ESI

Structure, resolution and chiroptical analysis of stable lanthanide complexes of a pyridylphenylphosphinate triazacyclononane ligand

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1. **Ligand and complex synthesis and characterisation.**
2. **X-ray crystallography.**
3. **Circular Dichroism : experimental and computational studies.**
4. **Representative 1-H NMR spectra of [Ln.L^3].**

1. Ligand and complex synthesis and characterisation.

General Experimental

All reagents were used as received from their respective suppliers. Acetonitrile was dried over calcium hydride when required. Air sensitive reactions were carried out under an atmosphere of argon.

Thin-layer chromatography was carried out on silica plates (Merck 5554) or neutral alumina oxide plates (Merck Art 5550) and visualised under irradiation at 254 nm or iodine staining. Preparative column chromatography was carried out using silica (Merck Silica Gel 60, 230 – 400 mesh) or neutral aluminium oxide (Merck Aluminium Oxide 90, activity II – III, 70 – 230 mesh), soaked in ethyl acetate prior to use.

^{1}H- and ^{13}C-NMR spectra were recorded on a Varian Mercury 400 (^{1}H at 399.97 MHz, ^{13}C at 100.61 MHz). Spectra were recorded in commercially available deuterated solvents. All chemical shifts are given in ppm and coupling constants in Hz.

Electrospray mass spectroscopy was carried out on a Thermo Finnigan LTQ and accurate masses recorded on a Thermo Finnigan LTQ-FT. Emission spectra were recorded on a ISA Joblin-Yvon Spex Fluorolog-3 luminescence spectrometer. Lifetime measurements were carried out using a Perkin Elmer LS55 spectrometer using FL Winlab software.

Quantum yield measurements were calculated by comparison with two standards (*see* J. W. Walton, L. Lamarque, D. Parker, J. Zwier *EJIC,* 2010 **25**, 3961). For the standards and each of the unknowns, five solutions with absorbances between 0.05 and 0.1 were used. The quantum yield was calculated according to the equation

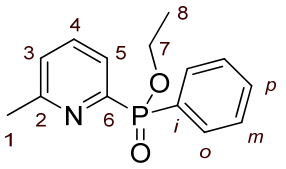
$$\Phi_x = \Phi_r \cdot \frac{A_r}{A_x} \cdot \frac{E_x}{E_r} \cdot \frac{I_r}{I_x} \cdot \frac{n_x^2}{n_r^2}$$

r and x refer to reference and unknown respectively
A = absorbance at λ_{ex}
E = corrected integrated emission intensity
I = corrected intensity of excitation light
n = refractive index of solution.

Chiral HPLC analyses were undertaken using a Chiralpak IC column, eluting using an isocratic gradient with a solvent system composed of EtOH/MeOH/HNEt$_2$, (50/50/0.1) at 15°C; the enantiomeric complexes eluted with

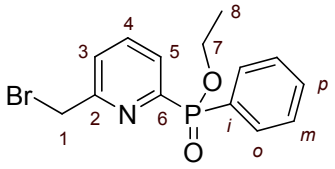
Δt_R = 1.6 min using a flow rate of 1 mLmin^{-1} . Analytical reverse phase HPLC analysis was performed at 298 K on a Perkin Elmer system using an XBridge C-18 10 cm 3.5 μm column at a flow rate of 1 mL / min using the following method:

Time (min)	H_2O + 0.1 % HCO_2H	CH_3CN + 0.1 % HCO_2H
0	95	5
1	95	5
9	0	100
11	0	100
12	95	5
13	95	5



Ethyl (6-methylpyridin-2-yl)(phenyl)phosphinate, 1

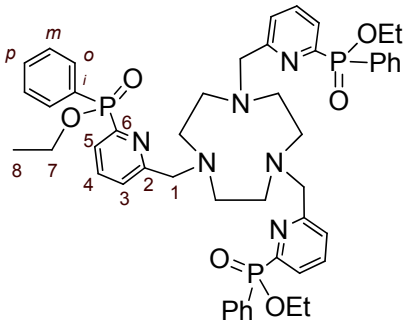
2-Bromo-6-methylpyridine (3.0 g, 17.4 mmol), ethyl phenylphosphinate (3.56 g, 20.9 mmol) and triethylamine (10 mL, 71 mmol) were added to dry degassed (freeze-thaw cycle) toluene (30 mL). Tetrakis(triphenylphosphine)palladium(0) (320 mg, 0.27 mmol) was added and the mixture was degassed three times before being stirred at 125 °C for 16 h under argon. The solution was diluted with CH_2Cl_2 (50 mL), washed with HCl (1M, 2 × 60 mL) and water (3 × 60 mL), dried over K_2CO_3, filtered and the solvent removed under reduced pressure to give a dark residue. Purification by column chromatography on silica (CH_2Cl_2 : 0.5 % MeOH) gave the *title compound* as a colourless oil (3.1 g, 66 %); δ_H ($CDCl_3$) 8.01 (2H, dd, $^3J_{H\text{-}H}$ 8.0 Hz $^3J_{H\text{-}P}$ 12.0 Hz, H^o), 7.91 (1H, dd, $^3J_{H\text{-}H}$ 7.0 Hz $^3J_{H\text{-}P}$ 14.0 Hz, H^5), 7.67 (1H, td, $^3J_{H\text{-}H}$ 7.0 Hz $^4J_{H\text{-}P}$ 3.0 Hz, H^4), 7.54 (1H, t, $^3J_{H\text{-}H}$ 8.0 Hz, H^p), 7.48 (2H, td, $^3J_{H\text{-}H}$ 8.0 Hz $^4J_{H\text{-}P}$ 4.0 Hz, H^m), 7.23 (1H, d, $^3J_{H\text{-}H}$ 7.0 Hz, H^3), 4.15 (2H, qd, $^3J_{H\text{-}H}$ 7.0 Hz $^3J_{H\text{-}P}$ 4.5 Hz, H^7), 2.60 (3H, s, H^1), 1.38 (3H, t, $^3J_{H\text{-}H}$ 7.0 Hz, H^8); δ_C ($CDCl_3$) 159.8 (d, $^3J_{C\text{-}P}$ 20 Hz, C^2), 154.0 (d, $^1J_{C\text{-}P}$ 167 Hz, C^6), 135.8 (d, $^3J_{C\text{-}P}$ 10 Hz, C^4), 132.6 (d, $^2J_{C\text{-}P}$ 12 Hz, C^o), 132.5 (d, $^4J_{C\text{-}P}$ 4 Hz, C^p), 130.6 (d, $^1J_{C\text{-}P}$ 136 Hz, C^i), 128.5 (d, $^3J_{C\text{-}P}$ 9 Hz, C^m), 125.8 (d, $^4J_{C\text{-}P}$ 4 Hz, C^3), 125.6 (d, $^2J_{C\text{-}P}$ 22 Hz, C^5), 61.9 (d, $^2J_{C\text{-}P}$ 6 Hz, C^7), 24.9 (C^1), 16.7 (C^8); δ_P ($CDCl_3$) 26.8; *m/z* (HRMS$^+$) 262.0999 $[M + H]^+$ ($C_{14}H_{17}O_2NP$ requires 262.0997); R_f = 0.37 (silica, CH_2Cl_2 : 5 % MeOH).



Ethyl [6-(bromomethyl)pyridin-2-yl](phenyl)phosphinate, 2

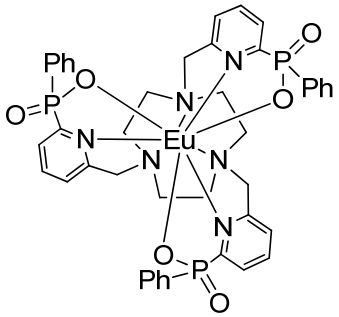
To a solution of ethyl (6-methylpyridin-2-yl)(phenyl)phosphinate (400 mg, 1.53 mmol) in carbon tetrachloride (25 mL) was added N-bromo-succinimde (327 mg, 1.84 mmol) and dibenzoyl peroxide (20 mg, 0.8 mmol). The mixture was stirred and irradiated by a 100 W lamp under an argon atmosphere. The reaction was monitored by ^{1}H-NMR and stopped after 16 h. The solvent was removed under reduced pressure and the crude product was dissolved in CH_2Cl_2 (20 mL) and washed with dilute K_2CO_3 solution (20 mL) to remove excess succinimide. The organic layer was dried over $MgSO_4$, filtered and the solvent removed under reduced pressure. Purification by column chromatography on silica (CH_2Cl_2, MeOH 0 – 1 % using 0.05 % increments) yielded the *title compound* as a colourless oil (198 mg, 38 %); δ_H ($CDCl_3$) 8.01 (1H, dd, $^3J_{H\text{-}H}$ 7.0 Hz $^3J_{H\text{-}P}$ 14.0 Hz, H^5), 8.00 (2H, dd, $^3J_{H\text{-}H}$ 8.0 Hz $^3J_{H\text{-}P}$ 12.0 Hz, H^o), 7.79 (1H, td, $^3J_{H\text{-}H}$ 7.0 Hz $^4J_{H\text{-}P}$ 3.0 Hz, H^4), 7.53 (1H, t, $^3J_{H\text{-}H}$ 8.0 Hz,

H^{p}), 7.52 (1H, d, $^{3}J_{H\text{-}H}$ 7.0 Hz, H^{3}), 7.46 (2H, td, $^{3}J_{H\text{-}H}$ 8.0 Hz $^{4}J_{H\text{-}P}$ 4.0 Hz, H^{m}), 4.57 (2H, s, H^{1}), 4.13 (2H, qd, $^{3}J_{H\text{-}H}$ 7.0 Hz $^{3}J_{H\text{-}P}$ 4.5 Hz, H^{7}), 1.37 (3H, t, $^{3}J_{H\text{-}H}$ 7.0 Hz, H^{8}); δ_C ($CDCl_3$) 158.0 (d, $^{3}J_{C\text{-}P}$ 20 Hz, C^{2}), 154.7 (d, $^{1}J_{C\text{-}P}$ 167 Hz, C^{6}), 137.3 (d, $^{3}J_{C\text{-}P}$ 10 Hz, C^{4}), 132.7 (d, $^{2}J_{C\text{-}P}$ 12 Hz, C^{o}), 132.6 (d, $^{4}J_{C\text{-}P}$ 4 Hz, C^{p}), 130.2 (d, $^{1}J_{C\text{-}P}$ 136 Hz, C^{i}), 128.5 (d, $^{3}J_{C\text{-}P}$ 9 Hz, C^{m}), 127.5 (d, $^{2}J_{C\text{-}P}$ 22 Hz, C^{5}), 125.8 (d, $^{4}J_{C\text{-}P}$ 4 Hz, C^{3}), 62.1 (d, $^{2}J_{C\text{-}P}$ 6 Hz, C^{7}), 33.6 (C^{1}), 16.7 (C^{8}); δ_P ($CDCl_3$) 26.0; *m/z* (HRMS^{+}) 340.0122 [M(^{79}Br) + H]$^{+}$ ($C_{14}H_{16}O_2NP^{79}Br$ requires 340.0102), 342.0098 [M(^{81}Br) + H]$^{+}$ ($C_{14}H_{16}O_2NP^{81}Br$ requires 342.0088); R_f = 0.57 (silica, CH_2Cl_2 : 5 % MeOH).



1,4,7-Tri[ethyl (6-methylpyridin-2-yl)(phenyl)phosphinate]-1,4,7-triazacyclononane,

1,4,7-Triazacyclononane (14 mg, 0.11 mmol), ethyl [6-(bromomethyl)pyridin-2-yl](phenyl)phosphinate, ***9***, (130 mg, 0.38 mmol) and K_2CO_3 (51 mg, 0.38 mmol) were stirred in dry CH_3CN (5 mL) at 80 °C for 20 h under argon. The reaction was monitored by TLC to confirm that all the brominated starting material had been consumed. The solvent was removed under reduced pressure and the resultant residue was dissolved in CH_2Cl_2 (30 mL) and washed with water (3 × 30 mL). The organic layer was dried over $MgSO_4$, filtered and the solvent was removed under reduced pressure. Purification by column chromatography on alumina (CH_2Cl_2 : 0 – 2 % MeOH in 0.05 % increments) gave the *title compound* as a glassy yellow solid (60 mg, 62 %); δ_H ($CDCl_3$) 7.96 (3H, dd, $^{3}J_{H\text{-}H}$ 7.0 Hz $^{3}J_{H\text{-}P}$ 14.0 Hz, H^{5}), 7.95 (6H, dd, $^{3}J_{H\text{-}H}$ 8.0 Hz $^{3}J_{H\text{-}P}$ 12.0 Hz, H^{o}), 7.74 (3H, td, $^{3}J_{H\text{-}H}$ 7.0 Hz $^{4}J_{H\text{-}P}$ 3.0 Hz, H^{4}), 7.54 (3H, d, $^{3}J_{H\text{-}H}$ 7.0 Hz, H^{3}), 7.47 (3H, t, $^{3}J_{H\text{-}H}$ 8.0 Hz, H^{p}), 7.39 (6H, td, $^{3}J_{H\text{-}H}$ 8.0 Hz $^{4}J_{H\text{-}P}$ 4.0 Hz, H^{m}), 4.11 (6H, qd, $^{3}J_{H\text{-}H}$ 7.0 Hz $^{3}J_{H\text{-}P}$ 4.5 Hz, H^{7}), 3.83 (6H, br s, H^{1}), 2.74 (12H, br s, *ring* Hs), 1.34 (9H, t, $^{3}J_{H\text{-}H}$ 7.0 Hz, H^{8}); δ_C ($CDCl_3$) 161.7 (d, $^{3}J_{C\text{-}P}$ 20 Hz, C^{2}), 153.9 (d, $^{1}J_{C\text{-}P}$ 167 Hz, C^{6}), 136.4 (d, $^{3}J_{C\text{-}P}$ 10 Hz, C^{4}), 132.6 (d, $^{4}J_{C\text{-}P}$ 4 Hz, C^{p}), 132.5 (d, $^{2}J_{C\text{-}P}$ 12 Hz, C^{o}), 130.5 (d, $^{1}J_{C\text{-}P}$ 136 Hz, C^{i}), 128.4 (d, $^{3}J_{C\text{-}P}$ 9 Hz, C^{m}), 126.6 (d, $^{2}J_{C\text{-}P}$ 22 Hz, C^{5}), 125.6 (d, $^{4}J_{C\text{-}P}$ 4 Hz, C^{3}), 64.1 (C^{1}), 61.8 (d, $^{2}J_{C\text{-}P}$ 6 Hz, C^{7}), 55.7 (*ring* Cs), 16.7 (C^{8}); δ_P ($CDCl_3$) 26.7; *m/z* (HRMS^{+}) 907.3641 [M + H]$^{+}$ ($C_{48}H_{58}O_6N_6P_3$ requires 907.3631); R_f = 0.56 (alumina, CH_2Cl_2 : 5 % MeOH).



Europium(III) complex of 1,4,7-tri[ethyl (6-methylpyridin-2-yl)(phenyl)phosphinate]-1,4,7-triazacyclononane, [EuL^{3}]

1,4,7-Tri[ethyl (6-methylpyridin-2-yl)(phenyl)phosphinate]-1,4,7-triazacyclononane (38 mg, 0.042 mmol) was dissolved in HCl (6M, 8 mL) and the solution was stirred at 100 °C for 16 h. The solvent was lyophilised to give a yellow solid, ***3***. Hydrolysis of the OEt groups was confirmed by ^{1}H- and ^{31}P-NMR (δ_P ($CDCl_3$) 16.0). The

solid was dissolved in H_2O – CH_3OH (1 : 1 v/v, 6 mL) and the pH of the solution adjusted to 5.8 using NaOH. $Eu(OAc)_3$ (18 mg, 0.046 mmol) was added and the solution was stirred at 50 °C for 18 h. After allowing the solution to cool to room temperature, the pH was raised to 10 by the addition of NH_3. The solution was stirred for 1 h causing excess Eu^{3+} to precipitate as $Eu(OH)_3$, which was removed by syringe filtration. Adjustment of the pH to 5.8 by the addition of CH_3CO_2H, followed by lyophilisation of the solvent, gave a solid, which was purified by column chromatography (silica, CH_2Cl_2: 20 % CH_3OH: 1 % NH_3) to give the *title compound* as a white solid (32 mg, 82 %); *m*/*z* (HRMS$^+$) 971.1675 [M + H]$^+$ ($C_{42}H_{43}O_6N_6P_3{}^{151}Eu$ requires 971.1656); δ_P (CD_3OD, 9.4T, 295K) +16.6; τ_{H_2O} = 1.26 ms, τ_{D_2O} = 1.54 ms, t_R = 6.81 min.

Cerium(III) complex of 1,4,7-tri[ethyl (6-methylpyridin-2-yl)(phenyl)phosphinate]-1,4,7-triazacyclononane, [CeL^3]

An analogous procedure to that described for the synthesis of [EuL^3] was followed using 1,4,7-tri[ethyl (6-methylpyridin-2-yl)(phenyl)phosphinate]-1,4,7-triazacyclononane (15 mg, 0.017 mmol) and $Ce(OAc)_3$ (7.0 mg, 0.018 mmol) to give the *title compound* as a white solid (12.2 mg, 77 %); *m*/*z* (ESI-MS$^+$) 960.3 [M (^{140}Ce) + H]$^+$; δ_P (CD_3OD, 9.4T, 295K) +27.8; t_R = 6.76 min.

Praseodymium(III) complex of 1,4,7-tri[ethyl (6-methylpyridin-2-yl)(phenyl)phosphinate]-1,4,7-triazacyclononane, [PrL^3]

An analogous procedure to that described for the synthesis of [EuL^3] was followed using 1,4,7-tri[ethyl (6-methylpyridin-2-yl)(phenyl)phosphinate]-1,4,7-triazacyclononane (15 mg, 0.017 mmol) and $Pr(OAc)_3$ (7.0 mg, 0.018 mmol) to give the *title compound* as a white solid (13.3 mg, 84 %); *m*/*z* (ESI-MS$^+$) 961.3 [M (^{141}Pr) + H]$^+$; δ_P (CD_3OD, 9.4T, 295K) +31.3; t_R = 6.78 min.

Neodymium(III) complex of 1,4,7-tri[ethyl (6-methylpyridin-2-yl)(phenyl)phosphinate]-1,4,7-triazacyclononane, [NdL^3]

An analogous procedure to that described for the synthesis of [EuL^3] was followed using 1,4,7-tri[ethyl (6-methylpyridin-2-yl)(phenyl)phosphinate]-1,4,7-triazacyclononane (15 mg, 0.017 mmol) and $Nd(OAc)_3$ (7.1 mg, 0.018 mmol) to give the *title compound* as a white solid (12.7 mg, 80 %); *m*/*z* (ESI-MS$^+$) 964.2 [M (^{144}Nd) + H]$^+$; δ_P (CD_3OD, 9.4T, 295K) +21.0; t_R = 6.78 min.

Samarium(III) complex of 1,4,7-tri[ethyl (6-methylpyridin-2-yl)(phenyl)phosphinate]-1,4,7-triazacyclononane, [SmL^3]

An analogous procedure to that described for the synthesis of [EuL^3] was followed using 1,4,7-tri[ethyl (6-methylpyridin-2-yl)(phenyl)phosphinate]-1,4,7-triazacyclononane (15 mg, 0.017 mmol) and $Sm(OAc)_3$ (7.2 mg, 0.018 mmol) to give the *title compound* as a white solid (12.5 mg, 78 %); *m*/*z* (ESI-MS$^+$) 972.2 [M (^{152}Sm) + H]$^+$; δ_P (CD_3OD, 9.4T, 295K) +31.4; t_R = 6.79 min.

Gadolinium(III) complex of 1,4,7-tri[ethyl (6-methylpyridin-2-yl)(phenyl)phosphinate]-1,4,7-triazacyclononane, [GdL^3]

An analogous procedure to that described for the synthesis of [EuL^3] was followed using 1,4,7-tri[ethyl (6-methylpyridin-2-yl)(phenyl)phosphinate]-1,4,7-triazacyclononane (15 mg, 0.017 mmol) and $Gd(OAc)_3$ (7.3 mg, 0.018 mmol) to give the *title compound* as a white solid (13.0 mg, 81 %); *m*/*z* (ESI-MS$^+$) 976.2 [M (^{156}Gd) + H]$^+$; t_R = 6.80 min.

Terbium(III) complex of 1,4,7-tri[ethyl (6-methylpyridin-2-yl)(phenyl)phosphinate]-1,4,7-triazacyclononane, [TbL^3]

An analogous procedure to that described for the synthesis of [EuL^3] was followed using 1,4,7-tri[ethyl (6-methylpyridin-2-yl)(phenyl)phosphinate]-1,4,7-triazacyclononane (15 mg, 0.017 mmol) and $Tb(OAc)_3$ (7.3 mg,

0.018 mmol) to give the *title compound* as a white solid (12.6 mg, 78 %); *m/z* (ESI-MS$^+$) 979.2 [M (^{159}Tb) + H]$^+$; δ_P (CD_3OD, 9.4T, 295K) -35.7; τ_{H_2O} = 1.63 ms, τ_{D_2O} = 1.84 ms, t_R = 6.81 min.

Dysprosium(III) complex of 1,4,7-tri[ethyl (6-methylpyridin-2-yl)(phenyl)phosphinate]-1,4,7-triazacyclononane, [DyL^3]

An analogous procedure to that described for the synthesis of [EuL^3] was followed using 1,4,7-tri[ethyl (6-methylpyridin-2-yl)(phenyl)phosphinate]-1,4,7-triazacyclononane (15 mg, 0.017 mmol) and $Dy(OAc)_3$ (7.4 mg, 0.018 mmol) to give the *title compound* as a white solid (13.0 mg, 80 %); *m/z* (ESI-MS$^+$) 984.2 [M (^{164}Dy) + H]$^+$; δ_P (CD_3OD, 9.4T, 295K) -13.9; t_R = 6.82 min.

Holmium(III) complex of 1,4,7-tri[ethyl (6-methylpyridin-2-yl)(phenyl)phosphinate]-1,4,7-triazacyclononane, [HoL^3]

An analogous procedure to that described for the synthesis of [EuL^3] was followed using 1,4,7-tri[ethyl (6-methylpyridin-2-yl)(phenyl)phosphinate]-1,4,7-triazacyclononane (15 mg, 0.017 mmol) and $Ho(OAc)_3$ (7.4 mg, 0.018 mmol) to give the *title compound* as a white solid (12.7 mg, 78 %); *m/z* (ESI-MS$^+$) 985.3 [M (^{165}Ho) + H]$^+$; δ_P (CD_3OD, 9.4T, 295K) -24.6; t_R = 6.82 min.

Erbium(III) complex of 1,4,7-tri[ethyl (6-methylpyridin-2-yl)(phenyl)phosphinate]-1,4,7-triazacyclononane, [ErL^3]

An analogous procedure to that described for the synthesis of [EuL^3] was followed using 1,4,7-tri[ethyl (6-methylpyridin-2-yl)(phenyl)phosphinate]-1,4,7-triazacyclononane (15 mg, 0.017 mmol) and $Er(OAc)_3$ (7.5 mg, 0.018 mmol) to give the *title compound* as a white solid (14.3 mg, 88 %); *m/z* (ESI-MS$^+$) 988.2 [M (^{168}Er) + H]$^+$; δ_P (CD_3OD, 9.4T, 295K) -10.5; t_R = 6.82 min.

Thulium(III) complex of 1,4,7-tri[ethyl (6-methylpyridin-2-yl)(phenyl)phosphinate]-1,4,7-triazacyclononane, [TmL^3]

An analogous procedure to that described for the synthesis of [EuL^3] was followed using 1,4,7-tri[ethyl (6-methylpyridin-2-yl)(phenyl)phosphinate]-1,4,7-triazacyclononane (15 mg, 0.017 mmol) and $Tm(OAc)_3$ (7.5 mg, 0.018 mmol) to give the *title compound* as a white solid (12.9 mg, 79 %); *m/z* (ESI-MS$^+$) 989.3 [M (^{169}Tm) + H]$^+$; δ_P (CD_3OD, 9.4T, 295K) +8.4; t_R = 6.82 min.

Ytterbium(III) complex of 1,4,7-tri[ethyl (6-methylpyridin-2-yl)(phenyl)phosphinate]-1,4,7-triazacyclononane, [YbL^3]

An analogous procedure to that described for the synthesis of [EuL^3] was followed using 1,4,7-tri[ethyl (6-methylpyridin-2-yl)(phenyl)phosphinate]-1,4,7-triazacyclononane (15 mg, 0.017 mmol) and $Yb(OAc)_3$ (7.6 mg, 0.018 mmol) to give the *title compound* as a white solid (13.6 mg, 83 %); *m/z* (ESI-MS$^+$) 994.2 [M (^{174}Yb) + H]$^+$; δ_P (CD_3OD, 9.4T, 295K $_3$) +17.7; t_R = 6.82 min.

2. X-ray crystallography.

Single crystal X-ray data for the complexes [Ln.L^3] were collected at 120K on a Bruker SMART-CCD 6000 (Ln = Ho, Sm, Tm, Yb) and Agilent Technologies Gemini S Ultra (Ln = Nd, Eu) diffractometers (ω-scan, 0.3-0.5°/frame) equipped with Cryostream (Oxford Cryosystems) open-flow nitrogen cryostates. The structures were solved by Patterson method and refined by full-matrix least squares on F^2 for all data using SHELXTL [Sheldrick, G.M. (2008) *Acta Cryst.*, A64, 112-122] and OLEX2 [O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, (2009) *J. Appl. Cryst.*, 42, 339-341] software. All non-disordered non-hydrogen atoms were refined with anisotropic displacement parameters, disordered atoms of Ph-rings and P=O groups were refined isotropically with fixed SOF = 0.5. All hydrogen atoms were placed into calculated positions and refined in "riding"-mode. All structures contain a number of severely disordered solvent

molecules. Their contribution to the scattering factors has been taken into account using the MASK procedure of OLEX2 software.

3. Electronic Circular Dichroism

CD spectra were recorded at room temperature on a Jasco J-715 Spectropolarimeter using 2.4 mM samples in methanol and a 0.02 cm quartz cell, with the following conditions: 50 nm/min scanning speed, 0.1 nm data pitch, 2.0 nm bandwith, 1 sec response time, 4 accumulations.
DFT calculations were run with Spartan '08 [Wavefunction, Inc., Irvine, CA] with defaults grids and convergence criteria. TDDFT calculations were run with Gaussian '09 [Revision A.02; Gaussian, Inc., Wallingford, CT, 2009] with default grids and convergence criteria. The input geometry for the calculations was obtained from the X-ray geometry of the TbL^3 complex by replacing Tb with La. Such geometry was symmetrised to C3 symmetry and optimized with DFT method using the B3LYP functional and the LanL2DZ basis set, consisting of a D95V set for hydrogen and first-row elements, and a Los Alamos effective core potential (ECP) plus a DZ set for the valence electrons of La [see Gaussian '09 documentation at www.gaussian.com/g_tech/g_ur/g09help.htm for references on DFT functionals and basis sets]. In the geometry optimization, the distances between La and N/O atoms were restrained to the values found by X-ray.
CD calculations were run with the TDDFT method using the CAM-B3LYP functional and the SVP basis set for H, C, N and O, and the Stuttgart-Dresden set SDD for La, including ECP for 48 core electrons (MWB48). Sixty excited states were included in the calculation. ECD spectra were generated using the program SpecDis [v. 1.50, T. Bruhn, V. Hemberger, A. Schaumlöffel, G. Bringmann, Univ. Wuerzburg, Germany, 2010] by applying a Gaussian band shape with 0.3 eV exponential half-width, from dipole-length rotational strengths; the difference fromdipole-velocity values was negligible (<10%) for most transitions.

4. Representative 1-H NMR spectra of [Ln.L^3] (next page)

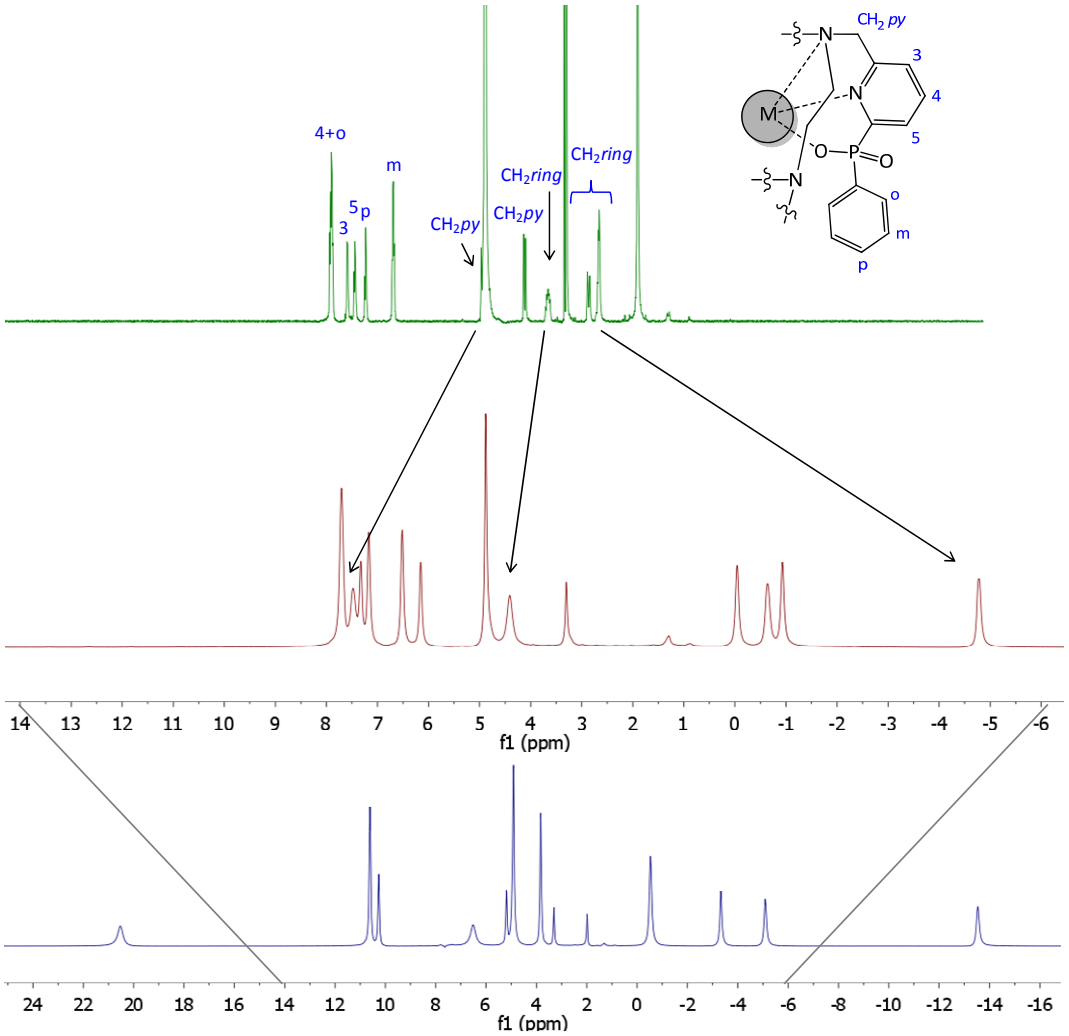


Figure ^{1}H-NMR traces for **[Y·L^{3}]** (*green*), **[Eu·L^{3}]** (*red*) and **[Yb·L^{3}]** (*blue*) (MeOH, 295 K, 9.4T).