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Mild, Selective Sulfoxidation with Molybdenum(VI) *cis*-Dioxo Catalysts

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S *Supporting Information*

ABSTRACT: Three molybdenum(VI) *cis*-dioxo catalysts (**8**−**10**) were synthesized with the goal of developing stable and selective oxidation catalysts for sulfoxidation. Their reactivities were investigated with a variety of substrates. We have demonstrated the usefulness of these catalysts for the chemoselective sulfoxidation of sulfides in the presence of reactive moieties, which has important applications for total synthesis processes. Notably, these catalysts are able to oxidize compounds analogous to sulfur mustard and can be used as an alternative to sodium periodate or *meta*-chloroperoxybenzoic acid (*m*-CPBA) for the oxidation of various organic sulfides without sacrificing total conversion. As the catalysts are tolerant of water and hydrogen peroxide, they allow for the design of completely green oxidation reactions, particularly for sulfur-containing amino acids.

R' = aliphatic, ClCH$_2$, aromatic, amino acid, benzylic, amide, amine

R'' = aliphatic or aromatic
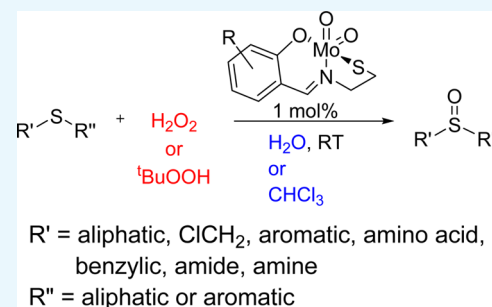
1. INTRODUCTION

Molybdenum(VI) dioxo complexes have been extensively studied. Much of the interest in these compounds is derived from their oxygen atom transfer chemistry and their relationship to biological oxotransferase enzymes, which feature sulfur ligands.[1,2] Consequently, molybdenum(VI) dioxo catalysts are often used for epoxidation and sulfoxidation reactions.[1,3−8] Rao et al. reported on molybdenum(VI) dioxo complexes with ONS-type ligands for the oxidation of olefins to epoxides (Figure 1).[1] A similar ONO-type ligand system was used in the synthesis of sulfoxides from sulfides (Figure 2).[9,10]
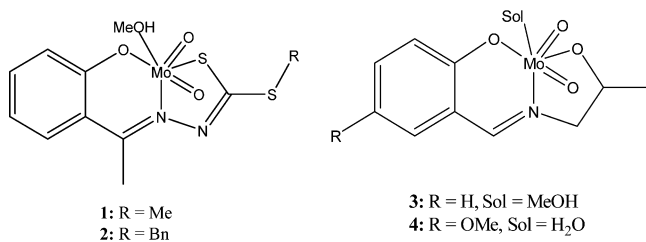

Figure 1. Mo(VI) dioxo catalysts used for the epoxidation of olefins1 (**1** and **2**)[1] and sulfoxidation reactions (**3** and **4**).[8,9]

Recyclable, inexpensive, and stable catalysts are desirable for industrial and synthetic applications. Selective oxidation of sulfides to sulfoxides is important. Sulfoxides are used prominently for the Mislow−Evans rearrangement in organic synthesis, involving a 2,3-sigmatropic rearrangement to transform allylic sulfoxides to allylic alcohols.[11] This transformation is used in the synthesis of various natural products of medicinal value.[11] One such application is in the synthesis of *β*-lactam PS-5-type antibiotics, where the sulfoxide is subjected to
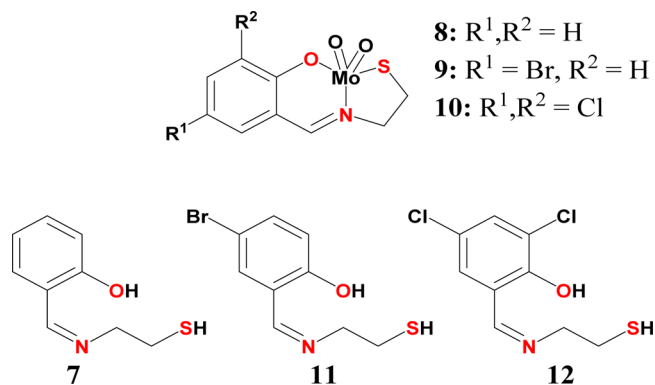

Figure 2. Structures of ONS-type ligand and molybdenum(VI) dioxo complex.

8: R^1,R^2 = H
**9:** R^1 = Br, R^2 = H
10: R^1,R^2 = Cl

substitution with a methyl ester to allow for further transformations. The oxidation of the sulfide, shown in Scheme 1, to the corresponding sulfoxide is performed with *meta*-chloroperoxybenzoic acid (*m*-CPBA), with yields ranging from 53 to 99%.[12] In the work by Kita et al., this particular step is conserved in the synthesis of optically pure (+)-PS-5 and (+)-thienamycin.[13] Solid peroxides such as *m*-CPBA, because of safety concerns, are more difficult to use on industrial scale than *t*BuOOH or H$_2$O$_2$, and *m*-CPBA generates chlorobenzoic acid (CBA) as a byproduct. The byproducts of oxidation from *t*BuOOH and H$_2$O$_2$ are *t*-butanol and water, respectively, which are environmentally much more friendly than CBA. In more complex total syntheses, great care must be taken during

Scheme 1. Sulfoxidation of β-Lactam Derivatives for the Synthesis of PS-5-Type Antibiotics[11]
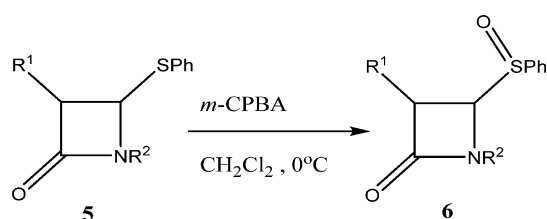
retrosynthesis to ensure that an oxidation step will not occur in the presence of other reactive functional groups. This leads to roundabout synthetic designs or routes that must use a large number of protecting groups that must then be deprotected. Both of these approaches significantly decrease the overall yield of a total synthesis.

Oxidation of sulfides has also been widely used in industry, the most general application being in the removal of sulfide impurities from oil, known as oxidative desulfurization.[14] More selective and efficient oxidative methods can allow industrial use of milder oxidants and conditions, allowing for the reduction of waste and toxic byproducts. A more specific application of sulfoxidation is in the synthesis of chiral vinylglycine from methionine. Rapoport and Afzali-Ardakani reported a synthesis of (L)-vinylglycine in 1980 with an overall yield of 54%, which stands so far as the highest reported overall yield and therefore the most widely used method for the synthesis of vinylglycine.[15−17] Chiral vinylglycine is useful as an enzyme inhibitor[16,18] and as a derivative for amide functionality[19] within enantiopure target organic molecules. As such, vinylglycine is produced on industrial scale. With a mild, direct sulfoxidation of methionine, it is possible to eliminate the necessity of protection/deprotection of both the carboxylic acid and amine functional groups. Removing these steps greatly increases the overall yield and atom economy and decreases excessive waste in the production of vinylglycine.

The ONS ligand scaffold, shown in Figure 2, was reported by Topich and Lyon for molybdenum(VI) cis-dioxo complexes.[20−23] The previously known complexes **8** and **9** have been shown to catalyze oxygen transfer to phosphines.[20,21,23] However, no further investigations into useful transformation or applications of these complexes have been reported. As the types of molybdenum dioxo complexes are able to catalyze oxygen transfer to sulfides,[9,10] we investigated the ability of these complexes for sulfoxidation. Herein, we report the first synthesis, characterization, and reactivity of Mo^{VI}(O)$_2$(H$_2$sal-eta) (**8**), Mo^{VI}(O)$_2$(H$_2$sal-eta-p-Br) (**9**), and Mo^{VI}(O)$_2$(H$_2$sal-eta-o,p-Cl) (**10**). These catalysts are able to oxidize sulfides to sulfoxides with excellent yield and selectivity and are tolerant to the presence of various reactive moieties, such as carboxylic acids, unprotected amines, and halides.

2. RESULTS AND DISCUSSION

2.1. Synthesis and Characterization. The synthesis of all three Mo(O)$_2$(ONS) catalysts proceeded smoothly, providing a high yield of pure complexes. The desired ONS ligand can be synthesized directly from the condensation of the corresponding salicylaldehyde derivative and cysteamine (2-aminoethanethiol). As shown in Scheme 2, these ligands can oxidatively cyclize to the thermodynamically stable five-membered dihydrothiazole. As the electron-withdrawing character of the aromatic substituents increases, the amount of dihydrothiazole formed increases because of the inductive effect at the imine carbon. However, formation of this side product does not affect metalation when the ligand is used crude. The tridentate linear ONS ligand metalates preferentially over the bidentate dihydrothiazole. This results in the precipitated complex being obtained analytically pure by ^{1}H NMR after simple filtration and washing.

Ligands **7**, **11**, and **12** are highly soluble in chloroform and acetonitrile, but their molybdenum complexes are less soluble and highly soluble only in dimethyl sulfoxide (DMSO) and dimethylformamide (DMF). Therefore, ^{1}H NMR analysis had to be conducted in DMSO. Metalation of ligand **7** saw the disappearance of the phenolic peak (10.6 ppm) and thiol peak (2.6 ppm) as these functional groups were now deprotonated and coordinated to molybdenum. The inductive effect from the coordinated molybdenum is the strongest for the protons alpha to the nitrogen, shifting each peak downfield approximately by 0.5 ppm. The protons alpha to the sulfur, however, shifted downfield only by 0.2 ppm. Complexes **9** and **10**, with bromide and chloride aromatic substituents respectively, experience a lesser deshielding effect on the protons alpha to the nitrogen, with a shift of approximately 0.3 ppm downfield. The protons alpha to the sulfur for complexes **10** and **11** experience a greater effect from the molybdenum, with downfield shifts of approximately 0.3 and 0.4 ppm, respectively.

2.1.1. X-ray Crystallography Data. All complexes were grown as single crystals in a vapor diffusion chamber with DMF and ether. Complete information regarding software and data collection can be found in the Supporting Information. The crystal structures are shown in Figure 3. The bond lengths calculated from the crystal structures of complexes **8−10** conform to the expected values for molybdenum(VI).

2.1.2. UV−Vis Spectroscopy Data. UV−vis data were obtained by preparing a 0.2 mM solution of catalyst **8** in DMSO. Maurya et al. had previously reported that the H$_2$sal-eta ligand has UV−vis peaks at 215, 255, and 316 nm, which were assigned to ϕ → ϕ*, π → π*, and n → π* transitions, respectively.[24] Figure 4 shows the UV−vis spectrum of complex **9**, which exhibits two distinct peaks at 360 and 270 nm. The broad lower energy band at 360 nm can be assigned to the now-present ligand-to-metal charge transfer[25] overlapping with

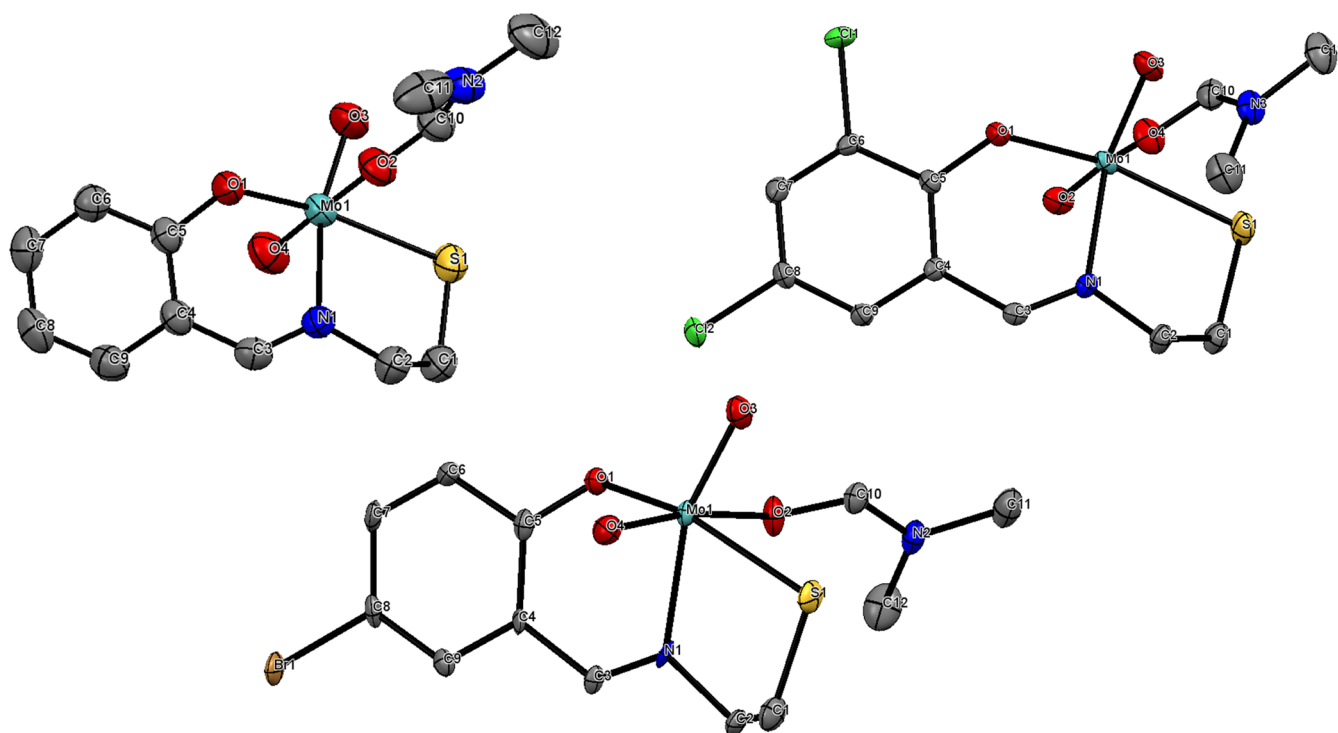**Scheme 2. Synthesis of the ONS-Type Ligands and Their Dihydrothiazole Side Product**
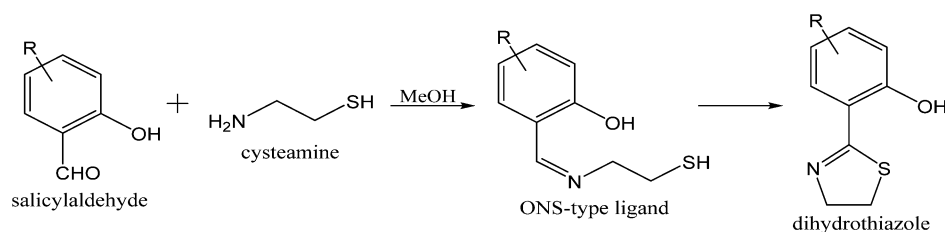
Figure 3. Catalyst **8** bond lengths in angstroms: Mo−O1 = 1.979, Mo−O2 = 2.341, Mo−O3 = 1.703, Mo−O4 = 1.694, Mo−N1 = 2.265, Mo−S1 = 2.411. Catalyst **9** bond lengths: Mo−O1 = 1.986, Mo−O2 = 2.313, Mo−O3 = 1.715, Mo−O4 = 1.698, Mo−N1 = 2.265, Mo−S1 = 2.413. Catalyst **10** bond lengths: Mo−O1 = 1.993, Mo−O2 = 1.702, Mo−O3 = 1.711, Mo−O4 = 2.298, Mo−N1 = 2.264, Mo−S1 = 2.410 [Oak Ridge thermal ellipsoid plot (ORTEP) diagram; thermal ellipsoids at 50% probability; and H atoms were omitted for clarity]. These crystal structures and their corresponding data include a coordinated DMF molecule. This DMF molecule is present from the conditions under which the crystals were grown and is not present in the dry samples, as is evident from ^{1}H NMR analyses.
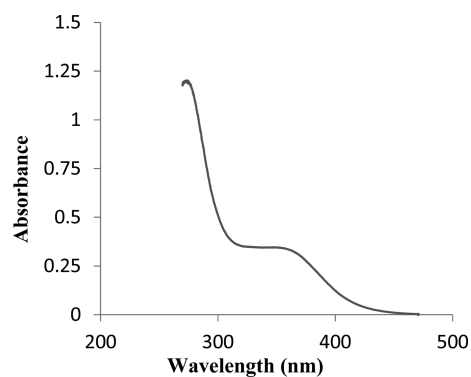

Figure 4. UV−vis spectrum of complex **8** taken at 25 °C in DMSO (0.2 mM). Peak maxima are at 270 and 360 nm.

an n → π* transition of the ligand. The higher energy 270 nm peak still corresponds to the π → π* of intraligand transitions.

2.2. Sulfoxidation. 2.2.1. Substrates and Scope of Reaction. Development of the reaction methodology was done with diethyl sulfide as a substrate representative. It should be noted that all Mo(O)$_2$(ONS-type) catalysts are sparingly soluble in most common organic solvents, with the exception of DMSO and DMF. Therefore, each reaction has at least two phases: solid, suspended catalyst and organic substrate. For solvents, the organic substrates are insoluble in, for example, diethyl sulfide in water, and the reaction becomes triphasic. As seen in Table 1, organic, aprotic solvents performed best when paired with tBuOOH, whereas H$_2$O performed best with H$_2$O$_2$. Although the reaction is not selective when performed neat with H$_2$O$_2$, it is selective with tBuOOH, as the organic peroxide

Table 1. Methodology Investigations with Diethyl Sulfide and Catalyst 8

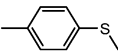| entry	solvent	peroxide	sulfoxide (%)[a]	sulfone (%)[a]
1	CD$_3$CN	1 equiv tBuOOH	97	3
2	CD$_3$CN	1 equiv H$_2$O$_2$	45	29
3	CDCl$_3$	1 equiv tBuOOH	98	2
4	CDCl$_3$	1 equiv H$_2$O$_2$	79.8	6.2
5	D$_2$O	1 equiv tBuOOH	27	10
6	D$_2$O	1 equiv H$_2$O$_2$	72	
7	D$_2$O	1.2 equiv H$_2$O$_2$	94	
8	none	1 equiv H$_2$O$_2$	62	37
9	none	1 equiv tBuOOH	98	2
10	EtOD	1 equiv H$_2$O$_2$	64	36

[a]Determined by NMR using diphenylmethane as an internal standard; remaining percent values refer to unreacted sulfide.

can act as a solvent for the substrate. Both of these conditions, H$_2$O$_2$ in water and tBuOOH neat without solvent, are noteworthy because they are "green", eliminating the need to use volatile and toxic organic solvents.[a]

It was possible to obtain over 90% sulfoxide yields with organic solvent and water (entries 1, 3, and 7). However, for water-insoluble sulfides, a slight excess of H$_2$O$_2$ was needed to drive the reaction further (entries 6 and 7). As shown later, this is not necessary for water-soluble sulfides. This eliminates the possibility of loss of H$_2$O$_2$ into O$_2$ and H$_2$O by the

molybdenum catalyst. This environmentally friendly, or green, condition was tested with other simple sulfides to investigate the scope of applicability. Table 2 summarizes these results.

Table 2. Substrate Compatibility under Green Reaction Conditions with Catalyst 8

sulfide + 1.2 eq H₂O₂ →(catalyst **8** (1 mol%) / D₂O, 1h, RT) sulfoxide

Entry	Sulfide	Sulfoxide (%)[a]	Sulfone (%)[a]
1	Et₂S	94	---
2	(aromatic sulfide)	no reaction	
3	tBu–S–	87[b]	---
4	Cl–S–	unknown product	
5	thiophene	no reaction[c]	
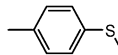
[a]Determined by NMR using diphenylmethane as an internal standard: remaining percents were unreacted sulfide. [b]Was only 32% complete after 1 h, so this entry was run for 5 h. [c]No reaction after 6 h.

Simple dialkyl substrates are tolerant of the green conditions. However, the aromatic sulfide did not react at all, and only the starting sulfide was observed by NMR after 8 h. Therefore, it was unsurprising that thiophene was also inert to these reaction conditions. It is unclear why (chloromethyl)(methyl)sulfide (Table 2, entry 4) decomposed under the reaction conditions. However, by NMR, there were no peaks corresponding to the sulfide, sulfoxide, sulfone, or hydrolysis derivatives. The peaks that were observed could not be assigned to any known, reasonable product. This substrate was successfully oxidized under the conditions discussed later.
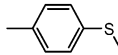
Because of the narrow scope of the hydrogen peroxide conditions with catalyst **8**, we turned our attention back to the high-yielding organic solvents. Table 1 (entries 1 and 3) shows acetonitrile and chloroform as the best candidates. Further substrate testing with both solvents revealed that chloroform was a superior choice for higher yields over a wider variety of substrates. Four simple organic sulfides were subjected to the chloroform/tBuOOH reaction conditions with each molybdenum catalyst. The results are shown in Table 3. All catalysts performed equally with all substrates, with the exception of a small drop in the conversion of (chloromethyl)(methyl)sulfide with catalyst **9** (entry 8). The excellent conversion for the oxidation of (chloromethyl)(methyl)sulfide is of particular importance as this sulfide is a model compound for sulfur mustard, which is a highly toxic chemical warfare agent. It is critical for the oxidation of sulfur mustards to be selective for the sulfoxide without overoxidation to the sulfone as the sulfone derivatives are nearly as toxic as the parent compounds.[26]

Three controls were performed for the sulfoxidation reaction. First, the reaction was performed in the absence of catalyst. Although sulfides will oxidize in the presence of an equimolar amount of peroxides, they must be stirred at least overnight or longer, and under noncatalytic conditions, they do not show selective oxidation. This slow oxidation is in stark contrast to the rapid 5−30 min completion times in the presence of Mo(O)₂(ONS-type) catalysts. Second, the reaction was performed in the absence of peroxide to verify that it was indeed the peroxide, not oxygen from the atmosphere, that was participating in the reaction. Finally, an equimolar amount of peroxide was stirred with catalyst **8** for 1 h (longer than the

Table 3. Substrate Testing with the Three Mo(O)₂(ONS-Type) Catalysts

Entry	Catalyst	Sulfide[a]	Sulfoxide (%)[b]	Sulfone (%)[b]
1	**8**	Et₂S	98	2
2	**8**	(aromatic sulfide)	100	---
3	**8**	tBu–S–	99	1
4	**8**	Cl–S–	98	1
5	**9**	Et₂S	99.8	0.2
6	**9**	(aromatic sulfide)	100	---
7	**9**	tBu–S–	98	2
8	**9**	Cl–S–	72	---
9	**10**	Et₂S	99.9	0.1
10	**10**	(aromatic sulfide)	100	---
11	**10**	tBu–S–	99.9	0.1
12	**10**	Cl–S–	99	1

[a]All reactions were performed with 1 mol % catalyst in CDCl₃ with tBuOOH (1 equiv) at room temperature for 30 min. [b]Determined by NMR using diphenylmethane as an internal standard; remaining percents were unreacted sulfide.

length of most reactions), at which point it was analyzed by ¹H NMR to determine whether the sulfur on the ligands of the catalysts are oxidized at all, thereby potentially changing the active catalyst species. However, there was no change in the NMR, particularly focusing on those protons alpha to the sulfur, so it can be concluded that the ligand structure is not affected by the presence of peroxide. It is probable that the peroxide instead changes the structure of the catalyst at the oxo moieties, resulting in an oxo-peroxo structure. These types of structures have been observed with other molybdenum dioxo catalysts in the presence of peroxides.[27,28]

2.2.2. Achiral Sulfoxide Intermediates in Total Synthesis. Encouraged by our initial results, we sought to broaden the substrate scope by examining more useful substrates from a synthesis viewpoint. Sulfoxides are used in organic synthesis for the Mislow−Evans rearrangement.[11] In these preparations, it is necessary to oxidize the sulfide to the sulfoxide. As such, it is extremely useful to have a mild oxidation reaction that is tolerant of various functional groups to eliminate the need for protecting the groups, which increases the number of linear steps required in a synthesis sequence. Figure 5 shows two sulfides (**5** and **14**) used as precursors for the Mislow−Evans rearrangement in total synthesis preparations[11] and their respective simplified model substrate structures. Only catalyst **8** was tested because all three catalysts have nearly identical reactivity. Both substrates **13** and **15** were successfully oxidized to their sulfoxide counterparts with catalyst **8**. Substrate **15** was converted only to 85% sulfoxide (**17**) in 30 min under the optimized conditions; however, after reacting for 90 min, no remaining sulfide was present and 100% conversion to the sulfoxide was observed by ¹H NMR. Substrate **13** was synthesized from 4-acetoxy-2-azetidinone according to the literature procedure.[29] The resultant sulfide **13** was converted
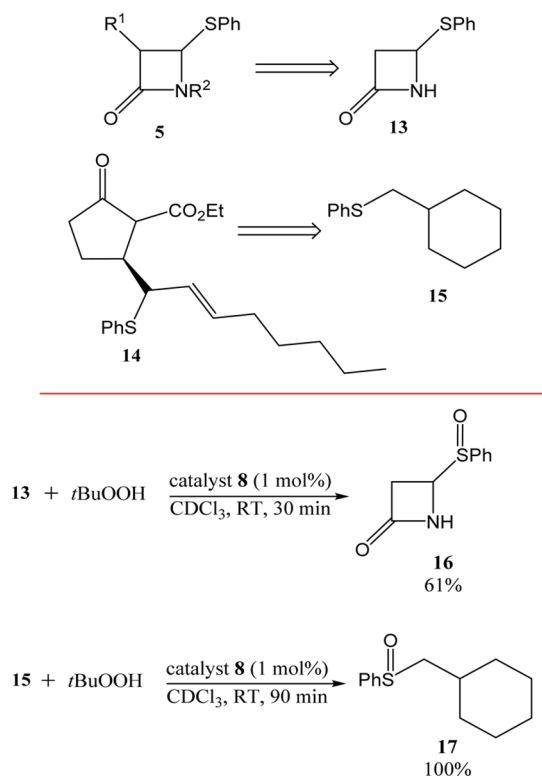
Figure 5. Model sulfides and the structures from which they were derived.

to corresponding sulfoxide **16** in 61% yield under our standard reaction conditions.

2.2.3. Sulfoxide Pyrolysis in the Synthesis of VinylGlycine. The next substrate we tested to examine the versatility and tolerance of catalyst **8** was D-methionine. The first attempt to oxidize D-methionine was done using the optimized CDCl$_3$ conditions that were successful for all previous organic substrates. However, no reaction was observed under these conditions. Upon examination of the reaction vessel, the reason became apparent. D-Methionine is not soluble in chloroform, resulting in a suspension of the substrate. As we had previously noted, the reaction works best when the substrate is dissolved in the liquid phase. From the experiments performed during optimization, we noted that reaction conditions with hydrogen peroxide, "green conditions", could work with varying degrees of success, depending on the substrate. Therefore, we decided to test the reaction in D$_2$O and H$_2$O$_2$ with D-methionine. Under these conditions, 100% of D-methionine was converted to the sulfoxide in 30 min. The ^{1}H NMR showed that the

catalyst was unreactive toward the carboxylic acid and free amine. This result has promising applications. Researchers trying to perform sulfoxidations late in total synthesis preparations could use this methodology to achieve direct sulfoxidation from sulfides without the need to protect and deprotect various functional groups on their compounds, thus simplifying their total synthesis and increasing their overall yield. More specifically, the successful direct oxidation of D-methionine could greatly improve the current method for the preparation of (R)-vinylglycine if the unprotected sulfoxide can be cleaved to give (R)-vinylglycine directly. Various literature procedures for the direct cleavage of sulfoxides[15,30−33] have proven unsuccessful thus far for this direct cleavage. Unable to achieve the direct cleavage of D-methionine sulfoxide, we sought to improve upon the total yield of the synthesis of vinylglycine reported by Rapoport (Scheme 3) and provide a more benign alternative to using NaIO$_4$ using our sulfoxidation procedure. Indeed, we were able to convert **18** to the corresponding sulfoxide (**19**) quantitatively.

3. CATALYST RECYCLABILITY

Finally, the recyclability of complex **8** was tested. As this complex did not hydrolyze in glacial acetic acid over 5 days, we expected a low catalyst deactivation and therefore a good recyclability. First, a basic sulfoxidation reaction was performed with methyl *p*-tolyl sulfide (run 1). For this reaction, the catalyst loading was decreased to 0.5 mol % to slow down the reaction so that consistent NMR data could be obtained over a longer reaction time. All other reaction parameters followed the standard sulfoxidation reaction protocol. The reaction solution was stirred at room temperature for 90 min, with points taken every 5 min for the first 30 min and then every 20 min for the remaining time. After 90 min, most of the catalyst had dissolved, and the reaction solution was filtered to remove the remaining insoluble catalyst. This supernatant was then subjected to another sulfoxidation reaction (run 2) with an additional equivalent of sulfide and oxidant, without the addition of any more catalyst. As shown in Figure 5, the catalyst remaining in the solution from run 1 was still highly active, with total conversion dropping only to 85% in run 2 from 97% conversion at the end of run 1. The insoluble catalyst that was isolated after run 1 was filtered and dried to yield 1.2 mg. A third sulfoxidation reaction (run 3) was scaled so that the 1.2 mg of insoluble catalyst was also 0.5 mol %. It is evident from the data, shown in Figure 6, that this insoluble catalyst is no longer useful as an active catalyst. Therefore, it can be concluded that the soluble homogenous complex is the active

Scheme 3. Literature Procedure for the Synthesis of Chiral Vinylglycine[14] Compared with Our Synthesis (in Red)
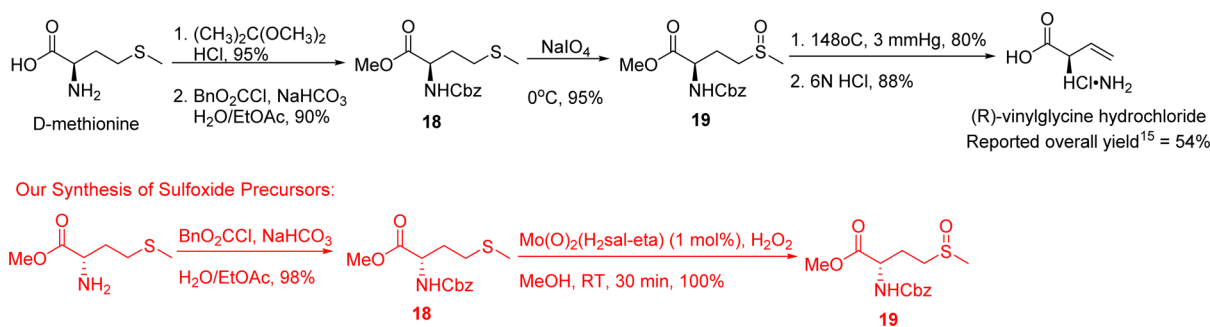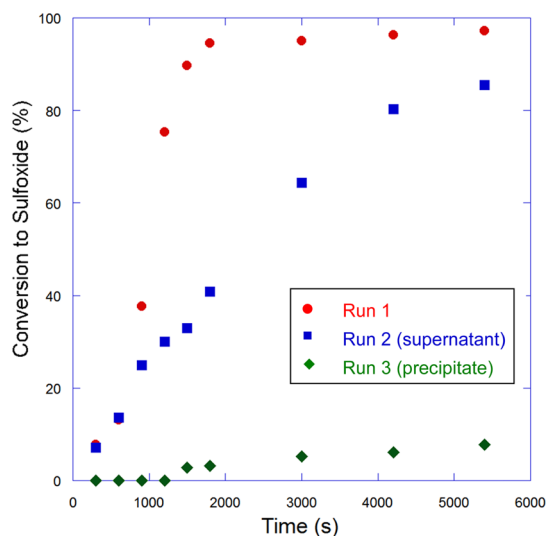
Figure 6. Recyclability of Mo(O)$_2$(H$_2$sal-eta) with methyl *p*-tolyl sulfide. Diphenylmethane was used as an internal standard in each reaction. Run 1: 1 equiv methyl *p*-tolyl sulfide, 1 equiv *t*BuOOH, 0.5 mol % catalyst **8**, CDCl$_3$, 90 min, RT. Run 2: filtered supernatant from run 1, additional 1 equiv sulfide, additional 1 equiv *t*BuOOH, no additional catalyst. Run 3: dried solid residue from run 1 (1.2 mg), sulfoxidation reaction scaled to 0.5 mol % catalyst loading.

catalyst and that this soluble complex retains most of its reactivity between subsequent reactions.

4. CONCLUSIONS

We have synthesized three molybdenum(VI) *cis*-dioxo catalysts based on the H$_2$sal-eta ancillary ligand and confirmed their structures. It has been shown that all three of these catalysts are able to selectively oxidize substituted sulfides to sulfoxides quickly and selectively, with low catalyst loading (0.5 mol %) and in excellent yields. These catalysts are air and water stable, allowing them to be stored for months without evidence of decomposition. These catalysts are tolerant of olefins, free amines, amides, and halogens. Sulfoxidation in the presence of chlorine allows these catalysts to be used for the neutralization of mustard gas and other similar compounds. With Mo-(O)$_2$(H$_2$sal-eta), we have been able to achieve direct, quantitative, green oxidation of D-methionine without the need for protecting groups. The successful cleavage of the sulfoxide group to the vinylidene would drastically increase the overall yield in the production of (*R*)-vinylglycine. As demonstrated by our model substrate studies, this sulfoxidation method can also be applied to the total synthesis of useful compounds that use achiral sulfoxide intermediates, which has the potential to simplify the total synthesis of various compounds, significantly increasing their overall yield and decreasing the cost of production. Our recyclability investigations have also shown that these catalyst types are durable, allowing them to retain most of their activity through successive reactions.

5. EXPERIMENTAL SECTION

5.1. Materials. All NMR and kinetics experiments were performed on a Bruker ARX400 NMR spectrometer. Elemental analyses were performed by Atlantic Microlab, Inc. UV−vis experiments were performed in DMSO with an Agilent Technologies Cary 60 UV−vis instrument, coupled with a

Quantum Northwest temperature control unit and using a 1 cm quartz cell. IR measurements were taken using a Thermo Nicolet Nexus FT-IR. Electron spray ionization mass spectrometry was performed by the interdepartmental mass spectrometry facility at Purdue University.

5.2. General Sulfoxidation Procedure. To a 20 mL vial were added Mo^{VI}(O)$_2$L (1 mg, 0.01 equiv), sulfide (1 equiv), CDCl$_3$ (1 mL), and diphenylmethane as an internal NMR standard. To this stirred suspension, *t*BuOOH (5 M in decane, 1 equiv) was added. The reaction solution was capped and stirred at room temperature under ambient atmosphere for 30 min, at which time the reaction solution was analyzed using NMR.

5.3. Synthesis of *cis*-Mo^{VI}(O)$_2$(H$_2$sal-eta) (8). The H$_2$sal-eta ligand (**7**) was prepared according to the previously reported literature procedure.[24] The crude ligand was used directly in the next reaction without further purification.[b]

The complex was prepared by dissolving ligand **7** (1.206 g, 6.654 mmol) and Mo(O)$_2$(acac)$_2$ (2.170 g, 6.654 mmol) in acetonitrile (40 mL) to make a yellow solution. Slightly heating the reaction solution at approximately 35 °C immediately gave a bright orange-red precipitate. The reaction solution was stirred for 15 min to ensure complete metalation. The resultant suspension was cooled to room temperature, filtered, washed with acetonitrile and hexane, and dried under vacuum to give the pure product (1.880 g, yield 92%). ^{1}H NMR (DMSO-d_6): δ (ppm) = 8.79 (s, 1H, imine =C−H), 7.59 (d, *J* = 7.6 Hz, 1H, Ar), 7.49 (t, *J* = 6.9 Hz, 1H, Ar), 6.97 (t, *J* = 7.5 Hz, 1H, Ar), 6.86 (d, *J* = 8.3 Hz, 1H, Ar), 4.15 (t, *J* = 5.5 Hz, 2H, N−CH$_2$), 3.15 (t, *J* = 5.8 Hz, 2H, S−CH$_2$). IR (cm^{-1}): ν(C=N) 2931, 2911, 1625, 1557, 1453, 1278, 1068, 923; ν(Mo=O) 904, 845. Elemental analysis for C$_9$H$_9$MoNO$_3$S: calculated C, 35.19; H, 2.95; N, 4.56; S, 10.44. Found: C, 35.27; H, 2.96; N, 4.64; S, 10.41. ESI-MS: *m/z* 309. CI-MS (M + H): *m/z* 310. Crystals were isolated as yellow prisms from vapor diffusion with DMF and diethyl ether.

5.4. Synthesis of *cis*-Mo^{VI}(O)$_2$(H$_2$sal-eta-*p*-Br) (9). Ligand **11** (500 mg, 1.922 mmol) and equimolar Mo-(O)$_2$(acac)$_2$ were dissolved in acetonitrile (10 mL) to make a bright yellow solution. The reaction began to proceed at ambient temperature but was gently heated at approximately 35 °C, which greatly increased the reaction rate. As the reaction progressed, a bright orange precipitate formed. The reaction suspension was cooled to room temperature, filtered, washed with acetonitrile and cold methanol, and dried under vacuum to give the pure product (680 mg, yield 92%). ^{1}H NMR (DMSO-d_6): δ (ppm) = 8.75 (s, 1H, imine =C−H), 7.80 (d, *J* = 2.6 Hz, 1H, Ar), 7.60 (dd, *J* = 8.8, 2.6 Hz, 1H, Ar), 6.85 (d, *J* = 8.8 Hz, 1H, Ar), 4.14 (t, *J* = 5.4 Hz, 2H, N−CH$_2$), 3.18 (t, *J* = 5.8 Hz, 2H, S−CH$_2$). Elemental analysis for C$_9$H$_8$BrMoNO$_3$S: calculated C, 28.00; H, 2.09; N, 3.63; S, 8.30; Br, 20.70. Found: C, 28.58; H, 2.11; N, 3.87; S, 8.31; Br, 20.24. ESI-MS (M+): *m/z* 387. CI-MS (M + H): *m/z* 388. Crystals were isolated as yellow needles from vapor diffusion with DMF and diethyl ether.

5.5. Synthesis of *cis*-Mo^{VI}(O)$_2$(H$_2$sal-eta-*o,p*-Cl) (10). Ligand **12** (500 mg, 1.999 mmol) and equimolar Mo-(O)$_2$(acac)$_2$ were dissolved in acetonitrile to make a bright yellow solution. The reaction solution was gently heated at approximately 40 °C. The solution turned dark, but no precipitate was observed, so pyridine (161 μL) was added. A precipitate immediately began to form, and the reaction solution was stirred for 1 h. The resultant suspension was

cooled to room temperature, filtered, washed with acetonitrile and cold methanol, and dried under vacuum to give the pure product (448 mg, yield 60%). ^{1}H NMR (DMSO-d_6): δ (ppm) = 8.80 (s, 1H, imine =C–H), 8.58 (d, J = 4.6 Hz, 1H, Ar), 7.82 (d, J = 2.7 Hz, 1H, Ar), 7.71 (d, J = 2.7 Hz, 1H, Ar), 4.18 (t, J = 4.9 Hz, 2H, N–CH$_2$), 3.24 (t, J = 5.8 Hz, 2H, S–CH$_2$). Elemental analysis for C$_9$H$_7$Cl$_2$MoNO$_3$S complexed to DMF (C$_3$H$_7$NO): calculated C, 32.09; H, 3.14; N, 6.24; S, 7.14; Cl, 15.78. Found: C, 32.43; H, 2.78; N, 5.99; S, 7.32; Cl, 15.62. ESI-MS (M+): m/z 377. CI-MS (M + H): m/z 378. Crystals were isolated as yellow needles from vapor diffusion with DMF and diethyl ether.

■ ASSOCIATED CONTENT

ⓈSupporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.7b00292.

Experimental, ^{1}H NMR, and crystallographic data (PDF)
Crytallographic data of compounds 8, 9 and 10 (CIF)

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Notes
The authors declare no competing financial interest.

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■ ADDITIONAL NOTES

^{a}It should be noted that because neat reactions must be dissolved in a deuterated solvent before analysis, the introduction of the solvent may have increased the overall yield but cannot account for the total conversion observed as analyses were performed promptly after the addition of deuterated solvent.
^{b}The side product of the ligand synthesis is the cyclized dihydrothiazole, which does not ligate to molybdenum.

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