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Efficient Conversion of Epoxides into Carbonates with CO₂ and a Single Organocatalyst: Laboratory and Kilogram-Scale Experiments

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► **To cite this version:**

Rabah Azzouz, Viviana Contreras Moreno, Clara Herasme-Grullon, Vincent Levacher, Lionel Estel, et al.. Efficient Conversion of Epoxides into Carbonates with CO₂ and a Single Organocatalyst: Laboratory and Kilogram-Scale Experiments. SYNLETT, 2020, 31 (02), pp.183-188. 10.1055/s-0039-1691405 . hal-02958227

HAL Id: hal-02958227

<https://normandie-univ.hal.science/hal-02958227v1>

Submitted on 21 Dec 2020

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**Efficient conversion of epoxides into carbonates with CO₂
and a single organocatalyst : laboratory and kg-scale
experiments**

Journal:	<i>SYNLETT</i>
Manuscript ID	ST-2019-08-0454-L.R2
Manuscript Type:	Letter
Date Submitted by the Author:	n/a
Complete List of Authors:	Azzouz, Rabah; Université de Rouen, UMR 6014 COBRA Contreras Moreno, Viviana; INSA Rouen, LSPC Herasme-Grullon, Clara; CNRS UMR 6014, COBRA Levacher, Vincent; CNRS UMR 6014, COBRA Estel, Lionel; INSA Rouen, LSPC Ledoux, Alain; INSA Rouen, LSPC Derrouiche, Salim; Veolia Environment Research and Innovation, Recherche et Innovation Marsais, Francis; VFP Therapies, research and development Bischoff, Laurent; Université de Rouen, UMR 6014 COBRA
Keywords:	carbon dioxide, pyridines, organocatalyst, cyclic carbonate, epoxides
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Efficient conversion of epoxides into carbonates with CO₂ and a single organocatalyst : laboratory and kilogram-scale experiments

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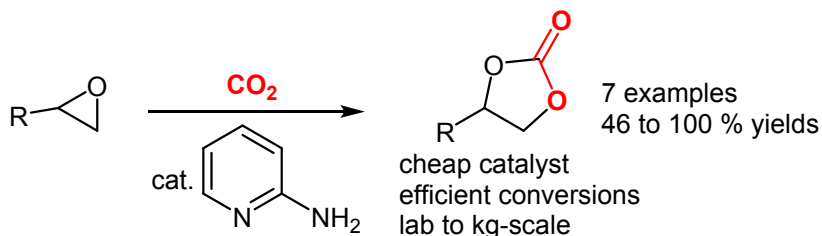
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Received:

Accepted:

Published online:

DOI:

Abstract Cheap and readily-available 2-aminopyridine and related compounds can be used as organocatalysts for the conversion of epoxides into cyclic carbonates. This reaction gives high conversions under solvent-free conditions, and is amenable to a kilogram-scale conversions under mild conditions.

Key words epoxides, cyclic carbonates, carbon dioxide, organocatalysis, aminopyridine

dimethylcarbonates.⁴ The latter are precursors of diphenyl carbonate, a useful surrogate for phosgene in the industrial preparation of polycarbonate materials. A representative example consists of the use of cerium oxide as a catalyst.

Increasingly over recent years, efforts have been made to reduce the industrial production of carbon dioxide and thus avoid its effects on climate change. Besides the capture followed by geological or ocean storage of CO₂,¹ several different products arising from its utilisation have been described. For instance, carbon dioxide can be reduced to produce formic acid derivatives,² carbon monoxide or methanol,³ products that are highly-valuable energetic materials, since formic acid can further release hydrogen and methanol can be used directly as a fuel. In the present study, we were interested in the preparation of cyclic carbonates, via incorporation of carbon dioxide into epoxides. Cyclic carbonates such as ethylene or propylene carbonate are known as industrial solvents and, from a general viewpoint, dialkyl carbonates are high-value starting materials for the synthesis of polycarbonates through transesterification with diols.

Due to the high chemical stability of carbon dioxide, its direct esterification with methanol involves high energy input, requiring high pressures and temperatures to yield

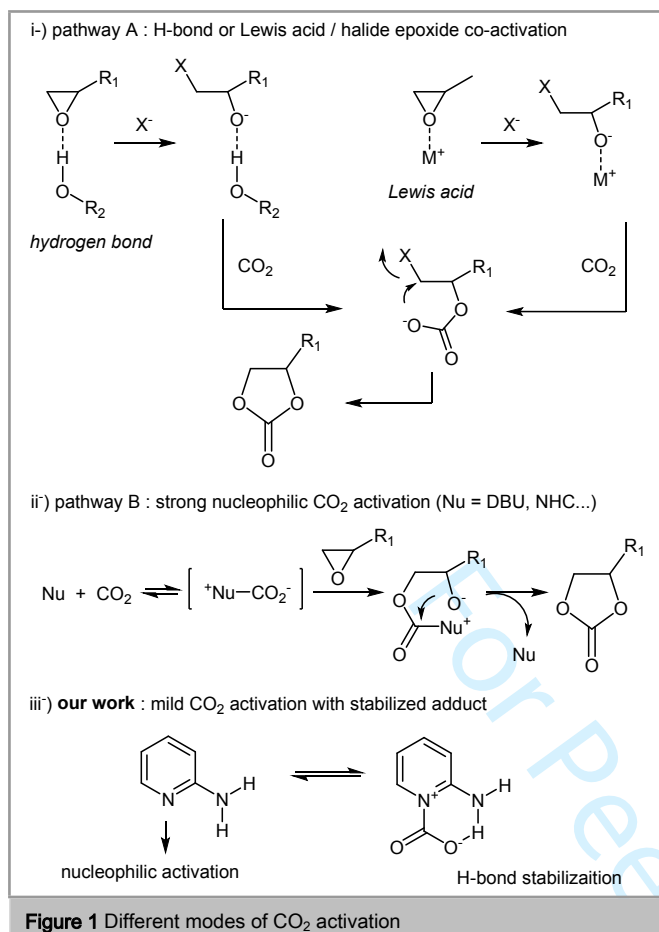


Figure 1 Different modes of CO₂ activation

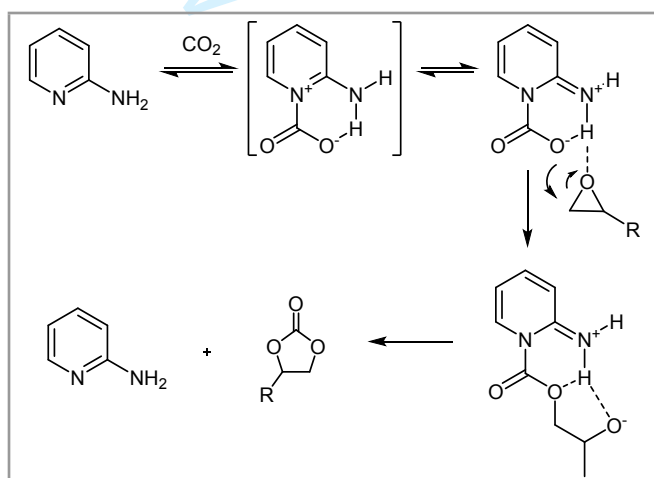
These energetic considerations have led several groups to focus on the reaction of carbon dioxide with molecules of higher reactivity, thus avoiding the requirement for an external source of energy. For instance, unstable carbamates can be trapped with electrophilic reagents and thus consumed in a stoichiometric amount.⁵ In particular, the reactivity of epoxides is interesting, since these incorporate both electrophilic carbon and subsequent nucleophilic oxygen atoms. Thus, in the presence of appropriate catalysts, CO₂ can be inserted into reactive epoxides to yield the corresponding cyclic carbonates, or, in some cases, directly provide polycarbonates.⁶

For this purpose, several catalytic systems have been described over the last decade.⁷ The main strategies explored to date are summarized in Figure 1. Dual activation is often required to achieve high conversions under atmospheric pressure. In the epoxide-activation strategy, opening with a halide and resulting formation of a transient halogeno (bromo and iodo) intermediate results in both the release of a nucleophilic alkoxide with a remaining C-X electrophilic bond. This preliminary opening pathway represents the most commonly encountered form of epoxide activation. However, when a halide ion-containing catalyst such as tetrabutylammonium bromide is used, either high pressures and temperatures are required, or the assistance of a Lewis acid is employed, in order to stabilize the strongly basic alkoxide ion before its reaction with carbon dioxide. This electrophilic activation and stabilization can be obtained either via H-bond formation from an alcohol moiety, or with a various metal catalysts.^{8,9}

Cooperative catalysis has been explored with both Lewis acid metal catalysis with halide as counter ion, and H-bond donors such as diphenolic ligands such as salophen.⁹ Cationic, organic solvent-soluble phosphonium salts, bearing an *ortho*-phenol group for H-bond activation of the epoxide, and bromide counter ion have been described.^{9b-c} Hirose and co-workers^{9d} also used organocatalysts encompassing both an alcohol as H-bond donor and nucleophilic assistance by iodide. Nucleophilic organocatalysts are also an efficient way to catalyse epoxide opening.¹⁰ Many catalytic systems can be supported on montmorillonite clay¹¹ or natural^{12a} or synthetic macromolecules,^{12b}. Most of these systems afford good results but often involve high costs, and structural or surface analyses to ensure reproducible reactions.

Another mechanistic strategy consists of activating CO₂ with strong nucleophiles such as amidines or guanidines;¹³ even NHCs can be employed.¹⁴ Unfortunately, strong nucleophiles also behave as fairly strong bases. Indeed, the reaction of CO₂ with DBU was thoroughly studied and shown to be particularly sensitive to moisture, enabling the transformation of CO₂ into hydrogencarbonate if water is present.¹⁵ However, in the case of industrial combustion exhausts, the removal of water will add an energy-consuming step. In addition, the cost of these reagents is generally too high for industrial applications.

2-aminopyridine is a relatively inexpensive compound (ca 15\$ / kg), easily accessible by the Chichibabin reaction of sodium amide with pyridine.¹⁶ It can exist as both tautomeric forms, and, in contrast to 2-hydroxy and 2-thio pyridines, 2-aminopyridine mostly exists mainly as the 2-amino- rather than 2-iminopyridine tautomer.¹⁷ Having a pKa value of 6.9, it is less basic than DBU or deprotonated NHCs, thus avoiding its acidobasic reaction with carbon dioxide and concomitant formation of hydrogencarbonate salt. It has a moderate toxicity and a good chemical stability towards water and most organic solvents. Owing to the electron-withdrawing properties of the pyridine nucleus, the amino group has a limited nucleophilic character, thus protecting this moiety from alkylation with epoxides or air-oxidation, as observed in the case of many amines.



Scheme 1 Catalysis of epoxide carbonatation with aminopyridine

Experiments conducted in NMR solvents (CDCl₃, DMSO or acetonitrile) provided no evidence of the formation of the CO₂ adduct with 2-aminopyridine. Thus, we believe that a limited

amount of 2-amino-pyridine/ CO_2 complex is present; nevertheless exhibiting sufficient reactivity to lead to the opening of the epoxide. Interestingly, when the reaction is carried out in a glass reactor, the formation of a precipitate is noticed when CO_2 under pressure is applied. This precipitate disappears during the course of the reaction. We believe that the sole pyridine nitrogen atom is not nucleophilic enough to react with CO_2 , as may occur in the case of DMAP or DBU. Thus, a hydrogen bond with the *vicinal* 2-amino group is required for carbamate stabilization. Indeed, as described in the literature,¹⁸ co-catalysis using both a phenol as the H-bond donor and DMAP as the nucleophilic catalyst has been described. In our case, the catalyst can be responsible for both activations (see Scheme 1). This is supported by the fact that 2-dimethylaminopyridine proved to be barely reactive under the same conditions; whereas 2-methylaminopyridine remained an effective catalyst, underlining the role of the hydrogen bond with the NH_2 or NHMe substituent

The catalytic properties of 2-aminopyridine were first examined using epichlorohydrin as a model substrate, on a 5 mL scale.²⁰ Epichlorohydrin is a widely-used synthon, mostly prepared as a monomer for epoxy paints.

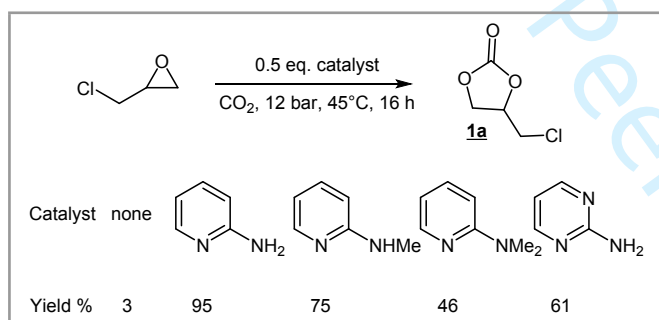


Figure 2 Catalyst comparison (isolated yields)

The corresponding cyclic carbonate is a high-value intermediate, especially if considered as a monomer for highly-functionalized polycarbonates. This preliminary work was aimed at determining which catalyst amongst the 2-aminopyridine analogues would be most suitable for this reaction. In this set of experiments, we used a large amount of catalyst, under 12-bar pressure of CO_2 , in order to exhibit the catalytic properties of the catalysts even with low activities.

These results clearly show the importance of the catalyst itself since, with no catalyst barely any reaction occurred. The hydrogen bond also seemed crucial, the lowest yield being obtained using 2-dimethylaminopyridine. 2-aminopyrimidine can also catalyse this reaction, though less efficiently. Further examinations of catalytic activities were only performed with N-H bearing catalysts.

Then the same reaction was conducted under 10 bar of CO_2 over 16 hrs, at various temperatures. We observed a rapid increase in reaction above 40°C; however we did not wish to use temperatures higher than 60°C in order to avoid side-reactions such as degradation of the epichlorohydrin. In the absence of catalyst, only traces of cyclic carbonate were observed. 2-Aminopyridine remained the most active catalyst, though 2-

methylaminopyridine and 2-aminopyrimidine also gave good yields at 60°C.

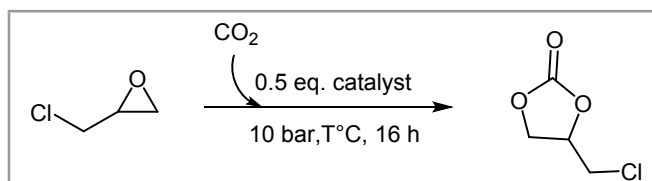


Figure 3 Role of the temperature

Table 1 Influence of the temperature with different catalysts

T°C	2-amino-pyridine % ^a	2-methylamino pyridine % ^a	2-amino-pyrimidine % ^a
25	8	5	0
40	25	28	25
60	90	81	66

a: isolated yields

As an important feature towards the possibility of industrial development, we next examined the catalyst loading, still working at 60°C under 10 bars of CO_2 pressure. These results clearly indicate that there is no requirement for high concentrations of catalyst, good yields being obtained even at 5% loading although, as expected, low concentrations of catalyst decreased the yields. Surprisingly, 2-methylaminopyridine remained effective at 2.5 mol %; whereas 2-aminopyridine only afforded a modest 52 % yield under the same conditions. When decreasing to 1 % ratio, we still noticed catalytic activity, although with low yields, except with 2-aminopyrimidine, which did not catalyse the reaction in such a concentration.

Having these results in hand, we wished to extend the scope of this transformation. Amongst commercially-available, suitably-substituted epoxides that would lead to useful monomers in polycarbonate chemistry, we focused on glycidol, glycidyl ethers, and phenyl-oxirane.

In each case, we revisited the reaction conditions, especially the catalyst loading, the reactivities of the epoxides exhibiting strong differences.

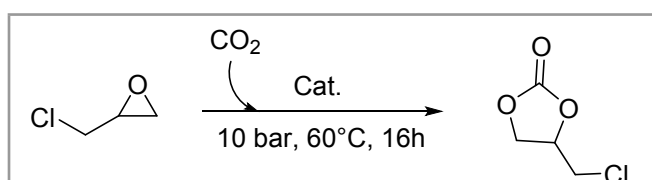


Figure 4 Catalyst loading

Table 2 Yields obtained with various catalyst concentrations

Mol % catalyst	2-amino-pyridine %	2-methylamino-pyridine %	2-amino-pyrimidine %
10	90	81	67

5	69	82	35
2.5	52	78	34
1	34	20	0

Glycidol is an important chemical intermediate, its carbonate represents a particularly interesting monomer for polycarbonate synthesis. When we studied carbonate formation from glycidol, we observed an unexpected reactivity of glycidol even if no catalyst is present. This may be due to self-activation by means of hydrogen bonding with the alcohol moiety. Pleasingly, the reactivity proved higher in the presence of the catalyst, as listed in the following table.

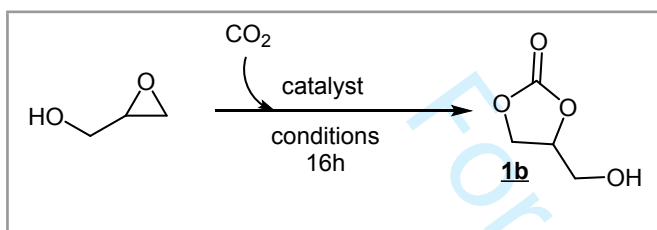


Figure 5 Carbonatation of glycidol

Table 3 Synthesis of glycidyl carbonate under various conditions

catalyst	no	2-amino-pyridine	2-methyl aminopyridine	2-amino-pyrimidine
20 bar, 50% cat., 45°C	60	80	70	83
20 bar, 10% cat. mol., 45°C	19	90	80	78
10 bar, 5% cat., 40°C	1.2	80	80	76
10 bars, 5% cat., 25°C	36	87	78	78

These results confirm the high catalytic activity of 2-aminopyridine, which remains the most efficient catalyst in this reaction, with 87 % yield being obtained at room temperature with a 5% catalyst loading under 10 bar pressure of CO₂.

Having these results in hand, we examined the reactivity of other commercially-available epoxides having sufficiently-high boiling points for reactions at 70-85°C. We focused on 2-aminopyridine, which allowed the formation of carbonates from every epoxide. Surprisingly, phenyl oxirane only gave a moderate yield, while having a high propensity for epoxide opening. Bis-glycidyl ether also lead to moderate yield of dicarbonate (62%), along with monocarbonate. Other epoxides gave good yields of carbonate formation, especially allyl glycidyl ether, which provided the carbonate in quantitative yield.

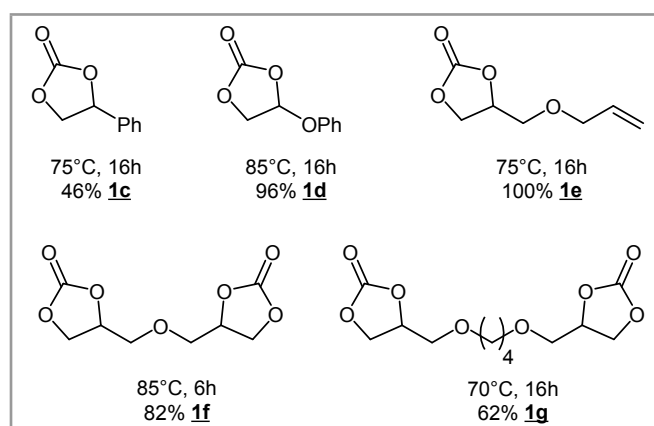


Figure 6 Other carbonates prepared under 20 bar CO₂, 10% 2-aminopyridine

Finally, with the aim of validating future industrial development, we examined the reactivity of epichlorohydrin in the presence of CO₂ and 2-aminopyridine at 1 kg-scale. The current commercial methods allowing production of cyclic carbonates require temperatures above 150 °C and high pressures of CO₂ between 50 – 80 bar. Using 2-aminopyridine as catalyst, we could reduce the operating conditions at laboratory scale. To verify the applicability of the reaction at large scale by only using an organo-catalyst, different operating conditions were evaluated and optimized to maximize the amount and the quality of the product obtained.

The reactions between CO₂ and epichlorohydrin (ECH) were carried out in a stainless-steel stirred-tank reactor (1.5 L) at a range of temperatures (50°C – 110°C) and pressures below 5 bar. The temperature in the reactor was maintained constant thanks to a carrier fluid circulating through a jacket. The accuracy of the temperature regulation inside of the reactor was ±0.1°C.

Stirring allowed the temperature and composition of the liquid phase to be kept homogeneous and improved the mass transfer. A reservoir of gas allowed continuous feeding into the reactor. The amount of gas-feed was controlled by regulating the pressure inside the stirred tank. Before every reaction, a vacuum was established to eliminate air contained in the reactor. The reactions were carried out under solvent-free conditions.

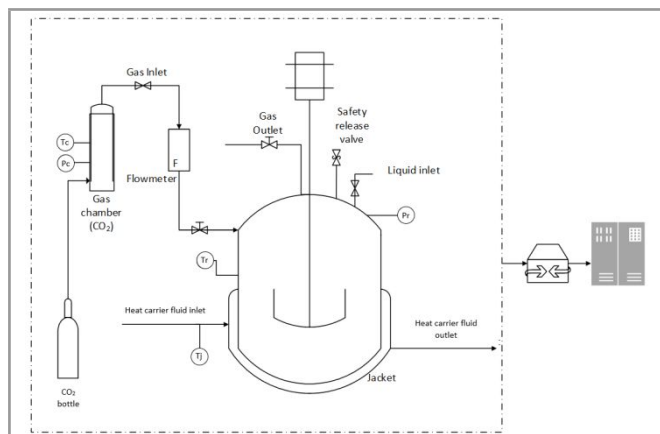


Figure 7 Stirred reactor diagram. T: temperature – P: Pressure C: chamber – j: jacket – r: reactor

Reactions performed at lab scale showed good conversions and yields at temperatures above 50 °C and concentrations of catalyst lower than 10% mol. We observed the behaviour of the reaction at pilot scale, by evaluating temperatures of between 50 and 110 °C. The pressure of the reaction and catalyst concentration were fixed to 5 bar and 5% mol., respectively.

Figure 8 shows the conversion of epichlorohydrin and additional information is given in Figure 9, which demonstrates the effect of temperature on the concentration of carbonate produced over time. At temperatures lower than 60 °C, the production of the carbonate was quite slow, reaction taking more than 6 hours with conversions lower than 30%. At temperatures above 70 °C, conversions were higher than 80% with a reaction time below 5 hours. We observed significant induction periods at temperatures lower than 70 °C.²¹ Indeed, we detected an optimal operating point over 80 °C at pilot-scale with a conversion and yield of around 90%, which was comparable to that obtained at laboratory scale. At temperatures higher than 90 °C, we observed a decrease in carbonate formation, which could be explained by thermal degradation of the catalyst.

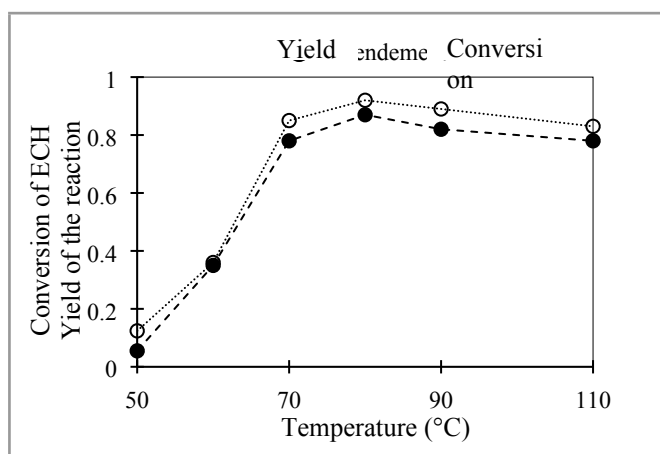


Figure 8 Effect of pressure on carbonate production over time at 80 °C bar and 5 mol% of 2-aminopyridine

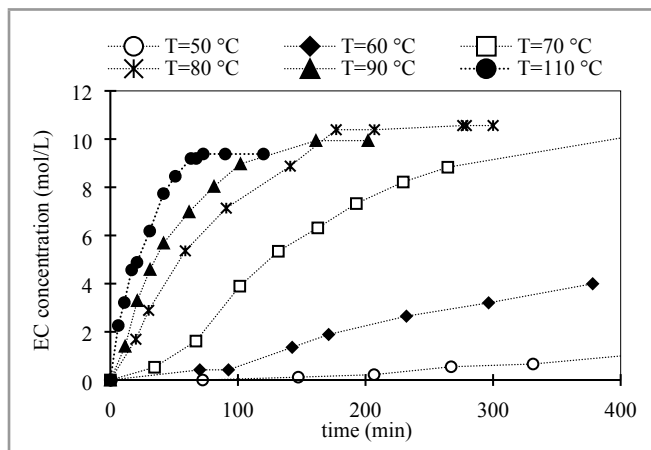


Figure 9 Effect of temperature on carbonate production over time at 5 bar and 5 mol% of 2-aminopyridine

The effect of CO₂ pressure on the reaction rate was observed at the optimal temperature of 80 °C and 5.0% mol. of 2-aminopyridine, the pressure of CO₂ into the reactor being varied from 1 to 5 bar. Figure 10 shows the variation of carbonate formation over time at these pressures. Using 2-aminopyridine as catalyst, a relatively insignificant effect of CO₂ pressure was observed on the production rate of carbonate. A similar effect has also been noticed, but at higher pressures when, below 150 bar, there was no effect on the formation rate of dimethyl carbonate from CO₂ and ethylene oxide.¹⁹

The conversions and yields were similar to that obtained at 5 bar (~90%). Under these conditions, we could minimize the pressure of the reaction without any consequence on the reaction performance.

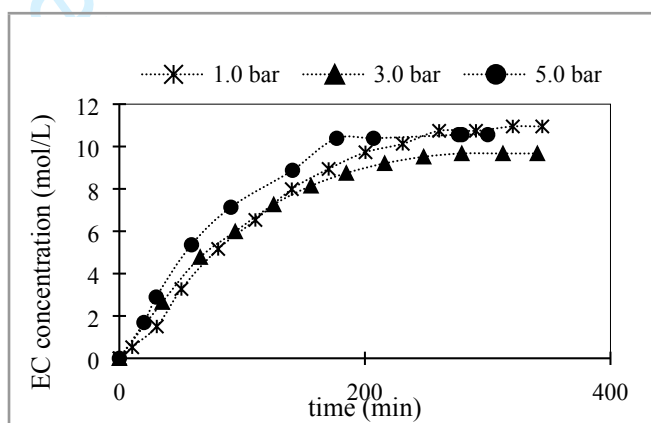


Figure 10 Effect of pressure on carbonate production over time at 80 °C and 5 mol% of 2-aminopyridine

According to the studies performed at lab scale, catalyst concentrations from 2.5 to 10% mol., could be used with success to obtain the cyclic carbonate at a temperature of 60 °C. However, at pilot-scale, the reaction requires a higher temperature to obtain similar yields. According to our study, we observed an optimal conversion at 80 °C. This temperature was used to study the performance of the catalyst. Two different concentrations of catalyst (5 and 7 mol %), were used during these reactions and the pressure of CO₂ was fixed at 5 bar.

Figure 11 shows the evolution of carbonate concentration over time according to the two catalyst concentrations used. An insignificant variation on the dynamic behaviour of carbonate formation was detected during the reaction. However, a slight difference was observed for the induction period. The concentration of carbonate was slightly lower when the concentration of catalyst was 7% mol. The yield of the reaction decreased to around 6%, but the overall conversion of epichlorohydrin remained relatively stable. We propose some catalyst degradation could occur during the last phases of the reaction, possibly due to the high temperature (80°C) and the higher concentration of catalyst (7 mol%).

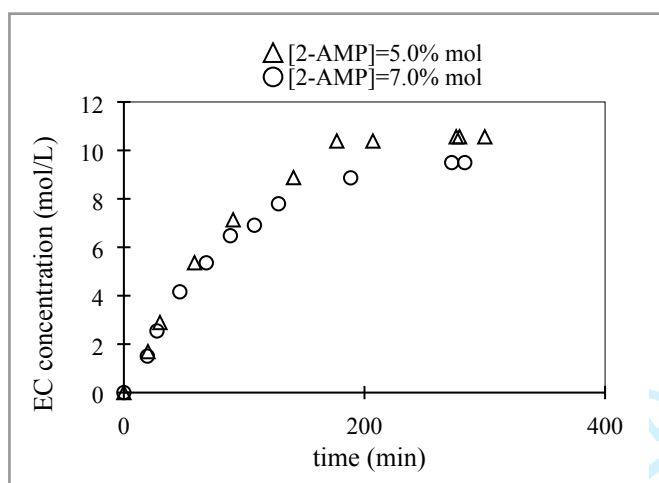


Figure 11 Effect of catalyst concentration on carbonate production over time at 80°C and 5 bar CO₂

This result showed that, at pilot-scale, the temperature had an impact more significant on the reaction performance compared to the catalyst concentration at the conditions studied. Under appropriate conditions, we could use a relatively low concentration of catalyst and obtain good yields and conversions.

This whole set of experiments allow us to conclude that the laboratory-scale reaction of epichlorohydrin with carbon dioxide can be carried out with high reliability on a pilot-scale, thus paving the way towards an industrial process. In terms of sustainable chemistry, this constitutes an additional example of synthesis of cyclic carbonates from epoxides, with a very simple and readily-available organocatalyst, exhibiting low basicity and avoiding hydrogen carbonate formation. Importantly, carbonates having both reactive moieties such as glycidyl or epichlorohydrin carbonates, available through this phosgene-free preparation, are of great interest in the manufacturing of polymers.

Funding Information

This work has been partially supported by INSA Rouen, Rouen University, CNRS, EFRD, European INTERREG IV A France (Channel) and Labex SynOrg (ANR-11-LABX-0029). Rabah Azzouz is grateful to FEDER BIOFLUORG and Viviana Contreras Moreno is grateful to Veolia Recherche et Innovation for financial support.

Acknowledgment

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Supporting Information

YES (this text will be updated with links prior to publication)

Primary Data

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An open glass Schlenk tube was charged with epichlorhydrin (5 mL, 61.8 mmol), 2-aminopyridine (580 mg, 6.18 mmol) and a magnetic stir bar. It was placed in a stainless-steel autoclave, then pressurized with carbon dioxide to 10 bar pressure. It was heated under stirring at 60°C (internal temperature) for 16 hrs. After cooling, the carbonate was purified by filtration through a short pad of silica, eluting with diethyl ether, followed by evaporation of

the solvent to yield 7.58 g of carbonate (90 %). 4-(chloromethyl)-1,3-dioxolan-2-one 1a: pale-yellow liquid; ¹H NMR (300 MHz, CDCl₃) δ 4.95-5.05 (m, 1H), 4.59 (t, J = 8.4 Hz, 1H), 4.38-4.44 (m, 1H), 3.71-3.80(m, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 154.6, 74.6, 67.0, 44.2

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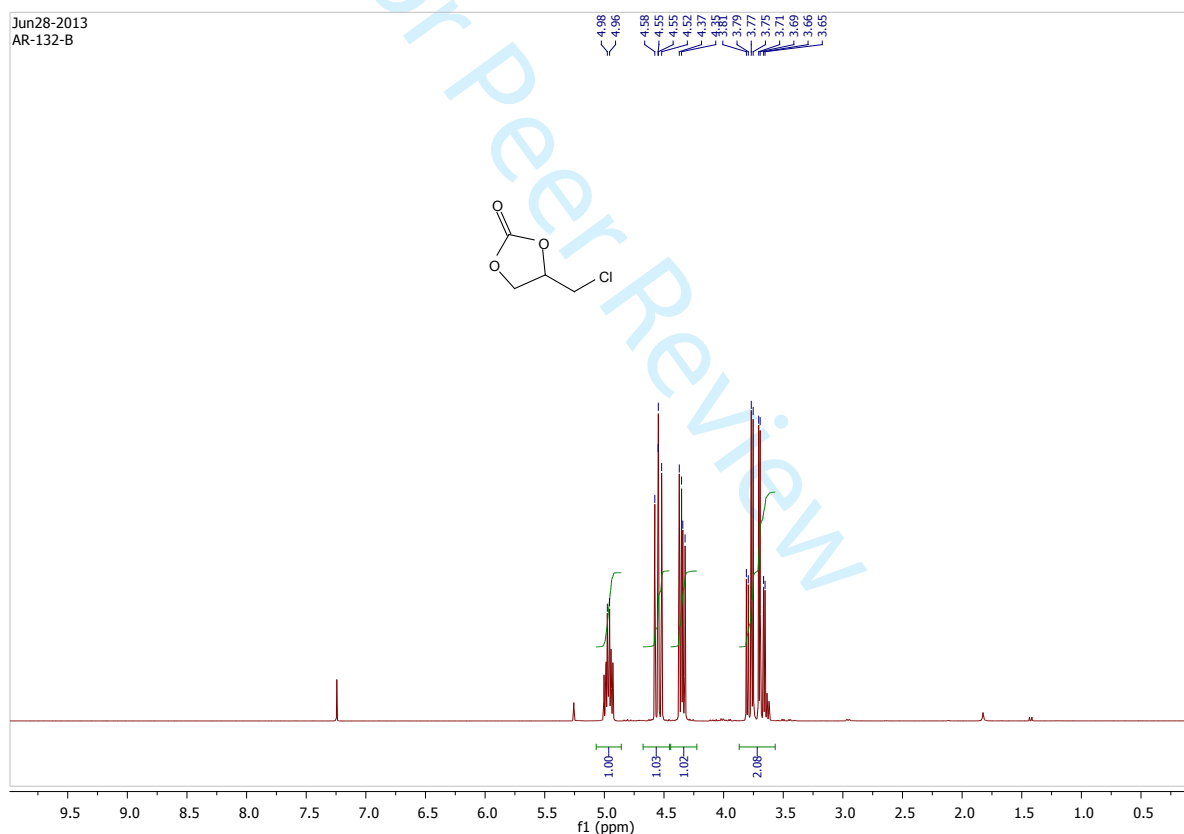
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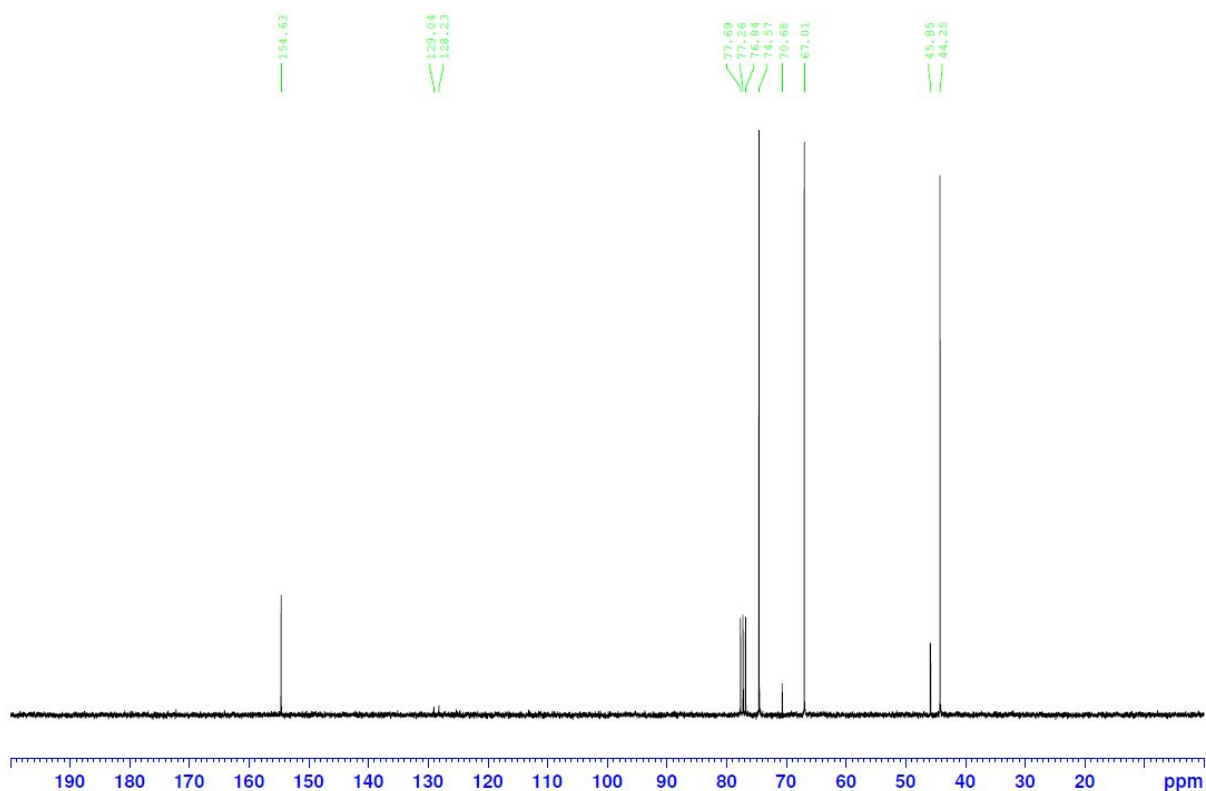
Rabah Azzouz, Viviana Contreras Moreno, Clara Herasme-Grullon, Vincent Levacher, Lionel Estel, Alain Ledoux, Salim Derrouiche, Francis Marsais, Laurent Bischoff

Experimental procedure: the carbonatation of epichlorhydrine is illustrative:

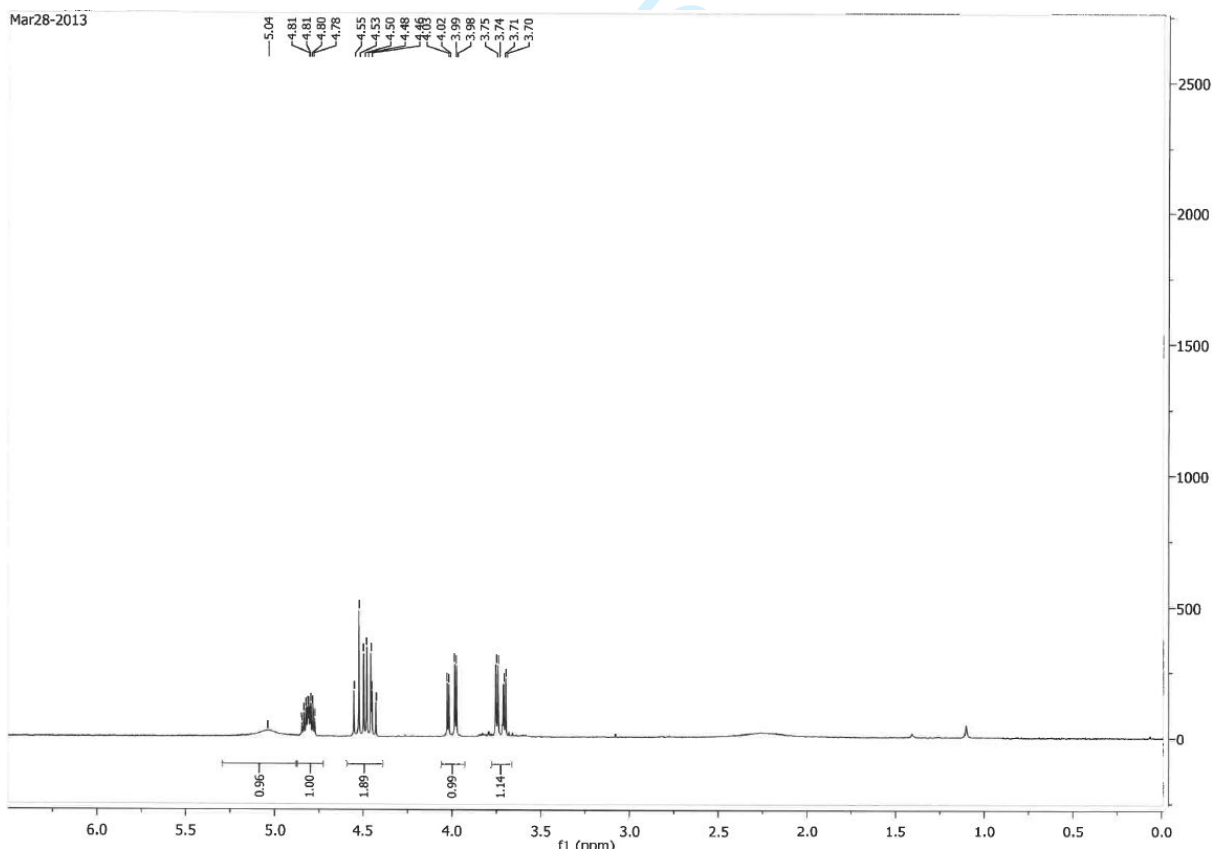
An open glass Schlenk tube is charged with 5 mL (61.8 mmol) epichlorhydrine, 580 mg (6.18 mmol) 2-aminopyridine and a magnetic stir bar. It is placed in a stainless-steel autoclave, then pressurized with carbon dioxide under 10 bar pressure. It is heated under stirring at 60°C (internal temperature) during 16 hrs. After cooling, the carbonate can be purified by filtration through a short pad of silica and eluting with diethyl ether followed by evaporation of the solvent to yield 7.58 g of carbonate (90 %).

4-(chloromethyl)-1,3-dioxolan-2-one 1a: light-yellow liquid liquid; ¹H NMR (300 MHz, CDCl₃) δ 4.94-5.02 (m, 1H), 4.56 (t, J = 8.4 Hz, 1H), 4.34-4.39 (m, 1H), 3.63-3.82(m, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 154.6, 74.6, 67.0, 44.2

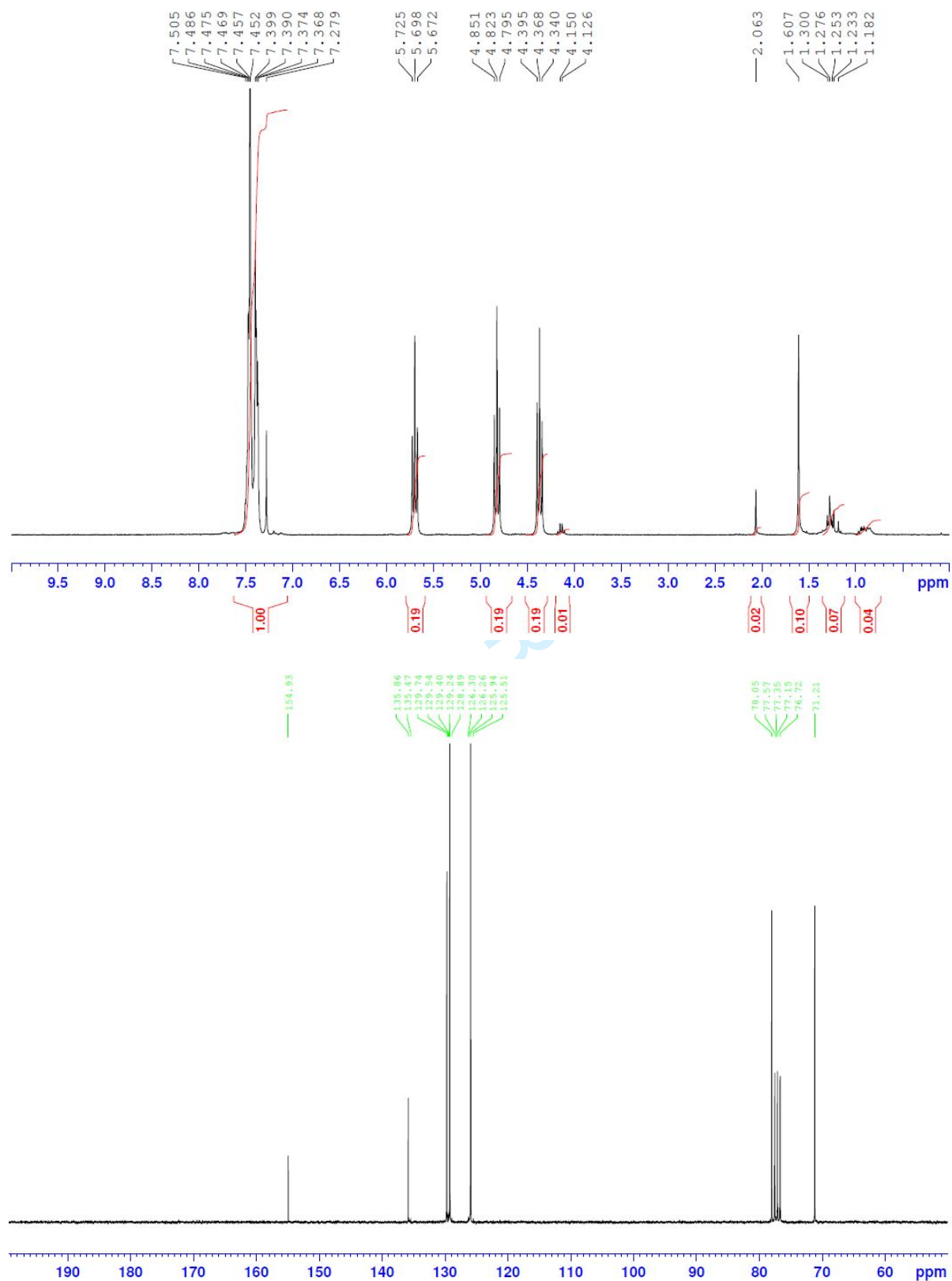




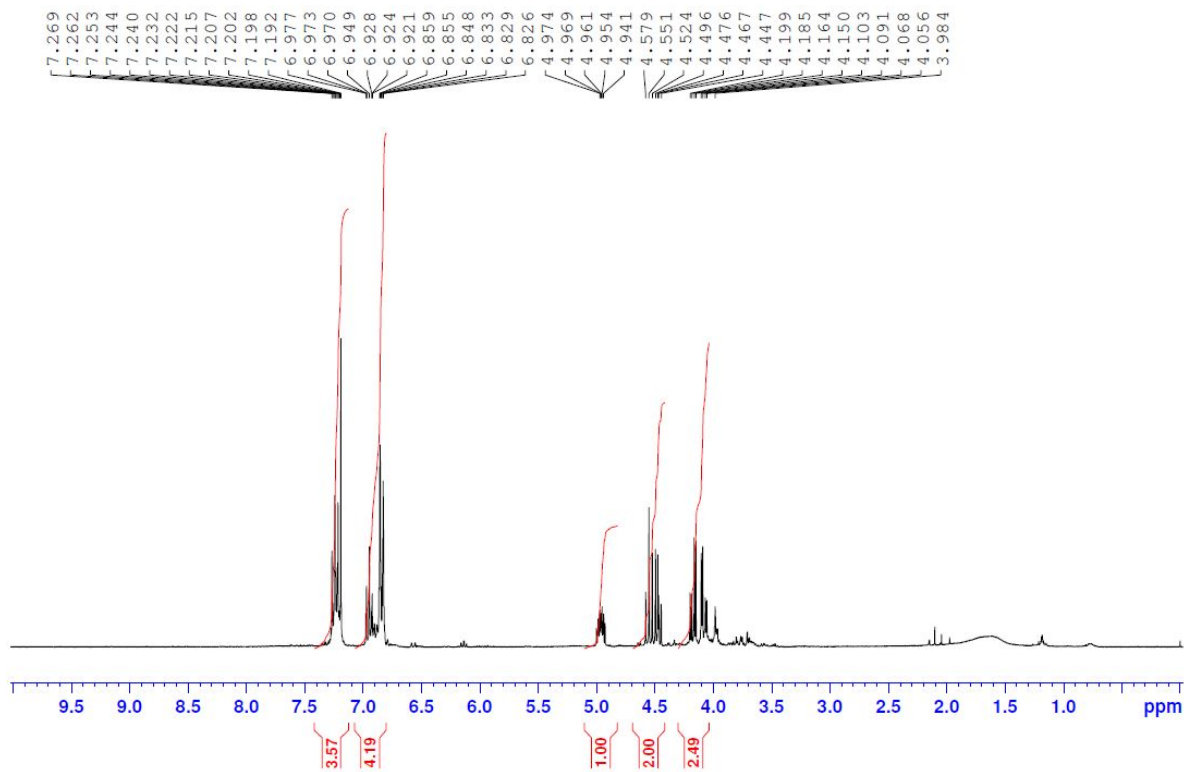
4-hydroxymethyl-1,3-dioxolan-2-one 1b: pale yellow liquid; 7.73 g obtained (87 %) from 5 mL (75.2 mmol) glycidol and 354 mg (3.8 mmol) 2-aminopyridine, under 5 bar CO₂ at 25°C during 16 hrs; ¹H NMR (300 MHz, CDCl₃) 5.04 (1H, brs), 4.78–4.81 (1H, m), 4.46–4.55 (2H, m), 4.01 (1H, dd *J* = 3.2, 13 Hz), 3.72 (1H, dd *J* = 3.5, 13 Hz); ¹³C NMR (75 MHz, CDCl₃): 155.2, 75.0, 65.8, 61.6



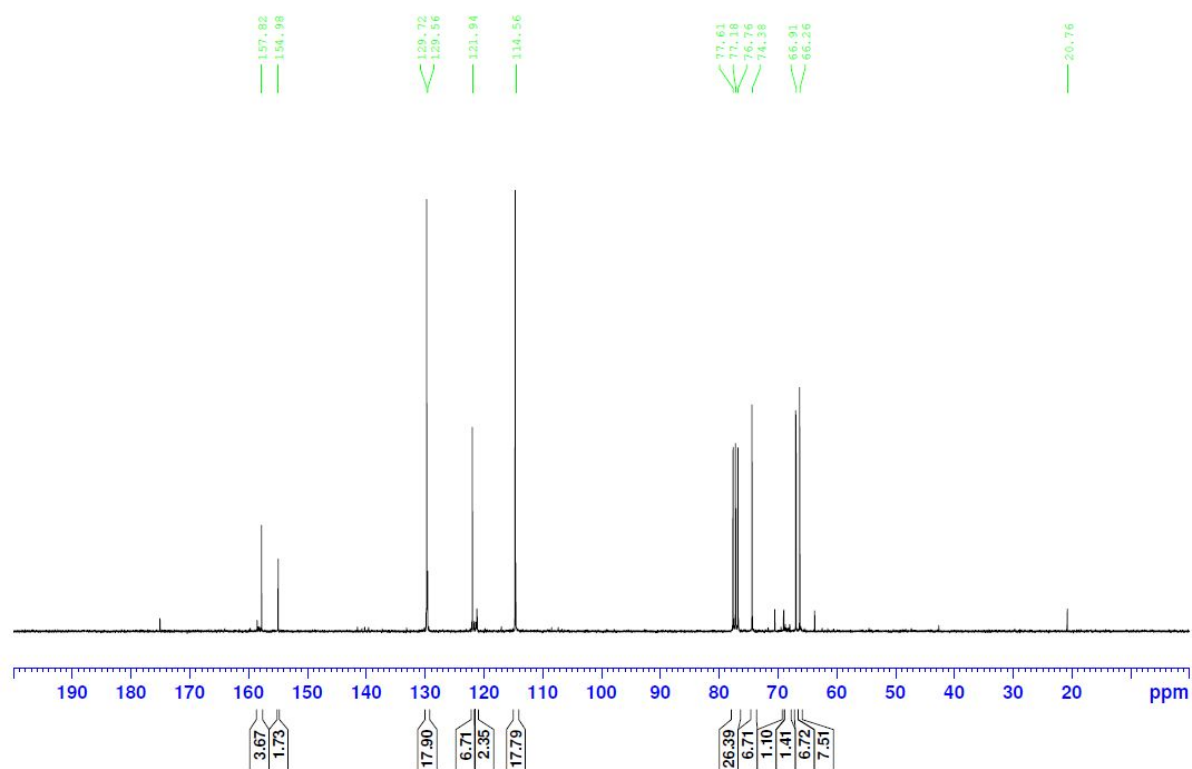
4-Phenyl-1,3-dioxolan-2-one **1c**: pale yellow liquid; 3.30 g obtained (46 %) from 5 mL (43.7 mmol) glycidol and 410 mg (4.4 mmol) 2-aminopyridine, under 20 bar CO₂ at 75°C during 16 hrs; ¹H NMR (300 MHz, CDCl₃): 7.42–7.37(m, 2H), 7.37–7.30(m, 3H), 5.70(t, 1H, *J*=7.9 Hz), 4.82(t, 1H, *J*=8.4 Hz), 4.37(t, 1H, *J*=8.4 Hz); ¹³C NMR (75 MHz, CDCl₃): 155.0, 135.9, 129.7, 129.2, 126.0, 76.8, 71.2



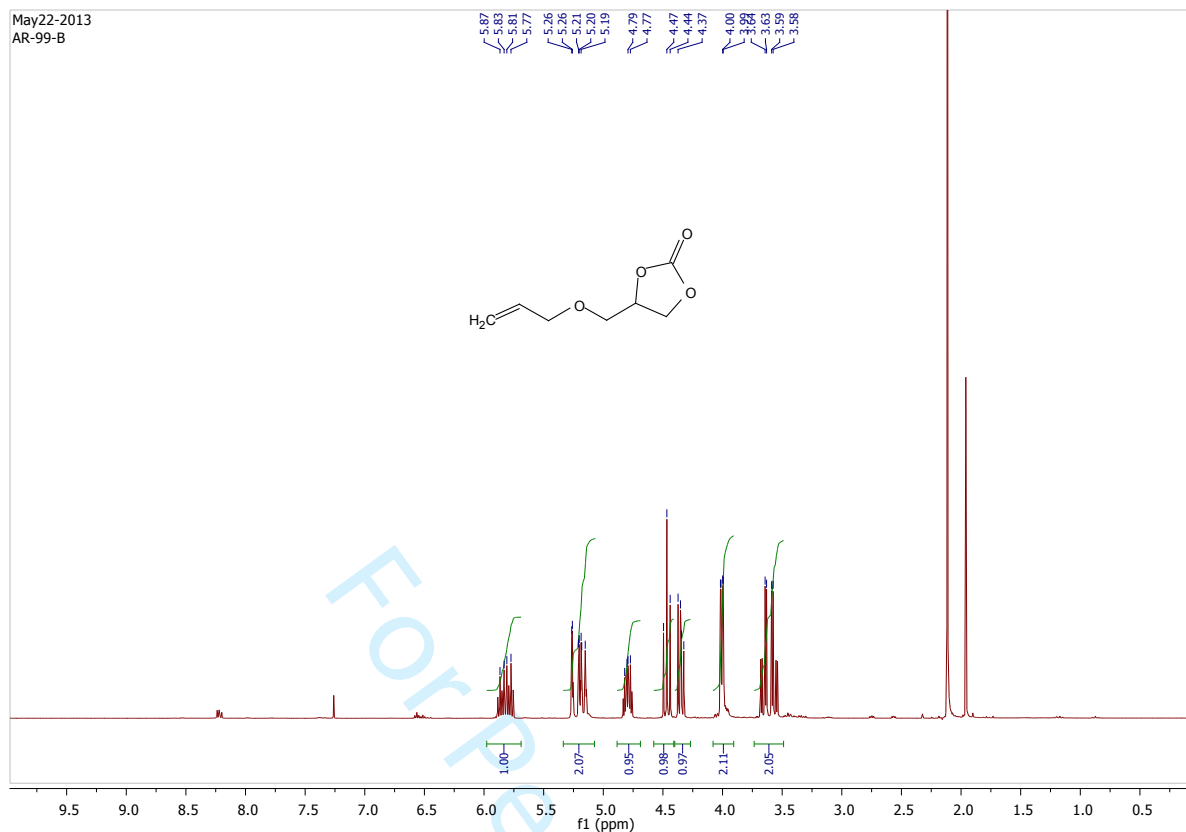
4-(Phenoxymethyl)-1,3-dioxolan-2-one 1d: pale brown solid; 6.84 g obtained (96 %) from 5 mL (36.6 mmol) phenyl glycidyl ether and 345 mg (3.7 mmol) 2-aminopyridine, under 20 bar CO₂ at 85°C during 16 hrs; ¹H NMR (300 MHz, CDCl₃): 7.36–7.22(m, 2H), 7.06–6.92(m, 1H), 6.91–6.85(m, 2H), 5.06–4.95(m, 1H), 4.65–4.56(m, 1H), 4.55–4.46(m, 1H), 4.22(dd, J = 10.5, 4.0Hz, 1H), 4.12 (dd, J = 10.5, 3.5Hz, 1H); ¹³C NMR (75 MHz, CDCl₃): 157.8, 155.0, 129.7, 122.0, 114.6, 74.4, 66.9, 66.3; HRMS: 194.0581



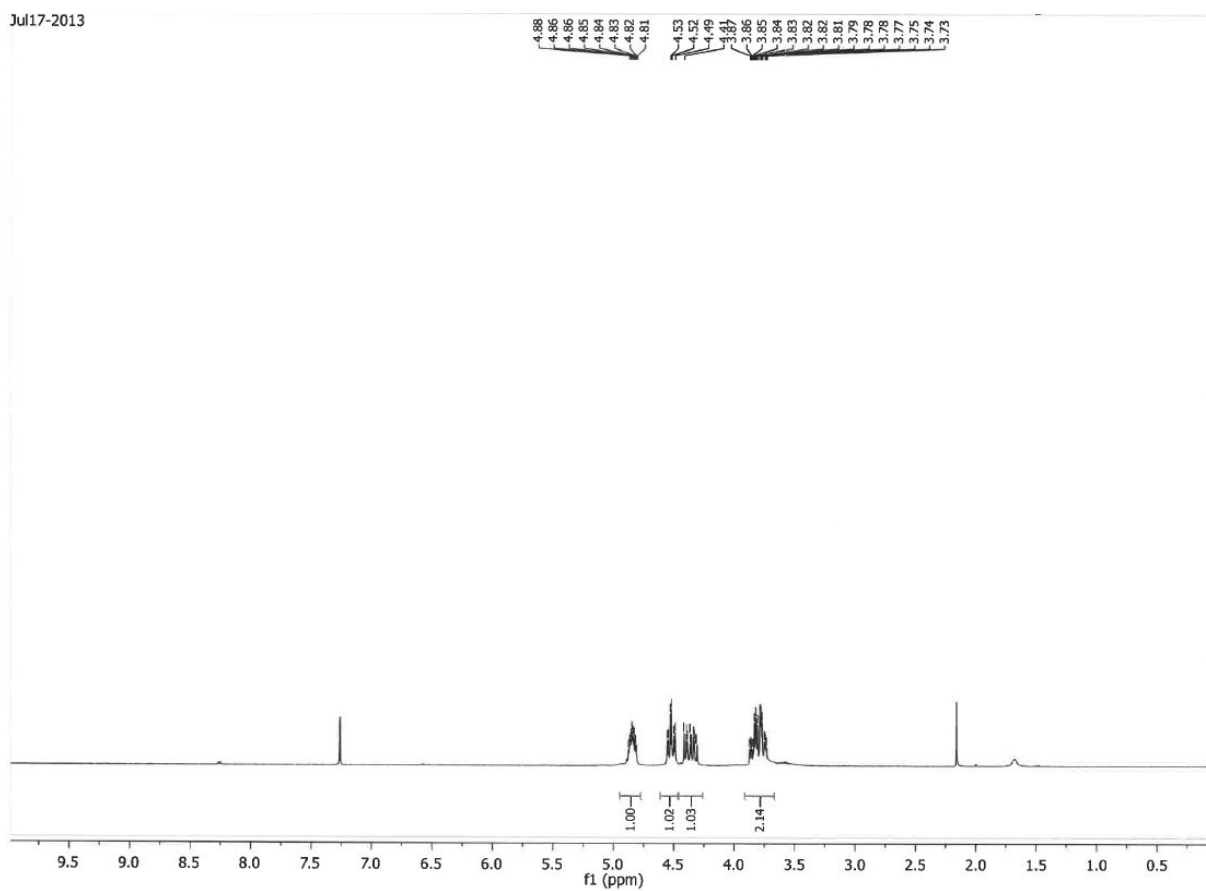
CHG carbonate carbon 13



4-(allyloxymethyl)-1,3-dioxolan-2-one: Colourless liquid; 6.72 g obtained (100 %) from 5 mL (42.5 mmol) glycidol and mg (mmol) 2-aminopyridine, under 20 bar CO₂ at 75°C during 16 hrs; ¹H NMR (300 MHz, CDCl₃) δ 5.71-5.83 (m, 1H), 5.13-5.21 (m, 2H), 4.71-4.81 (m, 1H), 4.43 (t, *J* = 8.4 MHz, 1H), 4.28-4.32 (m, 1H), 3.92-3.97(m, 2H), 3.49-3.64 (m, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 154.9, 133.6, 117.8, 75.0, 72.5, 68.8, 66.2



4,4'-(oxybis(methylene))bis(1,3-dioxolan-2-one): Colourless liquid; 7.68 g obtained (82 %) from 5 mL (43 mmol) diglycidyl ether and 405 mg (4.3 mmol) 2-aminopyridine, under 20 bar CO₂ at 85°C during 16 hrs; ¹H NMR (300 MHz, CDCl₃) δ 4.81-4.88 (m, 2H), 4.49-4.53 (m, 2H), 4.30-4.41 (m, 2H), 3.73-3.87 (m, 4H); ¹³C NMR (75 MHz, CDCl₃) δ 154.8, 133.5, 117.6, 75.0, 72.4, 68.7, 66.2



4,4'-((butane-1,4-diylbis(oxy))bis(methylene))bis(1,3-dioxolan-2-one): Colourless liquid; 7.68 g obtained (82 %) from 5 mL (43 mmol) diglycidyl ether and 405 mg (4.3 mmol) 2-aminopyridine, under 20 bar CO₂ at 85°C during 16 hrs