Tri- and tetra-substituted cyclen based lanthanide(III) ion complexes as ribonuclease mimics: A study into the effect of $\log K_a$, hydration and hydrophobicity on phosphodiester hydrolysis of the RNA-model 2-hydroxypropyl-4-nitrophenyl phosphate (HPNP)

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Supporting Information



Figure S1. ¹³ $C{^{1}_{4}H}$ decoupled NMR (CD₃OD, 100 MHz) of 4 exhibiting C₂ of symmetry through the N_1N_7 axis.



Figure S2 ¹*H NMR (D*₆-*DMSO, 400 MHz) of* **6** *exhibiting* C_4 *symmetry.*



Figure S3 ¹*H NMR (D₆-DMSO, 400 MHz) of* **6.***Eu exhibiting broad resonances over large ppm range*



Figure S4. Typical titration curves of the protonated ligand **3**, in the absence and presence of $La(ClO_4)_3$ and $Eu(ClO_4)_3$ against NEt₄OH at 25 °C. [**3**]_{total} = 9.4 x 10⁻⁴ M, [La(III)]_{total}, [Eu(III)]_{total}, = 1.0 x 10⁻³ M, [H⁺]_{total} = 8.17 x 10⁻³ M, [NEt₄OH] = 0.103 M, I = 0.10 M (NEt₄ClO₄), total volume = 10 cm³.



Figure S5. The pH-rate profile for the hydrolysis of 0.14 mM HPNP at 37 °C by **3.La** (0.18 mM) (pink) and **4.La** (0.18 mM) (blue). Each data point is an average of 2-3 measurements, agreeing to within 15%. The error bars are determined from the average of the 2-3 measurements.



Figure S6. Speciation variation of ligand **4**, showing the species present in H₂O at various pH in which $[\mathbf{4}]_{total} = 7.2 \times 10^{-4} \text{ M}$, $[\text{Eu}(\text{III})]_{total} = 7.0 \times 10^{-4} \text{ M}$, I = 0.10 M (NEt₄ClO₄) at 25 °C. Speciation is shown relative to the total concentration of ligand **4**.



Figure S7. The pH-rate profile for the hydrolysis of 0.14 mM HPNP at 37 °C by **5.La** (0.18 mM). Each data point is an average of 2-3 measurements, agreeing to within 15%. The error bars are determined from the average of the 2-3 measurements.