WORKSHOP DEI RICERCATORI - JOINTLABS

BIO-BASED BUILDING BLOCKS

POLITECNICO MILANO 1863

PIRELLI

150 YEARS

Renewable sources

Estimated global production of biomass: about 10^{11} ton/year. Only 3% is cultivated, harvested, and used. The agricultural dry biomass waste is about 20 Gton

Sustainable materials

Sustainable materials

1 Bio-based building blocks

2 Recycling

3 Energy sources with the lowest environmental impact

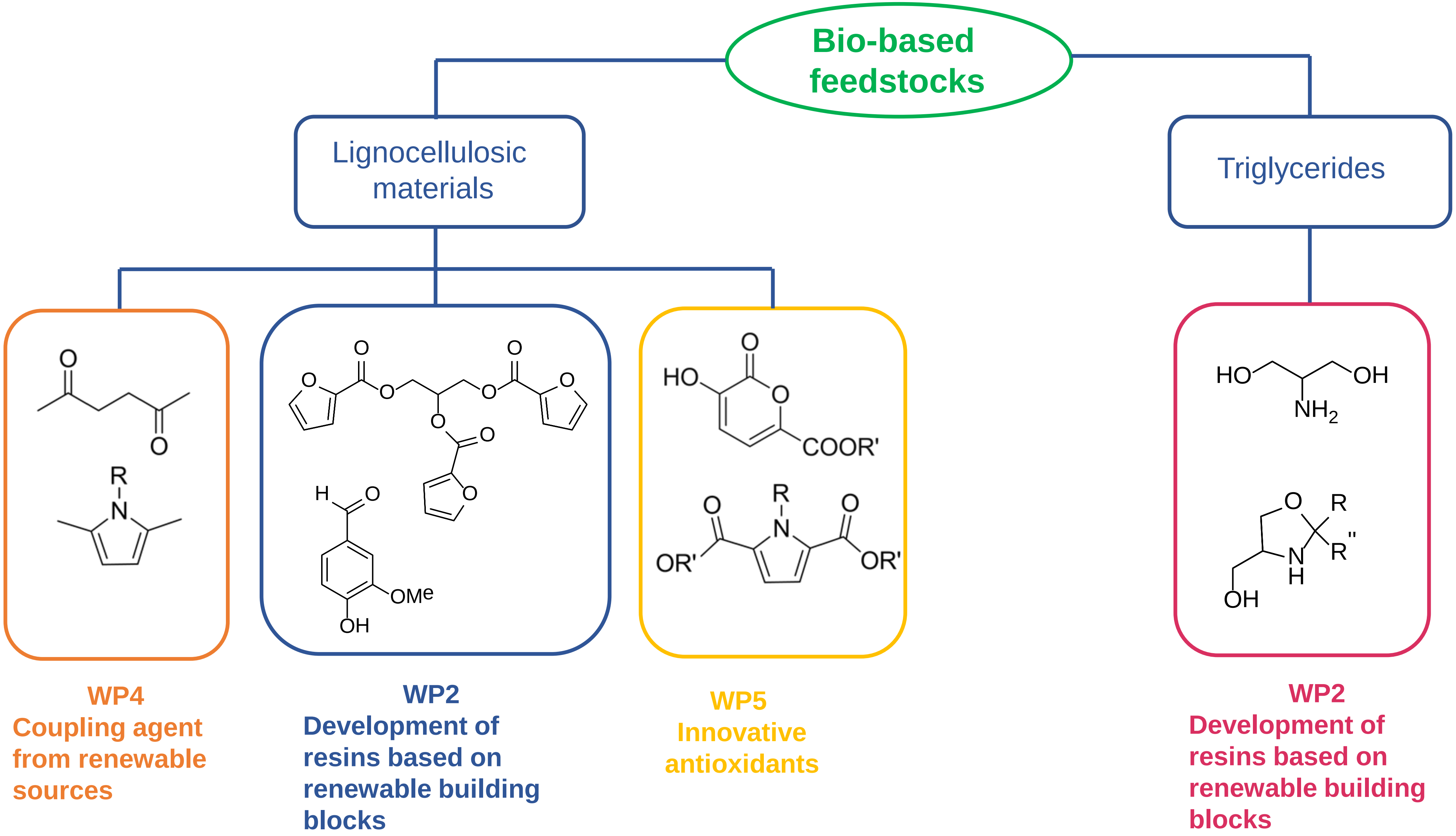
4 Capture of CO_2

Biomass feedstock

- Terpenes
- Lignocellulose
  - Carbohydrates
  - Lignin
- Proteins
- Triglycerides

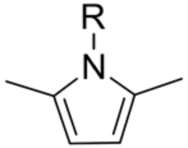
R. Meys, A. Kätelhön, M. Bachmann, B. Winter, C. Zibunas, S. Suh, A. Bardow, *Science*, **2021**, *374*, 71–76

Bio-based building blocks



Items of the presentation

1)



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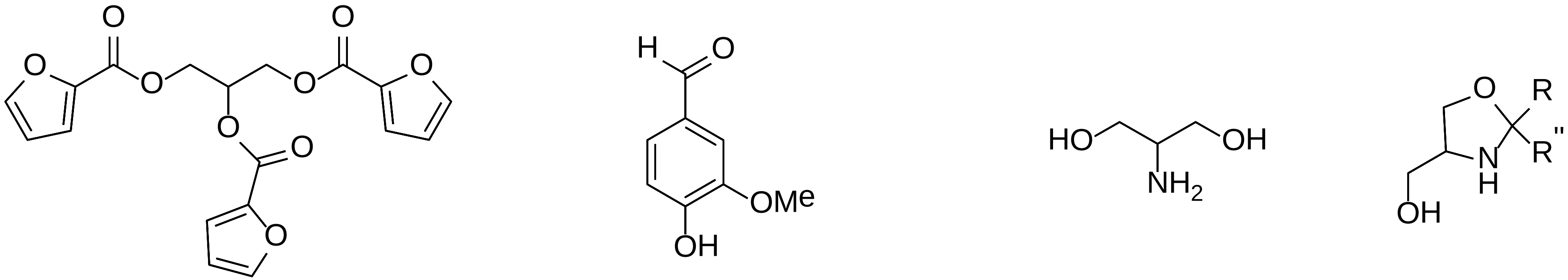

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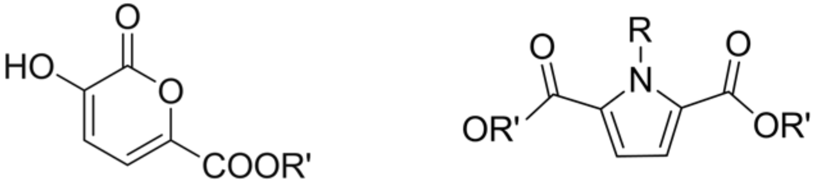
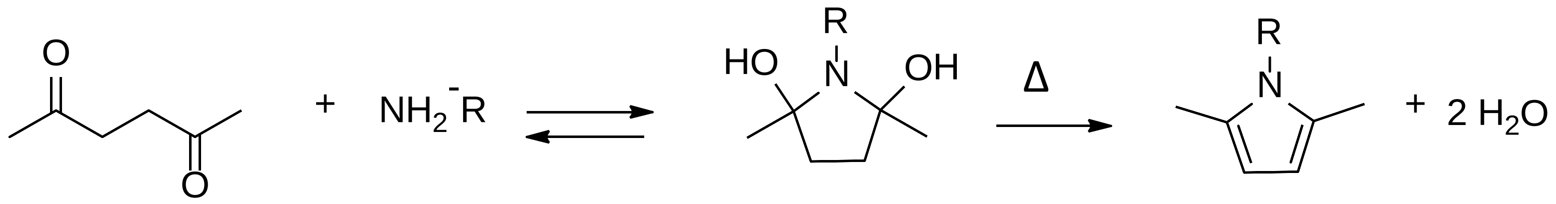


Paal-Knorr reaction



High yield: **85-96%**

Atom efficiency: **85%**

Easy procedure

No solvent

Co-product: **H_2O**

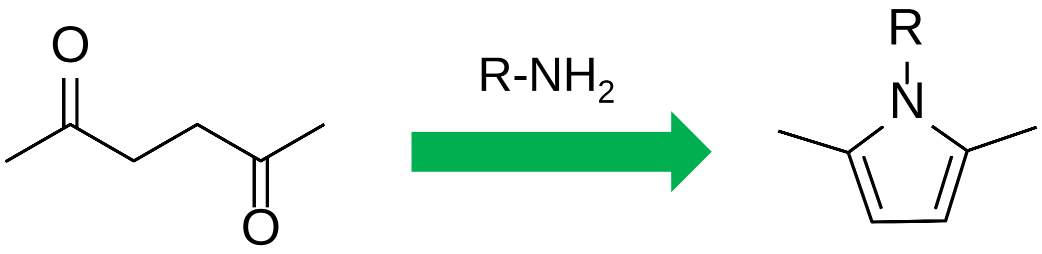
V. Barbera, A.Citterio, M. Galimberti, G. Leonardi, R. Sebastiano, S.U.Shisodia, A.M. Valerio ***WO 2015 189411 A1***

M. Galimberti, V. Barbera, A. Citterio, R. Sebastiano, A. Truscello, A. M. Valerio, L. Conzatti, R. Mendichi, *Polymer*, **2015,** *63*, 62–70

M. Galimberti, V. Barbera, S. Guerra, L. Conzatti, C. Castiglioni, L. Brambilla, A. Serafini,, *RSC Adv.*,**2015**, *5*, 81142-81152

V.Barbera, S.Musto, A.Citterio, L.Conzatti, M.Galimberti, *eXPRESSPolymerLetters,* **2016**,*10*(7), 548–558

Objective of the Project



Bio-based 2,5-hexanedione

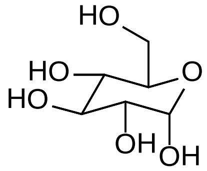
(HD)

Bio-based pyrroles

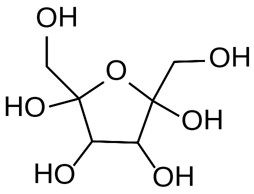
Lignocellulosic sources for preparing bio-HD

Lignocellulosic starting materials

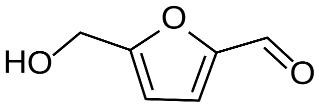
Step 1: depolymerization and hydrolysis



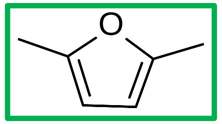
Step 2: isomerization to D-fructose



Step 3: dehydratation of D-fructose to 5-hydroxymethylfurfural



Step 4: hydrodeoxigenation

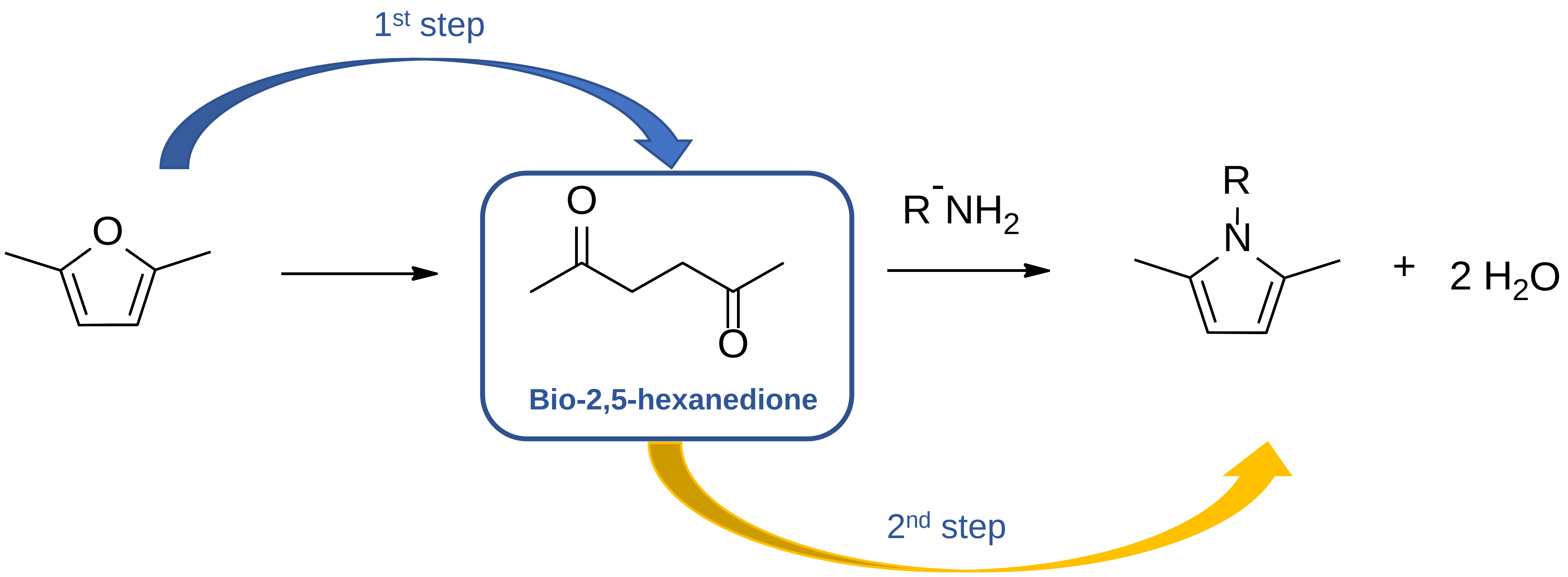


2,5-dimethylfuran

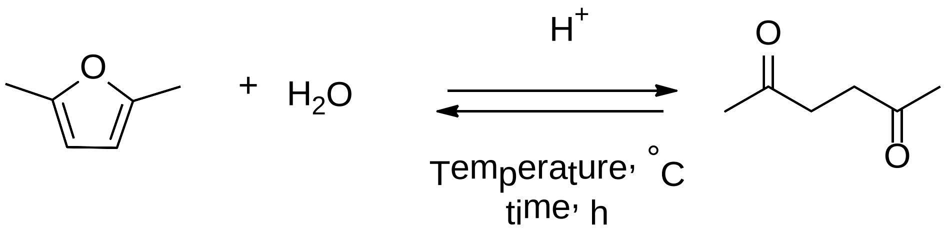
M. Moliner, Y. Roman-Leshkov, M. E. Davis, *Proc. Natl. Acad. Sci. U.S.A.* **2010**, *107*, 6164-6168
Y. Roman-Leshkov, J. N. Chheda, J. A. Dumesic, *Science* **2006**, *312*,1933-1937.
G. H. Wang, J. Hilgert, F. H. Richter, F. Wang, H. J. Bongard, B.Spliethoff, C. Weidenthaler, F. Schuth, *Nat. Mater*. **2014**, 13, 294-301

Technical objective: from dimethylfuran to hexanedione

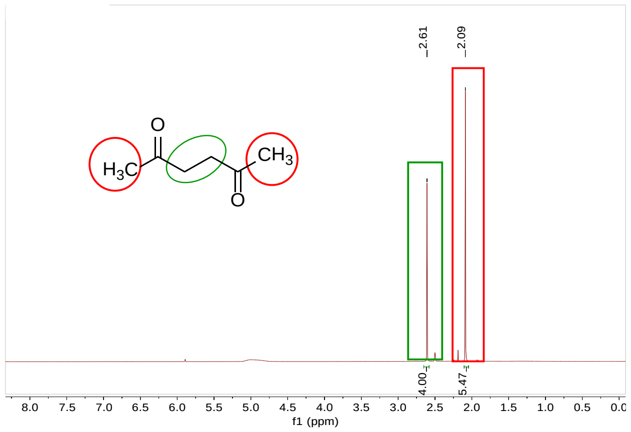
- HD ready as reagent for preparing pyrrole compounds. The role of H_2O !
- One pot two steps synthesis
- Green synthesis with high atom efficiency



Hexanedione for the preparation of pyrrole compounds



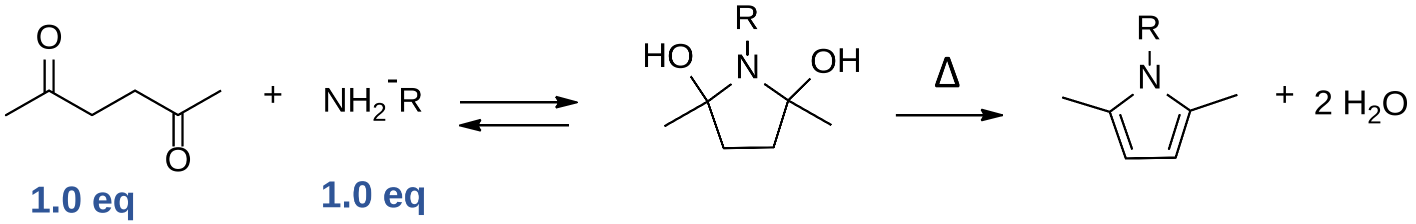
Stoichiometric amount of water

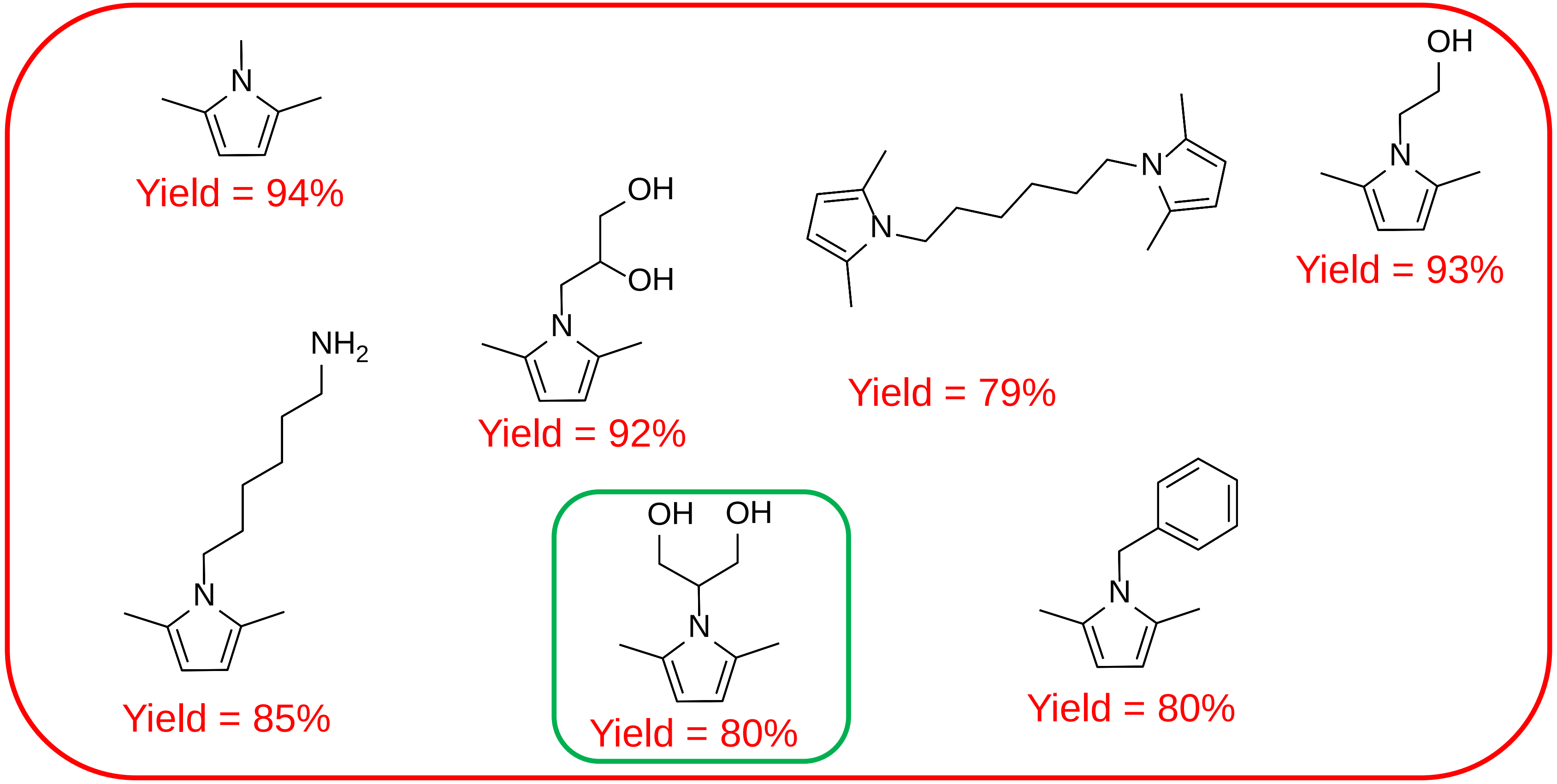


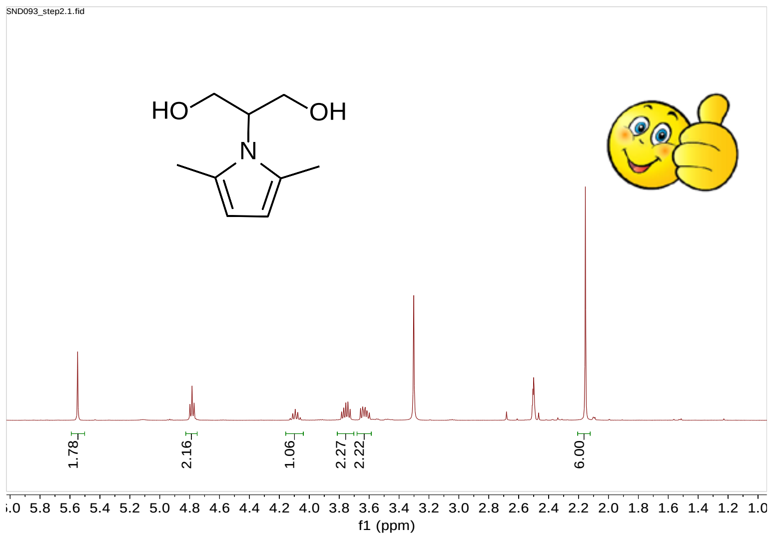
Time	24 h
Temperature	50 °C
Ratio 2,5-dimethylfuran / water (mmol)	**1 / 1**
Type and amount of acid	Strong mineral acid, in particular H_2SO_4, 4 mol%

Italian Patent Application n. 102021000032138, inventors: V. Barbera, M. Galimberti, L. Giannini, S. Naddeo

A library of pyrrole compounds

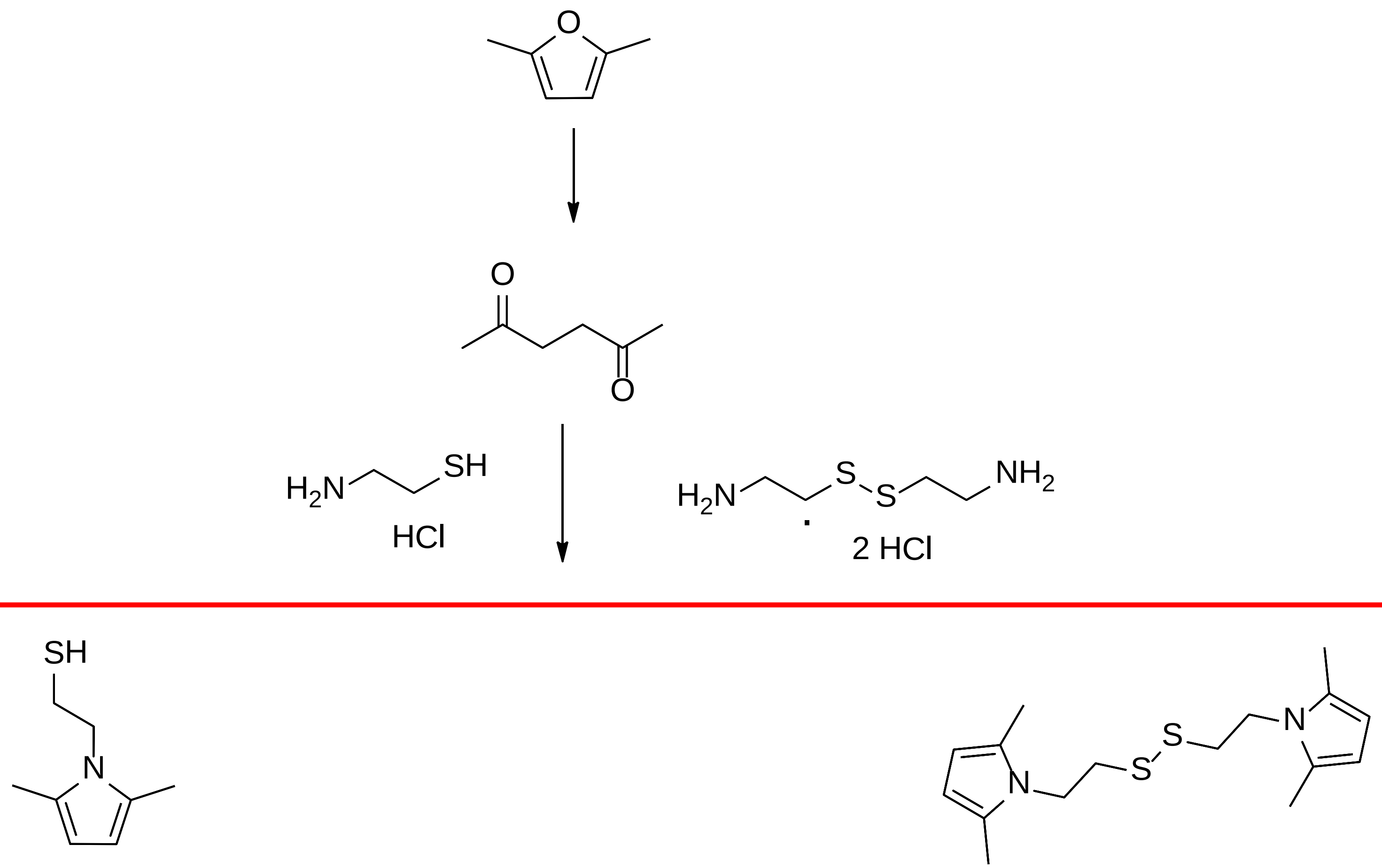






Italian Patent Application n. 102021000032138, inventors: V. Barbera, M. Galimberti, L. Giannini, S. Naddeo

A library of pyrrole compounds



Yield = 73%

Yield = 78%

All bio pyrrole compounds reactive with unsaturated elastomers

Conclusions

- **2,5-hexanedione** was successful synthesized starting from 2,5-dimethylfuran in **95% of yield**;

- **Pyrrole compounds** were obtained in yield from **73% - 93%** via one pot two steps synthesis;

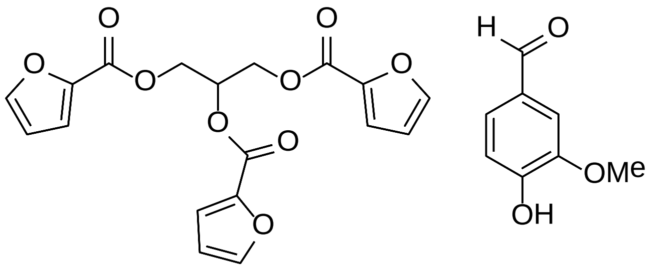
- A patent application was filed.

Resin based on renewable bio-sources

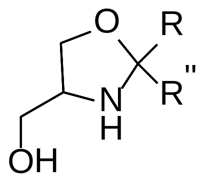
Objective of the project: to replace oil based resins with bio-based materials

Lignocellulosic starting materials

Triglycerides



Alternative aromatic substrates

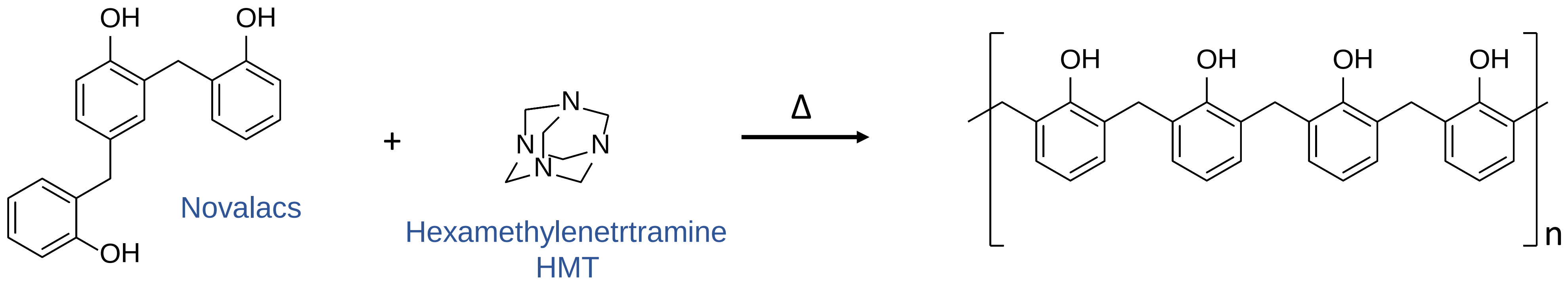


Innovative Methylene donors

Thermosetting Resins

Synthesis of thermosetting resins: state of the art

1)



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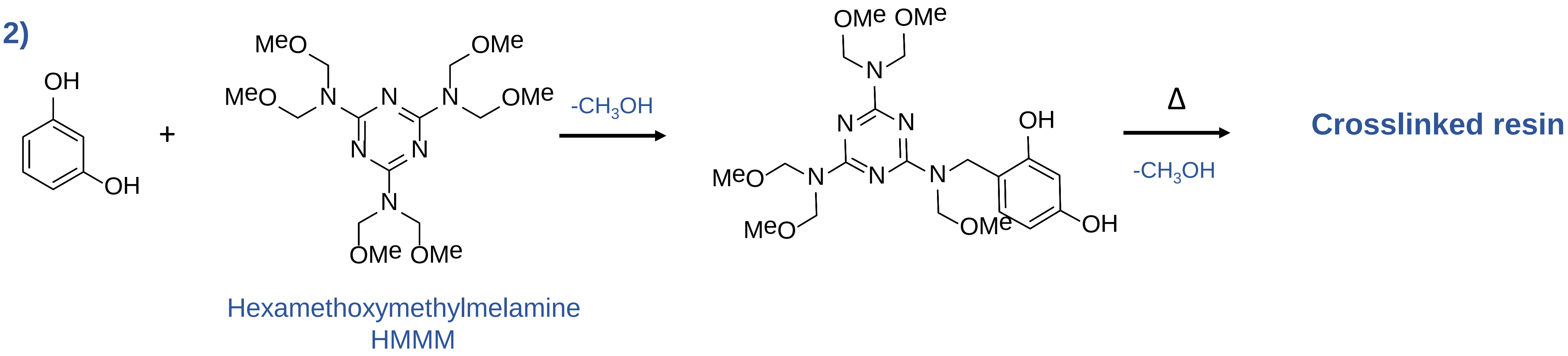


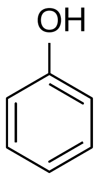
Akrochem. Reinforcing Phenolic Resins, **2017**

M. R. Acocella, A. Vittore, M. Maggio, G. Guerra, L. Giannini, L. Tadiello, *Polymers,* **2019**, 11, 1330

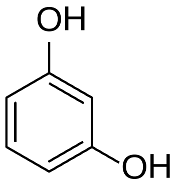
Classical thermosetting resins: some aspects to take into account

Drawbacks:

1)

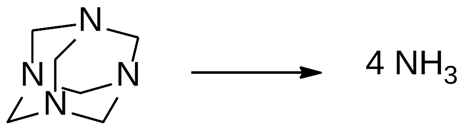


Phenol

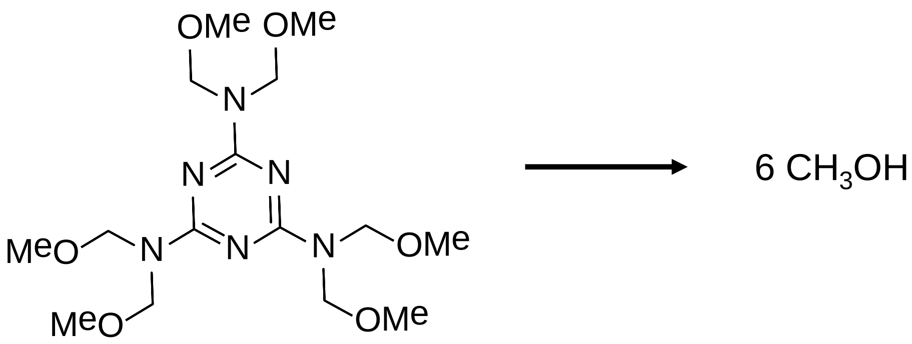


Resorcinol

2)



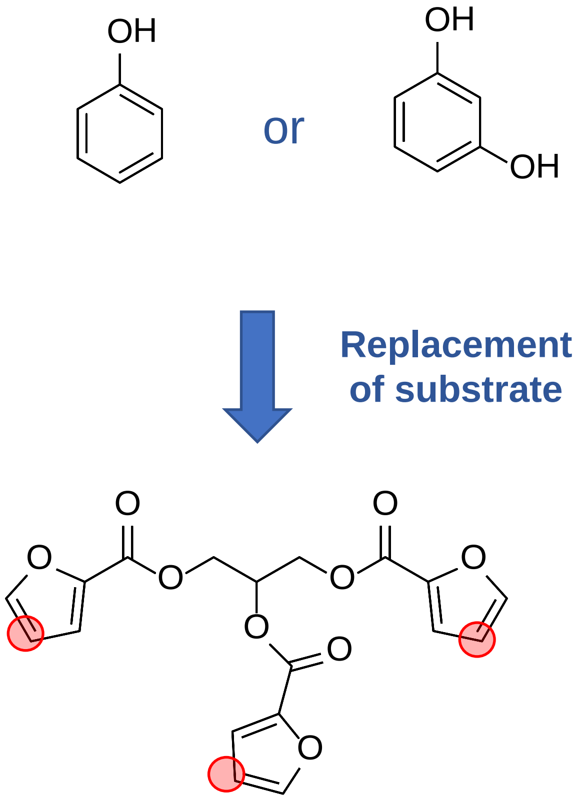
Hexamethylenetrtramine
HMT



Hexamethoxymethylmelamine
HMMM

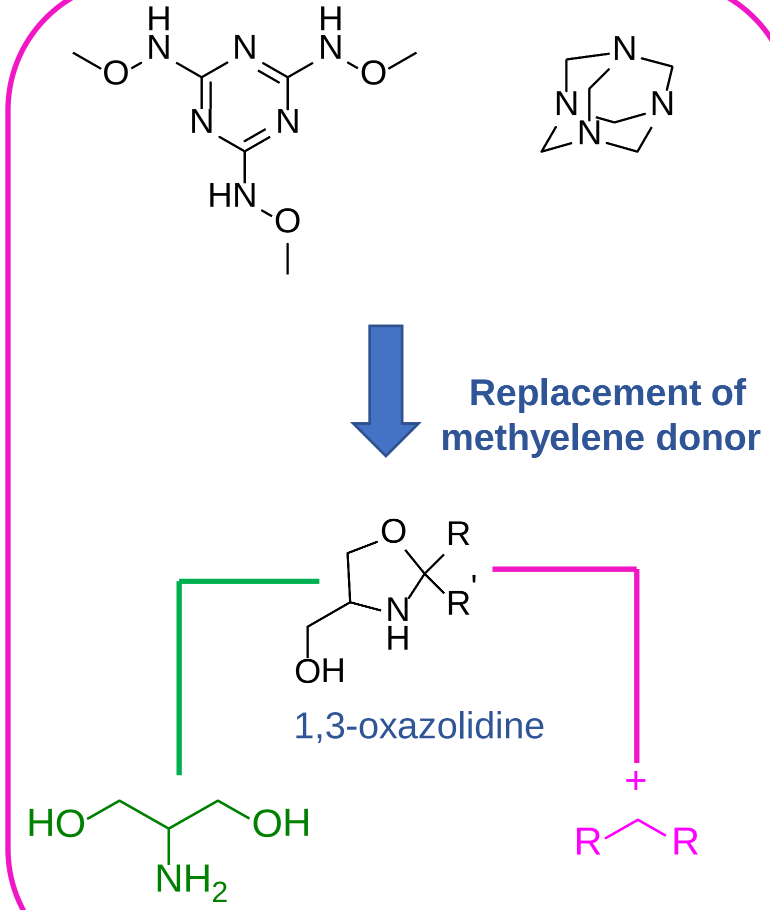
Technical objectives

1



Glyceryl furanoate

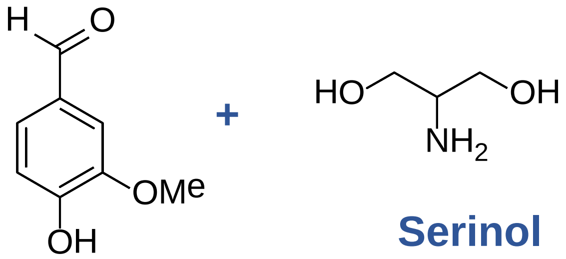
2



Serinol

3

***In situ* activation of bio-based substrate**

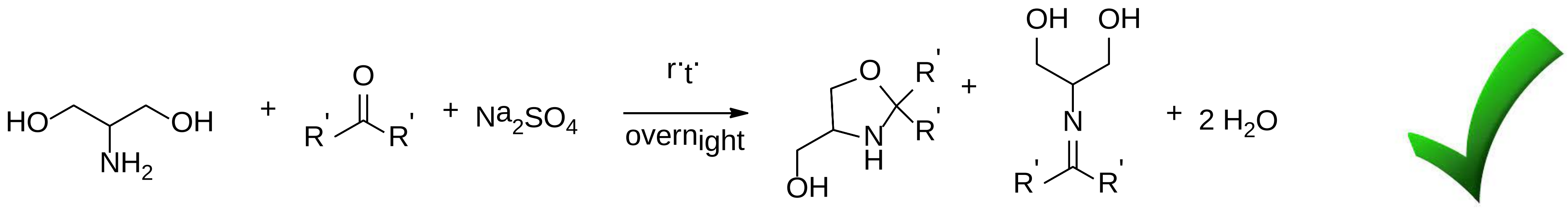


Vanillin

Serinol

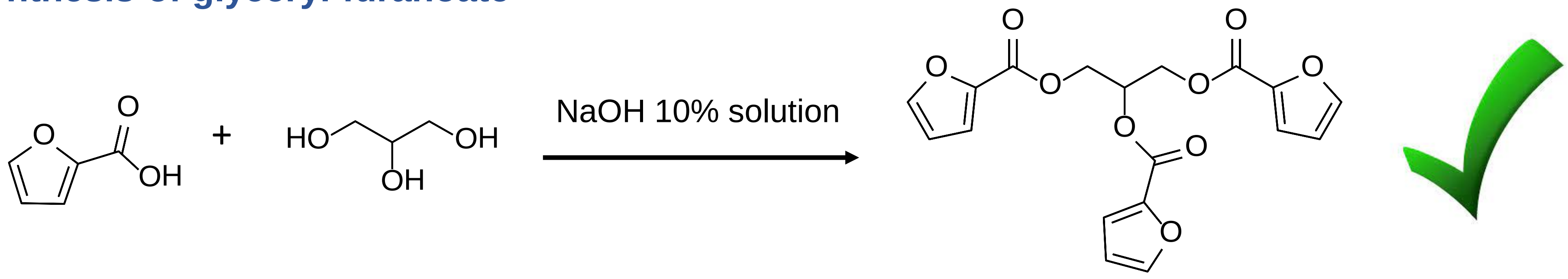
What has been done

1) Synthesis of 1,3-oxazolidine



Yield = 85% **Yield =15%**

2) Synthesis of glyceryl furanoate



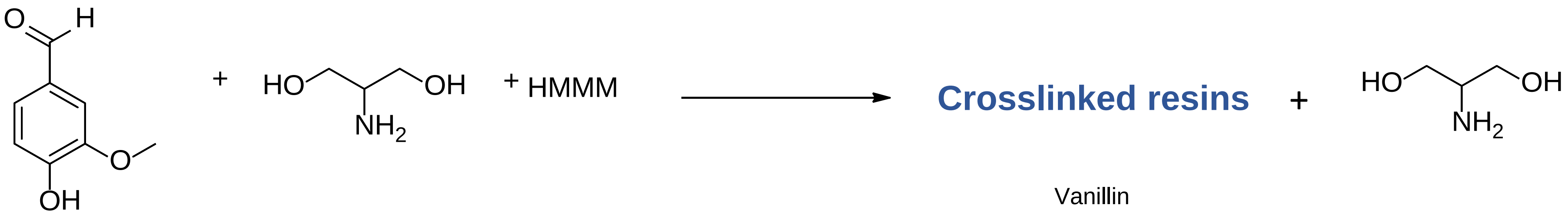
At present: Low yield

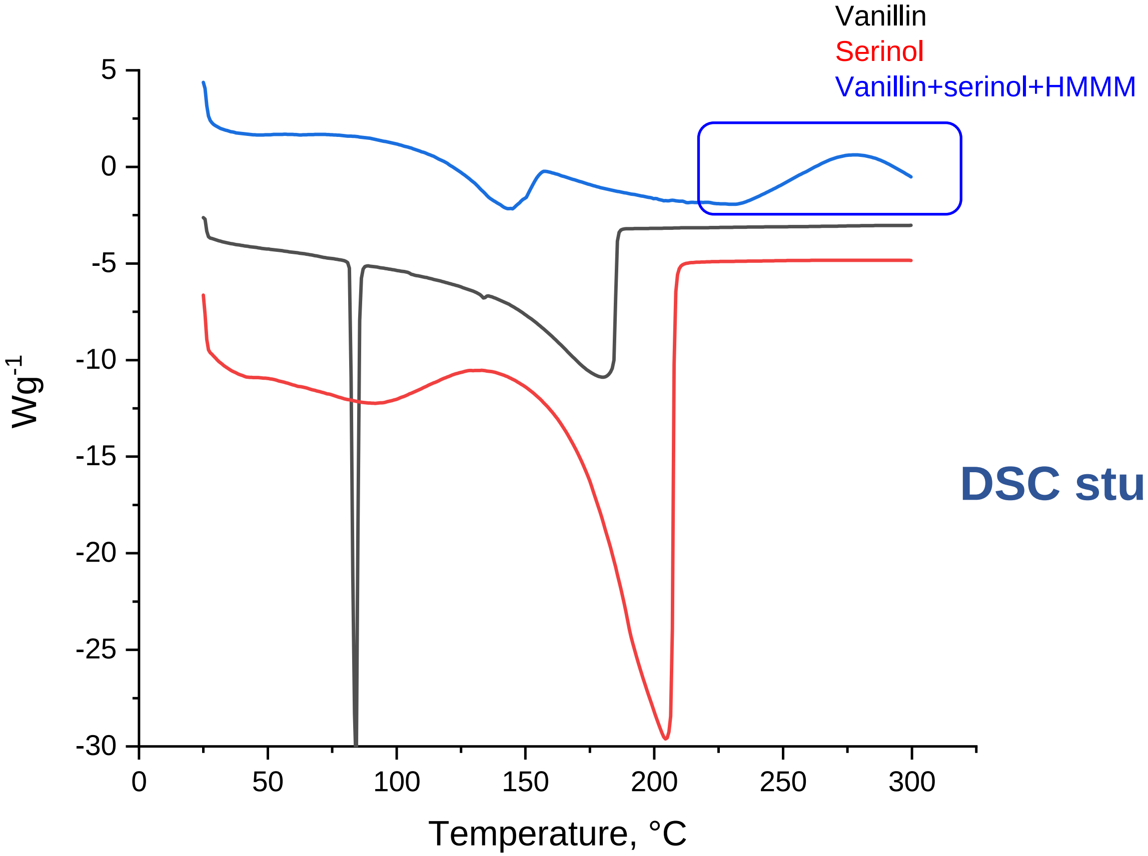
V. Barbera, G. Leonardi, A. M. Valerio, L. Rubino, S. Sun, A. Famulari, M. Galimberti, A. Citterio, R. Sebastiano, *ACS Sustainable Chem. Eng.*, **2020**, *8*, 9356−9366

Luella, "A study of furoyl chloride." Electronic Theses and Dissertations. Paper 1894.https://doi.org/10.18297/etd/1894 (1936).

What has been done

3) *in situ* activation of Vanillin





Exothermic peak

T = 277.94 °C

ΔH = 375.65 J/g

DSC studies

Conclusions

- **1,3-oxazolidine was successfully synthesized in 84% of yield;**

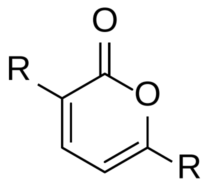
- Glyceryl furanoate was synthesized (low yield).

  DSC studies for the reaction of glyceryl furanoate with HMMM are in progress.

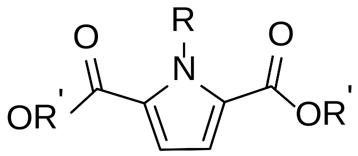
- **Reaction between Vanillin, HMMM and serinol**

  Promising indications

Antioxidant and antiozonants



2-pyrones



Pyrroles from pyrones

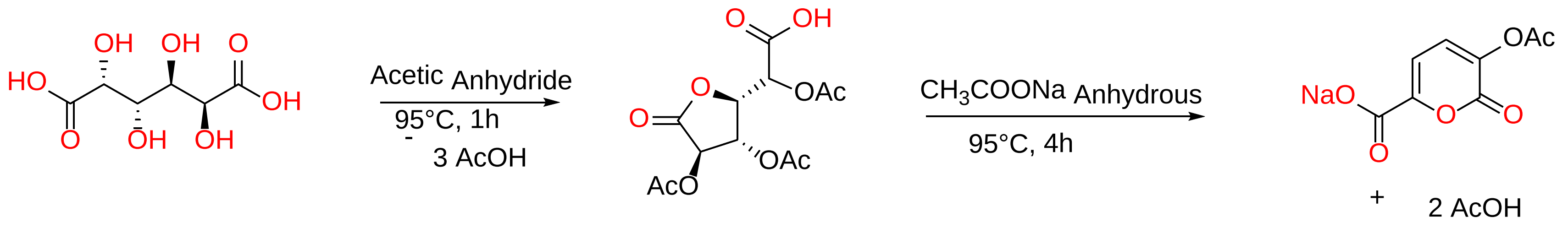
Antioxidant and Antiozonant activity

Functionalization of sp^2 carbon allotropes and inorganic oxyhydroxides

Synthesis of pyrones

Lab scale

Reaction scheme for the synthesis of sodium 3-acetoxy-2-oxo-2H-pyran-6-carboxylate (Pyr-Na)

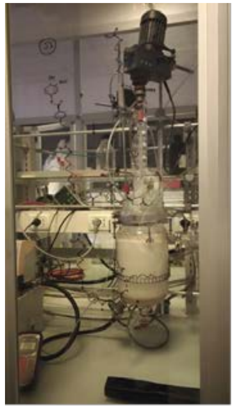


Mucic Acid

(*S*)-2-acetoxy-2-((2*S*,3*S*,4*R*)-3,4-diacetoxy-5-oxotetrahydrofuran-2-yl) acetic acid

sodium 3-acetoxy-2-oxo-2*H*-pyran-6-carboxylate

Pre industrial scale

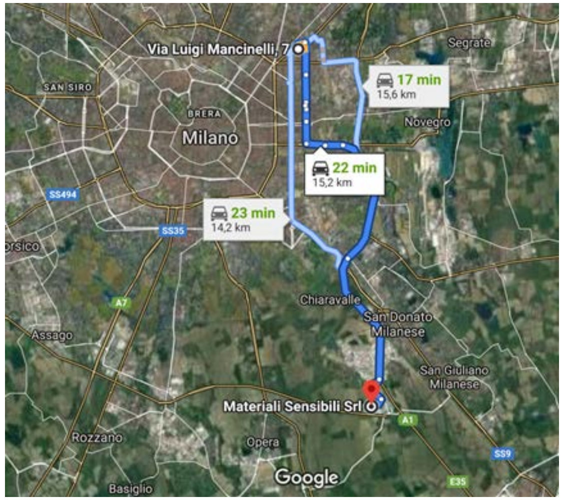


One Pot

4 hours

Yield = 75%

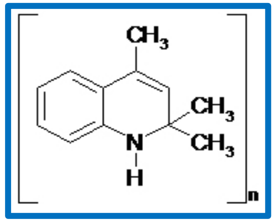
280 gr



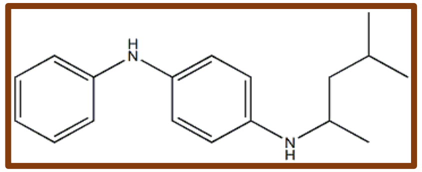
Pyrones as antioxidants and antiozonants for tire compounds

The objective of this work was to compare the behaviour of the following substances:

Traditional substances used in tire compounds

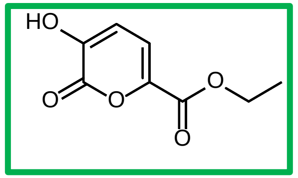


2,2,4-Trimethyl-1,2-Dihydroquinoline polymer
(TMQ)



N-(1,3-dimethylibutyl)-*N*'-phenyl-*p*-phenylenediamine
(6PPD)

Biosourced molecules



Pyr-Ester

Antioxidant agents: properties and results

PROJECT GOAL

To design and develop hardening resins from renewable sources, capable of similar performace of current «phenol-formaldehyde» resins

CURRENT STATUS

Furoic acid and esters and oxazolidines as alternative building blocks - supporting also faster kinetics and «SHORT VULCA PROJECT»

INTELLECTUAL PROPERTY

PIRELLI PATENT	COMPETITORS
Deposited from backgroud work in Pirelli 1 patent on Furoic Acid and derivatives	No specific patents known

CRITICAL ASPECTS	MITIGATION ACTIVITIES
Scale up of reactions to get enough material for technologichally relevant development	Engage companies capable of kg-scale preparations

2021 – Start PhD
2022 – SerinolPirrole from Renewable Molecules
Methylene Acceptor dev.
2023 – Methylene Donor dev.
Scale-up activity
2024 – Transfer to company of best solution
End of PhD
2025 – Indu decision

Ref. Pirelli: Giannini, Tadiello, Guerra
Ref. PoliMi: *Prof. Galimberti, Barbera, Margani, Naddeo*

PROJECT GOAL

Sustainability:

- Investigate potential of Innovative bio-sourced chemicals as antioxidants in rubber compounds
- Methods: define lab. screening methods for candidates antioxidant/antiozonants

CURRENT STATUS

- Pyrone derivatives and Naringerin identified as potential Antioxidants and Antiozonants

INTELLECTUAL PROPERTY

PIRELLI PATENT

Patent in preparation for Pyrone derivatives:
- Antioxydants
- Black fillers modifiers

COMPETITORS

No known activities on Pyrones and similar species.

CRITICAL ASPECTS

- Antioxidant/ozonant performance not fully evaluable by lab tests
- HSE profile to be fully evaluated

MITIGATION ACTIVITIES

- Investigation of Laboratory methods to assess Antioxydant activity performed
  - ✓ Different approaches confirm reactivity pattern