Choline-based eutectic mixtures as catalysts for effective synthesis of cyclic carbonates from epoxides and CO$_2$

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**A R T I C L E   I N F O**

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**A B S T R A C T**

CO$_2$ is a renewable, abundant and cheap C1-feedstock and its conversion to cyclic carbonates starting from epoxides has been widely explored in the last years. Nevertheless, conducting this reaction under mild and sustainable conditions is still a challenging task. Herein we present the use of choline-salt based eutectic mixtures as catalysts for the reaction of CO$_2$ with epoxides to give cyclic carbonates. Choline chloride and choline iodide have been coupled with various hydrogen bond donors (HBDs), mainly cheap and bio-based carboxylic acids and polyols, to form two classes of eutectic mixtures. Very good yields were achieved under mild conditions (80 °C in 7–22 h) for various terminal epoxides, with both classes of catalysts. While a pressure of 0.4 MPa of CO$_2$ is required to obtain appreciable conversions using choline chloride-based mixture, atmospheric pressure of CO$_2$ (balloon) has been successfully used with choline iodide-based mixtures. Furthermore, the catalysts could be recycled without appreciable loss of the catalytic activity. The improved catalytic performance of both choline-based eutectic mixtures is attributed to the synergistic activity of the halide, responsible for the opening of the epoxy-ring, and the HBD that has a role in the stabilization of the alkoxide intermediate.

**1. Introduction**

The possibility to capture and reuse CO$_2$ is a source of inspiration for numerous research studies [1,2]. CO$_2$ is a renewable, abundant and cheap C1-feedstock, but its fixation into chemical products is a challenging task because of its high thermodynamic stability [3]. CO$_2$ conversion to cyclic carbonates starting from epoxides has attracted a lot of attention as an alternative pathway to the use of phosgene [4] and cyanates, and a very large number of catalysts and conditions have been proposed to carry out this reaction [3,5,6]; among them, methods that involve the use of DBU-based organocatalysts, [7,8] organometallic catalysts, [9–13] alkali metal salts, [10] metaloxides [14] and phosphonium salts [15] have been recently reported. The challenge for this kind of reaction is to develop methods that use CO$_2$ at low pressure and temperature in sustainable solvents or under solventless conditions [16]; several good results have been achieved at room temperature (rt) or with CO$_2$ atmospheric pressure, especially in the field of organocatalysis [17–20], and also using ionic liquid-type catalysts [21–27].

Quaternary ammonium salts are among the most studied organocatalysts for the conversion of CO$_2$ in cyclic carbonates, i.e. tetraethylammonium bromide (TEABr) is industrially used to promote the synthesis of ethylene or propylene carbonate from CO$_2$ and epoxides since 1950s [28,29]. Their use in neat reactions, without any co-catalysts, usually requires high catalyst loading [30,31] or high temperature and CO$_2$ pressure [32–34]. Recently many improvements and insights have been made in this context, above all in terms of reaction conditions, due to the growing attention towards sustainable synthesis [6]; to this purpose, some works describe as beneficial the role of an alcoholic or acid component that can be used as a co-catalyst or included in the aliphatic quaternary ammonium salt [35–42]. In fact, the role of both the hydroxyl group and the hydrogen bonds that can be formed in the stabilization of the intermediate after the epoxy-ring opening, proved to be crucial [43,44]. Choline (2-hydroxy-N,N,N-trimethylethan-1-aminium) is a bio-based and non-toxic compound bearing both the ammonium and the alcoholic moieties. Choline chloride, bromide or iodide have been largely used for the coupling of various terminal epoxides with CO$_2$ [43,45–47]. However, Büttner et al. showed that choline halides are ineffective for the synthesis of cyclic carbonates in solventless conditions (2 h, 90 °C, 1 MPa) and an elongation of the alkyl chains of the ammonium ion is required for reaching good conversions [39]. Amaral et al. obtained good results using Choline Iodide (Chi) when ethanol was used as solvent (6 h, 85 °C, 1 MPa) [45].

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Choline derivatives are able to form strong hydrogen bonds acting as hydrogen bond acceptors (HBAs), in the presence of a great variety of hydrogen bond donors (HBDs) [48]. The mixture of the two components (HDB and HBA) has a lower melting point than the components alone, and constitutes what is commonly called Deep Eutectic Solvent (DES) [49–52]. When the components derive from renewable resources, these solvents are called NaDESs (Natural Deep Eutectic Solvents) and they become particularly attractive in the field of sustainable materials and green media for reactions and extraction processes [53,54].

H-bonds have a crucial role in the stabilization of the reaction intermediate formed in the epoxide-to-carbonate cyclization mechanism, so the presence of HBD could be useful to further improve catalytic efficiency of choline salts. In fact, Wu et al. used a choline chloride-supported catalyst and constitutes what is commonly called Deep Eutectic Solvent (DES) (HDB and HBA) has a lower melting point than the components alone, and DESs [55,56], the aim of the present paper is to exploit the double ability of biobased, non-toxic, recyclable choline-based HBD-HBA pairs to form eutectic mixtures and catalyze under homogeneous conditions the synthesis of cyclic carbonates from epoxides. The carbonation protocols here developed foresee solventless reactions that work in mild conditions of temperature and CO$_2$ pressure, thus combining efficiency and sustainability. To our knowledge this is the first time that all these aspects are combined together. A table comparing recent homogeneous/heterogeneous IL-type or ammonium-based catalysts appeared in the literature for the synthesis of styrene carbonate from CO$_2$ and styrene oxide is reported in the supplementary material (Table S2).

2. Experimental section

2.1. Material

All chemicals and solvents were purchased from Sigma–Aldrich or Alfa Aesar and used without any further purification. Particularly hygroscopic reagents (quaternary ammonium salts, glycerol, ethylene glycol and carboxylic acids) were used after vacuum drying and kept in a desiccator (see supplementary material, Table S1). CO$_2$ with ≥ 99.5% purity was purchased from Siad, Italy.

2.2. Synthesis of Choline Chloride (ChCl)-based DES

Choline Chloride (ChCl) was mixed with various HBDs in the appropriate molar ratios, heated at about 80–90 °C (60 °C when the HBD was a dicarboxylic acid) [57] and magnetically stirred until homogeneous liquids were obtained. DESs were cooled to rt before the use and stored in the fridge.

2.3. Representative procedure for the synthesis of carbonates at 0.4 MPa of CO$_2$ and at 0.1 MPa of CO$_2$ (ballon)

The reaction at 0.4 MPa was conducted in a stainless-steel, self-made, 25 mL autoclave equipped with a heating mantle. The preformed eutectic mixtures, or the two components of the same (5 mol in terms of ChCl respect to the epoxide), were weighed inside a 2 mL vial equipped with a magnetic stirring bar; then the epoxide (1.3 mmol) was added. The air in the reactor was firstly replaced with CO$_2$, then the vial was placed inside the steel autoclave. The autoclave was heated and filled with CO$_2$ (0.4 MPa), and the vial placed inside was kept stirring for the whole reaction time. After the completion of the reaction, the autoclave was cooled to rt and slowly depressurized.

The reaction at 0.1 MPa was conducted in a 25 mL Schlenk tube equipped with a CO$_2$ balloon. The two components of the eutectic mixture (5 % mol respect to the epoxide) were weighed and put inside the Schlenk with the epoxide (2.6 mmol). The air in the Schlenk tube was firstly replaced with CO$_2$, then the Schlenk was placed in an oil bath heated at 80 °C. The CO$_2$ of the balloon was then allowed to flow into the flask. After the completion of the reaction, the Schlenk tube was cooled to rt.

In both cases the reaction was conducted with the best performing mixture Choline Iodide (ChI): Glycerol (1:1) (5 mol%) in the conversion of benzyl glycidyl ether 1b (2.6 mmol) into the corresponding cyclic carbonate 2b at p(CO$_2$) = 0.1 MPa (ballon), 80 °C, for 7 h. After the reaction was completed, ethyl acetate was added to the crude mixture to recover the product while the aqueous phase was collected to recover the catalyst after removal of water by distillation. The recovered catalyst was used for more runs without further purification. The organic phase containing the product was analyzed by GC-MS, after dilution as before.

2.4. Procedure for catalyst recycle

The recycle of the catalyst was tested with the best performing mixture Choline Iodide (ChI): Glycerol (1:1) (5 mol%) in the conversion of benzyl glycidyl ether 1b (2.6 mmol) into the corresponding cyclic carbonate 2b at p(CO$_2$) = 0.1 MPa (ballon), 80 °C, for 7 h. After the reaction was completed, ethyl acetate was added to the crude mixture to recover the product while the aqueous phase was collected to recover the catalyst after removal of water by distillation. The recovered catalyst was used for more runs without further purification. The organic phase containing the product was analyzed by GC-MS, after dilution as before.

2.5. Instrumentation

GC-MS analyses of reaction mixtures were performed using an Agilent HP 6850 gas chromatograph connected to an Agilent HP 5975 quadrupole mass spectrometer. Analyses were separated on a HP-5MS fused-silica capillary column (stationary phase 5%-Phenyl)-methyl-polyisiloxane, 30 m, 0.25 mm i.d., 0.25 μm film thickness), with helium as the carrier gas (at constant pressure, 36 cm s$^{-1}$ linear velocity at 200 °C). Mass spectra were recorded under electron ionization (70 eV) at a frequency of 1 scan s$^{-1}$ within the 12–600 m/z range. The injection port temperature was 250 °C. The temperature of the column was kept at 50 °C for 5 min, then increased from 50 to 250 °C at 10 °C min$^{-1}$ and the final temperature of 250 °C was kept for 12 min. Epichlorohydrin 1c and allyl glycidyl ether 1d (more volatile than the other substrates) were analyzed through the following thermal program: the temperature of the column was kept at 40 °C for 6 min, then increased from 50 to 250 °C at 10 °C min$^{-1}$ until the final temperature of 250 °C. $^1$H NMR spectra were recorded on Varian 400 (400 MHz) spectrometers. $^{13}$C NMR spectra were recorded on a Varian 400 (100 MHz) spectrometers. Chemical shifts are reported in ppm from TMS with the solvent resonance as the internal standard (deuterchloroform: 7.26 ppm). Mesitylene (1,3,5 trimethylbenzene) was used as internal standard (see Supplementary material for more details).

3. Results and discussion

The reaction between CO$_2$ and epoxides catalyzed by eutectic mixtures has been initially studied with styrene oxide 1a as model substrate at different temperatures and CO$_2$ pressures.

Under the tested reaction conditions, ChCl and ChI were both insoluble in styrene oxide, but their solubilization increased by coupling
them with a hydrogen bond donor (HBD). Thus, several choline-based eutectic mixtures were prepared and their ability to catalyze epoxides carbonation was tested. Urea, glycerol, ethylene glycol, water and several carboxylic acids (oxalic, citric, maleic, malonic, tartaric, malic, fumaric, 3-hydroxybutyric, alpha-hydroxyisobutyric, crotonic, benzoic, octanoic, butanolic, and acetic acid), were all tested as HBD. Most of the chosen HBDs are non-toxic and biobased.

### 3.1. Choline chloride-based catalysts

The activity of ChCl-based catalysts was tested in stainless steel autoclave at maximum p(CO$_2$) = 0.4 MPa and T = 80 °C (Table 1), as described in the experimental Section 2.3. Eutectic mixtures were initially screened in sub-stoichiometric amounts (5 mol% in terms of choline component with respect to the starting material). A 5% catalyst loading is quite common when carbonatation reactions are performed under mild conditions [31,58,59], and allowed us to easily carry out the subsequent recyclability tests on this small scale.

As already observed [39], ChCl alone had no catalytic effect being very scarcely soluble in the reaction mixture (styrene oxide and CO$_2$) within 8 h (entry 1; ChCl/Urea (1:2) eutectic mixture behaved slightly better than ChCl alone (entry 2) but definitely better results have been obtained with catalysts containing acidic or alcoholic groups as HBD. All dicarboxylic acids here tested had an excellent activity in terms of both conversion and selectivity; the only exception was oxalic acid (entry 7). All the other ChCl: acids mixtures gave an almost quantitative conversion of 1a (entries 8-20), with a very good selectivity for the formation of 2a. When polyols were used as HBD, different behaviors were observed: glycerol had an activity similar to that of carboxylic acids (entry 5), while ethylene glycol (entry 3) was less reactive and less selective.

The activity of the catalysts when ChCl-eutectic mixture was pre-formed, as described in experimental Section 2.2 (entries 3, 5, 11, 13, 14, 15, 16, 17, 18, 19, 20), was also tested in presence of betaine, a zwitterion, containing both a quaternary ammonium salt, as choline, and an acidic group, but without the halide and hydroxyl groups. As ChCl tested alone (entry 1), also betaine was totally ineffective (data not shown).

### Table 1

| Entry | Catalyst ChCl:HBD | Conversion % | Selectivity % |
|-------|-------------------|--------------|---------------|
| 1a    | ChCl              | 0            | -             |
| 2a    | ChCl: Urea (1:2)  | 33           | >-99          |
| 3a    | ChCl: Ethylene Glycol (1:2) | 82 | 93:7          |
| 4a    | ChCl and Ethylene Glycol (1:2) | 80 | 89:11         |
| 5a    | ChCl and Glycerol (1:2) | 93 | 98:2          |
| 6a    | ChCl and Glycerol (1:2) | 72 | 92:8          |
| 7a    | ChCl: Oxalic Acid (1:1) | 76 | 93:7          |
| 8a    | ChCl: Citric Acid (1:1) | 95 | 98:2          |
| 9a    | ChCl: Maleic Acid (1:1) | 97 | 98:2          |
| 10a   | ChCl: Maleic Acid (1:1) | 91 | 99:1          |
| 11a   | ChCl: Malonic Acid (1:1) | 97 | 99:1          |
| 12a   | ChCl and Malonic Acid (1:1) | 92 | 99:1          |
| 13a   | ChCl: Tartaric Acid (1:1) | 95 | 95:5          |
| 14a   | ChCl and Tartaric Acid (1:1) | 83 | 95:5          |
| 15a   | ChCl: Malic Acid (1:1) | 97 | 99:1          |
| 16a   | ChCl: Malic Acid (1:1) | 92 | 98:2          |
| 17a   | ChCl: Malic Acid (1:1) | 26 | 98:2          |
| 18a   | ChCl and Malic Acid (1:1) | 22 | 98:2          |
| 19a   | ChCl: Malic Acid (1:1) 1.5% | 95 | 98:2          |
| 20a   | ChCl: Malic Acid (1:1) 3% | 96 | 98:2          |

Reaction conditions: 1.3 mmol 1a (148.6 μL), p(CO$_2$) = 0.4 MPa, neat.

- Catalyst was pre-formed as eutectic mixture and then added to 1a.
- Catalyst components were added separately in the reaction mixture.
- p(CO$_2$) = 0.2 MPa.
- p(CO$_2$) = 0.1 MPa (balloon).
- Conversion and selectivity calculated by GC-MS (see experimental section).

The two components are separated by the colon "::"); in comparison to its formation in situ by adding the components separately inside the reaction mixture (entries 4, 6, 12, 14, the two components are separated by "and"), was also analyzed. In some cases, the differences in terms of conversion between the two strategies were negligible (entries 3 and 4, 11 and 12), in other cases they were more relevant (entries 5 and 6, 13 and 14). In terms of selectivity for 2a formation, the two strategies gave similar results with acids-based mixtures (entries 11 and 12, 13 and 14), but better results were achieved when polyol-based mixture were pre-formed than when they were formed in situ (entries 3 and 4, 5 and 6). The reaction between CO$_2$ and 1a was also tested in presence of betaine, a zwitterion, containing both a quaternary ammonium salt, as choline, and an acidic group, but without the halide and hydroxyl groups. As ChCl tested alone (entry 1), also betaine was totally ineffective (data not shown).

Variations of pressure, time and amount of catalyst were further tested by using ChCl: Maleic acid (1:1) as catalyst. A decrease in CO$_2$ pressure proved to be detrimental (entries 10, 16, 17, 18) especially with the system operating at 0.1 MPa (balloon). The addition of the catalyst in the preformed eutectic mixture or as two separate components did not affect conversion if CO$_2$ pressure was kept at 0.1 MPa (balloon) (entries 17 and 18), whereas a slight decrease in both conversion and selectivity was observed by lowering the catalyst amount (entries 19 and 20). An in-depth study of the initial reaction rate demonstrated that 5–7 h were enough to get an almost quantitative conversion of 1a (Fig. 1).

On the basis of previous literature studies [6] and the experimental evidences here found, a plausible mechanism was proposed for ChCl-HBD catalyzed reaction of epoxides with CO$_2$ (Scheme 1). First, epoxide is activated via the hydrogen bond between the HBD and the...
nucleophilic attack of the choline halide with the formation of the oxygen of the epoxide, facilitating its ring opening that proceeds via Reaction conditions: 2.6 mmol

**Table 2**

**Synthesis of styrene carbonate 2a catalyzed by ChI-HBD catalysts.**

| Entry | Catalysts | ChI:HBD | Time (h) | Conversion % | Selectivity % |
|-------|-----------|---------|----------|--------------|---------------|
| 1     | ChI       | 5       | 16       | 99:1         |                |
| 2     | ChI and Malic Acid (1:1) | 5       | 88       | 99:1         |                |
| 3     | ChI and Maleic Acid (1:1) | 5       | 87       | 99:1         |                |
| 4     | ChI and Fumaric Acid (1:1) | 5       | 87       | 98:2         |                |
| 5     | ChI and Tartaric Acid (1:1) | 5       | 85       | 99:1         |                |
| 6     | ChI and 3-Hydroxybutyric Acid (1:1) | 5       | 86       | 99:1         |                |
| 7     | ChI and malic acid | 5       | 77       | 99:1         |                |
| 8     | ChI and Crotonic Acid (1:1) | 5       | 88       | >99          |                |
| 9     | ChI and Benzoic Acid (1:1) | 5       | 87       | >99          |                |
| 10    | ChI and Octanoic Acid (1:1) | 5       | 87       | >99          |                |
| 11    | ChI and Butanoic Acid (1:1) | 5       | 76       | >99          |                |
| 12    | ChI and Acetic Acid (1:1) | 5       | 90       | 98:2         |                |
| 13    | ChI and Ethylene Glycol (1:1) | 5       | 91       | >99          |                |
| 14    | ChI and H2O (1:2) | 5       | 88       | >99          |                |
| 15    | ChI and Glycoler (1:1) | 5       | 96       | 98:2         |                |
| 16    | ChI and Glycoler (1:1):2% | 7       | 99       | 96:4         |                |
| 17    | ChI and Glycoler (1:1):4% | 7       | 94       | 96:4         |                |
| 18    | ChI and Glycoler (1:1):5%, rt | 7       | 0        | 0            |                |
| 19    | ChI and Glycoler (1:1):5%, 50°C | 7       | 50       | 93:7         |                |
| 20    | Glycoler 5% | 22      | 0        | -            |                |
| 21    | TBAI 5%   | 7       | 64       | >99          |                |

Reaction conditions: 2.6 mmol 1a (297.2 μL), p(CO2) = 0.1 MPa (balloon), neat. 

**Fig. 2.** Effect of time on 1a conversion using 5 % ChI:Glycerol (1:1), 80°C, p (CO2) = 0.1 MPa (balloon). 

conditions ChI alone could effectively catalyze the reaction (5% mol, entry 1) giving a 95% conversion of 1a into 2a but at longer reaction times (22 h); the most commonly used TBAI (Tetrabutylammonium iodide) did not give a complete conversion in 7 h (entry 21). The coupling of ChI with a HDB forms a homogenous mixture in a short time, significantly decreasing the carbonatation time (entries 2-19, Table 2). Moreover, ChI-based mixtures proved to catalyze the reaction in milder conditions than what found with ChCl-based mixtures, allowing to decrease CO2 pressure from 0.4 MPa to 0.1 MPa (balloon). Notably, very good results and selectivity were found also by adding the components of the mixture separately inside the reaction system, being iodide a better leaving group than chloride, the product ring-closure is fastened despite the presence of water (Table 2, entry 14) [35,61].

Several HBDs were tested in combination with ChI. When dicarboxylic acids were used as HBDs (entries 2, 3, 4, 5), better conversions (close to 90 %) than those achieved with ChI alone (entry 1) were obtained in shorter reaction times (5 h), demonstrating that the presence of the HBD enhanced ChI activity. High conversions were reached also with other hydroxy-substituted carboxylic acids (entries 6 and 7), crotonic acid (entry 8), benzoic acid (entry 9) and some aliphatic acids (entries 10, 11, 12). Among the various acids, acetic acid seemed to be the most effective. The carboxylic acids tested alone were ineffective (data not shown). When polyols (glycerol and ethylene glycol, entries 13 and 15) or water (entry 14) were used as HBDs, very good results were obtained [35]. The best conversion (99 % in 7 h) was obtained with glycerol as HBD, whereas glycerol used alone (entry 20) was ineffective even after 22 h. By studying in more detail the effect of the catalyst amount, temperature and time it was found that: i) a slight decrease in product conversion was observed by decreasing the catalyst amount (entries 16 and 17); ii) the reaction did not run at rt (entry 18) and just 50 % conversion was achieved at 50°C after 7 h (entry 19); iii) a conversion of 90% was got after 3 h, becoming quantitative in 7 h (Fig. 2).

### 3.3. Substrates screening

The catalysts and conditions that gave the overall best results in the carbonatation of 1a (ChI-Malic Acid under pCO2 = 0.4 MPa; ChI-Glycerol under pCO2 = 0.1 MPa) were used for substrate scope (Table 3). Although many other HBDs performed well with ChI and others with ChI, Malic Acid and Glycerol have been chosen because they are bio-based, non-toxic, widely available and cheap.

Due to the different volatility of the substrates, the reaction with 1c and 1d was carried out inside the steel autoclave, in the condition optimized for ChCl-based eutectic mixtures (pCO2 = 0.4 MPa, 80°C); this approach guaranteed a greater insulation of the system than the Schlenk tube equipped with CO2 balloon. In this case it was not possible to carry out reactions inside the autoclave at lower pressures because the small size apparatus would have limited CO2 amount.

Generally, terminal epoxides could be transformed into the corresponding cyclic carbonates with good to very good yields (entries 1–5);
The catalyst could be recycled over four times without appreciable loss of catalytic activity (Fig. 3).

4. Conclusion

Herein sustainable catalysts composed by eutectic mixtures of choline salts and various bio based HBDs have been proved to be effective and recyclable catalysts for the synthesis of terminal cyclic carbonates from CO₂ and epoxides. The HBD, coupled with a choline salt has a dual role: 1) to form an eutectic mixture with the choline salt, soluble in the starting materials in our reaction conditions; 2) to be the co-catalyst in the cycloaddition reaction, being able to stabilize the alkoxide intermediate a (Scheme 1). Very good conversions of various terminal epoxides into the corresponding cyclic carbonates were obtained with choline chloride and choline iodide-based catalysts. With both catalysts carbonation reactions were conducted under solvent-free conditions, at 80 °C, in 7–22 h. While using choline chloride-based mixtures, a pressure of 0.4 MPa of CO₂ was required to obtain appreciable conversions, with iodide-based mixtures atmospheric pressure of CO₂ (balloon) has been successfully used.

The novelty of the present work in the wide panorama of previous studies about choline-based, ionic liquid- or DES- based catalysts is represented by the very mild conditions used (atmospheric CO₂ pressure and temperature below 100 °C) and the simplicity of the catalysts used. In fact, the use of these mixtures presents several advantages: they are very easily synthesized from commercially available, inexpensive and bio-based, non-toxic chemicals and do not require any particular purification step.

CRediT authorship contribution statement

Martina Vagnoni: Conceptualization, Methodology, Validation, Investigation, Writing - original draft, Visualization. Chiara Samorì: Supervision, Writing - review & editing. Paola Galletti: Conceptualization, Supervision, Project administration, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.jcou.2020.101302.

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Table 3

| Entry | Substrate | Product | By-product | Time (h) | Yield 2 [%] | Yield 3 or 4 [%] |
|-------|-----------|---------|------------|----------|-------------|-----------------|
| 1<sup>a</sup> | 1<sup>a</sup> | 2<sup>a</sup> | 3<sup>a</sup> | 7 | 90 (88) | 9 |
| 2<sup>b</sup> | 1<sup>b</sup> | 2<sup>b</sup> | 3<sup>b</sup> | 7 | 94 (87) | 5 |
| 3<sup>b</sup> | 1<sup>c</sup> | 2<sup>c</sup> | 3<sup>c</sup> | 7 | 80 (80) | 10 |
| 4<sup>c</sup> | 1<sup>d</sup> | 2<sup>d</sup> | 3<sup>d</sup> | 5 | 91 (80) | 8 |
| 5<sup>d</sup> | 1<sup>e</sup> | 2<sup>e</sup> | 3<sup>e</sup> | 22 | 95 (83) | 4 |
| 6<sup>e</sup> | 1<sup>f</sup> | 2<sup>f</sup> | - | 23 | 0 - |

<sup>a</sup> Reaction conditions: 2.6 mmol of substrate, Chl: Glycerol (1:1) 5%, 80 °C (5<sup>c</sup>) 100 °C, p(CO₂) = 0.1 MPa (balloon).

<sup>b</sup> Reaction conditions: 1.3 mmol of substrate, ChCl: Malic Acid (1:1) 5%, 80 °C, p(CO₂) = 0.4 MPa (autoclave).

<sup>c</sup> Calculated by <sup>1</sup>H-NMR (see experimental section), isolated yields in parentheses.

Fig. 3. Catalyst recycling for the conversion of 1b into 2b. Yield calculated by GC-MS (see experimental section).
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