

Mn(III)-salen complexes in the one-pot catalytic epoxidation/carboxylation of styrene in scCO₂

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

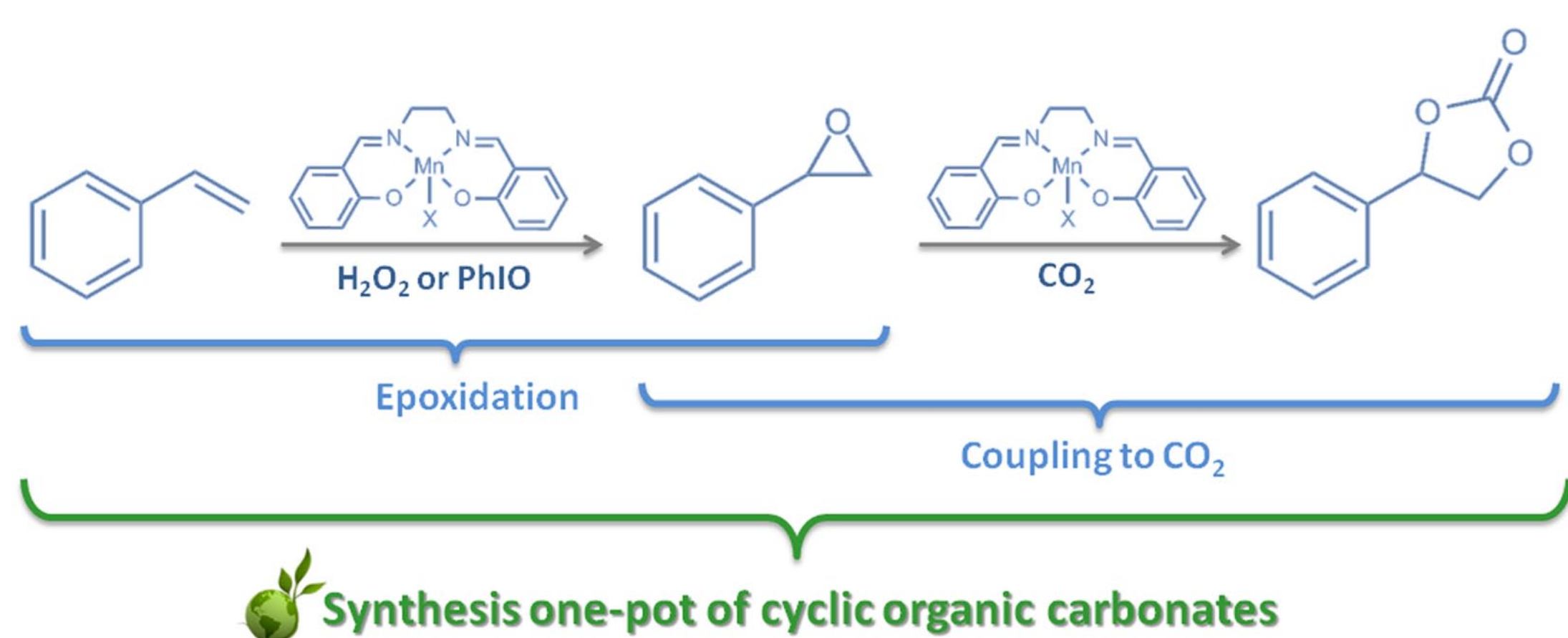
Research Group on Functional Materials and Catalysis-Department of Chemistry, University of Nariño. Pasto – Colombia



1. Introduction

The CO₂ 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, CO₂ can potentially replace other dangerous toxic and reactive gases, such as phosgene and carbon monoxide [1-2].

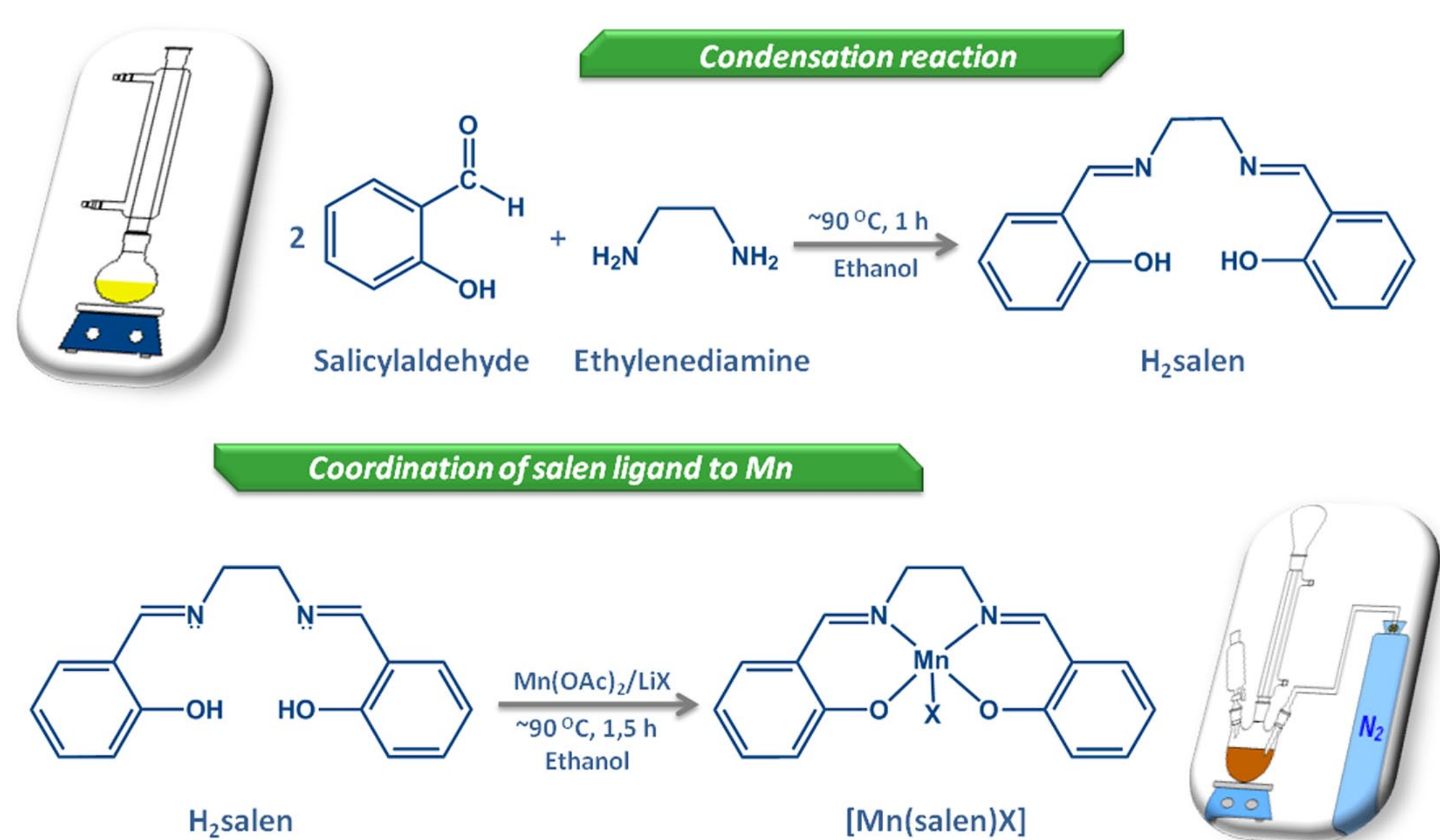
On the other hand, the Mn-salen type complexes are well known as catalysts in the epoxidation of olefins; recently, it has been reported their catalytic activity in the coupling reaction of epoxides to CO₂ [3-5].



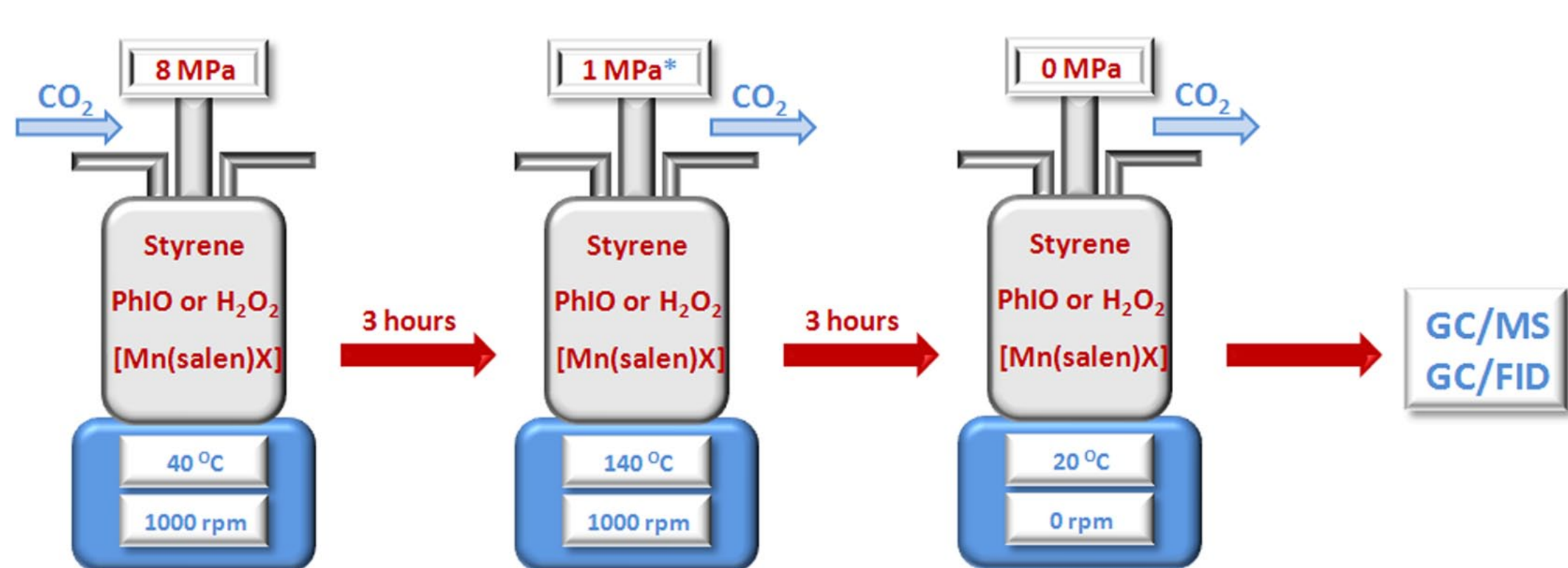
Thus, in this work we examined the effect of the halogen ligand on the catalytic behavior of [Mn(salen)X] (X = Cl, Br and I) complexes in the synthesis one-pot of styrene carbonate from styrene and CO₂ in the presence of an oxidizing agent (iodosylbenzene (PhIO) or hydrogen peroxide).

2. Experimental

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



2.2. Catalytic experiments



* Decreased in order to satisfy molar ratio epoxide:CO₂ (1:4) [5]

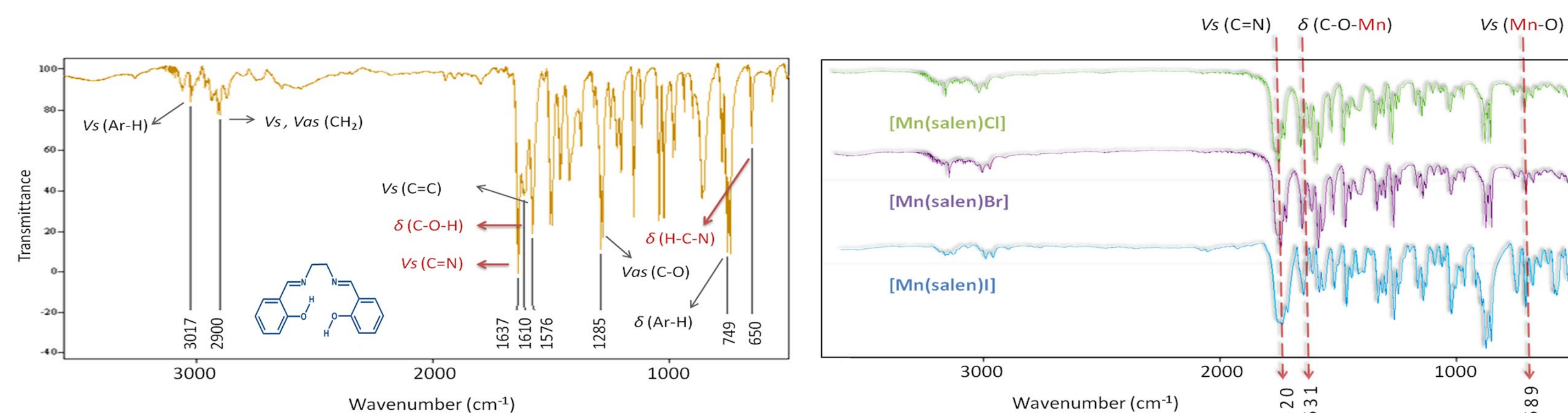
1. H₂O₂ experiments: 8.7 mmol of styrene (99.9% Sigma Aldrich), 26.1 mmol of H₂O₂ (30%; Panreac) and 0.0469 mmol of [Mn(salen)X].

2. PhIO experiments: 2.3 mmol of PhIO (prepared from (Diacetoxyiodo) benzene 98% Sigma-Aldrich) dissolved in 2 cm³ of CH₂Cl₂ (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.

3. Results and discussion

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

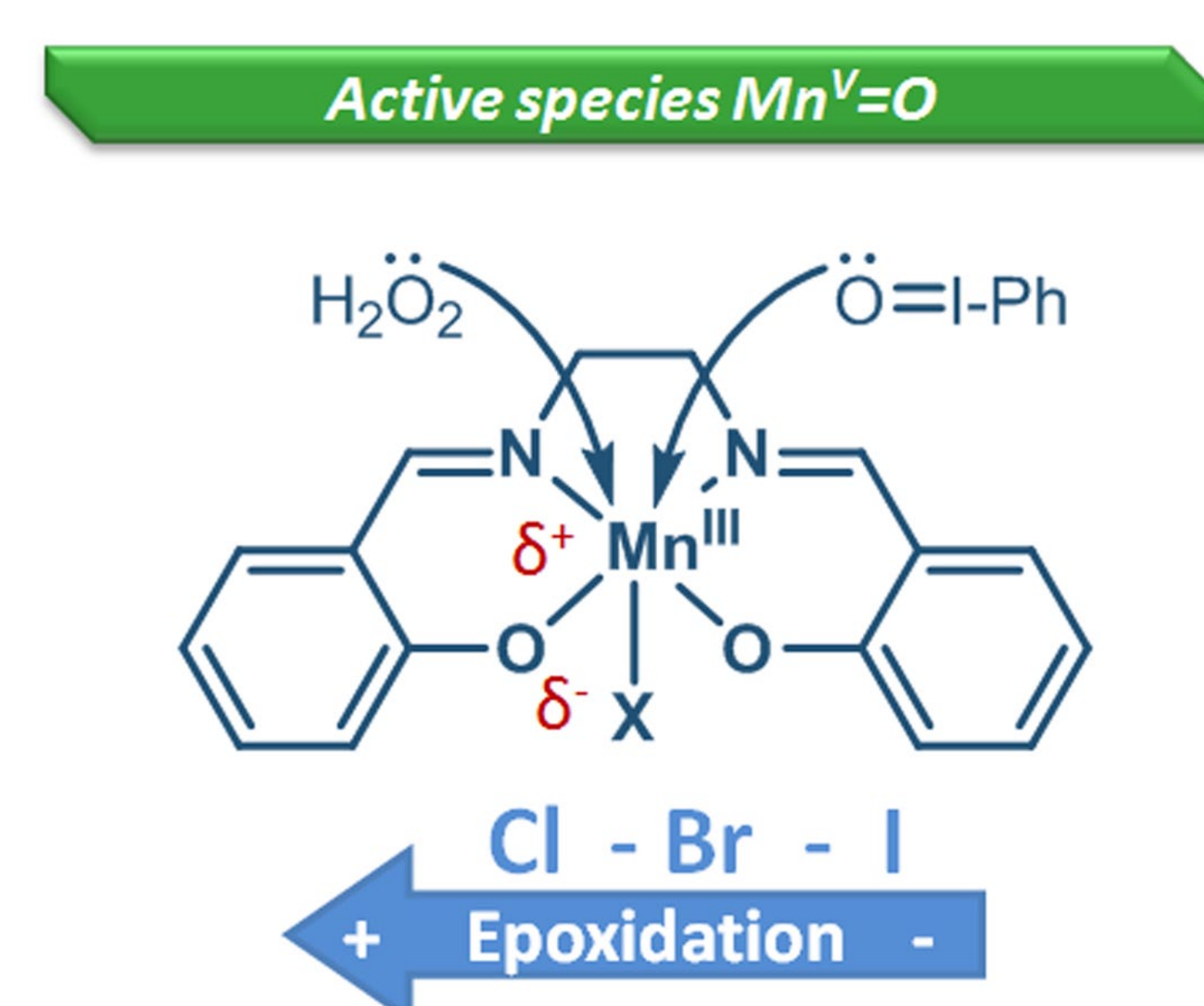


UV/Vis (CH₂Cl₂) ligand: band series at ~ 325 nm ($\pi^* \leftarrow \pi$, $\pi^* \leftarrow n$); UV/Vis (CH₂Cl₂) complexes: band series ~ 325 ($\pi^* \leftarrow \pi$, $\pi^* \leftarrow n$), 420 ($\pi^* \leftarrow d$) and 490 (d-d); ¹H-RMN ligand (400 MHz, CDCl₃) (ppm): 3.95 (s, 4H, CH₂), 6.86-6.90 (m, 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); ¹³C-RMN (125 MHz, CDCl₃) (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].

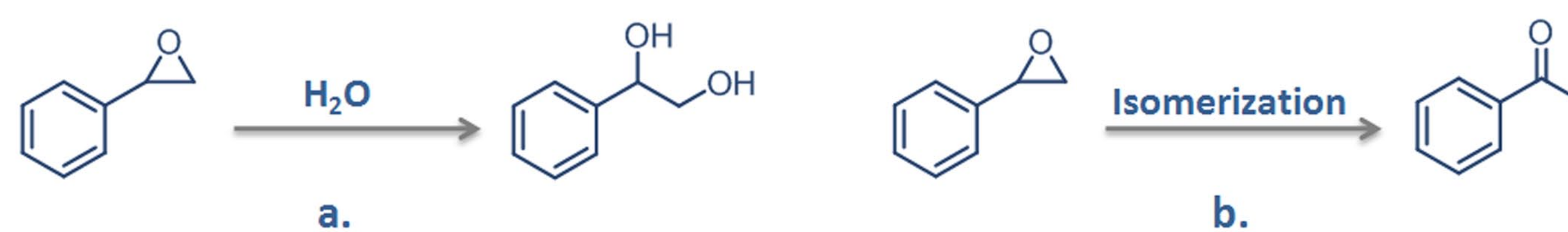
2.2. Catalytic performance of the Mn-complexes

Complex	Styrene Conversion (%)	Selectivity (%)					
		B	PMK	BA	SE	PED	Others
Hydrogen peroxide at 30 wt.%							
[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
Iodosylbenzene in CH₂Cl₂							
[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

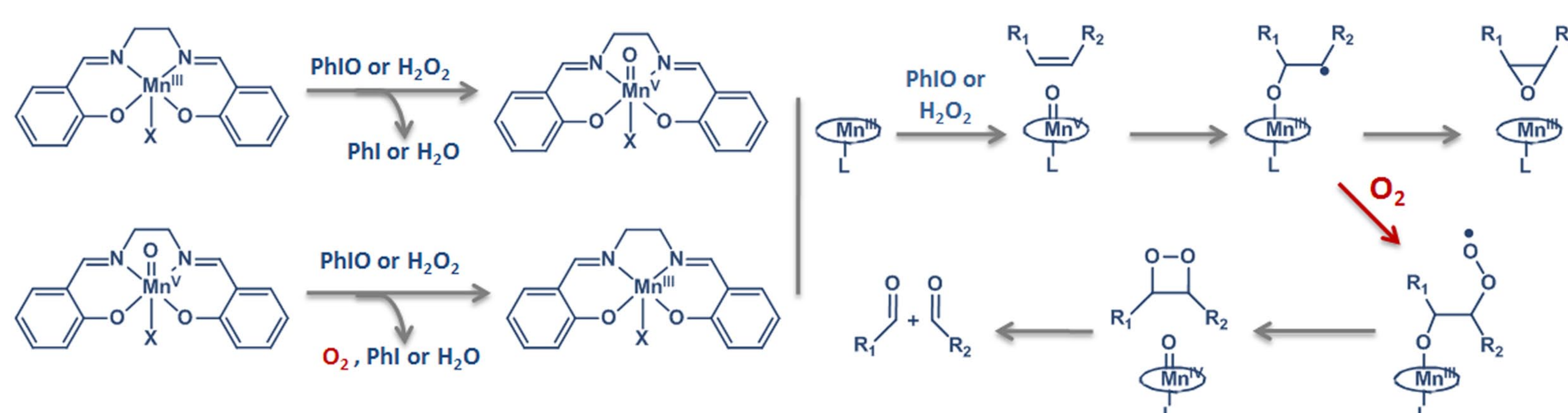
B: Benzaldehyde; PMK: Phenyl methyl ketone; BA: Benzoic acid; SE: Styrene epoxide; PED: 1-Phenyl-1,2-ethanediol; Others: Styrene polymers (dimers and trimers).



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 CO₂, 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 scCO₂ showed to play a fundamental role in the activation of the styrene epoxidation. The slightly better performance of PhIO compared to H₂O₂ as oxidizing agent is attributed to its lower polar character favoring increased solubility in scCO₂, while the active species Mn^V=O to be more easily formed. Decomposition of the oxidizing reagents promoted formation of byproducts.

Acknowledgement

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References

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* 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