Two steps one pot process for the conversion of dimethylfuran to pyrrole compounds with almost null E- factor

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Ancona, June 16-17

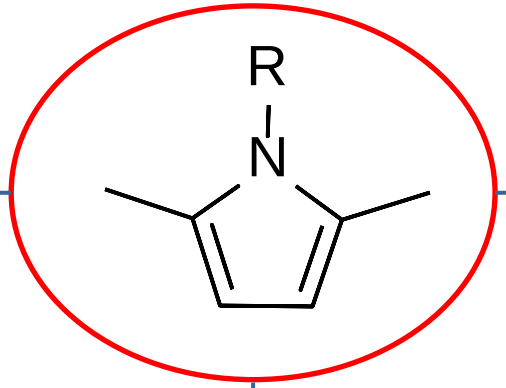
ISCaMaP

Innovative Sustainable Chemistry and Materials and Proteins Group

Innovative Sustainable Materials GROUP in ISCaMaP

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

Pyrrole compouds: multipurpose *Janus* molecules



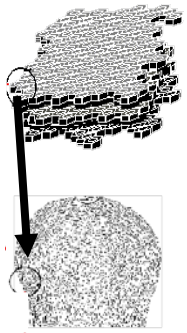
1) Fuctionalization of sp^2 carbon allotropes

2) Pyrrole compounds as monomers for chain and step growth polymerizations

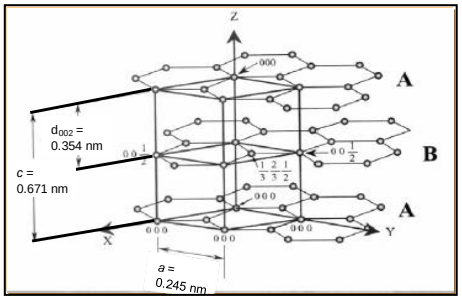
3) Fuctionalization of inorganic oxyhydroxides

Janus de Gennes P. G. *Angewandte Chemie International Edition in English*,**1992**, ***31***(7), 842-845
Galimberti M., Barbera V., Guerra S., Conzatti L., Castiglioni C., Brambilla L., Serafini A., 2015, *RSC Adv.,* **5**, 81142-81152.

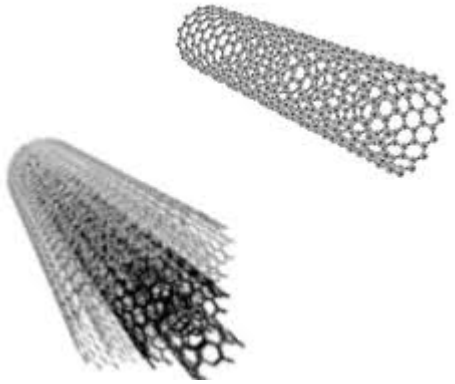
1) Pyrrole compounds for the functionalization of sp^2 carbon allotropes



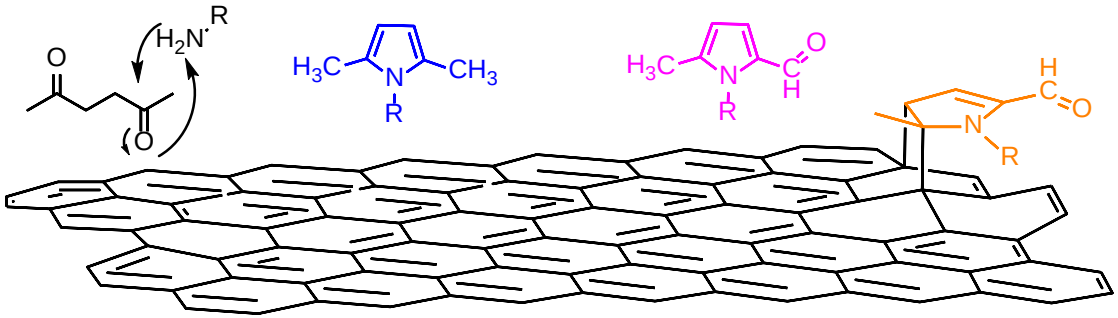
Carbon black



Few-layers graphene



CNT

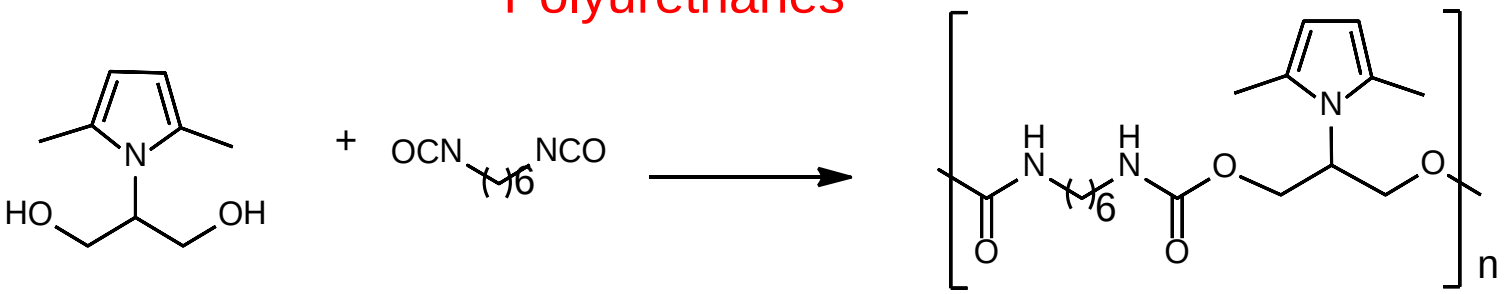


Proposed mechanism for the functionalization of sp^2 carbon allotropes with pyrrole compounds

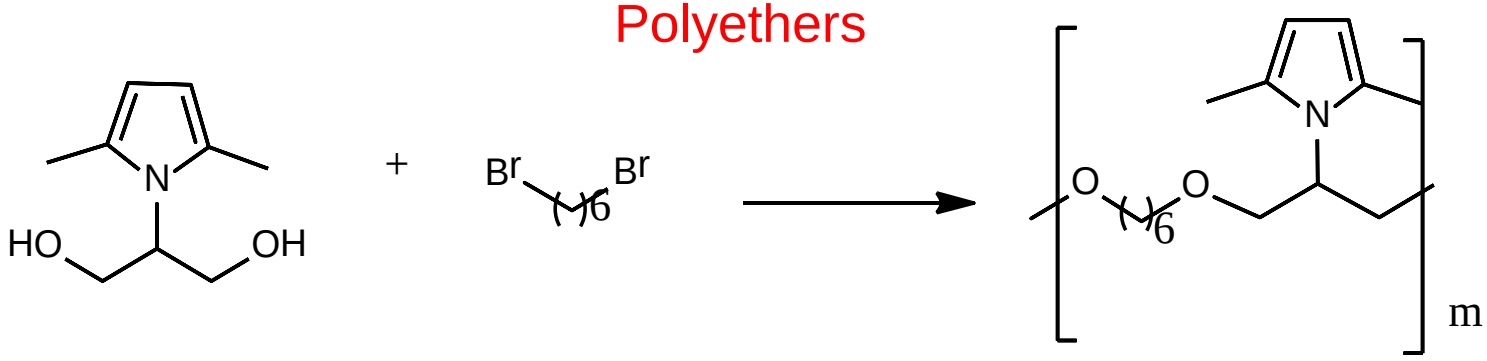
V. Barbera, L. Brambilla, A. Milani, A. Palazzolo, C. Castiglioni, A. Vitale, M. Galimberti, *Nanomaterials*, **2019**, *9*, 44.
EP3209604 B1; US10160652 B2. M. Galimberti, V. Barbera, R. Sebastiano, A. Citterio, G. Leonardi, A. M. Valerio.

2) Pyrrole compounds as monomers for chain and step growth polymerization

Polyurethanes

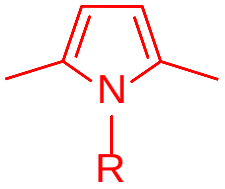


Polyethers



M. Galimberti, V. Barbera, A. Citterio, R. Sebastiano, …R. Mendichi, **2015**,Polymer, 63, 62–70.
V. Barbera, S. Musto, A. Citterio, L. Conzatti, M. Galimberti, **2016**, *eXPRESS Polymer Letters Vol.10, No.7,* 548–558
EP3180379 B1. M. Galimberti, V. Barbera, A. Truscello, R. Sebastiano, A. M. Valerio.

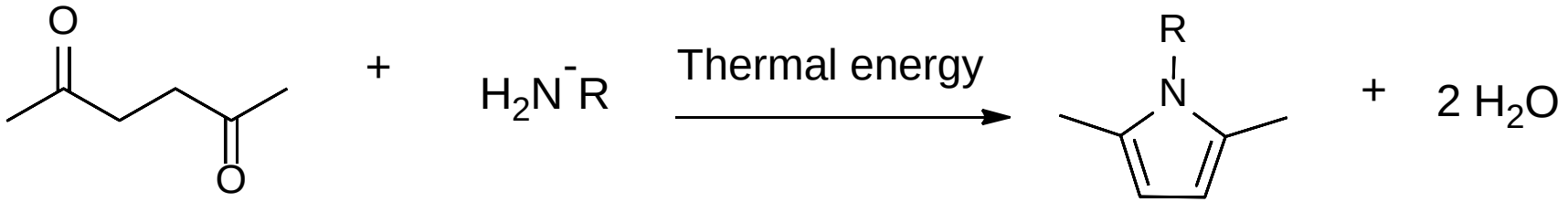
3) Pyrrole compounds for the functionalization of inorganic oxyhydroxydes



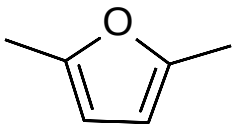
EP3755687B1 M.Galimberti, V.Barbera, A. Bernardi, D. Locatelli

Pyrrole compounds: synthetic pathway

Paal-Knorr reaction:



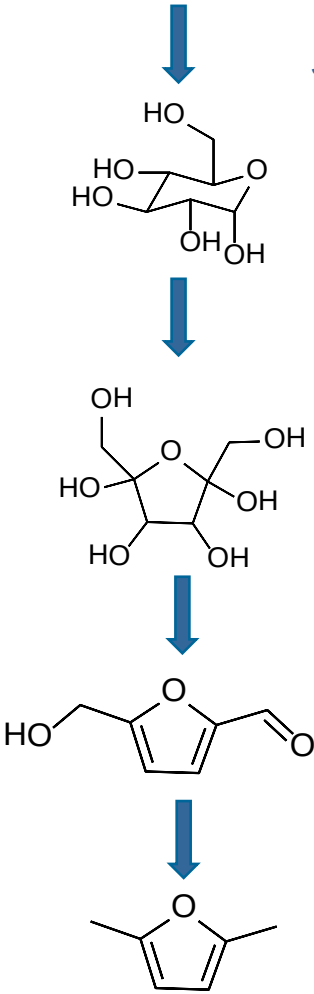
Bio-2,5-hexanedione: could it be obtained by bio-based feedstock?



2,5-dimethylfuran

Lignocellulosic materials as source for many furan compounds

Lignocellulosic starting materials



Step 1: depolymerization and hydrolysis

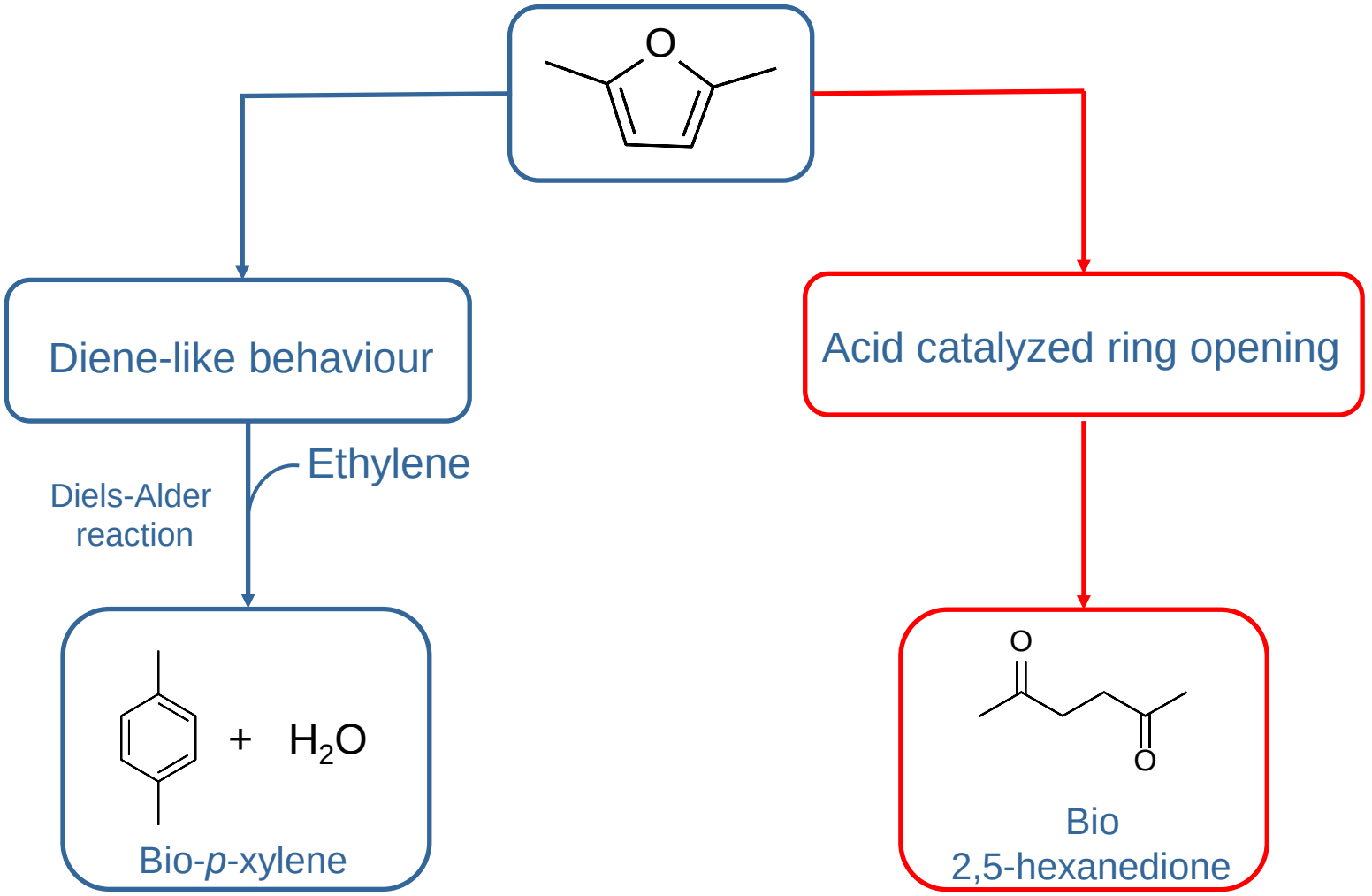
Step 2: isomerization to D-fructose

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

Step 4: hydrodeoxigenation to 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

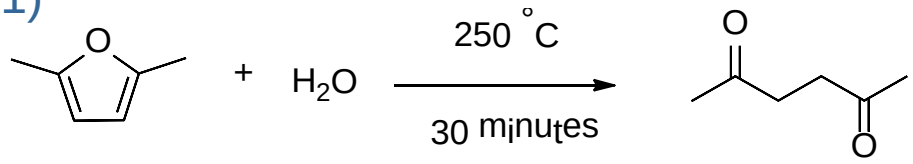
2,5-dimethylfuran: a versatile biobased building block



C. L. Williams, C.-C. Chang, P. Do, N. Nikbin, S. Caratzoulas, D. G. Vlachos,R. F. Lobo, W. Fan, P. J. Dauenhauer, *ACS Catal*. **2012**, *2*, 935−939
Y. Li, L. Guangqiang, Y. Wang, D. Tiansheng, Y. Wang, X. Hou, Y. Yang, *ChemistrySelect,* **2016**, *6*, 1252 – 1255

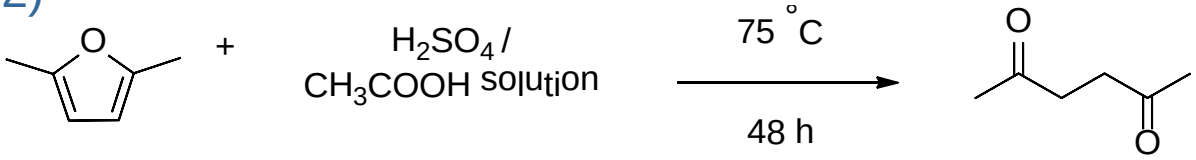
Synthesis of bio-2,5-hexanedione: screening of the literature

1)



95% of yield

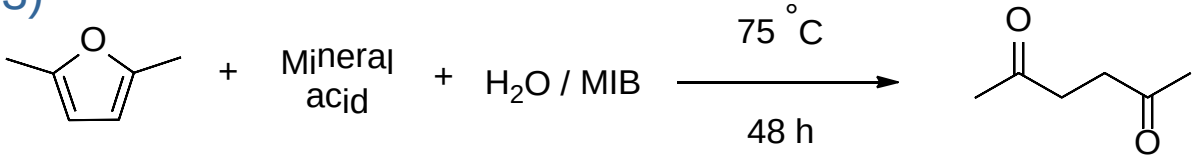
2)



95% of yield

Homoaldol by-products were observed

3)



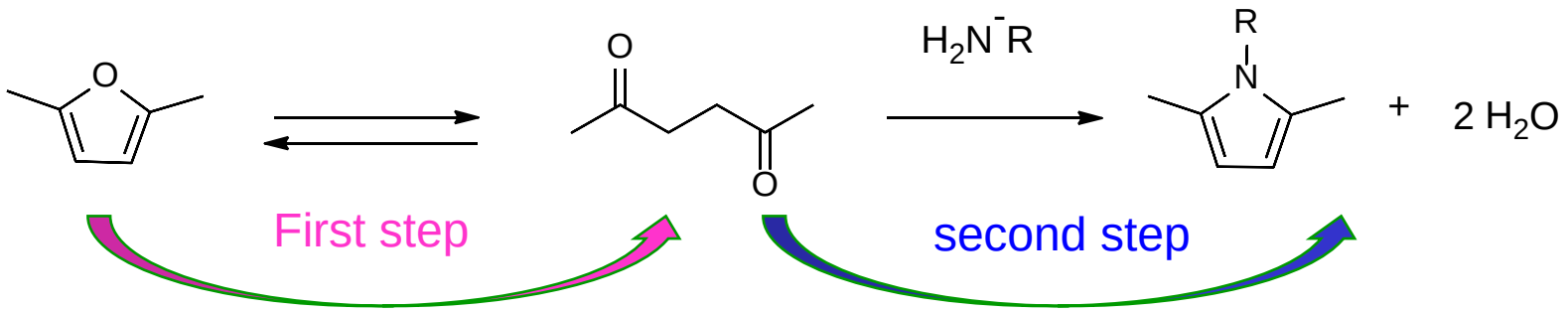
95% of yield

All these synthetic procedures require purification steps

B. Kuhlmann, E. M. Arnett, M. Siskin., *J. Org. Chem*. **1994**, *59*, 3098-3101
Y. Zhang, W. Li, S. Zong, H. Du, X. Shi, *Advanced Materials Research*, **2012**, *518-523*, 3947-3950
Y. Li , G. Lv, Y. Wang, T. Deng, Y. Wang, X. Hou, Y. Yang, *ChemistrySelect,* **2016**, *6*, 1252 – 1255

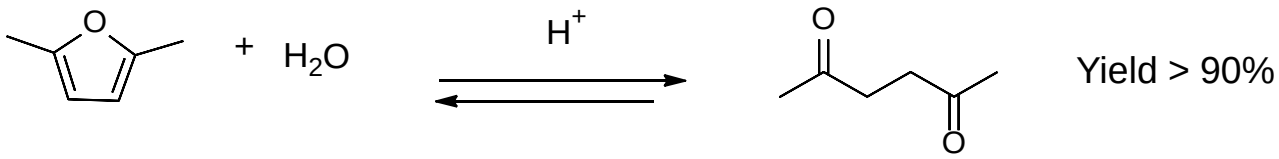
The objective of the work

Two steps - one pot synthesis of pyrrole compounds



Ring opening reaction: screening of the parameters

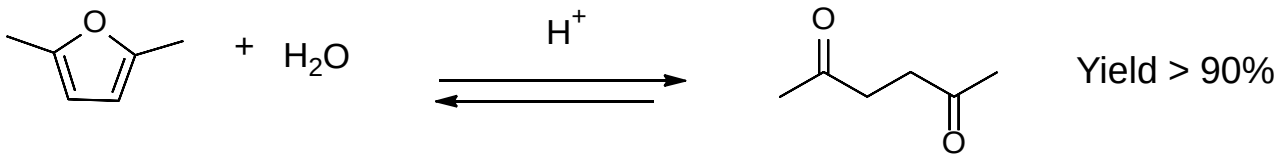
Ring opening reaction is an equilibrium reaction strongly dependent on reaction parameters



1) Time
2) Temperature
3) Amout of water
4) Type of acid
5) Amount of acid

Ring opening reaction: screening of the parameters

Ring opening reaction is an equilibrium reaction strongly dependent on reaction parameters

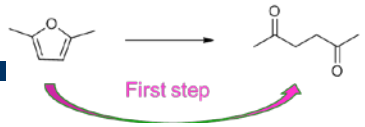


1) Time: 30 minutes – 48 hours;
2) Temperature: r.t – 250 °C
3) Amout of water: 1 - 3 eq. with respect to 2,5-dimethylfuran
4) Type of acid: strong and weak mineral and organic acid
5) Amount of acid: 0 – 15%

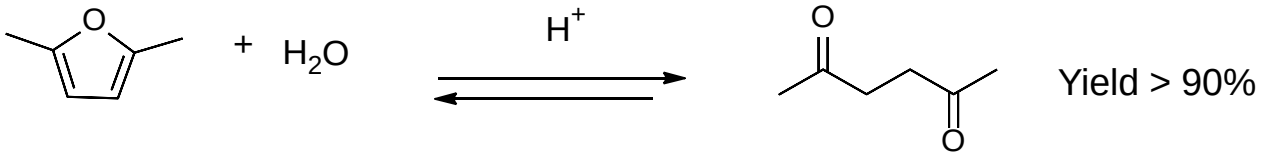
Ranges from prior art and our activity

- Italian Patent Application n. 102021000032138, *inventors: V. Barbera, M. Galimberti, L. Giannini, S. Naddeo*
- *S. Naddeo, M. Galimberti, V.Barbera, Manuscript in preparation 2022* ''Two steps one pot process for the conversion of dimethylfuran to pyrrole compounds with almost null E factor''

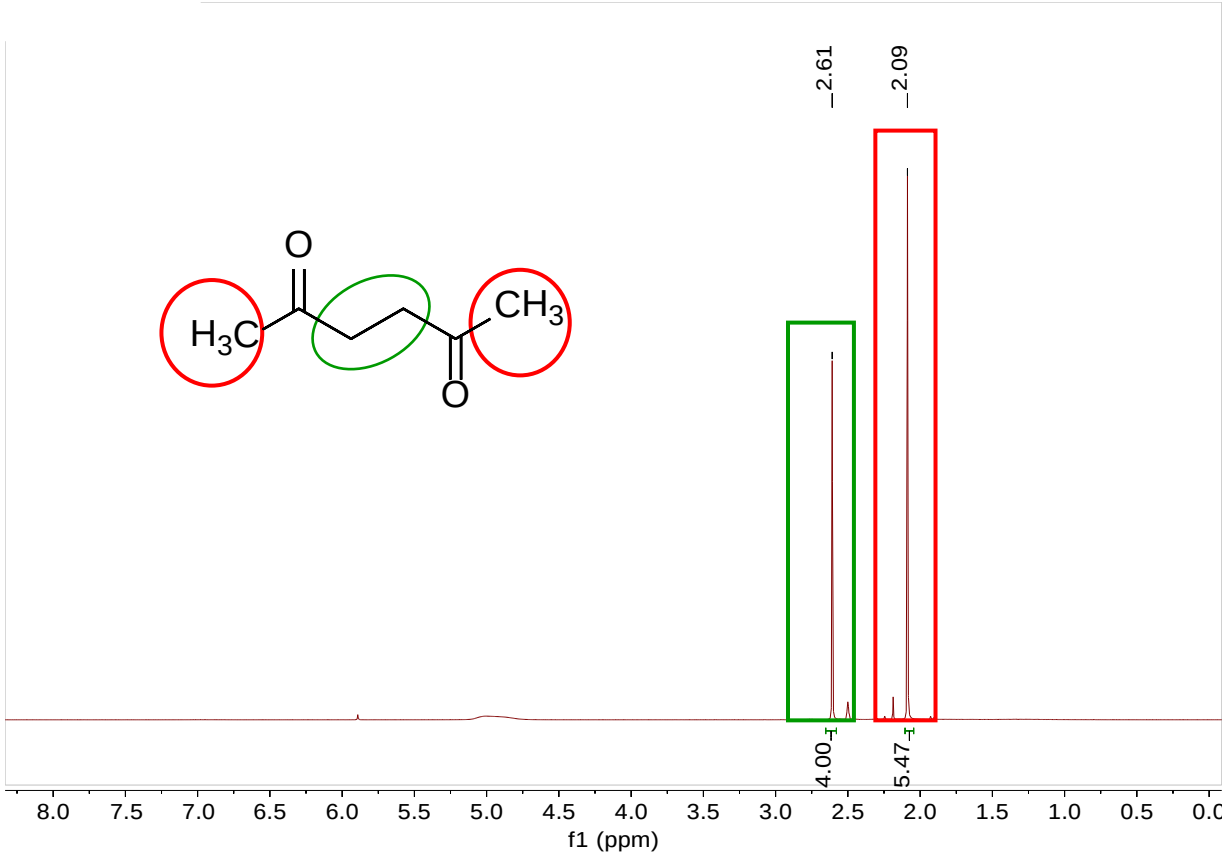
NMR characterization of bio-2,5-hexanedione



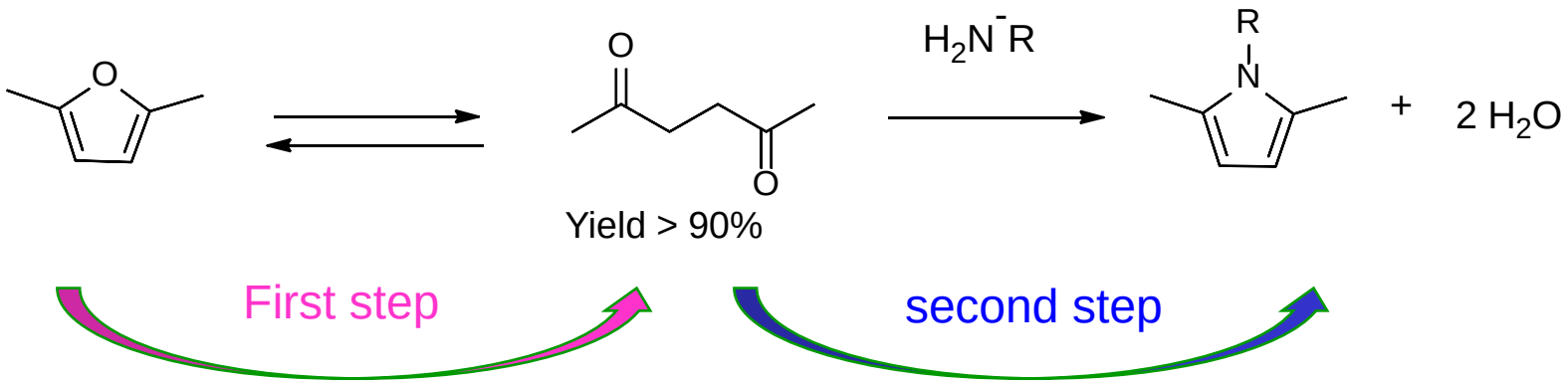
- Optimized conditions obtained after the screening of the parameters



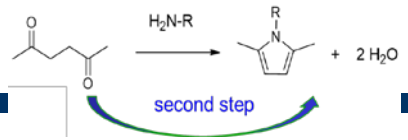
Yield > 90%



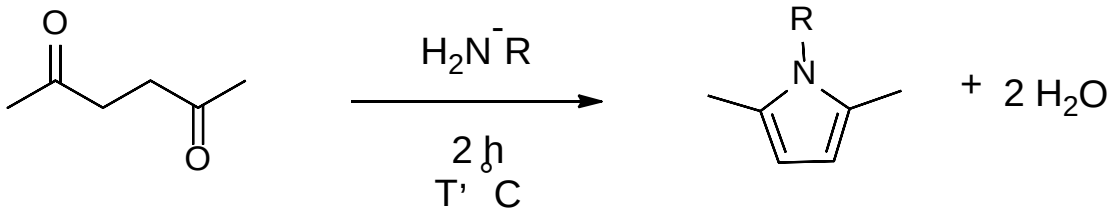
Synthesis of pyrrole compounds: second step



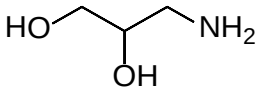
Synthesis of pyrrole compounds: second step



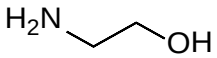
Primary amines were added to 2,5-hexanedione without any purification



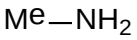
bio-2,5-hexanedione **pyrrole compounds**



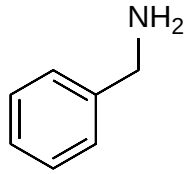
Yield = 92%



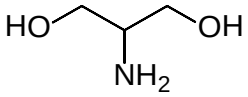
Yield = 93%



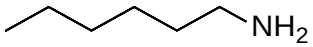
Yield = 94%



Yield = 80%

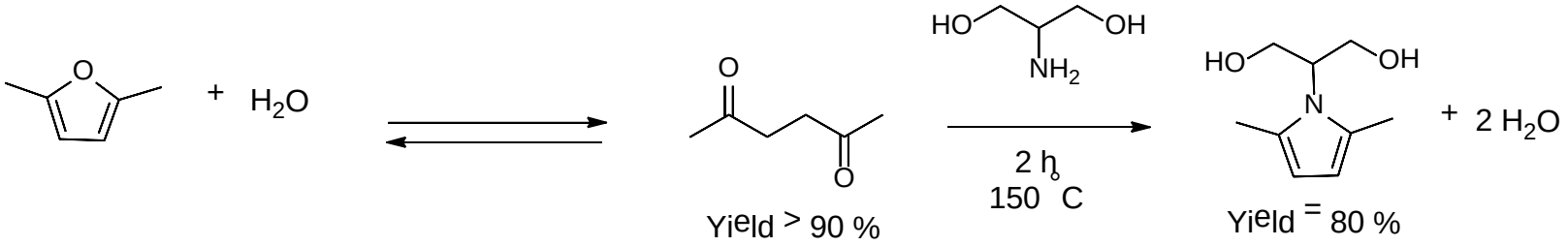


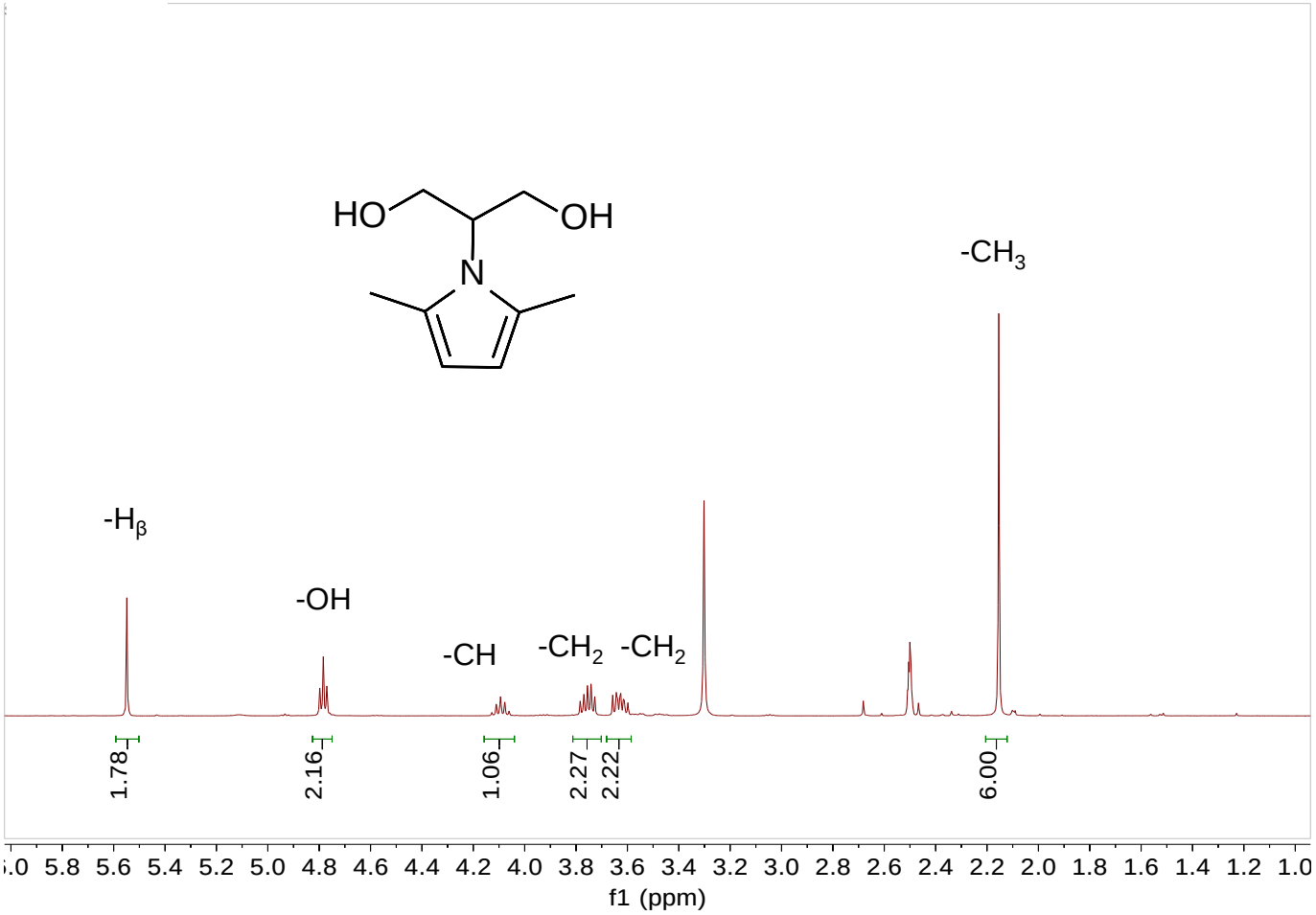
Yield = 80%



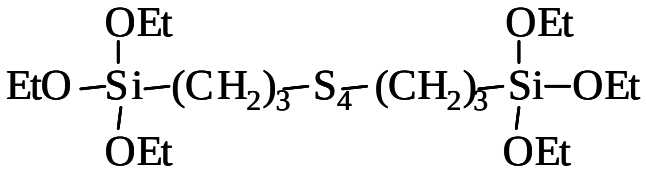
Yield = 85%

Synthesis of serinol-pyrrole via two steps - one pot process from 2,5-dimethylfuran



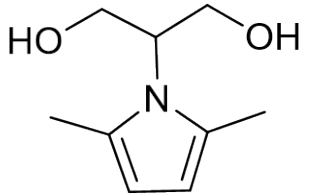


SP as coupling agent for silica in elastomer composites in place of TESPT



TESPT

vs



SP

TESPT: Bis(triethoxysilylpropyl)tetrasulfide

Elastomer composites with silica. Dynamic mechanical properties

Elastomer composite

Poly(styrene-co-butadiene) (SBR) 110, poly(1,4-cis-isoprene) (NR) 20

Silica 50

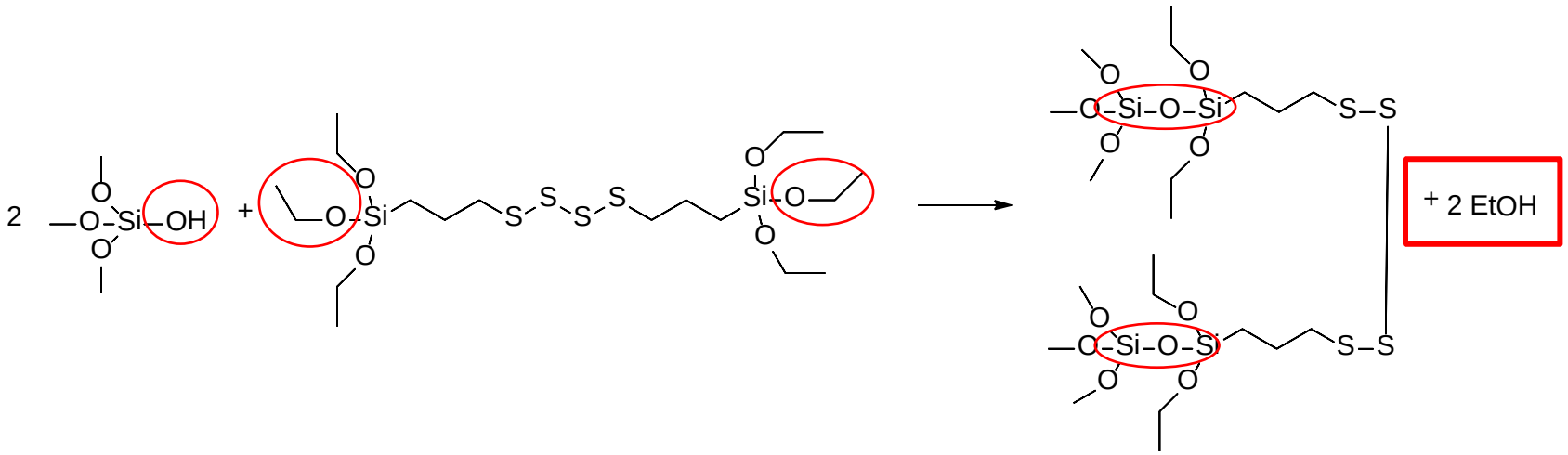
TESPT 8%, SP 9%

ZnO, S, Sulphenamide

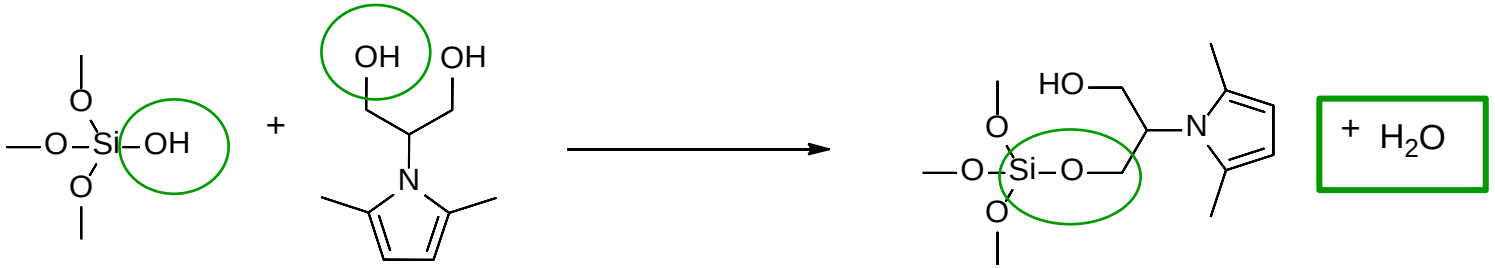
	Silica/TESPT	Silica/SP
$E'_{10\,°C}$	7.83	9.86
$E'_{23\,°C}$	5.86	7.13
$E'_{70\,°C}$	4.35	5.15
$(\text{Tan delta})_{10°C}$	0.58	0.61
$(\text{Tan delta})_{23°C}$	0.34	0.38
$(\text{Tan delta})_{70°C}$	0.10	0.11

SP as coupling agent for silica in elastomer composites in place of TESPT

Functionalization of silica with TESPT

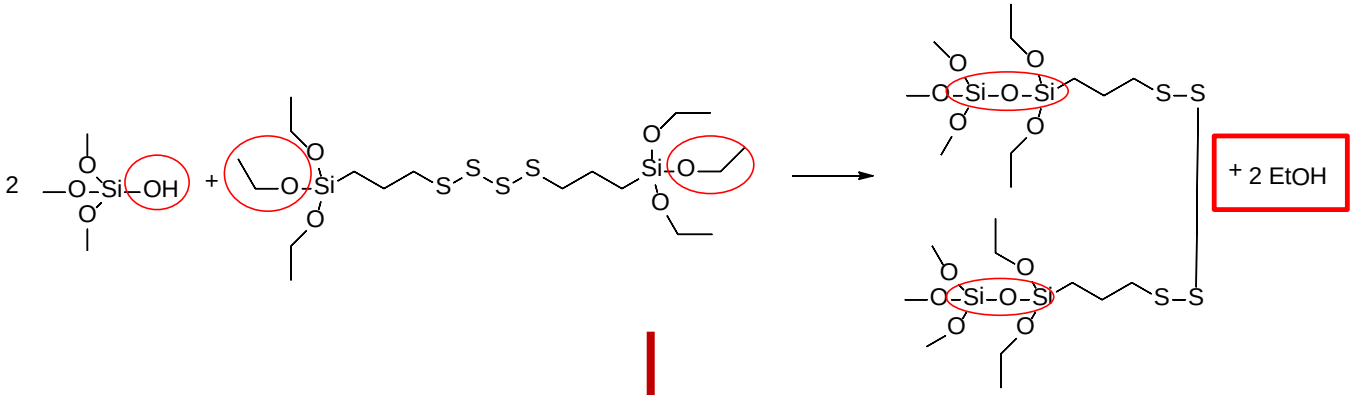


Functionalization of silica with serinol pyrrole



Amount of CO_2 released from TESPT condensation with silica

The global market for tires is expected to reach 2.7 billion units by 2025.



$$EtOH + 3\,O_2 \longrightarrow 2\,CO_2 + 3\,H_2O$$

Tons of CO_2 released = $8.44*10^4$

Conclusions

- Two steps one pot process for the conversion of dimethylfuran to pyrrole compounds with almost null E- factor was achieved

- 2,5-hexanedione was synthesized in yield up to 90% and the pyrrole compound with a global yield of about 80%, by using various primary amines

- SP behaves as an efficient coupling agent for silica and can be used in place of TESPT, in elastomer composites fior tyres

- In the whole process, from reagents to the silica/SP adduct, the only co-product is H_2O

Acknowledgments

Pirelli Tyre for the financial support to the *Ph*D activity

Innovative Sustainable Materials Group

ISMaterials group

AICIng
Associazione Italiana di Chimica per Ingegneria

Thanks for your attention!

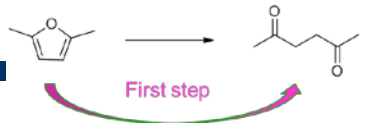
*ISM*aterials group
instagram: @ismaterials.polimi

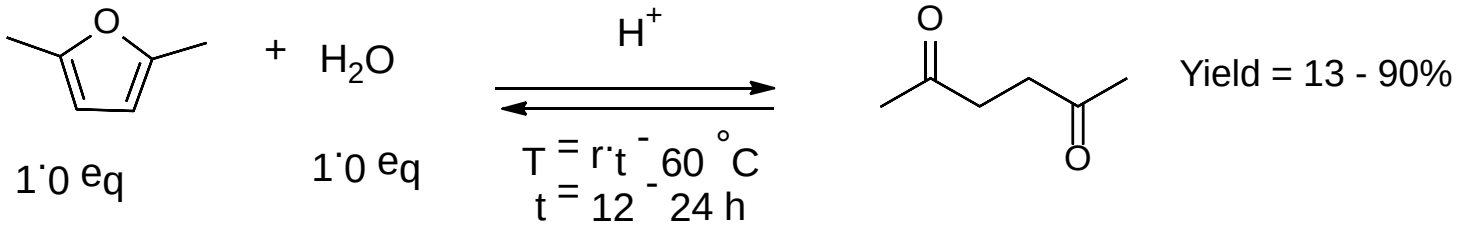
Politecnico di Milano, Department of Chemistry, Materials and Chemical Engineering “G. Natta”

EP3755687B1 ADDUCT BETWEEN A PYRROLIC COMPOUND AND AN INORGANIC OXIDE HYDROXIDE,
A SUPER-ADDUCT BETWEEN A PYRROLIC COMPOUND, AN INORGANIC OXIDE HYDROXIDE AND A CARBON ALLOTROPE,
ELASTOMERIC COMPOSITION COMPRISING THE SUPER-ADDUCT AND METHODS FOR PRODUCING THE SAME

Inventors: M.Galimberti, V.Barbera, A. Bernardi, D. Locatelli

Screening of parameters of the first step:
Amount of acid

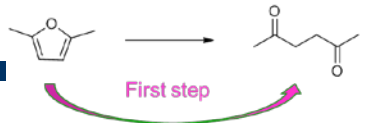


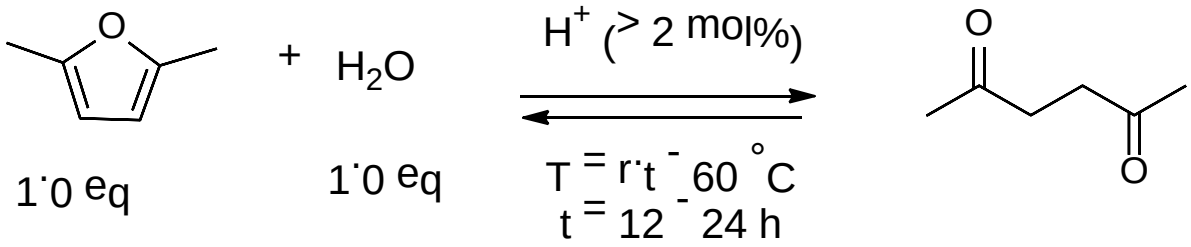


[Strong Mineral acid]	Yield of 2,5-hexanedione
Catalytic – 2 mol %	13 – 17 %
> 2 mol %	> 90 %

- *Italian Patent Application n. 102021000032138, inventors: V. Barbera, M. Galimberti, L. Giannini, S. Naddeo*
- *S. Naddeo, M. Galimberti, V.Barbera, Manuscript in preparation 2022* ‘Two steps one pot process for the conversion of dimethylfuran to pyrrole compounds with almost null E factor’’

Screening of parameters of the first step:
type of acid





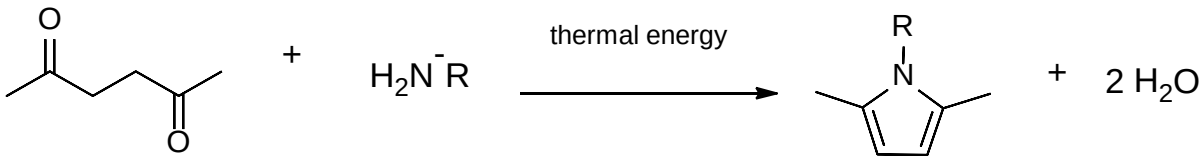
Type of acid	Yield of 2,5-hexanedione
Strong mineral acids	> 90%
Weak acids	< 2%

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

- S. Naddeo, M. Galimberti, V.Barbera, Manuscript in preparation 2022 ‘‘Two steps one pot process for the conversion of dimethylfuran to pyrrole compounds with almost null E factor’’

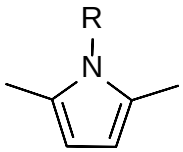
Prior art of our research group: synthesis of pyrrole compounds

Optimization of the Paal-Knorr reaction



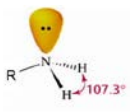
Primary amine
H_2N-R

Pyrrole compounds

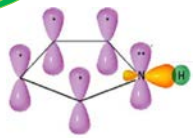


From sp^3

to sp^2



Paal-Knorr reaction



Yield: at least up to 90%

Atom efficiency: 85%

Easy procedure

No solvent

Co-product: H_2O

V. Barbera, A. Bernardi, A.Palazzolo, A. Rosengart, L. Brambilla, M. Galimberti *Pure and Applied Chemistry,* **2018**, *90(2)*, 253–270

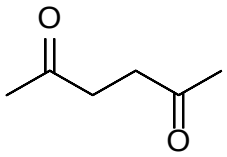
V. Barbera, A.Citterio, M. Galimberti, G. Leonardi, R. Sebastiano, S.U.Shisodia, A.M. Valerio *WO 2015 189411 A1*

M. Galimberti, V. Barbera, A. Citterio, R. Sebastiano, A. Truscello, A. M. Valerio, L. Conzatti, R. Mendichi, *Polymer*, vol 63, **20 April 2015**, Pages 62–70

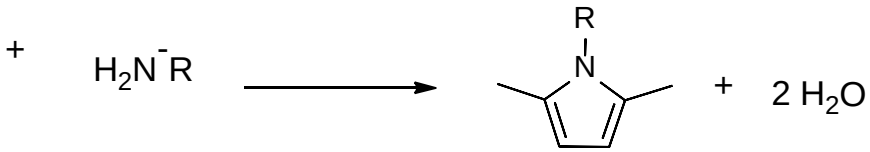
M. Galimberti, V. Barbera, S. Guerra, L. Conzatti, C. Castiglioni, L. Brambilla, A. Serafini,, *RSC Adv.,* **2015**, *5*, 81142-81152

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

Objectives of this work



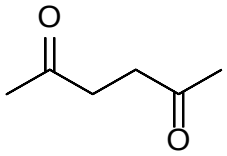
Oil-based
2,5-hexanedione



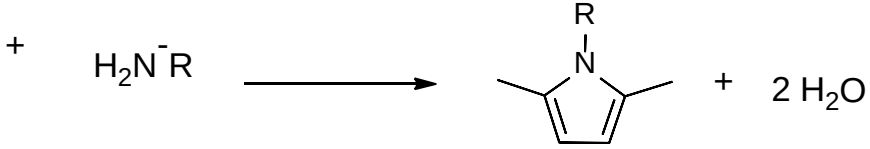
To develop a process for the conversion of dimethylfuran to pyrrole compounds with almost null E- factor

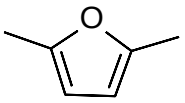
Objectives of this work

To develop a process for the conversion of dimethylfuran to pyrrole compounds with almost null E- factor

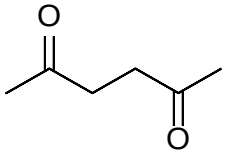


Oil-based
2,5-hexanedione

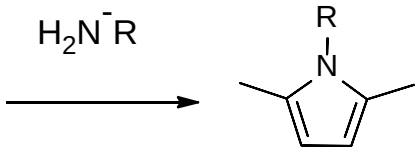




2,5-dimethylfuran
Bio-based starting material

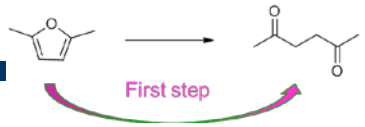


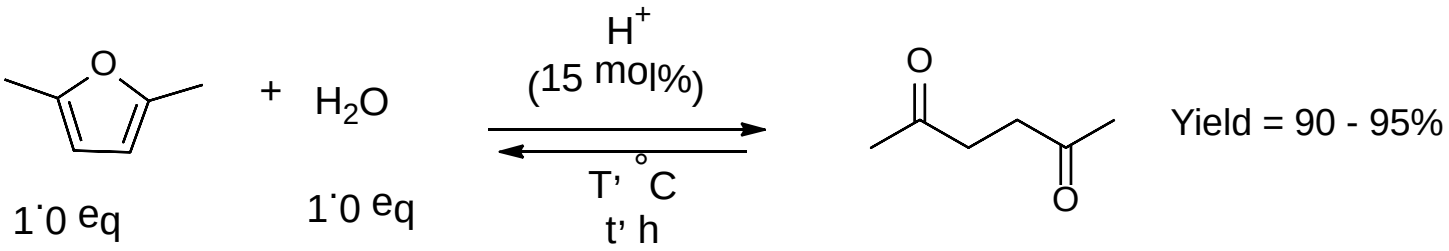
Bio-based
2,5-hexanedione



pyrrole compounds

Screening of parameters of the first step:
time and temperature





Best experimetal conditions:

Time = **12 – 24 hours**

Temperature = **25 – 70 °C**

the ratio of 2,5-dimethylfuran and water and the amount of mineral acid was kept constant in all the experiments.

This work is protected by a patent application. Results are not described in details.

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

Green metrics of Silica-Silane condensation