



From natural sources to materials: isocyanate-free polyurethanes from (*R*)-(+)-limonene oxide

Vincenzina Barbera^a

L. Rubino, ^a A. Rescifina, ^b V. Patamia, ^b M. Galimberti ^a

^a Politecnico di Milano, Department of Chemistry, Materials and Chemical Engineering “G. Natta”

^b Università di Catania, Dipartimento di Scienze del Farmaco e della Salute

vincenzina.barbera@polimi.it



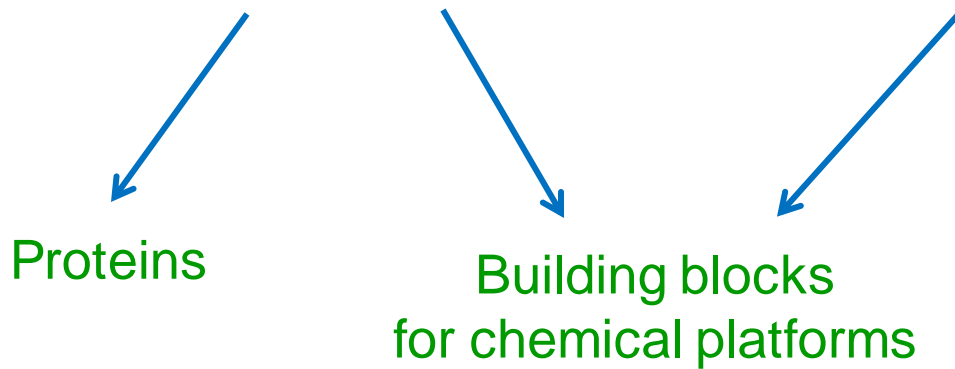
ISCaMaP

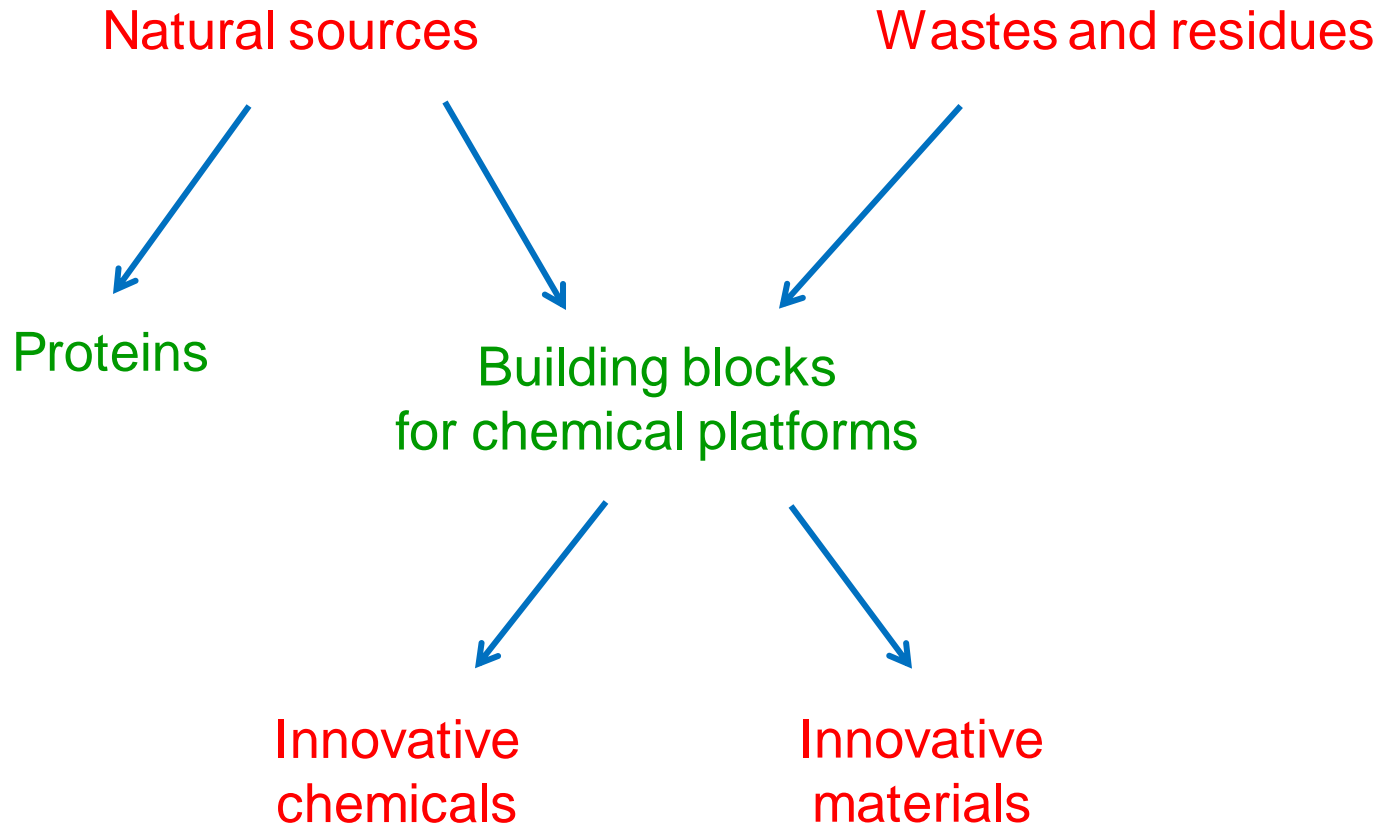
*Innovative **S**ustainable **C**hemistry and **M**aterials and **P**roteomics
Group*

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Natural sources

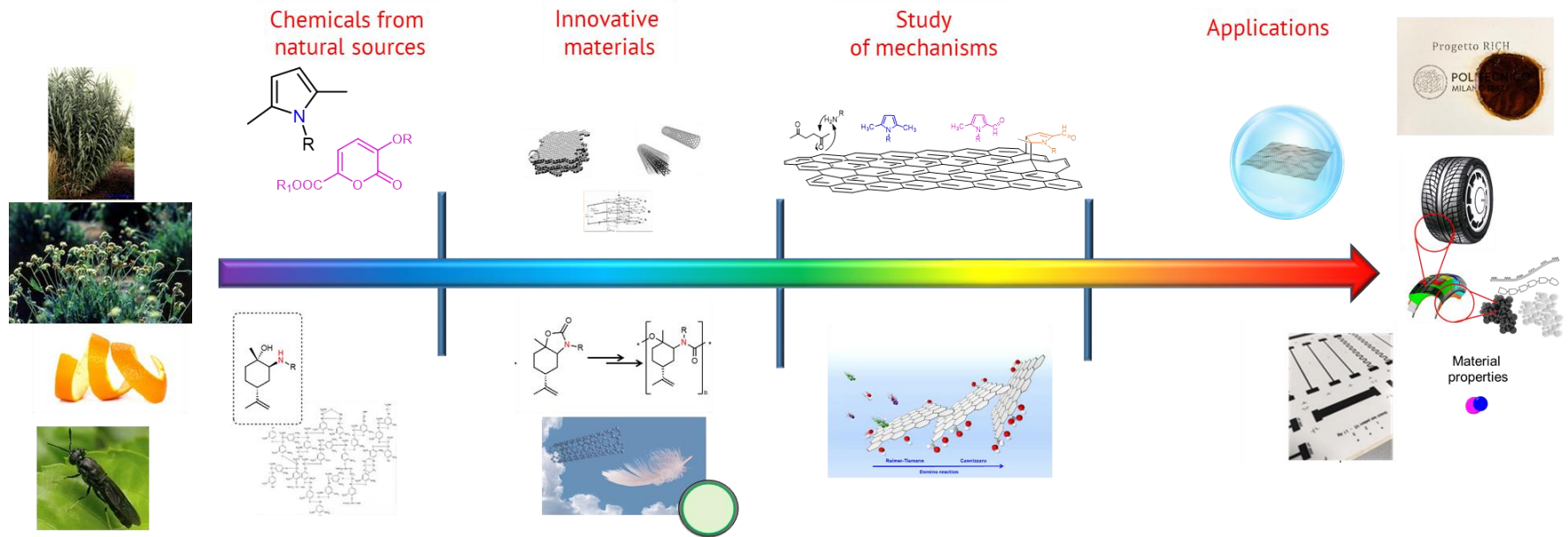
Wastes and residues





👉 Chemicals, Additives, Modifiers, Polymers

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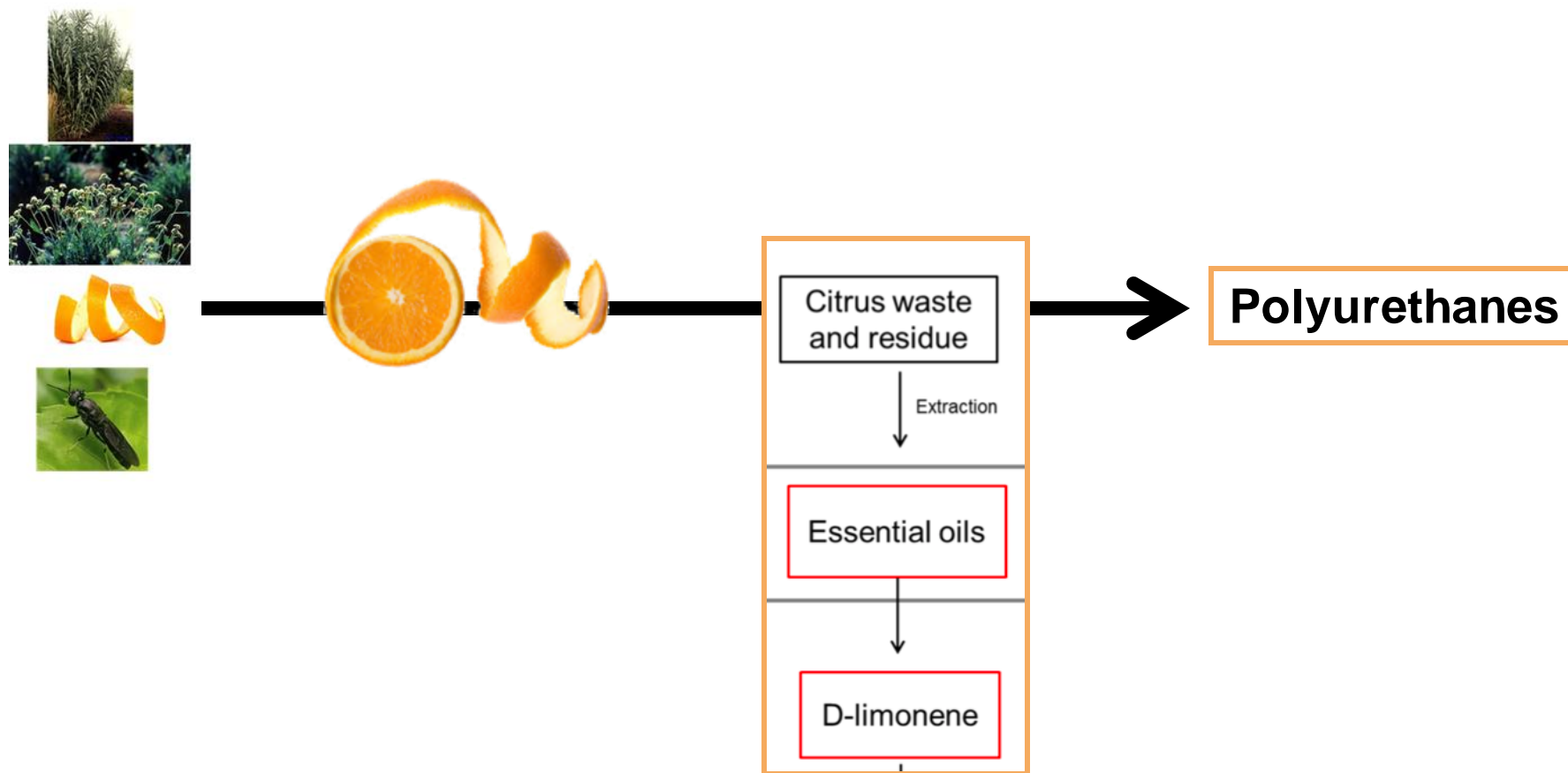


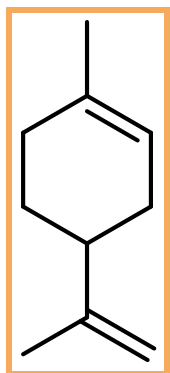
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From natural sources to materials

Wastes from **citrus fruits** processing industries generate large amounts of products.

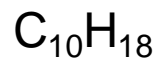
Terpenes, in particular Limonene, are the major components of essential oils of **citrus fruit**





Limonene: a biosourced building block

IUPAC: 1-methyl-4-(prop-1-en-2-yl)cyclohexene

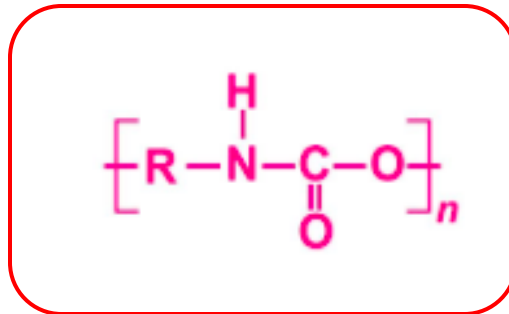


☞ Starting building block for many reaction pathways

☞ Reactivity

Why polyurethanes?

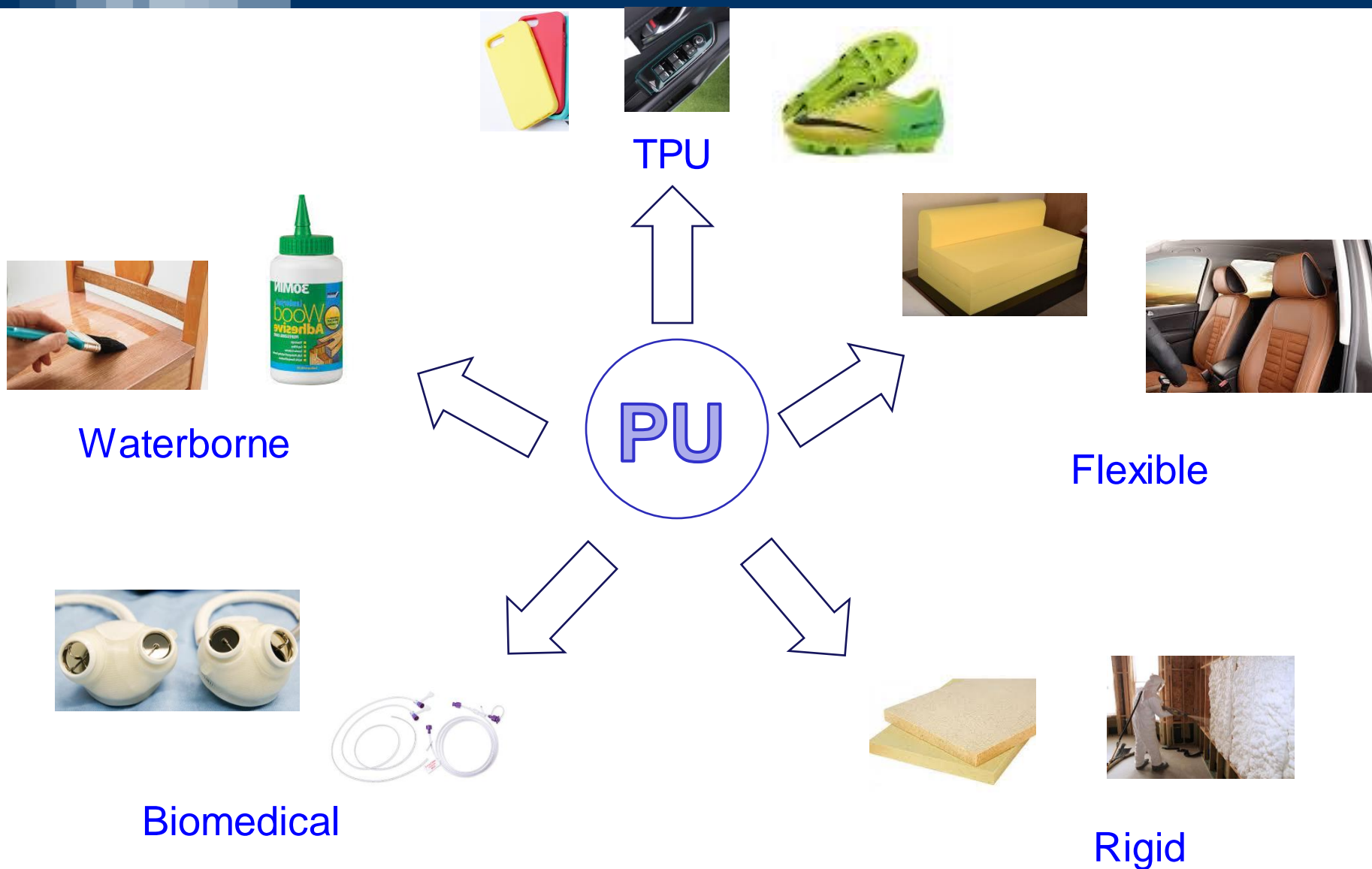
- no co-products (polyaddition!)
- versatile polymers
- commercial value



The urethane bond



The world of polyurethanes



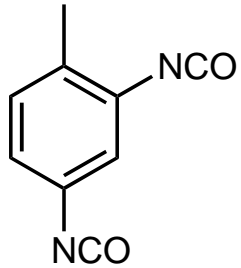
Concerns about polyurethanes

- Isocyanate production: phosgenation
- Isocyanate reactivity: storage
- Isocyanate toxicity
- Isocyanate reactivity: by-products

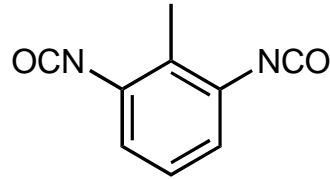


Isocyanate toxicity

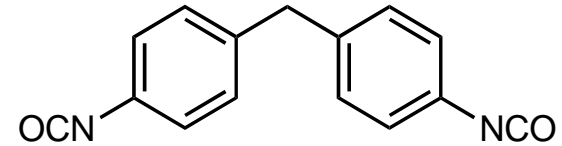
The most used isocyanates, TDI and MDI, are classified as CMR (Carcinogen, Mutagen, Reprotoxic) substances



2,4-TDI



2,6-TDI

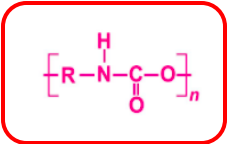
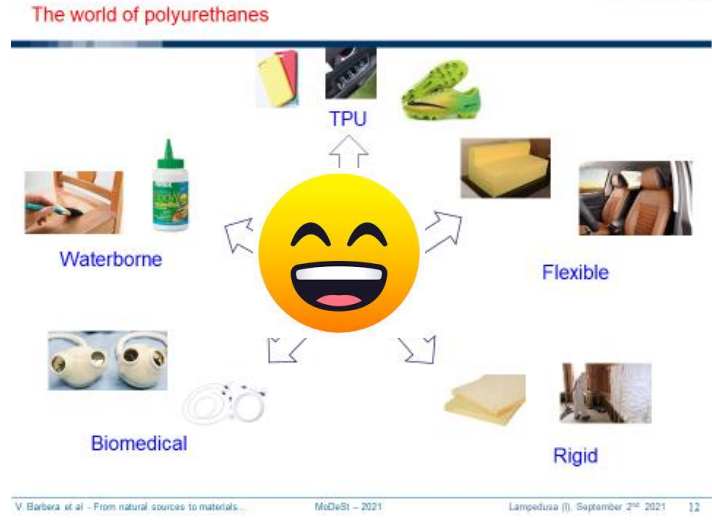


4,4'-MDI



This work. The rational design

objective



This work. The rational design

objective

The world of polyurethanes

Waterborne

TPU

Flexible

Biomedical

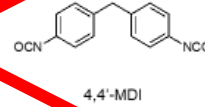
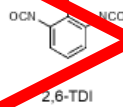
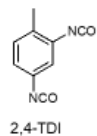
Rigid

$$\left[\text{R}-\overset{\text{H}}{\text{N}}-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\text{O} \right]_n$$

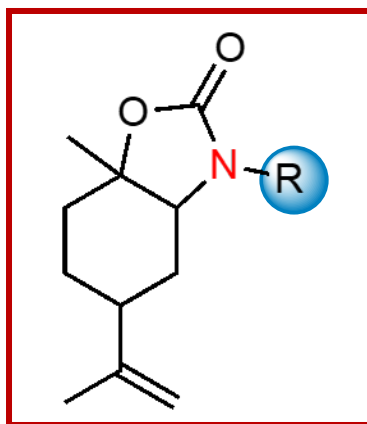
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Isocyanate toxicity

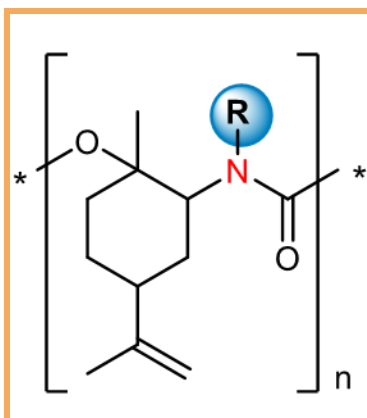
The most used isocyanates, TDI and MDI, are classified as CMR (Carcinogen, Mutagen, Reprotoxic) substances



The strategy



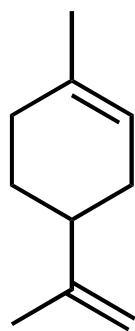
Cyclic carbamate



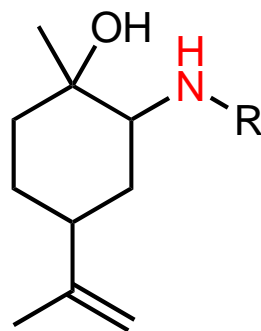
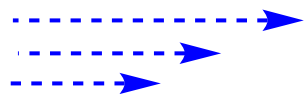
Isocyanate free PU

This work. Polyurethanes from (*R*)-(+)-limonene

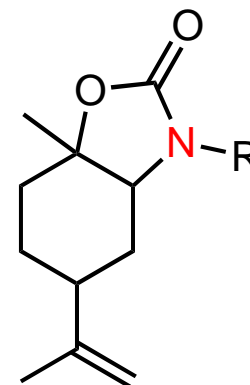
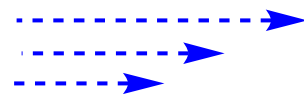
The strategy



(*R*)-(+)-limonene
bio-sourced building block



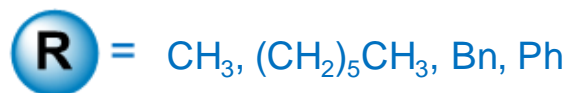
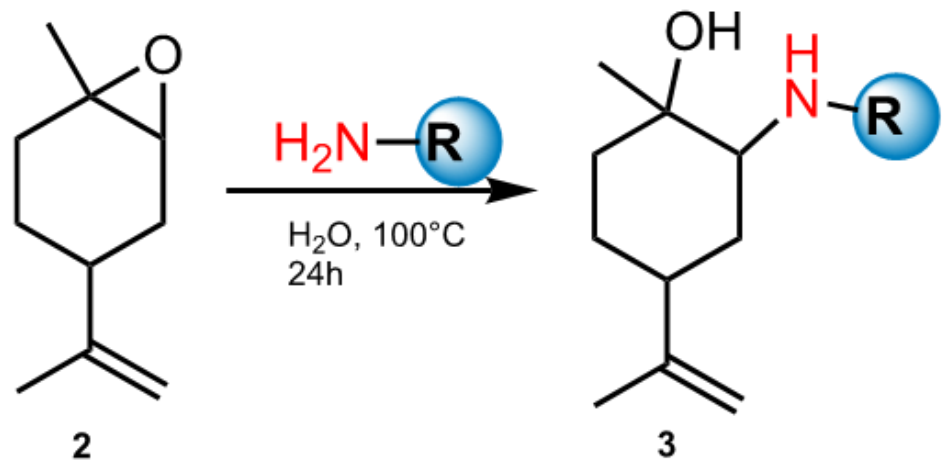
β -amino alcohols



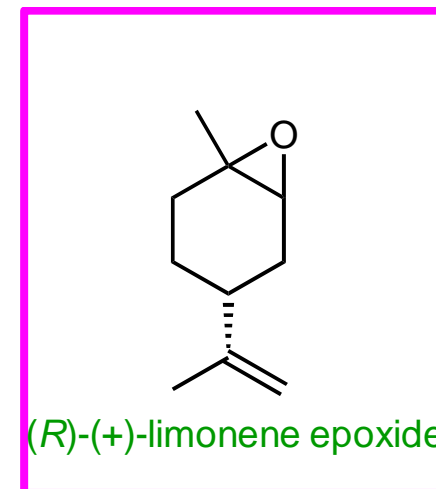
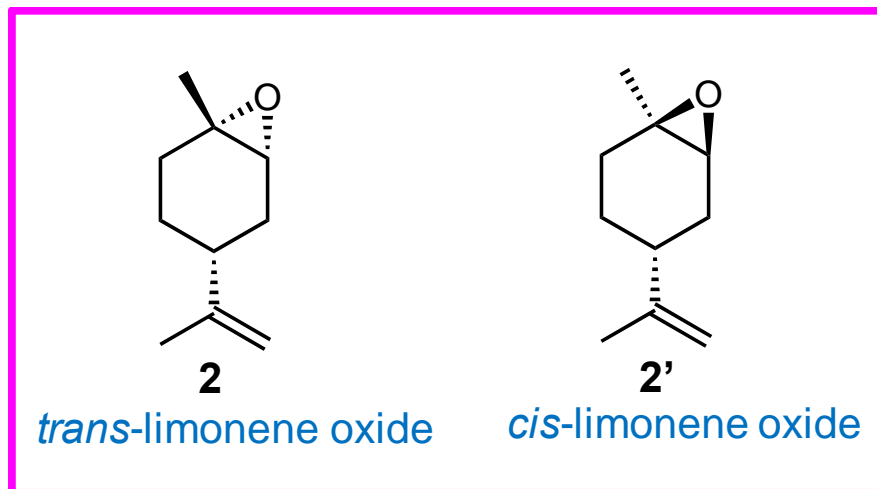
Cyclic carbamates



Polyurethanes from (*R*)-(+)-limonene



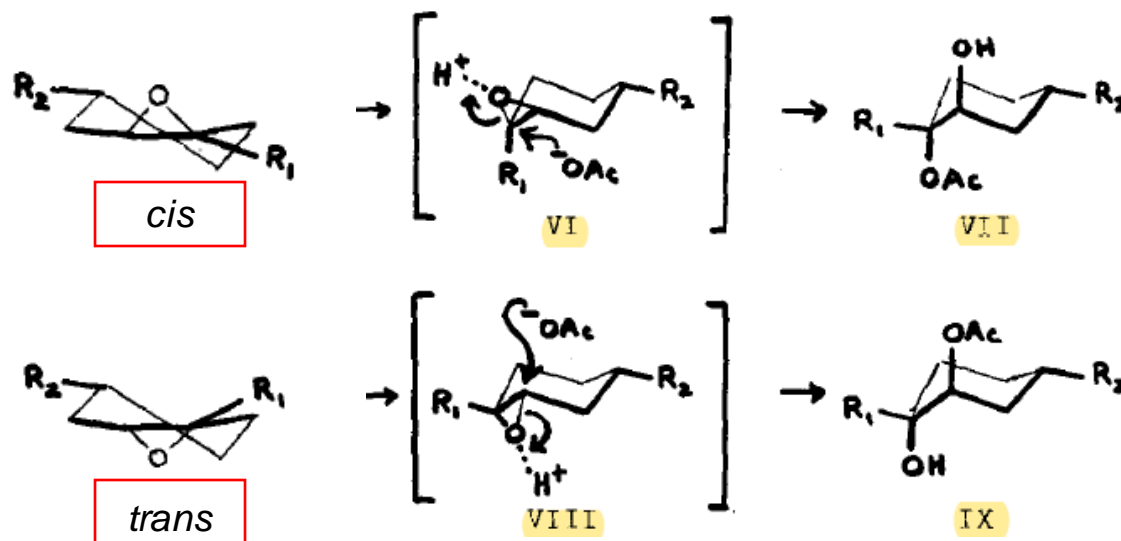
Polyurethanes from (*R*)-(+)-limonene



MIXTURE OF ISOMERS!!

Aminolysis of (*R*)-(+)-limonene oxide

The aminolysis is regio- and diastereoselective. The approach of the nucleophile is known to be *trans*-diaxial (Fürst-Plattner rule). In the case of *cis*-limonene oxide, the reaction occurs via a S_N1-type mechanism with inversion of configuration at the C-1. For *trans*-limonene oxide, a S_N2-type reaction can be envisioned at C-2.

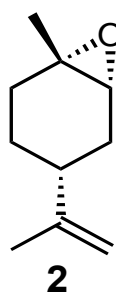
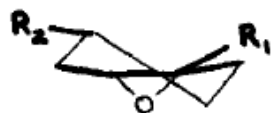


[1] Leffingwell, J. C., & Royals, E. E. (1965). Tetrahedron Letters, 6(43), 3829-3837.

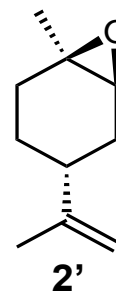
[2] Royals, E. E., & Leffingwell, J. C. (1966). The Journal of Organic Chemistry, 31(6), 1937-1944.

[3] Newhall, W. F. (1964). The Journal of Organic Chemistry, 29(1), 185-187.

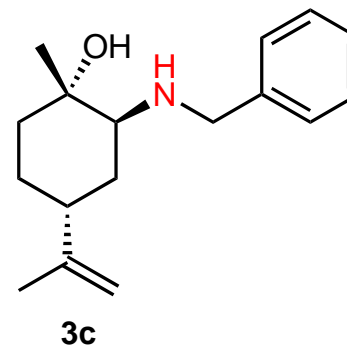
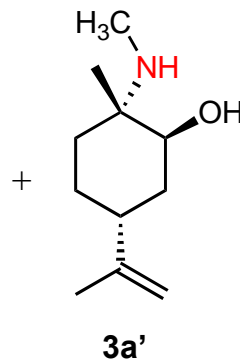
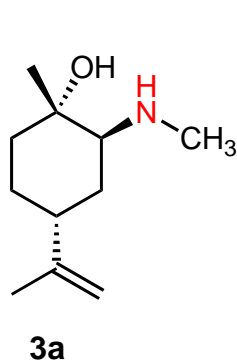
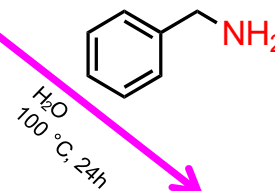
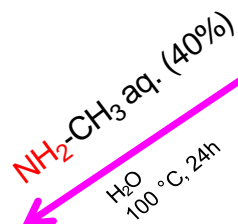
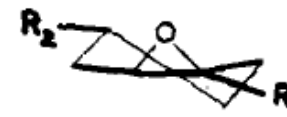
Aminolysis of (*R*)-(+)-limonene oxide



trans-limonene oxide

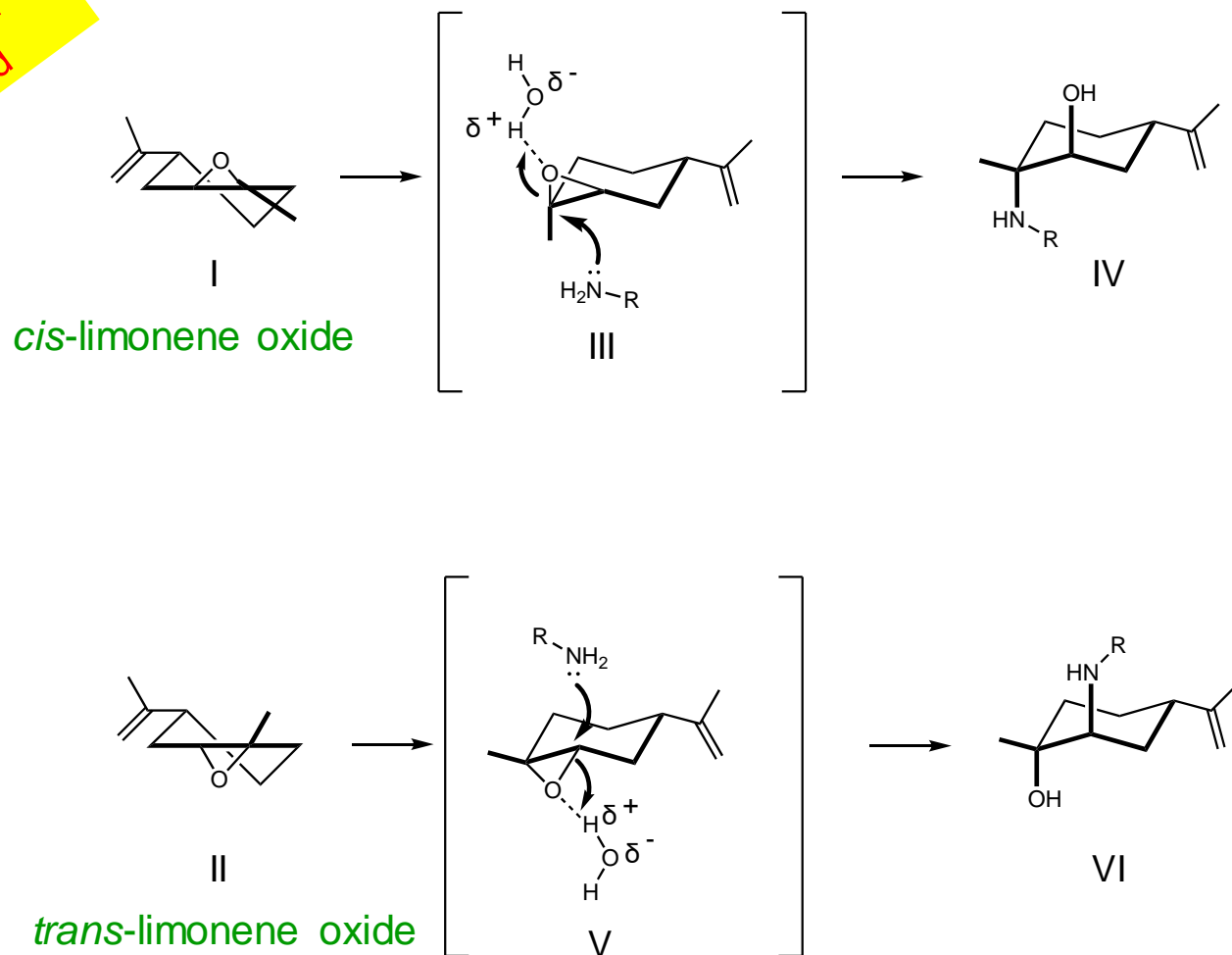


cis-limonene oxide

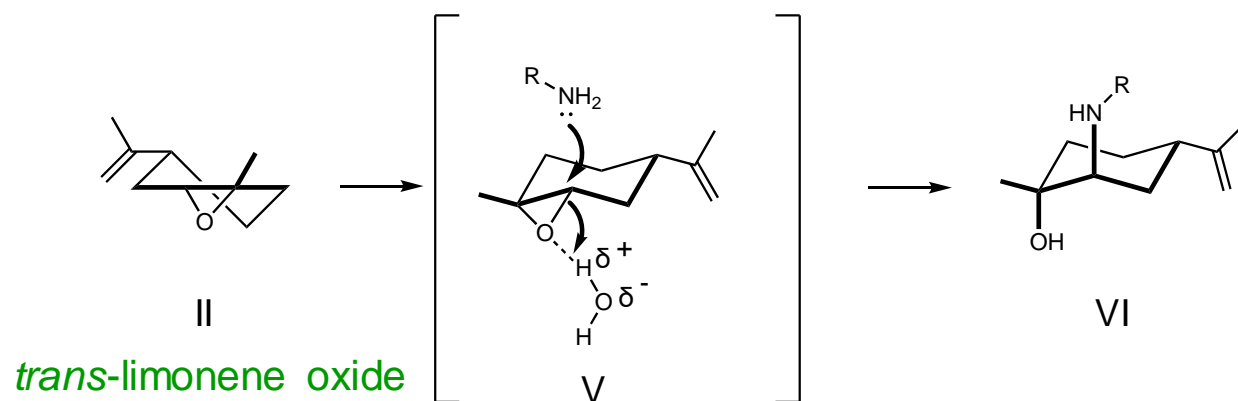


Aminolysis of (*R*)-(+)-limonene oxide: mechanism

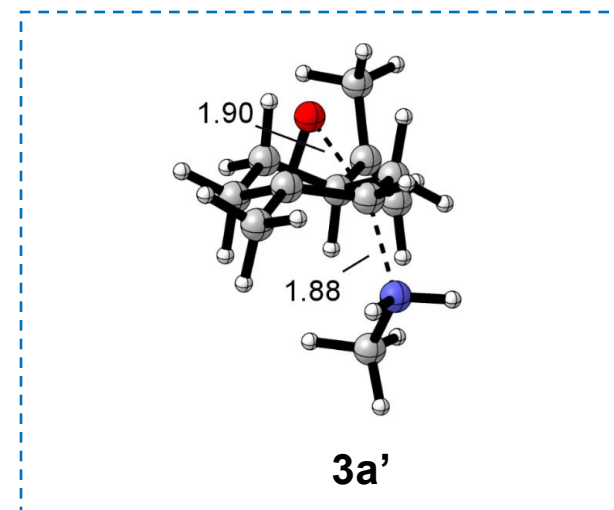
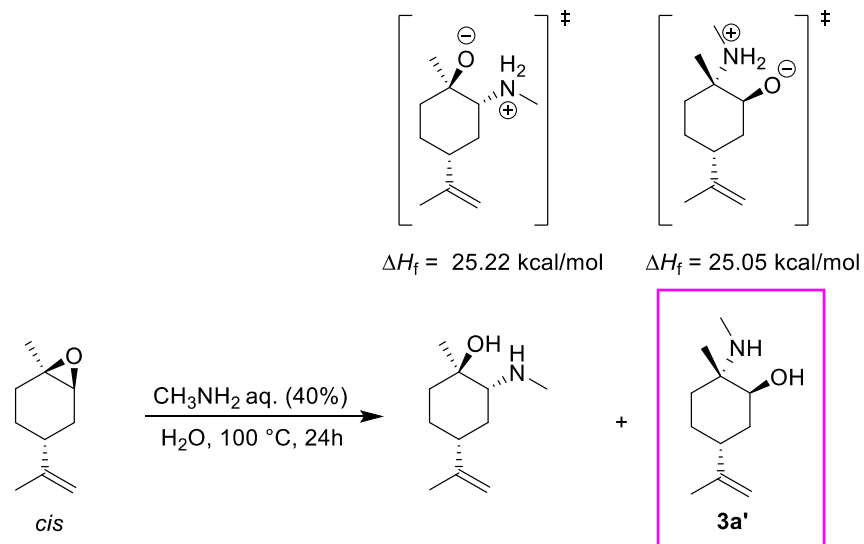
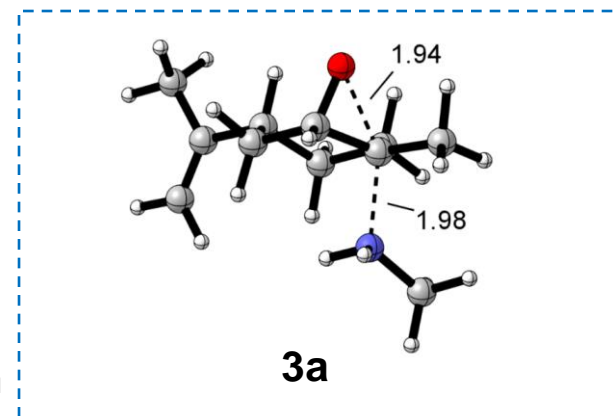
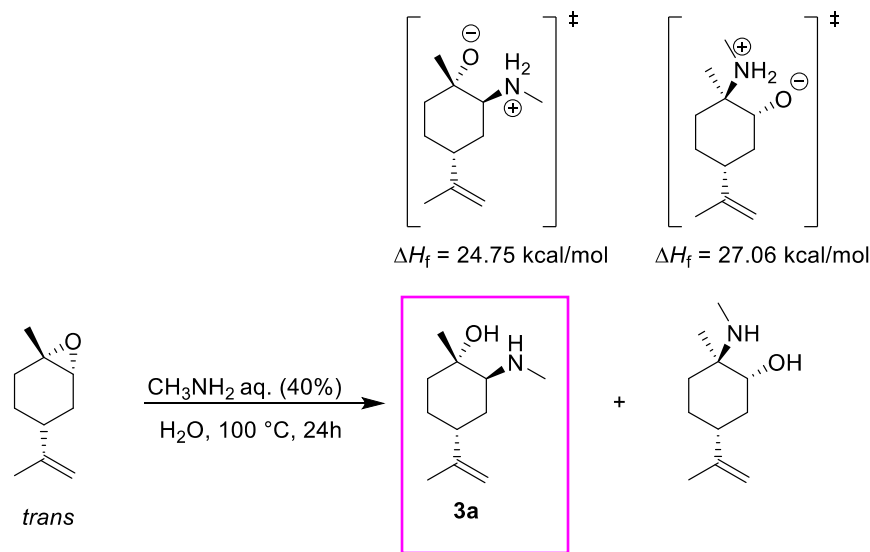
The mechanism of the epoxide ring opening in water with different primary amines is proposed



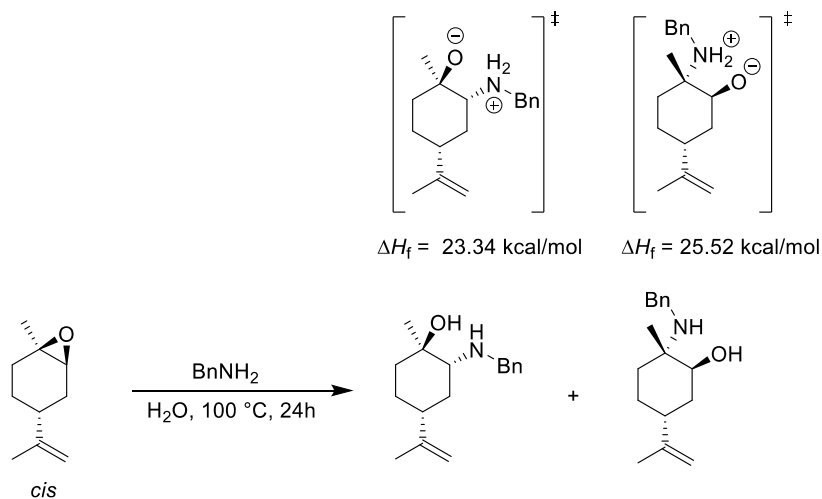
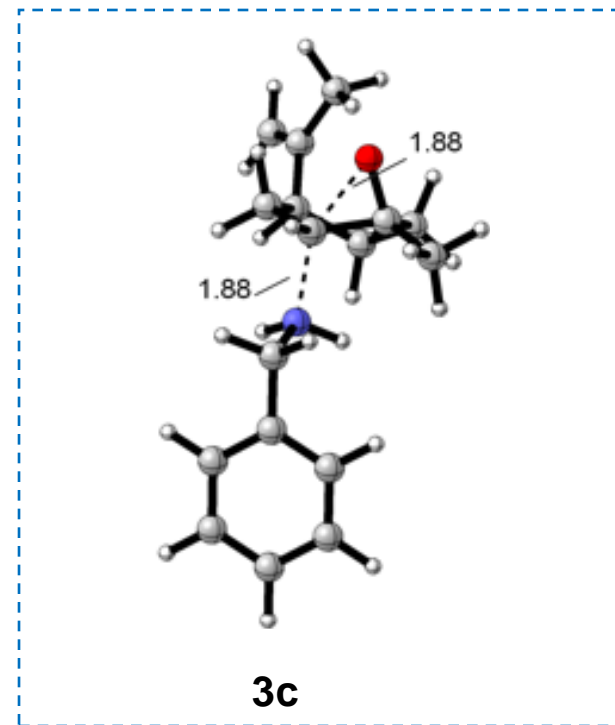
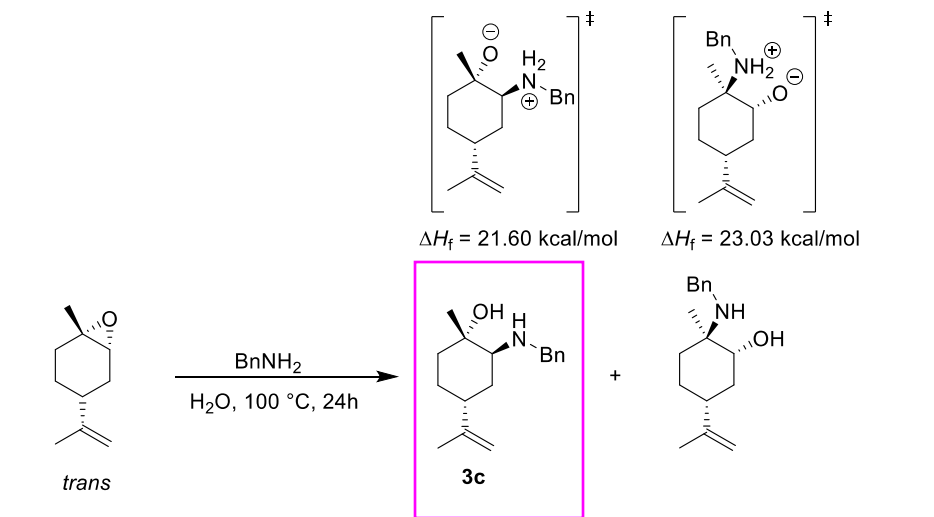
Aminolysis of (*R*)-(+)-limonene oxide: mechanism

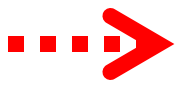
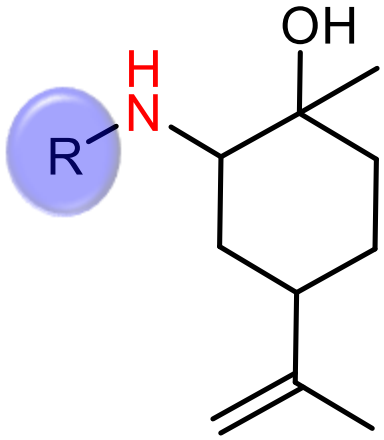
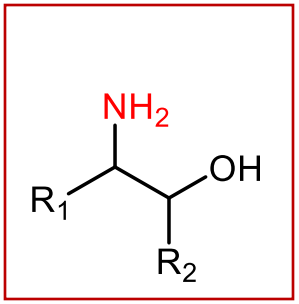


Aminolysis of (*R*)-(+)-limonene oxide: computational studies



Aminolysis of (*R*)-(+)-limonene oxide: computational studies





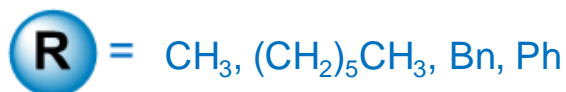
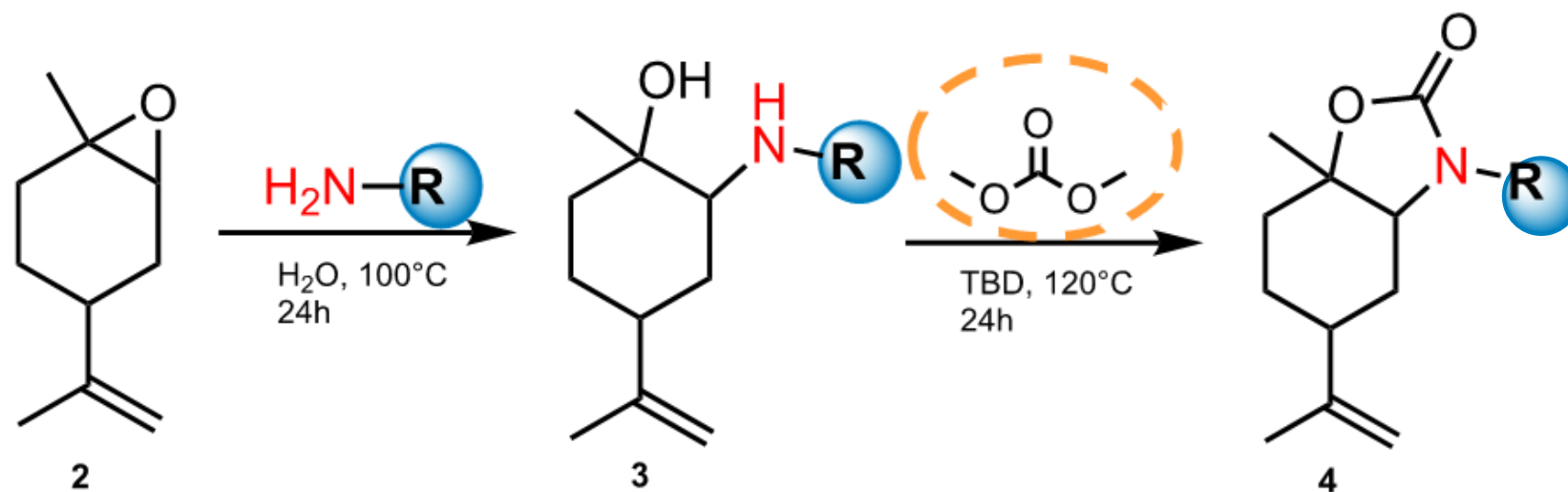
A Library of molecules

Four examples of substituted terpene derivatives:

- Primary amine: H2N-CH-CH(OH)-[terpene]
- Secondary amine (ethyl): Et-NH-CH-CH(OH)-[terpene]
- Secondary amine (benzyl): Bn-NH-CH-CH(OH)-[terpene]
- Secondary amine (phenyl): Ph-NH-CH-CH(OH)-[terpene]

... and so on!

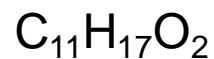
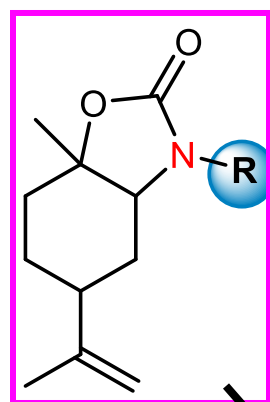
Polyurethanes from (*R*)-(+)-limonene



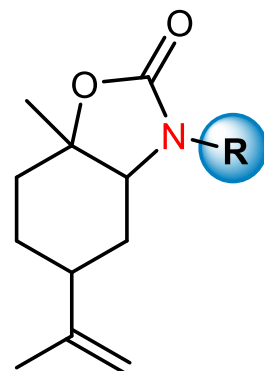
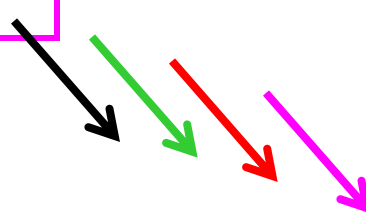
Synthesis of a library of
cyclic carbamates via
DAC chemistry

Green syntheses
No toxic reagents
High Yields

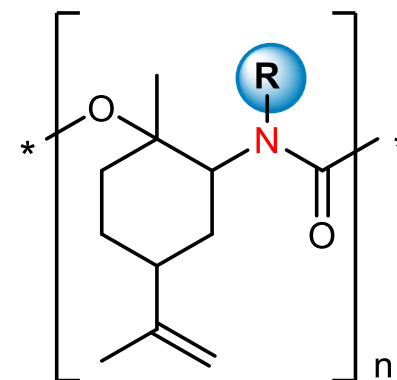
Polyurethanes from biosourced materials



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



ROP



Isocyanate-free Polyurethane via cationic ring opening polymerization of five-membered cyclic carbamates



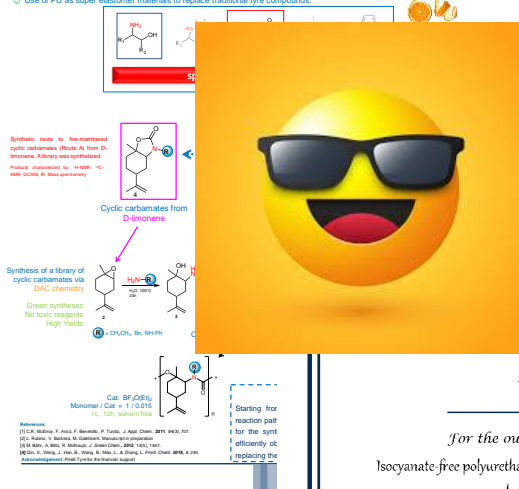
Lucia Rubino
(Post Doc)



 **Isocyanate-free polyurethanes from terpenes:
ROP of five-membered cyclic carbamates and cyclic carbonates**
Lucia Rubino, Vincenzina Barbera, Fatima Margani, Roberto Guadagnin, Maurizio Galimberti
Politecnico di Milano, Department of Chemistry, Materials and Chemical Engineering "G. Natta", Via Mancinelli 7, 20131 Milano, Italy
luciarita.rubino@polimi.it

Introduction
Polyurethanes (PU) represent one of the most versatile class of polymers, being suitable for a large variety of applications. They are industrially prepared by chemical reaction between polyols and isocyanates. Isocyanates are known to be highly toxic for health and environment.

- Objectives**
- Use of natural sources as building blocks for innovative platforms of chemicals;
 - Synthesis of isocyanate-free polyurethanes via Ring-Opening Polymerization (ROP) of 5-membered cyclic carbamates and carbonates;
 - Use of PU as super elastomer materials to replace traditional tyre compounds.



Polymer Days
15-17 July 2020
Poster Award




Lucia Rita Rubino

For the outstanding presentation entitled
Isocyanate-free polyurethanes from terpenes: ROP of five-membered cyclic carbamates and cyclic carbonates

THE AWARD COMMITTEE

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The Congress Chairs: *Professors Paolo Ferruti and Elisabetta Ranucci*  



Politecnico di Milano, Department of Chemistry, Materials and Chemical Engineering "G. Natta"