# Supporting Information for: Accessing Lanthanide-based, In Situ Illuminated Optical Turn-On Probes by Modulation of the Antenna Triplet State Energy

Alexia G. Cosby[a], Joshua J. Woods[b], Patrick Nawrocki[c], Thomas J. Sørensen[c], Justin J. Wilson[b], and Eszter Boros[a,*]

[a]Department of Chemistry, Stony Brook University, Stony Brook, New York, 11794, United States; [b]Department of Chemistry and Chemical Biology, Cornell University, Cornell University, Ithaca, New York, 14853, United States; [c] Nano-Science Center & Department of Chemistry, University of Copenhagen, Universitetsparken 5, 2100, København Ø, Denmark

*eszter.boros@stonybrook.edu

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**Table S1**. Summary of relevant discrete lanthanide turn-on probes

| "Off/On" | Probe | $\Phi_{Ln}$ | $\Phi_{Ln}$ x-fold increase | Em. x-fold increase | [Probe] | Analyte/ Concentration | Time-gated? (Y/N) | Ref |
|---|---|---|---|---|---|---|---|---|
| Off | EuBn | 0.0012 | -- | -- | -- | -- | | |
| On | EuCou | 0.0108 | **9** | ND | -- | -- | | |
| Off | TbBn | 0.0041 | -- | -- | -- | -- | | |
| On | TbCou | 0.0163 | **4** | ND | 50 μM | Various enzymes/0.1-5 U | Y | [1] |
| Off | EuL1 | 0.07 | -- | -- | -- | -- | | |
| On | EuL1-F | ND | ND | 9 | 20 μM | $F^-$/20-260 μM | N | [2] |
| Off | Tb-DO3A | ND | -- | -- | -- | -- | | |
| On | Tb-DO3A-trimesate | ND | ND | 11 | 50.9 μM | HO*/0.37 fM | Y | [3] |
| Off | Eu-Lys-HOPO | ND | -- | -- | -- | -- | | |
| On | Eu-Lys-HOPO + CN | ND | ND | 9 | 16 μM | $CN^-$/1.6 mM | Y | [4] |
| Off | EuL | 0.002 | | | | | | |
| On | F-(Eu)L2 | 0.047 | **24** | 22 | 49 μM | $F^-$/24 nM | N | [5] |
| Off | Eu-Lys-HOPO | ND | -- | -- | -- | -- | | |
| Off | Eu-Ser-HOPO | ND | -- | -- | -- | -- | | |
| Off | Eu-Gly-HOPO | ND | -- | -- | -- | -- | | |
| On | Eu-Lys-HOPO + $HPO_4^{2-}$ | ND | ND | 5 | -- | -- | | |
| On | Eu-Ser-HOPO + $HPO_4^{2-}$ | ND | ND | 36 | -- | -- | | |
| On | Eu-Gly-HOPO + $HPO_4^{2-}$ | ND | ND | 20 | 7.6 μM | $HPO_4^{2-}$/76 μM | Y | [6] |
| Off | Mito-NSTTA-Eu | 0.036 | -- | -- | -- | -- | | |
| Off | Mito-NSTTA-Tb | 0.0043 | -- | -- | -- | -- | | |
| On | Mito-HTTA-Eu | 0.035 | **1** | -- | -- | -- | | |
| On | Mito-HTTA-Tb | 0.147 | **34** | ND | 3.0 μM | glutathione / Cys // 5 uM | Y | [7] |
| Off | ANMTTA-Eu | 0.0023 | -- | -- | -- | -- | | |
| Off | ANMTTA-Tb | 0.0007 | -- | -- | -- | -- | | |
| On | HTTA-Eu | 0.163 | **71** | 100-600 | -- | -- | | |
| On | HTTA-Tb | 0.115 | **164** | 100-600 | 5 μM | HOCl / 70 μM | Y | [8] |
| Off | [Tb-1*$Zn_2$]$(NO_3)_4$ | 0.01 | -- | -- | -- | -- | | |
| On | [Tb-1*$Zn_2$]$(NO_3)_4$ +GMP | 0.48 | **48** | 87 | 20 μM | GMP / 20 μM | Y | [9] |
| Off | Eu.2 | 0.0045 | -- | -- | -- | -- | | |
| On | Eu.1 | 0.0056 | **1.24** | 20 | 10 μM | $HS^-$ / 250 μM | Y | [10] |
| Off | ATTA-Eu | 0.0058 | -- | -- | -- | -- | | |
| On | EP-ATTA-Eu | 0.10 | **17.2** | ND | 100 nM | $^1O_2$ / 2.8 nM | Y | [11] |

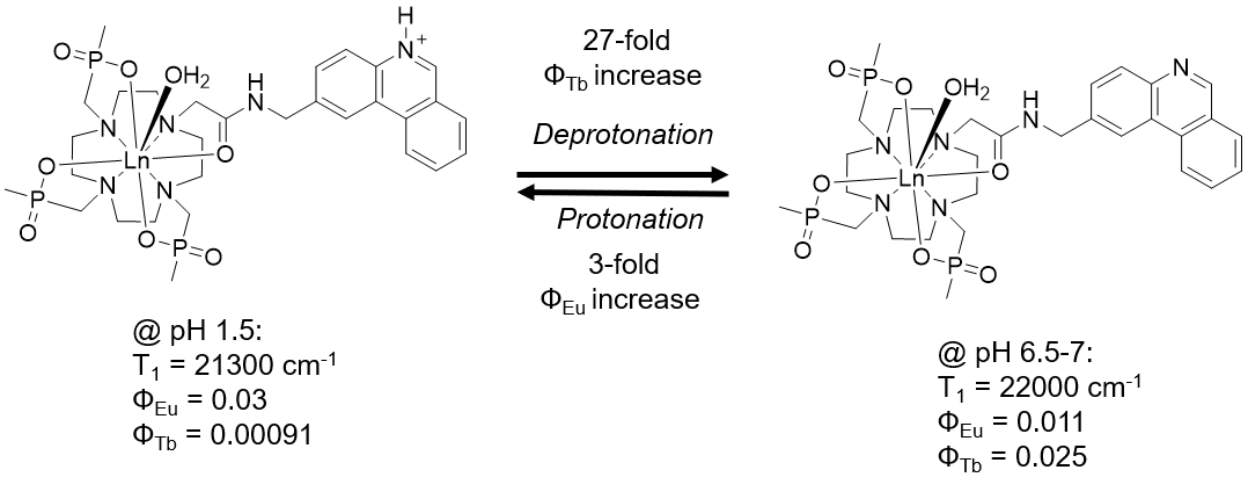



**Figure S1.** Structures and reactivity of pH-sensors developed by Parker and coworkers.[12]

## 3. Synthesis protocols, characterization, and HPLC traces

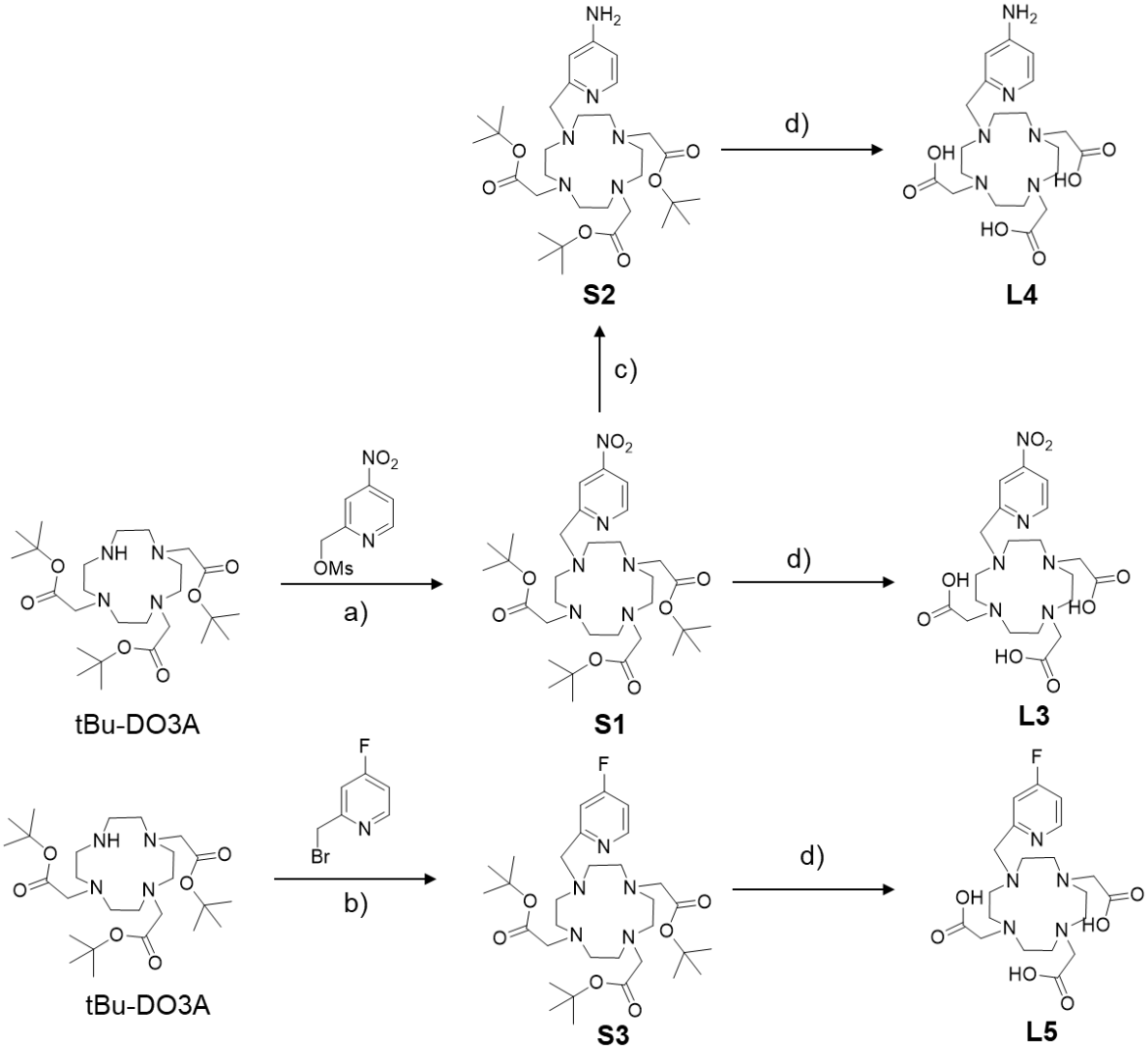



**Figure S2**. Synthetic scheme of ligands. a) dry MeCN, 8 eq. $K_2CO_3$, 90℃, 12 hr. b) dry MeCN, 8 eq. $K_2CO_3$, 90℃, 4 hr. c) 40% Pd/C, H2, dry MeOH, 2 hr. d) 2:1 TFA:DCM, RT, 12 hr.

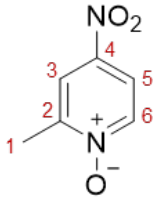
General protocols and methods featured in main mansucript.

Cryogenic phosphorescence measurements were recorded on an Cary Eclipse fluorescence spectrometer from Agilent Technologies. The spectrometer was equipped with a photomultiplier tube and a quartz cold finger dewar fitted for measurements on NMR tubes in liquid nitrogen temperatures. All complexes were dissolved in DPBS and flash frozen in an NMR tube. Phosphorescence spectra were recorded with a 2 nm data intervals and time-gated in the range 0.5 – 60 ms unless otherwise indicated. Due to large differences in quantum yields between samples

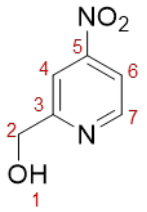
both slit sizes and detector voltage varied with the sample. The $T_1$ energy levels were determined from the gadolinium samples at 3 % of the maximum peak intensity on the high energy edge of the transition band. The Gd(**L3**) exhibited the presence of several emitting species and therefore a convolution on the high energy side of the band. Due to the greater error the $T_1$ energy level was determined at the 10 % intensity of the maxima.

Phosphorescence decays were collected in similar fashion as the phosphorescence spectra in the 0.5 – 80 ms range and fitted to single, double or tripple component exponential decay funtions using the Origin software.

### 3. Synthesis and characterization




**2-methyl-4-nitropyridine 1-oxide, 1.** Concentrated $H_2SO_4$ (9.19 g) was massed and put into a 100 ml RBF on a salt-ice bath, to which 2-methylpyridine N-oxide (1.45 g, 1.31 mL) was added dropwise with stirring. Concentrated $HNO_3$ (9.02 g) was massed and added slowly over 10 minutes. After an additional 10 minutes at 0℃, the flask was moved to a oil bath preheated to 45 ℃. The temperature was slowly increased to 110℃ over 1 hour, and then refluxed for 2 hours. After cooling to room temperature and allowing excess gases to dissipate, the mixture was poured over ice water (100 g). The aqueous phase was extracted with DCM (3x 50 mL), washed with saturated $K_2CO_3$ (120 mL) and extracted again with DCM (50 mL). After drying over $Na_2SO_4$, the final solution was concentrated in vacuo to yield a yellow crystalline solid (0.944g, 47%). $^1$H NMR ($CDCl_3$, 500 MHz): δ 8.31 (d, 1H, $H^5$), 8.14 (d, 1H, $H^3$), 7.99 (d, 1H, $H^6$), 2.57 (s, 3H, $H^1$).$^{13}$C NMR ($CDCl_3$, 125 MHz): δ 150.61 ($C^2$), 141.64 ($C^4$), 140.02($C^6$), 120.64 ($C^5$), 118.07 ($C^3$), 18.06 ($C^1$). ESI-MS: calcd. for $C_6H_6N_2O_3$: 154.04.




**2-(Hydroxymethyl)-4-nitropyridine, 2.** Trifluoroacetic acid anhydride (3 mL, 21.2 mmol, 3.5 eq) in 2 mL DCM was added dropwise, to a solution of **1** (0.944g, 6.10 mmol, 1 eq) in 10 mL dry DCM and refluxed overnight. The mixture was concentrated and then redissolved in 40 mL $H_2O$. The pH was brought up to 8 with $K_2CO_3$ and stirred at RT for 5 hours, after which KOH was added to increase the pH to 11. The aqueous phase was extracted with DCM (3x 50 mL), dried over $Na_2SO_4$, and concentrated to dryness in vacuo. The resutling orange crystalline solid was used without further purification (0.555 g, 59%). $^1$H NMR ($CDCl_3$, 500 MHz): δ 8.86 (d, 1H, $H^7$), 8.08 (s, 1H, $H^4$), 7.95 (d, 1H, $H^6$), 4.95 (s, 2H, $H^2$), 3.20 (br s, 1H, $H^1$).$^{13}$C NMR ($CDCl_3$, 125 MHz): δ 163.15 ($C^3$), 154.41 ($C^7$), 150.99 ($C^5$), 114.95 ($C^4$), 113.13 ($C^6$), 64.39 ($C^2$). ESI-MS: calcd. for $C_6H_6N_2O_3$: 154.02.

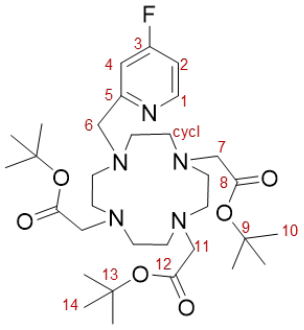
**2-[(Methylsulfonyloxy)methyl]-4-nitropyridine, 3**. Triethylamine (390 µL, 2.8 mmol, 3 eq) was added to a solution of **2** (0.143 g, 0.93 mmol, 1 eq) in 10 mL dry THF. The solution was cooled to 0℃ under an atmosphere of $N_2$. Methanesulfonyl chloride (110 µL, 1.39 mmol, 1.5 eq) was added dropwise and the solution stirred at 0℃ for 20 minutes. The residue was concentreated in vacuo, redissolved in DCM and washed with brine. The aqueous layer was further extracted with DCM, and the organic layers combined, dried over $Na_2SO_4$ and concentrated. The crude material was subject to silica column chromatography (10% MeOH in DCM, 8 cm x 3 cm silica plug) to afford a yellow oil (51%, 73.0 mg, 0.314 mmol, $R_t$ [2% MeOH in DCM]: 0.76). $^1$H NMR ($CDCl_3$, 400 MHz): δ 8.90 (d, 1H, $H^7$), 8.17 (s, 1H, $H^4$), 8.00, (d, 1H, $H^6$), 5.43 (s, 2H, $H^2$), 3.16 (s, 3H, $H^1$). $^{13}$C NMR ($CDCl_3$, 100 MHz): δ 157.33 ($C^3$), 154.51 ($C^7$), 151.82 ($C^5$), 116.06 ($C^4$), 114.49 ($C^6$), 69.66 ($C^1$), 37.98 ($C^2$).

***tert*-Butyl {4,10-bis(*tert*-butoxycarbonylmethyl)-7-[(4-nitro-2-pyridyl)methyl]-1,4,7,10-tetraaza-1-cyclododecyl}acetate, S1. 3** (74.5 mg, 0.32 mmol) was dissolved in anhydrous acetonitrile and added dropwise to a solution of tBu-DO3A (156 mg, 0.30 mmol) and $K_2CO_3$ (491 mg, 2.1 mmol) in 4 mL anhydrous acetonitrile. The mixture refluxed for 2 h and was then filtered and concentrated. The filtrate was purified using reverse-phase chromatography (method D), with the product eluting from 13-14 column volumes (CV). The fractions containing product were pooled and the solvent was removed in vacuo to afford **S1** as a yellow oil (23%, 47.8 mg, 0.074 mmol, $R_{CV}$ (method D) = 13-15 CV). $^1$H NMR ($CD_3OD$, 500 MHz): δ 8.86 (s, 1H, $H^1$), 8.23 (m, 2H, $H^{2,4}$), 4.21 (br s, 2H, $H^6$), 3.65-3.51 (m, 14H, $H^{cyc}$), 3.25-3.02 (m, 8H, $H^{7,11,cycl}$), 1.55 (s, 9H, $H^{14}$), 1.33 (s, 18H, $H^{10}$).$^{13}$C NMR ($CD_3OD$, 125 MHz): δ 172.51 ($C^8$), 166.95 ($C^{12}$), 156.15 ($C^5$), 152.16 ($C^1$), 117.11 ($C^3$), 116.06 ($C^4$), 114.20 ($C^2$), 86.08 ($C^9$), 83.40 ($C^{13}$), 58.17 ($C^7$), 56.14 ($C^{cycl}$), 55.18 ($C^6$), 53.22 ($C^{cycl}$), 50.05 ($C^{cycl}$), 28.51 ($C^{10}$), 28.39 ($C^{14}$). ESI-MS: calcd. for $C_{32}H_{54}N_6O_8$: 650.40. Found: 651.2 $[M+H]^+$.

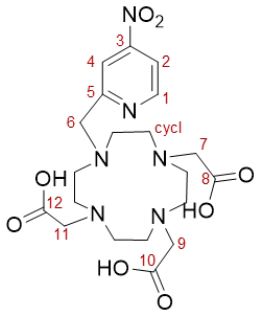
***tert*-Butyl {10-[(4-amino-2-pyridyl)methyl]-4,7-bis(*tert*-butoxycarbonylmethyl)-1,4,7,10-tetraaza-1-cyclododecyl}acetate, S2.** 40 mol % Pd/C (10.8 mg) was added to **S1** (27.4mg, 0.042 mmol) in 2.5 mL dry methanol and placed under $H_2$. Upon completion of the reaction after 2 hours as confirmed by LRMS, the mixture was filtered, and the filtrate was purified using semi-preparative HPLC (method A), with the product eluting at 10.1 minutes. The fractions containing product were pooled and the solvent was removed in vacuo to afford **S2** as a white solid (45%, 11.6 mg, 0.019 mmol, $R_t$ (method A) = 10.1 minutes). $^1$H NMR ($CD_3OD$, 500 MHz): 7.90 (d, 1H, $H^1$), 6.84 (m, 1H, $H^4$), 6.74 (s, 1H, $H^2$), 4.05 (s, 2H, $H^6$), 3.64 (m, 14H, $H^{cycl}$), 3.11-3.01 (m, 8H, $H^{7,11,cycl}$), 1.55 (s, 9H, $H^{14}$), 1.49 (s, 18H, $H^{10}$). $^{13}$C NMR ($CD_3OD$, 125 MHz): δ 170.38 ($C^{8,12}$), 161.80 ($C^5$), 141.19 ($C^1$), 140.93 ($C^3$), 110.05 ($C^4$), 109.34 ($C^2$), 84.48 ($C^9$), 84.02 ($C^{13}$), 56.39 ($C^7$), 55.54

($C^{cycl}$), 55.35 ($C^{cycl}$), 54.72 ($C^{11}$), 52.22 ($C^{cycl}$), 51.40 ($C^{cycl}$), 49.62 ($C^{6}$),28.51 ($C^{10}$), 28.39 ($C^{14}$). ESI-MS: calcd. for $C_{32}H_{56}N_6O_6$: 620.43. Found: 621.2 $[M+H]^+$.

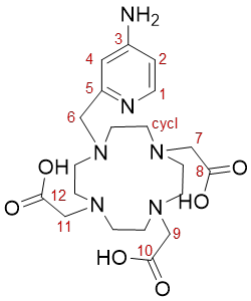
***tert*-Butyl {4,10-bis(*tert*-butoxycarbonylmethyl)-7-[(4-fluoro-2-pyridyl)methyl]-1,4,7,10-tetraaza-1-cyclododecyl}acetate, S3.** 2-methyl-4-fluoropyridine (19.2 mg, 0.102 mmol) and $K_2CO_3$ (67.3 mg, 0.510) mmol) was added dropwise to tBu-DO3A (52.5 mg, 0.102 mmol) in anhydrous acetonitrile and heat at reflux for 4 hours. Upon completion of the reaction as confirmed by LRMS, the mixture was filtered, and the filtrate was purified using semi-preparative HPLC (method A), with the product eluting at 14.1 minutes. The fractions containing product were pooled and the solvent was removed in vacuo to afford **6** as a yellow oil (24%, 15.2 mg, 0.023 mmol, $R_t$ (method A) = 14.1 minutes). $^1$H NMR ($CD_3OD$, 700 MHz): 8.56 (m, 1H, $H^1$), 7.29 (d, 2H, $H^{2,4}$), 4.76 (s, 2H, $H^6$), 4.22 (s, 2H, $H^{11}$), 3.75-3.49 (m, 12H, $H^{cycl}$), 3.23-3.03 (m, 8H, $H^{7,cycl}$), 1.57 (s, 9H, $H^{14}$), 1.35 (s, 18H, $H^{10}$). $^{13}$C NMR ($CD_3OD$, 175 MHz): δ 172.25 ($C^8$), 171.49 ($C^3$), 170.00 ($C^5$), 166.96 ($C^{12}$), 52.47 ($C^1$), 112.63 ($C^4$), 111.58 ($C^2$), 86.07 ($C^9$), 83.41 ($C^{13}$), 58.12 ($C^7$), 56.23 ($C^{cycl}$), 55.10 ($C^{11}$), 53.05 ($C^{cycl}$), 50.09 ($C^{cycl}$), 49.52 ($C^6$), 28.52 ($C^{10}$), 28.42 ($C^{14}$). $^{19}$F NMR: ($CD_3OD$, 376 MHz): -101.24. ESI-MS: calcd. for $C_{32}H_{54}FN_5O_6$: 623.41. Found: 624.1 $[M+H]^+$.




**{4,10-Bis(carboxymethyl)-7-[(4-nitro-2-pyridyl)methyl]-1,4,7,10-tetraaza-1-cyclododecyl}acetic acid, L3. S1** (34.1 mg, 0.023 mmol) was added to a 2:1 solution of TFA and DCM and stirred overnight at room temperature. The solvent was removed in vacuo, and the product was dissolved in $H_2O$. The solution was then lyophilized to yield **L3** as an off-white solid (11.1 mg, 0.022 mmo, $R_t$ (method C) = 3.0 minutes). $^1$H NMR ($CD_3OD$, 500 MHz): δ 8.88 (d, 1H, $H^1$), 8.23 (s, 1H, $H^4$), 8.10 (s, 1H, $H^2$), 4.13 (br s, 2H, $H^6$), 3.76-3.57 (m, 16H, $H^{9,cycl}$), 3.23-3.21 (m, 6H, $H^{7,11,cycl}$). $^{13}$C NMR ($CD_3OD$, 125 MHz): δ 173.12 ($C^{8,11}$), 169.36 ($C^{10}$), 159.54 ($C^5$), 156.12 ($C^1$), 152.71 ($C^3$), 117.43 ($C^4$), 116.77 ($C^2$), 58.33 ($C^6$), 55.34 ($C^{cycl}$), 54.12 ($C^{7,11}$), 52.25 ($C^{cycl}$), 50.48 ($C^{cycl}$), 49.62 ($C^9$). ESI-MS calcd. for $C_{20}H_{30}N_6O_8$: 482.2125. Found: 483.2198 $[M+H]^+$.

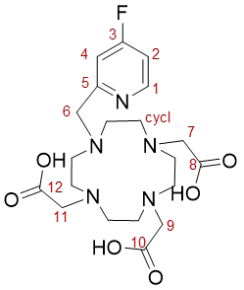



**{10-[(4-Amino-2-pyridyl)methyl]-4,7-bis(carboxymethyl)-1,4,7,10-tetraaza-1-cyclododecyl}acetic acid, L4. S2** (7.1 mg, 0.011 mmol) was added to a 2:1 solution of TFA and DCM and stirred overnight at room temperature. The solvent was removed in vacuo, and the product was dissolved in $H_2O$. The solution was then lyophilized to yield **L4** as an off-white solid (4.7 mg, 0.010 mmol, (method C) = 1.89 minutes). $^1$H NMR ($CD_3OD$, 400 MHz): 7.90 (d, 1H, $H^1$), 6.86 (s, 1H, $H^4$), 6.72 (d, 2H, $H^2$), 4.07 (br s, 2H, $H^6$), 3.96-3.66 (m, 4H, $H^{7,11}$), 3.26-2.93 (m, 18H, $H^{cycl,9}$). $^{13}$C NMR ($CD_3OD$, 100 MHz): δ 177.27 ($C^8$), 176.46 ($C^{12}$), 175.85 ($C^{10}$), 161.89 ($C^5$), 149.85 ($C^1$), 142.07 ($C^3$), 111.23 ($C^4$), 109.06 ($C^2$), 57.47 ($C^9$), 56.14 ($C^{cycl}$), 56.13 ($C^7$), 55.44



($C^{cycl}$), 54.34 ($C^{cycl}$), 51.785 ($C^{6}$). ESI-MS calcd. for $C_{20}H_{32}N_6O_6$: 452.2383. Found: 453.2457 $[M+H]^+$.

**{4,10-Bis(carboxymethyl)-7-[(4-fluoro-2-pyridyl)methyl]-1,4,7,10-tetraaza-1-cyclododecyl}acetic acid, L5. S3** (15.2 mg, 0.023 mmol) was added to a 2:1 solution of TFA and DCM and stirred overnight at room temperature. The solvent was removed in vacuo, and the product was dissolved in $H_2O$. The solution was then lyophilized to yield **L5** as an off-white solid (97%, 10.3 mg, 0.023 mmol, (method C) = 2.01 minutes). $^1$H NMR ($CD_3OD$, 400 MHz): δ 8.58 (m, 1H, $H^1$), 7.35 (d, 1H, $H^4$), 7.22 (m, 1H, $H^2$), 4.62 (br s, 2H, $H^6$), 4.11 (br s, 2H, $H^9$), 3.69-3.49 (m, 14H, $H^{cycl}$), 3.22 (m, 6H, $H^{cycl,7}$).$^{13}$C NMR ($CD_3OD$, 125 MHz): δ 173.05 ($C^8$), 172.01 ($C^{12}$), 169.91 ($C^{10}$), 158.79 ($C^3$), 153.12 ($C^5$), 120.96 ($C^1$), 118.64 ($C^4$), 116.34 ($C^2$), 58.17 ($C^7$), 55.77 ($C^{cycl}$), 53.82 ($C^9$), 52.61 ($C^{cycl}$), 51.37 ($C^{cycl}$), 50.75 ($C^6$), 50.17 ($C^{cycl}$). $^{19}$F NMR: ($CD_3OD$, 376 MHz): -100.16. ($CD_3OD$, 376 MHz): ESI-MS calcd. for $C_{20}H_{30}FN_5O_6$: 455.2180. Found: 456.2256 $[M+H]^+$.




*HPLC traces*

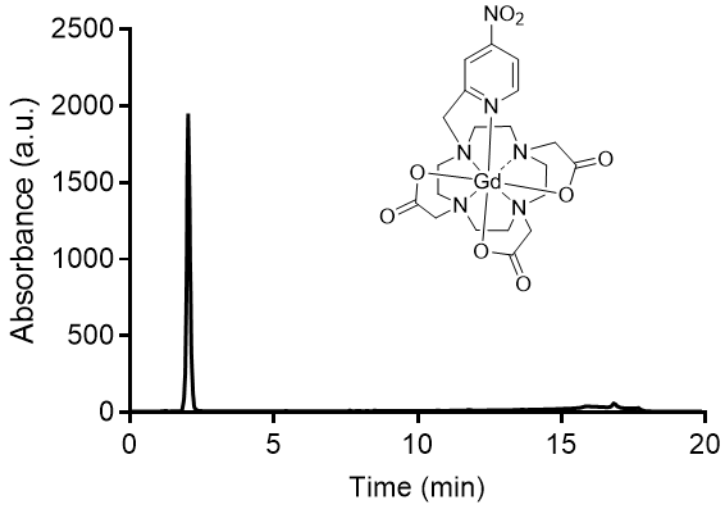



**Figure S3**. HPLC trace of Gd(**L3**). $\tau_r$ = 2.13 min.

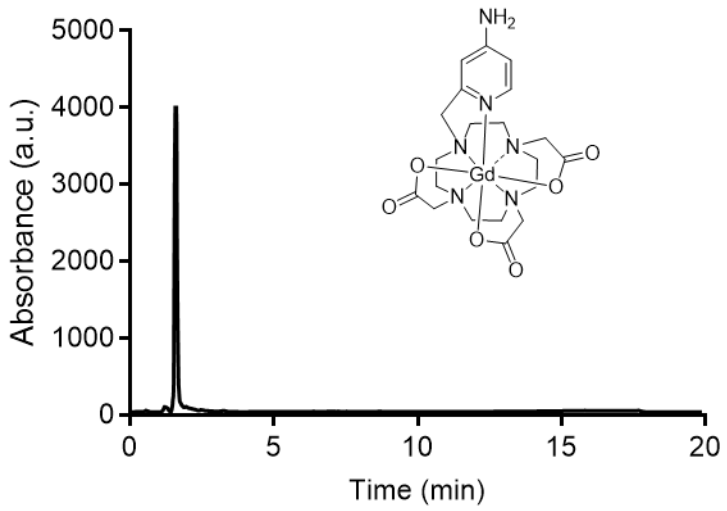



**Figure S4**. HPLC trace of Gd(**L4**). $\tau_r$ = 1.58 min.

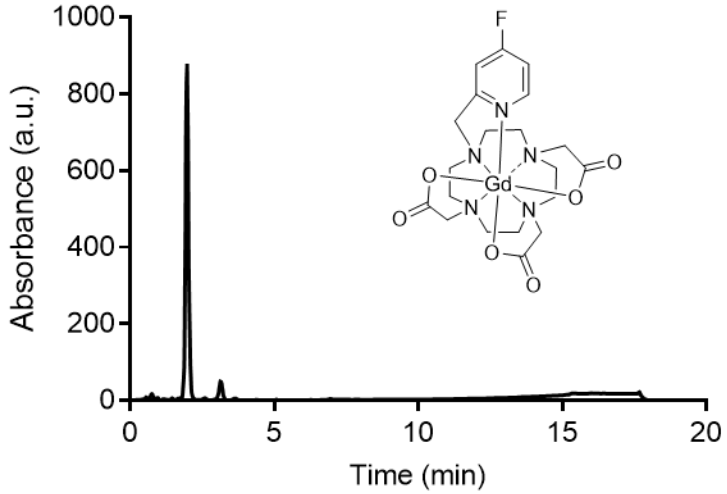



**Figure S5**. HPLC trace of Gd(**L5**). $\tau_r$ = 1.97 min.

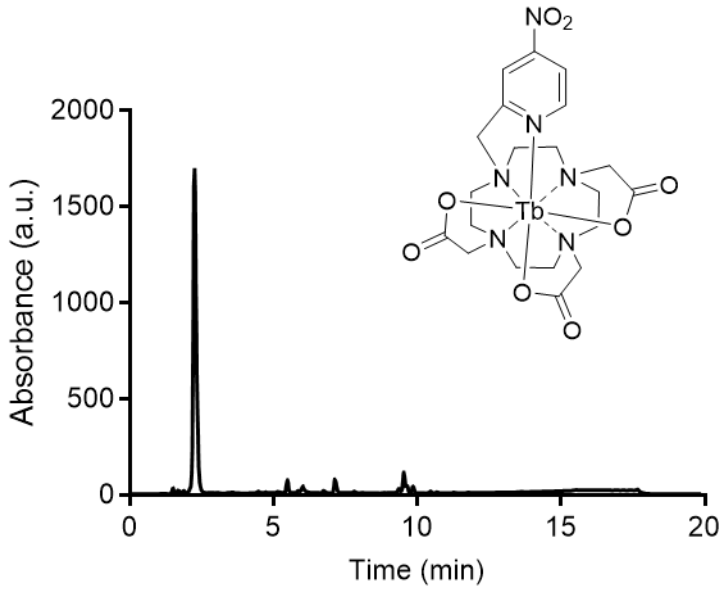



**Figure S6.** HPLC trace of Tb(**L3**). $\tau_r$ = 2.13 min.

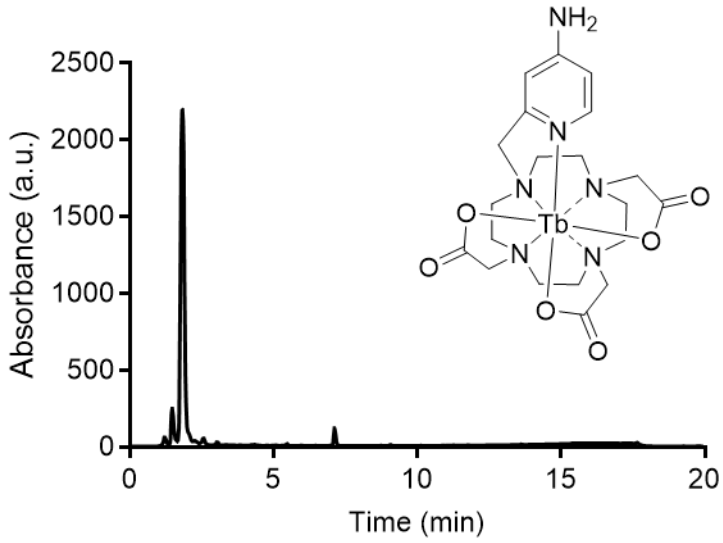



**Figure S7**. HPLC trace of Tb(**L4**). $\tau_r$ = 1.82 min.

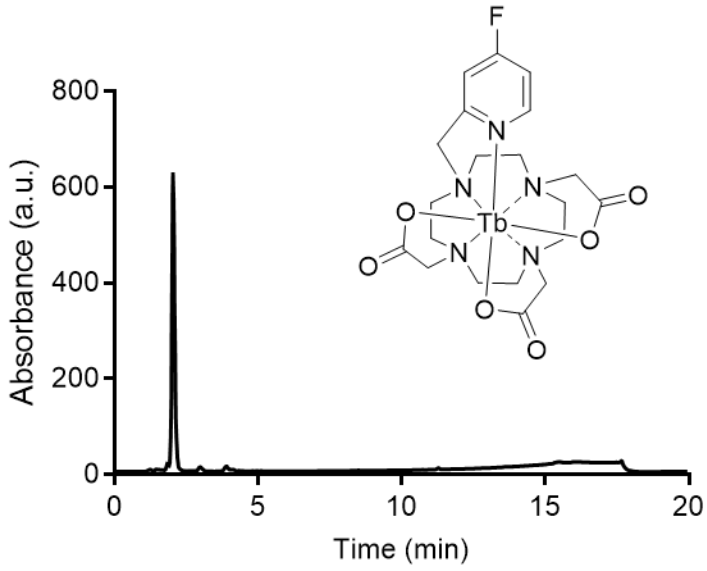



**Figure S8**. HPLC trace of Tb(**L5**). $\tau_r$ = 2.03 min.

## 4. Phosphorescence spectra and data analysis

### Phosphorescence data analysis

The $T_1$ energy levels of the pyridyl-functionalized groups were determined from the Gd(III) complexes to ensure that the observed transitions are ligand-based and unaffected by lanthanide(III) energy levels. The emission and excitation spectra of Gd(**L4**) and Gd(**L5**) complexes are unaffected by the selected excitation and emission wavelengths. The $T_1$ energy level can be directly determined at the 3 % intensity maxima at the onset of the high-energy side of the transition band.

Several features can be seen from the Gd(**L3)** emission spectra depending on the excitation wavelength and the selected time-gating of the measurement, indicating the presence of additional emitting species. However, the excitation spectra of the **L3** complexes seen in Figure S8 also exhibit the low intensity peak at ~330 nm indicating a charge transfer band that is also observed in the absorption spectrum. In order to correctly assign the **L3** $T_1$ state additional insight into the possible emitting species must be obtained. For this purpose, cryogenic spectra were recorded for Y-DOTA and the Tb(III) complexes along with phosphorescence decay measurements of all complexes.

From the phosphorescence measurements of Y-DOTA the emission of the carboxylate arms of the DOTA molecule is determined with a transition maxima at 430 nm, (Figure S11). The Tb(III)-based emission is characterized by high intensity and shorter lifetimes compared to their organic counterparts. A 15 ms time-gate can exclude the majority of Tb(III)-based emission and reveal the presence of underlying DOTA carboxylate emission.

The Tb(III) complexes reveal that the excitation spectra of the Gd(III) complexes are made of two distinct excitation spectra. Excitation spectra recorded by monitoring the emission of Tb(III) is blue-shifted compared with the pyridyl-based emission. These excitation profiles are consistent with those of pyridine: the blue-shifted excitation spectrum is consistent with the neutral form of pyridine and the red-shifted excitation spectrum consistent with the protonated version of pyridine, forming the pyridinium moiety and breaking the conjugated system. At the PBS moderated pH the neutral and protonated forms of the pyridyl exist in equilibrium.

By analyzing these spectra, the four key local excited states of Tb(III), DOTA, pyridine and pyridinium is determined. **DOTA-based emission is present in all complexes and should not be mistaken as the pyridyl $T_1$ state**. By exciting the neutral pyridyl group energy transfer to Tb(III) is favored and excitation of the pyridinium will favor emission via the DOTA carboxylic arms for Tb(**L3**) and Tb(**L4**). Tb(**L5**) exhibit both DOTA and pyridyl-based emission.

The excited state lifetimes of all complexes derived from the phosphorescent decays are given in Tables S3 to S6. From the Tb(**L3**) complex the lifetimes derived by exciting the pyridyl group at 275 nm (1.8 ms) is similar to the lifetime derived from exciting the charge transfer band (1.75 ms), when emission is observed through Tb(III). This indicates that the emission observed via the charge-transfer band ($S_1$) is representative of the **L3** triplet state. The $T_1$ energy level can therefore be obtained from Gd(**L3**) with 330 nm excitation. Even through with excitation through the charge transfer band contributions to the emission of other phosphorescent species could not be avoided.

This produce a partial convolution and an increased error on the energy level determination. The $T_1$ state is therefore determined at the 10 % onset instead.

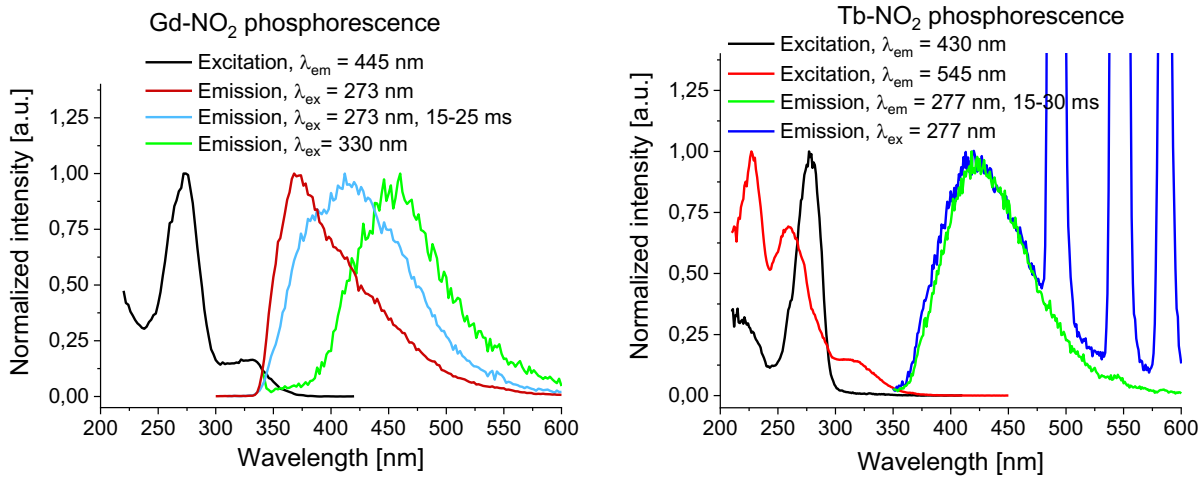



**Figure S9**. Phosphorescence spectra of Gd(**L3**) (left) and Tb(**L3**) (right) in PBS buffer at 77 K.

**Table S2.** Ln(**L3**), Ln = Gd(III), Tb(III) fitted lifetimes and amplitudes

| $NO_2$ | $\lambda_{ex}$ (nm) | $\lambda_{em}$ (nm) | $A_1$ | $\tau_1$ | $A_2$ | $\tau_2$ | $A_3$ | $\tau_3$ |
|---|---|---|---|---|---|---|---|---|
| Gd(III) | 273 | 370 | 9 | **1.3 ms** | 2 | **8.3 ms** | - | - |
| | 273 | 420 | 4 | **2.5 ms** | 2 | **21.6 ms** | - | - |
| | 273 | 455 | 8 | **2.7 ms** | 5 | **22.0 ms** | - | - |
| | 330 | 370 | 6 | **0.1 ms** | 0.01 | **5.9 ms** | - | - |
| | 330 | 420 | 8 | **0.2 ms** | 4 | **2.7 ms** | 1 | **14.4 ms** |
| | 330 | 455 | 3 | **2.2 ms** | 1 | **13.8 ms** | - | - |
| Tb(III) | 277 | 420 | 5 | **4.4 ms** | 11 | **51.0 ms** | - | - |
| | 317 | 420 | 3 | **0.2 ms** | 0.3 | **22.4 ms** | - | - |
| | 277 | 545 | 118 | **1.8 ms** | 5.7 | **0.2 ms** | 0.5 | **14.6 ms** |
| | 317 | 545 | - | **1.75 ms** | - | - | - | - |

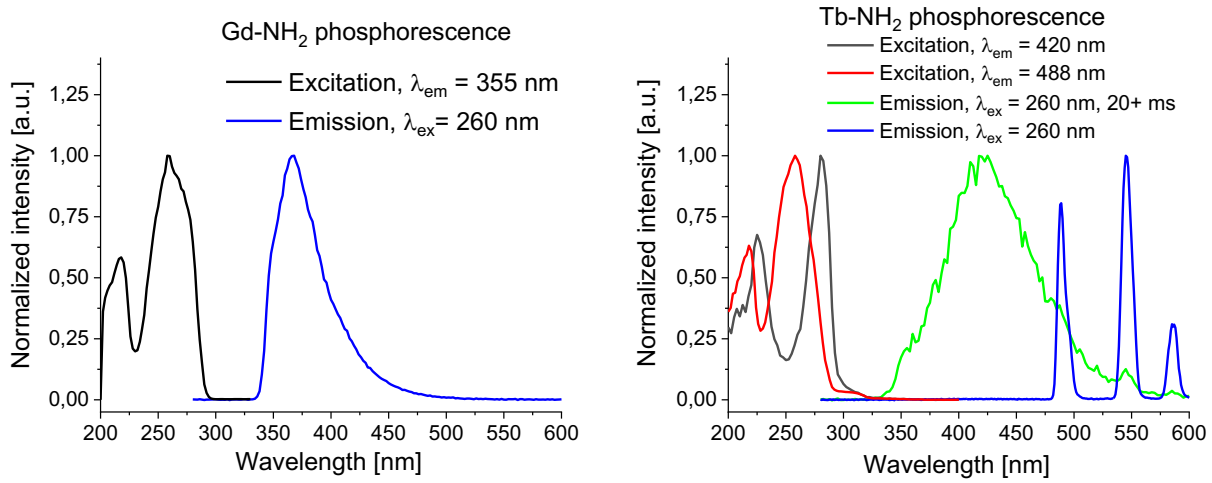



**Figure S10**. Phosphorescence spectra of Gd(**L4**) (left) and Tb(**L4**) (right) in PBS buffer at 77 K.

**Table S3.** Ln(**L4**), Ln = Gd(III), Tb(III) fitted lifetimes and amplitudes

| **$NH_2$** | **$\lambda_{ex}$ (nm)** | **$\lambda_{em}$ (nm)** | **$A_1$** | **$\tau_1$** | **$A_2$** | **$\tau_2$** | **$A_3$** | **$\tau_3$** |
|---|---|---|---|---|---|---|---|---|
| Gd(III) | 260 | 330 | 5 | **0.9 ms** | 3 | **3.5 ms** | - | **-** |
| Tb(III) | 250 | 420 | 19 | **0.1 ms** | 2 | **2.3 ms** | 0.5 | **36.7 ms** |
| | 285 | 420 | 6 | **3.1 ms** | 13 | **55.5 ms** | - | **-** |
| | 285 | 545 | - | **1.74 ms** | - | **-** | - | **-** |

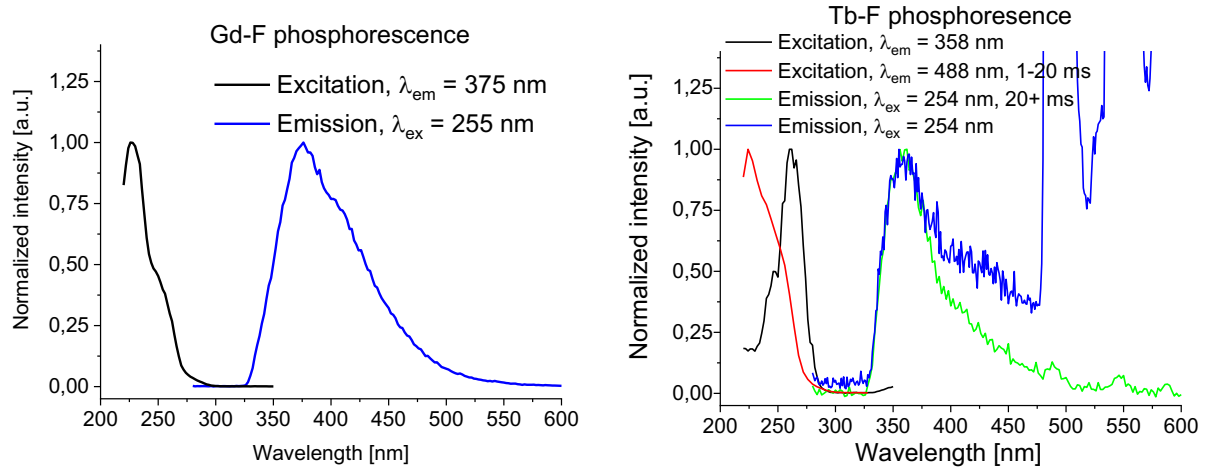



**Figure S11**. Phosphorescence spectra of Gd(**L5**) (left) and Tb(**L5**) (right) in PBS buffer at 77 K.

**Table S4.** Ln(**L5**), Ln = Gd(III), Tb(III) fitted lifetimes and amplitudes

| F | $\lambda_{ex}$ (nm) | $\lambda_{em}$ (nm) | $A_1$ | $\tau_1$ | $A_2$ | $\tau_2$ | $A_3$ | $\tau_3$ |
|---|---|---|---|---|---|---|---|---|
| Gd(III) | 255 | 340 | 25 | **1.8 ms** | 25 | **24.1 ms** | - | **-** |
| | 255 | 435 | 21 | **1.2 ms** | 19 | **17.3 ms** | - | **-** |
| Tb(III) | 255 | 435 | 118 | **0.2 ms** | 19 | **2.4 ms** | 5 | **24 ms** |
| | 275 | 358 | 5 | **1.9 ms** | 590 | **0.1 ms** | 6 | **62 ms** |

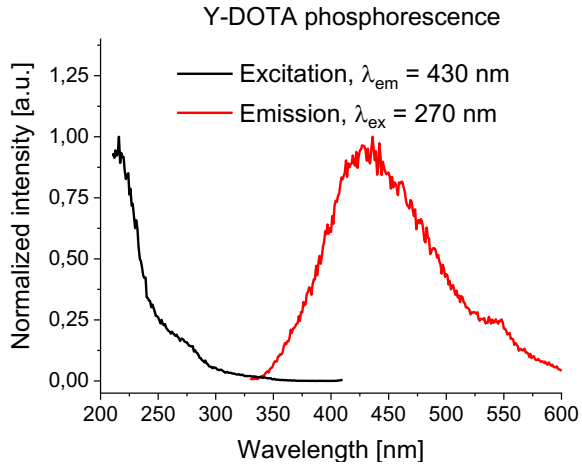



**Figure S12**. Phosphorescence spectra of Y.DOTA in DPBS buffer at 77 K. The small shoulder at 550 nm is likely a Tb(III) contamination.

**Table S5.** Y-DOTA fitted lifetimes and amplitudes

| Y-DOTA | $\lambda_{ex}$ (nm) | $\lambda_{em}$ (nm) | $A_1$ | $\tau_1$ | $A_2$ | $\tau_2$ | $A_3$ | $\tau_3$ |
|---|---|---|---|---|---|---|---|---|
| Y(III) | 270 | 430 | 1.3 | **0.5 ms** | 1.6 | **5.4 ms** | 0.6 | **30.9 ms** |

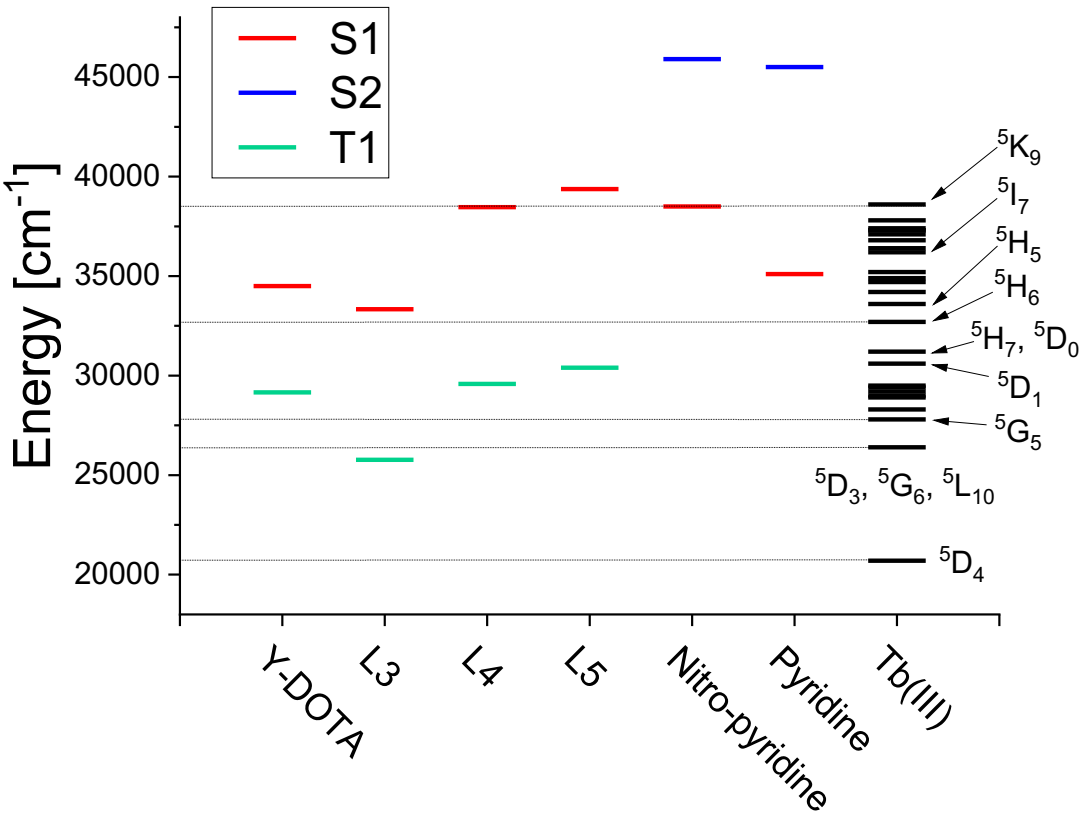



**Figure S13**. Energy level diagram of the obtained $S_1$ and $T_1$ energy levels of **L3**, **L4** and **L5** compared with the carboxylic DOTA energy levels, the pyridine and nitro-pyridine $S_1$ and $S_2$ levels and many of the Tb(III) excited energy levels.

## 5. Quantum yield, lifetime, and q measurements

Quantum yield for each complex was determined using the following equation:

$$QY_X = QY_S * \frac{Gradient_X}{Gradient_S} \qquad (S1)$$

where "S" refers to the $[Tb(L1)]^-$ ($\Phi = 0.47$) and "X" is the unknown. The gradient is the slope of the graph of integrated emission intensity versus the peak absorption value for a range of concentrations with abs < 0.1.

*Quantum yield gradients*

Gradients for quantum yield determination were measured using the following procedure: Complex was diluted in 1X DPBS and measuring absorbances ranging 0.01-0.10, followed by measurement of fluorescence emission. Total emission integrals were taken between 450-650 nm (only Tb-based emission), assuming a Gaussian distribution, and the integral of the second-order scattering peak was subtracted.

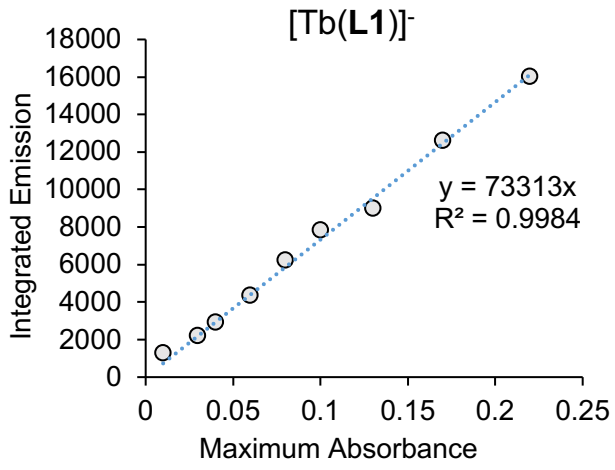



**Figure S14**. Quantum yield gradient of reference compound $[Tb(\mathbf{L1})]^-$.

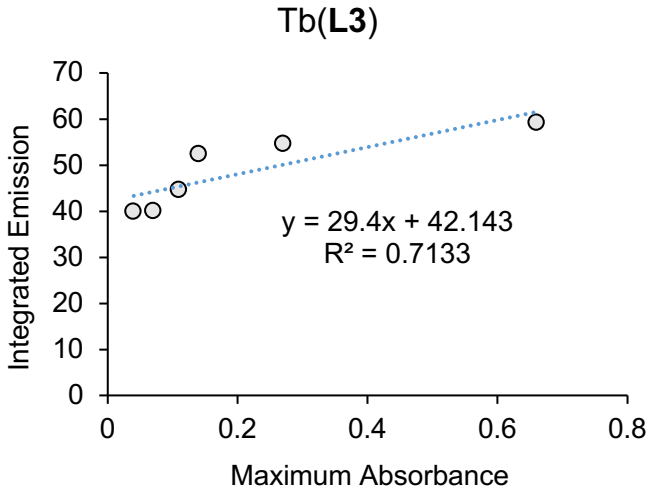



**Figure S15**. Quantum yield gradient of Tb(**L3**).

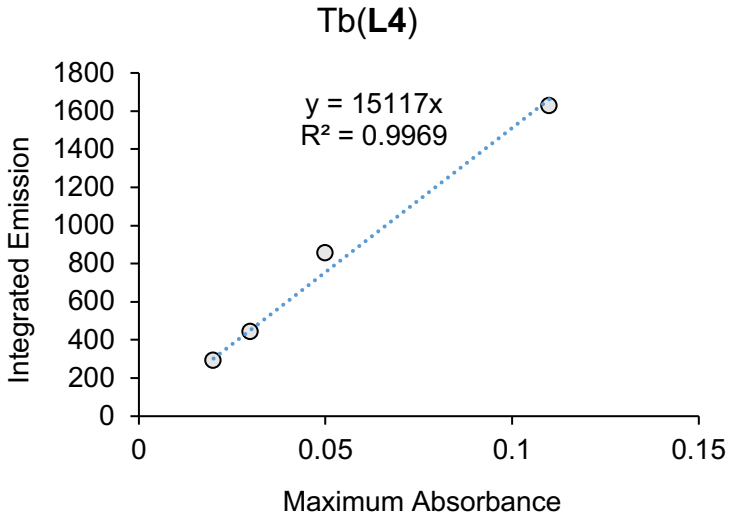



**Figure S16**. Quantum yield gradient of Tb(**L4**).

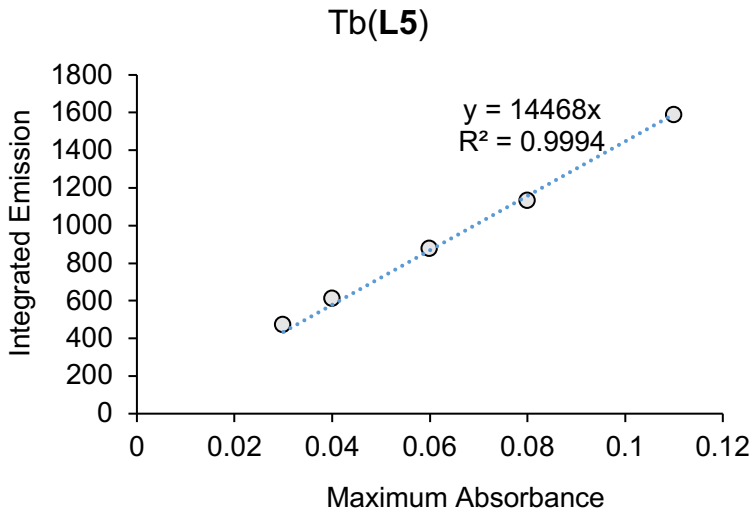



**Figure S17**. Quantum yield gradient of Tb(**L5**).

| **Table S6**. Gradient QY summary | | | |
|---|---|---|---|
| | $\lambda_{ex}$ | Gradient | $\Phi_{Tb}$ (%) |
| Tb(**L3**) | 300 | 29.4 | 0.02 |
| Tb(**L4**) | 260 | 15117 | 10 |
| Tb(**L5**) | 254 | 14468 | 9.3 |
| [Tb(**L1**)]$^-$ | 282 | 73315 | 47 |

*Lifetime and q measurements*

Lifetime values were extracted by fitting the luminescent decay curves with the equation:

$$I_t = I_0 * \exp\left(-\frac{x}{\tau}\right) \qquad \text{(S2)}$$

where $I_t$ is the initial luminescent emission intensity, $I_0$ is the intensity at time x = 0, and $\tau$ is the luminescence lifetime. Data was fit using Prism. Q was calculated using Horrocks' method, eq. 3.

$$q = 5.0\left(\frac{1}{\tau(H_2O)} - \frac{1}{\tau(D_2O)} - 0.06\right) \qquad \text{(S3)}$$

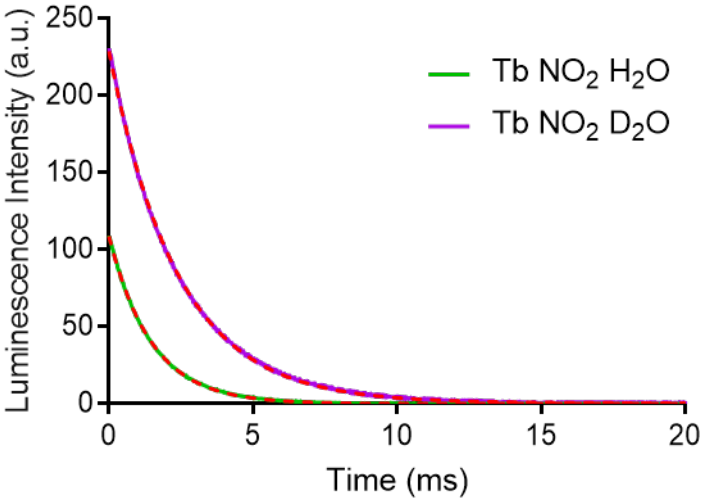



**Figure S18**. Luminescent lifetime decay curves of Tb(**L3**) in $H_2O$ (buffer) and $D_2O$. Fits of Equation S2 indicated as dashed red overlay.

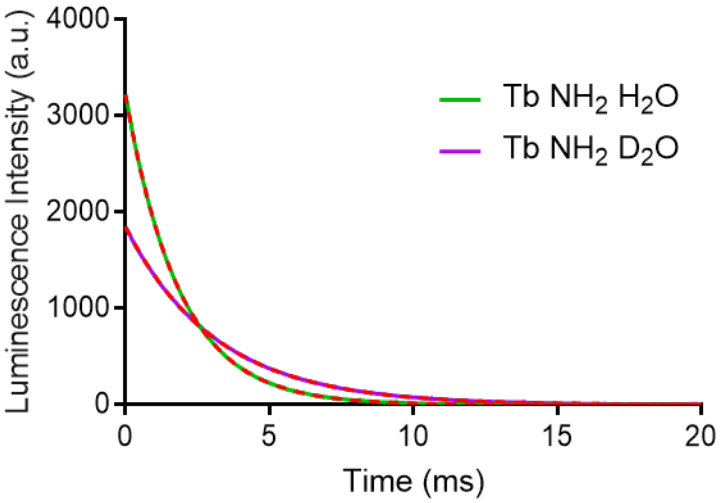



**Figure S19**. Luminescent lifetime decay curves of Tb(**L4**) in $H_2O$ (buffer) and $D_2O$. Fits of Equation S2 indicated as dashed red overlay.

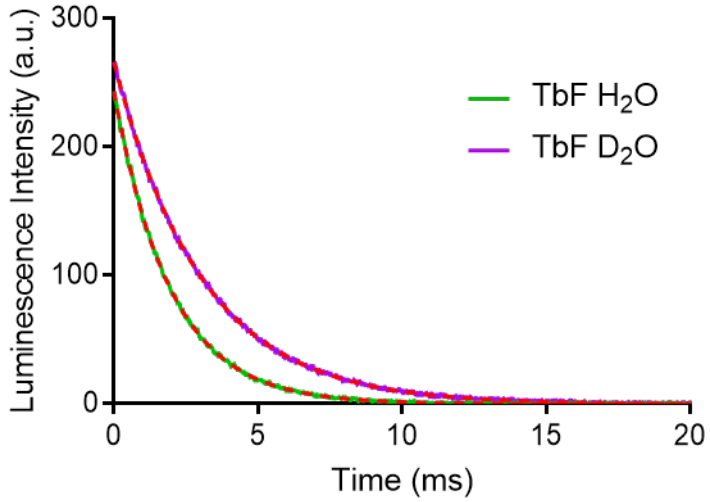



**Figure S20**. Luminescent lifetime decay curves of Tb(**L5**) in $H_2O$ (buffer) and $D_2O$. Fits of Equation S2 indicated as dashed red overlay.

**Table S7**. Luminescent Lifetimes and q values.

| Complex | Buffer lifetime (ms) | $D_2O$ lifetime (ms) | Buffer $\tau$ ($ms^{-1}$) | $D_2O$ $\tau$ ($ms^{-1}$) | q |
|---|---|---|---|---|---|
| Tb(**L3**) | 1.47 | 2.38 | 0.68 | 0.42 | 1.30 |
| Tb(**L4**) | 1.87 | 3.15 | 0.53 | 0.32 | 1.08 |
| Tb(**L5**) | 1.96 | 3.05 | 0.51 | 0.33 | 0.91 |

## 6. Characterization of hydrogen sulfide sensing

HPLC:

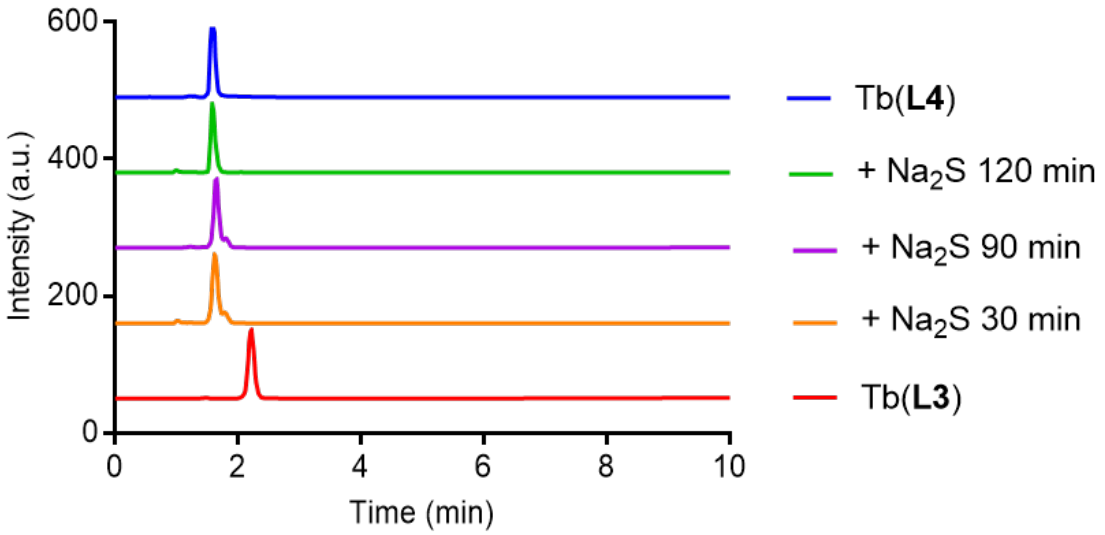



**Figure S21**. Normalized HPLC traces of Tb(**L3**) (red); Tb(**L3**) + 100 eq $Na_2S$ after 30 min (orange), after 90 min (purple), after 120 min (green); overlay of Tb(**L4**) as complexed from ligand **L2** (blue).

| **Table S8**. Average fold-increase (n = 3) of Tb(**L3**) + analyte/salt; | | |
|---|---|---|
| | Fold-increase | Std. deviation |
| Tb(**L3**) | 1.000 | 1.000 |
| NaOAc | 1.621 | 0.567 |
| NaI | 1.619 | 0.230 |
| $NaHCO_3$ | 1.792 | 0.163 |
| $Na_2CO_3$ | 1.863 | 0.110 |
| NaCl | 1.758 | 0.240 |
| Cys | 0.765 | 0.147 |
| $Na_2SO_4$ | 1.730 | 0.007 |
| $Na_2S$ | 31.321 | 5.421 |

## 7. ROI Analysis of CRET imaging

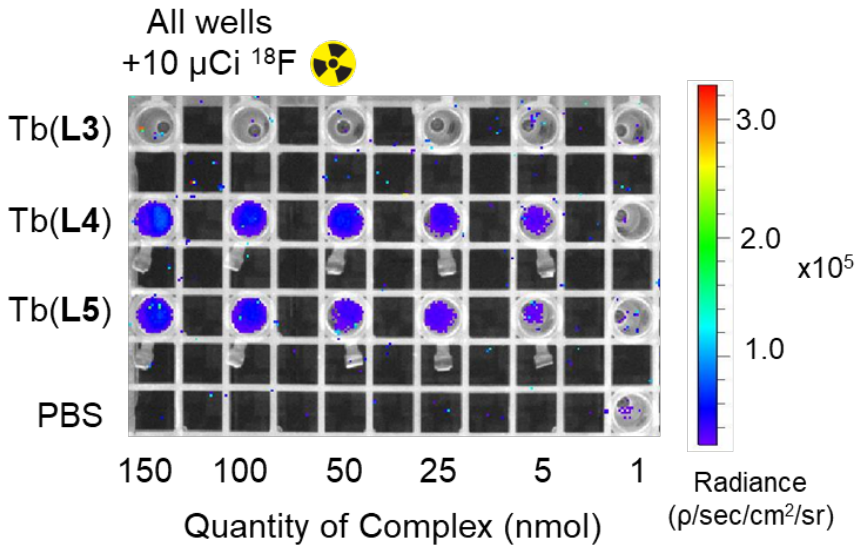



**Figure S22.** Plate of complexes featured in manuscript Figure 5, rewindowed to remove signal from buffer-only sample and Tb(**L3**) series.

| **Table S9**. Average radiance values of all complexes. N = 3. | | | |
|---|---|---|---|
| | Quantity (nmol) | Average Radiance (ρ/sec/cm²/sr) | Std. Deviation |
| Tb(**L3**) | 150 | 2530 | 2254 |
| | 100 | -2003 | 357 |
| | 50 | -2427 | 335 |
| | 25 | -3110 | 174 |
| | 5 | -1570 | 1876 |
| | 1 | -2840 | 528 |
| Tb(**L4**) | 150 | 36537 | 1152 |
| | 100 | 26970 | 743 |
| | 50 | 28160 | 1183 |
| | 25 | 14460 | 337 |
| | 5 | 8350 | 130 |
| | 1 | -2373 | 178 |
| Tb(**L5**) | 150 | 31717 | 1685 |
| | 100 | 26520 | 573 |
| | 50 | 13647 | 464 |
| | 25 | 10820 | 650 |
| | 5 | 6110 | 316 |
| | 1 | 483 | 849 |

| **Table S10.** Average radiance values of Tb(**L3**) in situ reduction with $Na_2S$ over time | | |
|---|---|---|
| Incubation time (hrs) | Average Radiance ($\rho$/sec/cm$^2$/sr) | Std. Deviation |
| 3 | 80467 | 12150 |
| 2.5 | 71467 | 1482 |
| 2 | 65900 | 2146 |
| 1.5 | 46900 | 6871 |
| 1 | 31233 | 3311 |
| 0 ($^{18}$F in PBS) | 167 | 3484 |

## 8. NMR spectra

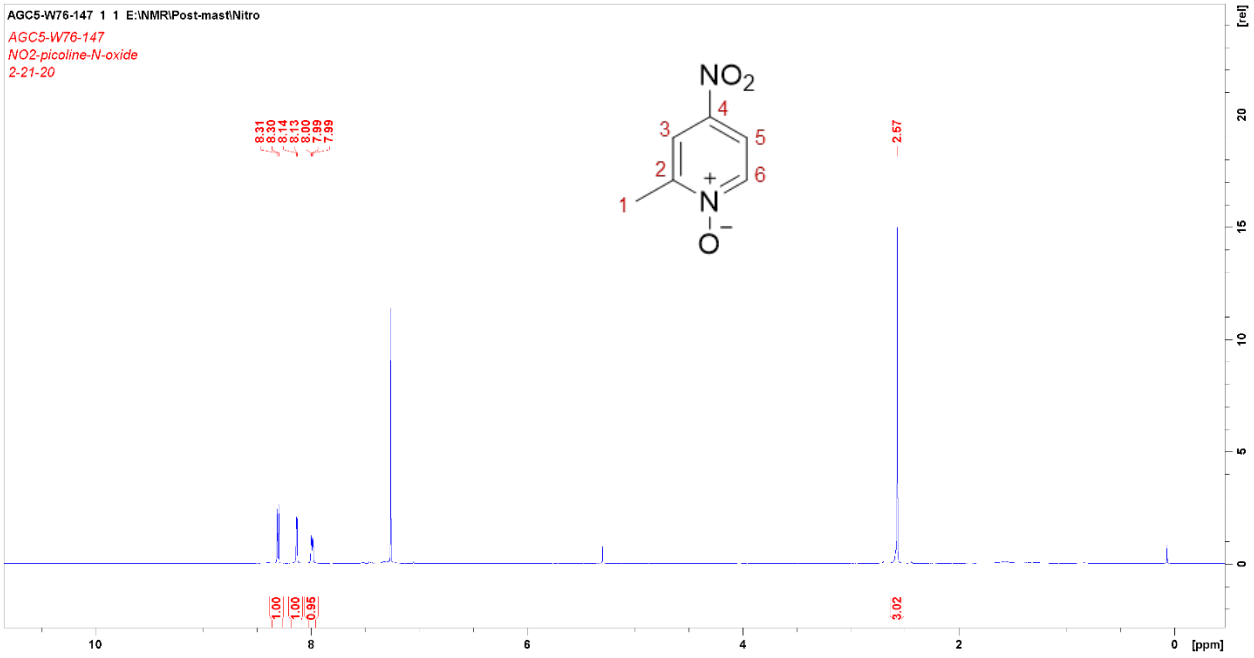



**Figure S23**. $^{1}$H NMR spectra of **2-methyl-4-nitropyridine 1-oxide, 1.**

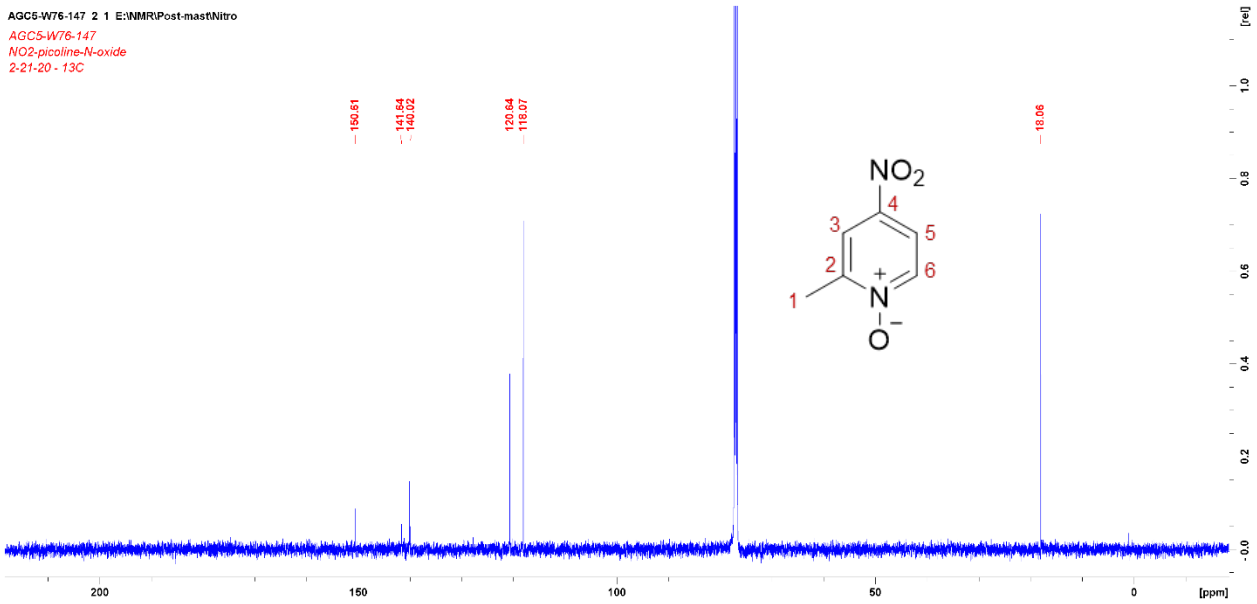



**Figure S24.** $^{13}$C NMR spectra of **2-methyl-4-nitropyridine 1-oxide, 1.**

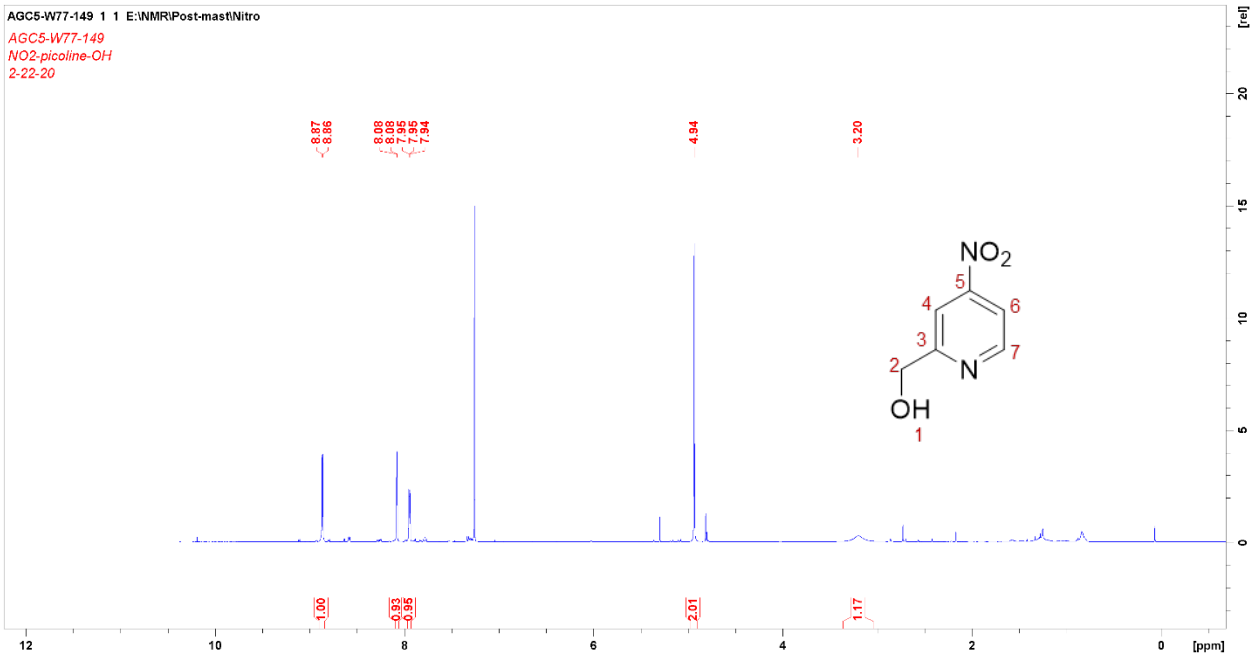



**Figure S25.** $^{1}$H NMR spectra of **2-(Hydroxymethyl)-4-nitropyridine, 2.**

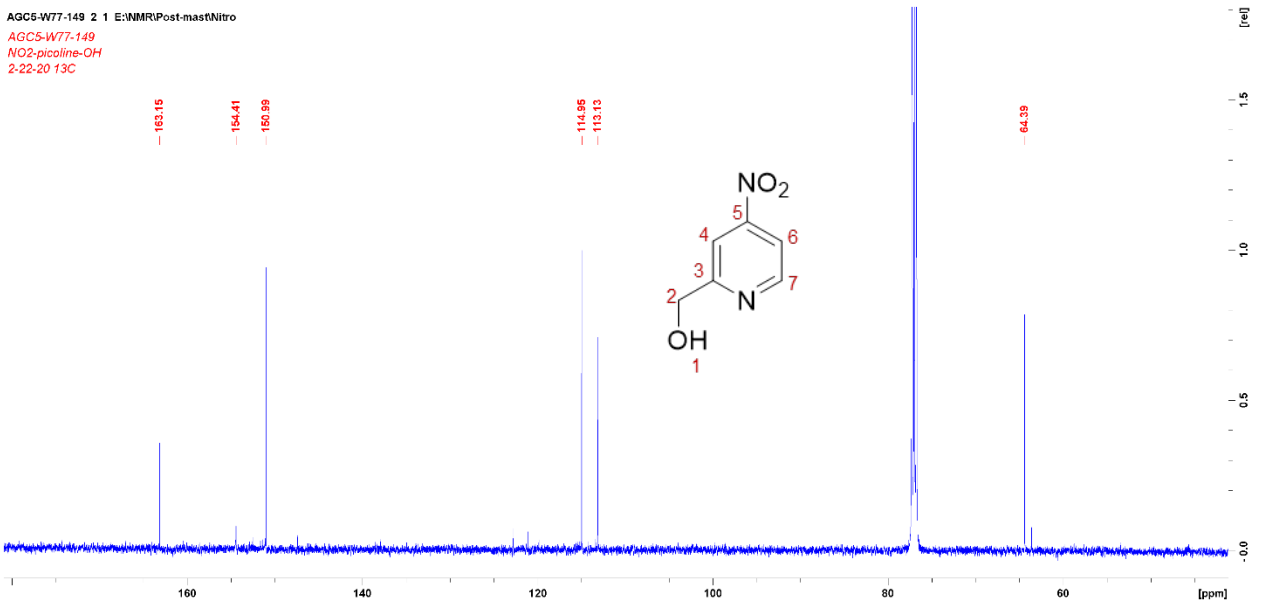



**Figure S26.** $^{13}$C NMR spectra of **2-(Hydroxymethyl)-4-nitropyridine, 2.**

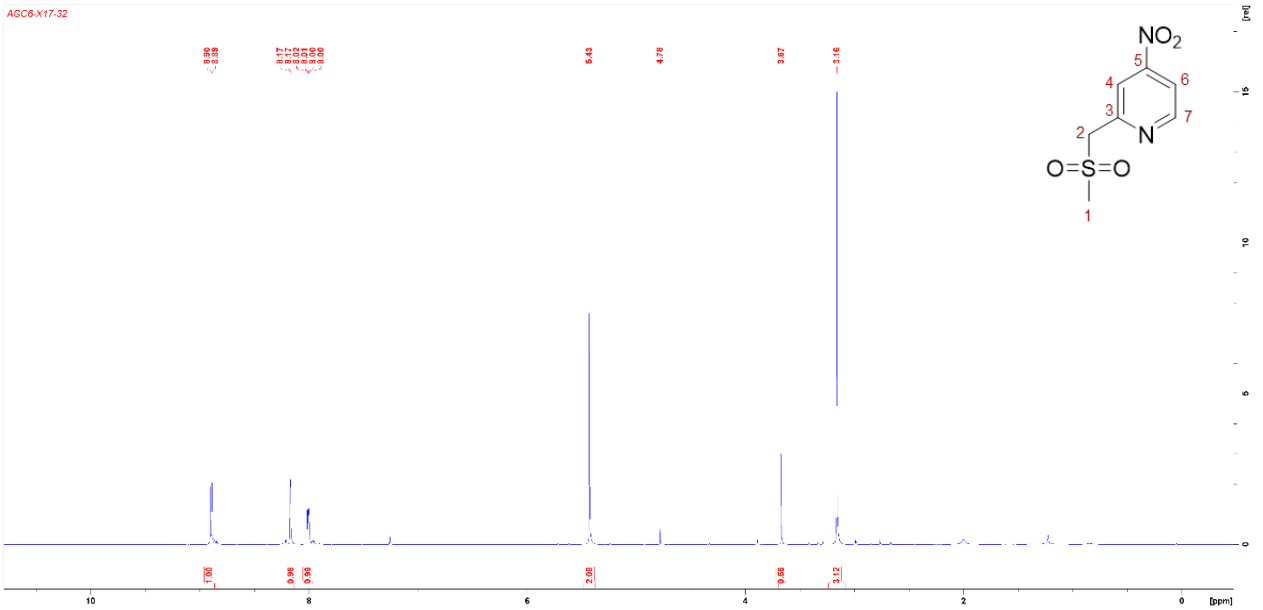



**Figure S27.** $^{1}$H NMR spectra of **2-[(Methylsulfonyloxy)methyl]-4-nitropyridine, 3**.

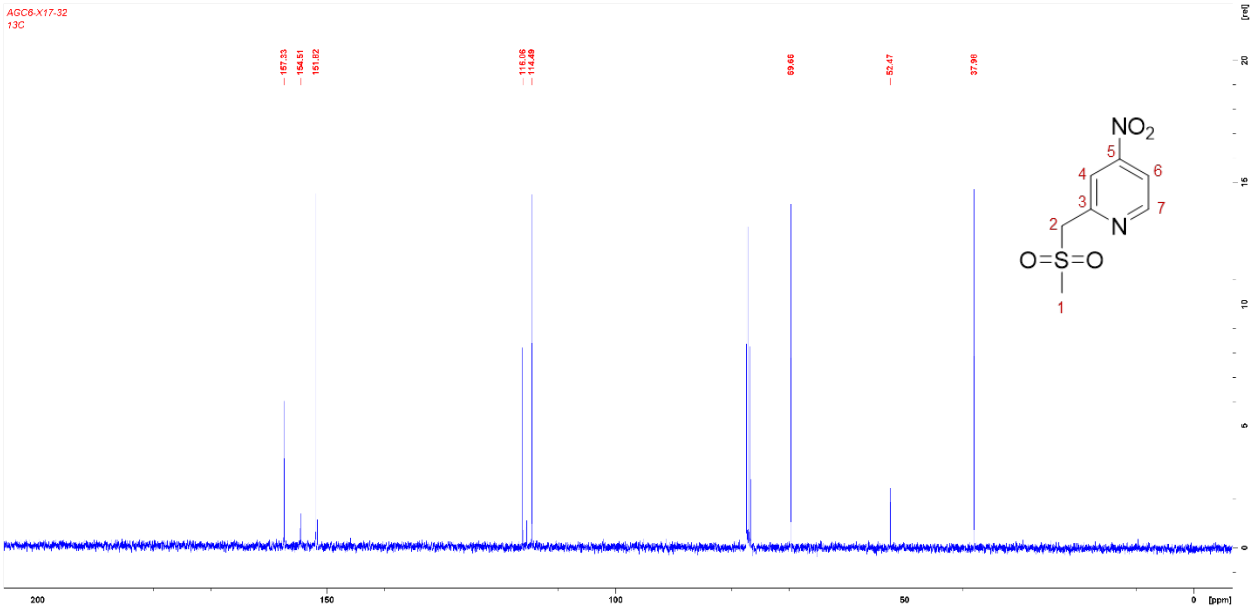



**Figure S28.** $^{13}$C NMR spectra of **2-[(Methylsulfonyloxy)methyl]-4-nitropyridine, 3**.

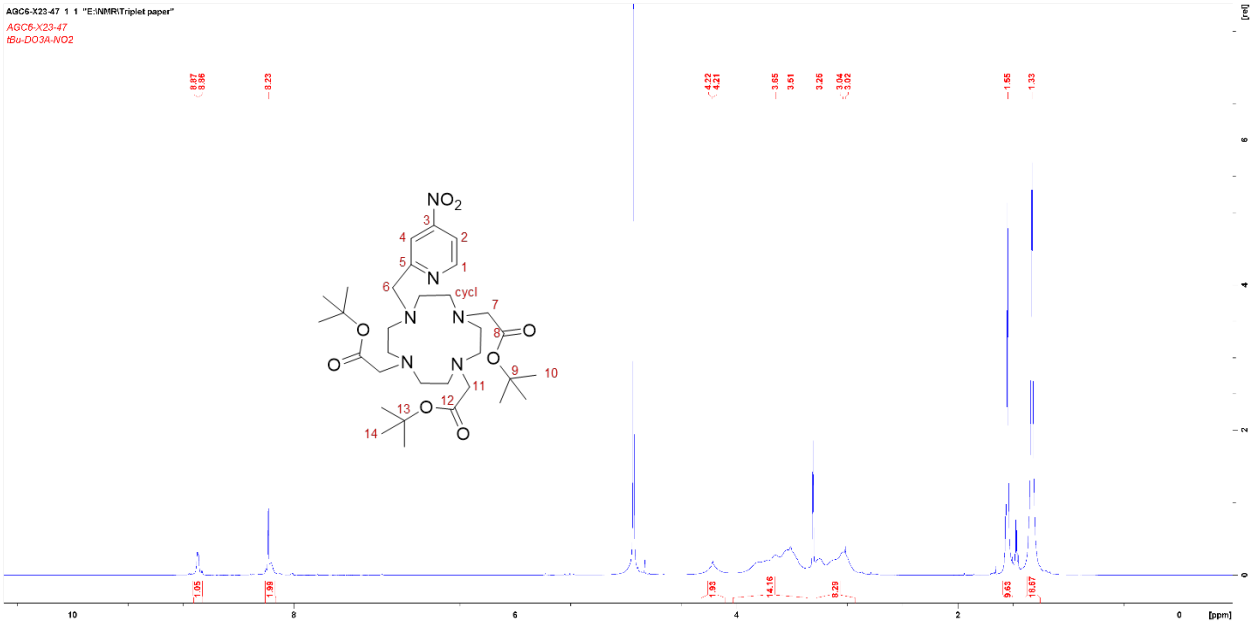



**Figure S29.** $^{1}$H NMR spectra of ***tert*-Butyl {4,10-bis(*tert*-butoxycarbonylmethyl)-7-[(4-nitro-2-pyridyl)methyl]-1,4,7,10-tetraaza-1-cyclododecyl}acetate, 4.**

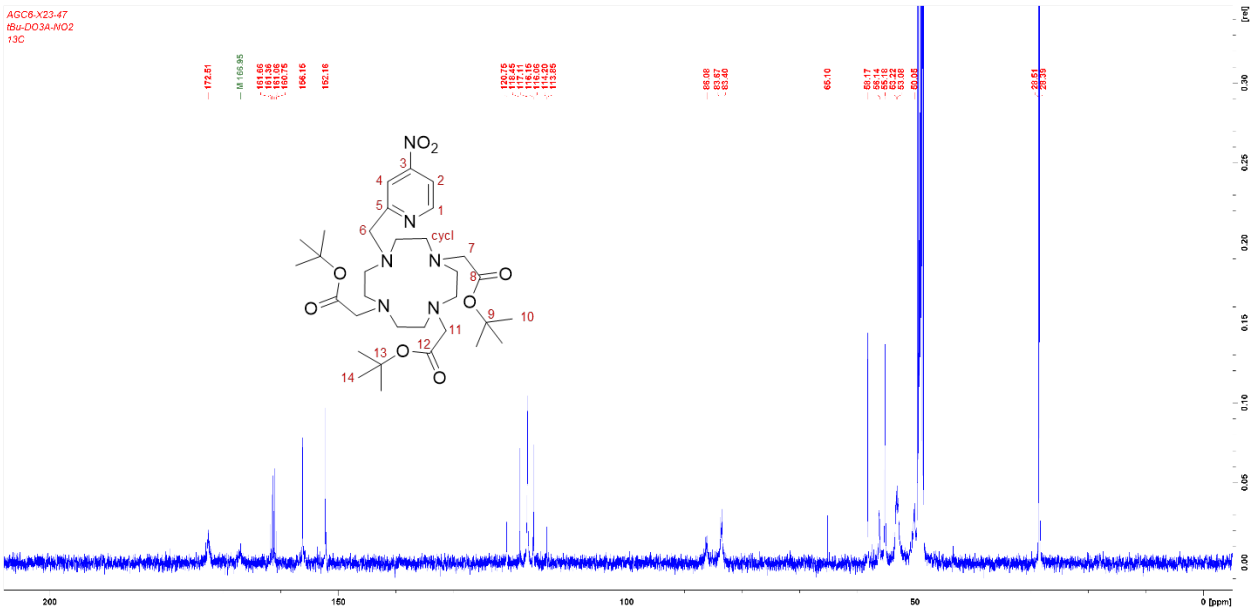



**Figure S30.** $^{13}$C NMR spectra of ***tert*-Butyl {4,10-bis(*tert*-butoxycarbonylmethyl)-7-[(4-nitro-2-pyridyl)methyl]-1,4,7,10-tetraaza-1-cyclododecyl}acetate, 4.**

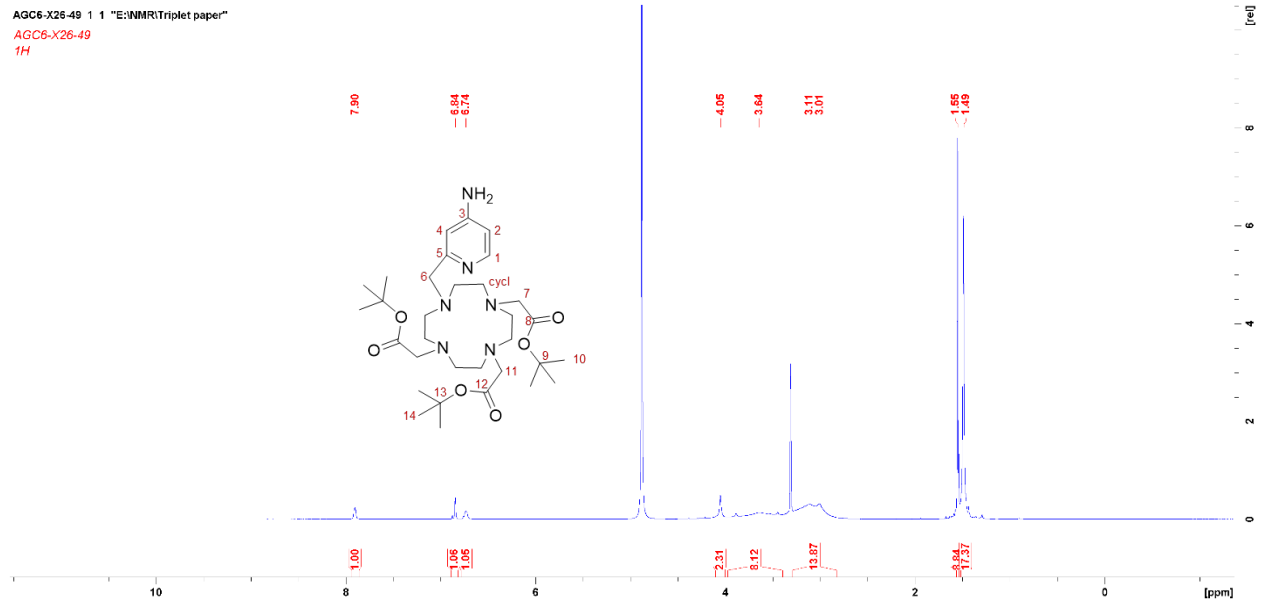



**Figure S31.** $^{1}$H NMR spectra of ***tert*-Butyl {10-[(4-amino-2-pyridyl)methyl]-4,7-bis(*tert*-butoxycarbonylmethyl)-1,4,7,10-tetraaza-1-cyclododecyl}acetate, 5.**

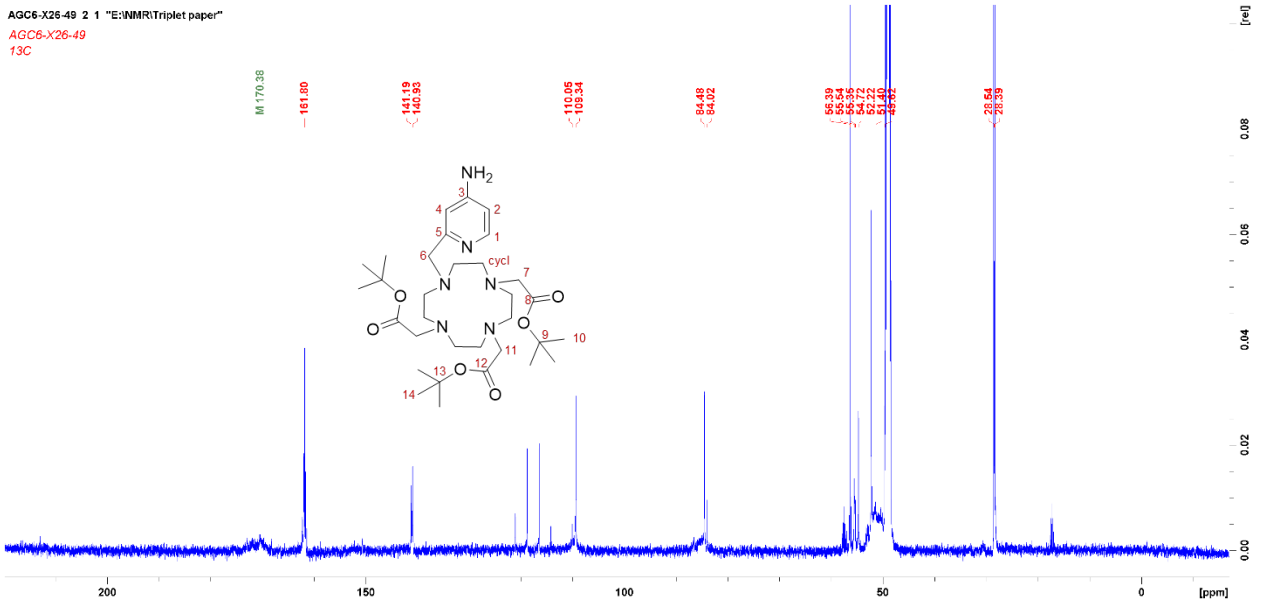



**Figure S32.** $^{13}$C NMR spectra of ***tert*-Butyl {10-[(4-amino-2-pyridyl)methyl]-4,7-bis(*tert*-butoxycarbonylmethyl)-1,4,7,10-tetraaza-1-cyclododecyl}acetate, 5.**

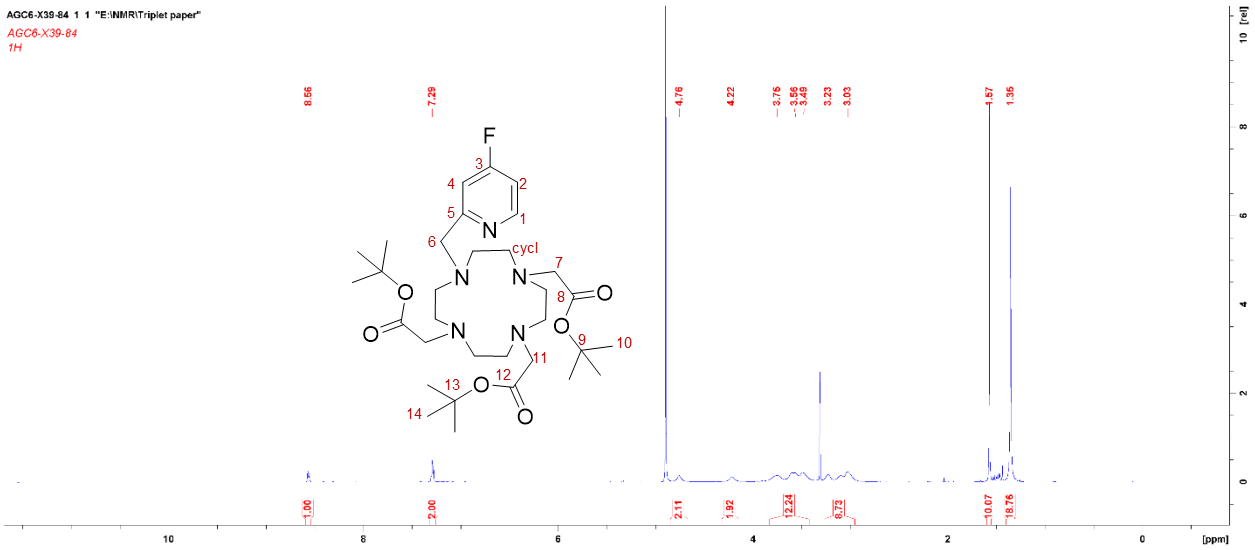



**Figure S33.** $^{1}$H NMR spectra of of ***tert*-Butyl {4,10-bis(*tert*-butoxycarbonylmethyl)-7-[(4-fluoro-2-pyridyl)methyl]-1,4,7,10-tetraaza-1-cyclododecyl}acetate, 6.**

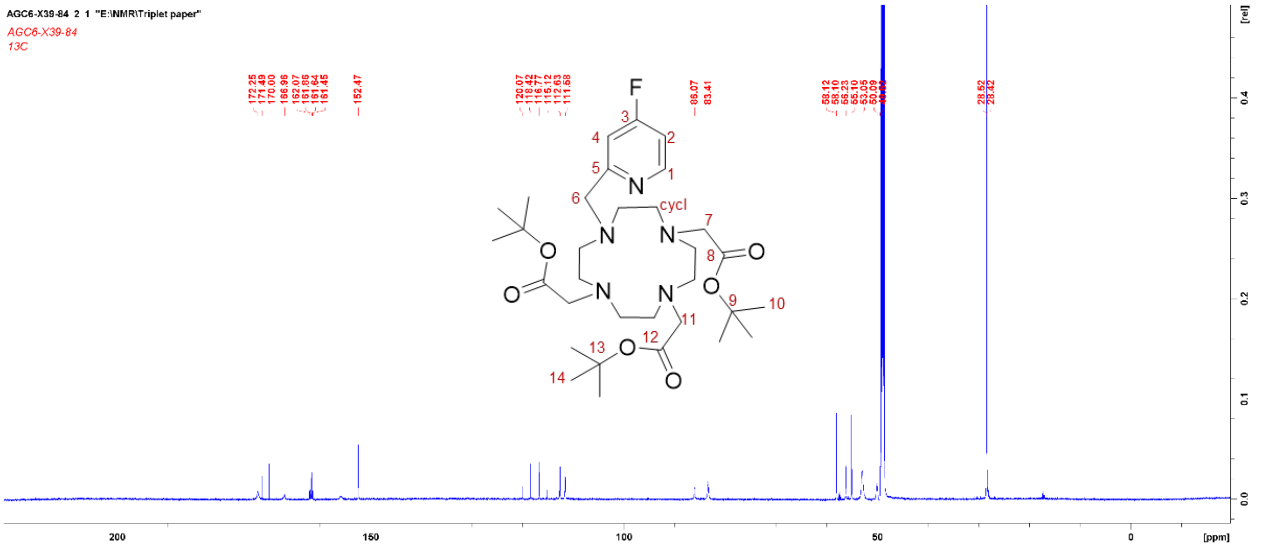



**Figure S34.** $^{13}$C NMR spectra of ***tert*-Butyl {4,10-bis(*tert*-butoxycarbonylmethyl)-7-[(4-fluoro-2-pyridyl)methyl]-1,4,7,10-tetraaza-1-cyclododecyl}acetate, 6.**

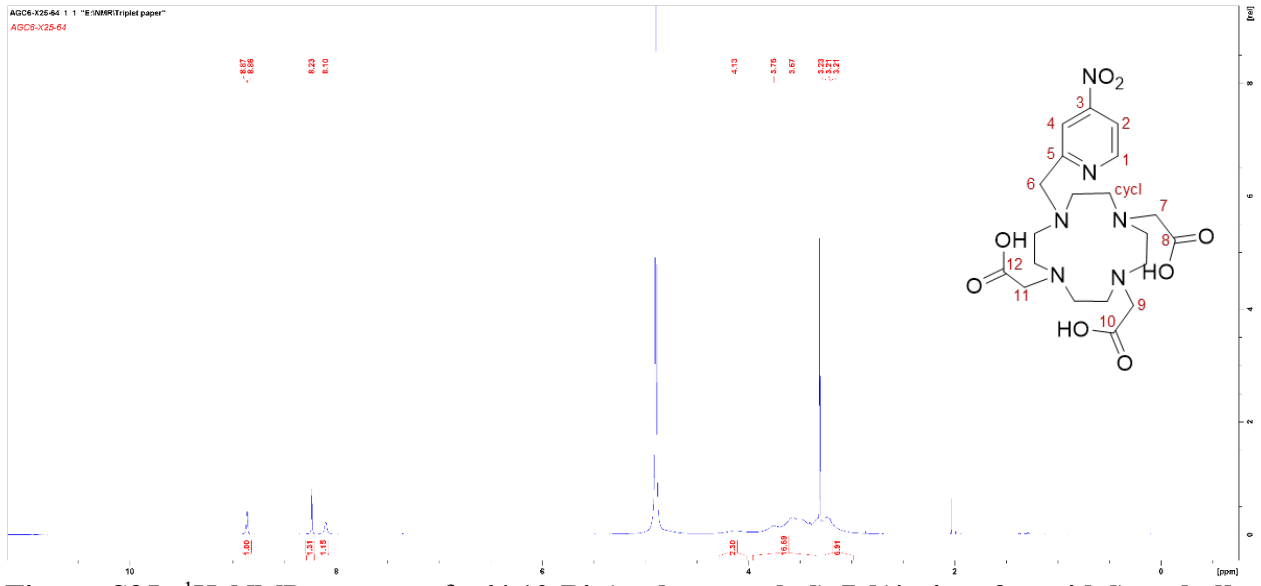


**Figure S35.** $^{1}$H NMR spectra of **{4,10-Bis(carboxymethyl)-7-[(4-nitro-2-pyridyl)methyl]-1,4,7,10-tetraaza-1-cyclododecyl}acetic acid, L3.**

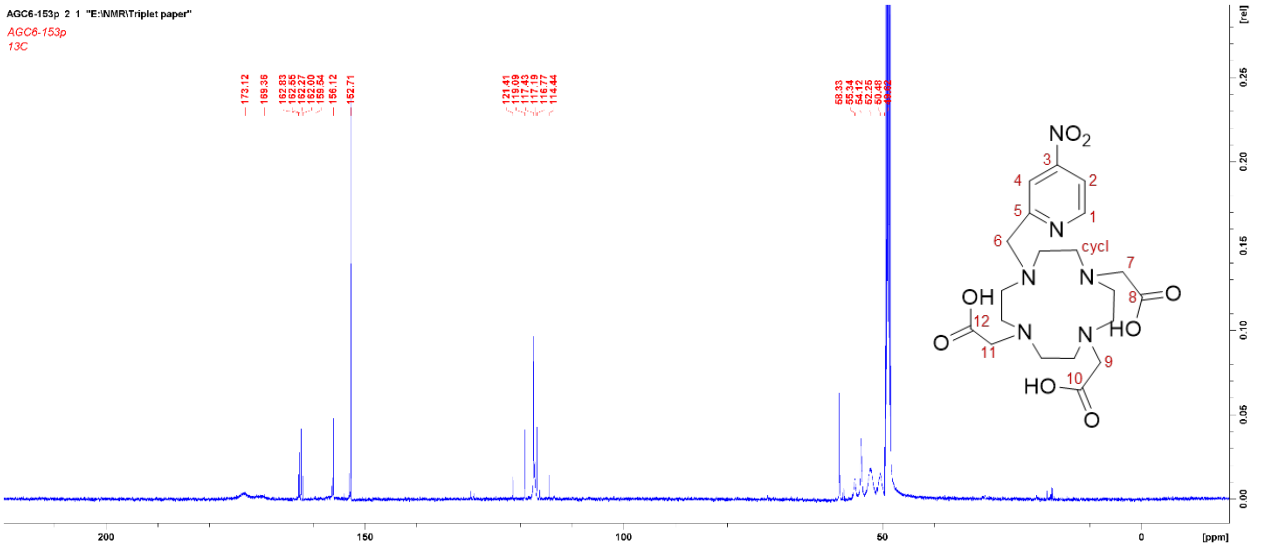


**Figure S36.** $^{13}$C NMR spectra of **{4,10-Bis(carboxymethyl)-7-[(4-nitro-2-pyridyl)methyl]-1,4,7,10-tetraaza-1-cyclododecyl}acetic acid, L3.**

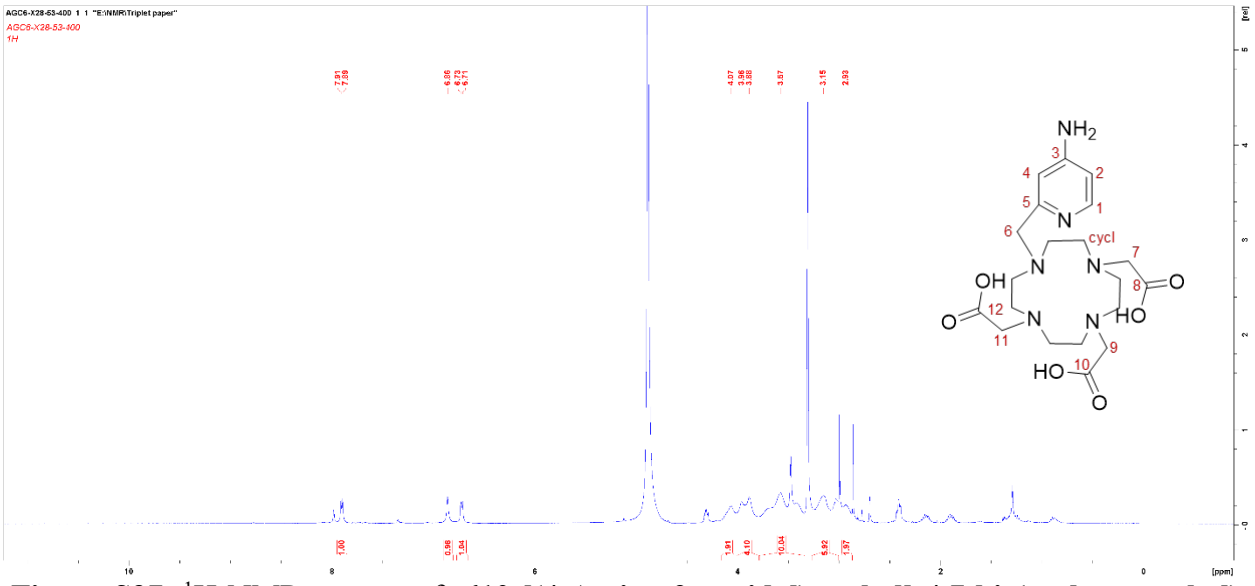


**Figure S37.** $^{1}$H NMR spectra of **{10-[(4-Amino-2-pyridyl)methyl]-4,7-bis(carboxymethyl)-1,4,7,10-tetraaza-1-cyclododecyl}acetic acid, L4.**

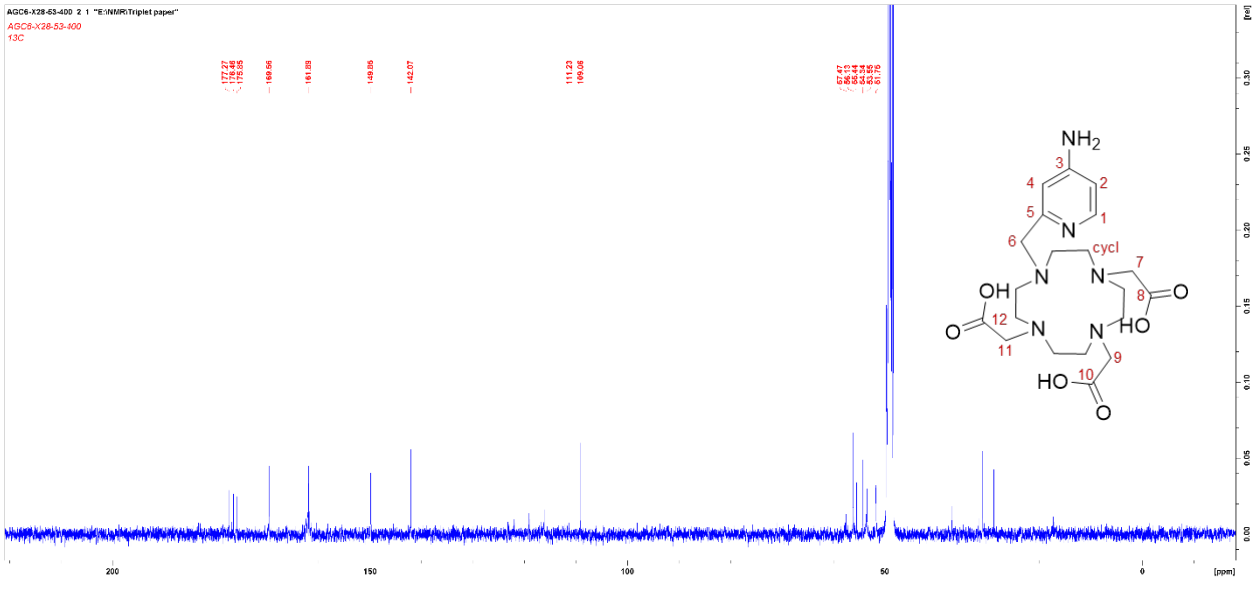


**Figure S38.** $^{13}$C NMR spectra NMR spectra of **{10-[(4-Amino-2-pyridyl)methyl]-4,7-bis(carboxymethyl)-1,4,7,10-tetraaza-1-cyclododecyl}acetic acid, L4.**

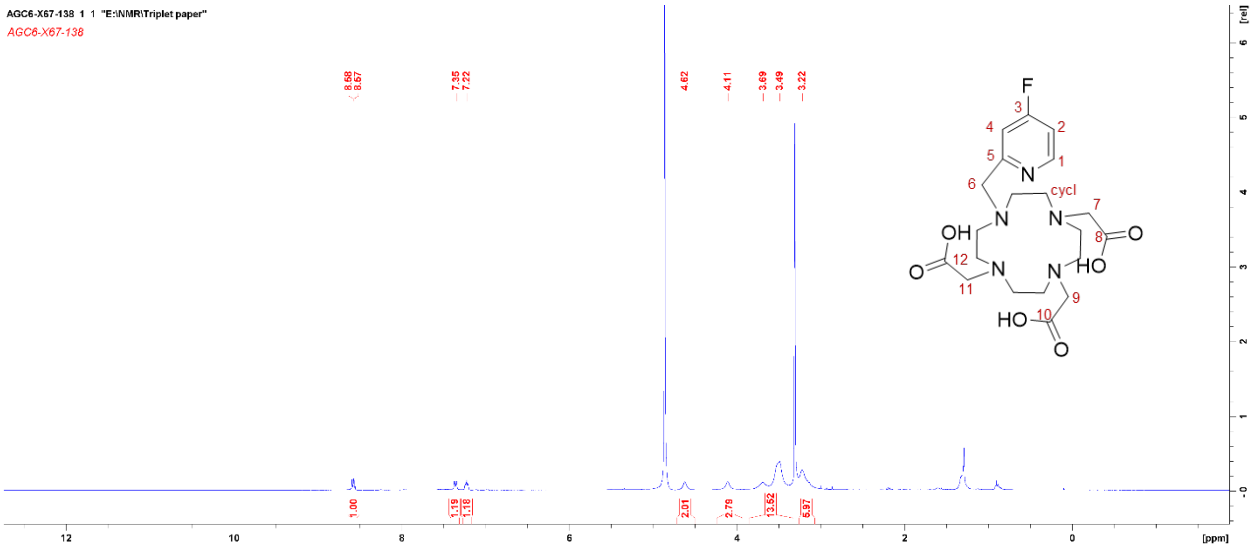



**Figure S39.** $^{1}$H NMR spectra of depro **{4,10-Bis(carboxymethyl)-7-[(4-fluoro-2-pyridyl)methyl]-1,4,7,10-tetraaza-1-cyclododecyl}acetic acid, L5**

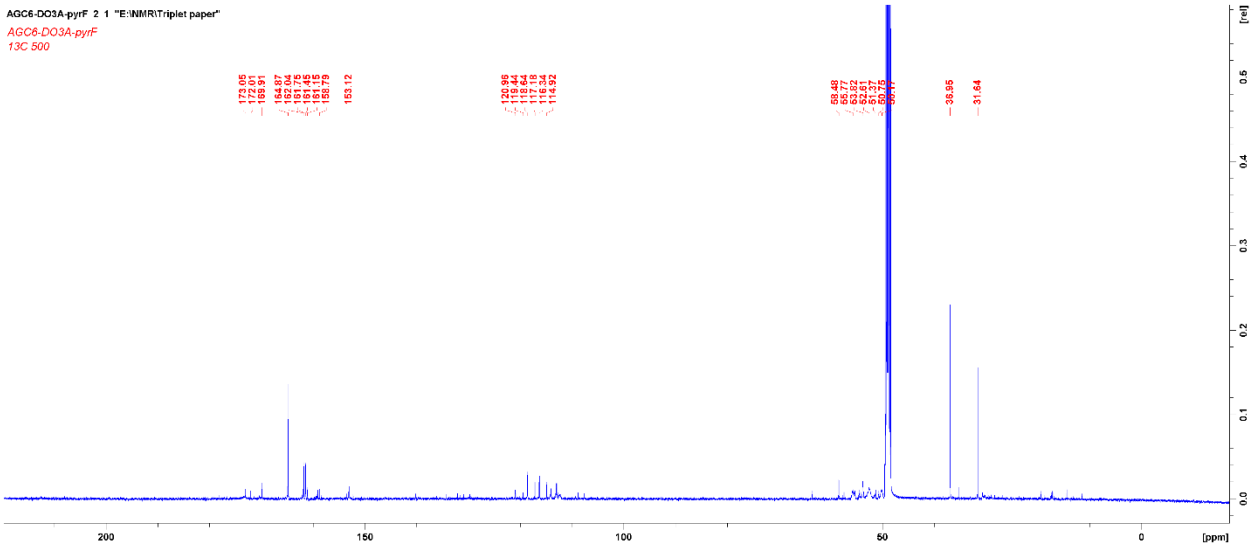



**Figure S40.** $^{13}$C NMR spectra of **{4,10-Bis(carboxymethyl)-7-[(4-fluoro-2-pyridyl)methyl]-1,4,7,10-tetraaza-1-cyclododecyl}acetic acid, L5**

## 9. Optimized Geometries

| Tb(**L3**) GS | | | 0 imaginary frequencies | |
|---|---|---|---|---|
| Center Number | Atom | X | Y | Z |
| 1 | Tb | 0.64118 | -0.03474 | -0.45863 |
| 2 | O | 0.24541 | -2.2408 | -0.95407 |
| 3 | C | -0.0333 | -3.23095 | -0.15762 |
| 4 | O | 0.11577 | -4.42966 | -0.375 |
| 5 | C | -0.6576 | -2.7871 | 1.1868 |
| 6 | N | -0.06154 | -1.52985 | 1.71647 |
| 7 | C | -1.02663 | -0.83199 | 2.59814 |
| 8 | C | -0.659 | 0.63124 | 2.83648 |
| 9 | N | -0.49694 | 1.42385 | 1.59162 |
| 10 | C | 0.36634 | 2.60744 | 1.87831 |
| 11 | C | 1.85536 | 2.26629 | 1.84982 |
| 12 | N | 2.31663 | 1.74302 | 0.54367 |
| 13 | C | 3.66755 | 1.13855 | 0.68302 |
| 14 | C | 3.6209 | -0.2414 | 1.3386 |
| 15 | N | 2.74391 | -1.20964 | 0.63006 |
| 16 | C | 2.33355 | -2.28734 | 1.56754 |
| 17 | C | 1.17972 | -1.84695 | 2.46826 |
| 18 | H | 0.98072 | -2.64023 | 3.20769 |
| 19 | H | 1.47444 | -0.95478 | 3.03098 |
| 20 | H | 3.17771 | -2.59724 | 2.20345 |
| 21 | H | 2.0409 | -3.1619 | 0.98299 |
| 22 | C | 3.44537 | -1.78345 | -0.5555 |
| 23 | C | 3.51851 | -0.79519 | -1.73812 |
| 24 | O | 2.43629 | -0.06792 | -1.88224 |
| 25 | O | 4.5136 | -0.76969 | -2.45029 |
| 26 | H | 2.85477 | -2.63829 | -0.9008 |
| 27 | H | 4.45492 | -2.12529 | -0.2924 |
| 28 | H | 4.64674 | -0.63669 | 1.40201 |
| 29 | H | 3.25826 | -0.15021 | 2.36781 |
| 30 | H | 4.32922 | 1.78889 | 1.27787 |
| 31 | H | 4.10086 | 1.06262 | -0.31483 |
| 32 | C | 2.3448 | 2.82541 | -0.48131 |
| 33 | C | 0.93848 | 3.18502 | -1.00205 |
| 34 | O | 0.16842 | 2.14325 | -1.19531 |
| 35 | O | 0.63703 | 4.35719 | -1.2039 |
| 36 | H | 2.90701 | 2.43747 | -1.33647 |
| 37 | H | 2.84305 | 3.72554 | -0.09719 |
| 38 | H | 2.42233 | 3.1715 | 2.12381 |
| 39 | H | 2.07708 | 1.51236 | 2.61328 |
| 40 | H | 0.12178 | 3.03065 | 2.86543 |
| 41 | H | 0.15129 | 3.38249 | 1.14165 |

| | | | | |
|---|---|---|---|---|
| 42 | C | -1.79913 | 1.90647 | 1.06748 |
| 43 | C | -2.61986 | 0.86669 | 0.33799 |
| 44 | N | -1.95339 | -0.01004 | -0.43827 |
| 45 | C | -2.63569 | -0.87392 | -1.21183 |
| 46 | C | -4.02988 | -0.91353 | -1.24355 |
| 47 | C | -4.69831 | -0.01675 | -0.41911 |
| 48 | N | -6.18072 | -0.02554 | -0.38841 |
| 49 | O | -6.72928 | 0.76614 | 0.37902 |
| 50 | O | -6.75114 | -0.82472 | -1.129 |
| 51 | C | -4.01762 | 0.88822 | 0.38622 |
| 52 | H | -4.56563 | 1.57945 | 1.01492 |
| 53 | H | -4.57433 | -1.60891 | -1.86924 |
| 54 | H | -2.02612 | -1.5423 | -1.81177 |
| 55 | H | -1.56705 | 2.67428 | 0.3204 |
| 56 | H | -2.40352 | 2.3637 | 1.86657 |
| 57 | H | -1.42038 | 1.0887 | 3.48953 |
| 58 | H | 0.28726 | 0.68561 | 3.38265 |
| 59 | H | -1.11301 | -1.3344 | 3.57598 |
| 60 | H | -2.00855 | -0.8934 | 2.12406 |
| 61 | H | -1.7196 | -2.59937 | 0.99595 |
| 62 | H | -0.58601 | -3.60271 | 1.91858 |
| 63 | O | -0.09087 | 0.10084 | -2.86276 |
| 64 | H | 0.80525 | -0.09881 | -3.19884 |
| 65 | H | -0.12529 | 1.07895 | -2.80822 |

| Tb(**L3**) $T_1$ | | | 0 imaginary frequencies | |
|---|---|---|---|---|
| Center Number | Atom | X | Y | Z |
| 1 | Tb | 0.63016 | -0.01655 | -0.46025 |
| 2 | O | 0.2712 | -2.24746 | -0.9724 |
| 3 | C | -0.15685 | -3.19887 | -0.21092 |
| 4 | O | -0.11964 | -4.40974 | -0.44341 |
| 5 | C | -0.81432 | -2.7326 | 1.10829 |
| 6 | N | -0.17201 | -1.51663 | 1.67166 |
| 7 | C | -1.13092 | -0.77913 | 2.53123 |
| 8 | C | -0.70172 | 0.66494 | 2.78475 |
| 9 | N | -0.47675 | 1.4532 | 1.54651 |
| 10 | C | 0.41236 | 2.60937 | 1.85797 |
| 11 | C | 1.88888 | 2.21947 | 1.88594 |
| 12 | N | 2.37987 | 1.67278 | 0.59851 |
| 13 | C | 3.69454 | 1.00818 | 0.79719 |

| | | | | |
|---|---|---|---|---|
| 14 | C | 3.55699 | -0.36886 | 1.44402 |
| 15 | N | 2.67572 | -1.29575 | 0.68787 |
| 16 | C | 2.19386 | -2.37034 | 1.59458 |
| 17 | C | 1.02523 | -1.90179 | 2.46028 |
| 18 | H | 0.76744 | -2.70148 | 3.17404 |
| 19 | H | 1.33325 | -1.03472 | 3.0537 |
| 20 | H | 3.00362 | -2.7191 | 2.25466 |
| 21 | H | 1.89299 | -3.22613 | 0.98724 |
| 22 | C | 3.40353 | -1.88363 | -0.47054 |
| 23 | C | 3.52964 | -0.90086 | -1.65289 |
| 24 | O | 2.49815 | -0.12947 | -1.83091 |
| 25 | O | 4.54665 | -0.93113 | -2.34453 |
| 26 | H | 2.80862 | -2.72435 | -0.84075 |
| 27 | H | 4.39777 | -2.24577 | -0.17869 |
| 28 | H | 4.56055 | -0.80797 | 1.55852 |
| 29 | H | 3.14624 | -0.26399 | 2.45334 |
| 30 | H | 4.35687 | 1.62709 | 1.42371 |
| 31 | H | 4.17122 | 0.91609 | -0.17951 |
| 32 | C | 2.51019 | 2.75393 | -0.41869 |
| 33 | C | 1.15569 | 3.17384 | -1.02186 |
| 34 | O | 0.33153 | 2.18033 | -1.22036 |
| 35 | O | 0.94969 | 4.35491 | -1.28842 |
| 36 | H | 3.10087 | 2.34674 | -1.24523 |
| 37 | H | 3.02566 | 3.63136 | -0.00616 |
| 38 | H | 2.47829 | 3.10461 | 2.17654 |
| 39 | H | 2.05574 | 1.46178 | 2.6593 |
| 40 | H | 0.14606 | 3.04872 | 2.83227 |
| 41 | H | 0.24704 | 3.38381 | 1.10784 |
| 42 | C | -1.75348 | 1.97719 | 0.98802 |
| 43 | C | -2.5958 | 0.94263 | 0.27779 |
| 44 | N | -1.92663 | 0.06773 | -0.51411 |
| 45 | C | -2.64583 | -0.7893 | -1.27819 |
| 46 | C | -4.02942 | -0.83721 | -1.27691 |
| 47 | C | -4.71032 | 0.05643 | -0.42501 |
| 48 | N | -6.08467 | 0.04196 | -0.35763 |
| 49 | O | -6.77585 | 0.81979 | 0.40848 |
| 50 | O | -6.82993 | -0.76216 | -1.04272 |
| 51 | C | -3.97991 | 0.96727 | 0.36657 |
| 52 | H | -4.49873 | 1.66704 | 1.01108 |
| 53 | H | -4.57492 | -1.53496 | -1.89978 |
| 54 | H | -2.06025 | -1.45206 | -1.90703 |
| 55 | H | -1.47462 | 2.7186 | 0.23162 |
| 56 | H | -2.34628 | 2.47567 | 1.77024 |
| 57 | H | -1.45893 | 1.15351 | 3.41924 |
| 58 | H | 0.23213 | 0.67586 | 3.35509 |

| | | | | |
|---|---|---|---|---|
| 59 | H | -1.26215 | -1.28171 | 3.50355 |
| 60 | H | -2.10079 | -0.79236 | 2.03119 |
| 61 | H | -1.85278 | -2.48606 | 0.86555 |
| 62 | H | -0.82193 | -3.55772 | 1.83256 |
| 63 | O | 0.0053 | 0.12958 | -2.8829 |
| 64 | H | 0.89798 | -0.07872 | -3.21905 |
| 65 | H | -0.03075 | 1.10783 | -2.85035 |

| Tb(**L4**) GS | | | 0 imaginary frequencies | |
|---|---|---|---|---|
| Center Number | Atom | X | Y | Z |
| 1 | Tb | 0.34407 | -0.02207 | -0.47022 |
| 2 | O | -0.00987 | -2.22641 | -1.02744 |
| 3 | C | -0.4216 | -3.21461 | -0.29132 |
| 4 | O | -0.35916 | -4.41487 | -0.54603 |
| 5 | C | -1.10124 | -2.77325 | 1.0269 |
| 6 | N | -0.48511 | -1.56018 | 1.62857 |
| 7 | C | -1.46639 | -0.85471 | 2.48516 |
| 8 | C | -1.06371 | 0.58949 | 2.77734 |
| 9 | N | -0.83184 | 1.40778 | 1.5623 |
| 10 | C | 0.0384 | 2.56589 | 1.91371 |
| 11 | C | 1.51945 | 2.19271 | 1.95499 |
| 12 | N | 2.03526 | 1.68077 | 0.66526 |
| 13 | C | 3.35654 | 1.03162 | 0.86611 |
| 14 | C | 3.23132 | -0.36279 | 1.47851 |
| 15 | N | 2.37313 | -1.28332 | 0.69099 |
| 16 | C | 1.89083 | -2.3828 | 1.56518 |
| 17 | C | 0.70507 | -1.94697 | 2.42563 |
| 18 | H | 0.44718 | -2.76542 | 3.11862 |
| 19 | H | 0.99515 | -1.08942 | 3.04217 |
| 20 | H | 2.69503 | -2.73898 | 2.22885 |
| 21 | H | 1.60557 | -3.22614 | 0.93341 |
| 22 | C | 3.12323 | -1.833 | -0.47501 |
| 23 | C | 3.28251 | -0.81093 | -1.61985 |
| 24 | O | 2.22835 | -0.05439 | -1.79999 |
| 25 | O | 4.31734 | -0.7899 | -2.27547 |
| 26 | H | 2.53014 | -2.6593 | -0.87977 |
| 27 | H | 4.10937 | -2.20879 | -0.17121 |
| 28 | H | 4.24033 | -0.78984 | 1.59358 |

| | | | | |
|---|---|---|---|---|
| 29 | H | 2.80828 | -0.28734 | 2.48582 |
| 30 | H | 4.00103 | 1.64564 | 1.51645 |
| 31 | H | 3.8467 | 0.9682 | -0.10598 |
| 32 | C | 2.15743 | 2.78271 | -0.33061 |
| 33 | C | 0.79822 | 3.20381 | -0.92489 |
| 34 | O | 0.00102 | 2.19808 | -1.17613 |
| 35 | O | 0.56088 | 4.39112 | -1.12988 |
| 36 | H | 2.75399 | 2.39337 | -1.16147 |
| 37 | H | 2.6636 | 3.6563 | 0.10223 |
| 38 | H | 2.09217 | 3.07978 | 2.27381 |
| 39 | H | 1.68478 | 1.42103 | 2.71502 |
| 40 | H | -0.24702 | 2.97867 | 2.89491 |
| 41 | H | -0.12295 | 3.35679 | 1.18013 |
| 42 | C | -2.10236 | 1.92453 | 0.99006 |
| 43 | C | -2.91129 | 0.90334 | 0.22085 |
| 44 | N | -2.21192 | 0.04605 | -0.55304 |
| 45 | C | -2.90736 | -0.78937 | -1.35442 |
| 46 | C | -4.29035 | -0.81779 | -1.41259 |
| 47 | C | -5.03018 | 0.06191 | -0.59359 |
| 48 | N | -6.3953 | 0.09217 | -0.63291 |
| 49 | H | -6.90596 | 0.60179 | 0.07103 |
| 50 | H | -6.89581 | -0.6459 | -1.1031 |
| 51 | C | -4.30069 | 0.93341 | 0.24377 |
| 52 | H | -4.81891 | 1.63899 | 0.88734 |
| 53 | H | -4.79165 | -1.50884 | -2.08275 |
| 54 | H | -2.30354 | -1.45404 | -1.96451 |
| 55 | H | -1.81914 | 2.69342 | 0.26296 |
| 56 | H | -2.72372 | 2.38905 | 1.77265 |
| 57 | H | -1.83683 | 1.05331 | 3.41282 |
| 58 | H | -0.13819 | 0.60044 | 3.36119 |
| 59 | H | -1.61034 | -1.37904 | 3.44511 |
| 60 | H | -2.42642 | -0.8691 | 1.96564 |
| 61 | H | -2.13948 | -2.53062 | 0.77759 |
| 62 | H | -1.1102 | -3.61099 | 1.7376 |
| 63 | O | -0.21746 | 0.19978 | -2.91428 |
| 64 | H | 0.70785 | 0.01772 | -3.17523 |
| 65 | H | -0.26085 | 1.17453 | -2.8207 |

| Tb(**L4**) $T_1$ | | | 0 imaginary frequencies | |
|---|---|---|---|---|
| Center Number | Atom | X | Y | Z |
| 1 | Tb | 0.34933 | -0.02154 | -0.46213 |
| 2 | O | -0.07635 | -2.21064 | -1.0403 |
| 3 | C | -0.58486 | -3.16832 | -0.3265 |
| 4 | O | -0.61132 | -4.36737 | -0.59642 |
| 5 | C | -1.26133 | -2.6936 | 0.98095 |
| 6 | N | -0.59118 | -1.52081 | 1.6045 |
| 7 | C | -1.55128 | -0.76882 | 2.44661 |
| 8 | C | -1.08903 | 0.65517 | 2.75186 |
| 9 | N | -0.79622 | 1.45758 | 1.54106 |
| 10 | C | 0.11458 | 2.57951 | 1.89469 |
| 11 | C | 1.57757 | 2.14622 | 1.9755 |
| 12 | N | 2.10321 | 1.59878 | 0.70351 |
| 13 | C | 3.38294 | 0.8837 | 0.94616 |
| 14 | C | 3.16892 | -0.50154 | 1.55435 |
| 15 | N | 2.2957 | -1.38033 | 0.73699 |
| 16 | C | 1.74046 | -2.46212 | 1.58975 |
| 17 | C | 0.55741 | -1.9756 | 2.42518 |
| 18 | H | 0.24088 | -2.78676 | 3.10233 |
| 19 | H | 0.87268 | -1.13977 | 3.05883 |
| 20 | H | 2.51103 | -2.86319 | 2.26766 |
| 21 | H | 1.42862 | -3.28409 | 0.94254 |
| 22 | C | 3.05407 | -1.9575 | -0.40897 |
| 23 | C | 3.27747 | -0.94544 | -1.55187 |
| 24 | O | 2.26394 | -0.14242 | -1.75202 |
| 25 | O | 4.32332 | -0.97509 | -2.19071 |
| 26 | H | 2.44234 | -2.76239 | -0.82864 |
| 27 | H | 4.01835 | -2.36852 | -0.08151 |
| 28 | H | 4.15158 | -0.97663 | 1.70497 |
| 29 | H | 2.71459 | -0.40327 | 2.54583 |
| 30 | H | 4.03706 | 1.46551 | 1.61612 |
| 31 | H | 3.90035 | 0.79334 | -0.00967 |
| 32 | C | 2.31467 | 2.68609 | -0.29211 |
| 33 | C | 1.00898 | 3.16444 | -0.9578 |
| 34 | O | 0.15553 | 2.2065 | -1.20473 |
| 35 | O | 0.86931 | 4.35412 | -1.22921 |
| 36 | H | 2.92821 | 2.26701 | -1.09561 |
| 37 | H | 2.84035 | 3.54047 | 0.15545 |
| 38 | H | 2.18184 | 3.01014 | 2.29973 |
| 39 | H | 1.69089 | 1.37558 | 2.74605 |
| 40 | H | -0.17319 | 3.02234 | 2.86235 |
| 41 | H | -0.0007 | 3.36296 | 1.14373 |
| 42 | C | -2.045 | 2.02975 | 0.93168 |

| | | | | |
|---|---|---|---|---|
| 43 | C | -2.91587 | 1.01227 | 0.28116 |
| 44 | N | -2.19017 | 0.15751 | -0.65911 |
| 45 | C | -2.89112 | -0.51294 | -1.57605 |
| 46 | C | -4.28431 | -0.56656 | -1.58465 |
| 47 | C | -5.03019 | 0.15817 | -0.51076 |
| 48 | N | -6.40555 | 0.07197 | -0.55301 |
| 49 | H | -6.93849 | 0.46355 | 0.21238 |
| 50 | H | -6.82275 | -0.74174 | -0.98706 |
| 51 | C | -4.30316 | 0.96258 | 0.36462 |
| 52 | H | -4.81707 | 1.57726 | 1.1009 |
| 53 | H | -4.8184 | -1.1199 | -2.34973 |
| 54 | H | -2.30501 | -1.06498 | -2.30633 |
| 55 | H | -1.68309 | 2.72935 | 0.16583 |
| 56 | H | -2.61827 | 2.59528 | 1.68458 |
| 57 | H | -1.85926 | 1.15063 | 3.36677 |
| 58 | H | -0.1792 | 0.62767 | 3.36049 |
| 59 | H | -1.7418 | -1.29232 | 3.39915 |
| 60 | H | -2.49709 | -0.72231 | 1.90342 |
| 61 | H | -2.27827 | -2.38979 | 0.71238 |
| 62 | H | -1.33386 | -3.53349 | 1.68559 |
| 63 | O | -0.12872 | 0.21618 | -2.93299 |
| 64 | H | 0.79467 | -0.01969 | -3.15594 |
| 65 | H | -0.11528 | 1.19192 | -2.83367 |

| Tb(**L5**) GS | | | 0 imaginary frequencies | |
|---|---|---|---|---|
| Center Number | Atom | X | Y | Z |
| 1 | Tb | 0.34383 | -0.02187 | -0.46558 |
| 2 | O | -0.01407 | -2.22021 | -1.03006 |
| 3 | O | -0.23038 | -4.42066 | -0.52575 |
| 4 | O | 2.20378 | -0.0228 | -1.81567 |
| 5 | O | 4.29874 | -0.72263 | -2.31776 |
| 6 | O | -0.07147 | 2.18339 | -1.16436 |
| 7 | O | 0.42333 | 4.39116 | -1.10465 |
| 8 | O | -0.27018 | 0.18501 | -2.89784 |
| 9 | N | -0.85604 | 1.3873 | 1.57687 |
| 10 | N | -0.44467 | -1.57274 | 1.63905 |
| 11 | N | 2.40072 | -1.24161 | 0.67295 |
| 12 | N | 1.99792 | 1.71539 | 0.65143 |

| | | | | |
|---|---|---|---|---|
| 13 | N | -2.2344 | 0.00821 | -0.53616 |
| 14 | F | -6.33198 | 0.00545 | -0.62868 |
| 15 | C | -1.06701 | 0.56287 | 2.79276 |
| 16 | C | -1.43711 | -0.89019 | 2.50182 |
| 17 | C | 0.76268 | -1.9247 | 2.42807 |
| 18 | C | 1.94829 | -2.34469 | 1.55949 |
| 19 | C | 3.25262 | -0.30107 | 1.44538 |
| 20 | C | 3.33684 | 1.09611 | 0.83168 |
| 21 | C | 1.48675 | 2.20979 | 1.95 |
| 22 | C | -0.0006 | 2.55857 | 1.92639 |
| 23 | C | -2.13668 | 1.8874 | 1.01593 |
| 24 | C | -1.03282 | -2.80591 | 1.04867 |
| 25 | C | -0.35666 | -3.22457 | -0.27866 |
| 26 | C | 3.1464 | -1.78364 | -0.49997 |
| 27 | C | 3.2741 | -0.76125 | -1.64845 |
| 28 | C | 2.07907 | 2.82329 | -0.34257 |
| 29 | C | 0.70057 | 3.21047 | -0.91519 |
| 30 | C | -2.93254 | 0.86472 | 0.23566 |
| 31 | C | -4.32917 | 0.88946 | 0.23994 |
| 32 | C | -4.99178 | 0.00687 | -0.60795 |
| 33 | C | -4.29016 | -0.87289 | -1.42622 |
| 34 | C | -2.90053 | -0.83462 | -1.34904 |
| 35 | H | 0.64657 | 0.00382 | -3.18643 |
| 36 | H | -0.3155 | 1.16032 | -2.81179 |
| 37 | H | -1.84799 | 1.00879 | 3.43086 |
| 38 | H | -0.14025 | 0.59455 | 3.37342 |
| 39 | H | -1.56403 | -1.41765 | 3.46209 |
| 40 | H | -2.40012 | -0.92891 | 1.98867 |
| 41 | H | 0.52937 | -2.74006 | 3.13289 |
| 42 | H | 1.04093 | -1.05361 | 3.03091 |
| 43 | H | 2.76544 | -2.68006 | 2.21769 |
| 44 | H | 1.67366 | -3.19847 | 0.93682 |
| 45 | H | 4.27231 | -0.70599 | 1.54201 |
| 46 | H | 2.84629 | -0.23528 | 2.46013 |
| 47 | H | 3.97686 | 1.72416 | 1.47269 |
| 48 | H | 3.81287 | 1.04449 | -0.14807 |
| 49 | H | 2.04705 | 3.10454 | 2.2689 |
| 50 | H | 1.67317 | 1.43617 | 2.7031 |
| 51 | H | -0.28283 | 2.95997 | 2.91284 |
| 52 | H | -0.18217 | 3.3517 | 1.20001 |
| 53 | H | -1.87302 | 2.67 | 0.29556 |
| 54 | H | -2.7662 | 2.33048 | 1.80387 |
| 55 | H | -2.08218 | -2.59648 | 0.81565 |
| 56 | H | -1.0052 | -3.64208 | 1.76026 |
| 57 | H | 2.56403 | -2.62234 | -0.89504 |

| | | | | |
|---|---|---|---|---|
| 58 | H | 4.14224 | -2.14112 | -0.20662 |
| 59 | H | 2.67435 | 2.45193 | -1.18257 |
| 60 | H | 2.56817 | 3.70835 | 0.08614 |
| 61 | H | -4.88752 | 1.57501 | 0.86704 |
| 62 | H | -4.80619 | -1.55664 | -2.08879 |
| 63 | H | -2.27737 | -1.49139 | -1.9481 |

| Tb(**L5**) $T_1$ | | | 0 imaginary frequencies | |
|---|---|---|---|---|
| Center Number | Atom | X | Y | Z |
| 1 | Tb | 0.32922 | -0.01383 | -0.45083 |
| 2 | O | 0.0417 | -2.22463 | -1.0739 |
| 3 | O | -0.43093 | -4.39701 | -0.67472 |
| 4 | O | 2.23472 | -0.02405 | -1.77468 |
| 5 | O | 4.31227 | -0.76559 | -2.27648 |
| 6 | O | 0.03706 | 2.21961 | -1.14564 |
| 7 | O | 0.69089 | 4.38213 | -1.19736 |
| 8 | O | -0.1965 | 0.23986 | -2.90389 |
| 9 | N | -0.82821 | 1.36945 | 1.59004 |
| 10 | N | -0.49191 | -1.60251 | 1.58368 |
| 11 | N | 2.36723 | -1.31036 | 0.68617 |
| 12 | N | 2.04229 | 1.65958 | 0.71299 |
| 13 | N | -2.21373 | 0.03982 | -0.59515 |
| 14 | F | -6.39362 | 0.02917 | -0.55364 |
| 15 | C | -1.05823 | 0.52468 | 2.78727 |
| 16 | C | -1.47064 | -0.90782 | 2.45318 |
| 17 | C | 0.68327 | -2.03166 | 2.38121 |
| 18 | C | 1.87862 | -2.43837 | 1.52111 |
| 19 | C | 3.20595 | -0.40763 | 1.51387 |
| 20 | C | 3.35427 | 0.99557 | 0.92873 |
| 21 | C | 1.51354 | 2.16661 | 2.00135 |
| 22 | C | 0.03068 | 2.52977 | 1.95097 |
| 23 | C | -2.12003 | 1.8871 | 1.02573 |
| 24 | C | -1.12769 | -2.78534 | 0.94254 |
| 25 | C | -0.44018 | -3.19982 | -0.37707 |
| 26 | C | 3.13861 | -1.82455 | -0.47872 |
| 27 | C | 3.28067 | -0.78473 | -1.61039 |

| | | | | |
|---|---|---|---|---|
| 28 | C | 2.19721 | 2.77022 | -0.26656 |
| 29 | C | 0.86796 | 3.19859 | -0.91608 |
| 30 | C | -2.94213 | 0.82066 | 0.39392 |
| 31 | C | -4.38535 | 0.79328 | 0.44017 |
| 32 | C | -5.05077 | 0.14459 | -0.54246 |
| 33 | C | -4.32565 | -0.51141 | -1.63503 |
| 34 | C | -2.90709 | -0.52835 | -1.56004 |
| 35 | H | 0.72572 | 0.05416 | -3.17071 |
| 36 | H | -0.23442 | 1.21447 | -2.80635 |
| 37 | H | -1.83207 | 0.97234 | 3.43257 |
| 38 | H | -0.1327 | 0.51847 | 3.37214 |
| 39 | H | -1.63414 | -1.46193 | 3.39264 |
| 40 | H | -2.42482 | -0.87989 | 1.9188 |
| 41 | H | 0.41001 | -2.87605 | 3.03546 |
| 42 | H | 0.96706 | -1.20269 | 3.03794 |
| 43 | H | 2.67706 | -2.81418 | 2.18064 |
| 44 | H | 1.60246 | -3.26106 | 0.85905 |
| 45 | H | 4.20956 | -0.8409 | 1.65128 |
| 46 | H | 2.75333 | -0.34652 | 2.50889 |
| 47 | H | 3.9907 | 1.59251 | 1.60194 |
| 48 | H | 3.86509 | 0.94516 | -0.03367 |
| 49 | H | 2.08167 | 3.05417 | 2.32592 |
| 50 | H | 1.67751 | 1.39369 | 2.76011 |
| 51 | H | -0.26389 | 2.94066 | 2.93014 |
| 52 | H | -0.13663 | 3.31819 | 1.21516 |
| 53 | H | -1.82079 | 2.61946 | 0.26015 |
| 54 | H | -2.70035 | 2.40923 | 1.80353 |
| 55 | H | -2.15561 | -2.51404 | 0.68342 |
| 56 | H | -1.16441 | -3.64236 | 1.62828 |
| 57 | H | 2.5695 | -2.65625 | -0.90566 |
| 58 | H | 4.13106 | -2.18309 | -0.17574 |
| 59 | H | 2.82216 | 2.39392 | -1.08229 |
| 60 | H | 2.68775 | 3.64086 | 0.18896 |
| 61 | H | -4.91834 | 1.30048 | 1.2379 |
| 62 | H | -4.8597 | -0.99947 | -2.4399 |
| 63 | H | -2.33056 | -1.05551 | -2.31676 |

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