
# Functionalization of graphene related materials with biosourced C-3 and C-6 building blocks. From synthesis to applications

Vincenzina Barbera

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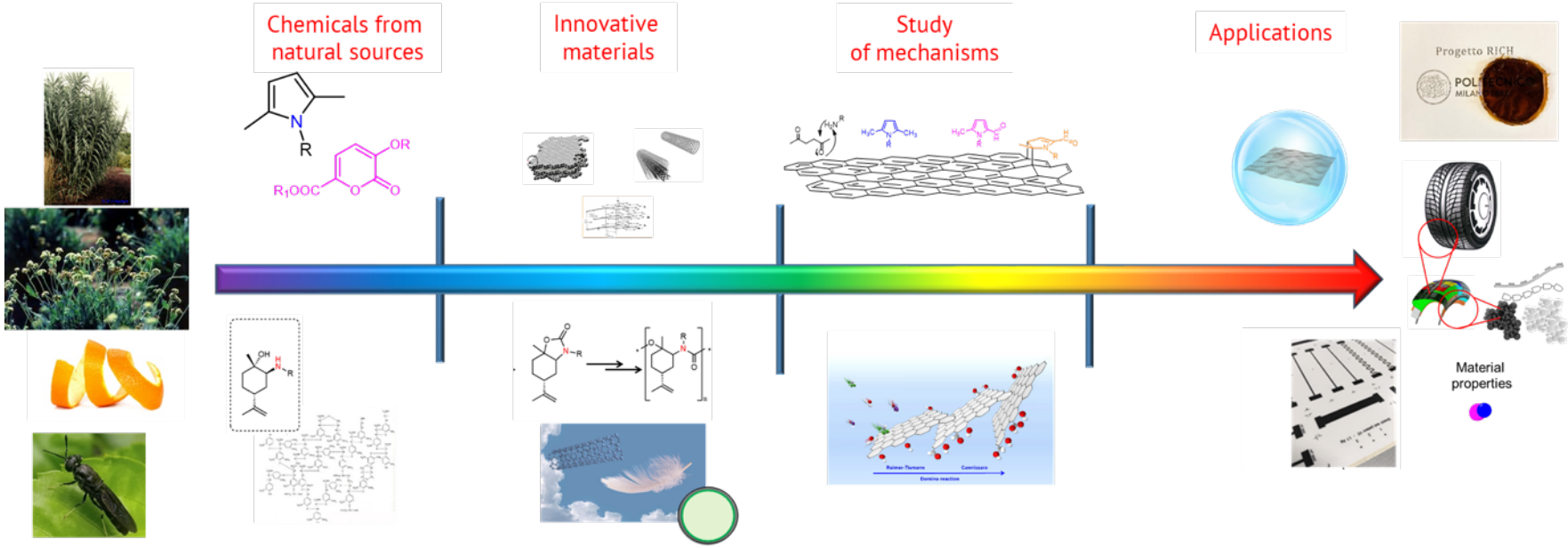
# *ISCaMaP*

*Innovative Sustainable Chemistry and Materials and Proteomics Group*

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

# *ISCaMaP*

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

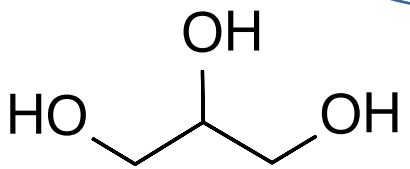


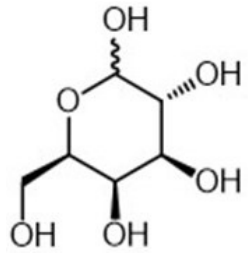

## ***ISMaterials*** group

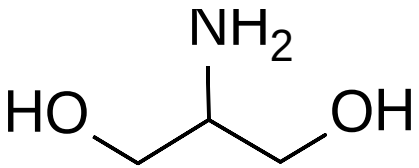
***ISM*aterials group**
instagram: @ismaterials.polimi

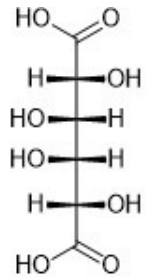
# The ISCaMaP Group. Some examples

Glycerol, Sugars

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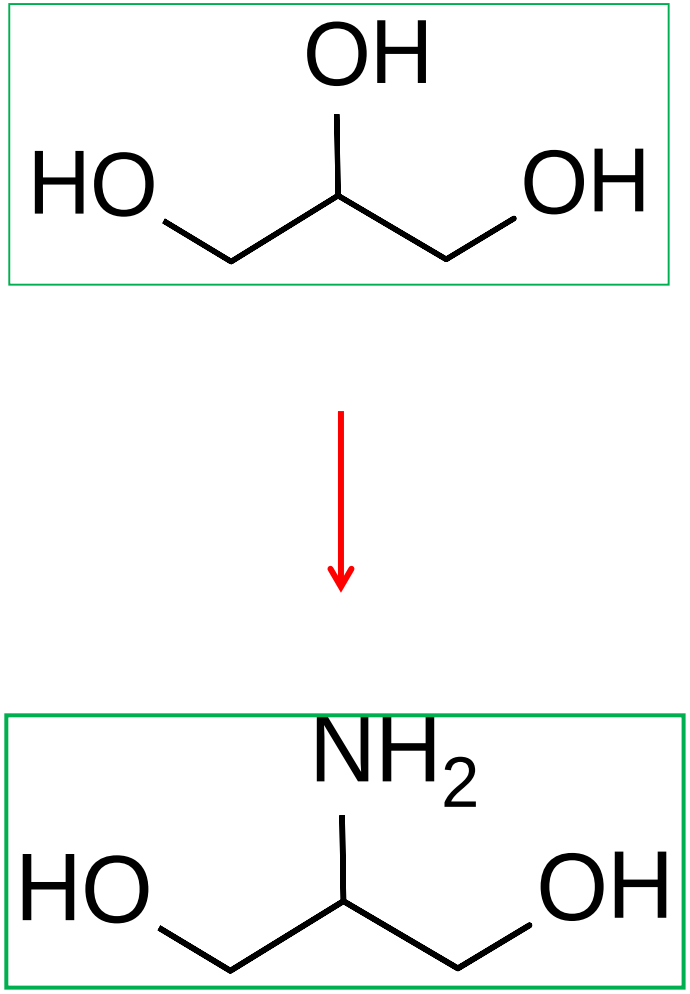
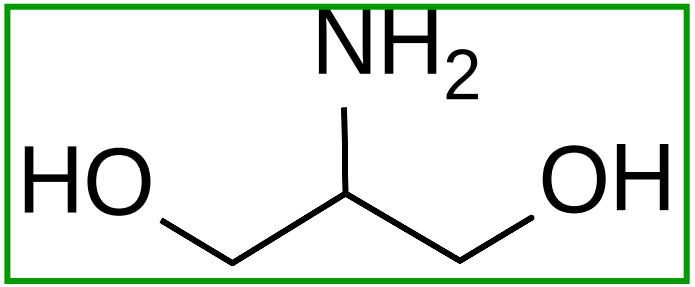
# C3 building blocks

# From glycerol to serinol



# Selection of the building block: serinol




- Starting building block for many reaction pathways: many derivatives

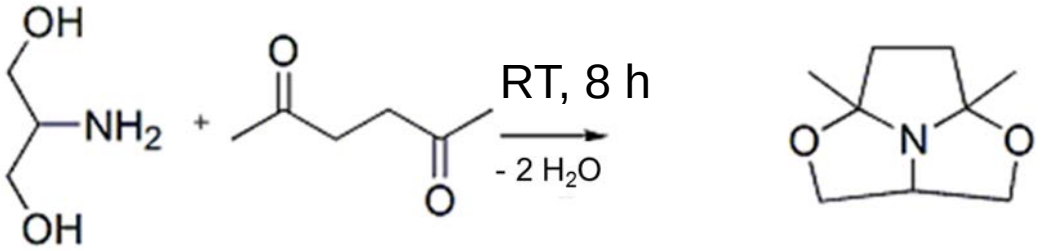
- Chemoselectivity

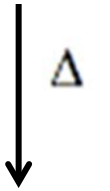
↓

Reactions of the amino group with carbonyl compounds

# Reaction of serinol with dicarbonyl compound

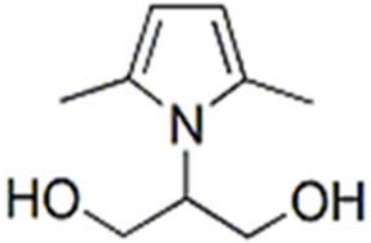
Sustainable synthesis




180°C, 3 h

No solvent
By product $H_2O$




Serinol pyrrole - SP

2-(2,5-dimethyl-1*H*-pirrol-1-yl) -1,3-propanediol

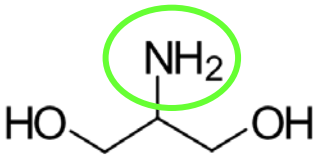

V. Barbera, A.Citterio, M. Galimberti, G. Leonardi, R. Sebastiano, S.U.Shisodia, A.M. Valerio *WO 2015 189411 A1*

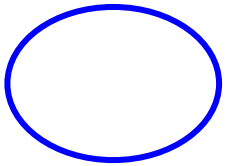
M. Galimberti, V. Barbera, A. Citterio, R. Sebastiano, A. Truscello, A. M. Valerio, L. Conzatti, R. Mendichi, *Polymer*, vol 63, 20 April 2015, Pages 62–70

M. Galimberti, V. Barbera, S. Guerra, L. Conzatti, C. Castiglioni, L. Brambilla, A. Serafini,, *RSC Adv.,* 2015, *5*, 81142-81152 DOI: 10.1039/C5RA11387C

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

# Neat synthesis of Serinol pyrrole



- Yield: at least 96%
- Atom efficiency: 85%
- Easy procedure
- No solvent
- By product: $H_2O$

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

# Pyrrole compounds (PyC) from neat Paal Knorr reaction

Same reaction conditions used for SP

PyC

Yield %

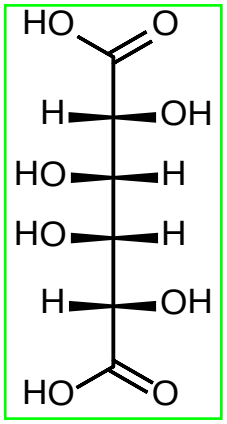
80 75 62 73

80 70

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

# C6 building blocks

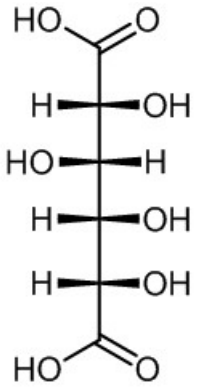
# Chemicals from sugars. Galactaric Acid




IUPAC: (2R,3S,4R,5S)-2,3,4,5-tetrahydroxyhexanedioic acid
Common nomenclature: mucic acid
Formula: $C_6H_{10}O_8$
210.14 Da

**Production (ton/a)** 38,000 (4-10 $/kg)*

- Symmetrical structure: achiral
- Platform molecule
- Not toxic, Biocompatible
- 25 times less expensive than glucaric acid

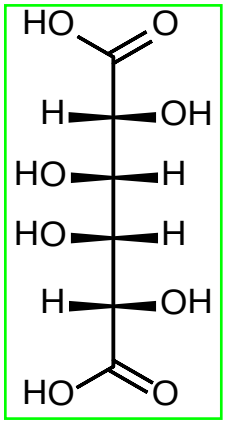



D-Glucaric

**Production (ton/a)** 100,000 (6-40 $/kg)*

J. LI – PhD thesis 2019 – Politecnico di Milano

# Galactaric Acid



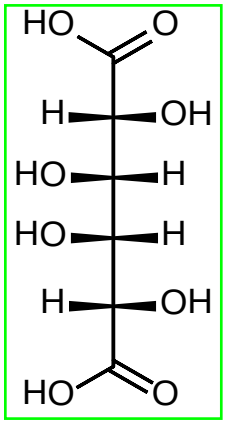

IUPAC: (2R,3S,4R,5S)-2,3,4,5-tetrahydroxyhexanedioic acid
Common nomenclature: mucic acid
Formula: $C_6H_{10}O_8$
210.14 Da

However …

pretty high price

J. LI – PhD thesis 2019 – Politecnico di Milano

# Galactaric Acid

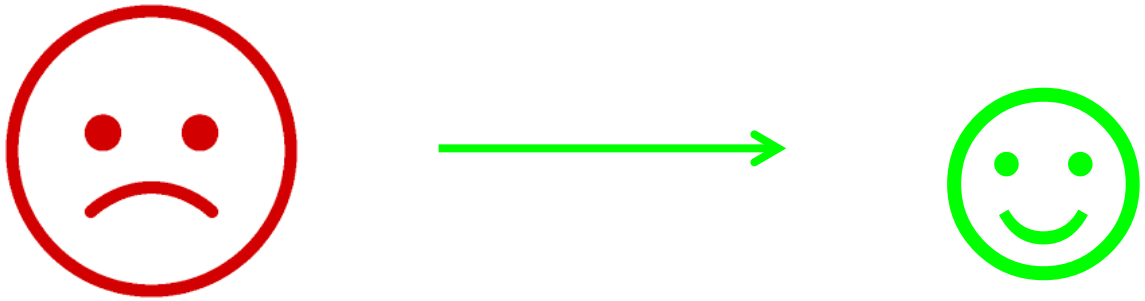



IUPAC: (2R,3S,4R,5S)-2,3,4,5-tetrahydroxyhexanedioic acid
Common nomenclature: mucic acid
Formula: $C_6H_{10}O_8$
210.14 Da

*Improvements in the production techniques* would unlock its potential **as a platform chemical**

pretty high price

low price



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# Galactaric Acid - Platform molecule

Derivatives from galactaric acid

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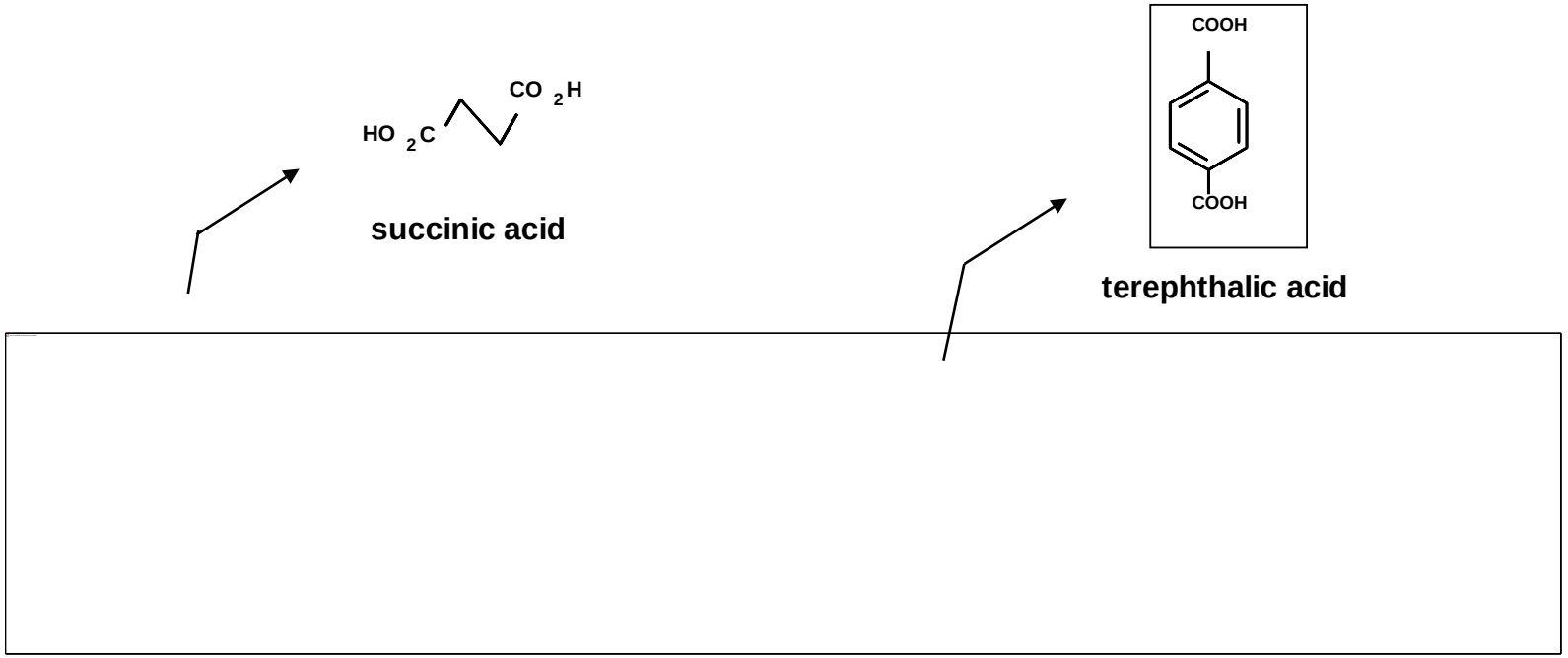
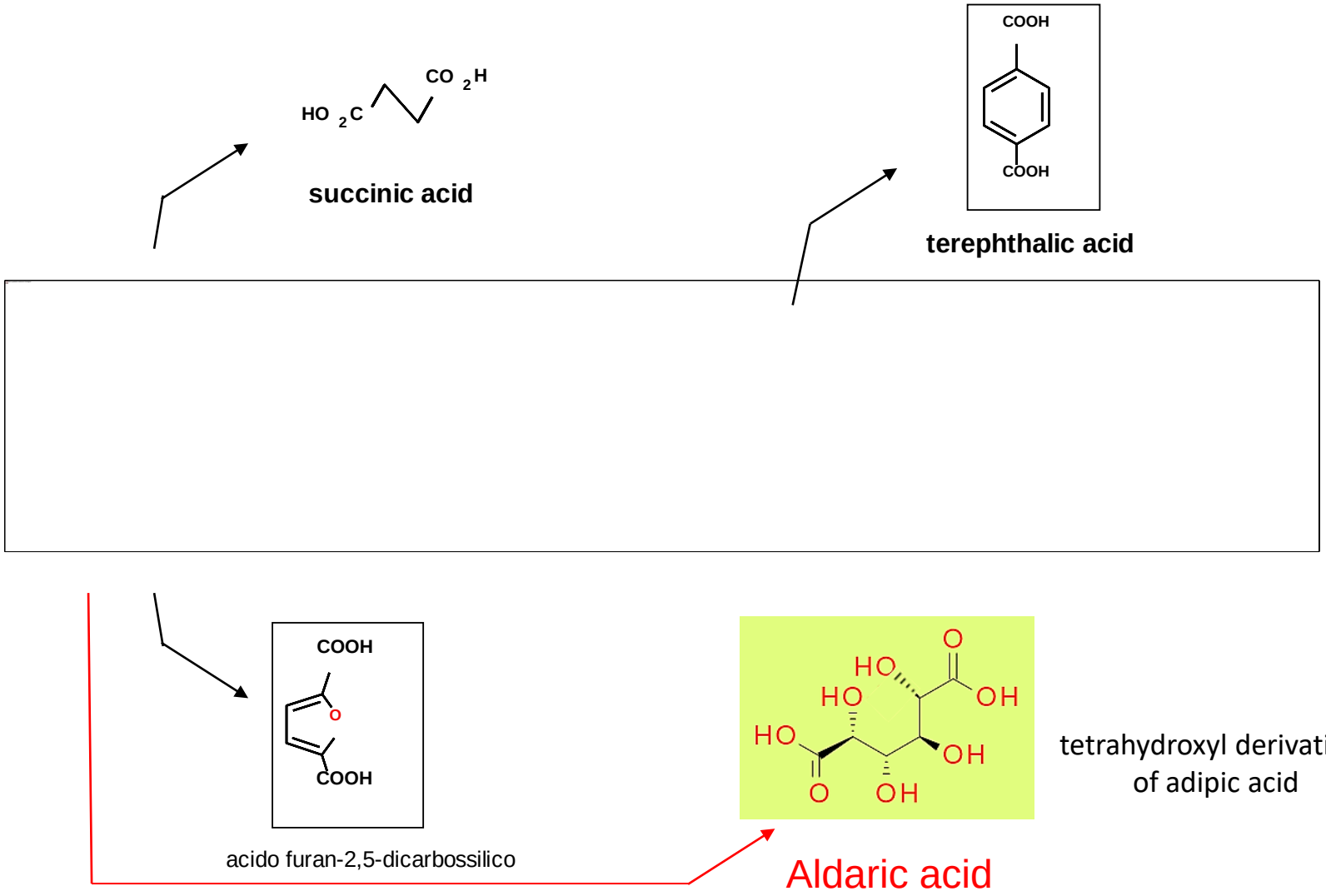
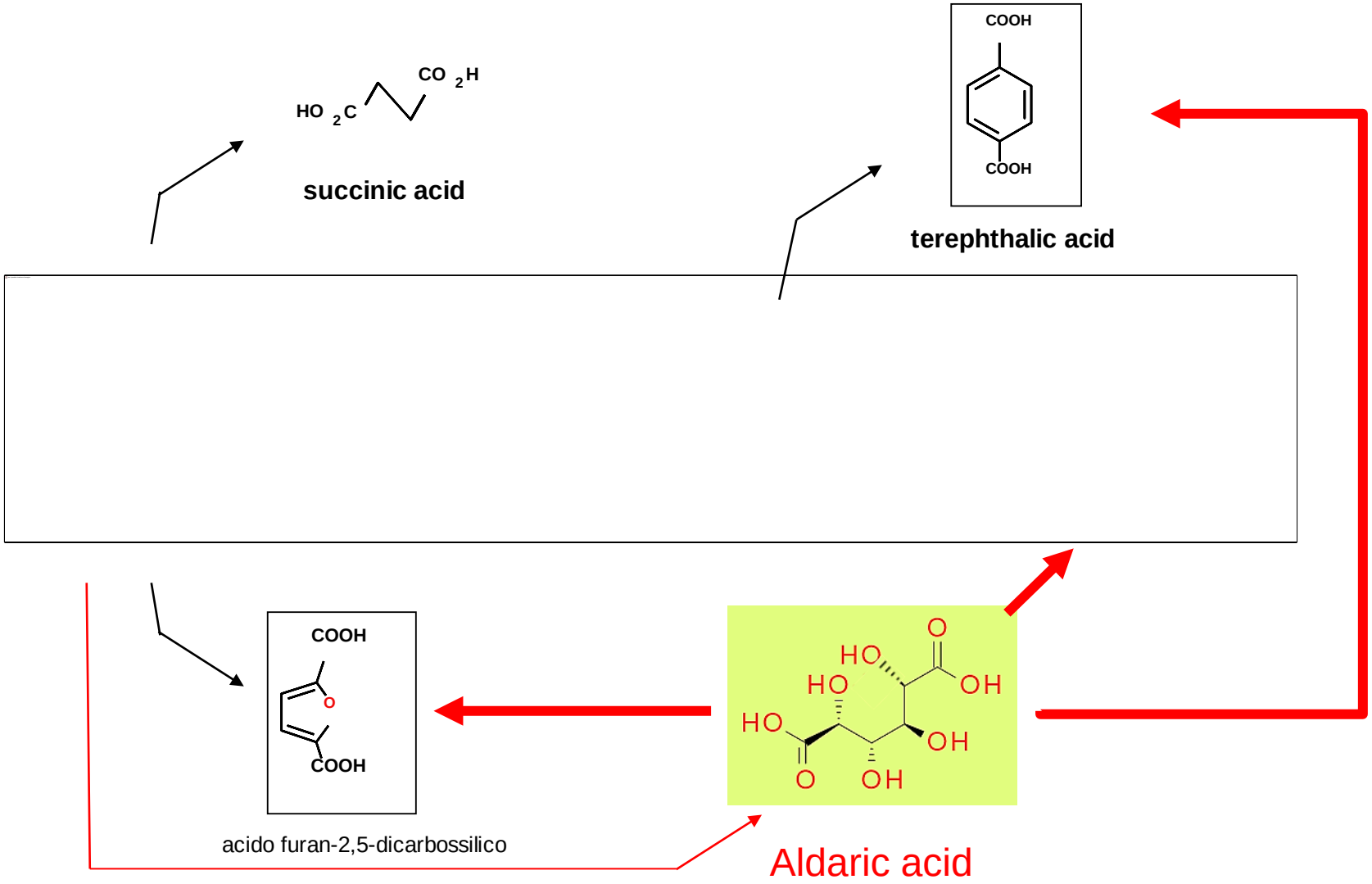
# Chemicals from sugar - Target molecules



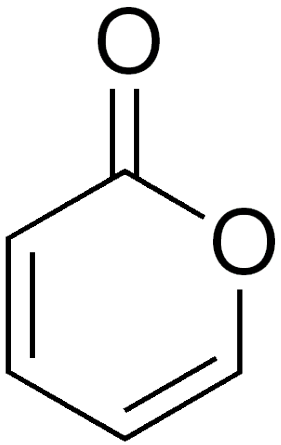
# Dicarboxylic Acids from Hydrolyzed Biomasses



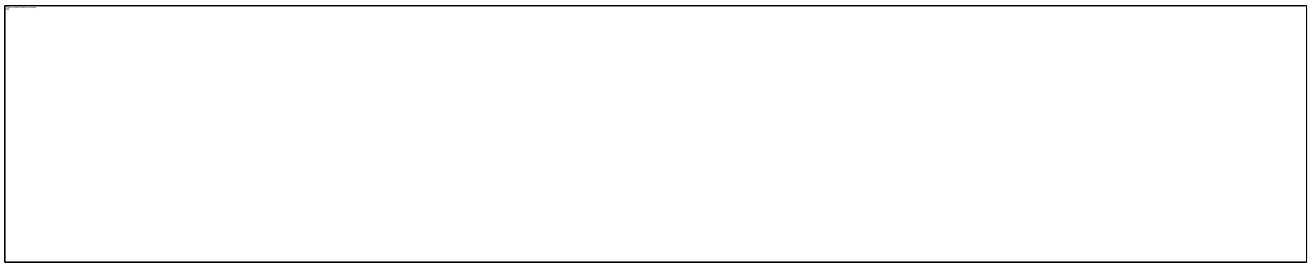
# Dicarboxylic Acids from Hydrolyzed Biomasses



# From aldaric acids to pyrones



# Synthesis of Pyrone Derivatives from Aldaric Acids @ ISCaMaP

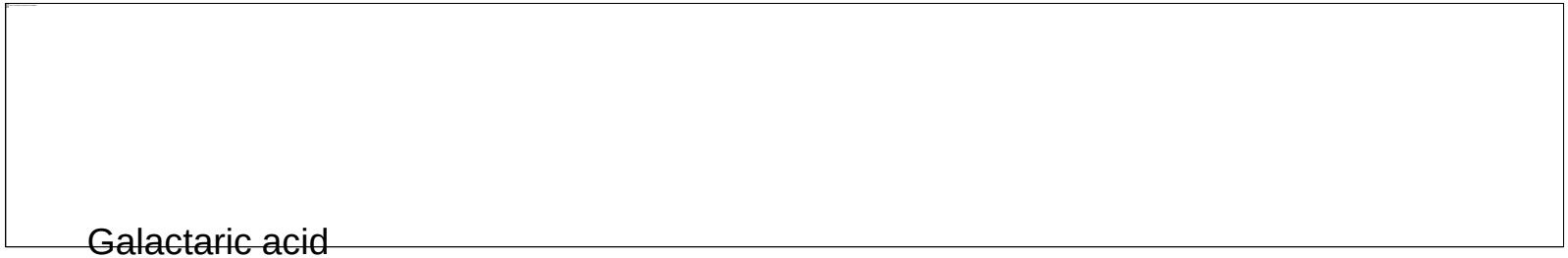


3-Acetoxy-2-oxo-2*H*-pyran-6-carboxylic salt (GAB-OAc)

- Easy procedure
- No solvent
- No catalyst
- High Conversion
- High Atom efficiency

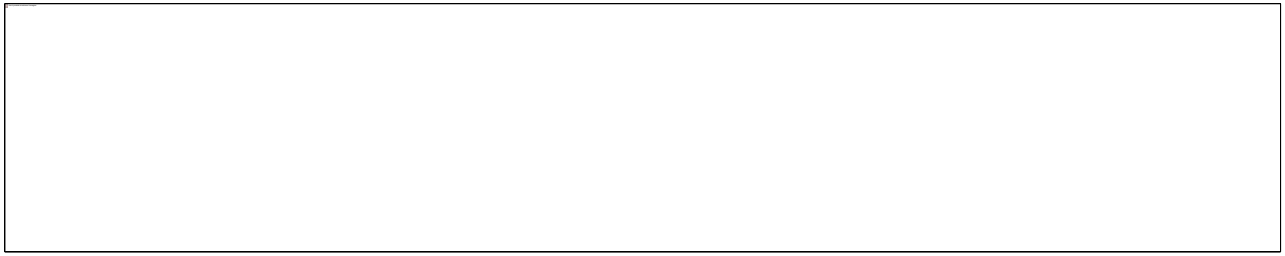
# Synthesis of Pyrone Derivatives from Aldaric Acids @ ISCaMaP

## First step




Yield = 99%; A.E. = 77%

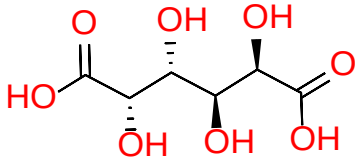
## Second step



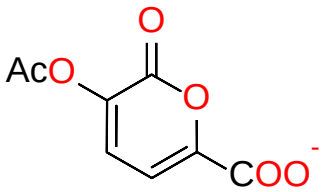
Yield = 65%; A.E. = 62%

Leonardi G., Li, J., Righetti, G. I. C., Truscello, A. M., Gambarotti, C., Terraneo, G., Citterio, A., Sebastiano, R., *Eur. J. Org. Chem.* **2020**, 241–251

# Synthesis of Pyrone Derivatives from Aldaric Acids @ ISCaMaP




Galactaric acid




GAB-OAc

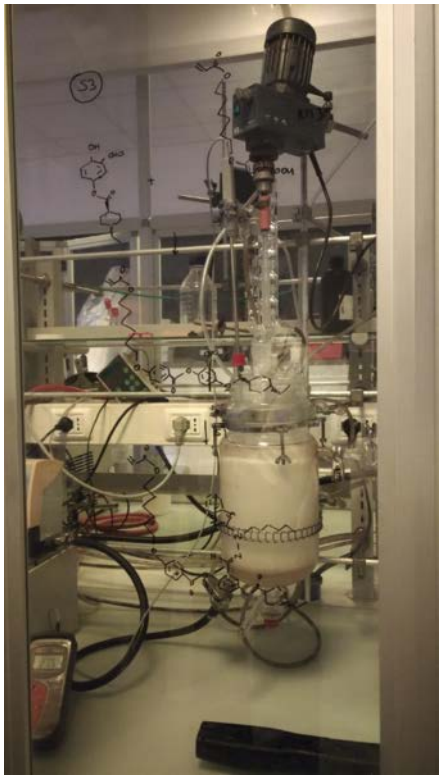
Yield
up to 73%

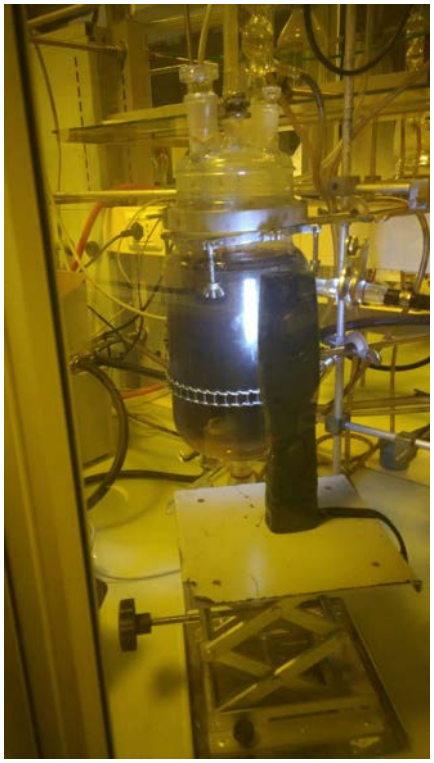
DEC

Yield
up to 90%

Leonardi et al. *Eur. J. Org. Chem.* **2020**, 241–251

# Synthesis of Pyrone - Scale up





One Pot

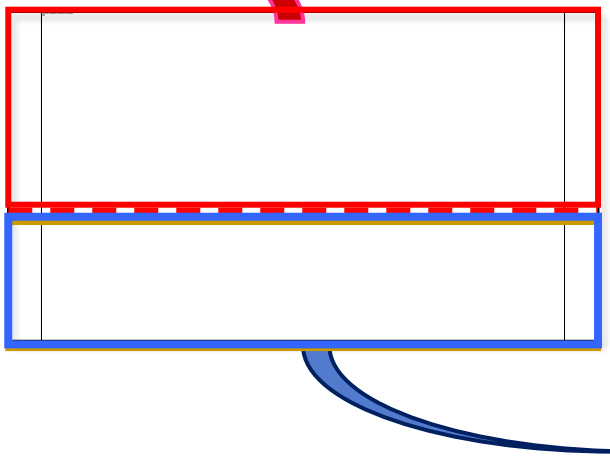
2 hours

Yield = 75%

# Functionalization of $sp^2$ carbon allotropes

# Serinolpyrrole: *Janus* molecule

INTERACTION
WITH
LIPOPHILIC MATRIX
AND
GRAPHITIC CARBONS



REACTIONS WITH
FUNCTIONAL GROUPS

INTERACTION
WITH POLAR
SURROUNDING

# Objective of the research

Sustainable and versatile functionalization of unperturbed graphene layers

# Carbon fillers from a layer of $sp^2$-bonded carbon atoms

graphene

stacked

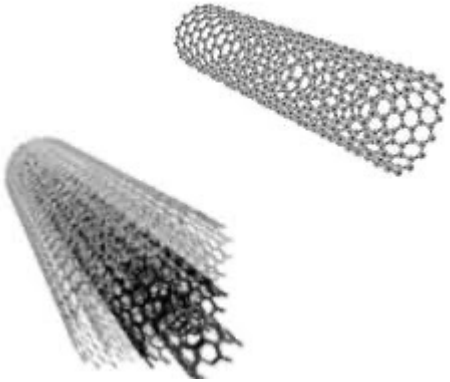
wrapped

stacked graphene layers

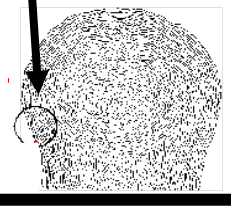
randomly arranged

with different shape anisotropy

CNT



carbon black

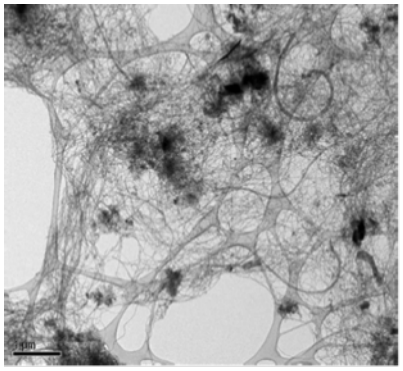


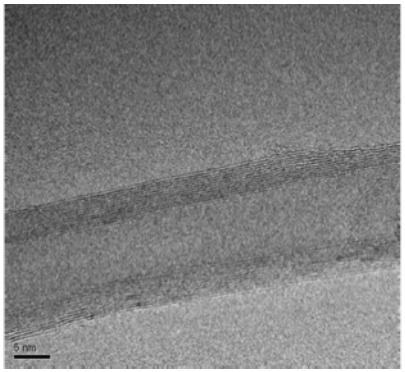
graphite,
nano-graphite,
graphene

# Carbon allotropes (CA)

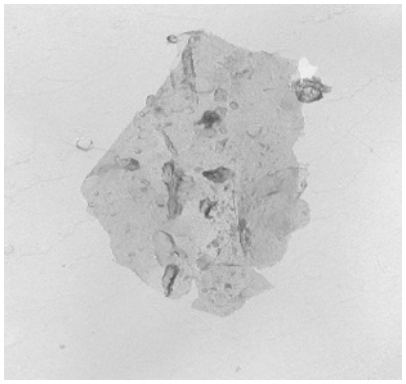
CB

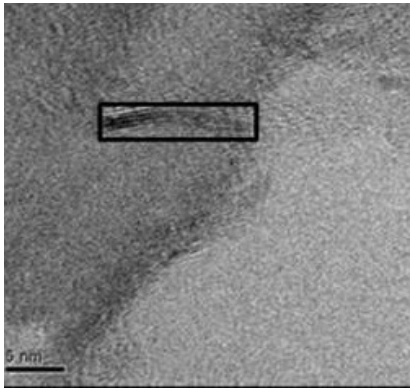
CNT





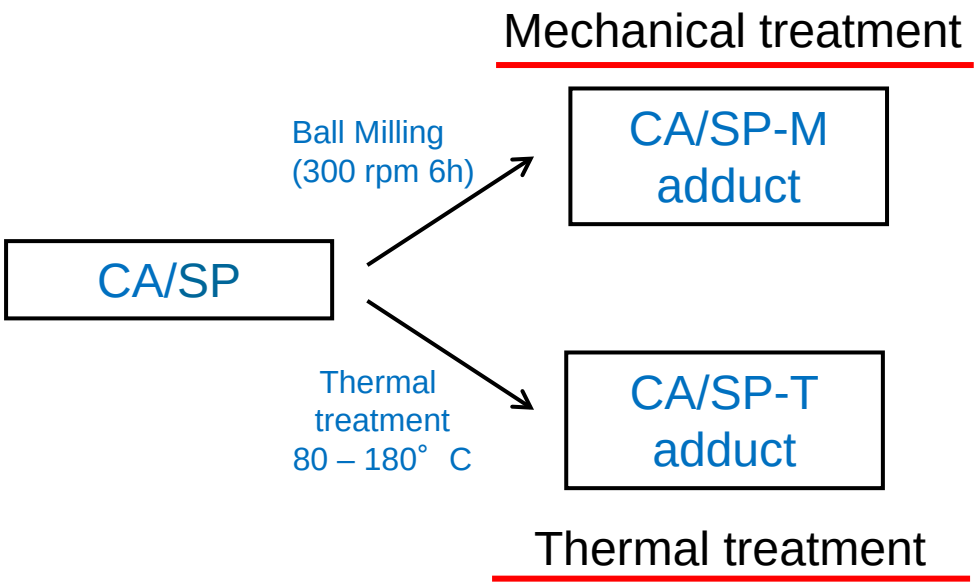
FEW LAYERS GRAPHENE





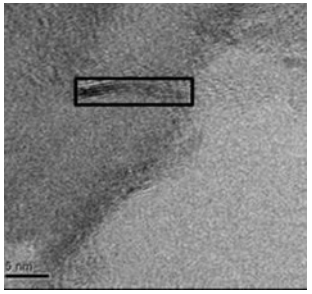
# Adducts of SP with CA - Preparation

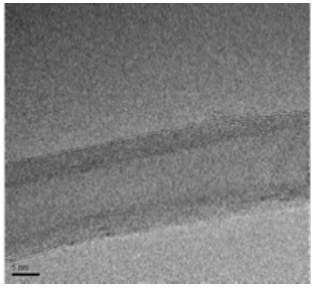

CA-SP




Barbera, V., Citterio, A., Galimberti, M., Leonardi, G., Sebastiano, R., Shisodia, S.U., Valerio A.M. WO 2015 189411 A1
Galimberti, M., Barbera, V., Guerra, S., Conzatti, L., Castiglioni, C., Brambilla, L., A. Serafini, RSC Advances, 5(99), (2015) 81142-81152

# High yield functionalization!





| | | | |
|---|---|---|---|
| **BET Surface area: [$m^2/g$]** | **300** | **77** | **275** |
| **Initial functional groups: [mmol/g]** | **1.7** | **0.9** | **2.0** |
| **Yields (%)*:** | **96** | **82** | **92** |

*was estimated through:

$$\text{Functionalization Yield } (\%) = 100 * \frac{\text{SP mass \% in (CA–SP adduct) after acetone washing}}{\text{SP mass \% in (CA–SP adduct) before acetone washing}}$$

Galimberti, M., Barbera, V., Sebastiano, R., Citterio, A., Leonardi, G. WO/2016/050887 A1 (2016)

# Adducts of SP with HSAG

- Functional groups up to 20%
- In plane order substantially unaltered
- No expansion of interlayer distance

HSAG-SP-M

HSAG-SP-T

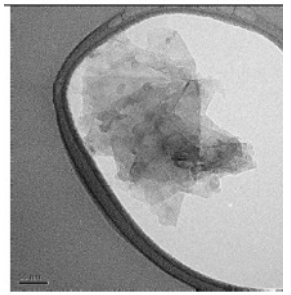
HSAG

HSAG

HSAG-SP-M

HSAG-SP-T

Few layers graphene

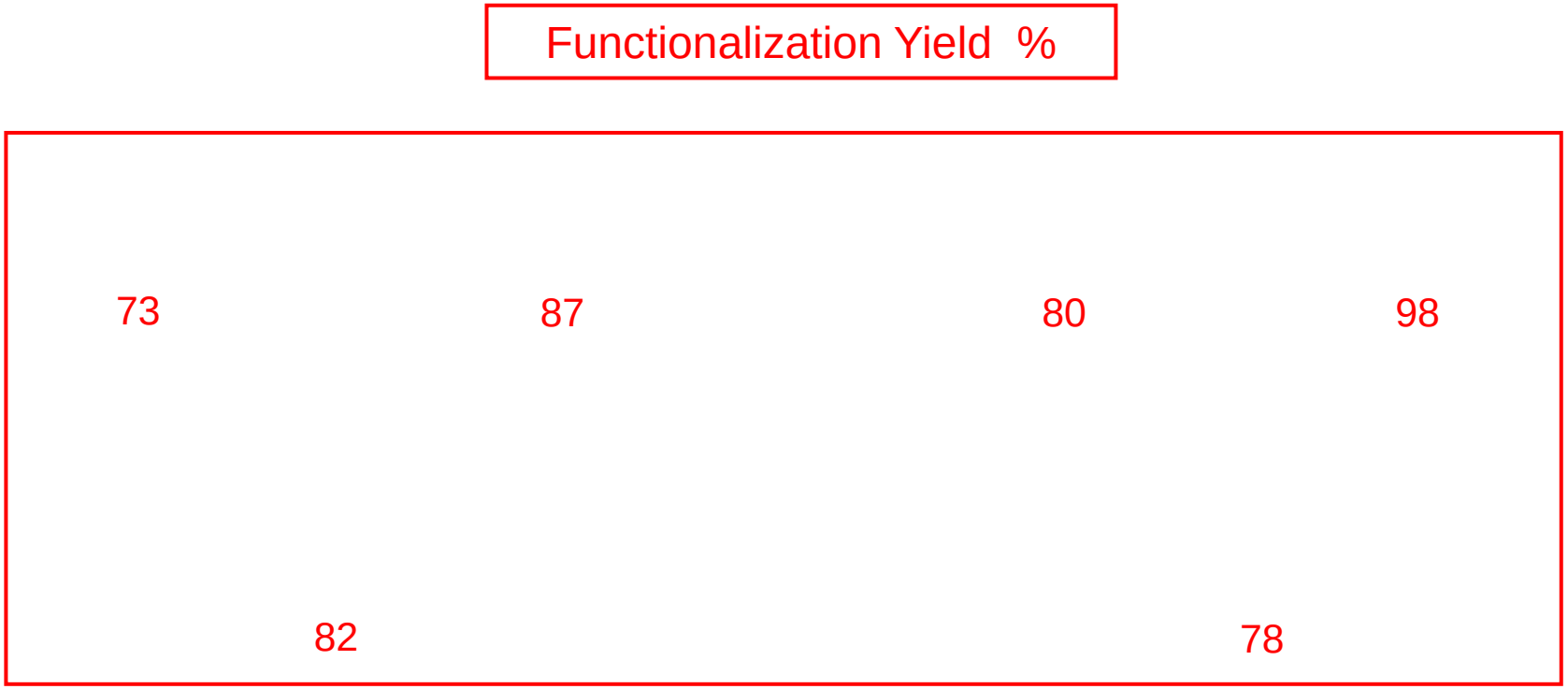


From water suspension

*Results from elemental, TGA, IR, XPS, Raman, XRD, HRTEM analysis*

M. Galimberti, V. Barbera, R. Sebastiano, A. Citterio, G. Leonardi, A.M. Valerio WO 2016 050887 A1
M. Galimberti, V. Barbera, S. Guerra, L. Conzatti, C. Castiglioni, L. Brambilla, A. Serafini, *RSC Adv.*, 2015, 5, 81142-81152

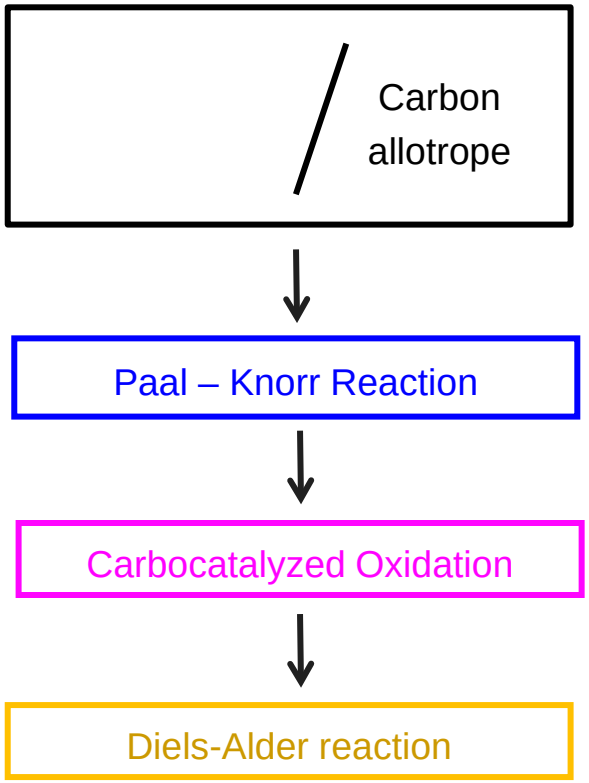
# HSAG / PyC adducts

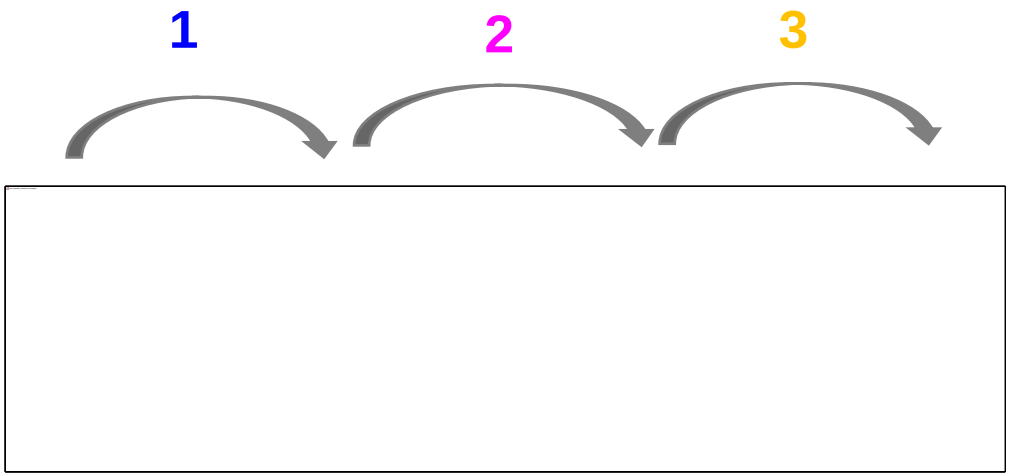



V. Barbera, A. Bernardi, A.Palazzolo, A. Rosengart, L. Brambilla, M. Galimberti Pure and Applied Chemistry 2018, 90(2), 253–270

# Mechanism for the formation of CA/PyC adducts

## Domino reaction

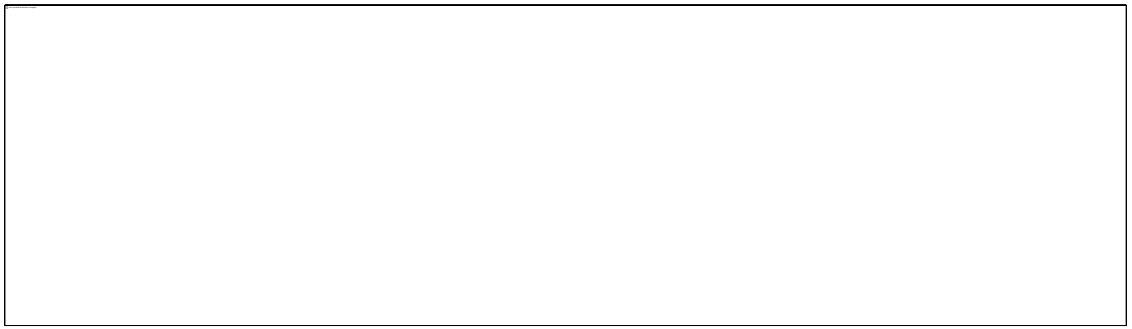



V. Barbera, L. Brambilla, M. Milani, A. Palazzolo, C. Castiglioni, A. Vitale, R. Bongiovanni, M. Galimberti, 2019. Nanomaterials, 9(1), p.44.

# Thanks to the carbon allotrope!

- Support: absorption of pyrrole ring thanks to π-π interaction
- Oxidation catalyst: protection of pyrrole ring and oxidation of lateral substituent
- Substrate for the cycloaddition reaction, i.e. for functionalization



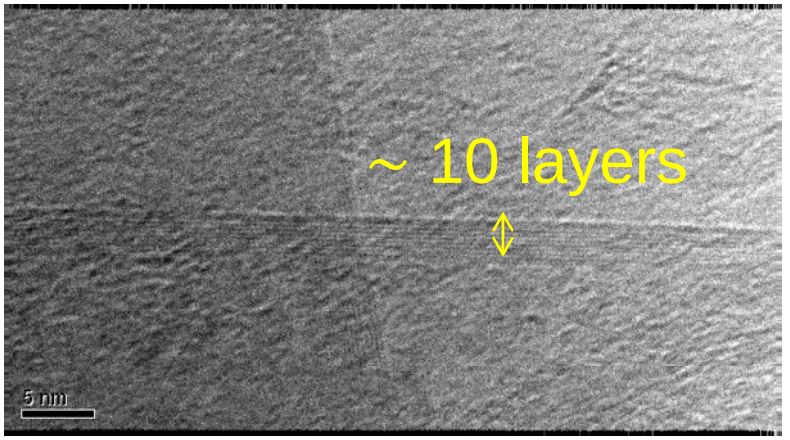
V. Barbera, L. Brambilla, M. Milani, A. Palazzolo, C. Castiglioni, A. Vitale, R. Bongiovanni, and M. Galimberti, 2019. Nanomaterials, 9(1), p.44.

# The CA/PyC adducts

- Functional group:
  from few % to 20%
- Functionalization yield:
  from 85% to quantitative
- Covalent bond
  between functional group
  and carbon allotrope
- Bulk structure of graphitic materials:
  substantially unaltered


V. Barbera, A. Citterio, M. Galimberti, G. Leonardi, R. Sebastiano, S.U. Shisodia, A.M. Valerio. *US10329253B2*
M. Galimberti, V. Barbera, R. Sebastiano, A. Citterio, G. Leonardi, A.M. Valerio. *US10160652B2*
M. Galimberti, V. Barbera, R. Sebastiano, A. Truscello, A.M. Valerio. *EP3180379B1*
M. Galimberti, V. Barbera, *EP3538511A1*
M. Galimberti, V. Barbera, *EP3538481A1*

# Production of few layers graphene




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

# Electrically conductive coating layers

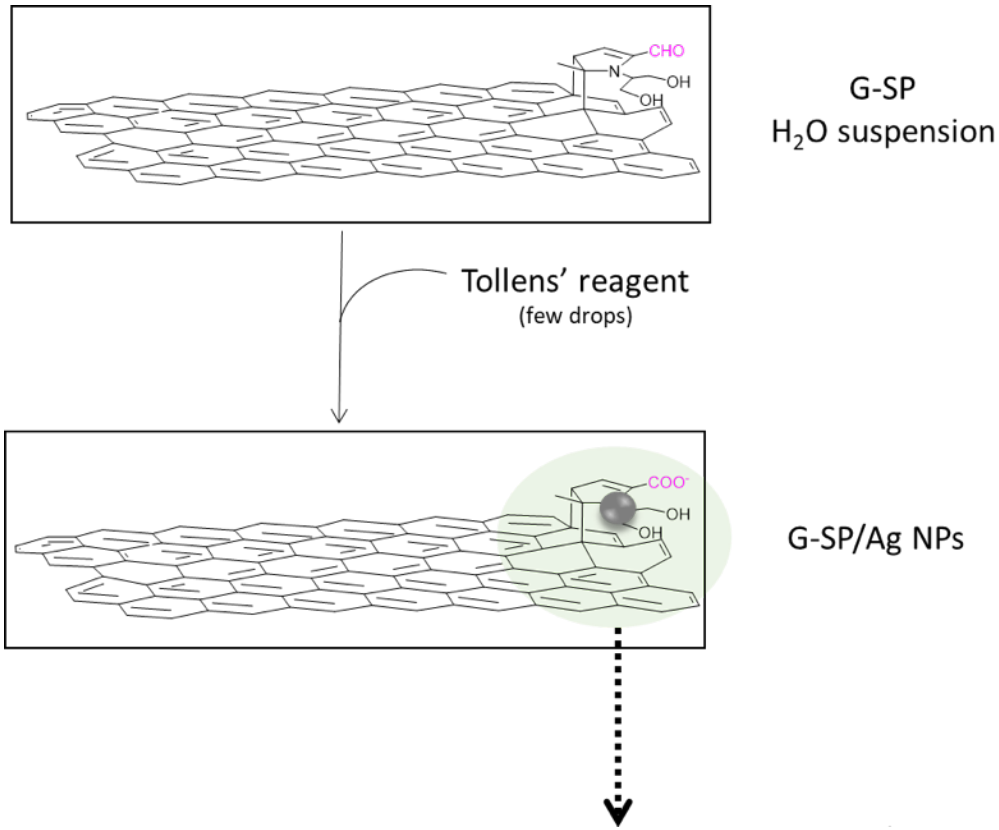
HSAG-K stearate

HSAG-SP

HSAG

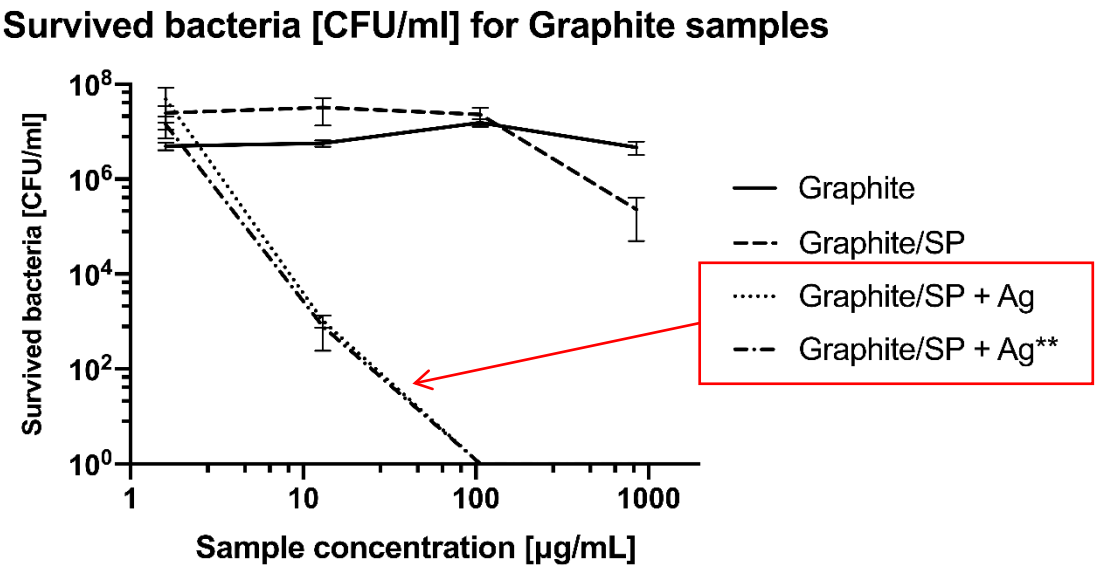
S. Guerra, V. Barbera, M. Galimberti, U. Giese, *KGK 2020, 04, 17-25*

# Antibacterial additives




Antibacterial additive

# Antibacterial activity




**The sample has been functionalized with an almost double quantity of Tollens' reagent.

**Test:** ASTM Standard Guide E2315 – 16

**Bacteria:** E. coli JM109 – DSM3423

**Material state:** Dispersions of powders

**Inoculum concentration:** ~$10^6$ CFU/mL

**Culture medium:** LB / PBS 1:100 (v/v)

**Culture conditions:** 24h, 37°C, 5% $CO_2$, 90% R.H. Dynamic conditions

V. Barbera, M. Galimberti, G. Candiani, *Italian Patent Application n. 102020000020113*

# Bionanocomposites

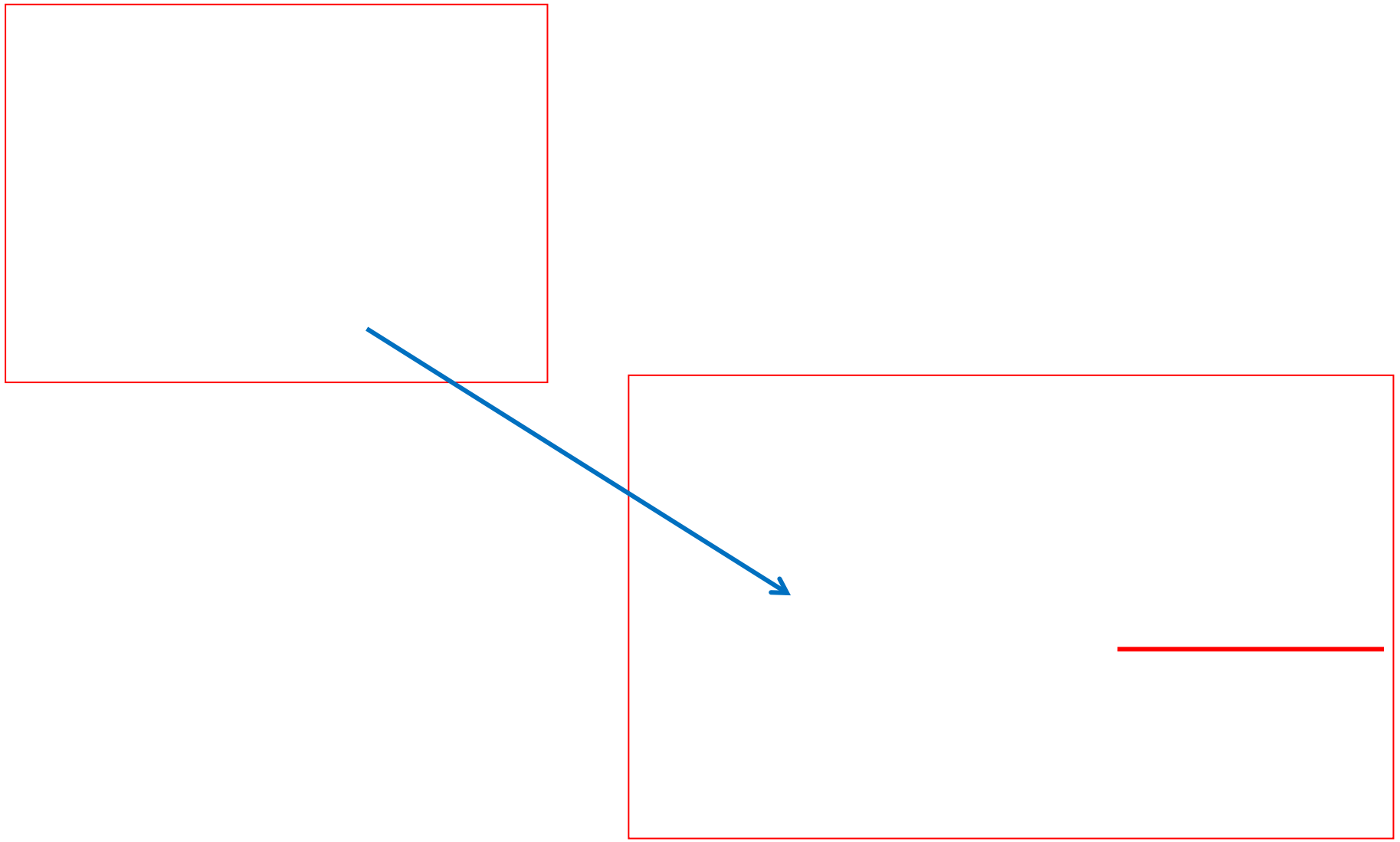
Carbon papers

Aerogels

V. Barbera, S. Guerra, L. Brambilla, M. Maggio, A. Serafini, L. Conzatti, A. Vitale, M. Galimberti, *Biomacromolecules, 2017, 18 (12), 3978–399*

S. Guerra, V. Barbera, A. Vitale, R. Bongiovanni, A. Serafini L. Conzatti, L. Brambilla, M. Galimberti, *Materials 2020, 13, 39*

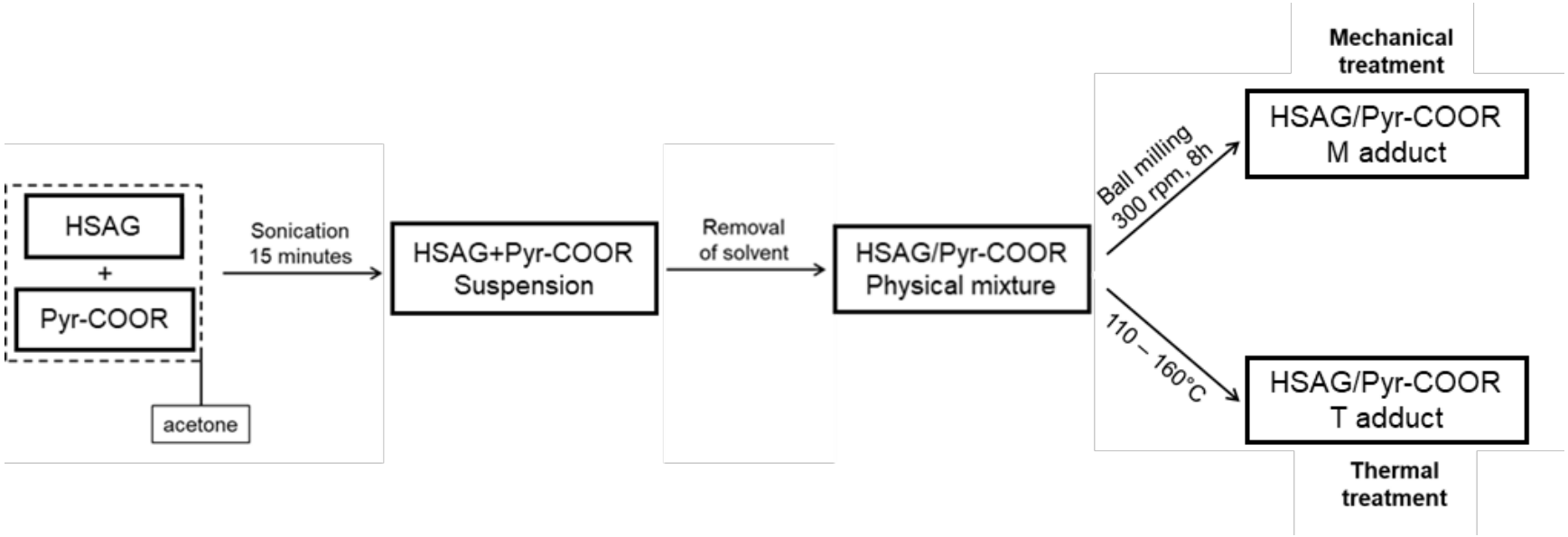
# Bionanocomposites



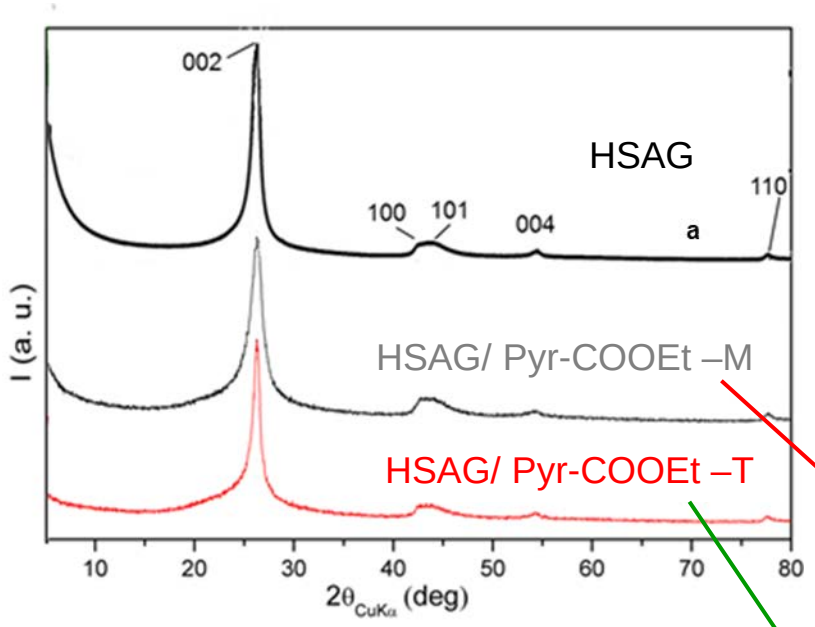
V. Barbera, S. Guerra, L. Brambilla, M. Maggio, A. Serafini, L. Conzatti, A. Vitale, M. Galimberti, *Biomacromolecules, 2017, 18 (12), 3978–399*

S. Guerra, V. Barbera, A. Vitale, R. Bongiovanni, A. Serafini L. Conzatti, L. Brambilla, M. Galimberti, *Materials 2020, 13, 39*

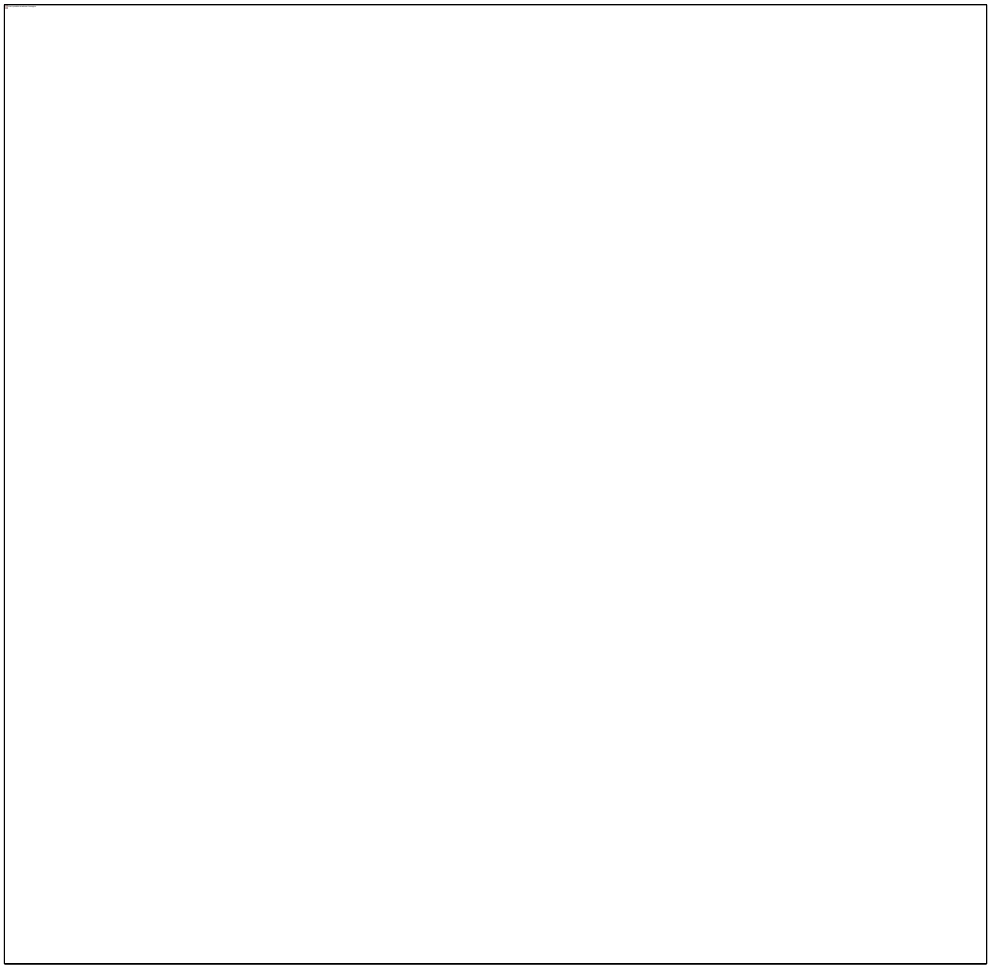
# Functionalization of HSAG with a Pyrone derivative



# Adduct of HSAG with Pyr-COOEt



# *EDGE-GO* - Functionalization of HSAG with a Pyrone derivative



# Preparation of few layers graphene

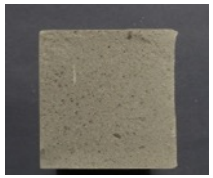
# Conclusions

## NanoCarbon Up Technology: 10 families of patents

**Rubber nanocomposites**


**Polyurethanes**

**Polyol dispersions**



**Concrete with high flexural strength**

**Carbon paper**

**Aerogels**

**Inks and varnishes**


## *Innovative Materials Group*


Innovative Sustainable Materials GROUP in ISCaMaP

**instagram:** @ismaterials.polimi

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