

## SUPPLEMENTARY INFORMATION

### **A simple one-pot route to stable formamidinatoiodidolanthanoid(III) complexes from lanthanoid metals**

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#### **Contents**

- 1. Syntheses**
- 2. <sup>1</sup>H and <sup>19</sup>F NMR Spectra of complexes**
- 3. X-ray crystallography**
- 4. Selected bond angles (°) and lengths (Å)**
- 5. References**

## 1. Syntheses

### General

The lanthanoid compounds described here are highly air and moisture sensitive, and were prepared and handled with vacuum-nitrogen line techniques and in a dry box in an atmosphere of purified nitrogen. N,N'-bis(2,6-difluorophenyl)formamidine and N,N'-bis(diisopropylphenyl)formamidinate were prepared by the literature method.<sup>1</sup> Lanthanoid metals were from Santoku/Molycorp/Eutectix. Large chunks were filed in the drybox before use. All other chemicals were purchased from Sigma Aldrich. Solvents (thf, C<sub>6</sub>D<sub>6</sub>) were pre-dried by distillation over sodium or sodium benzophenone ketyl before being stored under an atmosphere of nitrogen. Pyridine was distilled over potassium hydroxide, degassed and stored over dried 4Å molecular sieves. IR spectra were recorded as Nujol mulls between NaCl plates using an Agilent Technologies Cary 630 FTIR instrument within the range 4000–700 cm<sup>-1</sup>. <sup>1</sup>H NMR and proton decoupled <sup>19</sup>F NMR spectra were recorded with a Bruker DPX 300MHz spectrometer or a Bruker 400MHz instrument. Chemical shifts were referenced to the residual <sup>1</sup>H resonances of the deuterated solvents (<sup>1</sup>H) or external CCl<sub>3</sub>F (<sup>19</sup>F). Microanalyses were determined by the Elemental Analysis Service, London Metropolitan University, and all the samples were sealed in tubes under nitrogen. Melting points were determined in sealed glass capillaries under nitrogen and are uncalibrated. Crystals were immersed in crystallography oil, and were measured on a Bruker X8 APEXII SCXRD or the MX1 beamline at the Australian Synchrotron. Crystal data and refinement details are given in **Table S1**. CCDC 2082902-2082907 for compound **1-6**, CCDC 2082909-2082911 for compound **9-11**, 2099468 for compound **12**, 2099469-2099470 for compound **14-15**, 2082912 for compound **16**, CCDC 2082913 for compound **18**, CCDC 2082914 for compound **18a** contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

### General procedure for 1-11

Lanthanoid metal powder (1.0 mmol), iodine (0.1 mmol, 0.025 g), DFFormH (0.4 mmol, 0.107 g) (**1-7**) / iodine (0.5 mmol, 0.127 g), DFFormH (0.5 mmol, 0.134 g) (**8-11**) and dry THF (10ml) were stirred under nitrogen for three days at room temperature. After filtration of the reaction mixture, a small (0.3 ml) aliquot was monitored by <sup>19</sup>F NMR, and <sup>19</sup>F NMR

showed characteristic one resonance of  $[\text{Ln}(\text{DFForm})\text{nI}_{3-\text{n}}]$  ( $\text{n} = 1, 2$ ), which confirmed the consumption of DFFormH and formation of  $[\text{Ln}(\text{DFForm})\text{nI}_{3-\text{n}}]$  ( $\text{n} = 1, 2$ ) on completion. The filtrates were evaporated to half volume under vacuum, and the crystals were obtained. Yields were calculated based on the DFFormH ligand.

### **$[\text{Lu}(\text{DFForm})_2\text{I}(\text{thf})_2]$ 1**

Yellow crystals (0.149 g, 76%), M.p. 148-150 °C, (Found: C, 41.80; H, 2.93; N, 5.66;  $\text{C}_{34}\text{H}_{30}\text{F}_8\text{ILuN}_4\text{O}_2$  (980.49) requires C, 41.65; H, 3.08; N, 5.71 %). IR (Nujol): 1667m, 1586w, 1297m, 1261s, 1208m, 1092s, 1016s, 950m, 916m, 865m, 800s, 780s, 718m  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 300 MHz): 9.04 (s, 2H, NCHN), 6.48 (m, 8H, H(3,5)), 6.30 (m, 4H, H(4)), 3.83 (m, 8H, thf), 1.45 (m, 8H, thf).  $^{19}\text{F}$  NMR ( $\text{C}_6\text{D}_6$ , 300MHz, ppm):  $\delta = -123.8$  (s).

### **$[\text{Tm}(\text{DFForm})_2\text{I}(\text{thf})_2]$ 2**

Yellow crystals (0.160 g, 82%), M.p. 202-204 °C, (Found: C, 41.71; H, 3.09; N, 5.42;  $\text{C}_{34}\text{H}_{30}\text{F}_8\text{IN}_4\text{O}_2\text{Tm}$  (974.45) requires C, 41.91; H, 3.10; N, 5.75 %). IR (Nujol): 1665m, 1562s, 1291s, 1265s, 1222s, 1064s, 1008s, 953m, 918m, 864s, 800s, 777s, 720s  $\text{cm}^{-1}$ .  $^{19}\text{F}$  NMR (thf, ext.  $\text{CFCl}_3$ , ppm):  $\delta = -124.8$  (s).

### **$[\text{Er}(\text{DFForm})_2\text{I}(\text{thf})_2]$ 3**

Pink crystals (0.138 g, 71%), M.p.198-200 °C, (Found: C, 41.79; H, 3.28; N 5.54;  $\text{C}_{34}\text{H}_{30}\text{ErF}_8\text{IN}_4\text{O}_2$  (972.78) requires C, 41.98; H, 3.11; N, 5.76 %). IR (Nujol): 1668m, 1579s, 1296s, 1264s, 1219s, 1098s, 1014s, 952m, 918m, 865s, 801s, 770s, 718s  $\text{cm}^{-1}$ .  $^{19}\text{F}$  NMR (thf, ext.  $\text{CFCl}_3$ , ppm):  $\delta = -123.9$  (s).

### **$[\text{Ho}(\text{DFForm})_2\text{I}(\text{thf})_2]$ 4**

Pink crystals (0.172 g, 95%), M.p.180-182 °C, (Found: C, 41.84; H, 3.27; N, 5.48;  $\text{C}_{34}\text{H}_{30}\text{F}_8\text{HoIN}_4\text{O}_2$  (970.45) requires C, 42.08; H, 3.12; N, 5.77 %). IR (Nujol): 1667m, 1566s, 1294s, 1265s, 1218m, 1074s, 1013s, 952m, 918m, 863s, 802s, 777s, 721s  $\text{cm}^{-1}$ .  $^{19}\text{F}$  NMR (thf, ext.  $\text{CFCl}_3$ , ppm):  $\delta = -124.5$  (s).

### **$[\text{Dy}(\text{DFForm})_2\text{I}(\text{thf})_2]$ 5**

Colourless crystals (0.158 g, 81%), M.p.196-198 °C, (Found: C, 42.15; H, 3.07; N, 5.77;  $\text{C}_{34}\text{H}_{30}\text{DyF}_8\text{IN}_4\text{O}_2$  (968.02) requires C, 42.19; H, 3.12; N, 5.79 %). IR (Nujol): 1667m, 1579vs, 1294s, 1261vs, 1217m, 1095m, 1013s, 947m, 916m, 864s, 800s, 773s, 718s  $\text{cm}^{-1}$ .  $^{19}\text{F}$  NMR (thf, ext.  $\text{CFCl}_3$ , ppm):  $\delta = -124.2$  (s).

### **[Gd(DFForm)<sub>2</sub>I(thf)<sub>2</sub>] 6**

Colourless crystals (0.165 g, 85%), M.p.188-190 °C, (Found: C, 42.29; H, 3.09; N, 5.90; C<sub>34</sub>H<sub>30</sub>F<sub>8</sub>GdIN<sub>4</sub>O<sub>2</sub> (962.77) requires C, 42.42; H, 3.14; N, 5.82 %). IR (Nujol): 1667w, 1568s, 1294s, 1262s, 1217m, 1072s, 1011s, 952m, 915m, 858s, 802s, 778s, 719s cm<sup>-1</sup>. <sup>19</sup>F NMR (thf, ext. CFCl<sub>3</sub>, ppm): δ= -128.6 (s).

### **[Nd(DFForm)<sub>2</sub>I(thf)<sub>2</sub>] 7**

Purple crystals of **7** crystallized in the monoclinic space group C2/c, a = 16.3338(6) Å, b = 11.8553(3) Å, c = 19.2719(6) Å, β = 107.258(4) °, V = 3563.8(2) Å<sup>3</sup>, which had unit cell parameters in agreement with those of the other [Ln(DFForm)<sub>2</sub>I(thf)<sub>2</sub>] complexes (Table S1). The poor quality of the crystals precluded a structure determination.

### **[Lu(DFForm)<sub>2</sub>I<sub>2</sub>(thf)<sub>3</sub>] 8**

Colourless crystals (0.344 g, 75%), M.p.192-194 °C, (Found: C, 32.67; H, 3.31; N, 3.20; C<sub>25</sub>H<sub>31</sub>F<sub>4</sub>I<sub>2</sub>N<sub>2</sub>LuO<sub>3</sub> (912.29) requires C, 32.91; H, 3.42; N, 3.07 %). IR (Nujol): 1666m, 1616s, 1564s, 1297s, 1270s, 1217s, 1100m, 1065s, 1006s, 959m, 912m, 882s, 854s, 780s, 741s, 720s cm<sup>-1</sup>. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 300 MHz): 9.03 (s, 1H, NCHN), 6.43 (m, 4H, H(3,5)), 6.31 (m, 2H, H(4)), 3.65 (m, 12H, thf), 1.43 (m, 12H, thf). <sup>19</sup>F NMR (C<sub>6</sub>D<sub>6</sub>, 300MHz, ppm): δ= -123.8 (s).

### **[Gd(DFForm)<sub>2</sub>I<sub>2</sub>(thf)<sub>3</sub>] 9**

Colourless crystals (0.358 g, 80%), M.p.172-174 °C, (Found: C, 33.33; H, 3.24; N, 3.01; C<sub>25</sub>H<sub>31</sub>F<sub>4</sub>GdI<sub>2</sub>N<sub>2</sub>O<sub>3</sub> (894.57) requires C, 33.57; H, 3.49; N, 3.13 %). IR (Nujol): 1669s, 1615s, 1566s, 1298m, 1264s, 1214m, 1096m, 1067s, 1016s, 959w, 914m, 878s, 856s, 780s, 741m, 719s cm<sup>-1</sup>. <sup>19</sup>F NMR (thf, ext. CFCl<sub>3</sub>, ppm): δ= -124.5 (s).

### **[Sm(DFForm)<sub>2</sub>I<sub>2</sub>(thf)<sub>3</sub>] 10**

Colourless crystals (0.352 g, 79%), M.p.134-136 °C, (Found: C, 34.02; H, 3.26; N, 3.21; C<sub>25</sub>H<sub>31</sub>F<sub>4</sub>I<sub>2</sub>N<sub>2</sub>O<sub>3</sub>Sm (887.67) requires C, 33.83; H, 3.52; N, 3.16 %). IR (Nujol): 1666m, 1616s, 1559m, 1297s, 1270w, 1216m, 1108m, 1072s, 1030s, 954w, 915m, 871s, 856s, 776m, 739w, 721m cm<sup>-1</sup>. <sup>19</sup>F NMR (C<sub>6</sub>D<sub>6</sub>, 300MHz, ppm): δ= -125.2 (s).

### **[Nd(DFForm)<sub>2</sub>I<sub>2</sub>(thf)<sub>3</sub>] 11**

Purple crystals (0.389 g, 88%), M.p.146-148 °C, (Found: C, 33.89; H, 3.62; N, 2.86; C<sub>25</sub>H<sub>31</sub>F<sub>4</sub>I<sub>2</sub>N<sub>2</sub>NdO<sub>3</sub> (881.56) requires C, 34.06; H, 3.54; N, 3.18 %). IR (Nujol): 1668s,

1614m, 1556w, 1311s, 1263s, 1205m, 1096m, 1063s, 1002s, 956w, 914m, 875s, 856s, 775s, 740w, 722m cm<sup>-1</sup>. <sup>19</sup>F NMR (C<sub>6</sub>D<sub>6</sub>, 300MHz, ppm): δ= -124.5 (s).

### General procedure for 12-14

Lanthanoid metal powder (1.0 mmol), iodine (0.5 mmol, 0.127 g), DippFormH (0.5 mmol, 0.182) and dry THF (10ml) were placed in a Schlenk flask in a nitrogen-filled dry box. The mixture was ultrasonicated for one week. The reaction mixture was filtered. Crystals were obtained after the filtrates were evaporated to half volume under vacuum. Yields were calculated based on the DippFormH ligand.

### [Lu(DippForm)I<sub>2</sub>(thf)<sub>3</sub>]·2thf 12

Colourless crystals (0.403 g, 70%), M.p. 252-254 °C, (Found: C, 46.80; H, 6.92; N, 3.17; Lu, 15.04; C<sub>45</sub>H<sub>75</sub>I<sub>2</sub>LuN<sub>2</sub>O<sub>5</sub> (1152.84) requires C, 46.88; H, 6.56; N, 2.43; Lu, 15.18 %). IR (Nujol): 1666m, 1591w, 1524m, 1323w, 1272s, 1189m, 1100m, 1067s, 1018s, 935m, 915w, 865m, 803s, 756w, 722s cm<sup>-1</sup>. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 400 MHz): 8.32 (s, 1H, NCHN), 7.18-7.09 (m, 6H, H(3,4,5)), 4.30 (m, 4H, CH), 3.54 (m, 20H, thf), 1.47-1.26 (m, 24H, CH<sub>3</sub>), 1.18 (m, 20H, thf).

### [Dy(DippForm)I<sub>2</sub>(thf)<sub>3</sub>] 13

Colourless crystals (0.388g, 78%), M.p. 208-210 °C, (Found: C, 44.71; H, 6.15; N, 2.67; C<sub>37</sub>H<sub>59</sub>DyI<sub>2</sub>N<sub>2</sub>O<sub>3</sub> (996.18) requires C, 44.61; H, 5.97; N, 2.81 %). IR (crystal oil): 1666m, 1589m, 1528s, 1325s, 1276s, 1181s, 1106s, 1062s, 1018vs, 936s, 911s, 885s, 801s, 770s, 716m cm<sup>-1</sup>. **13** crystallized in the orthorhombic space group *Pbca*, *a*=19.469(4) Å, *b*=18.915(4) Å, *c*=24.240(5) Å, *V*=8927(3) Å<sup>3</sup>, which is similar to other [Ln(DippForm)I<sub>2</sub>(thf)<sub>3</sub>] complexes.

### [Gd(DippForm)I<sub>2</sub>(thf)<sub>3</sub>]·thf 14

Colourless crystals (0.355 g, 72%), M.p. 208-210 °C, (Found: C, 44.70; H, 6.18; N, 2.71; C<sub>37</sub>H<sub>59</sub>GdI<sub>2</sub>N<sub>2</sub>O<sub>3</sub> (990.91, loss of one thf in lattice) requires C, 44.80; H, 6.10; N, 2.82 %). IR (Nujol): 1666m, 1592m, 1525s, 1320s, 1272s, 1192s, 1102s, 1067s, 1019vs, 935s, 916s, 864s, 805s, 762s, 724m cm<sup>-1</sup>.

### [Nd(DippForm)I<sub>2</sub>(thf)<sub>3</sub>]·thf 15

Purple crystals (0.412 g, 81%), M.p. 226-228 °C. (Found: C, 46.19; H, 6.42; N, 3.97; Nd, 14.45; C<sub>41</sub>H<sub>67</sub>I<sub>2</sub>N<sub>2</sub>NdO<sub>4</sub> (1050.00) requires C, 46.90; H, 6.43; N, 2.67; Nd, 13.74 %). IR (Nujol): 1667m, 1592w, 1534w, 1319w, 1260s, 1182m, 1102s, 1072s, 1021s, 937w, 916w,

861m, 804s, 763s, 724m cm<sup>-1</sup>. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 400 MHz): 30.04 (s, 1H, NCHN), 10.13 (m, 4H, CH), 8.45 (m, 6H, H(3,4,5)), 4.67 (m, 18H, CH<sub>3</sub>), 3.06 (m, 12H, thf), 1.32 (m, 6H, CH<sub>3</sub>), -2.01 (m, 12H, thf), the solvated thf lost.

#### **Attempted reaction to obtain [Ln(DippForm)<sub>2</sub>I] (Ln = Gd, Dy)**

Lanthanoid metal powder (1.0 mmol), iodine (0.1 mmol, 0.025 g), DippFormH (0.4 mmol, 0.146) and dry THF (10ml) were placed in a Schlenk flask in a nitrogen-filled dry box. The mixture was ultrasonicated for one week. The reaction mixture was filtered. Crystals were obtained both [Ln(DippForm)<sub>2</sub>I<sub>2</sub>(thf)<sub>3</sub>] and DippFormH were obtained after the filtrates were evaporated to half volume under vacuum, which were checked by the unit cell.

#### **[Nd(DFForm)<sub>2</sub>Cp(thf)<sub>2</sub>].thf 16**

The crystals of **7** (0.1 mmol, 0.09 g) were directly reacted with TICp (0.1 mmol, 0.03 g), the reaction mixture was stirred in thf for three days. The resulting mixture was filtered and the filtrate was concentrated under vacuum. Purple crystals of [Nd(DFForm)<sub>2</sub>Cp(thf)<sub>2</sub>].thf were obtained after stored at -20 °C for one week, and identified by X-ray crystallography.

#### **[Yb(DFForm)<sub>2</sub>(thf)<sub>3</sub>] 17 and [YbI<sub>2</sub>(thf)<sub>4</sub>] 17a**

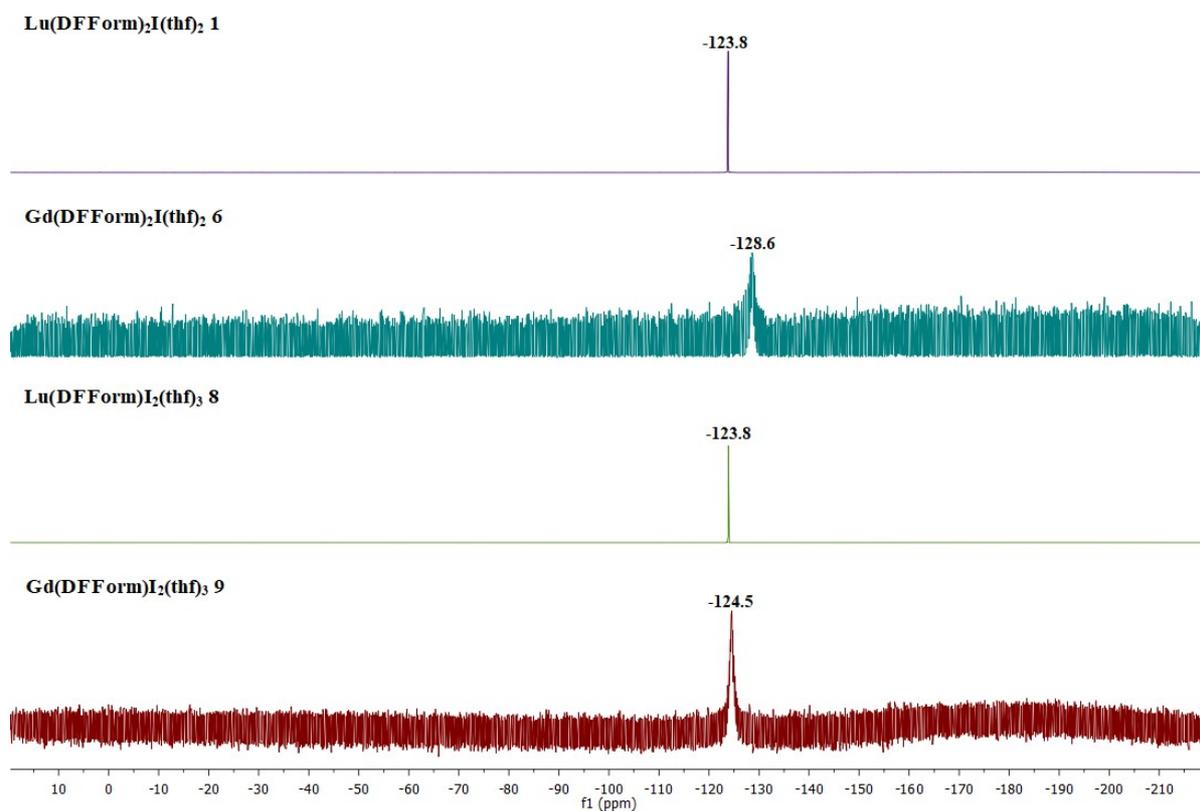
Ytterbium powder (2.00 mmol), iodine (0.5 mmol, 0.127 g), DFFormH (1.0 mmol, 0.134 g) and dry thf (10ml) were stirred for two days. The resulting mixture was filtered and the filtrate was concentrated under vacuum. Red crystals of a mixture of **17** and **17a** were obtained at -20 °C overnight. For **17** the unit cell is  $a=10.975(2)$  Å,  $b=13.271(3)$  Å,  $c=13.973(3)$  Å,  $\alpha=90.98(3)^\circ$ ,  $\beta=109.30(3)^\circ$ ,  $\gamma=103.50(3)^\circ$ ,  $V=1857.8(8)$  Å<sup>3</sup>, which similar to the one reported in 2016, unit cell is  $a=10.8778(8)$  Å,  $b=13.7732(6)$  Å,  $c=13.7857(6)$  Å,  $\alpha=88.907(4)^\circ$ ,  $\beta=71.716(5)^\circ$ ,  $\gamma=72.277(5)^\circ$ ,  $V=1861.36(18)$  Å<sup>3</sup>.<sup>2</sup> For **17a** the unit cell is  $a=8.3890(17)$  Å,  $b=9.829(2)$  Å,  $c=13.697(3)$  Å,  $\alpha=80.08(3)^\circ$ ,  $\beta=87.72(3)^\circ$ ,  $\gamma=86.99(3)^\circ$ ,  $V=1110.4(4)$  Å<sup>3</sup>. Reported unit cell is  $a=8.444(1)$  Å,  $b=9.810(<1)$  Å,  $c=13.618(1)$  Å,  $\alpha=79.67(<1)^\circ$ ,  $\beta=87.99(<1)^\circ$ ,  $\gamma=87.36(<1)^\circ$ ,  $V=1108.199$  Å<sup>3</sup>.<sup>3</sup> <sup>19</sup>F NMR (thf, C<sub>6</sub>D<sub>6</sub>, 300 MHz, ppm) of the reaction mixture:  $\delta=-122.8, 123.4$ .

#### **[Eu(DFForm)<sub>2</sub>(py)<sub>3</sub>] 18 and [EuI<sub>2</sub>(thf)<sub>2</sub>(py)<sub>3</sub>]·0.5thf 18a**

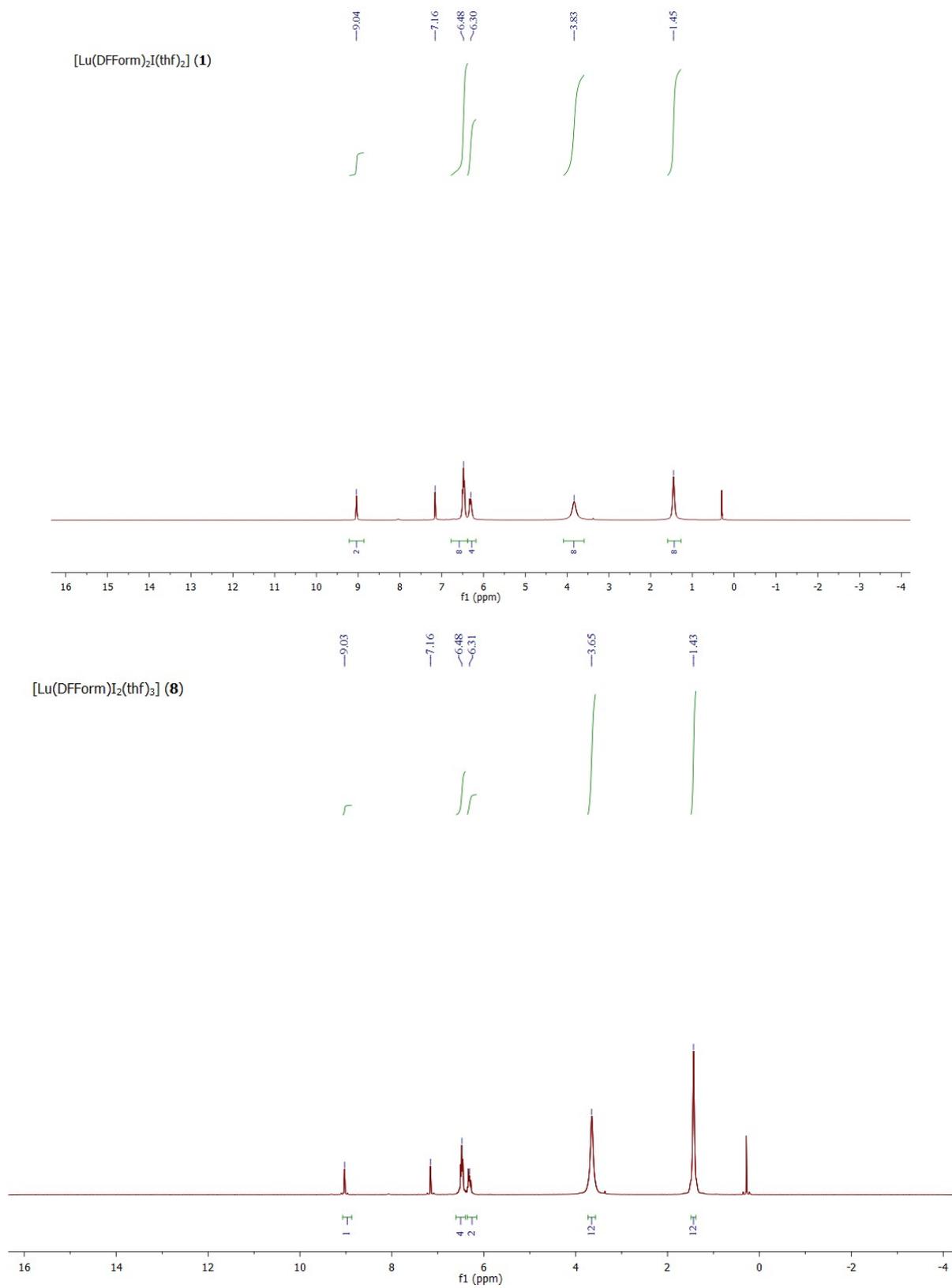
Europium powder (2.00 mmol), iodine (0.5 mmol, 0.127 g), DFFormH (1.0 mmol, 0.134 g) and dry py (10ml) were stirred under nitrogen for two days. The resulting mixture was filtered and the filtrate was concentrated under vacuum. Orange crystals of **18** were obtained after evaporation of the reaction mixture under vacuum, and identified by X-ray

crystallography. **18a** was obtained after the filtrate (which did not deposit crystals) was evaporated and the residua was recrystallized from thf.  $^{19}\text{F}$  NMR (thf,  $\text{C}_6\text{D}_6$ , 300 MHz, ppm) of the reaction mixture:  $\delta = -115.9, 121.4$ .

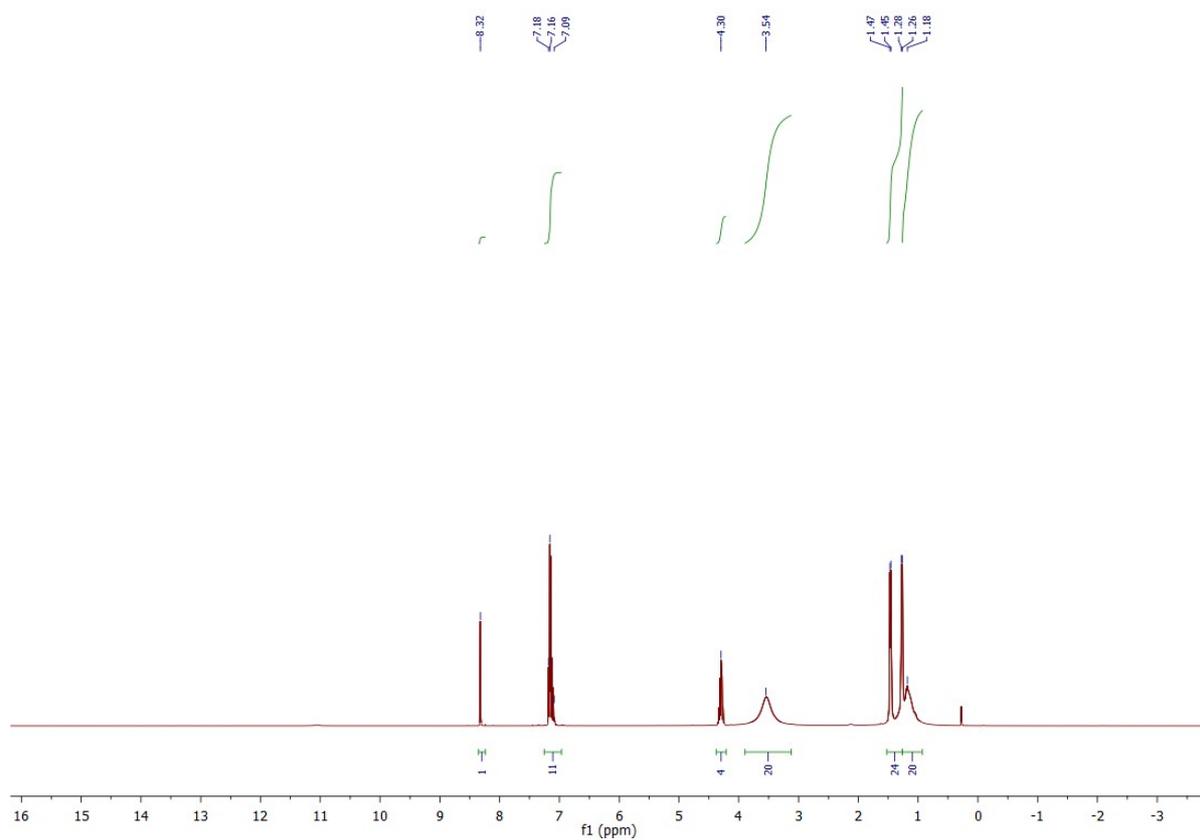
## 2. $^1\text{H}$ and $^{19}\text{F}$ NMR Spectra of complexes



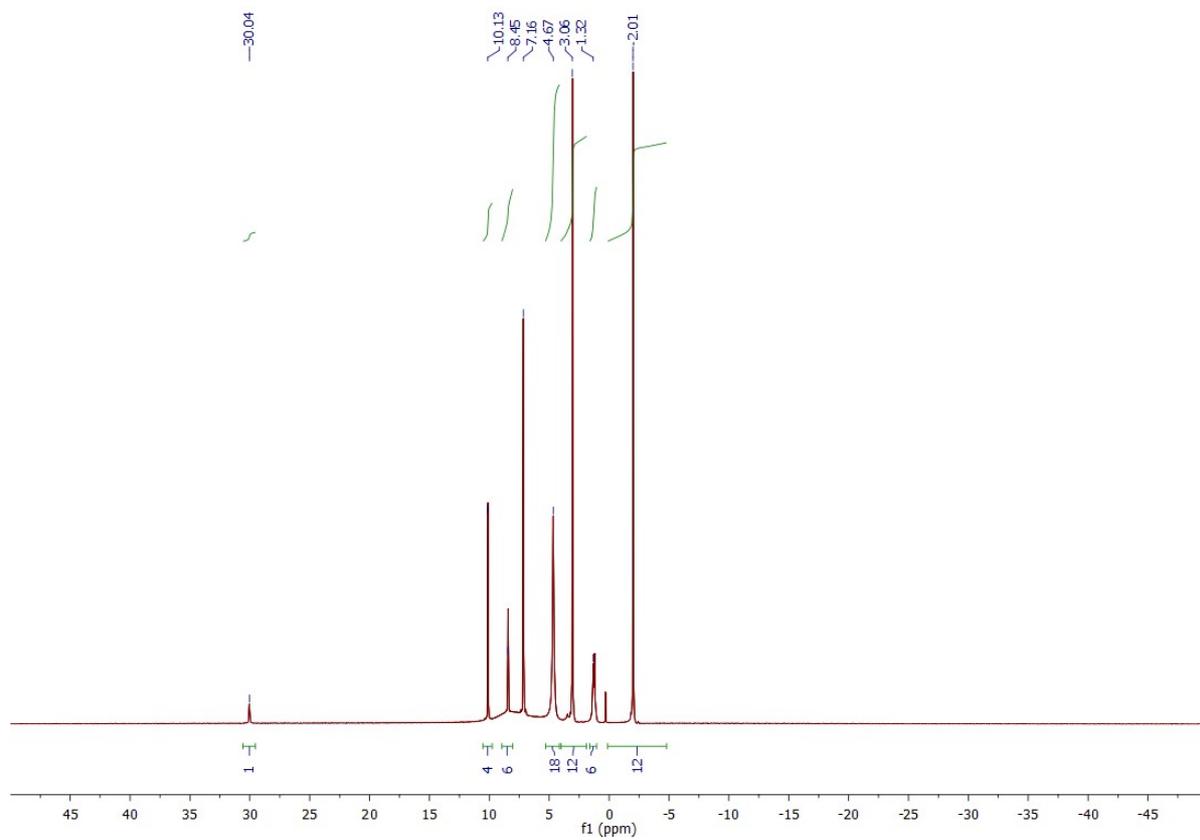
**Fig. S1** Typical  $^{19}\text{F}\{^1\text{H}\}$  NMR spectra of the reaction mixtures giving  $\text{Ln}(\text{DFForm})_2\text{I}(\text{thf})_2$  ( $\text{Ln} = \text{Lu}$ , **1**,  $\text{Gd}$ , **6**) and  $[\text{Ln}(\text{DFForm})\text{I}_2(\text{thf})_3]$  ( $\text{Ln} = \text{Lu}$ , **8**,  $\text{Gd}$ , **9**)



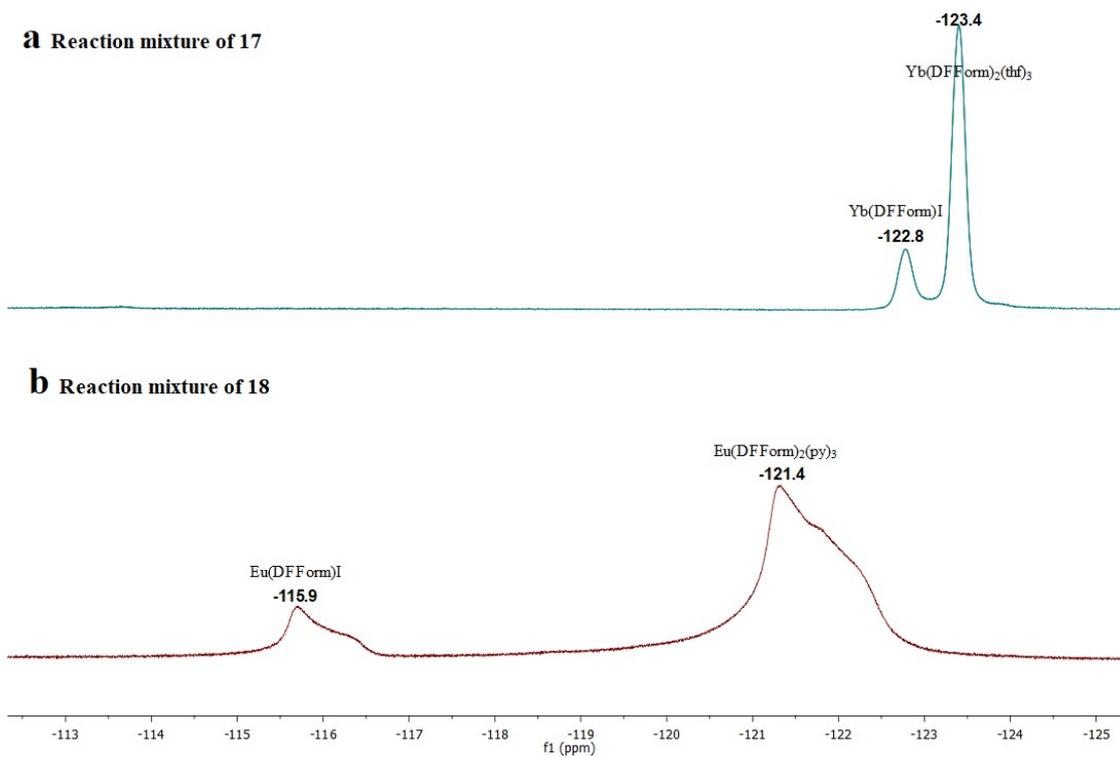
**Fig. S2** <sup>1</sup>H NMR spectra of (up) [Lu(DFForm)<sub>2</sub>I(thf)<sub>2</sub>] (1); (down) [Lu(DFForm)<sub>2</sub>I<sub>2</sub>(thf)<sub>3</sub>] (8)



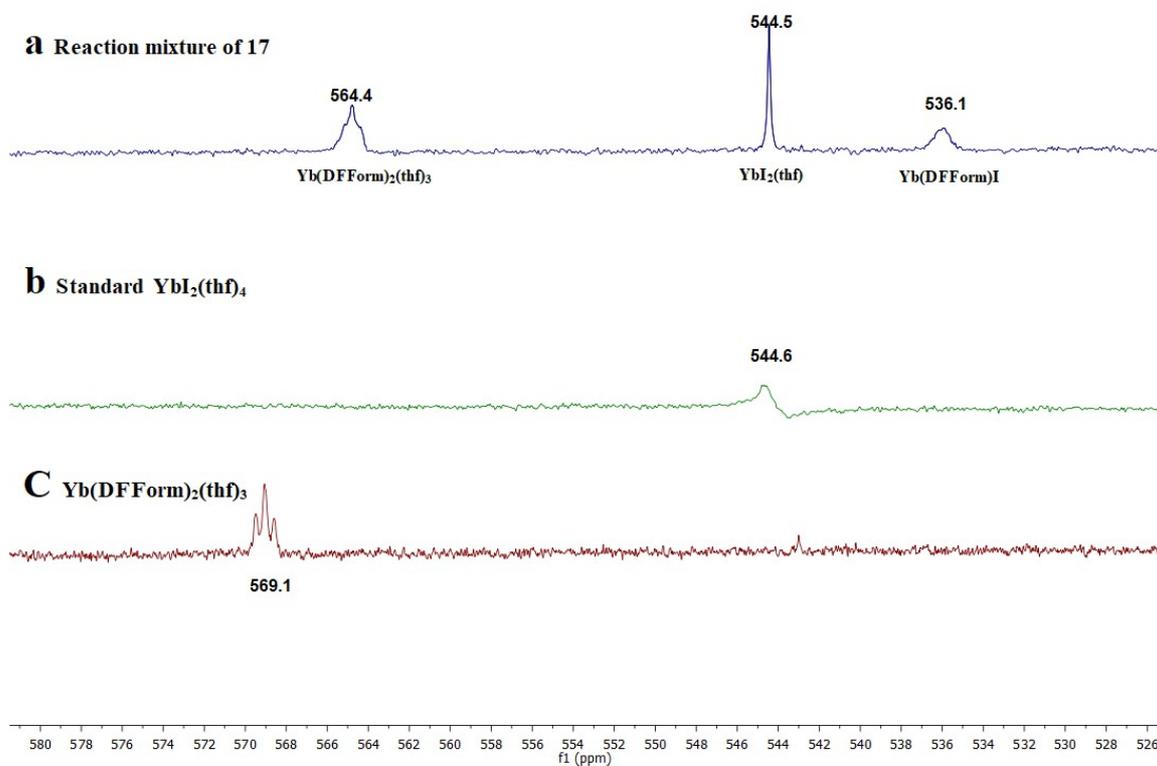
**Fig. S3**  $^1\text{H}$  NMR spectrum of  $[\text{Lu}(\text{DippForm})\text{I}_2(\text{thf})_3] \cdot 2\text{thf}$  (**12**)



**Fig. S4**  $^1\text{H}$  NMR spectrum of  $[\text{Nd}(\text{DippForm})\text{I}_2(\text{thf})_3] \cdot 0.5\text{thf}$  (**15**)

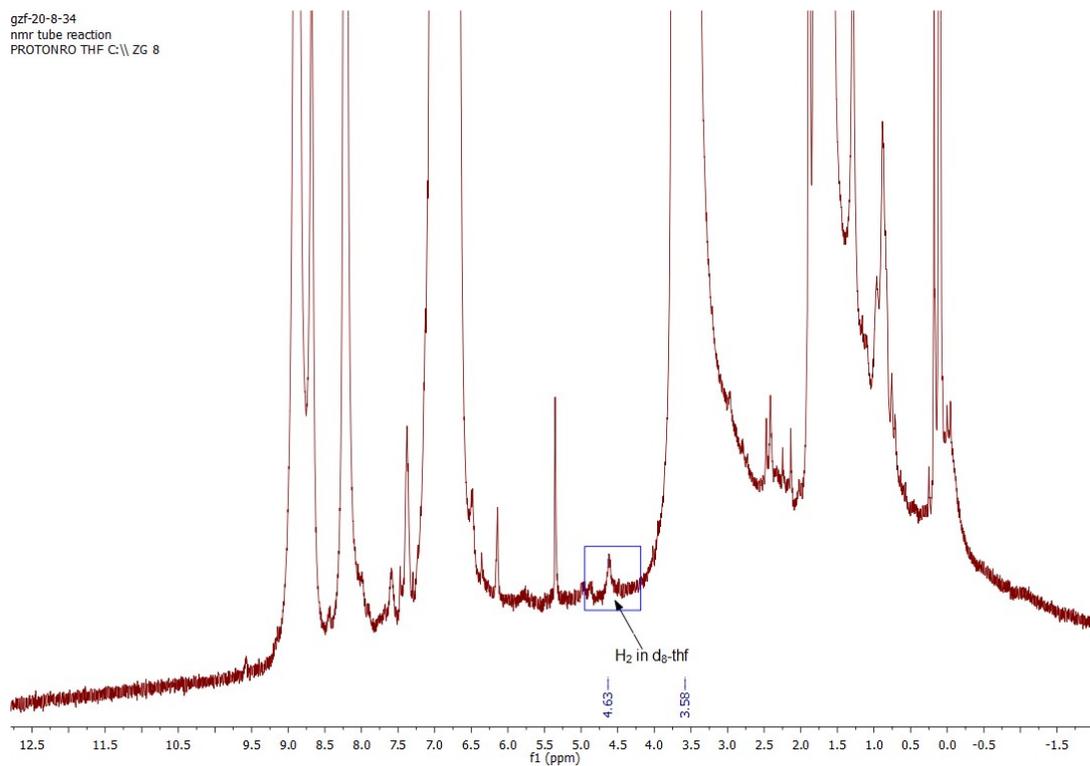


**Fig. S5.**  $^{19}\text{F}$  NMR spectra of the reaction mixture of (a) Yb with  $\text{I}_2$  and DFFormH; (b) Eu with  $\text{I}_2$  and DFFormH.

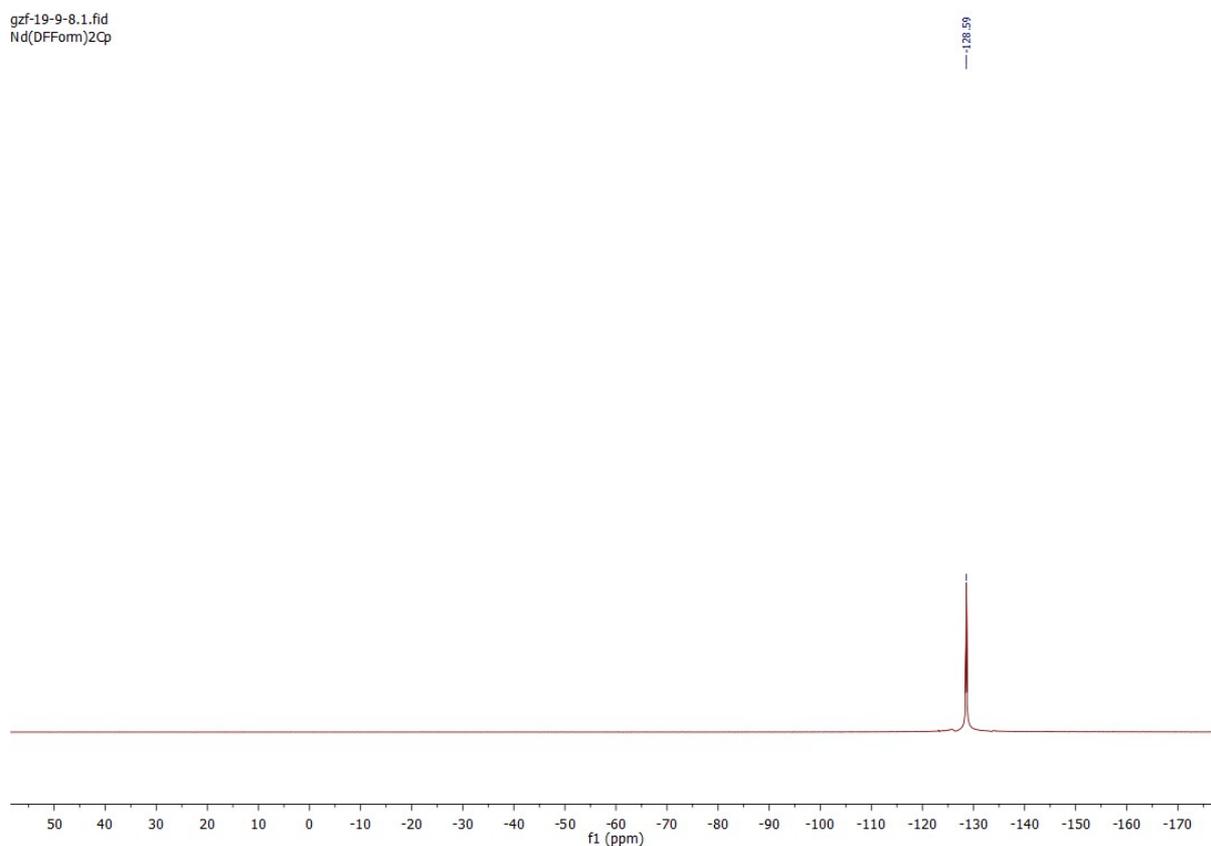


**Fig. S6.**  $^{171}\text{Yb}$  NMR spectra of (a) the reaction mixture of Yb with  $\text{I}_2$  and DFFormH; (b)

Standard  $\text{YbI}_2(\text{thf})_4$ ; (c)  $\text{Yb}(\text{DFForm})_2(\text{thf})_3$



**Fig. S7.**  $^1\text{H}$  NMR spectrum of the NMR tube scale reaction mixture of Lu,  $\text{I}_2$  and DFFormH in  $\text{d}_8$ -thf



**Fig. S8.** <sup>1</sup>H NMR spectrum of reaction mixture of Nd(DFForm)<sub>2</sub>I and NaCp

### 3. X-ray crystallography

Single crystals coated with viscous hydrocarbon oil were mounted on glass fibres or loops. Complexes **3**, **5** and **11** were measured on a “Bruker APEX-II CCD” diffractometer equipped with graphite-monochromated Mo-K radiation ( $\lambda = 0.71073 \text{ \AA}$ ) at 123 K, mounted on a fibre loop in crystallography oil. Absorption corrections were completed using Apex II program suite using SADABS.<sup>4</sup> Complexes **2**, **12** and **15** were measured on a Rigaku SynergyS diffractometer. The SynergyS operated using microsource Mo-K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) at 123 K. Data processing was conducted using CrysAlisPro.<sup>55</sup> software suite.<sup>5</sup> Others were measured at the Australian Synchrotron on the MX1 (**1**, **4**, **6**, **9-10**, **14**, **16**, **18**, **18a**) macromolecular beamlines, data integration was completed using Blue-ice<sup>6</sup> and XDS<sup>7</sup> software programs. Structural solutions were obtained by either direct methods<sup>8</sup> or charge flipping<sup>9</sup> methods and refined using full-matrix least-squares methods against  $F^2$  using SHELX2015,<sup>10</sup> in conjunction with the X-Seed<sup>11</sup> or Olex2<sup>9</sup> graphical user interface. All hydrogen atoms were placed in calculated positions using the riding model. Crystal data and refinement details are given in **Table S1**. contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

The crystal structure of **16** is reported for connectivity only, as we collected 6 datasets of the crystal data by different diffractometers (both synchrotron and Rigaku). The same problems continually arose, viz, there is a large residual peak near to one of the THF molecules. We attempted to find a suitable twin law in PLATON, but no sensible result was obtained. This could be an artefact of twinning.

**Table S1** Crystal data and structural refinement for lanthanoid complexes **1-18**

	<b>1</b>	<b>2</b>	<b>3</b>	<b>4</b>
Formula	C <sub>34</sub> H <sub>30</sub> F <sub>8</sub> ILuN <sub>4</sub> O <sub>2</sub>	C <sub>34</sub> H <sub>30</sub> F <sub>8</sub> IN <sub>4</sub> O <sub>2</sub> Tm	C <sub>34</sub> H <sub>30</sub> ErF <sub>8</sub> IN <sub>4</sub> O <sub>2</sub>	C <sub>34</sub> H <sub>30</sub> F <sub>8</sub> HoIN <sub>4</sub> O <sub>2</sub>
$M_r$	980.49	974.45	972.78	970.45
Crystal System	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	<i>C2/c</i>	<i>C2/c</i>	<i>C2/c</i>	<i>C2/c</i>
$a$ (Å)	15.937(3)	15.9539(4)	15.9339(5)	15.929(3)
$b$ (Å)	11.807(2)	11.8143(3)	11.8086(3)	11.845(2)

$c$ (Å)	18.619(4)	18.6508(4)	18.6639(5)	18.679(4)
$\alpha$ (°)	90	90	90	90
$\beta$ (°)	106.55(3)	106.585(1)	106.344(2)	106.19(3)
$\gamma$ (°)	90	90	90	90
$V$ (Å <sup>3</sup> )	3358.2(13)	3369.13(14)	3369.83 (17)	3384.5(13)
$Z$	4	4	4	4
$\rho_{\text{calc}}$ , g cm <sup>-3</sup>	1.939	1.921	1.917	1.905
$\mu$ , mm <sup>-1</sup>	3.942	3.632	3.489	3.332
$N_{\tau}$	30283	13890	13071	38696
$N$ ( $R_{\text{int}}$ )	4760(0.0198)	4056(0.0143)	3847(0.0321)	2988(0.0380)
$R_1(I > 2 \sigma(I))$	0.0251	0.0161	0.0205	0.0201
$wR_2$ (all data)	0.0694	0.0380	0.0445	0.0505
GOF	1.091	1.153	1.015	1.102
	<b>5</b>	<b>6</b>	<b>9</b>	<b>10</b>
Formula	C <sub>34</sub> H <sub>30</sub> DyF <sub>8</sub> IN <sub>4</sub> O <sub>2</sub>	C <sub>34</sub> H <sub>30</sub> F <sub>8</sub> GdIN <sub>4</sub> O <sub>2</sub>	C <sub>25</sub> H <sub>31</sub> F <sub>4</sub> GdI <sub>2</sub> N <sub>2</sub> O <sub>3</sub>	C <sub>25</sub> H <sub>31</sub> F <sub>4</sub> I <sub>2</sub> N <sub>2</sub> O <sub>3</sub> Sm
$M_r$	968.02	962.77	894.57	887.67
Crystal System	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	<b><i>C2/c</i></b>	<b><i>C2/c</i></b>	<b><i>P2<sub>1</sub>/c</i></b>	<b><i>P2<sub>1</sub>/n</i></b>
$a$ (Å)	15.9491(4)	16.009(3)	12.811(3)	9.6230(19)
$b$ (Å)	11.8365(3)	11.879(2)	9.4750(19)	23.486(5)
$c$ (Å)	18.7114(6)	18.931(4)	23.728(5)	12.883(3)
$\alpha$ (°)	90	90	90	90
$\beta$ (°)	106.203 (2)	106.04(3)	91.79(3)	92.89(3)
$\gamma$ (°)	90	90	90	90
$V$ (Å <sup>3</sup> )	3392.06 (17)	3460.1(13)	2878.8(10)	2907.9(10)
$Z$	4	4	4	4
$\rho_{\text{calc}}$ , g cm <sup>-3</sup>	1.896	1.848	2.064	2.028
$\mu$ , mm <sup>-1</sup>	3.195	2.890	4.503	4.197
$N_{\tau}$	31166	19110	32403	33855
$N$ ( $R_{\text{int}}$ )	3480(0.0526)	2861(0.0577)	5045(0.0392)	4978(0.0405)
$R_1(I > 2 \sigma(I))$	0.0225	0.0323	0.0335	0.0271
$wR_2$ (all data)	0.0413	0.0921	0.0797	0.0687

GOF	1.070	1.103	1.183	1.057
	<b>11</b>	<b>12</b>	<b>14</b>	<b>15</b>
Formula	C <sub>25</sub> H <sub>31</sub> F <sub>4</sub> I <sub>2</sub> N <sub>2</sub> NdO <sub>3</sub>	C <sub>45</sub> H <sub>75</sub> I <sub>2</sub> LuN <sub>2</sub> O <sub>5</sub>	C <sub>41</sub> H <sub>67</sub> GdI <sub>2</sub> N <sub>2</sub> O <sub>4</sub>	C <sub>41</sub> H <sub>67</sub> I <sub>2</sub> N <sub>2</sub> NdO <sub>4</sub>
<i>M<sub>r</sub></i>	881.56	1152.84	1063.01	1050.00
Crystal System	Monoclinic	Triclinic	Orthorhombic	Orthorhombic
Space group	<i>P2<sub>1</sub>/c</i>	<b>P-1</b>	<b>Pbca</b>	<b>Pbca</b>
<i>a</i> (Å)	12.8662(9)	11.6323(3)	18.831(4)	19.6958(3)
<i>b</i> (Å)	9.4950(6)	13.4896(3)	19.561(4)	18.9803(3)
<i>c</i> (Å)	23.7380(16)	16.2376(5)	24.134(5)	24.0171(5)
$\alpha$ (°)	90	99.391(2)	90	90
$\beta$ (°)	91.727(3)	106.182(3)	90	90
$\gamma$ (°)	90	97.937(2)	90	90
<i>V</i> (Å <sup>3</sup> )	2898.6(3)	2368.45(12)	8890(3)	8978.4(3)
<i>Z</i>	4	2	8	8
$\rho_{\text{calc}}$ , g cm <sup>-3</sup>	2.020	1.617	1.588	1.554
$\mu$ , mm <sup>-1</sup>	3.976	3.431	2.920	2.570
<i>N<sub>τ</sub></i>	22302	42943	93420	53865
<i>N</i> ( <i>R<sub>int</sub></i> )	7251(0.0150)	8330(0.1019)	7576(0.0651)	7909(0.0435)
<i>R</i> <sub>1</sub> ( <i>I</i> > 2 $\sigma$ ( <i>I</i> ))	0.0153	0.0492	0.0679	0.0309
<i>wR</i> <sub>2</sub> (all data)	0.0320	0.1391	0.1490	0.0750
GOF	1.117	1.062	1.137	1.071
	<b>16</b>	<b>18</b>	<b>18a</b>	
Formula	C <sub>43</sub> H <sub>43</sub> F <sub>8</sub> N <sub>4</sub> NdO <sub>3</sub>	C <sub>41</sub> H <sub>29</sub> EuF <sub>8</sub> N <sub>7</sub>	C <sub>25</sub> H <sub>35</sub> EuI <sub>2</sub> N <sub>3</sub> O <sub>2.5</sub>	
<i>M<sub>r</sub></i>	960.05	923.67	823.32	
Crystal System	Monoclinic	Monoclinic	Trigonal	
Space group	<i>P2<sub>1</sub>/c</i>	<i>C2/c</i>	<i>R-3c</i>	
<i>a</i> (Å)	19.141(4)	12.8569 (3)	18.997(3)	
<i>b</i> (Å)	10.909(2)	17.2704 (4)	18.997(3)	
<i>c</i> (Å)	38.732(8)	18.0267(5)	43.447(9)	
$\alpha$ (°)	90	90	90	
$\beta$ (°)	92.82(3)	107.775(1)	90	
$\gamma$ (°)	90	90	120	

$V (\text{\AA}^3)$	8078(3)	3811.64 (17)	13578(5)	
$Z$	8	4	18	
$\rho_{\text{calc}}, \text{g cm}^{-3}$	1.579	1.610	1.812	
$\mu, \text{mm}^{-1}$	1.368	1.725	4.150	
$N_{\tau}$	94237	42811	51472	
$N (R_{\text{int}})$	15170(0.0569)	5362(0.0459)	2669(0.0582)	
$R_1(I > 2 \sigma (I))$	0.0802	0.0229	0.0339	
$wR_2 (\text{all data})$	0.2256	0.0464	0.1009	
GOF	1.056	1.058	1.063	

#### 4. Selected bond angles (°) and lengths (Å)

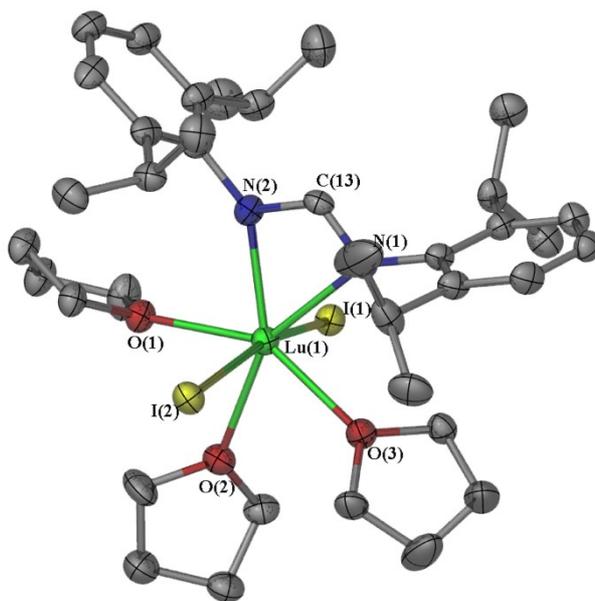
##### 4.1 The complexes [Ln(DFForm)<sub>2</sub>I(thf)<sub>2</sub>] (1-6)

**1** Lu-N(1) 2.363(3), Lu-N(2) 2.410(3), Lu-O(1) 2.272(3), Lu-I(1) 2.9754(7), O(1)-Lu-O(1)# 171.45(11), O(1)-Lu-I(1) 94.28(6), C(7)-Lu-O(1) 86.29(3), C(7)-Lu-I(1) 107.39(6), C(7)-Lu-C(7)# 145.22(13); **2** Tm-N(1) 2.3821(16), Tm-N(2) 2.4129(17), Tm-O(1) 2.2923(14), Tm-I(1) 2.9808(2), O(1)-Tm-O(1)# 170.83(8), O(1)-Tm-I(1) 94.59(4), C(7)-Tm-O(1) 86.77(5), C(7)-Tm-I(1) 107.41(4), C(7)-Tm-C(7)# 145.18(8); **3** Er-N(1) 2.432(2), Er-N(2) 2.392(2), Er-O(1) 2.3010(17), Er-I(1) 2.9879(3), O(1)-Er-O(1)# 171.26(9), O(1)-Er-I(1) 94.37(5), C(7)-Er-O(1) 90.98(7), C(7)-Er-I(1) 107.31(5), C(7)-Er-C(7)# 145.39(11); **4** Ho-N(1) 2.402(3), Ho-N(2) 2.450(3), Ho-O(1) 2.321(2), Ho-I(1) 3.0012(7), O(1)-Ho-O(1)# 170.91(11), O(1)-Ho-I(1) 94.55(5), C(7)-Ho-O(1) 86.05(9), C(7)-Ho-I(1) 107.47(6), C(7)-Ho-C(7)# 145.07(13); **5** Dy-N(1) 2.407(2), Dy-N(2) 2.449(2), Dy-O(1) 2.3292(19), Dy-I(1) 3.0038(3), O(1)-Dy-O(1)# 170.79(10), O(1)-Dy-I(1) 94.61(5), C(7)-Dy-O(1) 91.19(7), C(7)-Dy-I(1) 107.49(6), C(7)-Dy-C(7)# 145.02(12); **6** Gd-N(1) 2.485(4), Gd-N(2) 2.459(4), Gd-O(1) 2.367(4), Gd-I(1) 3.0307(7), O(1)-Gd-O(1)# 170.82(14), O(1)-Gd-I(1) 94.59(7), C(7)-Gd-O(1) 91.37(13), C(7)-Gd-I(1) 107.20(9), C(7)-Gd-C(7)# 145.59(18).

##### 4.2 The complexes [Ln(DFForm)I<sub>2</sub>(thf)<sub>3</sub>] (9-11)

**9** Gd-N(1) 2.399(5), Gd-N(2) 2.499(6), Gd-O(1) 2.390(4), Gd-O(2) 2.427(4), Gd-O(3) 2.460(5), Gd-I(1) 3.0343(7), Gd-I(2) 3.0401(8), O(1)-Gd-O(2) 71.42(16), O(1)-Gd-O(3) 145.65(16), O(2)-Gd-O(3) 74.34(16), I(1)-Gd-I(2) 172.242(11), C(7)-Gd-I(1) 98.67(14), C(7)-Gd-I(2) 89.07(14); **10** Sm-N(1) 2.430(3), Sm-N(2) 2.500(3), Sm-O(1) 2.420(3), Sm-O(2) 2.434(3), Sm-O(3) 2.492(3), Sm-I(1) 3.0512(6), Sm-I(2) 3.0553(6), O(1)-Sm-O(2) 71.78(10), O(1)-Sm-O(3) 145.94(10), O(2)-Sm-O(3) 74.16(10), I(1)-Sm-I(2) 170.351(11), C(7)-Sm-I(1) 99.96(8), C(7)-Sm-I(2) 89.47(8); **11** Nd-N(1) 2.435(2), Nd-N(2) 2.542(2), Nd-O(1) 2.4339(17), Nd-O(2) 2.4669(17), Nd-O(3) 2.5086(18), Nd-I(1) 3.0796(3), Nd-I(2) 3.0870(3), O(1)-Nd-O(2) 71.47(6), O(1)-Nd-O(3) 145.53(6), O(2)-Nd-O(3) 74.17(6), I(1)-Nd-I(2) 171.046(7), C(7)-Nd-I(1) 99.41(5), C(7)-Nd-I(2) 89.54(5).

##### 4.3 The complex [Ln(DippForm)<sub>2</sub>I<sub>2</sub>(thf)<sub>3</sub>] (12, 14, 15)



**Fig. S9.** Molecular diagram of  $[\text{Lu}(\text{DippForm})\text{I}_2(\text{thf})_3]\cdot 2\text{thf}$  (**12**) (representative of Lu, **12**, Gd, **14**, Nd, **15**) with non-hydrogen atoms represented by 50% thermal ellipsoids. The lattice thf molecules and hydrogen atoms have been omitted for clarity.

**12** Lu-N(1) 2.366(6), Lu-N(2) 2.330(6), Lu-O(1) 2.363(5), Lu-O(2) 2.422(5), Lu-O(3) 2.358(5), Lu-I(1) 2.9695(5), Lu-I(2) 2.9765(5), O(1)-Lu-O(2) 73.60(17), O(1)-Lu-O(3) 146.53(17), O(2)-Lu-O(3) 73.13(17), I(1)-Lu-I(2) 166.075(18), C(13)-Lu-I(1) 99.51(13), C(13)-Lu-I(2) 94.40(13); **14** Gd-N(1) 2.420(8), Gd-N(2) 2.433(9), Gd-O(1) 2.421(7), Gd-O(2) 2.474(8), Gd-O(3) 2.425(9), Gd-I(1) 3.0596(10), Gd-I(2) 3.068(8), O(1)-Gd-O(2) 74.5(4), O(1)-Gd-O(3) 148.2(3), O(2)-Gd-O(3) 73.7(3), I(1)-Gd-I(2) 167.34(17), C(13)-Gd-I(1) 96.11(8), C(13)-Gd-I(2) 96.47(10); **15** Nd-N(1) 2.462(4), Nd-N(2) 2.477(4), Nd-O(1) 2.472(3), Nd-O(2) 2.547(3), Nd-O(3) 2.478(4), Nd-I(1) 3.1115(4), Nd-I(2) 3.1155(4), O(1)-Nd-O(2) 73.86(12), O(1)-Nd-O(3) 147.58(12), O(2)-Nd-O(3) 73.79(11), I(1)-Nd-I(2) 167.663(12), C(13)-Nd-I(1) 95.5008(12), C(13)-Nd-I(2) 96.8340(12).

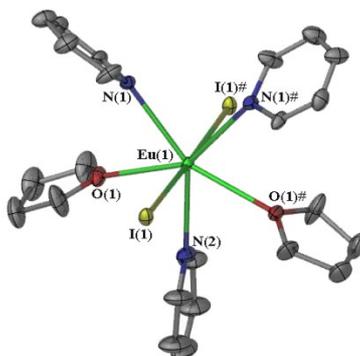
#### 4.4 The complex $[\text{Nd}(\text{DFForm})_2\text{Cp}(\text{thf})_2]\cdot \text{thf}$ **16**

We do not provide detailed bond lengths and angles for this compound as it is only submitted for connectivity only. As stated above there were issues in the refinement of this compound.

#### 4.5 The complexes $[\text{Eu}(\text{DFForm})_2(\text{py})_3]$ **18** and $[\text{EuI}_2(\text{thf})_3(\text{py})_2] \cdot 0.5\text{thf}$ **18a**

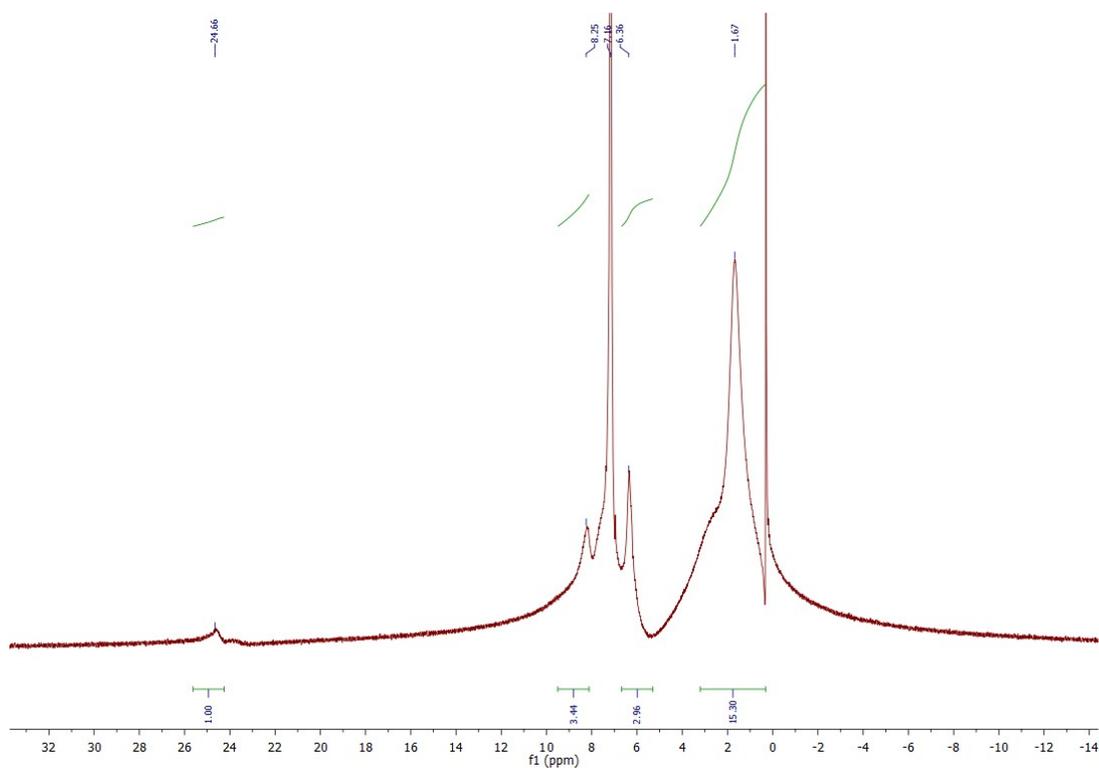
$[\text{EuI}_2(\text{thf})_3(\text{py})_3]\cdot 0.5\text{thf}$  **18a** crystallized in the trigonal space group  $R\bar{3}c$ . The Eu atom is seven coordinates with two *trans* iodide ligands (I1-Eu-I1# 177.47(3)°), three *mer* py ligands

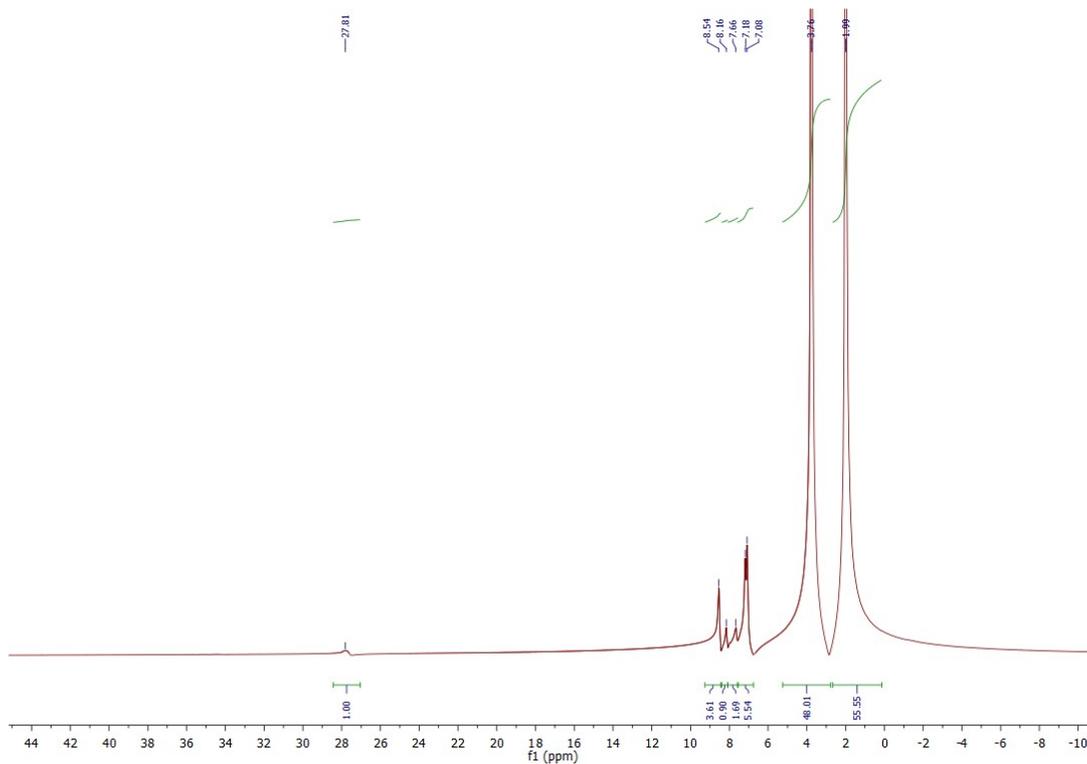
[N1-Eu-N1# 76.9(3), N1-Eu-N2 141.54(13)], and two *transoid* thf ligands [O-Eu-O1# 139.2(3)] (**Fig. S10**). The average bond distance for **18a** [Eu-O 2.629(6), Eu-I 3.2561(6), Eu-N 2.675(2)] is a little longer than the pentagonal bipyramid coordinated Eu complex [EuI<sub>2</sub>(thf)<sub>5</sub>] [Eu-O 2.598(14), Eu-I 3.234(2)], and the two iodide ligands are also in *trans* position [I1-Eu-I1# 177.83(6)<sup>o</sup>] in [EuI<sub>2</sub>(thf)<sub>5</sub>].<sup>11</sup>



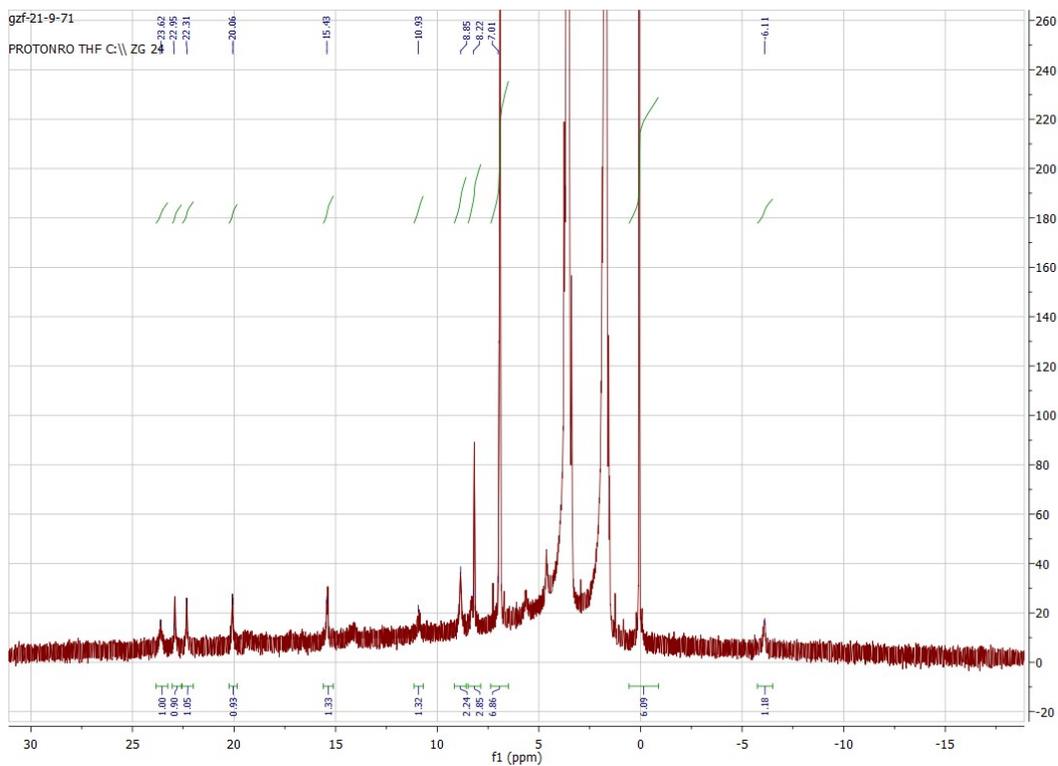
**Fig. S10** Molecular structure of [EuI<sub>2</sub>(thf)<sub>2</sub>(py)<sub>3</sub>]·0.5thf **18a** represented by 50% thermal ellipsoids. Hydrogen atoms and the lattice thf molecular have been omitted for clarity.

**18** Eu-N1 2.6072(14), Eu-N2 2.7329(14), Eu-N3 2.7023(16), Eu-N4 2.705(2), C7-Eu-C7#: 130.085; **18a** Eu-N1 2.672(6), Eu-N2 2.677(11), Eu-O1 2.629(6), Eu-I1 3.2561(6), I1-Eu-I1# 177.45(3), O1-Eu-O1# 139.2(3), N1-Eu-N2 141.53(13), N1-Eu-N1# 76.9(3).





**Fig. S11**  $^1\text{H}$  NMR spectra of **(up)**  $[\text{Nd}(\text{DFForm})_2\text{I}(\text{thf})_2]$  (**7**); **(down)**  $[\text{Nd}(\text{DFForm})\text{I}_2(\text{thf})_3]$  (**10**)



**Fig. S12**  $^1\text{H}$  NMR spectrum of  $[\text{Sm}(\text{DFForm})\text{I}_2(\text{thf})_3]$  (**11**)

## 5. References

- [1]. R. M. Roberts, *J. Org. Chem.*, 1949, **14**, 277.
- [2]. G. B. Deacon, P. C. Junk and D. Werner, *Chem. Eur. J.*, 2016, **22**, 160.
- [3]. S. Hamidi, G. B. Deacon, P. C. Junk and P. Neumann, *Dalton Trans.*, 2012, **41**, 3541.
- [4]. Sheldrick, G. M. SADABS; University of Gottingen, Gcottingen (Germany), 1996.
- [5]. CrysAlisPRO v.39. Agilent Technologies Ltd., Yarnton, Oxfordshire, England.
- [6]. T. M. McPhillips, S. E. McPhillips, H. J. Chiu, A. E. Cohen, A. M. Deacon, P. J. Ellis, E. Garman, A. Gonzalez, N. K. Sauter, R. P. Phizackerley, S. M. Soltis and J. P. Kuhn, *J. Synchrotron Radiat.*, 2002, **9**, 401.
- [7]. W. Kabsch, *J. Appl. Crystallogr.*, 1993, **26**, 795.
- [8]. G. M. Sheldrick, *Acta Crystallogr. Sect. A.*, 2008, **64**, 112.
- [9]. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Crystallogr.*, 2009, **42**, 339.
- [10]. G. M. Sheldrick, *Acta Cryst.*, 2015, **C71**, 3.
- [11]. L. J. Barbour, *J. Supramol. Chem.*, 2001, **1**, 189.
- [12]. G. Heckmann and M. Niemeyer, *J. Am. Chem. Soc.*, 2000, **122**, 4227.