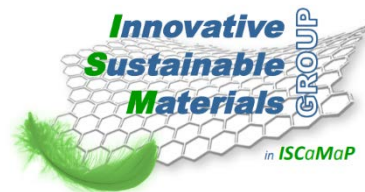




## Selective edge functionalization for preserving $sp^2$ carbon atoms in graphene layers

Vincenzina Barbera, Luigi Brambilla, Alberto Palazzolo, Chiara Castiglioni, Roberta Bongiovanni,  
Alessandra Vitale, M. Galimberti



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

# Objectives of the research activity



## Objectives of the research activity

To prepare **tailor made materials**, in view of the final application



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To prepare **tailor made materials**, in view of the final application

### Polymer composites

Lead to the macroscopic scale the exceptional properties of graphene and graphene related materials (nanoscale)

### Carbocatalysts

Are ideal when are characterized by:

high surface areas and large unperturbed aromatic basal planes

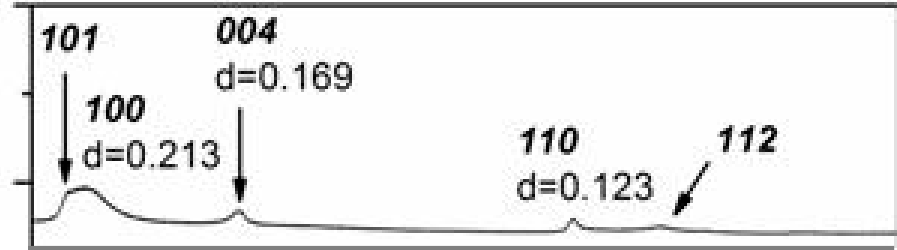
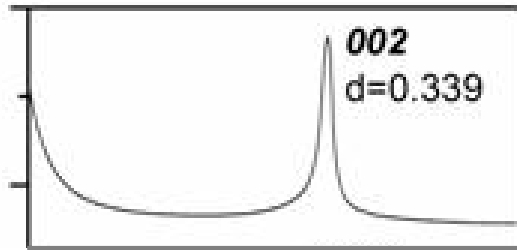


## Sustainable and versatile functionalization of unperturbed graphene layers



- 👍 Synthesis
- 👍 Characterizations
- 👍 Mechanisms
- 👍 Applications

# High Surface Area Graphite (HSAG)



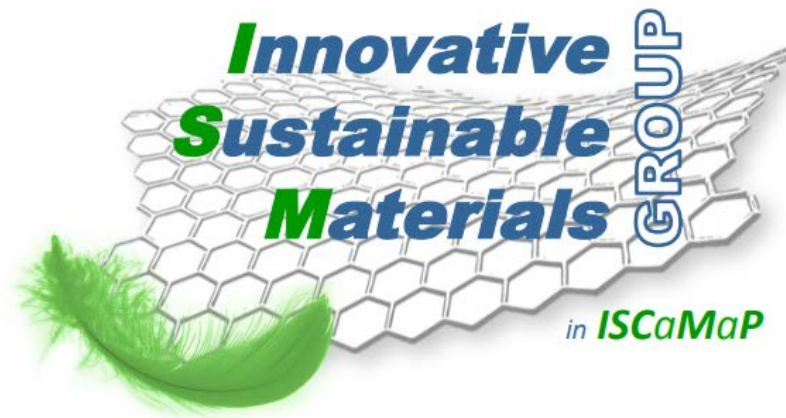
Sample	Surface area ( $\text{m}^2/\text{g}$ )	number of stacked layers	$D_{\parallel} / D_{\perp}$
HSAG	330	35	3.1

# Facile functionalization



+

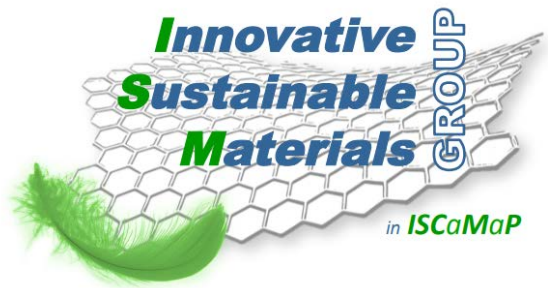
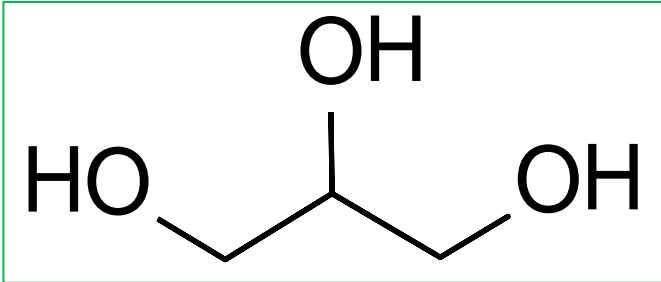




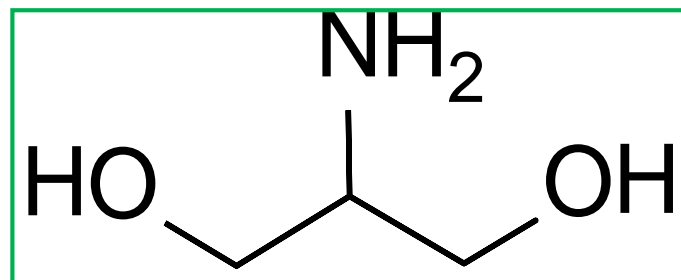
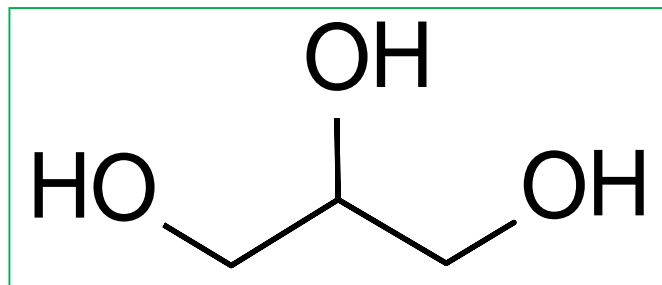
*Janus* molecules  
for the functionalization of graphene layers



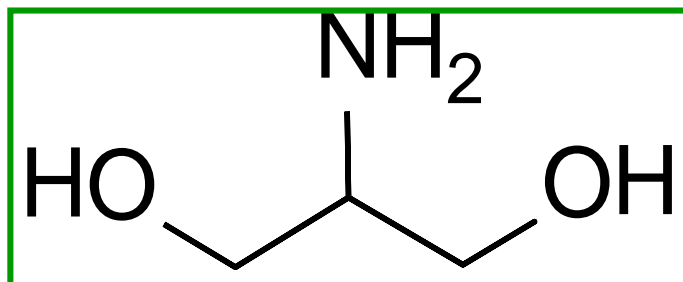
# C3 building block: glycerol



# From glycerol to serinol



## Selection of the building block: serinol



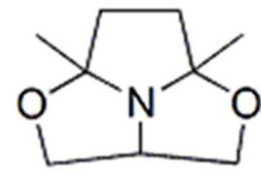
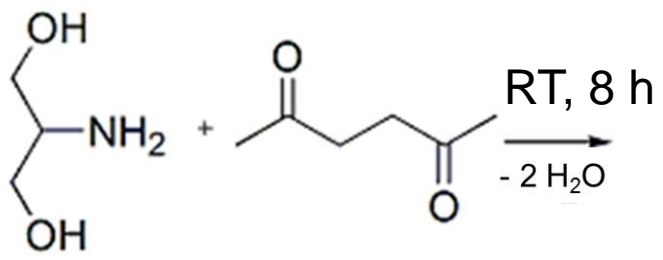
- ➔ Starting building block for many reaction pathways: many derivatives
- ➔ Chemoselectivity



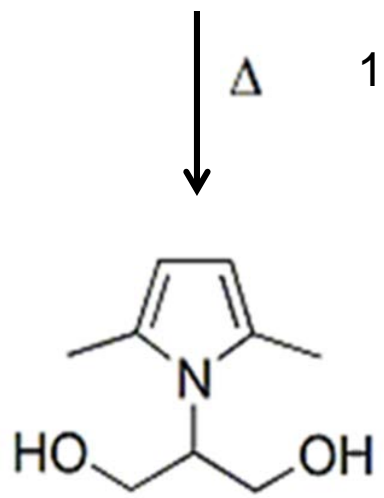
Reactions of the amino group with carbonyl compounds

# Reaction of serinol with dicarbonyl compound

Sustainable synthesis



180°C, 3 h



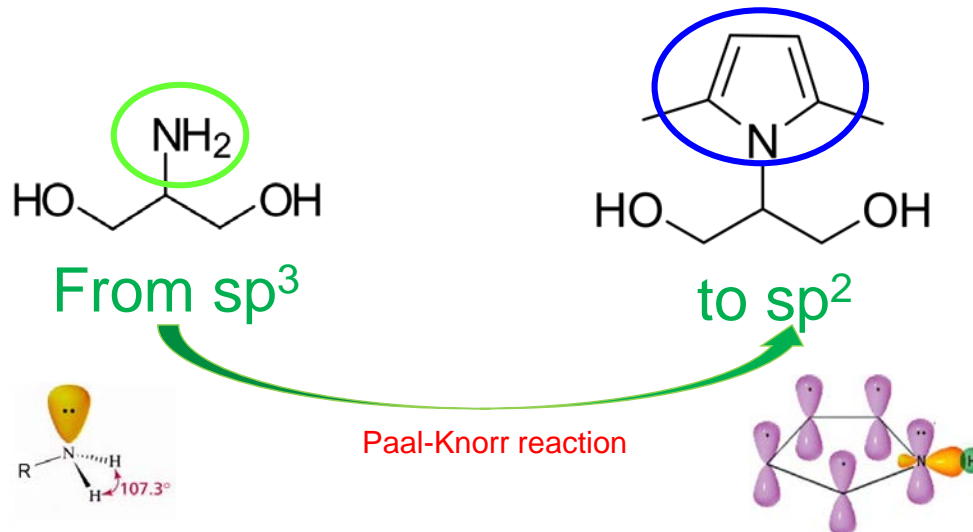
Serinol pyrrole - SP

No solvent  
By product H<sub>2</sub>O

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

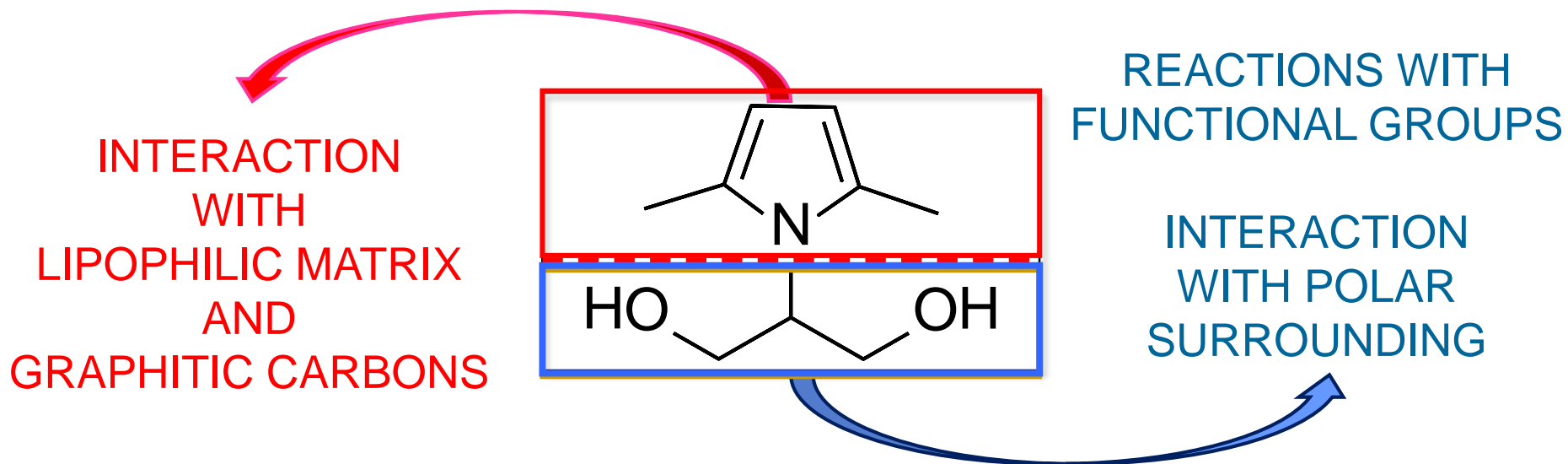
V. Barbera, A.Citterio, M. Galimberti, G. Leonardi, R. Sebastiano, S.U.Shisodia, A.M. Valerio *WO 2015 189411 A1*  
M. Galimberti, V. Barbera, A. Citterio, R. Sebastiano, A. Truscillo, A. M. Valerio, L. Conzatti, R. Mendichi, *Polymer*, vol 63, 20 April 2015, Pages 62–70  
M. Galimberti, V. Barbera, 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

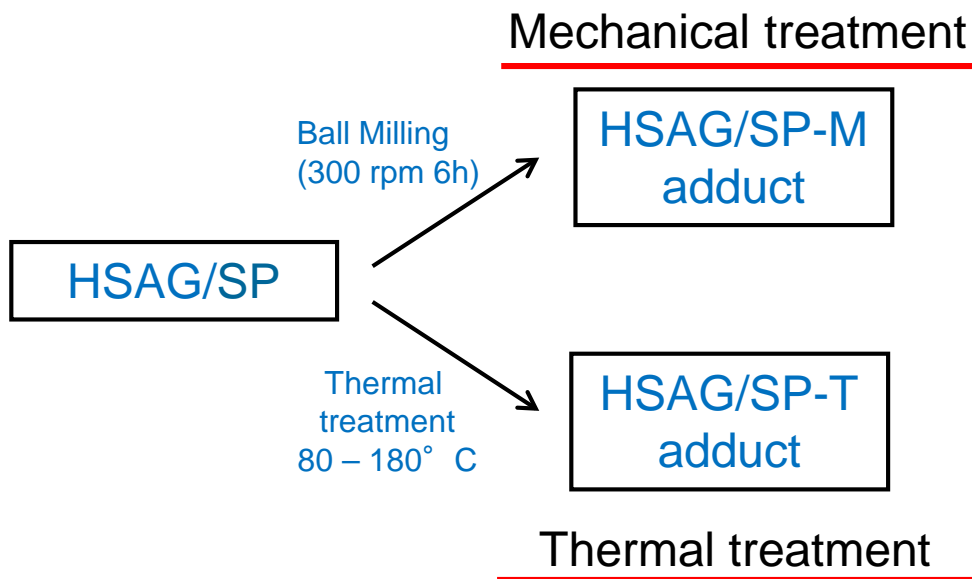


- ➡ Yield: at least 96%
- ➡ Atom efficiency: 85%
- ➡ Easy procedure
- ➡ No solvent
- ➡ By product:  $H_2O$

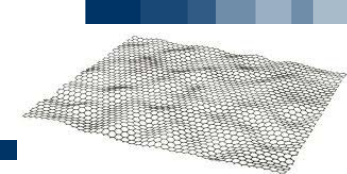
# Serinolpyrrole: *Janus* molecule



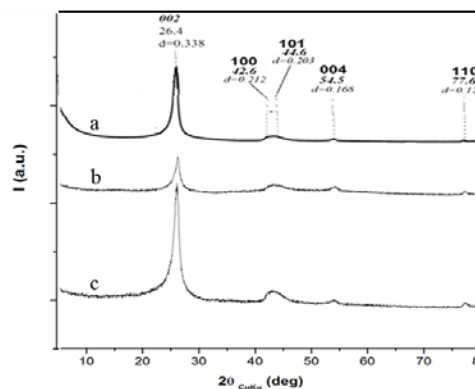
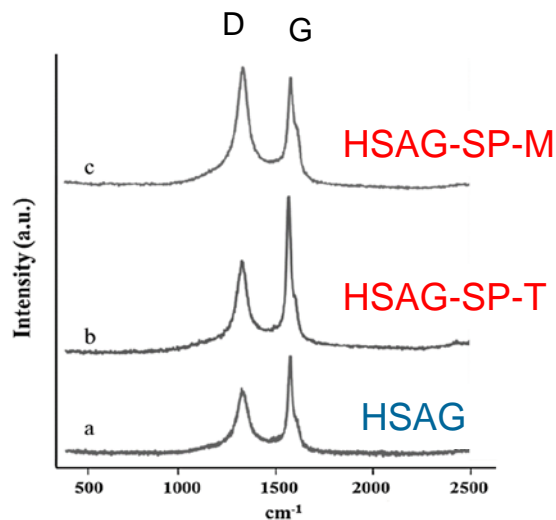
# Adducts of SP with HSAG - Preparation



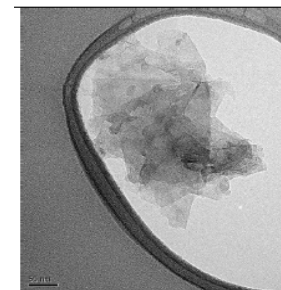
# Adducts of SP with HSAG



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



Few layers graphene

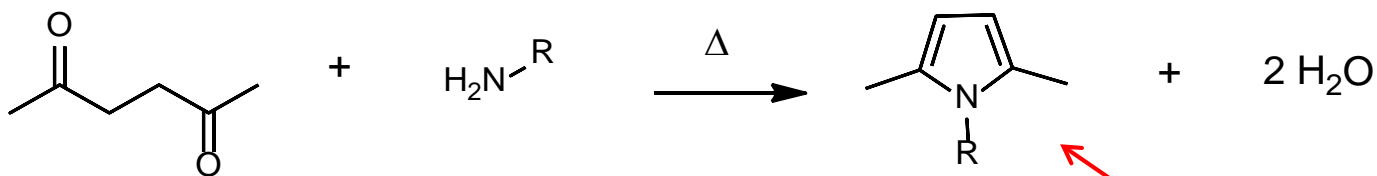


From water suspension

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



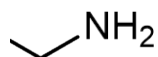
# Pyrrole compounds (PyC) from neat Paal Knorr reaction



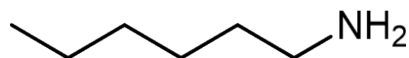
Same reaction conditions used for SP

PyC

Yield %



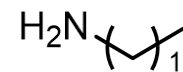
80



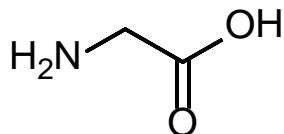
75



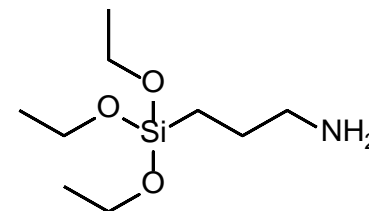
62



73

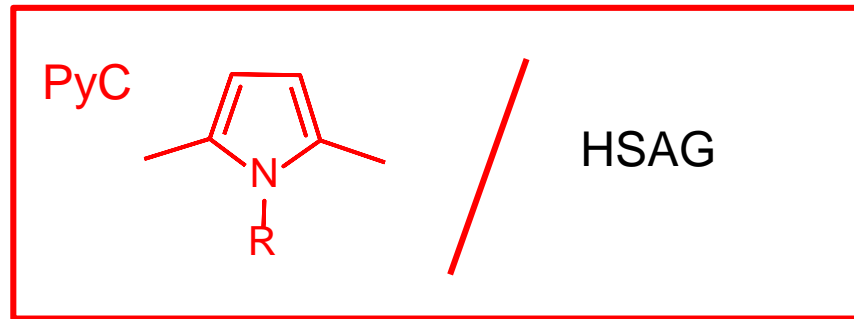


80



70

# Facile functionalization of carbon materials



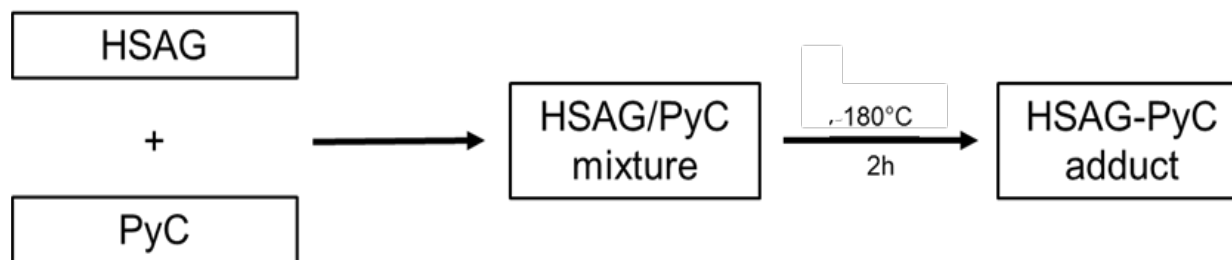
Mixing, energy, air

HSAG-PyC

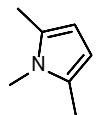
functional groups on surface

bulk structure substantially unaltered

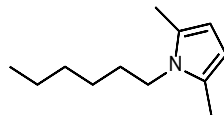
# HSAG / PyC adducts



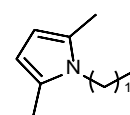
Functionalization Yield %



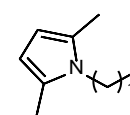
73



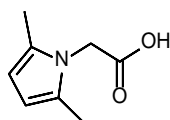
87



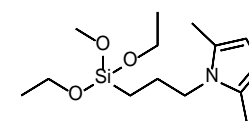
80



98



82

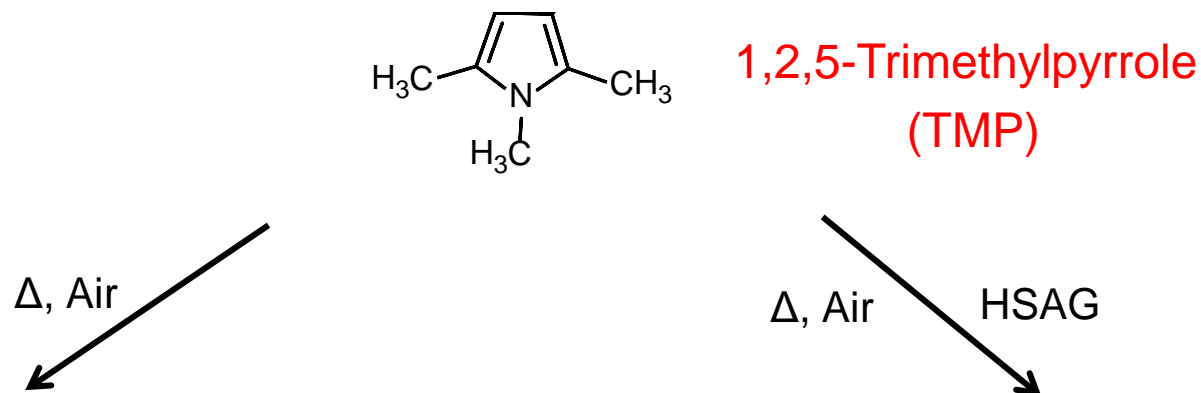


78

# Mechanistic considerations

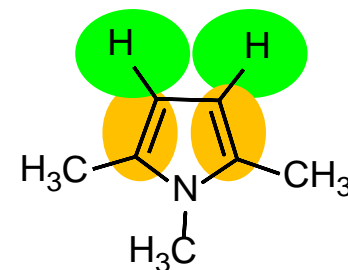
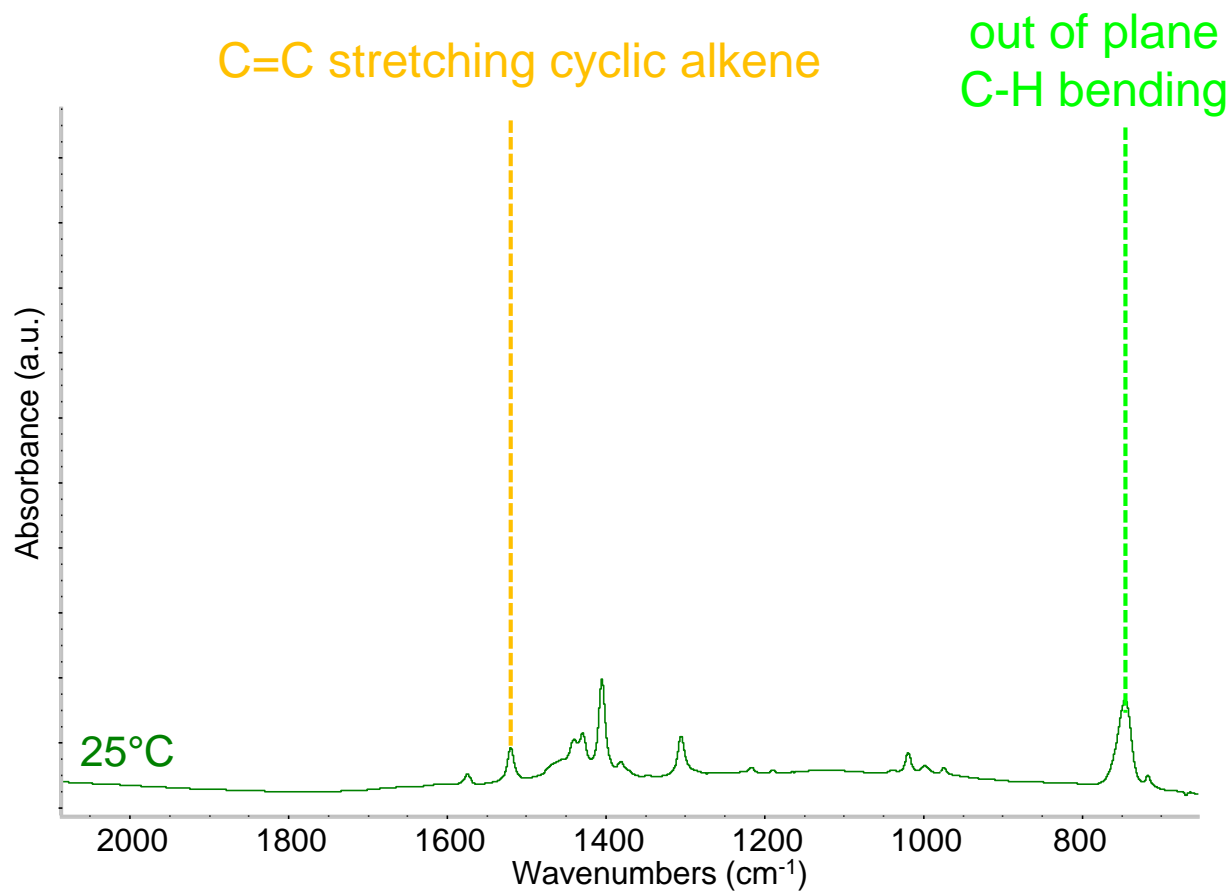
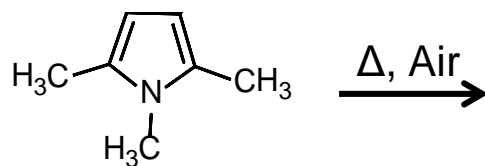
# Mechanism of the functionalization reaction

## Investigation with a model compound

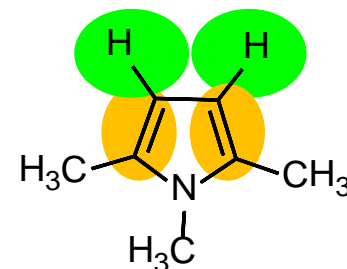
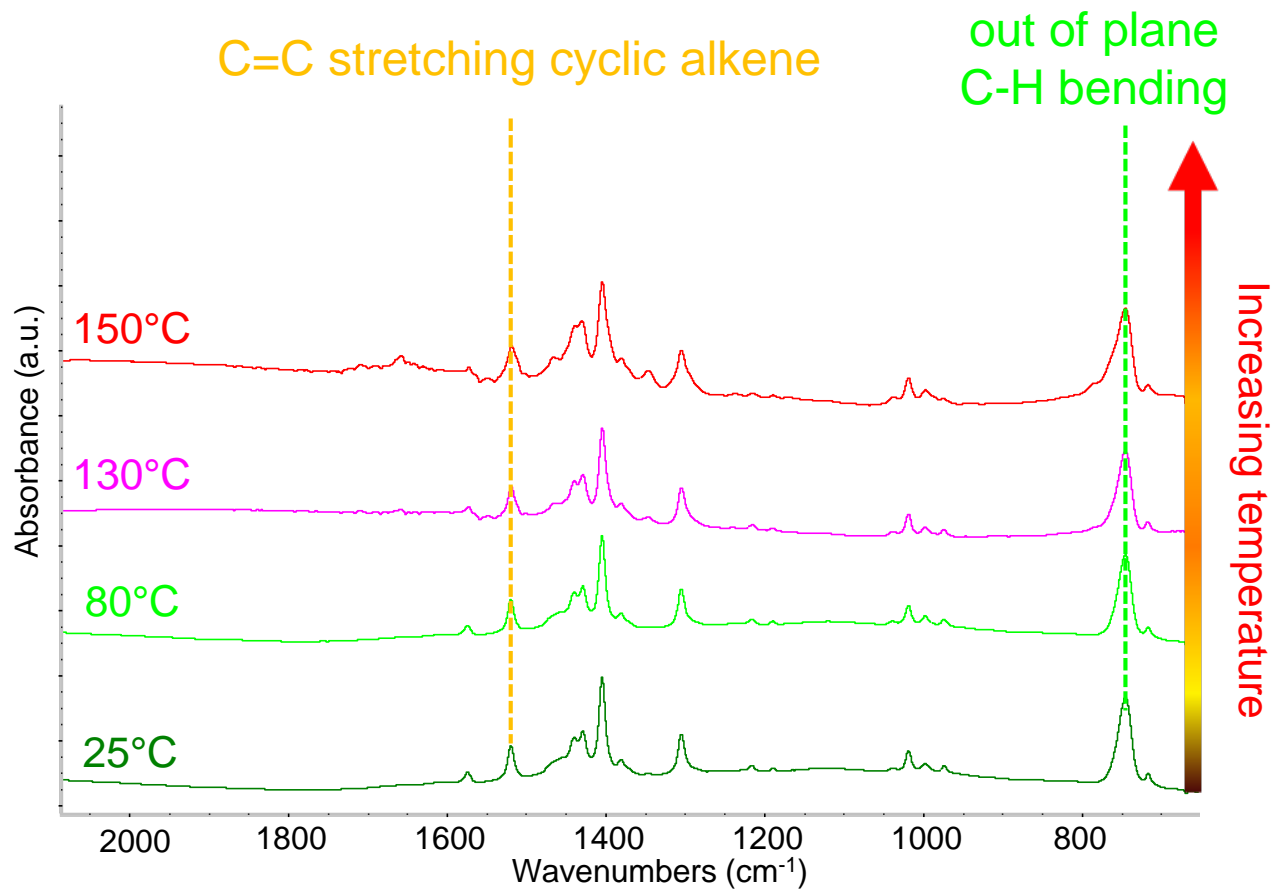
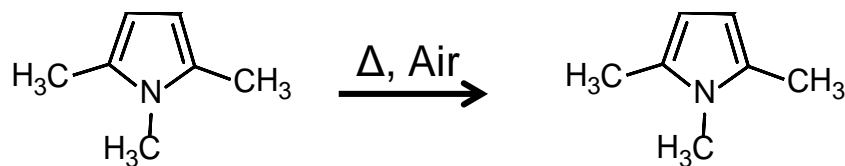


- ☞ Analysis of: liquids, HSAG/TMP adducts
- ☞ FT-IR and  $^1\text{H-NMR}$  spectroscopies
- ☞ FT-IR spectra generation with Density Functional Theory (DFT) quantum chemical modelling

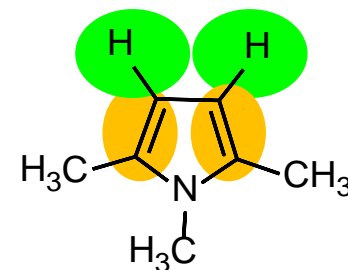
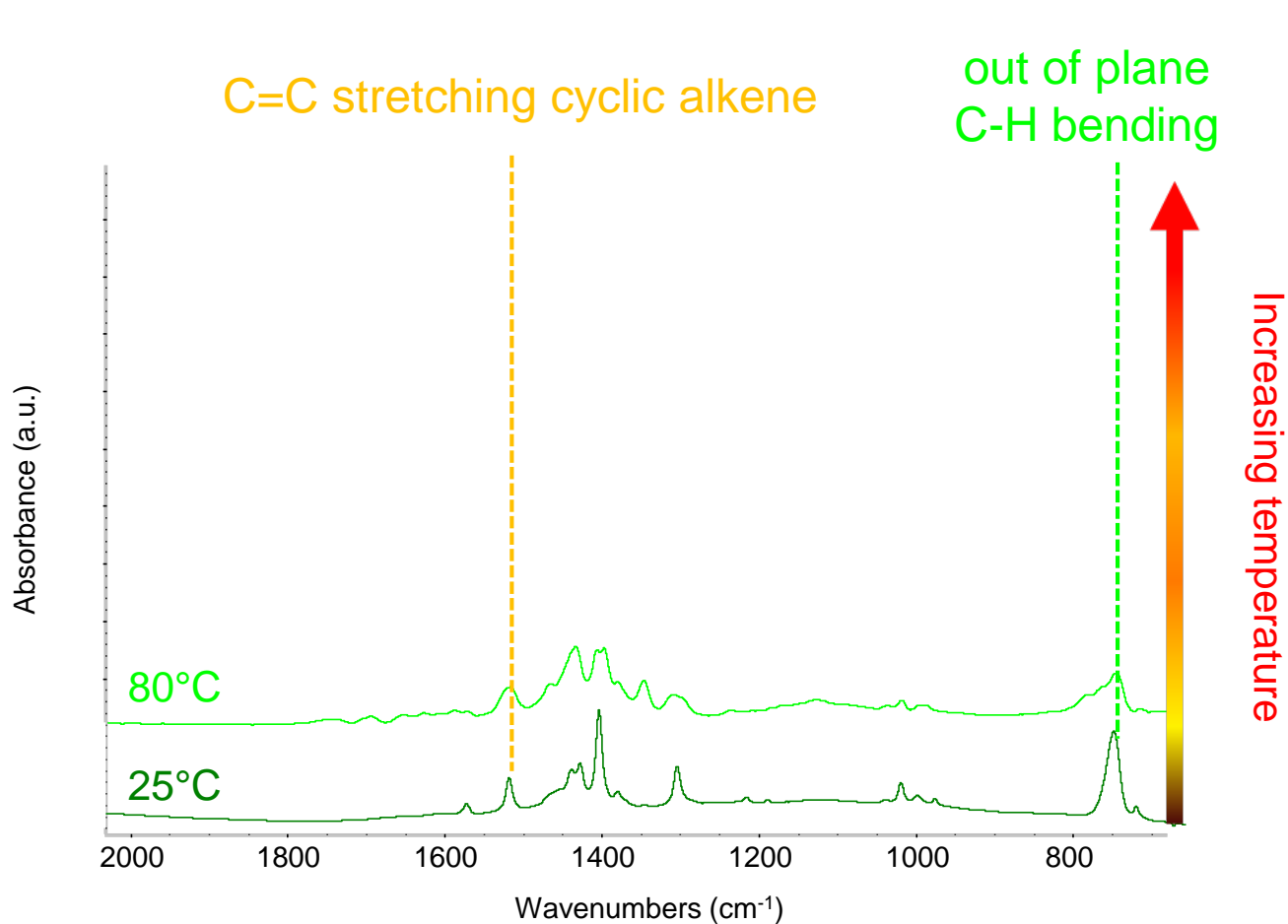
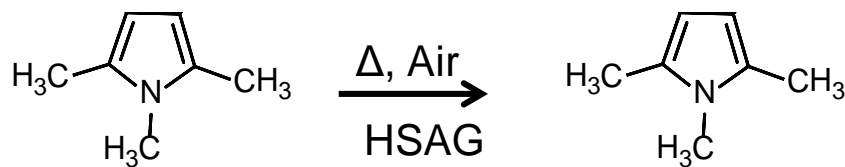
# 1,2,5-Trimethylpyrrole (TMP)



# TMP + Air - From 25°C to 150°C

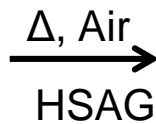
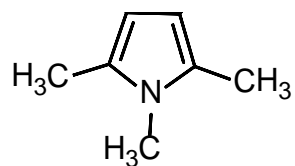


# TMP + HSAG / Air - From 25°C to 80°C

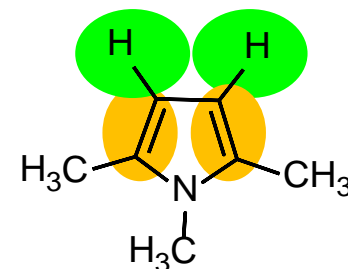
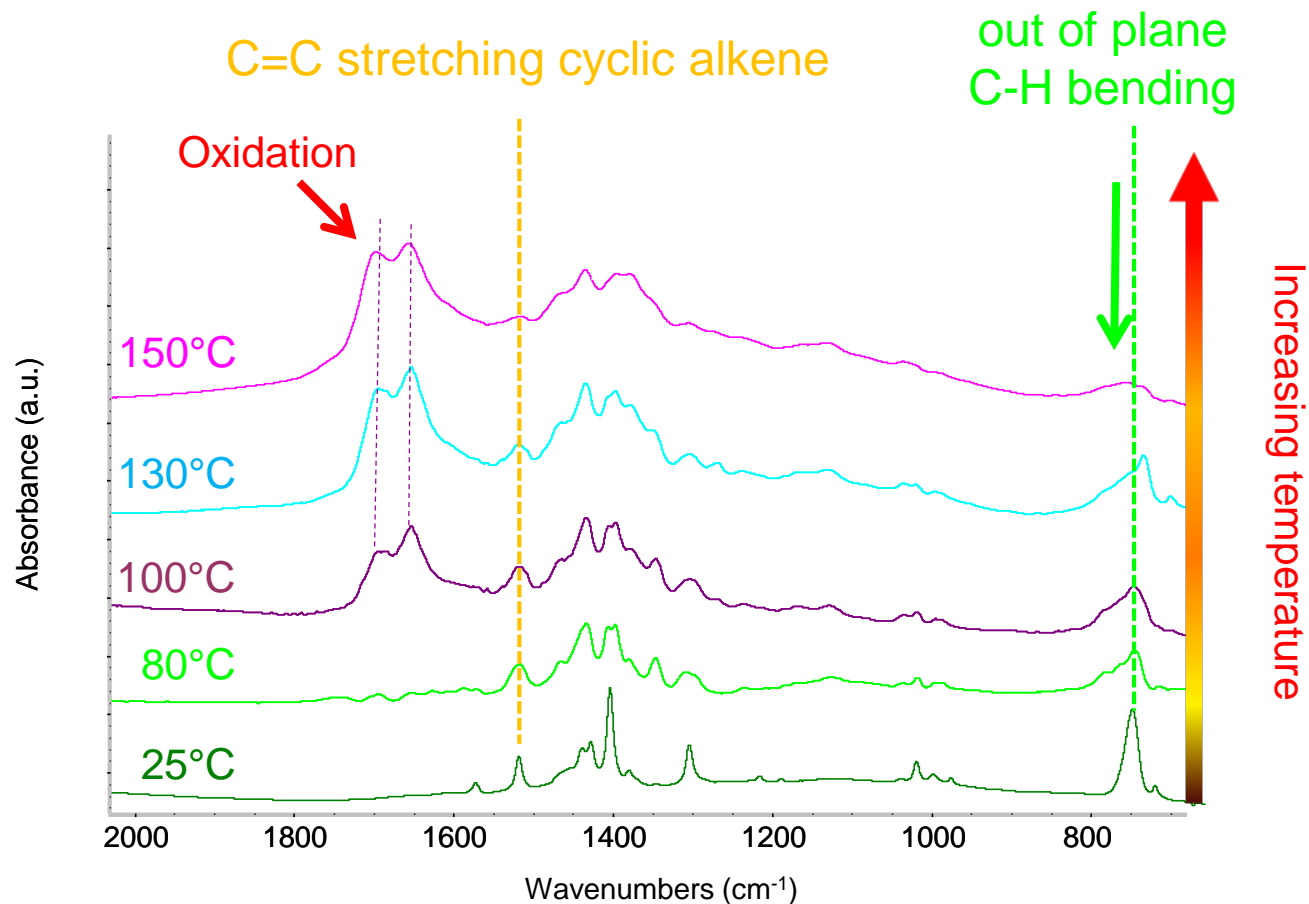




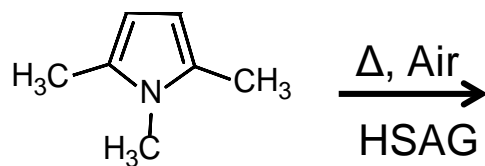
# TMP + HSAG - from 100°C to 150°C



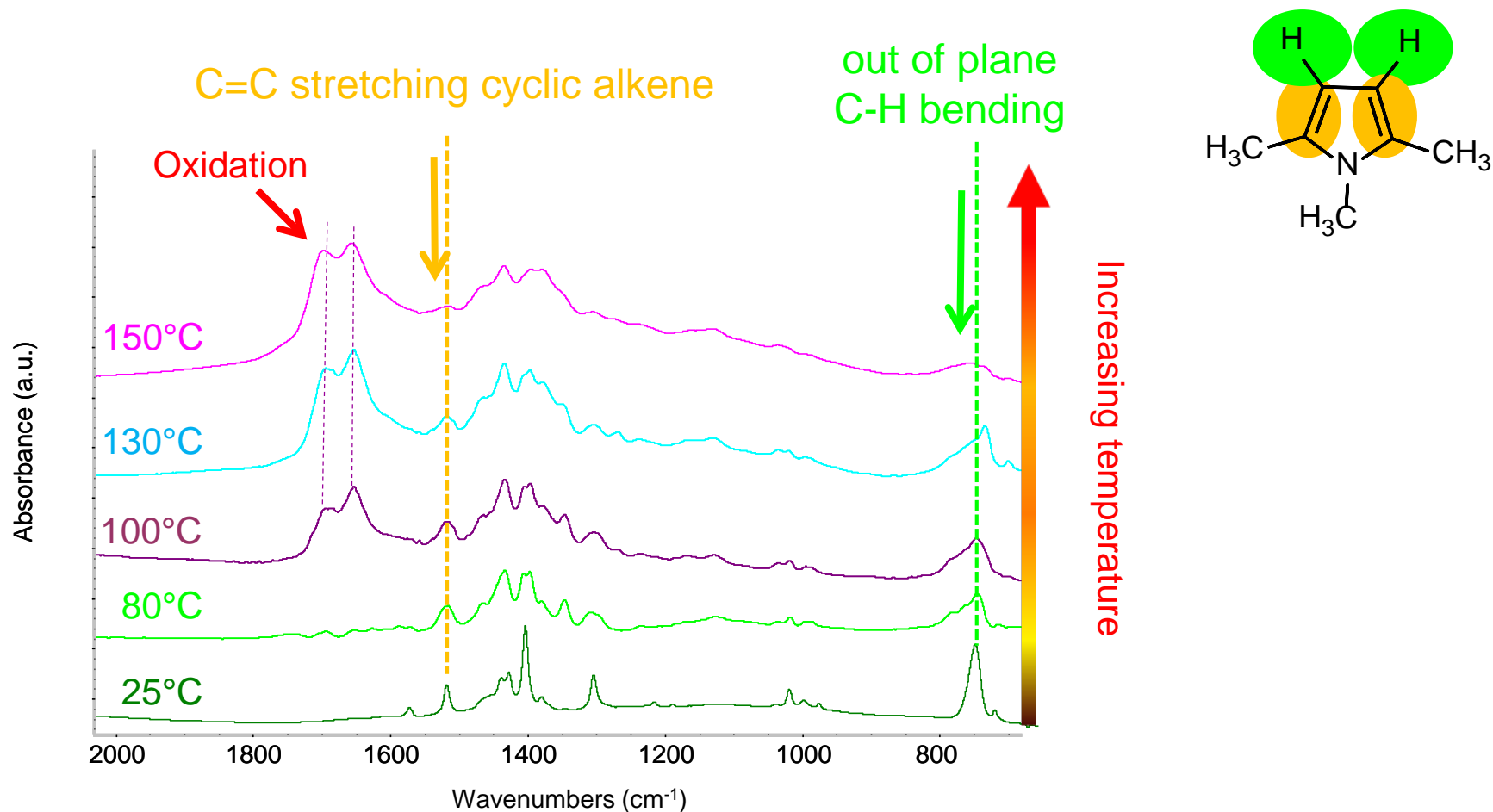
Oxidation products



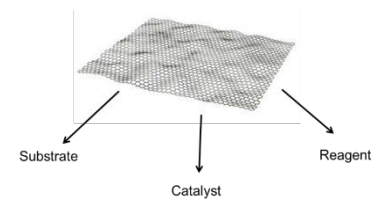
# TMP + HSAG - @ 150°C



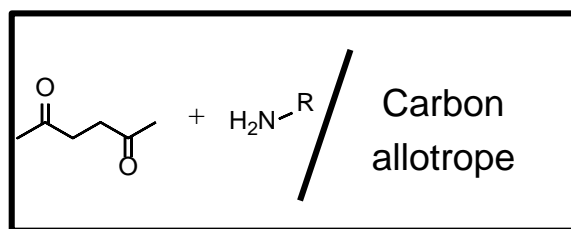
Reaction products of  
intra-annular double bonds



# Facile functionalization of carbon materials



## Hypothesis for the mechanism



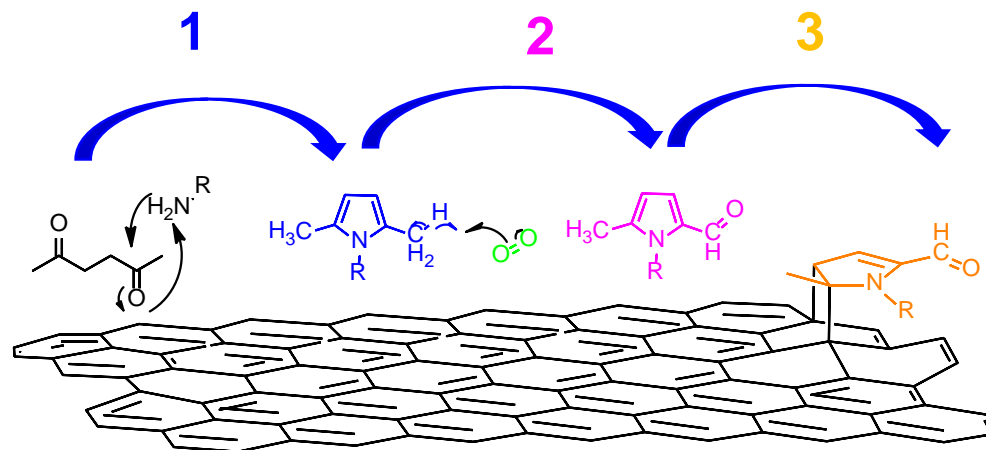
Paal – Knorr Reaction



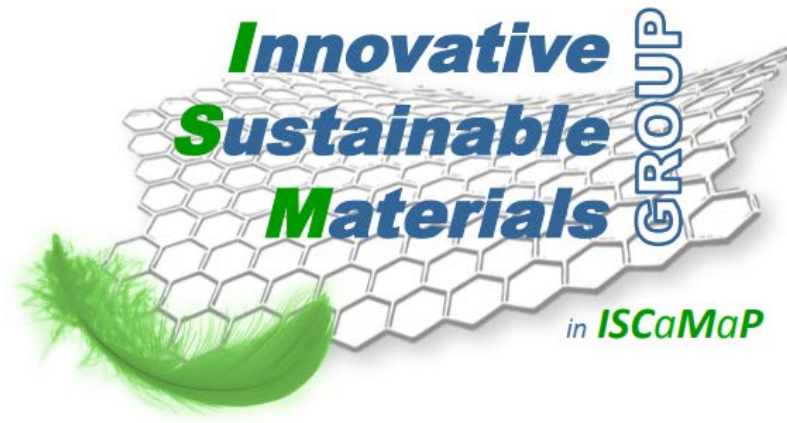
Carbocatalyzed Oxidation



Diels-Alder reaction

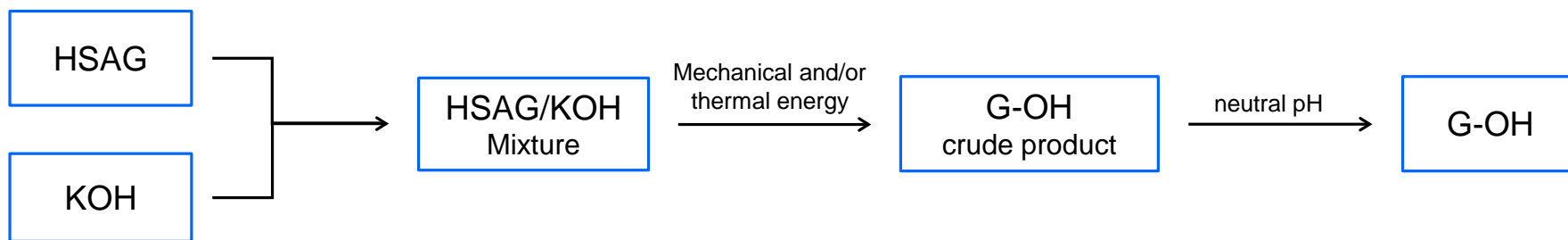
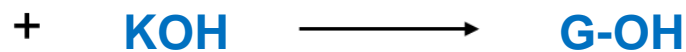


FT-IR and  $^1\text{H-NMR}$  spectroscopies; FT-IR spectra generation with Density Functional Theory (DFT) quantum chemical modelling



## Functionalization of carbon materials with KOH

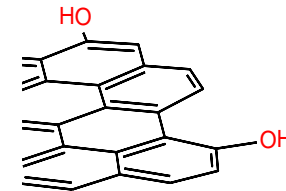
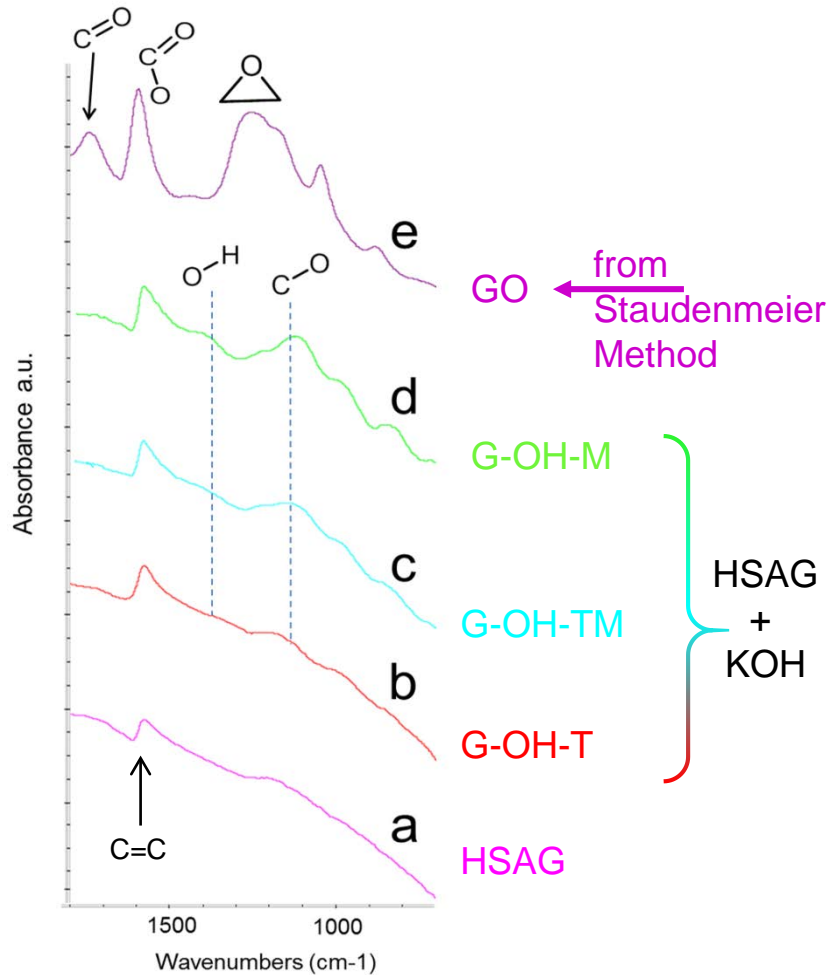
# Synthesis of G-OH



V. Barbera, A. Porta, L. Brambilla, S. Guerra, A. Serafini, A. M. Valerio, A. Vitale, M. Galimberti, [RSC Adv., 2016, 6, 87767-87777](#)

V. Barbera, A. Bernardi, G. Torrasi, A. Porta, M. Galimberti, [Elastomery, 2017, 21\(4\), 235-251](#)

# Preparation of G-OH



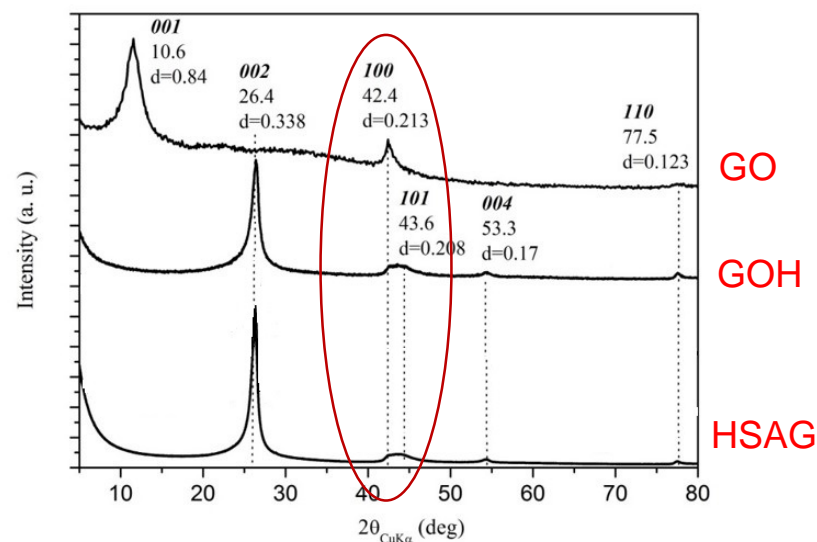
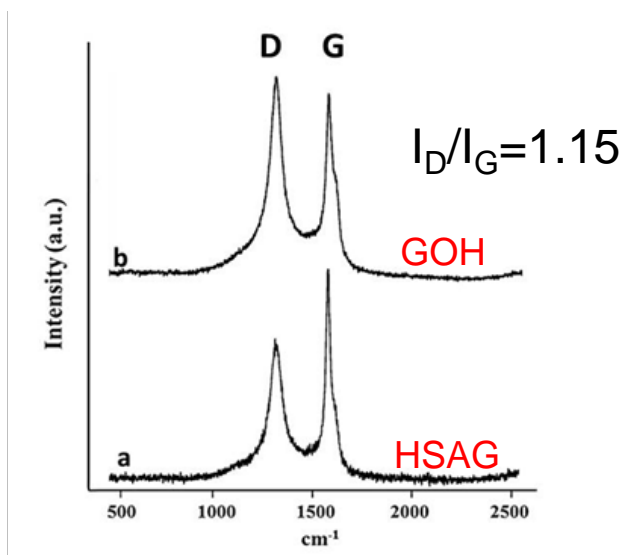
XPS → Increase of C-O / C=O ratio

	HSAG	G-OH-M
O1s / C1s atomic ratio	0.04	0.07
O atomic %	4.2	6.4

V. Barbera, A. Porta, L. Brambilla, S. Guerra, A. Serafini, A. M. Valerio, A. Vitale, M. Galimberti, *RSC Adv.*, 2016, 6, 87767-87777

V. Barbera, A. Bernardi, G. Torrisi, A. Porta, M. Galimberti, *Elastomery*, 2017, 21(4), 235-251

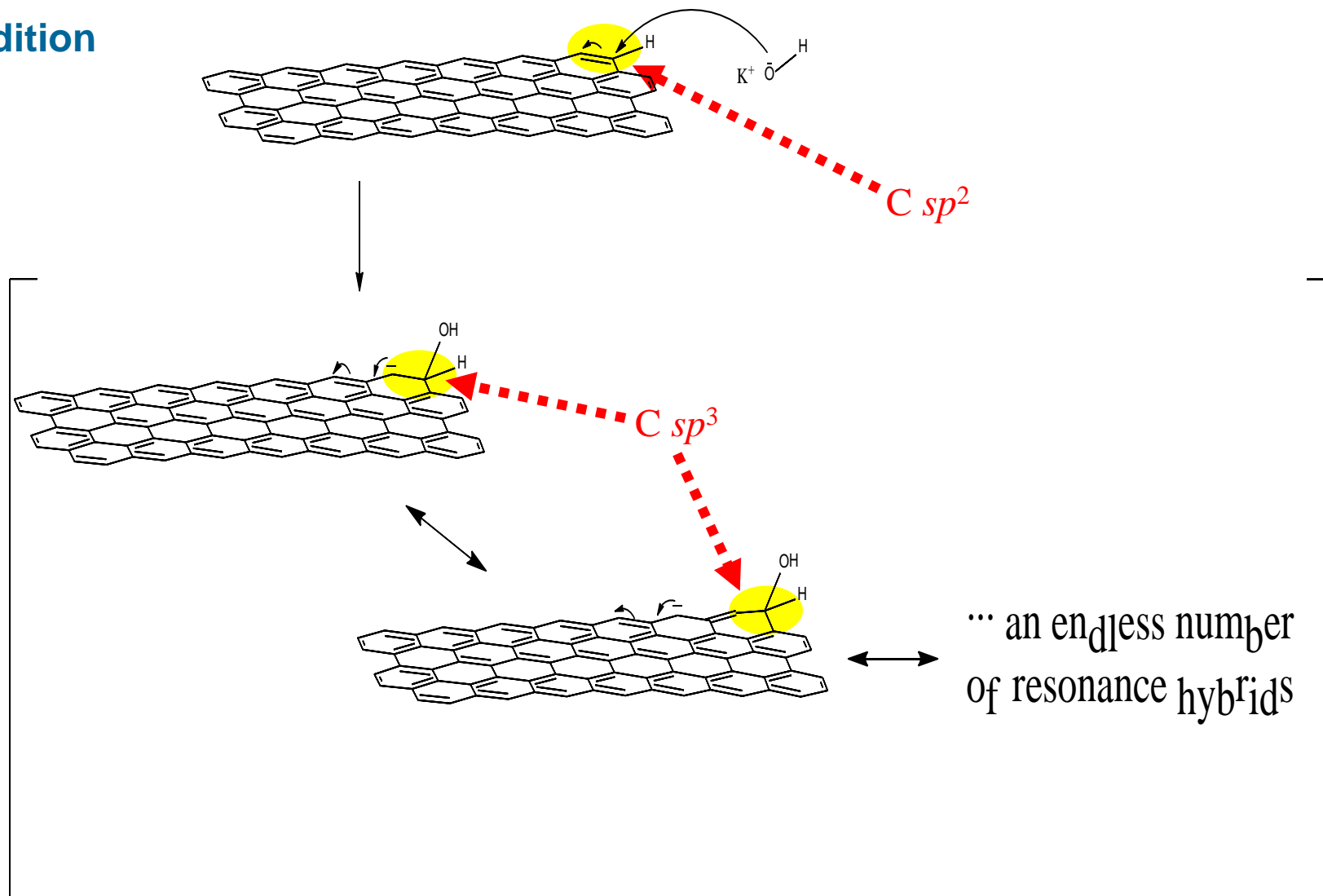
# Preparation of G-OH



- 👉 Selective introduction of OH groups up to 15 mass%
- 👉 In plane order substantially unaltered
- 👉 No expansion of interlayer distance

# Oxidation with KOH – Proposed mechanism

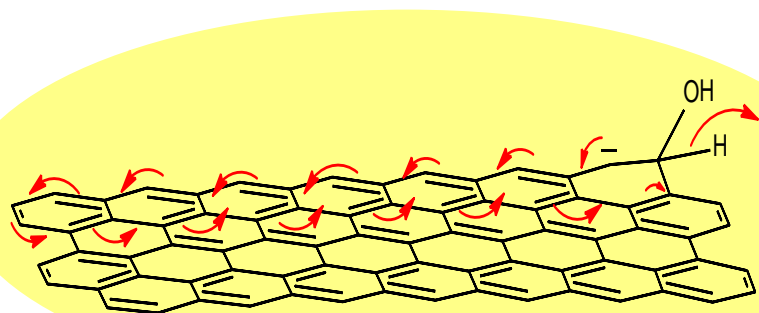
## Addition





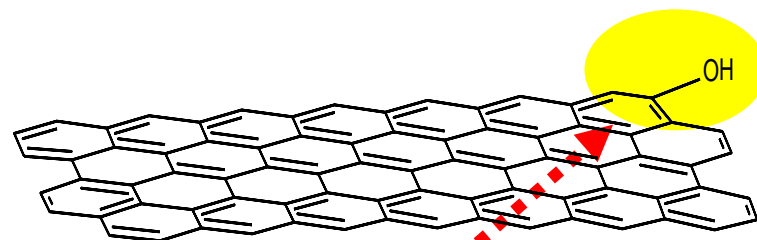
# Oxidation with KOH – Proposed mechanism

## Elimination



delocalization on the entire structure

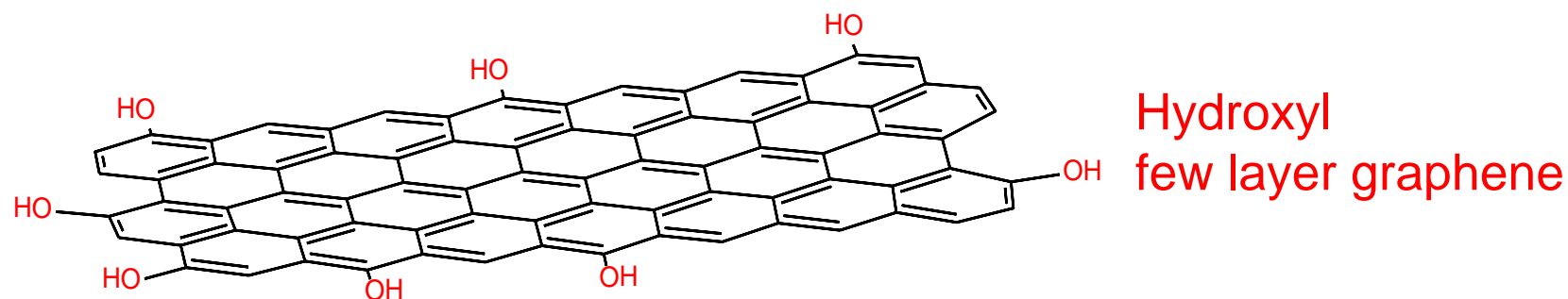
*“wave effect”*



$C\ sp^2$

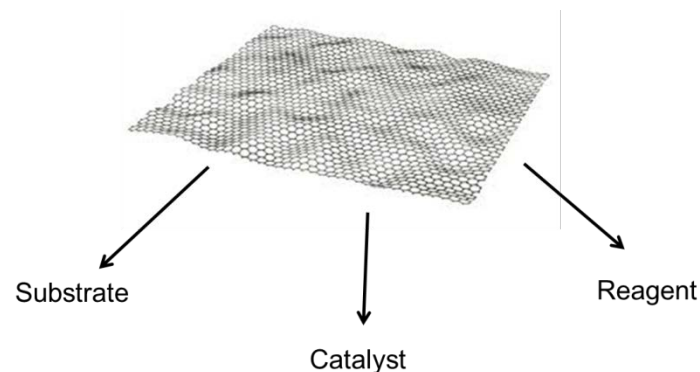
More electronrich structure,  
the oxygen lone pairs delocalized  
on the polyconjugated system

# Synthetic strategy



↓

“Polyphenolic” few layer graphene



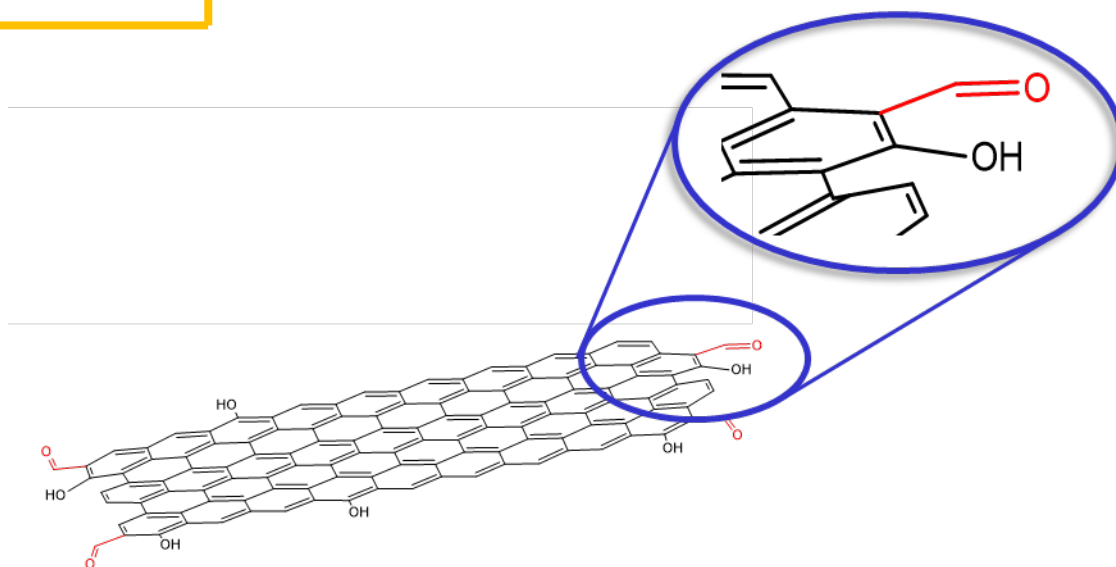
↓

Selective introduction of oxygenated functional groups by means of typical reactions performed on phenol ring

# Selective introduction of aldehydic functional groups

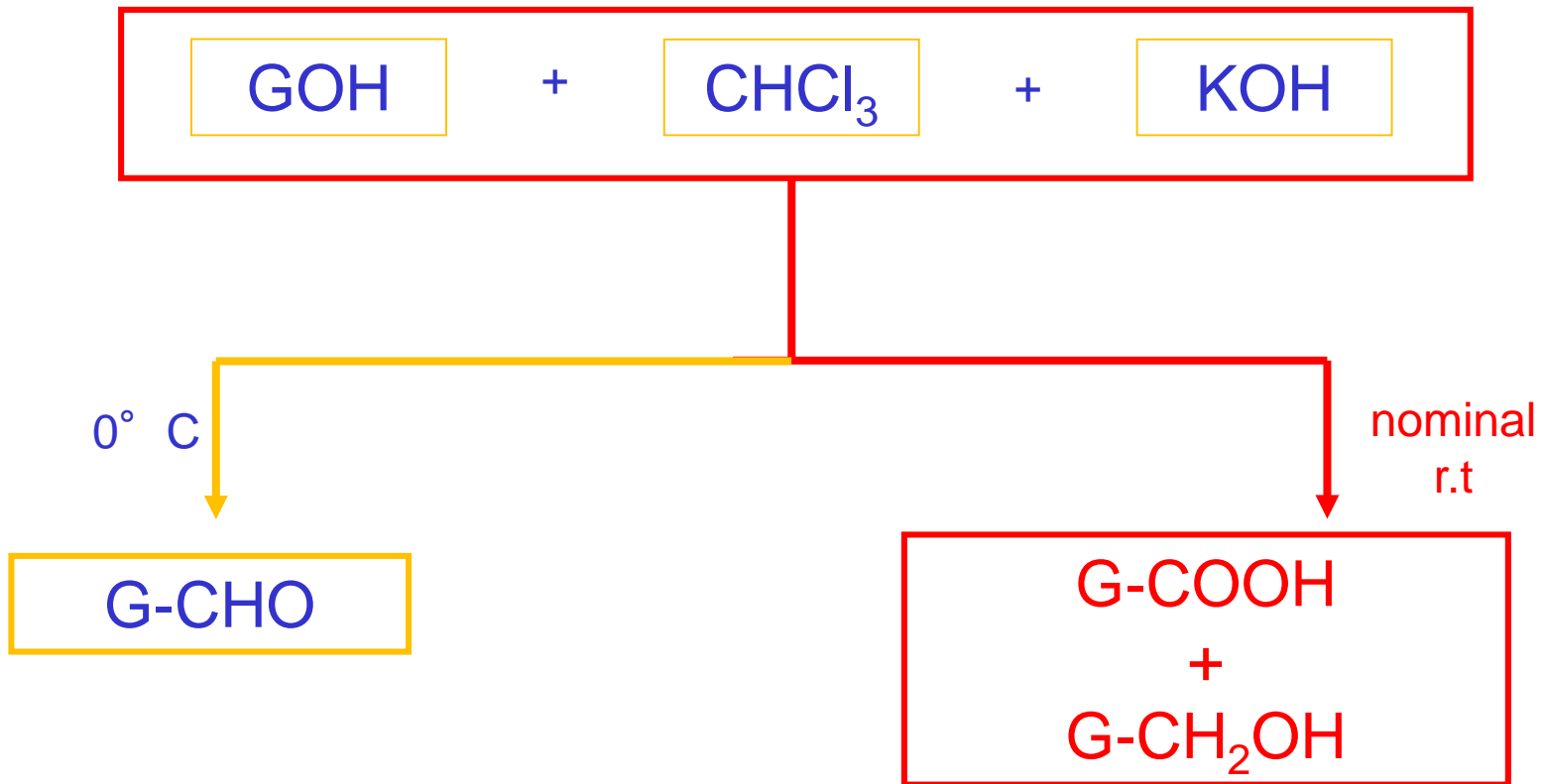


Selective ortho aldehyde



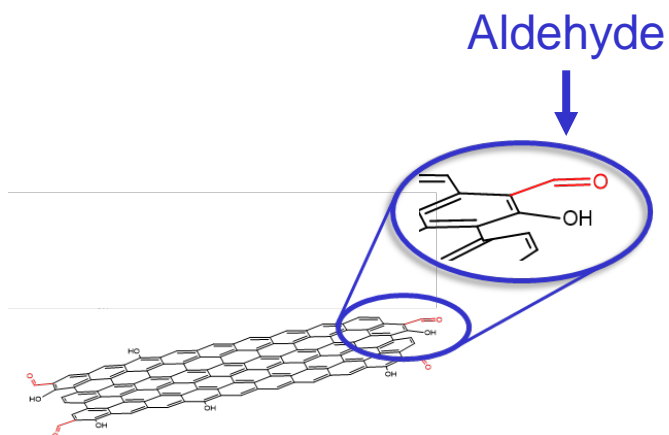
**Reimer-Tiemann  
reaction**

# Selective introduction of oxygenated functional groups

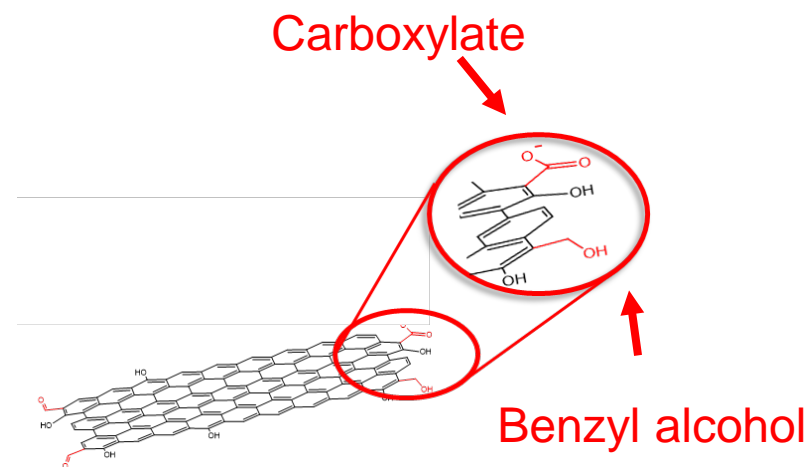


FT-IR, XPS analysis

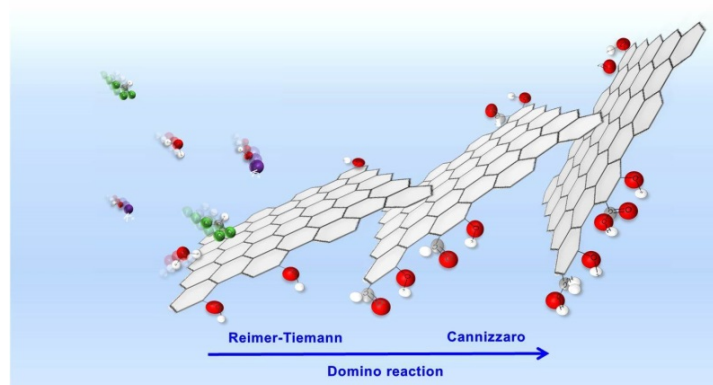
# GOH – Polyphenolic Graphite derivatives



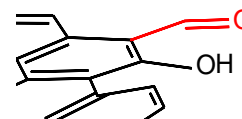
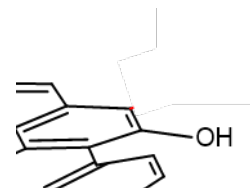
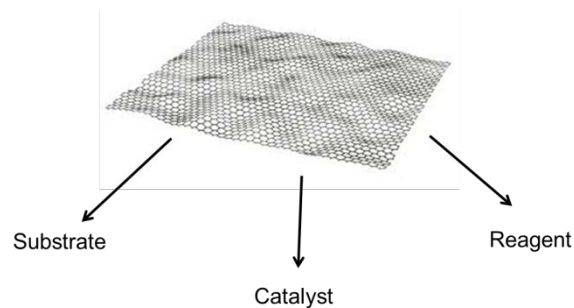
Reimer -Tiemann



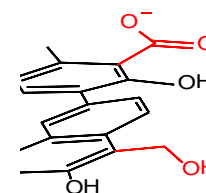
Cannizzaro



# Reimer-Tiemann - Cannizzaro Domino reaction



Reimer-Tiemann



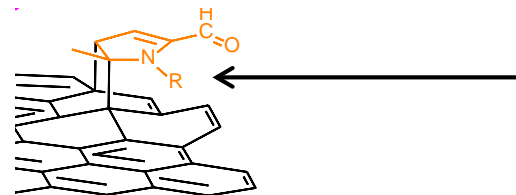
Domino Reimer-Tiemann/Cannizzaro



# Applications

# Tuning of solubility parameter of $sp^2$ carbon allotropes (CA)

Library PyC



CA-PyC  
adduct



Selection of PyC



Tuning of solubility parameter  
of  $sp^2$  carbon allotropes



# CA / PyC adducts - Tuning of solubility parameters

Experimental determination

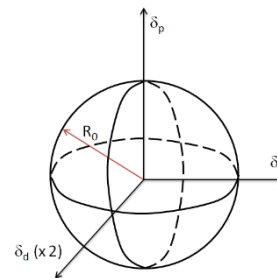


Stable suspensions  
in solvents  
with different  $\delta$

Theoretical predictions

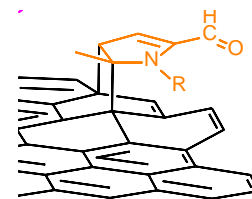


Computational model:  
Hansen solubility parameters

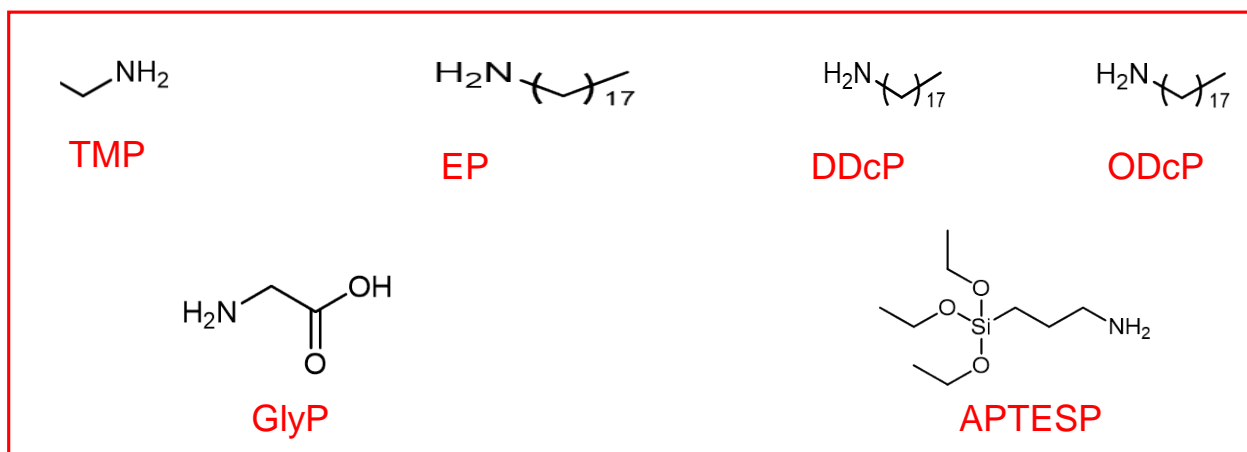


# Evaluation of solubility parameters of HSAG-PyC - $\delta$ values

Sample	$\delta_D$	$\delta_P$	$\delta_H$	Radius
HSAG	17.8	3.1	5.7	1.0
HSAG-TMP	14.6	10.3	5.6	11.6
HSAG-DDcP	8.5	7.5	8.3	12.3
HSAG-APTESP	12.7	2.3	0.5	8.3
HSAG-SP	12.8	2.0	8.9	13.8
HSAG-GlyP	6.9	12.1	5.3	15.3

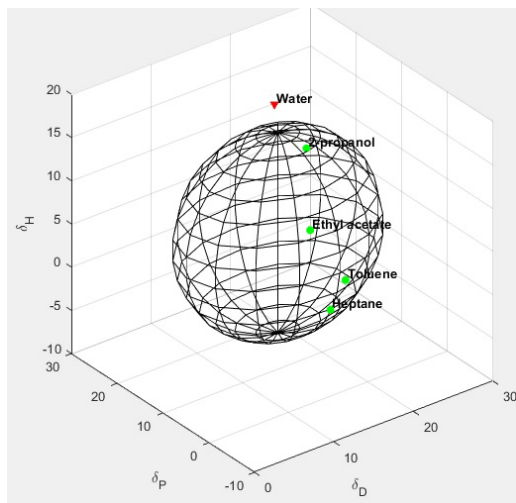


Amount of PyC on HSAG:  
about 5% mol

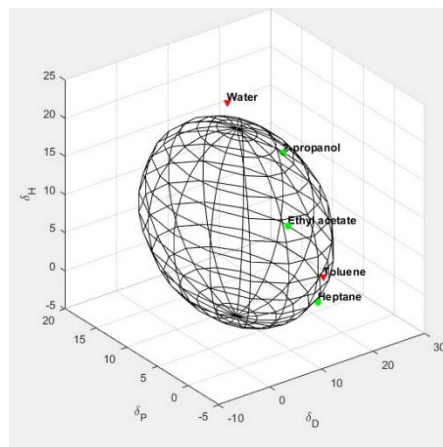


# Evaluation of solubility parameters of HSAG-PyC - Hansen sphere

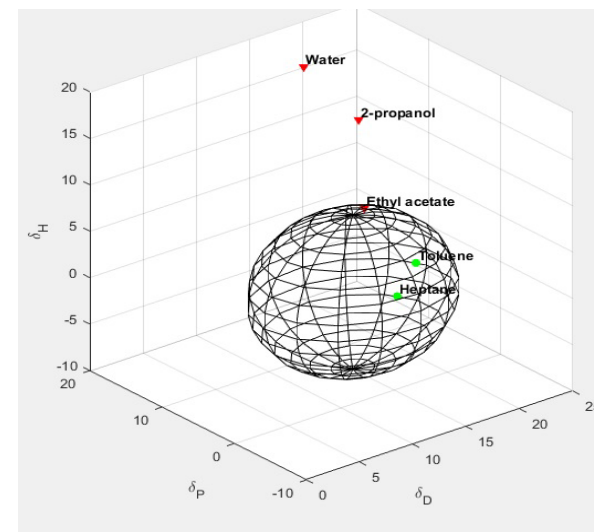
## HSAG-TMP



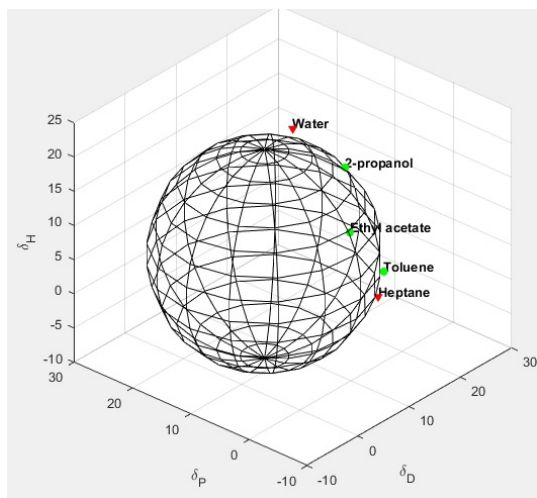
## HSAG-DDcP



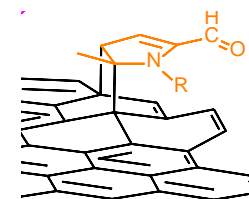
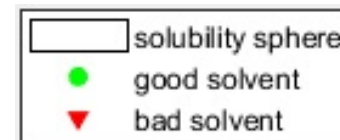
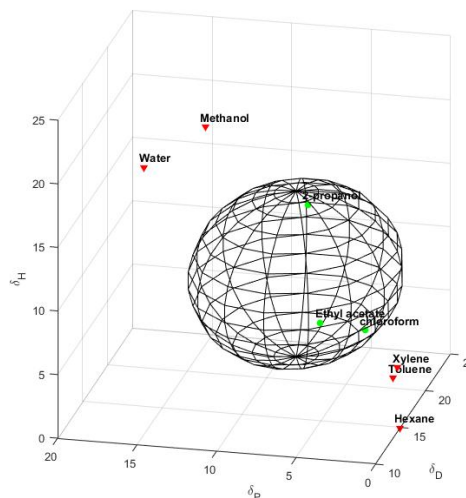
## HSAG-APTESP



## HSAG-GlyP



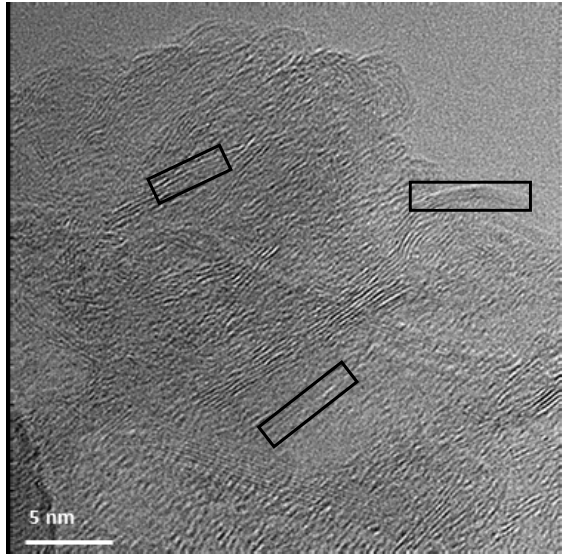
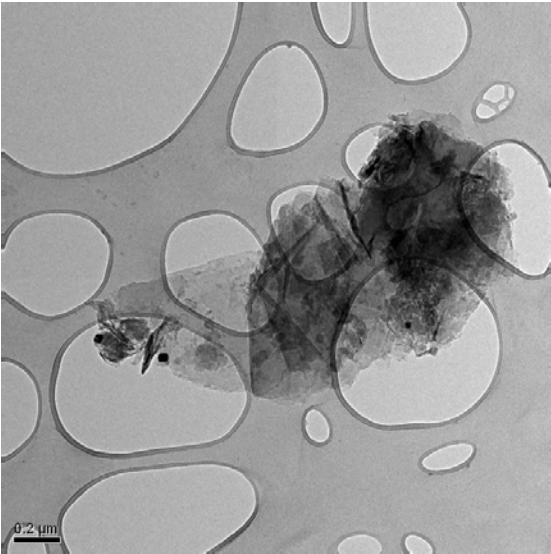
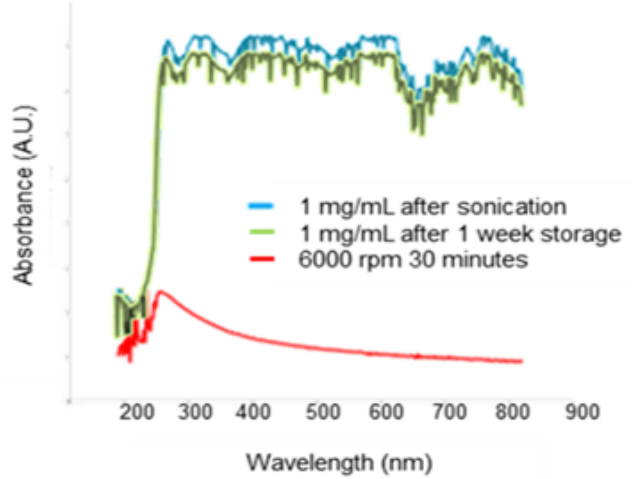
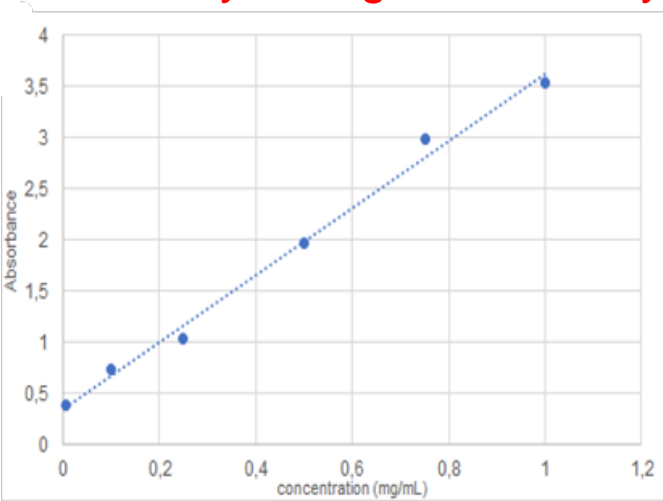
## HSAG-SP





# Ultimate dispersions in water of few layers graphene

By tuning the solubility parameter of graphene layers



2-3 stacked layers



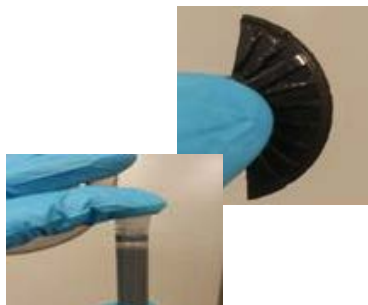
Polymer composites

Carbocatalysts



## Composites

Rubber nanocomposites



Concrete with high flexural strength



Carbon paper



Aerogels



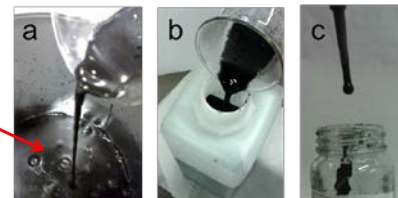
No HSAG HSAG HSAG-SP

Polyurethanes



Polyol dispersions

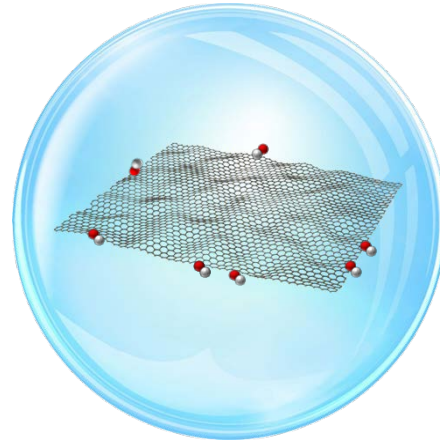
Large scale preparation



Conc (g/L): 10 g/L, 30 g/L, 200 g/L.

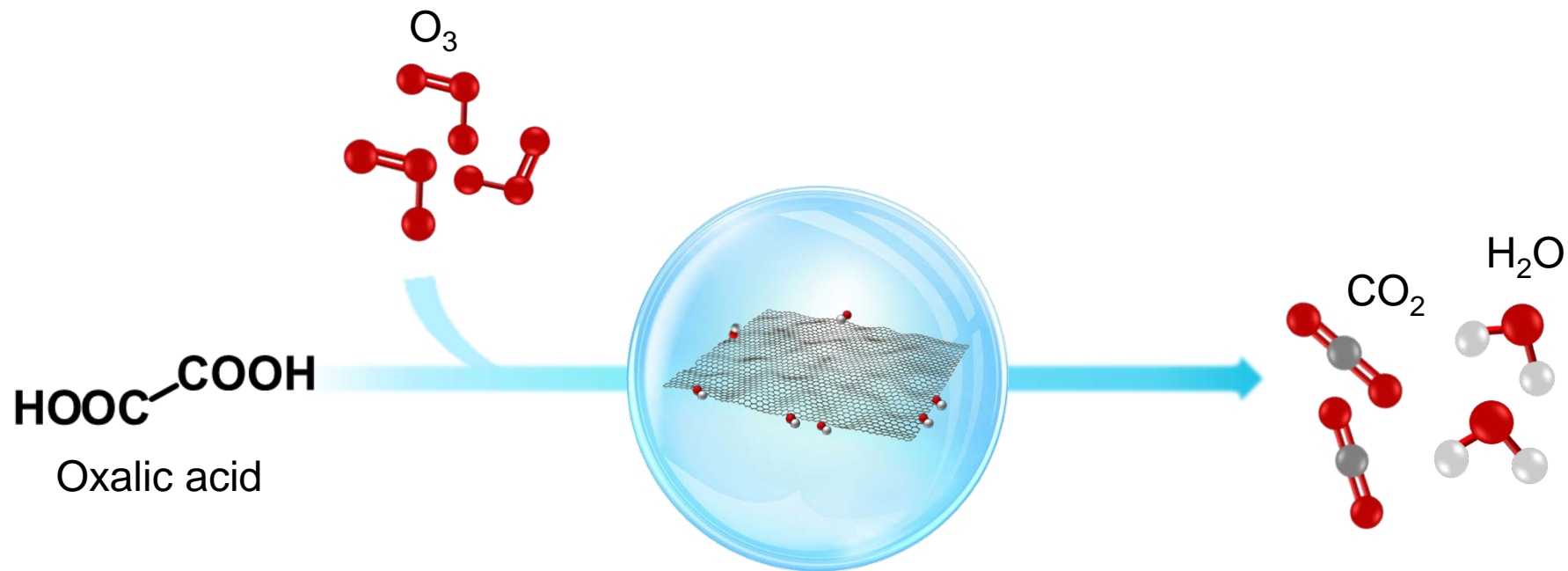
Inks and varnishes

## Carbocatalysis



G-OH and G-COOH  
in a water medium

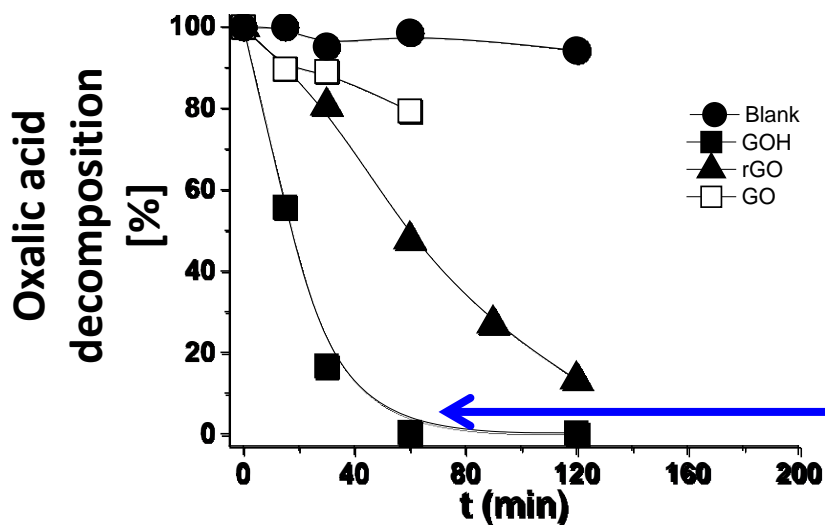
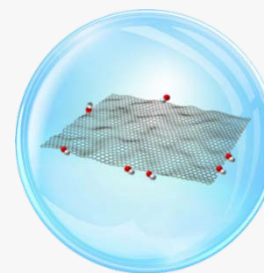
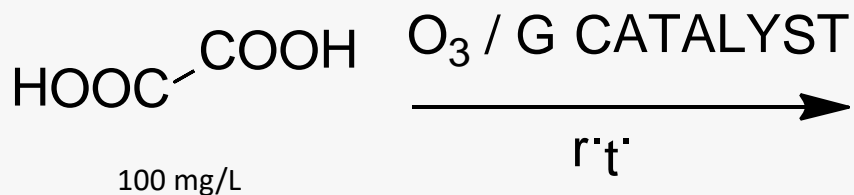
# G-OH and derivatives as catalyst for Ozonation



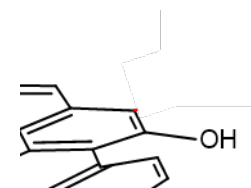


# G-OH and derivatives as catalyst for Ozonation

REACTION PERFORMED

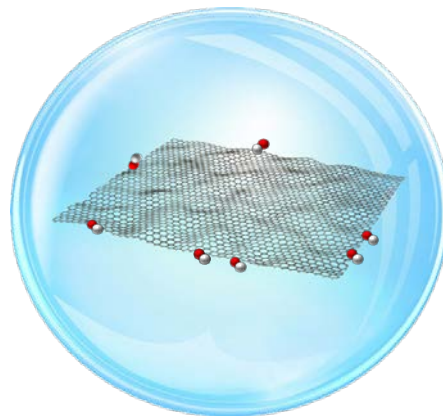
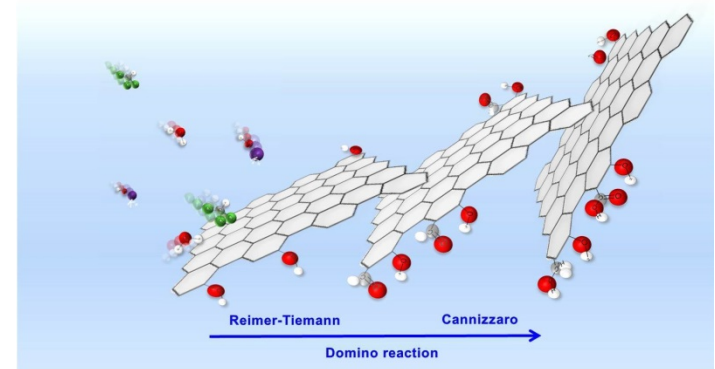
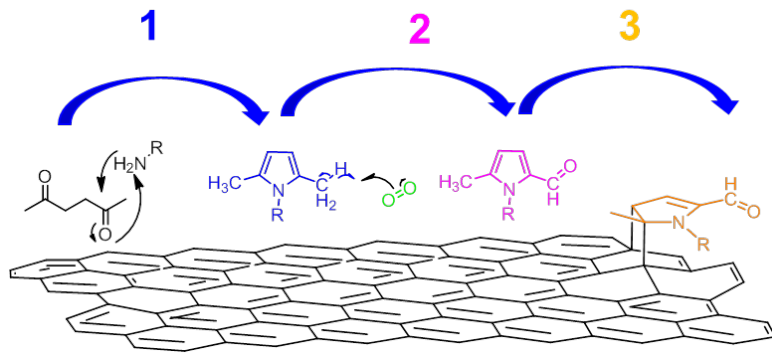


8 TIMES USED G-OH  
Almost the same activity!



G-OH

# Conclusions



*Thanks for the attention!*

