Electronic Supplementary Information

Ligand synthesis

2-Chloro-N-[(S)[1- ethoxycarbonyl-2-phenyl] ethyl] ethanamide

S-Phenylalaninethylester hydrochloride (3 g, 13.1 mmol) was dissolved in dry diethyl ether (100 ml) under argon and triethylamine (4.37 ml, 31.3 mmol) was added. The solution was cooled to –20 °C (acetone, CO_2 (s) bath) and chloroacetylchloride (1.25 ml, 15.7 mmol) in dry diethyl ether (60 ml) was added dropwise, maintaining the temperature at –20 °C. The reaction mixture was allowed to warm to room temperature and stirred for 1 h. The resulting white precipitate was dissolved in water (60 ml) and the organic layer washed with hydrochloric acid (0.1 M, 80 ml), water (3 x 80 ml), dried (K_2CO_3) and the solvent was removed in vacuo to give a pale yellow solid. The product was recrystallised from ether adding hexane and was isolated as white needles (2.47 g, 70%), m.p. 38-40 °C; (Found: C, 57.7; H, 5.98; N, 5.12. $C_{13}H_{16}NO_3Cl$ requires C, 57.9; H, 5.98; N, 5.16%); ν_{max} (solid)/cm^{-1} 3310 (NH), 1731 (*CO*O), 1650 (*CO*NH); δ_H (200 MHz, $CDCl_3$) 7.30-7.10 (5H, m, Ar), 7.00 (1H, br s, NH), 4.84 (1H, m, CH), 4.17 (2H, q, $^3J = 7.2$, CH_2O), 4.00 (2H, s, CH_2Cl), 3.14 (2H, d, $^3J = 5.8$, CH_2Ph), 1.24 (3H, t, $^3J = 7$, CH_3); δ_C (50.29 MHz, $CDCl_3$) 171.2 (CO_2Et), 166.4 (CONH), 136.0 (ipso-Ar), 129.5 (m-Ar), 128.7 (o-Ar), 127.3 (p-Ar), 61.8 (OCH_2), 53.9 (CH), 42.6 (CH_2Cl), 37.8 (CH_2Ph), 14.2 (CH_3); m/z (ES^+) 292 (100%, MNa^+), 561 (90%, M_2Na^+), 270 (20%, MH^+).

2-Chloro-N-[(S)[1-methoxycarbonyl-3-methyl] butyl] ethanamide

The title compound was prepared following a method similar to that above, using S-leucinemethylester hydrochloride (3 g, 16.5 mmol) and triethylamine (5.52 ml, 39.6 mmol) in dry diethyl ether (100 ml) and reacting with a solution of chloroacetylchloride

(1.58 ml, 19.8 mmol) in dry diethyl ether (60 ml). A brown oil resulted (3.21 g, 88%); ν_{max} (film)/cm^{-1} 3304 (NH), 1745 (*CO*O), 1680 (*CO*NH); δ_H (200 MHz, $CDCl_3$) 6.90 (1H, br s, NH), 4.68-4.56 (1H, br m, C*H*NH), 4.04 (2H, s, $ClCH_2CO$), 3.72 (3H, s, OCH_3), 1.69-1.50 (3H, br m, CH_2CH), 0.92 (6H, d, $^3J = 5.8$, CH_3); δ_C (50.29 MHz, $CDCl_3$) 172.8 (CO_2Me), 166.6 (CONH), 52.2 (OCH_3), 51.0 (CHNH), 42.4 ($ClCH_2CO$), 40.7 (CH_2CH), 24.7 (CH_2CH), 22.7 (CH_3), 21.6 (CH_3); m/z (ES^+) 244 (100%, MNa^+) (Found: MNa^+, 244.0739. $C_9H_{16}NO_3NaCl$ requires MNa^+, 244.0716).

General procedure for the preparation of tetraalkylated ligands.

1-Benzyl-4,7,10–Tris-[(S)-((1-ethoxycarbonyl-2-phenyl)ethyl)carbamoylmethyl]-1,4,7,10-tetraazacyclododecane

2-Chloro-N-[(S)[1- ethoxycarbonyl-2-phenyl] ethyl] ethanamide (2.68 g, 9.96 mmol) in dry N,N-dimethylformamide (5 ml) was added to a stirred solution of 1-benzyl-1,4,7,10-tetraazacyclododecane[14] (0.872 g, 3.32 mmol) and fine mesh anhydrous potassium carbonate (1.37 g, 9.96 mmol) in dry N,N-dimethylformamide (25 ml). The reaction mixture was heated at 60 °C under an argon atmosphere for 36 h. The solvent was distilled off under vacuum and the resulting brown oil was extracted into dichloromethane (40 ml), washed with purite water (3 x 40 ml), brine (40 ml), dried (K_2CO_3) and concentrated to dryness to give a yellow brown oil. The mixture was purified by alumina column chromatography (gradient elution from dichloromethane to 0.5% methanol-dichloromethane) and the product was isolated as a pale yellow oil (1.54 g, 48 %); R_f (Al_2O_3; 10% CH_3OH-CH_2Cl_2; I_2 and u.v. detection) 0.5; δ_H (200 MHz, $CDCl_3$) 7.8 (1H, br s, NHCO), 7.5 (2H, br s, NHCO), 7.3-7.0 (20H, m, Ar), 4.7 (3H, m, CH), 4.01 (6H, m, OCH_2), 3.8-2.2 (30H, m, ring-CH_2, CH_2CO, CH_2Ph, NCH_2Ph), 1.14 (9H, m, CH_3); δ_C (50.29 MHz, $CDCl_3$) 171.8 (CO_2Et), 171 (CONH), 138.1 (ipso-Ar), 136.6 (ipso-Ar), 129.6, 129.3, 128.5, 127.1 (C-Ar), 61.5 (OCH_2), 59.4-59.1 (br, NCH_2Ph, N*C*H_2CO), 53.9- 52.0 (br, CH, ring-CH_2), 37.0 (C*C*H_2Ph), 14.3 (CH_3); m/z (ES^+) 985 (100%, MNa^+), 963 (45%, MH^+), 501 (5%, MCa^{2+}).

1-Benzyl-4,7,10–tris-[(S)-((1-methoxycarbonyl-3-methyl)butyl)carbamoylmethyl]-1,4,7,10-tetraazacyclododecane L^6

The title compound was prepared following a method similar to that above, using 2-Chloro-N-[(S)[1-methoxycarbonyl-3-methyl] butyl] ethanamide (1.33 g, 6.00 mmol) in dry N,N-dimethylformamide (5 ml) and reacting with a solution of 1-benzyl-1,4,7,10-tetraazacyclododecane[14] (0.526 g, 2.00 mmol) and fine mesh anhydrous potassium carbonate (0.830 g, 6.00 mmol) in dry N,N-dimethylformamide (25 ml). The product was obtained, after purification, as a brown oil (0.821 g, 50%); R_f (Al_2O_3; 10% CH_3OH-CH_2Cl_2; I_2 and u.v. detection) 0.38; ν_{max} (film)/cm^{-1} 1741 (*CO*O), 1659 (*CO*NH); δ_H (200 MHz, $CDCl_3$) 8.0-7.8 (3H, br s, NHCO), 7.3-7.1 (5H, m, Ar), 4.5 (3H, m, C*H*NH), 3.70-2.40 (33H, br m, ring-CH_2, CH_2CO, OCH_3, CH_2Ph), 1.58-1.40 (9H, br m, C*H*$_2$CH, CH_2C*H*), 0.87 (18H, m, CH_3); δ_C (50.29 MHz, $CDCl_3$) 173.4 (CO_2Me), 173.2 (CO_2Me), 171.3 (CONH), 170.9 (CONH), 138.0 (ipso-Ar), 129.0, 128.5, 127.4 (C-Ar), 59.9-59.0 (br, NCH_2Ph, N*C*H_2CO), 53.4-52.3 (br, ring-CH_2, OCH_3), 50.5 (CHNH), 41.3 (*C*H_2CH), 25.1 (CH_2*C*H), 23.0 (CH_3), 22.1 (CH_3); m/z (ES^+) 429 (100%, MCa^{2+}), 840 (30%, MNa^+) 440 (20%, MK^+Na^+) (Found: $(MHK)^{2+}$, 428.7514. $C_{42}H_{72}N_7O_9K$ requires $(MHK)^{2+}$, 428.7542).

General procedure for the preparation of trialkylated ligands.

1,4,7–Tris-[(S)-((1-ethoxycarbonyl-2-phenyl)ethyl)carbamoylmethyl]-1,4,7,10-tetraazacyclododecane L^2

A hydrochloric acid solution (1 M, 1 ml) and a catalytic amount of palladium hydroxide on carbon were added to 1-Benzyl-4,7,10–Tris-[(S)-((1-ethoxycarbonyl-2-phenyl)ethyl)carbamoylmethyl]-1,4,7,10-tetraazacyclododecane (0.473 g, 0.49 mmol) in ethanol (25 ml) and the mixture was treated with hydrogen (45 psi) at room temperature for 48 h. The reaction mixture was filtered through celite and the solvent was removed under vacuum. The residue was taken into dichloromethane (30 ml) and washed with a solution of sodium bicarbonate (30 ml), brine (1 x 30 ml), dried (K_2CO_3) and concentrated to dryness to give the product as a pale yellow glassy solid (0.31 g, 71%), m.p. 84-88 ^oC; ν_{max} (solid)/cm^{-1} 1734 (*CO*O), 1656 (*CO*NH); δ_H (200 MHz, $CDCl_3$) 7.6 (2H, d, $^3J = 8$, NHCO), 7.4 (1H, d, $^3J = 8$, NHCO), 7.30-7.00 (15H, m, Ar), 4.80 (3H, m, CH), 4.12 (6H, m, OCH_2), 3.45-2.20 (29H, m, ring-CH_2, ring-NH, CH_2Ph, CH_2CO), 1.12 (9H, m, CH_3); δ_C (50.29 MHz, $CDCl_3$) 172.1 (CO_2Et), 171.4 (CONH), 136.8 (ipso-Ar), 129.6 (m-Ar), 128.6 (o-Ar), 127 (p-Ar), 61.5 (OCH_2), 59.7 (*C*H_2CO), 53.9-53.0 (ring-CH_2, CH), 47.3 (ring-CH_2), 37.8 (CH_2Ph), 14.3 (CH_3); m/z (ES$^+$) 456 (100%, MCa $^{2+}$) (A satisfactory accurate mass spectrum could not be obtained for this product).

1,4,7–Tris-[(S)-((1-methoxycarbonyl-3-methyl)butyl)carbamoylmethyl]-1,4,7,10-tetraazacyclododecane L^4

The title compound was prepared following a method similar to that for L^2, treating a solution of L^6 (1.07 g, 1.31 mmol) in ethanol (45 ml) with hydrogen (45 psi), in the presence of a hydrochloric acid solution (1 M, 1 ml) and a catalytic amount of palladium hydroxide on carbon. The product was obtained as a yellow orange glassy solid (0.77 g, 81%), m.p. 120-122 ^{o}C; ν_{max} (solid)/cm^{-1} 1739 (*CO*O), 1665 (*CO*NH); δ_H (200 MHz, CDCl$_3$) 8.0-7.84.(3H, br s, NHCO), 80-2.55 (35H, br m, ring-CH$_2$, CH$_2$CO, OCH$_3$, ring-NH, C*H*NH), 2.00-1.20 (9H, br m, C*H*$_2$CH, CH$_2$C*H*), 1.00-0.87 (18H, br, CH$_3$); δ_C (50.29 MHz, CDCl$_3$) 173.8 (*C*O$_2$Me), 173.4 (*C*O$_2$Me), 171.6 (CONH), 171.5 (CONH), 59.6 (br, N*C*H$_2$CO), 53.8-52.3 (br, ring-CH$_2$, OCH$_3$), 50.7 (CHNH), 47 (ring-CH$_2$), 41.3 (*C*H$_2$CH), 25.1 (CH$_2$*C*H), 23.0 (CH$_3$), 21.1 (CH$_3$); m/z (ES$^+$) 384 (100%, MCa^{2+}), 728 (15%, MH$^+$) 766 (5%, MK$^+$) (Found: MH$^+$, 728.4878. $C_{35}H_{66}N_7O_9$ requires MH$^+$, 728.4922).

Complex synthesis

Yb.L^2

Ytterbium (III) triflate (0.099 g, 0.16 mmol) in dry acetonitrile (1 ml) was added to a solution of L^2 (0.135 g, 0.16 mmol) in dry acetonitrile (4 ml) and the mixture was heated to reflux under argon overnight. The reaction solution was dropped onto stirring diethylether (50 ml) and the resulting white precipitate was collected by centrifugation and filtration. The solid was redissolved in the minimum amount of acetonitrile and the precipitation procedure repeated once more. A white solid resulted (0.134 g, 56%), m.p 142-144 °C; ν_{max} (solid)/cm^{-1} 1736 (*CO*O), 1625 (*CO*NH); δ_H (200 MHz, CD$_3$OD) partial assignment: major isomer 92.0 (1H, br s, ring-H$_{ax}$), 69.0 (1H, br s, ring-H$_{ax}$), 56.0 (1H, br s, ring-H$_{ax}$), 43.0 (1H, br s, ring-H$_{ax}$), 39.1 (1H, br s, ring-H$_{eq}$), 25.2 (1H, br s, ring-H$_{eq}$), 22.3 (1H, br s, ring-H$_{eq}$), 15.0 (1H, br s, ring-H$_{eq}$); minor isomer 96.0 (1H, br s, ring-H$_{ax}$), 67.0 (1H, br s, ring-H$_{ax}$), 59.0 (1H, br s, ring-H$_{ax}$), 43.0 (1H, br s, ring-H$_{ax}$), 41.0 (1H, br s, ring-H$_{eq}$), 27.0 (1H, br s, ring-H$_{eq}$), 23.0 (1H, br s, ring-H$_{eq}$), 19.0 (1H, br s, ring-H$_{eq}$);

m/z (ES^+) 522 (100%, M^{2+}), 349 (5%, M^{3+}) (Found: M^{2+}, 522.2077. $C_{47}H_{64}N_7O_9Yb$ requires M^{2+}, 522.2077).

Eu.L^2

The title compound was prepared using a similar method to that for Yb.L^2 using L^2 (0.057 g, 0.065 mmol) in dry acetonitrile (2 ml) and europium (III) triflate (0.039 g, 0.065 mmol) in dry acetonitrile (3 ml) to yield a white solid (0.056 g, 59%), m.p. 146-148 °C ; ν_{max} (solid)/cm^{-1} 1734 (*CO*O), 1619 (*CO*NH); δ_H (200 MHz, CD_3OD) partial assignment 24.1 (1H, br s, ring-H_{ax}), 14.0 (2H, br s, ring-H_{ax}), 12.3 (1H, br s, ring-H_{ax}), -5.20, -6.02, -9.34, -10.0, -12.4, -15.1, -20.0; m/z (ES^+) 512 (100%, M^{2+}), 587 (10%, $[M^{3+} + (CF_3SO_3^-)]^{2+}$ (Found: M^{2+}, 511.6971. $C_{47}H_{64}N_7O_9Eu$ requires M^{2+}, 511.6989).

Yb.L^3

Yb.L^2 (0.100 g, 0.067 mmol) was dissolved in the minimum amount of methanol and treated with an aqueous sodium hydroxide solution (0.02 M, 13.4 ml). The solution was brought to pH 6, reduced to small volume and loaded onto a cationic exchange column (Dowex, 50 WH$^+$), eluting with water and then aqueous ammonia solution (6%). The ammonia layer was dried giving the product as a yellow solid (0.035 g, 54%), m.p. > 250 °C; ν_{max} (solid)/cm^{-1} 1619 (br, *CO*NH, *CO*O); δ_H (200 MHz, CD_3OD) partial assignment 90.0 (1H, br s, ring-H_{ax}), 64.0 (1H, br s, ring-H_{ax}), 52.0 (1H, br s, ring-H_{ax}), 27.0 (1H, br s, ring-H_{ax}), -22.9, -25.1, -38.6, -46.7, -47.8, -49.9, -60.2, -82.3; m/z (ES^+) after addition of CF_3COOH: 959 (100%, MH^+) (Found: MH^+, 959.3137. $C_{41}H_{51}N_7O_9Yb$ requires MH^+ 951.3131).

Eu.L^3

The title compound was prepared following a method similar for Yb.L^3 using Eu.L^2 (0.150 g, 0.10 mmol), dissolved in the minimum amount of methanol and an aqueous sodium hydroxide solution (0.02 M, 20.4 ml). A yellow solid resulted (0.043 g, 45%), m.p. > 230 °C; ν_{max} (solid)/cm^{-1} 1612 (br, *CO*NH, *CO*O); δ_H (200 MHz, CD_3OD) partial assignment not available, the spectrum showed broad signals between +30 and –20; m/z (ES$^+$) after addition of CF_3COOH: 938 (100%, MH$^+$) (Found: MH$^+$, 938.2962. $C_{41}H_{51}N_7O_9Eu$ requires MH$^+$ 938.2962).

Yb.L^4

The title compound was prepared following a method similar for Yb.L^2, using ytterbium (III) triflate (0.44 g, 0.72 mmol) in dry acetonitrile (3 ml) and L^4 (0.512 g, 0.72 mmol) in dry acetonitrile (4 ml). A yellow solid resulted (0.70 g, 75%), m.p. 142-144 °C; ν_{max} (solid)/cm^{-1} 1742 (*CO*O), 1627 (*CO*NH); δ_H (200 MHz, CD_3OD) partial assignment 119.5 (1H, br s, ring-H$_{ax}$), 76.4 (1H, br s, ring-H$_{ax}$), 67.8 (1H, br, ring-H$_{ax}$), 53.9 (1H, br, ring-H$_{ax}$), 43.0 (1H, br s, ring-H$_{eq}$), 35.8 (1H, br s, ring-H$_{eq}$), 31.9 (1H, br s, ring-H$_{eq}$), 27.0 (1H, br, ring-H$_{eq}$), 12.1, -17.5, -19.1, -29.7, -33.8, -36.3, -41.1, -42.8, -48.5, -78.1, -91.0; m/z (ES$^+$) 450 (100%, M^{2+}) (Found: M^{2+}, 450.2109. $C_{35}H_{64}N_7O_9Yb$ requires M^{2+} 450.2077).

Ce.L^4

The title compound was prepared following a method similar for Yb.L^2, using cerium (III) triflate (0.056 g, 0.096 mmol) in dry acetonitrile (2 ml) and L^4 (0.070 g, 0.096 mmol) in dry acetonitrile (2 ml). A yellow solid resulted (0.090 g, 71%), m.p. > 174 °C (dec.); ν_{max} (solid)/cm^{-1} 1742 (*CO*O), 1627 (*CO*NH); δ_H (200 MHz, CD_3OD) partial assignment 15.0, 13.9, 10.4, 10.1, 8.14, 6.68, 6.1, -1.23, -3.92, -4.60, -8.12 (1H, br s, ring-H_{ax}), -12.1 (1H, br s, ring-H_{ax}); m/z (ES^+) 509 (100%, $[M^{3+} + (CF_3SO_3^-)]^{2+}$), 1164 (20%, $[M^{3+} + (CF_3SO_3^-)_2]^+$ (Found: M^{2+}, 433.1927. $C_{35}H_{64}N_7O_9Ce$ requires M^{2+} 433.1910).

Pr.L^4

The title compound was prepared following a method similar for Yb.L^2, using praseodymium (III) triflate (0.283 g, 0.48 mmol) in dry acetonitrile (3 ml) and L^4 (0.350 g, 0.48 mmol) in dry acetonitrile (3 ml). A yellow solid resulted (0.609 g, 96%), m.p. > 184 °C (dec.); ν_{max} (solid)/cm^{-1} 1742 (*CO*O), 1627 (*CO*NH); δ_H (200 MHz, CD_3OD) partial assignment 25.1, 24.0, 20.71, 14.6, 11.8, 11.04, 8.94, 6.35, -2.0, -5.0, -7.2, -11.2, -13.8 (2H, br s, ring-H_{ax}), -17.1 (1H, br s, ring-H_{ax}), -29.9 (1H, br s, ring-H_{ax}); m/z (ES^+) 434 (100%, M^{2+}), 509 (40%, $[M^{3+} + (CF_3SO_3^-)]^{2+}$) (Found: $[M^{3+} + (CF_3SO_3^-)_2]^+$, 1166.3008. $C_{37}H_{65}N_7O_{15}F_6S_2Pr$ requires $[M^{3+} + (CF_3SO_3^-)_2]^+$ 1166.2961).

Nd.L^4

The title compound was prepared following a method similar for Yb.L^2, using neodymium (III) triflate (0.057 g, 0.096 mmol) in dry acetonitrile (2 ml) and L^4 (0.070 g, 0.096 mmol) in dry acetonitrile (2 ml). A yellow solid resulted (0.093 g, 73%), m.p. > 180 °C (dec.); ν_{max} (solid)/cm^{-1} 1742 (*CO*O), 1627 (*CO*NH); δ_H (200 MHz, CD_3OD) partial assignment 16.3, 15.3, 13.5, 10.2, 9.58, 9.03, 8.66, 5.96, -2.45, -6.03, -8.81, -16.3 (1H, br s, ring-H_{ax}); m/z (ES^+) 511 (100%, $[M^{3+} + (CF_3SO_3^-)]^{2+}$) (Found: M^{2+}, 434.1938. $C_{35}H_{64}N_7O_9Nd$ requires M^{2+} 434.1922).

Sm.L^4

The title compound was prepared following a method similar for Yb.L^2, using samarium (III) triflate (0.074 g, 0.123 mmol) in dry acetonitrile (2 ml) and L^4 (0.090 g, 0.123 mmol) in dry acetonitrile (2 ml). A yellow solid resulted (0.120 g, 73%), m.p. > 184 °C (dec.); ν_{max} (solid)/cm^{-1} 1742 (*CO*O), 1627 (*CO*NH); m/z (ES$^+$) 514 (100%, $[M^{3+} + (CF_3SO_3^-)]^{2+}$), 1176 (10%, $[M^{3+} + (CF_3SO_3^-)_2]^+$) (Found: M^{2+}, 439.2024. $C_{35}H_{64}N_7O_9Sm$ requires M^{2+} 439.1982).

Eu.L^4

The title compound was prepared following a method similar for Yb.L^2, using europium (III) triflate (0.37 g, 0.62 mmol) in dry acetonitrile (3 ml) and L^4 (0.450 g, 0.62 mmol) in dry acetonitrile (3 ml). A yellow solid resulted (0.713 g, 87%), m.p. > 178 °C (dec.); ν_{max} (solid)/cm^{-1} 1742 (*CO*O), 1627 (*CO*NH); δ_H (200 MHz, CD_3OD) partial assignment 24.8 (1H, br s, ring-H$_{ax}$), 16.0 (1H, br s, ring-H$_{ax}$), 13.5 (1H, br s, ring-H$_{ax}$), 9.28 (1H, br s, ring-H$_{eq}$), -1.66, -4.83, -6.40, -7.33, -9.43, -11.6, -13.6, -14.9, -19.0; m/z (ES$^+$) 440 (100%, M^{2+}), 514 (40%, $[M^{3+} + (CF_3SO_3^-)]^{2+}$) (Found: $[M^{3+} + (CF_3SO_3^-)_2]^+$, 1178.3163. $C_{37}H_{65}N_7O_{15}F_6S_2Eu$ requires $[M^{3+} + (CF_3SO_3^-)_2]^+$ 1178.3097).

Tb.L^4

The title compound was prepared following a method similar for Yb.L^2, using terbium (III) triflate (0.075 g, 0.12 mmol) in dry acetonitrile (2 ml) and L^4 (0.090 g, 0.12 mmol) in dry acetonitrile (2 ml). A yellow solid resulted (0.137 g, 83%), m.p. > 160 °C (dec.); ν_{max} (solid)/cm^{-1} 1742 (*CO*O), 1627 (*CO*NH); δ_H (200 MHz, CD_3OD) partial assignment 81.3, -33.9, -55.6, -70.0, -85.2, -112.0, -126.4, -148.3, -166.9 (2H, br s, ring-H$_{ax}$), -234.8

(1H, br s, ring-H_{ax}), -319.7 (1H, br s, ring-H_{ax}); m/z (ES^+) 518 (100%, $[M^{3+} + (CF_3SO_3^-)]^{2+}$), 443 (60%, M^{2+}) (Found: M^{2+}, 442.7041. $C_{35}H_{64}N_7O_9Tb$ requires M^{2+} 442.7010).

Dy.L^4

The title compound was prepared following a method similar for Yb.L^2, using dysprosium (III) triflate (0.075 g, 0.12 mmol) in dry acetonitrile (2 ml) and L^4 (0.090 g, 0.12 mmol) in dry acetonitrile (2 ml). A yellow solid resulted (0.128 g, 77%), m.p. > 174 °C (dec.); ν_{max} (solid)/cm^{-1} 1742 (*CO*O), 1627 (*CO*NH); δ_H (200 MHz, CD_3OD) partial assignment 300.0, 216.0, 191.4, 147.4, 133.6, 120.6, 91.5, 70.9, -62.3, -88.44, -113.3, -138.2, -158.4, -191.0 (1H, br s, ring-H_{ax}), -213.0 (1H, br s, ring-H_{ax}), -237.7 (1H, br s, ring-H_{ax}), -379.4 (1H, br s, ring-H_{ax}); m/z (ES^+) 444 (100%, M^{2+}), 520 (80%, $[M^{3+} + (CF_3SO_3^-)]^{2+}$), 1188 (5%, $[M^{3+} + (CF_3SO_3^-)_2]^{2+}$) (Found: M^{2+}, 445.2023. $C_{35}H_{64}N_7O_9Dy$ requires M^{2+} 445.2028).

Ho.L^4

The title compound was prepared following a method similar for Yb.L^2, using holmium (III) triflate (0.29 g, 0.47 mmol) in dry acetonitrile (3 ml) and L^4 (0.348 g, 0.47 mmol) in dry acetonitrile (3 ml). A yellow solid resulted (0.62 g, 97%), m.p. > 158 °C (dec.); ν_{max} (solid)/cm^{-1} 1742 (*CO*O), 1627 (*CO*NH); δ_H (200 MHz, CD_3OD) partial assignment 191.3, 163.7, 110.8, 97.46, 81.0, 76.51, 74.0, 65.7, 61.0, 39.6, -14.8, -28.7, -59.10, -66.43, -79.81, -86.3 (1H, br s, ring-H_{ax}), -106.2 (1H, br s, ring-H_{ax}), -119.4 (1H, br s, ring-H_{ax}), -124.8 (1H, br s, ring-H_{ax}); m/z (ES^+) 446 (100%, M^{2+}) (Found: $[M^{3+} + (CF_3SO_3^-)_2]^+$, 1190.3165. $C_{37}H_{65}N_7O_{15}F_6S_2Ho$ requires $[M^{3+} + (CF_3SO_3^-)_2]^+$ 1190.3188).

Er.L^4

The title compound was prepared following a method similar for Yb.L^2, using erbium (III) triflate (0.076 g, 0.12 mmol) in dry acetonitrile (2 ml) and L^4 (0.090 g, 0.12 mmol) in dry acetonitrile (2 ml). A yellow solid resulted (0.134 g, 81%), m.p. > 150 °C (dec.); ν_{max} (solid)/cm^{-1} 1742 (*CO*O), 1627 (*CO*NH); δ_H (200 MHz, CD_3OD) partial assignment 117.6 (1H, br s, ring-H_{ax}), 78.1 (1H, br s, ring-H_{ax}), 54.2 (1H, br s, ring-H_{ax}), 50.8 (1H, br s, ring-H_{ax}), 30.2, 25.4, 20.6, -14.3, -17.9, -21.4, -28.4, -33.4, -41.9, -74.7; m/z (ES$^+$) 446 (100%, M^{2+}), 521 (80%, [M^{3+} + ($CF_3SO_3^-$)]$^{2+}$) (Found: M^{2+}, 446.2039. $C_{35}H_{64}N_7O_9Er$ requires M^{2+} 446.2034).

Tm.L^4

The title compound was prepared following a method similar for Yb.L^2, using thulium (III) triflate (0.076 g, 0.12 mmol) in dry acetonitrile (2 ml) and L^4 (0.090 g, 0.12 mmol) in dry acetonitrile (2 ml). A yellow solid resulted (0.130 g, 78%), m.p. > 164 °C (dec.); ν_{max} (solid)/cm^{-1} 1742 (*CO*O), 1627 (*CO*NH); δ_H (200 MHz, CD_3OD) partial assignment 293.0 (1H, br s, ring-H_{ax}), 261.9 (1H, br s, ring-H_{ax}), 228.0 (1H, br s, ring-H_{ax}), 179. (1H, br s, ring-H_{ax}), 136.5, 111.7, 70.7, 64.7, 30.6, -37.2, -44.1, -58.1, -77.3, -88.3, -96.8, -108.6, -130.7, -139.7, -175.2, -253.6; m/z (ES$^+$) 447 (100%, M^{2+}), 523 (15%, [M^{3+} + ($CF_3SO_3^-$)]$^{2+}$) (Found: M^{2+}, 447.7052. $C_{35}H_{64}N_7O_9Tm$ requires M^{2+} 447.7054).

Yb.L^5

The title compound was prepared following a method similar to that for Yb.L^3, using Yb.L^4 (0.25 g, 0.18 mmol), dissolved in the minimum amount of methanol and an aqueous sodium hydroxide solution (0.02 M, 37 ml). A yellow solid resulted (0.080 g, 50%), m.p. > 250 °C; ν_{max} (solid)/cm^{-1} 1625 (br, *CO*NH, *CO*O); δ_H (200 MHz, CD_3OD)

partial assignment 105.6 (1H, br s, ring-H_{ax}), 99.1 (1H, br s, ring-H_{ax}), 79.0 (1H, br s, ring-H_{ax}), 75.0 (1H, br s, ring-H_{ax}), 43.4 (1H, br s, ring-H_{eq}), 27.0 (3H, br s, ring-H_{eq}), 21.7, 18.7, 10.4, 8.15, -17.0, -22.8, -24.3, -33.0, -36.3, -46.7, -51.9, -54.3, -58.5, -61.7, -121.3; m/z (ES^+) after addition of CF_3COOH: 429 (100%, $[M + 2H^+]^{2+}$) (Found: MH^+, 857.3681. $C_{32}H_{57}N_7O_9Yb$ requires MH^+ 857.3607).

Ce.L^5

The title compound was prepared following a method similar to that for Yb.L^3, using Ce.L^4 (0.090 g, 0.068 mmol), dissolved in the minimum amount of methanol and an aqueous sodium hydroxide solution (0.02 M, 13.5 ml). A yellow solid resulted (0.032 g, 57%), m.p. > 250 °C; ν_{max} (solid)/cm^{-1} 1625 (br, *CO*NH, *CO*O); δ_H (200 MHz, CD_3OD) partial assignment 19.4, 18.2, 17.1, 15.9, 13.3, 9.62, 8.89, 7.23, 6.59, -1.2, -1.80, -2.2, -2.73, -3.32, -9.96 (1H, br s, ring-H_{ax}), -10.94 (1H, br s, ring-H_{ax}), -15.0 (2H, br s, ring-H_{ax}); m/z (ES^+) after addition of CF_3COOH: 412 (100%, $[M + 2H^+]^{2+}$) (Found: MH^+, 823.3288 $C_{32}H_{57}N_7O_9Ce$ requires MH^+ 823.3272).

Pr.L^5

The title compound was prepared following a method similar to that for Yb.L^3, using Pr.L^4 (0.400 g, 0.30 mmol), dissolved in the minimum amount of methanol and an aqueous sodium hydroxide solution (0.02 M, 76 ml). A yellow solid resulted (0.150 g, 60%), m.p. > 250 °C; ν_{max} (solid)/cm^{-1} 1625 (br, *CO*NH, *CO*O); δ_H (200 MHz, CD_3OD) partial assignment 34.2, 32.2, 31.8, 27.0, 26.42, 21.3, 20.86, 15.82, 14.2, 13.0, 12.65, 10.9, -7.62, -23.4 (1H, br s, ring-H_{ax}), -24.0 (1H, br s, ring-H_{ax}), -27.1 (1H, br s, ring-H_{ax}), -33.1 (1H, br s, ring-H_{ax}); m/z (ES^+) after addition of CF_3COOH: 413 (100%, $[M + 2H^+]^{2+}$) (Found: MH^+, 824.3298 $C_{32}H_{57}N_7O_9Pr$ requires MH^+ 824.3294).

Nd.L^5

The title compound was prepared following a method similar to that for Yb.L^3, using Nd.L^4 (0.090 g, 0.068 mmol), dissolved in the minimum amount of methanol, and an aqueous sodium hydroxide solution (0.02 M, 13.5 ml). A yellow solid resulted (0.025 g, 45%), m.p. > 260 °C; ν_{max} (solid)/cm^{-1} 1625 (br, *CO*NH, *CO*O); δ_H (200 MHz, CD_3OD) partial assignment 17.5, 16.1, 11.8, 10.2, 9.77, 7.77, 7.20, 6.54, 9.91, 5.67, -11.2 (1H, br s, ring-H_{ax}), -12.0 (1H, br s, ring-H_{ax}), -15.78 (1H, br s, ring-H_{ax}), -16.7 (1H, br s, ring-H_{ax}); m/z (ES$^+$) after addition of CF_3COOH: 413 (100%, $[M + 2H^+]^{2+}$) (Found: MH$^+$, 825.3299 $C_{32}H_{57}N_7O_9Nd$ requires MH$^+$ 825.3289).

Sm.L^5

The title compound was prepared following a method similar to that for Yb.L^3, using Sm.L^4 (0.090 g, 0.067 mmol), dissolved in the minimum amount of methanol and an aqueous sodium hydroxide solution (0.02 M, 13.6 ml). A yellow solid resulted (0.028 g, 50%), m.p. > 250 °C; ν_{max} (solid)/cm^{-1} 1625 (br, *CO*NH, *CO*O); m/z (ES$^+$) after addition of CF_3COOH: 418 (100%, $[M + 2H^+]^{2+}$) (Found: MH$^+$, 835.3412 $C_{32}H_{57}N_7O_9Sm$ requires MH$^+$ 835.3410).

Eu.L^5

The title compound was prepared following a method similar to that for Yb.L^3, using Eu.L^4 (0.500 g, 0.37 mmol), dissolved in the minimum amount of methanol and an aqueous sodium hydroxide solution (0.02 M, 75 ml). A yellow solid resulted (0.028 g, 50%), m.p. > 250 °C; ν_{max} (solid)/cm^{-1} 1625 (br, *CO*NH, *CO*O); δ_H (200 MHz, CD_3OD) partial assignment 25.7 (1H, br s, ring-H_{ax}), 23.4 (1H, br s, ring-H_{ax}), 18.0 (1H, br s, ring-H_{ax}), 17.6 (1H, br s, ring-H_{ax}), 11.03, -1.12, -2.34, -2.78, -3.32, -5.13, -5.37, -6.89, -7.28,

-8.84, -9.33, -11.1, -12.8, -14.6, -15.43; m/z (ES$^+$) after addition of CF_3COOH: 418 (100%, $[M + 2H^+]^{2+}$) (Found: MH$^+$, 836.3474 $C_{32}H_{57}N_7O_9Eu$ requires MH$^+$ 836.3430).

Tb.L^5

The title compound was prepared following a method similar to that for Yb.L^3, using Tb.L^4 (0.090 g, 0.067 mmol), dissolved in the minimum amount of methanol and an aqueous sodium hydroxide solution (0.02 M, 13.5 ml). A yellow solid resulted (0.030 g, 53%), m.p. > 260 °C; ν_{max} (solid)/cm^{-1} 1625 (br, *CO*NH, *CO*O); δ_H (200 MHz, CD_3OD) partial assignment 250.0, 232.0, 151.7, 141.1, 127.2, 69.8, 62.7, 49.4, 36.9, 31.4, 25.3, -16.4, -44.5, -53.7, -58.4, -89.2, -95.3, -128.6, -148.3 (1H, br s, ring-H$_{ax}$), -212.4 (1H, br s, ring-H$_{ax}$), -241.0 (1H, br s, ring-H$_{ax}$), -333.2 (1H, br s, ring-H$_{ax}$); m/z (ES$^+$) after addition of CF_3COOH: 422 (100%, $[M + 2H^+]^{2+}$) (Found: MH$^+$, 842.3519 $C_{32}H_{57}N_7O_9Tb$ requires MH$^+$ 842.3471).

Dy.L^5

The title compound was prepared following a method similar to that for Yb.L^3, using Dy.L^4 (0.090 g, 0.067 mmol), dissolved in the minimum amount of methanol and an aqueous sodium hydroxide solution (0.02 M, 13.5 ml). A yellow solid resulted (0.033 g, 58%), m.p. > 260 °C; ν_{max} (solid)/cm^{-1} 1625 (br, *CO*NH, *C*$\underline{O}$O); δ_H (200 MHz, CD_3OD) partial assignment 250.0, 246.0, 187.0, 100.8, 88.0, 73.4, 68.4, 43.8, 36.2, 28.2, -23.82, -49.54, -131.0, -151.9, -270.0 (2H, br s, ring-H$_{ax}$), -309.2 (1H, br s, ring-H$_{ax}$), -380.5 (1H, br s, ring-H$_{ax}$); m/z (ES$^+$) after addition of CF_3COOH: 424 (100%, $[M + 2H^+]^{2+}$) (Found: MH$^+$, 847.3553 $C_{32}H_{57}N_7O_9Dy$ requires MH$^+$ 847.3510).

Ho.L^5

The title compound was prepared following a method similar to that for Yb.L^3, using Ho.L^4 (0.40 g, 0.30 mmol), dissolved in the minimum amount of methanol and an aqueous sodium hydroxide solution (0.02 M, 74 ml). A yellow solid resulted (0.100 g, 40%), m.p. > 250 °C; ν_{max} (solid)/cm^{-1} 1625 (br, *CO*NH, *CO*O); δ_H (200 MHz, CD_3OD) partial assignment 142.4, 134.3, 88.3, 70.8, 44.5, 41.44, 38.2, 35.3, 30.0, -40.8, -49.8, -58.6, -78.2, -123.4 (1H, br s, ring-H$_{ax}$), -142.7 (1H, br s, ring-H$_{ax}$), -183.1 (1H, br s, ring-H$_{ax}$), -194.6 (1H, br s, ring-H$_{ax}$); m/z (ES$^+$) after addition of CF_3COOH: 425 (100%, $[M + 2H^+]^{2+}$) (Found: MH$^+$, 848.3534 $C_{32}H_{57}N_7O_9Ho$ requires MH$^+$ 848.3521).

Er.L^5

The title compound was prepared following a method similar to that for Yb.L^3, using Er.L^4 (0.090 g, 0.067 mmol), dissolved in the minimum amount of methanol and an aqueous sodium hydroxide solution (0.02 M, 13.5 ml). A yellow solid resulted (0.030 g, 53%), m.p. > 250 °C; ν_{max} (solid)/cm^{-1} 1625 (br, *CO*NH, *CO*O); δ_H (200 MHz, CD_3OD) partial assignment 122.8 (1H, br s, ring-H$_{ax}$), 106.3 (1H, br s, ring-H$_{ax}$), 66.86 (2H, br s, ring-H$_{ax}$), 52.2, 37.5, 31.7, 24.0, 19.4, 17.2, 14.2, -14.8, -27.7, -31.3, -32.8, -39.6, -45.6, -49.5, -56.2, -64.9; m/z (ES$^+$) after addition of CF_3COOH: 425 (100%, $[M + 2H^+]^{2+}$) (Found: MH$^+$, 849.3578 $C_{32}H_{57}N_7O_9Er$ requires MH$^+$ 849.3521).

Tm.L^5

The title compound was prepared following a method similar to that for Yb.L^3, using Tm.L^4 (0.090 g, 0.067 mmol), dissolved in the minimum amount of methanol and an aqueous sodium hydroxide solution (0.02 M, 13.4 ml). A yellow solid resulted (0.025 g, 44%), m.p. > 250 °C; ν_{max} (solid)/cm^{-1} 1625 (br, *CO*NH, *CO*O); δ_H (200 MHz, CD_3OD)

partial assignment 289.7 (2H, br s, ring-H_{ax}), 199.0 (1H, br s, ring-H_{ax}), 191.0 (1H, br s, ring-H_{ax}), 121.0, 78.2, 69.9, 56.9, 27.8, -35.5, -57.6, -65.5, -84.3, -94.7, -146.3, -164.3, -175.9, -182.5, -389; m/z (ES^+) after addition of CF_3COOH: 427 (100%, $[M + 2H^+]^{2+}$) (Found: MH^+, 852.3556 $C_{32}H_{57}N_7O_9Tm$ requires MH^+ 852.3560).

Yb.L^6

The title compound was prepared following a method similar for Yb.L^2, using ytterbium (III) triflate (0.099 g, 0.16 mmol) in dry acetonitrile (1 ml) and L^6 (0.131 g, 0.16 mmol) in dry acetonitrile (4 ml). A yellow solid resulted (0.200 g, 87%), m.p. > 140 °C (dec.); ν_{max} (solid)/cm^{-1} 1740 (*CO*O), 1622 (*CO*NH); δ_H (200 MHz, CD_3OD) partial assignment 140.0 (1H, br s, ring-H_{ax}), 134.0 (2H, br s, ring-H_{ax}), 112.3 (1H, br s, ring-H_{ax}), 34.8 (2H, br s, ring-H_{eq}), 29.0 (1H, br s, ring-H_{eq}), 24.65 (1H, br s, ring-H_{eq}), 23.8, 19.0, -9.63, -10.5, -15.7, -16.9, -28.9, -51.1, -60.5, -66.3, -69.1, -75.4, -79.6, -86.1, -89.69; m/z (ES^+) 495 (100%, M^{2+}) (Found: M^{2+}, 495.2322. $C_{42}H_{70}N_7O_9Yb$ requires M^{2+}, 495.2312).

Eu.L^6

The title compound was prepared following a method similar for Yb.L^2, using europium (III) triflate (0.088 g, 0.147 mmol) in dry acetonitrile (3 ml) and L^6 (0.120 g, 0.147 mmol) in dry acetonitrile (3 ml). A yellow solid resulted (0.181 g, 87%), m.p. > 150 °C (dec.); ν_{max} (solid)/cm^{-1} 1740 (*CO*O), 1622 (*CO*NH); δ_H (200 MHz, CD_3OD) partial assignment 21.5 (1H, br s, ring-H_{ax}), 20.4 (1H, br s, ring-H_{ax}), 17.8 (1H, br s, ring-H_{ax}), 16.9 (1H, br s, ring-H_{eq}), 12.0, 8.20, 7.60, -4.85, -5.50, -7.20, -8.50, -8.90, -9.50, -9.80, -10.8, -11.2, -12.0, -18.5; m/z (ES^+) 484 (100%, M^{2+}), 1119 (30%, $[M^{2+} + (CF_3SO_3^-)]^+$) (Found: M^{2+}, 484.7217. $C_{42}H_{70}N_7O_9Eu$ requires M^{2+}, 484.7218).

Tb.L^6

The title compound was prepared following a method similar for Yb.L^2, using terbium (III) triflate (0.037 g, 0.061 mmol) in dry acetonitrile (3 ml) and L^6 (0.050 g, 0.061 mmol) in dry acetonitrile (3 ml). A yellow solid resulted (0.060 g, 70%), m.p. > 168 °C (dec.); ν_{max} (solid)/cm^{-1} 1740 (*CO*O), 1622 (*CO*NH); δ_H (200 MHz, CD_3OD) partial assignment 380.0, 360.0, 300, 260.0, 200.0, 180.0, 140.0, -80.0, -110.0, -170.0, -160.0, -220.0, -250.0 (1H, br s, ring-H$_{eq}$), -266.0 (1H, br s, ring-H$_{eq}$), -320.0 (1H, br s, ring-H$_{eq}$), -330.0 (1H, br s, ring-H$_{eq}$); m/z (ES$^+$) 487 (100%, M^{2+}), 563 (20%, $[M^{3+} + (CF_3SO_3^-)]^{2+}$), 1275 (5%, $[M^{3+} + (CF_3SO_3^-)_2]^+$) (Found: M^{2+}, 487.7239. $C_{42}H_{70}N_7O_9Tb$ requires M^{2+}, 487.7239).

Yb.L^7

The title compound was prepared following a method similar to that for Yb.L^3, using Yb.L^6 (0.100 g, 0.069 mmol), dissolved in the minimum amount of methanol and an aqueous sodium hydroxide solution (0.02 M, 13.9 ml). A yellow solid resulted (0.035g, 40%), m.p. > 250 °C; ν_{max} (solid)/cm^{-1} 1623 (br, *CO*NH, *CO*O); δ_H (200 MHz, CD_3OD) partial assignment major isomer 107.1 (1H, br s, ring-H$_{ax}$), 102.7 (1H, br s, ring-H$_{ax}$), 83.2 (1H, br s, ring-H$_{ax}$), 61.74 (1H, br s, ring-H$_{ax}$), 59.3, 51.0, 42.0, 38.6, 37.0, 34.0, 28.3, 19.1, 17.1, -10.89, -12.06, -24.67, -28.95, -30.0, -43.0, -44.19, -46.3, -47.3, -55.8, -66.6, -72.1, -83.2, -98.6, -102.0, -105.3, -131.4; δ minor isomer 71.0 (1H, br s, ring-H$_{ax}$), 35.68 (1H, br s, ring-H$_{ax}$), 20.32 (1H, br s, ring-H$_{ax}$), 14.80 (1H, br s, ring-H$_{ax}$), -4.86, -6.58; m/z (ES$^+$) after addition of CF_3COOH: 474 (100%, $[M + 2H^+]^{2+}$) (Found: MH$^+$, 947.4077. $C_{39}H_{63}N_7O_9Yb$ requires MH$^+$ 947.4077).

Eu.L^7

The title compound was prepared following a method similar to that for Yb.L^3, using Eu.L^6 (0.080 g, 0.056 mmol), dissolved in the minimum amount of methanol and an aqueous sodium hydroxide solution (0.02 M, 11.3 ml). A yellow solid resulted (0.024 g, 46%), m.p. > 250 °C; ν_{max} (solid)/cm^{-1} 1623 (br, *CO*NH, *CO*O); δ_H (200 MHz, CD_3OD) partial assignment 21.27 (1H, br s, ring-H$_{ax}$), 11.67 (3H, br s, ring-H$_{ax}$), 9.03, 8.4, 6.06, -6.5, -9.33, -11.0, -13.63, -17.8, -18.25, -19.03; m/z (ES$^+$) after addition of CF_3COOH: 463 (100%, [M + 2H$^+$]$^{2+}$) (Found: MH$^+$, 926.3899. $C_{39}H_{63}N_7O_9Eu$ requires MH$^+$ 926.3894).

Tb.L^7

The title compound was prepared following a method similar to that for Yb.L^3, using Tb.L^6 (0.040 g, 0.028 mmol), dissolved in the minimum amount of methanol and an aqueous sodium hydroxide solution (0.02 M, 5.6 ml). A yellow solid resulted (0.010 g, 38%), m.p. > 250 °C; ν_{max} (solid)/cm^{-1} 1623 (br, *CO*NH, *CO*O); δ_H (200 MHz, CD_3OD) partial assignment 574.0, 404.3, 257.6, 235.5, 168.0, 131.4, -139.2, -157.9, -176.4, -185.9, -195.8, -214.7, -228.6, -250.6, -278.8, -291.6, -369.3 (1H, br s, ring-H$_{ax}$); m/z (ES$^+$) after addition of CF_3COOH: 466 (100%, [M + 2H$^+$]$^{2+}$) (Found: MH$^+$, 932.3937. $C_{39}H_{63}N_7O_9Tb$ requires MH$^+$ 932.3935).