Supplementary Information to Accompany:

Expanded Campestarene Hosts for Tetra- and Dinuclear Uranyl(VI) Complexes

Mohammad T. Chaudhry,[a] Francesco Lelj,*[b] and Mark J. MacLachlan*[a]

[a] Department of Chemistry, University of British Columbia, 2036 Main Mall, Vancouver, British Columbia, V6T 1Z1, Canada.

[b] La.M.I. and LaSCAMM INSTM Sezione Basilicata, Dipartimento di Chimica, Università della Basilicata, via dell'Ateneo Lucano 10, 85100 Potenza, Italy.

mmaclach@chem.ubc.ca, francesco.lelj@unibas.it

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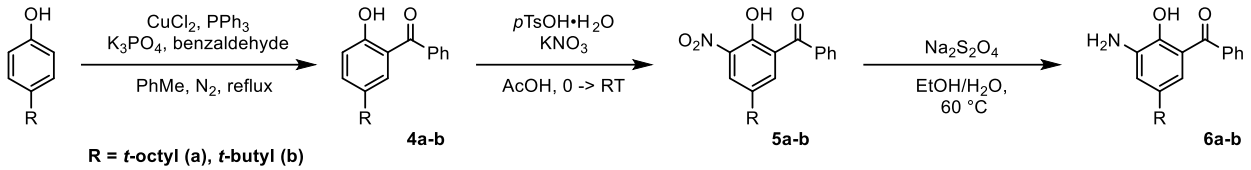
Materials and Equipment

All solvents and reagents were used as received from the supplier unless explicitly stated. $CDCl_3$ and 1,1,2,2-tetrachloroethane-d_2 were purchased from Cambridge Isotope Laboratories, and DCM-d_2 and DMSO-d_6 were purchased from Sigma-Aldrich. The MALDI matrix, *trans*-2-[3-(4-*t*-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB), was purchased from Sigma-Aldrich. All reactions were conducted under air unless explicitly stated. Dry toluene was obtained from a solvent purification system. Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AV-300 or AV-400 MHz spectrometer. Mass spectra (MS) were obtained using matrix assisted laser desorption/ionization (MALDI) on a Bruker Biflex IV time-of-flight (TOF) mass spectrometer. Electrospray ionization (ESI) mass spectra were obtained on a Bruker Esquire-LC ion trap mass spectrometer equipped with an electrospray ion source. Fourier transform infrared (FT-IR) spectra were obtained using a Thermo Scientific Nicolet 6700 FT-IR spectrometer equipped with a diamond Attenuated Total Reflectance (ATR) tip. Ultraviolet-Visible (UV-Vis) spectra were obtained on a Varian Cary 5000 UV-Vis-near-IR spectrophotometer using a 1 cm pathlength quartz cuvette.

Single crystal X-ray diffraction (SCXRD) data were obtained on a Bruker APEX X8 instrument, equipped with a Mo Kα source monochromated with graphite (λ = 0.71073 Å) to a resolution of 0.83 Å unless otherwise stated. Data were processed using Bruker APEX3 and an error model was prepared using SAINT V8.38A.[1] Structure solutions were done using SHELXT using the intrinsic-phasing method.[2] Structure refinement was done using SHELXL through least squares methods.[3] Both solution and refinement were done using Olex2 interface.[4] Heavily disordered solvent molecules were removed from the model with PLATON/SQUEEZE.[5] All non-hydrogen atoms are modeled anisotropically, with hydrogen atoms being modeled with geometric constraints for bond lengths and angles. Graphical representation of CIF data was prepared using Olex2.[4] CIF format data for all complexes are available, along with detailed responses to level A and B alerts.

Experimental:

Scheme S1. Synthesis of monomer 6



Synthesis of 4a

To an oven-dried 500 mL Schlenk flask equipped with a condenser was added *p*-*t*-octylphenol (30.0 g, 145.4 mmol, 1.3 eq), potassium phosphate tribasic (52.0 g, 246 mmol, 2.2 eq), triphenylphosphine (2.2 g, 8.3 mmol, 7.5 mol%), and copper(II) chloride (750 mg, 5.6 mmol, 5 mol%). The flask was then back-filled with nitrogen gas three times. Dry toluene (350 mL) was added *via* cannula transfer, then benzaldehyde (11.9 g, 111 mmol, 1 eq) was added *via* syringe to the stirring solution. The mixture was heated at reflux for 24 h, then the dull orange solution was cooled to room temperature, and the solvent was removed *in vacuo*. The orange-brown oil was partitioned between 150 mL of DCM and 150 mL of water. The aqueous phase was extracted with DCM (2 x 150 mL). The combined organic phase was dried with anhydrous $MgSO_4$, filtered, then solvent was removed *in vacuo* resulting in a viscous brown oil. Column chromatography on silica gel (1:4 toluene/hexanes) yielded **4a** as a viscous orange oil (16.3 g, 42.2 mmol, 38 %). This was a modified procedure based on work by Wang *et al*.[6]

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.80 (s, 1H), 7.68 (m, 2H), 7.60 (m, 1H), 7.54 (m, 3 H), 7.01 (d, 2H, *J* = 8.9 Hz), 1.66 (s, 2H), 1.28 (s, 6H), 0.73 (s, 9H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 201.83, 161.02, 140.45, 138.28, 134.86, 132.10, 130.60, 129.41, 128.44, 118.52, 117.80, 56.72, 38.08, 32.44, 32.00, 31.59. HR-ESI TOF (MeOH) = 333.1832 *m/z* (**4a** + Na)$^+$ calculated for $C_{21}H_{26}NaO_2$, 333.1830 *m/z*.

Synthesis of 4b

Compound **4b** was prepared by a similar procedure used for to **4a**, except *p*-*t*-butyl phenol (15.0 g, 99.9 mmol) was used and the purification was slightly modified (below). Following the extraction with DCM (2 x 150 mL), the solvent was removed *in vacuo*. The crude mixture was dissolved in toluene (50 mL) and combined with 2 g of sodium bisulfate in 50 mL water. The partitioned solution was heated at 50 °C for 2 h with vigorous stirring, then the organic phase was separated and washed with water (1 x 50 mL) and dried with $MgSO_4$. Solvent was removed *in vacuo* to afford a yellow-brown oil. Column chromatography on silica gel (1:1 DCM/hexanes) gave pure product as a yellow viscous oil **4b** (3.30 g, 10.0 mmol, 13 %).

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.84 (s, 1H), 7.75 – 7.66 (m, 2H), 7.66 – 7.47 (m, 5H), 7.02 (dd, *J* = 7.5, 1.7 Hz, 1H), 1.25 (s, 9H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 201.78, 161.10, 141.43, 138.19, 134.07, 132.09, 129.93, 129.41, 128.45, 118.52, 118.02, 34.22, 31.38. HR-ESI TOF (MeOH) = 255.1383 *m/z* (**4b** + 1H)$^+$, calculated for $C_{17}H_{19}O_2$, 255.1385 *m/z*.

Synthesis of 5a

p-Toluenesulfonic acid monohydrate (3.68 g, 19.3 mmol, 1.2 eq), **4a** (4.95 g, 16.1 mmol, 1 eq), and acetic acid (75 mL) were combined in a round-bottomed flask and cooled in an ice bath to 0 °C. Potassium nitrate (1.77 g, 17.5 mmol, 1.1 eq) was added slowly in portions over a few minutes and the solution turned green-yellow. The ice bath was removed, and the solution was stirred at room temperature. After 18 h, water (75 mL) was added to the reaction, generating a bright yellow precipitate. The solution was extracted with DCM (3 x 100 mL) and the combined organic phase was washed with saturated sodium bicarbonate solution until gas evolution had stopped. The organic phase was then washed with water (100 mL), dried with $MgSO_4$, and filtered. Solvent removal *in vacuo* yielded a red-orange vicious oil that solidified into a bright yellow solid **5a** (5.46 g, 95 %) on standing.

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.32 (s, 1H), 8.24 (d, *J* = 2.5 Hz, 1H), 7.83 – 7.75 (m, 3H), 7.63 (dd, *J* = 10.6, 4.3 Hz, 1H), 7.51 (t, *J* = 7.7 Hz, 2H), 1.73 (s, 2H), 1.38 (s, 6H), 0.77 (s, 9H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 196.07, 151.93, 142.43, 137.09, 136.11, 134.83, 133.69, 129.78, 128.77, 127.82, 125.79, 56.58, 38.53, 32.55, 32.07, 31.34. HR-ES TOF (MeOH) = 256.1856 *m/z* (**5a** + H)$^+$, calculated for $C_{21}H_{26}NO_4$, 256.1862 *m/z.*

Synthesis of 5b

Compound **5b** was synthesized using the same procedure as for **5a**, but the amount of **4b** used in the reaction was 2.30 g. The red oil was purified by column chromatography on silica gel (1:8 AcOEt/hexanes) to yield a yellow solid **5b** (1.90 g, 68 %).

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.32 (s, 1H), 8.25 (d, *J* = 2.5 Hz, 1H), 7.91 – 7.71 (m, 3H), 7.68 – 7.60 (m, 1H), 7.55 – 7.47 (m, 2H), 1.34 (s, 9H).^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 196.13, 152.03, 143.12, 137.03, 135.50, 134.93, 133.69, 129.84, 128.77, 128.01, 125.26, 34.69, 31.16. HR-ES TOF (MeOH) *m/z* = 300.1233 (**5b** + H)$^+$, calculated for $C_{17}H_{18}NO_4$, 300.1236 *m/z.*

Synthesis of 6a

Compound **3a** (1.66 g, 4.66 mmol, 1 eq) and ethanol/water (1:8, 50 mL) were combined in a round-bottomed flask, then sodium dithionite (4.87 g, 28 mmol, 6 eq) was added. The yellow solution was heated to 65 °C for 24 h. The resulting orange solution was cooled to room temperature, and the solvent was removed *in vacuo*. The resulting gummy orange oil was partitioned between DCM (100 mL) and water (100 mL) and the organic phase was washed with water (2 x 100 mL). The combined organic phase was dried over $MgSO_4$. Solvent was removed *in vacuo* resulting in an orange-brown viscous oil **6a** (1.33 g, 88 %).

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.95 (s, 1H), 7.71 – 7.66 (m, 2H), 7.63 – 7.56 (m, 1H), 7.54 – 7.46 (m, 3H), 7.00 (d, 1H, ^4J = 2.5 Hz), 6.96 (d, 1H, ^4J = 2.5 Hz), 3.92 (s (br), 2H), 1.63 (s, 2H), 1.24 (s, 6H), 0.75 (s, 9H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 202.26, 148.98, 140.45, 138.51, 135.68, 131.95, 129.43, 128.29, 120.34, 119.45, 117.99, 56.69, 38.09, 32.47, 31.97, 31.60. HR-ESI TOF (MeOH) = 331.1832 *m/z* (**6a** + Na)$^+$ calculated for $C_{21}H_{26}NaO_2$, 333.1830 *m/z.*

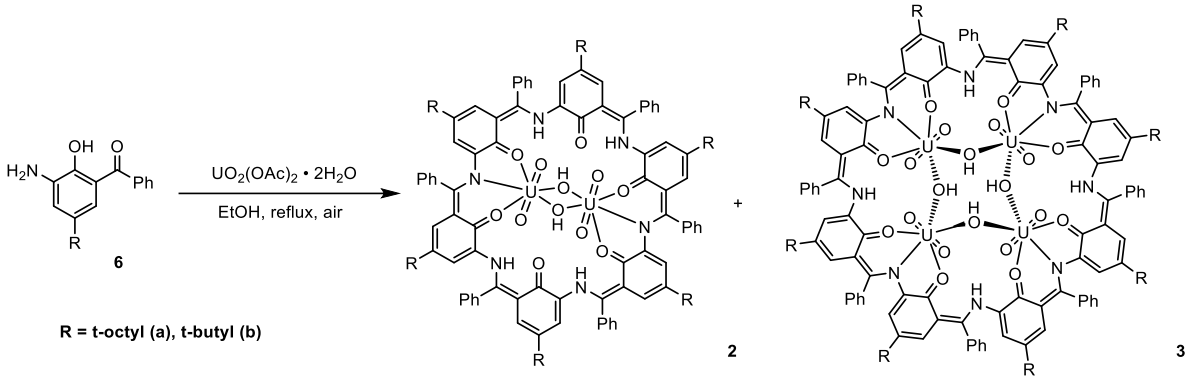
Synthesis of 6b

Compound **6b** was prepared using a procedure similar to that used for **6a**, but with the following amendments. Compound **5b** (200 mg) was used instead of **5a**. The mixture after drying was redissolved in $CHCl_3$ (3 x 5 mL) and the solvent was removed *in vacuo*. Product was isolated as a brown viscous oil **6b** (84%, 151 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 12.01 (s, 1H), 7.70 (m, 2H), 7.62 – 7.55 (m, 1H), 7.53 – 7.46 (m, 2H), 7.02 (d, *J* = 1.9 Hz, 1H), 6.99 (d, *J* = 2.2 Hz, 1H), 3.94 (s(br), 2H), 1.22 (s, 9H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 202.11, 149.47, 141.50, 138.39, 131.98, 129.43, 128.33, 120.22, 119.37, 118.14, 34.27, 31.40. HR-ESI TOF (MeOH) = 270.1495 *m/z* (**6b** + H)$^+$, calculated for $C_{17}H_{20}NO_2$, 270.1494 *m/z*.

Caution! Although the uranium precursor used contained depleted uranium, standard safety measures for handling highly toxic substances must be followed.

Scheme S2. Preparation of macrocyclic complexes 2 and 3 from monomer 6



Procedure for the preparation of 2a and 3a

Monomer **6a** (100 mg, 0.31 mmol, 1 eq) was dissolved in ethanol (2 mL, 150 mM) and added to a round bottomed flask, $UO_2(OAc)_2{\cdot}2H_2O$ (66 mg, 0.15 mmol, 0.5 eq) was then added all at once. The orange-brown solution was heated to gentle reflux for 36 h. The resulting dark red suspension was cooled to room temperature, after which the solvent was removed *in vacuo*, yielding a red-purple solid. The crude product was dissolved in DCM and, through column chromatography on basic alumina (1:200 EtOH/DCM), the two macrocyclic products **2a** (7%, 13 mg, R_f ~ 0.70) and **3a** (20%, 28 mg, R_f ~ 1.0) were isolated as purple and red solids, respectively.

Procedure for the preparation of 2b and 3b

The monomer **6b** (50 mg, 0.18 mmol, 1 eq) was dissolved in ethanol (1 mL, 180 mM) and added to a 5 mL round bottomed flask, followed by addition of $UO_2(OAc)_2{\cdot}2H_2O$ (39 mg, 0.09 mmol, 0.5 eq). The orange-brown solution was heated to reflux for 36 h. The resulting dark red was cooled to room temperature, after which the solvent was removed *in vacuo*, yielding a red-purple solid. The solution was flushed though a plug of alumina neutral (1:1 EtOAc/DCM), and the solvent removed *in vacuo*. The crude product was dissolved in DCM, and through column chromatography

on neutral alumina (1:200 EtOH/DCM) the two macrocyclic products **2b** (4%, 4 mg, R_f ~ 0.70) and **3b** (18%, 13 mg, R_f ~ 1.0) were isolated as purple and red solids, respectively.

Data for 2a

^{1}H NMR (400 MHz, DCM-d_2, 25 °C) δ 18.59 (s, 2H), 17.13 (s, 2H), 11.32 (s, 2H), 7.90 – 7.39 (m, 30H), 7.11 (d, *J* = 2.1 Hz, 2H), 6.97 (d, *J* = 2.2 Hz, 2H), 6.88 (d, *J* = 2.2 Hz, 2H), 6.87 (s, 4H), 6.80 (d, *J* = 2.2 Hz, 2H), 1.32 (s, 4H), 1.30 – 1.20 (m, 8H), 0.99 – 0.72 (m, 36H), 0.55 (s, 18H), 0.67 (s, 18H), 0.69 (s, 18H). UV-Vis (DCM) λ_{max} nm (ε M^{-1} cm^{-1}) = 541 (4.9 x 10^3), 502 (6.2 x 10^3), 306 (5.4 x 10^3). FT-IR (ATR) ν = 2953, 2901, 2869, 1530, 1515, 1365, 1247, 1228, 1179, 1025, 907, 765, 703 cm^{-1}. MALDI-TOF MS (DCTB) = 2377.7 *m/z* (**2a** – $2H_2O)^+$, calculated for $C_{126}H_{144}N_6O_{10}U_2$, 2377.2.

SCXRD quality crystals (purple plates) were grown by slow evaporation of **2a** in acetone/water.

Data for 2b

^{1}H NMR (400 MHz, DCM-d_2, 25 °C) δ 18.56 (s, 2H), 17.10 (s, 2H), 11.29 (s, 2H), 7.94 – 7.27 (m, 30H), 7.09 (d, *J* = 2.3 Hz, 2H), 7.04 (d, *J* = 2.3 Hz, 2H), 6.98 (d, *J* = 2.2 Hz, 2H), 6.84 (s, 4H), 6.83 (d, *J* = 2.3 Hz, 2H), 0.86 (s, 18H), 0.81 (s, 18H), 0.76 (s, 18H). ^{13}C{^{1}H} NMR (101 MHz, DCM-d_2, 25 °C) δ 173.35, 172.38, 169.12, 168.64, 167.02, 163.47, 143.05, 139.10, 137.17, 135.52, 133.22, 133.06, 132.46, 131.40, 130.91, 130.59, 130.35, 129.64, 129.04, 128.48, 128.23, 127.75, 125.35, 117.84, 117.71, 56.75, 56.30, 56.18, 38.04, 37.87, 37.76, 32.49, 32.46, 32.39, 31.93, 31.88. UV-Vis (DCM) λ_{max} nm (ε M^{-1} cm^{-1}) = 537 (4.3 x 10^3), 497 (5.7 x 10^3), 307 (5.1 x 10^3). FT-IR (ATR) ν = 2958, 2923, 2862, 1532, 1513, 1365, 1255, 1225, 1171, 1020, 905, 707 cm^{-1}. MALDI-TOF MS (DCTB) = 2042.4 *m/z* (**2b** – $2H_2O$ + 1H)$^+$, calculated for $C_{102}H_{97}N_6O_{10}U_2$, 2042.8 *m/z.*

SCXRD quality crystals were grown by slow evaporation from an NMR tube containing DMSO-d_6, to give red plates.

Data for 3a

^{1}H NMR (400 MHz, DCM-d_2, 25 °C) δ 18.44 (s, 2H), 18.19 (s, 1H), 17.86 (s, 1H), 12.80 (s, 1H), 12.70 (s, 1H), 7.85 – 7.47 (m, 32H), 7.87 – 7.29 (m, 8H), 7.04 – 6.80 (m, 12H), 6.72 (d, *J* = 1.9 Hz, 1H), 6.70 (d, *J* = 2.1 Hz, 1H), 6.68 (s, 1H), 1.24 – 1.01 (m, 16), 0.94 - 0.81 (m, 16H), 0.84 – 0.46 (m, 100H). ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C) δ 18.40 (s, 4H), 14.35 (s, 4H), 7.88 – 7.27 (m, 40H), 6.94 (d, *J* = 1.0 Hz, 4H), 6.77 (d, *J* = 1.0 Hz, 4H), 6.72 (d, *J* = 1.2 Hz, 4H), 6.59 (d, *J* = 1.2 Hz, 4H), 1.15 (s, 16H), 0.71 – 0.61 (m, 48H), 0.50 (s, 36H), 0.48 (s, 36H).UV-Vis (DCM) λ_{max} nm (ε M^{-1} cm^{-1}) = 541 (4.1 x 10^4), 513 (4.8 x 10^4), 329 (3.8 x 10^4). FT-IR (ATR) ν = 2954, 1560, 1525,1486, 1444, 1424, 1365, 1250, 1206, 1178, 1056, 1025, 956, 928, 706 cm^{-1}. MALDI-TOF MS (DCTB) = 3530.1 *m/z* (**3a** – $4H_2O$ + 1H)$^+$, calculated for $C_{168}H_{193}N_8O_{16}U_4$, 3530.6 *m/z*.

SCXRD quality crystals were grown by slow evaporation of a solution of **3a** in 1:3 acetone/pentane.

The high degree of asymmetry of the ^{1}H spectrum in DCM-d_2 and the poor solubility of the complex in DMSO-d_6, a solvent where the complex has higher symmetry in solution, prevented characterization of **3a** by ^{13}C{^{1}H} NMR spectroscopy.

Data for 3b

^{1}H NMR (400 MHz, DCM-d_2, 25 °C) δ 18.45 (s, 4H), 12.18 (s, 4H), 7.84 – 7.53 (m, 32H), 7.41 (t, *J* = 7.4 Hz, 4H), 7.34 (t, *J* = 7.2 Hz, 4H), 6.99 (d, *J* = 2.3 Hz, 4H), 6.93 (d, *J* = 2.3 Hz, 4H), 6.80 (d, *J* = 2.3 Hz, 4H), 6.75 (d, *J* = 2.3 Hz, 4H), 0.79 (s, 36H), 0.74 (s, 36H). ^{13}C{^{1}H} NMR (101 MHz, DCM-d_2, 25 °C) δ 173.11, 172.10, 167.79, 163.45, 143.84, 138.54, 137.73, 136.16, 133.47, 132.37, 131.37, 130.90, 130.50, 130.36, 129.88, 129.45, 129.27, 129.25, 129.08, 128.44, 128.41, 127.38, 127.20, 125.79, 123.87, 117.60, 34.02, 33.86, 30.93, 30.78. UV-Vis (DCM) λ_{max} nm (ε M^{-1} cm^{-1}) = 542 (1.3 x 10^4), 509 (1.6 x 10^4), 325 (1.1 x 10^4) FT-IR (ATR) ν = 2959, 2925, 2868, 1561, 1536, 1522, 1488, 1364, 1257, 1199, 1167, 1021, 925, 705 cm^{-1}. MALDI-TOF MS (DCTB) = 3080.4 *m/z* (**3b** – 4 H_2O + 1H)$^{+}$, calculated for $C_{136}H_{127}N_8O_{16}U_4$, 3080.1 *m/z*.

SCXRD quality crystals (red plates) were grown by vapour diffusion of hexanes into a solution of **3b** in 1,2-dichloroethane.

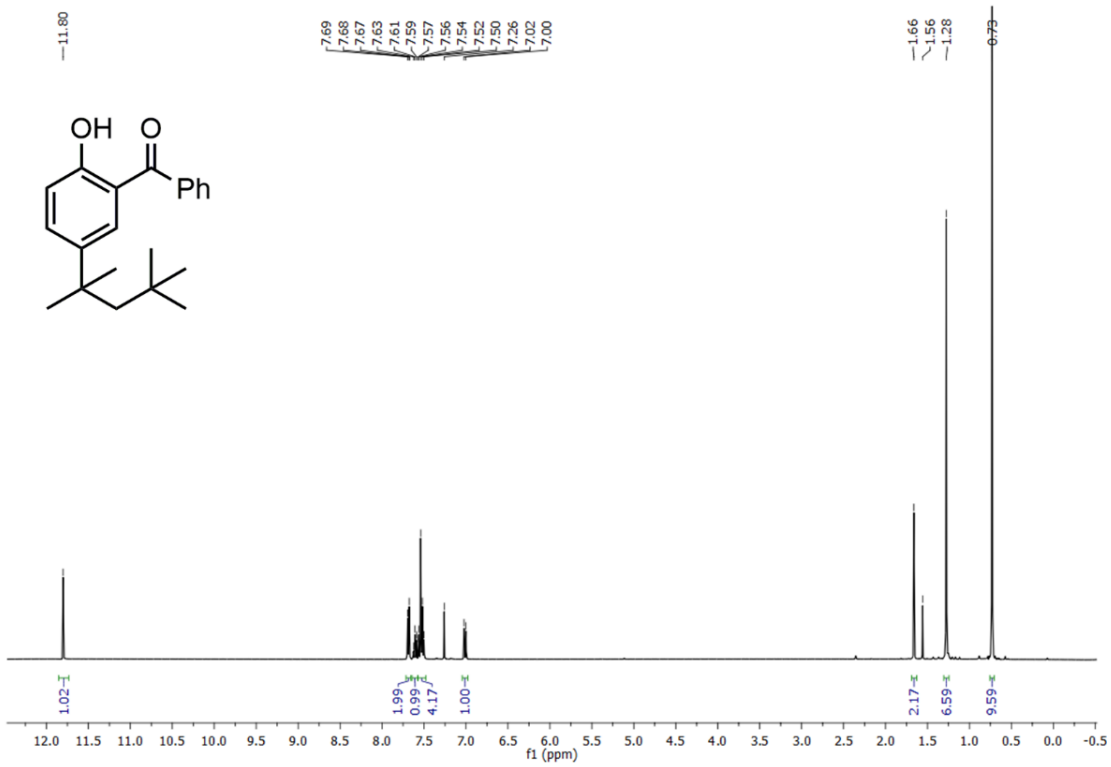


Figure S1. ^{1}H NMR spectrum of 4a in $CDCl_3$ (400 MHz).

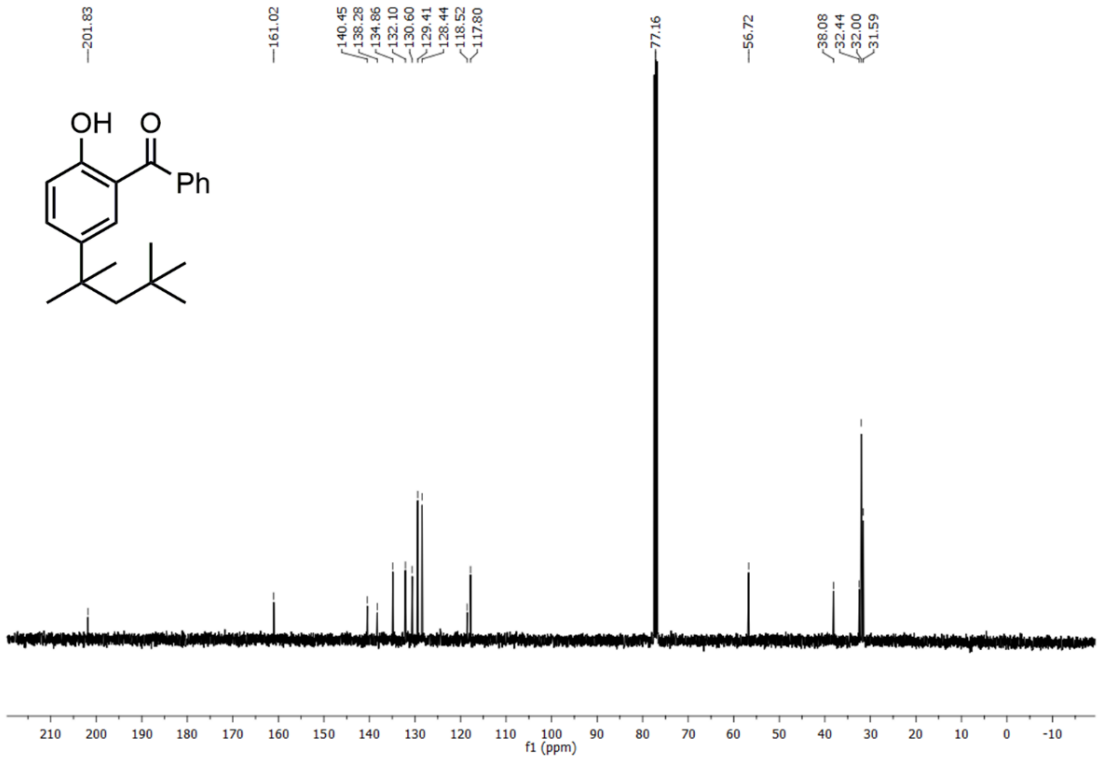


Figure S2. ^{13}C{^{1}H} NMR spectrum of 4a in $CDCl_3$ (101 MHz).

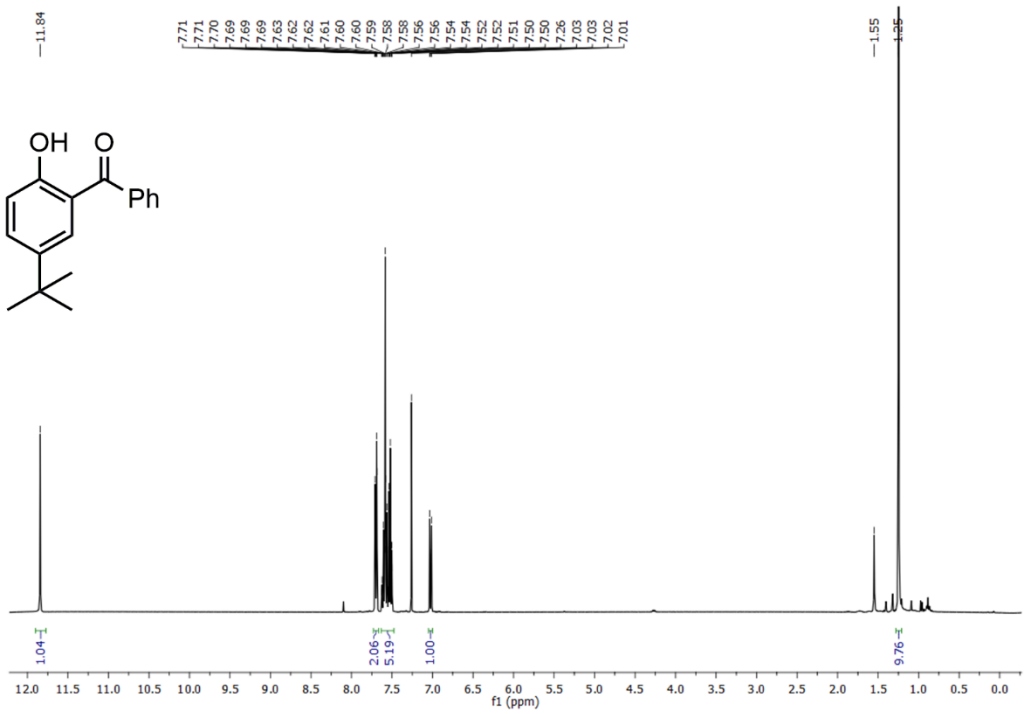


Figure S3. ^{1}H NMR of 4b in $CDCl_3$ (300 MHz).

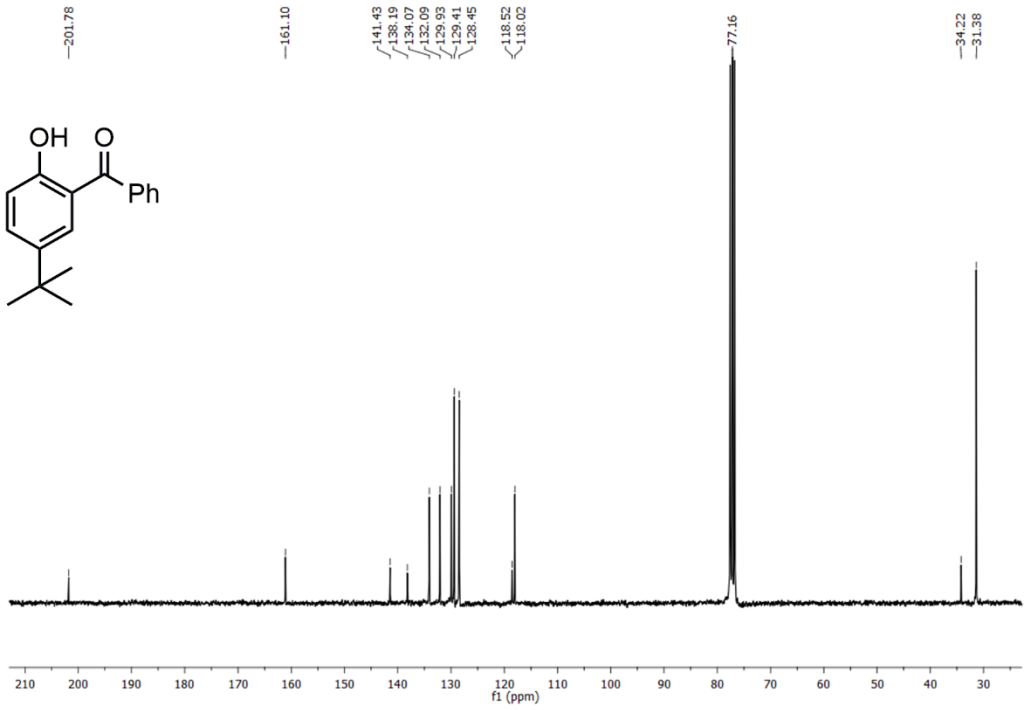


Figure S4. $^{13}C\{^{1}H\}$ NMR spectrum of compound 4b in $CDCl_3$ (75 MHz).

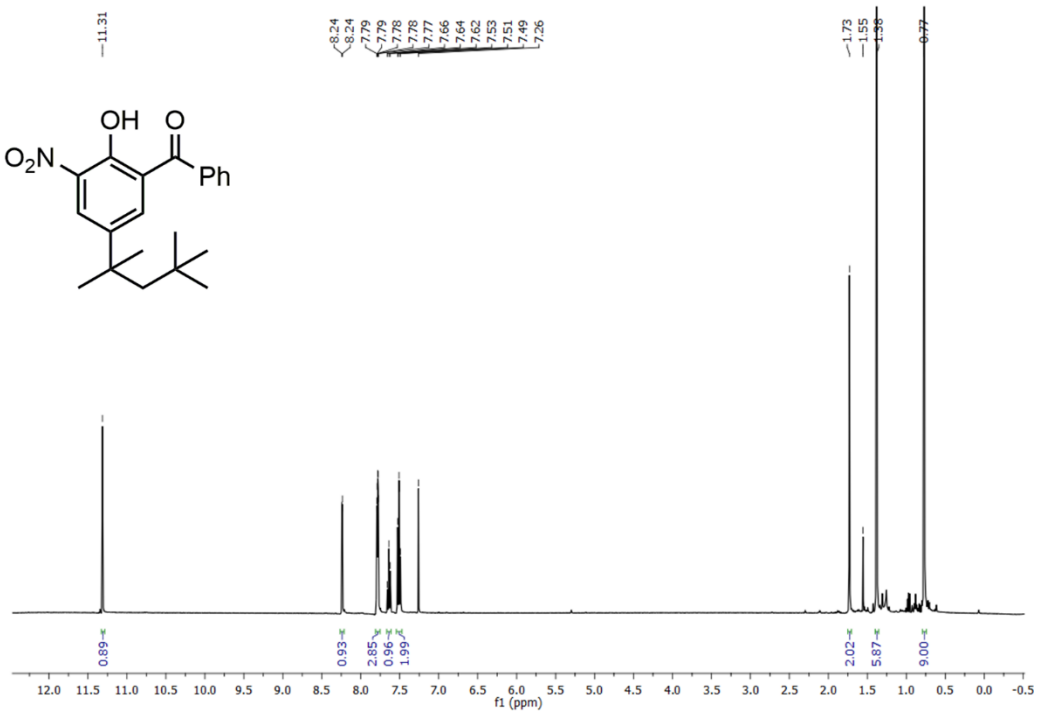


Figure S5. ^{1}H NMR spectrum of 5a in $CDCl_3$ (400 MHz).

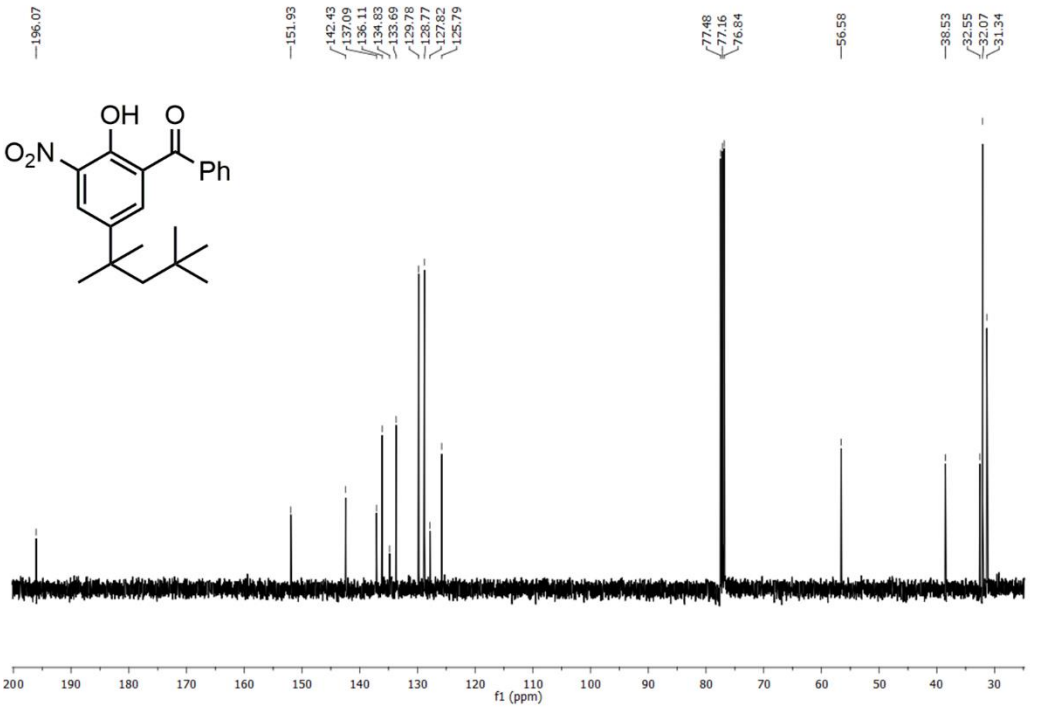


Figure S6. $^{13}C\{^{1}H\}$ NMR spectrum of 5a in $CDCl_3$ (101 MHz).

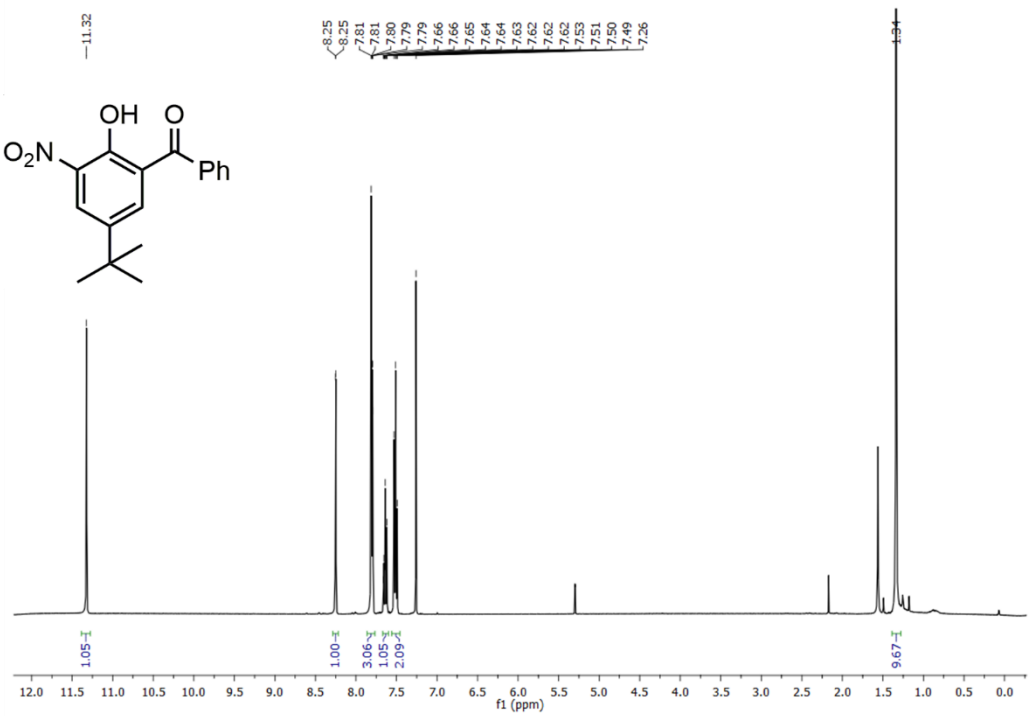


Figure S7. ^{1}H NMR spectrum of 5b in $CDCl_3$ (400 MHz).

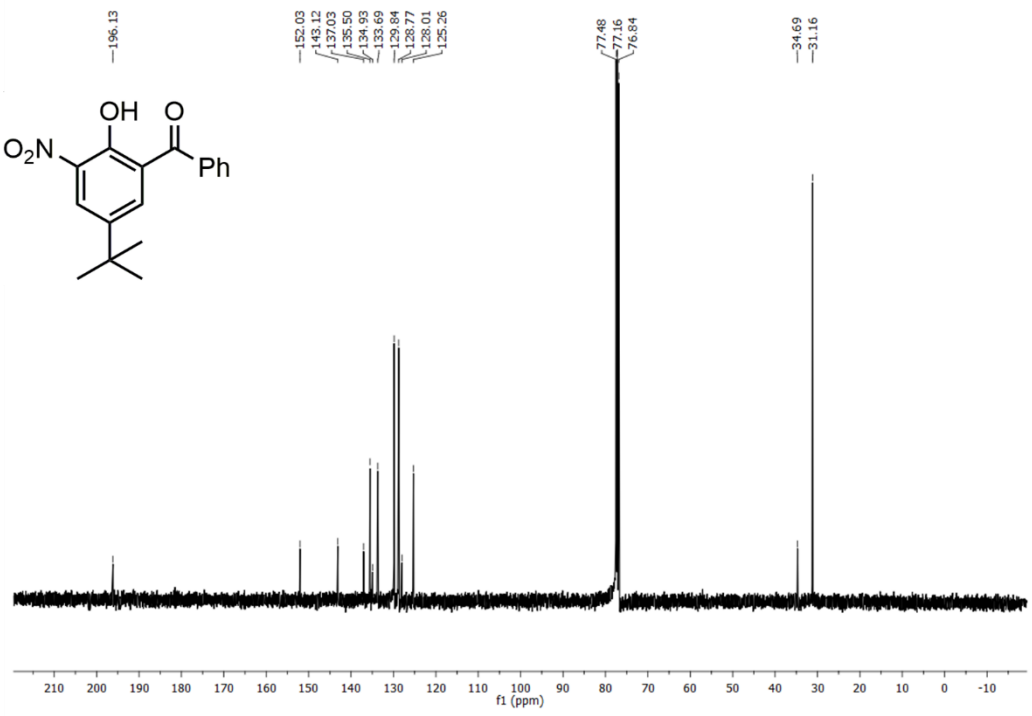


Figure S8. ^{13}C{^{1}H} NMR spectrum of 5b in $CDCl_3$ (101 MHz).

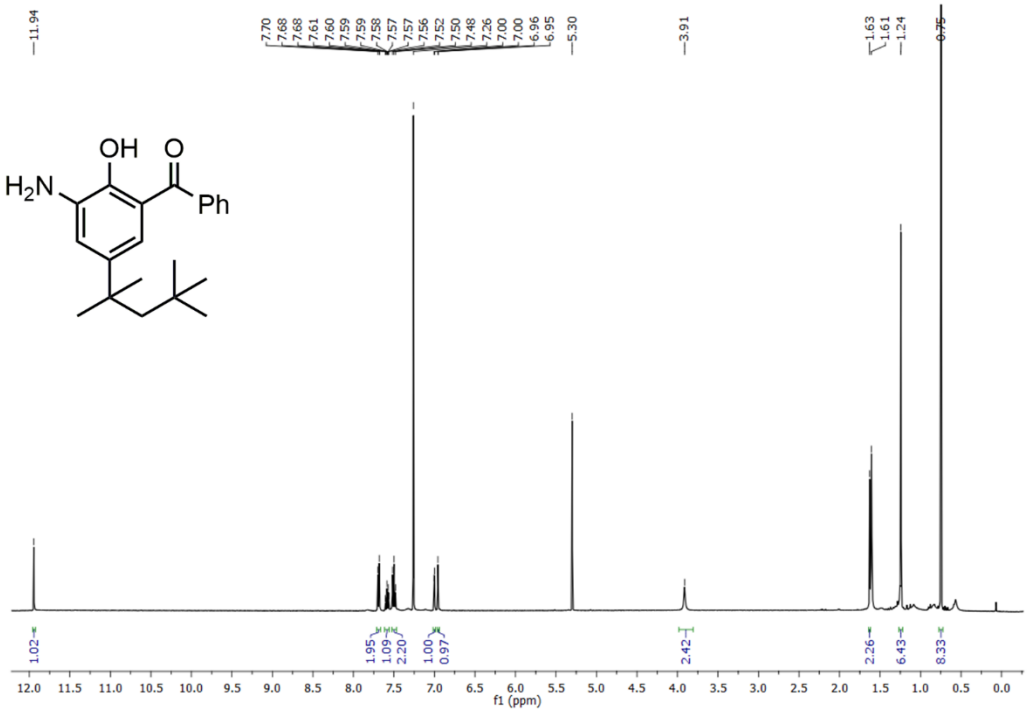


Figure S9. ^{1}H NMR spectrum of 6a in $CDCl_3$ (400 MHz).

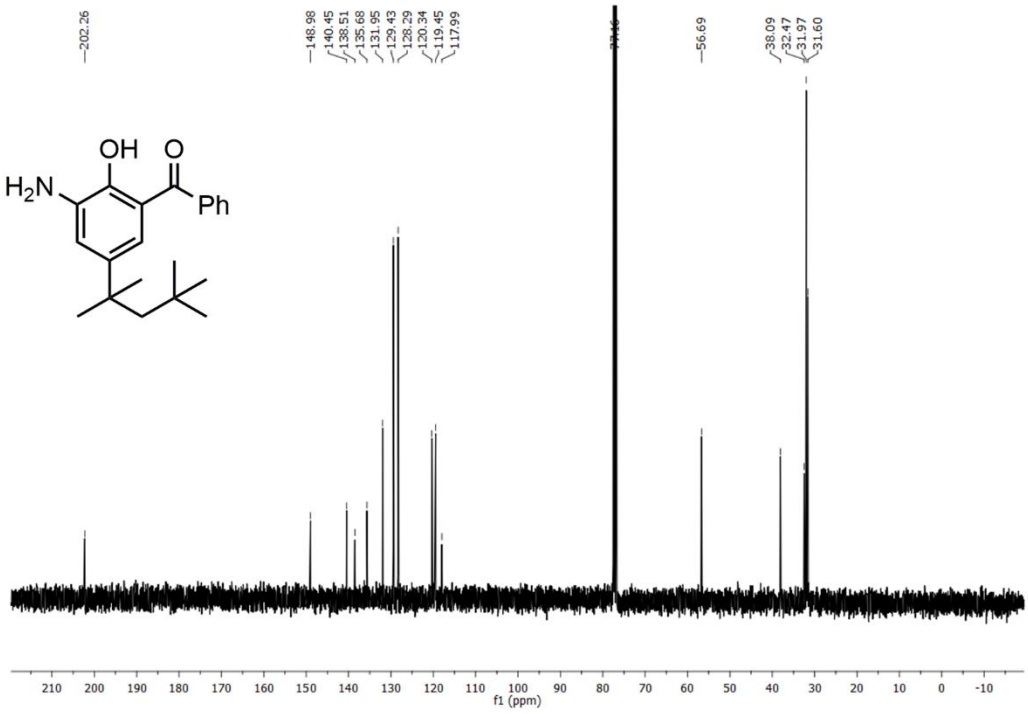


Figure S10. ^{13}C{^{1}H} NMR spectrum of 6a in $CDCl_3$ (101 MHz).

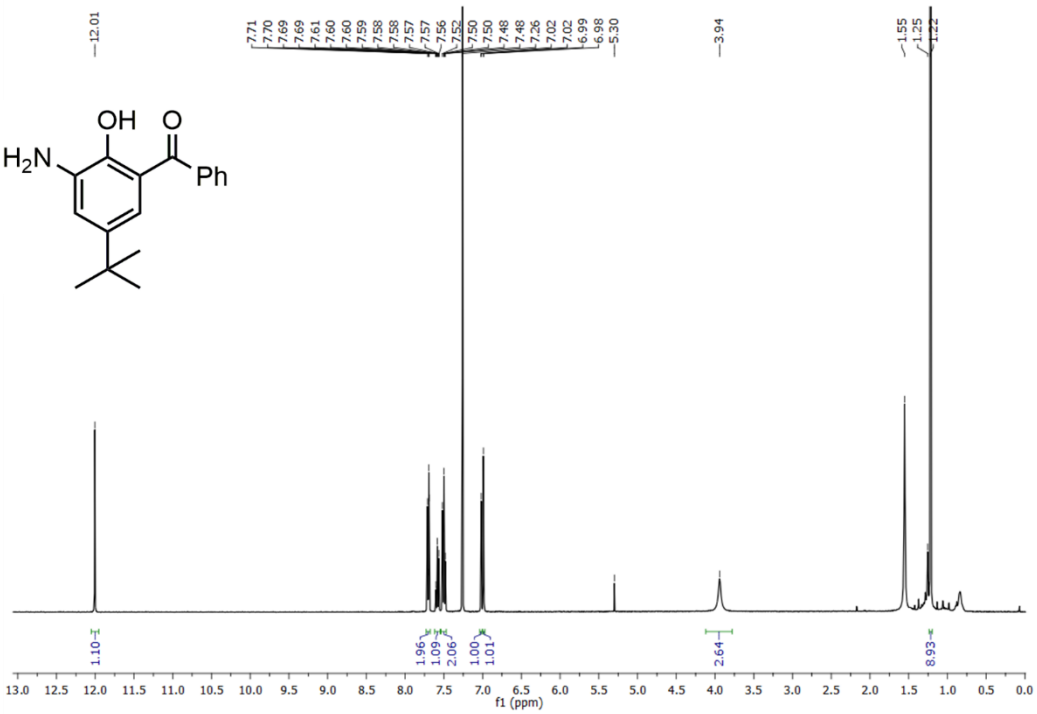


Figure S11. ^{1}H NMR spectrum of 6b in $CDCl_3$ (400 MHz).

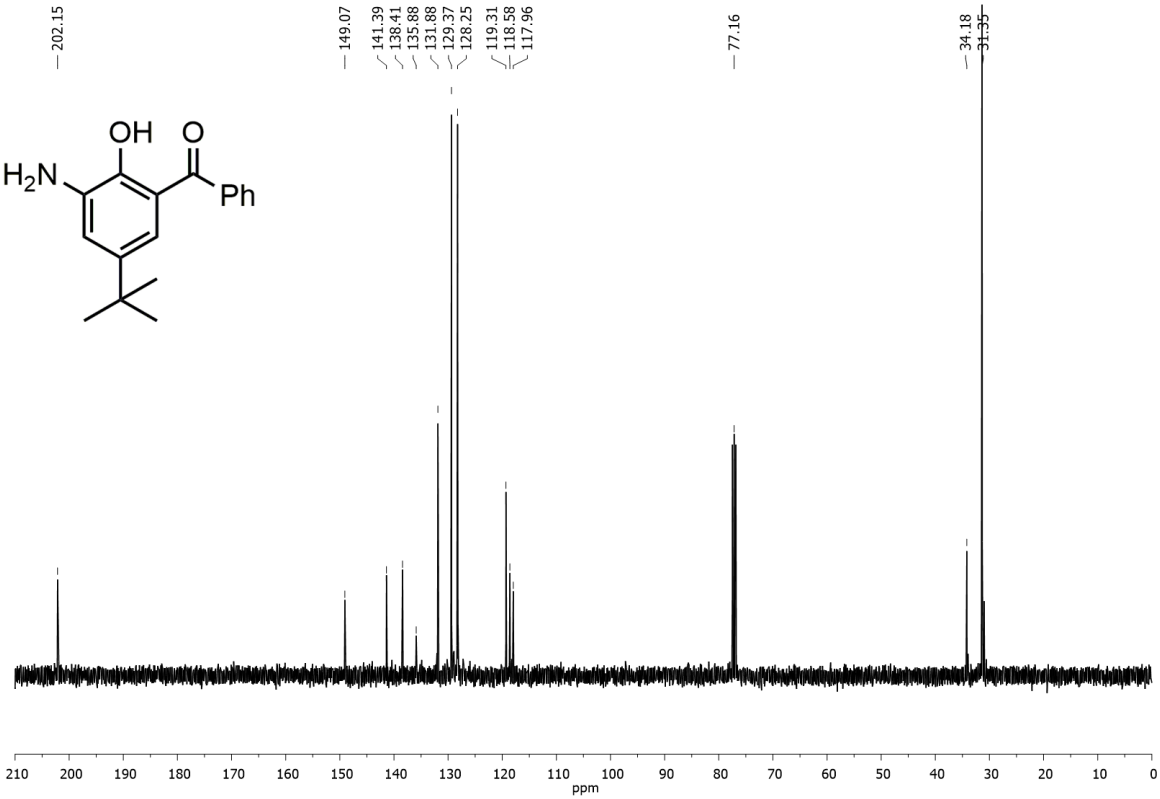


Figure S12. $^{13}C\{^{1}H\}$ NMR spectrum of 6b in $CDCl_3$ (101 MHz).

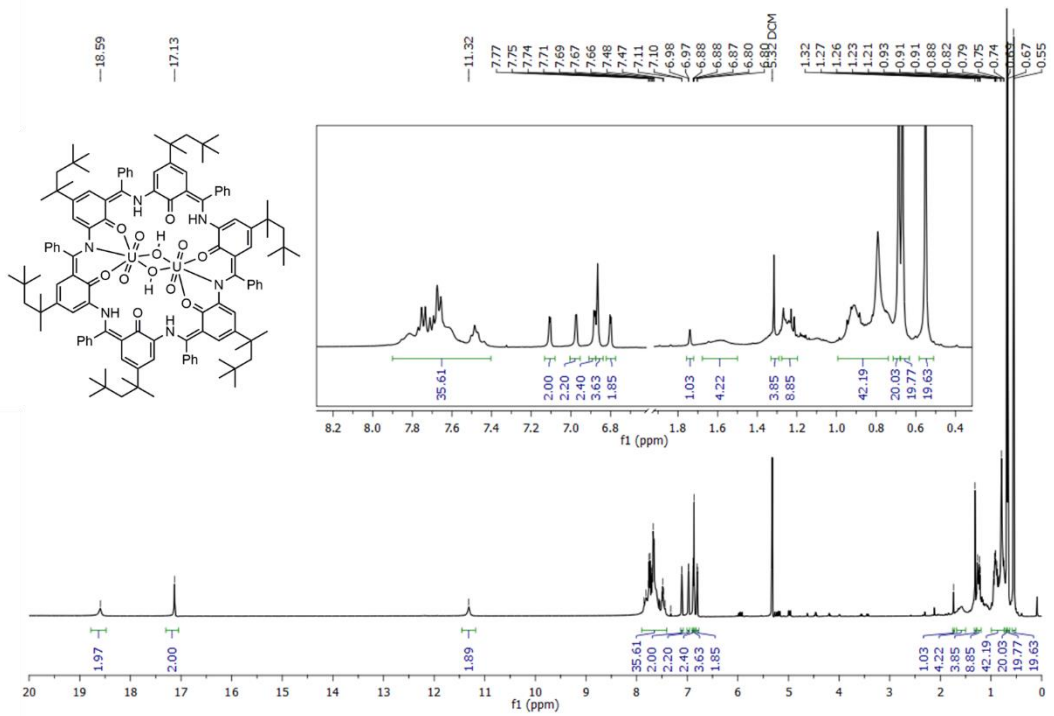


Figure S13. ^{1}H NMR spectrum of 2a in DCM-d_2 (400 MHz).

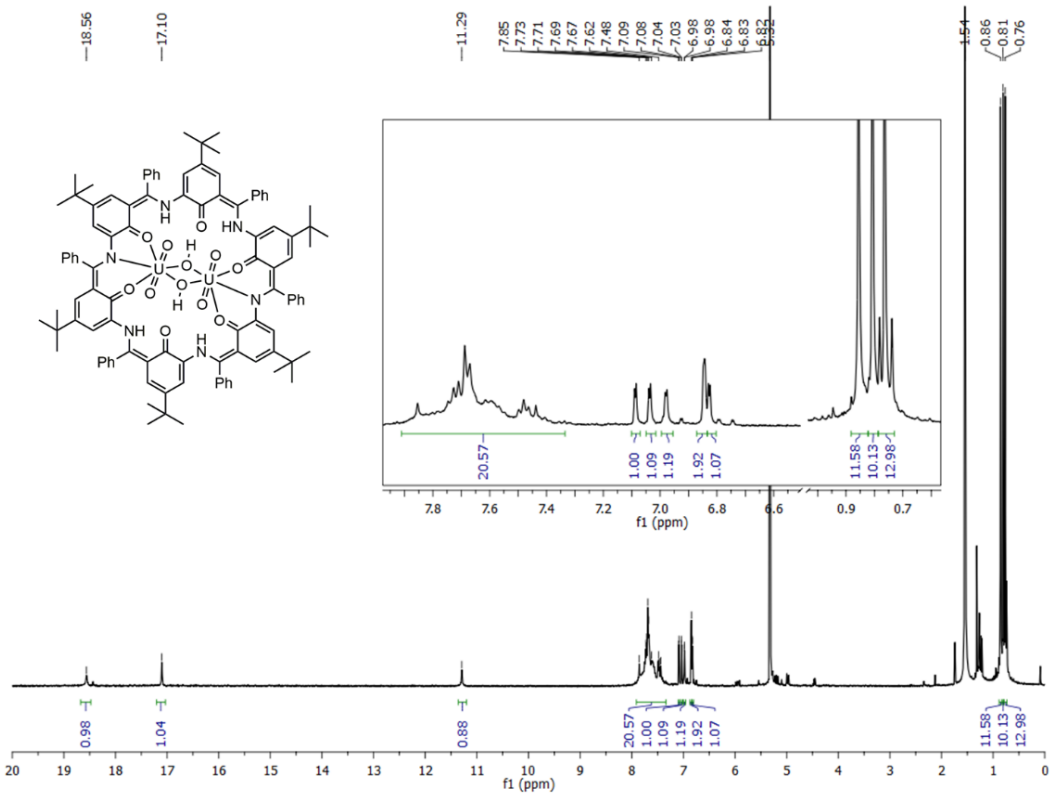


Figure S14. ^{1}H NMR spectrum of 2b in DCM-d_2 (400 MHz).

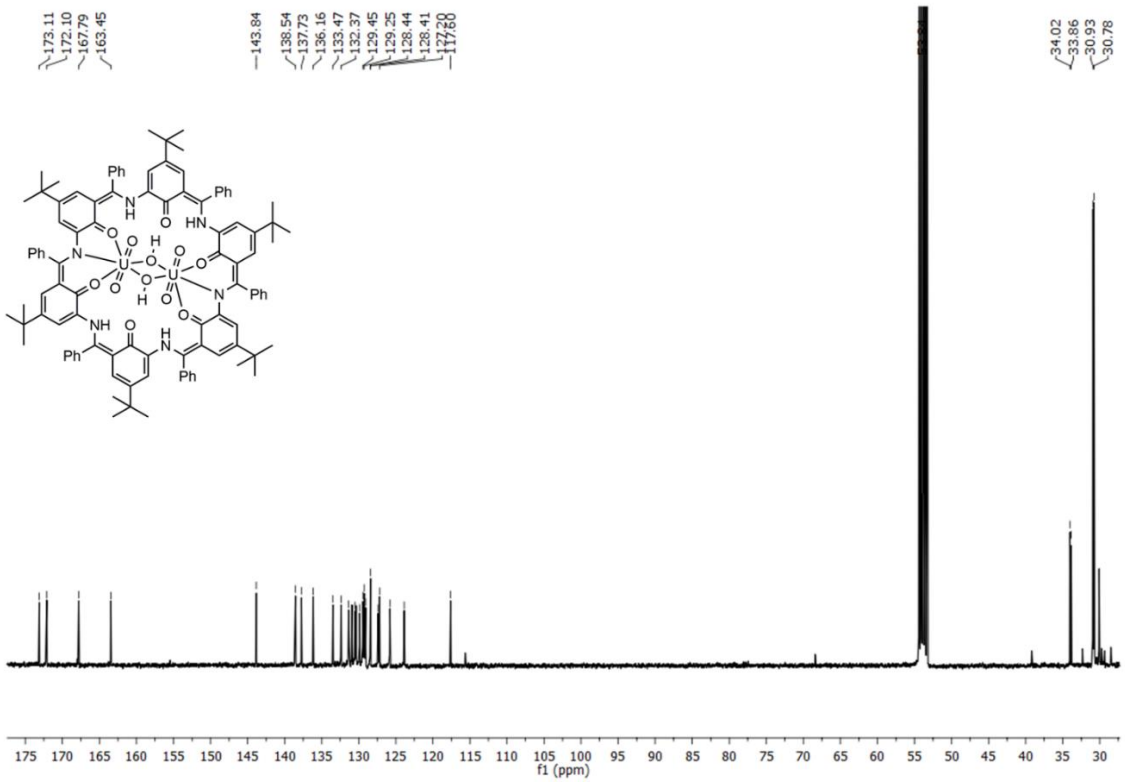


Figure S15. $^{13}C\{^{1}H\}$ NMR spectrum of 2b in DCM-d_2 (101 MHz).

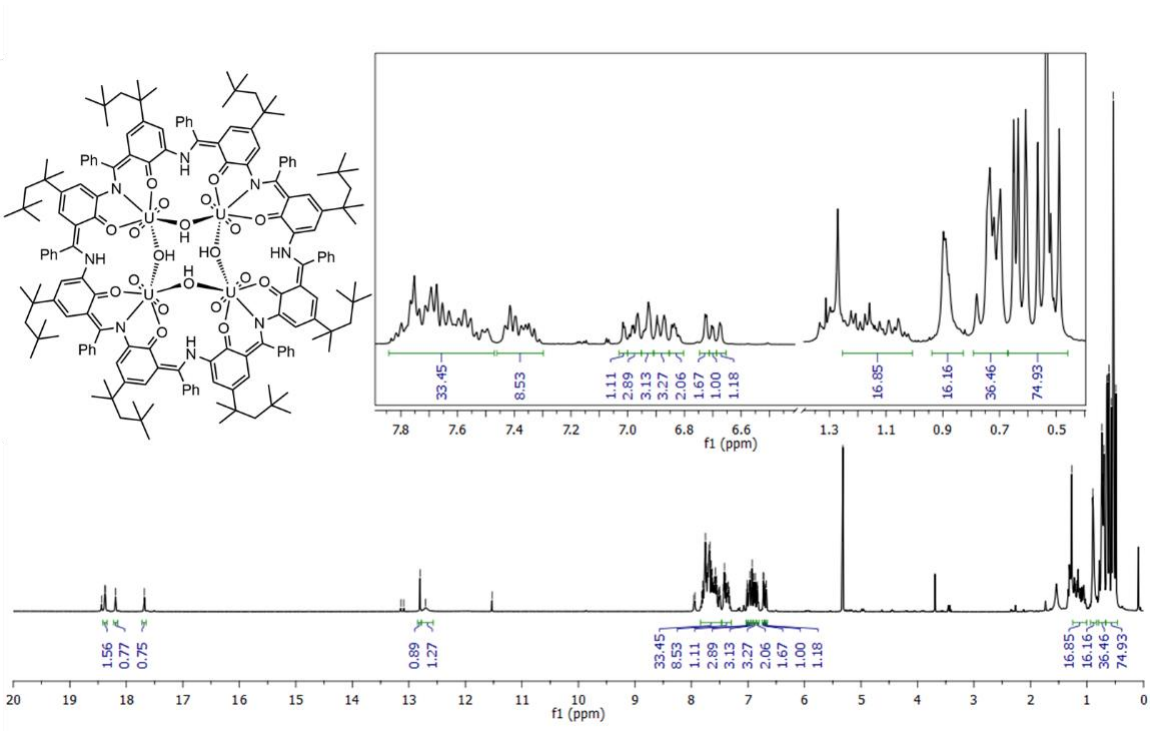


Figure S16. ^{1}H NMR spectrum of 3a in DCM-d_2 (400 MHz).

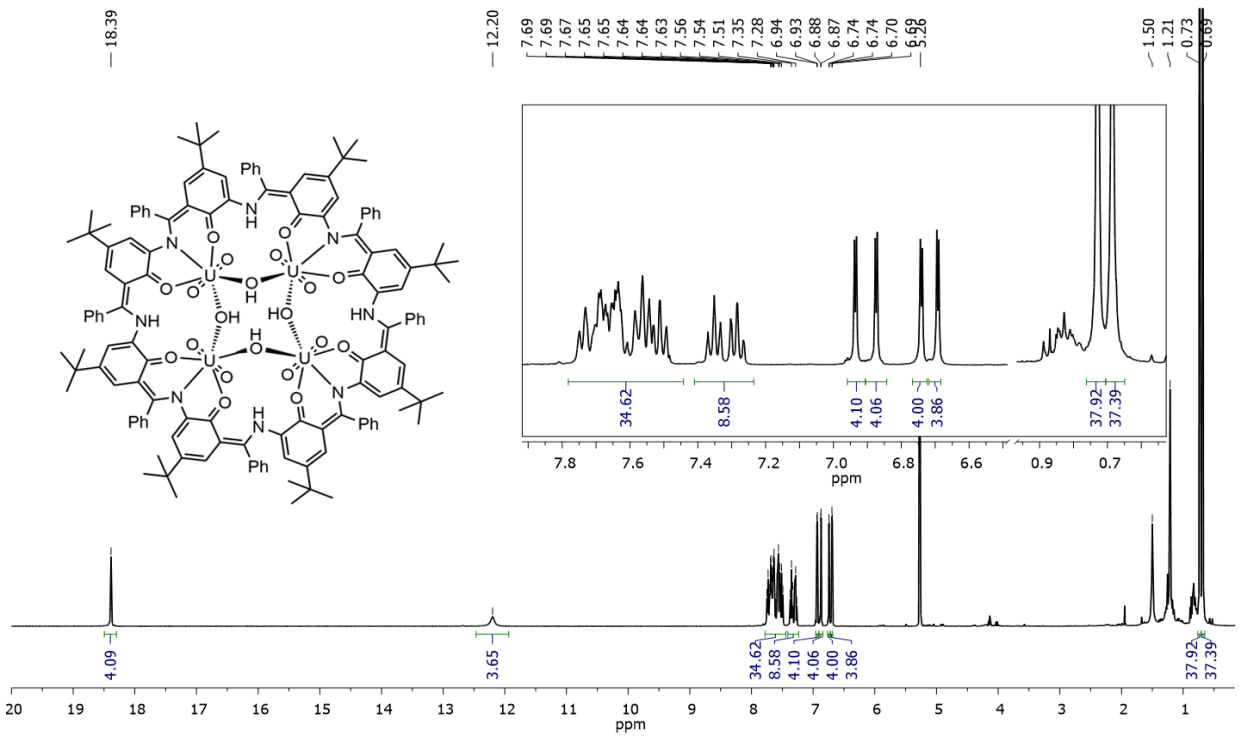


Figure S17. ^{1}H NMR spectrum of 3b in DCM-d_2 (400 MHz).

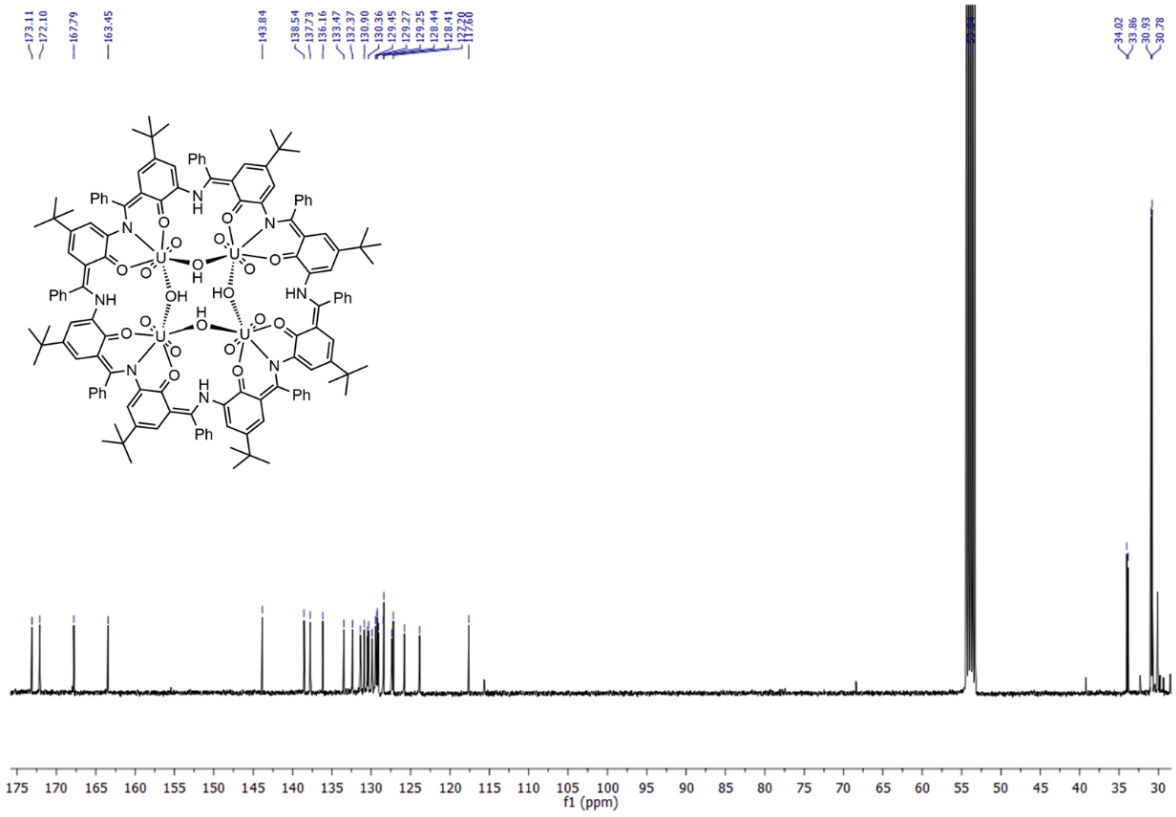


Figure S18. ^{13}C{^{1}H} NMR spectrum of compound 3b in DCM-d_2 (101 MHz).

D_2O Experiment on 2a

A drop of *D_2O* was added to an NMR tube containing **2a** in 1,1,2,2-tetrachloroethane-*d_2*. In the ^{1}H NMR spectra for **2a**, the lowered intensity of the corresponding downfield protons (18.23, 16.38, and 10.76 ppm) is a result of hydrogen-deuterium exchange. This is illustrated below in Figure S19 wherein the gradual decrease in intensity of the downfield singlets is seen, eventually resulting in a signal difficult to differentiate from baseline.

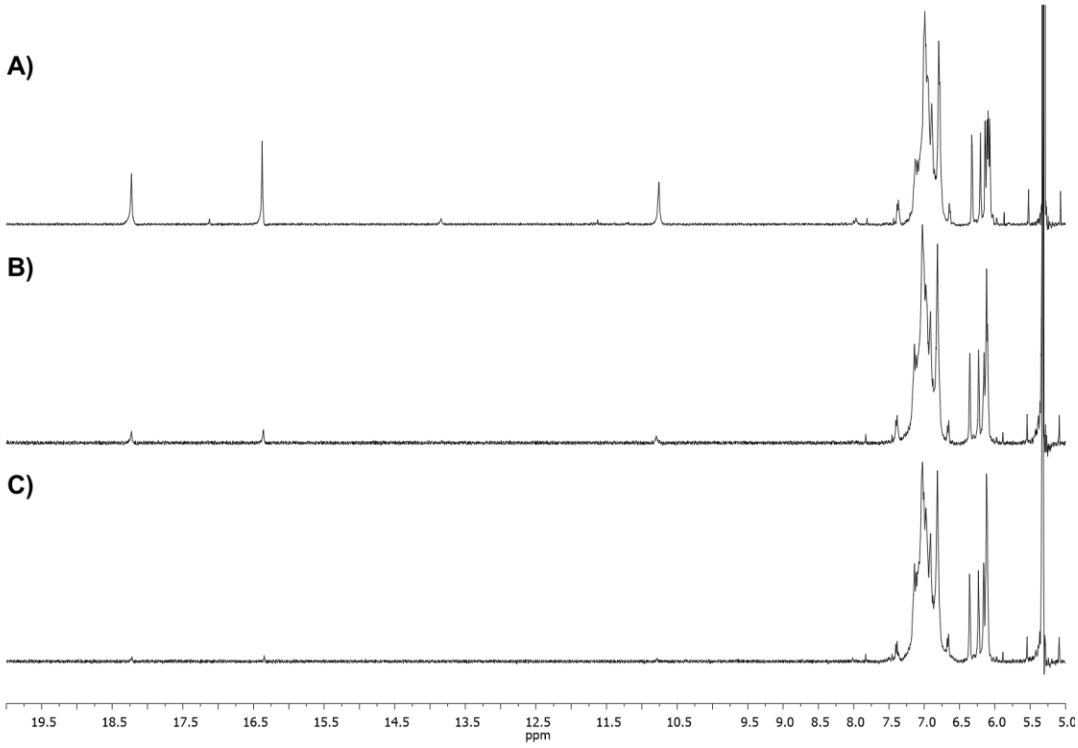


Figure S19. Partial ^{1}H NMR spectra of 2a in 1,1,2,2-tetrachloroethane-*d_2*, A) before addition of *D_2O*, B) *ca.* 1 minute after addition of *D_2O*, and C) *ca.* 1 day after addition of *D_2O*.

Shown in Figure S20 is the ^{1}H NMR spectrum of complex **2a** in DMSO-*d_6*, which was easier to interpret than **2a** in DCM-*d_2*. The splitting pattern is similar to that of complex **2b** with *t*-butyl groups in DCM-*d_2*. However, owing to the poor solubility of the complex in DMSO-*d_6*, analysis of all other uranyl complexes was done in DCM-*d_2*.

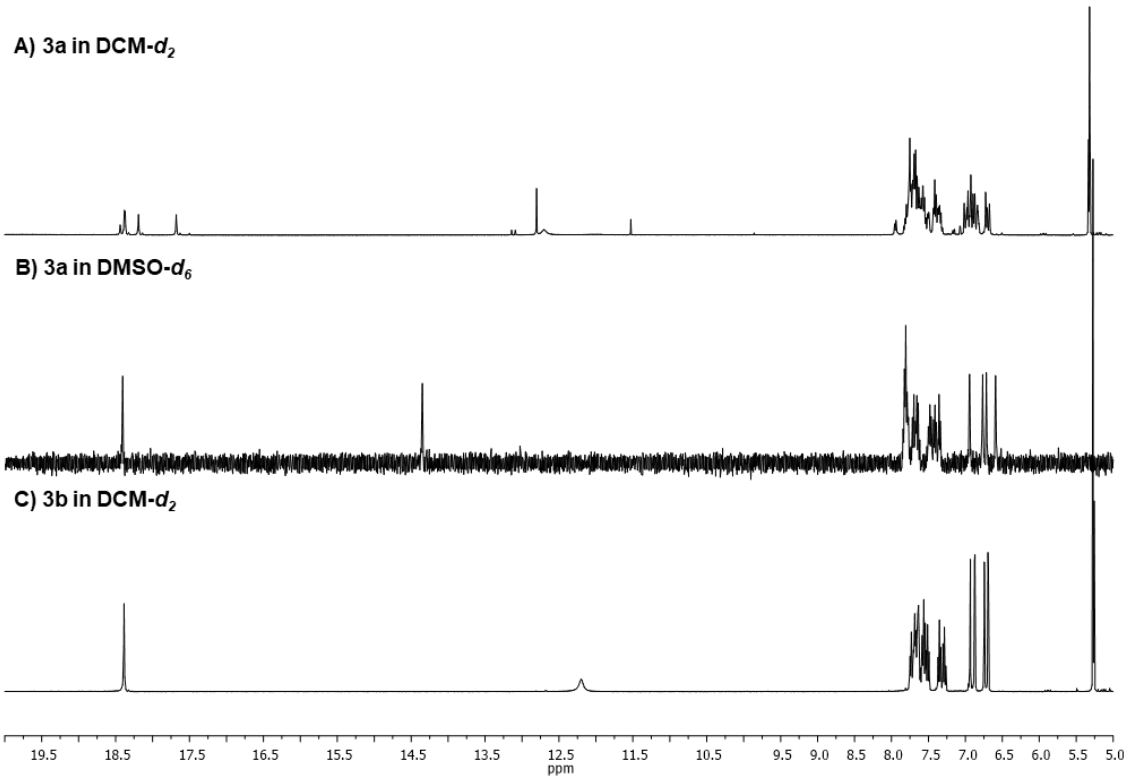


Figure S20. ^{1}H NMR spectra of A) complex 3a in DCM-d_2, B) complex 3a in DMSO-d_6, C) 3b in DCM-d_2.

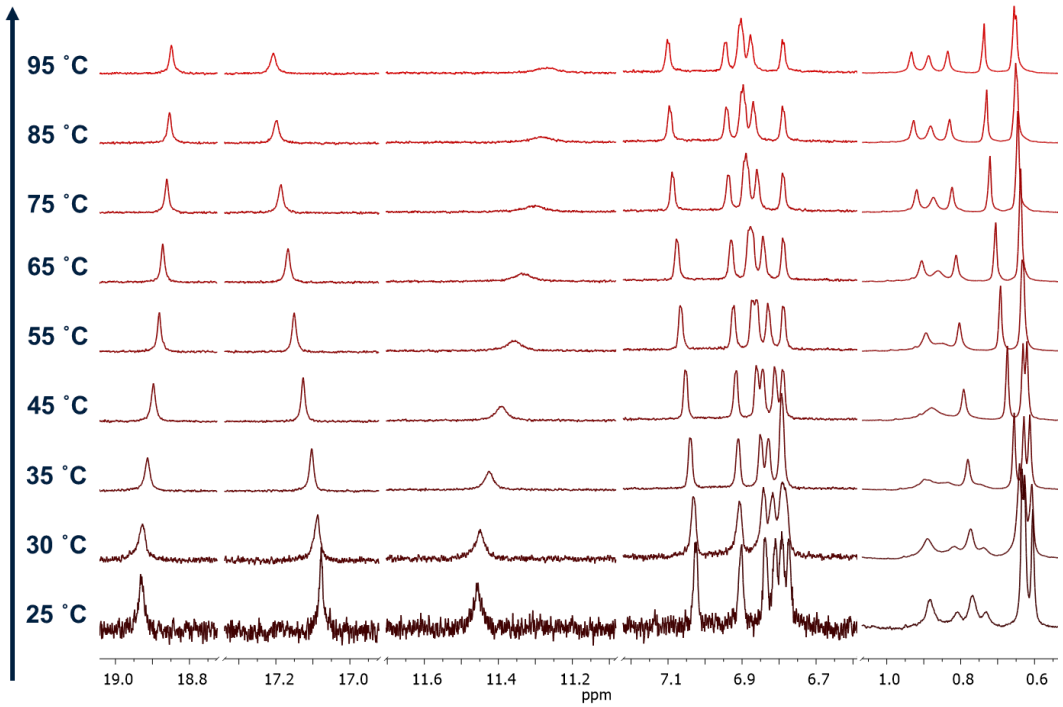


Figure S21. VT ^{1}H NMR spectra of 2a from in 1,1,2,2-tetrachloroethane-d_2 (400 MHz).

Peaks from *ca*. 0.8 to 1.0 ppm become well resolved giving three singlets, all equal in intensity. The aromatic resonances from δ 6.7 to 7.1 at 45 °C become well resolved showing eights doublets. The OH proton resonance at δ 11.4 ppm at 25 °C becomes broader as the temperature increases. The NH resonances at higher ppm (δ 18.9 and 17.2 ppm) remain singlets at increased temperatures. Note the spectra have been cut and the intensities adjusted purely for graphical representation.

Chair-like conformation of 2a and boat like conformation of 3a/b

When each of the main arene rings that compose the macrocyclic ligand in compound **2a** are treated as individual atoms and all arene and alkyl groups are removed, the resulting structure resembles a chair-conformer. The bond distances between the center of each "superatom" are roughly the same at *ca*. 6.5 Å.

When the same type of analysis is done on complex **3a/b** the resulting structure is more reminiscent of a boat-like conformation. Again, the bond distances between each of the "superatoms" in **3a** is almost identical at *ca*. 6.5 Å.

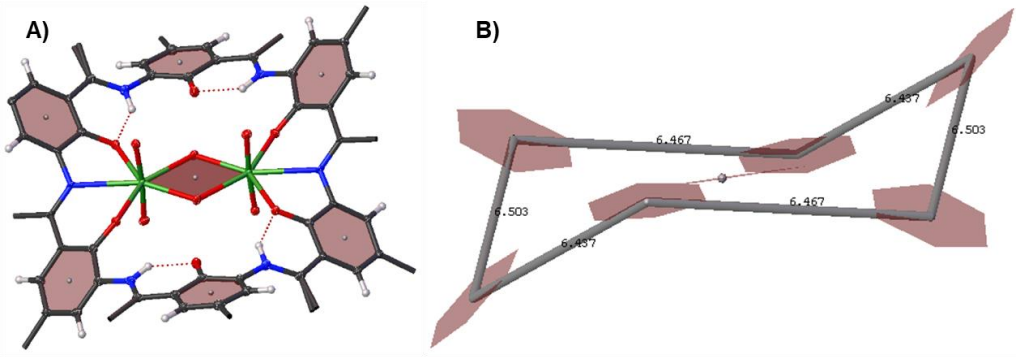


Figure S22. Chair-like conformation of 2.

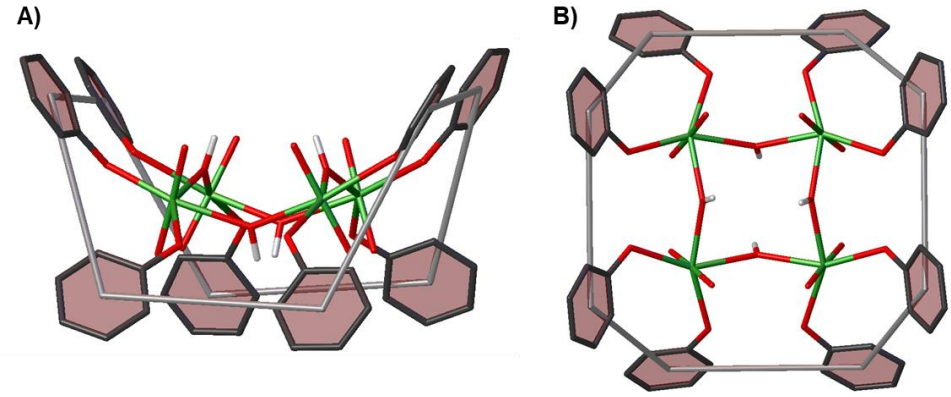


Figure S23. Boat-like conformation of 3.

Table S1. Summary of crystallographic data

Compound	**2a**	**2b**	**3a**	**3b**
Resolution (Å)	0.74	0.83	0.83	0.83
Chemical Formula	$C_{126}H_{146}N_6O_{12}U_2$, $10(C_3H_6O)$	$C_{102}H_{100}N_6O_{12}U_2$, $8(C_2D_6OS)$	$C_{42}H_{49}N_2O_5U$	$0.5(C_{136}H_{136}N_8O_{20}U_4)$, $2(C_2H_4Cl_2)$
Formula Weight	2993.32	2751.25	899.86	3550.55
a	14.0254(19)	14.1675(13)	29.7978(13)	35.7713(16)
b	16.697(3)	15.6425(13)	29.7978(13)	35.7713(16)
c	18.000(3)	15.7252(14)	21.0965(10)	28.7439(13)
α	69.218(4)	74.352(3)	90	90
β	72.211(4)	89.153(3)	90	90
γ	83.081(4)	79.490(3)	90	90
Unit cell volume ($Å^3$)	3752.3(9)	3297.3(5)	18731.8(19)	36780(4)
Temperature (K)	100	100	100	100
Crystal System	Triclinic	Triclinic	Tetragonal	Tetragonal
Space group	P-1	P-1	$I4_1/a$	$I4_1/acd$
Z	1	1	16	16
Absorption coefficient	2.221	2.641	3.503	3.680
Final R1 values ($I > 2\sigma(I)$)	0.0589	0.0567	0.0520	0.0569
Final wR(F2) values	0.1467	0.1537	0.1244	0.1210

Discussion about crystallographic refinement of compounds 2 and 3

Compound 2a.

Thermal similarity constrains were applied to several of the terminal *t*-butyl carbon atoms and one of the arene groups in the backbone.

Compound 2b

The uranium atoms were modelled in parts, due to positional disorder in the cavity of the molecule. This disorder is likely due to the large degree of rotational freedom of the macrocyclic ligand. Similar thermal constraints were applied to both uranium motifs, several of the carbon atoms in the macrocycle, and two carbon atoms on a DMSO molecule. A very disordered solvent molecule, which could not be modelled, was removed using PLATON/SQUEEZE.

Compound 3a.

A very disordered solvent molecule within the larger cavity of **3a** could not be modelled, so PLATON-SQUEEZE was used. Thermal similarity constraints were applied to several of the atoms. Due to positional disorder, the *t*-octyl groups were modelled in parts with constricted bond lengths and angles. Thermal similarity constraints were applied to some carbon atoms on the *t*-octyl groups and arene rings.

Compound 3b

Due to positional disorder of the terminal *t*-butyl groups similarity restraints were used on the bond lengths and angles. The *t*-butyl groups were modelled as parts, due to the disorder. One of the arene rings coordinated to the uranyl(VI) centers was disordered and modelled in parts. Several of the arene rings were disordered and were fixed to be hexagons and modelled in parts. A heavily disordered solvent molecule in the cavity of the molecule could not be successfully modelled, so PLATON-SQUEEZE was used.

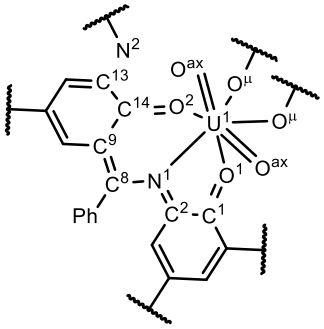


Image describing the naming scheme for the table of partial bond lengths

Table S2. Select crystallographic bond lengths

Compound	**2a**	**2b**	**3a**	**3b**
U1-U2	3.8916(5)	3.9089(6)	4.317	4.361
U1 O1	2.433(4)	2.444(4)	2.428(5)	2.452(6)
U1 O2	2.304(3)	2.236(5)	2.350(5)	2.322(6)
U1 Oμ#1	2.350(3)	2.353(5)	2.315(5)	2.352(7)
U1 Oμ#2	2.335(4)	2.353(5)	2.328(5)	2.344(7)
U1 Oax	1.790(4)	1.787(5)	1.779(5)	1.771(7)
U1 Oax	1.782(4)	1.791(5)	1.768(5)	1.740(7)
U1 N1	2.592(4)	2.639(6)	2.602(6)	2.573(8)
μO-μO	2.611	2.620	2.984	2.969
O1 C1	1.315(6)	1.300(9	1.290(9)	1.34(2)
O2 C14	1.305(6)	1.306(8)	1.284(9)	1.346(7)
C1 C2	1.418(7)	1.548(11)	1.428(11)	1.3900
N1 C2	1.444(6)	1.431(9)	1.401(10)	1.46(2)
N1 C8	1.298(6)	1.302(9)	1.304(10)	1.287(12)
C8 C9	1.458(6)	1.447(10)	1.458(12)	1.476(10)
C9 C14	1.420(7)	1.422(10)	1.451(11)	1.3900
C13 C14	1.419(7)	1.387(11)	1.414(11)	1.3900
N2 C13	1.416(7)	1.445(9)	1.420(10)	1.430(8)

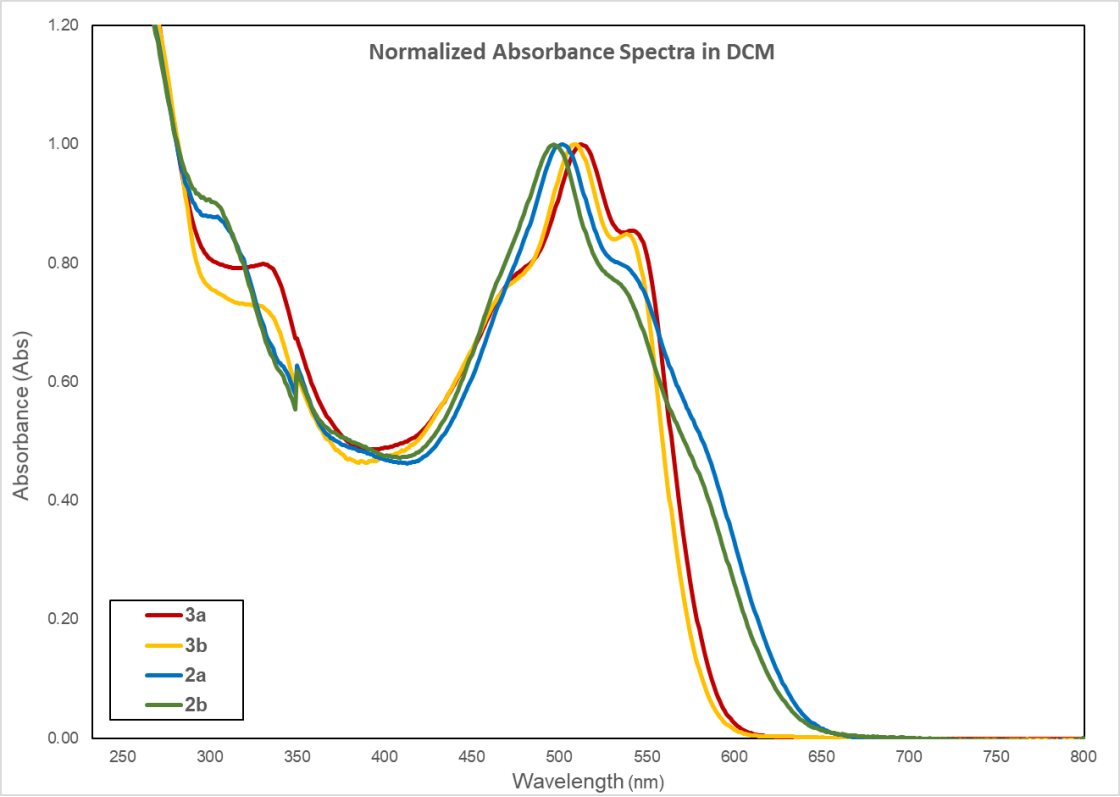


Figure S24. Normalized UV-Vis absorbance spectra of 2/3a-b in DCM.

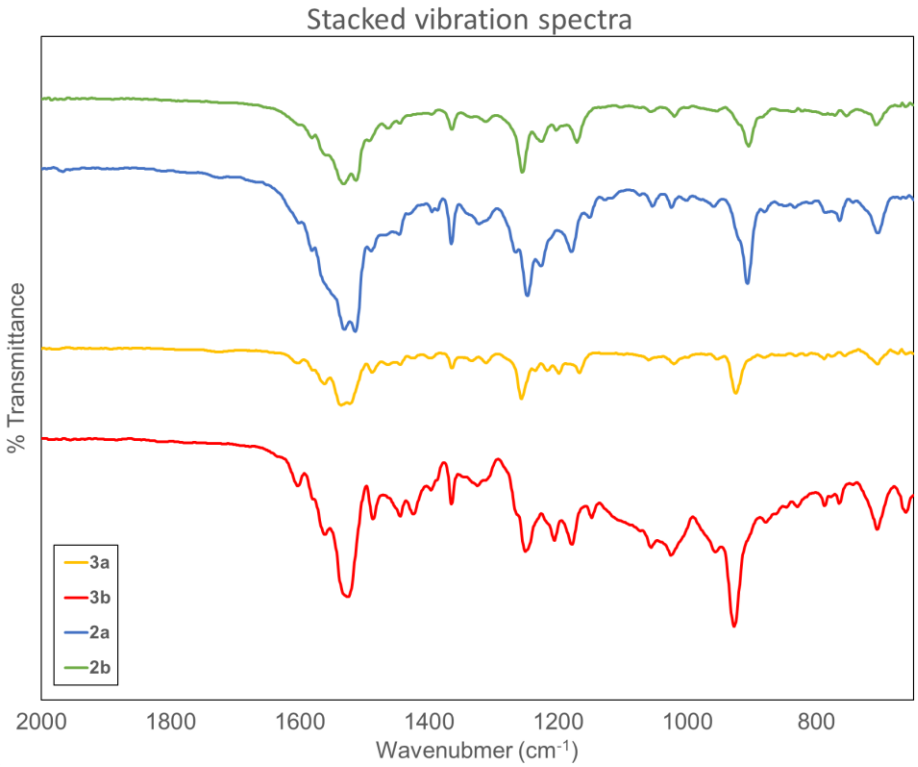


Figure S25. Stacked partial FT-IR spectra of complexes 2/3a-b.

Computational methods

There are many papers suggesting that in case of uranium and closely related actinides, compounds DFT coupled with quasi relativistic and fully relativistic pseudopotential describing inner electrons can be safely used for analyzing their structures and some electronic properties.[9-11.]

Geometries have been computed at different levels of theory ranging from range separated and meta-GGA (ωB97x[12] and M06[13]) xc functional. Basis sets for all atoms were 6-31g and 6-31g(d)[14] whereas for uranium atom the quasi relativistic medium core 78MWB[15] and the fully relativistic small core ECP (energy consistent pseudopotential) 60MDF[16] has been used. The 78MWB pseudopotential coupled with the relative (7s6p5d2f)/[5s4p4d2f][17] basis set and the 60MDF pseudopotential with a larger (14s13p10d8f6g)/[7s6p5d4f3g] basis set were both retrieved from University of Köln (Germany) web site[18]. All structures were checked being minima by computing the Hessian matrix at the same level of theory. All integrals have been computed using the "Ultrafine" integration grid. Calculations have been performed *in vacuo*, i.e., without the use of SCRF (Self Consistent Reaction Field) approach for continuum solvent model simulation.

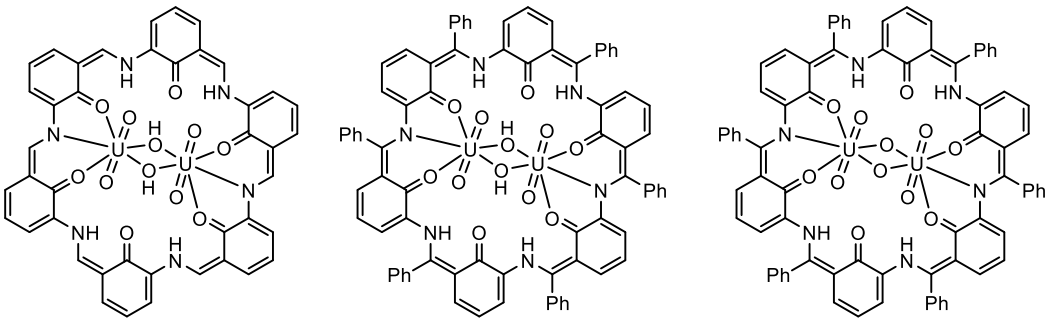
SCXRD geometries, if available, were used as input guesses for the optimization but increasing all the bond distances involving hydrogen atoms to 1.07 Å.

The Gaussian suite of programs G09.revE01 and G016.revB01[19] has been used for all geometry optimization and analytical Hessian calculations.

Optimized structures by DFT

Dinuclear uranyl models

In the case of **2a**/**2b** two model compounds have been compared. The former (**2c**) without the meso-ring substituents, *i.e*, missing the phenyl and alkyl substituents, the latter (**2d**) containing only the meso-phenyl substituents. A third (**2e**) has oxo bridging instead of the μ-OH one.



2c **2d** **2e**

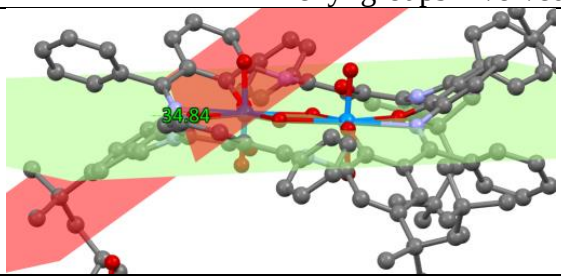
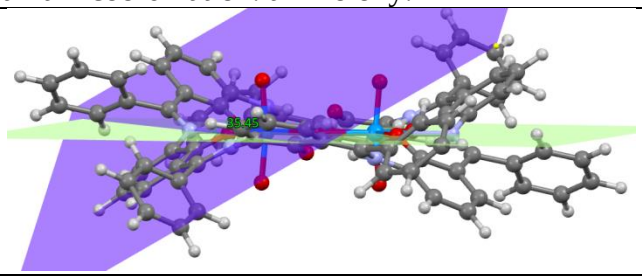
Figure 26. Structure of complexes 2c, 2d, and 2e

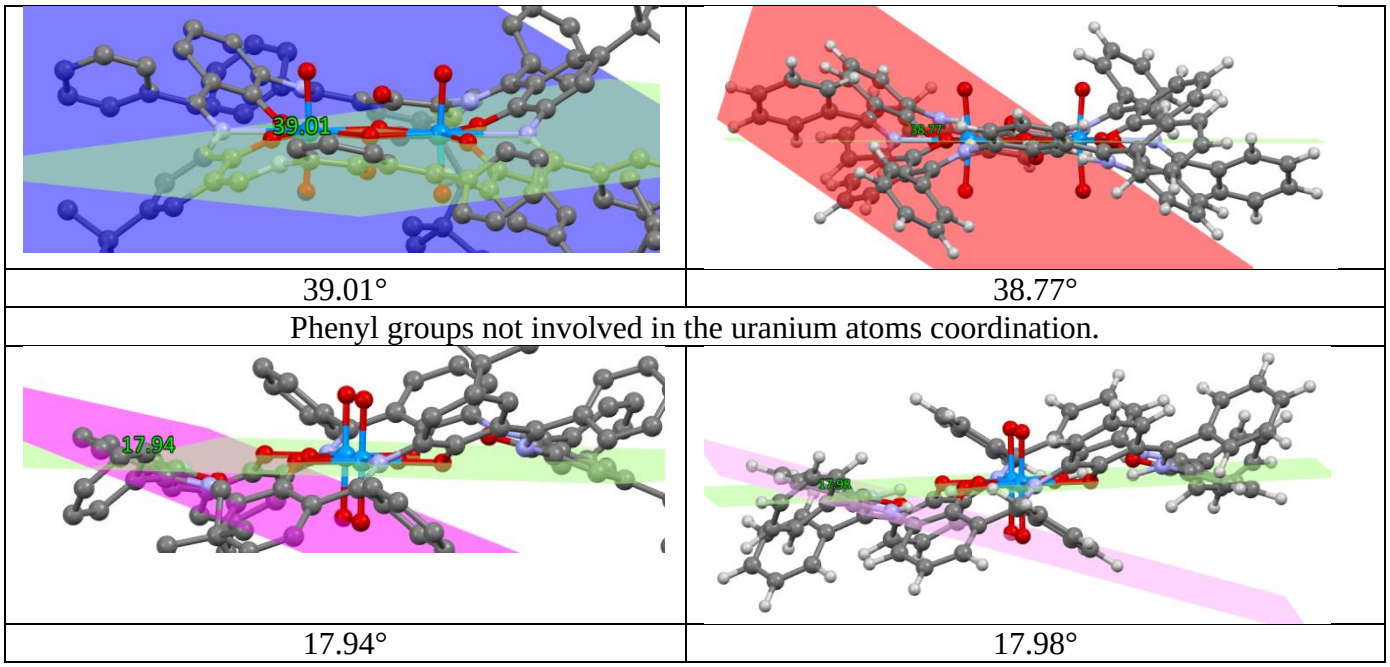
2e, irrespective of the level of theory used, shows a definite elongation of the rhombohedral geometry of the uranium μ-oxo core whereas **2c** shows a very close geometry as found in the SCXRD structure with (μ-OH)-U-(μ-OH) angle of 112° and a U-(μ-OH)-U angle of 67° suggesting a μ-OH bridging in agreement with the ^{1}H NMR findings. The conformation obtained starting from the SCXRD data belongs to the C_i point group symmetry and does not show any negative Hessian eigenvalue indicating that it is a real minimum on the molecular energy surface at the levels of theory used.

The difference shown by the uranium dimer core geometry does not seem very significant on changing the xc functional moving from range corrected to meta-hybrid functional whereas a larger basis set induces some modifications in oxygen and nitrogen atoms macrocycle coordination to uranium, distances increase significantly their values compared to the SCXRD data. Axial oxygen distances are better reproduced by the M06 xc correlation functional with the uranium atom described by the combination of the small core 78MWB pseudopotential and (7s6p5d2f)/[5s4p4d2f]) basis set and the 6-31g basis set on all the remaining atoms (1.771 and 1.768 Å ωB97X and M06 respectively vs. 1.783 Å SCXRD). However larger basis sets and small core pseudopotential give better account of the O-U-O angle being 173.63° and 173.74° (ωB97X and M06 respectively) vs. 174.84°, SCXRD, suggesting a better description of the relative role of f and d orbital[20] by the larger basis set.

Though **2c** shows a correct geometry of uranium oxygen core it has too small values of the dihedral between the average planes of uranium and the μ-OH atoms core and each of the three different kinds of phenyl rings around the macrocycle engendering a too flat conformation compared to the SCXRD structure.

2d on the other hand, because the presence of the meso-phenyl substituents, still retaining the C_i point group symmetry, bond distances and angles, gets the correct torsional value as indicated in Figure S27. This suggests that whereas the phenyl groups have a strong influence on the overall shape of the molecule the alkyl substituents play only a marginal role as far as the macrocycle conformation.

SCXRD data	78MWB((7s6p5d2f)/[5s4p4d2f]) /6-31g/m06
Phenyl groups involved in the uranium coordination: amino oxy.	
	
34.87°	35.45°
Phenyl groups involved in the uranium atoms coordination only by oxygen.	



39.01°	38.77°
Phenyl groups not involved in the uranium atoms coordination.	
17.94°	17.98°

Figure S27. Dihedral angles between the average uranium μ-oxygen core and the macrocycle phenyl moieties.

Cartesian coordinates of the optimized structures for the dinuclear system 2c (muOH_Ci_U_60MDF_631gdp_wB97x)

U	-0.0426288559	-1.9355397238	-0.0549697814
O	-2.1543064759	-2.9673701335	-0.3263532155
O	2.2197669119	-2.9466680997	0.2248971198
O	4.1179473304	0.1171095134	0.108847072
O	1.3016247636	-0.0366448819	0.2160110003
O	0.2564477436	-1.9811152106	-1.7895545691
O	-0.3084113291	-2.0822793475	1.6805155598
N	0.1484855437	-4.6445055829	-0.1156059275
N	4.8119157186	-2.4293450234	0.2300977717
N	-4.7249449413	-2.6459792011	0.0026305723
C	-2.7841836156	-4.0081346041	0.0844572767
C	-4.2025545711	-3.9312531879	0.2538527417
C	-4.9560221282	-5.0047694407	0.6849965605
C	-4.3404024263	-6.2323573631	0.9494315948
C	-2.9705740647	-6.3400502601	0.7980492714
C	-2.1756381379	-5.2586070251	0.3819820286
C	-0.7541886289	-5.4954255359	0.2271984127
C	2.5073303491	-4.149151214	-0.0992274833
C	1.4659234966	-5.1205690876	-0.3212618609
C	1.7873662727	-6.3791063452	-0.7702817025
C	3.1307183192	-6.797778211	-0.9418145006

C	4.1430748357	-5.9198861566	-0.6827937995
C	3.8627571695	-4.5881385067	-0.2662323433
C	4.9369287817	-3.6903075194	-0.0941574974
C	5.8366264478	-1.4677409064	0.3562309954
C	5.3490244344	-0.1084420629	0.25469114
C	6.3519952569	0.9231774618	0.3200066699
C	7.7166936737	0.5889845505	0.5116885941
C	8.1207494614	-0.7138019735	0.6399021462
C	7.159348967	-1.7512780215	0.5647376357
C	-5.9659532705	-2.2759948187	-0.1596219212
O	2.1543064759	2.9673701335	0.3263532155
O	-2.2197669119	2.9466680997	-0.2248971198
O	-4.1179473304	-0.1171095134	-0.108847072
N	-0.1484855437	4.6445055829	0.1156059275
N	-4.8119157186	2.4293450234	-0.2300977717
N	4.7249449413	2.6459792011	-0.0026305723
C	2.7841836156	4.0081346041	-0.0844572767
C	4.2025545711	3.9312531879	-0.2538527417
C	4.9560221282	5.0047694407	-0.6849965605
C	4.3404024263	6.2323573631	-0.9494315948
C	2.9705740647	6.3400502601	-0.7980492714
C	2.1756381379	5.2586070251	-0.3819820286
C	0.7541886289	5.4954255359	-0.2271984127
C	-2.5073303491	4.149151214	0.0992274833
C	-1.4659234966	5.1205690876	0.3212618609
C	-1.7873662727	6.3791063452	0.7702817025
C	-3.1307183192	6.797778211	0.9418145006
C	-4.1430748357	5.9198861566	0.6827937995
C	-3.8627571695	4.5881385067	0.2662323433
C	-4.9369287817	3.6903075194	0.0941574974
C	-5.8366264478	1.4677409064	-0.3562309954
C	-5.3490244344	0.1084420629	-0.25469114
C	-6.3519952569	-0.9231774618	-0.3200066699
C	-7.7166936737	-0.5889845505	-0.5116885941
C	-8.1207494614	0.7138019735	-0.6399021462
C	-7.159348967	1.7512780215	-0.5647376357
C	5.9659532705	2.2759948187	0.1596219212
U	0.0426288559	1.9355397238	0.0549697814
O	-1.3016247636	0.0366448819	-0.2160110003
O	-0.2564477436	1.9811152106	1.7895545691
O	0.3084113291	2.0822793475	-1.6805155598
H	9.1641972363	-0.9605134268	0.8022293946
H	6.7306554337	3.0532365113	0.1628434186

H -3.3393105382 7.8033765324 1.2913782533
H 5.9502943536 -4.0551386943 -0.2630187716
H 4.9305084513 7.0777157965 -1.2864128022
H 0.4533116414 6.532888778 -0.426039155
H -2.2565596569 0.0410529525 -0.0595347793
H 2.2565596569 -0.0410529525 0.0595347793
H -5.1813668248 6.2184423541 0.8145034436
H -0.9897872378 7.0723821507 1.0263772474
H -5.9502943536 4.0551386943 0.2630187716
H -7.4862557654 2.7820531073 -0.6865934152
H -9.1641972363 0.9605134268 -0.8022293946
H -8.4480040604 -1.3939569718 -0.5617698544
H -6.7306554337 -3.0532365113 -0.1628434186
H -6.026872483 -4.8958406652 0.8432019046
H -4.9305084513 -7.0777157965 1.2864128022
H -2.4810261189 -7.2888430834 1.0117531892
H -0.4533116414 -6.532888778 0.426039155
H 0.9897872378 -7.0723821507 -1.0263772474
H 3.3393105382 -7.8033765324 -1.2913782533
H 5.1813668248 -6.2184423541 -0.8145034436
H 7.4862557654 -2.7820531073 0.6865934152
H 8.4480040604 1.3939569718 0.5617698544
H 6.026872483 4.8958406652 -0.8432019046
H 2.4810261189 7.2888430834 -1.0117531892
H 4.0303694589 1.880003553 0.0591199678
H 3.8460090059 -2.0791216595 0.3146302112
H -4.0303694589 -1.880003553 -0.0591199678
H -3.8460090059 2.0791216595 -0.3146302112

2c (dimerH2_muOH_Ci_U_60MDF_631gdp_m06)
U -0.0364622509 -1.9256641182 -0.0524087122
O -2.1572192558 -2.9523440118 -0.3494010571
O 2.2287589659 -2.9228551035 0.2357492825
O 4.1282765019 0.1184377149 0.2253697739
O 1.3026452061 -0.0339580098 0.2379376674
O 0.2861012063 -1.9714086797 -1.7844123555
O -0.3354857129 -2.0714969233 1.6795266108
N 0.1569009499 -4.6210256047 -0.0943165215
N 4.8392928338 -2.4209363473 0.2299862906
N -4.7385311398 -2.660952265 -0.0810037577
C -2.7877672319 -3.9915290787 0.045439379
C -4.212131085 -3.9302640829 0.1792801889
C -4.965953138 -5.0172860452 0.5869170712

C -4.3450071518 -6.2340312515 0.8708854123
C -2.9695185366 -6.3278898371 0.7587402444
C -2.1732562549 -5.2404921161 0.3619050273
C -0.7594041209 -5.4693868736 0.2387338397
C 2.507247625 -4.1299013806 -0.0711107161
C 1.4656863764 -5.0968738966 -0.2840771062
C 1.7869483167 -6.3719780716 -0.7065823437
C 3.1224565751 -6.7989232025 -0.8576476462
C 4.1408407509 -5.9202561006 -0.6062966175
C 3.8661483463 -4.5823532517 -0.2209912342
C 4.9460222071 -3.6972656061 -0.0606168618
C 5.8587025083 -1.4665987394 0.3328709732
C 5.3634168233 -0.1105149044 0.2938738105
C 6.3721174617 0.9249896836 0.3176224553
C 7.7415333057 0.5908615837 0.427228943
C 8.1540152781 -0.7172983829 0.5067942596
C 7.1982349184 -1.7514778182 0.4571580158
C -5.9879851626 -2.2744785602 -0.1768589584
O 2.1572192558 2.9523440118 0.3494010571
O -2.2287589659 2.9228551035 -0.2357492825
O -4.1282765019 -0.1184377149 -0.2253697739
N -0.1569009499 4.6210256047 0.0943165215
N -4.8392928338 2.4209363473 -0.2299862906
N 4.7385311398 2.660952265 0.0810037577
C 2.7877672319 3.9915290787 -0.045439379
C 4.212131085 3.9302640829 -0.1792801889
C 4.965953138 5.0172860452 -0.5869170712
C 4.3450071518 6.2340312515 -0.8708854123
C 2.9695185366 6.3278898371 -0.7587402444
C 2.1732562549 5.2404921161 -0.3619050273
C 0.7594041209 5.4693868736 -0.2387338397
C -2.507247625 4.1299013806 0.0711107161
C -1.4656863764 5.0968738966 0.2840771062
C -1.7869483167 6.3719780716 0.7065823437
C -3.1224565751 6.7989232025 0.8576476462
C -4.1408407509 5.9202561006 0.6062966175
C -3.8661483463 4.5823532517 0.2209912342
C -4.9460222071 3.6972656061 0.0606168618
C -5.8587025083 1.4665987394 -0.3328709732
C -5.3634168233 0.1105149044 -0.2938738105
C -6.3721174617 -0.9249896836 -0.3176224553
C -7.7415333057 -0.5908615837 -0.427228943
C -8.1540152781 0.7172983829 -0.5067942596

C -7.1982349184 1.7514778182 -0.4571580158
C 5.9879851626 2.2744785602 0.1768589584
U 0.0364622509 1.9256641182 0.0524087122
O -1.3026452061 0.0339580098 -0.2379376674
O -0.2861012063 1.9714086797 1.7844123555
O 0.3354857129 2.0714969233 -1.6795266108
H 9.2067809184 -0.9627251881 0.6060813882
H 6.7633226316 3.0423979687 0.1279759834
H -3.3297853651 7.8119455971 1.189511649
H 5.9556072277 -4.0848573852 -0.2140757025
H 4.935174988 7.0870481053 -1.1913592468
H 0.4625573068 6.5084975546 -0.4547816314
H -2.2610255061 0.0388204012 -0.0919845894
H 2.2610255061 -0.0388204012 0.0919845894
H -5.1802633806 6.2243848416 0.7249790184
H -0.9853334399 7.0641341057 0.9582703871
H -5.9556072277 4.0848573852 0.2140757025
H -7.5337113745 2.7854264401 -0.5284977351
H -9.2067809184 0.9627251881 -0.6060813882
H -8.4727018494 -1.3987391055 -0.4495470396
H -6.7633226316 -3.0423979687 -0.1279759834
H -6.0438313319 -4.9214458899 0.7093789024
H -4.935174988 -7.0870481053 1.1913592468
H -2.4735445571 -7.2714264129 0.9861307765
H -0.4625573068 -6.5084975546 0.4547816314
H 0.9853334399 -7.0641341057 -0.9582703871
H 3.3297853651 -7.8119455971 -1.189511649
H 5.1802633806 -6.2243848416 -0.7249790184
H 7.5337113745 -2.7854264401 0.5284977351
H 8.4727018494 1.3987391055 0.4495470396
H 6.0438313319 4.9214458899 -0.7093789024
H 2.4735445571 7.2714264129 -0.9861307765
H 4.0389328035 1.9014560747 0.1837105389
H 3.8757582507 -2.0557533212 0.3111788101
H -4.0389328035 -1.9014560747 -0.1837105389
H -3.8757582507 2.0557533212 -0.3111788101

2c (dimerH2_muOH_Ci_U_60MDF_631g_wB97x)
U -0.0262784796 -1.9313809946 -0.0369913591
O -2.1279588344 -2.9508800848 -0.2101206508
O 2.2296951088 -2.9290387348 0.164152923
O 4.0945408428 0.1312440987 0.1409842553
O 1.3025799042 -0.0232785765 0.1292327682

O 0.1854099819 -2.0101463537 -1.796055461
O -0.1939650283 -2.0857565569 1.7229828056
N 0.1556309792 -4.6587643672 -0.0785527724
N 4.8069433608 -2.4286246908 0.1921165206
N -4.7174968764 -2.6520113223 0.0034445051
C -2.787872771 -4.0254629354 0.1380311612
C -4.2072668484 -3.9448750501 0.2533761404
C -4.9769194656 -5.0318433432 0.6288868635
C -4.3644944571 -6.2650864678 0.8849023943
C -2.9873373898 -6.3730379159 0.7703479112
C -2.1812380191 -5.2790179157 0.4035816993
C -0.7603173544 -5.5114437101 0.259008474
C 2.5209943793 -4.1669278964 -0.1250663301
C 1.4792438164 -5.136570896 -0.3031189031
C 1.7927102421 -6.4127427979 -0.7200966982
C 3.1351882733 -6.8306290007 -0.89755972
C 4.1534512188 -5.9432694485 -0.6680686313
C 3.8745313452 -4.6012474353 -0.2843726678
C 4.9469840801 -3.698207721 -0.1140536773
C 5.8318550782 -1.4660858574 0.3379817264
C 5.3543575207 -0.1084910875 0.2663663327
C 6.3496361716 0.9247794759 0.3230774694
C 7.7170807946 0.5898068304 0.500728012
C 8.1211886354 -0.7190690048 0.6131482306
C 7.1603889627 -1.7563746238 0.5289660365
C -5.9635337416 -2.2787340197 -0.1617152831
O 2.1279588344 2.9508800848 0.2101206508
O -2.2296951088 2.9290387348 -0.164152923
O -4.0945408428 -0.1312440987 -0.1409842553
N -0.1556309792 4.6587643672 0.0785527724
N -4.8069433608 2.4286246908 -0.1921165206
N 4.7174968764 2.6520113223 -0.0034445051
C 2.787872771 4.0254629354 -0.1380311612
C 4.2072668484 3.9448750501 -0.2533761404
C 4.9769194656 5.0318433432 -0.6288868635
C 4.3644944571 6.2650864678 -0.8849023943
C 2.9873373898 6.3730379159 -0.7703479112
C 2.1812380191 5.2790179157 -0.4035816993
C 0.7603173544 5.5114437101 -0.259008474
C -2.5209943793 4.1669278964 0.1250663301
C -1.4792438164 5.136570896 0.3031189031
C -1.7927102421 6.4127427979 0.7200966982
C -3.1351882733 6.8306290007 0.89755972

C -4.1534512188 5.9432694485 0.6680686313
C -3.8745313452 4.6012474353 0.2843726678
C -4.9469840801 3.698207721 0.1140536773
C -5.8318550782 1.4660858574 -0.3379817264
C -5.3543575207 0.1084910875 -0.2663663327
C -6.3496361716 -0.9247794759 -0.3230774694
C -7.7170807946 -0.5898068304 -0.500728012
C -8.1211886354 0.7190690048 -0.6131482306
C -7.1603889627 1.7563746238 -0.5289660365
C 5.9635337416 2.2787340197 0.1617152831
U 0.0262784796 1.9313809946 0.0369913591
O -1.3025799042 0.0232785765 -0.1292327682
O -0.1854099819 2.0101463537 1.796055461
O 0.1939650283 2.0857565569 -1.7229828056
H 9.1645209793 -0.9673356065 0.7641186958
H 6.7321635474 3.0488937066 0.1621606902
H -3.3423615536 7.8432152277 1.2223844952
H 5.959576781 -4.0669059309 -0.2643981765
H 4.9630147274 7.1183316538 -1.1803481766
H 0.4657473319 6.5500609464 -0.4505279429
H -2.280891209 0.0216195988 -0.1354747486
H 2.280891209 -0.0216195988 0.1354747486
H -5.189363266 6.2462757023 0.7977820488
H -0.9973506426 7.1165303764 0.9455883318
H -5.959576781 4.0669059309 0.2643981765
H -7.4922640722 2.7862752414 -0.628417334
H -9.1645209793 0.9673356065 -0.7641186958
H -8.4491108204 -1.3923107577 -0.5502072859
H -6.7321635474 -3.0488937066 -0.1621606902
H -6.0524061773 -4.9347260915 0.7480873675
H -4.9630147274 -7.1183316538 1.1803481766
H -2.5064565089 -7.3277251093 0.969970741
H -0.4657473319 -6.5500609464 0.4505279429
H 0.9973506426 -7.1165303764 -0.9455883318
H 3.3423615536 -7.8432152277 -1.2223844952
H 5.189363266 -6.2462757023 -0.7977820488
H 7.4922640722 -2.7862752414 0.628417334
H 8.4491108204 1.3923107577 0.5502072859
H 6.0524061773 4.9347260915 -0.7480873675
H 2.5064565089 7.3277251093 -0.969970741
H 4.0060449675 1.8977369348 0.0560191191
H 3.835286859 -2.080689537 0.2674988752
H -4.0060449675 -1.8977369348 -0.0560191191

H -3.835286859 2.080689537 -0.2674988752

2c (muOH_U_78MWB_631g _M06)

U 0.0329646392 -0.0638475231 -1.9142780933
O 0.1986603078 1.9952976507 -2.9878130607
O -0.1535077744 -2.3567312926 -2.7602090016
O -0.2628202499 -4.0994969038 0.311452548
O -0.1377261758 -1.2842957622 0.0377433068
O 1.7890214599 -0.2753889229 -2.0064803016
O -1.72288399 0.0983529782 -2.0920601901
N 0.0525909194 -0.3626824218 -4.5649301491
N -0.2244094691 -4.9361503263 -2.1951305077
N 0.0739016477 4.6089795407 -2.8541824973
C -0.1453539237 2.6029924387 -4.0868177821
C -0.2150916293 4.0294435842 -4.0966523033
C -0.5886823009 4.7418452248 -5.2269135857
C -0.8904620861 4.0642073365 -6.4121097151
C -0.8148732395 2.6796569791 -6.4383011124
C -0.4448170408 1.9310947557 -5.3046498303
C -0.3090163597 0.5123577946 -5.4608374439
C 0.1252217268 -2.6949011761 -3.9880881241
C 0.2946400171 -1.6910218881 -4.9910607987
C 0.7069926288 -2.0458430146 -6.265217423
C 0.878841491 -3.3955093469 -6.6392979533
C 0.6422419651 -4.3872500817 -5.7188303088
C 0.2668702982 -4.0668545132 -4.3871609595
C 0.0779060142 -5.1137207684 -3.466239133
C -0.3801621949 -5.9142751361 -1.2005868025
C -0.3504100891 -5.3711639121 0.1301365839
C -0.3904422286 -6.3239841149 1.2110459662
C -0.5342034293 -7.7053579023 0.9374994429
C -0.61887334 -8.1724255993 -0.3569032275
C -0.5329461899 -7.2652536991 -1.4333270073
C 0.2226831437 5.8798471573 -2.5395400972
O -0.1974139338 -1.995273569 2.9888388061
O 0.1547535801 2.3567540233 2.7612215212
O 0.264059587 4.0995309933 -0.3104239486
N -0.051236068 0.362703781 4.5659454346
N 0.2256194746 4.9361851583 2.196153701
N -0.0726792145 -4.6089525632 2.8551995695
C 0.1466248903 -2.6029719064 4.0878354636
C 0.216340435 -4.0294236545 4.0976666471
C 0.5899351067 -4.7418339748 5.2279210243

C	0.8917373558	-4.0642037152	6.413115899
C	0.8161698491	-2.6796524415	6.4393114218
C	0.4461172594	-1.9310815783	5.3056645048
C	0.3103449759	-0.5123423328	5.461856318
C	-0.1239457061	2.6949204278	3.9891076558
C	-0.2933105241	1.6910353628	4.9920836711
C	-0.7056477948	2.0458405142	6.2662483249
C	-0.8775304245	3.3955018931	6.6403337497
C	-0.6409790243	4.3872512793	5.7198629606
C	-0.2656230532	4.0668697043	4.3881852189
C	-0.0766981147	5.1137434312	3.4672637398
C	0.3813379548	5.9143159106	1.2016098935
C	0.3516016941	5.3712023171	-0.1291126973
C	0.391607497	6.3240207458	-1.2100245537
C	0.5353276166	7.7053995127	-0.9364795228
C	0.6199833169	8.1724715362	0.357922299
C	0.5340841285	7.2652988736	1.4343480906
C	-0.2214967882	-5.8798164025	2.540560033
U	-0.0317060174	0.0638685952	1.9152975265
O	0.139016288	1.2843107207	-0.0367240438
O	-1.787764143	0.2754082911	2.0074697419
O	1.7241401762	-0.0983323553	2.0931095103
H	-0.744094013	-9.2309053733	-0.5563789417
H	-0.1889033881	-6.6168865541	3.3430093671
H	-1.2027415858	3.6373650276	7.6464694579
H	0.2082738478	-6.1384207014	-3.8144938975
H	1.1887956523	-4.6183868909	7.2967002993
H	0.5191602464	-0.160395424	6.4816645314
H	0.2005507144	2.2602607013	-0.0776571312
H	-0.1992654843	-2.2602455548	0.078672451
H	-0.7603230491	5.4349106219	5.9893447777
H	-0.9308377044	1.2694152613	6.9929816111
H	-0.2070915837	6.1384392776	3.8155210841
H	0.5989876333	7.6458796795	2.4515058124
H	0.7451741656	9.2309551356	0.5573966608
H	0.5759689561	8.4002397334	-1.7735675309
H	0.1900765178	6.616916379	-3.3419897019
H	-0.6688545365	5.8260599748	-5.1936304964
H	-1.1875193574	4.6183838224	-7.2956986624
H	-1.0423118432	2.1439279802	-7.3583403525
H	-0.5178717978	0.1604010755	-6.4806336912
H	0.9322251625	-1.2694264146	-6.9919463466
H	1.2040645048	-3.6373841326	-7.6454270654

H 0.7615590444 -5.4349135917 -5.9883079187
H -0.5978549017 -7.6458307758 -2.4504857972
H -0.574864001 -8.4001984305 1.7745862961
H 0.6700916209 -5.8260497176 5.1946339024
H 1.043626788 -2.1439291553 7.3593494602
H -0.16147805 -3.9352297624 2.0640035315
H -0.2848365729 -3.95001763 -1.8727969667
H 0.1627063493 3.935258779 -2.0629851056
H 0.2860838977 3.9500554768 1.8738201142

2d Ci_muOH_6Phe_U_78MWB_631g_m06
U 0.0969282534 -1.9043885943 -0.0804718347
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O 2.4100174894 -2.7025430821 0.1862395275
O 4.0340632584 0.3863264123 0.1869068003
O 1.2760158226 0.0583725023 0.2234368154
O 0.4389249709 -1.9429265421 -1.820320465
O -0.2089261263 -2.1346885111 1.6531258045
N 0.4523929892 -4.4946465 -0.1161451965
N 4.9351932525 -2.0913848195 0.1652788708
N -4.4751601608 -2.9170004776 -0.1972589682
C -2.4406854351 -4.0716326382 0.2091553545
C -3.8649277845 -4.0683628165 0.3459734756
C -4.5296875691 -5.0368239428 1.0859322173
C -3.8046452791 -6.0714880901 1.6800050541
C -2.4320752834 -6.14023507 1.5013145545
C -1.7204123364 -5.1847397161 0.7454695463
C -0.3087409385 -5.4031622098 0.454039748
C 2.7491158671 -3.8350028466 -0.3793351046
C 1.739469288 -4.8164432444 -0.623115792
C 2.026210167 -5.9297168586 -1.390945673
C 3.3337136686 -6.1763763152 -1.8529326312
C 4.3520191892 -5.3155008728 -1.5203315706
C 4.1007259128 -4.1378892407 -0.7615804299
C 5.1757838984 -3.2551935298 -0.4338983301
C 5.8282334931 -1.0896907314 0.608720848
C 5.2637838837 0.2334565634 0.5424841698
C 6.1423349074 1.3381723984 0.8561697872
C 7.4295014451 1.0662243228 1.3830025877
C 7.8893993773 -0.2250195156 1.5323305747
C 7.0901851913 -1.3098499765 1.1239030498
C -5.7230959409 -2.6831062714 -0.5915580685
O 1.8817701356 3.0692283363 0.4146266291

O -2.4100174894 2.7025430821 -0.1862395275
O -4.0340632584 -0.3863264123 -0.1869068003
N -0.4523929892 4.4946465 0.1161451965
N -4.9351932525 2.0913848195 -0.1652788708
N 4.4751601608 2.9170004776 0.1972589682
C 2.4406854351 4.0716326382 -0.2091553545
C 3.8649277845 4.0683628165 -0.3459734756
C 4.5296875691 5.0368239428 -1.0859322173
C 3.8046452791 6.0714880901 -1.6800050541
C 2.4320752834 6.14023507 -1.5013145545
C 1.7204123364 5.1847397161 -0.7454695463
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H	9.0612773568	-2.4781452827	-2.7961335621
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Comparison between model tetranuclear SC-XRD C1 and optimized S_4

In the case of **3a/b** a model compound, **3c**, lacking the alkyl and meso-phenyl group has been used (Figure S28). Optimization of the structure starting from the SCXRD data was performed at the 78MWB/AVTZ/6-31g/M06 and ωB97x level of theory without imposing any symmetry in order to remove any constraint to the minimization procedure. The resulting optimized geometry turned out to belong to the S_4 point group symmetry and, after further optimization within this point group, frequencies have been computed confirming that the geometry was a true minimum on the molecular energy surface. Overlap of the computed and X-ray structures for the uranium core and the macrocycle shows that that the overall shape, unlike **2a/b** vs. **2c**, shows some differences in the torsion of the macrocycle phenyl rings though far smaller than in case of **2a/b**.

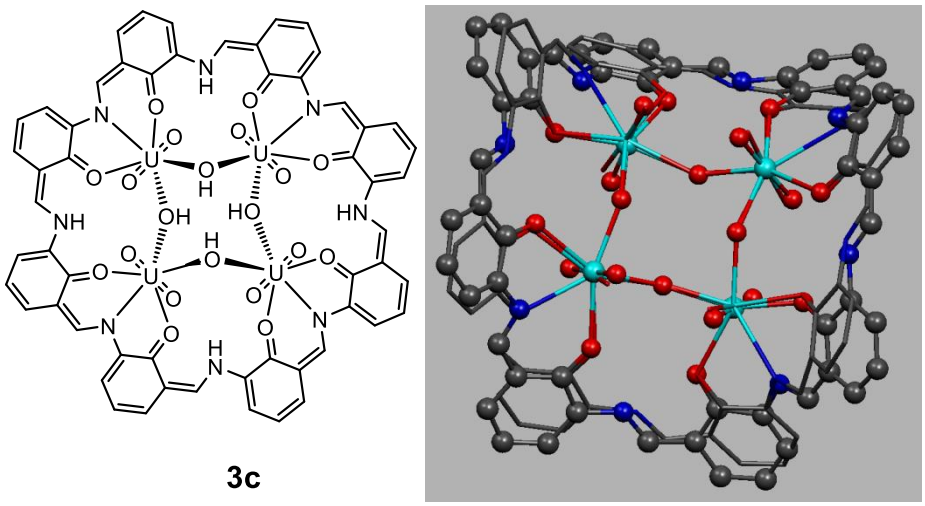


Figure S28. A) Image of complex 3c, and B) Overlap of the computed and experimental structure. Ball and stick computed, stick SCXRD. Hydrogen atoms and alkyl and exo-phenyl groups has been removed for clarity

Similar structure is shown by the same basis set and ωB97x functional with only small deviation from the two level of theory. Increasing the basis set including polarization functions to 6-31g(d) on the second period atoms does not change in any significant way the conformation and point group symmetry of **3c** geometry.

In case of M06 functional the overall RMSD (root mean square deviation between experimental and computed data excluding hydrogen atoms) are 0.0322 and 0.0363 Å for 6-31g and 6-31g(d) basis set and M06 functional suggesting that in case of smaller basis set there is some error cancellation that makes the value closer to the SCXRD. On the other hand, U-O bonds are better described by the larger basis set being the same RMSD 0.00626 and 0.0057 Å, respectively, for the two above mentioned basis sets with the largest deviation involve the U-N interactions that are -0.1111 and -0.0916 Å. The ligand bond length differences for the C-C bond range between -0.0453 and 0.0487 Å, the smallest absolute difference being 0.0022 Å in case of larger basis. Smaller basis set gives comparable deviations ranging between -0.0399 and 0.0475 Å. The largest deviations involving the N atoms interaction with U are -0.1111 and -0.0916 Å and those with C atoms of the imino bonds. These deviations are probably related to the absence of the meso-phenyl substituent of the model.

The agreement in case of bond angles is fair good being the largest deviation 2.34° in case of μ-OH-U-O_{ax} angle. The RMSD is 0.4558 and 0.8352° for 6-31g and 6-31g(d) basis set confirming that smaller basis set gives better result due to probably cancellation of errors.

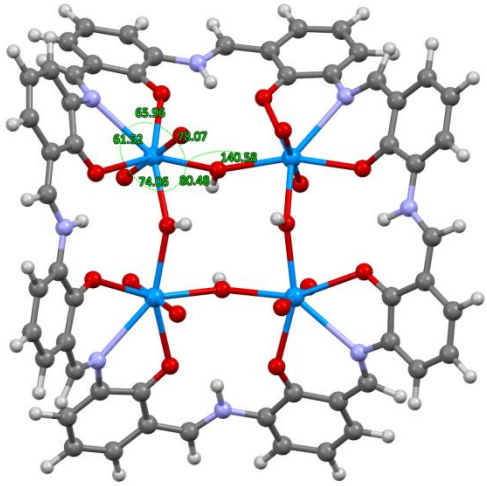
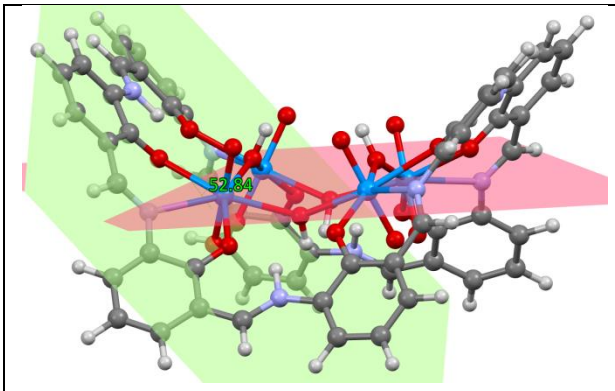
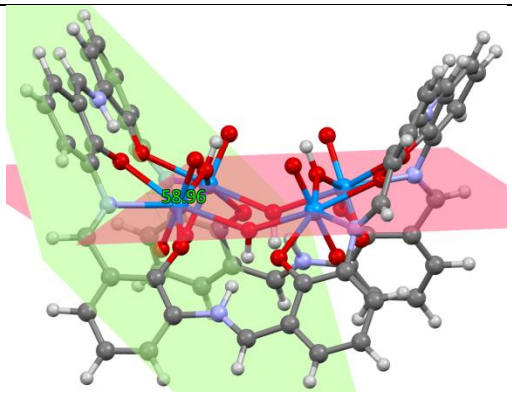


Figure S29. Some relevant angles in case of the DFT computed structure

Torsional angles show a RMSD of 1.5 and 1.8° for 6-31g and 6-31g(d) respectively, confirming the trend found in case of other internal geometrical parameters. The largest differences can be found in all cases in torsions involving the uranium atoms and the absolute values range between 0.1 and 7.3°. Hence these data suggest that the tetra uranium core induces large constraints to the overall shape of the macrocycle compared to the uranium dimer core.



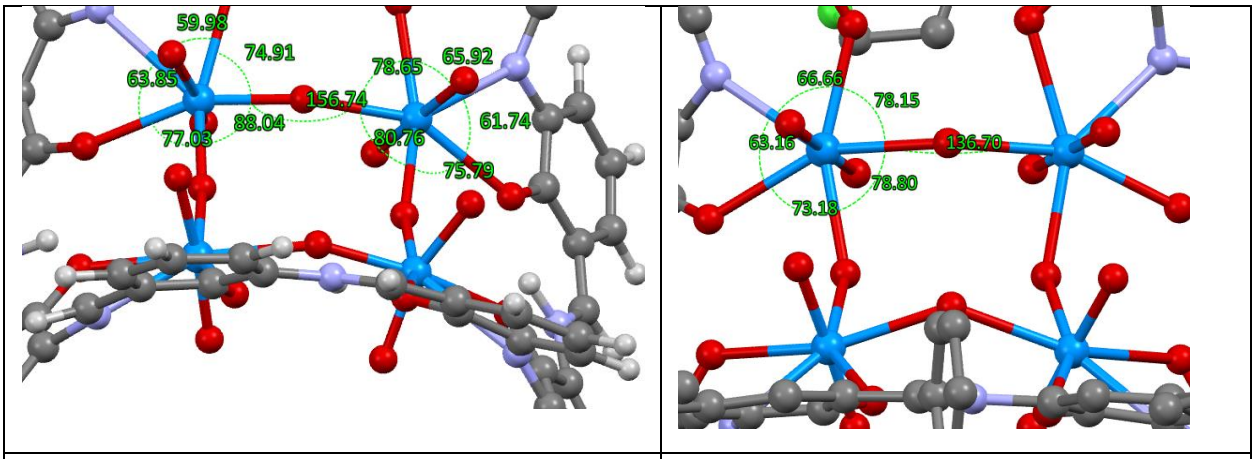
(78MWB/AVTZ/6-31g)M06 level of theory computed dihedral between the two plane 52.84°.



SCXRD with meso-phenyl and *t*-Butyl removed. The dihedral between the U atoms and the meso is 58.96°.

Figure S30. Dihedral comparison.

Calculations of the μ-oxo compound at the 78MWB/AVTZ/6-31g/M06 level of theory reduce the point group symmetry from S_4 to C_2. The RMSD of the bond angles in this case is 5.0° with the largest absolute deviation of 19.7° involving the U-μ-O-U angle. Torsional angles show a RMSD of 10.1° and all the dihedral angles involving at least one U atom differ from the SCXRD data by values ranging from -36.2 to 47.2°.



μ-O cluster	SCXRD

Figure S31. Comparison of some relevant geometrical parameters in case of μ-O (left) and SCXRD structure (right).

These very large differences compared to the μ-OH model complex suggest that in agreement with NMR data the complex has OH bridging groups between the uranium atoms.

Cartesian Coordinates for the optimized structures for the tetranuclear system 3c (78MWB_631gd_m06 S4)

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O 1.61091451 0.97118338 0.72054579
O -0.13358872 3.10943602 1.6548762
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H -2.4835300668 -7.2417306883 0.6375442659
H -1.1701082762 -7.9822114051 4.8321261978
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H 5.9496278713 3.0599604081 -4.1312763831
H 7.1768200002 1.1595188082 -5.061929916
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µ-oxo U4_78MWB_631g_m06

U1 0.67496949 2.7835263055 -0.0020940812
O2 -3.5298676937 2.7698916899 -1.2523323171
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O4 1.6213736117 1.0802728451 0.3857684014
O5 -0.1025780646 3.2548064908 1.5439435676
O6 1.6523125519 2.9361295396 -1.4982091536
N7 1.4335961334 5.4518098496 0.1308025479
N8 -2.6460255319 4.6234567519 -2.8329681525
C9 -4.8992831117 3.8279696923 -2.9225135802
C10 -4.697238446 2.9495599902 -1.8108994839
C11 -5.8295958961 2.2784122862 -1.2698556264
C12 1.3694019351 6.3330432694 -0.8242883801
C13 0.4902073938 6.2733397317 -1.9539796479
C14 -0.5543557887 5.30854524 -2.0103155684
C15 -1.5657755354 5.4954105908 -3.0062026917
C16 -1.4644697777 6.4782293726 -3.9776040827
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C18 0.5639112078 7.2711016935 -2.9407701106
C19 -3.8421229285 4.6429320237 -3.3840238576

O20	4.4560867031	0.7206961927	1.0343187308
N21	5.5329867162	-1.4932599768	-0.1358184995
N22	4.5897035889	2.5966190054	2.8202430955
C23	2.3025947361	6.9901671498	1.8715799803
C24	3.1117925122	7.1768510635	3.0121215448
C25	3.8274971018	6.116400626	3.5262813064
C26	3.7343920955	4.8269960876	2.9455931051
C27	2.8483040421	4.6120906496	1.8389889528
C28	2.1872532429	5.7434846064	1.2789875021
C29	6.4166986046	-1.3830023498	0.8135859903
C30	6.3340997716	-0.4875752584	1.9306166738
C31	5.3776314508	0.5627133436	1.9462334915
C32	5.4883399525	1.5351614633	2.9833117972
C33	6.425329264	1.4200084455	3.9995564909
C34	7.3274110186	0.3499855851	3.9953492341
C35	7.2900256767	-0.5724497691	2.958111638
C36	4.5774948973	3.7833060202	3.3898219077
O37	2.6712587599	3.4390888088	1.3036530402
O38	-4.4561355155	-0.720660866	1.0341649209
N39	-5.5331888856	1.4932811686	-0.1358565891
N40	-4.589740739	-2.5967011811	2.8200816358
C41	-2.302474733	-6.9902243211	1.8716907662
C42	-3.1117088682	-7.1768954751	3.0122108999
C43	-3.8274924752	-6.1164588953	3.5262925131
C44	-3.734434866	-4.8270798668	2.9455399995
C45	-2.8483369695	-4.6121909108	1.8389533578
C46	-2.1871891899	-5.743565885	1.2790347766
C47	-6.4168731596	1.3829781519	0.8135636707
C48	-6.3341857198	0.487525355	1.9305591409
C49	-5.3776753785	-0.5627355123	1.9461065392
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C51	-6.4253314112	-1.4201240337	3.999424114
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C54	-4.5775635414	-3.7833779212	3.3896901844
O55	-2.6714386813	-3.4392157026	1.3035140523
O56	0.6831138965	-4.3128984264	-1.1868909968
N57	-1.4335064632	-5.4518824322	0.1308651362
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C60	7.2544690541	-3.2228024974	-2.9965681685
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C66	-0.4901021664	-6.2733589833	-1.9539542602
C67	0.5544147208	-5.3085131736	-2.0103623152
C68	1.565813648	-5.4953741433	-3.0062729846
C69	1.4645101678	-6.4782143382	-3.9776517078
C70	0.3765884851	-7.360525512	-3.9591230713
C71	-0.5638027541	-7.2711389177	-2.9407280429
C72	3.8421436669	-4.6428610926	-3.3841491592
O73	3.5296881526	-2.7699624267	-1.2525207301
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O75	-1.6213432595	-1.0801882893	0.385642283
O76	0.102451162	-3.2548422192	1.5438253335
O77	-1.6521811932	-2.9359092377	-1.4984497247
U78	2.9874762259	-0.723532078	-0.0367067814
O79	0.9431560047	-1.7090675747	-0.424595146
O80	3.2192214793	-0.0027735102	-1.6344832728
O81	2.92803972	-1.5080949562	1.5476680502
U82	-2.9874391383	0.7236049135	-0.0368375799
O83	-0.9430825537	1.7091454713	-0.4246000575
O84	-3.2190996624	0.0028450396	-1.6346257225
O85	-2.9280740702	1.5081545692	1.5475484752
C86	-7.0718362434	2.3964904521	-1.8654529007
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C88	-7.2545114149	3.2229898103	-2.9966042658
C89	-6.1899592215	3.9332302959	-3.5041520552
H90	-6.3218675928	4.5878276464	-4.3635746782
H91	7.3296312218	-1.9937096797	0.7624346552
H92	8.0123122735	-1.3863605558	2.9293019082
H93	8.0563074288	0.2527322489	4.7925925113
H94	6.4609534631	2.1525612792	4.8028868175
H95	8.2331567498	-3.290233198	-3.4596544748
H96	6.3219536087	-4.5876457161	-4.3636245844
H97	7.9096902918	-1.8209739759	-1.4784868096
H98	4.0346446746	-5.3581115807	-4.1839199074
H99	2.5092582499	-3.9244835881	-2.0641284742
H100	0.2877623556	-8.1251637478	-4.7233057839
H101	2.2223054191	-6.5728480672	-4.7521104401
H102	-1.9970001399	-7.2347249678	-0.7638567302
H103	-1.3775924651	-7.9922336404	-2.8892622906
H104	-3.1699874904	-8.1562025853	3.4754234903
H105	-1.7350830716	-7.8274331484	1.471610563

H106	-4.4794136832	-6.25571614	4.3866556184
H107	-5.2950140034	-3.9847677291	4.1853840141
H108	-6.4609261973	-2.1527093431	4.8027261323
H109	-8.0563038793	-0.2529043811	4.7925543255
H110	-8.0123865072	1.3862501533	2.9293180396
H111	-3.8965888735	-2.4584496525	2.0467808646
H112	-7.3298137207	1.9936774842	0.7624767611
H113	-8.2331713638	3.2904731178	-3.4597416472
H114	-4.034605349	5.3581840902	-4.1837978041
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H117	3.1701147232	8.1561803213	3.4752818498
H118	1.7352714106	7.8273900228	1.4714320184
H119	3.8965866458	2.4583671243	2.0469116005
H120	1.9971690409	7.2346405467	-0.7639088354
H121	-0.2876897201	8.1251232635	-4.7233324388
H122	1.3777325952	7.9921639315	-2.8893498802
H123	-2.2222828268	6.5728668832	-4.7520449077
H124	-2.5092199616	3.9245303348	-2.0640306511

References

1 Bruker. Bruker AXS Inc.: Madison, Wisconsin, USA. 2012.
2 G. M. Sheldrick, *Acta Crystallogr. A*, 2015, **71**, 3–8.
3 G. M. Sheldrick, *Acta Crystallogr. C*, 2015, **71**, 3–8.
4 H. Puschmann, *J. Appl. Crystallogr.*, 2009, **42**, 330–341.
5 A. L. Spek, *Acta Crystallogr. C*, 2015, **71**, 9–18.
6 J. Hu, E. A. Adogla, Y. Ju, D. Fan and Q. Wang, *Chem. Commun.*, 2012, **48**, 11256–11258.
(9) L.-L. Yang, X.-H. Kong, Z.-L. Wu, Z.-L. Lin, L.-F. Liao and C.-M. Nie, *Appl. Organomet. Chem*., 2018, ***32***, e4387.
(10) S.-X. Hu, J.-J. Liu, J. K. Gibson and J. Li, *Inorg. Chem.*, 2018, **57**, 2899-2907.
(11) P. Di Pietro and A. Kerridge, *Phys. Chem. Chem. Phys.*, 2017, **19**, 7546-7559.
(12) (a) J.-D. Chai and M. Head-Gordon, *Phys. Chem. Chem. Phys.*, 2008, **10**, 6615-6620. (b) J.-D. Chai and M. Head-Gordon, *J. Chem. Phys.*, 2008, ***128***, 084106.
(13) Y. Zhao and D. G. Truhlar, *Theor. Chem. Acc*., 2008, ***120***, 215-241.
(14) M. M. Francl, W. J. Pietro, W. J. Hehre, J. S. Binkley, D. J. DeFrees, J. A. Pople and M. S. Gordon, *J. Chem. Phys.*, 1982, ***77***, 3654-3665.
(15) A. Moritz and M. Dolg, *Theor. Chem. Acc.*, 2008, ***121***, 297.
(16) M. Dolg and X. Cao, *J. Phys. Chem. A*, 2009, ***113***, 12573.
(17) K. A. Peterson, D. Figgen, M. Dolg and H. Stoll, *J. Chem. Phys.*, 2007, ***126***, 124101.
(18) http://www.tc.uni-koeln.de/PP/index.en.html (accessed on April 2018).
(19) M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li,

H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, Gaussian 09 Revision A.1, Gaussian Inc., Wallingford, CT, 2009.

(20) D. Wang, W. F. van Gunsteren, and Z. Chai, *Chem. Soc. Rev.*, 2012, ***41***, 5836–5865.