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Article

Enantioselective epoxidation of olefins with hydrogen peroxide catalyzed by bioinspired aminopyridine manganese complexes derived from L-proline

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ABSTRACT

Three chiral aminopyridine ligands derived from L-proline were prepared. Careful evaluation of the corresponding aminopyridine manganese complexes in asymmetric epoxidation of olefins revealed a broad substrate scope in the presence of 0.2 mol% manganese complex and 0.5 equiv. 2,2-dimethylbutyric acid, with aqueous hydrogen peroxide as an oxidant. A variety of olefins including styrenes, chromenes, and cinnamamides were transformed successfully into the target epoxides with moderate to excellent enantioselectivity (yield up to 95%, ee up to 99%).

1. Introduction

Metalloenzymes can promote a wide range of oxidative transformations, such as hydroxylation, epoxidation, and *cis*-dihydroxylation. Inspired by the properties of metalloenzymes, researchers have established biomimetic synthetic metal (e.g., Mn, Fe) complexes coordinated with tetradentate nitrogen (N4) ligands as excellent catalysts in oxidation reactions in the past decades [1–4]. The landmark investigations of epoxidation of olefins by biomimetic N4 metal complexes were begun in 2001 by Jacobsen and co-workers [5]. They reported that an Fe(II)(mep) complex (mep = *N*,*N*′-dimethyl-*N*,*N*′-bis(2-pyridinylmethyl)ethane-1,2-diamine) could rapidly mediate the epoxidation of aliphatic alkenes with aqueous hydrogen peroxide as the oxidant; note that acetic acid served as an important additive in the iron catalytic system. Earlier in the same year, Que and co-workers [6] first demonstrated enantioselective *cis*-dihydroxylation of olefins catalyzed by the iron complex of the aminopyridine N4 ligand. In 2003, Mn-MCP-$(OTf)_2$ [MCP = *N*,*N*-dimethyl-*N*,*N*-bis(2-pyridylmethyl) cyclohexane-*trans*-1,2-diamine] was used in the epoxidation of olefins with peracetic acid as an oxidant by Stack and co-workers; importantly, an ee of 10% was observed in the epoxidation of vinyl cyclohexane [7]. The development of novel elegant ligands is considered the key approach to obtaining highly efficient catalysts [8,9]. In this context, Costas [10–14], Talsi and Bryliakov [15–20], Gao [21,22], and our group [23–31] have developed many chiral N4 ligands, and their manganese and

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iron complexes exhibit good to excellent stereocontrol in the enantioselective epoxidation of various olefins (Scheme 1). Among them, the chiral N4 ligands derived from chiral 2,2′-bipyrrolidine play an important role in iron- or manganese-catalyzed asymmetric epoxidation of olefins (Scheme 1) [11,12,14,16–20]. However, these chiral 2,2′-bipyrrolidine skeletons are not easily available and are costly. In addition, the epoxidation catalyzed by manganese or iron complexes coordinated by these documented ligands requires a large quantity of acids as a vital additive [16,23]. It has been proposed that protonation of the hydroperoxide ligand by the coordinated carboxylic acid in metal-hydroperoxo intermediates facilitates O–O bond cleavage, generating high-valent metal-oxo species as reactive epoxidizing intermediates. Recently, Costas and co-workers reported that the quantity of carboxylic acid could be dramatically decreased to catalytic loading by including dimethylamino groups at the 4-position of the PDP ligand [Scheme 1, ^{NMe2}PDP, PDP = 2-({2-[1-(pyridin-2-ylmethyl)-pyrrolidin-2-yl]pyrrolidin-1-yl}methyl) pyridine] [12,13]. In 2012, we reported a series of facile N4 ligands (Scheme 1, *S*-PMP, *S*-PEB) derived from L-proline, which exhibited enantioselectivity comparable to those of chiral 2,2′-bipyrrolidine skeletons [28–32]. More importantly, L-proline is abundant in nature and easily transformed and diversified.

On the basis of our previous work, we hypothesized that modification of the substituents on the pyridyl groups and diamine backbone of the N4 ligand from L-proline would provide several new and practical N4 ligands. Herein, we report three structurally new aminopyridine ligands derived from L-proline and the catalytic performance of the corresponding manganese complexes in asymmetric epoxidation of a variety of olefins using aqueous hydrogen peroxide as an oxidant.

2. Experimental

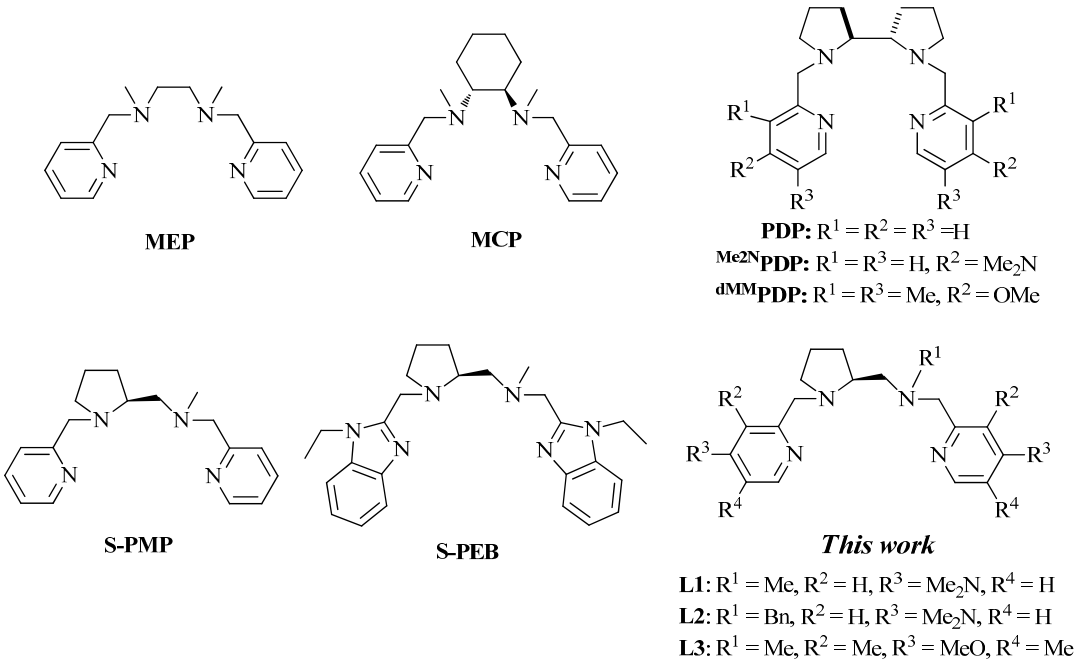
2.1. General

The starting materials were purchased from commercial suppliers and used without further purification. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance III 400 MHz spectrometer using $CDCl_3$ as the solvent with tetramethylsilane as an internal reference. Gas chromatography–mass spectrometry (GC–MS) spectra were recorded on an Agilent Technologies 7890A GC system with an Agilent 5975 inert mass-selective detector (EI) and an HP-5MS column (0.25 mm × 30 m, film: 0.25 μm). High-performance liquid chromatography (HPLC) analysis was performed on a Waters-Breeze instrument (2487 Dual λ absorbance detector and 1525 binary HPLC pump). Chiralpak OD-H, AS-H, and IC columns were purchased from Daicel Chemical Industries, Ltd. GC analysis was performed on an Agilent 6820 GC instrument with a CP-Chirasil-Dex CB column. Column chromatography was generally performed on silica gel (300–400 mesh), and thin-layer chromatography inspections were performed on silica gel GF_{254} plates.

L-proline-based diamines **1** and **2** were synthesized using a previously reported method [28,29,33].

2.2. Synthesis and characterization of ligands *L1–L3*

For **L1**, (*S*)-*N*-methyl-1-(pyrrolidin-2-yl)methanamine (**1**) (2.1 mmol) and 30 mL of dichloromethane (DCM) were added to a 100-mL round-bottom flask. Then K_2CO_3 (6 eq.) was added. Next, 2-(chloromethyl)-*N*,*N*-dimethylpyridin-4-amine (**3**) (5.0 mmol) was dissolved in 20 mL of DCM by addition through a constant-pressure dropping funnel at 0 °C. Then the mixture



Scheme 1. Tetradentate nitrogen (N4) ligands.