Electronic Supplementary Information for

“Nonclassical oxygen atom transfer reactions of oxomolybdenum(VI) bis(catecholate)”

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General Procedures. When necessary, CH_2Cl_2 was dried over molecular sieves, followed by CaH_2. Toluene was dried over sodium metal. Solvents were vacuum transferred from their drying agents and stored in an inert-atmosphere glovebox before use. Deuterated solvents (Cambridge Isotope Laboratories) were dried in the same manner as their protio analogues. Dioxomolybdenum bis(acetylacetonate) (Strem) and 4-picoline-*N*-oxide, 4-cyanopyridine-*N*-oxide, and 4-chloropyridine-*N*-oxide (Aldrich) were used as received. Pyridine-*N*-oxide (Acros) and 4-methoxy- and 4-dimethylaminopyridine-*N*-oxide (Aldrich) were sublimed before use. Mo_2O_2(3,5-DBCat)$_4$ was prepared by a literature method.[1] Routine ^{1}H and ^{13}C{^{1}H} NMR spectra (referenced to tetramethylsilane) were obtained on a Varian VXR-300 spectrometer. IR spectra were measured on a Jasco-6300 FT-IR spectrometer as powders on ATR plates and are reported in cm^{-1}. UV-visible spectra were measured using toluene solutions in 1-cm quartz cuvettes with a Beckman DU-7500 diode array spectrophotometer. The temperature of the solutions was regulated by circulation of ethylene glycol from a thermostatted bath through the metal cell block; temperatures were measured using a thermocouple inserted in a cuvette in the cell block. Elemental analyses were performed by M-H-W Laboratories (Phoenix, AZ).

Oxobis(3,5-di-*tert*-butylcatecholato)(4-picoline-*N*-oxide)molybdenum(VI), MoO(3,5-DBCat)$_2$(Opic). In the drybox, MoO_2(acac)$_2$ (Strem, 1.0064 g, 3.086 mmol), 3,5-di-*tert*-butylcatechol (1.42 g, 6.387 mmol, 2.07 equiv), and picoline-*N*-oxide (0.3450 g, 3.164 mmol, 1.02 equiv) are dissolved in CH_2Cl_2 (8 mL) in a 50-mL round-bottom flask. The solution is layered with 16 mL cyclohexane in the air and allowed to stand 18 h at room temperature. The mixture is evaporated to dryness, the residue washed with cyclohexane (2 × 5 ml) and then recrystallized in a minimum of benzene and cyclohexane. The dark purple solid is isolated by vacuum filtration, washed with 10 mL cyclohexane, and air-dried 15 min to yield 2.082 g

MoO(3,5-DBCat)$_2$(Opic) (85%). ^{1}H NMR (CDCl$_3$, 20 ºC): δ 1.24, 1.26 (s, 18H each, ^{t}Bu), 2.55 (s, 3H, C*H*$_3$), 6.59 (sl br, 2H, DBCat Ar*H*), 6.65 (d, 2 Hz, 2H, DBCat Ar*H*), 7.69 (d, 7 Hz, 2H, Opic 3,5-H), 8.69 (d, 7 Hz, 2H, Opic 2,6-H). ^{13}C{^{1}H} NMR (CDCl$_3$, 20 ºC): δ 21.58 (Opic C*H*$_3$), 29.81, 31.89 (C(*C*H$_3$)$_3$), 34.69, 34.79 (*C*(CH$_3$)$_3$), 109.78, 116.66 (br), 127.59, 136.08 (br), 140.72, 147.96 (v br), 151.05, 156.75 (br), 161.20 (br). IR: 2956 (s), 2906 (m), 2869 (m), 1738 (br, m), 1582 (m), 1495 (m), 1459 (m), 1411 (m), 1387 (w), 1362 (m), 1312 (m), 1284 (m), 1255 (w), 1233 (s), 1198 (s, $\nu_{\mathrm{N-O}}$), 1172 (w), 1099 (m), 1028 (m), 997 (w), 980 (m), 923 (s, $\nu_{\mathrm{Mo=O}}$), 853 (s), 831 (s), 815 (w), 765 (w), 753 (m), 685 (m), 665 (w), 636 (s), 586 (m). Anal. Calcd for $C_{34}H_{47}MoNO_6$: C, 61.72; H, 7.16; N, 2.12. Obsd: C, 62.17; H, 7.32; N, 2.15.

Measurement of kinetics of nonclassical OAT reactions of MoO(3,5-DBCat)$_2$(ONC$_5$H$_4$R). A solution of the desired pyridine-*N*-oxide dissolved in 2.0 mL toluene (5 - 50 × 10^{-3} mol L^{-1}) was placed in a cuvette sealed with a silicone septum and allowed to thermally equilibrate in the UV-Visible spectrophotometer. The reaction was initiated by injecting 0.100 mL of a solution of Mo$_2$O$_2$(3,5-DBCat)$_4$ into the cuvette to give a final molybdenum concentration of 0.5 - 1.0 × 10^{-4} mol L^{-1}. Absorbances at 500 and 800 nm were monitored and gave satisfactory fits to exponential decay over at least four half-lives.

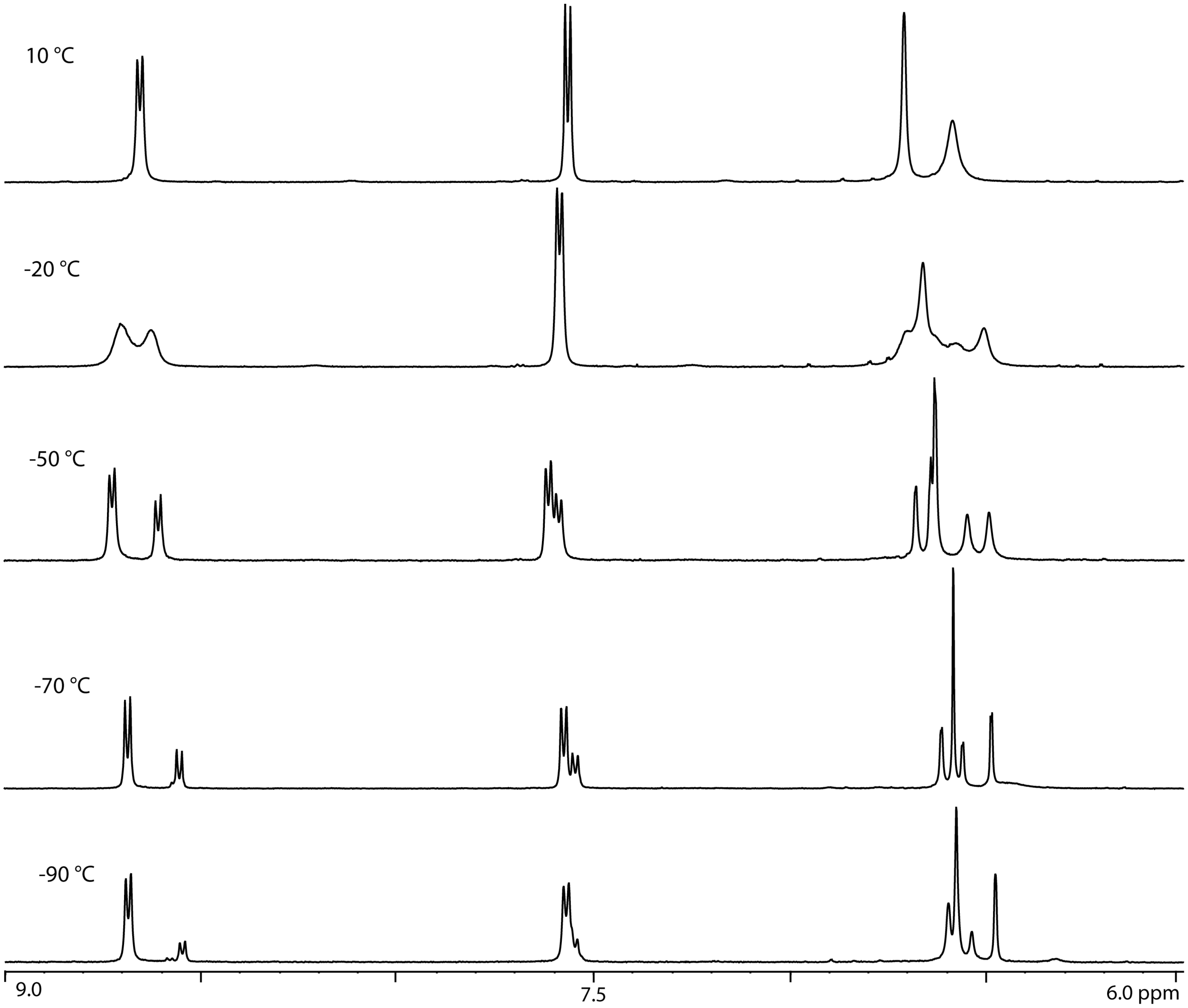


Fig. S1. ^{1}H NMR (500 MHz, CD_2Cl_2, aromatic region) of MoO(3,5-DBCat)$_2$(Opic) as a function of temperature.

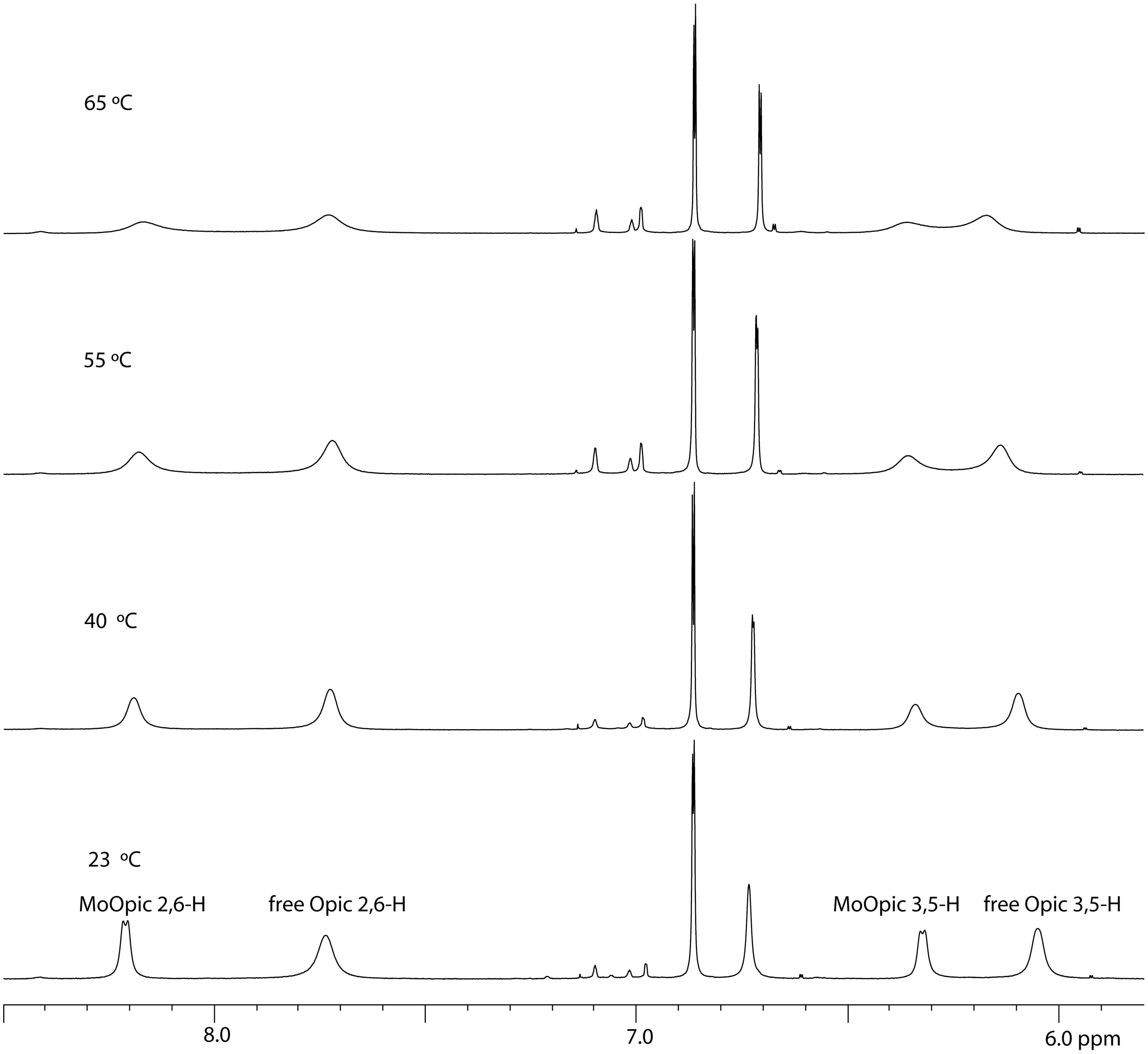


Fig. S2. ^{1}H NMR (500 MHz, toluene-d_8, aromatic region) of MoO(3,5-DBCat)$_2$(Opic) in the presence of free Opic (0.0344 mol L^{-1}).

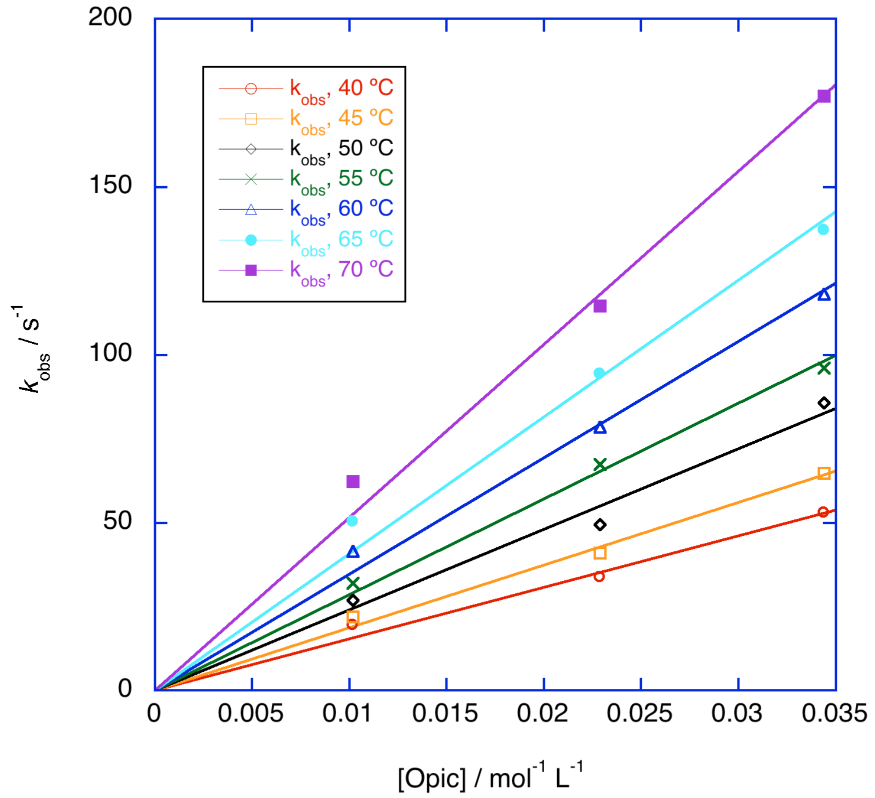
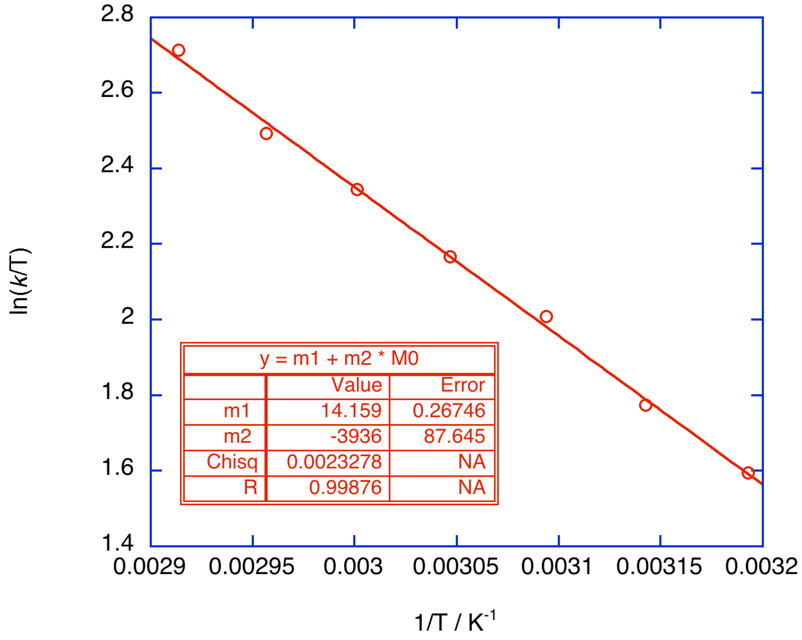


Fig. S3. Dependence of k_{obs} for exchange of free and bound Opic in MoO(3,5-DBCat)$_2$(Opic) on the concentration of free Opic (toluene-d_8). Values of k_{obs} were determined by NMR lineshape simulation using the program *g*NMR.[2]



y = m1 + m2 * M0

	Value	Error
m1	14.159	0.26746
m2	-3936	87.645
Chisq	0.0023278	NA
R	0.99876	NA

Fig. S4. Eyring plot for exchange of bound Opic in MoO(3,5-DBCat)$_2$(Opic) with free Opic (toluene-d_8).

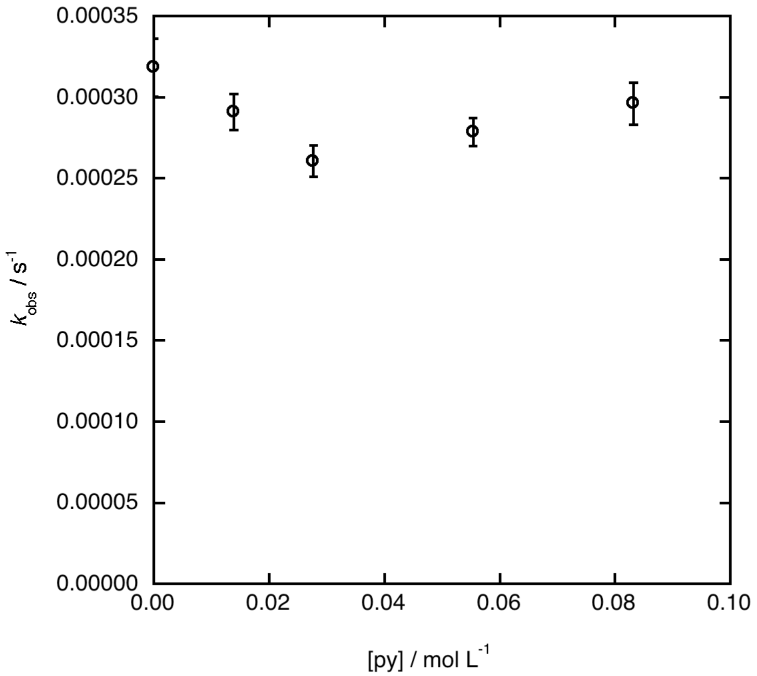


Fig. S5. Dependence of k_{obs} for oxidation of MoO(3,5-DBCat)$_2$(Opy) on [py] (toluene, 85 ºC, [Opy] = 0.050 mol L^{-1}).

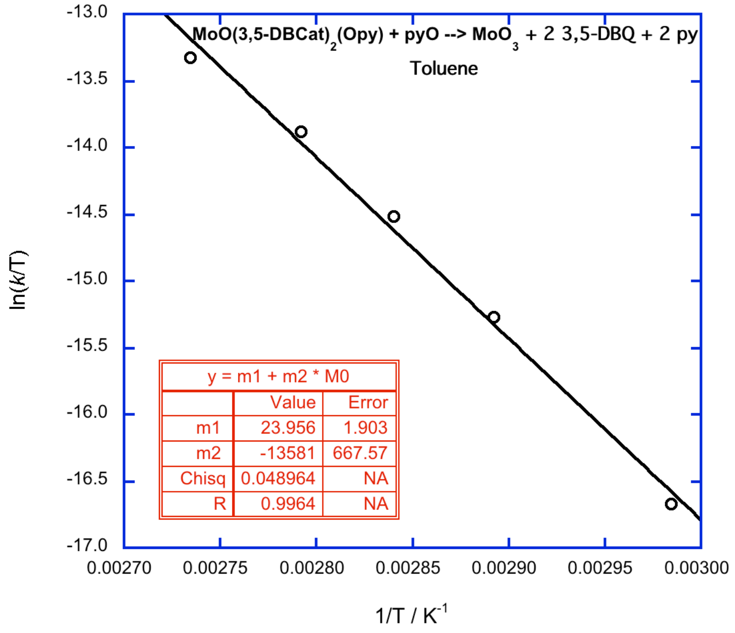


Fig. S6. Eyring plot for oxidation of MoO(3,5-DBCat)$_2$(Opy) in toluene.

References

(S1) R. M. Buchanan and C. G. Pierpont, *Inorg. Chem.*, 1979, **18**, 1616-1620.
(S2) P. H. M. Budzelaar, *gNMR*, v. 3.5.6., Cherwell Scientific Publishing, 1996.