

Supporting Information

Activation of Molecular Oxygen by a Molybdenum(IV) Imido Compound

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Experimental data and synthetic procedures.

General. Unless specified otherwise, all experiments were performed under inert conditions using standard Schlenk equipment. Commercially available chemicals were purchased from Sigma–Aldrich and used as received. No further purification or drying operations have been performed. The metal precursor $[\text{MoO}(\text{N}t\text{Bu})\text{Cl}_2(\text{dme})]^{1-3}$ was synthesized according to known procedures. Solvents were purified via a Pure–Solv MD–4–EN solvent purification system from Innovative Technology, Inc. Methanol was refluxed over activated magnesium for at least 24 h and then distilled prior to use. The ^1H , ^{13}C , ^{31}P and HSQC NMR spectra were recorded on a Bruker Optics instrument at 300/75/121 MHz. Peaks are denoted as singlet (s), broad singlet (bs), doublet (d), doublet of doublets (dd), triplet (t), pseudo–doublet (“d”), pseudo–triplet (“t”) and multiplet (m). Used solvents and peak assignment are mentioned at the specific data sets. ESI-MS measurements were performed at the University of Graz, Department of Analytical Chemistry using an Agilent 1100 Series LCMSD (SL type) mass spectrometer in positive ion mode, the used solvent was acetonitrile. Peaks are denoted as cationic mass peaks, and the unit is the according ions mass/charge ratio. Samples for infrared spectroscopy were measured on a Bruker Optics ALPHA FT–IR Spectrometer. IR bands are reported with wavenumber (cm^{-1}) and intensities (s, strong; m, medium; w, weak). All elemental analyses were measured at the Technical University of Graz, Institute of Inorganic Chemistry using a Heraeus Vario Elementar automatic analyzer.

Ligand Synthesis. Ligands **HL1**⁴ and **HL2**⁵ were synthesized according to known procedures. They are stable towards air and moisture and can be stored at ambient conditions for several weeks without decomposition. Proton NMR data in C_6D_6 is subsequently given for comparison reasons.

(E)-2,4-dimethyl-6-((phenylimino)methyl)phenol (HL1).

^1H -NMR (300 MHz, C_6D_6 , 25 °C) δ : 13.53 (bs, 1H, OH), 8.10 (s, 1H, CH=N), 7.13-6.90 (m, 5H, ArH), 6.86 (m, 1H, ArH), 6.65 (m, 1H, ArH), 2.39 (s, 3H, Me), 2.12 (s, 3H, Me) ppm.

(E)-2,4-di-tert-butyl-6-((phenylimino)methyl)phenol (HL2).

^1H NMR (300 MHz, C_6D_6 , 25 °C) δ : 14.14 (bs, 1H, OH), 8.08 (s, 1H, CH=N), 7.64 (d, 1H, ArH), 7.11-6.90 (m, 6H, ArH), 1.68 (s, 9H, *t*Bu), 1.34 (s, 9H, *t*Bu) ppm;

Complex Syntheses. The Mo(VI) complexes **1a**, **1b** and **3a** are sensitive towards moisture, the Mo(IV) complexes **2a** and **2b** are very sensitive towards moisture and air. All complexes can be stored at ambient temperature in a N_2 -filled glovebox for several weeks without decomposition.

Synthesis of [MoO(N*t*Bu)(L1)₂] (1a). For the synthesis of **1a**, a solution of 1 equiv of [MoO(N*t*Bu)Cl₂(dme)] (500 mg, 1.45 mmol) in 5 mL MeCN was added dropwise to a solution of 2 equiv **HL1** (655 mg, 2.90 mmol) and 2.2 equiv NEt₃ (0.45 mL, 3.19 mmol) in 5 mL MeCN with stirring. The addition was accompanied by an immediate color change from bright yellow to deep red. After 15 min of stirring at room temperature, a yellow precipitate started to form and the reaction mixture was left to stir for another 8 h. Subsequently, the precipitate was filtered off and washed with a small amount of cold MeCN. After addition of ~5 mL of THF and filtration of the resulting suspension to remove formed NEt₃·HCl, the filtrate was evaporated *in vacuo* to obtain **1a** as a dark yellow solid (582 mg, 63 %). Single crystals suitable for X-ray diffraction analysis were obtained via crystallization from a saturated MeCN solution of **1a** at -35 °C.

¹H NMR (C₆D₆, 25 °C, major isomer) δ: 7.75 (s, 1H, CH=N), 7.70 (s, 1H, CH=N), 7.43-7.37 (m, 2H, ArH), 7.12-6.73 (m, 10H, ArH), 6.44 (s, 1H, ArH), 6.38 (s, 1H, ArH), 2.20 (s, 3H, Me), 2.11 (s, 3H, Me), 2.02 (s, 3H, Me), 1.99 (s, 3H, Me), 1.31 (s, 9H, *Nt*Bu) ppm;

¹³C NMR (C₆D₆, 25 °C, major isomer, 2 Ar obscured) δ: 166.81, 166.73 (C=N), 163.78, 160.17 (Ar-O), 153.59, 153.39, 136.81, 136.58, 132.60, 131.35, 129.29, 127.92, 126.45, 126.26, 125.75, 125.46, 123.92, 123.26, 121.02, 120.33 (Ar), 71.85 (imido-*q-t*Bu), 29.74 (*t*Bu), 29.39, 20.28, 16.78, 16.57 (Me) ppm;

IR (ATR) $\tilde{\nu}$: 1618 s (C=N), 878 s (Mo=O) cm⁻¹;

Anal. Calcd. for C₃₄H₃₇MoN₃O₃: C, 64.65; H, 5.90; N, 6.65; Found: C, 64.29; H, 5.74; N, 6.34.

Synthesis of [MoO(N*t*Bu)(L2)₂] (1b). For the synthesis of **1b**, a solution of 1 equiv of [MoO(N*t*Bu)Cl₂(dme)] (200 mg, 0.58 mmol) in 5 mL toluene was added dropwise to a solution of 2 equiv **HL2** (359 mg, 1.16 mmol) and 2.1 equiv NEt₃ (0.17 mL, 1.28 mmol) in 5 mL toluene with stirring. The addition was accompanied by an immediate color change from bright yellow to deep red. The reaction mixture was stirred overnight and subsequently the formed NEt₃·HCl was filtered off and the residual deep red filtrate was evaporated *in vacuo*. Then 2 mL of pentane were added and the initially red solution was stored at -35 °C overnight. The formed precipitate was washed twice with little cold MeCN to obtain **1b** as yellow microcrystalline solid (238 mg, 65 %). Single crystals suitable for X-ray diffraction analysis were obtained via crystallization from a saturated MeCN solution of **1b** at -35 °C.

¹H NMR (C₆D₆, 25 °C, major isomer) δ: 7.96 (s, 1H, CH=N), 7.94 (s, 1H, CH=N), 7.58 (dd, 2H, ArH), 7.26-7.20 (m, 2H, ArH), 7.14-6.73 (m, 10H, ArH), 1.38 (s, 9H, *t*Bu), 1.34 (s, 9H, *t*Bu), 1.30 (s, 9H, *t*Bu), 1.27 (s, 9H, *t*Bu), 1.20 (s, 9H, *t*Bu) ppm; ¹H NMR (C₆D₆, 25 °C, minor isomer) δ: 7.73 (d, 1H, ArH), 7.71 (d, 1H, ArH), 7.69 (s, 1H, CH=N), 7.65 (s, 1H, CH=N), 7.14-6.73 (m, 12H, ArH), 1.72 (s, 9H, *t*Bu), 1.61 (s, 9H, *t*Bu), 1.34 (s, 9H, *t*Bu), 1.28 (s, 9H, *t*Bu), 1.27 (s, 9H, *t*Bu) ppm;

^{13}C NMR (C_6D_6 , 25 °C, 2 isomers, 3 Ar obscured) δ : 170.26, 169.09, 168.29 (C=N), 166.85 (Ar-O), 165.96 (C=N), 165.64, 162.22, 161.53 (Ar-O), 155.27, 154.31, 153.79, 153.70, 140.42, 140.25, 139.87, 139.63, 139.44, 139.23, 137.99, 131.26, 130.10, 130.00, 129.90, 129.72, 129.54, 128.85, 128.66, 128.53, 128.50, 127.68, 126.47, 125.79, 125.73, 125.56, 123.93, 123.60, 123.32, 122.93, 121.89, 121.74, 120.28 (Ar), 72.92, 72.12 (imido-*q-t*Bu), 35.90, 35.65, 35.63, 35.48 (*q-t*Bu), 34.27 (2x, *q-t*Bu), 34.21 (2x, *q-t*Bu), 31.65 (2x, *t*Bu), 31.61 (2x, *t*Bu), 30.32, 30.27 (*t*Bu), 30.00 (4x, *t*Bu) ppm;

IR (ATR) $\tilde{\nu}$: 1611 s (C=N), 890 s (Mo=O) cm^{-1} ;

Anal. Calcd. for $\text{C}_{46}\text{H}_{61}\text{MoN}_3\text{O}_3$: C, 69.07; H, 7.69; N, 5.25; Found: C, 69.45; H, 7.52; N, 5.31.

Synthesis of $[\text{Mo}(\text{PMe}_3)(\text{N}t\text{Bu})(\text{L1})_2]$ (2a**).** For the synthesis of **2a**, 5 equiv PMe_3 (0.12 mL, 1.15 mmol) were added dropwise to a solution of 1 equiv of **1a** (150 mg, 0.23 mmol) in 10 mL toluene. The addition was accompanied by an immediate color change from bright yellow to deep blue-purple. After 4 h of stirring at room temperature, the solvent was evaporated *in vacuo* to obtain a dark blue-purple solid. The crude product was washed five times with cold pentane (~ 5 mL each) and subsequently dissolved in toluene and filtered over a pad of celite. The filtrate was then evaporated *in vacuo* to obtain **2a** as a purple solid (83 mg, 52 %).

^1H NMR (C_6D_6 , 25 °C) δ : 7.94 (s, 1H, CH=N), 7.84 (s, 1H, CH=N), 7.82-7.76 (m, 2H, ArH), 7.71-7.65 (m, 2H, ArH), 7.21-7.03 (m, 5H, ArH), 6.99-6.92 (m, 2H, ArH), 6.83 (s, 2H, ArH), 6.63 (s, 1H, ArH), 2.39 (s, 3H, Me), 2.30 (s, 3H, Me), 2.23 (s, 3H, Me), 2.13 (s, 3H, Me), 0.95 (s, 9H, *t*Bu), 0.50 (d, 9H, PMe_3) ppm;

^{13}C NMR (C_6D_6 , 25 °C) δ : 168.24, 167.84 (C=N), 162.88, 161.36 (Ar-O), 161.26, 159.59, 137.83, 134.72, 134.13, 132.71, 130.38, 130.35, 128.71, 128.60, 125.55, 125.29, 124.94, 124.16, 122.49, 121.47, 120.14, 119.06 (Ar), 68.58 (d, imido-*q-t*Bu), 30.44 (d, *t*Bu), 20.76, 20.35, 18.68, 18.21 (Me), 17.43 (d, PMe_3) ppm;

$^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 25 °C) δ : 5.35 ppm;

Anal. calcd for $\text{C}_{37}\text{H}_{46}\text{MoN}_3\text{O}_2\text{P}$: C, 64.25; H, 6.70; N, 6.07. Found: C, 64.18; H, 6.36; N, 5.88;

Synthesis of $[\text{Mo}(\text{PMe}_3)(\text{N}t\text{Bu})(\text{L2})_2]$ (2b**).** For the synthesis of **2b**, 5 equiv PMe_3 (0.04 mL, 0.40 mmol) was added dropwise to a solution of 1 equiv of **1b** (60 mg, 0.08 mmol) in 5 mL toluene. The addition was accompanied by an immediate color change from orange-yellow to deep blue. After stirring overnight at room temperature, the solvent was evaporated *in vacuo* to obtain a dark blue solid. The crude product was subsequently dissolved in a small portion of cold heptane and filtered over a pad of celite. The filtrate was then evaporated *in vacuo* to obtain **2b** as a dark blue solid (48 mg, 74 %).

^1H NMR (C_6D_6 , 25 °C, major isomer) δ : 7.88 (d, 1H, CH=N), 7.77 (d, 1H, ArH), 7.52 (d, 1H, ArH), 7.29 (s, 1H, CH=N), 7.23-6.83 (m, 8H, ArH), 6.68-6.60 (m, 2H, ArH), 6.41-6.31 (m, 2H, ArH), 1.84 (s, 9H, *t*Bu), 1.69 (s,

¹H NMR (C₆D₆, 25 °C, minor isomer) δ: 8.15 (s, 1H, CH=N), 7.98 (s, 1H, CH=N), 7.72-7.66 (m, 2H, ArH), 7.60-7.55 (m, 2H, ArH), 7.54 (d, 1H, ArH), 7.42 (d, 1H, ArH), 7.23-6.83 (m, 8H, ArH), 1.48 (s, 9H, *t*Bu), 1.42 (s, 9H, *t*Bu), 1.37 (s, 9H, *t*Bu), 1.30 (s, 9H, *t*Bu), 1.00 (s, 9H, *t*Bu), 0.64 (d, 9H, PMe₃) ppm;

¹³C NMR (C₆D₆, 25 °C, 2 isomers) δ: 170.79, 170.52, 168.16, 167.62 (C=N), 162.65, 161.94, 161.67, 161.65, 161.42, 161.40, 161.14, 157.10, 154.41, 140.68, 140.65, 140.04, 139.44, 138.89, 136.58, 135.83, 134.63, 134.43, 131.54, 131.47, 130.65, 130.55, 130.07, 128.88, 128.54, 127.85, 126.96, 126.32, 125.72, 125.29, 125.09, 124.91, 124.80, 124.04, 123.73, 122.91, 122.90, 122.40, 120.51, 120.14 (Ar), 69.09, 68.58 (d, imido-*q-t*Bu), 36.23, 36.03, 35.81, 35.74, 34.49, 34.25, 33.98, 33.94 (*q-t*Bu), 32.04, 31.93, 31.71 (2x), 30.59, 30.54, 30.52, 30.23, 30.22, 30.08 (*t*Bu), 17.12, 16.30 (d, PMe₃) ppm;

³¹P {¹H} NMR (C₆D₆, 25 °C, 2 isomers) δ: 0.95, 0.64 ppm;

Anal. Calcd. for C₄₉H₇₀MoN₃O₂P: C, 68.43; H, 8.20; N, 4.89. Found: C, 69.12; H, 7.95; N, 4.88;

Synthesis of [Mo(η²-O₂)(*Nt*Bu)(L2)] (3a). For the synthesis of **3a**, 1 equiv of **2a** (75 mg, 0.10 mmol) was dissolved in 15 mL of dry toluene. After addition of activated molecular sieves (4 Å), the reaction vessel was subjected to three freeze-pump-thaw cycles and backfilled with dry O₂ gas (1.5 atm). The solution was subsequently stirred under O₂ atmosphere for 4 h, the reaction progress was indicated by a gradual color change from blue-purple to bright yellow. The reaction mixture was then filtered and evaporated *in vacuo*. After removal of residual OPMe₃ via dissolution of the residual yellow solid in little cold toluene and filtration over a pad of celite, **3a** was obtained as a dull yellow solid (42 mg, 65 %). Single crystals suitable for X-ray diffraction analysis were obtained via crystallization from a saturated MeCN solution of **3a** at -35 °C.

¹H NMR (C₆D₆, 25 °C) δ: 8.04-7.99 (m, 2H, ArH), 7.99 (s, 1H, CH=N), 7.93 (s, 1H, CH=N), 7.81-7.75 (m, 2H, ArH), 7.37-7.30 (m, 2H, ArH), 7.23-7.08 (m, 3H, ArH), 7.05-6.96 (m, 1H, ArH), 6.85 (d, 1H, ArH), 6.76 (d, 1H, ArH), 6.59 (d, 1H, ArH), 6.43 (d, 1H, ArH), 2.11 (s, 3H, Me), 2.07 (s, 3H, Me), 2.04 (s, 3H, Me), 1.97 (s, 3H, Me), 0.55 (s, 9H, *t*Bu) ppm;

¹³C NMR (C₆D₆, 25 °C) δ: 168.17, 167.99 (C=N), 164.46, 163.22 (Ar-O), 158.56, 152.41, 138.87, 138.74, 133.08, 131.95, 129.80, 129.09, 129.07, 128.57, 127.13, 126.87, 125.71, 124.79, 124.59, 123.68, 120.50, 119.20 (Ar), 71.02 (imido-*q-t*Bu), 28.28 (*t*Bu), 20.32, 20.18, 17.50, 16.89 (Me) ppm;

IR (ATR) $\tilde{\nu}$: 1617 s (C=N), 924 s (O-O), 523 s (Mo-O) cm⁻¹;

HR-MS: (ESI⁺) *m/z* [M+Na]⁺ calcd. for C₃₄H₃₇MoN₃O₄Na: 672.1738, found: 672.1739;

Anal. calcd for C₃₄H₃₇MoN₃O₄: C, 63.06; H, 5.76; N, 6.49. Found: C, 63.16; H, 5.68; N, 6.51;

NMR, IR and MS spectra.

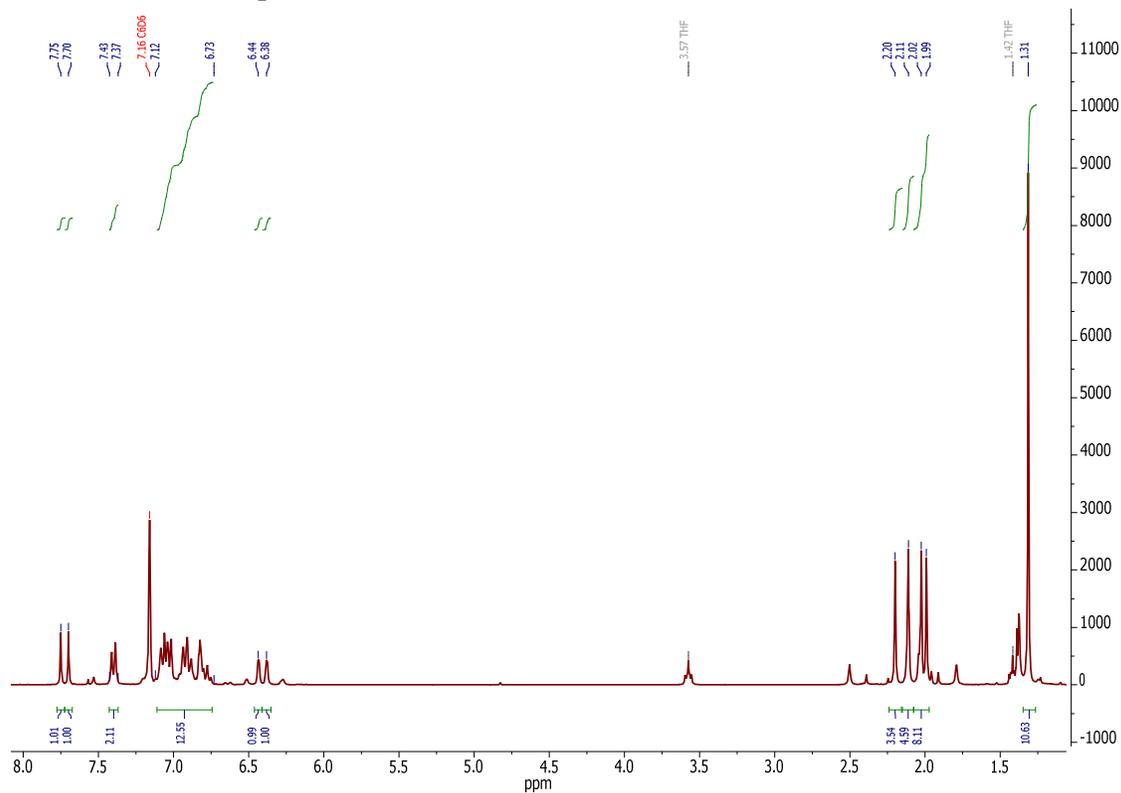


Figure S1. ¹H NMR spectrum of complex 1a.

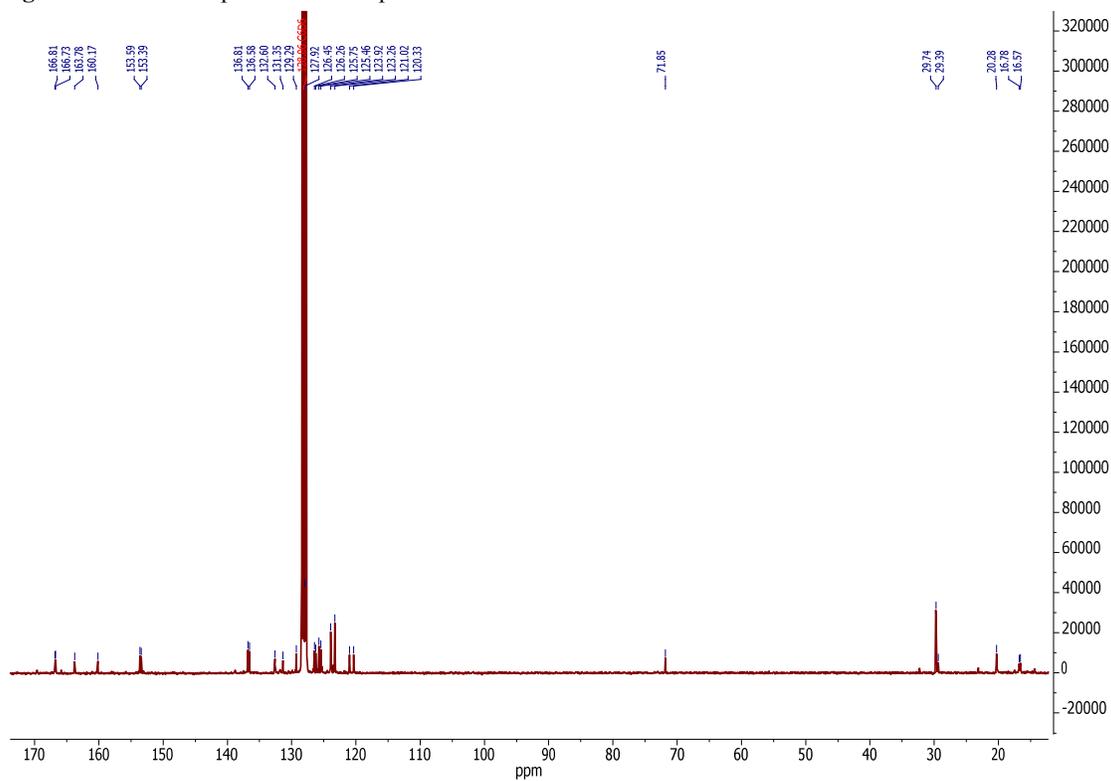


Figure S2. ¹³C NMR spectrum of complex 1a.

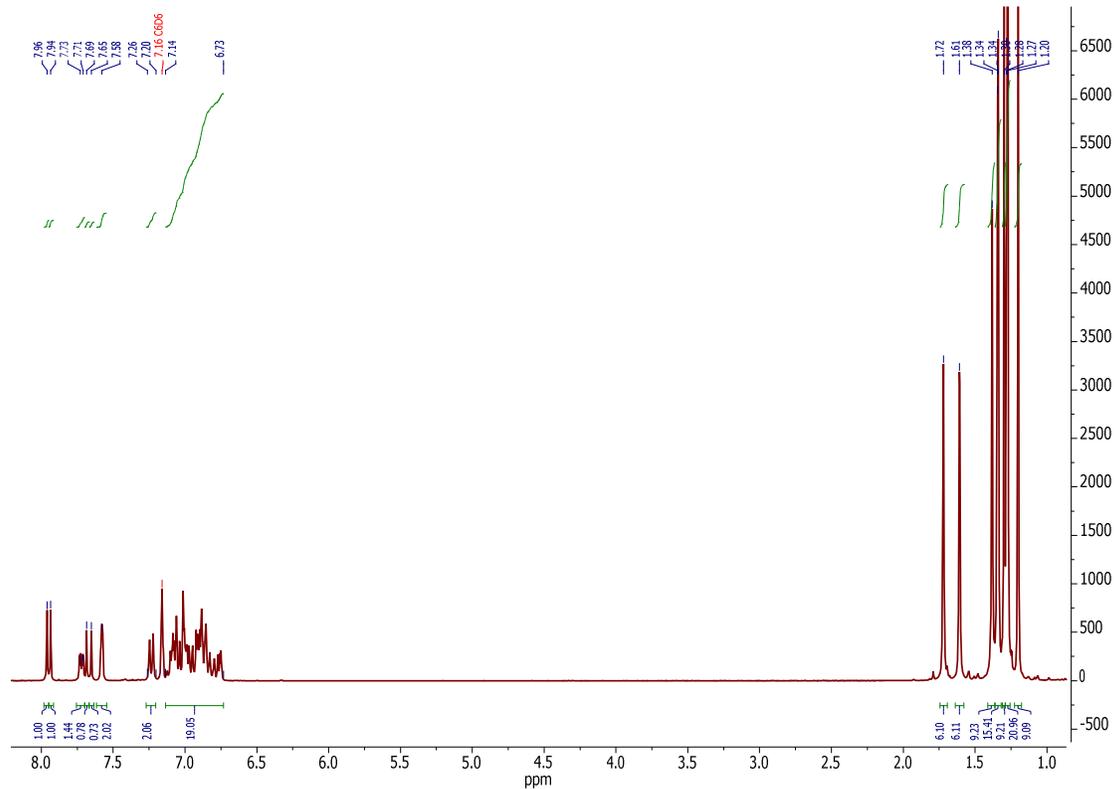


Figure S3. ¹H NMR spectrum of complex 1b.

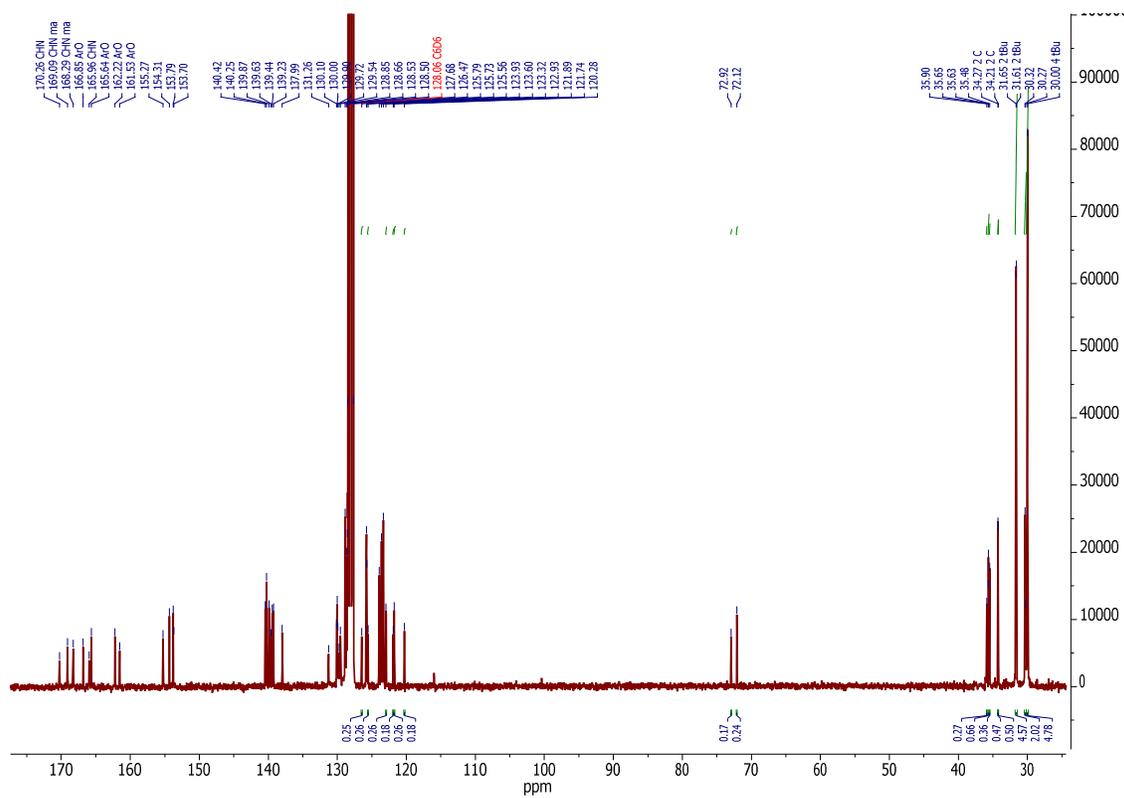


Figure S4. ¹³C NMR spectrum of complex 1b.

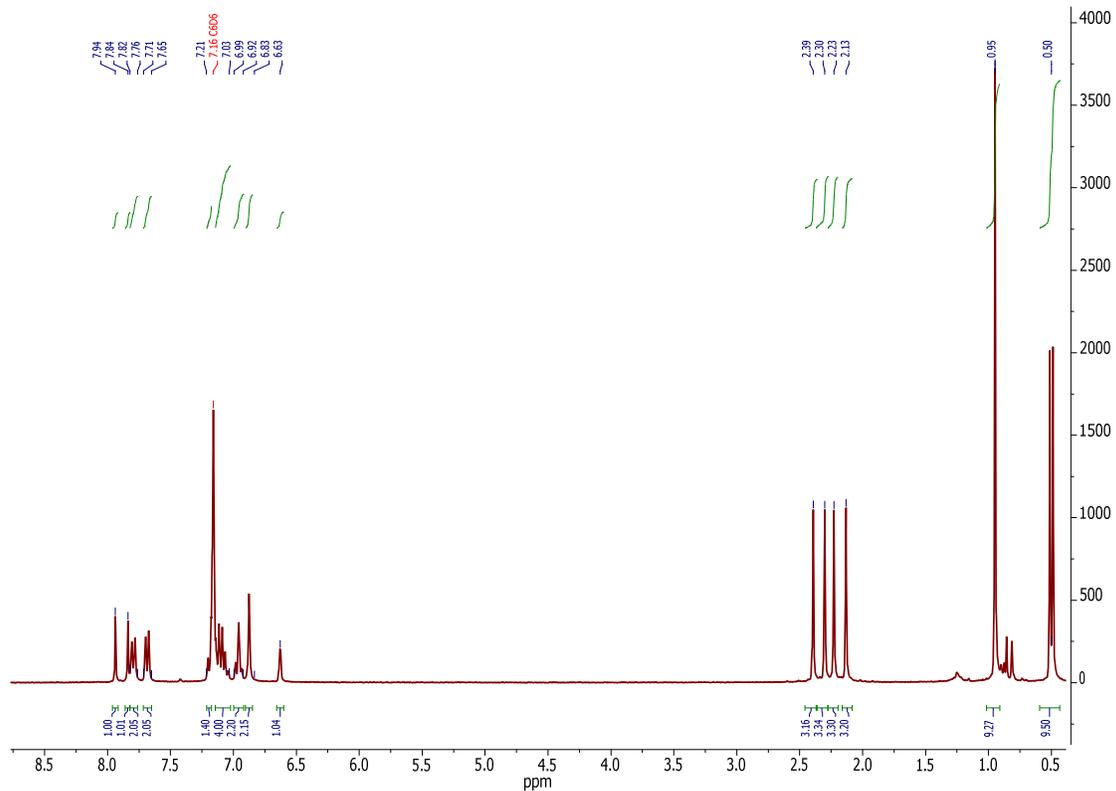


Figure S5. ^1H NMR spectrum of complex **2a**.

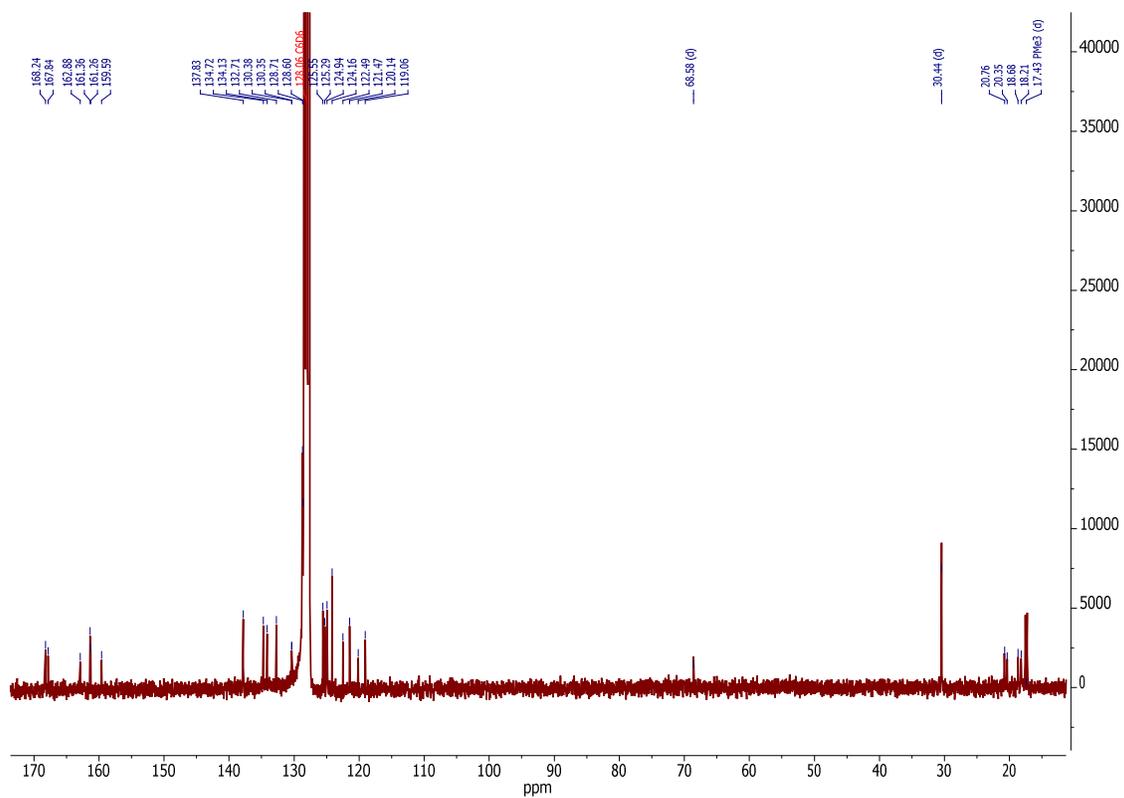


Figure S6. ^{13}C NMR spectrum of complex **2a**.

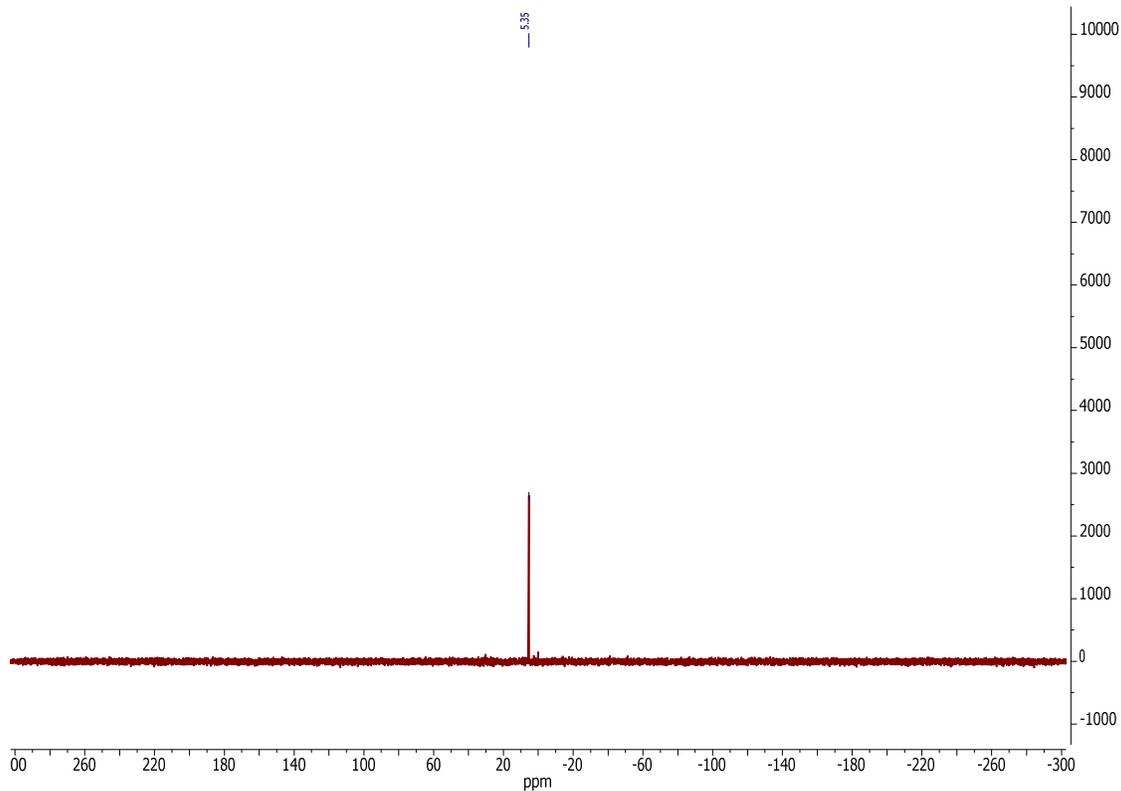


Figure S7. ³¹P NMR spectrum of complex 2a.

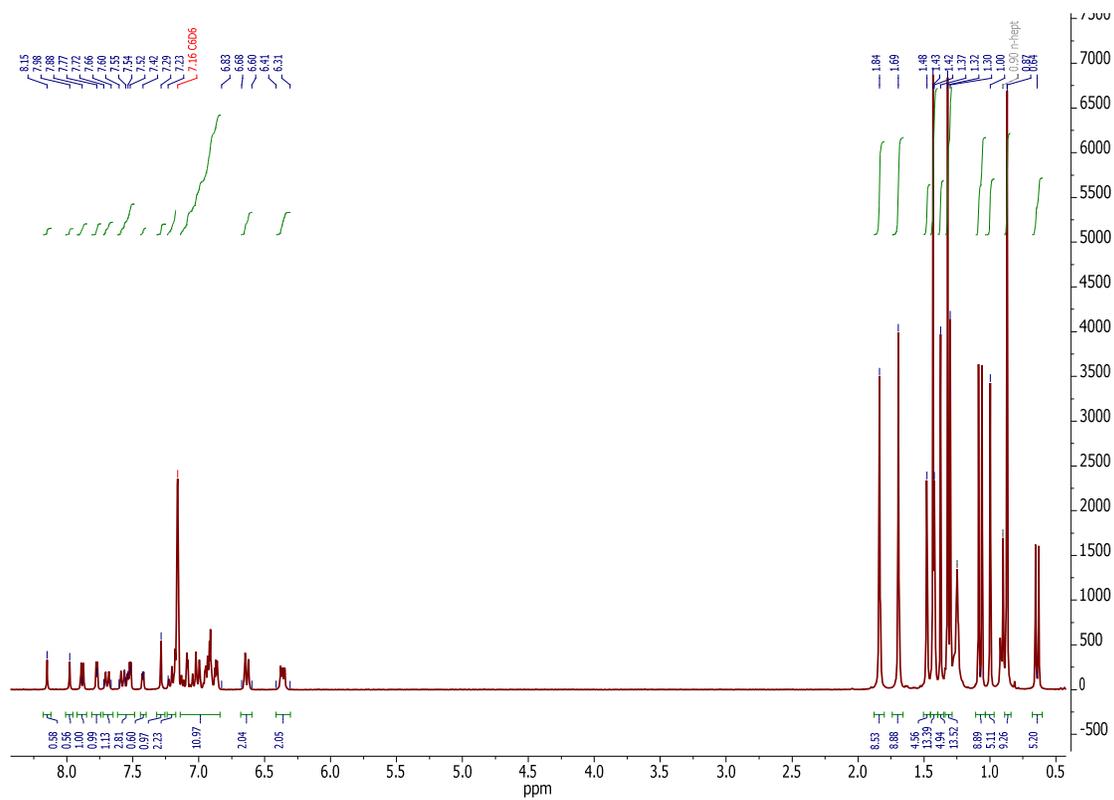


Figure S8. ¹H NMR spectrum of complex 2b.

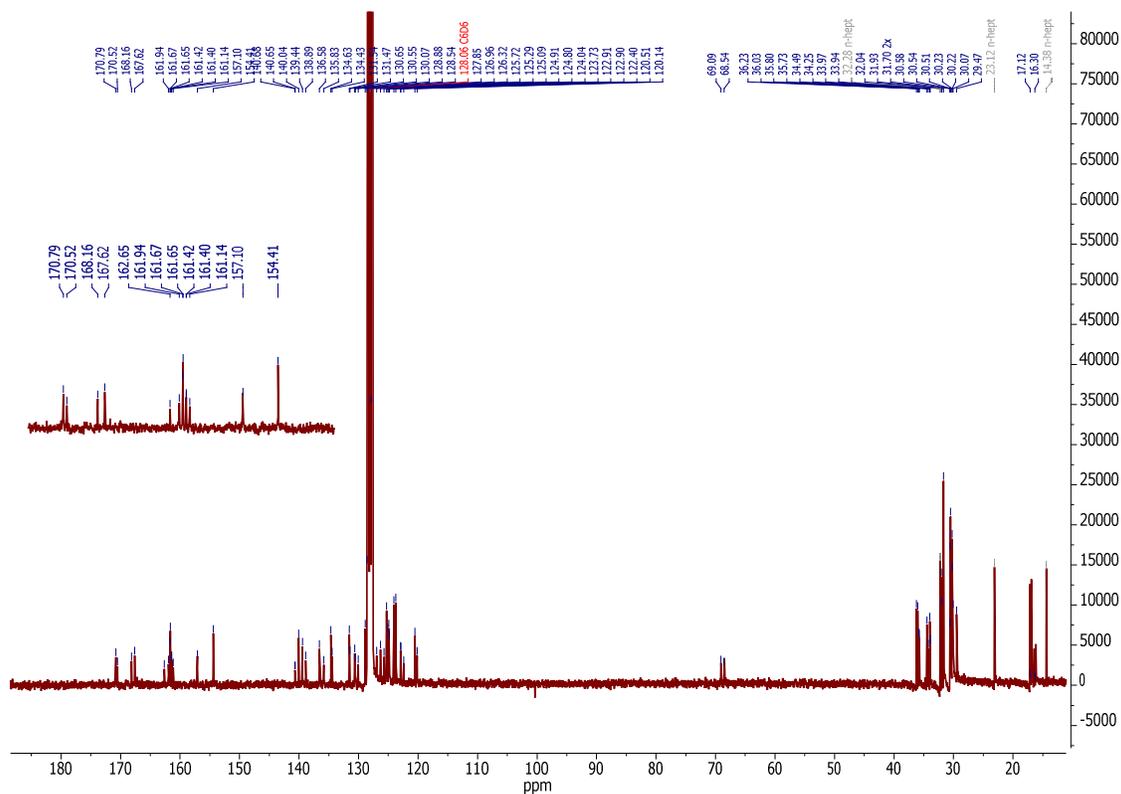


Figure S9. ^{13}C NMR spectrum of complex 2b.

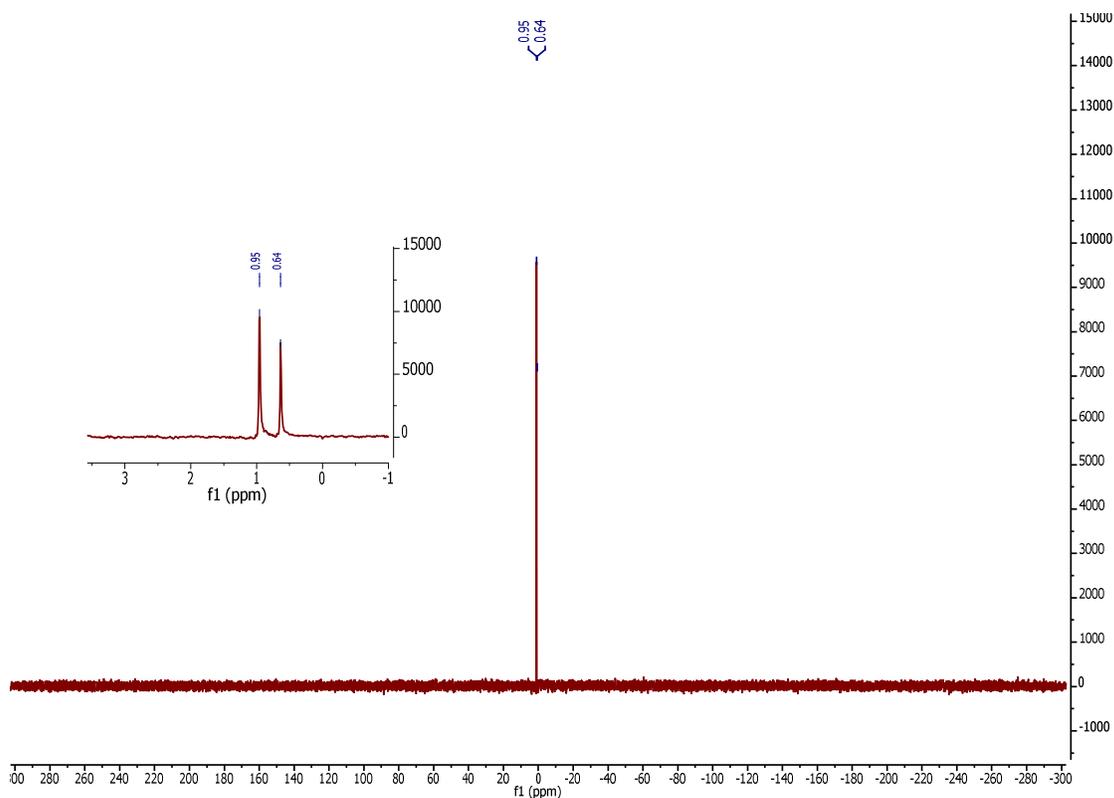


Figure S10. ^{31}P NMR spectrum of complex 2b.

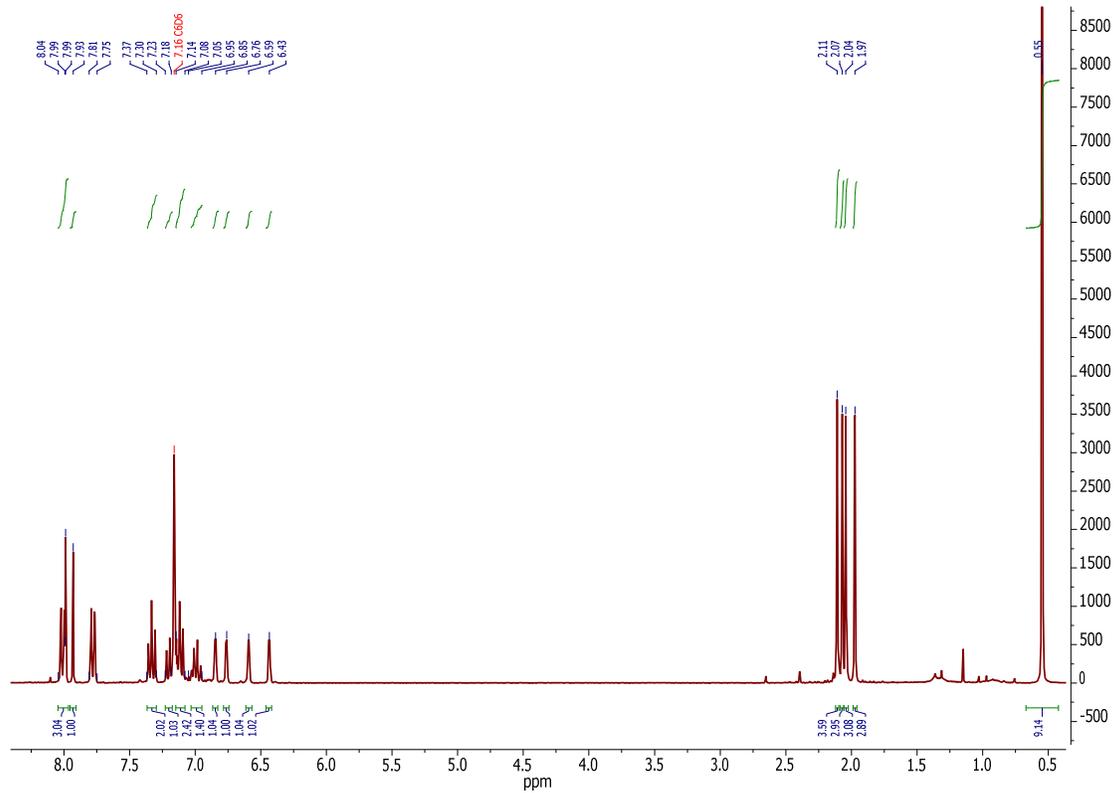


Figure S11. ^1H NMR spectrum of complex **3a**.

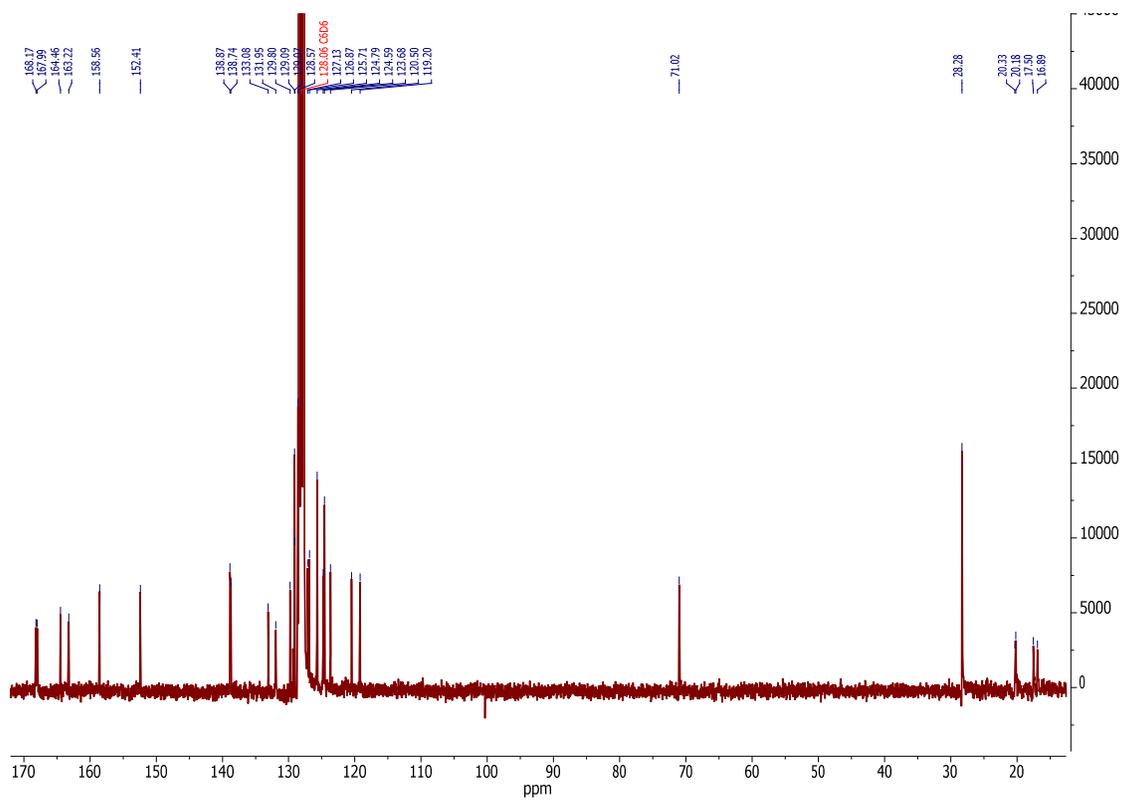


Figure S12. ^{13}C NMR spectrum of complex **3a**.

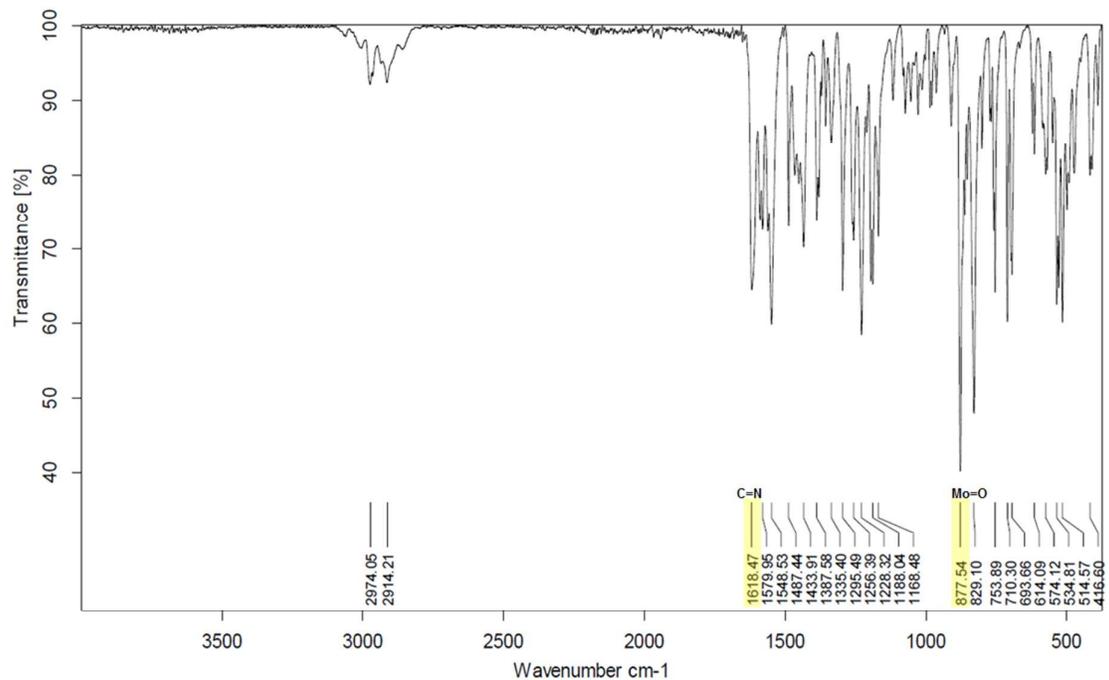


Figure S13. ATR-IR spectrum of complex **1a**.

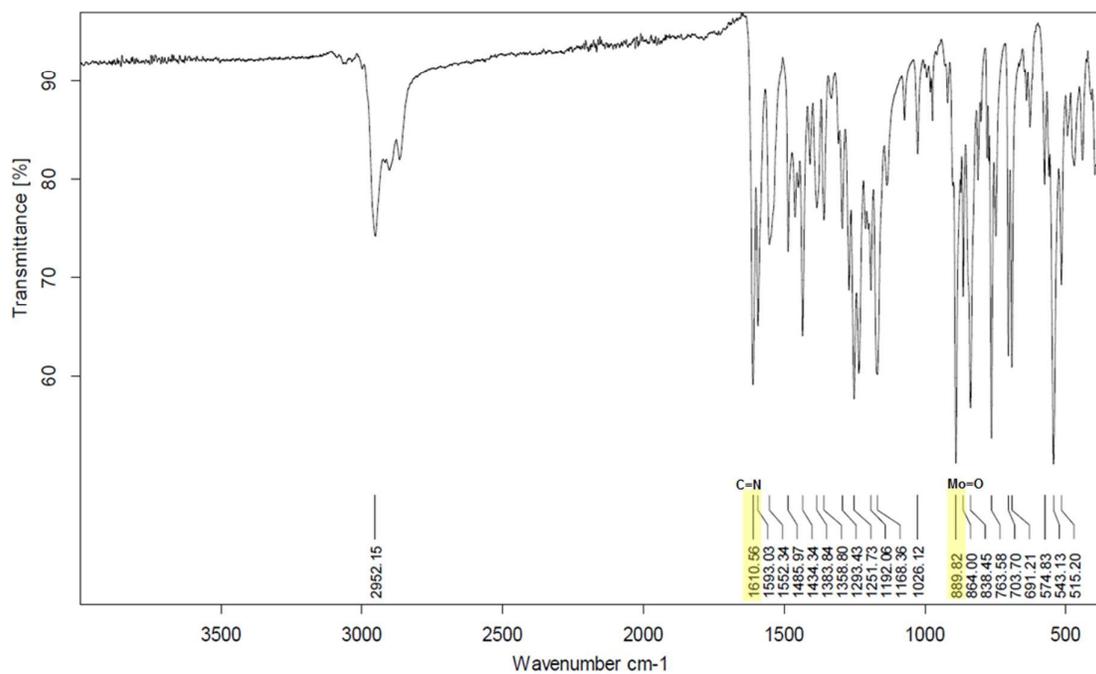


Figure S14. ATR-IR spectrum of complex **1b**.

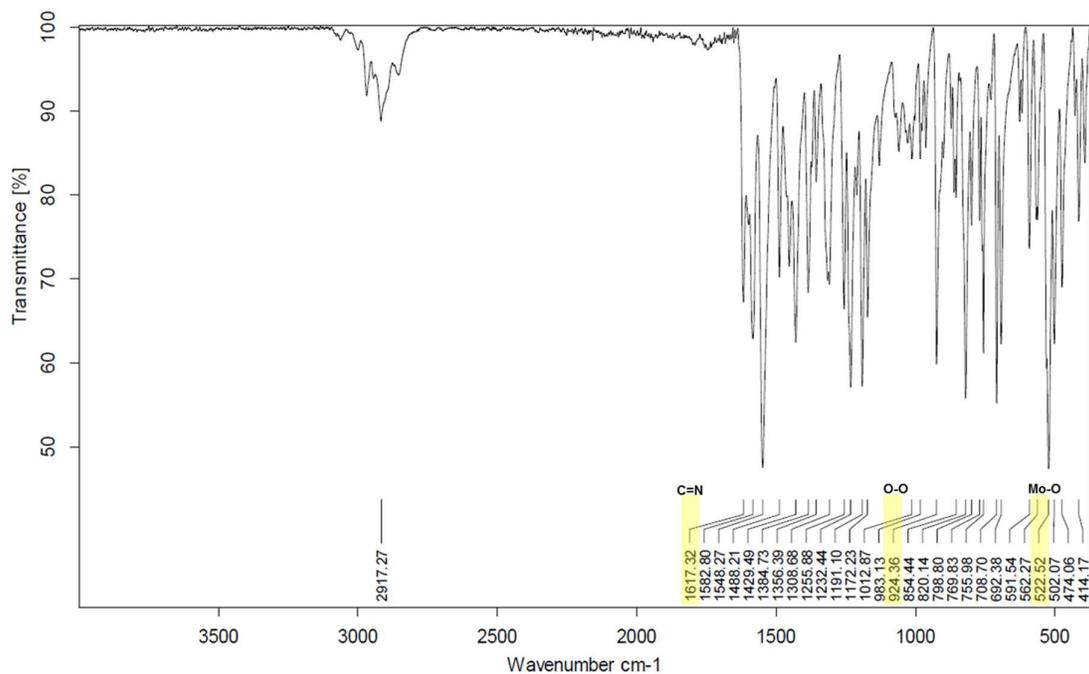


Figure S15. ATR-IR spectrum of complex **3a**.

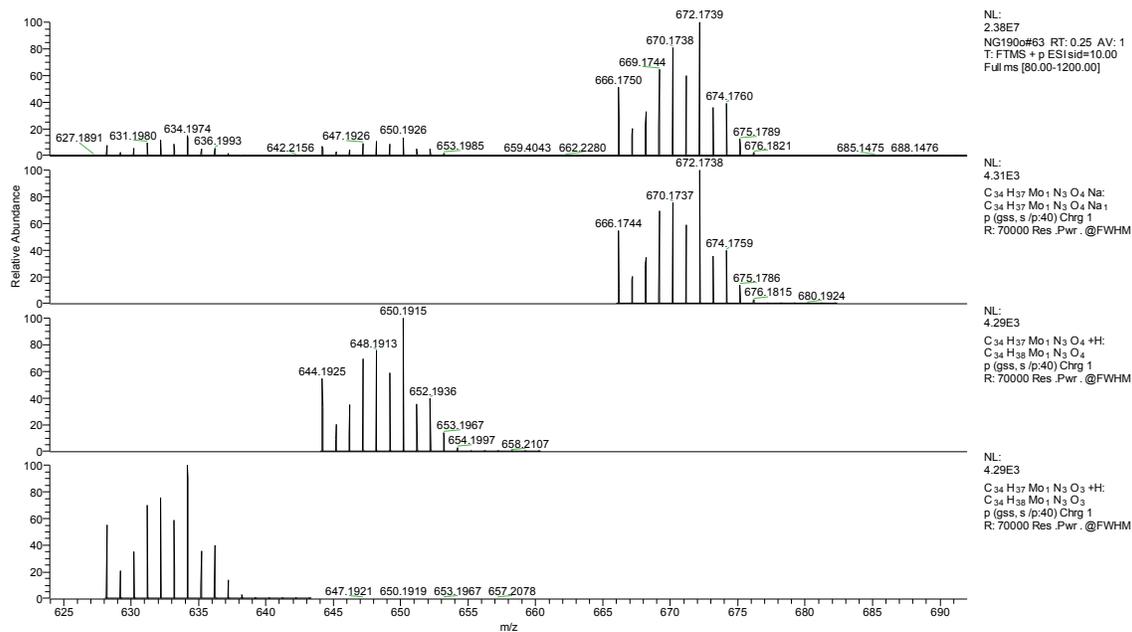


Figure S16. HR-MS (ESI⁺) spectrum of complex **3a**.

Single crystal X-ray diffraction analysis.

General. Single-crystal X-ray diffraction analyses were measured on a BRUKER-AXS SMART APEX II diffractometer equipped with a CCD detector. All measurements were performed using monochromatized Mo K_{α} radiation from an Incoatec microfocus sealed tube at 100K (cf. Table S1). Absorption corrections were performed semi-empirical from equivalents. Structures were solved by direct methods (SHELXS-97)⁶ and refined by full-matrix least-squares techniques against F^2 (SHELXL-2014/6).⁶ CCDC 1560457-1560459 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

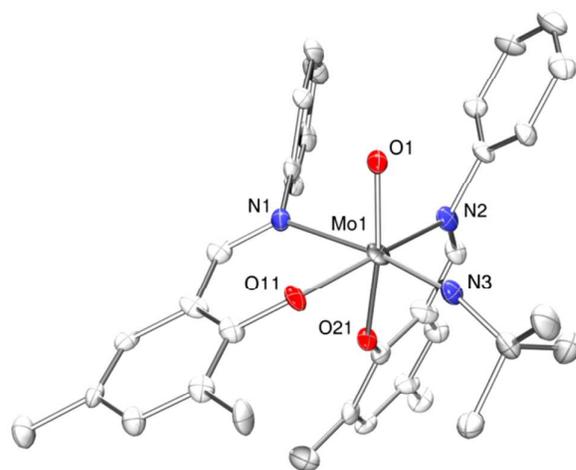


Figure S17. Molecular view (50% probability level) of oxido imido species **1a** depicting the (N,O) arrangement, with respect to the imido and oxido *trans* atoms; H atoms as well as solvent molecules are omitted for clarity reasons.

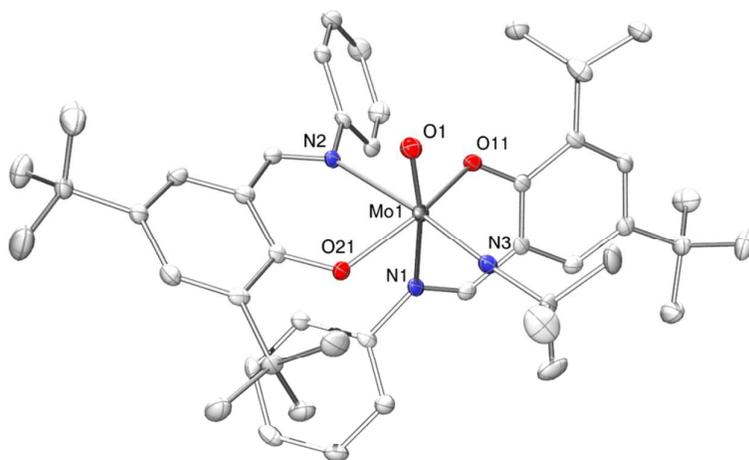


Figure S18. Molecular view (50% probability level) of oxido imido species **1b** depicting the (N,N) arrangement, with respect to the imido and oxido *trans* atoms; H atoms as well as solvent molecules are omitted for clarity reasons.

Theoretical Investigations.

General. The computational results presented have been achieved in part using the Vienna Scientific Cluster (VSC). Calculations were performed using the GAUSSIAN 09 software package,⁷ and the PBE0 functional without symmetry constraints. That functional uses a hybrid generalized gradient approximation (GGA), including 25 % mixture of Hartree-Fock⁸ exchange with DFT⁹ exchange-correlation, given by Perdew, Burke and Ernzerhof functional (PBE).^{10,11} The optimized geometries were obtained with the Stuttgart/Dresden ECP (SDD) basis set¹²⁻¹⁴ to describe the electrons of the molybdenum atoms. For all other atoms a standard 6-31G** basis set was employed.¹⁵⁻¹⁸ A Natural Population Analysis (NPA)¹⁹⁻²³ and the resulting Wiberg indices²⁴ were used to study the electronic structure and bonding of the optimized species. Three-dimensional representations of the orbitals were obtained with Molekel.²⁵

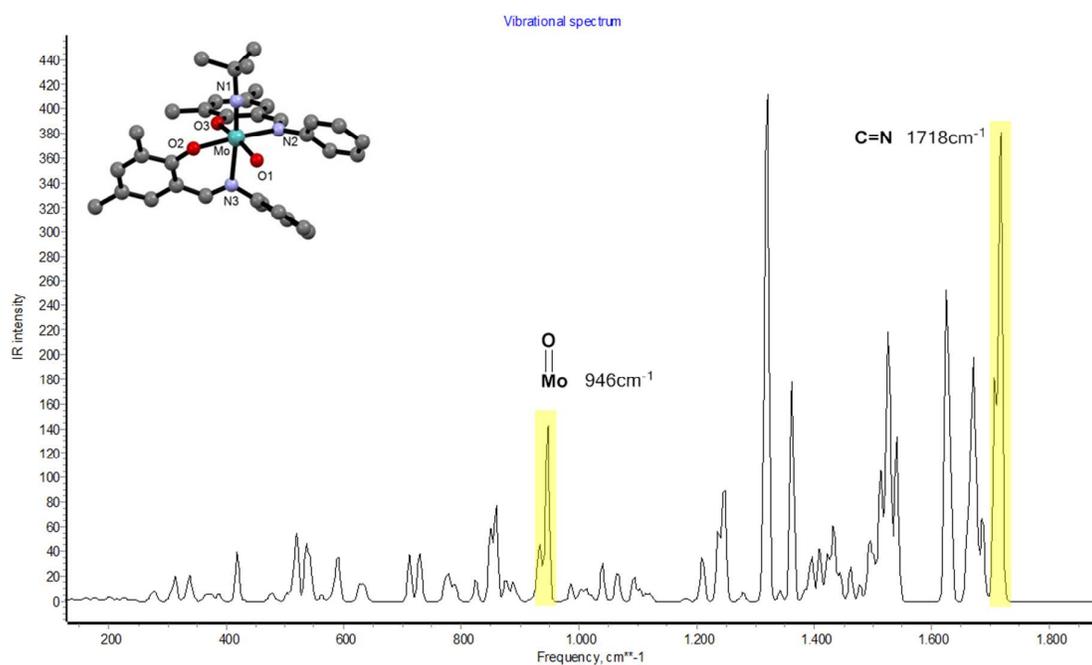


Figure S19. Calculated vibrational spectrum of complex 1a.

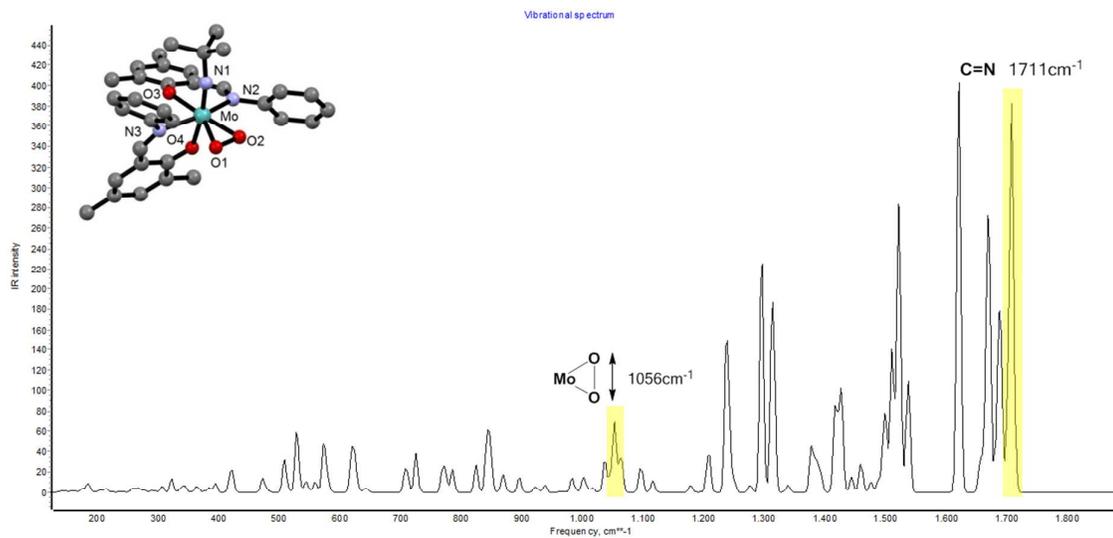


Figure S20. Calculated vibrational spectrum of complex **3a**.

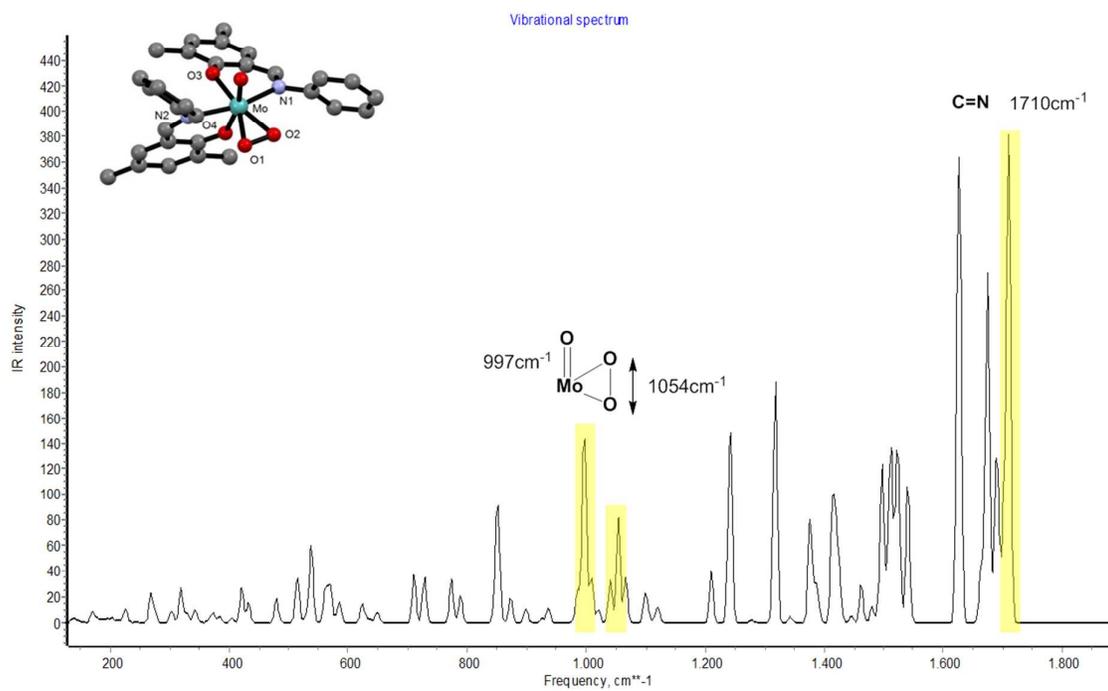


Figure S21. Calculated vibrational spectrum of complex **3a'**.

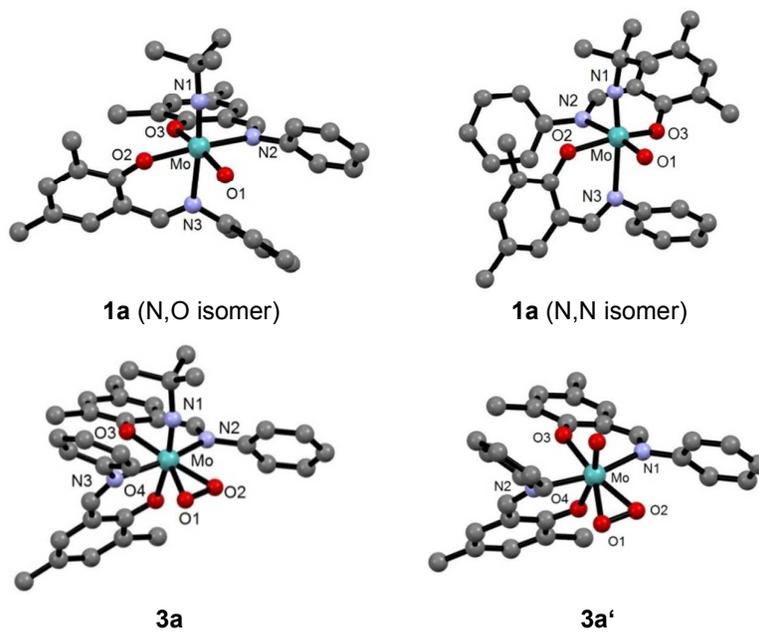


Figure S22. DFT calculated structures of **1a** (N,O isomer), **1a** (N,N isomer), **3a** and **3a'**.

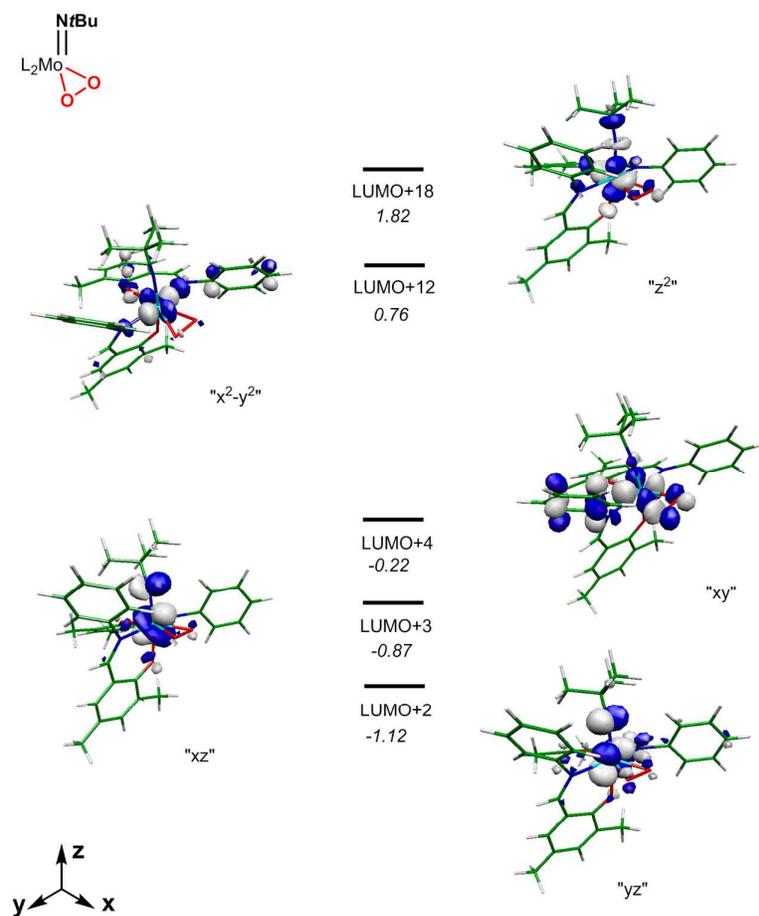


Figure S23. Frontier orbitals (d-splitting) for **3a**. Energy values in electron volts.

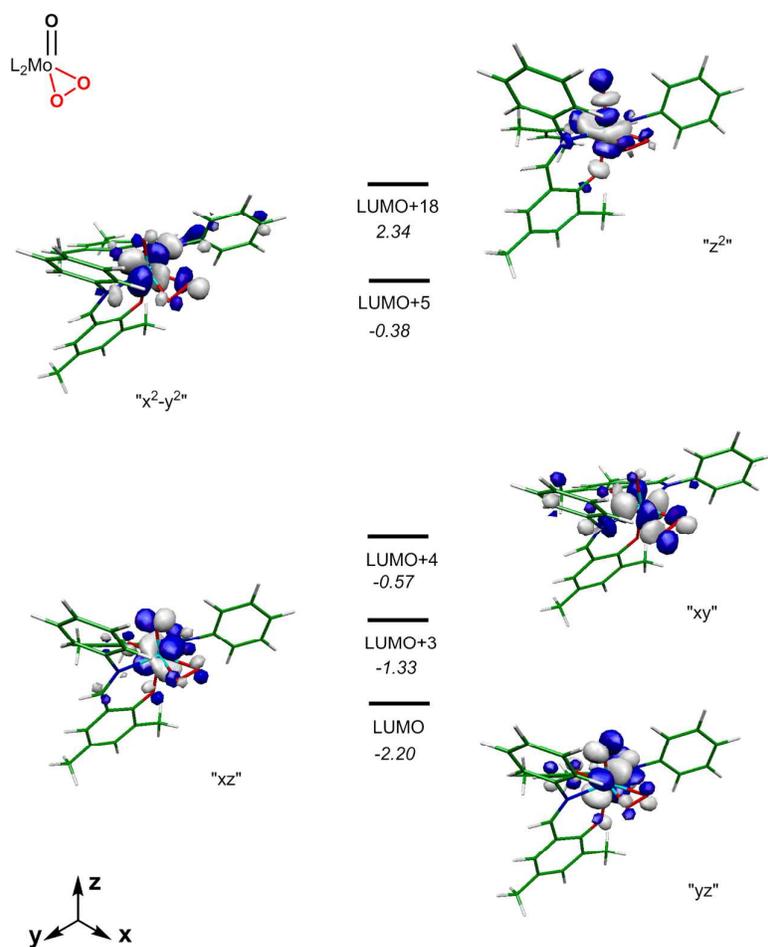


Figure S24. Frontier orbitals (d-splitting) for **3b**. Energy values in electron volts.

Additional crystallographic data for 1a, 1b and 3a.

Crystal Structure Determination of 1a. All the measurements were performed using monochromatized Mo K_{α} radiation at 100K: $C_{34}H_{37}MoN_3O_3$, M_r 631.60, orthorhombic, space group $Pca2_1$, $a = 22.105(13)\text{\AA}$, $b = 7.650(4)\text{\AA}$, $c = 17.467(10)\text{\AA}$, $V = 2954(3)\text{\AA}^3$, $Z = 4$, $d_{\text{calc}} = 1.420\text{g cm}^{-3}$, $\mu = 0.484\text{mm}^{-1}$. A total of 9704 reflections were collected ($\Theta_{\text{max}} = 25.0^\circ$), from which 4626 were unique ($R_{\text{int}} = 0.0611$), with 3989 having $I > 2\sigma(I)$. The structure was solved by direct methods (SHELXS-97)⁶ and refined by full-matrix least-squares techniques against F^2 (SHELXL-2014/6)⁶. The non-hydrogen atoms were refined with anisotropic displacement parameters without any constraints. The absolute configuration was established by anomalous dispersion effects in the diffraction measurements on the crystal. The H atoms of the phenyl rings and of the iminomethyl groups were put at the external bisectors of the C–C–C angles at C–H distances of 0.95Å and common isotropic displacement parameters were refined for the H atoms of the same phenyl ring including the iminomethyl atoms H17, H27. The H atoms of the methyl groups were refined with common isotropic displacement parameters for the H atoms of the same group and idealized geometries with tetrahedral angles, enabling rotation around the C–C bond, and C–H distances of 0.98Å. For 388 parameters final R indices of $R1 = 0.0508$ and $wR^2 = 0.1263$ ($\text{GOF} = 1.052$) were obtained. The largest peak in a difference Fourier map was 1.355\AA^{-3} .

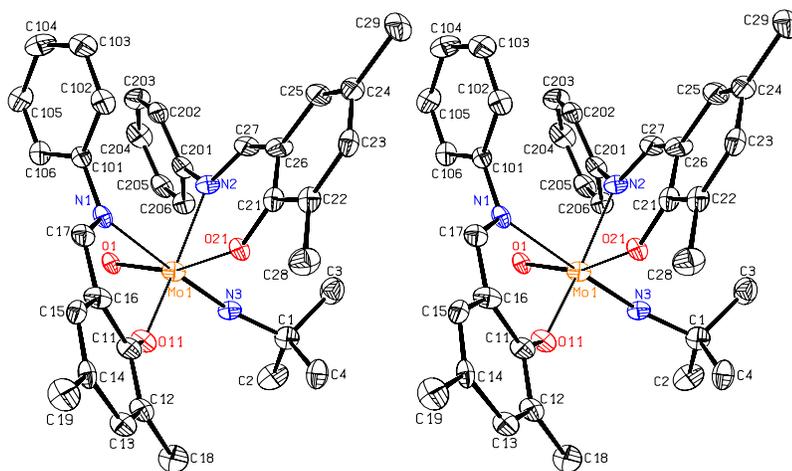


Figure S25. Stereoscopic ORTEP²⁶ plot of **1a** showing the atomic numbering scheme. The probability ellipsoids are drawn at the 50% probability level. The H atoms were omitted for clarity reasons.

Table S1. Crystal data and structure refinement for **1a**.

Crystal data	
Empirical formula	C ₃₄ H ₃₇ MoN ₃ O ₃
Formula weight	631.60
Crystal description	plate, yellow
Crystal size	0.17 x 0.12 x 0.06mm
Crystal system, space group	orthorhombic, P c a 2 ₁
Unit cell dimensions:	
a	22.105(13)Å
b	7.650(4)Å
c	17.467(10)Å
Volume	2954(3)Å ³
Z	4
Calculated density	1.420Mg/m ³
F(000)	1312
Linear absorption coefficient μ	0.484mm ⁻¹
Absorption correction	semi-empirical from equivalents
Max. and min. transmission	1.000 and 0.896
Unit cell determination	2.82° < Θ < 25.64° 2439 reflections used at 100K
Data collection	
Temperature	100K
Diffractometer	Bruker APEX-II CCD
Radiation source	Incoatec microfocus sealed tube
Radiation and wavelength	MoK α , 0.71073Å
Monochromator	multilayer monochromator
Scan type	ϕ and ω scans
Θ range for data collection	2.66 to 25.00°
Reflections collected / unique	9704 / 4626
Significant unique reflections	3989 with I > 2 σ (I)
R(int), R(sigma)	0.0611, 0.0997
Completeness to $\Theta = 25.0^\circ$	99.7%
Refinement	
Refinement method	Full-matrix least-squares on F ²
Data / parameters / restraints	4626 / 388 / 1
Goodness-of-fit on F ²	1.052
Final R indices [I > 2 σ (I)]	R1 = 0.0508, wR2 = 0.1206
R indices (all data)	R1 = 0.0604, wR2 = 0.1263
Absolute structure parameter	0.11(4)
Extinction expression	none
Weighting scheme	w = 1/[$\sigma^2(F_o^2) + (aP)^2$] where P = (F _o ² + 2F _c ²)/3
Weighting scheme parameter a	0.0439
Largest Δ/σ in last cycle	0.001
Largest difference peak and hole	1.355 and -0.830e/Å ³
Structure Solution Program	SHELXS-97 (Sheldrick, 2008)
Structure Refinement Program	SHELXL-2014/6 (Sheldrick, 2008)

Table S2. Selected bond lengths [Å] and angles [°] for **1a**.

Mo(1)-O(1)	1.727(6)
Mo(1)-N(3)	1.740(6)
Mo(1)-O(11)	1.982(5)
Mo(1)-O(21)	2.054(6)
Mo(1)-N(1)	2.358(7)
Mo(1)-N(2)	2.222(5)
N(3)-C(1)	1.434(10)
C(17)-N(1)	1.290(11)
C(27)-N(2)	1.302(12)
O(1)-Mo(1)-O(21)	157.9(2)
O(11)-Mo(1)-N(2)	163.6(3)
N(3)-Mo(1)-N(1)	172.0(3)
C(1)-N(3)-Mo(1)	161.3(6)
C(11)-O(11)-Mo(1)	132.6(5)
C(17)-N(1)-C(101)	117.2(7)
C(17)-N(1)-Mo(1)	123.9(6)
C(101)-N(1)-Mo(1)	118.7(5)
C(21)-O(21)-Mo(1)	138.4(5)
C(27)-N(2)-C(201)	114.5(6)
C(27)-N(2)-Mo(1)	127.8(7)
C(201)-N(2)-Mo(1)	117.6(6)
C(16)-C(17)-N(1)-C(101)	178.1(8)
C(16)-C(17)-N(1)-Mo(1)	-6.6(12)
C(26)-C(27)-N(2)-C(201)	175.1(8)
C(26)-C(27)-N(2)-Mo(1)	-1.7(13)

Crystal Structure Determination of 1b. All the measurements were performed using monochromatized Mo K α radiation at 100K: C₄₆H₆₁MoN₃O₃ · 2C₂H₃N, M_r 882.02, triclinic, space group P -1, $a = 9.9852(15)\text{\AA}$, $b = 16.369(3)\text{\AA}$, $c = 16.990(3)\text{\AA}$, $\alpha = 107.950(2)^\circ$, $\beta = 106.1874(19)^\circ$, $\gamma = 102.7576(19)^\circ$, $V = 2389.8(6)\text{\AA}^3$, $Z = 2$, $d_{\text{calc}} = 1.226\text{ g cm}^{-3}$, $\mu = 0.319\text{ mm}^{-1}$. A total of 29866 reflections were collected ($\Theta_{\text{max}} = 26.0^\circ$), from which 9374 were unique ($R_{\text{int}} = 0.0775$), with 7720 having $I > 2\sigma(I)$. The structure was solved by direct methods (SHELXS-97)⁶ and refined by full-matrix least-squares techniques against F^2 (SHELXL-2014/6).⁶ The non-hydrogen atoms were refined with anisotropic displacement parameters without any constraints. The H atoms of the phenyl rings and of the iminomethyl groups were put at the external bisectors of the C–C–C angles at C–H distances of 0.95 Å and common isotropic displacement parameters were refined for the H atoms of the same phenyl ring including the iminomethyl atoms H17, H27. The H atoms of the methyl groups were refined with common isotropic displacement parameters for the H atoms of the same group and idealized geometries with tetrahedral angles, enabling rotation around the C–C bond, and C–H distances of 0.98 Å. For 570 parameters final R indices of $R1 = 0.0447$ and $wR^2 = 0.1004$ (GOF = 1.033) were obtained. The largest peak in a difference Fourier map was $1.032\text{ e}\text{\AA}^{-3}$.

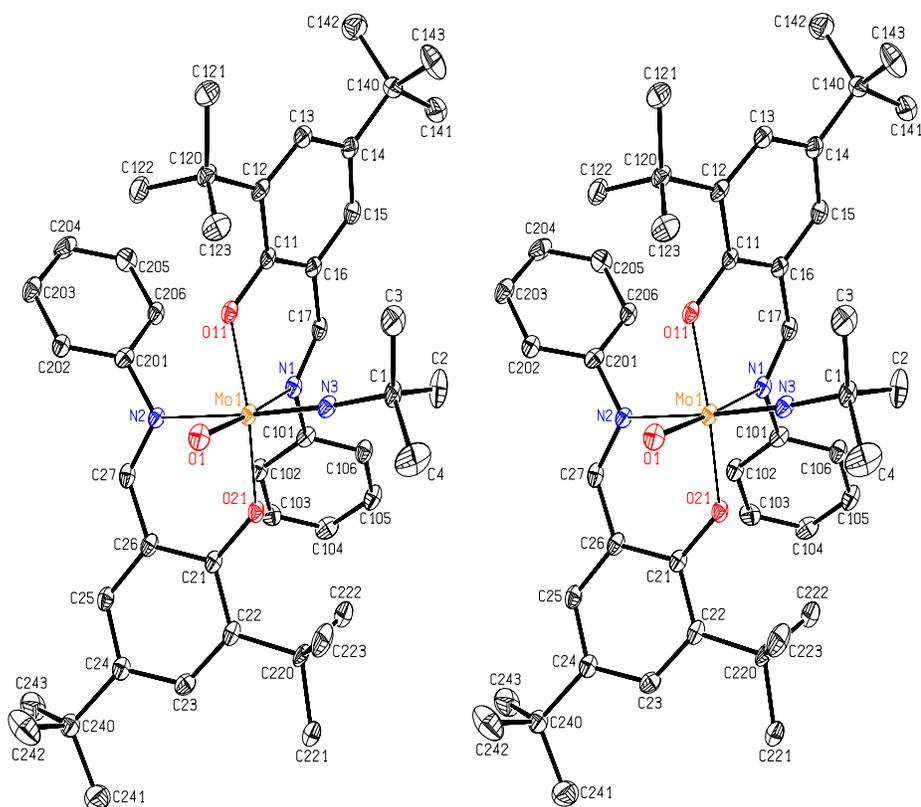


Figure S26. Stereoscopic ORTEP²⁶ plot of **1b** showing the atomic numbering scheme. The probability ellipsoids are drawn at the 50% probability level. The acetonitrile solvent molecules and the H atoms were omitted for clarity reasons.

Table S3. Crystal data and structure refinement for **1b**.

Crystal data	
Empirical formula	$C_{46}H_{61}MoN_3O_3 \cdot 2C_2H_3N$
Formula weight	882.02
Crystal description	needle, yellow
Crystal size	0.25 x 0.12 x 0.12mm
Crystal system, space group	triclinic, P -1
Unit cell dimensions:	
a	9.9852(15)Å
b	16.369(3)Å
c	16.990(3)Å
α	107.950(2)°
β	106.1874(19)°
γ	102.7576(19)°
Volume	2389.8(6)Å ³
Z	2
Calculated density	1.226Mg/m ³
F(000)	936
Linear absorption coefficient μ	0.319mm ⁻¹
Absorption correction	semi-empirical from equivalents
Max. and min. transmission	1.000 and 0.356
Unit cell determination	2.29° < Θ < 27.21°
	9890 reflections used at 100K

Data collection	
Temperature	100K
Diffractometer	Bruker APEX-II CCD
Radiation source	Incoatec microfocus sealed tube
Radiation and wavelength	MoK α , 0.71073Å
Monochromator	multilayer monochromator
Scan type	ϕ and ω scans
Θ range for data collection	2.68 to 26.00°
Reflections collected / unique	29866 / 9374
Significant unique reflections	7720 with $I > 2\sigma(I)$
R(int), R(sigma)	0.0775, 0.0827
Completeness to $\Theta = 26.0^\circ$	99.8%
Refinement	
Refinement method	Full-matrix least-squares on F ²
Data / parameters / restraints	9374 / 570 / 0
Goodness-of-fit on F ²	1.033
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0447, wR2 = 0.0950
R indices (all data)	R1 = 0.0600, wR2 = 0.1004
Extinction expression	none
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = (F_o^2 + 2F_c^2)/3$
Weighting scheme parameters a, b	0.0204, 1.5184
Largest Δ/σ in last cycle	0.001
Largest difference peak and hole	1.032 and -0.651 e/Å ³
Structure Solution Program	SHELXS-97 (Sheldrick, 2008)
Structure Refinement Program	SHELXL-2014/6 (Sheldrick, 2008)

Table S4. Selected bond lengths [Å] and angles [°] for **1b**.

Mo(1)-O(1)	1.7198(18)
Mo(1)-N(3)	1.739(2)
Mo(1)-O(11)	1.9680(18)
Mo(1)-O(21)	1.9953(18)
Mo(1)-N(1)	2.390(2)
Mo(1)-N(2)	2.366(2)
N(3)-C(1)	1.448(3)
C(17)-N(1)	1.294(3)
C(27)-N(2)	1.283(3)
O(11)-Mo(1)-O(21)	153.70(7)
N(3)-Mo(1)-N(2)	167.97(9)
O(1)-Mo(1)-N(1)	168.78(8)
C(1)-N(3)-Mo(1)	175.60(18)
C(11)-O(11)-Mo(1)	130.11(14)
C(17)-N(1)-C(101)	116.4(2)
C(17)-N(1)-Mo(1)	118.61(17)
C(101)-N(1)-Mo(1)	122.96(16)
C(21)-O(21)-Mo(1)	130.66(15)
C(27)-N(2)-C(201)	115.8(2)
C(27)-N(2)-Mo(1)	118.35(17)
C(201)-N(2)-Mo(1)	124.54(16)
C(16)-C(17)-N(1)-C(101)	178.5(2)
C(16)-C(17)-N(1)-Mo(1)	-17.1(3)
C(26)-C(27)-N(2)-C(201)	175.1(2)
C(26)-C(27)-N(2)-Mo(1)	-17.3(4)

Crystal Structure Determination of 3a. All the measurements were performed using monochromatized Mo K_{α} radiation at 100K: $C_{34}H_{37}MoN_3O_4$, M_r 647.60, monoclinic, space group $P 2_1/c$, $a = 11.9610(11)\text{\AA}$, $b = 15.2086(13)\text{\AA}$, $c = 17.8192(15)\text{\AA}$, $\beta = 106.700(2)^\circ$, $V = 3104.8(5)\text{\AA}^3$, $Z = 4$, $d_{\text{calc}} = 1.385\text{g cm}^{-3}$, $\mu = 0.464\text{mm}^{-1}$. A total of 57161 reflections were collected ($\Theta_{\text{max}} = 30.0^\circ$), from which 9043 were unique ($R_{\text{int}} = 0.0661$), with 7175 having $I > 2\sigma(I)$. The structure was solved by direct methods (SHELXS-97)⁶ and refined by full-matrix least-squares techniques against F^2 (SHELXL-2014/6).⁶ The non-hydrogen atoms were refined with anisotropic displacement parameters without any constraints. The H atoms of the phenyl rings including the H atoms of the adjacent iminomethyl groups were put at the external bisectors of the C–C–C angles at C–H distances of 0.95\AA and common isotropic displacement parameters were refined for these H atoms of the same ligand. The H atoms of the methyl groups were refined with common isotropic displacement parameters for the H atoms of the same group and idealized geometries with tetrahedral angles, enabling rotation around the C–C bond, and C–H distances of 0.98\AA . For 397 parameters final R indices of $R1 = 0.0317$ and $wR^2 = 0.0725$ ($\text{GOF} = 1.024$) were obtained. The largest peak in a difference Fourier map was $0.741\text{e}\text{\AA}^{-3}$.

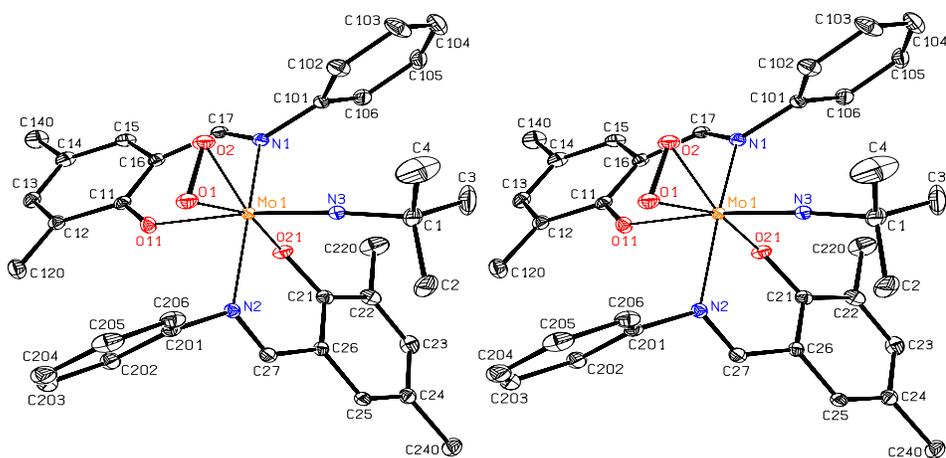


Figure S27. Stereoscopic ORTEP²⁶ plot of **3a** showing the atomic numbering scheme. The probability ellipsoids are drawn at the 50% probability level. The H atoms were omitted for clarity reasons.

Table S5. Crystal data and structure refinement for **3a**.

Crystal data	
Empirical formula	C ₃₄ H ₃₇ MoN ₃ O ₄
Formula weight	647.60
Crystal description	needle, yellow
Crystal size	0.31 x 0.14 x 0.11mm
Crystal system, space group	monoclinic, P 2 ₁ /c
Unit cell dimensions:	
a	11.9610(11)Å
b	15.2086(13)Å
c	17.8192(15)Å
β	106.700(2)°
Volume	3104.8(5)Å ³
Z	4
Calculated density	1.385Mg/m ³
F(000)	1344
Linear absorption coefficient μ	0.464mm ⁻¹
Absorption correction	semi-empirical from equivalents
Max. and min. transmission	1.000 and 0.887
Unit cell determination	2.53° < Θ < 30.39° 9991 reflections used at 100K
Data collection	
Temperature	100K
Diffractometer	Bruker APEX-II CCD
Radiation source	Incoatec microfocus sealed tube
Radiation and wavelength	MoK _α , 0.71073Å
Monochromator	multilayer monochromator
Scan type	φ and ω scans
Θ range for data collection	2.53 to 30.00°
Reflections collected / unique	57161 / 9043
Significant unique reflections	7175 with I > 2σ(I)
R(int), R(sigma)	0.0661, 0.0464
Completeness to Θ = 30.0°	99.9%
Refinement	
Refinement method	Full-matrix least-squares on F ²
Data / parameters / restraints	9043 / 397 / 0
Goodness-of-fit on F ²	1.024
Final R indices [I > 2σ(I)]	R1 = 0.0317, wR2 = 0.0659
R indices (all data)	R1 = 0.0499, wR2 = 0.0725
Extinction expression	none
Weighting scheme	w = 1/[σ ² (F _o ²)+(aP) ² +bP] where P = (F _o ² +2F _c ²)/3
Weighting scheme parameters a, b	0.0228, 2.3939
Largest Δ/σ in last cycle	0.001
Largest difference peak and hole	0.741 and -0.627e/Å ³
Structure Solution Program	SHELXS-97 (Sheldrick, 2008)
Structure Refinement Program	SHELXL-2014/6 (Sheldrick, 2008)

Table S6. Selected bond lengths [Å] and angles [°] for **3a**.

Mo(1)-O(1)	1.9764(13)
Mo(1)-O(2)	1.9754(13)
Mo(1)-N(3)	1.7261(15)
Mo(1)-O(11)	2.0940(13)
Mo(1)-O(21)	2.0440(12)
Mo(1)-N(1)	2.1954(15)
Mo(1)-N(2)	2.2053(14)
O(1)-O(2)	1.4399(17)
N(3)-C(1)	1.453(2)
C(17)-N(1)	1.304(2)
C(27)-N(2)	1.300(2)
O(1)-Mo(1)-O(21)	158.38(5)
O(2)-Mo(1)-O(21)	152.22(5)
N(3)-Mo(1)-O(11)	172.99(6)
O(2)-Mo(1)-N(1)	77.25(5)
O(1)-Mo(1)-N(2)	80.13(5)
N(1)-Mo(1)-N(2)	155.97(6)
C(1)-N(3)-Mo(1)	175.08(13)
C(11)-O(11)-Mo(1)	133.27(11)
C(17)-N(1)-C(101)	115.54(15)
C(17)-N(1)-Mo(1)	124.41(12)
C(101)-N(1)-Mo(1)	119.78(11)
C(27)-N(2)-C(201)	115.03(14)
C(27)-N(2)-Mo(1)	124.15(12)
C(201)-N(2)-Mo(1)	120.44(11)
O(1)-O(2)-Mo(1)-N(2)	3.67(10)
O(2)-O(1)-Mo(1)-N(1)	-12.10(10)
O(2)-O(1)-Mo(1)-N(2)	-176.87(8)
O(1)-O(2)-Mo(1)-N(1)	169.19(9)
C(16)-C(17)-N(1)-C(101)	-177.81(17)
C(16)-C(17)-N(1)-Mo(1)	8.1(3)
C(26)-C(27)-N(2)-C(201)	172.83(17)
C(26)-C(27)-N(2)-Mo(1)	0.0(3)

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