Electronic Supplementary Information for:

Catalytic NH_3 Oxidation to N_2 by Hydrogen Atom Abstraction using a Low-valent Molybdenum Complex

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I. General Procedures

Synthetic investigations were carried out under an atmosphere of N_2 or Argon (Ar), utilizing standard glovebox and/or Schlenk techniques unless otherwise noted. NMR experiments were conducted in J. Young NMR tubes with a PTFE valve and recorded at 298 K on a Bruker ASCEND AVANCE III HD 500 MHz (500.2 MHz for ^{1}H, 125.8 MHz for ^{13}C, and 50.0 MHz for ^{15}N NMR spectroscopy) spectrometer equipped with a Prodigy (liquid nitrogen cooled) cryoprobe, or a Bruker AVANCE NEO 400 MHz (400.1 MHz for ^{1}H NMR, 100.0 MHz for ^{13}C, 40.5 MHz for ^{15}N NMR spectroscopy) spectrometer unless otherwise noted. ^{1}H and ^{13}C NMR spectra were referenced to residual proton resonances in deuterated solvent. ^{15}N NMR chemical shifts were referenced to CH_3NO_2 (δ=0). Chemical shift (δ) values are expressed in parts per million (ppm) relative to tetramethylsilane (TMS). Infrared spectra were recorded on a ThermoScientific Nicolet iS50 FT-IR spectrometer at ambient temperature (25 °C) and under a purge stream of nitrogen gas. Solution-state FT-IR samples were run in an International Crystal Labs liquid IR cell with CaF_2 windows. Solid-state FT-IR samples were prepared as KBr pellets. Gas Chromatographic/Mass Spectrometry (GC-MS) analysis was performed on an Agilent Technologies 7890A GC system equipped with a 5975C inert XL El/Cl MSD with Triple-Axis Detector. Chromatographic separation of the mixture was carried out using an Agilent Technologies DB-5MS column (30m x 250 mm x 0.25 mm d_f). A 200 mL volume of each sample in a gas tight syringe was injected into a split/splitless injector operated in split mode using a 200:1 split ratio with a constant flow of 1 mL/min of ultra-high purity helium carrier gas throughout the run. The injector temperature was held at 200 °C and the MS transfer line at 280 °C. The GC oven was held at 35 °C for 4 min, ramped at 25 °C/min to 200 °C with a hold for 1.4 min. The ion source temperature was 230 °C with electron impact ionization energy of –70 eV. Following a 0.1 min delay, data was collected from *m/z* 12-250 using a detector voltage of 1089 V. Gas reaction products produced in catalytic trials and NMR tube experiments were quantified using an Agilent Technologies 7820A GC System. The GC parameters for N_2 quantification in the catalytic trials are as follows: Column: Supelco Analytical 60/80 Carboxen 1000, 15ft x 1/8 in x 2.1 mm SS. Inlet temperature: 230 °C; Flow: 30 mL/min; Oven temperature and ramp program: initial temperature 35 °C, hold 10 min, 20 °C to 220 °C. hold 10.75 min.; Carrier gas: Ar; Detector: TCD at 250 °C. Ultrahigh Purity He

gas (99.999%) was used as an internal standard for N_2 quantification. The gas response factors for N_2, H_2, and He were determined using a premixed primary gas standard of H_2 (0.500%), He (0.503%), N_2 (4.980%), with the balance gas of argon, which was purchased from PurityPlus Specialty Gases. The gas retention times of He, H_2, N_2 were recorded as ~0.9, 1.1 and 5.1 min, respectively using the GC method listed above. NH_3 gas could be detected in GC traces (retention time of ~t=21 min) but could not be quantified accurately due to significant tailing of the peak. Prior to each catalytic trial, a sample of the Ar glovebox atmosphere was injected into the GC to analyze for N_2 in the argon glovebox environment. Oxygen and nitrogen could be resolved using the GC parameters noted above. Thus, air contamination (oxygen and nitrogen from air) during sample injection, which was rarely noted, could accurately be subtracted from the GC data. $^{15}NH_3$ gas was tested using GC-MS analysis to confirm $^{15}N_2$ was not present as an impurity.

II. Synthesis and Materials

All chemicals were purchased from commercial chemical vendors and used without further purification unless otherwise noted. Molecular sieves (3A, 4-8 mesh) were obtained from Thermo-Fischer Scientific and activated *in vacuo* at 250 °C for 24 h. Proteo solvents tetrahydrofuran (THF), 1,2-dimethoxyethane (DME), fluorobenzene (PhF), acetonitrile, diethyl ether, and pentane were sparged and stored under Ultra High Purity (UHP) argon gas before being dried via passage through a CHEMBLY solvent purification system (formerly JC Meyer Solvent Systems) using UHP argon as the working gas. Deuterated solvents were purchased from Cambridge Isotope Laboratories, degassed by three freeze-pump-thaw cycles, and stored in an N_2 or Ar filled glovebox over activated molecular sieves. Ammonia gas (99.9995% purity, 5.5 Semiconductor Process Grade) was purchased from Praxair and used as received. $^{15}NH_3$(g) (98%-^{15}N) was purchased from Cambridge Isotope Labs. Anhydrous hydrazine was purchased from Sigma-Aldrich. $Mo(CO)_3$(CHT) was purchased from Strem Chemicals Inc. Celite was obtained from Sigma-Aldrich and dried at 160 °C overnight prior to use. All glassware was heated to 160 °C overnight prior to use. $P^{tBu}{}_2N^{Ph}{}_2$,[1] 2,4,6-tri-*tert*-butylphenoxyl radical,[2] and 2,6-di-*tert*-butyl-4-tritylphenoxyl radical[3] were prepared according to published literature procedures. *Caution: Anhydrous hydrazine is highly toxic and can be explosive. Please handle safely and be familiar with the dangers of hydrazine. All manipulations using anhydrous hydrazine in this work were conducted*

on a small scale in the glovebox at room temperature and were not heated. Please reference "Wiley Guide to Chemical Incompatibilities" (Pohanish, R. P. and Greene, S. A.; Wiley, 3rd edition) for more information about the hazards of anhydrous hydrazine.

Synthesis and Characterization of *fac*-[$(CO)_3Mo(P^{tBu}_2N^{Ph}_2)(NCCH_3)$]; Complex 1

A 100 mL Schlenk tube with a Teflon valve and equipped with a stir bar was charged with a suspension of $Mo(CO)_3$(CHT) (0.250 g, 0.919 mmol) and $P^{tBu}_2N^{Ph}_2$ (0.381 g, 0.919 mmol) in 1:1 MeCN/fluorobenzene (20 mL total). The vessel was sealed and the stirred suspension was heated at 80 °C for 3 d. After the reaction was complete the solvents were removed under vacuum. A 1:1 mixture of Et_2O/MeCN was added to the solid residue, stirred for 5 min, and dried under vacuum affording a tan powder. MeCN (10 mL) was added to the solid and the resulting suspension was transferred to a 25 mL Schlenk flask and sealed with a Teflon valve. The suspension was heated at 80 °C to dissolve all the material (some brown precipitate remained). The flask was brought into the argon glovebox and the solution was filtered through Celite. The filtrate was transferred to a 20 mL scintillation vial. Yellow crystals (suitable for X-ray diffraction) began forming immediately. After 3 h, the crystallization vial was stored at -35 °C overnight to produce a crystalline solid. The mother liquor was decanted into another vial, concentrated to 5 mL under vacuum, and stored in the freezer to yield an additional crop of crystals. Crystals were dried under vacuum. Yield: 0.284 g, 20%. ^{1}H NMR (500 MHz, THF-d_8, 35 °C): δ 7.26-7.15 (4H, m) 7.08 (2H, d, J = 8.0 Hz), 7.93 (2H, d, J = 8.0 Hz), 6.82 (1H, t, J = 7.2 Hz), 6.69 (1H, t, J = 7.2 Hz), 4.10-4.03 (2H, m), 3.83 (2H, d, J = 14.3 Hz), 3.69-3.54 (4H, m), 1.97 (1H, s), 1.36-1.32 (18H, m). ^{31}P{^{1}H} NMR (202 MHz, THF-d_8, 35 °C): δ 36.9 (s). ^{13}C{^{1}H} NMR (100 MHz, THF-d_8, 35 °C): 155.1 (m), 153.4 (m), 130.0 (d), 120.9 (s), 118.7 (s), 118.4 (s), 116.1 (s), 66.1 (s), 51.1 (m), 47.4 (m), 32.4 (m), 26.8 (m), 26.1 (t), 15.5 (s). IR (C_6D_6): ν_{CO} = 1932 (vs), 1844 (vs), 1813 (vs) cm^{-1} (Mo-CO).

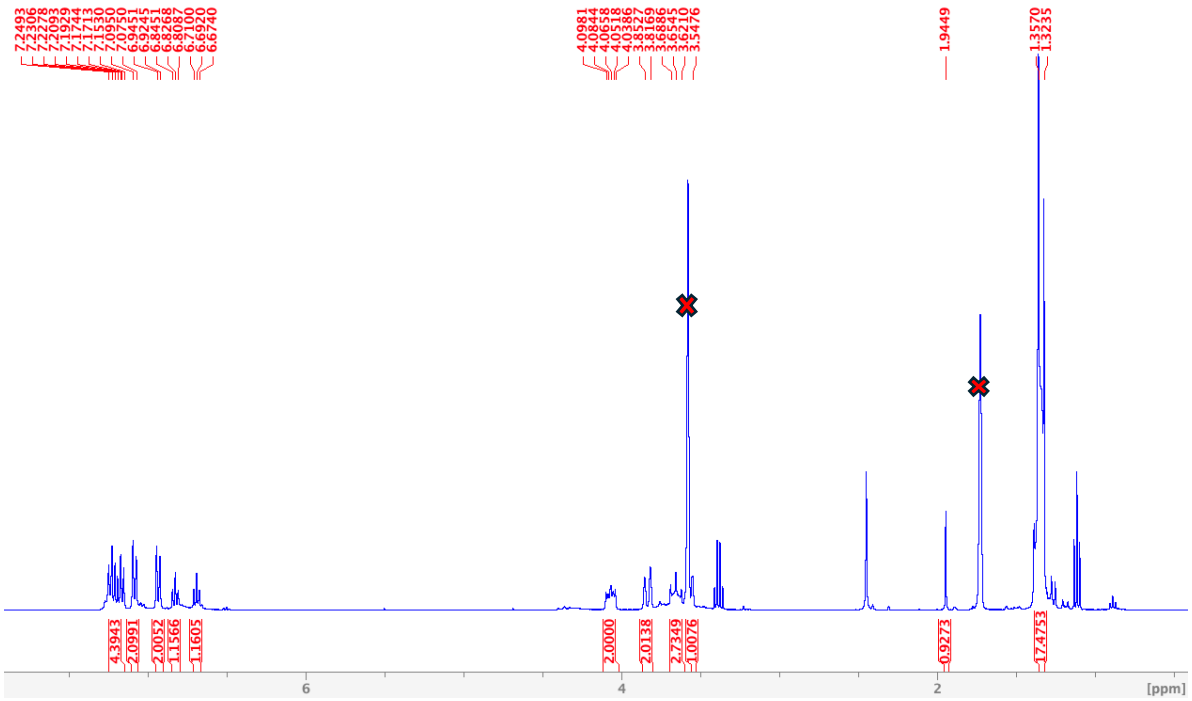


Figure S1. ^{1}H NMR spectrum of **1** in THF-d_8, at 500 MHz. Resonances marked with an X represent residual THF signals and unmarked resonances are solvent impurities present in the NMR solvent.

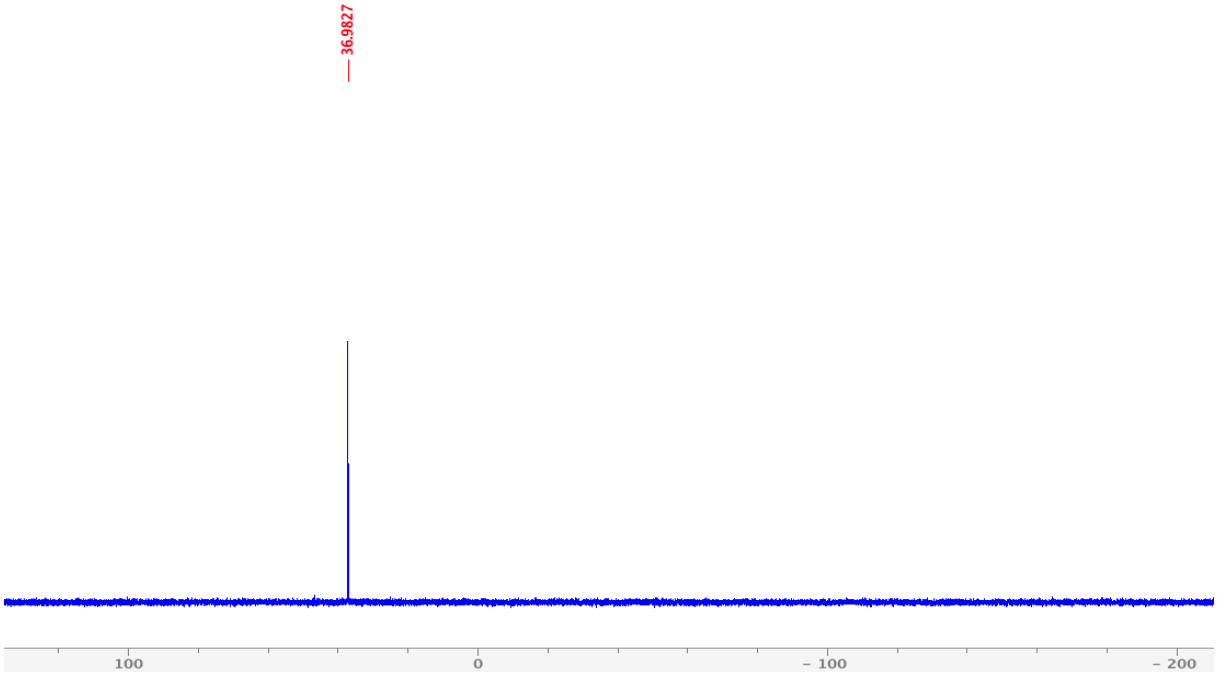


Figure S2. ^{31}P{^{1}H} NMR spectrum of **1** in THF-d_8, at 202 MHz.

Synthesis and Characterization of *fac*-[$(CO)_3Mo(P^{tBu}{}_2N^{Ph}{}_2)(NH_3)$]; Complex 2^{15N}

Working in an argon glovebox, complex **1** (0.025 g, 0.036 mmol) was added to a 20 mL scintillation vial and dissolved in 5 mL fluorobenzene. The vial was sealed and stirred vigorously until the complex was dissolved. NH_3 (g) was bubbled through the solution for 10 seconds, and the solution was stirred overnight. The solution was then filtered through Celite, and the filtrate was layered with pentane, resulting in the formation of yellow crystals over a period of two weeks. Yield: 0.020 g, 84%. ^{1}H NMR (500 MHz, THF-d_8, 25 °C): δ 7.36-7.30 (1H, m), 7.26-7.19 (4H, m), 7.11-7.02 (5H, m), 6.90 (1H, t, J = 7.3 Hz), 6.84 (1H, t, J = 7.3 Hz), 4.13-4.05 (2H, m), 3.73-3.66 (2H, m) 3.61-3.53 (2H, m), 2.0 (3H, dt, J= 67.1, 3.0 Hz), 1.36 (18H, m). ^{13}C{^{1}H} NMR (100 MHz, THF-d_8, 25 °C): 130.7 (d), 129.9 (s), 124.7 (d), 122.6 (s), 121.1 (s), 119.9 (s), 118.6 (s), 115.7 (d), 66.1 (s), 51.5 (m), 32.4 (m), 26.9 (m), 26.2 (s), 26.0 (t), 15.5 (s). ^{31}P{^{1}H} NMR (202 MHz, THF-d_8, 25 °C): δ 32.6 (s). ^{15}N NMR (51 MHz, THF-d_8, 25 °C) (^{15}N HSQC): -424.6. IR (KBr): ν_{CO} = 1918 (vs), 1823 (vs), 1764 (vs) cm^{-1} (Mo-CO).

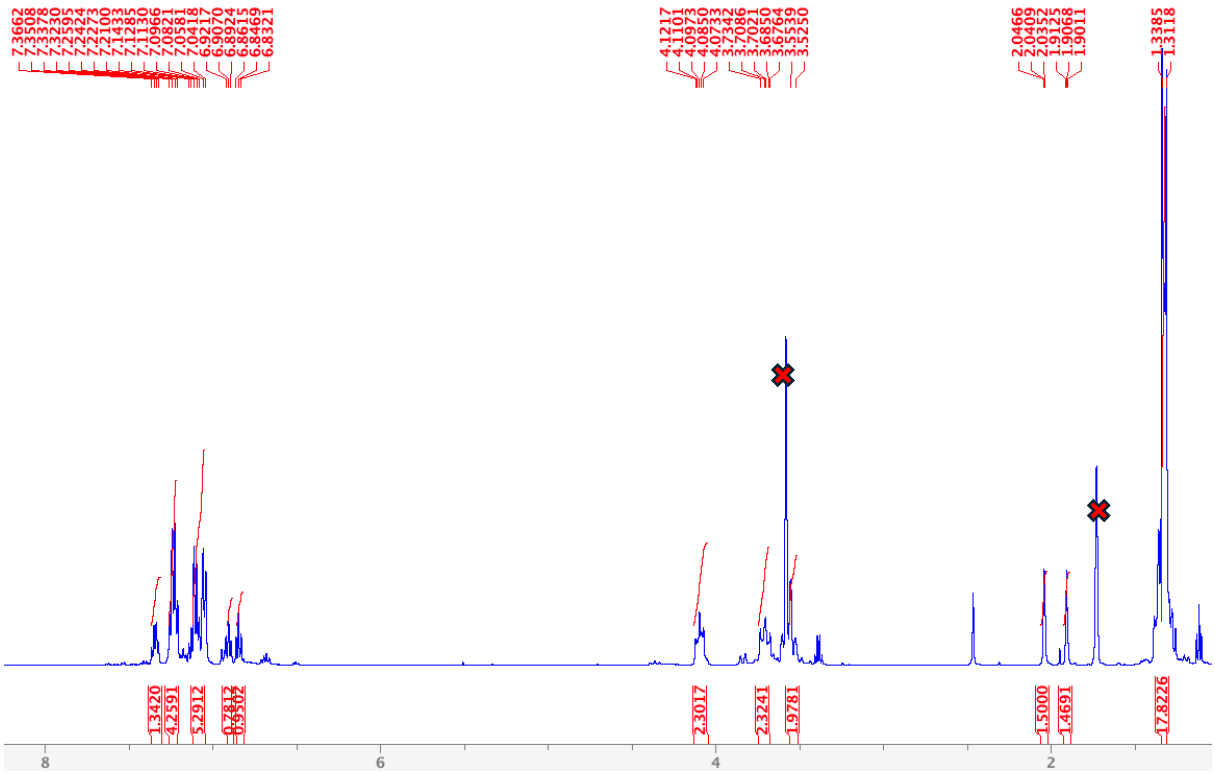


Figure S3. Representative ^{1}H NMR spectrum of **2^{15N}** in THF-d_8, at 500 MHz. Resonances marked with a X represent residual THF signals and unmarked resonances are solvent impurities present in the NMR solvent.

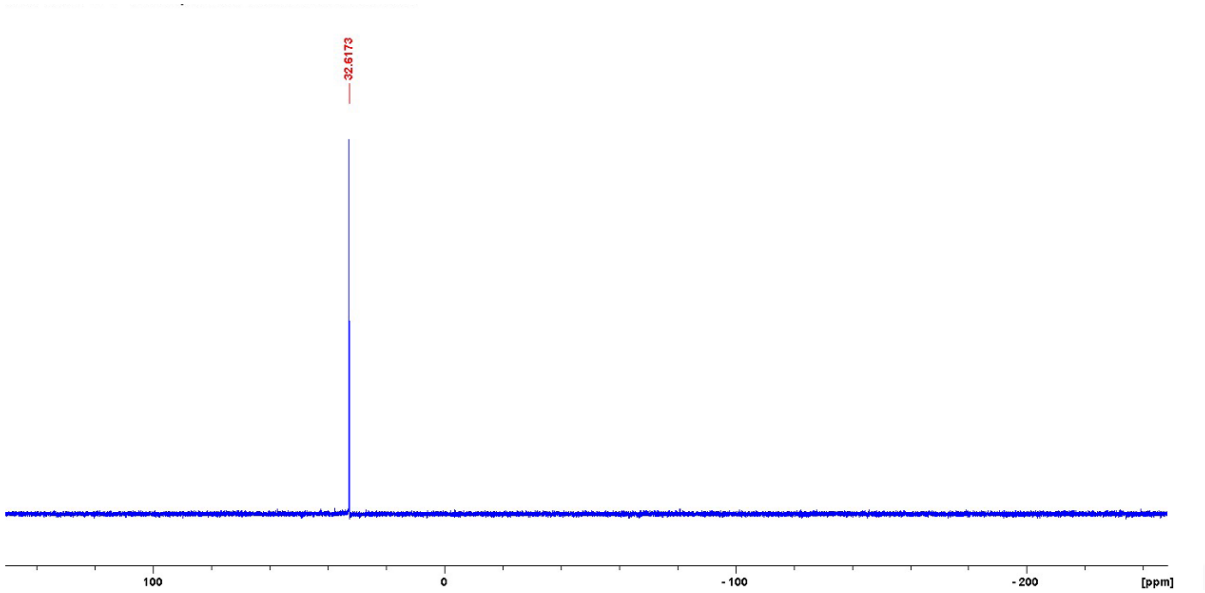


Figure S4. $^{31}P\{^{1}H\}$ NMR spectrum of **2^{15N}** recorded in THF-d_8 at 202 MHz.

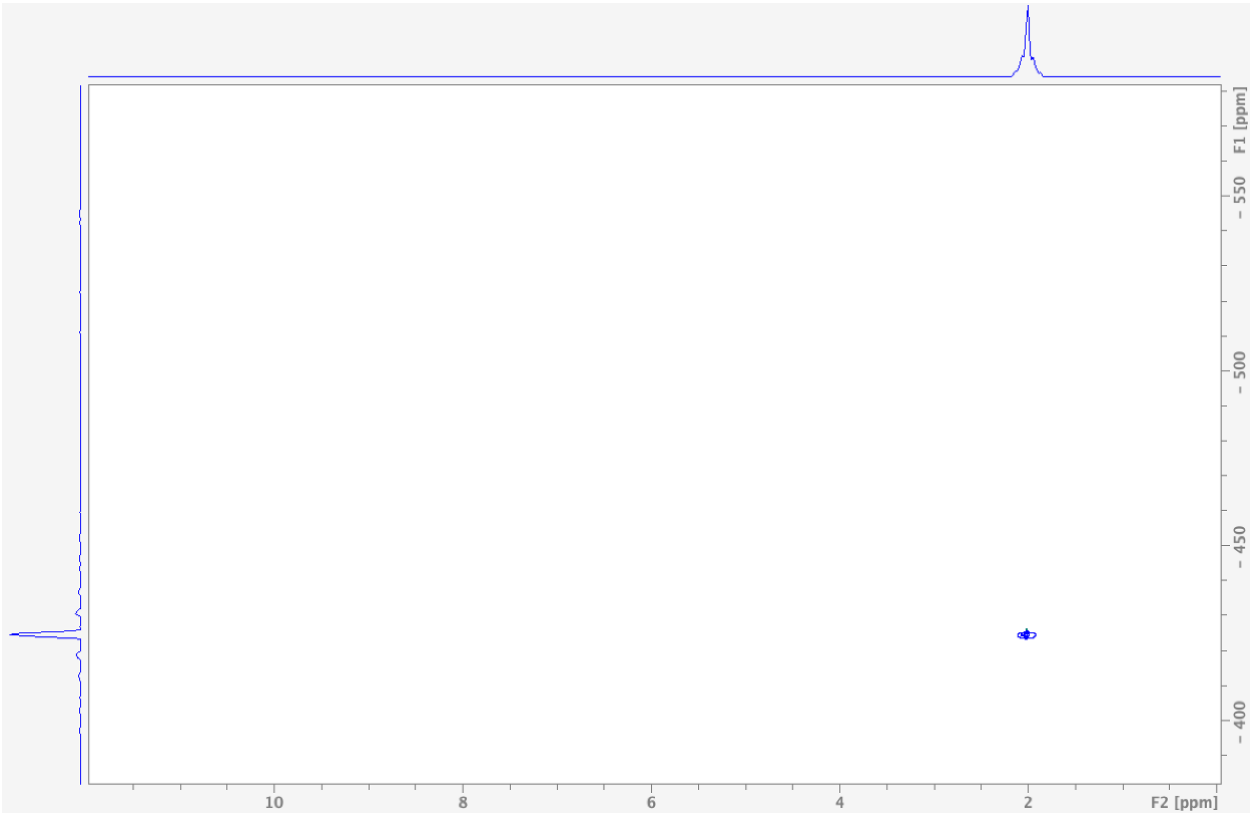


Figure S5. ^{1}H-^{15}N HSQC spectrum of **2^{15N}** recorded in THF-d_8.

Synthesis and Identification of $(CO)_4Mo(P^{tBu}{}_2N^{Ph}{}_2)$; **Mo(CO)$_4$**

Working in an argon glovebox, complex **1** (2 mg, 0.003 mmol) was added to an NMR tube equipped with Teflon-valve and dissolved in 0.5 mL $CDCl_3$. The NMR tube was then removed from the glovebox, the headspace was evacuated, and 1 equiv CO (g) was added to the headspace via a gas-tight syringe. ^{1}H NMR (500 MHz, $CDCl_3$, 35 °C): δ 7.30 (4H, t, J= 7.9 Hz) 7.01 (4H, d, J= 8.0 Hz) 6.96 (2H, m) 3.70-3.65 (4H, m) 3.44 (4H, d, J= 13.7 Hz) 1.29-1.24 (18H, m). ^{31}P{^{1}H} NMR (202 MHz, $CDCl_3$, 35 °C): 41.6 (s).

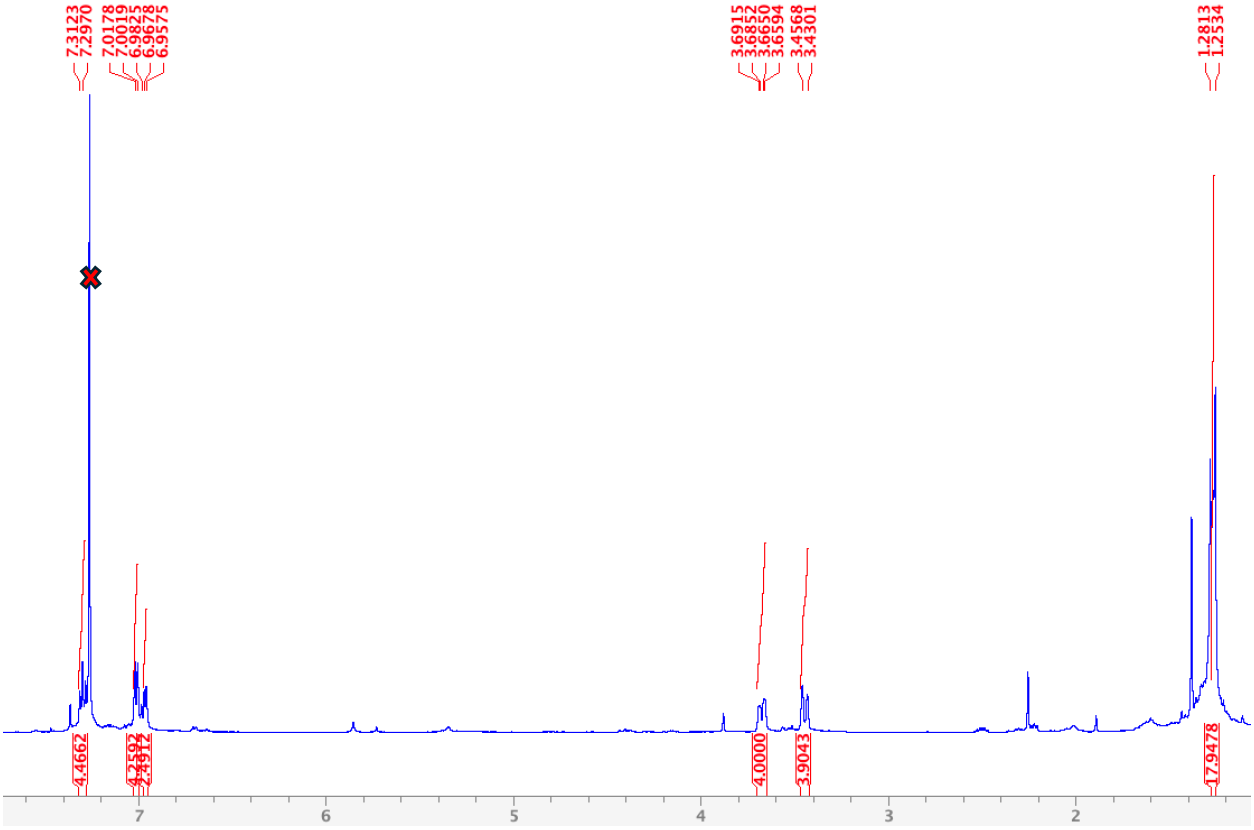


Figure S6. Representative ^{1}H NMR spectrum of **Mo(CO)$_4$($P^{tBu}{}_2N^{Ph}{}_2$)** in $CDCl_3$, at 500 MHz. Resonances marked with a red X represent $CDCl_3$ signal and unmarked resonances are solvent impurities present in the NMR solvent.

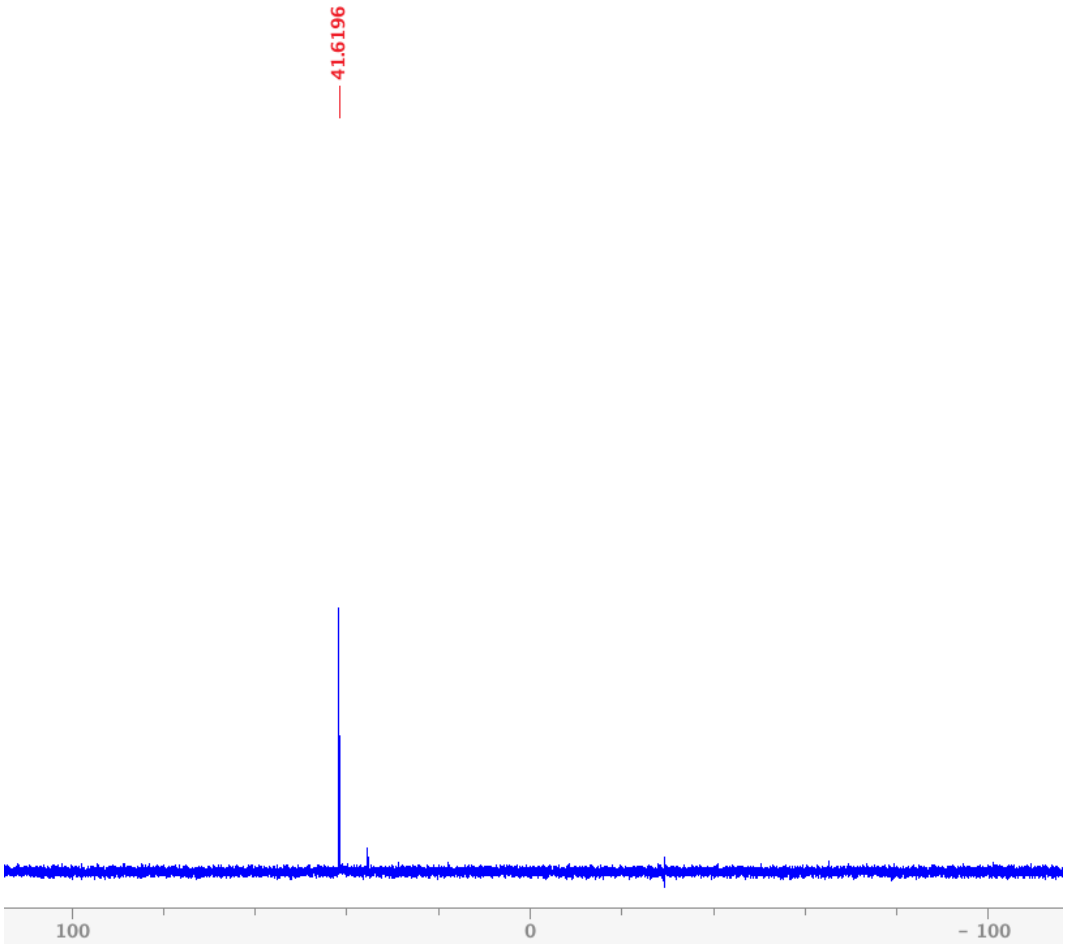


Figure S7. $^{31}P\{^{1}H\}$ NMR spectrum showing $Mo(CO)_4(P^{tBu}{}_2N^{Ph}{}_2)$ (41.6 ppm) recorded in $CDCl_3$ at 202 MHz.

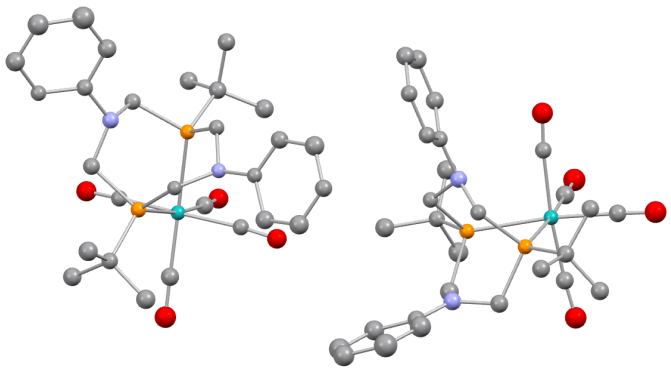


Figure S8. The atom connectivity of $Mo(CO)_4(P^{tBu}{}_2N^{Ph}{}_2)$ (**$Mo(CO)_4$**) determined by single crystal X-ray diffraction. A publishable molecular structure with reliable metric parameters was not attainable due to the weakly diffracting nature of the sample. In the molecular structure above the atoms are defined as the following: green (Mo); yellow (P); blue (N); red (O); grey (C).

Synthesis and Characterization of *fac*-[Mo(CO)$_3$(P$^{tBu}_2$N$^{Ph}_2$)(N$_2$H$_4$)] and *fac*-[Mo(CO)$_3$(P$^{tBu}_2$N$^{Ph}_2$)]$_2$(μ-N$_2$H$_4$); Complexes 4a and 4b

Working in an argon glovebox, complex **1** (10.5 mg, 0.017 mmol) was dissolved in approximately 1 mL fluorobenzene. Next, 1.0 equivalent N_2H_4 (1 M in fluorobenzene) was added to the solution and stirred overnight. The next day, the solution had notably turned a green-blue color. The solution was filtered through Celite, and the solvent removed under vacuum resulting in the isolation of **4a** and **4b** as a mixture in approximately a 1:2 ratio, respectively, as determined via integration of the N_2H_4 resonances in the ^{1}H NMR spectrum. ^{1}H NMR (500 MHz, THF-d_8, 35 °C): δ 7.40-7.35 (2H, m), 7.30- 7.25 (8H, m) 7.21 (2H, d, J = 8.3 Hz), 7.18- 7.10 (8H, m), 7.02 (1H, t, J= 7.05 Hz), 6.98 (1H, t, J= 7.05 Hz), 6.88 (1H, t, J= 7.05 Hz), 5.06 (**4b**, 2H, s), 4.82 (**4a**, 2H, s) 4.18-4.07 (4H, m), 3.74- 3.65 (4H, m) 3.56- 3.48 (4H, m), 3.29 (**4b**, 2H, s) 1.43-1.38 (**4a**, 9H, m), 1.37-1.33 (**4b**,18H, m) 1.30-1.26 (**4a**, 9H, m). ^{31}P{^{1}H} NMR (202 MHz, THF-d_8, 35 °C): δ 32.7 (**4a**), 32.5 (**4b**). ^{15}N NMR (51 MHz, THF-d_8, 25 °C) ^{15}N HSQC): δ -365.6 (**4b**), -321.8 (**4a**), -306.4 (**4b**).

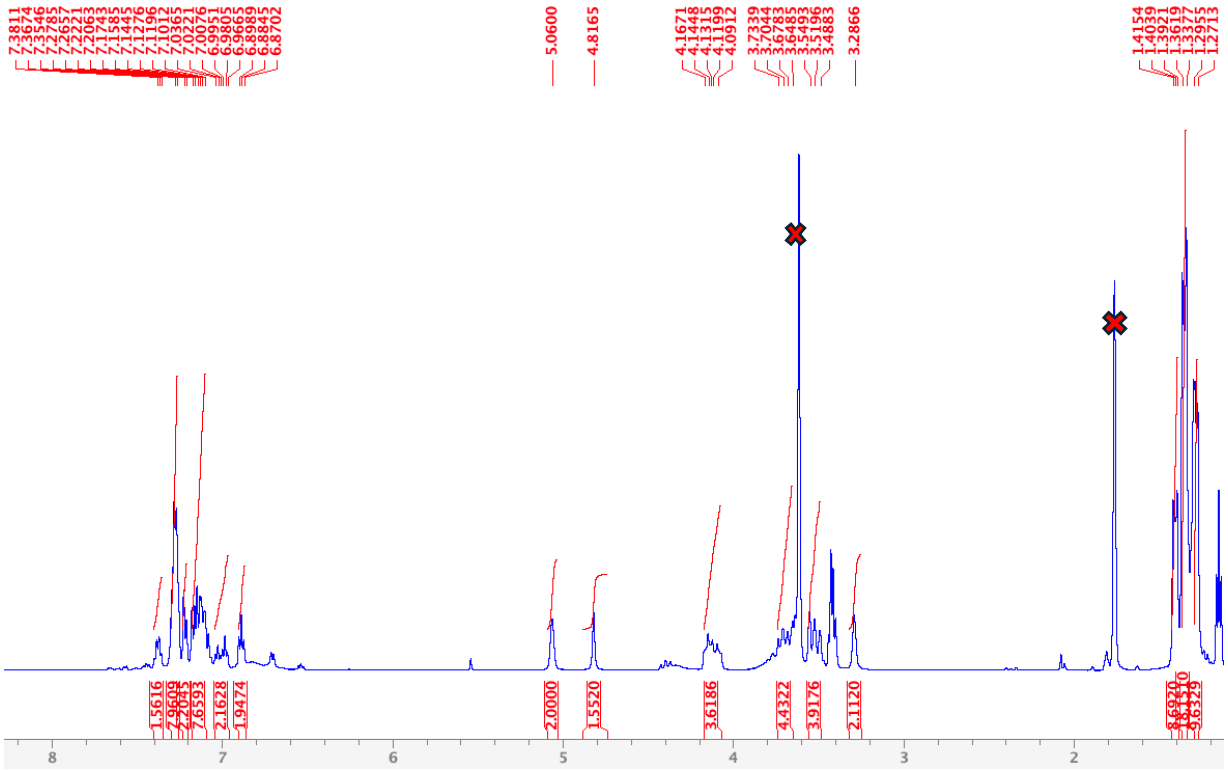


Figure S9. ^{1}H NMR spectrum of mixture of **4a** and **4b** in THF-d_8, at 500 MHz. Resonances marked with a X represent residual THF-d_8 signals and unmarked resonances are solvent impurities present in the NMR solvent. Minor resonances from free P$^{tBu}_2$N$^{Ph}_2$ are also noted.

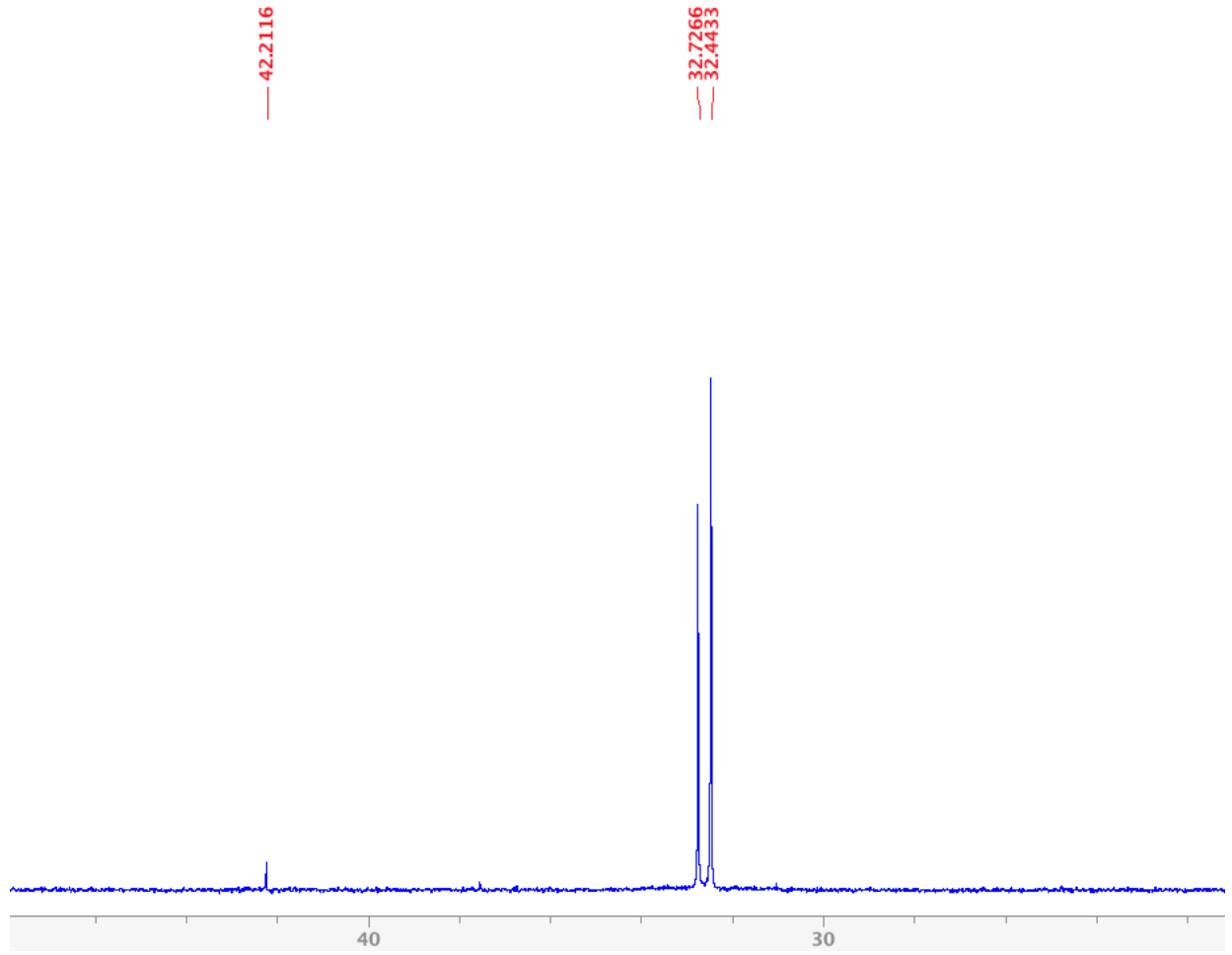


Figure S10a. $^{31}P\{^{1}H\}$ NMR spectrum of **4a** (32.7 ppm) and **4b** (32.4 ppm) recorded in THF-d_8 at 202 MHz. Minor resonances of **Mo(CO)$_4$** (42.2 ppm) and free $P^{tBu}{}_2N^{Ph}{}_2$ (-29.8 ppm).

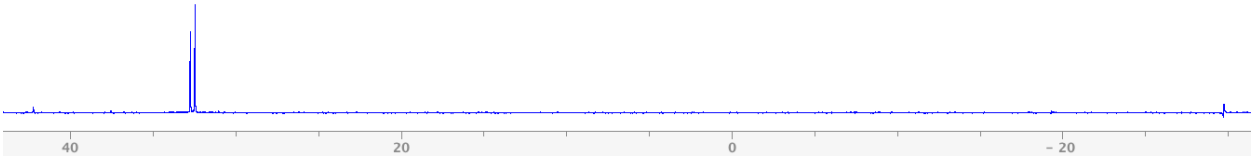


Figure S10b. Wide sweep $^{31}P\{^{1}H\}$ NMR spectrum of Figure 10a; **4a** (32.7 ppm) and **4b** (32.4 ppm) recorded in THF-d_8 at 202 MHz. Minor resonances of **Mo(CO)$_4$** (42.2 ppm) and free $P^{tBu}{}_2N^{Ph}{}_2$ (-29.8 ppm).

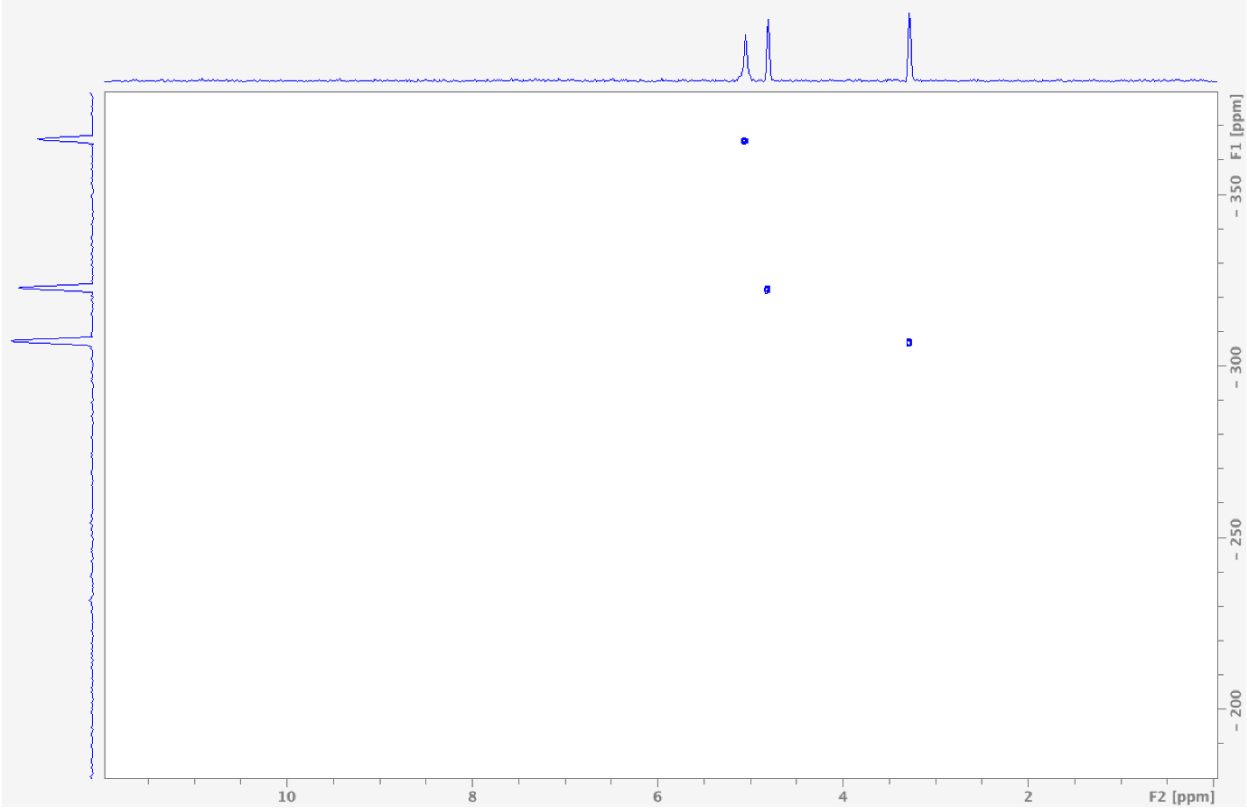


Figure S11. ^{1}H-^{15}N HSQC spectrum of **4a** (^{15}N: -321.8 and ^{1}H: 4.82) and **4b** (^{15}N: -365.6, -306.4 and ^{1}H: 5.06, 3.29 recorded in THF-d_8.

III. Catalytic NH_3 Oxidation

General Procedure for Catalytic NH_3 Oxidation Reactions:

Working in an Ar glovebox, a custom-made 10 mL round bottom flask equipped with a PTFE valve was charged with a stir bar and 2,4,6-tri-*tert*-butylphenoxyl radical (400-1200 equiv.) or 2,6-di-*tert*-butyl-4-tritylphenoxyl radical (400-1200 equiv.). A rubber septum was then affixed to the side arm with a hose clamp, the vessel sealed tightly and removed from the glovebox. 15 mL Ar headspace was taken from the glovebox to analyze by GC analysis for N_2. Outside the glovebox, the reaction vessel headspace was thoroughly evacuated and backfilled with anhydrous NH_3 (g) (1 atm) via the sidearm. The PTFE valve was closed, and the reaction flask brought back into the glovebox. A stock solution of **1** or **2** in DME was then added (2 mL total volume), the PTFE valve

closed, and the reaction was stirred vigorously for the duration of the catalytic trial. After 24 h, the reaction flask was removed from the glovebox, the PTFE valve was opened, and 200 μL of UHP He gas was injected into the flask headspace. After 30 minutes of equilibration time, 200 μL of the headspace gas was manually injected into the GC. No further attempts were made to quantify dissolved gases present in the reaction solvent.

General Procedure for Blank Trials:

Working in an Ar glovebox, a custom-made 10 mL round bottom flask equipped with a PTFE valve was charged with a stir bar and 2,4,6-tri-*tert*-butylphenoxyl radical or 2,6-di-*tert*-butyl-4-tritylphenoxyl radical. A rubber septum was then affixed to the side arm with a hose clamp, the vessel sealed tightly and removed from the glovebox. 15 mL Ar headspace was taken from the glovebox to analyze by GC analysis for N_2. Outside the glovebox, the reaction vessel headspace was thoroughly evacuated and backfilled with anhydrous NH_3 (g) (1 atm) via the sidearm. The PTFE valve was closed, and the reaction flask brought back into the glovebox. 2 mL DME was added to the reaction vessel via the sidearm and was stirred vigorously for the duration of the blank trial. After 24 h, the reaction flask was removed from the glovebox, the PTFE valve was opened, and 200 μL of UHP He gas was injected into the flask headspace. After 30 minutes of equilibration time, 200 μL of the headspace gas was manually injected into the GC. No further attempts were made to quantify dissolved gases present in the reaction media.

Analysis of $^{15}N_2$ gas formation by GC/MS:

Working in an Ar glovebox, 100 mg 2,4,6-tri-*tert*-butylphenoxyl radical was added to a Teflon-valved NMR tube. To this was added 0.8 mL DME and the tube sealed and agitated to fully dissolve the blue solid. Next, **1** (7.8 mg, 0.012 mmol) was added, and the reaction tube was resealed and removed from the glovebox. The reaction media was then frozen in LN_2 and the headspace was evacuated thoroughly. The reaction was allowed to warm to room temperature before being backfilled with 1 atm $^{15}NH_3$ (g) via a low-volume manifold and subsequently stirred for 48 h. The headspace was then sampled with a gas-tight syringe and manually injected into the GC/MS.

General Procedure for Stoichiometric HAA experiments:

Working in an Ar glovebox, **2^{15N}** (5 mg, 0.008 mmol) was dissolved in 1 mL THF-d_8 or CD_2Cl_2 and transferred to a Teflon-valved NMR tube. To this solution was added 2-5 equivalents of 2,4,6-tri-*tert*-butylphenoxyl or 2-6 equivalents 2,6-di-*tert*-butyl-4-tritylphenoxyl radical, the reaction vessel sealed and placed on an NMR tube rotator for 24 h. Reaction progress was monitored via ^{1}H, and ^{31}P NMR spectroscopy. Loss of the blue or green color of the solution were noted upon consumption of the 2,4,6-tri-*tert*-butylphenoxyl or 2,6-di-*tert*-butyl-4-tritylphenoxyl radical, respectively.

Reaction of 4a/4b with NH_3:

Working in an Ar glovebox, 5 mg of a 1:2 mixture of **4a** and **4b** was placed in a Teflon-valved NMR tube and dissolved in 0.8 mL THF-d_8. The headspace was evacuated, and the vessel backfilled with NH_3 (g). Reaction progress was monitored by ^{15}N and ^{31}P NMR spectroscopy.

Reaction of 4a/4b with excess 2,6-di-*tert*-butyl-4-tritylphenoxyl radical:

Working in an Ar glovebox, 4.2 mg of a 1:2 mixture **4a** and **4b** was placed in a Teflon-valved NMR tube and dissolved in 0.8 mL THF-d_8. To this solution was added 10 equiv. ***2,6-di-tert-butyl-4-tritylphenoxyl radical.*** The NMR tube was allowed to mix for 18 h on an NMR tube rotator, after which the headspace was then sampled with a gas-tight syringe and manually injected into the GC. Reaction progress was monitored by ^{31}P NMR spectroscopy.

Hydrazine Disproportionation experiment:

Working in an Ar glovebox, a 0.13 M solution of N_2H_4 in THF was prepared. 0.8 mL of this solution was transferred to a Teflon-valved NMR tube, and to the solution was added 2,6-di-*tert*-butyl-4-tritylphenoxyl radical (2.0 equiv) resulting in a rapid color change from green to yellow. The NMR tube was mixed for 12 h on an NMR tube rotator, after which the headspace was then sampled with a gas-tight syringe and manually injected into the GC.

NMR spectra of stoichiometric HAA experiments:

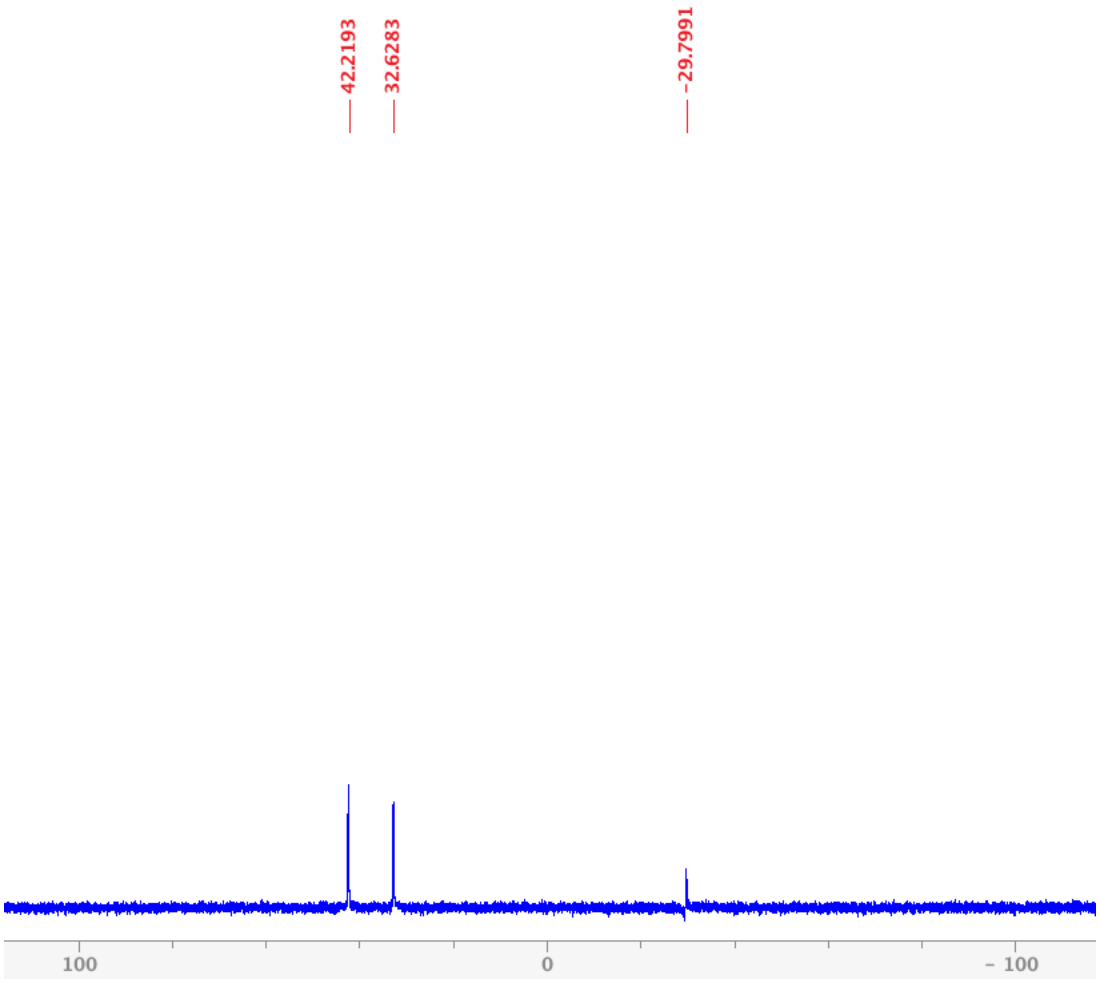


Figure S12. $^{31}P\{^{1}H\}$ NMR spectrum of Stoichiometric HAA (2 equiv. radical) reaction recorded 24 h after ***2,4,6-tri-tert-butylphenoxyl*** addition to $\mathbf{2^{15N}}$ in THF-d_8. The only products observed are $\mathbf{Mo(CO)_4(P^{tBu}{}_2N^{Ph}{}_2)}$ (42.2 ppm) and Free $P^{tBu}{}_2N^{Ph}{}_2$ (-29.8 ppm). $\mathbf{2^{15N}}$ is also present at 32.6 ppm.

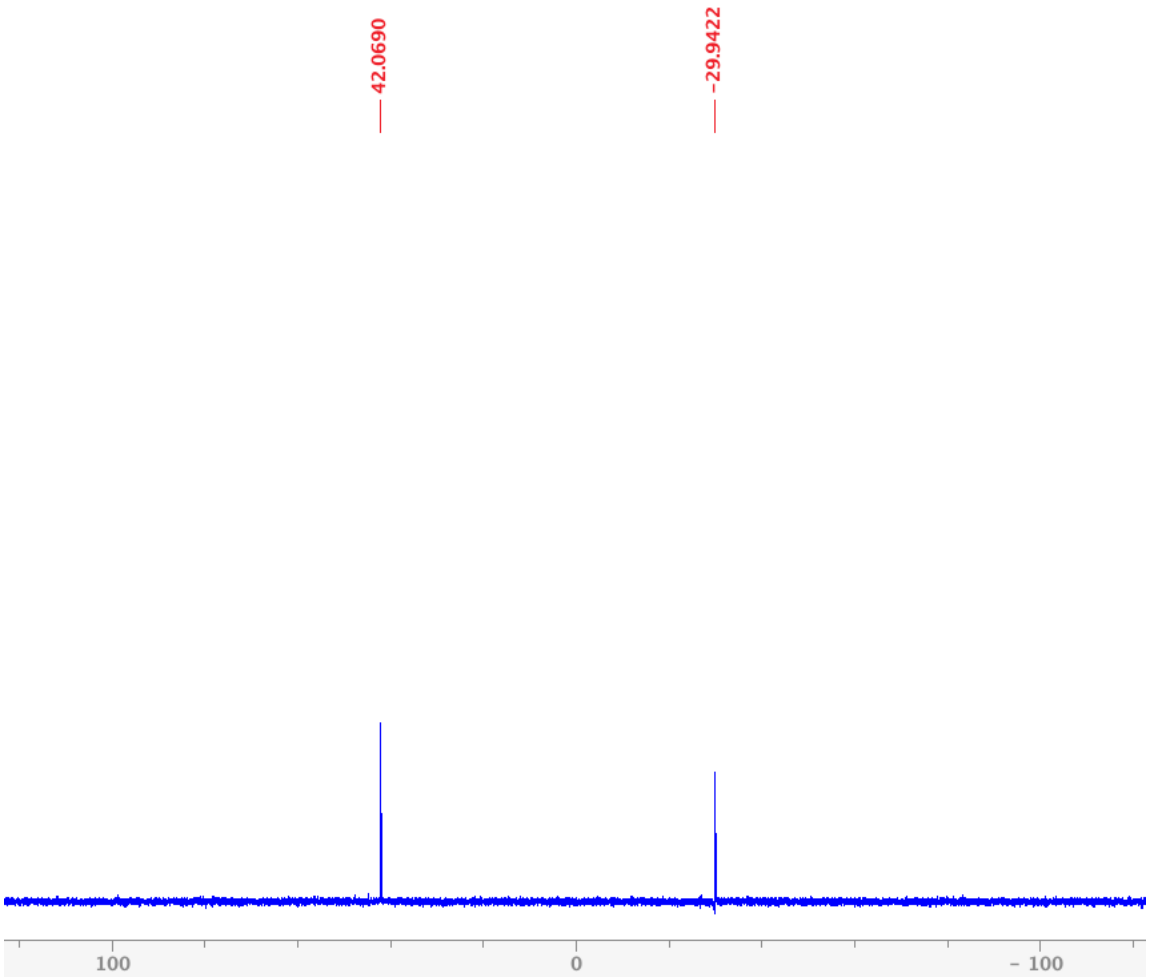


Figure S13. $^{31}P\{^{1}H\}$ NMR spectrum of stoichiometric HAA (5 equiv. radical) reaction recorded 1 h after ***2,4,6-tri-tert-butylphenoxyl*** addition to $\mathbf{2^{15N}}$ in CD_2Cl_2. The only products observed are $\mathbf{Mo(CO)_4(P^{tBu}{}_2N^{Ph}{}_2)}$ (42.2 ppm) and free $P^{tBu}{}_2N^{Ph}{}_2$ (-29.8 ppm). $\mathbf{2^{15N}}$ has notably been fully consumed.

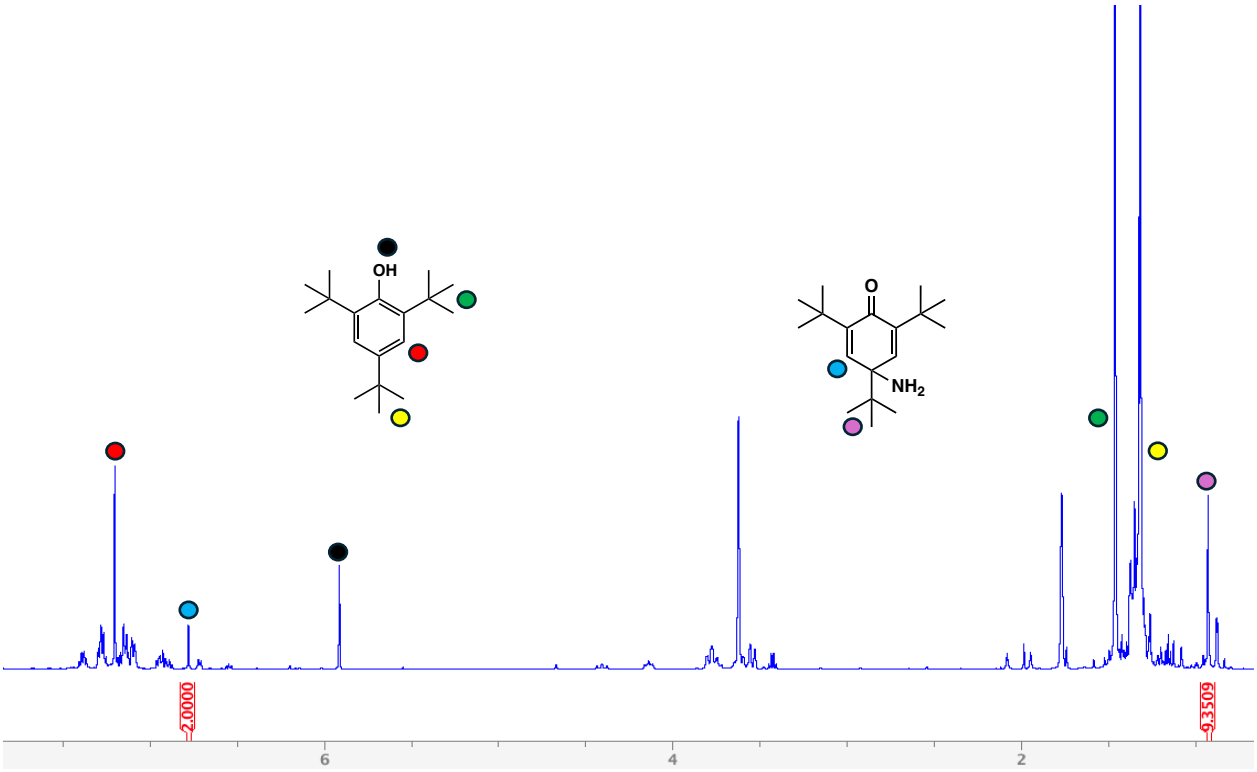


Figure S14. ^{1}H NMR spectrum of Stoichiometric HAA reaction recorded 24 h after ***2,4,6-tri-tert-butylphenoxyl*** addition to $\mathbf{2^{15N}}$ in THF-d_8. Resonances for relevant phenol and C-N coupling product 4-amino-2,4,6-tri-*tert*-butylcyclohexa-2,5-dien-1-one have been noted. Integrations for 4-amino-2,4,6-tri-*tert*-butylcyclohexa-2,5-dien-1-one are shown for clarity.

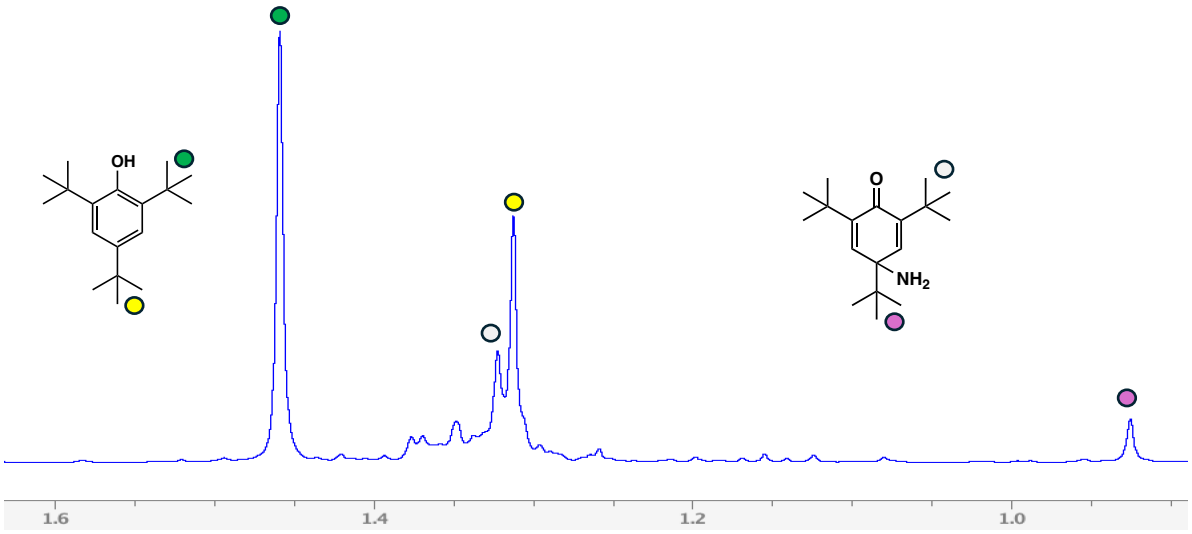


Figure S15. ^{1}H NMR of stoichiometric HAA reaction recorded 24 h after ***2,4,6-tri-tert-butylphenoxyl*** addition to $\mathbf{2^{15N}}$ in THF-d_8. Resonances for relevant phenol and C-N coupling product 4-amino-2,4,6-tri-*tert*-butylcyclohexa-2,5-dien-1-one have been noted; alkyl region has been enhanced for clarity.

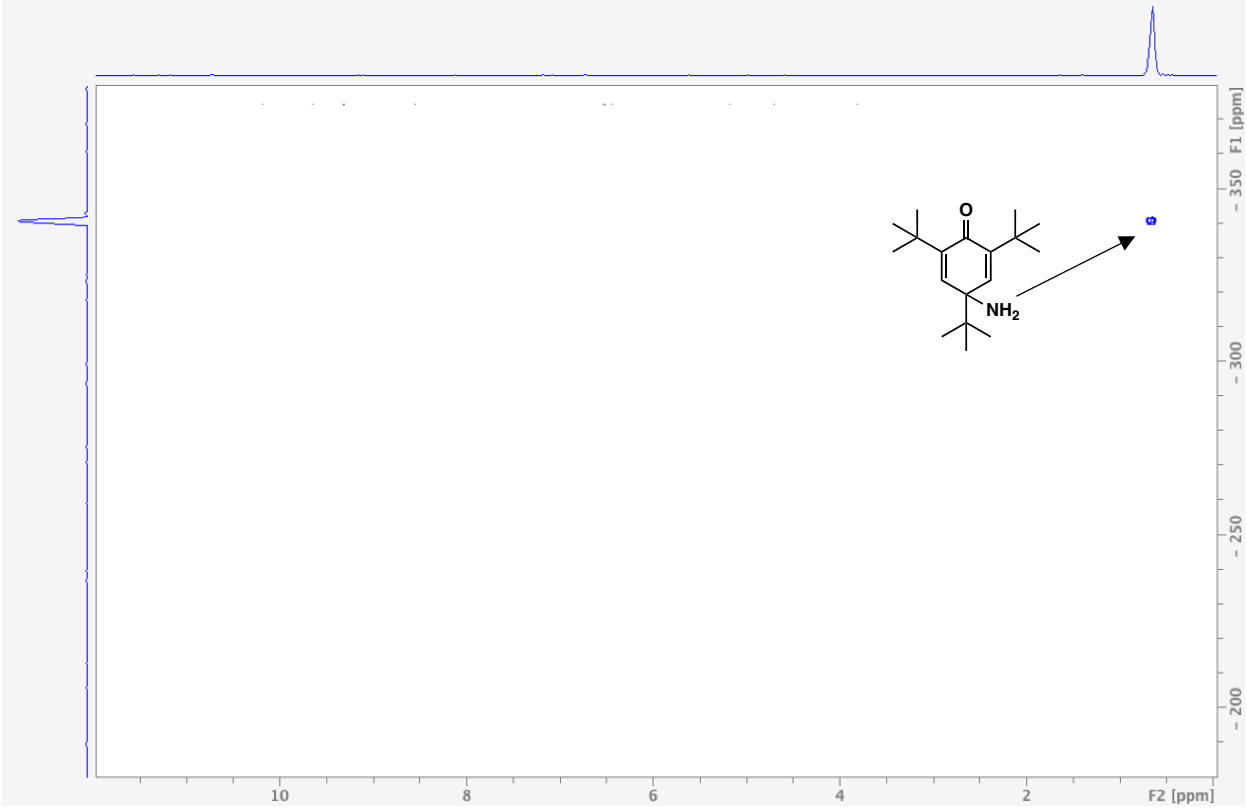


Figure S16. ^{1}H-^{15}N HSQC spectrum of stoichiometric HAA (2 equiv. radical) recorded 24 h after ***2,4,6-tri-tert-butylphenoxyl*** addition to $\mathbf{2^{15N}}$ in C_6D_6. Major cross peak: ^{1}H: 0.66 ^{15}N: -341 matches literature-reported value for C-N coupling product 4-amino-2,4,6-tri-*tert*-butylcyclohexa-2,5-dien-1-one.

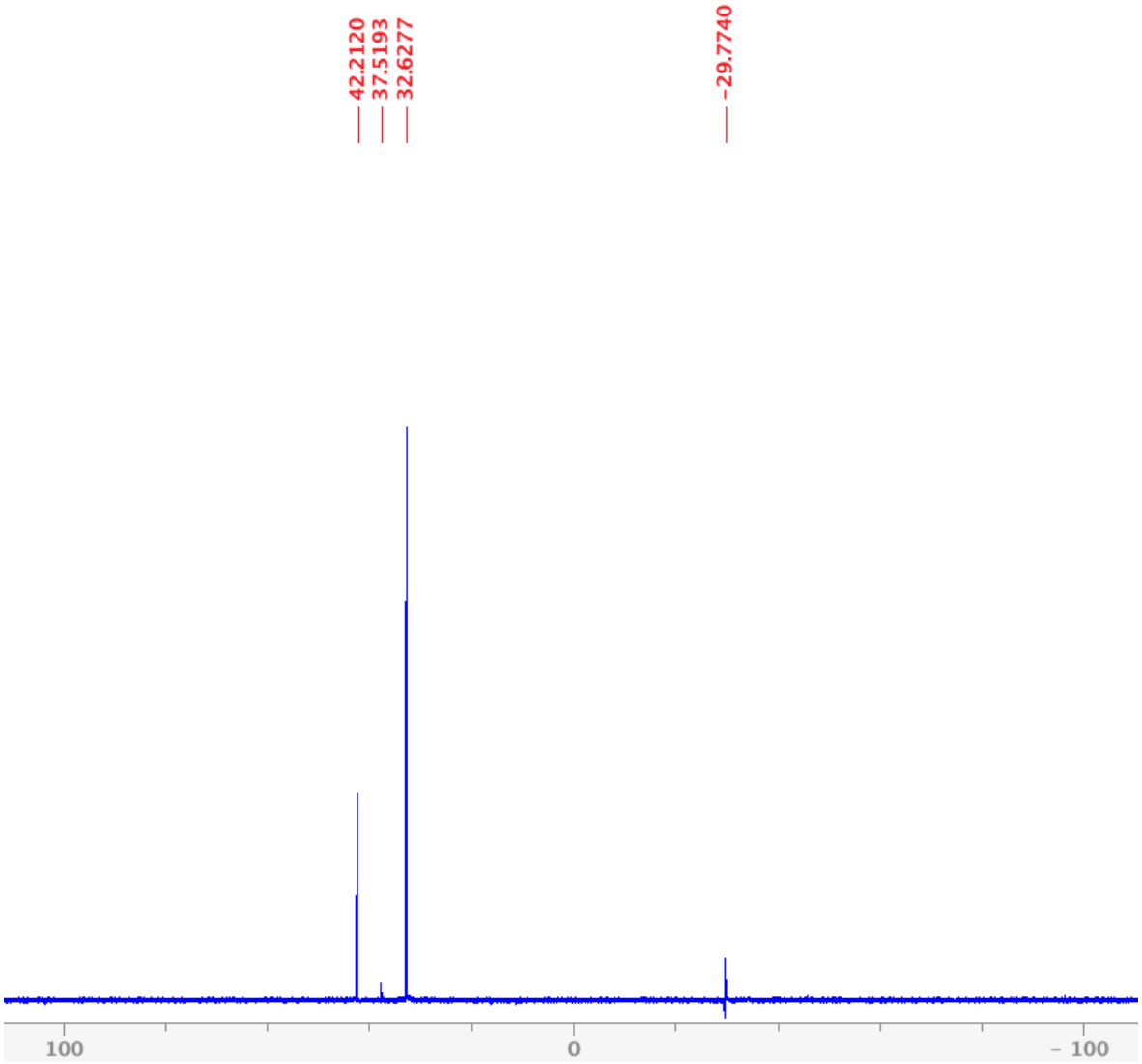


Figure S17. $^{31}P\{^{1}H\}$ NMR spectrum of Stoichiometric HAA (2 equiv radical) reaction recorded 24 h after ***2,6-di-tert-butyl-4-tritylphenoxyl*** addition to $\mathbf{2^{15N}}$ in THF-d_8. The only products observed are $\mathbf{Mo(CO)_4(P^{tBu}{}_2N^{Ph}{}_2)}$ (42.2) and free $P^{tBu}{}_2N^{Ph}{}_2$ (-29.8). Notably, $\mathbf{2^{15N}}$ is also present at 32.6 ppm. Minor resonance from **1** is noted at 37.5 ppm.

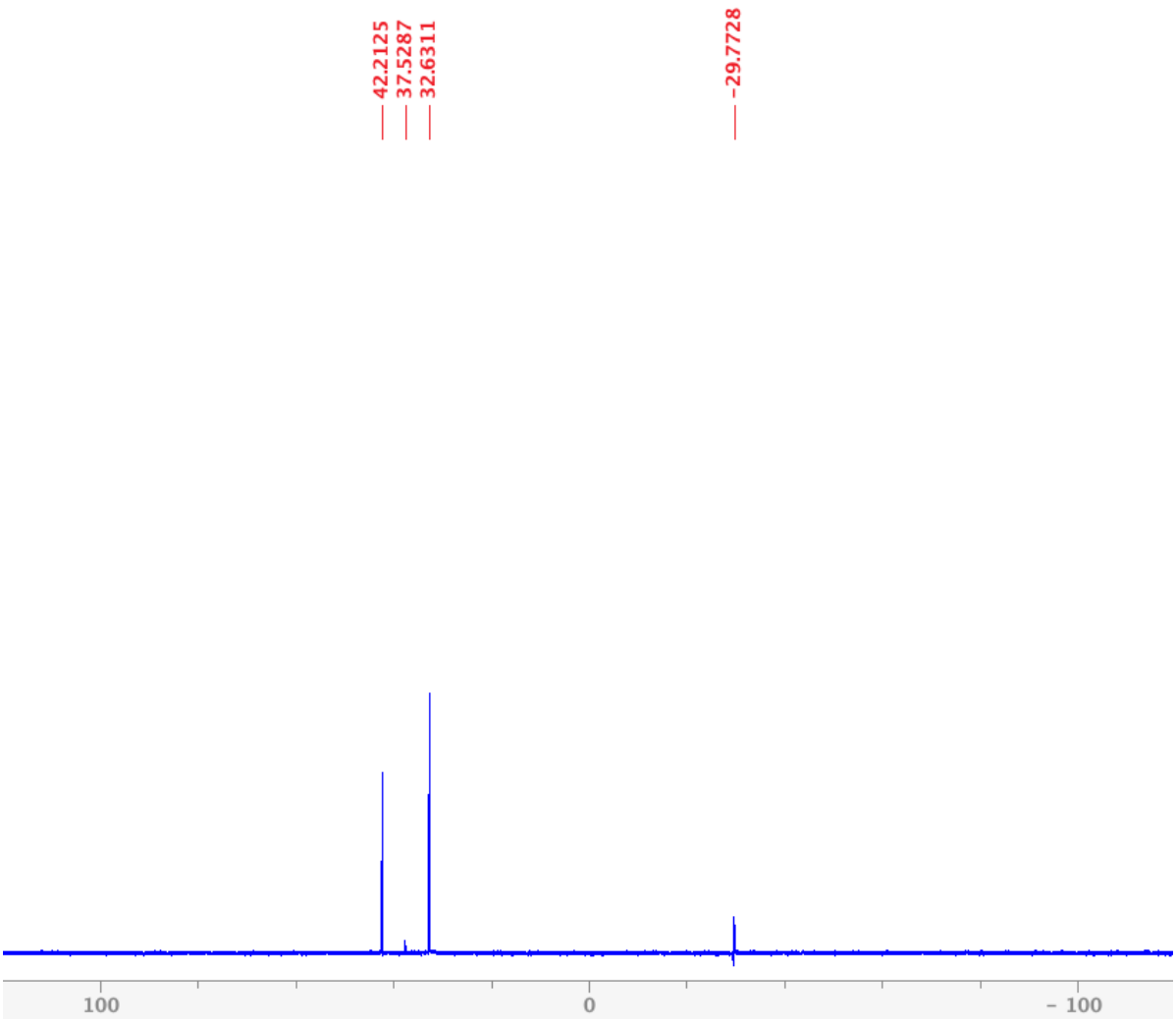


Figure S18. $^{31}P\{^{1}H\}$ NMR spectrum of stoichiometric HAA (6 equiv. radical) reaction recorded 1 h after ***2,6-di-tert-butyl-4-tritylphenoxyl*** addition to $\mathbf{2^{15N}}$ in THF-d_8. The products observed are $\mathbf{Mo(CO)_4(P^{tBu}{}_2N^{Ph}{}_2)}$ at 42.2 ppm, $\mathbf{2^{15N}}$ at 32.6 ppm. Minor resonances from **1** at 37.5 ppm and free $P^{tBu}{}_2N^{Ph}{}_2$ -29.8 ppm.

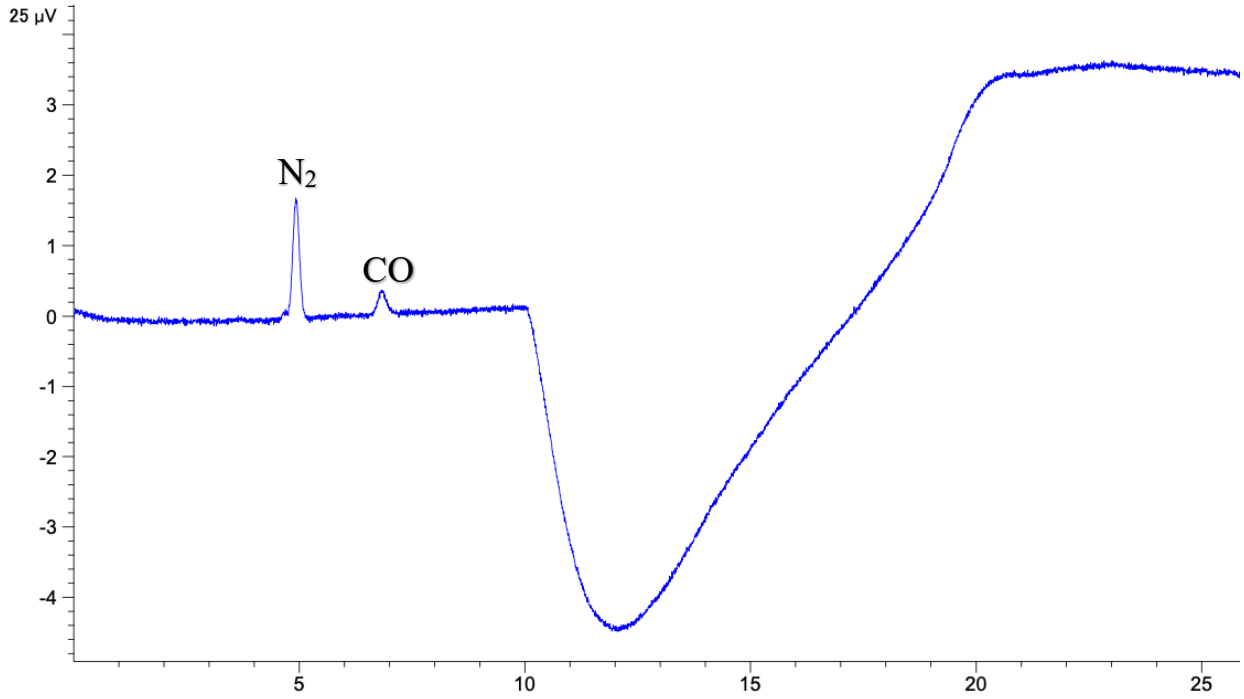


Figure S19. GC trace of headspace gases produces in stoichiometric HAA (6 equiv. radical) reaction recorded 1 h after ***2,6-di-tert-butyl-4-tritylphenoxyl*** addition to $\mathbf{2}^{\mathbf{15N}}$ in THF-d_8.

Reaction of 4a with NH_3 to form 4b and 2:

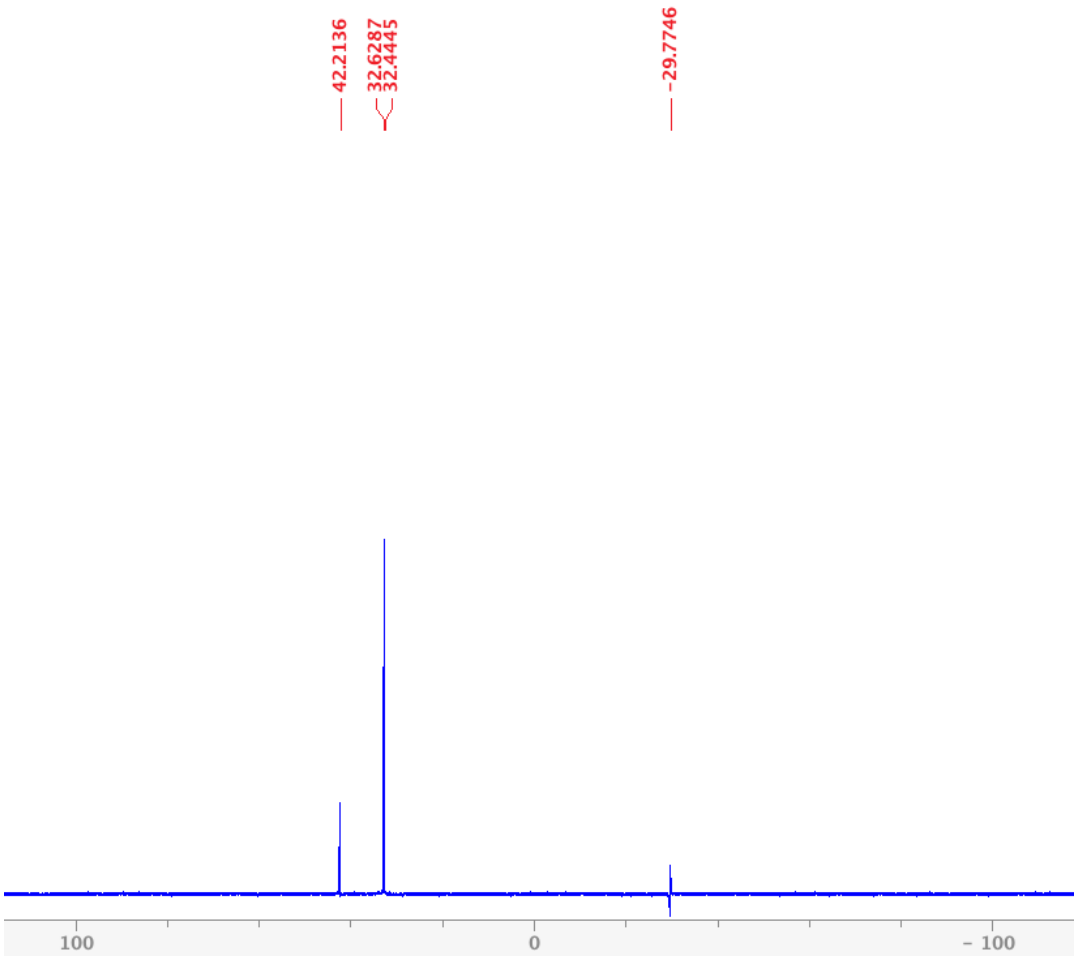


Figure S20a. $^{31}P\{^{1}H\}$ NMR spectrum of addition of 1 atm NH_3 (g) to the headspace of solution of **4a** and **4b** in THF-d_8. Major products are **2** (32.6 ppm) and **4b** (32.4 ppm). **$Mo(CO)_4(P^{tBu}{}_2N^{Ph}{}_2)$** and free $P^{tBu}{}_2N^{Ph}{}_2$ are noted. Notably, **4a** has been completely consumed.

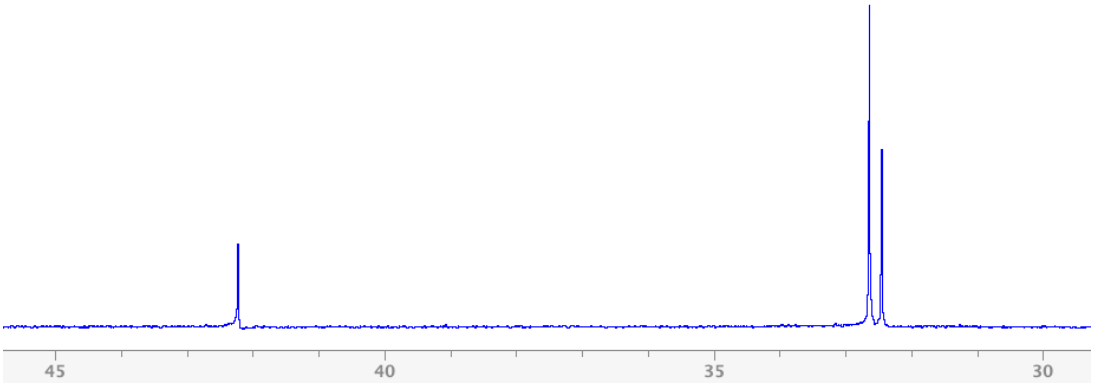


Figure S20b. Expanded region of ^{31}P NMR spectrum shown in Figure S20a.

Reaction of **4a** and **4b** mixture with excess ^{trityl}ArO$^{\bullet}$:

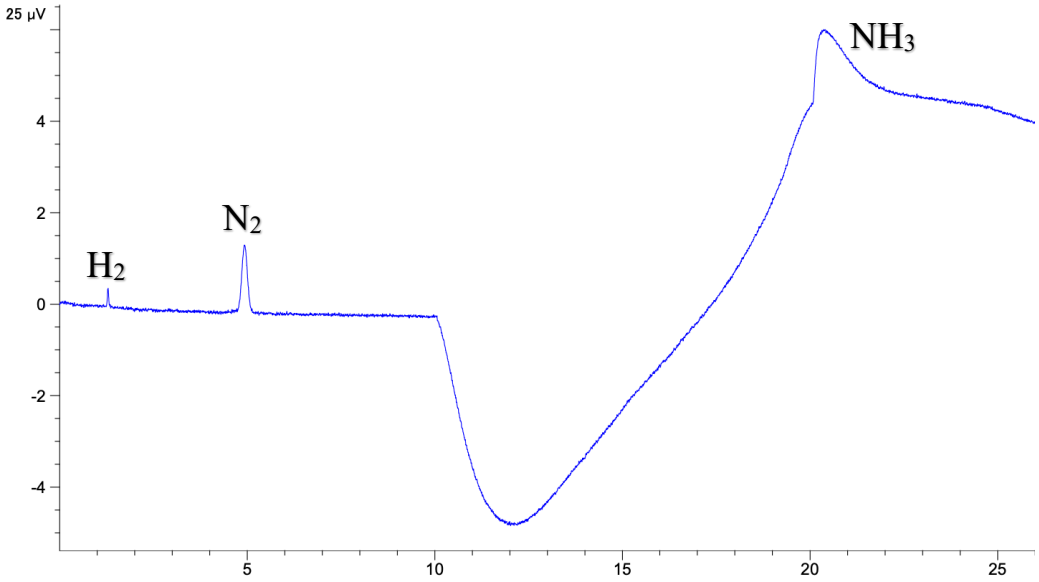


Figure S21. GC trace of headspace gas produced upon addition of 10 equiv. ***2,6-di-tert-butyl-4-tritylphenoxyl radical*** to $\mathbf{2^{15N}}$. N_2 and NH_3 are detected as the major gaseous products. Notably, a small amount of H_2 is noted and is presumed to arise from dissociation of the N_2H_4 ligand and subsequent disproportionation of free N_2H_4 in the reaction solvent by ^{trityl}ArO$^{\bullet}$.

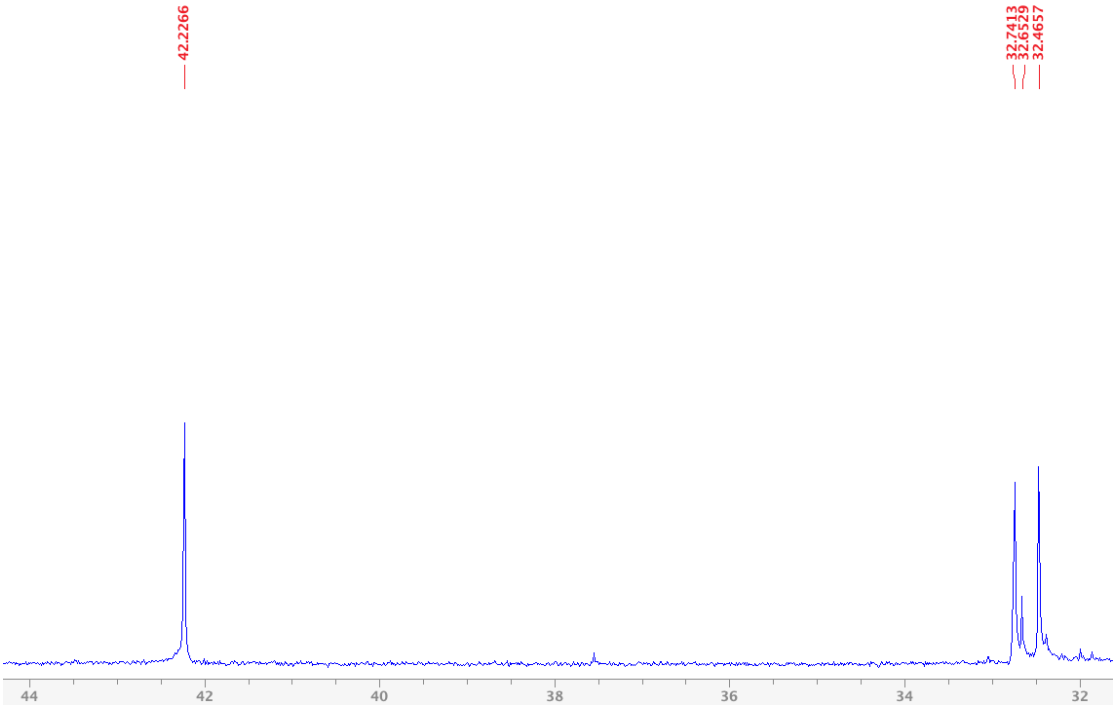


Figure S22. ^{31}P NMR spectrum recorded in THF-d_8 to accompany the GC trace in Figure S21. Major products observed are **$MoCO_4$** and **2** from the addition of 10 equiv. 2,6-di-*tert*-butyl-4-tritylphenoxyl radical to the mixture of **4a** and **4b**.

Addition of anhydrous hydrazine to *2,6-di-tert-butyl-4-tritylphenoxyl radical*

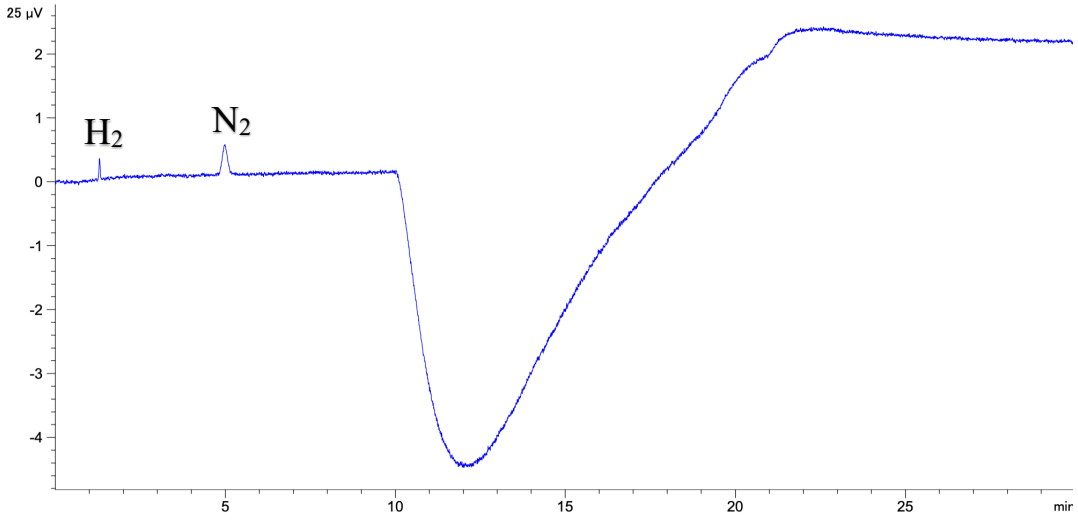


Figure S23. GC trace of headspace gas produced upon addition of ***2,6-di-tert-butyl-4-tritylphenoxyl radical*** to a solution of N_2H_4 in THF affording the gaseous products N_2 and H_2.

IV. Catalytic Results

Table S1. Summary of results for blank trials. Results are reported as average of three independent runs. [1] = 2,4,6-tri-*tert*-butylphenoxyl radical, [2] = 2,6-di-*tert*-butyl-4-tritylphenoxyl radical.

Solvent	Radical Loading	N_2 Detected
1,2-Dimethoxyethane (DME)	600 mg[1]; 700 mg[2]	$(4.2*10^{-6}$ Mol)[1] ; $(7.6*10^{-6}$ Mol)[2]

Table S2. Summary of catalytic results using 2,4,6-tri-*tert*-butylphenoxyl radical ($^{t\text{Bu}}$ArO$^{\bullet}$) or 2,6-di-*tert*-butyl-4-tritylphenoxyl radical ($^{\text{trityl}}$ArO$^{\bullet}$). All catalytic trials were performed in DME and 1 atm of NH_3. All results have been corrected for N_2 observed in blank reactions trials.

pre-catalyst	cat. loading (μmol)	NH_3 added	phenoxyl radical used	radical loading (equiv)	average quantified N_2 (mol)	individual trial results equiv N_2/Mo	average equiv. N_2/Mo
1	1.53	1 atm	$^{t\text{Bu}}$ArO$^{\bullet}$	400	1.19×10^{-5}	7.7, 7.9	7.8±0.1
1	3.06	1 atm	$^{t\text{Bu}}$ArO$^{\bullet}$	1200	2.51×10^{-5}	8.0, 8.5, 8.8	8.4±0.4
1	1.53	1 atm	$^{\text{trityl}}$ArO$^{\bullet}$	400	3.7×10^{-5}	18.2, 26.7, 28.3	24.4±5
1	1.53	1 atm	$^{\text{trityl}}$ArO$^{\bullet}$	800	8.0×10^{-5}	33.1, 58.0, 65.2	52.1±17
1[a]	1.53	1 atm	$^{\text{trityl}}$ArO$^{\bullet}$	1200	1.1×10^{-4}	59.3, 82.1, 88.3	76.6±15
1[a, b]	3.06	1 atm	$^{\text{trityl}}$ArO$^{\bullet}$	1200	6.6×10^{-5}	14.5, 24.5, 26.0	21.7±6
2[a]	1.53	1 atm	$^{\text{trityl}}$ArO$^{\bullet}$	1200	8.2×10^{-5}	45.8, 46.3, 59.2, 63.2	53.6±9

[a]3 mL reaction volume due to high radical loading. [b]48 h reaction time.

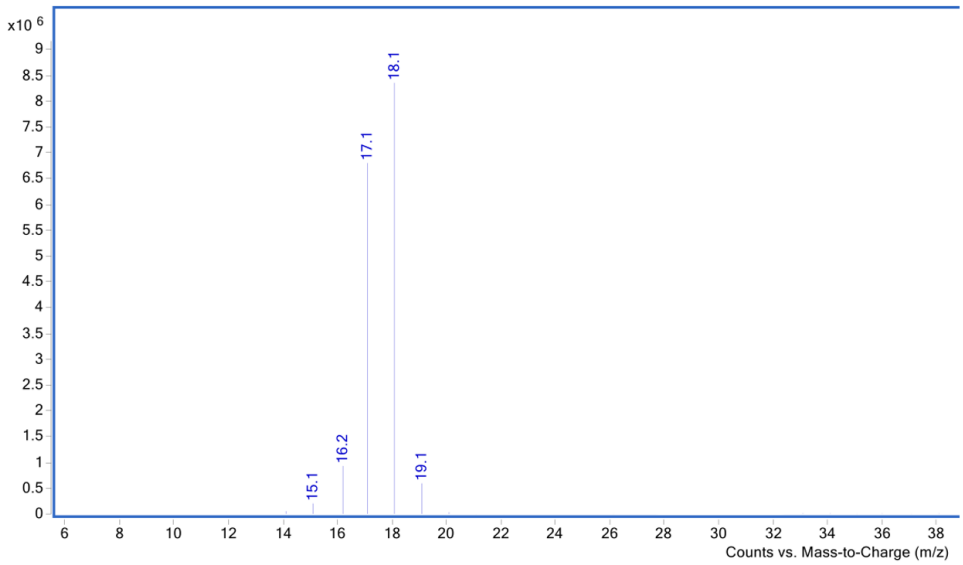


Figure S24. GC/MS trace of labeled $^{15}NH_3$ from standard gas tank noting the absence of $^{15}N_2$ (*m/z* =30) contaminant.

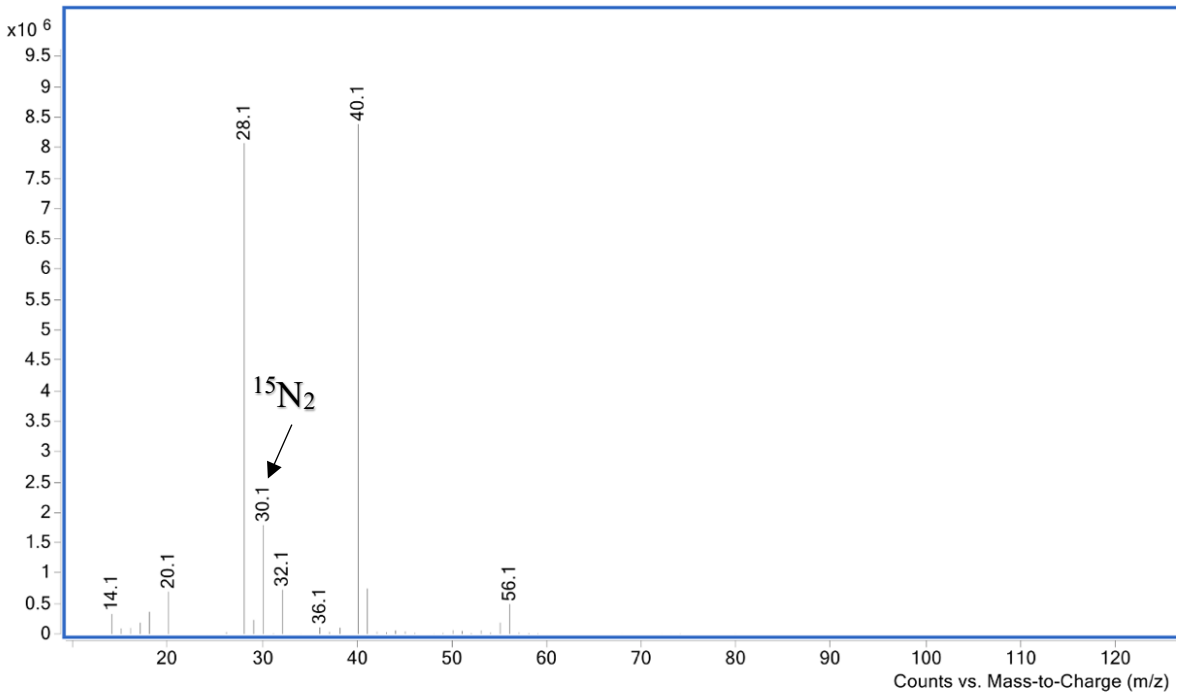


Figure S25. GC/MS headspace trace of catalytic reaction performed using $^{15}NH_3$. Note the diagnostic $^{15}N_2$ (*m/z* = 30).

V. Representative GC Headspace Injections

Standard calibration gas mixture:

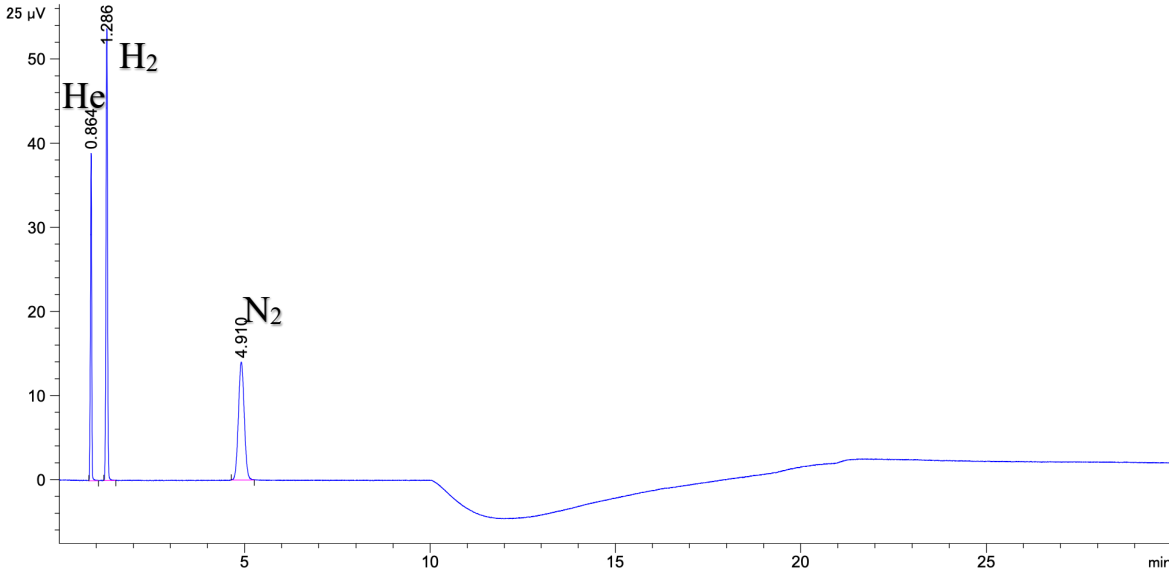


Figure S26. Representative GC trace of standard mixture gas used for gaseous product identification.

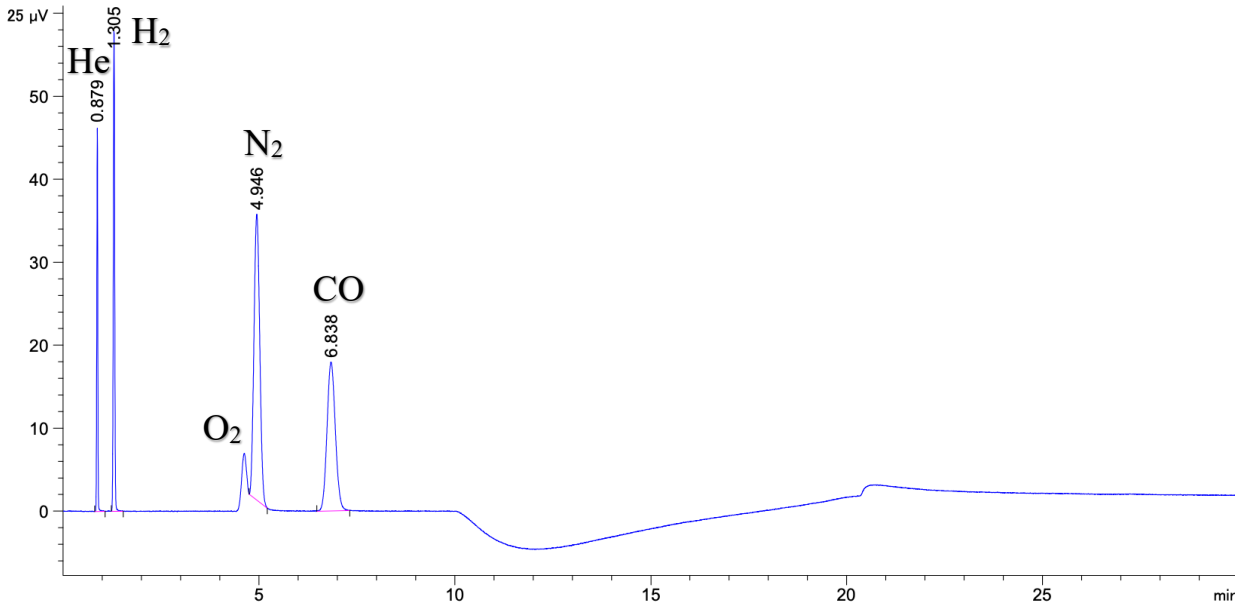


Figure S27. Representative GC trace of standard gas mixture spiked with CO (g). Note a small amount O_2 present from air contamination present in the trace.

Blank Trials:

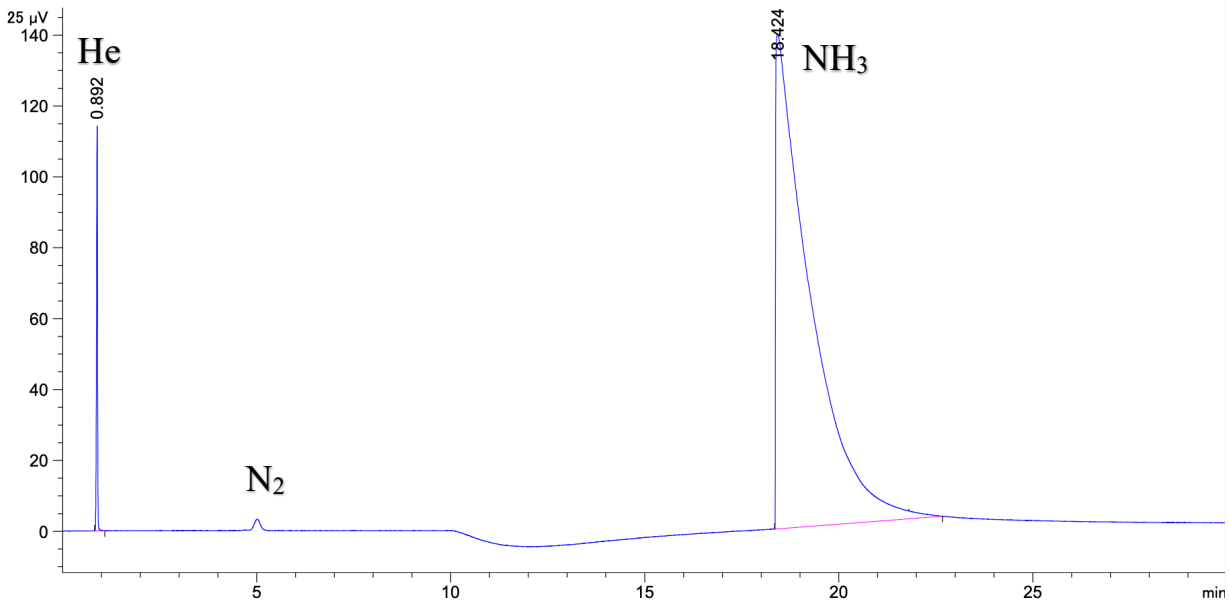


Figure S28. Representative GC trace of blank trial using ***2,4,6-tri-tert-butylphenoxyl*** radical. T = 0.9 (He), 5.0 (N_2), and 19.0 (NH_3).

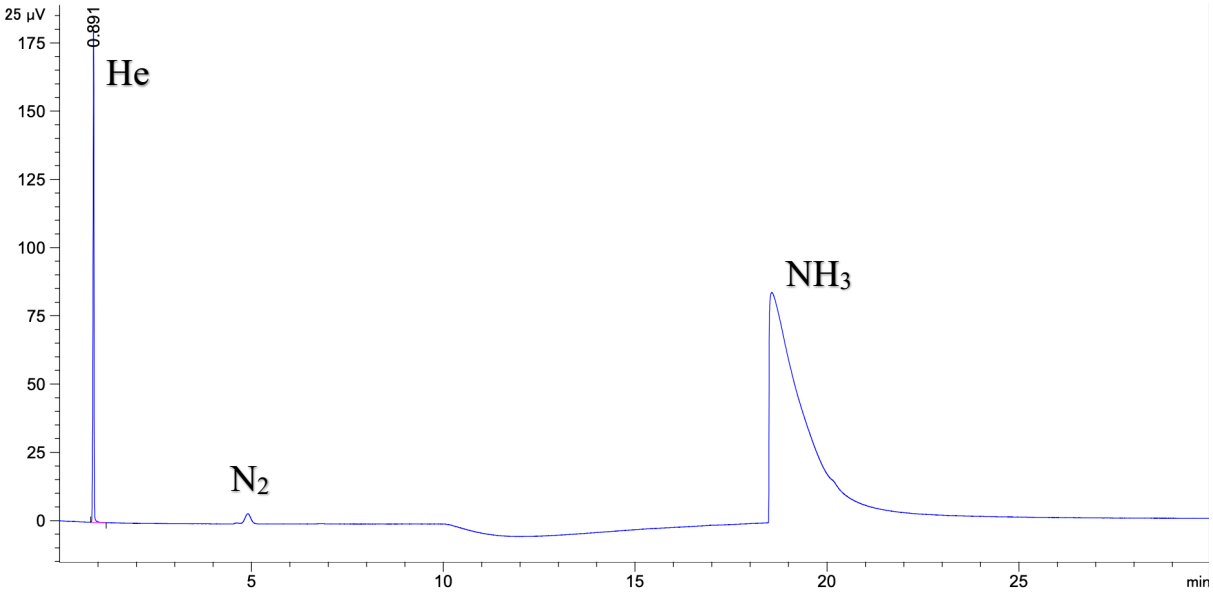


Figure S29. Representative GC trace of blank trial using ***2,6-di-tert-butyl-4-tritylphenoxyl*** radical. T = 0.9 (He), 5.0 (N_2), and 19.0 (NH_3).

Catalytic Trials:

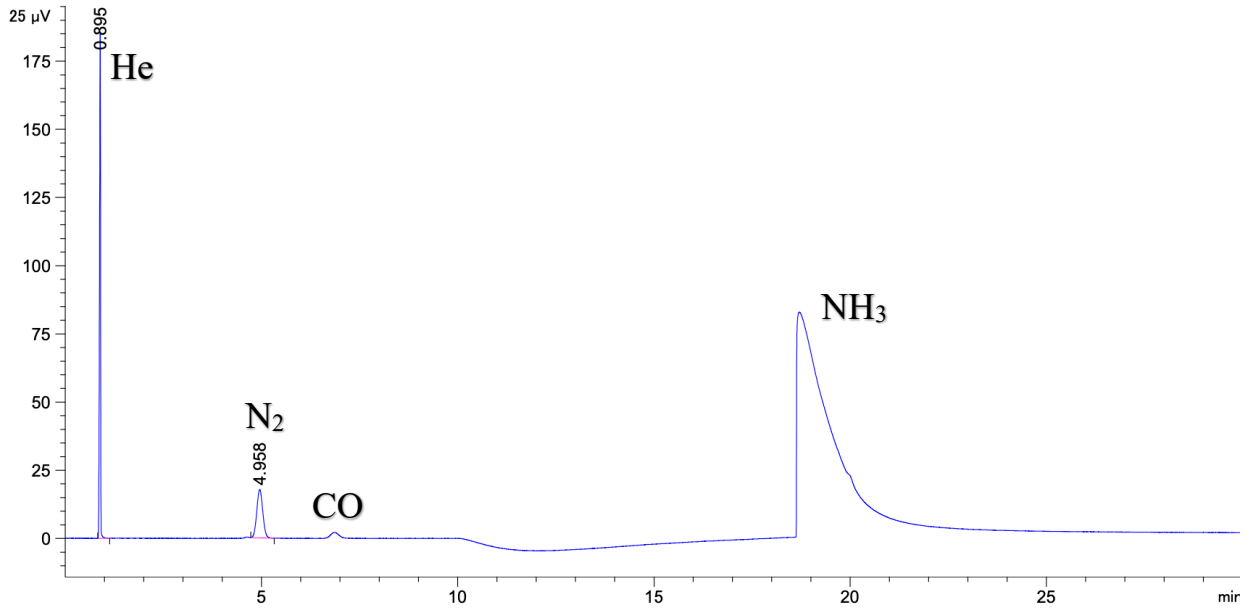


Figure S30. Representative GC trace of catalytic trial using **1** and ***2,4,6-tri-tert-butylphenoxyl*** radical. T = 0.9 (He), 5.0 (N_2), 6.9 (CO), and 19.0 (NH_3).

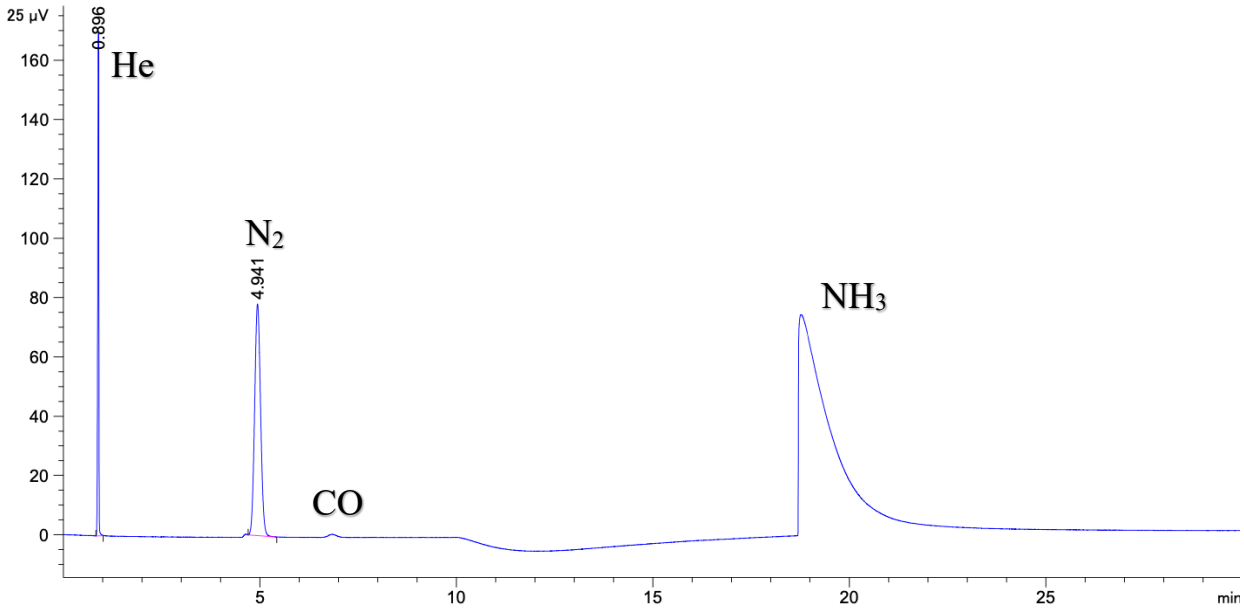


Figure S31. Representative GC trace of catalytic trial using **1** and 2,6-di-*tert*-butyl-4-tritylphenoxyl radical. T = 0.9 (He), 5.0 (N_2), 6.9 (CO), and 19.0 (NH_3).

Procedure for reaction of a 1:1 mixture of 2 and 2^{15N} with $^{trityl}ArO^{\bullet}$

Working in an argon glovebox, 2,6-di-tert-butyl-4-tritylphenoxyl radical (100.0 mg, 0.22 mmol) was added to an NMR tube equipped with a Teflon valve. Next, a solution containing a 1:1 ratio of **2** and $\mathbf{2^{15N}}$ was prepared (0.02 M in THF-d_8) and 0.6 mL was subsequently added to the NMR tube containing solid $^{trityl}ArO^{\bullet}$. The tube was quickly sealed and placed on an NMR tube rotator for 24 h. The headspace gas was then sampled using a gas-tight syringe and manually injected into the GC/MS.

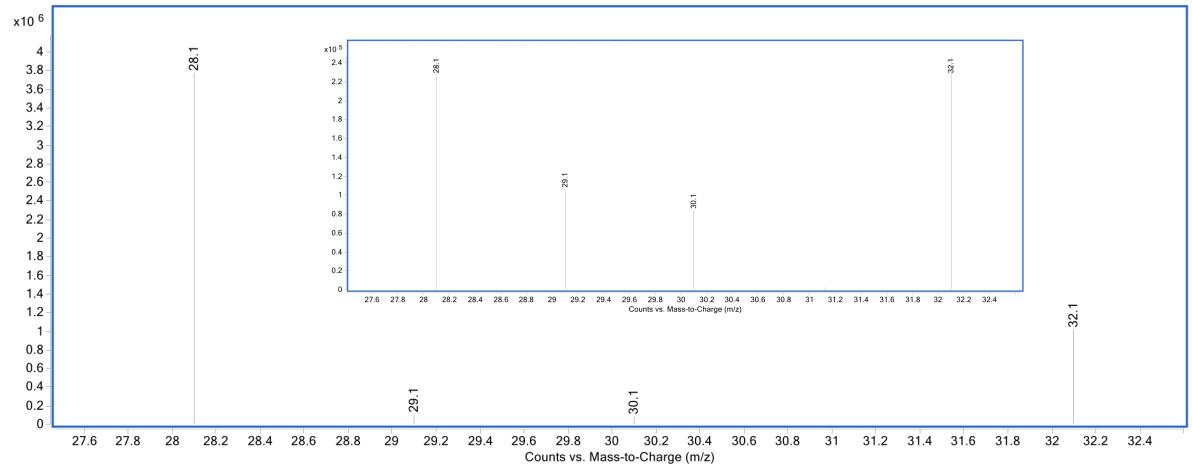


Figure S32. GC/MS trace of the region reaction of a 1:1 mixture of **2** and $\mathbf{2^{15N}}$ in THF-d_8 with 10 equiv of 2,6-di-*tert*-butyl-4-tritylphenoxyl radical. The formation of near equal amounts of $^{14}N^{15}N$ ($m/z = 29$) and $^{15}N_2$ ($m/z = 30$) were observed. A signal corresponding to $^{14}N_2$ ($m/z = 28$) (originates from both the reaction and from air) and $^{16}O_2$ ($m/z = 32$) are due to unavoidable air contamination during sample injection. Inset GC/MS plot shows an increased vertical scale of the region m/z 27.6 − 32.6 for clarity.

VI. X-Ray Crystallographic Data

CCDC: 2431617 (**1**) and 2431618 (**2**) contains the supplementary crystallographic data for this work. The data can be obtained free of charge from the Cambridge Crystallography Data Center via http://www.ccdc.cam.ac.uk/data_request/cif.

A colorless, prism-like specimen of **1**, approximate dimensions 0.276 mm × 0.423 mm × 0.686 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured (λ = 0.71073 Å) on a Bruker D8 Venture X-ray diffractometer equipped with a CMOS IμS 3.0 Mo source and PHOTON detector. A total of 2439 frames were collected. The total exposure time was 1.25 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 63691 reflections to a maximum θ angle of 33.73° (0.64 Å resolution), of which 11733 were independent

(average redundancy 5.428, completeness = 99.8%, R_{int} = 6.55%, R_{sig} = 5.04%) and 11407 (97.22%) were greater than 2σ(F^2). The final cell constants of a = 12.2585(15) Å, b = 21.027(3) Å, c = 11.8947(14) Å, β = 102.628(4)°, volume = 2991.8(6) Å^3, are based upon the refinement of the XYZ-centroids of 9609 reflections above 20 σ(*I*) with 6.738° < 2θ < 69.77°. Data were corrected for absorption effects using the Multi-Scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.901. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.6920 and 0.8560. The structure was solved and refined using the Bruker SHELXTL Software Package,[4] using the space group *Cc*, with Z = 4 for the formula unit, $C_{29}H_{39}MoN_3O_3P_2$. All non-hydrogen atoms were located in the Fourier maps and refined anisotropically. A well-ordered *fac*-[$(CO)_3Mo(P^{tBu}{}_2N^{Ph}{}_2)(MeCN)$] molecule is present in the asymmetric unit. The methyl H atoms of the acetonitrile ligand (C5), one of the *t*-butyl methyl groups (C21), and one of the methylene groups (C7) were placed in calculated positions and refined isotropically using a riding model with fixed C–H bond distances. The rest of the H atoms were located in successive Fourier maps and refined isotropically. The final anisotropic full-matrix least-squares refinement on F^2 with 475 variables converged at *R1* = 3.84%, for the observed data and *wR2* = 9.19% for all data. The goodness-of-fit was 1.078. The largest peak in the final difference electron density synthesis was 1.726 e$^-$/Å^3 and the largest hole was −0.918 e$^-$/Å^3 with an RMS deviation of 0.107 e$^-$/Å^3. On the basis of the final model, the calculated density was 1.411 g/cm^3 and F(000), 1320 e$^-$.

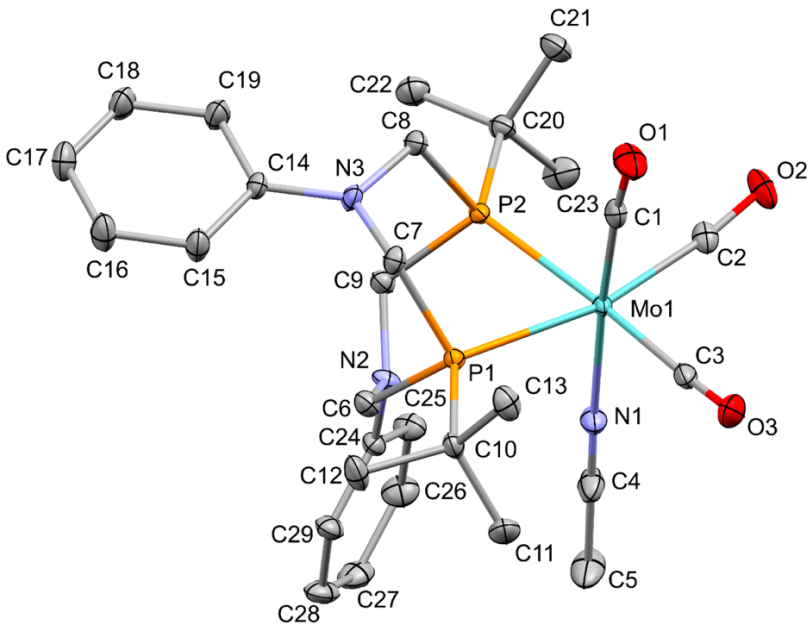


Figure S33. Molecular structure of *fac*-[$(CO)_3Mo(P^{tBu}{}_2N^{Ph}{}_2)(MeCN)$], compound **1**. All H atoms are omitted for clarity, and the thermal ellipsoids are drawn at 50% probability level.

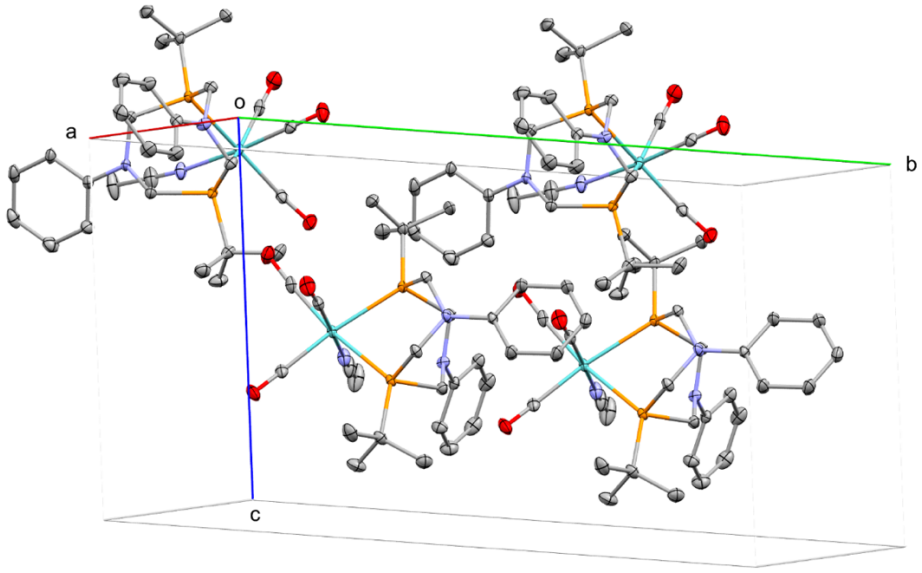


Figure S34. Packing in the crystals of *fac*-[$(CO)_3Mo(P^{tBu}{}_2N^{Ph}{}_2)(MeCN)$], compound **1**. All atoms are unlabeled, and H atoms omitted for clarity. The thermal ellipsoids are drawn at 50% probability level.

Table S3. Sample and crystal data for **1**.

Chemical formula	$C_{29}H_{39}MoN_3O_3P_2$	
Formula weight	635.51 g/mol	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal size	0.276 × 0.423 × 0.686 mm	
Crystal habit	colorless prism	
Crystal system	monoclinic	
Space group	*Cc*	
Unit cell dimensions	a = 12.2585(15) Å	
	b = 21.027(3) Å	α = 90°
	c = 11.8947(14) Å	β = 102.628(4)°
Volume	2991.8(6) Å^3	γ = 90°
Z	4	
Density (calculated)	1.411 g/cm^3	
Absorption coefficient	0.579 mm^{-1}	
F(000)	1320	

Table S4. Data collection and structure refinement for **1**.

Theta range for data collection	1.94 to 33.73°
Index ranges	$-19 \le h \le 19$, $-32 \le k \le 32$, $-18 \le l \le 18$
Reflections collected	63691
Independent reflections	11733 [R(int) = 0.0655]
Coverage of independent reflections	99.8%
Absorption correction	Multi-Scan
Max. and min. transmission	0.8560 and 0.6920
Structure solution technique	direct methods
Structure solution program	XT, VERSION 2018/2
Refinement method	Full-matrix least-squares on F^2
Refinement program	SHELXL-2019/1 (Sheldrick, 2019)
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	11733 / 2 / 475
Goodness-of-fit on F^2	1.078
Δ/σ_{max}	0.001
Final *R* indices	11407 data; $I > 2\sigma(I)$ $R1 = 0.0384$, $wR2 = 0.0914$
	all data $R1 = 0.0393$, $wR2 = 0.0919$
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0427P)^2 + 4.5200P]$ where $P = (F_o^2 + 2F_c^2)/3$
Absolute structure parameter	0.10(3)
Largest diff. peak and hole	1.726 and -0.918 eÅ^{-3}
R.M.S. deviation from mean	0.107 eÅ^{-3}

Table S5. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å^2) for **1**.

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	y/b	z/c	U(eq)
Mo1	0.55596(2)	0.25883(2)	0.49873(2)	0.01093(6)
C1	0.4219(3)	0.20881(15)	0.4389(3)	0.0164(5)
O1	0.3471(2)	0.17570(14)	0.4010(3)	0.0282(6)
C2	0.5917(3)	0.18739(15)	0.6097(3)	0.0171(5)
O2	0.5983(3)	0.14411(13)	0.6712(3)	0.0264(6)
C3	0.6131(3)	0.21172(14)	0.3792(3)	0.0174(5)
O3	0.6344(2)	0.18283(13)	0.3033(3)	0.0264(5)
P1	0.47429(6)	0.35147(3)	0.37474(6)	0.01107(13)
P2	0.45774(6)	0.32436(3)	0.62407(6)	0.01138(13)

N1	0.7158(2)	0.31261(13)	0.5514(3)	0.0192(5)
C4	0.8002(3)	0.33946(17)	0.5684(4)	0.0257(7)
C5	0.9064(3)	0.3734(2)	0.5871(6)	0.0397(12)
N2	0.5677(2)	0.43077(13)	0.5581(2)	0.0131(5)
C6	0.5172(3)	0.43222(16)	0.4358(3)	0.0149(5)
N3	0.2827(2)	0.37365(13)	0.4596(2)	0.0146(4)
C7	0.3194(2)	0.35254(14)	0.3580(3)	0.0143(5)
C8	0.3046(2)	0.32930(15)	0.5552(3)	0.0150(5)
C9	0.4945(3)	0.41100(14)	0.6328(3)	0.0144(5)
C10	0.4892(3)	0.35828(14)	0.2222(3)	0.0149(5)
C11	0.6149(3)	0.35591(18)	0.2223(3)	0.0222(6)
C12	0.4382(4)	0.41964(16)	0.1622(3)	0.0223(6)
C13	0.4304(3)	0.29982(16)	0.1585(3)	0.0203(6)
C14	0.2215(2)	0.42978(14)	0.4607(3)	0.0129(5)
C15	0.2100(3)	0.47400(16)	0.3706(3)	0.0208(6)
C16	0.1478(4)	0.52920(17)	0.3711(3)	0.0244(7)
C17	0.0958(3)	0.54352(17)	0.4609(3)	0.0231(6)
C18	0.1083(3)	0.50071(17)	0.5509(3)	0.0230(6)
C19	0.1699(3)	0.44464(17)	0.5518(3)	0.0206(6)
C20	0.4553(3)	0.30415(16)	0.7774(3)	0.0169(5)
C21	0.3880(4)	0.24218(18)	0.7749(4)	0.0253(7)
C22	0.4011(3)	0.35737(18)	0.8357(3)	0.0224(6)
C23	0.5764(3)	0.2933(2)	0.8439(3)	0.0249(7)
C24	0.6622(2)	0.46808(14)	0.6030(3)	0.0136(5)
C25	0.7244(3)	0.45744(17)	0.7160(3)	0.0195(6)
C26	0.8201(3)	0.4930(2)	0.7611(3)	0.0245(7)
C27	0.8584(3)	0.53982(19)	0.6957(4)	0.0251(7)
C28	0.7983(3)	0.54992(17)	0.5841(4)	0.0231(7)
C29	0.7011(3)	0.51529(15)	0.5380(3)	0.0175(5)

Table S6. Bond lengths (Å) for **1**.

Mo1-C1	1.949(3)	Mo1-C3	1.982(3)
Mo1-C2	1.984(3)	Mo1-N1	2.230(3)
Mo1-P1	2.5152(8)	Mo1-P2	2.5210(8)
C1-O1	1.162(4)	C2-O2	1.159(4)
C3-O3	1.164(4)	P1-C7	1.866(3)
P1-C10	1.868(3)	P1-C6	1.876(3)
P2-C9	1.874(3)	P2-C20	1.879(3)
P2-C8	1.880(3)	N1-C4	1.157(4)
C4-C5	1.458(5)	N2-C24	1.404(4)
N2-C6	1.452(4)	N2-C9	1.454(4)
N3-C14	1.400(4)	N3-C7	1.448(4)
N3-C8	1.450(4)	C10-C13	1.538(5)
C10-C12	1.540(4)	C10-C11	1.541(5)
C14-C15	1.403(4)	C14-C19	1.404(4)
C15-C16	1.390(5)	C16-C17	1.391(5)
C17-C18	1.381(5)	C18-C19	1.398(5)
C20-C23	1.538(5)	C20-C21	1.539(5)
C20-C22	1.542(5)	C24-C29	1.404(4)
C24-C25	1.411(5)	C25-C26	1.396(5)
C26-C27	1.397(6)	C27-C28	1.387(6)
C28-C29	1.401(5)		

Table S7. Bond angles (°) for **1**.

C1-Mo1-C3	82.56(13)	C1-Mo1-C2	83.12(13)
C3-Mo1-C2	92.14(14)	C1-Mo1-N1	174.07(13)
C3-Mo1-N1	91.62(12)	C2-Mo1-N1	98.30(12)
C1-Mo1-P1	90.47(9)	C3-Mo1-P1	97.14(10)
C2-Mo1-P1	167.97(10)	N1-Mo1-P1	89.12(8)
C1-Mo1-P2	92.14(10)	C3-Mo1-P2	170.64(10)
C2-Mo1-P2	94.88(10)	N1-Mo1-P2	93.47(8)
P1-Mo1-P2	75.12(3)	O1-C1-Mo1	175.0(3)
O2-C2-Mo1	171.4(3)	O3-C3-Mo1	172.5(3)
C7-P1-C10	102.08(14)	C7-P1-C6	102.89(14)
C10-P1-C6	103.15(14)	C7-P1-Mo1	109.70(10)
C10-P1-Mo1	121.18(10)	C6-P1-Mo1	115.60(11)
C9-P2-C20	102.74(14)	C9-P2-C8	100.11(14)
C20-P2-C8	102.07(14)	C9-P2-Mo1	115.08(10)
C20-P2-Mo1	124.14(11)	C8-P2-Mo1	109.47(11)
C4-N1-Mo1	173.5(3)	N1-C4-C5	178.8(5)
C24-N2-C6	120.3(3)	C24-N2-C9	119.7(3)
C6-N2-C9	115.7(3)	N2-C6-P1	113.0(2)
C14-N3-C7	122.1(3)	C14-N3-C8	122.8(3)
C7-N3-C8	114.8(2)	N3-C7-P1	114.2(2)
N3-C8-P2	111.9(2)	N2-C9-P2	114.7(2)
C13-C10-C12	110.0(3)	C13-C10-C11	109.6(3)
C12-C10-C11	109.4(3)	C13-C10-P1	106.4(2)
C12-C10-P1	113.5(2)	C11-C10-P1	107.9(2)
N3-C14-C15	121.1(3)	N3-C14-C19	121.9(3)
C15-C14-C19	117.1(3)	C16-C15-C14	120.9(3)
C15-C16-C17	121.9(3)	C18-C17-C16	117.5(3)
C17-C18-C19	121.6(3)	C18-C19-C14	121.0(3)
C23-C20-C21	109.7(3)	C23-C20-C22	109.8(3)
C21-C20-C22	109.9(3)	C23-C20-P2	108.3(2)
C21-C20-P2	107.1(3)	C22-C20-P2	111.9(2)
C29-C24-N2	122.5(3)	C29-C24-C25	117.3(3)
N2-C24-C25	120.2(3)	C26-C25-C24	121.0(3)
C25-C26-C27	121.3(4)	C28-C27-C26	117.9(3)
C27-C28-C29	121.5(3)	C28-C29-C24	121.0(3)

Table S8. Anisotropic atomic displacement parameters (Å^2) for **1**.

The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Mo1	0.00880(8)	0.00835(8)	0.01518(10)	0.00152(9)	0.00162(6)	0.00049(9)
C1	0.0169(12)	0.0132(12)	0.0187(14)	0.0033(10)	0.0030(11)	0.0037(9)
O1	0.0204(12)	0.0205(12)	0.0398(17)	0.0006(11)	-0.0022(11)	-0.0056(9)
C2	0.0151(12)	0.0140(12)	0.0194(14)	-0.0018(10)	-0.0024(10)	-0.0006(9)
O2	0.0313(13)	0.0162(11)	0.0267(13)	0.0071(9)	-0.0043(11)	0.0007(9)
C3	0.0147(12)	0.0111(11)	0.0265(16)	0.0025(10)	0.0048(11)	0.0003(9)
O3	0.0307(14)	0.0199(11)	0.0323(15)	-0.0022(10)	0.0152(11)	0.0049(10)
P1	0.0118(3)	0.0088(3)	0.0126(3)	0.0000(2)	0.0026(2)	0.0003(2)
P2	0.0102(3)	0.0107(3)	0.0130(3)	0.0023(2)	0.0019(2)	-0.0003(2)
N1	0.0127(10)	0.0144(11)	0.0296(15)	0.0007(10)	0.0022(10)	-0.0011(8)
C4	0.0147(13)	0.0171(14)	0.044(2)	-0.0020(14)	0.0025(14)	0.0013(11)
C5	0.0146(15)	0.0230(17)	0.080(4)	-0.010(2)	0.0062(18)	-0.0061(12)
N2	0.0151(11)	0.0118(10)	0.0128(11)	-0.0005(8)	0.0038(9)	-0.0059(8)
C6	0.0179(14)	0.0131(12)	0.0138(13)	0.0010(10)	0.0038(10)	-0.0013(10)
N3	0.0139(10)	0.0156(11)	0.0151(11)	0.0034(9)	0.0048(9)	0.0070(8)
C7	0.0128(11)	0.0149(12)	0.0143(13)	0.0000(9)	0.0009(9)	0.0027(9)
C8	0.0123(11)	0.0154(12)	0.0174(13)	0.0040(10)	0.0034(10)	0.0020(9)
C9	0.0168(12)	0.0122(11)	0.0146(12)	-0.0001(9)	0.0048(10)	-0.0012(9)
C10	0.0199(13)	0.0096(10)	0.0160(13)	0.0011(9)	0.0061(10)	0.0014(9)
C11	0.0243(15)	0.0227(15)	0.0235(16)	0.0031(12)	0.0137(13)	0.0020(12)
C12	0.0371(19)	0.0132(13)	0.0173(14)	0.0031(11)	0.0074(13)	0.0049(12)
C13	0.0289(16)	0.0150(13)	0.0160(14)	-0.0031(11)	0.0028(12)	-0.0011(11)
C14	0.0107(10)	0.0129(11)	0.0145(12)	0.0002(9)	0.0015(9)	0.0029(8)
C15	0.0271(16)	0.0175(13)	0.0193(15)	0.0030(11)	0.0081(12)	0.0092(11)
C16	0.0342(18)	0.0194(14)	0.0199(15)	0.0040(12)	0.0063(13)	0.0105(13)
C17	0.0270(16)	0.0163(13)	0.0248(16)	-0.0035(12)	0.0031(13)	0.0071(12)
C18	0.0271(16)	0.0200(14)	0.0245(16)	-0.0009(12)	0.0115(13)	0.0074(12)
C19	0.0244(15)	0.0193(14)	0.0203(15)	0.0025(11)	0.0101(12)	0.0072(11)
C20	0.0145(12)	0.0184(13)	0.0182(14)	0.0053(11)	0.0042(10)	0.0004(10)
C21	0.0269(17)	0.0212(15)	0.0296(19)	0.0107(13)	0.0102(15)	-0.0010(12)
C22	0.0238(15)	0.0254(15)	0.0191(15)	0.0003(12)	0.0074(12)	-0.0003(12)
C23	0.0187(14)	0.0372(19)	0.0171(15)	0.0065(14)	0.0004(12)	0.0021(13)
C24	0.0137(11)	0.0113(11)	0.0161(13)	-0.0009(9)	0.0038(10)	-0.0018(9)
C25	0.0167(13)	0.0222(14)	0.0184(14)	0.0008(11)	0.0013(11)	-0.0031(11)

C26	0.0186(15)	0.0298(18)	0.0235(17)	-0.0030(13)	0.0010(13)	-0.0048(12)
C27	0.0165(13)	0.0253(16)	0.035(2)	-0.0100(14)	0.0090(13)	-0.0080(12)
C28	0.0244(15)	0.0190(14)	0.0302(18)	-0.0053(13)	0.0153(14)	-0.0103(12)
C29	0.0196(13)	0.0130(11)	0.0217(14)	-0.0007(10)	0.0081(11)	-0.0052(10)

Table S9. Hydrogen atomic coordinates and isotropic atomic displacement parameters ($Å^2$) for **1**.

	x/a	y/b	z/c	U(eq)
H5A	0.9518	0.3623	0.6631	0.060000
H5B	0.8924	0.4193	0.5834	0.060000
H5C	0.9463	0.3613	0.5274	0.060000
H6A	0.575(4)	0.444(2)	0.398(4)	0.010(9)
H6B	0.452(5)	0.463(3)	0.414(5)	0.032(16)
H7A	0.2877	0.3083	0.3353	0.014(10)
H7B	0.2932	0.3711	0.3028	0.020(12)
H8A	0.280(4)	0.289(3)	0.534(4)	0.016(11)
H8B	0.265(5)	0.339(3)	0.614(5)	0.027(13)
H9A	0.424(5)	0.437(3)	0.619(5)	0.033(15)
H9B	0.528(4)	0.423(3)	0.713(5)	0.021(12)
H11A	0.624(7)	0.356(4)	0.148(7)	0.05(2)
H11B	0.647(4)	0.320(2)	0.258(4)	0.013(11)
H11C	0.651(4)	0.396(3)	0.257(5)	0.019(11)
H12A	0.449(5)	0.421(3)	0.079(6)	0.035(15)
H12B	0.467(5)	0.454(3)	0.200(5)	0.024(13)
H12C	0.365(5)	0.423(3)	0.155(5)	0.028(14)
H13A	0.449(5)	0.295(3)	0.083(5)	0.027(13)
H13B	0.364(5)	0.301(3)	0.147(5)	0.027(14)
H13C	0.453(6)	0.265(3)	0.207(6)	0.031(16)
H15	0.256(5)	0.464(3)	0.313(5)	0.033(15)
H16	0.146(5)	0.558(3)	0.314(5)	0.027(13)
H17	0.057(5)	0.582(3)	0.469(4)	0.022(13)
H18	0.071(5)	0.512(3)	0.610(5)	0.029(14)
H19	0.171(6)	0.413(3)	0.613(6)	0.049(19)
H21A	0.3929	0.2272	0.8539	0.027(14)
H21B	0.4186	0.2097	0.7313	0.049(19)
H21C	0.3096	0.2502	0.7379	0.047(18)
H22A	0.381(5)	0.337(3)	0.909(5)	0.026(13)

H22B	0.336(5)	0.368(3)	0.796(5)	0.033(15)
H22C	0.445(5)	0.400(3)	0.845(5)	0.032(15)
H23A	0.575(6)	0.277(3)	0.917(6)	0.036(16)
H23B	0.618(5)	0.327(3)	0.841(5)	0.031(15)
H23C	0.608(6)	0.258(3)	0.808(6)	0.026(14)
H25	0.703(5)	0.423(3)	0.760(5)	0.034(15)
H26	0.865(7)	0.486(4)	0.830(7)	0.05(2)
H27	0.919(5)	0.558(3)	0.730(6)	0.033(15)
H28	0.824(5)	0.575(3)	0.546(5)	0.028(14)
H29	0.659(4)	0.525(2)	0.460(4)	0.014(10)

A light yellow, prism-like specimen of **2**·C_6H_5F, approximate dimensions 0.063 mm × 0.101 mm × 0.162 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured (λ = 0.71073 Å) on a Bruker D8 Venture X-ray diffractometer equipped with a CMOS IμS 3.0 Mo source and a PHOTON detector. A total of 342 frames were collected. The total exposure time was 0.95 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 78535 reflections to a maximum θ angle of 27.10° (0.78 Å resolution), of which 7374 were independent (average redundancy 10.650, completeness = 99.8%, R_{int} = 17.53%, R_{sig} = 7.66%) and 5363 (72.73%) were greater than 2σ(F^2). The final cell constants of a = 14.868(2) Å, b = 13.2099(18) Å, c = 18.026(3) Å, β = 108.924(4)°, volume = 3349.0(8) $Å^3$, are based upon the refinement of the XYZ-centroids of 9963 reflections above 20 σ(I) with 4.715° < 2θ < 54.72°. Data were corrected for absorption effects using the Multi-Scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.813. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9190 and 0.9670. The structure was solved and refined using the Bruker SHELXTL Software Package,[4] using the space group *P2₁/c*, with Z = 4 for the formula unit, $C_{33}H_{44}FMoN_3O_3P_2$. The asymmetric unit consists of a *fac*-$[(CO)_3Mo(P^{tBu}{}_2N^{Ph}{}_2)(NH_3)]$ molecule and a fluorobenzene solvent molecule. Whereas the compound molecule is well-ordered and well-separated, the solvent exhibits some positional disorder with relatively high thermal parameters. However, no disorder model could be applied to treat the minor disorder of the solvent molecule. The non-hydrogen atoms were refined anisotropically. All H atoms were also located in successive Fourier maps and refined isotropically. The final anisotropic full-matrix least-squares refinement on F^2 with 564 variables converged at R_1 = 4.32%, for the observed data and wR_2 = 9.61% for all data. The goodness-of-fit was 1.035. The largest peak in the final difference electron density synthesis was 0.700 $e^-/Å^3$ and the largest hole was –0.519 $e^-/Å^3$ with an RMS deviation of 0.102 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.403 g/cm^3 and F(000), 1472 e^-.

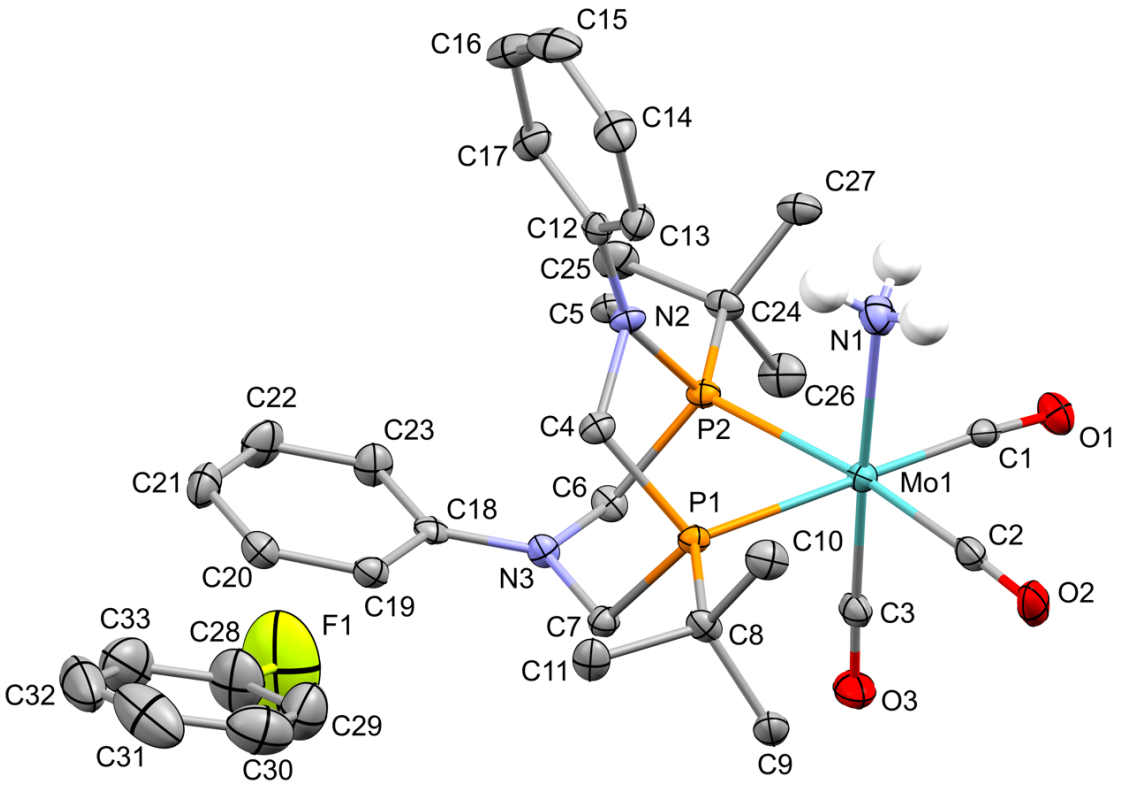


Figure S35. Molecular structure of *fac*-[$(CO)_3Mo(P^{tBu}{}_2N^{Ph}{}_2)(NH_3)$]·$C_6H_5F$, compound **2** with atom labelling. All H atoms except those of the NH_3 ligand are omitted for clarity. The thermal parameters are drawn at 50% probability level.

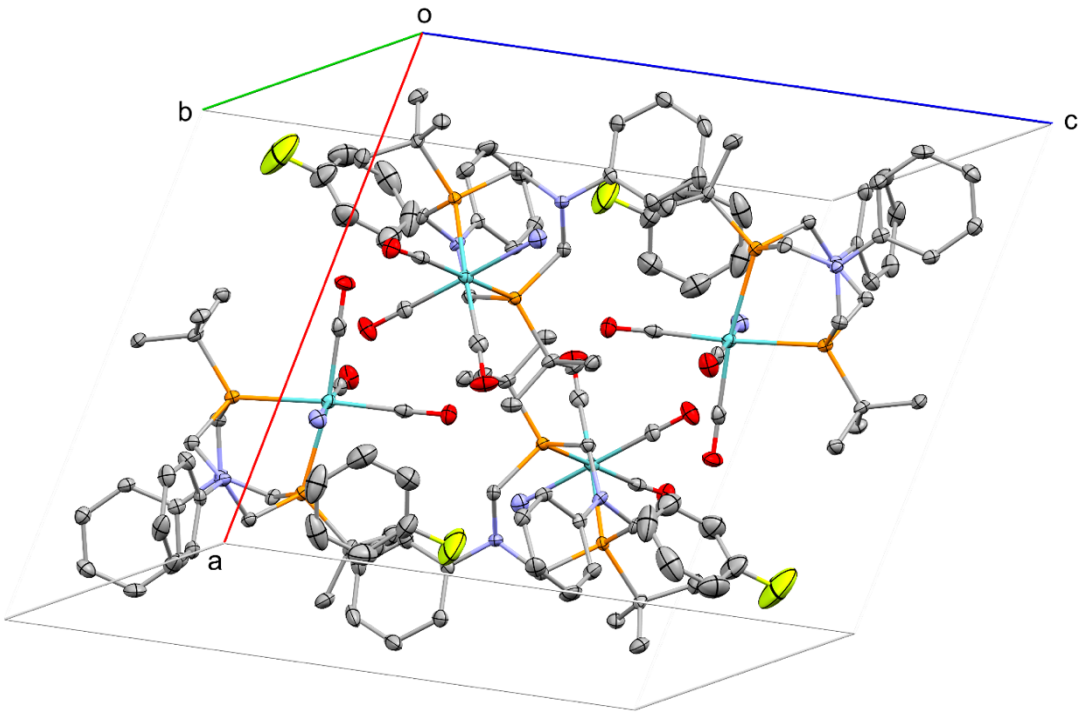


Figure S36. Packing in the crystals of *fac*-[$(CO)_3Mo(P^{tBu}{}_2N^{Ph}{}_2)(NH_3)$]·PhF, compound **2**. All atoms are unlabeled, H atoms are omitted for clarity and the thermal parameters are drawn at 50% probability level.

Table S10. Sample and crystal data for **2**·PhF.

Chemical formula	$C_{33}H_{44}FMoN_3O_3P_2$
Formula weight	707.59 g/mol
Temperature	100 (2) K
Wavelength	0.71073 Å
Crystal size	0.063 × 0.101 × 0.162 mm
Crystal habit	light yellow prism
Crystal system	monoclinic
Space group	$P2_1/c$
Unit cell dimensions	a = 14.868(2) Å

	b = 13.210(2) Å	α = 90°
	c = 18.026(3) Å	β = 108.924(4)°
Volume	3349.0(8) Å^3	γ = 90°
Z	4	
Density (calculated)	1.403 g/cm^3	
Absorption coefficient	0.530 mm^{-1}	
F(000)	1472	

Table S11. Data collection and structure refinement for **2**·PhF.

Theta range for data collection	1.95 to 27.10°
Index ranges	$-19 \leq h \leq 19$, $-16 \leq k \leq 16$, $-23 \leq l \leq 23$
Reflections collected	78535
Independent reflections	7374 [R(int) = 0.1753]
Coverage of independent reflections	99.8%
Absorption correction	Multi-Scan
Max. and min. transmission	0.9670 and 0.9190
Structure solution technique	direct methods
Structure solution program	XT, VERSION 2018/2
Refinement method	Full-matrix least-squares on F^2
Refinement program	SHELXL-2019/1 (Sheldrick, 2019)
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	7374 / 0 / 564
Goodness-of-fit on F^2	1.035
Δ/σ_{max}	0.001
Final R indices	5363 data; $I > 2\sigma(I)$ $R_1 = 0.0432$, $wR_2 = 0.0830$

	all data	$R_1 = 0.0720$, $wR_2 = 0.0961$
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0080P)^2 + 4.3781P]$ where $P = (F_o^2 + 2F_c^2)/3$	
Largest diff. peak and hole	0.700 and -0.519 eÅ^{-3}	
R.M.S. deviation from mean	0.102 eÅ^{-3}	

Table S12. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å^2) for **2**·PhF.

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	**y/b**	**z/c**	**U(eq)**
Mo1	0.58350(2)	0.86794(2)	0.75438(2)	0.01482(8)
N1	0.6468(3)	0.0071(2)	0.7087(2)	0.0235(7)
P1	0.57903(6)	0.76054(6)	0.63766(5)	0.01389(17)
P2	0.74399(6)	0.78336(6)	0.79246(5)	0.01439(17)
C1	0.5944(2)	0.9365(2)	0.8535(2)	0.0178(7)
O1	0.59695(17)	0.97305(17)	0.91302(14)	0.0250(5)
C2	0.4531(2)	0.9211(2)	0.7116(2)	0.0211(7)
O2	0.37474(17)	0.94819(18)	0.68702(16)	0.0312(6)
C3	0.5300(2)	0.7561(2)	0.79519(19)	0.0183(7)
O3	0.49714(18)	0.69036(18)	0.82145(16)	0.0300(6)
C4	0.6793(2)	0.7806(2)	0.5981(2)	0.0163(7)
N2	0.75339(17)	0.84762(18)	0.64805(15)	0.0150(6)
C5	0.8113(2)	0.8033(3)	0.72247(19)	0.0161(7)
C6	0.7307(2)	0.6430(2)	0.79053(19)	0.0159(6)
N3	0.69709(18)	0.60331(18)	0.71100(15)	0.0146(5)
C7	0.5978(2)	0.6247(2)	0.6682(2)	0.0156(6)
C8	0.4727(2)	0.7585(2)	0.54685(19)	0.0172(7)

C9	0.3864(2)	0.7295(3)	0.5715(2)	0.0214(7)
C10	0.4581(3)	0.8657(3)	0.5125(2)	0.0229(7)
C11	0.4835(3)	0.6835(3)	0.4855(2)	0.0216(7)
C12	0.8034(2)	0.9049(2)	0.60707(19)	0.0163(7)
C13	0.7518(3)	0.9695(2)	0.5468(2)	0.0212(7)
C14	0.7981(3)	0.0312(3)	0.5086(2)	0.0257(8)
C15	0.8956(3)	0.0308(3)	0.5300(2)	0.0316(9)
C16	0.9472(3)	0.9662(3)	0.5879(2)	0.0301(9)
C17	0.9026(2)	0.9029(3)	0.6262(2)	0.0217(7)
C18	0.7554(2)	0.5496(2)	0.67823(19)	0.0154(7)
C19	0.7223(2)	0.5171(2)	0.5995(2)	0.0178(7)
C20	0.7805(2)	0.4658(2)	0.5663(2)	0.0203(7)
C21	0.8737(3)	0.4441(3)	0.6086(2)	0.0264(8)
C22	0.9072(3)	0.4749(3)	0.6857(2)	0.0295(9)
C23	0.8501(2)	0.5271(3)	0.7200(2)	0.0229(8)
C24	0.8374(2)	0.8071(2)	0.88960(19)	0.0172(7)
C25	0.9306(3)	0.7510(3)	0.8982(2)	0.0255(8)
C26	0.7967(3)	0.7729(3)	0.9529(2)	0.0273(8)
C27	0.8561(3)	0.9218(3)	0.8969(2)	0.0227(8)
F1	0.8922(3)	0.2256(3)	0.92290(18)	0.1087(15)
C28	0.8654(3)	0.2223(4)	0.8438(3)	0.0491(12)
C29	0.7868(3)	0.2737(4)	0.8024(3)	0.0464(11)
C30	0.7574(4)	0.2694(4)	0.7222(3)	0.0489(12)
C31	0.8092(5)	0.2144(4)	0.6856(3)	0.0600(16)
C32	0.8887(4)	0.1636(4)	0.7287(4)	0.0560(15)
C33	0.9185(4)	0.1674(4)	0.8089(4)	0.0528(14)

Table S13. Bond lengths (Å) for **2**·PhF.

Mo1-C3	1.934(3)	Mo1-C1	1.963(4)
Mo1-C2	1.969(4)	Mo1-N1	2.333(3)
Mo1-P2	2.5202(9)	Mo1-P1	2.5205(9)
P1-C4	1.868(3)	P1-C8	1.871(3)
P1-C7	1.871(3)	P2-C6	1.864(3)
P2-C5	1.865(3)	P2-C24	1.875(3)
C1-O1	1.166(4)	C2-O2	1.161(4)
C3-O3	1.168(4)	C4-N2	1.471(4)
N2-C12	1.424(4)	N2-C5	1.461(4)
C6-N3	1.454(4)	N3-C18	1.391(4)
N3-C7	1.455(4)	C8-C11	1.531(5)
C8-C10	1.533(5)	C8-C9	1.536(5)
C12-C13	1.399(5)	C12-C17	1.401(5)
C13-C14	1.386(5)	C14-C15	1.374(5)
C15-C16	1.373(6)	C16-C17	1.383(5)
C18-C23	1.396(4)	C18-C19	1.410(5)
C19-C20	1.379(5)	C20-C21	1.378(5)
C21-C22	1.377(5)	C22-C23	1.385(5)
C24-C26	1.523(5)	C24-C25	1.534(5)
C24-C27	1.539(4)	F1-C28	1.351(5)
C28-C29	1.349(6)	C28-C33	1.366(7)
C29-C30	1.368(7)	C30-C31	1.373(8)
C31-C32	1.363(8)	C32-C33	1.369(8)

Table S14. Bond angles (°) for **2**·PhF.

C3-Mo1-C1	85.94(13)	C3-Mo1-C2	86.98(14)
C1-Mo1-C2	88.40(13)	C3-Mo1-N1	177.77(13)
C1-Mo1-N1	91.96(13)	C2-Mo1-N1	92.25(13)
C3-Mo1-P2	91.59(10)	C1-Mo1-P2	99.52(9)
C2-Mo1-P2	171.84(10)	N1-Mo1-P2	89.47(9)
C3-Mo1-P1	89.12(10)	C1-Mo1-P1	172.66(9)
C2-Mo1-P1	96.76(10)	N1-Mo1-P1	93.05(9)
P2-Mo1-P1	75.17(3)	C4-P1-C8	102.72(15)
C4-P1-C7	100.79(15)	C8-P1-C7	104.24(14)
C4-P1-Mo1	115.50(11)	C8-P1-Mo1	121.66(11)
C7-P1-Mo1	109.47(11)	C6-P2-C5	101.82(15)
C6-P2-C24	103.06(14)	C5-P2-C24	102.18(15)
C6-P2-Mo1	110.52(11)	C5-P2-Mo1	114.91(11)
C24-P2-Mo1	121.95(11)	O1-C1-Mo1	175.9(3)
O2-C2-Mo1	176.9(3)	O3-C3-Mo1	178.0(3)
N2-C4-P1	112.5(2)	C12-N2-C5	116.0(2)
C12-N2-C4	114.6(3)	C5-N2-C4	115.0(2)
N2-C5-P2	113.1(2)	N3-C6-P2	112.2(2)
C18-N3-C6	122.7(3)	C18-N3-C7	122.6(3)
C6-N3-C7	114.7(3)	N3-C7-P1	111.8(2)
C11-C8-C10	109.9(3)	C11-C8-C9	109.9(3)
C10-C8-C9	108.9(3)	C11-C8-P1	112.6(2)
C10-C8-P1	108.0(2)	C9-C8-P1	107.4(2)
C13-C12-C17	118.1(3)	C13-C12-N2	118.7(3)
C17-C12-N2	123.2(3)	C14-C13-C12	120.6(3)
C15-C14-C13	120.4(4)	C16-C15-C14	119.6(3)
C15-C16-C17	121.0(4)	C16-C17-C12	120.1(3)

N3-C18-C23	122.5(3)	N3-C18-C19	121.4(3)
C23-C18-C19	116.1(3)	C20-C19-C18	121.5(3)
C21-C20-C19	121.5(3)	C22-C21-C20	117.8(3)
C21-C22-C23	121.6(3)	C22-C23-C18	121.5(3)
C26-C24-C25	110.3(3)	C26-C24-C27	109.5(3)
C25-C24-C27	109.6(3)	C26-C24-P2	107.2(2)
C25-C24-P2	112.6(2)	C27-C24-P2	107.7(2)
C29-C28-F1	118.3(5)	C29-C28-C33	122.6(5)
F1-C28-C33	119.1(5)	C28-C29-C30	119.2(5)
C29-C30-C31	119.5(5)	C32-C31-C30	120.3(5)
C31-C32-C33	120.5(5)	C28-C33-C32	117.9(5)

Table S15. Anisotropic atomic displacement parameters ($Å^2$) for **2**·PhF.

The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Mo1	0.01479(14)	0.01385(13)	0.01563(14)	-0.00057(12)	0.00470(11)	-0.00088(11)
N1	0.0259(18)	0.0196(16)	0.0257(18)	0.0011(14)	0.0092(16)	0.0024(14)
P1	0.0128(4)	0.0138(4)	0.0139(4)	0.0010(3)	0.0028(3)	-0.0003(3)
P2	0.0151(4)	0.0149(4)	0.0133(4)	0.0015(3)	0.0048(3)	-0.0020(3)
C1	0.0126(16)	0.0134(15)	0.0268(19)	0.0013(14)	0.0056(14)	-0.0010(12)
O1	0.0310(14)	0.0228(12)	0.0210(13)	-0.0044(10)	0.0082(11)	0.0002(10)
C2	0.026(2)	0.0159(16)	0.0226(19)	-0.0068(14)	0.0096(16)	-0.0037(14)
O2	0.0177(13)	0.0281(13)	0.0421(17)	-0.0126(12)	0.0018(12)	0.0077(11)
C3	0.0225(18)	0.0167(15)	0.0166(17)	-0.0036(13)	0.0077(14)	-0.0018(13)
O3	0.0382(16)	0.0226(13)	0.0364(16)	-0.0031(11)	0.0221(13)	-0.0077(11)
C4	0.0162(16)	0.0182(16)	0.0145(17)	0.0031(14)	0.0051(14)	-0.0001(13)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
N2	0.0110(13)	0.0180(13)	0.0144(14)	0.0017(11)	0.0020(11)	-0.0018(10)
C5	0.0140(16)	0.0182(16)	0.0152(17)	0.0005(13)	0.0036(14)	-0.0018(13)
C6	0.0200(17)	0.0150(15)	0.0112(16)	0.0046(13)	0.0028(14)	0.0018(13)
N3	0.0145(13)	0.0149(13)	0.0116(13)	0.0001(10)	0.0002(11)	0.0019(10)
C7	0.0142(15)	0.0153(15)	0.0172(16)	0.0010(14)	0.0050(13)	0.0005(13)
C8	0.0156(16)	0.0148(15)	0.0163(17)	-0.0007(13)	-0.0017(14)	0.0010(12)
C9	0.0158(18)	0.0217(19)	0.025(2)	-0.0055(16)	0.0039(16)	-0.0008(14)
C10	0.0212(19)	0.0217(17)	0.0214(19)	0.0055(16)	0.0007(16)	0.0020(15)
C11	0.0189(19)	0.028(2)	0.0137(18)	-0.0032(15)	-0.0007(15)	0.0038(15)
C12	0.0205(17)	0.0159(15)	0.0148(16)	-0.0041(13)	0.0089(14)	-0.0027(13)
C13	0.0221(19)	0.0198(17)	0.0247(19)	0.0009(14)	0.0118(16)	0.0018(14)
C14	0.036(2)	0.0235(18)	0.0217(19)	0.0043(15)	0.0146(17)	-0.0004(16)
C15	0.041(2)	0.037(2)	0.022(2)	-0.0024(17)	0.0165(18)	-0.0198(18)
C16	0.023(2)	0.047(2)	0.021(2)	-0.0048(17)	0.0091(16)	-0.0146(17)
C17	0.0210(18)	0.0298(18)	0.0156(17)	-0.0026(15)	0.0077(15)	-0.0024(15)
C18	0.0173(16)	0.0088(14)	0.0187(17)	0.0031(12)	0.0039(14)	-0.0014(12)
C19	0.0149(17)	0.0152(15)	0.0197(18)	0.0005(13)	0.0007(14)	0.0003(13)
C20	0.0234(18)	0.0173(16)	0.0187(19)	-0.0002(14)	0.0049(15)	-0.0003(14)
C21	0.0238(19)	0.0259(18)	0.032(2)	0.0019(16)	0.0123(17)	0.0080(15)
C22	0.0163(18)	0.038(2)	0.030(2)	0.0029(17)	0.0007(16)	0.0083(16)
C23	0.0204(18)	0.0274(18)	0.0171(18)	-0.0005(15)	0.0009(15)	0.0043(14)
C24	0.0194(17)	0.0200(16)	0.0107(16)	-0.0017(13)	0.0026(13)	-0.0051(13)
C25	0.0201(19)	0.029(2)	0.021(2)	-0.0005(16)	-0.0025(16)	-0.0004(15)
C26	0.031(2)	0.033(2)	0.017(2)	0.0026(16)	0.0064(17)	-0.0028(18)
C27	0.0219(19)	0.0244(18)	0.0199(19)	-0.0017(15)	0.0042(16)	-0.0077(15)
F1	0.123(3)	0.147(3)	0.0308(18)	-0.014(2)	-0.010(2)	0.040(3)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C28	0.049(3)	0.064(3)	0.026(2)	-0.010(2)	0.000(2)	0.005(2)
C29	0.039(3)	0.055(3)	0.047(3)	-0.002(2)	0.016(2)	0.008(2)
C30	0.044(3)	0.046(3)	0.044(3)	0.007(2)	-0.003(2)	-0.007(2)
C31	0.107(5)	0.042(3)	0.031(3)	0.000(2)	0.022(3)	-0.016(3)
C32	0.083(4)	0.034(2)	0.073(4)	-0.014(3)	0.056(4)	-0.010(2)
C33	0.035(3)	0.048(3)	0.067(4)	0.000(3)	0.006(3)	0.008(2)

Table S16. Hydrogen atomic coordinates and isotropic atomic displacement parameters ($Å^2$) for **2**·PhF.

	x/a	y/b	z/c	U(eq)
H1A	0.686(3)	1.040(3)	0.742(3)	0.034(13)
H1B	0.606(3)	1.049(3)	0.688(3)	0.040(13)
H1C	0.677(4)	1.000(4)	0.678(3)	0.062(17)
H4A	0.706(2)	0.718(2)	0.5901(18)	0.007(8)
H4B	0.655(2)	0.808(2)	0.5510(19)	0.003(7)
H5A	0.859(2)	0.850(2)	0.7465(18)	0.006(8)
H5B	0.841(2)	0.742(3)	0.716(2)	0.018(9)
H6A	0.785(2)	0.613(2)	0.820(2)	0.016(9)
H6B	0.684(2)	0.626(2)	0.8170(18)	0.006(7)
H7A	0.562(2)	0.613(2)	0.7020(19)	0.009(8)
H7B	0.572(3)	0.578(3)	0.623(2)	0.026(10)
H9A	0.329(3)	0.733(3)	0.524(2)	0.032(11)
H9B	0.381(3)	0.771(3)	0.608(2)	0.027(11)
H9C	0.393(2)	0.663(3)	0.592(2)	0.021(9)
H10A	0.399(3)	0.868(3)	0.469(2)	0.029(10)

	x/a	y/b	z/c	U(eq)
H10B	0.507(2)	0.886(2)	0.4937(19)	0.011(8)
H10C	0.456(3)	0.911(3)	0.553(2)	0.032(11)
H11A	0.433(3)	0.692(3)	0.442(2)	0.028(10)
H11B	0.488(3)	0.613(3)	0.503(2)	0.034(11)
H11C	0.538(2)	0.695(2)	0.4688(19)	0.009(8)
H13	0.686(2)	0.966(2)	0.531(2)	0.015(9)
H14	0.758(3)	1.071(3)	0.469(2)	0.022(9)
H15	0.926(2)	1.068(3)	0.506(2)	0.022(10)
H16	1.019(3)	0.962(3)	0.600(2)	0.040(11)
H17	0.935(2)	0.855(2)	0.663(2)	0.014(9)
H19	0.662(2)	0.531(2)	0.567(2)	0.015(9)
H20	0.756(2)	0.446(2)	0.516(2)	0.019(9)
H21	0.914(2)	0.409(3)	0.588(2)	0.018(9)
H22	0.969(3)	0.466(3)	0.715(2)	0.028(10)
H23	0.876(2)	0.547(2)	0.772(2)	0.012(8)
H25A	0.977(3)	0.767(3)	0.947(3)	0.040(12)
H25B	0.959(3)	0.765(3)	0.857(3)	0.036(11)
H25C	0.919(3)	0.680(3)	0.898(2)	0.025(10)
H26A	0.836(3)	0.790(3)	0.998(3)	0.031(11)
H26B	0.786(3)	0.701(3)	0.955(2)	0.034(11)
H26C	0.741(3)	0.804(3)	0.948(2)	0.027(10)
H27A	0.902(3)	0.935(3)	0.947(2)	0.025(10)
H27B	0.799(3)	0.960(3)	0.892(2)	0.026(10)
H27C	0.885(3)	0.946(3)	0.861(2)	0.025(10)
H29	0.751(3)	0.312(3)	0.827(3)	0.056(14)
H30	0.698(5)	0.303(5)	0.689(4)	0.11(2)

	x/a	y/b	z/c	U(eq)
H31	0.788(3)	0.211(4)	0.631(3)	0.060(15)
H32	0.926(4)	0.126(4)	0.703(3)	0.072(16)
H33	0.967(4)	0.142(4)	0.844(3)	0.060(16)

VII. Computational Details

All computational structures were optimized without symmetry constraints in Gaussian 09[5] using the B3LYP[6] functional with the D2 dispersion corrections[7] with the Stuttgart basis set with effective core potential (ECP)[8] for Mo and the 6-31G** basis set[9] for all the remaining atoms. The ultrafine integration grid was employed in all calculations. Each stationary point was confirmed by a frequency calculation at the same level of theory to be a real local minimum on the potential energy surface without an imaginary frequency. Although for each species all the possible chair/boat conformations of the $P^{t\mathrm{Bu}}{}_2N^{\mathrm{Ph}}{}_2$ ligand were computed, only the lowest-free energy conformations are described here. Alternative conformations of the $P^{t\mathrm{Bu}}{}_2N^{\mathrm{Ph}}{}_2$ ligand noted above typically ranged 3-10 kcal/mol higher in free energy.[10] All reported free energies are for a THF solution at the standard state (T = 298 K, P = 1 atm of N_2, 1 M concentration of all species in THF) as modeled by the universal solvation model (SMD)[11] with standard correction for (harmonic) vibrational, rotational, and translational thermal free energy contributions. All BDFE's are anchored to the BDFE of 2,4,6-tri-*tert*-butyl-phenol with a value of 74.4 kcal/mol (THF).[12]

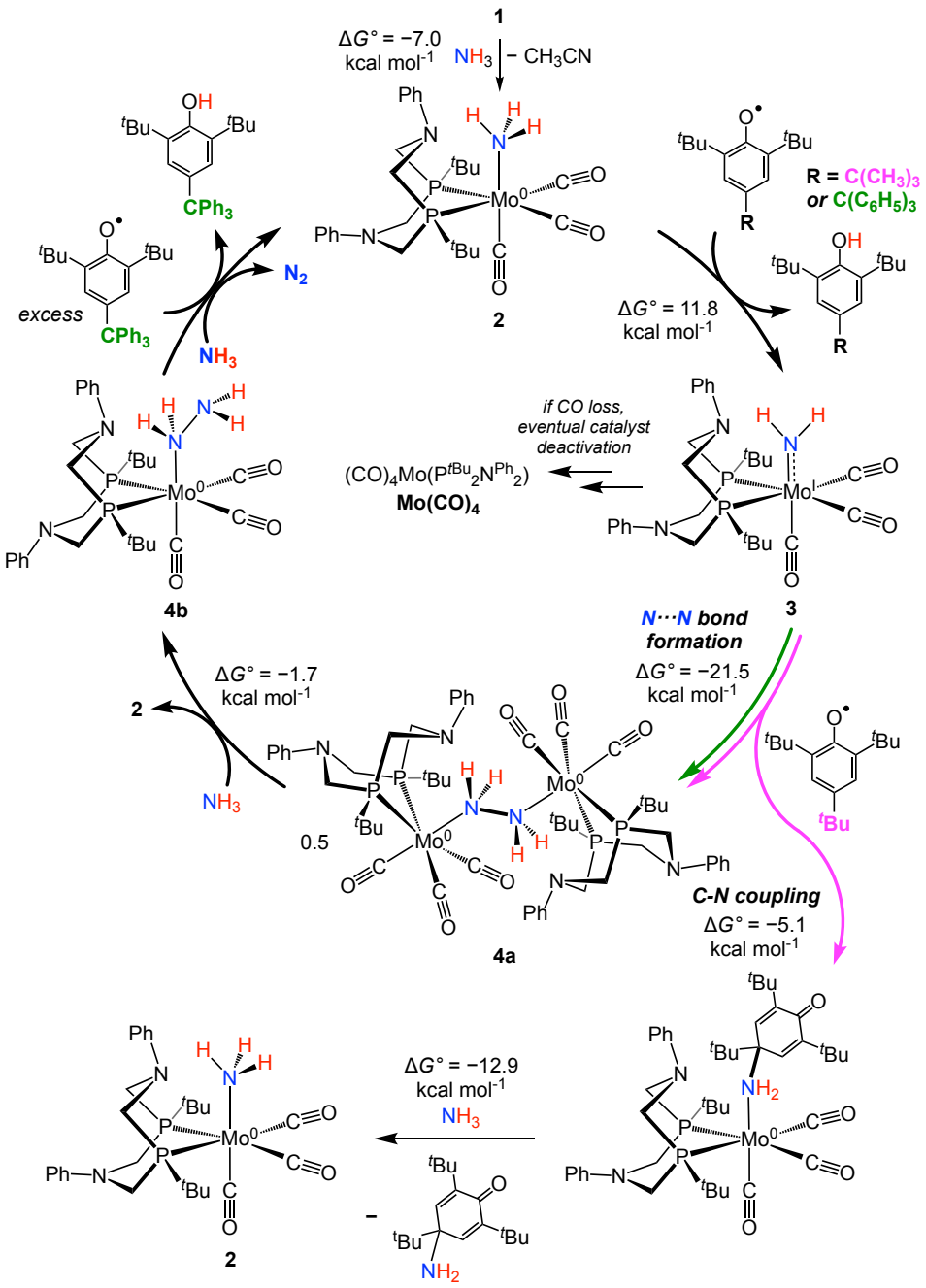
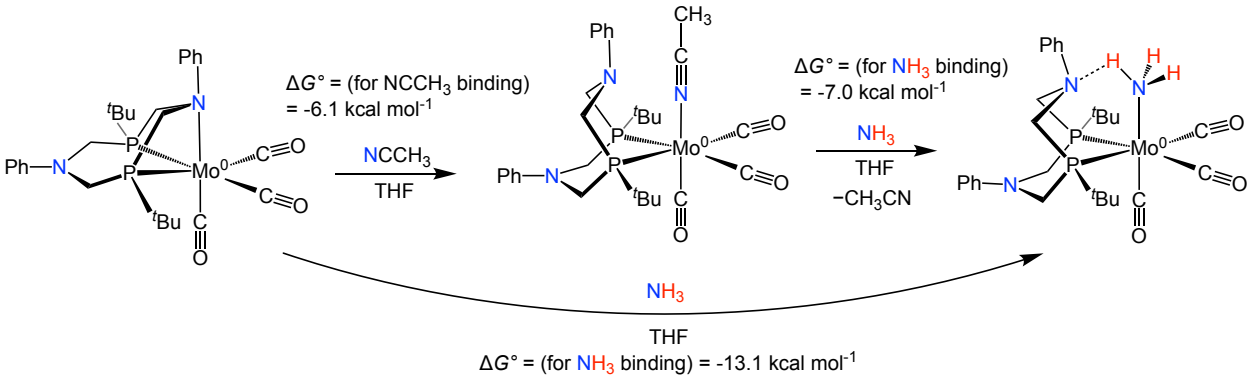
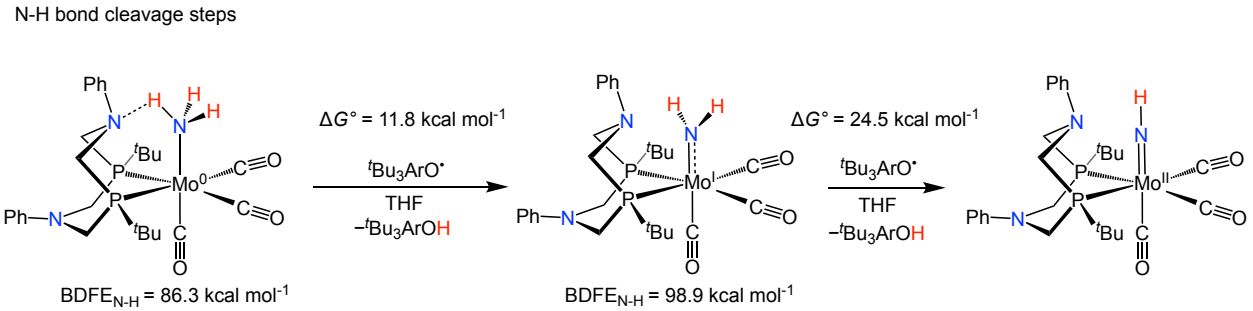


Figure S37. Proposed catalytic cycle for Mo catalyzed NH_3 oxidation to form N_2.

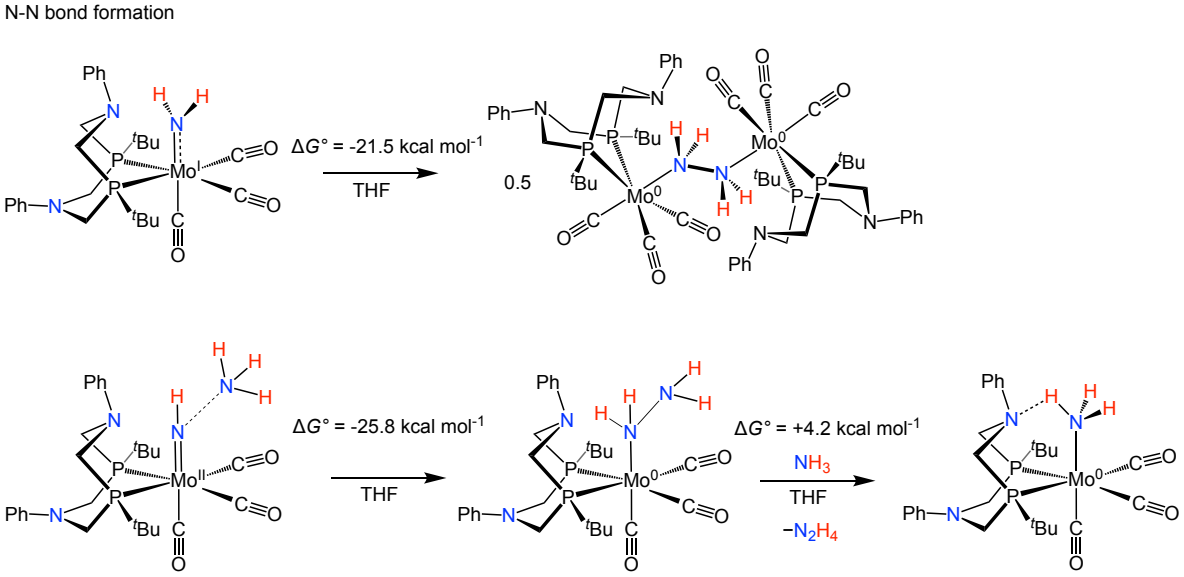
Schemes S1-S7: Tabulated thermochemical data from DFT calculations for various reaction steps relevant to NH_3 oxidation to form N_2 using **1** and **2**.



Scheme S1.

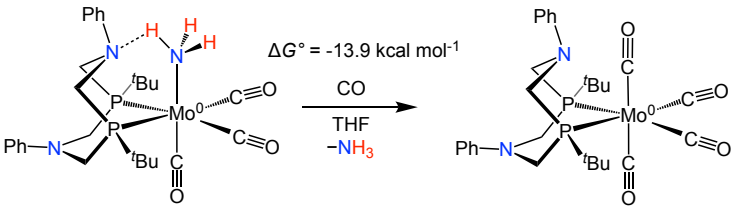


Scheme S2.



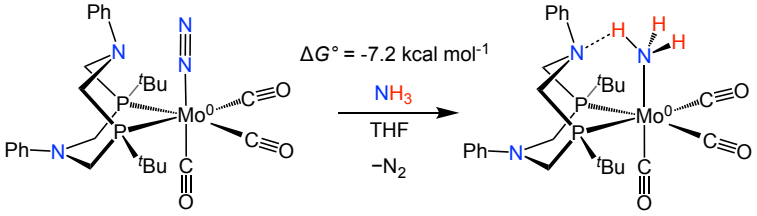
Scheme S3

Ligand substitution of NH_3 for CO.



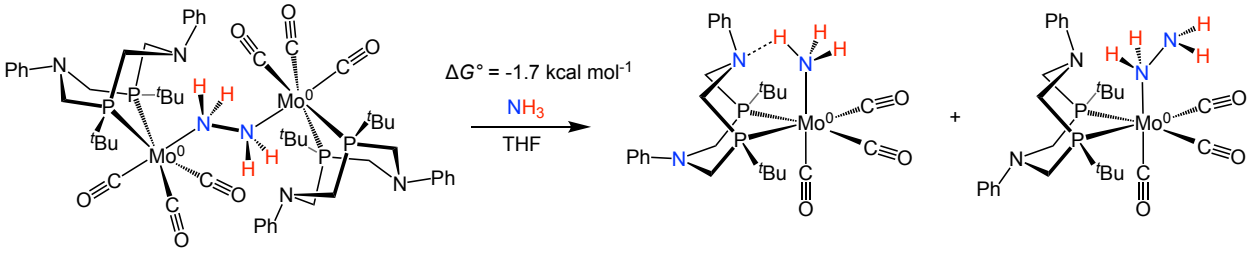
Scheme S4.

Ligand substitution of N_2 for NH_3.

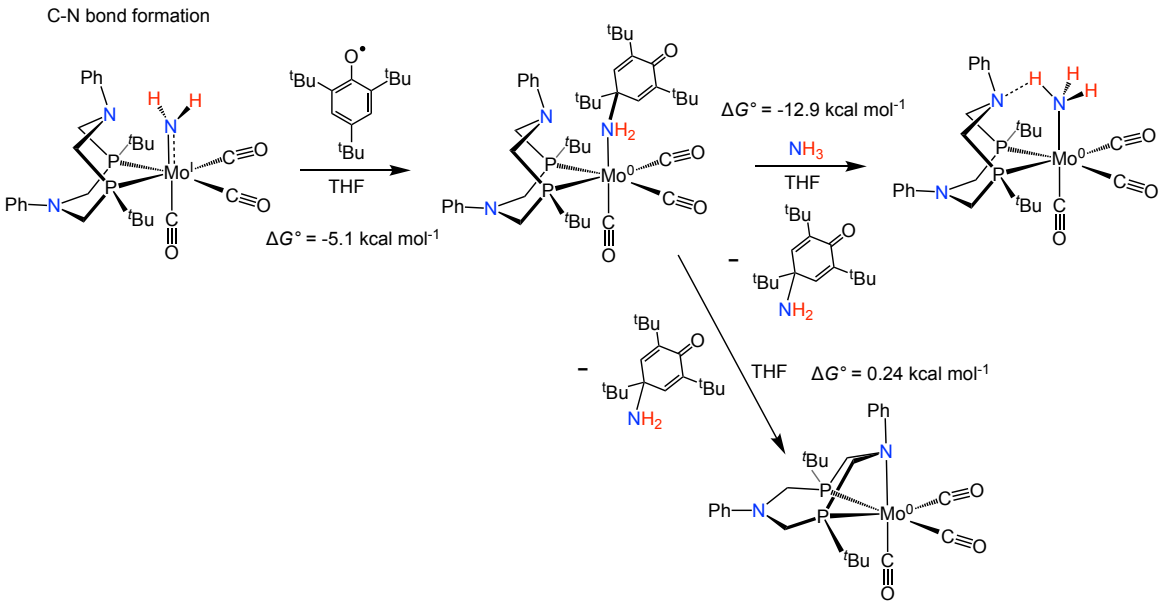


Scheme S5.

Conversion of **4a** to **2** and **4b**



Scheme S6.



Scheme S7.

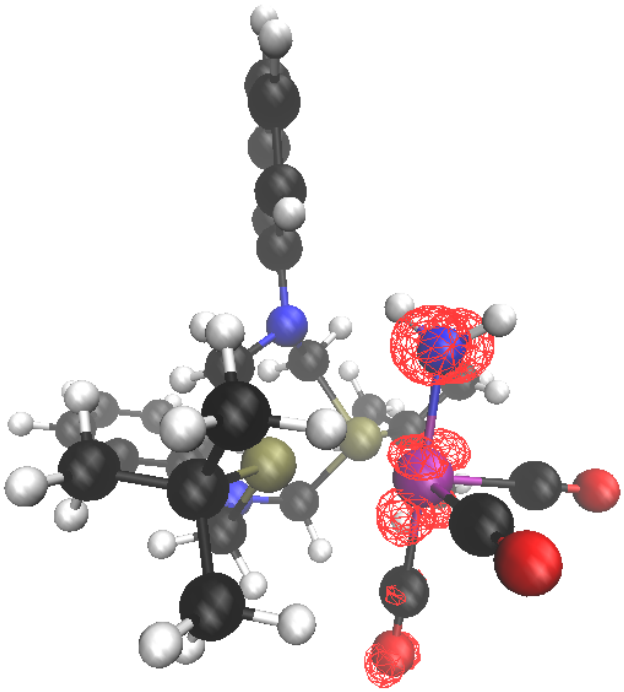


Figure S38. An unpaired spin density plot of **3**. The regions of unpaired spin density are shown as red mesh, isovalue = 0.01 e^- a.u.$^{-1}$. H: white, C: black, N: blue, P: gold, O: red, and Mo: purple. 43% unpaired spin-density resides on N of NH_2, 31% at Mo, 7% on C, 7% on O, less than 1% unpaired spin density on all other atoms.

Sample input file for geometry optimization and frequency calculation with Gaussian09

```
%chk=N2_B3LYP_GD2.chk
%nproc=16
%mem=512MW

#p b3lyp/6-31G** opt(maxcycles=100, verytight) freq integral(grid=ultrafine)
EmpiricalDispersion=GD2 gfinput  scf=(maxcycles = 1024)

N2_B3LYP_GD2

0 1
N 0   -0.014010    0.024266    0.000000
N 0   -0.541290    0.937542    0.000000
```

Sample input file for single point solvation with Gaussian09

```
%chk=N2_B3LYP_GD2_THF.chk
%nproc=16
%mem=512MW

#p B3LYP/6-31G** scrf=(smd,solvent=tetrahydrofuran) EmpiricalDispersion=GD2 gfinput
scf=(maxcycles = 1024)

N2_B3LYP_GD2_THF

0 1
 N    -0.001276     0.002209     0.000000
 N    -0.554024     0.959599     0.000000
```

xyz coordinates for DFT structures

```
   2
CO
 C     0.006835    -0.011838     0.000000
 O    -0.562135     0.973646     0.000000

   2
N2
 N    -0.001276     0.002209     0.000000
 N    -0.554024     0.959599     0.000000

   3
NH2-Radical
 N    -0.123558     3.416679     0.000000
 H    -0.493164     4.381782     0.000000
 H     0.897049     3.579142     0.000000
```

4

NH_3

N	-0.521314	0.923424	-0.034649
H	-0.551881	1.939836	0.018371
H	-1.489630	0.612953	0.018370
H	-0.082007	0.612953	0.829907

6

NCMe

C	-0.450345	0.591328	0.000000
C	0.434958	-0.572216	0.000000
N	1.137557	-1.495628	0.000000
H	0.139194	1.513978	0.000000
H	-1.087807	0.580399	0.890147
H	-1.087807	0.580399	-0.890147

6

NH_2NH_2

N	-0.957312	0.902823	-0.023852
H	-0.516497	-0.019454	-0.028627
H	-0.516335	1.359697	-0.824939
N	-0.322738	1.576538	1.143100
H	-0.763553	2.498815	1.147875
H	-0.763715	1.119665	1.944187

29

TEMPO

C	1.323020	-0.073200	-0.042807
N	0.004100	-0.754006	-0.255461
C	-1.315808	-0.074976	-0.043257
C	-1.238350	1.392345	-0.498287
C	0.002120	2.115912	0.026615
C	1.243742	1.394016	-0.497864
O	0.004932	-2.029917	-0.097950
C	-2.355032	-0.820224	-0.888983
C	-1.699057	-0.180191	1.444174
C	2.363534	-0.817047	-0.888178
C	1.705902	-0.177899	1.444755
H	-1.220144	1.419030	-1.595937
H	-2.159896	1.891159	-0.176621
H	0.001475	3.159161	-0.308327
H	0.001922	2.131714	1.122989
H	1.225874	1.420676	-1.595519
H	2.164506	1.894070	-0.175883
H	-2.072719	-0.792595	-1.946600
H	-2.425960	-1.862349	-0.572510
H	-3.329305	-0.334136	-0.770109
H	-2.736758	0.143956	1.579882
H	-1.604336	-1.221744	1.763361
H	-1.060104	0.442809	2.075392
H	2.081546	-0.789798	-1.945891
H	3.337112	-0.329648	-0.768972
H	2.435757	-1.859076	-0.571680
H	2.743120	0.147645	1.580817
H	1.065896	0.444240	2.075755
H	1.612475	-1.219578	1.763909

30

TEMPOH

C	1.283897	-0.052211	-0.040322
N	-0.000227	-0.666550	-0.469893
C	-1.284028	-0.051460	-0.040430
C	-1.245777	1.427218	-0.475238
C	0.000578	2.158027	0.029266
C	1.246547	1.426489	-0.475133
O	-0.000650	-2.043627	-0.016369
C	-2.393995	-0.766603	-0.826673
C	-1.596370	-0.176258	1.465493
C	2.393512	-0.768003	-0.826471
C	1.596039	-0.177192	1.465628
H	-1.255743	1.464005	-1.572353
H	-2.163468	1.910749	-0.119958
H	0.000896	3.195356	-0.325112
H	0.000543	2.196925	1.124868
H	1.256628	1.463271	-1.572246
H	2.164491	1.909483	-0.119775
H	-0.000757	-2.527860	-0.851624
H	-2.172767	-0.734264	-1.899009
H	-2.474659	-1.810415	-0.510277
H	-3.355200	-0.272506	-0.647369
H	-2.657032	0.042254	1.634052
H	-1.393943	-1.195643	1.803322
H	-1.014516	0.518556	2.073531
H	2.172393	-0.735534	-1.898826
H	3.354991	-0.274467	-0.647086
H	2.473540	-1.811862	-0.510068
H	2.656814	0.040701	1.634277
H	1.014540	0.517963	2.073617
H	1.392988	-1.196458	1.803440

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TBHT-Radical

C	-1.262670	0.651039	-0.011547
C	-1.232234	-0.732660	-0.005622
C	-0.030369	-1.466338	0.006168
C	1.196860	-0.761105	0.012214
C	1.273717	0.614080	0.007108
C	0.015505	1.384041	-0.005243
O	0.033862	2.641440	-0.010291
C	2.614853	1.350911	0.013855
C	-2.581414	1.427114	-0.024365
C	0.000992	-2.993676	0.012691
C	3.807999	0.379644	0.026561
C	2.740462	2.229731	-1.252444
C	2.722028	2.240143	1.274566
C	-3.804613	0.493532	-0.029441
C	-2.680380	2.319843	1.234938
C	-2.661944	2.309429	-1.292291
C	-1.402137	-3.620023	0.005039
C	0.760085	-3.491008	-1.238068
C	0.741731	-3.480638	1.278445
H	-2.164924	-1.277873	-0.010179
H	2.108480	-1.344687	0.021269
H	4.736041	0.960484	0.030937
H	3.802190	-0.256588	0.919224
H	3.815175	-0.263923	-0.860818
H	3.712673	2.737308	-1.243157
H	1.948061	2.978021	-1.286046
H	2.687155	1.609770	-2.155329
H	2.655518	1.627640	2.181656
H	3.694302	2.747685	1.275282
H	1.929267	2.988638	1.290437
H	-4.713567	1.103807	-0.038586
H	-3.819622	-0.149693	-0.916881
H	-3.832605	-0.142359	0.862957
H	-3.637100	2.855934	1.221144
H	-1.865902	3.044198	1.262351
H	-2.645697	1.706051	2.142918
H	-2.614055	1.688177	-2.194580
H	-3.618732	2.845558	-1.296874
H	-1.847109	3.033582	-1.313788
H	-1.310624	-4.711190	0.010203
H	-1.977620	-3.322173	0.888414
H	-1.964656	-3.329498	-0.889061
H	0.802978	-4.586482	-1.231182
H	1.785227	-3.108707	-1.263223
H	0.250999	-3.168576	-2.152930
H	0.219375	-3.150708	2.183096
H	0.784654	-4.576128	1.281214
H	1.766420	-3.098081	1.315398

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TBHT

C	-1.225393	0.675122	-0.011544
C	-1.207260	-0.728117	-0.005583
C	-0.026881	-1.466231	0.006141
C	1.178381	-0.755879	0.012032
C	1.246228	0.637635	0.006742
C	0.018717	1.343207	-0.005193
O	0.114521	2.718388	-0.010203
C	2.604489	1.364755	0.013684
C	-2.567191	1.437345	-0.024553
C	0.003425	-2.998426	0.012728
C	3.787052	0.378247	0.026456
C	2.757982	2.233340	-1.255299
C	2.739403	2.243861	1.277524
C	-3.780855	0.487752	-0.029512
C	-2.718865	2.304434	1.251366
C	-2.700078	2.293796	-1.309719
C	-1.403921	-3.614636	0.004962
C	0.757070	-3.503010	-1.235831
C	0.738639	-3.492575	1.276358
H	-2.148460	-1.257139	-0.010290
H	2.099241	-1.323683	0.021146
H	-0.760357	3.114208	-0.018264
H	4.721419	0.949511	0.030937
H	3.774339	-0.257717	0.918797
H	3.787391	-0.265110	-0.860660
H	3.736837	2.728646	-1.241199
H	1.981207	2.996328	-1.316847
H	2.705947	1.604423	-2.151779
H	2.674186	1.622410	2.178337
H	3.718390	2.739093	1.273670
H	1.961855	3.007287	1.321330
H	-4.699005	1.084990	-0.038728
H	-3.783544	-0.154689	-0.916094
H	-3.796590	-0.147301	0.862242
H	-3.661268	2.863154	1.211019
H	-1.909014	3.023959	1.409594

H	-2.737947	1.655636	2.133266
H	-2.706261	1.637693	-2.186385
H	-3.642938	2.852775	-1.287845
H	-1.887949	3.012031	-1.462021
H	-1.324735	-4.707201	0.010081
H	-1.976736	-3.309780	0.888139
H	-1.963698	-3.317161	-0.889026
H	0.802448	-4.599042	-1.232369
H	1.781824	-3.118425	-1.262053
H	0.248165	-3.178030	-2.150212
H	0.216392	-3.160043	2.180443
H	0.783997	-4.588595	1.282666
H	1.762921	-3.107722	1.314418

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TBHT-NH_2

C	-1.262670	0.651039	-0.011547
C	-1.232234	-0.732660	-0.005622
C	-0.030369	-1.466338	0.006168
C	1.196860	-0.761105	0.012214
C	1.273717	0.614080	0.007108
C	0.015505	1.384041	-0.005243
O	0.033862	2.641440	-0.010291
C	2.614853	1.350911	0.013855
C	-2.581414	1.427114	-0.024365
C	0.000992	-2.993676	0.012691
C	3.807999	0.379644	0.026561
C	2.740462	2.229731	-1.252444
C	2.722028	2.240143	1.274566
C	-3.804613	0.493532	-0.029441
C	-2.680380	2.319843	1.234938
C	-2.661944	2.309429	-1.292291
C	-1.402137	-3.620023	0.005039
C	0.760085	-3.491008	-1.238068
C	0.741731	-3.480638	1.278445
H	-2.164924	-1.277873	-0.010179
H	2.108480	-1.344687	0.021269
H	4.736041	0.960484	0.030937
H	3.802190	-0.256588	0.919224
H	3.815175	-0.263923	-0.860818
H	3.712673	2.737308	-1.243157
H	1.948061	2.978021	-1.286046
H	2.687155	1.609770	-2.155329
H	2.655518	1.627640	2.181656
H	3.694302	2.747685	1.275282
H	1.929267	2.988638	1.290437
H	-4.713567	1.103807	-0.038586
H	-3.819622	-0.149693	-0.916881
H	-3.832605	-0.142359	0.862957
H	-3.637100	2.855934	1.221144
H	-1.865902	3.044198	1.262351
H	-2.645697	1.706051	2.142918
H	-2.614055	1.688177	-2.194580
H	-3.618732	2.845558	-1.296874
H	-1.847109	3.033582	-1.313788
H	-1.310624	-4.711190	0.010203
H	-1.977620	-3.322173	0.888414
H	-1.964656	-3.329498	-0.889061
H	0.802978	-4.586482	-1.231182
H	1.785227	-3.108707	-1.263223
H	0.250999	-3.168576	-2.152930
H	0.219375	-3.150708	2.183096
H	0.784654	-4.576128	1.281214
H	1.766420	-3.098081	1.315398

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$Mo(CO)_3(P_2N_2$-tBuPh)

C	-0.346220	-2.561428	-0.265922
P	0.254296	-1.296985	1.010275
Mo	2.183063	0.016795	0.085663
P	0.330159	0.447047	-1.552440
C	-0.285137	-1.187992	-2.288867
N	-1.095921	-1.949670	-1.351458
C	-1.279557	-0.244562	1.311694
N	-1.184850	1.079708	0.719822
C	-1.227430	1.118570	-0.740352
C	3.490543	-0.510803	1.514069
O	4.232889	-0.839125	2.347686
C	3.549669	1.135855	-0.866406
O	4.323498	1.787801	-1.441162
C	2.772136	-1.592246	-1.002319
O	3.109171	-2.516054	-1.624295
C	1.653203	1.659941	1.213343
C	0.370586	-2.309816	2.593201
C	0.530828	1.559224	-3.057518
C	-1.846922	2.144057	1.386644
C	-2.859342	1.928280	2.335114
C	0.988727	2.944583	-2.570552
C	1.619029	0.936526	-3.948953
C	-0.980915	-2.936629	2.976911

C	0.848338	-1.387653	3.727401
C	-3.456378	3.008141	2.991861
C	-3.073749	4.317069	2.702237
C	-0.779479	1.701444	-3.850896
C	1.413569	-3.415073	2.352295
C	-2.073172	4.537994	1.749155
C	-1.460667	3.467876	1.105009
C	-3.207939	-1.286220	-2.415789
C	-2.494060	-1.948575	-1.388940
C	-3.262751	-2.610818	-0.402272
C	-4.655175	-2.625422	-0.460771
C	-5.345259	-1.981689	-1.488206
C	-4.600727	-1.310452	-2.458545
O	1.454570	2.597283	1.861252
H	-0.923129	-3.359873	0.197463
H	0.553879	-3.022691	-0.684483
H	-0.822016	-1.030755	-3.222457
H	0.607759	-1.773476	-2.529777
H	-1.316379	-0.121277	2.396376
H	-2.182874	-0.789821	1.003979
H	-1.305229	2.159920	-1.053730
H	-2.110875	0.594760	-1.129345
H	-3.199629	0.920988	2.549264
H	1.927190	2.881481	-2.014404
H	0.235172	3.420735	-1.931920
H	1.145766	3.594472	-3.440661
H	2.563595	0.832121	-3.407059
H	1.317388	-0.049348	-4.322466
H	1.790380	1.586115	-4.816471
H	-1.751384	-2.176553	3.144003
H	-1.344431	-3.636767	2.217277
H	-0.859942	-3.500100	3.910523
H	0.134960	-0.579379	3.925850
H	1.819767	-0.943900	3.497732
H	0.947542	-1.978175	4.646963
H	-4.237693	2.817151	3.722500
H	-3.542288	5.153505	3.211753
H	-0.612359	2.381269	-4.695732
H	-1.119139	0.745545	-4.263478
H	-1.585943	2.120726	-3.240199
H	1.096688	-4.103625	1.560011
H	1.540075	-3.998122	3.273053
H	2.384374	-2.989829	2.080344
H	-1.750412	5.550261	1.522324
H	-0.651340	3.645537	0.404645
H	-2.688733	-0.726667	-3.182726
H	-2.787224	-3.104884	0.434681
H	-5.201610	-3.147163	0.320255
H	-6.429549	-1.992894	-1.525200
H	-5.103946	-0.786225	-3.266407

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Mo(N2)(CO)$_3$(P$_2$N$_2$-tBuPh)

C	-0.449356	-2.560638	0.138281
P	0.206904	-1.135504	1.197540
Mo	2.162736	-0.058450	0.042680
P	0.284523	0.191685	-1.614624
C	-0.385991	-1.521233	-2.075319
N	-1.200767	-2.101284	-1.018796
C	-1.283846	0.009722	1.357746
N	-1.157087	1.215559	0.555500
C	-1.240014	1.022417	-0.890214
C	3.488347	-0.427889	1.497715
O	4.245172	-0.676901	2.347003
C	3.542892	0.845529	-1.092588
O	4.327137	1.362012	-1.781481
C	2.647706	-1.793372	-0.784418
O	2.913935	-2.822697	-1.270619
N	1.711486	1.818374	0.972481
C	0.322450	-1.896784	2.915296
C	0.484299	1.047458	-3.278652
C	-1.682056	2.424270	1.071059
C	-2.606443	2.457690	2.129115
C	0.992796	2.475815	-3.019266
C	1.536068	0.259187	-4.078082
C	-1.040779	-2.404681	3.414604
C	0.860163	-0.828926	3.882645
C	-3.063307	3.677467	2.634638
C	-2.629651	4.884595	2.087475
C	-0.836821	1.105982	-4.063939
C	1.320733	-3.064768	2.830846
C	-1.719966	4.858695	1.025350
C	-1.245053	3.648952	0.528231
C	-3.313542	-1.554217	-2.145540
C	-2.598369	-2.059215	-1.033561
C	-3.365774	-2.521338	0.062239
C	-4.758935	-2.498928	0.029051
C	-5.450831	-2.012785	-1.080557
C	-4.706991	-1.538348	-2.161402
N	1.583633	2.805453	1.480172
H	-1.039095	-3.262391	0.725918
H	0.432181	-3.103927	-0.215601

H	-0.934666	-1.495403	-3.014913
H	0.485884	-2.163129	-2.232590
H	-1.281069	0.303723	2.409202
H	-2.216141	-0.538779	1.163205
H	-1.313937	1.999144	-1.368162
H	-2.142375	0.460044	-1.163692
H	-2.992635	1.533699	2.545213
H	1.938809	2.467767	-2.471474
H	0.264442	3.069247	-2.453424
H	1.155337	2.978500	-3.981034
H	2.487831	0.210530	-3.541136
H	1.198787	-0.762920	-4.287367
H	1.708324	0.759596	-5.039323
H	-1.779423	-1.598528	3.477622
H	-1.446584	-3.196443	2.775905
H	-0.918956	-2.825194	4.420688
H	0.178713	0.025545	3.969758
H	1.839144	-0.462073	3.564410
H	0.966263	-1.273089	4.880425
H	-3.778842	3.675461	3.452419
H	-2.990438	5.829882	2.480891
H	-0.666768	1.636275	-5.009354
H	-1.214013	0.108319	-4.312160
H	-1.617542	1.643987	-3.515889
H	0.961213	-3.855841	2.162410
H	1.448934	-3.501372	3.829256
H	2.298894	-2.725000	2.477455
H	-1.358711	5.787950	0.593722
H	-0.504864	3.645245	-0.265308
H	-2.793745	-1.150270	-3.004322
H	-2.887501	-2.883844	0.962534
H	-5.304306	-2.864297	0.895023
H	-6.535511	-1.993814	-1.098027
H	-5.211156	-1.140365	-3.037843

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$Mo(NCMe)(CO)_3(P_2N_2$-tBuPh)

C	1.547120	-1.971827	-1.088007
P	0.170563	-0.734919	-1.520362
Mo	-1.773372	-1.104672	0.032320
P	0.122777	-0.545704	1.572156
C	1.512048	-1.811449	1.354785
N	2.264724	-1.608062	0.126165
C	1.084233	0.900528	-1.274713
N	0.630374	1.656553	-0.115004
C	0.981192	1.102881	1.181564
C	-3.109883	-1.450580	-1.410111
O	-3.865200	-1.646890	-2.278368
C	-3.126179	-1.424596	1.463864
O	-3.891089	-1.622772	2.323537
C	-1.315254	-3.016895	0.092068
O	-1.013494	-4.151071	0.144866
N	-2.338300	1.022265	0.088043
C	0.050318	-0.883724	-3.395382
C	-0.070471	-0.444926	3.443635
C	0.225555	2.984040	-0.254151
C	-0.459996	3.406045	-1.418751
C	-1.201329	0.550452	3.753126
C	-0.474496	-1.847140	3.932055
C	1.387094	-0.600071	-4.100499
C	-1.008774	0.118713	-3.883141
C	-0.861658	4.728478	-1.580928
C	-0.630820	5.679332	-0.581731
C	1.222098	0.003170	4.145606
C	-0.413891	-2.317223	-3.707230
C	0.023641	5.272036	0.582662
C	0.452910	3.953659	0.746960
C	4.117326	-0.503268	1.299946
C	3.505484	-0.968305	0.110194
C	4.214279	-0.750503	-1.096492
C	5.462250	-0.130708	-1.100190
C	6.060527	0.306090	0.082382
C	5.366926	0.113304	1.277474
C	-2.733055	2.105002	0.217850
C	-3.224844	3.461975	0.411857
H	2.239067	-2.104605	-1.917156
H	1.054913	-2.934336	-0.923455
H	2.179724	-1.841300	2.214682
H	1.017563	-2.786121	1.298469
H	0.942540	1.496345	-2.175309
H	2.159753	0.708823	-1.190306
H	0.614482	1.769866	1.960598
H	2.067605	1.004629	1.302825
H	-0.713671	2.681083	-2.182764
H	-2.135616	0.243312	3.276108
H	-0.954606	1.565375	3.417712
H	-1.359851	0.587161	4.838574
H	-1.390725	-2.187531	3.440727
H	0.317257	-2.581827	3.744688
H	-0.653773	-1.814589	5.014327
H	1.765375	0.403656	-3.878156

H	2.159769	-1.327243	-3.830072
H	1.240594	-0.668042	-5.186049
H	-0.693015	1.153980	-3.706257
H	-1.969765	-0.046566	-3.388546
H	-1.149398	-0.004052	-4.964743
H	-1.383907	5.010425	-2.491462
H	-0.951196	6.708529	-0.708211
H	1.047524	0.045573	5.228299
H	2.047369	-0.696285	3.974110
H	1.541791	0.999194	3.820528
H	0.324732	-3.058320	-3.379879
H	-0.543600	-2.426980	-4.791597
H	-1.368001	-2.538546	-3.220393
H	0.228845	5.990744	1.371601
H	1.008137	3.697066	1.641546
H	3.617228	-0.597535	2.254762
H	3.794288	-1.047632	-2.048427
H	5.966874	0.012672	-2.051908
H	7.031329	0.790603	0.071539
H	5.794678	0.452289	2.217260
H	-2.390512	4.122585	0.668748
H	-3.973355	3.476588	1.212056
H	-3.682343	3.830216	-0.511765

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$Mo(NH_3)(CO)_3(P_2N_2$-tBuPh)

C	-0.027699	-1.679967	-1.858659
P	0.411383	-1.600683	-0.016893
Mo	2.279057	0.036857	0.324495
P	0.445375	1.411593	-0.694288
C	-0.003114	0.705642	-2.395588
N	-0.785434	-0.518091	-2.299060
C	-1.240019	-1.106795	0.748271
N	-1.271328	0.274735	1.246756
C	-1.209615	1.318289	0.199191
C	3.555025	-1.262739	1.126179
O	4.281191	-2.053268	1.591524
C	3.580858	1.530012	0.511319
O	4.320943	2.431189	0.607187
C	2.975054	-0.364658	-1.460273
O	3.348781	-0.610169	-2.549399
N	1.381245	0.505504	2.441933
C	0.529236	-3.419205	0.466088
C	0.602933	3.259885	-1.028137
C	-2.284828	0.539458	2.224543
C	-3.398890	-0.289106	2.416729
C	0.953046	3.952489	0.299639
C	1.764878	3.437544	-2.021182
C	-0.774682	-4.190462	0.203940
C	0.881434	-3.493485	1.961155
C	-4.332832	0.006350	3.414880
C	-4.180326	1.132871	4.222002
C	-0.683038	3.872268	-1.607037
C	1.675910	-4.026837	-0.361158
C	-3.074387	1.968186	4.027829
C	-2.134171	1.671568	3.045502
C	-2.900364	0.623956	-2.802574
C	-2.172916	-0.539803	-2.453489
C	-2.922976	-1.726934	-2.269095
C	-4.305588	-1.743527	-2.443413
C	-5.006920	-0.591282	-2.800092
C	-4.282968	0.589010	-2.972677
H	-0.550631	-2.600531	-2.112163
H	0.927081	-1.693276	-2.392228
H	-0.511314	1.440351	-3.017696
H	0.947555	0.470984	-2.883071
H	-1.368101	-1.761273	1.614903
H	-2.064246	-1.314702	0.053864
H	-1.338384	2.284419	0.689877
H	-2.037320	1.202444	-0.512215
H	1.659501	-0.188189	3.128940
H	0.361781	0.486844	2.326566
H	1.671823	1.416361	2.782849
H	-3.548379	-1.156143	1.783730
H	1.884857	3.557596	0.713737
H	0.153307	3.834945	1.042232
H	1.083533	5.027651	0.122494
H	2.688493	3.000733	-1.630149
H	1.540631	2.971982	-2.988018
H	1.932277	4.508314	-2.193836
H	-1.615391	-3.782685	0.775564
H	-1.047199	-4.191670	-0.856719
H	-0.640565	-5.236081	0.508836
H	0.094456	-3.053986	2.587114
H	1.826342	-2.983197	2.166641
H	0.988392	-4.545628	2.254280
H	-5.189790	-0.647800	3.549168
H	-4.909450	1.358746	4.994036
H	-0.527055	4.946203	-1.770366
H	-0.950767	3.430505	-2.572655
H	-1.535236	3.758982	-0.928278
H	1.450407	-4.009633	-1.433814

H	1.819790	-5.073456	-0.064157
H	2.612669	-3.487274	-0.193169
H	-2.936306	2.845420	4.653578
H	-1.265889	2.311106	2.909391
H	-2.399745	1.575234	-2.925775
H	-2.440157	-2.647580	-1.969036
H	-4.836064	-2.679689	-2.290702
H	-6.083916	-0.610320	-2.930469
H	-4.795692	1.509213	-3.239608

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$Mo(NH_2)(CO)_3(P_2N_2$-tBuPh)

C	-0.164240	-0.167322	-2.517510
P	0.367163	-1.208506	-1.026573
Mo	2.232069	-0.041786	0.230723
P	0.289214	1.586035	0.288707
C	-0.224880	2.043808	-1.474956
N	-0.970588	0.981157	-2.131939
C	-1.244538	-1.351691	-0.069824
N	-1.279019	-0.559522	1.160993
C	-1.308684	0.887359	1.002330
C	3.637016	-1.461397	0.047032
O	4.445368	-2.290584	-0.072261
C	3.580989	1.070606	1.220796
O	4.358910	1.725887	1.785792
C	2.835220	0.788926	-1.511020
O	3.167120	1.271576	-2.523575
N	1.563594	-0.889994	2.020784
C	0.578367	-2.932522	-1.748778
C	0.419573	3.257272	1.144195
C	-2.022994	-1.113980	2.233745
C	-1.675834	-2.394178	2.709113
C	0.847710	3.016272	2.601290
C	1.513665	4.053557	0.411660
C	-0.710067	-3.455082	-2.405535
C	0.998904	-3.874825	-0.608360
C	-2.358396	-2.962738	3.780657
C	-3.391327	-2.264778	4.416210
C	-0.906652	4.034837	1.114923
C	1.705556	-2.850187	-2.792662
C	-3.733899	-0.993250	3.956638
C	-3.065725	-0.421844	2.870279
C	-3.133288	2.086674	-1.766571
C	-2.364544	0.993714	-2.233888
C	-3.076432	-0.084894	-2.811349
C	-4.464626	-0.053942	-2.929926
C	-5.207925	1.037173	-2.478805
C	-4.521067	2.101232	-1.893598
H	-0.681977	-0.769662	-3.261683
H	0.755669	0.196801	-2.984670
H	-0.782358	2.978433	-1.500920
H	0.702565	2.210299	-2.030866
H	-1.336220	-2.403885	0.200908
H	-2.094325	-1.109708	-0.722445
H	-1.378017	1.325084	2.001107
H	-2.173743	1.239060	0.422523
H	0.591865	-0.988234	2.294454
H	2.178471	-1.236216	2.751357
H	-0.847688	-2.923020	2.245666
H	1.793639	2.470920	2.650118
H	0.093222	2.448991	3.158864
H	0.975797	3.985201	3.100563
H	2.464358	3.511183	0.413740
H	1.233236	4.264929	-0.626931
H	1.663797	5.013398	0.921600
H	-1.539535	-3.512707	-1.692772
H	-1.023752	-2.833459	-3.251053
H	-0.530331	-4.466557	-2.791150
H	0.216830	-3.960824	0.155599
H	1.916369	-3.527387	-0.126135
H	1.176604	-4.876853	-1.019308
H	-2.068509	-3.948452	4.133976
H	-3.916155	-2.705793	5.258035
H	-0.771760	4.992549	1.633231
H	-1.232921	4.258243	0.093432
H	-1.710176	3.491412	1.623350
H	1.431917	-2.197776	-3.630364
H	1.898651	-3.852286	-3.195748
H	2.631298	-2.475037	-2.345442
H	-4.538528	-0.440339	4.433691
H	-3.368434	0.554623	2.508148
H	-2.661785	2.930646	-1.280534
H	-2.559525	-0.970173	-3.157755
H	-4.965652	-0.906790	-3.379827
H	-6.288909	1.052990	-2.570731
H	-5.066929	2.963182	-1.519430

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$Mo(NH_2)(CO)_3(P_2N_2$-tBuPh) Dimer

C	4.744867	1.417067	1.559704

P	2.935959	0.979124	1.260194
Mo	2.505002	0.420246	-1.140419
P	4.063727	-1.346867	-0.308474
C	5.614174	-0.633076	0.530257
N	5.642610	0.813724	0.601881
C	2.733653	-0.449593	2.495805
N	2.318983	-1.714883	1.889530
C	3.386867	-2.375776	1.115061
C	1.311300	1.912499	-1.647224
O	0.639864	2.812987	-1.998175
C	2.370272	-0.282136	-2.999917
O	2.336089	-0.691954	-4.092074
C	4.002139	1.574860	-1.730446
O	4.840971	2.283077	-2.131674
N	0.749357	-0.932718	-0.451122
C	2.058081	2.365536	2.194101
C	4.765586	-2.706385	-1.412301
C	1.624289	-2.628067	2.753065
C	1.575975	-2.487494	4.147384
C	3.587594	-3.468985	-2.044826
C	5.573950	-2.022697	-2.528305
C	2.612734	2.570252	3.612482
C	0.565208	2.005188	2.253384
C	0.838511	-3.392033	4.919521
C	0.154073	-4.449106	4.320312
C	5.660626	-3.682051	-0.631143
C	2.222802	3.660273	1.380215
C	0.207553	-4.595816	2.929964
C	0.934047	-3.695989	2.157785
C	7.530817	1.168624	-0.894899
C	6.851172	1.479544	0.297144
C	7.388089	2.467966	1.138127
C	8.570217	3.127033	0.790544
C	9.247452	2.802657	-0.384313
C	8.717719	1.815663	-1.222809
N	-0.585259	-0.336504	-0.338792
C	-5.453210	-1.176867	0.482042
P	-3.605508	-1.049804	0.871832
Mo	-2.279064	-1.703854	-1.145848
P	-3.613582	0.294686	-1.900606
C	-5.459737	-0.105600	-1.720306
N	-5.911749	-0.063569	-0.335925
C	-3.454653	0.752287	1.392538
N	-2.763484	1.634577	0.446236
C	-3.469270	1.832528	-0.838110
C	-1.479713	-3.365492	-0.422703
O	-1.094911	-4.411994	-0.051295
C	-3.720662	-2.860554	-1.802167
O	-4.605809	-3.541352	-2.167953
C	-1.308422	-1.953975	-2.872028
O	-0.772521	-2.107584	-3.898115
C	-3.398871	-1.912718	2.533610
C	-3.477947	1.000588	-3.639557
C	-2.347109	2.881296	1.019693
C	-2.727649	3.298973	2.305166
C	-2.005614	1.376007	-3.884139
C	-3.900098	-0.113224	-4.613660
C	-4.288047	-1.310082	3.632773
C	-1.916191	-1.790014	2.924865
C	-2.227179	4.490182	2.843025
C	-1.358459	5.295090	2.109141
C	-4.369345	2.237398	-3.842251
C	-3.757310	-3.394487	2.329559
C	-0.995833	4.894804	0.817488
C	-1.479750	3.707451	0.281536
C	-6.975916	2.135322	-0.597291
C	-6.598132	1.029323	0.201507
C	-6.949779	1.085289	1.571909
C	-7.648691	2.171328	2.095993
C	-8.024384	3.248654	1.293467
C	-7.674038	3.213184	-0.056724
H	5.006843	1.169714	2.605768
H	4.806806	2.501890	1.448312
H	5.689349	-1.078417	1.539057
H	6.481659	-0.976365	-0.033430
H	1.951213	-0.145618	3.191055
H	3.662956	-0.562262	3.081701
H	2.981898	-3.291096	0.683394
H	4.214426	-2.669751	1.783817
H	1.012021	-1.315740	0.466394
H	0.613041	-1.725100	-1.074955
H	2.117404	-1.688514	4.640974
H	2.945855	-2.802704	-2.626648
H	2.976377	-3.985355	-1.295434
H	3.985815	-4.233576	-2.723365
H	4.967717	-1.286044	-3.064124
H	6.466394	-1.523779	-2.135556
H	5.908130	-2.784654	-3.243392
H	2.518541	1.668404	4.227979
H	3.666702	2.866968	3.593639
H	2.047328	3.370332	4.106777
H	0.373954	1.115890	2.867572

H	0.171831	1.835241	1.248598
H	0.002007	2.837830	2.686518
H	0.812684	-3.266888	5.998527
H	-0.416931	-5.146785	4.925514
H	6.067796	-4.429923	-1.323105
H	6.506601	-3.171728	-0.157599
H	5.099735	-4.215633	0.143653
H	3.269849	3.979330	1.330298
H	1.644428	4.456188	1.863222
H	1.848789	3.538314	0.360800
H	-0.339003	-5.389020	2.430522
H	0.930830	-3.803944	1.080120
H	7.093497	0.454013	-1.582730
H	6.895504	2.714094	2.072723
H	8.966955	3.888719	1.456413
H	10.167597	3.314346	-0.649359
H	9.217695	1.566403	-2.154611
H	-0.725221	-0.062778	0.630429
H	-0.535771	0.543582	-0.845760
H	-6.054118	-1.268660	1.385489
H	-5.579255	-2.102531	-0.087714
H	-6.066909	0.548897	-2.342550
H	-5.593501	-1.122820	-2.098415
H	-2.850472	0.732554	2.302352
H	-4.444025	1.139173	1.671022
H	-2.890429	2.537410	-1.434375
H	-4.458112	2.279764	-0.672614
H	-3.421128	2.713464	2.895733
H	-1.647146	2.145219	-3.190859
H	-1.352412	0.503911	-3.799672
H	-1.904626	1.776424	-4.900779
H	-3.288068	-1.009904	-4.480989
H	-4.953991	-0.385717	-4.481015
H	-3.771010	0.243607	-5.643163
H	-4.067388	-0.252040	3.809315
H	-5.352941	-1.405031	3.393236
H	-4.112460	-1.848792	4.572643
H	-1.630829	-0.749338	3.125936
H	-1.270422	-2.189940	2.138744
H	-1.718604	-2.367897	3.834480
H	-2.535202	4.787441	3.841805
H	-0.973438	6.219281	2.529544
H	-4.243342	2.601039	-4.869649
H	-5.431742	2.008305	-3.703616
H	-4.100062	3.055214	-3.165801
H	-4.809865	-3.515166	2.046155
H	-3.596819	-3.935566	3.270777
H	-3.133931	-3.853042	1.557884
H	-0.310707	5.496768	0.228131
H	-1.138692	3.396357	-0.697674
H	-6.711802	2.179711	-1.645584
H	-6.665379	0.292906	2.251735
H	-7.894764	2.167443	3.154548
H	-8.564171	4.093401	1.708537
H	-7.939122	4.039281	-0.710953

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Mo(NH$_2$-TBHT)(CO)$_3$(P$_2$N$_2$-tBuPh)

C	2.284136	-1.106082	-2.329952
P	0.639717	-0.460800	-1.627689
Mo	-0.477575	-2.281203	-0.292982
P	1.710683	-1.870789	0.853986
C	3.162043	-2.194871	-0.320032
N	3.359072	-1.201554	-1.357001
C	1.184928	1.077033	-0.717567
N	2.129574	0.914046	0.396513
C	1.943151	-0.093516	1.423200
C	-2.131407	-2.362680	-1.391553
O	-3.063972	-2.438195	-2.095839
C	-1.087637	-3.819572	0.805315
O	-1.418236	-4.741793	1.448526
C	0.343643	-3.574765	-1.500458
O	0.864457	-4.358275	-2.205737
N	-1.424851	-0.935738	1.498988
C	-0.177831	0.263638	-3.171958
C	2.177739	-2.830643	2.412196
C	2.712252	2.128619	0.847973
C	3.356360	2.976240	-0.071658
C	1.046270	-2.628224	3.436082
C	2.248290	-4.314226	2.005697
C	0.629114	1.396188	-3.829642
C	-1.559431	0.806799	-2.783471
C	3.928756	4.172185	0.345743
C	3.888421	4.554971	1.691180
C	3.517766	-2.407742	3.035870
C	-0.338224	-0.906812	-4.160277
C	3.273725	3.710450	2.613636
C	2.688546	2.510199	2.200858
C	5.022585	0.007562	-0.020727
C	4.344664	-0.214571	-1.238276
C	4.729517	0.572064	-2.345251
C	5.744381	1.522202	-2.233638

C	6.411357	1.726609	-1.025209
C	6.036650	0.956191	0.076434
C	-2.416344	0.177565	1.500183
C	-2.225292	2.413492	0.375054
C	-3.069885	0.321827	2.973999
C	-3.509745	-0.150904	0.535679
C	-1.725541	1.466000	1.186108
C	-4.077214	0.735337	-0.300732
C	-3.965596	1.569190	3.052475
C	-1.963664	0.440933	4.040300
C	-3.937093	-0.908343	3.308725
C	-3.454942	2.093053	-0.431829
O	-3.909960	2.922729	-1.218943
C	-1.612524	3.817365	0.271493
C	-5.333160	0.409286	-1.118436
C	-5.038632	0.470404	-2.632872
C	-6.448227	1.419264	-0.758117
C	-5.867911	-0.997369	-0.797440
C	-2.677271	4.859347	0.689467
C	-1.128881	4.120770	-1.163613
C	-0.411175	3.985903	1.215476
H	2.582895	-0.476528	-3.163918
H	2.071663	-2.102623	-2.728257
H	4.093935	-2.348862	0.225642
H	2.897838	-3.143482	-0.800926
H	0.254932	1.563858	-0.394287
H	1.657259	1.734064	-1.446471
H	1.095337	0.129378	2.100316
H	2.837629	-0.059004	2.048317
H	-1.866187	-1.730118	1.953346
H	-0.662739	-0.677468	2.117878
H	3.462938	2.661850	-1.103022
H	0.086715	-2.958619	3.027093
H	0.965325	-1.576840	3.742201
H	1.256410	-3.220973	4.335347
H	1.316878	-4.646665	1.539700
H	3.073493	-4.496677	1.307755
H	2.424411	-4.923108	2.901481
H	0.642455	2.296902	-3.207568
H	1.663255	1.113667	-4.053531
H	0.146630	1.662411	-4.778236
H	-2.089285	1.131309	-3.687509
H	-2.167875	0.050074	-2.288188
H	-1.470062	1.671607	-2.123950
H	4.434346	4.798005	-0.384222
H	4.340335	5.488242	2.013181
H	3.757029	-3.092297	3.859338
H	4.343097	-2.456798	2.317729
H	3.480897	-1.396465	3.453866
H	0.631581	-1.283286	-4.505051
H	-0.894560	-0.553780	-5.037554
H	-0.893789	-1.734644	-3.710772
H	3.234716	3.984524	3.664479
H	2.195714	1.885672	2.937439
H	4.729443	-0.529786	0.872263
H	4.268551	0.424596	-3.314621
H	6.017691	2.099928	-3.112685
H	7.196131	2.471391	-0.941516
H	6.519448	1.109024	1.037586
H	-3.893043	-1.161182	0.607927
H	-0.821080	1.657918	1.754112
H	-4.491175	1.574842	4.013711
H	-4.711492	1.566596	2.252136
H	-3.381657	2.490085	2.974184
H	-2.428925	0.602256	5.018562
H	-1.297954	1.288416	3.845528
H	-1.362035	-0.472489	4.115001
H	-4.277787	-0.828783	4.346731
H	-3.391669	-1.856262	3.223142
H	-4.820245	-0.962198	2.665861
H	-5.967882	0.281015	-3.183800
H	-4.314247	-0.301469	-2.908383
H	-4.654734	1.450658	-2.920026
H	-7.360324	1.151533	-1.304588
H	-6.165642	2.438650	-1.022531
H	-6.672708	1.376022	0.315413
H	-6.779933	-1.166366	-1.379484
H	-6.123762	-1.093895	0.265379
H	-5.146866	-1.774473	-1.064459
H	-2.223864	5.857538	0.673980
H	-3.025991	4.660603	1.710481
H	-3.532286	4.847902	0.013207
H	-0.306342	3.452868	-1.441942
H	-1.939849	4.013323	-1.884921
H	-0.751217	5.149274	-1.203061
H	-0.026277	5.006481	1.123730
H	0.408624	3.306095	0.973758
H	-0.696847	3.825703	2.262330

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$Mo(NH)(CO)_3(P_2N_2$-tBuPh)

C	0.057121	1.216962	2.058456
P	0.574495	1.522301	0.264868
Mo	2.403610	0.000000	-0.516487
P	0.574494	-1.522301	0.264869
C	0.057121	-1.216962	2.058457
N	-0.721867	0.000000	2.231652
C	-1.016101	1.312675	-0.672812
N	-1.610466	0.000000	-0.891383
C	-1.016101	-1.312675	-0.672812
C	3.818561	1.358690	-1.053953
O	4.650680	2.114546	-1.336299
C	3.818560	-1.358691	-1.053954
O	4.650679	-2.114547	-1.336301
C	3.125065	0.000000	1.459787
O	3.396471	0.000001	2.590996
N	1.602922	0.000001	-2.292283
C	0.801491	3.392643	0.173848
C	0.801491	-3.392643	0.173848
C	-2.889901	0.000000	-1.468669
C	-3.566058	1.205981	-1.772886
C	1.208404	-3.776099	-1.259042
C	1.948945	-3.728430	1.143886
C	-0.461508	4.176119	0.569569
C	1.208405	3.776099	-1.259042
C	-4.858438	1.196456	-2.293289
C	-5.527543	0.000000	-2.549919
C	-0.461508	-4.176119	0.569570
C	1.948945	3.728431	1.143886
C	-4.858438	-1.196457	-2.293289
C	-3.566058	-1.205981	-1.772886
C	-2.854439	-1.203498	2.000535
C	-2.119850	0.000000	2.069075
C	-2.854438	1.203498	2.000533
C	-4.237325	1.195716	1.828449
C	-4.947512	0.000001	1.732757
C	-4.237325	-1.195715	1.828451
H	-0.476063	2.074715	2.466532
H	0.982031	1.113641	2.633488
H	-0.476063	-2.074714	2.466532
H	0.982031	-1.113641	2.633489
H	-0.828287	1.811735	-1.636094
H	-1.746937	1.919071	-0.131773
H	-0.828287	-1.811736	-1.636093
H	-1.746938	-1.919071	-0.131772
H	0.570086	0.000000	-2.347026
H	-3.095410	2.166044	-1.613137
H	2.091843	-3.224988	-1.588591
H	0.399218	-3.587056	-1.972517
H	1.436580	-4.849114	-1.285264
H	2.861281	-3.182073	0.883146
H	1.684315	-3.496850	2.182455
H	2.165483	-4.801881	1.083389
H	-1.281535	4.007925	-0.135517
H	-0.811363	3.928605	1.577340
H	-0.228495	5.247948	0.556817
H	0.399220	3.587055	-1.972518
H	2.091845	3.224989	-1.588590
H	1.436579	4.849114	-1.285265
H	-5.340773	2.147314	-2.503841
H	-6.534674	-0.000001	-2.954729
H	-0.228494	-5.247948	0.556817
H	-0.811361	-3.928607	1.577343
H	-1.281535	-4.007925	-0.135515
H	1.684314	3.496851	2.182455
H	2.165483	4.801881	1.083388
H	2.861280	3.182073	0.883147
H	-5.340772	-2.147315	-2.503841
H	-3.095410	-2.166045	-1.613136
H	-2.357303	-2.163139	2.053043
H	-2.357302	2.163140	2.053040
H	-4.758168	2.146490	1.759015
H	-6.020858	0.000001	1.576778
H	-4.758169	-2.146489	1.759018

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Mo(N)(CO)$_3$(P$_2$N$_2$-tBuPh)

C	-0.935255	1.309985	0.621738
P	0.593708	1.540493	-0.408140
Mo	2.527904	-0.000002	0.108220
P	0.593705	-1.540500	-0.408135
C	-0.935259	-1.309986	0.621741
N	-1.538639	0.000001	0.824391
C	0.029800	1.216965	-2.179981
N	-0.755051	-0.000006	-2.318445
C	0.029797	-1.216979	-2.179976
C	3.914471	1.397187	0.668084
O	4.703654	2.173894	1.009417
C	3.914473	-1.397186	0.668103
O	4.703660	-2.173885	1.009440
C	1.757683	0.000015	2.267977
O	1.482711	0.000035	3.391026

N	2.964537	-0.000016	-1.617173
C	0.812114	3.410437	-0.331048
C	0.812109	-3.410444	-0.331035
C	-2.141476	-0.000004	-2.087253
C	-2.870739	1.204020	-1.980600
C	1.884848	-3.755857	-1.380932
C	1.313352	-3.799296	1.069702
C	-0.484226	4.178998	-0.638630
C	1.884856	3.755845	-1.380944
C	-4.243420	1.196032	-1.740658
C	-4.948103	0.000001	-1.611250
C	-0.484234	-4.179004	-0.638612
C	1.313355	3.799294	1.069689
C	-4.243424	-1.196032	-1.740656
C	-2.870743	-1.204025	-1.980598
C	-3.445081	-1.205332	1.813199
C	-2.784978	0.000004	1.471762
C	-3.445076	1.205342	1.813198
C	-4.710125	1.196025	2.396838
C	-5.366491	0.000009	2.685682
C	-4.710130	-1.196009	2.396838
H	-1.687990	1.939082	0.141027
H	-0.690382	1.778876	1.588884
H	-1.687995	-1.939082	0.141031
H	-0.690389	-1.778876	1.588889
H	0.960475	1.091266	-2.741291
H	-0.504191	2.072705	-2.593161
H	0.960473	-1.091284	-2.741286
H	-0.504196	-2.072719	-2.593154
H	-2.374637	2.162548	-2.056468
H	2.805039	-3.187180	-1.215110
H	1.532183	-3.551214	-2.398097
H	2.117804	-4.825559	-1.312326
H	2.250447	-3.293764	1.315090
H	0.574412	-3.566164	1.844569
H	1.494165	-4.881200	1.093748
H	-0.913632	3.900792	-1.606867
H	-1.242574	4.025985	0.135829
H	-0.257705	5.251740	-0.673741
H	1.532193	3.551197	-2.398110
H	2.805047	3.187169	-1.215117
H	2.117811	4.825548	-1.312344
H	-4.760663	2.146546	-1.644692
H	-6.012558	0.000003	-1.402904
H	-0.257714	-5.251747	-0.673719
H	-1.242579	-4.025986	0.135848
H	-0.913641	-3.900800	-1.606849
H	0.574413	3.566168	1.844555
H	1.494171	4.881198	1.093730
H	2.250449	3.293762	1.315081
H	-4.760670	-2.146544	-1.644688
H	-2.374644	-2.162554	-2.056464
H	-2.983875	-2.166427	1.634066
H	-2.983865	2.166435	1.634066
H	-5.180351	2.147155	2.632150
H	-6.352366	0.000012	3.139802
H	-5.180361	-2.147137	2.632150

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$Mo(NH_2NH_2)(CO)_3(P_2N_2\text{-}tBuPh)$

C	-0.238136	-2.266138	-1.253731
P	0.280045	-1.612254	0.446917
Mo	2.239027	-0.050186	0.179790
P	0.433575	1.018728	-1.193303
C	-0.138406	-0.190247	-2.538020
N	-0.966579	-1.269332	-2.022594
C	-1.316864	-0.803050	1.034812
N	-1.226293	0.660329	1.080049
C	-1.152011	1.338296	-0.233820
C	3.465443	-1.058028	1.377364
O	4.163134	-1.669063	2.091427
C	3.638383	1.305261	-0.210997
O	4.445460	2.116374	-0.462494
C	2.843376	-1.100771	-1.361838
O	3.159265	-1.735327	-2.300219
N	1.441001	1.186745	2.002299
C	0.347790	-3.172358	1.501578
C	0.645382	2.615573	-2.174064
C	-2.158727	1.298318	1.964090
C	-3.348448	0.690421	2.385012
C	1.186455	3.705337	-1.235177
C	1.686757	2.329338	-3.271167
C	-0.992299	-3.925742	1.529090
C	0.738963	-2.765912	2.932189
C	-4.198958	1.356063	3.273657
C	-3.882812	2.632988	3.736672
C	-0.672671	3.090924	-2.808000
C	1.445361	-4.070139	0.903734
C	-2.698144	3.244264	3.309476
C	-1.837759	2.582814	2.436892
C	-3.052275	-0.203859	-2.759521
C	-2.359929	-1.255569	-2.112203

C	-3.150565	-2.293215	-1.561032
C	-4.539822	-2.280090	-1.670922
C	-5.207269	-1.242858	-2.323304
C	-4.442022	-0.207394	-2.860999
N	1.546253	2.622202	1.896647
H	-0.810800	-3.188071	-1.172438
H	0.687700	-2.506984	-1.784017
H	-0.643296	0.324008	-3.354246
H	0.776721	-0.625486	-2.950618
H	-1.465062	-1.144762	2.063182
H	-2.172282	-1.155902	0.445643
H	-1.154520	2.412901	-0.042505
H	-2.035796	1.103288	-0.841967
H	0.437589	0.971503	2.009571
H	-3.618837	-0.292291	2.014534
H	2.177757	3.436351	-0.863350
H	0.533153	3.870615	-0.372550
H	1.271352	4.645697	-1.795390
H	2.622314	1.960603	-2.838056
H	1.322303	1.592231	-3.995730
H	1.900246	3.258151	-3.815106
H	-1.800419	-3.311567	1.940776
H	-1.293363	-4.269514	0.534002
H	-0.890904	-4.813796	2.165685
H	-0.012450	-2.108488	3.387613
H	1.708918	-2.261597	2.946029
H	0.811778	-3.666578	3.554977
H	-5.118165	0.872735	3.592929
H	-4.547782	3.146826	4.424373
H	-0.483454	4.009453	-3.377827
H	-1.088814	2.354483	-3.503522
H	-1.431423	3.318414	-2.051794
H	1.189547	-4.395043	-0.111576
H	1.556971	-4.967019	1.526188
H	2.406986	-3.549452	0.870956
H	-2.436755	4.235343	3.670420
H	-0.900847	3.034847	2.119733
H	-2.517174	0.641316	-3.171284
H	-2.693608	-3.114617	-1.024970
H	-5.102334	-3.099721	-1.231709
H	-6.289425	-1.236970	-2.402084
H	-4.926910	0.623910	-3.365683
H	1.620005	3.034552	2.825770
H	1.892581	0.832308	2.842635
H	2.406723	2.818177	1.392879

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$Mo(NH_2NH_3)(CO)_3(P_2N_2\text{-}tBuPh)$

C	-0.197436	0.505684	2.519518
P	0.340974	1.348047	0.912062
Mo	2.240277	0.066584	-0.118331
P	0.377261	-1.606777	-0.020742
C	-0.172045	-1.824414	1.786253
N	-0.963145	-0.706202	2.275482
C	-1.254060	1.307023	-0.092160
N	-1.242301	0.352681	-1.228415
C	-1.231812	-1.066894	-0.836972
C	3.560860	1.563501	-0.038554
O	4.318987	2.445001	0.084893
C	3.569395	-1.183281	-0.918966
O	4.339320	-1.967150	-1.322938
C	2.843869	-0.517371	1.650285
O	3.168423	-0.860751	2.726702
N	1.398545	0.896027	-2.119036
C	0.458278	3.166200	1.393068
C	0.536144	-3.400250	-0.590993
C	-2.241728	0.689392	-2.207185
C	-2.069661	1.877265	-2.938123
C	0.994351	-3.418486	-2.057269
C	1.618713	-4.050217	0.289954
C	-0.869688	3.724390	1.930334
C	0.887223	3.957781	0.146430
C	-2.993927	2.253724	-3.908734
C	-4.099361	1.440737	-4.181475
C	-0.785128	-4.178064	-0.465309
C	1.551228	3.274258	2.471427
C	-4.269580	0.256483	-3.465269
C	-3.353535	-0.117686	-2.476448
C	-3.086668	-1.912623	2.019208
C	-2.357676	-0.742753	2.343945
C	-3.112429	0.388083	2.739237
C	-4.502782	0.337567	2.819647
C	-5.206710	-0.826314	2.508738
C	-4.477275	-1.945317	2.105622
N	2.071903	0.362944	-3.291226
H	-0.745305	1.187145	3.168144
H	0.726187	0.235064	3.039907
H	-0.701143	-2.763271	1.937480
H	0.749900	-1.878122	2.372027
H	-1.366110	2.308815	-0.510498
H	-2.121810	1.124319	0.553455
H	-1.306338	-1.650980	-1.758710

H	-2.093550	-1.323085	-0.207382
H	1.510590	1.914674	-2.194356
H	0.387930	0.657111	-2.164679
H	-1.200618	2.499168	-2.739358
H	1.960710	-2.919636	-2.173398
H	0.264750	-2.933253	-2.717914
H	1.104891	-4.459635	-2.388365
H	2.564997	-3.505428	0.219083
H	1.314428	-4.087250	1.342187
H	1.786509	-5.080598	-0.047822
H	-1.673491	3.661401	1.188929
H	-1.196522	3.205678	2.837874
H	-0.735904	4.782538	2.188156
H	0.142539	3.888130	-0.657388
H	1.851030	3.604324	-0.231983
H	0.991096	5.018574	0.407577
H	-2.841933	3.174783	-4.464201
H	-4.815614	1.728011	-4.945223
H	-0.627469	-5.207086	-0.811842
H	-1.139648	-4.233180	0.568991
H	-1.578616	-3.738733	-1.079466
H	1.273382	2.728563	3.380790
H	1.688176	4.329086	2.741136
H	2.506455	2.884226	2.108066
H	-5.126025	-0.381728	-3.663441
H	-3.515572	-1.030491	-1.915152
H	-2.580025	-2.805593	1.677913
H	-2.626720	1.327390	2.968563
H	-5.037080	1.232590	3.126706
H	-6.289558	-0.857342	2.569715
H	-4.991202	-2.867057	1.846150
H	1.674205	0.762082	-4.186364
H	1.953924	-0.677002	-3.249957
H	3.093199	0.604729	-3.179396

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Mo(NHNH$_3$)(CO)$_3$(P$_2$N$_2$-tBuPh)

C	-0.705142	-1.963517	1.621728
P	0.186689	-0.292994	1.617032
Mo	2.089744	-0.350422	-0.029973
P	0.043037	-0.817000	-1.434461
C	-0.808583	-2.382081	-0.787158
N	-1.544767	-2.146118	0.445893
C	-1.192984	0.896869	1.129994
N	-1.092208	1.417377	-0.232174
C	-1.335562	0.468535	-1.304667
C	3.528207	-0.044967	1.299366
O	4.368073	0.135642	2.101713
C	3.364782	-0.383610	-1.542890
O	4.100564	-0.397299	-2.462636
C	2.327199	-2.296210	0.208345
O	2.434423	-3.456809	0.362717
N	1.760655	1.909395	-0.125874
C	0.420869	0.077725	3.446581
C	0.126674	-1.127599	-3.291840
C	-1.396471	2.778216	-0.440930
C	-0.764947	3.755722	0.357683
C	0.799357	0.088346	-3.950910
C	1.002124	-2.374987	-3.504182
C	-0.911876	0.129373	4.211339
C	1.139551	1.432296	3.562889
C	-1.024897	5.108808	0.160007
C	-1.900211	5.530863	-0.847521
C	-1.262197	-1.344858	-3.914940
C	1.315517	-1.032851	4.024272
C	-2.519322	4.570869	-1.648042
C	-2.282939	3.208746	-1.444845
C	-3.715211	-2.063725	-0.699423
C	-2.925769	-1.946799	0.470592
C	-3.607762	-1.619958	1.667970
C	-4.990363	-1.447537	1.688773
C	-5.757052	-1.582182	0.530787
C	-5.096935	-1.887707	-0.660012
N	3.053082	2.505975	-0.493109
H	-1.279600	-2.121740	2.533346
H	0.083365	-2.722294	1.601907
H	-1.453671	-2.831129	-1.540323
H	-0.009143	-3.099342	-0.580596
H	-1.126967	1.735321	1.823058
H	-2.168653	0.418685	1.289041
H	-1.296930	1.010555	-2.251823
H	-2.319857	-0.014598	-1.236756
H	1.142828	2.209984	-0.878061
H	-0.031923	3.432352	1.088482
H	1.805090	0.242115	-3.551742
H	0.214108	1.005251	-3.806677
H	0.880244	-0.087567	-5.031354
H	1.992562	-2.241318	-3.059056
H	0.541020	-3.267959	-3.066432
H	1.124554	-2.552322	-4.580454
H	-1.580070	0.903283	3.818829
H	-1.440170	-0.829809	4.182050

H	-0.713029	0.362319	5.265360
H	0.527488	2.250898	3.166679
H	2.087872	1.418089	3.019861
H	1.340790	1.641657	4.621650
H	-0.524577	5.842487	0.787253
H	-2.094261	6.587765	-1.003293
H	-1.150162	-1.505736	-4.994840
H	-1.766107	-2.225837	-3.503820
H	-1.915340	-0.476993	-3.772925
H	0.826091	-2.012427	3.968601
H	1.519587	-0.818617	5.081282
H	2.269744	-1.089035	3.492179
H	-3.211726	4.876190	-2.428100
H	-2.810874	2.480700	-2.051290
H	-3.259307	-2.274891	-1.657683
H	-3.065564	-1.474454	2.592946
H	-5.467209	-1.196378	2.632472
H	-6.832876	-1.442610	0.553463
H	-5.658896	-1.988313	-1.584808
H	3.033064	3.533077	-0.544082
H	3.460135	2.123084	-1.362078
H	3.695063	2.221841	0.252750

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