Supporting Information to Accompany,
"Nitrogen Fixation to Cyanide at a Molybdenum Center"

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Contents:

General Considerations

All manipulations were carried out under an atmosphere of purified nitrogen in a Vacuum Atmospheres Model MO-40M glovebox equipped with the QP-30 accessory, or by standard Schlenk techniques.[1,2] Inside the MO-40M glovebox the ambient temperature ranged from 18–22 °C. All glassware was oven-dried at a temperature above 150 °C for at least 12 hours and allowed to cool under dynamic vacuum prior to use. Celite, alumina, and 4 Å sieves were activated by heating to a temperature greater than 180 °C under a dynamic vacuum for 2 d (Celite) or 5 d (alumina and 4 Å sieves). Et_2O, *n*-hexane, and *n*-pentane were bubble degassed with nitrogen and forced, under positive pressure, through a column of activated alumina followed by a column of activated Q5.[3] CH_2Cl_2 was bubble degassed with nitrogen and forced, under positive pressure, through two columns of activated alumina.[3] $CHCl_3$ was distilled from CaH_2. All solvents were stored over 4 Å sieves. C_6D_6 was degassed by three freeze-pump-thaw cycles and stored over 4 Å sieves for 3 d prior to use. $CDCl_3$ was refluxed over CaH_2 for 24 h then distilled and stored over 4 Å sieves. ^1H and ^{13}C NMR shifts are referenced against residual solvent resonances (for $CDCl_3$ 7.25 ppm and 77.23 ppm). All ^{15}N NMR spectra are externally referenced to neat $H_3CC^{15}N$ (δ = 245 ppm) in comparison to liquid NH_3 (δ = 0 ppm.[4] UV-vis spectra were obtained on an HP8453 spectrophotometer in 1 cm quartz cells manufactured by Starna. FT-IR spectra were obtained on a Bruker Tensor 37 Fourier Transform Infrared Spectrometer equipped with a Bruker Platinum ATR. Positive ion ESI-MS were obtained using a Bruker Daltonics APEXIV, 4.7 T Fourier Transform Ion Cyclotron Resonance Mass Spectrometer. Combustion analysis was performed by Midwest Microlab, LLC (Indianapolis, IN). Literature procedures were used for the preparation of $NMo(N[^tBu]Ar)_3$, **2**.[5] The following compounds were purchased from the indicated commercial source, and were used as received: $MeOCH_2I$ (Aldrich), $^iPr_3SiOTf$ (Oakwood Chemical), $LiN(SiMe_3)_2$ (Aldrich), $SnCl_2$ (Alfa Aesar), Me_3SiNMe_2 (Aldrich), and Me_3SiCN (Aldrich). No difference in reactivity was noted for $MeOCH_2Cl$ when it was prepared by a literature procedure[6] or purchased (Aldrich).

Synthesis of $[MeOCH_2NMo(N[^tBu]Ar)_3][OTf]$, [3][OTf]

At 20 °C, a solution of $NMo(N[^tBu]Ar)_3$ (2 g, 3.13 mmol) in 30 mL $CHCl_3$ was added to neat methoxymethyl chloride (252 mg, 3.13 mmol, 1 equiv) to form a yellow homogenos solution. This solution was then added to neat tri-*iso*propylsilyltriflate (959 mg, 3.13 mmol, 1 equiv) to form a dark red solution. The solution was stirred for 30 min before the solvent was removed by a placing the flask under a dynamic vacuum. The residue so-obtained was dissolved in a minimum of CH_2Cl_2 (approx. 10 mL) before 100 mL of *n*-hexane was added. The solvent was removed from this mixture under a dynamic vacuum. Twice more 100 mL *n*-hexane was added and the solvent removed under a dynamic vacuum to afford a red powder. This powder was transferred onto a sintered-glass frit and washed with *n*-pentane (50 mL × 6) to removed tri-*iso*propylsilylchloride. The yellow-orange powder that remained atop the frit was collected (2.283 g, 2.74 mmol, 87.5%). This material is can be stored as a solid at 20 °C for several weeks without noticeable decomposition. ^1H NMR ($CDCl_3$, 400 MHz, 20 °C): δ = 7.00 (3H, s, *p*-Ar), 6.09 (3H, s, CH_2OCH_3), 5.64 (6H, br s, *o*-Ar), 2.17 (18 H, s, Ar-Me), 1.26 (27 H, s, $C(CH_3)_3$) ppm. ^{19}F NMR ($CDCl_3$, 400 MHz, 20 °C): δ = –78 ppm. ^{13}C NMR ($CDCl_3$, 100 MHz, 20 °C): δ = 146.2, 138.8, 130.9, 128.2, 68.6, 77.4, 59.4, 32.0, 21.6 ppm. EA for $C_{39}H_{58}F_3MoN_4O_4S$, *calc* C, 56.3; H, 7.02; N, 6.73 *found* C, 55.9; H, 7.07; N, 6.4. Additional characterization data for ^{15}N-derivative: ^{15}N NMR ($CDCl_3$, 50 MHz, 20 °C): δ = 466 ppm. ESI-MS: 685.3775 (M^+, 685.375) amu.

Formation of $[MeOCH_2NMo(N[^tBu]Ar)_3][I]$, [3][I]

At 20 °C, into 0.5 mL of $CDCl_3$ was dissolved first methoxymethyl iodide (20 mg, 0.116 mmol, 1 equiv) and then $NMo(N[^tBu]Ar)_3$ (74 mg, 0.116 mmol). Upon dissolving $NMo(N[^tBu]Ar)_3$ an orange solution immediately formed, in contrast to yellow color typical of solutions of the NMo(N[^{t}Bu]Ar)$_3$. After 15 min, the sample was analyzed by ^{1}H NMR spectroscopy: both starting materials had been completely consumed and the observed resonances matched those given for [MeOCH$_2$NMo(N[^{t}Bu]Ar)$_3$][OTf]. The product is formulated as [MeOCH$_2$NMo(N[^{t}Bu]Ar)$_3$][I], although difficulty in obtaining crystalline material prevented full characterization of this product. Addition of LiN(SiMe$_3$)$_2$ to [MeOCH$_2$NMo(N[^{t}Bu]Ar)$_3$][I] in Et$_2$O gave MeO(H)CNMo(N[^{t}Bu]Ar)$_3$.

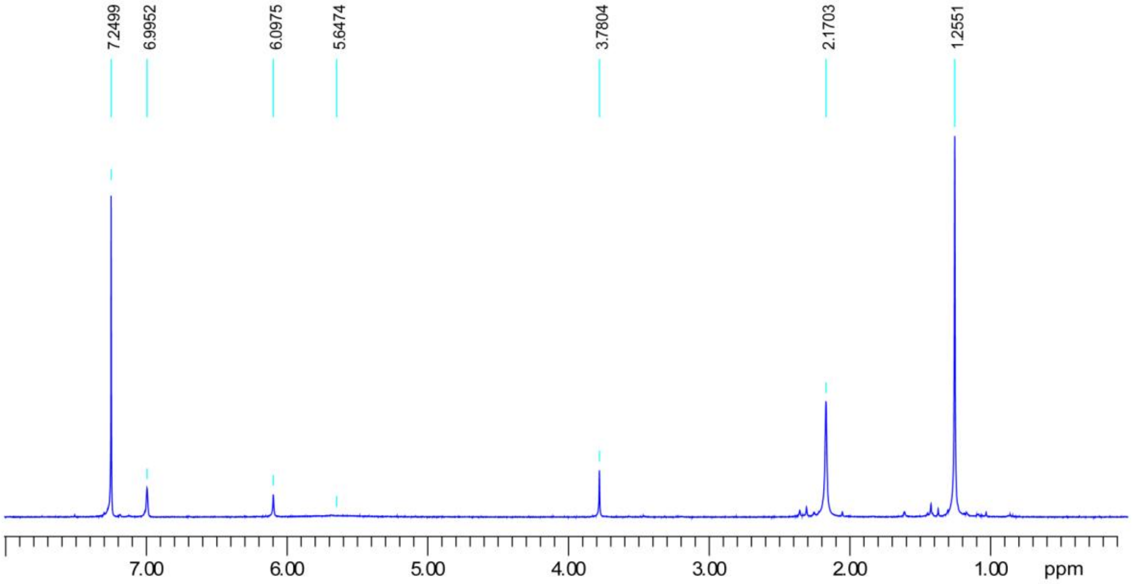

Figure S1. ^{1}H NMR spectrum (CDCl$_3$, 400 MHz, 20 °C) of [MeOCH$_2$NMo(N[^{t}Bu]Ar)$_3$][OTf], [**3**][OTf].

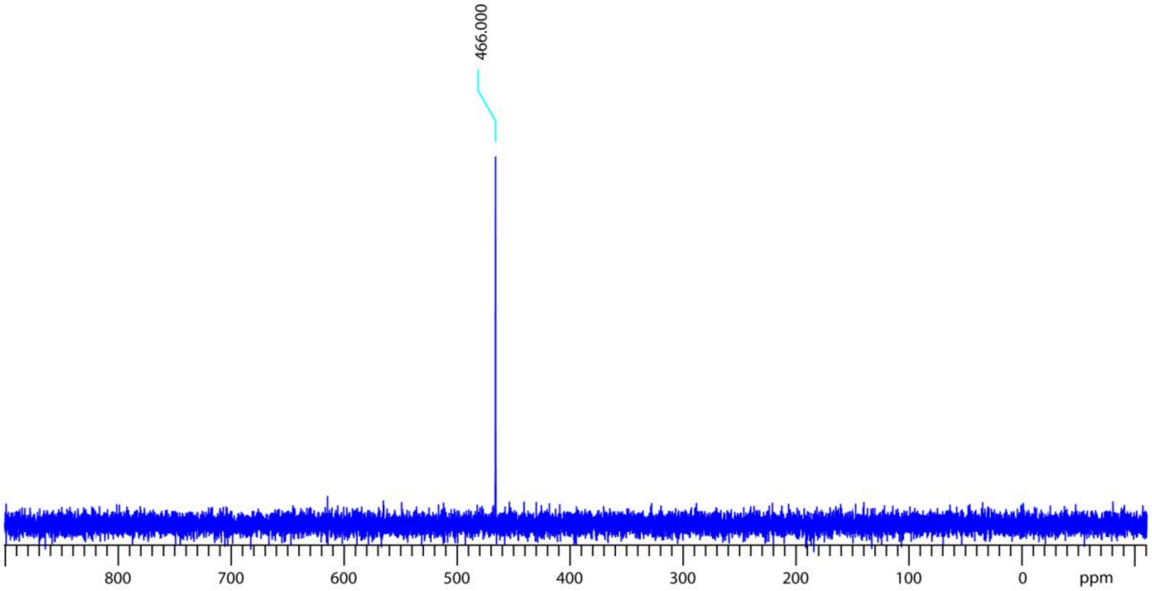

Figure S2. ^{15}N{^{1}H} NMR spectrum (CDCl$_3$, 50 MHz, 20 °C) of [MeOCH$_2$NMo(N[^{t}Bu]Ar)$_3$][OTf], [**3**][OTf]. No $^2J_{NH}$ was detected in the proton-coupled spectrum.

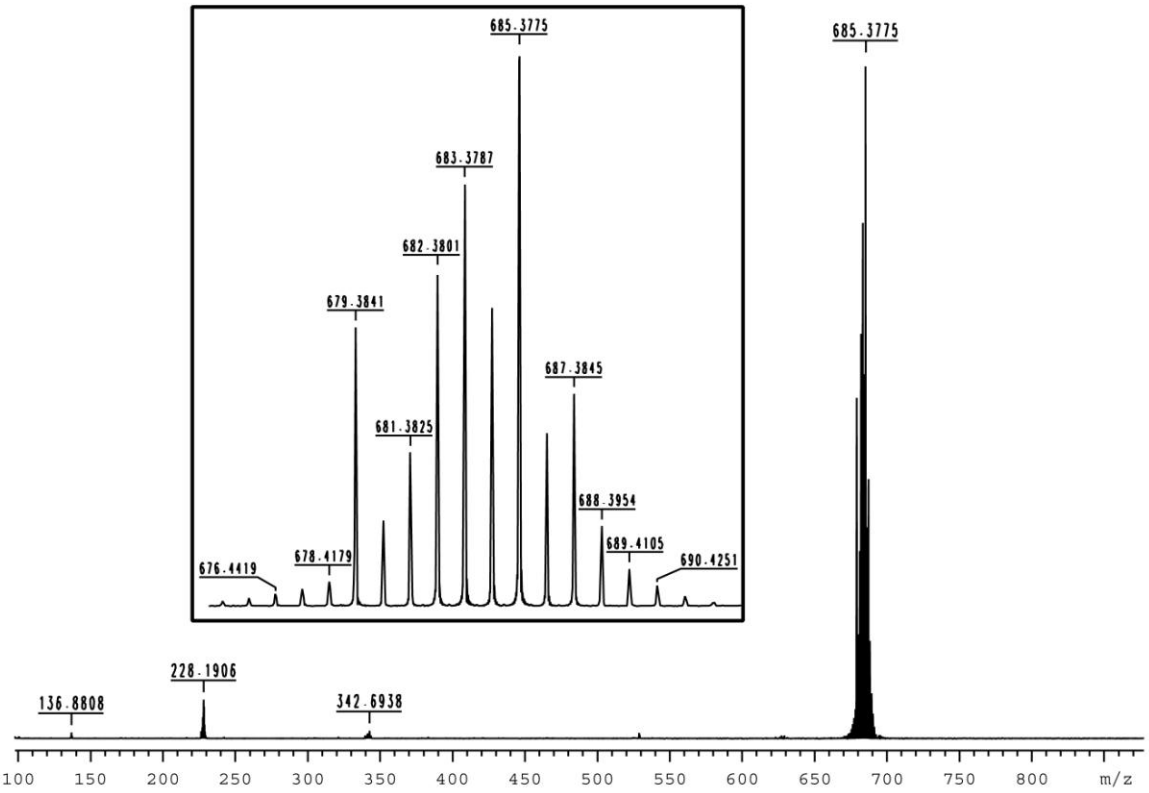

Figure S3. Positive-ion ESI-MS for [MeOCH$_2$NMo(N[^{t}Bu]Ar)$_3$][OTf], [**3**][OTf], in CH$_2$Cl$_2$.

Synthesis of MeOC(H)NMo(N[^{t}Bu]Ar)$_3$, 4

At 20 °C, to an orange solution of [MeOCH$_2$NMo(N[^{t}Bu]Ar)$_3$][OTf] (400 mg, 0.481 mmol) in Et$_2$O was added a slurry of LiN(SiMe$_3$)$_2$ (80.5, 0.481, 1 equiv) in 8 mL Et$_2$O. Upon addition, the solution immediately became dark blue in color. The blue solution was stirred for 10 min before 20 mL of *n*-hexane was added to the solution and the solvent was removed under dynamic vacuum. The resulting residue was extracted into thawing *n*-pentane (3 × 20 mL, –130 °C) and filtered through celite to remove an insoluble brown solid, presumably LiOTf. Removing the solvent from the filtrate under dynamic vacuum gave a sticky, blue solid (310 mg, 0.455 mmol, 95%). This material is pure, as assayed by ^{1}H NMR spectroscopy, but decomposes when stored at 20 °C for several hours. For the purposes of elemental analysis, the product was precipitated from a mixture of Et$_2$O and MeCN by storing the solution at –35 °C for 14 d to obtain a blue solid. ^{1}H NMR (C$_6$D$_6$, 400 MHz, 20 °C): δ = 7.37 (1H, s, *H*CN), 6.36 (9H, s, *p*-Ar and *o*-Ar), 3.10 (3H, s, OC*H*$_3$), 2.19 (18 H, s, Ar-Me), 1.30 (27 H, s, C(C*H*$_3$)$_3$) ppm. ^{13}C NMR (C$_6$D$_6$, 100 MHz, 20 °C): δ = 175.9, 153.3, 137.5, 137.1, 126.6, 63.5, 53.2, 32.3, 21.9 ppm. UV-vis (Et$_2$O, 20 °C): λ (ε) = 359 (9000, shoulder), 501 (1900), 615 (2500) nm (M^{-1}cm^{-1}). EA for C$_{38}$H$_{58}$MoN$_4$O, calc C, 66.84; H, 8.56; N, 8.21 found C, 66.78; H, 8.38; N, 8.47. Additional characterization data for ^{15}N-derivative: ^{15}N NMR (C$_6$D$_6$, 50 MHz, 20 °C): δ = 382 ppm, $^2J_{NH}$ = 2.5 Hz.

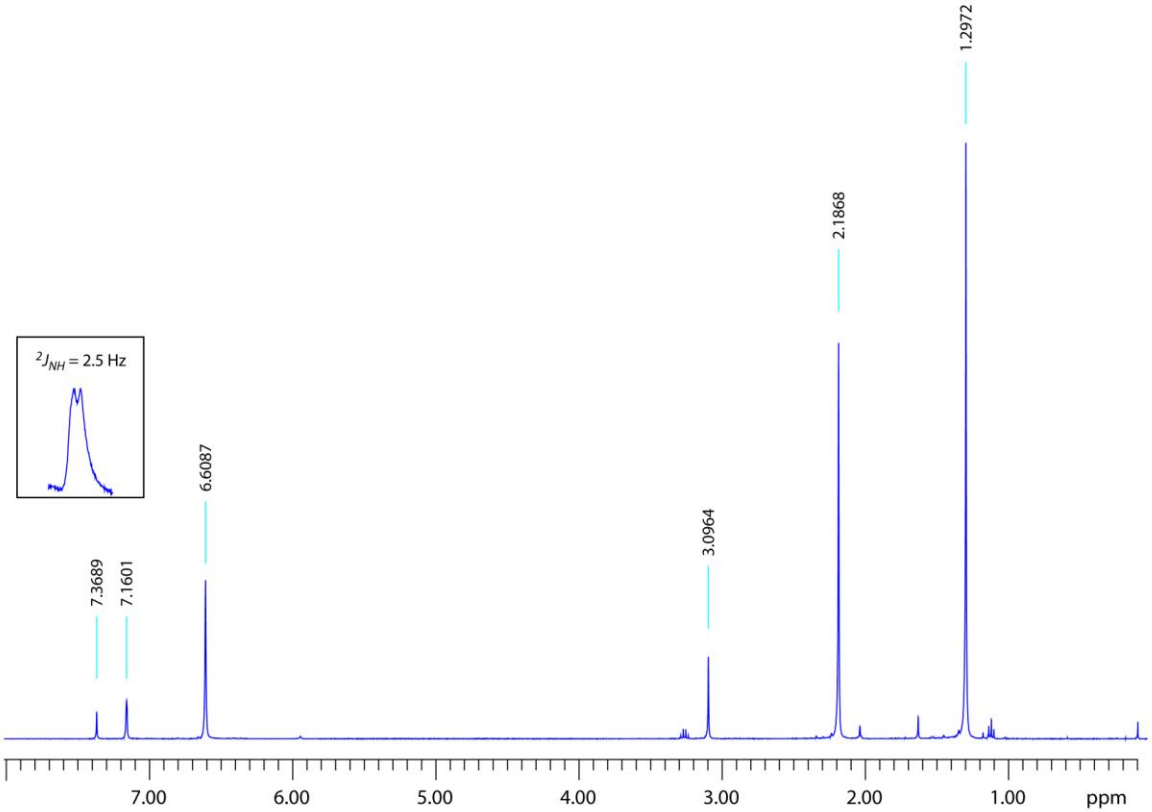

Figure S4. ^{1}H NMR spectrum (C_6D_6, 400 MHz, 20 °C of MeOC(H)NMo(N[^{t}Bu]Ar)$_3$, **4**, (inset) $^2J_{NH}$ observed for MeOC(H)^{15}NMo(N[^{t}Bu]Ar)$_3$, ^{15}N-**4**.

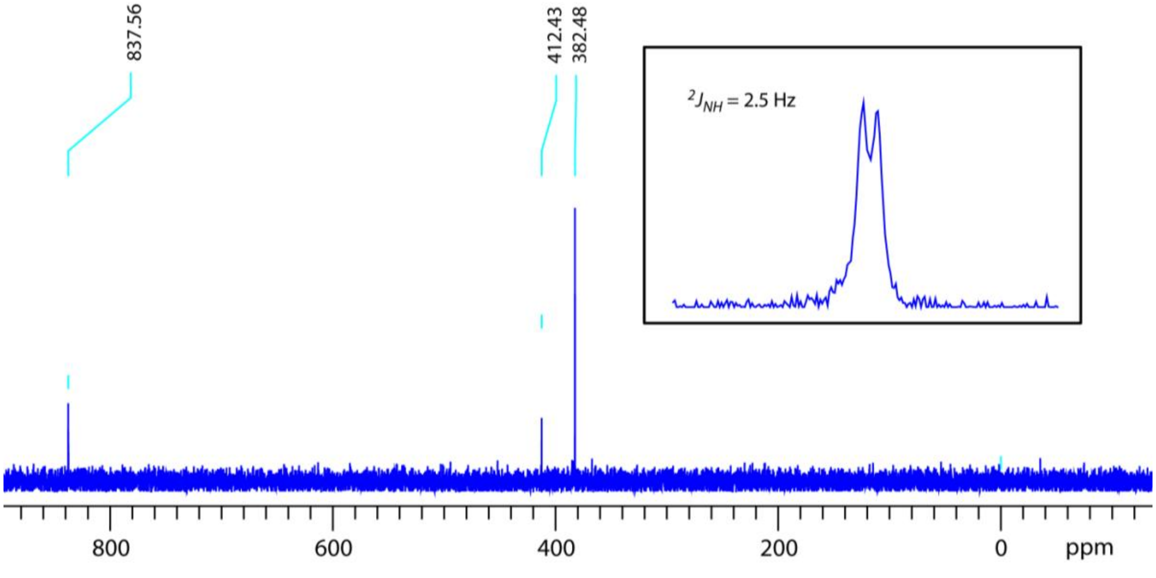

Figure S5. ^{15}N{^{1}H} NMR spectrum (C_6D_6, 50 MHz, 20 °C) of MeOC(H)^{15}NMo(N[^{t}Bu]Ar)$_3$, ^{15}N-**4**, shows a resonance at 382 ppm. Impurities in this spectrum are at 837 ppm (NMo(N[^{t}Bu]Ar)$_3$, **2**) and 412 ppm (unassigned). (inset) ^{15}N NMR spectrum taken in the absence of proton decoupling shows $^2J_{NH}$ = 2.5 Hz.

Treatment of MeOC(H)NMo(N[^{t}Bu]Ar)$_3$, 4, with 0.5 SnCl$_2$ and 10 Me$_3$SiNMe$_2$ to afford NCMo(N[^{t}Bu]Ar)$_3$, 5

To a rapidly stirred solution of MeOC(H)NMo(N[^{t}Bu]Ar)$_3$ (1.022 g, 1.5 mmol) in 80 mL Et$_2$O at 20 °C was added Me$_2$NSiMe$_3$ (1.755g, 15 mmol, 10 equiv). The SnCl$_2$ (285 mg, 1.5 mmol, 1 equiv) was added as a powder. The resulting reaction mixture was stirred for 30 min, over which time the initially blue solution took on a brown color. After that time, the reaction mixture was filtered through celite and the solvent was removed under a dynamic vacuum. Twice, 60 mL of *n*-hexane was added to the so obtained solids, and the solvent was again removed in vacuo. The remaining solids were dissolved in a minimum of Et$_2$O, and this solution was stored at –35 °C for several days to afford NCMo(N[^{t}Bu]Ar)$_3$ as a crystalline solid (527 mg, 0.8 mmol, 54%). This product was identified by its characteristic ^{1}H NMR spectrum.[7] No resonance was located in the ^{15}N NMR spectrum, nor was a ν_{CN} found in the FT-IR or Raman spectra of ^{15}N-**5**.

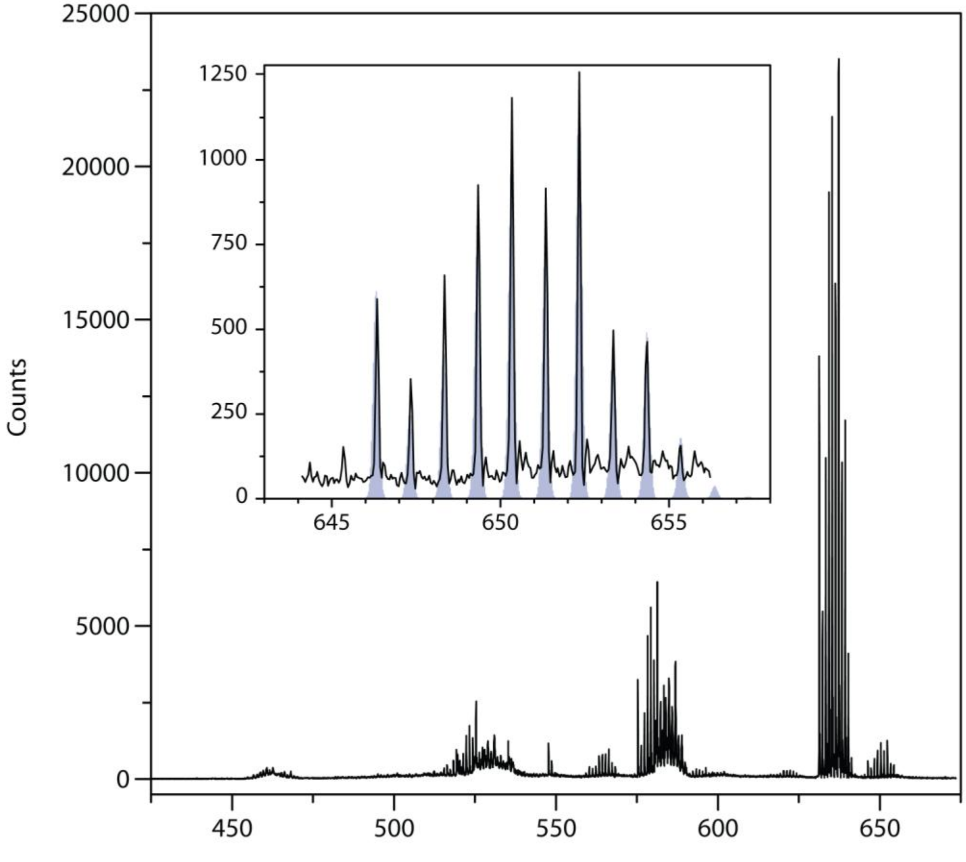

Figure S6. MALDI-TOF mass spectrograph of NCMo(N[^{t}Bu]Ar)$_3$, **5**, produced by the treatment of MeOC(H)NMo(N[^{t}Bu]Ar)$_3$, **4**, with a combination of SnCl$_2$ and Me$_2$NSiMe$_3$. The inset shows the isotope pattern observed for the molecular ion overlaid on the calculated pattern.

Conversion of MeOC(H)^{15}NMo(N[^{t}Bu]Ar)$_3$, ^{15}N-4, to ^{15}NCMo(N[^{t}Bu]Ar)$_3$, ^{15}N-5, in the presence of Me$_3$SiCN

Freshly prepared MeOC(H)^{15}NMo (295 mg, 0.300 mmol) was dissolved in 50 mL Et$_2$O that contained Me$_2$NSiMe$_3$ (350 mg, 10 equiv) and Me$_3$SiCN (30 mg, 0.303 mmol, 1 equiv) at 20 °C. To this solution was added SnCl$_2$ (56.5 mg, 0.298 mmol, 1 equiv). The mixture was stirred for 30 min, over which time it changed in color from blue to red-brown. An aliquot of the crude reaction mixture was removed and the solution analyzed by FT-IR. The spectrum showed a single band at 2195 cm^{-1} which was confirmed to be Me$_3$SiCN by comparison with an Et$_2$O solution of the pure material. Moreover, in the crude reaction mixture no bands were located that were consistent with the formation of Me$_3$SiC^{15}N during the course of the reaction.

The procedure described above was repeated on a 0.120 mmol scale, in the absence of added Me$_3$SiCN. Under these conditions the band attributed to Me$_3$SiCN at 2195 cm^{-1} was not observed in the FT-IR of the crude reaction mixture while all other bands were present in the spectrum.

UV-vis monitoring of the reaction MeOC(H)NMo(N[^{t}Bu]Ar)$_3$, 4 → NCMo(N[^{t}Bu]Ar)$_3$, 5

An Et$_2$O solution that was 0.3 mM in MeOC(H)NMo(N[^{t}Bu]Ar)$_3$ and 3 mM in Me$_3$SiNMe$_2$ was prepared, and *ca*. 3.5 mL of this solution was transferred into a cuvette containing a magnetic stirbar. To this mixture was added a single flake (5 mg, 0.026 mmol, 25 equiv) of SnCl$_2$. The cuvette was sealed placed in the diode-array UV-vis spectrometer equipped with a Peltier temperature-control. The cuvette was maintained at 20 °C while the mixture was magnetically stirred at a rate of 1000 rpm. The single flake of SnCl$_2$ did not dissolve during the course of the reaction. The reaction mixture was monitored by taking a UV-vis spectrum in 30-s intervals for 30 min after which time the reaction was judged to be complete. For clarity, spectra were plotted in 5 min intervals for Figure 1 of the main text.

Small Scale Reaction of ClMo(N[^{t}Bu]Ar)$_3$ with Me$_3$SiCN

To ClMo(N[^{t}Bu]Ar)$_3$ (50 mg, 0.078 mmol) was added 5 mL of a 20 mM Et$_2$O stock solution of Me$_3$SiCN (0.10 mmol, 1.3 equiv). The reaction mixture was stirred for 1 hour before the solvent was removed by a dynamic vacuum. The remaining solids were dissolved in C$_6$D$_6$. A ^{1}H NMR spectrum of the crude reaction mixture showed the presence of both ClMo(N[^{t}Bu]Ar)$_3$ and NCMo(N[^{t}Bu]Ar)$_3$. Approximately 33% of the ClMo(N[^{t}Bu]Ar)$_3$ starting material had been converted to NCMo(N[^{t}Bu]Ar)$_3$, as estimated by integration of the ^{t}Bu resonances at 24 ppm for ClMo(N[^{t}Bu]Ar)$_3$ and 31 ppm for NCMo(N[^{t}Bu]Ar)$_3$.

Preparation of NCMo(N[^{t}Bu]Ar)$_3$, 5, by treatment of ClMo(N[^{t}Bu]Ar)$_3$ with Me$_3$SiCN

A solution of ClMo(N[^{t}Bu]Ar)$_3$ (1.585 g, 2.404 mmol) in 20 mL Et$_2$O was added to neat Me$_3$SiCN (290 mg, 2.93 mmol, 1.2 equiv) at 20 °C. The mixture was stirred for 15 h after which time the solvent was removed by application of a dynamic vacuum. To the dried solids was added 30 mL of *n*-hexane which was immediately removed under dynamic vacuum. The remaining solids were extracted into a minimum of *n*-pentane and filtered through celite. This filtrate was concentrated to 15 mL to precipitate solids from solution. The resulting mixture was stored at –35

°C for 2 d to precipitate the product which was collected in a single crop (1.51 g, 2.32 mmol, 96.6%).

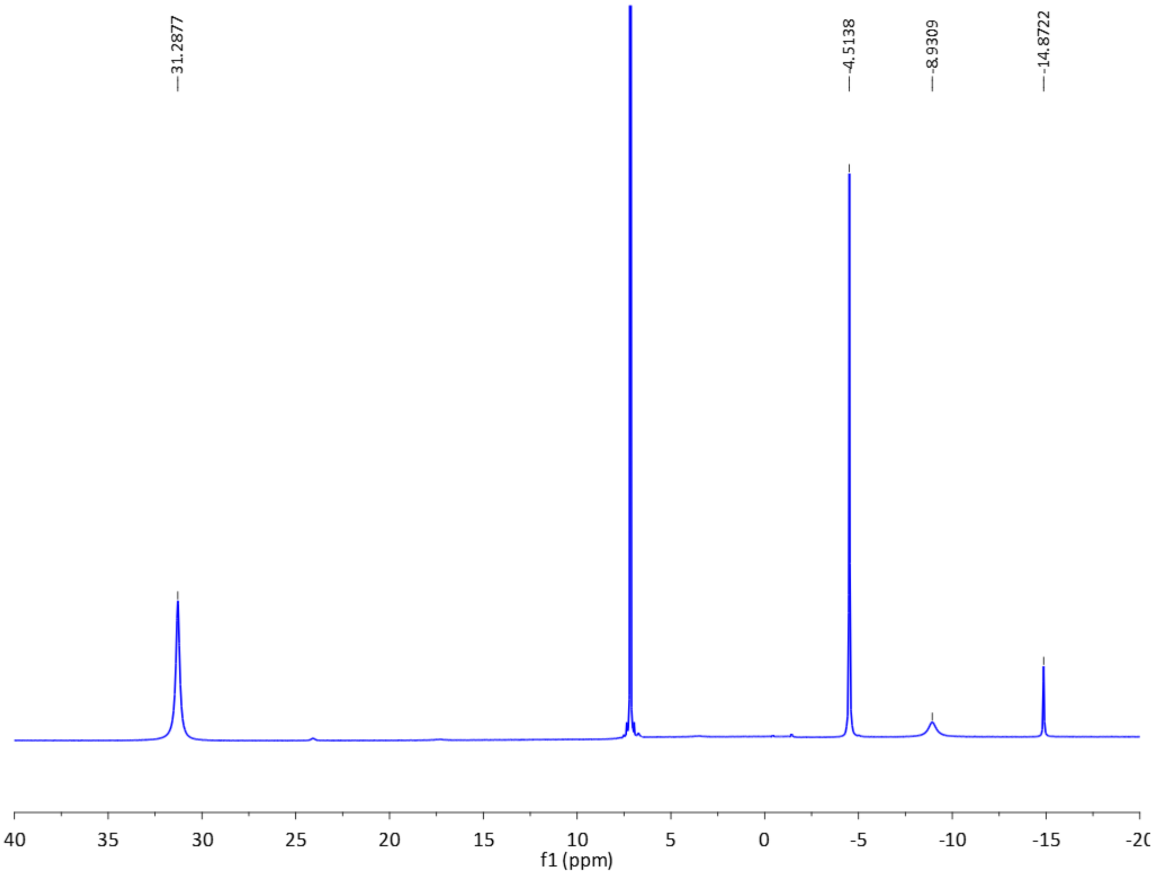

Figure S7. ^{1}H NMR spectrum (C_6D_6, 400 MHz, 20 °C) of NCMo(N[^{t}Bu]Ar)$_3$, **5**.

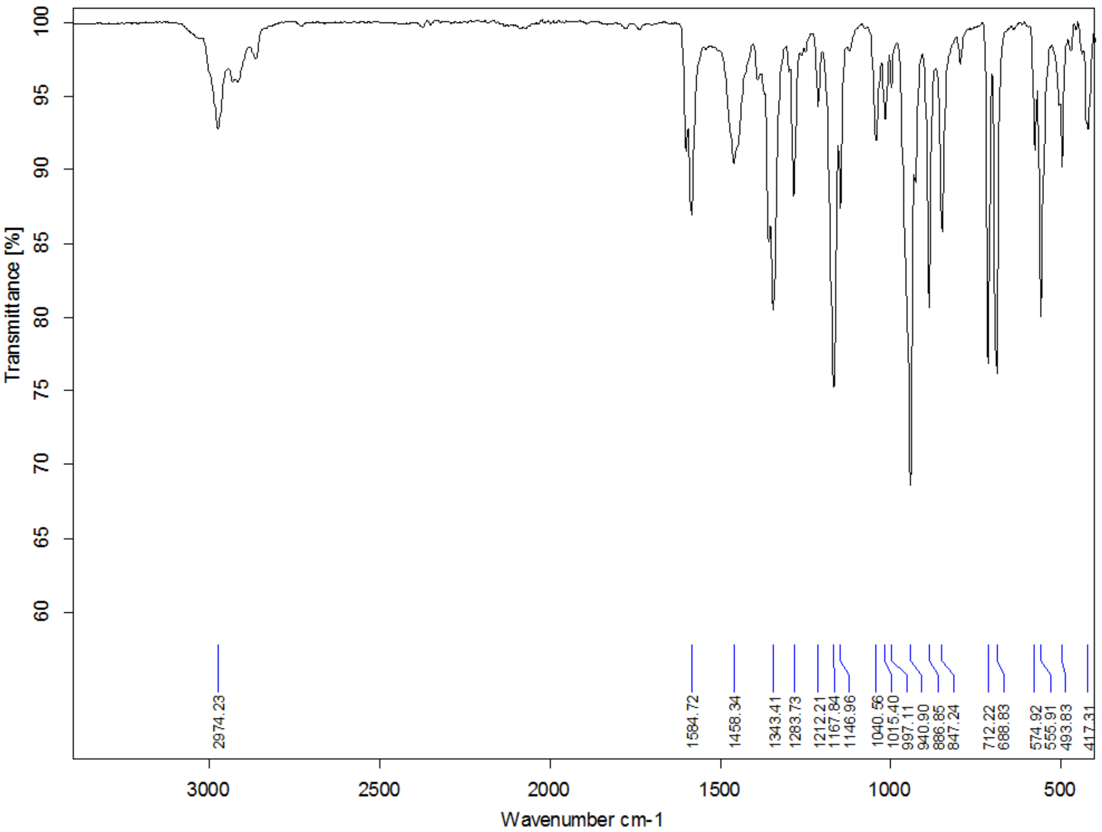

Figure S8. FT-IR spectrum (ATR) of NCMo(N[^{t}Bu]Ar)$_3$, **5**.

Crystallographic Structure Determination of NCMo(N[^{t}Bu]Ar)$_3$, 5

Diffraction quality crystals of **5** were grown from a saturated THF solution stored at -25 °C. The crystal was mounted on a MiTeGen MicroMount (Ithaca, NY) in oil. Low-temperature data were collected on a Siemens Platform three-circle diffractometer coupled to a Bruker-AXS Smart Apex CCD detector with graphite-monochromated Mo/κ radiation (l = 0.71073 Å), performing ω- and φ-scans. The structure was solved by direct methods using SHELXS and refined against F^2 on all data by full-matrix least squares with SHELXL-97.[8] A semi-empirical absorption correction (SADABS) was applied to the diffraction data.[9] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included in 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 value of the atoms they are linked to (1.5 times for methyl groups). The cyano ligand was initially modeled by including both linkage isomers in the model and allowing the occupancy to refine; a full occupancy for the cyano linkage isomer was identified.

Table S1. Crystal data and structure refinement for **5**.

Identification code	**5**	
Empirical formula	$C_{37}H_{54}MoN_4$	
Formula weight	650.78	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C 2/c	
Unit cell dimensions	a = 30.186(2) Å	α = 90°
	b = 10.5923(7) Å	β = 93.478(1)°
	c = 22.485 (2) Å	γ = 90°
Volume	7176.3(9) $Å^3$	
Z	8	
Density (calculated)	1.205 g/cm^3	
Absorption coefficient	0.394 mm^{-1}	
F(000)	2768	
Crystal size	0.60 x 0.60 x 0.30 mm^3	
Theta range for data collection	1.81 to 30.03°.	
Index ranges	-42<=h<=42, -14<=k<=14, -31<=l<=31	
Reflections collected	95861	
Independent reflections	10489 [R(int) = 0.0447]	
Completeness to θ = 30.03	100.00%	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8909 and 0.7978	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	10489 / 0 / 394	
Goodness-of-fit on F^2	1.04	
Final R indices [I>2σ(I)]	R1 = 0.0287, wR2 = 0.0691	
R indices (all data)	R1 = 0.0366, wR2 = 0.0745	
Largest diff. peak and hole	0.820 and -0.498 e·$Å^{-3}$	

Table S2. Bond lengths [Å] and angles [°] for **5**.

C(4)-N(41)	1.122(2)
C(4)-Mo(1)	2.0918(17)
C(11)-C(16)	1.398(2)
C(11)-C(12)	1.400(2)
C(11)-N(1)	1.4454(18)
C(12)-C(13)	1.400(2)
C(12)-H(12)	0.95
C(13)-C(14)	1.392(2)
C(13)-C(131)	1.510(2)
C(14)-C(15)	1.396(2)
C(14)-H(14)	0.95
C(15)-C(16)	1.396(2)
C(15)-C(151)	1.508(2)
C(16)-H(16)	0.95
C(17)-N(1)	1.5040(19)
C(17)-C(172)	1.519(3)
C(17)-C(173)	1.522(2)
C(17)-C(171)	1.539(3)
C(21)-C(26)	1.400(2)
C(21)-C(22)	1.402(2)
C(21)-N(2)	1.4435(18)
C(22)-C(23)	1.396(2)
C(22)-H(22)	0.95
C(23)-C(24)	1.391(2)
C(23)-C(231)	1.511(2)
C(24)-C(25)	1.394(2)
C(24)-H(24)	0.95
C(25)-C(26)	1.394(2)
C(25)-C(251)	1.509(2)
C(26)-H(26)	0.95
C(27)-N(2)	1.5003(18)
C(27)-C(273)	1.514(2)
C(27)-C(271)	1.521(2)

C(27)-C(272)	1.541(2)
C(31)-C(32)	1.3995(19)
C(31)-C(36)	1.403(2)
C(31)-N(3)	1.4434(18)
C(32)-C(33)	1.398(2)
C(32)-H(32)	0.95
C(33)-C(34)	1.391(2)
C(33)-C(331)	1.514(2)
C(34)-C(35)	1.400(2)
C(34)-H(34)	0.95
C(35)-C(36)	1.395(2)
C(35)-C(351)	1.510(2)
C(36)-H(36)	0.95
C(37)-N(3)	1.5020(19)
C(37)-C(373)	1.521(2)
C(37)-C(372)	1.523(2)
C(37)-C(371)	1.532(2)
C(131)-H(13A)	0.98
C(131)-H(13B)	0.98
C(131)-H(13C)	0.98
C(151)-H(15A)	0.98
C(151)-H(15B)	0.98
C(151)-H(15C)	0.98
C(171)-H(17A)	0.98
C(171)-H(17B)	0.98
C(171)-H(17C)	0.98
C(172)-H(17D)	0.98
C(172)-H(17E)	0.98
C(172)-H(17F)	0.98
C(173)-H(17G)	0.98
C(173)-H(17H)	0.98
C(173)-H(17I)	0.98
C(231)-H(23A)	0.98
C(231)-H(23B)	0.98

C(231)-H(23C)	0.98
C(251)-H(25A)	0.98
C(251)-H(25B)	0.98
C(251)-H(25C)	0.98
C(271)-H(27A)	0.98
C(271)-H(27B)	0.98
C(271)-H(27C)	0.98
C(272)-H(27D)	0.98
C(272)-H(27E)	0.98
C(272)-H(27F)	0.98
C(273)-H(27G)	0.98
C(273)-H(27H)	0.98
C(273)-H(27I)	0.98
C(331)-H(33A)	0.98
C(331)-H(33B)	0.98
C(331)-H(33C)	0.98
C(351)-H(35A)	0.98
C(351)-H(35B)	0.98
C(351)-H(35C)	0.98
C(371)-H(37A)	0.98
C(371)-H(37B)	0.98
C(371)-H(37C)	0.98
C(372)-H(37D)	0.98
C(372)-H(37E)	0.98
C(372)-H(37F)	0.98
C(373)-H(37G)	0.98
C(373)-H(37H)	0.98
C(373)-H(37I)	0.98
N(1)-Mo(1)	1.9574(12)
N(2)-Mo(1)	1.9530(12)
N(3)-Mo(1)	1.9637(12)
N(41)-C(4)-Mo(1)	178.95(15)
C(16)-C(11)-C(12)	119.26(13)
C(16)-C(11)-N(1)	120.56(13)

C(12)-C(11)-N(1)	120.14(13)
C(13)-C(12)-C(11)	120.57(14)
C(13)-C(12)-H(12)	119.7
C(11)-C(12)-H(12)	119.7
C(14)-C(13)-C(12)	118.82(14)
C(14)-C(13)-C(131)	120.53(14)
C(12)-C(13)-C(131)	120.66(15)
C(13)-C(14)-C(15)	121.80(14)
C(13)-C(14)-H(14)	119.1
C(15)-C(14)-H(14)	119.1
C(14)-C(15)-C(16)	118.45(14)
C(14)-C(15)-C(151)	121.29(14)
C(16)-C(15)-C(151)	120.24(14)
C(15)-C(16)-C(11)	121.08(14)
C(15)-C(16)-H(16)	119.5
C(11)-C(16)-H(16)	119.5
N(1)-C(17)-C(172)	110.74(13)
N(1)-C(17)-C(173)	109.00(13)
C(172)-C(17)-C(173)	109.24(17)
N(1)-C(17)-C(171)	109.06(13)
C(172)-C(17)-C(171)	109.94(18)
C(173)-C(17)-C(171)	108.83(15)
C(26)-C(21)-C(22)	119.18(13)
C(26)-C(21)-N(2)	121.10(13)
C(22)-C(21)-N(2)	119.70(13)
C(23)-C(22)-C(21)	120.66(14)
C(23)-C(22)-H(22)	119.7
C(21)-C(22)-H(22)	119.7
C(24)-C(23)-C(22)	118.80(14)
C(24)-C(23)-C(231)	120.22(15)
C(22)-C(23)-C(231)	120.96(15)
C(23)-C(24)-C(25)	121.82(14)
C(23)-C(24)-H(24)	119.1
C(25)-C(24)-H(24)	119.1

C(26)-C(25)-C(24)	118.65(14)
C(26)-C(25)-C(251)	120.95(15)
C(24)-C(25)-C(251)	120.40(15)
C(25)-C(26)-C(21)	120.88(14)
C(25)-C(26)-H(26)	119.6
C(21)-C(26)-H(26)	119.6
N(2)-C(27)-C(273)	110.60(13)
N(2)-C(27)-C(271)	109.25(12)
C(273)-C(27)-C(271)	109.88(14)
N(2)-C(27)-C(272)	109.09(13)
C(273)-C(27)-C(272)	110.90(18)
C(271)-C(27)-C(272)	107.03(15)
C(32)-C(31)-C(36)	119.04(13)
C(32)-C(31)-N(3)	120.13(13)
C(36)-C(31)-N(3)	120.82(12)
C(33)-C(32)-C(31)	120.63(14)
C(33)-C(32)-H(32)	119.7
C(31)-C(32)-H(32)	119.7
C(34)-C(33)-C(32)	119.24(14)
C(34)-C(33)-C(331)	120.85(14)
C(32)-C(33)-C(331)	119.87(15)
C(33)-C(34)-C(35)	121.33(14)
C(33)-C(34)-H(34)	119.3
C(35)-C(34)-H(34)	119.3
C(36)-C(35)-C(34)	118.70(14)
C(36)-C(35)-C(351)	119.80(14)
C(34)-C(35)-C(351)	121.48(14)
C(35)-C(36)-C(31)	121.04(13)
C(35)-C(36)-H(36)	119.5
C(31)-C(36)-H(36)	119.5
N(3)-C(37)-C(373)	110.94(14)
N(3)-C(37)-C(372)	109.68(12)
C(373)-C(37)-C(372)	109.18(16)
N(3)-C(37)-C(371)	109.15(13)

C(373)-C(37)-C(371)	110.18(18)
C(372)-C(37)-C(371)	107.64(14)
C(13)-C(131)-H(13A)	109.5
C(13)-C(131)-H(13B)	109.5
H(13A)-C(131)-H(13B)	109.5
C(13)-C(131)-H(13C)	109.5
H(13A)-C(131)-H(13C)	109.5
H(13B)-C(131)-H(13C)	109.5
C(15)-C(151)-H(15A)	109.5
C(15)-C(151)-H(15B)	109.5
H(15A)-C(151)-H(15B)	109.5
C(15)-C(151)-H(15C)	109.5
H(15A)-C(151)-H(15C)	109.5
H(15B)-C(151)-H(15C)	109.5
C(17)-C(171)-H(17A)	109.5
C(17)-C(171)-H(17B)	109.5
H(17A)-C(171)-H(17B)	109.5
C(17)-C(171)-H(17C)	109.5
H(17A)-C(171)-H(17C)	109.5
H(17B)-C(171)-H(17C)	109.5
C(17)-C(172)-H(17D)	109.5
C(17)-C(172)-H(17E)	109.5
H(17D)-C(172)-H(17E)	109.5
C(17)-C(172)-H(17F)	109.5
H(17D)-C(172)-H(17F)	109.5
H(17E)-C(172)-H(17F)	109.5
C(17)-C(173)-H(17G)	109.5
C(17)-C(173)-H(17H)	109.5
H(17G)-C(173)-H(17H)	109.5
C(17)-C(173)-H(17I)	109.5
H(17G)-C(173)-H(17I)	109.5
H(17H)-C(173)-H(17I)	109.5
C(23)-C(231)-H(23A)	109.5
C(23)-C(231)-H(23B)	109.5

H(23A)-C(231)-H(23B)	109.5
C(23)-C(231)-H(23C)	109.5
H(23A)-C(231)-H(23C)	109.5
H(23B)-C(231)-H(23C)	109.5
C(25)-C(251)-H(25A)	109.5
C(25)-C(251)-H(25B)	109.5
H(25A)-C(251)-H(25B)	109.5
C(25)-C(251)-H(25C)	109.5
H(25A)-C(251)-H(25C)	109.5
H(25B)-C(251)-H(25C)	109.5
C(27)-C(271)-H(27A)	109.5
C(27)-C(271)-H(27B)	109.5
H(27A)-C(271)-H(27B)	109.5
C(27)-C(271)-H(27C)	109.5
H(27A)-C(271)-H(27C)	109.5
H(27B)-C(271)-H(27C)	109.5
C(27)-C(272)-H(27D)	109.5
C(27)-C(272)-H(27E)	109.5
H(27D)-C(272)-H(27E)	109.5
C(27)-C(272)-H(27F)	109.5
H(27D)-C(272)-H(27F)	109.5
H(27E)-C(272)-H(27F)	109.5
C(27)-C(273)-H(27G)	109.5
C(27)-C(273)-H(27H)	109.5
H(27G)-C(273)-H(27H)	109.5
C(27)-C(273)-H(27I)	109.5
H(27G)-C(273)-H(27I)	109.5
H(27H)-C(273)-H(27I)	109.5
C(33)-C(331)-H(33A)	109.5
C(33)-C(331)-H(33B)	109.5
H(33A)-C(331)-H(33B)	109.5
C(33)-C(331)-H(33C)	109.5
H(33A)-C(331)-H(33C)	109.5
H(33B)-C(331)-H(33C)	109.5

C(35)-C(351)-H(35A)	109.5
C(35)-C(351)-H(35B)	109.5
H(35A)-C(351)-H(35B)	109.5
C(35)-C(351)-H(35C)	109.5
H(35A)-C(351)-H(35C)	109.5
H(35B)-C(351)-H(35C)	109.5
C(37)-C(371)-H(37A)	109.5
C(37)-C(371)-H(37B)	109.5
H(37A)-C(371)-H(37B)	109.5
C(37)-C(371)-H(37C)	109.5
H(37A)-C(371)-H(37C)	109.5
H(37B)-C(371)-H(37C)	109.5
C(37)-C(372)-H(37D)	109.5
C(37)-C(372)-H(37E)	109.5
H(37D)-C(372)-H(37E)	109.5
C(37)-C(372)-H(37F)	109.5
H(37D)-C(372)-H(37F)	109.5
H(37E)-C(372)-H(37F)	109.5
C(37)-C(373)-H(37G)	109.5
C(37)-C(373)-H(37H)	109.5
H(37G)-C(373)-H(37H)	109.5
C(37)-C(373)-H(37I)	109.5
H(37G)-C(373)-H(37I)	109.5
H(37H)-C(373)-H(37I)	109.5
C(11)-N(1)-C(17)	117.46(11)
C(11)-N(1)-Mo(1)	108.30(9)
C(17)-N(1)-Mo(1)	134.01(9)
C(21)-N(2)-C(27)	116.44(11)
C(21)-N(2)-Mo(1)	108.68(9)
C(27)-N(2)-Mo(1)	134.88(9)
C(31)-N(3)-C(37)	116.02(11)
C(31)-N(3)-Mo(1)	108.34(9)
C(37)-N(3)-Mo(1)	135.63(10)
N(2)-Mo(1)-N(1)	116.51(5)

N(2)-Mo(1)-N(3)	117.41(5)
N(1)-Mo(1)-N(3)	118.12(5)
N(2)-Mo(1)-C(4)	100.43(5)
N(1)-Mo(1)-C(4)	98.51(6)
N(3)-Mo(1)-C(4)	99.48(6)

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