

# Mn(III)-salen complexes in the one-pot catalytic epoxidation/carboxylation of styrene in scCO<sub>2</sub>

G. Morales, X. Delgado and L. A. Galeano\*

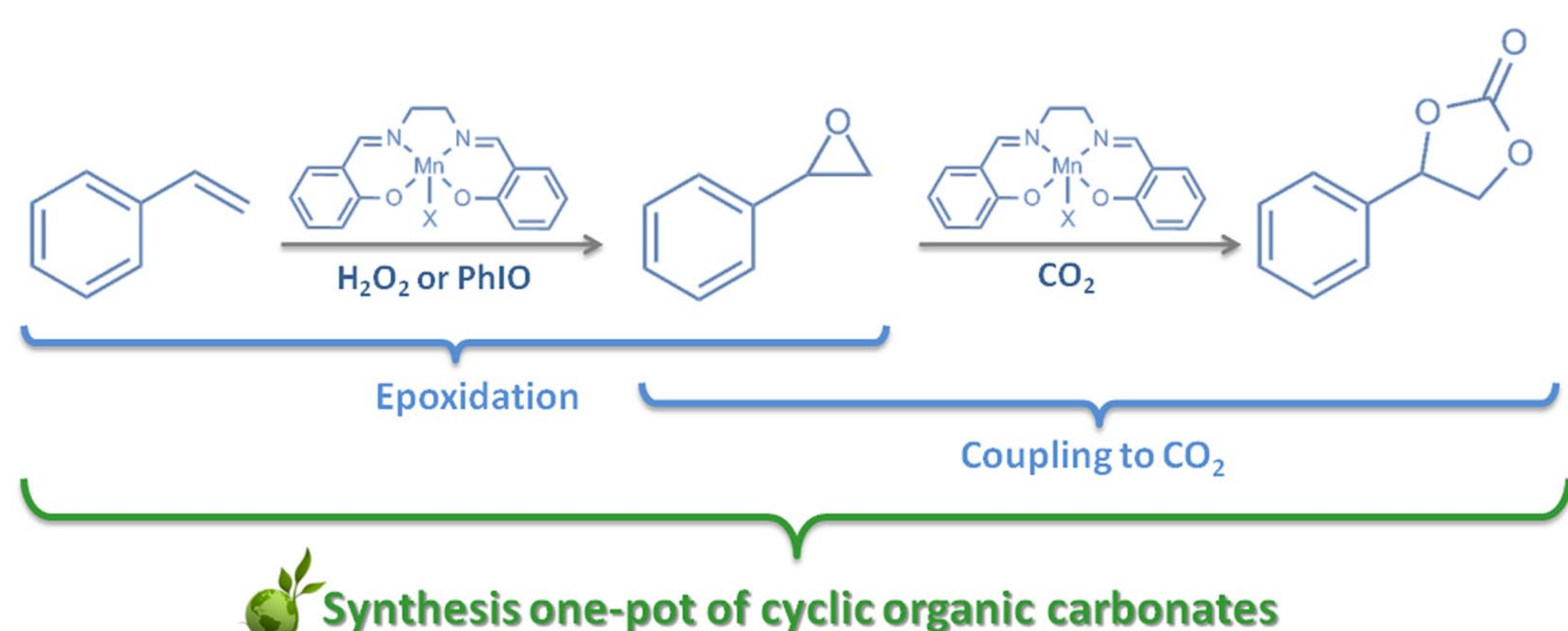
Research Group on Functional Materials and Catalysis-Department of Chemistry, University of Nariño. Pasto – Colombia



## 1. Introduction

The CO<sub>2</sub> is very attractive to be used as solvent or raw material in chemical synthesis; it is safe, harmless, nonflammable, abundant and inexpensive. Furthermore, as supercritical fluid can be used under relatively mild conditions of temperature and pressure (36.7 °C and 7.37 MPa). Thus, CO<sub>2</sub> can potentially replace other dangerous toxic and reactive gases, such as phosgene and carbon monoxide [1-2].

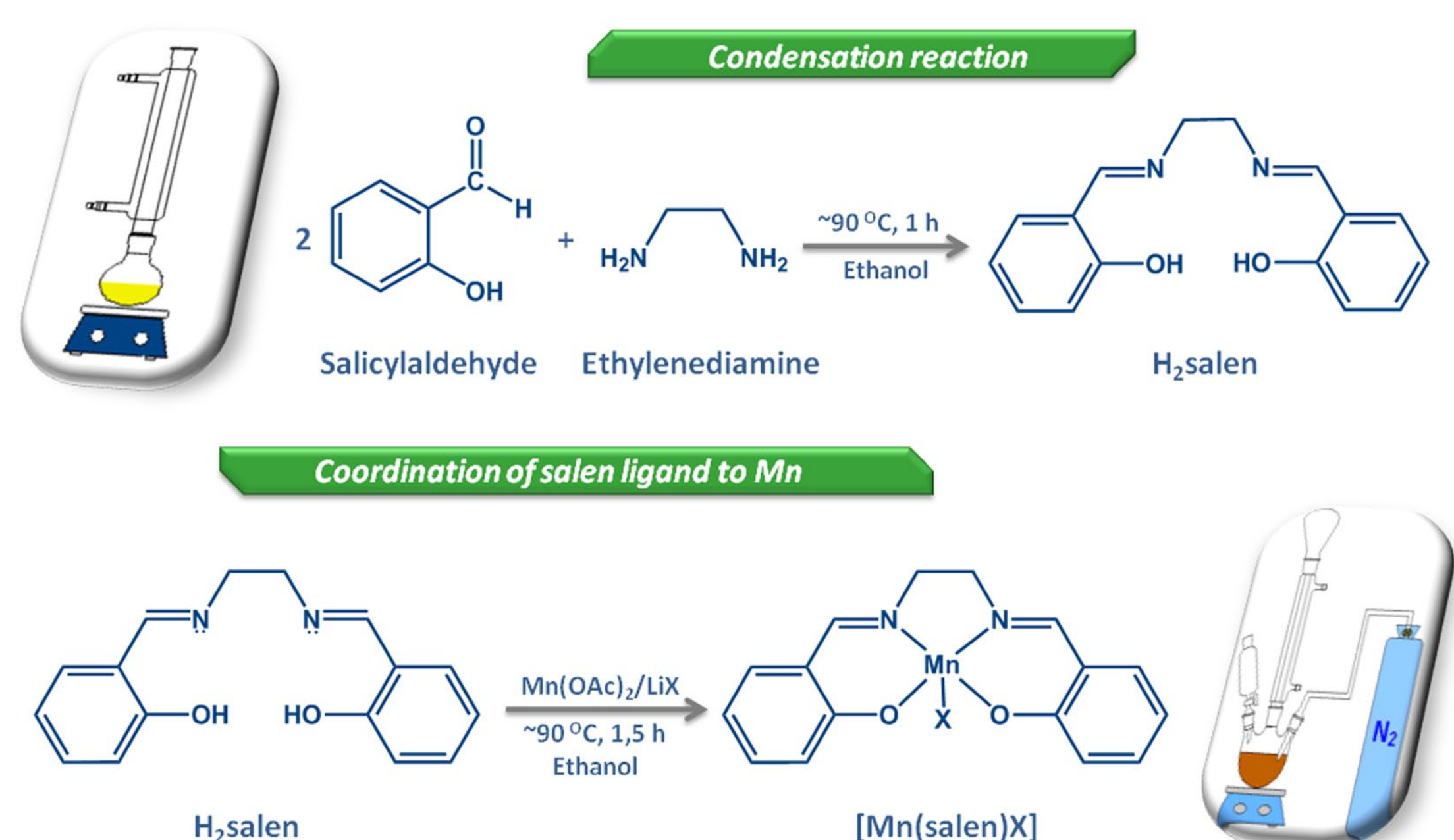
On the other hand, the Mn-salen type complexes are well known as catalysts in the epoxidation of olefins; recently, it has been reported their catalytic activity in the coupling reaction of epoxides to CO<sub>2</sub> [3-5].



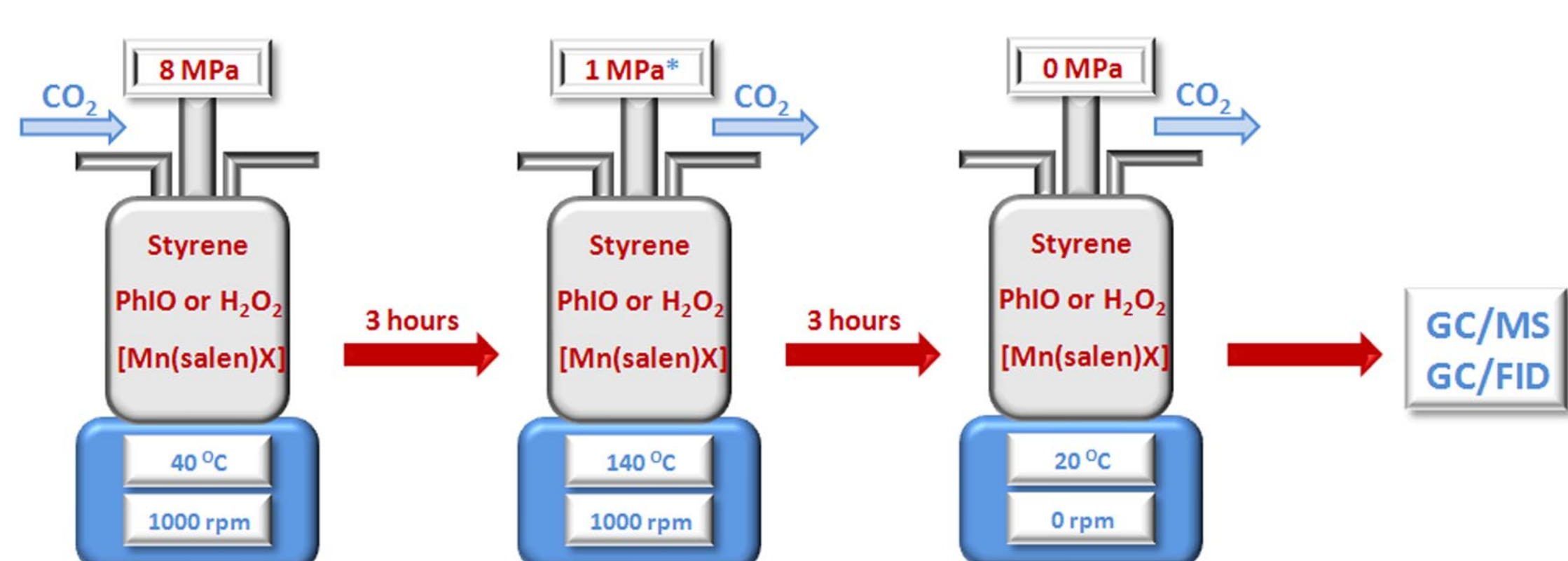
Thus, in this work we examined the effect of the halogen ligand on the catalytic behavior of [Mn(salen)X] (X = Cl, Br and I) complexes in the synthesis one-pot of styrene carbonate from styrene and CO<sub>2</sub> in the presence of an oxidizing agent (iodosylbenzene (PhIO) or hydrogen peroxide).

## 2. Experimental

### 2.1. Synthesis of the [Mn(salen)X] complexes



### 2.2. Catalytic experiments



\* Decreased in order to satisfy molar ratio epoxide:CO<sub>2</sub> (1:4) [5]

**1. H<sub>2</sub>O<sub>2</sub> experiments:** 8.7 mmol of styrene (99.9% Sigma Aldrich), 26.1 mmol of H<sub>2</sub>O<sub>2</sub> (30%; Panreac) and 0.0469 mmol of [Mn(salen)X].

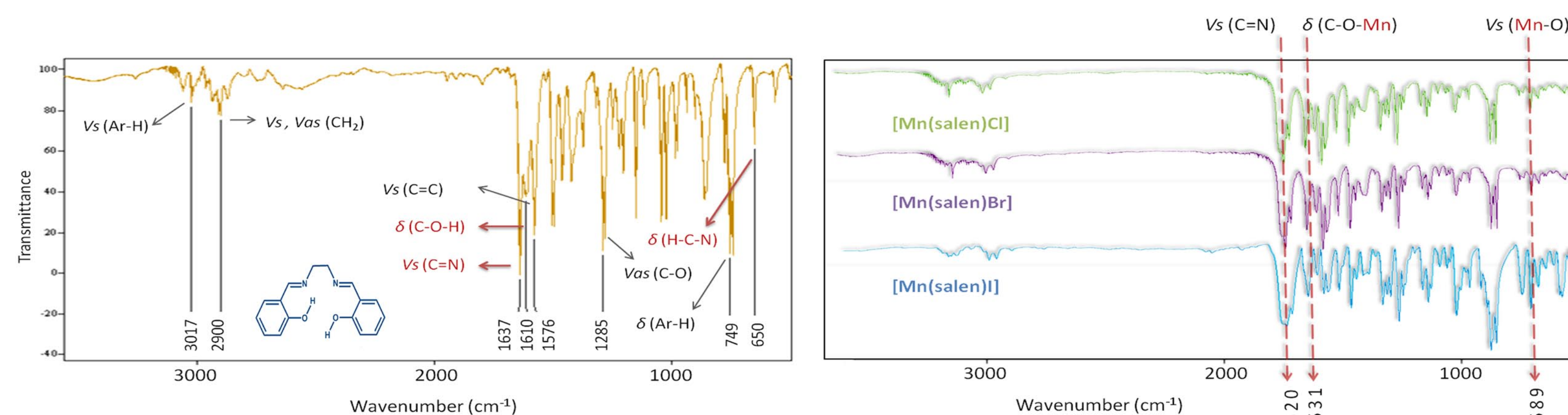
**2. PhIO experiments:** 2.3 mmol of PhIO (prepared from (Diacetoxyiodo) benzene 98% Sigma-Aldrich) dissolved in 2 cm<sup>3</sup> of CH<sub>2</sub>Cl<sub>2</sub> (99.8% Panreac), 1.2 mmol of styrene and 0.0162 mmol of [Mn(salen)X].

**3. GC/MS-FID conditions:** CP-Sil 8 CB Low Bleed/MS (30 m, 0.25 mm, i.d.; 0.25) and DB5-MS (30 m, 0.25 mm, i.d.; 0.25); temperature ramp; 40 °C (2 min) (10 °C/min ramp) 300 °C (2 min); injector and detector temperatures; 250 °C and 300 °C, respectively.

\* Corresponding author: Research Group on Functional Materials and Catalysis, Department of Chemistry, University of Nariño, Calle 18, Cra. 50 Campus Torobajo, Pasto, Colombia. Phone: + (57) 318 407 93 25; fax: + (57) 2 731 31 06. E-mail address: alejandrogaleano@udenar.edu.co

## 3. Results and discussion

### 2.1. Spectroscopic characteristics of the [Mn(salen)X] complexes

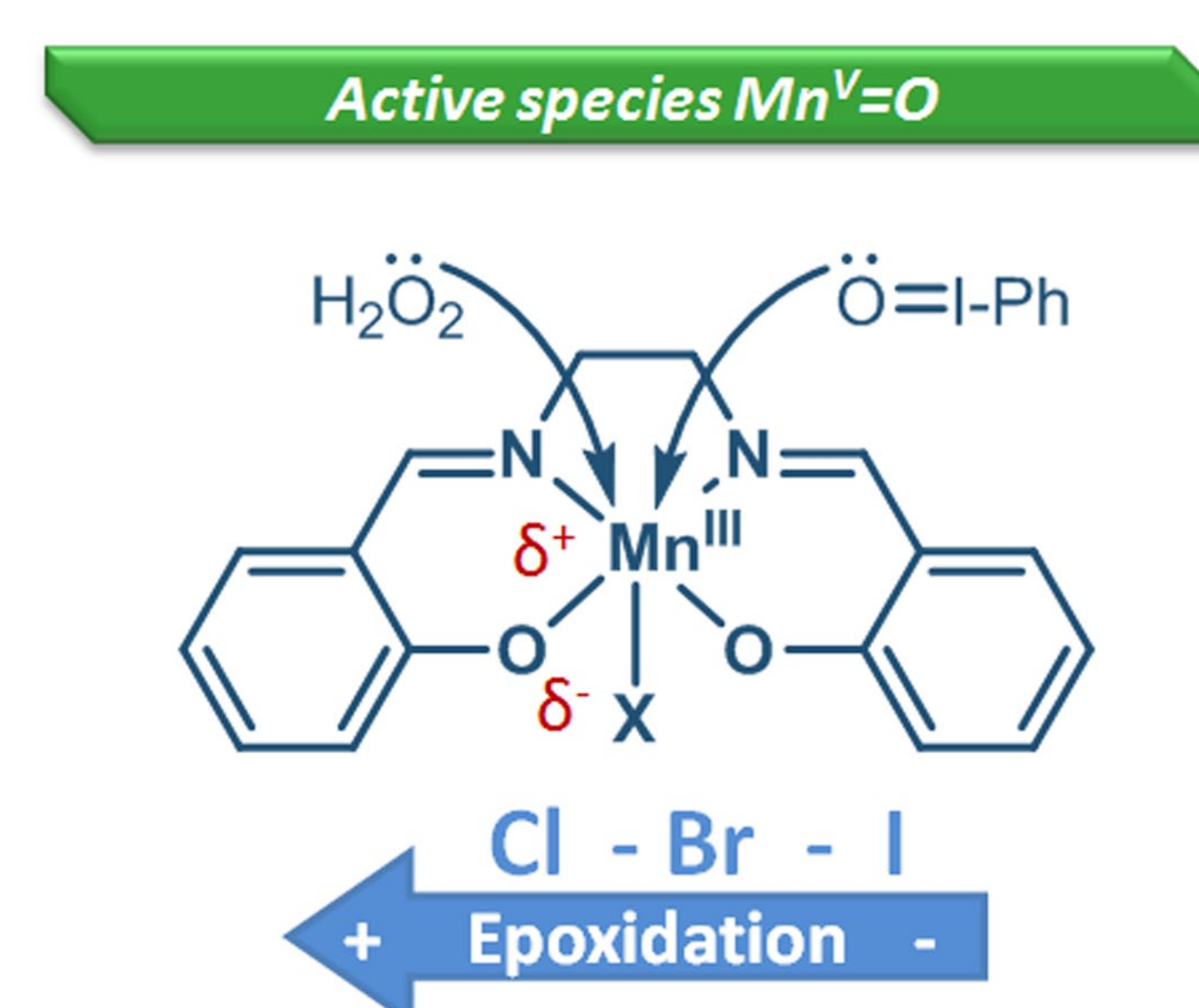


UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>) ligand: band series at ~ 325 nm ( $\pi^* \leftarrow \pi$ ,  $\pi^* \leftarrow n$ ); UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>) complexes: band series ~ 325 ( $\pi^* \leftarrow \pi$ ,  $\pi^* \leftarrow n$ ), 420 ( $\pi^* \leftarrow d$ ) and 490 (d-d); <sup>1</sup>H-RMN ligand (400 MHz, CDCl<sub>3</sub>) (ppm): 3.95 (s, 4H, CH<sub>2</sub>), 6.86-6.90 (m, 2H, Ar-H), 6.96-6.98 (d, 2H, Ar-H), 7.24-7.26 (d, 2H, Ar-H), 7.30-7.34 (m, 2H, Ar-H), 8.37 (s, 2H, H-C=N) and 13.23 (s, 2H, -OH); <sup>13</sup>C-RMN ligand (400 MHz, CDCl<sub>3</sub>) (ppm): 59.8, 116.5, 118.6, 118.7, 131.5, 132.4, 161.0 and 166.5; [Mn(salen)Cl]: yield 56%, AAS (total Mn) expected value 15.40%, experimental 14.74%; [Mn(salen)Br]: yield 50%, AAS (total Mn) expected value 13.70%, experimental 12.64%; [Mn(salen)I]: yield 47%, AAS (total Mn) expected value 12.26%, experimental 11.33%. Spectroscopic characteristics of the complexes coincided with those reported [5-6].

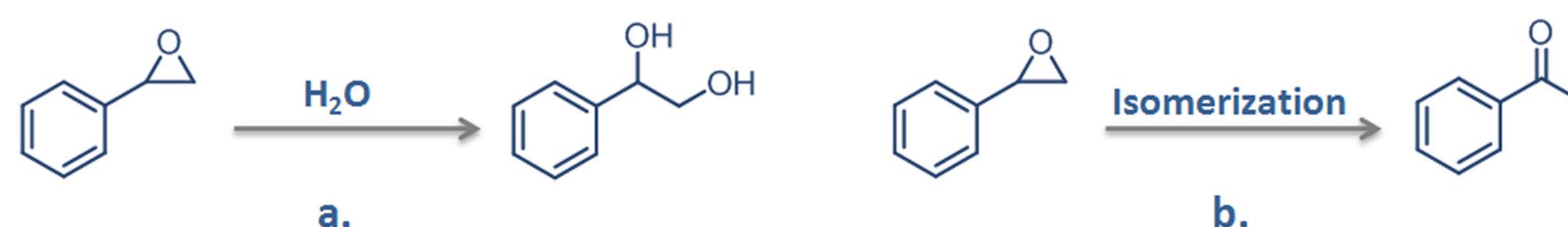
### 2.2. Catalytic performance of the Mn-complexes

Complex	Styrene Conversion (%)	Selectivity (%)					
		B	PMK	BA	SE	PED	Others
<b>Hydrogen peroxide at 30 wt.%</b>							
[Mn(salen)Cl]	15.0	52.1	1.8	5.3	14.5	18.9	7.4
[Mn(salen)Br]	3.0	73.0	2.0	3.0	2.0	0.0	20.0
[Mn(salen)I]	2.5	90.0	2.8	4.0	0.0	0.0	3.2
<b>Iodosylbenzene in CH<sub>2</sub>Cl<sub>2</sub></b>							
[Mn(salen)Cl]	9.0	66.1	4.7	0.0	16.7	0.0	12.6
[Mn(salen)Br]	7.1	69.4	0.0	0.0	4.2	0.0	26.3
[Mn(salen)I]	5.7	71.2	0.0	0.0	2.5	0.0	26.3

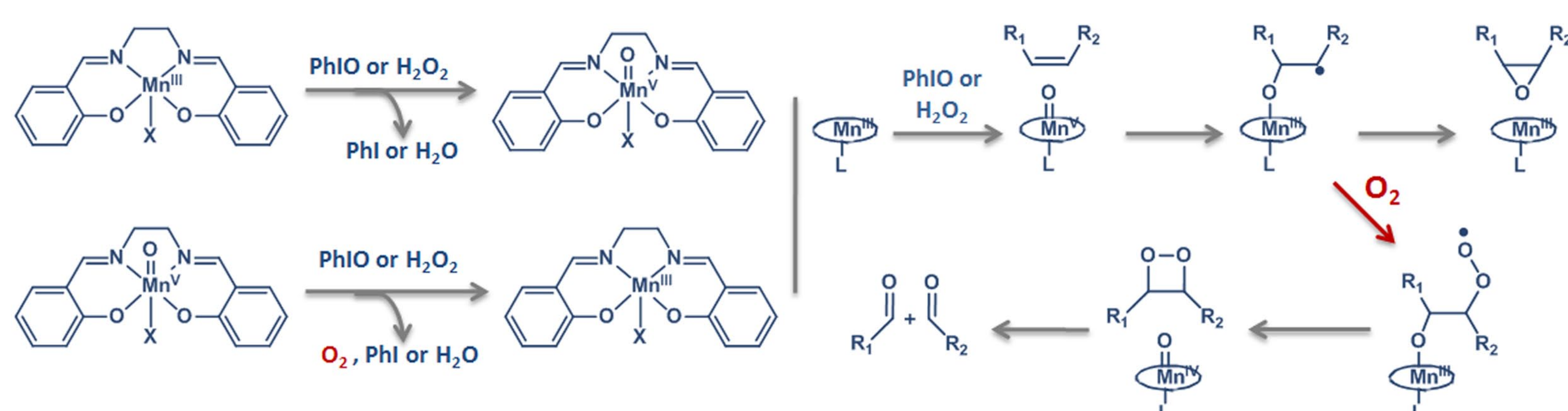
B: Benzaldehyde; PMK: Phenyl methyl ketone; BA: Benzoic acid; SE: Styrene epoxide; PED: 1-Phenyl-1,2-ethanediol; Others: Styrene polymers (dimers and trimers).



### Formation of byproducts



### Oxidizing agent decomposition followed by benzaldehyde formation



## 4. Conclusions

The styrene conversion and selectivity to the corresponding epoxide, as intermediate in the synthesis of organic carbonates from olefins and CO<sub>2</sub>, were proportional to the electronegativity of the halogen ligand in [Mn(salen)X] type complexes (Cl > Br > I). However, the opposite trend, already reported regarding the second stage of reaction, apparently prevented the styrene carbonate to be obtained in a one-pot process.

The solubilities of either the complexes and the oxidizing reagent in scCO<sub>2</sub> showed to play a fundamental role in the activation of the styrene epoxidation. The slightly better performance of PhIO compared to H<sub>2</sub>O<sub>2</sub> as oxidizing agent is attributed to its lower polar character favoring increased solubility in scCO<sub>2</sub>, while the active species Mn<sup>V</sup>=O to be more easily formed. Decomposition of the oxidizing reagents promoted formation of byproducts.

## Acknowledgement

The authors gratefully acknowledge the financial support from VIPRI - Udenar, as well as to Laboratory of organometallic compounds and homogeneous catalysis – Univalle, Colombia.

## References

- [1] E. J. Beckman, *J. Supercrit. Fluids* 28 (2004) 121-191.
- [2] T. Sakakura, J.-H. Choi, H. Yasuda. *Chem. Rev.* 107 (2007) 2365-2387.
- [3] A. R. Silva, C. Freire, B. Castro. *New J. Chem.* 28 (2004) 253-260.
- [4] C. Gao, S. Wooseob, J. Han, D. Han, C. Adharvana, H. Kim, K. Ahn. *Bull. Korean Chem. Soc.* 30 (2009) 541-542.
- [5] F. Jutz, J.-D. Grunwaldt, A. Baiker. *J. Mol. Catal. A: Chem.* 279 (2008) 94-103.
- [6] R. Tan, D. Yin, N. Yu, H. Zhao, D. Yina. *J. Catal.* 263 (2009) 284-291.