Supporting Information

Direct Photocatalytic C–H Functionalization Mediated by a Molybdenum Dioxo Complex

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Experimental Methods

I. General Considerations

All operations were conducted under an atmosphere of N_2 in a MBraun Unilab Pro glovebox or using Schlenk line techniques, unless otherwise stated. Acetonitrile was purchased from Honeywell, pentane and diethyl ether were purchased from VWR, and degassed with Ar and purified using Pure Process Technology solvent purification system. Acetonitrile was brought into an N_2-filled glovebox and stored under 4-Å molecular sieves. Deuterated solvents were purchased from Cambridge Isotope Laboratories and degassed through three cycles of freeze-pump-thaw except for D_2O. D_2O was sparged with N_2 for 30 min to replace dissolved oxygen. They were stored in an N_2-filled glovebox under 4-Å molecular sieves. Cyclohexene 99% was purchased from Alfa Aesar and distilled 5 times to remove trace impurities. It was further purified through a silica column to remove trace oxygenated impurities. Cyclohexene was degassed by three cycles of freeze-pump-thaw and brought in the glovebox, stored under 4-Å molecular sieves, and covered with aluminum foil to prevent reactivity with stray light. 1,4-cyclohexadiene 97% (stabilized BHT) was purchased from Acros Organics and stored in an N_2-filled glovebox under 4-Å molecular sieves and used without further purification. Cyclohexane was purchased from VWR, stored in an N_2-filled glovebox, and used without further purification. $Na_2MoO_4•(H_2O)_2$ 98% was purchased from Alfa Aesar and stored in a desiccator and used without further purification. Triphenylphosphine 99% was purchased from Aldrich and used without purification. 4,4'-ditertbtyl-2,2'-bipyridine and pyridine *N*-oxide were purchased from Acros Organics, stored in an N_2 filled glovebox and used without purification. 4-cyanopyridine *N*-oxide, 4-chloropyridine *N*-oxide, 4-methylpyridine *N*- oxide, 4-methoxyoxypyrdine *N*-oxide, and 2,6-lutadine *N*-oxide were purchased from TCI, stored in a glovebox and used without further purification.

^{1}H NMR spectra were taken on a Bruker 400MHz instrument at 25°C and referenced to CD_3CN signal (δ 1.94 ppm). Spectra were processed using the MestReNova software suit from Mestrelab Research S. L. UV-Vis measurements were made using an Ocean-FX-XR1-ES spectrometer from Ocean Optics with a DH-2000-BAL deuterium/tungsten source controlled by OceanView software. A ThorLabs High-Power 4-Wavelength LED Source was used for photolysis equipped with a 365 nm LED bulb. The organic products formed during photocatalytic assays were analyzed using an Agilent GC-MS system: 6890 N Agilent Technologies GC equipped with an HP-5ms 5% phenyl methyl silica column 30 m and 0.25 μm film attached to a 5975 B Agilent Technologies mass spectrometer. Elemental Analysis performed by Midwest Microlab, Indianapolis, IN.

II. Preparation of Complexes 1 and 2

Synthesis of Precursor $MoO_2Cl_2(DMSO)_2$

The synthesis of $MoO_2Cl_2(DMSO)_2$ was carried out in a hood by dissolving 6.26 g $Na_2MoO_4•(H_2O)_2$ in 50 mL of distilled water. 50 mL of 12 M $HCl_{(aq)}$ was added to the solution and refluxed for 2 hours at 98˚C. The clear green solution was then allowed to cool to room temperature. 25 mL of DMSO was added to the solution and stirred for 30 minutes. The precipitation of a light green solid product occurred after the addition of DMSO. The precipitate was filtered and washed with 100 mL of cold acetone until the slight greenish tint was removed yielding a white solid. The white solid product was dried in a Schleck flask under vacuum overnight and then was brought into the glovebox. Yield: 6.87 g, 62.9%. ^{1}HNMR (CD_3CN): δ 2.81 ppm (s, 6H) (Figure S1).

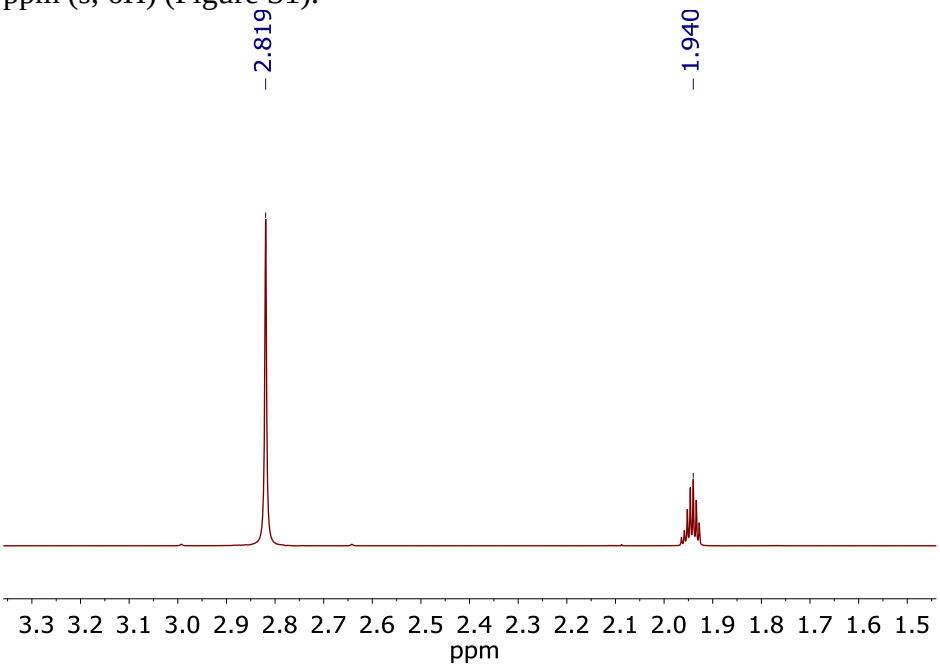


Figure S1. ^{1}H NMR spectrum of $MoO_2Cl_2(DMSO)_2$ taken in CD_3CN on a Bruker 400MHz instrument at room temperature

Synthesis of Complex 1, $MoO_2Cl_2(bpy\text{-}^tBu)$

A solution of 125 mg of $MoO_2Cl_2(DMSO)_2$ in 4 mL of acetonitrile was prepared. A solution of 1.1 equivalents (90 mg) of 4,4'-ditertbutyl 2,2'-bipyridine was made in 10 mL of acetonitrile and slowly added to the solution of $MoO_2Cl_2(DMSO)_2$. The solution was then stirred for two hours to ensure the reaction had gone to completion. Over the course of the reaction, a small amount of white precipitate formed. The solvent was evaporated under vacuum, leaving a white precipitate behind. The solid was then washed three times with 15 mL of toluene (5 mL ea) to remove any residual DMSO and dried under vacuum overnight. Yield: 84.4%. ^{1}H NMR (400 MHz, Acetonitrile-d_3) δ 9.35 (dd, J = 5.9, 0.7 Hz, 1H), 8.5 (dd, J = 1.9, 0.7 Hz, 1H), 7.85 (dd, J = 5.8, 1.9 Hz, 1H), 1.48 (s, 9H) (Figure S2). Elemental Analysis, found % (theoretical %): C, 46.05 (46.27); H 4.83(5.18); N 5.89 (6.00)

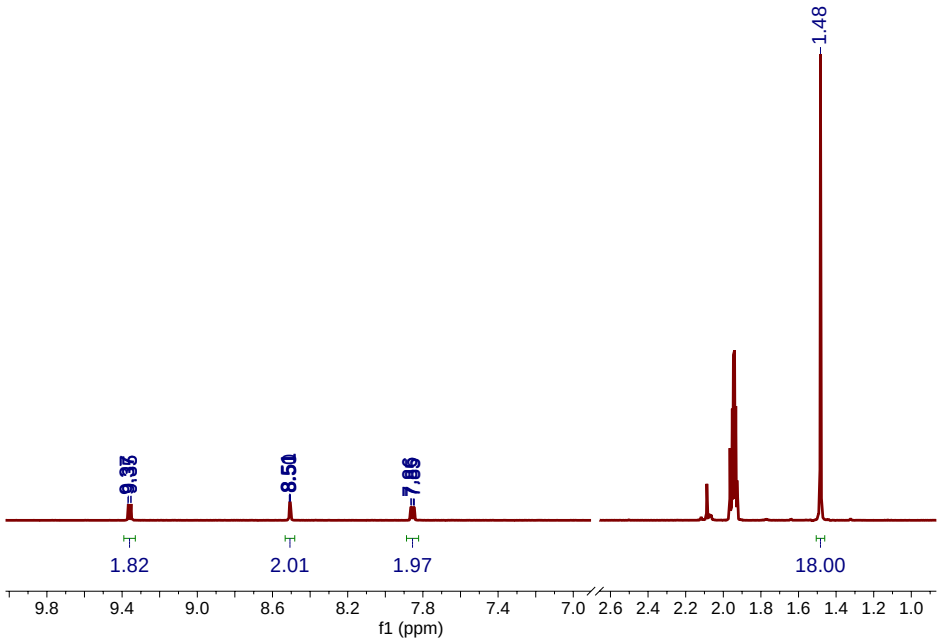


Figure S2 ^{1}H NMR spectrum of MoO_2Cl_2(bpy-^{t}Bu), **1**, taken in CD_3CN on a Bruker 400 MHz instrument at room temperature.

Synthesis of Complex 2, [$MoOCl_2$(bpy-^{t}Bu)]$_2$(μ-O)

A solution of 270 mg of MoO_2Cl_2(bpy-^{t}Bu) was dissolved in 40 mL of acetonitrile. 1 equivalent (150 mg) of triphenylphosphine was dissolved in 40 mL of acetonitrile. The two solutions were mixed together and stirred for 2 hours. Upon mixing the solution immediately turned a dark red. After the reaction was complete, the solvent was evaporated, leaving behind a dark red solid. The solid was then washed three times with 30 mL of pentane (10 mL ea). The solid was dried under vacuum again and then washed five times with 50 mL of diethyl ether (10 mL ea). The final product was dried under vacuum overnight. Yield 72.5%. ^{1}H NMR (400 MHz, Acetonitrile-d_3) δ 9.06 (dd, J = 21.8, 5.9 Hz, 0H), 8.46 – 8.29 (m, 1H), 7.84 – 7.65 (m, 1H), 7.62 (ddt, J = 14.5, 8.9, 2.8 Hz, 3H), 7.52 (dt, J = 8.9, 4.5 Hz, 2H), 1.63 (s, 1H), 1.58– 1.46 (m, 3H), 1.49 – 1.38 (m, 9H), 1.34 (s, 1H) (Figure S3). The ^{31}P NMR spectrum was also taken to ensure the PPh_3 and PPh_3O made during the reaction were removed. Elemental Analysis, found % (theoretical l%): C, 47.98 (47.08); H 4.95(5.27); N 5.93 (6.10).

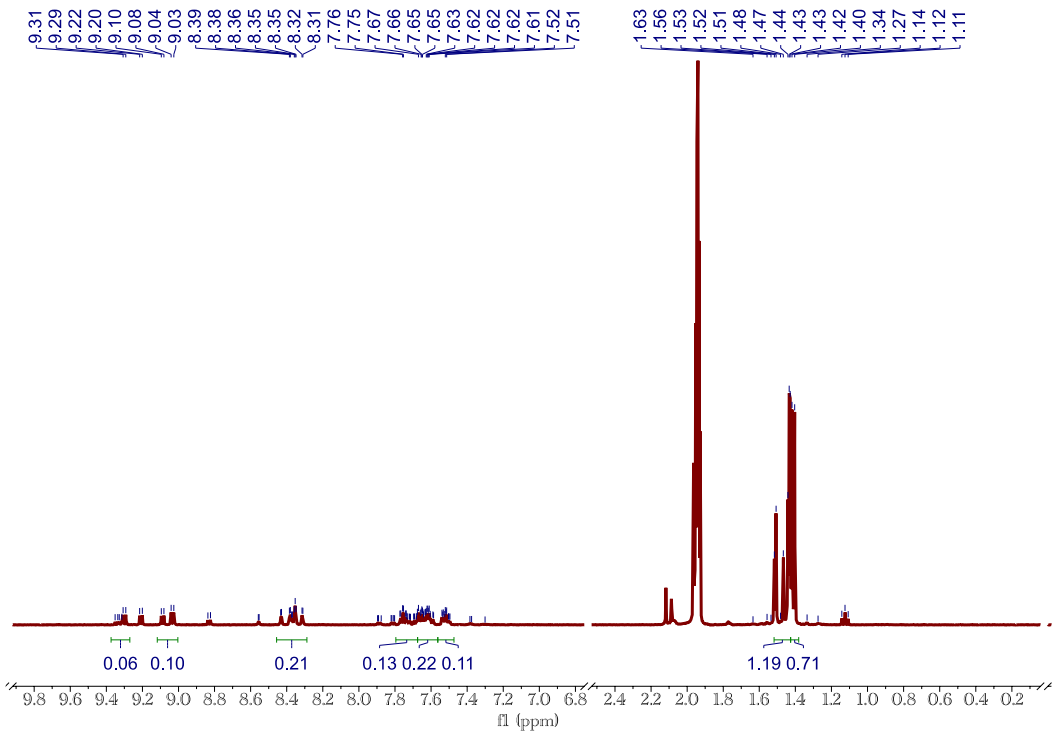


Figure S3. ^{1}H NMR spectrum of [$MoOCl_2$(bpy-^{t}Bu)]$_2$(μ-O) taken in CD_3CN on a Bruker 400 MHz instrument at room temperature. The data represents the equilibrium state of **2** in CD_3CN solution, in agreement with solution phase behavior observed in *J. Am. Chem. Soc.* 2022, 144, 44, 20472-20483.

III. Survey of Thermal Reactivity Between Complex 2 and Oxygen Atom Donors

Oxygen atom donors were added to solutions of $[MoOCl_2(bpy\text{-}^tBu)]_2(\mu\text{-}O)$, **2**, to determine which ones could reoxidize the $[MoO_2Cl_2(bpy\text{-}^tBu)_2](\mu\text{-}O)$ complex back to the starting material of $MoO_2Cl_2(bpy\text{-}^tBu)$, **1**. The ^1H NMR spectrum of the product between the oxygen atom donor and the bimetallic complex, was compared to that of the free ligand to ensure the bipyridine ligand doesn't fall off during oxidation. The product spectrum was also compared to that of the $MoO_2Cl_2(bpy\text{-}^tBu)$, **1**, to determine if oxidation occurs to the desired product. The spectrum of the $[MoOCl_2(bpy\text{-}^tBu)]_2(\mu\text{-}O)$, **2**, complex was also used to compare to see if oxidation had gone to completion.

Oxidation with Pyridine *N*-Oxide

A 2 mM (10 mg) solution of $[MoOCl_2(bpy\text{-}^tBu)]_2(\mu\text{-}O)$ was prepared in 5 mL of acetonitrile. A solution containing 3 equivalents (3 mg) of pyridine *N*-oxide in 5 mL of acetonitrile was added to the $[MoOCl_2(bpy\text{-}^tBu)]_2(\mu\text{-}O)$ solution. The solution was left to stir overnight at room temperature. After stirring overnight, the solution changed from a dark red to a light pink almost colorless solution. The solvent was evaporated under vacuum leaving a pale pink solid. Figure S4 and Figure S5 show the ^1H NMR (400 MHz, Acetonitrile-d_3) δ 9.36 (dd, J = 5.8, 0.7 Hz, 1H), 8.51 (dd, J = 1.9, 0.7 Hz, 1H), 7.86 (dd, J = 5.8, 1.9 Hz, 1H), 1.49 (s, 1H), 1.58 (s, 9H).

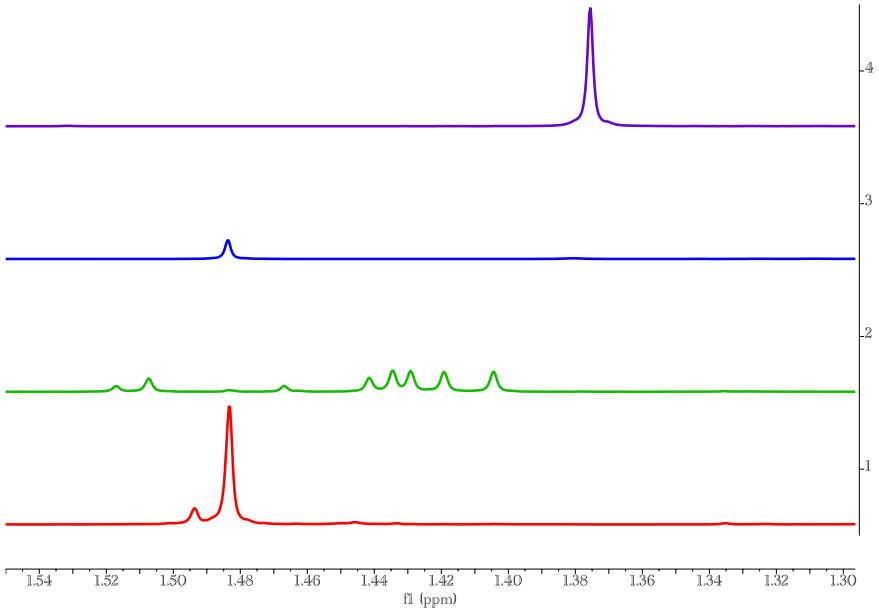


Figure S4 The aliphatic region of the ^1H NMR spectrum of the oxidation of $[MoOCl_2(bpy\text{-}^tBu)]_2(\mu\text{-}O)$ using pyridine *N*-oxide taken in CD_3CN on a Bruker 400 MHz instrument at room temperature. Product of oxidation (red), $[MoOCl_2(bpy\text{-}^tBu)]_2(\mu\text{-}O)$ (green), $MoO_2Cl_2(bpy\text{-}^tBu)$ (blue), $(bpy\text{-}^tBu)$ (purple).

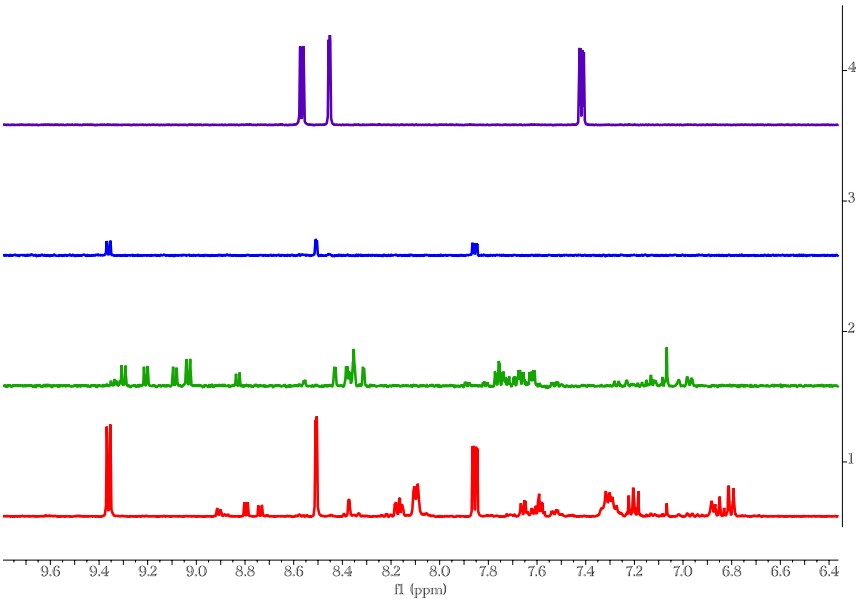


Figure S5 The aromatic region of the ^{1}H NMR spectrum of the oxidation of [$MoOCl_2$(bpy-^{t}Bu)]$_2$(μ-O) using pyridine *N*-oxide taken in CD_3CN on a Bruker 400 MHz instrument at room temperature. Product of oxidation (red), [$MoOCl_2$(bpy-^{t}Bu)]$_2$(μ-O) (green), MoO_2Cl_2(bpy-^{t}Bu) (blue), (bpy-^{t}Bu) (purple)

Oxidation with Iodosobenzene

A 2 mM (10 mg) solution of [$MoOCl_2$(bpy-^{t}Bu)]$_2$(μ-O) was prepared in 5 mL of acetonitrile. A solution containing 3 equivalents (6 mg) of iodosobenzene in 5 mL of acetonitrile was added to the [$MoOCl_2$(bpy-^{t}Bu)]$_2$(μ-O) solution. The solution was left to stir overnight at room temperature. After stirring overnight, the solution became a light pink almost colorless solution. The solvent was evaporated under vacuum leaving a pale pink solid. ^{1}H NMR (400 MHz, Acetonitrile-d_3) δ 9.36 (dd, J = 5.7, 0.7 Hz, 1H), 8.80 (dd, J = 5.8, 0.7 Hz, 1H), 8.51 (dd, J = 1.9, 0.7 Hz, 1H), 8.37 (d, J = 1.9 Hz, 1H), 7.86 (dd, J = 5.8, 1.9 Hz, 1H), 7.66 (dd, J = 5.7, 1.9 Hz, 1H), 1.49 (s, 5H), 1.48 (s, 9H), 1.40 (s, 2H) (Figure S6 and Figure S7).

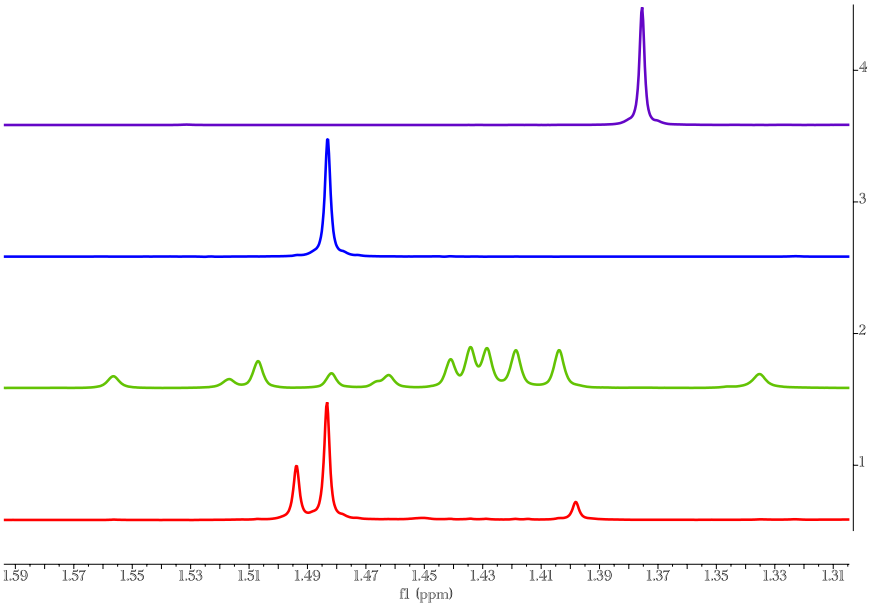


Figure S6 The aliphatic region of the ^{1}H NMR spectrum of the oxidation of $[MoOCl_2(bpy\text{-}^{t}Bu)]_2(\mu\text{-}O)$ using iodosobenzene taken in CD_3CN on a Bruker 400 MHz instrument at room temperature. Product of oxidation (red), $[MoOCl_2(bpy\text{-}^{t}Bu)]_2(\mu\text{-}O)$ (green), $MoO_2Cl_2(bpy\text{-}^{t}Bu)$ (blue), (bpy-^{t}Bu) (purple).

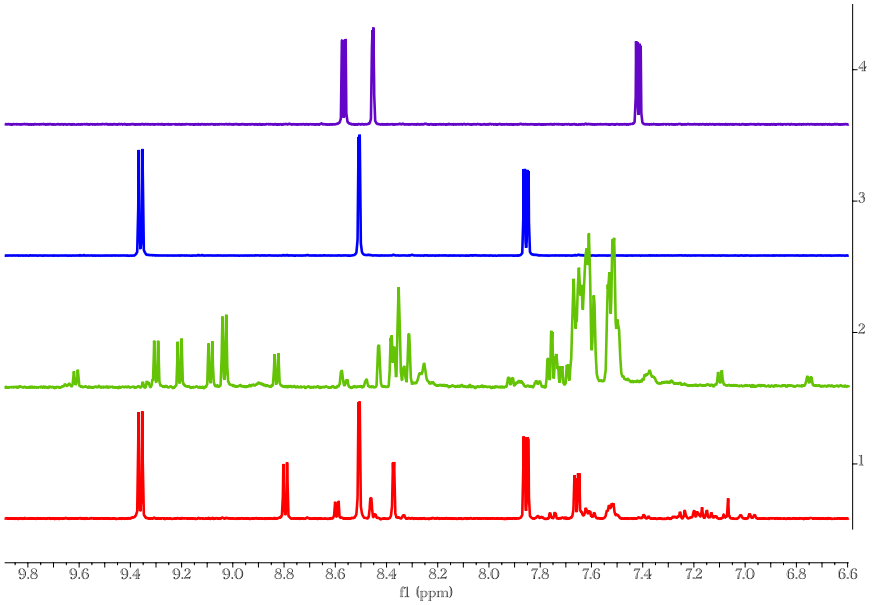


Figure S7. The aromatic region of the ^{1}H NMR spectrum of the oxidation of $[MoOCl_2(bpy\text{-}^{t}Bu)]_2(\mu\text{-}O)$ using iodosobenzene taken in CD_3CN on a Bruker 400 MHz instrument at room temperature. Product of oxidation (red), $[MoOCl_2(bpy\text{-}^{t}Bu)]_2(\mu\text{-}O)$ (green), $MoO_2Cl_2(bpy\text{-}^{t}Bu)$ (blue), (bpy-^{t}Bu) (purple).

Oxidation with Potassium Nitrate

A 2 mM (10 mg) solution of $[MoOCl_2(bpy\text{-}^tBu)]_2(\mu\text{-}O)$ was prepared in 5 mL of acetonitrile. A solution containing 3 equivalents (3 mg) of potassium nitrate in 5 mL of acetonitrile was added to the $[MoOCl_2(bpy\text{-}^tBu)]_2(\mu\text{-}O)$ solution. The solution was left to stir overnight at room temperature. After stirring overnight, the solution became a light pink almost colorless solution. The solvent was evaporated under vacuum leaving a pale pink solid. ^{1}H NMR (400 MHz, Acetonitrile-d_3) δ 9.37 (dd, J = 5.8, 0.6 Hz, 1H), 8.52 (dd, J = 1.9, 0.7 Hz, 1H), 7.86 (dd, J = 5.8, 1.9 Hz, 1H), 7.66 (dd, J = 5.7, 1.9 Hz, 1H), 1.49 (s, 4H), 1.48 (s, 9H) (Figure S8 and Figure S9).

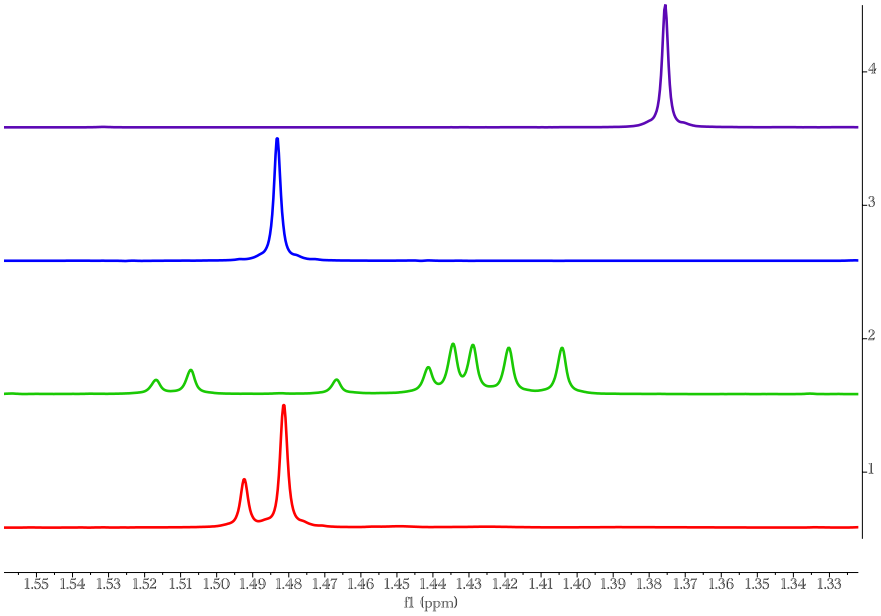


Figure S8. The aliphatic region of the ^{1}H NMR spectrum of the oxidation of $[MoOCl_2(bpy\text{-}^tBu)]_2(\mu\text{-}O)$ using potassium nitrate taken in CD_3CN on a Bruker 400MHz instrument at room temperature. Product of oxidation (red), $[MoOCl_2(bpy\text{-}^tBu)]_2(\mu\text{-}O)$ (green), $MoO_2Cl_2(bpy\text{-}^tBut)$ (blue), (bpy-^{t}Bu) (purple)

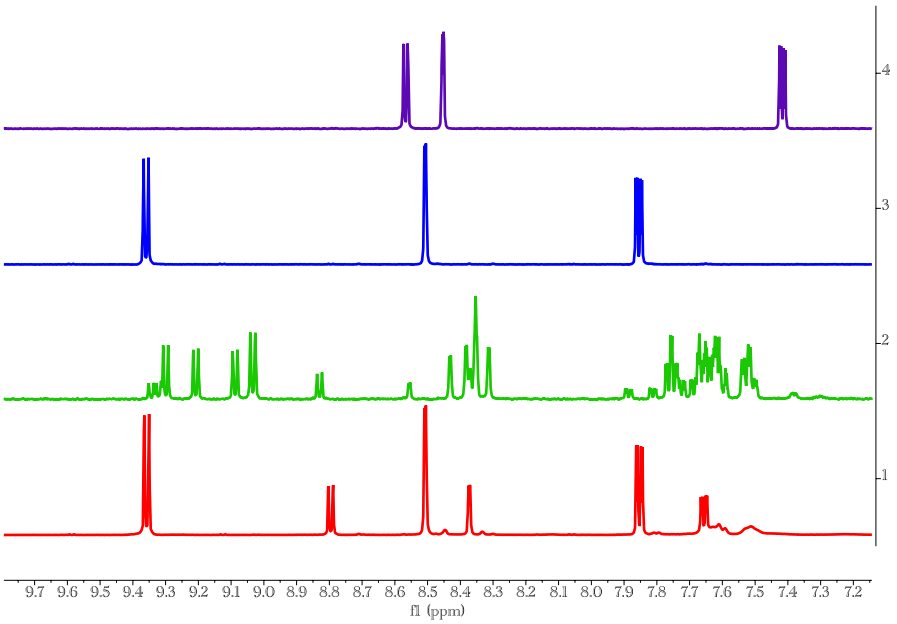


Figure S9. The aromatic region of the ^{1}H NMR spectrum of the oxidation of [$MoOCl_2$(bpy-^{t}Bu)]$_2$(μ-O) using potassium nitrate taken in CD_3CN on a Bruker 400 MHz instrument at room temperature. Product of oxidation (red), [$MoOCl_2$(bpy-^{t}Bu)]$_2$(μ-O) (green), MoO_2Cl_2(bpy-^{t}Bu) (blue), (bpy-^{t}Bu) (purple).

Oxidation with *tert*butyl hydrogen peroxide

A 2 mM (10 mg) solution of [$MoOCl_2$(bpy-^{t}Bu)]$_2$(μ-O) was prepared in 5 mL of acetonitrile. A solution containing 3 equivalents (30 μl) of *tert*butyl hydrogen peroxide in 5mL of acetonitrile was added to the [$MoOCl_2$(bpy-^{t}Bu)]$_2$(μ-O) solution. The solution was left to stir for 6h at room temperature. After stirring, the solution became a colorless solution. The solvent was evaporated under vacuum leaving a white solid. ^{1}H NMR (400 MHz, Acetonitrile-d_3) δ 9.37 (dd, J = 5.8, 0.7 Hz, 2H), 8.74 (s, 1H), 8.51 (dd, J = 1.9, 0.7 Hz, 2H), 7.86 (dd, J = 5.8, 1.9 Hz, 2H), 7.70 – 7.57 (m, 1H), 7.57 – 7.46 (m, 1H), 2.16 – 1.99 (m, 2H), 1.97 (d, J = 2.4 Hz, 3H), 1.51 (d, J = 8.3 Hz, 4H), 1.49 (s, 18H), 1.43 – 1.38 (m, 1H), 1.39 (s, 2H), 1.26 – 1.16 (m, 1H), 1.19 (s, 6H) (Figure S10 and Figure S11).

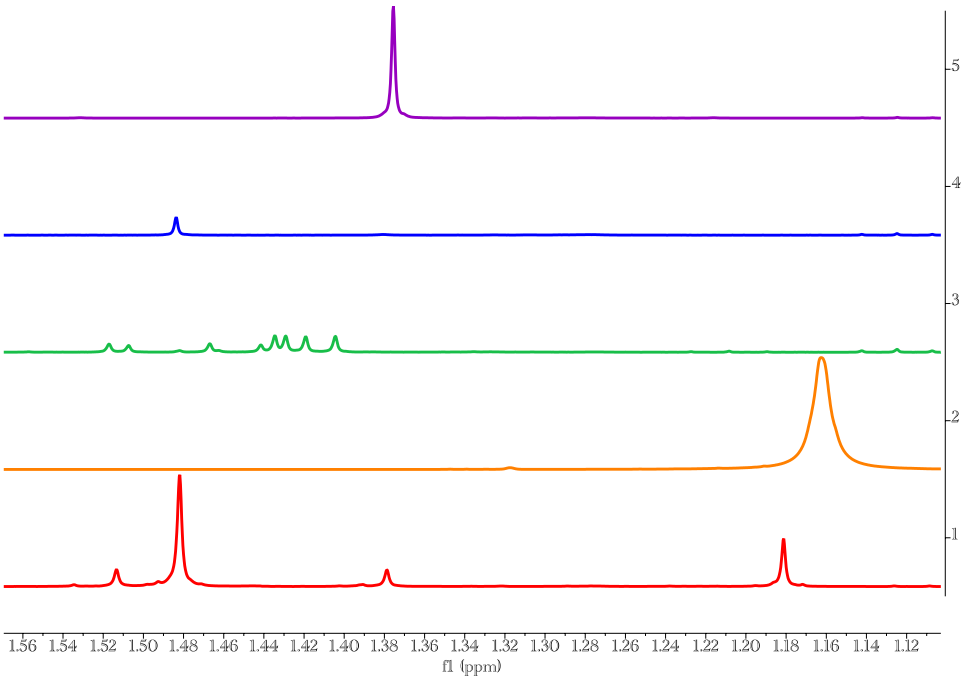


Figure S10. The aliphatic region of the ^{1}H NMR spectrum of the oxidation of $[MoOCl_2(bpy\text{-}^{t}Bu)]_2(\mu\text{-}O)$ using tertbutyl hydrogen peroxide taken in CD_3CN on a Bruker 400 MHz instrument at room temperature. Product of oxidation (red), tertbutyl hydrogen peroxide (orange), $[MoOCl_2(bpy\text{-}^{t}Bu)]_2(\mu\text{-}O)$ (green), $MoO_2Cl_2(bpy\text{-}^{t}Bu)$ (blue), (bpy-^{t}Bu) (purple)

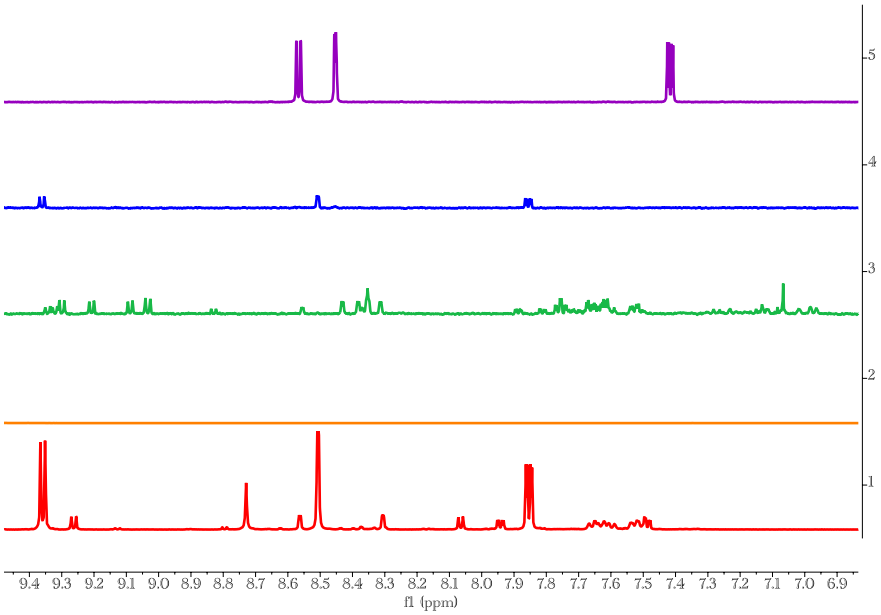


Figure S11. The aromatic region of the ^{1}H NMR spectrum of the oxidation of $[MoOCl_2(bpy\text{-}^{t}Bu)]_2(\mu\text{-}O)$ using tertbutyl hydrogen peroxide taken in CD_3CN on a Bruker 400 MHz instrument at room temperature. Product of oxidation (red), tertbutyl hydrogen peroxide (orange), $[MoOCl_2(bpy\text{-}^{t}Bu)]_2(\mu\text{-}O)$ (green), $MoO_2Cl_2(bpy\text{-}^{t}Bu)$ (blue), (bpy-^{t}Bu) (purple)

Oxidation with trimethylamine *N*-oxide

A 2 mM (10 mg) solution of $[MoOCl_2(bpy\text{-}^tBu)]_2(\mu\text{-}O)$ was prepared in 5 mL of acetonitrile. A solution containing 3 equivalents (2.1 mg) of trimethylamine *N*-oxide in 5 mL of acetonitrile was added to the $[MoOCl_2(bpy\text{-}^tBu)]_2(\mu\text{-}O)$ solution. The solution was left to stir overnight at room temperature. After stirring overnight, the solution became an almost colorless solution. The solvent was evaporated under vacuum leaving a white solid. ^{1}H NMR (400 MHz, Acetonitrile-d_3) δ 13.94 (s, 4H), 8.58 (s, 3H), 8.46 (s, 3H), 7.70 – 7.59 (m, 1H), 7.53 (ddd, J = 8.4, 6.6, 2.9 Hz, 1H), 7.43 (s, 3H), 3.30 (s, 1H), 2.95 (s, 4H), 2.20 (s, 0H), 2.12– 1.99 (m, 1H), 1.97 (d, J = 2.4 Hz, 7H), 1.85 (s, 1H), 1.48 (s, 2H), 1.54 – 1.40 (m, 1H), 1.438 (s, 26H), 1.29 (s, 1H) (Figure S12 and Figure S13).

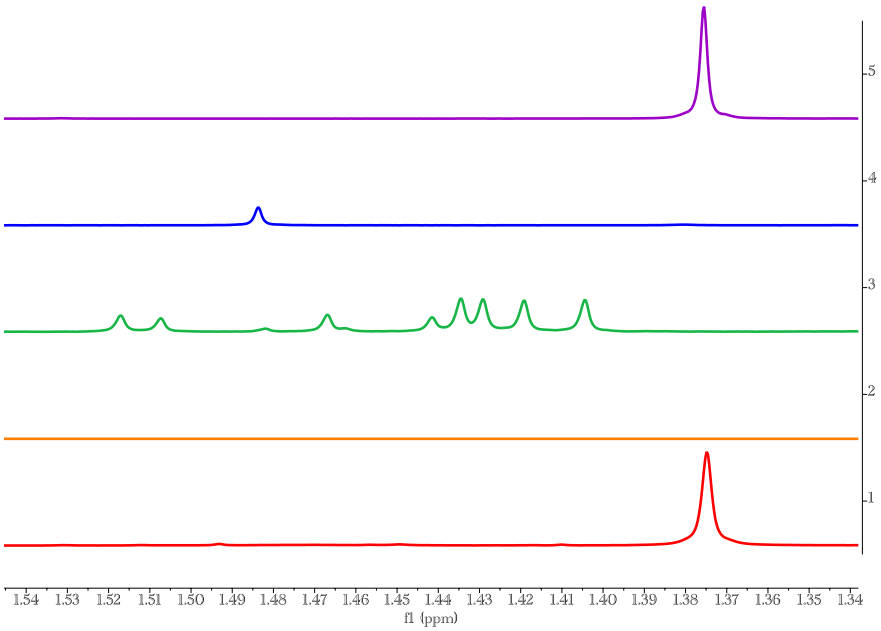


Figure S12. The aliphatic region of the ^{1}H NMR spectrum of the oxidation of $[MoOCl_2(bpy\text{-}^tBu)]_2(\mu\text{-}O)$ using triethylamine *N*-oxide taken in CD_3CN on a Bruker 400 MHz instrument at room temperature. Product of oxidation (red), triethylamine *N*-oxide (orange), $[MoOCl_2(bpy\text{-}^tBu)]_2(\mu\text{-}O)$ (green), $MoO_2Cl_2(bpy\text{-}^tBu)$ (blue), $(bpy\text{-}^tBu)$ (purple).

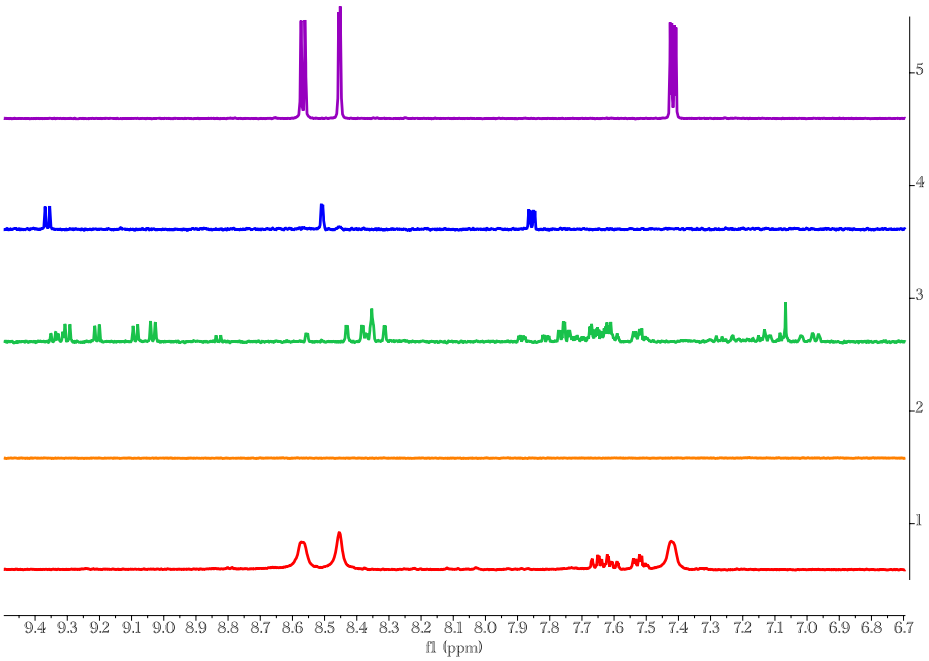


Figure S13. The aromatic region of the ^{1}H NMR spectrum of the oxidation of [$MoOCl_2$(bpy-^{t}Bu)]$_2$(μ-O) using triethylamine *N*-oxide taken in CD_3CN on a Bruker 400 MHz instrument at room temperature. Product of oxidation (red), triethylamine *N*-oxide (orange), [$MoOCl_2$(bpy-^{t}Bu)]$_2$(μ-O) (green), MoO_2Cl_2(bpy-^{t}Bu) (blue), (bpy-^{t}Bu) (purple).

Oxidation with cyanopyridine *N*-oxide

A 2 mM (10 mg) solution of [$MoOCl_2$(bpy-^{t}Bu)]$_2$(μ-O) was prepared in 5 mL of acetonitrile. A solution containing 3 equivalents (3.4 mg) of cyanopyridine *N*-oxide in 5 mL of acetonitrile was added to the [$MoOCl_2$(bpy-^{t}Bu)]$_2$(μ-O) solution. The solution was left to stir for 3 days at room temperature. After stirring 3 days, the solution was still a dark red solution. The solvent was evaporated under vacuum leaving a pink solid. ^{1}H NMR (400 MHz, Acetonitrile-d_3) δ 9.36 (t, *J* = 6.2 Hz, 1H), 9.31 (d, *J* = 6.1 Hz, 1H), 9.22 (d, *J* = 5.9 Hz, 1H), 9.07 (dd, *J* = 21.7, 5.9 Hz, 2H), 8.82 (dd, *J* = 15.9, 5.9 Hz, 1H), 8.52 (d, *J* = 1.9 Hz, 1H), 8.44 (d, *J* = 1.9 Hz, 1H), 8.41 – 8.33 (m, 3H), 8.32 (d, *J* = 1.8 Hz, 1H), 8.27 (d, *J* = 6.8 Hz, 1H), 8.22 – 8.15 (m, 3H), 7.91 – 7.80 (m, 1H), 7.80 – 7.72 (m, 2H), 7.75 – 7.62 (m, 4H), 7.63 (q, *J* = 2.4 Hz, 3H), 7.53 (dt, *J* = 8.4, 4.3 Hz, 1H), 2.15– 2.06 (m, 1H), 1.97 (s, 1H), 1.63 – 1.49 (m, 6H), 1.53 – 1.39 (m, 45H), 1.34 (s, 1H), 1.28 (s, 0H) (Figure S14 and Figure S15).

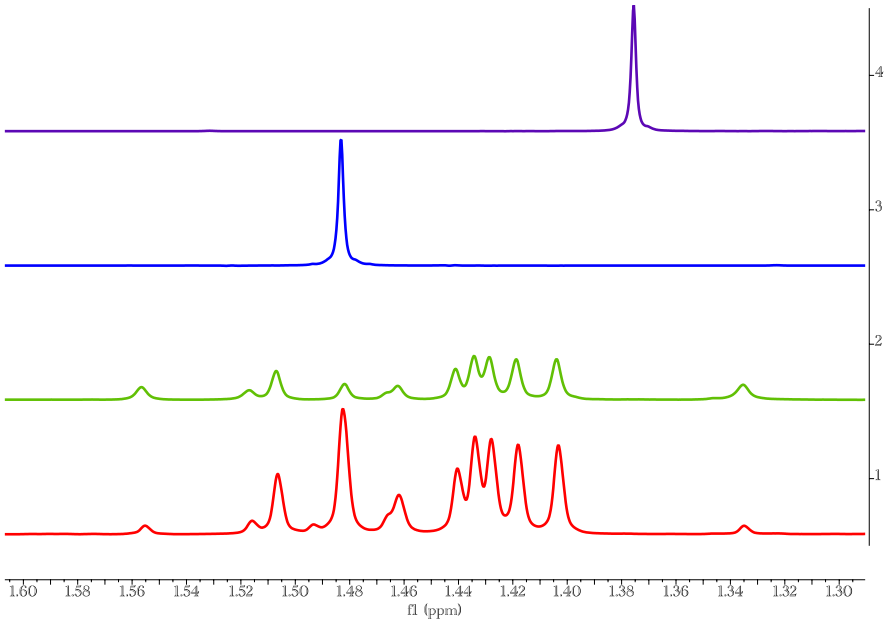


Figure S14. The aliphatic region of the ^{1}H NMR spectrum of the oxidation of [$MoOCl_2$(bpy-^{t}Bu)]$_2$(μ-O) using cyanopyridine *N*-oxide taken in CD_3CN on a Bruker 400 MHz instrument at room temperature. Product of oxidation (red), [$MoOCl_2$(bpy-^{t}Bu)]$_2$(μ-O) (green), MoO_2Cl_2(bpy-^{t}Bu) (blue), (bpy-^{t}Bu) (purple).

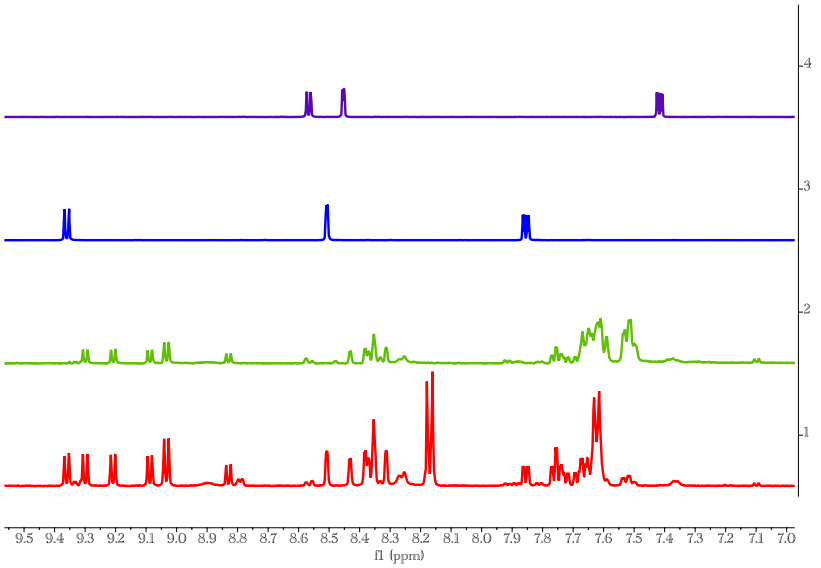


Figure S15. The aromatic region of the ^{1}H NMR spectrum of the oxidation of [$MoOCl_2$(bpy-^{t}Bu)]$_2$(μ-O) using cyanopyridine *N*-oxide taken in CD_3CN on a Bruker 400 MHz instrument at room temperature. Product of oxidation (red), [$MoOCl_2$(bpy-^{t}Bu)]$_2$(μ-O) (green), MoO_2Cl_2(bpy-^{t}Bu) (blue), (bpy-^{t}Bu) (purple).

Oxidation with lithium carbonate

A 2 mM (10 mg) solution of $[MoOCl_2(bpy\text{-}^tBu)]_2(\mu\text{-}O)$ was prepared in 5 mL of acetonitrile. A solution containing 3 equivalents (2.8 mg) of lithium carbonate in 5 mL of acetonitrile was added to the $[MoOCl_2(bpy\text{-}^tBu)]_2(\mu\text{-}O)$ solution. The solution was left to stir for 3 days at room temperature. After stirring, the solution remained a dark red solution. The solvent was evaporated under vacuum leaving a pink solid. ^{1}H NMR (400 MHz, Acetonitrile-d_3) δ 9.31 (d, J = 6.1 Hz, 0H), 9.13 – 9.01 (m, 1H), 8.46 – 8.35 (m, 1H), 8.39 – 8.32 (m, 1H), 8.30 (dd, J = 20.1, 4.0 Hz, 1H), 7.80 – 7.58 (m, 4H), 7.57 – 7.48 (m, 1H), 1.97 (d, J = 2.4 Hz, 2H), 1.88 (s, 1H), 1.54 (d, J = 15.4 Hz, 2H), 1.54 – 1.45 (m, 7H), 1.45 (s, 2H), 1.45 – 1.39 (m, 15H), 1.34 (s, 1H) (Figure S16 and Figure S17).

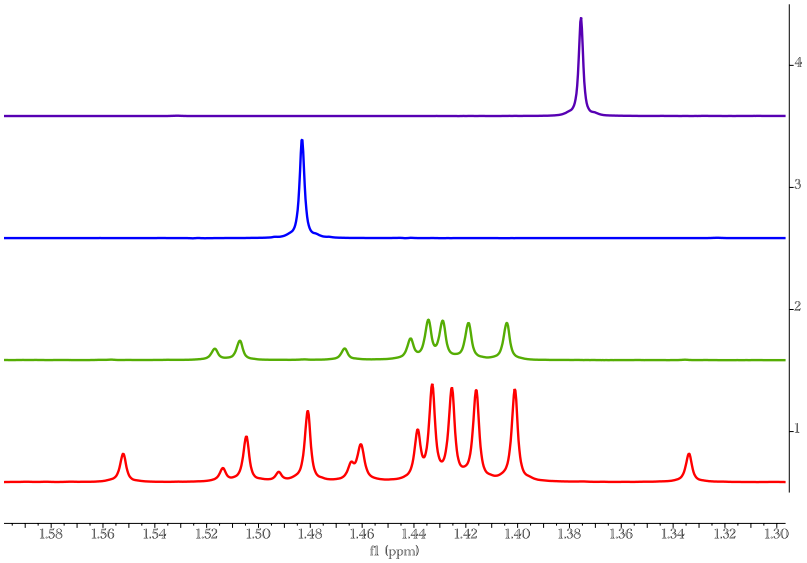


Figure S16. The aliphatic region of the ^{1}H NMR spectrum of the oxidation of $[MoOCl_2(bpy\text{-}^tBu)]_2(\mu\text{-}O)$ using lithium carbonate taken in CD_3CN on a Bruker 400 MHz instrument at room temperature. Product of oxidation (red), $[MoOCl_2(bpy\text{-}^tBu)]_2(\mu\text{-}O)$ (green), $MoO_2Cl_2(bpy\text{-}^tBu)$ (blue), (bpy-^{t}Bu) (purple).

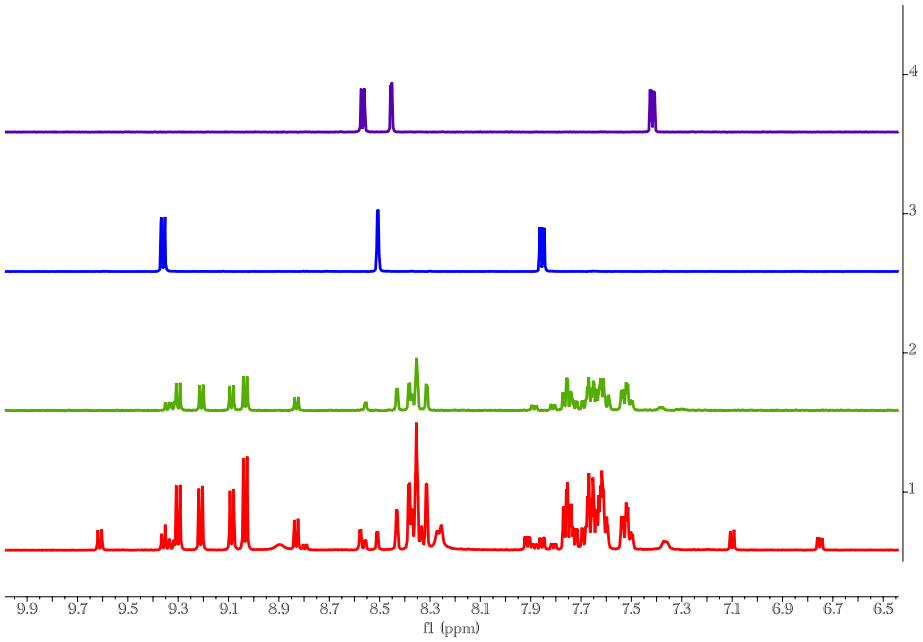
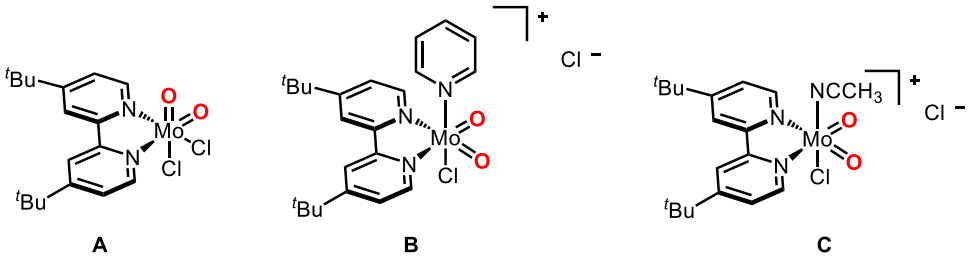


Figure S17. The aromatic region of the ^{1}H NMR spectrum of the oxidation of [$MoOCl_2$(bpy-^{t}Bu)]$_2$(μ-O) using lithium carbonate taken in CD_3CN on a Bruker 400MHz instrument at room temperature. Product of oxidation (red), [$MoOCl_2$(bpy-^{t}Bu)]$_2$(μ-O) (green), MoO_2Cl_2(bpy-^{t}Bu) (blue), (bpy-^{t}Bu) (purple).

IV. Identification of Minor Product Formed Upon Oxidation of Complex 2

During the oxidation reactions, it was observed that if oxidation occurred a peak corresponding to the ^{t}Butyl peak in MoO_2Cl_2(bpy-^{t}Bu) appeared at 1.48 ppm. Another peak slightly shifted to 1.49 ppm also appeared, indicating that another species was forming during these reactions. Several different reactions were explored to try and identify what this product could be. We primarily considered 3 possible products shown below: Chloride/Oxo structural isomers (*cis* chlorides), **A**; ionic isomer with an outersphere Cl^- and coordinated pyridine, **B**; ionic isomer with an outersphere Cl^- and coordinated solvent (CH_3CN), **C**.



To investigate the possible presence of *cis/trans* chloride isomers, samples of the product of the oxidation containing mixtures were heated based on the hypothesis that the unidentified product would readily convert to the more stable *trans* chloride isomer if the *cis* isomer were present.

To investigate the possibility of the inner sphere pyridine or solvent ligands, halide abstractions from **1** were attempted in the presence of pyridine or in the coordinating CH_3CN solvent.

Investigation of Isomerization of Chloride Ligands

A 2 mM solution (46 mg) of [$MoOCl_2$(bpy-^{t}Bu)]$_2$(μ-O) was made in 25 mL of acetonitrile. One equivalent of pyridine *N*-oxide (5 mg) in 25 mL of acetonitrile was added to this solution. The solution was stirred overnight and became a light pink solution. The resulting product was then refluxed at 80°C overnight. The solution turned a light orange solution after reflux. The product was dried under vacuum leaving a light-yellow solid. ^{1}H NMR (400 MHz, Acetonitrile-d_3) δ 9.36 (dd, J = 5.9, 0.6 Hz, 2H), 8.51 (dd, J = 1.9, 0.7 Hz, 2H), 8.16 (s, 1H), 7.85 (dd, J = 5.8, 1.9 Hz, 2H), 7.69 – 7.56 (m, 2H), 7.56 – 7.47 (m, 1H), 7.37 (s, 2H), 2.09 (s, 4H), 2.10 – 2.04 (m, 1H), 1.97 (d, J = 2.4 Hz, 1H), 1.48 (d, J = 4.2 Hz, 21H) (Figure S18 and Figure S19).

While some conversion of the unidentified species with a chemical shift at 1.49 ppm did occur, the retention of significant quantities of the minor product indicated that chloride isomerization was unlikely.

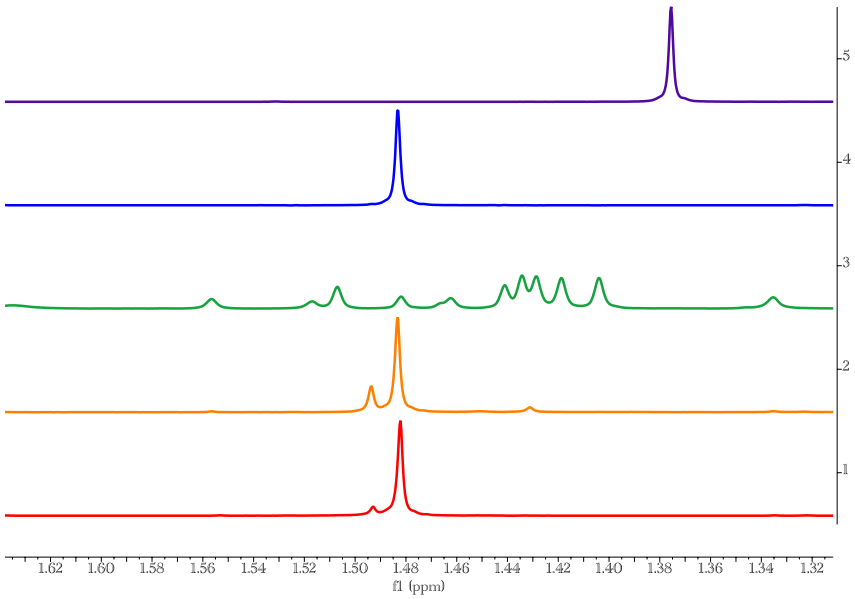


Figure S18. The aliphatic region of the ^{1}H NMR spectrum of the possible chloride isomerization of $[MoOCl_2(bpy\text{-}^{t}Bu)]_2(\mu\text{-}O)$ after heating in the presence of pyridine *N*-oxide taken in CD_3CN on a Bruker 400 MHz instrument at room temperature. Product after heating (red), product before heating (orange), $[MoOCl_2(bpy\text{-}^{t}Bu)]_2(\mu\text{-}O)$ (green), $MoO_2Cl_2(bpy\text{-}^{t}Bu)$ (blue), (bpy-^{t}Bu) (purple).

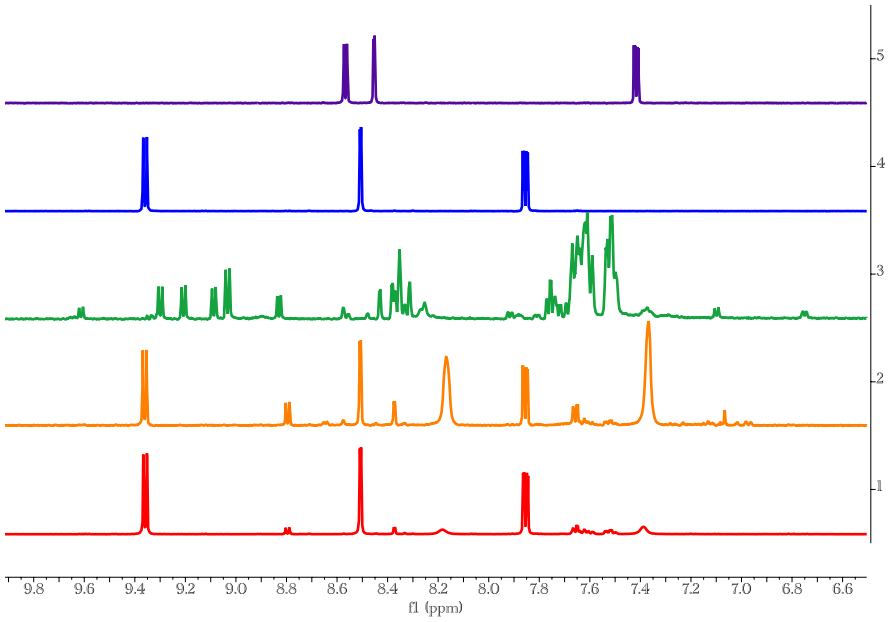


Figure S19. The aromatic region of the ^{1}H NMR spectrum of the possible chloride isomerization of $[MoOCl_2(bpy\text{-}^{t}Bu)]_2(\mu\text{-}O)$ after heating in the presence of pyridine *N*-oxide taken in CD_3CN on a Bruker 400 MHz instrument at room temperature. Product after heating (red), product before heating (orange), $[MoOCl_2(bpy\text{-}^{t}Bu)]_2(\mu\text{-}O)$ (green), $MoO_2Cl_2(bpy\text{-}^{t}Bu)$ (blue), (bpy-^{t}Bu) (purple)

Investigation of Coordination of Pyridine

The coordination of pyridine was investigated through a halide abstraction reaction. A 2 mM solution of MoO_2Cl_2(bpy-^{t}Bu) (5 mg) was made in 5 mL of acetonitrile. A one equivalent solution of pyridine (1 mL) and 1 equivalent of $AgPF_6$ (2.5 mg) was made in 5mL of acetonitrile. Both solutions were placed in the freezer and left for about an hour to allow them to cool to -30°C. Once the solutions were cooled the MoO_2Cl_2(bpy-^{t}Bu) solution was stirred. The pyridine and $AgPF_6$ solution was added dropwise to the MoO_2Cl_2(bpy-^{t}Bu) solution. The reaction was allowed to warm to room temperature and left to stir overnight. A white solid precipitated out of solution, which was the formation of AgCl. The solution was filtered through celite to remove the precipitate. The filtered solution was then dried under vacuum leaving a white solid behind. ^{1}H NMR (400 MHz, Acetonitrile-d_3) δ 12.42 (s, 0H), 8.60 – 8.54 (m, 4H), 7.90 (tt, J = 7.7, 1.9 Hz, 2H), 7.45 (dd, J = 7.7, 5.4 Hz, 4H), 1.52 – 1.38 (m, 3H), 1.42 – 1.25 (m, 2H) (Figure S20 and Figure S21).

The resulting ^{1}H NMR data indicates that pyridine coordination to Mo leads to a mixture of products and not the minor feature observed upon oxidation of **2** to **1**.

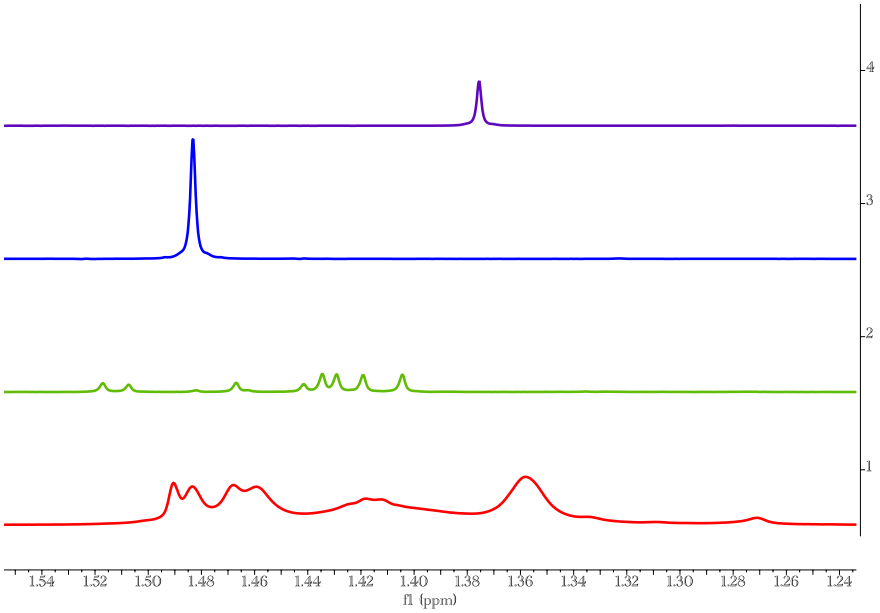


Figure S20. The aliphatic region of the ^{1}H NMR spectrum of the halide abstraction of MoO_2Cl_2(bpy-^{t}Bu) with $AgPF_6$ in the presence of pyridine taken in CD_3CN on a Bruker 400MHz instrument at room temperature. Product (red), [$MoOCl_2$(bpy-^{t}Bu)]$_2$(μ-O) (green), MoO_2Cl_2(bpy-^{t}Bu) (blue), (bpy-^{t}Bu) (purple)

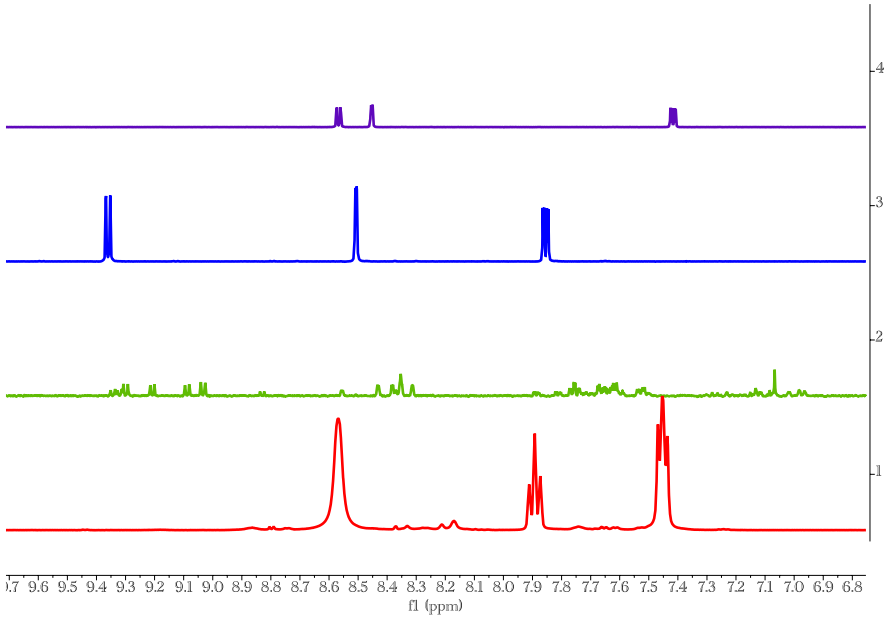


Figure S21. The aromatic region of the ^{1}H NMR spectrum of the halide abstraction of MoO_2Cl_2(bpy-^{t}Bu) with $AgPF_6$ in the presence of pyridine taken in CD_3CN on a Bruker 400MHz instrument at room temperature. Product (red), [$MoOCl_2$(bpy-^{t}Bu)]$_2$(μ-O) (green), MoO_2Cl_2(bpy-^{t}Bu) (blue), (bpy-^{t}Bu) (purple)

Investigation of Coordination of Acetonitrile

A 2 mM (5 mg) solution of MoO_2Cl_2(bpy-^{t}Bu) solution was made in 5 mL of acetonitrile. A one equivalent solution of $AgPF_6$ (2.5 mg) was made in 5 mL of acetonitrile. Both solutions were placed in the freezer for about an hour to cool to -30°C. After cooling the $AgPF_6$ solution was added dropwise to a stirring MoO_2Cl_2(bpy-^{t}Bu) solution. The reaction was allowed to warm to room temperature and left to stir overnight. A white precipitate formed indicating the formation of AgCl. The solution was filtered through celite to remove AgCl. The solution was then dried under vacuum overnight leaving behind a white solid. ^{1}H NMR (400 MHz, Acetonitrile-d_3) δ 8.79 (dd, J = 5.7, 0.7 Hz, 2H), 8.64 (d, J = 5.3 Hz, 6H), 8.38 (dd, J = 1.9, 0.6 Hz, 2H), 8.11 (tt, J = 7.8, 1.7 Hz, 2H), 7.65 (ddd, J = 7.4, 5.8, 1.6 Hz, 7H), 7.45 – 7.39 (m, 1H), 1.96 (d, J = 2.4 Hz, 2H), 1.85 (s, 1H), 1.49 (s, 19H), 1.48 (d, J = 12.6 Hz, 3H), 1.28 (s, 1H) (Figure S22 and Figure S23).

The product of halide abstraction results in a product with coincidental chemical shifts of as the unidentified product generated upon oxidation of **2**. It is thus proposed that the minor product observed is [MoO_2Cl(bpy-^{t}Bu)($NCCH_3$)]$^{+}$ with an outersphere anion.

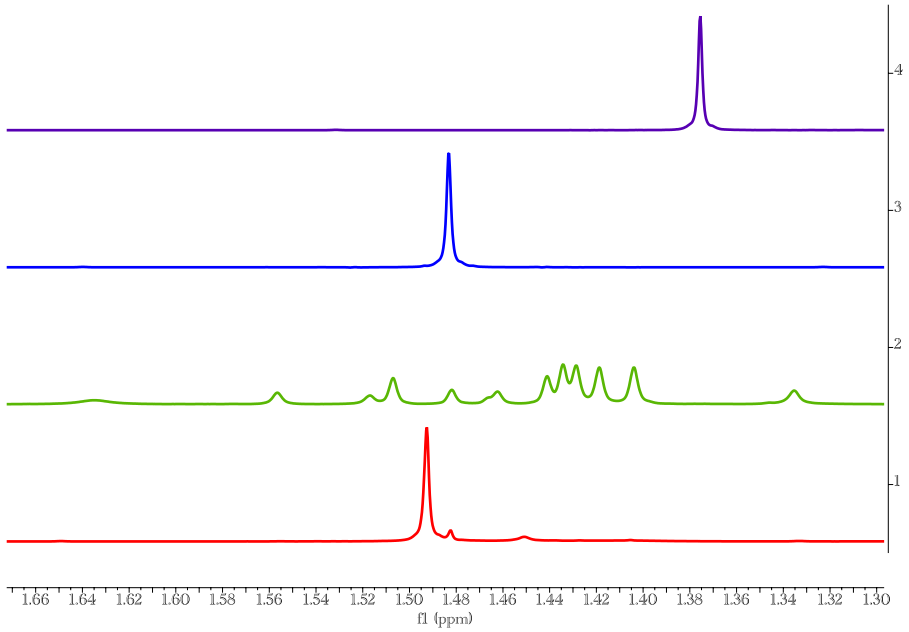


Figure S22. The aliphatic region of the ^{1}H NMR spectrum of the halide abstraction of MoO_2Cl_2(bpy-^{t}Bu) with $AgPF_6$ taken in CD_3CN on a Bruker 400 MHz instrument at room temperature. Product (red), [$MoOCl_2$(bpy-^{t}Bu)]$_2$(μ-O) (green), MoO_2Cl_2(bpy-^{t}Bu) (blue), (bpy-^{t}Bu) (purple)

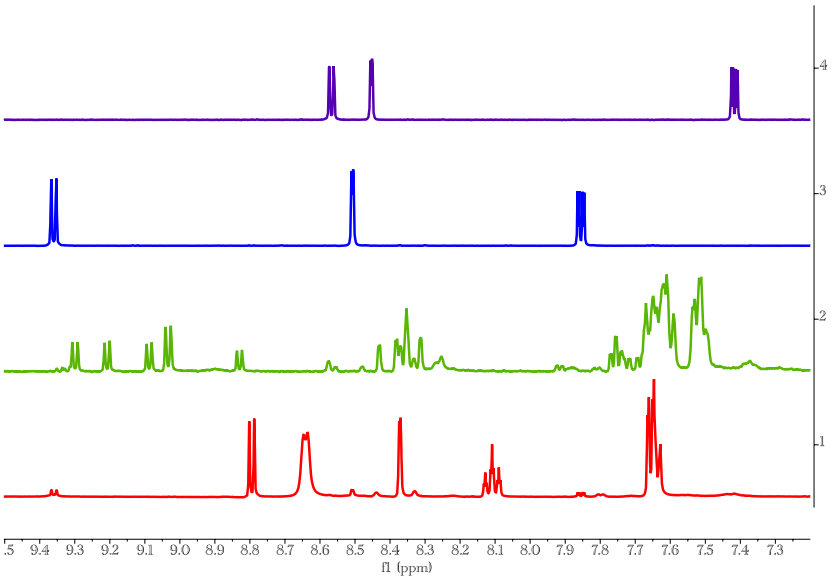


Figure S23. The aromatic region of the ^{1}H NMR spectrum of the halide abstraction of MoO_2Cl_2(bpy-^{t}Bu) with $AgPF_6$ taken in CD_3CN on a Bruker 400 MHz instrument at room temperature. Product (red), [$MoOCl_2$(bpy-^{t}Bu)]$_2$(μ-O) (green), MoO_2Cl_2(bpy-^{t}Bu) (blue), (bpy-^{t}Bu) (purple)

V. Kinetic Analysis of the Oxidation of Complex 2

Pyridine *N*-oxide was used as the oxygen atom donor for the remainder of these studies due to its ability to reoxidize the $[MoOCl_2(bpy\text{-}^tBu)]_2(\mu\text{-}O)$ complex without displacing a bipyridine ligand, and it is photostable. The rate of oxidation was monitored by UV-Vis by monitoring the decrease in absorbance at 520 nm due to the $[MoOCl_2(bpy\text{-}^tBu)]_2(\mu\text{-}O)$ complex.

Oxidation Rate with Pyridine *N*-Oxide

A 2 mM (10 mg) solution of $[MoOCl_2(bpy\text{-}^tBu)]_2(\mu\text{-}O)$ was prepared in 5 mL of acetonitrile. A 600 mM (285 mg) solution of pyridine *N*-oxide was prepared in 5 mL of acetonitrile. Both solutions were diluted by a factor of 5 to ensure absorbance at 520 nm was below 1. 1mL of the $[MoOCl_2(bpy\text{-}^tBu)]_2(\mu\text{-}O)$ solution was added to 6 different quartz cuvettes. A portion of the pyridine *N*-oxide solution was added to each cuvette to achieve solutions with a concentration between 10 eq-300 eq of pyridine *N*-oxide. Acetonitrile was added to the cuvettes to achieve a total volume of 2 mL in each cuvette. The cuvettes were wrapped in parafilm to prevent oxygen leaks. The change in absorbance of each solution was monitored over time by taking the UV-Vis every half an hour for 8 hours (Figure S24). The absorbance overtime was plotted for each sample. Using Beer's Law,

$$A = \varepsilon c l$$

A= absorbance (AU)
ε= extinction coefficient ($M^{-1}cm^{-1}$)
c= concentration (M)
l= path length (cm)

the absorbance at 520 nm was converted to moles of $[MoOCl_2(bpy\text{-}^tBu)]_2(\mu\text{-}O)$ using the extinction coefficient of 8.57 $M^{-1}cm^{-1}$. The decrease in moles of $[MoOCl_2(bpy\text{-}^tBu)]_2(\mu\text{-}O)$ was plotted against time giving the rate of oxidation.

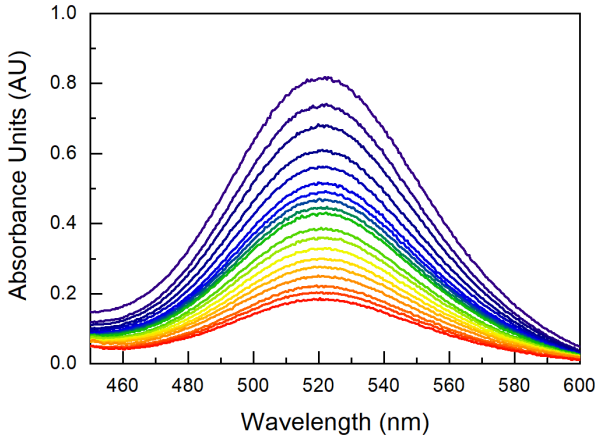


Figure S24. The UV-Vis spectra of $[MoOCl_2(bpy\text{-}^tBu)]_2(\mu\text{-}O)$ and 10 eq of pyridine N-oxide measured over time. UV-Vis spectra shown in 30 min increments from 0 min (purple) to 8 h (red)

Rate of Oxidation with Functionalized Pyridine *N*-Oxides

A 2 mM (10 mg) solution of $[MoO_2Cl_2(bpy\text{-}^tButyl)]_{2(}\mu\text{-}O)$ was prepared in 5 mL of acetonitrile. A 200 mM solution of *para* functionalized pyridine *N*-oxides were made in 5 mL of acetonitrile (R=OMe, Me, H, Cl, CN, lut (2,6-lutidine *N*-oxide)). All solutions were diluted by a

factor of 5 to ensure absorbance was below 1 at 520 nm. 1 mL of the $[MoOCl_2(bpy\text{-}^tBu)]_2(\mu\text{-}O)$ solution was added to 6 different quartz cuvettes. A 1 mL portion of each of the different pyridine *N*-oxide solutions was added to one of the cuvettes to achieve solutions with 100 eq for each pyridine *N*-oxide. The cuvettes were wrapped in parafilm to prevent oxygen leaks. The change in absorbance of each solution was monitored over time by taking the UV-Vis every half hour for 8 hours (Figure S25). The absorbance at 520 nm was converted to moles of $[MoOCl_2(bpy\text{-}^tBu)]_2(\mu\text{-}O)$ using the extinction coefficient of 8.57 $M^{-1}cm^{-1}$. The decrease in moles of bimetallic was plotted against time giving the rate of oxidation for each functionalized pyridine *N*-oxide.

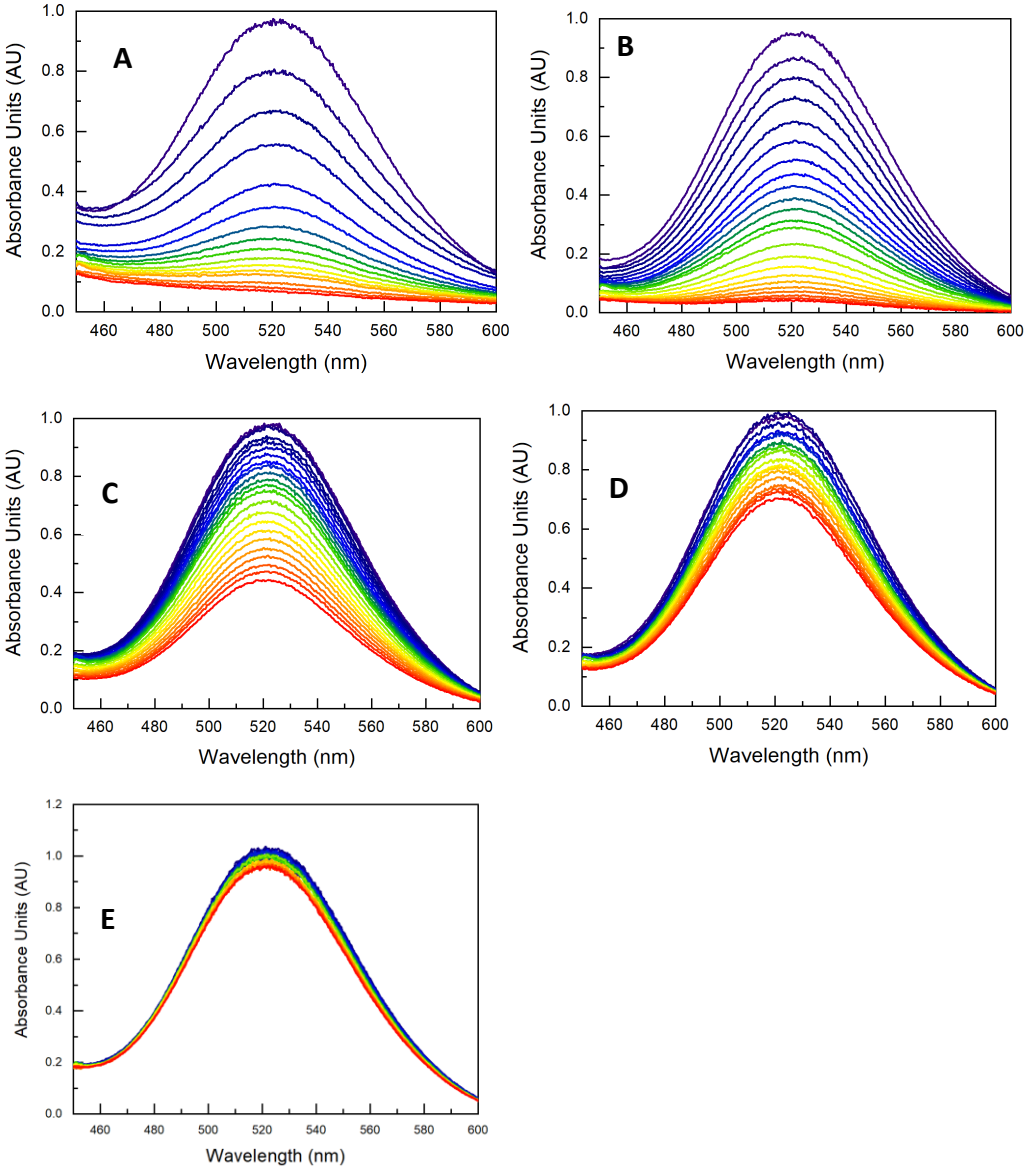


Figure S25. The UV-vis spectra of oxidation of $[MoOCl_2(bpy\text{-}^tBu)]_2(\mu\text{-}O)$ with 100 eq of a functionalized pyridine *N*-oxide. Spectra are shown in 30 min increments with 0 min in purple and 8 h in red. (A) OMe pyridine *N*-oxide (B) Me pyridine *N*-oxide (C) Cl pyridine *N*-oxide (D) lutidine *N*-oxide (E) CN pyridine *N*-oxide

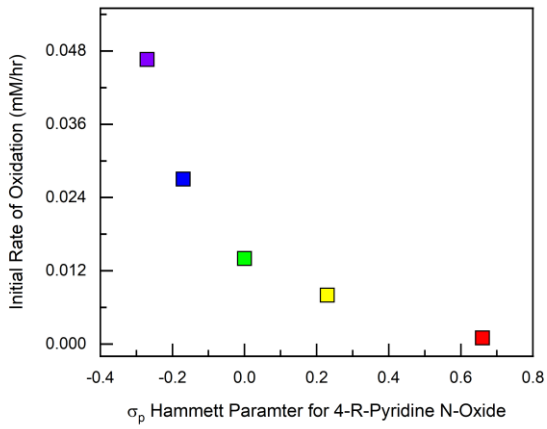


Figure S26. Hammett analysis for the initial rates of oxidation of $[MoOCl_2(bpy\text{-}^tBu)]_2(\mu\text{-}O)$ with 100 eq of a functionalized pyridine *N*-oxide. 4-R-Pyridine *N*-oxides used: R= OCH_3 (purple), CH_3 (blue), H (green), Cl (yellow), CN (red)

Oxidation Rate Law Dependence on Pyridine N-oxide

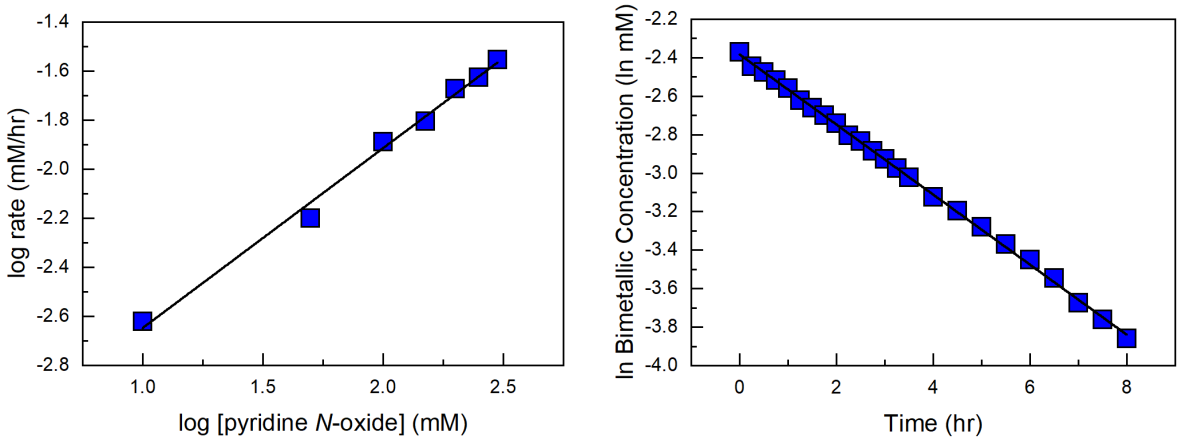


Figure S27. The log of the rate of oxidation vs the log of concentration of pyridine N-oxide. The linear plot shows the dependance of the reaction rate on pyridine *N*-oxide. y = 0.73x - 3.38 R^2 = 0.99 (left) The ln of $[MoOCl_2(bpy\text{-}^tBu)]_2(\mu\text{-}O)$ concentration vs time at 100 eq of pyridine *N*-oxide. The linear plot shows the first-order dependance of the reaction rate on pyridine *N*-oxide. y = -0.18x - 2.38 R^2 = 0.99

Oxidation Rate Law Dependence on Chloride

A 20 mL stock solution of 10 mM (19 mg) pyridine *N*-oxide was prepared in acetonitrile. A 2 mM (10 mg) solution of $[MoOCl_2(bpy\text{-}^tBu)]_2(\mu\text{-}O)$ was prepared in 5 mL of the stock solution. A 16 mM of solution of tetraphenyl phosphonium chloride (TPPCl was prepared in 5 mL of the stock solution. Both solutions were diluted by a factor of 10 to ensure absorbance was below 1 at 520 nm. 1 mL of the $[MoOCl_2(bpy\text{-}^tBu)]_2(\mu\text{-}O)$ solution was added to 6 different quartz cuvettes. A portion of the TPPCl solution was added to each cuvette to achieve solutions with 0.1 eq-2 eq

of TPPCl. Solutions were made in the same way to achieve another set of samples with TPPCl concentrations between 3 eq-32 eq. The diluted stock solution of pyridine *N*-oxide was added to the cuvettes to achieve a total volume of 2mL in each cuvette. The cuvettes were wrapped in parafilm to prevent oxygen leaks. The change in absorbance of each solution was monitored over time by taking the UV-Vis every hour for 8 hours (Figure S28). The absorbance at every time point for each solution was plotted. It was observed that the absorbance of bimetallic at 520 nm decreased over time. The absorbance at this wavelength was converted to moles of bimetallic using the extinction coefficient of 8.57 $M^{-1}cm^{-1}$. The decrease in moles of bimetallic was plotted against time giving the rate of oxidation. The log of the rate of each solution was plotted against the log of the concentration of TPPCl to determine the rection order in respect to TPPCl.

A 20 mL stock solution of 10 mM (25 μl) of 2,6-lutidine *N*-oxide was prepared in acetonitrile. A 2 mM (10 mg) solution of $[MoOCl_2(bpy\text{-}^tBu)]_2(\mu\text{-}O)$ was prepared in 5 mL of the stock solution. A 16 mM of solution of tetraphenyl phosphonium chloride (TPPCl was prepared in 5 mL of the stock solution. All solutions were diluted by a factor of 5 to ensure absorbance was below 1 at 520 nm. 1 mL of the $[MoOCl_2(bpy\text{-}^tBu)]_2(\mu\text{-}O)$ solution was added to 6 different quartz cuvettes. A portion of the TPPCl solution was added to each cuvette to achieve solution with 0.1 eq-2 eq of TPPCl. A similar process was done to test oxidation rate at higher concentrations, between 3 eq-32 eq of TPPCl. The diluted stock solution was added to the cuvettes to achieve a total volume of 2mL in each cuvette. The cuvettes were wrapped in parafilm to prevent oxygen leaks. The change in absorbance of each solution was monitored over time by taking the UV-Vis every hour for 8 hours (Figure S28). The rate of each solution was determined and the log of the rate of each solution was plotted against the log of the concentration of TPPCl to determine the rection order of TPPCl in lutidine *N*-oxide.

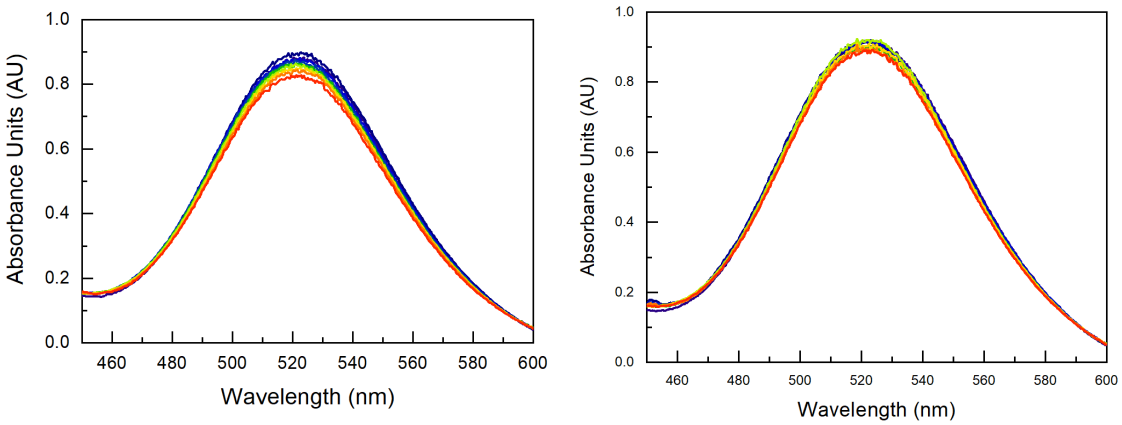


Figure S28. The UV-Vis of $[MoOCl_2(bpy\text{-}^tBu)]_2(\mu\text{-}O)$with 10 eq of pyridine N-oxide and 1 eq of TPPCl (left). The UV-Vis over time of $[MoOCl_2(bpy\text{-}^tBu)]_2(\mu\text{-}O)$ with 10 eq of lutidine N-oxide and 1eq of TPPCl (right). UV-Vis spectra shown in 1h increments from 0 min (purple) to 8 h (red)

Oxidation Rate Law Dependence on Bipyridine Ligand

A 100 mM (190 mg) stock solution of pyridine *N*-oxide was prepared in 20 mL of acetonitrile. A 2 mM (10 mg) solution of $[MoOCl_2(bpy\text{-}^tBu)]_2(\mu\text{-}O)$ was prepared in 5 mL of stock solution. A 400 mM (538 mg) solution of bpy-^{t}Bu was made in 5 mL of the stock solution. All solutions were diluted by a factor of 5. 1 mL portions of the $[MoOCl_2(bpy\text{-}^tBu)]_2(\mu\text{-}O)$ solution was added to 7 separate cuvettes. Portions of the (bpy-^{t}Bu) solution were added to each cuvette to achieve concentrations between 10 eq-200 eq. Stock solution was added to each cuvette to have a

total volume of 2 mL. The absorbance of each solution was taken every 30 min over the course of 8 h(Figure S29 left). The oxidation rate of each solution was determined and found to be constant despite the changing ligand concentration (Figure S29 right). The consistent rate across all solutions illustrates that the rate is not dependent on the loss of the bipyridine ligand.

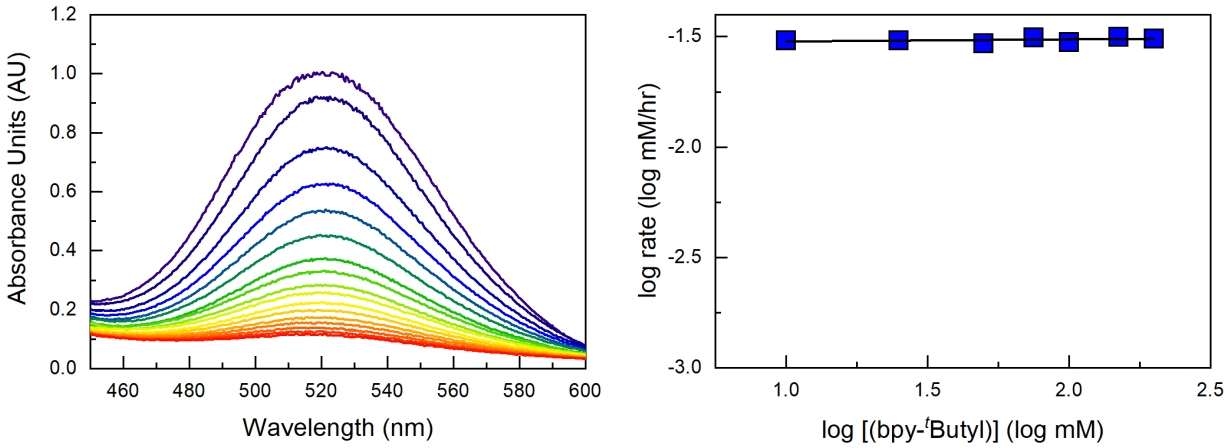


Figure S29. UV-Vis over time of a $[MoOCl_2(bpy\text{-}^tBu)]_2(\mu\text{-}O)$ solution with 100 eq of pyridine N-oxide and 100 eq of bpy-^{t}Bu. UV-Vis spectra shown in 30min increments from 0 min (purple) to 8h (red) (left) The log plot of the oxidation rate when varying the concentration of the bipyridine ligand y = 0.0095x - 1.53 R^2 = 0.16 (right)

Oxidation Rate Law Dependence on $MoO_2Cl_2(bpy\text{-}^tBu)$

A 100 mM (190 mg) stock solution of pyridine *N*-oxide was prepared in 20 mL of acetonitrile. A 2 mM (10 mg) solution of $[MoOCl_2(bpy\text{-}^tBu)]_2(\mu\text{-}O)$ was prepared in 5 mL of stock solution. These solutions were diluted by a factor of 5. A 100 mM (234 mg) solution of $MoO_2Cl_2(bpy\text{-}^tBu)$ was made in 5 mL of the diluted stock solution. 1 mL portions of the $[MoOCl_2(bpy\text{-}^tBu)]_2(\mu\text{-}O)$ solution was added to 7 separate cuvettes. Portions of the $MoO_2Cl_2(bpy\text{-}^tBu)$ solution were added to each cuvette to achieve concentrations between 10 eq-200 eq. Stock solution was added to each cuvette to have a total volume of 2 mL. The absorbance of each solution was taken every hour over the course of 8 h(Figure S30 left). The oxidation rate of each solution was determined, and the log rate was plotted against the log concentration of $MoO_2Cl_2(bpy\text{-}^tBu)$ (Figure S30 right). The rate remains relatively constant across all concentrations illustrating that the rate is not dependent on the breaking of the Mo–O bond.

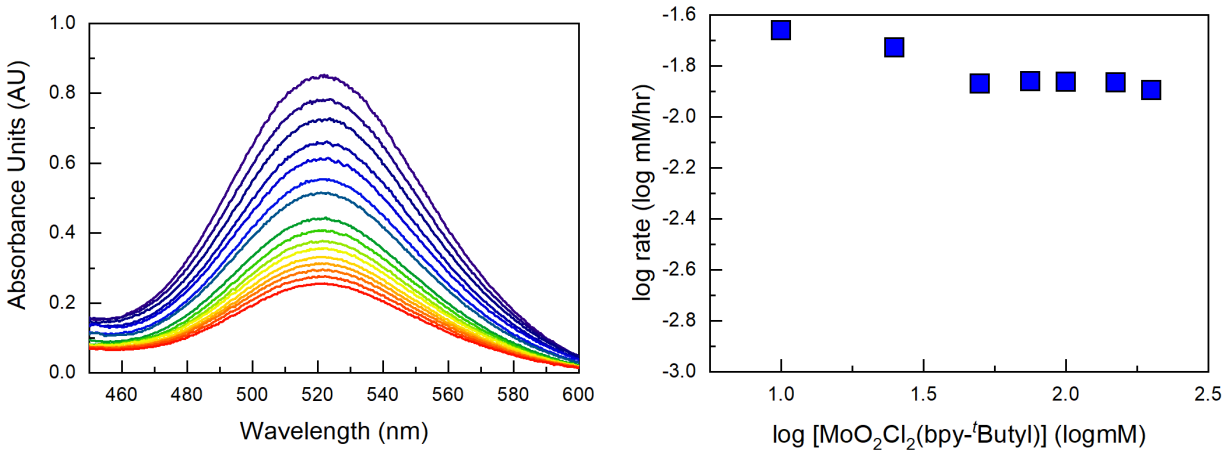


Figure S30. UV-vis over time of $[MoOCl_2(bpy\text{-}^tBu)]_2(\mu\text{-}O)$ with 100 eq of pyridine N-oxide and 100 eq of $MoO_2Cl_2(bpy\text{-}^tBu)$. UV-Vis spectra shown in 30 min increments from 0min (purple) to 8h (red) (left) The log plot of the oxidation rate when varying the concentration of $MoO_2Cl_2(bpy\text{-}^tBu)$ (right).

VI. Photocatalytic Assays

A stock solution of 500 mM of cyclohexene (1 mL, 9.9 mmol) was prepared in 19 mL of acetonitrile. 10 mL of the stock solution was added to 10 mg of MoO_2Cl_2(bpy-^{t}Bu) to make a 2 mM solution of **1** in the presence of 495 equiv of substrate. A 100 eq solution of pyridine *N*-oxide was prepared in 5mL of the stock solution. 1 mL of the MoO_2Cl_2(bpy-^{t}Bu) solution was added to three separate cuvettes. 1 mL of pyridine *N*-oxide was added to those cuvettes as well. Each sample was photolyzed at 365 nm for a given length of time. After photolysis 0.9 mL of each sample was added to a GC vial containing 0.1 mL of hexachloroethane, which is used as an internal standard. Each sample was run on the GC-MS to determine the amount of product produced. The concentration of product produced was averaged over three samples.

A stock solution of 500 mM of cyclohexadiene (1 mL, 10.6 mmol) was prepared in 19 mL of acetonitrile. 10 mL of the stock solution was added to 10mg of MoO_2Cl_2(bpy-^{t}Bu) to make a 2 mM solution of **1** in the presence of 530 equiv of substrate.. A 100 eq solution of pyridine *N*-oxide was prepared in 5 mL of the stock solution. 1 mL of the MoO_2Cl_2(bpy-^{t}Bu) solution was added to three separate cuvettes. 1 mL of pyridine *N*-oxide was added to those cuvettes as well. Each sample was photolyzed at 365 nm for a given length of time. After photolysis 0.9 mL of each sample was added to a GC vial containing 0.1 mL of hexachloroethane, which is used as an internal standard. Each sample was run on the GC-MS. The product concentrations obtained from these samples were averaged across three samples.

Control experiments were performed in which identical procedures were followed with either the omission of the oxidant or the omission of the MoO_2Cl_2(bpy-^{t}Bu).

A summary of the photocatalytic activity can be found in Table S1.

GC analyses were performed as previously reported in *J. Am. Chem. Soc.* 2022, 144, 44, 20472–20483.

Table S1. *Summary of photocatalytic activity of **1** in the presence and absence of pyridine-N-oxide as an oxidant.*

Entry	Substrate	Initial [1] mM	Initial [Oxidant] mM	Final [Product] mM	TON Product	TON C–H Activation
1	cyclohexene	1	100	6.0±0.5	6	12
2	cyclohexadiene	1	100	6.5±0.6	6.5	13
3	cyclohexene	1	0	0.4±0.1	0.4	0.8
4	cyclohexadiene	1	0	0.5±0.1	0.5	1
5	cyclohexene	0	100	0	0	0
6	cyclohexadiene	0	100	0	0	0

Stability of the Catalyst

A stock solution of 500 mM of cyclohexene (1mL) was prepared in 19 mL of acetonitrile. A 2 mM solution of MoO_2Cl_2(bpy-^{t}Bu) solution was prepared in 10 mL of stock solution (10 mg). A 100 eq solution of pyridine N-oxide (95 mg) was prepared in 10 mL of stock solution. 1 mL of each solution was added to a quartz cuvette. The solution was photolyzed at 365 nm for different amounts of time between 2 h-72 h. A new cuvette was prepared for each time interval (2 h, 4 h, 6

h, 8 h, 12 h, 16 h, 24 h, 48 h, 72 h,) For each time point 0.9 mL of the sample was added to a GC vial with 0.1 mL of an internal standard of hexachloroethane. The samples were run on the GC to determine product growth over time.

A stock solution of 500 mM of cyclohexene (1 mL) and 4 mM (0.1 mL) of water was prepared in 19 mL of acetonitrile. A 2 mM solution of MoO_2Cl_2(bpy-^{t}Bu) solution was prepared in 10 mL of stock solution (10 mg). A 100 eq solution of pyridine *N*-oxide (95 mg) was prepared in 10 mL of stock solution. 1 mL of each solution was added to a quartz cuvette. The solution was photolyzed at 365 nm for different amounts of time between 2 h-72 h. A new cuvette was prepared for each time interval (2 h, 4 h, 6 h, 8 h, 12 h, 16 h, 24 h, 48 h, 72 h,) For each time point 0.9 mL of the sample was added to a GC vial with 0.1 mL of an internal standard of hexachloroethane. The samples were run on the GC to determine product growth in the presence of water over time.

4 mg of the [$MoOCl_2$(bpy-^{t}Bu)]$_2$(μ-O) was dissolved in 2 mL of CD_3CN to make a 2 mM solution. A 20 mM (4 mg) solution of pyridine *N*-oxide was prepared in 2 mL of CD_3CN. 0.25 mL of each solution was added to two separate J Young NMR tubes. 2 μl of D_2O was added to one J young NMR tube to achieve a solution with 4mM of D_2O. The initial ^{1}H NMR spectrum of each tube was taken. The samples were wrapped in foil to shield them from stray light and ^{1}H NMR spectra were taken every hour for 8 h and at 24 h (Figure S31 and Figure S32). The integration ratio between the peak at 1.48ppm and 1.49 ppm were plotted for the reaction with and without D_2O (Figure S33).

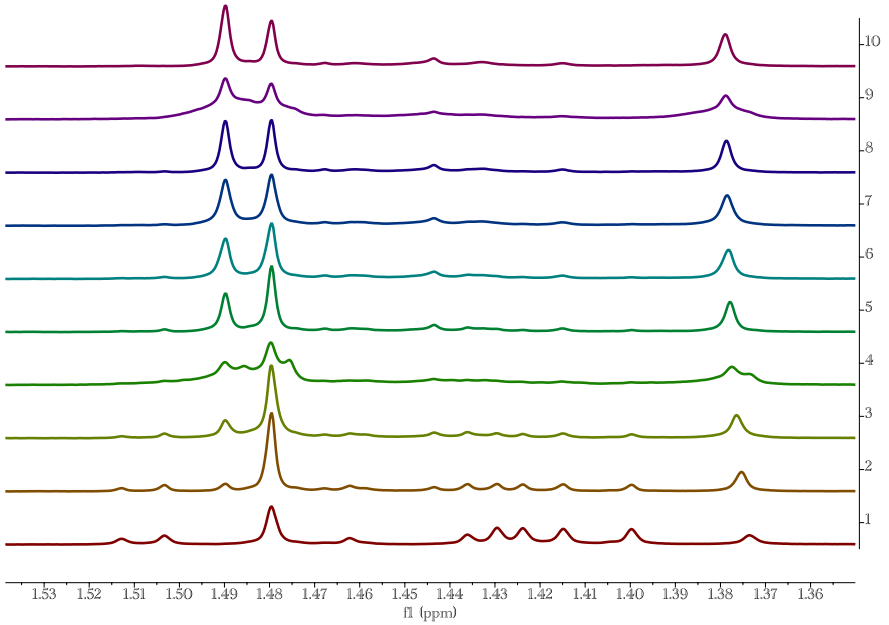


Figure S31. The aliphatic region of a ^{1}H NMR spectrum of MoO_2Cl_2(bpy-^{t}Bu) over time with 10 eq of pyridine *N*-oxide was taken in CD_3CN on a Bruker 400 MHz instrument. ^{1}H NMR spectra were taken every hour for 8 h and at 24 h. 0 min (red), 1 h (orange), 2 h (yellow), 3 h (light green), 4 h (dark green), 5 h (teal), 6 h (dark blue), 7 h (indigo), 8 h (purple) 24 h (pink). Growth of resonance at 1.375 ppm is assigned to free bpy-^{t}Bu. The resonance at 1.49 ppm is assigned to [MoO_2Cl(bpy-^{t}Bu)]$^+$.The diminishing resonance at 1.48 ppm is assigned to **1**.

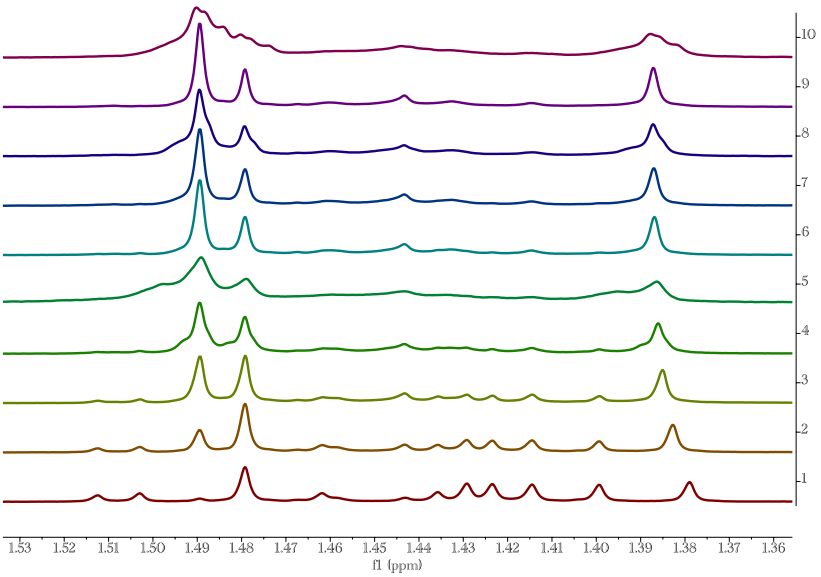


Figure S32. The aliphatic region of a ^{1}H NMR spectrum of MoO_2Cl_2(bpy-^{t}Bu) over time with 10 eq of pyridine *N*-oxide and 4 mM of D_2O was taken in CD_3CN on a Bruker 400 MHz instrument. ^{1}H NMR spectra were taken every hour for 8 h and at 24 h. 0 min (red), 1 h (orange), 2 h (yellow), 3 h (light green), 4 h (dark green), 5 h (teal), 6 h (dark blue), 7 h (indigo), 8 h (purple) 24 h (pink). Growth of resonance at 1.38 ppm is assigned to free bpy-^{t}Bu. The resonance at 1.49 ppm is assigned to $[MoO_2Cl(bpy\text{-}^{t}Bu)]^{+}$.The diminishing resonance at 1.48 ppm is assigned to **1**.

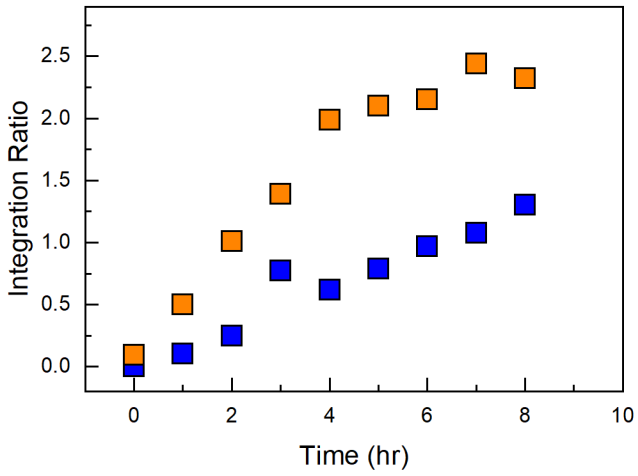


Figure S33. The integrated ratio of the MoO_2Cl_2(bpy-^{t}Bu) (1.48 ppm) and the solvated complex (1.49 ppm) over the course of oxidation. Blue $[MoOCl_2(bpy\text{-}^{t}Bu)]_2(\mu\text{-}O)$ and 10 eq pyridine *N*-oxide Orange $[MoOCl_2(bpy\text{-}^{t}Bu)]_2(\mu\text{-}O)$ 10 eq pyridine N oxide and 4 mM D_2O.

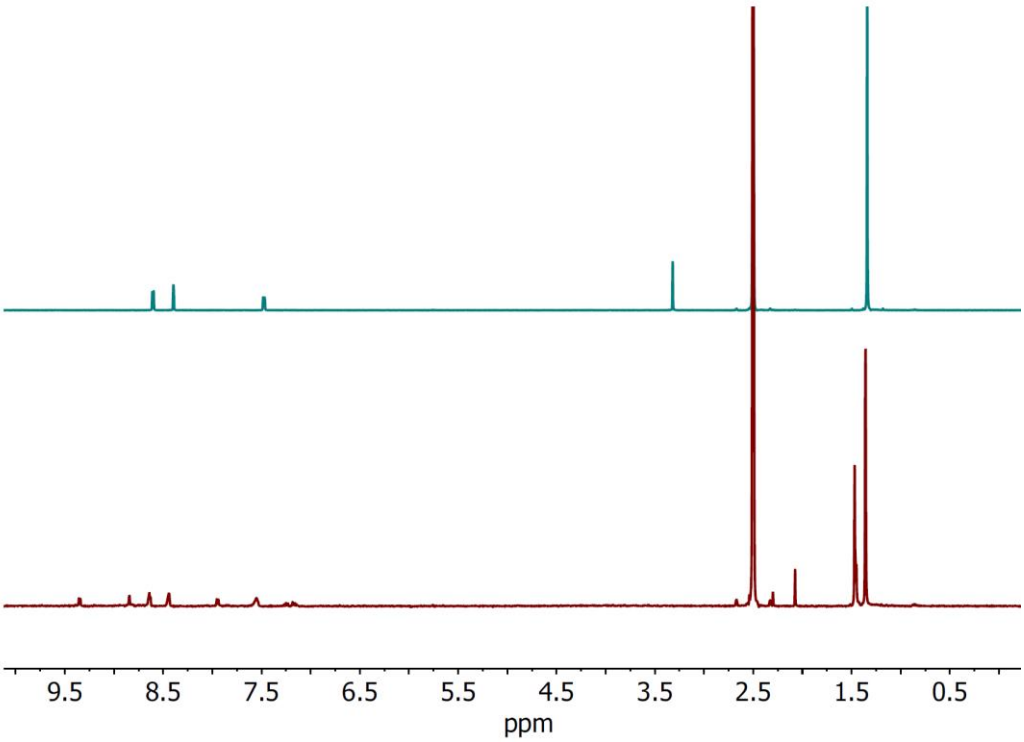


Figure S34. ^{1}H NMR spectra of bpy-^{t}Bu (top) and **1** (bottom) in DMSO-d_6. Resonances in the sample of **1** dissolved in DMSO-d_6 at 1.35 ppm, 7.5 ppm, 8.45 ppm, and 8.65 ppm are assigned to the presence of free bpy-^{t}Bu.

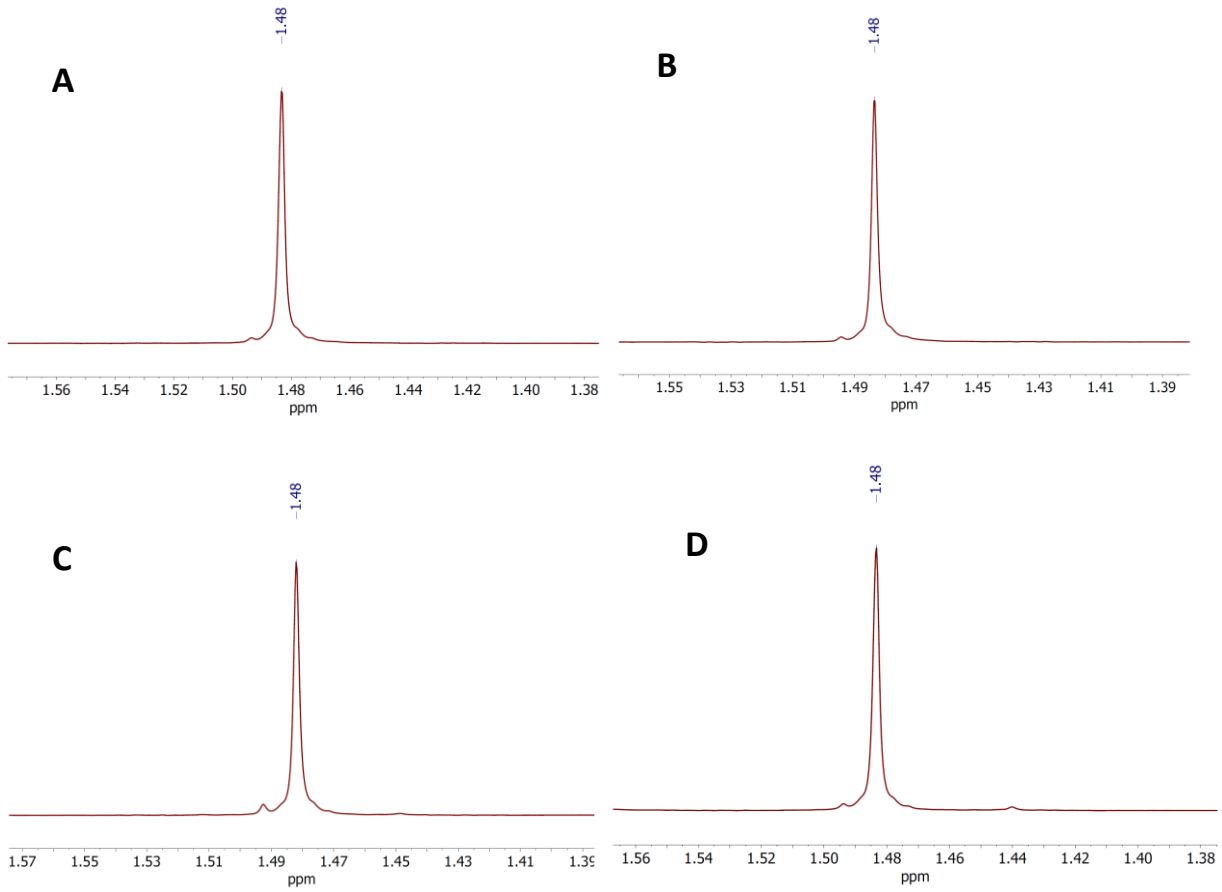


Figure S35. Chemical shift of the ^{t}Bu resonance in the 1H NMR spectra of **1** in CD_3CN in the presence/absence of various additives. (**A**) Complex **1** in the absence of any additive; (**B**) Complex **1** in the presence of 10 equiv of benzne; (**C**) Complex **1** in the presence of 10 equiv of pyridine; (**D**) Complex **1** in the presence of 10 equiv of cyclohexene. The common chemical shift corresponding to **1** indicates that benzene, pyridine, and cyclic alkenes do not readily degrade the complex.