

Sustainable Synthesis of Polymeric Materials versus Fine Chemicals via CO₂ Addition to Epoxides [†]

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[†] Presented at the 24th International Electronic Conference on Synthetic Organic Chemistry, 15 November–15 December 2020; Available online: <https://ecsoc-24.sciforum.net/>.

Abstract: The development of efficient chemical processes capable of transforming carbon dioxide (CO₂) into value-added products constitutes one of the greatest challenges for the scientific community. In this context, the use of carbon dioxide as a C1 source is a relevant topic and, over the last decade, there has been remarkable scientific and technological advances regarding the development of chemical processes for converting CO₂ into added value products. We highlight the reaction of CO₂ addition to epoxides, from which it is possible to selectively obtain two types of products: cyclic carbonates and polycarbonates, both with relevant applications as fine chemicals and polymeric materials, respectively.

Keywords: carbon dioxide; metallophthalocyanines; metalloporphyrins; CO₂ addition to epoxides; polycarbonates; cyclic carbonates

Citation: Gonzalez, A.C.S.; Aroso, R.T.; Carrilho, R.M.B.; Pereira, M.M. Sustainable Synthesis of Polymeric Materials Versus Fine Chemicals via CO₂ Addition to Epoxides. *Chem. Proc.* **2021**, *3*, 17. <https://doi.org/10.3390/ecsoc-24-08357>

Academic Editors: Julio A. Seijas and M. Pilar Vázquez-Tato

Published: 14 November 2020

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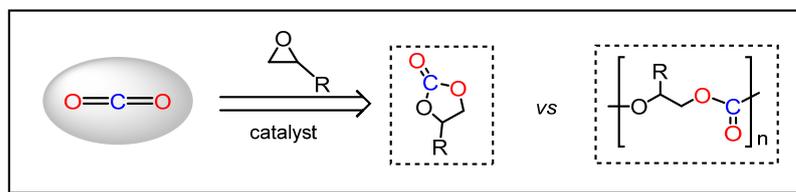
1. Introduction

CO₂ is considered an ideal reagent because it is renewable, abundant, and non-toxic. On the other hand, it is one of the main greenhouse gases, being responsible for the increase in earth temperature (global warming), due to its accumulation in the atmosphere [1,2]. For this reason, its consumption on a large scale may allow a reduction in its index in the terrestrial atmosphere, so its use as raw material in chemical synthesis is a notable advantage. However, CO₂ has high kinetic stability. Therefore, to turn carbon dioxide into a viable chemical reagent, it is necessary to develop efficient catalysts able to overcome the energy barrier and to promote its chemical conversion [3–6].

Due to its high abundance and reduced toxicity, an increasing number of applications of carbon dioxide as a reagent have been recently developed to produce added value chemicals, namely in the synthesis of carboxylic acids derivatives, carbamates, formamides, organic carbonates, cyclic carbonates and polycarbonates [7–9]. Among them, CO₂ addition to epoxides (Scheme 1) is particularly relevant since the resulting possible products, cyclic carbonates and polycarbonates, have numerous applications as “green” organic solvents and in the industry of plastics, respectively [10–12].

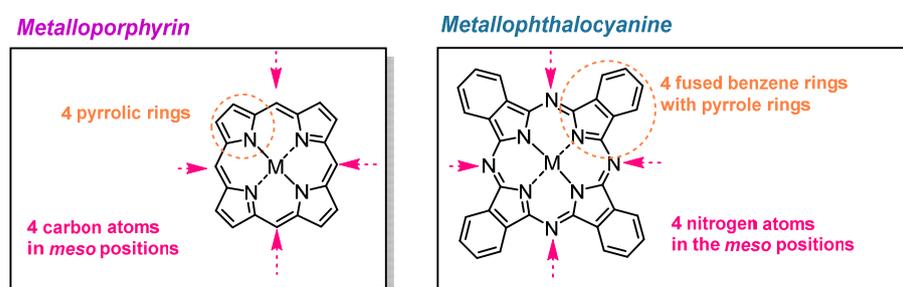
In the last decade, there have been countless scientific and technological advances regarding the development of efficient catalysts for converting CO₂ into value-added polycarbonates and cyclic carbonates, highlighting the organometallic complexes, based on salens [13], triphenolates [14], diiminates [15], and tetrapyrrolic macrocycles [16–19]

(metalloporphyrins and metallophthalocyanines). The latter are particularly interesting since their planar structure makes them suitable for efficient coordination of the oxygen atom of the epoxide with the metal center (Lewis acid).



Scheme 1. CO₂ addition to epoxides.

In the present work, we describe the synthesis and application of metalloporphyrins and metallophthalocyanines (Scheme 2) as catalysts in CO₂ addition reactions to epoxides. The effects of substrate, catalyst structure, as well as the reaction conditions (temperature and CO₂ pressure) on the modulation of the reaction selectivity are discussed.



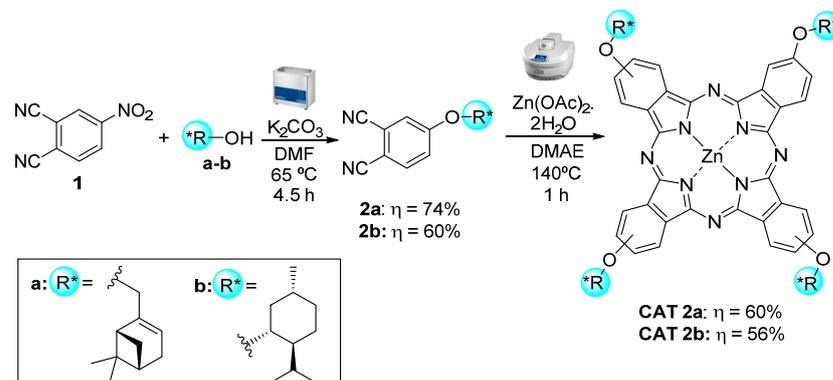
Scheme 2. General structure of a metalloporphyrin and a metallophthalocyanine.

2. Results and Discussion

2.1. Synthesis of the Catalysts

2.1.1. Monoterpene-Based Metallophthalocyanines

The synthesis of monoterpene-based metallophthalocyanines was performed in two steps: first, the preparation of phthalonitrile precursors, through nucleophilic aromatic substitution of (1*R*)-(-)-myrtenol and (1*R*,2*S*,5*R*)-(-)-menthol with 4-nitrothalonitrile (**1**), followed by cyclotetramerization reactions, using Zn(II) acetate as template. In order to increase energy efficiency and the sustainability of the synthesis of these catalysts, alternative approaches were used, such as the use of ultrasound irradiation to promote the synthesis of the phthalonitrile precursor and microwave irradiation to promote the subsequent cyclotetramerization reaction with the metal salt (Scheme 3).

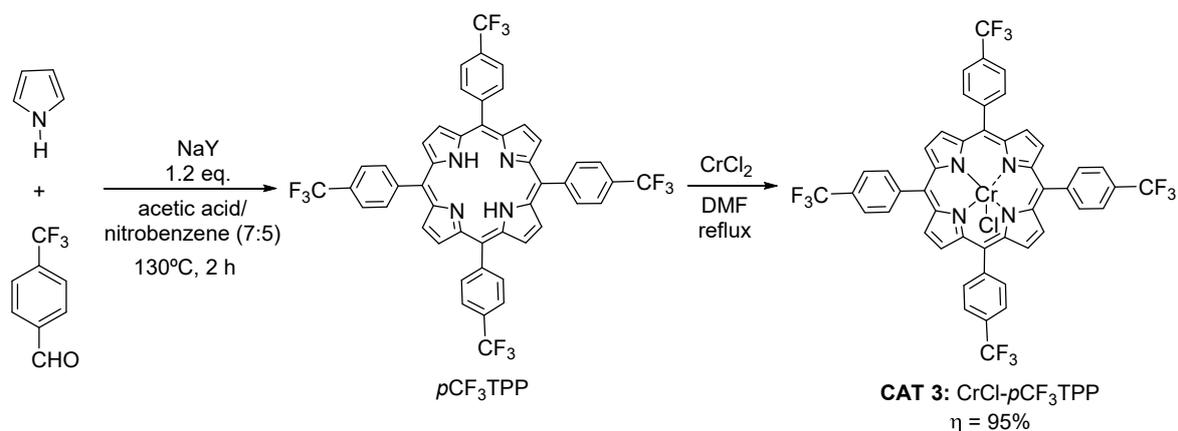


Scheme 3 General strategy for the synthesis of metallophthalocyanines derived from monoterpenes.

The first step consisted of the *ipso*-nitro substitution reaction between 4-nitrophthalonitrile and the intended alcohol, using ultrasound irradiation as heating source, with a complete reaction being observed after 4.5 h, with derivatives of phthalonitriles being obtained of (1*R*)-(-)-myrtenol and (1*R*,2*S*,5*R*)-(-)-menthol with yields of 74% and 60%, respectively. Next, we proceeded with the second step in the synthesis of the metallophthalocyanine type catalysts, which consisted in the condensation of the synthesized phthalonitriles with the desired metal salt. Thus, the cyclotetramerization reactions of phthalonitrile precursors derived from monoterpenes **2a** and **2b**, were carried out, using the metal salt Zn(OAc)₂ as a template and *N,N*-dimethylaminoethanol (DMAE) as solvent, using microwave irradiation as heating source. After 1 h of reaction, it was possible to observe the total consumption of the starting material, with yields of 60% for **CAT 2a** and 56% for **CAT 2b**, after purification by flash chromatography.

2.1.2. Fluorinated Metalloporphyrin

Regarding the metalloporphyrin catalyst **CAT 3**, it was synthesized in two steps, first through reaction of equimolar amounts of pyrrole with the desired aldehyde in a nitrobenzene and acetic acid mixture, using NaY zeolite as solid catalyst, following the method previously developed in the Coimbra group followed by metalation of the free base porphyrin with CrCl₂ in refluxing dimethylformamide (DMF) (Scheme 4) [17]. After purification by column chromatography over alumina with CHCl₃ as the eluent and solvents evaporation, the product was dried overnight under vacuum at 100 °C, yielding the chromium porphyrin complex CrCl-*p*-CF₃TPP (**CAT 3**) as a dark green solid, in 95% yield.

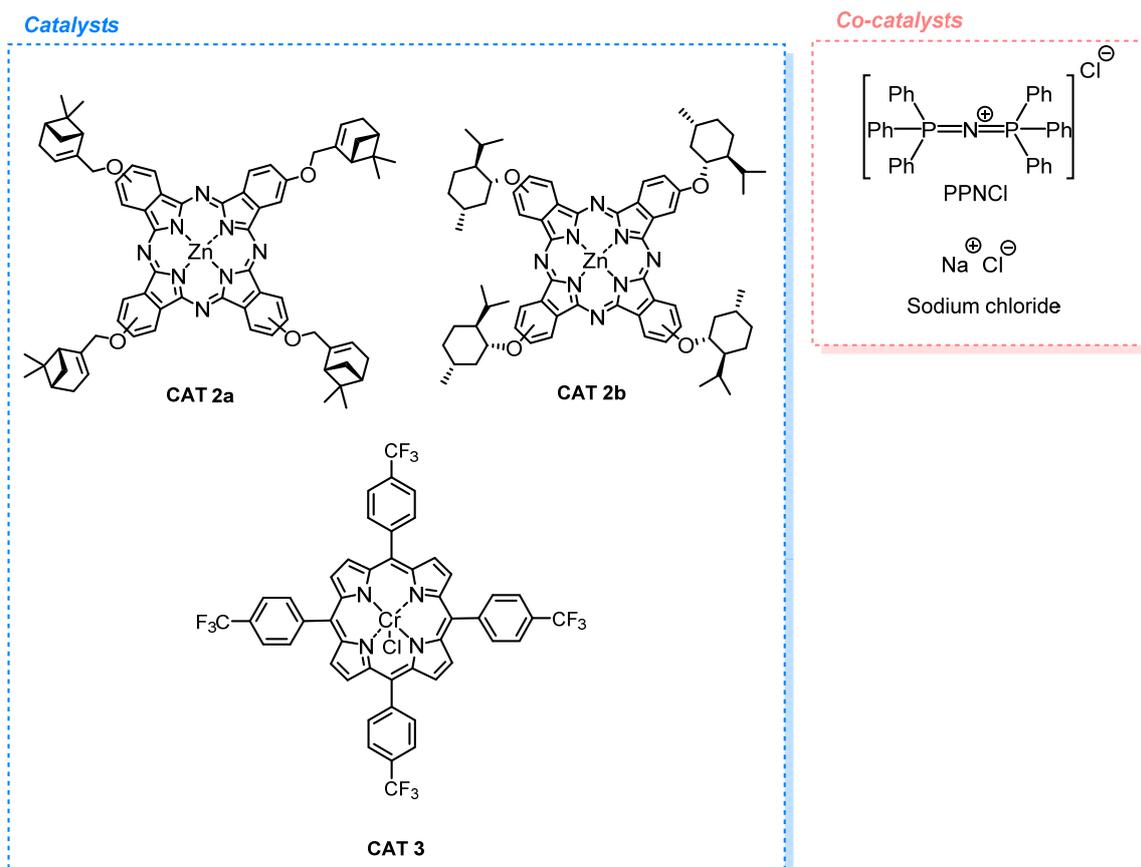


Scheme 4. Synthesis of the fluorinated metalloporphyrin catalyst.

2.2. CO₂ Addition Reaction to Epoxides

The evaluation of tetrapyrrolic macrocycle catalysts, in the presence of bis (tri-phenylphosphine) imine (PPNCl) or sodium chloride (NaCl) as co-catalysts (Scheme 5) was first performed using styrene oxide as substrate.

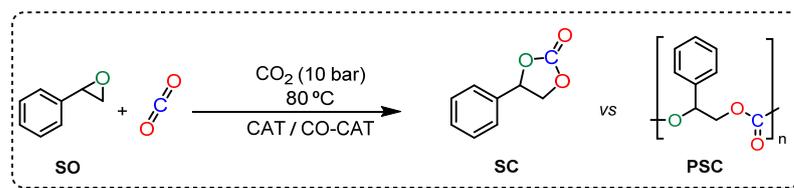
In a typical reaction, the tetrapyrrolic macrocycle catalyst and the co-catalyst (when used), were placed inside the reactor beaker. After 2 h under vacuum, at 80 °C, the epoxide was added via cannula. Then, the autoclave was pressurized with 10 bar of CO₂, and the reactor was kept at 80 °C, under stirring, for 24 h, without adding solvent. At the end of this time, the reactor was cooled and depressurized, and the reaction crude was analyzed by ¹H NMR, from which the conversion and selectivity values were calculated. The results obtained are shown in Table 1.



Scheme 5. Structures of catalysts and co-catalysts.

Using the metallophthalocyanine **CAT 2a** as a catalyst, in the absence of a co-catalyst, no conversion was observed under the conditions described above (Table 1, entry 1). Then, the reaction was performed under the same conditions, but in addition to **CAT 2a**, PPNCI was added as a co-catalyst, leading to 63% conversion in 24 h (TON = 900), with 100% selectivity for the cyclic carbonate (Table 1, entry 2). Then, NaCl was tested as a co-catalyst under the same reaction conditions, but no conversion was observed using the **CAT 2a**/NaCl catalytic system (Table 1, entry 3). Using **CAT 2b**, in the presence of PPNCI as co-catalyst, a similar conversion was obtained, comparing with the catalytic system **CAT 2a**/PPNCI, and 100% selectivity for the cyclic carbonate was also observed (Table 1, entries 2 and 4). Regarding the metallophthalocyanine-based catalysts, we were able to conclude that the presence of co-catalyst is essential for the addition of CO₂ to the styrene oxide, observing a synergistic effect between the metal center and the co-catalyst.

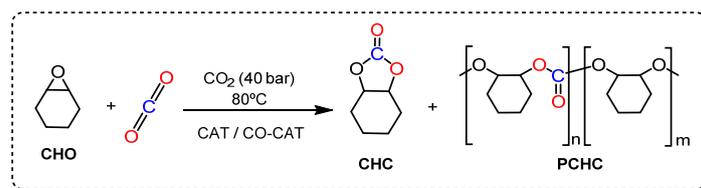
With the metalloporphyrin catalyst **CAT 3**, in the absence of co-catalyst, we observed 85% of conversion in 24 h, and it was possible to demonstrate a markedly different selectivity, with preferential formation (64%) for polycarbonate (Table 2, entry 5). Finally, the catalytic system **CAT 3**/PPNCI has been shown to have the highest catalytic activity (TON = 1425), with full conversion in 5 h and total selectivity for cyclic carbonate (Table 1, entry 6).

Table 1. Catalytic evaluation of in CO₂ addition to styrene oxide ^a.

Entry	Catalyst	Co-Catalyst	Conversion (%) ^b	TON ^c	Selectivity (%) ^d		Polymers		
					SC	PSC	% CO ₂ ^f	M _n ^g	PD ^g
1	CAT 2a	-	0	-	-	-	-	-	-
2	CAT 2a	PPNCl	63	900	100	-	-	-	-
3	CAT 2a	NaCl	0	-	-	-	-	-	-
4	CAT2b	PPNCl	59	843	100	-	-	-	-
5	CAT 3	-	85	1224	36	64	91	4200	1.20
6 ^e	CAT 3	PPNCl	100	1425	100	0	-	-	-
7	-	PPNCl	30	429	100	-	-	-	-

Reaction conditions: ^a styrene oxide (35 mmol, 4 mL); catalyst: 0.07 mol%; co-catalyst (when used): PPNCl or NaCl 0.07 mol%; T = 80 °C, P (CO₂) = 10 bar; t = 24 h; ^b % Conv. = Conversion determined by ¹H NMR, using the integrals ratio; ^c % TON (turnover number) = number of moles converted/number of moles catalyst. ^d % Cyclic carbonate selectivity determined by ¹H NMR. ^e t = 5 h. ^f % CO₂ content in polymers determined by ¹H NMR integral ratio of carbonate linkages/(carbonate linkages+ether linkages). ^g Number average molecular weight and polydispersity determined by GPC, using polystyrene as standard.

The catalysts were then evaluated in the CO₂ addition to cyclohexene oxide. The reactions were conducted at a pressure of 40 bar of CO₂, at a temperature of 80 °C, under stirring for 24 h. At the end, the reactor was cooled and depressurized, and the reaction crude was analyzed by ¹H NMR, from which the conversion value was calculated. The results obtained and the respective conversion values, as well as the TON and selectivity are presented in Table 2.

Table 2. Catalytic evaluation in the reaction of CO₂ addition to cyclohexene oxide ^a.

Entry	Catalyst	Co-Catalyst	Conversion (%) ^b	TON	Selectivity (%) ^c		% CO ₂	M _n (g/mol)	PD
					PCHC	CHC			
1	CAT 2a	PPNCl	0	-	-	-	-	-	
2	CAT 3	-	0	-	-	-	-	-	
3	CAT 3	PPNCl	86	1224	99	1	98	4800	1.25
4 ^d	CAT 3	PPNCl	86	1224	96	4	98	12,500	1.38
5	-	PPNCl	28	200	0	100	-	-	

Reaction conditions: ^a cyclohexene oxide (40 mmol, 4 mL); catalyst: 0.14 mol%; co-catalyst (when indicated): PPNCl or NaCl 0.14 mol%; T = 80 °C, P (CO₂) = 40 bar; t = 24 h; ^b % Conv. = Conversion determined by ¹H NMR; ^c % Selectivity determined by ¹H NMR through the ratio of the polycarbonate and cyclic carbonate signals. ^d P(CO₂) = 70 bar.

Using the CAT 2a and PPNCl catalytic system in cyclohexene oxide, under the conditions described, no conversion was observed after 24 h (Table 2, entry 1). With the metalloporphyrin catalyst CAT 3, in the absence of co-catalyst, no conversion was observed in 24 h (Table 2, entry 2). However, with CAT 3, in the presence of PPNCl as a co-catalyst,

86% conversion was observed, with high selectivity for the formation of polycarbonate (Table 2, entry 3). Then, with the reaction temperature set on 80 °C, the effect of the pressure was then evaluated using 70 bar of CO₂ (Table 2, entry 4) and we observed no significant effects, either in catalytic activity or selectivity for copolymers (Table 1, entries 3 and 4).

The polycarbonate structure was analyzed by ¹H NMR, ¹³C NMR and MALDI-TOF spectroscopy, which demonstrated high carbonate incorporation (98–99%). Gel permeation chromatography revealed number-average molecular weights (M_n) in the range of 4800 to 12,500 and narrow molecular weight distributions (M_w/M_n in the range 1.25 to 1.38).

3. Materials and Methods

3.1. Reagents

All reagents and solvents were purchased from Sigma-Aldrich (Lisbon, Portugal), and were used with the degree of purity described by the supplier. The solvents used in the synthesis reactions were, whenever necessary, purified, or dried according to the methods described in the literature. Air and moisture sensitive reagents were manipulated using Schlenk techniques, under a nitrogen or argon atmosphere, in a vacuum system. All glass material was dried in an oven at 100 °C.

3.2. Equipment

¹H and ¹³C NMR spectra were recorded in CDCl₃ on a Bruker DRX 400 spectrometer, operating at 400.13 MHz for ¹H and 100.61 MHz for ¹³C. Chemical shifts for ¹H and ¹³C are expressed in ppm, relatively to a tetramethylsilane (TMS) as internal standard, or relatively to residual peaks, present in the deuterated solvents used, CDCl₃ or DMSO-d₆. Microwave-assisted experiments were performed in an appropriate thick-walled glass vial (10 mL) under closed-vessel conditions, using a CEM Discover[®] SP Microwave System. Flash chromatography was performed by an Interchim[®] PuriFlash[®] XS 420 System (Interchim, France), equipped with a PuriFlash[®] SI-HP F0004 (15 μ) column, using CH₂Cl₂/EtOAc gradients, with a 10 mL/min flow. Ultrasound-assisted reactions were performed in a Bandelin Sonorex RK 100H apparatus. Gel permeation chromatography (GPC) measurements (URV, Tarragona, Spain) were made in toluene, versus polystyrene standards, on a Millipore–Waters 510 HPLC Pump device (Milford, MA, USA) using a three-serial column system (MZ-Gel 100 Å, MZ-Gel 1000 Å, MZ-Gel 10,000 Å linear columns, Millipore–Waters, Milford, MA, USA) with UV-Detector (ERC-7215) and IR-Detector (ERC-7515a, Millipore–Waters, Milford, MA, USA). The software used to get the data was NTeqGPC 5.1 (Millipore–Waters, Milford, MA, USA). Samples were prepared as follows: 5 mg of the copolymer was dissolved with 2 mL of toluene (HPLC grade). MALDI-TOF analyses were performed on a Voyager System 4412 instrument equipped with a 337 nm nitrogen laser (Applied Biosystems, Foster City, CA, USA). All spectra were acquired in the positive ion reflector mode. Dithranol (Sigma-Aldrich, Madrid, Spain) was used as matrix, which was dissolved in MeOH (Panreac, Barcelona, Spain) at a concentration of 10 mg·mL⁻¹. The polymer (5 mg) was dissolved in 1 mL of CHCl₃ (Euriso-Top, Saint-Aubin, France). Then, 1 μL of the sample, 1 μL of the matrix, and 1 μL of potassium trifluoroacetate (KTFA) solution in the case of polymers (1 mg of KTFA in 1 mL of THF) were deposited consecutively on the stainless-steel sample holder and allowed to dry before introduction into the mass spectrometer. The three independent measurements were made for each sample. For each spectrum, 100 laser shots were accumulated. Elemental analysis was done at the Serveis Tècnics de Recerca (Universitat de Girona, Spain).

3.3. Synthesis of Metallophthalocyanine Catalysts CAT 2a and CAT 2b

The monoterpene-based metallophthalocyanines 2(3),9(10),16(17),23(24)-tetrakis(((1R,5S)-6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl)methoxy) phthalocyanato zinc(II) (CAT 2a) and 2(3),9(10),16(17),23(24)-tetrakis(((1R,2S,5R)-2-isopropyl-5-methylcyclohexyl)oxy)

phthalocyanato zinc(II) (**CAT 2b**) were prepared by reacting the corresponding phthalonitrile (1.08 mmol) with zinc acetate (0.36 mmol), using *N,N*-dimethylaminoethanol (2.5 mL) as solvent, under microwave irradiation ($P = 120$ W, 140 °C, 1 h). The progress of the reaction was monitored by thin-layer chromatography (TLC), using a mixture of dichloromethane: ethyl acetate as the mobile phase and through UV-Vis absorption spectroscopy. After observing the total consumption of the starting phthalonitrile, the reaction mixture was cooled to room temperature and then a mixture of water: methanol (10:1) was added until precipitation occurred. The precipitate was subsequently vacuum filtered using a sintered plate glass funnel and dried under vacuum. The compounds were purified by flash chromatography using a mixture of dichloromethane: ethyl acetate as a gradient, starting with 100% dichloromethane (30 min), then the gradient was gradually changed to a mixture of dichloromethane: ethyl acetate (1: 1) with a flow of 10 mL/min and, finally, 100% ethyl acetate (45 min) to obtain the desired compounds. After solvent evaporation, we obtained the **CAT 2a** with 60% yield (0.191 g) and the **CAT 2b** with 56% yield (0.179 g). The spectroscopic data is in accordance with the literature [20].

3.4. Synthesis of Metalloporphyrin Catalyst **CAT 3**

The catalyst 5,10,15,20-tetrakis(4-trifluoromethylphenyl)porphyrinato chromium(III) chloride (**CAT 3**) was synthesized in two steps: first, free porphyrin was synthesized by adding pyrrole to the aldehyde. Then, free base porphyrin (5,10,15,20-tetra-(4-(trifluoromethyl) phenyl) porphyrin (p-CF₃TPP)) (0.5 g, 0.564 mmol), previously synthesized, was dissolved in DMF (10 mL) and left at reflux until reaching 170 °C. Then, CrCl₂ (0.111 g, 0.902 mmol) was added to the reflux solution. The progress of the reaction was analyzed by TLC and UV-Vis and after 1 h 30 m of reaction, the reaction mixture was cooled to room temperature. Approximately 100 mL of ice water was added and subsequently extracted with dichloromethane (2×50 mL) and ethyl acetate (2×50 mL). Finally, the organic phase was dried over anhydrous sodium sulfate and the solvents were evaporated. 0.411 g of a purple solid were obtained ($\eta = 75\%$). The spectroscopic data are in accordance with the literature [21].

3.5. CO₂ Addition to Epoxides

The catalytic reactions of adding CO₂ to epoxides were carried out in a high-pressure reactor (autoclave), made of stainless steel. The catalyst and co-catalyst were placed in a glass beaker, inside the autoclave and it was left in vacuum for approximately 4 h, at a temperature of 80 °C. Then, the epoxide (4 mL), previously dried over an alumina column, was injected via cannula. The autoclave was then pressurized with CO₂ (10–40 bar) and the reaction proceeded at the desired temperature (80 °C). After 24 h of reaction, the autoclave was cooled and depressurized slowly. The reaction crude was analyzed by ¹H NMR to determine the conversion of each catalytic system. To determine selectivity, the reaction mixture was placed under vacuum, in a bath at 100 °C, for 12 h, to evaporate the solvent and the substrate (epoxide) to be reacted, and was analyzed by ¹H NMR.

3.6. Styrene Carbonate (SC) and Styrene Polycarbonate (SPC)

Styrene carbonate was obtained by the addition reaction of CO₂ (10 bar) to styrene oxide (4 mL, 35 mmol), using **CAT 2a** or **CAT 3** (0.0245 mmol) and PPNCl (14 mg, 0.0245 mmol) as a co-catalyst. At the end of the reaction, the mixture was placed under vacuum at 100 °C for approximately 12 h, to eliminate unreacted starting material. After this procedure, styrene carbonate was obtained with high purity, without being subjected to any purification process, with 90% yield (5.18 g). The styrene polycarbonate was obtained through the same procedure but using **CAT 3** as catalyst, without any-cocatalyst. The polymer was precipitated from the reaction crude with chloroform and diethyl ether, it was washed with *n*-hexane and dried under vacuum at 50 °C (45% yield, 2.59 g). The spectroscopic data is in accordance with the literature [22].

3.7. Poly(cyclohexene carbonate) (PCHC)

Poly(cyclohexene carbonate) was obtained by adding CO₂ to the cyclohexene oxide (4 mL, 40 mmol), using the metalloporphyrin CrCl-pCF₃TPP (**CAT 3**) as catalyst (27 mg, 0.028 mmol), in the presence of PPNCl (16 mg, 0.028 mmol) as a co-catalyst. The reaction crude was evaporated and the residue was dried in vacuo at 100 °C for approximately 5 h. Then, it was washed with n-hexane, filtered and left under vacuum at 100 °C for 12 h. Finally, the product obtained in 89% yield (4.64 g) was characterized by ¹H NMR and ¹³C NMR spectroscopy. The spectroscopic data are in accordance with the literature [17]

4. Conclusions

We have developed sustainable synthetic methods for preparation of two Zn(II) phthalocyanines containing monoterpenes in their peripheral structure, using ultrasound and microwave irradiation. After purification, the metallophthalocyanines were isolated in yields around 60%. In addition, a fluorinated chromium (III) porphyrin was also synthesized with 95% yield, using NaY as acid catalyst. Subsequently, these tetrapyrrole macrocyclic metal complexes were evaluated as catalysts in CO₂ addition to epoxides. The Zn(II) metallophthalocyanines were moderately active in the reaction of CO₂ addition to styrene oxide, using PPNCl as co-catalyst. There was no effect of the monoterpene structure on both catalytic activity and selectivity, both of which led to conversions in the order of 60%, in 24 h, with 100% selectivity for cyclic carbonates. However, these catalysts were not active in CO₂ addition reaction to cyclohexene oxide. The Cr(III) metalloporphyrin (**CAT 3**) was highly active in both substrates, and a significant effect of the presence of the co-catalyst was observed on the catalytic activity and the selectivity. For styrene oxide, in the absence of co-catalyst, **CAT 3** gave rise to polycarbonate as a major product (64%), while in the presence of PPNCl, complete conversion with 100% selectivity for cyclic carbonate was observed. Using cyclohexene oxide as substrate, the **CAT 3**/PPNCl catalytic system led to high conversion and selectivity for the polymer, with a high CO₂ incorporation (>98%). In sum, the Cr(III) trifluoromethylporphyrin-based catalytic system is an attractive catalyst, considering its easy synthesis, high selectivity for copolymerization, and high solubility in the epoxide substrates, avoiding the use of any additional solvent. Although the studied Zn (II) metallophthalocyanine catalysts presented modest activity, additional studies regarding the modulation of metallophthalocyanine catalysts (metal center and phthalocyanine scaffold) are currently underway, in order to increase their catalytic activity.

Funding: This work was supported by national funds through FCT—Foundation for Science and Technology, I.P., under projects UID/QUI/00313/2019 to the Coimbra Chemistry Centre and PTDC/QUI-OUT/27996/2017.

Acknowledgments: R.T.A. thanks the FCT for his Ph.D. grant (PD/BD/143123/2019).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no conflicts of interest.

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