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Enantioselective Epoxidation of Olefins with H_2O_2 Catalyzed by Bioinspired Aminopyridine Manganese Complexes

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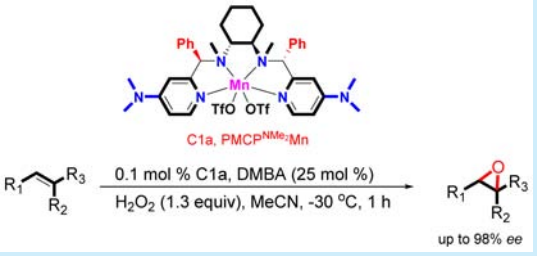
Supporting Information

ABSTRACT: A novel family of bioinspired manganese(II) complexes bearing chiral aminopyridine ligands that possessed additional aromatic groups and strong donating dimethylamino groups were synthesized and characterized. These manganese complexes exhibited efficient and improved activities in the asymmetric epoxidation of various olefins, such as styrene derivatives (up to 93% ee) with H_2O_2 as the oxidant, even with a catalytic amount of carboxylic acid as the additive.



Asymmetric epoxidation (AE) is undoubtedly one of the most significant reactions since one or even two stereogenic centers are constructed, and the resulting epoxides can be further transformed in the synthesis of chiral molecules.[1] Over the past decades, numerous efforts have been dedicated to the catalytic AE to achieve epoxides with high enantioselectivities and yields. For example, the Ti-catalyzed epoxidation by Sharpless,[2] the salen−Mn(III) complexes by Jacobsen[3] and Katsuki[4] independently, and the chiral ketones by Shi[5] are among the greatest breakthroughs in AE. Despite the tremendous progress of these recognized protocols, currently, the pursuit of efficient catalytic systems is still highly desirable from both the atom economic and ecological viewpoints.

Notably, natural nonheme enzymes can activate oxygen to carry out oxidation reactions under mild conditions, which may offer an alternative method to the sustainable goal of AE.[6] Inspired by these structure motifs and powerful oxidative properties of the active sites of such metalloenzymes, many biomimetic catalysts have been synthesized and applied to the AE.[7] Indeed, the bioinspired AE is an appealing method because low catalyst loadings (as low as 0.01 mol %) and environmentally benign oxidants such as hydrogen peroxide (H_2O_2) are often employed in this catalytic system. More importantly, probing into the concomitant metal−oxygen intermediates in bioinspired models will also benefit the illumination of mechanisms in nonheme enzymes in return.[8−10]

The landmark studies of AE catalyzed by bioinspired aminopyridine manganese complexes began at 2003 by Stack and co-workers.[11] They described that a manganese complex [Mn(*R*,*R*-MCP)$(OTf)_2$] (MCP = *N*,*N*′-bis(2-pyridylmethyl)-*N*,*N*′-dimethyl-*trans*-1,2-diaminocyclohexane, OTf = $CF_3SO_3^-$) could rapidly catalyze the epoxidation of electron-deficient olefins using peracetic acid (AcOOH) as the oxidant with high turnover numbers (TONs), while providing a 10% ee for the AE of vinyl cyclohexane. In order to enhance the stereoselectivity of this manganese catalyst for AE, one strategy was the ingenious modifications of the ligand MCP. Hence, after the pioneering work of Stack, versatile manganese and iron complexes containing aminopyridine N4 ligands were reported and proved to be active in the catalytic AE with H_2O_2 as the oxidant.[12] Gratifyingly, excellent yields and ee values (up to 99% ee) had been achieved for several types of olefins, such as chalcones, cinamates, and chromenes by combining modified manganese catalysts and appropriate carboxylic acid additives.[13] However, there is still substantial room for improvement in terms of simple aromatic or aliphatic olefins. For example, in the cases of styrene and stilbene derivatives, either the ee values were generally low or their derivatives were less scrutinized.[14] In this context, the discovery of more stereoselective manganese catalysts is highly desirable for this class of challenging substrates.

It was noteworthy that we previously found the *ee* value of styrene oxide was increased by about 20% when introducing aromatic rings into both of the 2-pyridylmethyl positions of [Mn(*R*,*R*-MCP)$(OTf)_2$] (Scheme 1).[11,12c] In addition, Costas and co-workers described that the amount of carboxylic acid could be dramatically decreased to substoichiometric levels (from 14 equiv to 0.35 equiv with respect to olefin substrate) by including dimethylamino groups to the 4-position of the PDP ligand (PDP^{NMe2}, PDP = 2-[[2-(1-(pyridin-2-ylmethyl)-pyrrolidin-2-yl)pyrrolidin-1-yl]methyl] pyridine).[13a,15,16] As such, it was envisioned that the development of manganese complexes bearing chiral N4 ligands that possessed aromatic rings in 2-pyridylmethyl positions and dimethylamino groups on pyridine rings was reasonable and feasible (Scheme 1). Meanwhile, such new manganese complexes not only would

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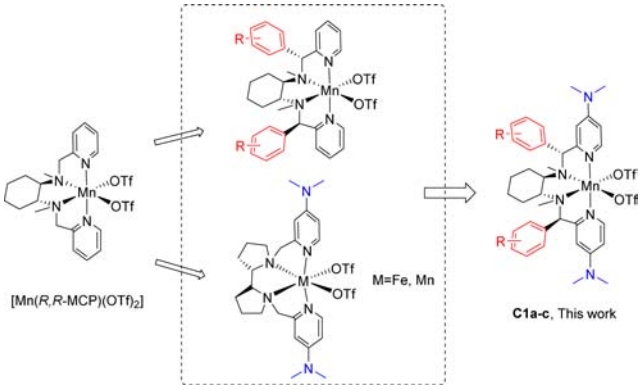
Scheme 1. Manganese(II) Complexes with Newly Designed Aminopyridine Ligands



retain the high efficiency of aminopyridine manganese catalysts but also exhibit potential in enhancing enantioselectivities in the AE of simple olefins with less carboxylic acid additives owing to the incorporation of the two beneficial substituents.

Herein, we report the preparation, reactivity, and substrate scope of bioinspired manganese complexes supported by a new family of aminopyridine ligands where the electronic properties can be tuned by the introduction of both aromatic rings and dimethylamino groups on the ligands. The present manganese catalysts (Figure 1) show improved catalytic activities and enantioselectivities in the AE of styrenes, *trans*-stilbenes, and aliphatic olefins, even in the presence of 25 mol % of carboxylic acid.

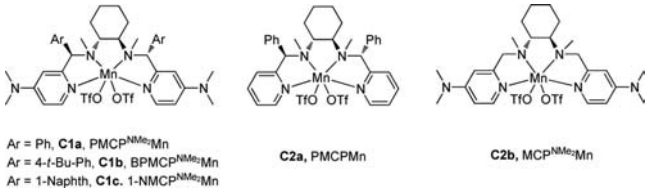
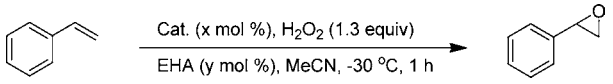


Figure 1. Manganese(II) complexes used in this study.

In exploratory experiments, we selected the AE of styrene as the model reaction and 2-ethylhexanic acid (EHA)[12h] as the additive to study the catalytic activity and stereoselectivity of several well-designed manganese catalysts. As can be seen in Table 1, almost no reaction occurred with the PMCPMn (**C2a**) catalyst in the presence of 25 mol % EHA (Table 1, entry 1). Then high conversion was observed only when the amount of EHA was increased to 5.0 equiv (Table 1, entry 2), which was consistent with our previous conditions.[12c] In the case of MCP^{NMe2} Mn (**C2b**) catalyst, a considerable yield was observed with only 25 mol % EHA (Table 1, entry 3). The PMCP^{NMe2} Mn (**C1a**) catalyst, which could be considered as an integrated one of **C2a** and **C2b**, was then tested in the AE of styrene. To our delight, full conversion and a further improved ee value (77%) were achieved with only 25 mol % of EHA and 0.1 mol % of catalyst at −30 °C (Table 1, entry 4). Lowering the catalyst loading and amount of EHA led to a decrease in conversion while the ee values remained unchanged (Table 1, entries 5 and 6). The series of manganese complexes with different aromatic rings, such as 4-*t*Bu-phenyl (BPMCP^{NMe2} Mn, **C1b**) and 1-naphthyl (1-NMCP^{NMe2} Mn, **C1c**), were also evaluated to study the stereo- and electro-properties of the

Table 1. Reaction Development with Various Aminopyridine Manganese Catalysts[a]



entry	cat. (x)	y	GC yield (%)	ee (%)[b]
1	**C2a** (0.1)	25	trace	–
2	**C2a** (0.1)	500	70	72
3	**C2b** (0.1)	25	63	63
4	**C1a** (0.1)	25	84	77
5	**C1a** (0.05)	25	28	77
6	**C1a** (0.1)	20	82	77
7	**C1b** (0.1)	25	50	73
8	**C1c** (0.1)	25	37	67

[a]Reaction conditions: H_2O_2 (30% aqueous solution, 1.3 equiv) diluted with 0.5 mL of MeCN was delivered through a syringe pump over 1 h to a stirred solution of catalyst (0.05−0.1 mol %), EHA (20−500 mol %), internal standard (decane), and substrate (0.5 mmol) in 1.0 mL of MeCN at −30 °C. [b]The ee values were determined by GC.

substituents. Both manganese complexes exhibited lower reactivity than that of PMCP^{NMe2} Mn, **C1a**.

In the case of nonheme iron or manganese catalysts, carboxylic acid as a coligand would lead to an efficient heterolytic O−O bond cleavage of M^{III}(OOH) (M = Fe, Mn) species to form high-valent metal-oxo species.[9a,c,12d,e] Despite the fact that mechanisms of epoxidation catalyzed by nonheme iron or manganese catalysts require further elucidation, the involvement of the carboxylate high-valent metal-oxo intermediates in the catalytic epoxidation reactions have been supported experimentally[9e] and theoretically,[9c] which are thought to be reactive epoxidizing intermediates. Bryliakov et al.[12e,h] and Costas et al.[15,16] had also demonstrated that the stereoselectivity of AE could be modulated by the use of carboxylic acid. In order to achieve high enantioselectivity, a variety of carboxylic acids were also screened. First, acetic acid (AA) was investigated in the AE of styrene, providing low conversion and a moderate ee value (Figure 2). With the

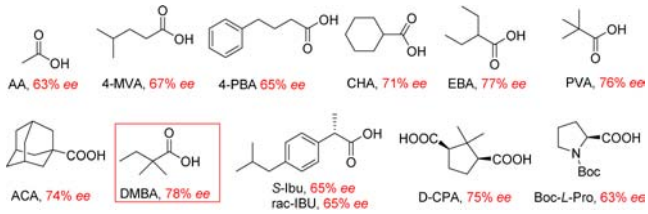


Figure 2. Screening the carboxylic acid for the AE of styrene. H_2O_2 (30% aqueous solution, 1.3 equiv) diluted with 0.5 mL of MeCN was delivered through syringe pump over 1 h to a stirred solution of PMCP^{NMe2} Mn, **C1a** (0.1 mol %), acid additive (25 mol %), internal standard (decane), and substrate (0.5 mmol) in 1.0 mL of MeCN at −30 °C.

increase in the steric bulk at the α-carbon of the carboxylic acid, the ee values could be enhanced clearly (Figure 2). The use of dimethylbutanic acid (DMBA) provided a comparable outcome with that of EHA (Figure 2, 78% ee), and this figure could be ascribed to the highest one in the AE of styrene in comparison with other nonheme iron or manganese catalysts so far.[12,13] In addition, racemic ibuprofen (Ibu) showed identical ee compared to *S*-Ibu. A chiral diacid, D-camphoric acid (D-CPA), was also involved to provide a good result compared

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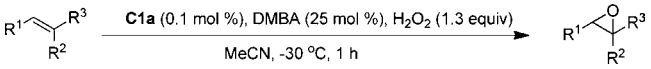
with that of DMBA. The AE of styrene was efficiently promoted by the use of Boc-protected L-proline except for the minimally lower ee value (Figure 2; for details see Table S1 in SI).[16]

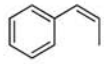
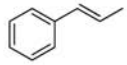
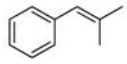
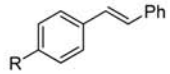
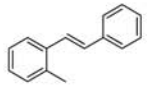
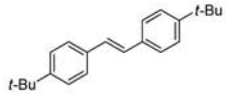
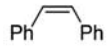
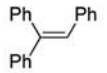
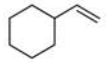
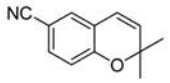
After the optimized conditions were identified, the asymmetric epoxidation of simple aromatic olefins including styrenes and *trans*-stilbenes were explored using this catalytic system. In general, the ee values of the epoxides of styrene derivatives were enhanced with regard to previous nonheme manganese systems. The halo atoms on the *para*-position of styrene nearly had no effect on the enantioselectivity, while the methyl group led to the decrease of the ee value (Table 2, entries 2−4). In the case of styrene bearing a methyl group on the *ortho*-position, 80% ee was observed (Table 2, entry 6). To our delight, an excellent ee value of 93% was obtained for the AE of *cis*-*β*-methylstyrene (Table 2, entry 7). However, the ee value dramatically declined to 52% when there were two methyl groups in the *β*-position (Table 2, entry 9). In the case of *trans*-*β*-methylstyrene, nearly racemic epoxide was produced (Table 2, entry 8). Presently, the application of the nonheme iron or manganese catalyst was limited by the lack of selectivity during the epoxidation of *trans*-stilbenes. It was noteworthy that AE of *trans*-stilbene with **C1a** under the same conditions provided quite good stereoselectivity (Table 2, entry 10, 88% ee). The reaction of *ortho*-Me-substituted *trans*-stilbene provided the epoxide in 90% ee (Table 2, entry 13). Furthermore, the *trans*-stilbenes with bulkier substituents resulted in diminished enantioselectivity (Table 2, entry 14). *cis*-Stilbene was often used as a probe substrate to simply study the reaction pathway for epoxidation.[17] In this work, the AE of *cis*-stilbene led to the formation of two stereoisomeric epoxides and the *ee* value of *trans*-epoxides was very low (Table 2, entry 15). It would point to the formation of a radical intermediate that would allow C−C bond rotation to give both stereoisomers.[18] In the cases of trisubstituted olefins, moderate to good yields as well as improved ee values were observed (Table 2, entry 16; Table S2 in SI, entry 1). In addition, this manganese catalyst **C1a** also exhibited good chemo- and enantioselectivities in the AE of other types of olefins. For example, simple aliphatic alkenes, which were always thought of as challenging substrates in bioinspired catalysis, could be converted to their epoxides with improved enantioselectivities (Table 2, entries 17−19).[11a,12c] As in the case of other state-of-the-art biomimetic procotols,[13a,b] as expected, excellent yields and stereoselectivities for the derivatives of chromene and chalcone were also achieved by using this manganese complex in a low loading of DMBA (Table 2, entries 20; Table S2, entries 2−4).

To demonstrate the utility of this reaction, a gram-scale AE reaction was performed. Treatment of 1.08 g of *trans*-stilbene produced epoxide in a 68% isolated yield and 88% ee under standard conditions (Scheme 2). The ee value of the epoxide reached 93% after recrystallization. Even though the reaction scale was magnified up to 20 times, a comparable ee value and synthetically valuable yield could be still obtained.

In summary, we have prepared and characterized several aminopyridine ligands and their manganese complexes that possessed additional aromatic groups and strong electron-donating dimethylamino groups. As expected, these manganese complexes exhibited excellent stereoselectivities in the asymmetric epoxidation of various olefins (e.g., styrenes, up to 93% ee), with environmental H_2O_2 as the oxidant in the catalytic amount of the carboxylic acid partner. Further elucidation of the reaction mechanism and development of more robust catalytic systems are underway.

Table 2. Asymmetric Epoxidation of Various Olefins by PMCP^{NMe2} Mn (C1a) and H_2O_2[a]



entry	substrate	conv (%)	GC yield (%)[b]	ee (%)[c]
1	R=H	99	84	78
2	R = *p*-F	99	85	78
3	R = *p*-Cl	99	89	76
4	R = *p*-Me	99	(70)	67
5	R = *m*-Me	99	79	77
6	R = *o*-Me	99	78	80
7		99	75	93
8[f]		99	71	2
9		99	85	52
10	 R = H	99	(86)	88
11	R = F	99	(80)	88
12	R = Me	99	(57)	80
13		99	(78)	90
14		99	(79)	52
15		85	(67)[d]	28[e]
16		66	(49)	64
17[f]		95	91	45
18[f]		99	94	54
19[f]		99	91	31
20		99	(95)	98

[a]Reaction conditions: For styrene derivatives, H_2O_2 (30% aqueous solution, 1.3 equiv) diluted with 0.5 mL of MeCN was delivered through a syringe pump over 1 h to a stirred solution of **C1a** (0.1 mol %), DMBA (25 mol %), internal standard (decane), and substrate (0.5 mmol) in 1.0 mL of MeCN in the air at −30 °C. For stilbene derivatives, the scale of substrates was 0.3 mmol, while the solvent was a mixture of MeCN and CH_2Cl_2 (v/v = 1:1). [b]Isolated yields were listed in the brackets. [c]The ee values were measured by GC and HPLC with chiral columns. [d]*cis*-Epoxides/*trans*-Epoxides = 7:3. [e]Ee value of *trans*-epoxides. [f]**C1a** (0.4 mol %), H_2O_2 (2.0 equiv), DMBA (100 mol %).

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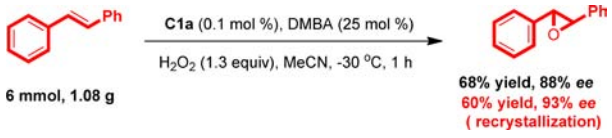
Scheme 2. Gram-Scale AE of *trans*-Stilbene Catalyzed by $PMCP^{NMe2}$ Mn (C1a) Complex with H_2O_2



■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.5b03309.

Synthetic procedures for the newly designed ligands and manganese(II) complexes, catalytic procedures, NMR, GC as well as HPLC spectra (PDF)

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) For reviews of asymmetric epoxidation, see: (a) Xia, Q.; Ge, H.; Ye, C.; Liu, Z.; Su, K. *Chem. Rev.* **2005**, *105*, 1603. (b) Wong, O.; Shi, Y. *Chem. Rev.* **2008**, *108*, 3958. (c) De Faveri, G.; Ilyashenko, G.; Watkinson, M. *Chem. Soc. Rev.* **2011**, *40*, 1722. (d) Zhu, Y.; Wang, Q.; Cornwall, R. G.; Shi, Y. *Chem. Rev.* **2014**, *114*, 8199. (e) Saisaha, P.; de Boer, J. W.; Browne, W. R. *Chem. Soc. Rev.* **2013**, *42*, 2059.

(2) Katsuki, T.; Sharpless, K. B. *J. Am. Chem. Soc.* **1980**, *102*, 5974.

(3) Zhang, W.; Loebach, J. L.; Wilson, S. R.; Jacobsen, E. N. *J. Am. Chem. Soc.* **1990**, *112*, 2801.

(4) Irie, R.; Noda, K.; Ito, Y.; Matsumoto, N.; Katsuki, T. *Tetrahedron Lett.* **1990**, *31*, 7345.

(5) Tu, Y.; Wang, Z.; Shi, Y. *J. Am. Chem. Soc.* **1996**, *118*, 9806.

(6) For reviews of metal sites and oxygen activation in nonheme enzymes, see: (a) Decker, A.; Solomon, E. I. *Curr. Opin. Chem. Biol.* **2005**, *9*, 152. (b) Que, L., Jr.; Tolman, W. B. *Nature* **2008**, *455*, 333. (c) Kovaleva, E. G.; Lipscomb, J. D. *Nat. Chem. Biol.* **2008**, *4*, 186. (d) Bugg, T. D. H. In *Iron-Containing Enzymes: Versatile Catalysts of Hydroxylation Reactions in Nature*; de Visser, S. P., Kumar, D., Eds.; The Royal Society of Chemistry: Cambridge, UK, 2011. (e) Bryliakov, K. P.; Talsi, E. P. *Coord. Chem. Rev.* **2014**, *276*, 73.

(7) For reviews of bioinspired catalysis of asymmetric epoxidation, see: (a) Talsi, E. P.; Bryliakov, K. P. *Coord. Chem. Rev.* **2012**, *256*, 1418. (b) Gelalcha, F. G. *Adv. Synth. Catal.* **2014**, *356*, 261. (c) Fingerhut, A.; Serdyuk, O. V.; Tsogoeva, S. B. *Green Chem.* **2015**, *17*, 2042. (d) Cussó, O.; Ribas, X.; Costas, M. *Chem. Commun.* **2015**, *51*, 14285.

(8) (a) Nam, W.; Lee, Y.-M.; Fukuzumi, S. *Acc. Chem. Res.* **2014**, *47*, 1146. (b) Mcdonald, A. R.; Que, L., Jr. *Coord. Chem. Rev.* **2013**, *257*, 414. (c) Ray, K.; Pfaff, F. F.; Wang, B.; Nam, W. *J. Am. Chem. Soc.* **2014**, *136*, 13942. (d) Oloo, W. N.; Que, L., Jr. *Acc. Chem. Res.* **2015**, *48*, 2612. (e) Chen, Z.; Yin, G. *Chem. Soc. Rev.* **2015**, *44*, 1083.

(9) (a) Mas-Ballesté, R.; Que, L., Jr. *J. Am. Chem. Soc.* **2007**, *129*, 15964. (b) Oloo, W. N.; Fielding, A. J.; Que, L., Jr. *J. Am. Chem. Soc.* **2013**, *135*, 6438. (c) Wang, Y.; Janardanan, D.; Usharani, D.; Han, K.; Que, L., Jr.; Shaik, S. *ACS Catal.* **2013**, *3*, 1334. (d) Prat, I.; Mathieson, J. S.; Güell, M.; Ribas, X.; Luis, J. M.; Cronin, L.; Costas, M. *Nat. Chem.* **2011**, *3*, 788. (e) Oloo, W. N.; Meier, K. K.; Wang, Y.; Shaik, S.; Münck, E.; Que, L., Jr. *Nat. Commun.* **2014**, *5*, 3046. (f) Park, J.; Lee, Y.-M.; Ohkubo, K.; Nam, W.; Fukuzumi, S. *Inorg. Chem.* **2015**, *54*, 5806. (g) Lyakin, O. Y.; Zima, A. M.; Samsonenko, D. G.; Bryliakov, K. P.; Talsi, E. P. *ACS Catal.* **2015**, *5*, 2702.

(10) (a) Nehru, K.; Kim, S. J.; Kim, I. Y.; Seo, M. S.; Kim, Y.; Kim, S.-J.; Kim, J.; Nam, W. *Chem. Commun.* **2007**, *44*, 4623. (b) Wu, X.; Seo, M. S.; Davis, K. M.; Lee, Y.-M.; Chen, J.; Cho, K.-B.; Pushkar, Y. N.; Nam, W. *J. Am. Chem. Soc.* **2011**, *133*, 20088.

(11) (a) Murphy, A.; Dubois, G.; Stack, T. D. P. *J. Am. Chem. Soc.* **2003**, *125*, 5250. (b) Murphy, A.; Pace, A.; Stack, T. D. P. *Org. Lett.* **2004**, *6*, 3119. (c) Murphy, A.; Stack, T. D. P. *J. Mol. Catal. A: Chem.* **2006**, *251*, 78.

(12) For selected examples of AE catalyzed by bioinspired manganese catalysts with MCP-derived ligands, see: (a) Guillemot, G.; Neuburger, M.; Pfaltz, A. *Chem.—Eur. J.* **2007**, *13*, 8960. (b) Gomez, L.; Garcia-Bosch, I.; Company, A.; Sala, X.; Fontrodona, X.; Ribas, X.; Costas, M. *Dalton Trans.* **2007**, 5539. (c) Wu, M.; Wang, B.; Wang, S.; Xia, C.; Sun, W. *Org. Lett.* **2009**, *11*, 3622. (d) Ottenbacher, R. V.; Bryliakov, K. P.; Talsi, E. P. *Inorg. Chem.* **2010**, *49*, 8620. (e) Ottenbacher, R. V.; Bryliakov, K. P.; Talsi, E. P. *Adv. Synth. Catal.* **2011**, *353*, 885. (f) Wang, B.; Miao, C.; Wang, S.; Kühn, F. E.; Xia, C.; Sun, W. *J. Organomet. Chem.* **2012**, *715*, 9. (g) Garcia-Bosch, I.; Gomez, L.; Polo, A.; Ribas, X.; Costas, M. *Adv. Synth. Catal.* **2012**, *354*, 65. (h) Lyakin, O. Y.; Ottenbacher, R. V.; Bryliakov, K. P.; Talsi, E. P. *ACS Catal.* **2012**, *2*, 1196. (i) Maity, N. C.; Bera, P. K.; Ghosh, D.; Abdi, S. H. R.; Kureshy, R. I.; Khan, N. H.; Bajaj, H. C.; Suresh, E. *Catal. Sci. Technol.* **2014**, *4*, 208.

(13) For selected examples of AE catalyzed by bioinspired manganese catalysts, see: (a) Cussó, O.; Garcia-Bosch, I.; Font, D.; Ribas, X.; Lloret-Fillol, J.; Costas, M. *Org. Lett.* **2013**, *15*, 6158. (b) Ottenbacher, R. V.; Samsonenko, D. G.; Talsi, E. P.; Bryliakov, K. P. *ACS Catal.* **2014**, *4*, 1599. (c) Dai, W.; Li, J.; Li, G.; Yang, H.; Wang, L.; Gao, S. *Org. Lett.* **2013**, *15*, 4138. (d) Wang, B.; Miao, C.; Wang, S.; Xia, C.; Sun, W. *Chem.—Eur. J.* **2012**, *18*, 6750. (e) Wang, X.; Miao, C.; Wang, S.; Xia, C.; Sun, W. *ChemCatChem* **2013**, *5*, 2489. (f) Shen, D.; Miao, C.; Wang, S.; Xia, C.; Sun, W. *Eur. J. Inorg. Chem.* **2014**, *2014*, 5777. (g) Dai, W.; Shang, S.; Chen, B.; Li, G.; Wang, L.; Ren, L.; Gao, S. *J. Org. Chem.* **2014**, *79*, 6688.

(14) (a) Gelalcha, F. G.; Bitterlich, B.; Anilkumar, G.; Tse, M. K.; Beller, M. *Angew. Chem., Int. Ed.* **2007**, *46*, 7293. (b) Niwa, T.; Nakada, M. *J. Am. Chem. Soc.* **2012**, *134*, 13538.

(15) Cussó, O.; Garcia-Bosch, I.; Ribas, X.; Lloret-Fillol, J.; Costas, M. *J. Am. Chem. Soc.* **2013**, *135*, 14871.

(16) Cussó, O.; Ribas, X.; Lloret-Fillol, J.; Costas, M. *Angew. Chem., Int. Ed.* **2015**, *54*, 2729.

(17) Castellino, A. J.; Bruice, T. C. *J. Am. Chem. Soc.* **1988**, *110*, 158.

(18) (a) Chang, S.; Galvin, J. M.; Jacobsen, E. N. *J. Am. Chem. Soc.* **1994**, *116*, 6937. (b) Zhang, W.; Lee; Lee, N. H.; Jacobsen, E. N. *J. Am. Chem. Soc.* **1994**, *116*, 425. (c) Ho, C.; Leung, W.-H.; Che, C.-M. *J. Chem. Soc., Dalton Trans.* **1991**, 2933. (d) Singh, K. K.; Tiwari, M. K.; Dhar, B. B.; Vanka, K.; Sen Gupta, S. *Inorg. Chem.* **2015**, *54*, 6112.

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