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## Process for CO<sub>2</sub> Removal and Valorisation from Cement Flue Gas

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## Imprint

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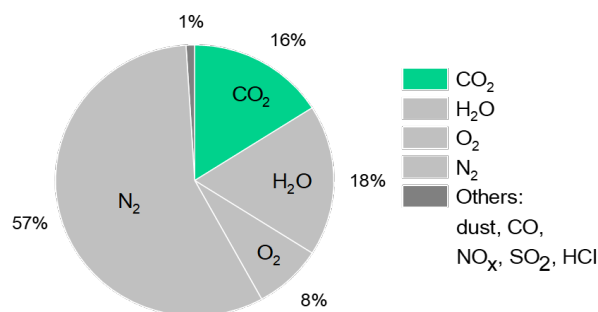
## 1 Abstract

Cement manufacturing accounts for a large portion of global greenhouse gas (CO<sub>2</sub>) emissions, changing the balance of life on earth and leading to global warming. Here, we developed a powerful catalytic method for the removal of CO<sub>2</sub> from gas streams, e.g. those generated during cement production, via a catalytic reaction between CO<sub>2</sub> and epoxides to afford useful cyclic carbonates. A continuous flow system employing a homogenous catalyst (tetrabutylammonium iodide, TBAI) and heterogenous catalyst (SiO<sub>2</sub>) were shown to efficiently promote the reaction in high yield. The process was successfully applied to a range of epoxides to generate a range of cyclic carbonates in excellent yield. These products have wide range of applications, e.g. as 'green' polar aprotic solvents, additives in lithium-ion batteries, and feedstocks to produce functional polymers. In order to model real flue gas, common impurities including O<sub>2</sub>, N<sub>2</sub>, NO<sub>2</sub>, CO and SO<sub>2</sub> were evaluated and shown to not to have a negative impact on the reaction (although water was found to be detrimental). Modelling using ASPEN demonstrates the economic viability and sustainability of the continuous flow system.

## 2 General introduction to the problem

CO<sub>2</sub> is a major greenhouse gas leading to global warming and its emission should be limited.<sup>1</sup> Global cement production accounts for about 1.4 Gt of CO<sub>2</sub> emissions per year,

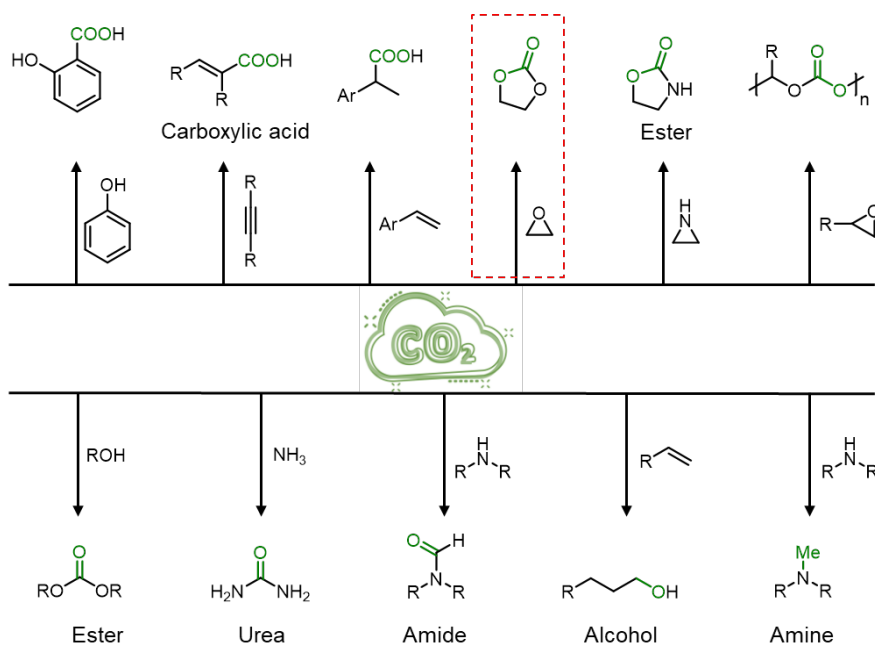
corresponding to roughly 5.8% of global anthropogenic emission.<sup>2</sup> Cement flue gas contains 16% CO<sub>2</sub>, which is far more than the average value of atmosphere of 0.04% (Fig. 1).<sup>2-3</sup>



**Figure 1.** Characteristics of cement plant flue gas.<sup>3</sup>

CO<sub>2</sub> capture and utilization of the flue gas is considered a sustainable strategy to reduce the CO<sub>2</sub> emission.<sup>4</sup> At present, the vast majority of carbon resources are based on crude oil, natural gas and coal, but CO<sub>2</sub> offers the possibility to create a renewable carbon economy and has become one of the most important industrial feedstocks due to its abundance, availability, nontoxicity and recyclability.

CO<sub>2</sub> as a source of single carbon atoms (termed C1 source) has received considerable interest over the last few decades, because it could potentially replace toxic C1 sources such as carbon monoxide, phosgene, etc.<sup>4-5</sup> In particular, incorporation of CO<sub>2</sub> into organic compounds and its transformation to value-added products has become an important topic in organic synthesis (Fig. 2).<sup>5</sup> However, activation and utilization of CO<sub>2</sub> is still problematic as the carbon in CO<sub>2</sub> is in the most oxidized form, which is thermodynamically stable and also kinetically inert in many reactions.<sup>6</sup> Consequently, most strategies use highly reactive substrates and/or forcing reaction conditions to activate CO<sub>2</sub>, limiting the application of such methods.



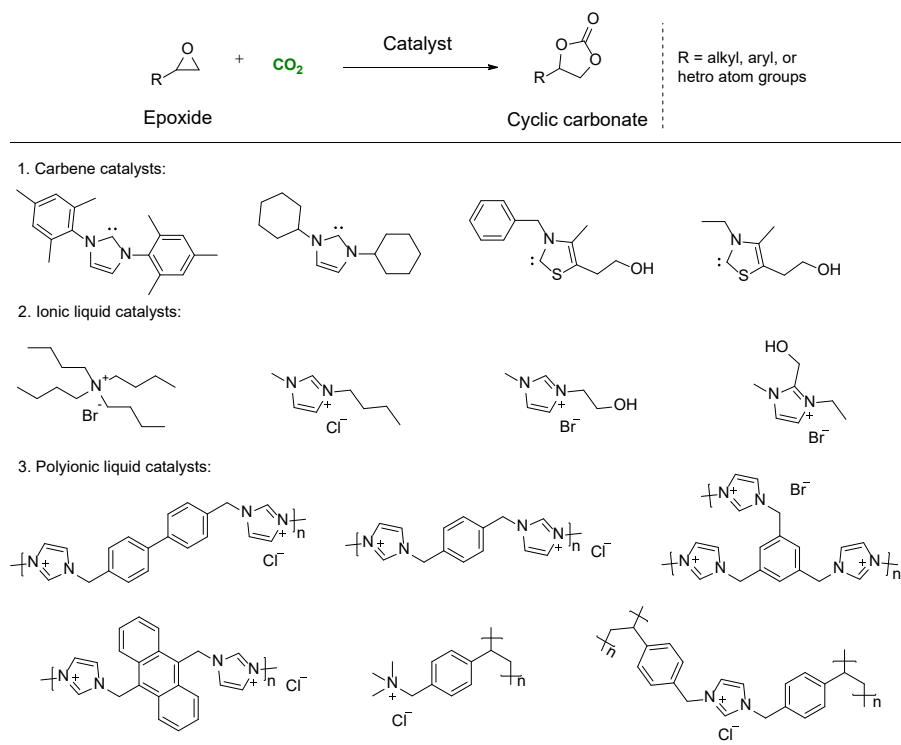
**Figure 2.** Applications of CO<sub>2</sub> in organic synthesis.

Moreover, all these reactions are performed in batch reactors, which is not suited to flue gas streams, and continuous flow methodologies would be advantageous, e.g. allowing reaction parameters to be monitored and optimized, resulting in reliable and reproducible processes.<sup>7-9</sup> Importantly, continuous flow systems provide very efficient heat and mass transfer, accelerating reaction rates, often leading to improved productivity with respect to batch systems.<sup>10</sup> However, switching chemical transformations from batch to continuous flow processes tend to be difficult (either reducing the product yield or in some cases is even considered impossible), primarily due to the limited interaction between the catalyst and substrates.

### 3 Solution

Cyclic carbonates have a continuously increasing market because of their extensive use as solvents, additives and as feedstocks used in the production of polymers, medicines and agricultural chemicals, etc.<sup>11-14</sup> Conventional synthesis of cyclic carbonates involves the reaction of diols with phosgene.<sup>15</sup> However, this reaction is not environment friendly due to the toxic and corrosive nature of phosgene. The formation of cyclic carbonates from epoxides and CO<sub>2</sub> involves fewer hazardous species, as it incorporates CO<sub>2</sub> as a C1 feedstock source instead of phosgene. The cycloaddition

reaction proceeds with 100% atom economy, i.e. there is no waste by-product, and thus constitutes one of the most efficient examples of artificial CO<sub>2</sub> fixation.



**Figure 3.** Fixation of CO<sub>2</sub> via cycloaddition with epoxides to produce cyclic carbonates and examples of catalysts used.

Our group have developed powerful catalytic tools for the removal of CO<sub>2</sub> from gas streams via cycloaddition with epoxides to form cyclic carbonates,<sup>16-25</sup> and carbene, ionic liquid and poly-ionic liquid catalysts have been intensely investigated (Fig. 3). These catalysts were developed using batch reaction conditions and in one case using a continuous flow process, enabling continuous CO<sub>2</sub> removal from flue gas streams. Although the demand for cyclic carbonates does not correspond to the amount of CO<sub>2</sub> produced globally, the demand for cyclic carbonates has been increasing rapidly,<sup>26-28</sup> and could contribute towards CO<sub>2</sub> mitigation.

## 4 Specific goals and plan

1. Fixed-bed reactor design and construction. The feedstock (gas and epoxide) will be injected into a fixed-bed reactor packed with the catalyst. The flow rates (and thus also the residence times) will be controlled using a pump (for the liquid epoxide) and mass flow meter (for the

gas). The product distribution will be monitored online (gas and liquid phase). Throughout the optimization process, flow-rates, reaction temperature and fixed-bed reactor pressure will be varied and the process parameters continuously monitored.

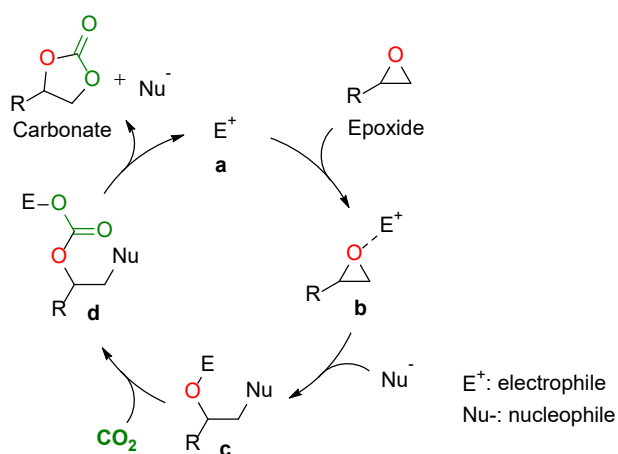
2. Catalyst design and optimization. Design and development of a highly active and selective catalytic system for the conversion of CO<sub>2</sub> into cyclic carbonates under continuous-flow conditions is essential.<sup>29</sup> The most common catalytic systems for this reaction have Lewis acid character, which activates the epoxide, and a Lewis base, which leads to ring opening of the epoxide. The Lewis acid is usually a metal complex or a hydrogen bond donor species and the Lewis base is usually a halide (Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>). The two types of active sites can be included within a bifunctional single component catalyst or in a binary system consisting of two separate components.
3. Determination of kinetic parameters. Once the reactor and catalytic system is operational, the kinetics of CO<sub>2</sub> extraction will be evaluated. To obtain the relevant kinetic parameters, a series of experiments will be conducted to study the reaction rate as a function of temperature, pressure and residence time in the reactor.
4. Development of a model for the process. The kinetic parameters will be implemented into a model for the process, using ASPEN, and will lead to key feasibility data. Heat optimization and energy consumption of the plant will be calculated to estimated CapEx and OpEx values.

## 5 Results

### 5.1 Continuous flow reactor design

Previously, we proposed a generalized catalytic cycle for the reaction of CO<sub>2</sub> and epoxides to yield cyclic carbonates (Fig. 4), which facilitates catalyst design. In this cycle, an electrophile **a** coordinates to the epoxide to form epoxide adduct **b**. A nucleophile then attacks the coordinated epoxide at the  $\beta$ -position to generate a ring-opened alkoxy intermediate **c**. Next, insertion of CO<sub>2</sub> into the metal–oxygen bond forms the carbonate intermediate **d**. Backbiting occurs with another inversion leading to ring closing and elimination to form the cyclic carbonate product. Thus, for the cycloaddition reaction, with two catalysts, acting as nucleophile and electrophile separately, or one bifunctional catalyst which could act as both nucleophile and electrophile simultaneously, are required. The nucleophile should also be a good leaving group to facilitate opening of the epoxide

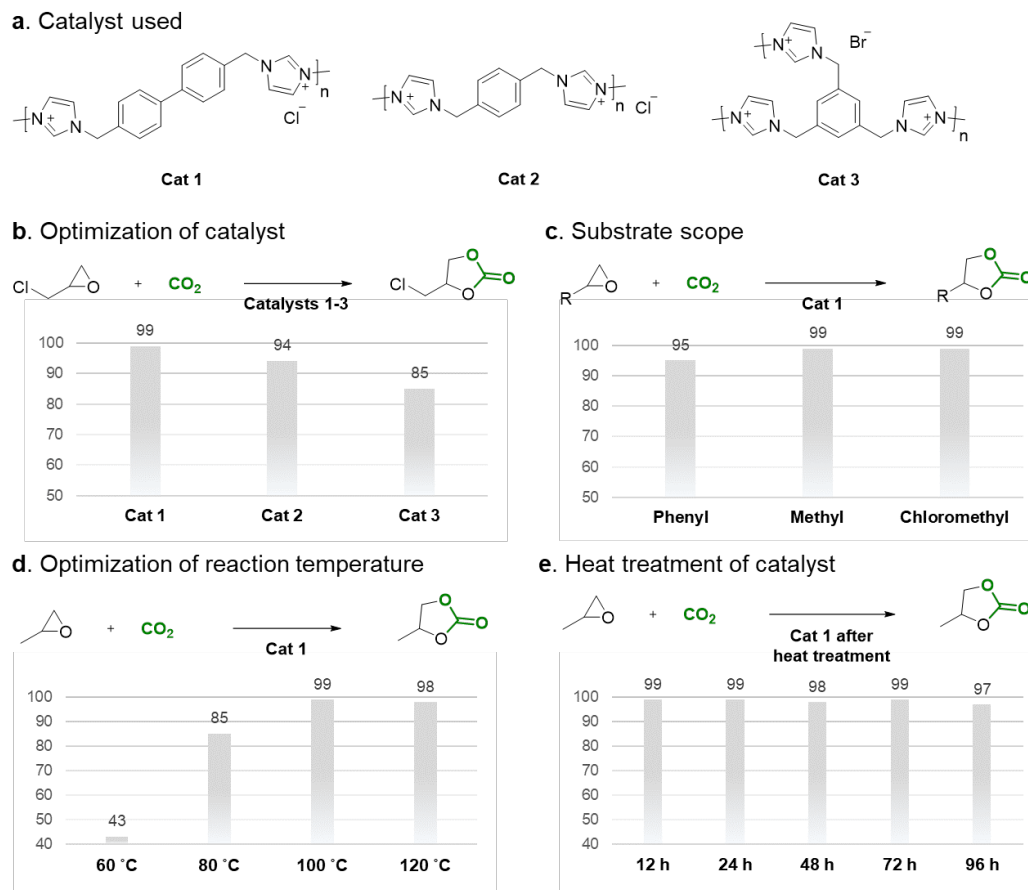
ring and ultimately allow cyclic carbonate formation. Similarly, to facilitate the  $\text{CO}_2$  insertion step, the electrophile should form favourable interactions that stabilize the ring-opened epoxide.



**Figure 4.** Mechanistic cycle for the catalytic cycloaddition reaction between  $\text{CO}_2$  and epoxides.

Regarding the reaction conditions, the influence of temperature on cyclic carbonate synthesis is difficult to predict. The reaction rate of the cycloaddition reaction generally increases with temperature due to an increase in catalyst activity at a higher temperature.<sup>30</sup> Moreover, increasing the temperature increases the gas diffusivity and decreases the viscosity of the reaction medium, both of which increase the gas-liquid mass transfer coefficient.<sup>31</sup> However, elevated temperatures may also accentuate side reactions such as isomerization and hydrolysis, leading to a significant decrease in product selectivity.<sup>32-36</sup> The effect of  $\text{CO}_2$  pressure in various homogeneous and heterogeneous catalytic systems has been extensively studied, and increasing the  $\text{CO}_2$  pressure results in an increase in reaction rate. Nevertheless, too high  $\text{CO}_2$  pressure increases equipment costs and reduces the epoxide concentration, leading to a decrease in the reaction rate.<sup>37-39</sup>

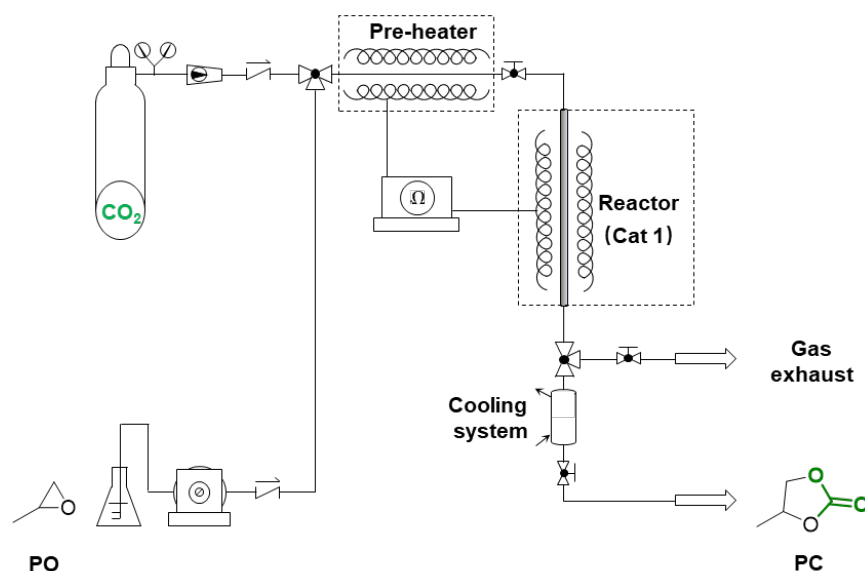
According to our previous studies, we initially selected polymeric ionic liquid catalysts, (Fig. 5a), and tested their efficiency under batch conditions. Polymeric ionic liquid catalysts are bifunctional catalysts, which act as both electrophile and nucleophile.



**Figure 5.** Optimization of the catalyst and reaction conditions in a batch reactor. (a) Polyimidazolium salt catalysts evaluated. (b) Catalytic activity tests. (c) Substrate scope evaluation. R = Phenyl, Methyl or Chloromethyl. (d) Reaction temperature tests. (e) Heat treatment of catalyst at 100 °C. Yields were determined by gas chromatography and each reaction was repeated for 2-3 times and average yield is provided.

The biphenyl-based polyimidazolium catalyst (Cat 1) was found to be the most efficient catalyst (Fig. 5b). The substrate scope was also investigated. Alkyl propylene oxide and epichlorohydrin are both transformed to their corresponding cyclic carbonates in high yield (Fig. 5c). Cycloaddition of CO<sub>2</sub> to propylene oxide was conducted at different reaction temperatures, with the highest conversion and yield achieved at 100 °C (Fig. 5d). In order to investigate thermal stability of Cat 1, heat treatment at 100 °C was conducted before using Cat 1 in the cycloaddition reaction (Fig. 5e). Cat 1 exhibits excellent thermal stability and was selected for further study in the fixed-bed reactor operating under continuous flow conditions.

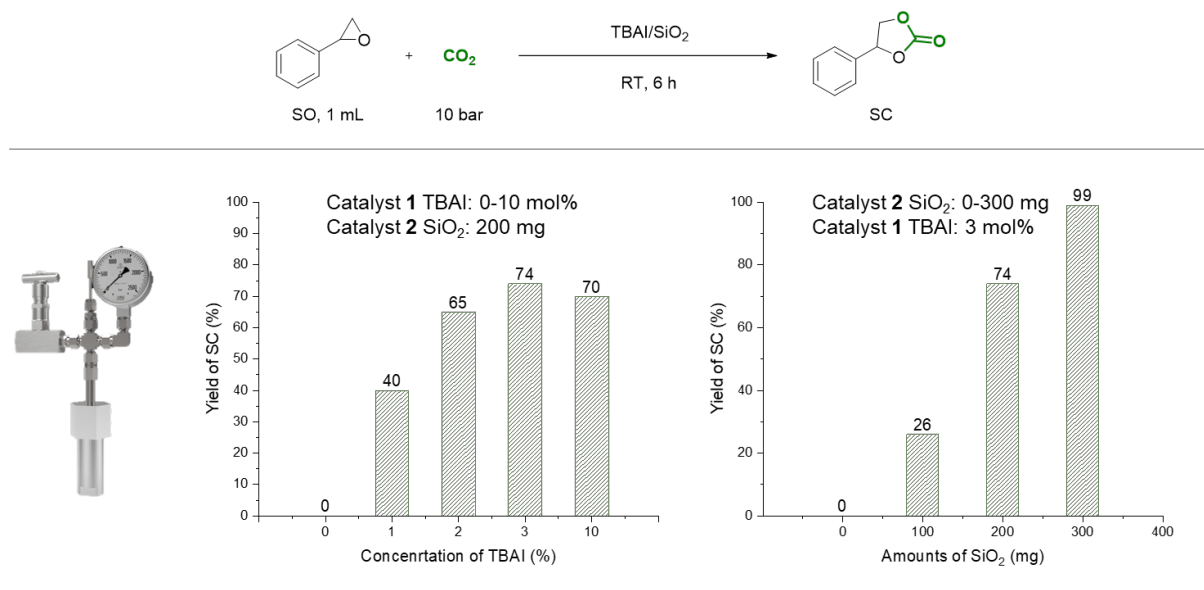
A fixed-bed reactor was then constructed (Fig. 6) and evaluated. Propylene oxide (PO) and commercially available CO<sub>2</sub> gas were used as substrates. The flow rates of liquid PO and CO<sub>2</sub> were controlled via a liquid pump and CO<sub>2</sub> mass flow meter. After mixing, the CO<sub>2</sub> and PO were preheated and then passed into the fixed-bed reactor, containing Cat 1. After entering the cooling unit, the liquid product generated was analysed. The fixed-bed reactor with biphenyl based polyimidazolium catalyst (Cat 1) works well, but the catalytic efficiency is not satisfactory (liquid flow rate < 1 mL/h, conversion of PO < 10%, reaction temperature = 100°C), which is not unusual when transferring a batch process to a continuous process.



**Figure 6.** Schematic of the fixed-bed reactor system.

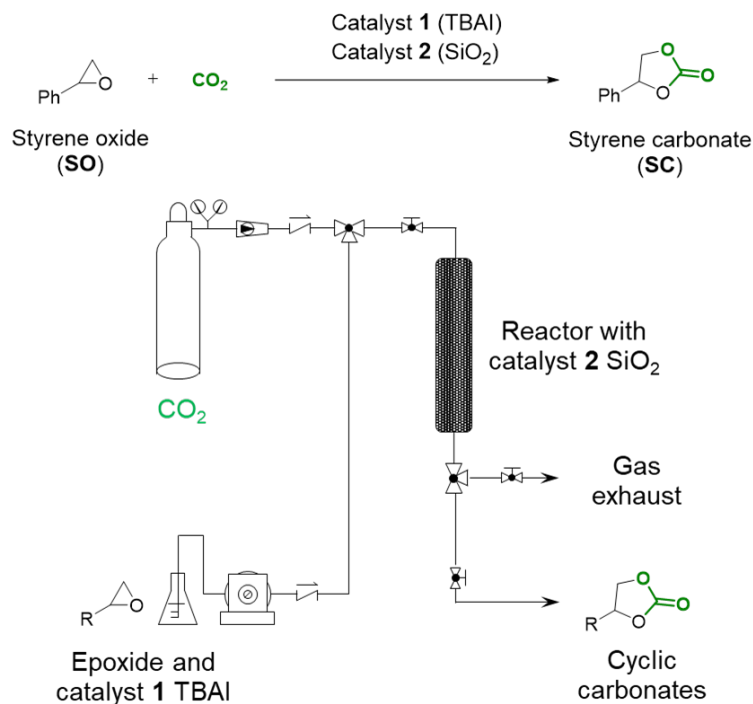
As mentioned above, compared to batch reactions, continuous flow processes provide a much lower retention time of substrate in the reactor, which requires a catalytic system with a short induction period and high turnover frequency. Hence, we hypothesized that a co-catalyst would be beneficial in a continuous flow process. Note that co-catalysts have been extensively studied in cyclic carbonate synthesis.<sup>40</sup> Commonly used co-catalyst for this reaction are nucleophile additives such as quaternary ammonium and phosphonium salts. The role of co-catalyst during cyclic carbonate formation is to open the epoxide ring, the rate determining step.<sup>41</sup> Following screening studies (see below), we discovered that using tetrabutylammonium iodide (TBAI) as a co-catalyst allows commercially available silica (SiO<sub>2</sub>) to be used as a highly efficient catalyst for the cyclic carbonate synthesis (notably a metal-free, non-toxic and inexpensive system). The effect of the

amount of TBAI and SiO<sub>2</sub> catalysts on the reaction between CO<sub>2</sub> and styrene oxide (SO) was initially studied in an autoclave batch reactor (Fig. 7). Reactions do not proceed in the absence of either the TBAI or SiO<sub>2</sub>, and from the catalyst concentration studies, a synergetic effect between the two catalysts appears to be in operation. In the batch reaction, the SiO<sub>2</sub> catalyst combined with the TBAI co-catalyst promotes the cycloaddition reaction to generate styrene carbonate (SC) in near stoichiometric yield (99%), even at room temperature.



**Figure 7.** Cycloaddition of CO<sub>2</sub> to styrene oxide (SO) in a batch reactor. Reaction conditions: SO (1 mL), TBAI (0-10 mol%), SiO<sub>2</sub> (0-300 mg), room temperature (RT), 6 h. Yields were determined by gas chromatography and each reaction was repeated for 2-3 times and average yield is provided.

The heterogeneous SiO<sub>2</sub> catalyst and homogeneous TBAI co-catalyst was then evaluated in a specially designed fixed-bed reactor as shown in Fig. 8. In the continuous process the TBAI is dissolved in the substrate solution (SO). As the liquid flows through the fixed-bed reactor packed with SiO<sub>2</sub> it is mixed with the gas containing CO<sub>2</sub>, promoting the reaction of CO<sub>2</sub> with SO to give the SC product in high yield.

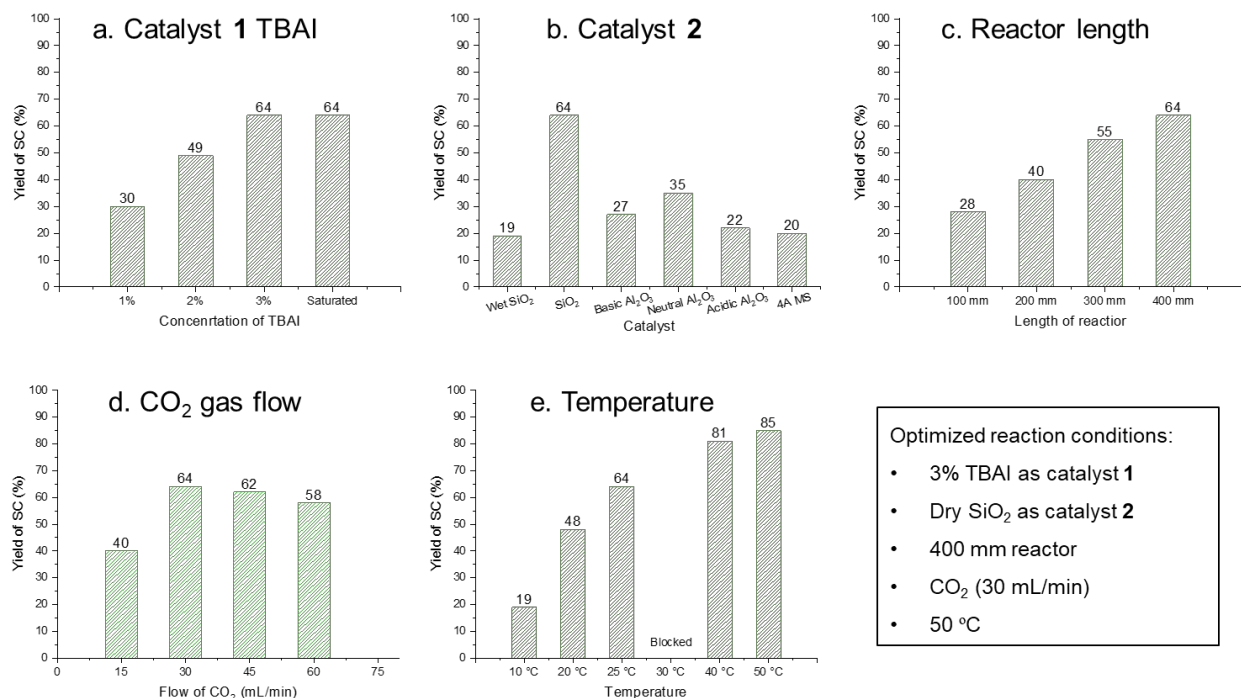


**Figure 8.** Reaction of styrene oxide (SO) and CO<sub>2</sub> to afford styrene carbonate (SC) (a valuable commodity chemical product) for direct CO<sub>2</sub> removal from gas streams (top). Outline of the fixed-bed reactor (bottom).

## 5.2 Parameter optimization

The type of heterogenous catalyst, concentration of the TBAI co-catalyst, reactor length, gas flow rate and reaction temperature, were further optimized as they significantly influence the cycloaddition reaction (Fig. 9). The concentration of the TBAI catalyst in the SO substrate solution was found to be a simple way to regulate the yield of the SC product (Fig. 9a). Since the TBAI concentration also impacts on the viscosity of the solution, a 3 mol% concentration was found to be optimal. Several solid catalysts were evaluated including Al<sub>2</sub>O<sub>3</sub> and molecular sieve, with SiO<sub>2</sub> providing the best performance (Fig. 9b). Notably, wet SiO<sub>2</sub> (commercially available product) gives a lower reaction yield of SC and water in the reaction system significantly reduces the reaction yield, see discussion below. As expected, the longer the reactor, the higher the yield of the product (Fig. 9c). The influence of the gas flow rate (Fig. 9d) and reaction temperature (Fig. 9e) were also optimized. At 25 °C, the yield reached to 64%, but at 30 °C, the reactor blocks due to the increased yield of SC (as the melting point of SC is ~50 °C the product solidified when its concentration is too high). However, at a higher temperature of 40 °C the SC product does not

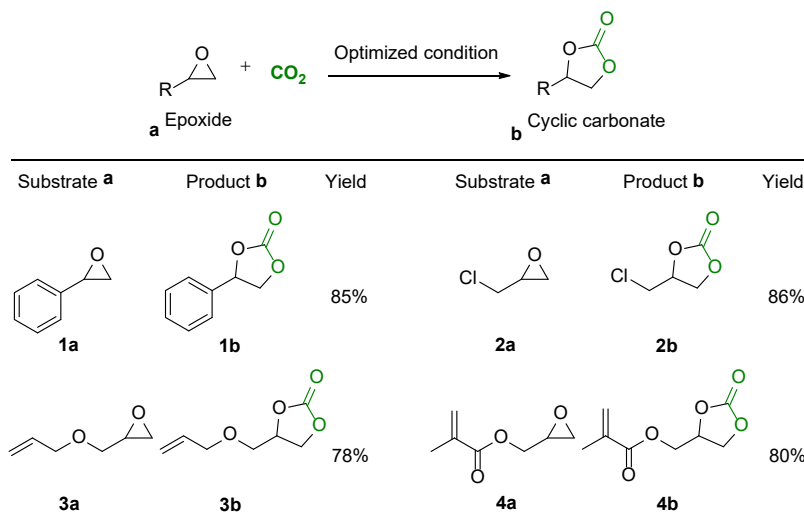
precipitate in the reactor, and only solidifies after cooling. Thus, the yield of SC reached 81% at 40 °C and 85 % at 50 °C.



**Figure 9.** Reaction parameter optimization under continuous flow conditions. Reaction conditions: TBAI (1-3mol%), SiO<sub>2</sub> (10-40 g), SO (0.1 mL/min), CO<sub>2</sub> (15-60 mL/min), 10-50 °C. Yields were determined by gas chromatography and each reaction was repeated for 2-3 times and average yield is provided.

### 5.3 Substrate scope

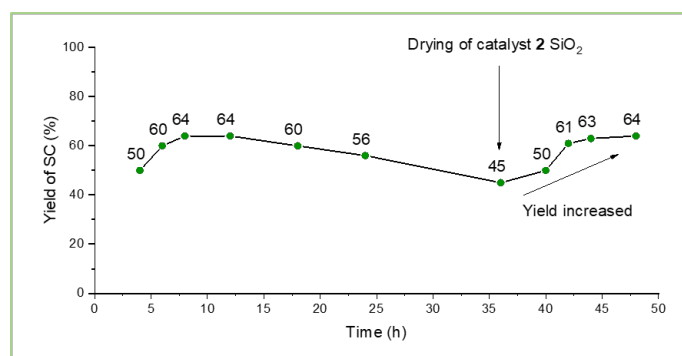
The substrate scope was expanded to other alkyl epoxides with heteroatoms or unsaturated bonds (Fig. 10). Similar to the aromatic epoxide **1a**, alkyl epoxides with a chloride (**2a**), vinyl (**3a**) or methacrylate (**4a**) group also produce the corresponding cyclic carbonate, i.e. 4-chloromethyl-dioxolan-2-one (**2b**), 4-((allyloxy)methyl)-1,3-dioxolan-2-one (**3b**), (2-oxo-1,3-dioxolane-4-yl)methyl methacrylate (**4b**) in high yield (78-85%). Styrene carbonate **1b** is widely used as an additive in lithium-ion traction batteries,<sup>42</sup> 4-chloromethyl-dioxolan-2-one (**2b**) is low-toxicity coating remover,<sup>43</sup> 4-((allyloxy)methyl)-1,3-dioxolan-2-one (**3b**) and (2-oxo-1,3-dioxolane-4-yl)methyl methacrylate (**4b**) are functional monomers used in the synthesis of polymers with high-end applications.<sup>43-46</sup>



**Figure 10.** Substrate scope of the continuous flow system. Reaction conditions: TBAI (3 mol%), fix-bed reactor (400 mm × 10 mm), epoxide (0.1 mL/min), CO<sub>2</sub> (30 mL/min), 50 °C. Yields were determined by gas chromatography and each reaction was repeated for 2-3 times and average yield is provided.

#### 5.4 Effect of gas impurities in cement flue gas

In addition to CO<sub>2</sub>, the main gases in cement flue gases include O<sub>2</sub>, N<sub>2</sub>, H<sub>2</sub>O and other relatively minor impurities including NO<sub>2</sub>, CO and SO<sub>2</sub>. Neither oxygen or nitrogen impact negatively on the reaction (see below), but water was found to be problematic. The evolution of the reaction yield over time in the flow reactor is summarized in Fig. 11.



**Figure 11.** Evolution of the yield of SC to illustrate the effect of water on the reaction. Reaction conditions: TBAI (3 mol%), fix-bed reactor (400 mm × 10 mm), SO (0.1 mL/min), CO<sub>2</sub> (30 mL/min), 25 °C.

Under the optimized reaction conditions, the maximum yield is reached in ca. 8 hours. After this time the reaction yield of SC slowly decreases to 45% at 36 h. The decrease in yield may be attributed to the accumulation of water in the system during the reaction, which originates from moisture in the CO<sub>2</sub> stream. To confirm the detrimental impact of water, the SiO<sub>2</sub> catalyst was dried after 36 h and replaced in the reactor, with the SC product yield recovering.

Other minor impurities including CO and SO<sub>2</sub> have no observable negative impact on the cycloaddition reaction (Table 1, entries 1-2). NO<sub>2</sub> even slightly improves the product yield (Table 1, entry 3) and the reason for this improvement currently remains unknown. To model the real flue gas, CO<sub>2</sub> gas diluted with air was also tested. The yield of SO is 70%, with the lower yield attributed to the increased gas flow. These results demonstrate diluted CO<sub>2</sub> gas or CO<sub>2</sub> with impurities (with the exception of H<sub>2</sub>O) can be used in the CO<sub>2</sub> and epoxide cycloaddition, confirming the potential application of the process to remove CO<sub>2</sub> from cement flue gas.

**Table 1.** Effect of other gas impurities on the reaction of CO<sub>2</sub> with SO under continuous flow conditions.

Entry	CO <sub>2</sub> with additives	Yield of SC (%)	Effect
1 <sup>a</sup>	10 ppm CO in CO <sub>2</sub>	83	None
2 <sup>a</sup>	2 ppm SO <sub>2</sub> in CO <sub>2</sub>	80	None
3 <sup>a</sup>	5 ppm NO <sub>2</sub> in CO <sub>2</sub>	89	Yield slightly increases
4 <sup>b</sup>	10% CO <sub>2</sub> , 72% N <sub>2</sub> , 18% O <sub>2</sub>	70	None

Reaction conditions (**a**): CO<sub>2</sub> gas mixture (30 ml/min, based on pure CO<sub>2</sub>), TBAI (3 mol%), SO (0.1 ml/min), 50°C, reactor (40 cm × 1 cm). (**b**): CO<sub>2</sub> gas mixture (150 ml/min), TBAI (3 mol%), SO (0.05 ml/min), 50°C, reactor (40 cm × 1 cm). Limited by the current instrument, the flow of SO have to be decreased. Decreased yield may be attributed to the increased gas flow.

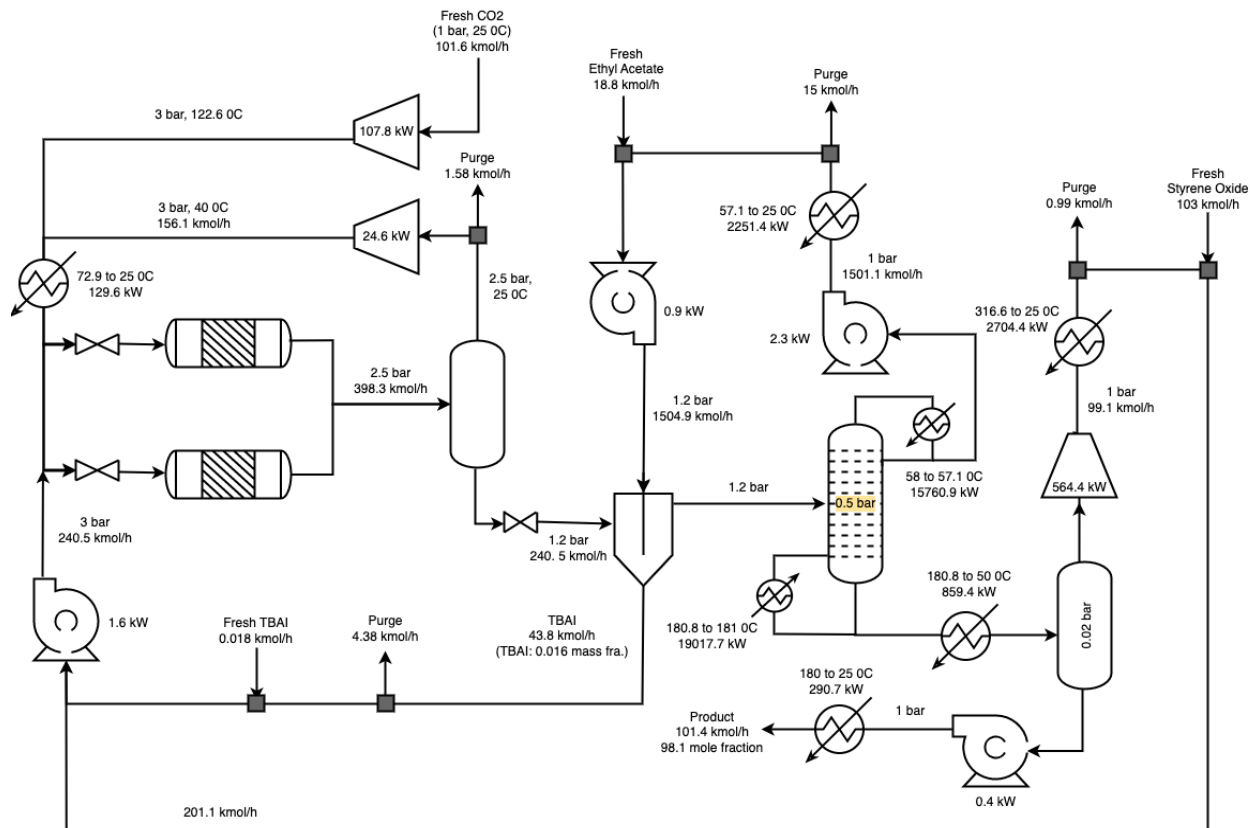
### 5.5 Modelling

In order to investigate the kinetics and economic viability of the reaction process, the experimental data was implemented into a model using ASPEN to analyze crucial parameters of the reaction process. A process model for the production of SC from SO and CO<sub>2</sub> was developed in Aspen Plus. SO and CO<sub>2</sub> react to form SC in the presence of SiO<sub>2</sub> (solid catalyst) and TBAI (co-catalyst). Ethyl

acetate is used to recover and recycle TBAI. In the Aspen Plus database, SO, CO<sub>2</sub> and ethyl acetate are available. SC was defined with properties estimated using the UNIFAC group contribution method, and TBAI was modelled as an inert solid.<sup>47</sup> In addition, the Peng-Robinson thermodynamic model was used to simulate the process flowsheet.<sup>22</sup>

The production process (Fig. 12) was designed for a production rate of 101.4 kmol/h. SO is mixed with TBAI (3 wt.%) and then reacts with CO<sub>2</sub> at 3 bar and 25 °C in a fixed-bed reactor. The volumetric flow ratio for the CO<sub>2</sub> and SO is set to 225, resulting in a SC yield of 58%. Subsequently, the reaction products enter a flash tank, where unconverted CO<sub>2</sub> is recovered and recycled back to the reactor inlet and mixed with fresh CO<sub>2</sub>. The co-catalyst, TBAI, which remains in the liquid stream, is recovered by precipitation in ethyl acetate, to be recycled with the SO flow at the reactor inlet. A distillation column is used to separate ethyl acetate from the SC and unreacted SO. The recovered ethyl acetate is mixed with make-up ethyl acetate. Finally, SC and SO are separated making use of their boiling point difference in a flash tank. The recovered SO is mixed with fresh SO, and the SC product is obtained with 98% purity, when cooled to ambient temperature. The production process has several compressors, pumps and heaters/coolers. In order to control the impurities, the process has several purge streams, and an overall product loss of 5% has been assumed. The process consumes 103 kmol/h SO, 101.6 kmol/h CO<sub>2</sub> and 6.8 kg/h TBAI.

The total installed cost of a plant is 5.68 million \$ (Aspen Economic Analyzer). And the minimum selling price of SC is 38.43 \$/kg. From the company Toronto Research Chemicals, the price of SC is over 10'000 times than SO. Thus, our simulation results show an economic viability of the CO<sub>2</sub> removal process established. Many other cyclic carbonates could be prepared via this process and in nearly all cases the price significantly exceeds that of the epoxide precursor. Hence, the price of cyclic carbonate products obtained by this process is competitive to those prepared by the usual methods. Since the cyclic carbonates prepared by this method also contain one renewable carbon atom derived from CO<sub>2</sub> (and some epoxide substrates are derived from biomass which would lead to entirely renewable cyclic carbonates), there would also be incentives to purchase cyclic carbonates prepared in this manner.



**Figure 12.** Process flow diagram for styrene carbonate production using SO and CO<sub>2</sub>.

## 6 Future work

The process should be patented and a demonstrator reactor constructed. Following optimization of the demonstrator, real cement flue gas should be studied and the economic viability of the process based on data from the demonstrator determined. The size of the demonstrator must also be defined, which will depend on future investment.

## 7 Financial

Funding support from FOEN and Cemsuisse was used for personal costs. One postdoc has been hired for the duration (two years) of the project. Other staff at EPFL (technician, PhD student, postdoc, senior scientist and admin) have been dedicated part of their time to this project. Furthermore, EPFL has contributed with costs of consumables and equipment.

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## 10 Supplementary information

### 10.1 Abbreviations and designations

TBAI, tetra-n-butylammonium iodide

TBAB, tetra-n-butylammonium bromide

C1, single carbon

Cat 1, catalyst 1

HPLC, high-performance liquid chromatography

GC-EI-MS, gas chromatography - electron ionization - mass spectrometry

SO, styrene oxide

SC, styrene carbonate, 4-phenyl-1,3-dioxolan-2-one

PO, propylene oxide

PC, propylene carbonate, 4-methyl-1,3-dioxolan-2-one

CapEx, capital expenditures

OpEx, operating expenses

RT, room temperature

**1a**, SO, styrene oxide, 2-phenyloxirane

**2a**, epichlorohydrin, 2-(chloromethyl)oxirane, chloropropylene oxide

**3a**, glycidyl vinyl ether

**4a**, glycidyl methacrylate, 2,3-epoxypropyl methacrylate

**1b**, styrene carbonate, 4-phenyl-1,3-dioxolan-2-one

**2b**, 4-chloromethyl-dioxolan-2-one

**3b**, 4-((allyloxy)methyl)-1,3-dioxolan-2-one

**4b**, (2-oxo-1,3-dioxolane-4-yl)methyl methacrylate

### 10.2 Materials

Epoxide substrates **1-4a**, propylene oxide, solvents and other organic compounds were purchased from Sigma-Aldrich. Silica gel was purchased from SiliCycle Inc. CO<sub>2</sub> gas or CO<sub>2</sub> gas mixtures were purchased from Carbagas AG. Fittings, valves, regulators and tubing for the reactor

construction were purchased from Swagelok Company. REAXUS HPLC reciprocating pump (LS-class) was purchased from IGZ Instruments AG. Gas mass flowmeter (EL-FLOW® Prestige) was purchased from Bronkhorst (Switzerland) AG.

### *10.3 Typical method of CO<sub>2</sub> and epoxide cycloaddition reaction*

Liquid substrate was prepared by dissolving TBAI (3 mol%) catalyst in epoxide and filtered to remove the impurities. Fix-bed reactor (10 × 400 mm) was filled with 8.7 g silica gel (Before use, commercially available silica gel was dried at 150 °C for 24 h to remove H<sub>2</sub>O). Liquid (0.1-0.5 mL/min) and gas (130 mol%) flow were mixed together and passed fix-bed reactor. Liquid and gas products were collected and analyzed per hour. Yield was determined by GC (error range ~5%) and reactions were repeated at least twice and up to 10 times to ensure reproducibility. Pure cyclic carbonates were isolated by Column Chromatography.

### *10.4 TBAI recovery*

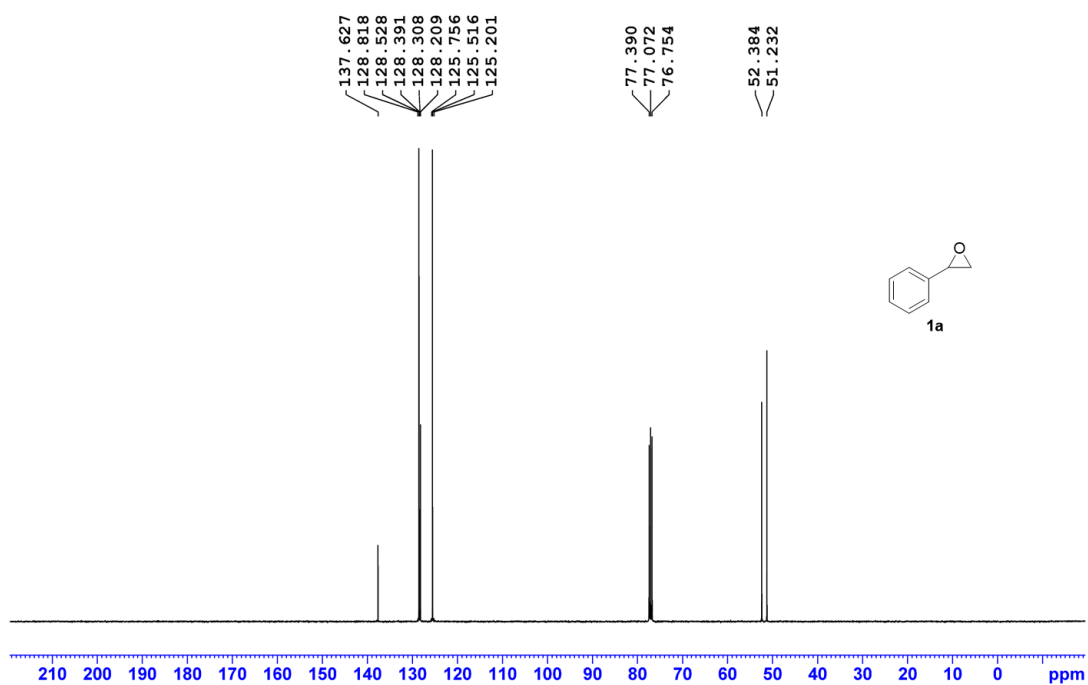
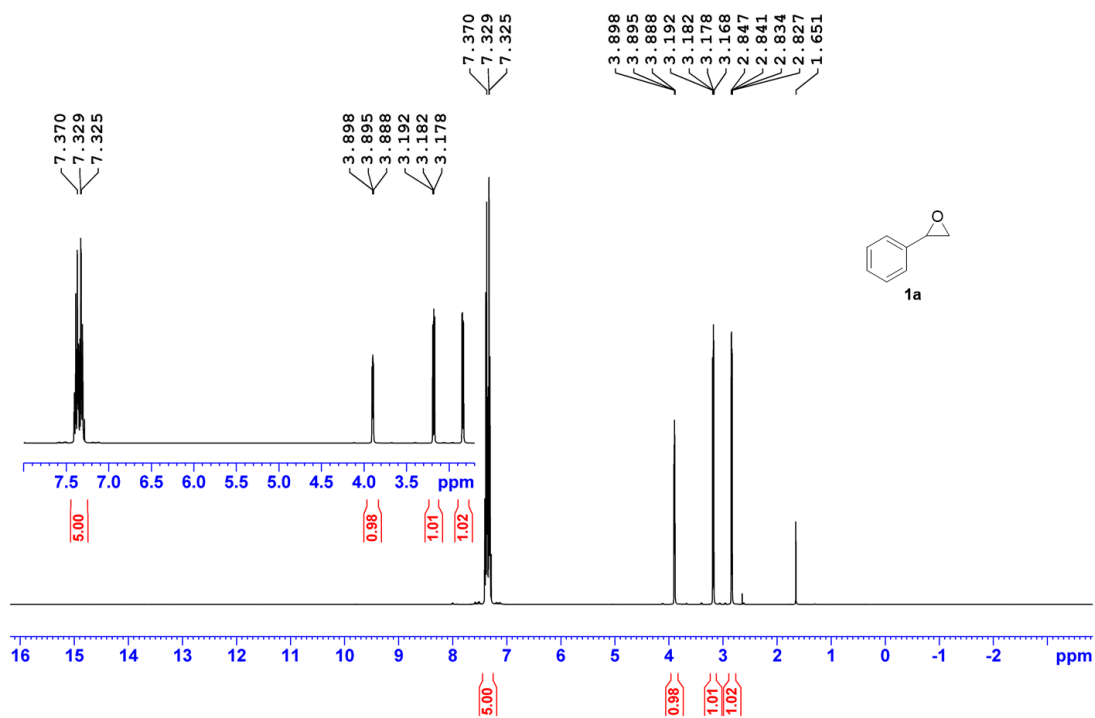
Mixture products containing TBAI solution (1 mL) were diluted with ethyl acetate (EA, 10 mL). Recovered TBAI precipitated and was dried in an oven (100 °C, overnight). The weight of recovered TBAI was recorded.

### *10.5 SiO<sub>2</sub> recovery*

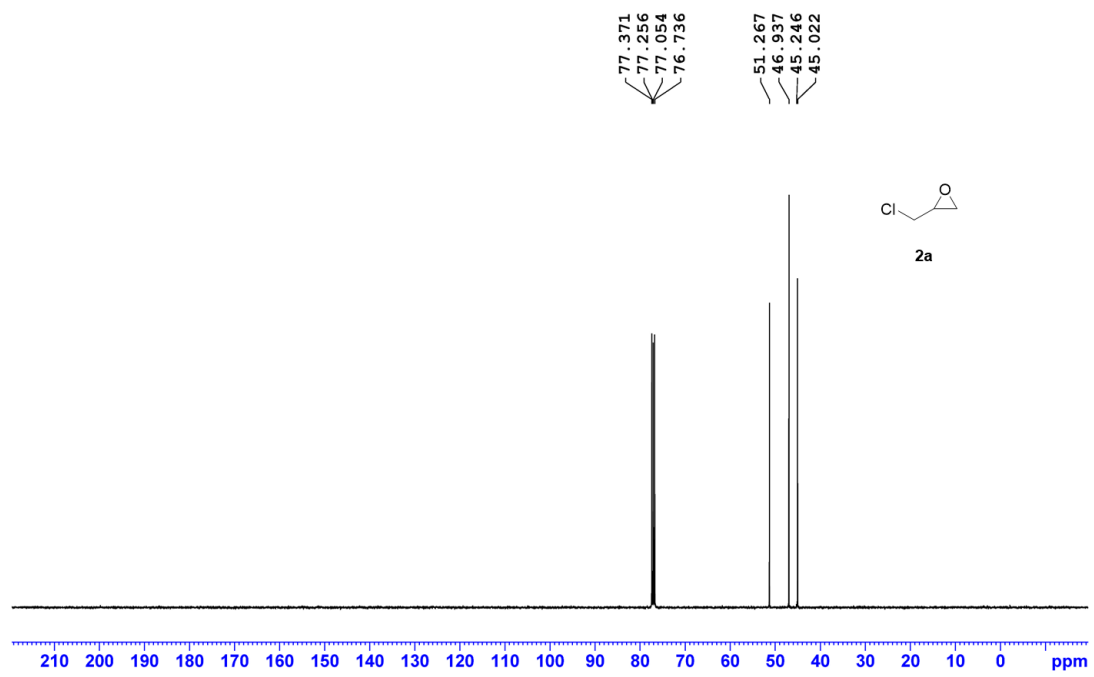
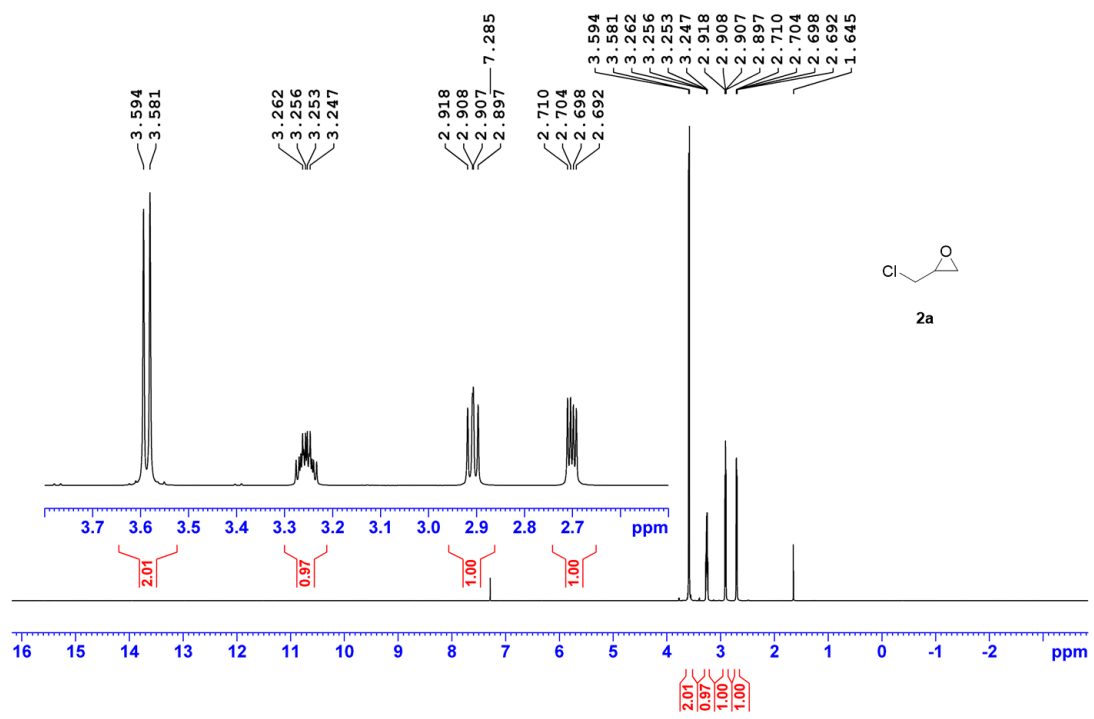
After reaction, the CO<sub>2</sub> gas flow was closed and the fix-bed reactor was washed with acetone (30 mL, 1 mL/min). Recovered SiO<sub>2</sub> was collected by drying in oven (100 °C, overnight).

## 10.6 NMR spectra of the substrates

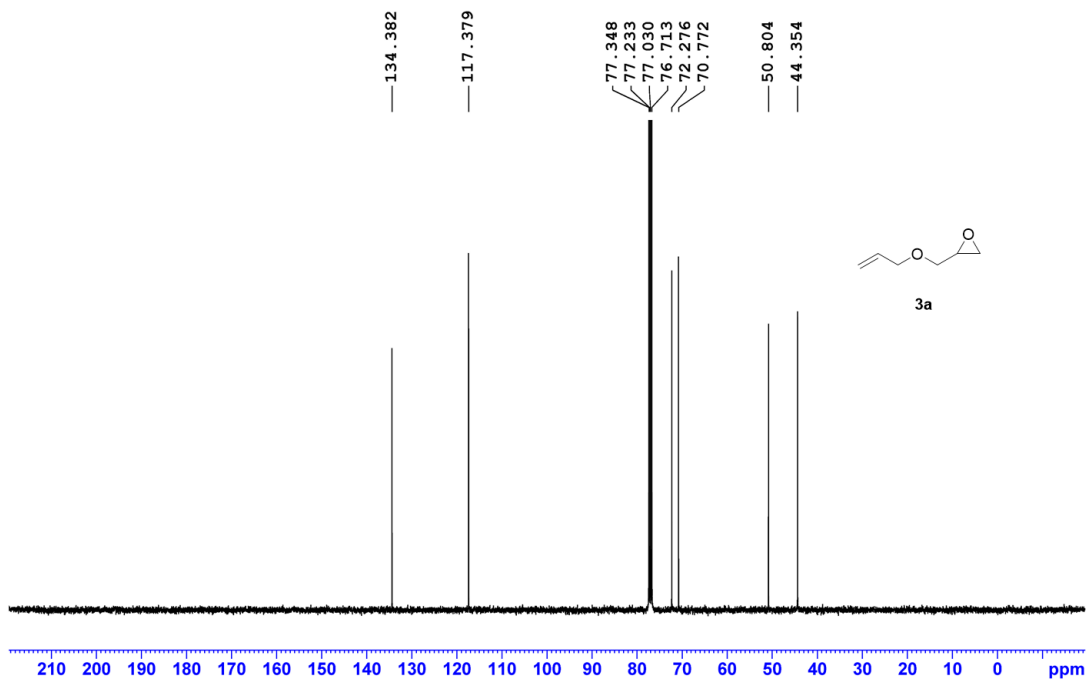
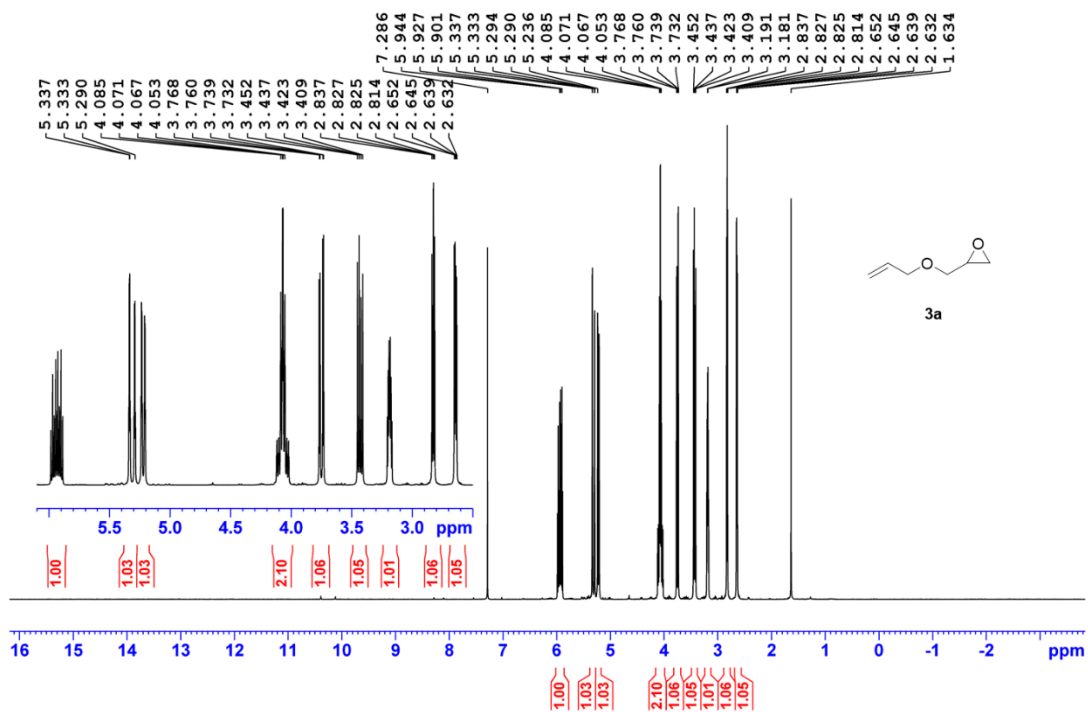
**1a**, styrene oxide



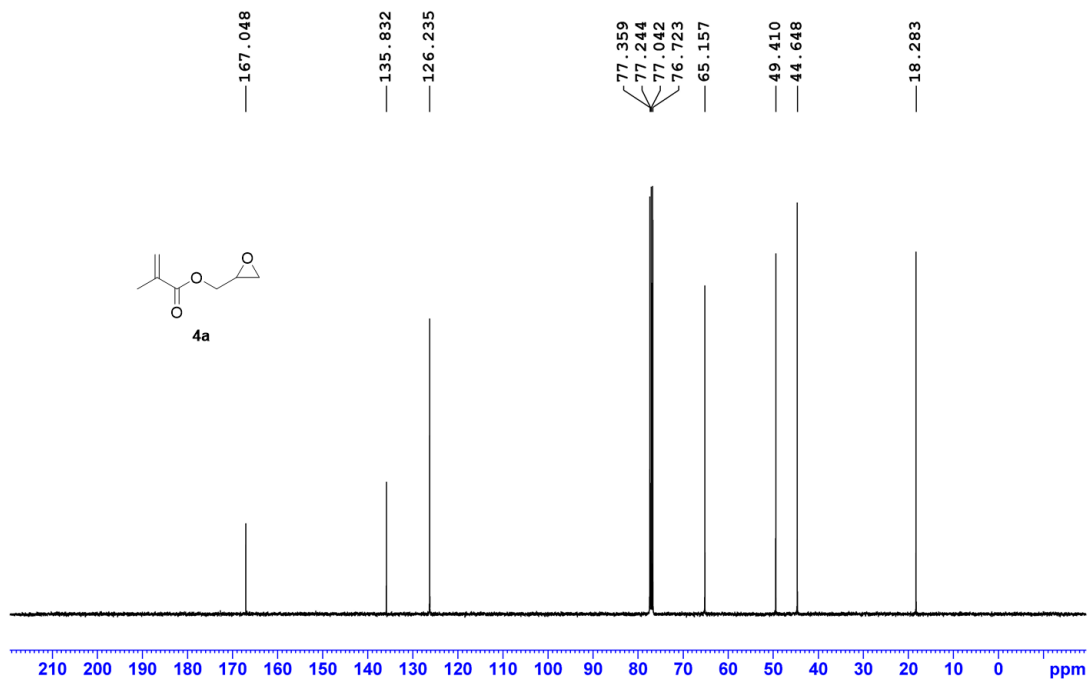
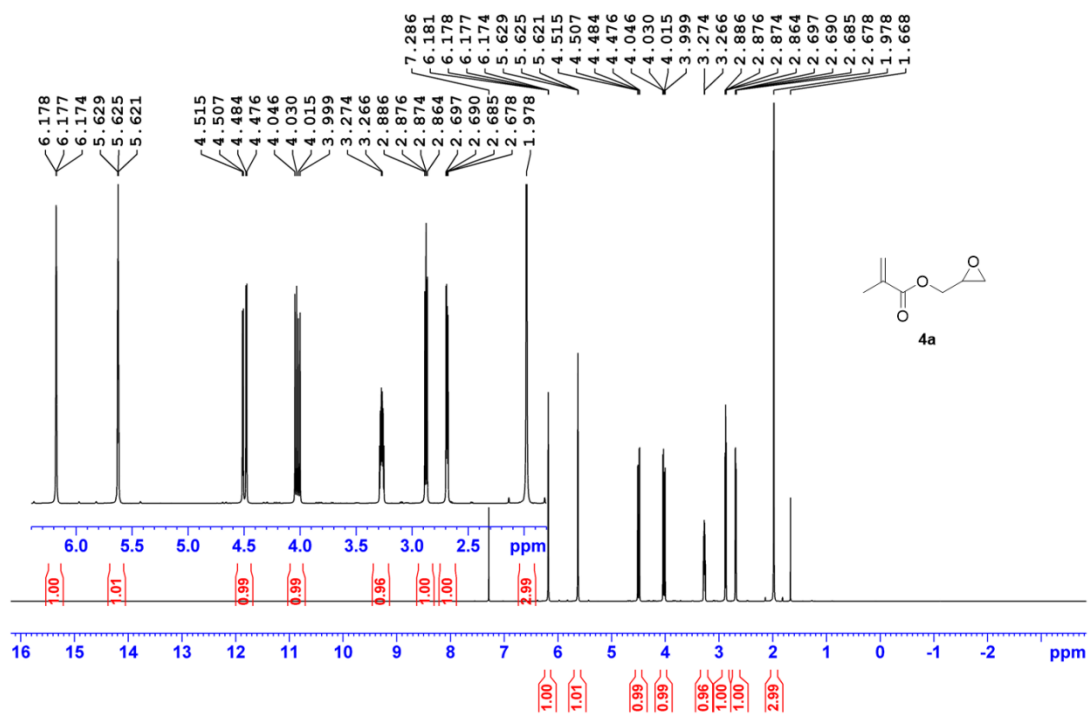
2a, epichlorohydrin



### 3a, glycidyl vinyl ether

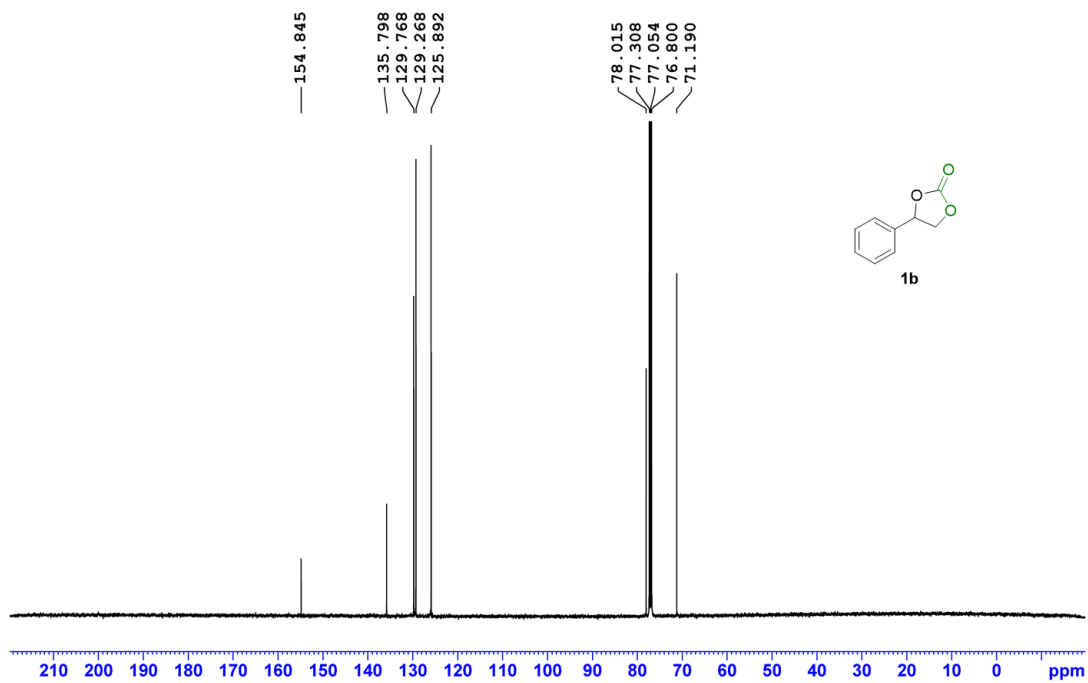
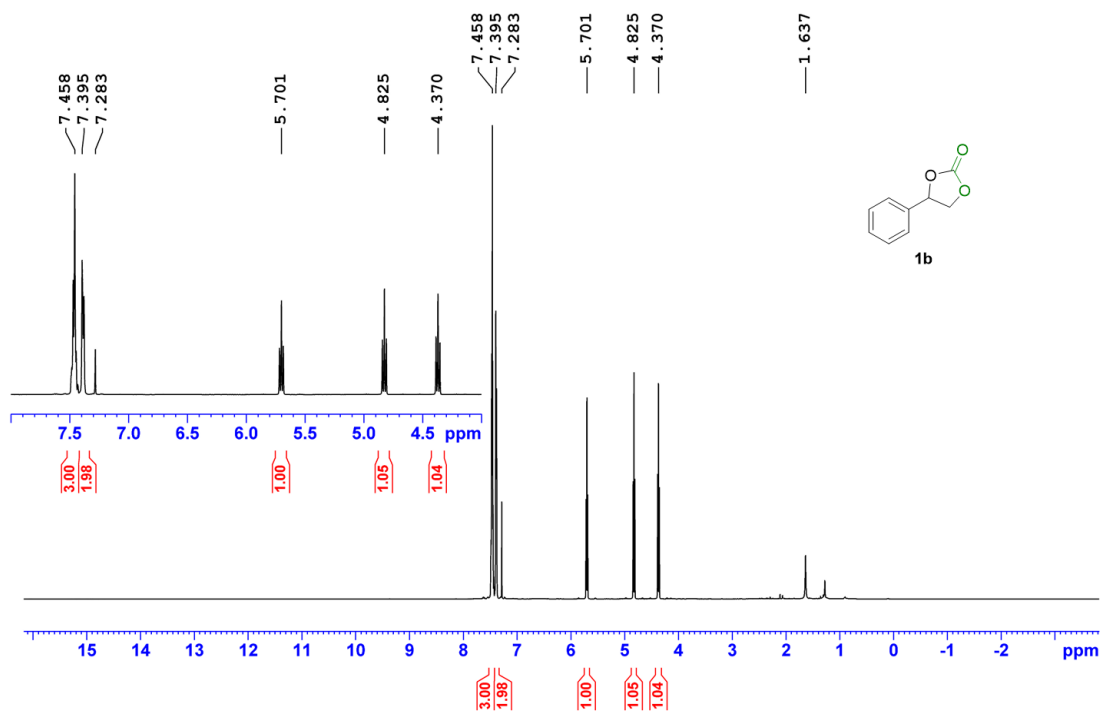


4a, glycidyl methacrylate

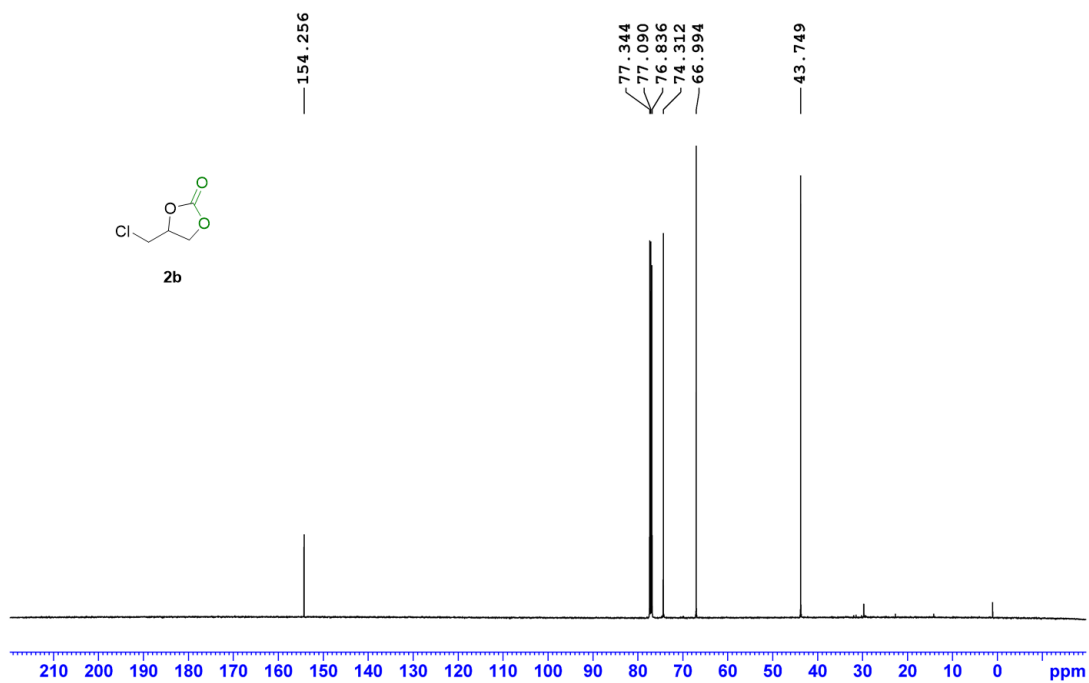
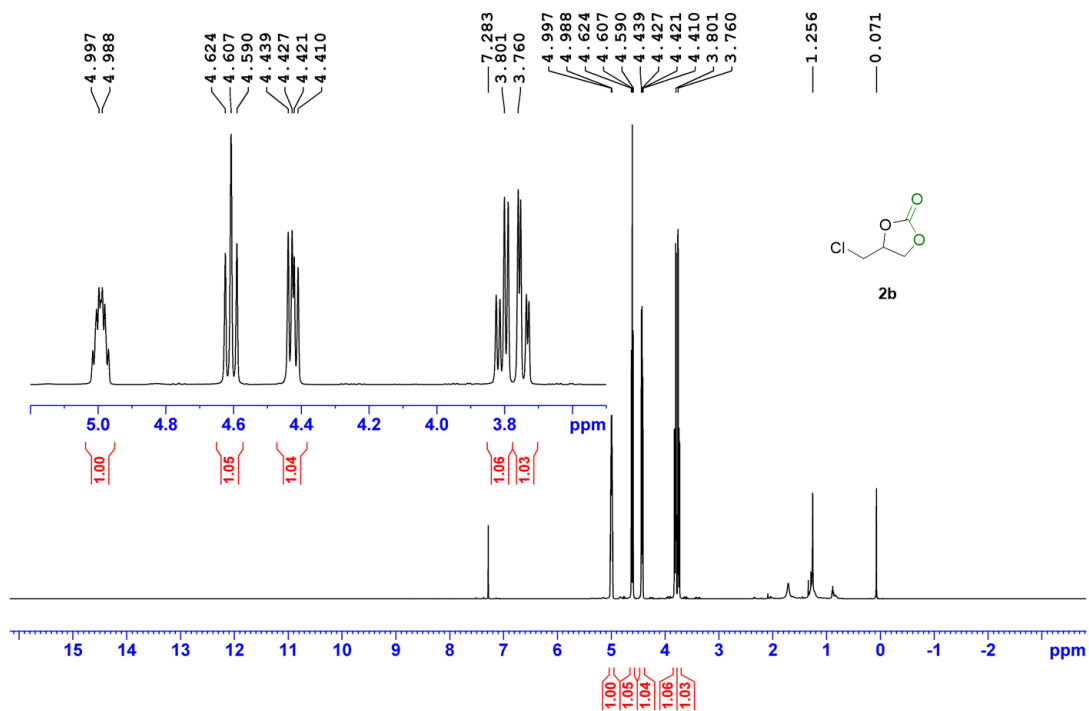


## 10.7 NMR spectra of the products

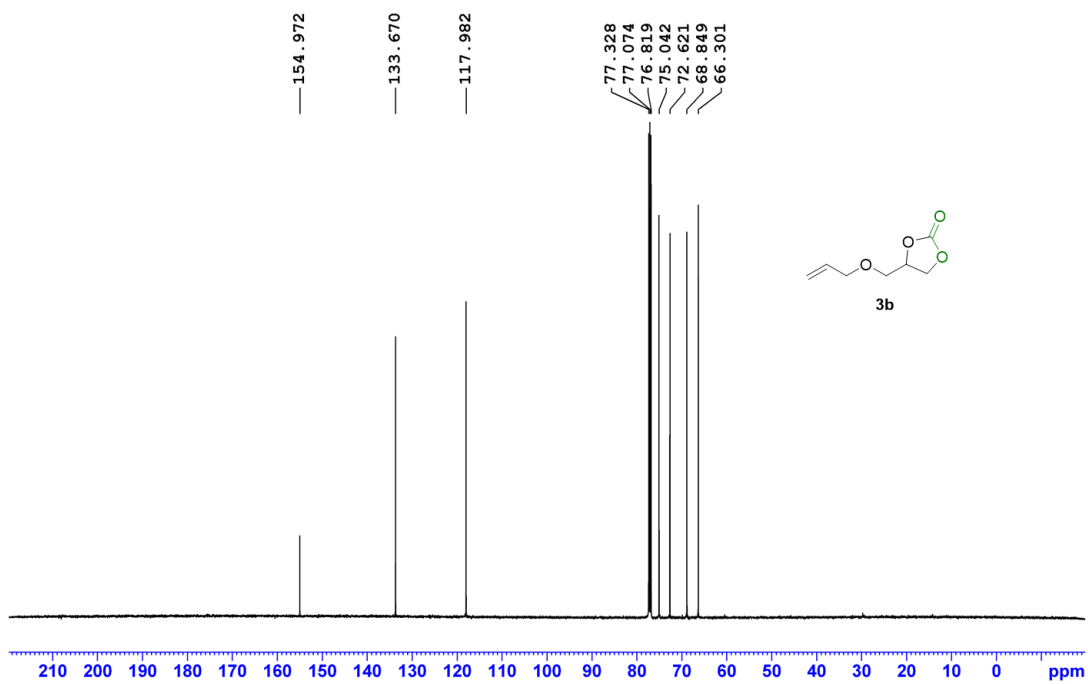
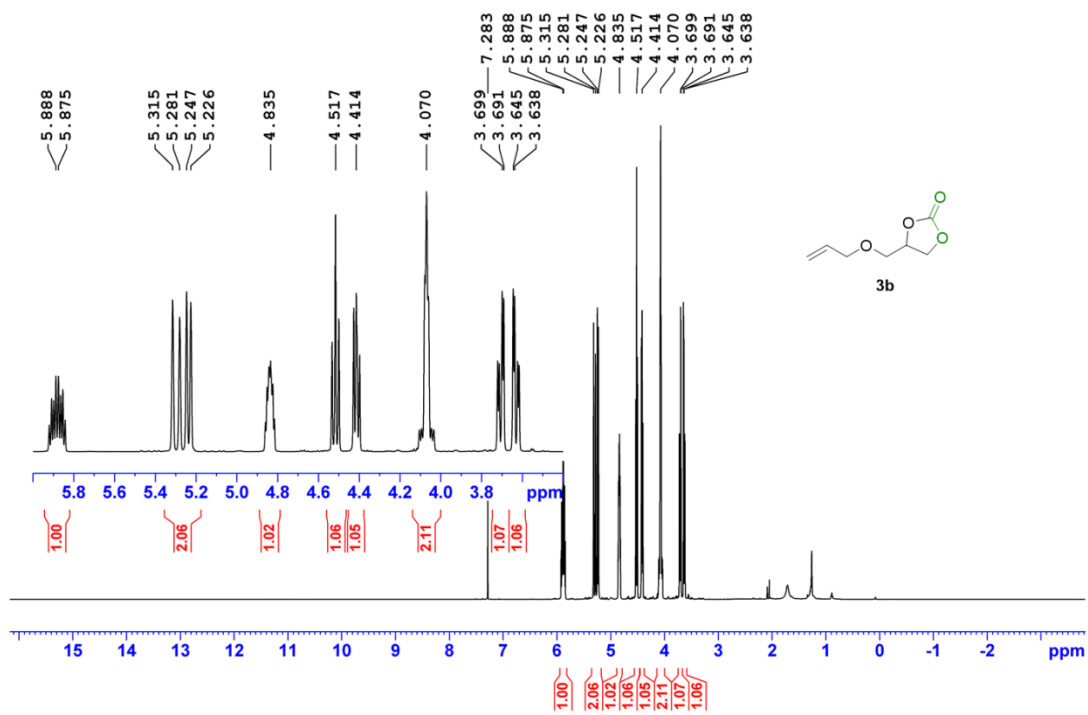
### 1b, 4-phenyl-1,3-dioxolan-2-one



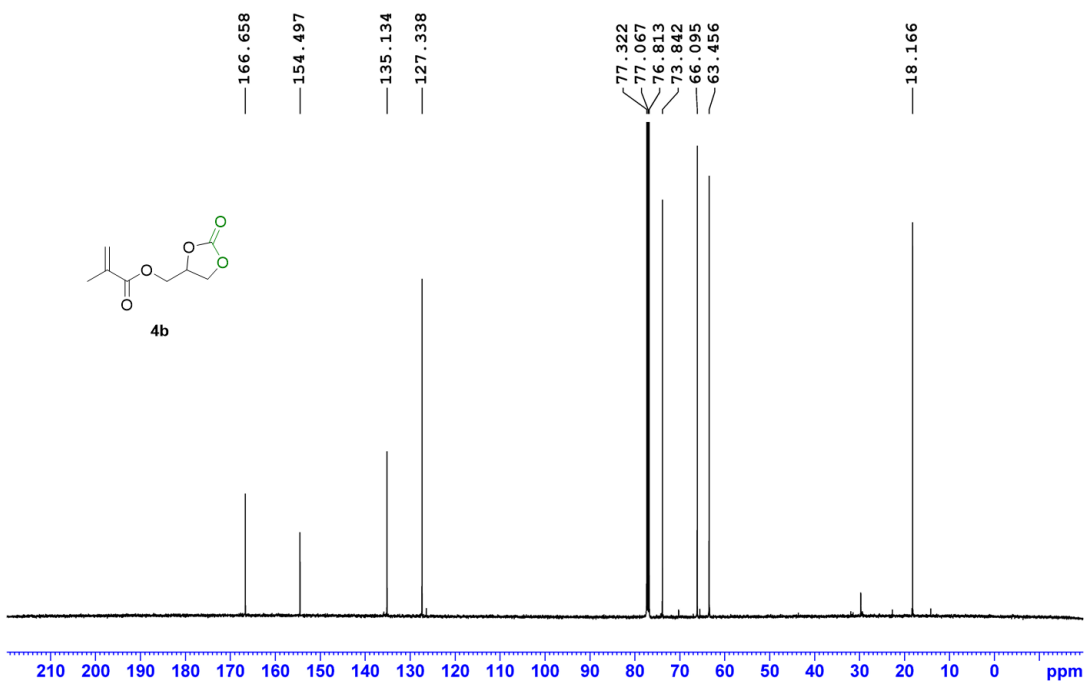
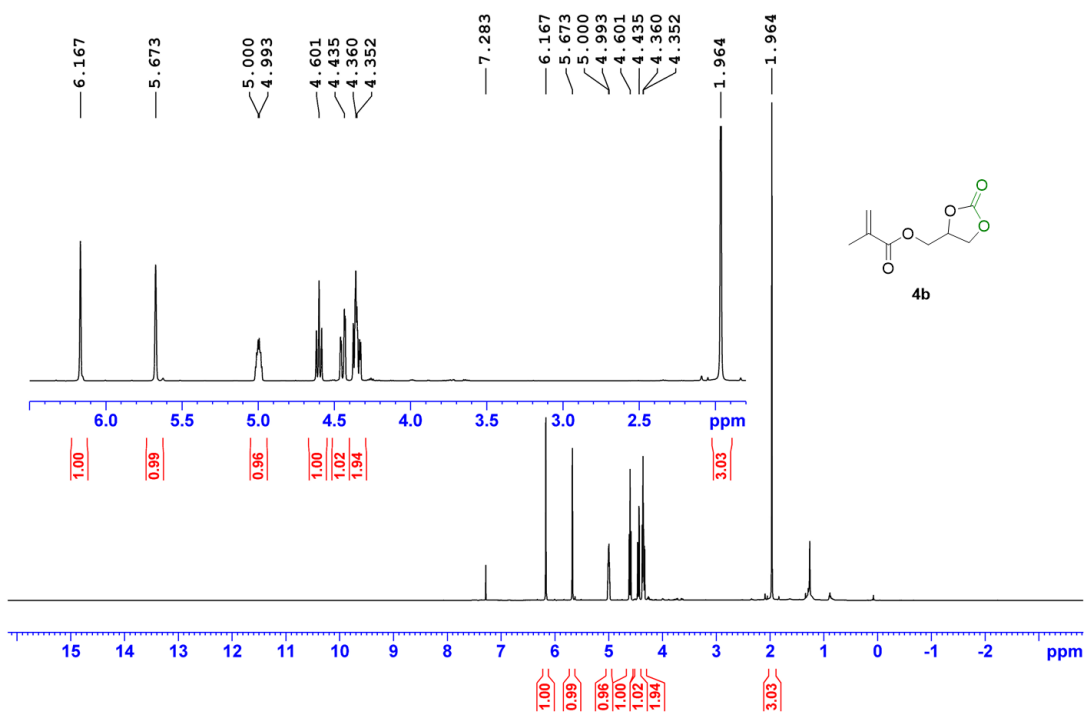
**2b**, 4-(chloromethyl)-1,3-dioxolan-2-one



**3b**, 4-((allyloxy)methyl)-1,3-dioxolan-2-one

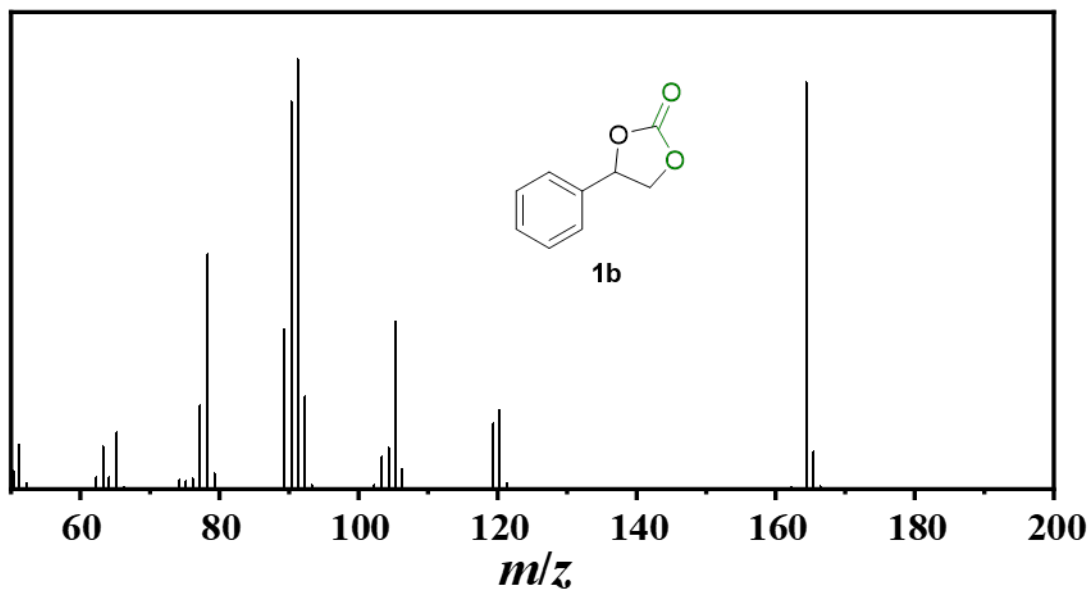


**4b**, (2-oxo-1,3-dioxolan-4-yl)methyl methacrylate

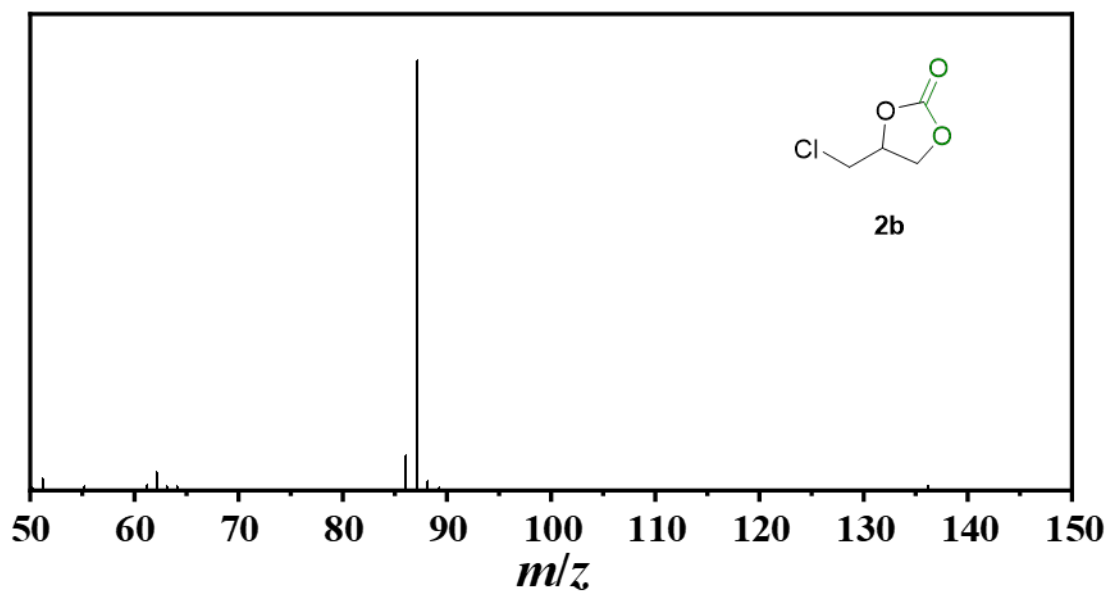


10.8 Mass spectra of the products

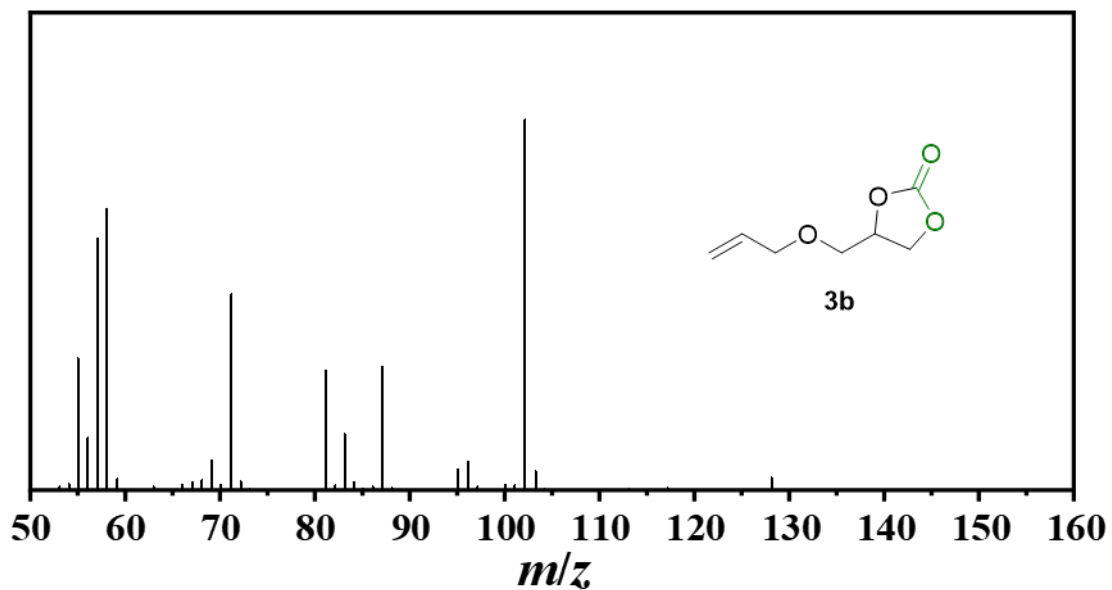
**1b**, 4-phenyl-1,3-dioxolan-2-one



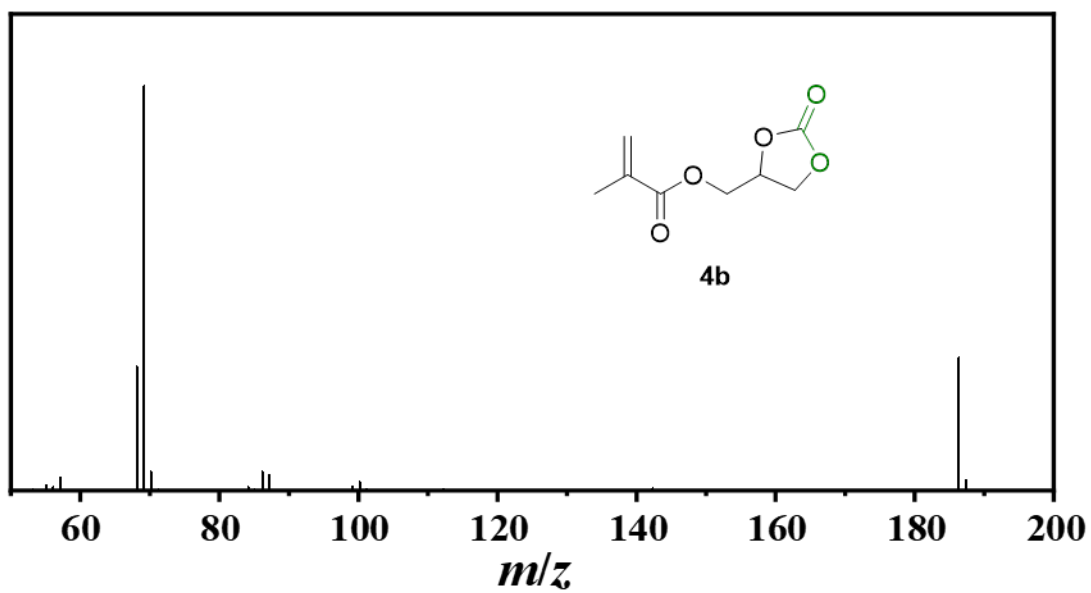
**2b**, 4-(chloromethyl)-1,3-dioxolan-2-one



**3b**, 4-((allyloxy)methyl)-1,3-dioxolan-2-one

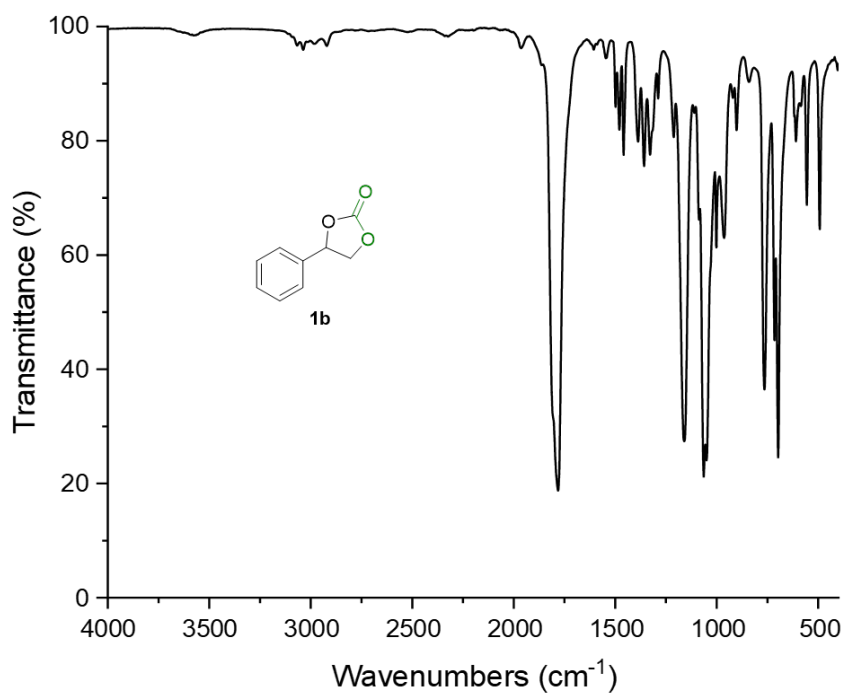


**4b**, (2-oxo-1,3-dioxolan-4-yl)methyl methacrylate

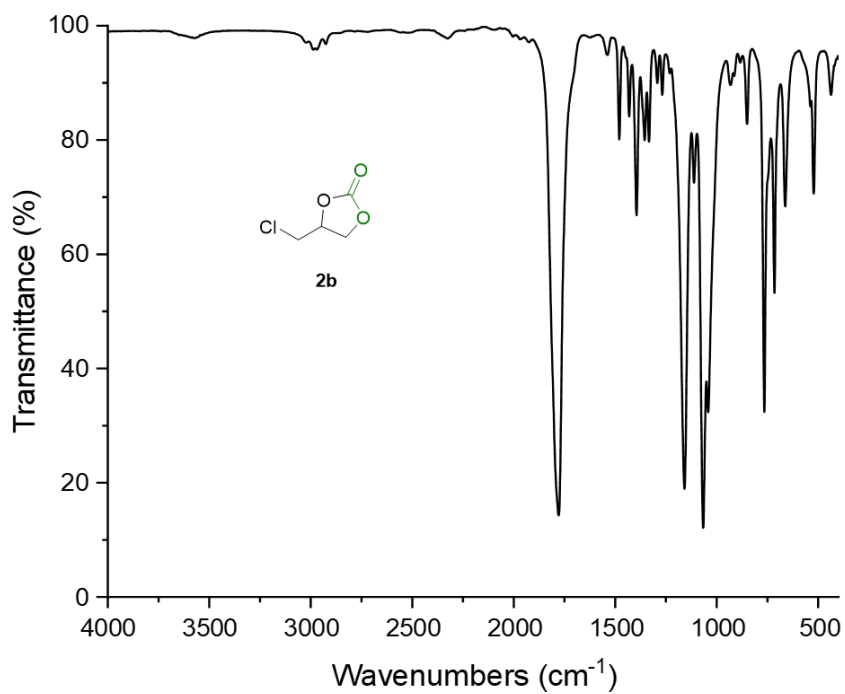


## 10.9 FT-IR spectra of the products

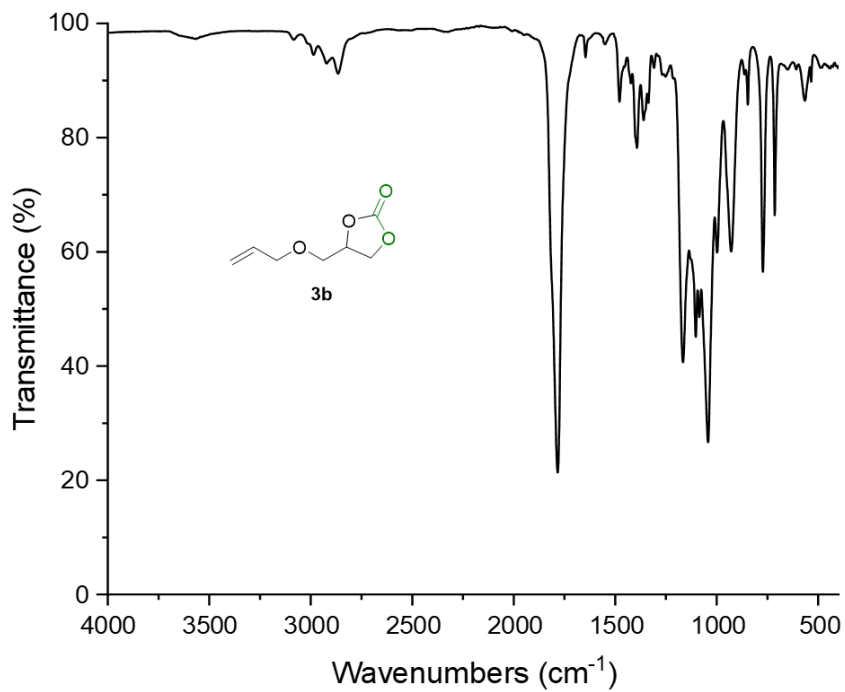
**1b**, 4-phenyl-1,3-dioxolan-2-one



**2b**, 4-(chloromethyl)-1,3-dioxolan-2-one



**3b**, 4-((allyloxy)methyl)-1,3-dioxolan-2-one



**4b**, (2-oxo-1,3-dioxolan-4-yl)methyl methacrylate

