

SI for Applications of boroxide ligands in supporting small molecule activation by U(III) and U(IV) complexes  
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## Contents

Numbering scheme.....	1
General Experimental Details .....	2
General procedures and techniques.....	2
Preparation of reagents.....	2
Other related compounds and reactions .....	3
Reaction of [U(OBMes <sub>2</sub> ) <sub>3</sub> ] <sub>2</sub> with CO <sub>2</sub> .....	3
Reaction of [U(OBMes <sub>2</sub> ) <sub>3</sub> ] <sub>2</sub> with PPh <sub>3</sub> .....	3
Reaction of [U(OBMes <sub>2</sub> ) <sub>3</sub> ] <sub>2</sub> with P <sub>4</sub> .....	3
Reaction of [U(OBMes <sub>2</sub> ) <sub>3</sub> ] <sub>2</sub> with Me <sub>3</sub> SiN <sub>3</sub> .....	3
Reaction of [OU(OBMes <sub>2</sub> ) <sub>3</sub> ] <sub>n</sub> with KC <sub>8</sub> , synthesis of K <sub>2</sub> [{(OBMes <sub>2</sub> ) <sub>3</sub> U} <sub>2</sub> (μ-O) <sub>2</sub> ] <b>10<sup>m</sup></b> .....	3
Reaction of [U(OBTrip <sub>2</sub> ) <sub>3</sub> ] <sub>2</sub> with CO .....	3
Selected NMR Spectra .....	4
[U(OBMes <sub>2</sub> ) <sub>3</sub> ] <sub>2</sub> <b>1<sup>m</sup></b> .....	4
[U(OBTrip <sub>2</sub> ) <sub>3</sub> ] <sub>2</sub> <b>1<sup>t</sup></b> .....	5
[U(OBTrip <sub>2</sub> ) <sub>3</sub> (OEt <sub>2</sub> )] <b>1<sup>t</sup>-OEt<sub>2</sub></b> .....	5
[U(OBMes <sub>2</sub> ) <sub>4</sub> ] <b>2<sup>m</sup></b> .....	7
[U(OBTrip <sub>2</sub> ) <sub>4</sub> ] <b>2<sup>t</sup></b> .....	8
[OU(OBMes <sub>2</sub> ) <sub>3</sub> ] <sub>n</sub> <b>3<sup>m</sup></b> .....	9
[U(OBMes <sub>2</sub> ) <sub>4</sub> (py-O) <sub>2</sub> ] <b>4<sup>m</sup></b> .....	10
[U(OBMes <sub>2</sub> ) <sub>3</sub> (OPPh <sub>3</sub> ) <sub>2</sub> ] <b>5<sup>m</sup></b> .....	11
[{(OBMes <sub>2</sub> ) <sub>3</sub> U} <sub>2</sub> (μ-η <sup>2</sup> :η <sup>2</sup> -S <sub>2</sub> ) <sub>2</sub> ] <b>7<sup>m</sup></b> .....	13
[U{η <sup>2</sup> -N(Cy)C(=NCy)N(Cy)}(OBMes <sub>2</sub> ) <sub>3</sub> ] <b>8<sup>m</sup></b> .....	14
[U(OBMes <sub>2</sub> )N <sup>n</sup> ] <sub>3</sub> <b>11<sup>m</sup></b> .....	15
[U(OBTrip <sub>2</sub> )N <sup>n</sup> ] <sub>3</sub> <b>11<sup>t</sup></b> .....	16
X-ray data.....	17
Crystallographic tables.....	17
[KOU(OBMes <sub>2</sub> ) <sub>3</sub> ] <sub>2</sub> <b>10<sup>m</sup></b> .....	20

## Numbering scheme

	number	yield	xray
[U(OBMes <sub>2</sub> ) <sub>3</sub> ] <sub>2</sub>	<b>1<sup>m</sup></b>	41	X-ray
[U(OBTrip <sub>2</sub> ) <sub>3</sub> ] <sub>2</sub>	<b>1<sup>t</sup></b>	32	
U(OBTrip <sub>2</sub> ) <sub>3</sub> (OEt <sub>2</sub> )	<b>1<sup>t</sup>.OEt<sub>2</sub></b>	11	X-ray
U(OBMes <sub>2</sub> ) <sub>4</sub>	<b>2<sup>m</sup></b>	12	X-ray
U(OBTrip <sub>2</sub> ) <sub>4</sub>	<b>2<sup>t</sup></b>	25	X-ray
(μ-O) <sub>2</sub> [U(OBMes <sub>2</sub> ) <sub>3</sub> ] <sub>2</sub>	<b>3<sup>m</sup></b>	100	
U(OBMes <sub>2</sub> ) <sub>4</sub> (OPy) <sub>2</sub>	<b>4<sup>m</sup></b>	65	X-ray
U(OBMes <sub>2</sub> ) <sub>3</sub> (OPPh <sub>3</sub> ) <sub>2</sub>	<b>5<sup>m</sup></b>	60	X-ray
[U(OBMes <sub>2</sub> ) <sub>3</sub> (B <sub>2</sub> O <sub>3</sub> Mes <sub>2</sub> )]	<b>and 6<sup>m</sup></b>		X-ray
(μ-η <sup>2</sup> :η <sup>2</sup> -S <sub>2</sub> ) <sub>2</sub> [U(OBMes <sub>2</sub> ) <sub>3</sub> ] <sub>2</sub>	<b>7<sup>m</sup></b>	18	X-ray
U(η <sup>2</sup> -DCC)(OBMes <sub>2</sub> ) <sub>3</sub> (DCC = N(Cy)C(=N(Cy))N(Cy))	<b>8<sup>m</sup></b>	69	
[U(OBTrip <sub>2</sub> ) <sub>3</sub> ] <sub>2</sub> (μ-CO <sub>3</sub> )	<b>9<sup>t</sup></b>	2	X-ray
K <sub>2</sub> [{(OBMes <sub>2</sub> ) <sub>3</sub> U] <sub>2</sub> (μ-O) <sub>2</sub> ]	<b>10<sup>m</sup></b>	2	X-ray
U(OBMes <sub>2</sub> )N <sup>''</sup> <sub>3</sub>	<b>11<sup>m</sup></b>	78	X-ray
U(OBTripp <sub>2</sub> )N <sup>''</sup> <sub>3</sub>	<b>11<sup>t</sup></b>	5	X-ray

## General Experimental Details

### General procedures and techniques

Standard high vacuum Schlenk-line techniques and MBraun and Vac glove boxes were used to store and manipulate air- and moisture-sensitive compounds under an atmosphere of air free and dried dinitrogen. Reactions and manipulations were carried out under an inert atmosphere unless stated otherwise. All gases were supplied by BOC gases UK. All glassware was dried in an oven at 160 °C, cooled under vacuum and purged with nitrogen prior to use. All Fisherbrand® 1.2 μm retention glass microfiber filters and cannula were dried in an oven at 160 °C before use.

Toluene, THF, diethyl ether and hexane for use with air- and moisture-sensitive compounds were stored in ampoules containing activated 4 Å molecular sieves from the Vac Atmospheres solvent tower drying system, where they had been passed over a column of molecular sieves for a minimum of 12 hours prior to collection. 1,4-dioxane and benzene were refluxed over potassium for 3 days, distilled and collected in an ampoule containing activated 4 Å molecular sieves. All solvents were degassed prior to use and stored. The solvents C<sub>6</sub>D<sub>6</sub>, THF-*d*<sub>5</sub> and pyridine-*d*<sub>5</sub> were heated under reflux over potassium for 24 hours, degassed and distilled by trap to trap distillation and stored under an atmosphere of nitrogen prior to use. All solvents were purchased by Sigma Aldrich or Fisher Scientific.

All NMR spectroscopic analyses were recorded at 198 K using Bruker Avance III 500.12 MHz spectrometers with <sup>1</sup>H NMR spectra run at 500.12 MHz, <sup>13</sup>C NMR spectra run at 125.76, <sup>29</sup>Si NMR spectra run at 99.37 MHz, <sup>11</sup>B NMR spectra run at 160.46 MHz, <sup>19</sup>F NMR spectra run at 470.59 MHz. The <sup>1</sup>H and <sup>13</sup>C NMR spectra are referenced internally to the residual solvent peaks or an external standard (Me<sub>4</sub>Si for <sup>29</sup>Si, Et<sub>2</sub>O•BF<sub>3</sub> for <sup>11</sup>B, CFC<sub>3</sub> for <sup>19</sup>F).

Elemental analyses were performed by Mr. Stephen Boyer at the London Metropolitan University.

Mass spectra measurements were carried out on a 12T Solarix FT-ICR-MS with an Infinity cell (Bruker Daltonics); fitted with an APPI II ion source (Bruker Daltonics) equipped with krypton lamp. Samples were prepared in a glovebox in toluene (10 μM) in a sealed sample vial. Infrared spectra were recorded on a Perkin Elmer Spectrum 65 FT-IR spectrometer as nujol mulls between KBr disks.

## Preparation of reagents

All commercially available solid reagents were dried under vacuum and liquids were either dried with alkali metal and purified by trap to trap distillation, or storage over activated molecular sieves when appropriate.  $\text{NaN}(\text{SiMe}_3)_2$ ,<sup>1</sup>  $\text{U}[\text{N}(\text{SiMe}_3)_2]_3$ ,<sup>2</sup>  $\text{HOBMe}_2$ ,<sup>3</sup>  $\text{HOB}(\text{Trip})_2$ ,<sup>3</sup>  $\text{HOBfMe}_2$ ,<sup>4</sup>  $[\text{Y}(\text{N}(\text{SiMe}_3)_2)_3]^{5-}$  were synthesised according to literature procedures, in some cases with slight modifications. Sodium salts of the boroxide ligands were prepared by deprotonation of the appropriate conjugate acid with  $\text{NaN}(\text{SiMe}_3)_2$  in toluene.

## Other related compounds and reactions

### Reaction of $[\text{U}(\text{OBMe}_2)_3]_2$ with CO

A purple solution of  $[\text{U}(\text{OBMe}_2)_2(\mu\text{-OBMe}_2)]_2$  (25 mg, 0.012 mmol) in  $\text{C}_6\text{D}_6$  (0.4 mL) was placed in a Young's NMR tube and degassed by three freeze pump thaw cycles. The solution was then exposed to 1 bar pressure of CO. The mixture was agitated and an immediate colour change was observed to light brown.  $^1\text{H}$ ,  $^{11}\text{B}$  and  $^{13}\text{C}$  NMR spectroscopy showed the formation of complex  $[\text{OU}(\text{OBMe}_2)_3]_n$  from oxygen traces.

### Reaction of $[\text{U}(\text{OBMe}_2)_3]_2$ with $\text{CO}_2$

A Young's NMR tube was charged with a purple solution of  $[\text{U}(\text{OBMe}_2)_2(\mu\text{-OBMe}_2)]_2$  (25 mg, 0.012 mmol) in  $\text{C}_6\text{D}_6$  (0.4 mL). The NMR tube was then degassed by three freeze pump thaw cycles and exposed to 1 bar pressure of  $\text{CO}_2$ . The reaction was allowed to react at room temperature, and at 80 °C for one day. No change was detected in the  $^1\text{H}$  NMR spectrum except for trace decomposition.

### Reaction of $[\text{U}(\text{OBMe}_2)_3]_2$ with $\text{PPh}_3$

In a 7 cm<sup>3</sup> vial in an inert atmosphere glovebox  $\text{PPh}_3$  (13 mg, 0.048 mmol, 2 eq.) was added to a purple solution of  $[\text{U}(\text{OBMe}_2)_2(\mu\text{-OBMe}_2)]_2$  (50 mg, 0.024 mmol) in benzene (1 mL). After stirring over 18 hours at room temperature. The formation of complex  $[\text{OU}(\text{OBMe}_2)_3]_n$  from oxygen traces was confirmed by  $^1\text{H}$  and  $^{11}\text{B}$  NMR spectroscopies.

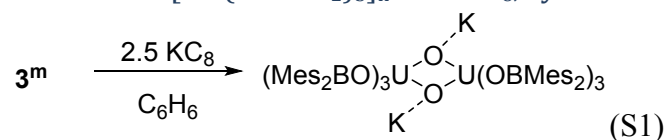
### Reaction of $[\text{U}(\text{OBMe}_2)_3]_2$ with $\text{P}_4$

$[\text{U}(\text{OBMe}_2)_2(\mu\text{-OBMe}_2)]_2$  (62 mg, 0.03 mmol) and  $\text{P}_4$  (4 mg, 0.03 mmol, 1 eq.) were placed in a Young's NMR tube in 0.4 mL of  $\text{C}_6\text{D}_6$ . The reaction was allowed to stand for one day at room temperature. No change was detected in the  $^1\text{H}$  NMR spectrum except for the formation of the decomposition product.

### Reaction of $[\text{U}(\text{OBMe}_2)_3]_2$ with $\text{Me}_3\text{SiN}_3$

$\text{Me}_3\text{SiN}_3$  (10  $\mu\text{L}$ , 0.076 mmol, 3 eq.) was added to a purple solution of  $[\text{U}(\text{OBMe}_2)_2(\mu\text{-OBMe}_2)]_2$  (52 mg, 0.025 mmol) in benzene (1 mL) in a 7 cm<sup>3</sup> vial in an inert atmosphere glovebox. The reaction was left stirring for 18 hours, after which the reaction had turned brown, and  $^1\text{H}$  and  $^{11}\text{B}$  NMR spectra show the decomposition product.

### Reaction of $[\text{OU}(\text{OBMe}_2)_3]_n$ with $\text{KC}_8$ , synthesis of $\text{K}_2[\{(\text{OBMe}_2)_3\text{U}\}_2(\mu\text{-O})_2]$ **10<sup>m</sup>**



To target reduction of the U centre in  $\mathbf{3^m}$ :

To a dark purple solution of  $[\text{U}(\text{OBMe}_2)_2(\mu\text{-OBMe}_2)]_2$  (50 mg, 0.024 mmol) in benzene (1 mL) in a 7 cm<sup>3</sup> vial was added  $\text{KC}_8$  (8 mg, 0.06 mmol, 2.5 eq.). The suspension was allowed to react for 18 hours. The reaction was centrifuged and the supernatant was filtered. Light brown crystals of  $\text{K}_2[\{(\text{OBMe}_2)_3\text{U}\}_2(\mu\text{-O})_2]$  **10<sup>m</sup>** suitable for single-crystal X-ray crystallography were grown by slow diffusion of hexanes into the reaction mixture, but in very low yield; Local code p18089. NMR spectra on this small sample are complicated and poorly resolved, so full characterisation was not pursued further.

### Reaction of $[\text{U}(\text{OBTrip}_2)_3]_2$ with CO

A purple-brown solution of  $[\text{U}(\text{OBTrip}_2)_3]_2$  (75 mg, 0.048 mmol, 1 eq.) in  $\text{C}_5\text{H}_{10}$  prepared *in situ* in a Young's NMR tube was degassed by three freeze pump thaw cycles and placed under a 1 bar pressure of CO at room temperature. The mixture was agitated to give a slight colour change to red-brown. The reaction mixture was

allowed to stand overnight at room temperature, affording X-ray quality crystals of  $[\text{U}(\text{OBTrip}_2)_4]$  directly from the reaction mixture. Yield: 4 mg, 2 %. X-ray local code 16121.

### Selected NMR Spectra

N.B.  $^{11}\text{B}$  NMR spectra were recorded in standard borosilicate NMR tubes which accordingly contain a broad absorption from the glass.

$[\text{U}(\text{OBMes}_2)_3]_2 \mathbf{1}^m$

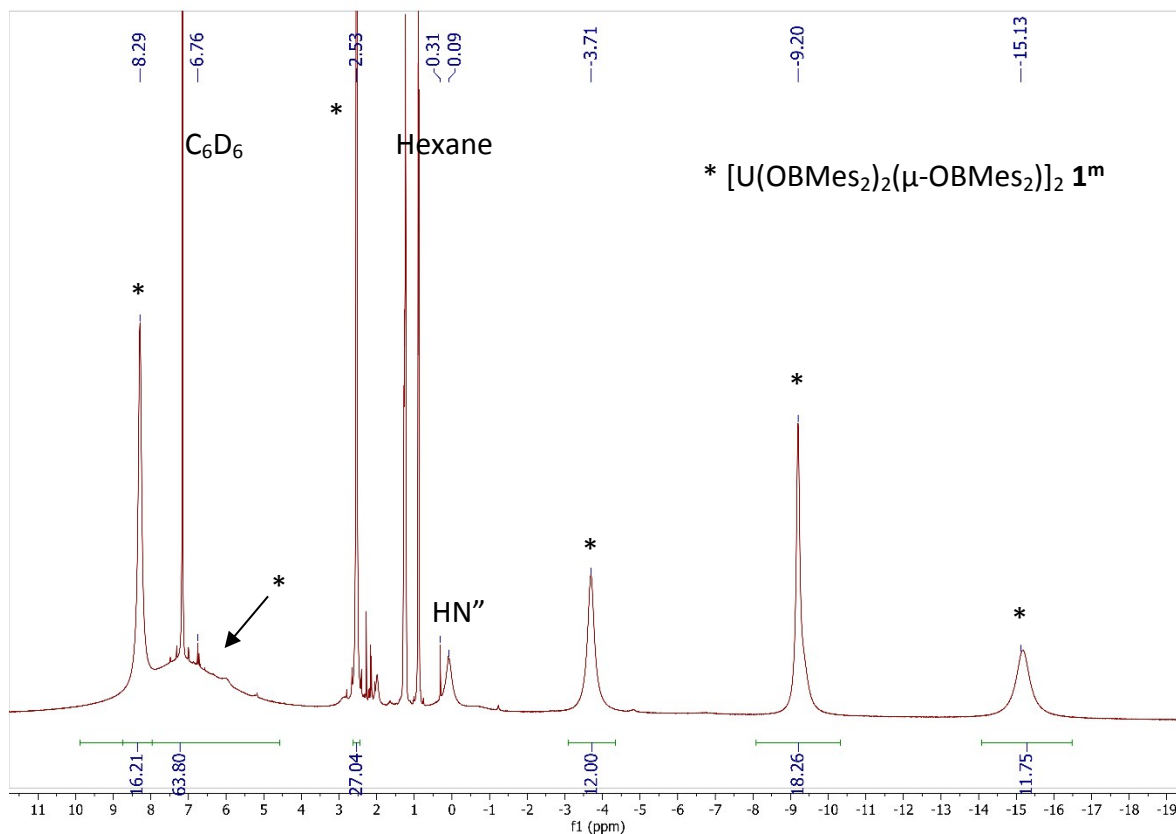


Figure S 1.  $^1\text{H}$  NMR spectrum (298 K,  $\text{C}_6\text{D}_6$ , 500 MHz) of complex  $[\text{U}(\text{OBMes}_2)_2(\mu\text{-OBMes}_2)]_2 \mathbf{1}^m$ .

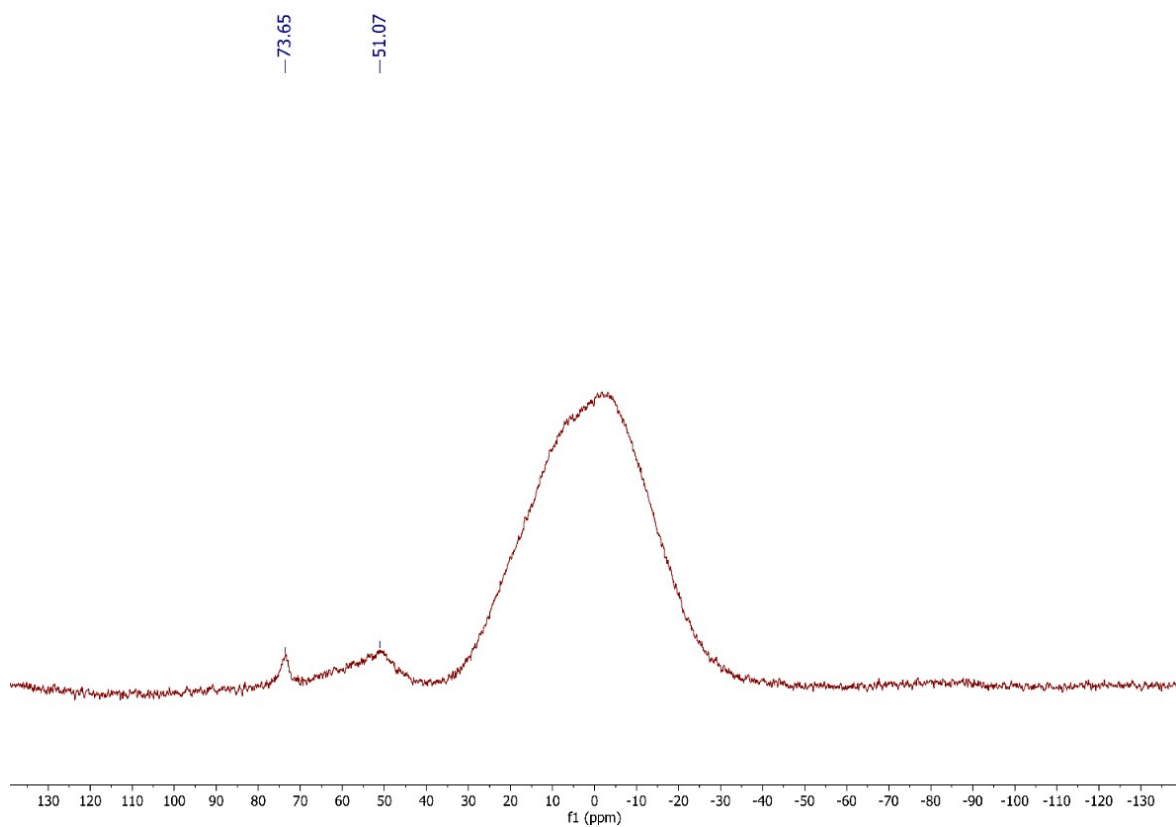


Figure S 2.  $^{11}\text{B}$  NMR spectrum of complex  $\mathbf{1}^m$ .

$[\text{U}(\text{OBTrip}_2)_3]_2 \mathbf{1}^t$

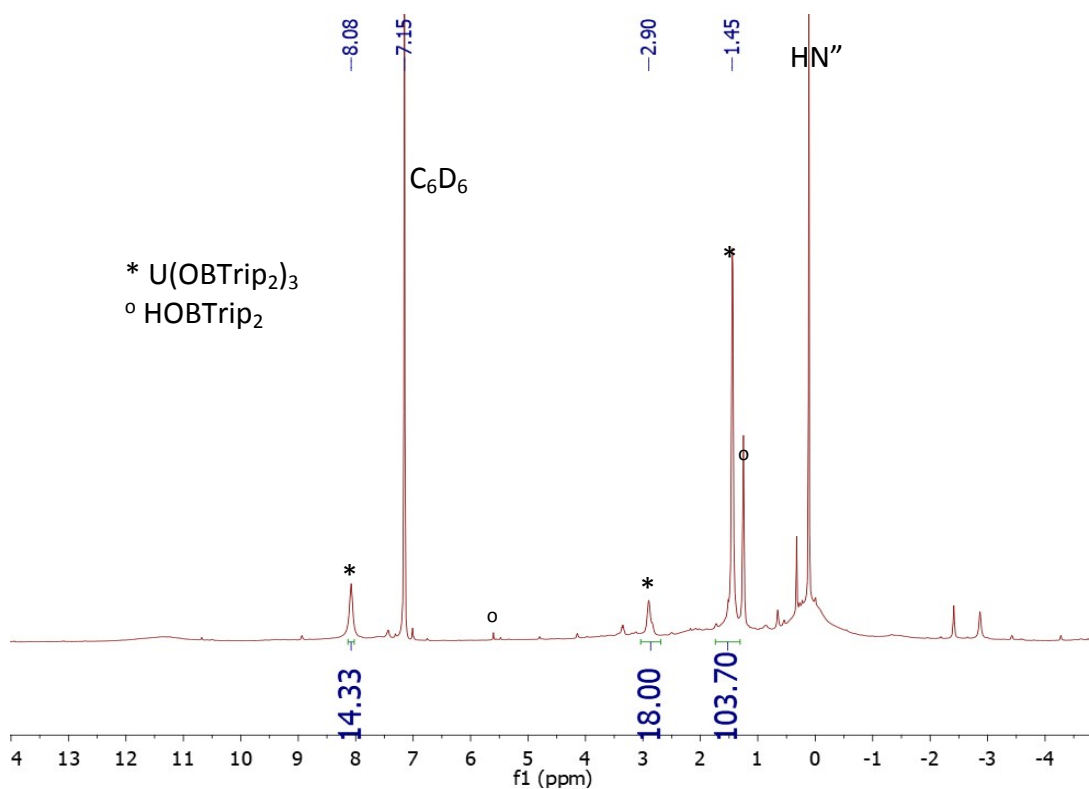


Figure S 3.  $^1\text{H}$  NMR spectrum of  $\text{C}_6\text{D}_6$  solution of complex  $[\text{U}(\text{OBTrip}_2)_3]_2 \mathbf{1}^t$ . Contamination with a small quantity of  $\mathbf{2}^t$  is visible, along with some free  $\text{HN}''$ .

[U(OBTrip<sub>2</sub>)<sub>3</sub>(OEt<sub>2</sub>)] **1<sup>t</sup>-OEt<sub>2</sub>**

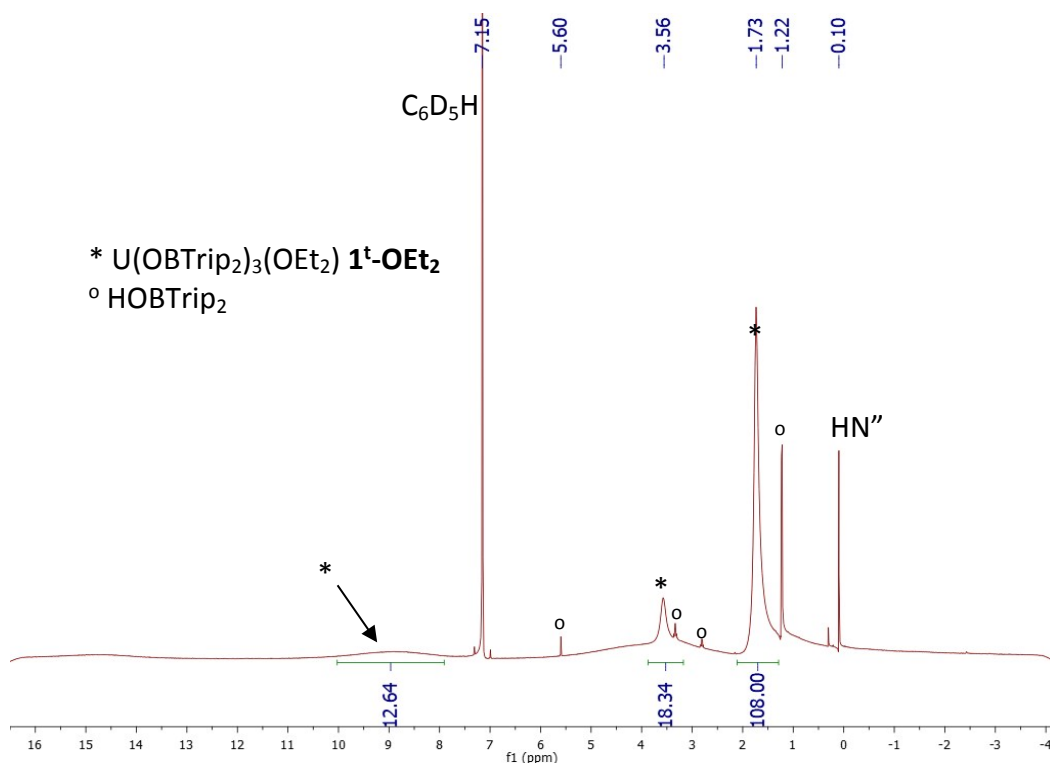


Figure S 4. <sup>1</sup>H NMR spectrum of C<sub>6</sub>D<sub>6</sub> solution of U(OBTrip<sub>2</sub>)<sub>3</sub>(OEt<sub>2</sub>) **1<sup>t</sup>-OEt<sub>2</sub>**. Contamination with a small quantity of another complex with broad resonances is visible when samples are dissolved in benzene, perhaps due to some Et<sub>2</sub>O decoordination.

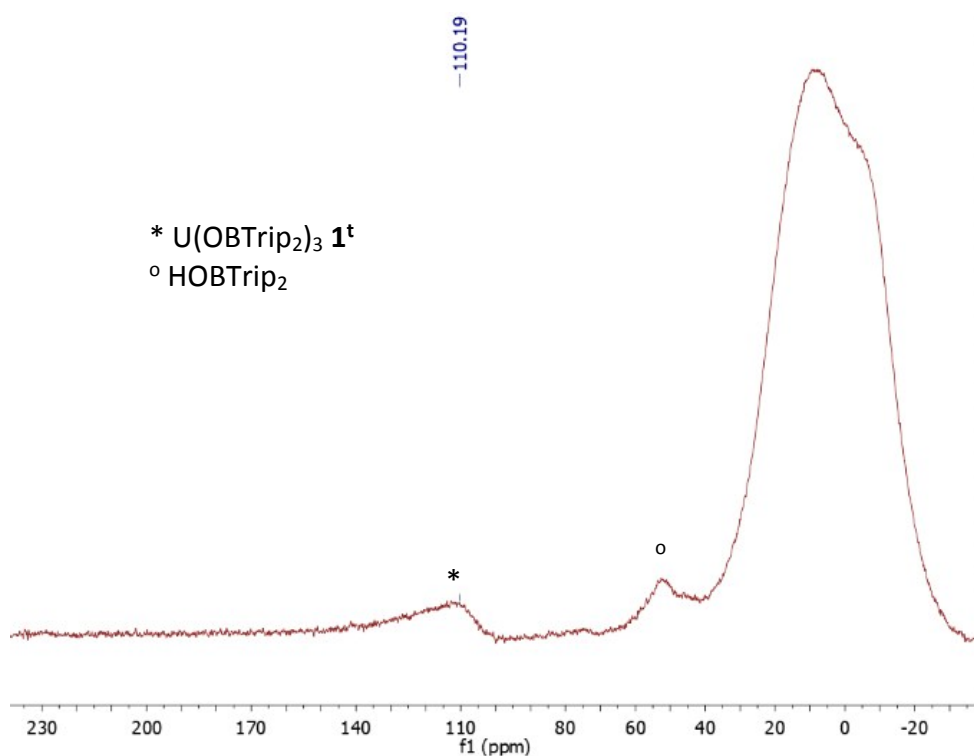


Figure S 5. <sup>11</sup>B NMR spectrum of complex **1<sup>t</sup>**.

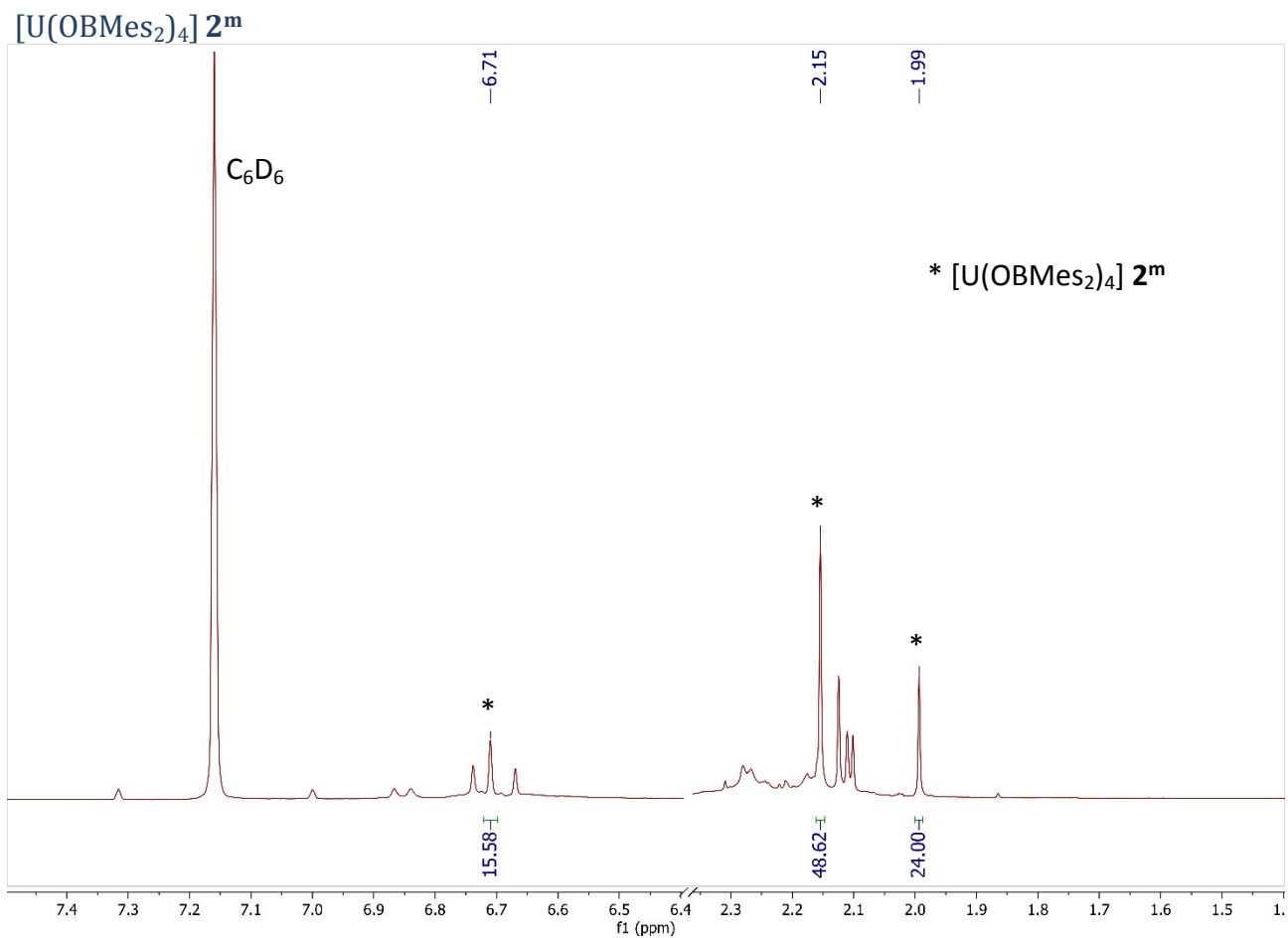


Figure S 6.  $^1H$  NMR spectrum of  $C_6D_6$  solution of  $U(OBMe_2)_4 2^m$ .

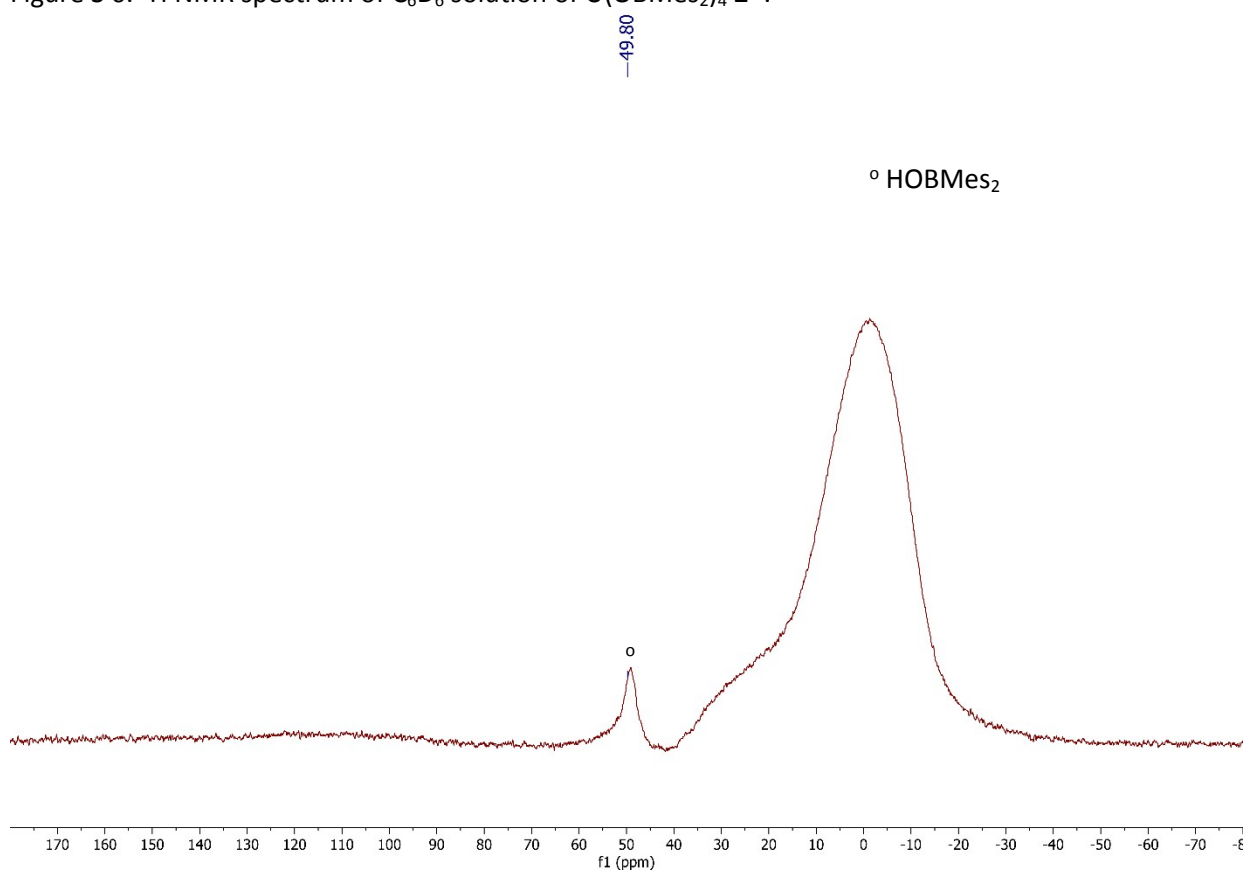


Figure S 7.  $^{11}B$  NMR spectrum of complex  $2^m$ .

[U(OBTrip<sub>2</sub>)<sub>4</sub>] 2<sup>t</sup>

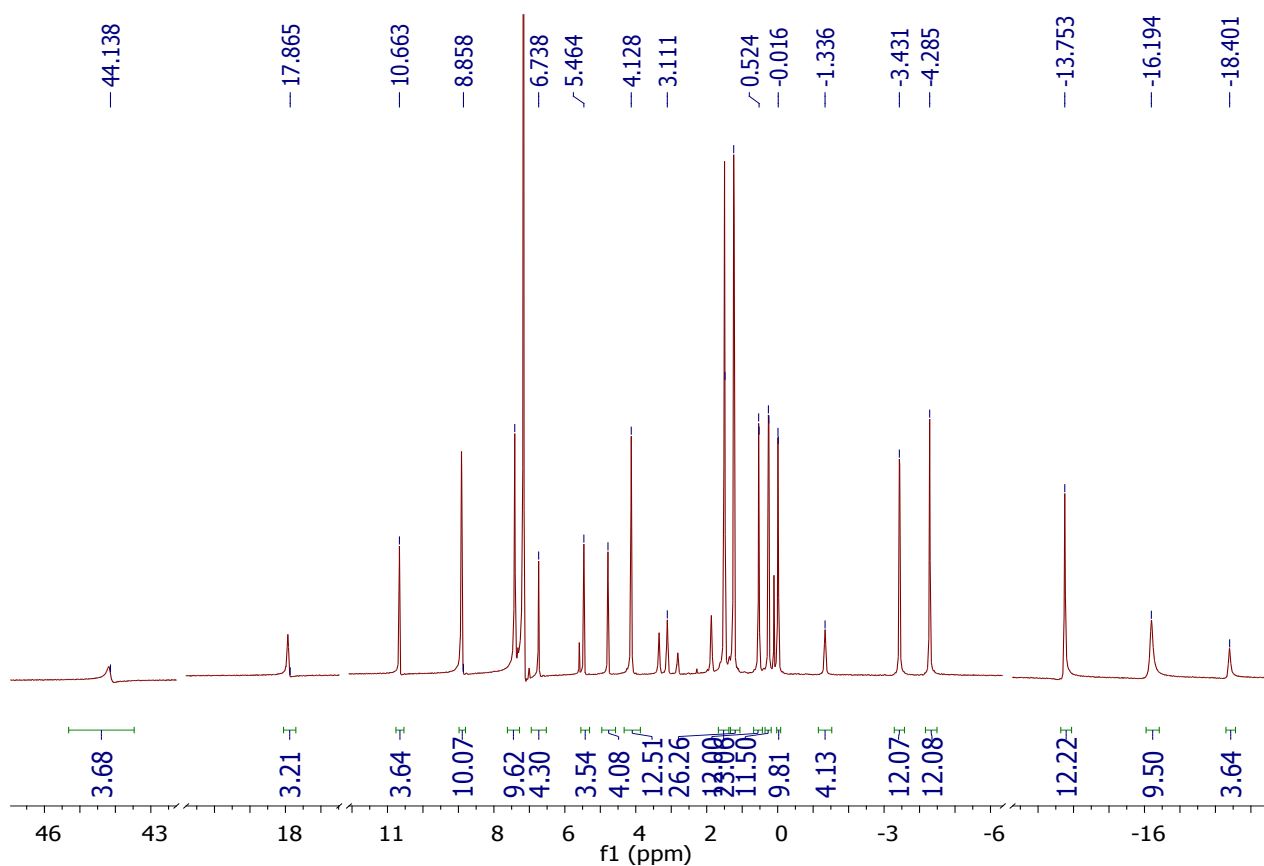


Figure S 8. <sup>1</sup>H NMR spectrum of complex 2<sup>t</sup>.

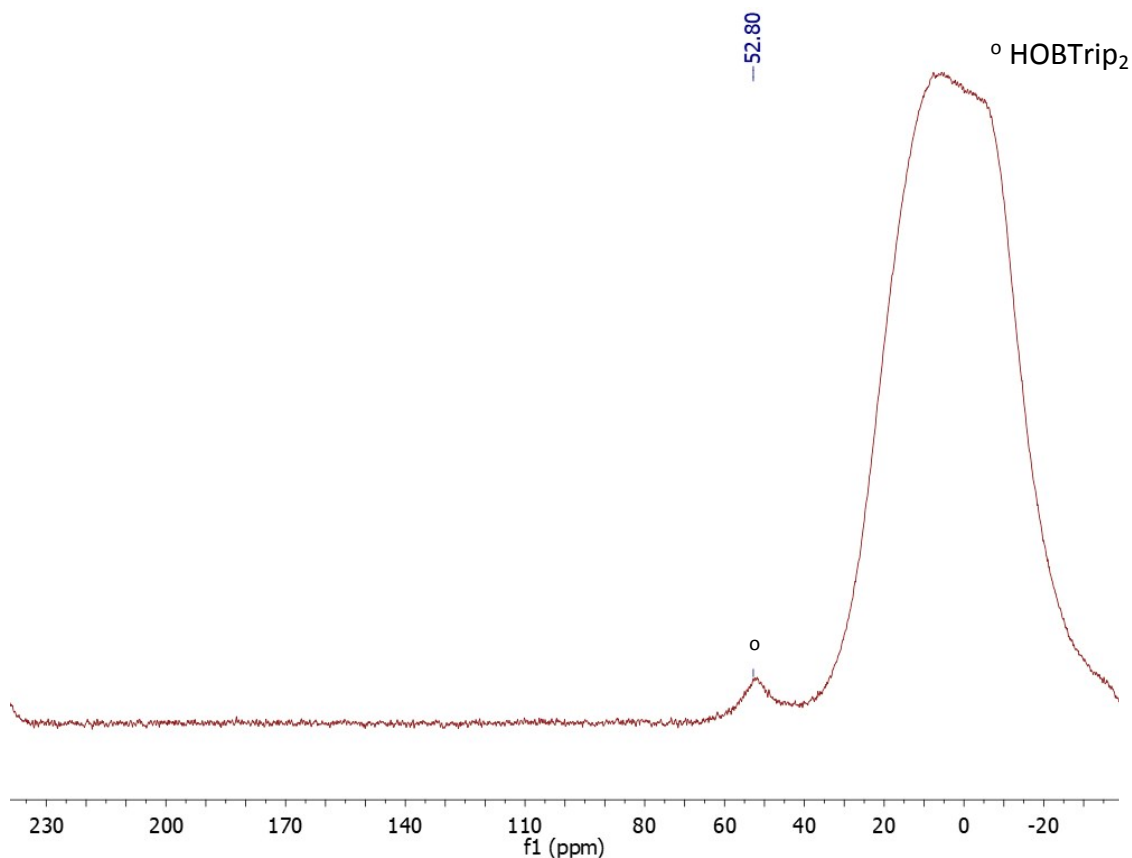


Figure S 9. <sup>11</sup>B NMR spectrum of complex 2<sup>t</sup>. No obvious signal in the range of 230--40 ppm except for that of HOBTrip<sub>2</sub>.



$[\text{OU}(\text{OBMe}_2)_3]_n \mathbf{3}^m$

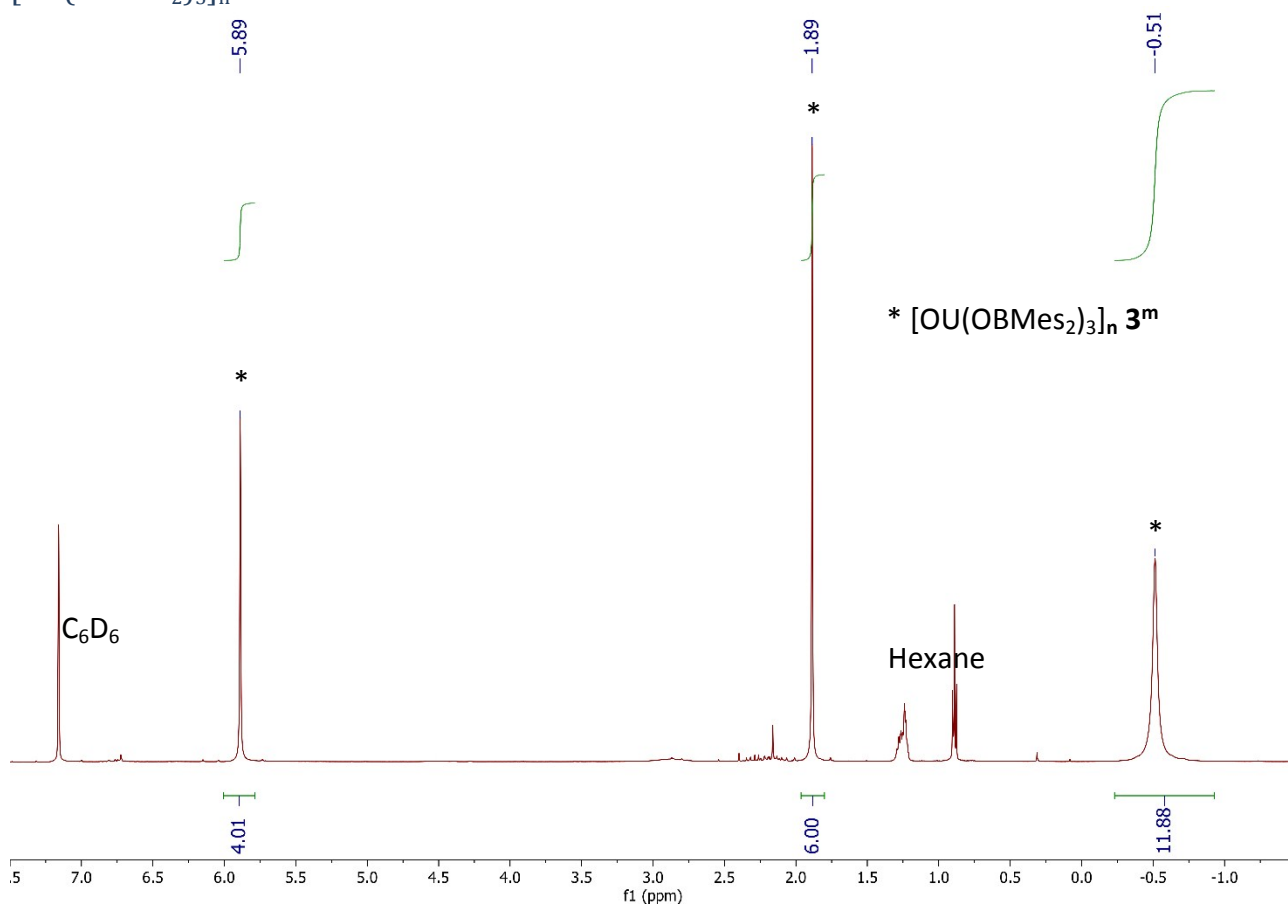


Figure S 10.  $^1\text{H}$  NMR spectrum of  $\text{C}_6\text{D}_6$  solution of  $[\text{OU}(\text{OBMe}_2)_3]_n \mathbf{3}^m$ .

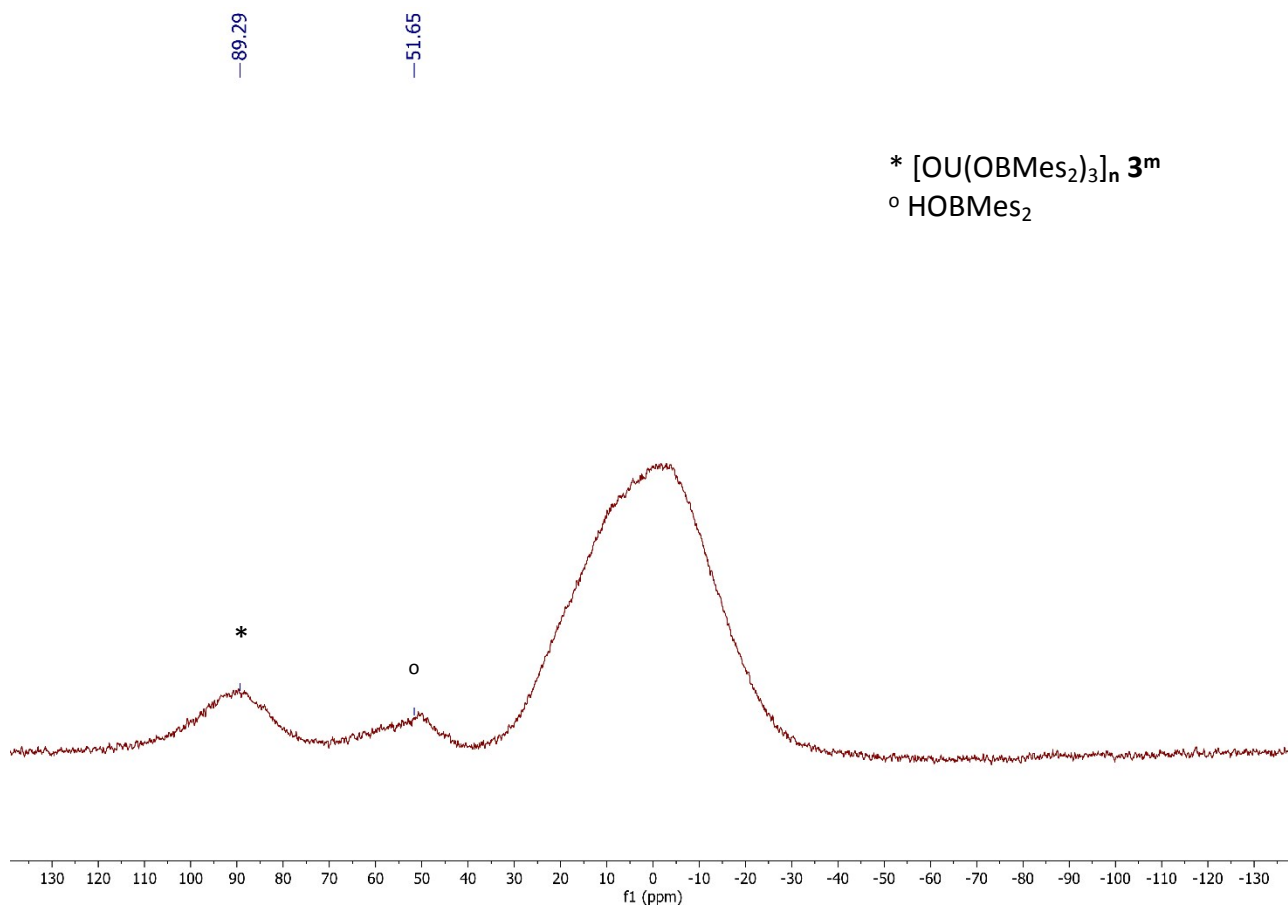


Figure S 11.  $^{11}\text{B}$  NMR spectrum of  $\text{C}_6\text{D}_6$  solution of complex  $\mathbf{3}^m$ .

[U(OBMe<sub>2</sub>)<sub>4</sub>(py-O)<sub>2</sub>] 4<sup>m</sup>

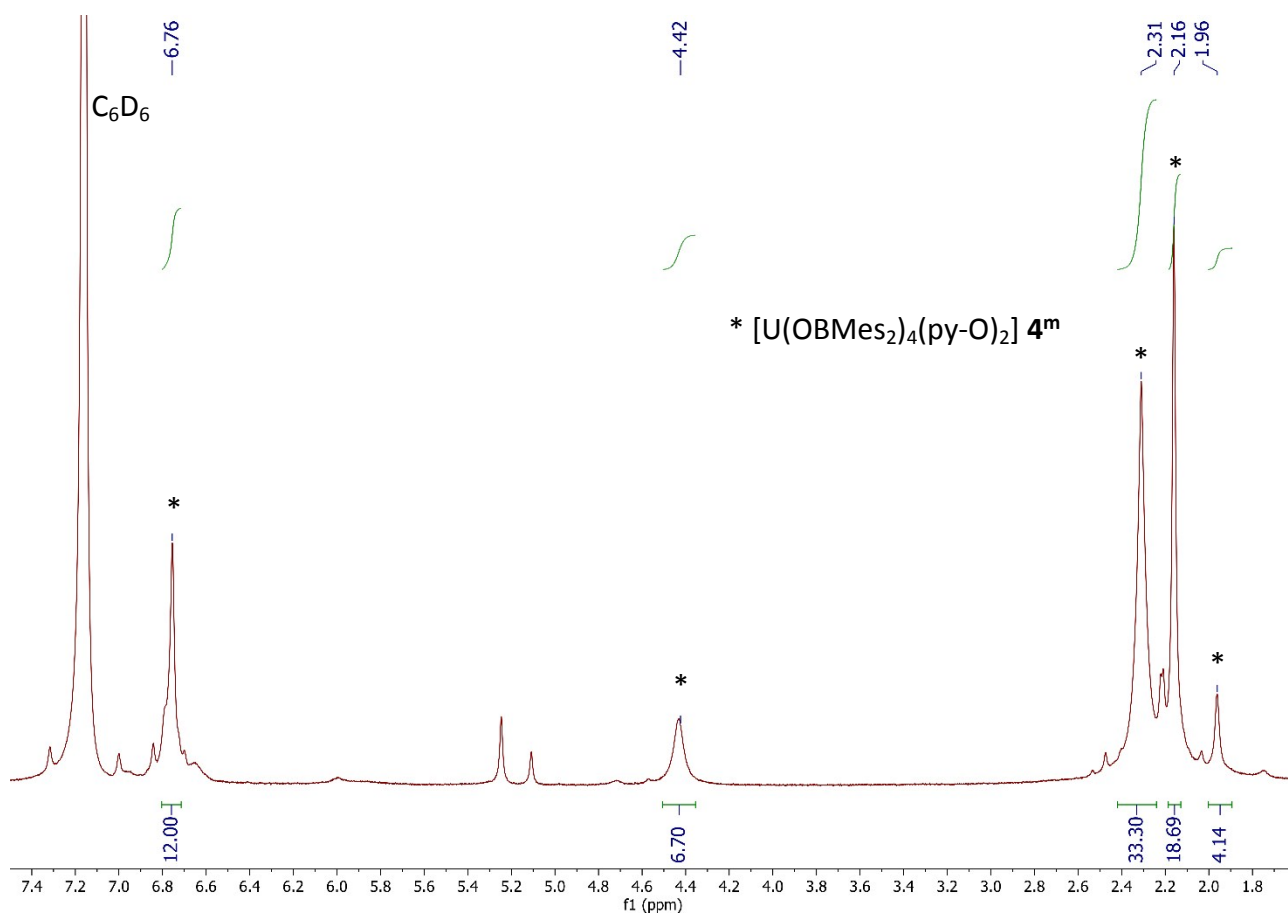


Figure S 12. <sup>1</sup>H NMR spectrum of C<sub>6</sub>D<sub>6</sub> solution of [U(OBMe<sub>2</sub>)<sub>4</sub>(py-O)<sub>2</sub>] 4<sup>m</sup>.

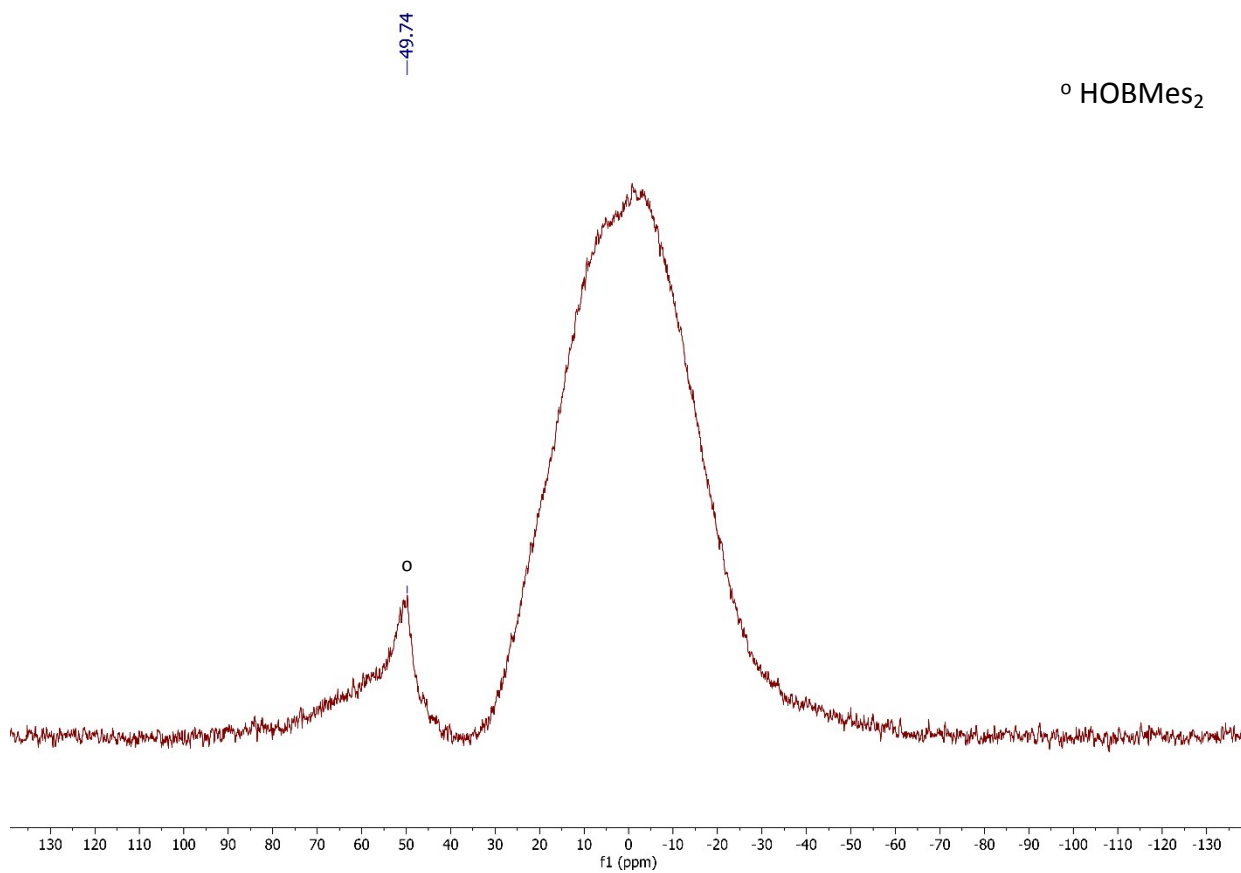


Figure S 13. <sup>11</sup>B NMR spectrum of C<sub>6</sub>D<sub>6</sub> solution of complex 4<sup>m</sup>.

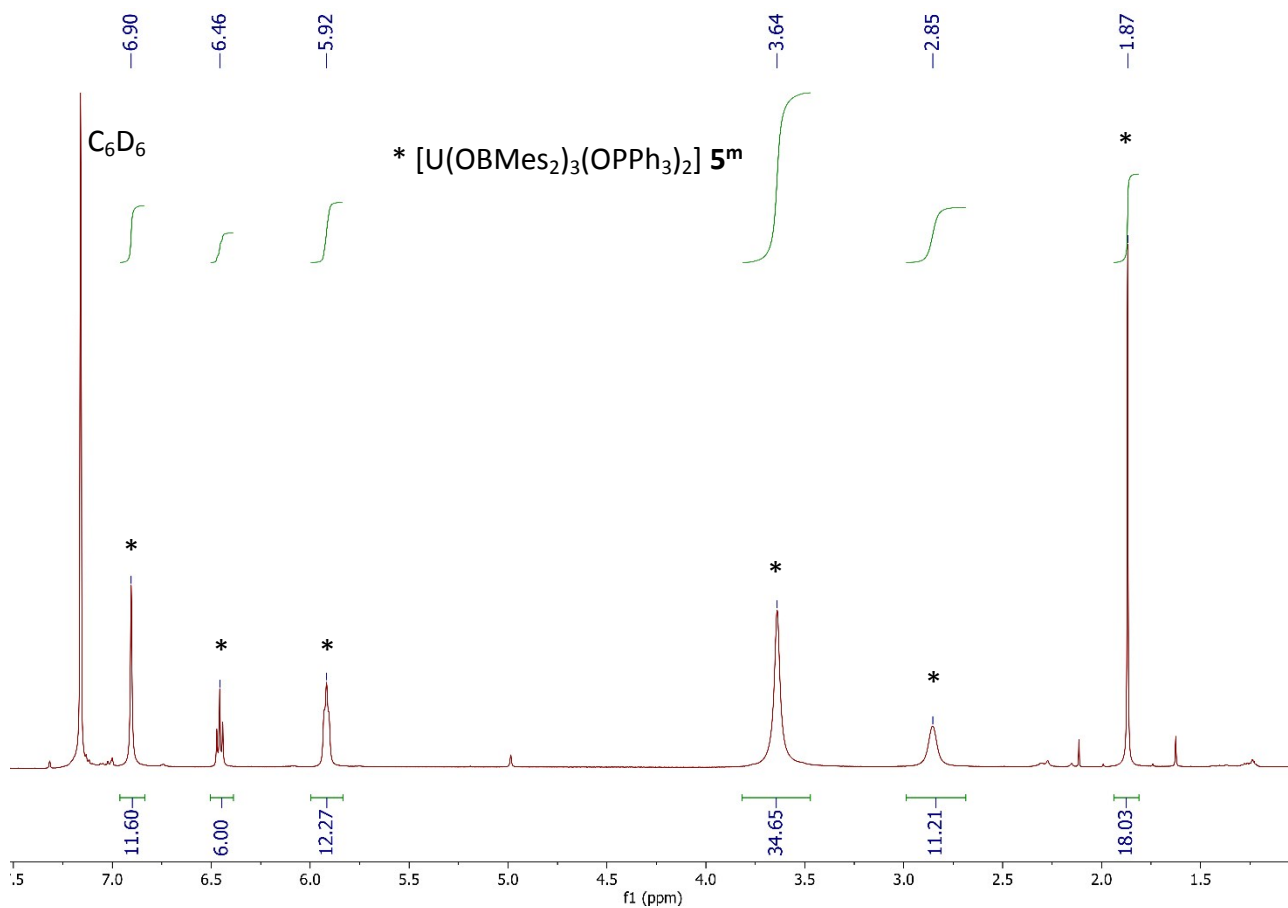


Figure S 14.  $^1H$  NMR spectrum of  $C_6D_6$  solution of  $[U(OBMe_2)_3(OPPh_3)_2] 5^m$ .

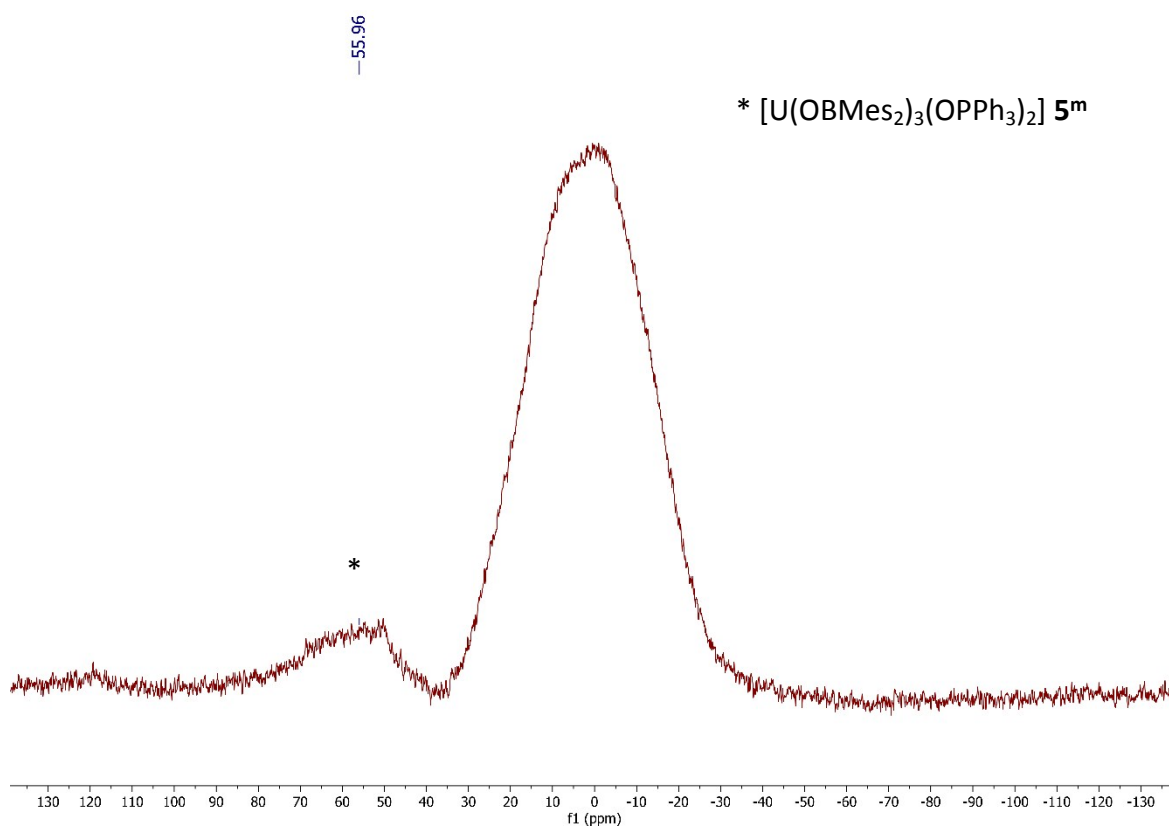


Figure S 15.  $^{11}B$  NMR spectrum of  $C_6D_6$  solution of complex  $5^m$ .

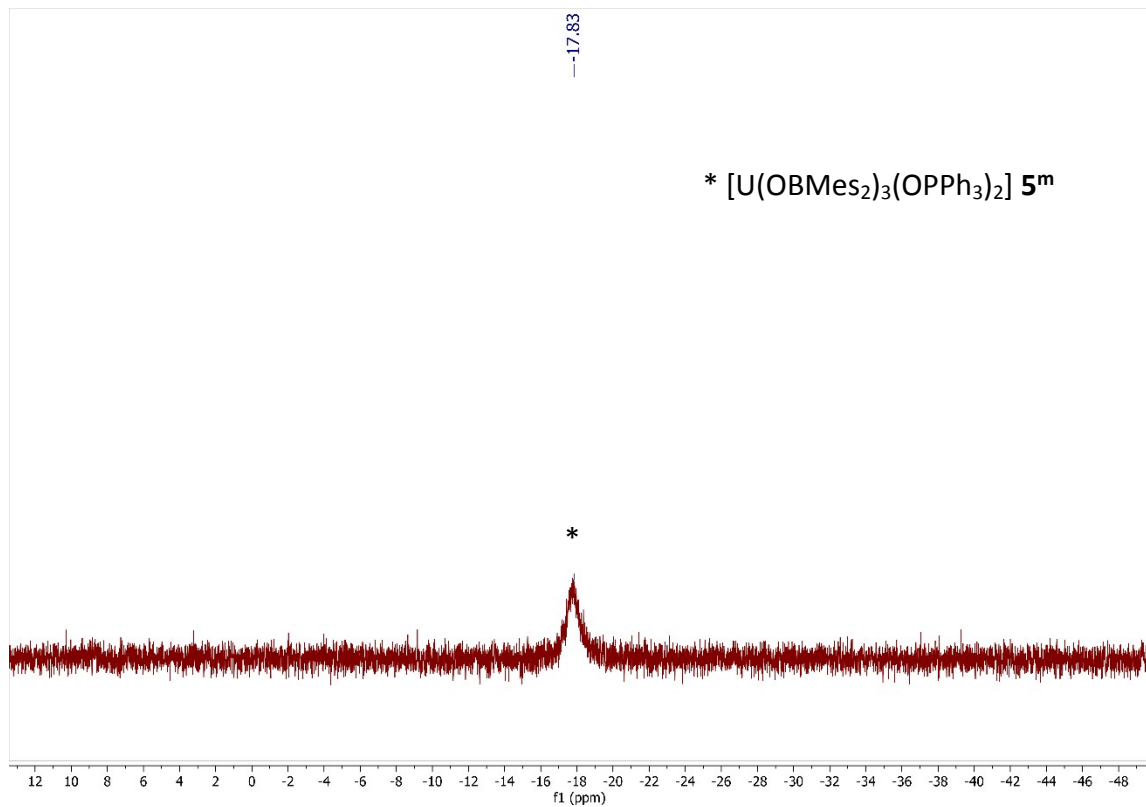


Figure S 16.  $^{31}\text{P}$  NMR spectrum of  $\text{C}_6\text{D}_6$  solution of complex  $\mathbf{5}^m$ .

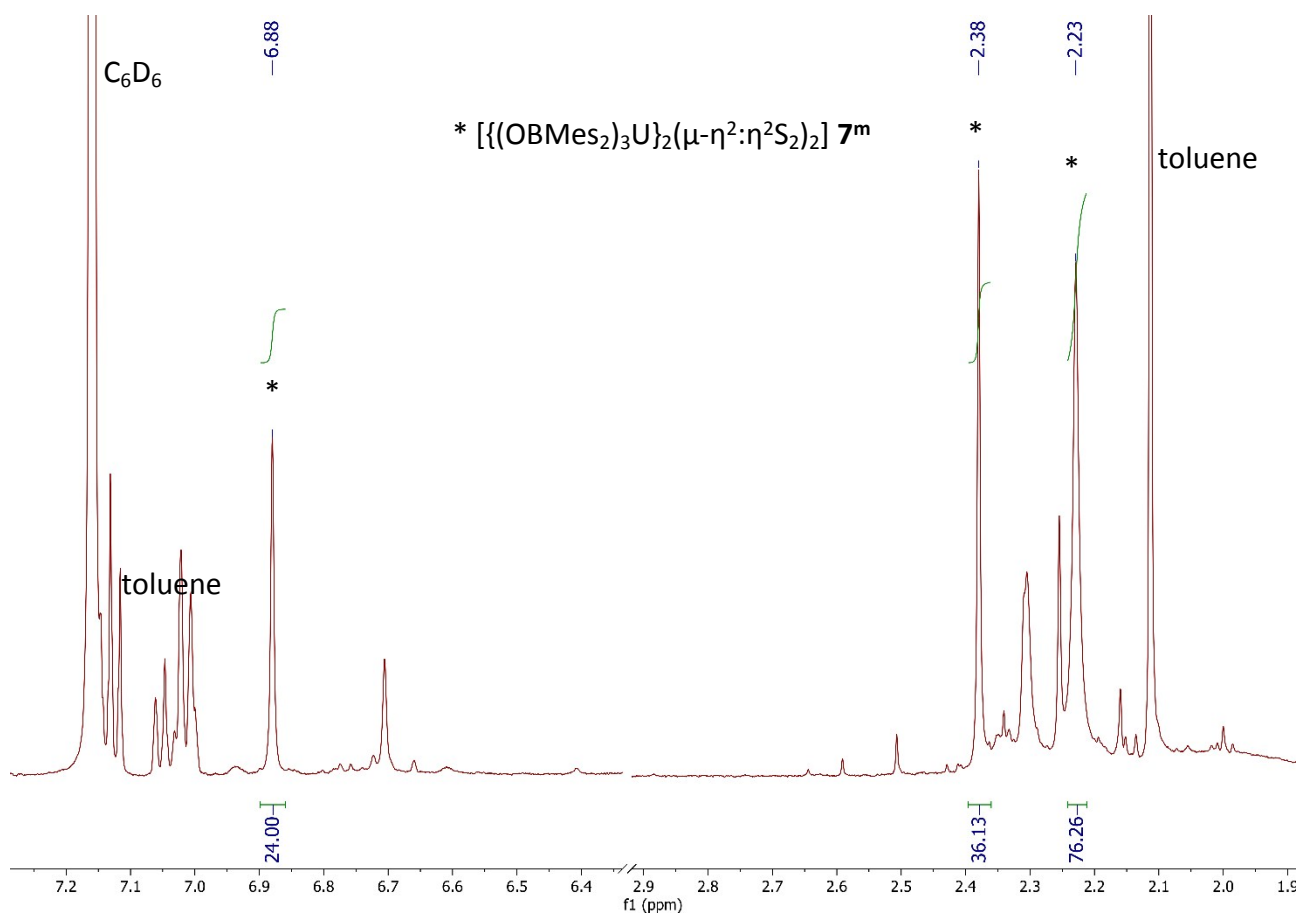


Figure S 17.  $^1H$  NMR spectrum of  $C_6D_6$  solution of  $[\{(OBMe_2)_3U\}_2(\mu-\eta^2:\eta^2-S_2)_2] \mathbf{7}^m$ .

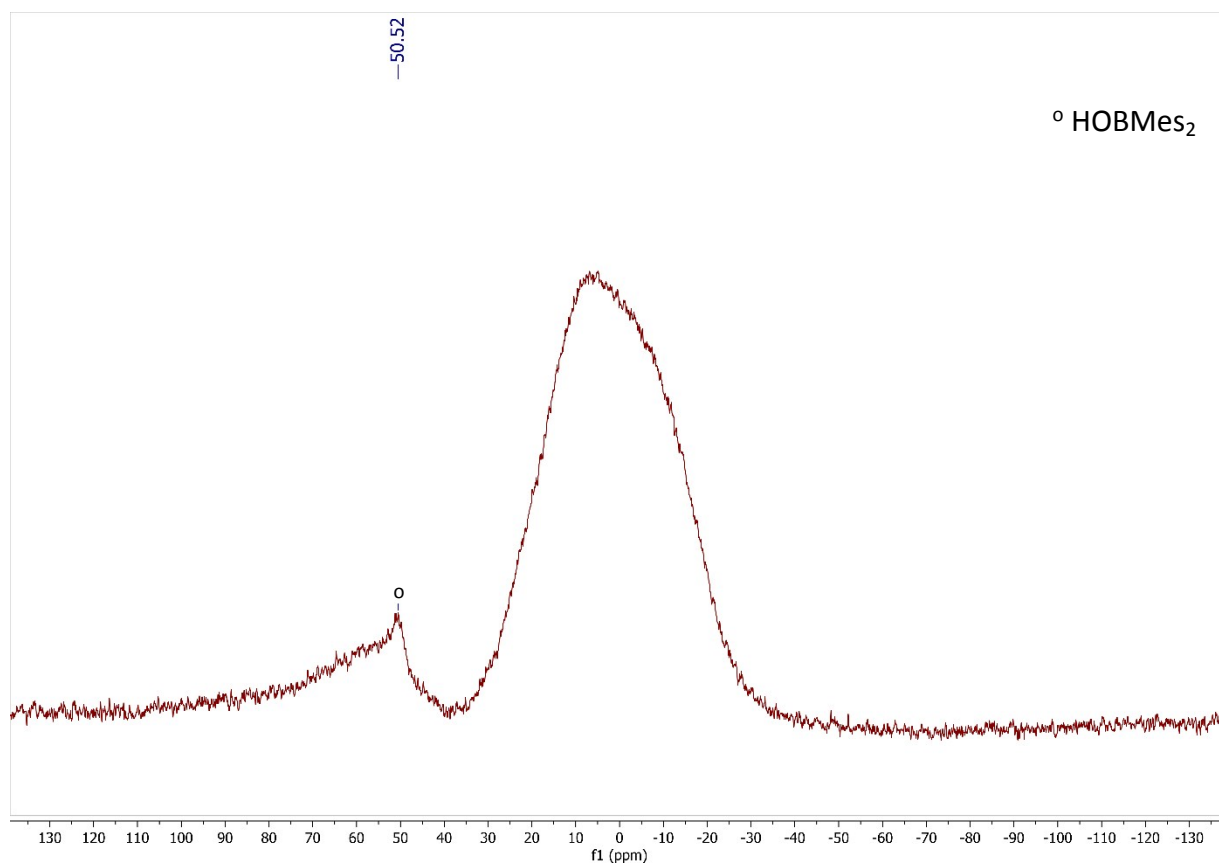


Figure S 18.  $^{11}B$  NMR spectrum of  $C_6D_6$  solution of complex  $\mathbf{7}^m$ .

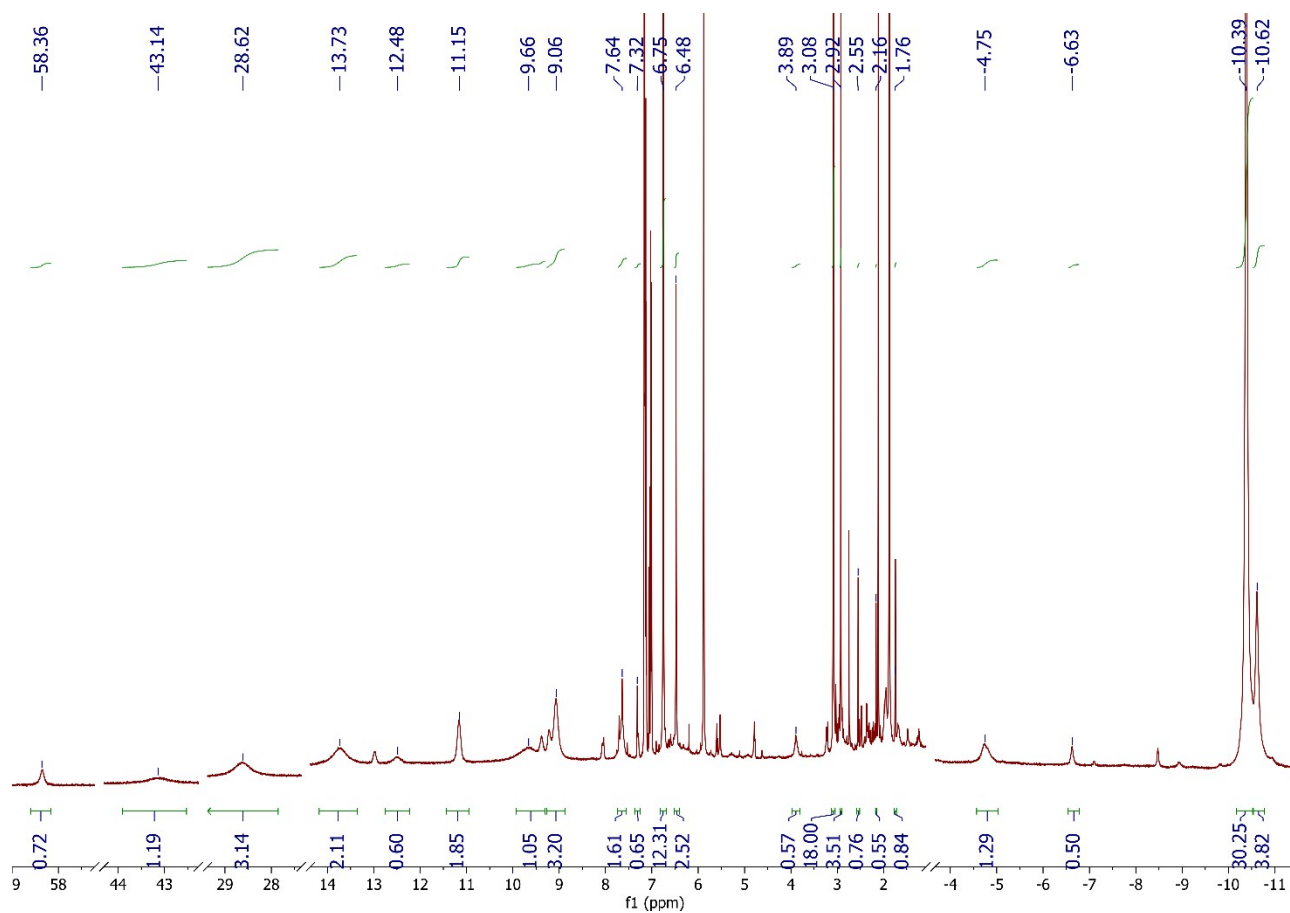


Figure S 19.  $^1H$  NMR spectrum of  $C_6D_6$  solution of  $[U\{\eta^2-N(Cy)C(=NCy)N(Cy)\}(OBMe_2)_3] 8^m$ .

[U(OBMe<sub>2</sub>)N<sub>3</sub>] **11<sup>m</sup>**

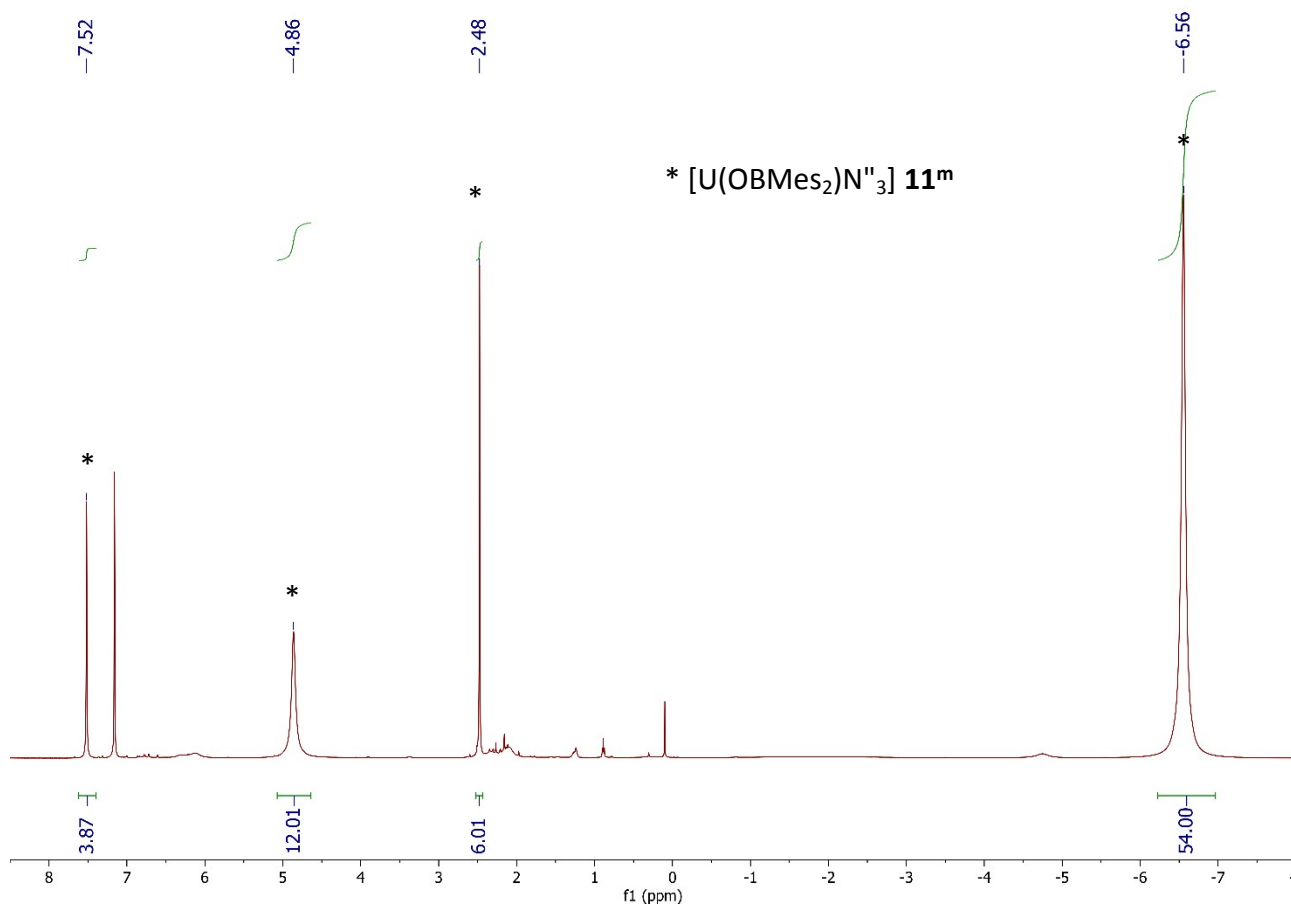


Figure S 20. <sup>1</sup>H NMR spectrum of C<sub>6</sub>D<sub>6</sub> solution of [U(OBMe<sub>2</sub>)N<sub>3</sub>] **11<sup>m</sup>**.

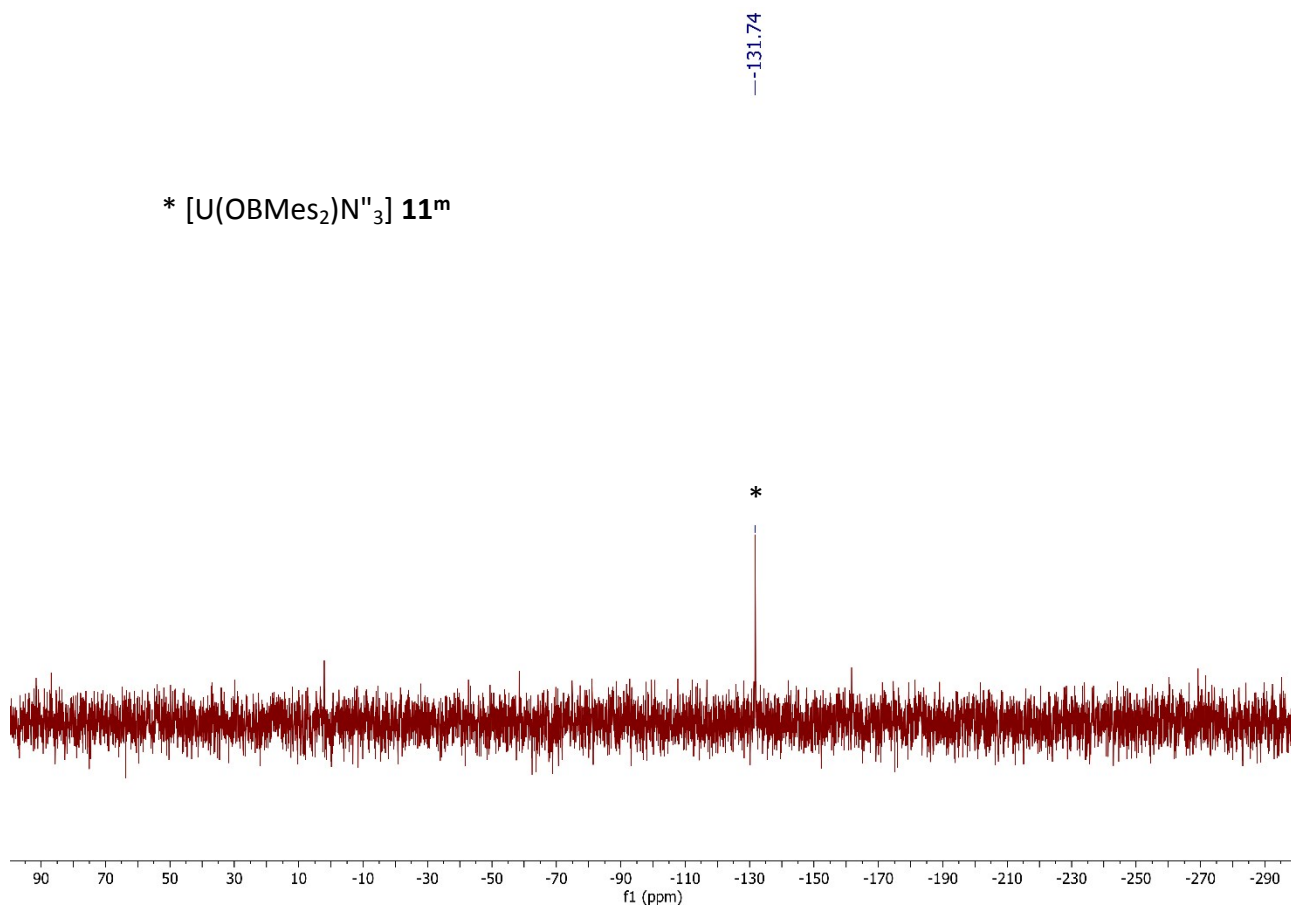


Figure S 21. <sup>29</sup>Si NMR spectrum of C<sub>6</sub>D<sub>6</sub> solution of complex **11<sup>m</sup>**.

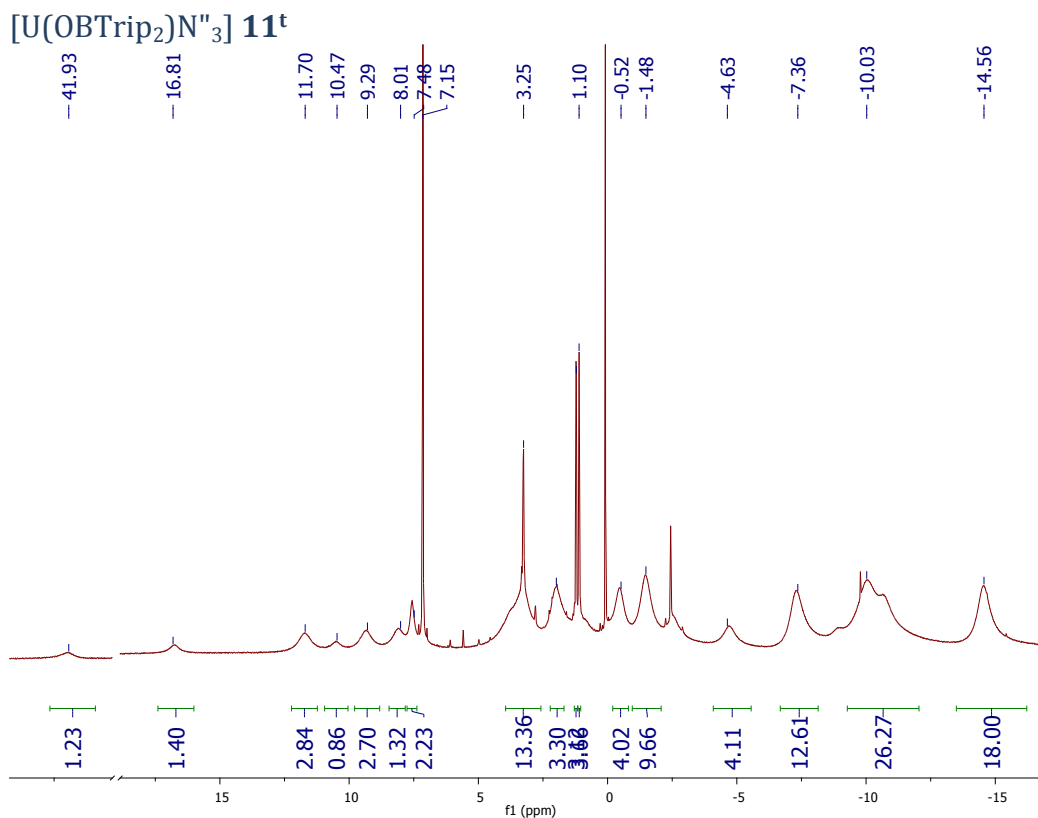


Figure S 22. <sup>1</sup>H NMR spectrum of C<sub>6</sub>D<sub>6</sub> solution of [U(OBTrip<sub>2</sub>)N<sup>3</sup>]<sub>3</sub> 11<sup>t</sup>.

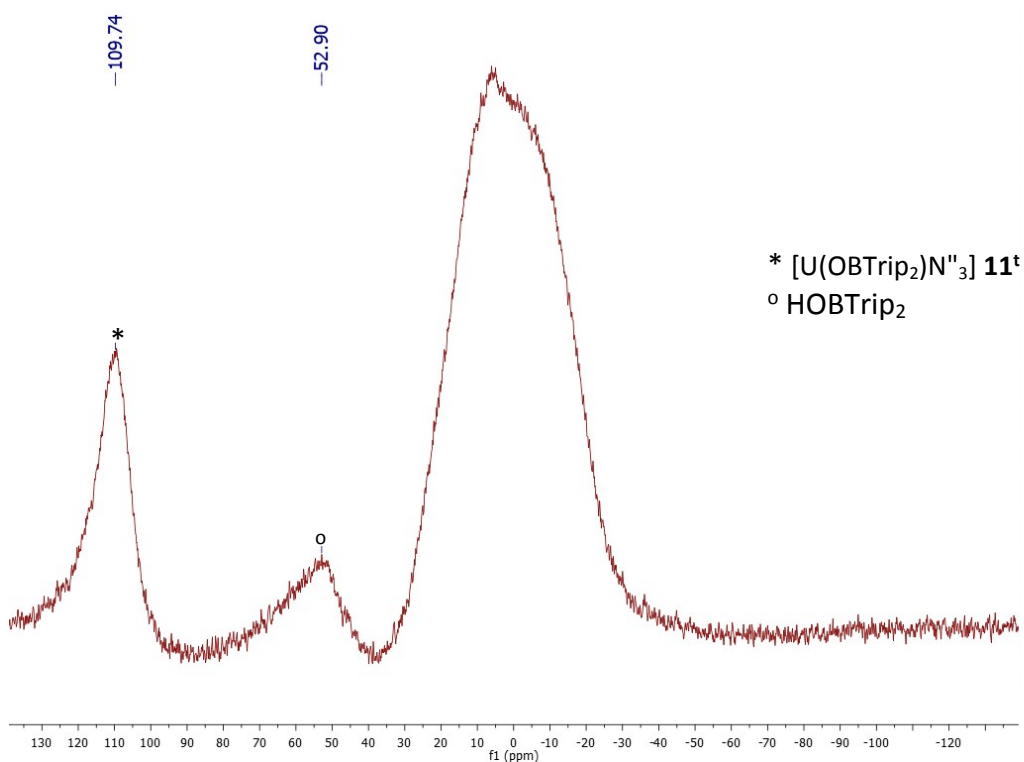


Figure S 23. <sup>11</sup>B NMR spectrum of C<sub>6</sub>D<sub>6</sub> solution of [U(OBTrip<sub>2</sub>)N<sup>3</sup>]<sub>3</sub> 11<sup>t</sup>.



## X-ray data

X-ray crystallographic data on compound **1<sup>m</sup>** was collected on a Rigaku Oxford diffraction SuperNova diffractometer fitted with an Atlas CCD detector with Mo K $\alpha$  radiation ( $\lambda = 0.7107 \text{ \AA}$ ) or Cu K $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ). X-ray crystallographic data on compounds **1<sup>t</sup>.OEt<sub>2</sub>**, **2<sup>m</sup>**, **2<sup>t</sup>**, **4<sup>m</sup>**, **5<sup>m</sup>** and **6<sup>m</sup>**, **7<sup>m</sup>**, **9<sup>t</sup>**, **10<sup>m</sup>** and **11<sup>m</sup>** were collected using an Oxford Diffraction Excalibur Eos diffractometer with Mo K $\alpha$  radiation at 120(2), 170(2) or 293(2) using a Mo K $\alpha$  source radiation source ( $\lambda = 0.71073 \text{ \AA}$ ). All structures were solved using SHELXT in Olex2.<sup>6-7</sup> Absorption corrections were completed using *CrysAlis PRO* 1.171.38.46 (Rigaku Oxford Diffraction, 2015) software. Analytical numeric absorption corrections used a multifaceted crystal model based on expressions derived by Clark and Reid.<sup>8</sup> Numerical absorption correction was based on a Gaussian integration over a multifaceted crystal model. Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm. The Olex2 solvent mask function was used for **2<sup>t</sup>** to remove a disordered toluene molecule (92.7 e<sup>-</sup>).

## Crystallographic tables

Table S 1

Complex	<b>1<sup>m</sup></b>	<b>2<sup>m</sup></b>	<b>4<sup>m</sup></b>
<b>Local code</b>	Po17030_refinalized	p18061	p17082_imo081
<b>Chemical formula</b>	0.67(C <sub>108</sub> H <sub>132</sub> B <sub>6</sub> O <sub>6</sub> U <sub>2</sub> )·1.33(C <sub>6</sub> H <sub>14</sub> )	C <sub>74</sub> H <sub>92</sub> B <sub>4</sub> O <sub>5</sub> U	0.5(B <sub>4</sub> C <sub>72</sub> O <sub>8</sub> U)·2(C <sub>5</sub> N)
<b>M<sub>r</sub></b>	1492.93	1342.74	999.37
<b>Crystal system, space group</b>	Monoclinic, <i>P2/c</i>	Triclinic, <i>P-1</i>	Monoclinic, <i>I2/m</i>
<b>Temperature (K)</b>	120	170	120
<b>a, b, c (Å)</b>	13.8450 (2)	14.1285 (10)	17.2362 (5)
	14.9545 (2)	15.8427 (12)	13.7651 (8)
	31.6940 (4)	16.6496 (12)	16.4420 (5)
<b><math>\alpha, \beta, \gamma</math> (°)</b>	96.521 (1)	103.798 (6)	90.156 (2)
		105.012 (6)	
		98.607 (6)	
<b>V (Å<sup>3</sup>)</b>	6519.63 (15)	3405.7 (5)	3901.0 (3)
<b>Z</b>	3	2	4
<b>Radiation type</b>	Mo K $\alpha$	Mo K $\alpha$	Mo K $\alpha$
<b><math>\mu</math> (mm<sup>-1</sup>)</b>	2.53	2.43	4.21
<b>Crystal size (mm)</b>	0.34 × 0.22 × 0.17	0.21 × 0.10 × 0.01	0.23 × 0.11 × 0.04
<b>Diffractometer</b>	SuperNova, Dual, Cu at zero, Atlas	Xcalibur, Eos	Xcalibur, Eos
<b>Absorption correction</b>	Gaussian	Analytical	Analytical
<b>T<sub>min</sub>, T<sub>max</sub></b>	0.519, 0.880	0.714, 0.972	0.978, 0.995
<b>No. of measured, independent and observed [<i>I</i> &gt; 2s(<i>I</i>)] reflections</b>	139328	78218	31319
	17270	15623	3992
	13836	11506	2962
<b>R<sub>int</sub></b>	0.072	0.152	0.128
<b>(sin <math>\theta/\lambda</math>)<sub>max</sub> (Å<sup>-1</sup>)</b>	0.698	0.649	0.617
<b>R[<i>F</i><sup>2</sup> &gt; 2s(<i>F</i><sup>2</sup>)], wR(<i>F</i><sup>2</sup>),</b>	0.041, 0.075, 1.04	0.069, 0.087, 0.99	0.335, 0.658, 4.80

<i>S</i>			
No. of reflections	17270	15623	3992
No. of parameters	624	781	74
No. of restraints	0	0	0
H-atom treatment	H-atom parameters not refined	H-atom parameters constrained	-
$\Delta\rho_{\max}, \Delta\rho_{\min}$ (e Å <sup>-3</sup> )	1.00, -1.42	2.04, -1.09	33.67, -13.92
Complex	<b>5<sup>m</sup> and 6<sup>m</sup></b>	<b>7<sup>m</sup></b>	<b>10<sup>m</sup></b>
Local code	p18047	p18033	p18089
Chemical formula	C <sub>90</sub> H <sub>96</sub> B <sub>3</sub> O <sub>5</sub> P <sub>2</sub> U·C <sub>72</sub> H <sub>88</sub> B <sub>5</sub> O <sub>6</sub> U·5(toluene)	C <sub>54</sub> H <sub>66</sub> B <sub>3</sub> O <sub>3</sub> S <sub>2</sub> U·C <sub>6</sub> H <sub>6</sub>	0.67(C <sub>108</sub> H <sub>132</sub> B <sub>6</sub> K <sub>2</sub> O <sub>8</sub> U <sub>2</sub> )
<i>M<sub>r</sub></i>	3233.95	1211.78	1451.50
Crystal system, space group	Triclinic, <i>P</i> -1	Triclinic, <i>P</i> -1	Monoclinic, <i>P</i> 2 <sub>1</sub> / <i>n</i>
Temperature (K)	170	170	170
<i>a, b, c</i> (Å)	17.2121 (4)	12.3086 (2)	15.3907 (2)
	23.0300 (4)	14.3349 (2)	22.7218 (2)
	23.4449 (6)	21.6092 (4)	16.9809 (3)
$\alpha, \beta, \gamma$ (°)	72.304 (2)	77.206 (1)	
	80.146 (2)	87.126 (1)	109.680 (2)
	70.091 (2)	84.907 (1)	
<i>V</i> (Å <sup>3</sup> )	8300.8 (4)	3701.62 (11)	5591.43 (13)
<i>Z</i>	2	2	3
Radiation type	Mo <i>K</i> α	Mo <i>K</i> α	Mo <i>K</i> α
$\mu$ (mm <sup>-1</sup> )	2.03	2.28	3.02
Crystal size (mm)	0.19 × 0.15 × 0.08	0.38 × 0.27 × 0.05	0.28 × 0.24 × 0.16
Diffractionmeter	Xcalibur, Eos	Xcalibur, Eos	Xcalibur, Eos
Absorption correction	Multi-scan	Analytical	Analytical
<i>T<sub>min</sub></i> , <i>T<sub>max</sub></i>	0.951, 1.000	0.267, 0.814	0.743, 0.840
No. of measured, independent and observed [ <i>I</i> > 2 <i>s</i> ( <i>I</i> )] reflections	190301	78705	109506
	33882	15098	10220
	21873	12610	8129
<i>R<sub>int</sub></i>	0.141	0.077	0.061
( <i>sin</i> θ/ <i>λ</i> ) <sub>max</sub> (Å <sup>-1</sup> )	0.625	0.625	0.602
<i>R</i> [ <i>F</i> <sup>2</sup> > 2 <i>s</i> ( <i>F</i> <sup>2</sup> )], <i>wR</i> ( <i>F</i> <sup>2</sup> ), <i>S</i>	0.058, 0.123, 1.00	0.044, 0.111, 0.96	0.030, 0.069, 1.02
No. of reflections	33882	15098	10220
No. of parameters	1708	638	586
No. of restraints	0	0	0
H-atom treatment	H-atom parameters constrained	H-atoms treated by a mixture of independent and constrained refinement	H-atom parameters constrained

$\Delta\rho_{\max}, \Delta\rho_{\min}$  ( $\text{e } \text{\AA}^{-3}$ )      1.51, -1.04      2.25, -0.77      0.80, -0.68

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Complex	11 <sup>m</sup>	1 <sup>t</sup> .OEt <sub>2</sub>	2 <sup>t</sup>	9 <sup>t</sup>
<b>Local code</b>	p18053_tri	P16133_087mono	P16121_087mono	P17058_tri087
<b>Chemical formula</b>	2(C <sub>36</sub> H <sub>76</sub> BN <sub>3</sub> OSi <sub>6</sub> U)	C <sub>94</sub> H <sub>148</sub> B <sub>3</sub> O <sub>4</sub> U	C <sub>120</sub> H <sub>184</sub> B <sub>4</sub> O <sub>4</sub> U· 2(C <sub>7</sub> H <sub>8</sub> )	B <sub>6</sub> C <sub>181</sub> O <sub>9</sub> U <sub>2</sub>
<b>M<sub>r</sub></b>	1968.75	1612.56	2064.06	2858.73
<b>Crystal system, space group</b>	Triclinic <i>P</i> <sup>-</sup> 1	Monoclinic <i>P</i> 2 <sub>1</sub> /n	Monoclinic <i>P</i> 2 <sub>1</sub> /c	Triclinic <i>P</i> <sup>-</sup> 1
<b>Temperature (K)</b>	293	170	170	170
<b>a, b, c (Å)</b>	12.0703 (2) 13.1641 (2) 15.6746 (3)	16.5344 (7) 27.8539 (8) 20.2709 (7)	22.0131 (4) 19.4020 (3) 30.6714 (6)	15.9113(3) 16.1748 (7) 36.3982 (10)
<b>a, β, γ (°)</b>	102.222 (2) 98.270 (1) 90.122 (1)	90 97.880 (4) 90	108.923 (2)	89.191 (3) 89.908 (2) 66.724 (3)
<b>V (Å<sup>3</sup>)</b>	2407.48 (7)	9247.6 (6)	12391.7(4)	8604.2 (5)
<b>Z</b>	1	4	4	2
<b>Radiation type</b>	Mo Kα	Mo Kα	Mo Kα	Mo Kα
<b>μ (mm<sup>-1</sup>)</b>	3.55	1.8	1.36	1.93
<b>Crystal size (mm)</b>	0.79 × 0.33 × 0.08	0.18 × 0.05 × 0.04	0.19 × 0.13 × 0.1	0.34 × 0.13 × 0.21
<b>Diffractometer</b>	Xcalibur, Eos	Xcalibur, Eos	Xcalibur, Eos	Xcalibur, Eos
<b>Absorption correction</b>	Multi-scan	Analytical	Analytical	Multi-scan
<b>T<sub>min</sub>, T<sub>max</sub></b>	0.483, 1.000	0.976, 0.994	0.955, 0.972	0.584, 1.00
<b>No. of measured, independent and observed [I &gt; 2σ(I)] reflections</b>	51203 9835 8900	131250 14671 8850	218483 19685 12561	151109 27315 14908
<b>R<sub>int</sub></b>	0.049	0,267	0,106	0,126
<b>(sin θ/λ)<sub>max</sub> (Å<sup>-1</sup>)</b>	0.625	0,575	0,575	0,579
<b>R[F<sup>2</sup> &gt; 2σ(F<sup>2</sup>)], wR(F<sup>2</sup>), S</b>	0.024, 0.055, 1.07	0.080, 0192, 0.93	0.047, 0.116, 1.05	0.116, 0.319, 1.06
<b>No. of parameters</b>	457	961	1262	809
<b>No. of restraints</b>	0	-	93	3
<b>H-atom treatment</b>	riding	riding	riding	-
<b>Dñ<sub>max</sub>, Δ<sub>min</sub> (e Å<sup>-3</sup>)</b>	0.80, -0.60	0.78, -0.53	2.49, -1.12	6.52, -6.77

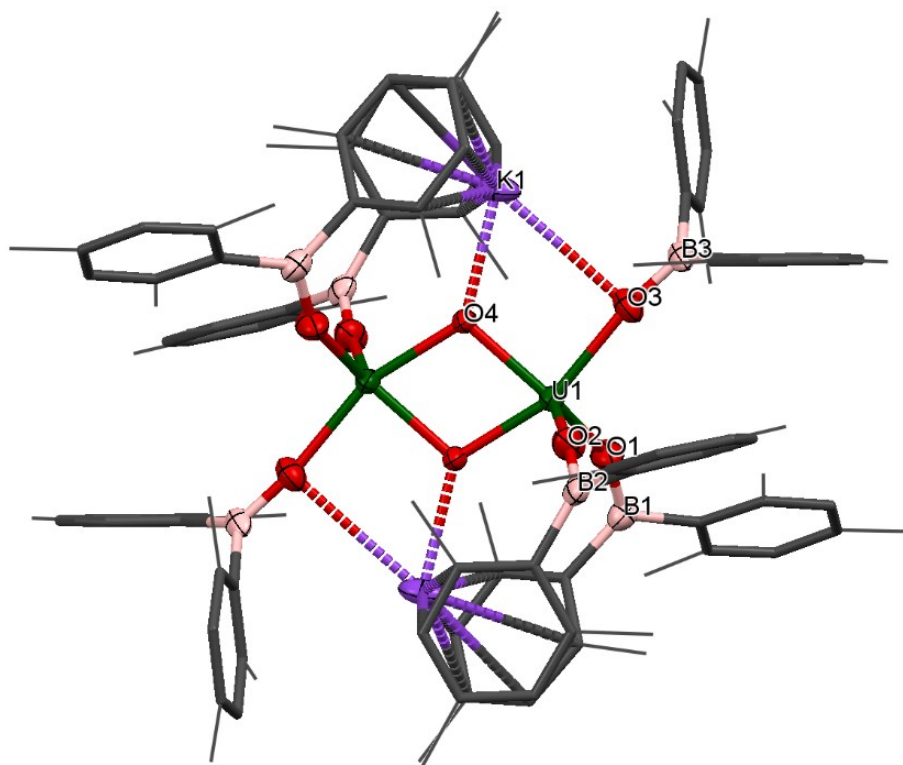


Figure S 24. Solid state structure of complex **10<sup>m</sup>**. Hydrogen atoms are omitted for clarity. The thermal ellipsoids are displayed at 50% probability.

Table S 2: Selected bond distances (Å) and angles (°) for crystallographically characterised uranium boroxide complexes.

	<b>1<sup>m</sup></b>	<b>1<sup>t</sup>-OEt<sub>2</sub></b>	<b>2<sup>m</sup></b>	<b>2<sup>t</sup></b>	<b>5<sup>m</sup></b>	<b>6<sup>m*</sup></b>	<b>7<sup>m</sup></b>
U-O <sub>(av)</sub>	2.196	2.183(7)	2.120	2.159(5)	2.124	2.172	2.078
B-O <sub>(av)</sub>	1.351	1.35(1)	1.356	1.364(7)	1.345	1.346	1.359
U-O-B	171.6	171.0(6)	167.1	171.0(5)	176.0	155.2-168.7	165

\* As noted in the text in the manuscript, there are different distances in the boroxine that make up these averages: O9-B9: 1.340(8); O10-B9: 1.376(9); O10-B10: 1.387(8); O11-B10 1.338(8)

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