

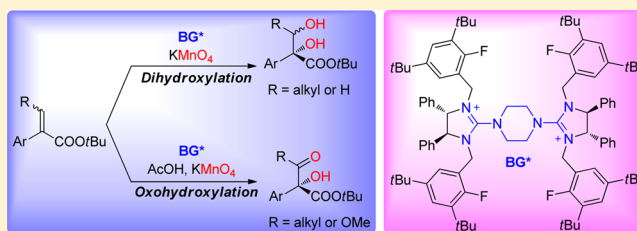
# Enantioselective Oxidation of Alkenes with Potassium Permanganate Catalyzed by Chiral Dicationic Bisguanidinium

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**S** Supporting Information

**ABSTRACT:** Chiral anion-controlled ion-pairing catalysis was demonstrated to be a wide-ranging strategy that can utilize a variety of cationic metal species. In a similar manner, we envision a complementary strategy using chiral cation in partnership with inorganic anionic metal salts. Herein, we report a chiral dicationic bisguanidinium-catalyzed asymmetric oxidation reaction of alkenes with potassium permanganate. Chiral induction is attributed to ion-pairing interaction between chiral cation and enolate anion. The success of the current permanganate oxidation reaction together with mechanistic insights should provide inspiration for expansion to other anionic metal salts and would open up new paradigms for asymmetric transition metal catalysis, phase-transfer catalysis, and ion-pairing catalysis.

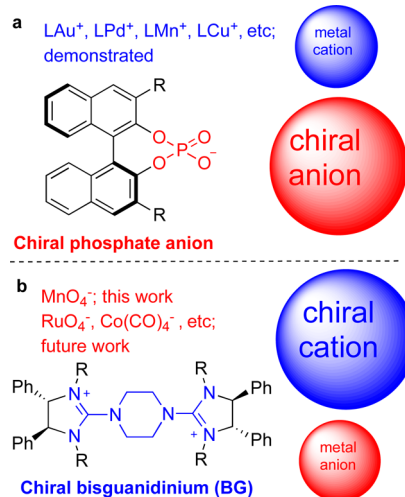


## INTRODUCTION

Asymmetric catalysis is one of the most efficient strategies to generate enantiomerically pure small molecules that are commercially important in the chemical and pharmaceutical industries.<sup>1</sup> Asymmetric phase-transfer catalysis is of particular interest because of its operational simplicity, ease of scalability, and environmental benignity.<sup>2–4</sup> Most asymmetric phase-transfer reactions are Brønsted base reactions; inorganic hydroxide bases are shuttled from the aqueous phase to generate an onium carbanion intermediate, which is subsequently trapped by electrophilic substrates.<sup>2</sup> Other inorganic salts were also used in phase-transfer reactions; however, they met with relatively less success in asymmetric versions.<sup>3</sup> High level of stereocontrol was restricted to only few transformations, such as asymmetric Strecker reaction using cyanide salt<sup>5</sup> and epoxidation with hypochlorite salt.<sup>6</sup> Asymmetric phase-transfer reactions are but a subset of a more general strategy of ion-pairing catalysis using chiral cation and a functional anion. A remarkable example of this approach is reported by Ishihara, in which the anionic (hypo)iodite reagent was utilized in catalytic amount and regenerated through *in situ* oxidation with co-oxidant.<sup>7</sup> Highly enantioselective cycloetherification can be accomplished together with the Maruoka catalyst, yielding enantio-enriched 2-acyl-2,3-dihydrobenzofurans. More recently, this (hypo)iodite catalysis was extended to an efficient, high turnover protocol for the synthesis of tocopherols.<sup>8</sup>

On the other hand, chiral anion-controlled ion-pairing catalysis has experienced tremendous progress recently owing mainly to the advances made in binaphthyl-derived chiral phosphate anion<sup>9–12</sup> and chiral thiourea anion-binding chemistries.<sup>13,14</sup> Along this line, the advent of chiral anion

phase-transfer catalysis is particularly interesting,<sup>10</sup> demonstrating the versatility of ion-pairing catalysis. More significantly, the strategy of using cationic metal species controlled by chiral anions thus forges a new direction for asymmetric metal catalyzed reactions (Figure 1a).<sup>11,12,15–19</sup> Inspired by these advancements, we envision a complementary strategy to control anionic metal species with chiral cations (Figure 1b).



**Figure 1.** Two distinct modes of chiral ion-pairing catalysis. (a) Cationic metal species and chiral phosphate anion. (b) Anionic metal species and chiral bisguanidinium cation.

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Chiral ammonium salts have been used in palladium catalyzed asymmetric allylation, wherein cationic metal intermediate is involved;<sup>20,21</sup> this strategy is dependent on the ammonium salt and metal catalyst to function fairly independent of each other. Conceptually, on the other extreme, ion-pairing catalysis using chiral cation and anionic metal species is dependent on the synergistic interaction between them. It also represents a different approach to exploit asymmetric organocatalysis to induce chirality with metals.<sup>22–25</sup>

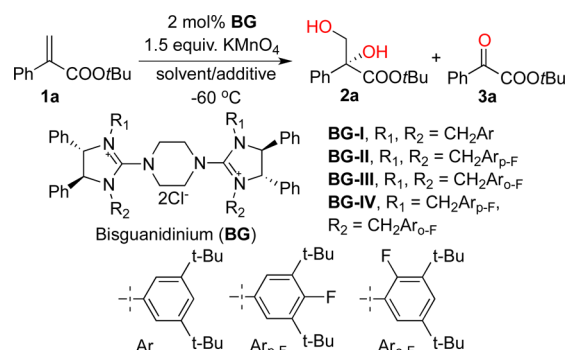
## RESULTS AND DISCUSSION

Metal-centered anionic reagents using achiral quaternary ammonium salts have had precedence in the literature. Carbonylation reaction using cobalt tetracarbonyl anion  $[\text{Co}(\text{CO})_4]^-$ <sup>26</sup> and oxidation reactions with perruthenate anion  $[\text{RuO}_4]^-$ <sup>27</sup> are such examples. The use of phase-transfer conditions for permanganate  $[\text{MnO}_4]^-$  oxidations is also known; stoichiometric amount of chiral *Cinchonidinium* salt was used to effect asymmetric dihydroxylation of alkenes, but these reactions suffered from moderate enantioselectivities and low yields.<sup>28</sup> Inspired by these works, we embark to demonstrate this ion-pairing strategy using permanganate oxidation as a platform.

It was observed that chiral *Cinchonidinium* salt decomposed under permanganate dihydroxylation condition. We realized that identification of a chiral cation that is compatible with permanganate anion is a prerequisite to achieve catalytic permanganate dihydroxylation. Our group has been interested in developing N-sp<sup>2</sup> hybridized pentanidinium salts as chiral phase-transfer catalysts<sup>29,30</sup> and a novel dicationic bisguanidinium (BG) evolved from this work serendipitously (Figure 1b). It is easily accessed in three synthetic steps from commercially available chiral diamine (Figure S1). We anticipated that the dicationic moiety, with its highly positive charge localized in small volume, would facilitate interactions with anionic reagents or intermediates. These interactions will enhance the ability of the catalyst to achieve high stereocontrol. We were thrilled to find out that these chiral bisguanidiniums are stable under permanganate oxidation condition and promoted the dihydroxylation of  $\alpha,\beta$ -unsaturated ketones catalytically in high conversion. We have conducted a stability test of bisguanidiniums in the presence of 50 equiv of  $\text{KMnO}_4$  and were able to recover the catalyst unchanged (see SI). We are aware of the significance of this reaction, as it is potentially a complementary approach to the renowned Sharpless Asymmetric Dihydroxylation (AD).<sup>31–33</sup>

After an extensive study, we decided to use  $\alpha,\beta$ -unsaturated esters as model substrates for our investigation and were encouraged by the preliminary results (Table 1). With the use of 2 mol % of dicationic bisguanidinium salt BG-I, *tert*-butyl 2-phenyl acrylate 1a was fully consumed, yielding dihydroxylation product 2a in satisfactory yield and promising enantioselectivity, together with C–C cleavage product 3a as the only detectable byproduct. A survey of solvents revealed that *tert*-butyl methyl ether (TBME) is the best choice (entries 1–4). Interestingly, we found that using different aqueous salts as additives has an impact on the reactivity and stereoselectivity of the reaction. Further structure modification of the bisguanidinium catalysts, in particular, introduction of fluoro-substitution on the side arms, led to increased levels of enantioselectivity (entries 5–8). Catalyst BG-IV together with 20 wt % aqueous potassium iodide (KI) provided the most ideal conditions (92% ee) (see Table S1 for more details). We have also prepared the

**Table 1. Optimization of Asymmetric Permanganate Dihydroxylation Conditions<sup>a</sup>**



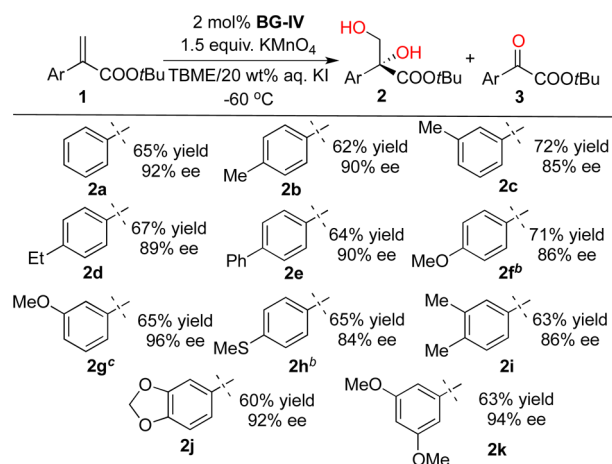
entry	catalyst	solvent	additive	ee of 2a (%) <sup>b</sup>
1	BG-I	DCM	H <sub>2</sub> O	26
2	BG-I	PhCH <sub>3</sub>	H <sub>2</sub> O	45
3	BG-I	THF	H <sub>2</sub> O	9
4	BG-I	TBME	H <sub>2</sub> O	71
5	BG-I	TBME	aq KI <sup>c</sup>	75
6	BG-II	TBME	aq KI <sup>c</sup>	88
7	BG-III	TBME	aq KI <sup>c</sup>	85
8	BG-IV	TBME	aq KI <sup>c</sup>	92

<sup>a</sup>Reactions were conducted on 0.025 mmol scale in 0.5 mL solvent and 0.05 mL aqueous additive. <sup>b</sup>Enantiomeric excess (ee) was determined by chiral HPLC. <sup>c</sup>20 wt % aqueous KI was used.

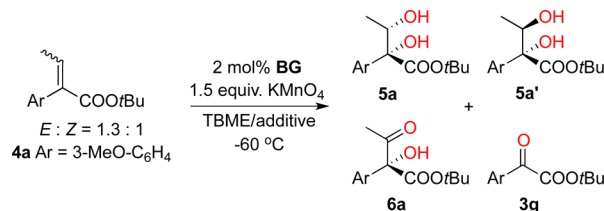
bisguanidinium iodide catalyst and shown that the activity is similar to the effect of adding of KI (see SI).

With the optimized condition in hand, *tert*-butyl acrylates with different  $\alpha$ -aryl groups were investigated (Scheme 1). Generally, the substrates with electron-neutral or electron-rich arenes showed high reactivity, provided diols 2a–2k in high enantioselectivities with moderate yields. The remaining yields are manifested as the C–C cleavage byproduct. Electron-rich arenes resulted in higher enantioselectivities in contrast with electron-deficient ones (Figure S2). Interestingly, methylthio

**Scheme 1. Substrate Scope of  $\alpha$ -Aryl Acrylates for Asymmetric Permanganate Dihydroxylation<sup>a</sup>**



<sup>a</sup>Reactions were carried out on 0.2 mmol scale at  $-60$  °C for 12 h unless otherwise noted; yield values refer to isolated yields after purification and ee was determined by chiral HPLC. <sup>b</sup>Reactions for 2f and 2h were carried out at  $-70$  °C for 36 h. <sup>c</sup>For absolute configuration determination, see Figure S4.

Table 2. Optimization of Reaction Conditions for Trisubstituted Enoates<sup>a</sup>

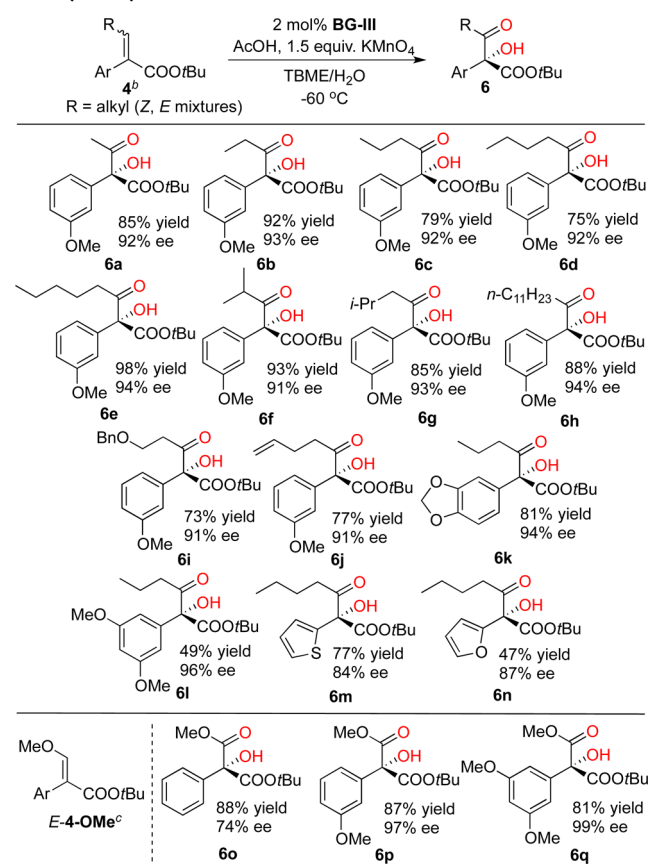
entry	catalyst	additive	ratio of 4a:(5a + 5a'):6a:3g <sup>b</sup>	ee of 5a/5a' (%) <sup>c</sup>	ee of 6a (%) <sup>c</sup>
1	BG-IV	H <sub>2</sub> O	17:33:0:50	84/89	-
2	BG-III	H <sub>2</sub> O	8:38:0:54	91/94	-
3	BG-III	1N aq HCl	11:32:41:16	85/93	92
4	BG-III	0.1N aq HCl	14:26:5:55	88/92	-
5	BG-III	H <sub>2</sub> O/AcOH	90% <sup>d</sup>	-	92

<sup>a</sup>The reaction was conducted on 0.05 mmol scale in 1 mL TBME and 0.05 mL aqueous additive. For substrate and products configuration determination, see Figures S3 and S4. <sup>b</sup>Ratios were determined by <sup>1</sup>H NMR analysis. <sup>c</sup>ee was determined by chiral HPLC. <sup>d</sup>Isolated yield of 6a.

ether group in diol 2h was well tolerated under the current dihydroxylation condition; although it was reported to be oxidized by permanganate under certain conditions.<sup>34,35</sup> Acrylates with an  $\alpha$ -alkyl group underwent reaction smoothly albeit with moderate enantioselectivities (Figure S2).

In the next stage, trisubstituted enoates were investigated and subjected to the permanganate oxidation condition (Table 2). We found that when a mixture of *Z*, *E*-trisubstituted enoates 4a were oxidized, both diastereomers 5a and 5a' were obtained in high enantioselectivities together with significant amount of C–C cleavage product 3g. Catalyst BG-III showed the highest catalytic activity and provided products with highest enantioselectivities (entry 1–2). When we were trying to improve the yields of the desired diols, we were pleasantly surprised that under acidic conditions, an unexpected 2-hydroxy-3-oxocarboxylic ester 6a was detected. The yield of 6a was influenced by the concentration of hydrochloric acid (entries 3–4). When acetic acid was used, 6a was obtained in both high yield and high enantioselectivity; both diols and C–C cleavage product formation were efficiently suppressed (entry 5) (see Table S2 for more details). Other organic acids with different pKa and structures were also tested and they are not significantly better than AcOH (see Table S3 for details). As far as we are aware, there are only a few reports describing this transformation.<sup>36,37</sup> We named this transformation oxohydroxylation as it is analogous to dihydroxylation. The high enantioselectivity observed indicates that both *Z*- and *E*-trisubstituted enoates 4a were transformed to the same enantiomer 6a under oxohydroxylation condition.

A series of trisubstituted enoates was then investigated under the oxohydroxylation condition (Scheme 2). Substrates with different alkyl groups, including long alkyl chain and secondary isopropyl group, uniformly gave high levels of enantioselectivity in good to excellent yields (6a–6j). Notably, isolated terminal double bond is well tolerated (6j). Different  $\alpha$ -aryl groups were also investigated; as anticipated, electron-rich aryl groups showed higher reactivity and selectivity (6k–6n). Interestingly, trisubstituted enoates with  $\alpha$ -heteroarene substituents including furyl and thienyl underwent oxohydroxylation in high enantioselectivity. As a further extension to this methodology, we found that methoxy-substituted enoates *E*-4-OME were transformed to  $\alpha$ -hydroxymalonates in high enantioselectivities (6o–6q). This transformation demonstrated that asymmetric oxohydroxylation could be used to prepare chiral  $\alpha$ -hydroxy carbonyl compounds from hetero-substituted alkenes. To

Scheme 2. Scope of Trisubstituted Enoates for Asymmetric Oxohydroxylation<sup>a</sup>

<sup>a</sup>Reactions were carried out on 0.2 mmol scale at  $-60$  °C with isolated yields reported and ee determined by chiral HPLC. A 4-mmol scale reaction of 4a (1 g) was conducted using 1 mol % of BG-III, yielding 6a in 81% yield and 92% ee. <sup>b</sup>For alkyl substituted enoates, *Z*, *E*-mixtures were used as substrates; for configuration determination, see Figure S3; for *Z*/*E* ratio, see Figure S9; <sup>c</sup>*E*-methoxy substituted enoates *E*-4-OME were used.

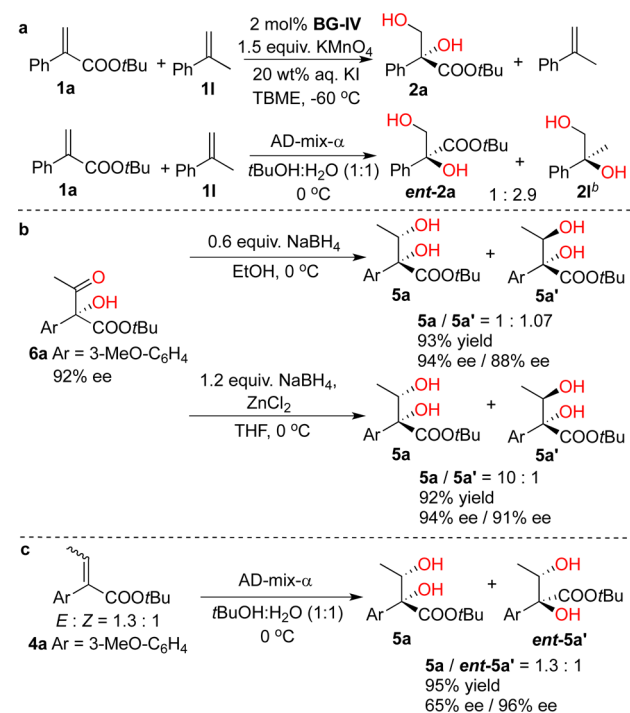
demonstrate the practicality of this new methodology, a 4-mmol reaction using 1 mol % BG-III was conducted, yielding 6a in 81% yield and 92% ee.

The difference between asymmetric permanganate dihydroxylation and Sharpless AD was then investigated. When an equal



amount of two alkenes, acrylate **1a** and  $\alpha$ -methylstyrene **1l**, was subjected to the permanganate dihydroxylation condition, only diol **2a** was obtained and  $\alpha$ -methylstyrene was recovered intact. In contrast, under standard Sharpless AD condition,<sup>32</sup>  $\alpha$ -methylstyrene was dihydroxylated preferentially, giving diol *ent*-**2a** and **2l** in a ratio of 1:2.9 (Scheme 3a). This newly developed permanganate dihydroxylation, thus, provides complementary selectivity to Sharpless AD.

**Scheme 3. Comparison between Asymmetric Permanganate Oxidation and Sharpless AD<sup>a</sup>**

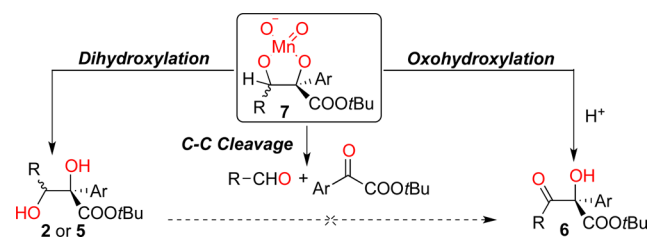


<sup>a</sup>All the ratios were determined with crude product by <sup>1</sup>H NMR analysis. <sup>b</sup>Absolute configuration of **2l** was determined according to ref 32.

When ketone **6a** was subjected to reduction with sodium borohydride, both diol **5a** and **5a'** were obtained in high optical purity (Scheme 3b). Moreover, reduction with NaBH<sub>4</sub>/ZnCl<sub>2</sub> yielded diol **5a** in excellent selectivity of 10:1 ratio and in excellent yield. On the other hand, when a *Z/E*-mixture of **4a** was subjected to standard Sharpless AD condition, it furnished diol **5a** in 65% ee and *ent*-**5a'** in 96% ee (Scheme 3c). This comparison indicated that asymmetric permanganate oxohydroxylation/reduction sequence provides a formal asymmetric dihydroxylation that is complementary to Sharpless AD and would be useful for some challenging substrates.

Mechanistically, it is widely recognized that a cyclic manganate diester **7** is the common intermediate that generates different products through diverse pathways<sup>34,35,38</sup> (Scheme 4). This is consistent with the experimental result that absolute configuration of the  $\alpha$ -chiral center of oxidation products from both dihydroxylation and oxohydroxylation is the same. Although the mechanism for oxohydroxylation from cyclic manganate diester is currently unclear, the possibility of *in situ* oxidation of dihydroxylation product to generate oxohydroxylation product can be ruled out. When the dihydroxylated alkenes were isolated and reintroduced to the reaction

**Scheme 4. Transformation of Cyclic Manganate Diester Intermediate **7** under Diverse Pathways**



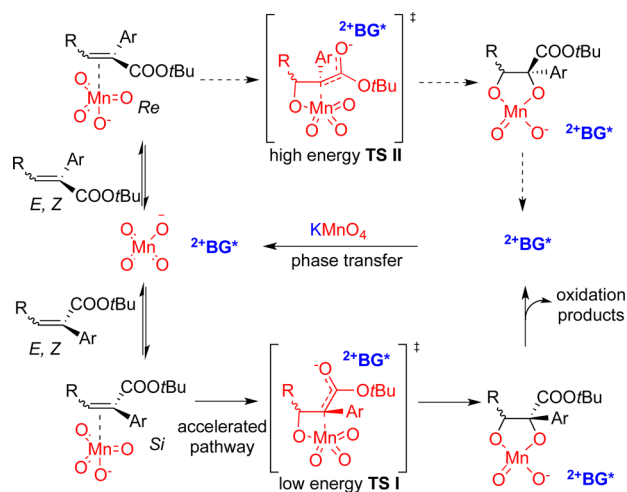
condition, they were not further oxidized to the oxohydroxylated products (Figure S5).

We then attempted to understand the origin of stereoinduction of this asymmetric permanganate oxidation. In Sharpless AD, chiral complex is formed through a covalent bond between chiral tertiary amine and osmium tetroxide.<sup>33</sup> However, it is unlikely for the bisguanidinium cation to form similar covalent type of chiral entity with the permanganate anion. On the other hand, most asymmetric phase-transfer catalyzed reactions are enantioselective nucleophilic addition reactions.<sup>2–4</sup> Previously, Jew and Park demonstrated a dimeric *Cinchona*-catalyzed epoxidation reaction and the authors proposed a transition state in which the two cationic centers of the catalyst interact with the anionic nucleophile and neutral electrophile simultaneously.<sup>39</sup> It seems also not likely for the bisguanidinium dication to form such transition complex, as it is oblivious to the configuration of trisubstituted alkenes as well as the size of alkyl substituents. Notably, we also did not observe *E/Z* isomerization under the permanganate oxidation conditions (Figure S6).

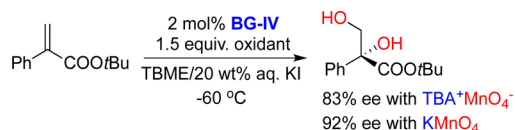
Lee and co-workers reported a mechanistic study of the reaction between methyl cinnamate and quaternary ammonium permanganate.<sup>40</sup> The authors found that the rate of reaction is fastest for those ions, which permit interionic distance in the quaternary ammonium ion pair to be minimized. Stabilization of the enolate transition state through ion pair formation was proposed for the rate enhancement. On the basis of this prior work, we propose that in the current catalytic system, the chiral catalyst accelerate oxidation reaction through the formation of an intimate ion pair with enolate anion in transition state (**TS-I** and **TS-II**) and chiral information is imparted through this interaction (Scheme 5). After shuttling to the organic phase, the permanganate anion dynamically coordinates to double bond from both prochiral faces of the substrate. The cationic centers of bisguanidinium are deeply buried in a chiral pocket, and as a result, only the matched transition state **TS-I** (*si* face approach) allows the formation of intimate ion pair and reaction through this pathway is accelerated selectively. In mismatched **TS-II** (*re* face approach), the interionic distance between enolate anion and cationic centers is much larger, which results in a higher energy transition state. This working model is in accordance with the experimental results that absolute configuration of  $\alpha$ -chiral center of oxidation products from both *Z*- and *E*-enoates is identical.

On the basis of the working model, we speculated that rate acceleration through ion-pairing formation rather than phase separation is crucial for reaction to go through the asymmetric pathway selectively. We envisaged that high level of asymmetric induction might be still applicable with an organic phase soluble permanganate source. To test this hypothesis, a control reaction using tetrabutylammonium permanganate as oxidant

Scheme 5. Working Model



was conducted. With only 2 mol % chiral catalyst and 1.5 equiv of tetrabutylammonium permanganate, the reaction provided high level of chiral induction (83% ee vs 92% ee) (Scheme 6).

Scheme 6. Comparison of Selectivity Using  $\text{TBA}^+\text{MnO}_4^-$  and  $\text{KMnO}_4$  as Oxidant

This demonstrates that the chiral bisguanidinium dication is much better in stabilizing the active anionic intermediates than tetrabutylammonium cation. This might be partially ascribed to its dicationic character, which forms stronger electrostatic interaction with enolate anion in the transition states.

## CONCLUSIONS

It is generally explained that phase-transfer catalysts accelerate reactions by enhancing organic solubility and nucleophilicity of the anionic reagents.<sup>2</sup> In this newly developed methodology, strong evidence suggests that rate acceleration is mainly attributed to transition state stabilization through attractive cation–anion interaction. This stereoselective rate acceleration makes the desired asymmetric pathway much favored. Charge-acceleration effect has been previously proposed in quaternary Cinchonidinium-catalyzed epoxidation reaction.<sup>41</sup> More recently, Jacobsen demonstrated that transition state charge stabilization strategy through multiple noncovalent interactions could be utilized in chiral anion-bonding catalysis to induce stereoselectivity.<sup>42</sup> Although the type of noncovalent interactions involved in this methodology remains to be elucidated, the enzyme-like mode of bisguanidinium, with active center deeply buried in a chiral pocket, should provide implications for catalyst design. A similar approach has already been utilized by List with imidodiphosphoric acid, which contains anionic sites buried within hydrophobic groups.<sup>43</sup>

In addition, the disclosure of asymmetric permanganate oxidation reaction together with mechanistic insights should provide inspiration for expansion to other anionic metal salts. Given the frequent occurrence of transition metal-centered anions in coordination complexes, the current chiral cation ion-

pairing strategy would open up new paradigms for asymmetric transition metal catalysis.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b05792.

Crystallographic data for *E*-4p, 5a', S1 and S2 (CIF)  
Experimental details and characterization data (PDF)

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### Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

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