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Molybdenum Catalysts based on Salan Ligands for the Deoxydehydration Reaction

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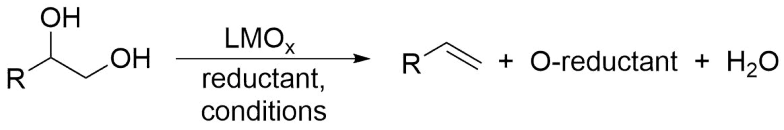
Abstract

Dioxomolybdenum complexes based on salan ligands have been evaluated for their potential in catalyzing the deoxydehydration (DODH) reaction. The DODH reaction is a formal reduction that converts vicinal diols into olefins using an oxometal catalyst and a sacrificial reductant. The reaction holds enormous potential in transforming biomass-derived molecules into platform chemicals. This study evaluated twenty (20) molybdenum complexes supported by salan ligands in the DODH reaction with the goal of establishing structure-activity relationships. Catalyst screenings were performed using styrene glycol as a model substrate and 1-10 mol% loading of the molybdenum complexes at 170 ^{o}C producing styrene in up to 54% yield. Aliphatic diols and *meso*-/*R,R*-hydrobenzoin were also converted to the corresponding alkenes in moderate to good yields (60-71%) that are comparable to previously reported molybdenum catalysts. A bio-derived glycol, (+)–diethyltartrate, could be converted to the alkene product (diethyl fumarate) in >98% yield using 10 mol% catalyst. A high yield of diethyl fumarate (78%) was also obtained with Na_2SO_3 (cheap, readily available, and benign) as a reductant. Quite significantly, diethyl fumarate was produced in a 42% yield at a 1 mol% catalyst loading which represents a turnover number (TON) of 42; this is one of highest activity in a DODH reaction observed with molybdenum catalysts. The catalytic studies along with preliminary kinetic investigations reveal significant ligand effects: sterically bulky *ortho*-substituents and electron-withdrawing *para*-substituents on the phenol arms resulted in enhanced catalytic activity while a rigid phenyl as well as an ethylene backbone featuring a tertiary amine were found to impede catalysis.

Introduction

Global concern regarding long-term implications associated with the use of fossil resources for meeting the energy and material demands of a growing population has resulted in scientific efforts aimed at identifying sustainable alternatives.[1] Biomass valorization to useful chemicals is identified to be crucial in this respect. However, this is a formidable task considering the highly oxygen-rich nature of biomass and its derivatives.[2] Of various deoxygenation strategies being explored for reducing the pre-existing functionality in biomass-derived molecules, the deoxydehydration (DODH) reaction is unique in its ability to furnish olefins from vicinal diols or glycols, a feature prevalent in sugars and sugar-derived molecules.[2–4] The reaction is an overall reduction of the diol and is catalyzed by high oxidation state oxometal complexes assisted by a stoichiometric reductant.



Scheme 1. Deoxydehydration of glycols to olefins.

First demonstrated in 1996 by Cook and Andrews[5] with an oxo-rhenium catalyst (Cp^*ReO_3) and triphenylphosphine (PPh_3) reductant, a variety of different variations of homogenous[6–12] and supported[13–16] rhenium (Re) catalysts have since then been explored and reported. The high cost of rhenium compounds has more recently driven research in the direction of non-precious metal catalysts based on vanadium (V) and molybdenum (Mo) in effecting the reaction.[17–20] A broad variety of chemical reductants have also been explored in mediating the reaction.[11,21–24] Mechanistically, the reaction is proposed to proceed *via* a sequence of condensation, reduction, and alkene extrusion steps.[25] The choice of the catalyst and reductant

has been shown to have a significant influence on the mechanistic sequence of the steps as well as on determining the rate-limiting (condensation *vs* reduction *vs* alkene extrusion) step.[26,27]

Catalytic systems based on V and Mo are attractive from an economic standpoint; however, compared to the Re counterparts they are plagued by poor reactivity compounded by harsher reaction conditions and higher catalyst loadings.[2,20] The use of metal catalysts supported over ancillary ligands has been explored to address the low catalytic activity of these metals. In the case of vanadium, the tridentate [ONO] coordinated dipic (dipic = 2,6-pyridinedicarboxlate) and related[-] ligands were found to impart catalytic activity for a wide range of substrates (15-95% yields) using a variety of reductants.[28,29] Typical reaction times ranged from 24-96 hours using 10 mol% of the catalyst at 150-170 ^{o}C. Although initial catalytic studies of molybdenum focused on commercially available molybdate salts as catalysts,[30–33] molybdenum complexes featuring supporting ligands have been evaluated recently with noted ligand effects. Galindo and coworkers reported the deoxydehydration of 1-phenyl-1,2-ethanediol (styrene glycol) and cyclooctane-1,2-diol using molybdenum complexes of acylpyrazolonate ligands (2 mol%) at 110 ^{o}C over 18 hours.[34] Although high diol conversions (60-100%) were observed, the alkene yield was found to be low (13-55%) under these conditions. Okuda *et al* evaluated the utility of dioxomolybdenum complexes based on [OSSO]-type bisphenolate ligands featuring various steric and electronic modulations as well as backbone flexibility.[35] With catalysts based on the 3-carbon (propylene) backbone, DODH reactions performed on 1,4-anhydroerythritol as a substrate using 5 mol% catalyst loading at 200 ^{o}C and 3-octanol as reductant, produced up to 57% yield of the olefin product 2,5-dihydrofuran. Catalysts based on the 2-carbon (ethylene) backbone furnished inferior yields of 1-3%. De Vos and Stalpert reported the use of β-diketones as ligands in the molybdenum catalyzed deoxydehydration.[36] The bulky β-diketone, 2,2,6,6-

tetramethylheptanedione (TMHD) when used in equivalent amounts demonstrated strong yield enhancements across a range of substrates at 150-200 ^{o}C using 10 mol% of $MoO_2(acac)_2$ as a precursor. The bulky ligand was proposed to inhibit oligomerization of the Mo catalyst which hindered catalytic activity. A five–coordinate dioxomolybdenum complex based on an [ONO] pincer ligand and its $OPPh_3$ adduct (a 6–coordinate complex) were explored in the DODH reaction by Kilyanek *et al*.[37] The complexes (10 mol%) were found to affect DODH reaction on a range of substrates at 150 or 190 ^{o}C producing the corresponding alkene in yields up to 62% over 48 hours. More recently, a related 6–coordinate complex, an HMPA adduct, resulted in styrene yields up to 69% (in addition to ~20% styrene that polymerized under these conditions) at 190 ^{o}C using PPh_3 as reductant.[38] A dinuclear dioxomolybdenum complex supported by the Cp* ligand, $(Cp^*MoO_2)_2O$, was reported by the Gebbink group for DODH of aliphatic diols using PPh_3 as a reductant in anisole at 200 ^{o}C over 15 hours.[39] Olefin yield as high as 65% (representing >30 turnovers) was recorded in *m*-dichlorobenzene as solvent and high olefin selectivity (up to 91%) was observed in trichlorobenzene as solvent for the formation of 1-octene from octane-1,2-diol using this cyclopentadienyl-Mo catalyst.

Given the potential of dioxomolybdenum complexes in affecting the DODH reaction under relatively mild condition (<200 ^{o}C) and the ease of steric and electronic modulation, we were interested in studying these complexes over other ancillary ligands.[40,41] Specifically, we sought to study dioxomolybdenum catalysts based on [ONNO] salan ligands in the DODH reaction. Such molybdenum complexes have found applications in a variety of other catalytic reactions, and more importantly the modular nature of ligand synthesis allows for facile tunability of steric and electronic properties.[42–45] In this work, we report our preliminary findings on the evaluation of ligand effects in deoxydehydration reaction catalyzed by dioxomolybdenum

complexes of salan ligands. These complexes were found to effectively catalyze the DODH reaction in high conversions (>90%) within short reaction times (2-24 hours) at 170 ^{o}C and yields as high as 98% could be achieved in case of the bio-derived glycol, (+)-diethyltartrate. The flexibility of the ligand backbone, steric bulk, and the electronic environment around the metal center are all found to be critical in modulating the catalytic activity of these complexes.

Results and Discussion

The successful use of [ONNO]-type salan ligands in supporting a variety of metal centers for establishing structure-activity relationships coupled with their easy and modular synthesis encouraged us to study their use in deoxydehydration catalysis.[46] These ligands allow for modular changes to be made to the diamine backbone which affects ligand flexibility as well as steric and electronic modulations (*o*-/*p*-substituents) to the phenol arms. All the complexes reported in this study are designated by the general notation $^{o,p}L_nMoO_2$, where the superscript on L denotes the *ortho*- and *para*- substituents on the phenol arms while the subscript refers to a unique backbone. The salan ligands were synthesized in 28-99% yield by either a reductive amination reaction between two equivalents of a suitably substituted salicylaldehyde and one equivalent of the respective diamine (**1a**-**18a**) or a Mannich condensation between a suitably substituted phenol, *N*,*N*'-dimethylethylenediamine, and formaldehyde. The dioxomolybdenum complexes were synthesized in 39-99% yield by stirring a mixture of the corresponding salan ligand and $MoO_2(acac)_2$ for 5-16 hours at room temperature. The ligands and corresponding molybdenum complexes were appropriately characterized by ^{1}H and $^{13}C\{^{1}H\}$ NMR spectroscopy, IR spectroscopy, mass spectrometry, and elemental analysis (Scheme S1 and Figures S1-S78).

Catalysis studies: We began our investigation by studying molybdenum complex **1b** ($^{H,H}L_1MoO_2$) based on the unsubstituted salan ligand derived from ethylene diamine (C2 backbone) and salicylaldehyde. Catalytic screening was performed on 1-phenyl-1,2-ethanediol (styrene glycol; 0.5 mmol) as a model substrate using 10 mol% loading of the molybdenum complex in toluene at 170 ^{o}C in presence of PPh_3 (1.5 equiv.) as reductant over 16 hours.[41] The olefin product, styrene, was obtained in 45% yield under these conditions (Table 1, entry 1). This was surprisingly significant as a *bis*(phenolato) molybdenum complex based on a similar [ONNO]-type ligand framework featuring a tertiary amine backbone was previously reported to be inefficient at converting 1,4-anhydroerythritol to 2,5-dihydrofuran (5% yield) at 200 ^{o}C over 18 hours using an alcohol reductant.[35] When the molybdenum precursor $MoO_2(acac)_2$ (10 mol%) was tested in the catalytic reaction, a 15% yield of styrene (Table 1, entry 16) was observed highlighting the significance of the ligated molybdenum center during catalysis.

Next, we investigated a series of molybdenum complexes supported over salan ligands featuring steric and electronic variations to elucidate structure-activity relationships. The presence of steric bulk (^{t}Bu = *tert*-butyl) at the *ortho*-position of the phenol arms (**2b**) did not influence deoxydehydration activity (Table 1, entry 2) producing styrene in 47% yield. The electronic nature of the *ortho*-/*para*-substituents on the phenol arms also did not exhibit any clear correlation with the electron–donating *vs* electron–withdrawing ability of the substituents (Table 1, entries 3-8). The catalyst bearing a *para*-Me substituent (**3b**) showed similar reactivity to **1b** and **2b**, again attesting to the earlier finding that steric bulk at the *ortho*-position of the phenol arms is inconsequential. The electron-donating –OMe substituent (**4b**) at the *para*-position of the phenol arm resulted in a marginally lower styrene yield of 34% while a –Cl substituent (**5b**) furnished a 41% yield under similar conditions. Quite interestingly, while a –F substituent (**6b**) at

the *para*-position yielded 50% styrene, a $-NO_2$ substituted (**7b**) catalyst resulted in only 5% yield of the product. This is interesting as both the fluoro- and nitro-group are highly electron–withdrawing although they operate through different mechanisms (inductive/field *vs* resonance). An *ortho*-/*para*-dichloro substituted complex $^{Cl,Cl}L_1MoO_2$ (**8b**) also produced styrene in 37% yield, only marginally lower than the mono *para*-Cl substituted complex, **5b**.

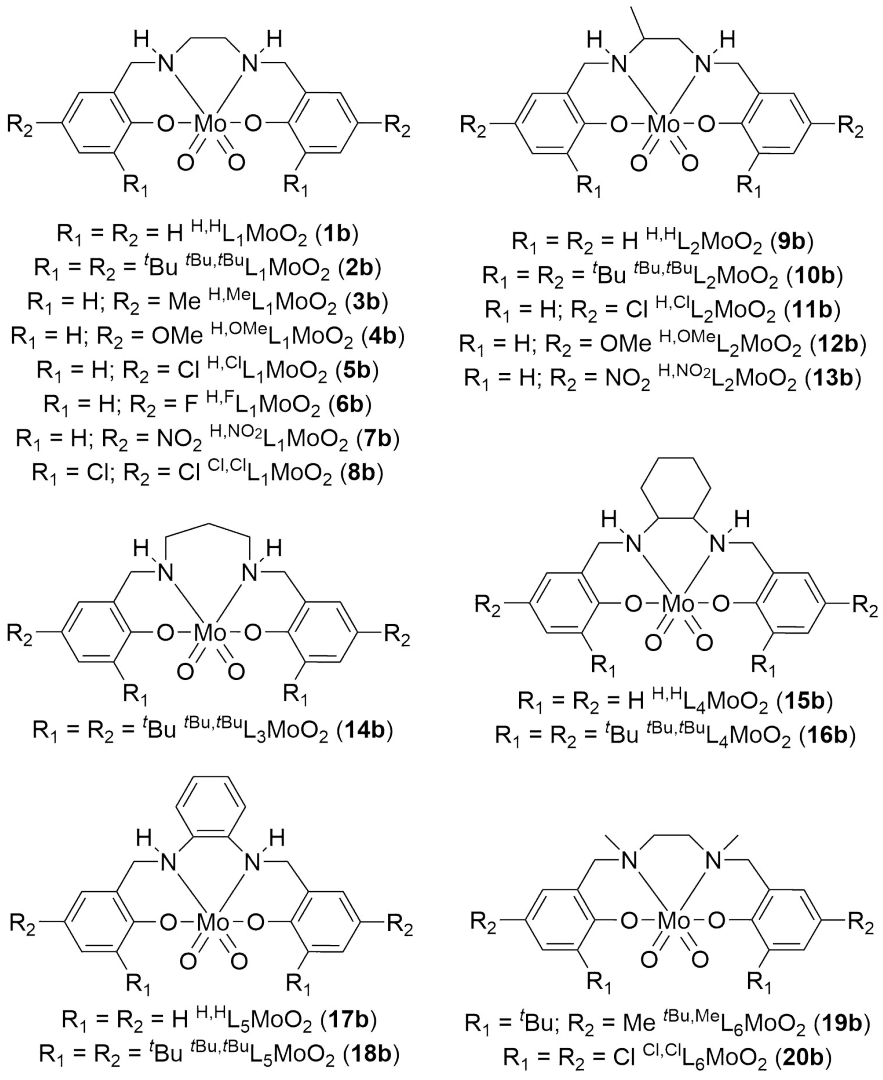
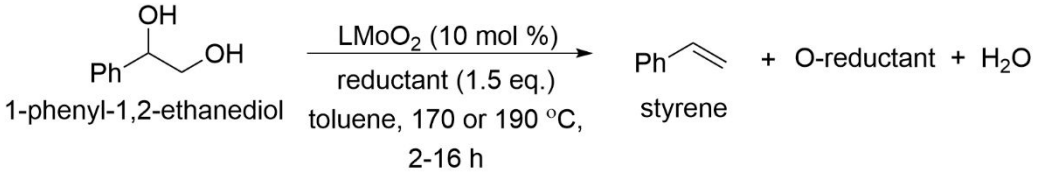


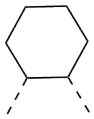
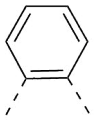
Figure 1. Molybdenum catalysts (**1b**-**20b**) evaluated in this study.

As no significant electronic or steric effects were observed in these catalytic results, and a clear correlation between catalytic activity and electronic nature of the *para*-substituent of the

phenol arm was lacking, we focused on the ligand backbone next. Introducing a –Me group on the C2 backbone (1,2-propylene; **9b**-**13b**) did not result in any notable difference in deoxydehydration activity across a variety of substituents on the phenol arms (Table S1, entries 1-5). The only notable difference was the catalytic activity observed using the *para*-NO_2 substituted catalyst (**13b**) which produced twice as much styrene (10%) as compared to the **7b**. Increasing the backbone length to a more flexible C3 backbone (1,3-propylene) with –^{t}Bu substituents on both the *ortho*- and *para*- positions of the phenol arms (**14b**) resulted in a marginally diminished activity (35%; Table 1, entry 9) as compared to **2b** which is based on a C2 backbone. Switching to a cyclohexyl (constrained) backbone while maintaining the steric and electronic features of the phenol arms (**15b** and **16b**) offered a slightly improved styrene yield of 50-54%. This set of catalysts based on the cyclohexyl backbone further support a lack of steric effect when switching between a –H and –^{t}Bu substituent at the *ortho*-position of the phenol arms. Finally, catalysts featuring a phenyl backbone (**17b** and **18b**), which represents a rigid backbone in the series, resulted in a notable drop in styrene yield (20-30%). It is worth pointing out that the steric bulk at the *ortho*-position did not result in any marked differences in catalytic activity (Table 1; entries 1&2 and 10&11) across the various backbones explored except for the phenyl backbone (Table 1, entries 12&13). Additionally, catalysts based on a 3^o–amine C2 backbone were also found to be inferior to those featuring a 2^o–amine C2 backbone yielding styrene in <5% yield even at 190 ^{o}C (Table 1, entries 14&15). This diminished activity could be attributed to reduced conformational flexibility of the 3^o–amine backbone and is in line with the previous report on a related molybdenum complex.[35] The observed effect of the phenyl and the 3^o–amine backbone suggests that the backbone effect is prominent in the reactivity of this class of dioxomolybdenum complexes in the DODH reaction.

Table 1. Deoxydehydration of styrene glycol catalyzed by molybdenum catalysts.[a]



entry	backbone	catalyst	styrene yield[b] PPh_3	styrene yield[b] Na_2SO_3
1.		$^{H,H}L_1MoO_2$ (**1b**)	45	34
2.		$^{t\text{Bu},t\text{Bu}}L_1MoO_2$ (**2b**)	47	46
3.[c]		$^{H,Me}L_1MoO_2$ (**3b**)	46	
4.		$^{H,OMe}L_1MoO_2$ (**4b**)	34 (54)	10
5.		$^{H,Cl}L_1MoO_2$ (**5b**)	41	23
6.		$^{H,F}L_1MoO_2$ (**6b**)	50	
7.		$^{H,NO_2}L_1MoO_2$ (**7b**)	5	5
8.		$^{Cl,Cl}L_1MoO_2$ (**8b**)	37	
9.		$^{t\text{Bu},t\text{Bu}}L_3MoO_2$ (**14b**)	35	
10.		$^{H,H}L_4MoO_2$ (**15b**)	54	
11.		$^{t\text{Bu},t\text{Bu}}L_4MoO_2$ (**16b**)	50	
12.		$^{H,H}L_5MoO_2$ (**17b**)	30	
13.		$^{t\text{Bu},t\text{Bu}}L_5MoO_2$ (**18b**)	20	
14.		$^{t\text{Bu},Me}L_5MoO_2$ (**19b**)	<1 (5)	<1 (<5)
15.		$^{Cl,Cl}L_6MoO_2$ (**20b**)	<5	<5
16.		$MoO_2(acac)_2$	15	

[a]Reaction conditions: Styrene glycol (0.50 mmol), catalyst (10 mol%) and reductant [PPh_3 or Na_2SO_3] (1.5 equiv.) in toluene (*ca*. 2.5 mL) at 170 °C for 2-16 hours. [b]Yields were determined by ^1H NMR spectroscopy using 1,3,5-trimethoxybenzene as an internal standard. [c]Yield in parentheses refers to the reaction at 190 °C.

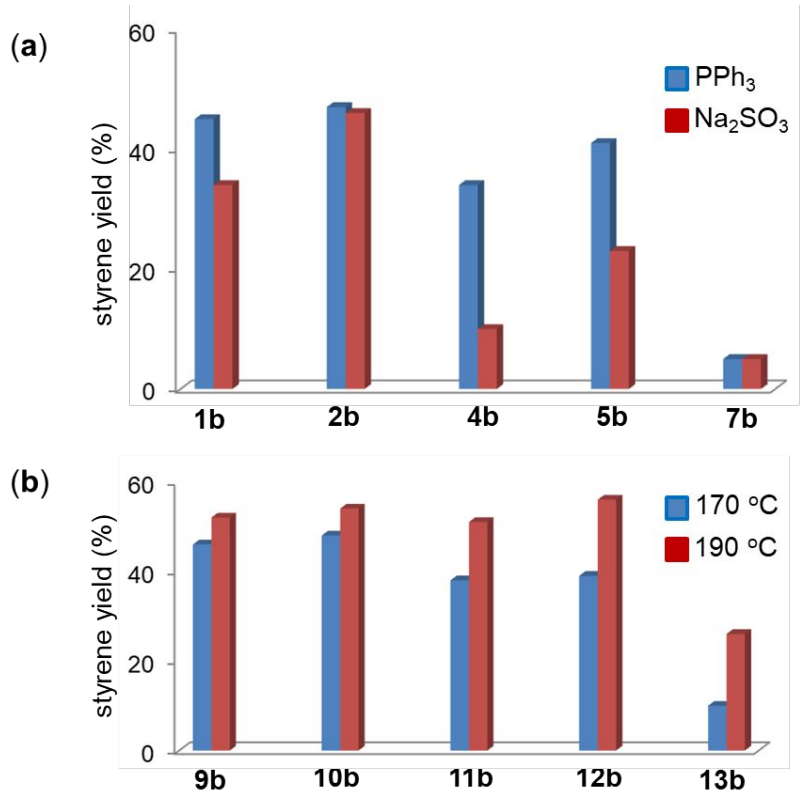


Figure 2. Effect of (**a**) reductant and (**b**) reaction temperature on styrene yield.

Reductant and temperature scope: The reductant being a crucial component of the reaction, we explored the use of Na_2SO_3 as a benign replacement for PPh_3.[11] While PPh_3 has been explored as a reductant in a variety of previous reports describing deoxydehydration reactions involving Re, Mo and V catalysts, its use is less than ideal considering the formation of $OPPh_3$ as a byproduct which needs to be laboriously separated from the olefin product (and reaction mixture) as opposed to the formation of Na_2SO_4 which can be easily separated by aqueous workup when Na_2SO_3 is the reductant. Under our optimized reaction conditions, the styrene product was obtained in marginally lower yields (4-46%) using Na_2SO_3 as the reductant (Figure 2 (**a**); Table 1, entries 1-2 & 4-5; Table 2, entries 2, 8 & 12; Table S1) as compared to PPh_3. A secondary alcohol, 3-octanol, was also tested as a reductant under our optimized conditions.[10]

The alkene product was obtained in a 23% yield when 3-octanol (1.5 equiv.) was used as the reductant and the yield decreased significantly (<5%) when 3-octanol was used both as a solvent and reductant (Table 2, entries 3 and 4). This suggests that 3-octanol is a less effective reductant for the dioxomolybdenum complexes used in this study although alcohols have been used as reductants in other Mo-catalyzed DODH reactions.[30] The effect of temperature was also explored using a series of catalysts (**9b**-**13b**) with the 1,2-diaminopropane backbone (Figure 2 (**b**), Table S1). Catalytic reactions proceeded in relatively higher yields (6-20% higher) at 190 ^{o}C compared to the standard reaction temperature of 170 ^{o}C across various catalysts evaluated (Table 1, entry 4 and Table S1, entries 1-5). Significantly lower styrene yields were observed at both lower (150 ^{o}C) and higher (210 ^{o}C) temperatures at high substrate conversions; hence, these conditions were not pursued for further studies.

Substrate scope: To showcase the general utility of dioxomolybdenum complexes supported over salan ligands in the deoxydehydration reaction, we next explored the substrate scope (Table 2) as well as the effect of catalyst loading on activity using $^{t\text{Bu},t\text{Bu}}L_1MoO_2$ (**2b**) as a model catalyst (at 170 ^{o}C in toluene as solvent). With our model substrate, styrene glycol, a reduced styrene yield of 36% was obtained at a 5 mol% loading of **2b** (Table 2, entry 5). However, no styrene was detected in a reaction carried out at a 1 mol% catalyst loading (Table 2, entry 6). The efficiency of **2b** in catalyzing the DODH of styrene glycol is comparable to previosuly reported dioxomolybdenum complexes.[36–38,41]

Aliphatic diols such as decane-1,2-diol and octane-1,2-diol when subjected to the reaction conditions produced the corresponding olefins in 28% and 17% yield respectively using 10 mol% of the catalyst (Table 2, entries 7 & 10). A 23% yield of 1-decene was attained when

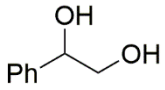
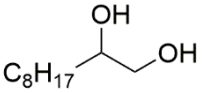
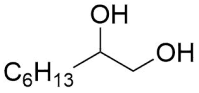
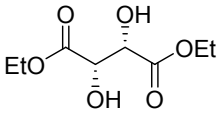
Na_2SO_3 was used reductant (comparable to yield obtained using PPh_3) while only a 16% yield of decene (at 55% conversion of decane-1,2-diol) was obtained when **1b** (10 mol%) was used as the catalyst (Table 2, entries 8 & 9). The decreased reactivity observed with **1b** could be a result of ligand effect suggesting that the bulky *tert*-butyl groups in **2b** result in enhanced reactivity. The observed alkene yields suggest low reactivity of the system towards aliphatic diols at 170 ^oC in line with previous reports. Successful DODH of aliphatic diols involving dioxomolybdenum catalysts usually requires higher temperatures (190-200 ^oC).[37,39] For example, the dioxomolybdenum complex of the bulky β-diketone 2,2,6,6-tetramethylheptanedione (TMHD) produced >90% yield of 1-hexene from hexane-1,2-diol at 200 ^oC using a stoichiometric amount of the β-diketone ligand (4 equiv.) while only a 23% yield of the alkene was obtained at 170 ^oC.[36]

When a bio-derived diol, (+)-diethyltartarate, was used as substrate the corresponding olefin product, diethyl fumarate, was obtained in >98% and 82% yield using 10 mol% and 5 mol% of **2b**, respectively in 16 hours (Table 2, entries 11 & 13). To the best of our knowledge, these results represent the highest yield of diethyl fumarate recorded to date using dioxomolybdenum catalysts at 170 ^oC; a 92% yield of diethyl fumarate was previously reported using a stoichiometric amount of β-diketone ligand (TMHDH, 4 equiv.) but at a higher temperature (200 ^oC).[36] Quite significantly, even at a catalyst loading as low as 1 mol% of **2b**, a 42% yield of the olefin product (TON = 42) was obtained in 24 hours (Table 2, entry 14) which is a noteworthy activity for DODH using an earth-abundant catalyst. Diethyl fumarate was also obtained in 78% yield when Na_2SO_3 (readily available, cost-effective, and ease of separation) was employed as the reductant at 10 mol% catalyst loading (Table 2, entry 12).

With the highly activated substrates *meso*- and *R*,*R*-hydrobenzoin, *trans*-stilbene was obtained in 60-71% yield under the reaction conditions (Table 2, entries 15 & 16). The formation of *trans*-stilbene as the olefin product from both *meso*- and *R*,*R*-hydrobenzoin is indicative of the stereoselective nature of the DODH reaction. Benzaldehyde was also obtained in 8-50% yield along with *trans*-stilbene suggesting that oxidative cleavage of the diol substrate is a competing pathway for these substrates under our reaction conditions (Table 2, entries 15 & 16).[36,39] The oxidative cleavage pathway could also explain the high conversions and low selectivity observed with styrene glycol as substrate; however, a significant amout of benzaldehyde was never detected in the reaction mixture.

Stereoisomeric cyclohexane-1,2-diols (Table 2, entries 17 & 18) were tested to gain insight into the stereochemical requirements for the DODH reaction. The alkene product (cyclohexene) was not detected by ^{1}H NMR spectroscopy when *trans*-cyclohexane-1,2-diol was employed. *Cis*-cyclohexane-1,2-diol on the other hand resulted in a 11% yield of cyclohexene product under identical conditions. Despite the low reactivity, this observation is in agreement with prior reports that suggest preferntial reactivity of *syn*/*cis*-diol substrates in the DODH reaction.[11,47] Biobased polyols, glycerol and erythritol, were also subjected to the DODH reaction under our optimized conditions. While no alkene product was obtained starting from glycerol, erythritol produced both the DODH product [2,5-dihydrofuran (2%)], and dehydration product [1,4-anhydrothreitol (25%)] under the reaction conditions (Table 2, entries 19 & 20). The reactivity observed with these polyol substrates is in line with previous studies using dioxomolybdenum complexes where marginally improved yields were obtained at higher temperatures (190-200 ^{o}C).[36,39]

Table 2. Deoxydehydration of glycols catalyzed by **2b**.[a]

	substrate	catalyst (mol%)	reductant	alkene yield[b] (%)
1.		10	PPh_3	47
2.		10	Na_2SO_3	46
3.		10	3-octanol	23
4.[c]		10	3-octanol	<5
5.		5	PPh_3	36
6.		1	PPh_3	nd
7.		10	PPh_3	28
8.		10	Na_2SO_3	23
9.[d]		10	PPh_3	16
10.		10		17
11.		10	PPh_3	>98
12.		10	Na_2SO_3	78
13.		5	PPh_3	82
14.		1	PPh_3	42
15.[e]	*R*,*R*-hydrobenzoin	10	PPh_3	71 (50)
16.[e]	*meso*-hydrobenzoin	10	PPh_3	60 (8)
17.	*trans*-cyclohexane-1,2-diol	10	PPh_3	0
18.	*cis*-cyclohexane-1,2-diol	10	PPh_3	11
19.	Glycerol	10	PPh_3	0
20.[f]	Erythritol	10	PPh_3	2, 25

[a]Reaction conditions: Glycol (0.50 mmol), **2b** (10 mol%) and reductant (1.5 equiv.) in toluene (*ca*. 2.5 mL) at 170 °C for 16 hours. [b]Yields were determined by ^{1}H NMR spectroscopy using 1,3,5-trimethoxybenzene as an internal standard. [c]Using 3-octanol (*ca*. 2.5 mL) as solvent and reductant. [d]Using **1b** (10 mol%) as catalyst at 55% conversion of decane-1,2-diol. [e]Yield in parentheses refers to the yield of benzaldehyde. [f]Both 2,5-dihydrofuran (2%) and 1,4-anhydrothreitol (25%) were obtained.

Kinetic studies: Preliminary qualitative kinetic studies were undertaken to further explore ligand effects in DODH of styrene glycol catalyzed by dioxomolybdenum complexes used in this study. Complexes **1b** (unsubstituted), **2b** (*o*-/*p*-di-*tert*-butyl), **6b** (*p*-fluoro) and **17b** (phenyl backbone) were chosen for this initial investigation. Yield/conversion data were recorded on aliquots drawn at 20, 40, 60, and 90 minutes as well as overnight (~16 hours) from catalytic reactions run in pressure reactors using 1,3,5-trimethoxybenzene as an internal standard (Figure 3 and S79-S85).

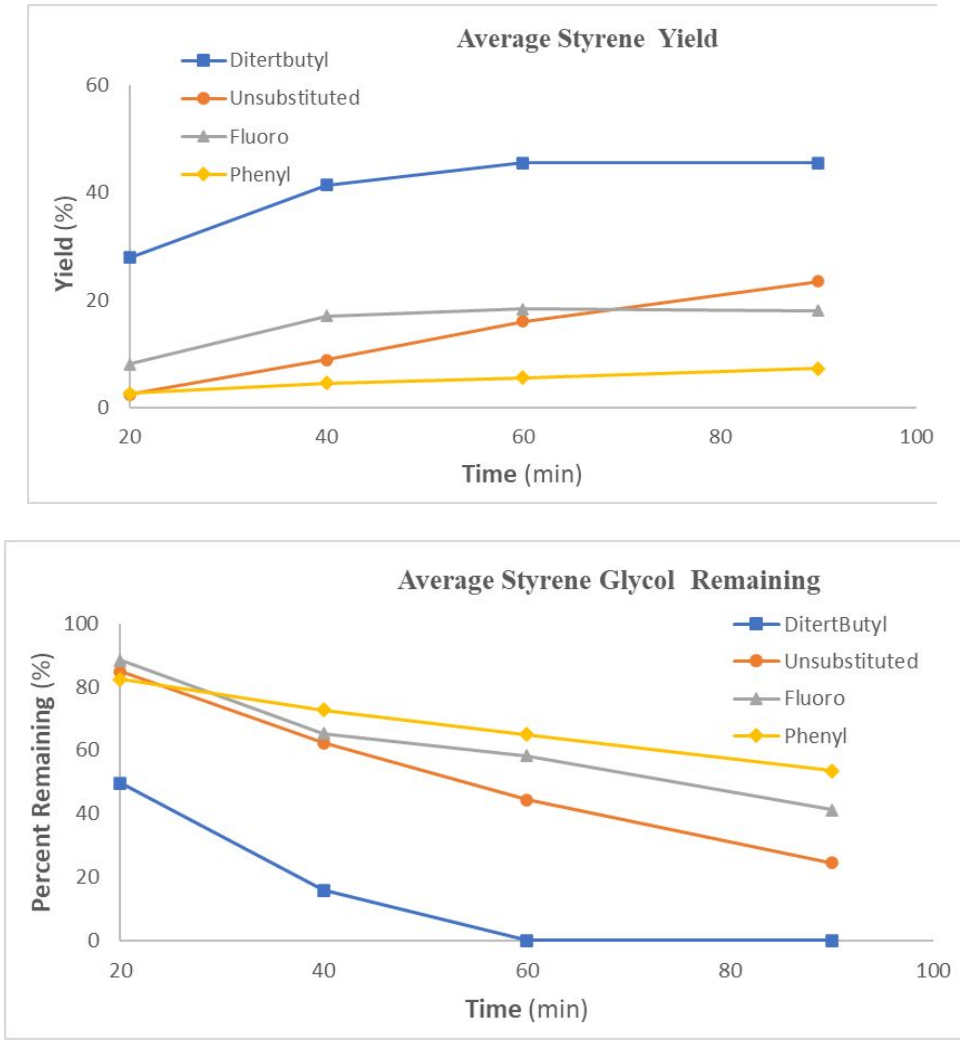


Figure 3. Kinetic profiles for conversion of styrene glycol to styrene using **1b** (●), **2b** (■), **6b** (▲), and **17b** (♦) at 170 °C; formation of styrene (top) and disappearence of styrene glycol (bottom).

The time-dependence data revealed a significant ligand effect and catalyst **2b** featuring the bulky *tert*-butyl groups in *ortho*-/*para*- positions of the phenol arm resulted in almost complete conversion of the glycol within 60 mins with concomitant production of styrene in ~45% yield which is similar to the yield observed from an overnight run (47%). We did not detect a significant amount of benzaldehyde under these conditions (in any of the aliquots collected). Since the styrene yield is practically the same after the overnight run, it can be concluded that the alkene product is not siphoned-off due to side reactions such as polymerization after it is formed. This is in contrast to a recent report from the Kilaynek group where the amount of polystyrene in the reaction mixture increased from 7-52% over a 6-hour period during catalysis (190 ^{o}C) in the absence of a polymerization inhibitor.[38] The time-dependent data collected using **1b** on the other hand exhibits a gradual change in glycol consumption as well as styrene yield reaching 23% over the initial 90 minutes and resulting in 40 % alkene yield overnight. The slightly reduced yield observed after the overnight run during the time-dependence study in comparison to a regular catalytic run (45%; Table 1, entry 1) could be indicative of loss in catalytic activity resulting from the periodic collection of aliquots; a similar effect is also observed when complex **6b** was used. The *para*-F substituted complex **6b** displayed a higher activity initially reaching 17% styrene yield in 40 mins (as opposed to 9% for **1b**) but then leveled off before attaining a ~40% yield overnight. Although a significant electronic effect was not apparent in styrene yields when using **1b** and **6b** duirng the catalytic reactions (Table 1), the kinetic results suggest that both steric and electronic factors are crucial in DODH reactions involving these catalysts based on salan ligands, with complexes featuring bulky *ortho*-substituents as well as electron-withdrawing *para*-substituents on the salan ligand displaying enhanced reactivity. The effect of the ligand backbone was confirmed using catalyst **17b** which

produced styrene in 7% yield (at 53% conversion) over the first 90 minutes in comparison to 23% styrene obtained using **1b**; only a 25% yield of styrene was obtained from the overnight run using **17b** which is consistent with earlier observation (Table 1). We hypothesize that the steric bulk from the ^{t}Bu groups at the *ortho*-position could be helpful in preventing a catalyst deactivation pathway such as comproportionation between a reduced Mo(IV) intermediate species with unreduced Mo(IV) center to generate a μ-oxo-Mo(V) dimer which is catalytically inefficient.[38] Alternatively, the steric bulk could also facilitate the alkene extrusion step which has been identified as one of the steps with a high activation barrier in the catalytic cycle in previous studies.[17,27,30,31] Overall, these preliminary kinetic studies highlight the importance of various ligand features (steric, electronics, backbone flexibility) in modulating the reactivity of these dioxomolybdenum complexes in the DODH reaction. The synthetic accessibility, ease of handling, and modular nature of this class of dioxomolybdenum complexes make them an ideal target for further exploration of ligand effects with the goal of improving efficacy of molybdneum catalysts to rival rhenium based systems.

Plausible Mechanism: The DODH reaction in general is proposed to proceed *via* a three-step sequence involving (*a*) initial condensation of the glycol with the metal-oxo to yield a glycolate complex, (*b*) which then is reduced by the sacrificial reductant to a lower oxidation state metal glycolate. Finally, an (*c*) oxidative extrusion/cycloreversion event releases the alkene product while regenerating the higher oxidation state metal-oxo species (Figure 4, *Path 1*). An alternate proposal suggests that the reduction event precedes glycolate formation involving a lower oxidation state metal center (reversal of the first two steps), which then generates the alkene *via* the extrusion step (Figure 4, *Path 2*). Molybdenum catalyzed DODH reactions are further

complicated since the glycol substrate can serve as a competing reductant via an oxidative cleavage of the glycol intermediate (Figure 4, *Path 3*). The actual path that is operative is dependent on several factors including the substrate, reductant, catalyst, temperature, etc.[9,25,48] While we do not have concrete evidence at this point to distinguish between *Path 1* or *Path 2*, the formation of benzaldehyde from oxidative cleavage of the diol when *R*,*R*-/*meso*-hydrobenzoin are subjected to DODH conditions (Table 2, entries 15 & 16) implies that *Path 3* is operational with this particular substrate. Detailed investigations using experimental and computational methods into the mechanism of DODH reaction catalyzed by dioxomolybdenum complexes supported over salan liagnds, in addition to gaining insights into the origin of the observed ligand effects are currently underway in our laboratory.

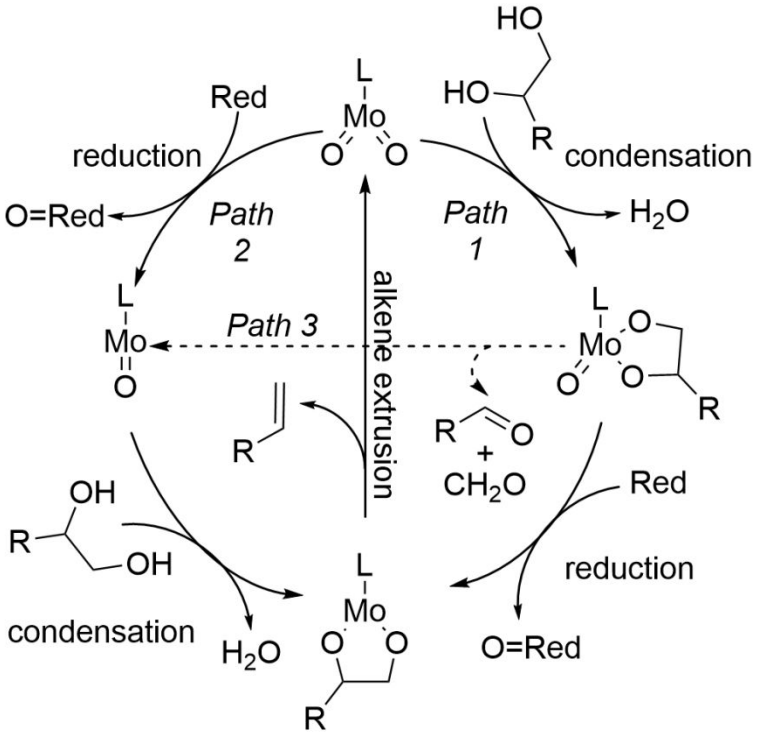


Figure 4. Proposed mechanism for the DODH reaction.

Conclusion

In summary, a variety of dioxomolybdenum complexes stabilized by salan ligands featuring variations in steric, electronics, and backbone flexibility were evaluated in the deoxydehydration reaction. The complexes catalyzed (10 mol% loading) the deoxydehydration of styrene glycol at 170 ^{o}C to produce styrene in 5-54% yield. The flexibility of the ligand backbone was found to be significant in modulating the reactivity of the molybdenum complexes based on catalytic results. However, preliminary kinetic studies suggest that ligand steric, electronics as well as backbone flexibility are all important parameters in controlling reactivity of these molybdenum complexes. A variety of reductants including PPh_3 (47%), Na_2SO_3 (46%), and 3-octanol (23%) could be successfully engaged in effecting the DODH reaction. The yield of styrene product was found to increase by 6-20% when catalysis was performed at a higher temperature of 190 ^{o}C. The substrate scope includes activated diols such as styrene glycol and hydrobenzoin to aliphatic glycols (decane-1,2-diol and octane-1,2-diol), diethyl tartrate, *cis*-/*trans*-cyclohexane-1,2-diol and polyols such as glycerol and erythritol. An almost quantitative mass balance (96%) was observed when *R*,*R*-hydrobenzoin was used as the substrate, including 71% *trans*-stilbene (DODH product) and 50% benzaldehyde (product from oxidative cleavage). Complex **2b** produced an almost quantitative yield (>98%) of diethyl fumarate when (+)-diethyl tartrate was used as the substrate using PPh_3 as reductant; a high yield (78%) was also achieved when Na_2SO_3 was employed as the reductant. Diethyl fumarate was also obtained in 42% yield when a 1 mol% loading of **2b** was used as catalyst along with PPh_3 a reductant representing a high TON of 42. To the best of our knowledge, this is one of the highest TONs reported with a homogeneous earth-abundant catalyst in the DODH reaction.

Conflict of Interest

The authors declare no conflicts of interest.

Author Contributions

Conceptualization: AJ; Investigation: NJW, WCT, JKW, BTN, JYL, SKG, ACM, SEM, TT, GMC, CAN, and IA performed the experimental work including synthesis and characterization of ligands/molybdenum complexes as well as catalytic studies; Methodology: NJW (synthesis/catalysis), WCT and BTN (kinetics); Formal Analysis: WCT, JKW, BTN, FXF, AJ (Kinetics data); Validation: WCT, JKW, BTN (Catalysis and Kinetic data); Supervision: AJ, FXF; Project Administration: AJ; Writing – Original draft: AJ; Writing – Review and Editing: AJ, FXF, KN; Funding Acquisition: AJ. KN engaged in discussions during various stages of the project and provided valuable insights and feedback.

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Experimental Section

General Procedures:

All air and water sensitive manipulations were conducted under a nitrogen atmosphere by using standard Schlenk line techniques or using an MBraun Labstar pro glovebox. All ^{1}H and $^{13}C\{^{1}H\}$ spectra were collected on a Varian 400-MR spectrometer. Chemical shifts (δ) for ^{1}H NMR spectra were referenced to the residual protons on deuterated chloroform (7.26 ppm) or dimethyl sulfoxide (2.50 ppm) and $^{13}C\{^{1}H\}$ NMR spectra were referenced to the residual chloroform (77.1 ppm) or dimethyl sulfoxide (39.5 ppm). Infra-red spectra were recorded on a Thermo Scientific NICOLET iS10 Spectrophotometer equipped with a SMART iTR. Gas Chromatography-Mass Spectrometric (GC-MS) analysis was performed on an Agilent 6850 series GC system connected to an Agilent 5973N Mass Selective Detector equipped with a HP-5MS column (30m × 0.25mm × 0.25μm). Elemental analysis was performed at Robertson Microlit Laboratories (New Jersey, USA). Precursors for ligand and complex synthesis were used as received. $CDCl_3$ and DMSO-d_6 were used as received from Sigma. ESI-MS data were collected on a Waters LCT Premier by flow injection analysis (FIA) in methanol and data analyzed with MassLynx v. 4.1 software. In ESI+ mode, analyte m/z ions (M+H)+ or (M+Na)+ were validated to less than ± 5 ppm relative to the nearest sodiated polyethylene glycol (CAS: 25322-68-3, av. Mwt 400)) or sodiated methoxypolyethyleneglycol (CAS: 990-74-4, av. Mwt 350) calibrant peak lockmass. Solvents (methanol, toluene, tetrahydrofuran, diethyl ether, and hexanes) were purchased from Fisher Scientific and used as received. All starting materials were procured from commercial sources and used without further purification. The ligands (**1a**-**20a**) and complexes **1b**, **2b**, **8b**, **10b**, **14b**-**17b**, and **20b** used in this study were synthesized by modifications of literature protocols.[46,49–62]

Representative procedure for the synthesis of salan ligands

A round bottom flask was charged with 1 mmol of diamine (1 equivalent), 10 mL methanol, and salicylaldehyde (2 equivalents). The solution was stirred overnight at room temperature. The yellow precipitate formed was separated by gravity filtration, and then dissolved in tetrahydrofuran (*ca*. 9 mL) and methanol (*ca*. 1 mL). $NaBH_4$ (5 equivalents) was added slowly, and the solution was stirred at room temperature until it turned colorless. The reaction was quenched with 5 mL of water, and the product was extracted with CH_2Cl_2. The organic layer was separated, and the combined organic layers were dried over anhydrous $MgSO_4$ or Na_2SO_4. The solvent was then removed under vacuum to obtain the product as a white solid.

$^{H,H}L_1$ (**1a**)[62]: Yield (0.439 g, 99%). ^{1}H NMR ($CDCl_3$, 400 MHz, 28 ^{o}C) δ 7.17 (t, $^3J_{HH}$ = 8 Hz, 2H), 6.97 (d, $^3J_{HH}$ = 8 Hz, 2H), 6.83 (d, $^3J_{HH}$ = 8 Hz, 2H), 6.78 (t, $^3J_{HH}$ = 8 Hz, 2H), 6.18 (br, 2H), 3.96 (s, 4H), 2.81 (s, 4H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz, 28 ^{o}C) δ 157.8, 128.9, 128.6, 122.0, 119.2, 116.4, 52.3, 47.5.

$^{tBu,tBu}L_1$ (2**a**)[62]: Yield (0.425 g, 85%). ^{1}H NMR ($CDCl_3$, 400 MHz, 28 ^{o}C) δ 7.23 (d, $^4J_{HH}$ = 4 Hz, 2H), 6.85 (d, $^4J_{HH}$ = 4 Hz, 2H), 3.96 (s, 4H), 2.87 (s, 4H), 1.41 (s, 18H), 1.28 (s, 18H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz, 28 ^{o}C) δ 154.4, 140.6, 135.9, 123.2, 123.1, 121.7, 53.5, 48.0, 34.9, 34.1, 31.7, 29.6.

$^{H,Me}L_1$ (**3a**)[46]: Yield (0.326 g, 47%). ^{1}H NMR ($CDCl_3$, 400 MHz, 28 ^{o}C) δ 6.97 (d, $^3J_{HH}$ = 8 Hz, 2H), 6.78 (s, 2H), 6.73 (d, $^3J_{HH}$ = 8 Hz, 2H), 3.95 (s, 4H), 2.83 (s, 4H), 2.23 (s, 6H).

$^{H,OMe}L_1$ (**4a**)[53]: Yield (0.117 g, 78%). ^{1}H NMR ($CDCl_3$, 400 MHz, 28 ^{o}C) δ 6.85 (d, $^3J_{HH}$ = 8 Hz, 2H), 6.40 (d, $^4J_{HH}$ = 4 Hz, 2H), 6.34 (dd,$^3J_{HH}$ = 8 Hz & $^4J_{HH}$ = 4 Hz, 2H), 3.90 (s, 4H), 3.75 (s, 6H), 2.80 (s, 4H). Selected IR (cm^{-1}): 3277 υ(2^o N-H / O-H); 1103 υ(O-CH_3) cm^{-1}.

$^{H,Cl}L_1$ (**5a**)[53]: Yield (0.307 g, 90%). ^{1}H NMR ($CDCl_3$, 400 MHz, 28 ^{o}C) δ 7.12 (dd, $^3J_{HH}$ = 8 Hz & $^4J_{HH}$ = 4 Hz, 2H), 6.95 (d, $^4J_{HH}$ = 4 Hz, 2H), 6.75 (d, $^3J_{HH}$ = 8 Hz, 2H), 3.95 (s, 4H), 2.82 (s, 4H). Selected IR (cm^{-1}): 3269 υ(2^o N-H / O-H) cm^{-1}.

$^{H,F}L_1$ (**6a**)[53]: Yield (0.461 g, 56%). ^{1}H NMR ($CDCl_3$, 400 MHz, 28 ^{o}C) δ 6.86 (dt, $^3J_{HH}$ = 8 Hz & $^4J_{HH}$ = 4 Hz, 2H), 6.77-6.74 (m, 2H), 6.70 (dd, $^3J_{HH}$ = 8 Hz & $^4J_{HH}$ = 4 Hz, 2H), 3.95 (s, 4H), 2.83 (s, 4H).

$^{Cl,Cl}L_1$ (**8a**)[51]: There was no need for extraction as the product precipitated out upon reduction. Yield (0.413 g, 81%). ^{1}H NMR (DMSO-d_6, 400 MHz, 28 ^{o}C) δ 7.30 (d, $^4J_{HH}$ = 4 Hz, 2H), 7.10 (d, $^4J_{HH}$ = 4 Hz, 2H), 3.88 (d, $^3J_{HH}$ = 8 Hz, 4H), 2.68 (d, $^3J_{HH}$ = 8 Hz, 4H).

$^{H,H}L_2$ (**9a**)[56]: Yield (0.504 g, 48%). ^{1}H NMR ($CDCl_3$, 400 MHz, 28 ^{o}C) δ 7.17 (t, $^3J_{HH}$ = 8 Hz, 2H), 6.97 (d, $^3J_{HH}$ = 8 Hz, 2H), 6.83 (d, $^3J_{HH}$ = 8 Hz, 2H), 6.78 (d, $^3J_{HH}$ = 8 Hz, 2H), 4.06-3.91 (m, 4H), 2.92 (hex, $^3J_{HH}$ = 8 Hz, 1H), 2.70 (d, $^3J_{HH}$ = 8 Hz, 2H), 1.18 (d, $^3J_{HH}$ = 8 Hz, 3H).

$^{tBu,tBu}L_2$ (**10a**)[58]: Yield (0.361 g, 99%). ^{1}H NMR ($CDCl_3$, 400 MHz, 28 ^{o}C) δ 7.22-7.21 (m, 2H), 6.86 (dd, J_{HH} = 4 Hz & 2Hz, 2H), 4.03-3.89 (m, 4H), 2.93 (m, 1H), 2.72 (d, $^3J_{HH}$ = 8 Hz, 2H), 1.40 (s, 18H), 1.28 (s, 18H), 1.20 (d, $^3J_{HH}$ = 8 Hz, 3H).

$^{H,Cl}L_2$ (**11a**)[49]: Yield (0.274 g, 63%). ^{1}H NMR ($CDCl_3$, 400 MHz, 28 ^{o}C) δ 7.09 (d, $^3J_{HH}$ = 8 Hz, 2H), 6.92 (s, 2H), 6.72 (d, $^3J_{HH}$ = 8 Hz, 2H), 6.16 (br, 2H), 3.98-3.81 (m, 4H), 2.85 (hex, $^3J_{HH}$ = 8 Hz, 1H), 2.65 (d, $^3J_{HH}$ = 8 Hz, 2H), 1.14 (d, $^3J_{HH}$ = 8 Hz, 3H).

$^{H,OMe}L_2$ (**12a**): Yield (0.260 g, 50%). ^{1}H NMR ($CDCl_3$, 400 MHz, 28 ^{o}C) δ 6.72-6.69 (m, 4H), 6.53 (s, 2H),5.85 (br, 2H), 3.96-3.80 (m, 4H), 3.71 (s, 6H), 2.85 (hex, $^3J_{HH}$ = 8 Hz, 1H), 2.64 (d, $^3J_{HH}$ = 8 Hz, 2H), 1.13 (d, $^3J_{HH}$ = 8 Hz, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz, 28 ^{o}C) δ 152.5, 151.6, 123.4, 123.0, 116.7, 116.6, 114.4, 114.2, 113.7, 113.6, 55.7, 53.7, 52.7, 51.8, 50.0. 18.1. HRMS (ESI/Q-TOF) m/z: $[M+H]^+$ Calcd. for $[C_{19}H_{26}N_2O_4+H]^+$ 347.1971; Found 347.1966.

$^{tBu,tBu}L_3$ (**14a**)[62]: Yield (2.34 g, 92%). ^{1}H NMR ($CDCl_3$, 400 MHz, 28 ^{o}C) δ 7.22 (s, 2H), 6.86 (s, 2H), 3.95 (s, 4H), 2.77 (t, $^3J_{HH}$ = 8 Hz, 4H),1.79 (quint, $^3J_{HH}$ = 8 Hz, 2H), 1.41 (s, 18H), 1.28 (s, 18H).

$^{H,H}L_4$ (**15a**)[54]: Yield (0.454 g, 99%). ^{1}H NMR ($CDCl_3$, 400 MHz, 28 ^{o}C) δ 7.18 (m, 2H), 7.00-6.94 (m, 4H), 6.80-6.76 (m, 2H), 4.06-3.86 (m, 4H), 2.52 (m, 2H), 2.03 (br, 2H), 1.74 (br, 2H), 1.25 (br, 2H).

$^{tBu,tBu}L_4$ (**16a**)[50]: Yield (0.577 g, 58%). ^{1}H NMR ($CDCl_3$, 400 MHz, 28 ^{o}C) δ 7.22 (d, $^4J_{HH}$ = 4 Hz, 2H), 6.87 (d, $^4J_{HH}$ = 4 Hz, 2H), 4.05 (d, $^2J_{HH}$ = 16 Hz, 2H), 3.90 (d, $^2J_{HH}$ = 16 Hz, 2H), 2.51 (br, 2H), 2.19 (br, 2H), 1.72 (br, 2H), 1.44-1.41 (m, 2H), 1.38 (s, 18H), 1.28 (s, 18H), 1.23-1.20 (m, 4H).

$^{H,H}L_5$ (**17a**)[50]: Yield (0.305 g, 76%). ^{1}H NMR ($CDCl_3$, 400 MHz, 28 ^{o}C) δ 7.24-7.19 (m, 4H), 6.96-6.94 (m, 4H), 6.89 (t, $^3J_{HH}$ = 8 Hz, 2H), 6.86 (t, $^3J_{HH}$ = 8 Hz, 2H), 4.40 (s, 4H).

$^{tBu,tBu}L_5$ (**18a**)[60]: Yield (0.328 g, 81%). ^{1}H NMR ($CDCl_3$, 400 MHz, 28 ^{o}C) δ 7.99 (s, 2H), 7.27 (s, 2H), 7.05 (s, 2H), 6.98 (s, 4H), 4.36 (br, 4H), 1.38 (s, 18H), 1.30 (s, 18H).

$^{tBu,Me}L_6$ (**19a**)[57]: Yield (0.764 g, 76%). ^{1}H NMR ($CDCl_3$, 400 MHz, 28 ^{o}C) δ 10.6 (br, 2H), 6.98 (s, 2H), 6.62 (s, 2H), 3.62 (s, 4H), 2.60 (s, 4H), 2.24 (s, 6H), 2.23 (s, 6H), 1.38 (s, 18H).

$^{Cl,Cl}L_6$ (**20a**)[55]: Yield (0.529 g, 39%). ^{1}H NMR ($CDCl_3$, 400 MHz, 28 ^{o}C) δ 7.27 (d, $^4J_{HH}$ = 4 Hz, 2H), 6.87 (d, $^4J_{HH}$ = 4 Hz, 2H), 3.69 (s, 4H), 2.70 (s, 4H), 2.32 (s, 6H).

Procedure for synthesis of nitro-substituted ligands

$^{H,NO2}L_1$(**7a**): A round bottom flask was charged with 1,2-ethylenediamine (0.60 mL, 0.898 mmol), 5-nitrosalicylaldehyde (0.301 g, 1.802 mmol), and 10 mL methanol. The solution was stirred overnight at room temperature. A yellow precipitate formed, which was separated by gravity filtration. The resulting yellow solid was dissolved in 9 mL tetrahydrofuran, 2 mL methylene chloride, and 1 mL methanol. $NaBH_4$ (0.142 g, 3.76 mmol) was added slowly. The solution was stirred overnight at room temperature. A yellow-orange precipitate formed, which was separated by gravity filtration. The resulting material was filtered through a silica plug, with 50% methanol in methylene chloride. The solvent was removed by evaporation under vacuum to yield the product as a light yellow solid (0.235 g, 72%).

$^{H,NO2}L_1$(**7a**)[59]: Yield (0.235 g, 72%). ^{1}H NMR ($CDCl_3$, 400 MHz, 28 ^{o}C) δ 7.77 (d, $^4J_{HH}$ = 4 Hz, 2H), 7.71 (dd, $^3J_{HH}$ = 8 Hz & $^4J_{HH}$ = 4 Hz, 2H), 5.96 (d, $^3J_{HH}$ = 8 Hz, 2H), 3.46 (s, 4H), 2.62 (s, 4H). $^{13}C\{^1H\}$ NMR (DMSO-d_6, 100 MHz, 28 ^{o}C) δ 179.6, 167.3, 128.5, 127.8, 127.0, 126.7, 119.2, 50.34, 47.83. Selected IR (cm^{-1}): 3560, 3340 υ(2º N-H / O-H); 1595, 1333 υ(N-O); 1270 υ(Ar-O) cm^{-1}.

$^{H,NO2}L_2$ (**13a**): Yield (0.183 g, 28 %). ^{1}H NMR (DMSO-d_6, 400 MHz, 28 ^{o}C) δ 8.10 (dd, $^3J_{HH}$ = 8 Hz & $^4J_{HH}$ = 4 Hz, 2H), 7.95 (dt, $^3J_{HH}$ = 8 Hz & $^4J_{HH}$ = 2 Hz, 2H), 6.68 (d, $^3J_{HH}$ = 8 Hz, 1H), 6.55 (d, $^3J_{HH}$ = 8 Hz, 1H), 3.98-3.78 (m, 4H), 3.05 (hex, $^3J_{HH}$ = 8 Hz, 1H), 2.81-2.66 (m, 2H), 1.14 (d, $^3J_{HH}$ = 8Hz, 3H). Selected IR (cm^{-1}): 3343(b) υ(O-H); 1591, 1337 υ(N-O) cm^{-1}. HRMS (ESI/Q-TOF) m/z: $[M-H]^-$ Calcd. for $[C_{17}H_{20}N_4O_6\text{-}H]^-$ 375.1305; Found 375.1310.

Representative procedure for the synthesis of molybdenum complexes

A round bottom flask equipped with magnetic stir bar was flame dried and flushed with nitrogen gas. The flask was charged with the ligand (1 equiv.), $MoO_2(acac)_2$ (1 equiv.), and methanol or acetonitrile (*ca*. 5mL), and the reaction mixture was stirred under nitrogen overnight at room temperature. The solvent was removed by evaporation under vacuum. The product was washed with methanol, leaving a yellow solid, which was separated by gravity filtration and was washed twice with cold methanol.

$^{H,H}L_1MoO_2$ (**1b**)[62]: Yield (0.230 g, 52%). ^{1}H NMR (DMSO-d_6, 400 MHz, 28 ^{o}C) δ 7.13-7.09 (m, 4H), 6.80 (t, $^3J_{HH}$ = 8 Hz, 2H), 6.70 (d, $^3J_{HH}$ = 8 Hz, 2H), 5.21 (br, 2H), 4.78 (d, $^2J_{HH}$

= 16 Hz, 2H), 3.87 (d, $^{2}J_{HH}$ = 16 Hz, 2H), 2.74–2.71 (m, 2H), 2.34–2.23 (m, 2H). $^{13}C\{^{1}H\}$ NMR (DMSO-d_6, 100 MHz, 28 ^{o}C) δ 160.3, 130.1, 128.2, 122.5, 120.4, 118.8, 53.0, 46.2. Selected IR (cm^{-1}): 879, 920 υ(Mo=O).

$^{tBu,tBu}L_1MoO_2$ (**2b**)[62]: Yield (1.43 g, 79%). ^{1}H NMR (DMSO-d_6, 400 MHz, 28 ^{o}C) δ 7.11 (s, 2H), 6.93 (s, 2H), 4.73 (d, $^{2}J_{HH}$ = 16 Hz, 2H), 4.43 (br, 2H), 3.88 (d, $^{2}J_{HH}$ = 16 Hz, 2H), 2.79–2.75 (m, 2H), 2.33–2.29 (m, 2H), 1.34 (s, 18H), 1.23 (s, 18H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz, 26 ^{o}C) δ 156.8, 142.5, 138.0, 124.2, 123.2, 120.6, 54.3, 46.2, 35.2, 34.3, 31.6, 29.9. Selected IR (cm^{-1}): 897, 911 υ(Mo=O).

$^{H,Me}L_1MoO_2$ (**3b**): Yield (0.464 g, 99%). ^{1}H NMR (DMSO-d_6, 400 MHz, 28 °C) δ 6.91-6.88 (m, 4H), 6.58 (d, $^{3}J_{HH}$ = 8 Hz, 2H), 5.12 (br, 2H), 4.74 (d, $^{2}J_{HH}$ = 16 Hz, 2H), 3.80 (d, $^{2}J_{HH}$ = 16 Hz, 2H), 2.71-2.68 (m, 2H), 2.30-2.25 (m, 2H), 2.19 (s, 6H). $^{13}C\{^{1}H\}$ NMR (DMSO-d_6, 100 MHz, 28 ^{o}C) δ 157.8, 129.8, 128.5, 128.1, 121.6, 118.0, 52.6, 45.7, 20.1. Selected IR (cm^{-1}): 885, 918 υ(Mo=O). Anal. Calcd. for $C_{18}H_{22}N_2O_4Mo$: C, 50.71%; H, 5.20%; N, 6.57%. Found: C, 50.49%; H, 5.21%; N, 6.66%.

$^{H,OMe}L_1MoO_2$ (**4b**): Yield (0.070 g, 48%). ^{1}H NMR (DMSO-d_6, 400 MHz, 28 ^{o}C) δ 6.97 (d, $^{3}J_{HH}$ = 8 Hz, 2H), 6.40 (dd, J = 8 Hz & 2 Hz, 2H), 6.27 (d, $^{4}J_{HH}$ = 2 Hz, 2H), 5.16 (br, 2H), 4.70 (d, $^{2}J_{HH}$ = 16 Hz, 2H), 3.80 (d, $^{2}J_{HH}$ = 16 Hz, 2H), 3.67 (s, 6H), 2.69-2.66 (m, 2H), 2.35-2.23 (m, 2H). $^{13}C\{^{1}H\}$ NMR (DMSO-d_6, 100 MHz, 28 ^{o}C) δ 160.5, 159.0, 130.0, 114.2, 106.6, 103.3, 54.9, 52.1, 45.4. Selected IR (cm^{-1}): 887, 898 υ(Mo=O). Anal. Calcd. for $C_{18}H_{22}N_2O_6Mo$: C, 47.17%; H, 4.84%; N, 6.11%. Found: C, 47.13%; H, 4.92%; N, 5.83%.

$^{H,Cl}L_1MoO_2$ (**5b**): Yield (0.276 g, 74%). ^{1}H NMR (DMSO-d_6, 400 MHz, 28 ^{o}C) δ 7.19 (s, 2H), 7.13 (d, $^3J_{HH}$ = 8 Hz, 2H), 6.71 (d, $^3J_{HH}$ = 8 Hz, 2H), 5.34 (br, 2H), 4.72 (d, $^2J_{HH}$ = 16 Hz, 2H), 3.90 (d, $^2J_{HH}$ = 16 Hz, 2H), 2.75 (br, 2H), 2.29-2.19 (m, 2H). ^{13}C{^{1}H} NMR (DMSO-d_6, 100 MHz, 28 ^{o}C) δ 158.7, 129.0, 127.4, 124.1, 123.2, 120.1, 52.0, 45.8. Selected IR (cm^{-1}): 3238 υ(2º N-H); 889, 909 υ(Mo=O). Anal. Calcd. for $C_{16}H_{16}N_2O_4Cl_2Mo$: C, 41.14%; H, 3.45%; N, 6.00%. Found: C, 41.63%; H, 3.78%; N, 6.38%.

$^{H,F}L_1MoO_2$ (**6b**): Yield (0.321 g, 50%). ^{1}H NMR (DMSO-d_6, 400 MHz, 28 ^{o}C) δ 6.99-6.90 (m, 4H), 6.71-6.68 (m, 2H), 5.27 (br, 2H), 4.73 (d, $^2J_{HH}$ = 16 Hz, 2H), 3.88 (d, $^2J_{HH}$ = 16 Hz, 2H), 2.74 (br, 2H), 2.26 (t, $^3J_{HH}$ = 8 Hz, 2H). ^{13}C{^{1}H} NMR (DMSO-d_6, 100 MHz, 28 ^{o}C) δ 156.7, 156.1 (d, $^1J_{CF}$ = 235 Hz), 123.7 (d, $^3J_{CF}$ = 7 Hz), 119.8 ($^3J_{CF}$ = 7 Hz), 115.9 ($^2J_{CF}$ = 23 Hz), 114.5 ($^2J_{CF}$ = 23 Hz), 52.7, 46.3. Selected IR (cm^{-1}): 884, 905 υ(Mo=O). Anal. Calcd. for $C_{16}H_{16}N_2O_4F_2Mo$: C, 44.25%; H, 3.71%; N, 6.45%. Found: C, 43.39%; H, 3.68%; N, 6.23%.

$^{H,NO2}L_1MoO_2$ (**7b**): Yield (0.147 g, 55%). ^{1}H NMR (DMSO-d_6, 400 MHz, 28 ^{o}C) δ 8.15 (d, $^4J_{HH}$ = 2 Hz, 2H), 8.03 (dd, $^3J_{HH}$ = 8 Hz & $^4J_{HH}$ = 2 Hz, 2H), 6.90 (d, $^3J_{HH}$ = 8 Hz, 2H), 5.71 (br, 2H), 4.80 (d, $^2J_{HH}$ = 16 Hz, 2H), 4.14 (d, $^2J_{HH}$ = 16 Hz, 2H), 2.85–2.77 (m, 2H), 2.27–2.21 (m, 2H). ^{13}C{^{1}H} NMR (DMSO-d_6, 100 MHz, 26 ^{o}C) δ 170.5, 145.2, 131.4, 129.2, 128.3, 124.8, 57.1, 51.0. Selected IR (cm^{-1}): 3238 υ(2º N-H); 1572, 1319 υ(N-O); 905, 920 υ(Mo=O). Anal. Calcd. for $C_{16}H_{16}N_4O_8Mo$: C, 39.36%; H, 3.30%; N, 11.47%. Found: C, 39.20%; H, 3.41%; N, 11.49%.

$^{Cl,Cl}L_1MoO_2$ (**8b**)[51]: Yield (0.369 g, 67%). ^{1}H NMR (DMSO-d_6, 400 MHz, 28 °C) δ 7.41 (d, $^4J_{HH}$ = 4 Hz, 2H), 7.22 (d, $^4J_{HH}$ = 4 Hz, 2H), 5.40 (br, 2H), 4.75 (d, $^2J_{HH}$ = 16 Hz, 2H), 3.99 (d, $^2J_{HH}$ = 16 Hz, 2H), 2.81-2.79 (m, 2H), 2.22 (t, $^3J_{HH}$ = 8 Hz, 2H). ^{13}C{^{1}H} NMR (DMSO-d_6, 100 MHz, 26 ^{o}C) δ 154.9, 128.6, 127.9, 125.9, 123.8, 123.5, 52.6, 46.5. Selected IR (cm^{-1}): 876, 913 υ(Mo=O).

$^{H,H}L_2MoO_2$ (**9b**): Yield (0.390 g, 67%). ^{1}H NMR ($CDCl_3$, 400 MHz, 28 ^{o}C) δ 7.18 (t, $^3J_{HH}$ = 8 Hz, 2H), 7.05 (t, $^3J_{HH}$ = 8 Hz, 2H), 6.89–6.82 (m, 4H), 5.30 (dt, $^2J_{HH}$ = 12 Hz & $^4J_{HH}$ = 4 Hz, 2H), 4.19 (d, $^2J_{HH}$ = 16 Hz, 1H), 4.04 (d, $^2J_{HH}$ = 12 Hz, 1H), 3.23 (d, $^2J_{HH}$ = 12 Hz, 1H), 2.94–2.81 (m, 2H), 2.60 (d, $^2J_{HH}$ = 12 Hz, 1H), 2.49 (q, $^3J_{HH}$ = 8 Hz, 1H), 1.16 (d, $^3J_{HH}$ = 8 Hz, 3H). ^{13}C{^{1}H} NMR (DMSO-d_6, 100 MHz, 26 ^{o}C) δ 160.4, 160.3, 130.2, 130.0, 128.4, 128.1, 122.3, 122.3, 120.4, 120.4, 118.7, 118.7, 53.1, 52.9, 50.1, 50.0, 14.1. Selected IR (cm^{-1}): 876, 915 υ(Mo=O). Anal. Calcd. for $C_{17}H_{20}N_2O_4Mo$: C, 49.52%; H, 4.89%; N, 6.79%. Found: C, 49.53%; H, 4.87%; N, 7.09%.

$^{tBu,tBu}L_2MoO_2$ (**10b**)[52]: Yield (0.348 g, 79%). ^{1}H NMR (DMSO-d_6, 400 MHz, 28 ^{o}C) δ 7.13 (s, 1H), 7.09 (s, 1H), 6.98 (s, 1H), 6.90 (s, 1H), 4.73 (dd, $^2J_{HH}$ = 12 Hz & $^3J_{HH}$ = 8 Hz, 2H), 4.65 (d, $^2J_{HH}$ = 12 Hz, 2H), 4.25 (d, $^2J_{HH}$ = 12 Hz, 1H), 4.08 (d, $^2J_{HH}$ = 12 Hz, 1H), 3.95 (d, $^2J_{HH}$ = 12 Hz, 1H), 3.88 (d, $^2J_{HH}$ = 12 Hz, 1H), 2.72 (d, $^2J_{HH}$ = 12 Hz, 1H), 2.10 (q, $^3J_{HH}$ = 12 Hz, 2H), 1.34 (s, 9H), 1.32 (s, 9H), 1.23 (s, 9H), 1.22 (s, 9H), 1.03 (d, $^3J_{HH}$ = 8 Hz, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz, 28 ^{o}C) δ 157.1, 156.5, 142.4, 142.4, 138.0, 137.7, 124.4, 123.9, 123.4, 122.8, 120.5, 119.8, 54.1, 52.6, 51.4, 49.6, 35.2, 34.2, 31.6, 29.9, 29.9, 16.3. Selected IR (cm^{-1}): 883, 902 υ(Mo=O).

$^{H,Cl}L_2MoO_2$ (**11b**): Yield (0.091 g, 92%). ^{1}H NMR (DMSO-d_6, 400 MHz, 26 ^{o}C) δ 7.92 (s, 2H), 7.39–7.31 (m, 4H), 7.01 (d, $^3J_{HH}$ = 8 Hz, 2H), 5.29 (d, $^2J_{HH}$ = 16 Hz, 2H), 5.20 (d, $^2J_{HH}$ = 16 Hz, 1H), 4.63 (d, $^2J_{HH}$ = 12 Hz, 1H), 4.37 (d, $^2J_{HH}$ = 16 Hz, 1H), 4.20 (d, $^2J_{HH}$ = 16 Hz, 1H), 3.10 (d, $^2J_{HH}$ = 12 Hz, 1H), 2.99-2.88 (m, 2H), 2.57 (q, $^3J_{HH}$ = 12 Hz, 1H), 1.40 (d, $^3J_{HH}$ = 12 Hz, 3H). $^{13}C\{^1H\}$ NMR (DMSO-d_6, 100 MHz, 26 ^{o}C) δ 159.2, 159.1, 129.6, 129.4, 128.1, 127.8, 124.6, 124.5, 123.7, 123.6, 120.5, 120.4, 53.1, 52.4, 50.3, 49.4, 14.1. Selected IR (cm^{-1}): 3263, 3215 υ(2º N-H); 882, 912 υ(Mo=O). Anal. Calcd. for $C_{17}H_{18}N_2O_4Cl_2Mo$: C, 42.43%; H, 3.77%; N, 5.82%. Found: C, 42.48%; H, 3.80%; N, 5.76%.

$^{H,OMe}L_2MoO_2$ (**12b**): Yield (0.134 g, 88%). ^{1}H NMR (DMSO-d_6, 400 MHz, 28 ^{o}C) δ 6.73-6.60 (m, 6H), 5.17 (d, $^2J_{HH}$ = 12 Hz, 2H), 4.78-4.72 (m, 3H), 4.03 (d, $^2J_{HH}$ = 16 Hz, 1H), 3.82 (d, $^2J_{HH}$ = 16 Hz, 1H), 3.66 (s, 6H), 2.66 (d, $^2J_{HH}$ = 16 Hz, 2H), 2.05 (q, $^3J_{HH}$ = 12 Hz, 1H), 0.97 (d, $^3J_{HH}$ = 4 Hz, 3H). $^{13}C\{^1H\}$ NMR (DMSO-d_6, 100 MHz, 26 ^{o}C) δ 154.7, 154.6, 153.1, 122.9, 122.8, 119.2, 119.1, 114.9, 114.3, 113.8, 55.8, 53.1, 53.0, 50.1, 14.2. Selected IR (cm^{-1}): 3244 υ(2º N-H); 896, 909 υ(Mo=O). Anal. Calcd. for $C_{19}H_{24}N_2O_6Mo$: C, 48.31%; H, 5.12%; N, 5.93%. Found: C, 48.18%; H, 5.00%; N, 5.99%.

$^{H,NO2}L_2$ MoO_2 (**13b**): Yield (0.171 g, 70%). ^{1}H NMR (DMSO-d_6, 400 MHz, 28 ^{o}C) δ 8.23 (d, $^4J_{HH}$ = 2 Hz, 2H), 8.15 (d, $^4J_{HH}$ = 2 Hz, 2H), 8.06-8.02 (m, 2H), 6.90 (d, $^3J_{HH}$ = 4 Hz, 1H), 6.88 (d, $^3J_{HH}$ = 4 Hz, 1H), 5.76 (d, $^2J_{HH}$ = 12 Hz, 1H), 5.35 (d, $^2J_{HH}$ = 12 Hz, 1H), 4.83-4.76 (m, 2H), 4.35 (d, $^2J_{HH}$ = 16 Hz, 1H), 4.13 (d, $^2J_{HH}$ = 16 Hz, 1H), 2.78 (d, $^2J_{HH}$ = 12 Hz, 1H), 2.00 (q, $^3J_{HH}$ = 12 Hz, 1H), 1.02 (d, $^3J_{HH}$ = 8 Hz, 3H). $^{13}C\{^1H\}$ NMR (DMSO-d_6, 100 MHz, 28 ^{o}C) δ 165.8,

165.7, 140.4, 140.4, 126.8, 126.6, 124.7, 124.4, 123.4, 123.4, 120.0, 119.9, 53.1, 52.2, 50.6, 49.3, 14.0. Selected IR (cm^{-1}): 3267, 3235 υ(2º N-H); 1572, 1337 υ(N-O); 880, 900 υ(Mo=O). Anal. Calcd. for $C_{17}H_{18}N_4O_8Mo$: C, 40.65%; H, 3.61%; N, 11.15%. Found: C, 40.45%; H, 3.89%; N, 10.91%.

$^{tBu,tBu}L_3MoO_2$ (**14b**)[62]: Yield (0.337 g, 56%). ^1H NMR ($CDCl_3$, 400 MHz, 28 ºC) δ 7.26 (d, $^4J_{HH}$ = 2 Hz, 2H), 6.90 (d, $^4J_{HH}$ = 2 Hz, 2H), 5.34 (dd, J_{HH} = 12 Hz & 4 Hz, 2H), 3.63 (d, $^2J_{HH}$ = 12 Hz, 2H), 3.27 (br, 2H), 2.88-2.78 (m, 4H), 1.46 (s, 18H), 1.28 (s, 18H), 1,16-1.11 (m, 2H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz, 28 ºC) δ 157.6, 142.7, 137.7, 124.3, 123.4, 123.1, 57.2, 51.9, 35.2, 34.3, 31.6, 30.0, 26.3. Selected IR (cm^{-1}): 891, 912 υ(Mo=O).

$^{H,H}L_4MoO_2$ (**15b**)[61]: Yield (0.310 g, 75%). ^1H NMR (DMSO-d_6, 400 MHz, 28 ºC) δ 7.12 (t, $^3J_{HH}$ = 8 Hz, 4H), 6.79 (t, $^3J_{HH}$ = 8 Hz, 2H), 6.70 (d, $^3J_{HH}$ = 8 Hz, 2H), 4.96 (d, $^3J_{HH}$ = 8 Hz, 2H), 4.78 (d, $^2J_{HH}$ = 16 Hz, 2H), 4.13 (d, $^2J_{HH}$ = 16 Hz, 2H), 4.06 (br, 2H), 2.11-2.01 (m, 2H), 1.57 (d, $^3J_{HH}$ = 8 Hz, 2H), 1.05-1.04 (m, 2H), 0.86-0.83 (m, 2H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz, 28 ºC) δ 160.3, 129.4, 128.7, 120.8, 120.4, 118.9, 57.8, 50.1, 29.6, 24.3. Selected IR (cm^{-1}): 881, 905 υ(Mo=O).

$^{tBu,tBu}L_4MoO_2$ (**16b**)[50]: Yield (0.130 g, 51%). ^1H NMR ($CDCl_3$, 400 MHz, 28 ºC) δ 7.26 (s, 2H), 6.86 (s, 2H), 5.28 (d, $^2J_{HH}$ = 16 Hz, 2H), 4.18 (d, $^2J_{HH}$ = 12 Hz, 2H), 2.34-2.28 (m, 4H), 1.43 (s, 18H), 1.30 (s, 18H), 1.19-1.17 (m, 4H), 0.88-0.85 (m, 4H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz, 28 ºC) δ 157.1, 152.1, 142.8, 142.3, 142.0, 138.0, 137.7, 137.6, 125.7, 125.4, 124.1, 124.0, 123.0, 122.9, 120.0, 119.6, 65.19, 58.9, 57.6, 53.4, 50.9, 50.5, 35.2, 35.1, 34.3, 34.2, 33.0, 31.6, 31.6,

31.5, 29.9, 29.9, 28.9, 24.5, 24.3, 24.1. Selected IR (cm^{-1}): 879, 904 υ(Mo=O). Anal. Calcd. for $C_{36}H_{56}N_2O_4Mo$: C, 63.89%; H, 8.34%; N, 4.15%. Found: C, 62.58%; H, 8.07%; N, 4.29%.

$^{H,H}L_5MoO_2$ (**17b**)[50]: Yield (1.45 g, 86%). ^1H NMR (DMSO-d_6, 400 MHz, 28 ^oC) δ 7.55 (d, $^3J_{HH}$ = 8 Hz, 1H), 7.37-7.35 (m, 1H), 7.19-7.10 (m, 4H), 7.07-7.05 (m, 1H), 7.02-6.98 (m, 2H), 6.91 (d, $^3J_{HH}$ = 8 Hz, 1H), 6.85-6.83 (m, 1H), 6.80 (d, $^3J_{HH}$ = 8 Hz, 1H), 6.76-6.68 (m, 2H), 6.63 (d, $^3J_{HH}$ = 8 Hz, 1H), 6.59 (d, $^3J_{HH}$ = 8 Hz, 1H), 6.42 (d, $^2J_{HH}$ = 12 Hz, 1H), 5.24 (d, $^2J_{HH}$ = 16 Hz, 1H), 5.16 (d, $^2J_{HH}$ = 16 Hz, 1H), 4.94 (d, $^2J_{HH}$ = 16 Hz, 1H), 4.20 (d, $^2J_{HH}$ = 12 Hz, 1H). $^{13}C\{^1H\}$ NMR (DMSO-d_6, 100 MHz, 28 ^oC) δ 163.0, 160.2, 155.6, 148.0, 141.1, 130.5, 129.1, 129.0, 128.9, 128.0, 127.9, 125.9, 124.3, 122.9, 120.1, 119.2, 119.1, 118.9, 117.8, 115.3, 111.1, 53.7, 53.6. Selected IR (cm^{-1}): 3127 υ(2º N-H); 916, 876 υ(Mo=O).

$^{tBu,tBu}L_5MoO_2$ (**18b**): Yield (0.069 g, 55%). ^1H NMR ($CDCl_3$, 400 MHz, 28 ^oC) δ 7.18-7.16 (m, 2H), 7.11 (s, 2H), 7.08-7.05 (m, 2H), 6.58 (s, 2H), 5.35 (d, $^2J_{HH}$ = 12 Hz, 2H), 4.40 (s, 2H), 4.22 (d, $^2J_{HH}$ = 12 Hz, 2H), 1.37 (s, 18H), 1.12 (s, 18H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz, 28 ^oC) δ 156.9, 142.5, 139.9, 138.1, 128.1, 125.2, 125.1, 123.4, 121.2, 54.4, 35.2, 34.1, 31.6, 30.0. Selected IR (cm^{-1}): 904, 879 υ(Mo=O). Anal. Calcd. For $C_{36}H_{50}N_2O_4Mo$: C, 64.46%; H, 7.51%; N, 4.18%. Found: C, 65.17%; H, 7.17%; N, 4.44%.

$^{tBu,Me}L_6MoO_2$ (**19b**): Yield (0.383 g, 39%). ^1H NMR ($CDCl_3$, 400 MHz, 28 ^oC) δ 7.08 (s, 2H), 6.71 (s, 2H), 4.83 (d, $^2J_{HH}$ = 12 Hz, 2H), 3.55 (d, $^2J_{HH}$ = 16 Hz, 2H), 3.15 (d, $^2J_{HH}$ = 12 Hz, 2H), 2.72 (s, 6H), 2.27 (s, 6H), 2.25 (d, $^2J_{HH}$ = 12 Hz, 2H), 1.41 (s, 18H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz, 28 ^oC) δ 157.8, 138.4, 129.0, 127.8, 127.6, 65.11, 53.23, 49.32, 34.87, 30.5, 20.8. Selected

IR (cm^{-1}): 897, 922 υ(Mo=O). HRMS (ESI/Q-TOF) m/z: $[M+H]^+$ Calcd. for $[C_{28}H_{42}MoN_2O_4+H]^+$ 563.2291; Found 563.2277.

$^{Cl,Cl}L_6MoO_2$ (**20b**)[55]: Yield (0.145 g, 53%). ^1H NMR (DMSO-d_6, 400 MHz, 28 °C) δ 7.51 (s, 2H), 7.23 (s, 2H), 4.61 (d, $^2J_{HH}$ = 16 Hz, 2H), 3.90 (d, $^2J_{HH}$ = 16 Hz, 2H), 2.73 (d, $^2J_{HH}$ = 12 Hz, 2H), 2.58 (s, 6H), 2.36 (d, $^2J_{HH}$ = 12 Hz, 2H).

Representative procedure for deoxydehydration reactions

A pressure tube reactor was charged with diol (0.500 mmol), reductant (0.750 mmol), molybdenum complex (0.050 mmol, 10 mol%) and 2.5 mL of solvent. The reactor tube was sealed, and the reaction mixture was stirred at 170 °C for the required amount of time. The reactions were cooled to room temperature before adding the internal standard for analysis {1,3,5-trimethoxybenzene (0.010 g, 0.059 mmol)}. An aliquot of the reaction mixture was analyzed by ^1H NMR using $CDCl_3$ as solvent. The integration of peaks corresponding to the diol and alkene product relative to the internal standard were used to determine yield of alkene product and conversion of the diol.

Representative procedure for Time-dependence reactions

A pressure tube reactor with substrate (0.500 mmol), reductant (0.750 mmol), molybdenum complex (0.050 mmol, 10 mol%) and 2.5 mL of solvent along with a stock solution of internal standard of 1,3,5-trimethoxybenzene equaling 0.010 g (0.059 mmol) was prepared first. The reactor tube was flushed with an inert gas, sealed, and the reaction mixture was stirred at 170 °C.

In time dependent studies the reaction time was reduced to 3 hours and aliquots were taken every 20 minutes for the first hour and subsequent aliquots were taken at 30-minute intervals. Before taking each aliquot, the reaction was cooled to room temperature by blowing compressed air on the tube to reduce possible reactions happening during the acquisition period. Once aliquots were taken, the reactor tubes were then flushed again with an inert gas and returned to the oil bath.

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