UNIVERSITÀ
DEGLI STUDI
DI PALERMO

Polyhedral Oligomeric Silsesquioxane Based Catalyst for the Efficient Synthesis of Cyclic Carbonates

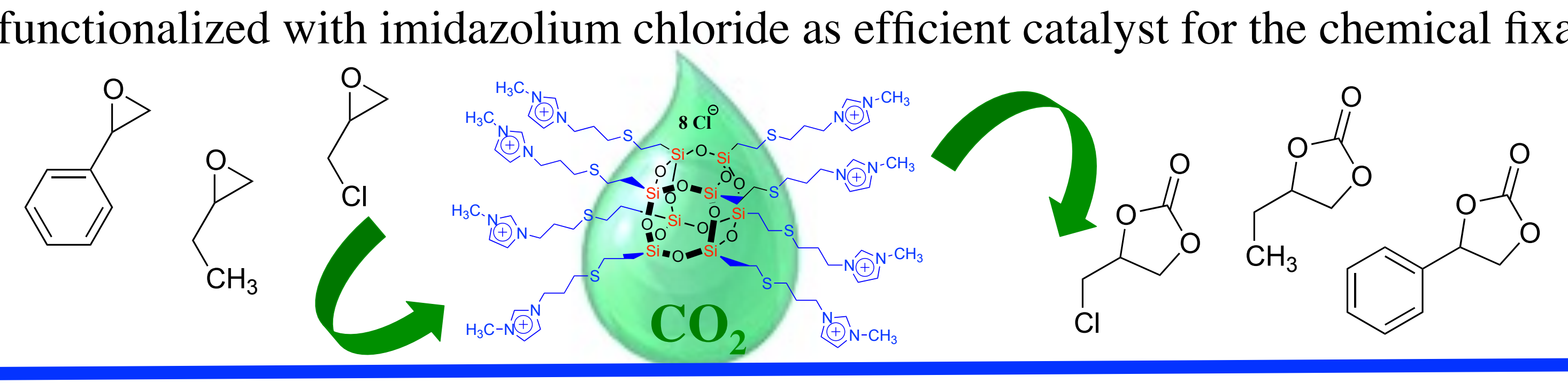
UNIVERSITÉ
DE NAMUR

L. A. Bivona,[1,2] **O. Fichera**,[1] **L. Fusaro**,[1] **F. Giacalone**,[2] **M. Buaki-Sogo**,[1,*] **M. Gruttadauria**,[2,*] **and C. Aprile**[1,*]

[1] **Laboratory of Applied Materials Chemistry, University of Namur (Unamur), 61 rue de Bruxelles, B5000, Namur, Belgium (*carmela.aprile@unamur.be, *mireia.buaki-sogo@unamur.be)**
[2] **Department of Biological Chemical and Pharmaceutical Sciences and Techologies (STEBICEF), Università di Palermo, Viale delle Scienze s/n, Ed. 17, I-90128, Palermo, Italy (*michelangelo.gruttadauria@unipa.it)**

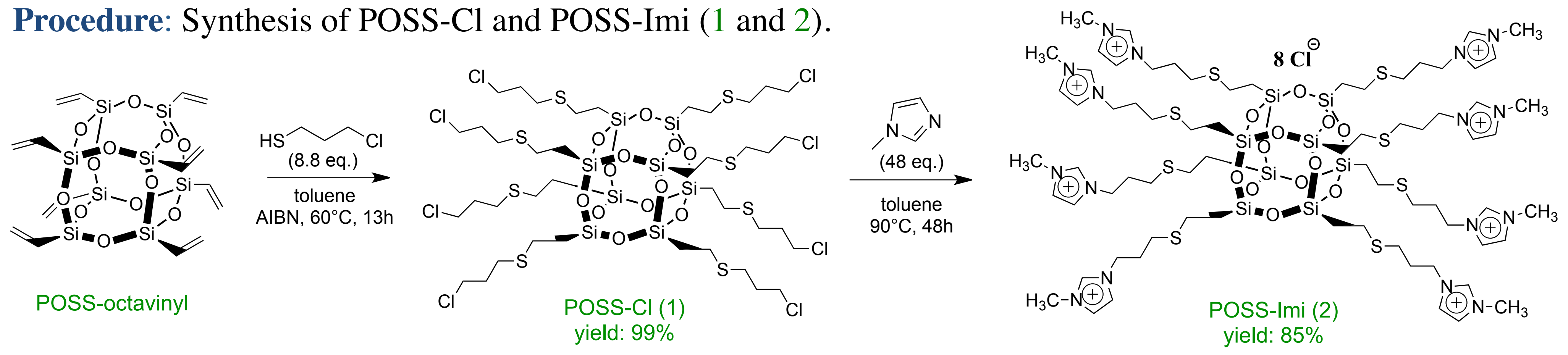
I. INTRODUCTION: Development of green processes based on chemical fixation of carbon dioxide has attracted the attention of the scientific community due to the possibility to transform a waste, such as CO_2, into useful products. Cyclic carbonates, synthetized through the reaction between CO_2 and epoxides, 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 CO_2 conversion to produce cyclic carbonate from epoxides.[2] Here the synthesis and applications of a novel class of imidazolium catalyst based on the functionalization of Polyehedral 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).

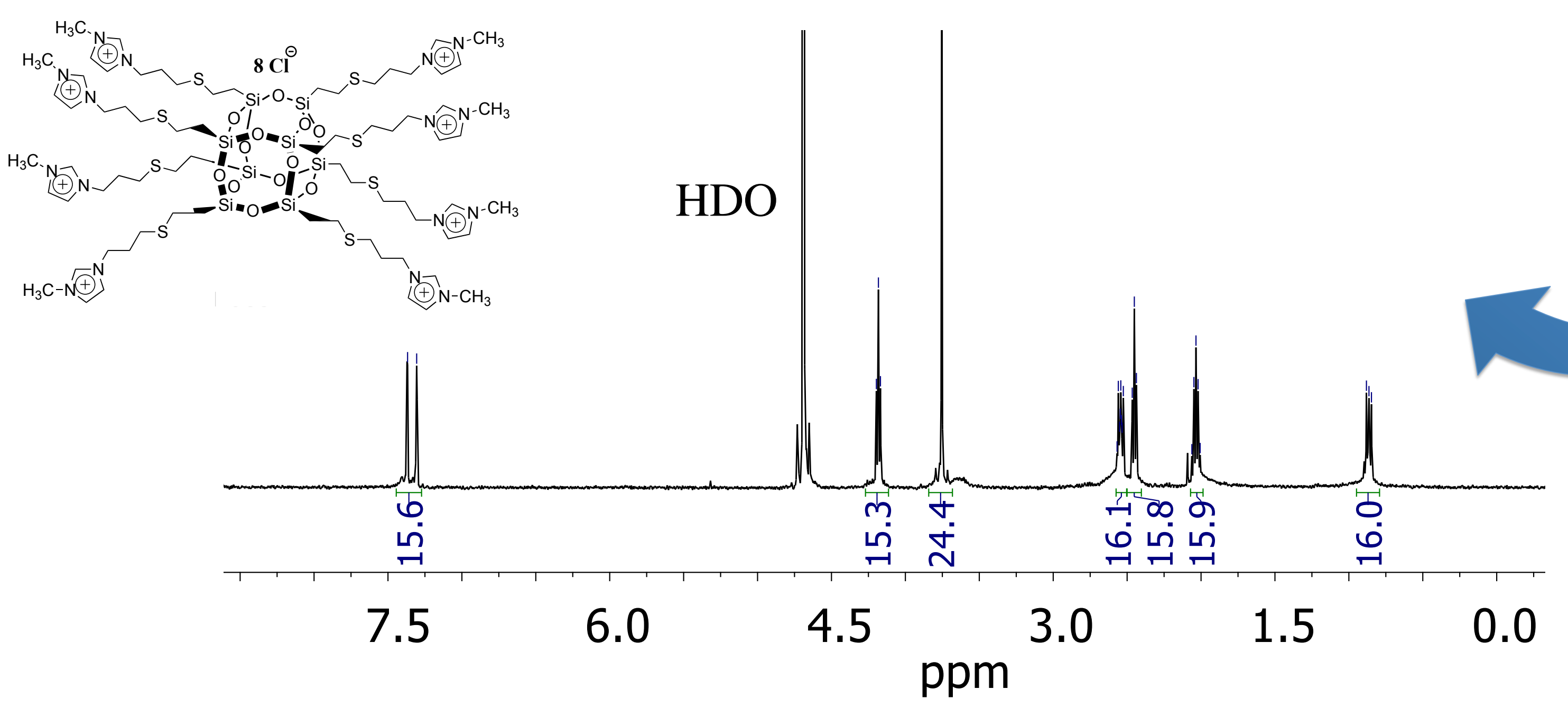


POSS-octavinyl

POSS-Cl (1)
yield: 99%

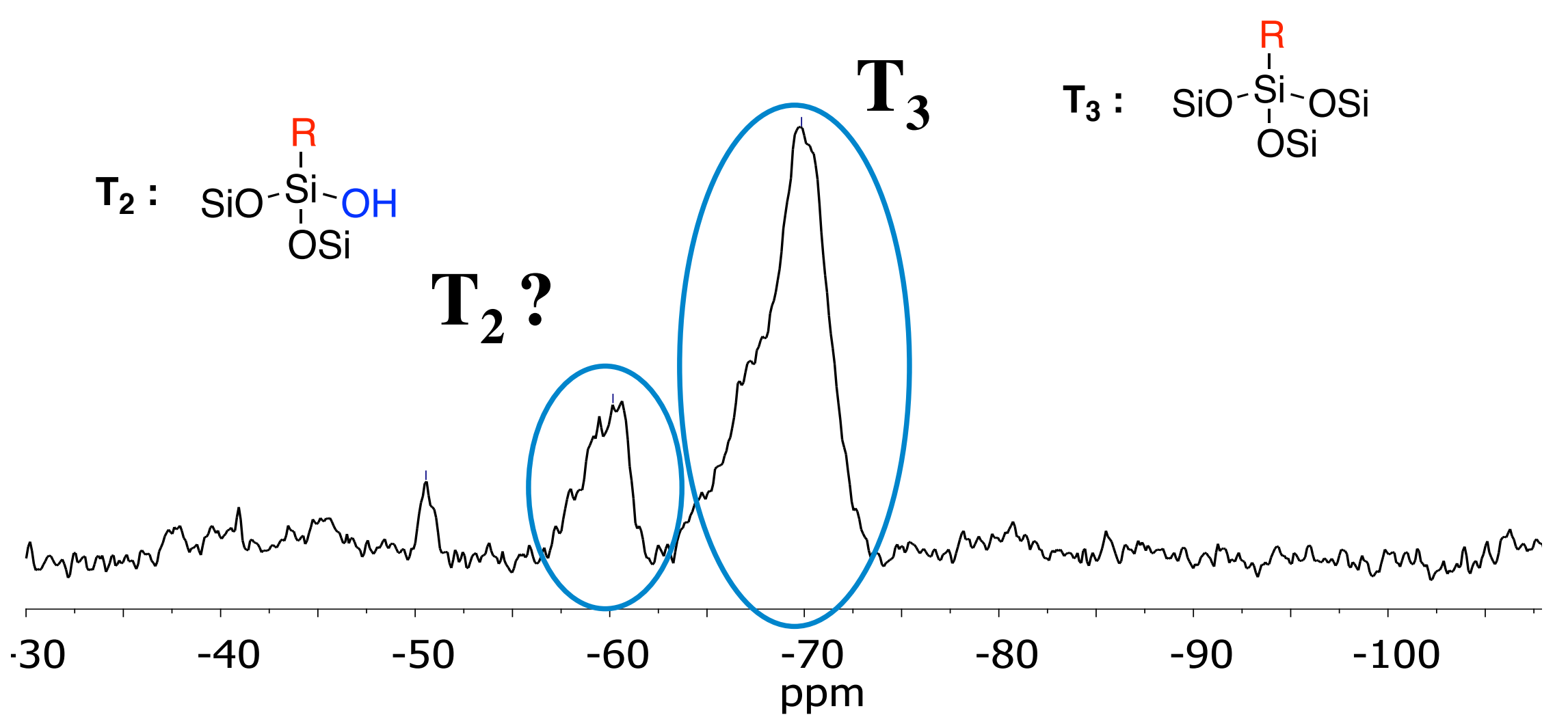
POSS-Imi (2)
yield: 85%

¹H-NMR (400MHz)

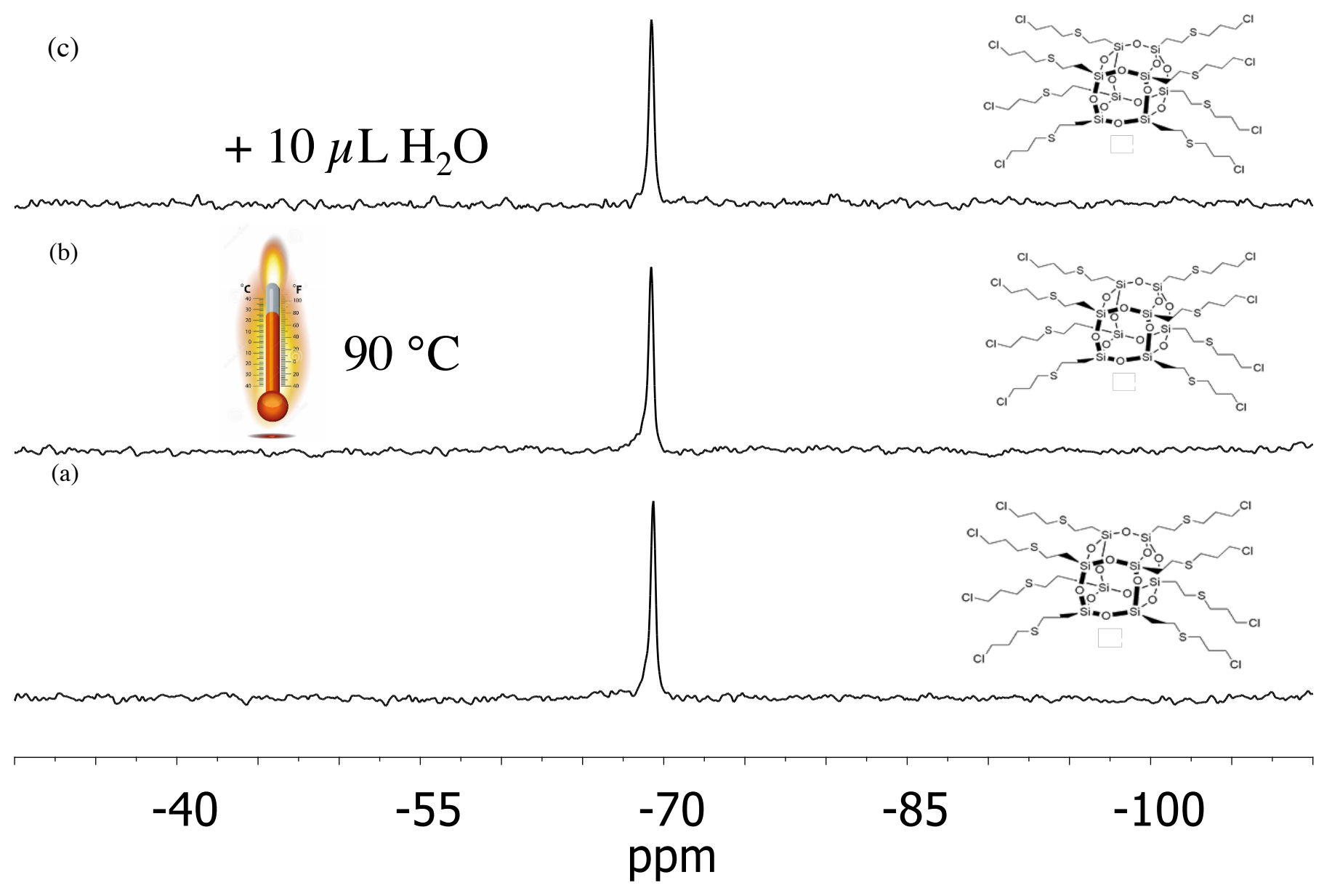


The anchoring of the imidazolium moieties is occurred?

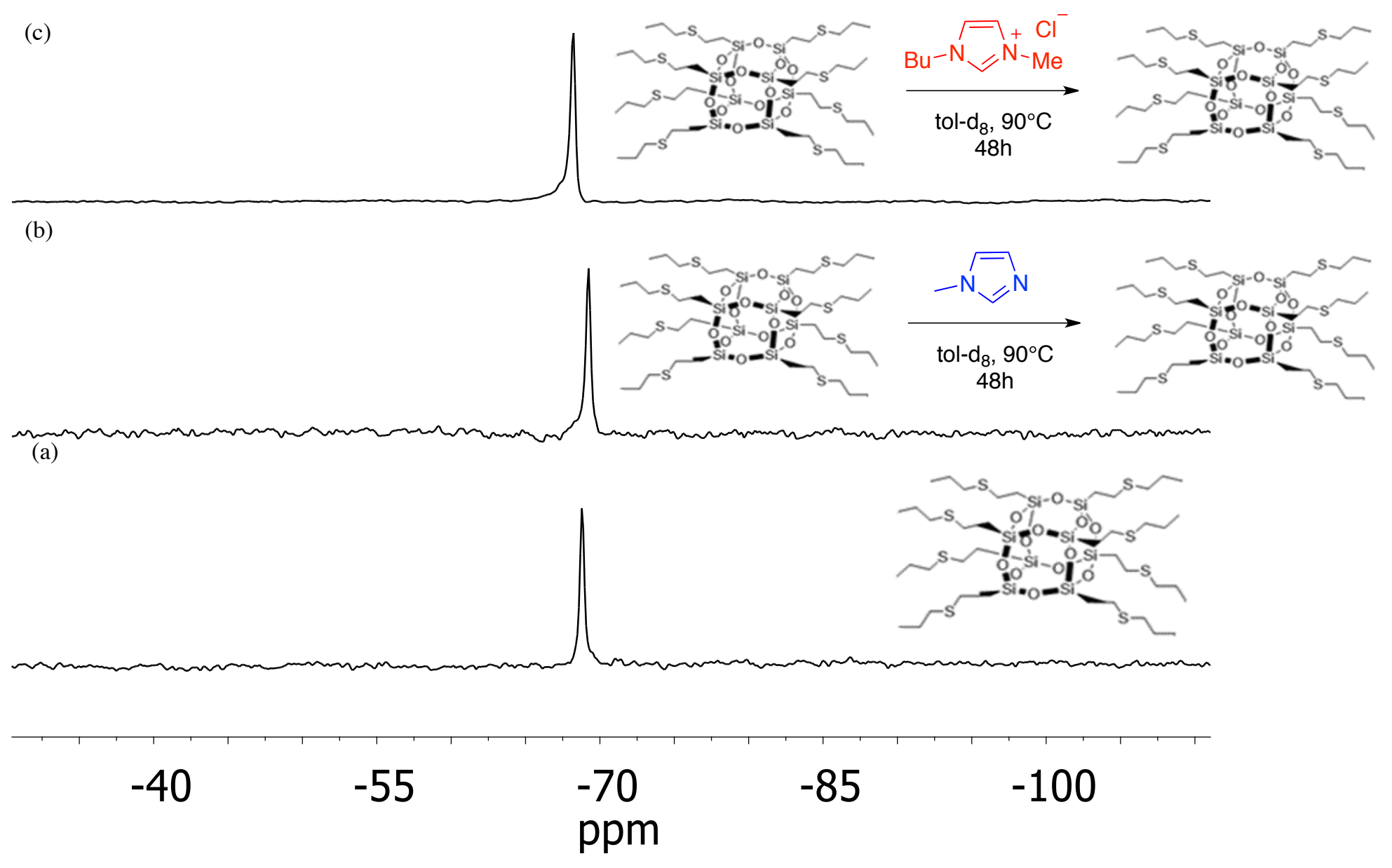
²⁹Si-NMR (500MHz)



Imidazolium based POSS is stable?

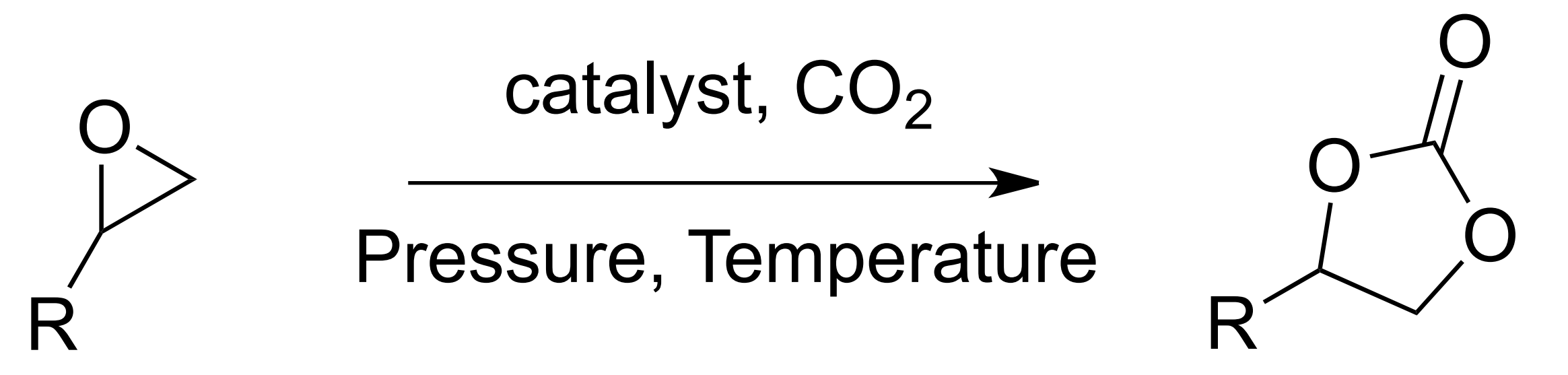


Experimental conditions: (a) POSS-Cl in tol-d8, (b) after 17 h at 90 °C, + 10 μL H2O after 48 h at 90 °C.

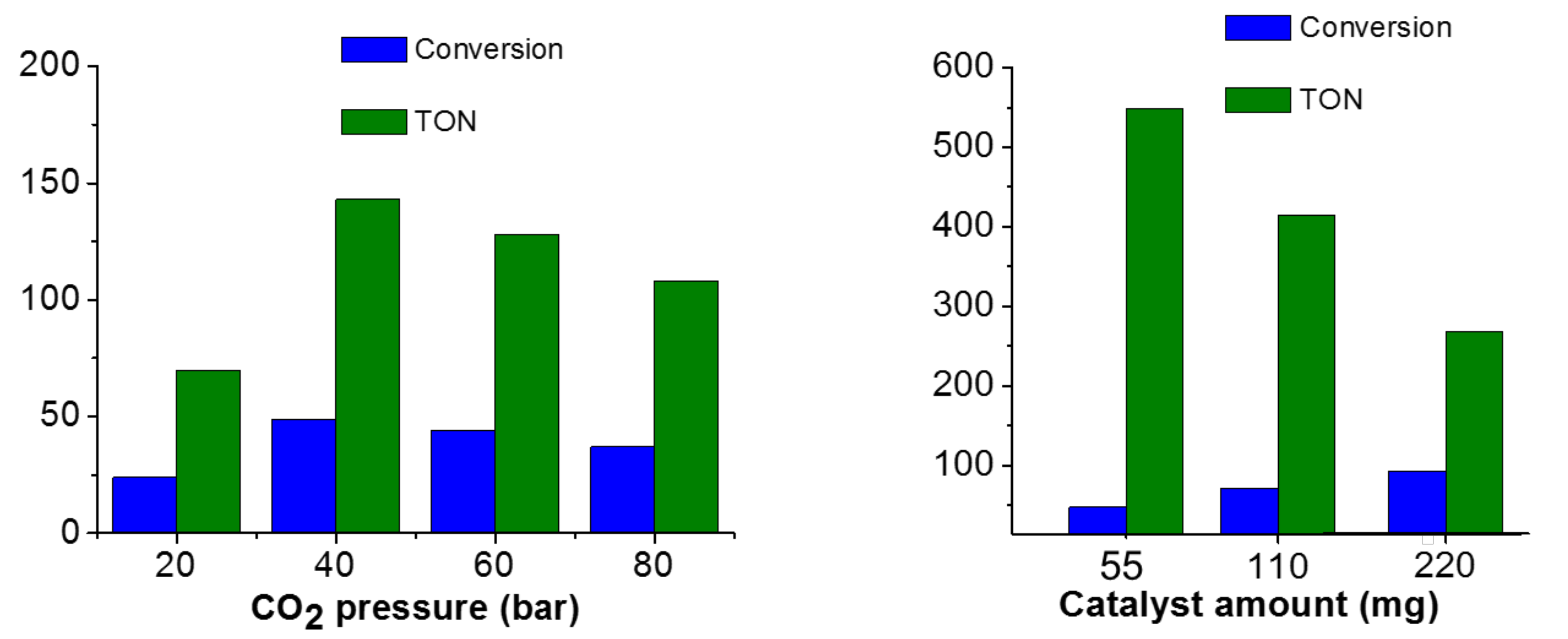


Experimental conditions: (a) POSS-CH_3 in tol-d_8, (b) POSS-CH_3 in tol-d_8 with 1-Me-Imi (24 eq.) after 48 h at 90°C, (c) POSS-CH_3 in tol-d_8 with 1-butyl-3-methyl imidazolium chloride (8 eq.) after 48 h at 90°C.

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 ($n_{converted}$ / $n_{active\ sites}$) of the reaction varying the CO_2 pressure at 125 °C, with 220 mg of catalyst in H_2O (a) and the catalyst amount at 40 bar, 150 °C, in H_2O (b).

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

Entry	Catalyst	Co-solvent (%)	Conversion (%)	Carbonate yield (%)	Selectivity (%)	TON
1	POSS-Imi	H_2O	71	51	72	410
2	POSS-Imi	MeOH	73	69	95	429
3	POSS-Imi	EtOH	85	81	95	299
4	POSS-Imi	^{i}PrOH	94	94	>99	553
5	BMim	^{i}PrOH	98	98	>99	326
6	POSS-Imi	EtOH (abs)	84	84	>99	490

Table 1: 110 mg of catalyst (which corrisponds to 0.36 mmol of imidazolium sites in POSS-Imi), 40 bar, 150°C, 24 mL (210 mmol) of styrene oxyde, 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 easly recovered from the reaction mixture by extraction and the structure was confirmed by ²⁹Si-NMR. In addition, POSS-Imi was tested with other epoxides (1-butene oxyde, epychlorohydrin) displaying exellent performances, even at lower temperature (100 °C, TON equal to 476) with epychloridrin as substrate.

IV. CONCLUSION: The synthesis of imidazolium functionalized polyhedral oligomeric silsesquioxane was successfully achieved. This system was full characterized in particular via ²⁹Si NMR spectroscopy and used as catalyst for the conversion of the CO_2 with epoxydes to obtain the corrisponding cyclic carbonates. Differents reaction conditions were investigated obtaining exellent 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 Academie Universitaire de Louvain co-funded by the Marie Curie Actions of the European Commision.