Supplementary Information

The Effects of the Increasing Number of the Same Chromophore on Photosensitization of Water-Soluble Cyclen-based Europium Complexes with Potentials for Biological Applications

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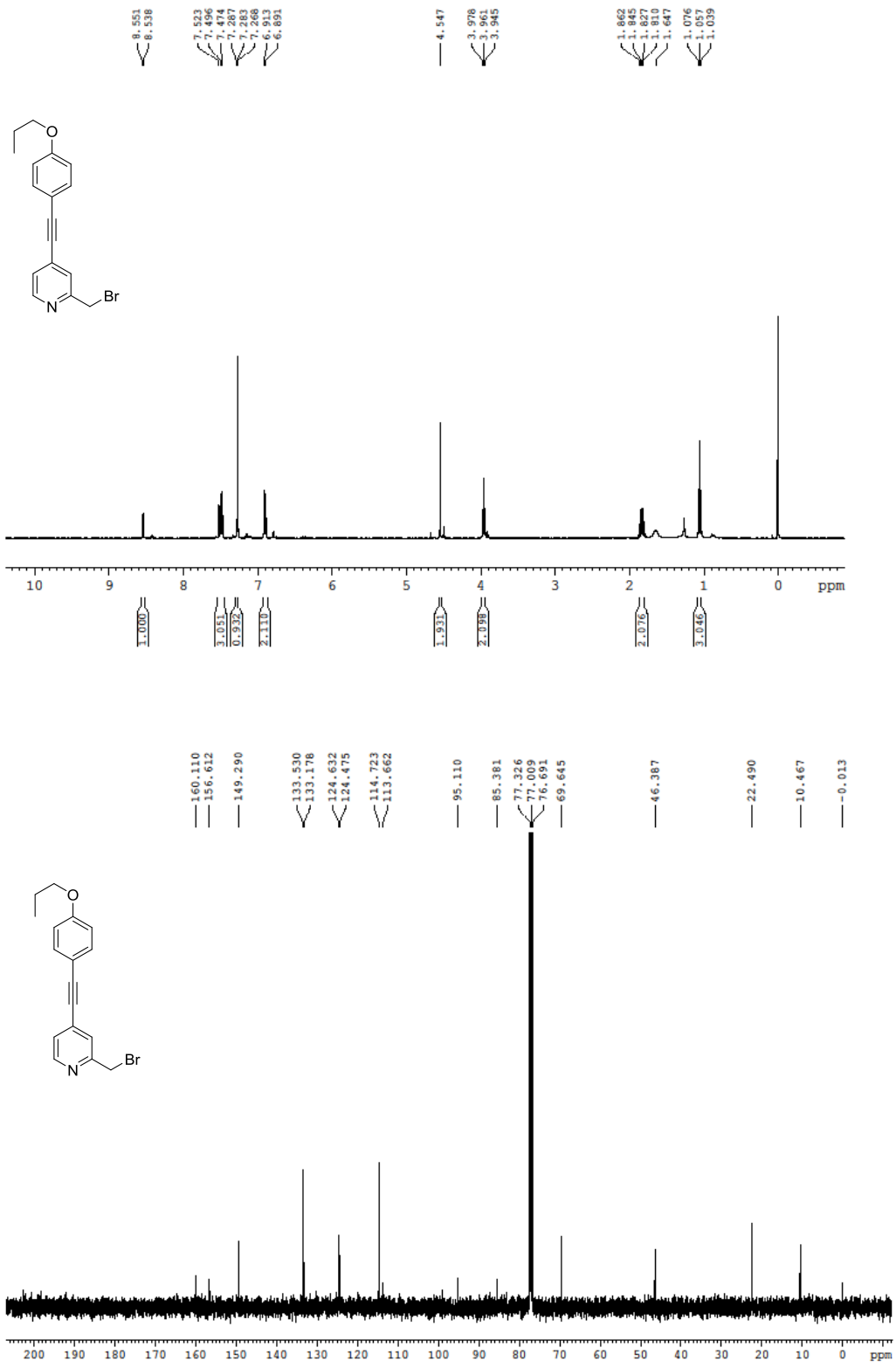
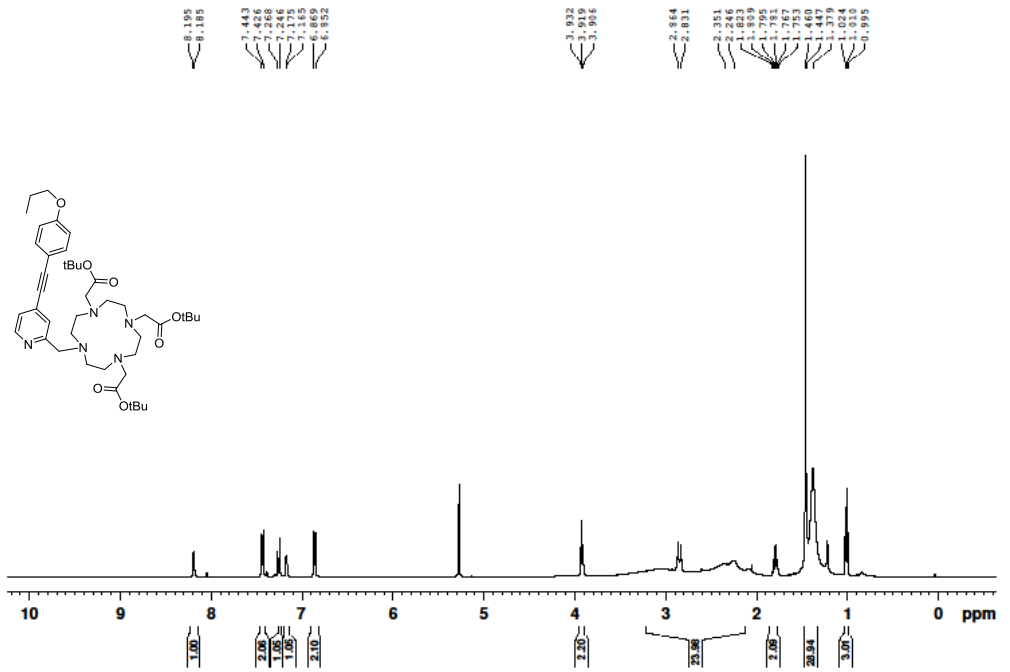
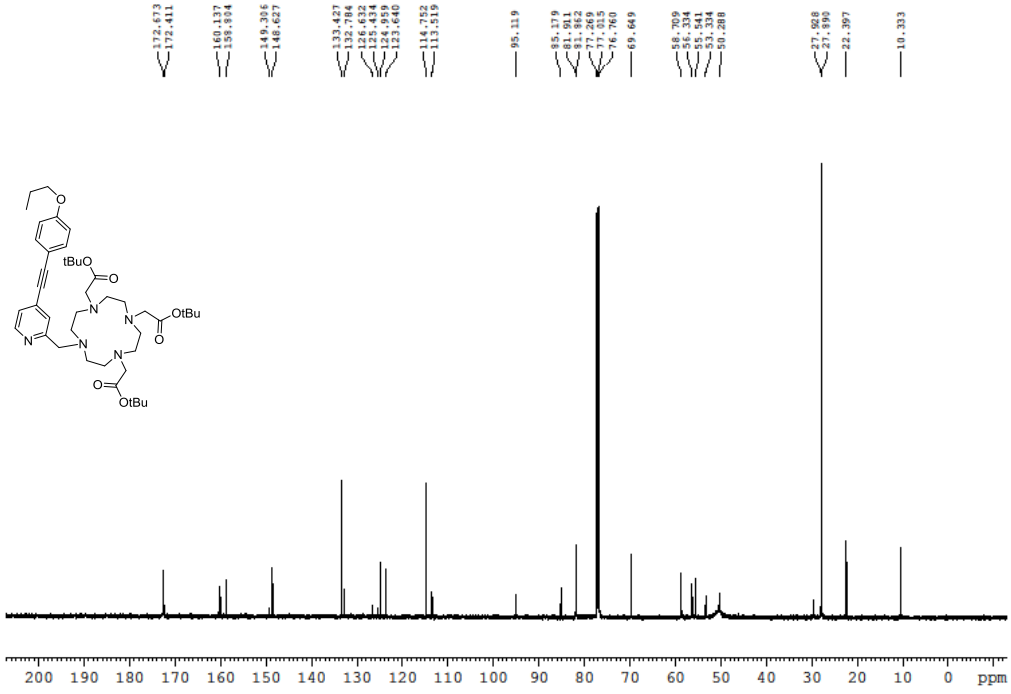
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) of Compound 2

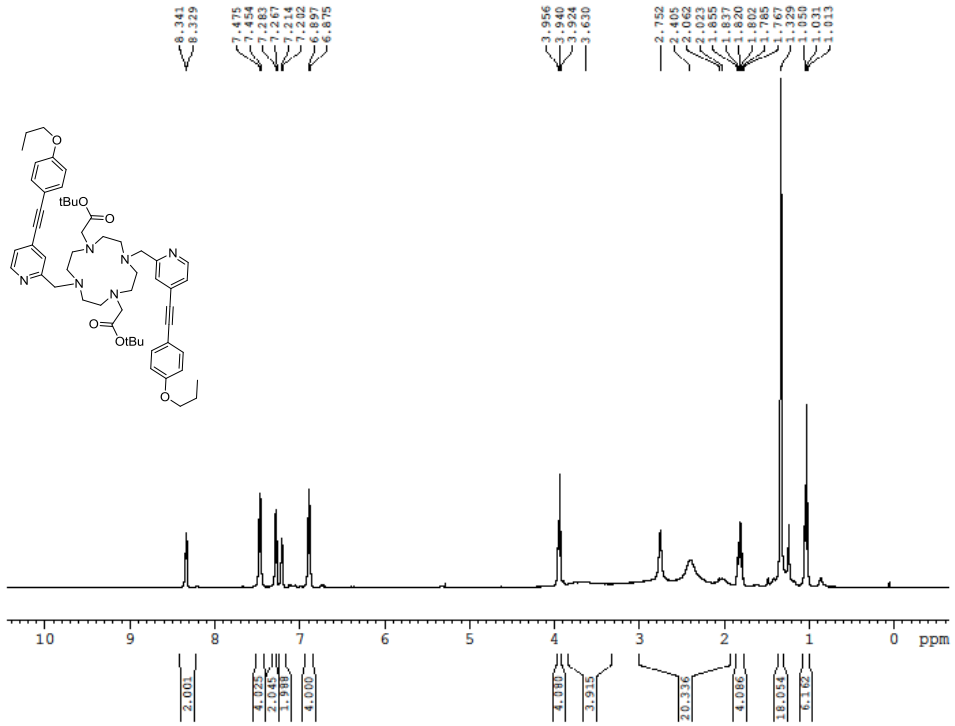


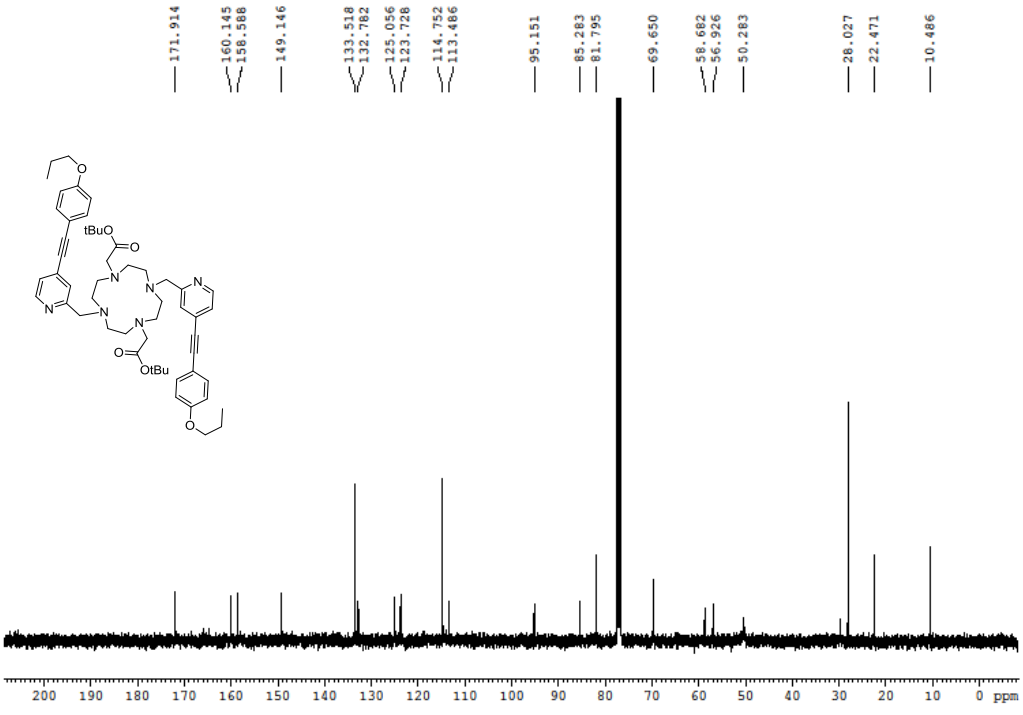
^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) of Ligand 1L



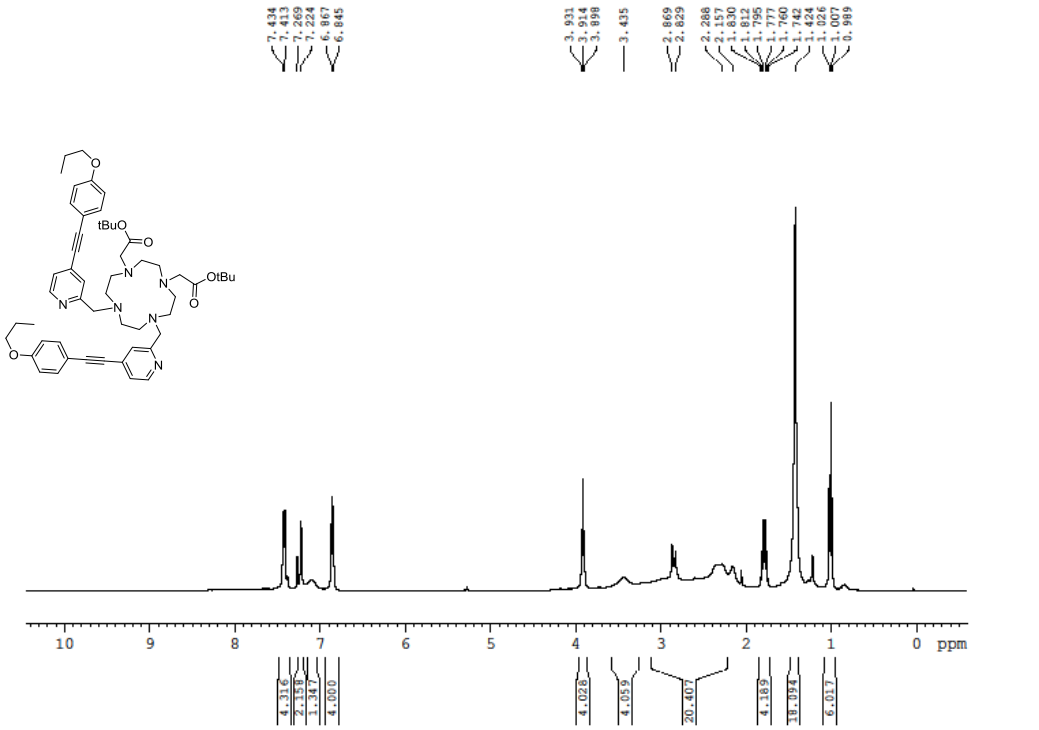


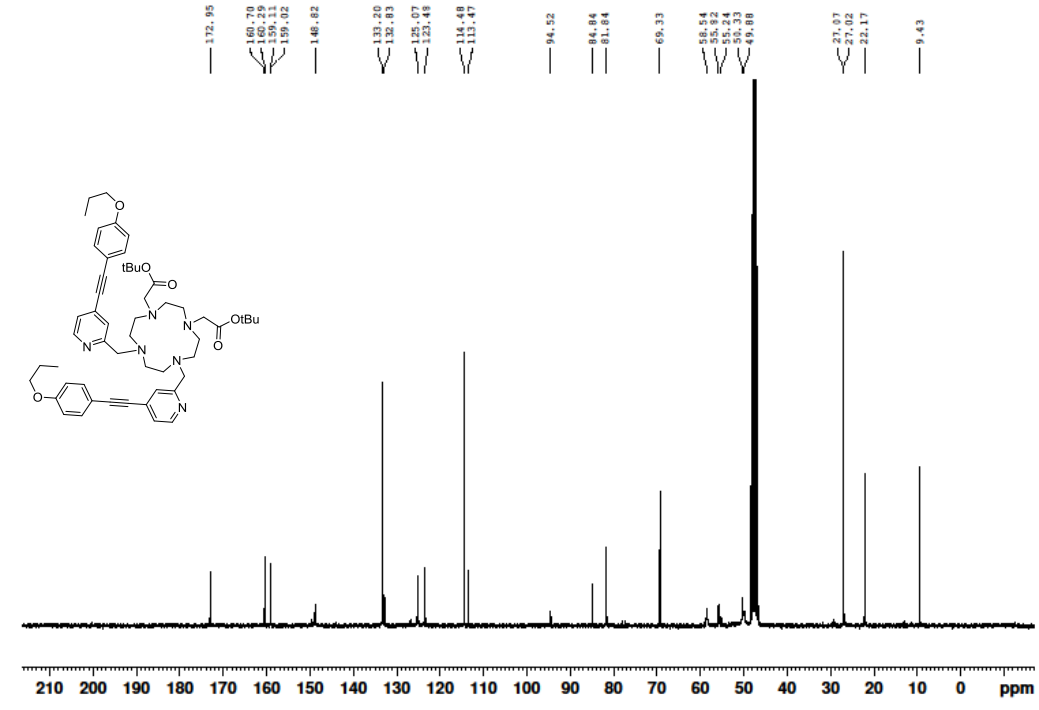
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) of Ligand p-2L



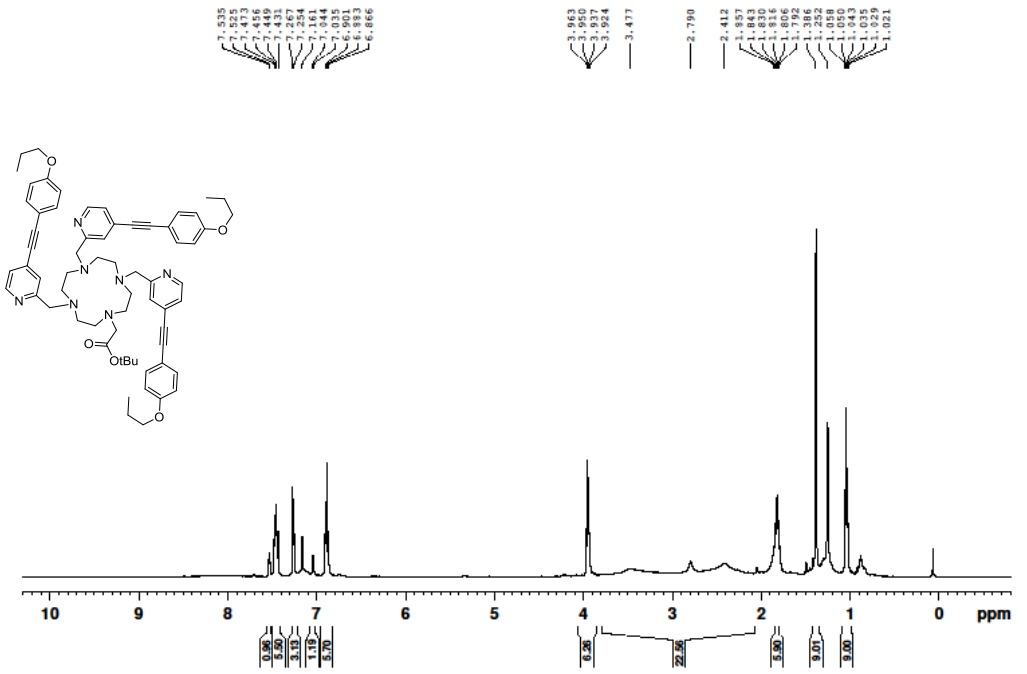


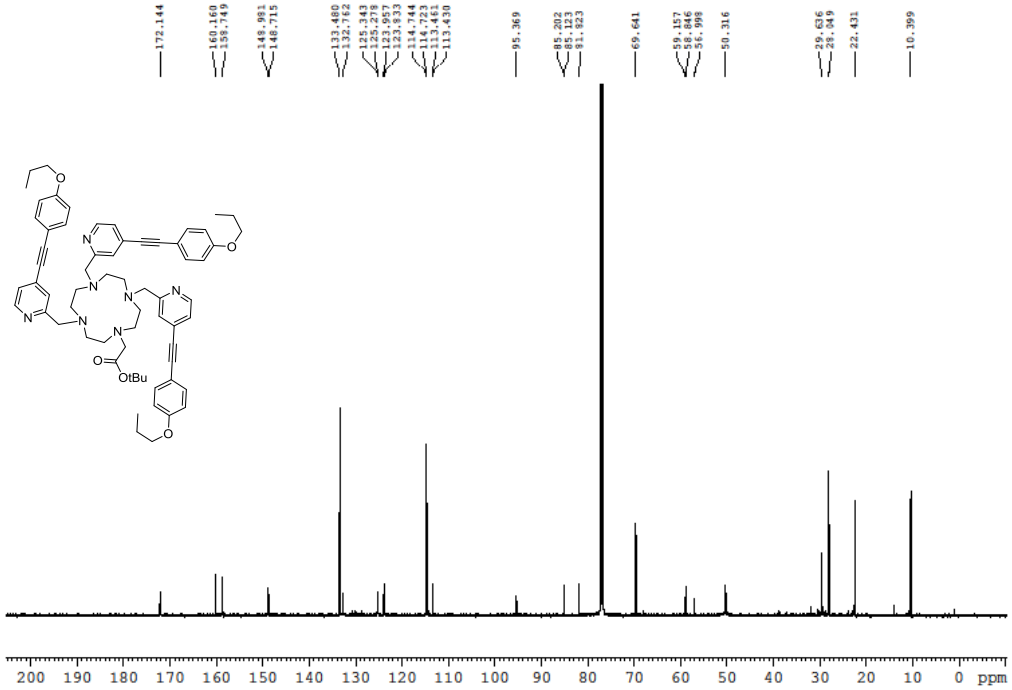
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (75 MHz, CD_3OD) of Ligand o-2L



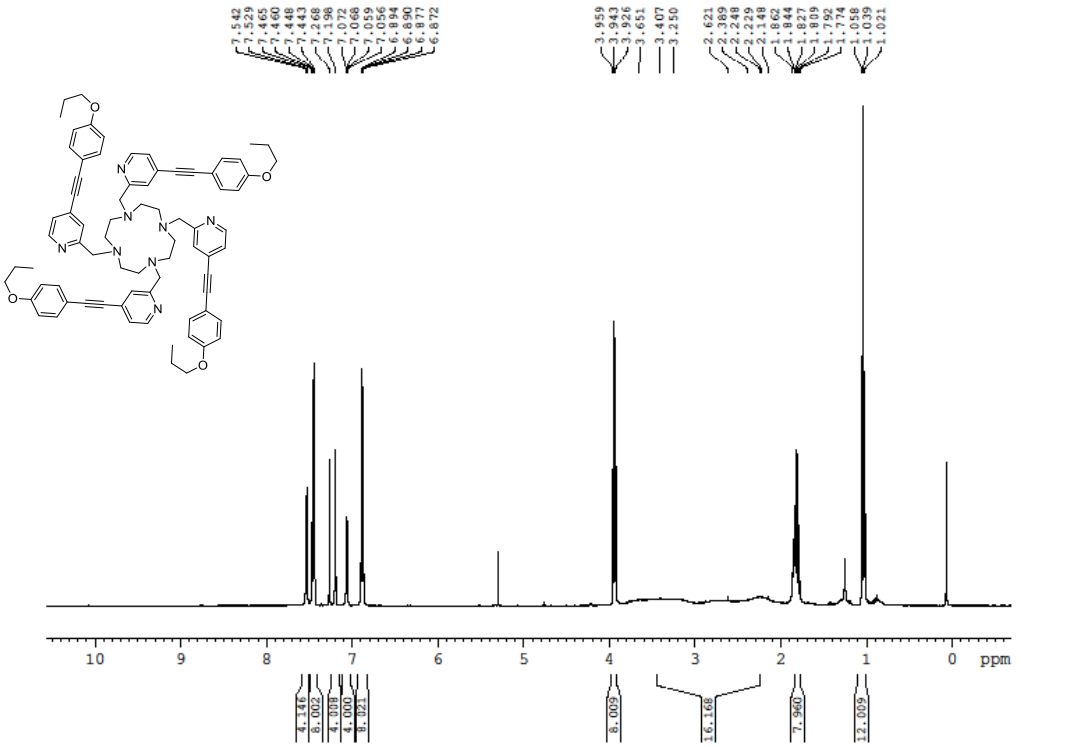


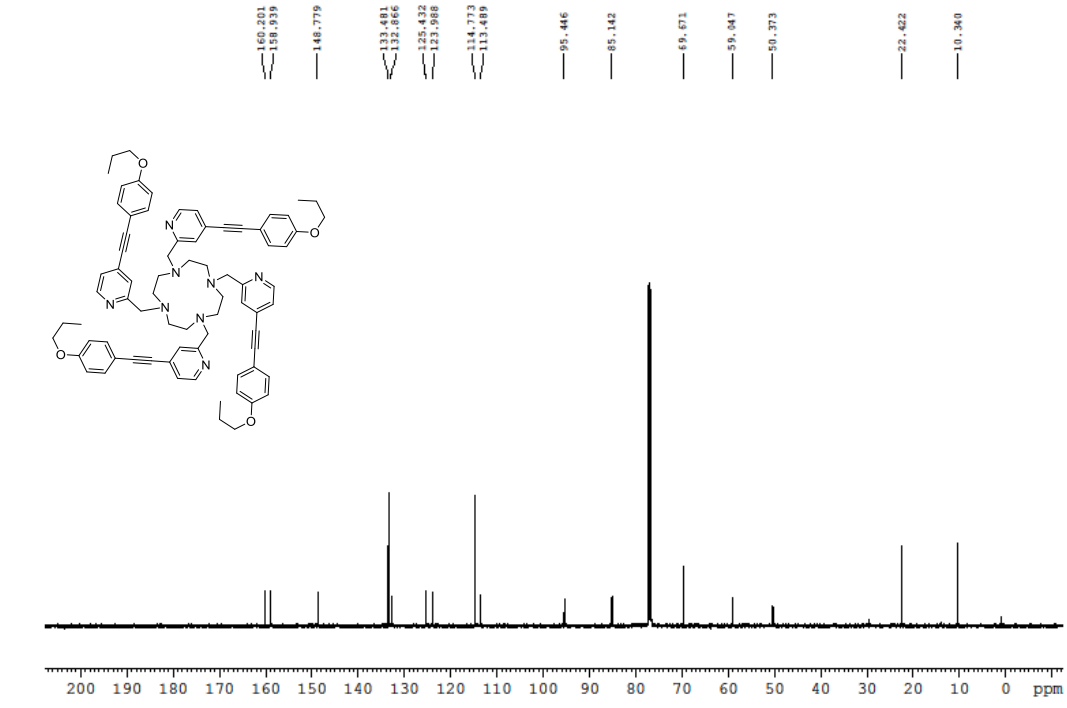
^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) of Ligand 3L



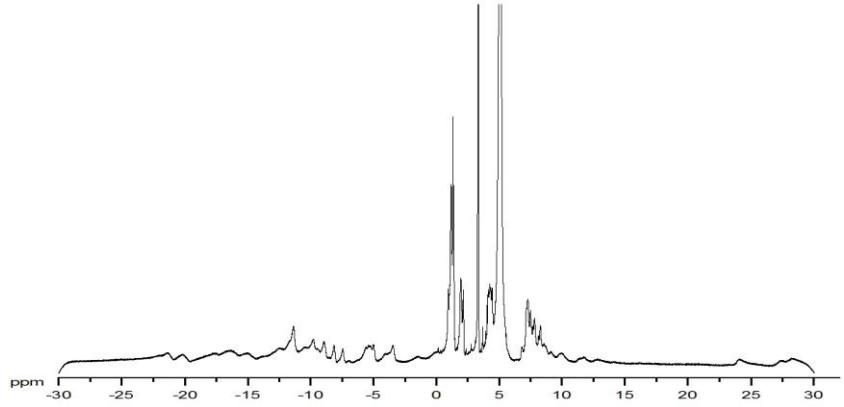


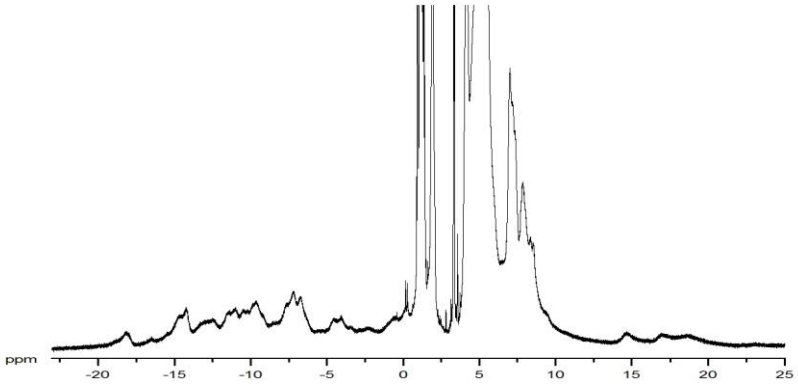
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) of Ligand 4L

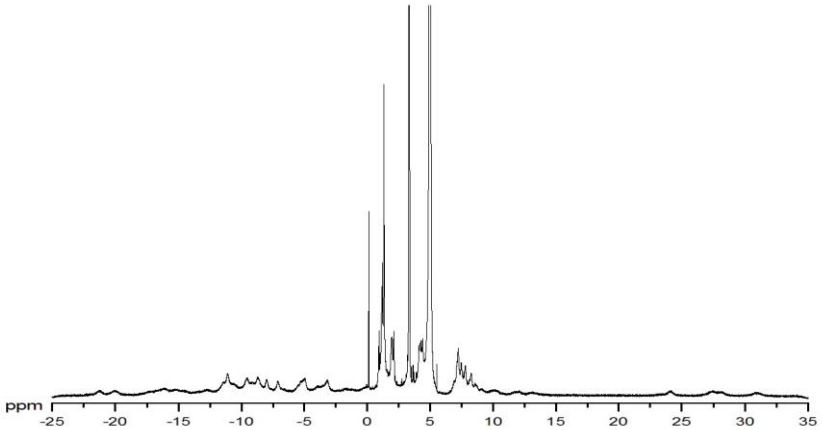




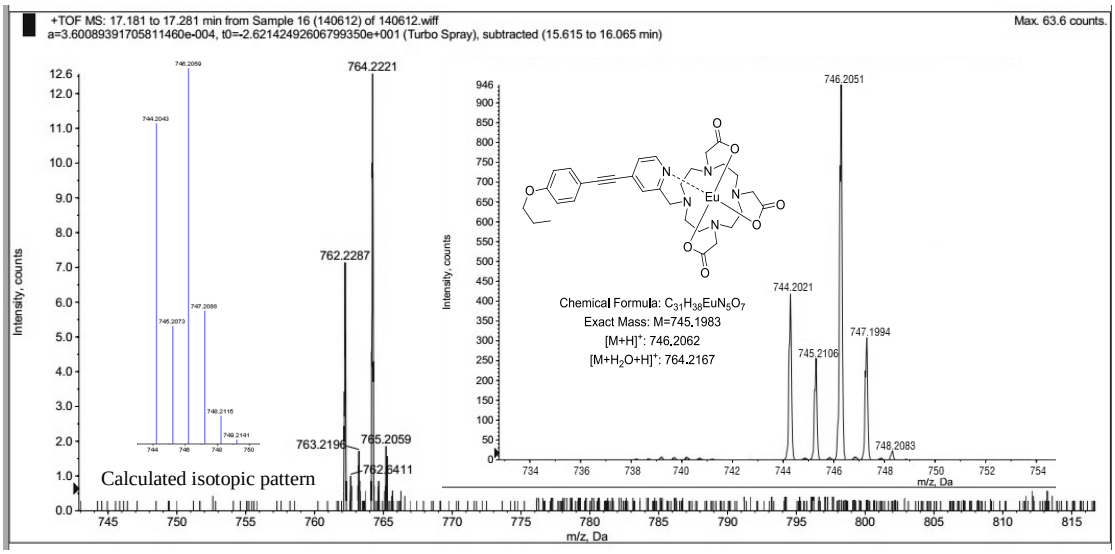
^{1}H NMR of Complexes Eu-nL (n = 1, o-2 and 3) in CD_3OD (500 MHz, 298 K) (top: Eu-1**L**, middle: Eu-o-2**L** and bottom: Eu-3**L**)

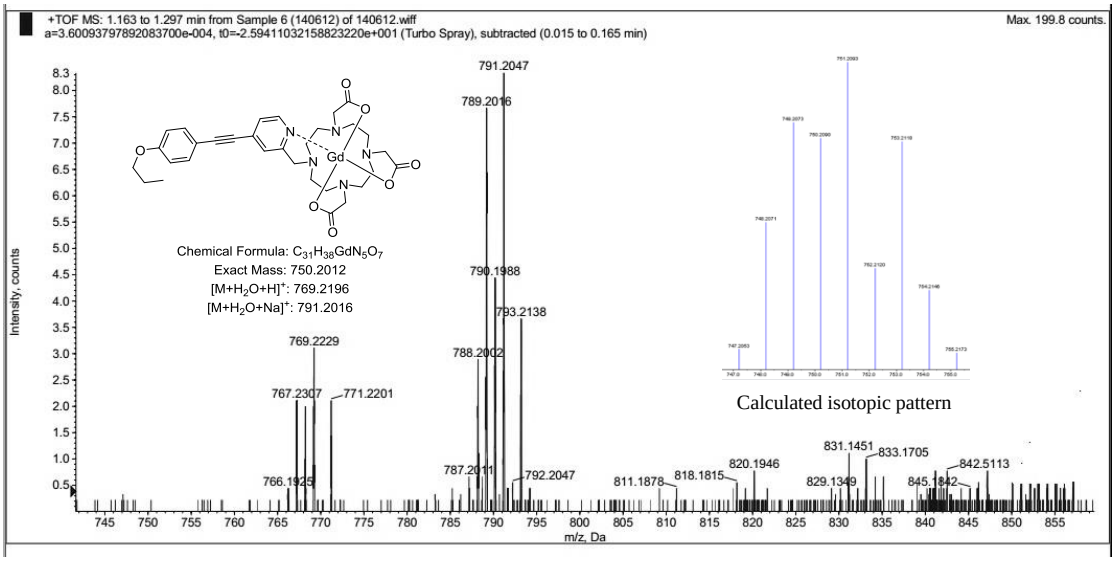


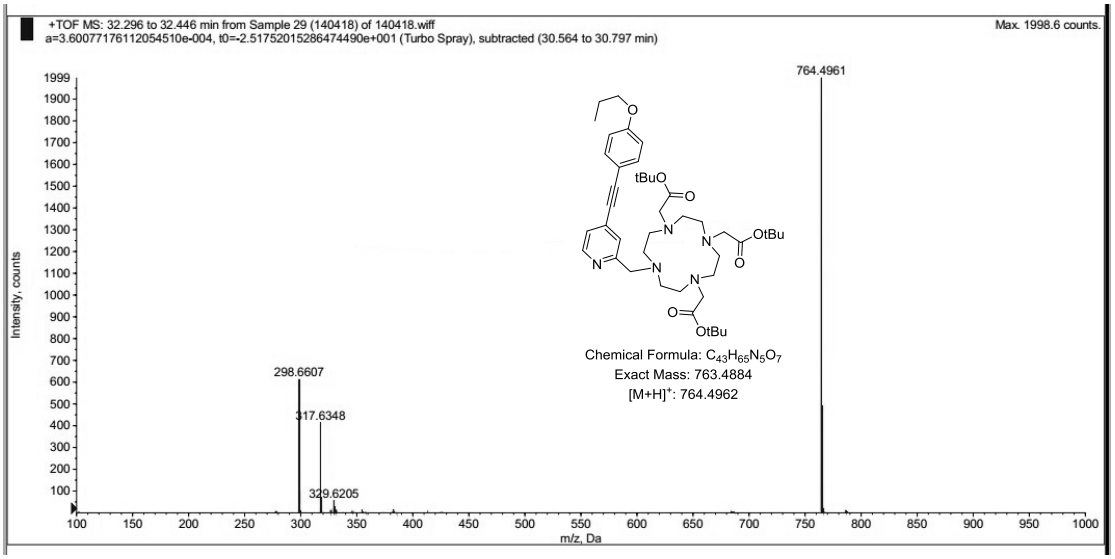




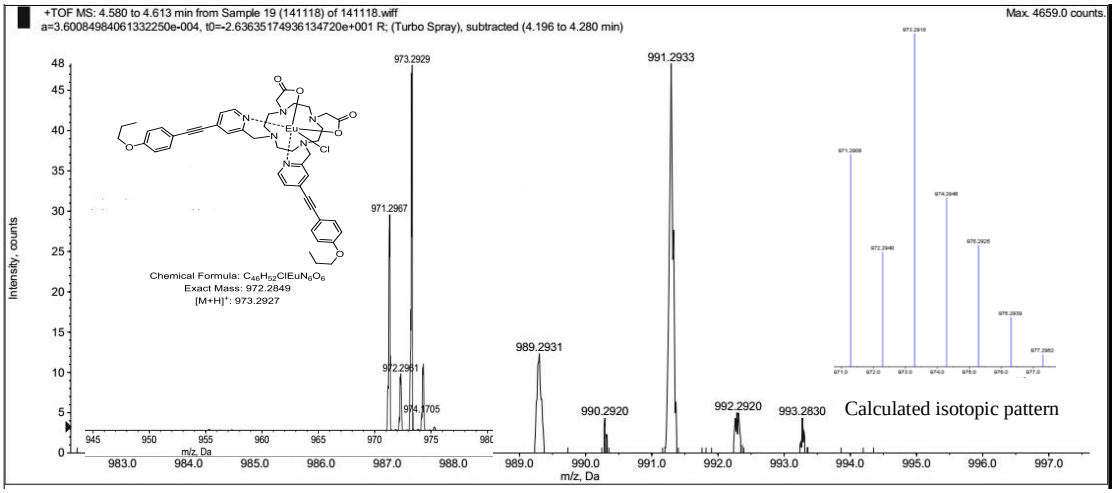
HRMS of Ln (Eu, Gd) complexes and the corresponding ligand (Top: the isotopic pattern of Eu-1**L**; Middle: the isotopic pattern of Gd-1**L**; Bottom: ligand 1**L**)

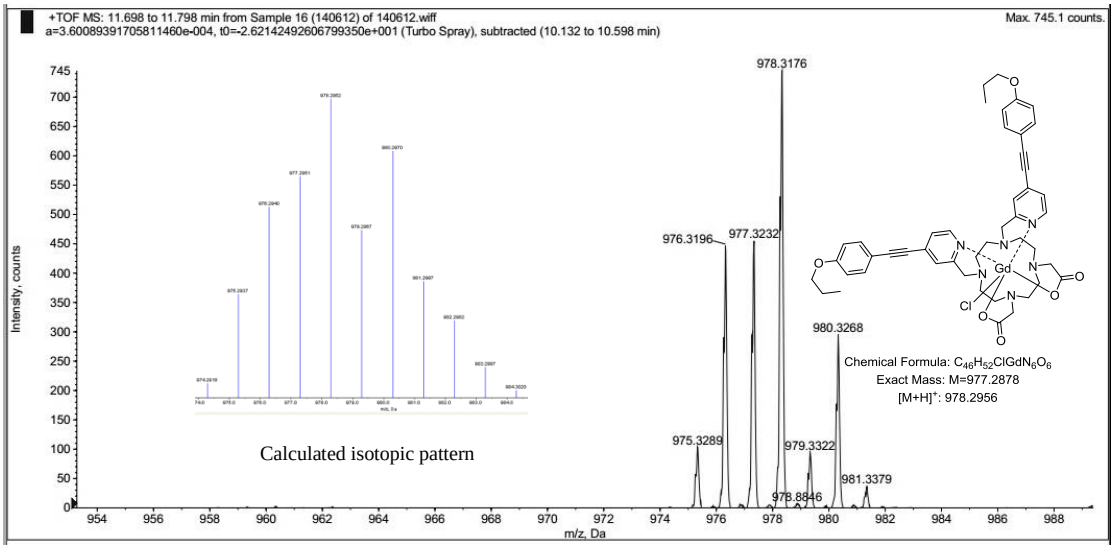


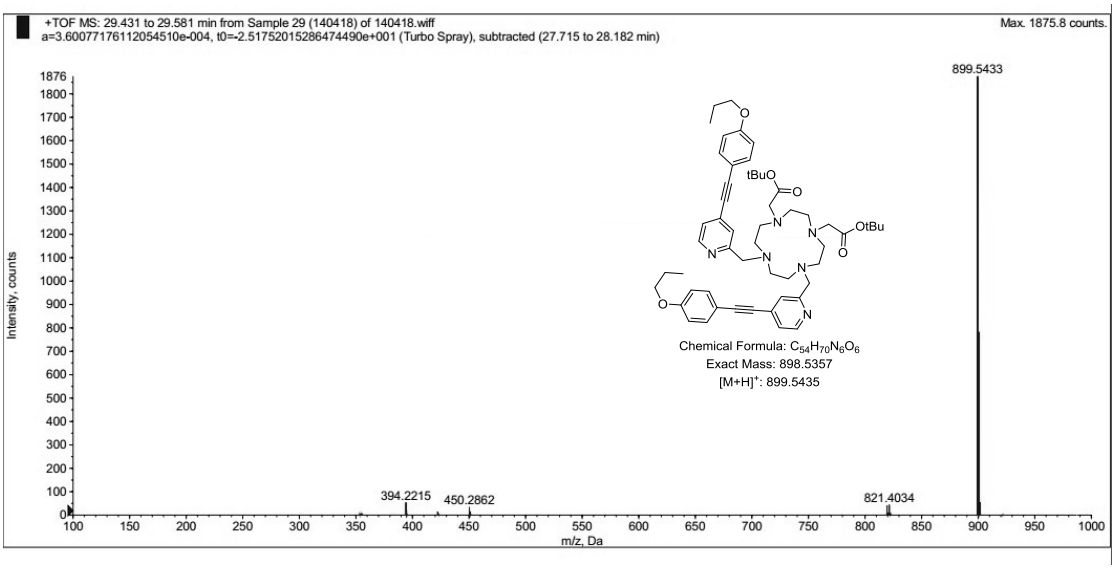




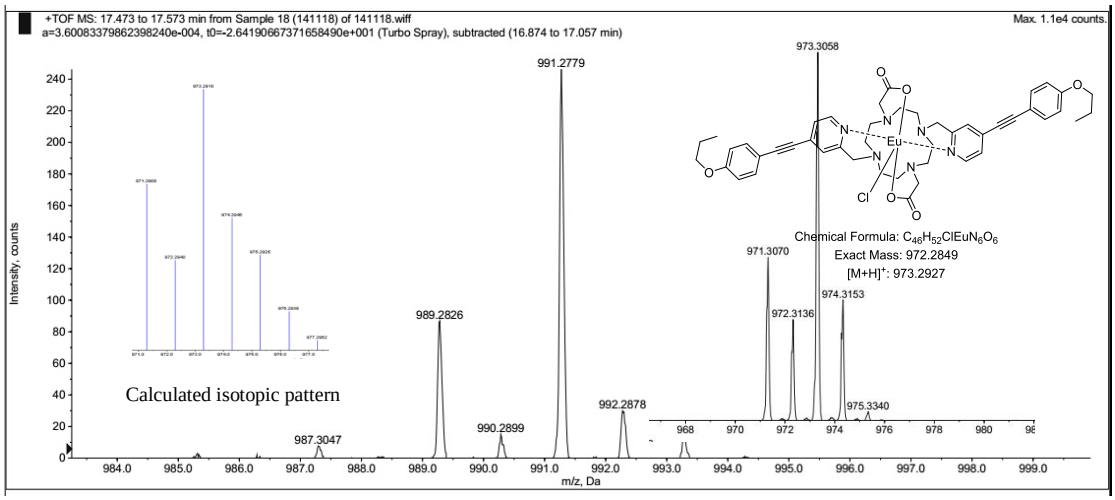
HRMS of Ln (Eu, Gd) complexes and the corresponding ligand (Top: the isotopic pattern of Eu-o-2**L**; Middle: the isotopic pattern of Gd-o-2**L**; Bottom: ligand o-2**L**)

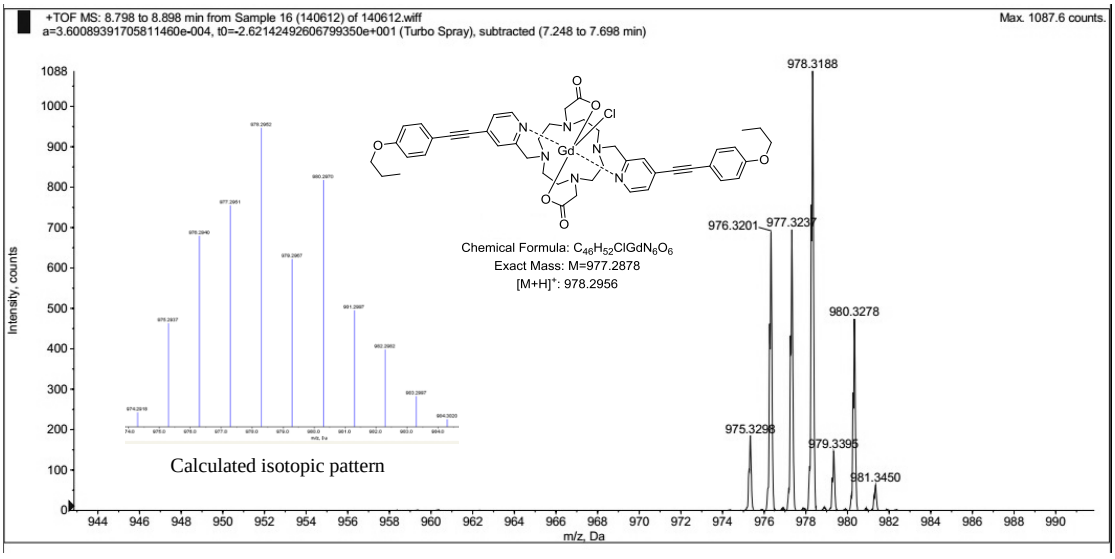


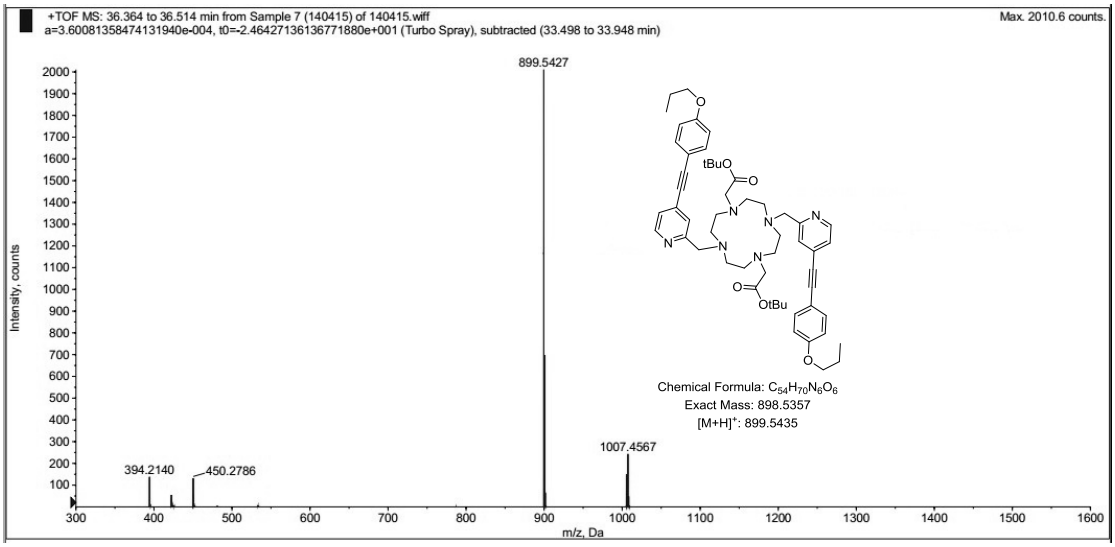




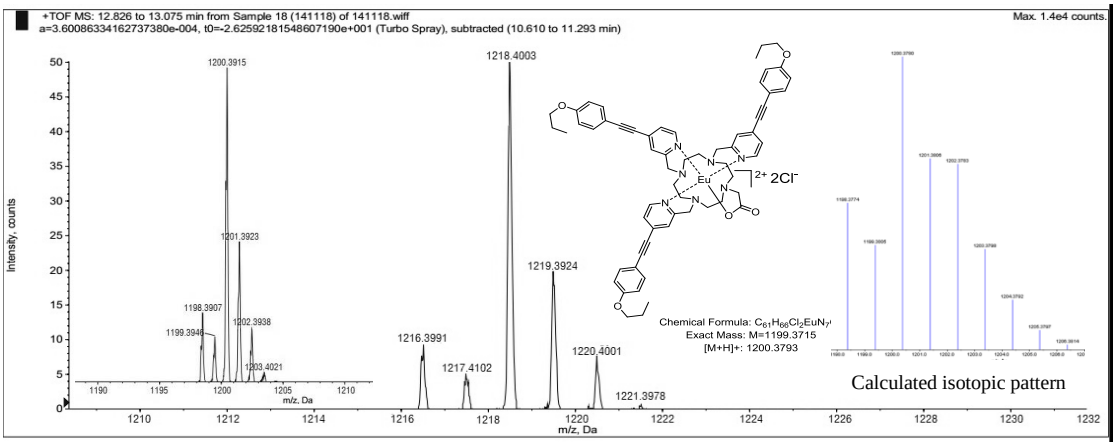
HRMS of Ln (Eu, Gd) complexes and the corresponding ligand (Top: the isotopic pattern of Eu-p-2**L**; Middle: the isotopic pattern of Gd-p-2**L**; Bottom: ligand p-2**L**)

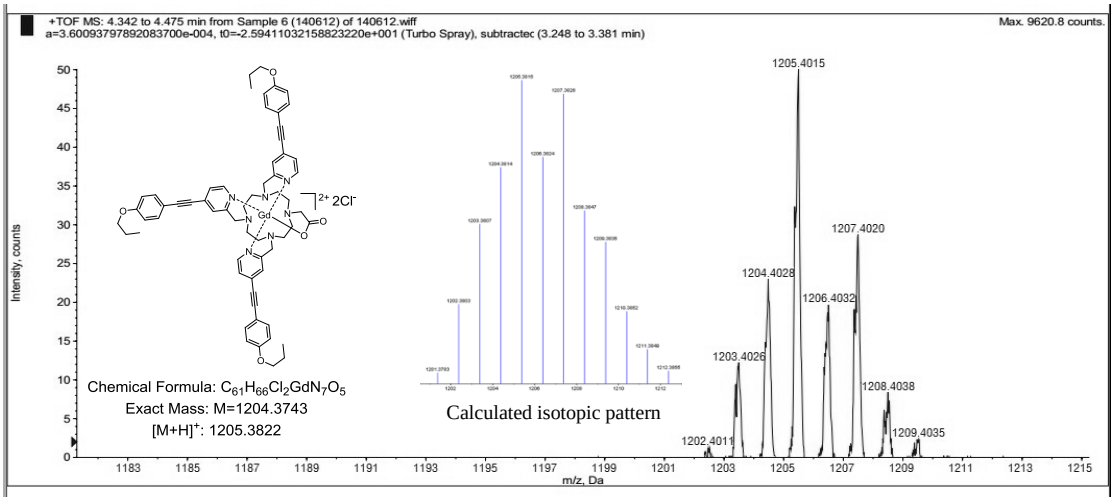


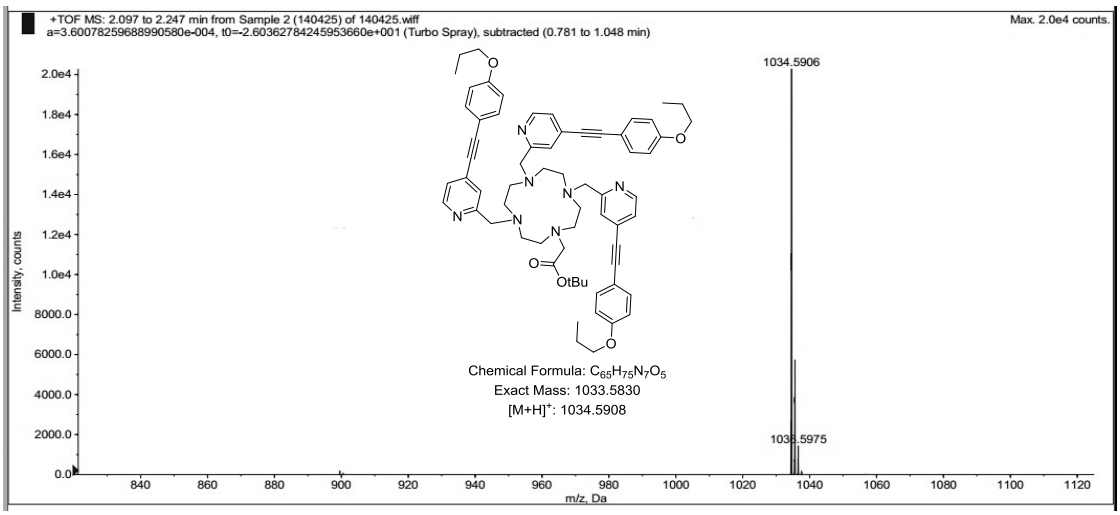




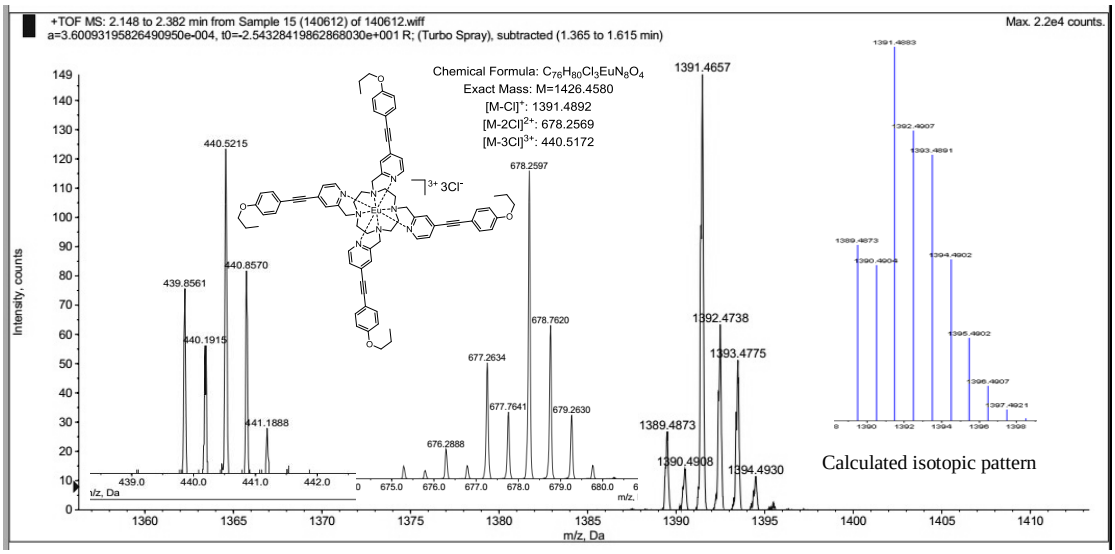
HRMS of Ln (Eu, Gd) complexes and the corresponding ligand (Top: the isotopic pattern of Eu-3**L**; Middle: the isotopic pattern of Gd-3**L**; Down: ligand 3**L**)

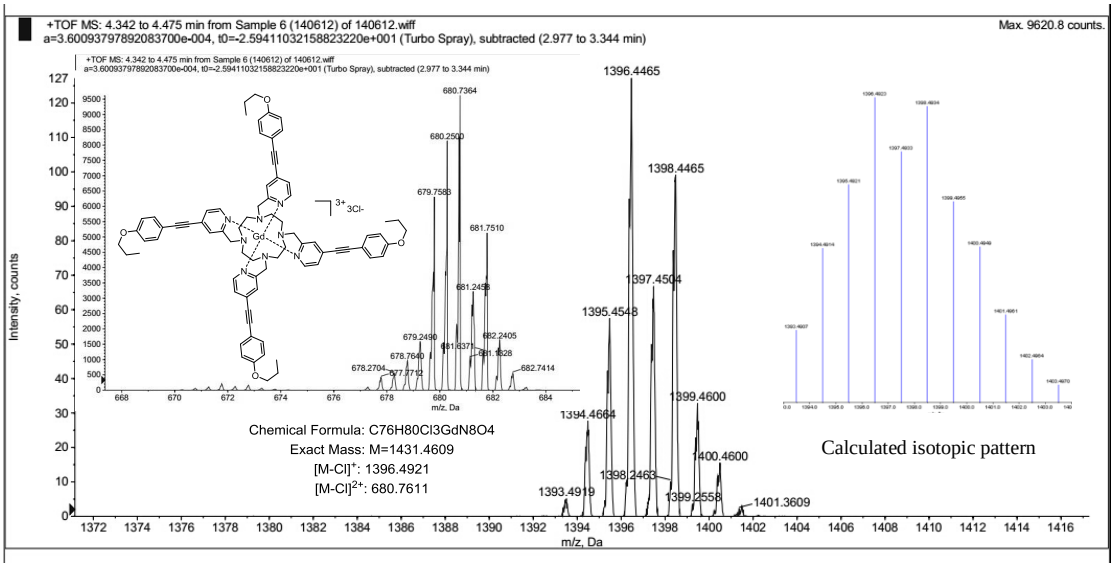






HRMS of Ln (Eu, Gd) complexes and the corresponding ligand (Top: the isotopic pattern of Eu-4**L**; Middle: the isotopic pattern of Gd-4**L**; Bottom: ligand 4**L**)





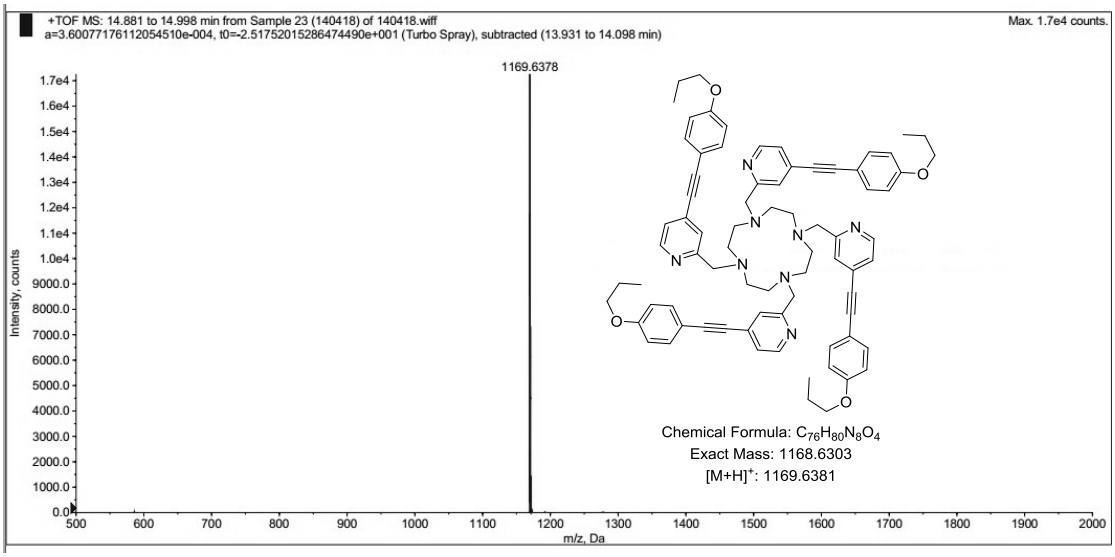


Table S1 Solvent gradient for HPLC

Time /min	0.1% CHOOH in mQ water /%	0.1% CHOOH in CH_3CN /%
0.0	95	5
14.0	50	50
15.0	50	50
20.0	0	100

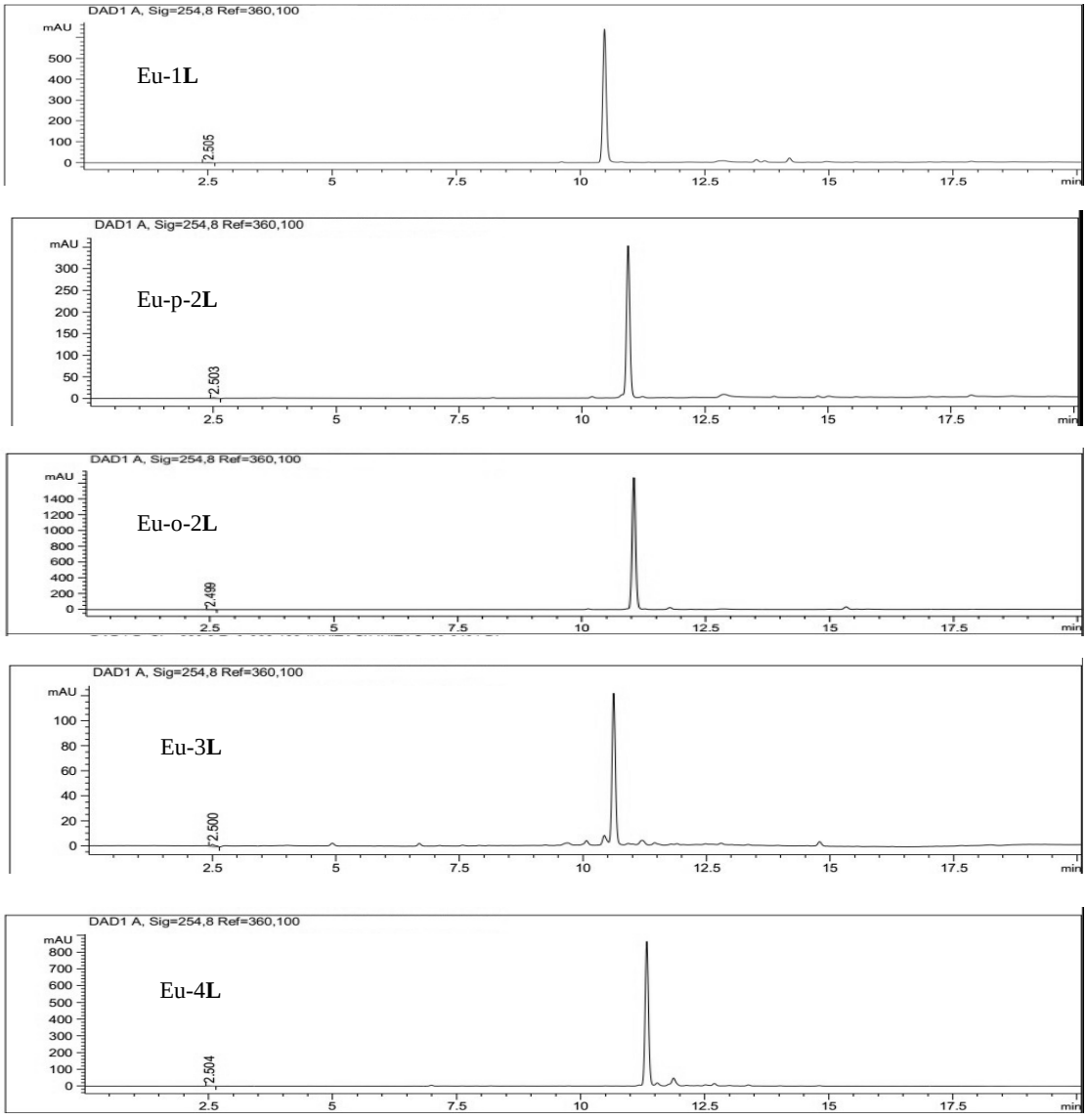
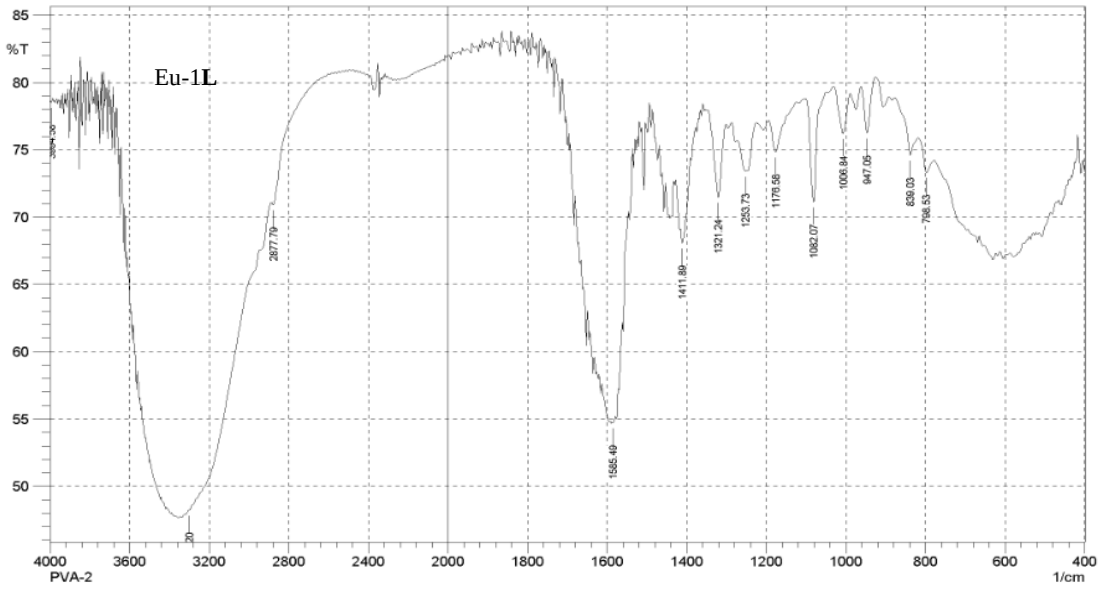
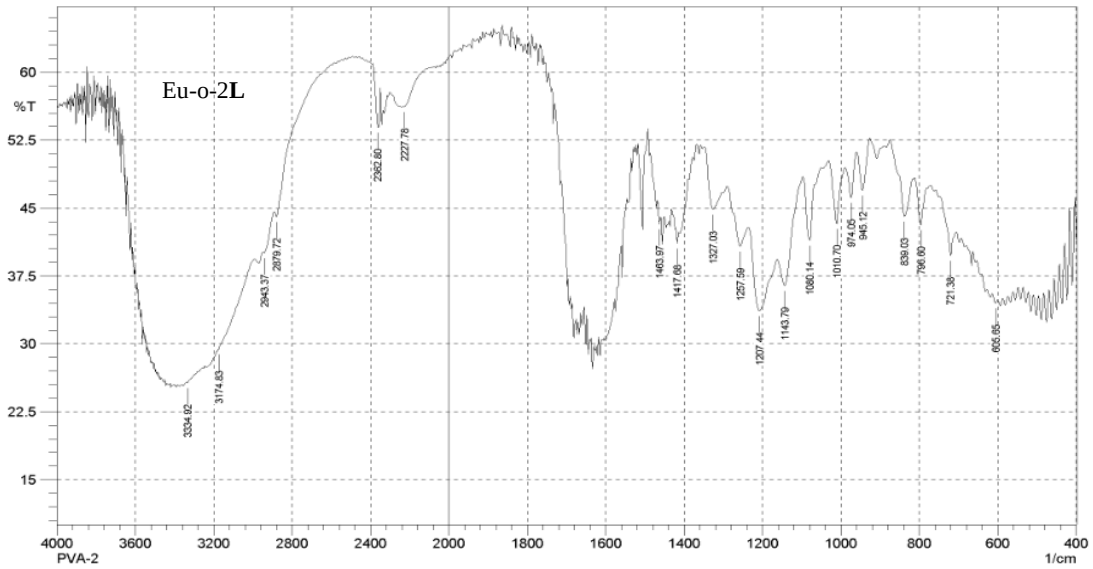
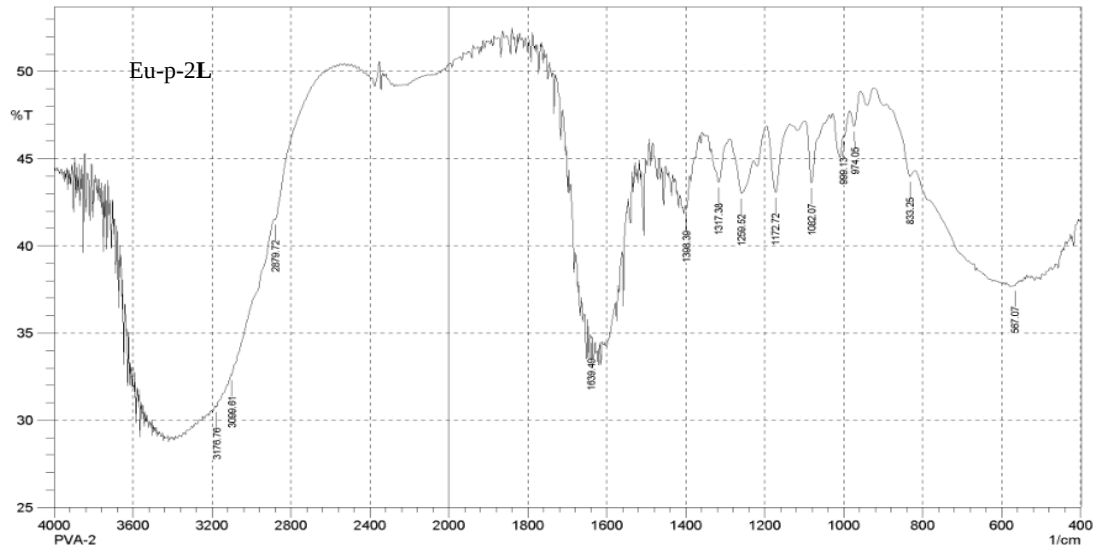


Fig. S1 HPLC trace of Eu complexes. Experimental conditions: Agilent ZORBAX SB-C18 Stable Bond Analytical 4.6 X 150mm 5-micron, 1.0mL/min flow rate, Retention Time: Eu-1**L** in 10.48 min, Eu-p-2**L** in 10.93 min, Eu-o-2**L** in 11.04 min, Eu-3**L** in 10.62 min and Eu-4**L** in 11.33 min.

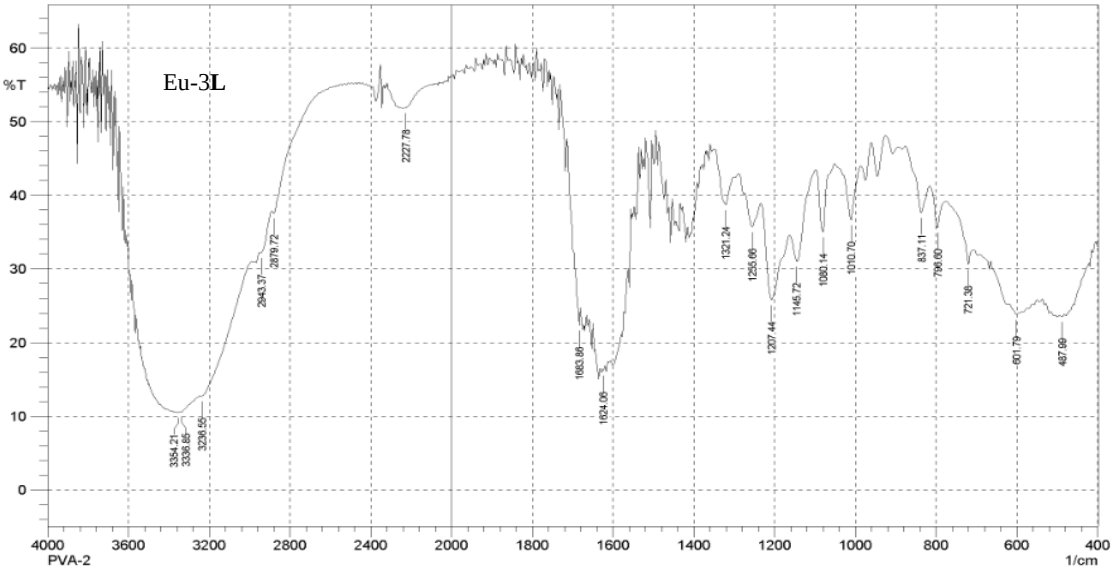
FT-IR Spectral of Complexes Eu-nL (n = 1, o-2 and p-2) (neat, 298 K) (top: Eu-1**L**, middle: Eu-o-2**L** and bottom: Eu-p-2**L**)

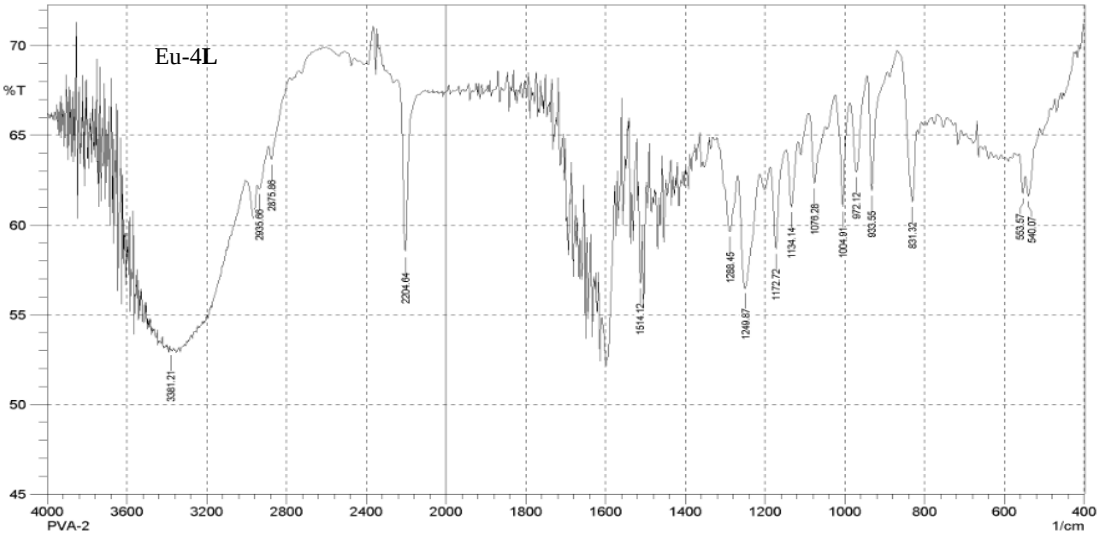






FT-IR Spectral of Complexes Eu-nL (3 and 4) (neat, 298 K) (upper: Eu-3**L**; down: Eu-4**L**)





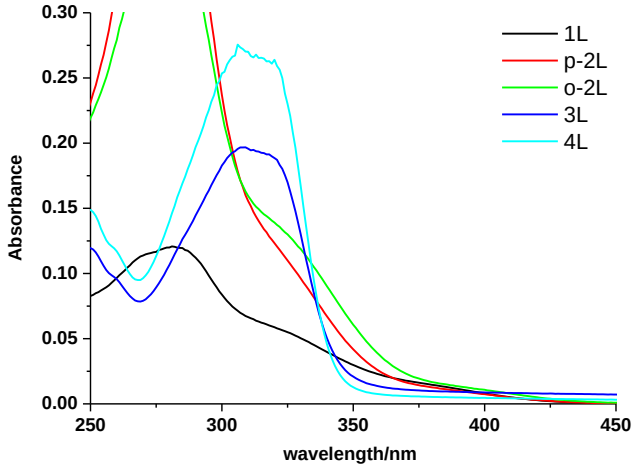


Fig. S2 UV absorption spectra of ligand n**L** (n = 1, p-2, o-2, 3 and 4, 10 μM) in aqueous solution.

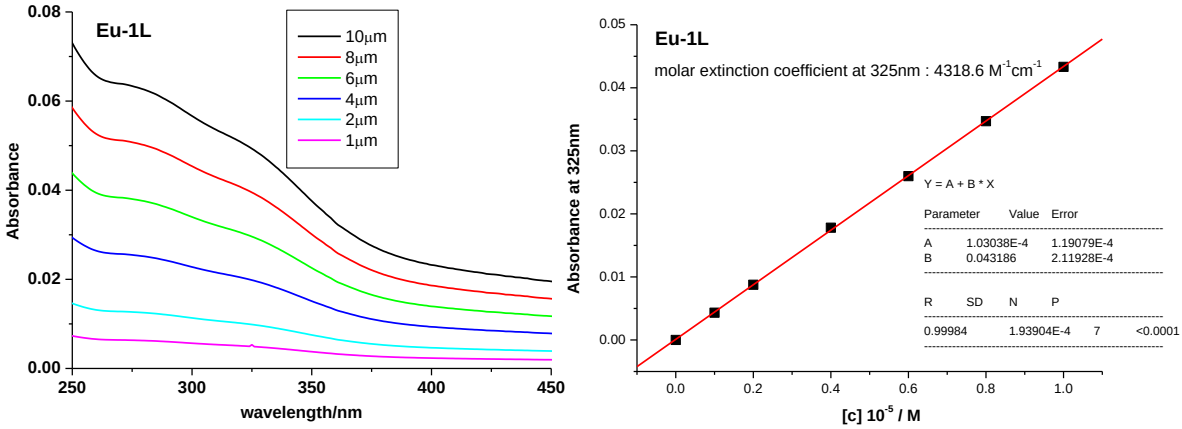


Fig. S3 Left: UV absorption spectra of Eu-1**L** in various of concentrations in water. Right: linear fit of the Absorbance at 325nm *versus* concentration.

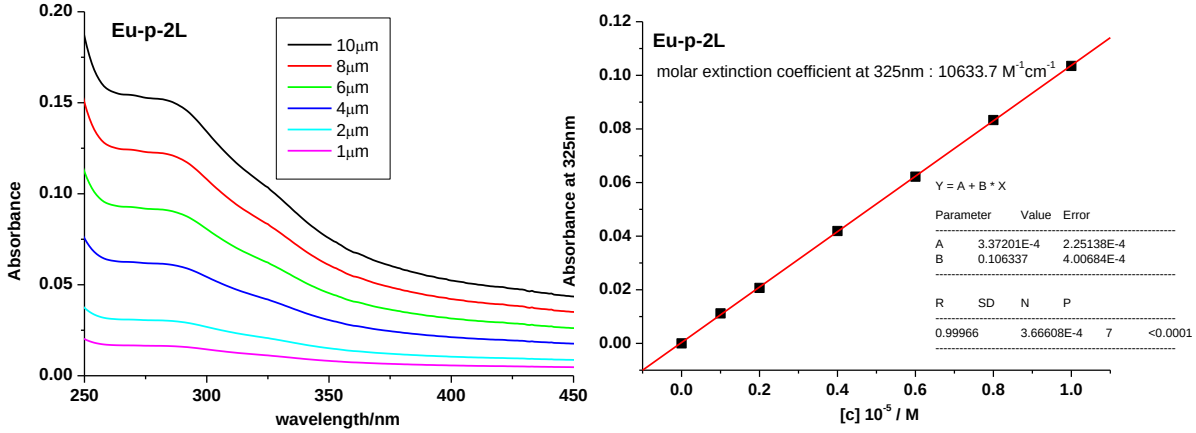


Fig. S4 Left: UV absorption spectra of Eu-p-2**L** in various of concentrations in water. Right: linear fit of the Absorbance at 325nm *versus* concentration.

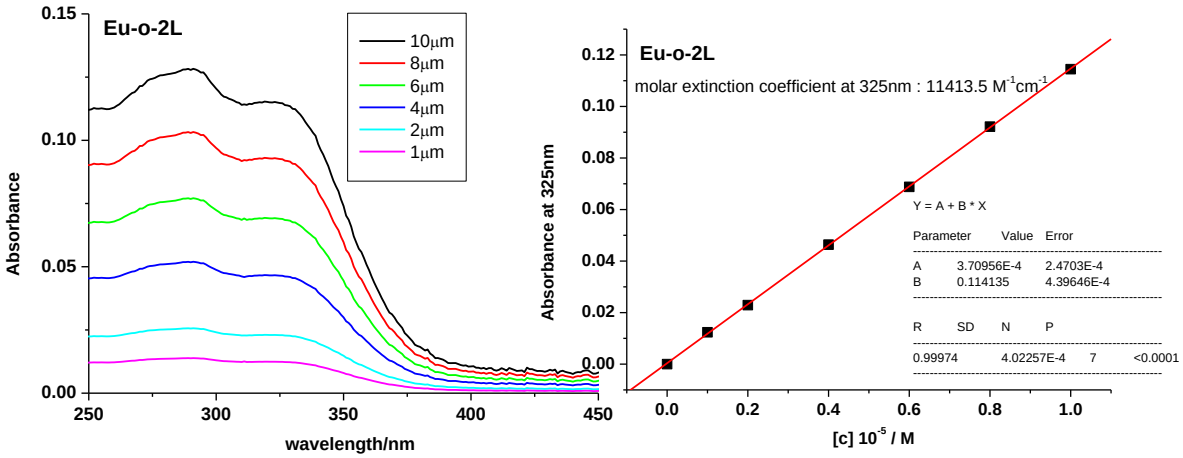


Fig. S5 Left: UV absorption spectra of Eu-o-2**L** in various of concentrations in water. Right: linear fit of the Absorbance at 325nm *versus* concentration.

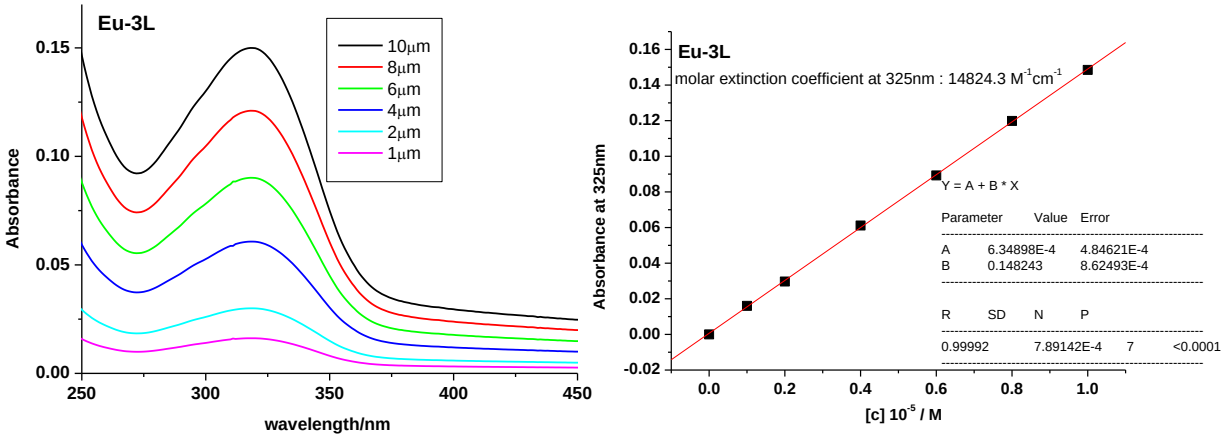


Fig. S6 Left: UV absorption spectra of Eu-3**L** in various of concentrations in water. Right: linear fit of the Absorbance at 325nm *versus* concentration.

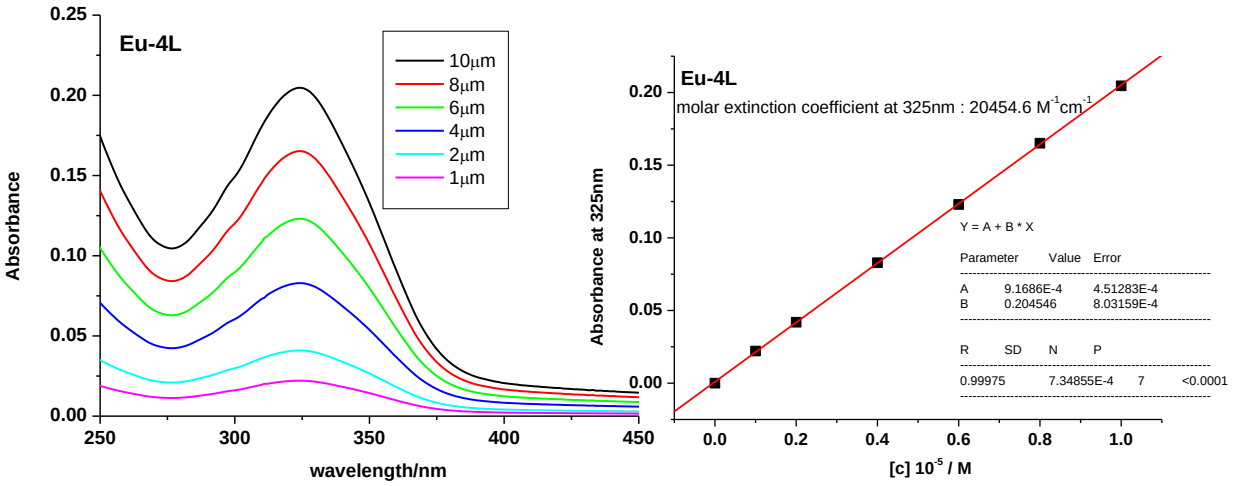


Fig. S7 Left: UV absorption spectra of Eu-4**L** in various of concentrations in water. Right: linear fit of the Absorbance at 325nm *versus* concentration.

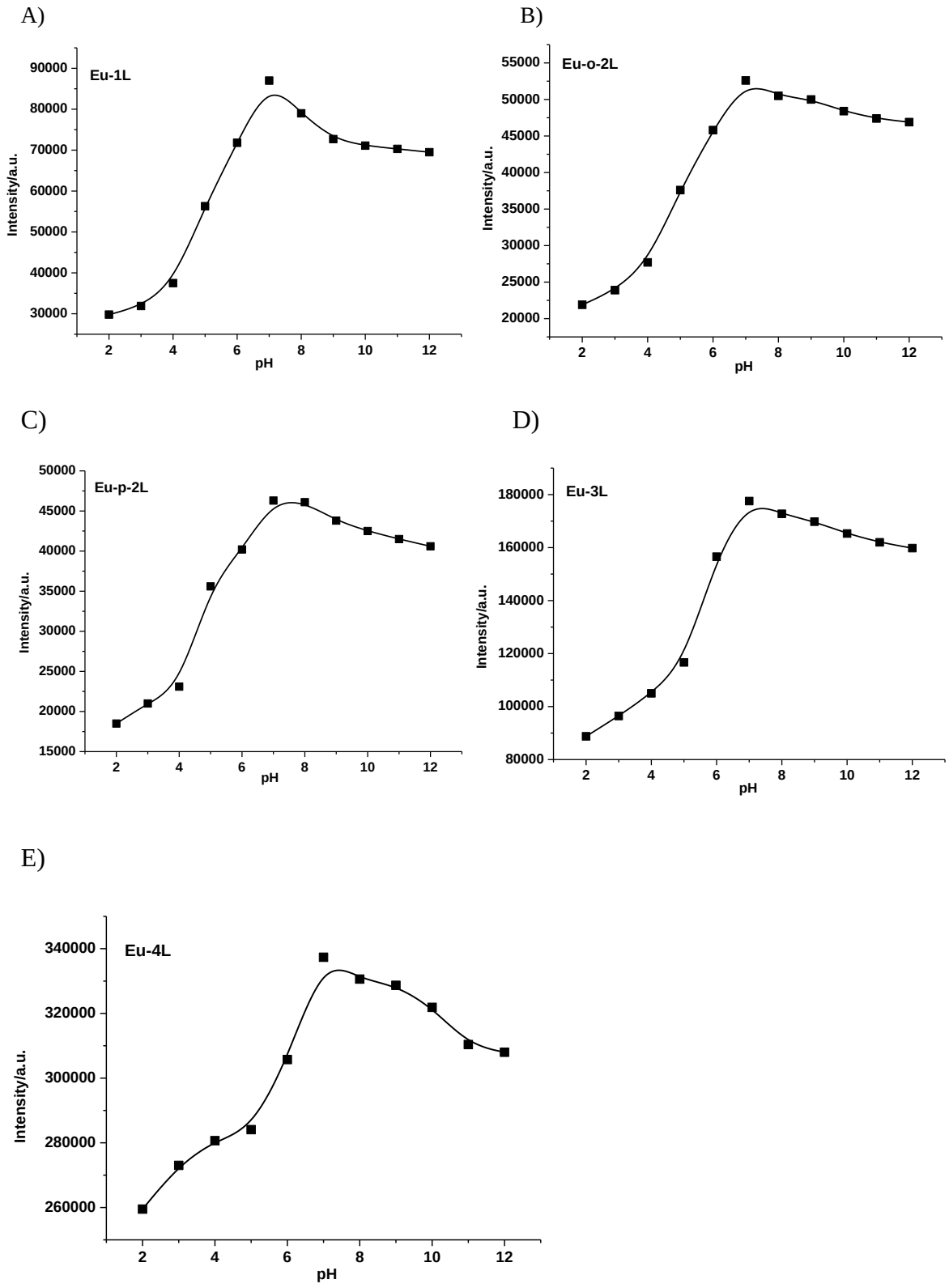


Fig. S8 Plot of intensity ($^5D_0$ to $^7F_2$) *versus* pH of five europium complexes , showing the fit to the observed data for an apparent pKa. A): Eu-1**L**, pKa = 5.1; B): Eu-o-2**L**, pKa = 4.9; C): Eu-p-2**L**, pKa = 4.6; D): Eu-3**L**, pKa = 5.4; E): Eu-4**L**, pKa = 5.3.