

Supplementary Information for:

Conversion of Trivalent Uranium Anilido to Tetravalent Uranium Imido Species via Oxidative Deprotonation

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Table of Contents:

General Considerations.....	S3
Synthesis of potassium tert-butyl(dimethylsilyl)amide (KTSA).....	S4
Synthesis of Tp^*_2U ptol-anilido (2-ptol).....	S4
Synthesis of Tp^*_2U terpy-anilido (2-terpy).....	S5
Synthesis of Tp^*_2U terpy-imido (3-terpy).....	S6
Synthesis of Tp^*_2U ptol-imido (3-ptol).....	S6
Figure S1. ^1H NMR spectrum (C_6D_6, 25°C) of 2-ptol	S7
Figure S2. ^{11}B NMR spectrum (C_6D_6, 25°C) of 2-ptol	S7
Figure S3. IR spectrum (KBr pellet) of 2-ptol	S8
Figure S4. ^1H NMR spectrum (C_6D_6, 25°C) of 2-terpy	S8
Figure S5. ^{11}B spectrum (C_6D_6, 25°C) of 2-terpy	S9
Figure S6. IR spectrum (salt plate) of 2-terpy	S9
Figure S7. ^1H NMR spectrum (C_6D_6, 25°C) of 3-terpy	S10
Figure S8. ^{11}B NMR spectrum (C_6D_6, 25°C) of 3-terpy	S10
Figure S9. IR spectrum (salt plate) of 3-terpy	S11
Table S1. Crystallographic details for 2-ptol	S13
Table S2. Crystallographic details for 2-terpy.....	S14
Table S3. Crystallographic details for 3-terpy	S16
References.....	S18

General Considerations. All air- and moisture-sensitive manipulations were performed using standard Schlenk techniques or using an MBraun inert atmosphere drybox with an atmosphere of purified nitrogen. The MBraun drybox was equipped with a cold well used for freezing samples in liquid nitrogen, making dry ice and acetone baths, as well as two $-35\text{ }^{\circ}\text{C}$ freezers for cooling samples and crystallizing compounds. Solvents for sensitive manipulations were dried and deoxygenated using literature procedures with a Seca solvent purification system.¹ Benzene- d_6 was purchased from Cambridge Isotope Laboratories, dried with molecular sieves and sodium, and degassed by three freeze–pump–thaw cycles. KTp*² and Tp*₂UBn (**1-Bn**)³ were synthesized using literature procedures. 4-(2,6-di(pyridin-2-yl)pyridin-4-yl)benzenamine (terpy-aniline) was prepared using a literature procedure.⁴ Potassium tert-butyl(dimethylsilyl)amide (KTSA) was prepared using a modified literature procedure.⁵ *tert*-butyl(dimethylsilyl)amine (HTSA) was prepared using a literature procedure.⁵

¹H NMR spectra were recorded on a Varian Inova 300 spectrometer operating at a frequency of 300 MHz. All chemical shifts are reported relative to the peak for SiMe₄, using ¹H residual chemical shifts of the solvent as a secondary standard. ¹¹B NMR spectra were recorded on a Varian Inova 300 spectrometer operating at a frequency of 96.24 MHz. ¹¹B chemical shifts are reported relative to the peak for BF₃·Et₂O. Spectra for paramagnetic molecules were obtained using an acquisition time of 0.5 s; thus, the peak widths reported have an error of ± 2 Hz. For paramagnetic molecules, the ¹H NMR data are reported with the chemical shift, followed by the peak width at half height in Hertz, the integration value, and, where possible, the peak assignment. Elemental analyses were performed by Midwest Microlab, Indianapolis, IN. Solid state infrared spectra were recorded using a Thermo Nicolet 6700 spectrophotometer; samples were made by using salt plates or by crushing the solids, mixing with dry KBr, and pressing into

a pellet. Electronic absorption spectroscopic measurements were recorded at 294 K in sealed 1 cm quartz cuvettes with a Cary 6000i UV–vis-NIR spectrophotometer.

Single crystals suitable for X-ray diffraction were coated with poly(isobutylene) oil in a glovebox and quickly transferred to the goniometer head of the specified instrument. Crystals of **2-terpy** were transferred to the goniometer head of a Bruker AXS D8 Quest CMOS diffractometer and examined with Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$). Crystals of **3-terpy** and **2-ptol** were transferred to the goniometer head of a Bruker AXS D8 Quest CMOS diffractometer examined with Cu K α radiation ($\lambda = 1.54184 \text{ \AA}$).

Synthesis of potassium tert-butyl(dimethylsilyl)amide (KTSA). A 20-mL scintillation vial was charged with benzylpotassium (1.09 g, 8.37 mmol), a stir bar, and 10 mL diethyl ether to make a suspension. While stirring, *tert*-butyl(dimethylsilyl)amine (HTSA) (1.00 g, 7.62 mmol) was added dropwise to this solution until all the suspended benzyl potassium was consumed as indicated by disappearance of the intense orange color. This orange suspension gradually changed to a pale-yellow solution. After 30 minutes of stirring, the solution was dried *in vacuo* leaving a pale-yellow powder (1.168 g, 91 %) assigned as potassium *tert*-butyl(dimethylsilyl)amide, KTSA. The solid was washed with pentane and dried to further remove toluene that was formed during the reaction. ^1H NMR (C_6D_6 , 25 °C): δ 0.32 (dd, 6.2H, SiH(CH_3)₂), 1.28 (s, 10.1H, C(CH_3)₃), 4.84 (sept, 1H, SiH). IR (KBr, cm^{-1}): 2946 m, 2853 m, 1929 s (ν_{SiH}), 1861 m, 1344 m, 1240 m, 1211 m, 1190 m, 1060 m, 939 m, 877 m, 823 m, 800 m, 757 m, 742 m.

Synthesis of Tp*₂U ptol-anilido (2-ptol). A 20-mL scintillation vial was charged with Tp*₂UBn (**1-Bn**) (0.025 g, 0.027 mmol), 5 mL of THF, and a stir bar. This green solution was cooled to -35° C. To this solution, 1 equivalent of *p*-toluidine (0.003 g, 0.027 mmol) was added as a solid,

and the reaction mixture was stirred for 1 hour at room temperature, turning the solution darker green. The volatiles were removed in vacuo to afford a blue-green powder assigned as Tp^*_2U ptol-anilido (0.023 g, 0.025 mmol, 90% yield). Blue-green block crystals of Tp^*_2U ptol-anilido suitable for X-ray diffraction were grown from a concentrated ether solution at -35°C . Elemental analysis of $\text{C}_{37}\text{H}_{52}\text{B}_2\text{N}_{13}\text{U}$, Calculated, C, 47.35; H, 5.58; N, 19.40. Found, C, 46.62; H, 5.48; N, 18.38. Repeated elemental analysis measurements always yield low carbon/nitrogen percentages for **2-ptol**. ^1H NMR (C_6D_6 , 25°C): δ = 77.88 (s, 1H, -NH), 35.22 (s 2H, *o*-CH), 18.88 (s, 2H, *m*-CH), 9.64 (s, 3H, *p*-CH₃), 2.71 (s, 2H, $\text{Tp}^*\text{-BH}$), 0.17 (s, 6H, $\text{Tp}^*\text{-CH}$), -2.42 (s, 18H, $\text{Tp}^*\text{-CH}_3$). The second set of methyl groups on the Tp^* ligand is not observed due to the paramagnetic uranium center. ^{11}B NMR (C_6D_6 , 25°C): δ -11.83. IR (KBr): $\nu_{\text{N-H}} = 3359\text{ cm}^{-1}$; $\nu_{\text{B-H}} = 2552, 2527\text{ cm}^{-1}$.

Synthesis of Tp^*_2U terpy-anilido (2-terpy). A 20-mL scintillation vial was charged with Tp^*_2UBn (**1-Bn**) (0.024 g, 0.027 mmol), 5 mL of toluene, and a stir bar. This green solution was cooled to -35°C . To this solution, 1 equivalent of terpy-aniline (0.009 g, 0.027 mmol) was added as a solid, and the reaction mixture was stirred for 1 hour at room temperature, turning the solution darker green. The volatiles were removed in vacuo, and the residue was taken up in pentane and filtered to remove impurities. The remaining solid was extracted with THF. Volatiles were removed in vacuo to afford a yellow-green powder assigned as Tp^*_2U terpy-anilido (0.03 g, 0.026 mmol, 91% yield). Yellow-green block crystals of Tp^*_2U terpy-anilido suitable for X-ray diffraction were grown from a concentrated ether solution at -35°C . Elemental analysis of $\text{C}_{51}\text{H}_{59}\text{B}_2\text{N}_{16}\text{U}$, Calculated C, 53.00; H, 5.15; N, 19.39, Found, C, 52.91; H, 5.55; N, 17.84. Repeated elemental analysis measurements always yield low nitrogen percentages for **2-terpy**. ^1H NMR (C_6D_6 , 25°C): δ 65.32 (s, 1H, -NH), 33.75 (d, 2H, *o*-Ph-CH), 18.98 (d, 2H, *m*-

Ph-CH), 14.32 (s, 2H, tpy), 10.26 (d, 2H, tpy), 9.73 (dd, 2H, tpy), 8.20 (dd, 2H, tpy), 7.55 (d, 2H, tpy), 2.69 (s, 2H, Tp*-BH), -1.83 (s, 18H, Tp*-CH₃). The second set of methyl groups on the Tp* ligand and the CH on the pyrazole is not observed due to the paramagnetic uranium center. ¹¹B NMR (C₆D₆, 25 °C): δ -8.62. IR (salt plate): ν_{N-H} = 3334 cm⁻¹; ν_{B-H} = 2556, 2526 cm⁻¹.

Synthesis of Tp*₂U terpy-imido (3-terpy). A 20-mL scintillation vial was charged with **2-terpy** (0.100 g, 0.087 mmol), 5 mL of tetrahydrofuran, and a stir bar. This yellow-green solution was cooled to -78° C. To this solution, 0.5 equivalent of I₂ (0.011 g, 0.043 mmol) was added as a solid, immediately turning the reaction mixture red. This mixture was stirred for 15 minutes at -78° C. After this time, 1 equivalent of KTSA (0.015 g, 0.087 mmol) was added as a solid, and the solution was stirred for 1 h at -78° C. Next, the solution was filtered and volatiles were removed in vacuo to afford a dark red powder that was assigned as **3-terpy** (0.096 g, 0.083 mmol, 96% yield). Red block crystals of Tp*₂U terpy-imido suitable for X-ray diffraction were grown from a concentrated ether solution at -35° C. Elemental analysis of C₅₁H₅₈B₂N₁₆U, Calculated, C, 53.05; H, 5.06; N, 19.41. Found, C, 47.18; H, 4.76; N, 16.83. These results are consistent with incomplete combustion of **3-terpy**, which is common for carbon-rich compounds. ¹H NMR (C₆D₆, 25 °C): δ 79.14 (d, 2H, *o*-Ph-CH), 54.73 (d, 2H, *m*-Ph-CH), 23.81 (s, 2H, tpy), 14.42 (d, 2H, tpy), 12.87 (dd, 2H, tpy), 10.66 (dd, 2H, tpy), 9.86 (s, 2H, tpy), 5.76 (s, 6H, Tp*-CH), 2.69 (s, 18H, Tp*-CH₃), -6.86 (s, 18H, Tp*-CH₃), -21.34 (s, 2H, Tp*-BH). ¹¹B NMR (C₆D₆, 25° C): δ -66.7. IR (salt plate): ν_{B-H} = 2556, 2522 cm⁻¹

Synthesis of Tp*₂U ptol-imido (3-ptol). A 20-mL scintillation vial was charged with **2-ptol** (0.100 g, 0.107 mmol), 5 mL of tetrahydrofuran, and a stir bar. This yellow-green solution was cooled to -78° C. To this solution, 0.5 equivalent of I₂ (0.014 g, 0.053 mmol) was added as a solid, immediately turning the reaction mixture red. This mixture was stirred for 15 minutes at -

78° C. After this time, 1 equivalent of KTSA (0.018 g, 0.107 mmol) was added as a solid, and the solution was stirred for 1 h at -78° C. Next, the solution was filtered and volatiles were removed in vacuo to afford a dark red powder that was assigned as **3-ptol**. Synthesis was confirmed by comparison to literature values.⁶

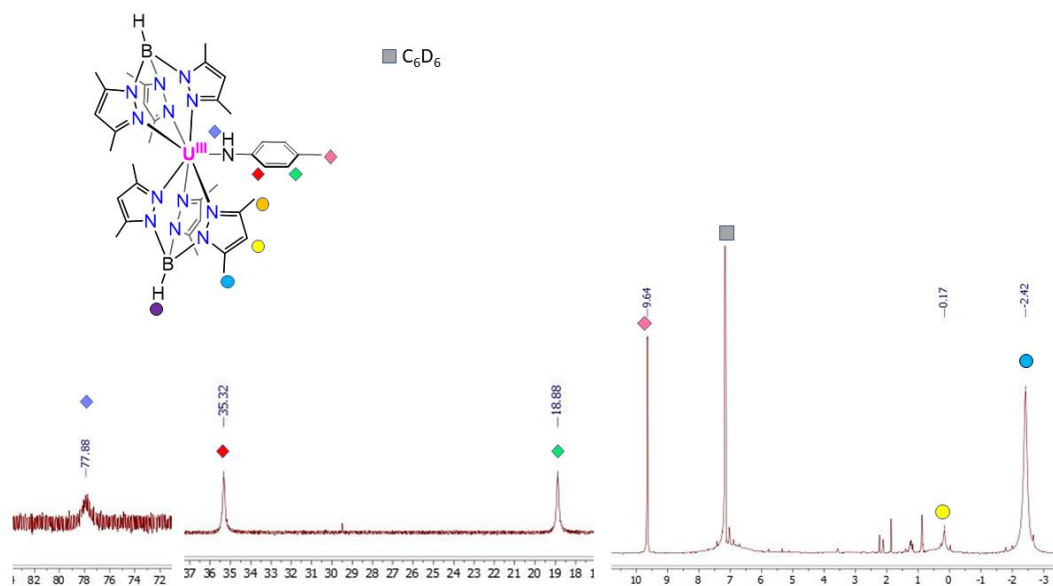


Figure S1. ¹H NMR spectrum (C₆D₆, 25°C) of **2-ptol**

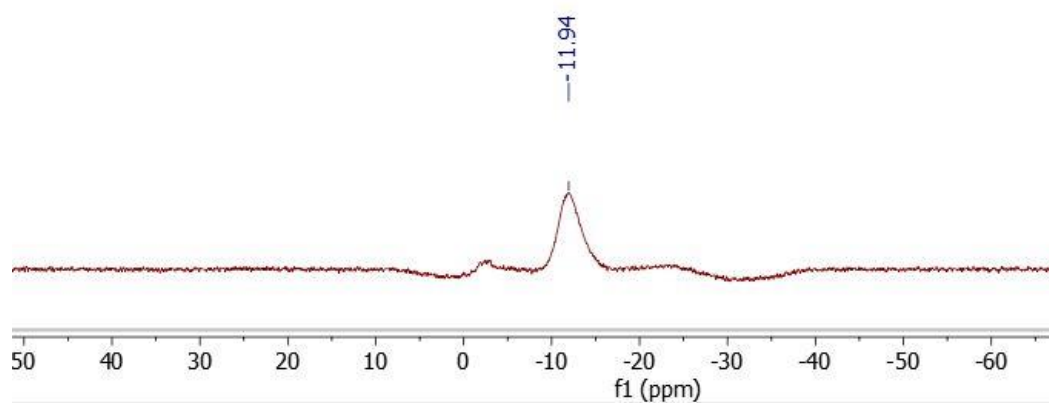


Figure S2. ¹¹B NMR spectrum (C₆D₆, 25°C) of **2-ptol**

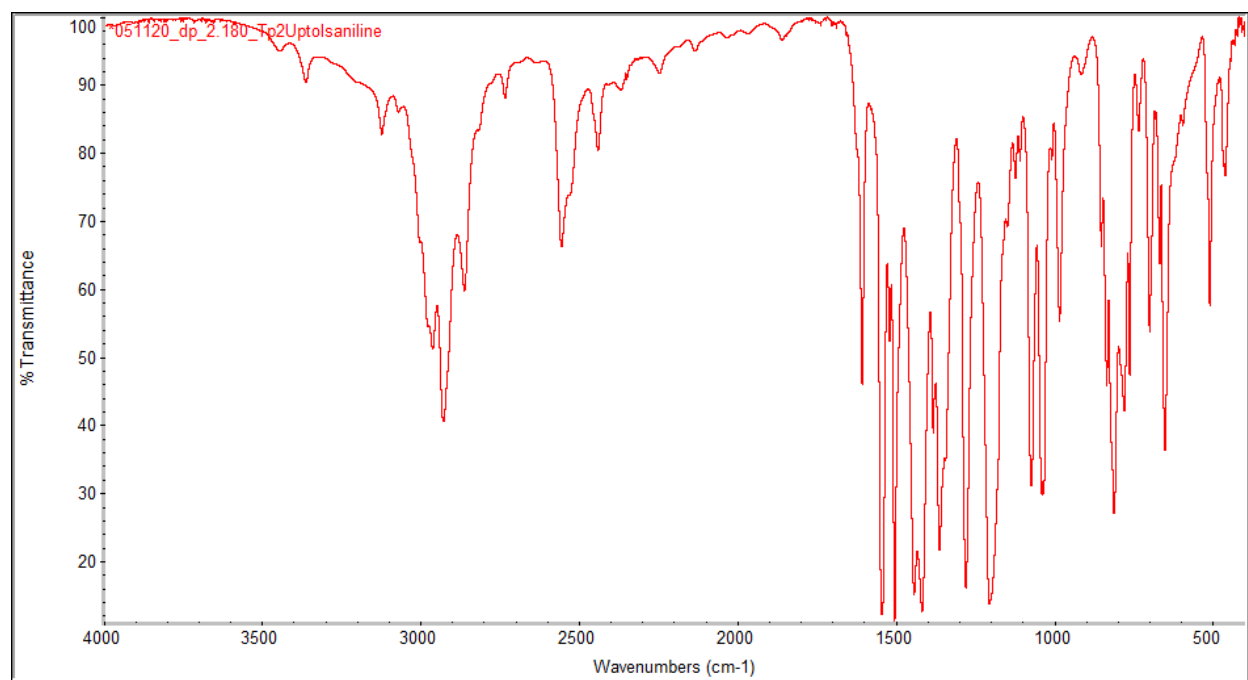


Figure S3. IR spectrum (KBr pellet) of **2-ptol**

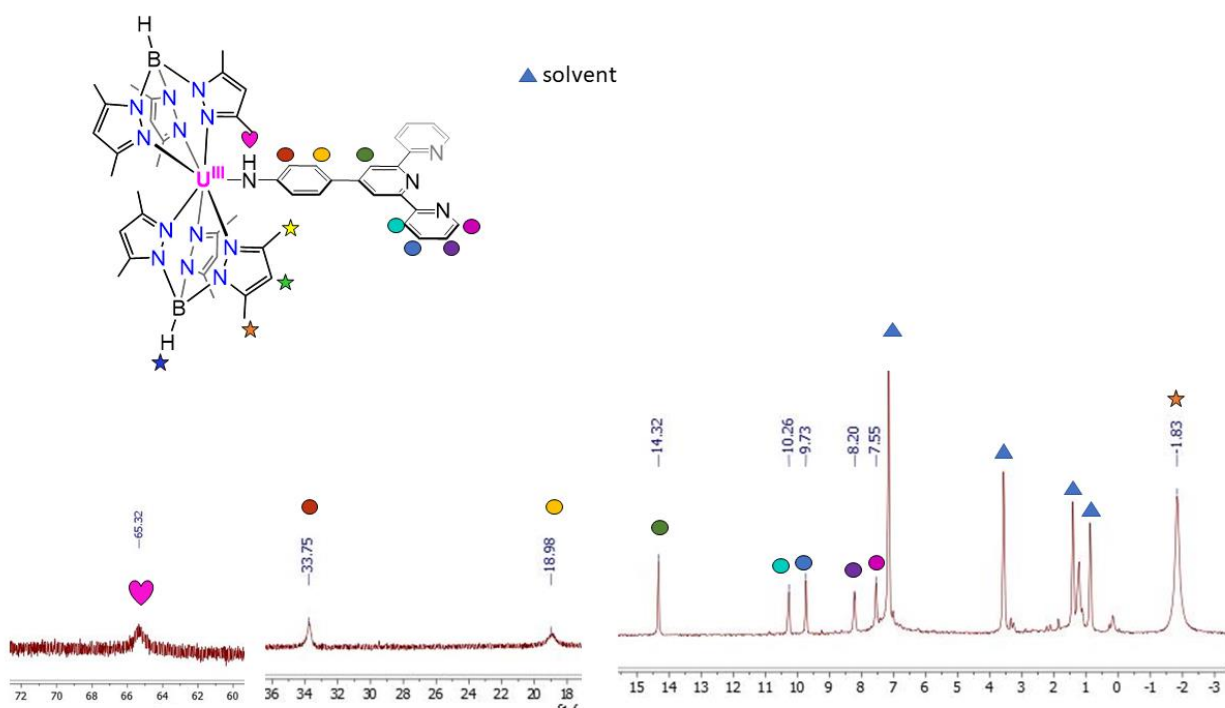


Figure S4. ^1H NMR spectrum (C_6D_6 , 25°C) of **2-terpy**

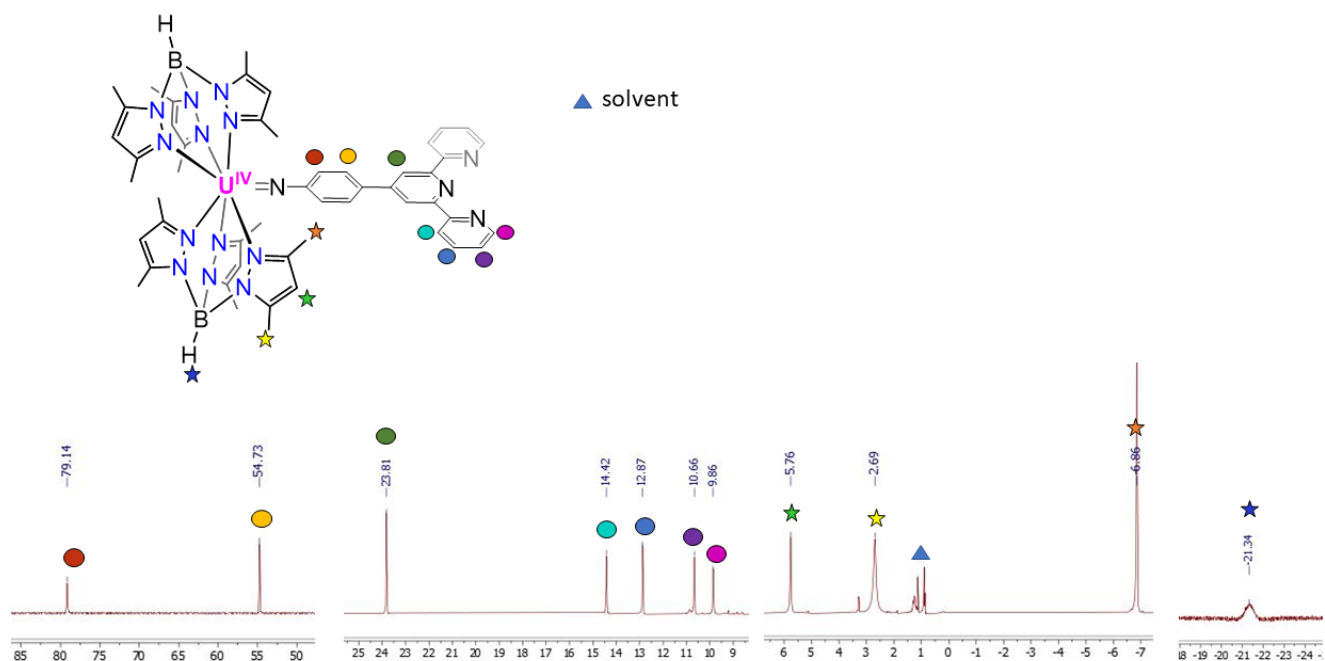


Figure S7. ^1H NMR spectrum (CDCl_3 , 25°C) of **3-terpy**

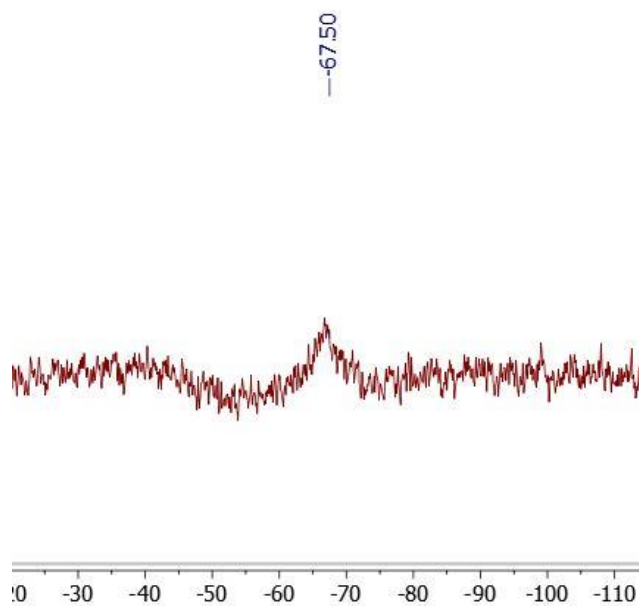


Figure S8. ^{11}B NMR spectrum (CDCl_3 , 25°C) of **3-terpy**

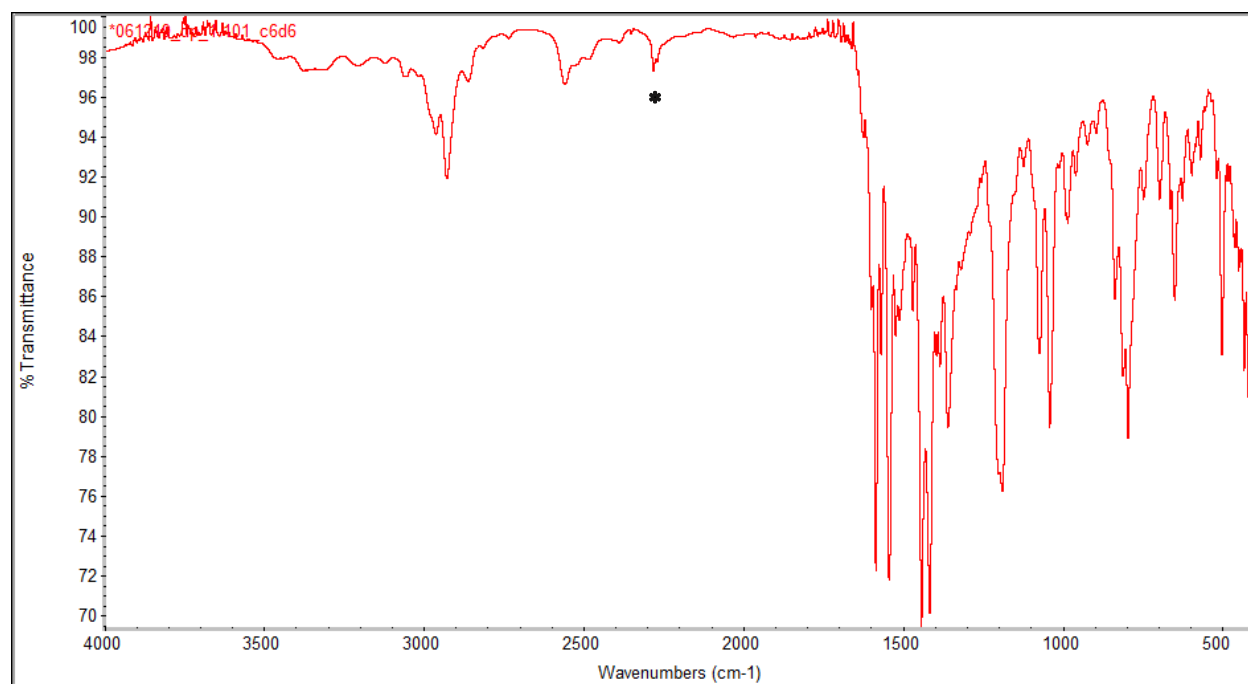


Figure S9. IR spectrum (salt plate) of **3-terpy** (*C₆D₆)

Data were collected at 150 K and reflections were indexed and processed, and the files scaled and corrected for absorption using APEX3⁷ and SADABS⁸. The space groups were assigned, and the structures were solved by direct methods using XPREP within the SHELXTL suite of programs⁹ and refined by full matrix least squares against F^2 with all reflections using Shelxl2018¹⁰ using the graphical interface Shelxle¹¹. H atoms attached to carbon and boron were positioned geometrically and constrained to ride on their parent atoms. C-H bond distances were constrained to 0.95 Å for aromatic and alkene C-H, and to 0.99 and 0.98 Å for aliphatic CH₂ and CH₃ moieties, respectively. B-H bond distances were constrained to 1.00 Å, and N-H distances to 0.88 Å. Methyl CH₃ were allowed to rotate but not to tip to best fit the experimental electron density. $U_{\text{iso}}(\text{H})$ values were set to a multiple of $U_{\text{eq}}(\text{C})$ with 1.5 for CH₃ and 1.2 for C-H, CH₂ and B-H units, respectively.

See Tables S1 to S3 and the cif data for additional data collection and refinement details, including description of disorder (where present). Complete crystallographic data, in CIF format, have been deposited with the Cambridge Crystallographic Data Centre. CCDC 1998751, 1998752 and 1998754 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Compound: **2-ptol**

Local Name: sf128

CCDC number: 1998751

Table S1. Crystallographic details for Tp*₂U ptol-anilido

Crystal data	
Chemical formula	C ₃₇ H ₅₂ B ₂ N ₁₃ U
<i>M_r</i>	938.56
Crystal system, space group	Triclinic, <i>P</i> $\bar{1}$
Temperature (K)	150
<i>a</i> , <i>b</i> , <i>c</i> (Å)	11.4262 (4), 12.8044 (4), 14.5233 (5)
α , β , γ (°)	85.778 (1), 81.849 (1), 74.456 (1)
<i>V</i> (Å ³)	2025.03 (12)
<i>Z</i>	2
Radiation type	Cu <i>K</i> α
μ (mm ⁻¹)	11.62
Crystal size (mm)	0.24 × 0.20 × 0.08
Data collection	
Diffractometer	Bruker AXS D8 Quest CMOS diffractometer
Absorption correction	Multi-scan, (SADABS 2016/2)
<i>T_{min}</i> , <i>T_{max}</i>	0.036, 0.179
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	47365, 8698, 8128
<i>R_{int}</i>	0.082
(sin θ/λ) _{max} (Å ⁻¹)	0.640
Refinement	
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.035, 0.092, 1.10
No. of reflections	8698
No. of parameters	491
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ (e Å ⁻³)	2.24, -0.94

Computer programs: Apex3 v2018.1-0 (Bruker, 2018), SADABS 2016/2,⁸ SAINT V8.38A

(Bruker, 2016), *SHELXS*97,⁹ *SHELXL*2018/3,¹⁰ *SHELXL*E Rev946.¹¹

Compound: **2-terpy**

Local Name: dp_1_42_ether

CCDC number: 1998754

Table S2. Crystallographic details for Tp*₂U terpy-anilido

Crystal data	
Chemical formula	C ₅₅ H ₆₉ B ₂ N ₁₆ O _U
<i>M_r</i>	1229.91
Crystal system, space group	Triclinic, <i>P</i> $\bar{1}$
Temperature (K)	150
<i>a</i> , <i>b</i> , <i>c</i> (Å)	11.4205 (5), 14.9959 (6), 17.6098 (8)
α , β , γ (°)	103.614 (2), 102.038 (2), 102.242 (2)
<i>V</i> (Å ³)	2756.4 (2)
<i>Z</i>	2
Radiation type	Mo <i>K</i> α
μ (mm ⁻¹)	3.00
Crystal size (mm)	0.24 × 0.20 × 0.08
Data collection	
Diffractometer	Bruker AXS D8 Quest CMOS diffractometer
Absorption correction	Multi-scan, (<i>SADABS</i> 2016/2)
<i>T_{min}</i> , <i>T_{max}</i>	0.390, 0.494
No. of measured, independent and observed [<i>I</i> > 2 σ (<i>I</i>)] reflections	52362, 13439, 12189
<i>R_{int}</i>	0.046
(<i>sin</i> θ / λ) _{max} (Å ⁻¹)	0.667
Refinement	
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.026, 0.064, 1.16
No. of reflections	13439
No. of parameters	788
No. of restraints	328
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ (e Å ⁻³)	3.43, -1.58

Refinement notes:

A diethyl ether molecule is disordered over three positions. The three disordered moieties were restrained to have similar geometries. In addition C-O distances and C-C distances were restrained to target values of 1.40(2) Å and 1.544(20) Å, respectively. *U*^{ij} components of ADPs for disordered atoms closer to each other than 2.0 Å were restrained to be similar. Subject to

these conditions the occupancy ratio refined to 0.418(3) (ether of O1), 0.127(3) (ether of O1A), and 0.455(3) (ether of O1B).

Computer programs: Apex3 v2018.1-0 (Bruker, 2018), SADABS 2016/2,⁸ SAINT V8.38A (Bruker, 2016), *SHELXS*97,⁹ *SHELXL*2018/3,¹⁰ *SHELXL*E Rev946.¹¹

Compound: **3-terpy**

Local Name: dp_101ether

CCDC number: 1998752

Table S3. Crystallographic details for Tp*₂U terpy-imido

Crystal data	
Chemical formula	C ₅₁ H ₅₈ B ₂ N ₁₆ U·C ₄ H ₁₀ O
<i>M_r</i>	1228.90
Crystal system, space group	Triclinic, <i>P</i> $\bar{1}$
Temperature (K)	150
<i>a</i> , <i>b</i> , <i>c</i> (Å)	10.4191 (4), 15.1878 (5), 19.7054 (7)
α , β , γ (°)	76.272 (2), 74.904 (2), 84.397 (1)
<i>V</i> (Å ³)	2922.50 (18)
<i>Z</i>	2
Radiation type	Cu <i>K</i> α
μ (mm ⁻¹)	8.22
Crystal size (mm)	0.24 × 0.20 × 0.08
Data collection	
Diffractometer	Bruker AXS D8 Quest CMOS diffractometer
Absorption correction	Multi-scan, (SADABS 2016/2)
<i>T_{min}</i> , <i>T_{max}</i>	0.046, 0.179
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	28956, 12136, 10684
<i>R_{int}</i>	0.067
(sin θ/λ) _{max} (Å ⁻¹)	0.642
Refinement	
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.056, 0.165, 1.07
No. of reflections	12136
No. of parameters	737
No. of restraints	129
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ (e Å ⁻³)	1.87, -2.18

Refinement notes:

A diethyl ether molecule is disordered over two positions. The two disordered moieties were restrained to have similar geometries, and the C-O distances, C-C distances, and 1,3-distances were restrained to 1.43(2) Å, 1.54(2) Å, and 2.55(2) Å, respectively. *U*^{ij} components of ADPs for disordered atoms closer to each other than 2.0 Å were restrained to be similar. Subject to these conditions the occupancy ratio refined to 0.454(18) to 0.546(18).

Computer programs: Apex3 v2018.1-0 (Bruker, 2018), SADABS 2016/2,⁸ SAINT
V8.38A (Bruker, 2016), *SHELXS*97,⁹ *SHELXL*2018/3,¹⁰ *SHELXL*E Rev946.¹¹

References:

1. Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J., Safe and convenient procedure for solvent purification. *Organometallics* **1996**, *15* (5), 1518-1520.
2. Woollins, J. D., *Inorganic Experiments*. 3rd, rev. ed. ed.; Wiley-VCH: Weinheim, 2010.
3. Matson, E. M.; Forrest, W. P.; Fanwick, P. E.; Bart, S. C., Functionalization of carbon dioxide and carbon disulfide using a stable uranium(III) alkyl complex. *J. Am. Chem. Soc.* **2011**, *133* (13), 4948-4954.
4. Trigo-López, M.; Muñoz, A.; Ibeas, S.; Serna, F.; García, F. C.; García, J. M., Colorimetric detection and determination of Fe(III), Co(II), Cu(II) and Sn(II) in aqueous media by acrylic polymers with pendant terpyridine motifs. *Sensors & Actuators: B. Chemical* **2016**, *226*, 118-126.
5. Pattenaude, S. A.; Coughlin, E. J.; Collins, T. S.; Zeller, M.; Bart, S. C., Expanding the Library of Uranyl Amide Derivatives: New Complexes Featuring the tert-Butyldimethylsilylamide Ligand. *Inorganic Chemistry* **2018**, *57* (8), 4543-4549.
6. Tatebe, C. J.; Zeller, M.; Bart, S. C., $2\pi+2\pi$ Cycloaddition of Isocyanates to Uranium(IV) Imido Complexes for the Synthesis of U(IV) κ -Ureato Compounds. *Inorg. Chem.* **2017**, *56* (4), 1956-1965.
7. Bruker (2018). Apex3, Saint, Bruker AXS Inc.: Madison (WI), USA.
8. Krause, L., Herbst-Irmer, R., Sheldrick G. M. & Stalke D., *J. Appl. Cryst.* **2015**, *48*, 3
9. Sheldrick, G. M., A short history of SHELX. *Acta Crystallographica Section A* **2008**, *64* (1), 112-122.
10. Sheldrick, G. M., Crystal structure refinement with SHELXL. *Acta Crystallographica Section C Structural Chemistry* **2015**, *71* (1), 3-8.
11. Hübschle, C. B.; Sheldrick, G. M.; Dittrich, B., ShelXle: a Qt graphical user interface for SHELXL. *Journal of Applied Crystallography* **2011**, *44* (6), 1281-1284.