Electronic Supplementary Information (ESI)

Tantalum, Easy as Pi: Understanding Differences in Metal-Imido Bonding Towards Improving Ta/Nb Separations

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General Synthetic Methods

All reactions and manipulations were performed under an inert atmosphere (N_2) using standard Schlenk techniques or in a dry and oxygen-free Vacuum Atmospheres Inc. Nexus II glovebox unless otherwise noted. All glassware, stir bars, and Celite were dried in an oven (150 °C) overnight prior to use. NMR spectra (^{1}H and ^{13}C{^{1}H}) were recorded on a Bruker UNI 400 or on a Bruker UNI 500 Fourier transform NMR spectrometer. Chemical shifts (δ) were recorded in units of parts per million (ppm) and referenced against residual *proteo* solvent peaks (for ^{1}H NMR spectra) or against the bulk NMR solvent peaks (for ^{13}C{^{1}H} NMR spectra). Elemental analyses were performed on a Costech ECS 4010 analyzer at the University of Pennsylvania. Prior to use, triethylamine (Et_3N) was stirred over calcium hydride (CaH_2) for 2 days, distilled under an atmosphere of N_2, and stored over 3 Å molecular sieves in the glovebox. ^{t}BuN=TaCl$_3$(pyridine)$_2$, ^{t}BuN=NbCl$_3$(pyridine)$_2$, and H_3TriNOx were prepared according to literature procedures,[1,2] and all other reagents were obtained from commercial sources and used without further purification. Solvents (benzene, toluene, *n*-pentane, diethyl ether) were purchased from Fisher Scientific, deoxygenated by sparging with argon (Ar) for 20 mins, dried via passage through a commercial two-column solvent purification system packed with Q5 reactant and neutral alumina (benzene, toluene, *n*-pentane), or two columns of neutral alumina (diethyl ether), and stored in the glovebox over 3 Å molecular sieves. Deuterated benzene (C_6D_6) and pyridine (pyr-d_5) were purchased from Cambridge Isotopes, dried with sodium/benzophenone or CaH_2 respectively, distilled under an N_2 atmosphere, and stored over 3 Å molecular sieves in the glovebox.

Synthetic Procedures

^{t}BuN=Ta(TriNOx) (**1-Ta**)

To a stirred benzene solution (3 mL) of H_3TriNOx (138 mg, 0.25 mmoles) in a 20 mL scintillation vial prepared in a glovebox was added triethylamine (Et_3N) (1 mL, 7.17 mmoles). A benzene solution (3 mL) of ^{t}BuN=$TaCl_3$(pyridine)$_2$ (127.1 mg, 0.25 mmoles) was added dropwise to the reaction vial and the resulting pale yellow mixture was stirred at room temperature for 7 h, during which time white [Et_3NH]Cl was observed to precipitate. Solid [Et_3NH]Cl was removed by filtration through a plug of Celite and the filtrate was concentrated under reduced pressure until ca. 1 mL of solvent remained. The resulting white precipitate was collected by filtration over a fine frit and was washed with pentane (3 x 5 mL). The analytically pure product was dried under reduced pressure for 1 h and used without further purification (46.1 mg, 23%). Single crystals of X-ray quality were obtained from a diethyl ether (Et_2O) solution of the complex at –20 °C. **^{1}H NMR** (C_6D_6, 400 MHz, 300 K): δ = 7.67 (dd, J_1 = 8 Hz, J_2 = 1 Hz, 3H), 7.09 (dt, J_1 = 7 Hz, J_2 = 2 Hz, 3H), 7.03 (dd, J_1 = 7 Hz, J_2 = 2 Hz, 3H), 6.94 (dt, J_1 = 7 Hz, J_2 = 1 Hz, 3H), 4.38 (d, J = 12 Hz, 3H), 2.41 (d, J = 11 Hz, 3H), 1.59 (s, 9H), 0.97 (s, 27H) ppm. **^{13}C{^{1}H} NMR** (C_6D_6, 101 MHz, 300 K): δ = 150.15 (s), 134.41 (s), 133.34 (s), 128.62 (s), 127.18 (s), 125.43 (s), 64.88 (s), 63.91 (s), 60.13 (s), 33.60 (s), 26.88 (s) ppm. **Anal. Calcd.** for $C_{37}H_{54}N_5O_3Ta$: C, 55.70; H, 6.82; N, 8.78. **Found:** C, 55.27; H, 6.15; N, 8.79.

^{t}BuN=Nb(TriNOx) (**1-Nb**)

To a stirred benzene solution (3 mL) of H_3TriNOx (132.8 mg, 0.24 mmoles) in a 20 mL scintillation vial prepared in a glovebox was added triethylamine (Et_3N) (1 mL, 7.17 mmoles). A benzene solution (3 mL) of ^{t}BuN=$NbCl_3$(pyridine)$_2$ (104.4 mg, 0.24 mmoles) was added dropwise to the reaction vial and the resulting pale yellow mixture was stirred at room temperature for 7 h, during which time white [Et_3NH]Cl was observed to precipitate. Solid [Et_3NH]Cl was removed by filtration through a plug of Celite and the filtrate was concentrated under reduced pressure until ca. 1 mL of solvent remained. The resulting white precipitate was collected by filtration over a fine frit and was washed with pentane (3 x 5 mL). The analytically pure product was dried under reduced pressure for 1 h and used without further purification (84.6 mg, 49%). Single crystals of X-ray quality were obtained from diffusion of pentane into a benzene solution of the complex at room temperature. **^{1}H NMR** (C_6D_6, 400 MHz, 300 K): δ = 7.74 (dd, J_1 = 8 Hz, J_2 = 1 Hz, 3H), 7.11 (dt, J_1 = 7 Hz, J_2 = 2 Hz, 3H), 7.03 (dd, J_1 = 7 Hz, J_2 = 2 Hz, 3H), 6.95 (dt, J_1 = 7 Hz, J_2 = 1 Hz, 3H), 4.36 (d, J = 12 Hz, 3H), 2.36 (d, J = 11 Hz, 3H), 1.56 (s, 9H), 0.96 (s, 27H) ppm. **^{13}C{^{1}H} NMR** (C_6D_6, 101 MHz, 300 K): δ = 150.44 (s), 134.51 (s), 132.97 (s), 128.89 (s), 127.13 (s), 125.37 (s), 63.91 (s), 60.16 (s), 31.88 (s), 26.68 (s) ppm. **Anal. Calcd.** for $C_{37}H_{54}N_5O_3Nb$: C, 62.61; H, 7.67; N, 9.87. **Found:** C, 62.34; H, 7.55; N, 9.75.

*(^{t}BuNCO$_2$)Ta(TriNOx) (**2-Ta**)*

A benzene solution (10 mL) of **1-Ta** (58 mg, 0.073 mmoles) was prepared in a 100 mL Schlenk bomb in an N_2 atmosphere glovebox. The solution was removed from the glovebox and degassed using three freeze-pump-thaw cycles. On the final cycle, 1 atm of CO_2 was flushed into the headspace of the reaction flask, and the reaction mixture was warmed to room temperature. The reaction mixture was then heated for 14 h at 50 °C in an oil bath, resulting in the precipitation of the product (**2-Ta**). The reaction mixture was degassed using three freeze-pump-thaw cycles, and the reaction bomb was returned to the glovebox. The pale-yellow product was collected by filtration over a fine porosity frit, washed with pentane (3 x 5 mL), and was dried under reduced pressure for 1 h. The product was found to be analytically pure, and was used without further purification (39 mg, 64 %). Single crystals of X-ray quality were obtained from slow evaporation of a DCM solution of the complex. **^{1}H NMR** (C_6D_6, 500 MHz, 300 K): δ = 7.64 (d, *J* = 8 Hz, 2H), 7.54 (t, *J* = 8 Hz, 1H), 7.48 (d, *J* = 8 Hz, 1H), 7.44 (d, *J* = 8 Hz, 1H), 7.38 (s, 2H), 7.34 (t, *J* = 8 Hz, 1H), 7.23 (m, 1H), 7.14 (d, J = 4 Hz, 2H), 6.89 (m, 1H), 5.68 (d, J = 11 Hz, 1H), 4.86 (d, J = 11 Hz, 1H), 4.31 (d, J = 11 Hz, 1H), 4.25 (d, J = 11 Hz, 1H), 3.57 (d, J = 11 Hz, 1H), 3.49 (d, J = 11 Hz, 1H), 1.92 (s, 9H), 1.37 (s, 9H), 1.24 (s, 9H), 0.78 (s, 9H) ppm. **^{13}C{^{1}H} NMR** (C_6D_6, 101 MHz, 300 K): δ = 161.72 (s), 145.84 (s), 137.48 (s), 135.44 (s), 134.71 (s), 133.83 (s), 132.79 (s), 131.14 (s), 130.28 (s), 130.12 (s), 130.02 (s), 129.22 (s), 128.40 (s), 127.99 (s), 126.33 (s), 125.73 (s), 71.19 (s), 68.47 (s), 64.33 (s) 64.01 (s), 63.24 (s), 63.18 (s), 58.11 (s), 33.39 (s), 29.80 (s), 28.51 (s), 28.01 (s) ppm. **IR** (KBr pellet): ν_{CO} = 1656 cm^{-1}. **Anal. Calcd.** for $C_{38}H_{54}N_5O_5Ta$: C, 54.22; H, 6.47; N, 8.32. **Found:** C, 54.59; H, 6.10; N, 8.18.

Kinetics Procedures

Pressurization procedure

A 7.0 mM stock solution of **1-Ta** was prepared in C_6D_6 in a glovebox and was stored frozen at –20 °C between kinetic trials. For a given kinetic trial, 0.35 mL of the stock solution was added to a medium-walled J-Young tube in the glovebox, leaving a total headspace of 1.65 mL above the solution. The sample was removed to a Schlenk line, and the sample degassed using three freeze-pump-thaw cycles. The solution was next frozen in an ice water bath (to prevent condensing of excess CO_2 upon pressurization), and the J-Young tube was pressurized with CO_2 that had been dried by passage of the gas through a column of Drierite. The pressure of gaseous CO_2 was determined *via* an Ashcroft 1702 differential pressure gauge. Overpressures of 15, 30, 45, and 60 psi were used depending on the kinetic trial. Concentrations of CO_2 in solution were determined based on the pressure of CO_2 added to the J-Young tube, as determined previously by Wendt and coworkers.[3] The J-young tube was sealed and was then immersed in liquid nitrogen for safe storage until the start of the NMR experiment.

NMR experimental setup

^{1}H NMR spectra for the kinetic study were obtained on a Bruker UNI 500 Fourier transform NMR spectrometer. For each kinetic trial, the frozen NMR sample containing **1-Ta** and frozen CO_2 was actively warmed to room temperature in a water bath and injected into the spectrometer; the spectrometer was pre-warmed to the experimental temperature (303, 313, or 323 K). A single NMR spectrum was obtained within 4 minutes and the exact time since sample injection was recorded. Following collection of the initial spectrum, automated spectra were collected every 5 minutes for 5 (303 K), 4 (313 K), or 3 (323 K) hours. Relaxation times (D1) of 3 seconds were chosen based on an experiment in which the ratio of the **1-Ta** and internal standard (toluene) resonance integrals were monitored as a function of increasing D1. Following completion of the experiment, the resonance at 4.38 ppm (corresponding to the methylene protons of **1-Ta**), the resonance at 4.01 ppm (corresponding to a methylene resonance of **2-Ta**), and the resonance at 2.10 ppm (corresponding to the toluene -CH_3) group were integrated, with the toluene integration standardized to 1.0000. The changing integrations of **1-Ta** and **2-Ta** with respect to internal standard were monitored and converted to concentration, and kinetic traces were obtained by plotting concentration versus time or LN(concentration) versus time (Fig. S1 and S2).

Kinetic Data

Representative rate plots

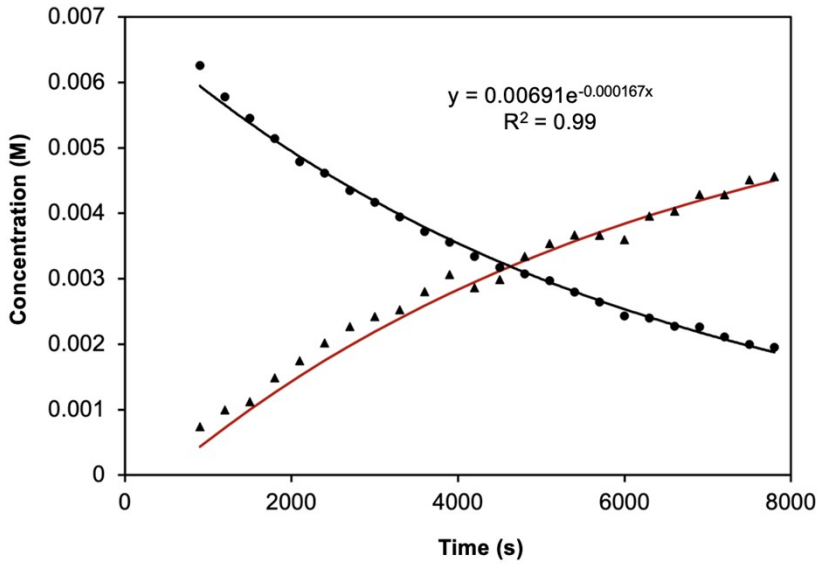

Fig. S1 Typical kinetic trace showing the decay of **1-Ta** (black circles) and the concomitant formation of **2-Ta** (black triangles). The black trace represents the fit to a single exponential function, and the red trace represents the theoretical yield of **2-Ta** according to this function (assuming a 1 → 1 transformation from **1-Ta** to **2-Ta**). Conditions: 50 °C, $[1\text{-Ta}]_0$ = 7 mM, $[CO_2]$ = 234 mM.

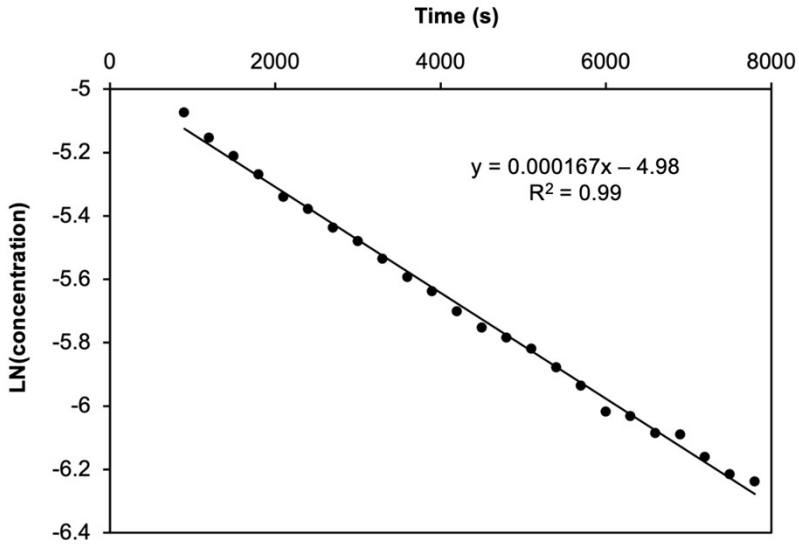

Fig. S2 First-order rate plot (natural log of concentration of **1-Ta** *vs*. time) for the same kinetic trial shown in Fig. S1. Conditions: 50 °C, $[1\text{-Ta}]_0$ = 7 mM, $[CO_2]$ = 234 mM.

Values of k_{obs} under various conditions

Table S1 Values of k_{obs} obtained under various conditions.

$[CO_2]$ (mM)	Temperature (K)	k_{obs} ($M^{-1}s^{-1}$)
0.154	303	0.0000191
0.154	303	0.0000276
0.154	303	0.0000152
0.231	303	0.0000270
0.231	303	0.0000293
0.231	303	0.0000289
0.308	303	0.0000361
0.308	303	0.0000401
0.308	303	0.0000426
0.386	303	0.0000430
0.386	303	0.0000595
0.386	303	0.0000520
0.225	313	0.0000780
0.225	313	0.000106
0.225	313	0.0000709
0.234	323	0.000167
0.234	323	0.000207
0.234	323	0.000174

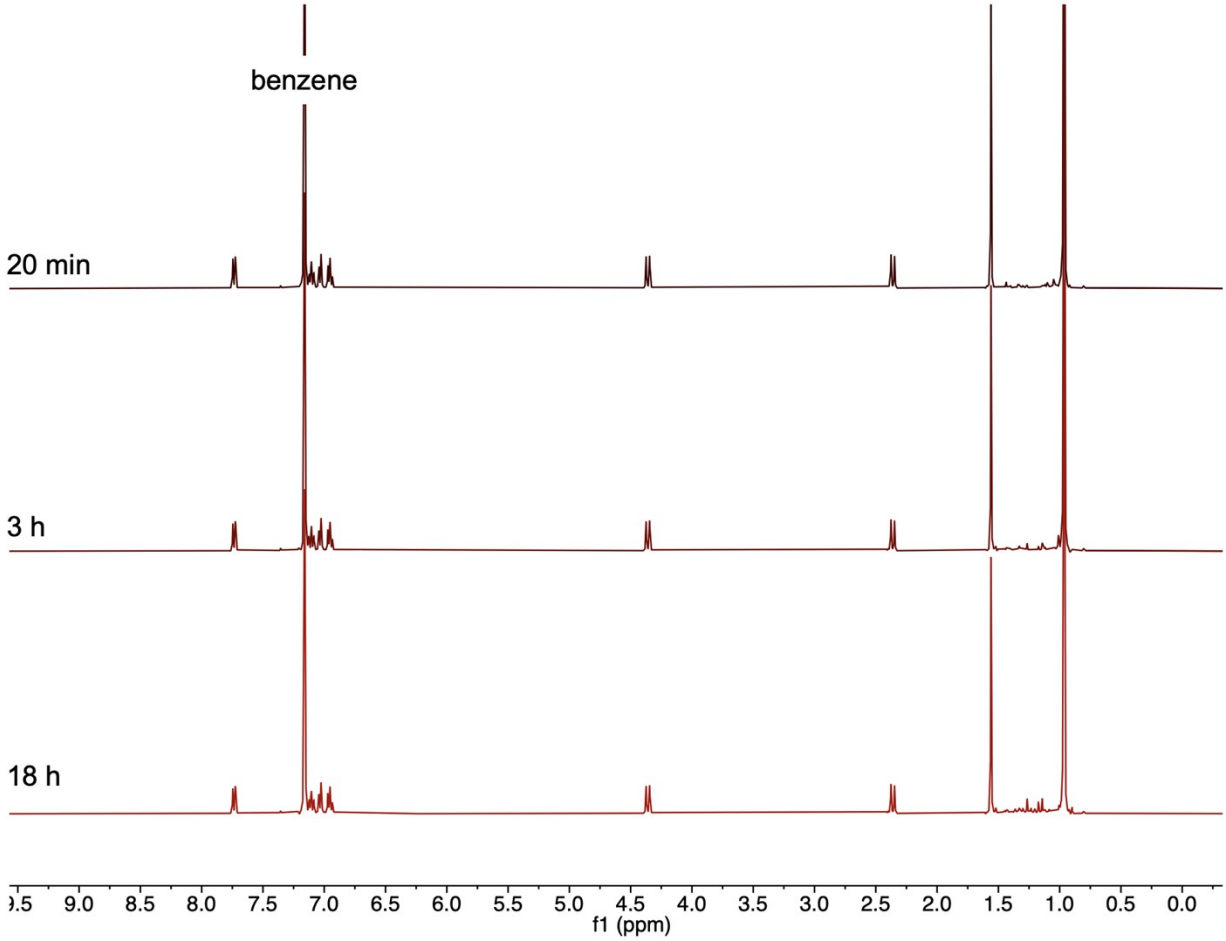

Fig. S3 ^{1}H NMR spectra of **1-Nb** under 1 atm of CO_2 at 80 °C for 18h (500 MHz).

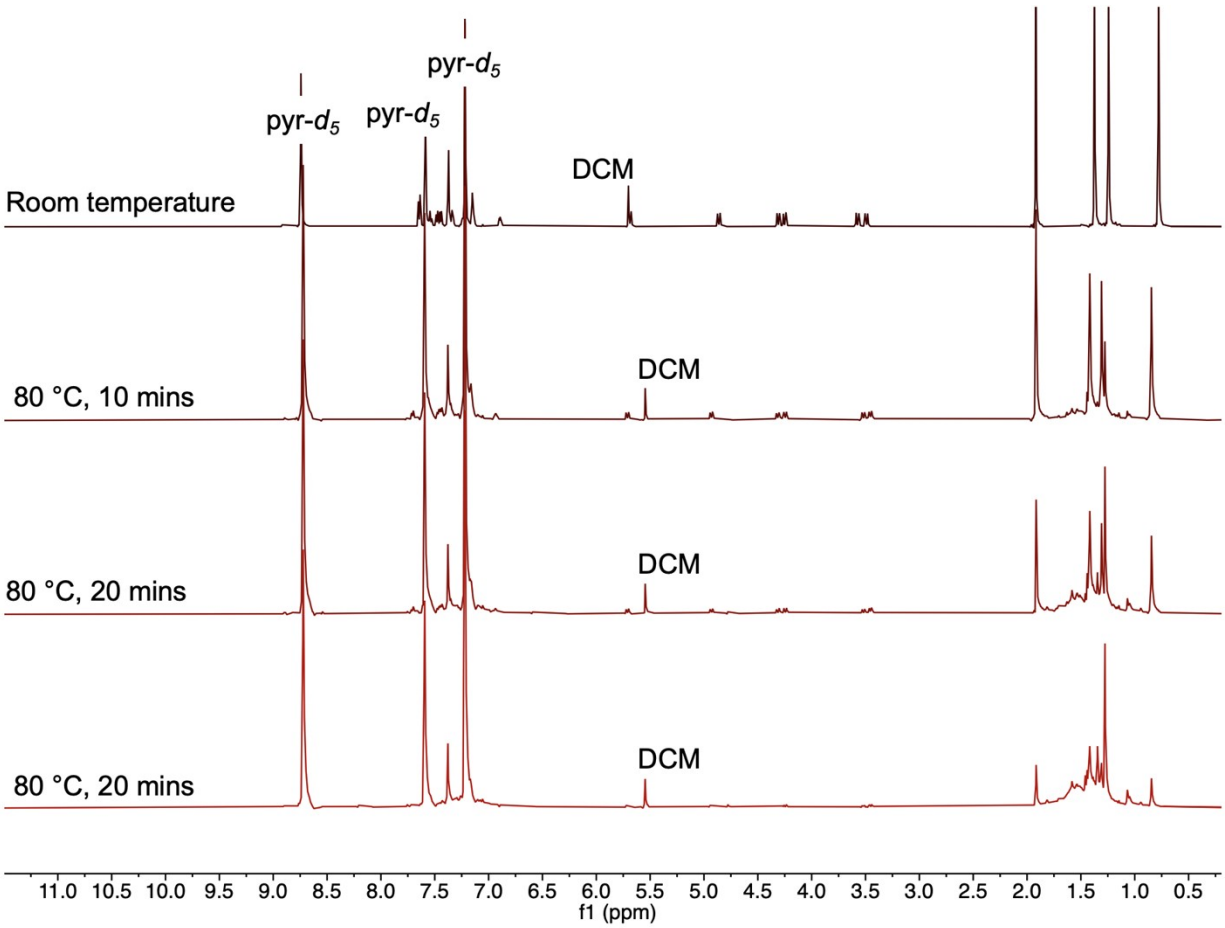

Fig. S4 ^{1}H NMR spectra of **2-Ta** in pyridine-d_5 at 80 °C for 50 minutes (500 MHz). Decomposition was observed, but spectral resonances corresponding to **1-Ta** were not observed to form, nor were spectral resonances consistent with the putative **3-Ta'** observed to form. The spectral resonance associated with ^{t}BuNCO were also not observed to form (1.18 ppm in pyridine-d_5).

Separations Procedure

A toluene solution (15 mL) containing **1-Ta** (78 mg, 0.1 mmoles) and **1-Nb** (69 mg, 0.1 mmoles) was prepared and divided into four equal volume fractions. Fraction 1: all volatiles were removed under reduced pressure, and the resulting solid material was analyzed for Ta/Nb content using ICP-OES. Fractions 2-4: the solutions were individually subjected to three freeze-pump-thaw cycles in Schlenk bomb flasks, and each reaction vessel was then back-filled with 1 atm of CO_2. The reaction vessels were heated to 50 °C for 18 h, and then subjected to three additional freeze-pump-thaw cycles to remove residual CO_2 from solution. The reaction vessels were brought into the glovebox and the solid precipitates were collected by filtration over fine frits, dried under reduced pressure, and were submitted for Ta/Nb content analysis by ICP-OES. All volatiles from the filtrates were removed under reduced pressure, and the resulting solid materials were submitted for Ta/Nb content analysis by ICP-OES. Enrichment factors (EF_M) and separation factors ($S_{Ta/Nb}$) were calculated according to standard procedures,[4] and are tabulated in Table S2 for each fraction.

Regeneration of H_3TriNOx:

Following the separation procedure described above, the major species in the sample are **1-Nb** and **2-Ta**. As such, ligand regeneration from these compounds was tested:

A THF solution (10 mL) of **1-Nb** (20 mg, 0.028 mmoles) was treated with 1 mL of deionized H_2O under an inert (N_2) atmosphere, and the resulting slurry was stirred at room temperature for 1 h. The white solid, presumably niobic acid, was removed via filtration, and all volatiles were removed under reduced pressure from the colorless filtrate. The resulting white solid was weighed (14.8 mg), and an NMR was obtained in C_6D_6, indicating the formation of pure H_3TriNOx in 96% yield (Figure SX).

A THF solution (10 mL) of **2-Ta** (23 mg, 0.027 mmoles) was treated with 1 mL of deionized H_2O under an inert (N_2) atmosphere, and the resulting slurry was stirred at room temperature for 1 h. The white solid, presumably tantalic acid, was removed via filtration, and all volatiles were removed under reduced pressure from the colorless filtrate. The resulting white solid was weighed (14.2 mg), and an NMR was obtained in C_6D_6, indicating the formation of pure H_3TriNOx in 95% yield (Figure SX).

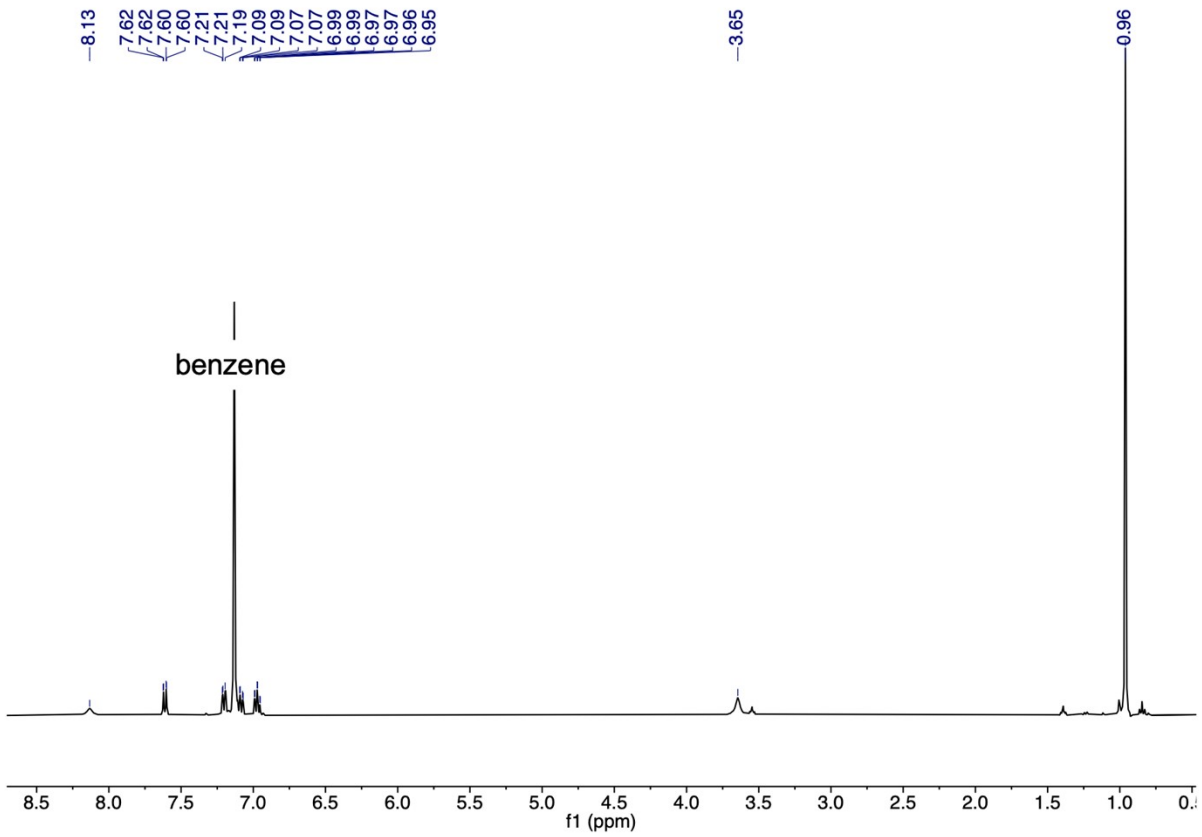

Figure S5 ^{1}H NMR spectrum of regenerated H_3TriNOx from **1-Nb** in C_6D_6 (400 MHz, 300 K).

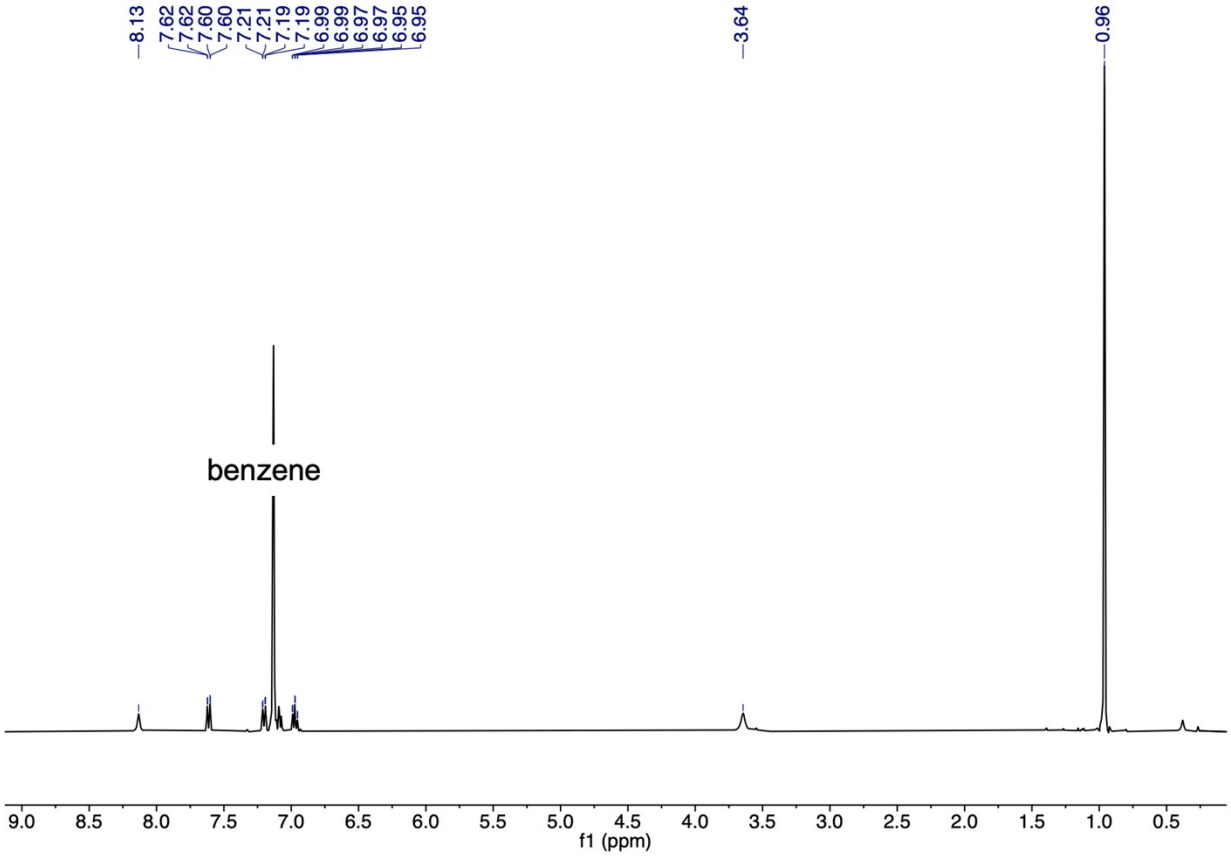

Figure S6 ^{1}H NMR spectrum of regenerated H_3TriNOx from **2-Ta** in C_6D_6 (400 MHz, 300 K).

ICP-OES Data

Table S2 Enrichment factors (EF_M) and separation factors ($S_{Ta/Nb}$) for the Ta/Nb separations. Fraction 1 represents the homogenized sample of **1-Ta**/**1-Nb** prior to the separation, which demonstrates an initial 1:1 mixture of Ta:Nb. Individual separations factors for Fractions 2 – 4 were determined by taking the product of EF_{Ta} in the precipitate, and EF_{Nb} in the filtrate. The final value of $S_{Ta/Nb}$ (404) was determined by averaging the three $S_{Ta/Nb}$ values for Fractions 2 – 4, with a corresponding standard deviation of 150.

Fraction #	Description	EF_{Ta}	EF_{Nb}	$S_{Ta/Nb}$
1	1:1 mixture	1.02	0.983	--
2	Precipitate	**135**	0.00738	
	Filtrate	0.253	**3.95**	**535**
3	Precipitate	**74.4**	0.0135	
	Filtrate	0.308	**3.25**	**241**
4	Precipitate	**100**	0.00999	
	Filtrate	0.231	**4.35**	**435**

NMR Spectra

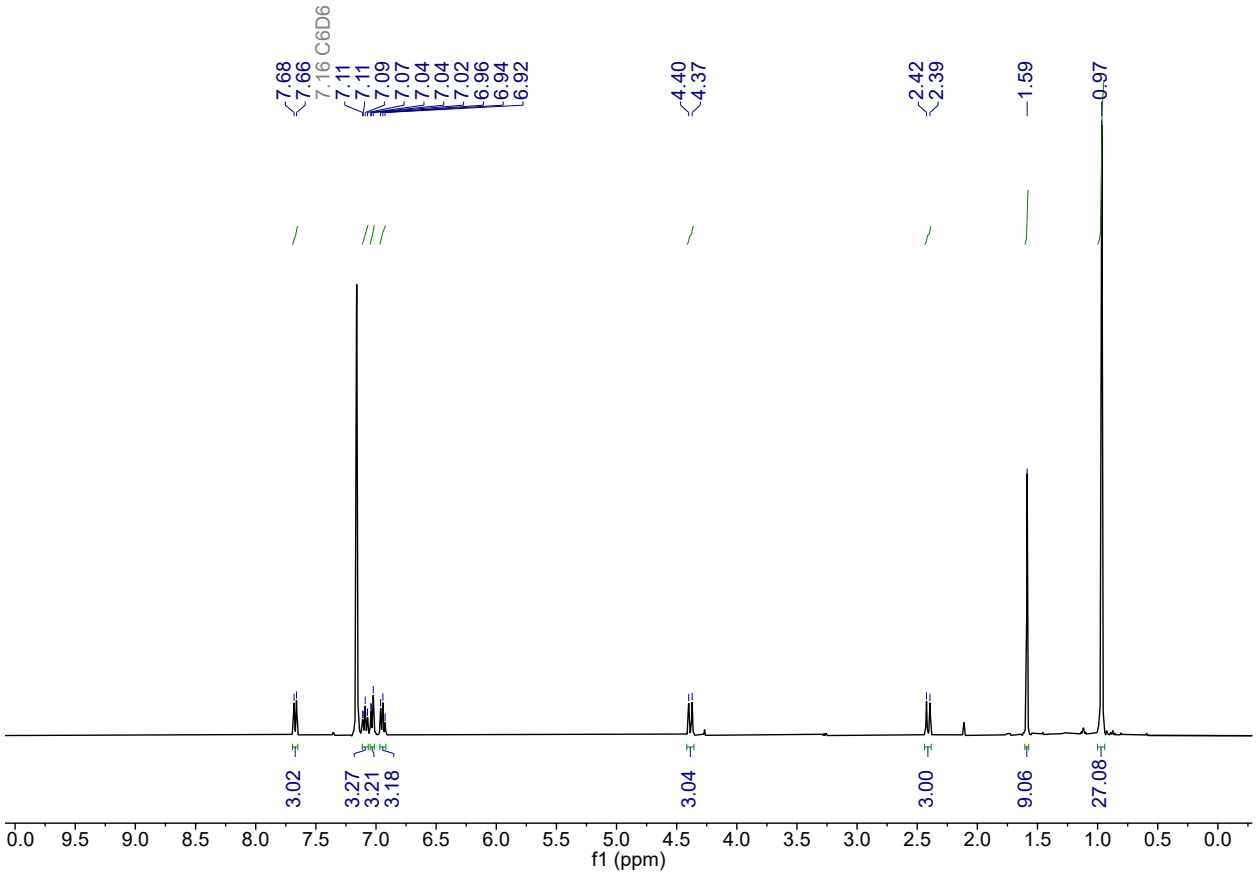

Fig. S7 ^{1}H NMR spectrum of **1-Ta** in C_6D_6 (400 MHz, 300 K).

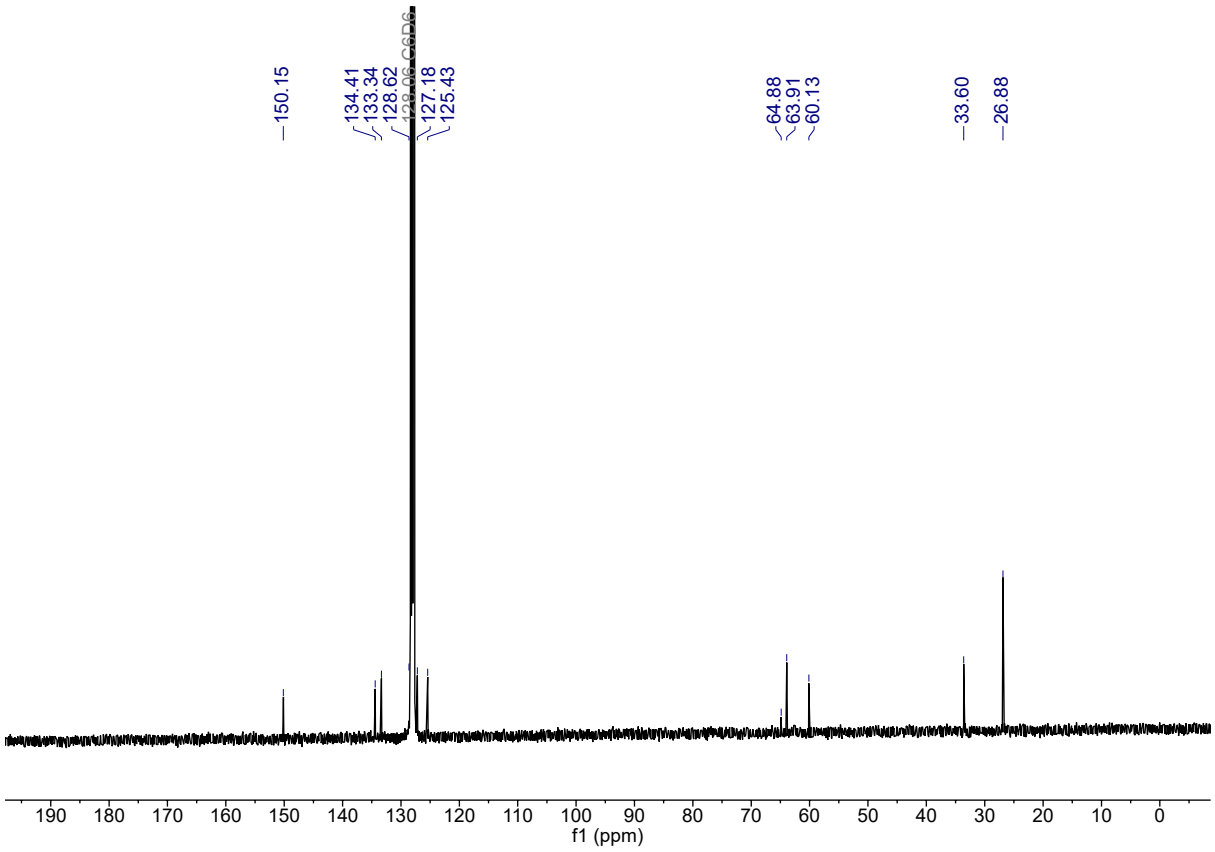

Fig. S8 $^{13}C\{^{1}H\}$ NMR spectrum of **1-Ta** in C_6D_6 (101 MHz, 300 K).

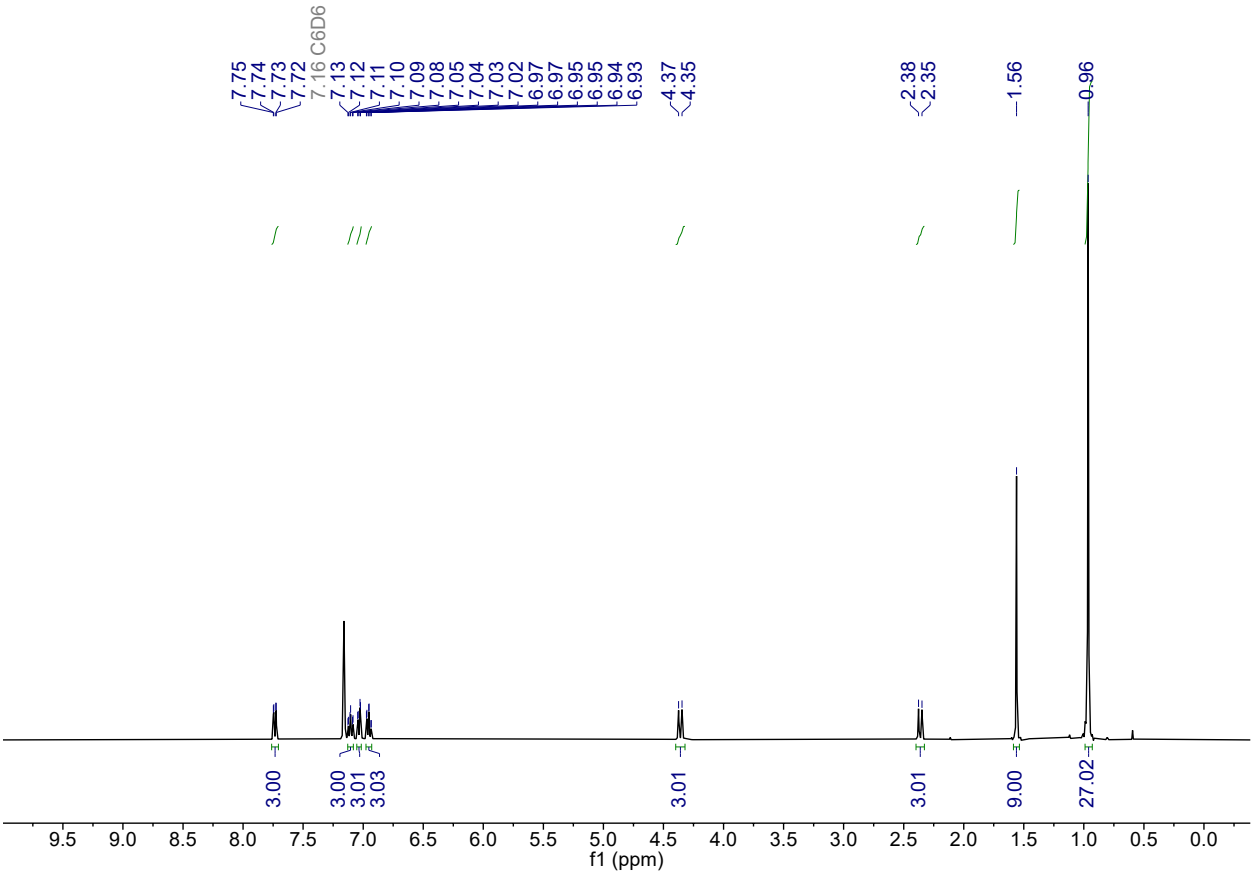

Fig. S9 ^{1}H NMR spectrum of **1-Nb** in C_6D_6 (400 MHz, 300 K).

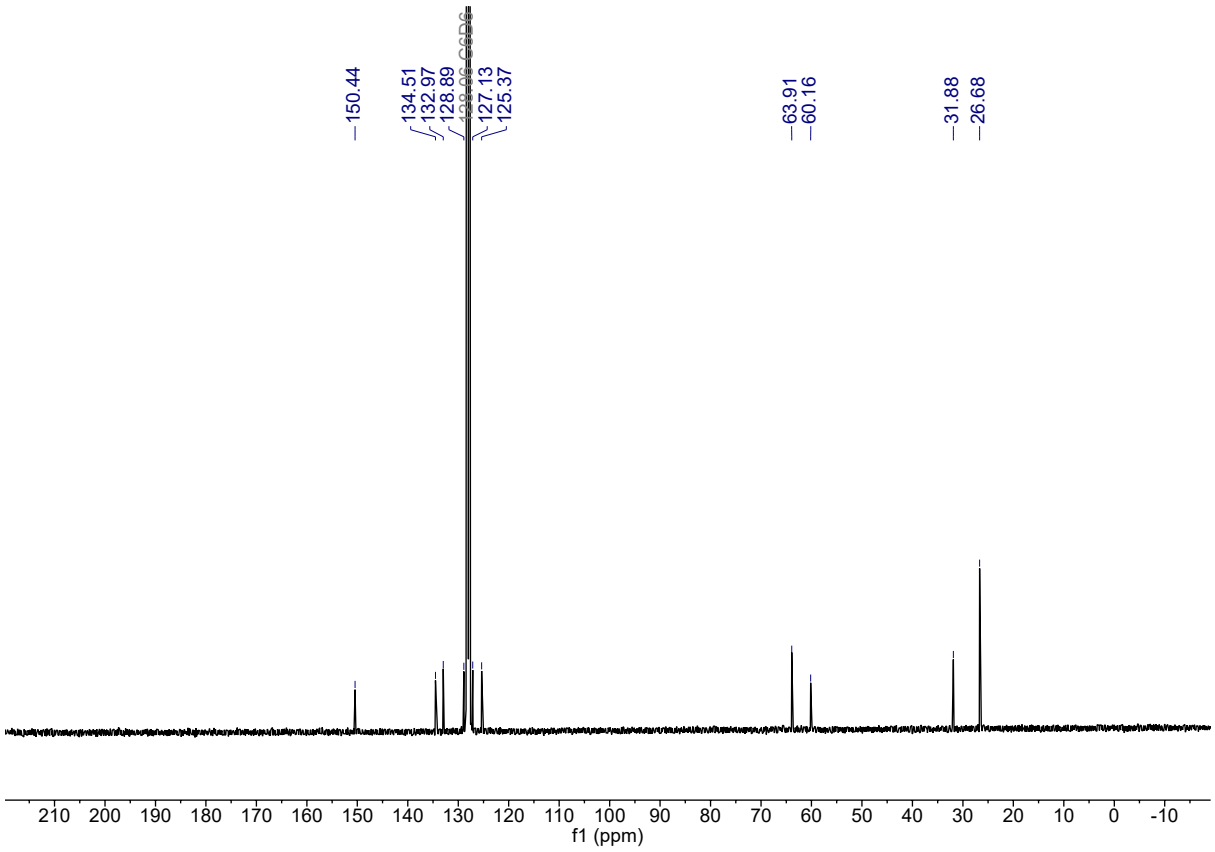

Fig. S10 $^{13}C\{^{1}H\}$ NMR spectrum of **1-Nb** in C_6D_6 (101 MHz, 300 K).

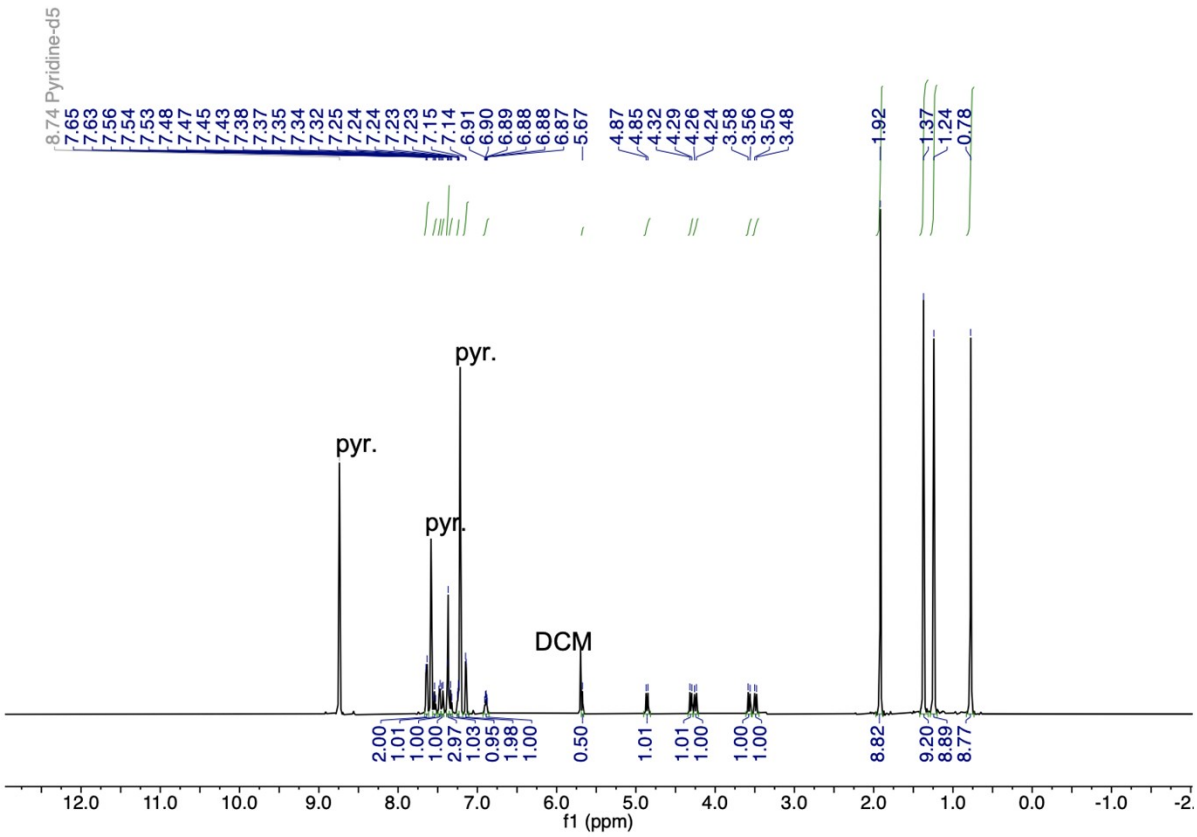

Fig. S11 ^{1}H NMR spectrum of **2-Ta** in pyridine-d_5 (500 MHz, 300 K). Note: only half of the resonance at 5.67 was integrated since the downfield side of the doublet overlaps with trace dichloromethane in the sample.

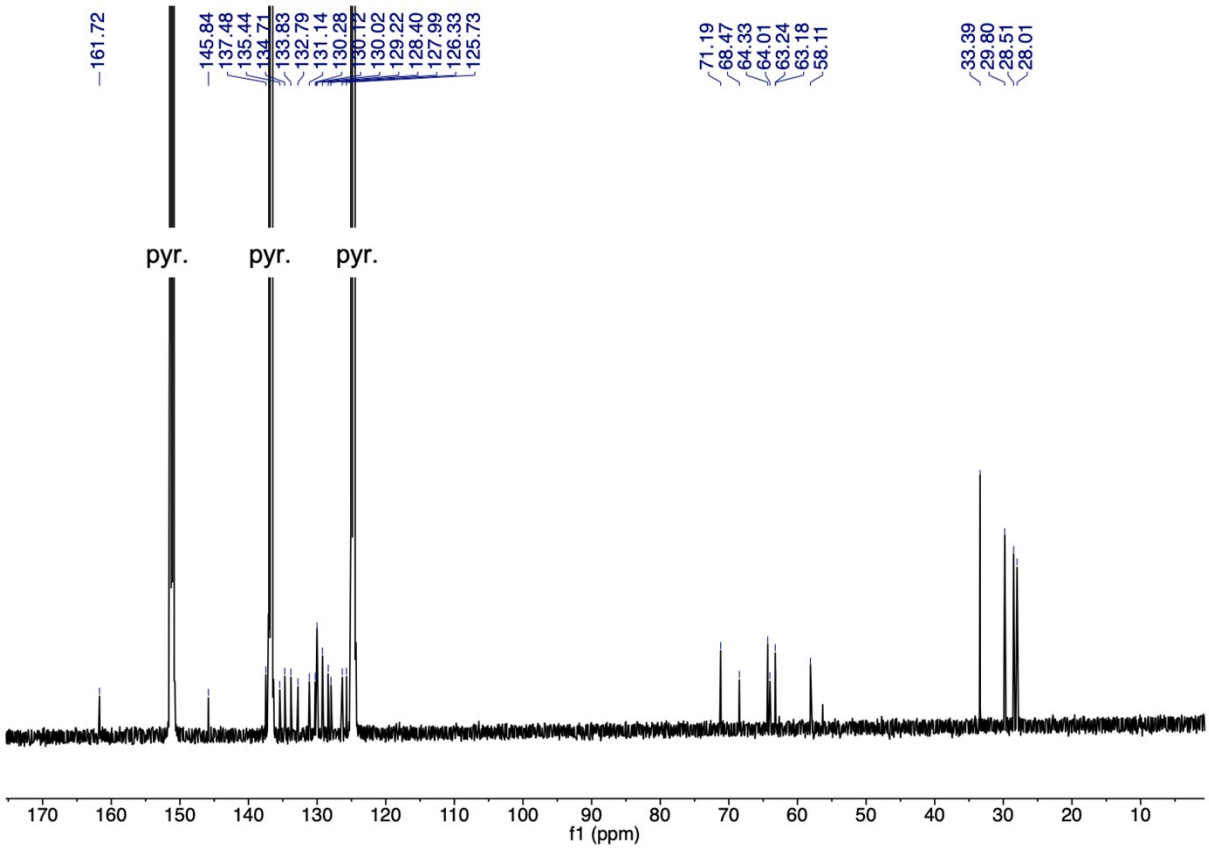

Fig. S12 $^{13}C\{^{1}H\}$ NMR spectrum of **2-Ta** in pyridine-d_5 (101 MHz, 300 K).

Infrared Spectra

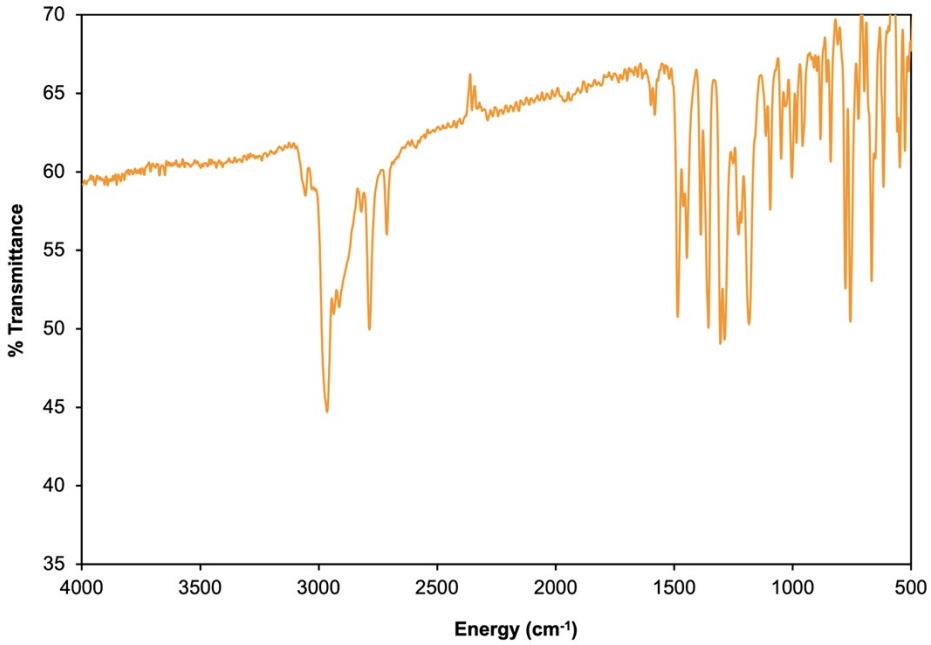

Fig. S13 IR spectrum of **1-Ta** (KBr pellet).

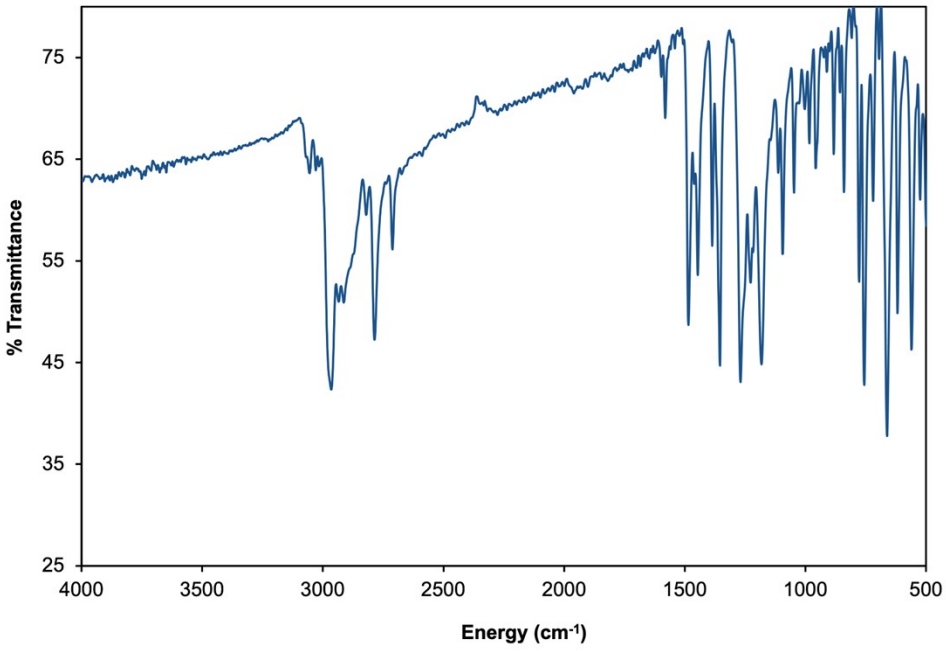

Fig. S14 IR spectrum of **1-Nb** (KBr pellet).

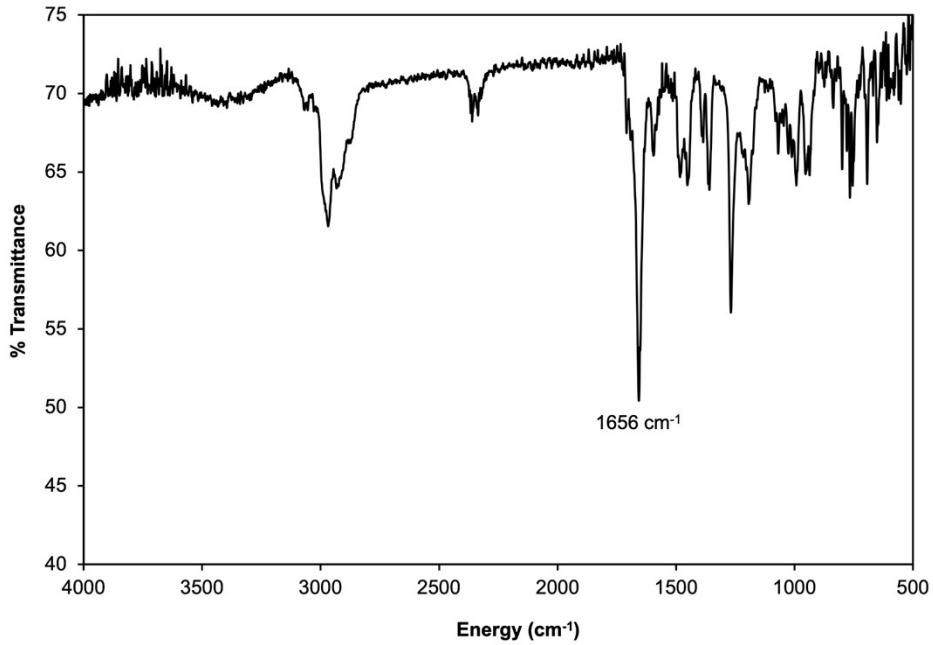

Fig. S15 IR spectrum of **2-Ta** (KBr pellet).

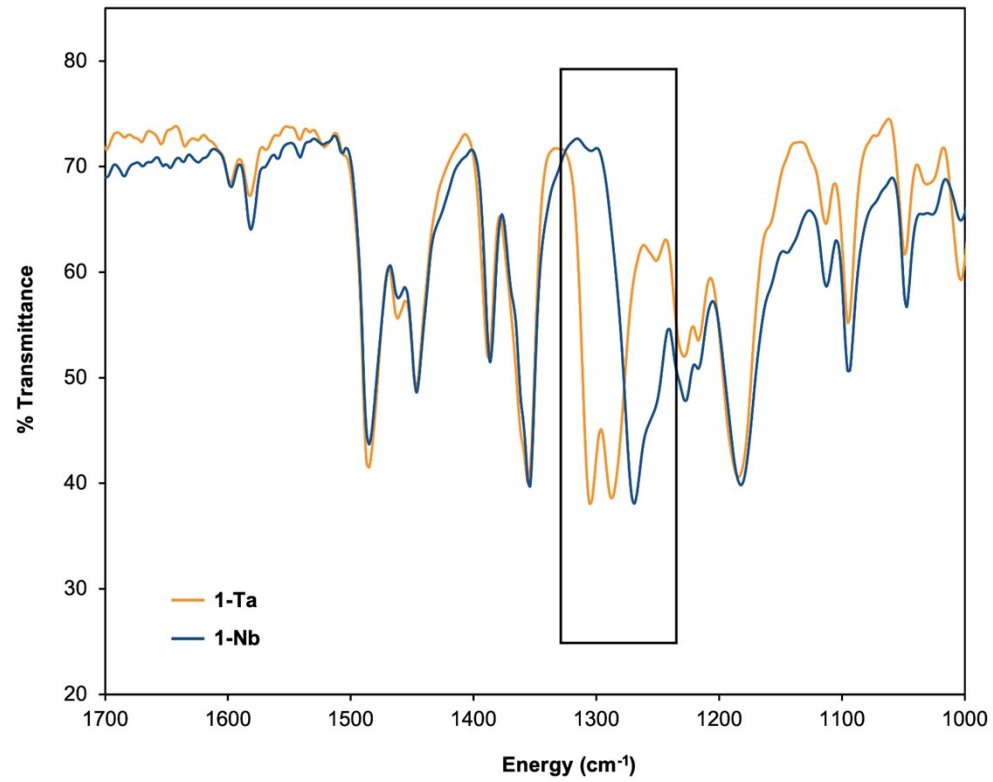

Fig. S16 Overlaid fingerprint regions of the IR spectra of **1-Ta** and **1-Nb** (KBr pellets).

Computational Details

Methods

All density functional theory (DFT) calculations were performed with QChem 5.3[5] at the B3LYP[6]/Def2-SVP[7] level of theory with a Def2 effective core potential (ECP). **1-M**, **2-M**, and **3-Ta** structures were obtained through geometry optimizations. Structures for **TS1-M** and **TS2-Ta** were obtained through constrained optimizations scanning relevant distances/bonds. All calculations were performed in a dielectric continuum of benzene. SCF and geometry optimization convergence was set to 10^{-8} and 10^{-6} respectively. Normal mode calculations were done on all structures to obtain entropy contributions to the energies and compute the IR spectra.

Computational Methods Testing

Several alternative functionals and basis sets were employed in probing the potential energy surface for the reaction of **1-M** + CO_2 → **2-M**. Single point energies were calculated at the different levels of theory in Orca 4.2.1 for the **1-M**, **TS1-M**, and **2-M** structures (obtained from geometry optimizations in QChem 5.3 at the B3LYP/Def2-SVP level of theory). For each combination, **TS1-Nb** was consistently higher in energy than **TS1-Ta**, and **2-Nb** was consistently higher in energy than **2-Ta** (Fig. S15).

The various levels of theory used were:

1. B3LYP/Def2-SVP
2. B3LYP(D3)/Def2-SVP
3. B3LYP/Def2-TZVP[5,7]
4. B3LYP/ZORA-Def2-SVP
5. ωB97XD[8]/Def2-SVP
6. ωB97XD/Def2-TZVP
7. M06-2X[9]/Def2-SVP
8. M06-2X/Def2-TZVP

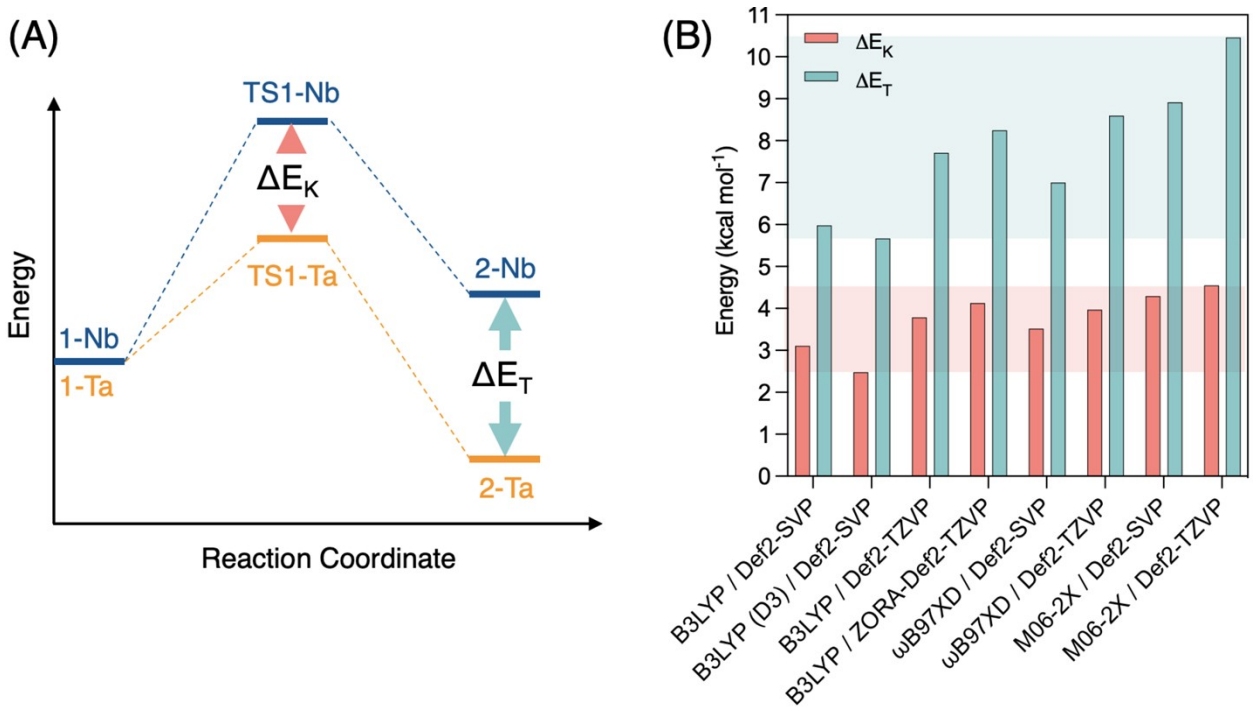

Fig. S17 Differences in the **TS1-M** electronic energies (ΔE_K) and **2-M** electronic energies (ΔE_T) calculated using various functional/basis set combinations. The consistently positive values show that **TS1-Nb** is consistently calculated to be higher in energy than **TS1-Ta**, and **2-Nb** is consistently calculated to be higher in energy than **2-Ta**.

Computed Vibrational Modes

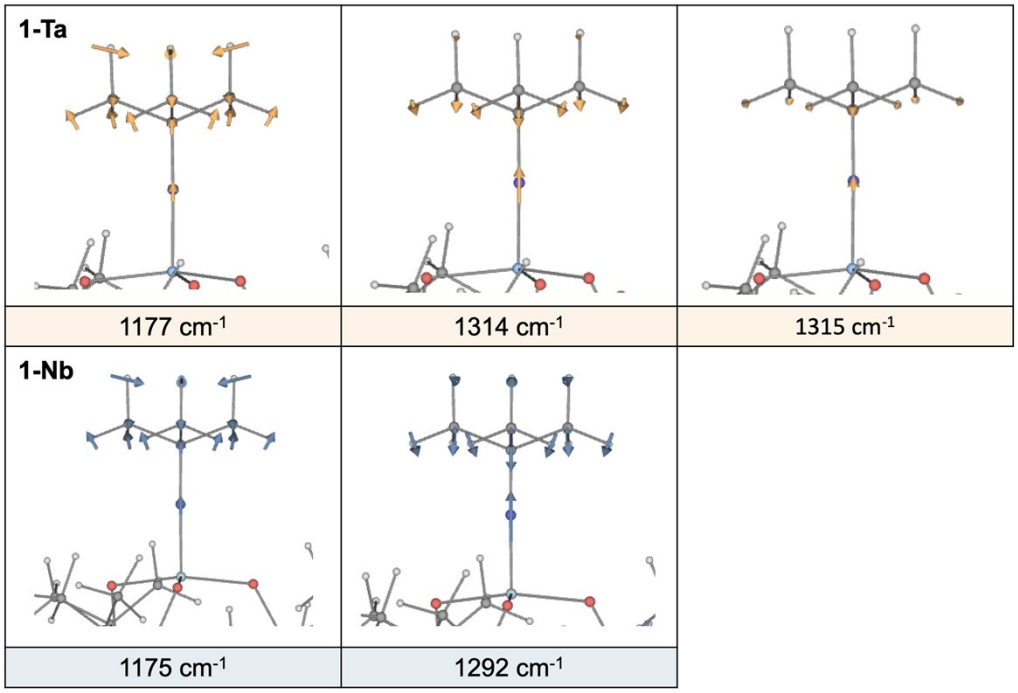

Fig. S18 Visualization of the metal-imido stretching modes for **1-M**. One symmetric stretching frequency is calculated at 1177 and 1175 cm^{-1} for **1-Ta** and **1-Nb** respectively. Two asymmetric stretching frequencies are calculated at 1314 and 1315 cm^{-1} for **1-Ta**, and one asymmetric stretching frequency is calculated at 1292 cm^{-1} for **1-Nb**.

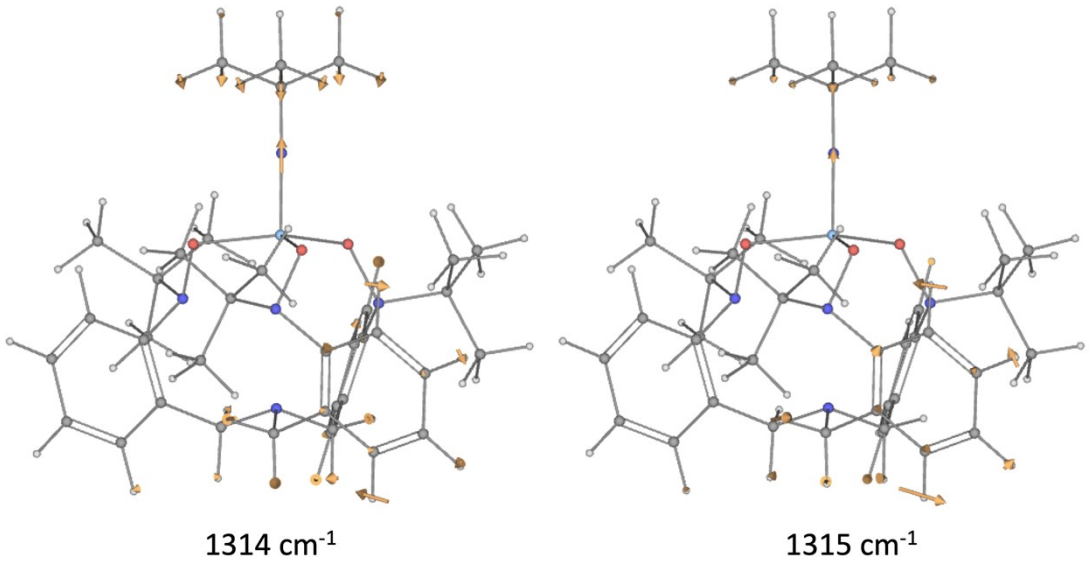

Fig. S19 Visualization of the two metal-imido asymmetric stretching modes calculated for **1-Ta**.

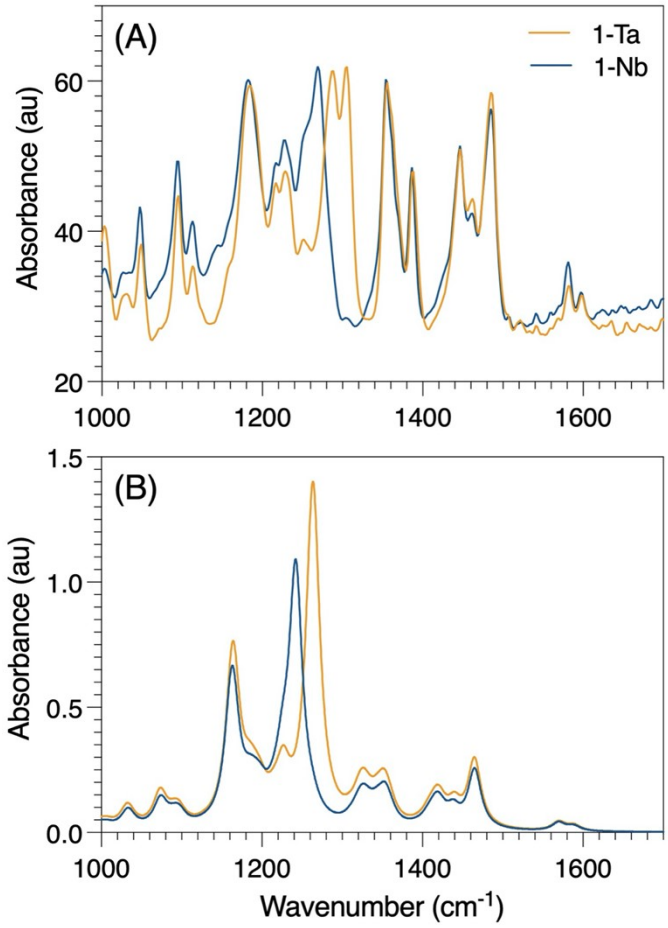

Fig. S20 Experimental IR spectra of **1-M** (A) and DFT-simulated IR spectra of **1-M** (B).

Computational Cartesian Coordinates (Å)

1-Ta

Energy = -1997.55016781288 Hartree

Atom	x	y	z
Ta	-0.0124329	-0.0481076	1.38317898
O	1.90992747	0.3898602	1.16152783
O	-0.5412688	-1.9521837	1.17994661
O	-1.3762976	1.37295245	1.0898813
N	2.45838288	-0.0767835	-0.0842219
N	-1.2087755	-2.0817411	-0.0898357

N	-1.1864696	2.09099687	-0.1410089
N	0.06315806	0.00628393	-2.3818294
N	-0.0291244	0.00649914	3.15504632
C	1.46562676	-0.0153052	-2.8256863
H	1.51826795	0.04491394	-3.93574
H	1.88475297	-0.9854655	-2.5403988
C	2.31385498	1.0959455	-2.244385
C	2.66284569	2.19592774	-3.0467338
H	2.34406506	2.2040492	-4.0931051
C	3.38626953	3.276259	-2.5379063
H	3.64134494	4.11968643	-3.1846223
C	3.76047219	3.27674529	-1.191075
H	4.30378901	4.12603435	-0.7682116
C	3.44311028	2.1843079	-0.3829473
H	3.71811581	2.18973746	0.67057011
C	2.7527207	1.07638761	-0.9035411
C	3.62805743	-0.9868608	0.22891153
C	3.08837501	-2.2028313	0.99667835
H	2.70945307	-1.9199302	1.98894418
H	3.89994829	-2.9319175	1.14398707
H	2.28184536	-2.6977888	0.43945863
C	4.72102116	-0.309742	1.08067706
H	4.29146665	0.14296656	1.98595177
H	5.27106758	0.46286398	0.52372848
H	5.45371221	-1.0684345	1.3976821
C	4.24007439	-1.4669427	-1.0960024
H	5.08399245	-2.1380567	-0.8747891
H	4.62448282	-0.6329262	-1.7008644
H	3.51329759	-2.0337489	-1.6953745
C	-0.6509019	-1.1937944	-2.8426811
H	-0.6145019	-1.2593808	-3.9533651
H	-1.7027791	-1.0683272	-2.5703431
C	-0.1317606	-2.4987538	-2.2768901
C	0.63740343	-3.3418999	-3.0979161
H	0.81980433	-3.0391235	-4.1329334
C	1.18206707	-4.536614	-2.6250436
H	1.77790101	-5.1690161	-3.2882323

C	0.97324498	-4.902702	-1.2926062
H	1.41122937	-5.8224264	-0.8958352
C	0.19997534	-4.0892383	-0.4639491
H	0.05637237	-4.361573	0.58036757
C	-0.3829599	-2.9047402	-0.9484755
C	-2.6149786	-2.5942731	0.17067939
C	-3.3300233	-1.575091	1.07032746
H	-2.907335	-1.5630506	2.0846021
H	-4.3940515	-1.8446226	1.15408355
H	-3.2646548	-0.5637601	0.6482432
C	-2.6360722	-3.9698708	0.86546637
H	-2.2928203	-4.7799271	0.2058646
H	-3.6694031	-4.2042604	1.16583661
H	-2.0140548	-3.9586169	1.7716924
C	-3.3592418	-2.6824746	-1.1701516
H	-3.4793054	-1.6916816	-1.6312692
H	-4.3650101	-3.0929418	-0.9925796
H	-2.8508731	-3.3484274	-1.8830885
C	-0.6105424	1.22247814	-2.8641416
H	-0.6375016	1.22951939	-3.9772341
H	0.00023818	2.07763592	-2.5584877
C	-2.0230089	1.39744456	-2.350121
C	-3.1101125	1.15625198	-3.2079473
H	-2.9090596	0.88253274	-4.2476507
C	-4.430338	1.23637707	-2.7614104
H	-5.255413	1.03958493	-3.4507786
C	-4.6837217	1.54739277	-1.4224819
H	-5.7103301	1.58765185	-1.0486309
C	-3.6195021	1.81236499	-0.5597179
H	-3.8114904	2.03877884	0.48769869
C	-2.2905268	1.77603874	-1.0174216
C	-0.9954558	3.55696975	0.19251285
C	0.27176729	3.67834389	1.05230886
H	1.13165506	3.21370291	0.5512147
H	0.1374226	3.20818482	2.03663186
H	0.50501358	4.74155855	1.21782343
C	-2.1810229	4.17179646	0.96467484

H	-1.9049322	5.18332668	1.30153011
H	-2.4247368	3.57431021	1.85498367
H	-3.0825603	4.26857641	0.34266258
C	-0.7839752	4.32935737	-1.1189063
H	0.11562704	3.98189625	-1.6465743
H	-0.6456872	5.39663014	-0.8881488
H	-1.6496222	4.24278155	-1.7918293
C	-0.0678161	0.06737789	4.59583929
C	-0.7850845	-1.1856433	5.13982582
H	-1.8108868	-1.2477683	4.74397926
H	-0.8390326	-1.1540822	6.24034252
H	-0.2476012	-2.1003442	4.84523677
C	1.37591747	0.11942657	5.13680961
H	1.93646205	-0.777507	4.830325
H	1.37792233	0.1703944	6.2379745
H	1.90353612	1.00388757	4.74717654
C	-0.8341939	1.3360189	5.02534674
H	-0.3388997	2.23775376	4.63278997
H	-1.8651309	1.31573826	4.63910227
H	-0.8761665	1.41373171	6.12409066

1-Nb

Energy = -1997.50088045929 Hartree

Atom	x	y	z
Nb	-0.0074822	-0.0340027	1.37047792
O	1.91260438	0.39589777	1.1679171
O	-0.5542858	-1.9278239	1.17995774
O	-1.3591313	1.39671636	1.11106689
N	2.44584841	-0.0823005	-0.0745918
N	-1.2227706	-2.0613105	-0.0826789
N	-1.159114	2.09693031	-0.12364
N	0.05883109	0.00499219	-2.3832102
N	-0.0235442	0.00623748	3.12235191
C	1.46024087	-0.0274589	-2.8270038
H	1.51391208	0.03179007	-3.9372212

H	1.87139979	-1.0011815	-2.542049
C	2.3174379	1.07735987	-2.246579
C	2.67921112	2.16971694	-3.0538928
H	2.36233217	2.17515845	-4.1008542
C	3.41198216	3.24582999	-2.5497332
H	3.67678433	4.08307288	-3.2005758
C	3.78385938	3.24952966	-1.2023293
H	4.33576184	4.0950367	-0.7829836
C	3.45292024	2.16506141	-0.3890303
H	3.72724836	2.17280874	0.66463726
C	2.75190388	1.06111853	-0.9040998
C	3.60661737	-1.0074851	0.23430411
C	3.05841577	-2.2121625	1.01376689
H	2.69290706	-1.9190726	2.00807627
H	3.86217853	-2.9509095	1.15627912
H	2.23977042	-2.6991859	0.46744422
C	4.71415323	-0.339099	1.07415657
H	4.29720651	0.12083449	1.98170107
H	5.26693828	0.42637528	0.51012761
H	5.44166105	-1.1044835	1.38696499
C	4.20408472	-1.5037875	-1.0910524
H	5.04030185	-2.1845336	-0.8700148
H	4.59668774	-0.6790784	-1.7033864
H	3.46641167	-2.0648707	-1.6822182
C	-0.664518	-1.1894202	-2.8420278
H	-0.6286575	-1.2580826	-3.9527156
H	-1.7154919	-1.0551415	-2.5702434
C	-0.1548106	-2.4961496	-2.2720427
C	0.60614788	-3.3484351	-3.0913095
H	0.78775221	-3.051468	-4.1281564
C	1.14359284	-4.544879	-2.6145385
H	1.7328977	-5.1847662	-3.2763983
C	0.93595004	-4.9028745	-1.2797275
H	1.36805528	-5.8240351	-0.8797727
C	0.17093201	-4.0798199	-0.4528066
H	0.02718504	-4.3475698	0.59269179
C	-0.4052752	-2.8933162	-0.9408375

C	-2.6322289	-2.5639872	0.18121115
C	-3.3386579	-1.5399523	1.0818505
H	-2.9077236	-1.5238586	2.09253776
H	-4.4025962	-1.8075341	1.17410209
H	-3.2742838	-0.5306616	0.65524371
C	-2.6604596	-3.9387695	0.87772792
H	-2.323126	-4.7515424	0.21842587
H	-3.6945108	-4.1667956	1.18054927
H	-2.0363699	-3.9304039	1.782626
C	-3.3816023	-2.6494836	-1.1570485
H	-3.4982881	-1.6583592	-1.6183489
H	-4.388874	-3.0549917	-0.9763247
H	-2.8787511	-3.3181532	-1.8713475
C	-0.6070125	1.22625792	-2.8602907
H	-0.6438231	1.23405616	-3.9732508
H	0.01382288	2.07628184	-2.5607335
C	-2.0133825	1.41319838	-2.3335804
C	-3.1083809	1.18124773	-3.1840502
H	-2.915845	0.906718	-4.225166
C	-4.4250665	1.27152837	-2.7293738
H	-5.2561177	1.08148442	-3.4134338
C	-4.666782	1.58471595	-1.3889193
H	-5.690436	1.63428025	-1.008111
C	-3.5946916	1.8405952	-0.5333049
H	-3.778466	2.06989561	0.51495934
C	-2.2685401	1.79221568	-0.9985106
C	-0.9477241	3.56631658	0.19221693
C	0.31377961	3.68456276	1.0605215
H	1.17571282	3.2141952	0.56888238
H	0.17005101	3.22065926	2.04623577
H	0.55025974	4.74792509	1.221045
C	-2.1313289	4.20496419	0.94792807
H	-1.8467951	5.21834046	1.27183502
H	-2.3854035	3.62227368	1.8450457
H	-3.0285267	4.30119641	0.31960822
C	-0.7146701	4.3212866	-1.1255315
H	0.18795065	3.95970551	-1.6382041

H	-0.5684212	5.38969862	-0.9049919
H	-1.573082	4.23614657	-1.8078135
C	-0.0704028	0.04805699	4.56511871
C	-0.453374	-1.3495022	5.0943997
H	-1.4410393	-1.653131	4.71385244
H	-0.4924864	-1.3477278	6.19575187
H	0.28461931	-2.1014715	4.7743916
C	1.3190634	0.45402898	5.09865219
H	2.08380636	-0.2756189	4.79020694
H	1.31011454	0.50197574	6.19957714
H	1.60959657	1.44250773	4.71022887
C	-1.1262148	1.08565301	4.99998146
H	-0.8680493	2.08569395	4.61901854
H	-2.1194441	0.81453003	4.6103218
H	-1.1852321	1.13752318	6.0991749

TS1-Ta

Energy = -2185.9721807663 Hartree

Atom	x	y	z
Ta	0.57538394	-0.4559421	-0.3135532
O	1.22209187	0.24889653	1.40802042
O	1.88205335	0.51589327	-1.4576406
O	-1.0223702	-0.8618727	-1.3971352
O	-0.6019763	-1.9176165	1.19367814
O	0.67042354	-3.8119827	1.55047739
N	1.45251013	-0.3010137	2.68174608
N	0.91407957	1.56279909	-1.5831183
N	-2.3772762	-1.2164594	-1.4286755
N	-1.2691919	1.3314757	0.79145523
N	1.50811926	-2.0480634	-0.4066951
C	-0.9400467	1.59656612	2.2251889
H	-1.6892095	2.31868261	2.60677083
H	0.02563683	2.10400641	2.23726285
C	-0.907274	0.43482264	3.19969251
C	-2.053704	0.203124	3.98106852

H	-2.9251221	0.84517903	3.82473718
C	-2.1135662	-0.7936418	4.95484209
H	-3.0240849	-0.938202	5.54146877
C	-0.9951186	-1.6061089	5.15566835
H	-1.0191809	-2.4136052	5.89240424
C	0.15135676	-1.4068239	4.39019738
H	0.99912014	-2.0817223	4.50328449
C	0.2337919	-0.3784117	3.43016245
C	2.65771211	0.3716398	3.29084245
C	2.44200237	1.88907566	3.45004163
H	2.24909899	2.36431875	2.4788024
H	3.34267263	2.35449011	3.88051874
H	1.5997418	2.10512424	4.12684803
C	3.85289645	0.10498645	2.36270025
H	4.03482951	-0.9761414	2.27641943
H	4.75727283	0.57654882	2.77763292
H	3.6821385	0.50826998	1.35659083
C	2.97304208	-0.2395241	4.66453948
H	2.18844937	-0.0369132	5.40664997
H	3.90700263	0.20836585	5.03771933
H	3.12539136	-1.3269594	4.59832343
C	-1.1774475	2.6363986	0.07978984
H	-1.5255436	2.47493679	-0.9422958
H	-1.867748	3.36708797	0.54525043
C	0.21250698	3.23820605	0.06166035
C	0.51105221	4.36551286	0.84367238
H	-0.28623	4.82472839	1.43460135
C	1.80327792	4.89218572	0.89964632
H	2.0099367	5.76786554	1.51991046
C	2.83384019	4.27132522	0.1881283
H	3.85706437	4.64974176	0.25387605
C	2.55489937	3.16348543	-0.6141788
H	3.35389813	2.66339487	-1.1600894
C	1.24528627	2.67536725	-0.7129644
C	0.76122263	1.91836924	-3.0686689
C	-0.301612	3.01310606	-3.2358175
H	-1.3065902	2.65479024	-2.9720289

H	-0.3279339	3.3117504	-4.294708
H	-0.0741622	3.91316497	-2.6463736
C	0.31977417	0.66886648	-3.8416898
H	1.07944906	-0.1234709	-3.7937295
H	0.18035626	0.94025217	-4.8991376
H	-0.6233044	0.26808274	-3.4530925
C	2.10156823	2.41217375	-3.6448964
H	2.38814913	3.39956255	-3.2560209
H	2.00278358	2.50460786	-4.7371542
H	2.90859233	1.69628679	-3.4353834
C	-2.65626	0.7689545	0.6931362
H	-2.6070454	-0.2888889	0.98438336
H	-3.29597	1.29189349	1.42831915
C	-3.3395548	0.89162967	-0.651348
C	-4.2038625	1.97796974	-0.8635258
H	-4.3471041	2.69742379	-0.0524795
C	-4.8910493	2.16019569	-2.0646175
H	-5.5599486	3.01459955	-2.1934646
C	-4.7068327	1.23526283	-3.0926812
H	-5.2182505	1.36071143	-4.0508608
C	-3.8589288	0.14204186	-2.903272
H	-3.7207169	-0.5559428	-3.7246395
C	-3.1855959	-0.0705643	-1.6837944
C	-2.5928209	-2.5328716	-2.1019334
C	-4.0996442	-2.8544448	-2.1207631
H	-4.5360278	-2.7121026	-1.1199458
H	-4.2289683	-3.9108792	-2.4003968
H	-4.6725945	-2.2501804	-2.8346531
C	-1.9191746	-3.606157	-1.2257953
H	-0.8365741	-3.4489847	-1.1702514
H	-2.0927903	-4.6018575	-1.6617435
H	-2.3347206	-3.5913406	-0.2079336
C	-1.9758315	-2.6114603	-3.5147431
H	-2.4502364	-1.9290623	-4.2338524
H	-2.0797335	-3.6340062	-3.9096759
H	-0.9037472	-2.3709061	-3.4736464
C	0.21942653	-2.7951554	1.18500985

C	2.5234545	-2.9697113	-0.9106357
C	3.25825788	-2.301759	-2.0940515
H	2.55937405	-2.0765013	-2.9142461
H	4.03989097	-2.974497	-2.4832939
H	3.73210329	-1.3599424	-1.7819381
C	1.8841919	-4.2813043	-1.4179284
H	1.3691797	-4.8199481	-0.6110191
H	2.6607253	-4.9456767	-1.8308227
H	1.15849481	-4.0712609	-2.2184818
C	3.55792182	-3.2875114	0.19039432
H	4.04560141	-2.3632948	0.53377853
H	4.33778018	-3.9608218	-0.2019083
H	3.08582297	-3.7755006	1.05409128

TS1-Nb

Energy = -2185.9174976065

Atom	x	y	z
Nb	0.57684245	-0.4428676	-0.3152948
O	1.20915849	0.25232509	1.40263158
O	1.93855888	0.4964149	-1.4198377
O	-1.0105987	-0.832598	-1.4155372
O	-0.612733	-1.9082209	1.17411239
O	0.66533217	-3.7997779	1.50433902
N	1.44540147	-0.3025205	2.66951546
N	0.95978146	1.51637806	-1.5585244
N	-2.3639492	-1.1803498	-1.4376947
N	-1.2730234	1.3421708	0.79963006
N	1.4872652	-2.0352552	-0.401447
C	-0.9383686	1.6055711	2.2301525
H	-1.6833387	2.33047722	2.61580708
H	0.02898666	2.11003447	2.24020305
C	-0.9068684	0.44195145	3.20281441
C	-2.0502916	0.21451889	3.98953514
H	-2.9187937	0.86214204	3.84008964
C	-2.1107153	-0.7855491	4.96002366

H	-3.0189853	-0.9269552	5.55092192
C	-0.995985	-1.6051614	5.152315
H	-1.0209036	-2.4149107	5.88653537
C	0.14784609	-1.4096821	4.38174647
H	0.99269841	-2.0891765	4.4891721
C	0.23023009	-0.3790261	3.4245662
C	2.65585551	0.36557464	3.27524713
C	2.44100897	1.88208936	3.44540253
H	2.24574239	2.36345095	2.47752597
H	3.34305364	2.34427633	3.87642427
H	1.60076142	2.09357397	4.12601902
C	3.84373449	0.10652901	2.33603074
H	4.0366696	-0.9729156	2.2535819
H	4.74753855	0.58917644	2.73917554
H	3.65660149	0.50287584	1.32999618
C	2.98010271	-0.2547636	4.64254283
H	2.20162873	-0.054376	5.39171878
H	3.91822342	0.18788404	5.01171848
H	3.12836068	-1.3422519	4.56833292
C	-1.1705941	2.64006757	0.08184721
H	-1.5268963	2.47856981	-0.9366279
H	-1.8497314	3.38311785	0.54509881
C	0.22489489	3.22956274	0.0531297
C	0.52254641	4.36899881	0.81914858
H	-0.2784596	4.83798449	1.39714251
C	1.81453693	4.89449736	0.87807096
H	2.01769833	5.77888593	1.48703284
C	2.84888762	4.26140133	0.18315851
H	3.87237992	4.63899713	0.24887836
C	2.5723864	3.14201837	-0.6025905
H	3.37271354	2.63351586	-1.1385676
C	1.26342789	2.65212297	-0.703601
C	0.78044008	1.84673124	-3.0521306
C	-0.4409849	2.75620092	-3.2331407
H	-1.3730014	2.23387983	-2.9747054
H	-0.5064778	3.04631721	-4.29272
H	-0.3653771	3.68062909	-2.6427367

C	0.5601354	0.54527299	-3.8345579
H	1.45300345	-0.0924341	-3.8098348
H	0.35141043	0.80126492	-4.8843533
H	-0.2877299	-0.0192833	-3.4324458
C	2.03692341	2.54607651	-3.6032101
H	2.17370981	3.55596885	-3.1917614
H	1.9346937	2.64231814	-4.6949259
H	2.94078615	1.95280323	-3.4017283
C	-2.660024	0.78499544	0.70389027
H	-2.6138625	-0.2738534	0.99193344
H	-3.2985306	1.3074297	1.44099813
C	-3.3421941	0.91544415	-0.6398374
C	-4.2142939	1.99753849	-0.8424091
H	-4.3646082	2.7067806	-0.0236931
C	-4.9000456	2.18724328	-2.0430729
H	-5.5764508	3.03691584	-2.1639362
C	-4.7040178	1.27632038	-3.0814523
H	-5.2139145	1.40793502	-4.0396326
C	-3.8455726	0.18957164	-2.9022003
H	-3.6996392	-0.4977313	-3.7312489
C	-3.1760138	-0.032996	-1.6821229
C	-2.5967828	-2.4957787	-2.1092933
C	-4.1071808	-2.8011898	-2.121794
H	-4.5381442	-2.6527366	-1.1195885
H	-4.2488228	-3.8564873	-2.399645
H	-4.6762486	-2.1916018	-2.8341961
C	-1.9309494	-3.5783203	-1.2390229
H	-0.8471888	-3.4303493	-1.1843525
H	-2.112659	-4.5699233	-1.6811869
H	-2.3446583	-3.5674948	-0.220524
C	-1.9889512	-2.5834054	-3.5259821
H	-2.4360869	-1.8735385	-4.2357867
H	-2.1384375	-3.5963366	-3.9307692
H	-0.9071496	-2.3905097	-3.4890106
C	0.21992564	-2.7767116	1.14159954
C	2.5114692	-2.9495105	-0.910747
C	3.26560729	-2.2689301	-2.0739849

H	2.58177046	-2.0193714	-2.8991766
H	4.0398817	-2.9492201	-2.4643351
H	3.75277578	-1.3414822	-1.7411665
C	1.87030361	-4.2493827	-1.4454634
H	1.34197379	-4.7968374	-0.6536791
H	2.6498284	-4.9105016	-1.8574874
H	1.15670185	-4.0243374	-2.2528228
C	3.53169849	-3.2868758	0.19785451
H	4.01089719	-2.3687384	0.56718615
H	4.31909147	-3.9462797	-0.2025431
H	3.05274733	-3.7973869	1.04382331

2-Ta

Energy = -2186.03033340307 Hartree

Atom	x	y	z
Ta	0.3869635	-0.3342779	-0.2293046
O	1.33182089	0.26890982	1.37125937
O	1.87324411	0.37296262	-1.4020632
O	-1.0976774	-0.7377595	-1.4439773
O	-0.3904439	-1.7933861	0.96846007
O	0.49953532	-3.8684571	1.15682599
N	1.52420599	-0.2106761	2.67256946
N	0.97078533	1.44594608	-1.5677755
N	-2.4416083	-1.1305511	-1.5150595
N	-1.2187672	1.27609277	0.75983467
N	1.35302115	-2.2084209	-0.28468
C	-0.8982056	1.56009611	2.2081815
H	-1.657636	2.27932216	2.56260042
H	0.06467818	2.07312056	2.21763028
C	-0.863727	0.39643527	3.17020681
C	-2.013499	0.10895337	3.92588271
H	-2.905746	0.72341769	3.77693473
C	-2.0456835	-0.916567	4.87007714
H	-2.9559961	-1.1106364	5.44237455
C	-0.9011572	-1.69597	5.0599771

H	-0.9081035	-2.526737	5.77045226
C	0.24769659	-1.4375215	4.31681765
H	1.11718896	-2.085403	4.41830398
C	0.3007797	-0.3809333	3.38854911
C	2.69090472	0.50159066	3.29975026
C	2.42214821	2.01062882	3.45887316
H	2.23306043	2.48021436	2.48379037
H	3.29858856	2.50647274	3.90513163
H	1.5610496	2.19811083	4.12040762
C	3.91067114	0.28007707	2.39032665
H	4.12286401	-0.7947682	2.29070522
H	4.79451616	0.76832111	2.82922151
H	3.7465999	0.69443132	1.3871734
C	2.99778488	-0.1060973	4.67699004
H	2.18577621	0.05698397	5.39910045
H	3.90214776	0.37785627	5.0766817
H	3.19572845	-1.1855374	4.60586235
C	-1.1239574	2.5936128	0.04308659
H	-1.4983475	2.43461937	-0.969273
H	-1.8038005	3.31306974	0.531233
C	0.26780802	3.18911359	0.00805279
C	0.56389606	4.34570303	0.74692762
H	-0.2345738	4.82836885	1.31674881
C	1.85710648	4.870864	0.78492945
H	2.06366198	5.77044441	1.36973983
C	2.88996051	4.21919876	0.10456466
H	3.91320894	4.59864353	0.16014297
C	2.61417507	3.07989202	-0.6532105
H	3.41315032	2.55730455	-1.1777196
C	1.30416907	2.59550193	-0.738546
C	0.79372741	1.75818276	-3.0741602
C	-0.4120858	2.68529171	-3.2673331
H	-1.3546757	2.18058388	-3.010435
H	-0.4671359	2.96634789	-4.3298142
H	-0.3247098	3.61474754	-2.6864711
C	0.55962666	0.45333662	-3.8432807
H	1.43587605	-0.2050419	-3.7921228

H	0.38046158	0.70435188	-4.8993891
H	-0.311679	-0.0838156	-3.4573027
C	2.06518808	2.42969834	-3.6230652
H	2.21698957	3.44224073	-3.2245745
H	1.96890709	2.51423714	-4.7160178
H	2.95673995	1.82190703	-3.4104313
C	-2.6349677	0.73852192	0.67731578
H	-2.5918538	-0.3314148	0.92248946
H	-3.2212144	1.24488805	1.46026299
C	-3.3681097	0.93552168	-0.6290324
C	-4.2386753	2.02887336	-0.758187
H	-4.3375779	2.72418355	0.08041794
C	-4.996747	2.24138992	-1.9109772
H	-5.6705861	3.09883811	-1.9774606
C	-4.8812652	1.33981918	-2.9698568
H	-5.453509	1.48869676	-3.8894677
C	-4.0242387	0.24248741	-2.8652914
H	-3.9404786	-0.4345711	-3.7109822
C	-3.2724138	0.00512619	-1.6976343
C	-2.6339602	-2.432655	-2.2197232
C	-4.1279355	-2.8065566	-2.1566015
H	-4.4996954	-2.7314507	-1.1232642
H	-4.2390198	-3.8514122	-2.4825612
H	-4.767822	-2.1890215	-2.7993101
C	-1.8644272	-3.5055325	-1.4290781
H	-0.7834744	-3.3376702	-1.4797002
H	-2.0705495	-4.4953684	-1.8639994
H	-2.16538	-3.5127261	-0.3730439
C	-2.11047	-2.4437766	-3.6724907
H	-2.6274037	-1.7306417	-4.3296894
H	-2.2444339	-3.4481423	-4.1031812
H	-1.0356428	-2.2132375	-3.6973917
C	0.50576631	-2.754791	0.66279737
C	2.513473	-2.9769344	-0.8008838
C	3.34335173	-2.1065024	-1.7530254
H	2.74631477	-1.7684483	-2.6114563
H	4.19140258	-2.695229	-2.1359773

H	3.74059452	-1.2179103	-1.2431341
C	2.01809598	-4.2180408	-1.5741664
H	1.40401108	-4.8602195	-0.9287579
H	2.87585309	-4.8067225	-1.938884
H	1.41708953	-3.915728	-2.4465281
C	3.41957998	-3.4173148	0.36893834
H	3.76706379	-2.5366778	0.93015777
H	4.30296267	-3.9517737	-0.016873
H	2.87967624	-4.0799253	1.05719037

2-Nb

Energy = -2185.97128581822 Hartree

Atom	x	y	z
Nb	0.38109474	-0.3261506	-0.2331029
O	1.32657985	0.25661207	1.35775722
O	1.86717643	0.36905277	-1.3963241
O	-1.0930364	-0.7333671	-1.4391049
O	-0.3996525	-1.7771124	0.96283296
O	0.48892453	-3.8492761	1.16469318
N	1.51738069	-0.2103792	2.65642221
N	0.97750939	1.43899905	-1.5613112
N	-2.4304492	-1.1246238	-1.5162192
N	-1.2239827	1.2829433	0.76153754
N	1.34447909	-2.199023	-0.2844488
C	-0.897811	1.56300722	2.20654088
H	-1.6512098	2.28650962	2.56641106
H	0.06800227	2.07092444	2.21415267
C	-0.865142	0.39827569	3.16694469
C	-2.0118246	0.11367673	3.92789742
H	-2.9027298	0.73143347	3.78480983
C	-2.0422276	-0.9137978	4.87023039
H	-2.9501264	-1.1058954	5.44703904
C	-0.8993149	-1.6971646	5.05332592
H	-0.9053157	-2.5287426	5.76281878
C	0.24706794	-1.4407407	4.30538384

H	1.1153939	-2.0908413	4.402371
C	0.29708369	-0.3836938	3.37799832
C	2.6905666	0.4957508	3.28068649
C	2.42345348	2.00394181	3.44999796
H	2.2310953	2.47910896	2.47823014
H	3.30215972	2.49639792	3.89546229
H	1.56522763	2.18801254	4.11608523
C	3.90394758	0.27942473	2.36188835
H	4.11804362	-0.7944354	2.25695827
H	4.78953865	0.76791345	2.79686435
H	3.731806	0.69707588	1.36146968
C	3.00472251	-0.1205322	4.65226367
H	2.19774419	0.0403377	5.38049123
H	3.91261259	0.35931725	5.04894601
H	3.19991784	-1.1999126	4.573539
C	-1.1256854	2.5977497	0.04452459
H	-1.5010819	2.43979894	-0.9675347
H	-1.8021755	3.32184246	0.53143977
C	0.26833863	3.18876429	0.00847881
C	0.56568452	4.34755403	0.74357165
H	-0.2333377	4.83429891	1.3091352
C	1.86005341	4.8697642	0.78401241
H	2.06670751	5.77126499	1.36583876
C	2.89355066	4.21292373	0.10982702
H	3.91750907	4.59023746	0.16664083
C	2.6170555	3.07117303	-0.6440351
H	3.41594816	2.5456574	-1.1659853
C	1.30630617	2.58937984	-0.7314274
C	0.79065911	1.75119479	-3.0680137
C	-0.4227371	2.66822048	-3.2594998
H	-1.3607632	2.15732498	-2.9989237
H	-0.4825872	2.94644245	-4.3224454
H	-0.340034	3.59957431	-2.6810817
C	0.56965456	0.44501959	-3.8385749
H	1.45247471	-0.2045252	-3.7893154
H	0.38759521	0.69655253	-4.8941279
H	-0.2961951	-0.1015691	-3.4539579

C	2.05524984	2.43609656	-3.61719
H	2.19949655	3.44798428	-3.2142011
H	1.95509925	2.52469584	-4.7094936
H	2.95317915	1.83567076	-3.4103087
C	-2.6360802	0.74240871	0.68070375
H	-2.588421	-0.3274192	0.92566737
H	-3.2259456	1.2464189	1.46308726
C	-3.3683501	0.93679922	-0.6263856
C	-4.2418834	2.02764457	-0.7574526
H	-4.3453454	2.72177277	0.08156355
C	-4.9963382	2.23931486	-1.9127089
H	-5.6726612	3.09471609	-1.9804434
C	-4.8736863	1.34013832	-2.9728831
H	-5.4425049	1.48887125	-3.8946219
C	-4.0132314	0.24573132	-2.8666767
H	-3.9225799	-0.4294076	-3.7132769
C	-3.2662403	0.0088909	-1.6958631
C	-2.6264274	-2.4311319	-2.213803
C	-4.1216944	-2.7995996	-2.1525962
H	-4.4960184	-2.7180908	-1.1206898
H	-4.234822	-3.8458115	-2.4734312
H	-4.7578214	-2.1835254	-2.8003945
C	-1.8619328	-3.5024519	-1.4169746
H	-0.7807403	-3.3356007	-1.463125
H	-2.0672362	-4.4929587	-1.8508629
H	-2.1678148	-3.5070306	-0.3624415
C	-2.1000104	-2.4492469	-3.6653603
H	-2.609444	-1.7323913	-4.3243717
H	-2.2421578	-3.4531304	-4.0944369
H	-1.0230862	-2.2283427	-3.6886231
C	0.49687873	-2.7373902	0.66351837
C	2.50643064	-2.9685043	-0.7935177
C	3.34488692	-2.1010598	-1.7408529
H	2.75293906	-1.7589552	-2.6010831
H	4.1912837	-2.6941523	-2.1208127
H	3.74475385	-1.2158143	-1.2273651
C	2.01141119	-4.2078747	-1.5706924

H	1.39043494	-4.8476468	-0.9295267
H	2.86952665	-4.7997046	-1.9295492
H	1.41767956	-3.902754	-2.4469836
C	3.40559434	-3.4140607	0.38005147
H	3.75430412	-2.5356618	0.94365057
H	4.28851854	-3.9513449	-0.002964
H	2.85974117	-4.0751624	1.06496679

TS2-Ta

Energy = -1860.30123122254 Hartree

Atom	x	y	z
Ta	0.22839269	-0.4163615	-0.1106648
O	1.35252232	0.19335357	1.42150346
O	1.7310677	0.30714853	-1.3782073
O	-1.1704813	-0.6317799	-1.5106476
O	-0.4523634	-1.7457975	0.87496203
O	0.98561109	-4.0319611	1.12243689
N	1.46429111	-0.2934203	2.73495106
N	0.96079706	1.47820932	-1.5886452
N	-2.4995953	-1.1016225	-1.5450993
N	-1.2160655	1.25773223	0.74948892
N	1.64430333	-2.3399686	-0.4490249
C	-0.9077871	1.52987183	2.20930043
H	-1.6525291	2.26892991	2.55095963
H	0.07066642	2.01130551	2.2312388
C	-0.9251603	0.35964789	3.16427119
C	-2.1005034	0.09647028	3.88793867
H	-2.9699039	0.73971624	3.72575729
C	-2.1879014	-0.9418947	4.81519594
H	-3.1172923	-1.1160312	5.36272477
C	-1.0725259	-1.7592377	5.01816627
H	-1.1215916	-2.6005483	5.71473504
C	0.10164569	-1.5226261	4.30763989
H	0.95043056	-2.1958322	4.42162956
C	0.21445965	-0.4523958	3.39886351
C	2.61259235	0.38738719	3.42380361

C	2.39360301	1.90870129	3.53978884
H	2.26905653	2.36419004	2.54825786
H	3.2634584	2.38223165	4.02213379
H	1.5074222	2.14110271	4.15230004
C	3.8759922	0.1026682	2.59494516
H	4.05182371	-0.9821071	2.5305407
H	4.75191315	0.569344	3.07202699
H	3.78085302	0.49686865	1.57553967
C	2.81736749	-0.197361	4.83014353
H	1.96401172	-0.0043605	5.4949323
H	3.70479129	0.27646065	5.27732884
H	2.9962045	-1.2821772	4.79619901
C	-1.0855327	2.57841269	0.0327
H	-1.4318341	2.41856247	-0.9913349
H	-1.7754663	3.29542289	0.50860093
C	0.31437465	3.15458522	0.04790245
C	0.61848231	4.27540185	0.83627357
H	-0.1786486	4.75685539	1.40967373
C	1.92254215	4.76936357	0.91497381
H	2.13940534	5.64341758	1.53397222
C	2.95173234	4.11657004	0.22933725
H	3.98225444	4.4702678	0.31726036
C	2.66445375	3.01172732	-0.5752927
H	3.46551517	2.49464199	-1.1022744
C	1.34477901	2.55929407	-0.7080782
C	0.92812299	1.84903639	-3.0692435
C	0.12116822	3.14367983	-3.257708
H	-0.9241853	3.02079595	-2.9390533
H	0.10978586	3.39509306	-4.328947
H	0.56015622	3.99665361	-2.7208681
C	0.24509185	0.73181564	-3.8659019
H	0.78093108	-0.2201596	-3.7650204
H	0.23748595	1.0080738	-4.9315838
H	-0.7849444	0.57630682	-3.5285682
C	2.35503662	2.05147613	-3.6186646
H	2.83485328	2.95687894	-3.2205484
H	2.30903911	2.16152481	-4.7132514

H	2.98773707	1.18241862	-3.3891906
C	-2.6520296	0.75757173	0.65711403
H	-2.6303261	-0.3117715	0.90512599
H	-3.2173894	1.28172063	1.44219297
C	-3.404301	0.95967293	-0.6378347
C	-4.273457	2.05652943	-0.7415127
H	-4.3178712	2.77078386	0.08593382
C	-5.1038363	2.24617401	-1.847988
H	-5.7733607	3.10821717	-1.8952092
C	-5.0694599	1.30850726	-2.880362
H	-5.7046457	1.43164824	-3.7618028
C	-4.2106207	0.21016542	-2.8050042
H	-4.1935194	-0.4886287	-3.6361878
C	-3.3707521	0.00370732	-1.6923503
C	-2.638278	-2.3866302	-2.2879532
C	-4.0819797	-2.894158	-2.109781
H	-4.3313129	-2.9661995	-1.0399738
H	-4.1644753	-3.9005534	-2.5479146
H	-4.8344907	-2.259535	-2.5944932
C	-1.7083921	-3.4181535	-1.619011
H	-0.653259	-3.1873884	-1.8136771
H	-1.9178925	-4.4159399	-2.0340983
H	-1.8589838	-3.4404823	-0.531739
C	-2.2412721	-2.3018788	-3.7794506
H	-2.9308723	-1.700778	-4.3881746
H	-2.2196508	-3.313352	-4.2151212
H	-1.2339318	-1.8728735	-3.8787448
C	1.20701022	-3.1438014	0.40542565
C	2.87267019	-2.724999	-1.2679918
C	2.52193267	-2.5022624	-2.7430095
H	1.6969277	-3.1613621	-3.0548821
H	3.39862042	-2.7281542	-3.370095
H	2.22702912	-1.4591662	-2.9085606
C	3.24520174	-4.1985189	-1.0422103
H	3.52486466	-4.3985151	0.00353817
H	4.11312466	-4.4467114	-1.6716503
H	2.42318519	-4.8760026	-1.3220662

C	4.03219078	-1.8205649	-0.8327312
H	3.77123049	-0.7639701	-0.9742367
H	4.92516548	-2.0516973	-1.435076
H	4.27881993	-1.9862385	0.22671255

3-Ta

Energy = -2185.98386198675 Hartree

Atom	x	y	z
Ta	-0.0167969	-0.0605246	1.37592719
O	1.87544906	0.36006552	1.10177289
O	-0.5221748	-1.9461788	1.15892335
O	-1.3501324	1.33785757	1.02052804
N	2.48922902	-0.0983143	-0.1169188
N	-1.2220398	-2.0934774	-0.0942529
N	-1.1914237	2.11489418	-0.1788296
N	0.06434241	0.00943712	-2.3828151
C	1.46726917	-0.0264364	-2.8308733
H	1.51661837	0.02239414	-3.9412627
H	1.88204131	-0.9952818	-2.5341262
C	2.32333036	1.08502085	-2.2619368
C	2.66292925	2.18707152	-3.0651424
H	2.33551284	2.19781356	-4.1087521
C	3.38817064	3.26728079	-2.5585304
H	3.63572781	4.11313809	-3.2049622
C	3.77395668	3.26616909	-1.2149155
H	4.31691336	4.1168031	-0.7945993
C	3.46868002	2.17004232	-0.4069659
H	3.75302038	2.17554248	0.64409127
C	2.77775636	1.06244456	-0.9268021
C	3.65597504	-0.9891282	0.24253604
C	3.10065189	-2.2125201	0.98738751
H	2.6838655	-1.9366464	1.96683155
H	3.91396314	-2.9328466	1.16378647
H	2.32161139	-2.7146233	0.39799301
C	4.71142746	-0.3029989	1.13297547

H	4.24554629	0.14816927	2.02125885
H	5.27756489	0.47134256	0.59529277
H	5.43655412	-1.0558124	1.47983139
C	4.3098645	-1.4559335	-1.067269
H	5.15046157	-2.1245801	-0.8272273
H	4.70549707	-0.6140143	-1.6537837
H	3.60212196	-2.0202496	-1.6922049
C	-0.661166	-1.1877161	-2.8388405
H	-0.6349046	-1.2516964	-3.9495661
H	-1.7100706	-1.0580552	-2.5563177
C	-0.1449059	-2.4977368	-2.2815642
C	0.62545492	-3.3355396	-3.1070089
H	0.8114539	-3.0251059	-4.1390193
C	1.16767428	-4.5340754	-2.6415084
H	1.76570406	-5.161148	-3.307703
C	0.95361811	-4.912222	-1.3133103
H	1.38996059	-5.8352489	-0.9227889
C	0.17780844	-4.1055532	-0.4806384
H	0.03228942	-4.3872352	0.56092329
C	-0.400854	-2.916436	-0.9582788
C	-2.6204246	-2.6022063	0.2054172
C	-3.3163538	-1.5631896	1.09799245
H	-2.8771422	-1.5327219	2.10568215
H	-4.3784385	-1.8298653	1.20873055
H	-3.2603501	-0.5604097	0.65372334
C	-2.6302512	-3.9634706	0.92667012
H	-2.3016417	-4.787182	0.27680902
H	-3.658117	-4.1893773	1.25090852
H	-1.9926415	-3.9366286	1.82195417
C	-3.3819911	-2.7108631	-1.123771
H	-3.4974661	-1.7278925	-1.6027939
H	-4.3890123	-3.1083242	-0.9258624
H	-2.8875003	-3.3958509	-1.8285029
C	-0.5987966	1.22932459	-2.8763976
H	-0.6109532	1.23312224	-3.9893306
H	0.01037156	2.08306584	-2.5622735
C	-2.0169638	1.41222767	-2.3815027

C	-3.0966448	1.17127944	-3.2483983
H	-2.8880722	0.89227106	-4.2851269
C	-4.4201202	1.25752055	-2.8123618
H	-5.2400876	1.06118134	-3.5079008
C	-4.6847069	1.57295625	-1.4765446
H	-5.714348	1.61528295	-1.1116887
C	-3.6274782	1.83950952	-0.6054314
H	-3.8296807	2.06918923	0.43938995
C	-2.2958621	1.7998904	-1.0541586
C	-1.0147093	3.56507349	0.20955292
C	0.2679529	3.66690327	1.04963609
H	1.12410482	3.23547594	0.5130606
H	0.15954955	3.15669143	2.01782855
H	0.49136106	4.72490399	1.25618499
C	-2.1922151	4.14117188	1.02187035
H	-1.9174877	5.1402873	1.39448503
H	-2.4212161	3.50895116	1.89233546
H	-3.1021166	4.25706679	0.41577768
C	-0.8351617	4.37662355	-1.0830088
H	0.05386211	4.04942225	-1.6417834
H	-0.698664	5.43769636	-0.824637
H	-1.7147973	4.30230556	-1.739159
O	-0.0348912	0.0059864	3.10862958

X-ray Crystallographic Details

Structures of **1-Ta** and **2-Ta**:

X-ray data were collected on a on a Rigaku XtaLAB Synergy-S diffractometer[10] equipped with an HPC area detector (Dectris Pilatus3 R 200K) and employing confocal multilayer optic-monochromated MoKα radiation (λ = 0.71073 Å) at a temperature of 100 K. Preliminary indexing was preformed from a series of thirty 0.5° rotation frames with exposures of 0.625 seconds (**1-Ta**) or 15 seconds (**2-Ta**). A total of 1168 frames (9 runs, **1-Ta**) or 1248 frames (13 runs, **2-Ta**) were collected employing ω scans with a crystal to detector distance of 34.0 mm, rotation widths of 0.5° and exposures of 8.53 seconds (**1-Ta**) or 60 seconds (**2-Ta**).

Rotation frames were integrated using CrysAlisPro,[10] producing a listing of unaveraged F^2 and $\sigma(F^2)$ values. The intensity data were corrected for Lorentz and polarization effects and for absorption using SCALE3 ABSPACK[11] (minimum and maximum transmission 0.9260, 1.0000 (**1-Ta**) or 0.0718, 0.0972 (**2-Ta**)). The structures were solved by direct methods (**1-Ta**) or by dual methods (**2-Ta**) – SHELXT.[12] Refinement was by full-matrix least squares based on F^2 using SHELXL.[12] All reflections were used during refinement. The weighting scheme used was $w = 1/[\sigma^2(F_o^2) + (0.0184P)^2 + 16.1343P]$ (**1-Ta**) or $w = 1/[\sigma^2(F_o^2) + (0.0231P)^2 + 0.4969P]$ (**2-Ta**) where $P = (F_o^2 + 2F_c^2)/3$. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined using a riding model.

Table S3 Summary of Structure Determination of **1-Ta**.

Empirical formula	$C_{37}H_{54}N_5O_3Ta$
Formula weight	797.80
Diffractometer	Rigaku XtaLAB Synergy-S (Dectris Pilatus3 R 200K)
Temperature	100 K
Crystal system	triclinic
Space group	P**Error!**
a	10.1780(3) Å
b	12.1307(4) Å
c	15.7705(5) Å
α	91.362(2)°
β	90.315(3)°
γ	114.430(3)°
Volume	1772.04(10) $Å^3$
Z	2
d_{calc}	1.495 g/cm^3
μ	3.144 mm^{-1}
F(000)	816.0
Crystal size, mm	0.1 × 0.05 × 0.02
2θ range for data collection	4.564 - 56.564°
Index ranges	-13 ≤ h ≤ 13, -16 ≤ k ≤ 16, -21 ≤ l ≤ 20
Reflections collected	35950
Independent reflections	8790[R(int) = 0.0547]
Data/restraints/parameters	8790/0/427
Goodness-of-fit on F^2	1.147
Final R indexes [I>=2σ (I)]	R_1 = 0.0488, wR_2 = 0.1068
Final R indexes [all data]	R_1 = 0.0559, wR_2 = 0.1090
Largest diff. peak/hole	4.12/-2.56 $eÅ^{-3}$

Table S4 Summary of Structure Determination of **2-Ta**.

Empirical formula	$C_{38}H_{54}N_5O_5Ta$
Formula weight	841.81
Diffractometer	Rigaku XtaLAB Synergy-S (Dectris Pilatus3 R 200K)
Temperature	100 K
Crystal system	monoclinic
Space group	$P2_1$
a	10.8852(4) Å
b	15.2484(4) Å
c	12.4719(5) Å
β	114.466(5)°
Volume	1884.22(14) $Å^3$
Z	2
d_{calc}	1.484 g/cm^3
μ	2.965 mm^{-1}
F(000)	860.0
Crystal size, mm	0.53 × 0.02 × 0.02
2θ range for data collection	4.904 - 56.63°
Index ranges	-14 ≤ h ≤ 14, -20 ≤ k ≤ 20, -16 ≤ l ≤ 16
Reflections collected	35379
Independent reflections	9120[R(int) = 0.0526]
Data/restraints/parameters	9120/1/455
Goodness-of-fit on F^2	1.027
Final R indexes [I>=2σ (I)]	R_1 = 0.0313, wR_2 = 0.0556
Final R indexes [all data]	R_1 = 0.0440, wR_2 = 0.0582
Largest diff. peak/hole	2.78/-1.22 $eÅ^{-3}$
Flack parameter	0.052(9)

Structure of **1-Nb**:

X-ray data were collected on a on a Bruker D8QUEST CMOS[13] area detector employing graphite-monochromated MoKα radiation (λ = 0.71073 Å) at a temperature of 100 K. Preliminary indexing was

preformed from a series of twenty four 0.5° rotation frames with exposures of 10 seconds. A total of 1818 frames were collected with a crystal to detector distance of 34.0 mm, rotation widths of 0.5 ° and exposures of 30 seconds.

Rotation frames were integrated using SAINT,[14] producing a listing of unaveraged F^2 and $\sigma(F^2)$ values. The intensity data were corrected for Lorentz and polarization effects and for absorption using SADABS[15] (minimum and maximum transmission 0.6705, 0.7456). The structure was solved by direct methods – SHELXT.[12] Refinement was by full-matrix least squares based on F^2 using SHELXL.[12] All reflections were used during refinement. The weighting scheme used was $w = 1/[\sigma^2(F_o^2) + (0.0688P)^2 + 10.1392P]$ where $P = (F_o^2 + 2F_c^2)/3$. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined using a riding model.

Table S5 Summary of Structure Determination of **1-Nb**.

Empirical formula	$C_{37}H_{54}N_5O_3Nb$
Formula weight	709.76

Diffractometer	Bruker D8Quest (CMOS detector)
Temperature	100 K
Crystal system	triclinic
Space group	P**Error!**
a	10.1693(4) Å
b	12.0732(5) Å
c	15.7690(6) Å
α	91.220(2)°
β	90.450(2)°
γ	114.455(2)°
Volume	1761.67(12) $Å^3$
Z	2
d_{calc}	1.338 g/cm^3
μ	0.384 mm^{-1}
F(000)	752.0
Crystal size, mm	0.1 × 0.04 × 0.03
2θ range for data collection	2.584 - 55.114°
Index ranges	-13 ≤ h ≤ 13, -15 ≤ k ≤ 15, -20 ≤ l ≤ 20
Reflections collected	59771
Independent reflections	8136[R(int) = 0.2128]
Data/restraints/parameters	8136/0/427
Goodness-of-fit on F^2	1.129
Final R indexes [I>=2σ (I)]	R_1 = 0.0752, wR_2 = 0.1823
Final R indexes [all data]	R_1 = 0.1172, wR_2 = 0.1946
Largest diff. peak/hole	1.50/-0.85 $eÅ^{-3}$

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