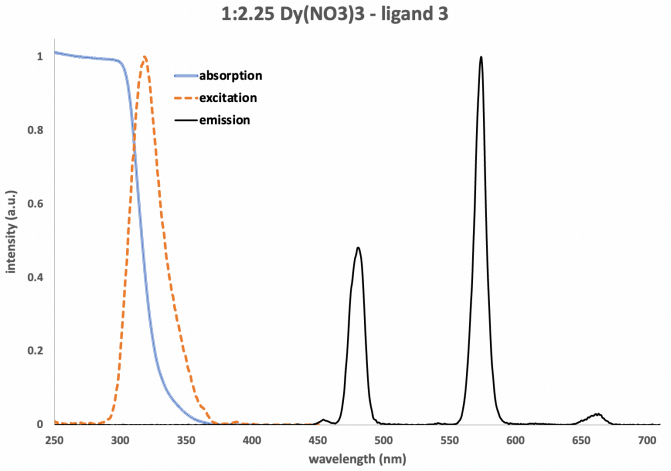


Ligand 3 complexes

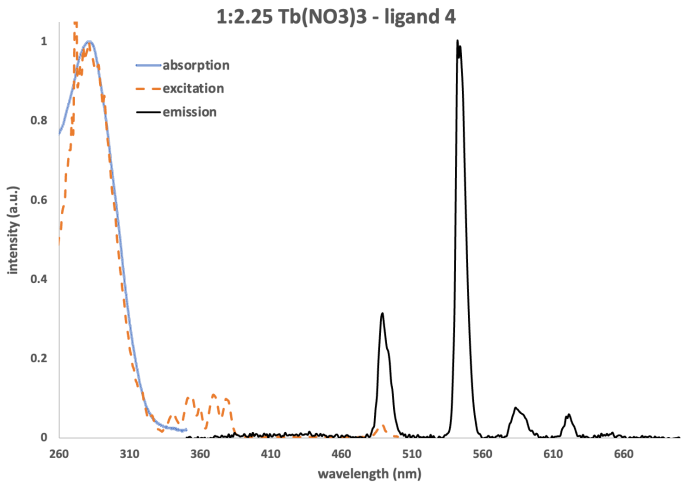


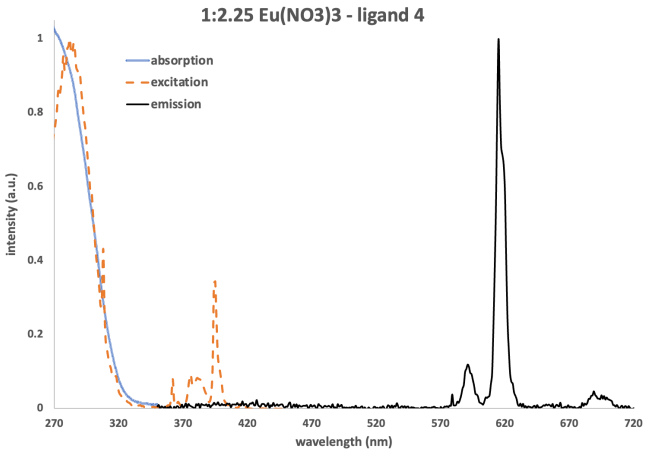


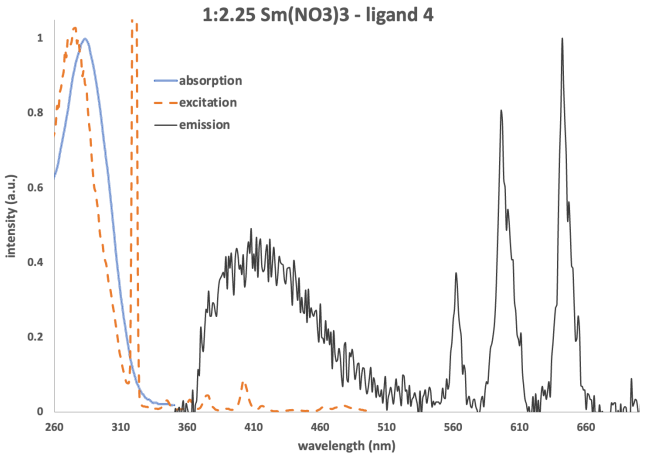


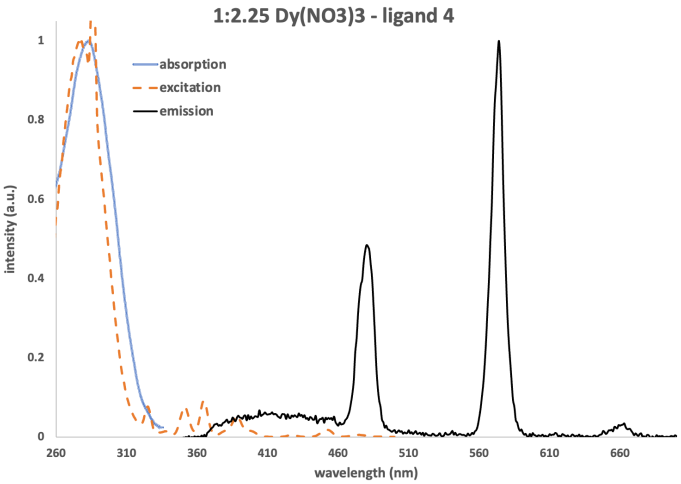


Ligand 4 complexes

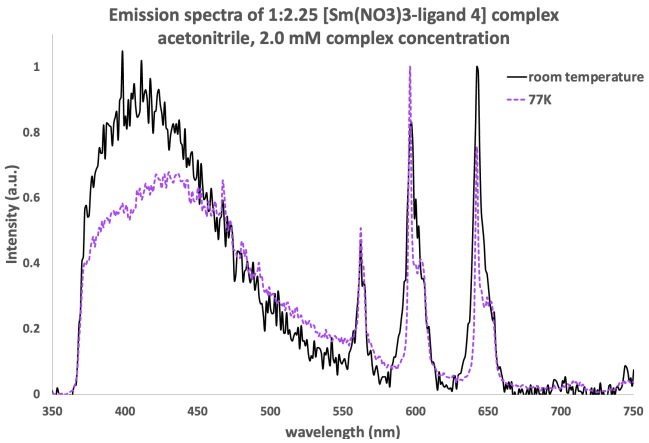








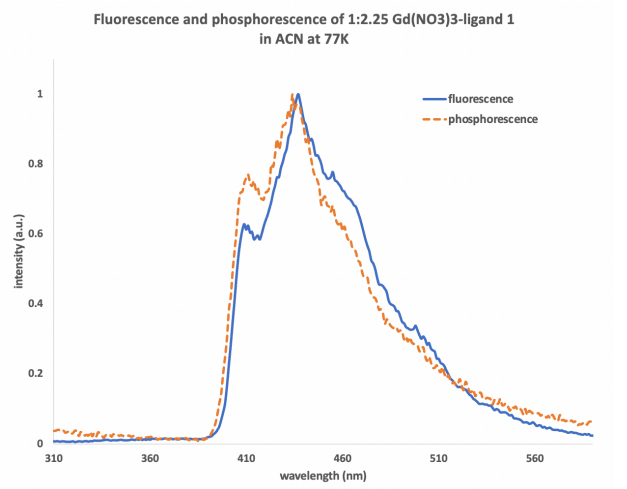
Emission spectra of $Sm(4)_{2.25}(NO_3)_3$ complex at room temperature vs. 77 K

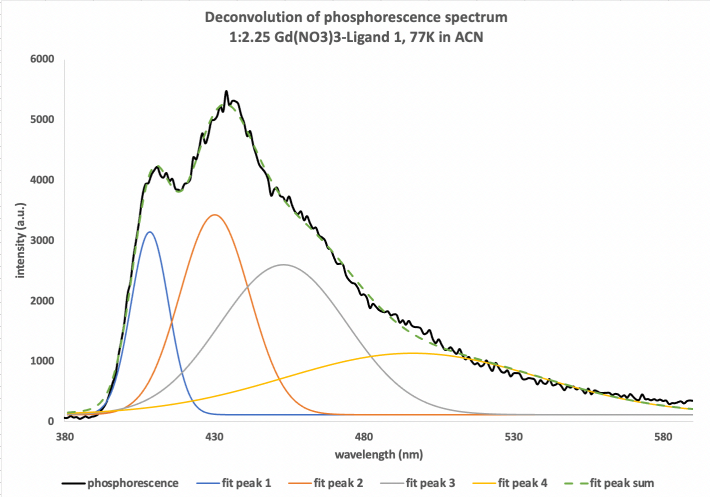


Determination of singlet and triplet state energies

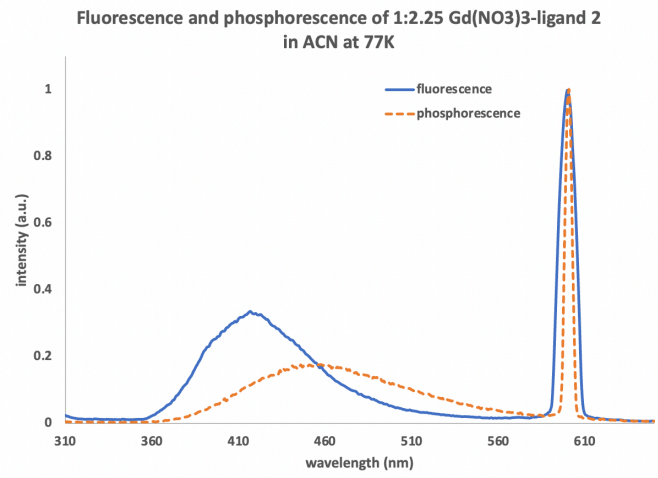
General note: the charts showing emission in fluorescence vs. phosphorescence mode have had the emission intensities normalized to unity for ease of comparison, and the signal at 600 nm is the double excitation peak.

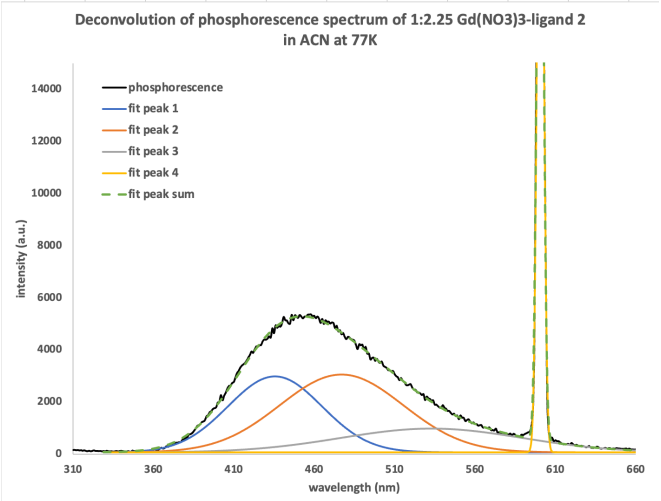
Ligand 1: [Gd(**1**)$_{2.25}$(NO$_3$)$_3$] 2.0 mM complex in CH_3CN at 77K
Slit widths = 1.0 nm, excitation wavelength = 300 nm, phosphorescence details = delay time = 0.05 ms; time per flash = 41.0 ms; sample window = 1.50 ms; flash count = 100





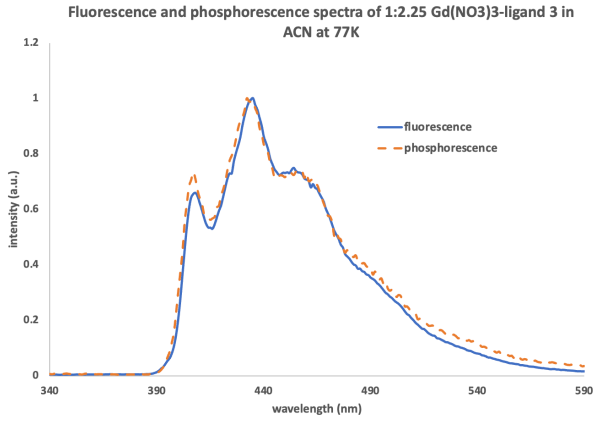
Ligand 2: [Gd(**2**)$_{2.25}$(NO$_3$)$_3$] 2.0 mM complex in CH_3CN at 77K
Slit widths = excitation: 3 nm, emission: 1.5 nm, excitation wavelength = 300 nm, phosphorescence details = delay time = 0.05 ms; time per flash = 41.0 ms; sample window = 1.50 ms; flash count = 100

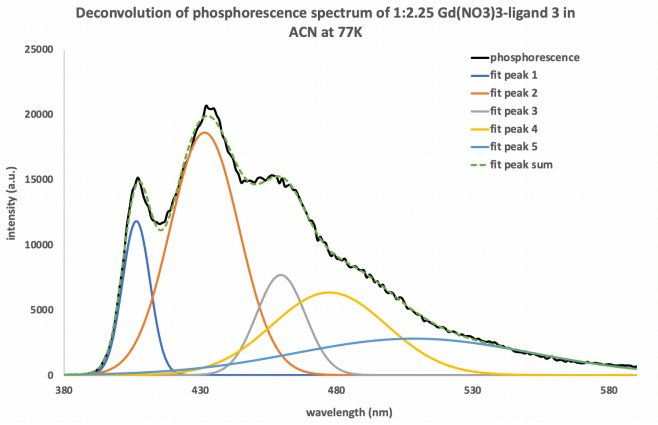




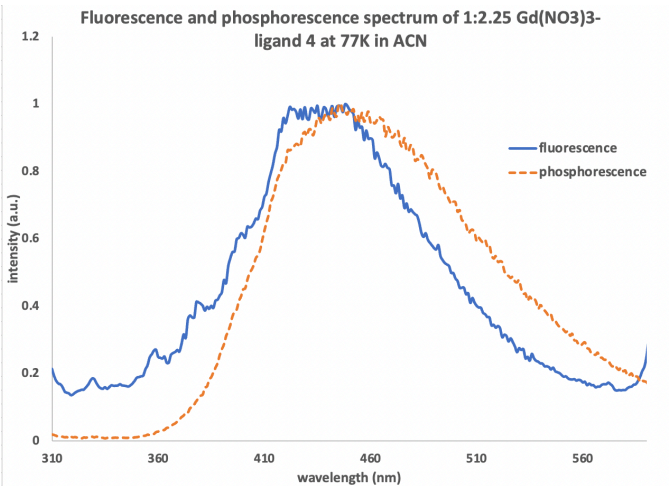
Note: the double excitation peak at 600 nm was included in the multi-peak fitting since it overlapped significantly with the ligand emission, so although there are four fit peaks shown only three correspond to the phosphorescence of ligand **2**.

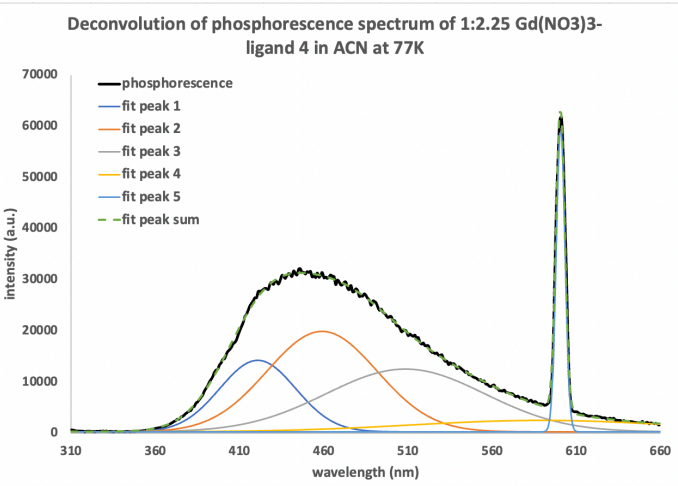
Ligand 3: [Gd(**3**)$_{2.25}$(NO$_3$)$_3$] 2.0 mM complex in CH_3CN at 77K
Slit widths = 1 nm, excitation wavelength = 300 nm, phosphorescence details = delay time = 0.05 ms; time per flash = 41.0 ms; sample window = 1.50 ms; flash count = 100





Ligand 4: [Gd(**4**)$_{2.25}$(NO$_3$)$_3$] 2.0 mM complex in CH_3CN at 77K
Slit widths = excitation: 1 nm, emission: 2 nm; excitation wavelength = 300 nm, phosphorescence details = delay time = 0.05 ms; time per flash = 41.0 ms; sample window = 1.50 ms; flash count = 100

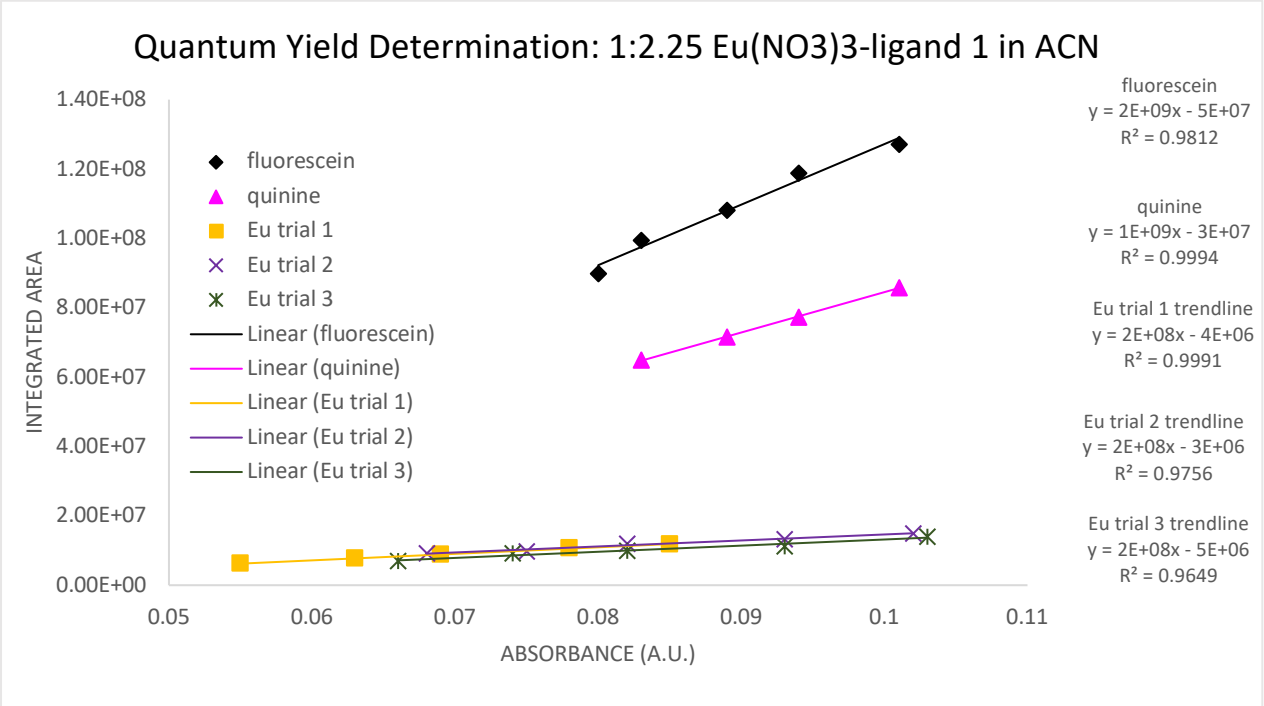


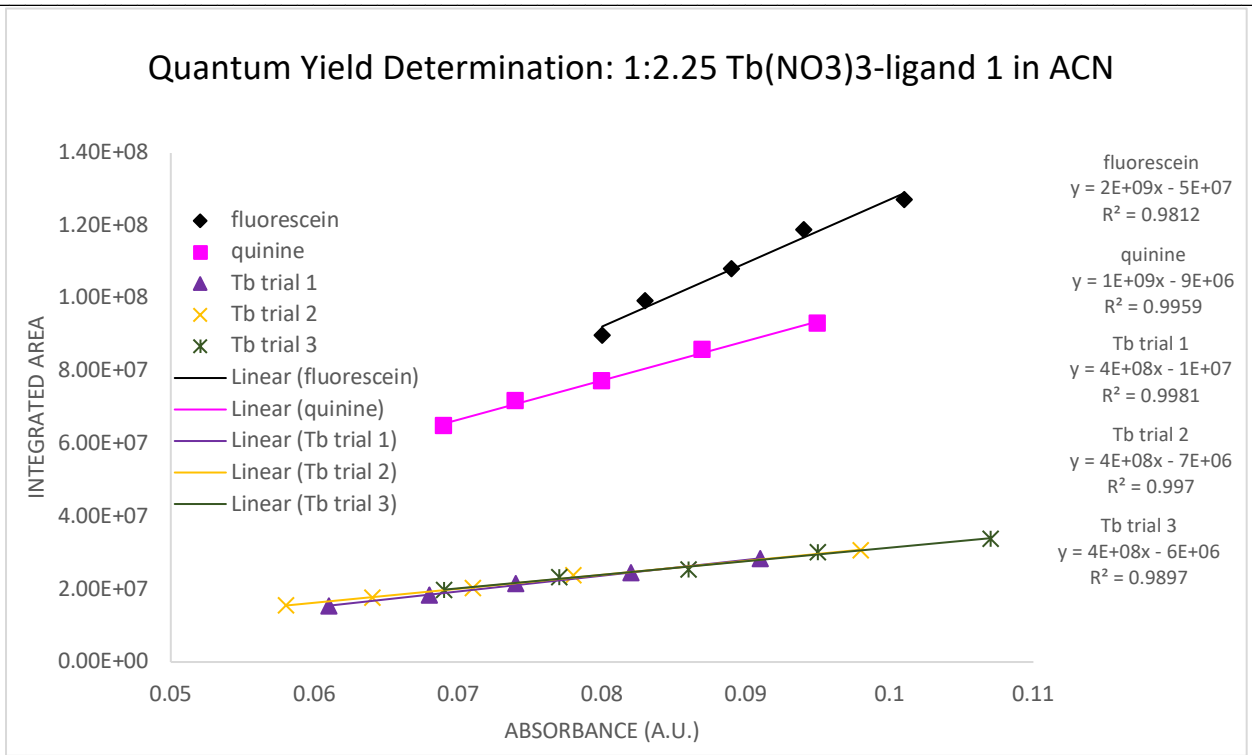


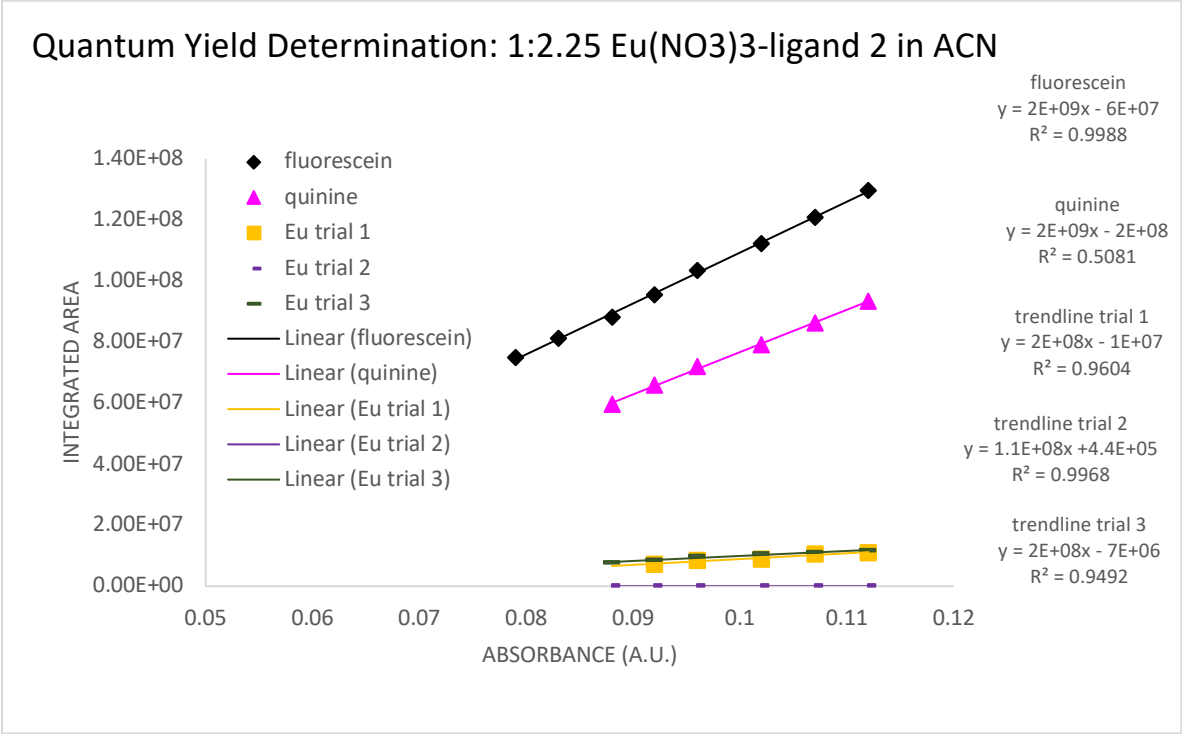
note: the double excitation peak at 600 nm was included in the multi-peak deconvolution calculation, so although there are five fit peaks shown, only four correspond to the phosphorescence of ligand **4**.

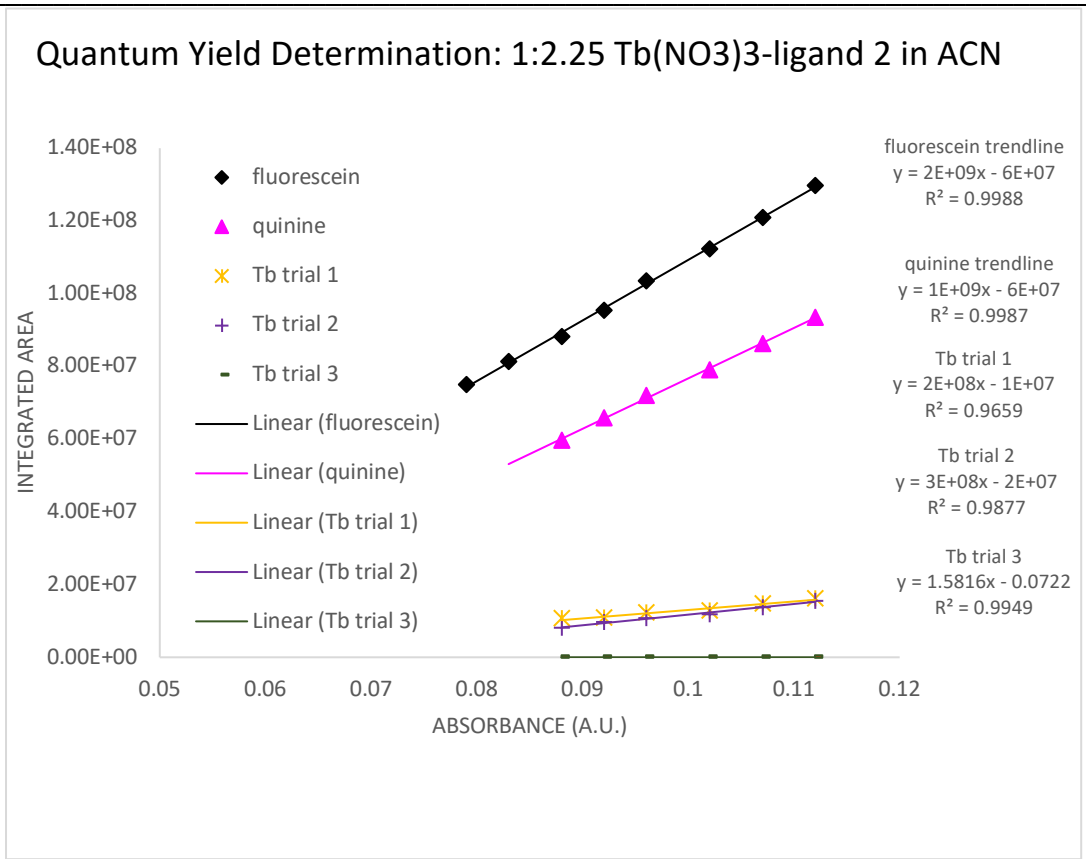
B. Quantum Yield determination.

The ligand (**1**-**4**) of interest and metal nitrate ($Tb(NO_3)_3$, $Eu(NO_3)_3$) were dissolved in acetonitrile in a 2.25:1 ratio to create 20 mM stock solutions. The cuvette was filled with 0.3 mL of the stock complex and 2.7 mL of acetonitrile. The solution was analyzed in the UV Vis spectrophotometer to determine the absorbance at the excitation wavelength of 284 nm. The solution was diluted to 0.1 ABS and a corrected emission spectrum was taken from 320-800 nm with 1 nm slit widths. A corrected emission spectrum of the blank solvent was also taken from 320-800 nm with 1 nm slit widths. Integrated areas of the blank solvent and the complexes were taken from the emission spectra. The complex was then diluted by removing 0.3 mL of the contents and replacing it with 0.3 mL of acetonitrile. The absorbance and integrated area were collected and again the integrated area of the blank solvent was subtracted. This was repeated five times with different absorbances. The slope of the integrated area versus the absorbance was determined. This procedure was repeated with the standards fluorescein in 0.1 M NaOH and quinine in 0.1 M H_2SO_4. The quantum yields were determined using the relative method.[1] The equation used was $\phi_u = \phi_{st}(\frac{Grad_u}{Grad_{st}})(\frac{\eta_u^2}{\eta_{st}^2})$. The quantum yield of the unknown is ϕ_u. The quantum yield of the standard is ϕ_{st}. The slope of the integrated area versus the absorbance of the unknown solutions is $Grad_u$. The slope of the integrated area versus the absorbance of the standard solution is $Grad_{st}$. The refractive index of the solvent for the unknown solution is η_u. The refractive index of the solvent for the standard solution is η_{st}. The values used for each known quantity were taken from the literature as: $\Phi_{\text{quinine}} = 0.54$; $\Phi_{\text{fluorescein}} = 0.79$;[2] $\eta_{\text{acetonitrile}} = 1.3441$; $\eta_{\text{0.1 M NaOH}} = 1.3344$; $\eta_{\text{0.1 M H2SO4}} = 1.3355$.

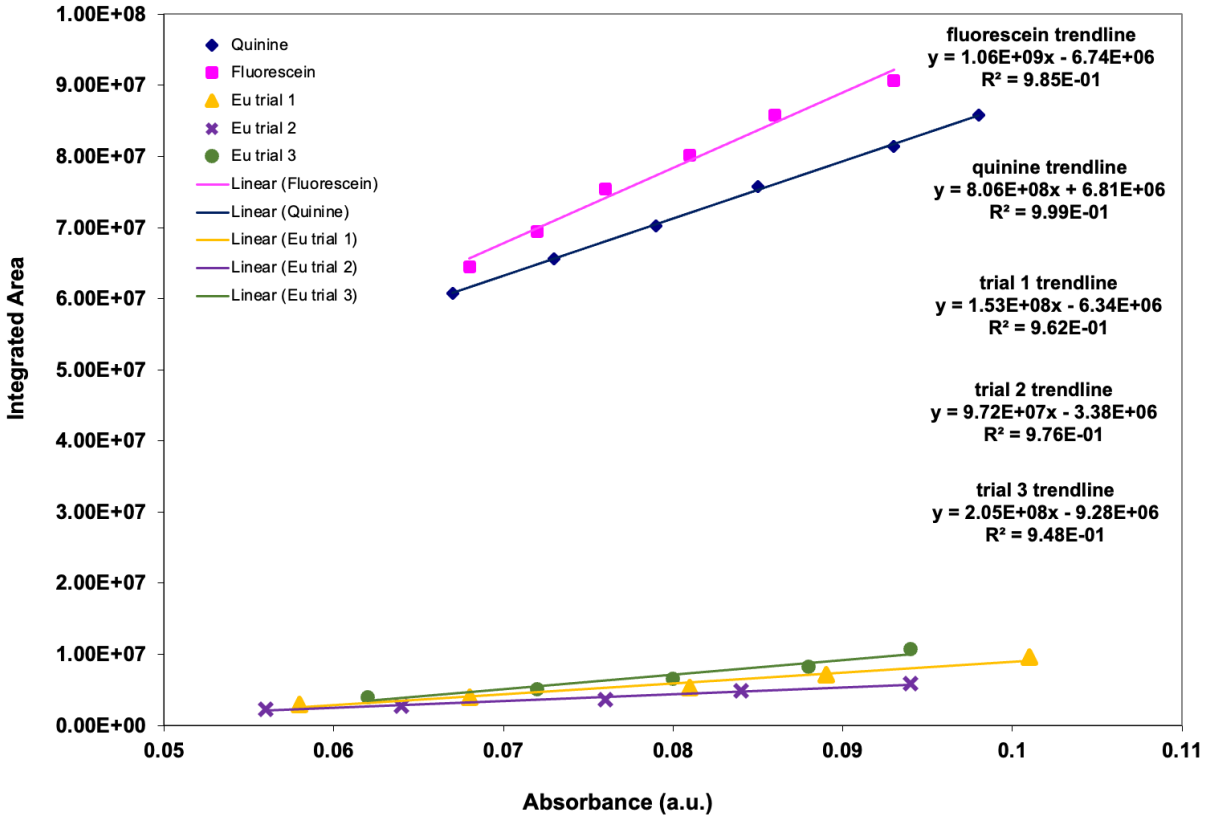

Quantum Yield Determination: 1:2.25 Eu(NO3)3-ligand 1 in ACN
INTEGRATED AREA
ABSORBANCE (A.U.)
1.40E+08
1.20E+08
1.00E+08
8.00E+07
6.00E+07
4.00E+07
2.00E+07
0.00E+00
0.05
0.06
0.07
0.08
0.09
0.1
0.11
fluorescein
quinine
Eu trial 1
Eu trial 2
Eu trial 3
Linear (fluorescein)
Linear (quinine)
Linear (Eu trial 1)
Linear (Eu trial 2)
Linear (Eu trial 3)
fluorescein
y = 2E+09x - 5E+07
R² = 0.9812
quinine
y = 1E+09x - 3E+07
R² = 0.9994
Eu trial 1 trendline
y = 2E+08x - 4E+06
R² = 0.9991
Eu trial 2 trendline
y = 2E+08x - 3E+06
R² = 0.9756
Eu trial 3 trendline
y = 2E+08x - 5E+06
R² = 0.9649


Quantum Yield Determination: 1:2.25 Tb(NO3)3-ligand 1 in ACN
INTEGRATED AREA
ABSORBANCE (A.U.)
1.40E+08
1.20E+08
1.00E+08
8.00E+07
6.00E+07
4.00E+07
2.00E+07
0.00E+00
0.05
0.06
0.07
0.08
0.09
0.1
0.11
fluorescein
quinine
Tb trial 1
Tb trial 2
Tb trial 3
Linear (fluorescein)
Linear (quinine)
Linear (Tb trial 1)
Linear (Tb trial 2)
Linear (Tb trial 3)
fluorescein
y = 2E+09x - 5E+07
R² = 0.9812
quinine
y = 1E+09x - 9E+06
R² = 0.9959
Tb trial 1
y = 4E+08x - 1E+07
R² = 0.9981
Tb trial 2
y = 4E+08x - 7E+06
R² = 0.997
Tb trial 3
y = 4E+08x - 6E+06
R² = 0.9897

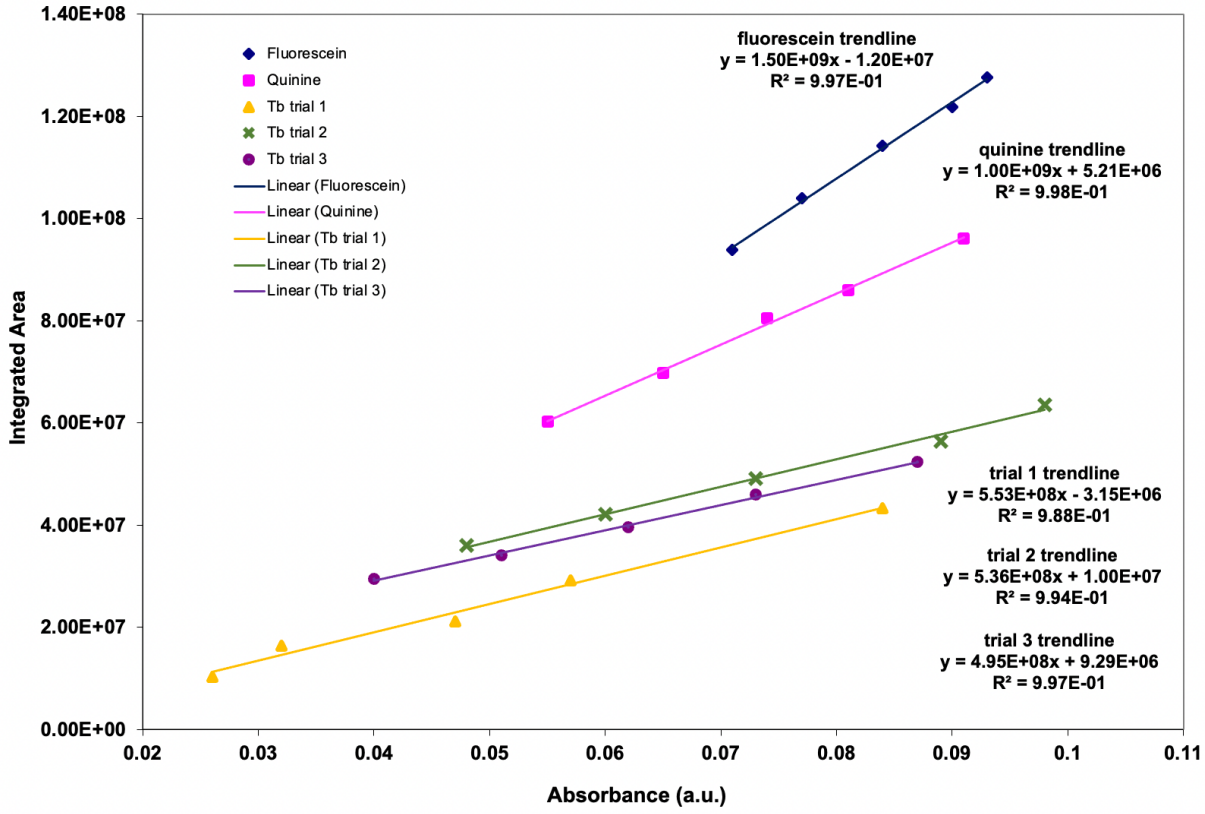

Quantum Yield Determination: 1:2.25 Eu(NO3)3-ligand 2 in ACN
fluorescein
y = 2E+09x - 6E+07
R² = 0.9988
quinine
y = 2E+09x - 2E+08
R² = 0.5081
trendline trial 1
y = 2E+08x - 1E+07
R² = 0.9604
trendline trial 2
y = 1.1E+08x +4.4E+05
R² = 0.9968
trendline trial 3
y = 2E+08x - 7E+06
R² = 0.9492
1.40E+08
1.20E+08
1.00E+08
8.00E+07
6.00E+07
4.00E+07
2.00E+07
0.00E+00
INTEGRATED AREA
fluorescein
quinine
Eu trial 1
Eu trial 2
Eu trial 3
Linear (fluorescein)
Linear (quinine)
Linear (Eu trial 1)
Linear (Eu trial 2)
Linear (Eu trial 3)
0.05
0.06
0.07
0.08
0.09
0.1
0.11
0.12
ABSORBANCE (A.U.)

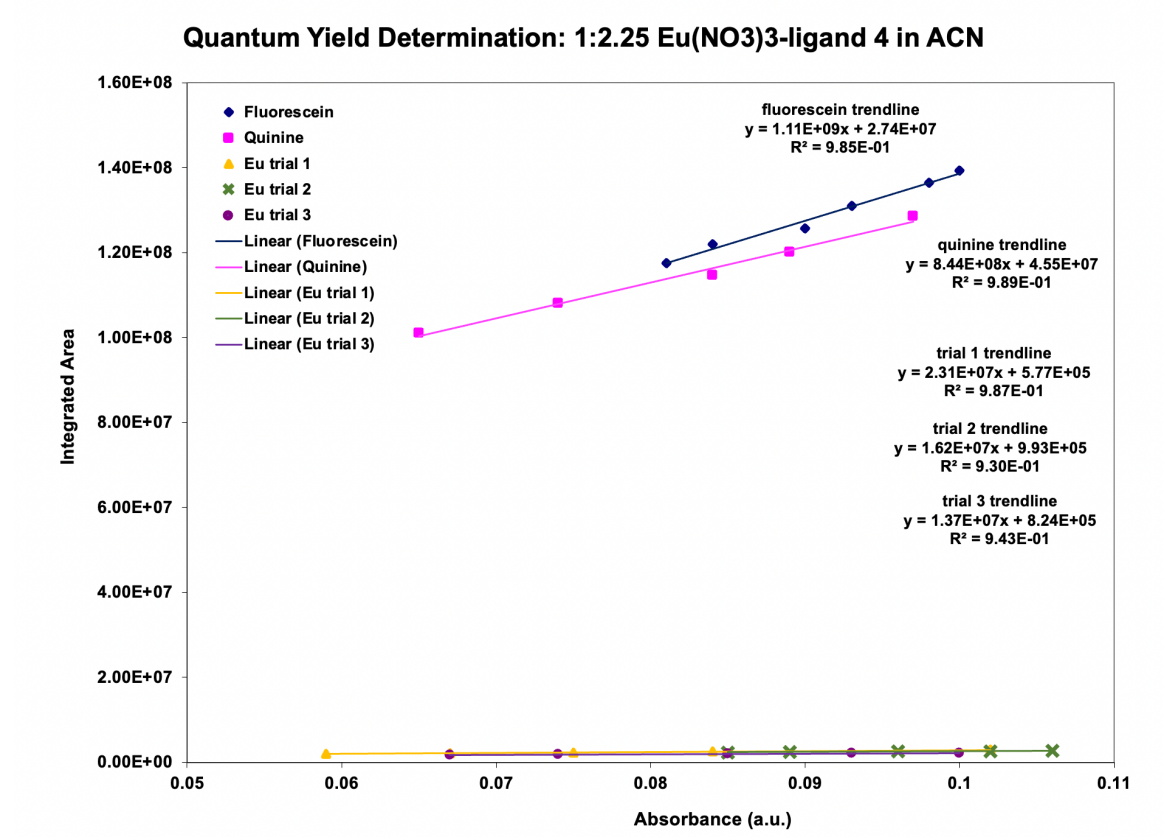

Quantum Yield Determination: 1:2.25 Tb(NO3)3-ligand 2 in ACN
fluorescein trendline
y = 2E+09x - 6E+07
R² = 0.9988
quinine trendline
y = 1E+09x - 6E+07
R² = 0.9987
Tb trial 1
y = 2E+08x - 1E+07
R² = 0.9659
Tb trial 2
y = 3E+08x - 2E+07
R² = 0.9877
Tb trial 3
y = 1.5816x - 0.0722
R² = 0.9949
1.40E+08
1.20E+08
1.00E+08
8.00E+07
6.00E+07
4.00E+07
2.00E+07
0.00E+00
INTEGRATED AREA
fluorescein
quinine
Tb trial 1
Tb trial 2
Tb trial 3
Linear (fluorescein)
Linear (quinine)
Linear (Tb trial 1)
Linear (Tb trial 2)
Linear (Tb trial 3)
0.05
0.06
0.07
0.08
0.09
0.1
0.11
0.12
ABSORBANCE (A.U.)

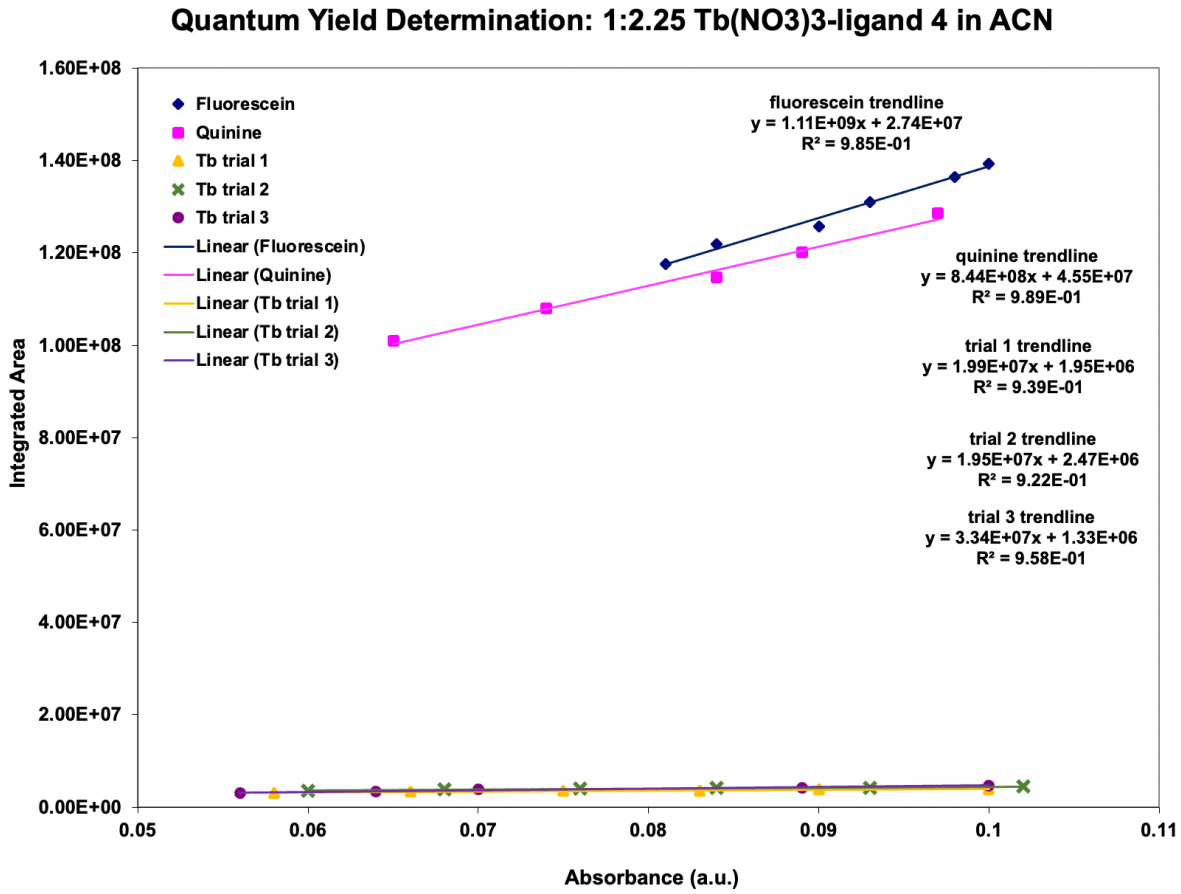
Quantum yield determination: 1:2.25 Eu(NO3)3-ligand 3 in ACN



Quantum Yield Determination: 1:2.25 Tb(NO3)3-ligand 3 in ACN




Quantum Yield Determination: 1:2.25 Eu(NO3)3-ligand 4 in ACN
Fluorescein
Quinine
Eu trial 1
Eu trial 2
Eu trial 3
Linear (Fluorescein)
Linear (Quinine)
Linear (Eu trial 1)
Linear (Eu trial 2)
Linear (Eu trial 3)
fluorescein trendline
y = 1.11E+09x + 2.74E+07
R² = 9.85E-01
quinine trendline
y = 8.44E+08x + 4.55E+07
R² = 9.89E-01
trial 1 trendline
y = 2.31E+07x + 5.77E+05
R² = 9.87E-01
trial 2 trendline
y = 1.62E+07x + 9.93E+05
R² = 9.30E-01
trial 3 trendline
y = 1.37E+07x + 8.24E+05
R² = 9.43E-01
Integrated Area
1.60E+08
1.40E+08
1.20E+08
1.00E+08
8.00E+07
6.00E+07
4.00E+07
2.00E+07
0.00E+00
0.05
0.06
0.07
0.08
0.09
0.1
0.11
Absorbance (a.u.)


Quantum Yield Determination: 1:2.25 Tb(NO3)3-ligand 4 in ACN
Fluorescein
Quinine
Tb trial 1
Tb trial 2
Tb trial 3
Linear (Fluorescein)
Linear (Quinine)
Linear (Tb trial 1)
Linear (Tb trial 2)
Linear (Tb trial 3)
fluorescein trendline
y = 1.11E+09x + 2.74E+07
R² = 9.85E-01
quinine trendline
y = 8.44E+08x + 4.55E+07
R² = 9.89E-01
trial 1 trendline
y = 1.99E+07x + 1.95E+06
R² = 9.39E-01
trial 2 trendline
y = 1.95E+07x + 2.47E+06
R² = 9.22E-01
trial 3 trendline
y = 3.34E+07x + 1.33E+06
R² = 9.58E-01
Integrated Area
1.60E+08
1.40E+08
1.20E+08
1.00E+08
8.00E+07
6.00E+07
4.00E+07
2.00E+07
0.00E+00
0.05
0.06
0.07
0.08
0.09
0.1
0.11
Absorbance (a.u.)

C. Luminescence lifetime decay curves, residuals and fitting statistics

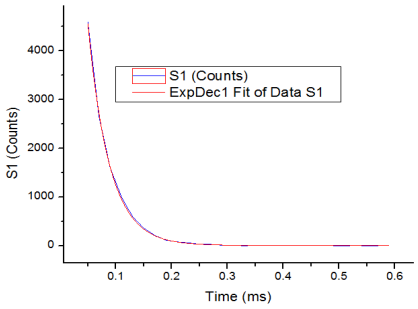
General considerations. All complex solutions were prepared by combining appropriate volumes of 20.0 mM stock solutions of the ligand and $Ln(NO_3)_3(H_2O)_6$ in HPLC grade CH_3CN to reach a 2.0 mM complex concentration with a 1:2.25 molar ratio between the $Ln(NO_3)_3$ salt and the ligand (unless otherwise noted). Spectra were acquired within 12 hours of stock solution preparation at ambient temperature. The temperature was not controlled in these experiments.

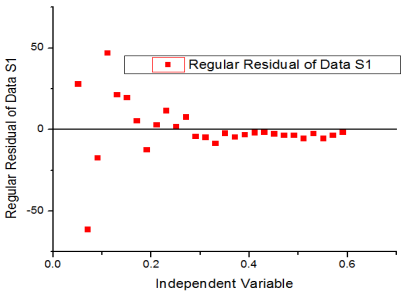
For some Ln(**1**-**4**)$_{2.25}(NO_3)_3$ complexes, the fitting of the decay data to a single exponential decay produced a curve which gave residuals that had shape (did not appear to be random). We attribute this to the fluxional nature of the Ln-ligand systems in solutions of acetonitrile, and that there is likely varying amounts of free metal and free ligand present in solution. In these instances, we attempted to fit the decay curve to a double exponential equation to try to capture the lifetimes of different complex stoichiometries or free metal in solution. Unfortunately, most of these attempts to fit the data were unsuccessful (did not converge).

Complexes of Ligand 1

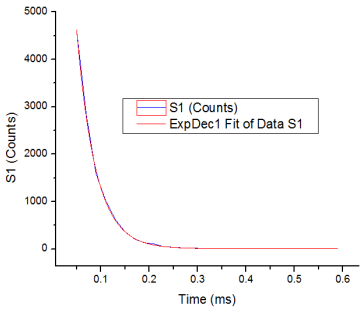
$Sm(1)_{2.25}(NO_3)_3$ complex

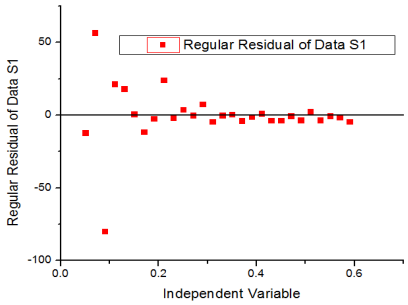
Fluorimeter settings: excitation: 300 nm; emission: 642 nm; excitation and emission slit widths: 2.5 nm; sample window: .08 ms; time between flashes: 41 ms; count (averages): 100; initial delay: 0.05 ms; max delay: .6 ms; delay increment: 0.02 ms



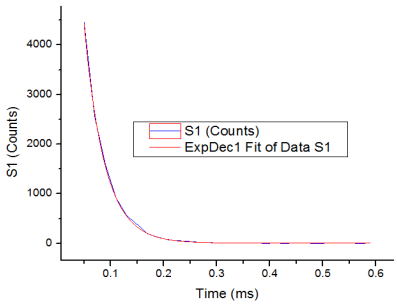


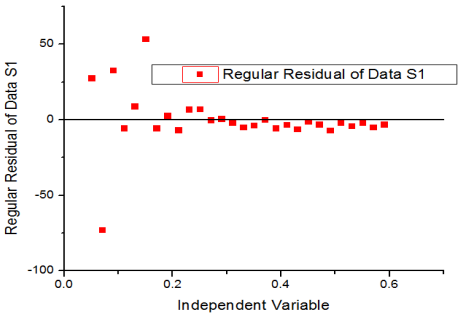
Trial 1





Trial 2





Trial 3

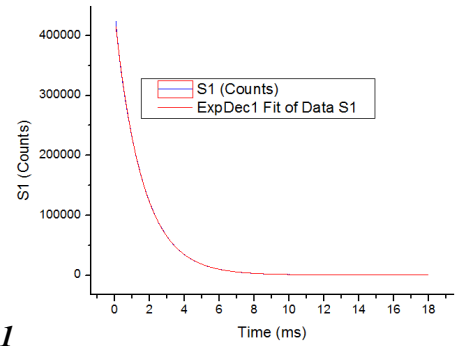
Fitting statistics, all trials

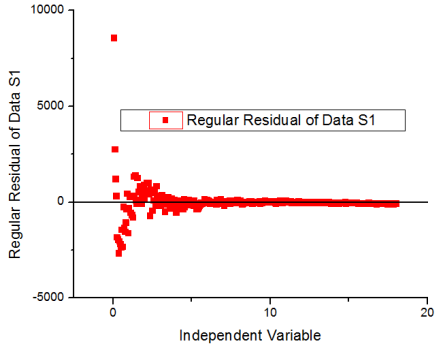
Model: ExpDec1; Equation: Y=A1*exp(-x/t1)+y0

		Trial 1		Trial 2		Trial 3	
Reduced Chi-Sqr		340.63046		457.87038		421.94201	
Adj R-Square		0.99967		0.99957		0.99956	
		Value	***Standard Error***	***Value***	***Standard Error***	***Value***	***Standard Error***
S1	**y0**	5.28326	4.11201	4.36238	4.7835	6.86838	4.57392
S1	**A1**	16733.87059	197.11505	16630.58374	219.40647	16313.59973	220.95257
S1	**t1**	0.03841	2.86385E-4	0.0391	3.30814E-4	0.03829	3.27526E-4

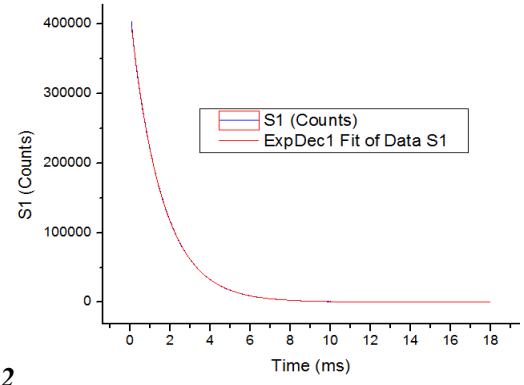
$Tb(1)_{2.25}(NO_3)_3$ complex

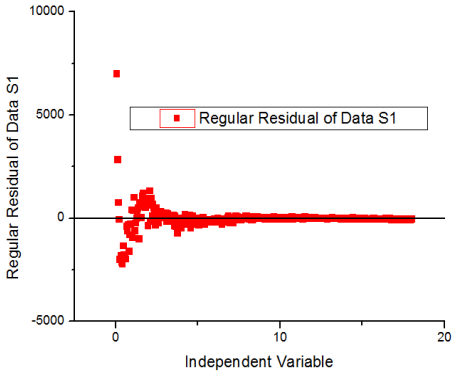
Fluorimeter settings for all trials: excitation: 300 nm; emission: 543 nm; slits: 1.5 nm; sample window: 1.8 ms; time between flashes: 41 ms; count (averages): 100; initial delay: 0.05 ms; max delay: 18 ms; delay increment: 0.05 ms



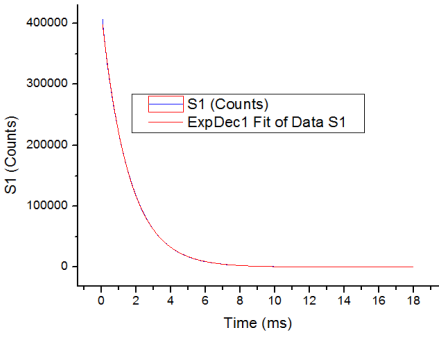


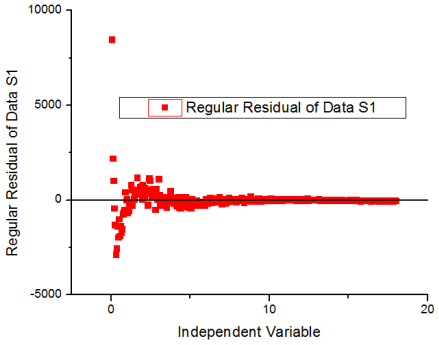
Trial 1





Trial 2





Trial 3

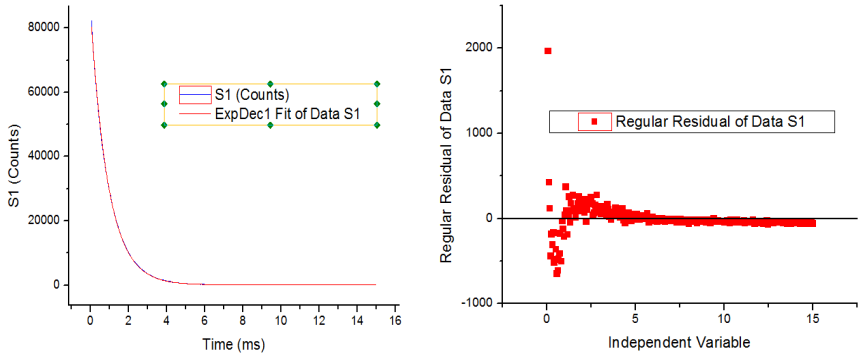
Fitting statistics, all trials

Model: ExpDec1; Equation: Y=A1*exp(-x/t1)+y0

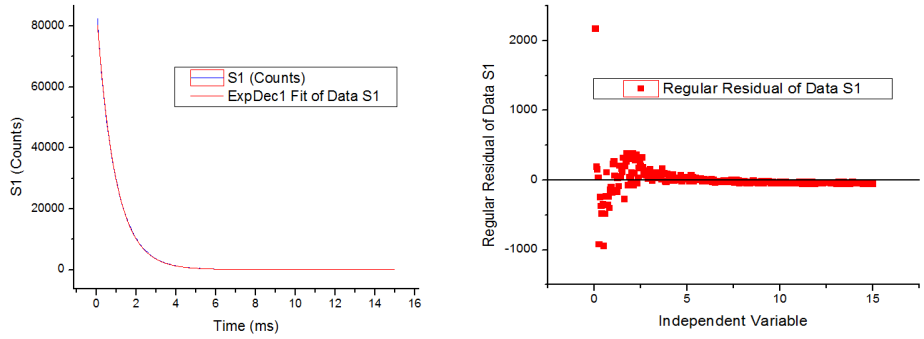
		Trial 1		Trial 2		Trial 3	
Reduced Chi-Sqr		408368.79316		304206.68984		361298.46499	
Adj R-Square		0.99994		0.99995		0.99994	
		Value	***Standard Error***	***Value***	***Standard Error***	***Value***	***Standard Error***
S1	**y0**	302.95793	41.75663	264.71653	36.03579	271.1433	39.24274
S1	**A1**	428678.03703	235.34384	409502.51672	203.16999	411557.23198	221.74466
S1	**t1**	1.57269	0.00135	1.57202	0.00122	1.56764	0.00132

$Eu(1)_{2.25}(NO_3)_3$ complex

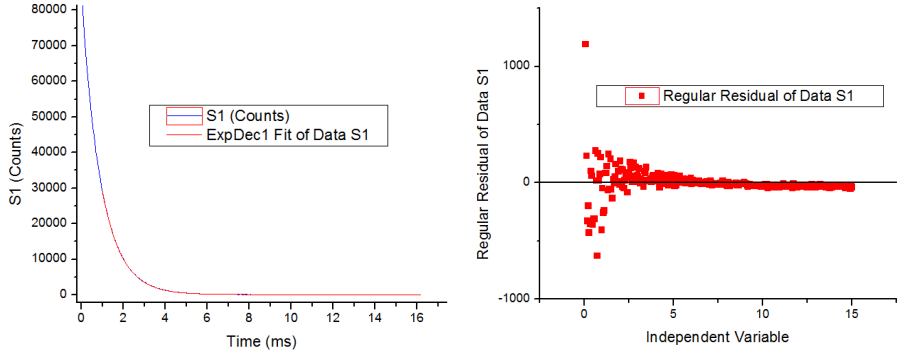
Fluorimeter settings for all trials: excitation: 300 nm; emission: 616 nm; slits: 1 nm; sample window: 1.5 ms; time between flashes: 41 ms; count (averages): 100; initial delay: 0.05 ms; max delay: 15 ms; delay increment: 0.05 ms. After taking a look at the residuals for these fittings, we attempted to fit the lifetime decay data to a second order exponential decay. Unfortunately, this fitting procedure did not converge.



Trial 1



Trial 2



Trial 3

Fitting statistics, all trials

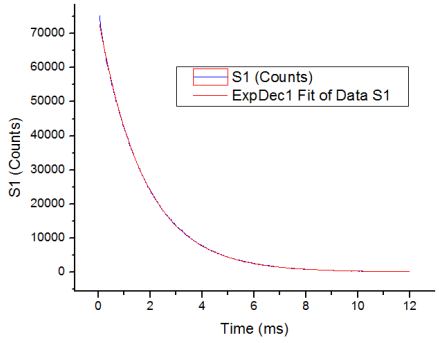
Model: ExpDec1; Equation: Y=A1*exp(-x/t1)+y0

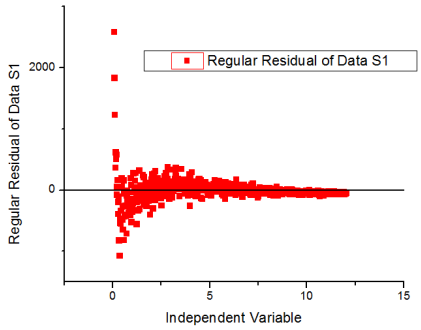
		Trial 1		Trial 2		Trial 3	
Reduced Chi-Sqr		27395.9651		32730.70221		12674.92178	
Adj R-Square		0.99985		0.99982		0.99993	
		Value	***Standard Error***	***Value***	***Standard Error***	***Value***	***Standard Error***
S1	**y0**	111.18162	11.01981	108.61075	12.05029	95.61468	7.50317
S1	**A1**	84778.62061	81.09453	84729.45582	88.50965	84550.77829	54.97165
S1	**t1**	0.92979	0.00132	0.93224	0.00145	0.93551	9.04111E-4

Complexes of ligand 2

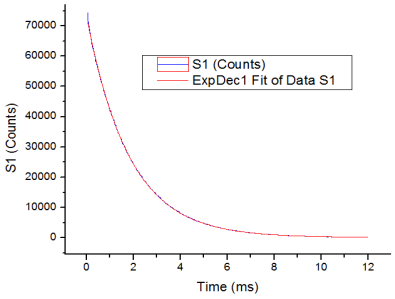
$Tb(2)_{2.25}(NO_3)_3$ complex

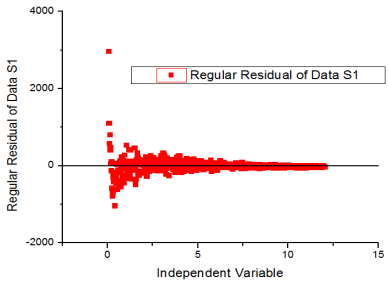
Fluorimeter settings for trials 1 and 2: excitation: 300 nm; emission: 543 nm; slits: 1.5 nm; sample window: 1.8 ms; time between flashes: 41 ms; count (averages): 100; initial delay: 0.05 ms; max delay: 12 ms; delay increment: 0.05 ms. For trial 3, all settings were the same except for the max delay was set at 18 ms. After taking a look at the residuals for these fittings, we attempted to fit the lifetime decay data to a second order exponential decay. Unfortunately, this fitting procedure did not converge.



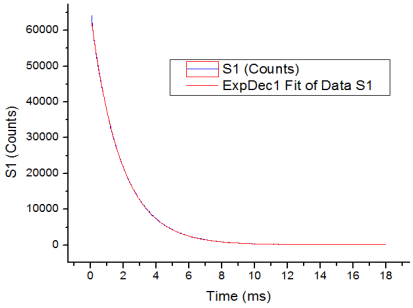


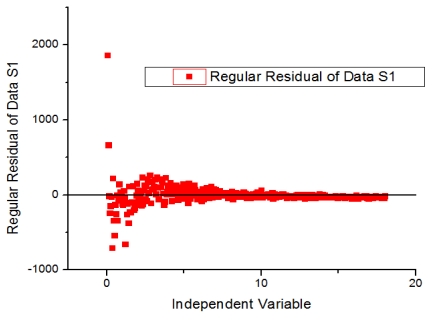
Trial 1





Trial 2





Trial 3

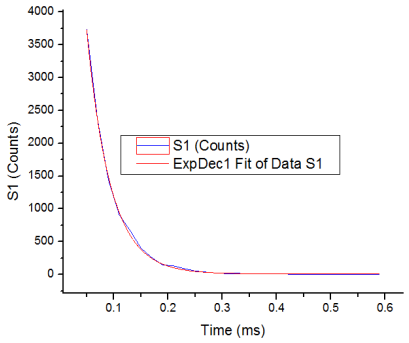
Fitting statistics, all trials

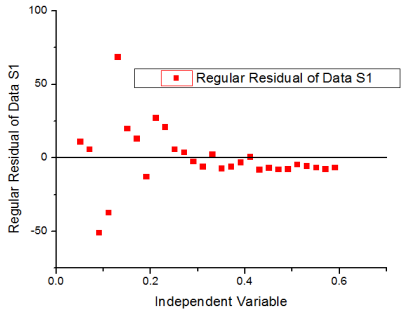
Model: ExpDec1; Equation: Y=A1*exp(-x/t1)+y0

		Trial 1		Trial 2		Trial 3	
Reduced Chi-Sqr		41102.97423		36519.34808		20510.44722	
Adj R-Square		0.99985		0.99987		0.99987	
		Value	***Standard Error***	***Value***	***Standard Error***	***Value***	***Standard Error***
S1	**y0**	144.56769	12.71484	115.46353	12.24454	98.14075	9.79112
S1	**A1**	74718.81633	45.34502	73231.29061	41.95349	64030.7066	48.70523
S1	**t1**	1.75288	0.0019	1.81377	0.00188	1.82762	0.00225

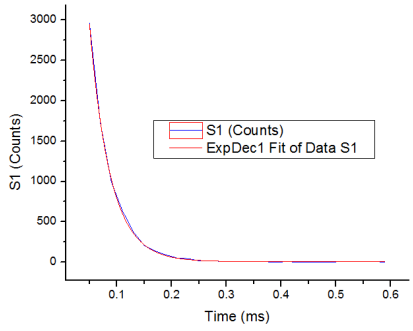
$Sm(2)_{2.25}(NO_3)_3$ complex

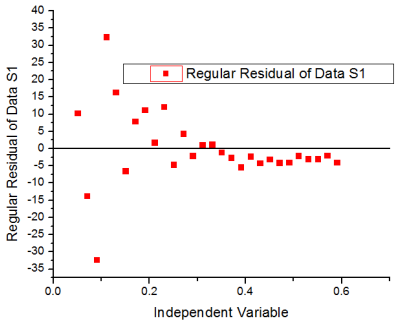
Fluorimeter settings for all trials: excitation: 300 nm; emission: 642 nm; slits: 2.5 nm; sample window: .08 ms; time between flashes: 41 ms; count (averages): 100; initial delay: 0.05 ms; max delay: .6 ms; delay increment: 0.02 ms



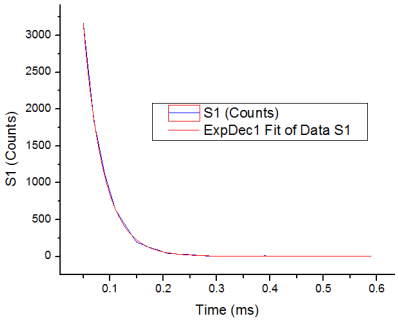


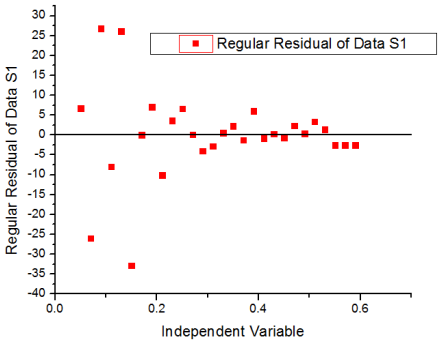
Trial 1





Trial 2





Trial 3

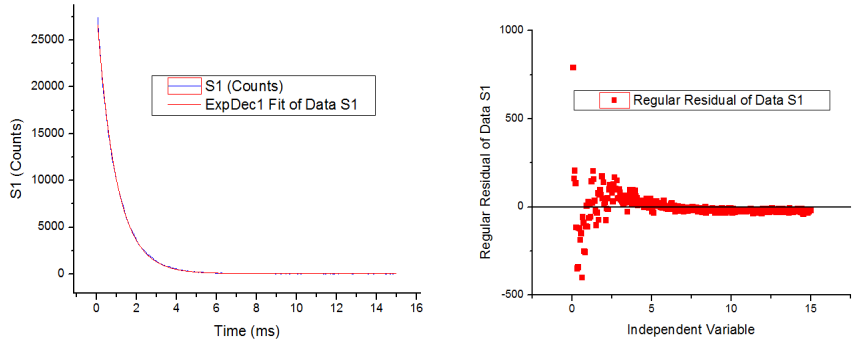
Fitting statistics, all trials

Model: ExpDec1; Equation: Y=A1*exp(-x/t1)+y0

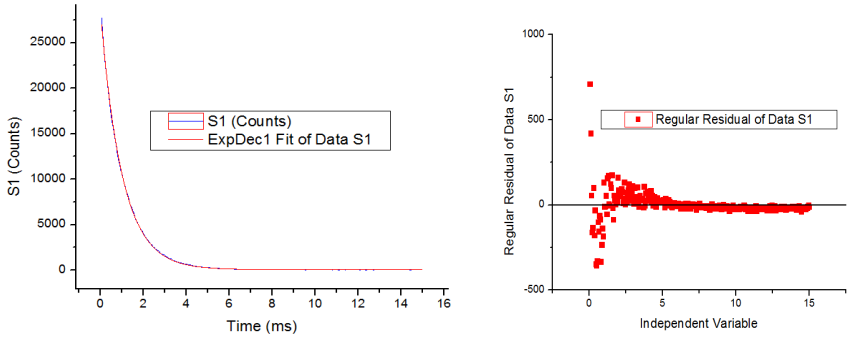
		Trial 1		Trial 2		Trial 3	
Reduced Chi-Sqr		454.95636		129.06651		143.36329	
Adj R-Square		0.99937		0.9997		0.99971	
		Value	***Standard Error***	***Value***	***Standard Error***	***Value***	***Standard Error***
S1	**y0**	8.21952	4.87499	6.98255	2.52236	3.56626	2.65907
S1	**A1**	11755.39227	173.02696	11100.37932	126.7737	11880.92591	133.17041
S1	**t1**	0.04352	4.43875E-4	0.03769	2.68687E-4	0.03774	2.64352E-4

$Eu(2)_{2.25}(NO_3)_3$ complex

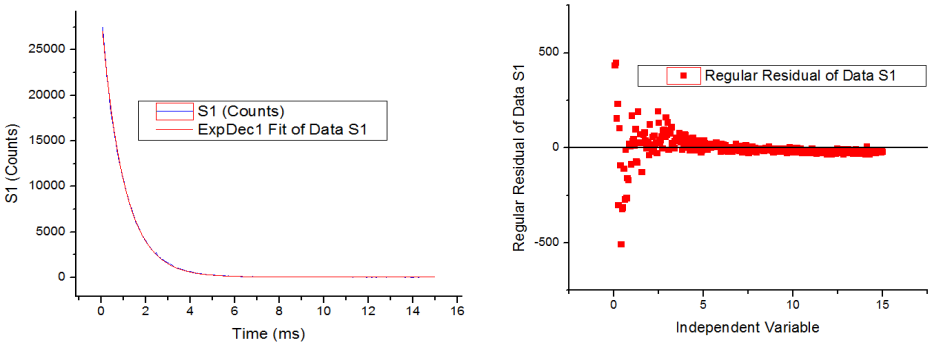
Fluorimeter settings for all trials: excitation: 300 nm; emission: 642 nm; slits: 2.5 nm; sample window: .08 ms; time between flashes: 41 ms; count (averages): 100; initial delay: 0.05 ms; max delay: .6 ms; delay increment: 0.02 ms



Trial 1



Trial 2



Trial 3

Fitting statistics, all trials

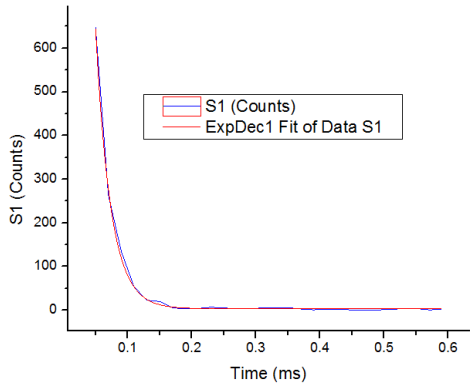
Model: ExpDec1; Equation: Y=A1*exp(-x/t1)+y0

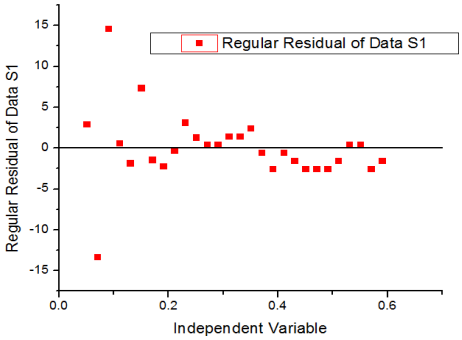
		Trial 1		Trial 2		Trial 3	
Reduced Chi-Sqr		6431.35629		6191.76007		5631.90326	
Adj R-Square		0.99969		0.99972		0.99975	
		Value	***Standard Error***	***Value***	***Standard Error***	***Value***	***Standard Error***
S1	**y0**	63.09063	5.36887	61.61247	5.31182	58.74251	5.06575
S1	**A1**	28007.53318	38.58279	28342.75055	36.89285	28418.02167	35.19017
S1	**t1**	0.9608	0.00197	1.00673	0.00197	1.00648	0.00187

Complexes of ligand 3

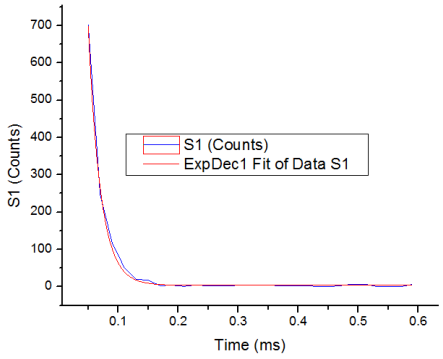
$Sm(3)_{2.25}(NO_3)_3$ complex

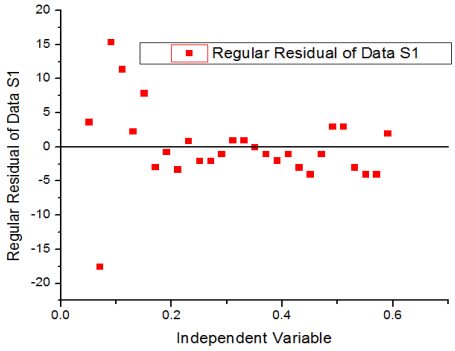
Fluorimeter settings for all trials: excitation: 300 nm; emission: 642 nm; slits: 1.5 nm; sample window: .08 ms; time between flashes: 41 ms; count (averages): 100; initial delay: 0.05 ms; max delay: .6 ms; delay increment: 0.02 ms



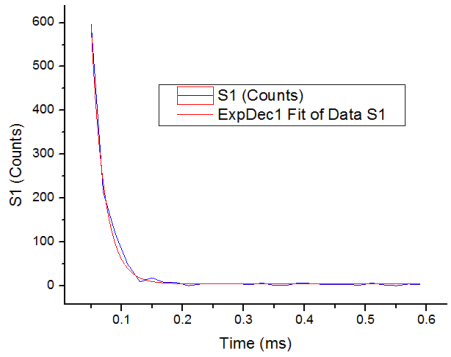


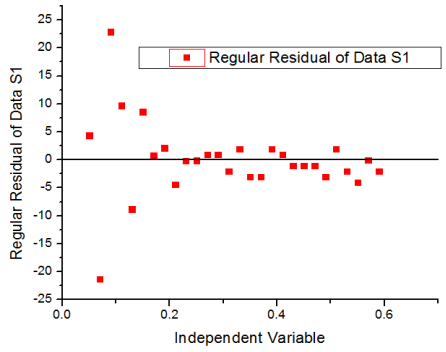
Trial 1





Trial 2





Trial 3

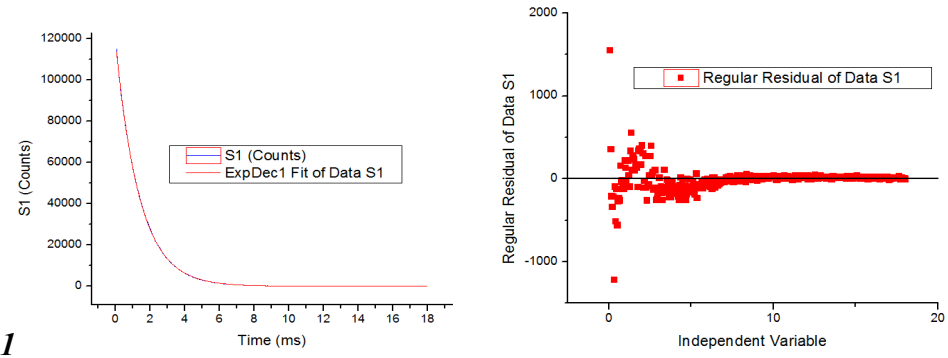
Fitting statistics, all trials

Model: ExpDec1; Equation: Y=A1*exp(-x/t1)+y0

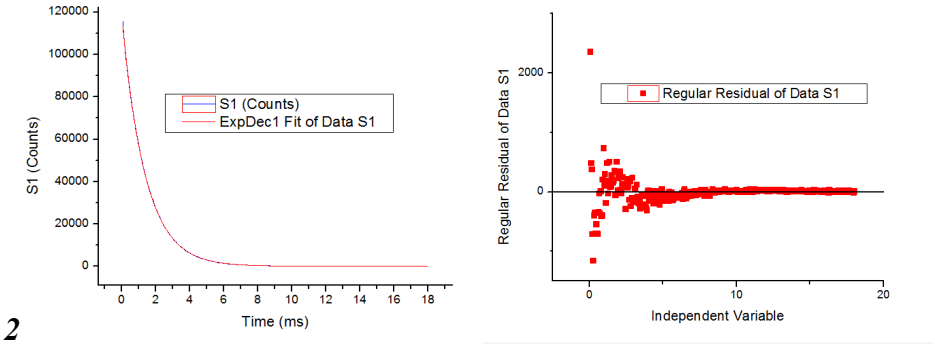
		Trial 1		Trial 2		Trial 3	
Reduced Chi-Sqr		21.10132		35.27255		53.61898	
Adj R-Square		0.99876		0.99817		0.99616	
		Value	***Standard Error***	***Value***	***Standard Error***	***Value***	***Standard Error***
S1	**y0**	3.53126	0.95737	3.96589	1.22245	4.04266	1.51278
S1	**A1**	5392.31249	191.73856	8092.71168	409.21405	6148.72889	427.83219
S1	**t1**	0.02349	3.60327E-4	0.02037	3.9421E-4	0.02131	5.89647E-4

$Tb(3)_{2.25}(NO_3)_3$ complex

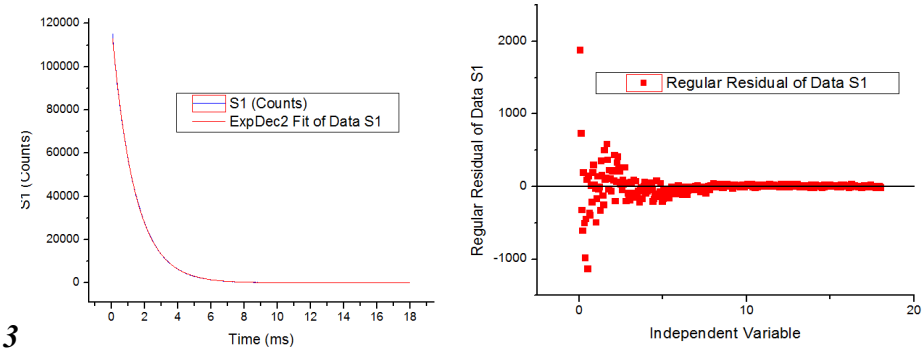
Fluorimeter settings for all trials: excitation: 300 nm; emission: 543 nm; slits: .75 nm; sample window: 1.8 ms; time between flashes: 41 ms; count (averages): 100; initial delay: 0.05 ms; max delay: 18 ms; delay increment: 0.05 ms



Trial 1



Trial 2



Trial 3

Fitting statistics, all trials

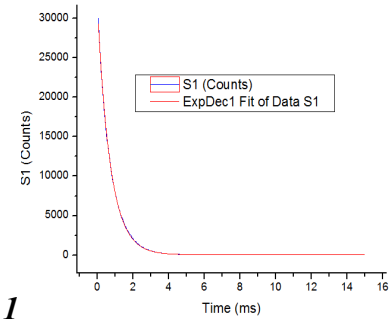
Model: ExpDec1; Equation: Y=A1*exp(-x/t1)+y0

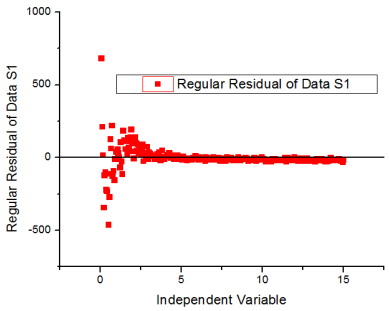
		Trial 1		Trial 2		Trial 3	
Reduced Chi-Sqr		23385.88265		39436.59431		30197.97934	
Adj R-Square		0.99995		0.99991		0.99993	
		Value	***Standard Error***	***Value***	***Standard Error***	***Value***	***Standard Error***
S1	**y0**	68.5946	9.66221	69.67499	12.53864	78.50292	10.9764
S1	**A1**	117983.69232	60.663	117463.08122	78.91029	117373.31888	68.98472
S1	**t1**	1.36872	0.00108	1.36441	0.0014	1.36687	0.00123

$Eu(3)_{2.25}(NO_3)_3$ complex

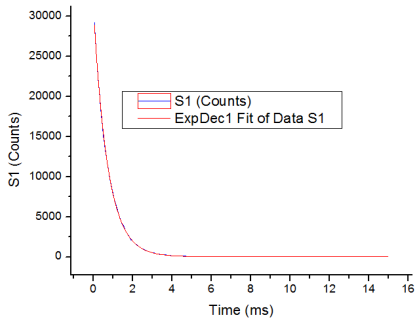
Fluorimeter settings for all trials: excitation: 300 nm; emission: 616 nm; slits: .75 nm; sample window: 1.5 ms; time between flashes: 41 ms; count (averages): 100; initial delay: 0.05 ms; max delay: 15 ms; delay increment: 0.05 ms

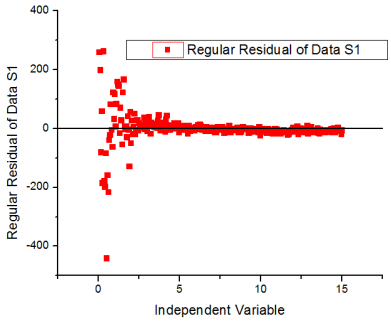
For this experiment the data from Trials 1 and 2 were fit successfully to a second exponential decay. These fits are shown on the next page. In both cases, t1 was in good agreement with the t1 values obtained when the data was fit to a single exponential decay.



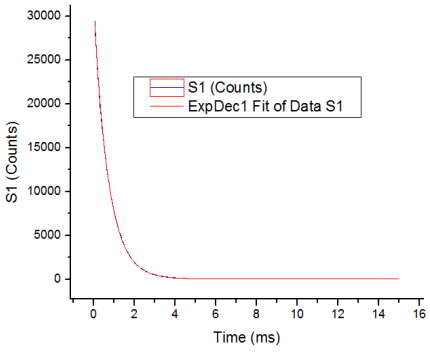


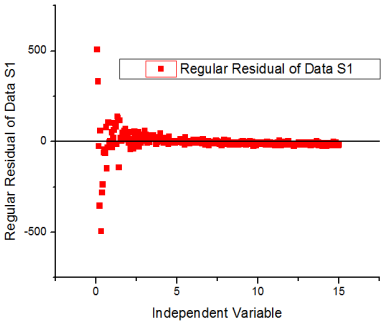
Trial 1





Trial 2





Trial 3

Fitting statistics, all trials

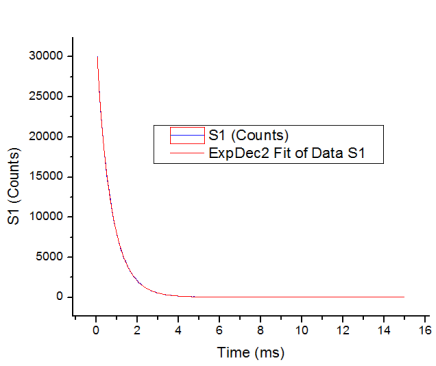
Model: ExpDec1; Equation: Y=A1*exp(-x/t1)+y0

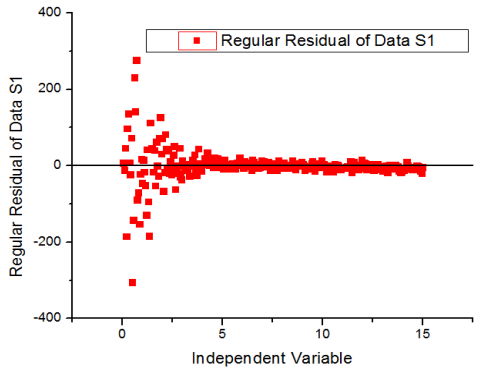
		Trial 1		Trial 2		Trial 3	
Reduced Chi-Sqr		5120.01461		2677.98507		3735.47624	
Adj R-Square		0.99974		0.99986		0.99981	
		Value	***Standard Error***	***Value***	***Standard Error***	***Value***	***Standard Error***
S1	**y0**	45.29091	4.59373	39.73116	3.32449	41.91381	3.92097
S1	**A1**	31406.23784	40.59663	30972.95485	29.26522	30990.15405	34.79618
S1	**t1**	0.71686	0.00134	0.72093	9.83799E-4	0.71255	0.00115

$Eu(3)_{2.25}(NO_3)_3$ complex – data fit to a double exponential decay

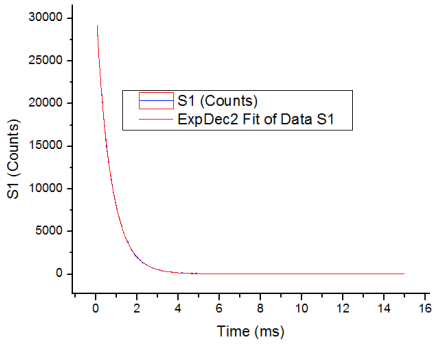
Fluorimeter settings for all trials: excitation: 300 nm; emission: 616 nm; slits: .75 nm; sample window: 1.5 ms; time between flashes: 41 ms; count (averages): 100; initial delay: 0.05 ms; max delay: 15 ms; delay increment: 0.05 ms

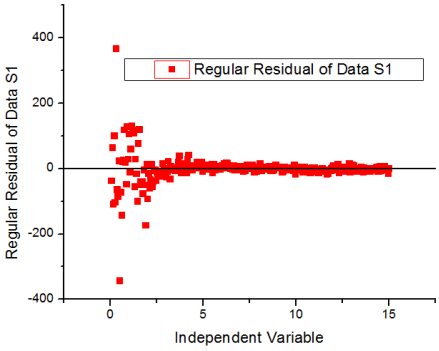
The same data as Trials 1 and 2 from the previous page





Trial 1





Trial 2

Fitting statistics, all trials

Model: ExpDec2; Equation: Y=A1*exp(-x/t1)+ A2*exp(-x/t2)+y0

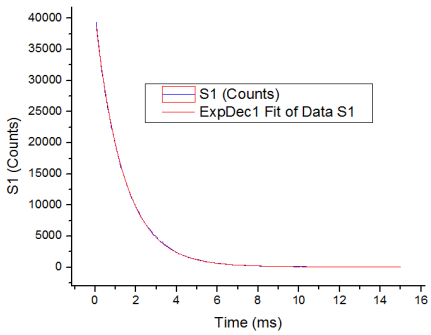
		Trial 1		Trial 2	
Reduced Chi-Sqr		1825.68693		1829.30411	
Adj R-Square		0.99991		0.99991	
		Value	***Standard Error***	***Value***	***Standard Error***
S1	**y0**	36.64729	2.79981	34.25805	2.83128
S1	**A1**	30579.58749	72.07539	30330.45863	130.13592
S1	**t1**	0.73384	0.00148	0.73296	0.00209
S1	**A2**	2296.71762	107.6578	1181.67579	113.57519
S1	**t2**	0.1026	0.00914	0.16294	0.02783

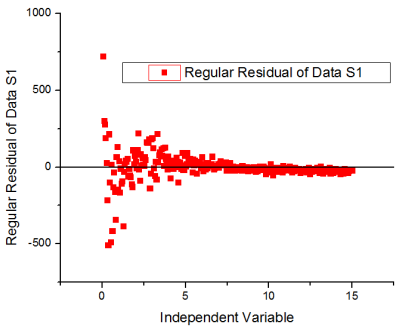
Complexes of ligand 4

$Eu(4)_{2.25}(NO_3)_3$ complex

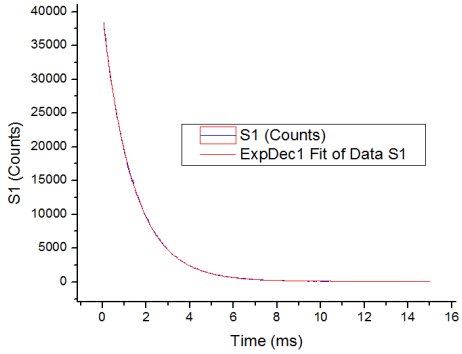
Fluorimeter settings for all trials: excitation: 300 nm; emission: 616 nm; slits: 1.5 nm; sample window: 1.5 ms; time between flashes: 41 ms; count (averages): 100; initial delay: 0.05 ms; max delay: 15 ms; delay increment: 0.05 ms

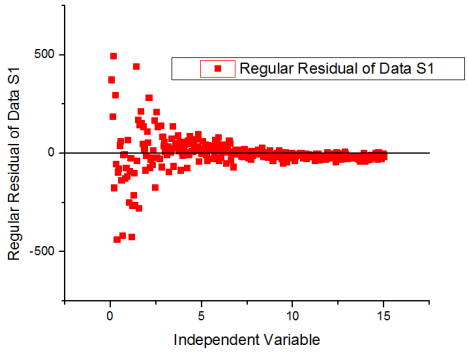
Trial 1



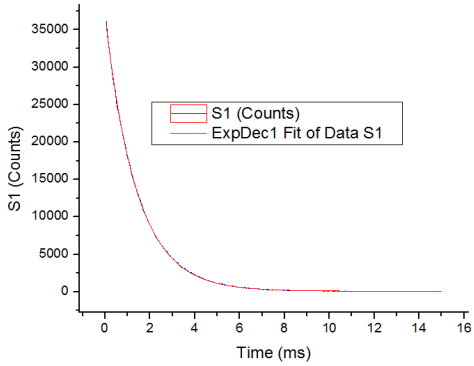


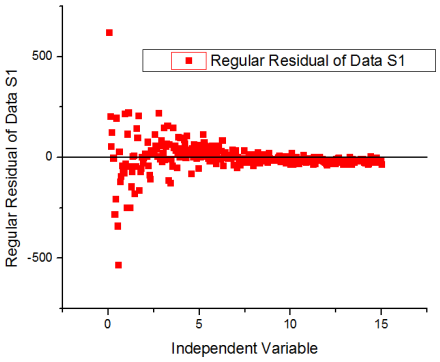
Trial 2





Trial 3





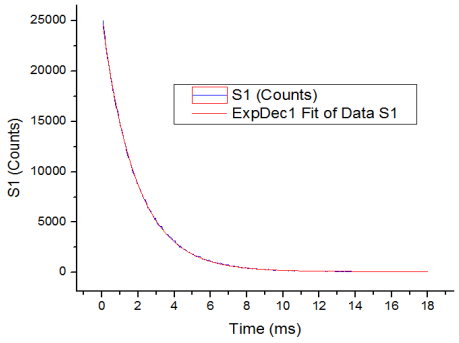
Fitting statistics, all trials

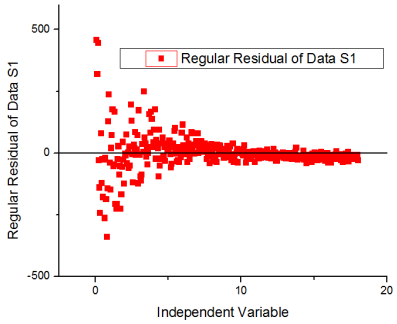
Model: ExpDec1; Equation: Y=A1*exp(-x/t1)+y0

		Trial 1		Trial 2		Trial 3	
Reduced Chi-Sqr		8648.40778		7942.10798		6278.68431	
Adj R-Square		0.99985		0.99986		0.99987	
		Value	***Standard Error***	***Value***	***Standard Error***	***Value***	***Standard Error***
S1	**y0**	95.92135	6.77917	99.00669	6.50647	83.59217	5.78213
S1	**A1**	40033.48051	36.4706	39343.93061	34.85244	36747.04954	31.0172
S1	**t1**	1.39827	0.00201	1.40554	0.00197	1.40312	0.00187

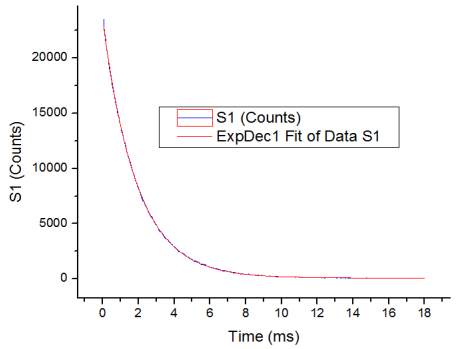
$Tb(4)_{2.25}(NO_3)_3$ complex

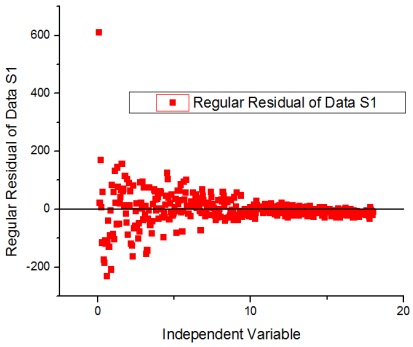
Fluorimeter settings for all trials: excitation: 300 nm; emission: 543 nm; slits: 1.5 nm; sample window: 1.8 ms; time between flashes: 41 ms; count (averages): 100; initial delay: 0.05 ms; max delay: 18 ms; delay increment: 0.05 ms



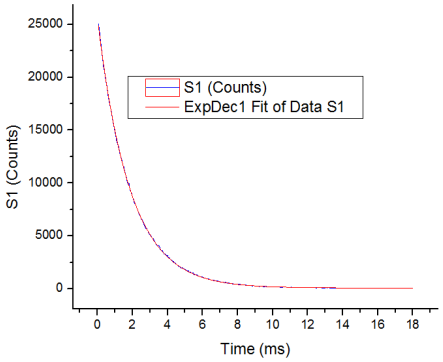


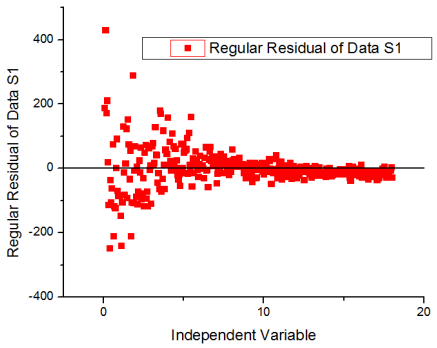
Trial 1





Trial 2





Trial 3

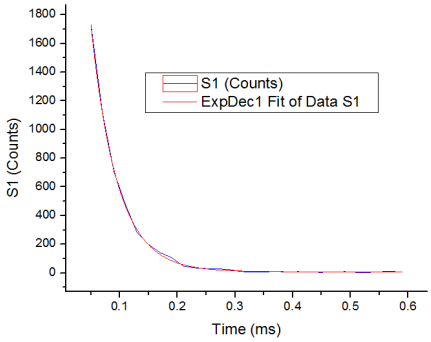
Fitting statistics, all trials

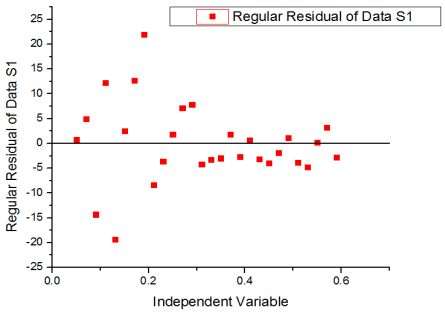
Model: ExpDec1; Equation: Y=A1*exp(-x/t1)+y0

		Trial 1		Trial 2		Trial 3	
Reduced Chi-Sqr		5254.64282		3398.47988		3640.70355	
Adj R-Square		0.99979		0.99985		0.99986	
		Value	***Standard Error***	***Value***	***Standard Error***	***Value***	***Standard Error***
S1	**y0**	93.72161	4.98835	86.308	4.03096	94.22244	4.1429
S1	**A1**	25184.85202	24.40563	23429.18793	19.48692	25466.67154	20.38417
S1	**t1**	1.8628	0.00293	1.88834	0.00256	1.85079	0.0024

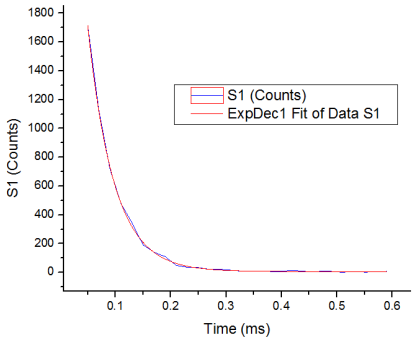
$Sm(4)_{2.25}(NO_3)_3$ complex

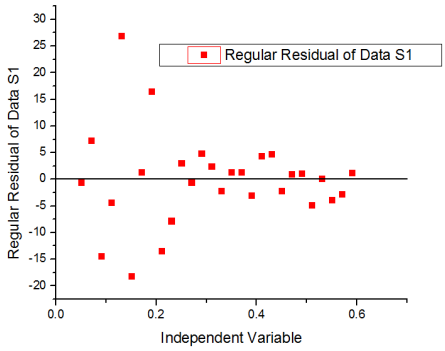
Fluorimeter settings for all trials: excitation: 300 nm; emission: 642 nm; slits: 2.5 nm; sample window: 0.08 ms; time between flashes: 41 ms; count (averages): 100; initial delay: 0.05 ms; max delay: 0.6 ms; delay increment: 0.02 ms



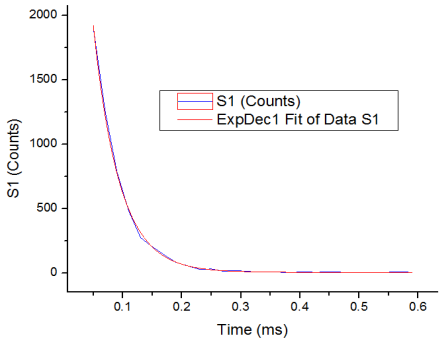


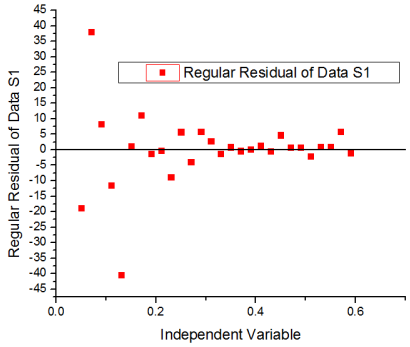
Trial 1





Trial 2





Trial 3

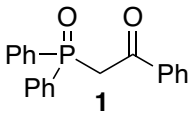
Fitting statistics, all trials

Model: ExpDec1; Equation: Y=A1*exp(-x/t1)+y0

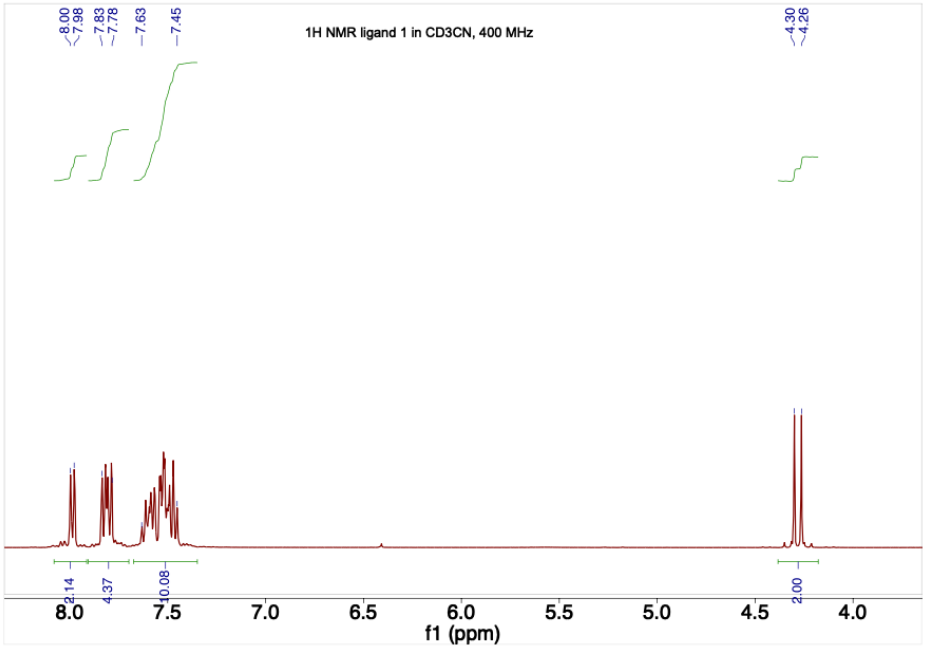
		Trial 1		Trial 2		Trial 3	
Reduced Chi-Sqr		69.48354		79.99371		160.20744	
Adj R-Square		0.99956		0.99949		0.99916	
		Value	***Standard Error***	***Value***	***Standard Error***	***Value***	***Standard Error***
S1	**y0**	7.75449	1.92061	6.76289	2.08128	5.04246	2.89868
S1	**A1**	5230.48446	62.83446	4957.93123	62.05835	5991.36847	100.77227
S1	**t1**	0.04508	3.84845E-4	0.04697	4.30012E-4	0.04391	5.15037E-4

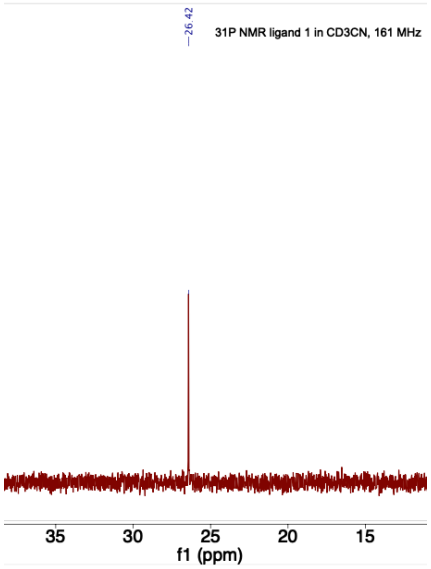
D. NMR and IR data for ligands 1-4 and their Ln-complexes

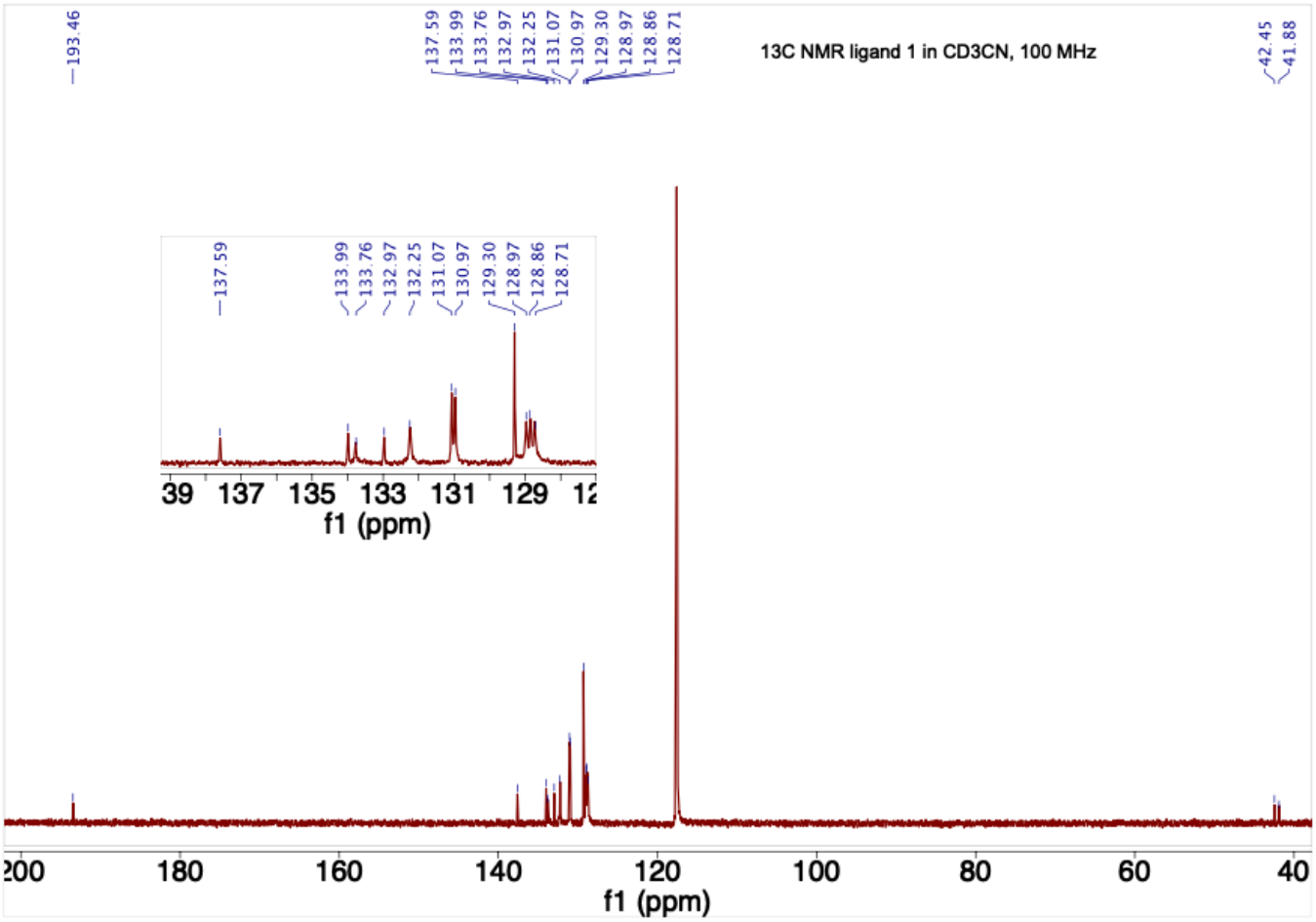
1. Ligand 1

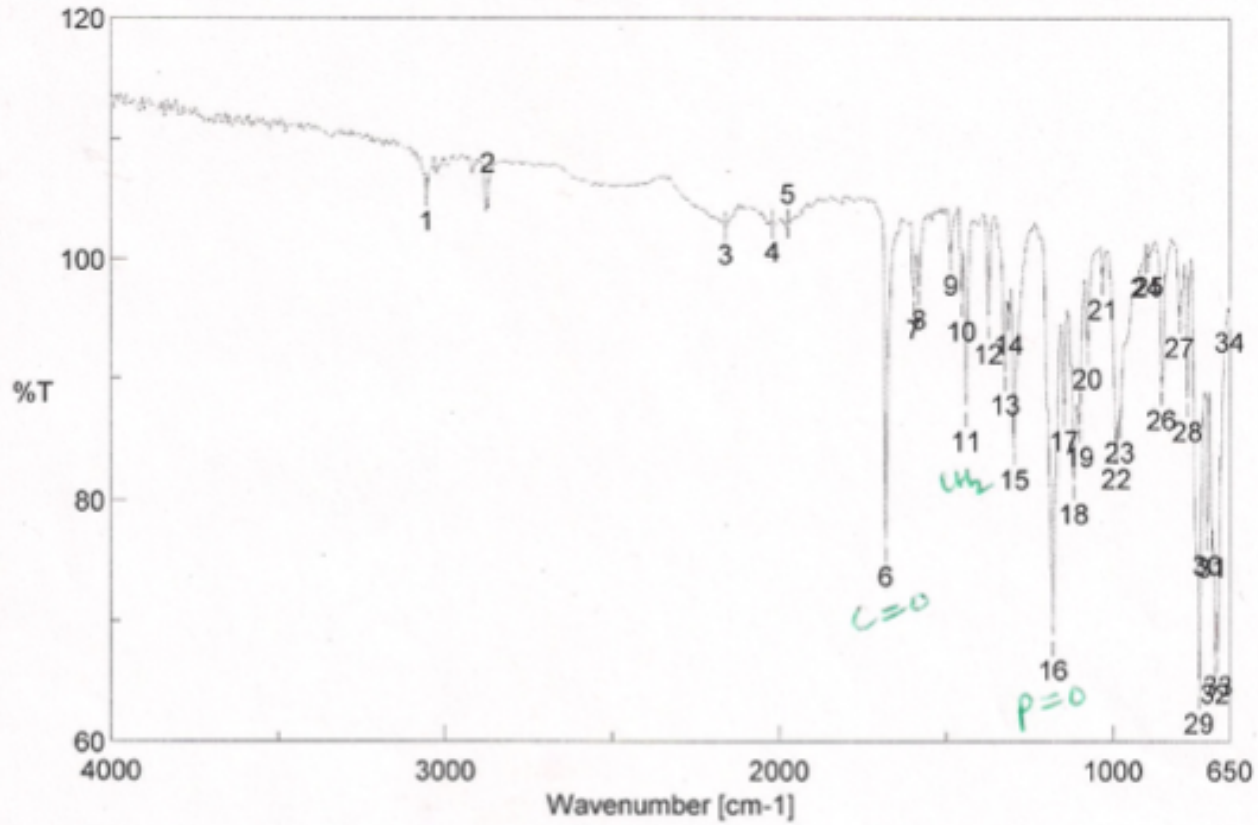


1









[Detailed Information]

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Vertical axis	%T
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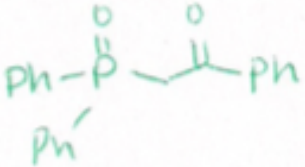
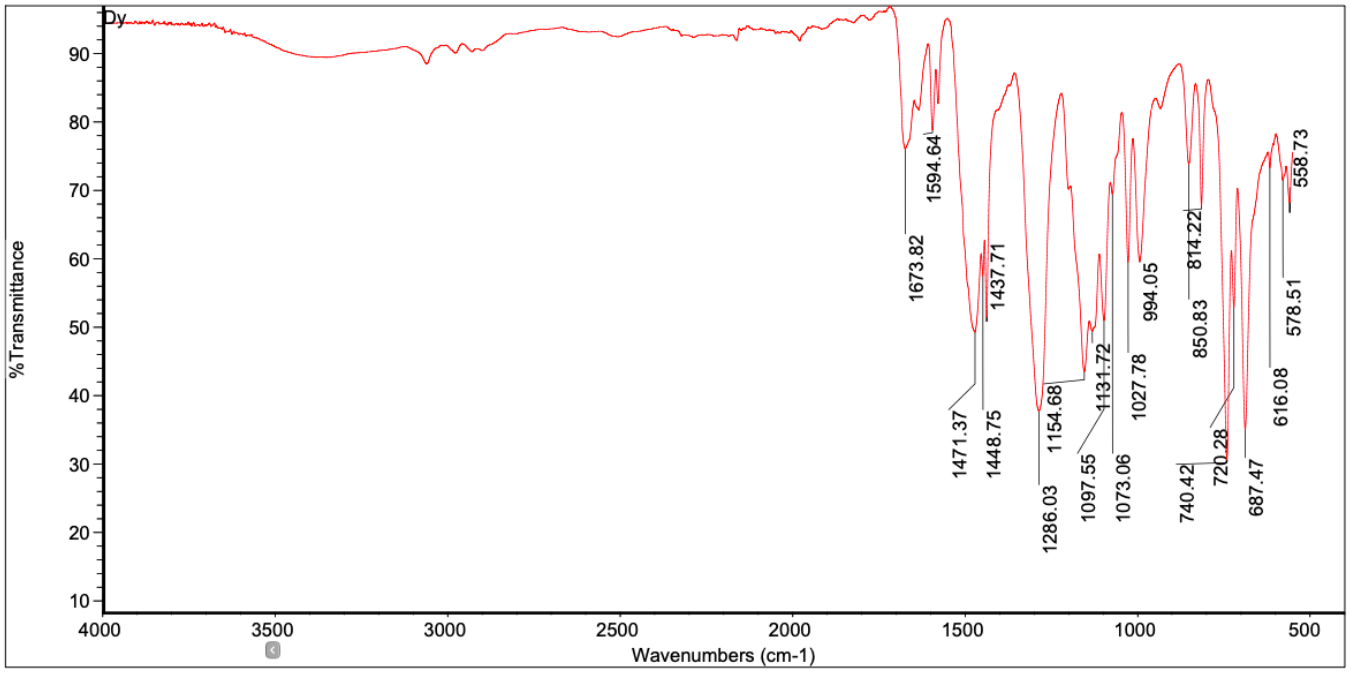
Data points	3476



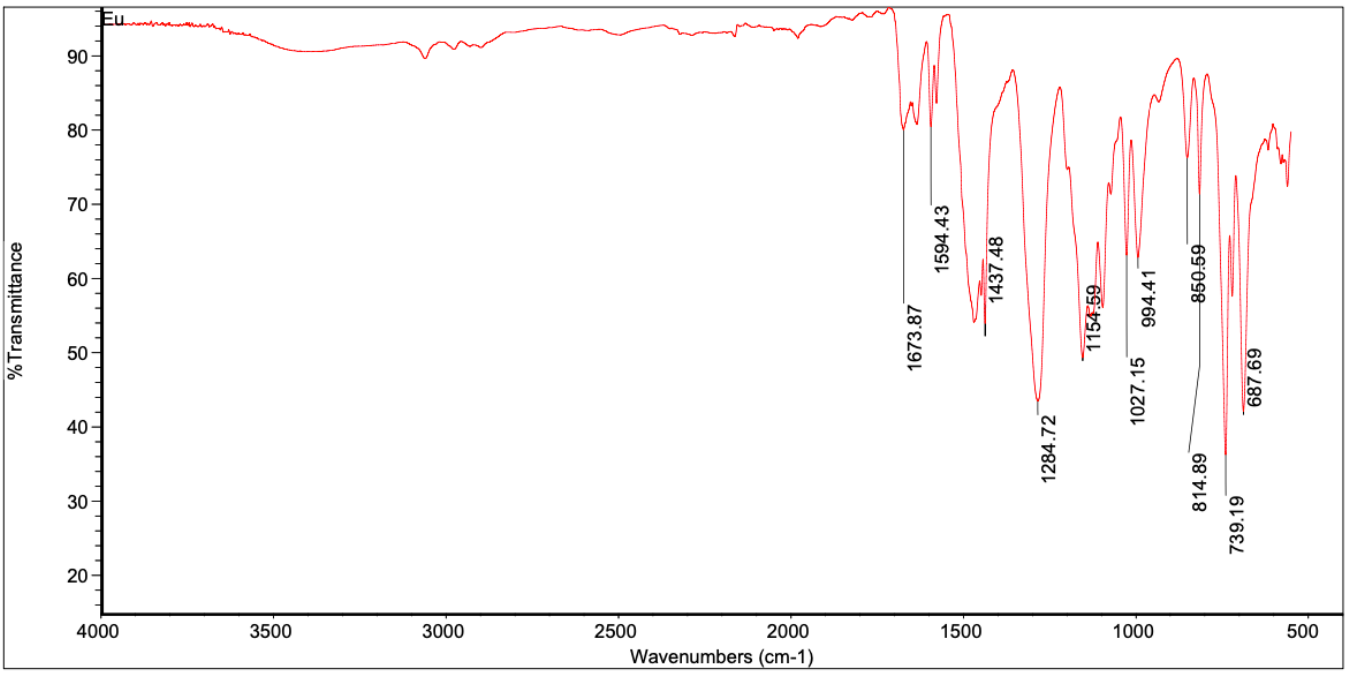
[Result of Peak Picking]

No.	Position	Intensity	No.	Position	Intensity
1	3055.66	105.557	2	2871.49	105.52
3	2160.85	102.777	4	2019.1	103.005
5	1972.82	102.963	6	1679.69	76.1143
7	1595.81	96.5224	8	1580.38	97.3496
9	1484.92	100.197	10	1454.06	96.3512
11	1439.6	87.218	12	1372.1	94.5051
13	1321.96	90.226	14	1311.36	95.2685
15	1295.93	84.094	16	1179.26	68.3544
17	1146.47	87.2427	18	1117.55	81.2567
19	1101.15	85.9478	20	1076.08	92.3742
21	1029.8	98.1853	22	989.304	84.1331
23	978.697	86.3355	24	901.558	100.03
25	891.916	100.127	26	853.347	88.9687

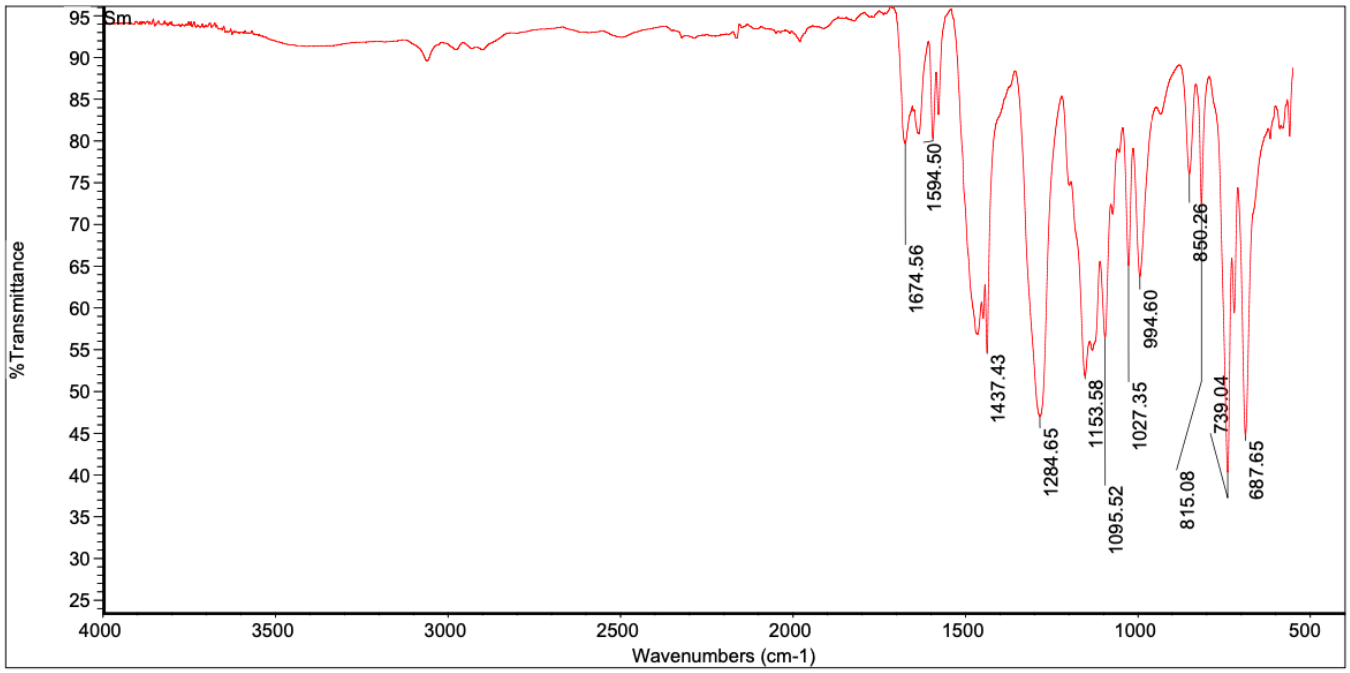
$Dy(1)_2(NO_3)_3$



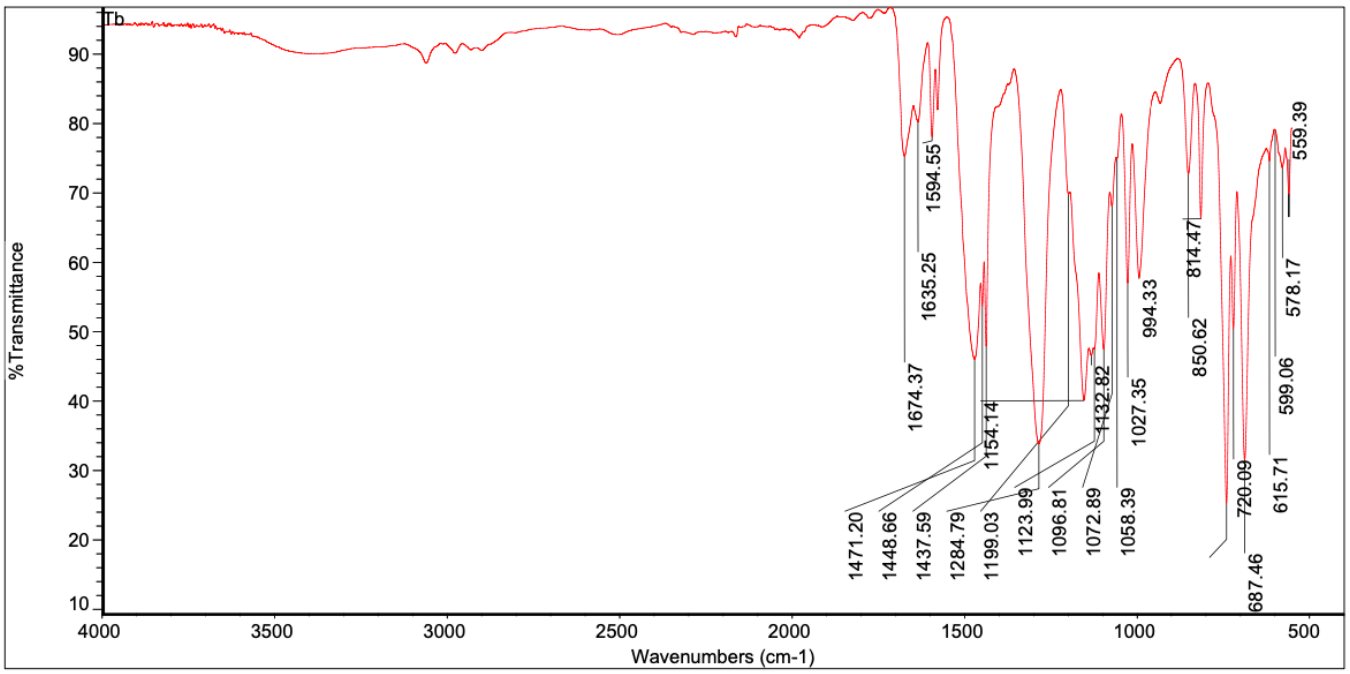
$Eu(1)_2(NO_3)_3$



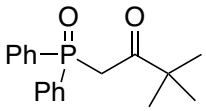
$Sm(1)_2(NO_3)_3$

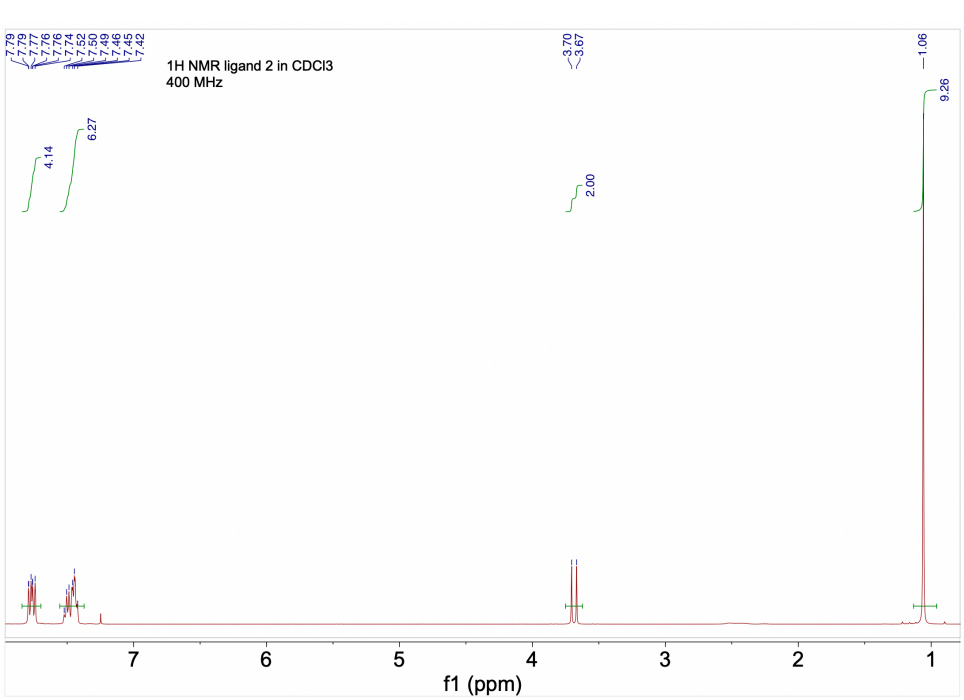


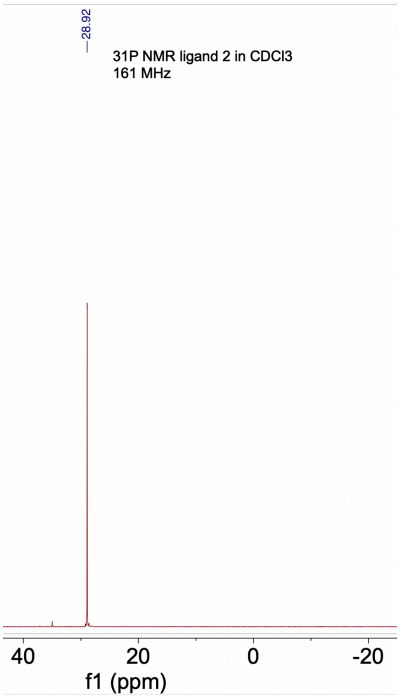
$Tb(1)_2(NO_3)_3$

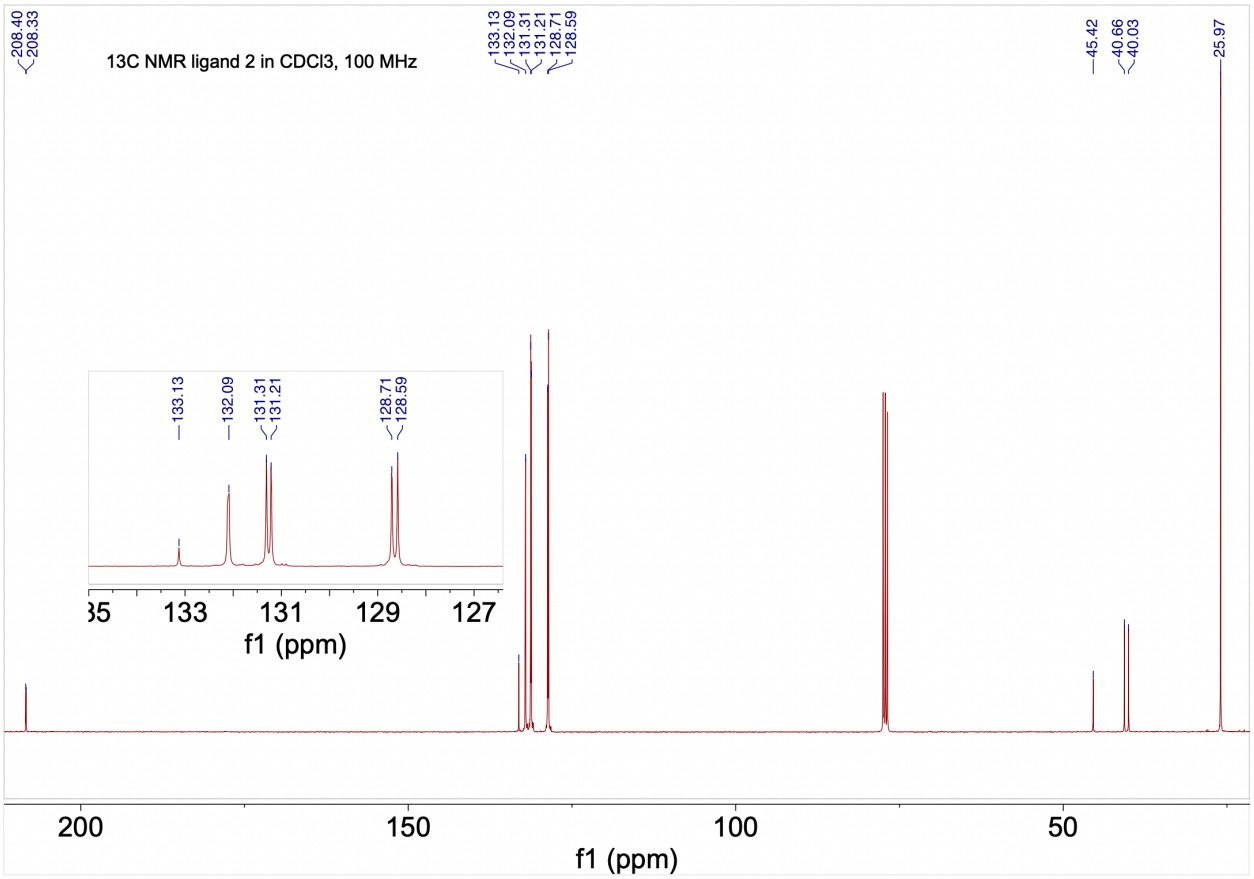


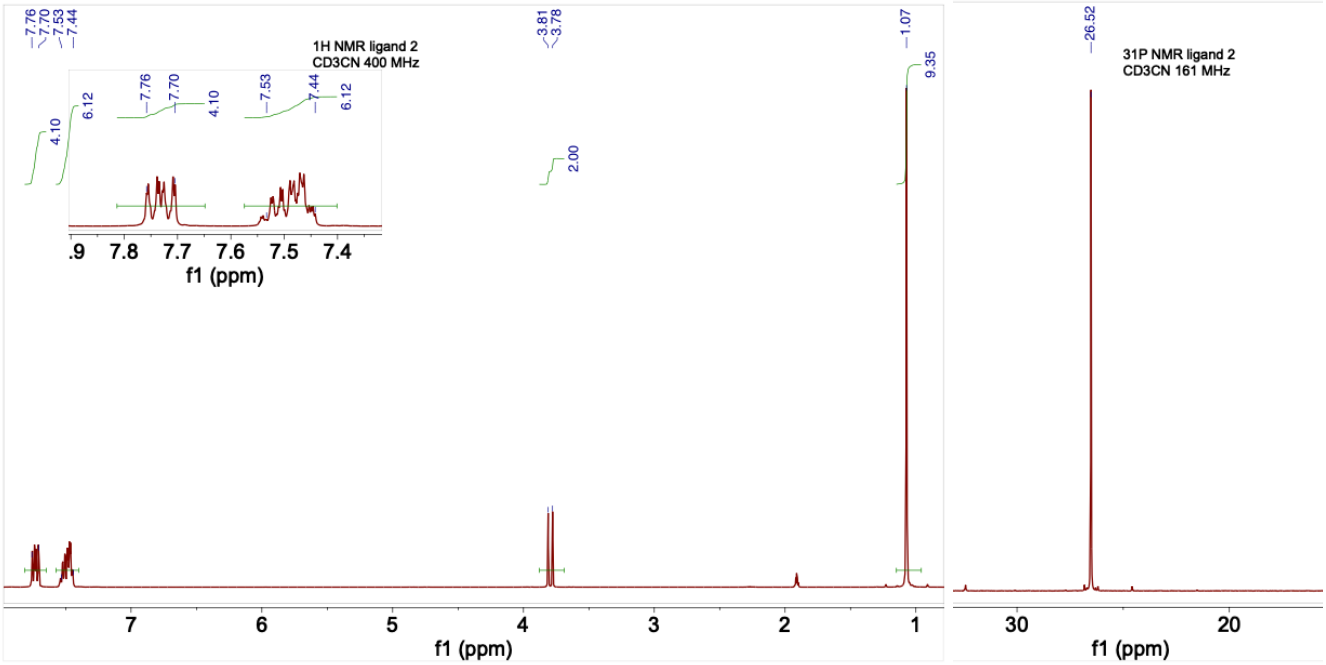
1. Ligand 2

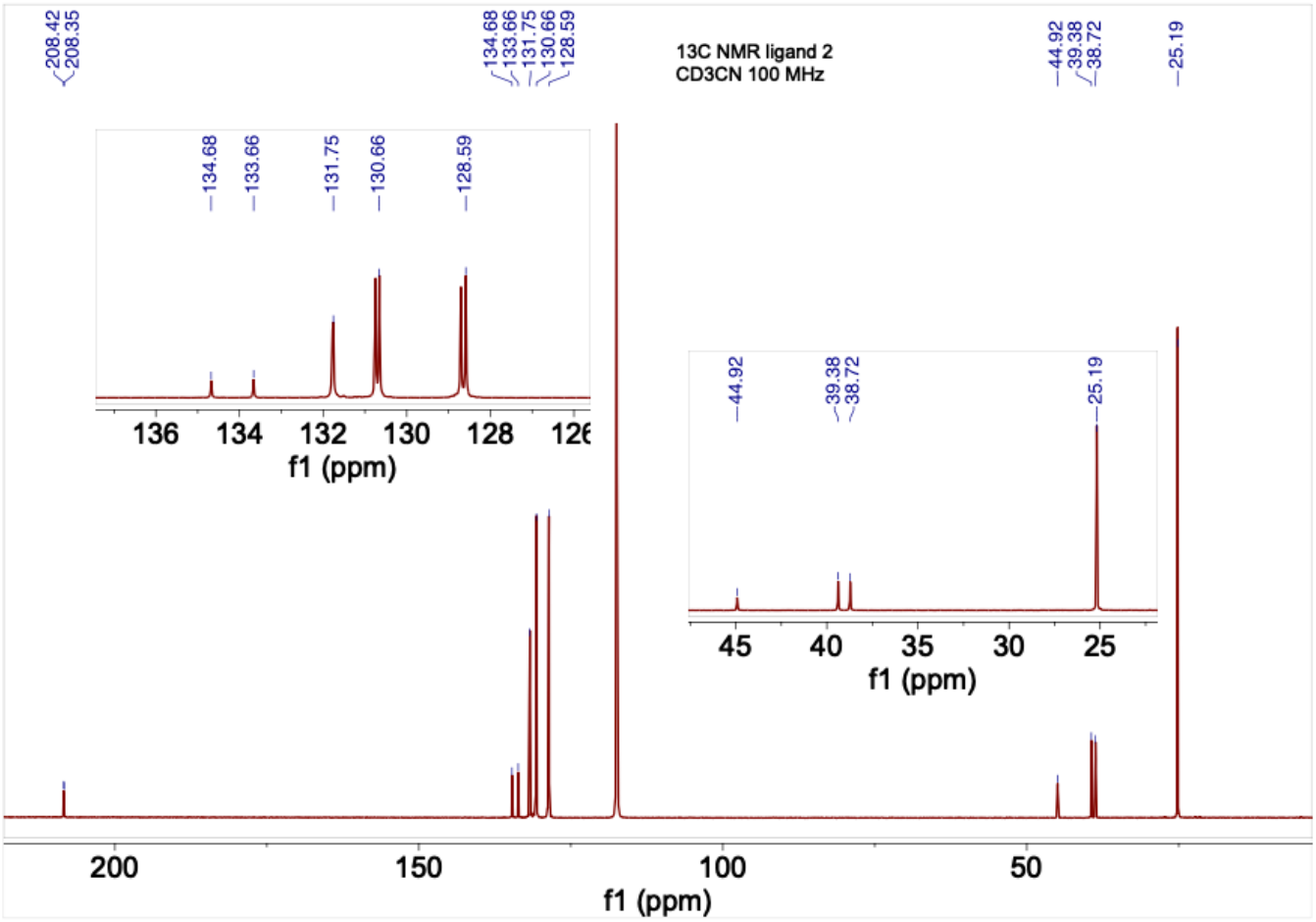

O
O
Ph
P
Ph

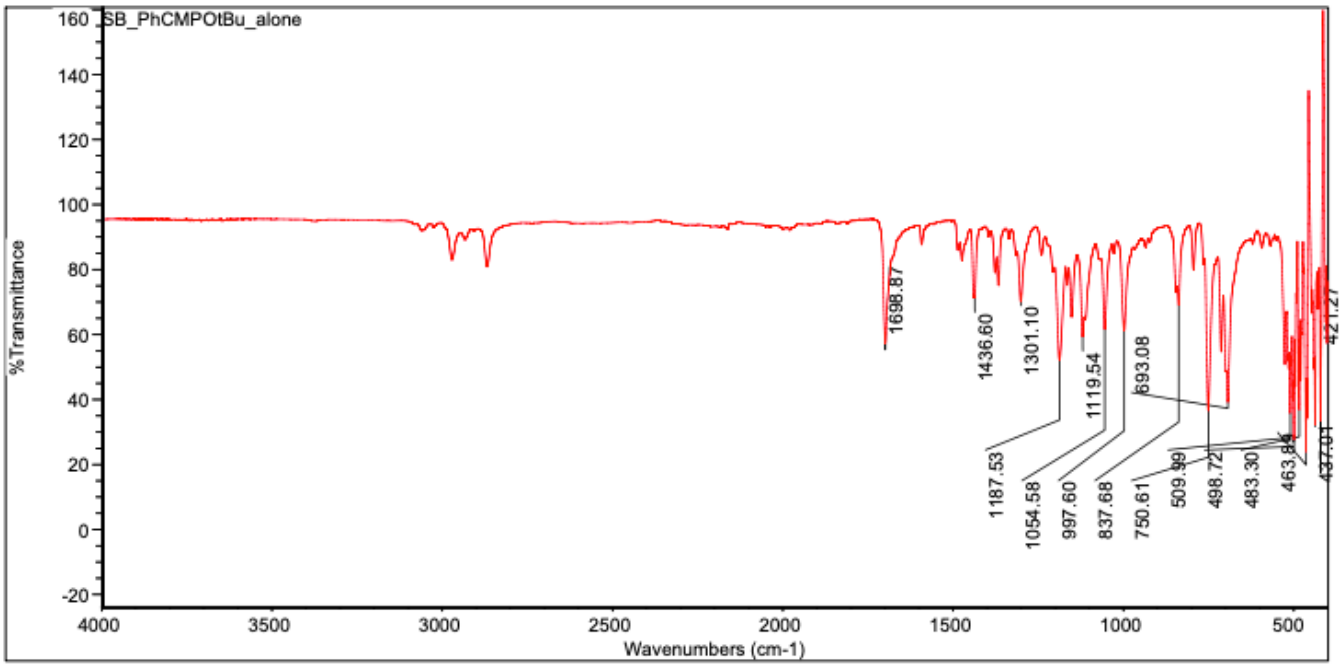

1H NMR ligand 2 in CDCl3
400 MHz
7.79
7.79
7.77
7.76
7.76
7.74
7.52
7.50
7.49
7.46
7.45
7.42
3.70
3.67
1.06
9.26
6.27
4.14
2.00
7
6
5
4
3
2
1
f1 (ppm)


28.92
31P NMR ligand 2 in CDCl3
161 MHz
40
20
0
-20
f1 (ppm)

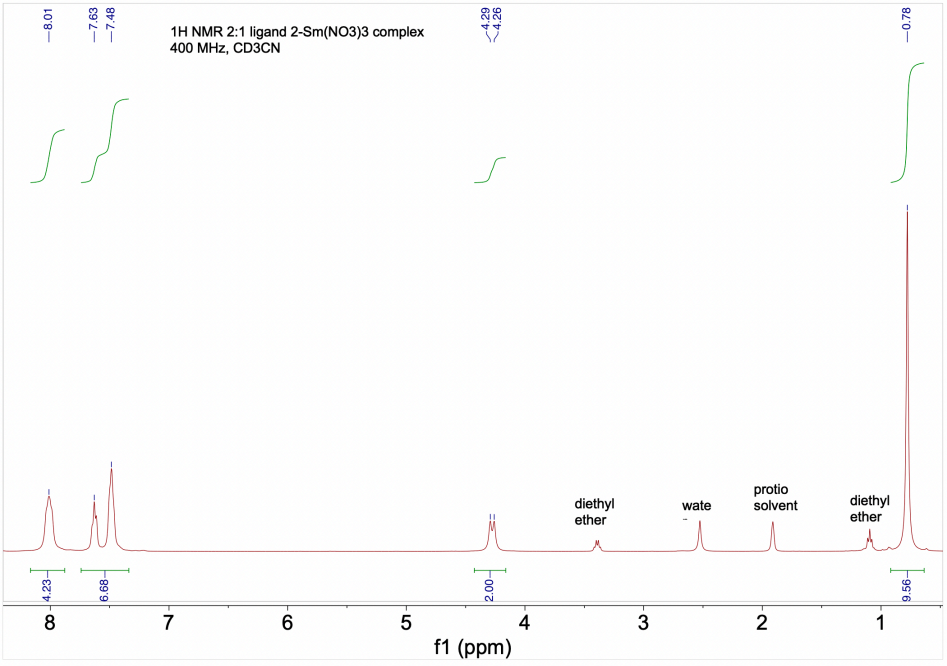

208.40
208.33
13C NMR ligand 2 in CDCl3, 100 MHz
133.13
132.09
131.31
131.21
128.71
128.59
45.42
40.66
40.03
25.97
133.13
132.09
131.31
131.21
128.71
128.59
35
133
131
129
127
f1 (ppm)
200
150
100
50
f1 (ppm)

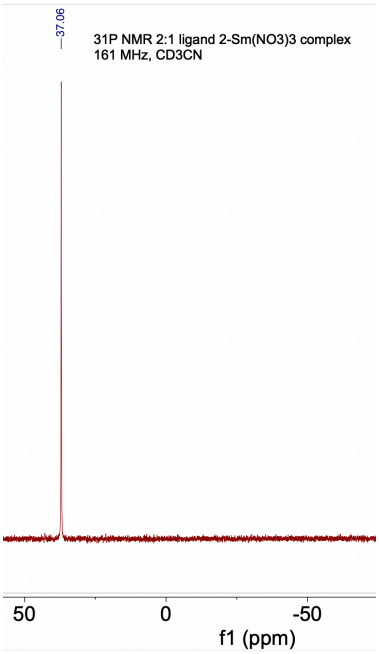

1H NMR ligand 2
CD3CN 400 MHz
7.76
7.70
7.53
7.44
6.12
4.10
3.81
3.78
2.00
1.07
9.35
f1 (ppm)
31P NMR ligand 2
CD3CN 161 MHz
26.52
f1 (ppm)

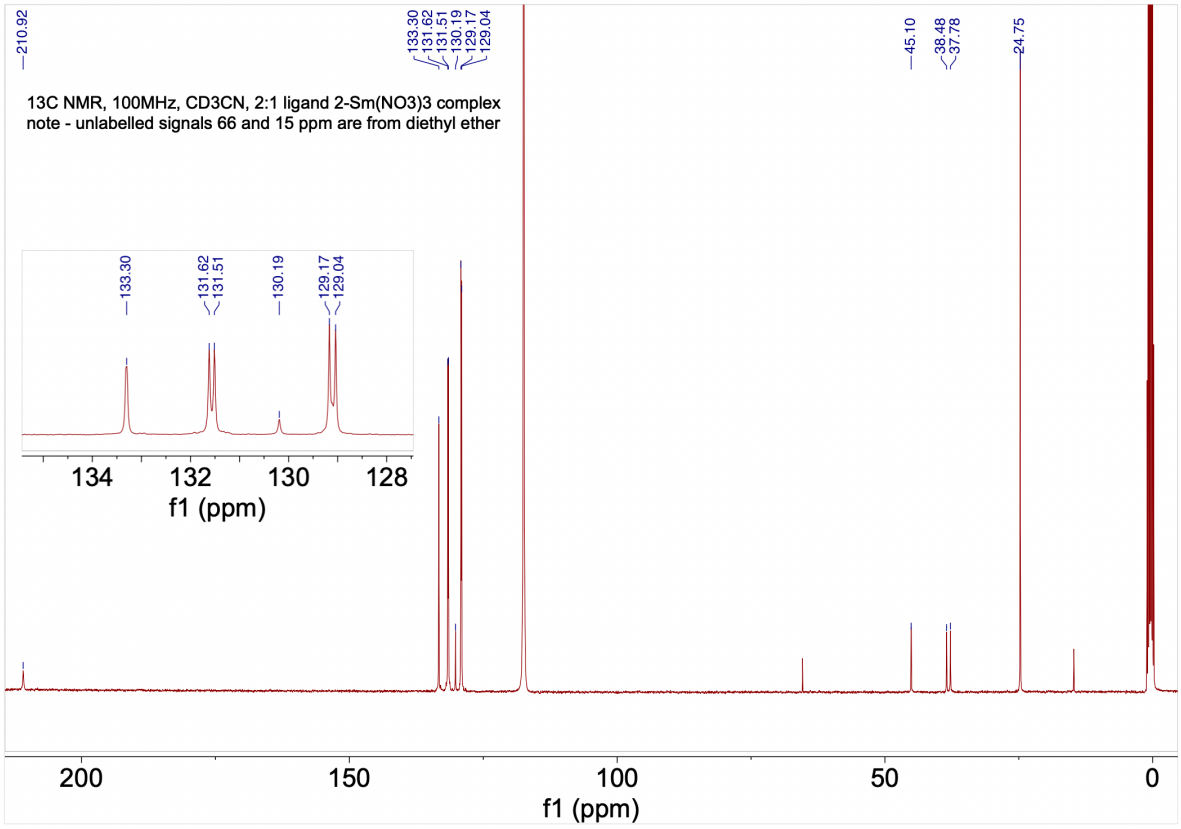

13C NMR ligand 2
CD3CN 100 MHz
208.42
208.35
134.68
133.66
131.75
130.66
128.59
44.92
39.38
38.72
25.19
f1 (ppm)

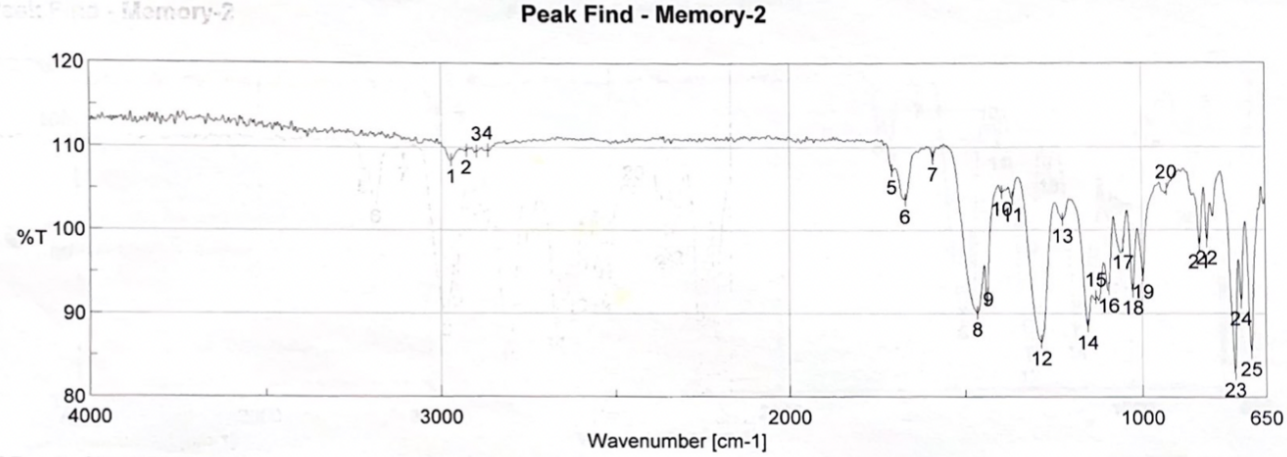

SB_PhCMPOtBu_alone
%Transmittance
Wavenumbers (cm-1)
1698.87
1436.60
1301.10
1187.53
1119.54
1054.58
997.60
837.68
750.61
693.08
509.99
498.72
483.30
463.84
437.01
421.27

2. $Sm(2)_2(NO_3)_3$


1H NMR 2:1 ligand 2-Sm(NO3)3 complex
400 MHz, CD3CN
8.01
7.63
7.48
4.29
4.26
0.78
diethyl ether
wate
protio solvent
diethyl ether
4.23
6.68
2.00
9.56
f1 (ppm)

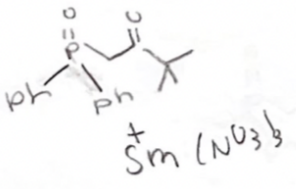

31P NMR 2:1 ligand 2-Sm(NO3)3 complex
161 MHz, CD3CN
37.06
f1 (ppm)



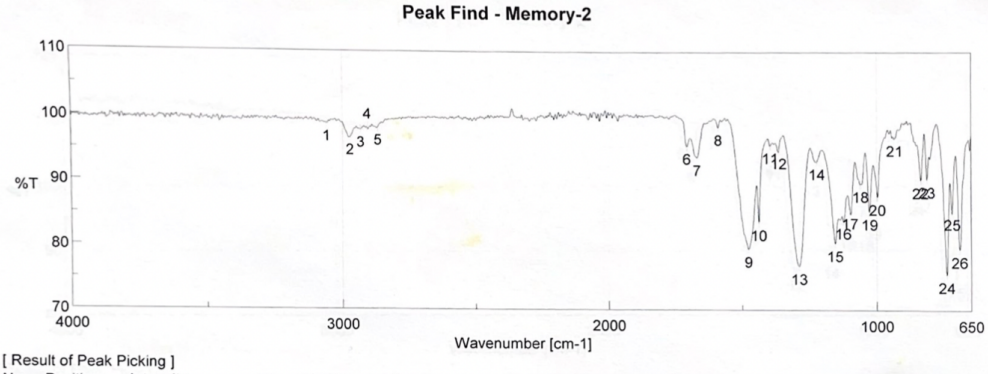


[Result of Peak Picking]

No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity
1	2972	108	2	2928	110	3	2899	110
4	2867	110	5	1708	107	6	1669	104
7	1591	109	8	1466	90	9	1435	94
10	1395	105	11	1365	104	12	1284	87
13	1224	101	14	1153	89	15	1130	92
16	1093	93	17	1053	98	18	1026	93
19	997	95	20	930	105	21	837	98
22	816	99	23	738	83	24	720	91
25	691	85						

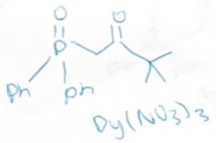


3. $Dy(2)_2(NO_3)_3$

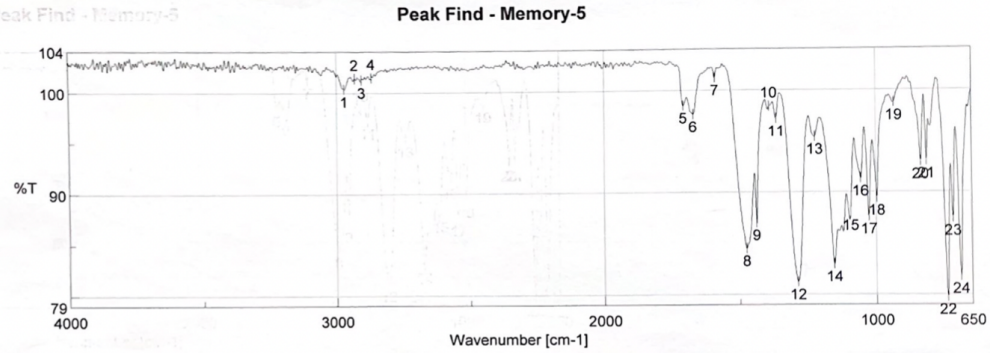


[Result of Peak Picking]

No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity
1	3060	99	2	2971	97	3	2931	98
4	2907	98	5	2868	98	6	1708	96
7	1670	94	8	1591	98	9	1477	79
10	1439	84	11	1396	96	12	1364	95
13	1288	77	14	1223	93	15	1154	80
16	1124	84	17	1099	85	18	1061	90
19	1027	85	20	997	88	21	933	97
22	837	90	23	814	90	24	741	76
25	720	85	26	693	79			

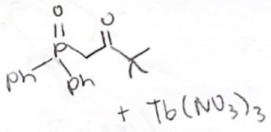


4. $Tb(2)_2(NO_3)_3$

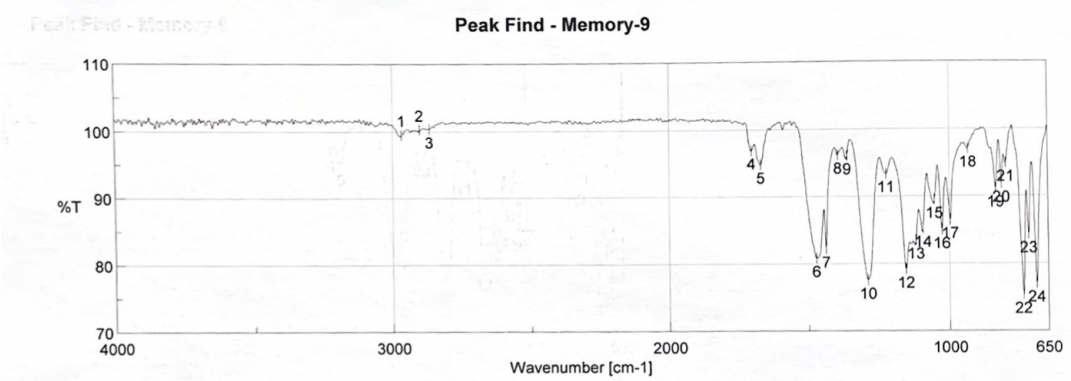


[Result of Peak Picking]

No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity
1	2972	100	2	2932	101	3	2906	101
4	2870	101	5	1708	99	6	1671	98
7	1591	101	8	1475	85	9	1439	87
10	1391	98	11	1365	97	12	1288	81
13	1224	95	14	1154	83	15	1093	88
16	1057	91	17	1027	88	18	997	89
19	933	99	20	836	93	21	815	93
22	741	80	23	719	87	24	691	82

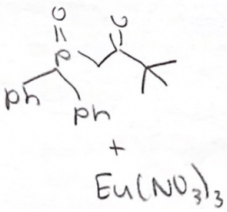


5. $Eu(2)_2(NO_3)_3$

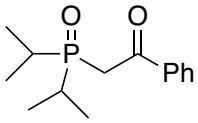


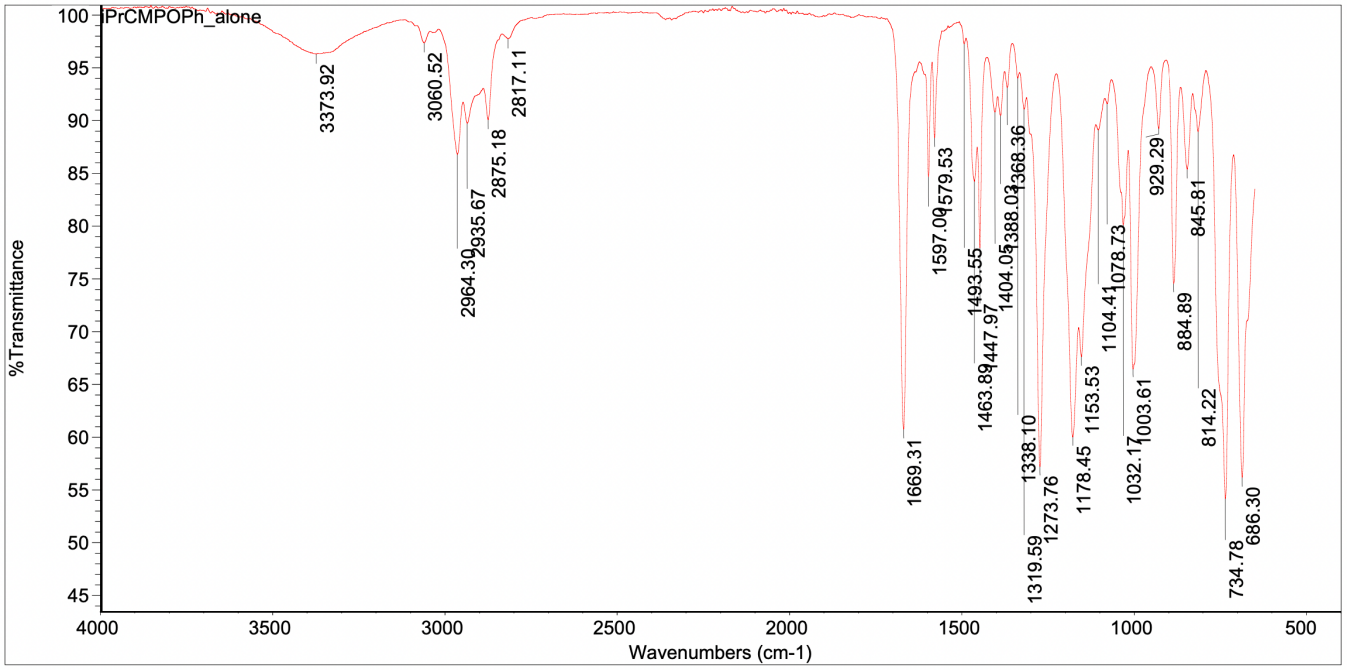
[Result of Peak Picking]

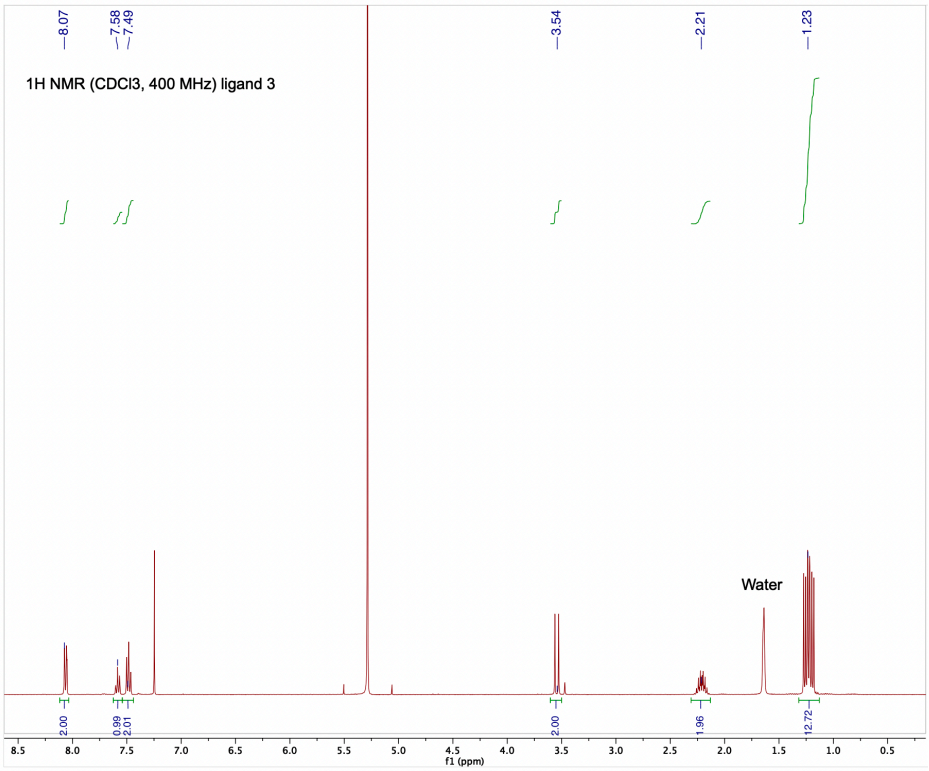
No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity
1	2968	100	2	2902	100	3	2867	100
4	1704	97	5	1671	95	6	1472	81
7	1438	82	8	1395	96	9	1362	96
10	1289	78	11	1224	93	12	1154	79
13	1119	83	14	1093	85	15	1053	89
16	1027	85	17	997	86	18	933	97
19	836	91	20	815	92	21	799	95
22	739	75	23	719	84	24	691	77

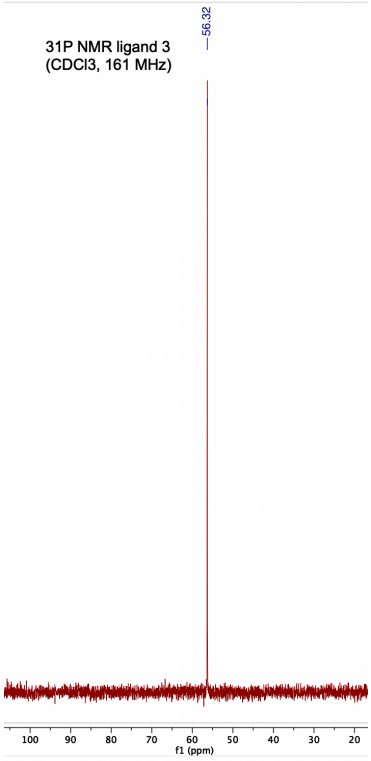


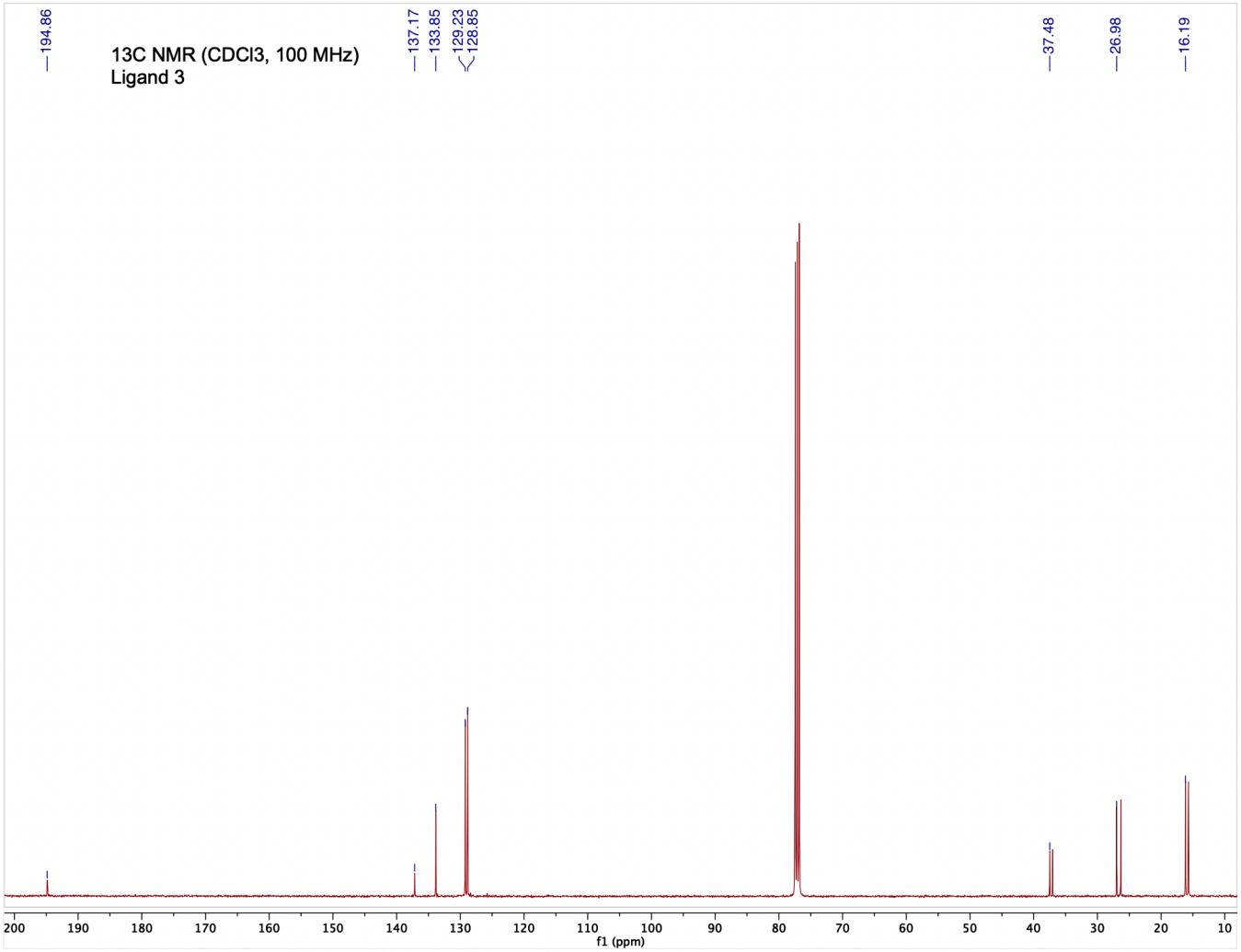
6. Ligand 3

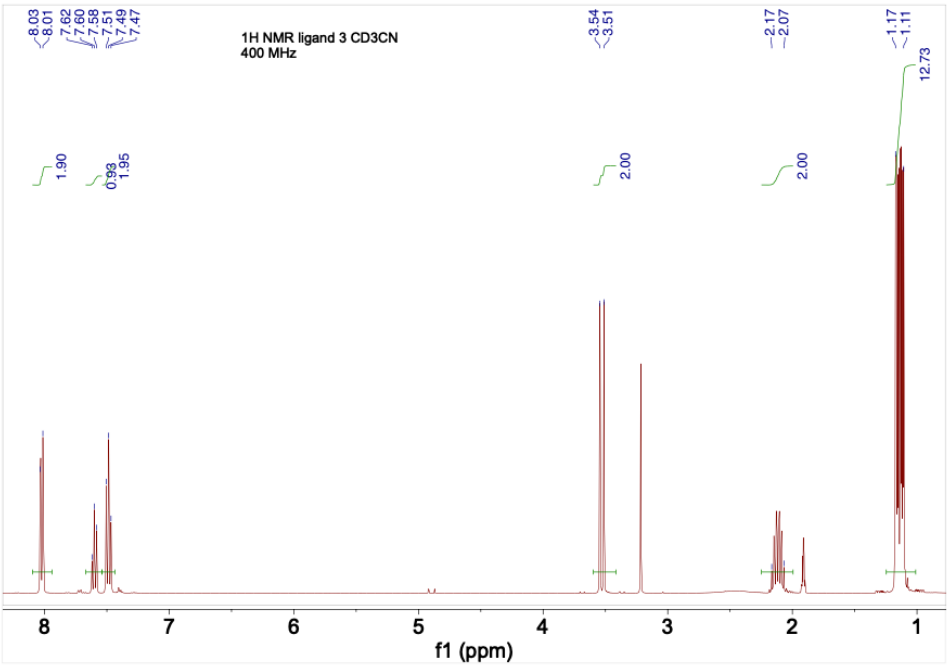


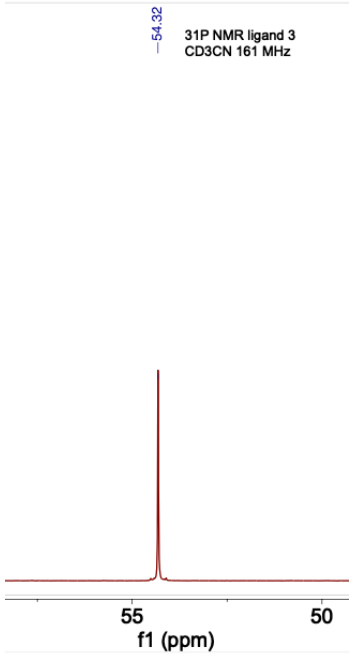


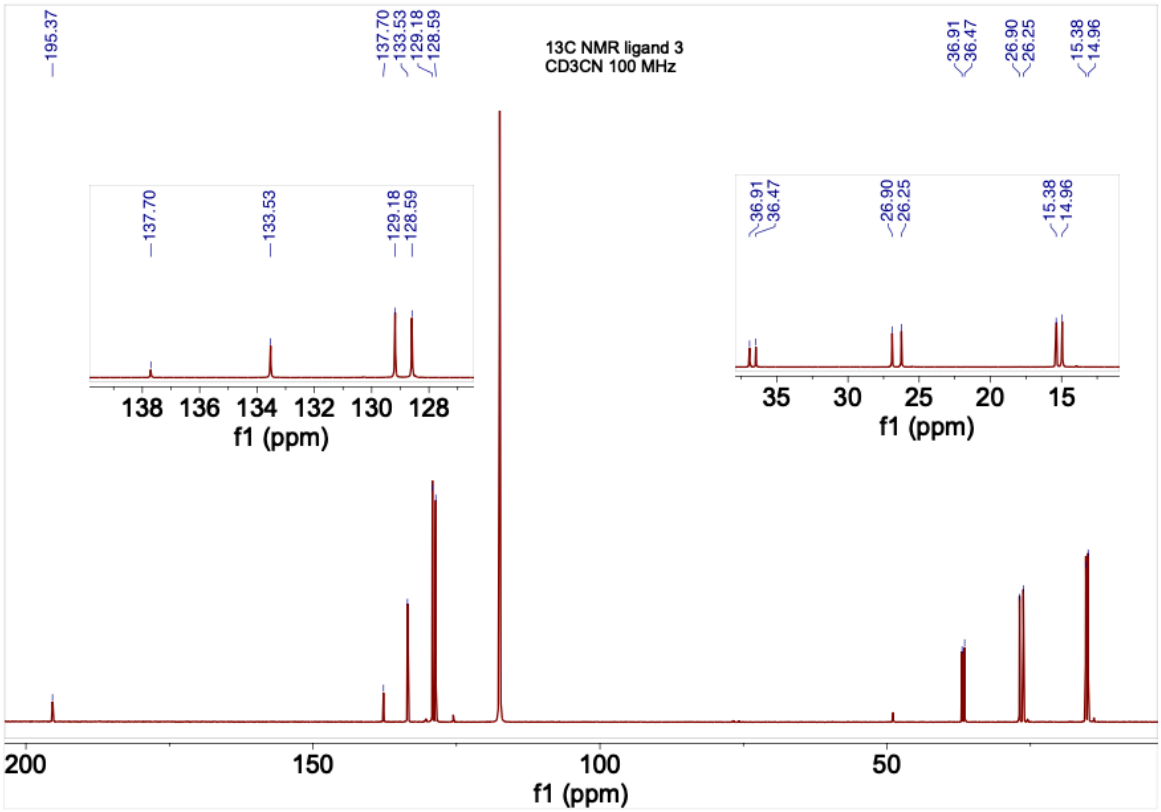

1H NMR (CDCl3, 400 MHz) ligand 3
8.07
7.58
7.49
3.54
2.21
1.23
Water
2.00
0.99
2.01
2.00
1.96
12.72
f1 (ppm)


31P NMR ligand 3
(CDCl3, 161 MHz)
56.32
f1 (ppm)

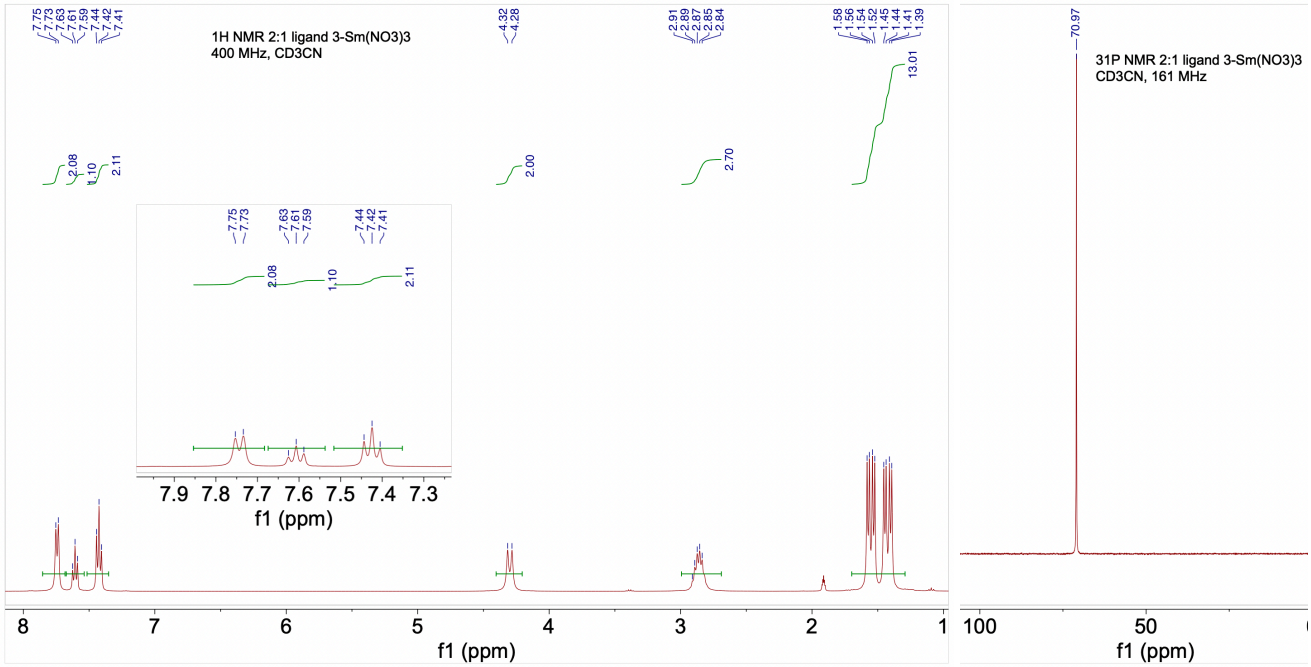

13C NMR (CDCl3, 100 MHz)
Ligand 3
194.86
137.17
133.85
129.23
128.85
37.48
26.98
16.19
f1 (ppm)

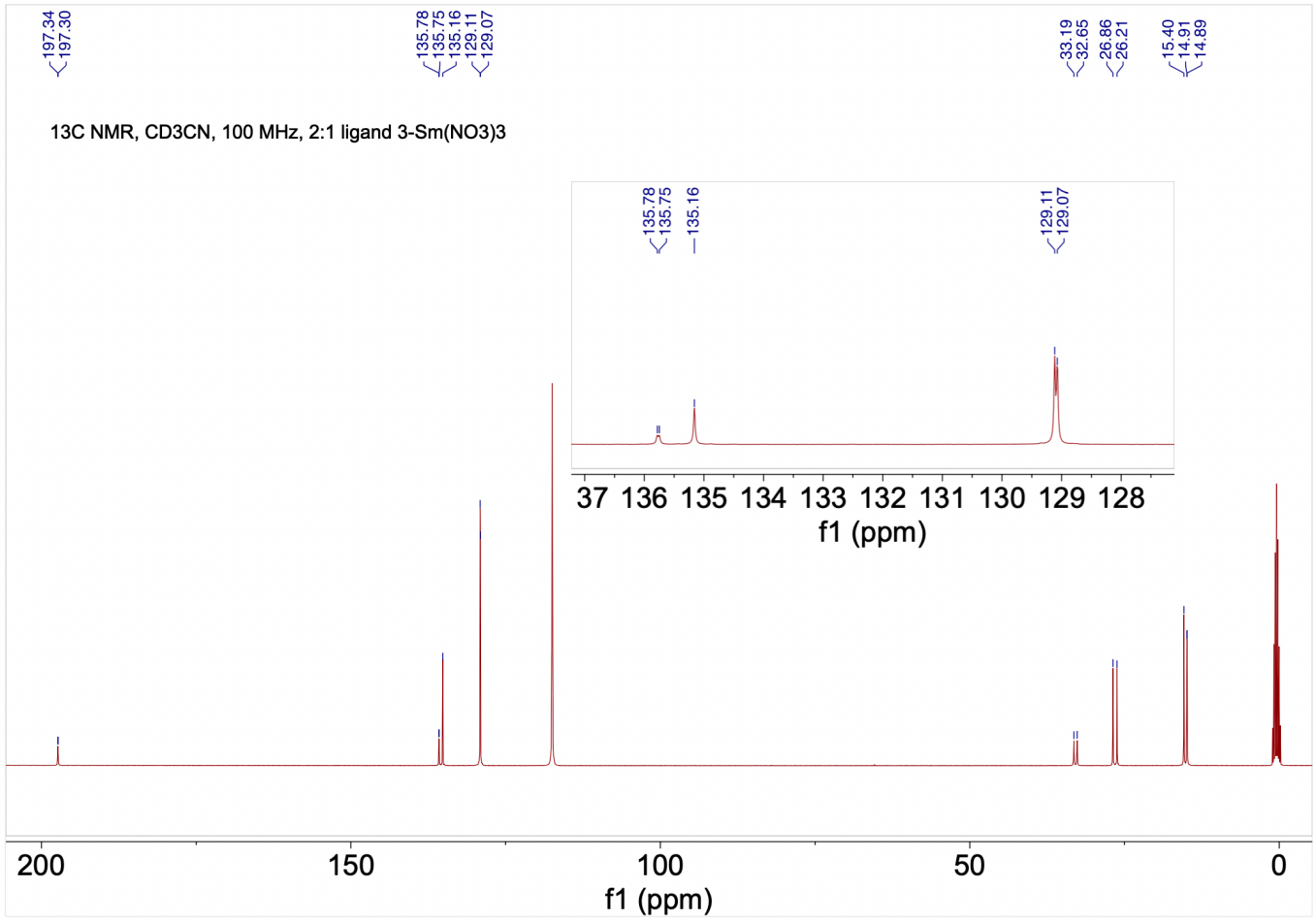

1H NMR ligand 3 CD3CN
400 MHz
8.03
8.01
7.62
7.60
7.58
7.51
7.49
7.47
3.54
3.51
2.17
2.07
1.17
1.11
12.73
1.90
0.93
1.95
2.00
2.00
f1 (ppm)

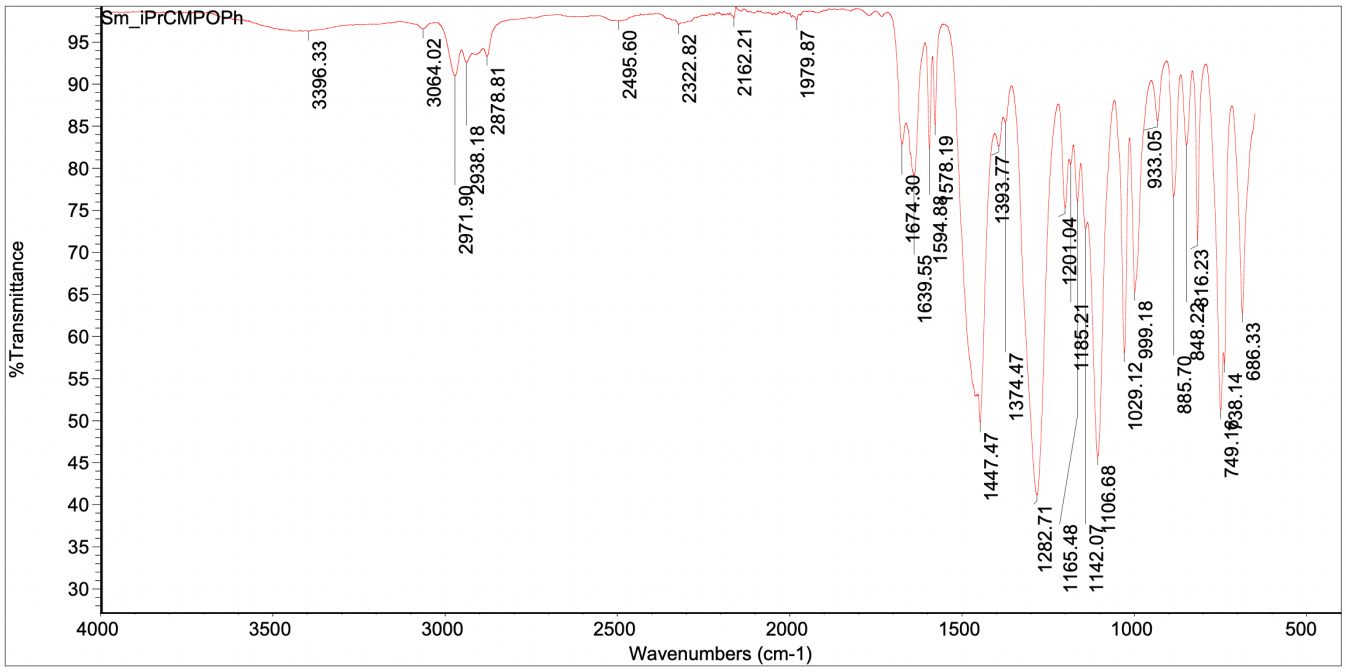

31P NMR ligand 3
CD3CN 161 MHz
54.32
f1 (ppm)


195.37
137.70
133.53
129.18
128.59
13C NMR ligand 3
CD3CN 100 MHz
36.91
36.47
26.90
26.25
15.38
14.96
f1 (ppm)

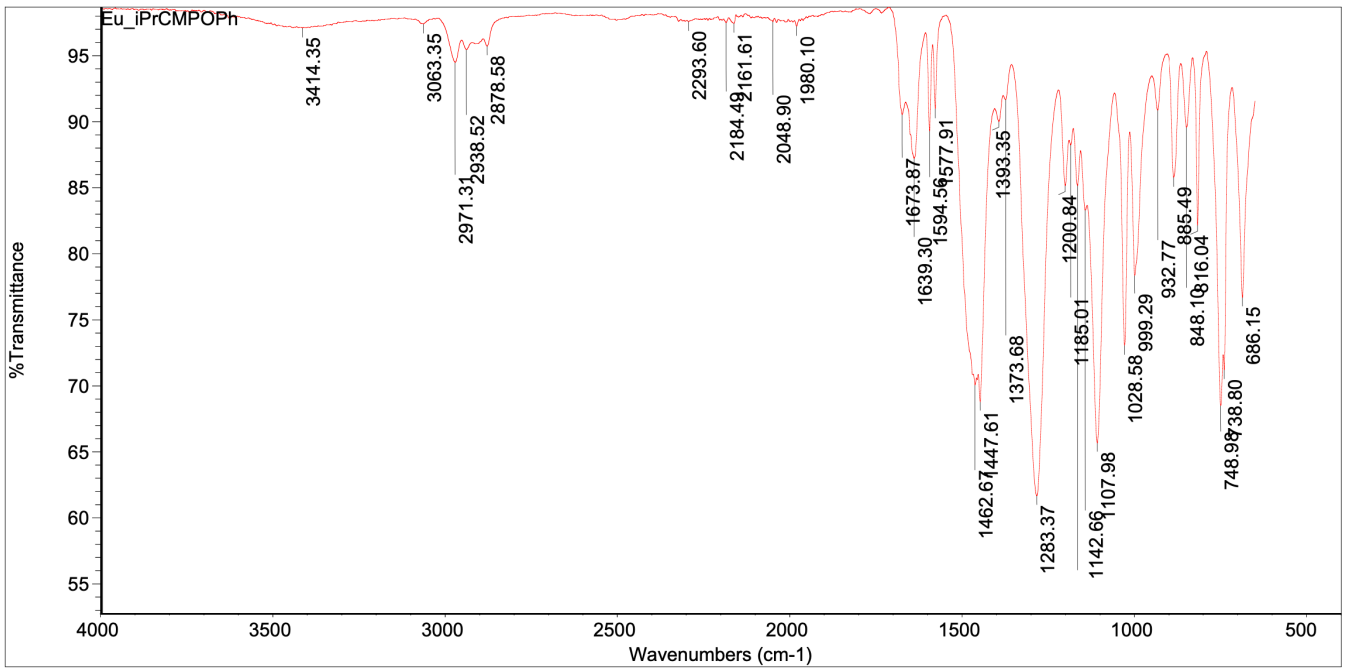
7. $Sm(3)_2(NO_3)_3$


1H NMR 2:1 ligand 3-Sm(NO3)3
400 MHz, CD3CN
f1 (ppm)
31P NMR 2:1 ligand 3-Sm(NO3)3
CD3CN, 161 MHz
f1 (ppm)

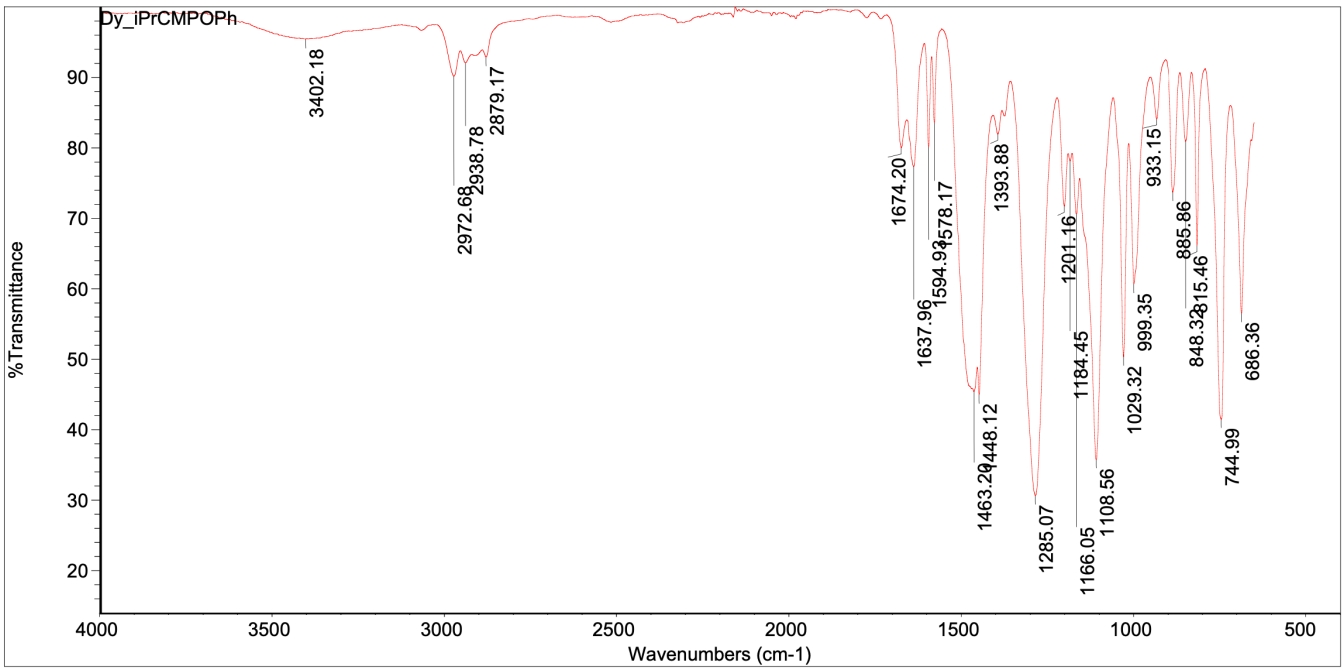

13C NMR, CD3CN, 100 MHz, 2:1 ligand 3-Sm(NO3)3
f1 (ppm)


Sm_iPrCMPOPh
%Transmittance
Wavenumbers (cm-1)
3396.33
3064.02
2971.90
2938.18
2878.81
2495.60
2322.82
2162.21
1979.87
1674.30
1639.55
1594.88
1578.19
1447.47
1393.77
1374.47
1282.71
1201.04
1185.21
1165.48
1142.07
1106.68
1029.12
999.18
933.05
885.70
848.22
816.23
749.19
738.14
686.33

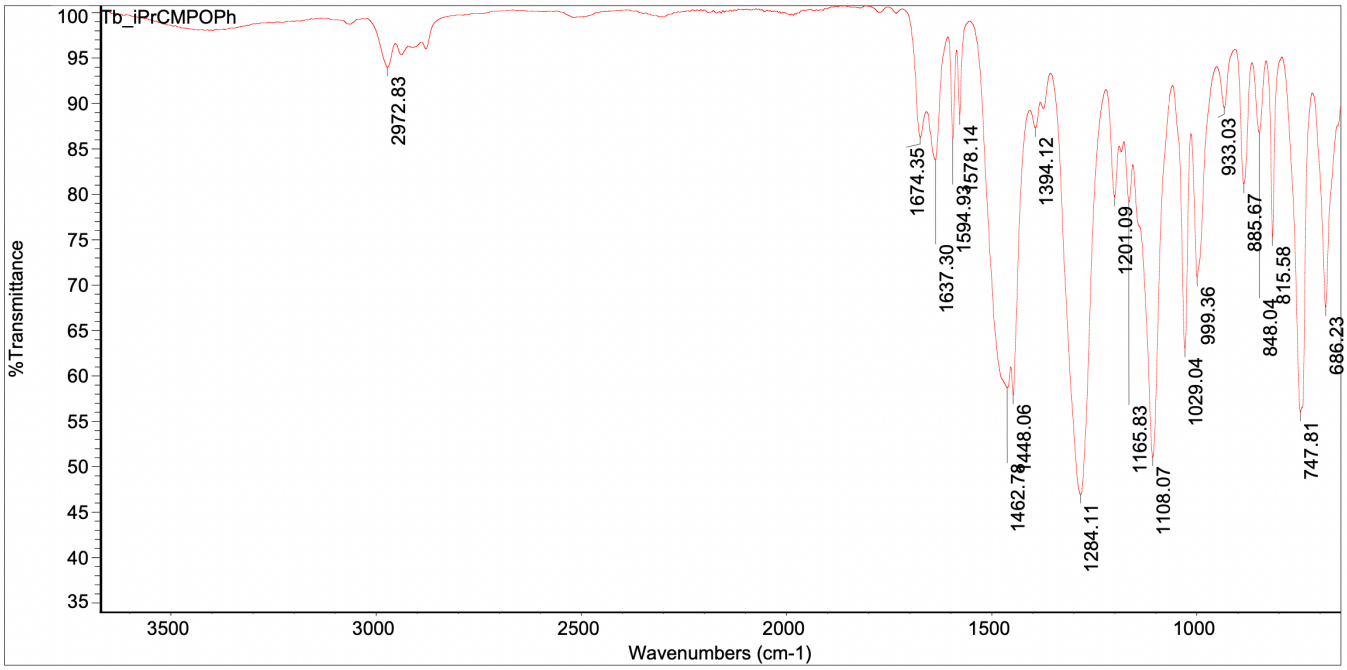
8. $Eu(3)_2(NO_3)_3$


Eu_iPrCMPOPh
%Transmittance
Wavenumbers (cm-1)
3414.35
3063.35
2971.31
2938.52
2878.58
2293.60
2184.49
2161.61
2048.90
1980.10
1673.87
1639.30
1594.56
1577.91
1462.67
1447.61
1393.35
1373.68
1283.37
1200.84
1185.01
1142.66
1107.98
1028.58
999.29
932.77
885.49
848.10
816.04
748.98
738.80
686.15

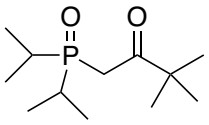
9. $Dy(3)_2(NO_3)_3$

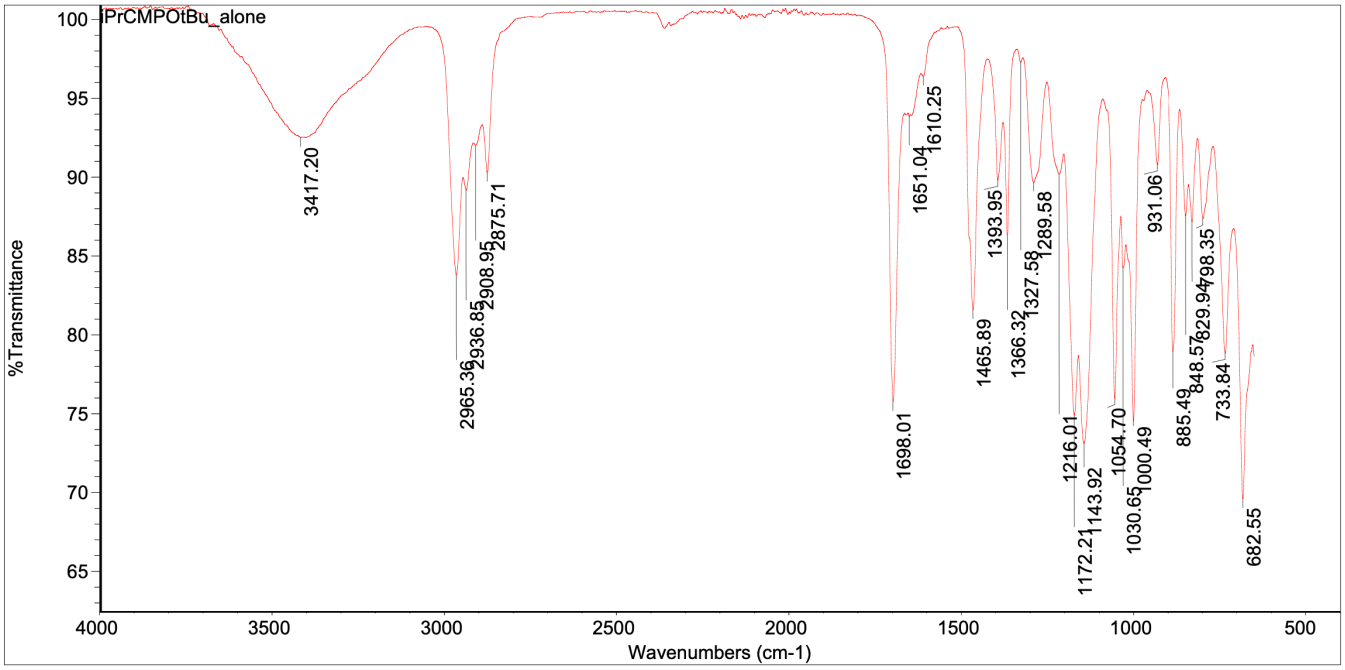


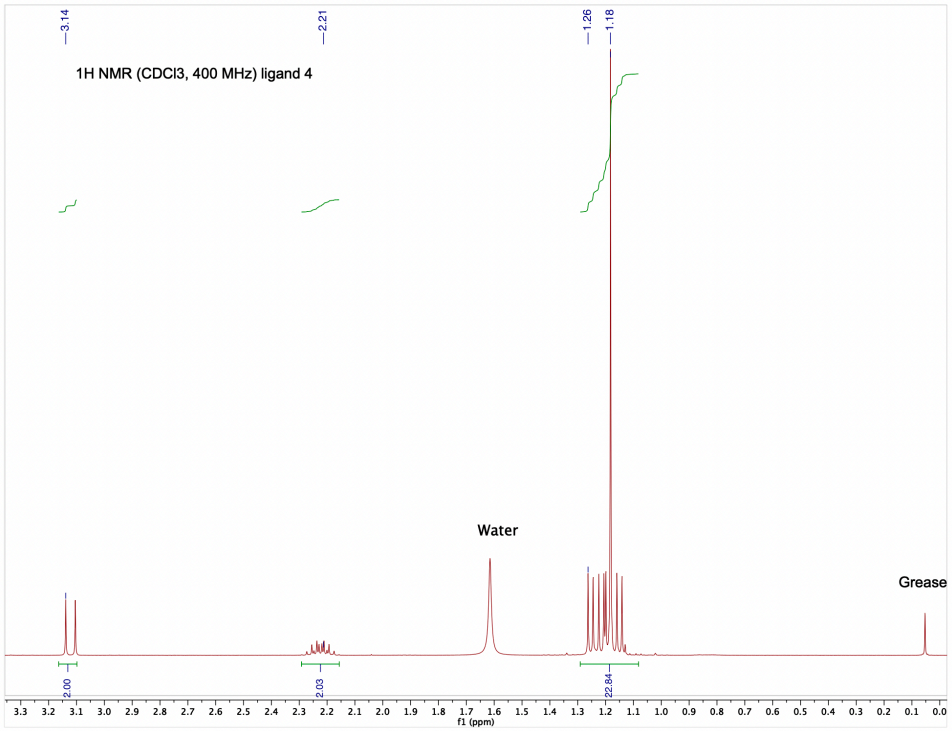
10. $Tb(3)_2(NO_3)_3$

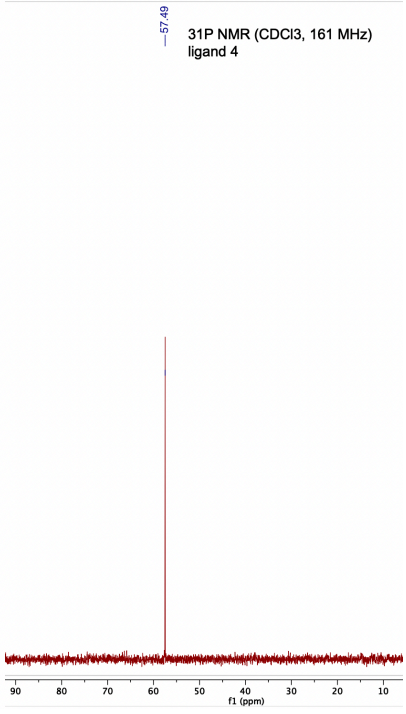


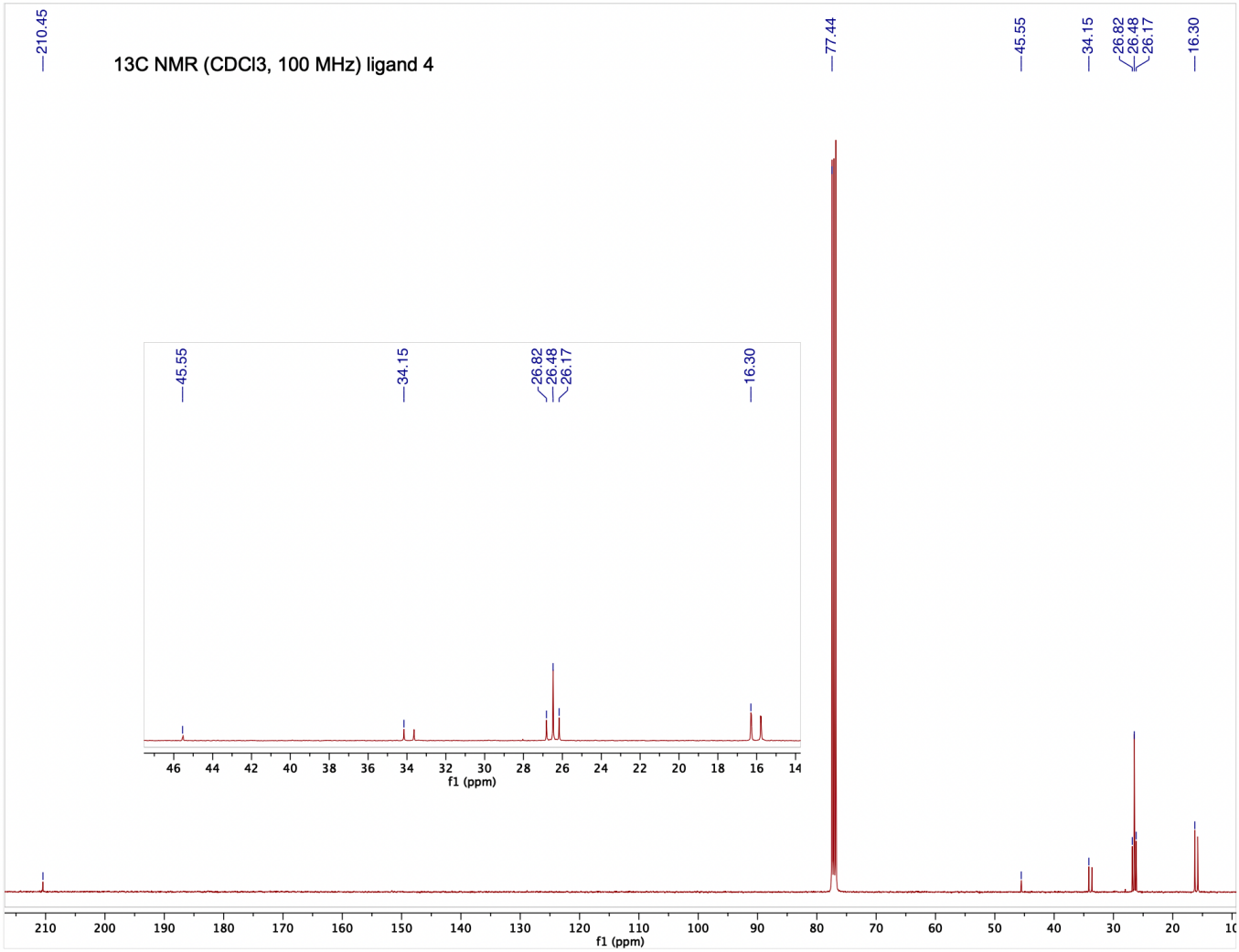
11. Ligand 4

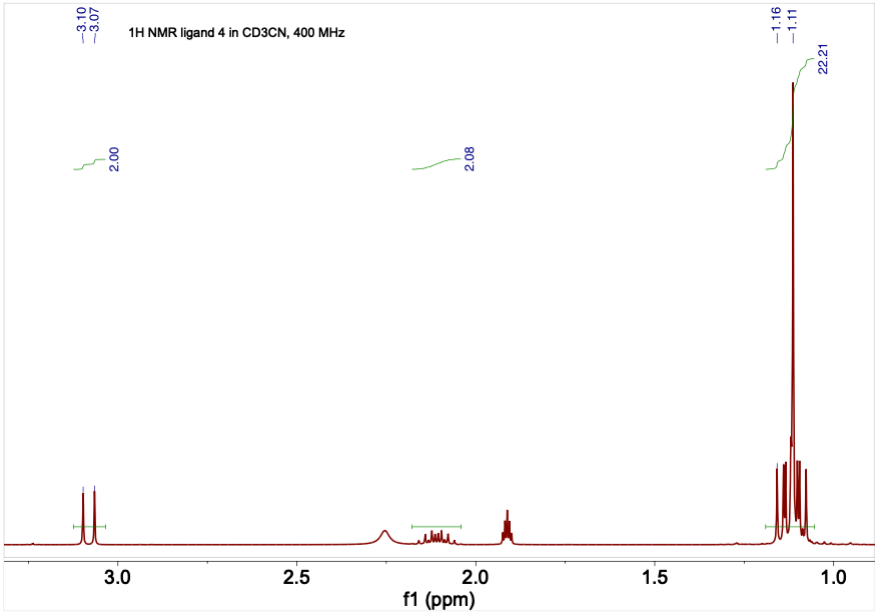


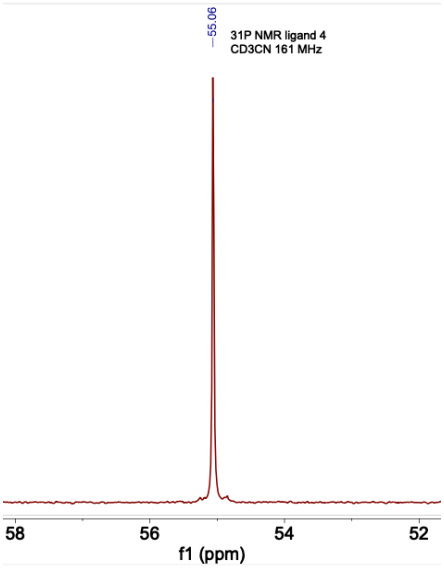

iPrCMPOtBu_alone
%Transmittance
Wavenumbers (cm-1)
3417.20
2965.36
2936.85
2908.95
2875.71
1698.01
1651.04
1610.25
1465.89
1393.95
1366.32
1327.58
1289.58
1216.01
1172.21
1143.92
1054.70
1030.65
1000.49
931.06
885.49
848.57
829.94
798.35
733.84
682.55

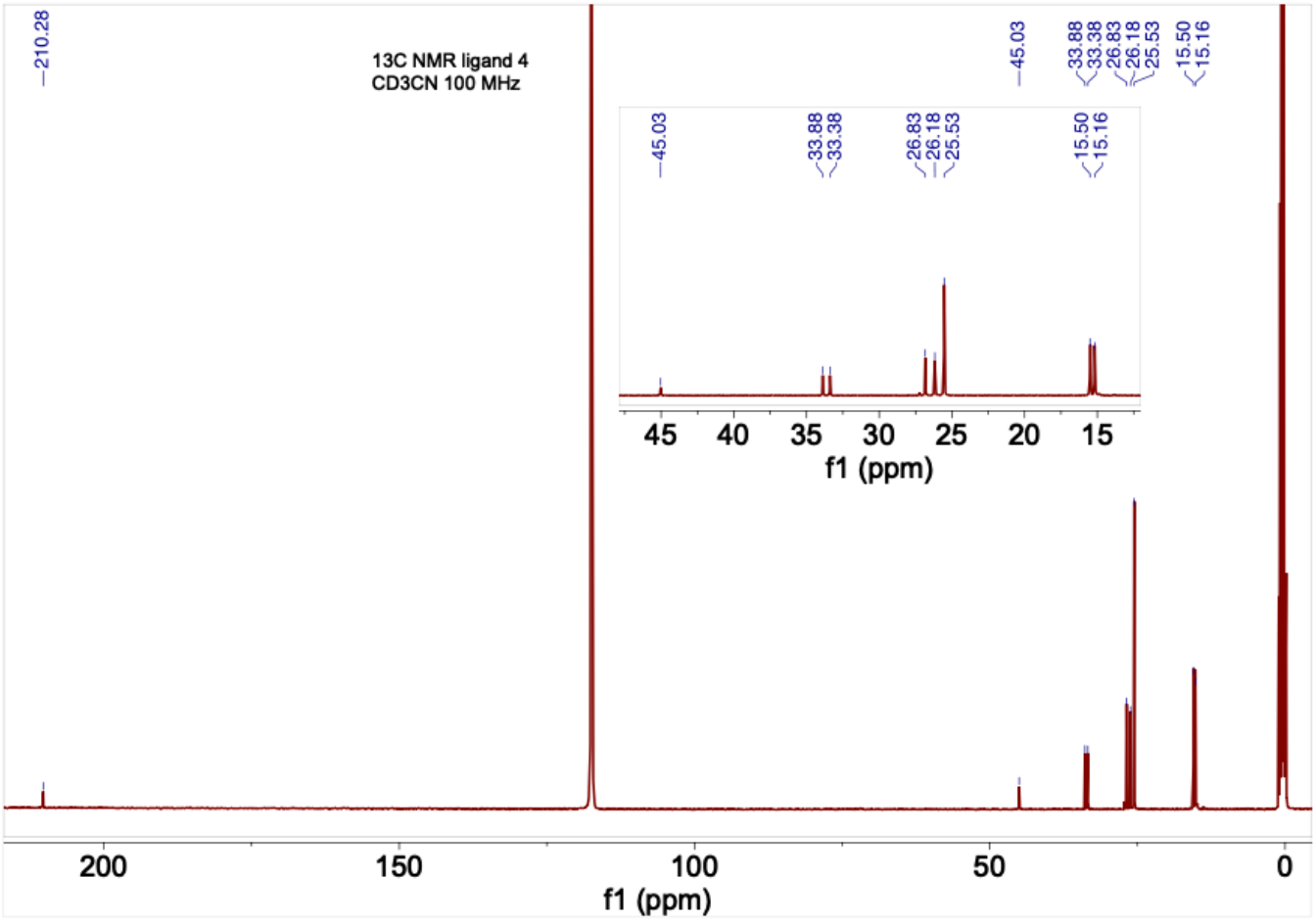

1H NMR (CDCl3, 400 MHz) ligand 4
Water
Grease
f1 (ppm)


31P NMR (CDCl3, 161 MHz)
ligand 4
f1 (ppm)

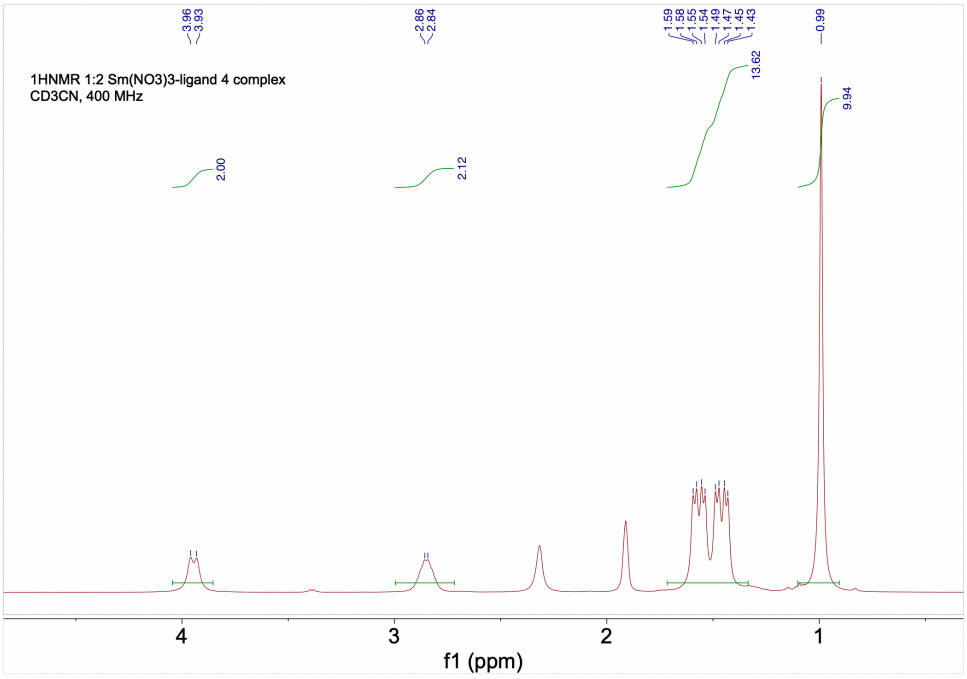

13C NMR (CDCl3, 100 MHz) ligand 4
210.45
77.44
45.55
34.15
26.82
26.48
26.17
16.30
f1 (ppm)

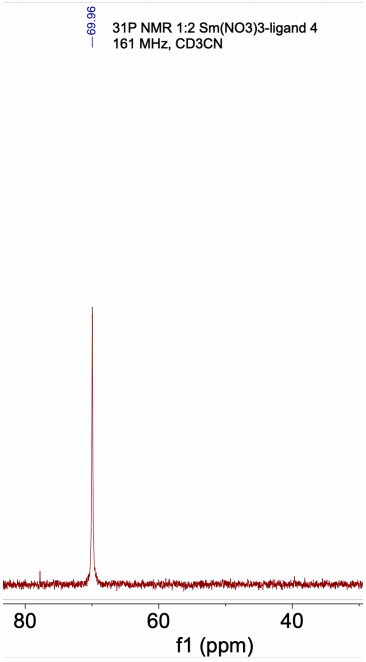

1H NMR ligand 4 in CD3CN, 400 MHz
3.10
3.07
1.16
1.11
22.21
2.00
2.08
f1 (ppm)

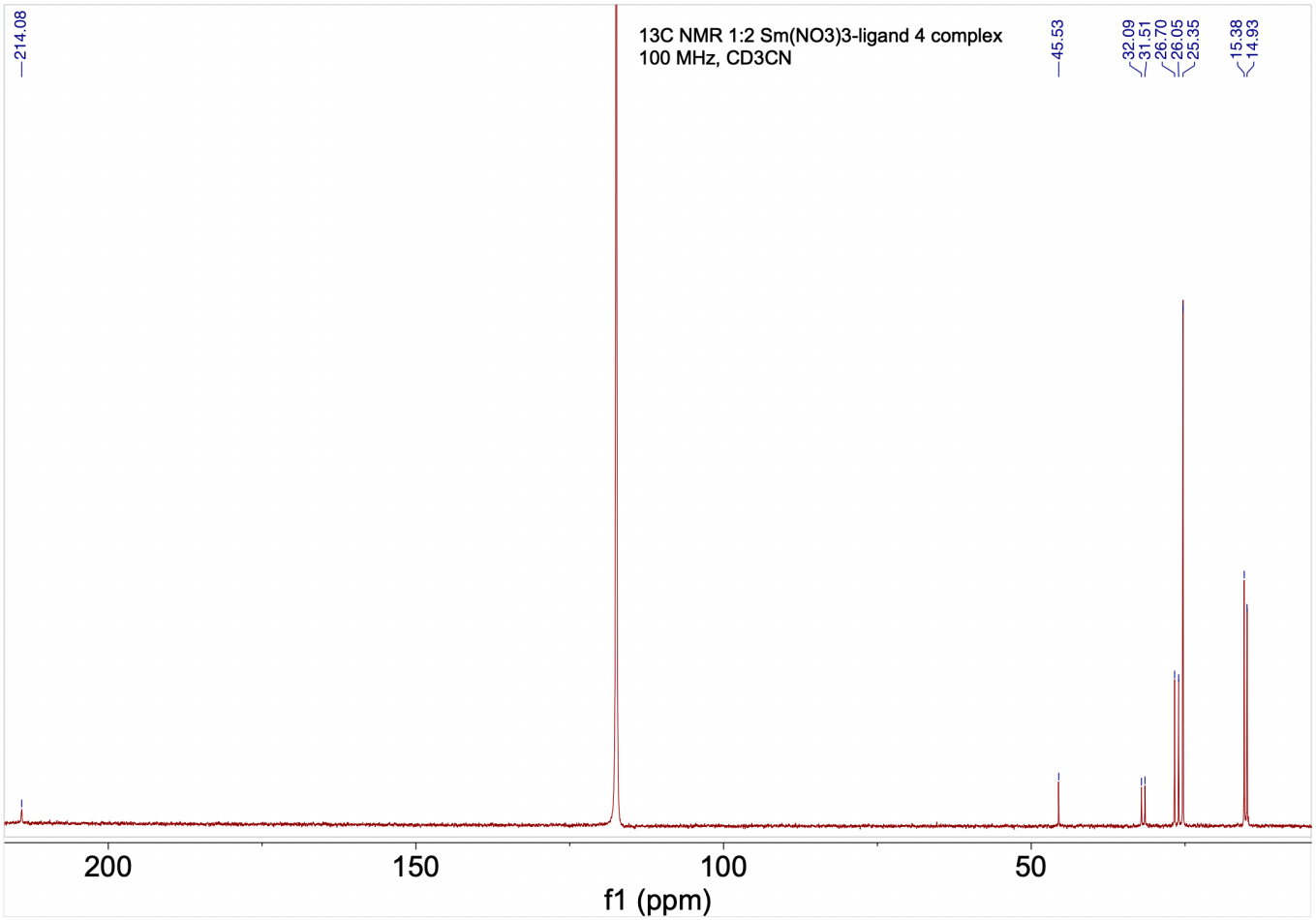

55.06
31P NMR ligand 4
CD3CN 161 MHz
f1 (ppm)

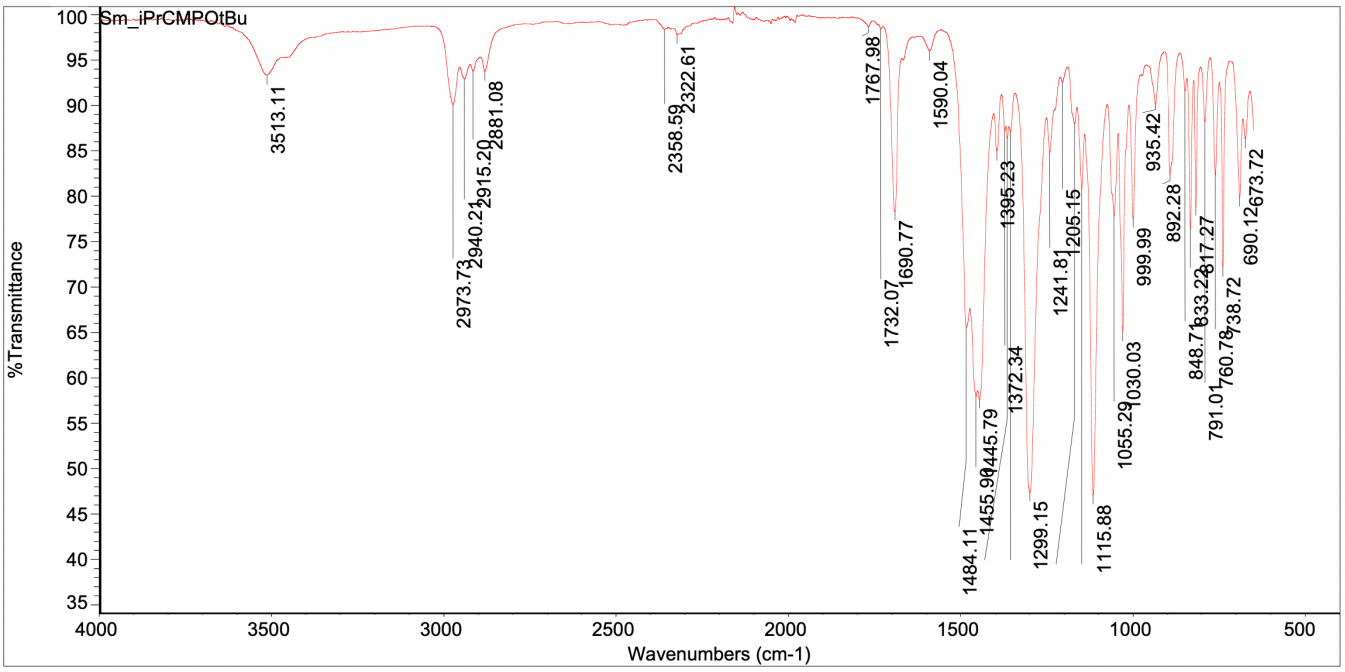

13C NMR ligand 4
CD3CN 100 MHz
210.28
45.03
33.88
33.38
26.83
26.18
25.53
15.50
15.16
f1 (ppm)

12. $Sm(4)_2(NO_3)_3$

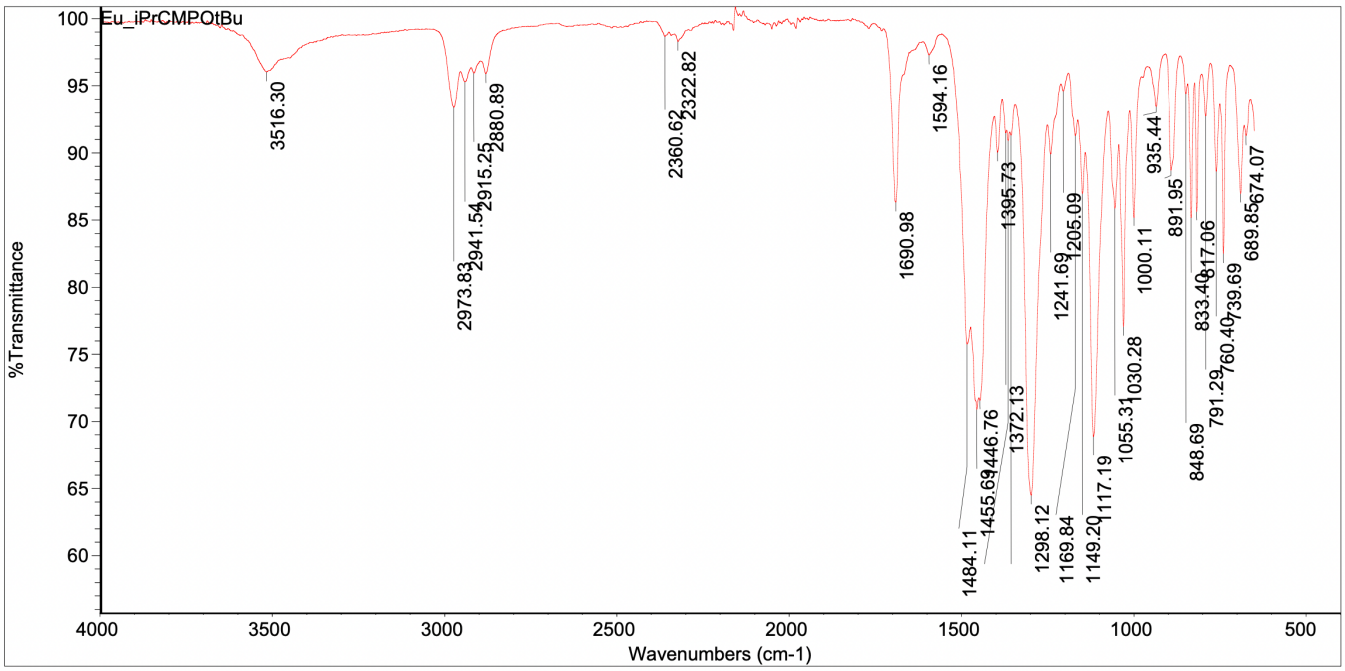

1HNMR 1:2 Sm(NO3)3-ligand 4 complex
CD3CN, 400 MHz
3.96
3.93
2.86
2.84
1.59
1.58
1.55
1.54
1.49
1.47
1.45
1.43
0.99
2.00
2.12
13.62
9.94
f1 (ppm)


69.96
31P NMR 1:2 Sm(NO3)3-ligand 4
161 MHz, CD3CN
f1 (ppm)

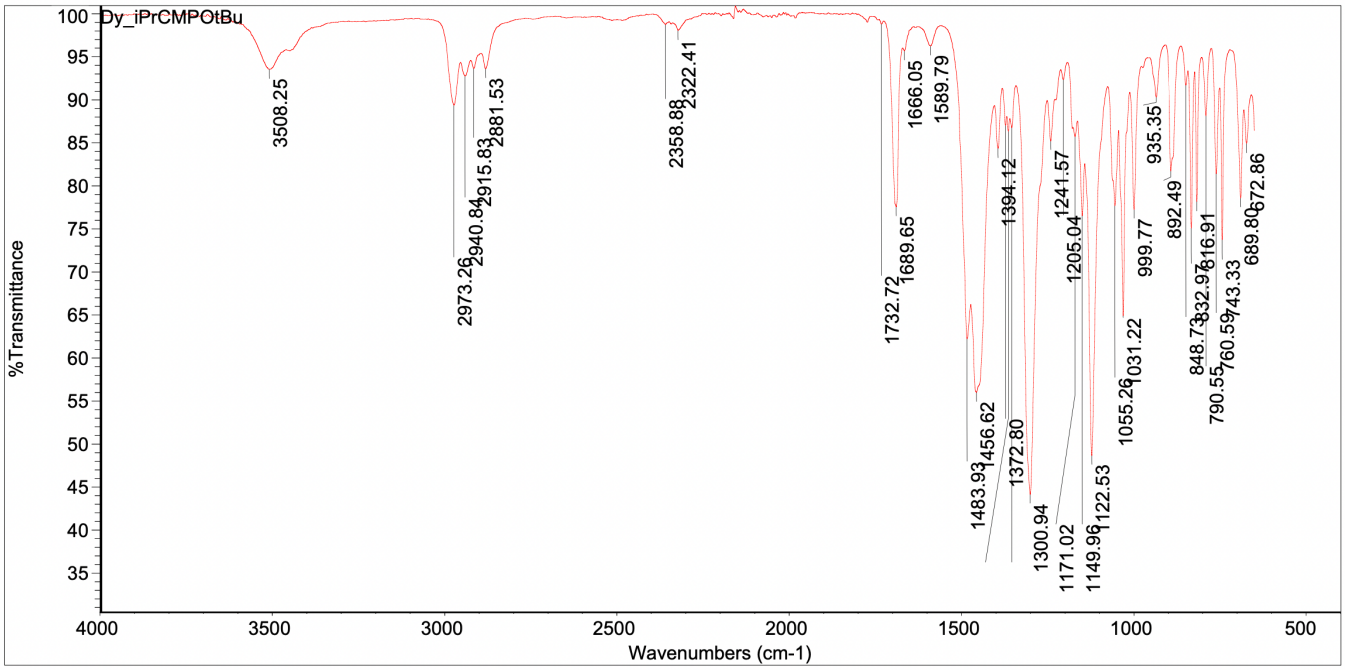

13C NMR 1:2 Sm(NO3)3-ligand 4 complex
100 MHz, CD3CN
214.08
45.53
32.09
31.51
26.70
26.05
25.35
15.38
14.93
200
150
100
50
f1 (ppm)


Sm_iPrCMPOtBu
%Transmittance
Wavenumbers (cm-1)
3513.11
2973.73
2940.21
2915.20
2881.08
2358.59
2322.61
1767.98
1732.07
1690.77
1590.04
1484.11
1455.99
1445.79
1395.23
1372.34
1299.15
1241.81
1205.15
1115.88
1055.29
1030.03
999.99
935.42
892.28
848.71
833.22
817.27
791.01
760.78
738.72
690.12
673.72

13. $Eu(4)_2(NO_3)_3$


Eu_iPrCMPOtBu
%Transmittance
Wavenumbers (cm-1)
3516.30
2973.83
2941.54
2915.25
2880.89
2360.62
2322.82
1690.98
1594.16
1484.11
1455.69
1446.76
1395.73
1372.13
1298.12
1241.69
1205.09
1169.84
1149.20
1117.19
1055.31
1030.28
1000.11
935.44
891.95
848.69
833.40
817.06
791.29
760.40
739.69
689.85
674.07

14. $Dy(4)_2(NO_3)_3$


Dy_iPrCMPOtBu
%Transmittance
Wavenumbers (cm-1)
3508.25
2973.26
2940.84
2915.83
2881.53
2358.88
2322.41
1732.72
1689.65
1666.05
1589.79
1483.93
1456.62
1394.12
1372.80
1300.94
1241.57
1205.04
1171.02
1149.96
1122.53
1055.26
1031.22
999.77
935.35
892.49
848.73
832.97
816.91
790.55
760.59
743.33
689.80
672.86

15. Tb $(4)_2(NO_3)_3$

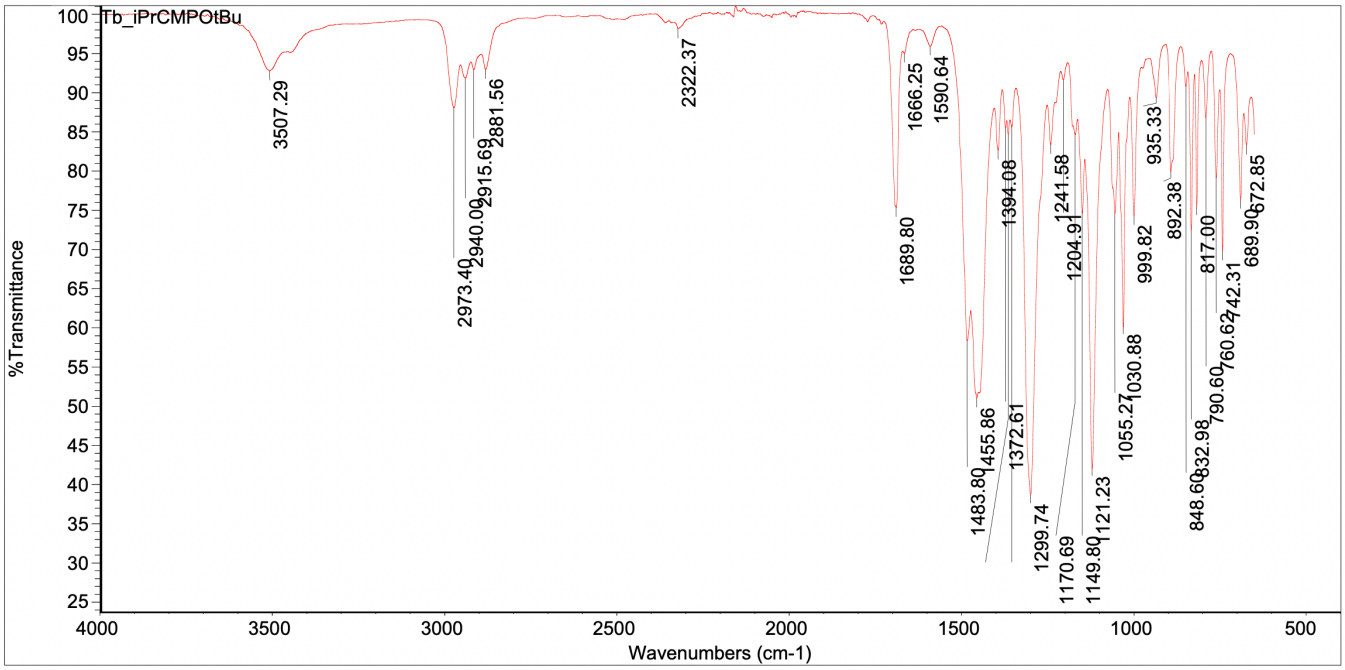

Tb_iPrCMPOtBu
%Transmittance
Wavenumbers (cm-1)
3507.29
2973.40
2940.00
2915.69
2881.56
2322.37
1689.80
1666.25
1590.64
1483.80
1455.86
1394.08
1372.61
1299.74
1241.58
1204.91
1170.69
1149.80
1121.23
1055.27
1030.88
999.82
935.33
892.38
848.60
832.98
817.00
790.60
760.62
742.31
689.90
672.85

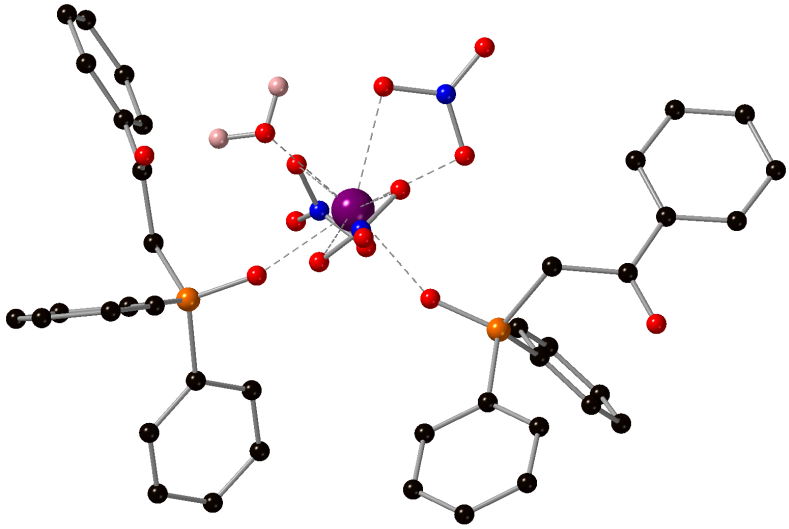
Table containing assigned absorption bands in the IR for each complex

Ligand or Complex	Ligand		Coordinated nitrate				**Δν** ν(N=O) and $\nu_a(NO_2)$
	ν(C=O)	**ν(P=O)**	**ν(N=O)**	**$\nu_a(NO_2)$**	**$\nu_s(NO_2)$**	**ν(NO)[b]**	
ligand **1**	1680	1179	---	---	---	---	---
Tb(**1**)$_3$(NO$_3$)$_3$	1677	1143	1458	1294	1030	815	164
Eu(**1**)$_3$(NO$_3$)$_3$	1676	1138	1467	1290	1028	816	177
Sm(**1**)$_3$(NO$_3$)$_3$	1677	1138	1464	1291	1029	817	173
Dy(**1**)$_3$(NO$_3$)$_3$	1676	1140	1472	1292	1030	815	180
ligand **2**	1700	1187	---	---	---	---	---
Tb(**2**)$_2$(NO$_3$)$_3$	1671	1154	1475	1288	1027	815	187
Eu(**2**)$_2$(NO$_3$)$_3$	1671	1154	1472	1289	1027	815	183
Sm(**2**)$_2$(NO$_3$)$_3$	1684	1156	1466	1284	1026	815	182
Dy(**2**)$_2$(NO$_3$)$_3$	1670	1154	1477	1288	1027	814	189
ligand **3**	1669	1178	---	---	---	---	---
Tb(**3**)$_2$(NO$_3$)$_3$	1637	1108	1463	1284	1029	816	179
Eu(**3**)$_2$(NO$_3$)$_3$	1639	1108	1463	1283	1029	816	180
Sm(**3**)$_2$(NO$_3$)$_3$	1640	1107	1457	1283	1029	816	174
Dy(**3**)$_2$(NO$_3$)$_3$	1638	1109	1463	1285	1029	815	178
ligand **4**	1698	1689	---	---	---	---	---
Tb(**4**)$_2$(NO$_3$)$_3$	1689	1121	1483	1300	1031	817	183
Eu(**4**)$_2$(NO$_3$)$_3$	1691	1117	1484	1298	1030	817	186
Sm(**4**)$_2$(NO$_3$)$_3$	1690	1123	1484	1299	1030	817	185
Dy(**4**)$_2$(NO$_3$)$_3$	1691	1116	1484	1301	1031	817	183

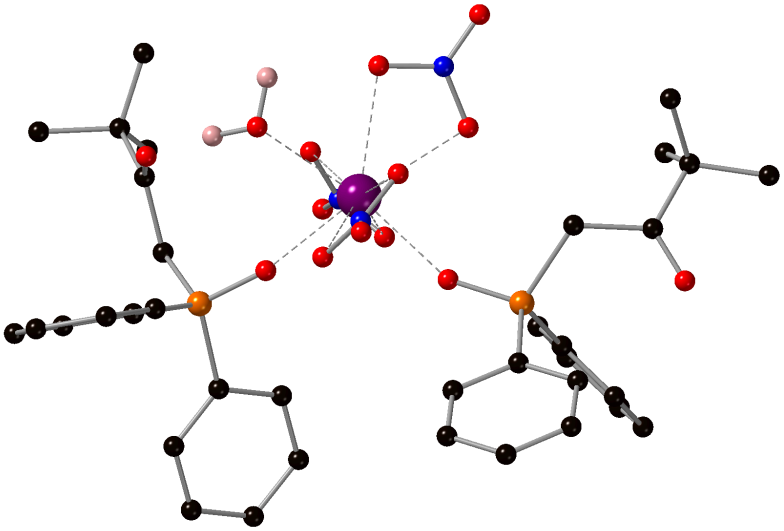
E. Structures of minimized $Gd(1\text{-}4)_2(NO_3)_3(H_2O)$ complexes - singlet state

These figures were drawn using a ball-and-stick model with standard CPK colors (Gd = purple). All hydrogen atoms other than those of the water molecule have been omitted for clarity.

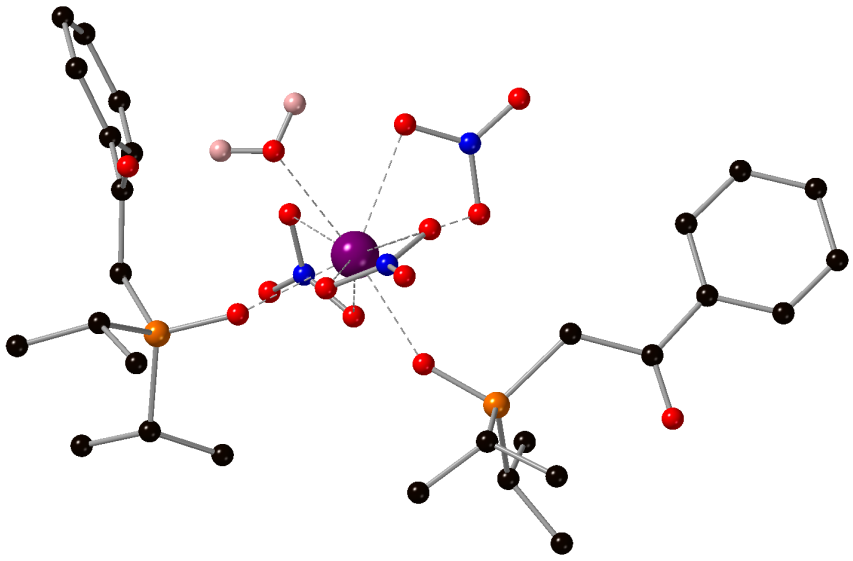
Complex of ligand 1



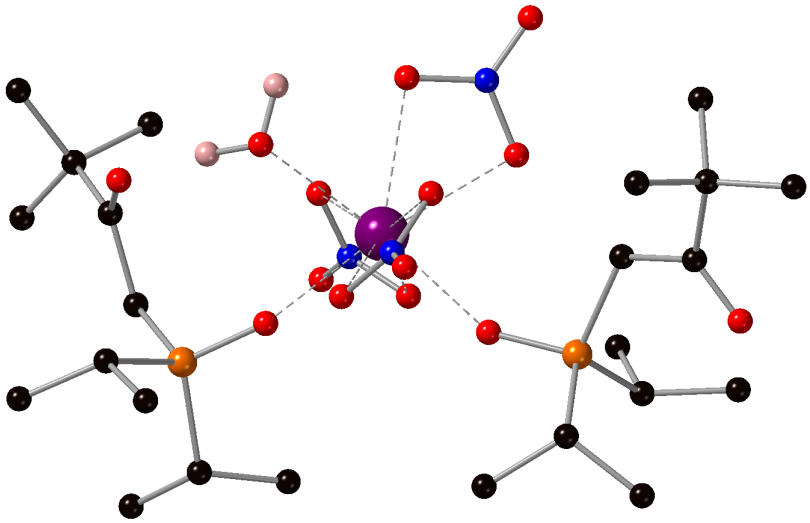
Complex of ligand 2



Complex of ligand 3



Complex of ligand 4



Literature Cited.

1. Montalti, M.; Credi, A.; Prodi, L.; Gandolfi, M. *Handbook of Photochemistry, 3rd ed.* Taylor & Francis.
2. Montalti, M.; Credi, A.; Prodi, L.; Gandolfi, M. T. *Handbook of Photochemistry*. 3rd ed.; Taylor & Francis.