Bisguanidinium dinuclear oxodiperoxomolybdosulfate ion pair-catalyzed enantioselective sulfoxidation

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Catalytic use of peroxomolybdate for asymmetric transformations has attracted increasing attention due to its catalytic properties and application in catalysis. Herein, we report chiral bisguanidinium dinuclear oxodiperoxomolybdosulfate $[\text{BG}]^{2+} \cdot [(\mu-\text{SO}_4)\text{Mo}_2\text{O}_2(\mu-\text{O}_2)\text{O}_2]^{2-}$ ion pair, as a catalyst for enantioselective sulfoxidation using aqueous $\text{H}_2\text{O}_2$ as the terminal oxidant. The ion pair catalyst is isolatable, stable and useful for the oxidation of a range of dialkyl sulfides. The practical utility was illustrated using a gram-scale synthesis of armodafinil, a commercial drug, with the catalyst generated in situ from 0.25 mol% of bisguanidinium and 2.5 mol% of $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$. Structural characterization of this ion pair catalyst has been successfully achieved using single-crystal X-ray crystallography.

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Metalloenzymes containing molybdenum, responsible for nitrogen and sulfur metabolism, continue to fuel interest in the exploration of novel molybdenum complexes with catalytic activities. Various neutral coordination complexes of Mo(VI) containing chiral organic ligands have been synthesized and studied extensively for enantioselective reactions. In particular, one interesting example of highly enantioselective sulfoxidation of alkyl aryl sulfides was demonstrated using a complex derived from MoO$_2$(acac)$_2$ and chiral bis-hydroxamic acids. In contrast to their neutral counterparts, there have been no successful attempts to utilize peroxomolybdate for asymmetric reactions, even though many of these species have been comprehensively characterized.

It is well known that peroxomolybdates are formed on the treatment of molybdate salts with aqueous H$_2$O$_2$ oxidant. Monomeric, oligomeric and polymeric peroxomolybdate species could be generated under similar conditions. The addition of different organic ligands can further increase the structural and functional diversity of peroxomolybdate complexes. Other ligands such as silanol, phosphate, arsenate and sulfate have been used to bridge molybdates to construct dinuclear or trinuclear peroxomolybdate complexes. Peroxomolybdates species have been shown to be excellent catalysts for the oxidation of numerous substrates, including alkenes, alcohols and sulfides. The complexity of peroxomolybdates is thus recognized to be a challenging obstacle for elaborating them into highly enantioselective catalysts.

We have recently developed pentanidium and dicatonic bisguanidinium (BG) as efficient phase-transfer agents and ion pair catalysts. We have utilized bisguanidinium permanganate ion pair catalyst for the enantioselective oxidation of alkenes. The precise stereocontrol exhibited by bisguanidinium encouraged us to explore other anionic metallic species for asymmetric transformations. Herein, we describe our serendipitous discovery of chiral bisguanidinium dinuclear oxodiperoxomolybdosulfate [BG]$^{2+}$-[(μ-SO$_4$)Mo$_2$O$_7$(μ-O$_2$)$_2$(O$_2$)$_2$]$_{2-}$ ion pair catalyst (Fig. 2). This ion pair catalyst is stable and isolatable or it can be generated in situ. In a continuation of our current efforts towards developing practical approaches to enantiopure sulfoxides, we report a simple and scalable methodology for enantioselective sulfoxidation using this ion pair catalyst.

Results

Catalytic application of molybdate in sulfoxidation. At the onset of this work, we realized that we were unable to approach enantiopure 2-sulfinyl esters through enantioselective alkylation of sulfinic anion, as the reaction was incompatible with z-halogenated carboxylates. We were attracted to the low cost and easy accessibility of molybdate salts and thus we attempted to investigate the direct sulfoxidation of 2-sulfinyl acetate, by utilizing a catalytic amount of molybdate salts and aqueous H$_2$O$_2$ as terminal oxidant. Methyl 2-(benzydrylsulfinyl)acetate 2a was chosen as the model substrate (Table 1), since 2-sulfinyl acetate 3a could be easily transformed to armodafinil, a commercial drug used for the treatment of narcolepsy and shift work sleep disorder.

When the reaction was performed in the presence of 1 mol% of (S,S)-1a, 5 mol% of (NH$_4$)$_2$Mo$_2$O$_7$·4H$_2$O and 1.05 equiv. 35% aqueous H$_2$O$_2$, poor yield and no enantioselectivity were observed (Table 1, entry 1). With the addition of acetic acid, the enantioselectivity was slightly improved, albeit with low yield (entries 2 and 3). Using trifluoroacetic acid as additive, a marked enhancement of the reactivity was achieved, but with negligible enantioselectivity (entry 4). With the addition of sodium or potassium hydrogen sulfate, we observed significant improvement of yield, as well as enantioselectivity (entries 5 and 6). Switching to other additives, such as dihydrogen phosphate or hydrogen phosphate led to poor results (entries 7 and 8). Further investigation of reaction parameters (entries 9–14), such as the source of molybdate, solvent and stoichiometry of KH$_2$PO$_4$, led to the enhancement of reactivity, as well as enantioselectivity (entry 14, 93% ee; Supplementary Table 1).

The optimal condition was established by lowering the...
temperature to 0 °C and using just 1 mol% of (S,S)-1a together with 2.5 mol% Na₂MoO₄·2H₂O in ¹H₂O₂, affording 2-sulfinyl acetate 3a in 99% yield with 94% ee (entry 15). The absolute configuration of 3a was confirmed to be S through comparison with the reported data 46.

**Substrate scope of various sulfides using (S,S)-1a.** The reaction scope was examined using a series of substrates with a relatively low reactivity, in which the electron density of sulfur is reduced, due to strong electron-withdrawing groups like ester, ketone and nitrile (Table 2). The reactions performed efficiently and were generally completed within 1 h. For benzyl 2-sulfinylacetates with different substituents on the aromatic ring, dialkyl sulfoxides 3b–3i were obtained in high yields and excellent enantioselectivities. Sulfoxide 3j bearing 2-thienyl was obtained in high yield and good enantioselectivity without oxidation at the thiophene. With a slight variation of reaction conditions, using 0.25 equiv. of KHSO₄ and 2.5 mol% of K₂MoO₄, various aromatic 2-sulfinylacetates were efficiently converted to alkyl aryl sulfoxides 3k–3q in high yields with good enantioselectivities. For the oxidation of sulfide-bearing para-OMe substituent, leading to sulfoxide 3i, slight over-oxidation to sulfoxide was observed. For a less reactive substrate 2r, the reaction was conducted at room temperature using 1.5 equiv. H₂O₂, affording sulfoxide 3r with good enantioselectivity. With less favourable substrates such as tert-butyl substituted 2-sulfinyl acetate 2s, low enantioselective induction was observed (Table 2, 3s).

To further explore the scope, a diverse range of substrates bearing different functional groups were examined (Table 2, 3t–3y). 3-Sulfinyl propanoate 3t was produced with excellent enantioselectivity. Sulfoxides 3u–3y bearing amide, ketone, acrylate, nitrile and aldehyde moieties were furnished with good to excellent enantioselectivities. The absolute configurations of 3f and 3o were confirmed to be R and S, respectively, using single-crystal X-ray diffraction; thus, absolute configurations of sulfoxides 3 were assigned by analogy to either 3f or 3o. The practical utility was successfully demonstrated using a gram-scale synthesis of (R)-modafinil (armodafinil), a commercial drug, using 0.25 mol% of (R,R)-1a (Fig. 3).

**Identification and characterization of ion pair (R,R)-1b.** We attempted to identify the reactive catalytic species by mimicking the reaction conditions in the absence of sulfide substrate (Fig. 4). After a simple workup procedure, (R,R)-1b was isolated and a single crystal suitable for X-ray diffraction was grown by vapour diffusion of Et₂O into a dimethylformamide (DMF) solution of (R,R)-1b. The structure of (R,R)-1b was fully characterized using X-ray analysis (Fig. 2b), Mo nuclear magnetic resonance (NMR) (Fig. 5b) and fourier transform-infrared spectroscopy (FT-IR) (Supplementary Fig. 2).

The achiral anionic metallic species [(μ-SO₄)Mo₂O₅ (μ-O₂)₂(μ₂-O)₂]⁻ is revealed by X-ray crystallography to be embedded within the chiral cavity formed by two side arms of the chiral bisguanidinium dication (Fig. 2b). The coordination geometry surrounding the Mo was clearly elucidated (Fig. 5a). The SO₄²⁻ ligand plays a crucial role in constructing the dimeric symmetric structure. Each Mo centre comprises one bridging peroxo ligand, one side-on peroxo group and a terminal oxo ligand, with the sulfate group acting as a bipodal ligand to the two Mo atoms. Each Mo atom is 7-coordinated with oxygen atoms in a pentagonal bipyramidal arrangement. The two associated pentagonal bipyramids share one edge [O₅–O₁₀], and the two Mo atoms are connected by two μ–η¹:η² peroxo-bridges, [O₅–O₁₀ and O₁₁–O₁₆]. Both Mo₁–O₁ and Mo₂–O₁₂ bonds have the same length (1.659(7) Å) that falls in a typical range for the Mo–O bond. Generally, the bridging peroxo O₅–O₁₀ (1.482(9) Å) and O₁₁–O₁₆ (1.473(10) Å) bond lengths are slightly longer than the other side-on peroxo O₂–O₂ (1.458(10) Å) and O₁₃–O₁₄ (1.467(10) Å) bond lengths. Mo NMR spectrum of (R,R)-1b was also obtained in DMF-d₂ at 22 °C, using 2 M Na₂MoO₄·2H₂O solution in D₂O as an external reference (assigned to 0 p.p.m.). The chemical shift at ~199.3 p.p.m. is characteristic of oxodiperoxomolybdate species (Fig. 5b) 52.

We found that (R,R)-1b (1.0 equiv.), prepared using the method in Fig. 4, can be used directly as the oxidant for

### Table 1 | Optimization of bisguanidinium-catalyzed asymmetric sulfoxidation of 2a.

| Entry | [Mo] (5 mol%) | Additive (x equiv.) | Time (h) | Yield (%)* | ee (%)† |
|-------|--------------|---------------------|----------|-------------|---------|
| 1     | (NH₄)₆Mo₇O₂₄·4H₂O | —                   | 24       | 15          | 0       |
| 2*    | (NH₄)₆Mo₇O₂₄·4H₂O | CH₃CO₂H (1.0)       | 24       | 0           | 0       |
| 3     | (NH₄)₆Mo₇O₂₄·4H₂O | CH₃CO₂H (1.0)       | 24       | 14          | 20      |
| 4     | (NH₄)₆Mo₇O₂₄·4H₂O | Cs₂CO₃H (1.0)       | 8        | 80          | 4       |
| 5     | (NH₄)₆Mo₇O₂₄·4H₂O | NaHSO₄ (1.0)        | 19       | 99          | 69      |
| 6     | (NH₄)₆Mo₇O₂₄·4H₂O | KHSO₄ (1.0)         | 19       | 99          | 75      |
| 7     | (NH₄)₆Mo₇O₂₄·4H₂O | Li₂HPO₄ (1.0)       | 19       | 50          | 40      |
| 8     | (NH₄)₆Mo₇O₂₄·4H₂O | Na₂HPO₄ (1.0)       | 19       | 28          | 0       |
| 9     | Li₂MoO₄         | KHSO₄ (1.0)         | 3        | 85          | 88      |
| 10    | K₂MoO₄          | KHSO₄ (1.0)         | 2        | 99          | 86      |
| 11    | Na₂MoO₄·2H₂O   | KHSO₄ (1.0)         | 2        | 99          | 88      |
| 12    | Na₂MoO₄·2H₂O   | KHSO₄ (0.5)         | 2        | 99          | 89      |
| 13    | Na₂MoO₄·2H₂O   | KHSO₄ (0.25)        | 2        | 99          | 83      |
| 14†   | Na₂MoO₄·2H₂O   | KHSO₄ (0.5)         | 1        | 99          | 93      |
| 15‡‡‡| Na₂MoO₄·2H₂O   | KHSO₄ (0.5)         | 1        | 99          | 94      |

*Yield of the isolated product.
†Determined by high-performance liquid chromatography analysis using CHIRALPAK AD-H column.
*Without (S,S)-1a.
‡PhO as the solvent.
‡‡‡Reaction was performed with 0.2 mmol of 2a at 0 °C with 2.5 mol% Na₂MoO₄·2H₂O with 99% isolated yield without sulfone byproduct.

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NATURE COMMUNICATIONS | DOI: 10.1038/ncomms13455 | www.nature.com/naturecommunications
sulfoxidation, without additional aqueous H₂O₂, providing sulfoxide ent-3a in 90% yield and 80% ee in 0.5 h (Fig. 6a, equation 1). This result indicates that (R,R)-1b is the actual oxidizing specie providing high enantiodiscrimination. Utilizing 0.25 equiv. (R,R)-1b led to the formation of ent-3a in 50% yield in 24 h with 31% ee (Fig. 6a, equation 2), demonstrating that two out of four peroxo moieties on (R,R)-1b are active oxygen donors, as two equivalent of active oxygen from (R,R)-1b are transferred to

**Table 2 | Substrate scope of sulfides in asymmetric sulfoxidation.**

| R₁, R₂ | Compound | Yield (%) | ee (%) |
|--------|----------|-----------|--------|
| Ph      | 3b        | 99%       | 90%    |
| Cl      | 3f        | 92%       | 91%    |
| Cl      | 3j        | 94%       | 89%    |
| Cl      | 3n        | 93%       | 90%    |
| Cl      | 3r        | 79%       | 74%    |
| Ph      | 3v        | 99%       | 90%    |
| MeO     | 3c        | 92%       | 92%    |
| MeO     | 3d        | 96%       | 83%    |
| Cl      | 3e        | 94%       | 96%    |
| Br      | 3h        | 98%       | 93%    |
| Br      | 3i        | 99%       | 93%    |
| Ph      | 3k        | 91%       | 86%    |
| Ph      | 3l        | 94%       | 79%    |
| Ph      | 3m        | 93%       | 89%    |
| Ph      | 3n        | 93%       | 90%    |
| Ph      | 3o        | 95%       | 91%    |
| Ph      | 3p        | 99%       | 89%    |
| Ph      | 3q        | 97%       | 83%    |
| Ph      | 3r        | 94%       | 89%    |
| Ph      | 3s        | 92%       | 92%    |
| Ph      | 3t        | 96%       | 82%    |
| Ph      | 3u        | 99%       | 90%    |
| Ph      | 3v        | 84%       | 77%    |
| Ph      | 3w        | 87%       | 80%    |
| Ph      | 3x        | 82%       | 65%    |
| Ph      | 3y        | 82%       | 65%    |
| Ph      | 3y        | 84%       | 77%    |
| Ph      | 3x        | 87%       | 80%    |
| Ph      | 3y        | 82%       | 65%    |
| Ph      | 3y        | 84%       | 77%    |
| Ph      | 3x        | 87%       | 80%    |
| Ph      | 3y        | 82%       | 65%    |
| Ph      | 3y        | 84%       | 77%    |
| Ph      | 3x        | 87%       | 80%    |
| Ph      | 3y        | 82%       | 65%    |
| Ph      | 3y        | 84%       | 77%    |
| Ph      | 3x        | 87%       | 80%    |
| Ph      | 3y        | 82%       | 65%    |
| Ph      | 3y        | 84%       | 77%    |
| Ph      | 3x        | 87%       | 80%    |
| Ph      | 3y        | 82%       | 65%    |
| Ph      | 3y        | 84%       | 77%    |
| Ph      | 3x        | 87%       | 80%    |
| Ph      | 3y        | 82%       | 65%    |
| Ph      | 3y        | 84%       | 77%    |
| Ph      | 3x        | 87%       | 80%    |
| Ph      | 3y        | 82%       | 65%    |
| Ph      | 3y        | 84%       | 77%    |
| Ph      | 3x        | 87%       | 80%    |
| Ph      | 3y        | 82%       | 65%    |
| Ph      | 3y        | 84%       | 77%    |
| Ph      | 3x        | 87%       | 80%    |
| Ph      | 3y        | 82%       | 65%    |
| Ph      | 3y        | 84%       | 77%    |
| Ph      | 3x        | 87%       | 80%    |
| Ph      | 3y        | 82%       | 65%    |
| Ph      | 3y        | 84%       | 77%    |
| Ph      | 3x        | 87%       | 80%    |
| Ph      | 3y        | 82%       | 65%    |
| Ph      | 3y        | 84%       | 77%    |
| Ph      | 3x        | 87%       | 80%    |
| Ph      | 3y        | 82%       | 65%    |
| Ph      | 3y        | 84%       | 77%    |
| Ph      | 3x        | 87%       | 80%    |
| Ph      | 3y        | 82%       | 65%    |
| Ph      | 3y        | 84%       | 77%    |
| Ph      | 3x        | 87%       | 80%    |
| Ph      | 3y        | 82%       | 65%    |
| Ph      | 3y        | 84%       | 77%    |
| Ph      | 3x        | 87%       | 80%    |
| Ph      | 3y        | 82%       | 65%    |
| Ph      | 3y        | 84%       | 77%    |
| Ph      | 3x        | 87%       | 80%    |
| Ph      | 3y        | 82%       | 65%    |
| Ph      | 3y        | 84%       | 77%    |
| Ph      | 3x        | 87%       | 80%    |
| Ph      | 3y        | 82%       | 65%    |
| Ph      | 3y        | 84%       | 77%    |
| Ph      | 3x        | 87%       | 80%    |
| Ph      | 3y        | 82%       | 65%    |
| Ph      | 3y        | 84%       | 77%    |
| Ph      | 3x        | 87%       | 80%    |
| Ph      | 3y        | 82%       | 65%    |
| Ph      | 3y        | 84%       | 77%    |
| Ph      | 3x        | 87%       | 80%    |
| Ph      | 3y        | 82%       | 65%    |
| Ph      | 3y        | 84%       | 77%    |
| Ph      | 3x        | 87%       | 80%    |
| Ph      | 3y        | 82%       | 65%    |
| Ph      | 3y        | 84%       | 77%    |

**Figure 3 | Gram-scale synthesis of R-modafinil (armodafinil).** Reaction conditions: (i) (R,R)-1a (0.25 mol%), Na₂MoO₄·2H₂O (2.5 mol%), 35% aq. H₂O₂ (1.05 equiv.), KHSO₄ (0.5 equiv.), ¹Bu₂O (4 mL), 0°C, 1 h; (ii) NH₃ (10.0 equiv., 2 M in MeOH), rt, 24 h.

- **Conditions:** reaction was performed with 0.2 mmol of 2, H₂O₂ (1.05 equiv.), KHSO₄ (0.5 equiv.), 2.5 mol% Na₂MoO₄·2H₂O, 1 mol% (S,S)-1a in 4.0 ml of solvent at 0°C.
- *¹Bu₂O as the solvent.
- ²K₂MoO₄ as [MoO₄]²⁻ source.
- ³0.25 equiv. of KHSO₄.
- ⁴The reaction was conducted at room temperature for 24 h using 1.5 equiv. of 35% aqueous H₂O₂.
Figure 4 | Preparation of \([\text{BG}]^2+[\text{S(O}_2\text{)}\text{Mo}_2\text{O}_2(\mu\text{-O}_2\text{)}_2\text{O}_2]^2^–\) \((R,R)-1\text{b}\). Conditions: \(\text{Na}_2\text{MoO}_4\cdot2\text{H}_2\text{O}\) (2.5 mol%), 35% aq. \(\text{H}_2\text{O}_2\) (1.0 equiv.), KHSO\(_4\) (0.5 equiv.) or \(\text{H}_2\text{SO}_4\) (0.25 equiv.), \(\text{Et}_2\text{O}\) (2 ml), rt, 2 h.

Figure 5 | Characterization of the anionic cluster \([\text{S(O}_2\text{)}\text{Mo}_2\text{O}_2(\mu\text{-O}_2\text{)}_2\text{O}_2]^2^–\) in \((R,R)-1\text{b}\). (a) ORTEP view of \([\text{S(O}_2\text{)}\text{Mo}_2\text{O}_2(\mu\text{-O}_2\text{)}_2\text{O}_2]^2^–\) dianion in \((R,R)-1\text{b}\) with the atom numbering scheme. (b) \(^{95}\text{Mo}\) NMR spectrum of \((R,R)-1\text{b}\) in DMF-d\(_7\) (0.05 M, 22 °C).

Figure 6 | Mechanistic insights. (a) \([\text{BG}]^2^+[\text{S(O}_2\text{)}\text{Mo}_2\text{O}_2(\mu\text{-O}_2\text{)}_2\text{O}_2]^2^–\) \((R,R)-1\text{b}\) as the sole oxidant. (b) 1 mol% \((R,R)-1\text{b}\) as catalyst.

Figure 7 | Geometry optimization of ion pair \((R,R)-1\text{b}\) with ONIOM method. Structure of \((R,R)-1\text{b}\) obtained from ONIOM geometry optimization, where atoms are color-coded as follows: C (grey), N (blue), H (white), S (yellow), O (red) and Mo (pink). The displayed NCI surface of bisguanidinium indicates interactions between the anionic cluster \([\text{S(O}_2\text{)}\text{Mo}_2\text{O}_2(\mu\text{-O}_2\text{)}_2\text{O}_2]^2^–\) and bisguanidinium.
enantioenriched dialkyl sulfoxides and alkyl aryl sulfoxides have been catalyzed by peroxomolybdate for enantioselective sulfoxidation; a series of compounds in the article, see Supplementary Figs 14–70 and Supplementary Data availability. CCDC 1456997-1456990 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre www.ccdc.cam.ac.uk/data_request/cif. The data that support the findings of this study are available from the corresponding authors on request.

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