From natural sources to materials:

isocyanate-free polyurethanes from (*R*)-(+)-limonene oxide

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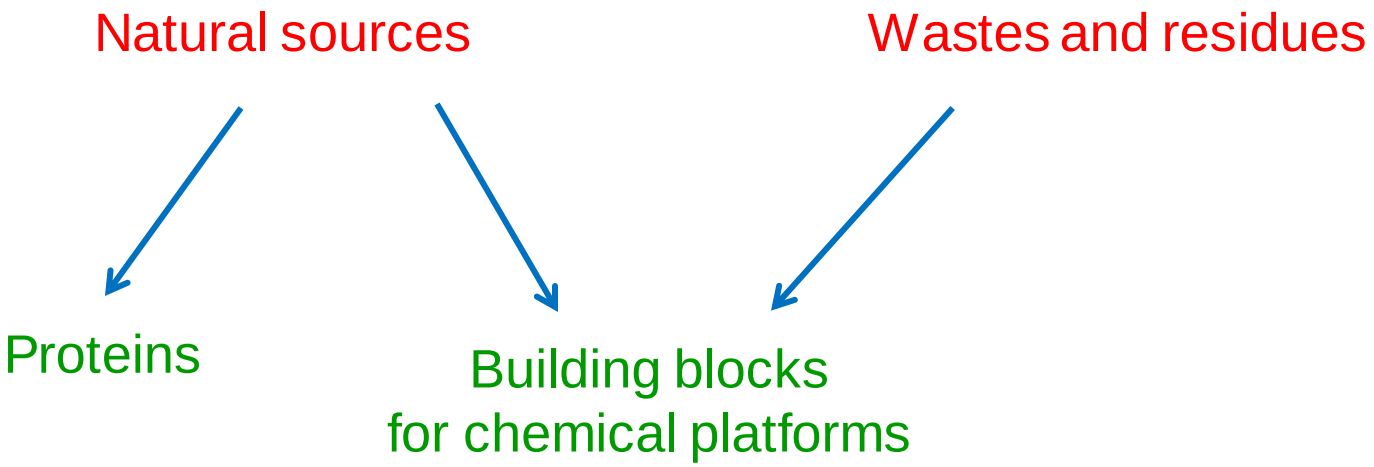
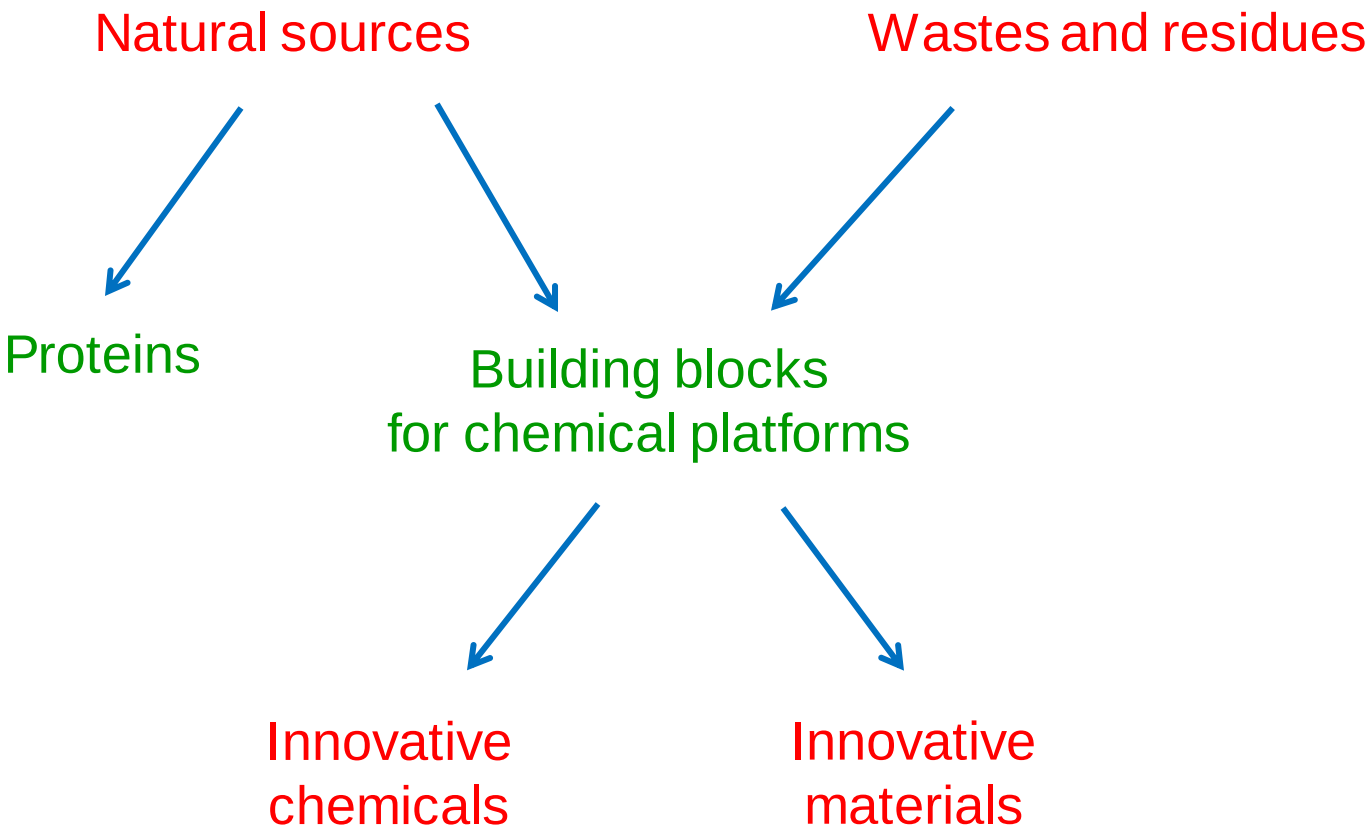
ISCaMaP

Innovative Sustainable Chemistry and Materials and Proteomics Group

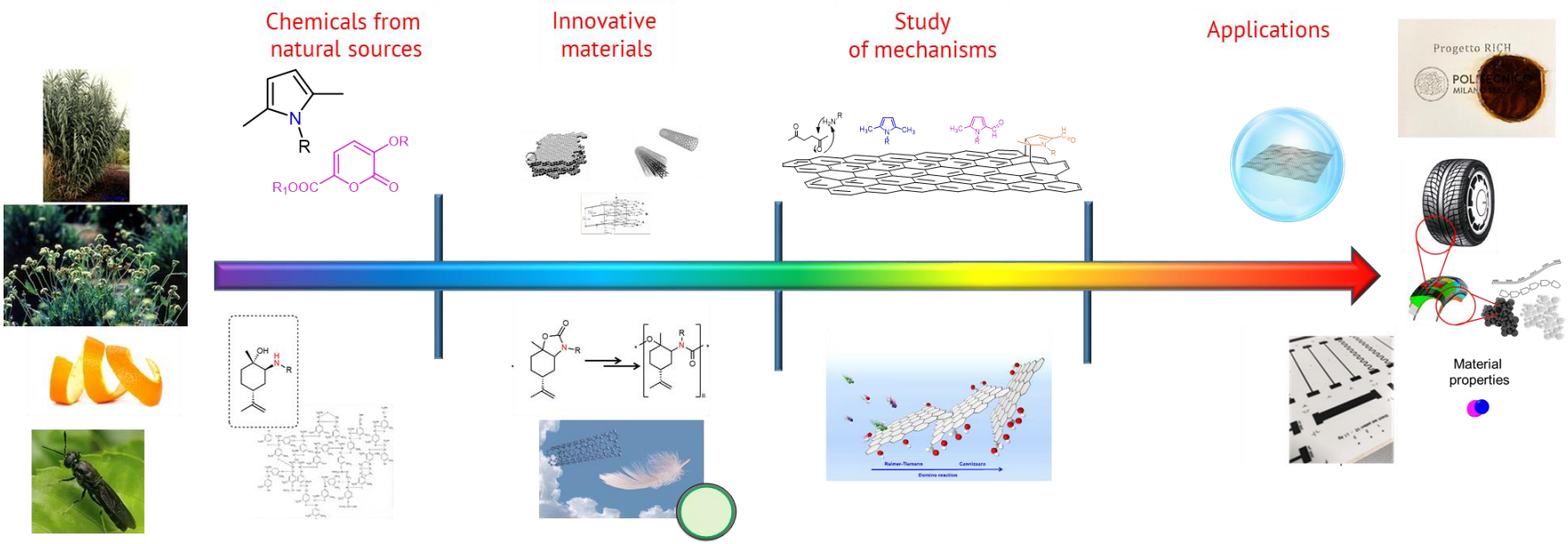
Politecnico di Milano, Department of Chemistry, Materials and Chemical Engineering "G. Natta"


Natural sources
Wastes and residues
Proteins
Building blocks
for chemical platforms



☞ Chemicals, Additives, Modifiers, Polymers

ISMaterials group



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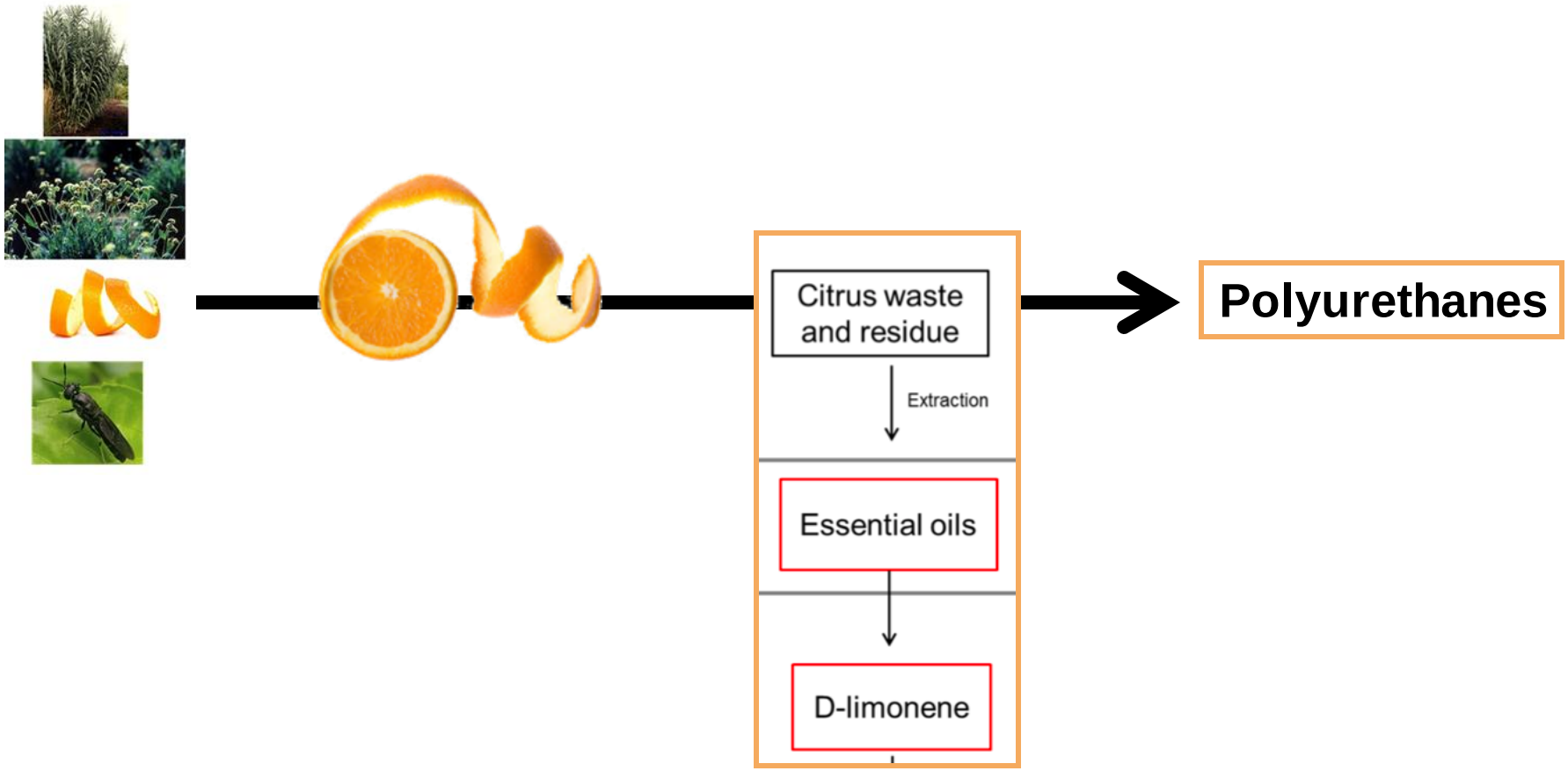
instagram: @ismaterials.polimi

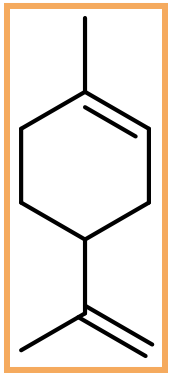
From natural sources to materials

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



A rational design



Limonene: a biosourced buiding block

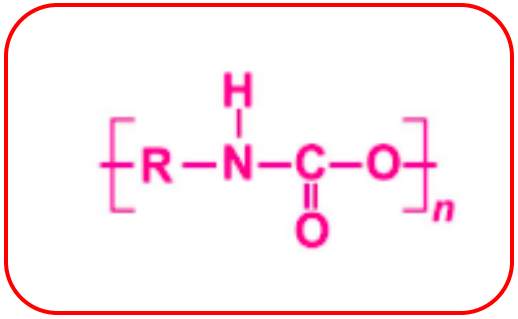
IUPAC: 1-methyl-4-(prop-1-en-2-yl)cyclohexene

$C_{10}H_{18}$

- 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



TPU




PU

Waterborne

Flexible




Biomedical

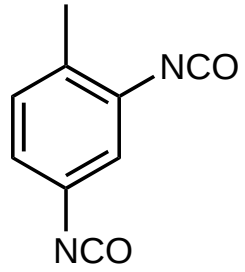
Rigid

Concerns about polyurethanes

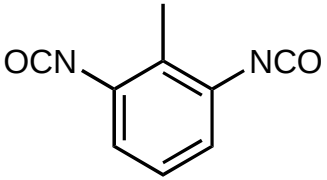
- Isocyanate production: phosgenation
- Isocyanate reactivity: storage
- Isocyanate toxicity
- Isocyanate reactivity: by-products

Isocyanate toxicity

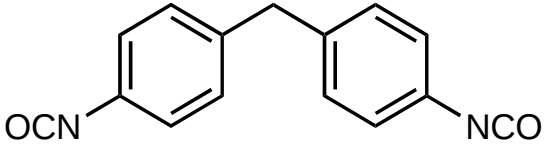
The most used isocyanates, TDI and MDI, are classified as CMR (Carcinogen, Mutagen, Reprotoxic) substances



2,4-TDI



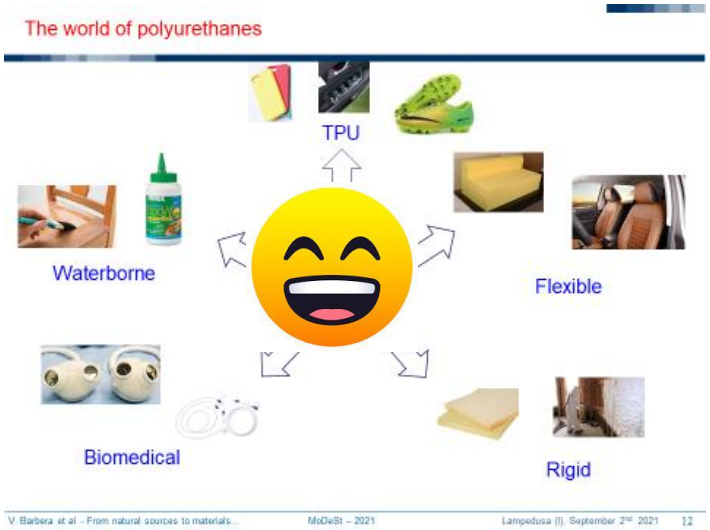
2,6-TDI

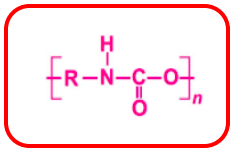


4,4'-MDI

This work. The rational design

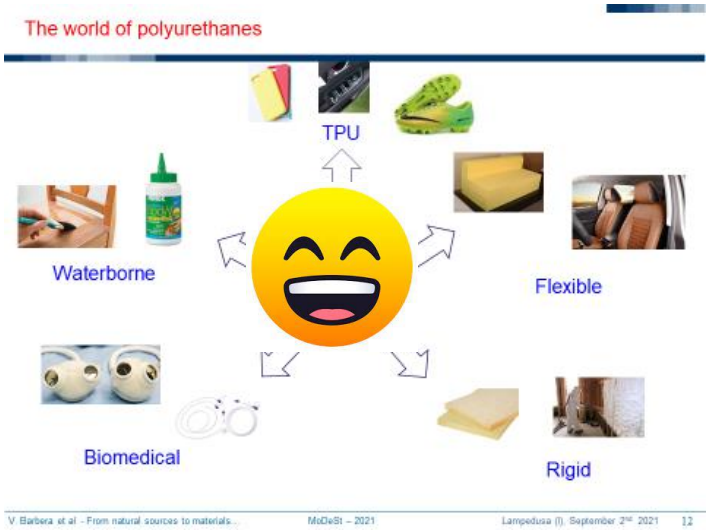
objective

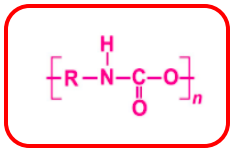


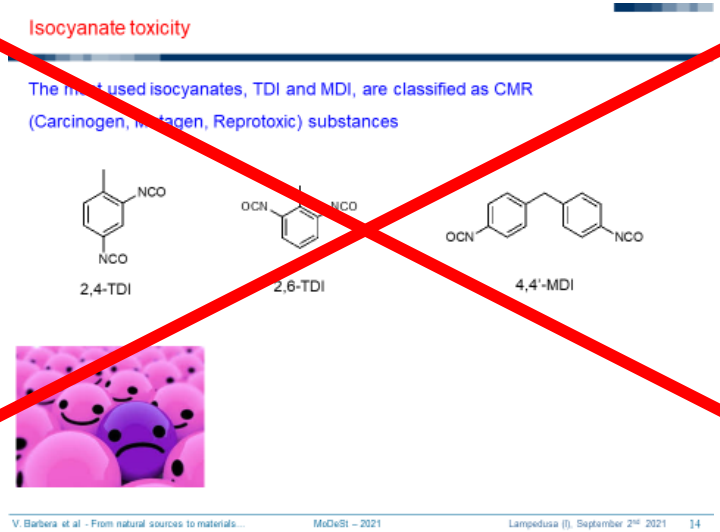


This work. The rational design

objective

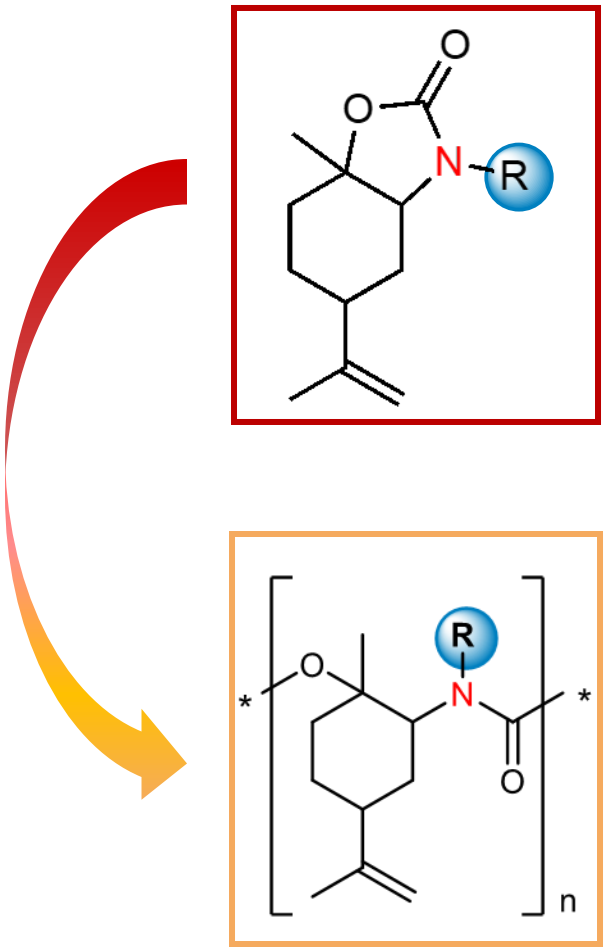






This work. Polyurethanes from (*R*)-(+)-limonene

The strategy

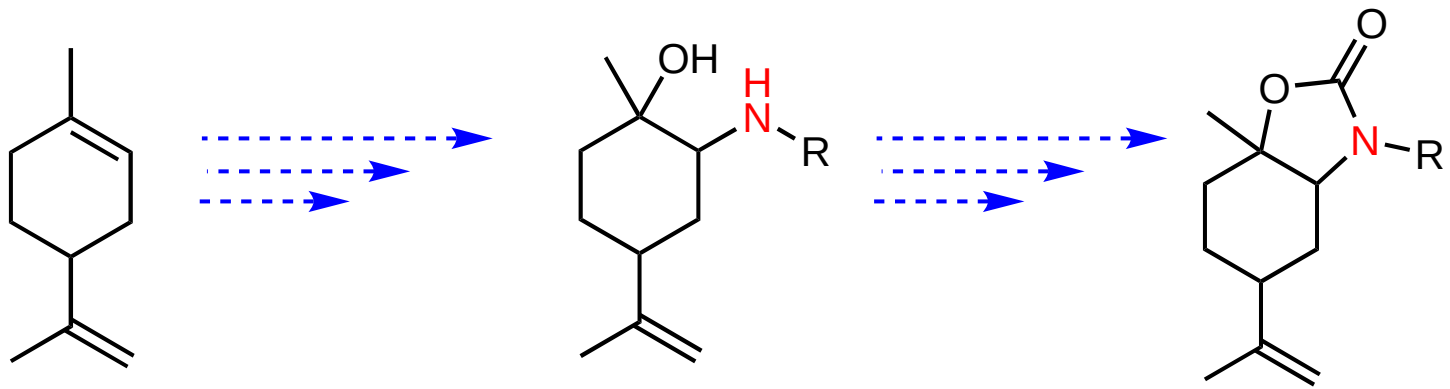


Cyclic carbamate

Isocyanate free PU

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

The strategy

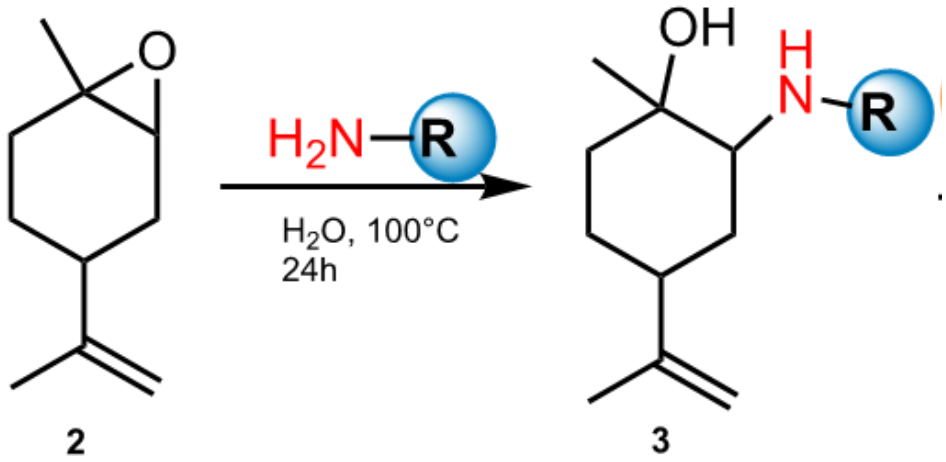


(*R*)-(+)-limonene
bio-sourced building block

β-amino alcohols

Cyclic carbamates

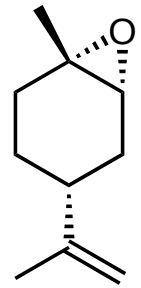
Polyurethanes from (*R*)-(+)-limonene



R = CH_3, $(CH_2)_5CH_3$, Bn, Ph

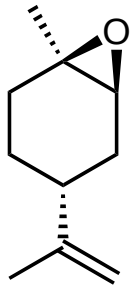
L. Rubino, A.Rescifina, V. Patamia, M. Galimberti, V. Barbera (2021). Submitted for pubblication

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



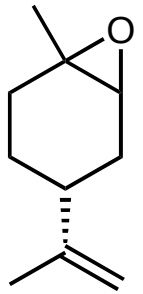
2

trans-limonene oxide



2’

cis-limonene oxide

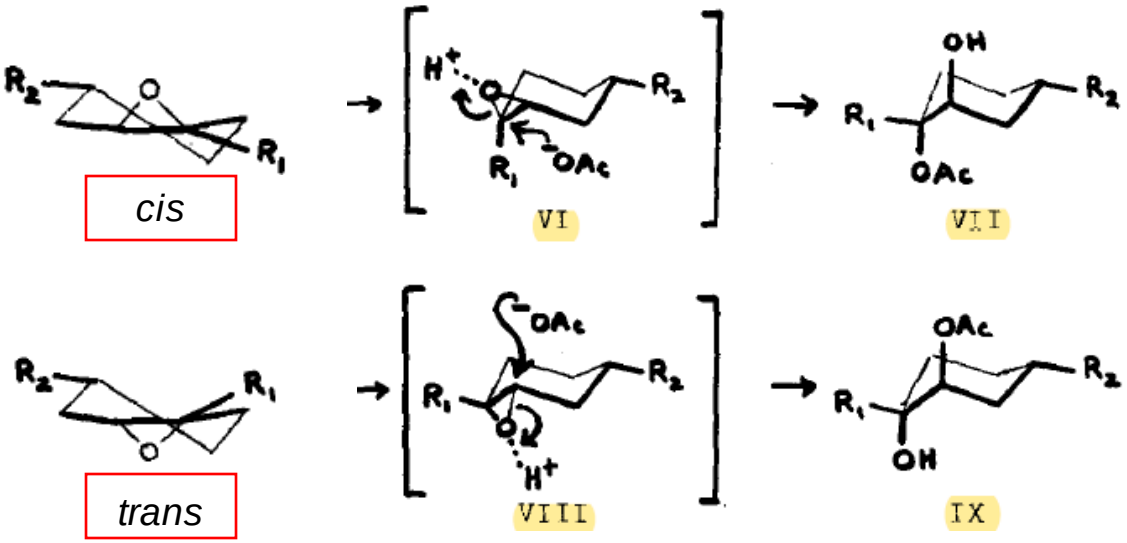


(*R*)-(+)-limonene epoxide

MIXTURE OF ISOMERS!!

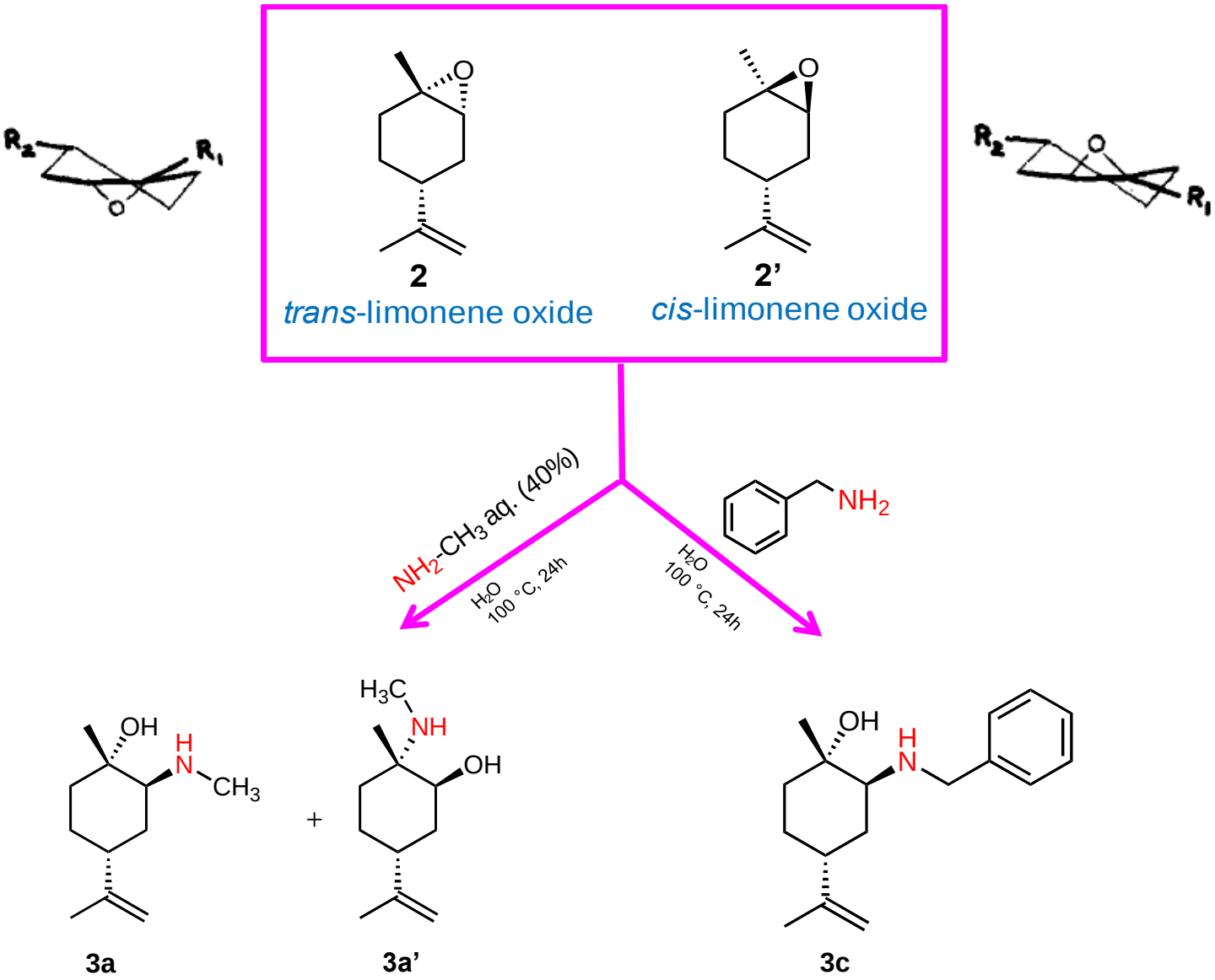
Aminolysis of (*R*)-(+)-limonene oxide

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.



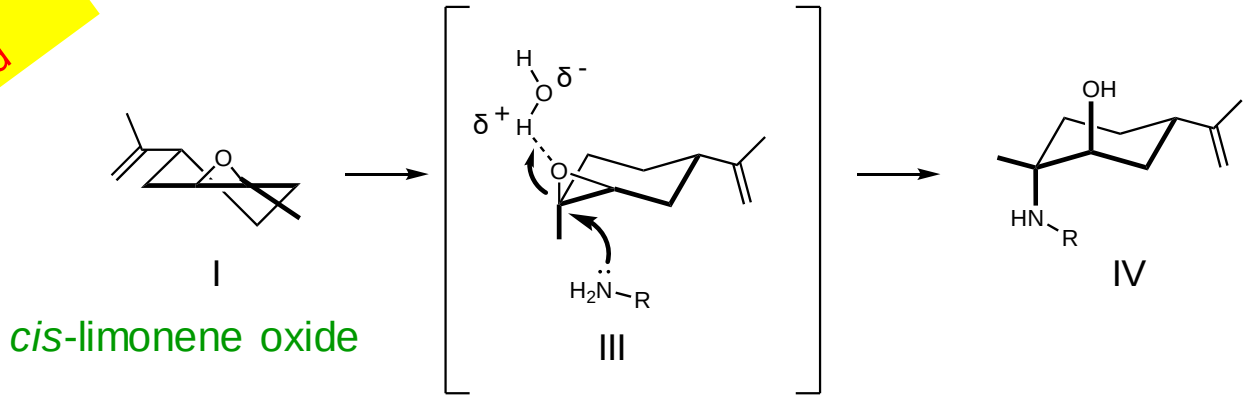
[1] Leffingwell, J. C., & Royals, E. E. (1965). Tetrahedron Letters, 6(43), 3829-3837.
[2] Royals, E. E., & Leffingwell, J. C. (1966). The Journal of Organic Chemistry, 31(6), 1937-1944.
[3] Newhall, W. F. (1964).. The Journal of Organic Chemistry, 29(1), 185-187.

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

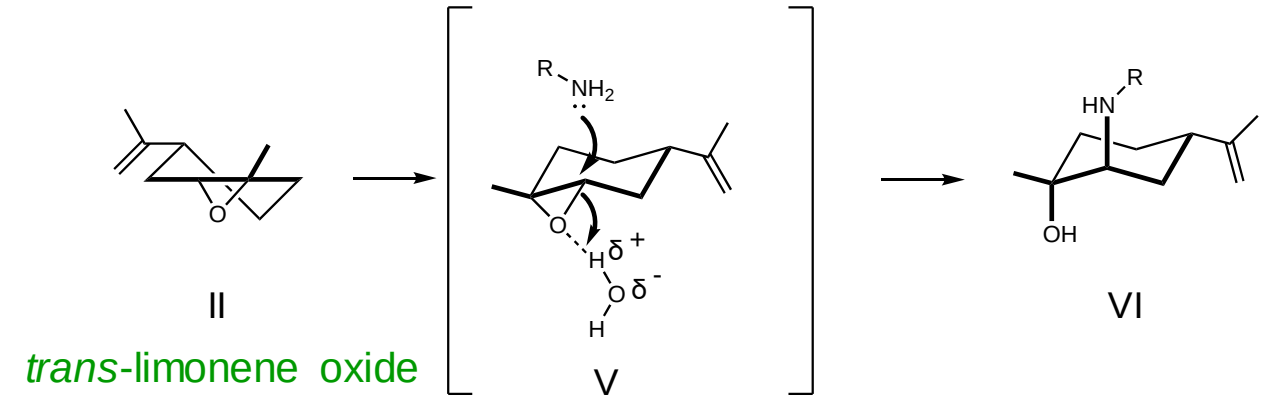


Aminolysis of (*R*)-(+)-limonene oxide: mechanism

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

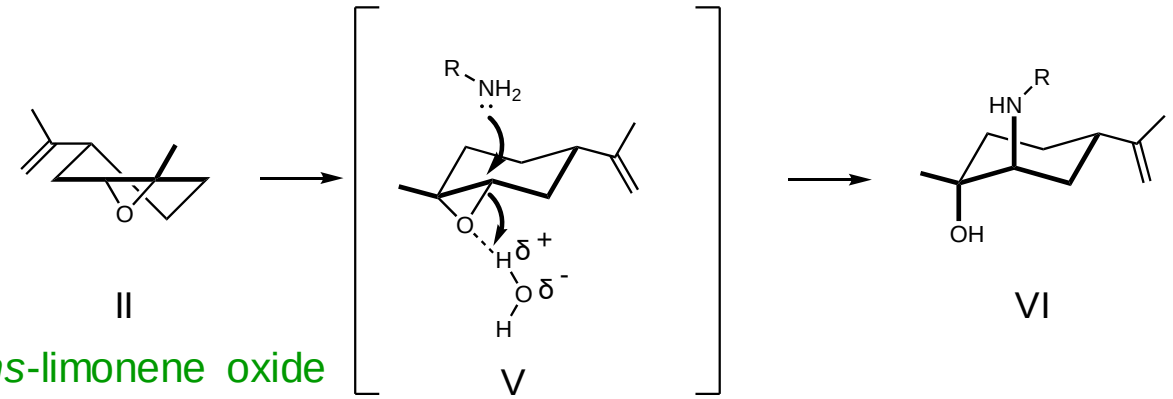


cis-limonene oxide



trans-limonene oxide

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



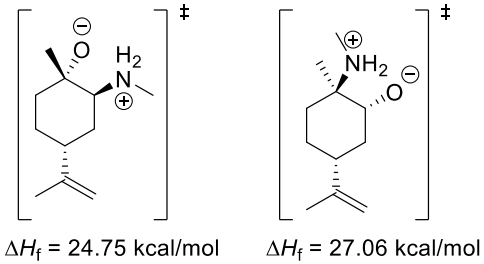
II

trans-limonene oxide

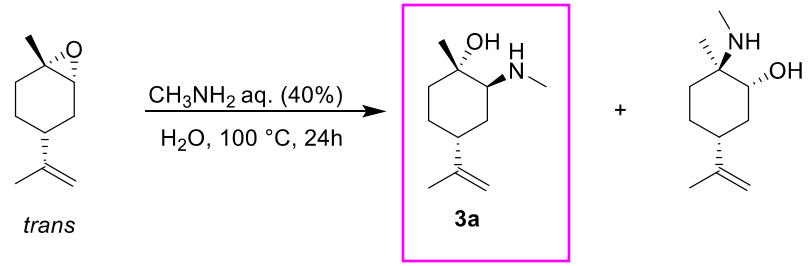
V

VI

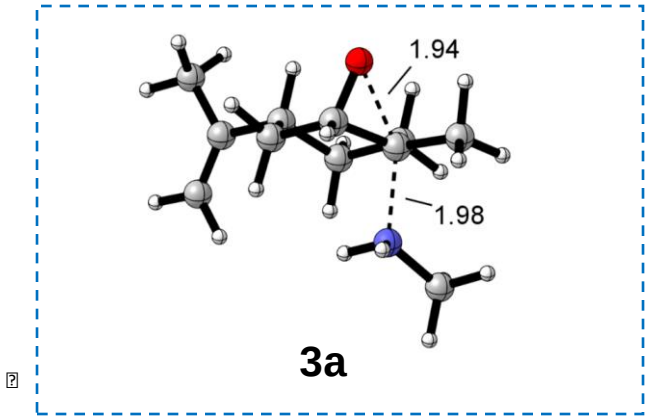
Aminolysis of (*R*)-(+)-limonene oxide: computational studies

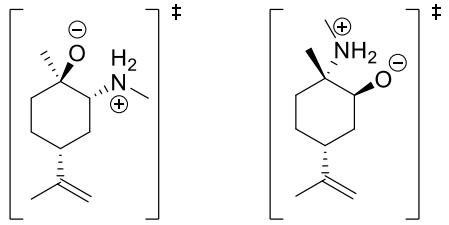


ΔH_f = 24.75 kcal/mol ΔH_f = 27.06 kcal/mol

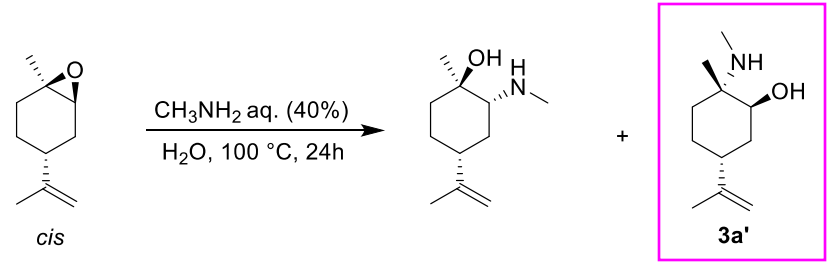


trans **3a**

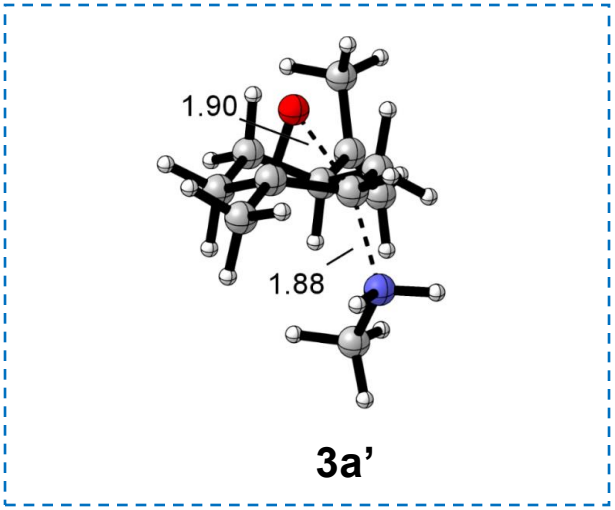




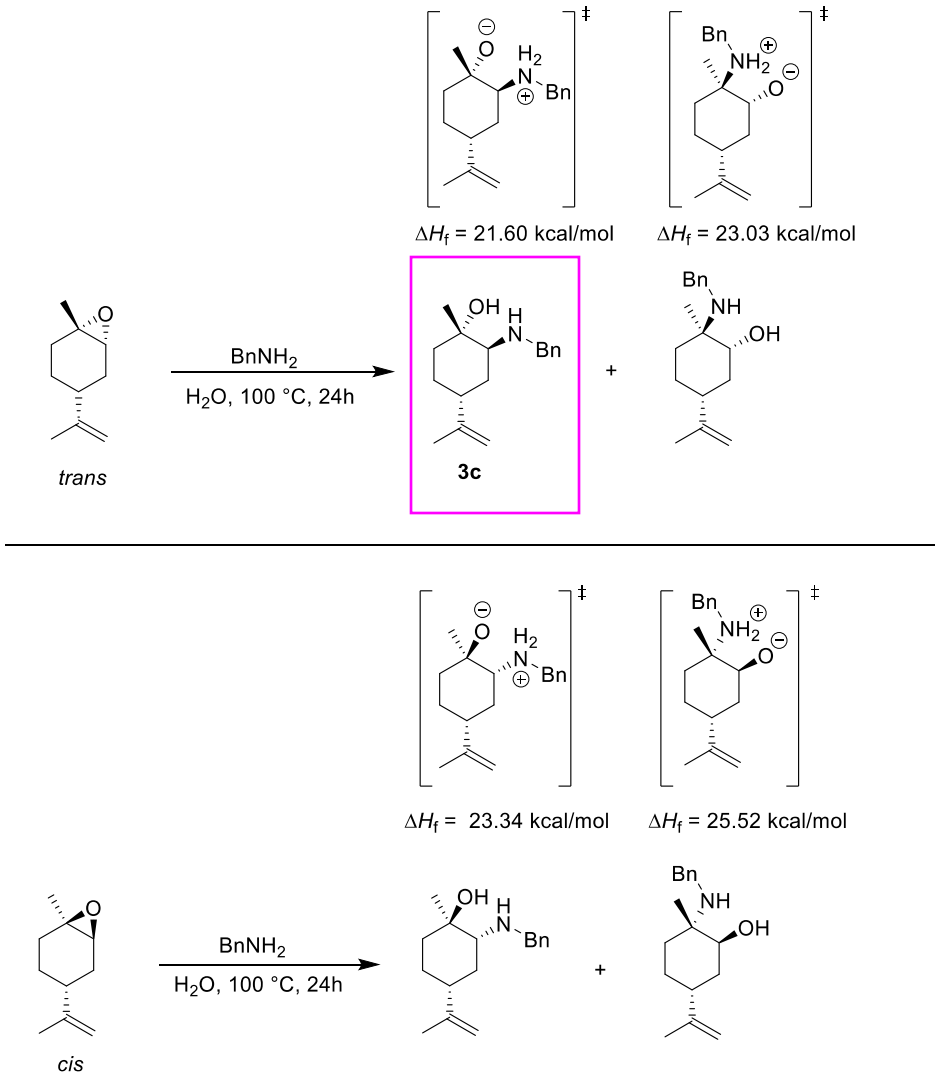
ΔH_f = 25.22 kcal/mol ΔH_f = 25.05 kcal/mol

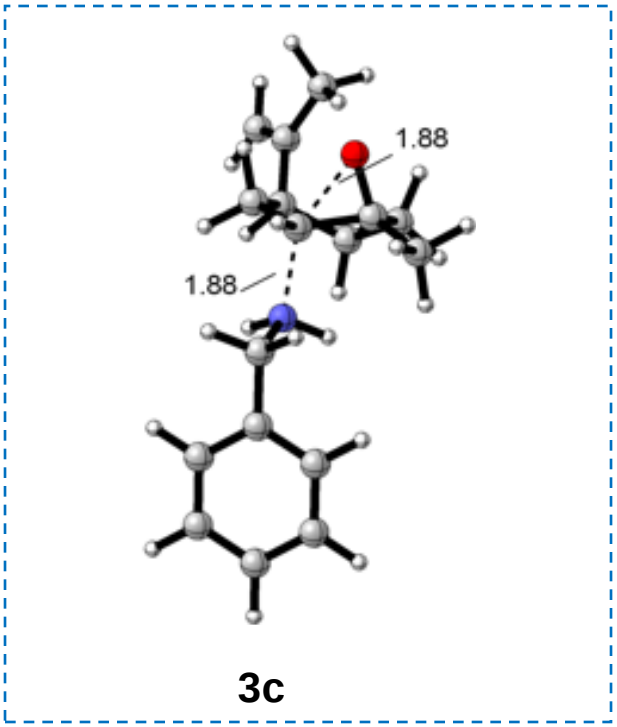


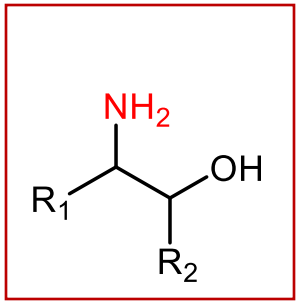
cis **3a'**

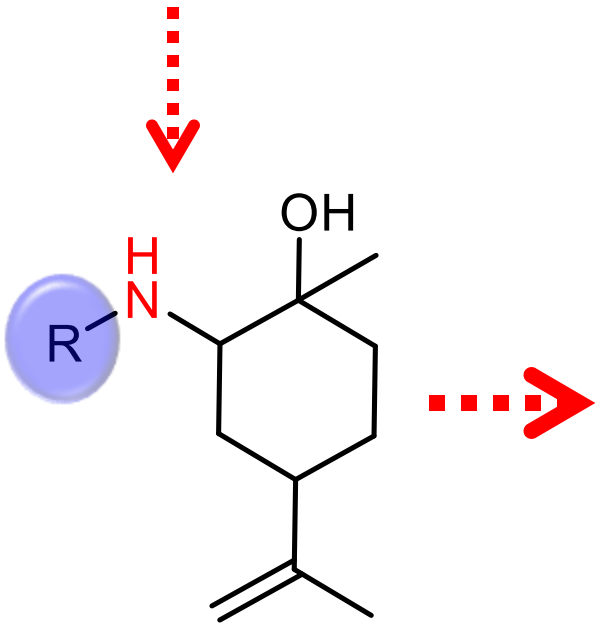


Aminolysis of (*R*)-(+)-limonene oxide: computational studies

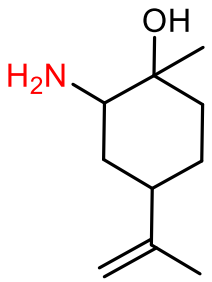


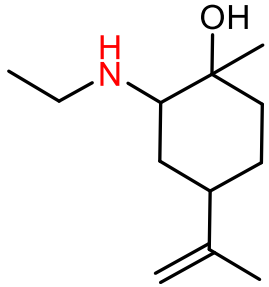


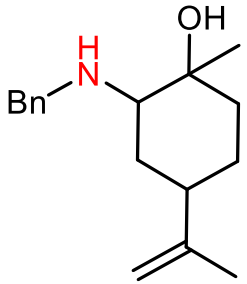


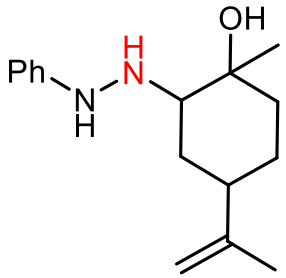


A Library of molecules



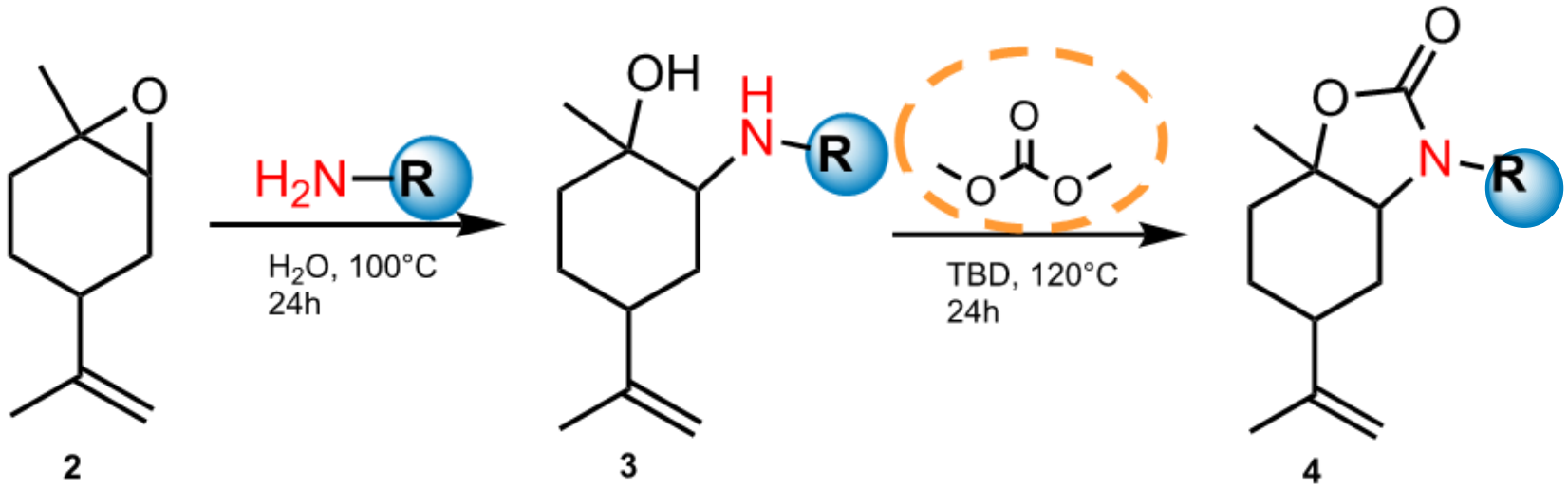






… and so on!

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



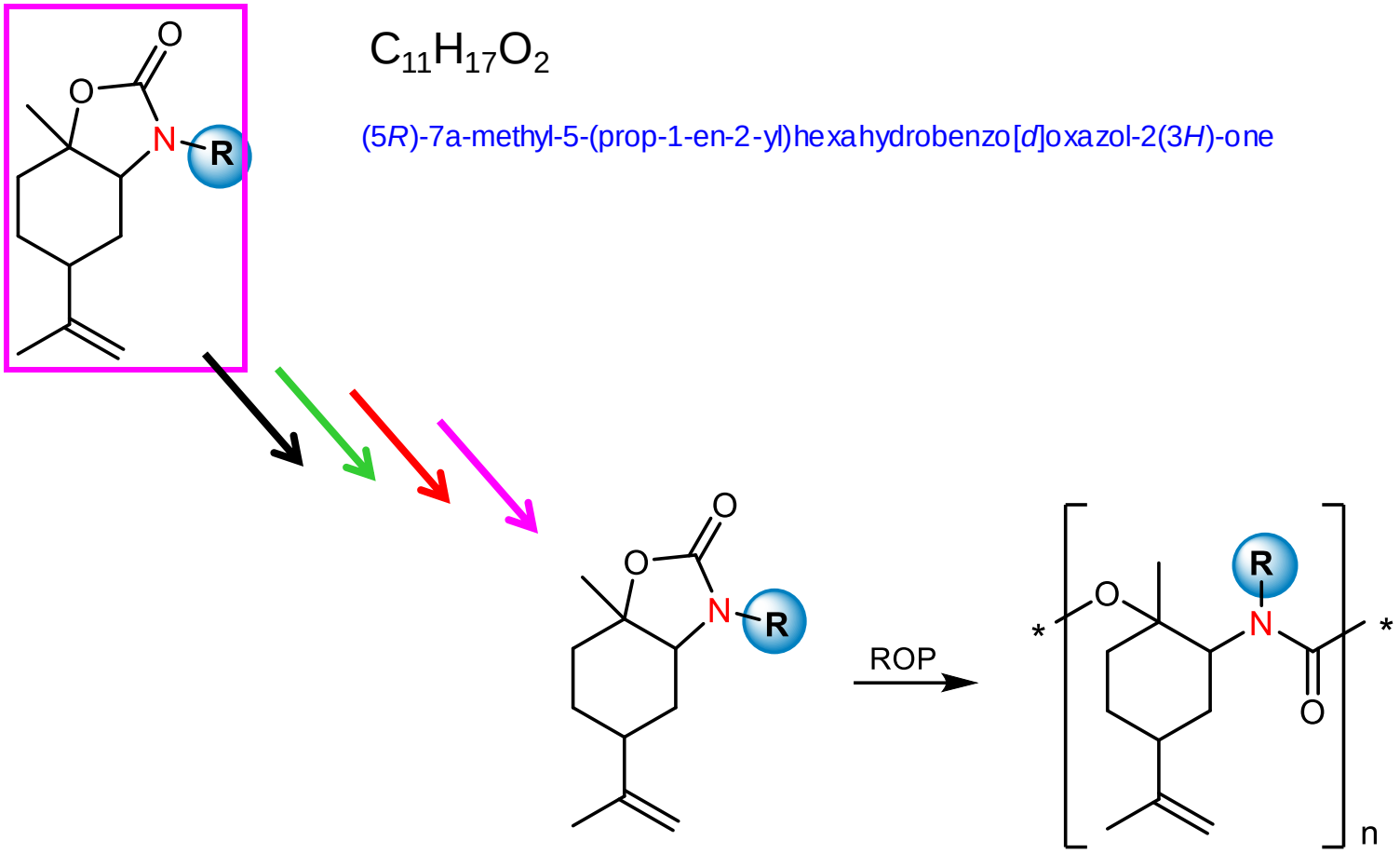
R = CH_3, $(CH_2)_5CH_3$, Bn, Ph

Synthesis of a library of cyclic carbamates via DAC chemistry

Green syntheses
No toxic reagents
High Yields

L. Rubino, A.Rescifina, V. Patamia, M. Galimberti, V. Barbera (2021). Manuscript in preparation

Polyurethanes from biosourced materials



$C_{11}H_{17}O_2$

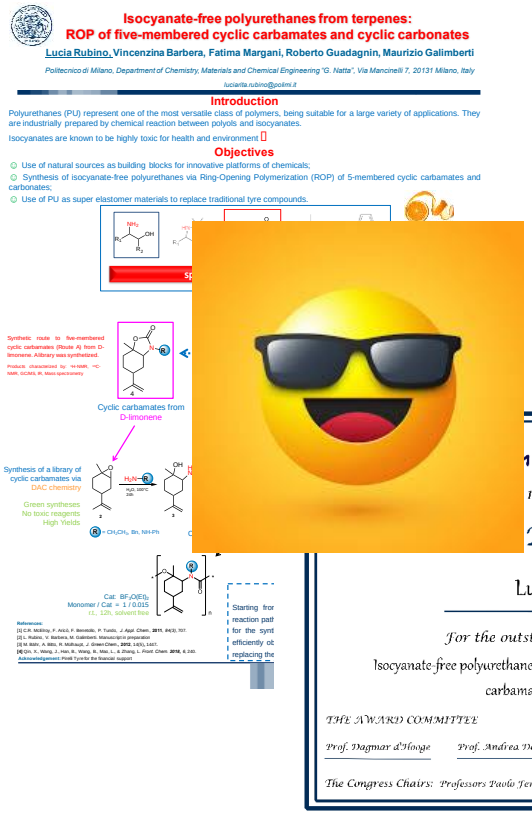
(5*R*)-7a-methyl-5-(prop-1-en-2-yl)hexahydrobenzo[*d*]oxazol-2(3*H*)-one

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

Polyurethanes from terpenes: award

PhD Project

Lucia Rubino
(Post Doc)



Innovative Materials Group

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