

SUPPLEMENTARY INFORMATION for

A rational investigation of the Lewis acid promoted coupling of carbon dioxide with cyclohexene oxide: towards CO₂-sourced polycyclohexene carbonate under solvent and co-catalyst free conditions

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ESI 1: Coupling of cyclohexene oxide with CO₂: determination of the conversion and selectivity

The conversion of cyclohexene oxide and the selectivity towards the formation of the cyclic carbonate, the polycarbonate and the polyether were determined by comparing the relative intensities of characteristic peaks of each species according to the following formula:

$$\text{Conversion (\%)} = 1 - \frac{\left[\frac{A_{534}}{A_{CH_2(2934)}} \right]_{\text{Reaction mixture}}}{\left[\frac{A_{534}}{A_{CH_2(2934)}} \right]_{\text{Neat CHO}}}$$

$$\text{Yield CHC: } Y_{CHC}(\%) = \frac{\left[\frac{A_{1803}}{A_{CH_2(2934)}} \right]_{\text{Reaction mixture}}}{\left[\frac{A_{1803}}{A_{CH_2(2934)}} \right]_{\text{Neat CHC}}}$$

$$\text{Yield PCHC: } Y_{PCHC}(\%) = \frac{\left[\frac{A_{1740}}{A_{CH_2(2934)}} \right]_{\text{Reaction mixture}}}{\left[\frac{A_{1740}}{A_{CH_2(2934)}} \right]_{\text{Neat PCHC}}}$$

$$\text{Yield PE: } Y_{PE}(\%) = \frac{\left[\frac{A_{1080}}{A_{CH_2(2934)}} \right]_{\text{Reaction mixture}}}{\left[\frac{A_{1080}}{A_{CH_2(2934)}} \right]_{\text{Neat PE}}}$$

$$\text{Selectivity CHC: } S_{CHC} = \frac{Y_{CHC}}{Y_{CHC} + Y_{PCHC} + Y_{PE}} \times 100$$

$$\text{Selectivity PCHC: } S_{PCHC} = \frac{Y_{PCHC}}{Y_{CHC} + Y_{PCHC} + Y_{PE}} \times 100$$

$$\text{Selectivity PE: } S_{PE} = \frac{Y_{PE}}{Y_{CHC} + Y_{PCHC} + Y_{PE}} \times 100$$

ESI 2: Coupling of cyclohexene oxide with CO₂: characterization of the polymer by ¹H NMR

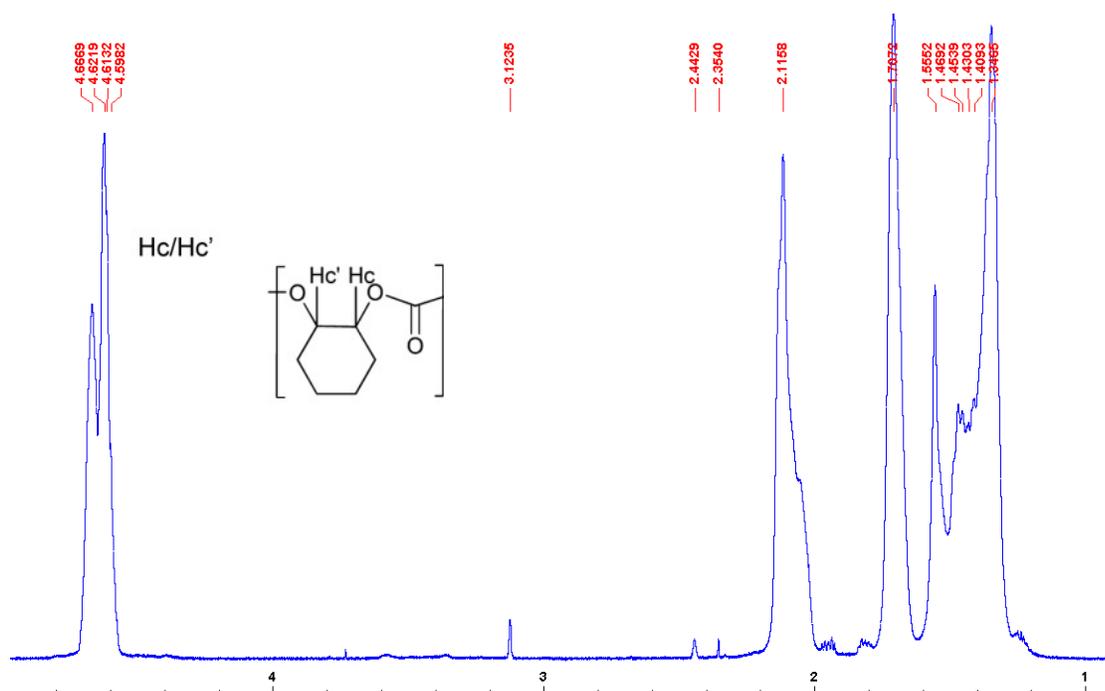


Figure S1: ¹H NMR spectra in CDCl₃ of the purified product obtained after 20h of reaction of cyclohexene oxide with CO₂ catalyzed by ZnTos. Conditions: 70 °C, 40 bar and 1 mol% of catalyst. The residual broad barely detected signal at 3.4-3.5 ppm corresponds to less than 1% of ether linkages in PCHC. [1, 2]

ESI 3: Influence of the nature of the co-catalyst on the Sc and Y complexes

Preliminary investigations of the influence of a co-catalyst on the selectivity of the Sc and Y complexes towards the formation of PCHC have been performed and put in evidence only a slight improvement of their selectivity towards the formation of PCHC.

Table S1: Catalytic studies performed with Y(OTf)₃ and Sc(OTf)₃ catalysts using various cocatalysts^a

Entry	Cat./co-cat.	Cat.:co-cat ratio	Conv ^b (%)	S _{CHC} ^c (%)	S _{PCHC} ^d (%)	S _{PE} ^e (%)
1	Sc(OTf) ₃ /Et ₄ NCl	1:1	85	0	6	94
2	"	1:10	15	52	7	41
3	Sc(OTf) ₃ /BMIBr	1:1	88	0	7	93
4	"	1:10	48	100	0	0
5	Y(OTf) ₃ /PPNCl	1:0.5	90	0	5	95
6	"	1:1	66	0	14	86
7	"	1:2	76	0	2	98

^a Conditions: 5 mmoles cyclohexene oxide, 1 mol% catalyst, 60°C, 20 h, 4MPa CO₂.

^b Conv: CHO conversion.

^c S_{CHC}: selectivity to cyclic carbonate.

^d S_{PCHC}: selectivity to polycarbonate.

^e S_{PE}: selectivity to polyether.

ESI 4: Influence of solvents of different polarity on the activity of the Zn(OTf)₂/Et₄NTos catalytic platform

The influence of solvents of different polarity on the activity of the Zn(OTf)₂/Et₄NTos catalytic platform for the synthesis of PCHC was evaluated. Toluene, Tetrahydrofuran (THF) and Dichloromethane (CH₂Cl₂) have been chosen as PCHC is known to be soluble in these solvents. Experimental results obtained for different solvent concentration at 70°C, 4 MPa after 20 h are summarized in Table S2. At 0.2ml of solvent and whatever the nature of the solvent, the selectivity towards the formation of PCHC is only moderately improved in comparison with the one reported under neat conditions. At higher solvent concentration, the selectivity towards the formation of PCHC is further slightly improved in the presence of Toluene (entries 2-4) and CH₂Cl₂ (entries 8-10) but a decrease is clearly observed with THF (entries 5-7). Therefore, even though the better results were obtained in toluene, the conversion and selectivity towards the formation of PCHC remain relatively comparable to the one reported under neat conditions.

Table S2: Catalytic studies performed with Zn(OTf)₂/Et₄NTos catalytic platforms using various solvents at different concentration^a

Entry	Cat./co-cat.	Solvent (ml)	Conv ^b (%)	S _{CHC} ^c (%)	S _{PCHC} ^d (%)	S _{PE} ^e (%)
1	Zn(OTf) ₂ / Et ₄ NTos	No solvent	83	0	78	22
2	"	Toluene (0.2)	84	4	79	17
3	"	Toluene (0.4)	87	6	82	12
4	"	Toluene (0.6)	90	7	82	11
5	"	THF (0.2)	78	2	84	14
6	"	THF (0.4)	70	2	50	48
7	"	THF (0.6)	67	1	13	86
8	"	CH ₂ Cl ₂ (0.2)	71	6	81	13
9	"	CH ₂ Cl ₂ (0.4)	72	6	80	14
10	"	CH ₂ Cl ₂ (0.6)	77	8	82	10

^a Conditions: 5 mmoles cyclohexene oxide, 1 mol% catalyst, 1:2 Cat./Co-cat ratio, 70°C, 20 h, 4MPa CO₂.

^b Conv: CHO conversion.

^c S_{CHC}: selectivity to cyclic carbonate.

^d S_{PCHC}: selectivity to polycarbonate.

^e S_{PE}: selectivity to polyether.

1. Buchard, A.; Kember, M.R.; Sandeman, K.G.; Williams, C.K., A bimetallic iron(iii) catalyst for CO₂/epoxide coupling. *Chem. Comm.*, **2011**, *47*, 212-214.
2. Taherimehr, M.; Pescarmona, P.P., Green polycarbonates prepared by the copolymerization of CO₂ with epoxides. *J. Appl. Polym. Sci.*, **2014**, *131*, 41141.

