SUPPORTING INFORMATION

Synthesis of Bulky Hydride Ligands: *m*-Terphenylborohydride Complexes with Uranium and Neodymium

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I. Experimental

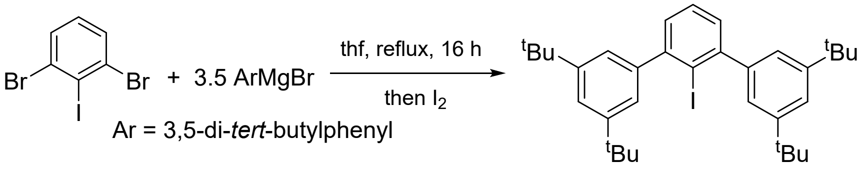
General Considerations.

Caution! Depleted uranium (primarily U-238, $t_{1/2}$ = 4.47 x 10^9 y) contains weak alpha emitters and α-, β-, and γ-emitting decay products that present radiological health risks. All manipulations should be conducted in gloveboxes or well-ventilated fume hoods with appropriate radiological monitoring controls. $LiAlH_4$, the borohydride ligand salt, and the metal complexes are water and acid sensitive and may enflame on exposure to air. All manipulations should be carried out in an inert atmosphere until the chemicals are ready to be quenched in a controlled manner for disposal.

All reactions were carried out under an atmosphere of N_2 or Ar using glovebox or standard Schlenk techniques. All glassware was heated to 150 °C for at least two hours and allowed to cool under vacuum before use. Solvents were dried and deoxygenated using a Pure Process Technologies Solvent Purification System and stored over 3 Å molecules sieves. Deuterated solvents were deoxygenated on the Schlenk line by three freeze-pump-thaw cycles and stored over 3 Å for at least 3 days before use. $LiAlH_4$ was purchased from Strem Chemicals and was purified by extraction with Et_2O. $UI_3(thf)_4$ was prepared from UCl_4 as described previously.[1] All other reagents were purchased from commercial sources and used as received.

^{1}H NMR data were collected on a Bruker NEO-500 spectrometer operating at 500 MHz (^{1}H) or on a Bruker NEO-300 spectrometer operating at 300 MHz (^{1}H). ^{11}B NMR data were collected on a Bruker NEO-300 spectrometer operating at 96 MHz. Chemical shifts are reported in δ units relative to residual NMR solvent peaks (^{1}H) or δ units relative to an external standard (^{11}B; $BF_3{\cdot}Et_2O$, 0.0 ppm). IR spectra were collected with a Thermo Scientific Nicolet iS5 as Nujol mulls between KBr salt plates. Electronic absorption spectra were collected with an Agilent Cary 6000i UV-Vis-NIR Spectrophotometer. Microanalytical data (CHN) were collected using an EAI CE-440 elemental analyzer at the University of Iowa's MATFab Facility.

Synthesis of I-Ar^{tBu4}.

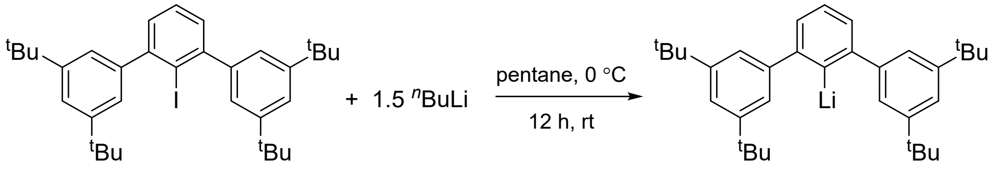


Magnesium turnings (5.0 g, 0.17 mol) were rinsed with 1M HCl until shiny, then rinsed with acetone, and transferred to a hot 250 mL Schlenk round bottom flask with a large stir bar. The flask was evacuated and heated for 5 minutes with a heat gun to ensure all HCl/acetone was evaporated. Once cooled, THF (100 mL) and one crystal of I_2 was added, and the flask was fitted with a condenser and heated to a reflux. In a separate Schlenk round bottom flask, $C_{14}H_{21}Br$ (30 g, 0.11 mol) was dissolved in THF (100 mL) and slowly cannula transferred to the flask containing Mg turnings through the top of the condenser. On initiation, the reaction was removed from heating and allowed to continue stirring. Once frothing had stopped, the flask was heated to a reflux with stirring for 2 h. After this time, stirring was stopped and the mixture was allowed to settle at 60-80 °C. Once sufficiently settled, this hot mixture was carefully cannula transferred to a 500 mL Schlenk flask containing 1,3-dibromo-2-iodo-benzene (11.5 g, 0.0318 mol) dissolved in THF (100 mL) cooled in an ice bath. After addition, the flask was fitted with a condenser and heated to a reflux overnight.

The next day, the flask was removed from heating, and I_2 (16 g, 0.063 mol) was added in portions with strong stirring. This mixture was refluxed for an additional 30 min, then allowed to cool to room temperature. To this, a saturated solution of aqueous sodium sulfite was added to quench remining I_2 until little to no red color remained. The mixture was filtered to remove magnesium salts, which were washed with diethyl ether (2 x 30 mL) and added to the filtrate. The organic layer was then separated, and the aqueous layer was extracted with diethyl ether (2 x 100 mL). All organic layers were then combined and dried over anhydrous $MgSO_4$. The organic layers were then filtered, and the solvent was removed under vacuum.

The resulting thick yellow/orange oil was vacuum distilled up to ~130 °C to remove $C_{14}H_{21}Br$, which left a dark orange solid in the boiling flask. To this methanol was added (50 – 100 mL) and the solid was broken up, then heated to a boil for 15-20 min. The precipitated solid was then filtered and washed with additional room temperature methanol (2 x 50 mL) and dried overnight under vacuum to yield I-Ar^{tBu4} as a fluffy white solid. If the isolated solid was still yellow, the washing procedure was repeated until the pure product was obtained. Yield 10.4 g (57%). ^1H NMR (C_6D_6) 300 MHz: 7.56 (2H, t), 7.43 (4H, d), 7.23 (2H, d), 7.05 (1H, t), 1.31 (36H, s). ^{13}C NMR (C_6D_6, 75 MHz): 150.2 (s), 149.5 (s), 145.3 (s), 128.6 (s), 124.2 (s), 120.9 (s), 104.9 (s), 34.7 (s), 31.3 (s).

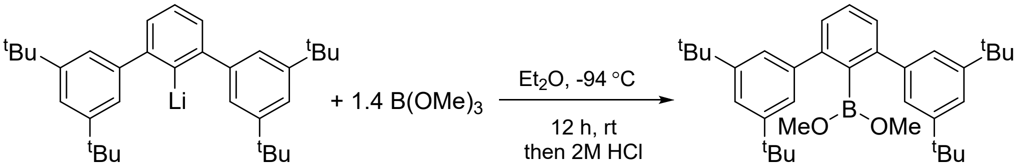
Synthesis of Li-$Ar^{tBu4}(Et_2O)_{1.5}$.



To a 250 mL Schlenk flask containing I-Ar^{tBu4} (2.6 g, 4.5 mmol) dissolved in pentane (60 mL) cooled in an ice bath, was syringed ^nBuLi (2.7 mL, 6.7 mmol, 2.5 M). This mixture was allowed to slowly warm to room temperature overnight at which point the solution had become cloudy with suspended solids. The flask was transferred to a glovebox, and the solid was isolated by centrifugation. The yellow supernatant after centrifuging was discarded, and the white solid was washed with additional pentane (3 x 20 mL) until the washings were no longer yellow. The resulting white solid was dried under vacuum for 2h to afford $LiAr^{tBu4}$ as a white powder. This was crystallized from a concentrated Et_2O solution cooled to -30° C to yield large transparent crystals. ^1H NMR data collected on the isolated solid revealed that the complex co-crystalizes with 1.5 equivalents of Et_2O. Yield 1.75 g (92%). ^1H NMR (C_6D_6, 300 MHz): 7.80 ppm (4H, d), 7.64 (2H, d), 7.47 (1H, t), 7.25 (2H, t), 3.28 (6H, q, Et_2O), 1.22 (36H, s), 1.11 (9H, t, Et_2O). ^{13}C NMR

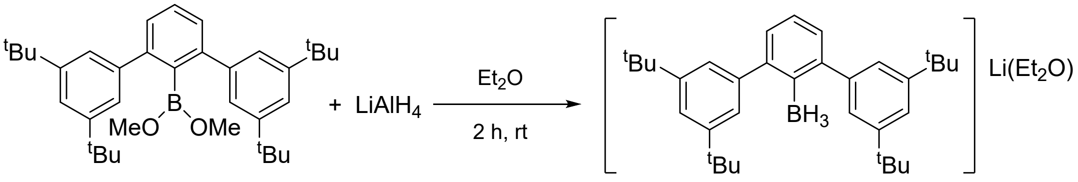
(C_6D_6, 75 MHz): 153.1 (s), 152.0 (s), 146.5 (s), 126.5 (s), 125.2 (s), 120.7 (s), 65.5 (s), 34.8 (s), 31.2 (s), 15.2 (s).

Synthesis of $(MeO)_2BAr^{tBu4}$.



To a 500 mL Schlenk flask containing $LiAr^{tBu4}(Et_2O)_{1.5}$ (11.0 g, 19.1 mmol) dissolved in Et_2O (100 mL) cooled in an acetone/liquid nitrogen bath, was syringed $B(OMe)_3$ (2.8 g, 3 mL, 26.9 mmol). This mixture was allowed to slowly warm to room temperature overnight at which point the solution had become slightly cloudy. 2 M HCl (~25 mL) was added to the flask and the biphasic mixture was stirred at room temperature for 2 hours, which resulted in a yellow organic layer and a colorless aqueous layer. The solution was transferred to a separatory funnel and the organic layer was isolated. The aqueous layer was extracted with diethyl ether (6 x 50 mL) or until almost no yellow color was extracted. The combined organic extracts were washed with H_2O (2 x 150 mL), brine (150 mL), and dried over anhydrous $MgSO_4$. The filtered organic solution was brought to near dryness on a rotary evaporator which left a dark orange/red oil. This was heated just under 50 °C and a strong vacuum was pulled which solidified the oil as a pinkish solid. Yield 7.80 g (92%). ^1H NMR (C_6D_6, 300 MHz): 7.56 (m, 6H), 7.52 (d, 2H), 7.36 (t, 1H), 3.22 (s, 5H), 1.37 (s, 36H). ^{11}B NMR (C_6D_6, 96 MHz): 33.2 (s).

Synthesis of $Li(H_3BAr^{tBu4})(Et_2O)$.



To a 50 mL Schlenk flask containing $(MeO)_2BAr^{tBu4}$ (7.16 g, 13.6 mmol) dissolved in Et_2O (~15 mL) was dropwise added a solution of 1.1 equiv. $LiAlH_4$ (0.56 g, 14.9 mmol) dissolved in Et_2O (~5 mL). Additions were conducted slowly to ensure no uncontrollable exotherm was observed. After complete addition, the mixture was allowed to stir at room temperature for 2 h (this may be left to stir overnight without reduction in yield). Filtration of the diethyl ether from a porous white precipitate, followed by evaporation under vacuum, washings with pentane (2 x 10 mL), and drying for 1h under vacuum yielded a free flowing white solid. ^1H NMR data indicates that the complex co-crystallizes with an equivalent of Et_2O to give the formula $Li(H_3BAr^{tBu4})(Et_2O)$. Yield: 5.58 g (75%). ^1H NMR ($CDCl_3$, 300 MHz): 7.24 (t, 2H), 7.14-7.10 (m, 7H), 3.48 (q, 4H, Et_2O), 1.26 (s, 36H), 1.20 (t, 6H, Et_2O). ^{13}C

NMR (C_6D_6, 125 MHz): 150.0 (s), 148.4 (s), 146.6 (s), 126.9 (s), 123.8 (s), 123.4 (s), 119.8 (s), 65.8 (s), 34.9 (s), 31.5 (s), 15.0 (s). ^{11}B NMR ($CDCl_3$, 96 MHz): -29.1 (q, $^1J_{BH}$ = 75 Hz).

Synthesis of U(H_3BAr^{tBu4})$_3$(thf)$_2$ (1-U).

$UI_3(thf)_4$ (0.306 g, 0.33 mmol) and Li(H_3BAr^{tBu4})(Et_2O) (0.55 g, 1.00 mmol) were added to a Schlenk tube and 50 mL chlorobenzene was added and the mixture was stirred at room temperature for 16 h. The resulting brown/grey solution was brought to dryness under vacuum to leave a brown residue. This residue was extracted with toluene (~100 mL) filtered then brought to complete dryness over 24 h to leave an orange residue. The orange residue was stirred in 20 mL of pentane, allowed to settle, and the slightly orange pentane washing was discarded. The resulting orange powder was dried under vacuum for 1 h to leave a free-flowing microcrystalline orange powder (0.268 g; crude yield: 44%.). The orange powder was dissolved in benzene (20 mL) and allowed to slowly evaporate in a vapor chamber surrounded by toluene. Every 2-3 days crops of red/orange crystals were collected and combined to yield 0.168 g (crystalline yield: 27%). ^1H NMR (500 MHz, C_6D_6, δ): 134.3 (s, BH_3), 74.07 (s), 72.75(s) 39.55 (s), 37.79 (s), 16.93 (s), 16.24 (s), 15.44 (s), 14.20 (s), 12.81 (s), 8.87 (s), 8.69 (s), 8.17 (s), 7.87 (s), 7.72 (d, J_{HH} = 7.6 Hz), 7.47 (s), 7.00 (s), 6.71 (t, J_{HH} = 7.6 Hz), 5.00 (s), 4.53 (s), 4.10 (s), 1.95 (s), 1.30 (m), 0.87 (t, J_{HH} = 7.5 Hz), 0.38 (s), -2.72 (s), -3.87 (s), -6.03 (s), -6.97 (s), -16.34(s), -20.25(s), -73.60(s). ^{13}C NMR (C_6D_6, 125 MHz): 155.9 (s), 150.1 (s), 148.3 (s), 145.6 (s), 130.7 (s), 125.1 (s), 120.6 (s), 118.8 (s). 37.4 (s), 35.8 (s), 34.1 (s), 32.2 (s), 27.3 (s), 25.8 (s), 22.7 (s), 14.25 (s). ^{11}B NMR (96 MHz, C_6D_6, δ): 181.0 (s, fwhm = 220 Hz). IR (Nujol) $\bar{\upsilon}_{max}$ (cm^{-1}): 3043, 2970, 2852, 2726, 2663, 2373, 2172, 2070, 1590, 1561, 1459, 1419, 1377, 1361, 1303, 1243, 1200, 1145, 1078, 1017, 923, 898, 875, 857, 840, 804, 762, 734, 717, 655, 617, 576, 544. Anal. Calcd for $UB_3C_{110}H_{160}O_2$: C, 74.02; H, 9.04. Found: C, 66.36; H, 8.29. The low %C and %H is attributed to incomplete combustion, which is typical for U complexes containing arylborohydride ligands.[2] Despite the lower-than-expected values, the C:H molar ratio is $C_{110}H_{164}$, which is consistent with the proposed formula.

Synthesis of U(H_3BAr^{tBu4})$_3$(DME)$_2$ (2-U).

U(H_3BAr^{tBu4})$_3$(thf)$_2$ (30 mg, 0.015 mmol) and excess dimethoxyethane (5 mL) were added to a 20 mL scintillation vial with a small stir bar. This solution was stirred at room temperature for 10 min at which point the solid material was dissolved. The red/orange solution was filtered through a pad of celite and brought to dryness under vacuum. The oily residue was dissolved in ~1 mL of pentane, filtered, and set in the freezer at -30 °C. After 2 days, small orange prisms were formed, one of which was picked and used for structure determination. The rest of the material was separated from the slightly orange pentane mother liquor and dried under vacuum to yield 22 mg (61%). ^1H NMR (300 MHz, C_6D_6, δ): 19.15 (s), 16.06 (s), 12.68 (s), 8.33 – 6.68 (m), 5.38 (s), 5.01 (s), 4.54 (s), 4.47 (s), 4.10 (s), 2.34 (br, s), 1.96 (br, s), 1.49 (s), 1.39 – 1.29 (m), 1.29 (s), -3.58 (s), -6.82 (s). ^{11}B NMR (96 MHz, C_6D_6, δ): 271.3 (s, fwhm = 231 Hz), 216.7 (s, fwhm = 215 Hz), 194.4 (s), 181.7 (s, fwhm 211 Hz). Elemental analysis was not attempted due to the issues with incomplete combustion described above for **1-U**.

Synthesis of Nd(H_3BAr^{tBu4})$_3$(thf)$_2$ (1-Nd).

$NdCl_3$ (0.033 g, 0.13 mmol) and Li(H_3BAr^{tBu4})(Et_2O) (0.229 g, 0.40 mmol) were added to a 20 mL scintillation vial with a stir bar. To this was added thf (8 mL) and the mixture was allowed to stir at room temperature overnight. The next day, the solution was evaporated to dryness in vacuo to reveal beige powder. To this was added pentane (15 mL) and the mixture was stirred for 15 min. After allowing the vial to settle for 5 min, the visually colorless pentane was filtered and evaporated to dryness to reveal a very pale blue oil. This process of extracting with pentane (40 mL total), filtering, and drying was repeated. To the combined blue pasty solid was added benzene (7 mL) which was then filtered and allowed to slowly evaporate overnight. The next day a crop of very light blue blocks had formed. The benzene mother liquor was pipetted away, and the crystals were dried in vacuo for 1 h. Yield: 70 mg (31%). ^{1}H NMR (300 MHz, C_6D_6, δ): 98.5 (br, s), 13.6 (s), 12.8 (s), 8.31 (s), 8.13 (s), 7.64 – 7.23 (m), 6.12 (t), 3.71 (s), 2.23 (s), 1.32 (s), 0.93 (br, s), 0.30 (s). ^{11}B NMR (96 MHz, C_6D_6, δ) 197.4 (s, fwhm = 260 Hz). IR (Nujol) $\bar{\upsilon}_{max}$ (cm^{-1}): 3043, 2951, 2913, 2850, 2191, 2081, 1591, 1563, 1456, 1421, 1374, 1361, 1304, 1244, 1201, 1146, 1200, 1144, 1077, 1015, 895, 875, 799, 731, 714, 663, 651, 573.

II. Single-crystal X-ray diffraction studies

Single crystals isolated from pentane ($[Li(H_3BAr^{tBu4})]_2$ and **2-U**) and benzene (**1-U** and **1-Nd**) were mounted on a MiTeGen micromount with ParatoneN oil. The data were collected on a Bruker D8 Venture Duo equipped with a Bruker photon III detector. The samples were cooled to 100 K by an Oxford Cryostreams 700 low-temperature device. The diffractometers were equipped with a graphite monochromatized Mo Kα X-ray source (λ = 0.71073). A hemisphere of data was collected using phi and omega scans. Data collection, initial indexing, and cell refinement were conducted using the Bruker Apex II suite. The data were corrected for absorption using redundant reflections and the SADABS program.[3] Structure solution and refinement were performed in Olex2[4] using SHELXT[5] and SHELXL.[6] Hydrogen atoms attached to carbon were idealized and allowed to ride on the attached carbon atom. Hydrogen atoms attached to boron were placed in idealized positions with B-H = 1.20 Å and allowed to rotate about the B-C bond to find the best least-squares position. *HKL* reflections with error/esd values ± 10 were omitted from the models. The final refinement included anisotropic temperature factors on all non-hydrogen atoms. Isotropic extinction parameters were not needed for any of the refinements. Crystallographic details are summarized in Table S1.

Special refinement details. 1-U: *tert*-Butyl groups on C66 contain carbon atoms that were positionally disordered and modeled over two sites. The refinement occupancies for the A and B sites were 0.678 and 0.322, respectively. **2-U**: *tert*-Butyl groups on C18, C31, C38, C59, contain carbon atoms that were positionally disordered and modeled over two sites. The refinement occupancies for each of the *tert*-butyl groups on the A and B sites were 0.558 and 0.442, 0.865 and 0.135, 0.907 and 0.093, and 0.819 and 0.181, respectively. Carbon atoms on dme molecules were positionally disordered and were modeled over two sites. The refinement occupancies for each of the carbon atoms on the A and B sites were 0.712 and 0.288, respectively. **1-Nd**: *tert*-Butyl groups on C51 contain carbon atoms that were positionally disordered and modeled over two sites. The refinement occupancies for the A and B sites were 0.712 and 0.288, respectively. $[Li(H_3BAr^{tBu4})]_2$: A solvent mask was applied to account for disordered interstitial solvent that could not be modeled satisfactorily. *tert*-Butyl groups on C47 and C61 contained carbon atoms that were positionally disordered and modeled over two sites. The refinement occupancies for the A and B sites were 0.891 and 0.109, and 0.739 and 0.261, respectively. To help maintain reasonable bond length and ADP values on the disordered sites, SIMU, RIGU, and SADI restraints were applied to all structures.

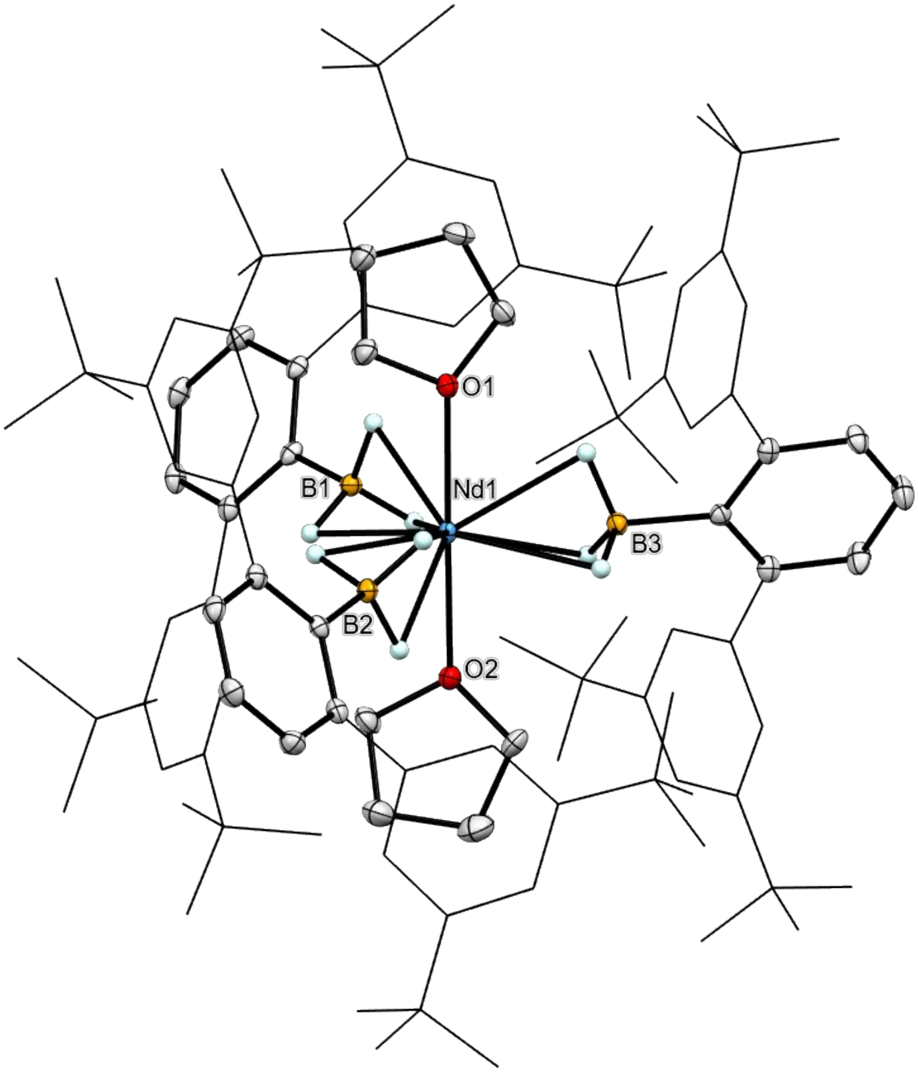


Figure S1. Truncated molecular structure of Nd^{III}(H$_3$BAr^{tBu4})$_3$(thf)$_2$ (**1-Nd**). Ellipsoids are drawn at 50% probability, except hydrogens which are drawn as arbitrary sized spheres. Flanking aryl groups have been made wireframe, and hydrogen atoms on carbon have been omitted for clarity.

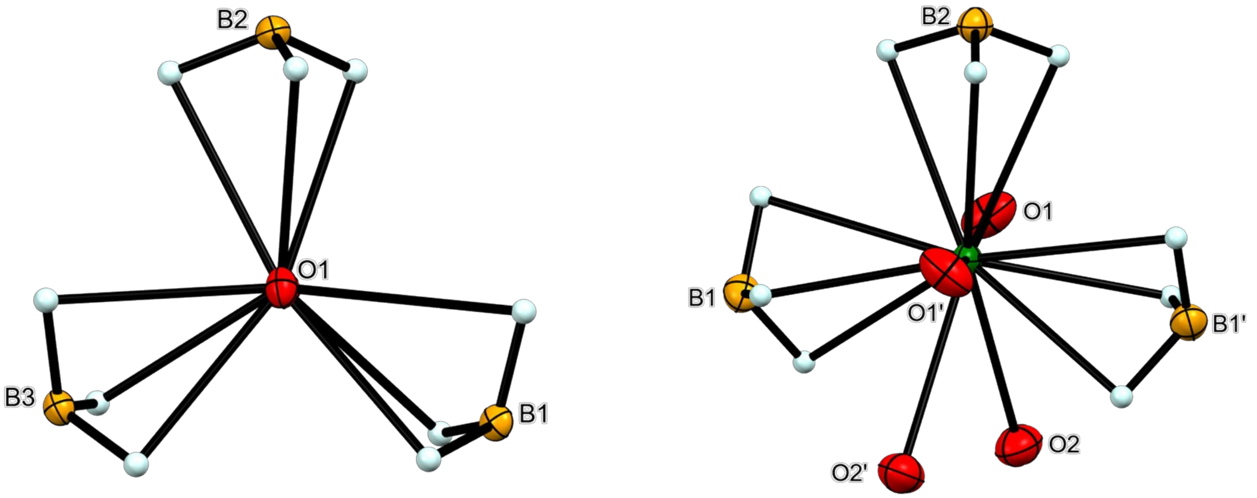


Figure S2. Truncated molecular structures of $\mathrm{U^{III}(H_3BAr^{tBu4})_3(thf)_2}$ (**1-U**, left), and $\mathrm{U^{III}(H_3BAr^{tBu4})_3(dme)_2}$ (**2-U**, right) as viewed down the O-U-O bonds in both complexes. Ellipsoids are drawn at 50% probability, except hydrogens which are drawn as arbitrary sized spheres. Carbon atoms and co-crystallized solvent molecules have been omitted for clarity. Selected angles (deg). 1-U: B(1)-U(1)-B(2) = 123.93(8), B(1)-U(1)-B(3) = 119.33(8), B(2)-U(1)-B(3) = 116.71(8), O(1)-U(1)-O(2) = 178.95(5). 2-U: B(1/1')-U(1)-B(2) = 102.03(7), B(1)-U(1)-B(1') = 155.95(8), B(1)-U(1)-O(1) = 83.11(9), B(1)-U(1)-O(2) = 86.82(8), B(1)-U(1)-O(1') = 98.57(8), B(1)-U(1)-O(2') = 73.08(8).

Table S1. Crystallographic data.

	U(H_3BAr^{tBu4})(thf)$_2$	**U(H_3BAr^{tBu4})(dme)$_2$**	**Nd(H_3BAr^{tBu4})$_3$(thf)$_2$**	**Li_2(H_3BAr^{tBu4})$_2$**
Empirical formula	$C_{110}H_{151}B_3O_2U$	$C_{120}H_{186}B_3O_4U$	$C_{110}H_{160}B_3NdO_2$	$C_{77}H_{117}B_2Li_2$
Formula weight	1775.76	1963.14	1691.04	1078.2
Crystal system	monoclinic	monoclinic	monoclinic	triclinic
Space group	$P2_1/n$	C2/c	$P2_1/n$	P-1
a/Å	14.4250(5)	22.7381(6)	14.4185(6)	10.6910(6)
b/Å	30.4588(11)	16.4819(5)	30.3781(12)	13.2184(8)
c/Å	23.2285(8)	30.7694(10)	23.2224(11)	27.5291(15)
α/°	90	90	90	94.734(2)
β/°	96.2370(10)	92.2340(10)	96.375(2)	95.397(2)
γ/°	90	90	90	108.591(2)
Volume/Å^3	10145.5(6)	11522.6(6)	10108.7(8)	3644.8(4)
Z	4	4	4	2
ρ_{calc}g/cm^3	1.163	1.132	1.111	0.982
μ/mm^1	1.646	1.456	0.56	0.054
F(000)	3736	4180	3644	1190
2Θ range for data collection/°	3.75 to 56.636	3.996 to 52.822	3.756 to 52.858	3.758 to 56.754
Final R indexes [I>=2σ (I)]	R_1 = 0.0314, wR_2 = 0.0681	R_1 = 0.0335, wR_2 = 0.0821	R_1 = 0.0338, wR_2 = 0.0780	R_1 = 0.0605, wR_2 = 0.1481
Final R indexes [all data]	R_1 = 0.0390, wR_2 = 0.0707	R_1 = 0.0354, wR_2 = 0.0830	R_1 = 0.0361, wR_2 = 0.0793	R_1 = 0.0796, wR_2 = 0.1589
Largest diff. peak/hole / e Å^{-3}	0.66/-2.34	2.14/-0.87	0.80/-1.24	0.27/-0.22
Temperature/K	100(1)	100(1)	100(1)	100(1)

Table S2. Select atomic distances and angles from single-crystal XRD studies.

$U(H_3BAr^{tBu4})_3(thf)_2$

Distances (Å)		Angles (deg)	
U(1)-B(1)	2.638(3)	B(1)-U(1)-B(2)	123.93(8)
U(1)-B(2)	2.646(3)	B(1)-U(1)-B(3)	119.33(8)
U(1)-B(3)	2.622(2)	B(2)-U(1)-B(3)	116.71(8)
U(1)-O(1)	2.4573(15)	O(1)-U(1)-O(2)	178.95(5)
U(1)-O(2)	2.4848(15)		

$U(H_3BAr^{tBu4})_3(dme)_2$

Distances (Å)		Angles (deg)	
U(1)-B(1)/B	2.695(3)	B(2)-U(1)-B(1)	102.03(7)
U(1)-B(2)	2.712(4)	B(1)-U(1)-O(1)	83.11(9)
U(1)-O(1)	2.596(2)	B(1)-U(1)-O(2)	86.82(8)
U(1)-O(2)	2.788(2)	B(1)-U(1)-O(1')	98.57(8)
		B(1)-U(1)-O(2')	73.08(8)

$Nd(H_3BAr^{tBu4})_3(thf)_2$

Distances (Å)		Angles (deg)	
Nd(1)-B(1)	2.604(2)	B(1)-Nd(1)-B(2)	116.85(6)
Nd(1)-B(2)	2.628(2)	B(2)-Nd(1)-B(3)	123.80(6)
Nd(1)-B(3)	2.623(2)	B(3)-Nd(1)-B(1)	119.32(7)
Nd(1)-O(1)	2.4475(12)	O(1)-Nd(1)-O(2)	179.10(4)
Nd(1)-O(2)	2.4467(12)		

III. NMR spectra

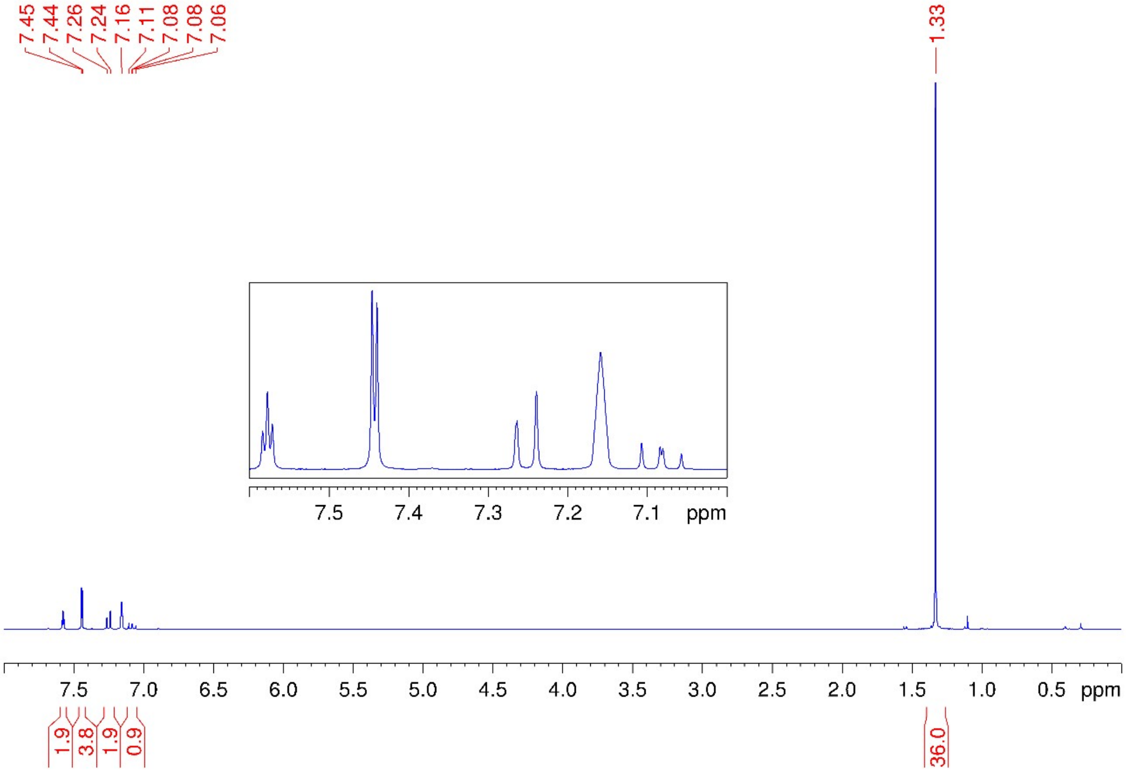


Figure S3. ^{1}H NMR spectrum of I-Ar^{tBu4} in C_6D_6.

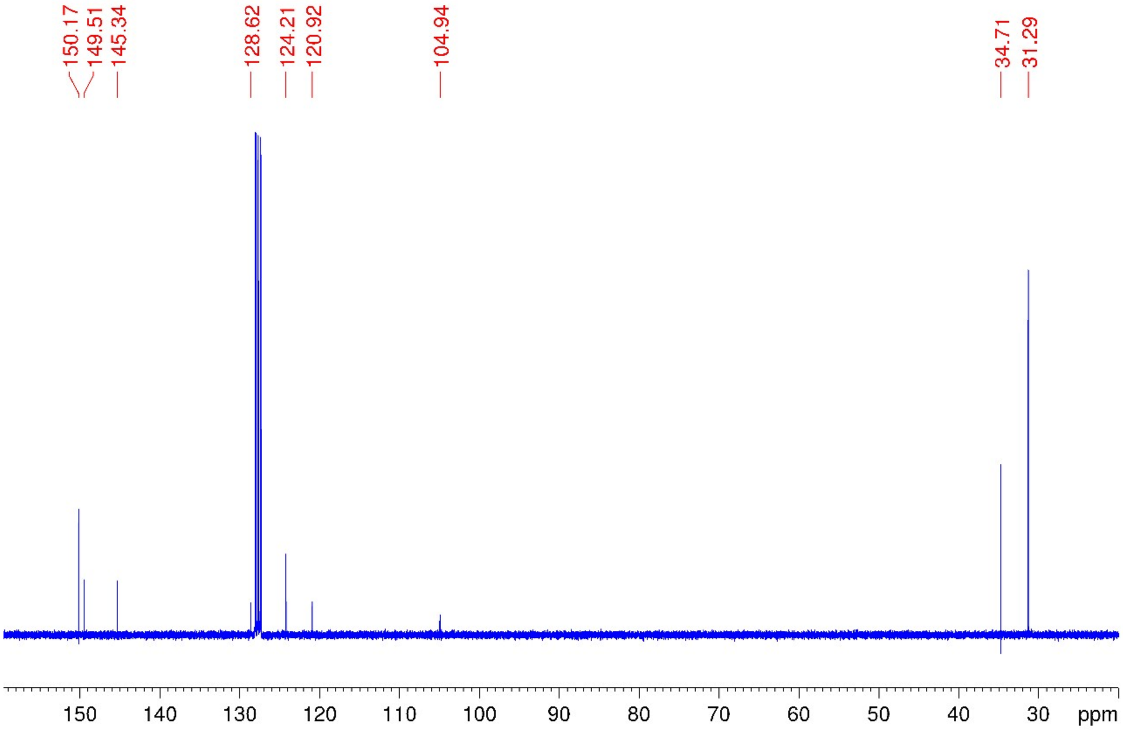


Figure S4. $^{13}C\{^1H\}$ NMR spectrum of I-Ar^{tBu4} in C_6D_6.

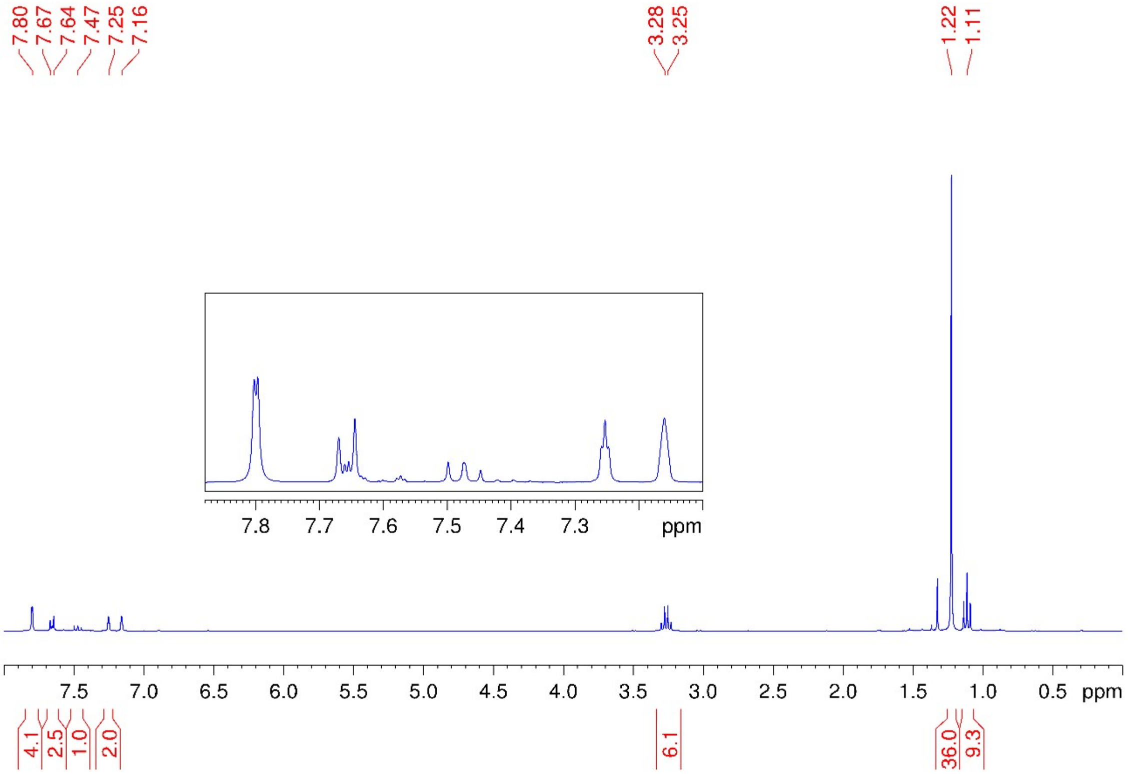


Figure S5. ^{1}H NMR spectrum of LiAr^{tBu4}(Et$_2$O)$_{1.5}$ in C$_6$D$_6$.

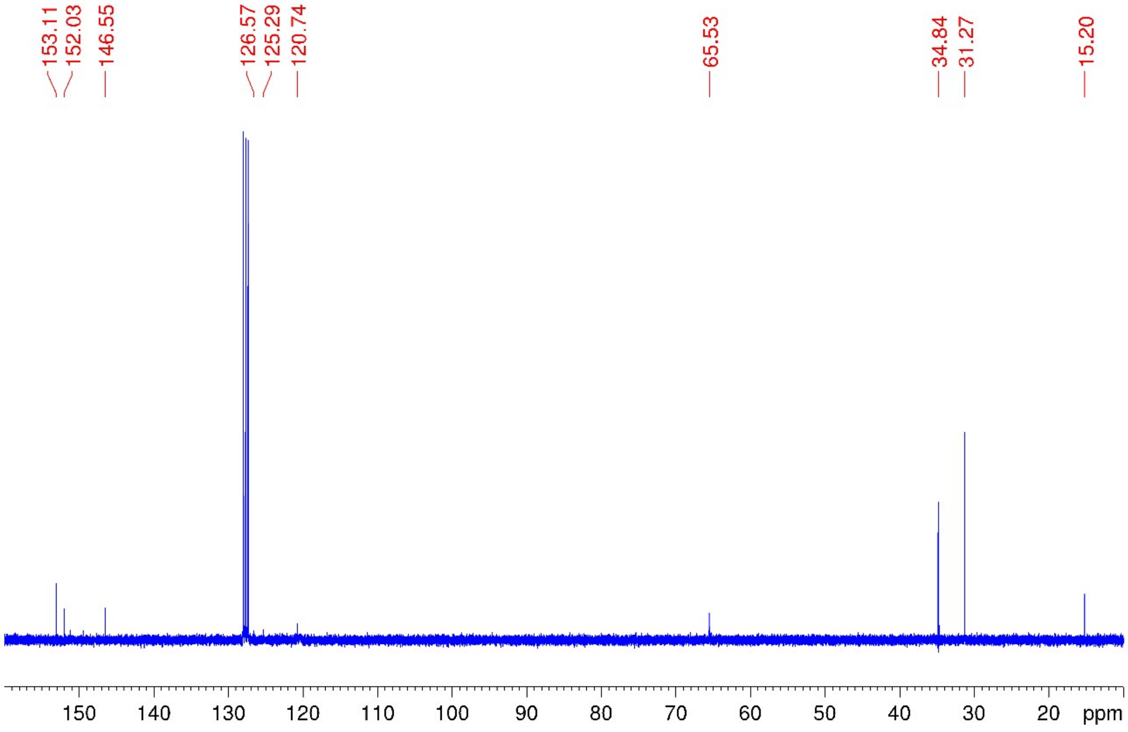


Figure S6. ^{13}C{^{1}H} NMR spectrum of LiAr^{tBu4}(Et$_2$O)$_{1.5}$ in C$_6$D$_6$.

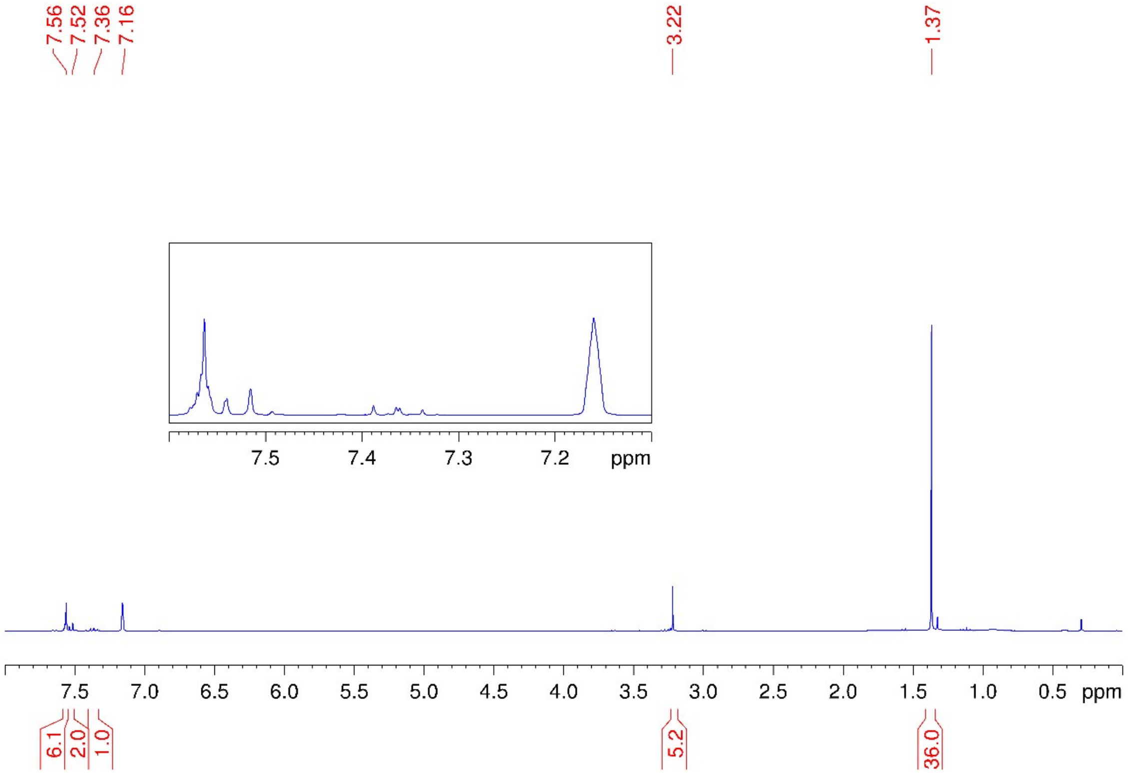


Figure S7. ^{1}H NMR spectrum of $(MeO)_2BAr^{tBu4}$ in C_6D_6.

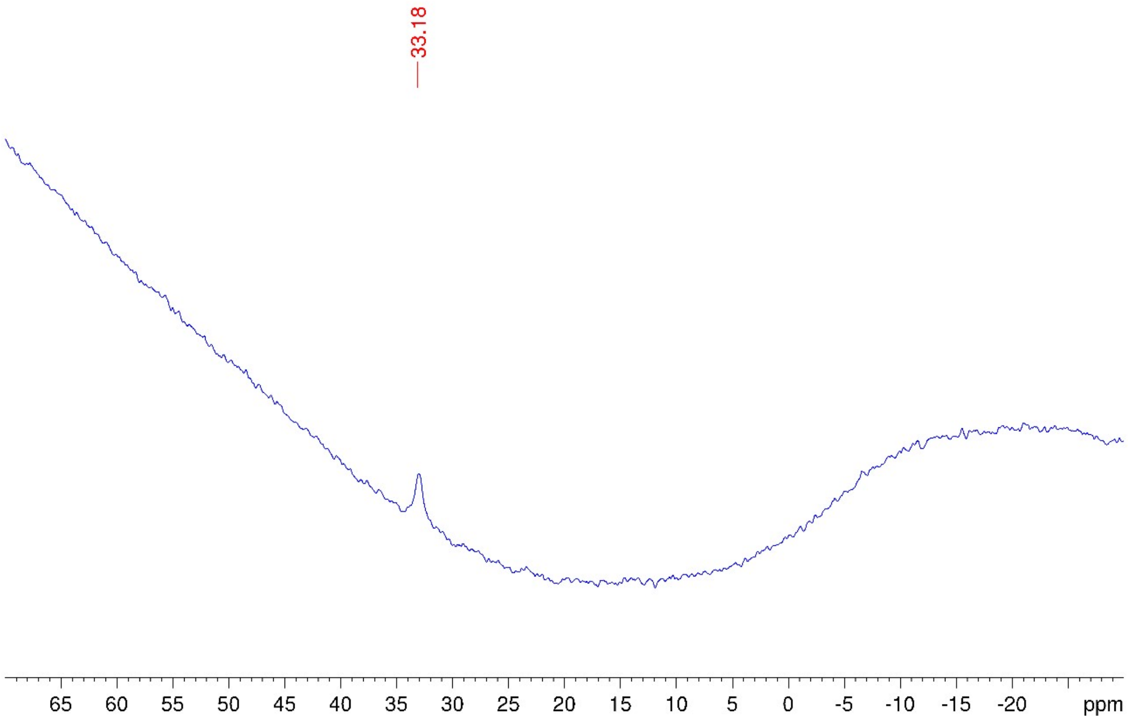


Figure S8. ^{11}B NMR spectrum of $(MeO)_2BAr^{tBu4}$ in C_6D_6.

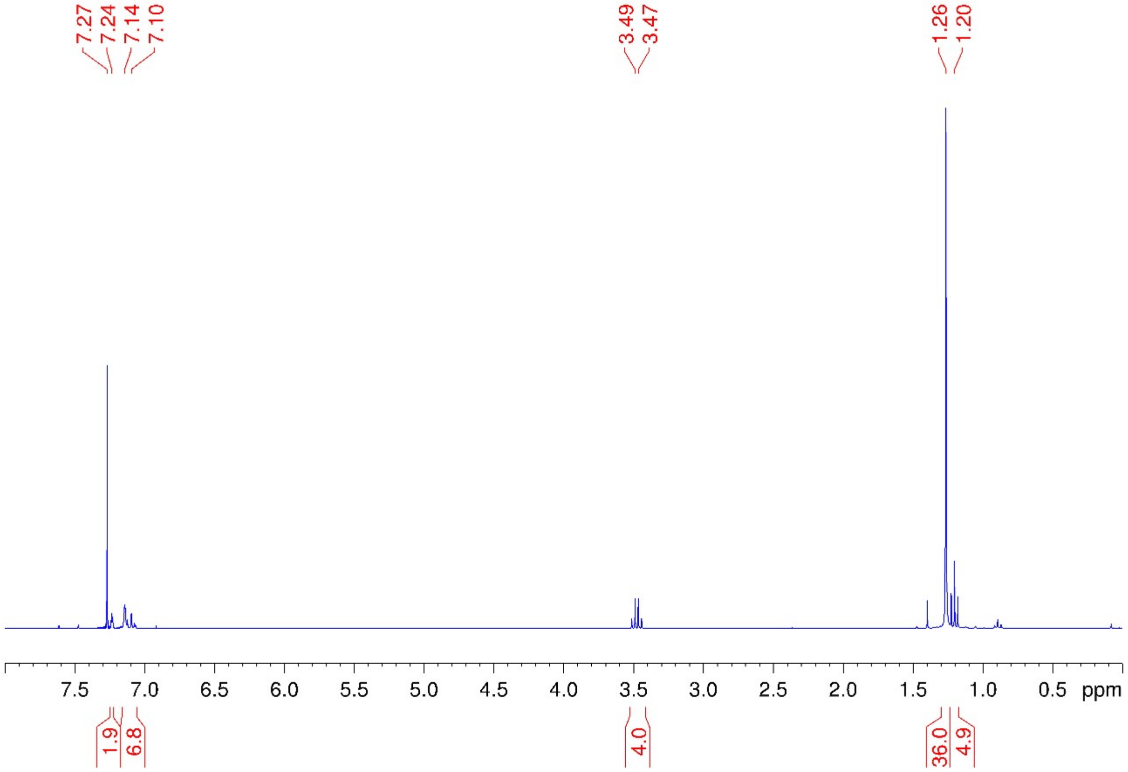


Figure S9. ^{1}H NMR spectrum of Li(H_3BAr^{tBu4})(Et_2O) in $CDCl_3$.

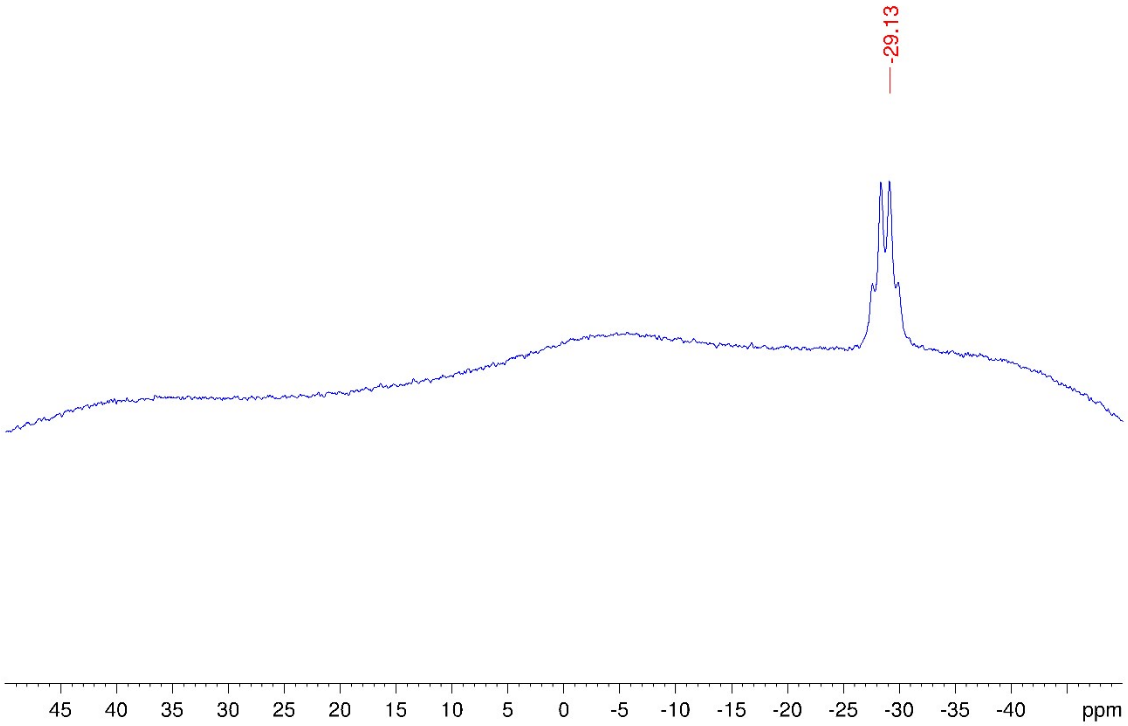


Figure S10. ^{11}B NMR spectrum of Li(H$_3$BAr^{tBu4})(Et$_2$O) in CDCl$_3$.

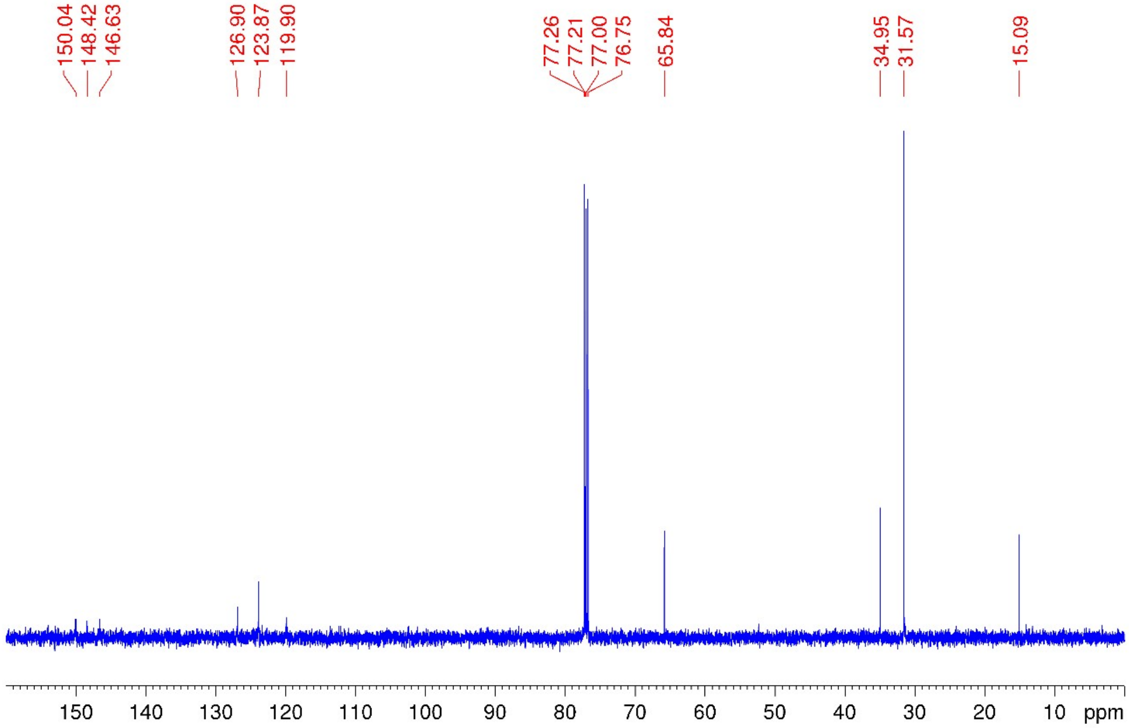


Figure S11. $^{13}C\{^{1}H\}$ NMR spectrum of $Li(H_3BAr^{tBu4})(Et_2O)$ in $CDCl_3$.

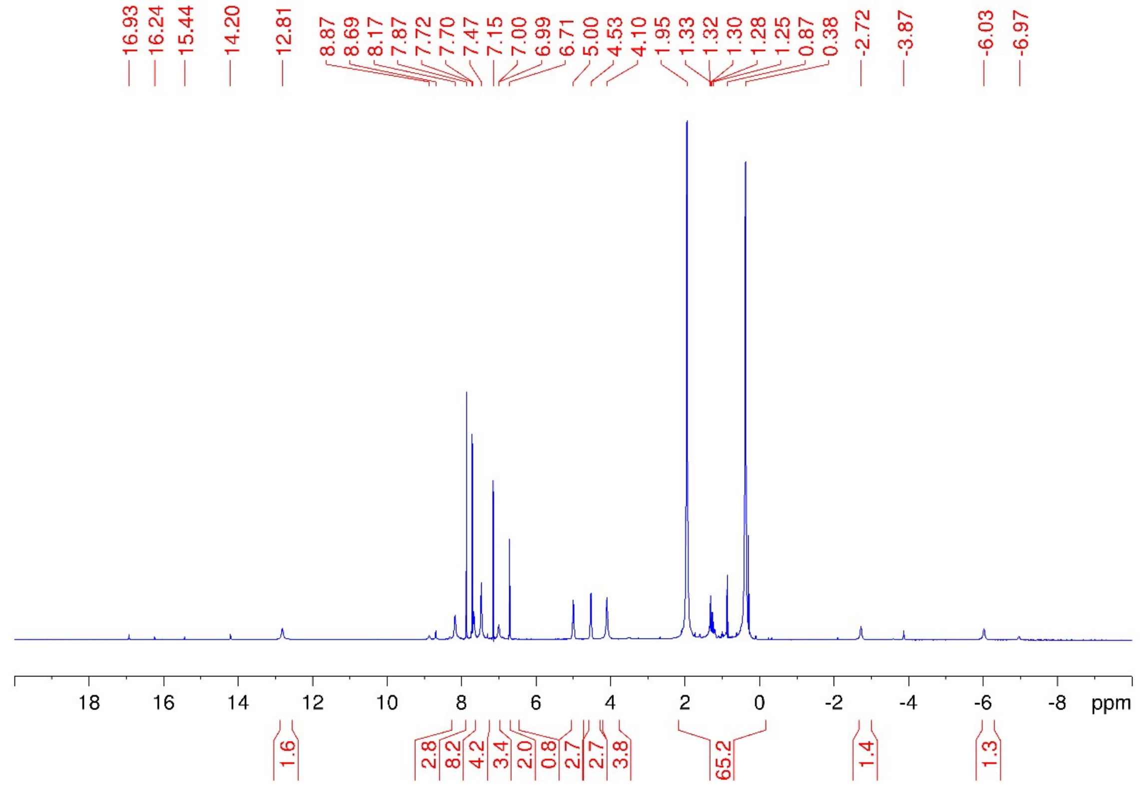


Figure S12. ^{1}H NMR spectrum of $U(H_3BAr^{tBu4})_3(thf)_2$ in C_6D_6.

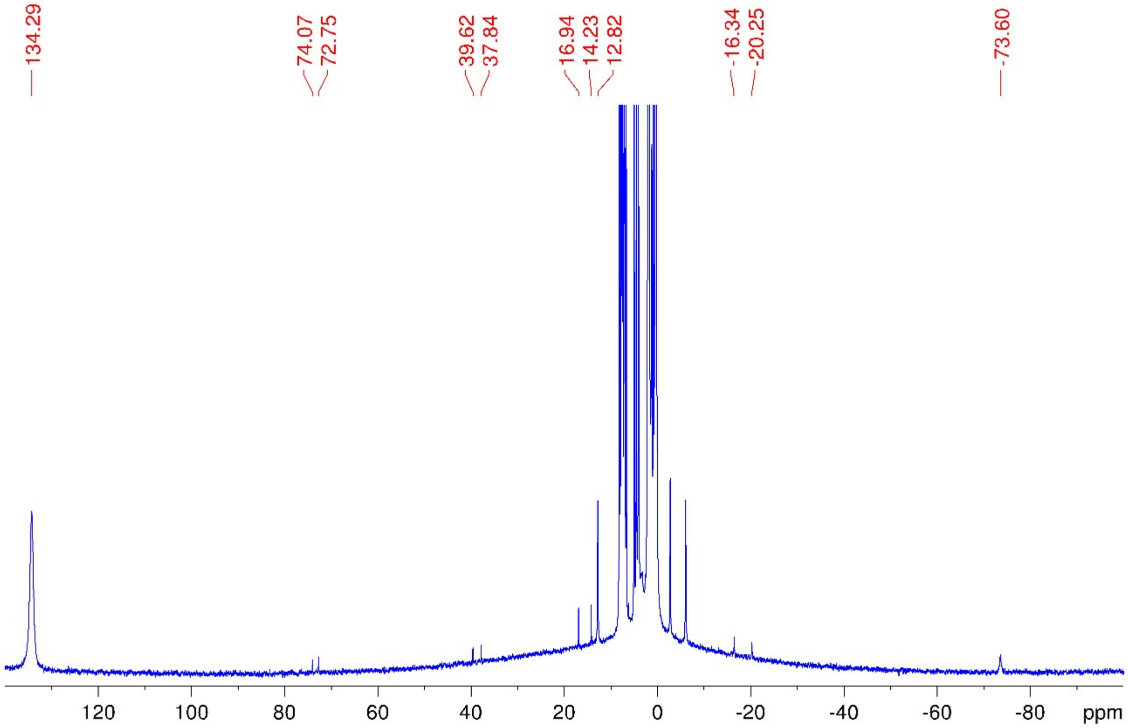


Figure S13. ^{1}H NMR spectrum (expanded window) of U(H$_3$BAr^{tBu4})$_3$(thf)$_2$ in C$_6$D$_6$. Line broadening of 10 Hz was applied to the spectrum.

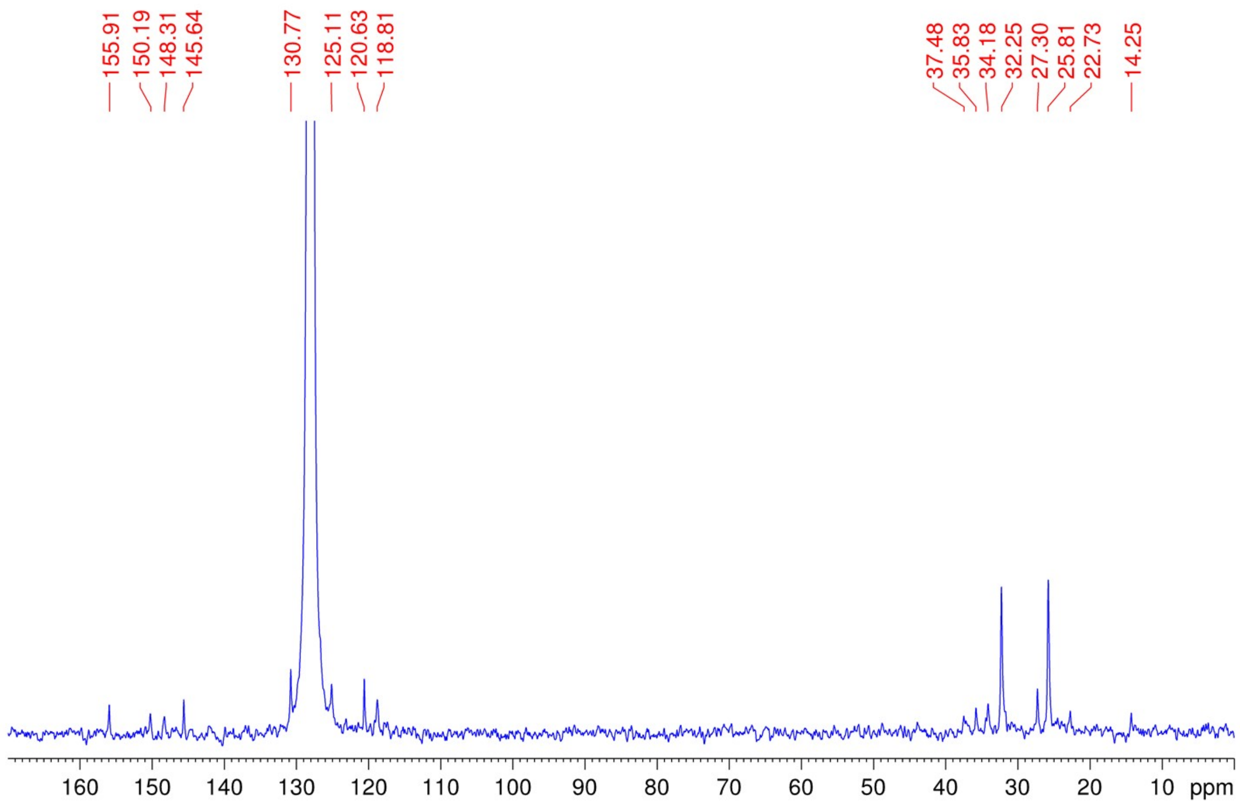


Figure S14. $^{13}C\{^1H\}$ NMR spectra of $U(H_3BAr^{tBu4})_3(thf)_2$ in C_6D_6. Line broadening of 20 Hz was applied to the spectrum.

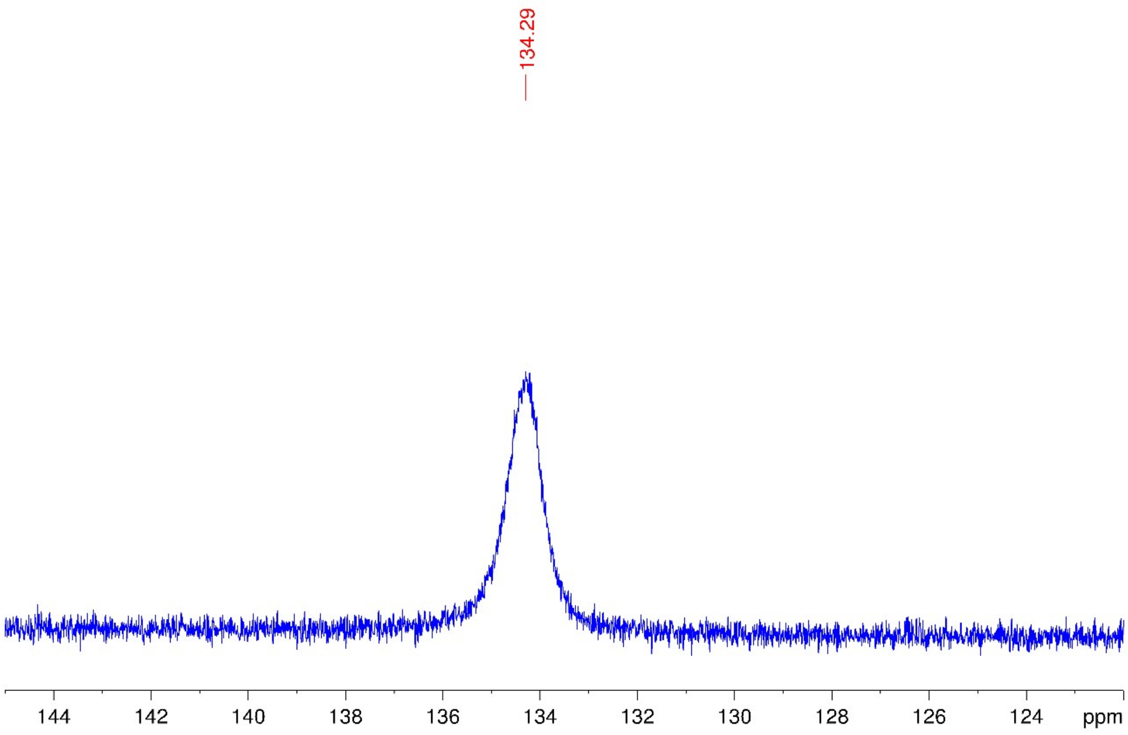


Figure S15. ^{1}H NMR spectrum of $U(H_3BAr^{tBu4})_3(thf)_2$ (BH_3 region) in C_6D_6.

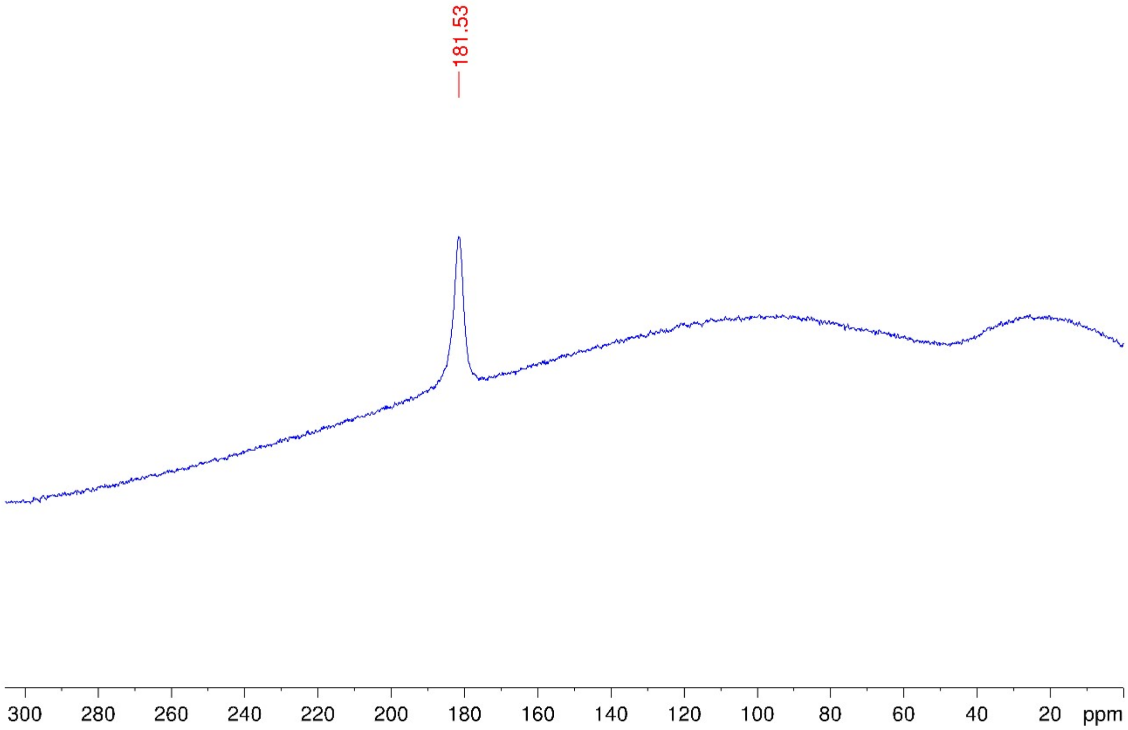


Figure S16. ^{11}B NMR spectra of $U(H_3BAr^{tBu4})_3(thf)_2$ in C_6D_6.

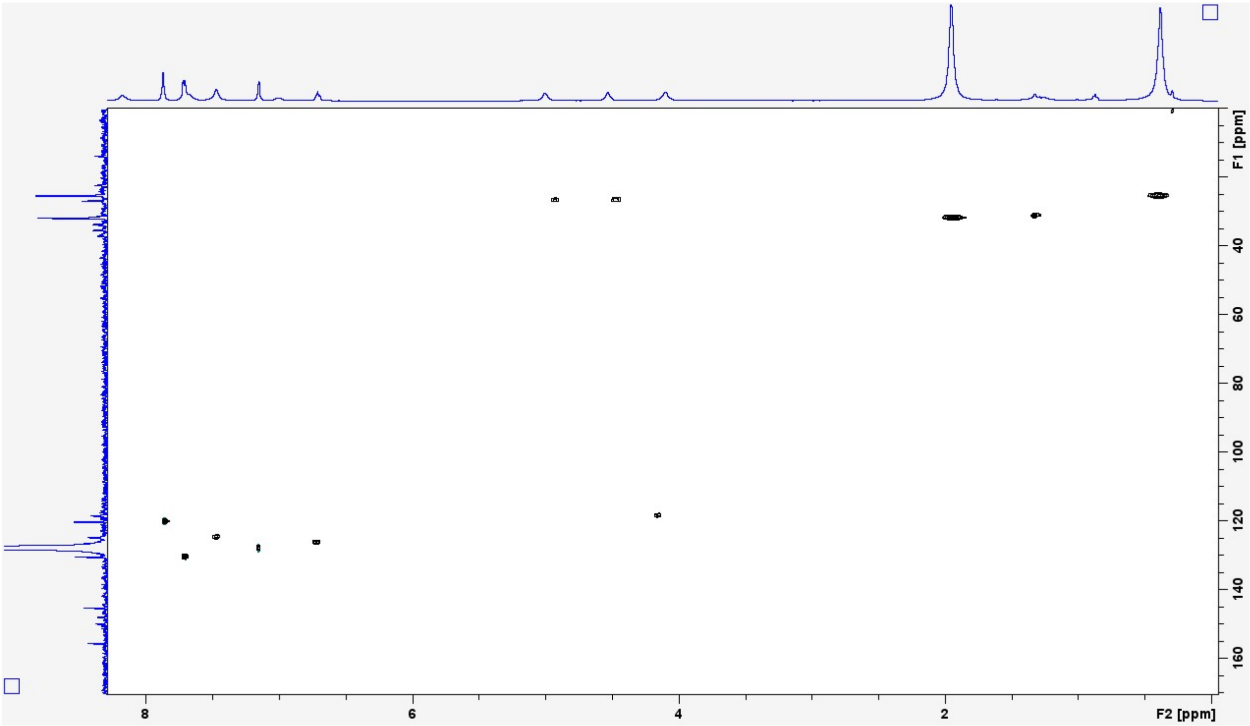


Figure S17. HSQC NMR spectrum of U(H_3BAr^{tBu4})$_3$(thf)$_2$ in C_6D_6.

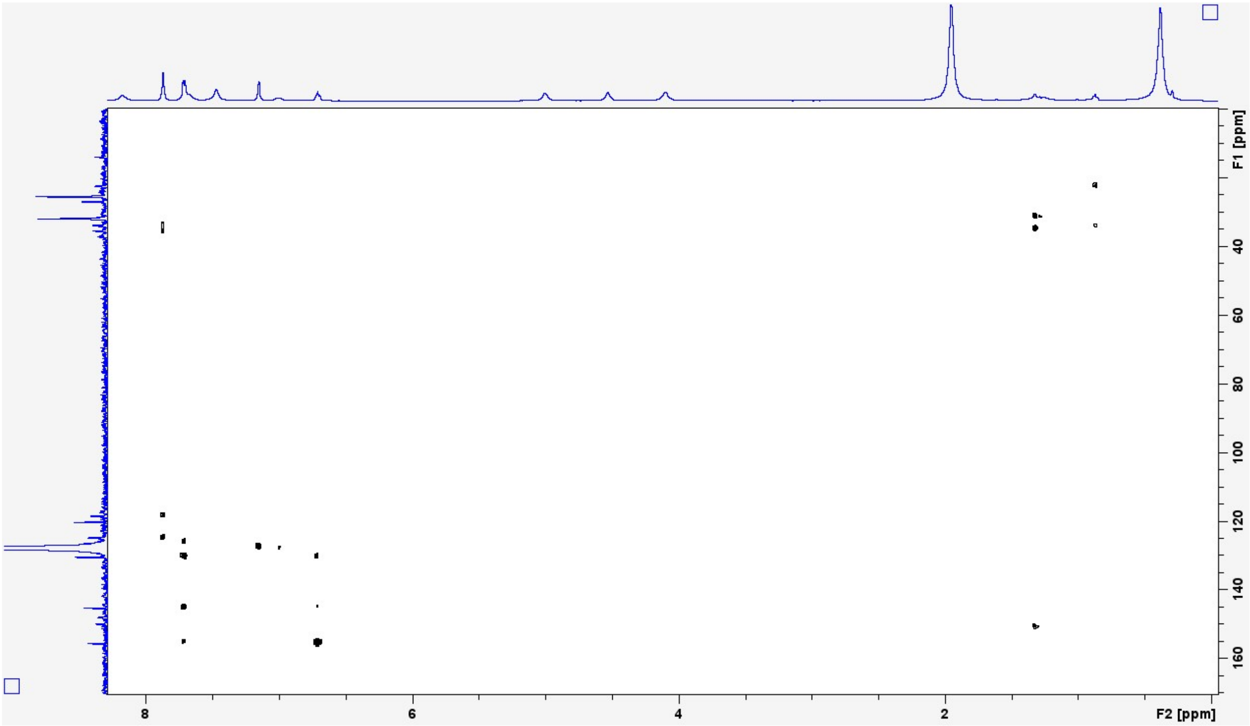


Figure S18. HMBC spectrum of $U(H_3BAr^{tBu4})_3(thf)_2$ in C_6D_6.

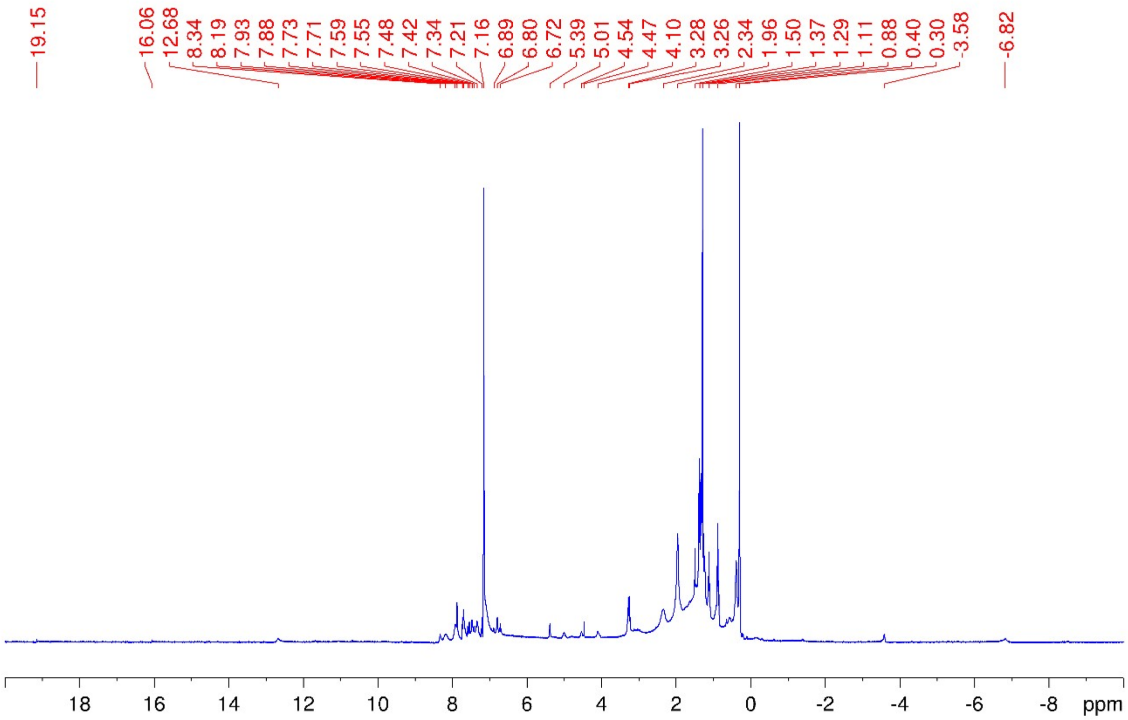


Figure S19. ^{1}H NMR spectra of U(H$_3$BAr^{tBu4})$_3$(dme)$_2$ in C$_6$D$_6$.

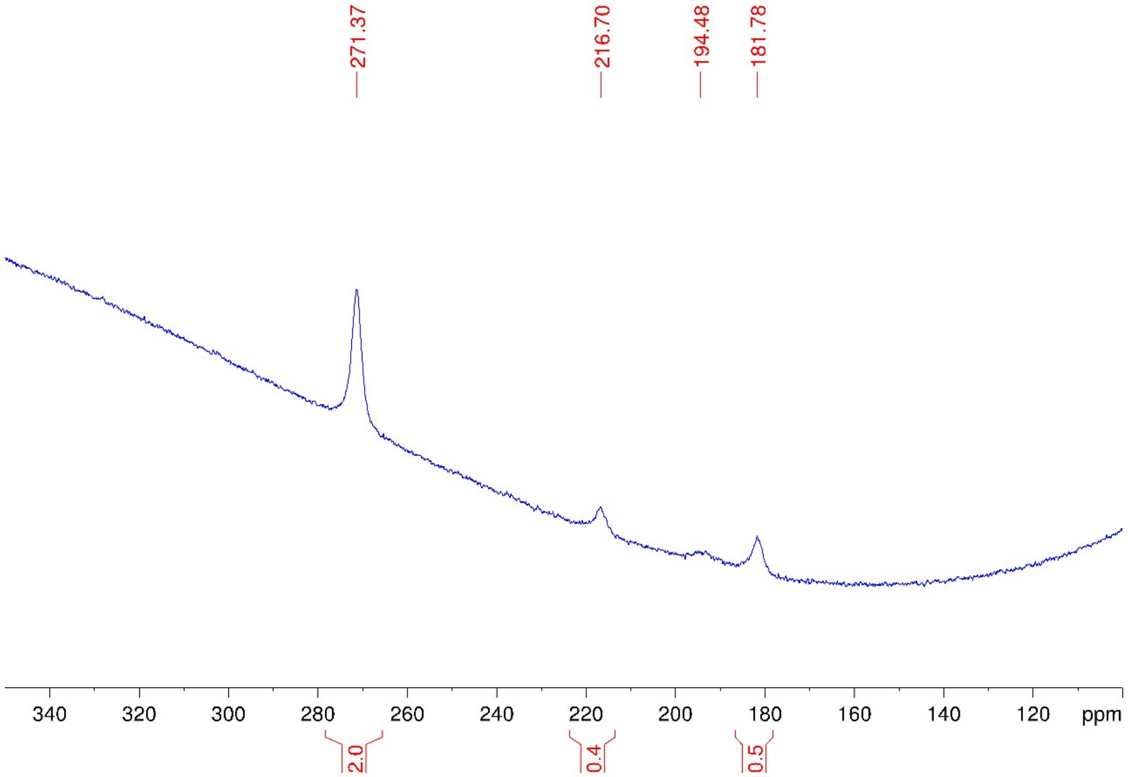


Figure S20. ^{11}B NMR spectra of U(H_3BAr^{tBu4})$_3$(dme)$_2$ in C_6D_6.

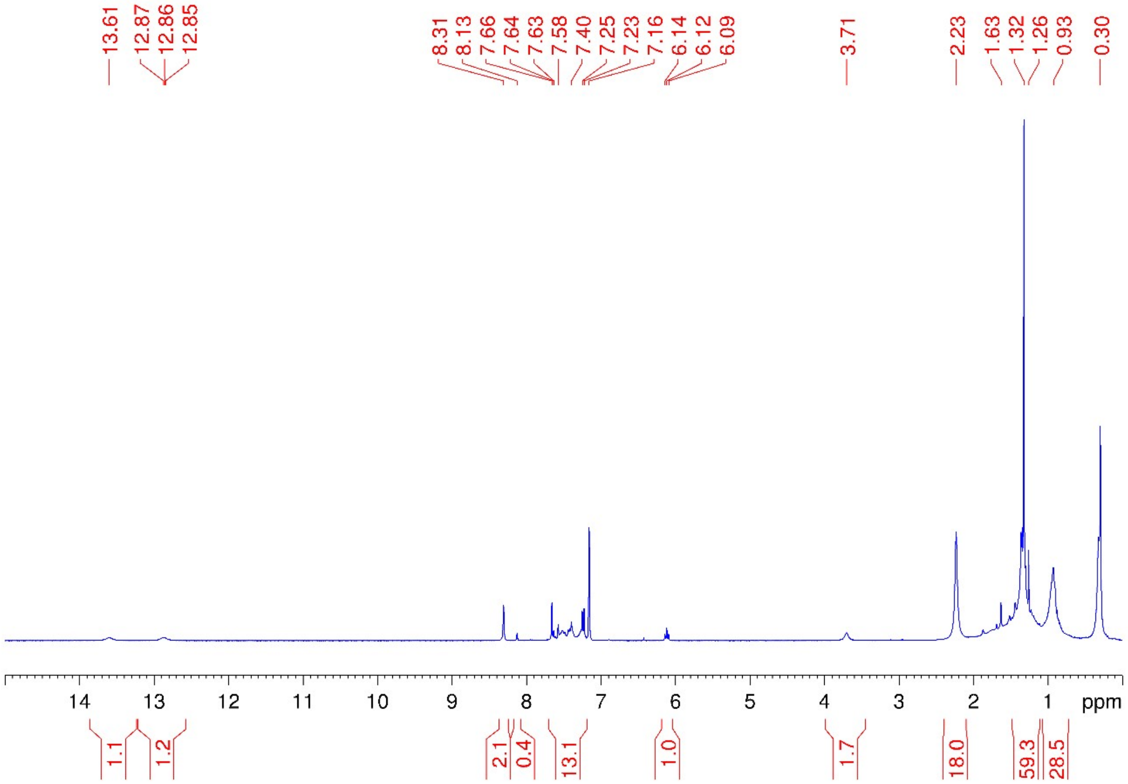


Figure S21. ^{1}H NMR spectra of Nd(H_3BAr^{tBu4})$_3$(thf)$_2$ in C_6D_6.

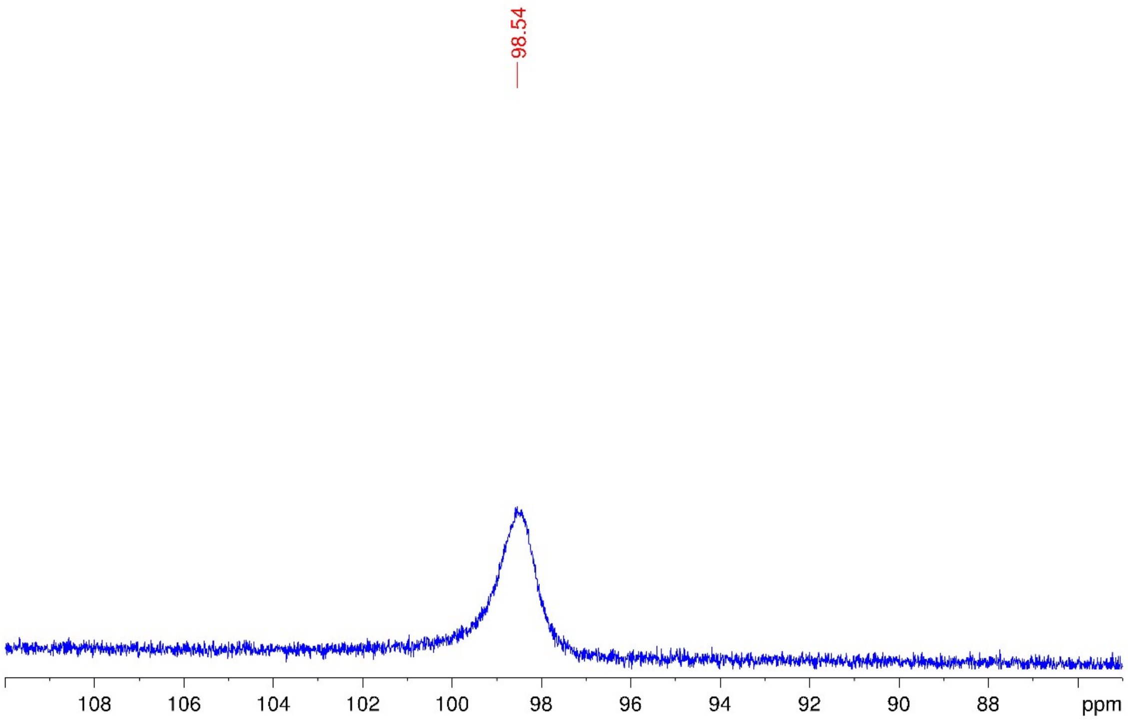


Figure S22. ^{1}H NMR spectrum of Nd(H$_3$BAr^{tBu4})$_3$(thf)$_2$ (BH$_3$ region) in C$_6$D$_6$.

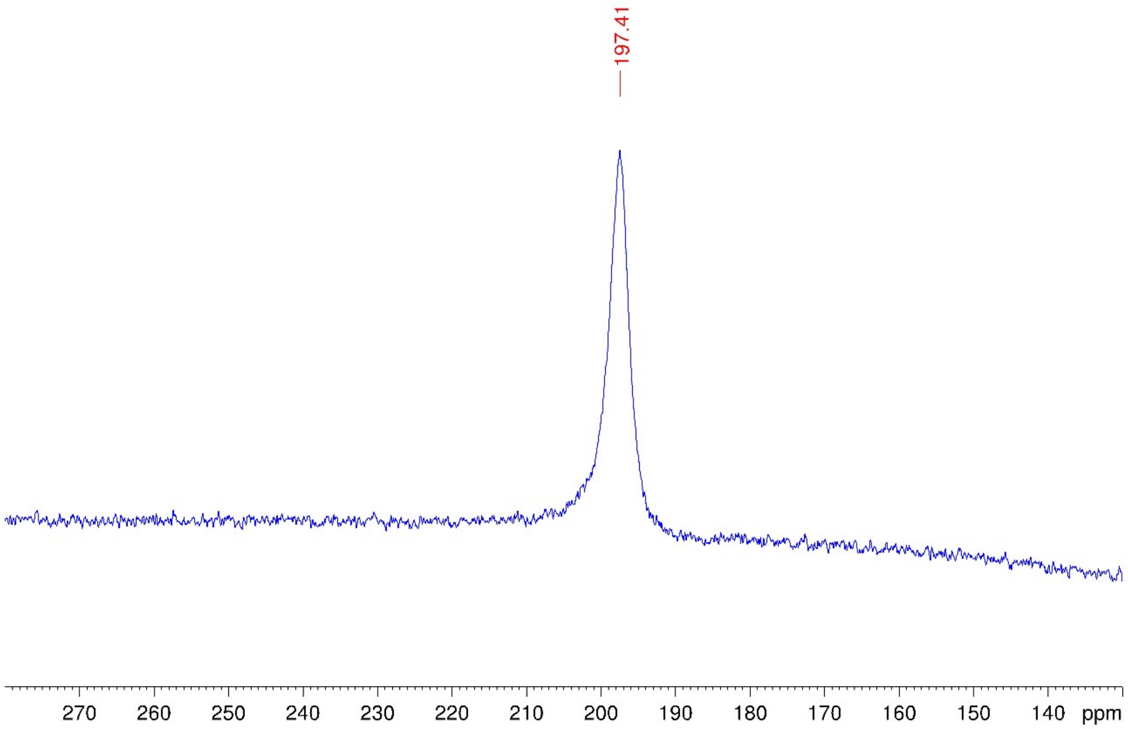


Figure S23. ^{11}B NMR spectra of Nd(H$_3$BAr^{tBu4})$_3$(thf)$_2$ in C$_6$D$_6$.

IV. IR spectra

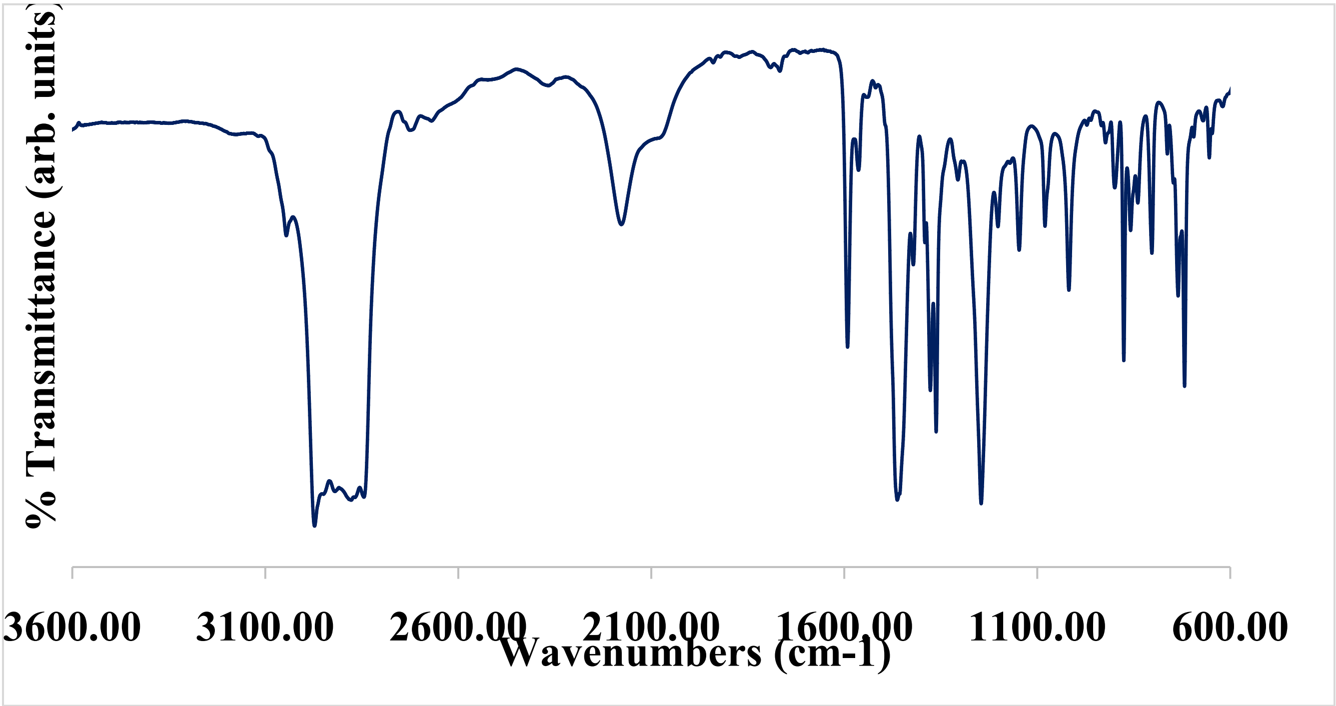


Figure S24. Nujol mull IR spectra of U(H_3BAr^{tBu4})$_3$(thf)$_2$.

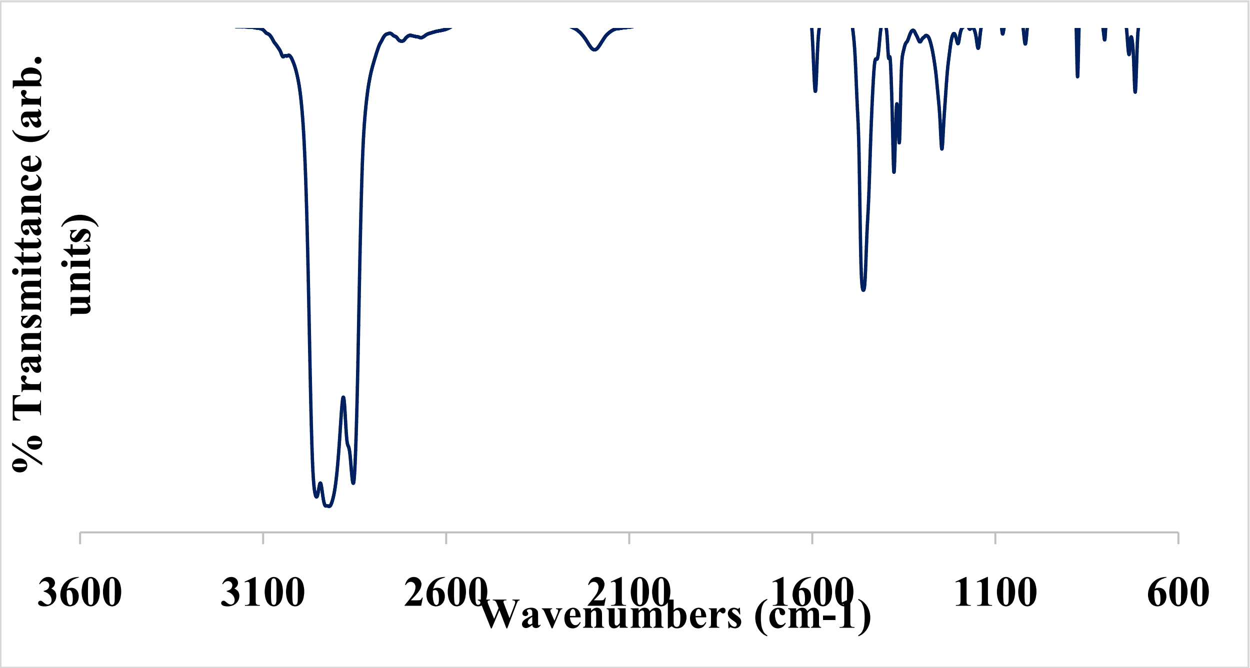


Figure S25. Nujol mull IR spectra of Nd(H_3BAr^{tBu4})$_3$(thf)$_2$.

V. UV-vis-NIR spectrum of $U(H_3BAr^{tBu4})_3(thf)_2$ (1-U)

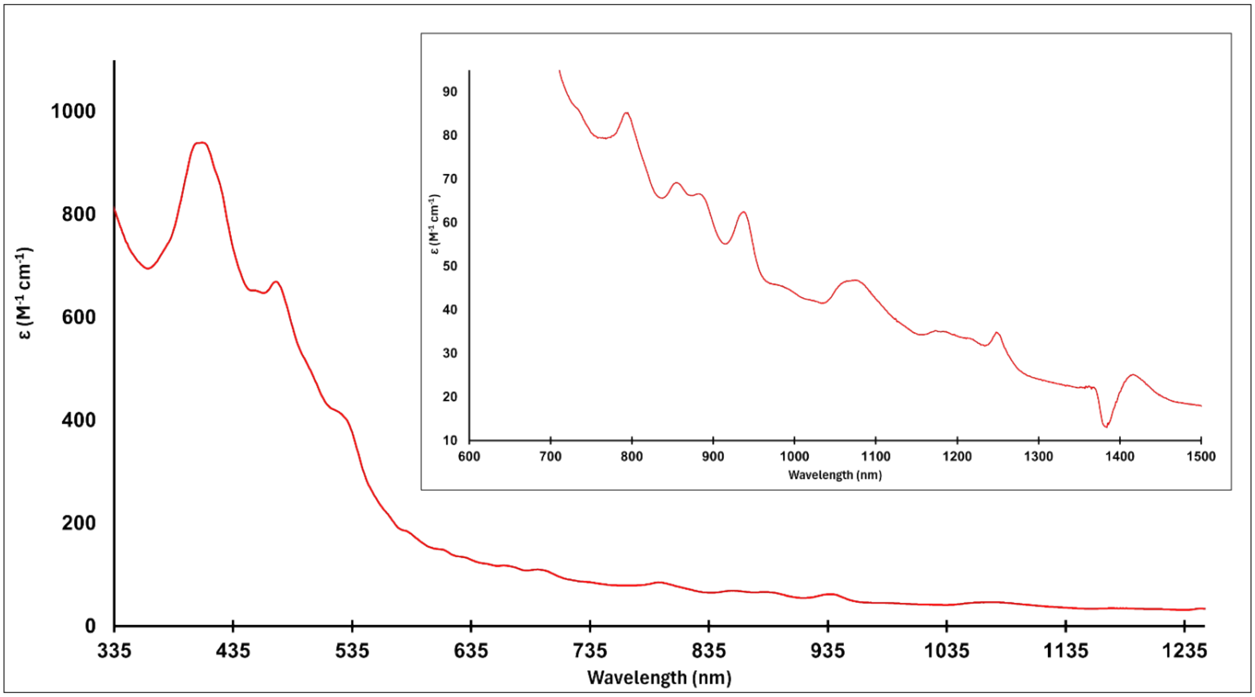


Figure 26. UV-vis/NIR electronic absorption spectrum of $U^{III}(H_3BAr^{tBu4})_3(thf)_2$ (**1-U**) (1.01 mM in thf), inset showing the scaled *f* – *f* transitions.

VI. Supporting information references

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(5) Sheldrick, G. *Acta Crystallogr., Sect. A: Found. Crystallogr.* **2015**, *71*, 3-8.
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