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Synthesis of Molybdenum and Tungsten Alkylidene Complexes that Contain the 2,6-(2,4,6-tri-*iso*-propylphenyl)$_2$phenylimido (NHIPT) Ligand

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ABSTRACT: Molybdenum and tungsten alkylidene complexes that contain the sterically demanding hexaisopropylterphenylimido ligand, N-2,6-(2,4,6-*i*-Pr$_3$C$_6$H$_2$)$_2$C$_6$H$_3$ (NHIPT), have been prepared from Mo(N-*t*-Bu)$_2$Cl$_2$(1,2-dimethoxyethane) or W(N-t-Bu)$_2$Cl$_2$(pyridine)$_2$, employing *t*-butylimido ligands as sacrificial proton acceptors. These complexes include M(NHIPT)(CH-*t*-Bu)Cl$_2$ (M = Mo or W), Mo(NHIPT)(CH-*t*-Bu)(pyrrolide)$_2$, and Mo(NHIPT)(CH-*t*-Bu)(pyrrolide)(OC$_6$F$_5$). In all cases only *anti* alkylidene isomers are observed in solution as a consequence of the steric demands of the NHIPT ligand. An X-ray structure of W(NHIPT)(CH-*t*-Bu)Cl$_2$ showed it to be a monomer with a disordered alkylidene that is 86% in the *anti* configuration and 14% in the *syn* configuration.

A characteristic of all 14 electron "d^0" alkylidene (M=CHR) complexes of molybdenum and tungsten is the possibility of forming two isomers, one (*syn*) in which R is pointed toward X (oxo or imido) and one (*anti*) in which R is pointed away

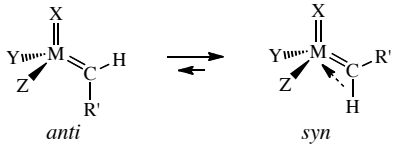


Figure 1. M = Mo or W; X = imido or oxo (W only); Y and Z are the same or different monoanionic monodentate ligands.

from X (Figure 1).[1,2] The agostic interaction[3] of the CH$_\alpha$ electrons with the metal in the *syn* isomer reduces the value of $^1J_{CH_\alpha}$ to 120-130 Hz compared to 140-150 Hz in the *anti* isomer, which is part of the reason why the *syn* form is usually the more stable of the two by a few kcal mol^{-1} and therefore the one observed in many circumstances. *Syn* and *anti* isomers can interconvert in the absence of an olefin at rates that vary from ~10^{-5} s^{-1} to ~100 s^{-1}.[4] *Syn* and *anti* isomers also are likely to have dramatically different reactivities. An untested feature of an *anti* alkylidene *versus* a *syn* alkylidene is the possible lower acidity of the H$_\alpha$ proton in the *anti* alkylidene and therefore a reduced tendency for it to be abstracted to form an alkylidyne ligand.[5] Abstraction of a relatively acidic α proton from an alkylidene or alkyl ligand as a consequence of a CH agostic interaction in a sterically crowded coordination sphere is the basis for forming high oxidation state alkylidyne and alkylidene ligands, respectively.[6]

In the last several years we have reported MonoAryloxide Pyrrolide (MAP) catalysts for the Z-selective metathesis reactions of disubstituted olefins,[7] an example being Mo(N-1-adamantyl)(CHCMe$_2$Ph)(Pyr)(OHIPT) (OHIPT = O-2,6-(2,4,6-*i*-Pr$_3$C$_6$H$_2$)$_2$C$_6$H$_3$).[8] The theory is to limit the substitution pattern in the intermediate TBP metallacyclobutane to one in which any single substituent on a metallacycle carbon atom points away from a large axial aryloxide ligand and toward a relatively small X ligand (imido or oxo (W only); Figure 2). An "inversion" of the roles of a "large" aryloxide and a "small" imido group would be another way to limit formation of metallacyclobutane intermediates to those with substituents all on one side and at the same time could limit formation of *syn* alkylidene isomers in favor of *anti* alkylidene isomers. Inversion of the relative steric influences became possible with the synthesis by Gavenonis and Tilley of relatively large 2,6-disubstituted anilines in which the substituents in the 2 and 6 positions are 2,4,6-trimethylphenyl (Mes) or 2,4,6-triisopropylphenyl (Trip) groups.[9]

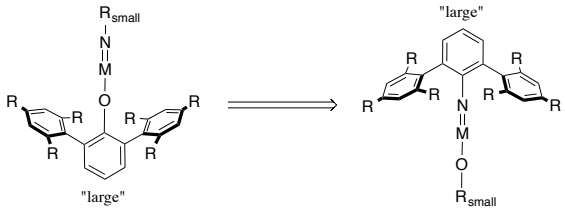
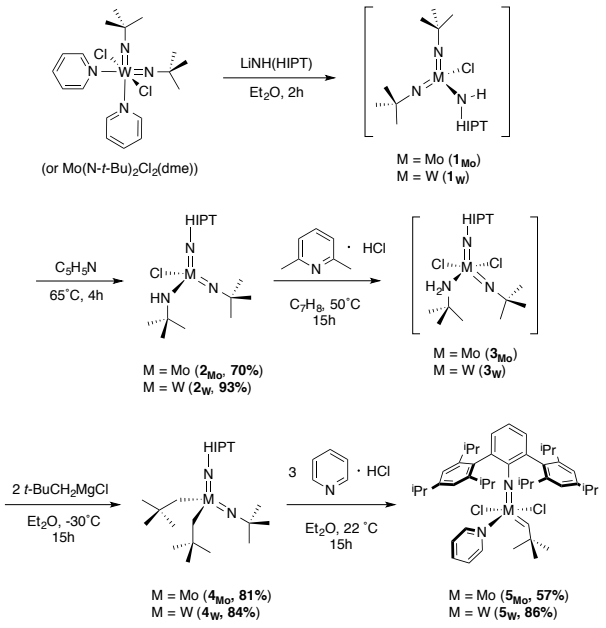


Figure 2. Exchanging the "large/small" roles of the imido and aryloxide (R = Me or *i*-Pr).

The large size of the NHMT (hexamethylterphenylimido or N-2,6-Mes$_2$C$_6$H$_3$) ligand prevented synthesis of Mo(NHMT)$_2$(CH$_2$-t-Bu)$_2$ and other bisimido intermediates that are required in a traditional synthesis of an imido alkylidene complex. Therefore, an entirely new synthesis (inspired by a report by Gibson[10]) had to be devised that employed two *t*-butylimido ligands as "sacrificial" imido groups in order to prepare Mo and W complexes that contain the NHMT ligand.[11] We found that the NHMT ligand was not sufficiently large to completely prevent formation of *syn* isomers in the complexes that were prepared. Therefore, we turned to the synthesis of Mo and W NHIPT complexes.

We were pleased to find that essentially the same methods employed for the synthesis of NHMT complexes are successful for the synthesis of NHIPT complexes. As shown in Scheme 1, Mo(N-*t*-Bu)$_2$Cl$_2$(dme)[10] and W(N-*t*-Bu)$_2$Cl$_2$py$_2$,[12] which are readily prepared on a large scale, serve as starting points. Intermediates **1$_{Mo}$** and **1$_W$** were not isolated and characterized, but converted to **2$_{Mo}$** (70%) and **2$_W$** (93%) by dissolving crude **1$_{Mo}$** and **1$_W$** in pyridine and heating the mixture to 65°C for 4 h. Pyridine-catalyzed transfer of the proton from



Scheme 1. Synthesis of the M(NHIPT)(CH-*t*-Bu)Cl_2(py) complexes.

the N(H)HIPT to a *t*-butylimido ligand is a key to formation of $\mathbf{2_{Mo}}$ and $\mathbf{2_W}$ in good yields (70% and 93%, respectively). The *t*-butylamido ligand in **2** could then be protonated selectively with 2,6-lutidinium chloride to generate M(NHIPT)(N-*t*-Bu)(NH_2-*t*-Bu)Cl_2 ($\mathbf{3_{Mo}}$ and $\mathbf{3_W}$), which were alkylated (without isolation) employing two equivalents of *t*-$BuCH_2MgCl$ to give $\mathbf{4_{Mo}}$ and $\mathbf{4_W}$ in 81% and 84% yields, respectively. An X-ray structural study of $\mathbf{4_{Mo}}$ showed it to be the proposed monomeric complex (Figure 3). Bond distances and angles are not unusual. (See SI for a full list and description.)

Treatment of $\mathbf{4_{Mo}}$ and $\mathbf{4_W}$ with three equivalents of finely-ground pyridinium chloride afforded the desired alkylidene complexes, $\mathbf{5_{Mo}}$ and $\mathbf{5_W}$ in 57% and 86% yields, respectively. Complex $\mathbf{5_W}$ is obtained as the *cis* isomer shown, which is readily apparent from the presence of six different isopropyl groups in the HIPT group in the proton NMR spectrum. The alkylidene proton in $\mathbf{5_W}$ is found at 10.65 ppm with $^1J_{CH}$ = 147 Hz, a value that is characteristic of an *anti* alkylidene; no *syn* alkylidene proton resonance could be found.

Proton NMR spectra of $\mathbf{5_{Mo}}$ in C_6D_6 (Figure 4) show that two isomers are present in approximately a 1:1 ratio. One is *cis*-$\mathbf{5_{Mo}}$ (analogous to *cis*-$\mathbf{5_W}$), while the second has mirror symmetry and therefore must contain *trans* chlorides (*trans*-$\mathbf{5_{Mo}}$). The large $^1J_{CH}$ values (148 Hz for *cis*-$\mathbf{5_{Mo}}$, 158 Hz for *trans*-$\mathbf{5_{Mo}}$) are characteristic of *anti* alkylidenes; again no alkylidene resonance for a *syn* isomer could be found. The two alkylidene resonances broaden at temperatures up to 80 °C, consistent with interconversion of *cis*-$\mathbf{5_{Mo}}$ and *trans*-$\mathbf{5_{Mo}}$. Because the rate of interconversion of the two isomers is slower at any given temperature when pyridine is added to the sample, *cis*-$\mathbf{5_{Mo}}$ and *trans*-$\mathbf{5_{Mo}}$ must interconvert through loss of pyridine. Evidently, M(NHIPT)$(py)_2Cl_2$ is too crowded to form, and even five-coordinate **5** loses pyridine in solution. The main isomer of $\mathbf{5_{Mo}}$ in a proton NMR spectrum in CD_2Cl_2 is the *cis* isomer, which might be expected in view of the likely larger dipole moment for *cis*-$\mathbf{5_{Mo}}$ versus *trans*-$\mathbf{5_{Mo}}$.

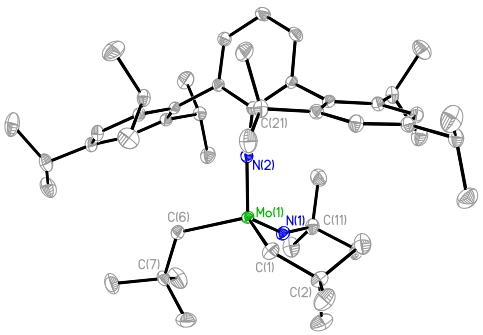


Figure 3. Thermal ellipsoid drawing (50%) of Mo(NHIPT)(N-*t*-Bu)(CH_2-*t*-Bu)$_2$ ($\mathbf{4_{Mo}}$). Selected bond distances (Å) and angles (˚): Mo1-N1 = 1.7477(17), Mo1-N2 = 1.7641(17), Mo1-N1-C11 = 156.88(15), Mo1-N2-C21 = 162.53(14).

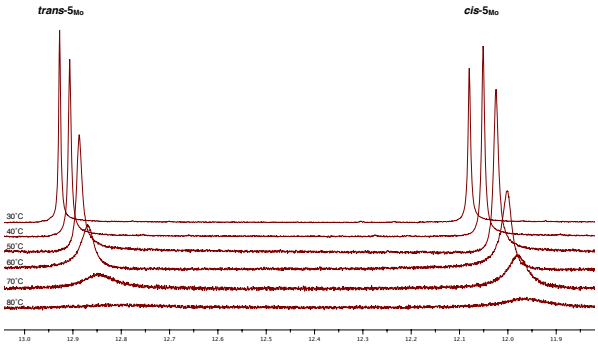
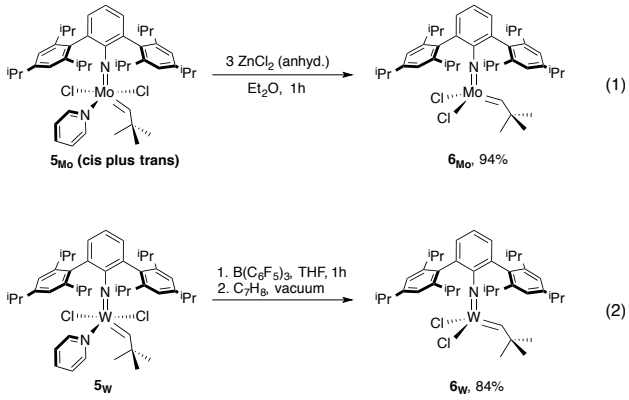


Figure 4. Variable-temperature ^{1}H NMR of $\mathbf{5_{Mo}}$ in C_6D_6.



(1)

(2)

Treatment of $\mathbf{5_{Mo}}$ in diethyl ether with three equivalents of $ZnCl_2$ in 1h resulted in formation of Mo(NHIPT)$(CHCMe_3)Cl_2$ ($\mathbf{6_{Mo}}$, equation 1); this reaction is successful as a consequence of the lability of pyridine in $\mathbf{5_{Mo}}$. The alkylidene in $\mathbf{6_{Mo}}$ is also an *anti* isomer ($^1J_{CH}$ = 158 Hz). Treatment of $\mathbf{5_W}$ with one equivalent of $B(C_6F_5)_3$ in THF cleanly converted $\mathbf{5_W}$ to the THF adduct of $\mathbf{6_W}$ (equation 2). The THF can be removed under vacuum after dissolution of the THF adduct in toluene to give 14-electron $\mathbf{6_W}$. A value of $^1J_{CH}$ = 155 Hz suggests that the alkylidene in $\mathbf{6_W}$ is also the *anti* isomer.

An X-ray crystallographic study of $\mathbf{6_W}$ was complicated by whole molecule disorder. Two structures contribute to the disorder, *anti*-$\mathbf{6_W}$ (~86%) and *syn*-$\mathbf{6_W}$ (~14%). Drawings of *anti*-$\mathbf{6_W}$ are shown in Figures 5a and 5b. The geometry at the metal is pseudotetrahedral. One of the Trip rings is positioned approximately over the alkylidene (Figure 5b). The bond lengths and angles are unexceptional for an *anti* alkylidene complex. The N1-W1-C1-C2 dihedral angle (177.7(7)°) is consistent with essentially no twisting (within 3σ) of the alkylidene out of the N1-W1-C1-C2 plane.

The overall structure of *syn*-$\mathbf{6_W}$, as described in the Supporting Information, is similar to that of *anti*-$\mathbf{6_W}$, although the standard deviations for various bond lengths and angles are much larger than they are for *anti*-$\mathbf{6_W}$. The N1-W1-C1-C2 dihedral angle in *syn*-$\mathbf{6_W}$ is 17(6)°, which again suggests that within experimental error the alkylidene is not "twisted" out of the N1-W1-C1-C2 plane, in spite of the steric interaction between the *t*-butyl group of the neopentylidene ligand and one of the Trip groups in the NHIPT ligand. Even though some *syn*-$\mathbf{6_W}$ is found in the solid state, we were unable to observe any resonances for the *syn* isomer in solution by proton NMR, even at -80 °C, where *syn* and *anti* interconversion is expected to be slow on the NMR time scale.[4] Because both isomers are found in the solid state, it seems likely that both are accessible in solution, although the equilibrium clearly overwhelmingly favors *anti*-$\mathbf{6_W}$.

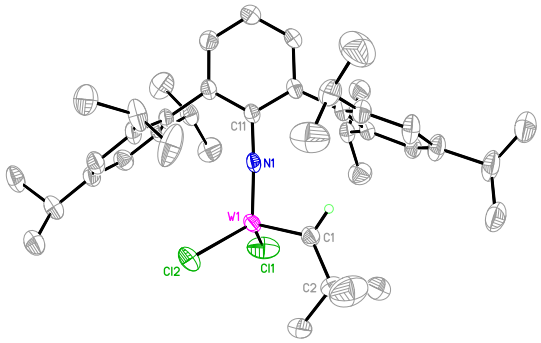


Figure 5a. Solid-state structure of *anti*-$\mathbf{6_W}$. Selected bond distances (Å) and angles (°): W1-C1 1.892, W1-N1 1.702, W1-Cl1 2.274, W1-Cl2 2.272; W1-C1-C2 126.88, W1-N1-C11 178.37, N1-W1-C1 98.31.

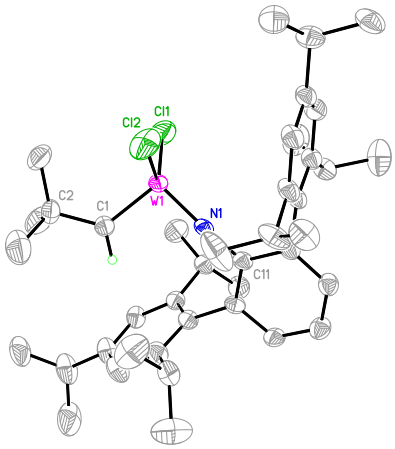
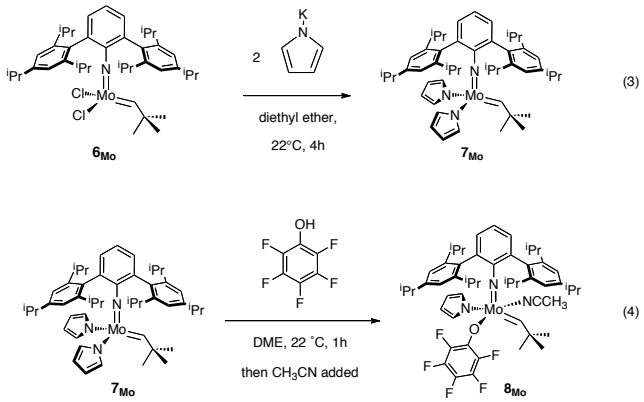


Figure 5b. Solid-state structure of *anti*-$\mathbf{6_W}$ showing the position of one of the NHIPT Trip rings approximately over the *anti* alkylidene proton.

To our knowledge $\mathbf{6_W}$ and (we presume isostructural) $\mathbf{6_{Mo}}$ are the only 14-electron imido alkylidene dihalide complexes in the literature. We propose that formation of dimers or higher oligomers in which halides or imido ligands bridge between metals is not possible in $\mathbf{6_W}$ and $\mathbf{6_{Mo}}$ for steric reasons. Complexes analogous to $\mathbf{6_W}$ and $\mathbf{6_{Mo}}$ that contain the NHMT ligand were not reported,[11] although no attempts to make them by methods analogous to or related to those shown in equations were attempted at the time.

We were interested in preparing other M(NHIPT) complexes that contain relatively small anionic ligands, in particular, bispyrrolide and MAP species. We have shown that both can be prepared, so far with Mo. The reaction between $\mathbf{6_{Mo}}$ and potassium pyrrolide gave $\mathbf{7_{Mo}}$ (equation 3), while subsequent treatment of $\mathbf{7_{Mo}}$ in diethyl ether at -30˚C with one equivalent of pentafluorophenol, followed by crystallization from acetonitrile, led to Mo(NHIPT)(CH-*t*-Bu)(pyr)(OC_6F_5)(CH_3CN) ($\mathbf{8_{Mo}}$; equation 4). Proton NMR spectra of $\mathbf{8_{Mo}}$ (see SI) suggest that the acetonitrile is dissociating on the NMR time scale, but efforts to obtain a sample completely free of acetonitrile have not yet been successful.



In summary, we have taken advantage of a synthetitic route in which *t*-butylimido ligands are employed as sacrificial proton acceptors to prepare Mo and W alkylidene complexes that contain the NHIPT imido ligand. Alkylidene NHIPT complexes reported here exist exclusively as *anti* isomers in solution, in contrast to the previously reported closely analogous M(NHMT) complexes,[11] which are mixtures of *syn* and *anti* isomers in solution. We are in the process of exploring olefin metathesis reactions with M(NHIPT) complexes. Our hope is that they will be especially stable and long-lived as a consequence of the steric protection toward bimolecular decomposition reactions afforded by the NHIPT ligand.

ASSOCIATED CONTENT

Supporting Information. Experimental details for the synthesis of all compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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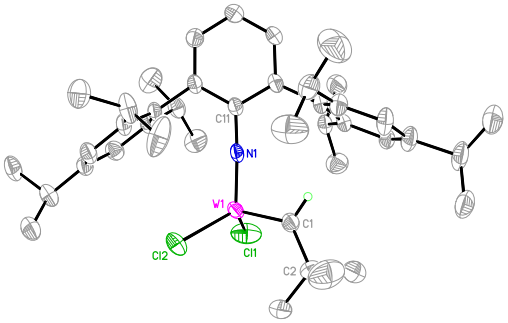

Supporting Information for

Synthesis of Molybdenum and Tungsten Alkylidene Complexes that Contain the 2,6-(2,4,6-tri-*iso*-propylphenyl)$_2$phenylimido (NHIPT) Ligand

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General Procedures. All manipulations of air- and moisture-sensitive materials were performed either in a Vacuum Atmospheres glovebox (N_2 atmosphere) or on a dual-manifold Schlenk line. All solvents were sparged with nitrogen, passed through activated alumina, and stored over activated 4 Å molecular sieves. HIPTNHLi[1], $Mo(N^tBu)_2Cl_2(DME)$[2], and $W(N^tBu)_2Cl_2(py)_2$[3] were prepared according to reported procedures. All other reagents were used as received unless otherwise noted. Methylene chloride-d_2 and benzene-d_6 were stored over 4 Å molecular sieves. NMR measurements of air- and moisture-sensitive materials were carried out in Teflon-valve-sealed J. Young NMR tubes. NMR spectra were recorded using spectrometers at 500 or 300 MHz (^1H), 125 MHz (^{13}C), and 282 (^{19}F) MHz, reported in δ (parts per million) relative to tetramethylsilane (^1H, ^{13}C) or PhF (^{19}F) and referenced to residual $^1H/^{13}C$ signals of the deuterated solvent (^1H (δ), benzene 7.160, methylene chloride 5.320); ^{13}C (δ), benzene 128.06, methylene chloride 53.84. Elemental analyses were carried out by the CENTC Elemental Analysis Facility at the University of Rochester.

Mo(NHIPT)(N^tBu)(NH^tBu)Cl (2_{Mo}). This product can be made without isolating $\mathbf{1_{Mo}}$. A solution of HIPTNHLi (3.40g, 6.74 mmol) in ~15mL Et_2O was added to a solution of $Mo(N^tBu)_2Cl_2(dme)$ (2.69g, 6.74 mmol) in ~15mL Et_2O and the mixture was stirred for 2h, during which time a yellow-orange mixture with precipitate was formed. The solvents were removed *in vacuo*, pentane was added to the residue, and the mixture was filtered through Celite. All solvents were removed from the filtrate *in vacuo* and the residue was dissolved in pyridine. The red solution was heated to 65˚C for 4h in a Schlenk bomb and then all pyridine was removed *in vacuo*. The red residue was extracted with pentane, and all volatiles were removed from the filtrate *in vacuo*. Minimal Et_2O was added to give some yellow precipitate, and to this stirred mixture was added acetonitrile to encourage further precipitatation of the yellow product. This mixture was stirred for an additional 6h and the yellow product was isolated by filtration and washed with acetonitrile; yield 3.61g (70%): ^1H NMR (C_6D_6, 500MHz) δ 7.71 (s, 1H, NH), 7.27 (overlapping singlets, 2H, Ar), 7.25 (overlapping singlets, 2H, Ar), 7.06 (d, 2H, Ar), 6.84 (t, 1H, Ar), 3.12 (sept, 4H, C*H*Me_2), 2.88 (sept, 2H, C*H*Me_2), 1.52 (d, 6H, ^{i}Pr), 1.46 (d, 6H, ^{i}Pr), 1.31 (d, 6H, ^{i}Pr), 1.29 (d, 6H, ^{i}Pr), 1.20 (d, 6H, ^{i}Pr), 1.13 (d, 6H, ^{i}Pr), 1.09 (s, 9H, ^{t}Bu), 1.06 (s, 9H, ^{t}Bu); ^{13}C NMR (CD_2Cl_2, 500 MHz, 20˚C) 155.37, 148.16, 147.52, 147.08, 136.15, 135.75, 131.16, 124.04, 121.41, 121.30, 71.11, 58.22, 34.56,

32.20, 31.46, 31.15, 31.08, 25.85, 25.33, 24.28, 24.06, 24.05, 23.83. Anal. Calcd for $C_{44}H_{68}ClMoN_3$: C, 68.59; H, 8.90; N, 5.45. Found: C, 68.23; H, 8.65; N, 5.04.

W(N^{t}Bu)(NHIPT)(NH^{t}Bu)Cl (2_W). This product can be made without isolating $\mathbf{1_W}$. A solution of HIPTNHLi (3.59g, 7.13 mmol) in ~15mL Et_2O was added to a solution of $W(N^tBu)_2Cl_2py_2$ (3.96g, 7.13 mmol) in ~50mL Et_2O. The resulting yellow-brown mixture was stirred for 4h. The suspension was then filtered through a Celite plug, which was rinsed with Et_2O. The volatiles were removed from the filtrate *in vacuo*. Pyridine was added to the residue and the solution was transferred to a Schlenk bomb. The Schlenk bomb was heated at 65˚C for 4h. The solvent was then removed *in vacuo*, pentane was added, and the solvent was again removed *in vacuo*. Minimal Et_2O was added to give some yellow precipitate, and to this stirred mixture was added acetonitrile to further precipitate the yellow product. This mixture was stirred for an additional 6h and the yellow product was isolated by filtration and washed with acetonitrile; yield 5.70g (93%): ^{1}H NMR (C_6D_6, 500 MHz) δ 7.26 (s, 2H, Ar), 7.25 (s, 2H, Ar), 7.12 (d, 2H, Ar), 6.82 (t, 1H, Ar), 6.56 (s, 1H, N*H*^{t}Bu), 3.10 (overlapping sept, 4H, C*H*Me$_2$), 2.88 (sept, 2H, C*H*Me$_2$), 1.51 (d, 6H, ^{i}Pr), 1.46 (d, 6H, ^{i}Pr), 1.32 (d, 6H, ^{i}Pr), 1.30 (d, 6h, ^{i}Pr), 1.21 (d, 2H, ^{i}Pr), 1.14 (d, 6H, ^{i}Pr), 1.11 (s, 9H, ^{t}Bu), 1.05 (s, 9H, ^{t}Bu); ^{13}C NMR (C_6D_6, 125 MHz) 154.57, 148.05, 147.73, 147.28, 137.17, 136.21, 130.73, 123.53, 121.31, 121.17, 67.99, 56.82, 34.63, 32.69, 32.58, 31.26, 31.16, 25.85, 25.17, 24.44, 24.34, 24.18, 24.11. Anal. Calcd for $C_{44}H_{68}ClN_3W$: C, 61.57; H, 7.99; N, 4.90. Found: C, 61.91; H, 7.95, N, 4.73.

Mo(NHIPT)(N^{t}Bu)(CH$_2$CMe$_3$)$_2$ (4_{Mo}). This product can be made without isolating $\mathbf{3_{Mo}}$. 2,6-Lutidinium chloride (677 mg, 4.71 mmol) was added to a solution of Mo(N^{t}Bu)(NHIPT)(NH^{t}Bu)Cl (3.63g, 4.71 mmol) in ~75mL toluene. The resulting mixture was stirred for 15h at 50˚C in a Schlenk bomb. The orange mixture was filtered and the solvents were removed from the filtrate *in vacuo*. The residue was extracted with pentane and filtered through Celite into a tared vial. All solvent was removed *in vacuo*, diethyl ether was added, the mixture was chilled at -30˚C for 1h, and 2.05 equivalents of neopentylmagnesium chloride (2.42M, 3.88 mL) was then added dropwise to the stirred solution. The resulting mixture was stirred for 16h. The mixture was filtered and the solvents removed from the filtrate *in vacuo*. A small amount of CH_3CN was added and the mixture was stirred for 2h. The yellow product was then isolated by filtration; yield 728 mg (81%): ^{1}H NMR (C_6D_6, 500MHz) δ 7.24 (s, 4H, Ar), 7.09 (d, 2H, Ar), 6.83 (t, 1H, Ar), 3.21 (sept, 4H, C*H*Me$_2$),

2.92 (sept, 2H, C*H*Me$_2$), 2.27 (d, 2H, C*H*$_2$), 1.52 (d, 12H, ^{i}Pr), 1.40 (s, 9H, ^{t}Bu), 1.35 (d, 12H, ^{i}Pr), 1.16 (d, 12H, ^{i}Pr), 0.96 (s, 18H, ^{t}Bu), 0.38 (d, 2H, C*H*$_2$); ^{13}C NMR: 156.24, 147.88, 147.29, 136.79, 135.37, 132.12, 123.01, 121.16, 81.07, 69.81, 34.67, 33.59, 33.52, 32.83, 31.04, 26.30, 24.48, 24.42. Crystals of **4$_{Mo}$** obtained from toluene were found to contain one toluene of crystallization. Anal. Calcd for $C_{57}H_{88}MoN_2$: C, 76.30; H, 9.89; N, 3.12. Found: C, 76.12; H, 9.84; N, 3.07.

W(N^{t}Bu)(NHIPT)(CH$_2$CMe$_3$)$_2$ (4$_W$). This compound can be made without isolating **3$_W$**. 2,6-lutidinium chloride (878mg, 6.11 mmol) was added to W(N^{t}Bu)(NHIPT)(NH^{t}Bu)Cl (5.00g, 5.82 mmol) in ~75mL toluene and the mixture was heated to 50˚C for 15h in a Schlenk bomb. All solvents were removed *in vacuo*, the residue was extracted with pentane, and the mixture was filtered through Celite. The volatiles were removed *in vacuo* and the residue was redissolved in ~75mL Et$_2$O. The solution was chilled for 1h in a freezer kept at -30˚C. Neopentylmagnesium chloride (2.42M, 4.57 mL) was added and the resulting mixture was stirred overnight. The solvent was removed under vacuum and the residue was extracted with pentane. The suspension was filtered through Celite and the solvents were removed from the filtrate *in vacuo*. Acetonitrile was added to the residue and the resulting tan product was isolated by filtration; yield 4.38g (84%): ^{1}H NMR (C_6D_6, 500 MHz) δ 7.24 (s, 4H, Ar), 7.12 (d, 2H, Ar), 6.82 (t, 1H, Ar), 3.18 (sept, 4H, C*H*Me$_2$), 2.92 (sept, 2H, C*H*Me$_2$), 2.13 (d, 2H, C*H*$_2$), 1.51 (d, 12H, ^{i}Pr), 1.43 (s, 9H, ^{t}Bu), 1.35 (d, 12H, ^{i}Pr), 1.16 (d, 12H, ^{i}Pr), 0.96 (s, 18H, ^{t}Bu), 0.08 (d, 2H, C*H*$_2$); ^{13}C NMR (CD_2Cl_2, 125 MHz) 156.07, 147.60, 147.26, 136.70, 135.34, 131.75, 121.78, 121.07, 89.88, 68.15, 34.45, 34.04, 33.80, 33.45, 30.88, 25.94, 24.45, 24.19. Crystals of **4$_W$** obtained from toluene contain one molecule of toluene. Anal. Calcd for $C_{57}H_{88}N_2W$: C, 69.49; H, 9.00; N, 2.84. Found: C, 69.04; H, 8.98; N, 2.90.

Mo(NHIPT)(CHCMe$_3$)Cl$_2$(py) (5$_{Mo}$). Pyridinium chloride (1.26g, 10.9 mmol) was added to a solution of Mo(NHIPT)(N^{t}Bu)(CH$_2$CMe$_3$)$_2$ (2.92g, 3.63 mmol) in ~175 mL Et$_2$O and the mixture was stirred for 12h. The solvents were removed *in vacuo* and the residue was extracted with pentane. The mixture was filtered through Celite, washed with pentane, and the filtrate taken to dryness *in vacuo*. A small amount of acetonitrile was added to the residue and a yellow solid was isolated by filtration; yield 1.69g (57%) as a mixture of isomers: ^{1}H NMR (CD_2Cl_2, 500 MHz, Major (*cis*) isomer) δ 12.55 (s, 1H, Mo=CH), 7.74 (tt, 1H, py), 7.54 (d, 2H, py), 7.30 (t, 1H, Ar), 7.22 (s, 2H, Ar), 7.19 (d, 2H, Ar), 7.16 (t, 2H, py), 7.11 (s, 2H, Ar),

3.01 (sept, 2H, C*H*Me$_2$), 2.86 (sept, 2H, C*H*Me$_2$), 2.50 (sept, 2H, C*H*Me$_2$), 1.37 (d, 6H, CH*Me*$_2$), 1.35 (d, 6H, CH*Me*$_2$), 1.28 (d, 6H, CH*Me*$_2$), 1.05 (d, 6H, CH*Me*$_2$), 0.95 (d, 6H, CH*Me*$_2$), 0.94 (s, 9H, ^{t}Bu), 0.71 (bs, 6H CH*Me*$_2$); ^{13}C NMR 331.54, 156.38, 155.53, 148.96, 147.80, 147.73, 139.36, 134.94, 131.36, 127.31, 125.18, 125.17, 121.79, 121.26, 45.40, 34.79, 31.10, 30.95, 28.78, 25.82, 25.72, 24.62, 24.22, 23.11, 23.04. Anal. Calcd for $C_{46}H_{64}Cl_2N_2Mo$: C, 68.05; H, 7.95; N, 3.45. Found: C, 67.99; H, 8.09; N, 3.32.

W(NHIPT)(CHCMe$_3$)Cl$_2$(py) (5$_W$). Pyridinium chloride (1.16g, 10.1 mmol) was added to a solution of W(NHIPT)(N^{t}Bu)(CH$_2$CMe$_3$)$_2$ (3.00g, 3.36 mmol) in ~75 mL Et$_2$O and the resulting mixture was stirred for 18h. The mixture was filtered through Celite and the solvents was removed from the filtrate *in vacuo.* A small amount of pentane was added to precipitate a yellow solid which was isolated by filtration; yield 2.60g (86%): ^{1}H NMR (C_6D_6, 500 MHz) δ 10.65 (s, 1H, W=CH, $^1J_{CH}$ = 147Hz), 7.81 (d, 2H, py), 7.37 (s, 2H, Ar), 7.19 (s, 2H, Ar), 7.18 (d, 2H, Ar), 6.86 (t, 1H, Ar), 6.79 (t, 1H, py), 6.53 (t, 2H, py), 3.21 (sept, 2H, C*H*Me$_2$), 2.90 (sept, 2H, C*H*Me$_2$), 2.82 (sept, 2H, C*H*Me$_2$), 1.54 (d, 6H, ^{i}Pr), 1.34-1.31 (m, 12H, ^{i}Pr), 1.19 (s, 9H, ^{t}Bu), 1.13 (d, 6H, ^{i}Pr), 1.06 (d, 6H, ^{i}Pr), 0.91 (br s, 6H, ^{i}Pr); ^{13}C NMR (C_6D_6, 125 MHz) 298.90 (W=CH), 156.63, 155.30, 148.61, 148.05, 147.84, 138.60, 138.40, 135.81, 130.87, 125.67, 124.97, 121.72, 121.01, 41.04, 34.86, 31.72, 31.20, 30.98, 26.04, 25.83, 24.83, 24.32, 23.44, 23.43. Anal. Calcd for $C_{46}H_{64}Cl_2N_2W$: C, 61.41; H, 7.17; N, 3.11. Found: C, 61.72; H, 7.51; N, 2.95.

Mo(NHIPT)(CHCMe$_3$)Cl$_2$ (6$_{Mo}$). Mo(NHIPT)(CHCMe$_3$)Cl$_2$(py) (281mg, 0.346 mmol) was charged with 25mL Et$_2$O, followed by ZnCl$_2$ (142mg, 1.04 mmol). The resulting red mixture was stirred for 1h, then dried under vacuum, extracted with pentane, and filtered through Celite. The filtrate was dried to afford a red/orange solid; yield 238mg (94%): ^{1}H NMR (C_6D_6, 500 MHz) δ 11.85 (s, 1H, Mo=CH, $^1J_{CH}$ = 158 Hz), 7.26 (s, 4H, Ar), 7.09 (d, 2H, Ar), 6.92 (t, 1H, Ar), 2.97 (sept, 4H, C*H*Me$_2$), 2.84 (sept, 2H, C*H*Me$_2$), 1.42 (d, 12H, ^{i}Pr), 1.28 (d, 12H, ^{i}Pr), 1.16 (d, 12H, ^{i}Pr), 1.07 (s, 9H, ^{t}Bu); ^{13}C NMR (C_6D_6, 125 MHz) 317.76, 158.16, 149.64, 147.39, 138.09, 133.55, 130.53, 127.44, 121,56, 44.98, 34.82, 31.54, 28.15, 25.64, 24.36, 23.54; Anal. Calcd for $C_{41}H_{59}Cl_2MoN$: C 67.20; H, 8.12; N, 1.91. Found: C, 67.08; H, 8.41; N, 1.75.

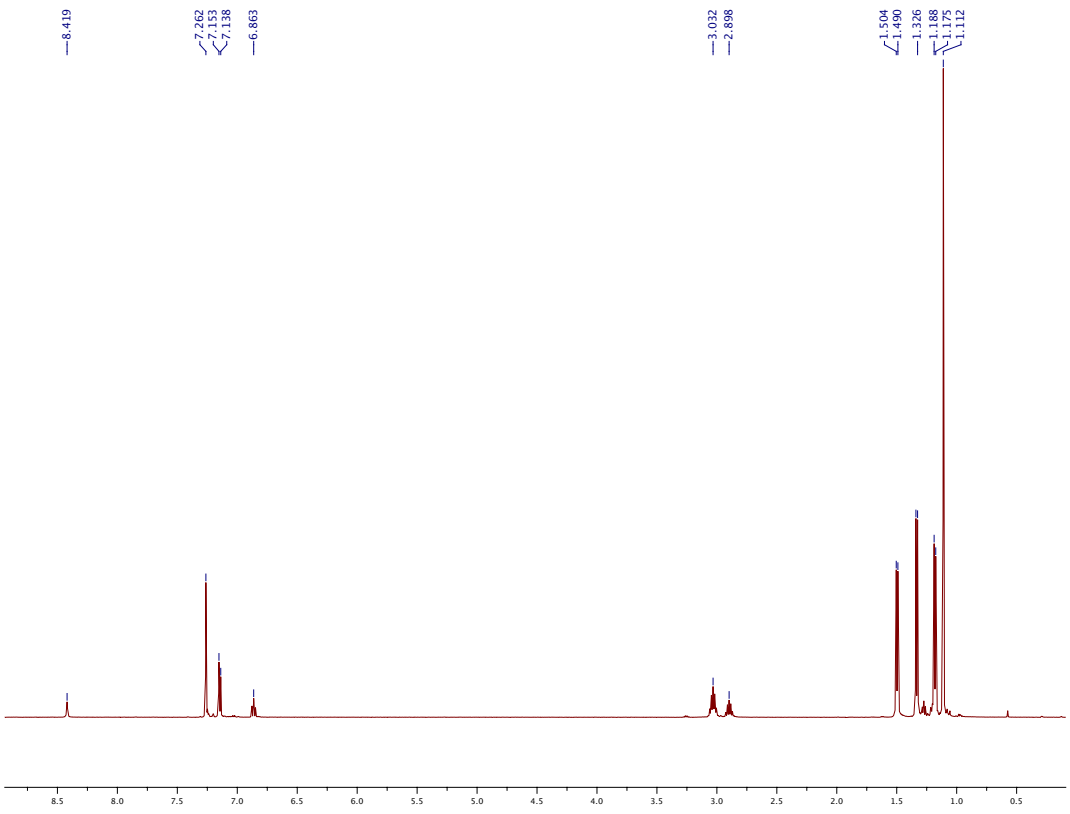
W(NHIPT)(CHCMe$_3$)Cl$_2$ (6$_W$). B(C_6F_5)$_3$ (285mg, 0.556 mmol) was added to a solution of W(NHIPT)(CHCMe$_3$)Cl$_2$(py) (500mg, 0.556 mmol) in 20mL THF. The

orange solution was stirred for 30 minutes and all volatiles were removed *in vacuo*. The resulting solid was then extracted with pentane and the mixture was filtered through a Celite plug. The volatiles were removed from the filtrate *in vacuo*. Toluene (~10mL) was added and removed again *in vacuo* to give the red product; yield 384mg (84%): ^{1}H NMR (C_6D_6, 500MHz) δ 9.93 (s, 1H, W=CH, $^2J_{WH}$ = 40.5 Hz, $^1J_{CH}$ = 155 Hz), 7.25 (s, 4H, Ar), 7.16 (d, 2H, Ar), 6.93 (t, 1H, Ar), 2.96 (sept, 4H, C*H*Me$_2$), 2.86 (sept, 2H, C*H*Me$_2$), 1.40 (d, 12H, ^{i}Pr), 1.29 (d, 12H, ^{i}Pr), 1.17 (d, 12H, ^{i}Pr), 1.08 (s, 9H, ^{t}Bu); ^{13}C NMR (C_6D_6, 125MHz) 284.06 (W=CH), 155.51, 149.26, 147.33, 137.82, 134.11, 130.21, 126.45, 121.38, 40.21, 34.84, 31.43, 30.96, 25.61, 24.41, 23.60. Anal. Calcd for $C_{41}H_{59}Cl_2NW$: C, 60.01; H, 7.25; N, 1.71. Found: C, 59.94; H, 7.05; N, 1.56.

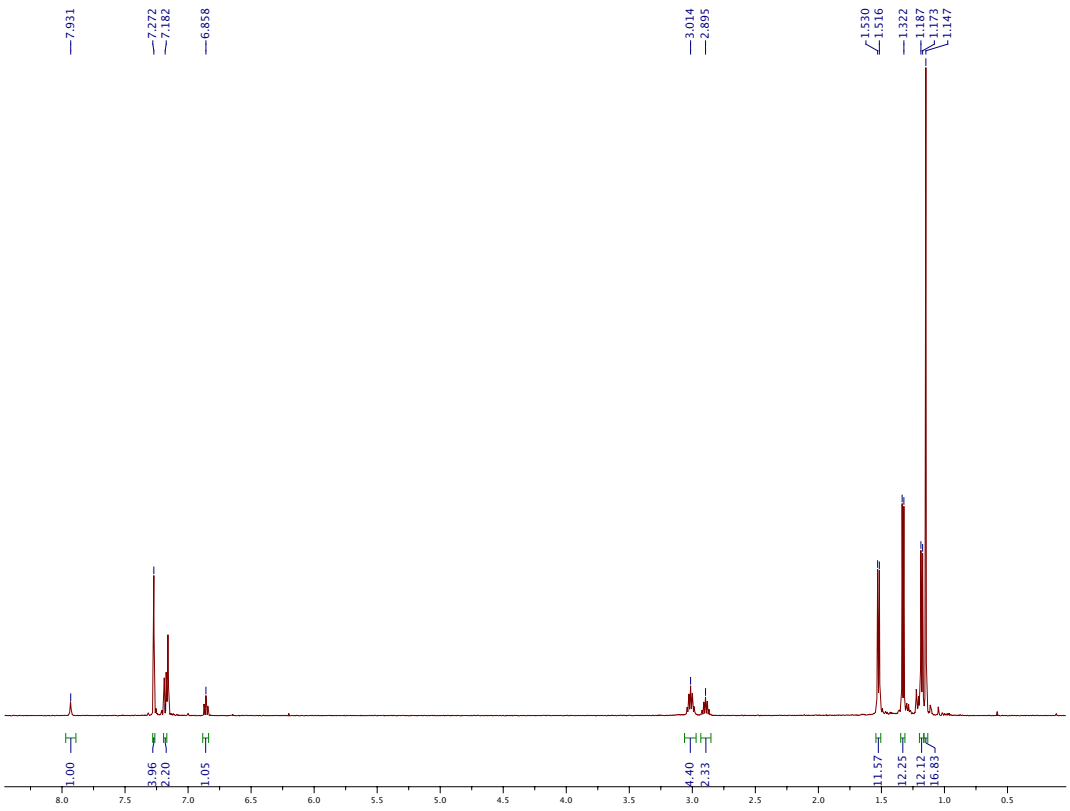
Mo(NHIPT)(CHCMe$_3$)(pyr)$_2$ (7$_{Mo}$). Mo(NHIPT)(CHCMe$_3$)Cl$_2$ (132mg, 0.180 mmol) in ~10mL Et$_2$O was treated with Kpyr (38mg, 0.360 mmol) and was allowed to stir for 4h. The resulting mixture was then filtered through a Celite plug, washed with Et$_2$O, and dried under vacuum to afford the desired product; yield 110mg (77%): ^{1}H NMR (C_6D_6, 500 MHz) δ 12.35 (s, 1H, Mo=CH), 7.25 (s, 4H, Ar), 7.01 (d, 2H, Ar), 6.83 (t, 1H, Ar), 6.59 (t, 4H, pyr), 6.22 (t, 4H, pyr), 2.90 (m, 6H, C*H*Me$_2$), 1.34 (d, 12H, CH*Me*$_2$), 1.15 (d, 12H, CH*Me*$_2$), 1.10 (d, 12H, CH*Me*$_2$), 1.04 (s, 9H, ^{t}Bu); ^{13}C NMR (125 MHz) 314.29, 156.16, 148.78, 147.41, 137.16, 135.16, 131.19, 129.97, 125.28, 121.82, 109.47, 48.46, 34.78, 31.52, 25.71, 24.39, 22.91. Anal. Calcd for $C_{49}H_{67}MoN_3$: C, 74.12; H, 8.51; N, 5.29. Found: C, 73.88; H, 8.79; N, 5.06.

Mo(NHIPT)(CHCMe$_3$)(pyr)(OC$_6$F$_5$)(CH$_3$CN) (8$_{Mo}$). 7$_{Mo}$ (50mg, 0.0630 mmol) in ~5mL DME was charged with C_6F_5OH (11mg, 0.0630 mmol) in ~3mL DME. After one hour the volatiles were removed *in vacuo*. The residue was charged with MeCN and stirred for 3h to precipitate a yellow solid. The volatiles were removed *in vacuo* to yield the desired product; yield 43mg (72%): ^{1}H NMR (500 MHz, C_6D_6, ~0.01M): δ 12.57 (brs, 1H, Mo=CH), 7.28 (s, 2H, Ar), 7.27 (s, 2H, Ar) 7.06 (d, 2H, Ar), 6.84 (t, 1H, Ar), 6.44 (bs, 2H, pyr), 6.42 (bs, 2H, pyr), 2.99 (m, 4H, C*H*CMe$_2$), 2.80 (sept, 2H, C*H*CMe$_2$), 1.41 (d, 6H, CHC*Me*$_2$), 1.38 (d, 6H, CHC*Me*$_2$), 1.21 (d, 6H, CHC*Me*$_2$), 1.15 (d, 6H, CHC*Me*$_2$), 1.12 (d, 6H, CHC*Me*$_2$), 1.06 (s, 9H, ^{t}Bu), 0.97 (d, 6H, CHC*Me*$_2$); ^{13}C NMR (125 MHz, ~0.09M) 334.19 (Mo=CH), 155.27, 148.91, 147.10, 146.49, 140.02 ($^1J_{CF}$ = 240Hz), 140.00 (m), 138.37 ($^1J_{CF}$ = 244 Hz), 138.18, 134.82, 133.45 ($^1J_{CF}$ = 241 Hz), 131.00, 130.85, 128.35, 125.61, 121.98, 121.65, 107.72, 47.36, 34.84, 31.45, 31.20, 30.15, 26.08, 26.02, 24.69, 24.00, 23.28, 22.66,

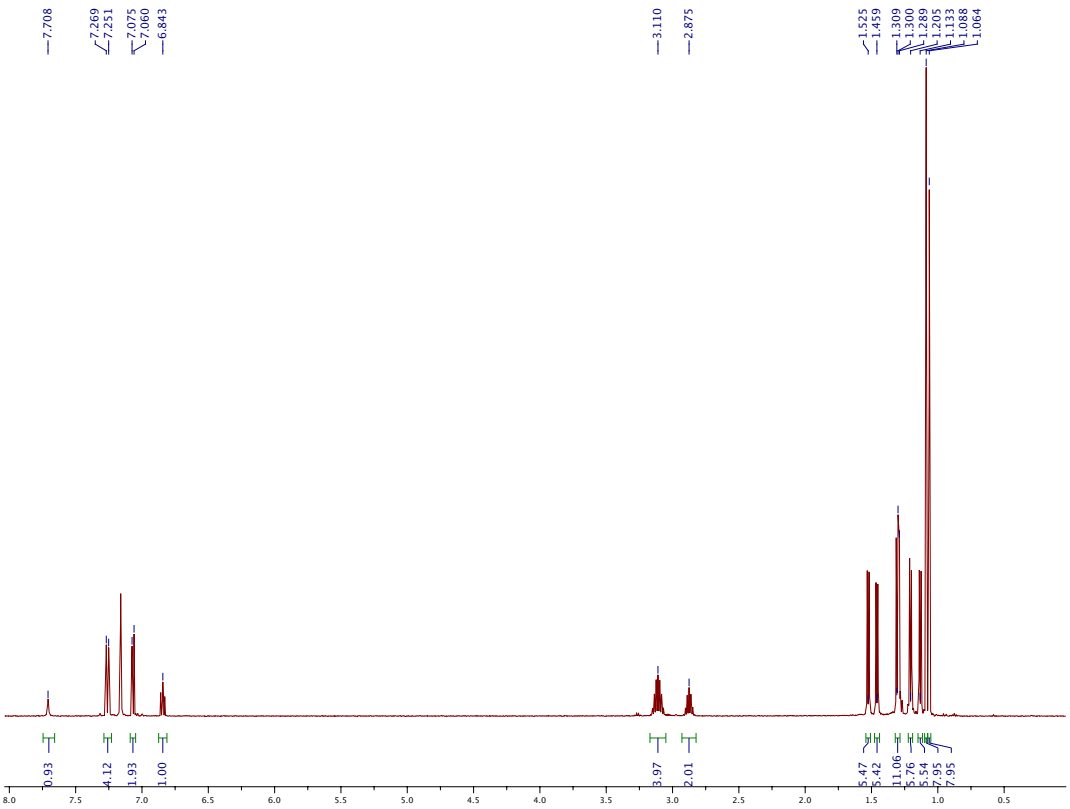
0.93; ^{19}F NMR (282 MHz, ~0.09M) -157.92 (d, 2F), -167.30 (t, 2F), -174.01 (bs, 1F). The broad alkylidene resonance in the proton NMR spectrum suggests that acetonitrile is dissociating on the NMR time scale; therefore, the breadth of the alkylidene resonance and details in the spectrum change slightly with concentration. Anal. Calcd for $C_{53}H_{66}F_5MoN_3O$: C, 66.86; H, 6.99; N, 4.41. Found: C, 66.87; H, 6.93; N, 4.30.



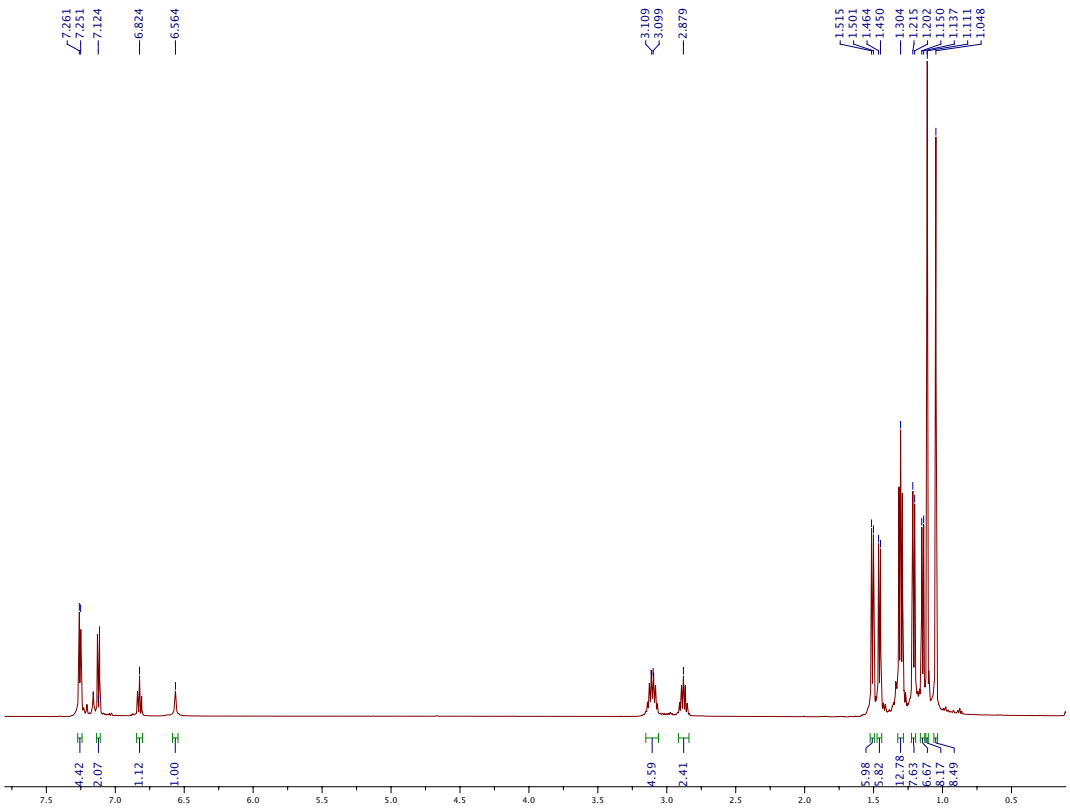
^{1}H NMR spectrum of $\mathbf{1_{Mo}}$ before treatment with pyridine.



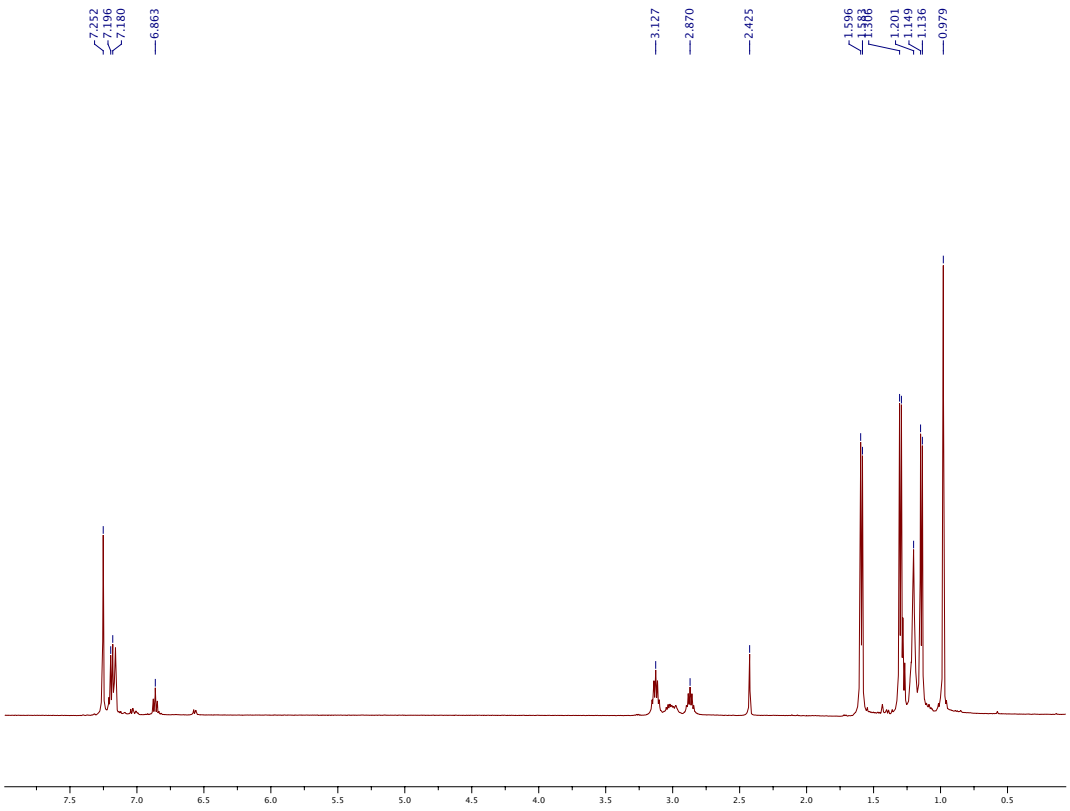
^{1}H NMR spectrum of $\mathbf{1_W}$ before treatment with pyridine.



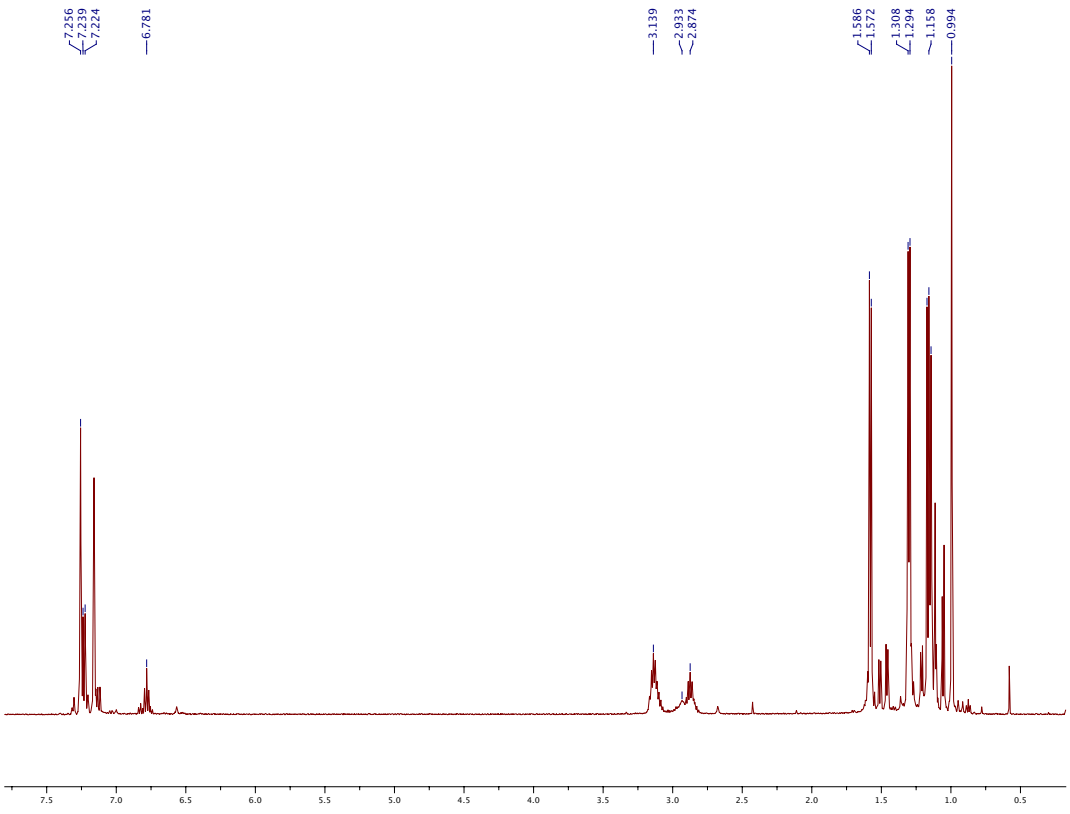
^{1}H NMR spectrum of $\mathbf{2_{Mo}}$.



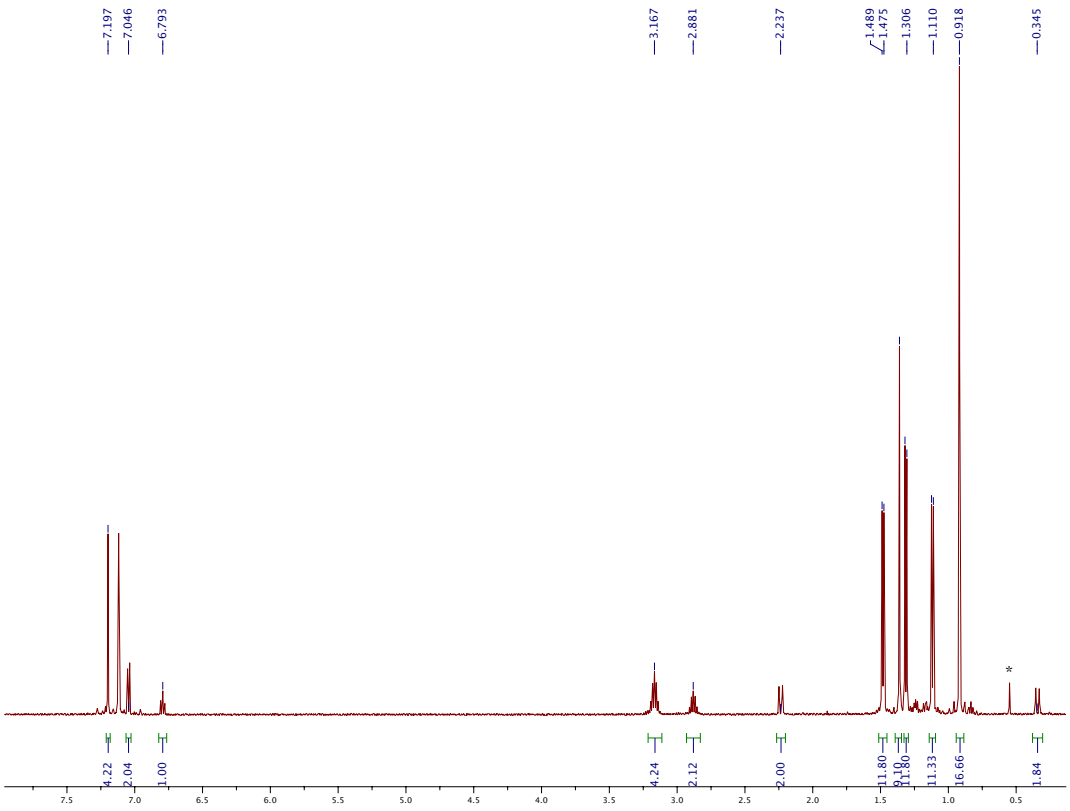
^{1}H NMR spectrum of $\mathbf{2_W}$.



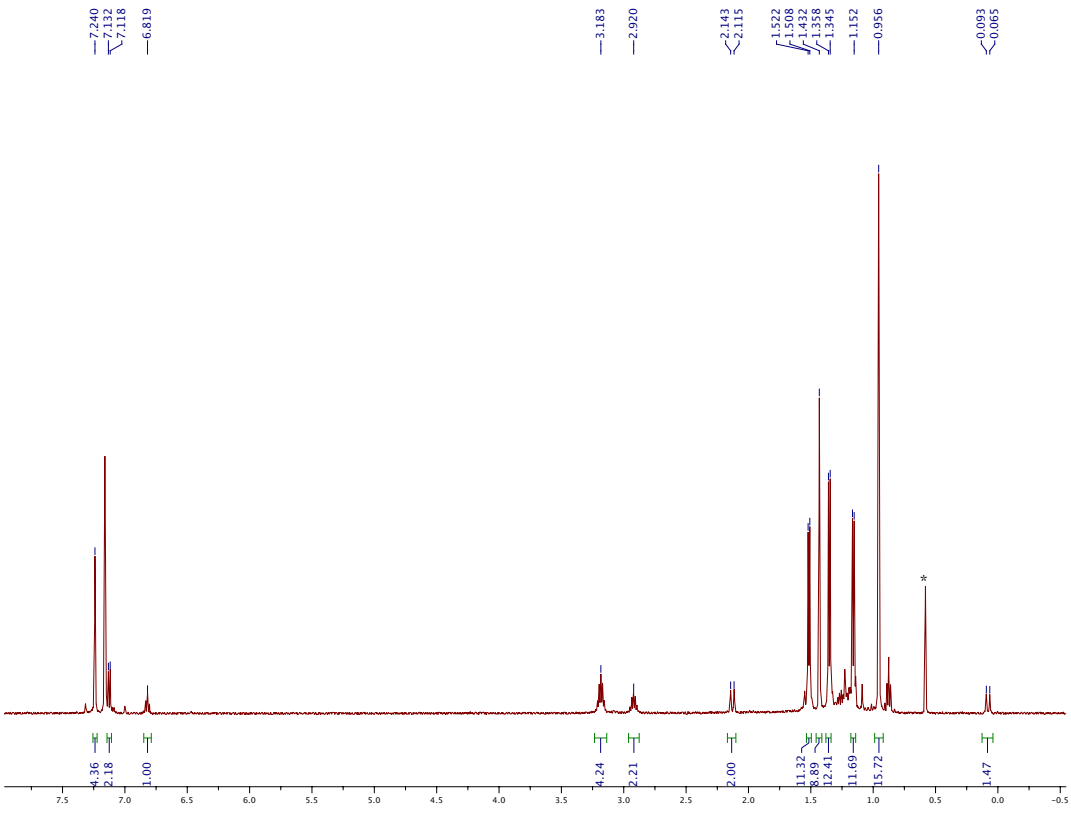
^{1}H NMR spectrum of $\mathbf{3_{Mo}}$ before treatment with $ClMgCH_2$-*t*-Bu.



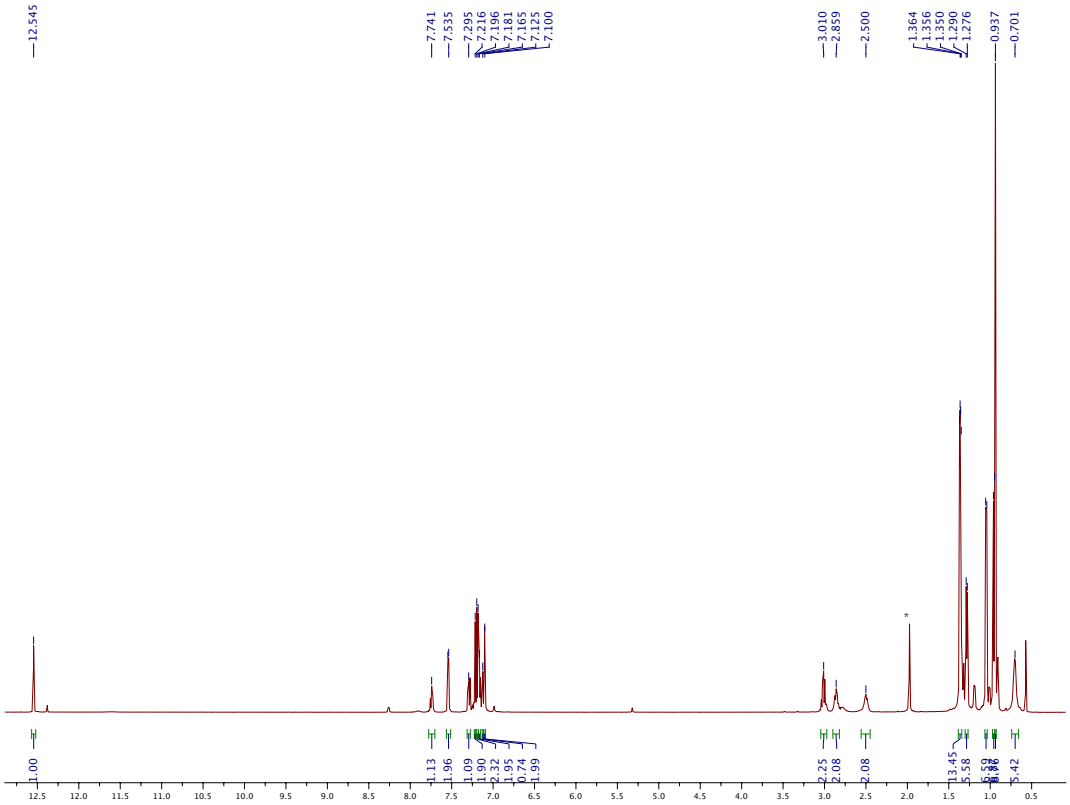
^{1}H NMR spectrum of $\mathbf{3_W}$ before treatment with $ClMgCH_2$-*t*-Bu.



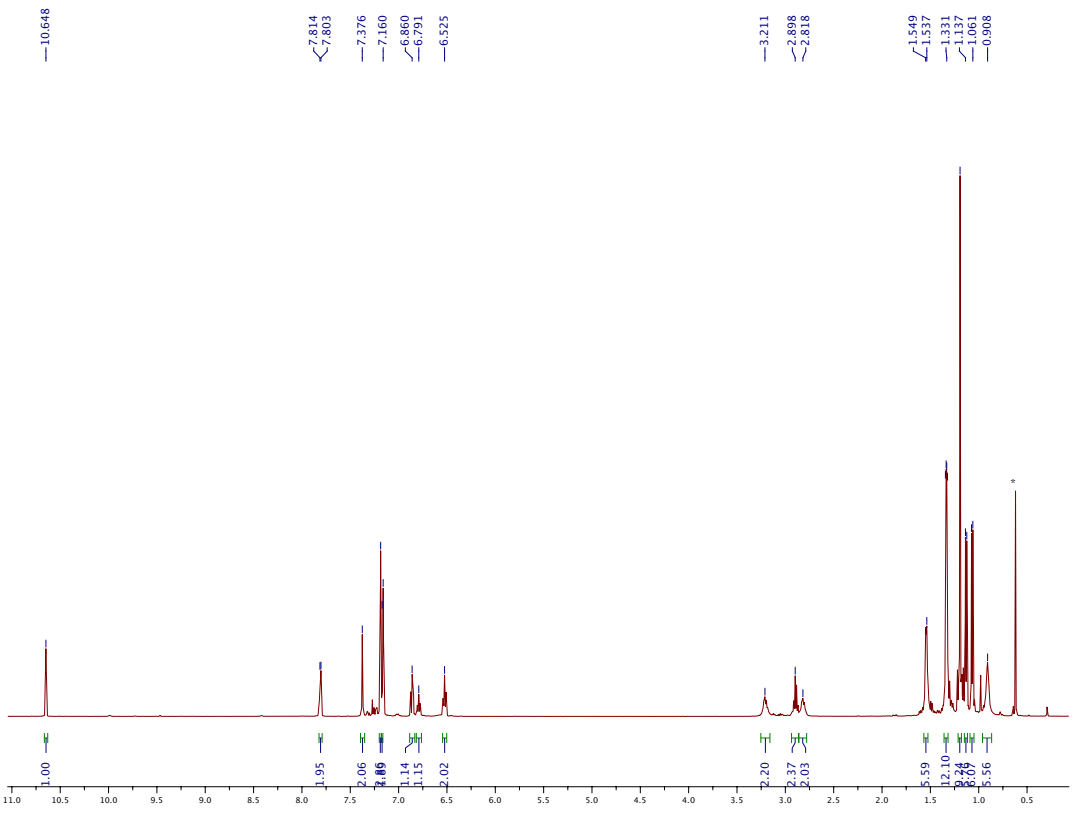
^{1}H NMR spectrum of $\mathbf{4_{Mo}}$.



^{1}H NMR spectrum of $\mathbf{4_W}$.



^{1}H NMR spectrum of $\mathbf{5_{Mo}}$ in CD_2Cl_2.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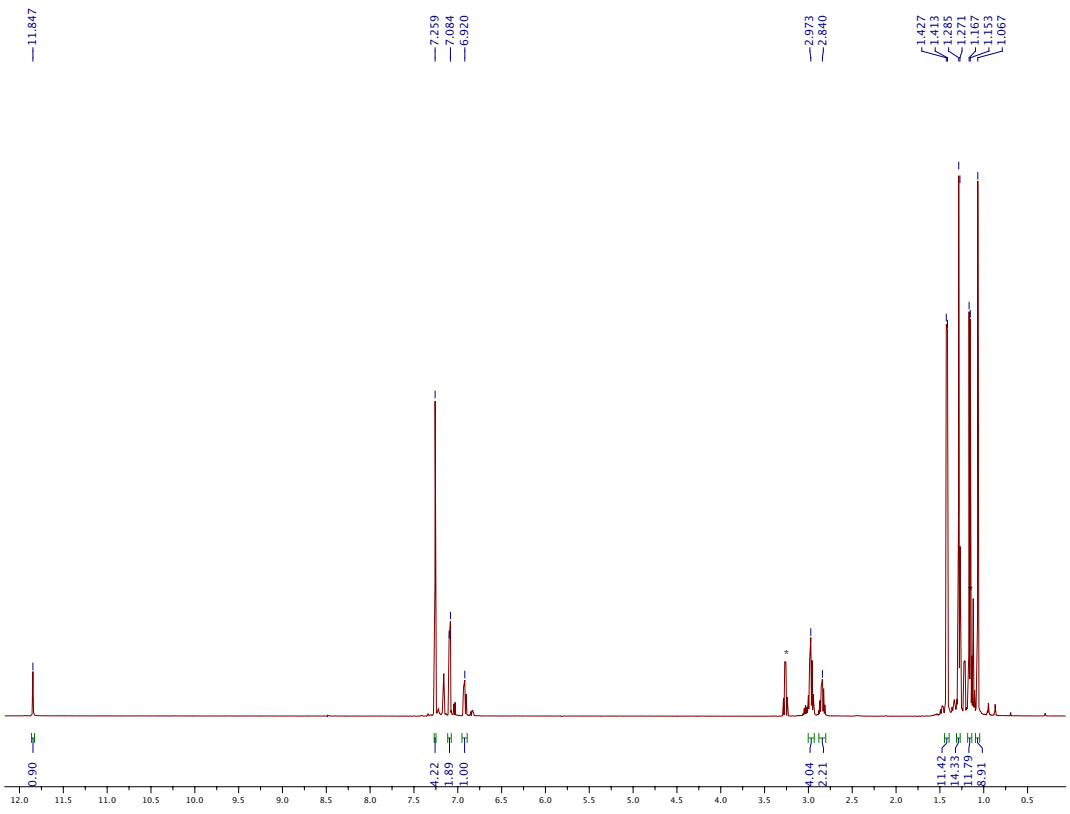
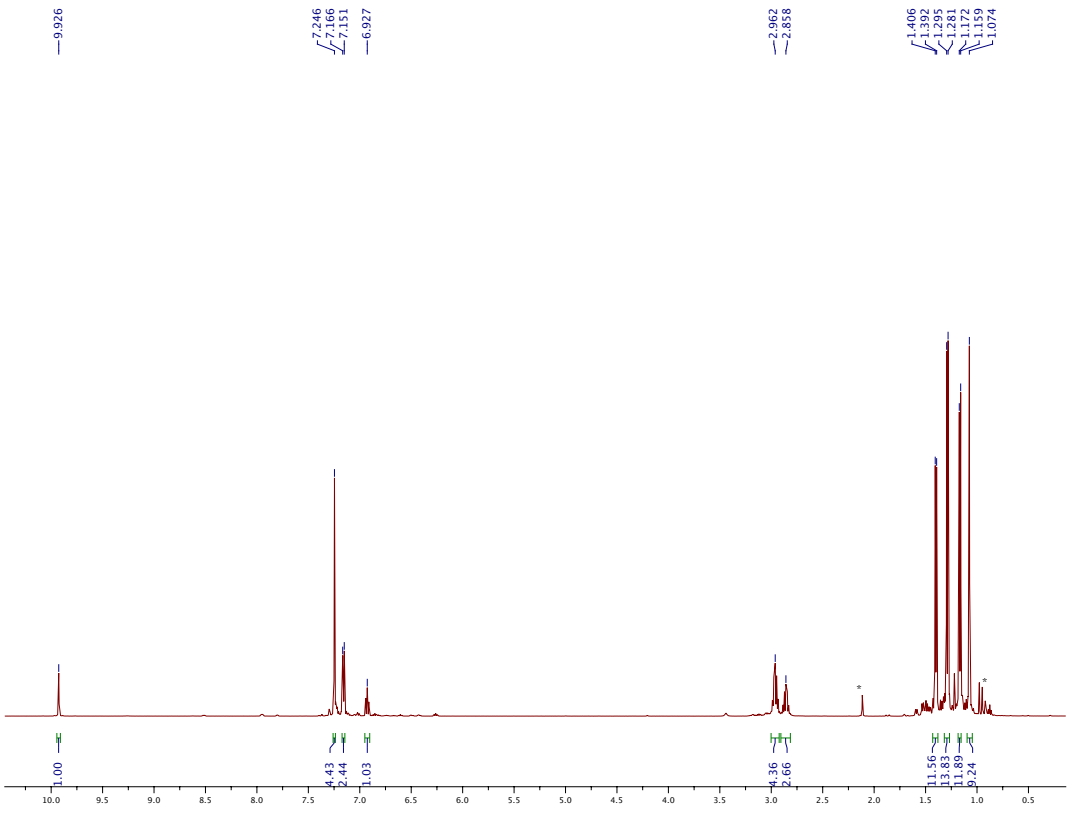
7.803
7.376
7.160
6.860
6.791
6.525
3.211
2.898
2.818
1.549
1.537
1.331
1.137
1.061
0.908
1.00
1.95
2.06
1.14
1.15
2.02
2.20
2.37
2.03
5.59
12.10
5.56

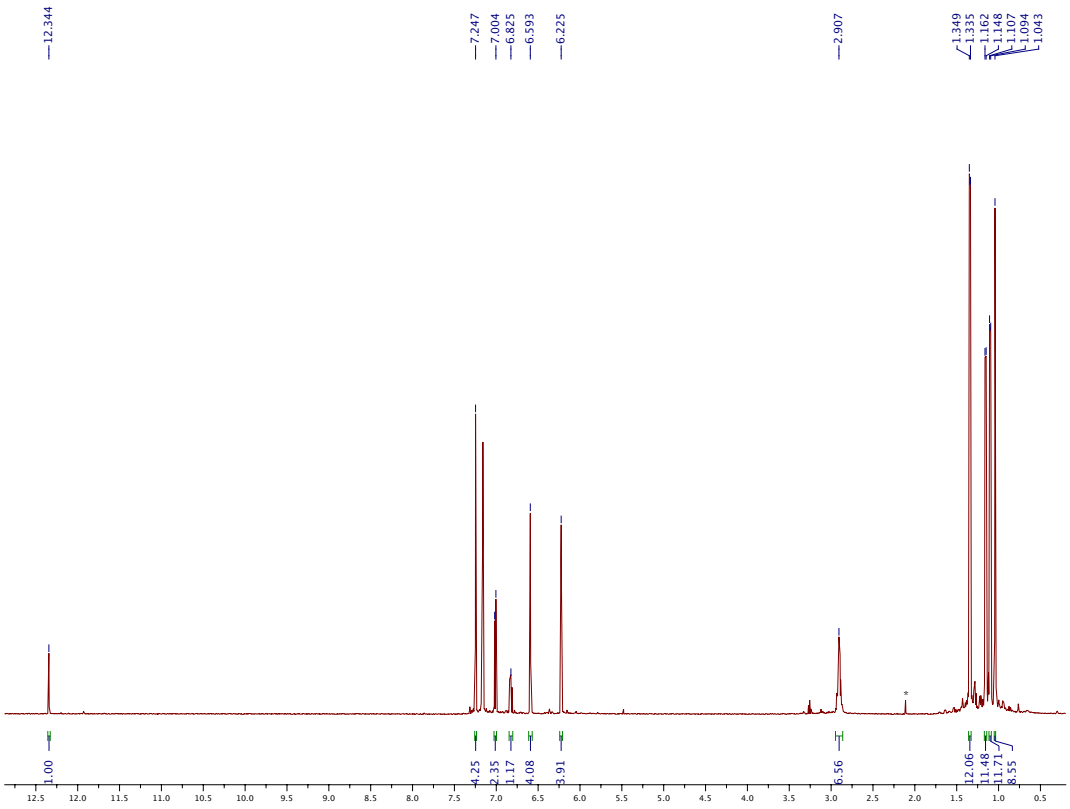
^{1}H NMR of **5$_{W}$**.



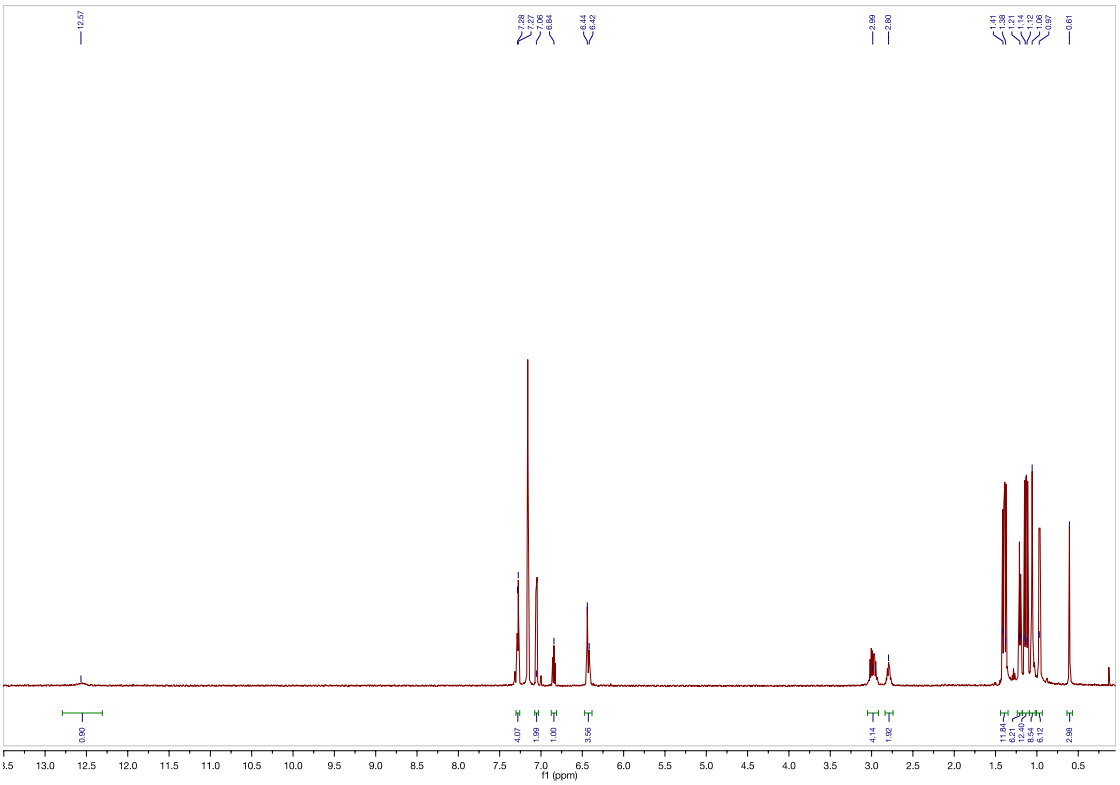
^{1}H NMR spectrum of $\mathbf{6_{Mo}}$.



^{1}H NMR spectrum of $\mathbf{6_W}$.



^{1}H NMR spectrum of $\mathbf{7_{Mo}}$.



^{1}H NMR spectrum of $\mathbf{8_{Mo}}$.

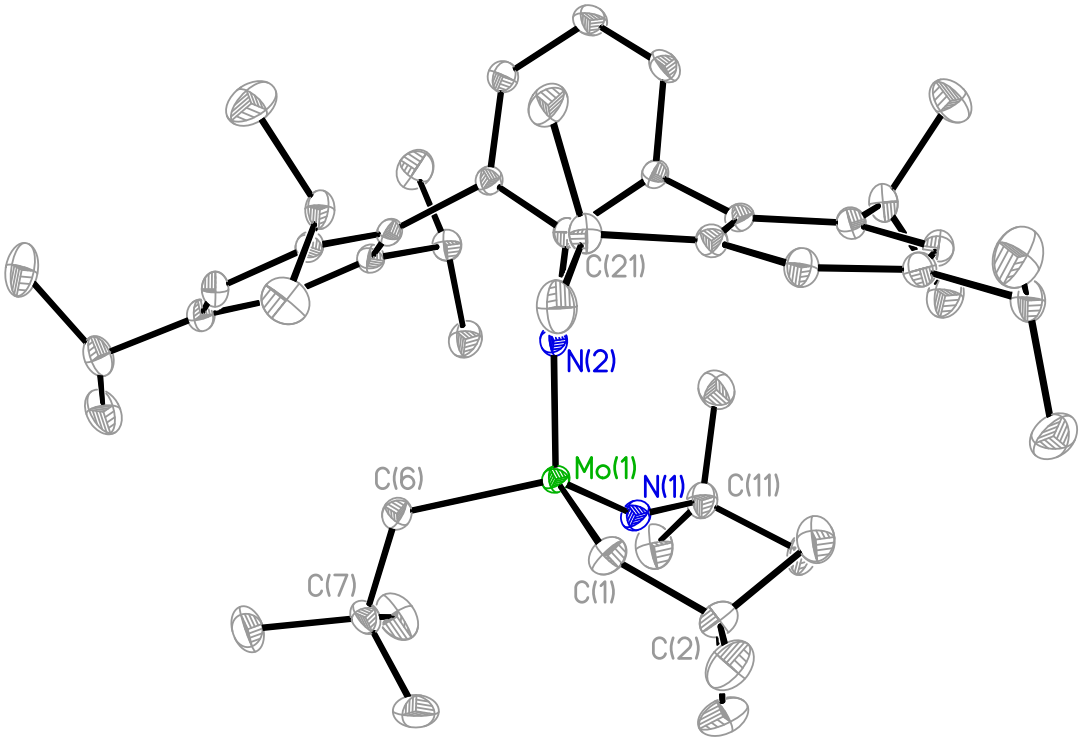


Figure S1. Thermal ellipsoid drawing (50%) of Mo(NHIPT)(N^{t}Bu)(CH_2-*t*-Bu)$_2$ (**4$_{Mo}$**). Hydrogen atoms and cocrystallized toluene have been omitted for clarity. Select bond distances (Å) and angles (˚): Mo1-N1 = 1.7477(17), Mo1-N2 = 1.7641(17), Mo1-C1 = 2.122(2), Mo1-C6 = 2.133(2); Mo1-N1-C11 = 156.88(15), Mo1-N2-C21 = 162.53(14), N2-Mo1-N1 = 114.00(8), Mo1-C1-C2 = 127.36(16), Mo1-C6-C7 = 122.70(15).

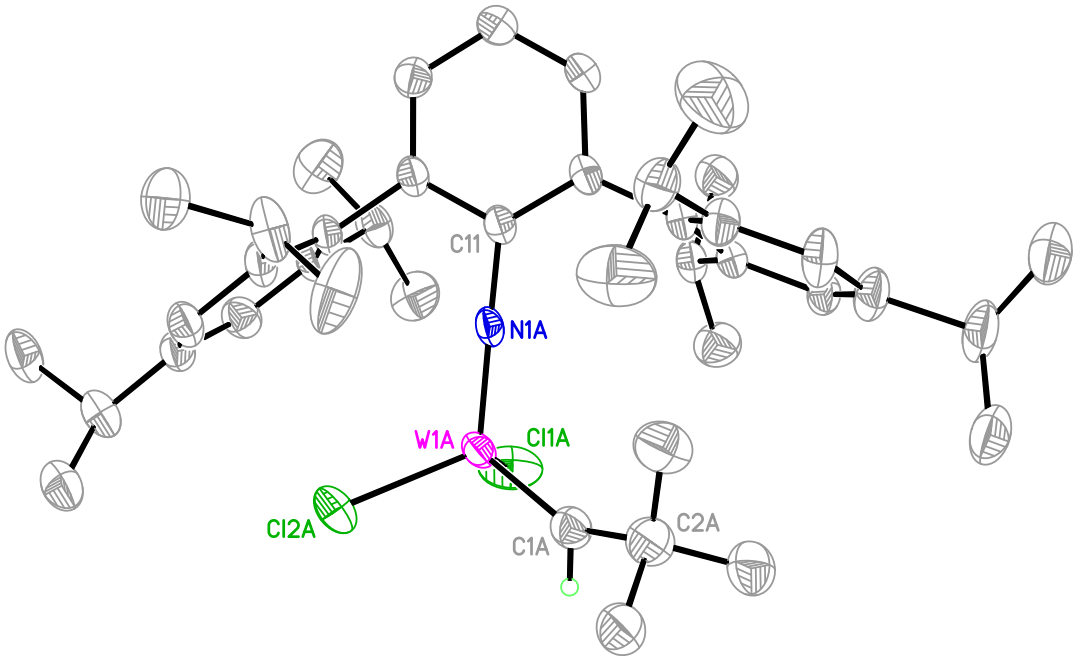


Figure S2. Thermal ellipsoid drawing of *syn*-W(NHIPT)(CH-*t*-Bu)Cl_2 (**6**$_W$). Hydrogen atoms have been omitted for clarity. Select bond distances (Å) and angles (˚): W1A-N1A = 1.760(14), W1A-C1A = 1.879(18), W1A-Cl1A = 2.256(11), W1A-Cl2A = 2.233(10); W1A-N1A-C11 = 179(8), W1A-C1A-C2A = 149(2), N1A-W1A-C1A = 114(3).

X-ray crystal structure determination details.

Low-temperature diffraction data (ϕ-and ω-scans) were collected on a Siemens Platform three-circle diffractometer coupled to a Bruker-AXS Smart Apex CCD detector with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) for the structure of $\mathbf{4_{Mo}}$ and on a Bruker-AXS X8 Kappa Duo diffractometer coupled to a Smart APEX2 CCD detector with Mo Kα radiation (λ = 0.71073 Å) from an IμS micro-source for the structure of compound $\mathbf{6_W}$. Absorption and other corrections were applied using TWINABS[4] for the structure of $\mathbf{4_{Mo}}$ and SADABS[5] for the structure of $\mathbf{6_W}$. All structures were solved by direct methods using SHELXT[6] and refined against F^2 on all data by full-matrix least squares with SHELXL-2013[7] using established refinement methods.[8] Unless noted otherwise below, all hydrogen atoms were included into the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U_{eq} value of the atoms they are linked to (1.5 times for methyl groups). Details about crystal properties, diffraction data and crystal structures can be found in the tables below.

$\mathbf{4_{Mo}}$ crystallizes in the triclinic centrosymmetric space group $P\bar{1}$ with one molecule of $\mathbf{4_{Mo}}$ and one molecule of toluene per asymmetric unit. The crystal was non-merohedrally twinned; two independent orientation matrices for the unit cell were found using the program CELL_NOW[9], and data reduction taking into account the twinning was performed with SAINT[10]. The program TWINABS[i] was used to set up the HKLF5 format file for structure refinement. The twin ratio was refined freely and converged at a value of 0.3988(6). Advanced rigid bond restraints[11] were applied to all atoms in order to counteract correlation effects caused by the twinning. Coordinates for hydrogen atoms bound to carbon directly attached to the central molybdenum atom (carbon atoms C1 and C6) were taken from the difference Fourier synthesis and those hydrogen atoms were subsequently refined semi-freely with the help of distance restraints.

$\mathbf{6_W}$ crystallizes in the orthorhombic centrosymmetric space group *Pbca* with one molecule of $\mathbf{6_W}$ per asymmetric unit. The structure shows substantial disorder and the refinement was challenging. Most importantly, the structure is a mixture of the of *syn* and *anti* isomers. Because the geometries of the two isomers are significantly different, the best description of this mixture would be a whole molecule disorder (WMD). Probably owing to additional disorders in the NHIPT ligand that are independent of the *syn-anti* disorder, a complete WMD model was not stable. Therefore, only the positions of the tungsten, chlorine and alkylidene carbon atoms (C1 to C10) were included in this "partial whole-molecule disorder". The ratio between *syn* and *any* isomers was refined

freely and converged at 0.860(3), corresponding to *ca*. 14% *syn* and 86% *anti*. Due to the much lower occupancy of the *syn* isomer, the *anti* molecule is described significantly better and the structural parameters obtained for the *syn* isomer are therefore much less precise that those of the *anti* isomer. This is evident from the higher standard uncertainties for all structural parameters of the *syn* isomer. In addition, it should be noted that the NHIPT ligand position belongs to the *anti* isomer, as the coordinates of this ligand could not be included in the *syn-anti* disorder. As mentioned above, the NHIPT ligand shows disorders unrelated to the described *syn-anti* disorder. Namely one full tri-isopropyl-phenyl group and two of the three iPr groups on the other tri-isopropyl-phenyl moiety were independently refined as disordered over two positions. All disorders were refined with the help of similarity restraints on 1-2 and 1-3 distances and displacement parameters as well as rigid bond restraints for anisotropic displacement parameters.

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Table S1. Crystal data and structure refinement for $\mathbf{4_{Mo}}$.

Identification code	14012_t5	
Empirical formula	C_{57} H_{88} Mo N_2	
Formula weight	897.23	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	$P\bar{1}$	
Unit cell dimensions	a = 11.366(2) Å	α = 88.474(4)°
	b = 13.229(3) Å	β = 89.275(3)°
	c = 18.298(3) Å	γ = 72.197(3)°
Volume	2618.6(8) Å^3	
Z	2	
Density (calculated)	1.138 Mg/m^3	
Absorption coefficient	0.286 mm^{-1}	
F(000)	972	
Crystal size	0.380 x 0.250 x 0.120 mm^3	
Theta range for data collection	1.113 to 30.508°.	
Index ranges	-16<=h<=16, -18<=k<=18, 0<=l<=26	
Reflections collected	16197	
Independent reflections	16197 [R_{int} = 0.0537]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	16197 / 473 / 576	
Goodness-of-fit on F^2	1.042	
Final R indices [I>2σ(I)]	R1 = 0.0359, wR2 = 0.0952	
R indices (all data)	R1 = 0.0417, wR2 = 0.1001	
Largest diff. peak and hole	0.538 and -0.732 e.Å^{-3}	

Table S2. Crystal data and structure refinement for $\mathbf{6_w}$.

Identification code	X14136	
Empirical formula	C_{41} H_{59} Cl_2 N W	
Formula weight	820.64	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	*Pbca*	
Unit cell dimensions	a = 19.2637(18) Å	α = 90°
	b = 16.7591(18) Å	β = 90°
	c = 24.480(3) Å	γ = 90°
Volume	7903.2(14) Å^3	
Z	8	
Density (calculated)	1.379 Mg/m^3	
Absorption coefficient	3.086 mm^{-1}	
F(000)	3360	
Crystal size	0.170 x 0.110 x 0.075 mm^3	
Theta range for data collection	1.813 to 30.506°.	
Index ranges	-13<=h<=27, -23<=k<=23, -34<=l<=34	
Reflections collected	141820	
Independent reflections	12060 [R_{int} = 0.0966]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.4942 and 0.3487	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	12060 / 2343 / 622	
Goodness-of-fit on F^2	1.103	
Final R indices [I>2σ(I)]	R1 = 0.0587, wR2 = 0.1315	
R indices (all data)	R1 = 0.0823, wR2 = 0.1428	
Largest diff. peak and hole	2.382 and -2.089 e.Å^{-3}	