

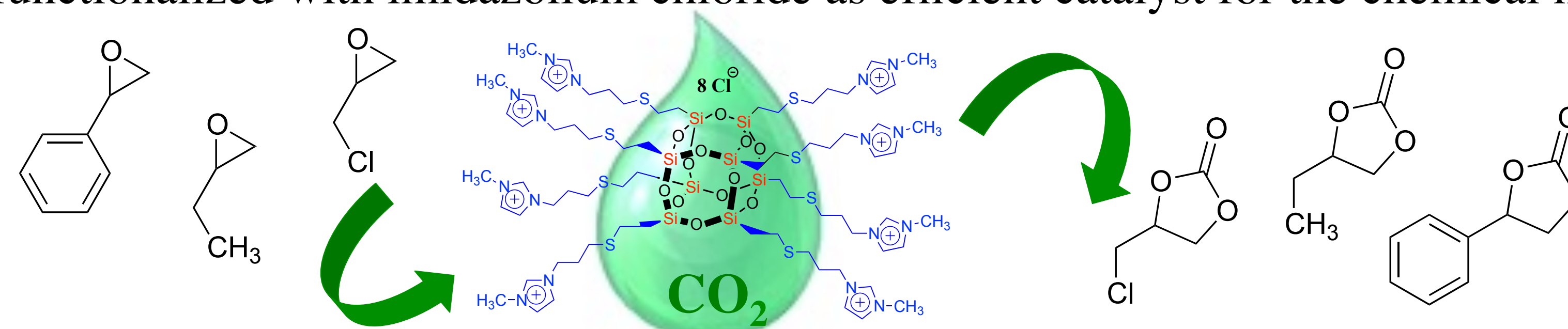
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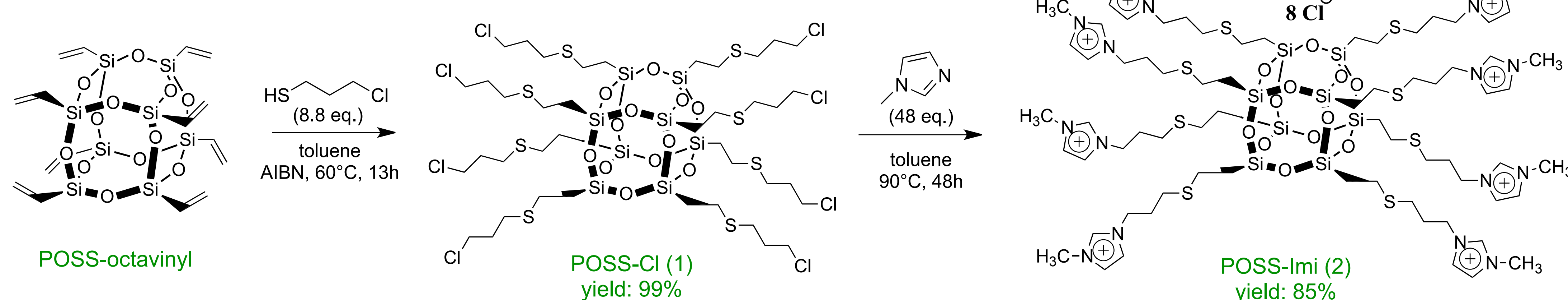
I. INTRODUCTION: Development of green processes based on chemical fixation of carbon dioxide has attracted the attention of the scientific community due to the possibility to transform a waste, such as CO₂, into useful products. Cyclic carbonates, synthesized through the reaction between CO₂ and epoxides, are interesting compounds that can be used for several applications, such as electrolytes for lithium batteries and polar aprotic solvents. Due to its thermodynamic and kinetic stability, carbon dioxide conversion is difficult to achieve and an efficient catalyst is required.¹ Various homogeneous and heterogeneous catalysts have been proposed for this reaction. Recently, ionic liquids have emerged as a novel class of organocatalysts. In particular, imidazolium-based ionic liquids have become very attractive since they are one of the most efficient catalysts for CO₂ conversion to produce cyclic carbonate from epoxydes.² Here the synthesis and applications of a novel class of imidazolium catalyst based on the functionalization of Polyhedral Oligomeric Silsesquioxane (POSS) is presented.³

AIM: In the present work we present a silsesquioxane based nanostructure functionalized with imidazolium chloride as efficient catalyst for the chemical fixation of carbon dioxide.

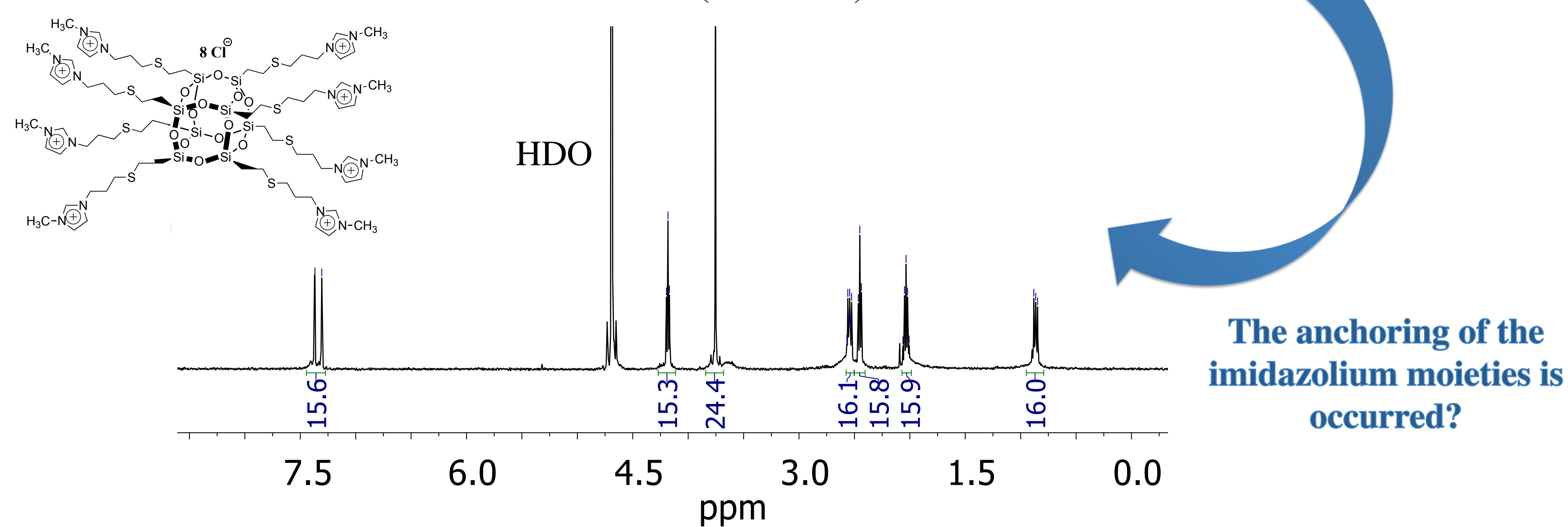


II. SYNTHETIC STRATEGY AND CHARACTERISATION

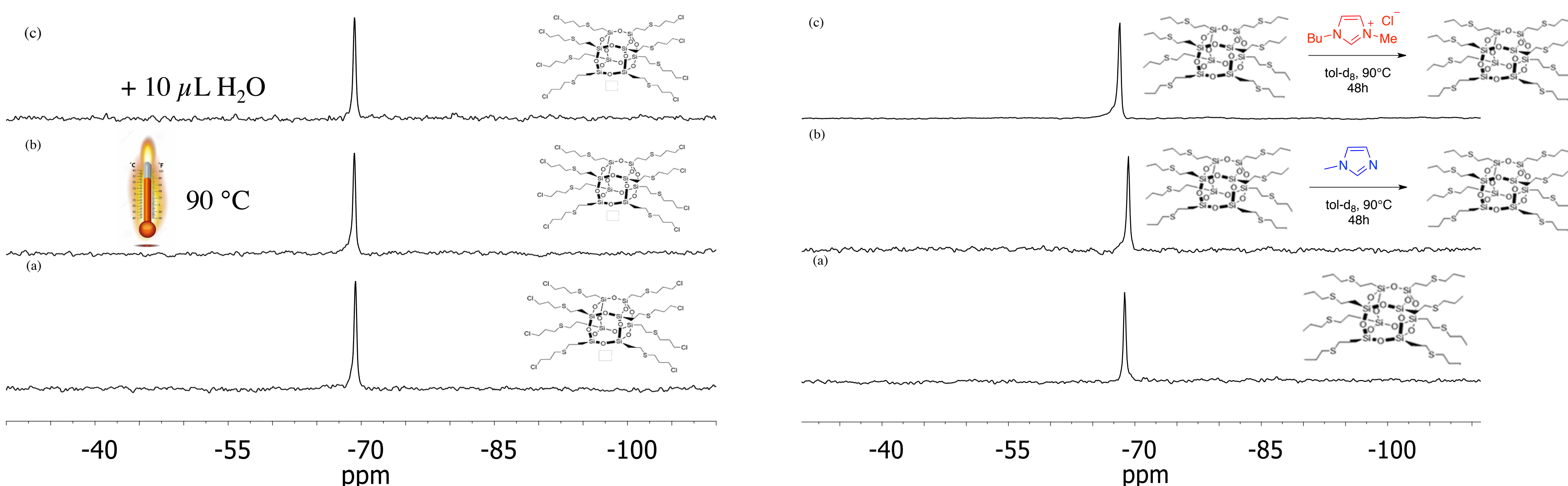
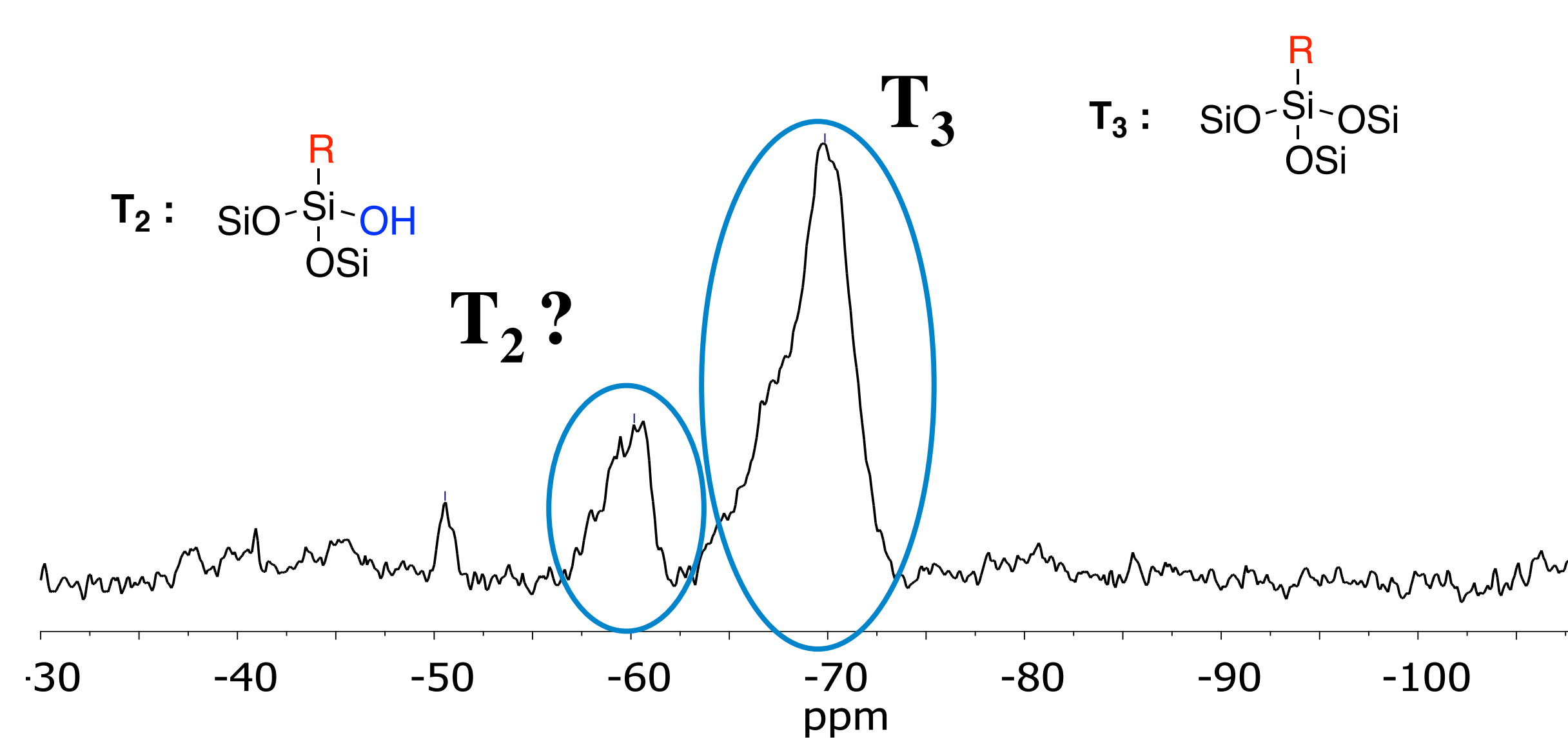
Procedure: Synthesis of POSS-Cl and POSS-Imi (1 and 2).



¹H-NMR (400MHz)



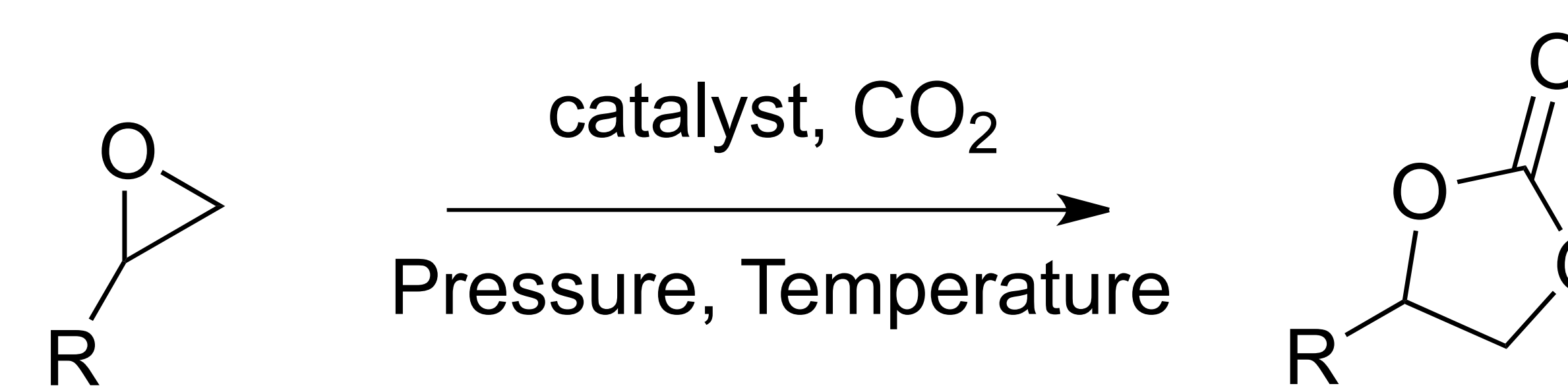
²⁹Si-NMR (500MHz)



Experimental conditions: (a) POSS-Cl in tol-d₈, (b) after 17 h at 90 °C, + 10 µL H₂O after 48 h at 90 °C.

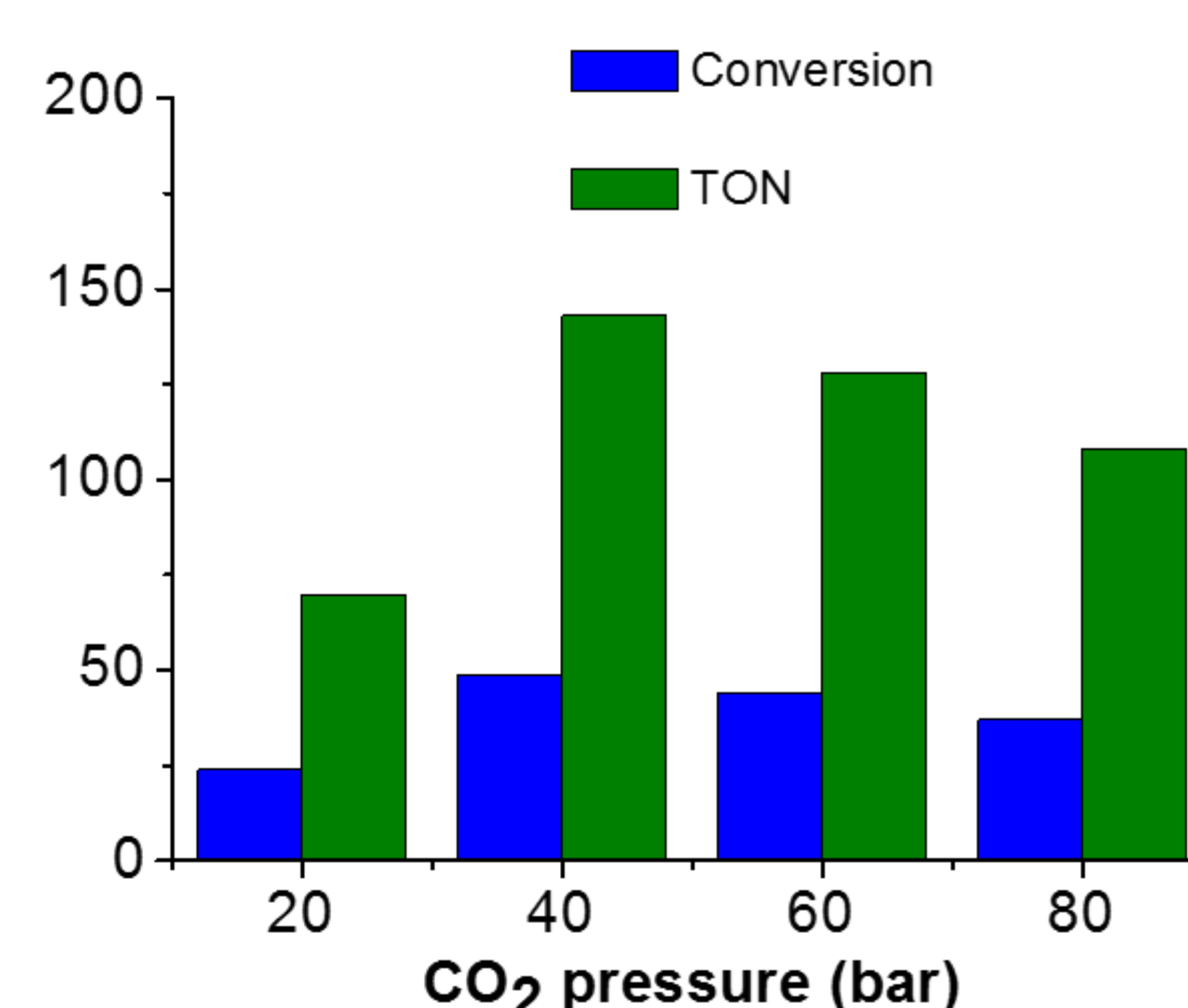
Experimental conditions: (a) POSS-Cl in tol-d₈, (b) POSS-Cl in tol-d₈ with 1-Me-Imi (24 eq.) after 48 h at 90 °C, (c) POSS-Cl in tol-d₈ with 1-butyl-3-methylimidazolium chloride (8 eq.) after 48 h at 90 °C.

III. CATALYTIC TESTS

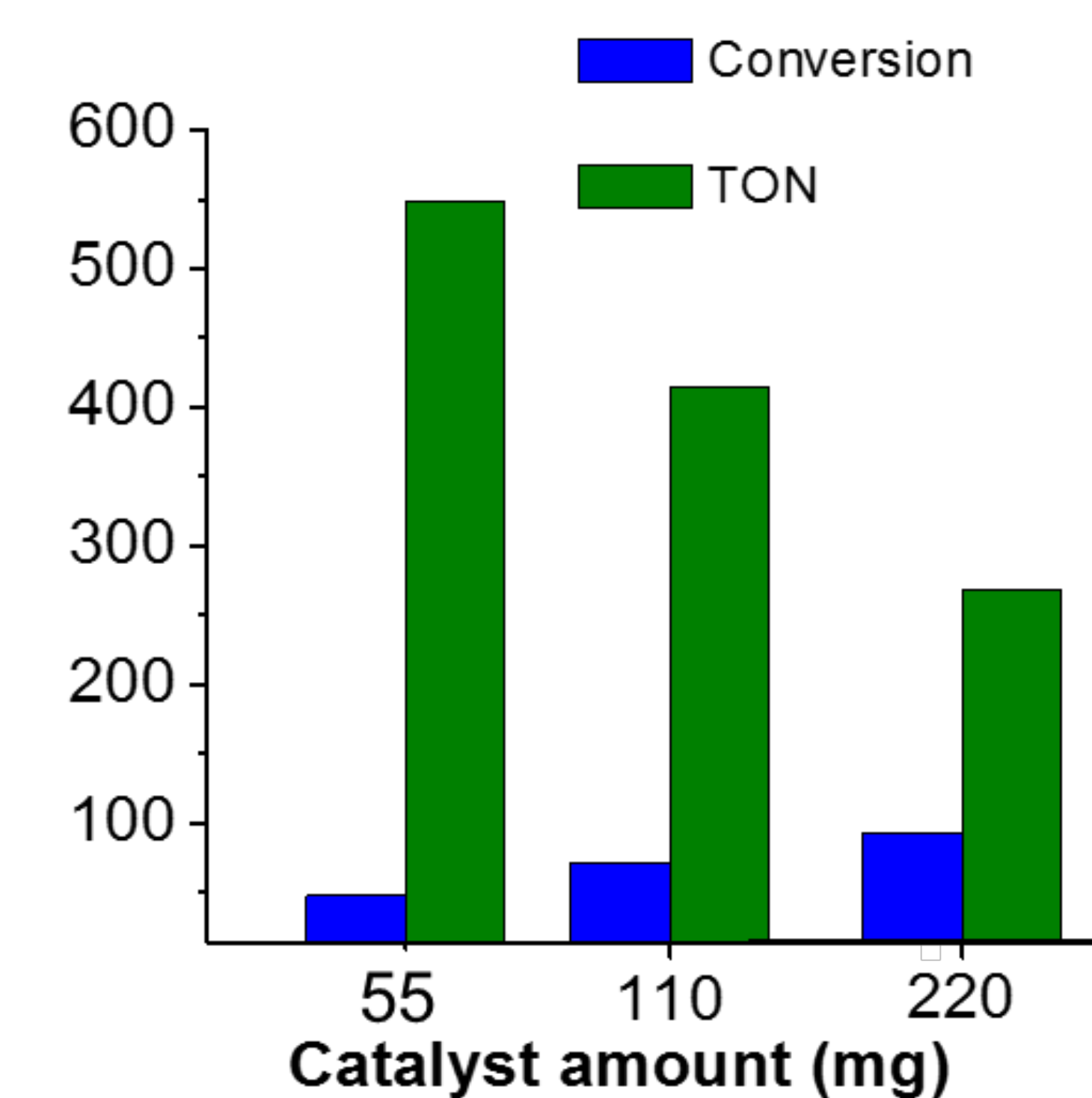


Procedure: Investigation of reaction conditions with POSS-Imi.

(a) In function of the pressure



(b) In function of the amount of the catalyst



Conversion and TON ($n_{\text{converted}} / n_{\text{active sites}}$) of the reaction varying the CO₂ pressure at 125 °C, with 220 mg of catalyst in H₂O (a) and the catalyst amount at 40 bar, 150 °C, in H₂O (b).

Procedure: Study of the catalytic activity of the POSS-Imi in function of the solvent and the comparison with the unsupported 1-butyl-3-methyl imidazolium chloride (BMim).

Entry	Catalyst	Co-solvent (%)	Conversion (%)	Carbonate yield (%)	Selectivity (%)	TON
1	POSS-Imi	H ₂ O	71	51	72	410
2	POSS-Imi	MeOH	73	69	95	429
3	POSS-Imi	EtOH	85	81	95	299
4	POSS-Imi	iPrOH	94	94	>99	553
5	BMim	iPrOH	98	98	>99	326
6	POSS-Imi	EtOH (abs)	84	84	>99	490

Table 1: 110 mg of catalyst (which corresponds to 0.36 mmol of imidazolium sites in POSS-Imi), 40 bar, 150 °C, 24 mL (210 mmol) of styrene oxide, 3 h and 1.5 mL of solvent were used in all the tests. For Bmim, 0.63 mmol.

After the reaction, the catalyst was easily recovered from the reaction mixture by extraction and the structure was confirmed by ²⁹Si-NMR. In addition, POSS-Imi was tested with other epoxydes (1-butene oxide, epichlorohydrin) displaying excellent performances, even at lower temperature (100 °C, TON equal to 476) with epichlorohydrin as substrate.

IV. CONCLUSION: The synthesis of imidazolium functionalized polyhedral oligomeric silsesquioxane was successfully achieved. This system was fully characterized in particular via ²⁹Si NMR spectroscopy and used as catalyst for the conversion of the CO₂ with epoxydes to obtain the corresponding cyclic carbonates. Different reaction conditions were investigated obtaining excellent results. The catalyst was also recovered from the reaction mixture. A further comparison with the unsupported Bmim highlights the positive effect of the nano-cage on the catalytic activity.

REFERENCES: ¹ T. Sakakura, J.-C. Choi, H. Yasuda, *Chemical Reviews* 107 (2007) 2365-2387. ² C. Aprile, F. Giacalone, P. Agrigento, L. F. Liotta, J. A. Martens, P. P. Pescarmona, M. Gruttadauria, *ChemSusChem* 4 (2011) 1830-1837. ³ L. A. Bivona, O. Fichera, L. Fusaro, F. Giacalone, M. Buaki-Sogo, M. Gruttadauria, C. Aprile, *Catalysis Science & Technology*, 2015, Accepted.

ACKNOWLEDGEMENTS: The authors acknowledge in the frame of the program FSR-FNRS "Research Credit Project". L. A. Bivona thanks University of Namur and University of Palermo for a co-funded PhD fellowship. M.B-S is gratefully acknowledged for an Incoming Post-Doctoral Fellowship of the Académie Universitaire de Louvain co-funded by the Marie Curie Actions of the European Commission.