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General Considerations:

Caution! ^{237}Np represents a health risk due to its α and γ emission and its decay to the short-lived ^{233}Pa isotope ($t_{1/2} = 27.0$ days), which is a strong β and γ emitter. All studies with Np were conducted in a laboratory equipped for radioactive materials. All studies were modeled on depleted uranium prior to working with ^{237}Np .

All air- and moisture-sensitive manipulations were performed using standard Schlenk techniques or in an MBraun negative pressure argon atmosphere glovebox. The MBraun glovebox was equipped with a cold well designed for freezing samples in liquid nitrogen as well as a -35 °C freezer for cooling samples and crystallizations. Solvents for sensitive manipulations were dried and deoxygenated using literature procedures with a Seca solvent purification system.¹ Benzene- d_6 were purchased from Cambridge Isotope Laboratories, dried with molecular sieves and sodium, and degassed by six freeze-pump-thaw cycles. CDCl_3 and pyridine- d_5 were purchased from Cambridge Isotope Laboratories, dried over molecular sieves and degassed by six freeze-pump thaw cycles. Uranium tetrachloride (UCl_4) was prepared according to literature procedures.²

All chemical shifts were reported relative to the peak for SiMe_4 using ^1H (residual) chemical shifts of the solvent as a secondary standard. The 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.

Electronic absorption measurements were recorded at room temperature in toluene in sealed 1 cm short path quartz cuvettes with data collection being performed on a JASCO V-770 UV-Vis-NIR Spectrophotometer. Single crystals suitable for X-ray diffraction for all samples were coated with poly(isobutylene) oil in the glovebox and quickly transferred to the goniometer head of a Bruker Quest diffractometer with a fixed chi angle, a sealed tube fine focus X-ray tube, single crystal curved graphite incident beam monochromator, a Photon II area detector and an Oxford Cryosystems low temperature device. Examination and data collection were performed with $\text{Mo K}\alpha$ radiation ($\lambda = 0.71073$ Å) at 150 K.

Synthetic Procedures

Synthesis of $\text{NpCl}_4(\text{MeCN})_4$: A vial was charged with $\text{NpCl}_4(\text{dme})_2$ (8.0 mg). 1 mL of acetonitrile was added. The solution changed to a very light pink color. The reaction was stirred overnight. Volatiles were removed in vacuo. A very light pink, almost white, powder remained. Single crystals were grown from slow cooling of concentrated acetonitrile solution heated at 100 °C to room temperature. Quantitative yield (95%), 7.4 mg. CCDC 2335544

Synthesis of $\text{NpCl}_4\text{pyr}_4$: A vial was charged with $\text{NpCl}_4(\text{dme})_2$ (9.3 mg). 1 mL of pyridine was added. The solution changed to a yellow/brown color. The reaction stirred overnight. Volatiles were removed in vacuo. A light yellow powder remained. Single crystals were grown from slow cooling of a concentrated pyridine solution heated at 100 °C to room temperature. Quantitative yield (93%), 10.8 mg. CCDC 2335543

Synthesis of $\text{NpCl}_4(\text{tert-butylbipy})_2$: $\text{NpCl}_4(\text{dme})_2$ (8.3 mg) was dissolved in THF (~1mL). In a separate vial 4,4'-di-tert-butyl-2,2'-bipyridine was dissolved in 0.5mL of THF. The ligand was added dropwise to the $\text{NpCl}_4(\text{dme})_2$ solution. An immediate color change from light pink to a brighter, darker pink (described as "Barbie pink") was observed. After stirring overnight, the reaction was filtered through glass filter paper and volatiles were removed in vacuo. A pink powder remained. Single crystals were grown from a concentrated solution of THF layered pentane at -35 °C. Yield 81%, 11.0 mg. CCDC 2335545

Synthesis of $\text{NpCl}_4(\text{OPPh}_3)_2$: $\text{NpCl}_4(\text{dme})_2$ (9.1 mg) was dissolved in THF (~ 1 mL). In a separate vial OPPh_3 (9.1 mg) was dissolved in THF (~ 1 mL). The ligand was added dropwise to the $\text{NpCl}_4(\text{dme})_2$ solution. An immediate color change from light pink to colorless to light blue was observed. The reaction was homogeneous and stored in the freezer at -35 °C for 2 hours before volatiles removed in vacuo. After 2 hours a crystalline solid was observed at the bottom of the vial. After volatiles were removed a blue/green powder remained. Single crystals were grown from the reaction mixture at -35 °C. Yield 92%, 14.1 mg. CCDC 2345808

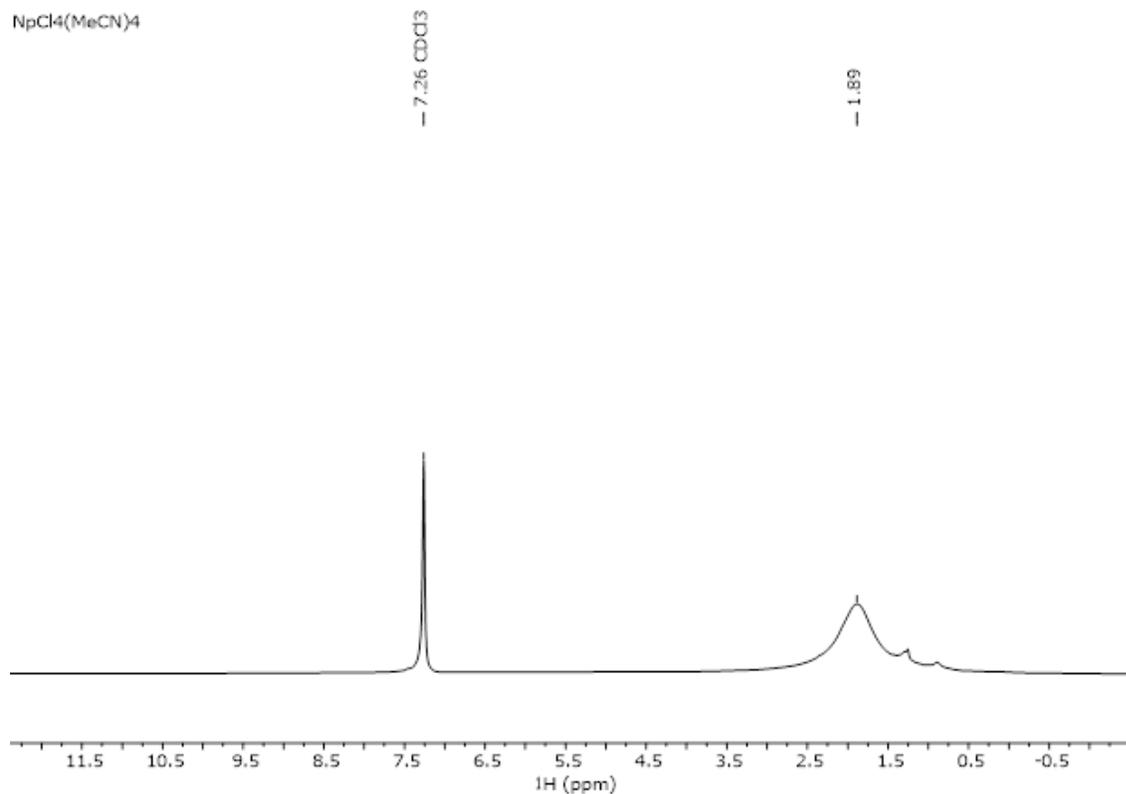


Figure S1. ¹H NMR Spectrum of **1**. (chloroform-*d*, 25 °C)

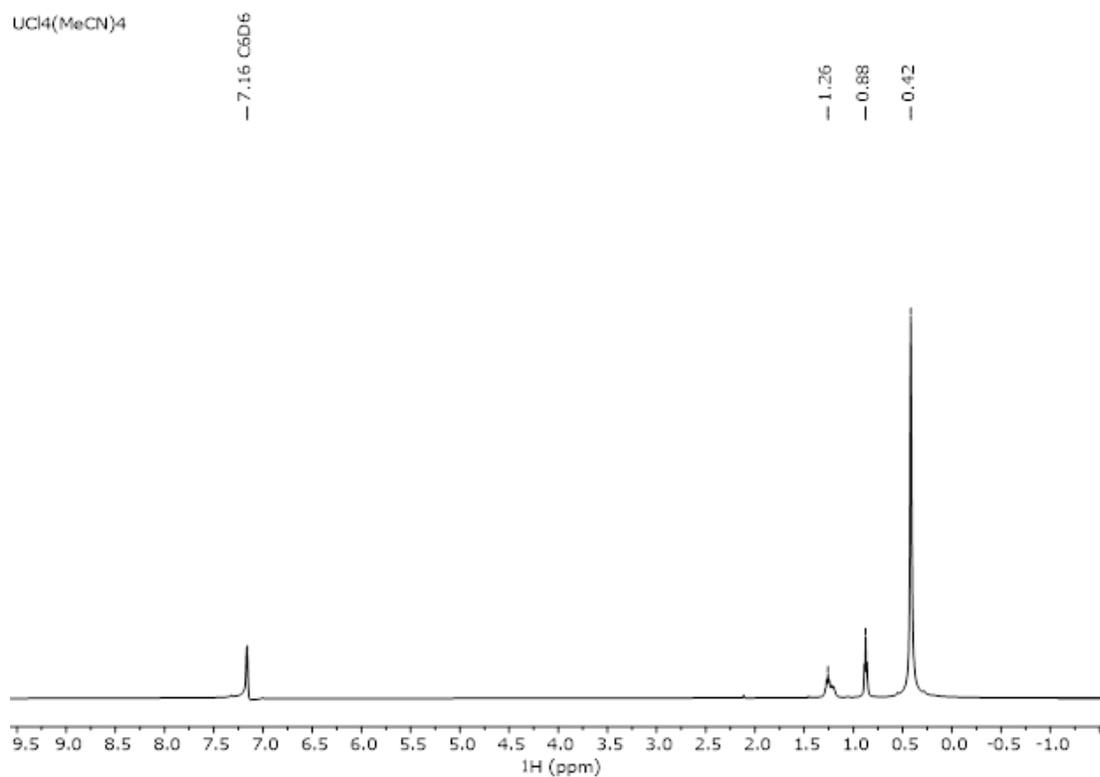


Figure S2. ¹H NMR Spectrum of **UCl₄(MeCN)₄**. (benzene-*d*₆, 25 °C)

NpCl₄(pyr)₄

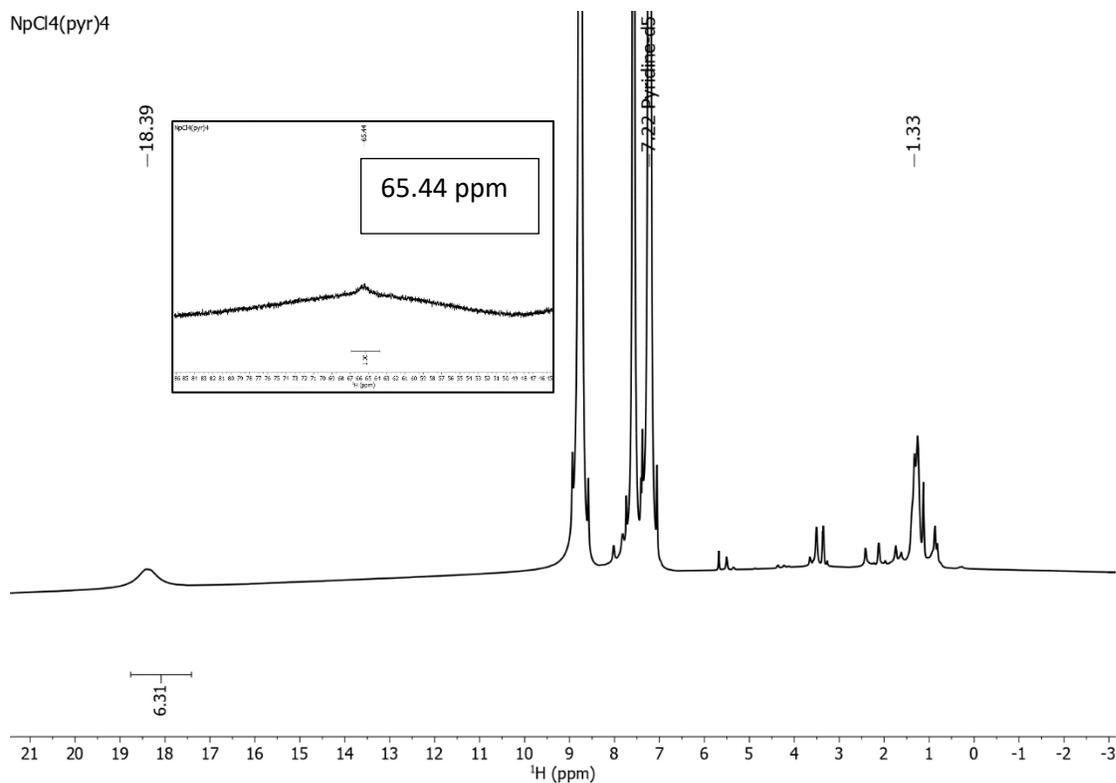


Figure S3. ¹H NMR Spectrum of **2**. (pyridine-*d*₅, 25 °C)

UCl₄(pyr)₄

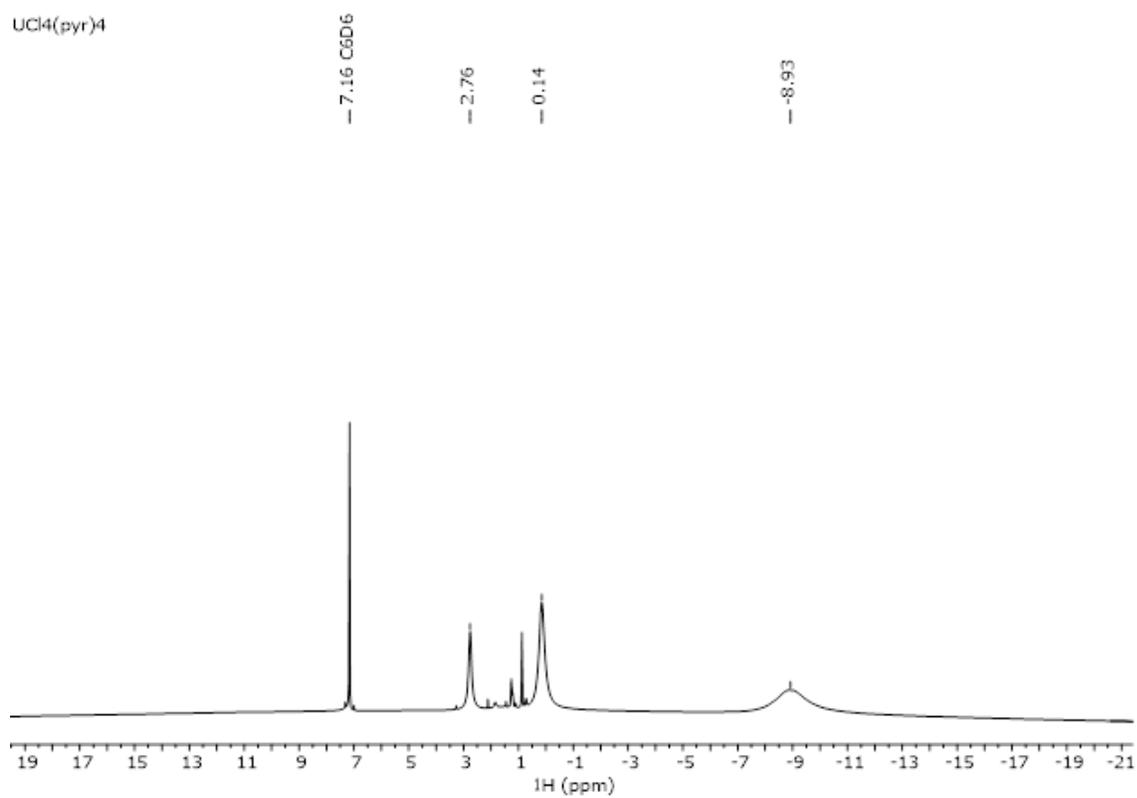


Figure S4. ¹H NMR Spectrum of **UCl₄(pyr)₄**. (benzene-*d*₆, 25 °C)

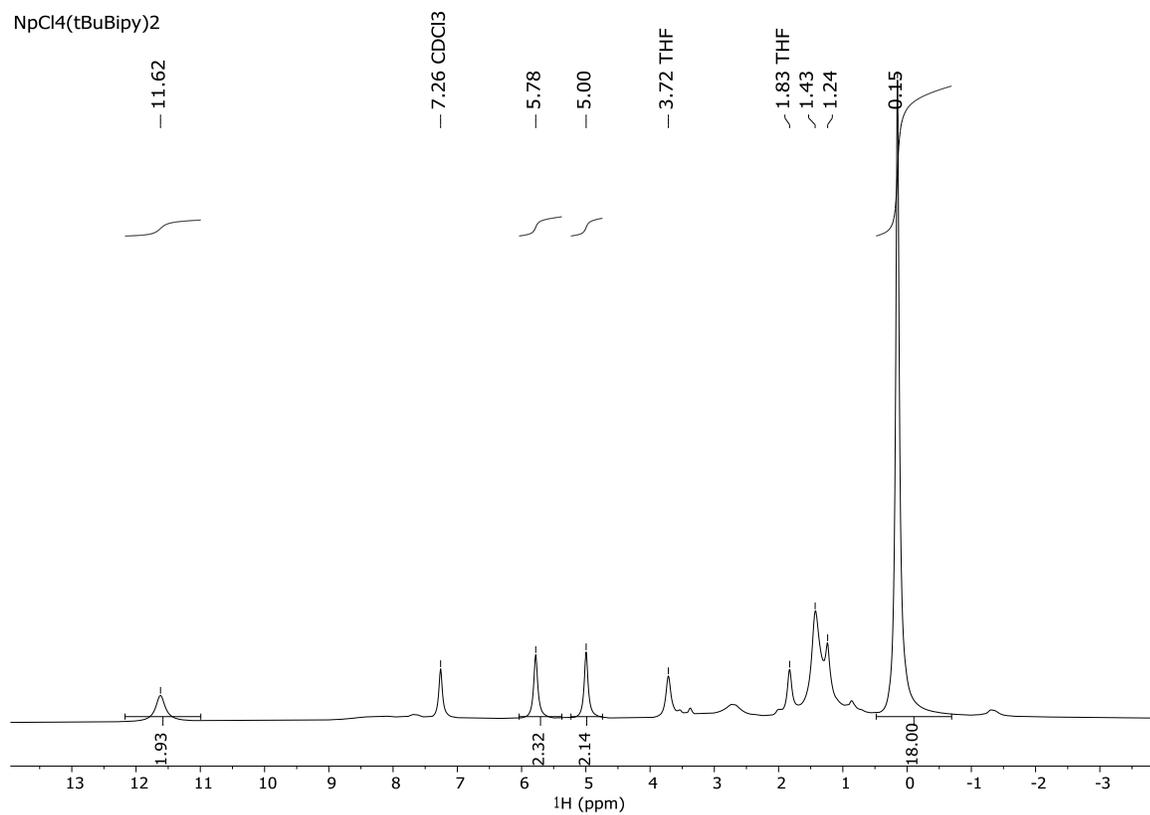


Figure S5. ¹H NMR Spectrum of **3**. (chloroform-*d*, 25 °C)

NpCl₄(OPPh₃)₂

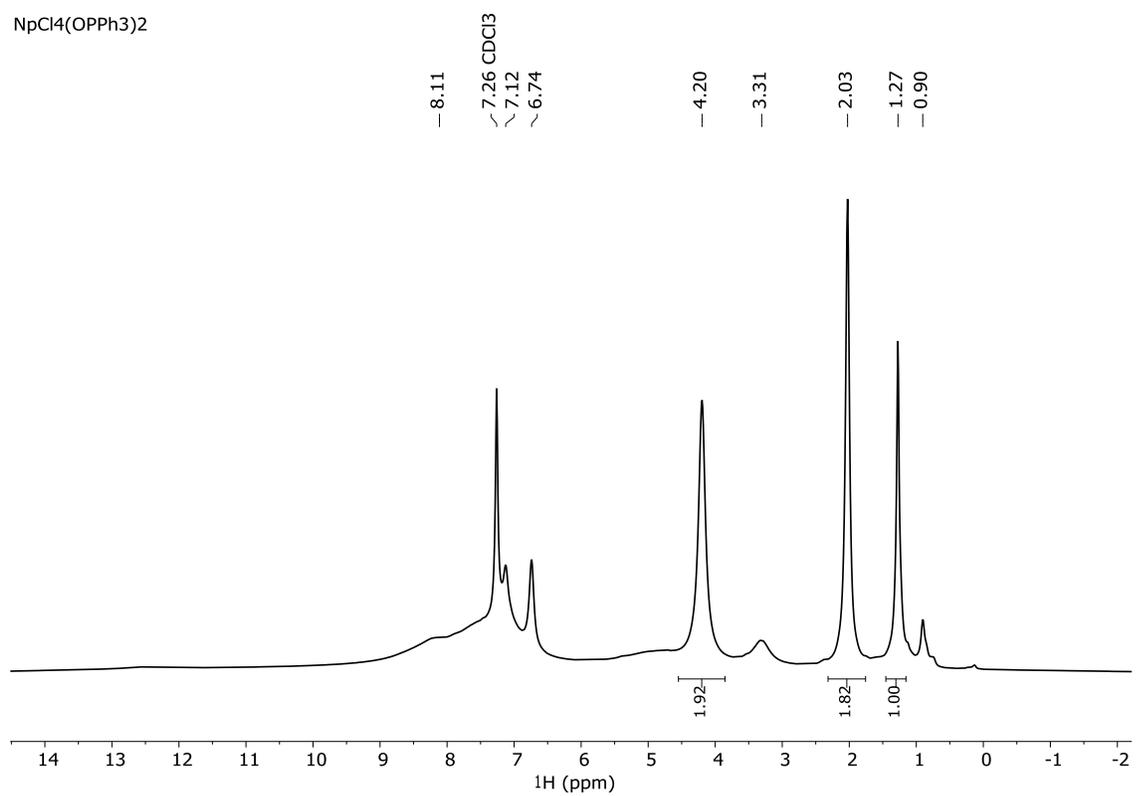


Figure S6. ¹H NMR spectrum of **4**. (chloroform-*d*, 25° C).

NpCl₄(OPPh₃)₂

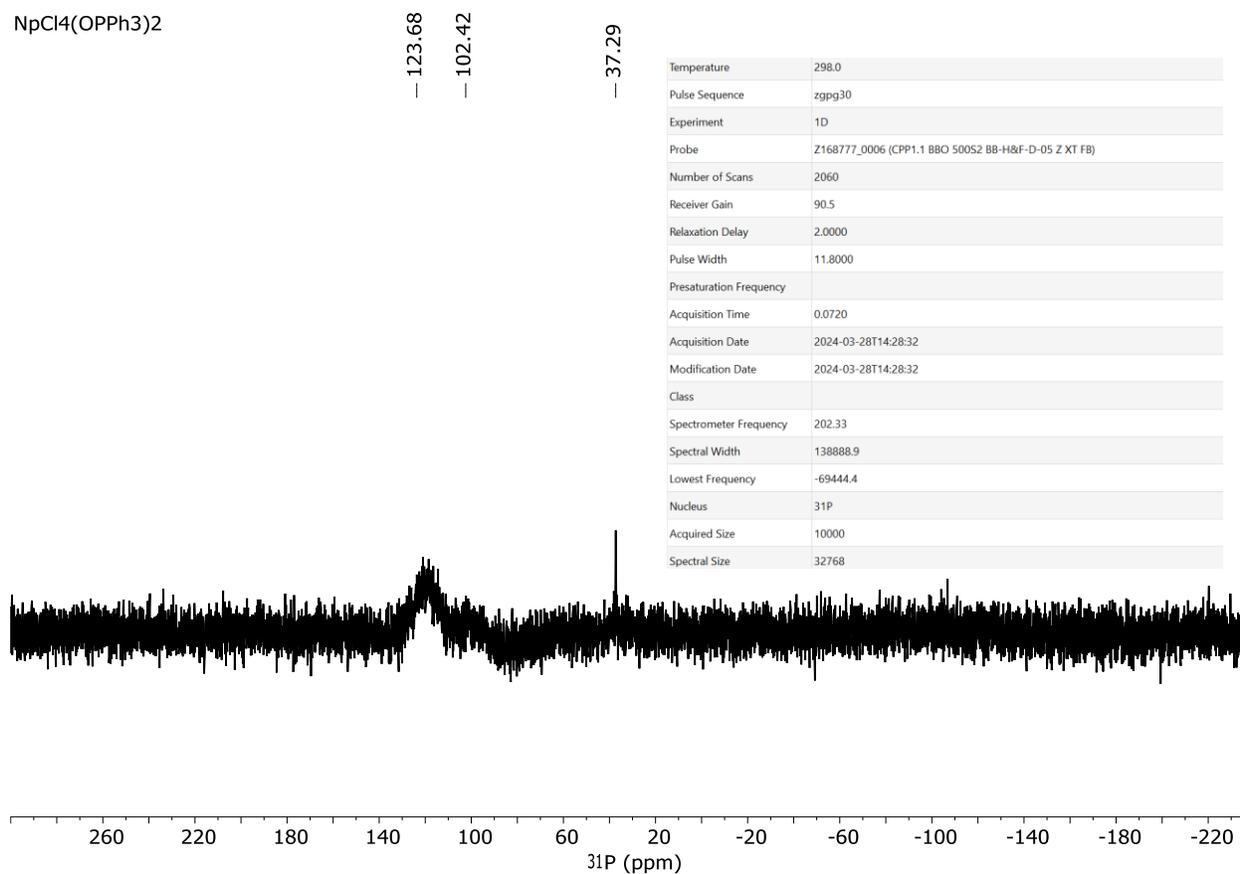


Figure S7. ³¹P NMR spectrum of **4** (chloroform-*d*, 25° C) with 5 Hz line broadening. The shifts are relative to phosphoric acid at 0 ppm. The NMR experiment parameters are shown in the inset.

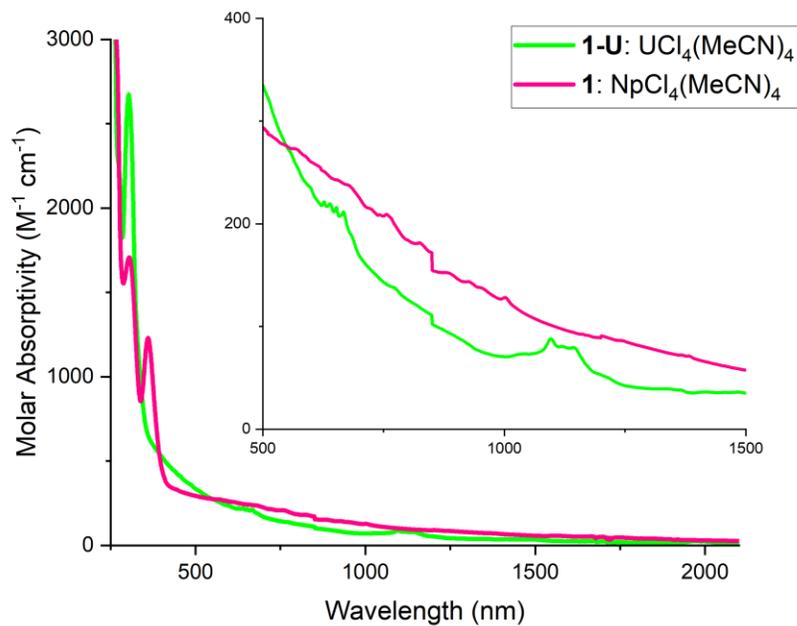


Figure S8. UV-vis/NIR Spectrum of **1** (1.27 mM) and $\text{UCl}_4(\text{MeCN})_4$ (1.51 mM) in acetonitrile at 25 °C.

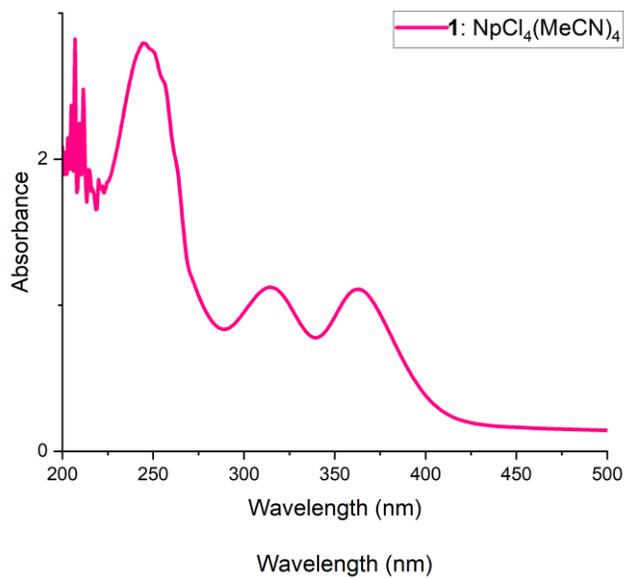


Figure S9. UV-vis Spectrum of **1** (2.32 mM) in dichloromethane at 25 °C.

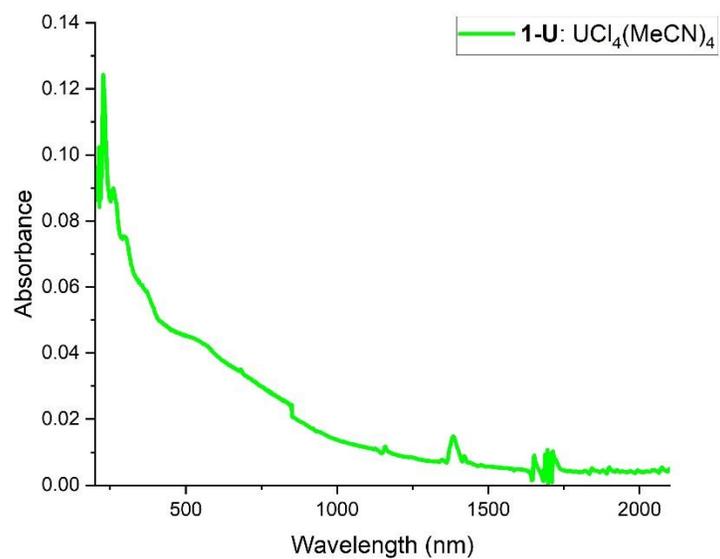


Figure S10. UV-vis/NIR spectrum of $\text{UCl}_4(\text{MeCN})_4$ (saturated) in dichloromethane at 25 °C.

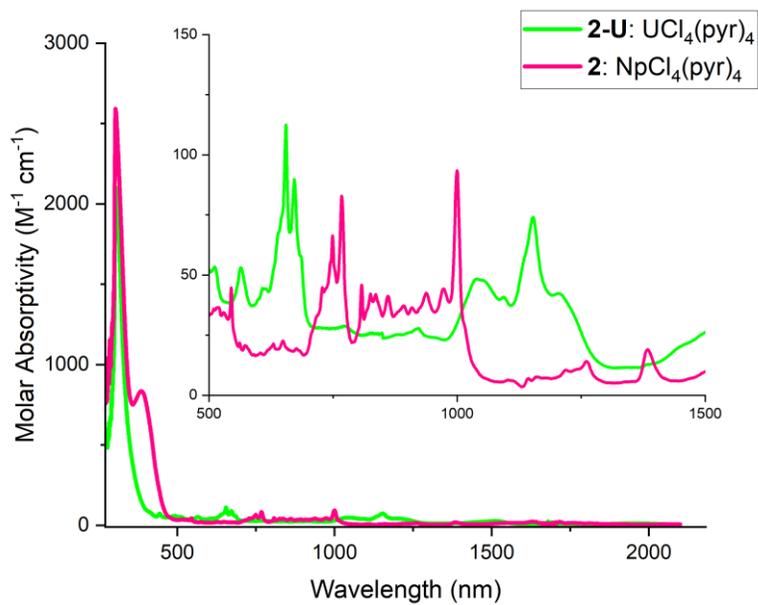


Figure S11. UV-vis/NIR Spectrum of **2** (0.86 mM) and $\text{UCl}_4(\text{pyr})_4$ (1.15 mM) in pyridine at 25 °C.

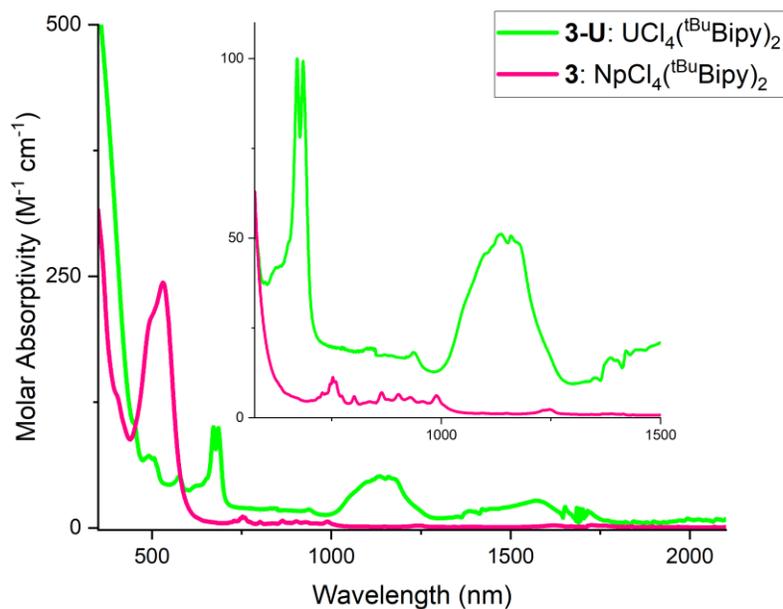


Figure S12. UV-vis/NIR Spectrum of **3** (0.89 mM) and $\text{UCl}_4(\text{tBuBipy})_2$ (0.82 mM) in dichloromethane at 25 °C.

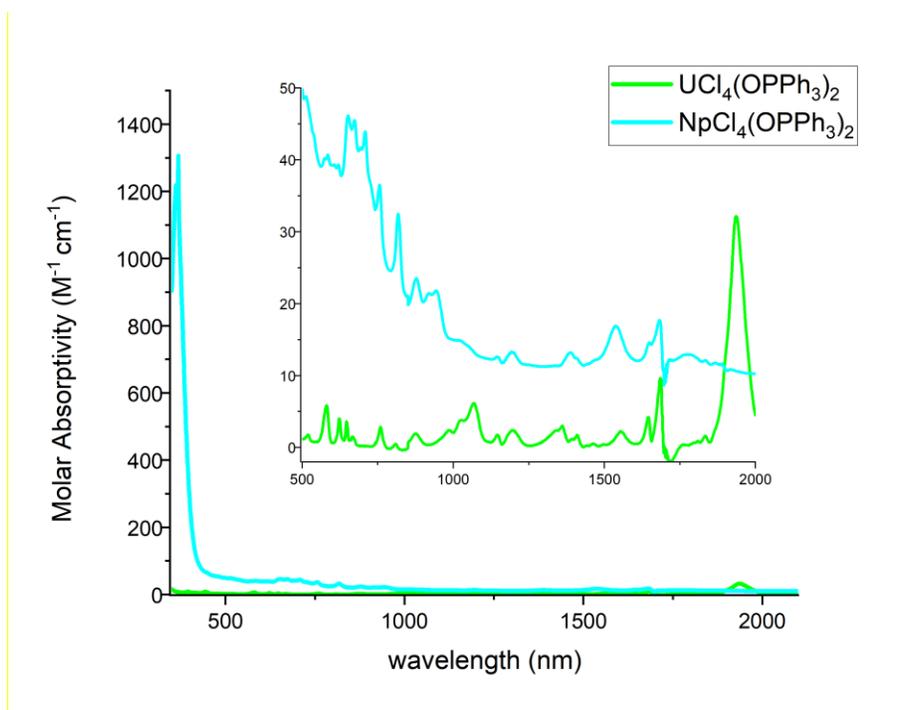


Figure S13. UV-vis/NIR Spectrum of **4** (0.3 mM) and $\text{UCl}_4(\text{OPPh}_3)_2$ (0.3 mM) in dichloromethane at 25 °C.

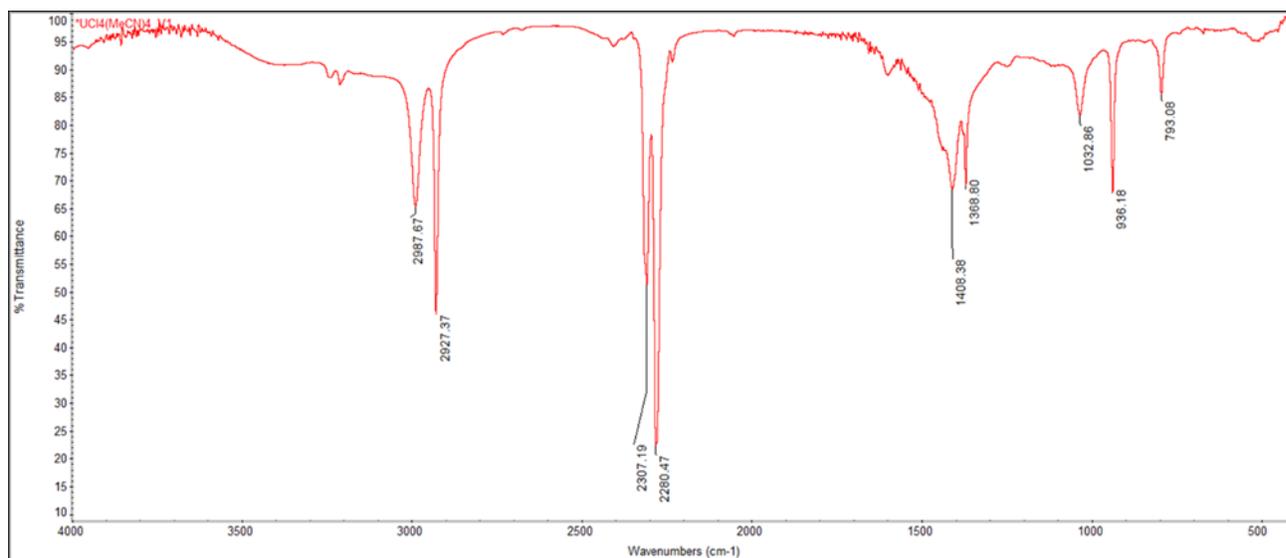


Figure S14. IR Spectrum of $\text{UCl}_4(\text{MeCN})_4$ obtained by using a KBr pellet.

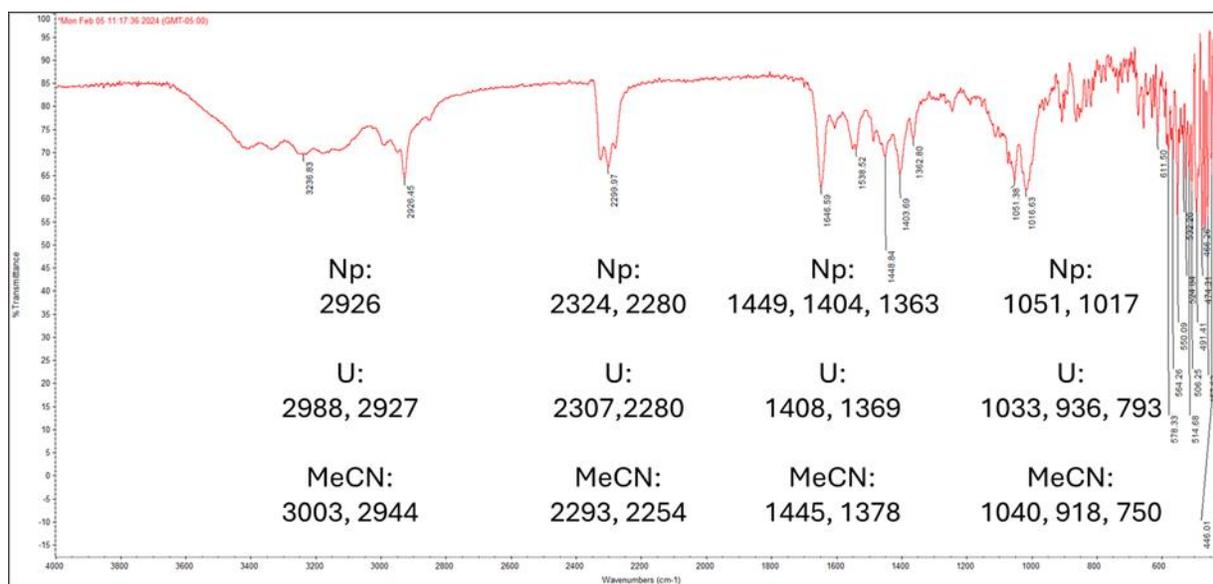


Figure S15. IR Spectrum of **1** obtained by using a KBr pellet. Data called out for “Np”, “U”, and “MeCN” are provided in wavenumbers for convenience of comparison.

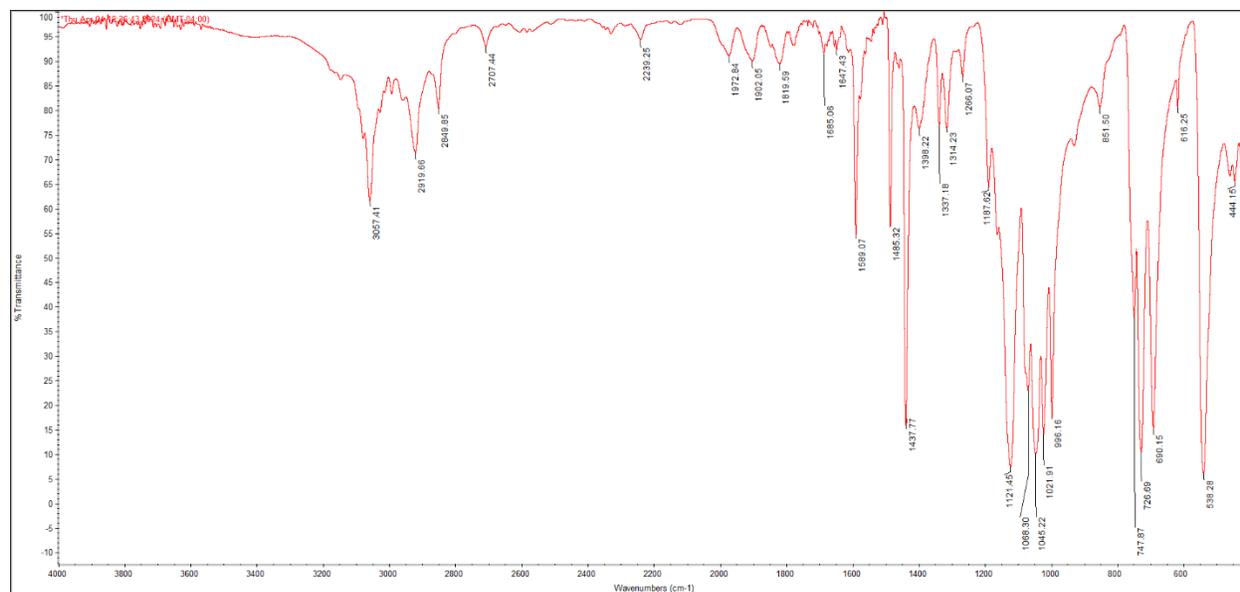


Figure S16. IR Spectrum of **4** using a KBr pellet.



Figure S17. 1, 2, and 3 during synthesis in acetonitrile, pyridine, and toluene respectively.

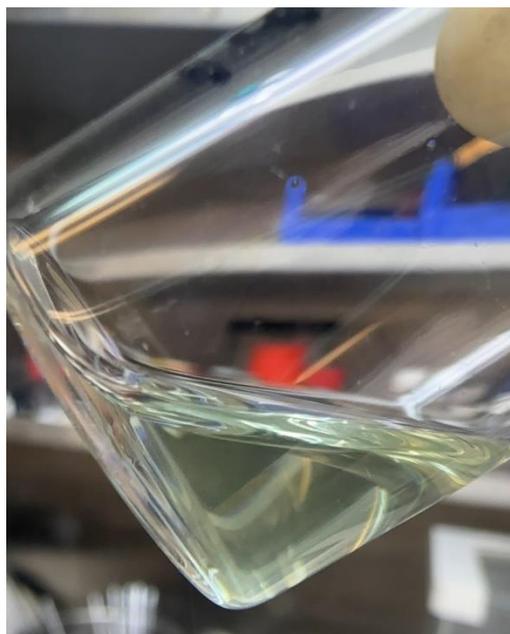


Figure S18. 4 during synthesis in THF.

Crystallographic Information:

NpCl₄(MeCN)₄ (1)	
Crystal data	
Chemical formula	C ₈ H ₁₂ Cl ₄ N ₄ Np
<i>M_r</i>	543.02
Crystal system, space group	Monoclinic, <i>C2/c</i>
Temperature (K)	150
<i>a</i> , <i>b</i> , <i>c</i> (Å)	14.6308 (5), 8.4327 (3), 13.7095 (5)
β (°)	91.687 (1)
<i>V</i> (Å ³)	1690.71 (10)
<i>Z</i>	4
Radiation type	Mo <i>K</i> α
μ (mm ⁻¹)	6.76
Crystal size (mm)	0.57 × 0.45 × 0.15
Data collection	
Diffractometer	Bruker AXS D8 Quest
Absorption correction	Multi-scan <i>SADABS</i> 2016/2: Krause, L., Herbst-Irmer, R., Sheldrick G.M. & Stalke D., <i>J. Appl. Cryst.</i> 48 (2015) 3-10
<i>T_{min}</i> , <i>T_{max}</i>	0.379, 0.747
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	10988, 3213, 3174
<i>R_{int}</i>	0.024
(sin θ/λ) _{max} (Å ⁻¹)	0.769
Refinement	
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.016, 0.038, 1.26
No. of reflections	3213
No. of parameters	81
H-atom treatment	H-atom parameters constrained
Δ _{max} , Δ _{min} (e Å ⁻³)	0.97, -0.82

Computer programs: Apex4 v2022.10-1 (Bruker, 2022), *SAINT* V8.40B (Bruker, 2020), *SHELXT* (Sheldrick, 2015b), *SHELXL2019/2* (Sheldrick, 2019).

NpCl₄(pyr)₄ (2)	
Crystal data	
Chemical formula	C ₂₀ H ₂₀ Cl ₄ N ₄ Np
<i>M_r</i>	695.20
Crystal system, space group	Monoclinic, <i>C2/c</i>
Temperature (K)	150
<i>a</i> , <i>b</i> , <i>c</i> (Å)	19.2449 (8), 9.5303 (4), 15.6081 (11)
β (°)	127.522 (1)
<i>V</i> (Å ³)	2270.4 (2)
<i>Z</i>	4
Radiation type	Mo <i>K</i> α
μ (mm ⁻¹)	5.06
Crystal size (mm)	0.30 × 0.26 × 0.24
Data collection	
Diffractometer	Bruker AXS D8 Quest
Absorption correction	Multi-scan <i>SADABS</i> 2016/2: Krause, L., Herbst-Irmer, R., Sheldrick G.M. & Stalke D. (2015). <i>J. Appl. Cryst.</i> 48, 3-10.
<i>T_{min}</i> , <i>T_{max}</i>	0.647, 0.747
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	35651, 4351, 4231
<i>R_{int}</i>	0.030
(sin θ/λ) _{max} (Å ⁻¹)	0.770
Refinement	
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.016, 0.040, 1.18
No. of reflections	4351
No. of parameters	133
H-atom treatment	H-atom parameters constrained
Δ _{max} , Δ _{min} (e Å ⁻³)	1.54, -1.21

Computer programs: Apex4 v2021.4-0 (Bruker, 2021), *SAINT* V8.40B (Bruker, 2020), *SHELXT* (Sheldrick, 2015), *SHELXL2019/3* (Sheldrick, 2015, 2019), *SHELXLE* Rev1275 (Hübschle *et al.*, 2011).

NpCl₄(^tBuBipy)₂ (3)	
Crystal data	
Chemical formula	C ₃₆ H ₄₈ Cl ₄ N ₄ Np·2.441(C ₄ H ₈ O)
<i>M_r</i>	1091.64
Crystal system, space group	Monoclinic, <i>P2₁/n</i>
Temperature (K)	150
<i>a</i> , <i>b</i> , <i>c</i> (Å)	16.6555 (6), 11.5350 (4), 25.7510 (9)
β (°)	94.5345 (14)
<i>V</i> (Å ³)	4931.8 (3)
<i>Z</i>	4
Radiation type	Mo <i>K</i> α
μ (mm ⁻¹)	2.36
Crystal size (mm)	0.24 × 0.24 × 0.04
Data collection	
Diffractometer	Bruker AXS D8 Quest diffractometer with PhotonII charge-integrating pixel array detector (CPAD)
Absorption correction	Multi-scan <i>SADABS</i> 2016/2: Krause, L., Herbst-Irmer, R., Sheldrick G.M. & Stalke D., <i>J. Appl. Cryst.</i> 48 (2015) 3-10
<i>T_{min}</i> , <i>T_{max}</i>	0.578, 0.746
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	89329, 15071, 12148
<i>R_{int}</i>	0.047
(sin θ/λ) _{max} (Å ⁻¹)	0.715
Refinement	
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.036, 0.094, 1.06
No. of reflections	15071
No. of parameters	740
No. of restraints	828
H-atom treatment	H-atom parameters constrained
	$w = \frac{1}{[\sigma^2(F_o^2) + (0.0421P)^2 + 10.2109P]}$ where $P = (F_o^2 + 2F_c^2)/3$
Δ _{max} , Δ _{min} (e Å ⁻³)	2.29, -0.87

Computer programs: Apex4 v2021.4-0 (Bruker, 2021), *SAINTE* V8.40B (Bruker, 2020), *SHELXT* (Sheldrick, 2015), *SHELXL2019/3* (Sheldrick, 2015, 2019), *SHELXL* Rev1275 (Hübschle *et al.*, 2011).

NpCl₄(OPPh₃)₂ (4)	
Crystal data	
Chemical formula	C ₃₆ H ₃₀ Cl ₄ NpO ₂ P ₂
<i>M_r</i>	935.34
Crystal system, space group	Monoclinic, <i>P</i> 2 ₁
Temperature (K)	150
<i>a</i> , <i>b</i> , <i>c</i> (Å)	9.9552 (5), 15.3552 (8), 11.9194 (6)
β (°)	98.955 (2)
<i>V</i> (Å ³)	1799.84 (16)
<i>Z</i>	2
Radiation type	Cu <i>K</i> α
μ (mm ⁻¹)	17.73
Crystal size (mm)	0.15 × 0.07 × 0.05
Data collection	
Diffractometer	Bruker AXS D8 Quest
Absorption correction	Multi-scan <i>SADABS</i> 2016/2: Krause, L., Herbst-Irmer, R., Sheldrick G.M. & Stalke D. (2015). <i>J. Appl. Cryst.</i> 48, 3-10.
<i>T_{min}</i> , <i>T_{max}</i>	0.527, 0.754
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	63868, 7672, 7496
<i>R_{int}</i>	0.050
(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>	0.021, 0.052, 1.07
No. of reflections	7672
No. of parameters	408
No. of restraints	1
H-atom treatment	H-atom parameters constrained

$\Delta_{\max}, \Delta_{\min}$ ($e \text{ \AA}^{-3}$)	1.02, -1.49
Absolute structure	Refined as an inversion twin.
Absolute structure parameter	0.324 (5)

Computer programs: Apex4 v2022.10-1 (Bruker, 2022), *SAINTE* V8.40B (Bruker, 2020), *SHELXT* 2014/4 (Sheldrick, 2014), *SHELXL2019/2* (Sheldrick, 2019).

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*, 1518-1520.
2. Monreal, M. J.; Thomson, R. K.; Cantat, T.; Travia, N. E.; Scott, B. L.; Kiplinger, J. L. " $U_i_4(1,4\text{-Dioxane})_2$, $[UCl_4(1,4\text{-Dioxane})]_2$, and $U_i_3(1,4\text{-Dioxane})_{1.5}$: Stable and Versatile Starting Materials for Low- and High-Valent Uranium Chemistry." *Organometallics* **2011**, *30*, 2031-2038.