Selective Oxo Ligand Functionalisation and Substitution Reactivity in an Oxo/Catecholate-Bridged U^{IV}/U^{IV} Pacman Complex

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1.1.1 General Details

All manipulations were carried out under a dry, oxygen-free atmosphere of either dinitrogen, using standard glovebox technique, or argon, using standard Schlenk techniques. Pyridine was distilled from potassium and stored over 4 Å molecular sieves. THF, toluene, hexanes, 1,2-dimethoxyethane (dme) and dichloromethane were degassed and purified by passage through activated alumina towers and stored over 4 Å molecular sieves. All gases were supplied by BOC gases UK. All glassware items, cannulae and Fisherbrand 1.2 µm retention glass microfibre filters were dried in a 150 °C oven overnight before use.

The deuterated solvent d_5-pyridine was boiled over potassium for 24 hours, freeze-pump-thaw degassed and vacuum-transferred prior to use. ^{1}H, ^{2}H, ^{13}C{^{1}H}, ^{11}B, ^{19}F and ^{29}Si_INEPT NMR spectra were recorded on Bruker AVA500, PRO500 or AVA600 spectrometers between 300 and 360 K, as indicated on the respective NMR spectra/data. Chemical shifts are reported in parts per million, δ. All ^{1}H NMR and ^{13}C{^{1}H} NMR spectra were referenced relative to external $SiMe_4$, and internal proteo resonances of the solvent; 8.74, 7.58 and 7.22 ppm for d_5-pyridine in ^{1}H NMR, and 150.35, 135.91 and 123.87 ppm for d_5-pyridine in ^{13}C{^{1}H} NMR spectra. ^{11}B, ^{19}F and ^{29}Si NMR spectra were referenced using an external standard of $BF_3(OEt_2)$ (0.0 ppm), α,α,α-trifluorotoluene (–63.8 ppm) and $SiMe_4$ (0.0 ppm), respectively. Please see the NMR Spectra section below for specific details pertaining to the collection of NMR data for complexes **1**-**6**. Infrared spectra were recorded on a Perkin Elmer Spectrum 65 FT-IR spectrometer as nujol mulls between NaCl disks. Elemental analyses were carried out at Pascher Labor, Germany or at the London Metropolitan University.

^{1}H NMR chemical shifts are provided for [{(py)U^{IV}(µ-OMe)(µ-OH)U^{IV}(µ-$O_2C_6H_4$)(py)}(L^A)] (**2**), [{(py)U^{IV}(µ-F_2)U^{IV}(µ-$O_2C_6H_4$)(py)}(L^A)] (**5**) and [{(py)U^{IV}(µ-F)(µ-OBcat)U^{IV}(µ-$O_2C_6H_4$)(py)}(L^A)] (**5A**) at 300 K, but integrations were not defined due to inaccuracies caused by dynamic behaviour in solution (i.e. line broadening). As a result, high temperature data (360 K) were recorded since the line broadening was significantly decreased at elevated temperatures. A multiplet located between 0 and 3 ppm in the ^{1}H NMR spectrum of [{(py)U^{IV}(µ-η^2:η^2-Se_2)U^{IV}(µ-$O_2C_6H_4$)(py)}(L^A)] (**4**) has been assigned as a mixture of hydrocarbyl impurities (i.e. toluene, hexanes, silicon grease). A ^{1}H NMR spectrum of [{(py)U^{IV}(µ-Cl)$_2U^{IV}$(µ-$O_2C_6H_4$)(py)}(L^A)] (**6**) generated *in situ* was used for the assignment as once precipitated, it is almost completely insoluble in common solvents. Insufficient **6** could be retained in solution to allow meaningful ^{13}C{^{1}H} NMR spectra to be obtained. No ^{19}F resonance for **5**, and no ^{11}B resonance for **5A** could be located, even when samples were heated to 360 K.

Single crystal X-ray diffraction data for **1·3THF**, **2·C_6H_6**, **3·5py**, **4·2CH_2Cl_2**, **5·4py**, **6·solvent** and **8·solvent** were collected using an Excalibur Eos diffractometer, fitted with a CCD area detector and using Mo Kα radiation; data for **1·3THF**, **3·5py**, **6·solvent** and **8·solvent** was collected at 120.0(1) K, whereas data for **2·C_6H_6**, **4·2CH_2Cl_2** and **5·4py** was collected at 173(2) K. Single crystal X-ray data for **5'·3dme** was collected using an Oxford Diffraction Supernova instrument at 120.0(1) K, fitted with a CCD area detector using Mo Kα radiation.

B_2cat_2, $BF_3(OEt_2)$, selenium powder, α,α,α-trifluorotoluene, S_8, Me_3SiCl and [PyH]Cl were purchased from Sigma-Aldrich; α,α,α-trifluorotoluene was used as was, selenium powder, S_8 and [PyH]Cl were stored in the glove box prior to use, and $BF_3(OEt_2)$ and Me_3SiCl were distilled and stored in the glove box prior to use. XeF_2 and tellurium powder were purchased from Alfa Aesar and stored in the glove box prior to use. Ph_3P=Se was purchased from Merck and stored in the glove box prior to use. P_4 was provided by the University of Sussex as a gift and stored in the glove box prior to use. [{(py)U^{IV}OU^{IV}(µ-$O_2C_6H_4$)(py)}(L^A)] (**A**) and [{(py)(pinBO)U^{IV}OU^{IV}(OBpin)(py)}(L^A)] (**B**) were prepared according to the literature procedures.[1]

1.1.2 Syntheses

[{(py)U^{IV}(μ-OH)$_2$U^{IV}(μ-O$_2$C$_6$H$_4$)(py)}(L^A)] (1): A solution of water in pyridine (0.0250 mL, 5.56 M) was added to [{(py)U^{IV}OU^{IV}(μ-O$_2$C$_6$H$_4$)(py)}(L^A)] (204 mg, 0.126 mmol) in pyridine (20 mL) in a 100 mL Schlenk flask under an argon atmosphere. The reaction was stirred for 30 minutes at room temperature. The solvent was then removed under a reduced pressure, and hexanes (30 mL) were added to the crude product. The resulting slurry was sonicated, then the hexanes were removed under a reduced pressure, providing [{(py)U^{IV}(μ-OH)$_2$U^{IV}(μ-O$_2$C$_6$H$_4$)(py)}(L^A)] as a yellow solid. Yield = 151 mg (73 %). X-ray quality crystals of [{(py)U^{IV}(μ-OH)$_2$U^{IV}(μ-O$_2$C$_6$H$_4$)(py)}(L^A)]·2THF were obtained by vapour diffusion of hexanes into a solution of [{(py)U^{IV}(μ-OH)$_2$U^{IV}(μ-O$_2$C$_6$H$_4$)(py)}(L^A)] in THF at room temperature. **Elemental Analysis:** Found: C, 54.60; H, 4.17; N, 8.49. Calc. for $C_{74}H_{64}N_{10}O_4U_2$: C, 54.41; H, 3.95; N, 8.58 %. **IR (Nujol Mull, ν_{max}/cm^{-1}):** 1718w, 1596s, 1555m, 1484s, 1459s, 1377s, 1354w, 1315w, 1290m, 1273w, 1257w, 1236w, 1212w, 1171w, 1150w, 1097w, 1084w, 1055s, 1037m, 1016w, 1007w, 980w, 970w, 960w, 905w, 895w, 880w, 837m, 799m, 791m, 758w, 736s, 722w, 697m, 659w, 632w, 618w, 607w, 588w. **^{1}H NMR (500 MHz; d$_5$-pyridine; 298 K; SiMe$_4$):** δ 95.46 (s, 2H), 57.41 (s, 2H), 36.87 (s, 4H), 33.92 (s, 4H), 29.82 (s, 2H), 25.86 (s, 8H), 22.66 (br s, 6H), 21.88 (s, 6H), 8.99 (br s, 4H), 4.36 (s, 4H), –29.85 (br s, 4H), –34.71 (s, 4H), –36.08 (br s, 2H). **^{13}C{^{1}H} NMR (126 MHz; d$_5$-pyridine; 298 K; SiMe$_4$):** δ 283.2 (br s), 212.4 (br s), 207.0 (br s), 206.3 (br s), 188.4 (br s), 168.7 (br s), 162.1 (s), 157.0 (s), 153.8 (s), 152.7 (s), 151.6 (s), 147.7 (s), 144.7 (s), 137.6 (s), 129.9 (s), 129.2 (s), 127.7 (s), 127.6 (s), 125.8 (s), 122.1 (s), 121.7 (s), 120.6 (s), 119.6 (s), 118.8 (s), 117.7 (s), 111.3 (s), 110.3 (s), 109.4 (s), 106.6 (s), 102.8 (br s), 9.77 (s), 2.39 (s).

[{(py)U^{IV}(μ-OMe)(μ-OH)U^{IV}(μ-O$_2$C$_6$H$_4$)(py)}(L^A)] (2): A solution of methanol in pyridine (0.110 mL, 1.24 M) was added to [{(py)U^{IV}OU^{IV}(μ-O$_2$C$_6$H$_4$)(py)}(L^A)] (225 mg, 0.139 mmol) in pyridine (20 mL) in a 100 mL Schlenk flask under an argon atmosphere. The reaction was stirred for 30 minutes at room temperature. The solvent was then removed under a reduced pressure, and hexanes (30 mL) were added to the crude product. The resulting slurry was sonicated, then the hexanes were removed under a reduced pressure, providing [{(py)U^{IV}(μ-OMe)(μ-OH)U^{IV}(μ-O$_2$C$_6$H$_4$)(py)}(L^A)] as a yellow solid. Yield = 124 mg (54 %). X-ray quality crystals of [{(py)U^{IV}(μ-OMe){(μ-OMe)$_{0.69}$(μ-OH)$_{0.31}$}U^{IV}(μ-O$_2$C$_6$H$_4$)(py)}(L^A)]·C$_6$H$_6$ were obtained by vapour diffusion of hexanes into a solution of [{(py)U^{IV}(μ-OMe)(μ-OH)U^{IV}(μ-O$_2$C$_6$H$_4$)(py)}(L^A)] in benzene at room temperature. **Elemental Analysis:** Found: C, 54.77; H, 4.02; N, 8.32. Calc. for $C_{75}H_{66}N_{10}O_4U_2$: C, 54.68; H, 4.04; N, 8.50 %. **IR (Nujol Mull, ν_{max}/cm^{-1}):** 1599s, 1556m, 1485s, 1457s, 1377m, 1367w, 1354w, 1316w, 1304w, 1290w, 1274w, 1256w, 1243w, 1234w, 1214w, 1169w, 1149w, 1098w, 1085w, 1057m, 1037w, 1015w, 1008w, 978w, 964w, 909w, 895w, 879w, 863w, 839m, 798w, 791w, 761w, 736m, 724w, 698m, 661w, 646w, 638w, 624w, 619w, 606w, 589w. **^{1}H NMR (500 MHz; d$_5$-pyridine; 298 K; SiMe$_4$):** δ 96.65 (s), 58.18 (s), 37.40, 37.28 (2×s), 34.96 (s), 33.71 (s), 30.66 (s), 29.48 (s), 26.04 (s), 23.56 (s), 22.62 (s), 21.50 (s), 9.79 (s), 4.76 (s), 4.36 (s), 3.64 (s), –28.08, –28.55 (2×br s), –32.32 (br s), –33.36 (s), –35.89 (s). **^{1}H NMR (500 MHz; d$_5$-pyridine; 360 K; SiMe$_4$):** δ 78.48 (s, 1H), 47.87 (s, 2H), 30.53 (s, 2H), 30.20 (s, 2H), 29.35 (s, 2H), 28.59 (s, 2H), 25.89 (s, 1H), 25.01 (s, 1H), 21.27 (s, 8H), 19.43 (s, 2H), 18.71 (2, 6H), 18.57 (s, 2H), 9.16 (s, 1H), 5.24 (s, 2H), 4.65 (s, 2H), 3.64 (s, 6H), –21.69 (s, 2H), –24.63 (s, 2H), –25.01 (s, 2H), –26.47 (s, 1H), –27.28 (s, 2H). **^{13}C{^{1}H} NMR (126 MHz; d$_5$-pyridine; 298 K; SiMe$_4$):** δ 289.0 (br s), 209.6 (br s), 191.8 (br s), 173.8 (br s), 167.6 (br s), 164.2 (s), 162.9 (s), 161.6 (s), 161.0 (s), 160.0 (br s), 158.0 (br s), 157.0 (br s), 151.6 (s), 146.5 (s), 145.9 (s), 144.6 (s), 138.5 (s), 137.6 (s), 134.0 (s), 133.8 (s), 133.0 (br s), 132.3 (s), 127.8 (s), 127.6 (s), 127.3 (s), 126.9 (s), 126.7 (s), 126.6 (br s), 126.4 (s), 126.2 (s), 125.7 (s), 122.1 (s), 121.8 (s), 121.7 (s), 120.6 (br s), 119.9 (br s), 119.4 (br s), 118.0 (s), 117.2 (s), 116.1 (s), 113.6 (s), 113.1 (s), 111.2 (s), 110.4 (br s), 109.9 (br s), 106.7 (s), 104.3 (br s), 50.2 (br s), 45.6 (br s), 24.2 (br s), 9.3 (br s).

[{(py)U^{IV}(μ-η^2:η^2-S$_2$)U^{IV}(μ-O$_2$C$_6$H$_4$)(py)}(L^A)] (3): Pyridine (20 mL) was added to [{(py)U^{IV}OU^{IV}(μ-O$_2$C$_6$H$_4$)(py)}(L^A)] (188 mg, 0.117 mmol) and S$_8$ (15.0 mg, 5.85×10^{-2} mmol) in a 100 mL ampoule under an argon atmosphere. The reaction was stirred overnight at room temperature then overnight at 80 ^{o}C. The reaction solution was then cannulated into a Schlenk flask and the solvent was removed under a reduced pressure. The crude product was sonicated in hexanes (20 mL) and filtered, providing [{(py)U^{IV}(μ-η^2:η^2-S$_2$)U^{IV}(μ-O$_2$C$_6$H$_4$)(py)}(L^A)] as a brown/yellow powder which was washed with hexanes (2×10 mL) and dried under a reduced pressure. Yield = 107 mg (55 %). X-ray quality crystals of [{(py)U^{IV}(μ-η^2:η^2-S$_2$)U^{IV}(μ-O$_2$C$_6$H$_4$)(py)}(L^A)]·5py were obtained from a concentrated solution of [{(py)U^{IV}(μ-η^2:η^2-S$_2$)U^{IV}(μ-O$_2$C$_6$H$_4$)(py)}(L^A)] in pyridine at room temperature. **Elemental Analysis:** Found: C, 53.21; H, 3.81; N, 8.30. Calc. for $C_{74}H_{62}N_{10}O_2S_2U_2$: C, 53.43; H, 3.76; N, 8.42 %. **IR (Nujol Mull, ν_{max}/cm^{-1}):** 1714w, 1597s, 1553m, 1481s, 1458s, 1377s, 1353w, 1314w, 1305w, 1281m, 1252w, 1236w, 1210w, 1167w, 1149w, 1091m, 1056s, 1039m, 1008m, 973w, 958w, 905w, 892w, 874m, 840m, 784w, 751w, 735s, 699m, 658w, 625w, 612w, 603w, 589w, 533w. **^{1}H NMR (600 MHz; d$_5$-pyridine; 298 K; SiMe$_4$):** δ 62.24 (s, 2H), 39.03 (s, 4H), 37.38 (s, 8H), 32.37 (s, 6H), 32.05 (s, 2H), 22.98 (s, 4H), 15.44 (s, 6H), 7.01, 6.95 (2×s, 10H), –11.87 (br s, 2H), –28.81 (s, 4H), –40.90 (s, 4H). **^{13}C{^{1}H} NMR (126 MHz; d$_5$-pyridine; 298 K; SiMe$_4$):** δ 176.3 (s), 167.0 (s), 156.9 (s), 153.8 (s), 149.9 (s), 146.8 (br s), 145.8 (s), 138.5 (s), 137.6 (s), 136.5 (s), 136.4 (s), 135.5 (s), 134.0 (s), 127.6 (s), 127.5 (s), 127.3 (s), 126.2 (s), 124.6 (s), 124.5 (s), 124.4 (s), 121.6 (s), 120.6 (s), 120.0 (s), 119.8 (s), 119.6 (s), 118.7 (s), 117.7 (s), 116.1 (s), 111.2 (s), 110.3 (s), 109.4 (s), 107.7 (s), 106.6 (s), 32.2 (s), 23.3 (s), 14.7 (s), 2.36 (s).

Synthesis of [{(py)U^{IV}(μ-η^2:η^2-S$_2$)U^{IV}(μ-O$_2$C$_6$H$_4$)(py)}(L^A)] (3) from CS$_2$: CS$_2$ (3.6 mg, 4.73×10^{-2} mmol) was added to [{(py)U^{IV}OU^{IV}(μ-O$_2$C$_6$H$_4$)(py)}(L^A)] (24.6 mg, 1.52×10^{-2} mmol) dissolved in d$_5$-pyridine (~0.6 mL) in a J-Young NMR tube, and heated to 120 °C for 4 days. The resulting ^{1}H NMR spectrum (in d$_5$-pyridine) was the same as that of complex **3**.

[{(py)U^{IV}(μ-η^2:η^2-Se$_2$)U^{IV}(μ-O$_2$C$_6$H$_4$)(py)}(L^A)] (4): Pyridine (50 mL) was added to [{(py)U^{IV}OU^{IV}(μ-O$_2$C$_6$H$_4$)(py)}(L^A)] (231 mg, 0.143 mmol) and elemental selenium (90.5 mg, 1.15 mmol (8 equiv., excess)) in a 100 mL ampoule under an argon atmosphere. The reaction was stirred for 48 hours while heated to 125 ^{o}C. The reaction solution was then cannulated into a Schlenk flask and the solvent was removed under a reduced pressure. The crude product was sonicated in hexanes (50 mL) and filtered, providing [{(py)U^{IV}(μ-η^2:η^2-Se$_2$)U^{IV}(μ-O$_2$C$_6$H$_4$)(py)}(L^A)] as a hickory coloured powder which was washed with hexanes (2×20 mL) and dried under a reduced pressure. Yield = 107 mg (55 %). X-ray quality crystals of [{(py)U^{IV}(μ-η^2:η^2-Se$_2$)U^{IV}(μ-O$_2$C$_6$H$_4$)(py)}(L^A)]·2CH$_2$Cl$_2$·solvent were obtained by vapour diffusion of hexanes into a solution of [{(py)U^{IV}(μ-η^2:η^2-Se$_2$)U^{IV}(μ-O$_2$C$_6$H$_4$)(py)}(L^A)] in CH$_2$Cl$_2$ at room temperature; residual electron density from highly disordered lattice solvent was removed from the structure using the "solvent mask" feature of Olex2 (84.6 electrons/unit cell), rendering the lattice solvent unidentified. **Elemental Analysis:** Found: C, 50.77; H, 3.68; N, 7.86. Calc. for $C_{74}H_{62}N_{10}O_2Se_2U_2$: C, 50.58; H, 3.56; N, 7.97 %. **IR (Nujol Mull, ν_{max}/cm^{-1}):** 1716w, 1627w, 1592s, 1550m, 1481m, 1458s, 1377s, 1352w, 1313w, 1286m, 1274w, 1263w, 1252w, 1244w, 1235w, 1210m, 1167w, 1150w, 1106w, 1088w, 1054m, 1037m, 1019w, 1011m, 978w, 959w, 903w, 894w, 875m, 861w, 840m, 780w, 758w, 743w, 732m, 721w, 701m, 658w, 627w, 617w, 604w, 587w, 531w. **^{1}H NMR (500 MHz; d$_5$-pyridine; 298 K; SiMe$_4$):** δ 62.49 (s, 2H), 39.10 (s, 4H), 37.99 (s, 4H), 37.65 (s, 4H), 33.57 (s, 6H, 2×CH$_2$C*H*$_3$), 31.94 (s, 2H), 22.83, 22.81 (2×s, 4H), 15.18 (s, 6H, 2×CH$_2$C*H*$_3$), 7.46 (br s, 4H), 6.11 (br s, 2H), 3.02 (br s, 4H, tentatively assigned), –2.81 (br s, 2H), –28.55 (s, 4H), –41.70 (s, 4H). **^{13}C{^{1}H} NMR (126 MHz; d$_5$-pyridine; 298 K; SiMe$_4$):** δ 236.7 (br s), 235.7 (br s), 217.3 (br s), 201.8 (br s), 177.9 (s), 167.6 (s), 164.1 (br s), 163.9 (br s), 157.0 (s), 154.0 (s), 153.0 (s), 152.0 (s), 151.5 (s), 147.0 (br s), 145.9 (s), 138.5 (s), 137.6 (s), 134.0 (s), 129.9 (s), 129.2 (s), 127.7 (s), 127.3 (s), 126.2 (s), 123.1 (s), 121.7 (s), 119.6 (s), 118.6 (s), 117.7 (s), 116.1 (s), 110.3 (s), 109.3 (s), 108.2 (s), 106.6 (s), 100.9 (br s), 98.5 (br s), 94.7 (br s), 32.2 (s), 31.7 (br s), 23.3 (s), 21.8 (s), 14.7 (s), 10.5 (br s), 2.4 (s), –9.9 (s).

[{(py)U^{IV}(μ-F)$_2$U^{IV}(μ-O$_2$C$_6$H$_4$)(py)}(L^A)] (5): XeF_2 (26.6 mg, 0.157 mmol) was added to [{(py)U^{IV}OU^{IV}(μ-O$_2$C$_6$H$_4$)(py)}(L^A)] (253 mg, 0.157 mmol) dissolved in pyridine (25 mL) in a 100 mL ampoule and the reaction was stirred for 24 hours at room temperature followed by 24 hours at 80 °C. The reaction solution was then brought into the glove box, layered with hexanes (~25 mL) and left at room temperature for recrystallisation. Following several days of hexanes diffusion into the pyridine solution, lime green crystals of needle morphology were obtained; recrystallised [{(py)U^{IV}(μ-F)$_2$U^{IV}(μ-O$_2$C$_6$H$_4$)(py)}(L^A)] was isolated by decanting the mother liquors and drying the collected solid under a reduced pressure. Yield = 103 mg (40 %). X-ray quality crystals of [{(py)U^{IV}(μ-F)$_2$U^{IV}(μ-O$_2$C$_6$H$_4$)(py)}(L^A)]·4py·solvent were obtained by vapour diffusion of hexanes into a solution of [{(py)U^{IV}(μ-F)$_2$U^{IV}(μ-O$_2$C$_6$H$_4$)(py)}(L^A)] in pyridine at room temperature; residual electron density from highly disordered lattice solvent was removed from the structure using the "solvent mask" feature of Olex2 (90.6 electrons/unit cell), rendering the lattice solvent unidentified. **Elemental Analysis:** Found: C, 53.99; H, 3.83; N, 8.64. Calc. for $C_{74}H_{62}F_2N_{10}O_2U_2$: C, 54.28; H, 3.94; N, 8.56 %. **IR (Nujol Mull, ν_{max}/cm^{-1}):** 1740w, 1721w, 1616w, 1597m, 1555w, 1481m, 1460s, 1377s, 1312w, 1259w, 1235w, 1214w, 1147w, 1095w, 1056m, 1007w, 990w, 913w, 873w, 840w, 796w, 736m, 702m. **^{1}H NMR (600 MHz; d$_5$-pyridine; 298 K; SiMe$_4$):** δ 64.89 (s), 41.46 (s), 38.76 (s), 33.19 (s), 29.84 (s), 24.19 (s), 21.20 (br s), 5.00 (br s), –35.75 (br s), –41.64 (s), –55.51 (br s). **^{1}H NMR (500 MHz; d$_5$-pyridine; 360 K; SiMe$_4$):** δ 88.91 (s, 2H), 53.03 (s, 2H), 50.40 (broad s, 4H), 33.51 (s, 4H), 32.32 (s, 4H), 27.79 (s, 2H), 24.37 (s, 6H), 20.61 (s, 4H), 16.57 (s, 6H), 8.57, 8.56 (2×s, 4H), 4.07 (s, 4H), –27.19 (s, 4H), –31.82 (s, 4H), –43.00 (br s, 2H). **^{13}C{^{1}H} NMR (126 MHz; d$_5$-pyridine; 298 K; SiMe$_4$):** 201.3 (br s), 174.4 (br s), 167.5 (s), 162.9 (s), 161.0 (s), 156.9 (s), 153.9 (br s), 153.7 (br s), 153.1 (br s), 153.0 (s), 152.3 (s), 151.6 (s), 145.9 (s), 145.2 (s), 143.5 (br s), 138.5 (s), 137.6 (s), 134.0 (s), 133.7 (s), 132.3 (s), 127.8 (s), 127.7 (s), 127.6 (s), 127.3, 127.3 (2×s), 126.7 (s), 126.4 (s), 125.7 (s), 122.1 (s), 121.7 (s), 120.6 (s), 120.0 (s), 119.6 (s), 118.7 (br s), 118.0 (s), 117.7 (s), 117.2 (s), 116.1 (s), 113.1 (s), 106.7 (s), 106.6 (s), 99.2 (br s), 10.4 (br s).

[{(py)U^{IV}(μ-F)(μ-OBcat)U^{IV}(μ-O$_2$C$_6$H$_4$)(py)}(L^A)] (5A): XeF_2 (23.0 mg, 0.136 mmol) was added to [{(py)U^{IV}OU^{IV}(μ-O$_2$C$_6$H$_4$)(py)}(L^A)] (220 mg, 0.136 mmol) containing approximately 1 equiv. of catBOBcat byproduct dissolved in pyridine (20 mL) in a 100 mL Schlenk flask inside the glove box and the reaction was stirred for 24 hours at room temperature. The reaction solution was then evaporated to dryness under a reduced pressure and the crude product was sonicated in hexanes (30 mL), producing a yellow/brown slurry. The hexanes were then removed under a reduced pressure, providing [{(py)U^{IV}(μ-F)$_2$U^{IV}(μ-O$_2$C$_6$H$_4$)(py)}(L^A)] as a brown/yellow solid. Yield = 162 mg (68 %). X-ray quality crystals of [{(py)U^{IV}(μ-F)(μ-OBcat)U^{IV}(μ-O$_2$C$_6$H$_4$)(py)}(L^A)]·3dme were obtained from a concentrated solution of [{(py)U^{IV}(μ-F)(μ-OBcat)U^{IV}(μ-O$_2$C$_6$H$_4$)(py)}(L^A)] in 1,2-dimethoxyethane cooled to –30 °C. **Elemental Analysis:** Found: C, 54.60; H, 4.07; N, 8.26. Calc. for $C_{80}H_{66}BFN_{10}O_5U_2$: C, 54.80; H, 3.79; N, 7.99 %. **IR (Nujol Mull, ν_{max}/cm^{-1}):** 1714w, 1600s, 1556s, 1485s, 1459s, 1398w, 1378s, 1355w, 1315w, 1290m, 1275m, 1254w, 1235m, 1212m, 1170w, 1152w, 1097m, 1086w, 1056s, 1037w, 1016m, 1006m, 980w, 965w, 959w, 909m, 896w, 881w, 837m, 790w, 760w. 737s, 723w, 696m, 658w, 652w, 627w, 619w, 607w, 589w. **^{1}H NMR (600 MHz; d$_5$-pyridine; 298 K; SiMe$_4$):** δ 102.25 (s), 60.80 (s), 39.82 (br s), 38.13 (s), 36.28, 35.96 (2×br s), 31.49 (s), 31.15 (s), 27.76 (s), 22.90 (br s), 21.39 (br s), 3.55 (s), –38.01 (s). **^{1}H NMR (500 MHz; d$_5$-pyridine; 360 K; SiMe$_4$):** δ 81.60 (s, 2H), 52.95 (br s, 2H), 49.54 (s, 2H), 49.20 (s, 2H), 31.65 (s, 2H), 30.66 (s, 2H), 29.99 (s, 4H), 26.36 (s, 1H), 25.82 (s, 1H), 22.33 (s, 6H), 19.59 (s, 2H), 19.33 (s, 2H), 16.81 (s, 6H), 8.56 (br s, 2H), 8.46, 8.45 (2×br s, 2H), 7.00 (br s, 4H), 4.50 (s, 2H), 4.27 (s, 2H), 0.36 (s, 1H), –23.08 (s, 2H), –25.27 (s, 2H), –28.29 (s, 2H), –28.48 (s, 2H), –42.64 (br s, 1H). **^{13}C{^{1}H} NMR (126 MHz; d$_5$-pyridine; 298 K; SiMe$_4$):** δ 213.0 (br s), 211.9 (br s), 194.4 (br s), 171.3 (br s), 164.4 (br s), 157.0 (s), 152.7 (s), 151.6 (s), 146.0 (br s), 143.5 (br s), 127.6 (s), 126.9 (s), 126.6 (br s), 122.1 (s), 121.7 (s), 120.1 (s), 118.7 (s), 111.3 (s), 110.9 (s), 109.4 (s), 102.7 (br s), 71.0 (br s), 36.4 (br s), 11.0 (br s), 9.4 (br s). **^{19}F NMR (471 MHz; d$_5$-pyridine; 300 K; α,α,α-trifluorotoluene):** δ 141 (broad s, $\omega_{1/2}$ ~100 Hz).

[{(py)U^{IV}(μ-Cl)$_2$U^{IV}(μ-O$_2$C$_6$H$_4$)(py)}(L^A)] (6): Pyridine (50 mL) was added to [{(py)U^{IV}OU^{IV}(μ-O$_2$C$_6$H$_4$)(py)}(L^A)] (427 mg, 0.264 mmol) and Me$_3$SiCl (57.5 mg, 0.529 mmol) in a 100 mL ampoule under an argon atmosphere and the reaction was stirred for 48 hours at 80 °C. The reaction solution was then cannulated into a Schlenk flask and the solvent was removed under a reduced pressure. The crude product was sonicated in toluene (50 mL) and filtered, providing [{(py)U^{IV}(μ-Cl)$_2$U^{IV}(μ-O$_2$C$_6$H$_4$)(py)}(L^A)] as a brown/yellow solid which was washed with hexanes (2×20 mL) and dried under a reduced pressure. Yield = 252 mg (57 %). X-ray quality crystals of [{(py)U^{IV}(μ-Cl)$_2$U^{IV}(μ-O$_2$C$_6$H$_4$)(py)}(L^A)]·solvent were obtained from vapour diffusion of hexanes into a solution of [{(py)U^{IV}(μ-Cl)$_2$U^{IV}(μ-O$_2$C$_6$H$_4$)(py)}(L^A)] in pyridine at room temperature; residual electron density from highly disordered lattice solvent was removed from the structure using the "solvent mask" feature of Olex2 (393.3 electrons/unit cell), rendering the lattice solvent unidentified. **Elemental Analysis:** Found: C, 53.35; H, 3.95; N, 8.26. Calc. for $C_{74}H_{62}Cl_2N_{10}O_2U_2$: C, 53.21; H, 3.86; N, 8.39 %. **IR (Nujol Mull, ν_{max}/cm^{-1}):** 1713w, 1591s, 1552s, 1481s, 1456s, 1378s, 1353w, 1312w, 1288m, 1273m, 1252w, 1242w, 1210m, 1169w, 1085w, 1055m, 1037m, 1017w, 1005w, 980w, 958w, 895w, 880w, 866w, 841m, 757m, 736s, 696m, 657w, 625w, 613w, 606w, 589w. **^{1}H NMR (500 MHz; d$_5$-pyridine; 298 K; SiMe$_4$):** δ 65.90 (s, 2H), 50.54 (broad s, 2H), 41.01 (s, 4H), 39.86 (s, 4H), 33.45 (s, 2H), 32.16 (s, 6H), 24.09 (s, 4H), 18.21 (s, 6H), 8.87 (s, 4H), 8.28 (s, 4H), 5.36 (s, 4H), –12.62 (broad s, 2H), –39.25 (s, 8H).

Synthesis of [{(py)U^{IV}(μ-Cl)$_2$U^{IV}(μ-O$_2$C$_6$H$_4$)(py)}(L^A)] (6) from 1 and [PyH]Cl: [PyH]Cl (3.5 mg, 3.03×10^{-2} mmol) was added to [{(py)U^{IV}(μ-OH)$_2$U^{IV}(μ-O$_2$C$_6$H$_4$)(py)}(L^A)] (24.8 mg, 1.52×10^{-2} mmol) dissolved in d$_5$-pyridine (~0.6 mL) in a J-Young NMR tube, and sonicated for 1 hour. The resulting ^{1}H NMR spectrum (in d$_5$-pyridine) is the same as that of complex **6**.

[{(py)U^{IV}(μ-Cl)(μ-OBcat)U^{IV}(μ-O$_2$C$_6$H$_4$)(py)}(L^A)] (6A): Pyridine (20 mL) was added to [{(py)U^{IV}OU^{IV}(μ-O$_2$C$_6$H$_4$)(py)}(L^A)] (216 mg, 0.134 mmol) containing approximately 1 equiv. of catBOBcat byproduct and Me$_3$SiCl (29.1 mg, 0.268 mmol) in a 100 mL ampoule under an argon atmosphere and the reaction was stirred for 24 hours at room temperature. The reaction solution was then cannulated into a Schlenk flask and the solvent was removed under a reduced pressure. The crude product was sonicated in hexanes (20 mL) and filtered, providing [{(py)U^{IV}(μ-Cl)(μ-OBcat)U^{IV}(μ-O$_2$C$_6$H$_4$)(py)}(L^A)] as a brown/yellow solid which was washed with hexanes (2×10 mL) and dried under a reduced pressure. Yield = 135 mg (57 %). **Elemental Analysis:** Found: C, 54.42; H, 3.91; N, 7.86. Calc. for $C_{80}H_{66}BClN_{10}O_5U_2$: C, 54.29; H, 3.76; N, 7.92 %. **IR (Nujol Mull, ν_{max}/cm^{-1}):** 1720w, 1623w, 1596s, 1554m, 1484s, 1463s, 1377m, 1352w, 1315w, 1283m, 1275m, 1253m, 1212w, 1098w, 1087w, 1056m, 1039w, 1013w, 1009w, 978w, 961w, 912w, 894w, 874m, 842m, 805w, 760w, 739s, 698m. **^{1}H NMR (600 MHz; d$_5$-pyridine; 298 K; SiMe$_4$):** δ 100.84 (s, 2H), 60.69 (s, 2H), 38.31 (s, 4H), 36.86 (s, 2H), 35.98 (s, 2H), 32.00 (s, 1H), 30.82 (s, 1H), 28.26 (broad s, 6H), 23.38 (s, 2H), 22.23 (s, 2H), 21.62 (broad s, 6H), 9.62 (s, 4H), 6.17 (s, 2H), 5.77 (s, 2H), 3.68 (s, 2H), 3.10 (s, 6H), –31.37 (broad s, 2H), –34.48 (s, 2H), –36.62 (s, 2H), –38.30 (s, 2H). **^{13}C{^{1}H} NMR (126 MHz; d$_5$-pyridine; 298 K; SiMe$_4$):** δ 195.9 (broad s), 176.8 (broad s), 172.1 (broad s), 166.8 (s), 164.7 (s), 157.0 (s), 154.0 (broad s), 153.1 (broad s), 153.0 (broad s), 152.8 (s), 147.6 (broad s), 145.4 (broad s), 145.1 (broad s), 137.7 (s), 129.8 (broad s), 127.6 (broad s), 126.3 (s), 123.1 (s), 122.3 (s), 122.2 (s), 121.7 (s), 120.7 (s), 120.1 (s), 119.6 (s), 118.8 (s), 115.9 (broad s), 111.3 (s), 110.5 (s), 110.3 (s), 109.5 (s), 102.9 (broad s), 71.0 (broad s), 45.8 (broad s), 43.9 (broad s), 35.2 (broad s), 10.8 (broad s). **^{11}B NMR (161 MHz; d$_5$-pyridine; 300 K; BF$_3$·OEt$_2$):** δ 435 (broad s, $\omega_{1/2}$ ~470 Hz).

[{(py)U^{IV}OU^{IV}(μ-O$_2$C$_6$H$_4$)(py)}(L^A)] + 4Te: [{(py)U^{IV}OU^{IV}(μ-O$_2$C$_6$H$_4$)(py)}(L^A)] (21.2 mg, 1.31×10^{-2} mmol) and Te (6.7 mg, 5.25×10^{-2}) were mixed together in a J-Young NMR tube with d$_5$-pyridine (~0.6 mL) and heated to 120 °C for 3 days. No reaction had occurred, as determined by ^{1}H NMR spectroscopy (in d$_5$-pyridine).

[{(py)U^{IV}OU^{IV}(μ-$O_2C_6H_4$)(py)}(L^A)] + P_4: [{(py)U^{IV}OU^{IV}(μ-$O_2C_6H_4$)(py)}(L^A)] (24.6 mg, 1.52×10^{-2} mmol) and P_4 (2.0 mg, 1.61×10^{-2}) were mixed together in a J-Young NMR tube with d_5-pyridine (~0.6 mL) and heated to 105 °C for 4 days. No reaction had occurred, as determined by ^{1}H NMR spectroscopy (in d_5-pyridine). UV irradiation was also attempted, deploying wavelengths of 410, 365 and 254 nm for periods of 16 hours each, however still no reaction occurred.

[{(py)U^{IV}OU^{IV}(μ-$O_2C_6H_4$)(py)}(L^A)] + Ph_3P=Se: [{(py)U^{IV}OU^{IV}(μ-$O_2C_6H_4$)(py)}(L^A)] (23.9 mg, 1.48×10^{-2} mmol) and Ph_3P=Se (5.1 mg, 1.50×10^{-2}) were mixed together in a J-Young NMR tube with d_5-pyridine (~0.6 mL) and heated to temperatures of 80, 100 and 130 °C for time periods of 16 hours at each temperature. No reaction had occurred, as determined by ^{1}H NMR spectroscopy (in d_5-pyridine).

[{(py)(pinBO)U^{IV}OU^{IV}(OBpin)(py)}(L^A)] + XeF_2: XeF_2 (2.9 mg, 1.71×10^{-2} mmol) was added to [{(py)(pinBO)U^{IV}OU^{IV}(OBpin)(py)}(L^A)] (30.2 mg, 1.68×10^{-2} mmol) dissolved in d_5-pyridine (~0.6 mL) in a J-Young NMR tube, and left at room temperature for 30 minutes. The resulting ^{1}H NMR spectrum was the same as [UO_2(py)(H_2L^A)] and other unidentifiable diamagnetic species (in d_5-pyridine).

[{(py)(OH)U^{IV}OU^{IV}(OH)(py)}(L^A)] (7) from [{(py)(pinBO)U^{IV}OU^{IV}(OBpin)(py)}(L^A)] and Excess H_2O: A solution of H_2O in pyridine (0.04 mL, 2.78 M) was added to [{(py)(pinBO)U^{IV}OU^{IV}(OBpin)(py)}(L^A)] (18.8 mg, 1.05×10^{-2} mmol) dissolved in d_5-pyridine in an NMR tube, and left to sit at room temperature for 30 minutes. The resulting ^{1}H and ^{11}B NMR spectra indicated the formation of **7** and 2 equiv. of HOBpin as the reaction byproduct had occurred, and were unchanged after at least 24 hours at room temperature. **^{1}H NMR (600 MHz; d_5-pyridine; 298 K; $SiMe_4$):** 48.23 (broad s, 2H), 36.81 (s, 4H), 35.07 (s, 4H), 28.20 (s, 2H), 26.06 (broad s, 4H), 19.79 (s, 4H), 14.99 (broad s, 6H), 10.44 (s, 2H), 6.91 (s, 4H), 6.59 (s, 6H), 5.21 (s, 4H), –31.31 (s, 4H), –34.34 (s, 4H). **^{13}C{^{1}H} NMR (126 MHz; d_5-pyridine; 298 K; $SiMe_4$):** 217.4 (broad s), 193.3 (s), 178.8 (s), 170.9 (s), 166.0 (broad s), 160.2 (s), 158.7 (s), 158.4 (s), 157.3 (s), 156.6 (s), 154.5 (s), 152.1 (s), 151.0 (s), 142.5 (s), 142.4 (s), 133.3 (s), 132.4 (s), 132.2 (s), 128.6 (s), 126.8 (s), 126.6 (s), 125.4 (s), 122.5 (s), 121.2 (broad s), 112.1 (s), 111.9 (s), 110.9 (s), 110.8 (s), 110.6 (s), 104.4 (broad s), 98.6 (broad s), 97.5 (broad s), 95.0 (broad s), 76.1 (broad s), 69.8 (broad s), 46.1 (s), 45.6 (s), 31.9 (s), 30.4 (s), 30.1 (s), 28.8 (broad s), 23.0 (s), 14.4 (s), 9.5 (s), 9.3 (s), 9.2 (s), 9.0, 9.0 (2 × s), 8.9 (s).

[{(py)ClU^{IV}OU^{IV}Cl(py)}(L^A)] (8) from [{(py)(pinBO)U^{IV}OU^{IV}(OBpin)(py)}(L^A)] and Me_3SiCl: Me_3SiCl (3.8 mg, 3.50×10^{-2} mmol) in d_5-pyridine (~0.2 mL) was added to [{(py)(pinBO)U^{IV}OU^{IV}(OBpin)(py)}(L^A)] (31.2 mg, 1.74×10^{-2} mmol) dissolved in d_5-pyridine (~0.4 mL) in a J-Young NMR tube, and left at room temperature overnight. The resulting reaction solution appeared to be a mixture of products, given the presence of Me_3SiO*B*pin and other paramagnetic boron-containing species in the resulting ^{11}B NMR spectrum. A third equiv. of Me_3SiCl was then added (2.0 mg, 1.84×10^{-2} mmol) and the reaction solution was left at room temperature for 30 minutes. The resulting ^{11}B NMR spectrum only contained Me_3SiO*B*pin and the ^{29}Si_INEPT NMR spectrum contained Me_3*Si*OBpin and (Me_3*Si*)$_2$O in an approximate 6:1 ratio, along with unreacted Me_3*Si*Cl (all NMR spectra were recorded in d_5-pyridine). X-ray quality crystals of **[{(py)ClU^{IV}OU^{IV}Cl(py)}(L^A)]·solvent** (**8·solvent**) were obtained via vapour diffusion of hexanes into the pyridine reaction mixture at room temperature; residual electron density from highly disordered lattice solvent was removed from the structure using the "solvent mask" feature of Olex2 (81.1 electrons/unit cell), rendering the lattice solvent unidentified.

[{(py)(pinBO)U^{IV}OU^{IV}(OBpin)(py)}(L^A)] + 10 equiv. of Me_3SiCl: Me_3SiCl (14.4 mg, 0.133 mmol) in d_5-pyridine (~0.2 mL) was added to [{(py)(pinBO)U^{IV}OU^{IV}(OBpin)(py)}(L^A)] (23.7 mg, 1.32×10^{-2} mmol) dissolved in d_5-pyridine (~0.4 mL) in a J-Young NMR tube, and left at room temperature overnight. The resulting ^{11}B NMR spectrum contained Me_3SiO*B*pin and an unknown compound giving rise to a singlet at 7.51 ppm in an approximate 3:1 ratio, and the ^{29}Si_INEPT NMR spectrum contained Me_3*Si*OBpin

and $(Me_3Si)_2O$ in an approximate 1:1 ratio, along with unreacted Me_3SiCl (all NMR spectra were recorded in d_5-pyridine).

1.1.3 Crystallographic Details

General X-ray Experimental Details

The molecular structures of **1·3THF**, **2·C_6H_6**, **3·5py**, **4·2CH_2Cl_2**, **5·4py**, **5A·3dme**, **6** and **8** were solved using SHELXT[2] and least-square refined using SHELXL[3] in Olex2.[4] Hydrogen atoms were treated by constrained refinement, except for H(3) in **1·3THF** which was located in the difference map.

A molecule of THF in the asymmetric unit of [{(py)U^{IV}(μ-OH)$_2U^{IV}$(μ-$O_2C_6H_4$)(py)}(L^A)]·3THF (**1·3THF**) was positionally disordered over two positions. As a result, it was split into two parts and refined with an occupancy ratio of 0.73:0.27. In addition, the thermal parameters of the carbon atoms were restrained to be similar to one another through the use of the SIMU command. C(10) was also positionally disordered over two positions, and was split into two parts and refined with a 0.69:0.31 ratio. The thermal parameters of C(10) and C(10A) were restrained to be similar to one another through the use of the SIMU command.

A molecule of lattice benzene in [{(py)U^{IV}(μ-OMe)$_{1.69}$(μ-OH)$_{0.31}U^{IV}$(μ-$O_2C_6H_4$)(py)}(L^A)]·C_6H_6 (**2-OMe/OH·C_6H_6**) was positionally disordered over two positions. As a result, it was split into two parts and refined with an occupancy ratio of 0.58:0.42. In addition, the thermal parameters of the carbon atoms were restrained to be similar to one another through the use of the SIMU command. C(8) was also positionally disordered over two positions, and was split into two parts and refined with a 0.58:0.42 ratio. The thermal parameters of C(8) and C(8A) were restrained to be similar to one another through the use of the SIMU command, and the C(7)-C(8) and C(7)-C(8A) distances were restrained to be similar to one another using the SADI command. The thermal ellipsoids of the carbon atoms of the bridging catecholate ligand (C(69)-C(74)) were restrained using the RIGU command, and the thermal ellipsoids of the carbon atoms of one of the anthracenyl ligand linkers (C(45)-C(58)) were restrained using the RIGU command. Finally, one of the bridging methoxy ligands possesses full occupancy (C(75)) whereas the other only possesses partial occupancy (C(76)). C(76) was refined freely with an occupancy of 0.69, and the remainder of the 0.31 occupancy bound to O(4) is attributed to a hydrogen atom (based on a ^{1}H NMR spectrum indicating that there is one methoxy and one hydroxy ligand bridging the two U centres). However, the hydrogen atom with 0.31 occupancy could not be located in the difference map.

[{(py)U^{IV}(μ-η^2:η^2-S_2)U^{IV}(μ-$O_2C_6H_4$)(py)}(L^A)]·5py (**3·5py**) was refined as a 2-component twin with component 1 being equal to 78% (BASF = 0.2209(2)) using SADABS. The thermal ellipsoids of the carbon atoms of one of the U-coordinated pyridine ligands (N(10), C(70), C(71), C(72), C(73), C(74)) were restrained using the RIGU command. Furthermore, two of the lattice pyridine molecules (C(886), C(887), C(888)/N(888) and C(997), C(998), C(999)/N(999)) reside on special positions. Therefore, one carbon atom per pyridine molecule (C(888) and C(999)) was assigned as both a carbon atom and a nitrogen atom with 50% occupancy. The positional and thermal parameters of the N/C refined atoms were fixed using the EXYZ and EADP commands, respectively.

The molecule of pyridine coordinated to U(2) in [{(py)U^{IV}(μ-η^2:η^2-Se_2)U^{IV}(μ-$O_2C_6H_4$)(py)}(L^A)]·2CH_2Cl_2·solvent (**4·2CH_2Cl_2·solvent**; N(10), C(70), C(71), C(72), C(73), C(74)) was positionally disordered over two positions. As a result, it was split into two parts and refined with an occupancy ratio of 0.58:0.42. In addition, the thermal parameters of the carbon and nitrogen atoms were restrained to be similar to one another, respectively, through the use of the SIMU command. In addition, residual lattice electron density (presumably from highly disordered lattice solvent) was modelled using the "solvent mask" feature of Olex2 (84.6 electrons/cell).

A molecule of lattice pyridine in [{(py)U^{IV}(μ-F)$_2U^{IV}$(μ-$O_2C_6H_4$)(py)}(L^A)]·4py (**5·4py·solvent**) was positionally disordered over two positions. As a result, it was split into two parts and refined with an occupancy ratio of 0.59:0.41. In addition, the thermal parameters of the carbon atoms were restrained to be similar to one another through the use of the SIMU command. In addition, residual lattice electron density (presumably from highly disordered lattice solvent) was modelled using the "solvent mask" feature of Olex2 (90.6 electrons/cell).

All three molecules of lattice 1,2-dme in [{(py)U^{IV}(μ-F)(μ-OBcat)U^{IV}(μ-$O_2C_6H_4$)(py)}(L^A)]·3dme (**5A·3dme**) were positionally disordered over two positions. The molecule of 1,2-dme with carbons C(100)-C(103) and oxygens O(10) and O(11) was split into two parts and refined with an occupancy ratio of 0.8:0.2. The thermal parameters of the part with the highest occupancy were refined anisotropically, whereas the thermal parameters of the lower occupancy part were refined using ISOR. Furthermore, the thermal ellipsoids of the carbon atoms were refined to be similar to one another using the SIMU command. The molecule of 1,2-dme with carbons C(200)-C(203) and oxygens O(20) and O(21) was split into two parts and refined with an occupancy ratio of 0.62:0.38. The thermal parameters of atoms O(20) and O(20A), O(21) and O(21A), and C(200) and C(1F) were restrained to be similar to one another through the use of the SIMU command. The molecule of 1,2-dme with carbons C(300)-C(303) and oxygens O(30) and O(31) were split into two parts and refined in a 0.75:0.25 ratio. In addition, the thermal parameters of the carbons C(300), C(301), C(302), C(1B), C(1K) and C(1L), and oxygens O(30), O(30A), O(31) and O(31A) were restrained to be similar to one another using the SIMU command. The C(1B)-O(31A), C(1A)-O(31A), C(1L)-O(30A) and C(1K)-O(30A) bond lengths of one of the disordered molecules of 1,2-dme were restrained to be similar to one another using the SADI command. The C(202)-C(201), C(1E)-C(1C), C(201)-O(20), C(1E)-O(20A), O(20)-C(200), O(20A)-C(1F), C(301)-O(30), C(102)-O(11), O(10)-C(101), C(101)-C(102), C(1A)-O(31A), O(31A)-C(1B), C(1B)-C(1K), C(1K)-O(30A), O(30A)-C(1L), C(1I)-C(1H), C(1J)-O(10A), O(10A)-C(1H), C(1H)-C(1I), C(1I)-O(11A) and O(11A)-C(1G) bond lengths of the disordered molecules of 1,2-dme were restrained to ~1.4 Angstroms using the DANG command. Finally, the thermal parameters of C(1A) and C(303), and O(10) and O(11) were constrained to be equal to each other, respectively, using the EADP command due to unstable refinement in the absence of it.

C(8) in [{(py)U^{IV}(μ-Cl)$_2U^{IV}$(μ-$O_2C_6H_4$)(py)}(L^A)]·solvent (**6·solvent**) is positionally disordered over two positions, so it has been split into two parts and refined in a 0.53:0.47 ratio. In addition, a U-coordinated molecule of pyridine is positionally disordered over two positions, so it has been split into two parts and refined in a 0.84:0.16 ratio; the thermal ellipsoids have been restrained to be similar to one another through the use of the SIMU command. Furthermore, the geometry of N(5), C(59), C(60), C(61), C(62) and C(63) was constrained using AFIX 66. Finally, the lattice solvent exhibited unresolvable disorder and was removed using the "solvent mask" feature of Olex 2 (393.3 electrons per cell).

Residual lattice electron density (presumably from highly disordered lattice solvent) in [{(py)ClUOUCl(py)}(L^A)]·solvent (**8·solvent**) was modelled using the "solvent mask" feature of Olex2 (81.1 electrons/cell). In addition, the SIMU command was used on carbon atoms C(31)-C(34) (a pyrrolic ring) because the thermal ellipsoid of C(31) was non-positive definite when refined anisotropically, and the SIMU command was used on carbon atoms C(9) and C(10) due to a failed Hirshfield test.

Experimental Single Crystal X-Ray Diffraction Details

Table S1. Crystallographic data summary for complexes **1·3THF**, **2·C_6H_6** and **3·5py**. CCDC codes 1984900-1984902.

Complex	[{(py)U^{IV}(μ-OH)$_2U^{IV}$(μ-$O_2C_6H_4$)(py)}(L^A)]·3THF (**1·3THF**)	[{(py)U^{IV}(μ-OMe)$_{1.69}$(μ-OH)$_{0.31}U^{IV}$(μ-$O_2C_6H_4$)(py)}(L^A)]·C_6H_6 (**2·C_6H_6**)	[{(py)U^{IV}(μ-η^2:η^2-S_2)U^{IV}(μ-$O_2C_6H_4$)(py)}(L^A)]·5py (**3·5py**)
Name in cif	compound1	compound2	compound3
Local code	p17104_cmono080	P18088	p17131_twin_refinalized_twin1_hklf4
Chemical formula	$C_{74}H_{64}N_{10}O_4U_2$, 3(C_4H_8O)	$C_{75.69}H_{67.06}N_{10}O_4U_2$, C_6H_6	$C_{74}H_{63}N_{10}O_2S_2U_2$, 5($C_5H_5N$)
Lattice Solvent	THF	Benzene	Pyridine
M_r	1849.72	1734.84	2060.02
Crystal system, space group	Monoclinic, *C*2/*c*	Triclinic, *P*–1	Triclinic, *P*–1
Temperature (K)	120.0(1)	173(2)	120.0(1)
a, *b*, *c* (Å)	16.9463(3), 24.3235(4), 17.9675(3)	10.6363(6), 14.9997(8), 21.849(1)	13.7332(2), 17.5327(3), 18.0598(3)
α, β, γ (°)	90, 98.758(2), 90	90.546(4), 102.195(5), 94.113(5)	77.619(1), 85.469(1), 88.925(1)
V (Å^3)	7319.8(2)	3397.3(3)	4234.0(1)
Z	4	2	2
Radiation type	Mo Kα	Mo Kα	Mo Kα
μ (mm^{-1})	4.485	4.822	3.922
Crystal size (mm)	0.191 × 0.058 × 0.034	0.140 × 0.062 × 0.036	0.266 × 0.101 × 0.080
Diffractometer	Xcalibur, Eos	Xcalibur, Eos	Xcalibur, Eos
Absorption correction	Analytical *CrysAlis PRO* 1.171.38.42b (Rigaku Oxford Diffraction, 2015) Analytical numeric absorption correction using a multifaceted crystal model based on expressions derived by R.C. Clark & J.S. Reid. (Clark, R. C. & Reid, J. S. (1995). Acta Cryst. A51, 887-897) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.	Analytical *CrysAlis PRO* 1.171.38.42b (Rigaku Oxford Diffraction, 2015) Analytical numeric absorption correction using a multifaceted crystal model based on expressions derived by R.C. Clark & J.S. Reid. (Clark, R. C. & Reid, J. S. (1995). Acta Cryst. A51, 887-897) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.	Analytical *CrysAlis PRO* 1.171.38.42b (Rigaku Oxford Diffraction, 2015) Analytical numeric absorption correction using a multifaceted crystal model based on expressions derived by R.C. Clark & J.S. Reid. (Clark, R. C. & Reid, J. S. (1995). Acta Cryst. A51, 887-897) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.
T_{min}, T_{max}	0.91925, 1.00000	0.965, 0.988	0.88725, 1.00000
θ_{min}, θ_{max}	2.791, 26.370	2.862, 25.350	2.808, 29.395
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	74194, 7484, 6009	66944, 12421, 8941	142230, 58720, 33537
R_{int}	0.0856	0.1173	0.0937
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.0336, 0.0615, 1.034	0.0520, 0.0700, 1.019	0.0385, 0.0511, 0.765
No. of reflections	7484	8941	58720
No. of parameters	510	932	1086
No. of restraints	36	349	21
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.959, –0.775	1.601, –0.942	2.757, –1.815

Table S2. Crystallographic data summary for complexes **4·2CH$_2$Cl$_2$·solvent**, **5·4py·solvent** and **5A·3dme**. CCDC codes 1984903-1984905.

Complex	[{(py)U^{IV}(μ-η^2:η^2-Se$_2$)U^{IV}(μ-O$_2$C$_6$H$_4$)(py)}(L^A)]·2CH$_2$Cl$_2$·solvent (**4·2CH$_2$Cl$_2$·solvent**)	[{(py)U^{IV}(μ-F)$_2$U^{IV}(μ-O$_2$C$_6$H$_4$)(py)}(L^A)]·4py (**5·4py.solvent**)	[{(py)U^{IV}(μ-F)(μ-OBcat)U^{IV}(μ-O$_2$C$_6$H$_4$)(py)}(L^A)]·3dme (**5'·3dme**)
Name in cif	compound4	compound5	compound5A
Local code	p18107	p18071	po18009_refinalized
Chemical formula	$C_{74}H_{62}N_{10}O_2Se_2U_2$, 2($CH_2Cl_2$)	$C_{74}H_{62}F_2N_{10}O_2U_2$, 4($C_5H_5N$)	$C_{80}H_{66}BFN_{10}O_5U_2$, 3($C_4H_{10}O_2$)
Lattice Solvent	CH_2Cl_2 Olex2 "solvent mask" feature was used to remove 84.6 electrons per unit cell	Pyridine Olex 2 "solvent mask" feature was used to remove 90.6 electrons per unit cell	1,2-Dimethoxyethane
M_r	1927.16	1953.79	2023.65
Crystal system, space group	Monoclinic, *P*21/*c*	Monoclinic, *P*21/*n*	Triclinic, *P*–1
Temperature (K)	173(2)	173(2)	120.0(1)
a, *b*, *c* (Å)	10.9153(2), 19.1212(4), 34.2194(6)	17.5381(4), 26.2280(6), 17.8435(4)	14.6146(3), 16.3896(4), 18.1536(4)
α, β, γ (°)	90, 92.935(2), 90	90, 91.942(2), 90	77.518(2), 78.699(2), 82.007(2)
V (Å^3)	7132.7(2)	8203.1(3)	4141.9(2)
Z	4	4	2
Radiation type	Mo Kα	Mo Kα	Mo Kα
μ (mm^{-1})	5.760	4.007	3.975
Crystal size (mm)	0.148 × 0.078 × 0.063	0.254 × 0.102 × 0.041	0.612 × 0.154 × 0.066
Diffractometer	Xcalibur, Eos	Xcalibur, Eos	SuperNova, Dual, Cu at zero, Atlas
Absorption correction	Analytical *CrysAlis PRO* 1.171.38.42b (Rigaku Oxford Diffraction, 2015) Analytical numeric absorption correction using a multifaceted crystal model based on expressions derived by R.C. Clark & J.S. Reid. (Clark, R. C. & Reid, J. S. (1995). Acta Cryst. A51, 887-897) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.	Analytical *CrysAlis PRO* 1.171.38.42b (Rigaku Oxford Diffraction, 2015) Analytical numeric absorption correction using a multifaceted crystal model based on expressions derived by R.C. Clark & J.S. Reid. (Clark, R. C. & Reid, J. S. (1995). Acta Cryst. A51, 887-897) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.	Gaussian *CrysAlis PRO* 1.171.38.42b (Rigaku Oxford Diffraction, 2015) Numerical absorption correction based on gaussian integration over a multifaceted crystal model Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.
T_{min}, T_{max}	0.999, 1.000	0.852, 0.967	0.201, 1.000
θ_{min}, θ_{max}	2.834, 25.350	2.795, 25.350	2.802, 32.951
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	133959, 13030, 10932	161248, 15008, 10867	105405, 28789, 21060
R_{int}	0.0851	0.1286	0.0478
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.0424, 0.0787, 1.064	0.0449, 0.0784, 1.011	0.0407, 0.0838, 1.045
No. of reflections	13030	15008	28789
No. of parameters	900	1086	1194
No. of restraints	132	138	174
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.571, –1.739	1.242, –0.906	1.820, –1.282

Table S3. Crystallographic data summary for complexes **6·solvent** and **8·solvent**. CCDC codes 1984906 and 1984907.

Complex	[{(py)U^{IV}(μ-Cl)$_2U^{IV}$(μ-$O_2C_6H_4$)(py)}(L^A)]·solvent (**6·solvent**)	[{(py)ClU^{IV}OU^{IV}Cl(py)}(L^A)]·solvent (**8·solvent**)
Name in cif	compound6	compound8
Local code	p18017_08_mono	p19029
Chemical formula	$C_{74}H_{62}Cl_2N_{10}O_2U_2$	$C_{68}H_{58}Cl_2N_{10}OU_2$
Lattice Solvent	Olex2 "solvent mask" feature was used to remove 393.3 electrons per unit cell	Olex2 "solvent mask" feature was used to remove 81.1 electrons per unit cell
M_r	1670.29	1578.20
Crystal system, space group	Monoclinic, *P*21/*m*	Triclinic, *P*–1
Temperature (K)	120.0(1)	120.0(1)
a, *b*, *c* (Å)	14.0058(3), 21.7361(5), 14.7736(3)	12.2163(5), 13.1548(5), 21.166(1)
α, β, γ (°)	90, 105.395(2), 90	77.753(4), 76.263(4), 72.589(4)
V (Å^3)	4336.2(2)	3116.0(2)
Z	2	2
Radiation type	Mo Kα	Mo Kα
μ (mm^{-1})	3.833	5.327
Crystal size (mm)	0.346 × 0.138 × 0.095	0.124 × 0.085 × 0.037
Diffractometer	Xcalibur, Eos	Xcalibur, Eos
Absorption correction	Analytical *CrysAlis PRO* 1.171.38.42b (Rigaku Oxford Diffraction, 2015) Analytical numeric absorption correction using a multifaceted crystal model based on expressions derived by R.C. Clark & J.S. Reid. (Clark, R. C. & Reid, J. S. (1995). Acta Cryst. A51, 887-897) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.	Analytical *CrysAlis PRO* 1.171.38.42b (Rigaku Oxford Diffraction, 2015) Analytical numeric absorption correction using a multifaceted crystal model based on expressions derived by R.C. Clark & J.S. Reid. (Clark, R. C. & Reid, J. S. (1995). Acta Cryst. A51, 887-897) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.
T_{min}, T_{max}	0.793, 0.928	0.833, 0.941
θ_{min}, θ_{max}	2.857, 26.372	2.926, 25.349
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	47380, 9110, 6549	60766, 11386, 8593
R_{int}	0.0670	0.1020
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.0382, 0.0814, 1.022	0.0590, 0.1241, 1.054
No. of reflections	9110	11386
No. of parameters	471	752
No. of restraints	120	24
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.658, –0.925	4.186, –2.058

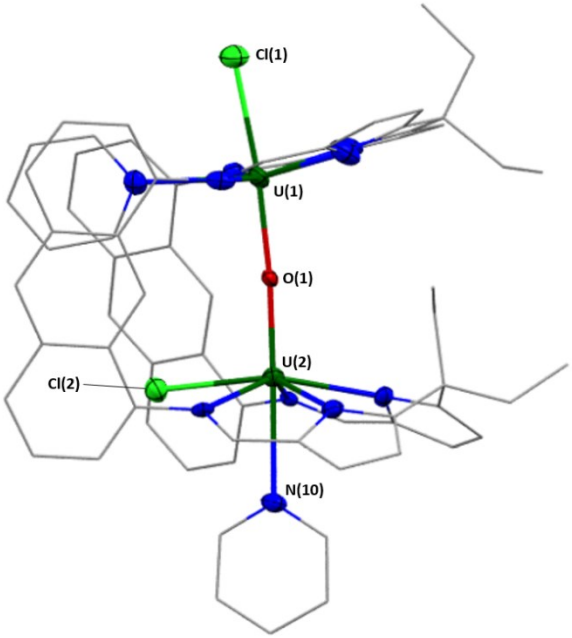

Figure S1. Solid-state structure of **8**·solvent. Displacement ellipsoids are drawn at 50 % probability and carbon atoms are drawn wireframe. The solvent mask feature of Olex2 was deployed to remove unresolvable disorder in the lattice solvent (81.1 electrons per unit cell). For clarity, hydrogen atoms are omitted. Selected bond lengths [Å] and bond angles [°]: U(1)–Cl(1), 2.630(3); U(2)–Cl(2), 2.663(2); U(1)–O(1), 2.158(6); U(2)–O(1), 2.103(6); U(1)···U(2), 4.2579(6); U(1)–O(1)–U(2), 175.4(3); Cl(1)–U(1)–O(1), 174.9(2); Cl(2)–U(2)–O(1), 95.1(2).

1.1.4 NMR Spectra

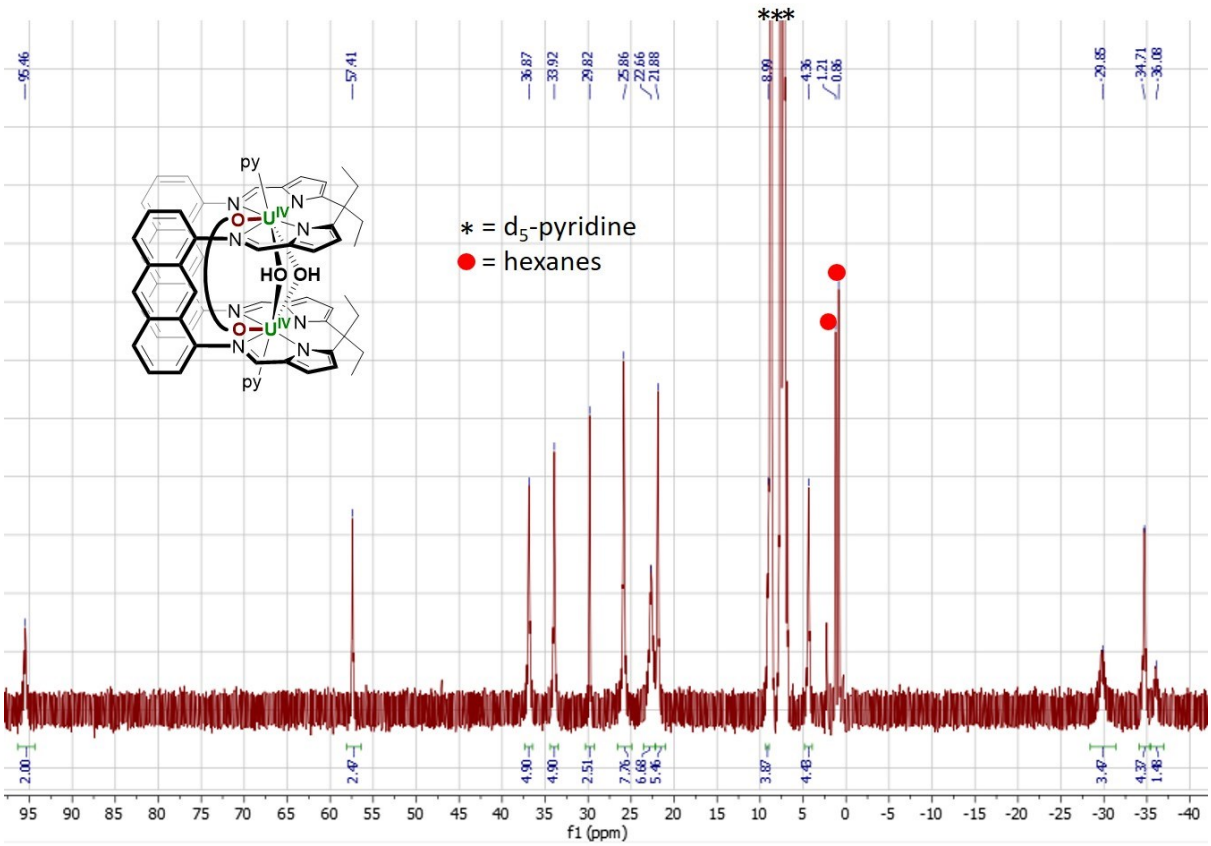

Figure S2. ^{1}H NMR spectrum of **1** (500 MHz; d_5-pyridine; 300 K; $SiMe_4$).

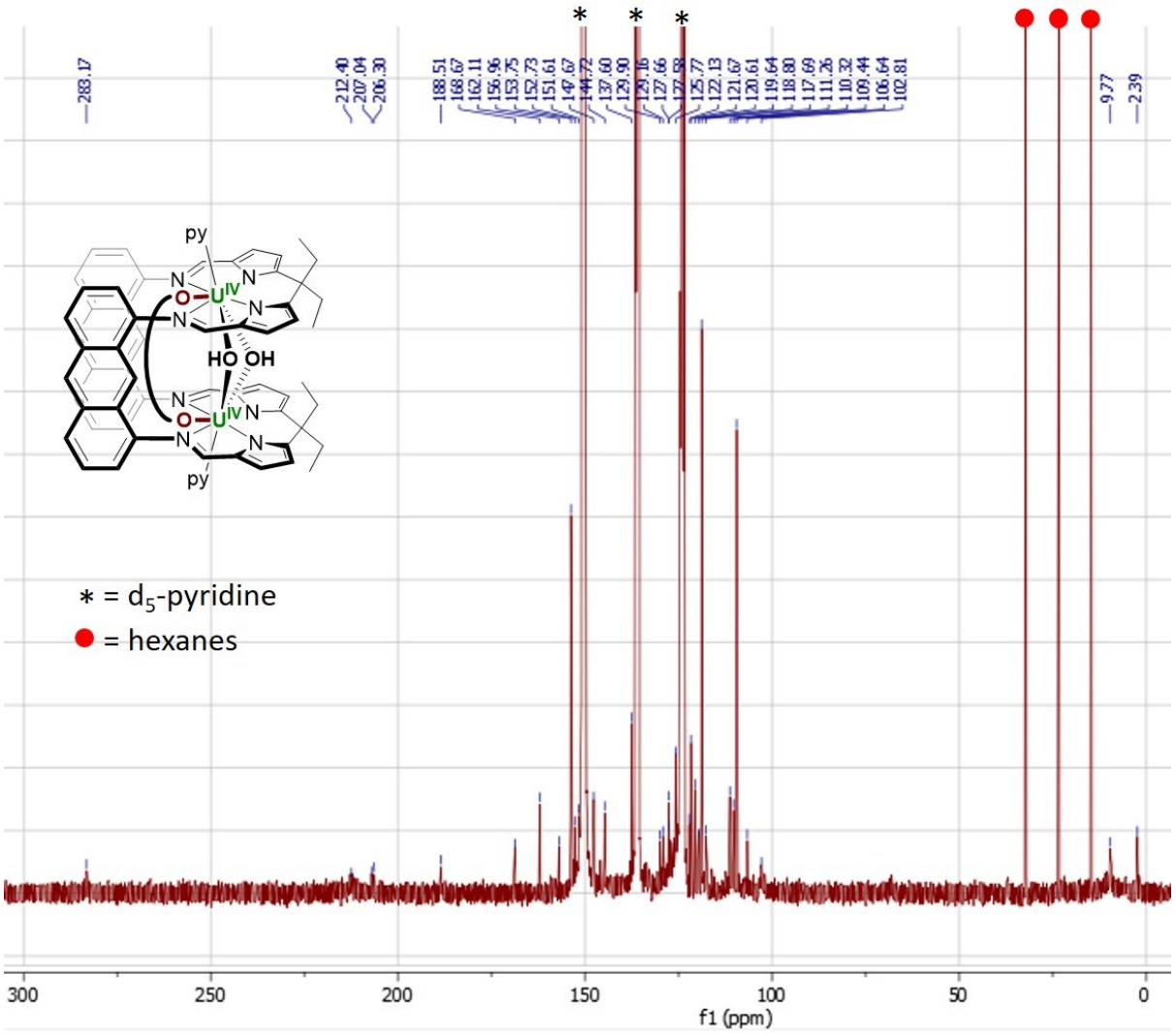

Figure S3. $^{13}C\{^{1}H\}$ NMR spectrum of **1** (126 MHz; d_5-pyridine; 300 K; $SiMe_4$).

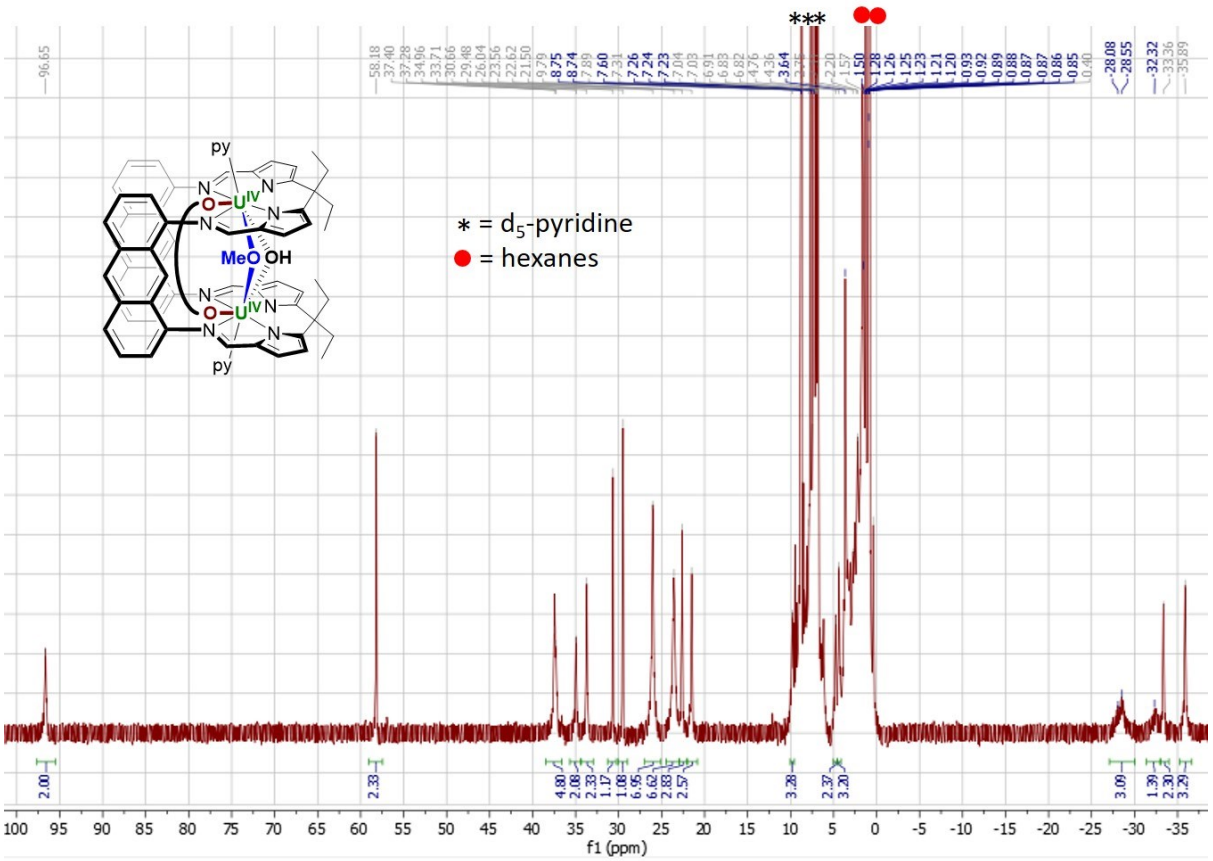

Figure S4. ^{1}H NMR spectrum of **2** (500 MHz; d_5-pyridine; 300 K; $SiMe_4$).

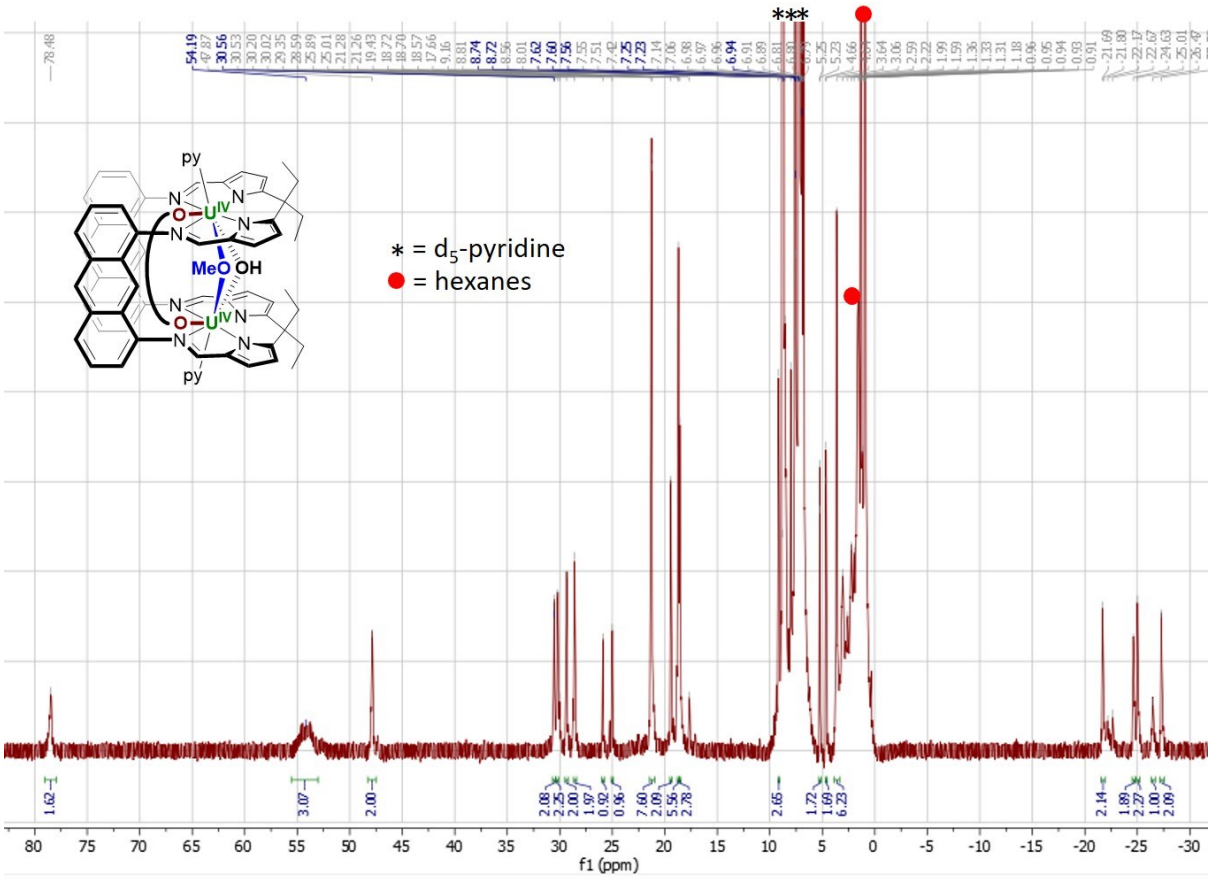

Figure S5. ^{1}H NMR spectrum of **2** (500 MHz; d_5-pyridine; 360 K; $SiMe_4$).

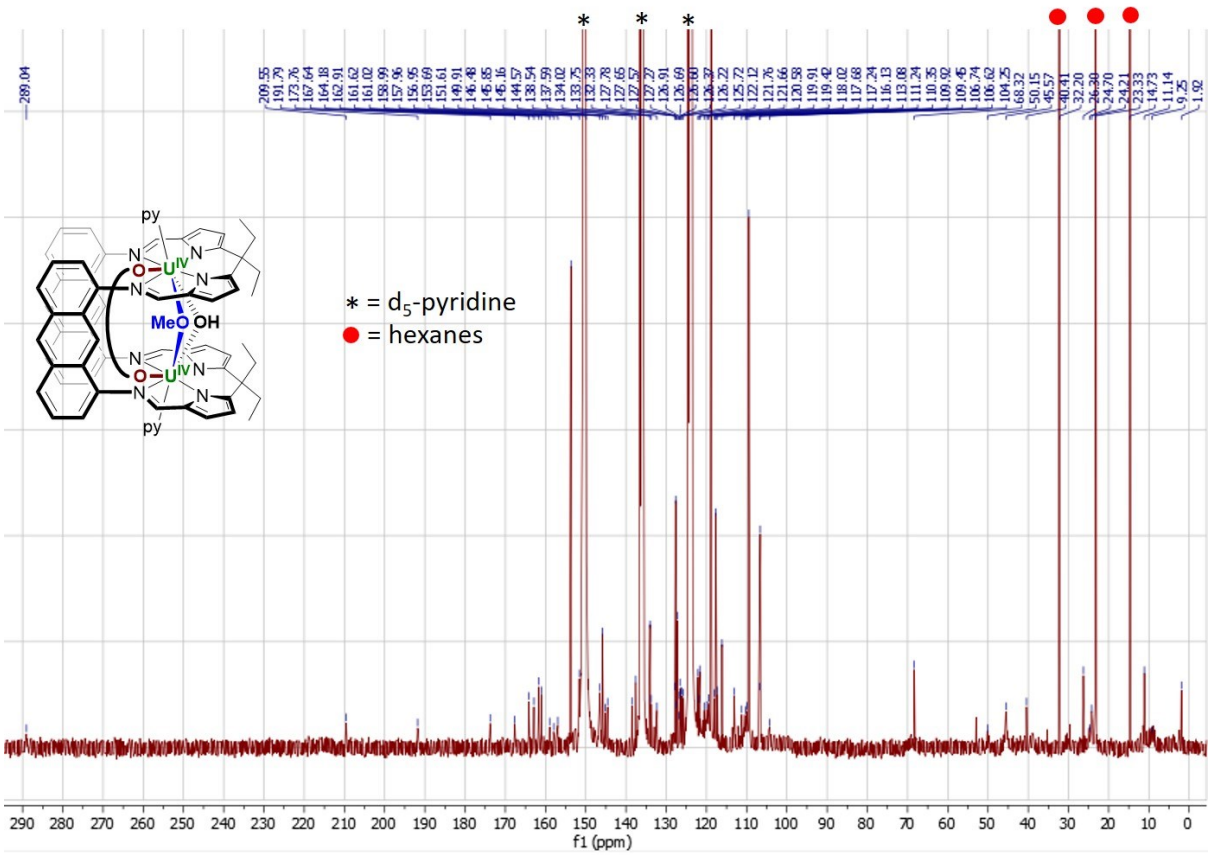

Figure S6. $^{13}C\{^{1}H\}$ NMR spectrum of **2** (126 MHz; d_5-pyridine; 300 K; $SiMe_4$).

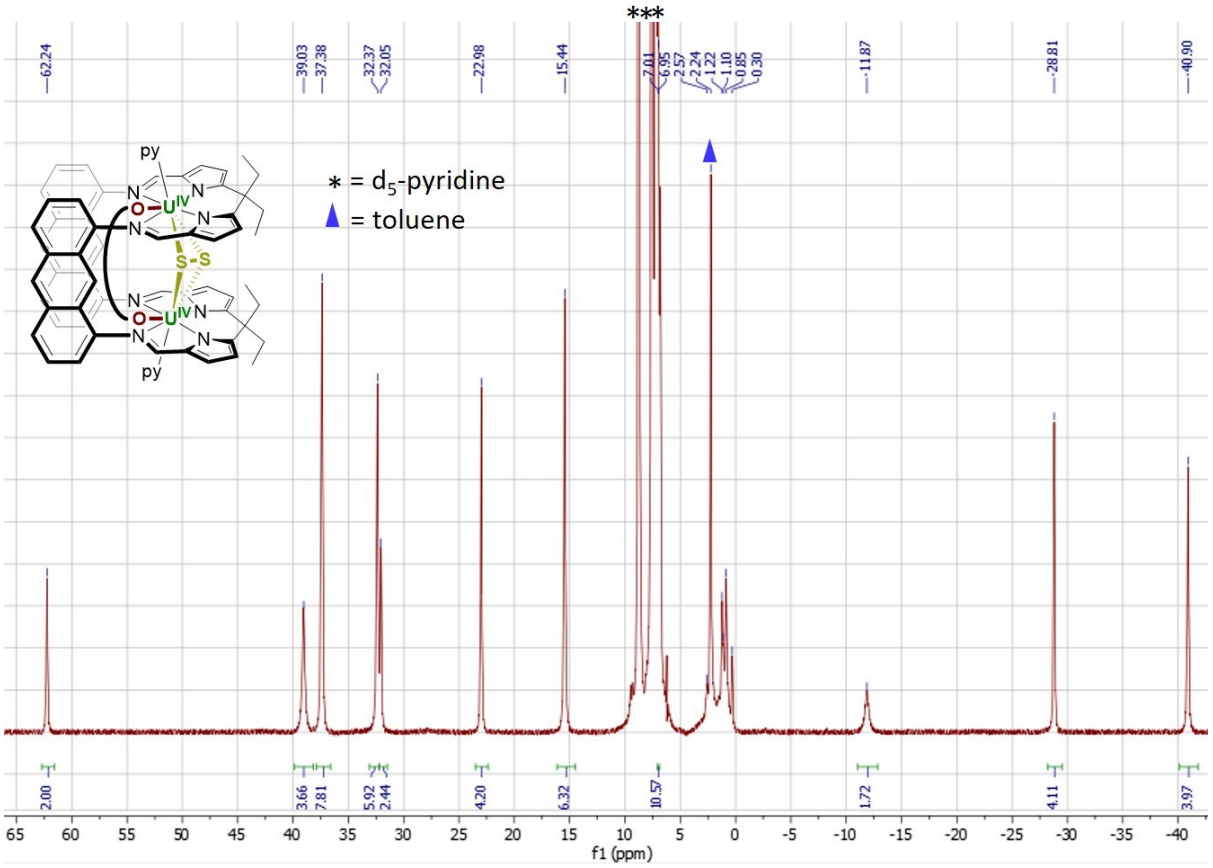

Figure S7. ^{1}H NMR spectrum of **3** (600 MHz; d_5-pyridine; 300 K; $SiMe_4$).

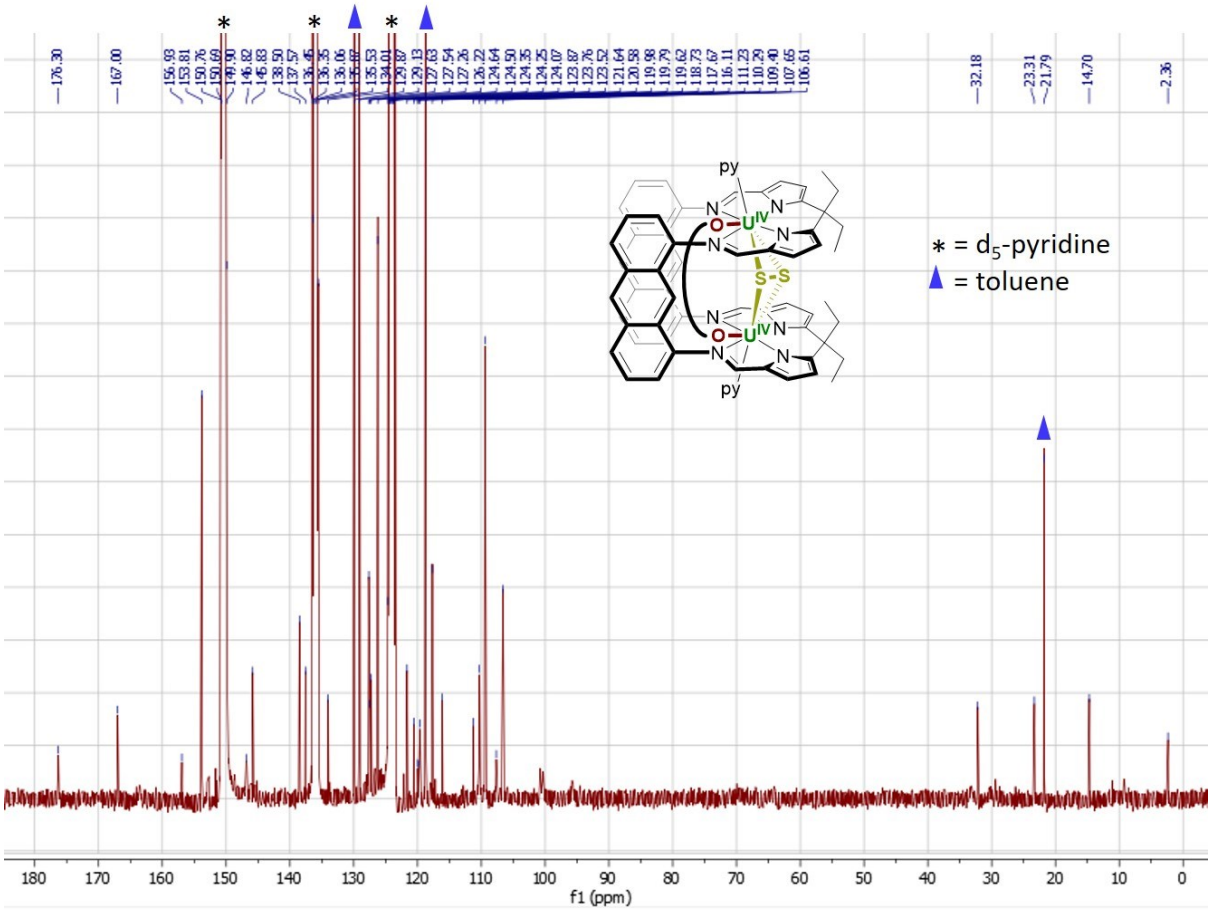

Figure S8. $^{13}C\{^{1}H\}$ NMR spectrum of **3** (126 MHz; d_5-pyridine; 300 K; $SiMe_4$).

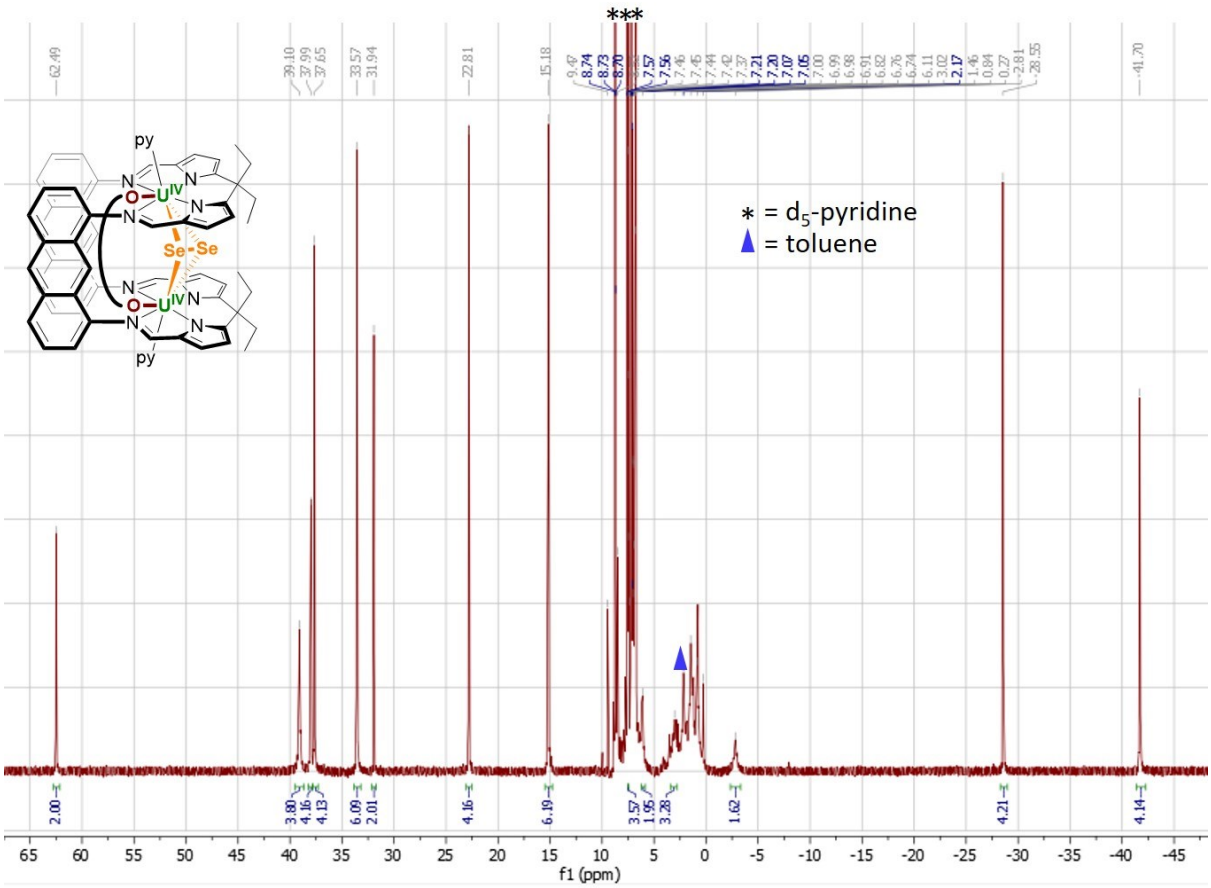

Figure S9. ^{1}H NMR spectrum of **4** (500 MHz; d_5-pyridine; 300 K; $SiMe_4$).

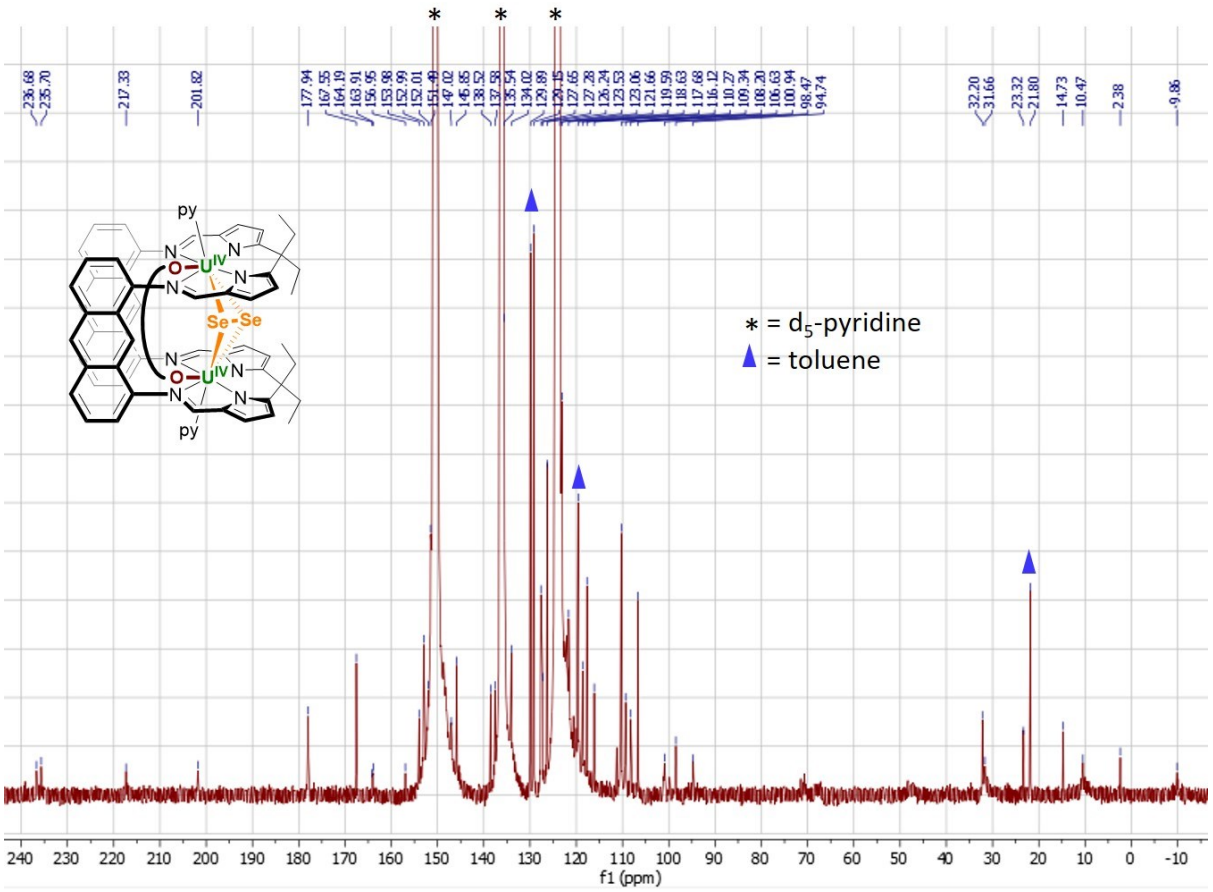

Figure S10. $^{13}C\{^{1}H\}$ NMR spectrum of **4** (126 MHz; d_5-pyridine; 300 K; $SiMe_4$).

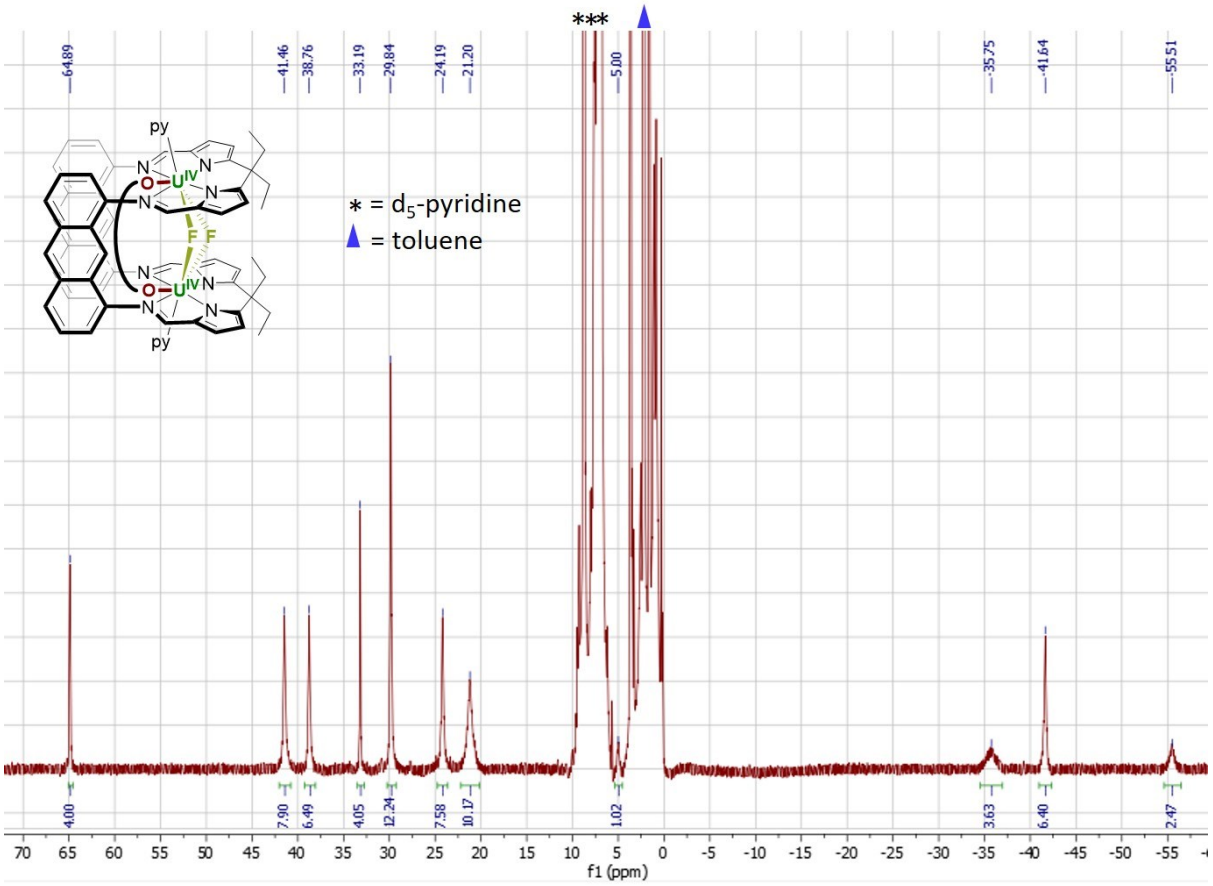

Figure S11. ^{1}H NMR spectrum of **5** (500 MHz; d_5-pyridine; 300 K; $SiMe_4$).

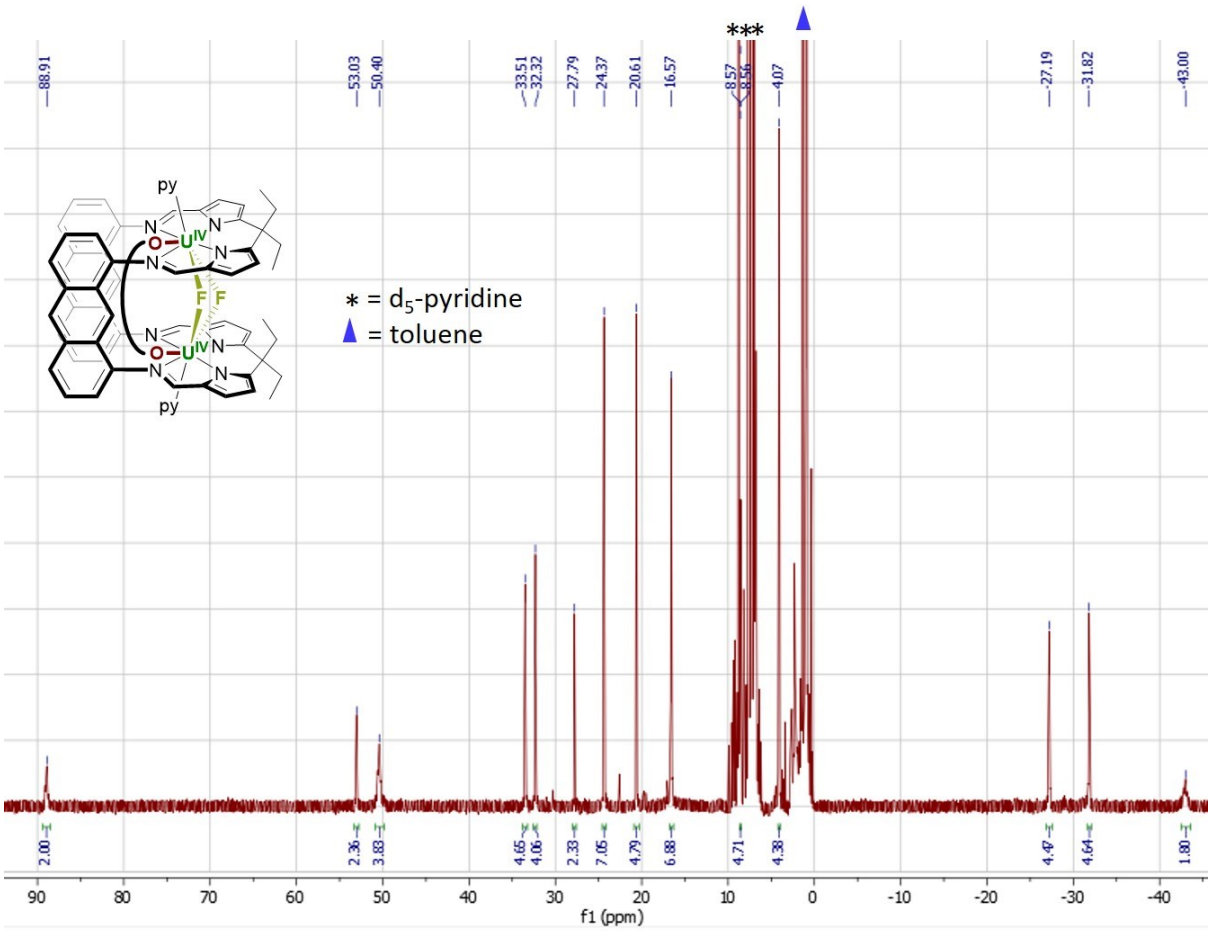

Figure S12. ^{1}H NMR spectrum of **5** (500 MHz; d_5-pyridine; 360 K; $SiMe_4$).

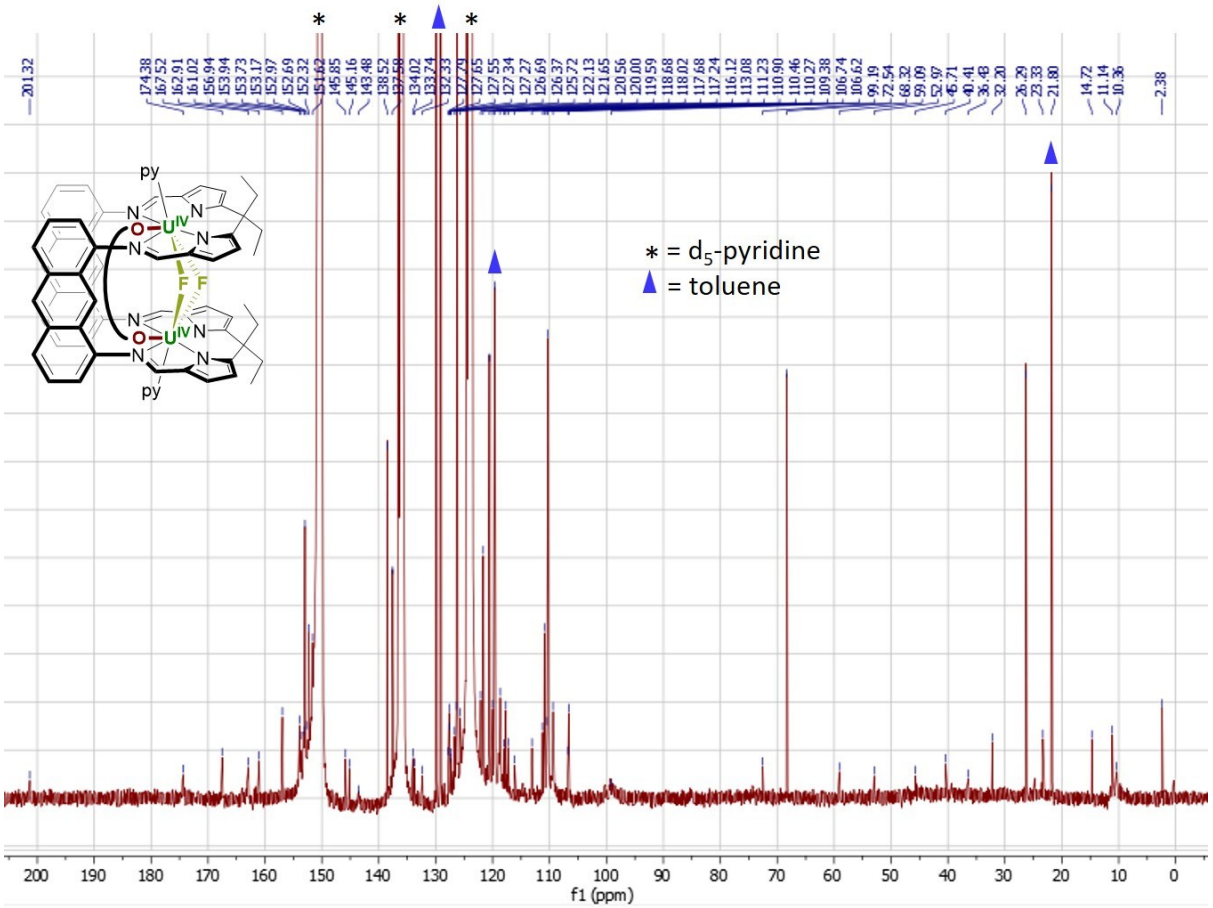

Figure S13. $^{13}C\{^{1}H\}$ NMR spectrum of **5** (126 MHz; d_5-pyridine; 300 K; $SiMe_4$).

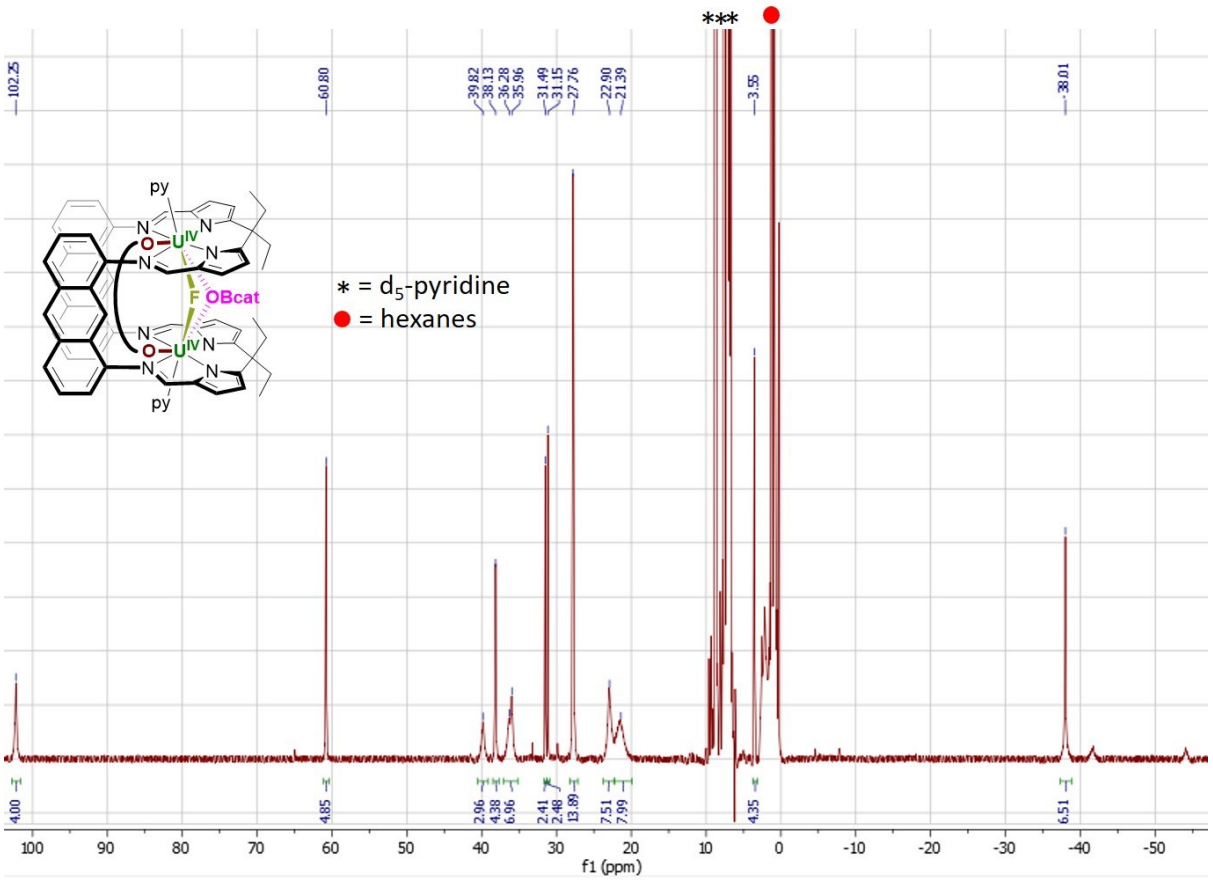

Figure S14. ^{1}H NMR spectrum of **5A** (600 MHz; d_5-pyridine; 300 K; $SiMe_4$).

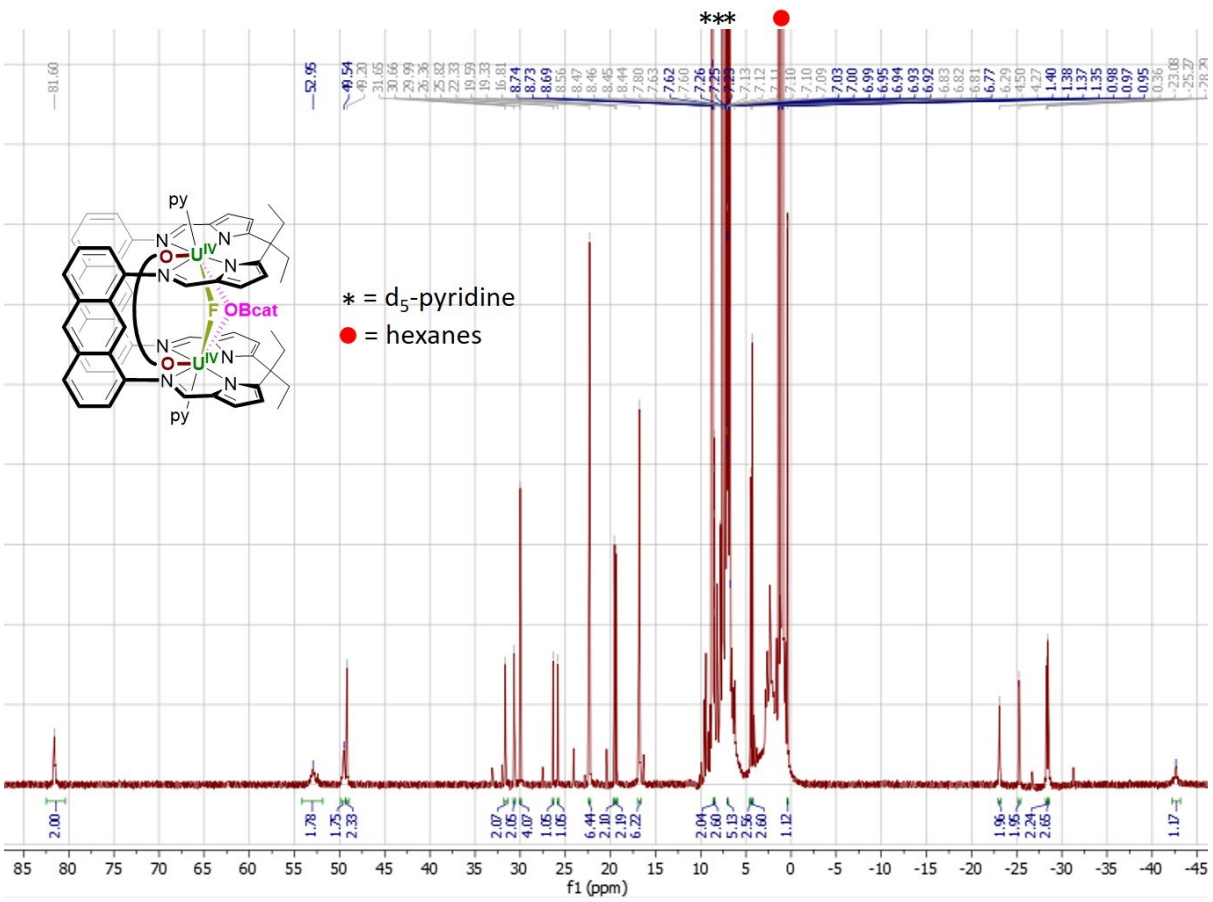

Figure S15. ^{1}H NMR spectrum of **5A** (500 MHz; d_5-pyridine; 360 K; $SiMe_4$).

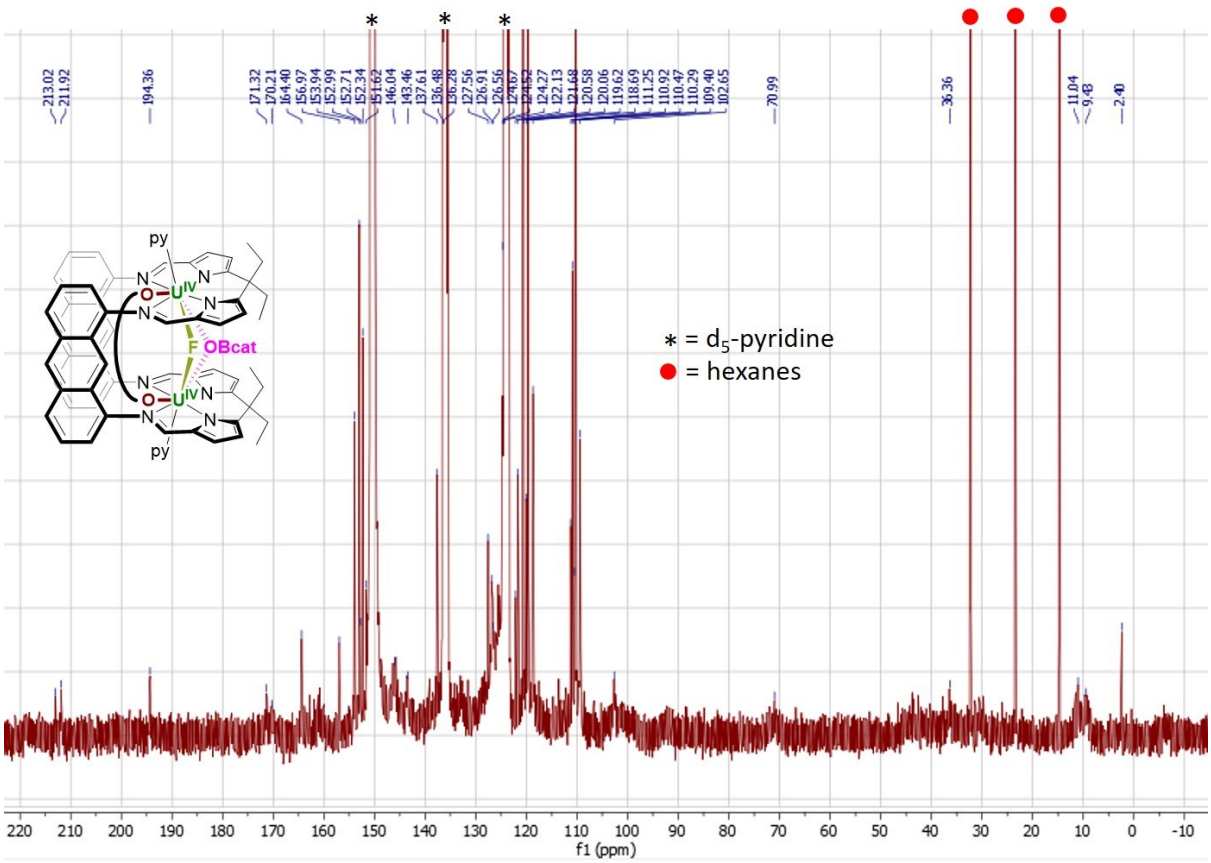

Figure S16. $^{13}C\{^{1}H\}$ NMR spectrum of **5A** (126 MHz; d_5-pyridine; 300 K; $SiMe_4$).

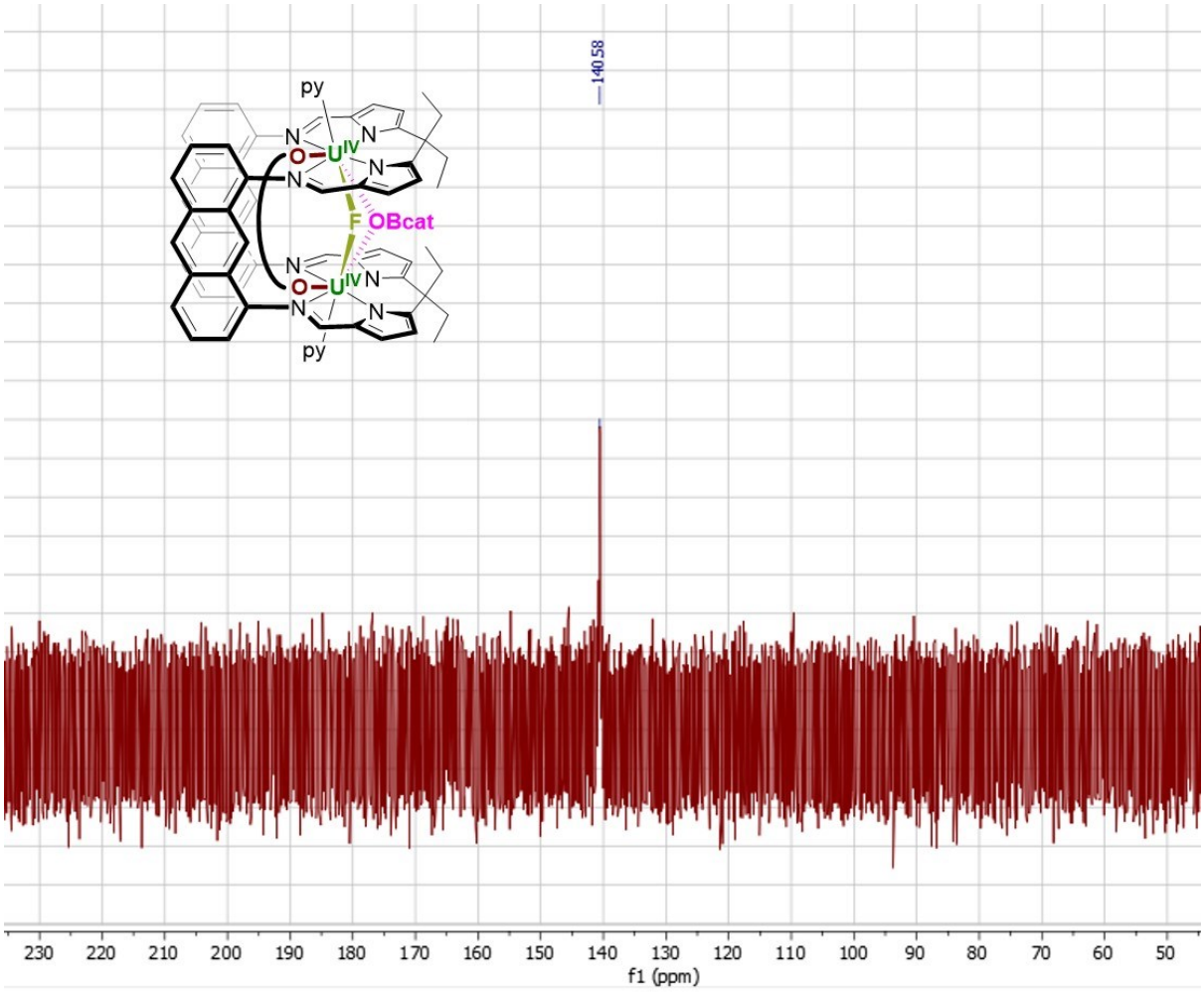

Figure S17. ^{19}F NMR spectrum of **5A** (471 MHz; d_5-pyridine; 300 K; α,α,α-trifluorotoluene).

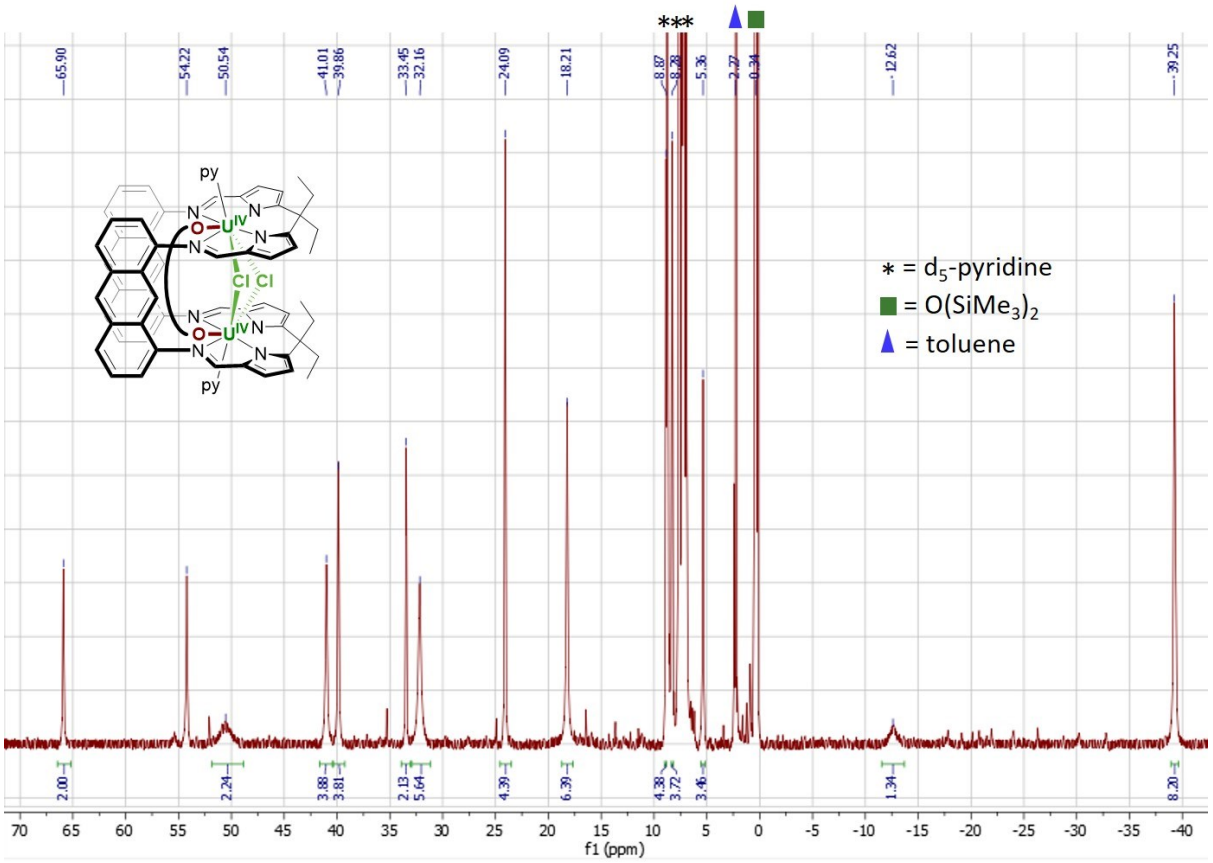

Figure S18. ^{1}H NMR spectrum of **6** (500 MHz; d_5-pyridine; 300 K; $SiMe_4$) generated *in situ*. Characterisation of **6** was achieved using an *in situ* generated sample due to its insolubility once isolated.

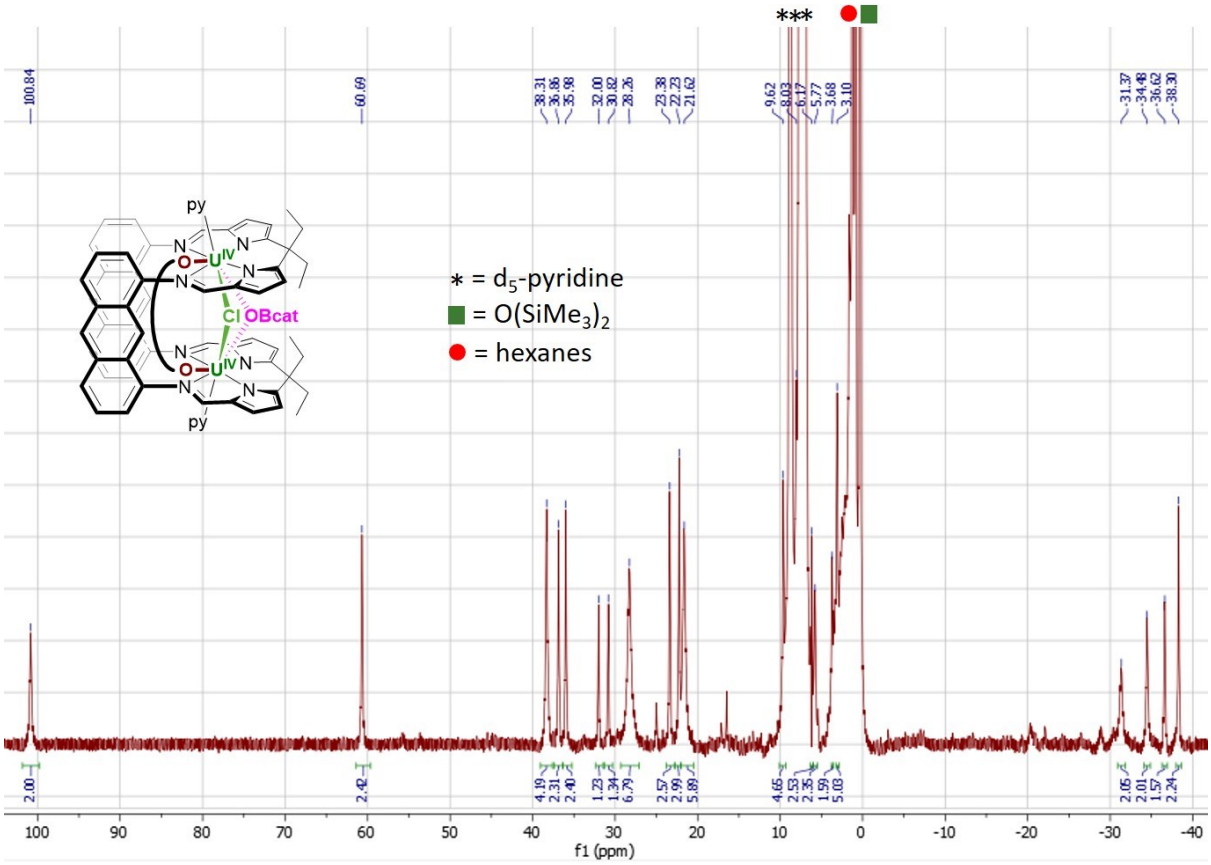

Figure S19. ^{1}H NMR spectrum of **6A** (600 MHz; d_5-pyridine; 300 K; $SiMe_4$).

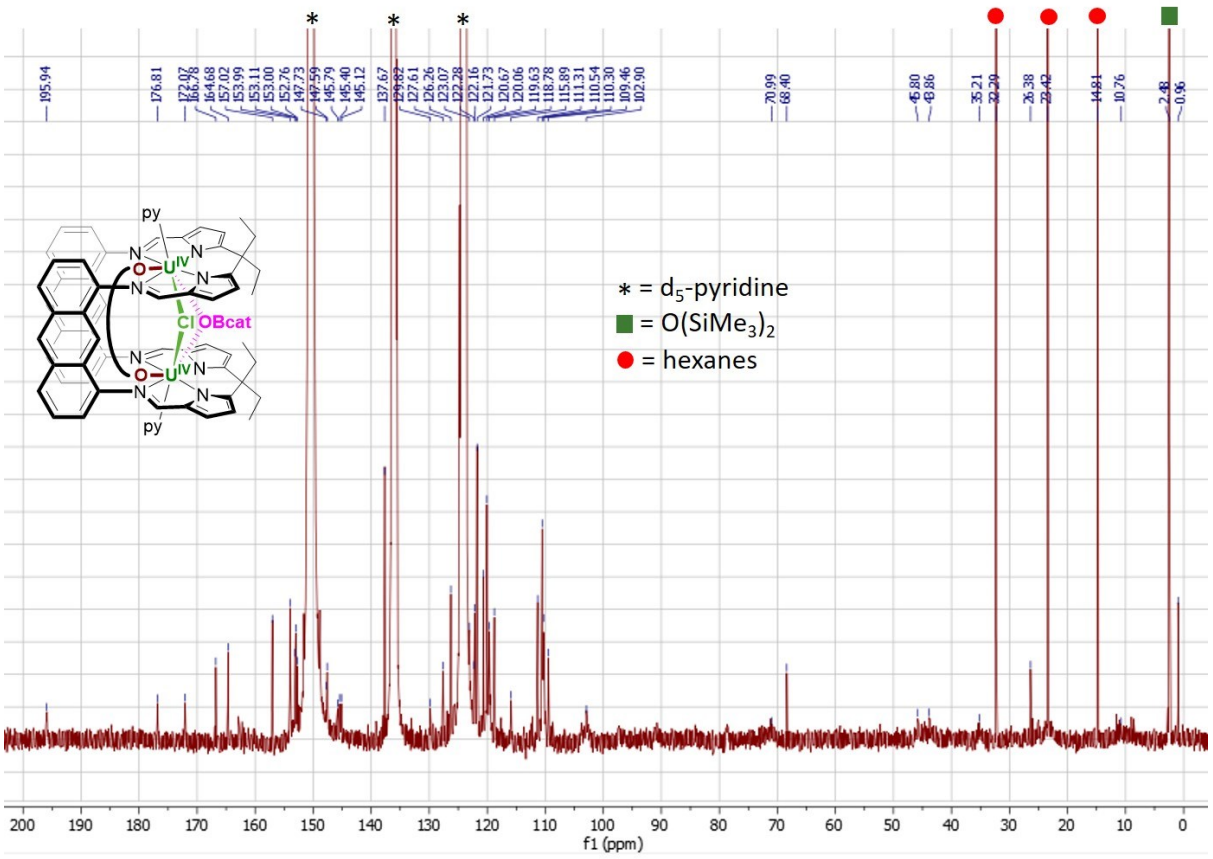

Figure S20. $^{13}C\{^{1}H\}$ NMR spectrum of **6A** (126 MHz; d_5-pyridine; 300 K; $SiMe_4$).

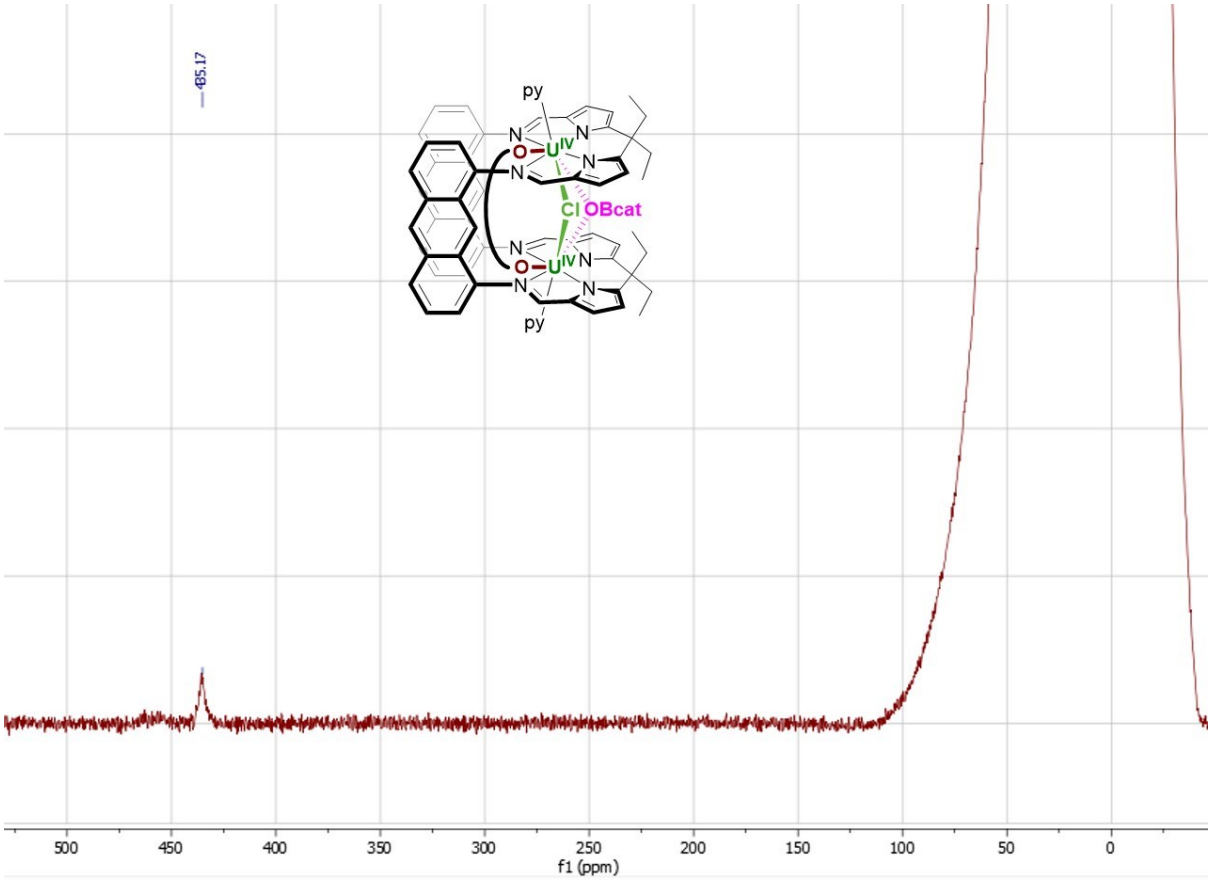

Figure S21. ^{11}B NMR spectrum of **6A** (161 MHz; d_5-pyridine; 300 K; $BF_3(OEt_2)$).

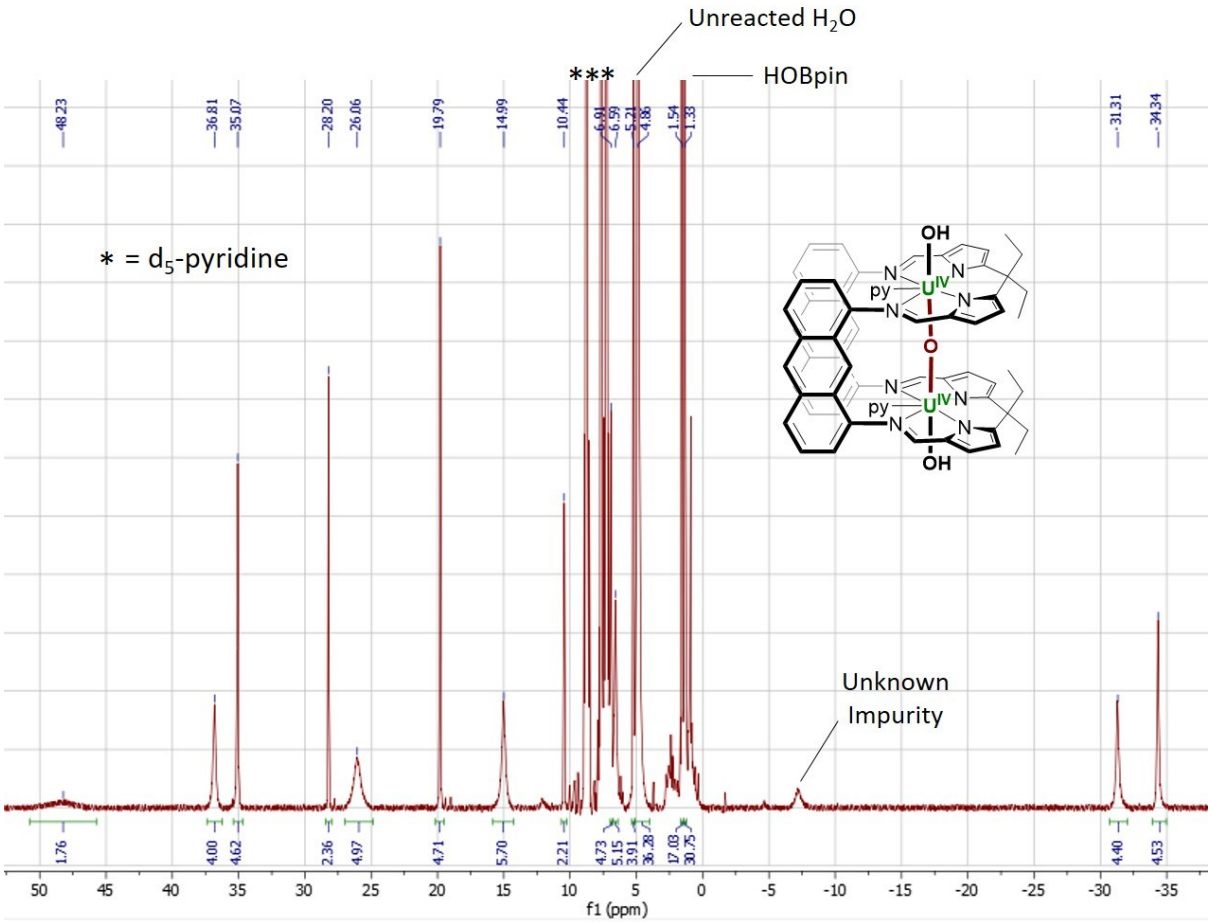

Figure S22. ^{1}H NMR spectrum of [{(py)(pinBO)U^{IV}OU^{IV}(OBpin)(py)}(L^A)] (**B**) + 2 equiv. of H_2O, forming [{(py)HOU^{IV}OU^{IV}OH(py)}(L^A)] (**7**) and 2 equiv. *H*OBpin (500 MHz; d_5-pyridine; 300 K; $SiMe_4$).

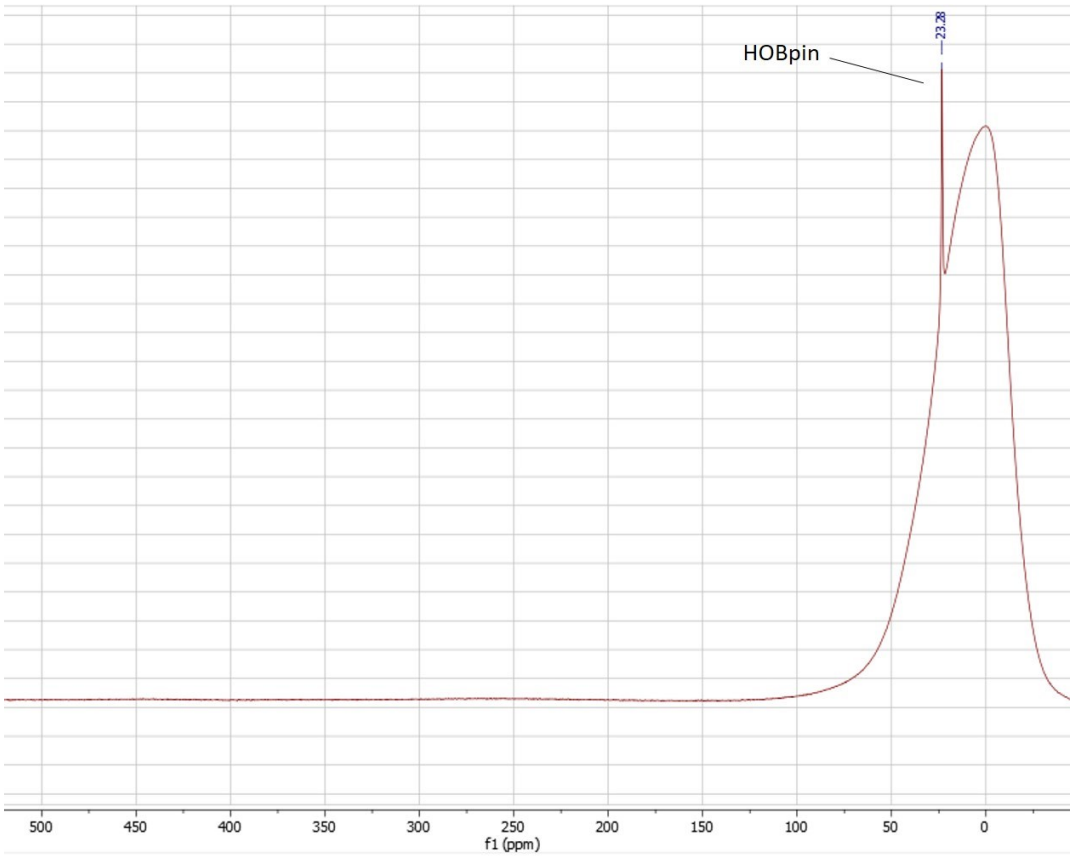

Figure S23. ^{11}B NMR spectrum of **B** + 2 equiv. of H_2O, forming HO*B*pin (161 MHz; d_5-pyridine; 300 K; $BF_3(OEt_2)$).

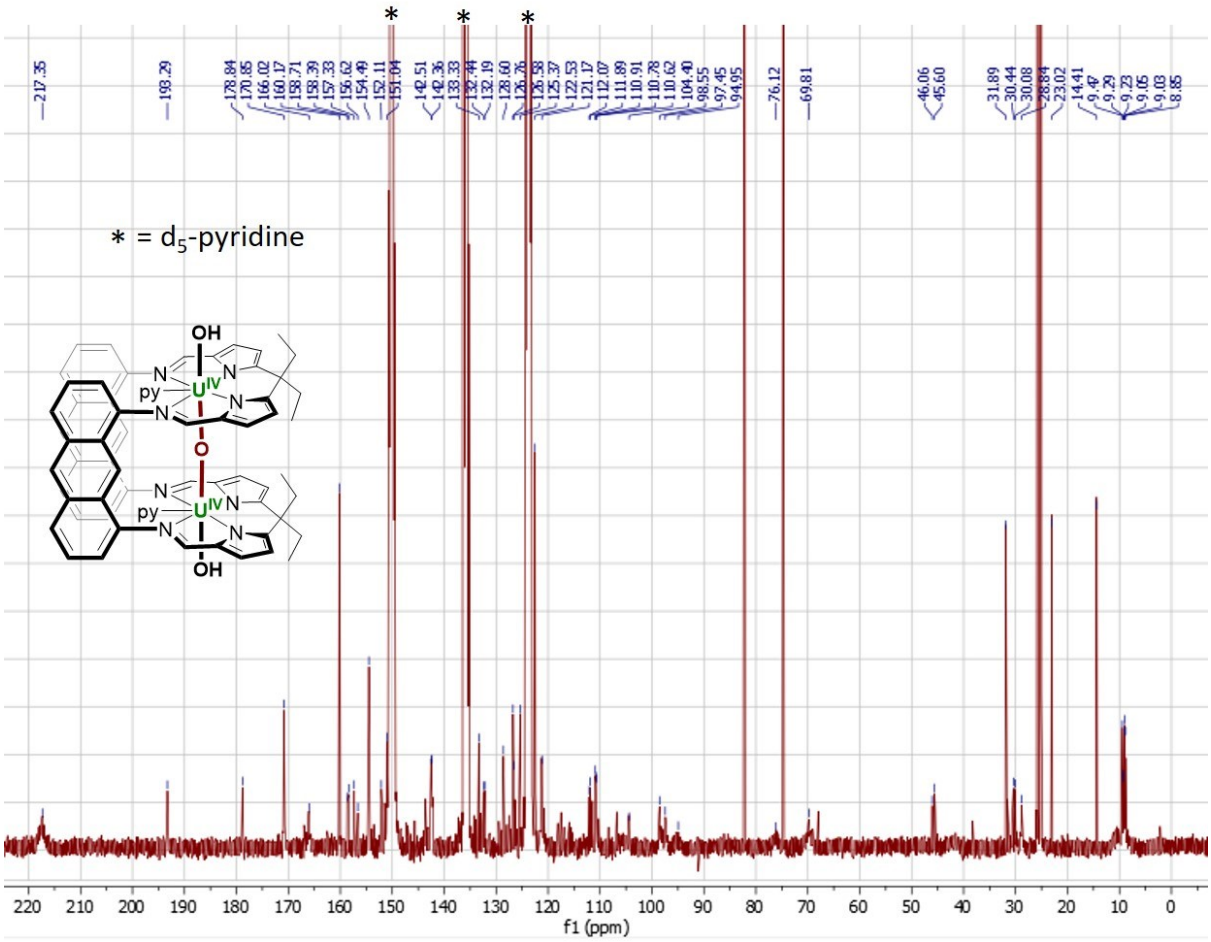

Figure S24. $^{13}C\{^{1}H\}$ NMR spectrum of **7** (126 MHz; d_5-pyridine; 300 K; $SiMe_4$). The unknown impurity present in the ^{1}H NMR spectrum in Figure S22 is still present in this spectrum, however, without the use of standard 2D NMR techniques the ^{13}C signals corresponding to the impurity could not be identified.

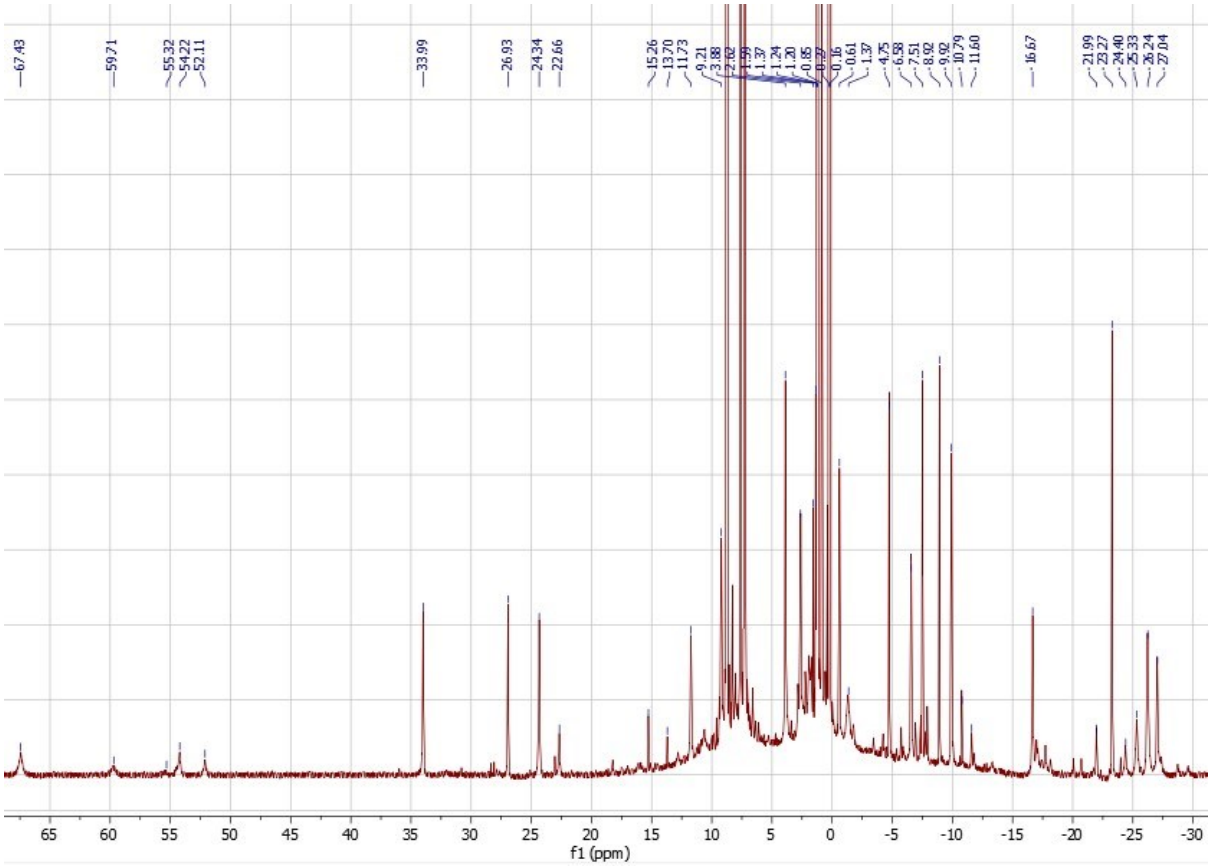

Figure S25. ^{1}H NMR spectrum of [{(py)(pinBO)U^{IV}OU^{IV}(OBpin)(py)}(L^{A})] (**B**) + 2 equiv. of Me_3SiCl, forming a mixture of **8** and other unidentifiable products (500 MHz; d_5-pyridine; 300 K; $SiMe_4$).

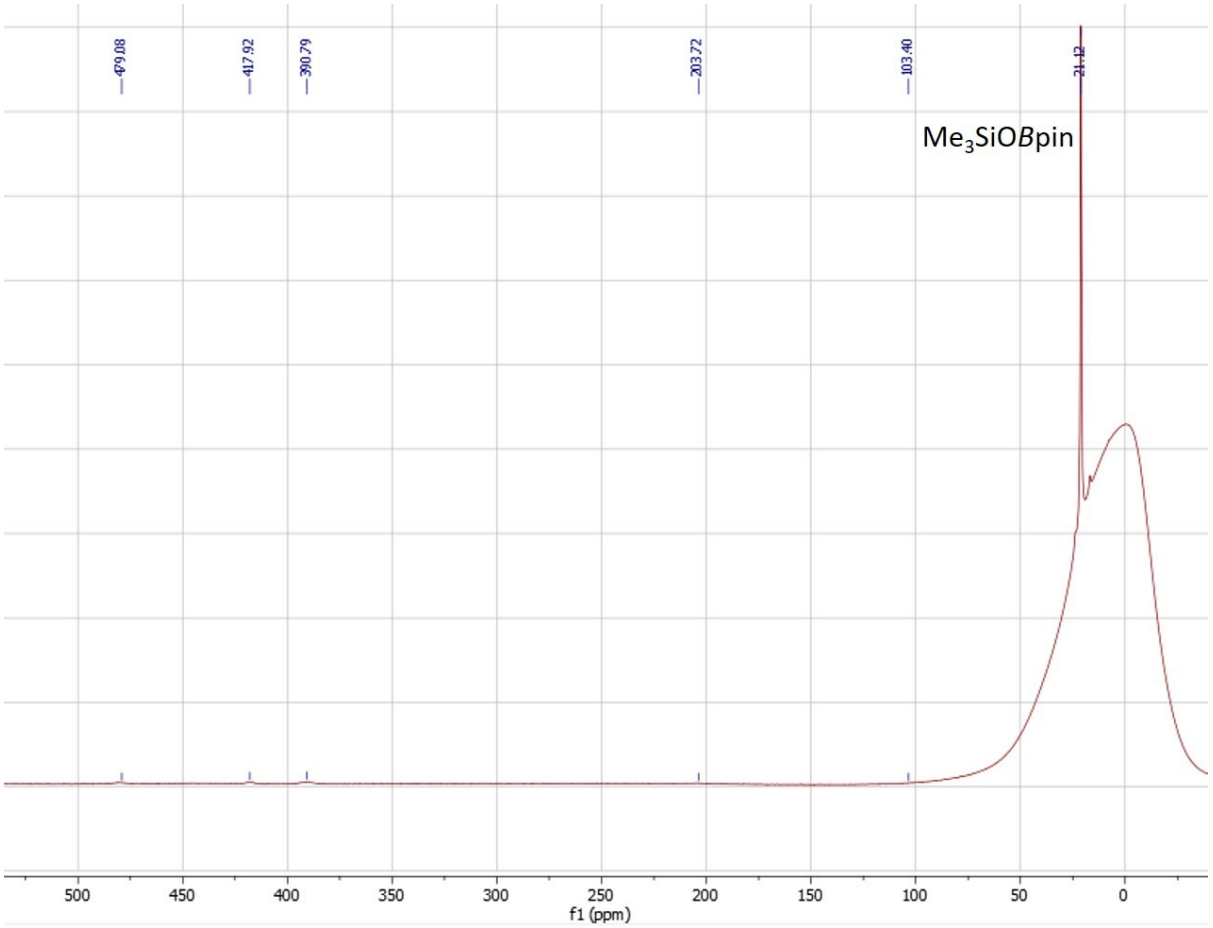

Figure S26. ^{11}B NMR spectrum of **B** + 2 equiv. of Me_3SiCl, forming $Me_3SiOBpin$ and other boron-containing paramagnetic species (161 MHz; d_5-pyridine; 300 K; $BF_3(OEt_2)$).

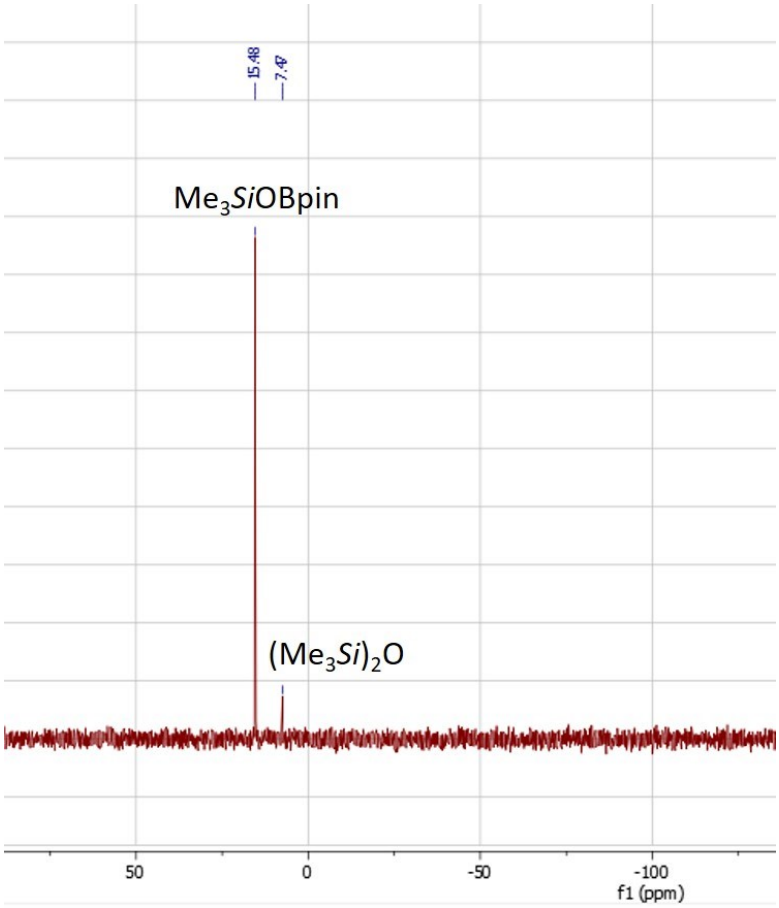

Figure S27. ^{29}Si_INEPT NMR spectrum of **B** + 2 equiv. of Me_3SiCl, forming $Me_3SiOBpin$ and $(Me_3Si)_2O$. The formation of both Si-containing species indicates that Me_3SiCl reacts at both the boroxido- and bridging oxo ligands, with the far greater quantity of $Me_3SiOBpin$ indicating that the boroxido ligands are the preferred site of reactivity (99 MHz; d_5-pyridine; 300 K; $SiMe_4$).

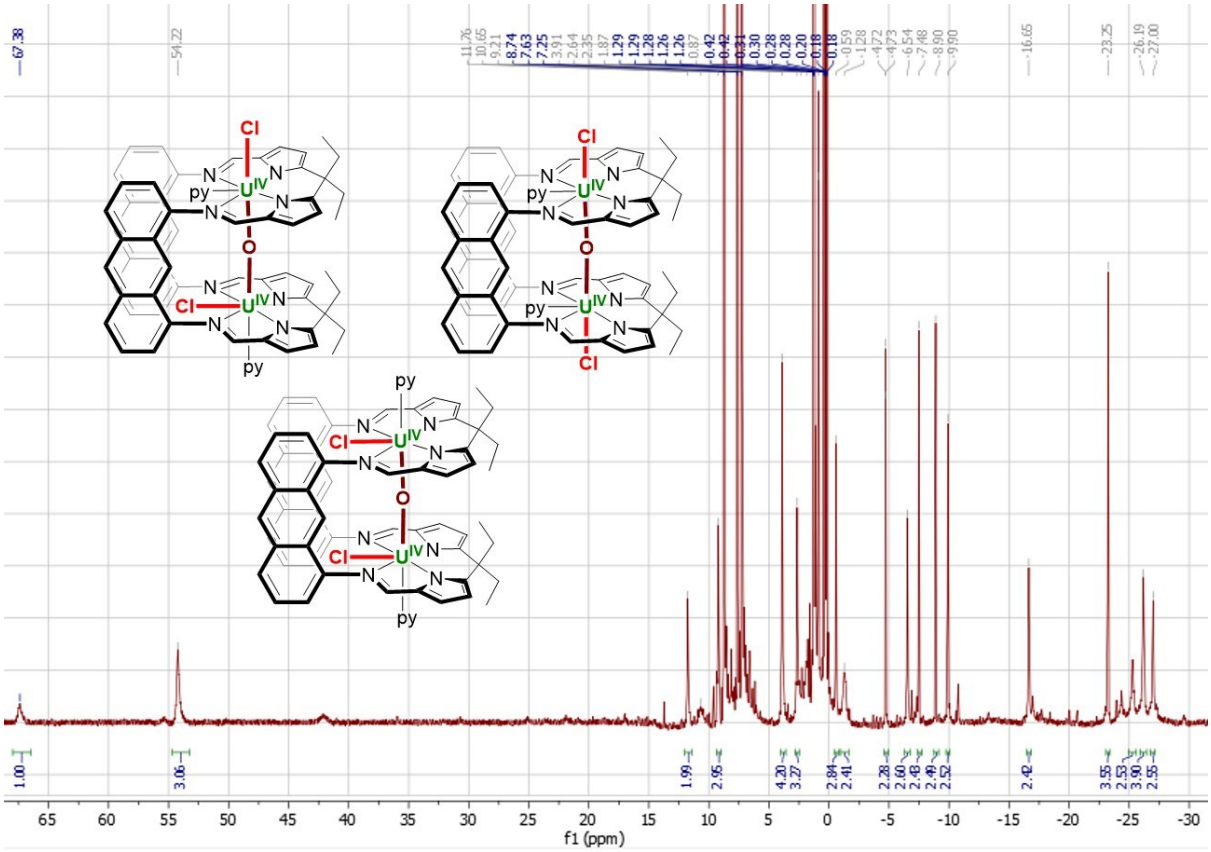

Figure S28. ^{1}H NMR spectrum of **B** + 3 equiv. of Me_3SiCl, forming **8**. We were unable to determine if this reaction formed a mixture of products, or if **8** exists as a mixture of isomers in solution with the chloride ligands coordinated in both axial and equatorial positions (500 MHz; d_5-pyridine; 300 K; $SiMe_4$).

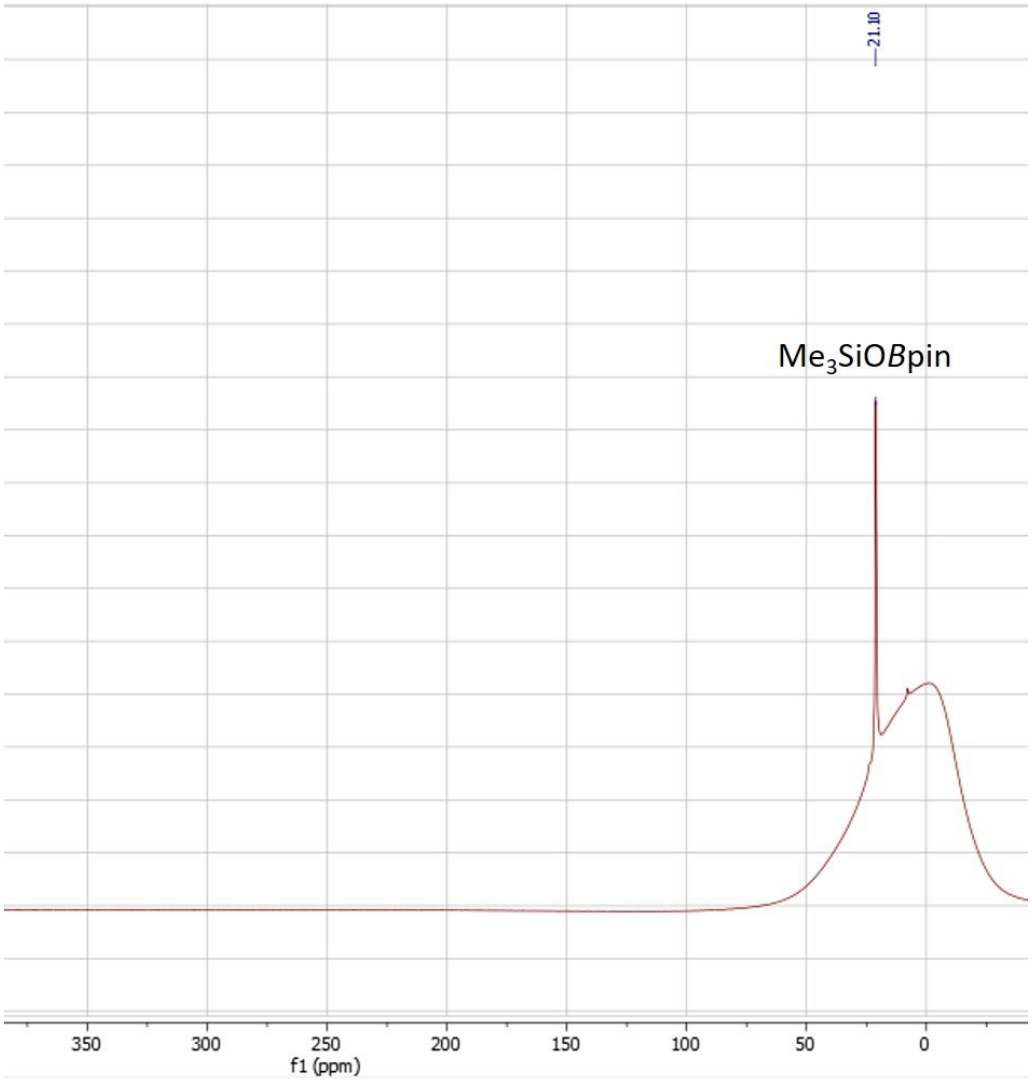

Figure S29. ^{11}B NMR spectrum of **B** + 3 equiv. of Me_3SiCl, forming only $Me_3SiOBpin$ (161 MHz; d_5-pyridine; 300 K; $BF_3(OEt_2)$).

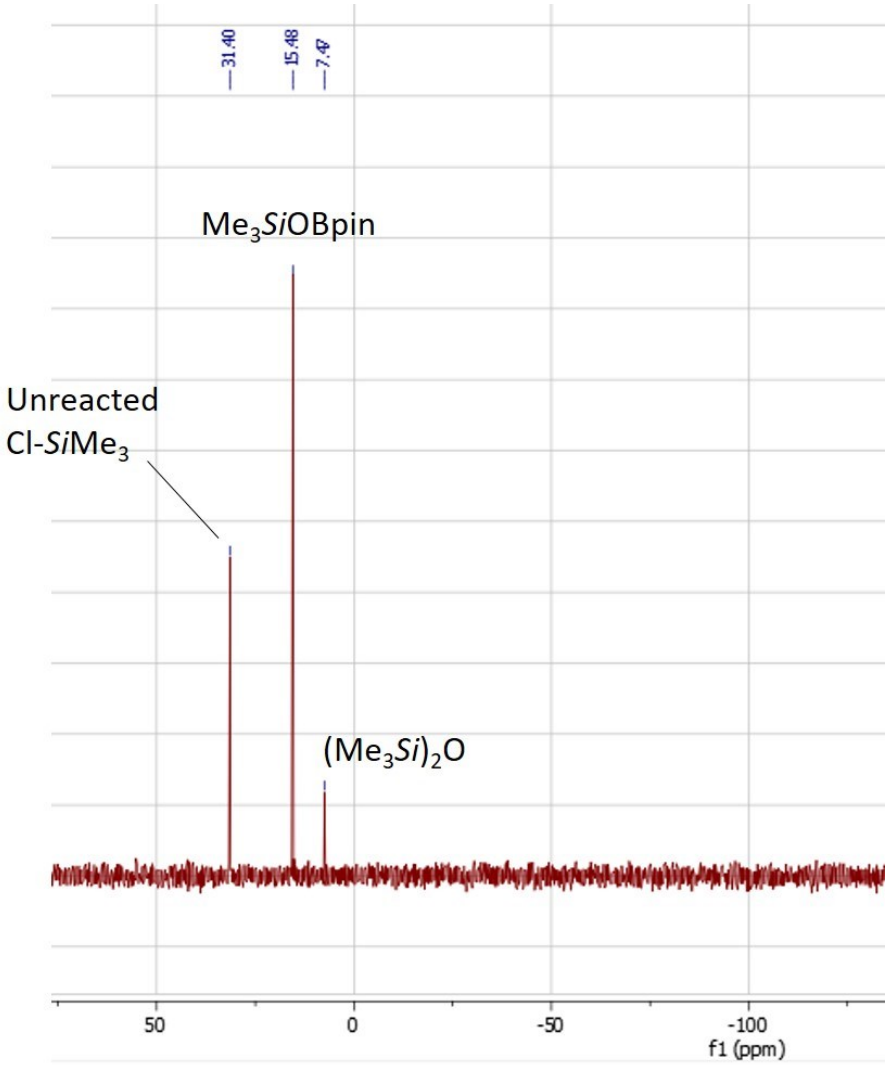

Figure S30. ^{29}Si_INEPT NMR spectrum of **B** + 3 equiv. of Me_3SiCl; $Me_3SiOBpin$, $(Me_3Si)_2O$ and unreacted Me_3SiCl are present in the NMR spectrum (99 MHz; d_5-pyridine; 300 K; $SiMe_4$).

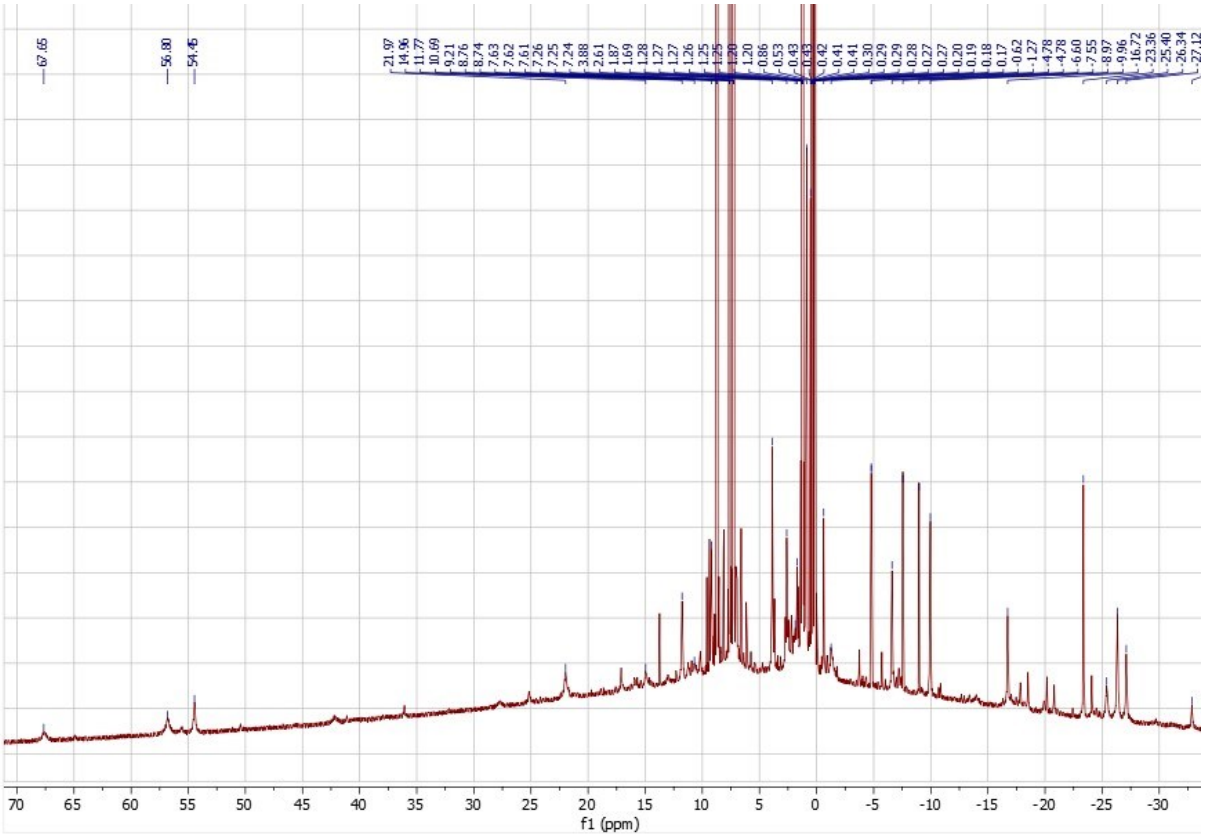

Figure S31. ^{1}H NMR spectrum of **B** + 10 equiv. of Me_3SiCl, forming **8** and a mixture of other species (500 MHz; d_5-pyridine; 300 K; $SiMe_4$).

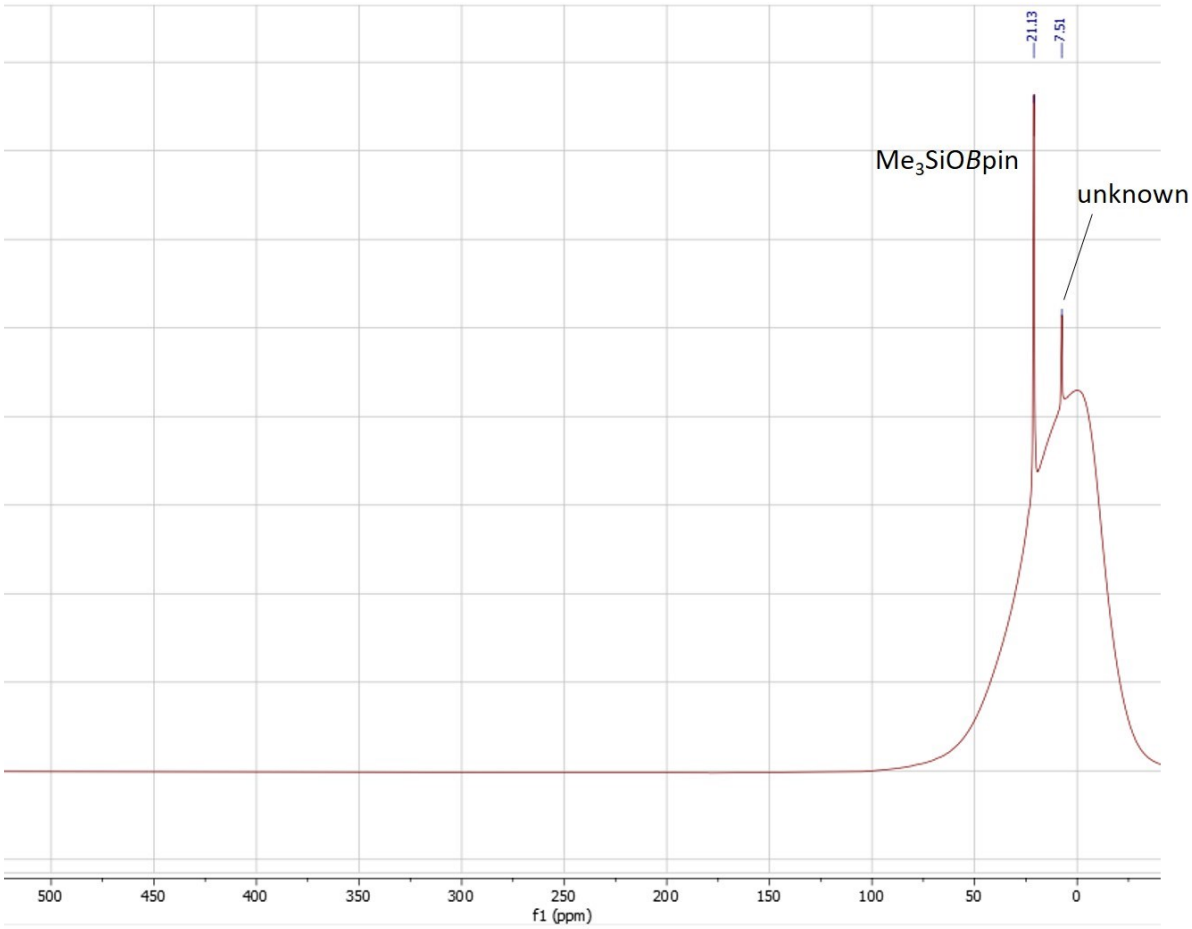

Figure S32. ^{11}B NMR spectrum of **B** + 10 equiv. of Me_3SiCl, forming $Me_3SiOBpin$ and an unknown species at 7.5 ppm (161 MHz; d_5-pyridine; 300 K; $BF_3(OEt_2)$).

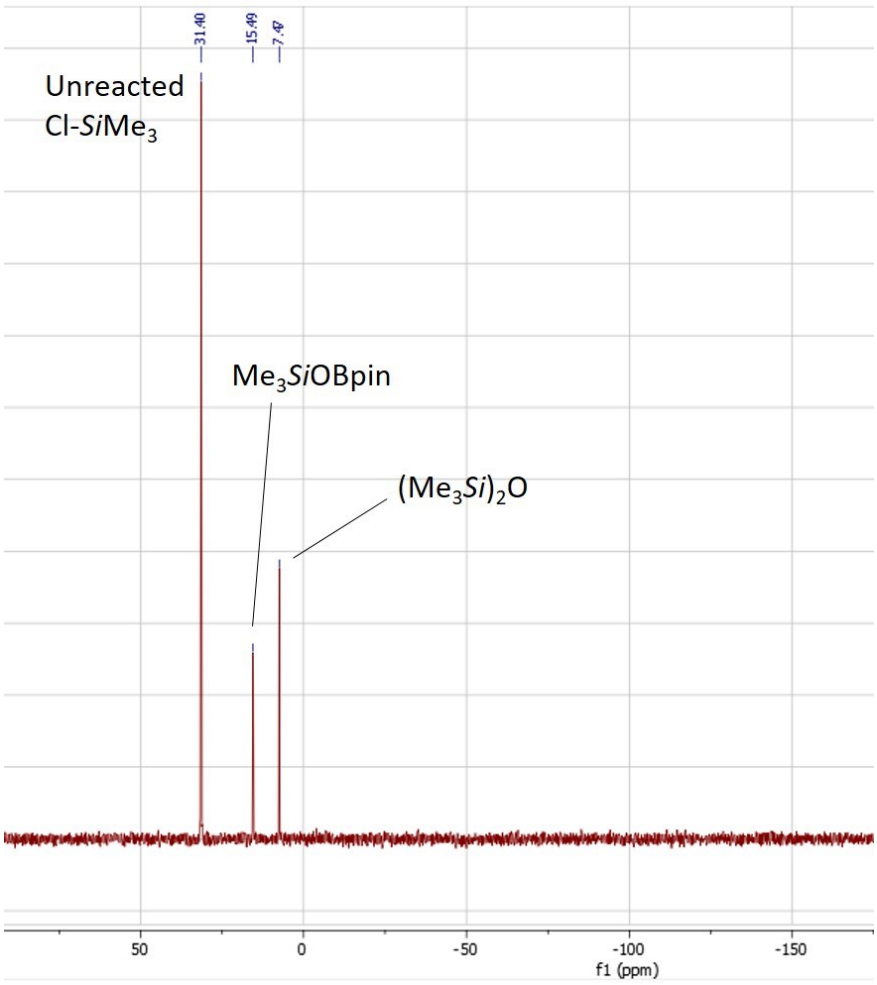

Figure S33. ^{29}Si_INEPT NMR spectrum of **B** + 10 equiv. of Me_3SiCl; $Me_3SiOBpin$ and $(Me_3Si)_2O$ are present in the NMR spectrum in a 1:1 ratio alongside unreacted Me_3SiCl (99 MHz; d_5-pyridine; 300 K; $SiMe_4$).

1.1.5 FTIR Spectra

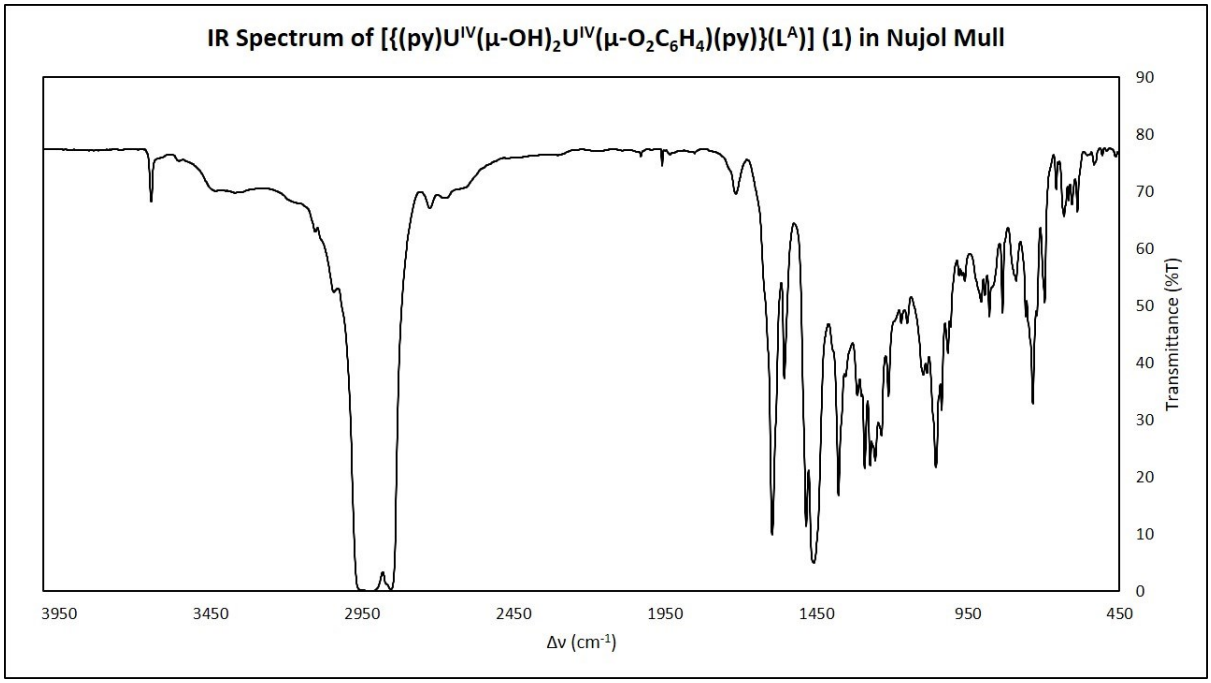

Figure S34. IR spectrum of **1** in nujol mull.

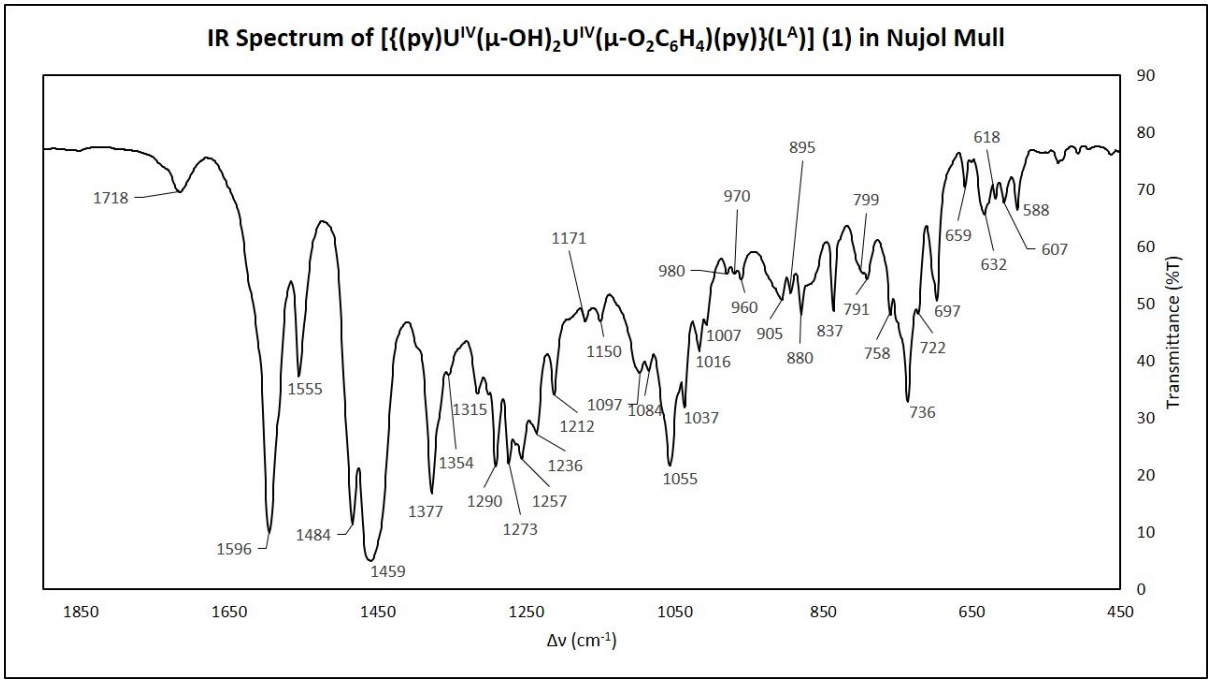

Figure S35. Expanded view of the IR spectrum of **1** in nujol mull.

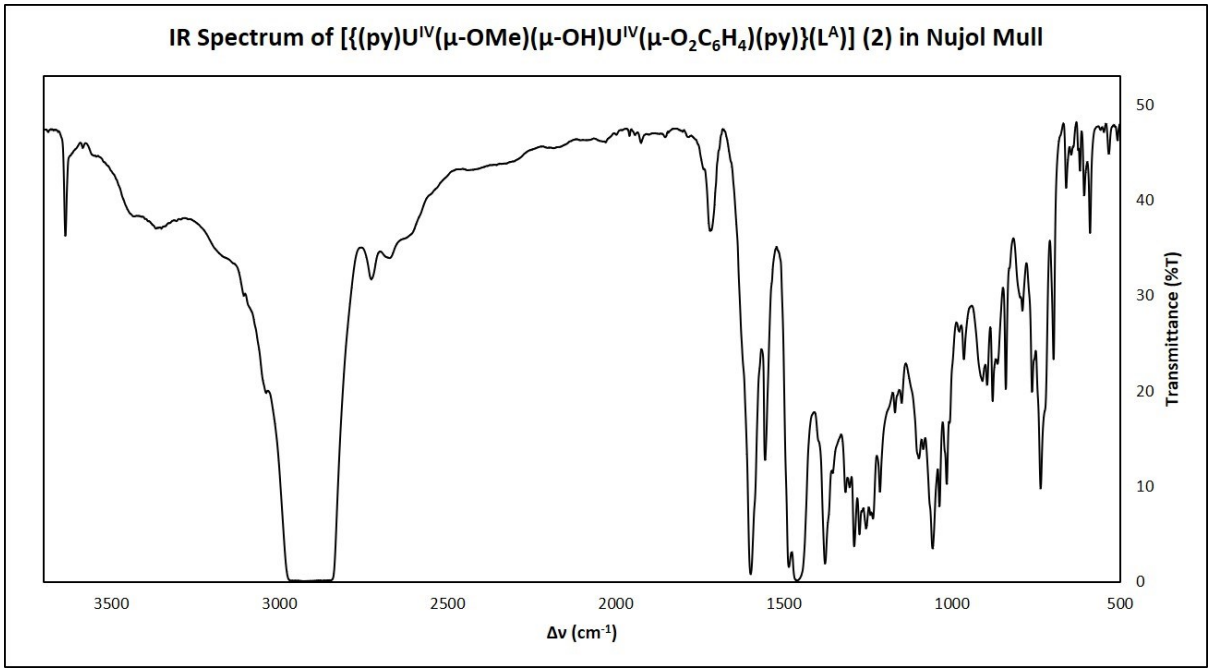

Figure S36. IR spectrum of **2** in nujol mull.

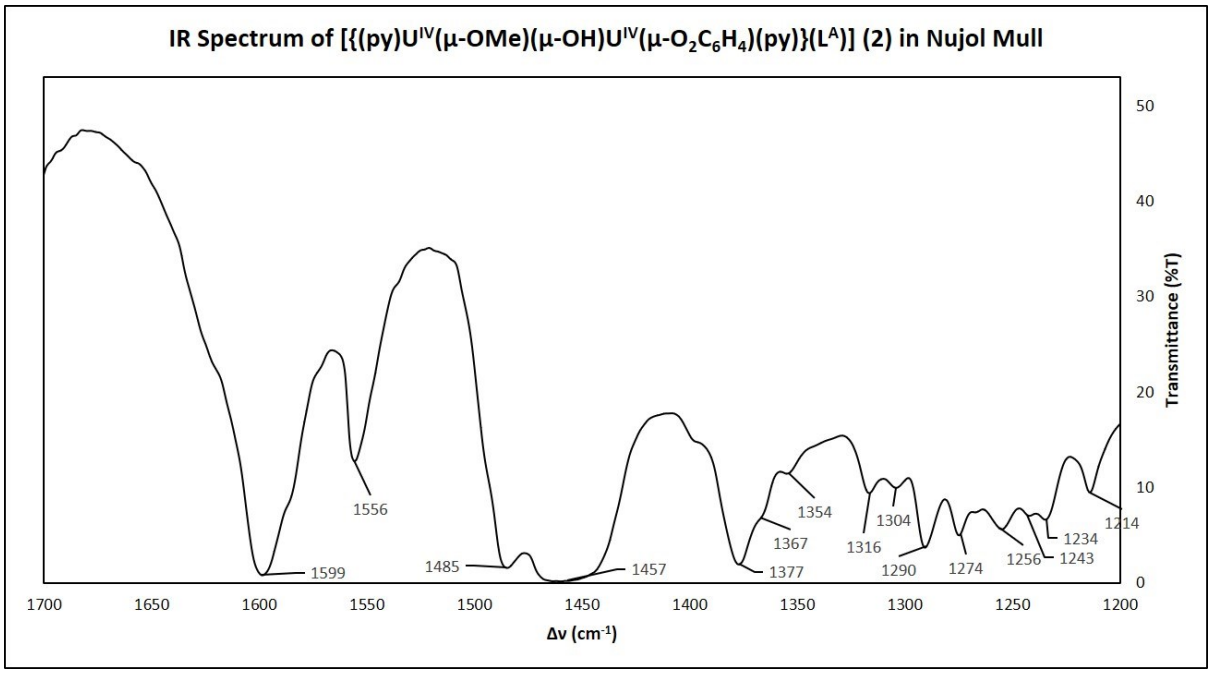

Figure S37. Expanded view of the IR spectrum of **2** in nujol mull.

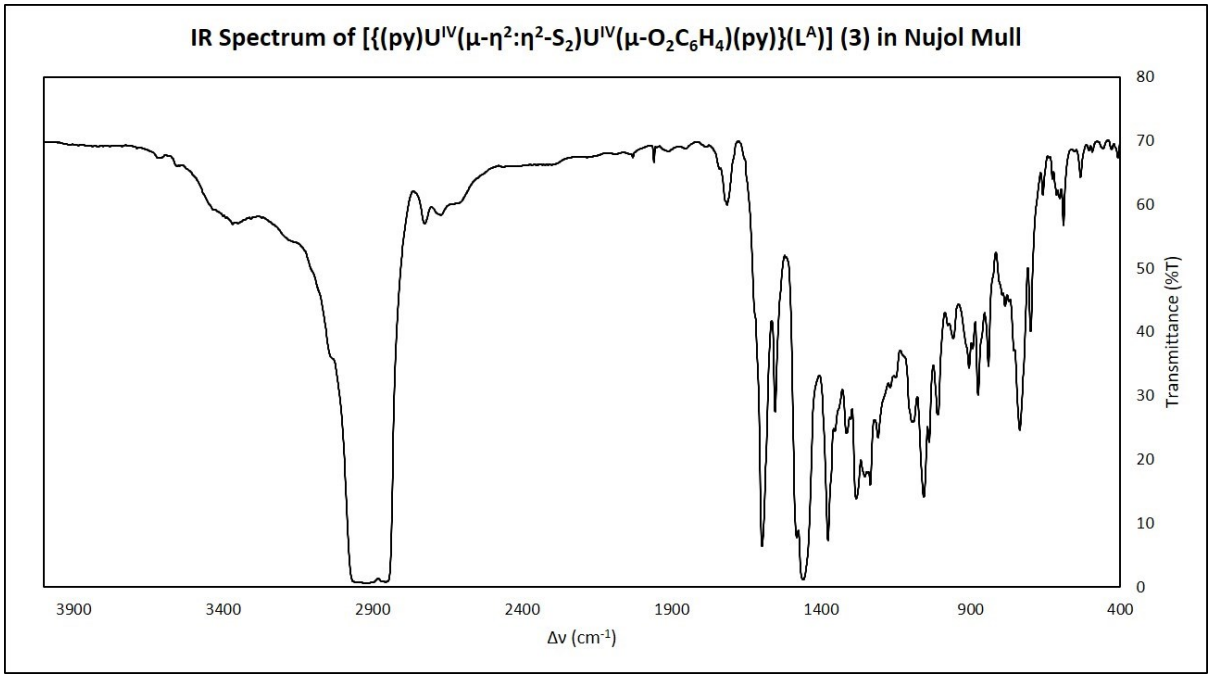

Figure S38. IR spectrum of **3** in nujol mull.

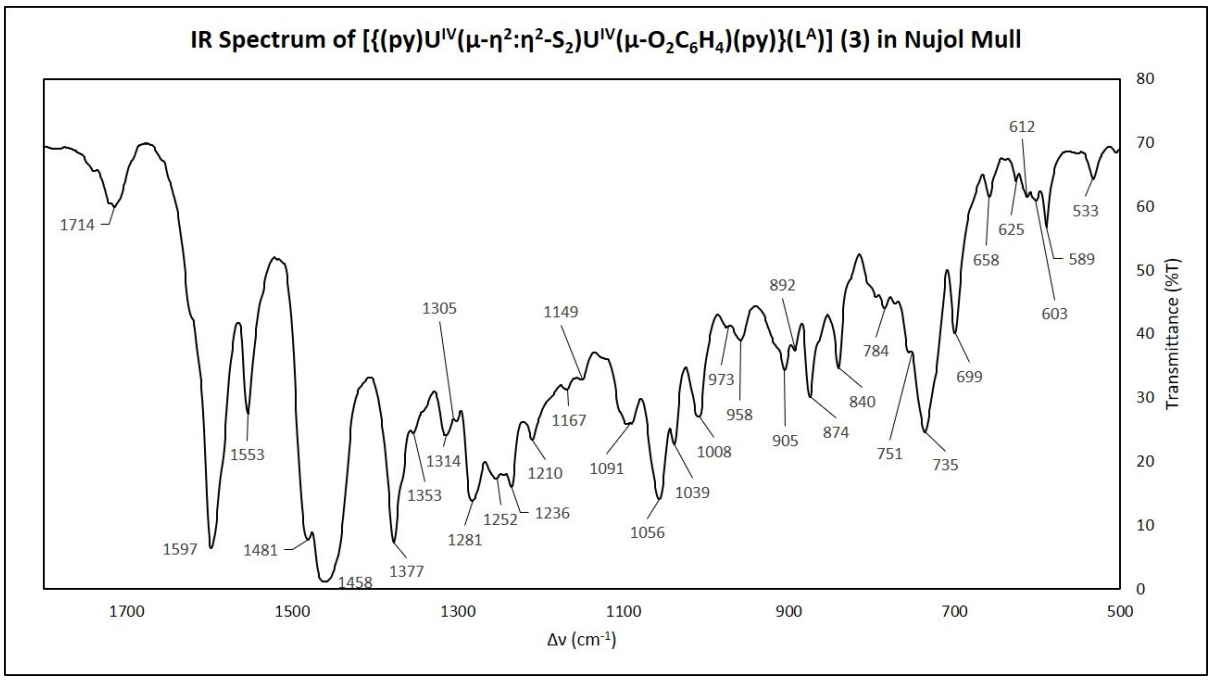

Figure S39. Expanded view of the IR spectrum of **3** in nujol mull.

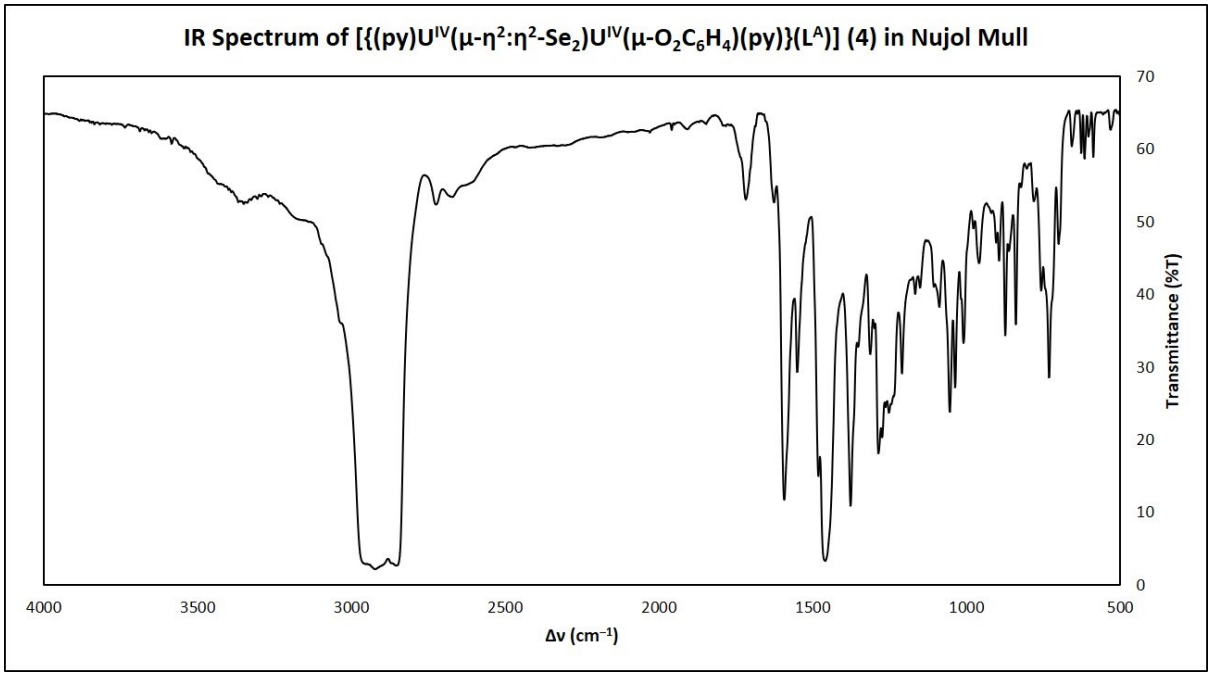

Figure S40. IR spectrum of **4** in nujol mull.

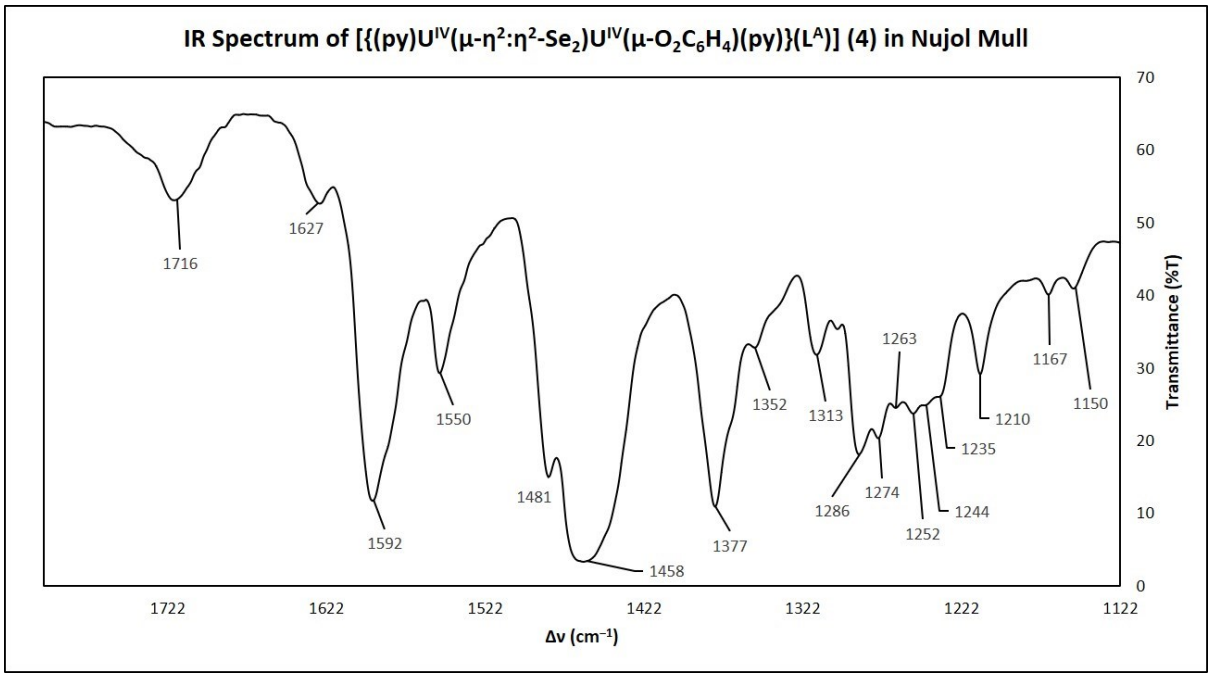

Figure S41. Expanded view of the IR spectrum of **4** in nujol mull.

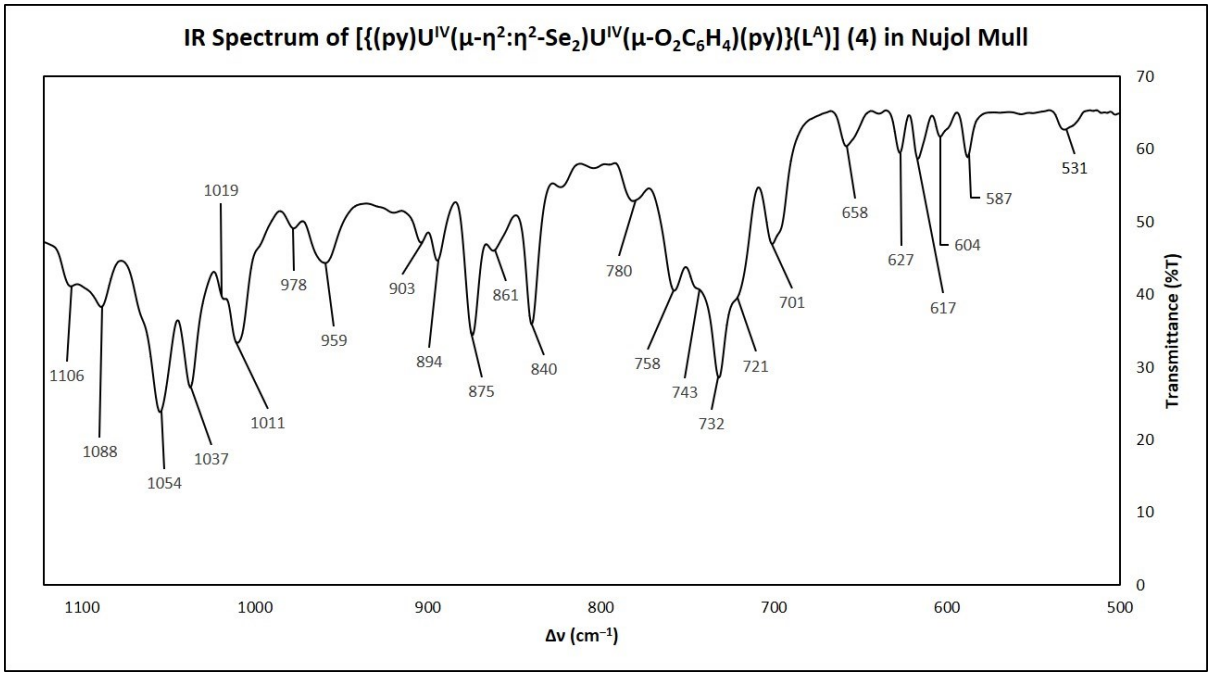

Figure S42. Expanded view of the IR spectrum of **4** in nujol mull.

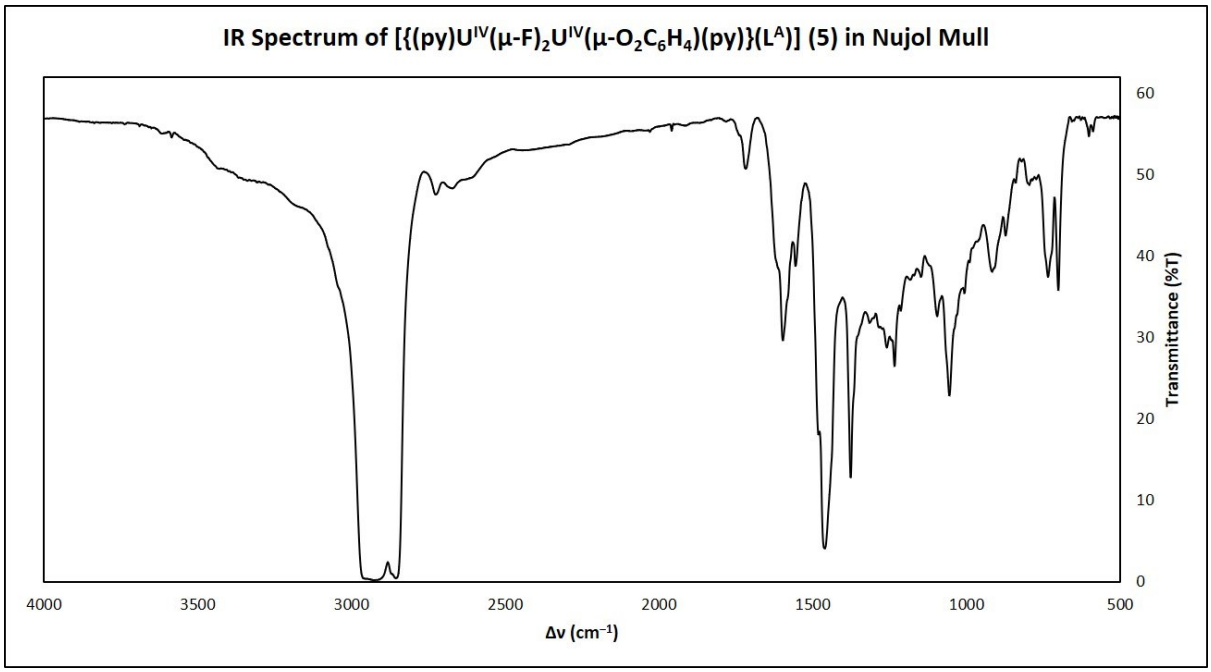

Figure S43. IR spectrum of **5** in nujol mull.

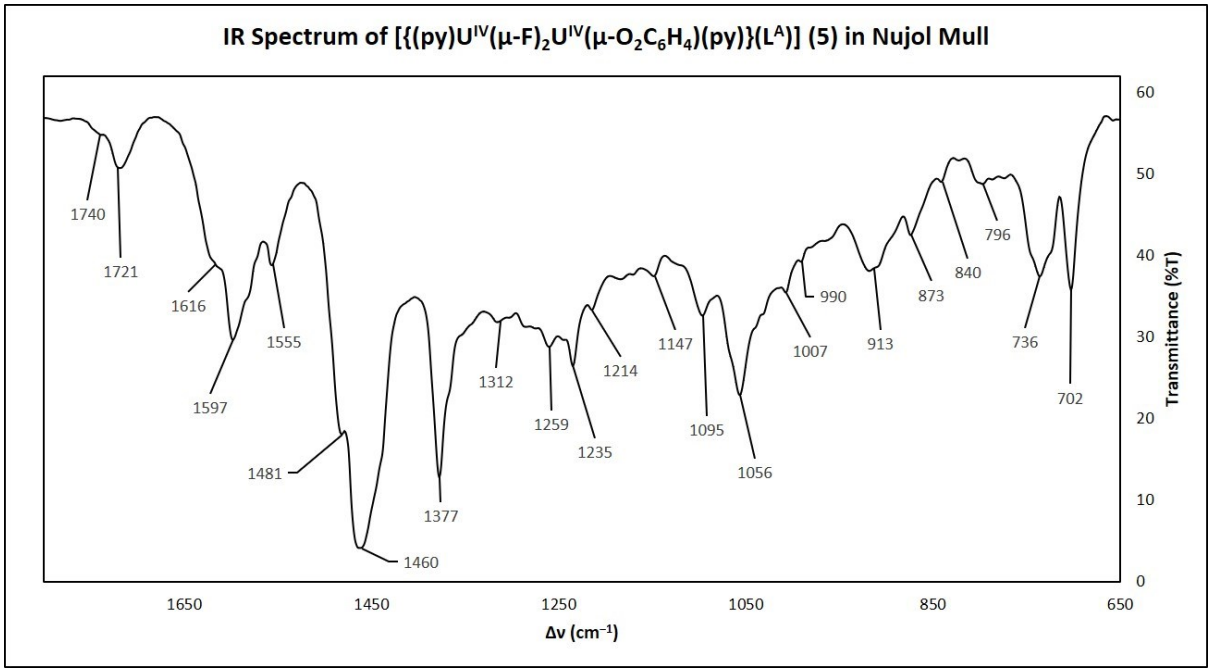

Figure S44. Expanded view of the IR spectrum of **5** in nujol mull.

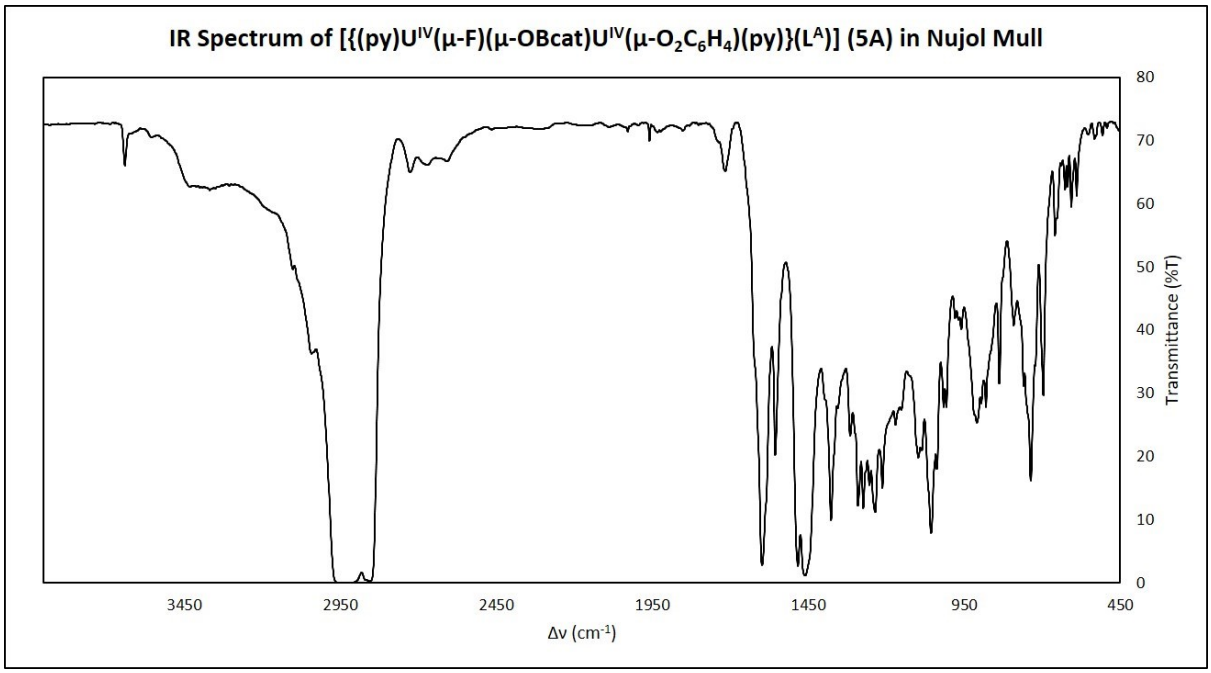

Figure S45. IR spectrum of **5A** in nujol mull.

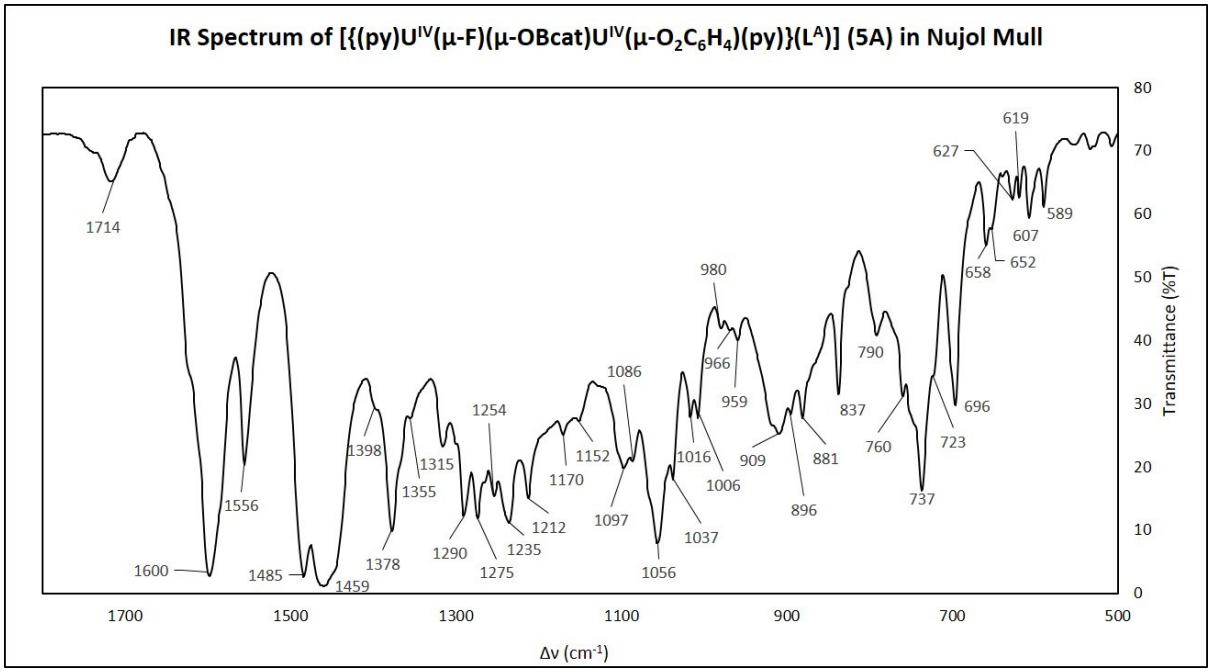

Figure S46. Expanded view of the IR spectrum of **5A** in nujol mull.

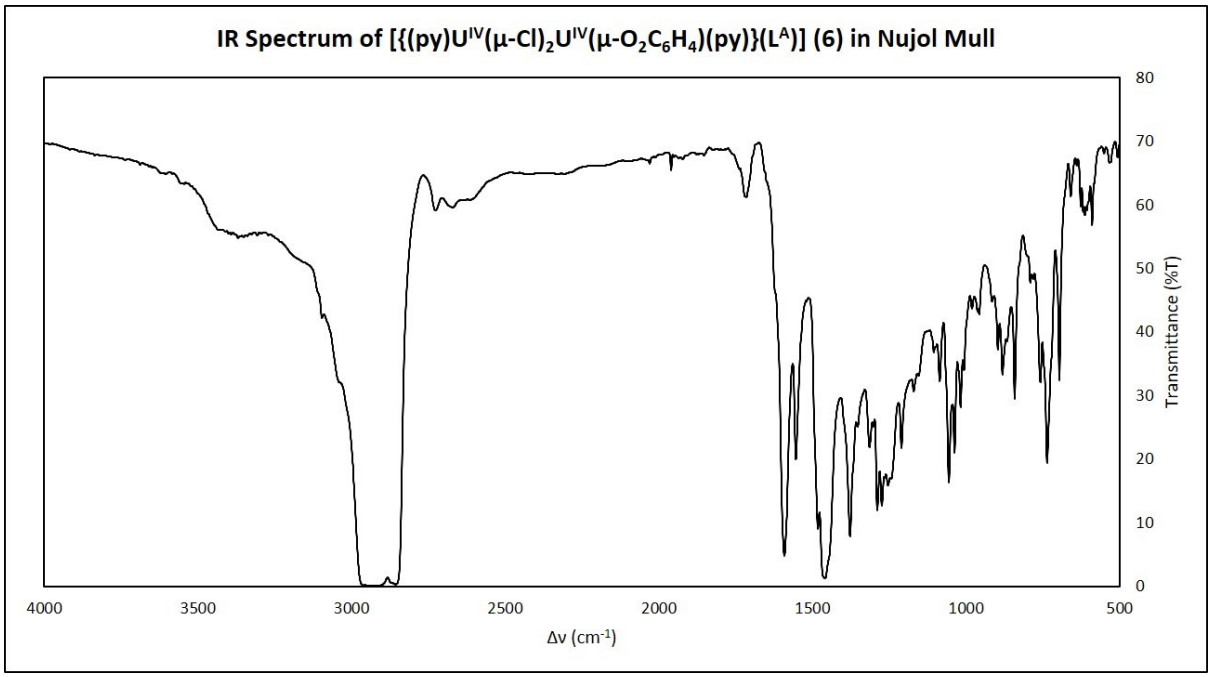

Figure S47. IR spectrum of **6** in nujol mull.

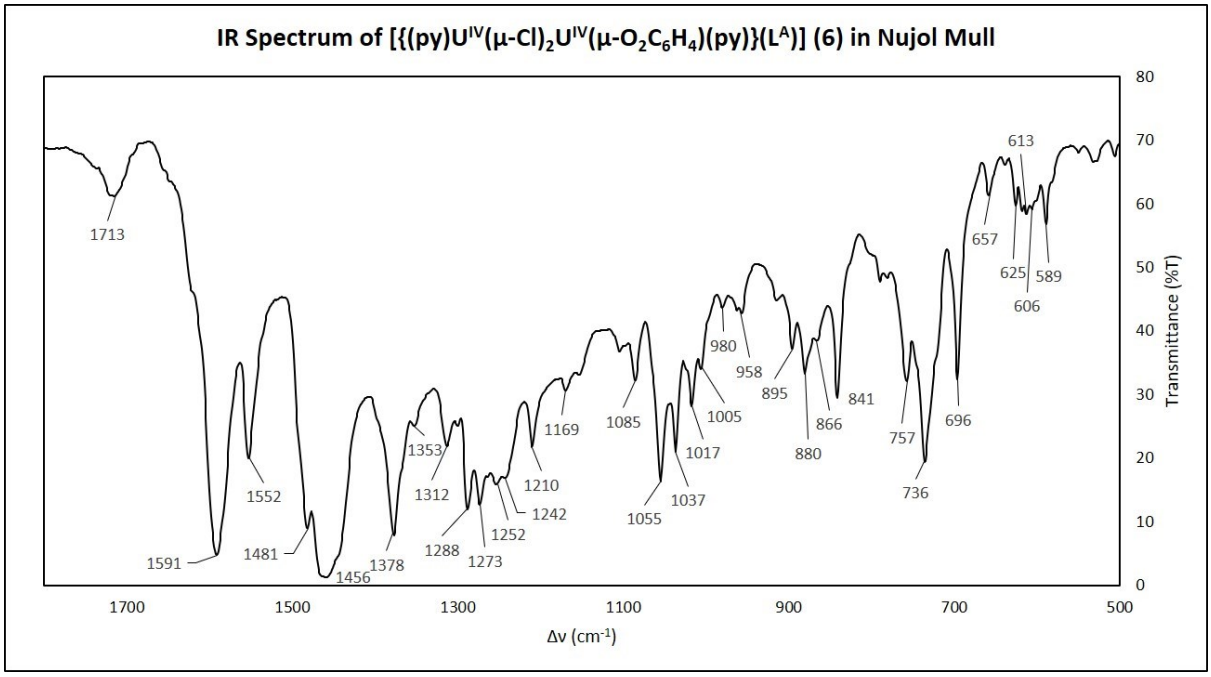

Figure S48. Expanded view of the IR spectrum of **6** in nujol mull.

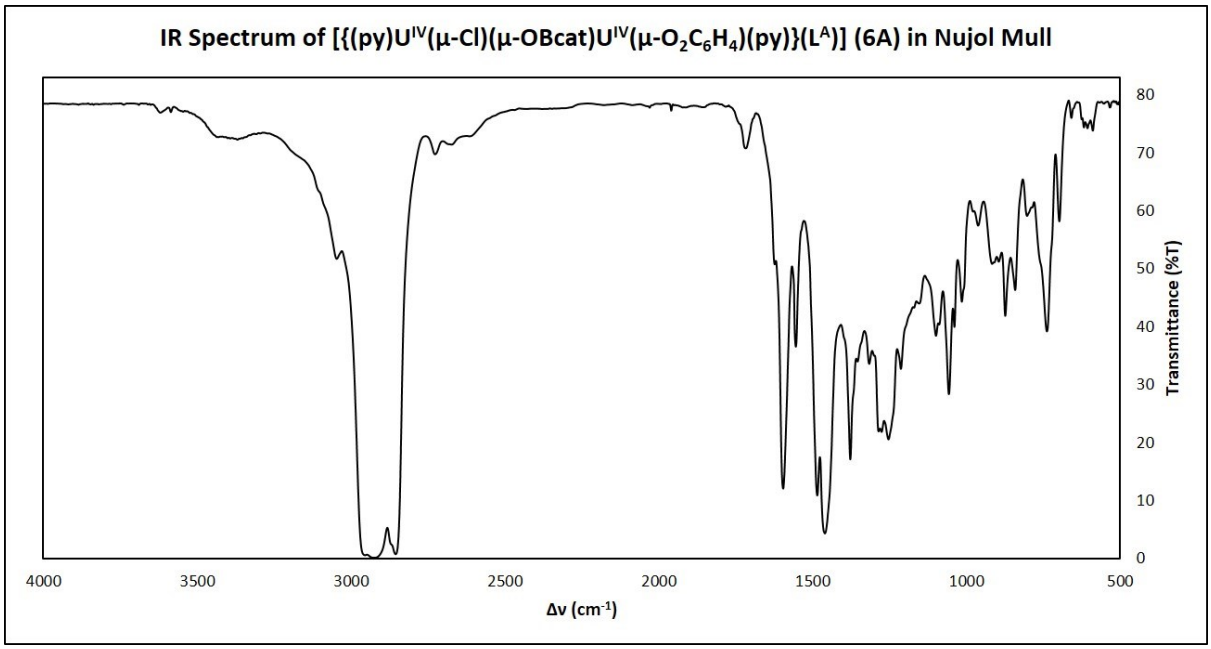

Figure S49. IR spectrum of **6A** in nujol mull.

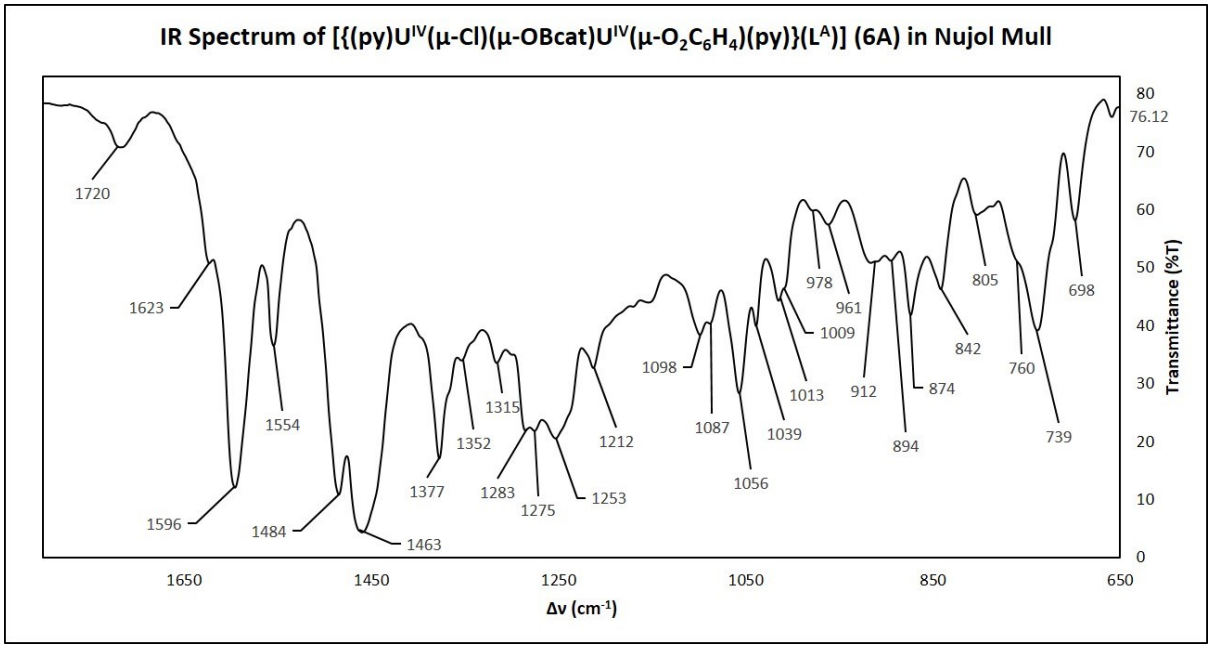

Figure S50. Expanded view of the IR spectrum of **6A** in nujol mull.

1.1.6 Computational details

All quantum-chemical calculations were conducted using the Gaussian09 program suite.[5] Becke's 3-parameter hybrid functional was employed, combined with the non-local correlation functional provided by Perdew/Wang, denoted as B3PW91.[6] The relativistic energy-consistent small-core pseudopotential of the Stuttgart-Köln ECP library was used in combination with its adapted segmented basis.[7] For all other atoms, a standard 6-31G** basis set was used.[8] All stationary points have been identified as minima (number of imaginary frequencies $N_{imag} = 0$) by frequency calculations. Natural Bonding Orbital (NBO) analyses were also carried out.[9] The enthalpy energy was computed at T=298 k in the gas phase.

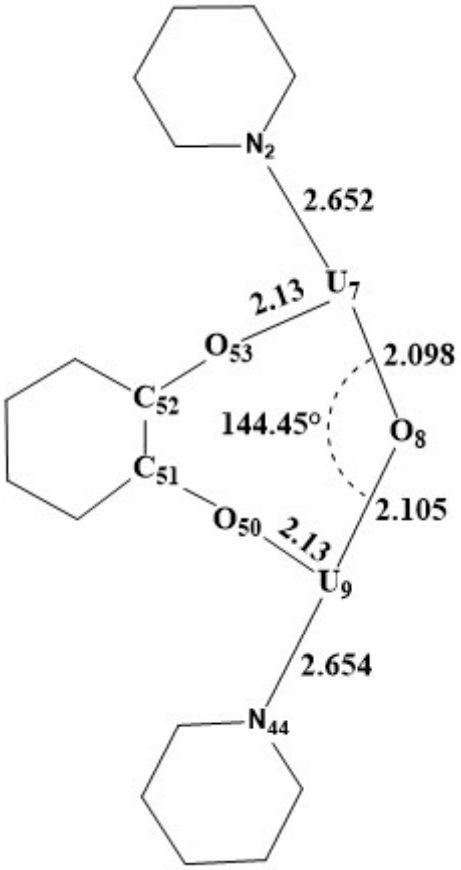

Figure S51. Main geometrical parameters of the optimised structure

Natural Charge

U_7 = 1.67807	U_9 = 1.66253	O_8 = -0.90719	O_{50}= -0.70735
O_{53}= -0.70744	N_{44}= -0.47801	N_2= -0.47822	

Natural Electron Configuration

U_7 [core]7S(0.18)5f(2.72)6d(1.04)7p(0.25)
U_9 [core]7S(0.18)5f(2.73)6d(1.05)7p(0.26)
O_8 [core]2S(1.71)2p(5.19)
O_{50} [core]2S(1.61)2p(5.09)3p(0.01)
O_{53} [core]2S(1.61)2p(5.09)3p(0.01)
N_{44} [core]2S(1.31)2p(4.15)3p(0.01)
N_2 [core]2S(1.31)2p(4.15)3p(0.01)

Wiberg Bond Indexes

U7-O8 = 0.9075	U7-U9 = 0.1560	U7-N2 = 0.3217	U7-O53 = 0.8294
U9-O8 = 0.8959	U9-U7 = 0.1560	U9-N44 = 0.3205	U9-O50 = 0.8355

Donation

		Energy (kcal/mol)	
Donor	Acceptor	Alpha	Beta
O_8	U_7	*198,40 (8% CR + 92% LP)*	*193,25(9% CR + 91% LP)*
O_8	U_9	*196,46 (8% CR + 92% LP)*	*190,66(9% CR + 91% LP)*

Spin Density

	U1	U2
Complex A	2.126115	2.126821
Complex B	2.126527	2.128697

Figure S52. Frontier orbital diagram of complex **A**. Atom colours: grey, carbon; blue, nitrogen; red, oxygen; green, uranium.

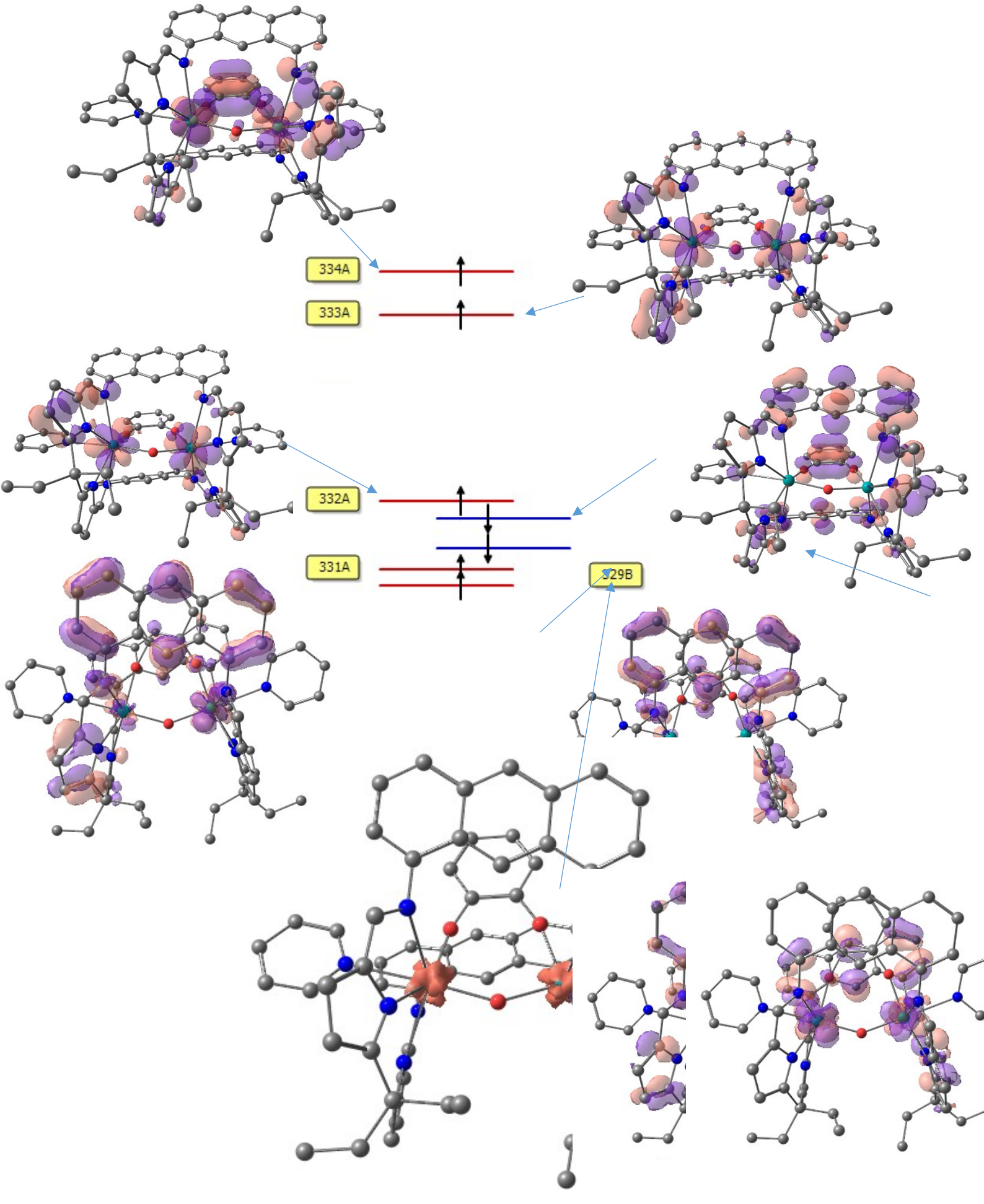

Figure S53. Depiction of the unpaired spin density of complex **A**.

Computed Atomic Coordinates

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151
U2C74N10H62O3
C       13.234715000     -1.279210000     -2.584204000
N       13.679407000     -0.035818000     -2.341360000
C       14.776370000      0.390202000     -2.986206000
C       15.466599000     -0.402612000     -3.896731000
C       15.003911000     -1.692293000     -4.145633000
C       13.867984000     -2.138904000     -3.475597000
U       12.402327000      1.504152000     -0.600020000
O       11.512302000      2.670582000      0.899331000
U       11.572377000      4.529660000      1.884859000
N       11.081422000      3.866532000      4.247149000
C       12.075823000      4.160181000      5.166098000
C       11.603078000      3.988768000      6.476115000
C       10.280679000      3.572208000      6.353053000
C        9.993021000      3.508998000      4.970354000
C       13.363117000      4.526384000      4.737820000
N       13.681746000      4.606228000      3.469323000
C       15.006669000      5.007195000      3.190651000
C       15.856813000      4.131398000      2.430922000
C       17.225422000      4.517861000      2.203189000
C       17.692761000      5.764778000      2.713775000
C       16.853695000      6.579705000      3.422858000
C       15.508147000      6.198545000      3.667849000
C       15.400415000      2.908113000      1.937802000
C       16.230588000      2.061060000      1.202225000
```

C	17.612288000	2.417580000	1.010699000
C	18.066591000	3.641960000	1.510337000
C	18.480200000	1.507594000	0.337104000
C	18.004568000	0.310054000	-0.123023000
C	16.634724000	-0.032146000	0.028713000
C	15.752572000	0.822895000	0.653084000
N	14.380464000	0.495723000	0.732584000
C	14.060527000	-0.574035000	1.421002000
C	12.772287000	-1.136942000	1.392307000
N	11.807986000	-0.673217000	0.507350000
C	10.743401000	-1.501252000	0.640828000
C	11.008598000	-2.479706000	1.630889000
C	12.296603000	-2.251784000	2.099900000
C	9.464734000	-1.418773000	-0.173797000
C	8.352871000	-0.642527000	0.617463000
C	7.782253000	-1.330116000	1.855086000
C	8.733300000	2.972697000	4.324848000
C	7.595863000	2.845423000	5.368544000
C	7.071261000	4.146608000	5.978351000
N	11.492073000	6.918949000	3.036973000
C	12.306850000	7.918928000	2.667124000
C	12.270141000	9.175306000	3.262337000
C	11.347002000	9.406529000	4.279305000
C	10.497705000	8.372309000	4.663053000
C	10.604054000	7.143957000	4.018920000
O	13.137007000	5.194220000	0.603517000
C	14.191465000	5.269833000	-0.222345000
C	14.590787000	4.138628000	-0.982245000
O	13.900804000	2.990805000	-0.906860000
N	10.215247000	6.046220000	0.267804000
C	10.698991000	7.041593000	-0.608827000
C	11.428408000	6.658527000	-1.785616000
C	12.002005000	7.685668000	-2.614764000
C	11.781816000	9.054469000	-2.278025000
C	11.034785000	9.385475000	-1.180234000
C	10.495636000	8.377218000	-0.337550000
C	12.740672000	7.306945000	-3.740445000
C	12.920752000	5.965476000	-4.091740000
C	12.305144000	4.946992000	-3.280372000
C	11.565320000	5.321092000	-2.158389000
C	12.439701000	3.570939000	-3.672177000
C	13.160918000	3.252898000	-4.801822000
C	13.781883000	4.261582000	-5.585262000
C	13.666302000	5.581329000	-5.245292000
N	11.787145000	2.567272000	-2.919169000
C	10.878269000	1.880172000	-3.567745000
C	10.180529000	0.805811000	-2.995640000
N	10.440589000	0.374936000	-1.701866000
C	9.617656000	-0.680057000	-1.489971000
C	8.821174000	-0.921496000	-2.635666000
C	9.182377000	0.019294000	-3.590327000
N	9.120848000	4.489942000	2.336616000
C	8.329769000	5.138149000	1.399468000
C	6.972431000	4.861751000	1.630766000
C	6.936012000	4.020982000	2.737953000
C	8.273056000	3.828836000	3.158232000
C	8.914657000	5.964442000	0.424592000
C	9.059647000	1.553233000	3.749886000

C	9.570137000	0.522040000	4.754350000
C	8.961533000	-2.862241000	-0.458717000
C	9.887051000	-3.734089000	-1.304399000
H	14.820418000	-1.067938000	2.034394000
H	12.840539000	-2.818141000	2.845674000
H	10.345135000	-3.275594000	1.939023000
H	8.783293000	-3.363113000	0.496594000
H	7.974983000	-2.795271000	-0.932778000
H	10.049103000	-3.301948000	-2.296503000
H	9.456697000	-4.732239000	-1.440230000
H	10.860720000	-3.854867000	-0.818648000
H	8.070284000	-1.691351000	-2.744764000
H	8.789026000	0.134088000	-4.592776000
H	10.631229000	2.150902000	-4.599035000
H	13.259752000	2.209406000	-5.087923000
H	14.349276000	3.971046000	-6.465552000
H	14.135175000	6.355373000	-5.847151000
H	13.183184000	8.079591000	-4.365699000
H	11.086970000	4.555058000	-1.560011000
H	8.254454000	6.553040000	-0.219575000
H	6.134307000	5.237704000	1.057078000
H	6.052710000	3.603811000	3.201421000
H	6.766653000	2.305605000	4.894916000
H	7.944526000	2.188333000	6.171758000
H	8.150091000	1.183165000	3.262535000
H	9.805205000	1.681928000	2.958180000
H	10.436697000	0.897846000	5.306798000
H	9.882637000	-0.385219000	4.228469000
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H	9.608875000	3.320755000	7.161509000
H	12.167445000	4.142898000	7.387469000
H	14.122103000	4.721686000	5.501745000
H	14.853966000	6.858138000	4.231396000
H	17.211686000	7.530143000	3.809829000
H	18.724622000	6.051995000	2.529519000
H	19.107697000	3.919606000	1.359693000
H	16.260600000	-0.965548000	-0.382125000
H	14.376339000	2.607641000	2.125743000
H	9.968672000	6.304655000	4.285259000
H	9.941136000	8.655181000	0.554244000
H	19.523796000	1.781015000	0.203904000
H	18.669997000	-0.386891000	-0.625759000
H	13.005201000	7.690490000	1.869270000
H	12.211276000	9.825538000	-2.912552000
H	10.858834000	10.429083000	-0.932712000
H	9.763876000	8.504745000	5.451101000
H	12.951338000	9.950836000	2.928059000
H	11.290996000	10.376948000	4.764725000
H	6.293370000	3.932520000	6.719476000
H	7.866091000	4.704530000	6.481222000
H	6.639078000	4.802324000	5.217899000
H	7.537037000	-0.445389000	-0.089026000
H	8.765251000	0.335075000	0.889643000
H	7.069772000	-0.664960000	2.353238000
H	7.239437000	-2.246989000	1.604704000
H	8.561978000	-1.582793000	2.579071000
H	15.095730000	1.400614000	-2.756302000
H	16.348276000	-0.011075000	-4.393268000

H	15.519966000	-2.338391000	-4.850409000
H	13.469492000	-3.134856000	-3.637739000
H	12.343101000	-1.577548000	-2.041667000
C	15.714397000	4.244994000	-1.808181000
C	16.430834000	5.435002000	-1.911724000
C	16.028329000	6.548385000	-1.179539000
C	14.917340000	6.458660000	-0.344290000
H	16.022524000	3.370451000	-2.372472000
H	17.298416000	5.486700000	-2.563744000
H	16.574252000	7.484897000	-1.252397000
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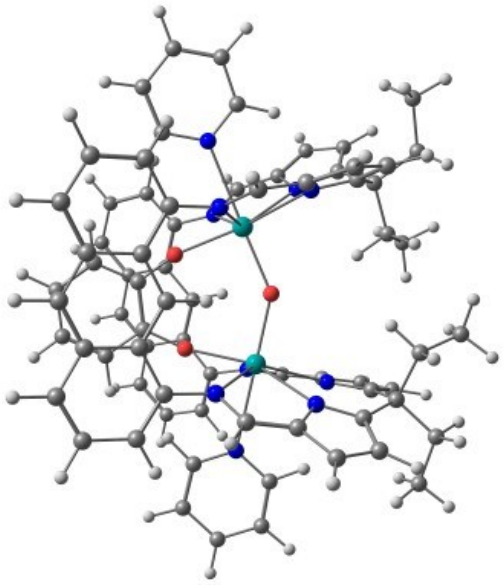

Figure S54. Geometry optimisation of bent complex **A**.

183
U2B2C80N10H82O7

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U	11.787197000	4.788668000	1.846064000
O	13.672342000	8.499195000	0.694904000
O	14.843847000	-1.789364000	-2.556298000
O	15.258896000	7.015386000	-0.035774000
O	13.189635000	6.146127000	0.887922000
O	12.743318000	-1.870621000	-3.492192000
O	13.283872000	-0.059314000	-1.982165000
O	12.120889000	3.132245000	0.605010000
N	14.790756000	2.550731000	-1.539025000
N	10.337371000	0.796188000	-1.622613000
N	11.984246000	2.772439000	-2.901870000
N	11.590702000	-0.372078000	0.628023000
N	14.297717000	0.543271000	0.924006000
N	13.920210000	4.788462000	3.424211000
N	11.368127000	3.901894000	4.153285000
N	9.378479000	4.271393000	2.201541000
N	10.230357000	6.087663000	0.220228000

N	11.007017000	6.966391000	3.235715000
C	14.455117000	-4.110873000	-2.136177000
C	16.075171000	-3.373453000	-3.894734000
C	13.953760000	-2.209074000	-5.523179000
C	12.682079000	-4.080228000	-4.454655000
C	13.535348000	-2.845877000	-4.195159000
C	14.746471000	-3.067277000	-3.216502000
C	17.230326000	8.399859000	-0.148845000
C	14.447153000	10.586188000	-0.222582000
C	15.479702000	9.588238000	1.822282000
C	14.853859000	9.285550000	0.459343000
C	7.506805000	-1.052823000	1.869466000
C	8.079109000	-0.283241000	0.681031000
C	15.098074000	3.823093000	-1.238223000
C	16.296817000	4.419016000	-1.615342000
C	17.214138000	3.673075000	-2.345461000
C	16.899305000	2.356001000	-2.668131000
C	15.684500000	1.833774000	-2.243203000
C	7.284603000	3.749000000	5.726009000
C	7.999673000	2.498820000	5.212666000
C	8.878382000	0.791294000	-3.395306000
C	8.449900000	-0.142634000	-2.467357000
C	9.378022000	-0.123628000	-1.393248000
C	10.048944000	1.355912000	-2.860621000
C	10.878547000	2.314333000	-3.451467000
C	9.709007000	-3.157832000	-1.474585000
C	8.739394000	-2.389933000	-0.581239000
C	9.220545000	-0.973980000	-0.145801000
C	11.934643000	-2.034526000	2.172109000
C	10.654002000	-2.167228000	1.654850000
C	10.475851000	-1.136894000	0.695011000
C	12.500603000	-0.924762000	1.521956000
C	13.833041000	-0.485373000	1.595595000
C	13.573292000	4.743435000	4.686811000
C	10.266086000	0.415664000	4.799900000
C	9.682060000	1.327420000	3.723402000
C	9.153490000	2.720418000	4.201616000
C	8.975338000	5.712355000	0.288912000
C	15.471158000	8.478355000	-1.920901000
C	15.733061000	8.320846000	-0.423421000
C	15.697923000	0.711965000	0.892997000
C	16.514467000	-0.268617000	0.371762000
C	17.916092000	-0.070395000	0.267146000
C	18.493251000	1.106201000	0.662823000
C	18.245214000	3.351853000	1.670254000
C	17.694012000	2.145555000	1.224412000
C	16.276188000	1.939585000	1.367113000
C	15.500759000	2.917545000	1.992126000
C	16.059181000	4.110991000	2.455895000
C	17.470052000	4.341756000	2.284763000
C	18.045201000	5.542108000	2.798257000
C	17.269846000	6.448740000	3.469645000
C	15.881533000	6.218345000	3.662342000
C	15.276553000	5.083077000	3.170881000
C	12.292734000	4.331603000	5.091391000
C	11.799324000	4.154365000	6.392613000
C	10.536711000	3.587114000	6.245949000
C	10.306555000	3.442193000	4.858840000

C	8.628268000	3.454887000	2.980072000
C	7.305059000	3.387287000	2.485129000
C	7.238601000	4.225697000	1.377825000
C	8.525419000	4.763703000	1.222795000
C	13.637342000	5.858028000	-5.303468000
C	13.915192000	4.544681000	-5.573863000
C	13.391115000	3.499968000	-4.763719000
C	12.622745000	3.787079000	-3.661337000
C	11.621608000	5.481556000	-2.177996000
C	12.366086000	5.156488000	-3.311611000
C	12.840181000	6.207468000	-4.172943000
C	12.467718000	7.527436000	-3.887256000
C	10.132065000	8.417246000	-0.480459000
C	10.489579000	9.449318000	-1.389537000
C	11.257358000	9.186420000	-2.492539000
C	11.690882000	7.854595000	-2.767933000
C	11.303165000	6.801757000	-1.866638000
C	10.542417000	7.121915000	-0.691776000
C	10.088087000	6.844140000	4.209048000
C	9.579775000	7.932801000	4.908851000
C	10.039992000	9.208024000	4.595035000
C	10.992497000	9.340389000	3.589450000
C	11.448316000	8.200157000	2.933811000
B	13.997948000	7.154346000	0.527718000
B	13.590529000	-1.190103000	-2.636692000
H	12.245018000	-4.466882000	-3.532242000
H	13.273486000	-4.873274000	-4.924759000
H	11.861891000	-3.823136000	-5.131253000
H	14.500808000	-2.911184000	-6.160104000
H	14.582218000	-1.328777000	-5.356439000
H	13.055550000	-1.885758000	-6.056518000
H	16.857469000	-3.488823000	-3.138453000
H	16.376202000	-2.570240000	-4.570503000
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H	13.503535000	-3.906642000	-1.637280000
H	15.246789000	-4.071266000	-1.382354000
H	14.423372000	-5.124738000	-2.546751000
H	8.279418000	-1.332076000	2.591327000
H	6.988074000	-1.965210000	1.558437000
H	6.772965000	-0.429358000	2.391948000
H	8.455040000	0.690727000	1.011682000
H	7.264802000	-0.066396000	-0.020486000
H	6.810436000	4.303144000	4.911424000
H	7.975772000	4.428668000	6.233369000
H	6.504199000	3.473126000	6.443656000
H	13.850658000	10.398502000	-1.116770000
H	13.841953000	11.186758000	0.463503000
H	15.327491000	11.176507000	-0.497872000
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H	15.777956000	8.667419000	2.329282000
H	14.741371000	10.099328000	2.447513000
H	9.663699000	10.079899000	5.123355000
H	11.383979000	10.311376000	3.303783000
H	8.838419000	7.771149000	5.684285000
H	10.151637000	10.463123000	-1.191794000
H	11.534253000	9.982317000	-3.179441000
H	12.186589000	8.278041000	2.142005000
H	17.606251000	9.412099000	-0.332169000

H	15.858389000	9.429449000	-2.299834000
H	18.527590000	-0.862739000	-0.156494000
H	19.564457000	1.263083000	0.564797000
H	9.553266000	8.651716000	0.407950000
H	17.766359000	7.720932000	-0.819278000
H	17.466326000	8.110926000	0.876691000
H	14.404524000	8.417855000	-2.146725000
H	15.970506000	7.668397000	-2.460105000
H	9.755702000	5.835354000	4.425158000
H	14.366627000	4.387586000	-0.667976000
H	16.478595000	5.440669000	-1.307825000
H	18.161902000	4.106851000	-2.653216000
H	17.584287000	1.729391000	-3.229731000
H	15.408069000	0.807328000	-2.453294000
H	14.442933000	2.730800000	2.135316000
H	16.063823000	-1.170877000	-0.029821000
H	19.316209000	3.512983000	1.563675000
H	19.110837000	5.711173000	2.666339000
H	17.715125000	7.353592000	3.875243000
H	15.282396000	6.944245000	4.205277000
H	14.309919000	4.969231000	5.464055000
H	12.315740000	4.395225000	7.313466000
H	9.872354000	3.281775000	7.041976000
H	9.516519000	0.109466000	5.537152000
H	10.656443000	-0.492080000	4.330416000
H	11.088275000	0.898784000	5.336594000
H	10.441366000	1.506953000	2.955230000
H	8.851289000	0.819044000	3.225326000
H	8.397677000	1.937497000	6.063943000
H	7.268140000	1.829348000	4.744110000
H	6.493377000	2.809614000	2.905377000
H	6.376573000	4.436654000	0.757325000
H	8.242889000	6.142044000	-0.400816000
H	11.274223000	4.686872000	-1.529260000
H	12.782697000	8.321544000	-4.561540000
H	14.011408000	6.649230000	-5.948248000
H	14.522128000	4.284468000	-6.437069000
H	13.575951000	2.462091000	-5.023960000
H	10.569362000	2.702667000	-4.426515000
H	8.424795000	1.039948000	-4.346692000
H	7.572081000	-0.768684000	-2.546236000
H	10.646556000	-3.357982000	-0.946937000
H	9.276863000	-4.120533000	-1.769578000
H	9.951435000	-2.598854000	-2.382406000
H	7.772730000	-2.281560000	-1.086306000
H	8.531835000	-2.981653000	0.315223000
H	9.936756000	-2.934263000	1.910924000
H	12.421579000	-2.662766000	2.907711000
H	14.513764000	-1.057034000	2.233985000

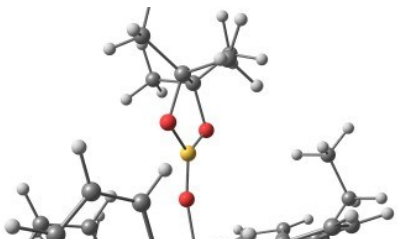

Figure S55. Geometry optimisation of linear complex **B**.

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237
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U       16.059449000      2.950902000     13.332996000
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O       15.828711000      2.993048000     15.478361000
O       13.920224000      2.213277000     13.208740000
O       16.484960000      5.176985000     13.445383000
O       17.732257000      1.450678000     13.633410000
O       17.766594000      2.253617000     17.723611000
O       15.193683000      5.197443000     17.515853000
O       13.924476000      1.491651000     17.347009000
N       15.779014000      1.329988000     11.136750000
N       15.193969000      4.164854000     11.033533000
N       17.926547000      3.257080000     11.355998000
N       15.939190000      1.351103000     19.808116000
N       16.525467000      4.184899000     19.912911000
N       13.787221000      3.280604000     19.643815000
C       21.151923000     -1.932040000     19.584066000
C       20.838061000      4.168138000     18.434859000
C       22.754596000      2.614785000     18.011102000
C       21.991689000      4.167334000     16.204204000
C       21.521404000      3.286294000     17.379505000
C       20.508224000      2.250323000     16.808241000
C       18.897940000     -0.776189000     19.432493000
C       20.245683000     -0.829330000     19.076435000
C       20.731577000      0.173436000     18.230671000
C       19.942182000      1.236992000     17.782462000
C       18.567649000      1.280277000     18.149524000
C       18.059962000      0.239941000     18.966988000
C       16.578084000      0.132796000     19.235596000
C       16.838299000     10.320002000     19.383963000
C       11.971537000      6.903682000     17.543889000
C       11.793960000      7.752670000     15.187567000
C       12.413129000      9.316486000     17.041029000
C       12.566502000      7.877542000     16.516553000
C       14.051714000      7.510600000     16.226720000
C       16.965292000      7.785349000     19.399326000
C       16.418233000      8.956360000     18.875465000
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C	15.469680000	8.828028000	17.854563000
C	15.018723000	7.588948000	17.390287000
C	15.577176000	6.399907000	17.938267000
C	16.578371000	6.526371000	18.932925000
C	17.349364000	5.314428000	19.398917000
C	8.410942000	0.519970000	18.397910000
C	13.925373000	-2.206769000	17.713261000
C	13.744625000	-2.912042000	15.308162000
C	11.741326000	-3.020291000	16.801300000
C	13.015032000	-2.218330000	16.476371000
C	12.697693000	-0.762215000	16.023501000
C	10.548146000	1.847871000	18.708499000
C	9.885071000	0.758945000	18.140362000
C	10.615826000	-0.067608000	17.281763000
C	11.975581000	0.126197000	17.015360000
C	12.639590000	1.243871000	17.592028000
C	11.890623000	2.109580000	18.428111000
C	12.493260000	3.404521000	18.915879000
C	13.735051000	2.200157000	20.655902000
C	14.581377000	0.979974000	20.257525000
C	16.738587000	1.900681000	20.928399000
C	17.435838000	3.221682000	20.565658000
C	15.491213000	4.662587000	20.860966000
C	14.073730000	4.586507000	20.272417000
C	10.549239000	-1.926674000	11.224970000
C	10.884741000	4.154264000	12.505856000
C	8.947702000	2.609724000	12.864893000
C	9.697183000	4.115622000	14.717836000
C	10.176345000	3.256176000	13.530177000
C	11.169937000	2.197055000	14.093105000
C	12.805355000	-0.784164000	11.433521000
C	11.451679000	-0.837066000	11.766515000
C	10.956788000	0.151575000	12.623622000
C	11.744039000	1.202590000	13.104265000
C	13.123167000	1.248629000	12.755939000
C	13.640104000	0.219918000	11.929852000
C	15.126179000	0.109626000	11.687724000
C	14.839997000	10.299980000	11.577162000
C	19.704060000	6.911330000	13.445932000
C	19.855200000	7.747265000	15.809363000
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C	16.103683000	6.379459000	13.021228000
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C	18.924684000	-0.816938000	14.965779000
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C	21.794466000	0.734252000	12.949871000

C	21.040890000	-0.102837000	13.777925000
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C	19.023674000	1.206702000	13.421281000
C	19.793950000	2.081578000	12.614286000
C	19.202322000	3.378408000	12.116600000
C	18.002250000	2.179583000	10.341960000
C	17.145162000	0.958669000	10.714254000
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H	11.868479000	6.731006000	14.794529000
H	10.732360000	7.989984000	15.336179000
H	12.899277000	9.431151000	18.016013000
H	12.853066000	10.036088000	16.337811000
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H	18.058644000	5.635338000	20.182005000
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H	14.875286000	-1.713365000	17.479725000
H	13.439541000	-1.664896000	18.533840000
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H	13.995945000	-3.947372000	15.573174000
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H	14.632440000	0.283820000	21.115490000
H	16.084010000	2.049411000	21.795140000
H	17.515433000	1.182097000	21.225131000
H	18.251822000	3.014617000	19.869718000
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H	15.685053000	5.708957000	21.135527000
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H	13.341170000	4.802525000	21.072611000
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H	9.771594000	-2.188116000	11.952362000
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H	11.698781000	4.706780000	12.988815000
H	11.304542000	3.543399000	11.697560000
H	8.242242000	3.392628000	12.555767000
H	9.239544000	2.036647000	11.978116000
H	8.432404000	1.940476000	13.566640000
H	10.548203000	4.608687000	15.203928000
H	8.997774000	4.889086000	14.374375000
H	9.191546000	3.489720000	15.464176000
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H	10.656320000	1.640378000	14.889412000
H	13.232519000	-1.559962000	10.801113000
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H	15.647078000	-0.125761000	12.628518000
H	15.303526000	-0.739421000	11.004261000
H	15.560121000	10.688095000	10.843172000
H	13.857910000	10.252870000	11.092584000
H	14.779469000	11.022378000	12.400085000
H	19.693616000	5.887203000	13.835766000
H	19.125312000	6.938524000	12.514828000
H	20.743213000	7.190066000	13.226236000
H	19.429969000	8.425881000	16.559720000
H	19.786118000	6.722768000	16.195848000
H	20.915962000	7.994248000	15.671008000
H	18.761918000	9.433735000	12.981511000
H	18.785968000	10.028320000	14.663982000
H	20.303651000	9.565438000	13.858876000
H	17.235963000	8.143186000	15.553161000
H	17.588414000	6.465358000	15.135578000
H	13.966430000	7.828221000	10.772769000
H	16.576544000	9.708111000	13.591583000
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H	13.663273000	5.611767000	10.734346000
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H       16.801607000     -1.766144000     13.433507000
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H       16.931842000     -2.456363000     15.847818000
H       17.632352000     -4.013658000     15.345621000
H       18.476927000     -2.994323000     16.542969000
H       20.582115000     -3.063548000     15.074649000
H       19.665879000     -4.104566000     13.959303000
H       20.456891000     -2.635199000     13.345496000
H       19.491127000     -0.874210000     15.905702000
H       17.966557000     -0.337233000     15.198243000
H       21.708150000      2.515733000     11.745644000
H       21.541098000     -0.923711000     14.282771000
H       19.955758000      3.884758000     11.488159000
H       18.995797000      4.047919000     12.965925000
H       17.685028000      2.578938000      9.371312000
H       19.041409000      1.839271000     10.231628000
H       17.617402000      0.436181000     11.549099000
H       17.111414000      0.268187000      9.850779000
H       15.677109000      2.042410000      9.151889000
H       14.234909000      1.168503000      9.682992000
H       13.470290000      2.989009000     11.042452000
H       13.875043000      3.643700000      9.438509000
H       16.209169000      4.054421000      9.184311000
H       16.061030000      5.692162000      9.834116000
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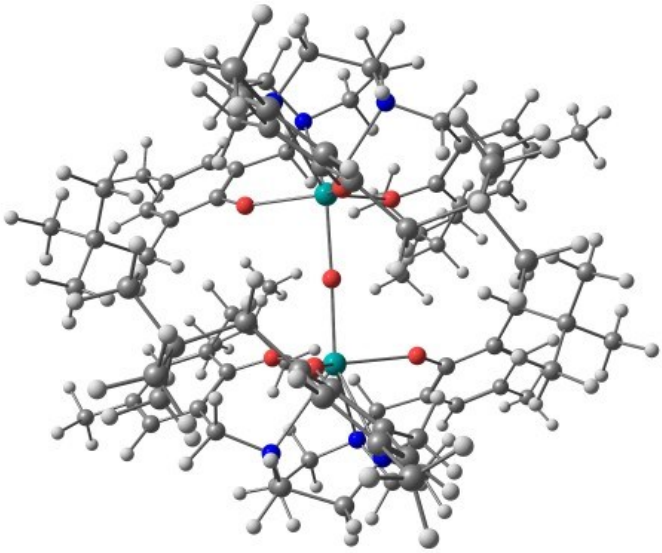

Figure S56. Geometry optimisation of linear [{((Neop,MeArO)$_3$tacn)U^{IV}}$_2$(μ-O)].

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C       -1.599017000      0.956378000      1.714950000
C       -0.743216000      0.925131000      2.831268000
C        0.631345000      1.206662000      2.672704000
C        1.117198000      1.531631000      1.409023000
C        0.286943000      1.588843000      0.284569000
C       -3.052002000      0.518111000      1.783453000
```

C	-3.905292000	1.013531000	2.936408000
C	-4.612748000	0.083176000	3.732232000
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C	-5.305280000	1.903094000	5.220343000
C	-4.726788000	2.845252000	4.327277000
C	-4.047292000	2.399620000	3.171892000
C	-6.147719000	-0.462251000	5.673851000
C	-5.461747000	-1.642224000	6.343594000
C	-4.111130000	-1.628684000	6.732974000
C	-3.550193000	-2.765083000	7.361911000
C	-4.353552000	-3.875989000	7.597913000
C	-5.704183000	-3.911968000	7.228979000
C	-6.228785000	-2.786436000	6.598853000
O	-3.330834000	-0.565143000	6.511519000
U	-2.410603000	1.285215000	5.749016000
O	-1.201381000	0.618132000	4.062874000
C	-2.100088000	-2.743097000	7.751684000
C	-6.553266000	-5.123857000	7.511986000
C	-4.610590000	-1.378415000	3.349050000
C	-3.488253000	3.386027000	2.178394000
C	-4.899513000	4.332214000	4.579217000
C	-3.662393000	5.208546000	4.623699000
C	-2.430682000	4.742163000	5.117681000
C	-1.296047000	5.587138000	5.070354000
C	-1.441160000	6.891940000	4.604401000
C	-2.667734000	7.394365000	4.155551000
C	-3.756448000	6.524840000	4.159343000
C	-5.951116000	2.382200000	6.506227000
O	-2.300472000	3.497717000	5.594199000
C	0.050054000	5.049716000	5.464501000
C	-2.801109000	8.819942000	3.687227000
C	1.536621000	1.139429000	3.868310000
C	0.835616000	1.961899000	-1.067951000
O	-1.093404000	1.411757000	7.431175000
U	-0.785626000	2.457207000	9.272315000
O	-0.189157000	0.974072000	10.751648000
C	0.780081000	0.648901000	11.632336000
C	1.605009000	-0.461817000	11.351160000
C	2.605584000	-0.806759000	12.256277000
C	2.820771000	-0.089636000	13.438019000
C	1.984383000	0.994929000	13.694457000
C	0.965048000	1.383596000	12.817733000
C	1.375621000	-1.252611000	10.094687000
C	3.924327000	-0.473352000	14.389192000
C	0.022891000	2.500195000	13.237058000
C	-0.332646000	3.573522000	12.220256000
C	0.678362000	4.269983000	11.523743000
C	0.327782000	5.152127000	10.476069000
C	-1.035821000	5.325740000	10.122156000
C	-2.049066000	4.767113000	10.949105000
C	-1.691250000	3.920634000	12.021605000
C	2.121950000	4.080971000	11.913504000
C	1.413747000	5.941277000	9.772674000
C	2.510933000	5.186094000	9.043592000
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C	3.403235000	3.251435000	7.858881000
C	4.619408000	3.915463000	7.732702000
C	4.821550000	5.205486000	8.237864000

C	3.755726000	5.810185000	8.899133000
C	-1.419264000	6.153288000	8.909975000
C	-3.504654000	5.130691000	10.705187000
C	-4.518006000	4.005963000	10.630800000
C	-4.196445000	2.755692000	10.071243000
C	-5.136500000	1.700003000	10.145722000
C	-6.398906000	1.952261000	10.678979000
C	-6.766768000	3.209353000	11.172140000
C	-5.798136000	4.211260000	11.156848000
C	-2.736225000	3.409621000	12.985559000
O	-3.001733000	2.534921000	9.510431000
C	-4.740086000	0.321353000	9.702385000
C	-8.153162000	3.463267000	11.703763000
O	1.153286000	3.261594000	8.611483000
C	3.221653000	1.847450000	7.358952000
C	6.142747000	5.908492000	8.065877000
H	-6.738471000	-5.244376000	8.586575000
H	0.959716000	6.660844000	9.087942000
H	1.895765000	6.564755000	10.538599000
H	2.065908000	-2.098266000	10.031847000
H	0.351850000	-1.639573000	10.052090000
H	1.511006000	-0.637992000	9.197204000
H	-0.902665000	2.026416000	13.573305000
H	0.446777000	2.980332000	14.129967000
H	2.122172000	1.562706000	14.614162000
H	3.236865000	-1.665175000	12.031577000
H	4.913467000	-0.260849000	13.965097000
H	3.847372000	0.075532000	15.332423000
H	3.899417000	-1.543348000	14.623846000
H	-5.587786000	-0.367620000	9.742462000
H	-3.950116000	-0.084426000	10.346525000
H	-4.334311000	0.305361000	8.687034000
H	-3.578775000	5.742107000	9.803439000
H	-3.810389000	5.802266000	11.520005000
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H	-8.532912000	2.601989000	12.263404000
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H	3.131073000	1.142662000	8.194903000
H	4.072505000	1.533179000	6.748218000
H	5.440352000	3.405491000	7.230600000
H	6.983459000	5.252962000	8.318445000
H	6.292511000	6.236778000	7.029664000
H	6.209309000	6.795958000	8.702412000
H	-3.534732000	0.807368000	0.839913000
H	-3.059554000	-0.573877000	1.786501000
H	1.245296000	1.868816000	4.632383000
H	2.574108000	1.340262000	3.588411000
H	-5.475362000	4.481622000	5.495042000
H	-5.549384000	4.716765000	3.780473000
H	0.398646000	4.303046000	4.740561000
H	0.036844000	4.545019000	6.435058000
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H	-0.561389000	7.533489000	4.576014000
H	-2.866225000	9.518019000	4.531667000
H	-3.701297000	8.959329000	3.080900000

H	-1.940693000	9.127099000	3.083236000
H	-4.716034000	6.875888000	3.780203000
H	1.690990000	1.334146000	-1.342617000
H	-1.728844000	1.316650000	-0.394739000
H	0.078559000	1.851275000	-1.849848000
H	1.181975000	3.002374000	-1.089202000
H	2.179063000	1.747357000	1.300185000
H	1.490507000	0.155056000	4.346725000
H	2.307831000	1.747634000	6.767199000
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H	-6.901733000	-0.867224000	4.984741000
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H	-1.820045000	-3.661283000	8.275316000
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H	-7.526735000	-5.053916000	7.017560000
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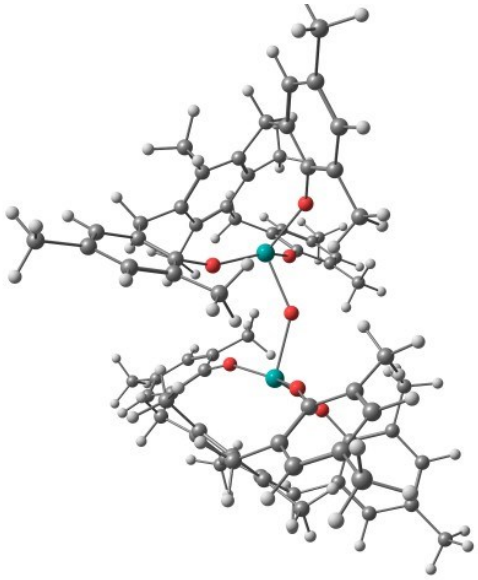

Figure S57. Geometry optimisation of bent [{((MeArO)$_3$mes)U^{IV}}$_2$(μ-O)].

1.1.7 References

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