Supplementary Materials

Complexation Behavior of Pinene–Bipyridine Ligands towards Lanthanides: The Influence of the Carboxylic Arm

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Contents

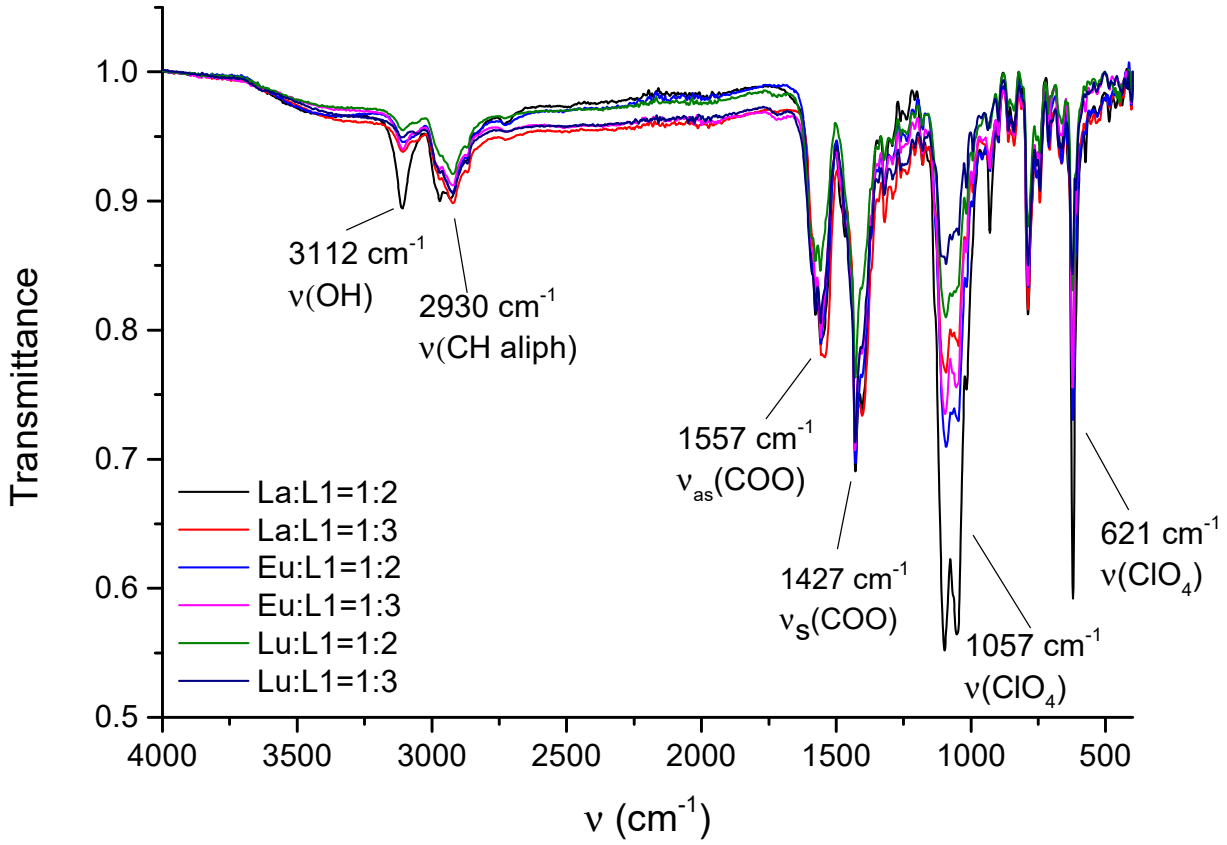


Figure S1. Superposition of IR spectra of complexes with **(-)-L1**$^{-}$

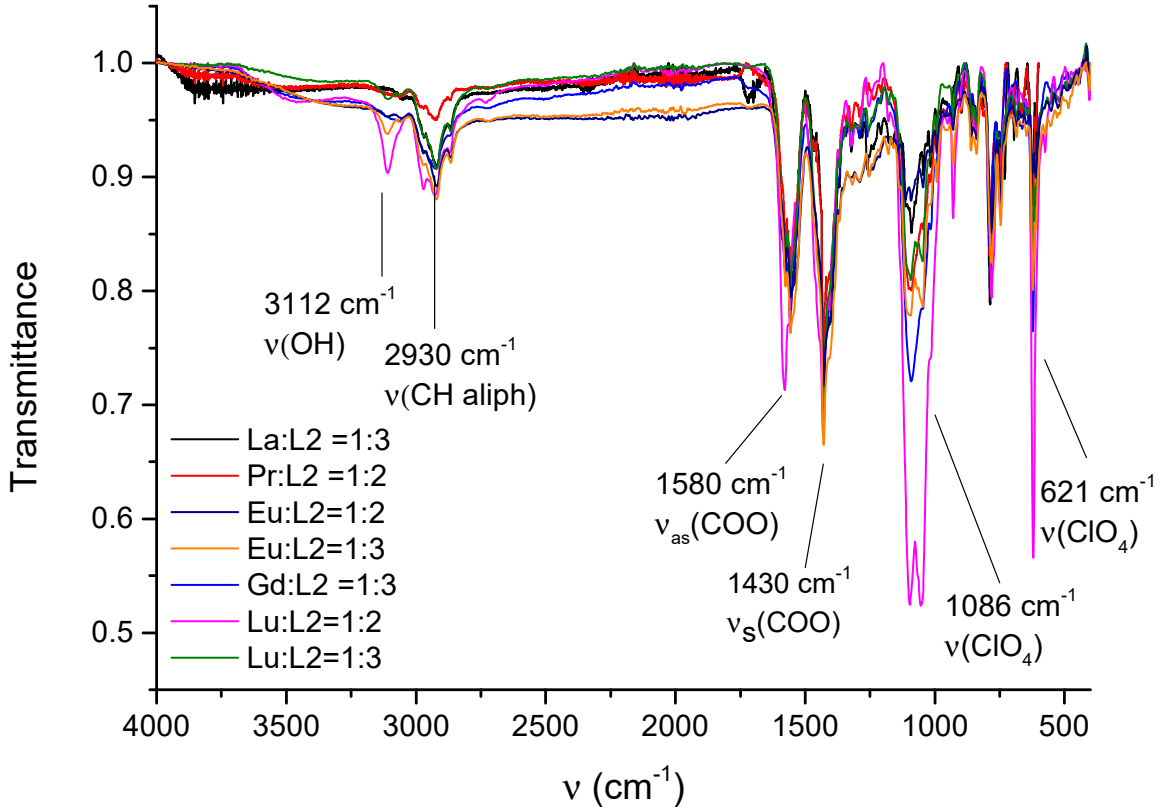


Figure S2. Superposition of IR spectra of complexes with **(-)-L2**$^{-}$

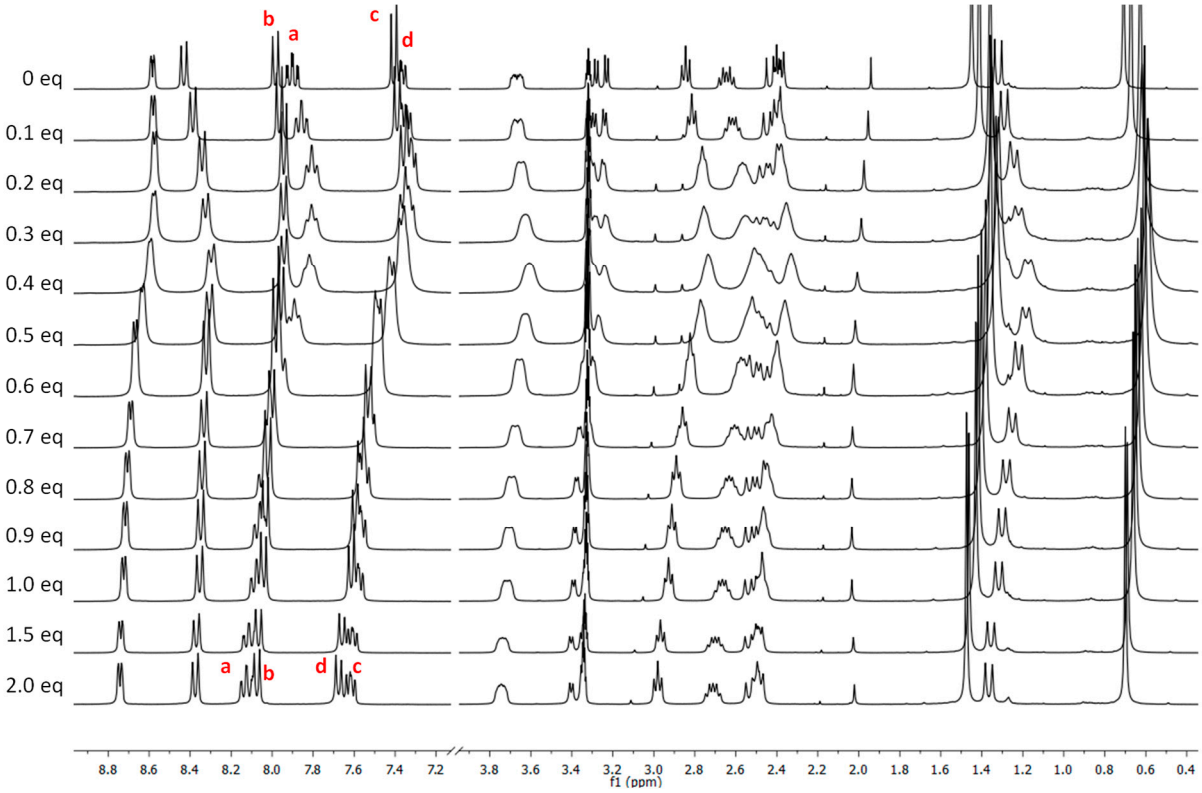


Figure S3. ^{1}H-NMR titration of **(-)-L1**$^{-}$ with La(III) in MeOD.

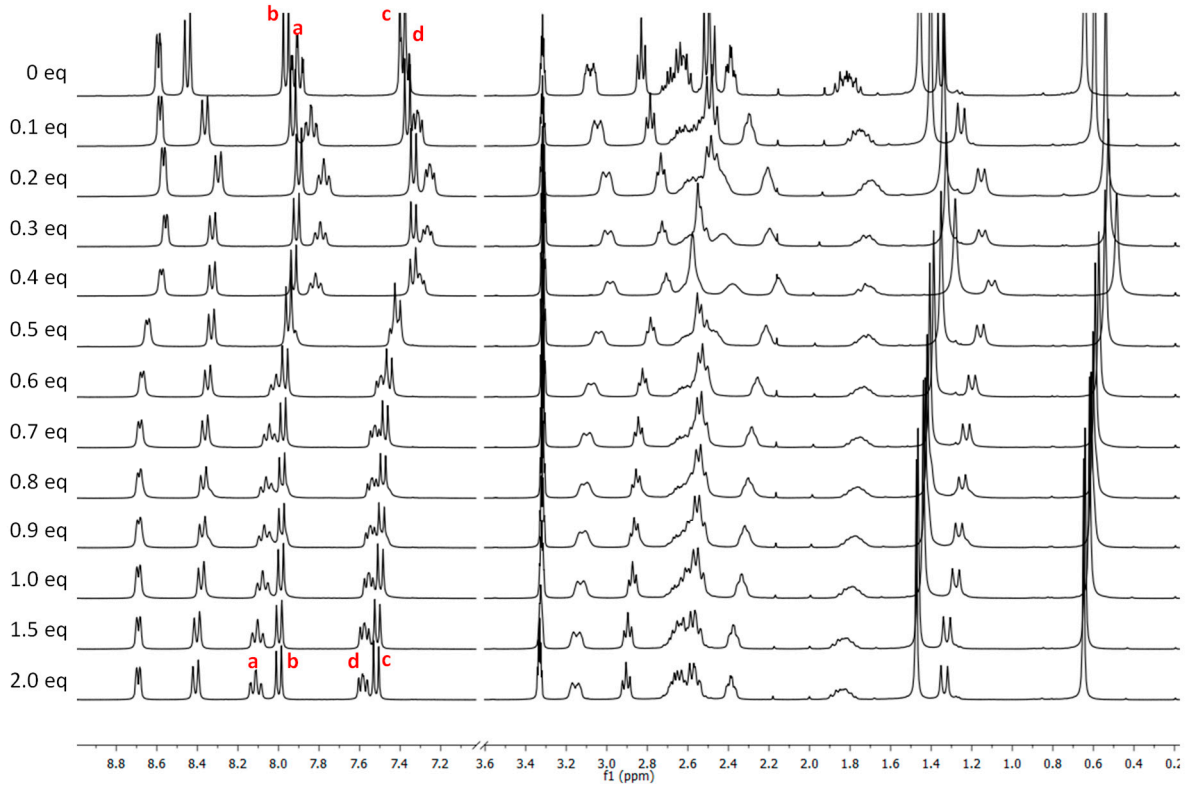


Figure S4. ^{1}H-NMR titration of **(-)-L2**$^{-}$ with La(III) in MeOD.

NMR spectra

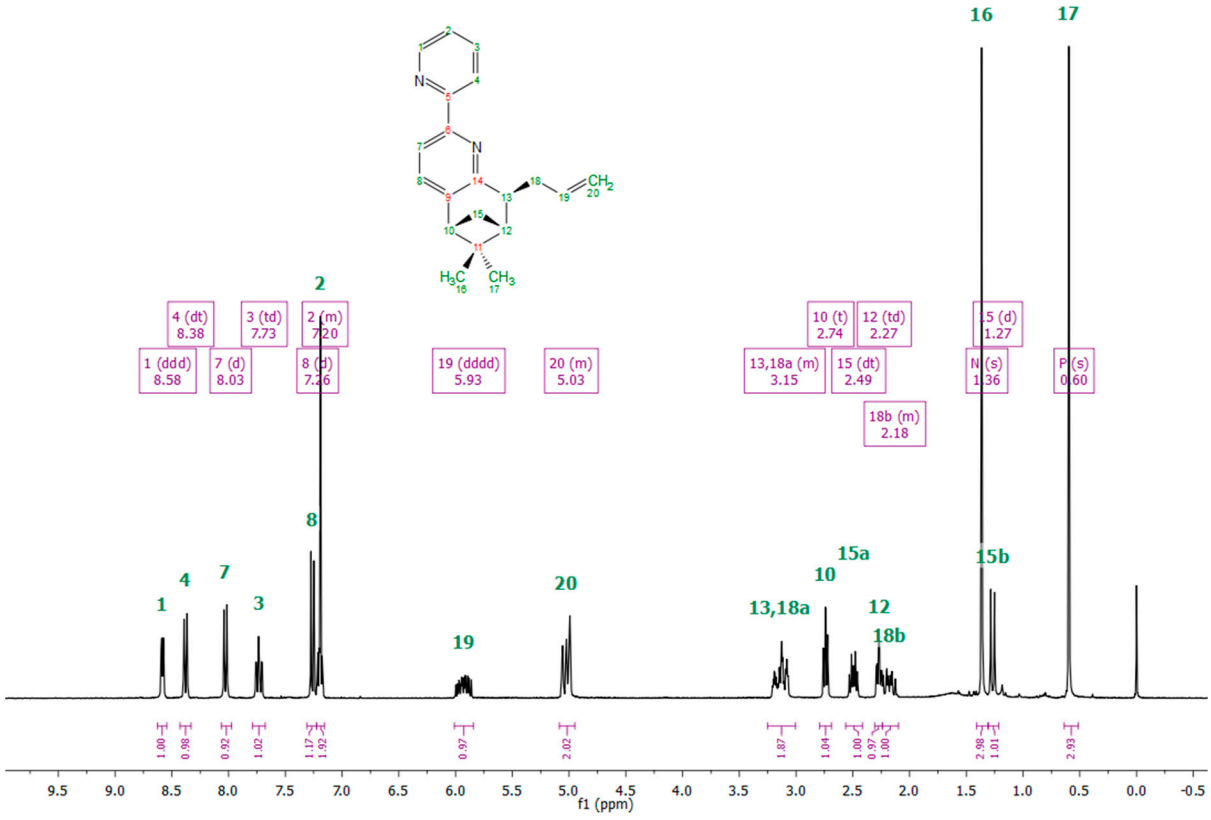


Figure S5. ^{1}H-NMR spectrum of **(-)-PL1.**

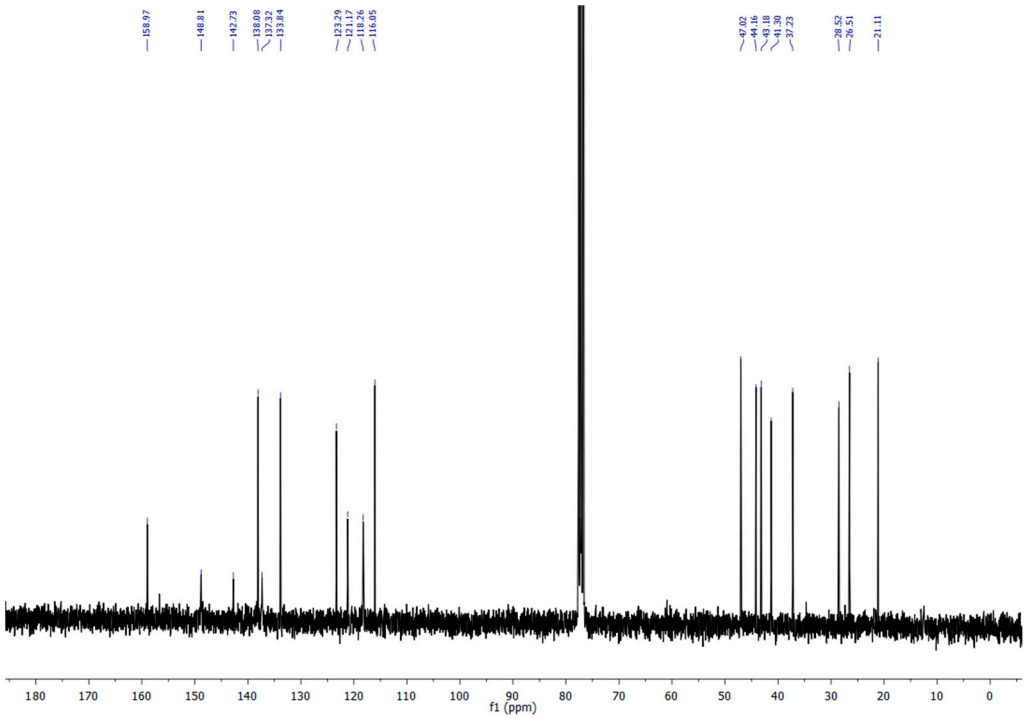


Figure S6. ^{13}C-NMR spectrum of **(-)-PL1.**

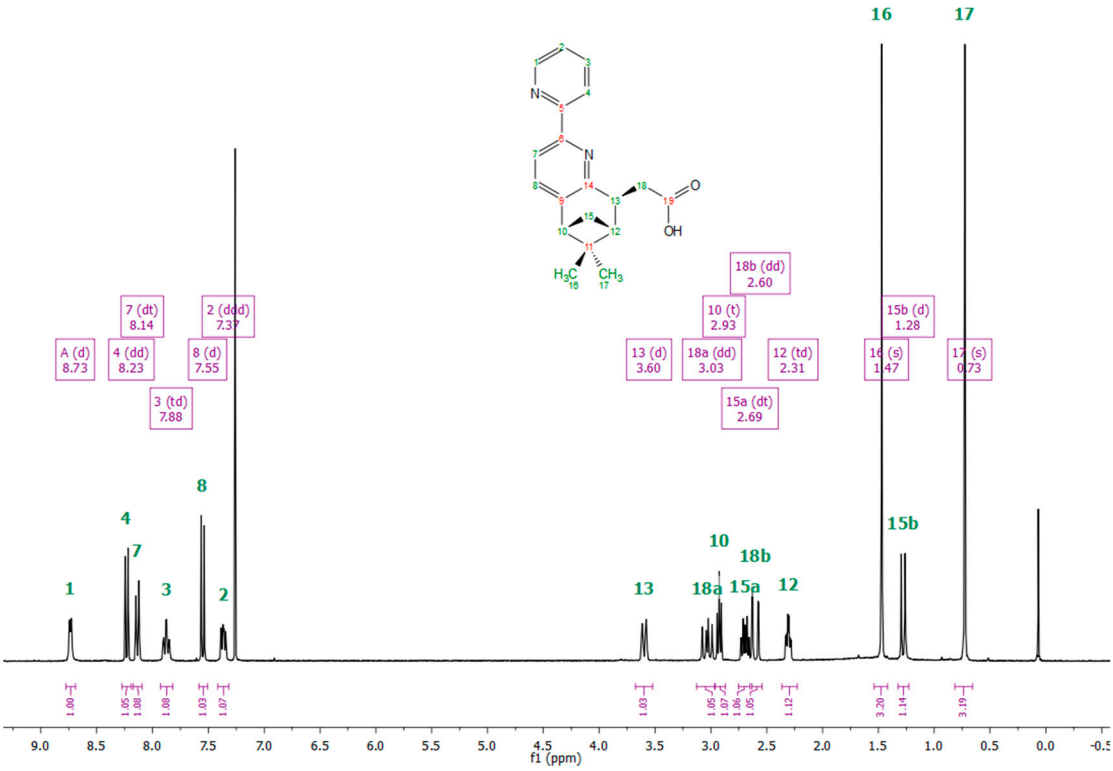


Figure S7. ^{1}H-NMR spectrum of **(-)-HL1.**

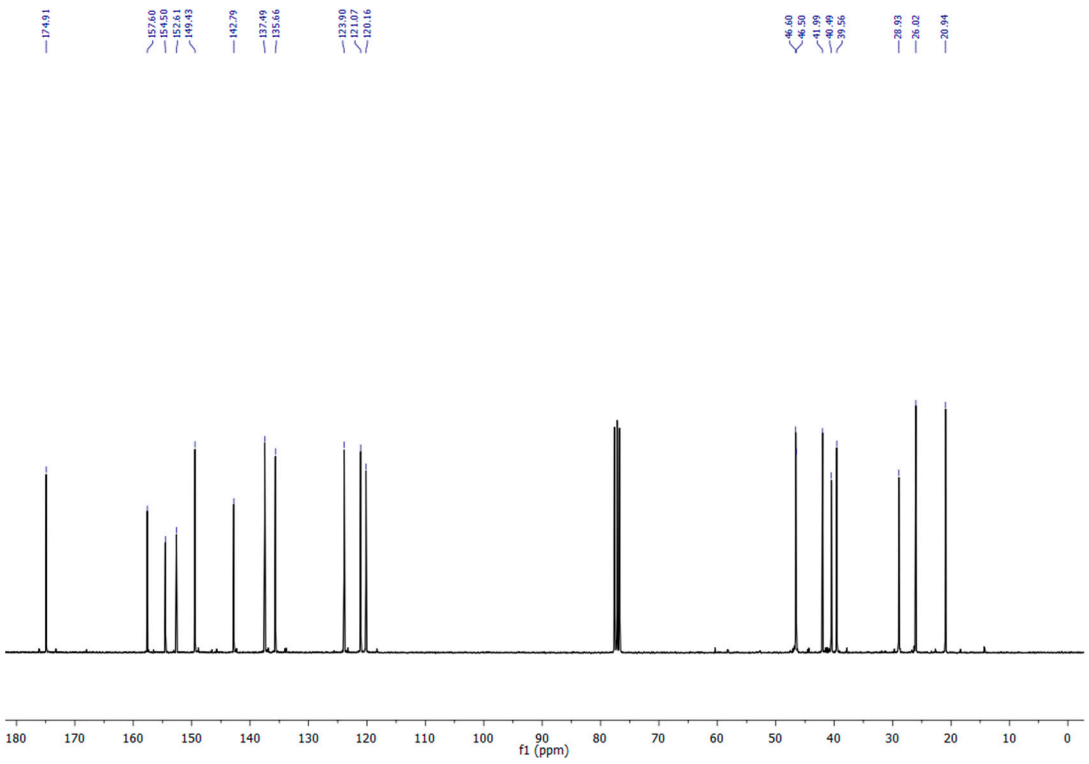


Figure S8. ^{13}C-NMR spectrum of **(-)-HL1.**

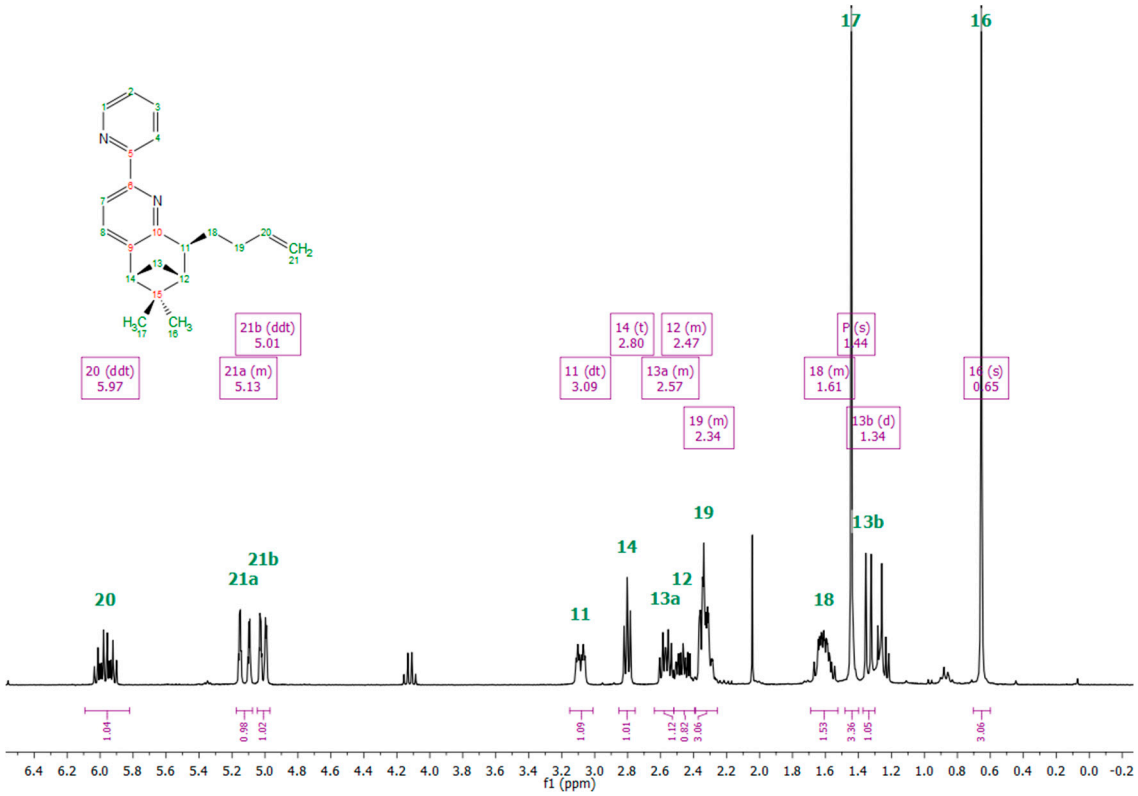


Figure S9. ^{1}H-NMR spectrum of **(-)-PL2.**

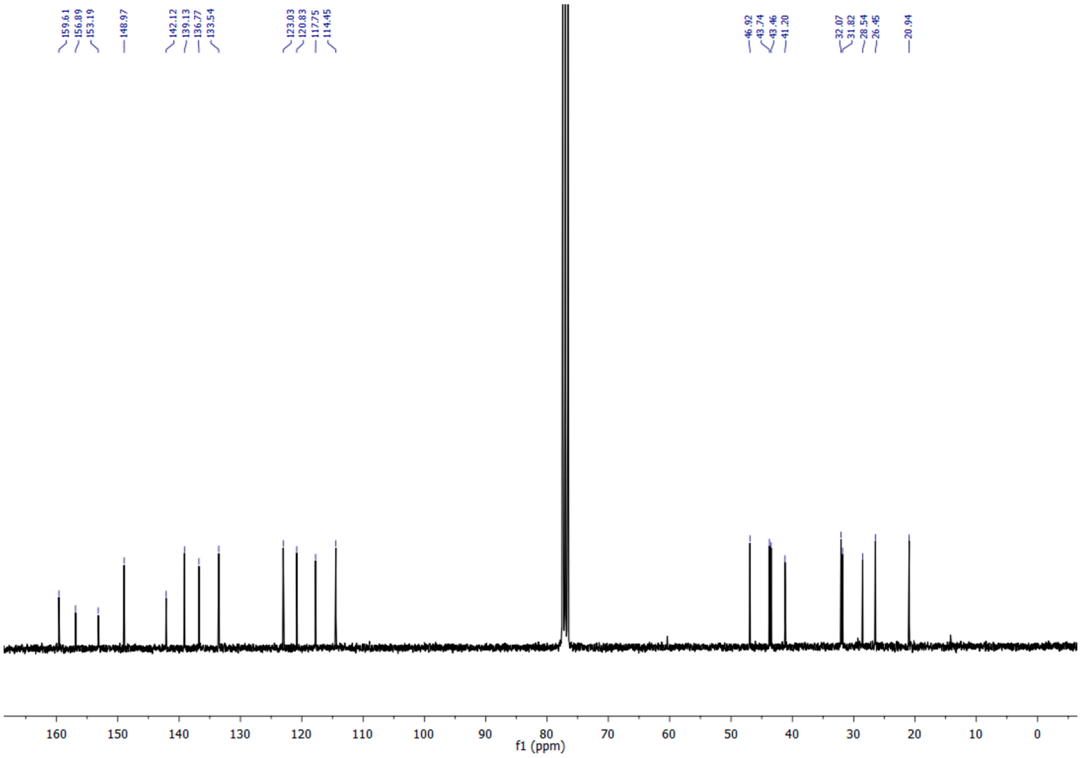


Figure S10. ^{13}C-NMR spectrum of **(-)-PL2.**

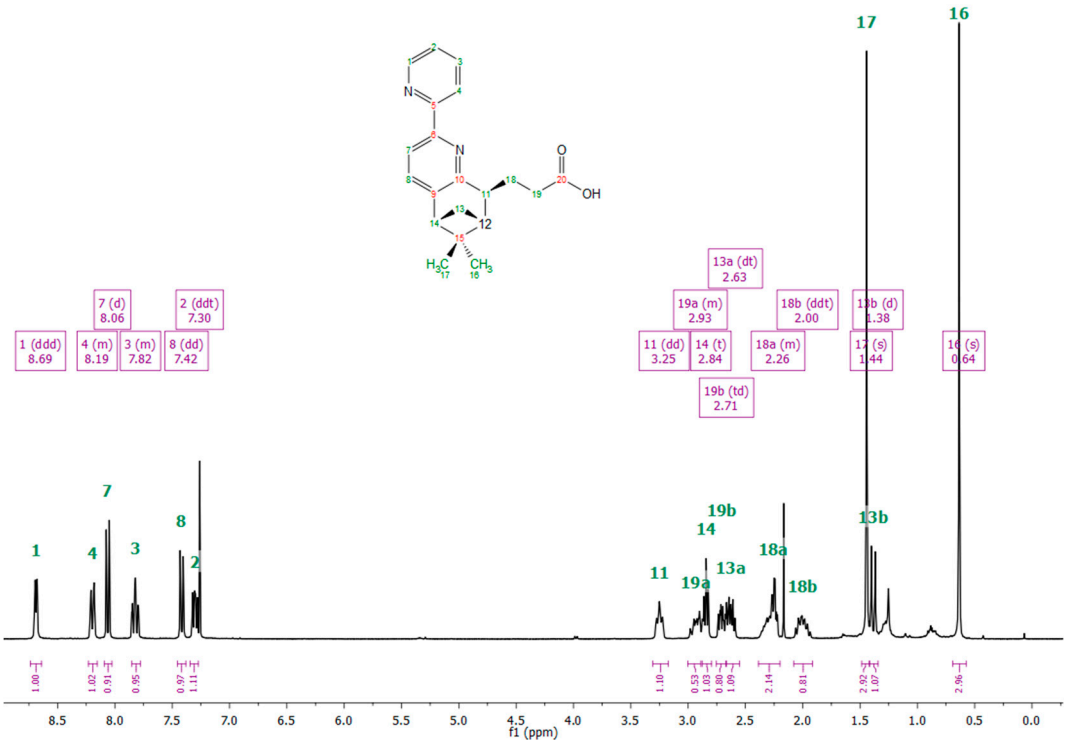


Figure S11. ^{1}H-NMR spectrum of **(-)-HL2.**

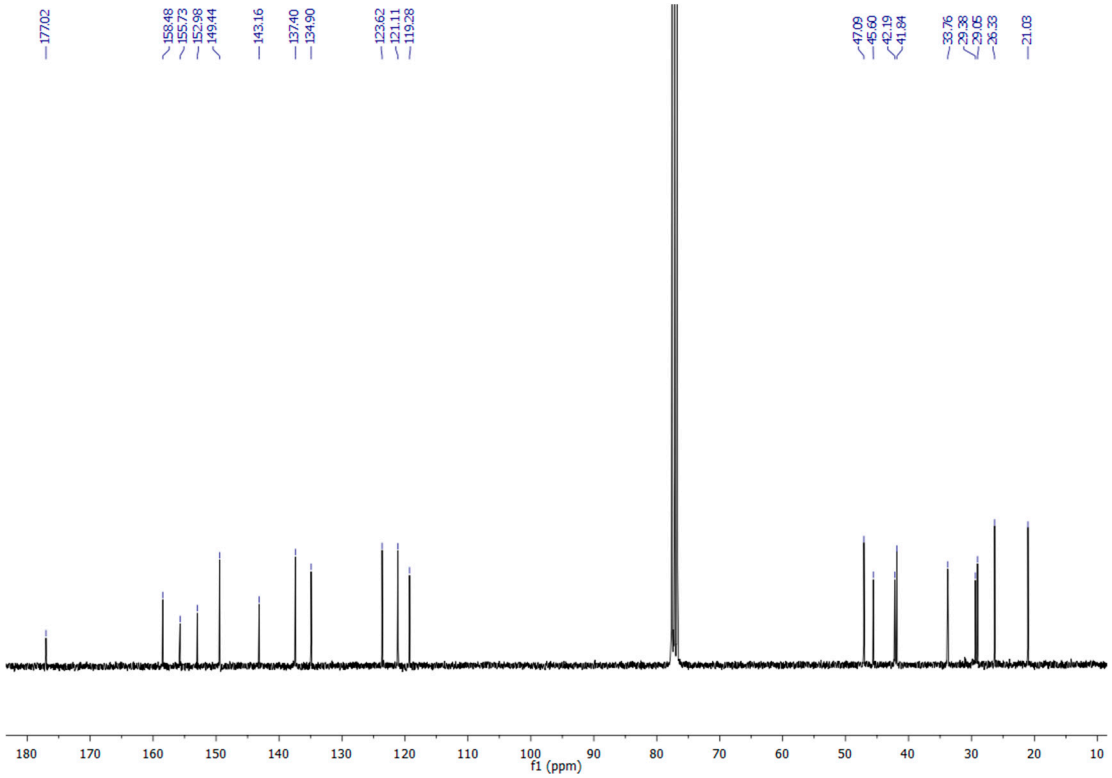


Figure S12. ^{13}C-NMR spectrum of **(-)-HL2.**

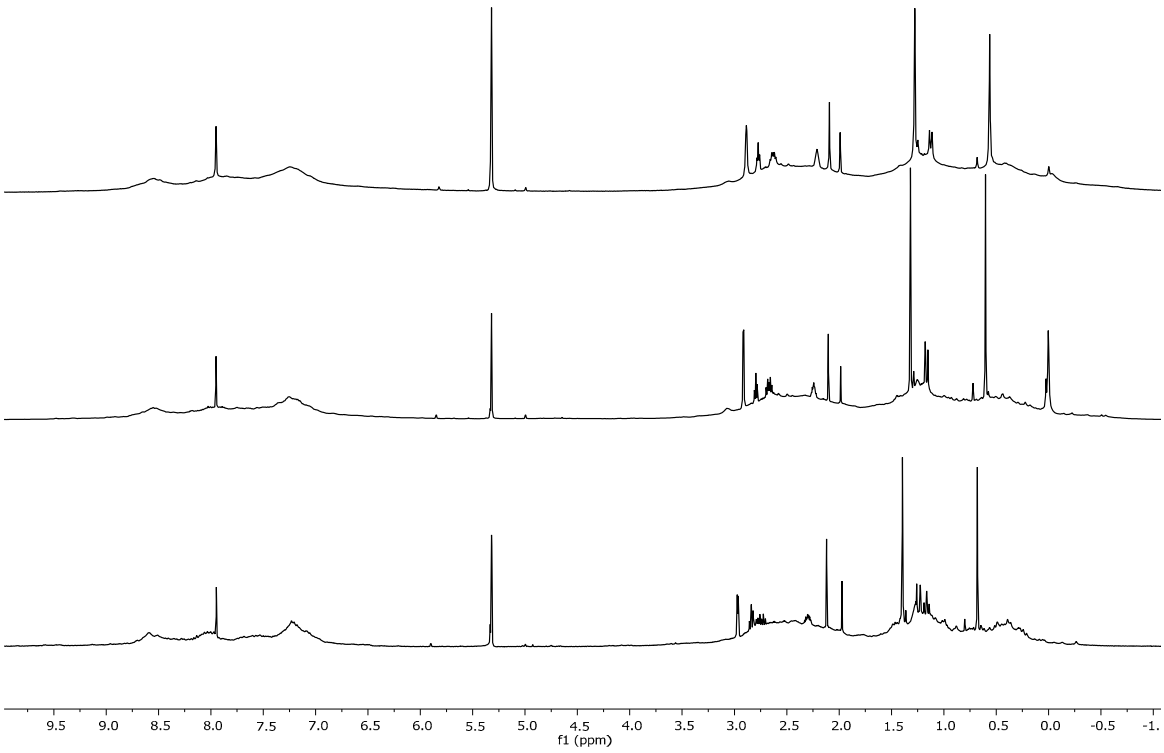


Figure S13. Stacked ^{1}H-NMR spectra of [La{(-)-L2}$_2$]ClO$_4$ in CD_2Cl_2 at 298 K (top), 233 K (middle) and 183 K (bottom).

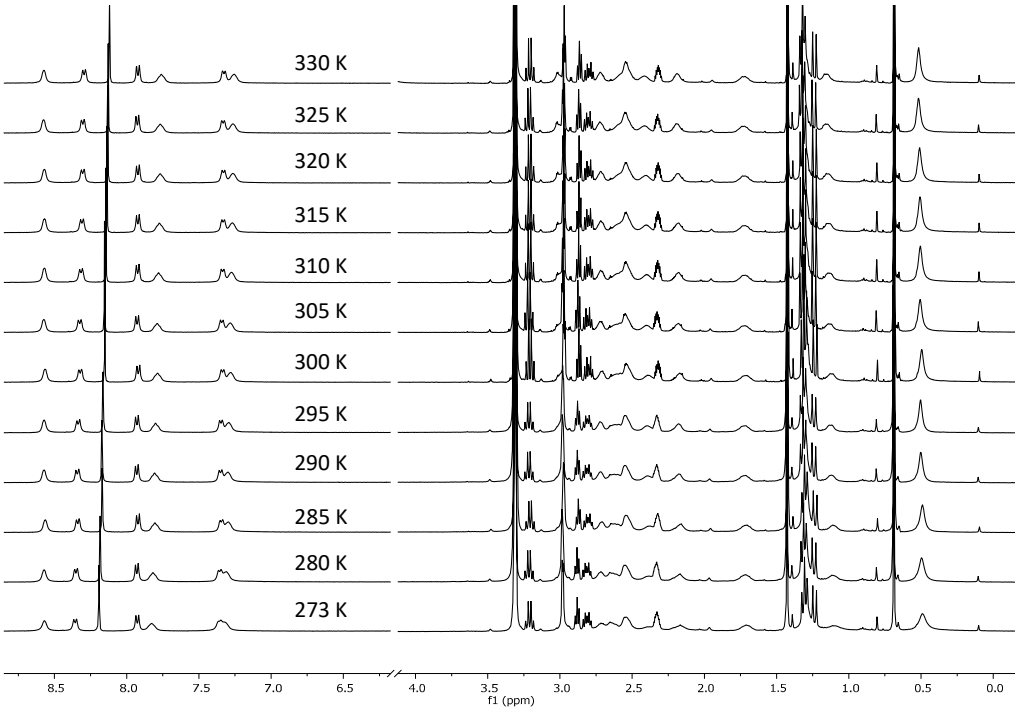


Figure S14. Stacked ^{1}H-NMR spectra of [La{(-)-L1}$_2$]ClO$_4$ in MeOD.

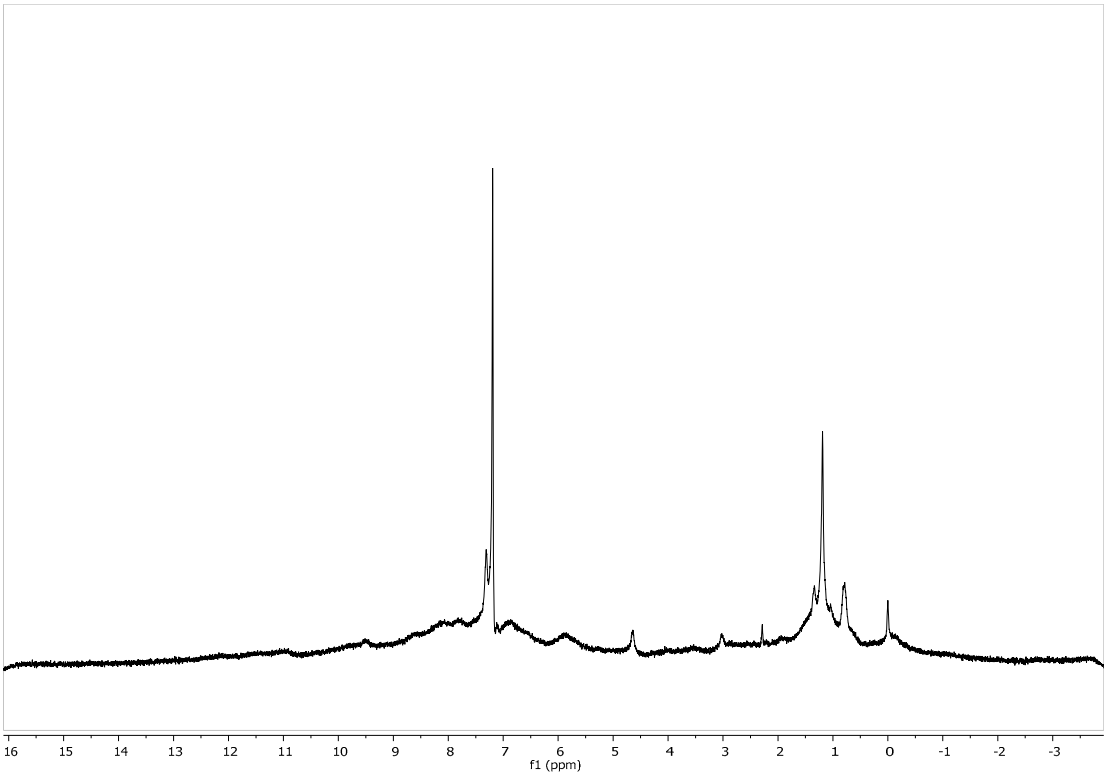


Figure S15. ^{1}H-NMR spectrum of [Eu{(-)-L1}$_2$]ClO$_4$ in CDCl$_3$.

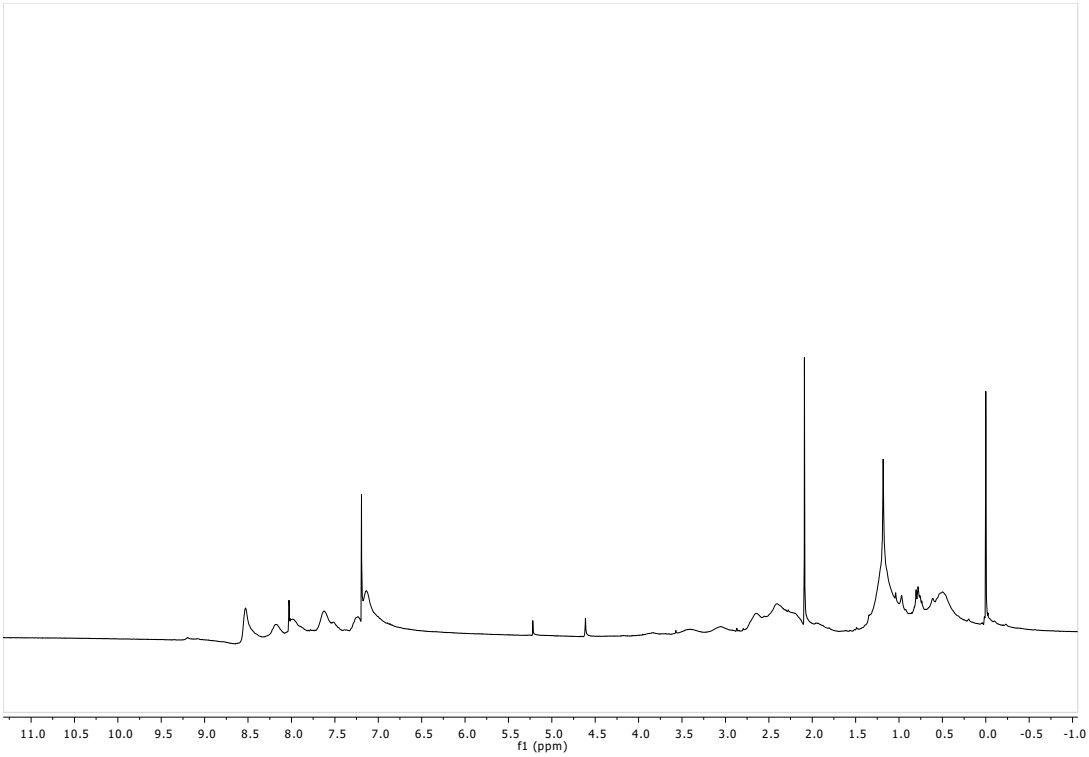


Figure S16. ^{1}H-NMR spectrum of [Lu{(-)-L1}$_2$]ClO$_4$ in CDCl$_3$.

(+)-ESI-MS spectra

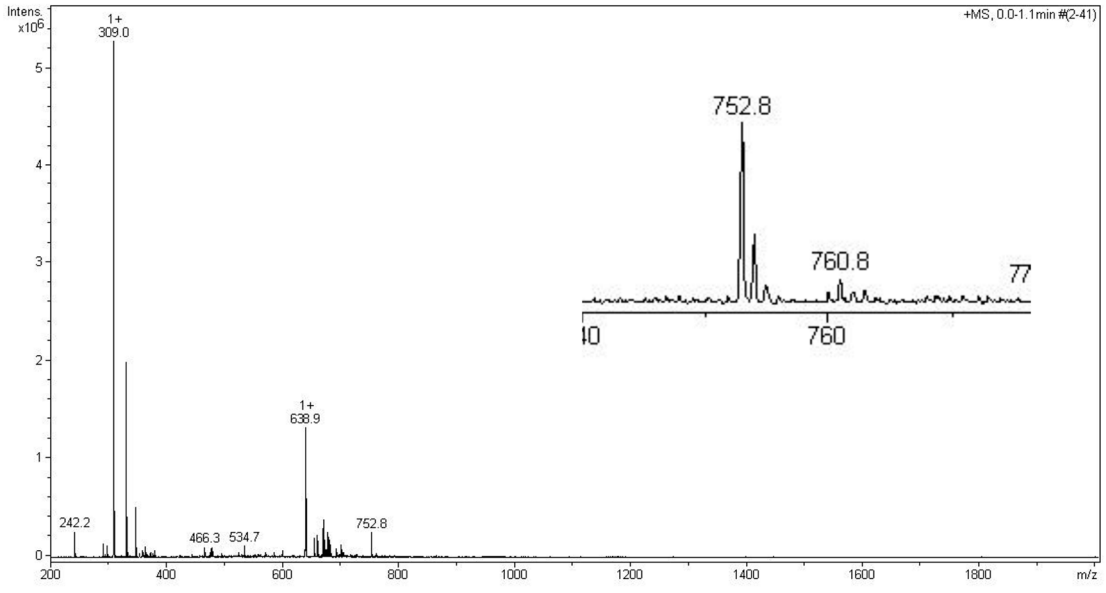


Figure S17. (+)-ESI-MS spectrum of the complex formed at La:L1 = 1:2 ratio.

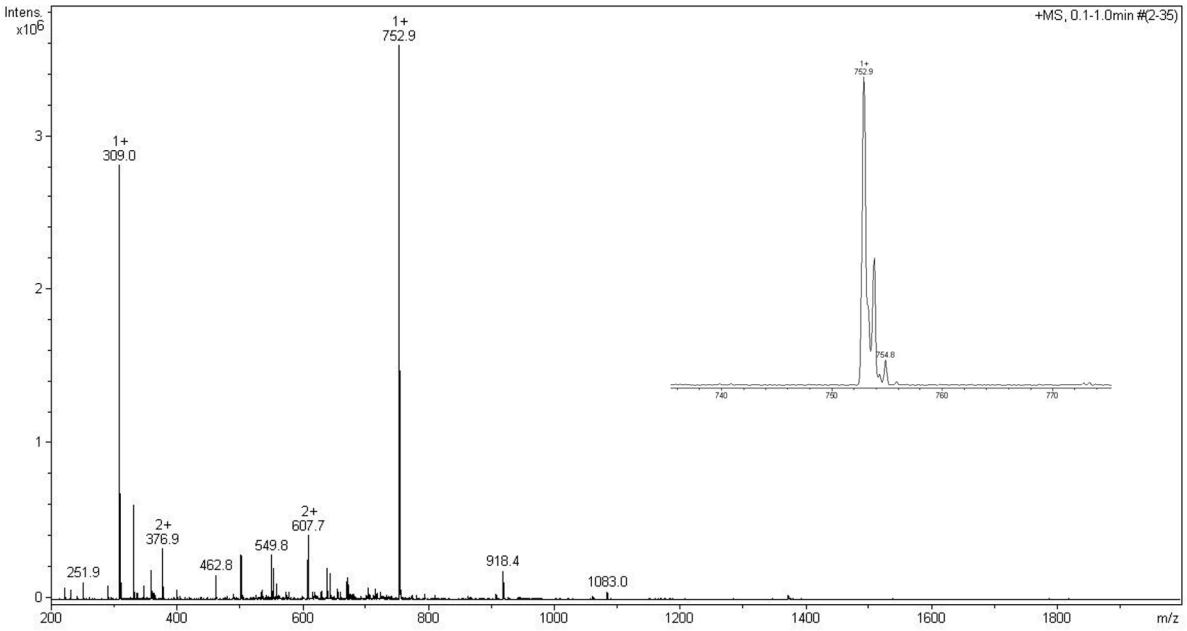


Figure S18. (+)-ESI-MS spectrum of the complex formed at La:L1 = 1:3 ratio.

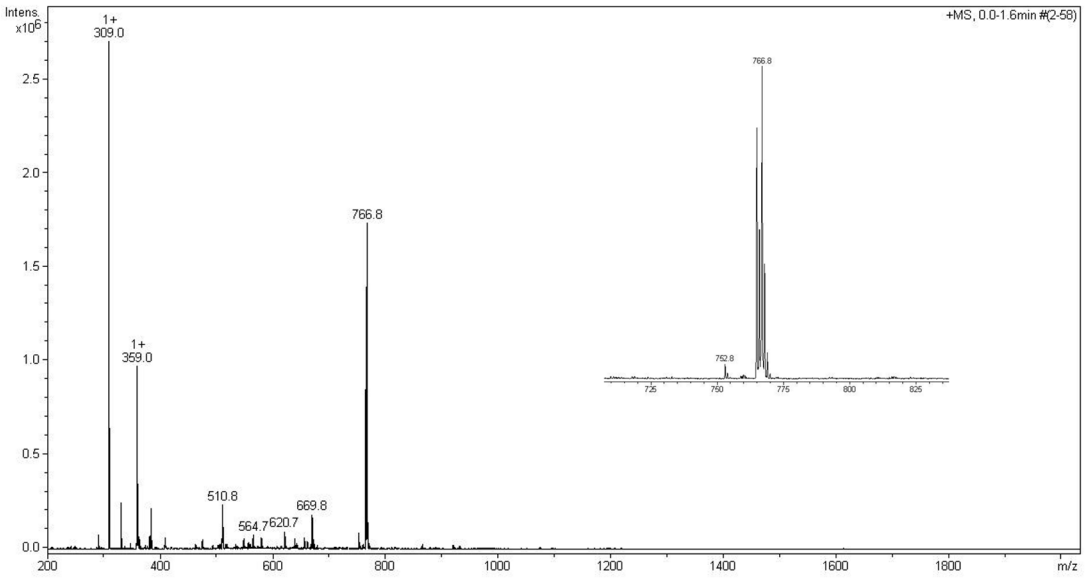


Figure S19. (+)-ESI-MS spectrum of the complex formed at Eu:L1 = 1:2 ratio.

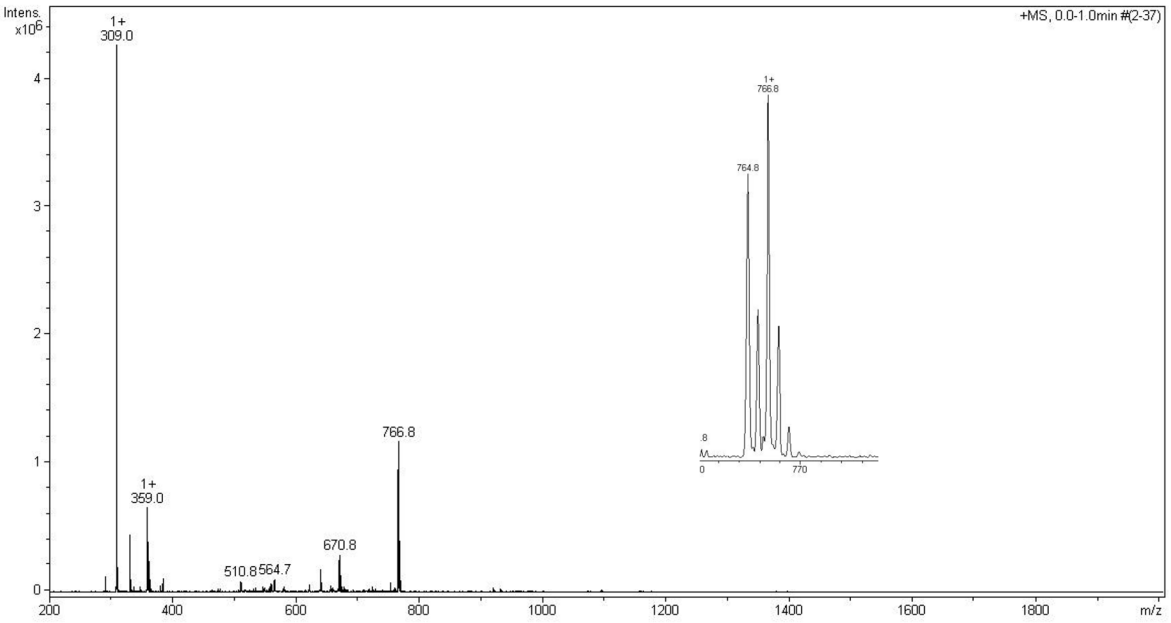


Figure S20. (+)-ESI-MS spectrum of the complex formed at Eu:L1 = 1:3 ratio

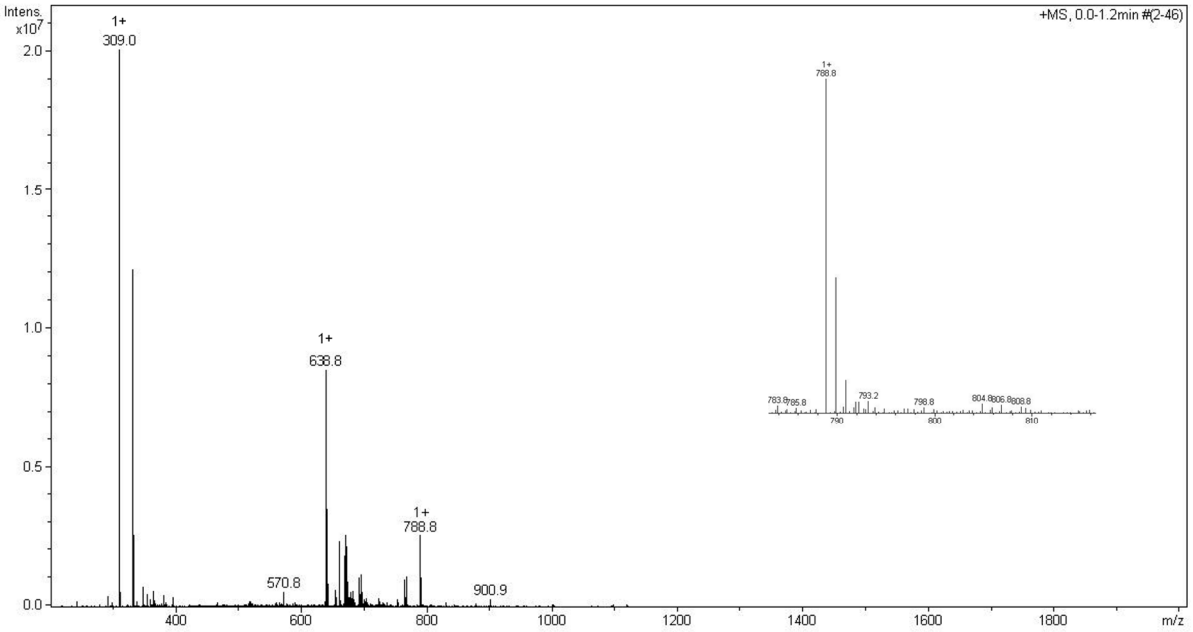


Figure S21. (+)-ESI-MS spectrum of the complex formed at Lu:L1 = 1:2 ratio.

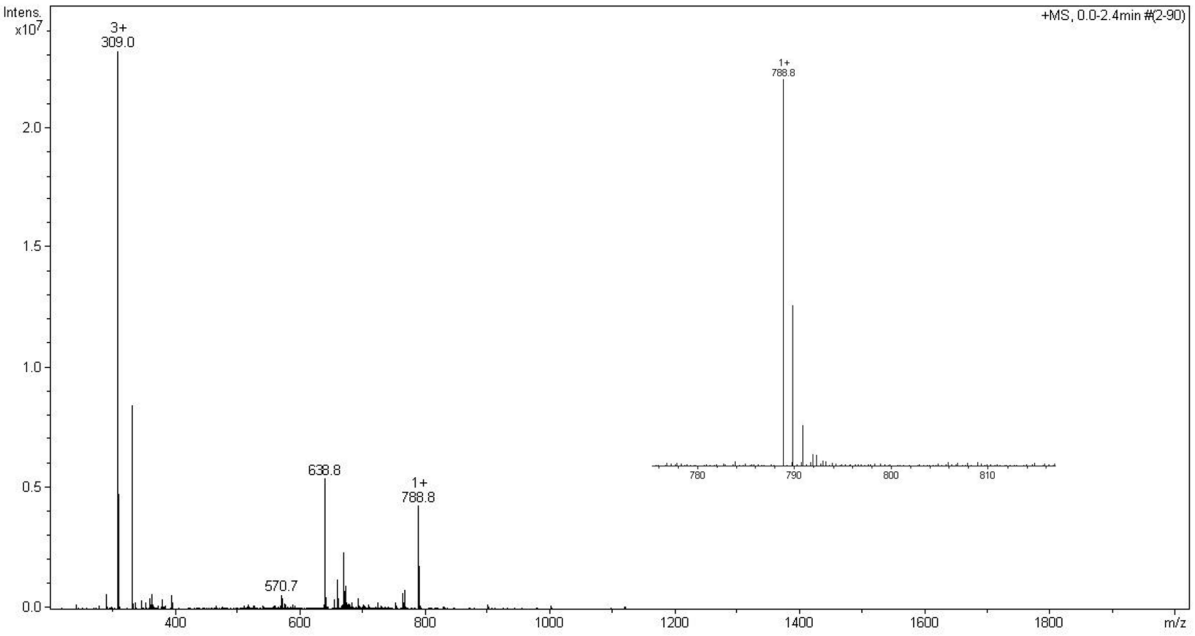


Figure S22. (+)-ESI-MS spectrum of the complex formed at Lu:L1 = 1:3 ratio.

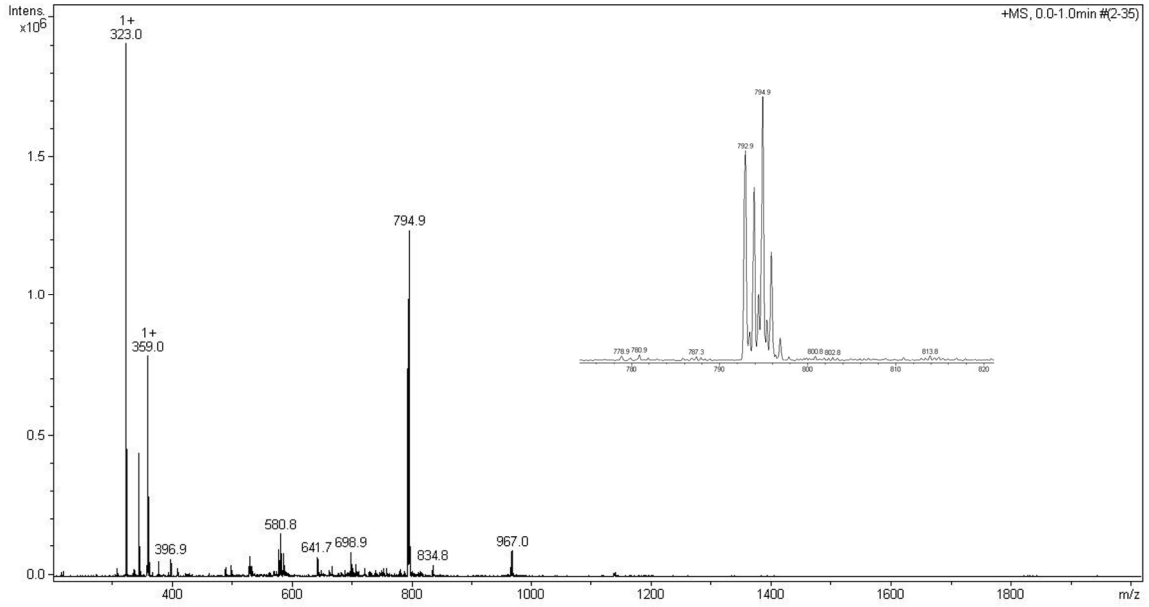


Figure S23. (+)-ESI-MS spectrum of the complex formed at Eu:L2 = 1:2 ratio.

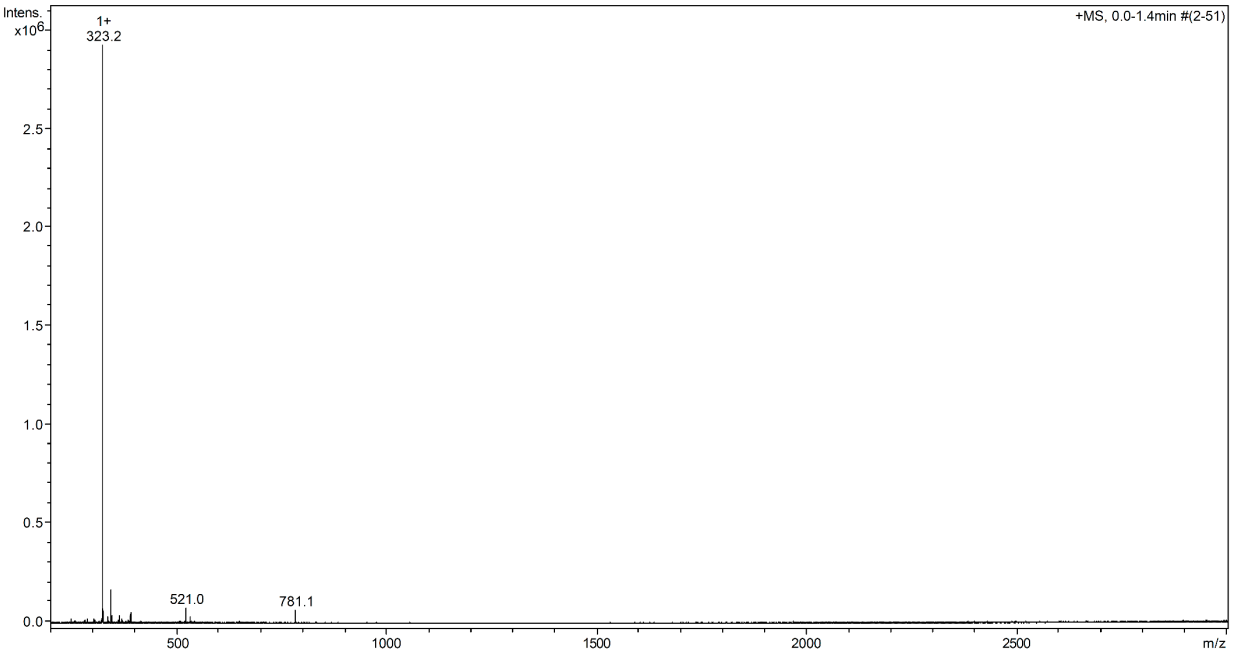


Figure S24. (+)-ESI-MS spectrum of the complex formed at La:L2 = 1:2 ratio.

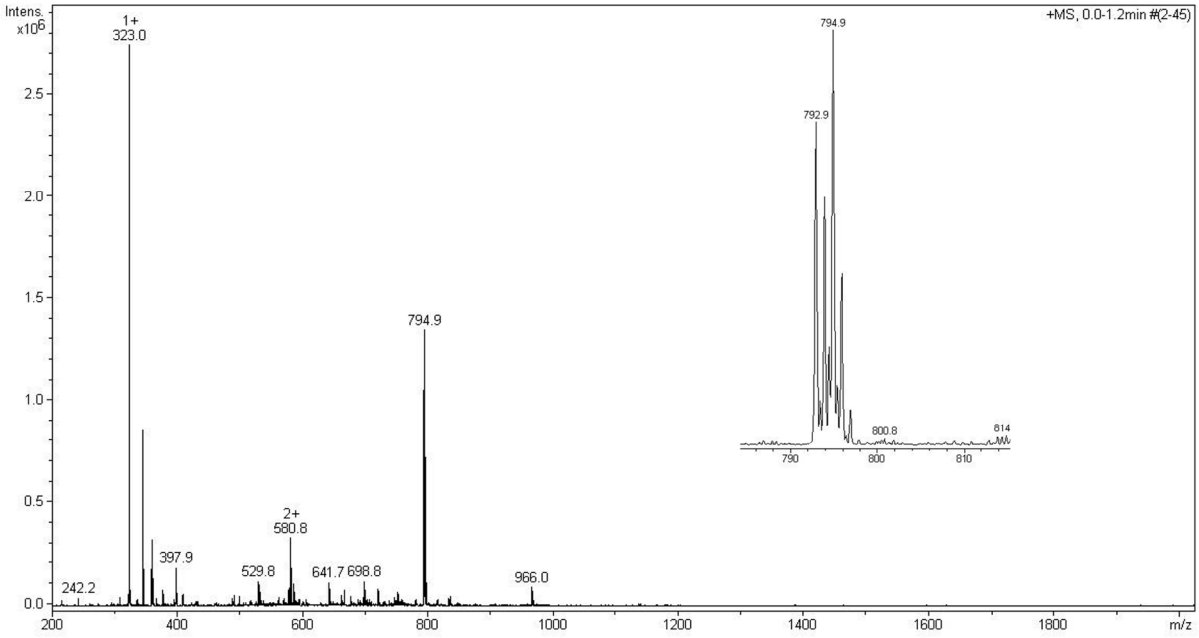


Figure S25. (+)-ESI-MS spectrum of the complex formed at Eu:L2 = 1:3 ratio.

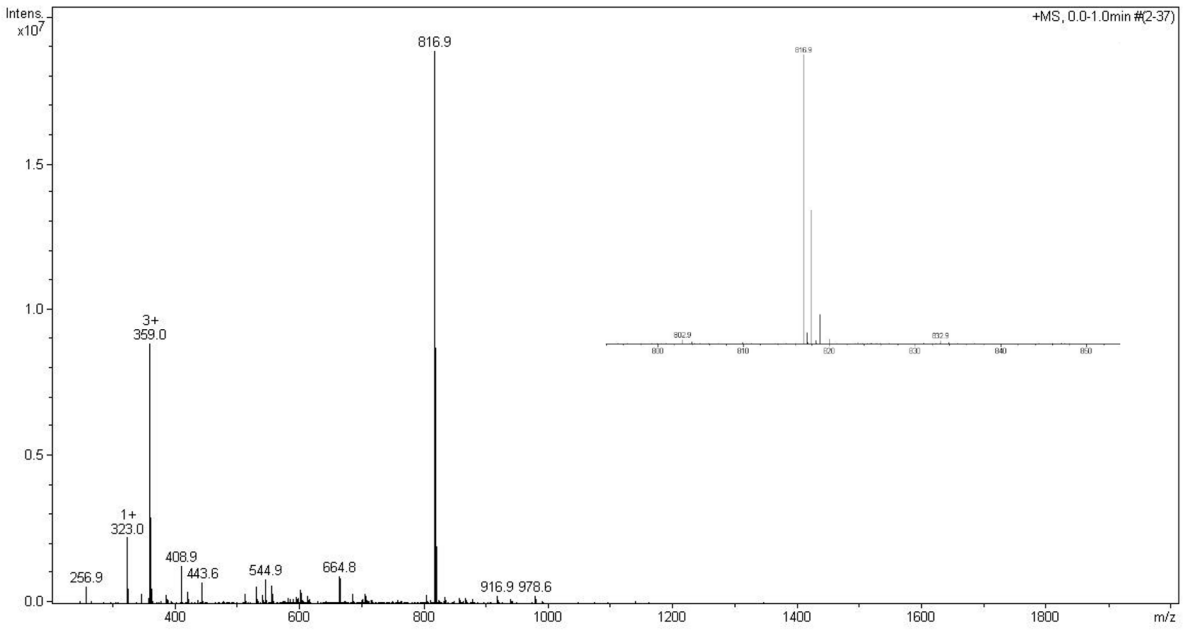


Figure S26. (+)-ESI-MS spectrum of the complex formed at Lu:L2 = 1:2 ratio.

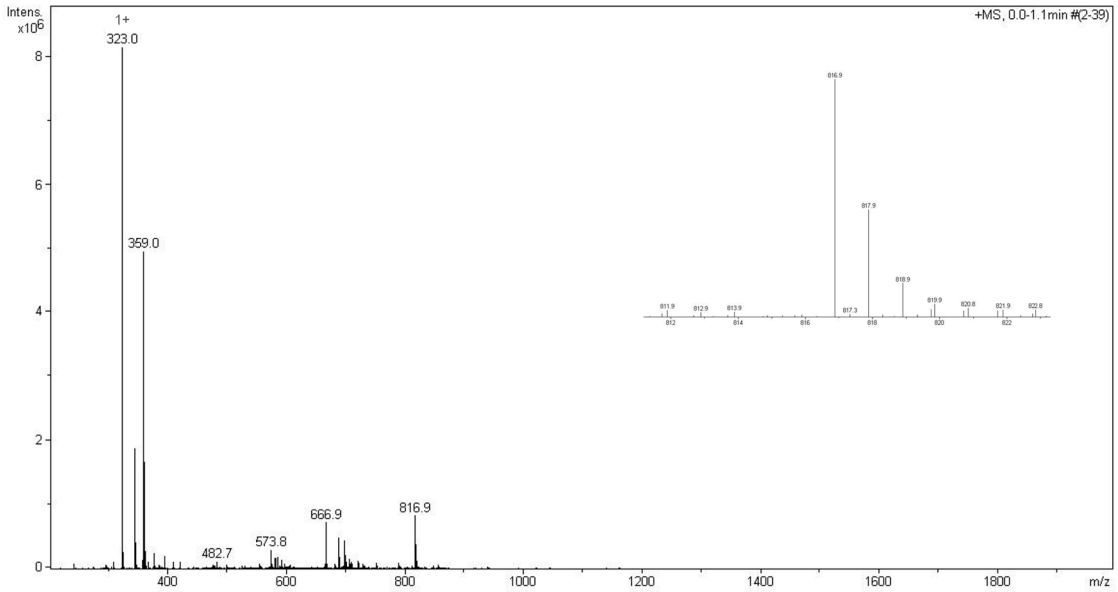
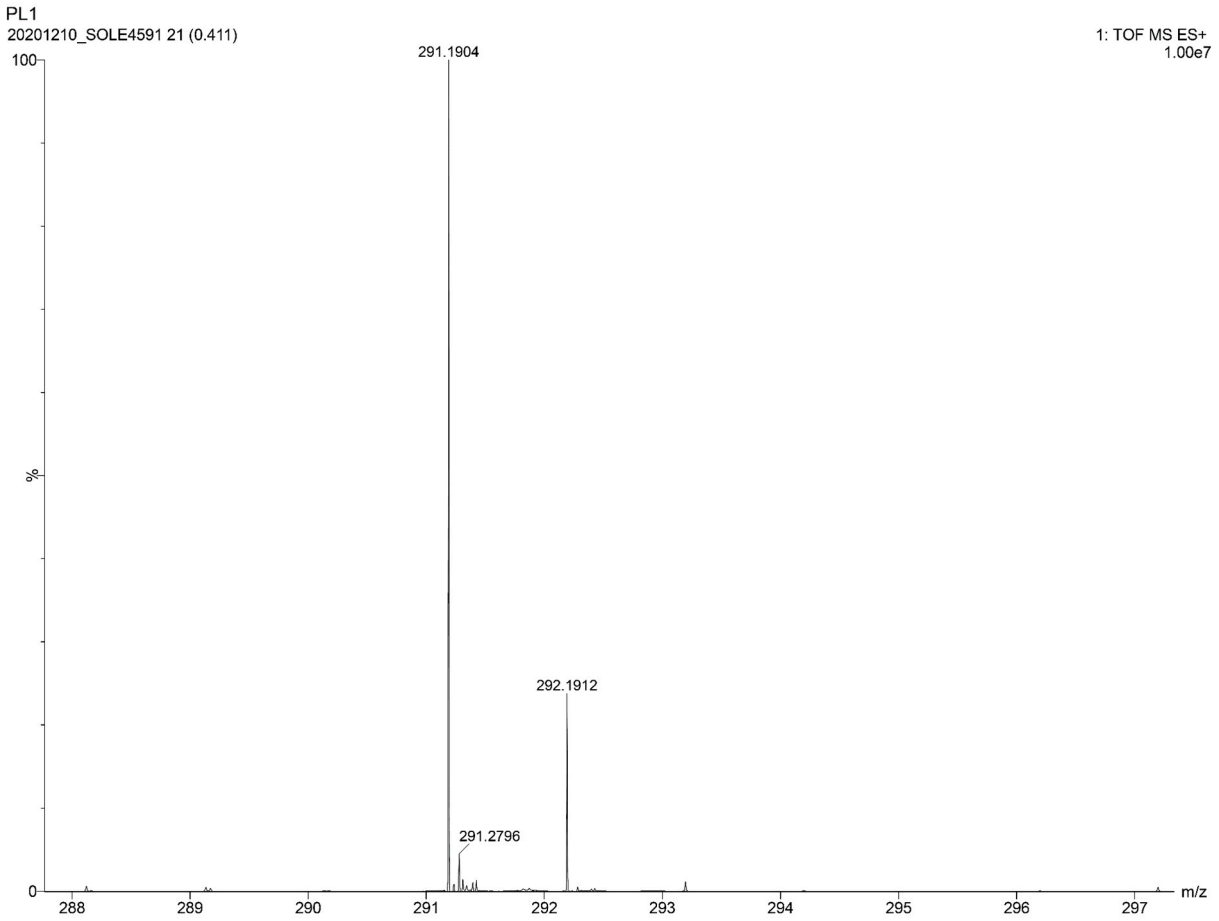


Figure S27. (+)-ESI-MS spectrum of the complex formed at Lu:L2 = 1:3 ratio.

HRMS spectra

(-)-PL1

Mass	Calc. Mass	mDa	PPM	DBE	Formula
291.1904	291.1861	4.3	14.8	10.5	C20 H23 N2
	291.1610	29.4	101.0	11.5	C18 H19 N4
	291.2549	-64.5	-221.5	4.5	C17 H31 N4
	291.2800	-89.6	-307.7	3.5	C19 H35 N2
	291.0922	98.2	337.2	17.5	C21 H11 N2
	291.0671	123.3	423.4	18.5	C19 H7 N4



(-)-PL2

Ion mass = 305.2009120

Charge = +1

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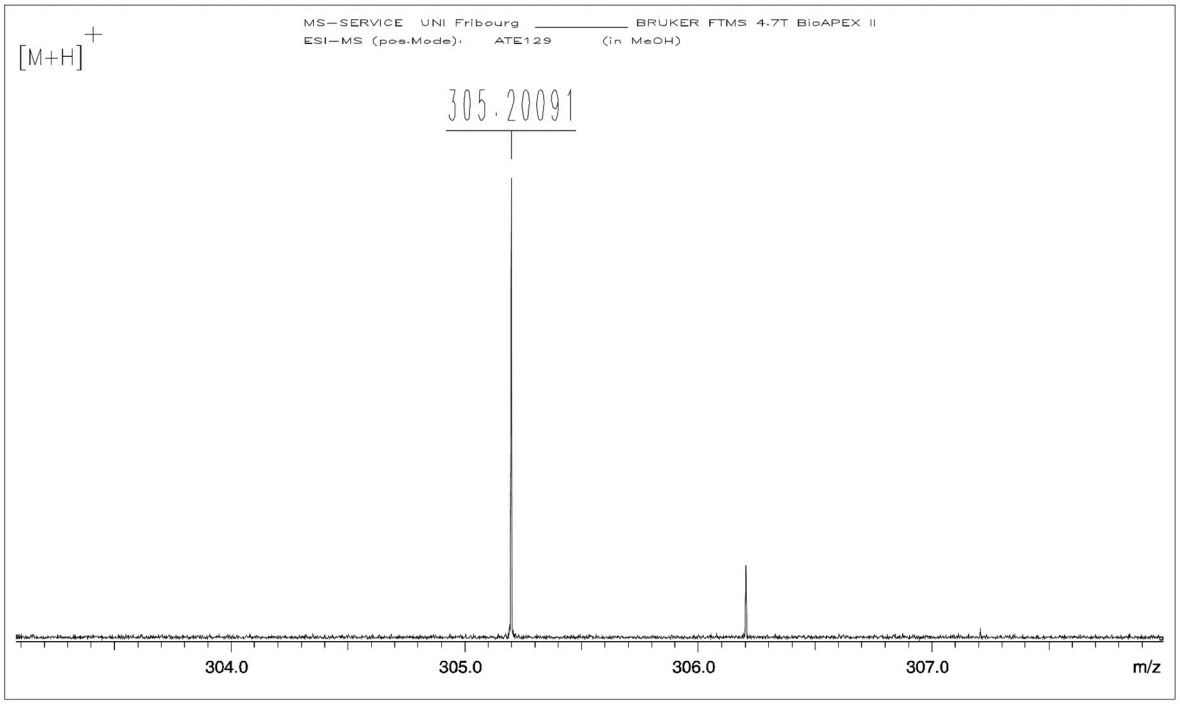
*** Mass Analysis for mass 305.2009120						
1	**21**	**25**	**2**	**305.2012252**	10.5	3.132e-04
2	13	23	9	305.2070932	7.0	6.181e-03
3	12	21	10	305.1945171	7.5	6.395e-03
4	20	23	3	305.1886492	11.0	1.226e-02
5	22	27	1	305.2138013	10.0	1.289e-02
6	14	25	8	305.2196693	6.5	1.876e-02
7	19	21	4	305.1760731	11.5	2.484e-02
8	15	27	7	305.2322453	6.0	3.133e-02
9	18	19	5	305.1634971	12.0	3.741e-02
10	16	29	6	305.2448214	5.5	4.391e-02



(-)-HL1

XMASS Mass Analysis for /Data/UNI_FR/SOLE2553_ESI/2/pdata/1/massanal.res:
XMASS Mass Analysis Constraints

Ion mass = 309.1595820

Charge = +1

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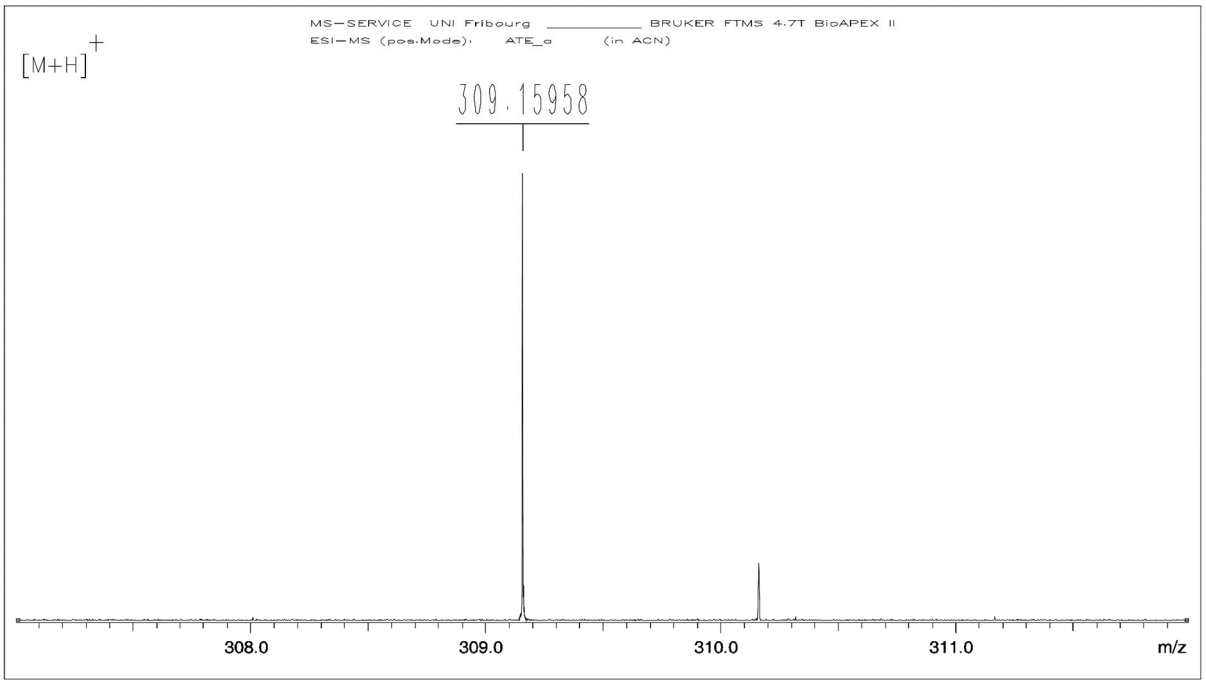
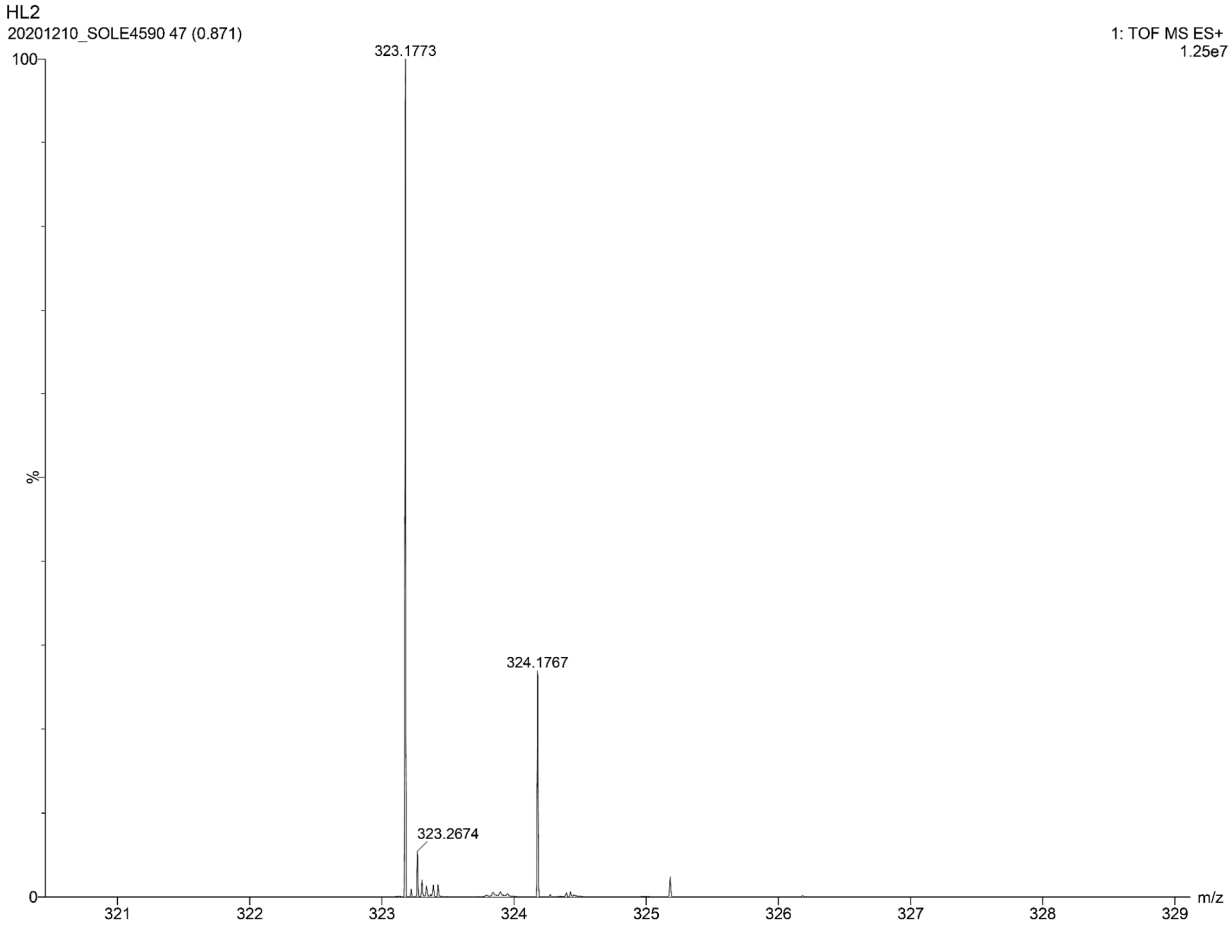
2	5	23	7	8	309.1602622	-2.0	6.802e-04
3	17	19	5	1	309.1584117	11.0	1.170e-03
4	7	25	4	9	309.1616048	-2.5	2.023e-03
5	16	23	1	5	309.1570743	6.0	2.508e-03
6	8	21	8	5	309.1629422	2.5	3.360e-03
7	14	21	4	4	309.1557316	6.5	3.850e-03
8	10	23	5	6	309.1642849	2.0	4.703e-03
9	12	19	7	3	309.1543889	7.0	5.193e-03
10	11	19	9	2	309.1656223	7.0	6.040e-03



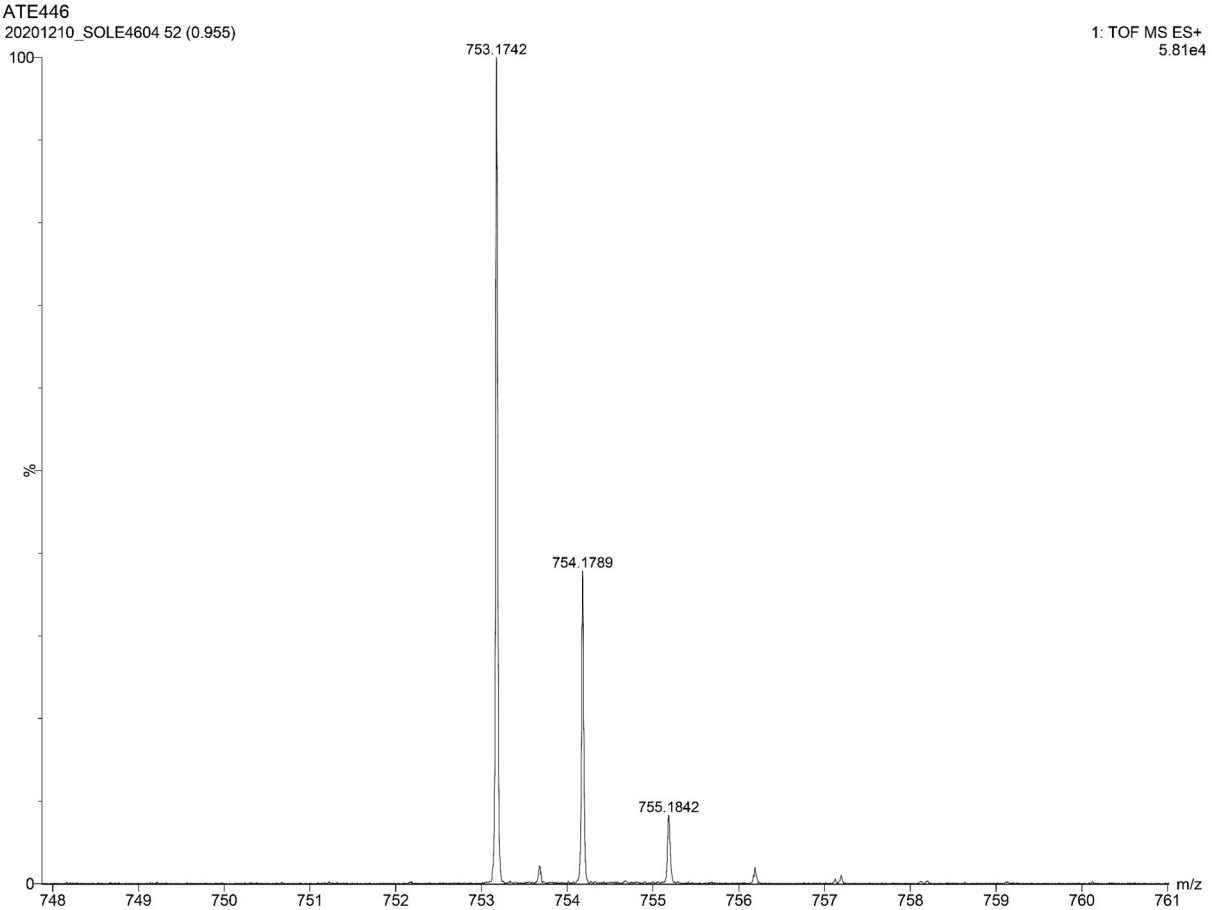
(-)-HL2

Mass	Calc. Mass	mDa	PPM	DBE	Formula
323.1773	323.1760	1.3	4.0	10.5	C20 H23 N2 O2
	323.1818	-4.5	-13.9	1.5	C13 H27 N2 O7
	323.1719	5.4	16.7	6.5	C15 H23 N4 O4
	323.1872	-9.9	-30.6	10.5	C19 H23 N4 O
	323.1931	-15.8	-48.9	1.5	C12 H27 N4 O6
	323.1607	16.6	51.4	6.5	C16 H23 N2 O5
	323.1971	-19.8	-61.3	5.5	C17 H27 N2 O4
	323.1567	20.6	63.7	2.5	C11 H23 N4 O7
	323.1508	26.5	82.0	11.5	C18 H19 N4 O2
	323.2083	-31.0	-95.9	5.5	C16 H27 N4 O3



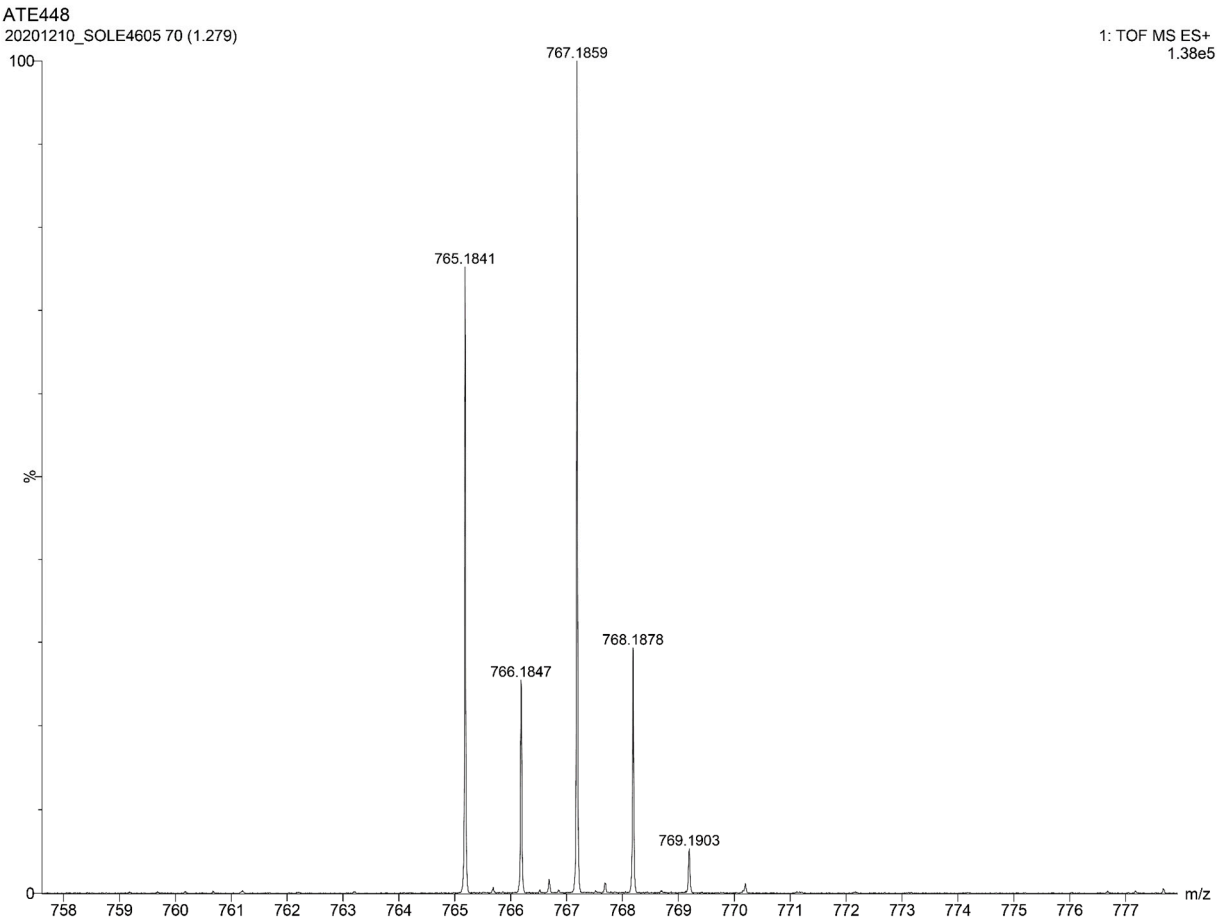
[La{(-)-L1}$_2$](ClO$_4$)

Mass	Calc. Mass	mDa	PPM	DBE	Formula
753.1742	753.1745	-0.3	-0.4	27.5	C41 H34 N4 O2 La
	753.1844	-10.2	-13.5	22.5	C39 H38 N2 O5 La
	753.1633	10.9	14.5	27.5	C42 H34 N2 O3 La
	753.1957	-21.5	-28.5	22.5	C38 H38 N4 O4 La
	753.1997	-25.5	-33.9	26.5	C43 H38 N2 O2 La
	753.1480	26.2	34.8	23.5	C38 H34 N2 O6 La
	753.1422	32.0	42.5	32.5	C45 H30 N2 O La
	753.1381	36.1	47.9	28.5	C40 H30 N4 O3 La
	753.2109	-36.7	-48.7	26.5	C42 H38 N4 O La
	753.2208	-46.6	-61.9	21.5	C40 H42 N2 O4 La



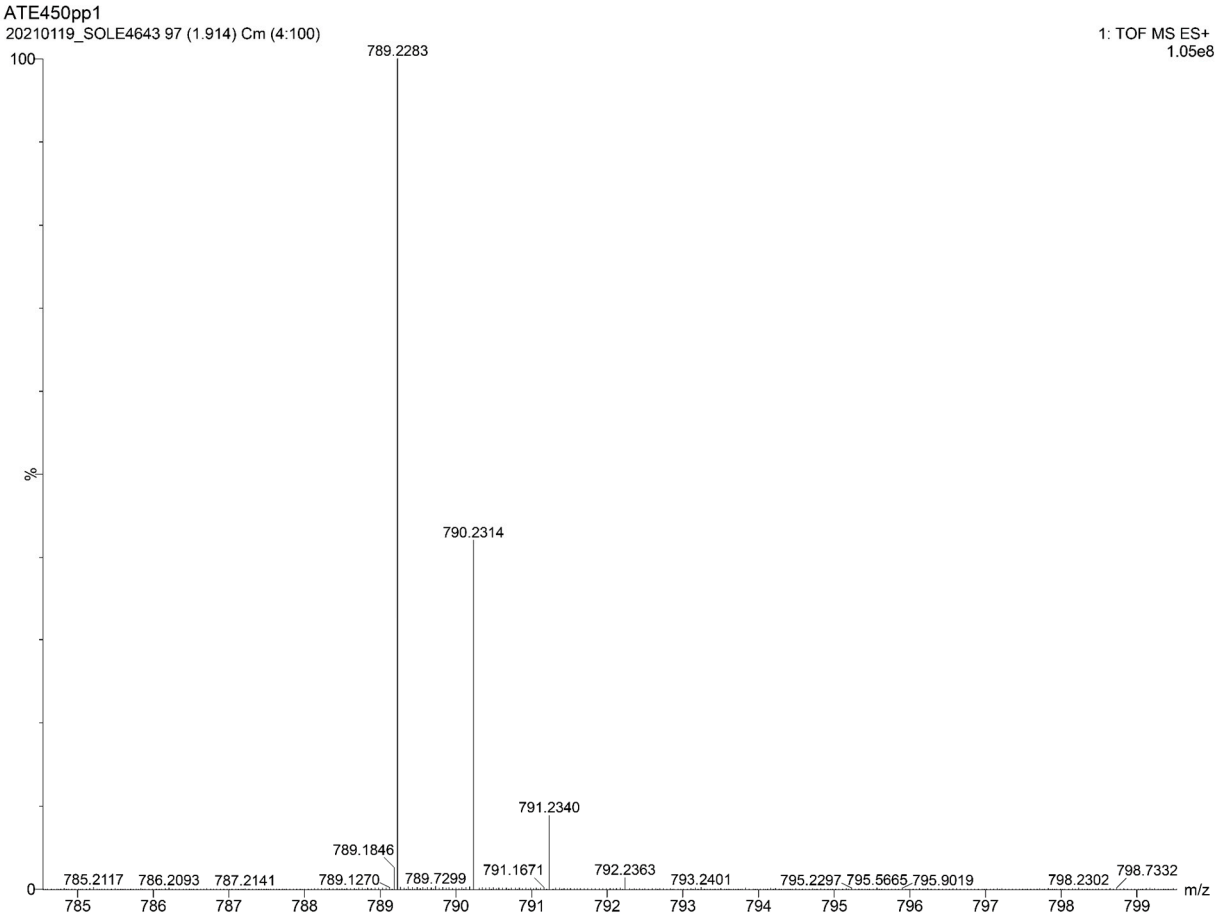
[Eu{(-)-L1}$_2$](ClO$_4$)

Mass	Calc. Mass	mDa	PPM	DBE	Formula
765.1841	765.1880	-3.9	-5.1	27.5	C41 H34 N4 O2 151Eu
	765.1768	7.3	9.5	27.5	C42 H34 N2 O3 151Eu
	765.1979	-13.8	-18.0	22.5	C39 H38 N2 O5 151Eu
	765.1615	22.6	29.5	23.5	C38 H34 N2 O6 151Eu
	765.2092	-25.1	-32.8	22.5	C38 H38 N4 O4 151Eu
	765.1557	28.4	37.1	32.5	C45 H30 N2 O 151Eu
	765.2132	-29.1	-38.0	26.5	C43 H38 N2 O2 151Eu
	765.1516	32.5	42.5	28.5	C40 H30 N4 O3 151Eu
	765.2244	-40.3	-52.7	26.5	C42 H38 N4 O 151Eu
	765.1404	43.7	57.1	28.5	C41 H30 N2 O4 151Eu



[Lu{(-)-L1}$_2$](ClO$_4$)

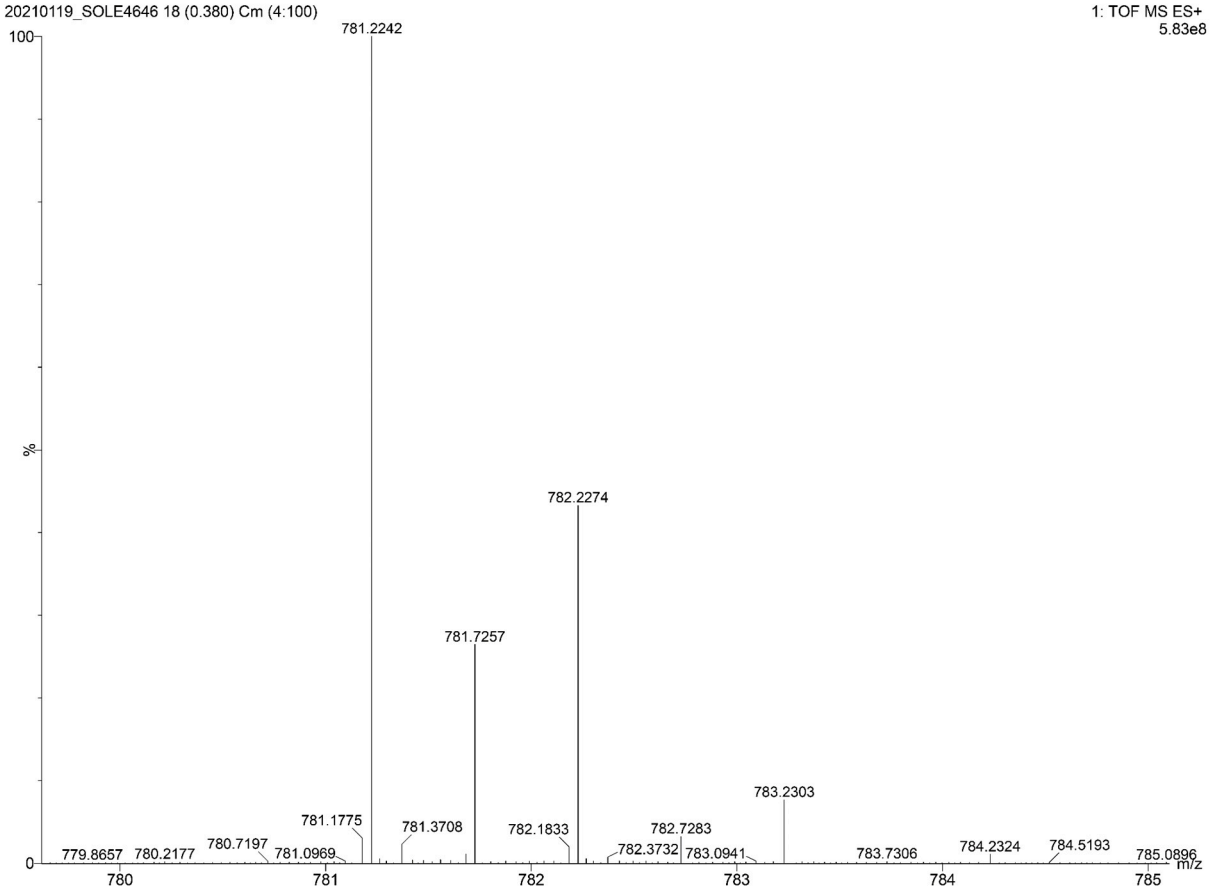
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
789.2283	789.2301	-1.8	-2.3	22.5	1434.0	4.164	1.55	C38 H38 N4 O4 Lu
	789.2247	3.6	4.6	13.5	1432.0	2.195	11.14	C32 H42 N2 O10 Lu
	789.2341	-5.8	-7.3	26.5	1436.6	6.843	0.11	C43 H38 N2 O2 Lu
	789.2359	-7.6	-9.6	13.5	1432.0	2.243	10.61	C31 H42 N4 O9 Lu
	789.2188	9.5	12.0	22.5	1434.6	4.793	0.83	C39 H38 N2 O5 Lu
	789.2400	-11.7	-14.8	17.5	1432.3	2.528	7.98	C36 H42 N2 O7 Lu
	789.2148	13.5	17.1	18.5	1430.6	0.819	44.08	C34 H38 N4 O7 Lu
	789.2453	-17.0	-21.5	26.5	1436.2	6.392	0.17	C42 H38 N4 O Lu
	789.2089	19.4	24.6	27.5	1435.8	5.990	0.25	C41 H34 N4 O2 Lu
	789.2512	-22.9	-29.0	17.5	1431.2	1.457	23.29	C35 H42 N4 O6 Lu



[La{(-)-L2}$_2$](ClO$_4$)

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
781.2243	781.2270	-2.7	-3.5	22.5	1755.2	3.667	2.55	C40 H42 N4 O4 La
	781.2310	-6.7	-8.6	26.5	1758.6	7.094	0.08	C45 H42 N2 O2 La
	781.2328	-8.5	-10.9	13.5	1758.1	6.621	0.13	C33 H46 N4 O9 La
	781.2157	8.6	11.0	22.5	1755.7	4.192	1.51	C41 H42 N2 O5 La
	781.2117	12.6	16.1	18.5	1755.4	3.866	2.09	C36 H42 N4 O7 La
	781.2369	-12.6	-16.1	17.5	1751.9	0.333	71.66	C38 H46 N2 O7 La
	781.2422	-17.9	-22.9	26.5	1758.4	6.913	0.10	C44 H42 N4 O La
	781.2058	18.5	23.7	27.5	1757.9	6.371	0.17	C43 H38 N4 O2 La
	781.2481	-23.8	-30.5	17.5	1753.2	1.718	17.95	C37 H46 N4 O6 La
	781.2005	23.8	30.5	18.5	1754.8	3.284	3.75	C37 H42 N2 O8 La

ATE169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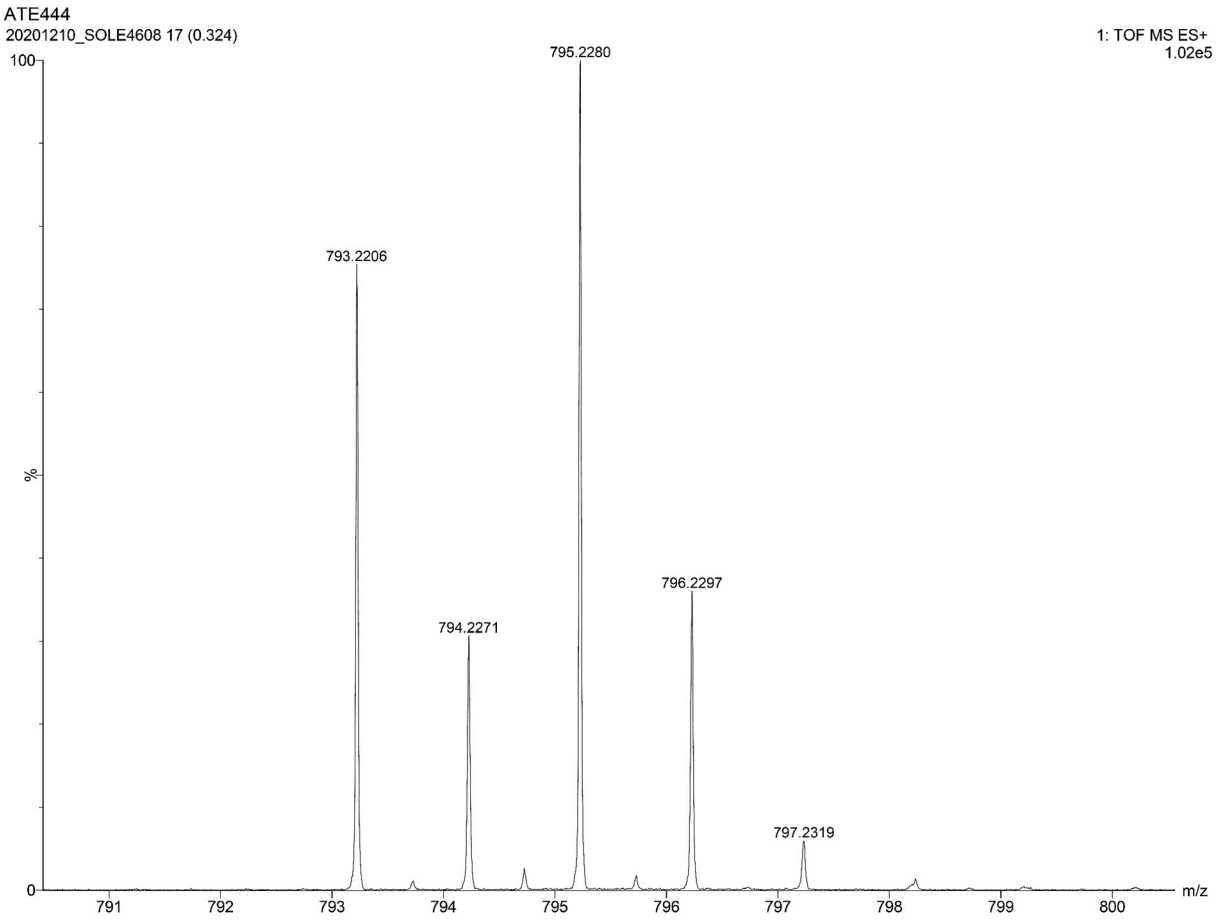
784.5193
785.0896
m/z
780
781
782
783
784
785

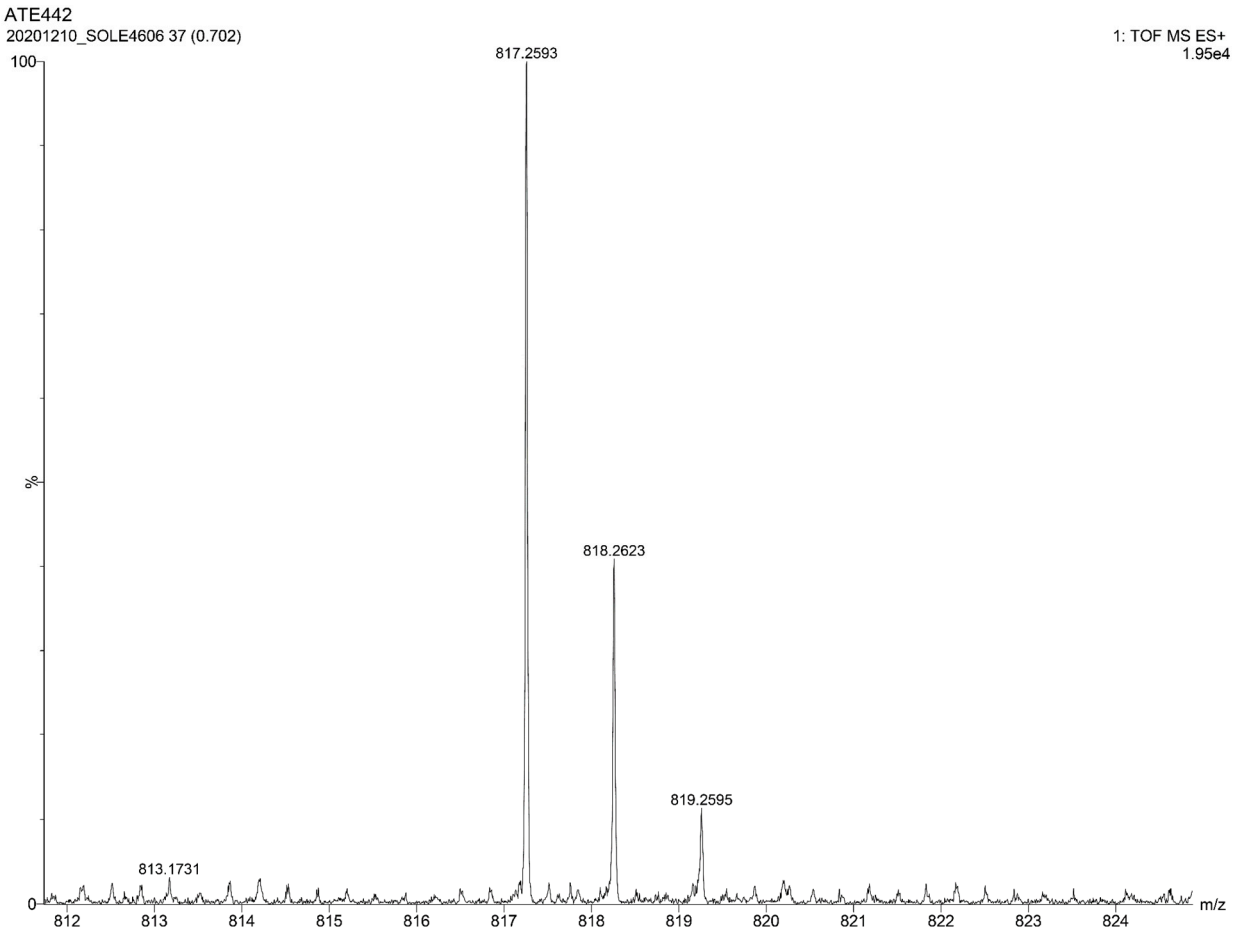
[Eu{(-)-L2}$_2$](ClO$_4$)

Mass	Calc. Mass	mDa	PPM	DBE	Formula
793.2206	793.2193	1.3	1.6	27.5	C43 H38 N4 O2 151Eu
	793.2292	-8.6	-10.8	22.5	C41 H42 N2 O5 151Eu
	793.2081	12.5	15.8	27.5	C44 H38 N2 O3 151Eu
	793.2041	16.5	20.8	23.5	C39 H38 N4 O5 151Eu
	793.2405	-19.9	-25.1	22.5	C40 H42 N4 O4 151Eu
	793.2445	-23.9	-30.1	26.5	C45 H42 N2 O2 151Eu
	793.1928	27.8	35.0	23.5	C40 H38 N2 O6 151Eu
	793.2503	-29.7	-37.4	17.5	C38 H46 N2 O7 151Eu
	793.1870	33.6	42.4	32.5	C47 H34 N2 O 151Eu
	793.2557	-35.1	-44.2	26.5	C44 H42 N4 O 151Eu



[Lu{(-)-L2}$_2$](ClO$_4$)

Mass	Calc. Mass	mDa	PPM	DBE	Formula
817.2593	817.2614	-2.1	-2.6	22.5	C40 H42 N4 O4 Lu
	817.2654	-6.1	-7.5	26.5	C45 H42 N2 O2 Lu
	817.2501	9.2	11.3	22.5	C41 H42 N2 O5 Lu
	817.2713	-12.0	-14.7	17.5	C38 H46 N2 O7 Lu
	817.2766	-17.3	-21.2	26.5	C44 H42 N4 O Lu
	817.2402	19.1	23.4	27.5	C43 H38 N4 O2 Lu
	817.2865	-27.2	-33.3	21.5	C42 H46 N2 O4 Lu
	817.2290	30.3	37.1	27.5	C44 H38 N2 O3 Lu
	817.2250	34.3	42.0	23.5	C39 H38 N4 O5 Lu
	817.2978	-38.5	-47.1	21.5	C41 H46 N4 O3 Lu



X-Ray tables

	(-)-PL1	(-)-HL1	(-)-HL2
CCDC number	2084719	2084720	2084721

Empirical formula	$C_{20}H_{22}N_2$	$C_{19}H_{20}N_2O_2$	$C_{40}H_{44}N_4O_4$
Form. weight ($g.mol^{-1}$)	290.39	308.37	644.79
Temperature (K)	250(2)	200(2)	250(2)
Wavelength (Å)	0.71073	1.54186	0.71073
Crystal system	Orthorhombic	Orthorhombic	Monoclinic
Space group	$P2_12_12_1$	$P2_12_12_1$	$P2_1$
a (Å)	7.2613(5)	6.50130(10)	11.3097(8)
b (Å)	9.0056(6)	10.1527(3)	6.2574(5)
c (Å)	25.277(2)	24.2770(5)	24.2538(19)
β (°)	90	90	95.828(6)
Volume ($Å^3$)	1652.9(2)	1602.42(6)	1707.6(2)
Z	4	4	2
Density (calc.) (g/mm^3)	1.167	1.278	1.254
Abs. coef. (mm^{-1})	0.068	0.668	0.082
$F(000)$	624	656.0	688.0
Theta range for data collection	1.611 to 25.125°.	14.102 to 137.64	3.376 to 50.516
Reflections collected	21498	16497	5874
Independent reflections	2947 [R_{int} = 0.1080]	2908 [R_{int} = 0.0181]	5874 [Twinning: 0.732(6)]
Data / restraints / parameters	2947 / 0 / 202	2908/0/211	5874/1/441
Goodness-of-fit on F^2	0.923	1.045	1.076
Final R indices [I>2sigma(I)]	R_1 = 0.0400 wR_2 = 0.0698	R_1 = 0.0317 wR_2 = 0.0790	R_1 = 0.0896 wR_2 = 0.2301
R indices (all data)	R_1 = 0.0965 wR_2 = 0.0850	R_1 = 0.0343 wR_2 = 0.0805	R_1 = 0.1079 wR_2 = 0.2532
Largest diff. peak and hole ($e.Å^{-3}$)	0.139/-0.124	0.20/-0.20	0.39/-0.32