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Electronic Supplementary Information for

Mn(III)-porphyrin catalysts for the cycloaddition of CO_2 with epoxides at atmospheric pressure: effects of Lewis acidity and ligand structure

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1. Characterization of Mn(III)-porphyrin complexes

1.1. Elemental analysis of H$_3$[Mn(Br$_x$T4CPP)] (x = 2, 4, and 6)

Elemental analysis data are given in Table S1. The proposed molecular formulas for the complexes present water and inorganic salts since the final step of the purification is accomplished by adding aqueous HCl and NaOH. The presence of NaCl or water does not modify the C/N ratio, although it contributes to changes in C, N, H data of the complexes.[45] In this way, we verified the C/N ratio for the new β-brominated Mn(III)-porphyrins and the theoretical percentage of carbon and nitrogen for the respective pure complexes (in the absence of other molecules). When comparing these values, we observed a small difference in the C/N ratio (error less than 2%), confirming that the proposed molecular formulas correspond to the obtained complexes.

Table S1. Elemental analysis of H$_3$[Mn(Br$_x$T4CPP)] (x = 2, 4, and 6; complexes **6**, **7**, and **8**, respectively).

Compound	Experimental Values		Theoretical Values[a]		C/N[b]		Error[c]
	C (%)	N (%)	C (%)	N (%)	Exp.	Theor.	(%)
6	55.31	5.29	57.62	5.60	12.1931	11.9992	1.62
7	47.57	4.55	49.77	4.84	12.1924	11.9919	1.67
8	41.35	3.96	43.81	4.26	12.1772	11.9930	1.54

[a] Theoretical values were calculated considering the pure complexes H$_3$[Mn(Br$_x$T4CPP)] (x = 2, 4, and 6).
[b] Calculated as (14.007 x C%) / (12.011 x N%) [1].
[c] The difference between the experimental and the theoretical C/N mole ratio divided by the theoretical value.

1.2. UV-Vis spectra of H$_3$[Mn(Br$_x$T4CPP)] (x = 2, 4, and 6)

The UV-vis spectra for this series of porphyrin H$_3$[Mn(Br$_x$T4CPP)] (x = 2, 4, and 6) in phosphate buffer (pH = 7.45), show similar behavior to that of its analogs in ester form [Mn(Br$_x$T4CMPP)Cl] in methanol, as shown in Table S2. Our group has previously shown that there is a correlation between the data of UV-vis spectra of Mn(III)-porphyrins anionic (carboxylate form, Figures S1-S3) in phosphate buffer and those of the corresponding neutral porphyrins (as methyl ester) in methanol. This is particularly useful for characterization of porphyrins containing carboxylate groups, which, like the novel compounds di, tetra and hexabrominated series of H$_3$[Mn(Br$_x$T4CPP)] (x = 2, 4, and 6) are handling and purification more difficult than their analogs in ester form.

Table S2. Comparison of data from the Soret band of porphyrins $H_3[Mn(Br_xT4CPP)]$ (in phosphate buffer pH = 6.5) and $[Mn(Br_xT4CMPP)Cl]$ (in methanol).

	Soret[a] Wavelength (nm) for $H_3[Mn(Br_xT4CPP)]$	Soret[b] Wavelength (nm) for $[Mn(Br_xT4CMPP)Cl]$
x = 0	466	466
x = 2	474	471
x = 4	476	476
x = 6	479	487
x = 8	493	494

[a] solvent: phosphate buffer (pH = 6.5);
[b] solvent: methanol.
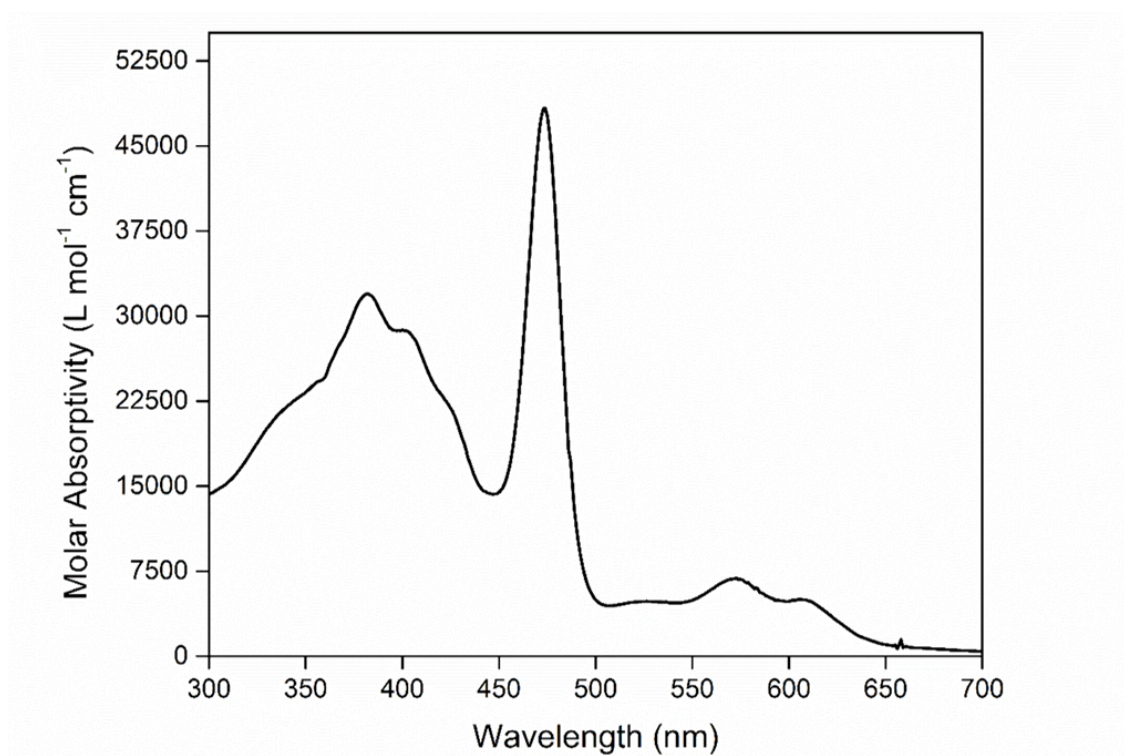
Figure S1. UV-Vis spectra of $H_3[Mn(Br_2T4CPP)]$ in phosphate buffer (pH = 7,45).
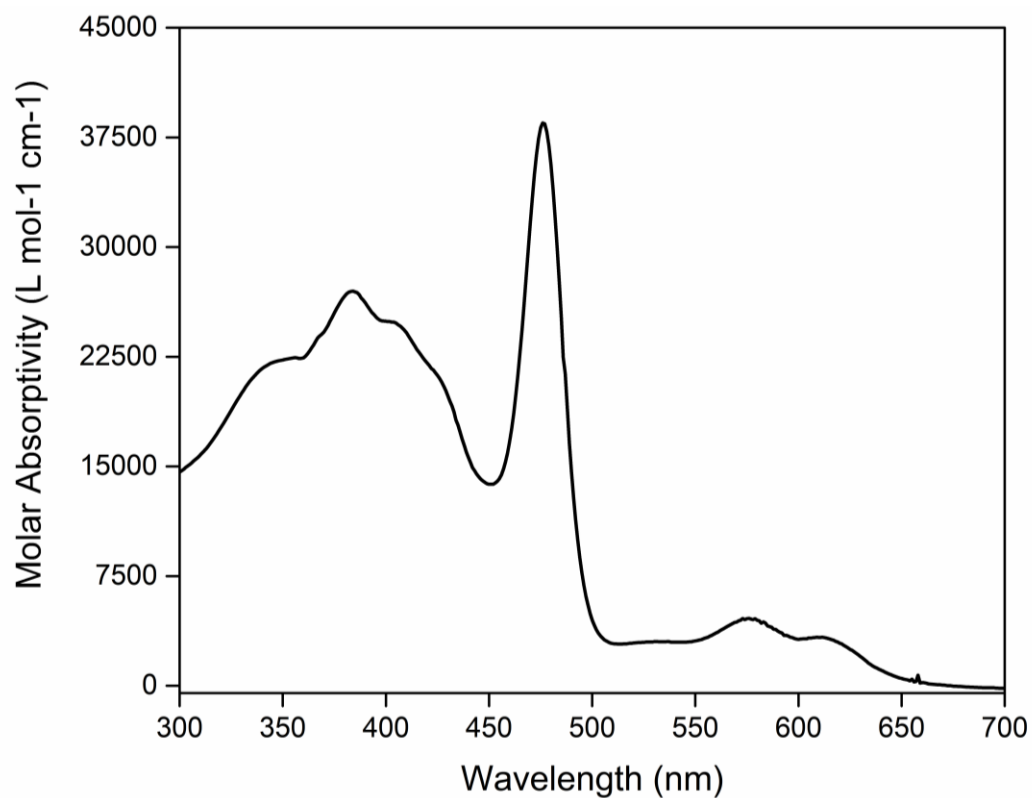
Figure S2. UV-Vis spectra of $H_3[Mn(Br_4T4CPP)]$ in phosphate buffer (pH = 7,45).
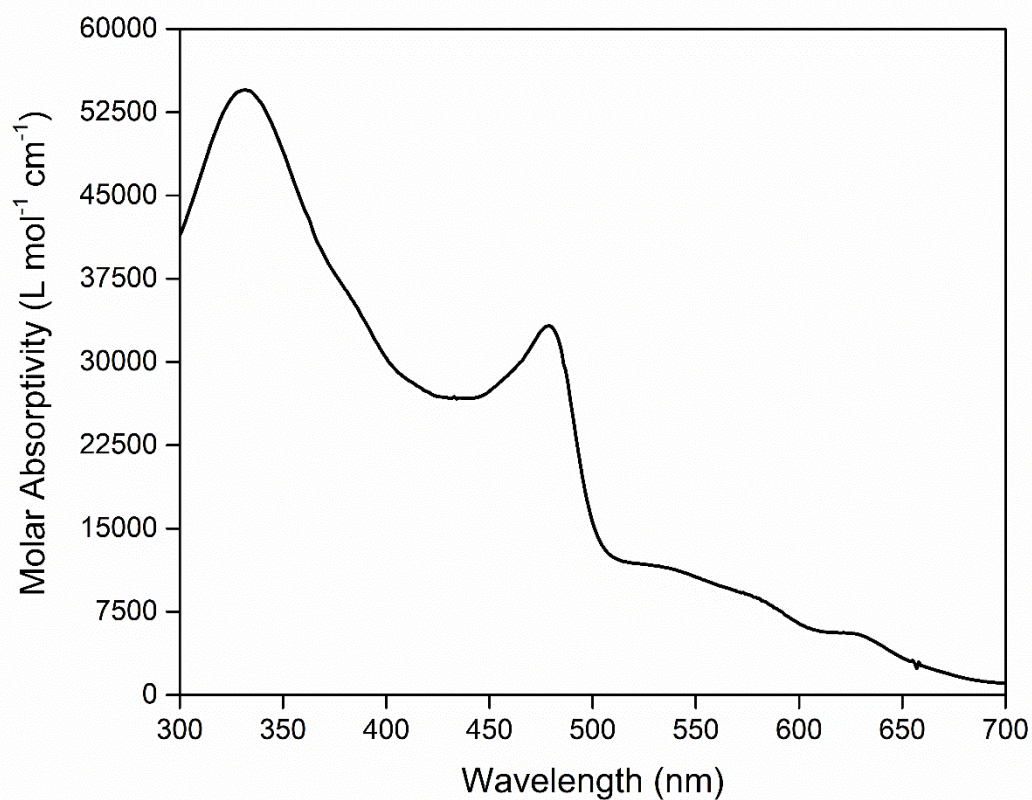

Figure S3. UV-Vis spectra of $H_3[Mn(Br_6T4CPP)]$ in phosphate buffer (pH = 7,45).

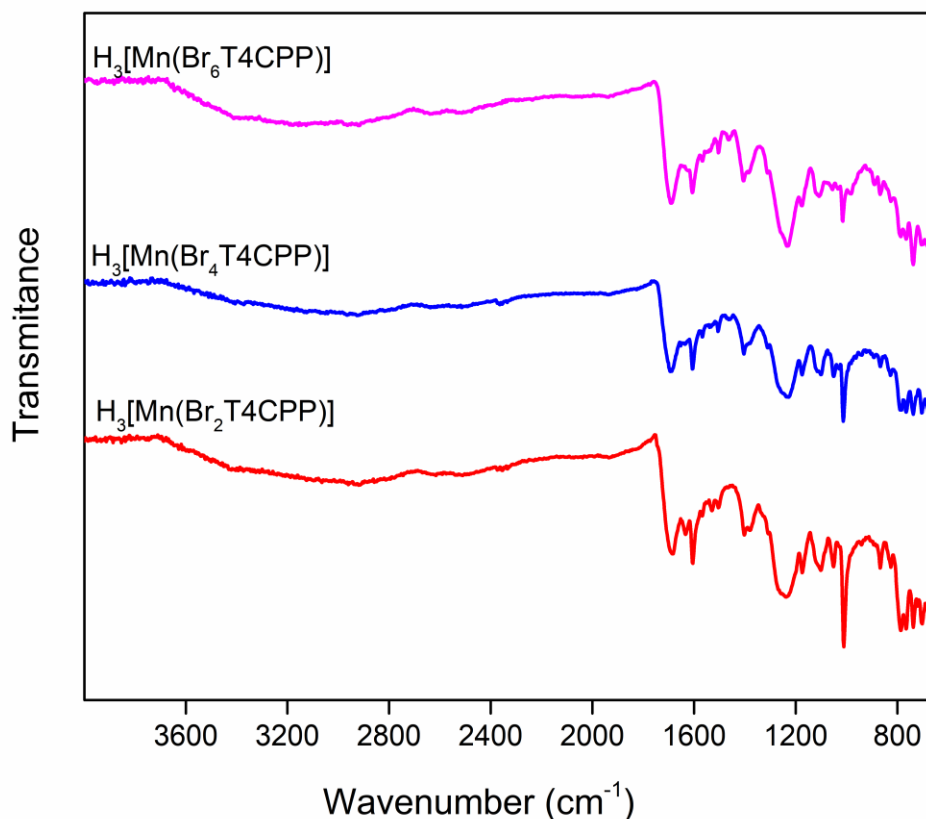**1.3. IR-FT-ATR spectra of H$_3$[Mn(Br$_x$T4CPP)] (x = 2, 4, and 6)**

Figure S4. IR-FT-ATR spectra of H$_3$[Mn(Br$_x$T4CPP)] (x = 2, 4, and 6).

2. Catalytic tests: cycloaddition reactions between CO$_2$ and epoxides

CO$_2$ gas (99.99%) was purchased from Líder Oxigênio and used without further purification. TBAB, TBAI, TBAC, PPNC and epoxides: propylene oxide (PO), styrene oxide (SO); epichlorohydrin (ECH); glycidyl 2-methylphenyl ether (GME); allyl glycidyl ether (AGE); 1,2-epoxyhexane (EH); 1,2- epoxydodecane (ED); resorcinol diglycyl ether (RDE) and 1,2-epoxy-3-phenoxypropane (EPP) were purchased from Merck and used without further purification.

Solution NMR spectra were collected at 25 ºC using Bruker Avance III 11.75 Tesla spectrometer (500 MHz) in deuterated chloroform (CDCl$_3$) with tetramethylsilane (TMS) as an internal reference.

2.1. Catalytic tests under high pressure

Catalytic tests were conducted in a Parr reactor system (model 4560 with controller model 4848) equipped with a 300 mL stainless steel vessel. In a general procedure, the vessel was charged with one of the catalysts, cocatalyst (nucleophile source), and the epoxide propylene oxide (PO). Carbon dioxide was pressurized into the mixture and the reaction was performed under predetermined conditions. When the reaction was complete, the vessel was cooled to 0 °C and the pressure was slowly released. The conversion was calculated based on the ^{1}H NMR spectrum of the crude reaction mixture thus obtained, in $CDCl_3$, by the integral ratio between epoxide and cyclic carbonate. The results are presented below in Table S3.

Table S3. Cycloaddition reactions using **1-5**/PO in 3 hours.[a]

Entry	Catalyst	Conv. (%)	Selectivity (%)	TON[c]	TOF[d]
1	[b]	13	93	-	-
2	H_3[Mn(T4CPP)] (**1**)	60	>99	15,060	5,020
3	H_3[Mn(Br$_8$T4CPP)] (**2**)	39	75	4,194	1,398
4	[Mn(Br$_8$T4CMPP)Cl] (**3**)	25	>99	5,307	1,769
5	[Mn(TPFPP)Cl] (**4**)	33	>99	8,361	2,787
6	[Mn(T2,6CFPP)Cl] (**5**)	66	>99	16,447	5,482

[a] 0.004 mol% of Mn catalyst, 0.08 mol% of TBAB, 50.0 mmol of PO, 100 °C, 30 atm of CO_2.
[b] Blank experiment using only TBAB.
[c] Turnover number (mol of carbonate produced/mol catalyst).
[d] Turnover frequency (TON h^{-1}).

2.2. Representative ^{1}H NMR spectrum of a catalytic test with PO, under high pressure
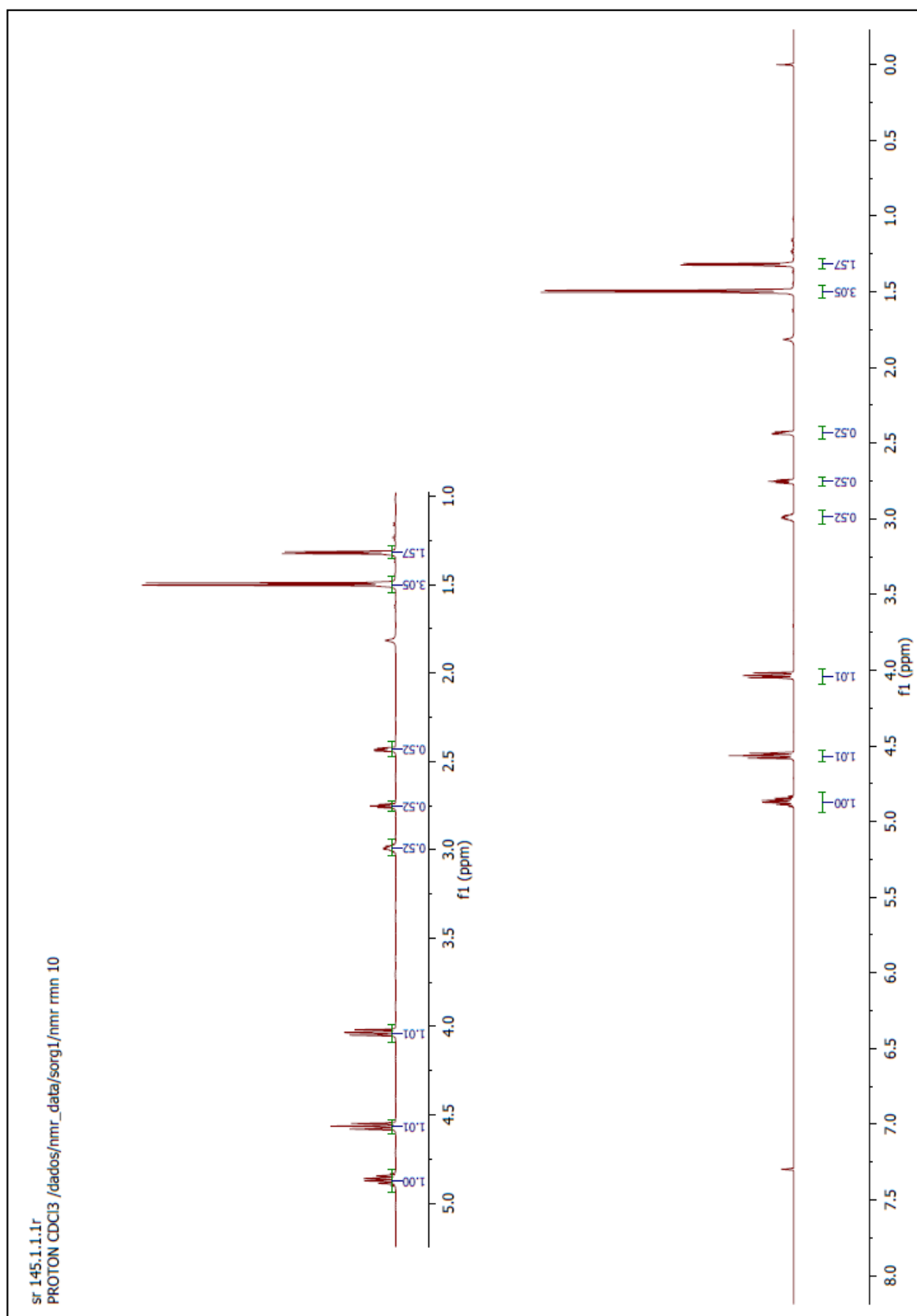

Figure S5. ^{1}H NMR spectrum of the reaction mixture of entry 6 (Table S3), showing the formation of propylene carbonate.

2.3. ^{1}H NMR spectra of the catalytic tests at atmospheric pressure using catalyst 1 with different epoxides

In a general procedure, a round bottom flask (10 mL) was charged with complex **1** (0.00125 mmol, 0.001 g, 0.02 mol%), cocatalyst (TBAI, 0.0625 mmol, 0.023 g, 1 mol%) and the appropriate epoxide (6.25 mmol, 0.7 mL – SO, 0.8 mL – AGE, 1.1 mL – EPP, 1.389 g – RDE, 0.5 mL – ECH, 0.95 mL – GME, 1.3 mL – ED, 0.75 mL – EH). The round bottom flask was pressurized with carbon dioxide (1 atm) with a balloon and the reaction was stirred at 90 ºC for 36 hours. After the given time, the reaction was stopped, cooled to room temperature (25-30 °C) and a sample was prepared for ^{1}H NMR analysis. The conversion was calculated based on ^{1}H NMR spectroscopy of the crude reaction mixture thus obtained, in $CDCl_3$. The ^{1}H NMR profile of all cyclic carbonates was compared to spectra already reported, as referenced after each figure.
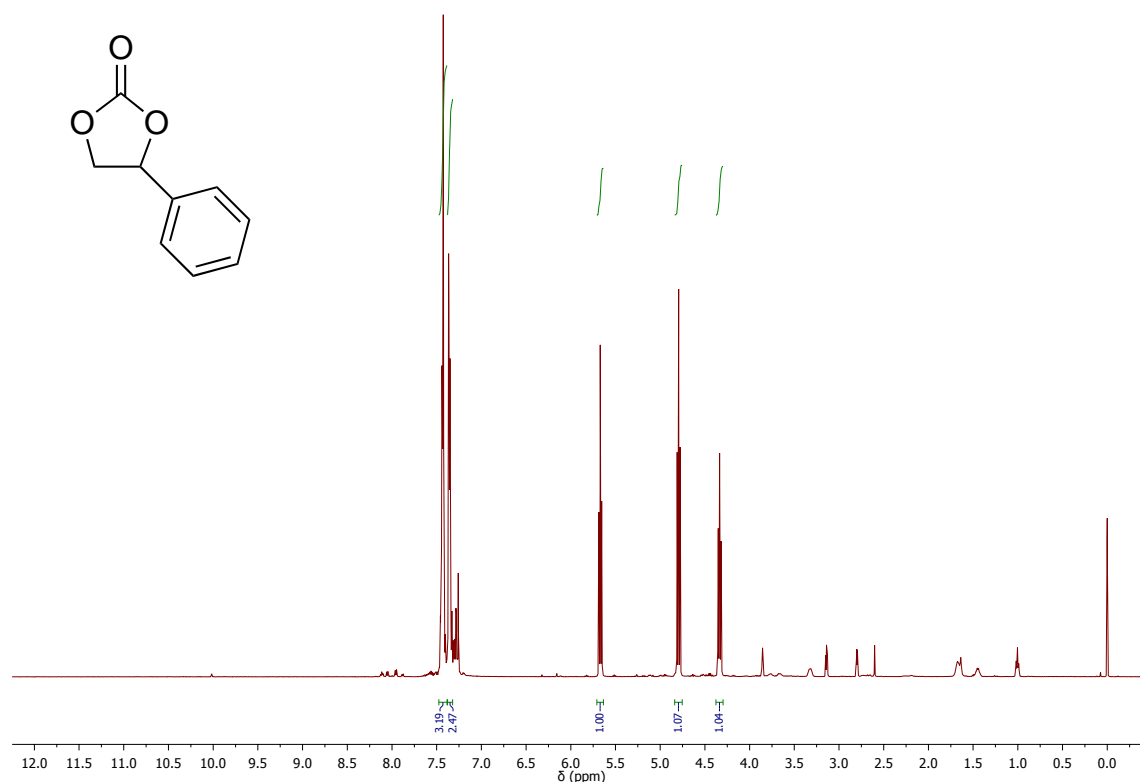

Figure S6. ^{1}H NMR spectrum of the reaction mixture showing the formation of styrene carbonate (SC). Conversion: 90%. [2]
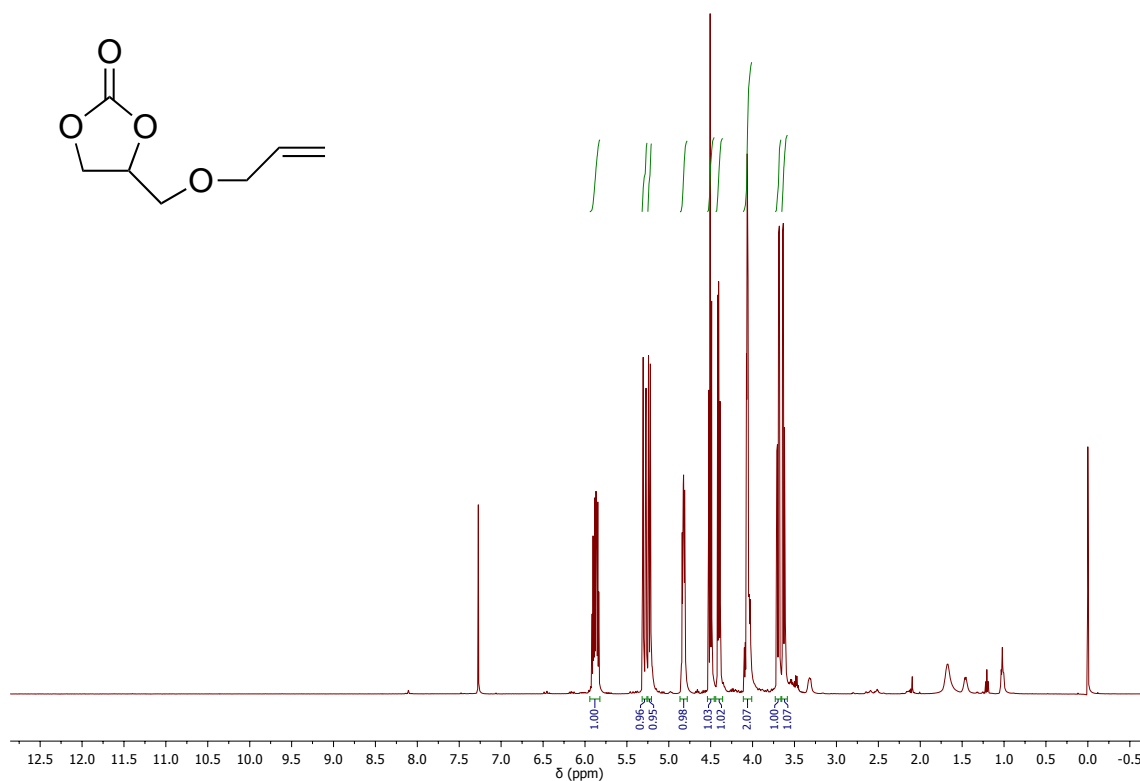
Figure 7 ^{1}H NMR spectrum of the reaction mixture showing the formation of allylpropylene carbonate (APC). Conversion: > 99%. [3]
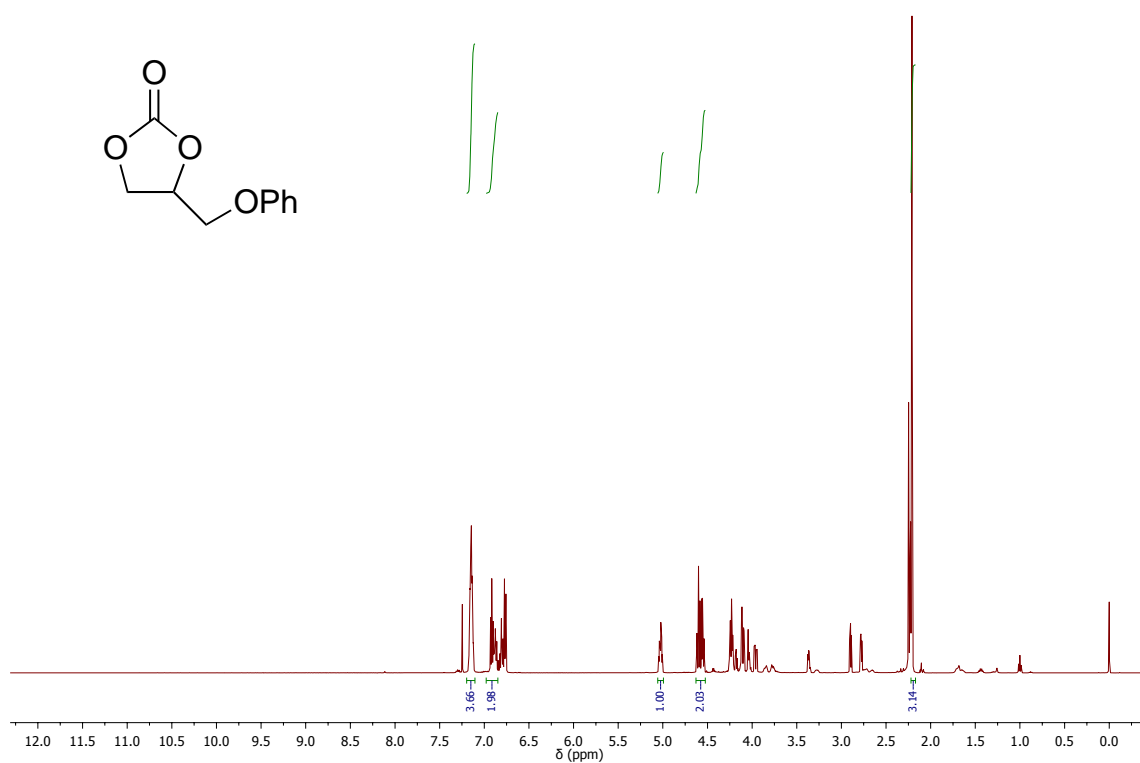

Figure S8. ^{1}H NMR spectrum of the reaction mixture showing the formation of phenoxypropylene carbonate (PPC). Conversion: 87%. [2]
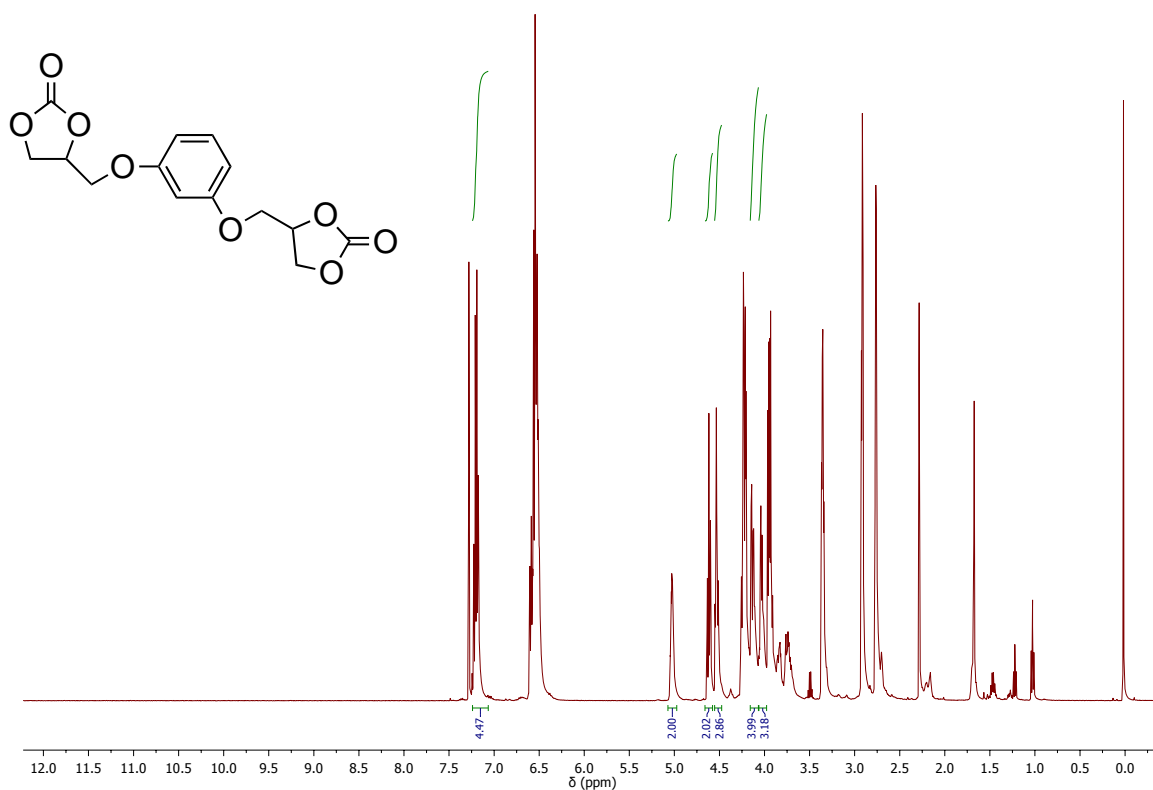
Figure S9. ^{1}H NMR spectrum of the reaction mixture showing the formation of resorcinol bis carbonate (RBC). Conversion: 41%. [4]
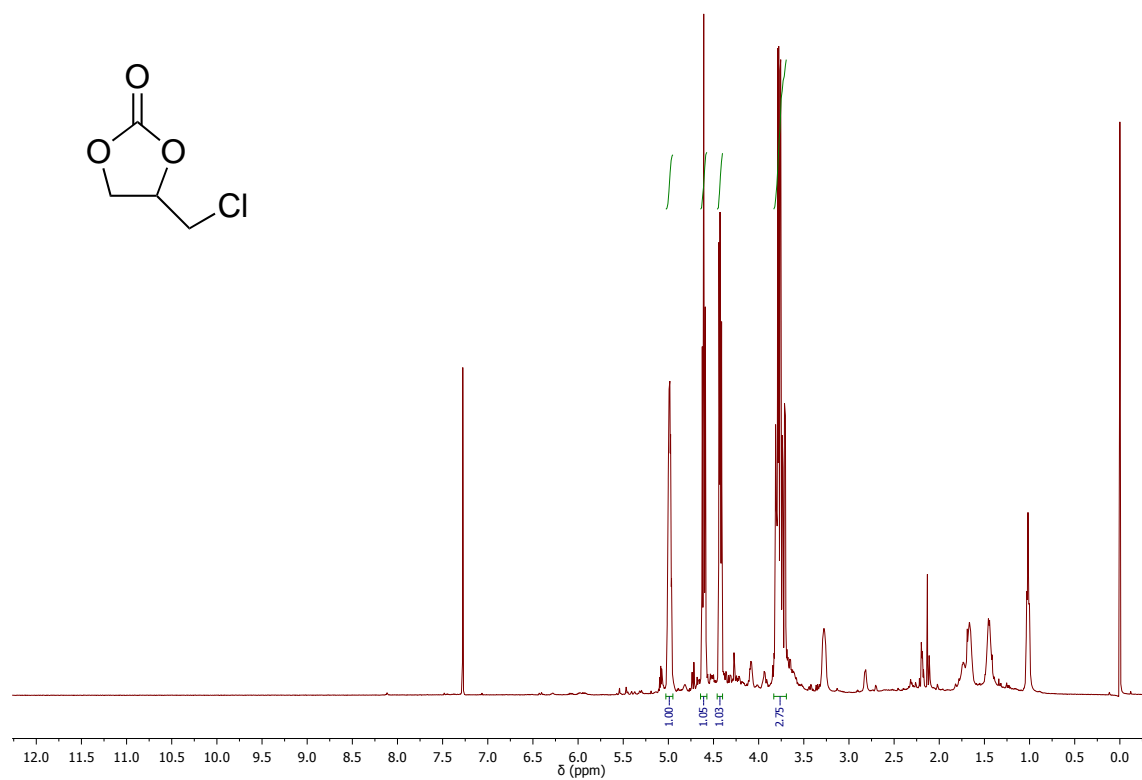

Figure S10. ^{1}H NMR spectrum of the reaction mixture showing the formation of chloropropylene carbonate (CPC). Conversion: > 99%. [2]
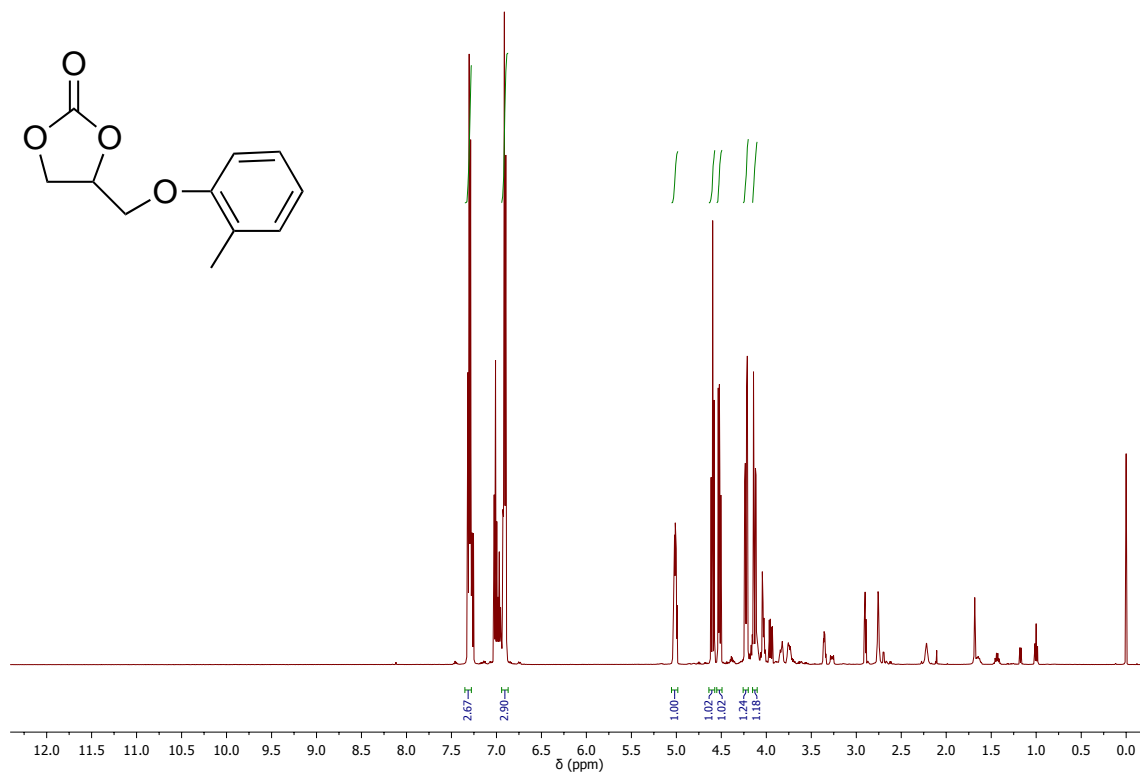
Figure S11. ^{1}H NMR spectrum of the reaction mixture showing the formation of *o*-tolyloxypropylene carbonate (TPC). Conversion: 75%. [5]
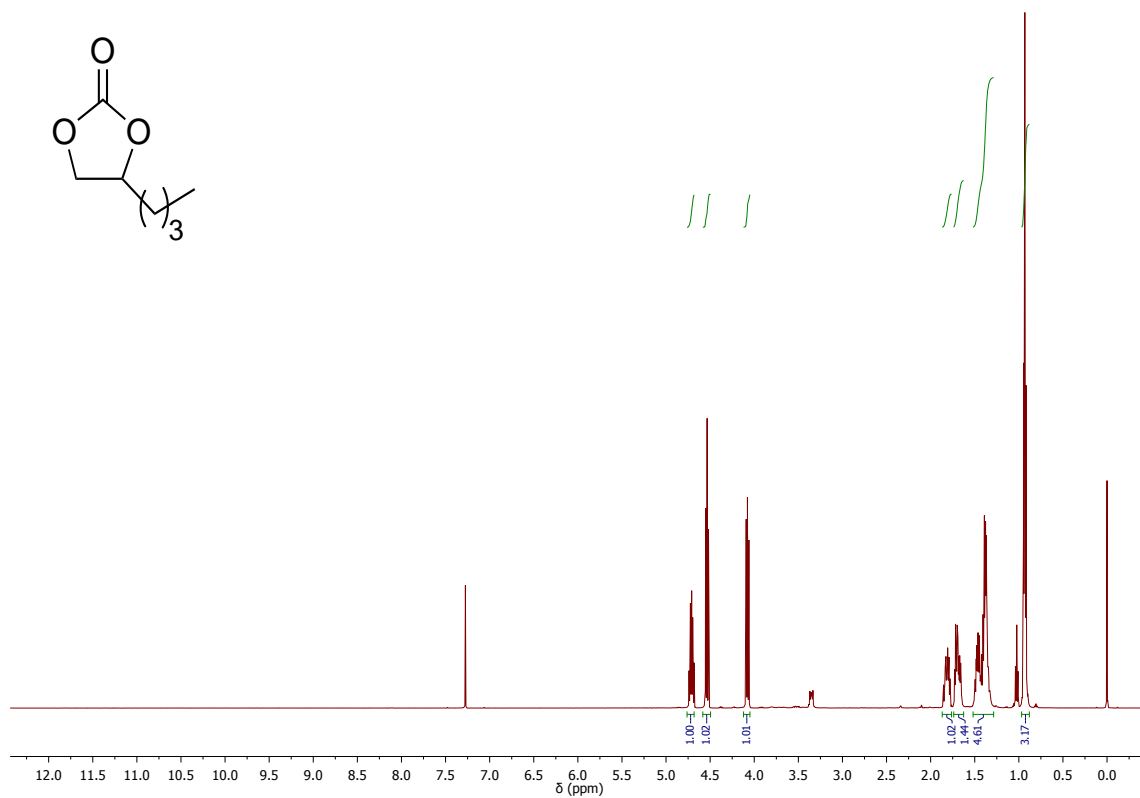

Figure S12. ^{1}H NMR spectrum of the reaction mixture showing the formation of hexylene carbonate (HC). Conversion: >99%. [2]
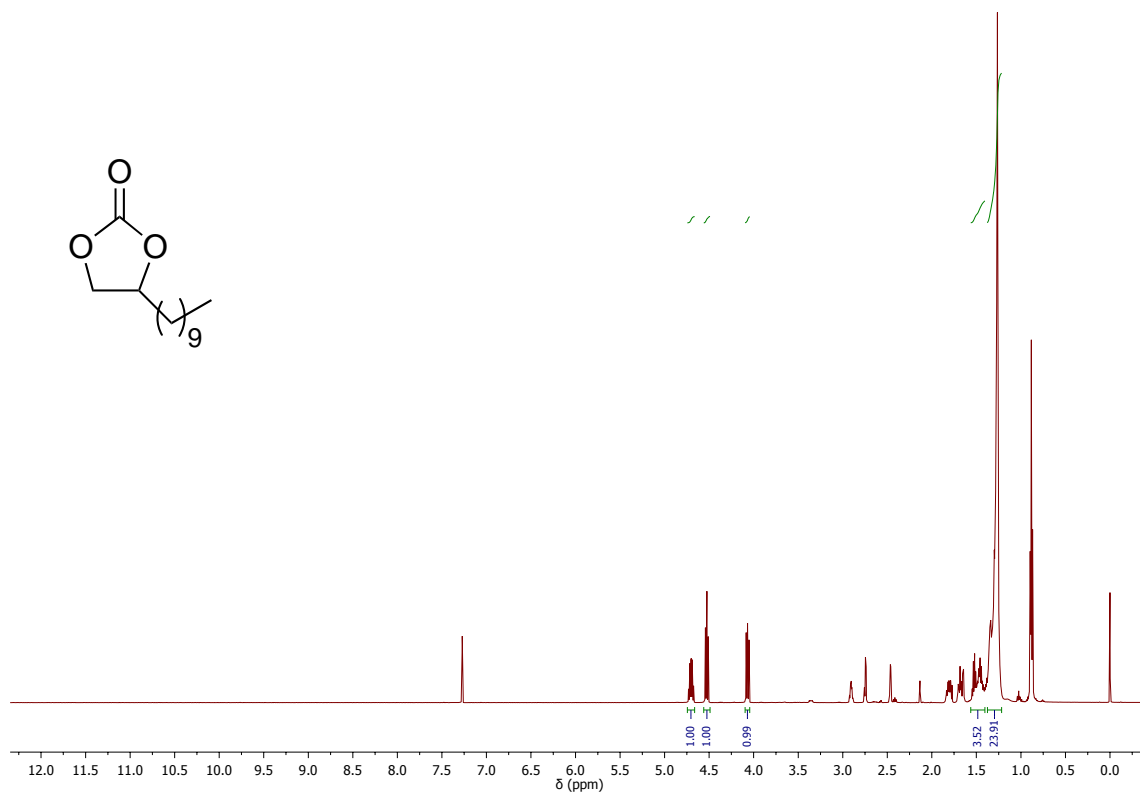
Figure S13. ^{1}H NMR spectrum of the reaction mixture showing the formation of dodecanylene carbonate (DC). Conversion: 65%. [2]

3. References

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