



OPEN Cyclic carbamates based on (*R*)-(+)-limonene oxide for ring-opening polymerization

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A novel synthetic pathway for synthesizing isocyanate-free polyurethanes is reported here. β -Amino alcohols were efficiently synthesized from the aminolysis of the epoxide ring of (*R*)-(+)-limonene oxide with different primary amines as nucleophiles and hot water as catalysts. The regio- and diastereoselectivities of the reactions were investigated and supported by computational studies. DFT calculations were performed to understand the experimental results more deeply. It confirmed the crucial roles of water molecules and the nature of the nucleophile in forming the products. The formation of the product is entirely driven by the free energy of activation that affects the reaction rate. Cyclic carbamates were prepared from β -amino alcohols using the dialkyl carbonate (DAC) chemistry. An oligourethane was obtained from Anionic Ring-Opening Polymerization (AROP) of a cyclic carbamate derived from (*R*)-(+)-limonene-oxide. All the products were characterized by employing ¹H and ¹³C NMR spectroscopies. The assignments of the signals in ¹H and ¹³C NMR spectra were also supported by 2D NMR spectroscopy.

Keywords Isocyanate free, Dimethyl carbonate, Sustainable, Polyurethane, Density functional theory

Polyurethanes (PU) are one of the most important classes of polymers, with an annual production of more than 18 million tons, about 5 mass % of total worldwide polymer production¹. They are very versatile polymers, as they can be thermoplastic, elastomeric, thermoset, and foams². PU are typically prepared by step-growth polymerization between polyols and isocyanates. Isocyanates present concerns regarding their impact on the environment, health, and safety^{3–6}. They are produced from the reaction of amines with toxic phosgene² and have several potential adverse effects on human health^{4–6}. Currently, with the governmental regulatory environment and the general European goal of using the least toxic effective components available, there has been increasing industrial and academic emphasis on obtaining urethane properties from systems that do not employ isocyanates. Bio-based polyurethanes are generally prepared using polyols from natural sources as an alternative to oil-based ones^{7,8}. The most common approaches reported in the literature to obtain isocyanate-free PU are (1) polyaddition of cyclic dicarbonates and diamines (*i.e.*, ring-opening polymerization of cyclic carbonates); (2) polycondensation of linear activated dicarbonates and diamines (*i.e.*, bis(dialkyl carbonate) route); (3) polycondensation of linear activated carbamates and diols (*i.e.*, transurethanization route); (4) ring-opening polymerization (ROP) of cyclic carbamates (*i.e.*, ROP route)^{9–11}. Among them, the ROP of cyclic carbamates is only scarcely investigated. In particular, 5- and 6-membered cyclic carbamates can undergo cationic ROP^{12–14}. More recently, the anionic ROP of cyclic carbamates was reported^{15,16}. However, cyclic carbamates have been limited by very laborious or low-yielding synthetic procedures for their preparation, involving phosgene or its derivatives¹⁷, alkyl halide chemistry^{18–20}, and isocyanate compounds^{21,22}. Recently, new approaches to cyclic carbamates via dialkyl carbonate (DAC) chemistry have been reported^{23,24}.

Herein we report a novel methodology for the synthesis of cyclic carbamates starting from (*R*)-(+)-limonene oxide, a biorenewable derivative of the naturally abundant terpene (*R*)-(+)-limonene. Furthermore, the attempt of Anionic Ring-Opening Polymerization (AROP) of a cyclic carbamate derived from (*R*)-(+)-limonene oxide is described and discussed.

Results and discussion

The Anionic Ring-Opening Polymerization (AROP) of cyclic carbamates based on (*R*)-(+)-limonene oxide yields isocyanate-free (oligo)PU (Fig. 1).

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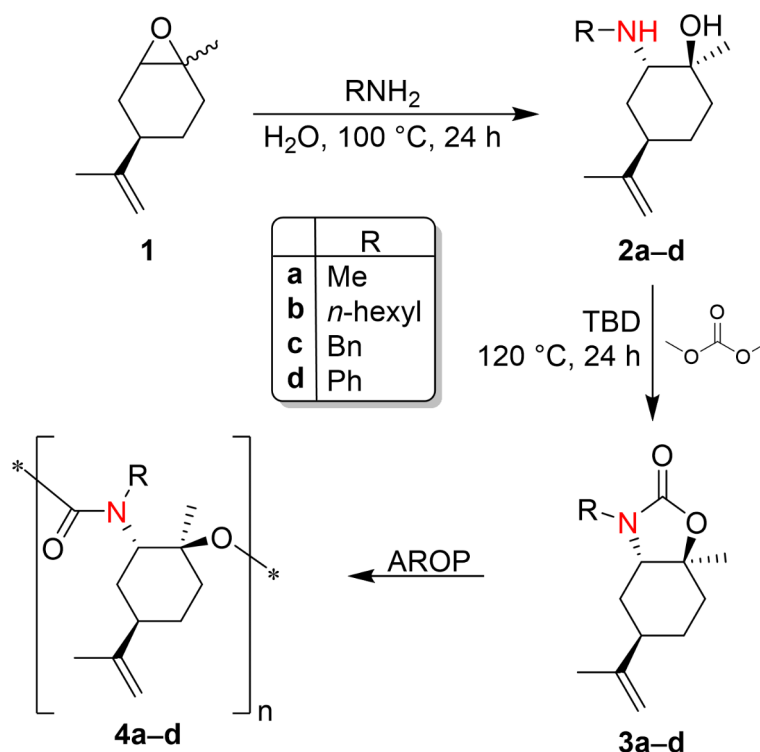


Fig. 1. Reactions pathway for the synthesis of isocyanate-free PU from (*R*)-(+)-limonene oxide.

Entry	Amine	2 (%) ^b	2' (%) ^b	Yield %
1	Methylamine	53	47	97
2	Hexylamine	100	n.d. ^c	50
3	Benzylamine	100	n.d.	50
4	Aniline	73	27	59

Table 1. Aminolysis reaction of (*R*)-(+)-limonene oxide with different amines^a. ^aReaction conditions: (*R*)-(+)-limonene oxide (1 eq.), amine (2 eq. for entries 1 and 4, 1.2 eq. for entries 2,3), water, 100 °C, 24 h. ^bCalculated by integrating the signals in the ¹H NMR spectrum of the crude reaction mixture and by considering their relative abundance. Not detected.

A library of β -amino alcohols was efficiently prepared from the opening of the epoxide of (*R*)-(+)-limonene oxide with primary amines (methylamine, hexylamine, benzylamine, aniline) and in the presence of water as a catalyst with high yields, as highlighted in Table 1.

Without water, the reaction proceeded with very low yields, even after long reaction times and temperatures²⁵. Hot water acts as a mild Brønsted acid catalyst, favoring the epoxide ring-opening by nucleophiles, such as amines^{26–28}. The nucleophile attack occurred preferentially at the less hindered carbon atom. In the case of hexylamine and benzylamine (entries 2 and 3 of Table 1), the lone pair on the nitrogen atom is entirely available, and the activation of the oxirane by hydrogen bonding with water is lost. With methylamine and aniline (entries 1 and 4 of Table 1), 2 equivalents of nucleophile are necessary for the aminolysis of (*R*)-(+)-limonene oxide due to the formation of hydrogen bonding with water (solvent effect) and the low nucleophilicity of aniline (delocalization of the lone pair over the benzene ring). Minimal work-up of the reactions was required by extracting with an organic solvent (diethyl ether or dichloromethane) or by direct water evaporation, leading to the pure ring-opened products with no further purification. It is worth mentioning that commercially available (*R*)-(+)-limonene oxide is a 1:1 mixture of *cis*- and *trans*- isomers (Fig. 2). The separation of the two diastereomers by physical methods (fractional distillation, gas chromatography) is troublesome²⁹.

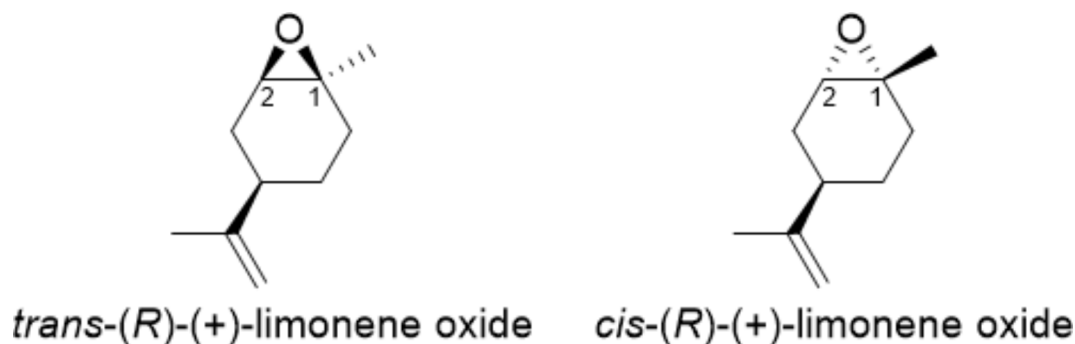


Fig. 2. Chemical structures of *trans*- and *cis*-limonene oxide. The numbers refer to the carbon atoms involved in the amine addition.

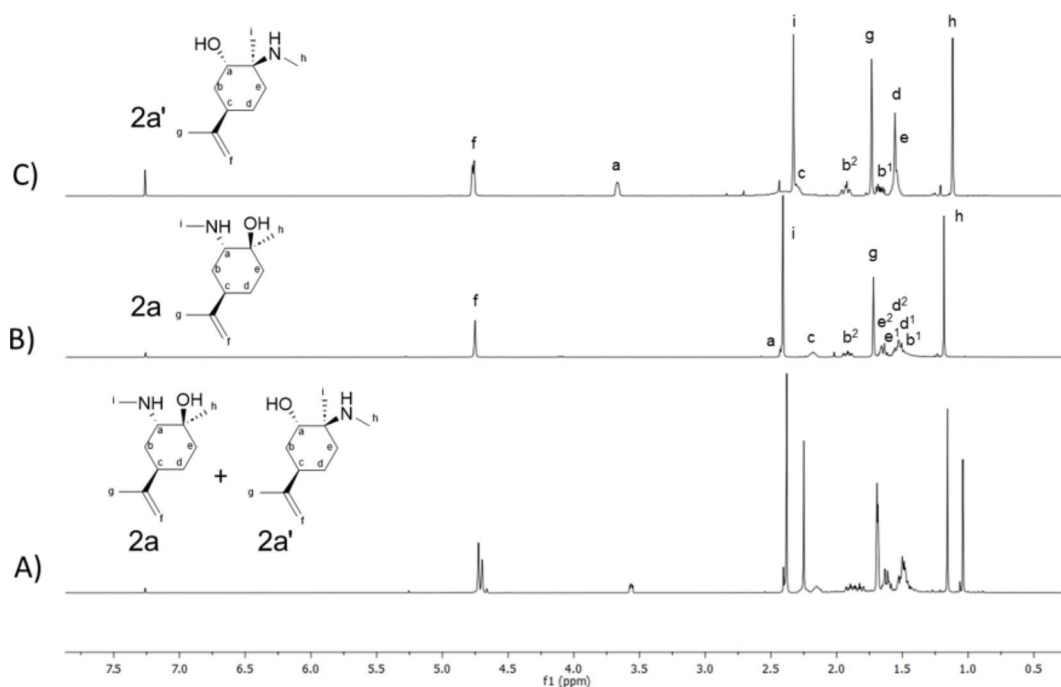


Fig. 3. ^1H NMR spectra (CDCl_3 , 400 MHz) of (A) mixture of **2a** and **2'a** regioisomers; (B) single regioisomer **2a**; (C) single regioisomer **2'a**.

However, the aminolysis reaction of limonene oxide is reported to be regio- and diastereoselective^{28,30–37}. According to the Fürst-Plattner rule, the approach of the nucleophile to cyclohexene oxide derivatives is *trans*-diaxial, leading substantially to *trans*-diaxial opening products favoring a chair-like transition state^{38,39}. The bulky isopropenyl group of (*R*)-(+)-limonene oxide is equatorial in both *cis*- and *trans*-isomers. Generally, nucleophilic amines' aminolysis of limonene oxide occurs preferentially on the *trans*-isomer in an $\text{S}_{\text{N}}2$ -type reaction at the less hindered secondary C-2, leaving the *cis*-isomer substantially unreacted (kinetic resolution)^{31,33,34}. This case was observed for forming β -amino alcohols **2b** and **2c**, where R is a *n*-hexyl and a benzyl substituent, respectively. Contrarily, the $\text{S}_{\text{N}}2$ -type reaction at the less hindered C-2 of the *cis*-isomer would have to occur *via* a boat-like transition state, which is energetically more demanding and unfavorable. However, when utilizing non-nucleophilic amines, the aminolysis reaction does not occur, and the water acts as a nucleophile only on *cis*-limonene oxide at the most hindered tertiary C-1 carbon atom through a chair-like transition state^{31,34}. In this case, an $\text{S}_{\text{N}}1$ -type reaction occurs due to the electronic state of the C-1 carbon but maintains the features of an $\text{S}_{\text{N}}2$ -type reaction, leading to an inversion of configuration at the C-1 atom^{31,34}. Indeed, a mixture of the two regioisomers, **2** and **2'**, was obtained when (*R*)-(+)-limonene oxide was reacted with methylamine and aniline (Table 1, Entries 1 and 4).

2a and **2'a** were separated by flash chromatography and characterized by ^1H NMR spectra (Fig. 3).

To shed light on the experimental outcome, we conducted computational studies at the density functional theory (DFT) level of theory. To obtain as accurate activation energies as possible, the three-dimensional models of all reagents, products, and transition states were fully geometrically optimized at a high level of theory by

employing the PW6B95D3 functional with def2TZVPP basis set implemented in the Gaussian 16 software package. Frequency calculation was used to confirm the nature of the stationary points. Transition structures were found to have only one negative eigenvalue.

To choose the best system to simulate the catalytic action of water, we conducted a molecular dynamics (MD) study under the experimental conditions reported in Table 1 Entry 1 employing the structure of the transition state (TS) for both regioisomeric approach and using water as an explicit solvent (see SI). After 300 ns of MD simulation, the trajectories were analyzed to individuate the most recurrent and reliable water molecules/TS arrangement. This arrangement, containing the first layer of water molecules around the TS, was extrapolated by the MD frame and fully minimized at the GFN2-xTB level of theory. The result, depicted in Fig. 4, shows a network of water molecules, three establishing a hydrogen bond bridge between the oxygen of the epoxide and one of the amine hydrogens and another coordinated by hydrogen bonding with the oxygen of the epoxide, that we retain essential for the correct reproduction of the experimental conditions.

So, all DFT calculations were conducted using an implicit-explicit solvation model using SMD implicit solvation and four explicit water molecules. The two TS conducting to products **2a** and **2'a** are shown in Fig. 5.

Considering that the reactions studied are sufficiently exergonic and, therefore, difficult to reversible, it is evident that the results we observed must depend exclusively on the free activation energies. It is presumable that in the reactions that exclusively produce the compounds **2b** and **2c**, the activation energies for the transition states that lead to the compounds **2'b** and **2'c** must be higher and insurmountable at the reaction temperature of 100 °C; that is, for the latter, the reaction is kinetically much slower and in the reaction time of 24 h the formation of the products is not appreciated.

The enthalpies, free energies, and entropies of activation for all studied TSs, reported in Table 2, support this hypothesis. All the reactions show an elevated free energy of activation heavily penalized by the activation entropy due to the high order of the molecules in the transition state. On the contrary, all the TSs-2 possess an enthalpy of activation almost null (TS-2a) or slightly exothermic (TSs-2b-c), whereas in all the TSs-2' it is slightly endothermic (Table 2).

Activation energies around 50 kcal/mol result in very long reaction times, even at 100 °C. For example, the reaction leading to compounds **2a/2'a** has a 97% yield with a **2a:2'a** ratio close to unity, indicating a nearly complete reaction of both *trans* and *cis* reagents. The reaction for compounds **2d/2'd** has a 59% yield with a

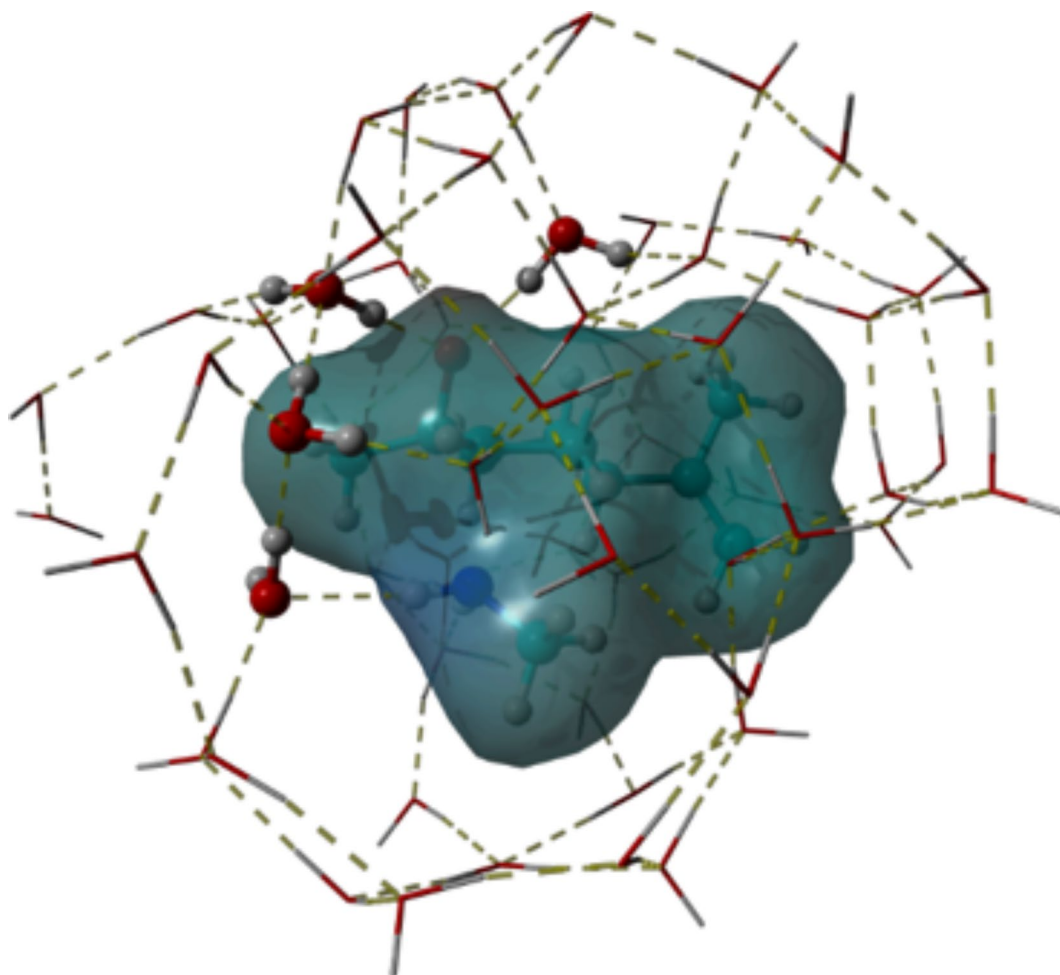


Fig. 4. Representative 3D-geometry for the first-layer solvation of TS conducting to product **2a**.

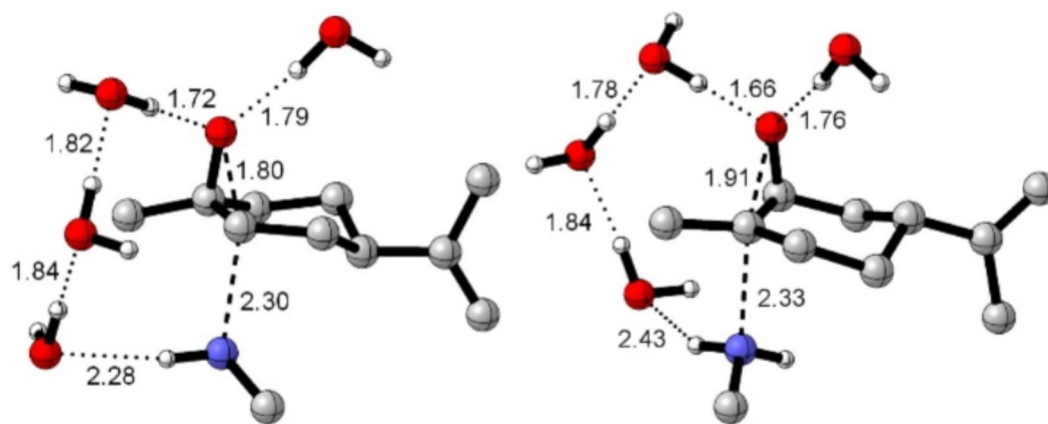


Fig. 5. TSs for the reaction of the *trans* and *cis*-limonene oxides with methylamine. Aliphatic hydrogens were omitted for clarity. Distances were in Å. Dashed lines represent bonds involved in transition states, and dotted lines are hydrogen bonds. Carried out with CYLview20⁴⁰.

TS	DH ^{‡a} (kcal/mol)	DG ^{‡a} (kcal/mol)	DS [‡] (cal/mol/K)
2a	0.004	49.55	−166.18
2'a	2.01	50.40	−162.28
2b	−1.12	50.50	−173.16
2'b	0.37	51.83	−172.61
2c	−0.19	50.11	−168.72
2'c	1.86	51.89	−161.07
2d	−0.34	50.89	−169.85
2'd	1.39	51.11	−164.05

Table 2. Enthalpies, free energies, and entropies of activation for transition states involved in the aminolysis reactions^a. ^aCalculated with respect to the enthalpies, free energies, and entropies of the reactants.

2d:2'd ratio of 2.7, showing that almost 100% of the *trans* reagent converts to **2d** (yielding 43%), while only 15.9% of **2'd** is obtained. Reactions for **b** and **c** yield 50%, producing only **2c** and **2b**, with the *trans* reagent fully converted and the *cis* reagent unreacted. This data suggests a maximum activation barrier beyond which reactions do not occur at 100 °C, producing no detectable products within 24 h. Based on our calculations, this limit is slightly higher than 51.11 kcal/mol, the activation energy for the reaction leading to compound **2'd** (Table 2). Thus, reactions leading to compounds **2'b** and **2'c**, with activation energies of 51.83 and 51.89 kcal/mol, respectively, do not occur.

Cyclic carbamates were obtained by reaction of limonene β-amino alcohols previously prepared with dimethyl carbonate (DMC) in the presence of a catalytic amount of a bicyclic nitrogen base, 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD). Dimethyl carbonate is a versatile, non-toxic, biodegradable chemical belonging to the dialkyl carbonate family (DACs). DACs are ambident electrophiles, meaning they can undergo B_{Ac}2- or B_{Al}2-nucleophilic substitution under appropriate conditions to give alkoxycarbonylation and alkylation reactions, respectively. In this work, the reaction proceeded by a selective double B_{Ac}2 mechanism to obtain the desired cyclic carbamate. Cyclic carbamates were obtained from the reaction of limonene β-amino alcohols and DMC at a bath temperature of 120 °C for 24 h in the presence of 0.5% mol of TBD. The reaction was conducted in a vessel equipped with a magnetic stirrer and reflux condenser. Reaction time and temperature were adjusted and optimized to have a high conversion of the reactants. The reactions performed were monitored through TLC and GC-MS. Cyclic carbamates **3a–d** were characterized by employing ¹H, ¹³C NMR, and ESI-MS spectroscopies.

The assignments of all the signals in ¹H and ¹³C NMR were also supported by ¹H, ¹H COSY, and HSQC (Heteronuclear Single Quantum Coherence) analyses (SI). After the end of each reaction, a simple work-up procedure was adopted, and the pure product was collected with no further purification. In brief, the reaction mixture was dissolved in diethyl ether and washed with deionized water. The dried organic phase was filtered and concentrated under reduced pressure (details are in the experimental part). Notably, the synthetic methodology developed does not use the typical toxic reagents involved in synthesizing cyclic carbamates such as phosgene, alkyl halides, and isocyanates. A library of cyclic carbamates based on (*R*)-(+)-limonene oxide was efficiently synthesized with the above-described method (Table 3), with high yields. The ¹H NMR spectra (Fig. 6) of the synthesized cyclic carbamates **3a–d** are in accordance with the theoretical structures (Fig. 5). The formation of the open carbamates/carbonates was observed when an excess of dimethyl carbonate was used in the reaction mixture. In this latter case, a strong peak near 3.79 ppm due to the −CH₃ protons of DMC was observed. Hence,

Entry	β -amino alcohol	Amine	Yield %
1	3a	Methylamine	69
2	3'a	Methylamine	65
3	3b	Hexylamine	80
4	3c	Benzylamine	70
5	3d	Aniline	80

Table 3. Preparation of cyclic carbamates^a. ^aReaction conditions: β -amino alcohol (1 eq), DMC (1 eq), TBD (0.5 eq), 120 °C, 24 h.

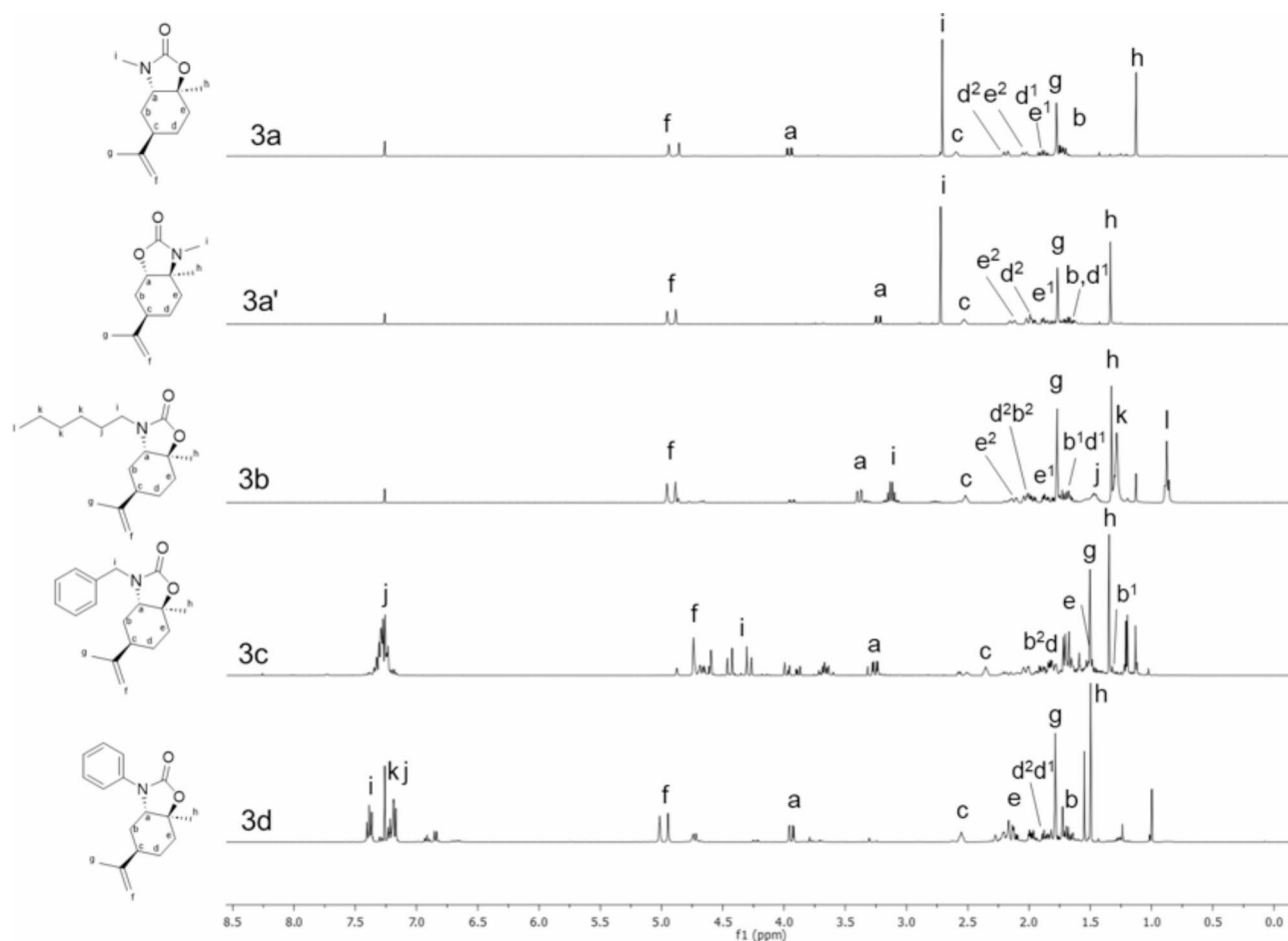


Fig. 6. ¹H NMR spectra (CDCl₃, 400 MHz) of cyclic carbamates **3a–d**.

the absence of this peak in the ¹H NMR spectrum suggests the formation of cyclic carbamate. Another evidence of the formation of the cycle is given by the presence of the C=O of the urethane bond, confirmed by ¹³C NMR spectroscopy, as shown in Table S1. By comparing the ¹H NMR spectra of β -amino alcohols with the corresponding ¹H NMR spectra of cyclic carbamates, it was noticed that in the case of β -amino alcohols, the hydrogens *f* of the isoprenyl group give rise to a single signal, which indicates the equatorial orientation of the isoprenyl group. In the case of cyclic carbamates, two well-separated signals for hydrogens *f* of the isoprenyl group can be distinguished, indicating that the isoprenyl group has an axial orientation³³. Indeed, in β -amino alcohols, the –OH and amino substituents are *trans*-diaxial, and the bulky isoprenyl group is equatorial, as explained above. Probably, a change in the conformation of the cyclohexane ring occurs when the β -amino alcohols react with dimethyl carbonate, and the –OH and amino substituents assume a *trans*-diequatorial orientation to be able to form the cyclic carbamate.

Cyclic carbamates based on (*R*)-(+)-limonene oxide were then investigated as potential monomers to prepare polyurethanes (PU) via Ring-Opening Polymerization (ROP). Monomer **3a** was selected for the polymerization reaction (Fig. 7).

Different types of ROP can be distinguished according to the mechanism involved: Radical Ring-Opening Polymerization (RROP), Cationic Ring Opening Polymerization (CROP), Anionic Ring-Opening

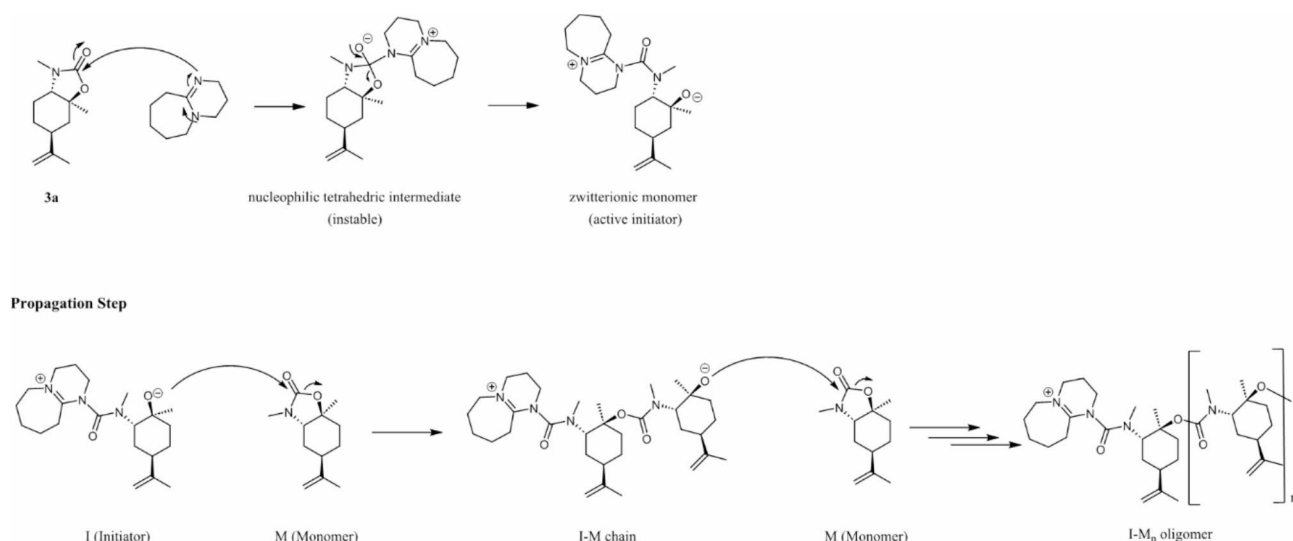


Fig. 7. Chemical structure of monomer (5*R*)-3,7*a*-dimethyl-5-(prop-1-en-2-yl)hexahydrobenzo[d]oxazol-2(3*H*)-one (**3a**), initiation Step of the Anionic Polymerization of Cyclic Carbamate Monomer **3a** with DBU and propagation Step of the Anionic ROP of Cyclic Carbamate **3a** (in the figure labeled as M).

Polymerization (AROP), and Ring-Opening Metathesis Polymerization (ROMP). Some examples of Cationic ROP of cyclic carbamates^{12–14,39}, and Anionic Ring-Opening Polymerization (AROP)^{15,16} are reported in the scientific literature. CROP of 5- and 6-membered cyclic carbamates to yield polyurethanes is generally performed efficiently using boron trifluoride diethyl etherate $\text{BF}_3\text{O}(\text{Et})_2$ or trifluoromethane sulfonate $\text{CF}_3\text{SO}_2\text{R}$ ($\text{R}=\text{OH}$, OCH_3) as initiators in the melt. The polymerization mechanism first involves forming the cationic species via an acid-base reaction between the monomer and the initiator. Then, the propagation step occurs via the nucleophilic attack of a monomer molecule on the electrophilic species. The polymerization continues until the monomer is consumed or with the addition of a nucleophile. However, our system is more complex with respect to what is reported in the literature due to the presence of the cyclohexane ring and the presence of the isoprenyl group. In particular, the double bond of the isoprenyl group is relevant. Since $\text{BF}_3\text{O}(\text{Et})_2$ and triflates are weak and strong acids, respectively, these catalysts were supposed to be inefficient for the ROP of monomer **3a** because they can react well with alkenes. For this reason, it was decided to perform Anionic ROP to polymerize monomer **3a**. At the same time, some experiments of CROP of monomer **3a** were also conducted to verify our hypothesis. Typically, the initiation step of the Anionic ROP of cyclic carbamates occurs via hydrogen abstraction of the N-H proton with a basic initiator (*t*-BuOK, *n*-BuLi) and, in some cases, a co-initiator is needed^{15,16}. In our system, the nitrogen of the urethane bond is substituted with a $-\text{CH}_3$ group in the case of monomer **3a**. Hence, another strategy was performed for the Anionic ROP of monomer **3a**. Cyclic carbonates are polymerized via Anionic ROP using amine initiators (DMAP, DABCO, DBU)⁴¹. In a typical polymerization reaction, the cyclic monomer is weighed into a reaction vessel. The catalyst is added to the monomer in a 0.4% molar ratio. The mixture is magnetically stirred at the selected temperature for 12 h. 1,8-Diazabicyclo(5.4.0)undec-7-ene (DBU) was used as the catalyst for the Anionic ROP of cyclic carbamate **3a**. Table 4 resumes the experimental conditions adopted for the ROP of cyclic carbamate **3a**.

To follow the progression of the polymerization via NMR spectroscopy, first trials were performed using $\text{DMSO}-d_6$ as the solvent. The initiation step of the polymerization (Fig. 7) involves the reaction between **3a** and DBU to obtain a nucleophilic tetrahedral intermediate, which is unstable and gives an alkoxide anion, the active initiator of the polymerization.

The propagation step can occur once the active initiator is formed, as shown in Fig. 7.

By inspecting the ^1H (Fig. 8) and ^{13}C NMR (Figure S13) spectra, the opening of the carbamate ring and the propagation give a PU oligomer. As shown in the ^1H NMR spectrum of the Anionic ROP of monomer **3a** with DBU (spectrum C of Fig. 8), the $-\text{CH}_3$ group bonded to the nitrogen atom at 2.6 ppm belongs to the repeating unit, whereas the peak at 2.8 ppm is the $-\text{CH}_3$ group and represents the terminal group. Integrating these two signals shows that the PU oligomer has 3.82 (~4) repeat units. Further, by inspecting the ^{13}C NMR spectrum of Figure S13, the peak at 165.40 ppm indicates the urea linkage's presence. The low molecular weight of the product is consistent with the steric hindrance of the cyclic carbamate **3a** as the monomer. It should also be noted that a neat polymerization was carried out. In anionic polymerizations, a solvent can strongly influence the nature of the active growing species, favoring the formation of solvated ion pairs or ion clusters. In this work, the anionic ROP of the cyclic carbamate **3a** was carried out under neat conditions to understand the ability of the monomer to form the active initiator species and to propagate without the influence of any solvent. Further research could elucidate the influence of the solvent on the anionic ROP of cyclic carbamate monomers derived from (*R*)-(+)-limonene.

Entry	Catalyst	T (°C)	Time (h)	ROP	\bar{M}_n (Kg mol ⁻¹) ^b
1	DBU	rt.	12	Not observed	/
2	DBU	150	12	Observed	1.197
3	BF ₃ O(Et) ₂	rt.	12	Not observed	/
4	BF ₃ O(Et) ₂	150	12	Mixture of oligomers ^c	n.d. ^d
5	CF ₃ SO ₂ OCH ₃	rt.	12	Not observed	/
6	CF ₃ SO ₂ OCH ₃	150	12	Mixture of oligomers ^c	n.d. ^d

Table 4. Attempted ROP of monomer **3a**.

^aReaction conditions: monomer **3a**: catalyst 1:0.004. ^bDetermined through ¹H NMR spectroscopy (chain end determination). ^cMixed cationic propagations: ROP and electrophilic addition to the alkene. ^dNot determined.

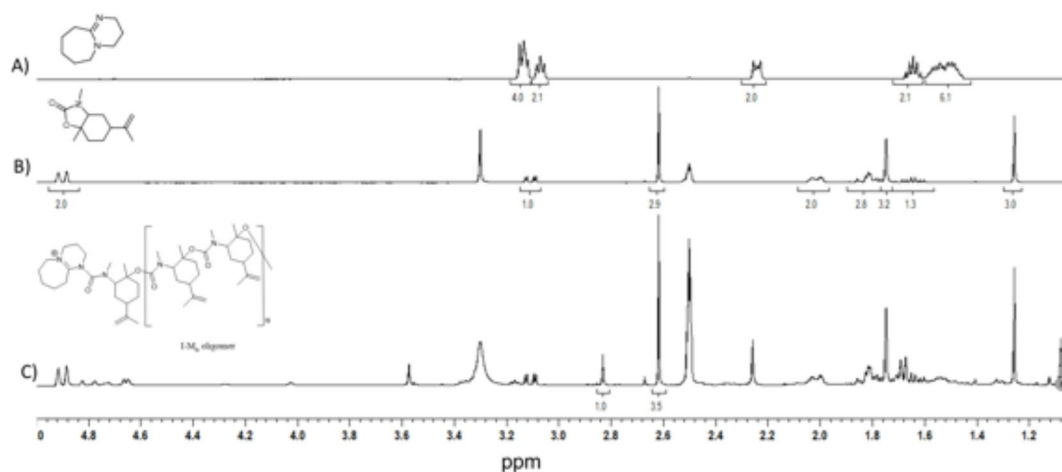


Fig. 8. ¹H NMR spectra (DMSO-d₆, 400 MHz) of: (A) DBU; (B) monomer **3a**; (C) Anionic ROP of monomer **3a** with DBU.

Conclusions

A novel synthetic pathway for the synthesis of polyurethanes without using toxic reagents, *i.e.*, isocyanates, was designed and performed starting from limonene as a natural source. In particular, the enantiomer (*R*)-(+)-limonene was used. A library of β -amino alcohols was efficiently synthesized from the aminolysis of the epoxide ring of (*R*)-(+)-limonene-oxide with different amines as nucleophiles and water as solvent and catalyst. The regio- and diastereoselectivity of the reactions were investigated and supported by computational studies. The β -amino alcohols obtained were then used for the synthesis of 5-membered cyclic carbamates by using the dialkylcarbonate (DAC) chemistry. A library of cyclic carbamates was obtained. Cyclic carbamates are suitable monomers for the Ring-Opening Polymerization (ROP) to yield isocyanate-free polyurethanes. One of the cyclic carbamates derived from (*R*)-(+)-limonene was used as a monomer, and Anionic Ring-Opening Polymerization (AROP) was performed. A polyurethane oligomer was obtained, thus validating the synthetic pathway designed in this work to synthesize polyurethanes from natural sources without using toxic reagents and solvents, following the principles of green chemistry. Combining the experimental results and the DFT calculations, it is clear that the presence of water as an acid catalyst at a temperature of 100 °C and the nature of the nucleophile have a crucial role in forming the products; interestingly, the formation of the product is entirely driven by the free energy of activation that affects the rate of reaction. Above an approximate value of 51.6 kcal/mol, the reaction, at a temperature of 100 °C, is extremely slow for forming products **2'b** and **2'c**.

Experimental part

Materials. Reagents and solvents commercially available were purchased and used without further purification:

Methylamine 40% w/w in water (Sigma Aldrich – Merck), hexylamine (Sigma Aldrich – Merck), ethanolamine (Sigma Aldrich – Merck), ammonium hydroxide solution 30% w/w in water (Sigma Aldrich – Merck), limonene (Sigma Aldrich – Merck), limonene epoxide (Sigma Aldrich – Merck), benzylamine (Sigma Aldrich – Merck), aniline (Sigma Aldrich – Merck), dimethylcarbonate (Sigma Aldrich – Merck), 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD, Sigma Aldrich – Merck), 1,8-Diazabicyclo(5.4.0)undec-7-ene (DBU, Sigma Aldrich – Merck), boron trifluoride diethyl etherate (Sigma Aldrich – Merck), methyl trifluoromethanesulfonate (Sigma Aldrich – Merck), dichloromethane (Sigma Aldrich – Merck), diethyl ether (Sigma Aldrich – Merck), sodium sulphate anhydrous (Sigma Aldrich – Merck), acetone (Sigma Aldrich – Merck), deuterated chloroform (CDCl_3 , Sigma Aldrich – Merck), deuterated dimethyl sulfoxide ($\text{DMSO}-d_6$, Sigma Aldrich – Merck).

General procedure for β -amino alcohols

In a 50 mL round bottomed flask equipped with magnetic stirrer and reflux condenser were added in sequence (R)-(+)-limonene oxide and the selected primary amine (methylamine solution 40 wt % in H_2O , hexylamine, benzylamine, aniline), in H_2O as catalyst and solvent. The reaction mixture was left stirring at 100 °C for 24 h. The reaction was monitored by means of GC-MS. After the reaction was complete, the product was isolated by removal of water or by extracting with dichloromethane or diethyl ether. The products were characterized by means of ^1H , ^{13}C NMR, and ESI-MS spectroscopies.

Synthesis of (1S,2S,4R)-2-amino-1-methyl-4-(prop-1-en-2-yl)cyclohexan-1-ol (**3a**) and (1S,2S,5R)-2-amino-2-methyl-5-(prop-1-en-2-yl)cyclohexan-1-ol (**3a'**).

In a 50 mL round bottomed flask equipped with magnetic stirrer and reflux condenser were added in sequence (R)-(+)-limonene oxide (5 g, 0.033 mol) in H_2O and methylamine solution 40 wt % in H_2O (3 mL, 0.04 mol). The reaction mixture was left stirring at 100 °C for 24 hours. After this time, the product was extracted from water using dichloromethane. A yellow viscous liquid was obtained (5.84 g, 97% yield), comprising of regioisomers (1S,2S,4R)-2-amino-1-methyl-4-(prop-1-en-2-yl)cyclohexan-1-ol (**3a**) and (1S,2S,5R)-2-amino-2-methyl-5-(prop-1-en-2-yl)cyclohexan-1-ol (**3a'**). The two regioisomers were separated by flash chromatography, eluting with EtOAc/EtOH 1:1.

(1S,2S,4R)-2-amino-1-methyl-4-(prop-1-en-2-yl)cyclohexan-1-ol (**3a**). Yellow oil. ^1H NMR (CDCl_3 , 400 MHz) δ (ppm) 4.75 (s, 2 H), 2.41 (s, 3 H), 2.20 (dd, 1 H), 1.92 (ddd, 1 H), 1.72 (s, 3 H), 1.59–1.71 (m, 2 H), 1.42–1.59 (m, 4 H), 1.19 (s, 3 H). ^{13}C NMR (CDCl_3 , 100 MHz) δ (ppm) 148.89, 109.39, 72.11, 64.26, 37.86, 35.06, 34.79, 29.51, 26.30, 25.59, 21.58. ESI mass spectra, m/z (MeOH): 184.2 ($[\text{M} + \text{H}]^+$).

(1S,2S,5R)-2-amino-2-methyl-5-(prop-1-en-2-yl)cyclohexan-1-ol (**3a'**). Yellow oil. ^1H NMR (CDCl_3 , 400 MHz) δ (ppm) 4.68 (s, 2 H), 3.60 (dd, 1 H), 2.26 (s, 3 H), 1.80–1.95 (ddd, 1 H), 1.67 (s, 3 H), 1.59 (ddd, 1 H), 1.41–1.53 (m, 4 H), 1.11–1.25 (m, 1 H), 1.05 (s, 3 H). ^{13}C NMR (CDCl_3 , 100 MHz) δ (ppm) 148.63, 109.34, 71.88, 63.69, 37.78, 33.17, 29.79, 27.50, 25.43, 21.52, 20.20. ESI mass spectra, m/z (MeOH): 184.2 ($[\text{M} + \text{H}]^+$), 206.2 ($[\text{M} + \text{Na}]^+$).

Synthesis of (1S,2S,4R)-2-(hexylamino)-1-methyl-4-(prop-1-en-2-yl)cyclohexan-1-ol (**3b**).

In a 50 mL round bottomed flask equipped with magnetic stirrer and reflux condenser were added in sequence (R)-(+)-limonene oxide (0.55 g, 3.62 mmol) in H_2O and hexylamine (0.44 g, 4.34 mmol) in H_2O as catalyst and solvent. The reaction mixture was left stirring at 100 °C for 24 h. After this time, the unreacted starting materials were separated from the product by distillation. (1S,2S,4R)-2-(hexylamino)-1-methyl-4-(prop-1-en-2-yl)cyclohexan-1-ol (**3b**) was obtained as a dark yellow viscous liquid (0.54 g, 59% yield). ^1H NMR (CDCl_3 , 400 MHz) δ (ppm) 4.78 (s, 2 H), 2.77–2.70 (m, 1 H), 2.52–2.45 (m, 2 H), 2.23 (s, 1 H), 1.99–1.93 (m, 1 H), 1.74 (s, 3 H), 1.69–1.64 (m, 2 H), 1.56–1.45 (m, 5 H), 1.33–1.30 (m, 6 H), 1.20 (s, 3 H), 0.88 (t, 3 H). ^{13}C NMR (CDCl_3 , 100 MHz) δ (ppm) 148.52, 109.42, 72.09, 61.97, 48.23, 38.01, 34.59, 31.75, 30.74, 30.31, 27.13, 26.99, 26.05, 22.63, 21.61, 14.03. ESI mass spectra, m/z (MeOH): 254.2 ($[\text{M} + \text{H}]^+$), 276.1 ($[\text{M} + \text{Na}]^+$).

Synthesis of (1S,2S,5R)-2-methyl-2-(methylamino)-5-(prop-1-en-2-yl)cyclohexan-1-ol (**3c**).

In a 50 mL round bottomed flask equipped with magnetic stirrer and reflux were added in sequence (R)-(+)-limonene oxide (3 g, 0.02 mol) in H_2O and benzylamine (2.53 g, 0.024 mol) in H_2O as catalyst and solvent. The reaction mixture was left stirring at 100 °C for 24 h. After this time, the unreacted starting materials were separated from the product by distillation. (1S,2S,5R)-2-methyl-2-(methylamino)-5-(prop-1-en-2-yl)cyclohexan-1-ol (**3c**) was obtained as a yellow oil (3.5 g, 69% yield). ^1H NMR (CDCl_3 , 400 MHz) δ (ppm) 7.34 (m, 5 H), 4.77 (s, 2 H), 3.85–3.60 (m, 2 H), 2.62 (m, 1 H), 2.26 (m, 1 H), 1.99 (m, 1 H), 1.73 (s, 3 H), 1.66–1.70 (m, 2 H), 1.50–1.64 (m, 3 H), 1.24 (s, 3 H). ^{13}C NMR (CDCl_3 , 100 MHz) δ (ppm) 148.86, 141.01, 128.52, 128.33, 128.27, 127.10, 109.46, 72.28, 65.98, 61.49, 52.39, 38.13, 34.65, 30.30, 26.29, 21.62. ESI mass spectra, m/z (MeOH): 260.1 ($[\text{M} + \text{H}]^+$), 282.1 ($[\text{M} + \text{Na}]^+$).

Synthesis of (1S,2S,4R)-1-methyl-2-(phenylamino)-4-(prop-1-en-2-yl)cyclohexan-1-ol (**3d**) and (1S,2S,5R)-2-methyl-2-(phenylamino)-5-(prop-1-en-2-yl)cyclohexan-1-ol (**3d'**).

In a 50 mL round bottomed flask equipped with magnetic stirrer and reflux were added in sequence (R)-(+)-limonene oxide (0.3 g, 1.97 mmol) in H_2O and aniline (0.37 g, 3.95 mmol) in H_2O as catalyst and solvent. The reaction mixture was left stirring at 100 °C for 24 hours. After this time, the unreacted starting materials were separated from the product by distillation. A mixture of (1S,2S,4R)-1-methyl-2-(phenylamino)-4-(prop-1-en-2-yl)cyclohexan-1-ol (**3d**) and (1S,2S,5R)-2-methyl-2-(phenylamino)-5-(prop-1-en-2-yl)cyclohexan-1-ol (**3d'**) was obtained as amber oil (0.28 g, 59% yield). ^1H NMR (CDCl_3 , 400 MHz) δ (ppm) 7.19–7.15 (m, 4 H), 6.83–6.80 (m, 2 H), 6.71–6.65 (m, 4 H), 4.75 (d, 4 H), 3.64 (t, 1 H), 3.52 (t, 1 H), 2.36–2.25 (m, 1 H), 2.14–2.09 (m, 1 H), 2.0–1.90 (m, 2 H), 1.74 (s, 3 H), 1.71 (s, 3 H), 1.68–1.65 (m, 2 H), 1.62–1.55 (m, 2 H), 1.28 (s, 6 H). ^{13}C NMR (CDCl_3 , 100 MHz) δ (ppm) 149.44, 149.21, 148.70, 147.78, 129.48, 129.13, 117.72, 117.56, 113.57, 109.56, 109.11, 74.05, 72.06, 71.85, 71.43, 38.44, 37.59, 34.73, 34.15, 33.82, 33.62, 33.13, 31.31, 26.95, 26.78, 26.33, 26.12, 26.08, 23.23, 21.40, 21.28, 21.19. ESI mass spectra, m/z (MeOH): 246.1 ($[\text{M} + \text{H}]^+$), 268.1 ($[\text{M} + \text{Na}]^+$).

General procedure for cyclic carbamates

In a 50 mL round bottomed flask equipped with magnetic stirrer and reflux condenser were added in sequence the selected β -amino alcohol (**3a-d**), dimethylcarbonate (DMC) and the catalyst 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD). The reaction mixture was left stirring at 120 °C for 24 h. The reaction was monitored by means of GC-MS. After the reaction was complete, the residue was dissolved in diethyl ether and washed with deionized water (15 mL) for three times. The organic phase was dried over anhydrous Na_2SO_4 , filtered through filter paper and concentrated under reduced pressure. The products were characterized by means of ^1H , ^{13}C NMR, and ESI-MS spectroscopies.

Synthesis of (5*R*)-3,7a-dimethyl-5-(prop-1-en-2-yl)hexahydrobenzo[d]oxazol-2(3*H*)-one (**4a**).

In a 50 mL round bottomed flask equipped with magnetic stirrer and reflux condenser were added in sequence (1*S*,2*S*,4*R*)-2-amino-1-methyl-4-(prop-1-en-2-yl)cyclohexan-1-ol (**3a**, 0.101 g, 0.55 mmol), dimethylcarbonate (DMC, 0.05 g, 0.055 mmol) and the catalyst 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD, 0.04 g, 0.28 mmol). The reaction mixture was left stirring at 120 °C for 24 h. The reaction was monitored by means of GC-MS. After the reaction was complete, the residue was dissolved in diethyl ether and washed with deionized water (15 mL) for three times. The organic phase was dried over anhydrous Na_2SO_4 , filtered through filter paper and concentrated under reduced pressure. Pure (5*R*)-3,7a-dimethyl-5-(prop-1-en-2-yl)hexahydrobenzo[d]oxazol-2(3*H*)-one (**4a**) was obtained as a brownish solid (0.08 g, 69% yield). ^1H NMR (CDCl_3 , 400 MHz) δ (ppm) 4.95 (s, 1 H), 4.88 (s, 1 H), 3.23 (dd, 1 H), 2.72 (s, 3 H), 2.55–2.52 (m, 1 H), 2.18–2.11 (m, 1 H), 2.03–1.95 (m, 2 H), 1.90–1.83 (m, 1 H), 1.74 (s, 3 H), 1.72–1.62 (m, 2 H), 1.34 (s, 3 H). ^{13}C NMR (CDCl_3 , 100 MHz) δ (ppm) 160.91, 146.65, 111.93, 82.72, 62.73, 38.29, 32.62, 29.65, 25.78, 25.53, 22.78, 17.71. ESI mass spectra, m/z (MeOH): 232.1 ($[\text{M} + \text{Na}]^+$).

Synthesis of (6*R*)-3,3a-dimethyl-6-(prop-1-en-2-yl)hexahydrobenzo[d]oxazol-2(3*H*)-one (**4a'**).

In a 50 mL round bottomed flask equipped with magnetic stirrer and reflux condenser were added in sequence (1*S*,2*S*,5*R*)-2-amino-2-methyl-5-(prop-1-en-2-yl)cyclohexan-1-ol (**3a'**, 0.05 g, 0.27 mmol), dimethylcarbonate (DMC, 0.025 g, 0.27 mmol) and the catalyst 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD, 0.02 g, 0.14 mmol). The reaction mixture was left stirring at 120 °C for 24 h. The reaction was monitored by means of GC-MS. After the reaction was complete, the residue was dissolved in diethyl ether and washed with deionized water (15 mL) for three times. The organic phase was dried over anhydrous Na_2SO_4 , filtered through filter paper and concentrated under reduced pressure. Pure (6*R*)-3,3a-dimethyl-6-(prop-1-en-2-yl)hexahydrobenzo[d]oxazol-2(3*H*)-one (**4a'**) was obtained as a white solid (0.04 g, 65% yield). ^1H NMR (CDCl_3 , 400 MHz) δ (ppm) 4.94 (s, 1 H), 4.86 (s, 1 H), 3.96 (dd, 1 H), 2.71 (s, 3 H), 2.61–2.59 (m, 1 H), 2.22–2.16 (m, 1 H), 2.06–2.02 (m, 1 H), 1.92–1.84 (m, 1 H), 1.78 (s, 3 H), 1.75–1.73 (m, 2 H), 1.70–1.68 (m, 1 H), 1.13 (s, 3 H). ^{13}C NMR (CDCl_3 , 100 MHz) δ (ppm) 159.49, 146.54, 111.56, 79.87, 62.61, 39.11, 31.18, 26.34, 25.09, 24.11, 22.80, 13.03. ESI mass spectra, m/z (MeOH): 232.1 ($[\text{M} + \text{Na}]^+$).

Synthesis of (5*R*)-3-hexyl-7a-methyl-5-(prop-1-en-2-yl)hexahydrobenzo[d]oxazol-2(3*H*)-one (**4b**).

In a 50 mL round bottomed flask equipped with magnetic stirrer and reflux condenser were added in sequence (1*S*,2*S*,4*R*)-2-(hexylamino)-1-methyl-4-(prop-1-en-2-yl)cyclohexan-1-ol (**3b**, 0.2 g, 0.79 mmol), dimethylcarbonate (DMC, 0.07 g, 0.79 mmol) and the catalyst 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD, 0.05 g, 0.4 mmol). The reaction mixture was left stirring at 120 °C for 24 h. The reaction was monitored by means of GC-MS. After the reaction was complete, the residue was dissolved in diethyl ether and washed with deionized water (15 mL) for three times. The organic phase was dried over anhydrous Na_2SO_4 , filtered through filter paper and concentrated under reduced pressure. Pure (5*R*)-3-hexyl-7a-methyl-5-(prop-1-en-2-yl)hexahydrobenzo[d]oxazol-2(3*H*)-one (**4b**) was obtained as dark yellow oil (0.18 g, 80% yield). ^1H NMR (CDCl_3 , 400 MHz) δ (ppm) 4.96 (s, 1 H), 4.89 (s, 1 H), 3.39 (dd, 1 H), 3.19–1.08 (m, 2 H), 2.53–2.50 (m, 1 H), 2.20–2.10 (m, 1 H), 2.05–1.95 (m, 2 H), 1.88–1.81 (m, 1 H), 1.77 (s, 3 H), 1.74–1.66 (m, 2 H), 1.48–1.44 (m, 1 H), 1.33 (s, 3 H), 1.28 (m, 6 H), 0.88 (t, 3 H). ^{13}C NMR (CDCl_3 , 100 MHz) δ (ppm) 159.98, 146.53, 111.82, 82.37, 60.95, 42.88, 38.28, 32.44, 32.01, 31.61, 28.26, 26.71, 25.66, 25.56, 22.71, 22.62, 17.57, 14.10. ESI mass spectra, m/z (MeOH): 301.1 ($[\text{M} + \text{Na}]^+$).

Synthesis of (5*R*)-3-benzyl-7a-methyl-5-(prop-1-en-2-yl)hexahydrobenzo[d]oxazol-2(3*H*)-one (**4c**).

In a 50 mL round bottomed flask equipped with magnetic stirrer and reflux condenser were added in sequence (1*S*,2*S*,5*R*)-2-methyl-2-(methylamino)-5-(prop-1-en-2-yl)cyclohexan-1-ol (**3c**, 1 g, 3.86 mmol), dimethylcarbonate (DMC, 0.35 g, 3.86 mmol) and the catalyst 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD, 0.27 g, 1.93 mmol). The reaction mixture was left stirring at 120 °C for 24 h. The reaction was monitored by means of GC-MS. After the reaction was complete, the residue was dissolved in diethyl ether and washed with deionized water (20 mL) for three times. The organic phase was dried over anhydrous Na_2SO_4 , filtered through filter paper and concentrated under reduced pressure. (5*R*)-3-benzyl-7a-methyl-5-(prop-1-en-2-yl)hexahydrobenzo[d]oxazol-2(3*H*)-one (**4c**) was obtained as dark orange oil (0.87 g, 70% yield). ^1H NMR (CDCl_3 , 400 MHz) δ (ppm) 7.27 (m, 5 H), 4.74 (s, 2 H), 4.47–4.27 (m, 2 H), 3.25 (dd, 1 H), 2.36 (m, 1 H), 2.05–2.01 (m, 1 H), 1.87–1.79 (m, 2 H), 1.61–0.51 (m, 2 H), 1.51 (s, 3 H), 1.49–1.41 (m, 1 H), 1.35 (s, 3 H). ^{13}C NMR (CDCl_3 , 100 MHz) δ (ppm) 160, 146.26, 136.7, 128.52, 127.98, 111.5, 82.39, 60.51, 47.43, 38.13, 32.70, 31.98, 27.04, 25.25, 22.18, 17.54. ESI mass spectra, m/z (MeOH): 308.1 ($[\text{M} + \text{Na}]^+$).

Synthesis of (5*R*)-7a-methyl-3-phenyl-5-(prop-1-en-2-yl)hexahydrobenzo[d]oxazol-2(3*H*)-one (**4d**).

In a 50 mL round bottomed flask equipped with magnetic stirrer and reflux condenser were added in sequence (1*S*,2*S*,4*R*)-1-methyl-2-(phenylamino)-4-(prop-1-en-2-yl)cyclohexan-1-ol (**3d**) and (1*S*,2*S*,5*R*)-2-methyl-2-(phenylamino)-5-(prop-1-en-2-yl)cyclohexan-1-ol (**3d'**, 0.08, 0.33 mmol), dimethylcarbonate (DMC, 0.03 g, 0.33 mmol) and the catalyst 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD, 0.023 g, 0.165 mmol). The reaction mixture was left stirring at 120 °C for 24 h. The reaction was monitored by means of GC-MS. After the reaction was complete, the residue was dissolved in diethyl ether and washed with deionized water (20 mL) for three times. The organic phase was dried over anhydrous Na_2SO_4 , filtered through filter paper and concentrated under reduced pressure. (5*R*)-7a-methyl-3-phenyl-5-(prop-1-en-2-yl)hexahydrobenzo[d]oxazol-2(3*H*)-one (**4d**) was

obtained as white solid (0.02 g, 80% yield). ^1H NMR (CDCl_3 , 400 MHz) δ (ppm) 7.40–7.37 (m, 2 H), 7.30–7.28 (m, 1 H), 7.23–7.7 (m, 2 H), 5.01 (s, 1 H), 4.95 (s, 1 H), 3.94 (dd, 1 H), 2.55 (m, 1 H), 2.27–2.09 (m, 2 H), 2.0–1.96 (m, 1 H), 1.89–1.82 (m, 1 H), 1.79 (s, 3 H), 1.73–1.64 (m, 2 H), 1.50 (s, 3 H). ^{13}C NMR (CDCl_3 , 100 MHz) δ (ppm) 158.17, 146.64, 129.21, 125.98, 123.72, 112.01, 83.14, 61.93, 38.41, 32.57, 25.65, 25.52, 22.86, 18.0. ESI mass spectra, m/z (MeOH): 294.0 ($[\text{M} + \text{Na}]^+$).

Polymerization of cyclic carbamate **4a** via Anionic Ring-Opening Polymerization.

The glass vessel used for the polymerization reaction was first heated to 80 °C *in vacuo*, then filled with dry nitrogen and, during the reaction, handled in a stream of dry nitrogen. The monomer (5*R*)-3,7a-dimethyl-5-(prop-1-en-2-yl)hexahydrobenzo[d]oxazol-2(3*H*)-one (**4a**, 0.07 g, 0.35 mmol) was weighed directly into the reaction vessel, the catalyst 1,8-Diazabicyclo(5.4.0)undec-7-ene (DBU, 0.2 mg, 1.4×10^{-3} mmol) was added to the monomer. The reaction was carried out in $\text{DMSO}-d_6$ in order to check the progress of the polymerization. The mixture was left magnetically stirring at 150 °C for 12 h. After this time, the mixture was analyzed by means of ^1H and ^{13}C NMR spectroscopies. ^1H NMR (CDCl_3 , 400 MHz) δ (ppm) 4.91 (s, 4 H), 4.88 (s, 4 H), 3.10 (dd, 4 H), 2.83 (s, 3 H, CH_3 -N terminal), 2.61 (s, 12 H, CH_3 -N repeating unit), 2.03–1.99 (m, 8 H), 1.85–1.78 (m, 12 H), 1.74 (s, 12 H), 1.40–1.45 (m, 4 H), 1.25 (s, 12 H). ^{13}C NMR (CDCl_3 , 100 MHz) δ (ppm) 165.40 (C=O urea), 159.71 (C=O urethane), 147.34, 146.72, 111.17, 81.99, 62.01, 52.21, 47.83, 45.95, 37.40, 36.81, 31.94, 29.16, 28.20, 25.89, 24.99, 24.82, 24.63, 23.29, 22.26, 17.43.

Data availability

All data generated or analysed during this study are included in this published article [and its supplementary information files].

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Author contributions

Conceptualization, L.R. and V.B.; methodology, L.R., V.P., A.R., M.G. and V.B.; investigation, L.R., A.R. and V.B.; re-sources, M.G. and V.B.; writing—original draft preparation, V.B., A.R., V.P. and L.R.; writing—review and editing, M.G., V.B., L.R., A.R. and V.P.; supervision, M.G., A.R. and V.B. All authors have read and agreed to the published version of the manuscript.

Declarations

Competing interests

The authors declare no competing interests.

Additional information

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