



Short communication

# Chiral oligomers of spiro-salenCo(III)X for catalytic asymmetric cycloaddition of epoxides with CO<sub>2</sub>



Zhouhe Zhu<sup>a,b</sup>, Yuqian Zhang<sup>a,b</sup>, Kai Wang<sup>a,b</sup>, Xiyong Fu<sup>a,b</sup>, Fengjuan Chen<sup>a,b</sup>, Huanwang Jing<sup>a,b,c,\*</sup>

<sup>a</sup> State Key Laboratory of Applied Organic Chemistry, Key Laboratory of Nonferrous Metals Chemistry and Resources Utilization, Gansu, People's Republic of China

<sup>b</sup> College of Chemistry and Chemical Engineering, Lanzhou University, 222 South Tianshui Road, Lanzhou, Gansu 730000, People's Republic of China

<sup>c</sup> State Key Laboratory of Coal Conversion, Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan 030001, People's Republic of China

## ARTICLE INFO

## Article history:

Received 29 January 2016

Received in revised form 9 April 2016

Accepted 11 April 2016

Available online 14 April 2016

## Keywords:

Asymmetric cycloaddition

Chiral oligomer catalyst

Carbon dioxide

Epoxide

Kinetic resolution

## ABSTRACT

Several new chiral oligomers of spiro-salenCo(III)X (spiro = 1.1'-spirobiindane-7,7'-diol) complexes have been designed, synthesized, and characterized by nuclear magnetic resonance (NMR), infrared (IR), and elemental analyses, in which, the chiral spiro moieties are first introduced into a scaffold of chiral salenCo catalysts. They were used to catalyze the asymmetric cycloaddition of epoxides with carbon dioxide. Under very mild reaction conditions, a kinetic resolution of racemic epoxides with CO<sub>2</sub> was smoothly initiated by these chiral oligomer catalysts with good enantioselectivities, which can be attributed to the match effect between chiral backbones of salen and spiro. High stability and easy recyclability are their major advantages.

© 2016 Elsevier B.V. All rights reserved.

## 1. Introduction

Carbon dioxide (CO<sub>2</sub>) fixation has attracted much research attention because of its relative abundance, low cost, nontoxicity, and renewability.[1–3] In the past decades, >20 reactions with CO<sub>2</sub> as a starting material have been developed. Among them, the synthesis of cyclic carbonates *via* cycloaddition of epoxides and CO<sub>2</sub> is one of the most promising strategies [4], because of its 100% atom economy. The cyclic carbonates are widely used as aprotic polar solvents, monomers, organic synthetic intermediates, and fine chemical intermediates. Chiral cyclic carbonates might be applied to produce pharmaceuticals and useful chiral organic intermediates.[5–7]

Optically pure cyclic carbonates were traditionally fabricated by chiral diols and phosgene in the presence of zinc [8–10] or palladium complexes [11]. Some chiral salenCo(III) complexes were shown to be a highly efficient catalyst for the asymmetric ring-opening and kinetic resolution of aliphatic terminal epoxides.[12–14] Efficient bifunctional chiral catalysts were also reported by our group [15,16]. Recently, Lu and coworkers have reported a new type of chiral salenCo(III) complexes as efficient catalysts for the preparation of chiral cyclic carbonates [17]. In order to investigate the effect of more chiral centers in one molecule, chiral ionic liquids were used in these reactions as

cocatalysts [18], the polymeric binol-salenCo(III) catalysts with multiple chiral centers exhibited more activity, and enantioselectivity and easy recyclability were documented by our group [19]. It is well known that the spirocyclic framework as chiral backbones is widely used in the area of asymmetric catalysis [20,21]. In this study, we report several new oligomeric spiro-based salenCo(III)X catalysts (Fig. 1) and their application to the kinetic resolution of epoxides.

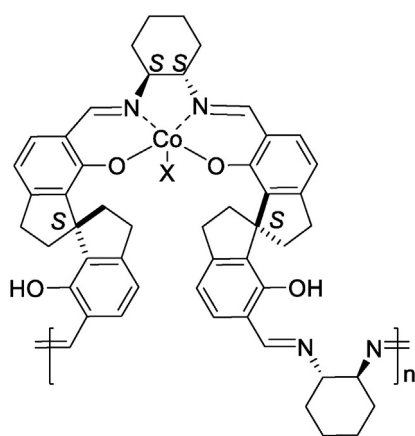
## 2. Experimental

## 2.1. General

Racemic epoxides were distilled from CaH<sub>2</sub> before use. Other commercially available chemicals and reagents were used without purification unless specified. <sup>1</sup>H and <sup>13</sup>C nuclear magnetic resonance (NMR) spectra were recorded on a Varian Mercury Plus 300-MHz spectrometer using CDCl<sub>3</sub>, DMSO-*d*<sub>6</sub>, or acetone-*d*<sub>6</sub> as the solvent and tetramethylsilane (TMS) as an internal standard. Mass spectrometry data were obtained with a HP-5988 spectrometer and ZAB-HS spectrometer. Gel permeation chromatography (GPC) was performed using a Waters 1515 chromatograph at 35 °C with tetrahydrofuran (THF) as eluent at a flow rate of 1.0 ml/min calibrated by polystyrene standards. Infrared (IR) spectra were recorded on a Fourier transform infrared (FTIR) spectrometer and reported in cm<sup>-1</sup> (%T). Gas chromatographic (GC) analyses were carried out on a Varian CP-3800 gas chromatograph equipped with a flame ionization detector (FID) using Supelco-DEX series (225) chiral columns. High-performance liquid

\* Corresponding author at: State Key Laboratory of Applied Organic Chemistry, Key Laboratory of Nonferrous Metals Chemistry and Resources Utilization, Gansu, People's Republic of China.

E-mail address: [hwjing@lzu.edu.cn](mailto:hwjing@lzu.edu.cn) (H. Jing).



(*S,S,S,S*)-ZSS-1 (*S,R,R,S*)-ZSS-2  
 (*R,S,S,R*)-ZSS-3 (*R,R,R,R*)-ZSS-4

**a** X = OAc; **b** X = CCl<sub>3</sub>CO<sub>2</sub>; **c** X = CF<sub>3</sub>CO<sub>2</sub>

Fig. 1. Configurations of chiral catalysts.

chromatography (HPLC) analyses (Daicel Chiralcel OD chiral column) were conducted on a Water 600 controller with 2996 Photodiode Array Detector.

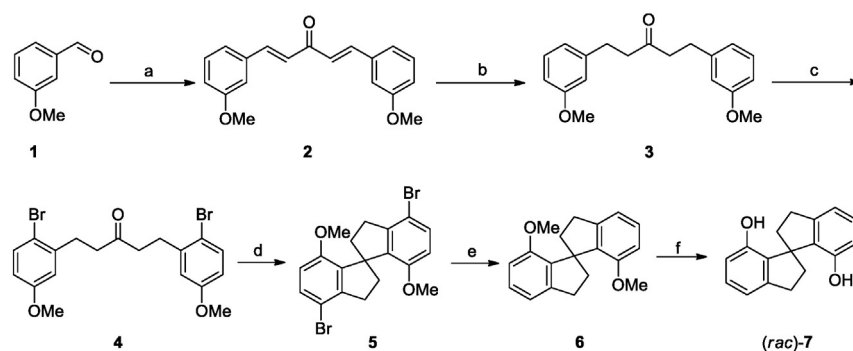
## 2.2. Synthesis of catalysts

Following the synthetic routes (Scheme 1) reported in the literature [22,23,24], compounds 2–7 were successfully produced and purified, and their fully characterized data are listed in supporting information.

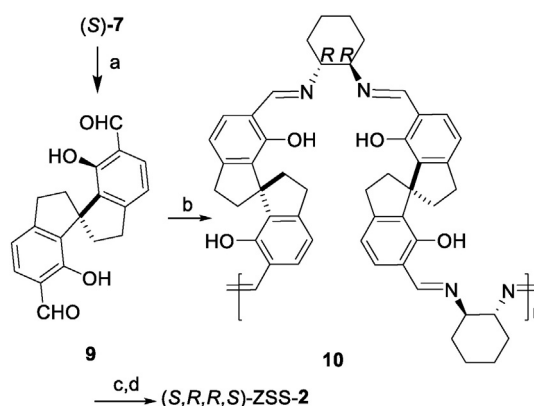
The synthetic routes for the chiral compounds 7–10 are shown in Scheme 2, and their data of characterization are listed in supporting information.

## 2.3. General procedure for coupling of epoxides with CO<sub>2</sub>

Catalyst of (*S,R,R,S*)-ZSS-2b (631 mg, 0.1 mmol), cocatalyst of tetrabutylammonium fluoride (TBAF, 0.0522 g, 0.2 mmol), and racemic propylene oxide (PO, 7 mL, 100 mmol) were introduced into a 100-mL stainless steel autoclave to form a brown solution. The reactor was purged thrice with carbon dioxide, and charged it to 0.8 MPa. Then, the asymmetric catalytic reaction took place at room temperature. After some time, the pressure in the reactor decreased to an expected value, and it was vented to terminate the reaction. After removing the unreacted epoxide, chiral cyclic carbonate (R = Me, Et, CH<sub>2</sub>Cl), weighed to calculate the yield of cyclic carbonate, was distilled under vacuum as a colorless liquid or it (R = Ph, PhOCH<sub>2</sub>) was obtained by column chromatography through a short silica gel column (ethyl acetate:petroleum ether = 5:1).



Scheme 1. Synthetic routes for *rac*-1,1'-spirobiindane-7,7'-diol: (a) acetone, NaOH, EtOH–H<sub>2</sub>O, r.t., 4 h; (b) Raney Ni, acetone, r.t., 1 atm. H<sub>2</sub>, 24 h; (c) NaBr, H<sub>2</sub>O<sub>2</sub>, HOAc, r.t.; (d) CH<sub>3</sub>SO<sub>3</sub>H, 50 °C, 12 h; (e) *n*-BuLi, THF, –78 °C, 1 h; EtOH (quench); (f) BBr<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>, –78 °C to r.t. overnight.



Scheme 2. (a) MgCl<sub>2</sub>, paraformaldehyde, Et<sub>3</sub>N, THF, 12 h, reflux; (b) (1*R*,2*R*)-(+)–1,2-diaminocyclohexane *L*-tartrate, K<sub>2</sub>CO<sub>3</sub>, water/ethanol, THF, 4 h; (c) Co(OAc)<sub>2</sub>·4H<sub>2</sub>O, CH<sub>3</sub>OH, Ar, reflux, 4 h; (d) CCl<sub>3</sub>COOH, CH<sub>2</sub>Cl<sub>2</sub>, O<sub>2</sub>, room temperature, 12 h.

## 3. Results and discussion

The synthetic routes of the new oligomeric chiral catalysts are shown in Schemes 1 and 2. Compounds 2–4 were fabricated *via* routine strategies in high yields. For synthesizing the key racemic spiro compound 5, cyclization of symmetric ketone 4 was first performed in the presence of polyphosphoric acid at 105 °C for 6 h, which led to only 20–30% yield [21]. Alternatively, when the catalyst polyphosphoric acid was replaced by MsOH, this cyclization generated 5 in 62% yield under mild reaction conditions (50 °C, 6 h) [22]. Therefore, four chiral oligomer catalysts with various absolute configurations of spiro and diaminocyclohexane were fabricated and named as (*S,S,S,S*)-ZSS-1, (*R,R,R,R*)-ZSS-4, (*S,R,R,S*)-ZSS-2, and (*R,S,S,R*)-ZSS-3. Asymmetric cycloaddition of racemic PO and CO<sub>2</sub> in the presence of the aforementioned chiral catalysts was then carefully investigated. Data in Table 1 reveal the enantioselective effects between the chirality of spiro and diaminocyclohexane. Catalysts 1a and 2a with OAc as counterion were used in this reaction with TBAF as cocatalyst (Table 1, entries 1, 6). Catalyst 2a is superior to 1a and exhibits a higher enantioselectivity (57.1% vs. 48.5% *ee* of chiral propylene carbonate, CPC). It is evident that the enantioselectivity is mainly affected by the chirality of spiro skeleton. It can also be observed that catalysts 2a (*S,R,R,S*) and 3b (*R,S,S,R*) possessing mixed chirality exhibit higher *ee* values (Table 1, entries 6 and 13, 57.1% (*S*) and 60.3% (*R*) of CPC). Catalysts 1a (*S,S,S,S*) and 4b (*R,R,R,R*) having the same absolute configurations exhibit lower *ee* values (Table 1, entries 14, 48.5% (*R*) and 50.2% (*S*) of CPC). The cocatalyst effect was also screened by using catalysts 1a and 2a (Table 1, entries 1–5, entries 6–10). The obtained reactivity order is PTAT > TBAI > TBAB > TBAC > TBAF; however, the enantioselectivity order shows an opposite trend: TBAF > TBAC > TBAB > TBAI > PTAT. The results also reveal that the anion of the cocatalyst in the binary

Download English Version:

<https://daneshyari.com/en/article/49774>

Download Persian Version:

<https://daneshyari.com/article/49774>

[Daneshyari.com](https://daneshyari.com)