The coupling of CO_2 with diols promoted by organic dual systems: towards products divergence via benchmarking of the performance metrics

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ABSTRACT

Herein, we propose a critical study balancing two metal-free dual activating systems, namely DBU/EtBr and TEA/TsCl, for the coupling of CO_2 with 1,x-diols to afford (a)cyclic carbonates. *In-situ* ATR-IR monitoring correlated with DFT calculations led to mechanism propositions for the model formation of propylene carbonate from propylene glycol. Kinetics upon various experimental conditions were established for the first time, leading to an optimized synthetic protocol. The substrates scope was then investigated and selectivities toward the formation of cyclic or linear carbonates were correlated to the dual activating system and the diol structure. By choosing the suitable organic dual activating system, one is able to control the product selectivity to substituted ethylene- or trimethylene carbonate and/or acyclic compounds, providing a powerful tool to synthesize CO_2-based precursors that are highly relevant for organic and polymer chemistry from ubiquitous building blocks.

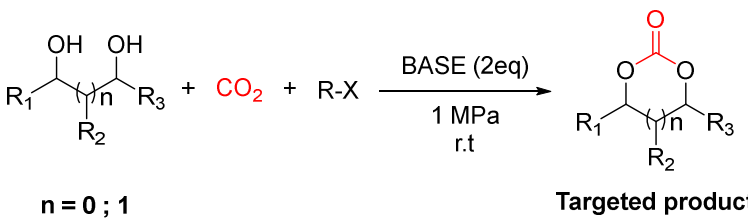
Keywords: Carbon dioxide, diols, carbonates, metal-free, mild conditions, selectivity

1. Introduction

It is widely known that carbon dioxide concentration in the atmosphere, among other greenhouse gases, keeps increasing every year, partly due to the petrochemical industry and combustion of fossil fuels.[1,2] New scientific challenges have risen to mitigate such anthropogenic emissions and prevent the environmental concerns. Among them, Carbon Dioxide Utilization (CDU) has emerged as a solution to valorise CO_2 as a key intermediate for chemistry.[3-12] In this context, converting CO_2 into organic cyclic carbonates was extensively investigated to design CO_2-based materials with a lower carbon footprint finding wide applications as intermediates in the organic and polymer chemistry[13-21], as well as promising green aprotic polar solvents.[22,23] Various synthetic pathways were developed to access (functional) 5- or 6-membered cyclic carbonates such as the [3+2] coupling of CO_2 with epoxides[24-29] or via the fixation of CO_2 into oxetanes.[26,30,31] Although terminal epoxides are easily converted into 5-membered cyclic carbonates, the conversion of internal di-, tri- and tetra-substituted epoxides or (substituted) oxetanes into their corresponding five- and six-membered cycles still remained very challenging.[31] To broaden the scope and

functionality of cyclic carbonates, other substrates such as propargylic alcohols[15,32-37], 1,2 and 1,3-diols[38-41] were subjected to carbonation in order to afford α-alkylidene cyclic carbonates, five- and six-membered cyclic carbonates, respectively. Although the use of diols is a promising alternative, their reaction with CO_2 is kinetically and thermodynamically limited due to the formation of water as a by-product. To surpass these hurdles, catalytic platforms based on both homogeneous and heterogeneous organometallic catalysts (Bu_2SnO, K_2CO_3, CeO_2…) used in combination with dehydrating systems (molecular sieves, zeolites, 2-Cyanopyridine…) were developed.[42,43] To the best of our knowledge, the most efficient system involved CeO_2 as the catalyst and 2-Cyanopyridine as dehydrating agent.[43] The main drawback related to this process is the use of harsh reaction conditions (150 °C, 5 MPa) and an expensive dehydrating agent used in large excess. Alternative protocols have been recently proposed to displace the reaction equilibrium and to overcome the limitation induced by the formation of water by combining the use of an organic base and an alkylating agent under mild conditions. Such strategy has been shown by Zhang et al. [44] and Buchard et al. [45,46] by combining strong Lewis bases and Tosyl chloride (TsCl) as the alkylating agent to promote the synthesis of 6-membered cyclic carbonates with the formation of the TsO- anion as a by-product. A similar protocol has been proposed by Kitamura et al.[47] and Dyson et al. [41] using alkyl halides as the alkylating agents that allow the synthesis of cyclic carbonates in good yields from different substrates. Gnanou et al. also investigated the cyclization or polymerization of glycoside and diols with a larger spacer in a similar fashion. [48-50] Addition of ionic liquids to these systems to promote CO_2 activation to afford cyclic carbonates from diols was also studied.[51] Although plausible mechanisms have been proposed for the carbonation of 1,2-diols promoted by organic bases/alkyl halide dual system, a molecular level understanding of the reaction mechanism and the determination of the key structural parameter of the reactants and the organic activating system that governs the yields and the selectivity of the reaction is still missing.

To this aim, we propose a detailed investigation and comparison of the coupling of CO_2 and various 1,x-diols in a one pot/one step fashion under mild conditions promoted by two different organic dual activating systems (Scheme 1).



Scheme 1: Strategy for the synthesis of 5 to 6 membered cyclic carbonates from diols and CO_2 promoted by organic bases and alkyl halides under mild conditions.

A mechanism of the model carbonation of propylene glycol using DBU and bromoethane is first proposed by correlation of *in-situ* ATR-IR kinetic monitoring and DFT calculations. The effects of the temperature, the pressure, the solvent and the nature of the alkyl halide on the kinetics, the carbonate yields and selectivities were then evaluated. In a similar fashion,

the model carbonation of propylene glycol was studied using a second dual activating system with triethylamine (TEA) as a base and TsCl as the alkylating agent. Extension of the synthetic protocols to the carbonation of challenging mono-, di- and tetrasubstituted vicinal diols, to 1,3- and 1,4 diols or isosorbide, a bio-based diol with a two fused furan rings structure, was then investigated using both dual systems. The benchmarking of their performance metrics will guide us opting to the most appropriate activating system regarding the nature of the diol substrate and the desired product selectivity, i.e. a cyclic or a linear carbonate.

2. Material and Methods

2.1 Material

Propylene glycol (PG, Sigma Aldrich), Ethylene glycol (Sigma Aldrich), 2,3-butanediol (Sigma Aldrich), Pinacol (Sigma Aldrich), Glycerol (Sigma Aldrich), 1,3-butanediol (Sigma Aldrich), Hexylene glycol (Arkema), 1,4-butanediol (Sigma Aldrich), Isosorbide (Alfa Aesar), trans-1,2-Cyclohexanediol (Alfa Aesar), Pyrocatechol (Sigma Aldrich), Bromoethane (Sigma Aldrich), Bromobutane (Sigma Aldrich), Chlorobutane (Sigma Aldrich), Benzyl bromide (Sigma Aldrich), Benzyl chloride (Sigma Aldrich), Methyl iodide (Sigma Aldrich), Dichloromethane (CH_2Cl_2, Sigma Aldrich) Acetonitrile (CH_3CN, Sigma Aldrich), Chloroform ($CHCl_3$ Sigma Aldrich), Anisole (Alfa Aesar), Dimethyl sulfoxide (DMSO, Sigma Aldrich) were used without further purification.

2.2 Methods

General procedure for kinetic studies:

The reactions were monitored *in-situ* by IR spectroscopy using a home-made Ge ATR accessory suitable for high-pressure measurements (up to 5 MPa) and high temperature (up to 100 °C) coupled with a ThermoOptek interferometer (type 6700) equipped with a globar source, a KBr/Ge beamsplitter and a DTGS (Deuterated TriGlycine Sulphate) detector. Single beam spectra recorded in the spectral range (400-4000 cm^{-1}) with a 4 cm^{-1} resolution were obtained after the Fourier transformation of 20 accumulated interferograms for the first hundred spectra (one spectra every 75 sec), and then Fourier transformation of 80 accumulated intereferograms until the end of reaction time (one spectra every 5 min).

Diol (0.5 mmol) was solubilized in a 2 mL vial with 200 µL of solvent. Organic base (1 mmol) was added to the vial. Alkyl halide (1.2 mmol) was added to the vial. The whole mixture was then transferred to the reaction chamber (volume: 5 mL) which is directly fixed on the Ge crystal of the ATR-IR device. The setup is sealed with the CO_2 feed pipe so it can be put under pressure. To best avoid side reactions between the base and the alkyl halide, it is worth noting that the faster the system is pressurized, the less side reactions are observed. Experiments where cyclic carbonates were obtained in good yields (> 50 %) were carried out again on a larger scale for further purification. Products were purified by column

chromatography (100 % Ethyl acetate for glycerol carbonate, 5 % Acetone / 95 % Chloroform for others) and weighted to get the isolated yield.

General procedure for batch reactions:

Diol (0.5 mmol) was solubilized in a 2mL vial with 200 µL of solvent. Organic base (1 mmol) was added to the vial. Alkyl halide (1.2 mmol) was added to the vial. A stir bar was added to the vial. The vial was sealed with a septum cap which was perforated to let CO_2 enter the vial and dissolve in the solution. Up to 8 vials were transferred into the high pressure reacting chamber, placed on a magnetic stirrer. A pressure of 1 MPa CO_2 was initially applied to the chamber, which volume is large enough to keep the pressure quasi constant throughout the reaction (pressure drops as CO_2 dissolves in the media). At the end of the reaction time, the reaction chamber was slowly depressurized and the vials were taken out. Septum caps were replaced by sealed caps. All products were analysed by both ATR-IR spectroscopy and ^{1}H NMR spectroscopy without further purification. To best avoid side reactions between the base and the alkyl halide, it is worth noting that the faster the system is pressurized, the less side reactions are observed.

Nuclear magnetic resonance spectroscopy (NMR)

^{1}H and ^{13}C NMR spectra were recorded at 298 K with a Bruker advance DRX 400 spectrometer operating at 400.13 MHz, on the Fourier transform mode. All NMR spectra were phased and baseline-corrected. The samples were prepared by dissolving 15-20 mg of product in 0.7 ml of a deuterated solvent ($CDCl_3$) and were calibrated with the 7.26ppm residual signal of $CDCl_3$.

Density Functional Theory (DFT) computational details

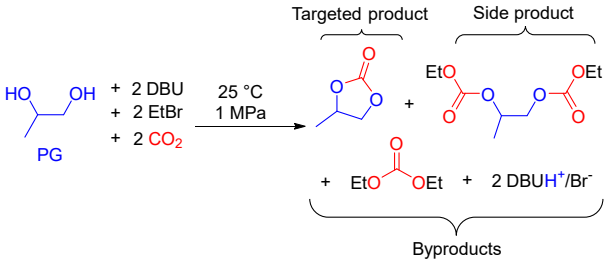
Preliminary calculations of equilibrium structures were performed using a semi-empirical model (AM1-D3H4) to determine the most stable conformations. These semi-empirical calculations were performed using the AMPAC software. The CHAIN algorithm was used for locating intermediates and transition states along the reaction path. The lowest energy structures obtained at the AM1-D3H4 level were further investigated using the Density Functional Theory method (DFT) implemented in the Gaussian 16 package. DFT calculations of geometries, energies, and vibrational frequencies reported in this article were carried out with the M06-2X functional using the 6-311G(d,p) basis set. All frequencies of each structure have also been calculated to verify the presence of a single imaginary frequency for transition states and the absence of imaginary frequency for ground states. The intrinsic reaction coordinate (IRC) method has been used to verify that the obtained transition states were effectively connected to the desired minima. For all activating systems, a wide range of possible configurations and interactions have been modelled and the more stable of them are reported in this work. To consider entropic effects, the energies mentioned in this study correspond to the Gibbs free energy (ΔG).

3. RESULTS AND DISCUSSION

3.1 Dual system DBU/R-X

3.1.1 Synthesis of propylene carbonate from propylene glycol : mechanistic study

Insights into the mechanisms and the kinetics of the carbonation of 1,x-diols to access (a)cyclic carbonates were first performed for a model reaction between propylene glycol (PG) and CO_2 promoted by a dual system composed of an organic superbase, i.e. 1,8-diazabicyclo-[5.4.0]-undec-7-ene (DBU) and an alkylating agent, i.e. bromoethane (EtBr) (Scheme 2). The model reactions were performed in dichloromethane under low CO_2 pressure (0.5 – 4 MPa) and monitored by in-situ ATR-IR spectroscopy (Figure 1).



Scheme 2: One pot/one step model reaction studied for the synthesis of propylene carbonate from PG and CO_2. Diethyl carbonate is obtained as a by-product.

Typical spectra recorded at different reaction times are depicted in Fig. 1. Fine interpretation of the spectral footprints enabled us to identify several key intermediates formed at 25°C under 1 MPa CO_2 pressure. First, before the introduction of CO_2 in the reaction mixture, a well-defined band observed at 1613 cm^{-1} is characteristic of the C=N stretching mode of DBU which indicates that there is no specific interaction and/or reaction between DBU and another reactive species (red curve). In particular, neither spontaneous deprotonation of the alcohol moiety by DBU nor a possible alkylation of DBU by EtBr were observed. Addition of CO_2 to the system at 1 MPa pressure (green curve) induced a DBU absorption band shifts toward 1636 cm^{-1}, which has been assigned to the $C=NH^+$ stretching mode of protonated DBU.[52,53] Concomitantly, a shoulder of this broad peak appears around 1660 cm^{-1} and was attributed to the C=O stretching of the alkyl carbonate anion RCO_3^- species.[53-55] These spectral changes highlight a trimolecular reaction between CO_2, PG and DBU forming the $RCO_3^-/DBUH^+$ organic salt (see ESI 1 for further investigations). Indeed, the hydrogen bonding between sp^2 N atom from DBU and the alcohol moiety of PG will increase the nucleophilicity of the O atom and thus promotes its attack on the C atom of CO_2. It should be noted that the formation of the carbonate salt occurs within 5 minutes and is regulated by the CO_2 solubilisation in the organic phase, which is known to be high in dichloromethane.[56,57] By ATR-IR, it was however not possible to discriminate which of the primary or the secondary alcohol is preferentially involved in the formation of the carbonate salt. When the reaction goes on, around 30 min after introduction of CO_2, the absorption band of protonated DBU starts shifting from 1636 cm^{-1} to higher wavenumbers of 1645 cm^{-1} (purple curve). The peak got thinner and the shoulder tended to disappear. This was attributed to a change in the anionic environment of protonated DBU, due to the time consumption of the

RCO_3^- species that are progressively replaced by the bromine anion of EtBr. Concomitantly, two novel absorption bands appeared around 1743 cm^{-1} and 1796 cm^{-1} and were respectively assigned to the C=O stretching mode of a linear alkyl carbonate[58] **IntLC** (see Scheme 3) and to the vibrational stretching of the C=O function of a 5-membered cyclic carbonate[58], i.e. propylene carbonate (PC) (See ESI 2).

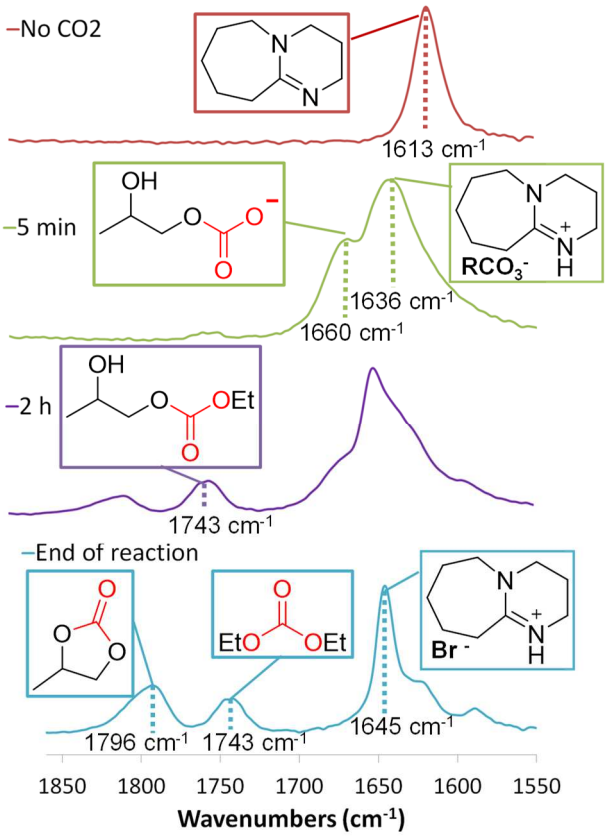
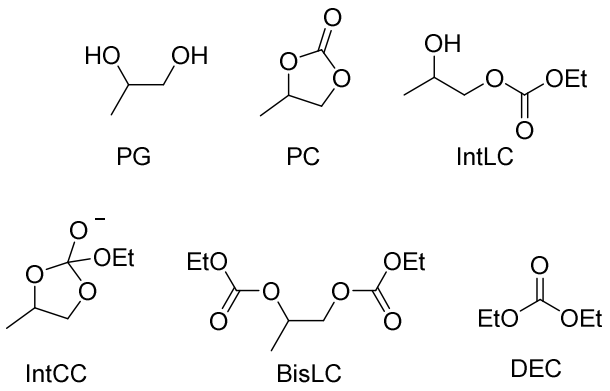


Figure 1: Monitoring of the model reaction between PG and CO_2 promoted by a dual DBU/EtBr system using ATR-IR spectroscopy. Conditions: PG (0.5mmol) ; DBU (1mmol) ; EtBr (1.2mmol) ; CH_2Cl_2 (200µL) ; 1 MPa ; 25°C



Scheme 3: Substrate (PG), reaction intermediates (IntLC ; IntCC) and products (PC ; BisLC ; DEC) of the model reaction

So far, the ATR-IR analysis could not differentiate **IntLC** from diethyl carbonate (**DEC**) co-produced at the end of the reaction. To get clues about the formation of **DEC** by-product,

kinetic profiles were drawn from the time evolution of the intensity of the specific signals of both the linear and the cyclic carbonate (Fig. 2). As a matter of fact, the absorption band $\nu_{C=O}$ = 1743 cm^{-1} of **IntLC** started increasing after only 5 min., i.e. far before the formation of PC ($\nu_{C=O}$ = 1796 cm^{-1}) that appears at t = 60 min, suggesting that PC is produced from **IntLC**. Then, one would expect that the consumption of **IntLC** should be accompanied with a progressive decrease of the intensity of the peak at $\nu_{C=O}$ = 1743cm^{-1}. But, this specific signal reached a quasi-plateau as soon as PC started to be synthesized confirming that each mole of **IntLC** that is consumed produces PC but also one mole of **DEC** co-product, both intermediate **IntLC** and **DEC** having the same absorption band. We believe that the absorbance of the peak at $\nu_{C=O}$ = 1743cm^{-1} keeps increasing very slightly because of the formation of side products (See Scheme 2), namely **BisLC** (Scheme 3). Indeed, a linear biscarbonate **BisLC**, which absorption band of the C=O stretching mode is around 1743 cm^{-1}, is obtained in low yields (~15 %) from carbonation of each alcohol moieties, followed by double alkylation. This study led to consistent proofs for the prior formation of **IntLC** before PC and **DEC**.

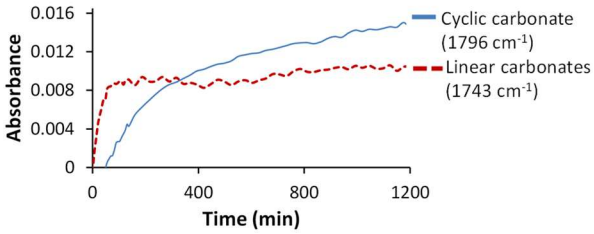
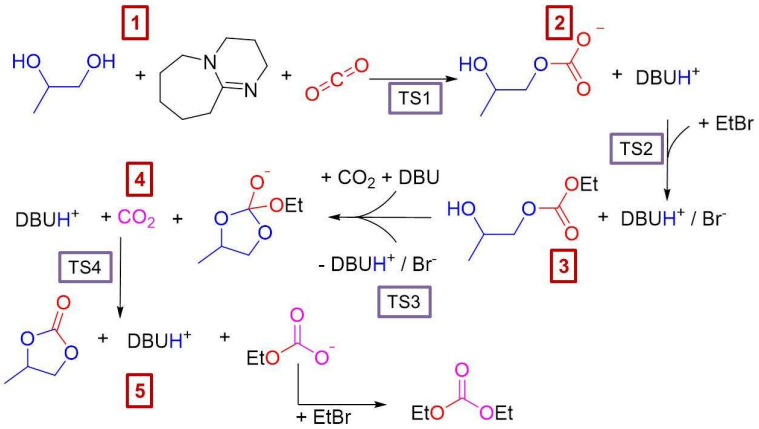


Figure 2: Kinetic study of the carbonation of PG promoted by DBU/EtBr system: time evolution of the absorption bands relative to PC and linear carbonates (**DEC, IntLC** and **BisLC**). Conditions: PG (0.5 mmol) ; DBU (1 mmol) ; EtBr (1.2 mmol) ; CH_2Cl_2 (200 µL) ; 1 MPa ; 25°C

The ^1H NMR characterization of the crude reaction medium after 20 h confirmed the presence of PC, **DEC** and **BisLC** (yield of PC = 73 %, PC/DEC = 2, yield of biscarbonated products **BisLC** = 15 %) (See ESI 3). Control experiment for the synthesis of **DEC** from ethanol and CO_2 promoted by dual system composed of DBU/EtBr in the same experimental conditions was carried out. **DEC** was obtained in 55 % yield after 23 h, which explain the origin of the PC/DEC ratio of 2 at the end of reaction time. The identification of the specific intermediates correlated to the kinetic data obtained through ATR-IR monitoring led to a mechanism proposal (Scheme 4).



Scheme 4: Mechanism proposal for the formation of propylene carbonate from PG, based on reaction intermediates identified from Fig.1. The presence of IntCC was not shown by ATR-IR experiments but was proposed regarding DFT calculations (Fig. 3).

As proposed before, the first step relies on the carbonation of one alcohol moiety of PG to generate an alkyl carbonate ion /$DBUH^+$ adduct. The second step consists of a SN_2 addition of the generated alkyl carbonate ion on EtBr, leading to the linear alkyl carbonate **IntLC**. Then, a second equivalent of DBU creates an hydrogen bonding with the second alcohol moiety rendering the oxygen atom more reactive and capable of an intramolecular attack onto the carbonyl group of the acyclic carbonates. This reaction generates the cyclic intermediate **IntCC** that expelled ethanolate with concomitant formation of propylene carbonate. Ethanolate undergoes a carbonation reaction with the CO_2 dissolved in the medium to generate an anionic alkyl carbonate, which will react with a second equivalent of EtBr through a SN_2 reaction to generate the acyclic diethyl carbonate as a co-product.

To confirm our predictions deduced from the experimental ATR-IR results, this mechanism was confronted to molecular modelling through DFT calculations at the M062X/6-311g(d,p) level (Fig. 3). As expected from experimental results, TS1 involves a trimolecular reaction

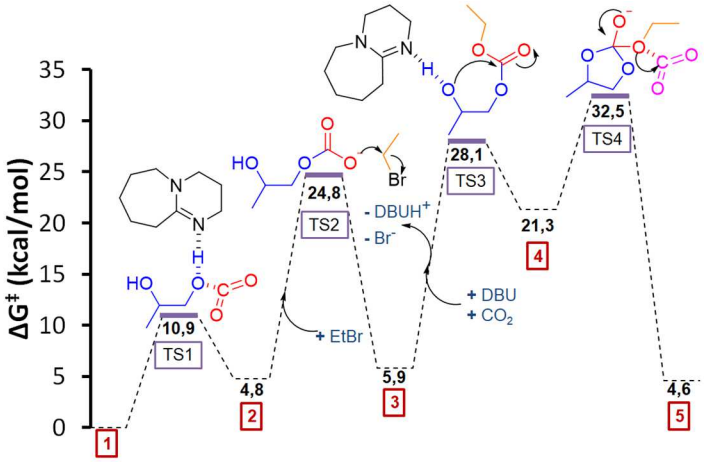


Figure 3: DFT computed pathway (*M062X/6-311g(d,p)*) of model reaction as depicted in Scheme 4. Red numbers correspond to optimized reaction intermediates shown in Scheme 4 (Van Der Waals interactions were accounted). Transition states (TS) were optimized using the same molecular species as in the intermediates.

through hydrogen bonding which activates the alcohol function and induces angular deformation of CO_2 ($\Delta G_{TS1}^{\ddagger}$ = 10.9 kcal/mol). TS2 confirms the SN_2 hypothesis on EtBr with

simultaneous addition of RCO_3^- and elimination of Br^- ($\Delta G_{TS2}^{\ddagger}$ = 20.0 kcal/mol). TS3 involves another hydrogen bonding to promote the cyclization ($\Delta G_{TS3}^{\ddagger}$ = 22.2 kcal/mol). Finally, TS4 is related to the cyclization of propylene carbonate with the release of an ethyl carbonate anion formed from the addition of an excess CO_2 to the released ethanolate. Thus, although DFT calculation results show that the cyclization (TS3) and the formation of the cyclic carbonate (TS4) are two different steps, the intermediate **IntCC** was not identified by ATR-IR spectroscopy probably due to the high Gibbs Free Energy of intermediate 4 and the low activation barrier of TS4 ($\Delta G_{TS4}^{\ddagger}$ = 11.2 kcal/mol).

The low activation barrier of $\Delta G_{TS1}^{\ddagger}$ is well correlated with the fast formation of the anionic alkyl carbonate RCO_3^- (~ 5min for carbonation of the alcohol moiety). As **IntLC** is very stable (linear alkyl carbonate), $\Delta G_{TS3}^{\ddagger}$ has the highest activation barrier and is thus the rate limiting step of the reaction. Once again, it is well correlated with kinetic profiles obtained by ATR-IR, since absorption band of **IntLC** ($\nu_{C=O}$ = 1743 cm^{-1}) appears before and increases faster than absorption band of the cyclic product ($\nu_{C=O}$ = 1796 cm^{-1}).

It should be noted that the DFT energetic profile of Fig. 3 was modelled with (R)-1,2-propanediol and assuming that the carbonation would first occur on the primary alcohol function. Yet, all the possible reaction pathways were modelled for both the (R) and (S) stereoisomers of propylene glycol and by assuming either the carbonation of the primary or secondary alcohol upon CO_2 addition (see ESI 4). No major differences in the activation barrier of each transition states were found, and we concluded that all paths could occur, with a slight preference over carbonation of primary alcohol of (R)-1,2-propanediol (see ESI 4). To further understand how the experimental parameters may affect the DBU-promoted carbonation of 1,x-diols, the influences of the temperature, the pressure, the solvent, the alkylating agent and the substrate scope were investigated through ATR-IR and results were complemented by quantitative ^1H NMR characterization of the crude media (see ESI 3 and ESI 5). Full conversion of the diol was never observed. In most of the spectra, a small fraction of the intermediate **IntLC** obtained from the corresponding 1,x-diol remained not converted into the cyclic product.

3.1.2 Temperature, pressure and solvent effect on kinetics and yields

Effect of the temperature:

At a fixed pressure of 1 MPa, an increase of the temperature from 25 °C to 50 °C slightly increases the overall yield (from 70 % to 76 % after 20h) but considerably increases the kinetics (Table 1, entries 1-2). Fig. 4a (green curve) highlights a two-fold acceleration of the formation of propylene carbonate by simple doubling of the temperature. In contrast, heating up to 70 °C do not increase the kinetic of the reaction but has a detrimental effect on the yield (Table 1, entry 3 ; Fig. 4a, red curve). In both cases, increasing the temperature led to lower yields of **BisLC** biscarbonated side-products (2 % and 5% for 50 °C and 70 °C respectively).

Table 1: Effect of the temperature, pressure and solvent on the reaction of propylene glycol to afford propylene carbonate. Reaction conditions: Propylene glycol (0.5 mmol in 200µL solvent), DBU (1 mmol), EtBr (1.2 mmol).

Entry	P_{CO2} (MPa)	T (°C)	Solvent	PG conv. (%)[1,2]	PC yield (%)[1,3]	Biscarbonate yield (%)[1,4]
1	1	25	CH_2Cl_2	90	73	15
2	1	50	CH_2Cl_2	78	76	2
3	1	70	CH_2Cl_2	70	49	5
4	0.5	25	CH_2Cl_2	74	62	12
5	2	25	CH_2Cl_2	40	35	0
6	3	25	CH_2Cl_2	20	16	2
7	4	25	CH_2Cl_2	41	34	7
8	1	25	neat	87	61	26
9	3	25	neat	56	22	22
10	1	25	anisole	72	46	16
11	1	25	ACN	78	30	19
12	1	25	$CHCl_3$	70	45	10
13	1	25	DMSO	69	15	14

[1] Determined after 20h
[2] Conversion of propylene glycol calculated from ^{1}H NMR with 1,3,5-trimethoxybenzene as internal standard
[3] PC yield calculated from ATR-IR and from ^{1}H NMR with 1,3,5-trimethoxybenzene as internal standard
[4] Yield of the biscarbonated product BisLC calculated from ^{1}H NMR with 1,3,5-trimethoxybenzene as internal standard

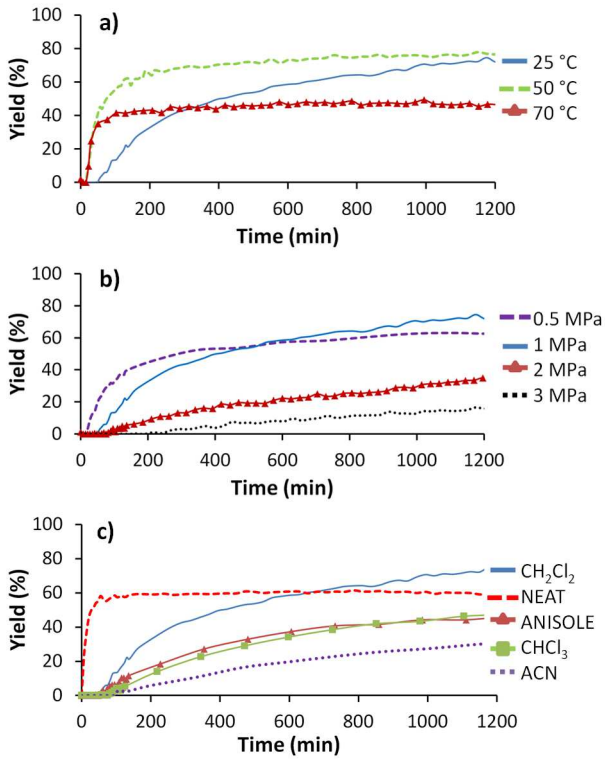


Figure 4 : Yield of propylene carbonate (PC) with the reaction time for different (a) temperatures, (b) pressures and (c) solvent conditions. Reaction conditions are described in Table 1.

Effect of the pressure:

Increasing the pressure from 1 MPa to 4 MPa had a detrimental effect on both the kinetics and PC yields for the model reaction promoted by DBU/EtBr in CH_2Cl_2 at 25°C for 20 h (Figure 4b). While the CO_2 solubility increases with the pressure in CH_2Cl_2 [56], a two-fold decrease of the reaction yield (PC yields from 70 % to 35 %, Table 1, entries 1 and 5) was noticed upon simple doubling the CO_2 pressure from 1 MPa to 2 MPa and the reaction was quasi inhibited at 3 MPa of CO_2. Such experimental observations were assigned to a "salting out effect" presumably caused by the formation of a CO_2-expanded reaction medium provoking the precipitation of the $RCO_3^-/DBUH^+$ organic salt (see ESI 6). Attempts to improve the addition of CO_2 onto PG by decreasing the pressure from 1 MPa to 0.5 MPa also gave mitigated results. If the kinetic is faster during initial course of the reaction (below 500 min) at 0.5 MPa, the PC yield ceiled at 50-60 % after 500-600 min while it continued to increase up to ~ 70 % at 1 MPa. Therefore, we set up the optimal pressure and temperature for this reaction in CH_2Cl_2 to 1 MPa and 25°C, respectively. Regarding the formation of **BisLC** side product, lower yields were unexpectedly obtained with higher pressures, which indicate that the CO_2 concentration in the reaction mixture is not decisive for this side reaction.

Effect of the solvent:

To study the influence of the solvent on the system, the model reactions were reproduced at 1 MPa and 25°C in neat condition or using anisole, $CHCl_3$, DMSO or acetonitrile (ACN) (Table 1, entries 8-13). Even though CO_2 is poorly soluble in glycols [59], reactions performed under neat conditions at 1 MPa and 25 °C displayed faster kinetics, and PC yields up to 60 % were obtained after only 2 h (Table 1, entry 8, Fig. 4C red curve). Alike the model reactions carried out in CH_2Cl_2, increasing the pressure had a negative impact on both the kinetic and PC yields (Table 1, entries 8-9). Switching from CH_2Cl_2 to other solvents (Table 1, entries 10-13) led systematically to lower/moderate PC yields (from 16 % in DMSO to 46 % in anisole after 20 h). The benchmarking of the kinetic profiles recorded for each solvent clearly highlighted slower reaction rates in solvents other than CH_2Cl_2 (Fig. 4C). Interestingly, when the reaction was carried out in anisole, precipitation of organic salts $DBUH^+/Br^-$ occurred after 30 min of reaction. When DMSO was used instead of CH_2Cl_2, PC was synthesized in very low yield (Table 1, entry 15). We believe the variation of the PC yields in the various solvents was caused by the occurrence of side-reactions (enhanced alkylation of DBU by EtBr), that will be discussed below. Unlike neat conditions that favoured the formation of **BisLC** side-product with a yield up to 27 % (Table 1, entry 8-11), its formation remained limited to ~15 % by switching from CH_2Cl_2 to other solvents.

Influence of the alkylating agent:

As shown by our DFT calculations, the R-X alkylating agent is expected to play an important role on the carbonation of diols. It was expected that the nature of the halide would dictate the reactivity for the alkylation of the carbonate anion (step 2 in Scheme 4) whereas the R motif is expected to trigger the cyclization step prior formation of PC by providing a good RO^-

leaving group (step 4 in Scheme 4). To verify this hypothesis, different alkyl halides were screened for the DBU promoted synthesis of PC from PG and CO_2 at 25 °C and 1 MPa in CH_2Cl_2.

When bromobutane replaced bromoethane, a slower kinetic was observed (Fig. 5, dark red curve), resulting in lower PC yield of 50 % after 20 h (Table 2, entry 2). Extending the reaction time to 39 h led to similar yield with regard to bromoethane (76 % yield of PC). Replacing bromobutane by its chlorinated analogue dramatically decreased the reaction rate with a marginal PC yield of only 3 % after 20 h (Table 2, entries 2 and 3, Fig. 5 orange curve). This result is consistent with the proposed mechanism that involved the formation of the intermediate **IntLC** by a SN_2 reaction (step 2, see Scheme 4). Chlorine being a poorer leaving group than bromine, the nucleophilic substitution is disfavoured.

Table 2 : Effect of the alkyl halide on the carbonation of propylene glycol under a pressure of 1 MPa CO_2 at 25 °C. Reaction conditions: diol (0.5 mmol in 200 µL CH_2Cl_2), DBU (1 mmol), Alkyl halide R-X (1.2 mmol)

Entry	R-X	PG conv. (%)[1,2]	PC yield (%)[1,3]	Biscarbonate yield (%)[1,4]
1	EtBr	90	73	15
2	BuBr	60	50	10
3	BuCl	3	3	0
4	BzCl	65	65	0
5	BzBr	0	0	0
6	MeI	0	0	0
7[a]	EtBr	28	10	0
8[b]	EtBr	35	32	0
9[c]	/	3	3	0

[1] Determined after 20 h
[2] Conversion of propylene glycol calculated from ^{1}H NMR with 1,3,5-trimethoxybenzene as internal standard
[3] PC yield calculated from ATR-IR and from ^{1}H NMR with 1,3,5-trimethoxybenzene as internal standard
[4] Yield of the biscarbonated product BisLC calculated from ^{1}H NMR with 1,3,5-trimethoxybenzene as internal standard
[a] 0.5 mmol DBU.
[b] 0.5 mmol R-X.
[c] No R-X.

Unlike chlorobutane, a higher PC yield of 65 % was obtained with benzyl chloride. Indeed, the benzyl group displays better leaving group capability in comparison with the butyl group for the cyclization step. Surprisingly, with the more reactive benzyl bromide (BzBr) or methyl iodide (MeI), no PC was formed (Table 2, entries 5-6). We therefore postulate that the possible quaternization of DBU by these alkyl halides might explain this lack of reactivity. This quaternization is typically used for the synthesis of ionic liquids[60]. This hypothesis was further confirmed by ATR-IR analysis. The C=N stretching mode at 1613cm^{-1} of DBU shifts toward 1622cm^{-1} upon alkylation (see ESI 7) and is favoured with more reactive alkyl halides. From these experiments, BzCl and EtBr are the best candidates in combination with DBU for the synthesis of PC. Still, presence of quaternized DBU salts can be shown at the end of reaction time in Fig. 1 with a shoulder at 1622 cm^{-1} of the protonated-DBU peak, probably due to the presence of an excess of alkylating agent (2.4 eq) and non-reacted base (diol not

fully converted). Control experiments (Table 2, entries 7-8) highlighted the need of using 2 equivalents of DBU and 2.4 equivalents of R-X to reach the highest PC high yields, as previously described. [47] In the absence of alkylating agent, only traces of PC (yield of 3 %, Table 2, entry 9) was measured, excluding any role of CH_2Cl_2 as an alkylating agent in promoting the carbonation of PG.

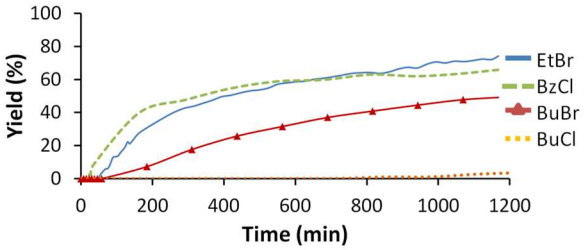


Figure 5: Yield of propylene carbonate (PC) with the reaction time for different alkylating agents. Reaction conditions: Propylene glycol (0.5 mmol in 200 µL CH_2Cl_2), DBU (1 mmol), R-X (1.2 mmol), 1 MPa, 25 °C, 20 h. One pot/one step reactions.

3.2 Dual system TEA/TsCl

To increase the versatility of the coupling between diols and CO_2 for the synthesis of cyclic carbonates, other tertiary amines than DBU were tested as bases, such as N,N,N',N'-tetramethylethylenediamine (TMEDA), triethylamine (TEA), N,N-diisopropylethylamine (DIPEA) and N-methyl pyrrolidine. In all cases, carbonation of the alcohol of PG occurred as highlighted by *in-situ* ATR-IR by the formation of RCO_3^- species at 1660 cm^{-1}. But no propylene carbonate was formed when EtBr was used as alkylating agent. Surprisingly, no absorption band could be observed around 1743 cm^{-1}, indicating that step 2 (SN_2 reaction with EtBr) did not occur. Further investigations were carried out with TEA as the model organic base to compare with DBU, using PG as the diol. DFT calculations (Fig. 6) showed that TEA poorly stabilises TS2, rendering the oxygen atom involved in SN_2 less reactive than in the case of DBU (Mulliken charges of -0.451 vs -0.467), highlighting the important role of the base in every step of the reaction and not only for the protonation steps. This leads to a consistent increase of the Gibbs Free Energy of TS2 for TEA (36.5 kcal/mol vs 24.8 kcal/mol) which is now the highest energetic barrier of the overall reaction ($\Delta G_{TS2}^{\ddagger}$ = 27.4 kcal/mol), explaining why SN_2 doesn't occur in the case of TEA and EtBr.

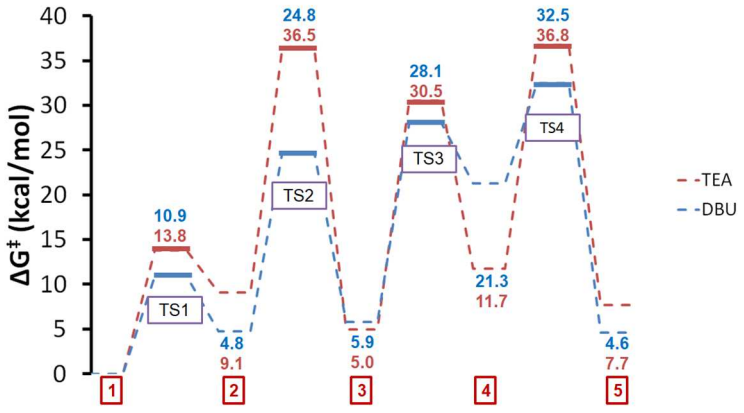


Figure 6: DFT computed pathway (*M062X/6-311g(d,p)*) of model reaction as depicted in Scheme 4 with two different organic bases (DBU or TEA). Red squares correspond to optimized reaction intermediates shown in Scheme 4 (Van Der Waals interactions were accounted). Transition states (TS) were optimized using the same molecular species as in the intermediates.

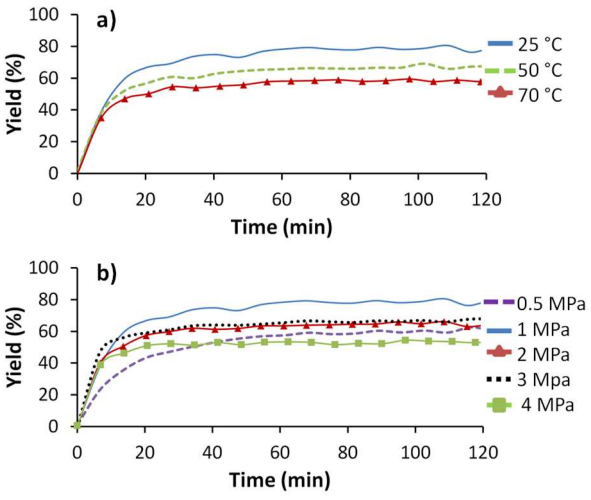
TEA being a less nucleophilic base than DBU, other more reactive R-X could be tested while avoiding side reactions mentioned above (quaternization of the base). Tosyl chloride (TsCl) was selected as a good candidate due to previous research [44-46]. Similarly to the synthetic pathway with DBU/EtBr, the model carbonation reaction of propylene glycol into propylene carbonate was studied using the dual system TEA/TsCl. As the mechanism was already demonstrated by Buchard *et al*[45] for the carbonation of 2,2-dimethyl-1,3-propanediol, the experimental confirmation of this mechanism is presented in ESI 8 with propylene glycol. Kinetic studies are reported for the first time by ATR-IR *in-situ* monitoring in pressurized reactors that enabled to identify important reaction intermediates and to confirm the reaction mechanism.

At room temperature and a fixed pressure of 1 MPa, a maximum PC yield of 79 % is obtained after only 70 min (Fig. 7a, blue curve). When the reaction media was heated up to 50 °C and 70 °C, the yield decreased to 70 % and 60 % respectively (Table 3, entries 2-3).

Table 3: Effect of the temperature, pressure and solvent on the reaction of propylene glycol to afford propylene carbonate Reaction conditions: Propylene glycol (0.5 mmol in 200µL solvent), TEA (1 mmol), TsCl (0.5 mmol).

Entry	P_{CO2} (MPa)	T (°C)	Solvent	PG conv. (%)[1,2]	PC yield (%)[1,3]
1	1	25	CH_2Cl_2	80	79
2	1	50	CH_2Cl_2	79	70
3	1	70	CH_2Cl_2	62	60
4	0.5	25	CH_2Cl_2	80	62
5	2	25	CH_2Cl_2	66	65
6	3	25	CH_2Cl_2	70	68
7	4	25	CH_2Cl_2	70	55
8	1	25	neat	90	90
9	1	25	anisole	90	85
10	1	25	ACN	80	75
11	1	25	$CHCl_3$	79	60

[1] Determined after 3h
[2] Conversion of propylene glycol calculated from ^{1}H NMR with 1,3,5-trimethoxybenzene as internal standard
[3] PC yield calculated from ATR-IR and from ^{1}H NMR with 1,3,5-trimethoxybenzene as internal standard



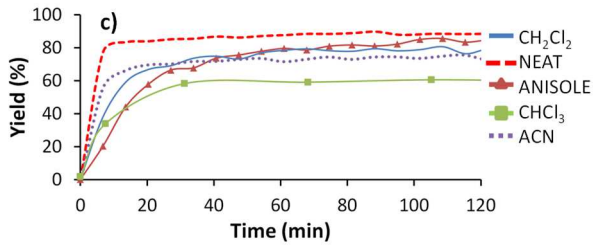


Figure 7: Yield of propylene carbonate (PC) with the reaction time for different (a) temperatures, (b) pressures and (c) solvent conditions. Reaction conditions are described in Table 3.

Regarding pressure effects, at the optimized temperature of 25 °C, an optimum yield for 1 MPa was observed (Table 3, entry 1 and entries 4-7) and increasing the pressure had a detrimental effect on the overall PG conversion and yield. No major differences were observed in terms of kinetics for both heating and increasing the pressure (Fig 7a and 7b), unless for a low pressure of 0.5 MPa (Fig 7b, purple curve) that displayed slow kinetics.

The optimized conditions were applied in neat conditions, which gave the best results so far with 90 % PC yield after only 70 min (Fig 7c, red dashed curve; Table 3, entry 8). Other solvents were tested resulting in a drop of the PC yields to 85 % in anisole (Table 3, entry 9). Switching to acetonitrile or $CHCl_3$ gave PC yields of 75 % and 60 % respectively (Table 3, entries 10-11), with slower kinetics in chloroform (Fig 7c, green curve).

As for the DBU/EtBr dual system, side reactions are expected. In this case, with propylene glycol as a substrate, the main side reaction is the tosylation of one or both alcohol groups, as it is a known reaction for protecting alcohol groups in organic chemistry when a base is involved. Nevertheless, yields of tosylated alcohol never exceeded 3 % for all experiments listed in Table 3.

Other kinetics were performed with tertiary amines such as DIPEA, TMEDA and N-methyl pyrrolidine. Best results were obtained with TEA when dichloromethane was used as solvent. Still, DIPEA could afford propylene carbonate with a yield of 75 % in 150 min (Table 4 entry 2; Fig 8 red curve). TMEDA and N-methyl pyrrolidine displayed lower activity as figured out by lower yields and slower kinetics (Table 4, entries 3-4).

Table 4: Effect of the organic base for the carbonation reaction of propylene glycol to afford propylene carbonate. Reaction conditions: Propylene glycol (0.5 mmol in 200 µL CH_2Cl_2), base (1 mmol), TsCl (0.5 mmol), 25 °C, 1 MPa.

Entry	Base	PG conv. (%)[1,2]	PC yield (%)[1,3]
1	TEA	80	80
2	DIPEA	75	75
3	TMEDA	58	58
4	N-Methyl Pyrrolidine	ND	45

[1] Determined after 3h
[2] Conversion of propylene glycol calculated from ^{1}H NMR with 1,3,5-trimethoxybenzene as internal standard
[3] PC yield calculated from ATR-IR and from ^{1}H NMR with 1,3,5-trimethoxybenzene as internal standard

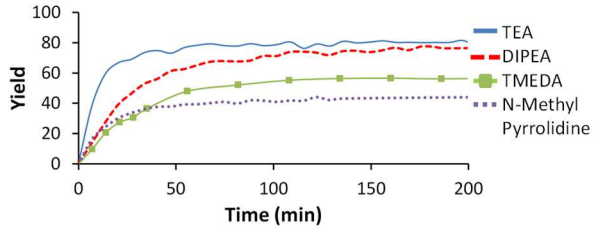
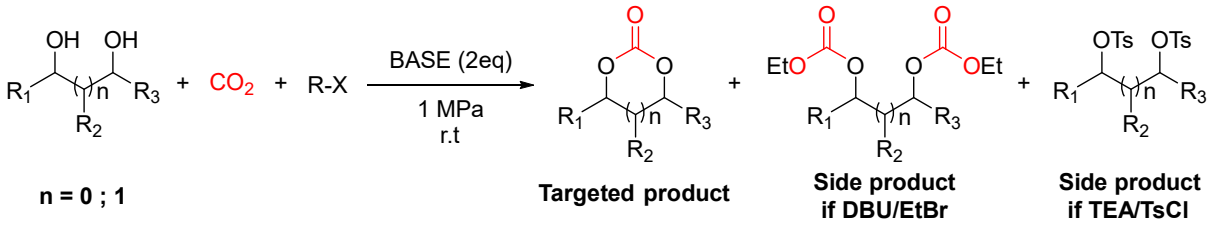


Figure 8: Yield of propylene carbonate (PC) with the reaction time for various organic bases. Reaction conditions are described in Table 4.

3.3 Substrate scope

Even if DBU/EtBr and TEA/TsCl promote the carbonation of diols under mild operative conditions, the benchmarking of their performances as well as their influence on the product selectivities has never been assessed. The coupling chemistry of different classes of alcohols (1,x-diols with x = 2, 3 or ≥ 4) with CO_2 to afford di-, tri- and tetrasubstituted ethylene carbonates, (substituted) trimethylene carbonates or acyclic biscarbonated compounds (Scheme 5) was then balanced regarding both activating systems. Insights into the products yield and selectivity (linear vs cyclic carbonates) are highlighted by benchmarking the performance metrics of both dual activation systems. This study will guide the reader to select the most efficient dual system and the optimal operating conditions to drive the selective formation of the envisioned (a)cyclic carbonate.



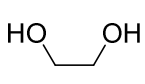
Scheme 5: Substrate scope comparison between the two dual agents DBU/EtBr and TEA/TsCl. Side products directly depend on the method used.

3.3.1 Selectivity for 1,2-diols substrates

Vicinal diols were expected to give ethylene carbonates analogues as the main product due to their known stability. However, depending on the structure of the 1,2-diol, a different selectivity toward the cyclic or biscarbonated linear product was observed (Table 5, entries 1-4) when DBU/EtBr was used. The carbonation of ethylene glycol (product A) afforded a mixture of biscarbonate and ethylene carbonate for DBU/EtBr as the activating system with a low selectivity in cyclic carbonate (39 %). When TEA/TsCl was used however, the yield in cyclic carbonate was improved from 19 % up to 44 % with a greater selectivity of 69 % (Table 5 entry 1). Side products (tosylated alcohols) were still observed at a 20 % yield. When the substrate was switched to propylene glycol (PG), great selectivity toward the cyclic carbonate was observed for both systems (Table 5 entry 2). Best results were obtained with TEA/TsCl as the dual system with a 79 % yield and 100 % selectivity of propylene carbonate. In a similar fashion as for product A, 2,3-butanediol (product C) displayed a poor yield and

selectivity toward the cyclic carbonate when DBU/EtBr was used. Yet, the dual system TEA/TsCl provides a satisfying way to obtain mainly the corresponding cyclic carbonate with a moderate yield of 46 % with 100 % selectivity (Table 5 entry 3). We believe that double carbonation occurs in the case of products A and C when DBU/EtBr was used since both

Table 5: Substrate scope for the carbonation of diols for both dual activating systems DBU/EtBr and TEA/TsCl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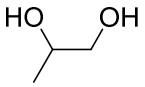
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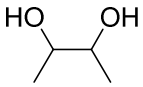
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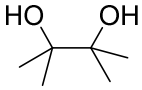
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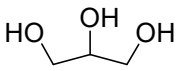
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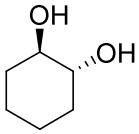
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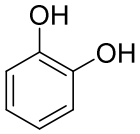
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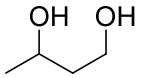
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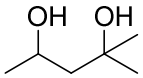
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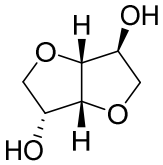
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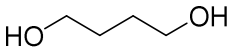

K

Entry	Substrate	DBU/EtBr			TEA/TsCl		
		Yield cyclic carbonate[1] (%)	Yield biscarbonated[2] (%)	Selectivity cyclic carbonate	Yield cyclic carbonate[3] (%)	Yield tosylated alcohol[4] (%)	Selectivity cyclic carbonate (%)
1	A	19	29	39	44	20	69
2	PG	73	15	83	79 (55)[5]	0	100
3	C	20	27	42	46	0	100
4	D	27	0	100	67 (50)[5]	0	100
5	E	75 (60)[5]	0	100	55	20	73
6	F	0	54	0	90 (60)[5]	4	96
7	G	0	0	0	0	0	0
8	H	17	31	35	64 (39)[5]	12	84
9	I	15	54	22	84 (58)[5]	0	100
10	J	0	56	0	0	ND	/
11	K	0	51	0	0	ND	/

[1]: Yield of the corresponding carbonate after 20 h, estimated by quantitative ^{1}H NMR. Conditions: Diol (0.5 mmol); DBU (1 mmol); EtBr (1.2 mmol); CH_2Cl_2 (200 µL); 1,3,5-trimethoxybenzene (0.166 mmol) as internal standard ; 1 MPa, r.t.

[2]: Yield of the corresponding biscarbonated compound after 20h, estimated by quantitative NMR. Conditions: Diol (0.5 mmol); DBU (1 mmol); EtBr (1.2 mmol); CH_2Cl_2 (200 µL); 1,3,5-trimethoxybenzene (0.166 mmol) as internal standard ; 1 MPa, r.t.

[3]: Yield of the corresponding carbonate after 3h, estimated by quantitative NMR. Conditions: Diol (0.5 mmol); TEA (1 mmol); TsCl (0.5 mmol); CH_2Cl_2 (200 µL); 1,3,5-trimethoxybenzene (0.166 mmol) as internal standard ; 1 MPa, r.t.

[4]: Yield of the corresponding tosylated alcohol after 3h, estimated by quantitative NMR. Conditions: Diol (0.5 mmol); TEA (1 mmol); TsCl (0.5 mmol); CH_2Cl_2 (200 µL); 1,3,5-trimethoxybenzene (0.166 mmol) as internal standard ; 1 MPa, r.t.

[5]: Isolated yields after purification for a couple of best results. Experiments were carried out again on a larger scale and products purified by column chromatography. See ESI for NMR spectra.

alcohol functions are equivalent due to the molecular symmetry. Moreover, small steric hindrance due to the presence of hydrogens or only one methyl must allow the double insertion of CO_2. Whereas no huge differences were observed between carbonation of the primary or secondary alcohol with DBU as a base when DFT calculations were performed (see ESI 3), experimental results tend to demonstrate that non-equivalent alcohol functions

favour the formation of 5 membered cyclic carbonates, as it is the case for PG. In the case of TEA, no double carbonation are expected as it was previously reported for 2,2-dimethylpropane-1,3-diol with a 100 % selectivity toward monocarbonated species, versus 41 % toward biscarbonated species when DBU was used as a base[45]. Tetrasubstituted Pinacol (product D) was poorly converted into the corresponding cyclic carbonate (diol conversion: 27 %) with however no double carbonation (Table 5, entry 4) with DBU/EtBr activating system, due to greater steric hindrance. However, the cyclic carbonate yield was greatly improved up to 67 % when TEA/TsCl was used, with 100 % selectivity toward the cyclic product. To the best of our knowledge, 4,4,5,5-tetramethyl-1,3-dioxolan-2-one was successfully synthesized from CO_2 for the first time, while other attempts using the CO_2/epoxide coupling failed to obtain this product [61]. Interestingly, glycerol (product E) was selectively converted into glycerol carbonate with a yield of 75 % using the dual system DBU/EtBr (Table 5, entry 5). This alkylating agent/organobase activating system surpasses the performance of TEA/TsCl that only afforded glycerol carbonate with a yield of 55 % with concomitant formation of 20 % of tosylated alcohols as side products, highlighting the substrate dependence for each method and the differences in selectivity. These differences are even more highlighted when *trans*-1,2-cyclohexanediol (product F) was used as the substrate. In this case, cyclisation is disfavoured compared to other vicinal diols due to the trans configuration. Interestingly, the cyclic carbonate could still be synthetized in excellent yield (90 %, Table 5 entry 6) and selectivity close to 100 % with TEA/TsCl but not in the case of DBU/EtBr. For the latter, biscarbonation is favoured and biscarbonated compounds were selectively synthetized in good yield (54 %, Table 5 entry 6). Unfortunately, pyrocatechol (product G) could not be converted into any carbonates (Table 5 entry 7).

3.3.2 Selectivity for 1,3-diols substrates

When the DBU/EtBr protocol was applied to the carbonation of 1,3 diols such as 1,3-butanediol (product H) and hexylene glycol (product I), linear biscarbonates were found as the major products (yield = 31 and 54 %, respectively) (Table 5, entries 8 and 9). The formation of the biscarbonated products was favoured due to a larger spacer between both alcohol moieties, in accordance to previous studies[45,46]. Experimentally, 6-membered cyclic carbonates were formed in good yields with great selectivities (Table 5, entries 8 and 9) using TEA/TsCl. Thus, one can tailor the selectivity toward the biscarbonated compounds or substituted trimethylene carbonate by opting for the adequate dual system. This study is particularly relevant as 6-membered cyclic carbonates are modular building blocks for polymer synthesis via ring-opening polymerization[19].

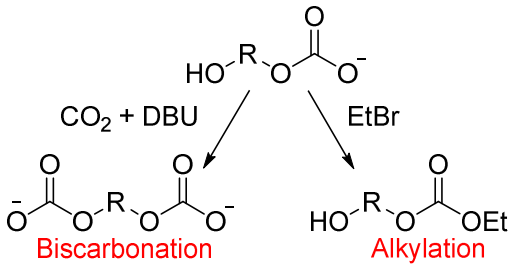
3.3.3 Selectivity for 1,x-diols substrates ($x \geq 4$)

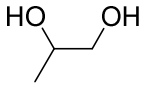
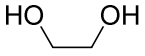
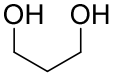
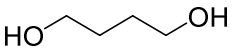
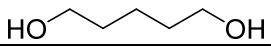
Coupling CO_2 with diols with a larger spacer is expected to favour the carbonation of both alcohol moieties with the formation of acyclic biscarbonates. These compounds are indeed exclusively obtained from 1,4-butanediol or isosorbide in moderate yields (Table 5, entries 10 and 11) with no formation of the 7-membered cyclic carbonates. No cyclic products were

detected in the case of the TEA/TsCl system. A small fraction of dimers and trimers were detected indicating the system is still reactive for this class of diols.

In order to deeply understand the selectivity between cyclisation or biscarbonation depending on the nature of the diol when DBU is used as the base, DFT calculations were performed at the *M062X/6-311g(d,p)* level. For each diol, the activation barriers of the alkylation and biscarbonation steps were compared. For both calculations, the starting point was the optimized geometry of monocarbonated species (product of step 1, see Scheme 4 and Fig. 3). Firstly, biscarbonation was not considered in the reaction pathway with PG as the diol, since its activation barrier is 3.3 kcal/mol higher than the activation barrier of alkylation (Table 6, entry 1), which explains the low percentage of biscarbonated products (≤ 15 %). Moreover, all other activation barriers for the conversion of PG into propylene carbonate are lower than 23.3 kcal/mol (Fig. 4). For ethylene glycol (Table 6, entry 2), both activation barriers are of similar magnitude, indicating that both pathways would compete, which is consistent with experimental results (Table 5, entry 1). As the length of the spacer between both alcohol functions is increased, the activation barrier for biscarbonation decreases whereas alkylation barrier remains around 20 kcal/mol (Table 6, entries 3, 4 and 5). These results support the experimental data collected in Table 5 where 1,3 diols yielded a mixture of (substituted) trimethylene carbonates and biscarbonated products, whereas 1,4-butanediol and Isosorbide only yielded the biscarbonated product.

Table 6: DFT calculation (M062X/6-311g(d,p)) for the comparison between monocarbonation followed by alkylation versus carbonation of both alcohol moieties (biscarbonation).



Entry	Substrate	$\Delta G_2^{\ddagger}$ (kcal/mol)[1] **Alkylation**	$\Delta G_2^{\ddagger}$ (kcal/mol)[1] **Biscarbonation**
1		20.0	23.3
2		20.0	19.7
3		22.2	13.3
4		23.0	16.1
5		22.6	11.9

[1]: Gibbs Free Energy activation were calculated by the difference of Gibbs Free Energy of the transition state and the corresponding optimized reaction intermediates. The optimized structures of the transition states are reported at the end of the ESI.

4. Conclusion

In this work, deep investigations of a model reaction for the coupling of propylene glycol and CO_2 under mild conditions (25 °C ; 1 MPa) promoted by two different metal-free dual activating systems led to a fine understanding of these carbonation reactions. The protocol was optimized thanks to mechanistic and kinetic studies of various parameters reported for the first time, such as influence of the pressure, temperature, solvent and nature of the alkyl halide. Most importantly, extension to other diols using both synthetic pathways provided a powerful guide for the reader to choose the best dual activating system regarding the desired product. If cyclic carbonates are highly desired, TEA/TsCl gives the most interesting results with fast kinetics to afford selectively 5- and 6- membered carbonates. However, DBU/EtBr must be used for the selective synthesis of glycerol carbonate from glycerol. The latter is also effective to tailor selectivity toward biscarbonated compounds when 1,x diols (x ≥ 3) are used as substrates, as for instance to obtain biscarbonated isosorbide. DFT calculations supported the experimental results obtained. This benchmarking highlights the versatility of these organic based dual activating systems and demonstrates the substrate dependency of such carbonation reactions. Perspectives to improve the efficiency of the process would be to recycle these activating systems which are currently used in stoichiometric amounts. To this aim, polymer-supported organic (super)bases could be an alternative way to improve the recyclability of the system.

Acknowledgements

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SUPPLEMENTARY INFORMATION for

The coupling of CO_2 with diols promoted by organic dual systems: towards products divergence via benchmarking of the performance metrics

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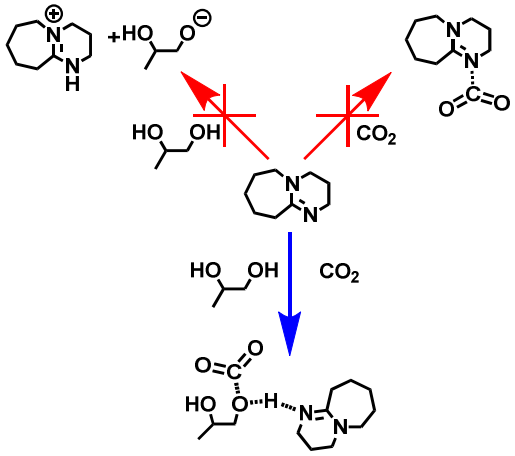
ESI 1 : Evidences of the trimolecular interaction between CO_2, DBU and PG



Scheme S1: Trimolecular reaction between PG, DBU and CO_2. No adduct or special interaction is observed with only two species at the same time.

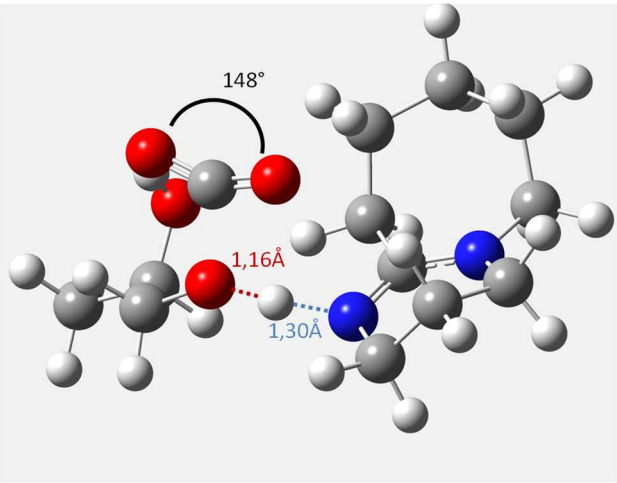


Figure S1: Molecular modelling of the transition state TS1 with trimolecular interaction between PG, DBU and CO_2. Hydrogen bonding between PG and DBU, and angular deformation of CO_2 occur at the same time.

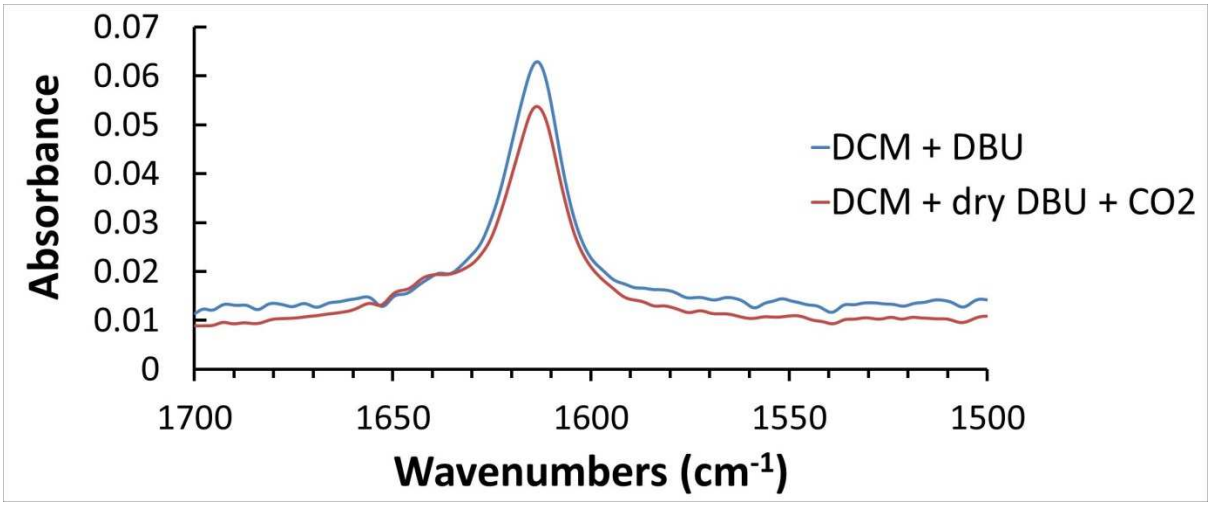


Figure S2: ATR-IR spectra of the DBU/CO_2 system in dichloromethane (DCM). A pressure of 1 MPa CO_2 was applied. When DBU was dried, no interaction or adduct between DBU and CO_2 can be observed. In the presence of water, $DBUH^+/HCO_3^-$ salts are formed.

ESI 2 : Molar attenuation coefficient determination of propylene carbonate for quantitative ATR-IR measurements

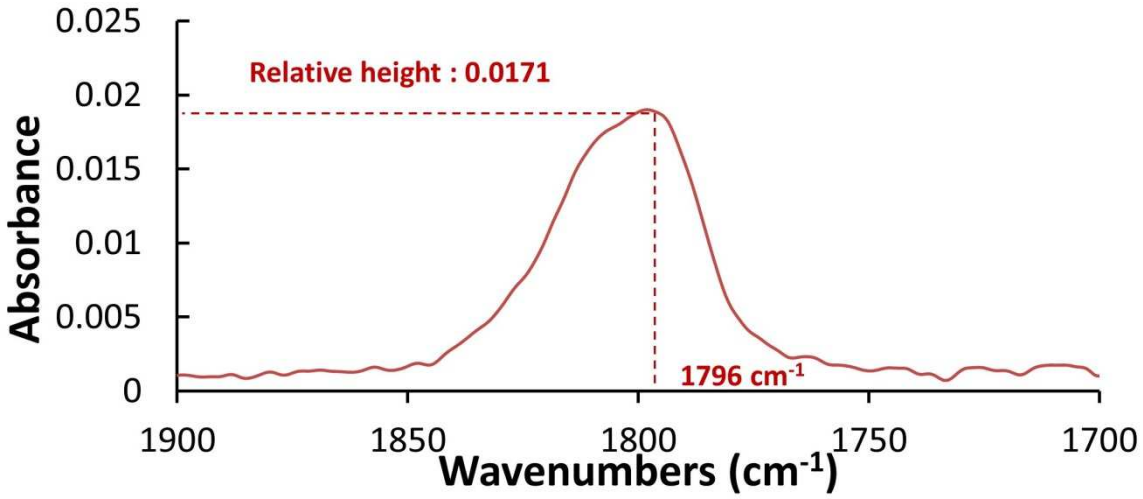


Figure S3: Experimental determination of the molar attenuation coefficient of propylene carbonate by ATR-IR : Propylene carbonate (0.5mmol ; 42.3µL) ; DBU (1mmol ; 149.2µL) ; BuBr (1.2mmol ; 130µL) ; CH_2Cl_2 : (200µL).

Table S1: Results obtained for the determination of ε*l of propylene carbonate. Concentration of propylene carbonate (PC) in all experiments was calculated through Beer-Lambert law using a value of ε*l for pure propylene carbonate (0.0192mL/mmol) since no significant difference was observed for other molecular environments.

Molecular species	Carbonate concentration	Peak height	ε*l (mL/mmol)
PC ; DBU ; BuBr ; CH_2Cl_2	0.96 mol/L	0.0171	0.0178
PC	11.85 mol/L	0.227	0.0192

ESI 3 : ^{1}H NMR characterization of the crude reaction mixture

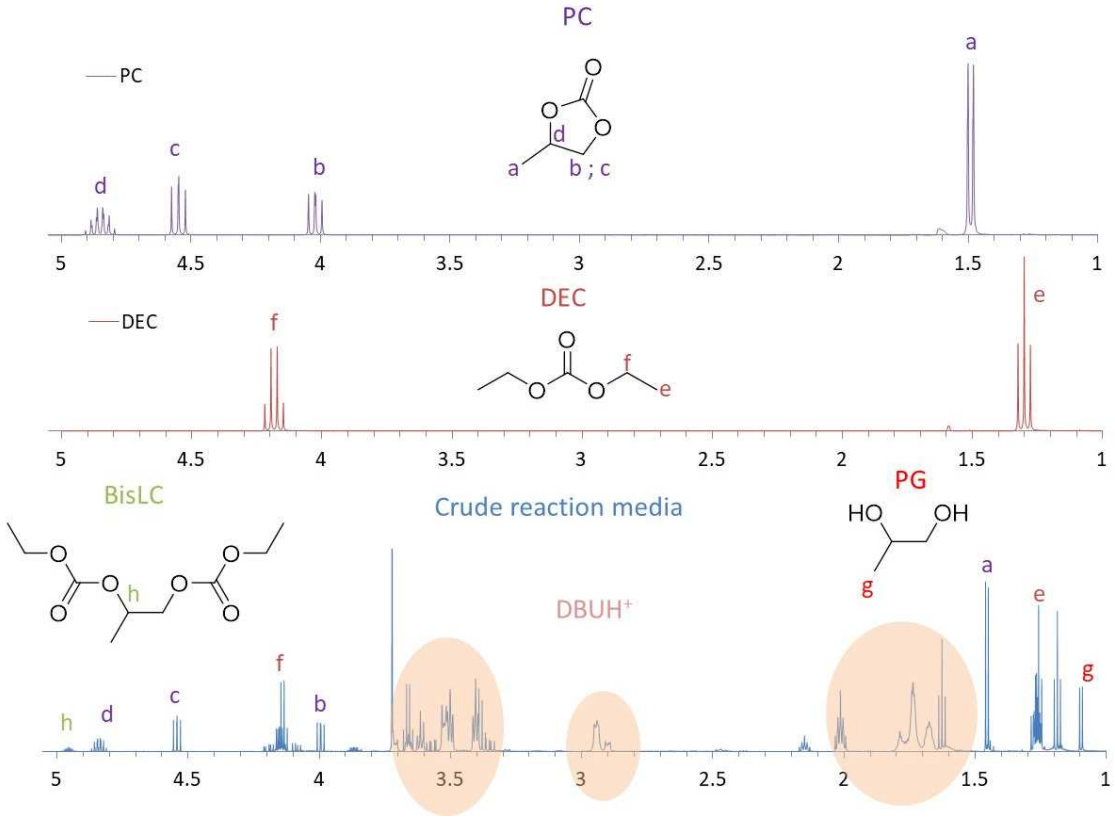


Figure S4: ^{1}H NMR (300MHz, $CDCl_3$) of (a) propylene carbonate (PC), (b) diethyl carbonate (DEC) and (c) the crude reaction mixture (sample entry 1, Table 1)

Chemical shifts ($CDCl_3$) :

PC:

a: 1.48 – 1.42 ppm (3H, d, C*H*$_3$CHO) ; b: 4.02 – 3.95 ppm (1H, dd, C*H*HO) ; c: 4.57 – 4.50 ppm (1H, dd, CH*H*O) ; d: 4.9 – 4.77 ppm (1H, m, MeC*H*O)

DEC:

e: 1.27 – 1.24 ppm (6H, t, *CH*$_3$CH$_2$); f: 4.16 – 4.12 ppm (4H, q, CH$_3$*CH*$_2$)

PG:

g: 1.11 – 1.09 ppm (3H, d, *CH*$_3$CHOH)

BisLC:

h: 4.98 – 4.93 ppm (1H, m, CH$_3$C*H*O)

ESI 4 : DFT discrimination of (R) and (S) configurations and of primary and secondary alcohol reactivities of PG.

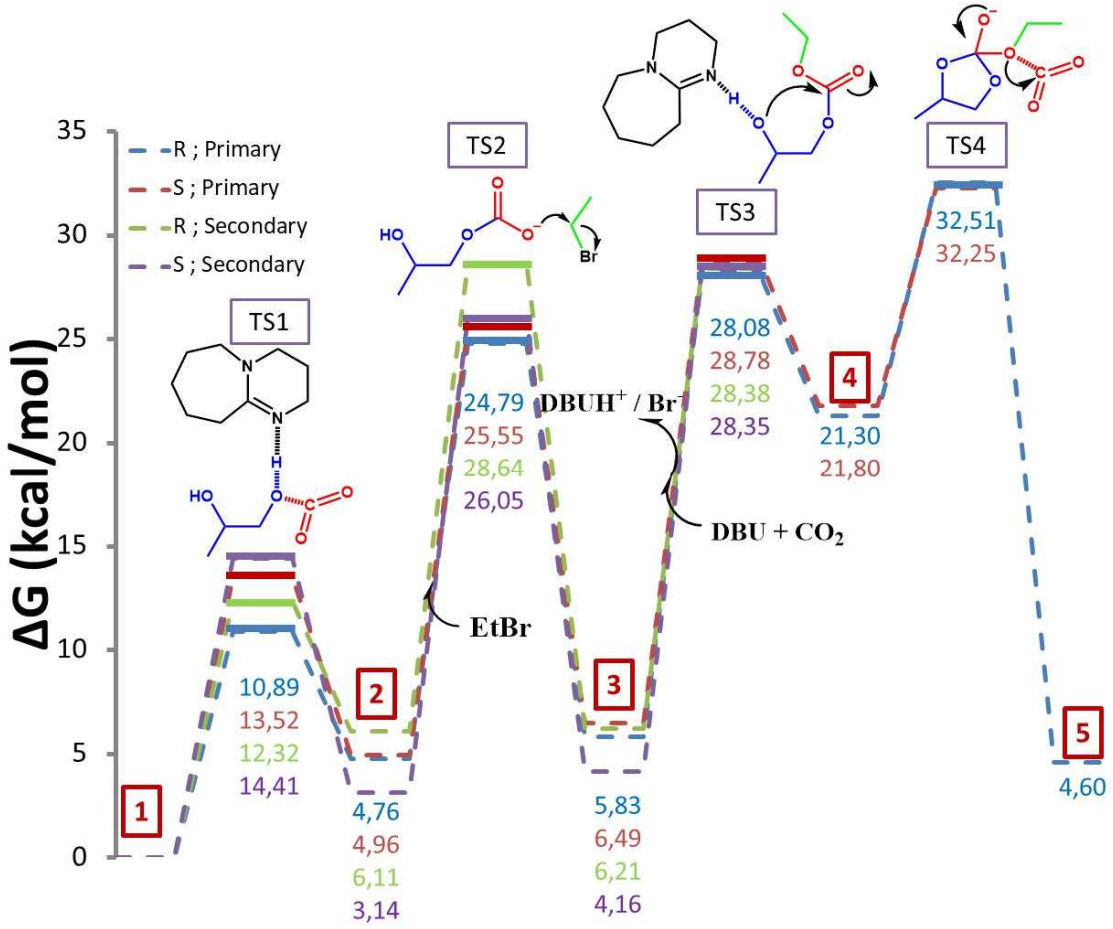


Figure S5: DFT computed pathway (*M062X/6-311g(d,p)*) of model reaction as depicted in Scheme 4. All pathways were considered for the monocarbonation of propylene glycol: carbonation on the primary or secondary alcohol moiety, with either (R) or (S) stereochemistry. Red numbers correspond to optimized reaction intermediates shown in Scheme 4 (Van Der Waals interactions were accounted). Transition states (TS) were optimized using the same molecular species as in the intermediates. The optimized structures of the intermediates and transition states for the reaction path calculated with the (R) primary alcohol are reported at the end of the ESI.

ESI 5 : Comparison between quantitative ATR-IR and quantitative ^{1}H NMR

All yields were determined by quantitative ^{1}H NMR using 1,3,5-trimethoxybenzene (TMB) as internal standard, except for the synthesis of propylene carbonate where the yield was determined by both ^{1}H quantitative NMR and ATR-IR. A known mass of TMB (0.333 equivalent) was added to the reaction mixture before the introduction of CO_2. Here are presented ^{1}H NMR spectrum and ATR-IR spectrum of the same sample at the end of reaction time to compare the yields obtained and confirm both methods work as quantitative methods. Attribution of peaks is detailed in ESI 3.

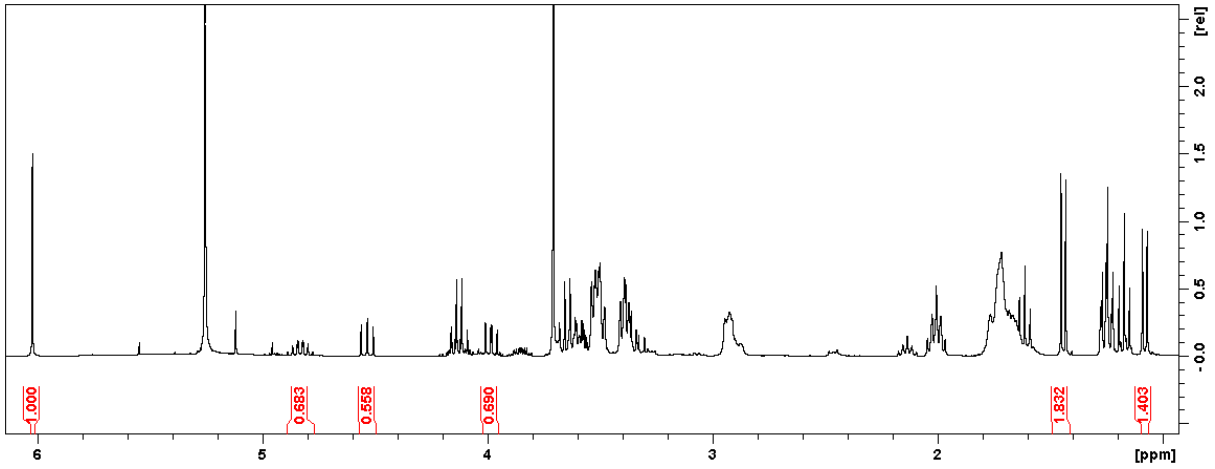


Figure S9: ^{1}H NMR spectrum of model reaction in $CDCl_3$ (Scheme 2) after 20h for the synthesis of Propylene carbonate. Propylene glycol (0.5mmol ; 36.7µL) ; DBU (1mmol ; 149.2µL) ; EtBr (1.2mmol ; 89.4µL) ; CH_2Cl_2 (200µL) ; 1,3,5-trimethoxybenzene (0.162mmol ; 27.22mg) as internal standard. 50µL of the reaction mixture are mixed with 600µL $CDCl_3$ to perform ^{1}H NMR analysis.

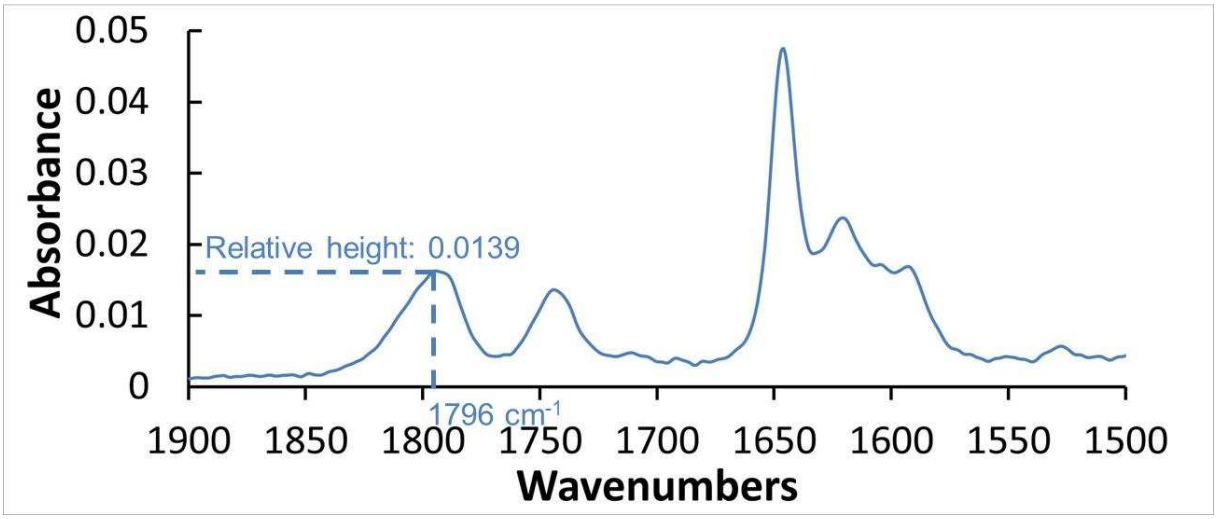


Figure S10: ATR-IR spectra of model reaction (same sample that for ^{1}H NMR spectrum, Fig. S9).

- Yield obtained from ^{1}H NMR analysis :

Propylene carbonate: δ: 4.9 – 4.77 (1 H, m, MeC*H*O), 4.57 – 4.50 (1 H, dd, CH*H*O), 4.02 – 3.95 (1 H, dd, C*H*HO), 1.48 – 1.42 (3 H, d, C*H*$_3$CHO).

Propylene glycol: δ: 3.91 – 3.8 (1H, m, MeC*H*OH), 3.63 – 3.55 (1H, m, CH*H*OH), 3.42 – 3.2 (1H, m, C*H*HOH), 1.10 – 1.06 (3H, d, CH_3CHOH)

TMB: δ: 6.02 (3H, Ar*H*), 3.71 (9H, OCH_3)

Proton signals of propylene carbonate were integrated with aromatic protons signal of TMB (3H) as reference (integration value of 1). As TMB was introduced with a known mass (0.333 equivalent of propylene glycol), one can calculate the exact mole number of propylene carbonate.

$$n(PC) = \frac{\sum_i \frac{\int_i PC}{N_H^i}}{i} * 3 * n_{TMB}$$

$n(PC)$: $Mole\ number\ of\ propylene\ carbonate$

$\int_i PC$: $integration\ value\ of\ signal$ "i" $relative\ to\ propylene\ carbonate$

N_H^i : $number\ of\ hydrogen\ taken\ into\ account\ for\ signal$ "i"

n_{TMB} : $mole\ number\ of\ TMB\ initially\ introduced\ in\ the\ reaction\ media$

Yield obtained from Fig. 12 is of **62 %**.

- Yield obtained from ATR-IR analysis :

Propylene carbonate: ν(C=O) : 1796cm^{-1}

As we calculated the value of ε*l for propylene carbonate (see ESI 5), one can calculate the concentration of propylene carbonate in the reaction media using Beer-Lambert law with the absorbance at 1796cm^{-1}.

Yield obtained from Fig. 13 is of **69 %**.

Both methods lead to the same yield with only small differences attributed to experimental factors.

ESI 6 : Evidence of the $DBUH^+/RCO_3^-$ salt precipitation at 4 MPa

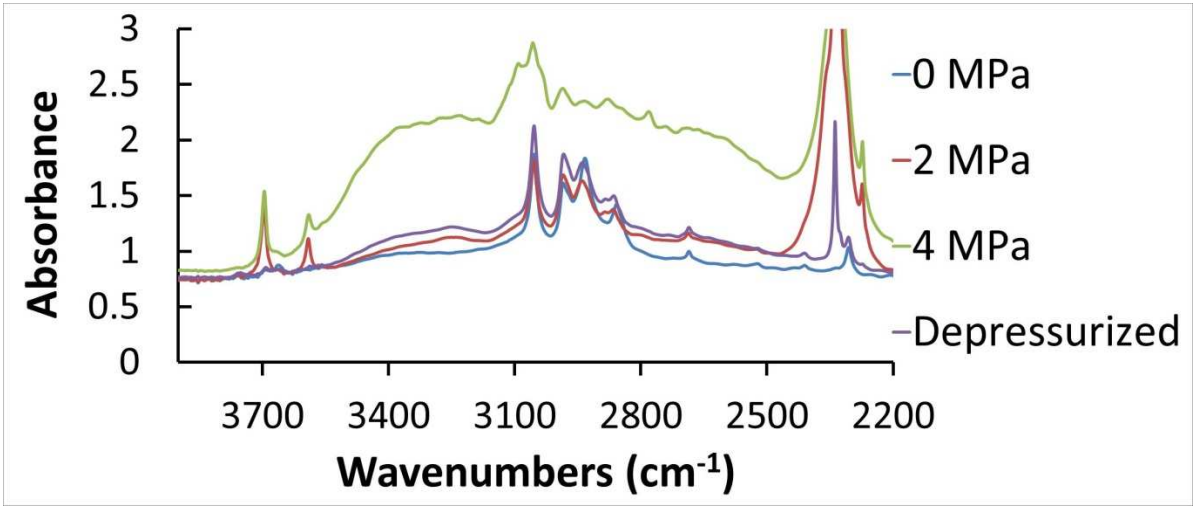
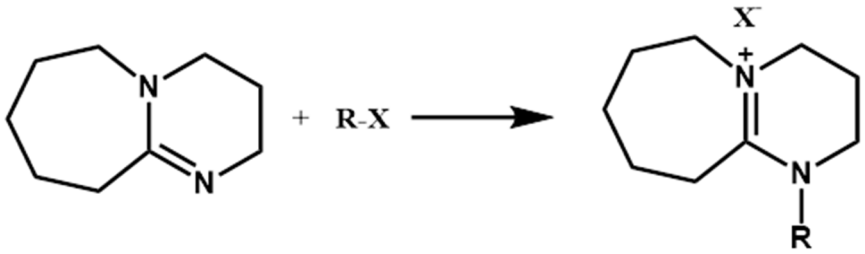


Figure S6: FT-IR (transmission) spectra collected at the equilibrium over different pressure. Purple curve was collected after depressurizing the cell at 4 MPa. Conditions: PG (0.67 mmol ; 49.2 µL), DBU (0.67 mmol ; 100 µL), CH_2Cl_2 (850 µL)

As the system is under pressure, carbonation of the alcohol moiety occurs. Around 4 MPa, large absorption band between 2400cm^{-1} and 3500cm^{-1} appears, characteristic of the formation of solid organic salts (here $RCO_3^-/DBUH^+$) that interferes with the infrared beam as it deposits on the FT-IR cell window. When the system is depressurized, FT-IR profile is nearly fully recovered from the initial state, indicating organic salts are well solubilized in dichloromethane.

ESI 7 : Evidences of the DBU quaternization with alkylating agents R-X



Scheme S2: Side reaction between DBU and alkyl halide (R-X): formation of ionic liquid.

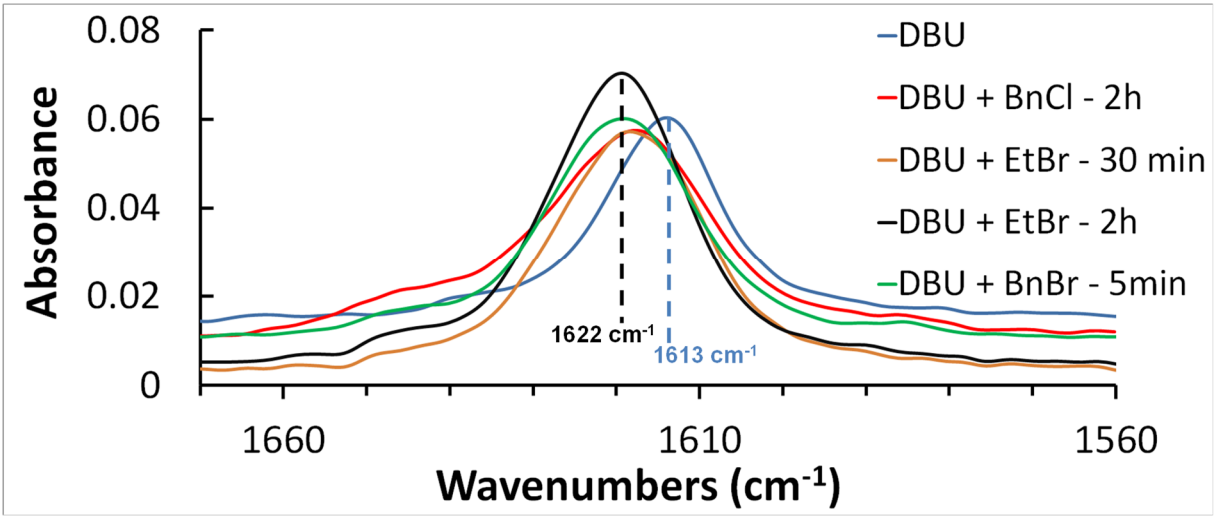


Figure S7 : ATR-IR spectra of the DBU/BnCl, DBU/BnBr and DBU/EtBr systems over time. DBU absorption band is shifted from 1613cm^{-1} to 1622cm^{-1} while alkylation occurs. Depending on the reactivity of R-X, reaction time varies greatly (5min for BnBr, several hours for BnCl).

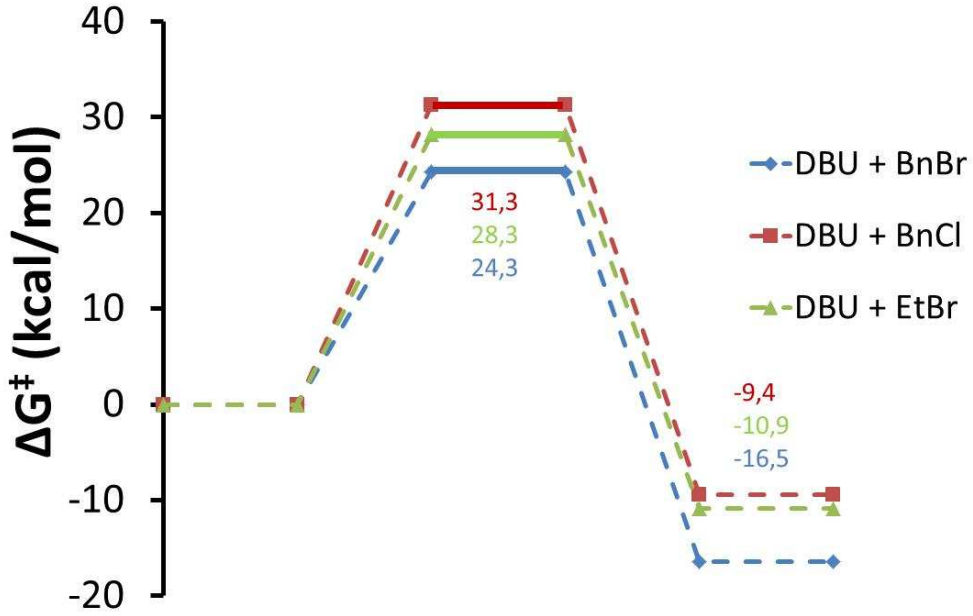


Figure S8 : DFT computed pathway (*M062X/6-311g(d,p)*) of side reaction depicted in Scheme S2.

ESI 8: *In-situ* ATR-IR monitoring of the carbonation reaction of PG to afford PC

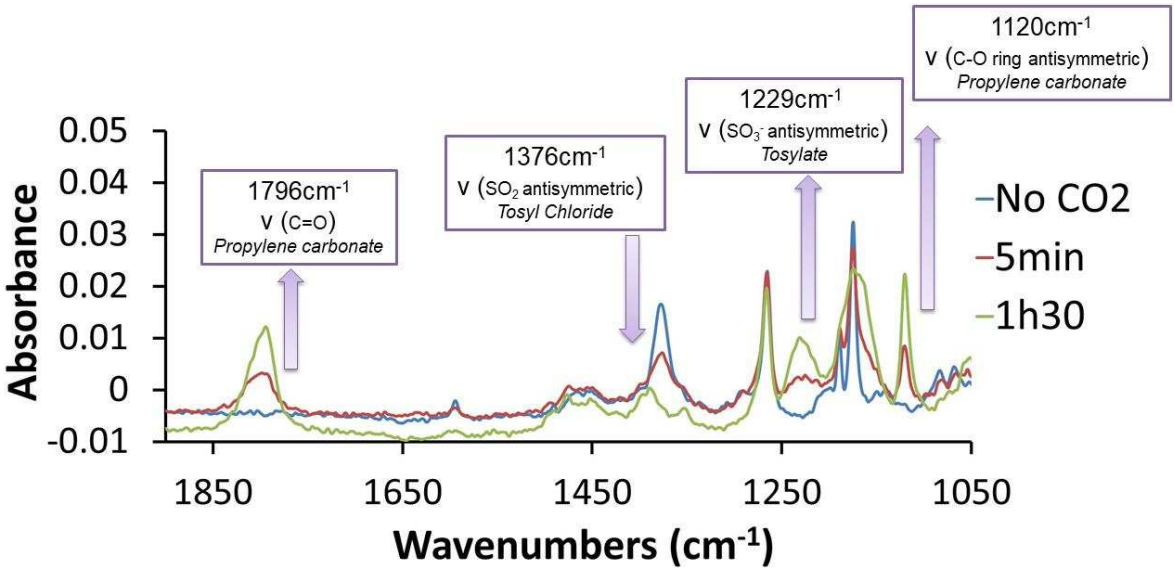
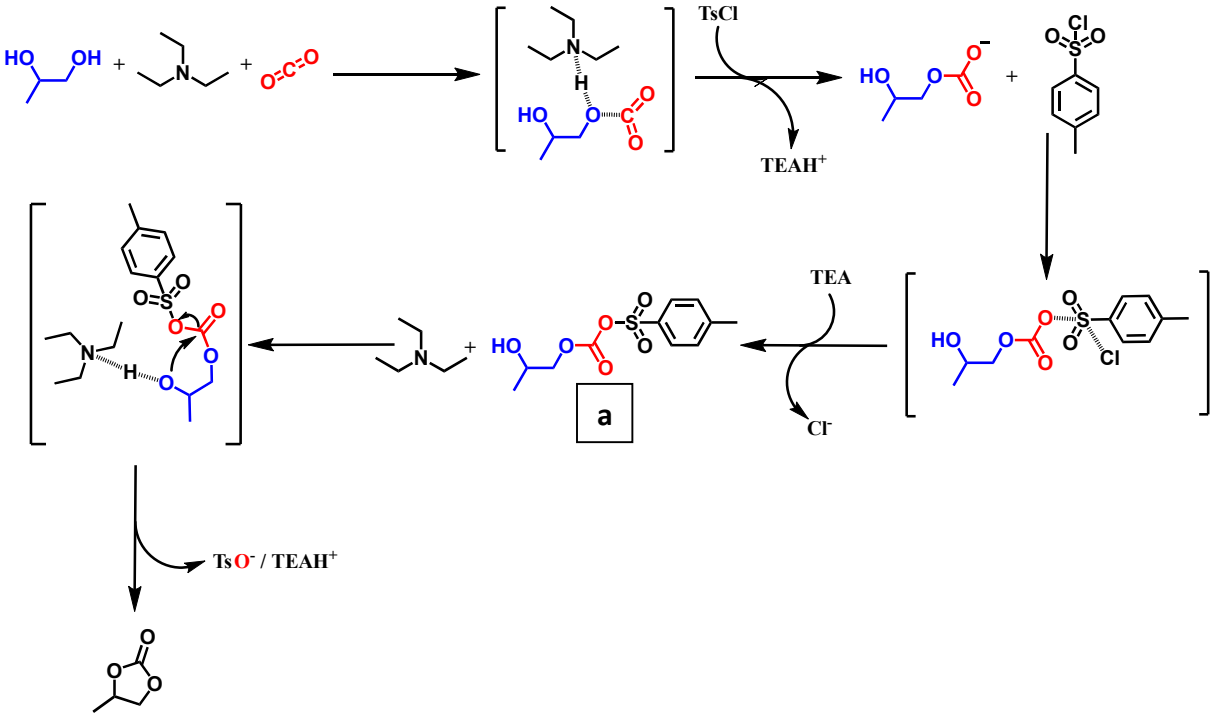


Figure S11: Monitoring of the model reaction between PG and CO2 promoted by a dual TEA/TsCl system using ATR-IR spectroscopy. Conditions: PG (0.5 mmol) ; TEA (1 mmol) ; TsCl (0.5 mmol) ; CH_2Cl_2 (200 µL) ; 1 MPa ; 25°C

Identification of product formation and reactant consumption could confirm the mechanism already proposed in the literature[1]

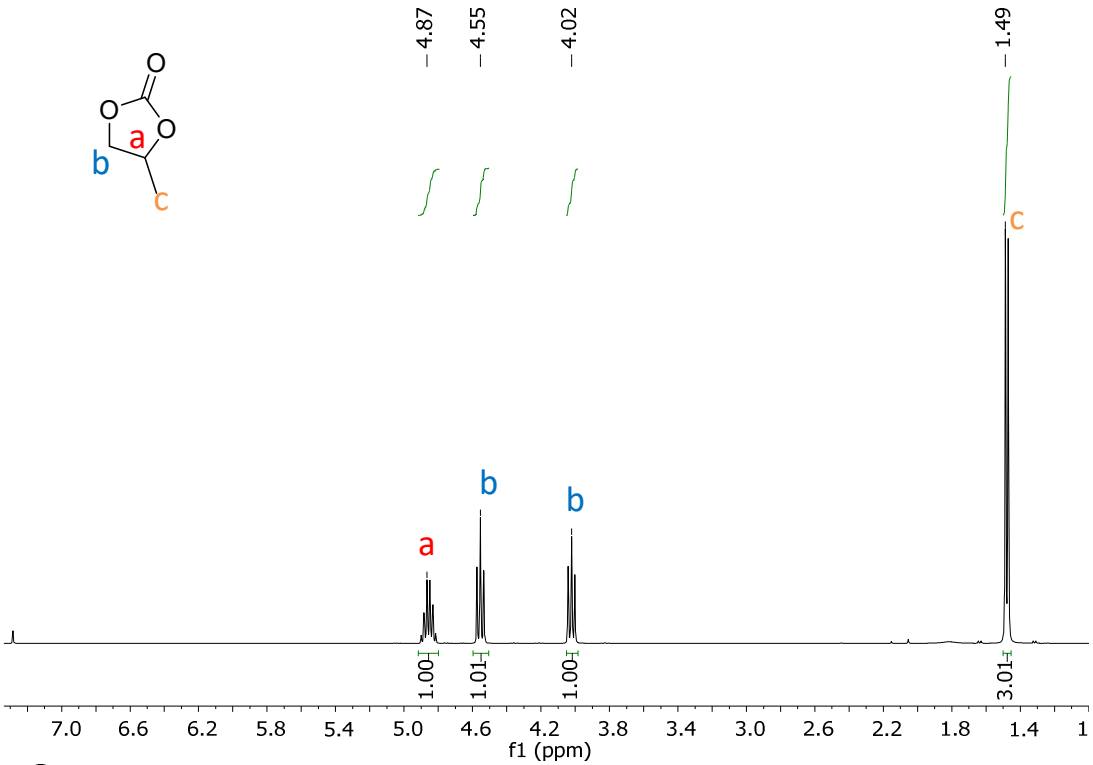


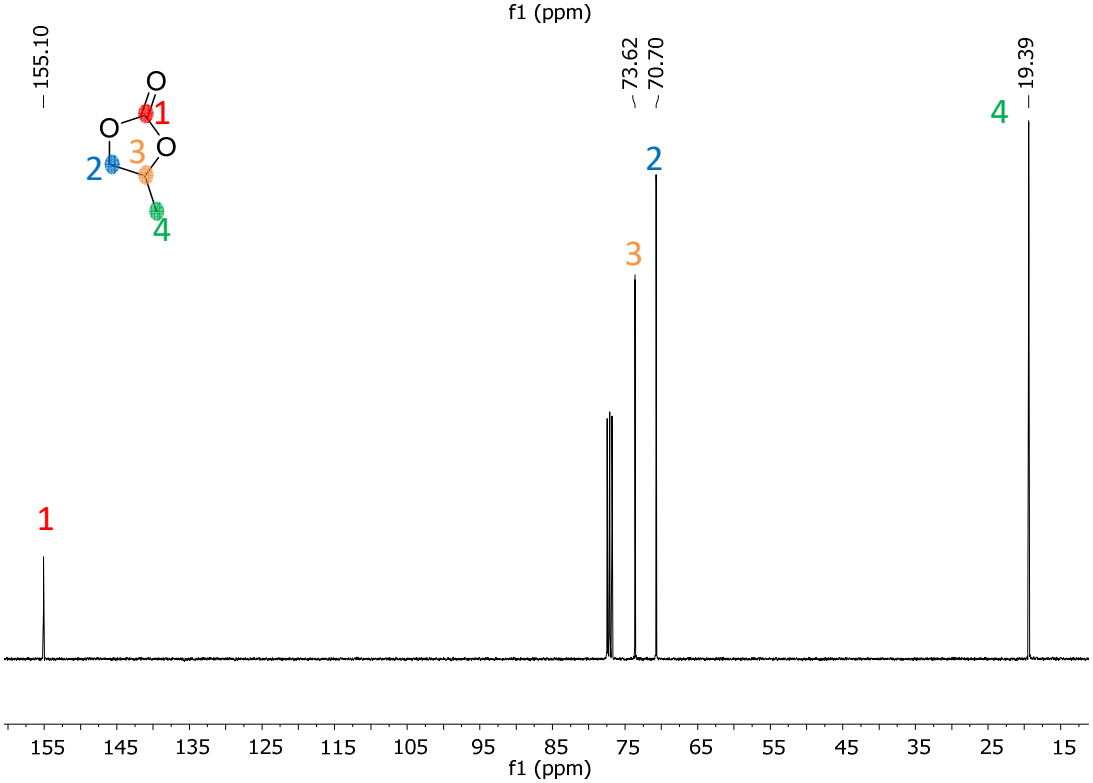
Scheme S3 : Mechanism proposal for the formation of propylene carbonate from PG, inspired from Buchard *et al* [1]. The presence of **a** was not shown by ATR-IR experiments but was proposed regarding preliminaries DFT calculations.

Characterization of organic carbonates

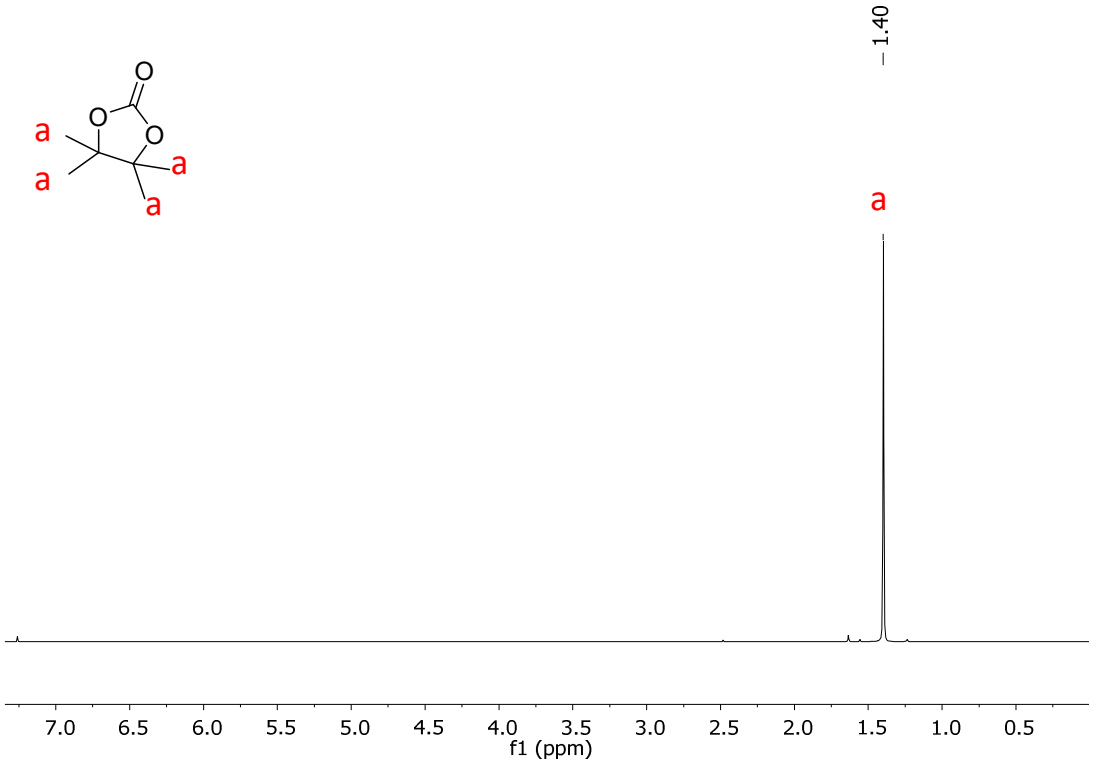
4-Methyl-1,3-dioxolan-2-one : The product was isolated as a colourless oil, 2.136 g (isolated yield 55 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 4.82-4.90 (m, 1 H), 4.55 (dd, *J* = 7.8 Hz, *J* = 8.3 Hz, 1 H), 4.02 (dd, *J* = 7.4 Hz, *J* = 8.3 Hz, 1 H), 1.49 (d, *J* = 6.2 Hz, 3 H).

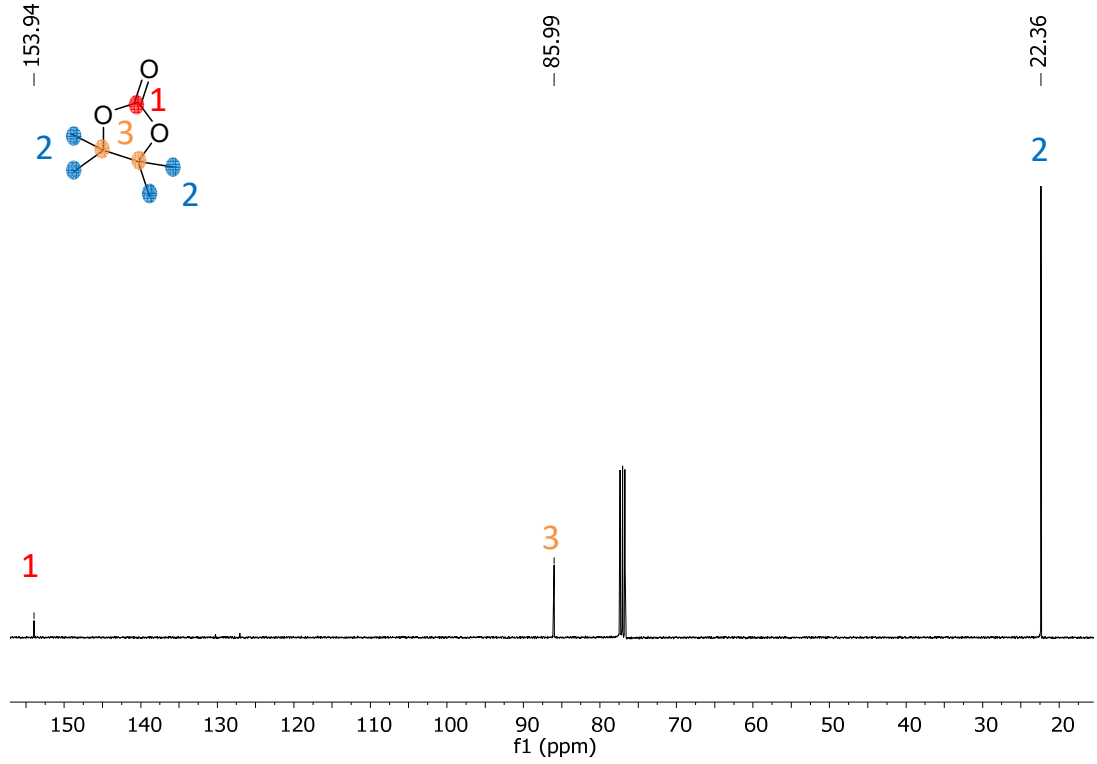
^{13}C NMR (400 MHz, $CDCl_3$) δ (ppm): 155.0, 73. 5, 70.6, 19.2





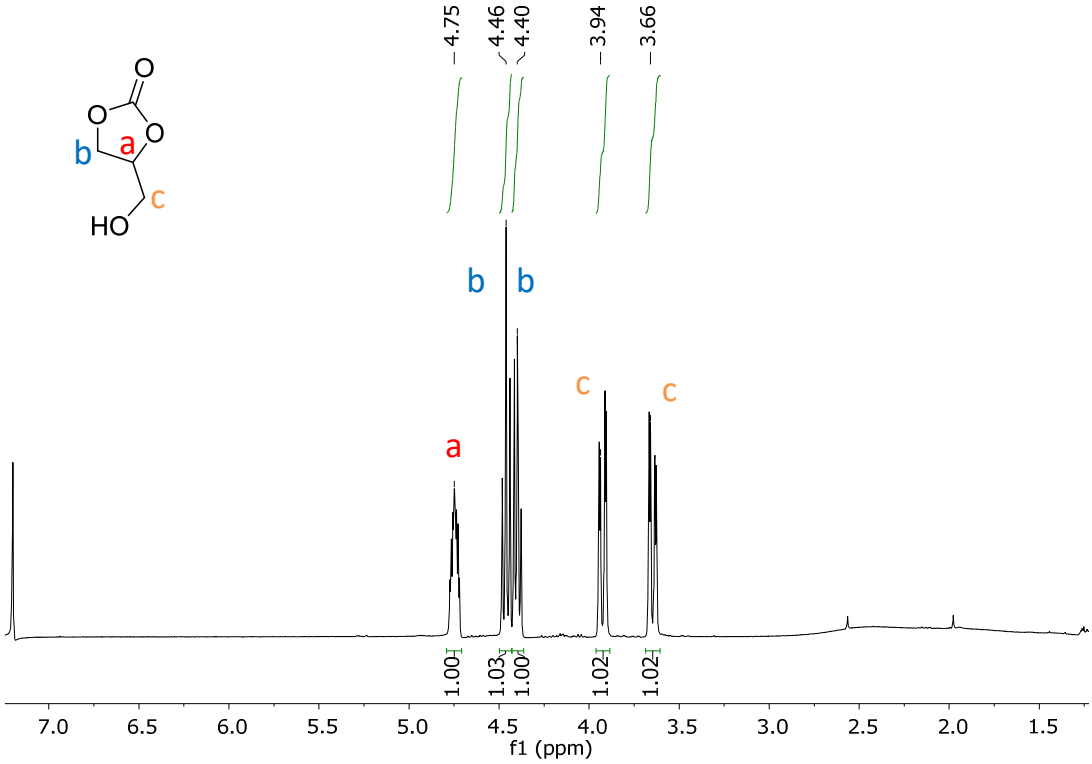
4,4,5,5-Tetramethyl-1,3-Dioxolan-2-one : The product was isolated as a white solid, 1.2976 g (isolated yield 50 %). ^{1}H NMR (400 MHz, CDCl3) δ (ppm): 1.40 (s, 12 H).
^{13}C NMR (400 MHz, CDCl3) δ (ppm): 153.9, 88.99, 22.36

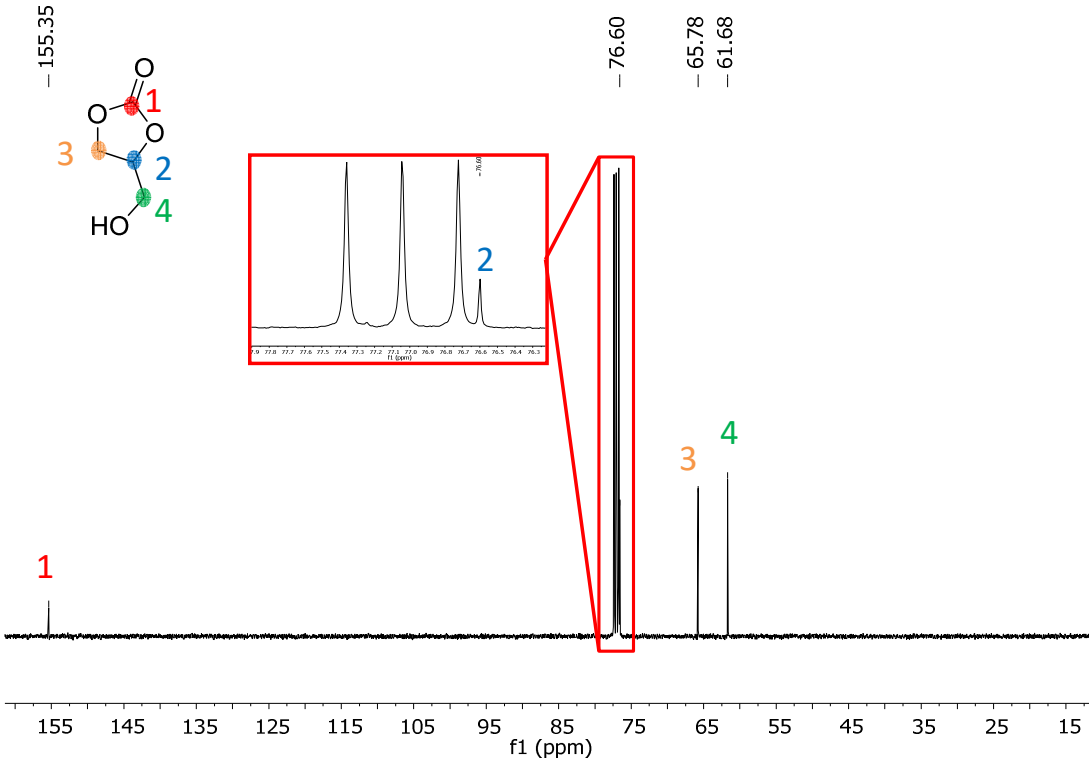




4-(Hydroxymethyl)-1,3-Dioxolan-2-one : The product was isolated as a colourless oil, 0.215 g (isolated yield 60 %). ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 4.75 (m, 1 H), 4.46 (dd, *J* = 8.30 Hz, *J* = 8.46 Hz, 1 H); 4.40 (dd, *J* = 6.74 Hz, *J* = 8.23 Hz, 1 H); 3.94 (dd, *J* = 2.99 Hz, *J* = 9.91 Hz, 1 H); 3.66 (dd, *J* = 3.14 Hz, *J* = 9.38 Hz, 1 H).

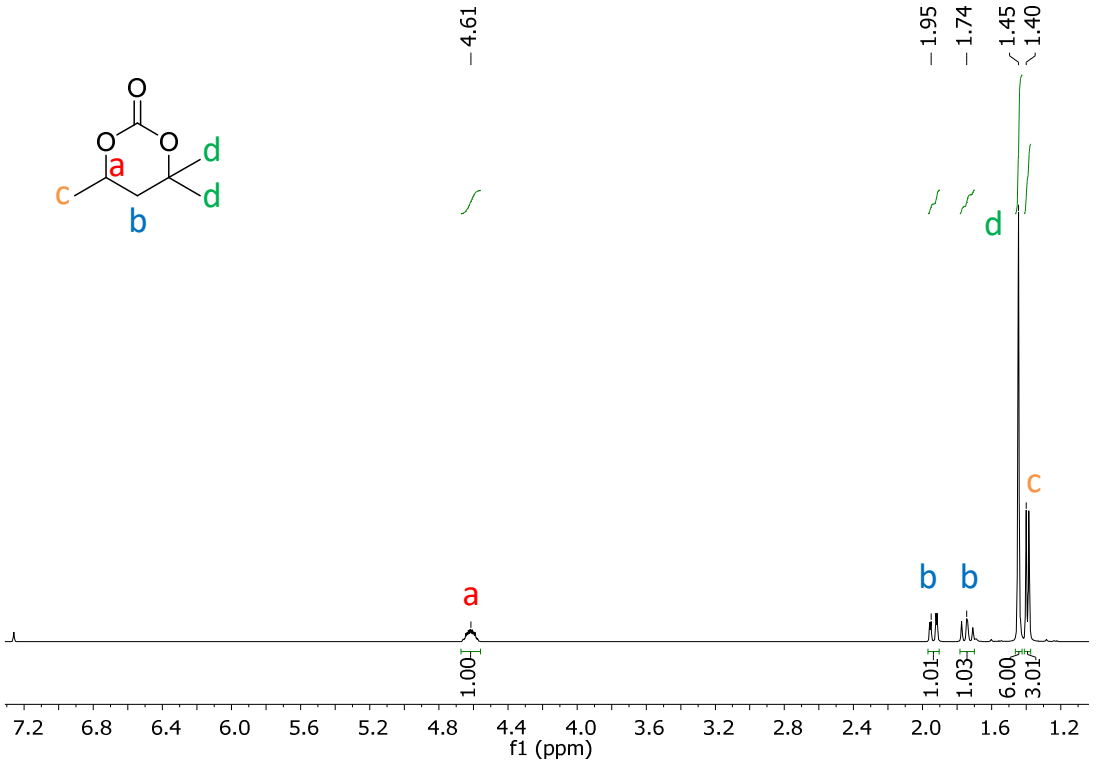
^{13}C NMR (400 MHz, $CDCl_3$) δ (ppm): 155.3, 76.6, 65.8, 61.7

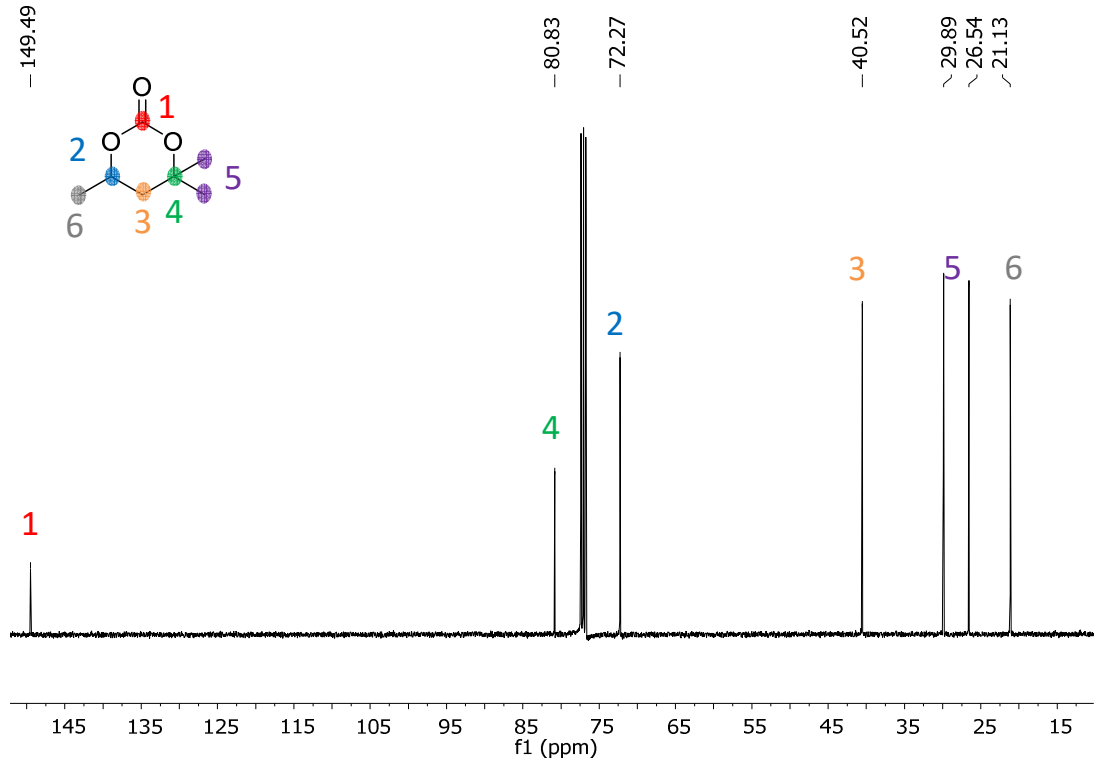




4,4,6-Trimethyl-1,3-Dioxan-2-one : The product was isolated as a white solid, 0.850 g (isolated yield 59 %). ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 4.63 (m, 1 H), 1.95 (dd, *J* =3.0 Hz, *J* = 11.1 Hz, 1 H); 1.74 (dd, *J* = 12.2 Hz, *J* = 13.8 Hz, 2 H); 1.45 (s, 6H); 1.40 (d, *J* = 6.2 Hz, 3 H).

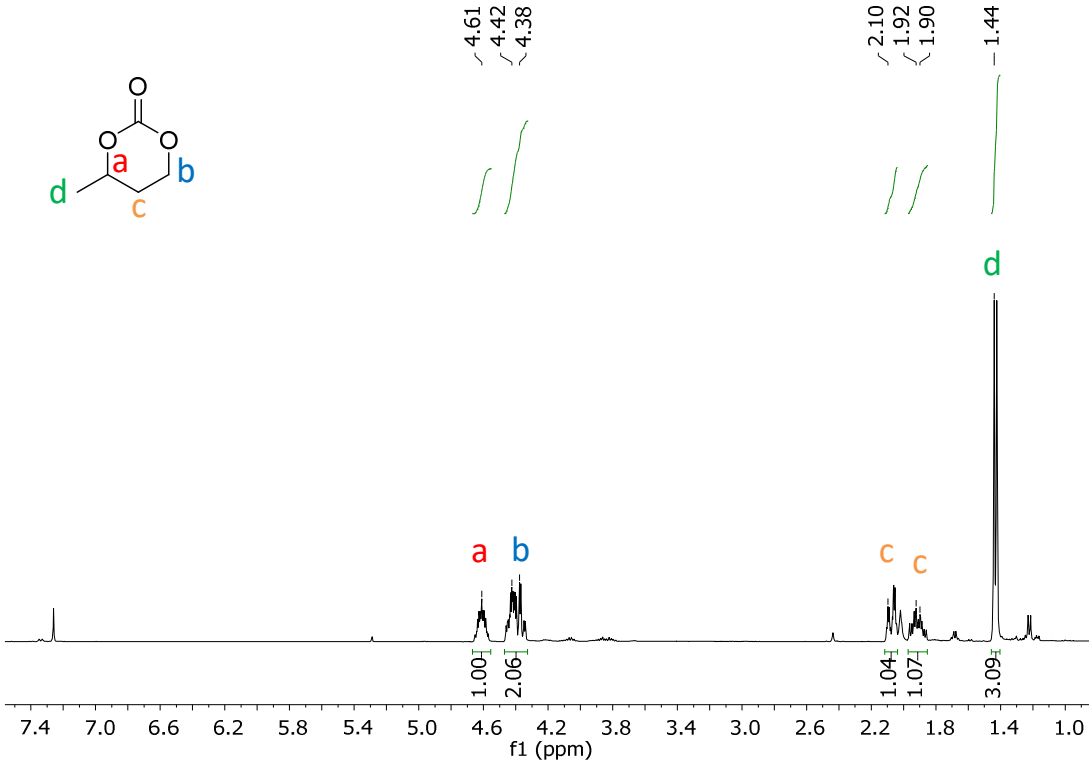
^{13}C NMR (CDCl3, 100 MHz) δ (ppm): 149.5, 80.9, 72.3, 40.5, 29.9, 26.5, 21.1.

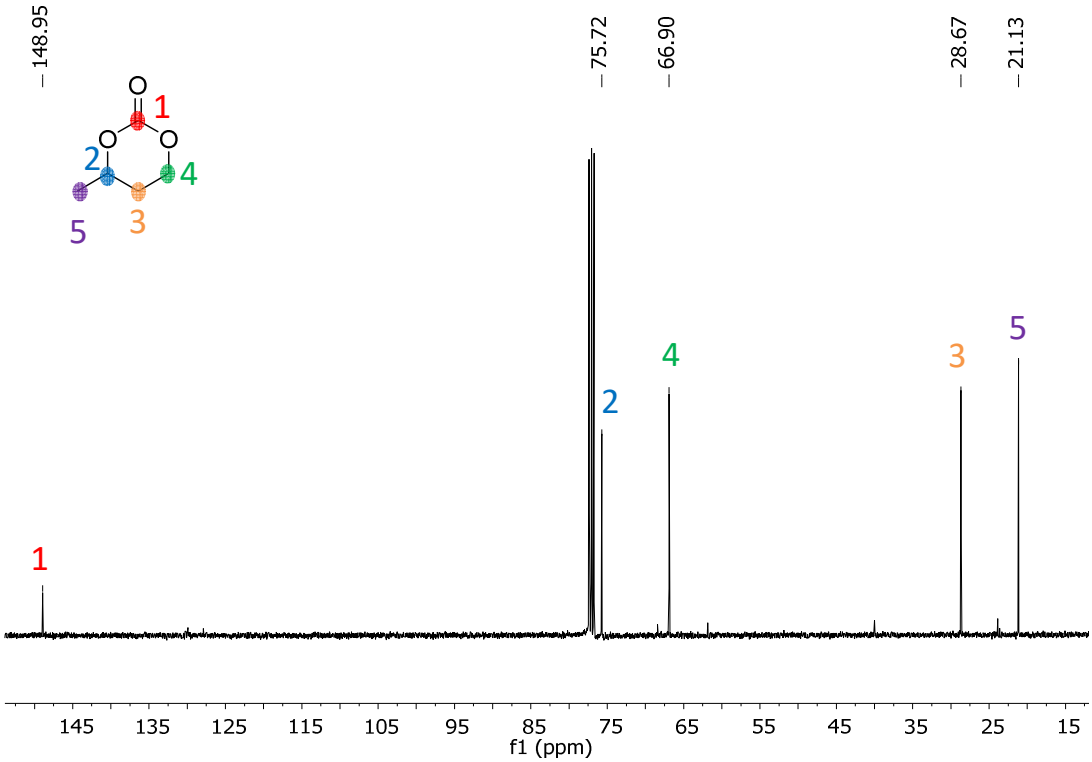




4-Methyl-[1,3]-dioxan-2-one : The product was isolated as a colourless oil, 0.452 g (isolated yield 39 %). ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 4.57-4.65 (m, 1 H), 4.34-4.46 (m, 2 H), 2.04-2.11 (m, 1 H), 1.86-1.96 (m, 1 H), 1.44 (d, J = 6.3, 3 H.

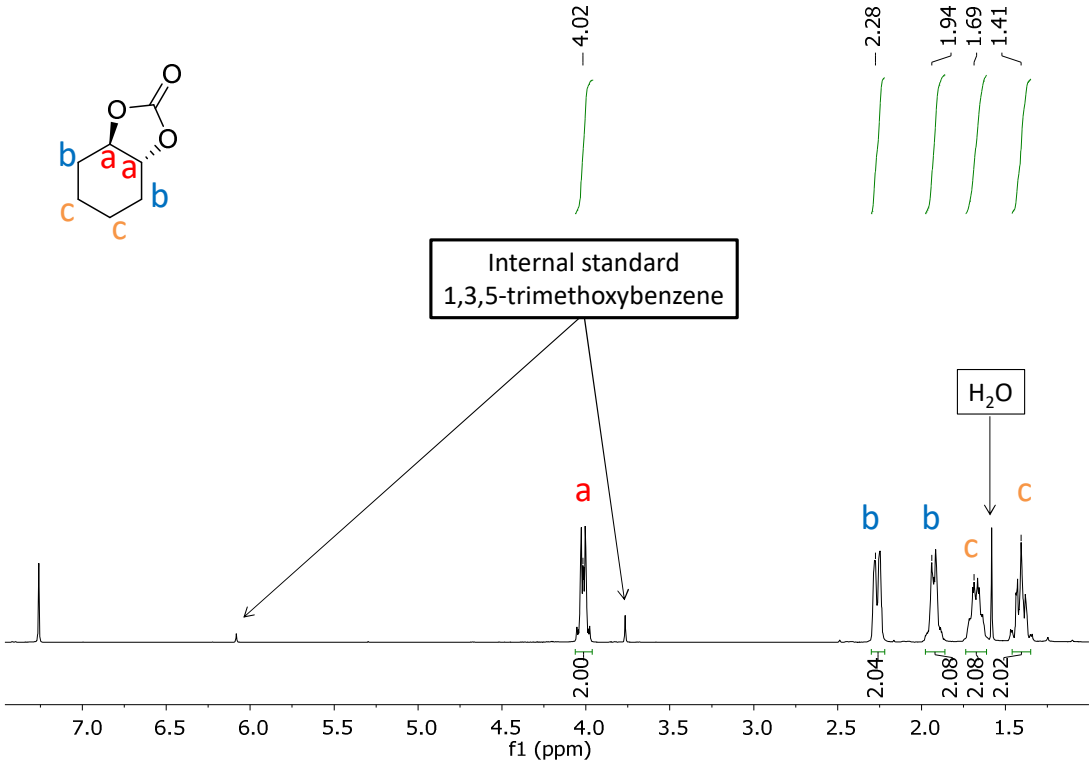
^{13}C NMR ($CDCl_3$, 400 MHz) δ (ppm): 148.9, 75.7, 66.9, 28.7, 21.1

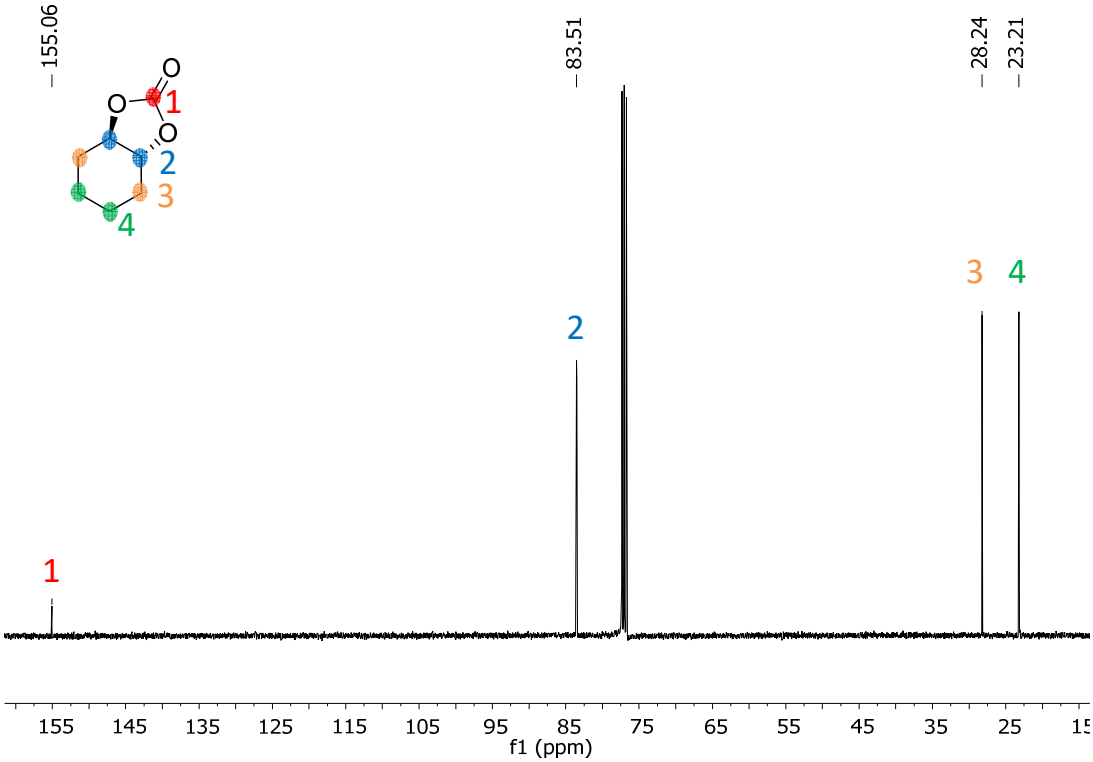




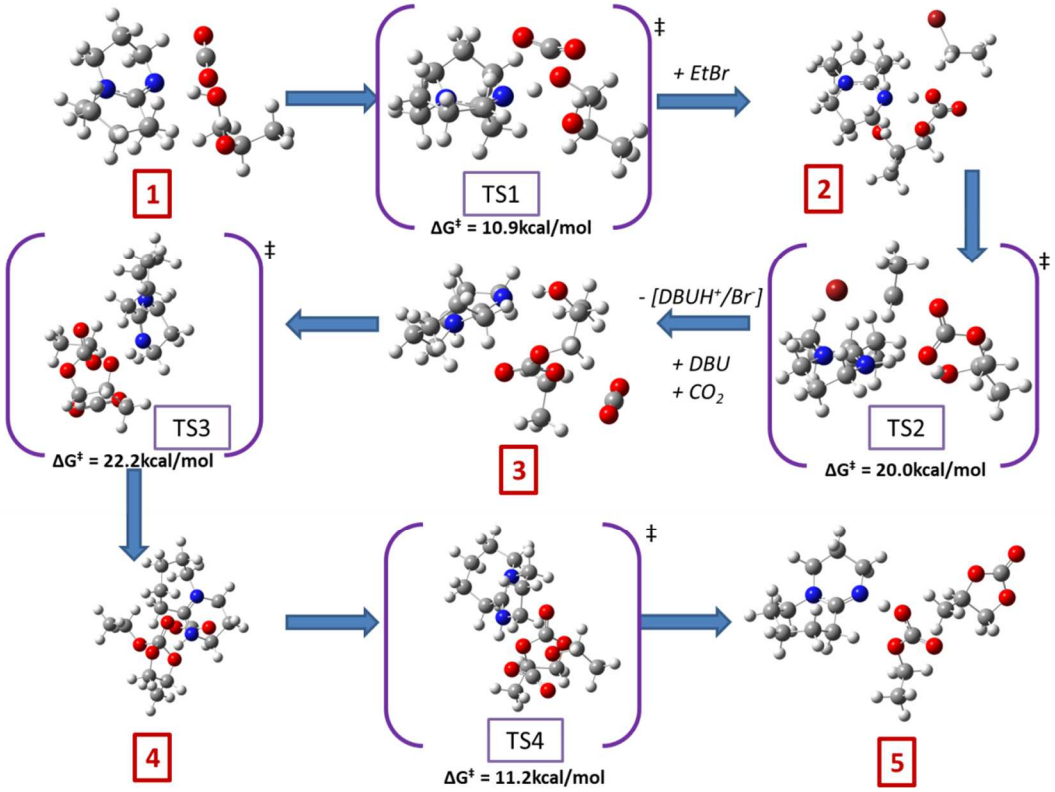
Hexahydro-,(3aR,7aR)-1,3-benzodioxol-2-one : The product was isolated as a white solid, 0.255 g (isolated yield 60 %). ^{1}H NMR (400 MHz, CDCl3) δ (ppm): 3.98-4.05 (m, 2 H), 2.23-2.30 (m, 2 H), 1.88-1.98 (m, 2 H), 1.63-1.73 (m, 2 H), 1.37-1.44 (m, 2 H).

13C NMR (400 MHz, CDCl3) δ (ppm): 155.0, 83.5, 28.2, 23.2





Optimized structures at the *M062X/6-311g(d,p)* level of the intermediates and transition states for the reaction path of the model reaction with PG, DBU (2eq), EtBr (2eq), CO_2 (2eq) calculated with the (R) primary alcohol



TS1:

0 1	X	Y	Z
C	2.131972	2.698591	0.561076
C	0.782169	1.984667	0.481838
C	0.541781	1.216272	-0.829914
C	3.345475	1.769619	0.505221
C	1.15716	-0.156586	-0.819161
C	3.379772	0.906746	-0.758819
H	2.20289	3.415736	-0.266263
H	0.670566	1.290371	1.320702
H	-0.530051	1.093669	-0.965639
H	4.259698	2.369188	0.542358
H	4.385729	0.517461	-0.926521
C	3.132229	-1.523168	-0.306941
H	3.87726	-1.294355	0.460566

N	2.498979	-0.259608	-0.699927
N	0.362704	-1.181172	-0.875277
H	3.130596	1.509612	-1.636259
H	3.358062	1.108922	1.379163
H	2.173047	3.283835	1.483312
H	-0.020046	2.719926	0.574655
H	0.918097	1.790429	-1.683401
H	3.659529	-1.947433	-1.169278
C	2.097072	-2.495229	0.231218
H	2.542476	-3.484619	0.344494
C	0.916804	-2.521114	-0.730691
H	1.225831	-2.904408	-1.710414
H	0.116935	-3.160955	-0.355121
H	1.733431	-2.155891	1.203923
C	-3.077203	-0.884805	-0.325922
C	-3.119033	0.477034	-1.013414
O	-2.616829	1.497644	-0.165286
H	-2.820106	1.260354	0.749464
O	-1.822015	-1.183555	0.236565
H	-0.854198	-1.106923	-0.408683
C	-1.454922	-0.578585	1.862149
O	-2.436452	-0.035301	2.262553
O	-0.327381	-0.898716	2.049309
H	-3.352522	-1.667483	-1.041387
H	-3.810681	-0.89677	0.487984
C	-4.530072	0.803158	-1.48287
H	-4.544155	1.785059	-1.956278
H	-4.893028	0.061776	-2.199415
H	-5.212556	0.825563	-0.62911
H	-2.446406	0.452219	-1.880181

TS2:

0 1	X	Y	Z
C	-1.191798	-3.372695	-1.77191
C	-0.044413	-2.732394	-0.992781
C	-0.223771	-1.22361	-0.756683
C	-2.547553	-3.30416	-1.069561
C	-1.093386	-0.891681	0.420131
C	-2.997998	-1.883584	-0.728372
H	-1.274761	-2.873759	-2.744455
H	0.095199	-3.234067	-0.029666
H	0.750408	-0.767309	-0.59035
H	-3.306682	-3.749059	-1.718749
H	-4.065809	-1.875245	-0.510709
C	-3.235212	-0.941706	1.567959

H	-3.940383	-1.760491	1.721915
N	-2.345186	-1.329502	0.467637
N	-0.553778	-0.205981	1.404724
H	-2.847194	-1.193071	-1.563889
H	-2.52956	-3.894883	-0.147544
H	-0.948403	-4.418088	-1.977661
H	0.891805	-2.86323	-1.537757
H	-0.66589	-0.739169	-1.635065
H	-3.785707	-0.048606	1.253362
C	-2.444847	-0.671267	2.83811
H	-3.109522	-0.261544	3.599
C	-1.326004	0.309269	2.526558
H	-1.738328	1.284739	2.247606
H	-0.649721	0.4329	3.371897
H	-2.021177	-1.603476	3.220157
C	4.570644	0.245832	0.498269
H	4.284749	0.085738	1.542232
H	5.620421	0.536557	0.454507
C	4.371512	-1.037392	-0.302589
O	3.868629	1.365384	-0.043208
H	0.409249	0.145826	1.266274
O	3.104534	-1.636201	-0.063259
H	2.591566	-0.999923	0.456793
C	2.55058	1.505023	0.234454
O	2.031733	2.523689	-0.261793
O	1.984931	0.624136	0.930069
C	-0.063206	3.806582	-1.169093
H	-0.413953	3.696377	-2.193163
H	0.929264	4.257975	-1.172603
H	-0.75487	4.452823	-0.632352
C	0.02985	2.470683	-0.498742
H	0.201953	1.573898	-1.067401
H	-0.070264	2.380349	0.569241
Br	-2.39103	1.871764	-0.682047
H	4.443627	-0.771081	-1.364781
C	5.45089	-2.05147	0.046046
H	5.239966	-2.991326	-0.4646
H	6.44115	-1.702178	-0.254328
H	5.451302	-2.244691	1.121983

TS3:

0 1	X	Y	Z
C	-1.191798	-3.372695	-1.77191
C	-0.044413	-2.732394	-0.992781
C	-0.223771	-1.22361	-0.756683

C	-2.547553	-3.30416	-1.069561
C	-1.093386	-0.891681	0.420131
C	-2.997998	-1.883584	-0.728372
H	-1.274761	-2.873759	-2.744455
H	0.095199	-3.234067	-0.029666
H	0.750408	-0.767309	-0.59035
H	-3.306682	-3.749059	-1.718749
H	-4.065809	-1.875245	-0.510709
C	-3.235212	-0.941706	1.567959
H	-3.940383	-1.760491	1.721915
N	-2.345186	-1.329502	0.467637
N	-0.553778	-0.205981	1.404724
H	-2.847194	-1.193071	-1.563889
H	-2.52956	-3.894883	-0.147544
H	-0.948403	-4.418088	-1.977661
H	0.891805	-2.86323	-1.537757
H	-0.66589	-0.739169	-1.635065
H	-3.785707	-0.048606	1.253362
C	-2.444847	-0.671267	2.83811
H	-3.109522	-0.261544	3.599
C	-1.326004	0.309269	2.526558
H	-1.738328	1.284739	2.247606
H	-0.649721	0.4329	3.371897
H	-2.021177	-1.603476	3.220157
C	4.570644	0.245832	0.498269
H	4.284749	0.085738	1.542232
H	5.620421	0.536557	0.454507
C	4.371512	-1.037392	-0.302589
O	3.868629	1.365384	-0.043208
H	0.409249	0.145826	1.266274
O	3.104534	-1.636201	-0.063259
H	2.591566	-0.999923	0.456793
C	2.55058	1.505023	0.234454
O	2.031733	2.523689	-0.261793
O	1.984931	0.624136	0.930069
C	-0.063206	3.806582	-1.169093
H	-0.413953	3.696377	-2.193163
H	0.929264	4.257975	-1.172603
H	-0.75487	4.452823	-0.632352
C	0.02985	2.470683	-0.498742
H	0.201953	1.573898	-1.067401
H	-0.070264	2.380349	0.569241
Br	-2.39103	1.871764	-0.682047
H	4.443627	-0.771081	-1.364781
C	5.45089	-2.05147	0.046046
H	5.239966	-2.991326	-0.4646

H	6.44115	-1.702178	-0.254328
H	5.451302	-2.244691	1.121983

TS4:

0 1	X	Y	Z
C	-1.191798	-3.372695	-1.77191
C	-0.044413	-2.732394	-0.992781
C	-0.223771	-1.22361	-0.756683
C	-2.547553	-3.30416	-1.069561
C	-1.093386	-0.891681	0.420131
C	-2.997998	-1.883584	-0.728372
H	-1.274761	-2.873759	-2.744455
H	0.095199	-3.234067	-0.029666
H	0.750408	-0.767309	-0.59035
H	-3.306682	-3.749059	-1.718749
H	-4.065809	-1.875245	-0.510709
C	-3.235212	-0.941706	1.567959
H	-3.940383	-1.760491	1.721915
N	-2.345186	-1.329502	0.467637
N	-0.553778	-0.205981	1.404724
H	-2.847194	-1.193071	-1.563889
H	-2.52956	-3.894883	-0.147544
H	-0.948403	-4.418088	-1.977661
H	0.891805	-2.86323	-1.537757
H	-0.66589	-0.739169	-1.635065
H	-3.785707	-0.048606	1.253362
C	-2.444847	-0.671267	2.83811
H	-3.109522	-0.261544	3.599
C	-1.326004	0.309269	2.526558
H	-1.738328	1.284739	2.247606
H	-0.649721	0.4329	3.371897
H	-2.021177	-1.603476	3.220157
C	4.570644	0.245832	0.498269
H	4.284749	0.085738	1.542232
H	5.620421	0.536557	0.454507
C	4.371512	-1.037392	-0.302589
O	3.868629	1.365384	-0.043208
H	0.409249	0.145826	1.266274
O	3.104534	-1.636201	-0.063259
H	2.591566	-0.999923	0.456793
C	2.55058	1.505023	0.234454
O	2.031733	2.523689	-0.261793
O	1.984931	0.624136	0.930069
C	-0.063206	3.806582	-1.169093

H	-0.413953	3.696377	-2.193163
H	0.929264	4.257975	-1.172603
H	-0.75487	4.452823	-0.632352
C	0.02985	2.470683	-0.498742
H	0.201953	1.573898	-1.067401
H	-0.070264	2.380349	0.569241
Br	-2.39103	1.871764	-0.682047
H	4.443627	-0.771081	-1.364781
C	5.45089	-2.05147	0.046046
H	5.239966	-2.991326	-0.4646
H	6.44115	-1.702178	-0.254328
H	5.451302	-2.244691	1.121983

XYZ coordinates of the optimized structures at the *M062X/6-311g(d,p)* level of the transition states for comparison between biscarbonation or alkylation

- Propylene glycol as substrate

TS ALKYLATION

0 1	X	Y	Z
C	-1.191798	-3.372695	-1.77191
C	-0.044413	-2.732394	-0.992781
C	-0.223771	-1.22361	-0.756683
C	-2.547553	-3.30416	-1.069561
C	-1.093386	-0.891681	0.420131
C	-2.997998	-1.883584	-0.728372
H	-1.274761	-2.873759	-2.744455
H	0.095199	-3.234067	-0.029666
H	0.750408	-0.767309	-0.59035
H	-3.306682	-3.749059	-1.718749
H	-4.065809	-1.875245	-0.510709
C	-3.235212	-0.941706	1.567959
H	-3.940383	-1.760491	1.721915
N	-2.345186	-1.329502	0.467637
N	-0.553778	-0.205981	1.404724
H	-2.847194	-1.193071	-1.563889
H	-2.52956	-3.894883	-0.147544
H	-0.948403	-4.418088	-1.977661
H	0.891805	-2.86323	-1.537757
H	-0.66589	-0.739169	-1.635065

H	-3.785707	-0.048606	1.253362
C	-2.444847	-0.671267	2.83811
H	-3.109522	-0.261544	3.599
C	-1.326004	0.309269	2.526558
H	-1.738328	1.284739	2.247606
H	-0.649721	0.4329	3.371897
H	-2.021177	-1.603476	3.220157
C	4.570644	0.245832	0.498269
H	4.284749	0.085738	1.542232
H	5.620421	0.536557	0.454507
C	4.371512	-1.037392	-0.302589
O	3.868629	1.365384	-0.043208
H	0.409249	0.145826	1.266274
O	3.104534	-1.636201	-0.063259
H	2.591566	-0.999923	0.456793
C	2.55058	1.505023	0.234454
O	2.031733	2.523689	-0.261793
O	1.984931	0.624136	0.930069
C	-0.063206	3.806582	-1.169093
H	-0.413953	3.696377	-2.193163
H	0.929264	4.257975	-1.172603
H	-0.75487	4.452823	-0.632352
C	0.02985	2.470683	-0.498742
H	0.201953	1.573898	-1.067401
H	-0.070264	2.380349	0.569241
Br	-2.39103	1.871764	-0.682047
H	4.443627	-0.771081	-1.364781
C	5.45089	-2.05147	0.046046
H	5.239966	-2.991326	-0.4646
H	6.44115	-1.702178	-0.254328
H	5.451302	-2.244691	1.121983

TS BISCARBONATION

0 1	X	Y	Z
C	5.896744	1.359414	-1.903946
C	5.024955	2.004856	-0.829043
C	3.688607	1.284353	-0.597751
C	6.358428	-0.053251	-1.557666
C	3.760553	0.08221	0.294017
C	5.215029	-1.028819	-1.290168
H	5.328612	1.32664	-2.840262
H	5.577257	2.075755	0.113981
H	2.958881	1.970261	-0.166499
H	6.944597	-0.449664	-2.391289
H	5.591697	-2.049927	-1.340484

C	4.495979	-2.165692	0.78889
H	5.480564	-2.635499	0.790064
N	4.614807	-0.899063	0.050304
N	2.964974	0.062173	1.351386
H	4.407006	-0.95379	-2.024184
H	7.01813	-0.035031	-0.683815
H	6.770471	1.990207	-2.086803
H	4.794102	3.02824	-1.131903
H	3.238466	0.929614	-1.531684
H	3.785867	-2.78449	0.230736
C	4.01142	-1.930887	2.208776
H	3.839216	-2.891332	2.695156
C	2.721877	-1.130748	2.163204
H	1.909698	-1.705114	1.704843
H	2.417671	-0.801266	3.156752
H	4.76878	-1.388223	2.780524
C	-5.298428	0.529742	-2.402024
C	-4.171841	1.11781	-1.55056
C	-4.371047	0.965437	-0.031171
C	-5.496946	-0.978921	-2.250731
C	-3.929269	-0.385877	0.463336
C	-5.772205	-1.406317	-0.807146
H	-6.235879	1.033186	-2.135955
H	-3.212075	0.670785	-1.833
H	-3.794358	1.71619	0.509356
H	-6.340402	-1.291637	-2.873106
H	-6.220196	-2.400978	-0.785455
C	-4.018381	-2.828531	0.248242
H	-4.154602	-3.400846	-0.673422
N	-4.567612	-1.486535	0.018716
N	-2.907218	-0.430579	1.262175
H	-6.494646	-0.729949	-0.341934
H	-4.614337	-1.519004	-2.610851
H	-5.109661	0.761246	-3.453531
H	-4.089372	2.184864	-1.769565
H	-5.421059	1.132234	0.229858
H	-4.597547	-3.322226	1.037384
C	-2.545644	-2.754172	0.611999
H	-2.196297	-3.730297	0.95088
C	-2.346352	-1.706251	1.694993
H	-2.821613	-2.009813	2.634696
H	-1.280509	-1.557714	1.865918
H	-1.935412	-2.46759	-0.247162
C	-0.19774	1.13551	0.964638
H	0.177181	0.248929	1.493437
H	0.514016	1.967457	1.082967

C	-0.322104	0.791649	-0.52256
H	-1.119333	0.050039	-0.631825
C	-0.622878	2.023628	-1.355642
H	0.180004	2.757701	-1.253214
H	-0.724534	1.755042	-2.409
H	-1.549601	2.491378	-1.015065
O	-1.424447	1.527791	1.509109
H	-2.253652	0.57373	1.441913
O	0.896338	0.233458	-0.995253
H	2.289821	0.812114	1.409946
C	1.143527	-1.128694	-0.69968
C	-1.764537	3.272339	1.650742
O	2.229516	-1.516098	-1.152518
O	0.300543	-1.718982	-0.009215
O	-2.936498	3.327547	1.842114
O	-0.730463	3.835544	1.503142

- Ethylene glycol as substrate

TS ALKYLATION

0 1	X	Y	Z
C	-1.69809	-3.190549	-1.743564
C	-0.439784	-2.811879	-0.964656
C	-0.280289	-1.298278	-0.744921
C	-3.006964	-2.814481	-1.049823
C	-1.058394	-0.76918	0.423807
C	-3.131658	-1.325515	-0.726048
H	-1.66494	-2.697384	-2.722013
H	-0.418232	-3.320969	0.004435
H	0.770118	-1.067675	-0.576675
H	-3.843979	-3.087187	-1.698434
H	-4.171679	-1.077793	-0.514762
C	-3.16146	-0.327583	1.558696
H	-4.03311	-0.965497	1.715637
N	-2.376278	-0.916906	0.468131
N	-0.382915	-0.211116	1.405368
H	-2.828317	-0.695355	-1.567777
H	-3.123437	-3.38362	-0.12142
H	-1.692106	-4.266295	-1.936313
H	0.445795	-3.154044	-1.502497
H	-0.600402	-0.736965	-1.63039
H	-3.49586	0.662829	1.231718
C	-2.336171	-0.228312	2.83149
H	-2.895317	0.327613	3.584441
C	-1.024589	0.473485	2.518979

H	-1.20665	1.514258	2.230852
H	-0.341325	0.449447	3.367433
H	-2.134083	-1.227885	3.224542
C	4.717277	-0.902138	0.504683
H	4.428592	-0.995488	1.554981
H	5.804386	-0.865654	0.434121
C	4.203295	-2.087375	-0.299111
O	4.291155	0.360101	-0.013711
H	0.634177	-0.081899	1.26704
O	2.867351	-2.453586	-0.006299
H	2.493896	-1.713749	0.494351
C	3.030718	0.77638	0.252013
O	2.751229	1.89307	-0.225873
O	2.276988	0.02456	0.920124
C	0.992474	3.586829	-1.172658
H	0.639607	3.545694	-2.201109
H	2.058712	3.814488	-1.164049
H	0.448798	4.371125	-0.649757
C	0.787426	2.267981	-0.493504
H	0.769295	1.349993	-1.054127
H	0.657004	2.210798	0.57347
Br	-1.702824	2.202563	-0.707916
H	4.308537	-1.845174	-1.363375
H	4.847171	-2.946622	-0.083987

TS BISCARBONATION

0 1	X	Y	Z
C	-5.89962	1.565235	1.828121
C	-4.987354	2.151637	0.753075
C	-3.670255	1.383194	0.569735
C	-6.399029	0.158017	1.513298
C	-3.76419	0.15907	-0.289447
C	-5.282406	-0.860236	1.296546
H	-5.350967	1.542434	2.776251
H	-5.51895	2.212201	-0.202523
H	-2.910536	2.03359	0.135699
H	-7.012988	-0.195485	2.346221
H	-5.692209	-1.86719	1.368234
C	-4.557025	-2.078599	-0.734465
H	-5.553168	-2.523216	-0.73605
N	-4.653113	-0.788082	-0.035046
N	-2.950746	0.084414	-1.330935
H	-4.486269	-0.789058	2.043839
H	-7.041331	0.171224	0.626473
H	-6.756449	2.227811	1.975169

H	-4.729643	3.175613	1.031111
H	-3.251629	1.041102	1.522792
H	-3.870766	-2.69878	-0.148428
C	-4.04802	-1.896919	-2.153653
H	-3.897914	-2.874735	-2.611931
C	-2.735873	-1.134211	-2.112305
H	-1.946102	-1.72097	-1.631426
H	-2.412124	-0.837302	-3.110018
H	-4.78248	-1.34842	-2.749249
C	5.534567	0.860639	2.113606
C	4.437112	1.401058	1.194898
C	4.581097	0.972617	-0.275051
C	5.626539	-0.665671	2.183659
C	4.016003	-0.397929	-0.521109
C	5.850779	-1.327408	0.820127
H	6.499722	1.249802	1.766906
H	3.449219	1.096943	1.558459
H	4.048907	1.672277	-0.917073
H	6.455562	-0.939968	2.842479
H	6.241467	-2.337636	0.949945
C	3.988849	-2.789195	0.040375
H	4.150357	-3.225239	1.029834
N	4.625117	-1.464839	0.032199
N	2.92904	-0.480428	-1.228644
H	6.600917	-0.775904	0.2472
H	4.715088	-1.083915	2.625326
H	5.386314	1.254483	3.122459
H	4.453101	2.492714	1.222633
H	5.633465	0.999004	-0.574566
H	4.491586	-3.429864	-0.693085
C	2.502833	-2.680091	-0.25252
H	2.082061	-3.668838	-0.438126
C	2.287743	-1.773272	-1.453359
H	2.699556	-2.222579	-2.364287
H	1.22054	-1.606231	-1.588267
H	1.960408	-2.25549	0.594402
C	0.233754	1.08772	-0.948069
H	-0.10212	0.198834	-1.499087
H	-0.492166	1.901006	-1.088468
C	0.31726	0.748253	0.537897
H	1.113308	0.015579	0.695569
O	1.473385	1.513757	-1.441167
H	2.287241	0.536541	-1.411508
O	-0.912688	0.261721	1.040605
H	-2.248737	0.808844	-1.393862
C	-1.215557	-1.095671	0.780311

C	1.802656	3.275844	-1.267954
O	-2.312887	-1.429815	1.24692
O	-0.398971	-1.732947	0.100054
O	2.954461	3.39591	-1.532914
O	0.777736	3.774934	-0.94126
H	0.54816	1.660396	1.093749

- 1,3-propanediol as substrate

TS ALKYLATION

0 1	X	Y	Z
C	-2.54722	-3.465127	-1.273719
C	-1.023686	-3.3707	-1.379176
C	-0.486416	-1.928639	-1.38996
C	-3.144041	-2.862643	-0.000718
C	-0.38421	-1.355706	-0.006558
C	-2.81679	-1.381868	0.185226
H	-2.986321	-2.95432	-2.138305
H	-0.55076	-3.931008	-0.5653
H	0.503015	-1.86942	-1.843063
H	-4.23156	-2.963445	-0.039561
H	-3.49543	-0.898892	0.885548
C	-1.385939	-0.687497	2.12103
H	-2.167506	-1.211502	2.674332
N	-1.462671	-1.16054	0.725058
N	0.829905	-1.126188	0.475905
H	-2.92497	-0.826463	-0.748988
H	-2.805504	-3.415996	0.88242
H	-2.844372	-4.514106	-1.348266
H	-0.707779	-3.847672	-2.309175
H	-1.119648	-1.274917	-1.994284
H	-1.628506	0.379113	2.122344
C	-0.021621	-0.97525	2.72438
H	0.062774	-0.461487	3.681932
C	1.066238	-0.502301	1.775081
H	1.062051	0.586725	1.657972
H	2.055012	-0.807607	2.116698
H	0.096538	-2.047505	2.901638
C	3.849702	0.280894	-1.332413
H	4.077968	1.334671	-1.505519
O	2.490714	0.02731	-1.687138
H	1.588291	-1.143191	-0.200152
C	1.570481	1.015795	-1.320401
O	0.446325	0.804947	-1.855489
O	1.906346	1.881743	-0.528411

C	4.143258	-0.083953	0.114564
C	5.613775	0.081397	0.471755
H	3.86271	-1.12719	0.304287
H	3.539986	0.564954	0.755792
H	6.227798	-0.598528	-0.122805
H	5.941255	1.104382	0.246682
H	4.443515	-0.330616	-2.01473
O	5.86618	-0.249297	1.825287
H	5.445009	0.418877	2.370962
C	-1.022346	1.744117	-0.890129
C	-0.883765	3.125617	-1.455703
H	-1.653088	1.01816	-1.370848
H	-0.516193	1.48484	0.023496
H	-1.822644	3.445173	-1.903924
H	-0.605768	3.827398	-0.672419
H	-0.102773	3.115998	-2.216065
Br	-3.004423	2.155092	0.567686

TS BISCARBONATION

0 1	X	Y	Z
C	4.490922	-2.074216	1.331298
C	3.512593	-0.924629	1.573395
C	3.594576	0.216584	0.542402
C	4.273414	-2.820393	0.016395
C	2.830198	-0.055889	-0.727286
C	4.385177	-1.906821	-1.204854
H	5.515431	-1.682209	1.346711
H	2.486914	-1.30392	1.60929
H	3.184355	1.13592	0.959927
H	5.02013	-3.614247	-0.074175
H	4.56304	-2.497594	-2.104617
C	2.340666	-1.602796	-2.579702
H	2.261295	-2.689529	-2.483212
N	3.178797	-1.122425	-1.473016
N	1.858522	0.743894	-1.048569
H	5.24398	-1.237127	-1.09986
H	3.288302	-3.299052	0.008
H	4.415381	-2.780495	2.161713
H	3.725575	-0.495772	2.5559
H	4.64025	0.428086	0.293354
H	2.850555	-1.385899	-3.52507
C	0.966636	-0.95742	-2.54512
H	0.456271	-1.138595	-3.492464
C	1.136002	0.533576	-2.300198
H	1.693193	1.011572	-3.112821

H	0.187279	1.058025	-2.228472
H	0.354297	-1.391341	-1.749313
C	0.728443	0.794553	2.49328
H	0.923729	0.48704	1.468263
C	0.752578	4.00457	-0.968499
O	0.642177	3.424527	-2.003133
O	0.779668	5.02789	-0.375768
C	0.311314	2.253006	2.51095
C	1.200279	3.054092	1.562388
H	0.354368	2.659547	3.524769
H	-0.719794	2.337783	2.1579
H	0.988509	4.122017	1.655529
H	2.259832	2.917351	1.834445
H	1.634529	0.638578	3.086749
O	0.968336	2.678826	0.227958
H	1.502029	1.671284	-0.364586
C	-3.480345	2.212756	-0.762782
C	-2.21569	1.455364	-1.164163
C	-1.752482	0.40402	-0.143624
C	-4.724844	1.339838	-0.621583
C	-2.443599	-0.938019	-0.24223
C	-4.546513	0.195967	0.376927
H	-3.291384	2.715241	0.193659
H	-2.356991	0.975091	-2.139947
H	-0.685533	0.220527	-0.268719
H	-5.562236	1.960648	-0.28937
H	-5.523544	-0.194166	0.666383
C	-4.548802	-2.193702	-0.27753
H	-5.481616	-1.971704	-0.804024
N	-3.797119	-0.946771	-0.150407
N	-1.697787	-1.986371	-0.415469
H	-4.072944	0.553771	1.296944
H	-5.004807	0.912521	-1.590659
H	-3.670325	3.002267	-1.494273
H	-1.404682	2.178328	-1.279178
H	-1.883209	0.79722	0.872294
H	-4.804738	-2.567113	0.721463
C	-3.733799	-3.226775	-1.034437
H	-4.234164	-4.195934	-0.994579
C	-2.346671	-3.291641	-0.411035
H	-2.419362	-3.642255	0.62668
H	-1.708949	-3.992751	-0.952953
H	-3.645962	-2.931482	-2.083831
O	-0.30834	-0.028354	3.04585
H	-0.506469	-1.864046	0.642088
C	-0.750146	-1.094726	2.361228

O	-1.818673	-1.584318	2.611586
O	0.080724	-1.517279	1.41238

➢ 1,4-butanediol as substrate

TS ALKYLATION

0 1	X	Y	Z
C	-4.58571300	-2.17616200	-1.52771300
C	-3.21198100	-2.59302500	-1.00423400
C	-2.22412300	-1.42871100	-0.82044500
C	-5.36229800	-1.25251100	-0.59174600
C	-2.40092900	-0.66653000	0.46144300
C	-4.62069700	0.04040900	-0.25671500
H	-4.45348900	-1.66976700	-2.49080000
H	-3.31365000	-3.13481600	-0.05818200
H	-1.19975500	-1.80330800	-0.82616500
H	-6.31073300	-0.98363500	-1.06482000
H	-5.31741000	0.77352000	0.14956500
C	-3.73075100	0.69344400	1.97424400
H	-4.76020400	0.57753200	2.31862500
N	-3.57679600	-0.12411600	0.76568500
N	-1.36718600	-0.60246700	1.26718600
H	-4.17458500	0.49724000	-1.14561000
H	-5.60531900	-1.77054100	0.34199000
H	-5.18119500	-3.07136700	-1.72446900
H	-2.76376100	-3.29168500	-1.71351200
H	-2.31518000	-0.70590800	-1.64024100
H	-3.56321200	1.73953600	1.69530800
C	-2.75280400	0.25897100	3.05383800
H	-2.79938100	0.95800500	3.88929100
C	-1.35213500	0.22447900	2.46423100

H	-1.03134600	1.23544400	2.18966700
H	-0.62955500	-0.20299100	3.15892500
H	-3.02013500	-0.73413400	3.42362300
C	4.20654200	-1.62565300	-0.69044800
H	4.04714100	-1.03695300	-1.59605200
O	2.95360500	-2.07676000	-0.17877800
H	-0.46439800	-1.01184900	0.92374200
C	1.92378700	-1.19539400	-0.16234300
O	0.85515100	-1.64749100	0.28231100
O	2.14501600	-0.03456500	-0.59961300
C	4.98265100	-0.81933500	0.33798100
C	6.35911200	-0.42193300	-0.18663300
H	5.08216500	-1.42021700	1.24797400
H	4.40159200	0.07217900	0.58861300
C	7.15055000	0.38118000	0.82618600
H	6.94151100	-1.31099000	-0.44904600
H	6.26111300	0.17707300	-1.09732000
H	6.59552000	1.29306400	1.08469600
H	7.27745300	-0.20867000	1.74426700
H	4.74749600	-2.53822000	-0.94711100
C	1.22158900	2.22081900	-1.57818200
H	2.25860800	1.91393300	-1.71560200
H	1.19252800	3.18288500	-1.07043500
H	0.74422700	2.32872100	-2.55020200
C	0.52148200	1.17594000	-0.76303600
H	0.52801900	1.21844400	0.31199700
H	0.02969300	0.33926500	-1.22816500
Br	-1.68918100	2.28798900	-0.68785000
O	8.40488600	0.69501800	0.24579400
H	8.91048400	1.20913400	0.87782800

TS BISCARBONATION

0 1	X	Y	Z
C	7.06411800	1.05617700	-1.74019600
C	5.87277100	1.84333100	-1.19916300
C	4.62293400	0.98532400	-0.95197000
C	7.59333000	-0.00136800	-0.77579600
C	4.61582900	0.23487000	0.34557200
C	6.55048000	-1.03584900	-0.35991900
H	6.76324400	0.56600200	-2.67270900
H	6.15223700	2.36791200	-0.27923400
H	3.72876200	1.60838400	-0.97537300
H	8.41832900	-0.53620600	-1.25429900
H	7.05221600	-1.90037300	0.07335100
C	5.44481100	-1.48622400	1.81280100
H	6.43953600	-1.75359000	2.17098000
N	5.61763000	-0.56354800	0.68019900
N	3.58994500	0.43816700	1.15767100
H	5.95236600	-1.40384900	-1.19916900
H	7.99938800	0.47262300	0.12396400
H	7.86996500	1.74998100	-1.99337700
H	5.60131300	2.61210800	-1.92569800
H	4.47415900	0.22784700	-1.72966000
H	4.93721300	-2.37238200	1.41618000
C	4.63090400	-0.83996500	2.92000600
H	4.45430500	-1.56767000	3.71241100
C	3.30640700	-0.36899400	2.34707500
H	2.67480400	-1.21054700	2.04483600
H	2.76681200	0.26118500	3.05480200
H	5.18213800	0.00302000	3.34529200
C	0.75789300	-0.31003800	-1.39971100
H	0.13211300	-1.19672200	-1.26789900

O	2.12002600	-0.68491500	-1.46009200
H	2.82607200	0.97453200	0.77032900
C	2.53254900	-1.70057200	-0.55536600
O	3.72828100	-1.99631500	-0.70420900
O	1.69497200	-2.09114900	0.26227900
C	0.46866500	0.67212100	-0.27030500
C	-0.99939000	1.07615400	-0.22955200
H	1.08616800	1.57163100	-0.40543400
H	0.74297000	0.18350800	0.67108800
C	-1.33779400	2.00165000	0.93248500
H	-1.27712500	1.58588900	-1.15982800
H	-1.61611300	0.17289300	-0.14946900
H	-1.08906600	1.51855600	1.88594200
H	-0.76555700	2.92981200	0.85353600
H	0.52594900	0.15301400	-2.36318200
C	-4.58023900	-1.82541000	-2.71471400
C	-3.64647200	-0.85456500	-1.99024100
C	-4.36473700	0.29274100	-1.25754600
C	-5.54758400	-2.57878300	-1.80132800
C	-4.85217400	-0.11035900	0.10652400
C	-6.43936500	-1.65163700	-0.97322500
H	-5.16328000	-1.26423100	-3.45461000
H	-3.01630200	-1.40194500	-1.28068800
H	-3.70137400	1.14140900	-1.11650300
H	-6.18968600	-3.21894900	-2.41287700
H	-7.30527100	-2.19770400	-0.59615600
C	-6.14069400	-1.66883900	1.49969000
H	-6.23766900	-2.74919700	1.36370900
N	-5.77276500	-1.08897600	0.20421900
N	-4.32520000	0.46968000	1.14233600
H	-6.82938600	-0.84148800	-1.59526200

H	-4.99682800	-3.23586500	-1.11923000
H	-3.98076100	-2.54810100	-3.27376000
H	-2.96681000	-0.40896600	-2.72042000
H	-5.20563400	0.66731300	-1.84908900
H	-7.11892900	-1.28028500	1.80430000
C	-5.08747400	-1.35965400	2.55196800
H	-5.46005800	-1.63885700	3.53820100
C	-4.75067600	0.12300000	2.48828900
H	-5.62100100	0.72916800	2.76237900
H	-3.94072500	0.38269000	3.17061300
H	-4.18368700	-1.94079300	2.35150400
O	-2.70822200	2.33373500	0.94470500
H	-3.54587200	1.36910000	1.01629900
C	-3.19928900	3.50911200	-0.12635500
O	-4.38325800	3.35811800	-0.26722800
O	-2.25492700	4.15784300	-0.47306700

- 1,5-pentanediol as substrate

TS ALKYLATION

0 1	X	Y	Z
C	-5.085124	-2.134001	-1.262159
C	-3.709531	-2.573967	-0.762948
C	-2.667874	-1.444367	-0.69886
C	-5.784564	-1.115602	-0.364469
C	-2.761204	-0.591072	0.53353
C	-4.977022	0.163001	-0.148153
H	-4.971303	-1.700801	-2.262587
H	-3.79482	-3.044603	0.221964
H	-1.660596	-1.862304	-0.718189
H	-6.739311	-0.837932	-0.819393
H	-5.625467	0.952128	0.232228
C	-3.972015	0.923676	1.998362
H	-4.991157	0.87707	2.38684
N	-3.900196	0.021945	0.843192
N	-1.694652	-0.519821	1.294946
H	-4.548946	0.538367	-1.082812

H	-6.011022	-1.557714	0.611497
H	-5.724259	-3.013677	-1.373345
H	-3.319979	-3.338737	-1.437833
H	-2.763406	-0.775243	-1.562484
H	-3.77121	1.940331	1.643042
C	-2.971856	0.517955	3.068763
H	-2.956026	1.271895	3.856223
C	-1.597956	0.382236	2.432574
H	-1.24591	1.357876	2.079666
H	-0.867539	-0.030666	3.127867
H	-3.266276	-0.435603	3.514285
C	3.769637	-1.88155	-0.750687
H	3.613243	-1.333546	-1.682234
O	2.511489	-2.256473	-0.192914
H	-0.824596	-0.9895	0.946454
C	1.516434	-1.335573	-0.203798
O	0.442968	-1.718776	0.29015
O	1.770941	-0.211038	-0.712753
C	4.597512	-1.056102	0.220574
C	5.972616	-0.721116	-0.351503
H	4.706606	-1.617023	1.154326
H	4.053468	-0.135323	0.446815
C	6.831202	0.09034	0.615089
H	6.49908	-1.648051	-0.609313
H	5.850486	-0.162905	-1.287413
C	8.194504	0.441189	0.037371
H	6.303835	1.016217	0.878153
H	6.981168	-0.464711	1.546286
H	8.740167	-0.471833	-0.211506
H	8.06943	1.012889	-0.892642
H	4.269061	-2.826858	-0.971339
O	9.011494	1.140854	0.958053
H	8.55285	1.949655	1.197002
C	0.899475	2.008577	-1.8121
H	1.919035	1.652822	-1.96168
H	0.923402	3.002432	-1.369486
H	0.393061	2.070971	-2.773347
C	0.189712	1.047863	-0.90655
H	0.234395	1.1615	0.162351
H	-0.350065	0.203225	-1.298211
Br	-1.973494	2.250266	-0.836248

TS BISCARBONATION

0 1	X	Y	Z
C	-7.496279	-0.475588	2.481507
C	-5.976871	-0.479424	2.633625
C	-5.220532	-0.639482	1.306433
C	-8.031134	0.702109	1.672015
C	-5.058029	0.621541	0.512425
C	-7.458521	0.791626	0.259718
H	-7.799708	-1.408031	1.992803
H	-5.645683	0.431549	3.143593
H	-4.224003	-1.041743	1.489521
H	-9.117009	0.607889	1.584299
H	-8.082813	1.451629	-0.341573
C	-5.938996	2.431194	-0.809854
H	-6.741806	3.153411	-0.657579
N	-6.103481	1.371157	0.196808
N	-3.826034	0.9744	0.180559
H	-7.429676	-0.173631	-0.255314
H	-7.833317	1.64423	2.193999
H	-7.957946	-0.47288	3.472394
H	-5.690897	-1.316397	3.274229
H	-5.706401	-1.351926	0.630255
H	-6.046768	1.948996	-1.787709
C	-4.581957	3.099495	-0.677364
H	-4.45706	3.828493	-1.478421
C	-3.500289	2.038803	-0.77235
H	-3.454789	1.595046	-1.771954
H	-2.522847	2.438826	-0.500921
H	-4.516512	3.625893	0.278746
C	5.736753	3.353137	0.469447
C	4.666358	2.271695	0.311318
C	4.824504	1.402133	-0.949634
C	7.167819	2.829755	0.601623
C	5.817144	0.287343	-0.746241
C	7.602668	1.971067	-0.588741
H	5.692313	4.025746	-0.396471
H	4.639911	1.611264	1.183297
H	3.873915	0.928695	-1.18936
H	7.852304	3.678507	0.688098
H	8.690721	1.900485	-0.633459
C	8.033902	-0.395544	0.042663
H	8.614298	0.105217	0.822249
N	7.108355	0.595597	-0.521543
N	5.358277	-0.928161	-0.744699

H	7.282627	2.429951	-1.52798
H	7.271998	2.236472	1.516657
H	5.498931	3.960754	1.346282
H	3.689728	2.758207	0.256537
H	5.115044	2.014169	-1.809762
H	8.730813	-0.722638	-0.737184
C	7.270829	-1.571926	0.626433
H	7.966173	-2.373498	0.878977
C	6.239914	-2.03345	-0.394892
H	6.730558	-2.415214	-1.297391
H	5.617345	-2.833927	0.008749
H	6.738136	-1.26241	1.528655
C	-2.809138	-2.439547	-1.473536
H	-2.601632	-2.446865	-2.546228
O	-4.113545	-1.944716	-1.235068

References

[1] T.M. McGuire, E.M. López-Vidal, G.L. Gregory, A. Buchard, J. CO2 Util., 27 (2018) 283-288.

Suitable organic dual activating system are proposed to enable the coupling of CO_2 with diols to produce selectively substituted ethylene- or trimethylene carbonate and/or acyclic carbonates, providing a powerful tool to synthesize CO_2-based precursors.