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Salen manganese (III) complexes as catalysts for R-(+)-limonene oxidation

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ABSTRACT

The epoxidation of R-(+)-limonene using *in situ* generated dimethyldioxirane (DMD) as the oxidizing agent and four Jacobsen-type catalysts ((R,R)-Jacobsen, (S,S)-Jacobsen, racemic Jacobsen and achiral Jacobsen) was examined. The effect of the amount of $KHSO_5$ and acetone in the catalyzed and uncatalyzed reaction was also assessed. The main reaction products were diepoxide and endocyclic monoepoxide. In the absence of catalyst, the amount of $KHSO_5$ did not significantly influence conversion and selectivity. The catalyst can be segregated to a different phase and separated from the reaction media when the amount of $KHSO_5$ is above the stoichiometric ratio, R-(+)-limonene/$KHSO_5$ = 0.5 mmol/mmol, and acetone/mmol R-(+)-limonene = 2 mL/mmol. However, when the amount of $KHSO_5$ is below the stoichiometric ratio (R-(+)-limonene/$KHSO_5$ = 1.5 mmol/mmol) the catalyst is difficult to separate. Under the reaction conditions of this study, when the catalyst is segregated, no effect of the catalyst chiral center, (R,R)-Jacobsen or (S,S)-Jacobsen, was found on conversion and selectivity. Additionally, the (R,R)-Jacobsen's catalyst proved to be very stable to oxidative degradation.

1. Introduction

Limonene derivatives functionalized with oxygen are important intermediates in the preparation of pharmaceuticals, food additives, and agrochemicals [1]. Fig. 1 shows the main products from the oxidation of limonene which are classified in two groups. The first group comprises products from the epoxidation of the double bonds denoted as epoxides [2]. Additionally, epoxides can be classified as monoepoxides if a double bond is oxidized and diepoxides if both double bonds are oxidized. If the double bond between carbons 1 and 2 is oxidized, the monoepoxide corresponds to the endocyclic epoxide. If the double bond between carbons 8 and 9 is oxidized, the resulting monoepoxide is the exocyclic epoxide [2]. The second group corresponds to allylic oxidation products, which include carveol and carvone [2].

Due to the existence of a chiral center in the chemical structure of limonene (carbon 4, Fig. 1), this compound has two enantiomers with optical configurations R and S [3]. Orange peels are the main source of R-(+)-limonene, while lime peels mostly contain S-(−)-limonene [4]. Either limonene enantiomer has eight optically pure epoxides [4]. Fig. 2 shows the chemical structure of these epoxides and their corresponding optical configuration. It is important to note that each monoepoxide has two isomers (*cis*/*trans*) known as diastereomers. Just like any pair of enantiomers, the cyclic diasteromers *cis*/*trans* show different behavior when interacting with a biological receptor, mainly due to the orientation of the substituents [5]. This is how a diasteromer can be effective in the treatment of an illness; while its counterpart may be inactive or even produce opposite effects. For this reason, there is much interest on the development of efficient processes for obtaining optically pure epoxides [6].

The Jacobsen–Katsuki epoxidation is used in the production of optically pure epoxides [7]. The success of this method is based on the use of manganese (III)–salen complexes, as catalysts. Fig. 3 shows the chemical structure of the Jacobsen's catalyst [7]. The most common solvents used are dichloromethane and acetonitrile and the most used oxidizing agents are sodium hypochlorite, iodosylbenzene, and *meta*-chlorobenzoic acid. In spite of the satisfactory results achieved with this method (enantiomeric excess $\geq$95%), no industrial process still exists because reaction products and catalyst are in the same phase and are difficult to separate by physical–mechanical methods [8]. Therefore, various methods for the heterogenization of Jacobsen–Katsuki type catalysts have been proposed. The immobilization of the catalyst on the surface of a solid (support) by covalent chemical bond is mostly used [9]. With this method, the complete separation of the catalyst from the reaction products has been proved. However, no successful immobilization method has been established that keeps the catalytic properties of the homogeneous catalyst or the preservation of the initial catalytic activity of the immobilized catalyst [10].

It is generally recognized that the solid support prevents the geometric reception of the active catalytic species attained in a homogeneous phase, which is interpreted as a poor chiral

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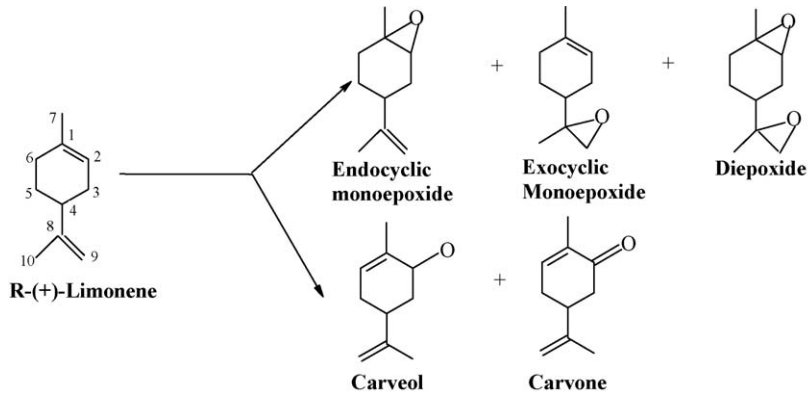

Fig. 1. Main oxygenated products from limonene.

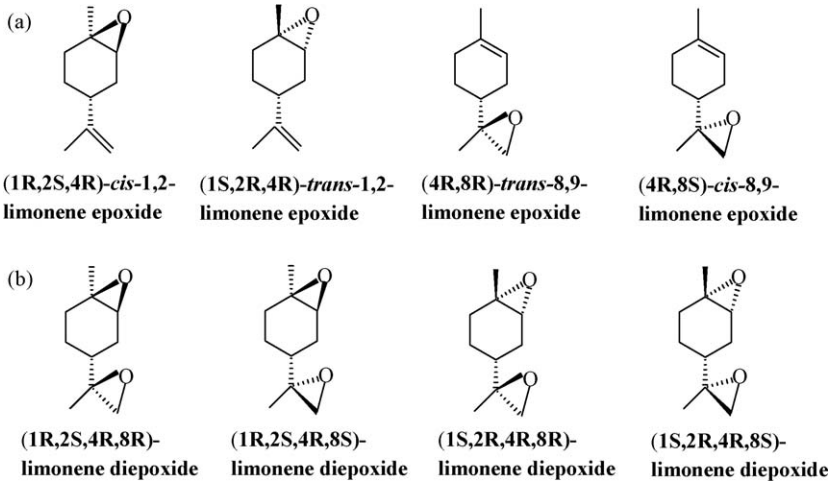

Fig. 2. Epoxides derived from R-(+)-limonene: (a) monoepoxides; (b) diepoxides.

communication between the catalyst and the olefin [11]. On the other hand, it has been established that oxidizing agents such as sodium hypochlorite and iodosylbenzene promote the deactivation of the catalyst because of the oxidative degradation of the salen ligand [11]. To overcome these difficulties, the use of dimethyldioxirane (DMD) generated *in situ* as an oxidizing agent improves the stability of the catalyst because of the moderate oxidation conditions that can be attained [12,13]. Additionally, the catalyst initially soluble in the reaction medium, can be segregated depending on reaction conditions.

In this paper we report on the asymmetric oxidation of R-(+)-limonene using *in situ* generated DMD as oxidizing agent in the

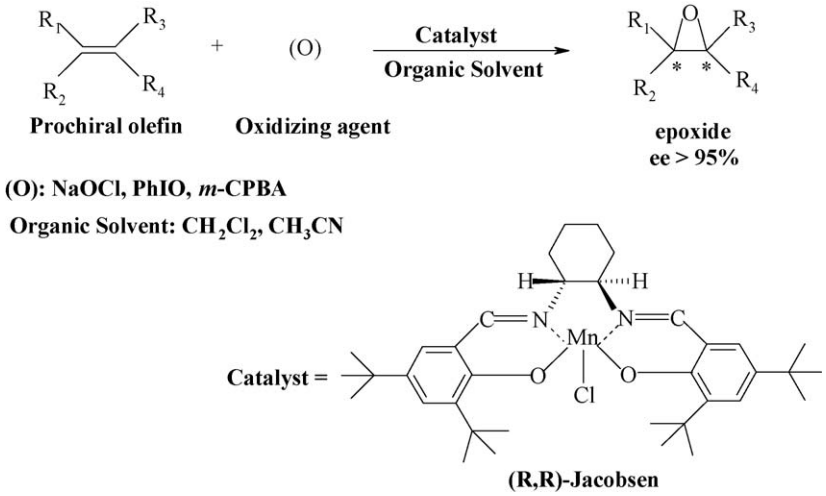

Fig. 3. Jacobsen asymmetric epoxidation.

presence of Jacobsen-type catalysts. Reaction conditions affect product selectivity as well as catalyst recoverability. The catalyst was easily recovered when the ratio R-(+)-limonene/$KHSO_5$ = 0.5 and the ratio acetone/R-(+)-limonene was 2 mL/mmol. Under these conditions, the chiral center of the catalyst did not appear to influence catalytic activity. Additionally, the catalyst was successfully reused three times suggesting improvement of catalyst stability to oxidative degradation.

2. Experimental

2.1. Catalyst synthesis

2.1.1. Preparation of (R,R)-Jacobsen's catalyst

The preparation of this catalyst is divided into three steps [14]. The first step is the racemic resolution of the optically active amine. In the second step, the amine previously obtained reacts with 3,5-di-tert-butyl-2-hidroxy-benzaldehyde to form the salen ligand. In the last step, the salen ligand is treated with a manganese source under an oxidizing atmosphere to produce (R,R)-Jacobsen's catalyst. The synthesis procedure is illustrated in Fig. 4.

The resolution of the optically active amine ((R,R)-1,2-diaminocyclohexane L-(+)-tartrate) was obtained by the following procedure. 150 g of L-(+)-tartaric acid and 400 mL of distilled water were mixed in a beaker with continuous stirring at room temperature until complete dissolution. Next, 240 mL of a mixture of *cis*/*trans* 1,2-diaminocyclohexane was added at a speed such that the reaction temperature did not exceed 70 °C. Then, 100 mL of glacial acetic acid was added at a speed such that the reaction temperature did not exceed 90 °C. After the addition of acetic acid, a white precipitate formed. This mixture was stirred vigorously for 2 h without heating. Then, the precipitate was filtered, washed with 100 mL of water at 5 °C and with 100 mL of methanol for about five times. Next, the solid was dried, first in flowing air for 1 h and then under vacuum at 40 °C.

The salen ligand ((R,R)-Jacobsen's ligand) was obtained as follows. In a 100 mL round-bottom vessel 1.11 g of (R,R)-1,2-diaminocyclohexane mono-(+)-tartrate, 1.16 g of potassium carbonate and 6.0 mL of water was added. The resulting mixture was magnetically stirred until complete dissolution. Then, 22 mL of ethanol was added and the turbid mixture heated under reflux. Next, a solution of 2.0 g of 3,5-di-tert-butyl-2-hidroxy-benzaldehyde dissolved in 10 mL of ethanol was added through the condenser with a Pasteur pipette, and the pipette and the beaker rinsed with 2.0 mL of hot ethanol. After heating under reflux for 1 h, 6 mL of water was added, the mixture allowed to cool and then introduced into an ice bath for 30 min. The yellow solid was recovered by filtration and washed with 5 mL of ethanol. This solid was dissolved in 25 mL of dichloromethane and the solution washed twice with 5 mL of water followed by 5 mL of a saturated saline solution. The organic layer was dried with sodium sulfate and the solvent removed by rotary evaporation to obtain a purified yellow solid.

Finally, the (R,R)-Jacobsen's catalyst was prepared as follows: 1.0 g of (R,R)-Jacobsen's ligand and 25 mL of absolute ethanol was added to a 100 mL round-bottom vessel. After heating and magnetically stirring this mixture under reflux (105 °C) for 20 min, 2.0 equiv. of $Mn(OAc)_2{\cdot}4H_2O$ was added and the reflux continued for 30 min. Afterwards, a low flow of air was bubbled through the reaction mixture for 1 h in order to oxidize Mn^{2+} to Mn^{3+}. Then, 3 equiv. of LiCl was added to neutralize the organometallic cationic complex. After heating and stirring for 30 additional minutes, the solvent was removed by rotary evaporation. The product was dissolved in 25 mL of dichloro-

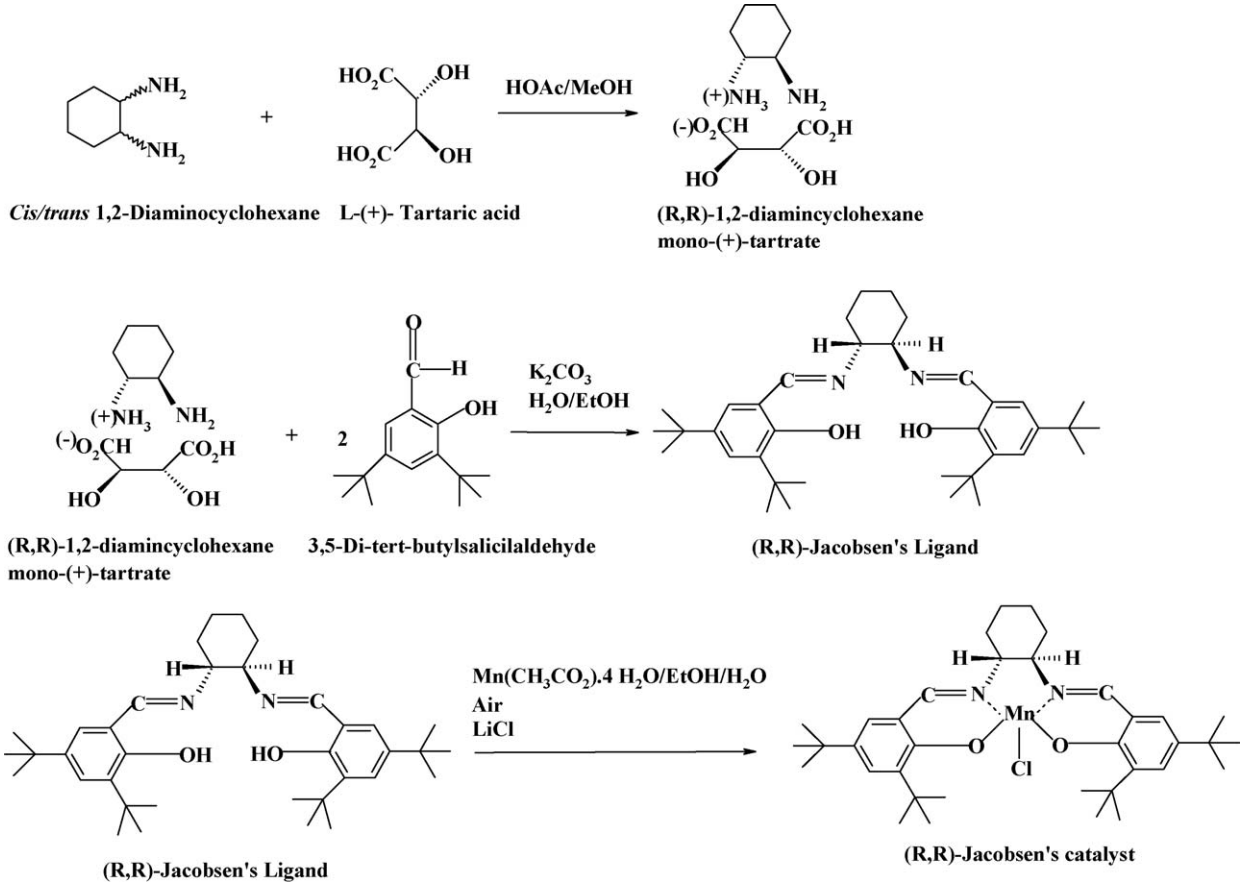

Fig. 4. Preparation of (R,R)-Jacobsen's catalyst.

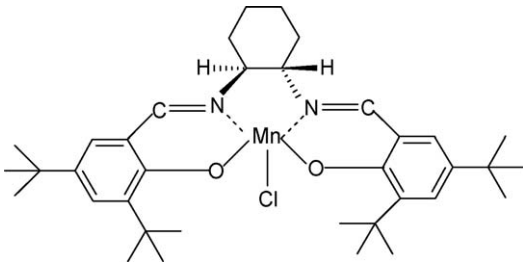

Fig. 5. Chemical structure of (S,S)-Jacobsen's catalyst.

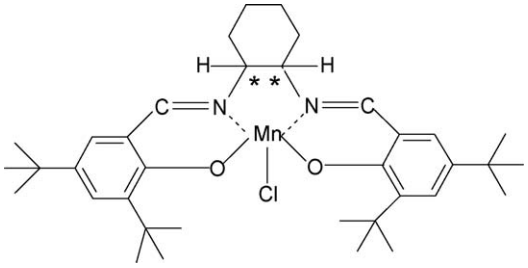

Fig. 6. Chemical structure of Jacobsen's racemic catalyst.

methane, washed twice with water, and once with a saturated saline solution. After drying the organic phase with sodium sulfate, 30 mL of heptane was added as the crystallization solvent. Dichloromethane was removed by rotary evaporation and the brown-colored mixture cooled in an ice bath for 30 min, to obtain the (R,R)-Jacobsen's catalyst.

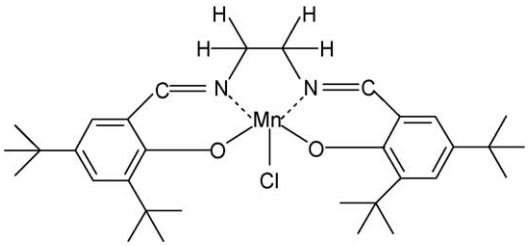

Fig. 7. Chemical structure of Jacobsen's achiral catalyst.

2.1.2. Preparation of (S,S)-Jacobsen's catalyst

The (S,S)-Jacobsen's catalyst and (S,S)-Jacobsen's ligand were prepared following the same procedure described above, but D-(−)-tartaric acid was used instead of L-(+)-tartaric acid. Fig. 5 shows the chemical structure of the (S,S)-Jacobsen's catalyst.

2.1.3. Preparation of the Jacobsen's racemic catalyst

The Jacobsen's racemic catalyst and Jacobsen's racemic ligand were prepared following a procedure similar to that of the pure enantiomeric catalyst but, the first step was not performed. Fig. 6 shows the chemical structure of the Jacobsen's racemic catalyst.

2.1.4. Preparation of Jacobsen's achiral catalyst

Jacobsen's achiral catalyst and Jacobsen's achiral ligand were prepared following a procedure similar to that used for the Jacobsen's racemic catalyst. In this case, 1,2-diaminoethane was used instead of 1,2-diaminocylohexane. Fig. 7 shows the chemical structure of the Jacobsen's achiral catalyst.

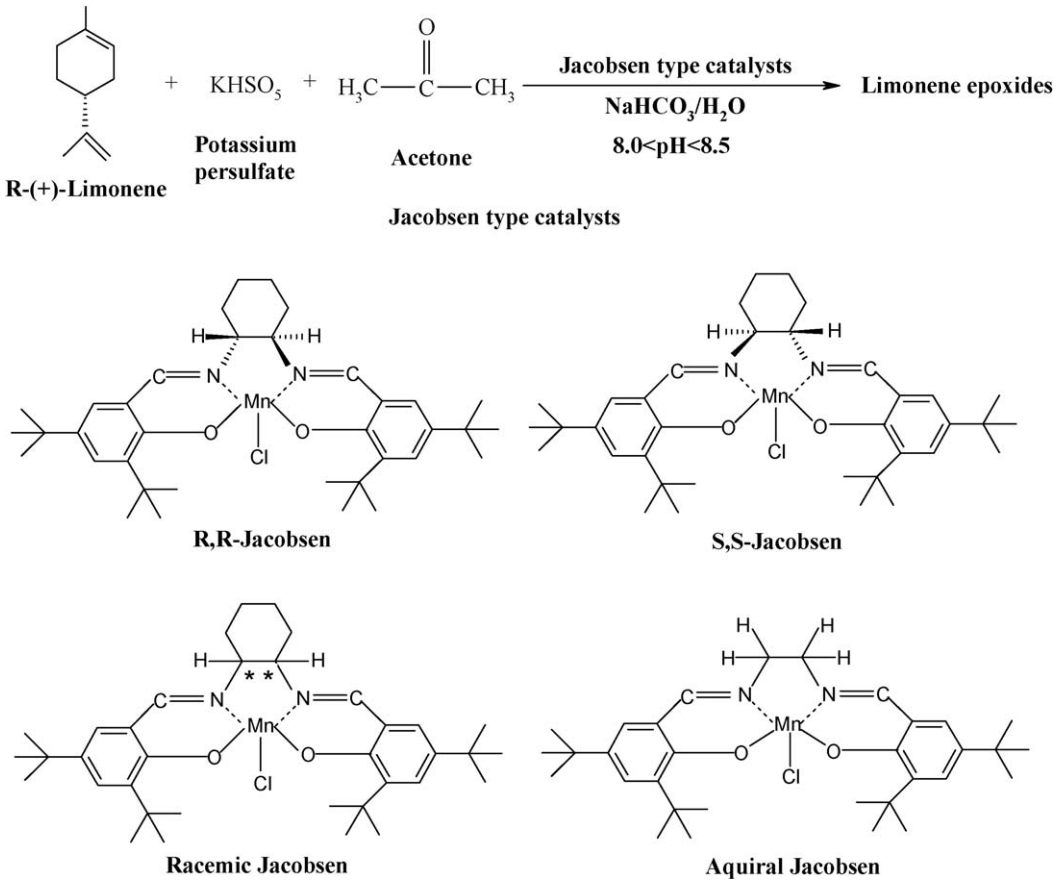

Fig. 8. Asymmetric oxidation of R-(+)-limonene with Jacobsen-type catalysts.

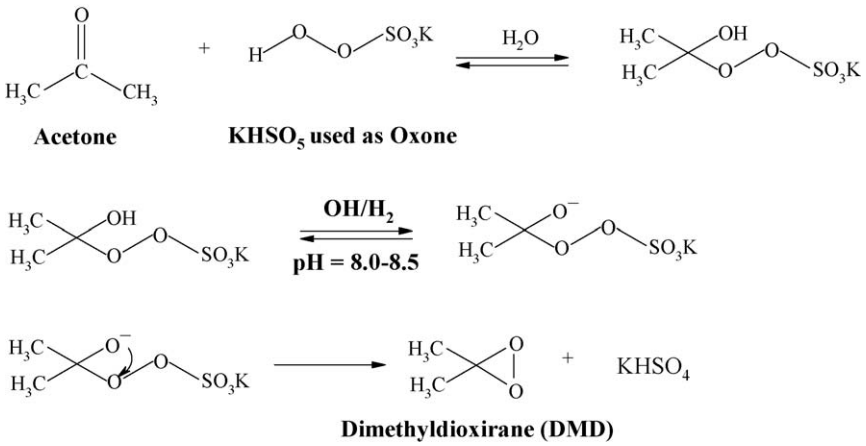

Fig. 9. *In situ* formation of DMD from $KHSO_5$ and acetone [15].

2.2. Catalyst characterization

Catalyst samples were characterized by infrared spectroscopy in a FT-IR Nicolet Avatar 330 equipped with a dispersion cell. Samples were diluted with potassium bromide to obtain a solid mixture of approximately 3% (w/w). The spectra were registered in the aromatic region 1200–1800 cm^{-1}. UV–vis spectra were recorded in the range 200–700 nm in a Lamda 4B PerkinElmer spectrophotometer equipped with a diffuse reflectance attachment, using $BaSO_4$ as reference. Differential thermogravimetric analysis (DTA) curves were obtained on a TGA 2950 thermal analyzer. Samples were heated from room temperature up to 700 °C under flowing air using alumina sample holders. The sample weight was ca. 10 mg and the heating rate was 5 °C/min. A reference sample holder contained alumina. The bulk Mn content was determined by atomic absorption spectroscopy (AAS) in a Model S4 Thermo Electron Corporation spectrometer. Typically one sample of 20 mg of solid, previously dried at 100 °C, was mixed with 2 cm^3 of HF and 2 cm^3 of aqua regia. Finally, the sample was adjusted to a known volume (100 mL) with deionized water.

2.3. Catalytic tests

The catalytic activity of the synthesized catalysts was examined on the asymmetric oxidation of R-(+)-limonene using *in situ* generated dimethyldioxirane (DMD) as the oxidizing agent. The pH control during the catalytic tests is important since the formation of DMD by reaction between acetone and $KHSO_5$ takes place in a narrow pH range (8.0–8.5). pH measurements were performed with a Metrohom 691 pH meter. Reproducibility of the pH measurements was assured by calibrating the pH meter before measurements, using standard buffer solution of pH 4.0 and 7.0. In a standard procedure, 2.0 mmol of R-(+)-limonene, 1.2 mmol of sodium bicarbonate and 0.05 mmol of catalyst were dissolved in the required amount of acetone (mixture A). The pH was difficult to measure due to the organic nature of this liquid mixture. For this reason, a buffer solution (aqueous $NaHCO_3$, 5 wt.%) was added to bring the pH in the range between 8.0 and 8.5. In another vessel, the required amount of $KHSO_5$ (Oxone®) was dissolved in 4–8 mL of water (mixture B). While mixture A was being stirred, mixture B was slowly added, keeping the pH in the range 8.0–8.5 using $NaHCO_3$ solution (5% (w/w) aqueous). When mixture B was completely added, stirring was stopped and the formed solids separated by filtration and/or centrifugation. In homogeneous phase experiments, 30 mL of dichloromethane was added to the reaction mixture obtaining two phases. The aqueous phase was discarded and the organic phase was vacuum distilled (160 °C and 0.08 MPa) in order to separate the catalyst from the reaction products. When the catalyst was recoverable (Fig. 16b), the solid and liquid phases were separated by filtration and/or centrifugation. The solid was washed with large amounts of deionized water in order to remove inorganic salts produced from Oxone® and buffer solution. In both cases, the liquid mixture free of catalyst was concentrated under vacuum and the reaction products analyzed in a gas chromatograph coupled to a mass spectrometer (Agilent Technologies 5975C GC–MS), and equipped with a FID and a capillary column Beta-dex GTA (60 m length, 250 μm internal diameter and 0.25 μm film thickness). The reactions involved are illustrated in Fig. 8. The *in situ* formation of DMD from the reaction between $KHSO_5$ and acetone in a slightly basic medium [15] is illustrated in Fig. 9.

3. Results and discussion

3.1. Catalyst characterization

Fig. 10 shows the FT-IR spectra of the salen ligands and their corresponding catalysts. The salen ligands show a characteristic band around 1640 cm^{-1}, which is associated with the vibrations of the imine group (HC=N) [16]. In the catalyst samples, this band is displaced towards a lower wavelength (1620 cm^{-1}) as the first evidence of the formation of the organometallic complex. Additionally, characteristic bands at 1540 (C–O), 575 (Mn–O)

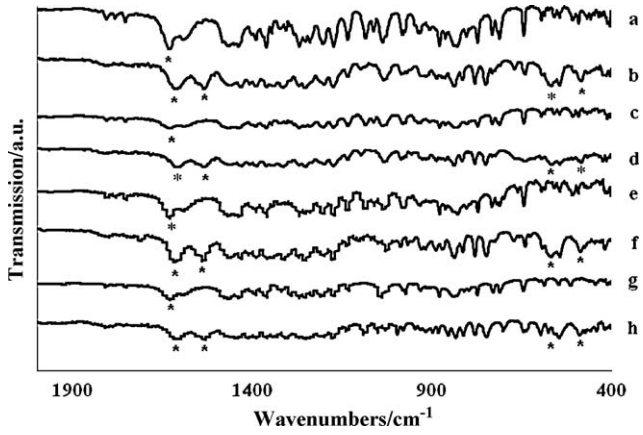

Fig. 10. FT-IR spectra of (R,R)-Jacobsen's ligand (a), (R,R)-Jacobsen's catalyst (b), (S,S)-Jacobsen's ligand (c), (S,S)-Jacobsen's catalyst (d), Jacobsen's racemic ligand (e), Jacobsen's racemic catalyst (f), Jacobsen's achiral ligand (g) and Jacobsen's achiral catalyst (h).

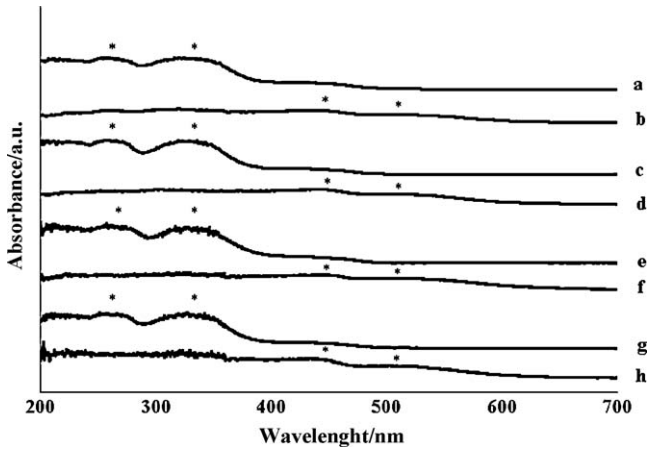

Fig. 11. DR UV–vis spectra of (R,R)-Jacobsen's ligand (a), (R,R)-Jacobsen's catalyst (b), (S,S)-Jacobsen's ligand (c), (S,S)-Jacobsen's catalyst (d), Jacobsen's racemic ligand (e), Jacobsen's racemic catalyst (f), Jacobsen's achiral ligand (g) and Jacobsen's achiral catalyst (h).

and 492 cm^{-1} (Mn–N) are also associated with the complexation of manganese by the salen ligand [16].

Fig. 11 shows DR UV–vis spectra of the salen ligands and their corresponding catalysts. The salen ligands exhibit absorption bands at 265 nm and 335 nm. These bands are attributed to $\pi \rightarrow \pi^*$ transitions. The band at 265 nm has been assigned to the benzene ring and the one at 335 nm, to the imino groups [17]. The imino $\pi \rightarrow \pi^*$ transitions in the Mn salen complexes is shifted to larger wavelengths due to metal coordination, confirming the formation of Mn(III)–salen complex [17]. UV–Vis and FT-IR spectra revealed that the salen ligands are unaffected and are not decomposed upon coordination of the organo-funtional groups with manganese.

Thermogravimetric analysis (TGA–DTA) has been used to monitor the decomposition profiles of all materials and to evaluate the ligand loading of Mn(III)–salen complexes. The DTA curves of Jacobsen's achiral ligand and Jacobsen's achiral catalyst materials are shown in Fig. 12. The salen ligand exhibits one main step of weight loss when heated under flowing air [18]. The main weight loss (ca. 93.1%) centers at 290 °C. DTA profile indicates that the Jacobsen's achiral ligand is thermally stable up to about 170 °C. The DTA profiles of the other three ligands are similar to that shown for the Jacobsen's achiral ligand. On the other hand, the Jacobsen's achiral catalyst is apparently stable up to about 280 °C. The enhanced thermal stability of the Jacobsen's achiral catalyst can be assigned to the complexation of the salen ligand with manganese [18]. The DTA curves of the other three Mn(III)–salen complexes are similar to that of the Jacobsen's achiral catalyst. Overall, the decomposition profiles of Mn(III)–salen complexes are completed at about 550 °C with the residues amounting to manganese oxides.

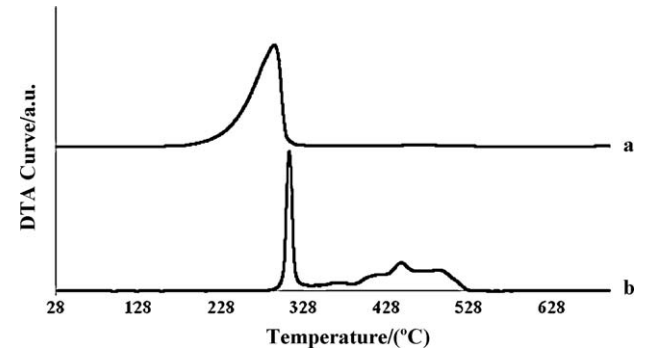

Fig. 12. DTA curves of Jacobsen's achiral ligand (a) and Jacobsen's achiral catalyst (b).

Table 1
Chemical and thermal analysis of Jacobsen catalysts.

Catalyst	Mn loading[a] (wt.%)	Ligand loading[b] (wt.%)	Mn/ligand[c]
(R,R)-Jacobsen	7.5	76	0.98
(S,S)-Jacobsen	7.9	80	0.98
Jacobsen racemic	7.9	81	0.96
Jacobsen achiral	9.0	81	0.94

[a] Determined by AAS.
[b] Determined by TGA–DTA.
[c] Molar ratio.

Table 1 collects the salen ligand loading of the four Mn(III)–salen complexes.

The manganese contents of the Mn(III)–salen complexes are summarized in Table 1. The Mn loadings are in the range 7.5–9.0 wt.% Mn elemental analysis of the Mn(III)–salen complexes in combination with TGA–DTA suggests that neither free ligand nor free manganese appear to be present in the samples, because the Mn/ligand molar ratio is close to 1.

3.2. Catalytic activity

The choice of oxygen donor and solvent is crucial in the catalytic oxidation of olefins. It is known that the best solvents for the Jacobsen epoxidation are: dichloromethane, acetonitrile and toluene when NaOCl, PhIO and *m*-CPBA are used as oxidizing agents [8]. However, the use of these oxidizing agents leads to the oxidative degradation of the catalyst [8]. On the other hand, the formation of *in situ* dioxiranes requires a ketone derivative. In the case of *in situ* DMD, acetone is used [15]. We conducted the test reaction using dichloromethane, acetonitrile, toluene and equimolar mixtures of these together with $KHSO_5$ as oxygen source, but the reaction was poor and the catalyst was degraded by action of $KHSO_5$. In contrast, when acetone is used, $KHSO_5$ does not act as oxidizing agent. Instead, $KHSO_5$ reacts with acetone in a slightly basic medium to give DMD (Fig. 9). Thus, DMD as oxidizing agent delivers the active oxygen towards the metal center of the catalyst to give oxo-manganese (V) moieties and then it transfers the atomic oxygen to the olefinic double bond. Therefore, $KHSO_5$ deactivates the catalyst when it acts as oxidizing agent. On the other hand, DMD improves catalyst stability. This finding can be explained by the following two facts. First, DMD reacts with the catalyst as it is formed so its life time is short. Second, $KHSO_5$ reacts preferentially with acetone instead of the catalyst.

The asymmetric oxidation of R-(+)-limonene using *in situ* generated DMD was first examined in the absence of catalyst. Fig. 11 shows the results for two different ratios of $KHSO_5$; below the stoichiometric amount (R-(+)-limonene/$KHSO_5$ = 1.5) and above the stoichiometric amount (R-(+)-limonene/$KHSO_5$ = 0.5). In these experiments, the acetone/R-(+)-limonene ratio was maintained at 2 mL/mmol. As can be observed in Fig. 13 in the absence of catalyst there is a moderate conversion of R-(+)-limonene. Diepoxides were the main reaction products and endocyclic monoepoxides were the secondary products. No exocyclic epoxides were detected. Fig. 13 also suggests that there is no significant effect of the amount of $KHSO_5$ on reaction parameters when the reaction occurs without catalyst.

Fig. 14 shows the effect of acetone/R-(+)-limonene ratio on the oxidation of R-(+)-limonene using *in situ* generated DMD in the absence of catalyst. In these experiments, the ratio of R-(+)-limonene/$KHSO_5$ was kept at 0.5. As can be observed in Fig. 14, conversion and selectivity to diepoxides slightly improved when the acetone/R-(+)-limonene ratio was 10 mL/mmol instead of 2 mL/mmol. Acetone contributes to DMD formation (see Fig. 9), which act as oxidizing agent. At the same time, acetone favors the

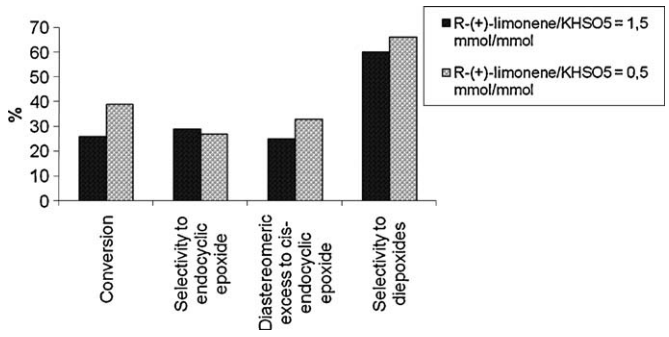

Fig. 13. The effect of the amount of $KHSO_5$ on the oxidation of R-(+)-limonene using *in situ* generated DMD in the absence of catalyst. Reaction conditions: R-(+)-limonene = 2.0 mmol; $NaHCO_3$ = 1.2 mmol; catalyst = 0.05 mmol; acetone = 4.0 mL; H_2O = 4 mL; room temperature; pH ~ 8.0–8.5; reaction time ~ 20–25 min.

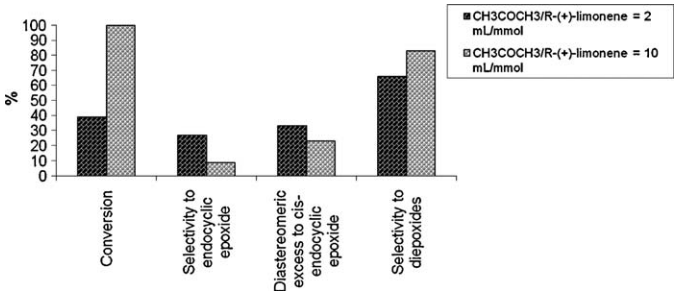

Fig. 14. Effect of the amount of acetone on the oxidation of R-(+)-limonene using *in situ* generated DMD in the absence of catalyst. Reaction conditions: R-(+)-limonene = 2.0 mmol; $KHSO_5$ = 4 mmol; $NaHCO_3$ = 1.2 mmol; catalyst = 0.05 mmol; H_2O = 4 mL; room temperature; pH ~ 8.0–8.5; reaction time ~ 20–25 min.

interaction between DMD and R-(+)-limonene in the organic phase.

Fig. 15 shows the effect of the amount of $KHSO_5$ on the oxidation of R-(+)-limonene in the presence of the (R,R)-Jacobsen's catalyst. In these experiments, we used acetone/R-(+)-limonene = 2 mL/mmol. Similarly to the reaction without catalyst, there is no significant effect of the amount of $KHSO_5$ on conversion and selectivity to diepoxides. The best selectivity towards diepoxides (90%) was reached when the stoichiometric ratio R-(+)-limonene/$KHSO_5$ = 1 was used; above this value the selectivity did not further improve. A total conversion of the R-(+)-limonene (100%) was reached with the (R,R)-Jacobsen's catalyst when R-(+)-limonene/$KHSO_5$ = 0.5, while in the absence of catalyst 38% conversion was

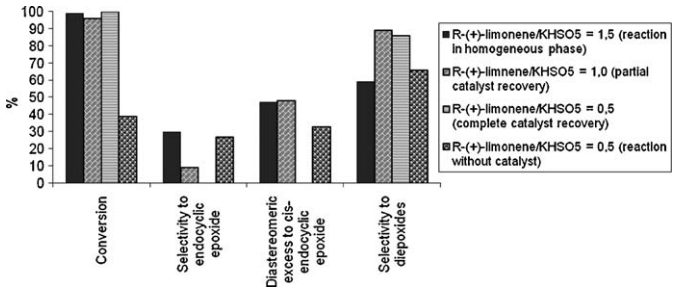

Fig. 15. Effect of the amount of $KHSO_5$ on the catalytic activity of (R,R)-Jacobsen's catalyst. Reaction conditions: R-(+)-limonene = 2.0 mmol; $NaHCO_3$ = 1.2 mmol; catalyst = 0.05 mmol; acetone = 4 mL; H_2O = 4 mL; room temperature; pH ~ 8.0–8.5; reaction time ~ 20–25 min.

obtained. Besides, diepoxide selectivity increased by 22%. A very important result from these experiments was the total recovery of the catalyst, which was favored by increasing the amount of $KHSO_5$. This way, when an amount of $KHSO_5$ below the stoichiometric ratio was used (R-(+)-limonene/$KHSO_5$ = 1.5), the catalyst and the reaction products remained in the same phase, i.e. homogenous catalysis (Fig. 16a). In this case the reaction products and the catalyst cannot be separated by physical–mechanical methods, so it was necessary to use a vacuum distillation process in order to separate the catalyst. When the stoichiometric ratio (R-(+)-limonene/$KHSO_5$ = 1.0) was used there was a partial distribution of the catalyst between the solid and liquid phases, which was entitled as partial recovery of the catalyst. Above the stoichiometric ratio (R-(+)-limonene/$KHSO_5$ = 0.5), total recovery of the catalyst was achieved (Fig. 16b). In this case, the catalyst is present in the solid phase (brown color), which also contains inorganic salts coming from the oxygen source and the buffer solution. These salts are easily removed from the solid phase by washing with enough water. After this, the catalyst was dried in flowing air at 60 °C and reused.

Fig. 16 shows pictures of the homogeneous and heterogeneous systems. In the homogeneous system, both the catalyst and the reaction products coexist in the upper phase. The bottom phase is primarily composed of water. The photograph on the right side corresponds to reaction conditions where the catalyst is recoverable. Here a solid phase that adheres to the walls of the tube can be observed, as well as a liquid phase. The solid phase was composed of catalyst and inorganic salts that accompany the process, while the liquid phase contains the reaction products. This was determined by extraction, vacuum distillation, and chromatographic analysis. The catalyst can be recovered from the solid phase by washing it with abundant water to remove inorganic salts.

Fig. 16. (a) Catalyst in homogeneous phase; (b) recoverable catalyst in heterogeneous phase.

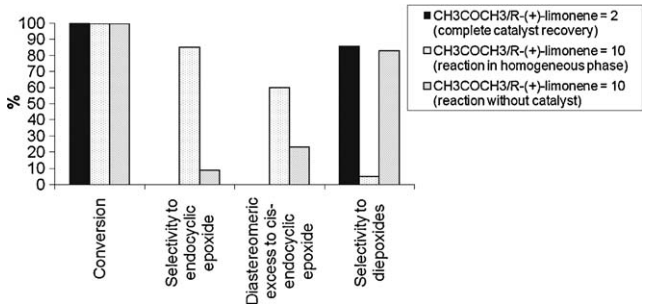

Fig. 17. Effect of the amount of acetone on the catalytic activity of (R,R)-Jacobsen's catalyst. Reaction conditions: R-(+)-limonene = 2.0 mmol; $KHSO_5$ = 4 mmol; $NaHCO_3$ = 1.2 mmol; catalyst = 0.05 mmol; H_2O = 4 mL; room temperature; pH ~ 8.0–8.5; reaction time ~ 20–25 min.

The effect of the amount of acetone on the oxidation of R-(+)-limonene in the presence of the (R,R)-Jacobsen's catalyst was also examined. In these experiments, the ratio of $KHSO_5$ was above stoichiometry, i.e. R-(+)-limonene/$KHSO_5$ = 0.5. Fig. 17 shows almost complete conversion when either amount of acetone was used. However, the selectivity was different. Selectivity to diepoxides was 86% when the ratio of acetone/R-(+)-limonene = 2 mL/mmol while the endocyclic monoepoxide was obtained (85% selectivity) when the ratio of acetone/R-(+)-limonene = 10 mL/mmol. Comparing the catalyzed and un-catalyzed reaction using the same ratio of acetone/R-(+)-limonene (10 mL/mmol) it can be seen that the presence of the catalyst favors the endocyclic monoepoxide with a diasteromeric excess of 58% for the *cis*-epoxide. In the absence of catalyst diepoxides were the main products. Also, in these experiments the recovery of the catalyst was dependent on the amount of acetone. The catalyst was totally recovered when acetone/R-(+)-limonene = 2 mL/mmol. On the other hand, when acetone/R-(+)-limonene = 10 mL/mmol the catalyst and reaction products remained in the same phase.

The oxidation of R-(+)-limonene using the (R,R)Jacobsen's catalyst, (S,S)-Jacobsen's catalyst, Jacobsen's racemic catalyst, and Jacobsen's achiral catalyst at reaction conditions under which the catalyst was recoverable (R-(+)-limonene/$KHSO_5$ = 0.5 mmol/mmol and CH_3COCH_3/R-(+)-limonene = 2 mL/mmol) are shown in Fig. 18. As can be seen in Fig. 18, similar conversion and selectivity to diepoxide were observed with tested catalysts suggesting that the chiral center of the enantiomerically pure catalysts ((R,R) and (S,S)-Jacobsen) appear to have little or no influence on conversion and selectivity to diepoxide; rather the state of coordination given by the salen ligand to the manganese appears to be crucial [19]. Here, the contribution of the catalyst is proven once again by an increase of R-(+)-limonene conversion but

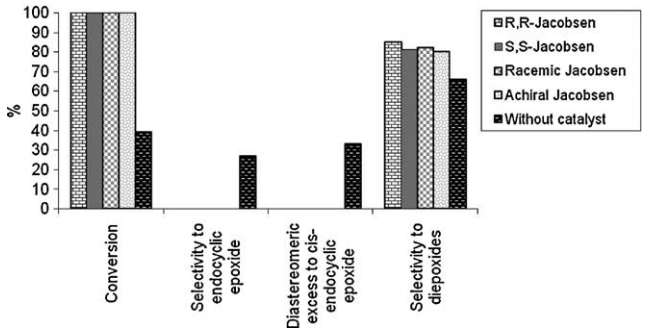

Fig. 18. Effect of the catalysts' chirality on the catalytic activity. Reaction conditions: R-(+)-limonene = 2.0 mmol; $KHSO_5$ = 4 mmol; $NaHCO_3$ = 1.2 mmol; catalyst = 0.05 mmol; acetone = 4 mL; H_2O = 4 mL; room temperature; pH ~ 8.0–8.5; reaction time ~ 20–25 min.

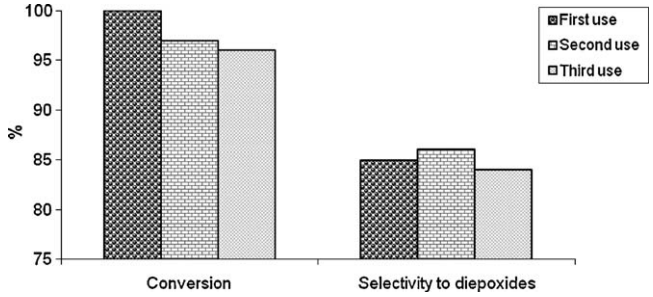

Fig. 19. Reuse of (R,R)-Jacobsen's catalyst.

the main product is the diepoxide. In the absence of catalyst, monoepoxide was also obtained with a poor selectivity (28%) and a poor diasteromeric excess (35%).

Finally, the reuse of (R,R)-Jacobsen's catalyst was investigated at reaction conditions under which the catalyst was recoverable. As can be observed in Fig. 19 the catalyst experienced a slight decrease in conversion through three consecutive runs. However, the high level of conversion remained. On the other hand, the obtained selectivity values are close to the initial selectivity. Given that the percent recovery of catalyst varied between 85 and 90%, the slight loss of catalytic activity is mainly associated with the physical loss of the catalyst during the recovery process. These results indicate the good stability of the catalyst towards the oxidative degradation.

We recently reported that using *in situ* generated dimetildioxyrane (DMD) as oxidizing agent the catalyst is stable to the oxidative degradation [20]. By FT-IR and DR UV–vis it was demonstrated that the chemical structure of the catalyst was retained after reusing it [20]. In the present work, the lack of demetalation is proved by AAS since no Mn is detected in the solid-free liquid phase (Fig. 16b). This fact makes unlikely the occurrence of the hydrolysis. It is well known that the salycilidene imine group is prone to undergo acid-catalyzed hydrolysis, reverting to the corresponding salicylaldehyde and diamine in the presence of water [11]. However, the stability of the salycilidene imine group increases considerably upon coordination with a manganese ion and formation of the Mn(III)–salen complex [11]. Therefore, in contrast to the ligand salen, the Mn(III)–salen complex can be used in wet solvents or even in aqueous media without undergoing hydrolysis.

4. Conclusions

The main conclusions from this work are:

1. Under the studied conditions, diepoxides and endocyclic monoepoxides are the main products of the oxidation of R-(+)-limonene using *in situ* generated DMD as the oxidizing agent.
2. In the presence of the Jacobsen-type catalysts, the R-(+)-limonene/$KHSO_5$ and CH_3COCH_3/R-(+)-limonene ratios affect the selectivity and recovery of the catalyst. In this way, the selectivity towards diepoxides and the total recovery of the catalyst is favored above the stoichiometric ratio of R-(+)-limonene/$KHSO_5$. On the other hand, the increase of the amount of acetone favors the selectivity towards the endocyclic epoxide and the diasteromeric excess of the endocyclic *cis*-epoxide. However, under these conditions catalyst is not recoverable. In contrast, decreasing the amount of acetone favors the selectivity towards diepoxides and catalyst recovery.
3. No effect of catalyst chirality on the catalytic activity was found. Therefore, the origin of the activity of these catalysts is mostly

associated with the high coordination state of the manganese instead of the chiral center of the salen ligand.
4. The (R,R)-Jacobsen's catalyst exhibited good stability to oxidative degradation.

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