

## Turning waste into resources. Efficient synthesis of biopolyurethanes from used cooking oils and CO<sub>2</sub> <sup>☆☆,☆</sup>

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### ABSTRACT

The coupling reaction of carbon dioxide and highly-substituted epoxides derived from renewable resources such as fatty acids and waste vegetable oils (cooking oils derived from olive and sunflower) leads to the synthesis of new bio-derived cyclic carbonates using efficient metal-free bifunctional organocatalysts under mild and solvent-free reaction conditions. Once cyclic carbonates derived from biobased sources were synthesized, the design of non-isocyanate polyurethanes (NIPUs) with different chemical structures was investigated by their reaction with a broad substrate scope of diamines. The NIPUs materials were characterized by spectroscopic techniques (NMR and IR) and their molecular weights and polydispersities were determined by GPC studies. Finally, thermal properties of the polymers were studied by DSC and TGA analyses.

### 1. Introduction

Carbon dioxide (CO<sub>2</sub>) has become the principal anthropogenic gas responsible for global warming [1]. The concentration of CO<sub>2</sub> in the atmosphere has been continuously increasing since the Industrial Revolution from 280 to 420.4 ppm, principally due to the use of fossil fuels [2]. This fact is of great concern to society, therefore greener and more sustainable synthetic processes and methodologies respectful with the environment should be developed to accomplish the “Twelve Principles of Green Chemistry” [3]. As a result, it is necessary to focus on the chemical fixation and transformation of CO<sub>2</sub> into value-added products with the aim to reduce its concentration in the atmosphere which would help to mitigate climate change [4,5]. CO<sub>2</sub> is a non-toxic, non-flammable, and renewable C1 resource that can be used as starting material

for the preparation of a wide variety of organic molecules such as methanol, urea, and salicylic acid, among others [4,6]. Nevertheless, the reactivity of CO<sub>2</sub> is quite hampered because of its thermodynamic stability, which means that the use of high pressures and temperatures is required, for these reasons, it is highly desirable to carry out the synthesis of novel effective catalytic systems to overcome the elevated energy barriers related with reactions of CO<sub>2</sub> [7–9].

In that sense, the catalytic formation of cyclic carbonates by cycloaddition of CO<sub>2</sub> into epoxides is one of the most promising reactions since it is a 100% atom-economy reaction in which CO<sub>2</sub> is used as efficient feedstock [10]. The industrial preparation of ethylene or propylene carbonates catalyzed by quaternary ammonium salts has been performed since the 1950 s, however, it requires high temperatures and high CO<sub>2</sub> pressures [11]. The 5-membered ring cyclic carbonates, which

**Abbreviations:** BDA, 1,4-diaminobutane; CVOs, carbonated vegetable oils; DBU, 1,8-diazabicyclo(5.4.0)undec-7-ene; DFT, density functional theory; DMSO, dimethyl sulfoxide; DSC, differential scanning calorimetry; EVOs, epoxidized vegetable oils; FTIR, Fourier transform infrared spectroscopy; GC-FID, gas chromatography with flame-ionization detection; GPC, gel permeation chromatography; HBDs, hydrogen-bond donors; IR, infrared spectroscopy; MOFs, metal organic frameworks;  $M_n$ , molecular weight number; NIPUs, non-isocyanate polyurethanes; NMR, nuclear magnetic resonance spectroscopy; PDI, polydispersity; PHUs, polyhydroxyurethanes; PMMA, polymethylmethacrylate; TBD, 1,5,7-triazabicyclo[4.4.0]dec-5-ene;  $T_d$ , thermal decomposition;  $T_g$ , glass transition temperature; TGA, thermogravimetric analyses; TMS, tetramethyl silane; WVOs, waste vegetable oils.

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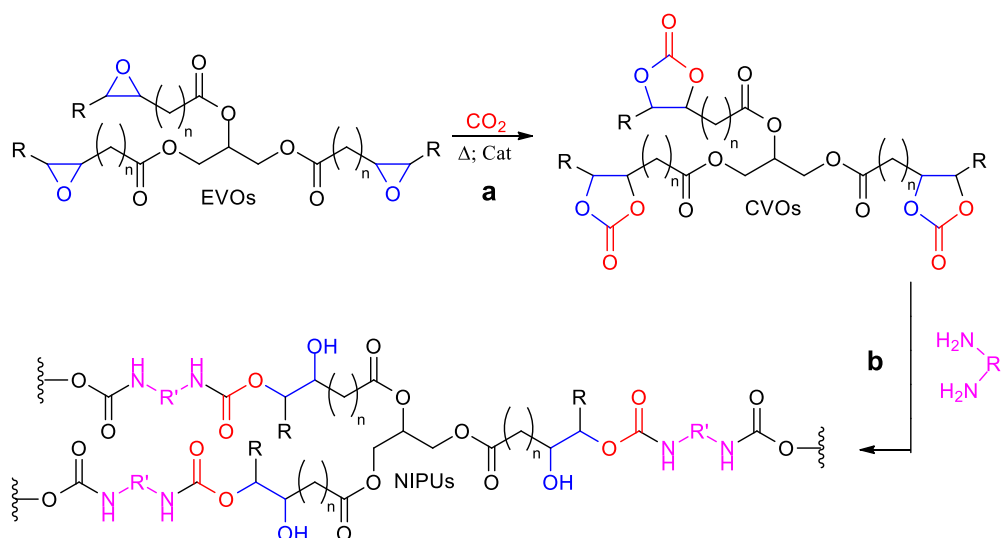
have noteworthy properties such as high solubility, low toxicity, and low vapor pressure [12], were broadly used as polar aprotic solvents, monomers for the production of polymers, in electrolyte batteries, to mention some applications [13–15]. A huge variety of metal catalysts [16–18], organocatalysts [19–24], metal organic framework (MOFs) [25–29], and ionic liquids, [30–32] among others, have been recently reported for the obtention of cyclic carbonates from epoxides and CO<sub>2</sub>. Lately, scientific groups have centered their efforts towards the preparation of bio-based cyclic carbonates obtained from renewable starting materials since waste generation has grown enormously in the last few years, thus it is necessary to develop new tactics to reduce waste production and increment residue valorization [33–38]. Among the produced waste, residues derived from vegetable oils, which are mainly generated in homes, restaurants, and hotels, are the most plentiful food residue, therefore used vegetable oils can get a “second chance”, firstly for food purposes and then for disposal. It is estimated that around 67 million tons per year of waste vegetable oils (WVOs) are generated worldwide [39,40], and normally WVOs are dumped in ocean or rivers, producing significant environmental complications. For these reasons, it must be priority to find new ways to recycle and reuse these WVOs. It should be highlighting that WVOs have the potential to be a renewable resource for the preparation of high value-added products such biodiesel [41–43], soap [44], or cyclic carbonates [19,45–47]. In particular, carbonated vegetable oils (CVOs) could be synthesized by the reaction between epoxidized vegetable oils (EVOs) derived from WVOs and CO<sub>2</sub> (Scheme 1 a) [19,45–47]. EVOs can be easily prepared by epoxidation of the double bonds present in the triglyceride units [48], which allows vegetable oils to be chemically transformed and increase their potential applications. Furthermore, CVOs have gain huge relevance since they have been used for the synthesis of non-isocyanate polyurethanes (NIPUs) by their reaction with diamines (Scheme 1b) [45,49–57]. These polymers could have potential applications in biomedicine, industrial coating, foams and adhesive [45,49–57].

Metal-free organocatalysts have received special attention and could be an interesting alternative to metal compounds since these catalysts are generally prepared in larger amounts. Hydrogen-bond donors (HBDs) organocatalysts have been widely used for the preparation of cyclic carbonates since the presence of proton-containing groups, such as, –COOH, –OH, or –NH– have the ability to activate the epoxide ring through the formation of hydrogen bonds, enabling its opening by the attack of a nucleophile. D’Elia *et al.* studied the relation between the catalytic activity of the hydroxyl group of the HBDs and their Brønsted acidity in the reaction of CO<sub>2</sub> with epichlorohydrin discovering that an elevated Brønsted acidity had a positive effect on hydrogen bond

formation facilitating the ring opening of the epoxide, although, it slowed down the release of cyclic carbonate in the cyclization stage [58]. Therefore, the principal challenge will consist in designing HBDs organocatalysts with adequate Brønsted acidity. These catalysts have exhibited excellent catalytic activities for the cyclic carbonate formation as a bifunctional [19,20,59–64] or binary [23,65,66] catalytic systems. In this context, HBDs catalysts based on protic organic salts containing –COOH, –OH, or –NH– groups and a nucleophilic counterion are exceptional candidates to act as a bifunctional organocatalysts for the cycloaddition of CO<sub>2</sub> and epoxides.

Related to that, organocatalysts based on salts of N-heterocycles have proven to be efficient for the preparation of cyclic carbonates [60,67,68]. Kühn *et al.* reported through DFT calculations and experimental results that the presence of –OH groups in the bisimidazolium salts performed a positive effect on the catalytic activity of these organocatalysts [69]. Additionally, this fact was also observed by our research group in the development of hydroxy-containing imidazole salts which were exceptional bifunctional organocatalysts for the synthesis of a broad variety of cyclic carbonates [20]. An iodide imidazole-based organocatalyst derived from this family of compounds was able to carry out a set of carbonated vegetable oils from WVOs which could be employed as potential bio-derived feedstock in different chemical processes [19,45]. It is important to mention that this family of organocatalysts has not only been used to obtain cyclic carbonates from the reaction between epoxides and CO<sub>2</sub>, since the formation of oxazolidin-2-ones, by [3 + 2] cycloaddition of epoxides and isocyanates was also achieved demonstrating the versatility of this type of systems [70].

Therefore, inspired by the brilliant catalytic activity showed by these hydroxy-containing mono-imidazole salts in various catalytic processes, we explored the synthesis of a second generation of catalysts 1 – 6 based on bis-imidazole salts (bromide and iodide) where the presence of two –OH groups in their structure significantly increases the catalytic activity. In this work, we have prepared an important substrate scope of cyclic carbonates derived from mono- or disubstituted epoxides, terpenes, waste fatty acid bis-epoxide *n*-pentyl ester and waste vegetable oils (from cooking oils), as starting materials for the synthesis of different NIPUs materials by polyaddition reaction of carbonated vegetable oils with a variety of diamines. The obtained organocatalysts and cyclic carbonates were characterized by NMR, IR, GPC, and their thermal properties were studied by TGA and DSC.



Scheme 1. Synthetic routes for the formation of CVOs (a) and NIPUs (b).

## 2. Experimental

### 2.1. Materials and methods

All reactions involving CO<sub>2</sub> were carried out in a stainless-steel reactor with a magnetic stirrer bar. Solvents were pre-dried over sodium wire (CH<sub>3</sub>CN, hexane and EtOAc) or CaCl<sub>2</sub> and CHCl<sub>3</sub> (CH<sub>2</sub>Cl<sub>2</sub>). Deuterated solvents were stored over activated 4 Å molecular sieves and degassed by several freeze-thaw cycles. <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra were performed on a Varian Inova FT-500 spectrometer and referenced to the residual deuterated solvent. Chemical shifts are given in parts per million (ppm) relative to TMS [<sup>1</sup>H and <sup>13</sup>C, δ(SiMe<sub>4</sub>) = 0]. All coupling constants (J) are represented in Hz. Multiplicities are shown by brs (broad singlet), s (singlet), d (doublet), t (triplet), dd (double doublet), and m (multiplet). FTIR spectra were afforded on a Shimadzu IR Prestige-21 spectrophotometer armed with a Pike Technology ATR system. The instrument was set to acquire 32 scans per spectrum at a resolution of 4 cm<sup>-1</sup>. Elemental analysis was carried out with a Perkin-Elmer 2400 CHN analyzer. Molecular weight estimations of synthesized polymers were assessed by gel permeation chromatography (GPC, Jasco, Japan) equipped with a refractive index detector (RI-4030, Jasco) and a divinylbenzene based column (DVB column, Jordi Labs) enclosed in a column oven at 40 °C (CO-4060, Jasco). 10 mg of polymeric sample were dissolved in 1.0 mL of chloroform and stirred overnight up to the total dissolution of polymer into the solvent. Samples were measured in GPC running with chloroform as mobile phase at 1.0 mL/min. Molecular weight calculations (Mw, Mn, and polydispersity index), were done by using ChromNAV-GPC software (Jasco), using a molecular weight calibration curve made using different narrow polymethylmethacrylate (PMMA) standard (ReadyCal Kit, Polymer Standard Service GmbH). Thermogravimetric analyses were done in a Perkin Elmer TGA-4000. The heating rate for the sample was 10 °C/min from 30.0 °C to 500 °C, and the nitrogen flow rate was 20 mL/min. Thermal characterization was done in a differential scanning calorimeter (TA Instruments DSC Q200). Around 10 mg of sample was deposited in an alumina crucible, and first applying a first cooling cycle from room temperature up to - 50 °C at 10 °C/min, followed by heating from - 50 °C up to 150 °C at 10 °C/min under a nitrogen atmosphere. This cycle was repeated two times. Commercially available chemicals (Sigma Aldrich) were used as received.

### 2.2. General procedure for the synthesis of bis-imidazolium salts 1 – 6

Bisimidazolium organocatalysts have been synthesized from neutral imidazole derived from 5-(2-hydroxyphenyl)-1H-imidazole, which have been widely described in previous works developed by our research group [70]. A suspension of 1-dibromomethane (10 mL) and the corresponding 5-(2-hydroxyphenyl)-1-butyl-1H-imidazole derived (2.30 mmol) was heated at 95 °C for 7 h, resulting in the formation of a brown precipitate. Then the following solvents CHCl<sub>3</sub>/Et<sub>2</sub>O/acetone were added to the product formed in a 1/0.2/1 ratio, which caused the precipitation of a white solid, which was filtered and dried to afford the bis-imidazolium bromide salts (1, 3 and 5). The bis-imidazolium iodide salts were obtained by the ionic exchange reaction between bis-imidazolium bromide with KI, using CH<sub>2</sub>Cl<sub>2</sub> as solvent at rt for 30 min. Finally, a brown solid was obtained and filtered, affording bis-imidazolium iodide salts (2, 4 and 6).

1,1'-Methylenebis[4-(2-hydroxyphenyl)-3-phenyl-1H-imidazol-3-ium] dibromide (1). Obtained as pale brown solid, (1.45 g) 97% yield. An analytically pure sample was obtained by recrystallization from CHCl<sub>3</sub>. Monocrystals were grown from a CHCl<sub>3</sub>/EtOAc solution. Mp 273–274 °C. Anal. Calcd. for C<sub>31</sub>H<sub>26</sub>Br<sub>2</sub>N<sub>4</sub>O<sub>2</sub> (646.37): C, 57.60; H, 4.05; N, 8.67. Found: C, 57.66; H, 4.10; N, 8.61. <sup>1</sup>H NMR (500 MHz, [D<sub>6</sub>] DMSO) δ = 10.25 (s, 2 H), 10.12 (m, 2 H), 8.52 (m, 2 H), 7.56 (d, J=4.5 Hz, 6 H), 7.43 (s, 4 H), 7.31 (t, J=8.0 Hz, 2 H), 7.17 (d, J=7.0 Hz, 2 H), 6.92–6.85 ppm (m, 6 H). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, [D<sub>6</sub>]DMSO)

δ = 156.1, 139.2, 134.8, 132.7, 132.2, 132.1, 130.7, 130.2, 130.1, 125.5, 121.7, 119.7, 116.5, 112.0 ppm.

1,1'-Methylenebis[4-(2-hydroxyphenyl)-3-phenyl-1H-imidazol-3-ium] diiodide (2). Obtained as white solid, (1.65 g) 97% yield. An analytically pure sample was obtained by recrystallization from CHCl<sub>3</sub>. Monocrystals were grown from a CHCl<sub>3</sub>/EtOAc solution. Mp 277–278 °C. Anal. Calcd. for C<sub>31</sub>H<sub>26</sub>I<sub>2</sub>N<sub>4</sub>O<sub>2</sub> (740.37): C, 50.29; H, 3.54; N, 7.57. Found: C, 50.33; H, 3.60; N, 7.52. <sup>1</sup>H NMR (500 MHz, [D<sub>6</sub>] DMSO) δ = 10.22 (s, 2 H), 8.52 (s, 2 H), 7.58 (m, 6 H), 7.54 (s, 4 H), 7.29 (t, J=7.5 Hz, 2 H), 7.25 (d, J=7.0 Hz, 2 H), 6.84–6.82 ppm (m, 6 H). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, [D<sub>6</sub>]DMSO) δ = 156.1, 139.1, 134.8, 132.7, 132.3, 132.2, 132.1, 130.7, 130.2, 130.1, 129.9, 125.8, 125.6, 121.7, 119.7, 116.4, 112.1 ppm.

1,1'-Methylenebis[3-butyl-4-(2-hydroxyphenyl)-1H-imidazol-3-ium] dibromide (3). Obtained as brown solid, (1.36 g) 98% yield. Mp 238–239 °C. Anal. Calcd. for C<sub>27</sub>H<sub>34</sub>Br<sub>2</sub>N<sub>4</sub>O<sub>2</sub> (606.40): C, 53.48; H, 5.65; N, 9.24. Found: C, 53.43; H, 5.59; N, 9.27. <sup>1</sup>H NMR (500 MHz, [D<sub>6</sub>] DMSO) δ = 10.43 (s, 2 H), 9.80 (s, 2 H), 8.21 (s, 2 H), 7.44 (t, J=6.5 Hz, 2 H), 7.29 (d, J=6.5 Hz, 2 H), 7.07 (d, J=8.0 Hz, 1 H), 6.99 (t, J=7.0 Hz, 2 H), 6.83 (s, 2 H), 4.10 (t, J=6.5 Hz, 4 H), 1.67–1.62 (m, 4 H), 1.22–1.18 (m, 4 H), 0.77 ppm (t, J=7.0 Hz, 6 H). <sup>13</sup>C{<sup>1</sup>H}-NMR (125 MHz, [D<sub>6</sub>]DMSO) δ = 156.2, 138.2, 133.0, 132.8, 132.5, 121.0, 120.1, 116.6, 112.2, 58.9, 47.9, 31.1, 19.2, 13.6 ppm.

1,1'-Methylenebis[3-butyl-4-(2-hydroxyphenyl)-1H-imidazol-3-ium] diiodide (4). Obtained as brown solid, (1.51 g) 94% yield. An analytically pure sample was obtained by recrystallization from CHCl<sub>3</sub>. Monocrystals were grown from a CHCl<sub>3</sub>/EtOAc solution. Mp 207–208 °C. Anal. Calcd. for C<sub>27</sub>H<sub>34</sub>I<sub>2</sub>N<sub>4</sub>O<sub>2</sub> (700.40): C, 46.30; H, 4.89; N, 8.00. Found: C, 46.38; H, 4.93; N, 7.92. <sup>1</sup>H NMR (500 MHz, [D<sub>6</sub>] DMSO) δ = 10.44 (s, 2 H), 9.77 (s, 2 H), 8.24 (s, 2 H), 7.45–7.42 (m, 2 H), 7.29 (d, J=8.0 Hz, 2 H), 7.07 (d, J=8.0 Hz, 2 H), 6.99 (t, J=7.5 Hz, 2 H), 6.81 (s, 2 H), 4.11 (t, J=7.0 Hz, 4 H), 1.68–1.62 (m, 4 H), 1.24–1.16 (m, 4 H), 0.78 ppm (t, J=7.5 Hz, 6 H). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, [D<sub>6</sub>]DMSO) δ = 156.2, 138.2, 133.0, 132.9, 132.5, 120.9, 120.1, 116.6, 112.2, 58.9, 47.9, 31.1, 19.2, 13.6 ppm.

1,1'-Methylenebis[3-butyl-4-(3,5-difluoro-2-hydroxyphenyl)-1H-imidazol-3-ium] dibromide (5). Obtained as white solid, (1.54 g) 99% yield. An analytically pure sample was obtained by recrystallization from CHCl<sub>3</sub>. Monocrystals were grown from a CHCl<sub>3</sub>/EtOAc solution. Mp 258–260 °C. Anal. Calcd. for C<sub>27</sub>H<sub>30</sub>Br<sub>2</sub>F<sub>4</sub>N<sub>4</sub>O<sub>2</sub> (678.36): C, 47.81; H, 4.46; N, 8.26. Found: C, 47.65; H, 4.41; N, 8.29. <sup>1</sup>H NMR (500 MHz, [D<sub>6</sub>]DMSO) δ = 10.52 (s, 2 H), 10.01 (s, 2 H), 8.30 (s, 2 H), 7.52 (t, J=8.5 Hz, 2 H), 7.21 (d, J=8.5 Hz, 2 H), 6.90 (s, 2 H), 4.12 (t, J=7.2 Hz, 4 H), 1.67–1.62 (m, 4 H), 1.24–1.18 (m, 4 H), 0.79 ppm (t, J=7.3 Hz, 6 H). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, [D<sub>6</sub>]DMSO) δ = 154.4 (dd, J= 312.5, 15.1 Hz), 153.2 (dd, J=309.4, 16.1 Hz), 150.5 (d, J=16.4 Hz), 141.1 (d, J=19.0 Hz), 138.6, 130.1, 122.1, 115.3 (dd, J=18.9, 13.9 Hz), 114.3 (d, J=30.2 Hz), 107.9 (d, J= 29.9 Hz), 58.8, 48.1, 31.0, 19.2, 13.7 ppm.

1,1'-Methylenebis[3-butyl-4-(3,5-difluoro-2-hydroxyphenyl)-1H-imidazol-3-ium] diiodide (6). Obtained as pale brown solid, (1.49 g) 85% yield. An analytically pure sample was obtained by recrystallization from CHCl<sub>3</sub>. Monocrystals were grown from a CHCl<sub>3</sub>/EtOAc solution. Mp 259–262 °C. Anal. Calcd. for C<sub>27</sub>H<sub>30</sub>F<sub>4</sub>I<sub>2</sub>N<sub>4</sub>O<sub>2</sub> (772.37): C, 41.99; H, 3.92; N, 7.25. Found: C, 41.93; H, 3.89; N, 7.30. <sup>1</sup>H NMR (500 MHz, [D<sub>6</sub>]DMSO) δ = 10.54 (s, 2 H), 9.83 (s, 2 H), 8.27 (s, 2 H), 7.51 (t, J=7.0 Hz, 2 H), 7.25 (d, J=5.0 Hz, 2 H), 6.89 (s, 2 H), 4.11 (t, J=7.0 Hz, 4 H), 1.75–1.72 (m, 4 H), 1.26–1.22 (m, 4 H), 0.75 ppm (t, J=7.0 Hz, 6 H). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, [D<sub>6</sub>]DMSO) δ = 154.1 (dd, J= 297.5, 15.1 Hz), 152.2 (dd, J= 288.5, 16.4 Hz), 150.5 (t, J=16.3 Hz), 141.1 (t, J= 4.0 Hz), 138.6, 130.1, 122.1, 115.4–115.3 (m), 114.3 (d, J=33.8 Hz), 107.8 (t, J= 34.0 Hz), 58.9, 48.1, 31.0, 19.2, 13.7 ppm.

### 2.3. Synthesis of epoxidized vegetable oils

Epoxidized olive oil (13) and epoxidized sunflower oil (14) were prepared following a synthetic route previously reported in the

literature [19,71].

#### 2.4. General procedure for the optimization of reaction conditions for the preparation of cyclic carbonates 8a-c, 10, 15 and 16

Styrene oxide (7a), epichlorohydrin (7b), 1,2-epoxydodecane (7c) 8-[2-(2-pentyl-3-oxacyclopropylmethyl)-3-oxacyclopropyl]octanoate (9), epoxidized olive oil (13) or epoxidized sunflower oil (14) (1.7 mmol), organocatalysts 1–6 (12.75–85.0 μmol) were located in a 30 mL stainless steel reactor with a magnetic stirrer bar. The reaction mixture was stirred at 60–100 °C and 20 bar CO<sub>2</sub> pressure for 1–44 h, then the conversions of the epoxides into their corresponding cyclic carbonates were determined by analysis of a sample by <sup>1</sup>H NMR spectroscopy.

#### 2.5. General procedure for the synthesis of cyclic carbonates

An epoxide (1.7 mmol) and organocatalyst 4 (12.75–85.0 μmol) were placed in a 100 mL stainless steel 4790 Parr reactor with a magnetic stirrer bar inside and connected to a high pressure CO<sub>2</sub> line. The reaction mixture was heated at 60–100 °C with a Radleys TECH stirring hot plate, pressurized a 20 bar CO<sub>2</sub> pressure and left stirring for 1–44 h. After the allotted time period, the reactor was cooled to ambient temperature over 1 h and was carefully released by a gradual depressurization over the time. The transformation of epoxide to cyclic carbonate was then followed by analysis of a sample by <sup>1</sup>H NMR spectroscopy. The remaining sample was filtered through a plug of silica, eluting with CH<sub>2</sub>Cl<sub>2</sub> to eliminate the catalyst. The eluent was then evaporated under reduced pressure to give either the pure cyclic carbonate or a mixture of cyclic carbonate and unreacted epoxide. As later option, the mixture was purified by flash chromatography using a solvent system of first hexane, then hexane:EtOAc (9:1), then hexane:EtOAc (6:1), then hexane:EtOAc (3:1), then hexane:EtOAc (1:1), then EtOAc to give the pure cyclic carbonate.

#### 2.6. Recyclability study

To investigate the recyclability and stability of the catalysts, the epoxidized olive oil 13 and catalyst 4 were used under the optimal reaction conditions previously determined. Epoxide 13 (1.7 mmol) and organocatalyst 4 (1.7 μmol) were placed in the reactor connected to a high pressure CO<sub>2</sub> line. The reaction mixture was heated at 100 °C, pressurized at 20 bar CO<sub>2</sub> pressure and left stirring for 9 h. After the allotted time period, the reactor was cooled to ambient temperature over 1 h and was carefully released by a gradual depressurization over the time. The transformation of epoxide to cyclic carbonate was then followed by analysis of a sample by <sup>1</sup>H NMR spectroscopy. The catalyst was precipitated by adding Et<sub>2</sub>O and the reaction mixture was centrifuged to recover the catalyst 4. Subsequently, the catalyst was subjected to vacuum drying at 80 °C for 7 h for the subsequent cycle experiment. The <sup>1</sup>H NMR spectrum of the recovered catalyst 4 showed no changes compared to freshly prepared compound. This procedure was repeated for each cycle.

#### 2.7. General procedure for the synthesis of poly(hydroxyurethane)s 10a-d, 15a,e, 16a,b,d,e

In a 10 mL vial flask equipped with a small stir bar pentyl 8-(2-oxo-5-((2-oxo-5-pentyl-1,3-dioxolan-4-yl)methyl)-1,3-dioxolan-4-yl)octanoate (10), carbonated olive oil (15) or carbonated sunflower oil (16) (0.86 mmol), the corresponding diamine (0.86–1.72 mmol), 10 mol% of 1,8-diazabicyclo(5.4.0)undec-7-ene, DBU, (0.086 mmol) and MeCN (4 mL) were added. The reaction mixture was then heated up at 80 °C and left stirring for 16 h. After that time, the solvent was removed under reduced pressure and the residue was washed with MeOH. The mixture was filtered, and the solvent was dried in vacuo to give the

corresponding poly(hydroxyurethane).

### 3. Results and discussion

#### 3.1. Synthesis and structural characterization of organocatalysts 1–6

A series of methylenebisimidazolium dibromides (1, 3 and 5) and diiodides (2, 4 and 6) (Fig. 1) were synthesized according to the methodology depicted in point 2.2 of the Experimental Section and were characterized by spectroscopic methods (see Supplementary data for more information). It is relevant to mention that only one set of resonances for the butyl or phenyl protons was observed in the <sup>1</sup>H and <sup>13</sup>C {<sup>1</sup>H} NMR spectra of compounds 1–6 at room temperature, proving that both imidazolium rings are equivalent. When compared to their dibromide analogues, the chemical shifts for the methylenebisimidazolium diiodides 2, 4, and 6 slightly differ and some signals also appear wider. In contrast to its dibromide analogue 5, the imidazole proton resonances from compound 6 are, for instance, shifted to higher field.

#### 3.2. Catalytic results for the preparation of cyclic carbonates

Once the bis-imidazole compounds 1–6 were synthesized, it was investigated their potential use as bifunctional organocatalysts for CO<sub>2</sub> fixation into a wide diversity of cyclic carbonates. Initially, the catalytic activity of 1–6 was tested and compared with different terminal epoxides (Table 1). In general, iodide bis-imidazole derivatives 2 and 4 were more active than bromide derivatives 1 and 3, respectively, however, this trend was not observed with catalysts 5 and 6. The lower reactivity of 5 and 6 has been previously observed by our group in the cycloaddition of epoxides and isocyanates [70]. This suggests that the increase in acidity due to the presence of the fluor atoms, makes that the limiting step of the reaction is the cyclisation to obtain the cyclic carbonate, similar to what has been observed by Poater and D'Elia [58]. Thus the higher acidity of 5 and 6 would slow down the reaction rate. Amongst the catalysts under study, iodide bis-imidazole compound 4 was the most effective and it transformed an aryl, halide, and alkyl epoxides 7a–c into their corresponding cyclic carbonates 8a–c in outstanding conversions under the experimental reaction conditions.

As can be seen in the data shown in Table 1 catalyst 4 was the most active, therefore we decided to increase the substrate scope with others monosubstituted epoxides with ether functionality 7d, and 7e where excellent catalytic results were also afforded (Fig. 2). At this point, we opted to submit catalyst 4 to further challenges by preparing a range of disubstituted cyclic carbonates 8f–h from epoxides 7f–h in good to excellent yields (Fig. 2). Cyclopentane carbonate, 8f was isolated with a high yield (98%) in the presence of 0.75 mol% of 4 in 16 h, which represents a notable improvement with respect to the catalytic result previously obtained by mono-imidazole organocatalyst [20]. It is relevant to mention that owing to the solid nature of *trans*-stilbene oxide 7g, the preparation of *trans*-1,2-diphenylethylene carbonate 8g was performed at 100 °C and a good yield was obtained. 9-Oxabicyclo[6.1.0]non-4-ene epoxide 7h was also employed as substrate to give its carbonate 8h in 40% yield with a 59:41 mixture of *cis/trans* isomers in 16 h. As far as we know, there are only three previously reported examples for the preparation of 8h by the reaction of CO<sub>2</sub> and epoxide 7h

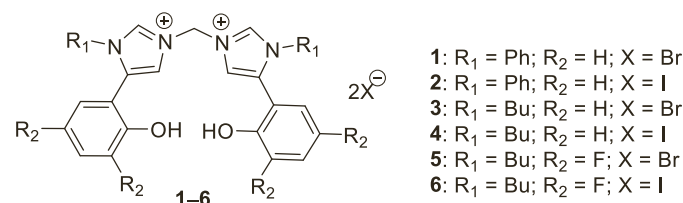
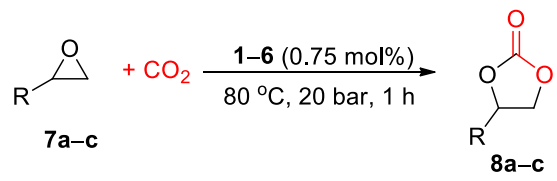


Fig. 1. Bifunctional organocatalysts 1–6.

**Table 1**  
Preparation of cyclic carbonates **8a–c** using organocatalysts **1–6**.<sup>a</sup>

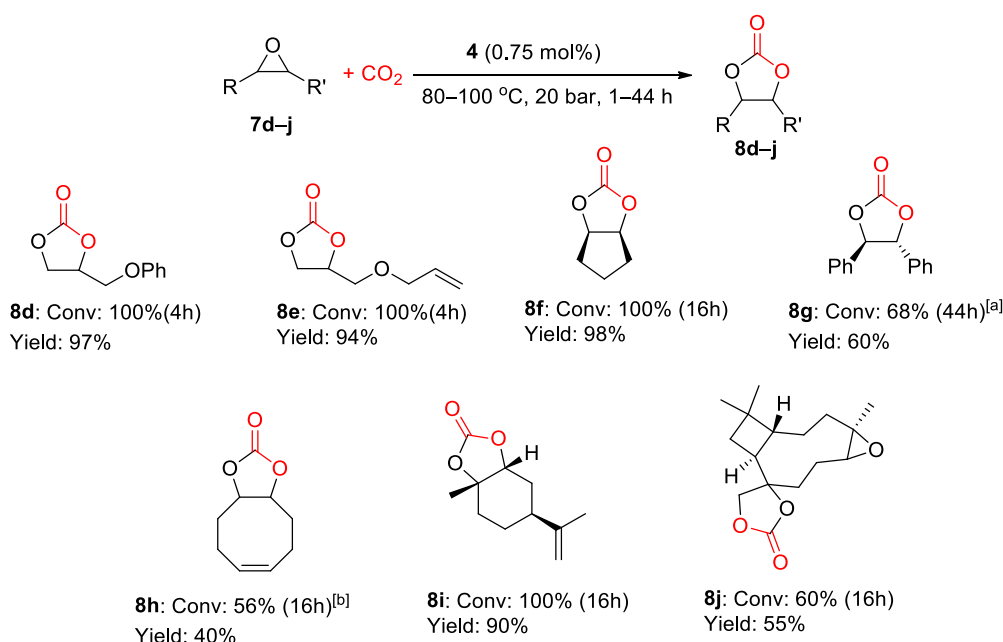


Organocatalyst	1	2	3	4	5	6
Entry	Epoxide	Conv. <sup>b</sup> (%)	Conv. <sup>b</sup> (%)	Conv. <sup>b</sup> (%)	Conv. <sup>b</sup> (%)	Conv. <sup>b</sup> (%)
1	7a (R = Ph)	80	90	79	98 (96) <sup>c</sup>	54
2	7b (R = CH <sub>2</sub> Cl)	79	85	86	100 (98) <sup>c</sup>	80
3	7c (R = Oct)	7	69	18	100 (98) <sup>c</sup>	5

<sup>a</sup> Reactions were carried out at 80 °C, 20 bar CO<sub>2</sub> pressure for 1 h using 0.75 mol% of catalyst **1–6** under solvent free conditions.

<sup>b</sup> Determined by <sup>1</sup>H NMR spectroscopy.

<sup>c</sup> Isolated yield from purified cyclic carbonate.



**Fig. 2.** Cyclic carbonates **8d–j** obtained from their corresponding epoxides **7d–j** by using organocatalyst **4**. Unless otherwise stated, reactions were carried out at 80 °C and 20 bar CO<sub>2</sub> pressure under solvent free conditions for 1–44 h. [a] T = 100 °C. [b] *cis/trans* = 59:41.

[72–74], and it is the first organocatalyst to achieve it, which highlights the ability of this catalyst to convert challenge epoxides into their corresponding cyclic carbonates.

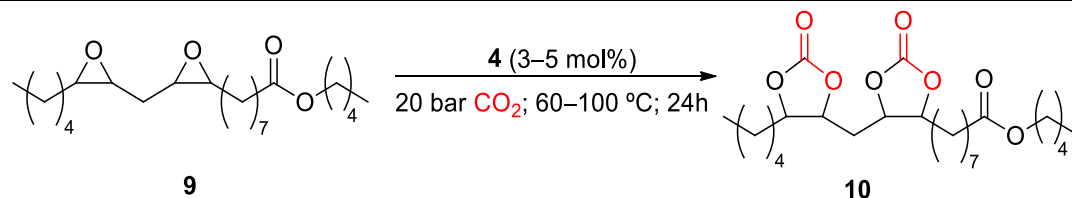
Taking into consideration that catalyst **4** was able to accomplish the formation of mono- and di-substituted cyclic carbonates, we explored its use as organocatalyst for the preparation of highly hindered cyclic carbonates derived from terpenes oxides. Thus, the synthesis of two tri-substituted cyclic carbonates **8i** and **8j** obtained from natural starting materials was carried out (Fig. 2). *cis*-Limonene carbonate **8i** was prepared from commercially available *cis*-limonene oxide and was isolated in 90% yield. Additionally, polycyclic carbonate **8j** derived from (1*R*,4*R*,6*R*,10*S*)-9-methylene-4,12,12-trimethyl-5-oxatricyclo [8.2.0.0<sub>4,6</sub>]dodecane, caryophyllene oxide was obtained in 55% yield. It is important to highlight that the formation of a bis(cyclic carbonate) has not been observed in **8j** because the appearance of a cyclic organic carbonate moiety is not favored on rings bigger than cyclooctane [72]. This cyclic carbonate was isolated diastereoselectively and a unique stereoisomer was obtained with a specific rotation value of  $[\alpha]_{D25}$

= -85.3° (See Fig. S38 in the Supplementary data).

### 3.3. Catalytic results for the preparation of a fatty acid biobased bis(cyclic carbonate)

Catalyst **4** has demonstrated excellent versatility for the synthesis of a broad selection of cyclic carbonates, with these results in mind we then focused our interest to the obtention of a fatty acid biobased bis(cyclic carbonate) **10** derived from a waste fatty acid bis-epoxide *n*-pentyl ester **9** (*cis/trans* ratio of 39:61) (Table 2). The use of biobased precursors for their transformation into the corresponding cyclic carbonates is getting much consideration nowadays [19,34,38,46,54,75–77]. Firstly, the catalytic reaction was studied employing 5 mol% of organocatalyst **4** at 100 °C and 20 bar CO<sub>2</sub> pressure achieving a quantitative conversion of the bis(cyclic carbonate) **10** (Table 2, entry 1). Interestingly, the same results were observed when decreasing the catalytic loading to 3 mol% and the temperature to 80 °C (Table 2, entries 2 and 3), however a slight increase to the *cis* orientation was detected when the temperature went

**Table 2**  
Screening and optimization for the synthesis of bis(cyclic carbonate) **10**.<sup>a</sup>



Entry	Cat (mol%)	Temperature (°C)	Conv. [%] <sup>c</sup>	<i>cis/trans</i> % <sup>d</sup>	TOF (h <sup>-1</sup> ) <sup>e</sup>
1	4 (5)	100	100	32/68	13
2	4 (3)	100	100	38/62	21
3	4 (3)	80	100 (95) <sup>f</sup>	45/55	21
4 <sup>b</sup>	4 (3)	80	46	45/55	17
5	4 (3)	60	19	80/20	4

<sup>a</sup> Reactions were carried out at 60–100 °C and 20 bar CO<sub>2</sub> pressure using 3–5 mol% of **4** for 24 h in the absence of a solvent.

<sup>b</sup> time = 9 h.

<sup>c</sup> Determined by <sup>1</sup>H NMR spectroscopy.

<sup>d</sup> *Cis/trans* ratios were determined by <sup>1</sup>H NMR spectroscopy.

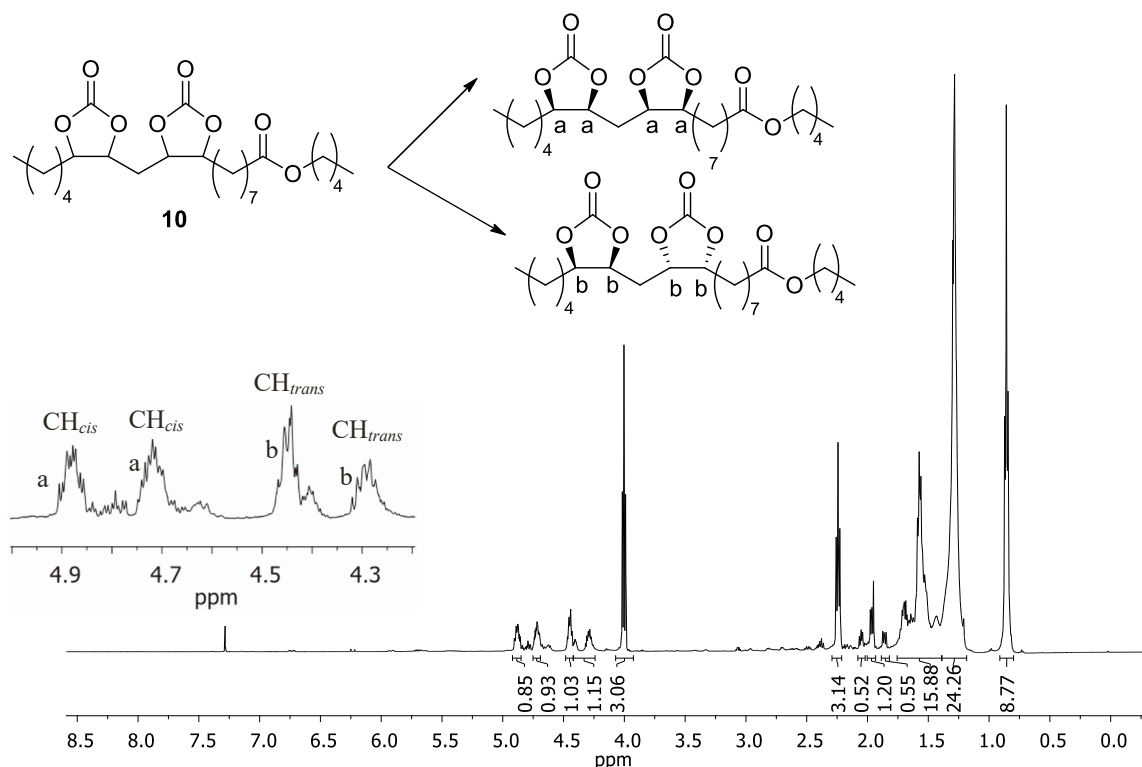
<sup>e</sup> TOF=moles of product/(moles of catalyst × time),

<sup>f</sup> Isolated yield from purified cyclic carbonate in parenthesis.

down (Table 2, entry 3) (Fig. 3). Finally, lower conversions of product **10** were afforded by reducing the reaction time to 9 h and the temperature to 60 °C, respectively (Table 2, entries 4 and 5). It is remarkable to comment that the use of an iodide ion as a nucleophile gave the *trans* isomer as a major product under the optimal reaction conditions as previously reported [34].

To elucidate the reaction mechanism, the interactions amongst bis-imidazole organocatalyst **4** and bis-epoxide **9** with CO<sub>2</sub> were studied spectroscopically in CDCl<sub>3</sub> using a Young valve NMR tube (Fig. 4). Firstly, it was investigated the probable formation of hydrogen bonds

between the –OH groups of the catalyst **4** and the oxygen atom of the bis-epoxide **9**. As can be seen in Fig. 4b, the resonance from the –OH groups of catalyst **4** at 9.40 ppm is broadened. Based on this spectroscopic result, it is possible to conclude the formation of hydrogen bonds between the catalyst **4** and the bis-epoxide **9**. This finding has already been observed by using other imidazole salt-based catalysts for the synthesis of cyclic carbonates [20]. The ring-opening of the internal epoxide was not observed in the absence of CO<sub>2</sub> even submitting to the sample to elevated temperatures (90 °C) and long reaction times (24 h), contrary to what has been previously detected with terminal epoxides [20,66,70,



**Fig. 3.** <sup>1</sup>H NMR spectrum of bis(cyclic carbonate) **10** in CDCl<sub>3</sub> (Table 2, entry 3).

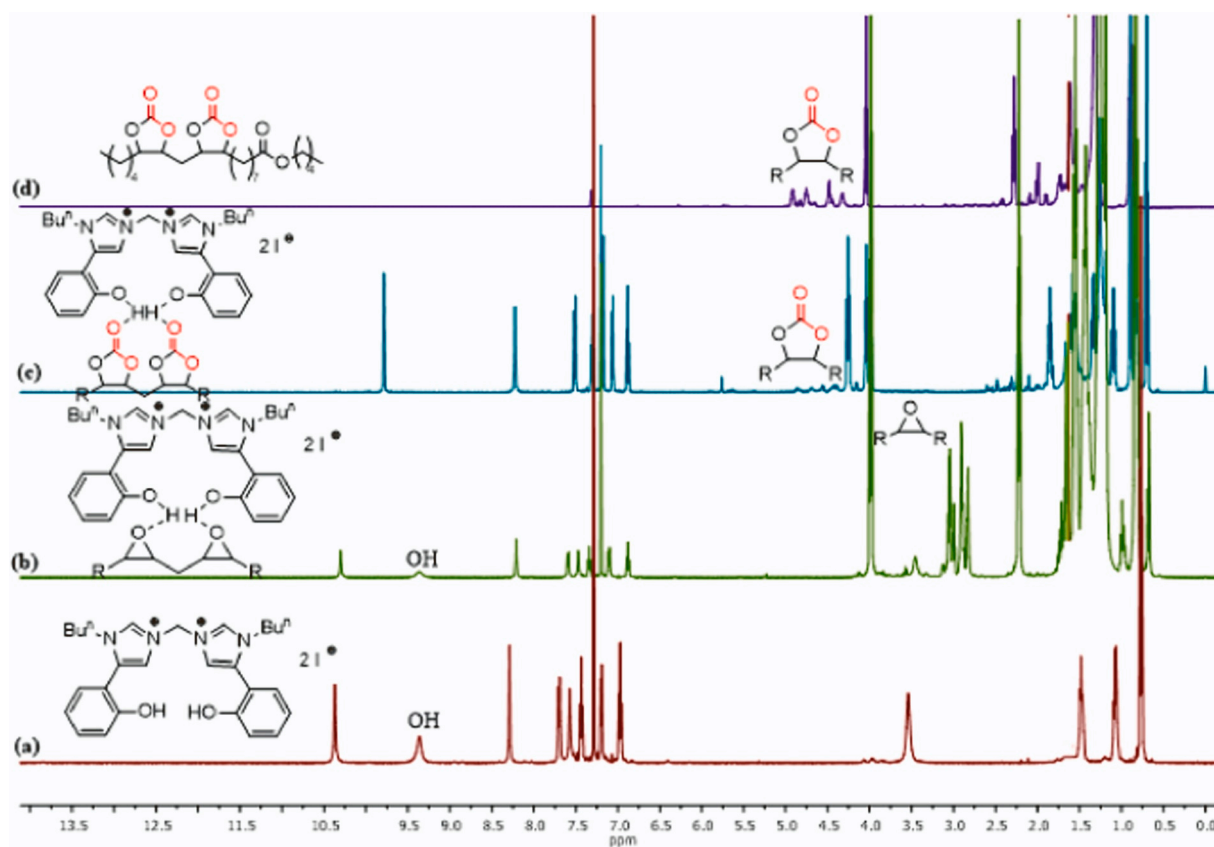
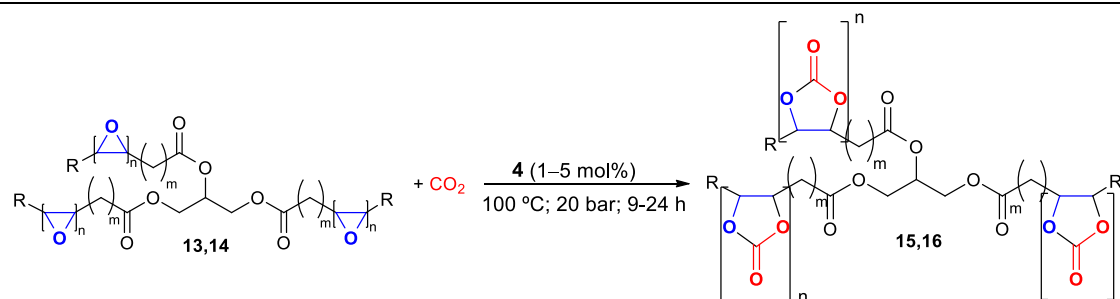


Fig. 4. (a)  $^1\text{H}$  NMR spectrum of catalyst 4 in  $\text{CDCl}_3$ ; (b)  $^1\text{H}$  NMR spectrum of catalyst 4 + bis-epoxide 9 at rt and  $t = 0$  h in  $\text{CDCl}_3$ ; (c)  $^1\text{H}$  NMR spectrum of catalyst 4 + bis-epoxide 9 at  $80^\circ\text{C}$  and 20 bar  $\text{CO}_2$  pressure for 5 h in  $\text{CDCl}_3$ ; (d)  $^1\text{H}$  NMR spectrum of bis(cyclic carbonate) 10 in  $\text{CDCl}_3$ .

Table 3

Catalytic formation of carbonated cooking oils by reaction of epoxidized cooking vegetable oils and  $\text{CO}_2$ .<sup>a</sup>



Entry	Oil-derived epoxides	Cat (mol%)	Time (h)	Conversion (%) <sup>b</sup>
1	13 (olive)	4 (5)	16	100
2	13 (olive)	4 (3)	16	100
3	13 (olive)	4 (1)	16	100
4	13 (olive)	4 (1)	3	35
5	13 (olive)	4 (1)	9	100 (90) <sup>c</sup>
6	14 (sunflower)	4 (1)	9	55
7	14 (sunflower)	4 (2)	9	100 (88) <sup>c</sup>

<sup>a</sup> Reactions were carried out at  $100^\circ\text{C}$  and 20 bar  $\text{CO}_2$  pressure using catalyst 4 (1–5 mol%) for 3–24 h in the absence of a solvent.

<sup>b</sup> Determined by  $^1\text{H}$  NMR spectroscopy.

<sup>c</sup> Isolated yield from purified cyclic carbonate in parenthesis.

78]. Finally, CO<sub>2</sub> was added to the reaction mixture and the synthesis of the corresponding bis(cyclic carbonate) **10** were observed along with a strong interaction through hydrogen bonds between **10** and catalyst **4**, since several of the resonances belonging to the catalyst were clearly shifted in the <sup>1</sup>H NMR spectrum (Fig. 4c). The aforementioned results indicated that the activation of the epoxide by hydrogen bonding was crucial for the formation of cyclic carbonate catalyzed by bis-imidazole salt **4**.

### 3.4. Synthesis of non-isocyanate polyurethanes by polyaddition reaction of fatty acid biobased bis(cyclic carbonate) or carbonated vegetable oils with diamines

Initially, waste vegetable oils (cooking oils derived from olive **11** and sunflower **12**), respectively, were employed as renewable starting material for the synthesis of their corresponding epoxides **13** (olive) and **14** (sunflower). Their fatty acids composition was established by GC-FID and the analysis showed that **11** and **12** had 2.92 and 4.06 double bonds per gram of triglyceride unit, respectively. This analysis also confirmed that oleic acid in **11** and linoleic acid in **12** were the major fatty acid in these waste cooking oils (See Supplementary data, Table S1 and Fig. S1), and after that, **11** and **12** were epoxidized under previously reported conditions [19,71], and the epoxidized olive oil **13** and sunflower oil **14** were obtained quantitatively (See Supplementary data for further details). Then, **13** and **14** were transformed into their corresponding carbonated vegetable oils **15** (olive) and **16** (sunflower) using catalyst **4** in a 30 mL stainless steel reactor at 100 °C and 20 bar CO<sub>2</sub> pressure (Table 3). Exceptional results were afforded for the obtention of **15** at different catalytic loads of 1, 3 and 5 mol% of bis-imidazole **4** at 16 h reaction time (Table 3, entries 1–3). Considering the elevated catalytic activity showed by **4**, then the reaction time was reduced to 9 and 3 h, respectively, (Table 3, entries 4 and 5) obtaining an isolated yield of 90% of carbonated from cooking olive oil at 9 h. Moreover, carbonated from cooking sunflower oil **16** was also obtained with excellent performance using a 2 mol% of catalyst under the same reaction conditions (Table 3, entry 7), since the presence of a greater number of epoxide units implies that obtaining this cyclic carbonate is more challenging.

After that, we decided to investigate the ability of catalyst **4** to be reused in this catalytic process according to a methodology previously reported in the literature [19], and epoxidized olive oil **13** was used as substrate under the optimal reaction conditions previously determined. Thus, the epoxide **13** and organocatalyst **4** were introduced in the reactor at 100 °C and 20 bar of CO<sub>2</sub> pressure for 9 h, and the transformation of epoxide **13** into its corresponding cyclic carbonate **15** was followed by NMR spectroscopy. It is relevant to comment that this reaction was repeated five times and fresh epoxide **13** and the recovered catalyst **4** from the previous cycle were subsequently added to the reactor with the aim to maintain the concentration of catalyst constant at 1 mol%. As it is shown in Fig. 5, the catalytic activity did not decrease significantly over the six consecutive cycles, which demonstrated that

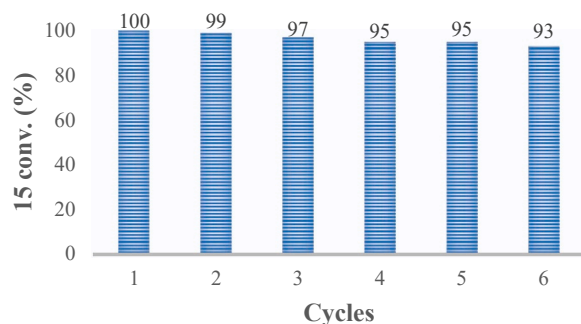


Fig. 5. Reusability investigation of catalyst **4**.

the catalyst **4** did not lose its effectiveness after being reused several times. In addition, the <sup>1</sup>H NMR spectrum of the recovered catalyst **4** did not show any structural modification compared to the compound **4** used in the first catalytic cycle (see Fig. S105 for further details).

The cyclic carbonates derived from biobased source (**10**, **15** and **16**) were used as a carbon source derived from CO<sub>2</sub> for the preparation of non-isocyanate polyurethanes (NIPUs) by their reaction with different diamines (Scheme 2). Firstly, bis(cyclic carbonate) **10** was chosen along with 1,4-diaminobutane (BDA) (a) in a 1:1 molar ratio to select the optimal conditions for the formation of NIPUs. It is worth mentioning that acetonitrile was selected as solvent because of its availability and elevated polarity which would facilitate the solubility of cyclic carbonate and diamine. The reactions were carried out at 80 °C for 16 h using a 10 mol% of 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) as initiator since in its absence the reaction did not take place (Table 4, entry 1) as previously reported, in which the presence of a strong base such as DBU or TBD (1,5,7-triazabicyclo[4.4.0]dec-5-ene) catalyzed this reaction [14,79]. Consequently, several NIPUs were synthesized using a broad range of commercially available diamines (Scheme 2) and the results were shown in Table 4. It is important to comment that according to the fatty acid composition of waste vegetable oils **11** and **12** (Table S1), the molar ratio of carbonated vegetable oil versus diamine was 1/1.5 in the case of **15** and 1/2 with **16**. Ten novel NIPUs were obtained in quantitative conversions after 16 h under aforementioned reaction conditions, four derived from cyclic carbonate **10** (**10a–d**), two derived from carbonated cooking olive oil (**15a,e**) and four derived from carbonated cooking sunflower oil (**16a,b,d,e**) as can be seen in Table 4.

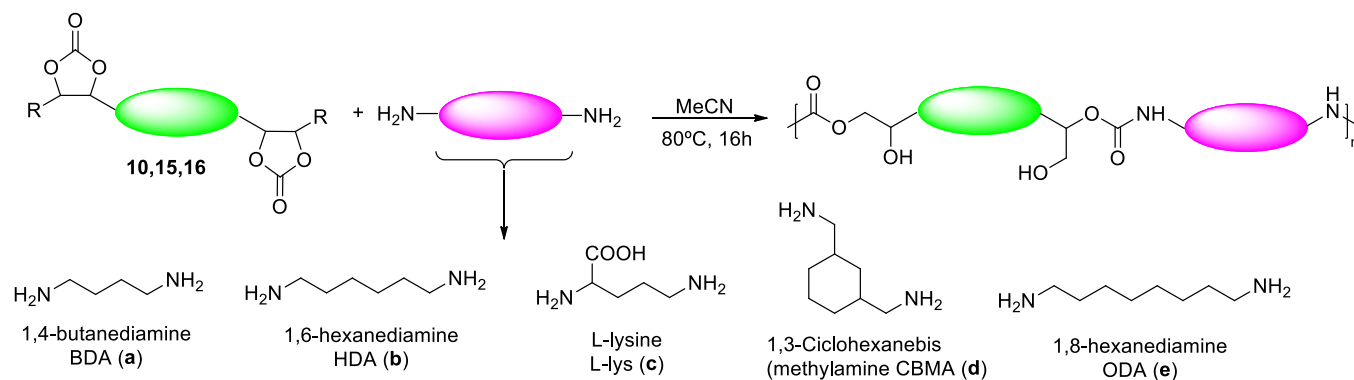
Chemical structures of the synthesized NIPUs were determined by FTIR (Fig. 6 and Supplementary data), <sup>1</sup>H NMR and <sup>13</sup>C-{<sup>1</sup>H}-NMR spectroscopy (Fig. 7 and Supplementary data) and gel permeation chromatography (GPC) (see Supplementary data). The FTIR spectra of carbonated cooking olive oil **15** showed two classic bands at 1802 and 1174 cm<sup>-1</sup>, respectively, corresponding to the cyclic carbonate product (Fig. 6, blue). Nevertheless, those bands did not appear in the FTIR spectrum of PHU **15a** in which a new band were obtained at 1711 cm<sup>-1</sup>, proving the existence of urethane groups (Fig. 6, black). In addition, the band at 1740 cm<sup>-1</sup> was assigned to the C=O stretching vibration of the ester group of the triglyceride unit, which is present in both cyclic carbonate **15** and PHU **15a**. Additionally, another band around 1645 cm<sup>-1</sup> was detected in some PHUs, which corresponds to the C=O stretching vibration of the urea group, revealing the presence of polyurethane-polyurea chains (See Supplementary data for further details) [14,80].

The formation of PHUs was also confirmed by <sup>1</sup>H NMR spectroscopy in which it is observed the presence of the urethane moieties. The appearance of characteristic broadened resonances at 7.06 ppm and 6.75 ppm belonging to the protons of the urethane groups confirmed their existence in the final polymer (Fig. 7). Furthermore, we realized the broadening of the O–H signal at 4.73 and 4.49 ppm corresponding to the hydroxyl groups present in the polymer. Finally, the signal at 2.94 ppm was assigned to the methylene protons of the butanodiamine fragment and the signals at 3.98 ppm, 2.25 ppm and between 1.78–1.10 ppm belonging to the CH<sub>2</sub> groups of the bis(cyclic carbonate) **10**.

The low molecular weights obtained by PHUs between 601 and 1726 g/mol with a polydispersity (PDI) in the range 1.25–2.24 (Table 4) revealed that these polymers were produced as oligomers. These results are probably due to the fact that no catalyst was used during the polyaddition process, and the epoxides used as starting materials (**13** and **14**) are formed by different chains of fatty acids, therefore there was not a control in the polymerization reaction and numerous chains with a wide variety of molecular weights can be produced, which would explain the PDI values found.

Thermal properties of the NIPUs were studied by DSC and TGA (Table 5). DSC thermograms exhibited low glass temperature *T*<sub>g</sub> of the PHUs obtained as previously reported as well for other PHUs, due to the elevated molecular flexibility existing by the hydroxyurethane groups





**Table 4**  
GPC data for synthesized NIPUs.<sup>a</sup>

Entry	Cyclic carbonate	Diamine	NIPU	Conversion (%) <sup>b</sup>	$M_n$ , exp. <sup>c</sup>	PDI <sup>c</sup>
1 <sup>d</sup>	10	BDA (a)	10a	0	-	-
2	10	BDA (a)	10a	100	939	1.94
3	10	HDA (b)	10b	100	1138	1.75
4	10	L-Lys (c)	10c	100	601	1.25
5	10	CBMA (d)	10d	100	747	1.66
6	15	BDA (a)	15a	100	1166	1.96
7	15	ODA (e)	15e	100	1726	2.24
8	16	BDA (a)	16a	100	1108	1.99
9	16	HDA (b)	16b	100	821	1.77
10	16	CBMA (d)	16d	100	1071	2.01
11	16	ODA (e)	16e	100	1271	2.09

<sup>a</sup> Reactions were carried out at 80 °C for 16 h and 10 mol% of DBU as initiator using a molar ratio of 1:1 (10/diamine), 1:1.5 (15/diamine) and 1:2 (16/diamine).

<sup>b</sup> Determined by <sup>1</sup>H NMR spectroscopy.

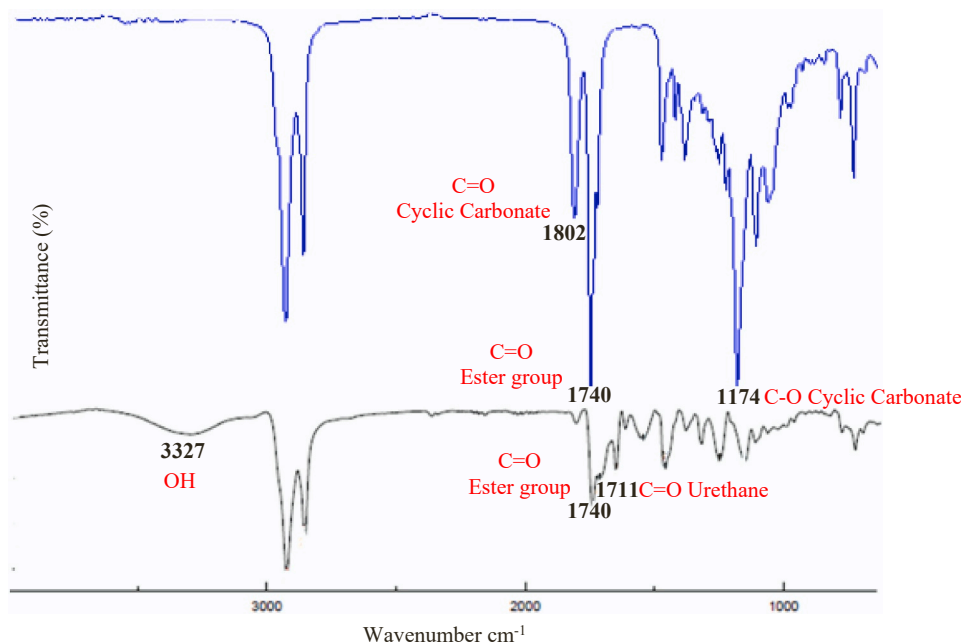
<sup>c</sup> Determined by GPC relative to PMMA standards in chloroform.

<sup>d</sup> No DBU was added.

[14,81,82]. PHUs derived from bis(cyclic carbonate) 10 showed a  $T_g$  around 10 °C (Table 5, entries 1–4), however PHUs derived from carbonated cooking oils (15 and 16) presented various  $T_g$  possibly because of the complex chemical structure displayed by these polymers (Table 5, entries 5–10). Also, in Table 5 the thermal decomposition temperature at 5% loss mass ( $T_{d5\%}$ ) is informed, showing that PHUs prepared using bis(cyclic carbonate) 10 showed a  $T_{d5\%}$  between 170 – 212 °C, meanwhile, the PHUs derived from carbonated cooking oils (15 and 16) presented a higher  $T_{d5\%}$  between 190 to 239 °C.

#### 4. Conclusions

We have designed novel bifunctional bis-imidazole organocatalysts 1 – 6, which acted as efficient catalysts for the preparation of cyclic carbonates from epoxides and carbon dioxide under solvent-free conditions. Iodide derived compound 4 showed the best performance for the formation of monosubstituted cyclic carbonates (8a–e) under moderate reaction conditions (80 °C, 20 bar, 1 h) using just 0.75 mol% of catalyst 4. This catalyst had also the ability to perform the synthesis of more challenging products such as di- (8 f–h) and trisubstituted cyclic carbonates (8i and 8j) in good to excellent yields in most cases. After that, the transformation of the bis-epoxide wasted fatty acid 9 into its corresponding bis(cyclic carbonate) 10 was achieved at 80 °C and 20 bar



**Fig. 6.** IR spectra for 15 (blue) and PHU 15a (black).

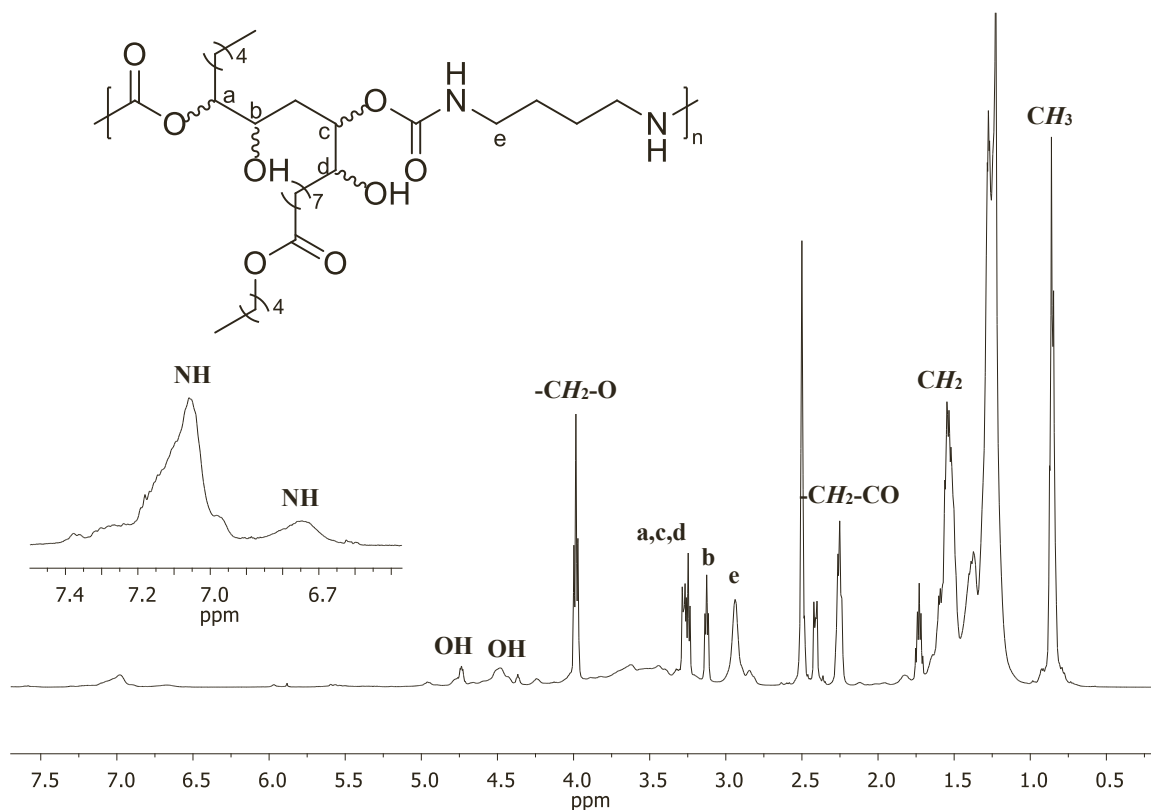


Fig. 7. <sup>1</sup>H NMR spectrum for poly(hydroxyurethane) **10a** in DMSO-d<sub>6</sub>.

**Table 5**  
DSC and TGA analyses for selected PHUs.

Entry	Poly(hydroxyurethane)	T <sub>g</sub> (°C) <sup>a</sup>	T <sub>d</sub> 5% (°C) <sup>b</sup>
1	<b>10a</b>	9	173
2	<b>10b</b>	11	203
3	<b>10c</b>	10	212
4	<b>10d</b>	10	184
5	<b>15a</b>	-20, 8, 18	212
6	<b>15e</b>	-18, 2, 9	226
7	<b>16a</b>	-10, 12	230
8	<b>16b</b>	-10	191
9	<b>16d</b>	-5	239
10	<b>16e</b>	-5, 10	205

<sup>a</sup> Determined by differential scanning calorimetry.

<sup>b</sup> Determined by thermogravimetric analysis.

CO<sub>2</sub> pressure in exceptional conversions, achieving a ratio of *cis/trans* isomers of 45/55. In addition, a set of experiments were carried out between bis-epoxide **9** and catalyst **4** to elucidate the reaction mechanism, and strong interactions by hydrogen bonds were observed between catalyst **4** and bis-epoxide **9** or bis(cyclic carbonate) **10**. It is also relevant to comment that the ring-opening of the internal epoxide was not detected in the absence of CO<sub>2</sub> even at high temperatures (90 °C) and long reaction times (24 h), contrary to what has been previously observed with terminal epoxides. Alternatively, the preparation of carbonated cooking olive oil **15** and cooking sunflower oil **16**, respectively, was successfully carried out from their precursor cooking oils by catalyst **4**.

Finally, we achieved the formation of a wide range of non-isocyanate polyurethanes by the polyaddition reaction of cyclic carbonates **10**, **15** and **16** with different diamines under moderate reaction conditions. All PHUs were obtained quantitatively at 80 °C for 16 h in CH<sub>3</sub>CN as solvent under the presence of 10 mol% of DBU as initiator. The polymers were fully characterized by spectroscopic techniques (NMR and IR), their

molecular weights and polydispersities were determined by GPC and their thermal properties were also studied by DSC and TGA. PHUs were synthesized as oligomers with low molecular weights (601–1726 g/mol) and moderate polydispersities (1.25–2.24) due to there was not a good control in the polymerization reaction and various chains with a huge variety of different molecular weights could be produced.

#### CRediT authorship contribution statement

**Moreno-Villoslada Ignacio:** Investigation, Formal analysis, Methodology. **De la Cruz-Martínez Felipe:** Investigation, Resources. **Castro Osma José Antonio:** Formal analysis, Investigation, Methodology. **Werlinger Francisca:** Formal analysis, Investigation, Methodology. **Caballero María del Prado:** Formal analysis, Investigation, Methodology. **Trofymchuk Oleksandra S.:** Formal analysis, Investigation, Methodology. **Flores Mario E:** Formal analysis, Investigation, Methodology. **Lara-Sánchez Agustín:** Conceptualization, Funding acquisition, Project administration, Visualization, Writing – review & editing, Supervision. **Martínez Javier:** Conceptualization, Investigation, Methodology, Supervision, Validation, Writing – original draft. **Tejeda Juan:** Resources, Supervision.

#### 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.

#### Data availability

No data was used for the research described in the article.

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## Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.jcou.2023.102659](https://doi.org/10.1016/j.jcou.2023.102659).

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