



Facile and sustainable functionalization of sp^2 carbon allotropes, as fillers for rubber composites

Maurizio Galimberti

Vincenzina Barbera, Andrea Bernardi, Daniele Locatelli, Giulio Torrisi

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

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Acknowledgments



ISCaMaP

*Innovative Sustainable Chemistry and Materials and Proteomics
Group*



Vincenzina Barbera



Andrea Bernardi



Daniele Locatelli



Giulio Torrasi

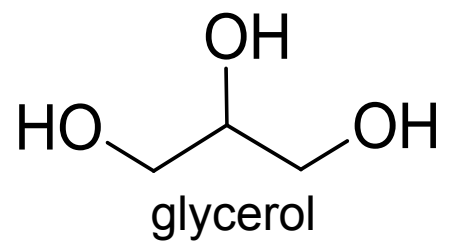
Prof. Attilio Citterio

Pirelli Tyre

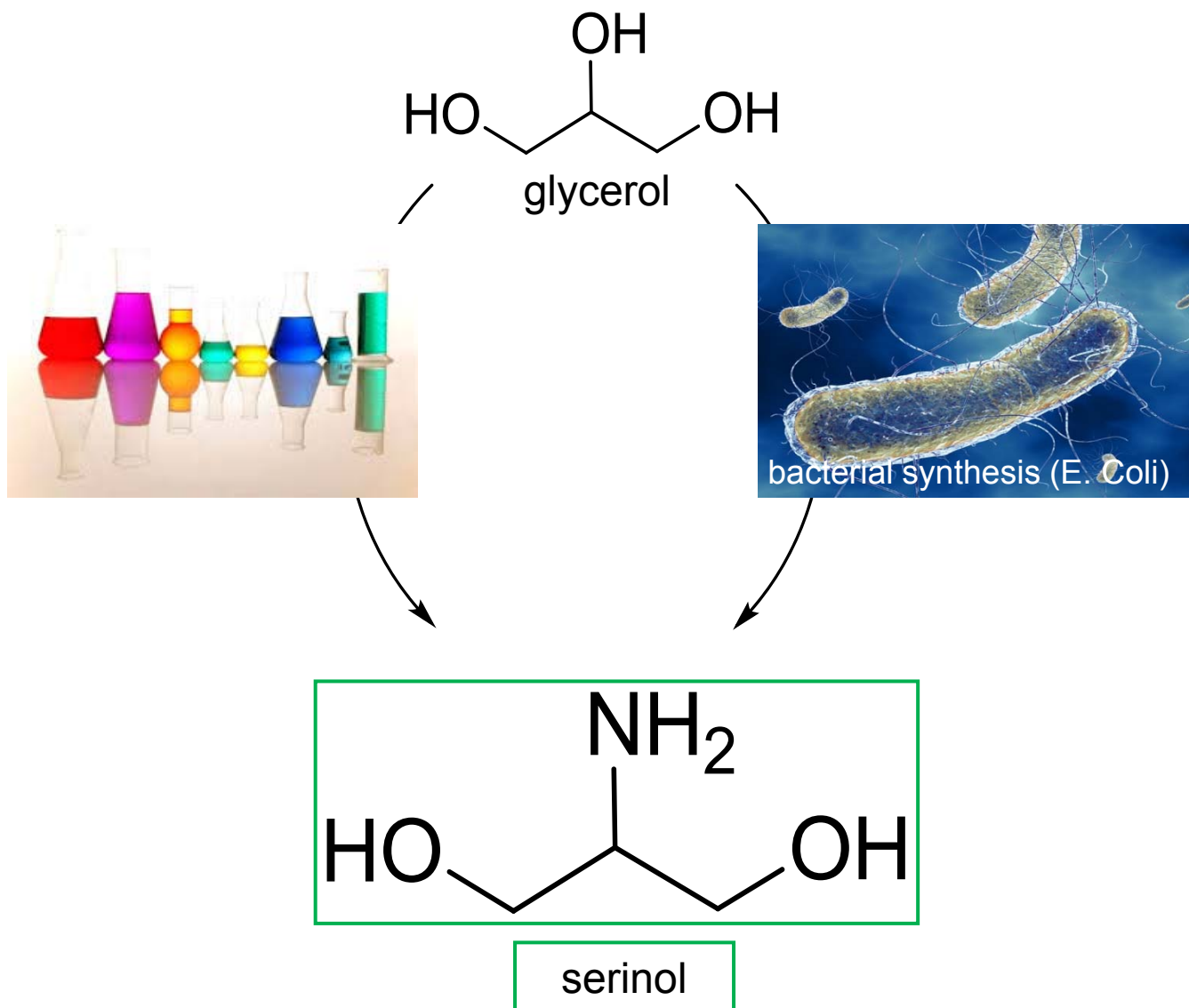
Objectives of the research activity

- Functionalization of sp^2 carbon allotropes
 - without waste
 - through a sustainable process
 - preserving the sp^2 hybridization
 - with a fine tuning of the solubility parameters
- Preparation of rubber composites, with improved properties

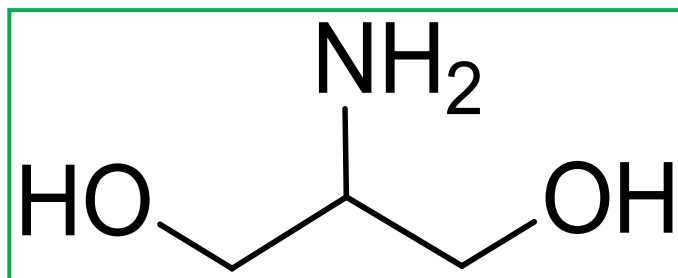
Selection of the building block: serinol



Selection of the building block: serinol

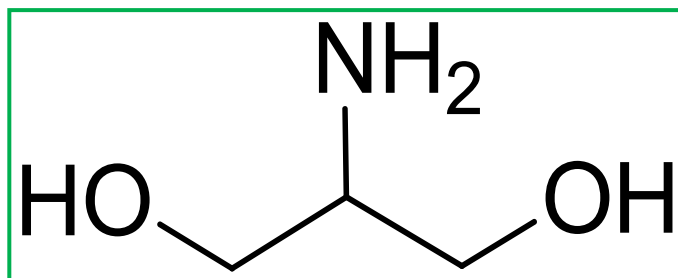


Selection of the building block: serinol

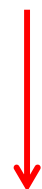


- ☞ Starting building block for many reaction pathways: many derivatives
- ☞ Chemoselectivity

Selection of the building block: serinol



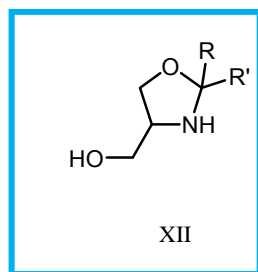
- ☞ Starting building block for many reaction pathways: many derivatives
- ☞ Chemoselectivity



Reactions of the amino group with carbonyl compounds

Reaction of serinol with carbonyl compounds.

Without steric hindrance
and aromatic substituents



Oxazolidines

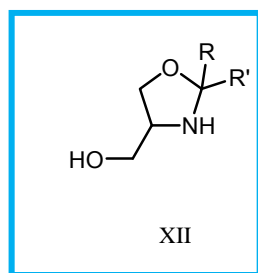
Neat synthesis. No solvent. No catalyst

M. Galimberti, V. Barbera, G. Infortuna, V. Cipolletti, A. Citterio, S. Sun [Proceedings of International Elastomer Conference Cleveland \(OH\), October 9-12, 2017](#)

M. Galimberti, V. Barbera, S. Musto, G. Infortuna, V. Cipolletti, A. Citterio, S. Sun, [Rubber Chemistry and Technology, Frontiers Edition, accepted](#)

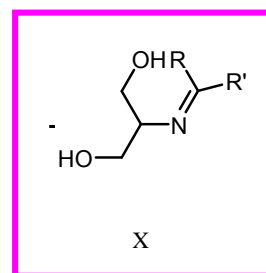
Reaction of serinol with carbonyl compounds.

Without steric hindrance
and aromatic substituents



Oxazolidines

With steric hindrance
and aromatic substituents



Imines

Neat synthesis. No solvent. No catalyst

M. Galimberti, V. Barbera, G. Infortuna, V. Cipolletti, A. Citterio, S. Sun [Proceedings of International Elastomer Conference Cleveland \(OH\), October 9-12, 2017](#)

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Reaction of serinol with carbonyl compounds – Hypothesis of a mechanism

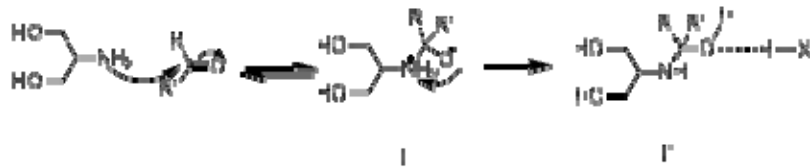
The nucleophilic nitrogen reacts with carbonyl group

Proton transfer



Reaction of serinol with carbonyl compounds – Hypothesis of a mechanism

Release of a water molecule



H—X = General or specific acid cat.

Reaction of serinol with carbonyl compounds – Hypothesis of a mechanism

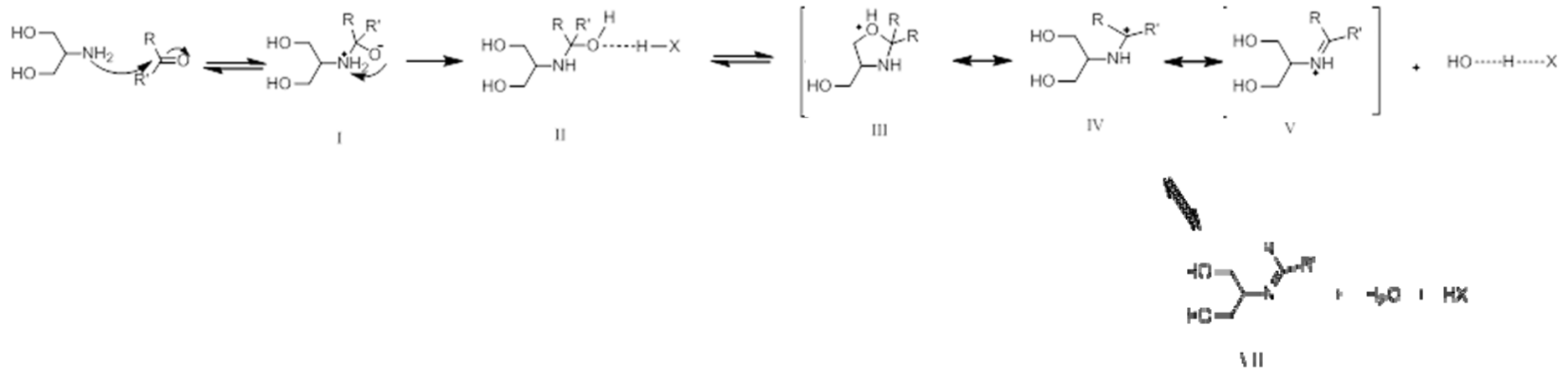
Formation of a cationic species



H—X = General or specific acid cat.

Reaction of serinol with carbonyl compounds – Hypothesis of a mechanism

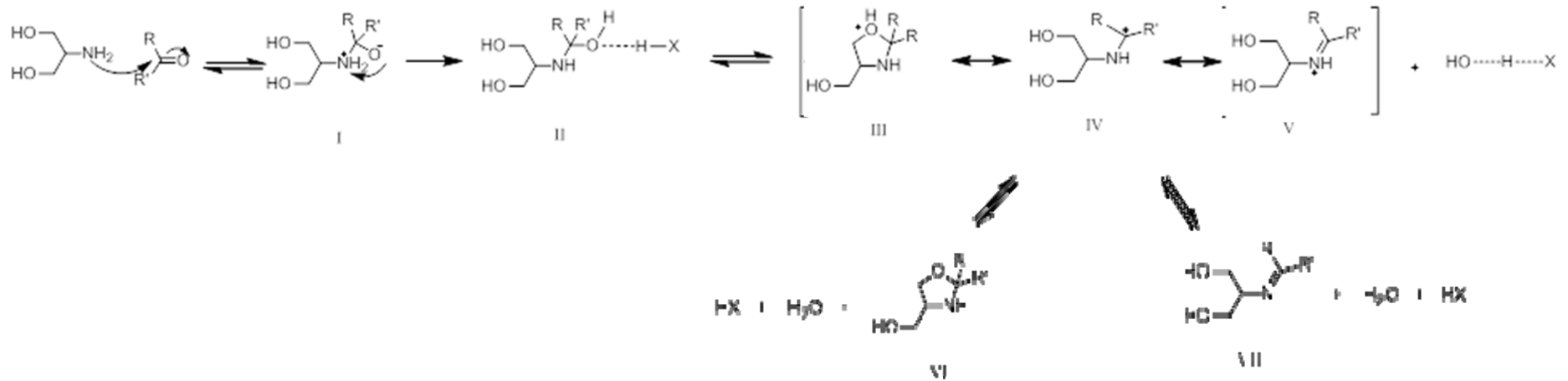
Proton abstraction. Formation of an imine



H—X = General or specific acid cat.

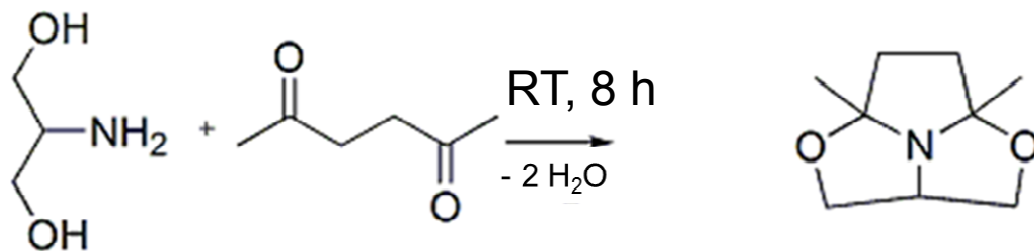
Reaction of serinol with carbonyl compounds – Hypothesis of a mechanism

Proton abstraction. Formation of an oxazolidine



H—X = General or specific acid cat.

Reaction of serinol with dicarbonyl compound



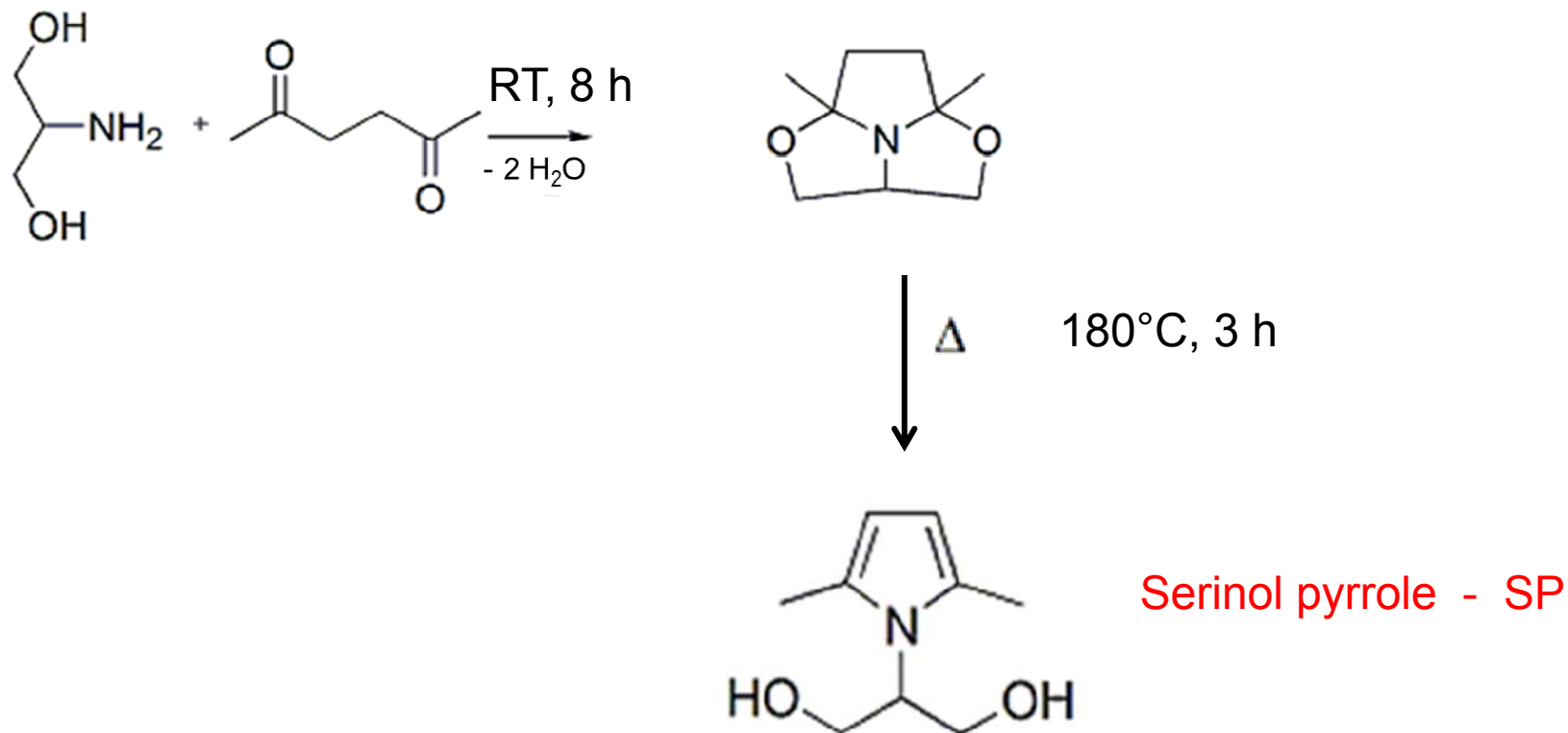
V. Barbera, A. Citterio, M. Galimberti, G. Leonardi, R. Sebastiano, S.U. Shisodia, A.M. Valerio *WO 2015 189411 A1*

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

Reaction of serinol with dicarbonyl compound



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

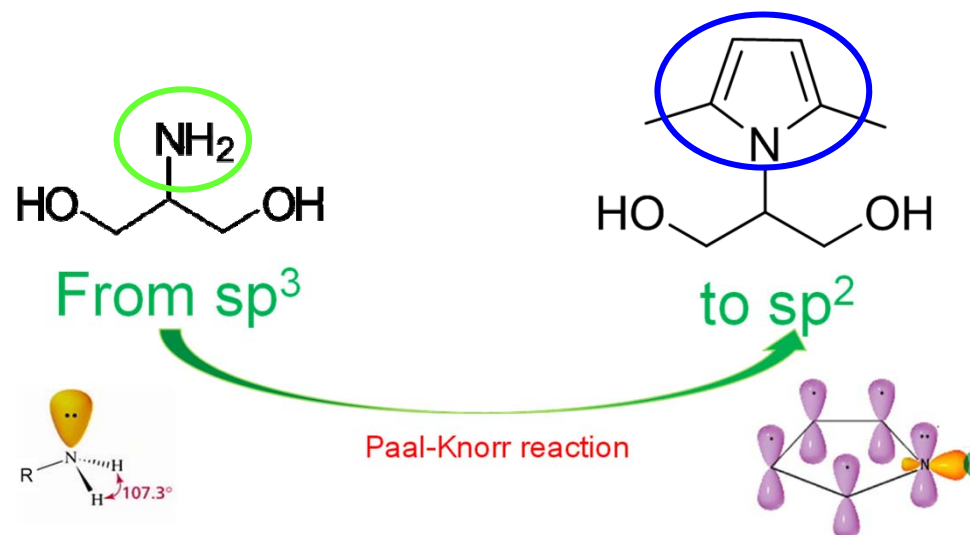
V. Barbera, A. Citterio, M. Galimberti, G. Leonardi, R. Sebastiano, S.U. Shisodia, A.M. Valerio *WO 2015 189411 A1*

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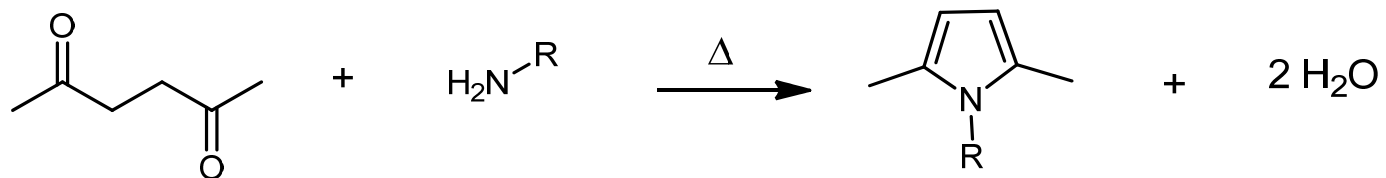
V. Barbera, S. Musto, A. Citterio, L. Conzatti, M. Galimberti, *eXPRESS Polymer Letters* 2016, 10 (7) 548–558

Neat synthesis of Serinol pyrrole

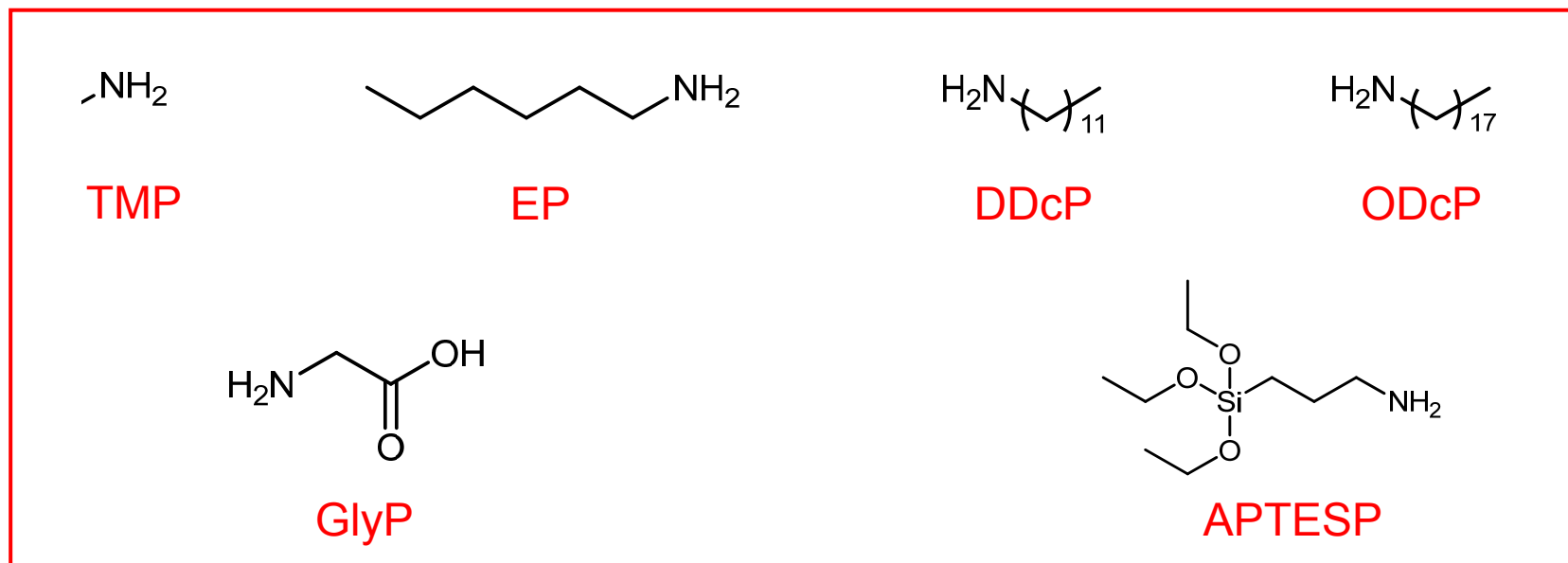
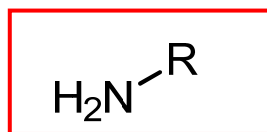
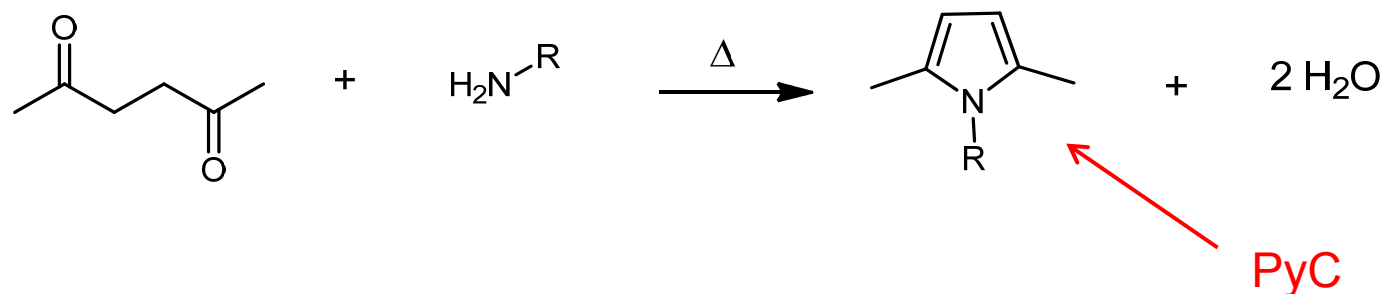


- Yield: at least 96%
- Atom efficiency: 85%
- Easy procedure
- No solvent
- By product: H_2O

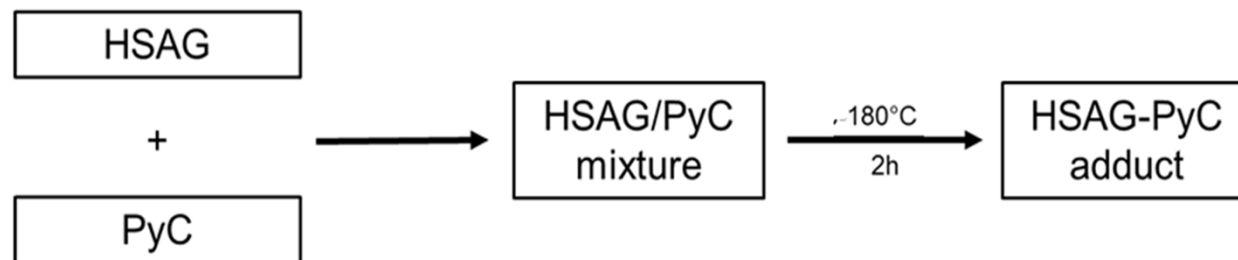
Pyrrole compounds (PyC) from neat Paal Knorr reaction



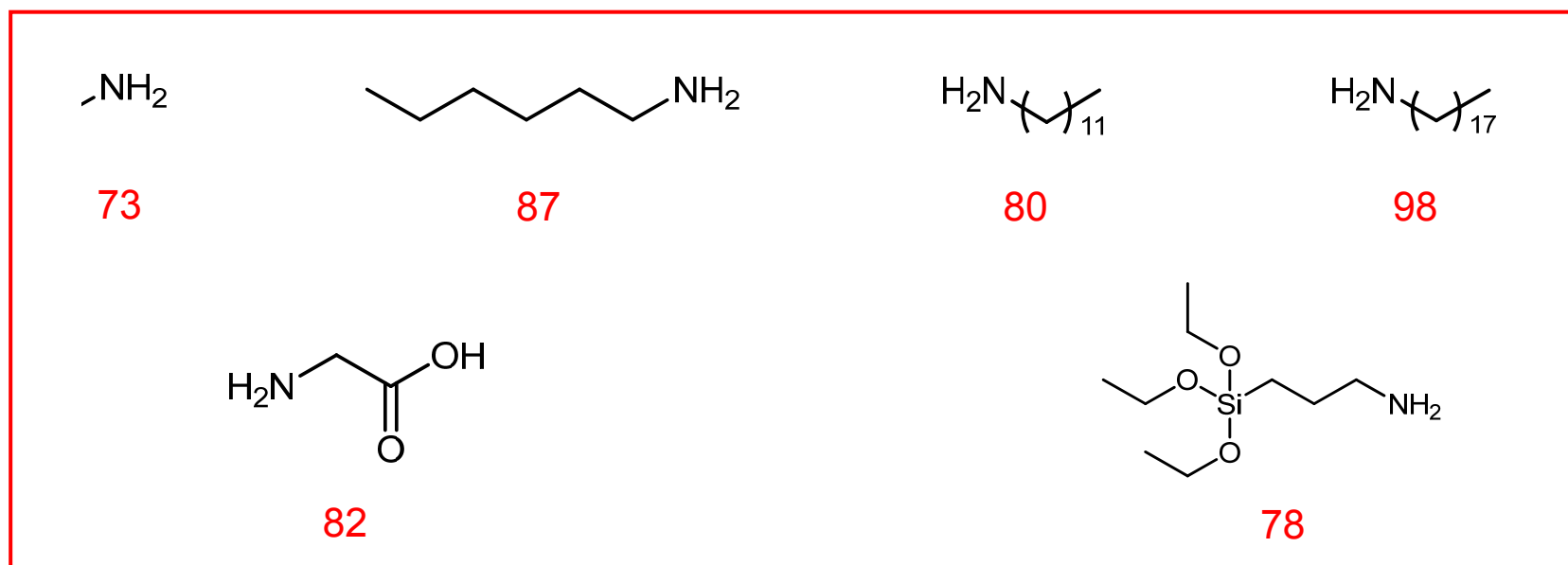
Pyrrole compounds (PyC) from neat Paal Knorr reaction

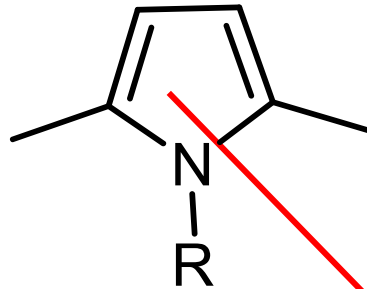


HSAG / PyC adducts



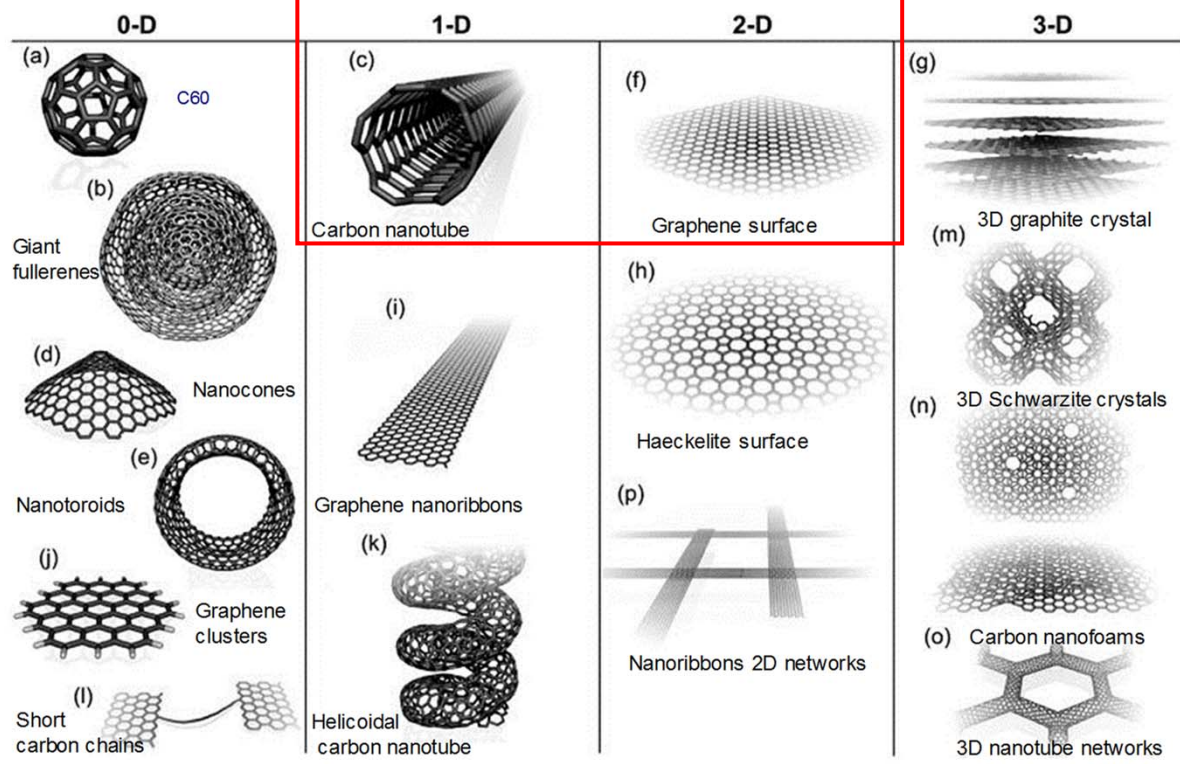
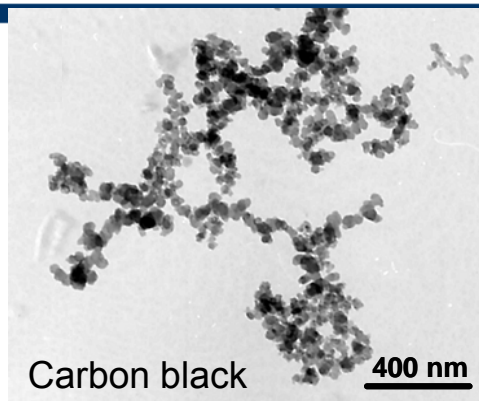
Functionalization Yield %





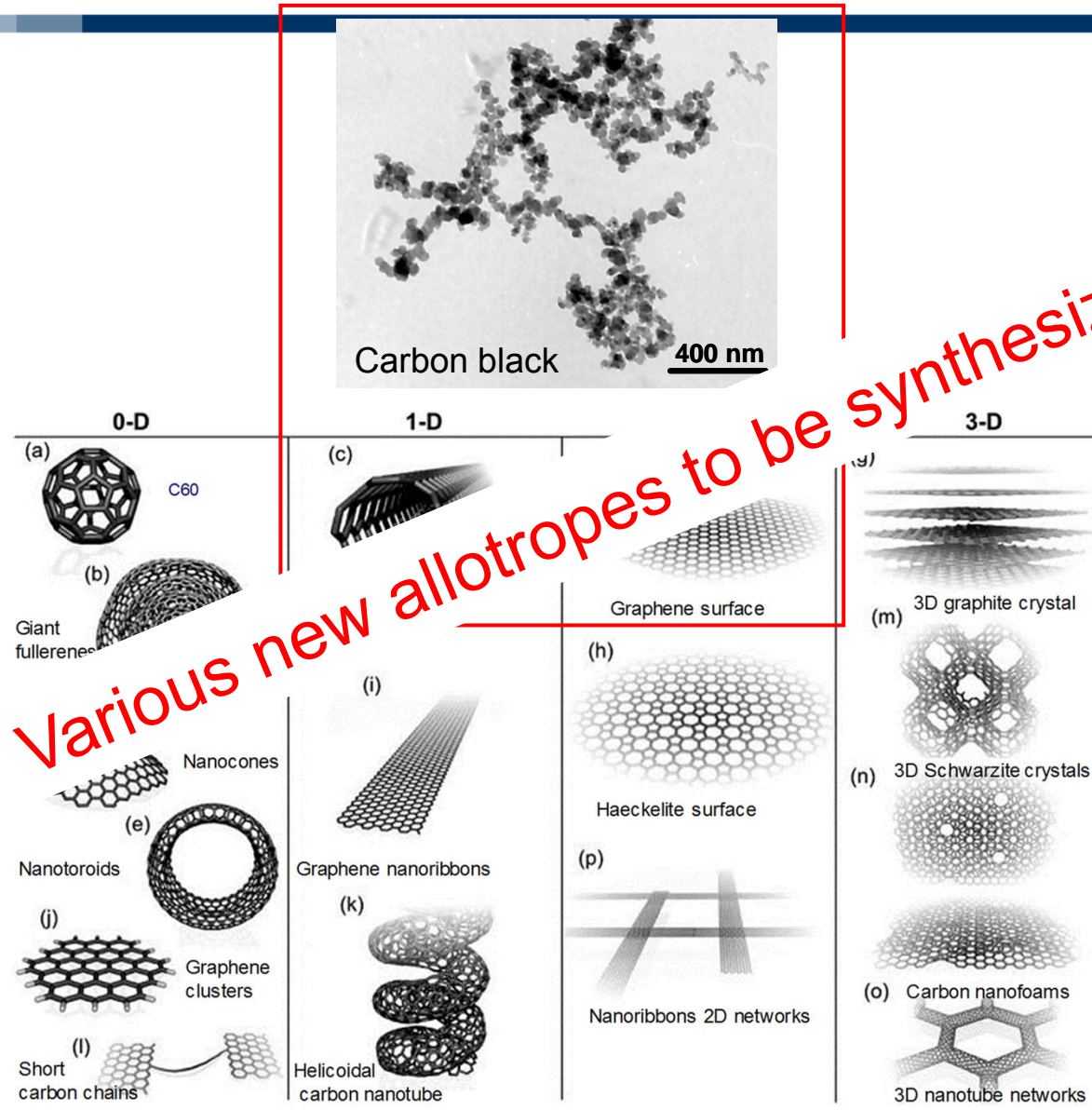
Functionalization
of sp^2 carbon allotropes (CA)

sp² Carbon allotropes (CA)



M. Terrones, et al. *Nano Today* 5 (4) (2010) 351e372.

sp² Carbon allotropes (CA)

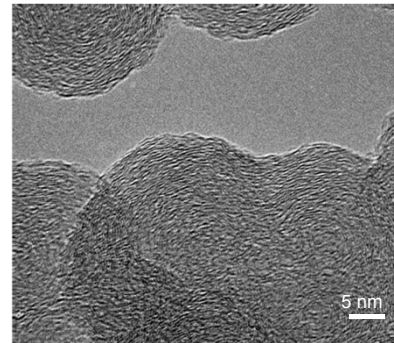
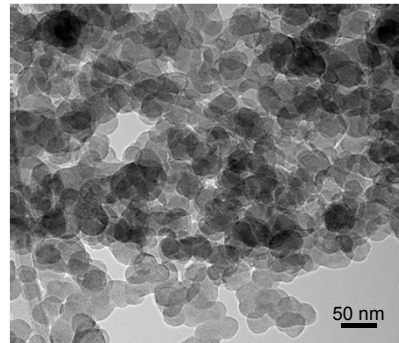


Carbon allotropes

Carbon black N326

CB

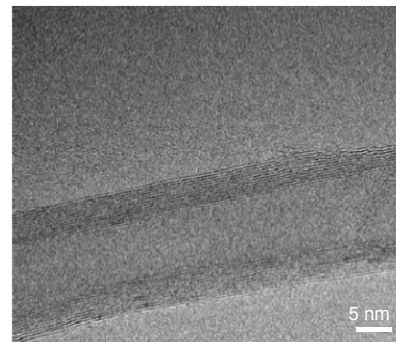
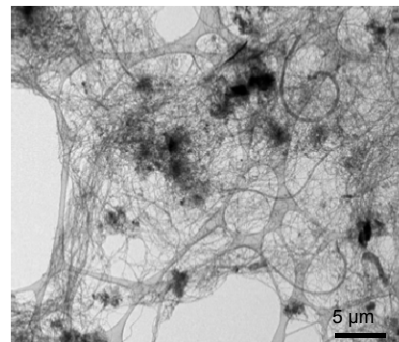
Cabot



Multi walled
Carbon Nanotubes

CNT

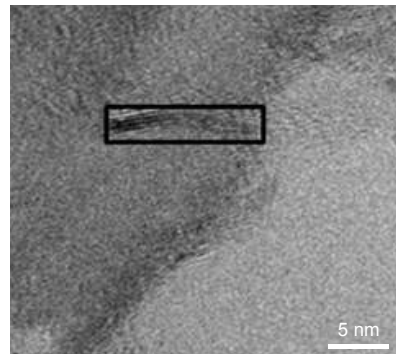
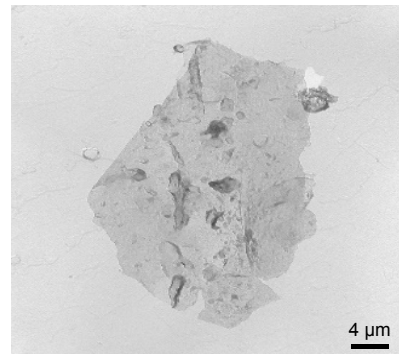
Nanocyl 7000



High surface area
Nanographite

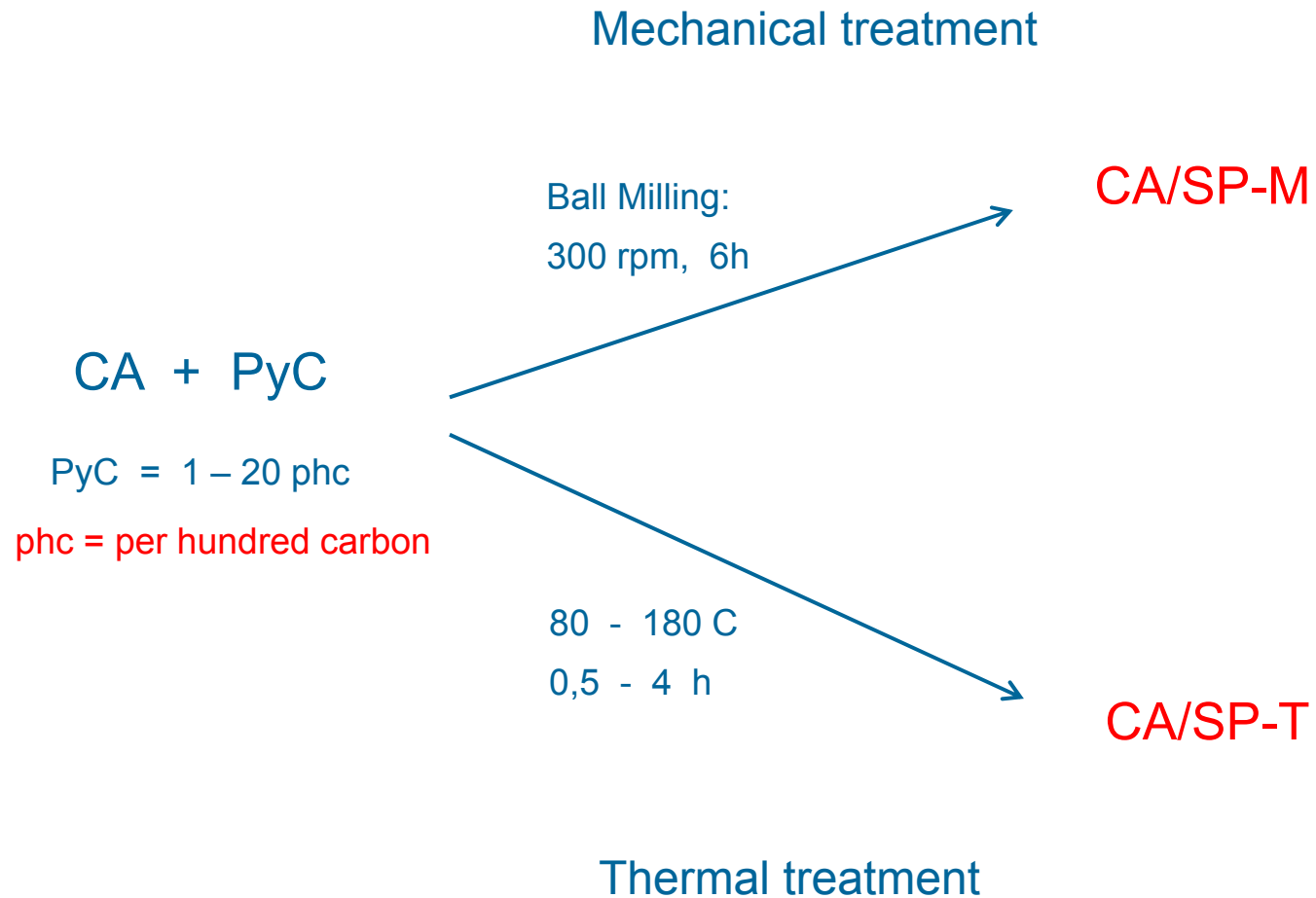
HSAG

Asbury



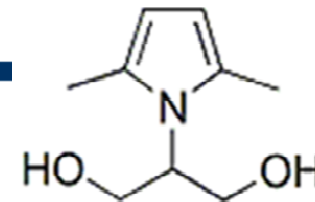
High-resolution
transmission electron microscopy
(HR-TEM)

CA-SP Adducts - Preparation



Galimberti, M., Barbera, V., Guerra, S., Conzatti, L., Castiglioni, C., Brambilla, L., A. Serafini, *RSC Advances*, 5(99), (2015) 81142-81152
Galimberti, M., Barbera, V., Sebastiano, R., Valerio A.M. Leonardi, G., Citterio, *EP 3209604 B1 - US 2017 0275169 A1*
Galimberti M., Barbera V., Guerra S., Bernardi A., *Rubber Chemistry and Technology*, 2017, 90(2), 285-307.

CA-SP Adducts - Yield of functionalization*



Thermal treatment

SP = 5 phc; 150°C, 2 h

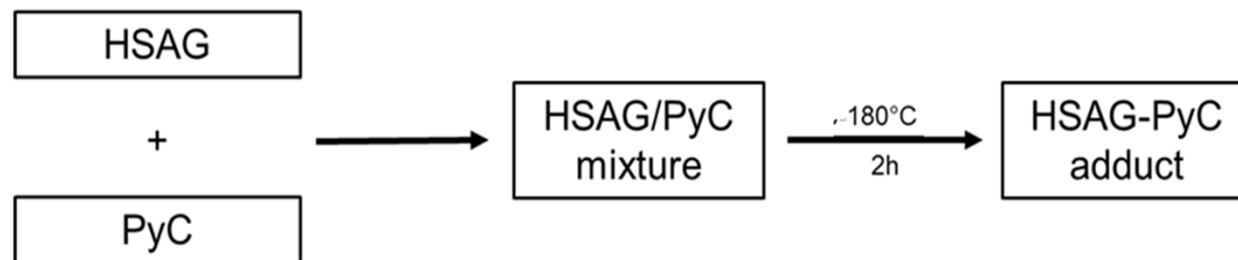
	HSAG	CB	MWCNT
BET Surface area: [m ² /g]	300	77	275
Functionalization Yield(%)*:	96	82	92

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

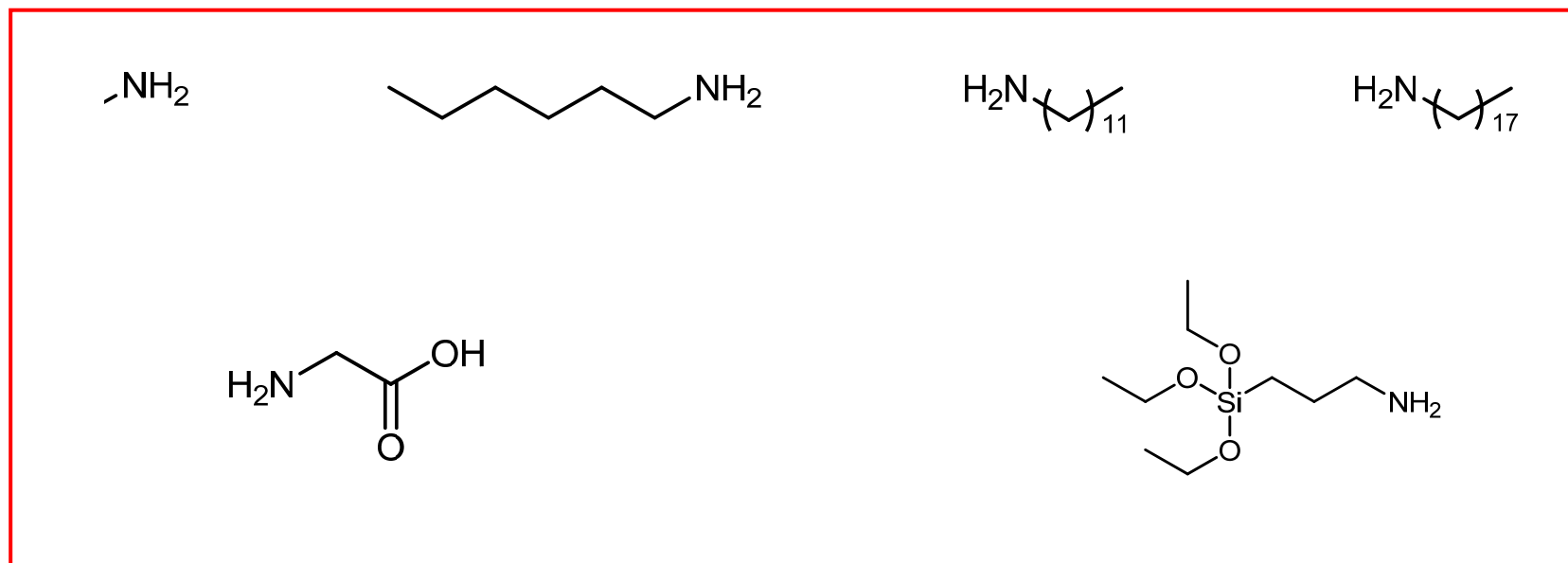
from TGA

HSAG from Asbury, CB from Cabot, CNT from Nanocyl

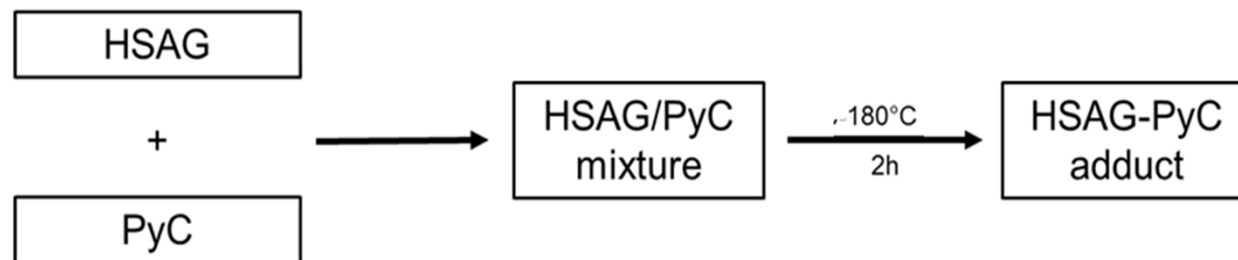
HSAG / PyC adducts



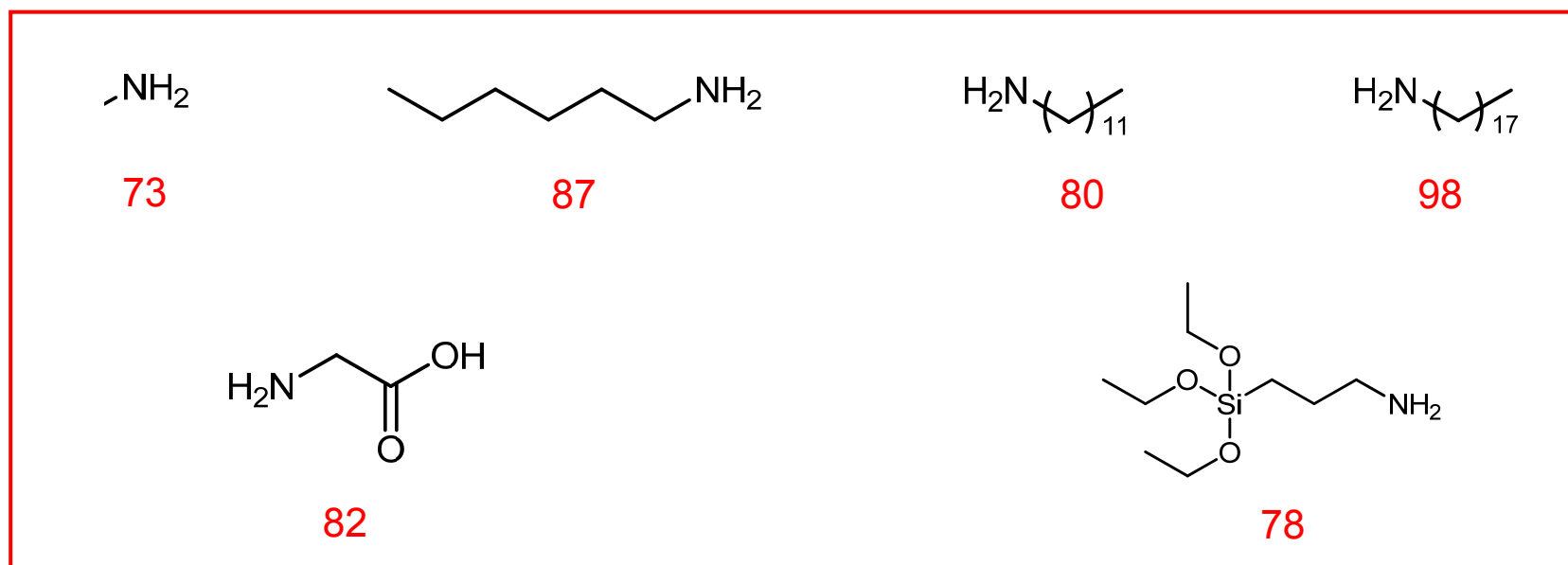
Functionalization Yield %



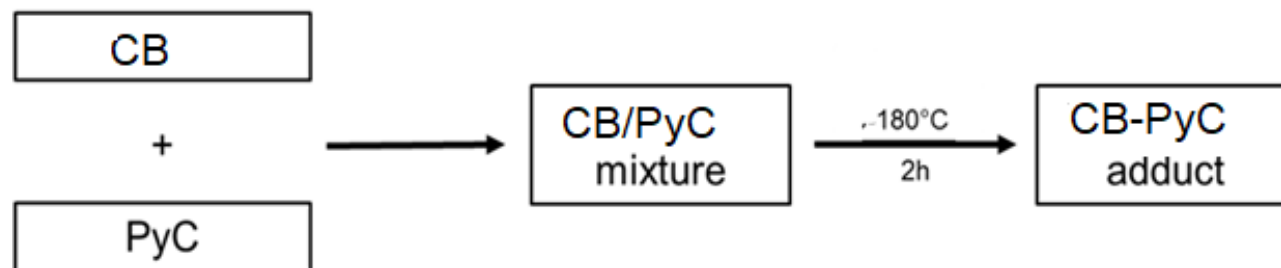
HSAG / PyC adducts



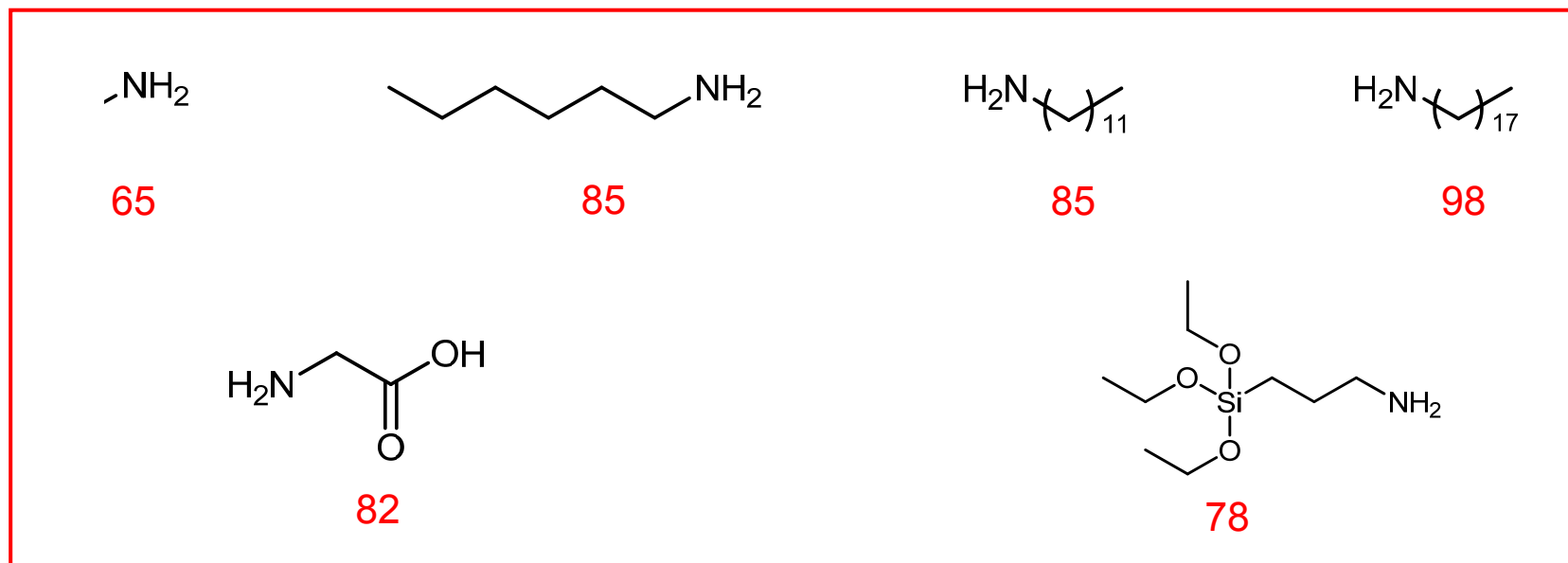
Functionalization Yield %



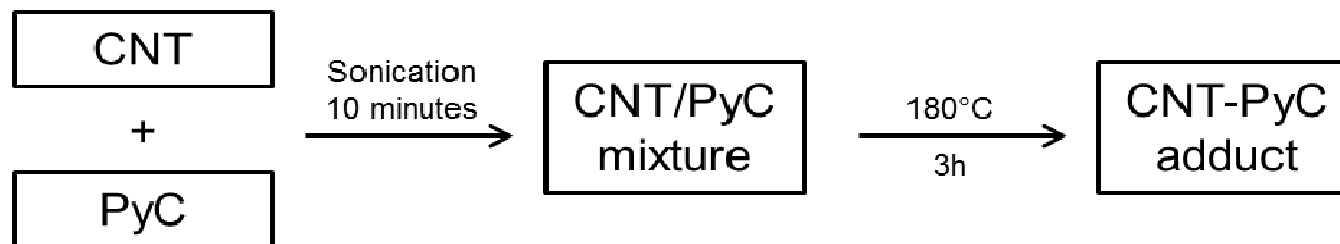
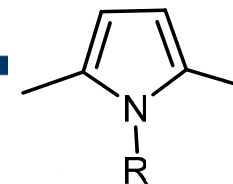
CB / PyC adducts



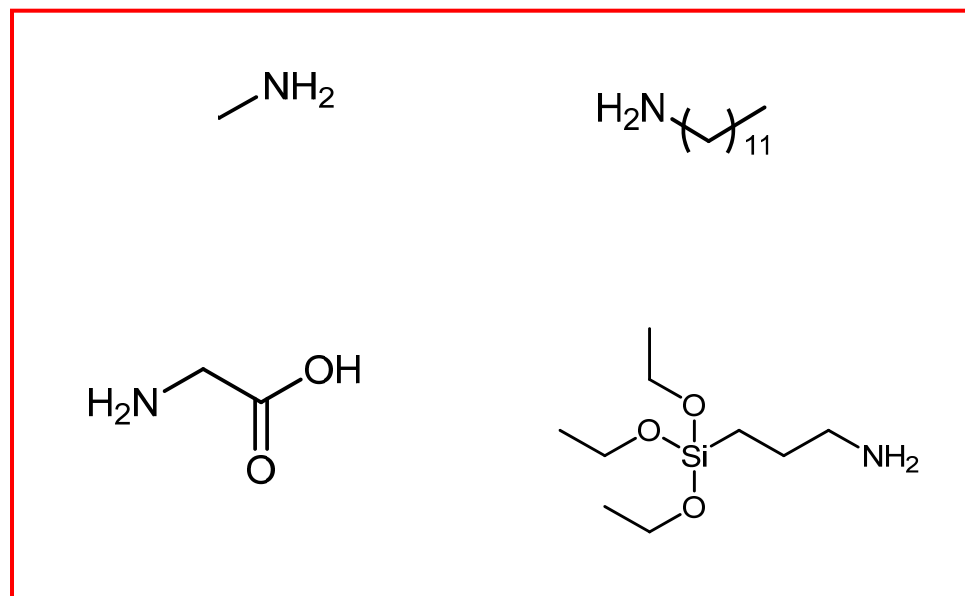
Functionalization Yield %



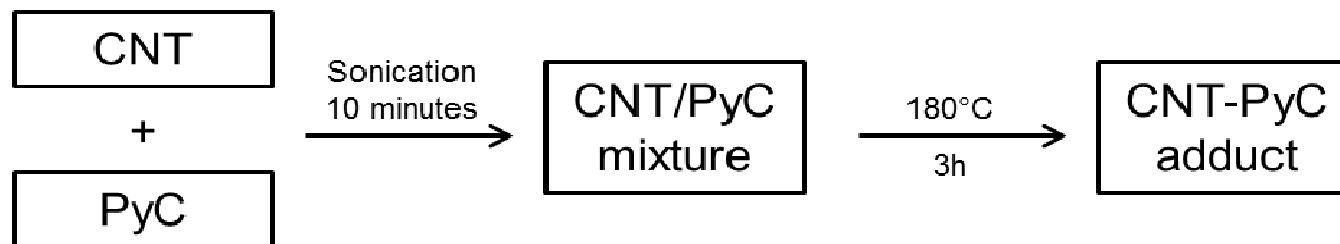
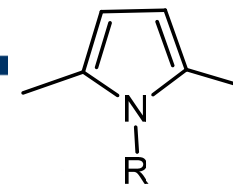
CNT / PyC adducts



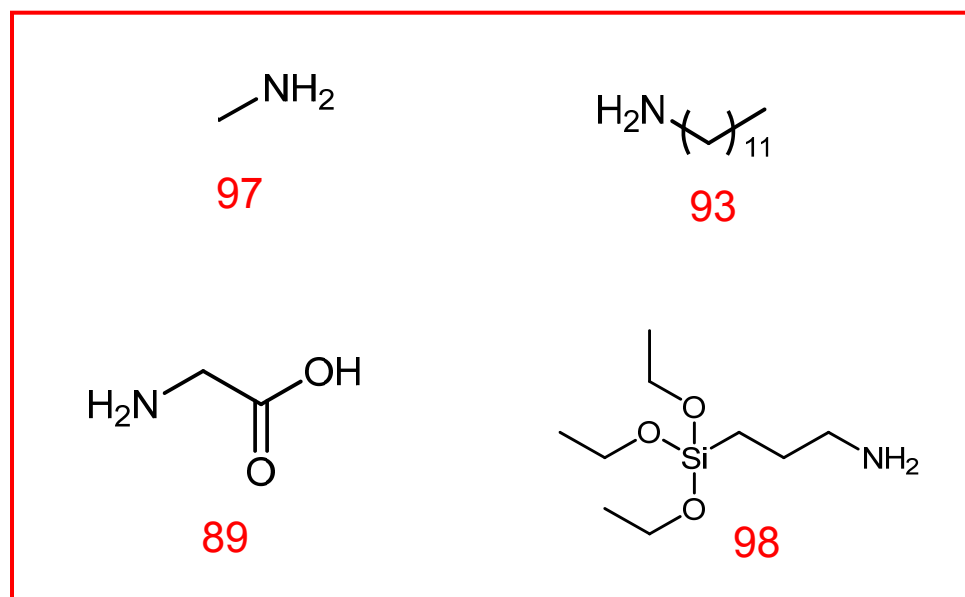
Functionalization Yield %



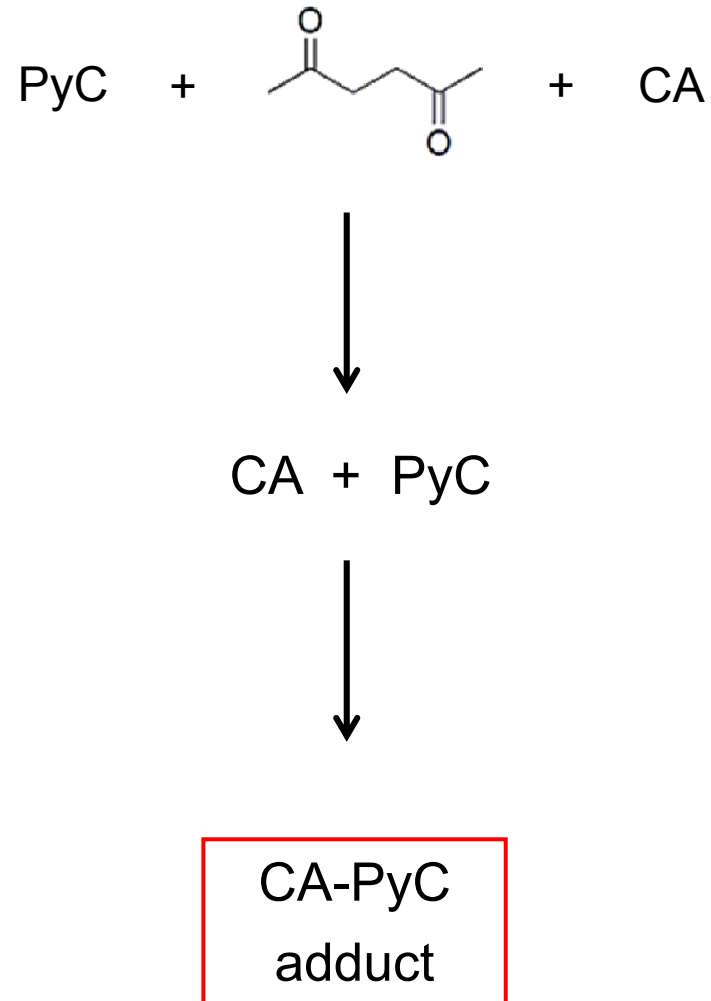
CNT / PyC adducts



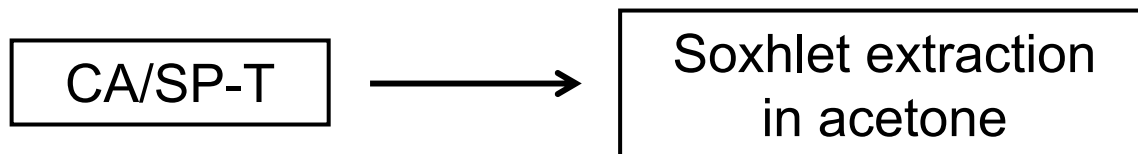
Functionalization Yield %



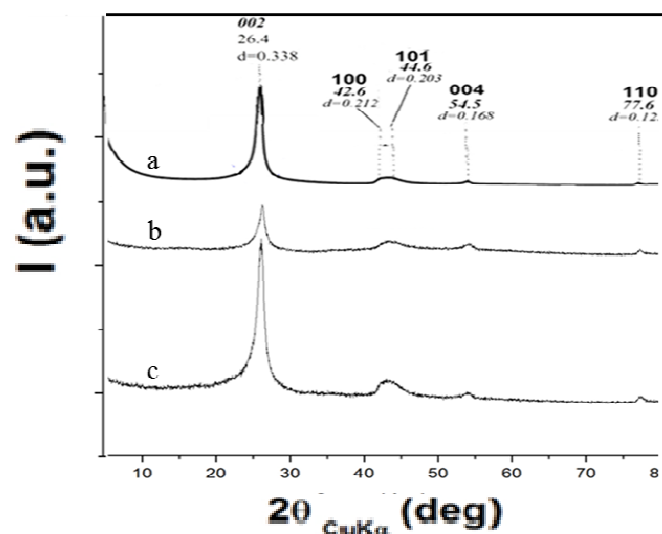
CA-PyC Adducts - PyC formed *in situ*



Adducts of SP with high surface area graphite (HSAG)



WAXD

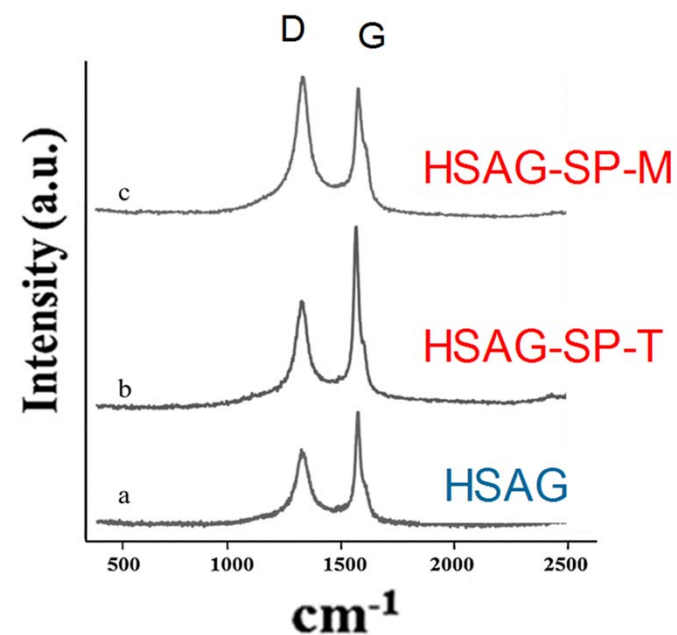


HSAG

HSAG-SP-M

HSAG-SP-T

Raman



HSAG-SP-M

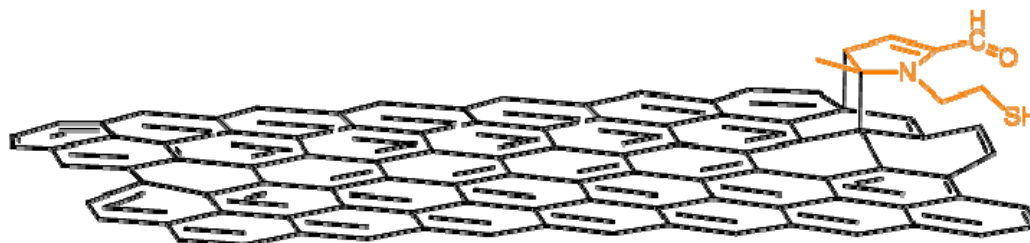
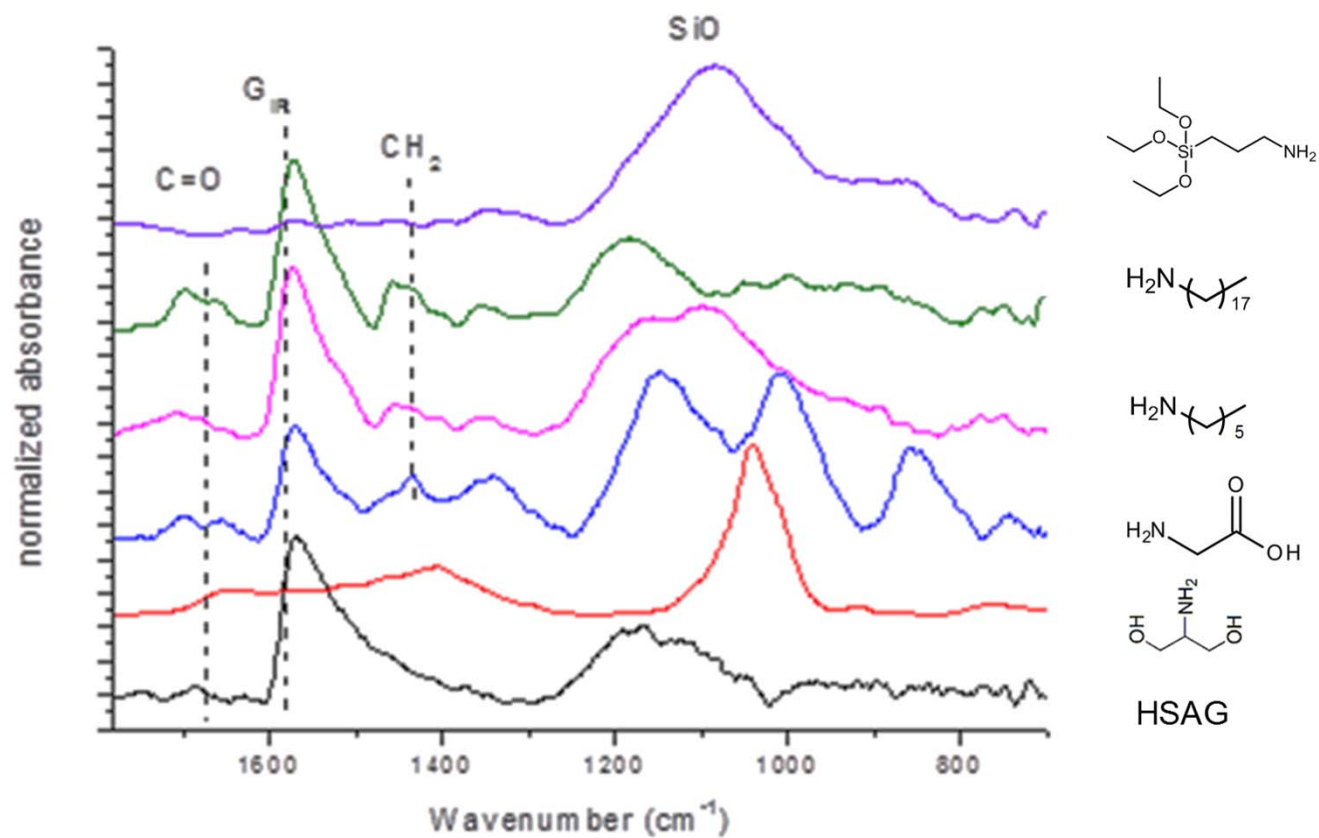
HSAG-SP-T

HSAG

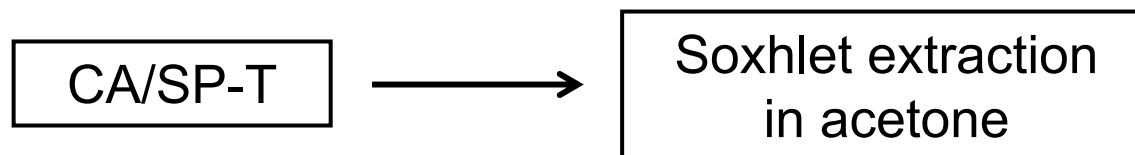
Galimberti, M., Barbera, V., Guerra, S., Conzatti, L., Castiglioni, C., Brambilla, L., A. Serafini, *RSC Advances*, 5(99), (2015) 81142-81152

Galimberti M., Barbera V., Guerra S., Bernardi A., *Rubber Chemistry and Technology*, 2017, 90(2), 285-307.

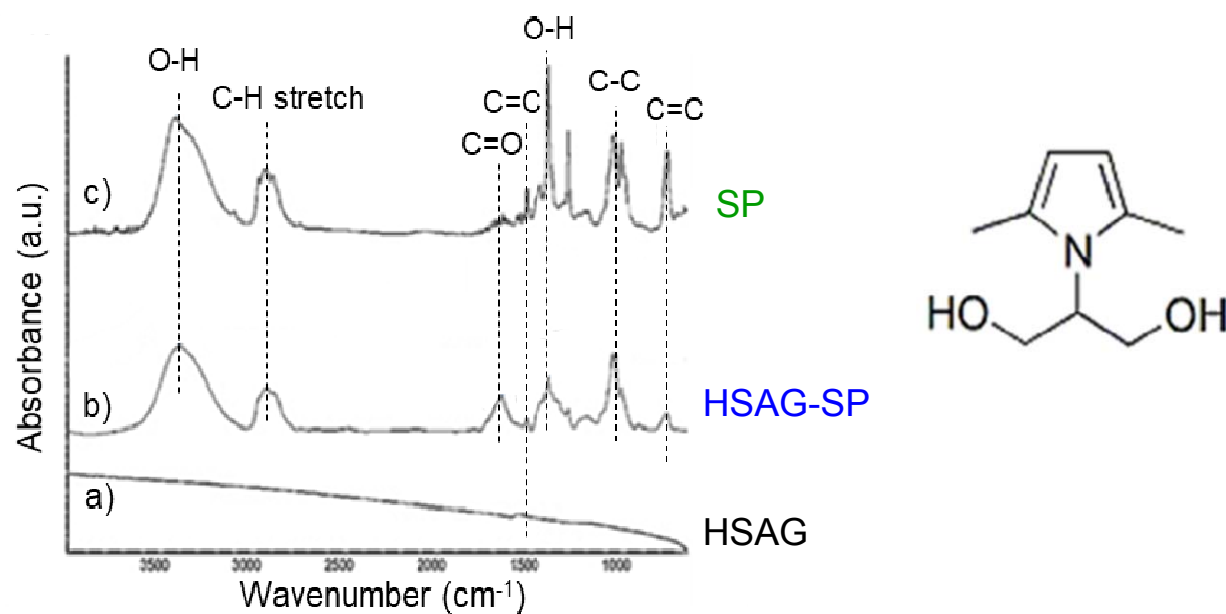
Adducts of PyC with high surface area graphite (HSAG)



Adducts of SP with high surface area graphite (HSAG)



FT-IR

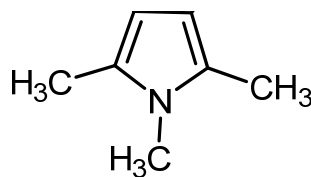


Galimberti, M., Barbera, V., Guerra, S., Conzatti, L., Castiglioni, C., Brambilla, L., A. Serafini, *RSC Advances*, 5(99), (2015) 81142-81152

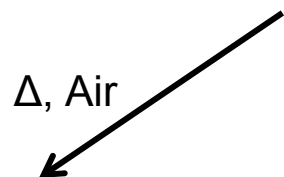
Galimberti M., Barbera V., Guerra S., Bernardi A., *Rubber Chemistry and Technology*, 2017, 90(2), 285-307.

Mechanism of the functionalization reaction

Investigation with a model compound

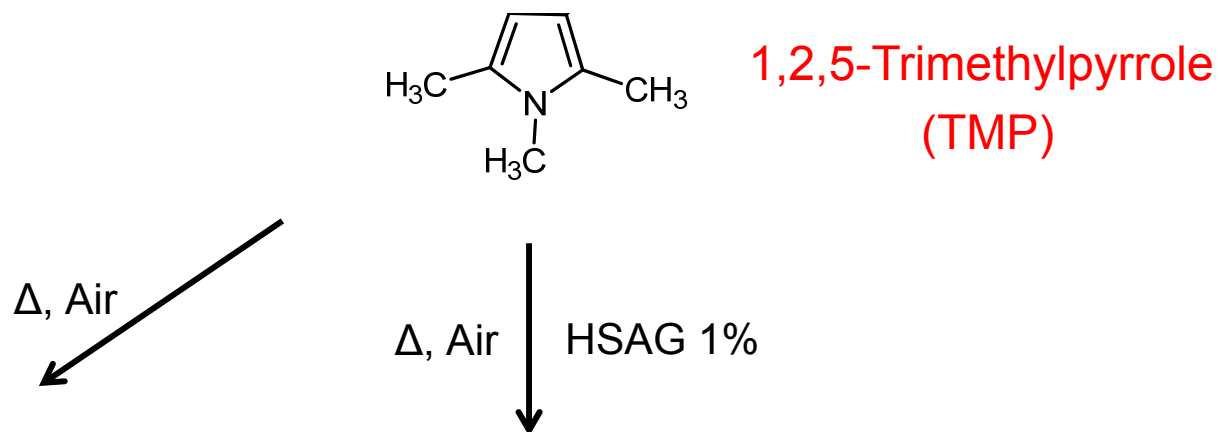


1,2,5-Trimethylpyrrole
(TMP)



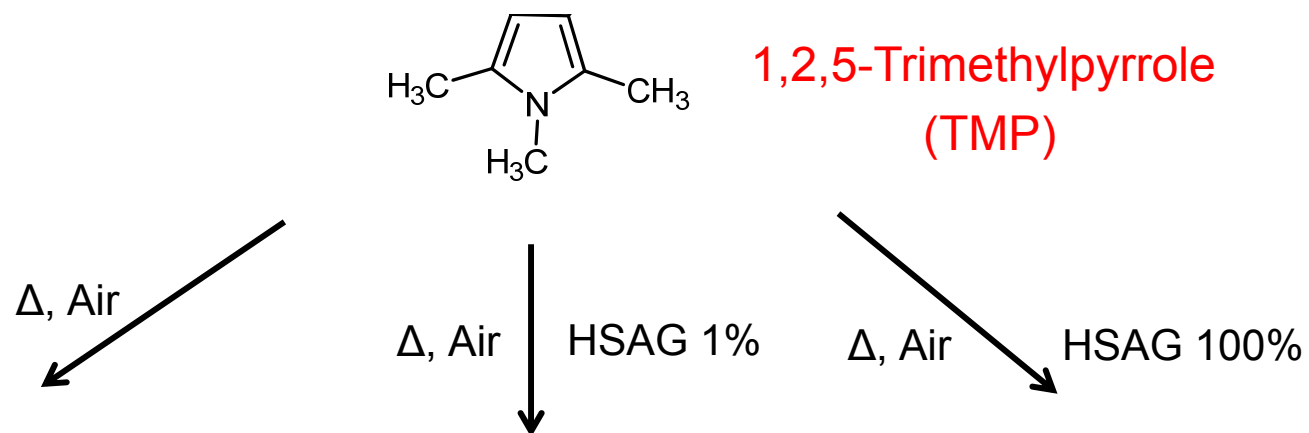
Mechanism of the functionalization reaction

Investigation with a model compound



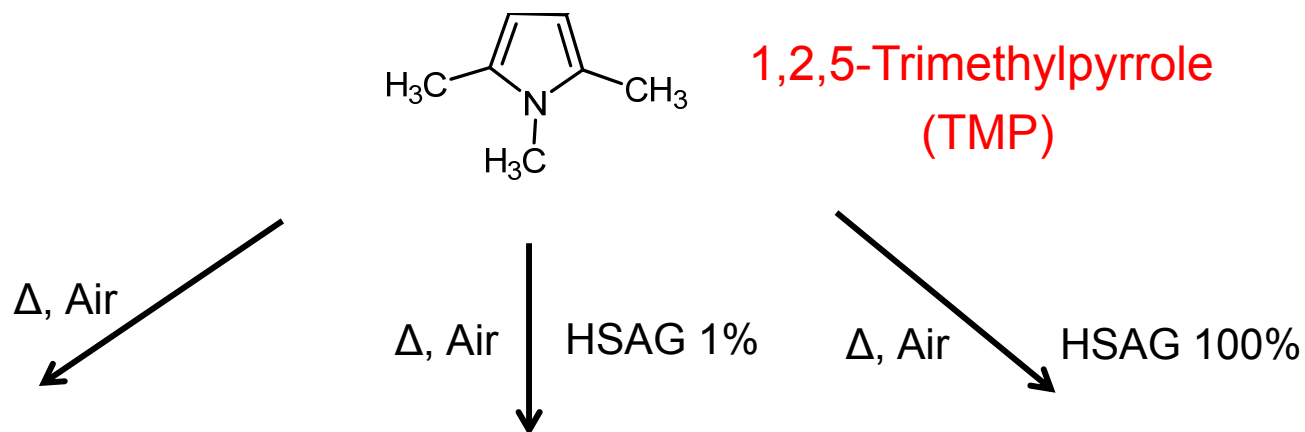
Mechanism of the functionalization reaction

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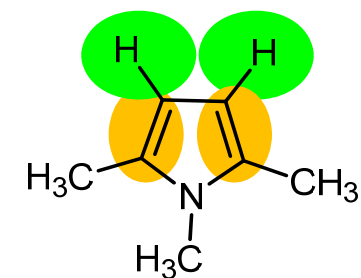
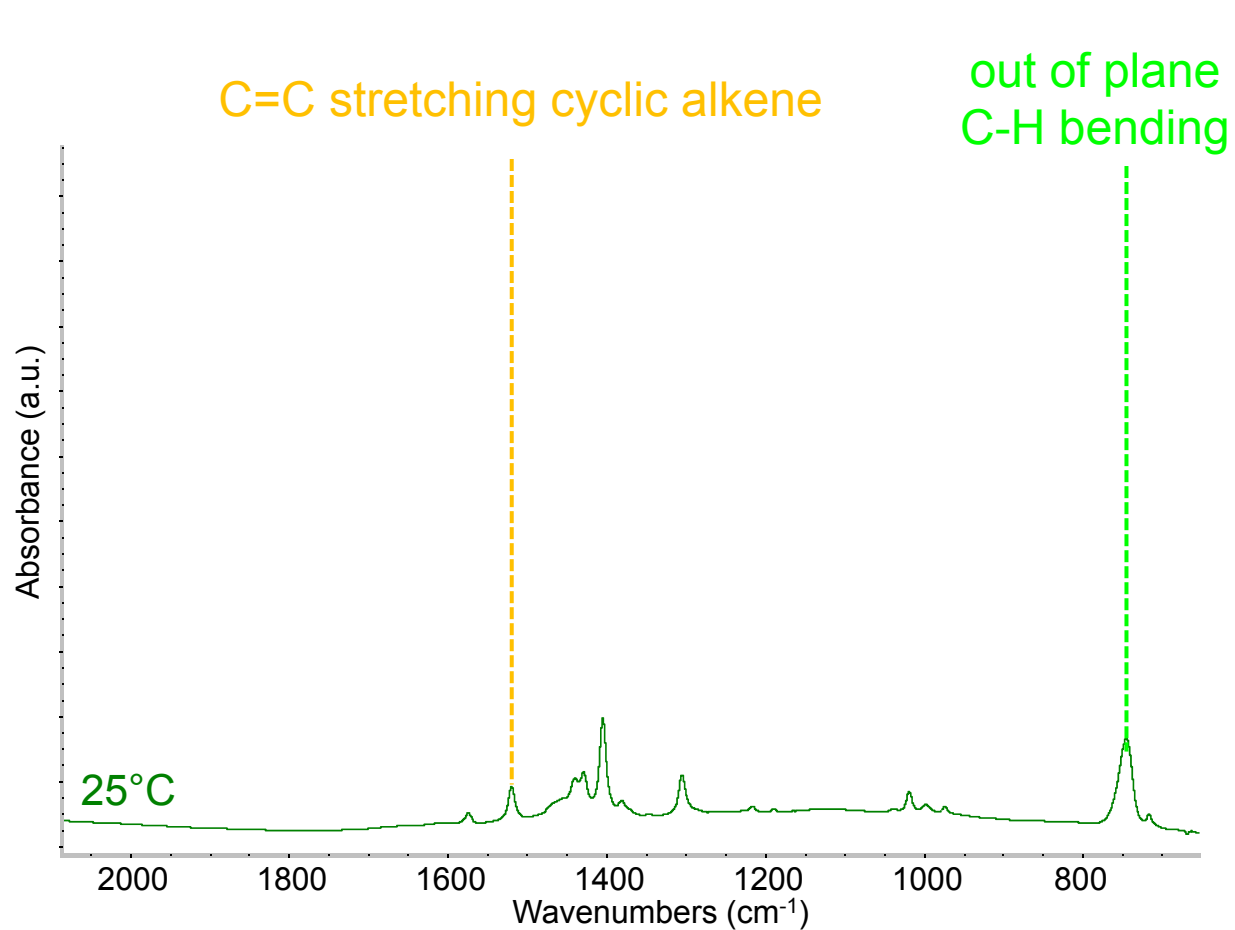
Mechanism of the functionalization reaction

Investigation with a model compound

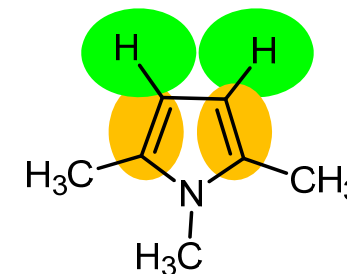
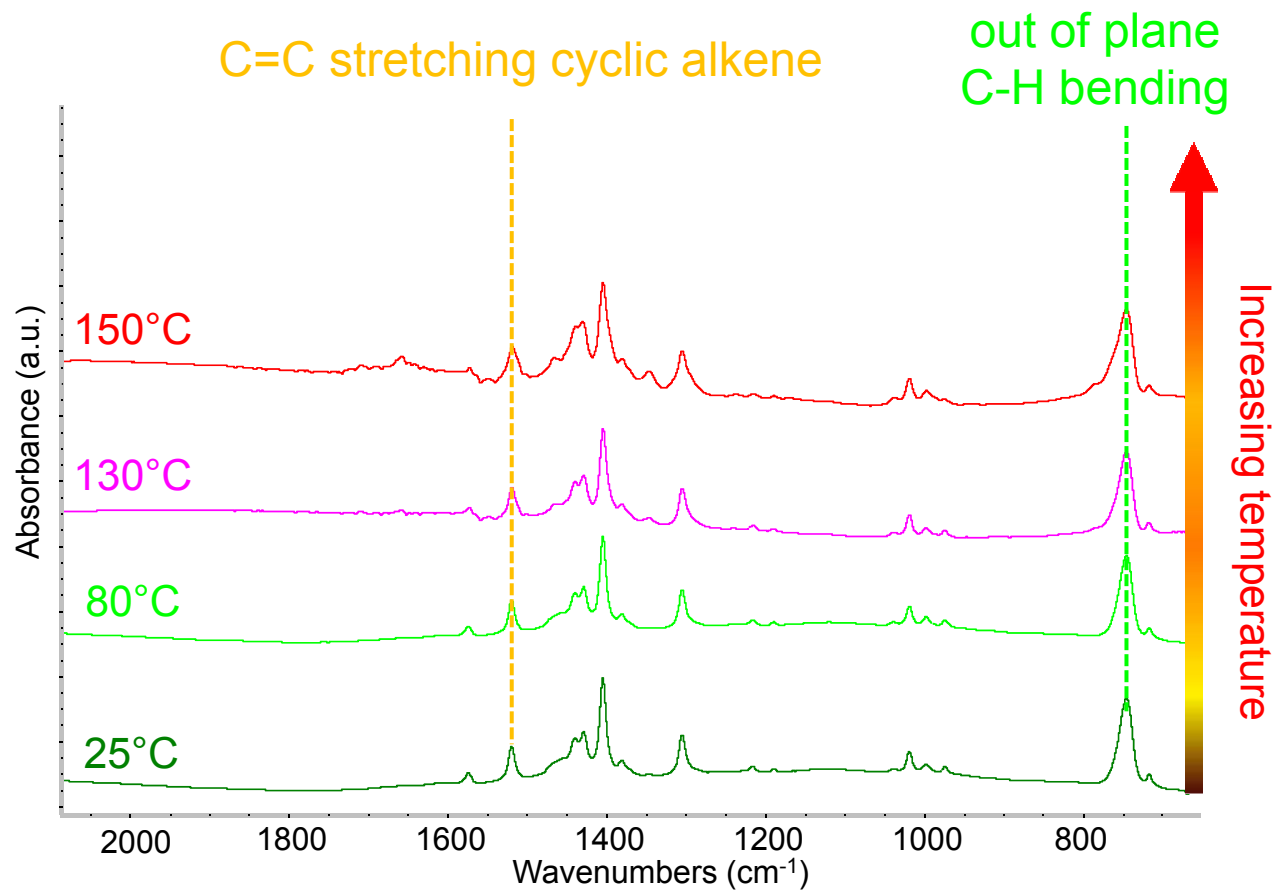
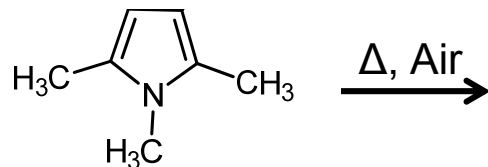


- ☞ Analysis of: liquids, HSAG/TMP adducts
- ☞ FT-IR, XPS and $^1\text{H-NMR}$ spectroscopies
- ☞ FT-IR spectra generation with Density Functional Theory (DFT) quantum chemical modelling

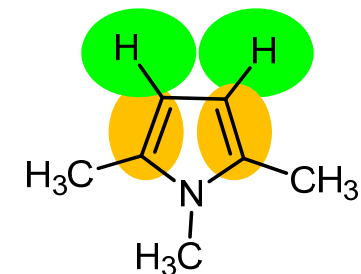
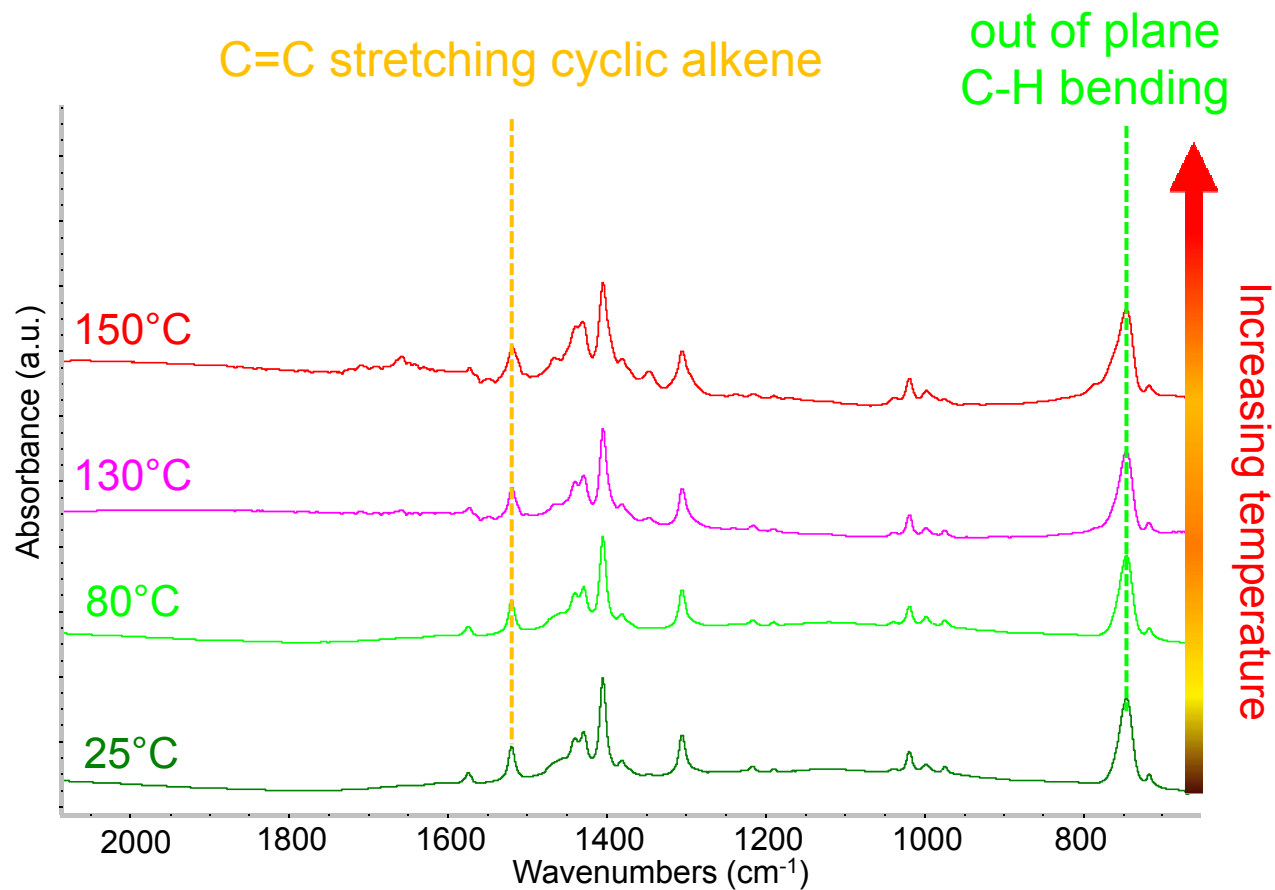
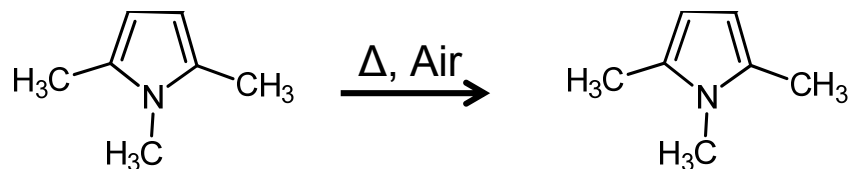
1,2,5-Trimethylpyrrole (TMP)



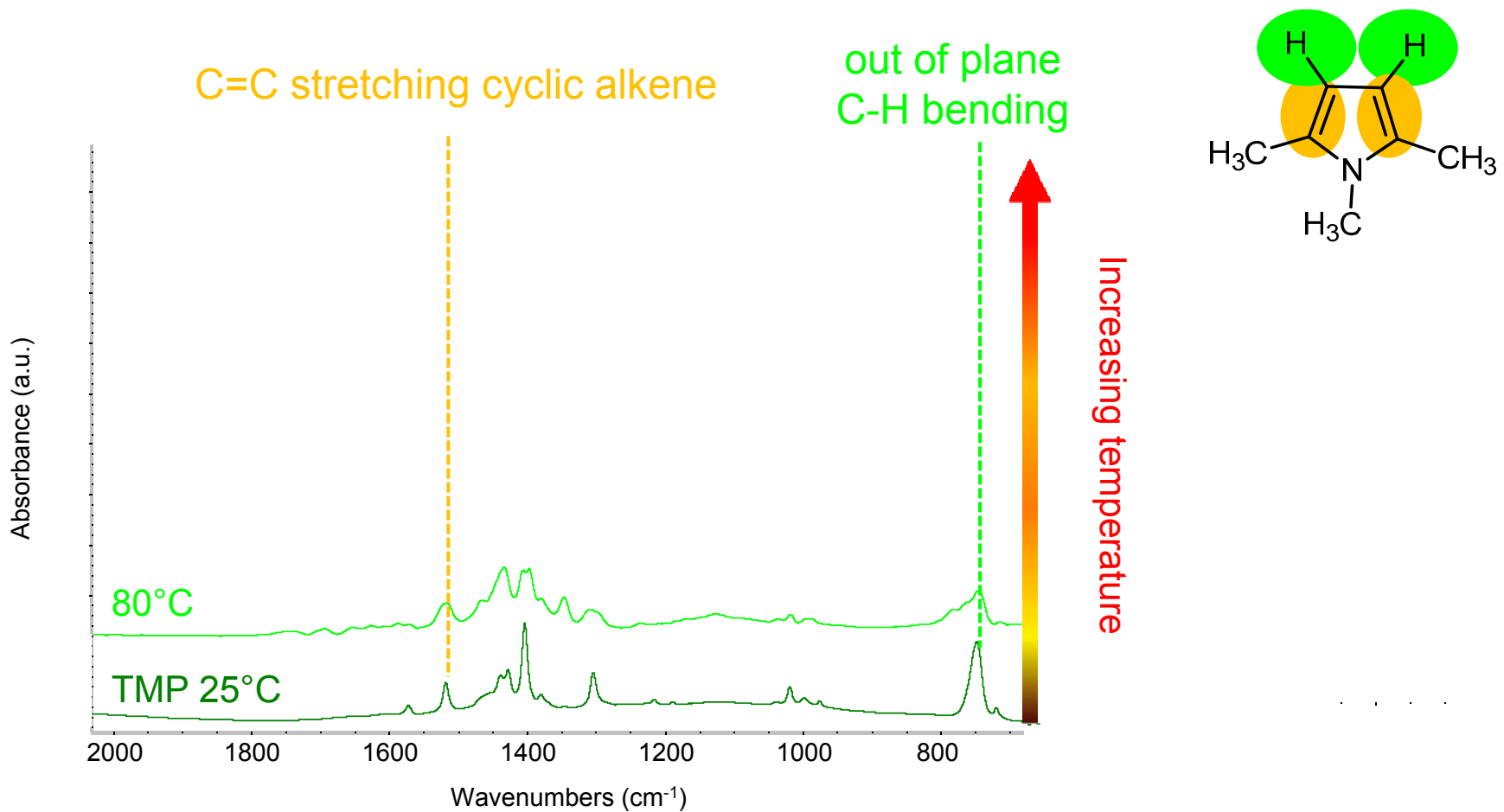
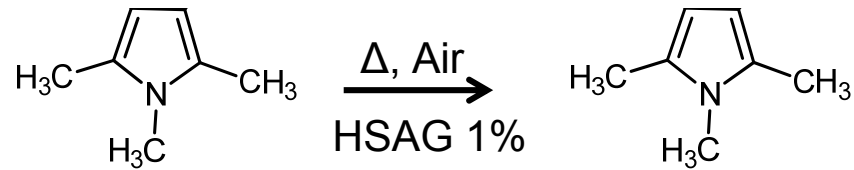
TMP + Air - From 25°C to 150°C



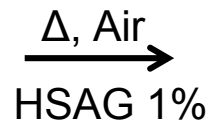
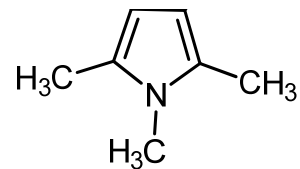
TMP + Air - From 25°C to 150°C



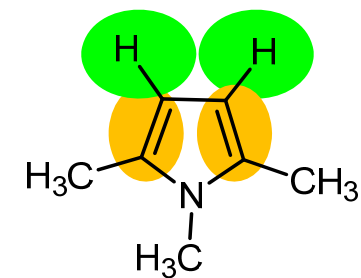
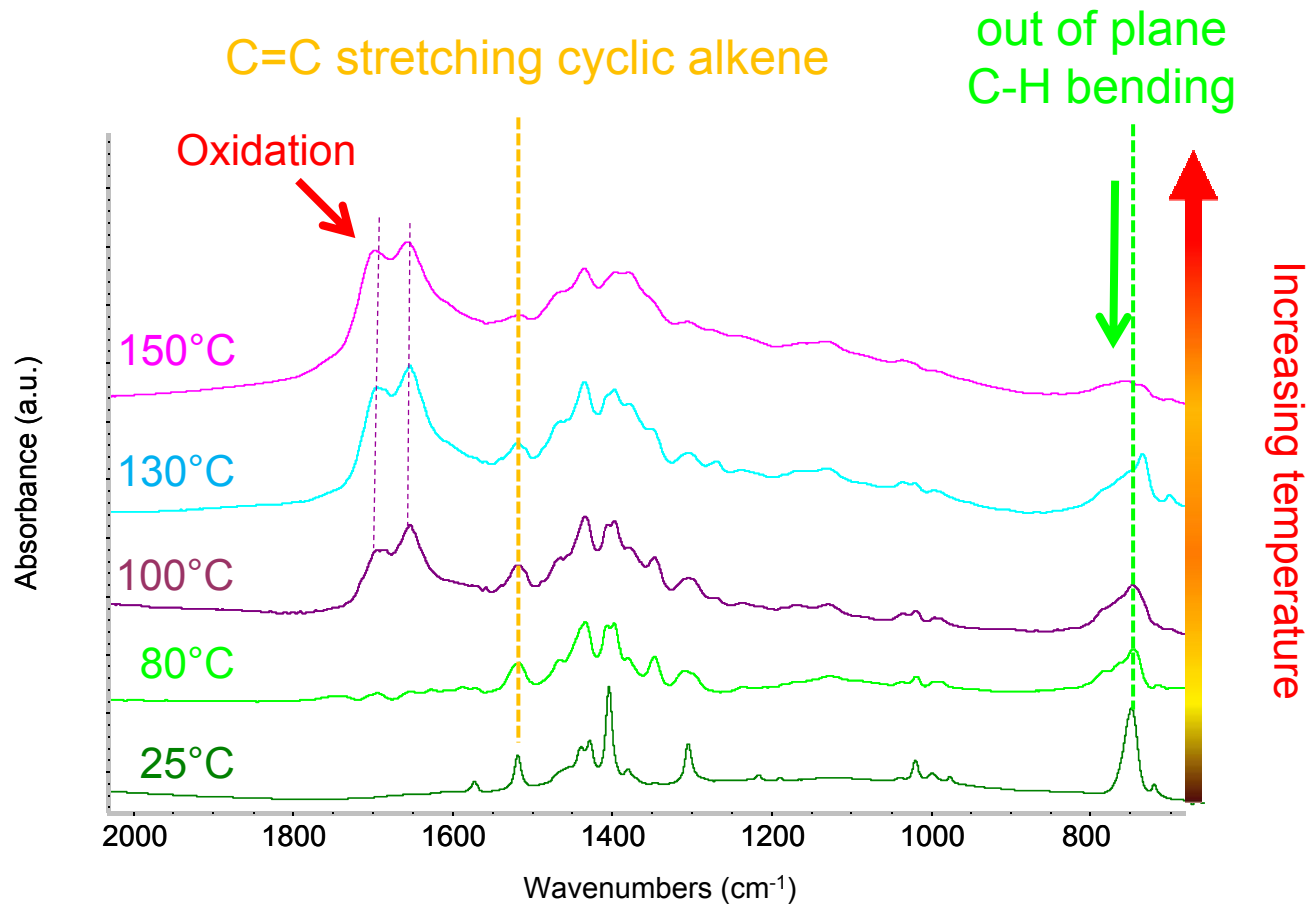
TMP + HSAG 1% / Air - From 25°C to 80°C - Solid product



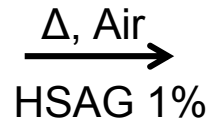
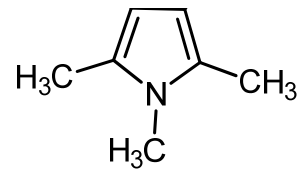
TMP + HSAG 1% / Air - from 100°C to 150°C - Solid product



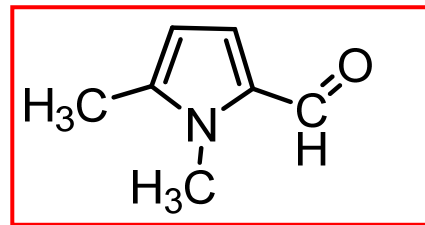
Oxidation products



TMP + HSAG 1% / Air - from 100°C to 150°C

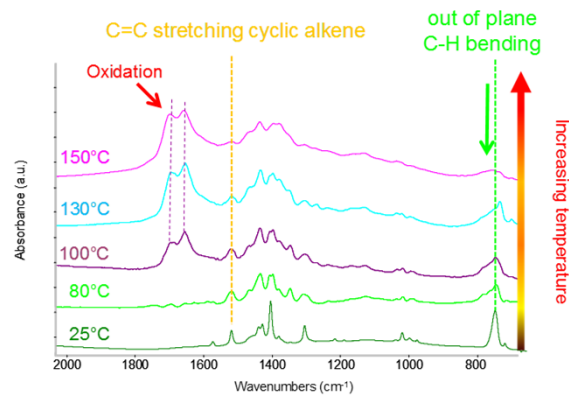


Oxidation products

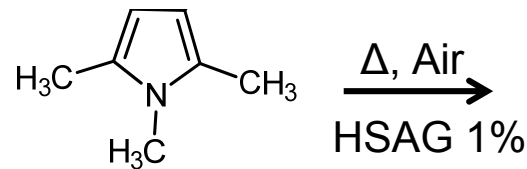


1-methyl-1*H*-pyrrole-2-carbaldehyde

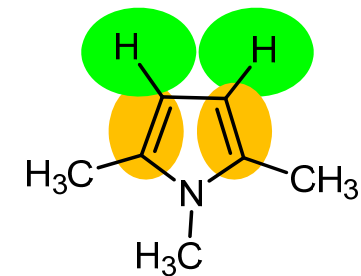
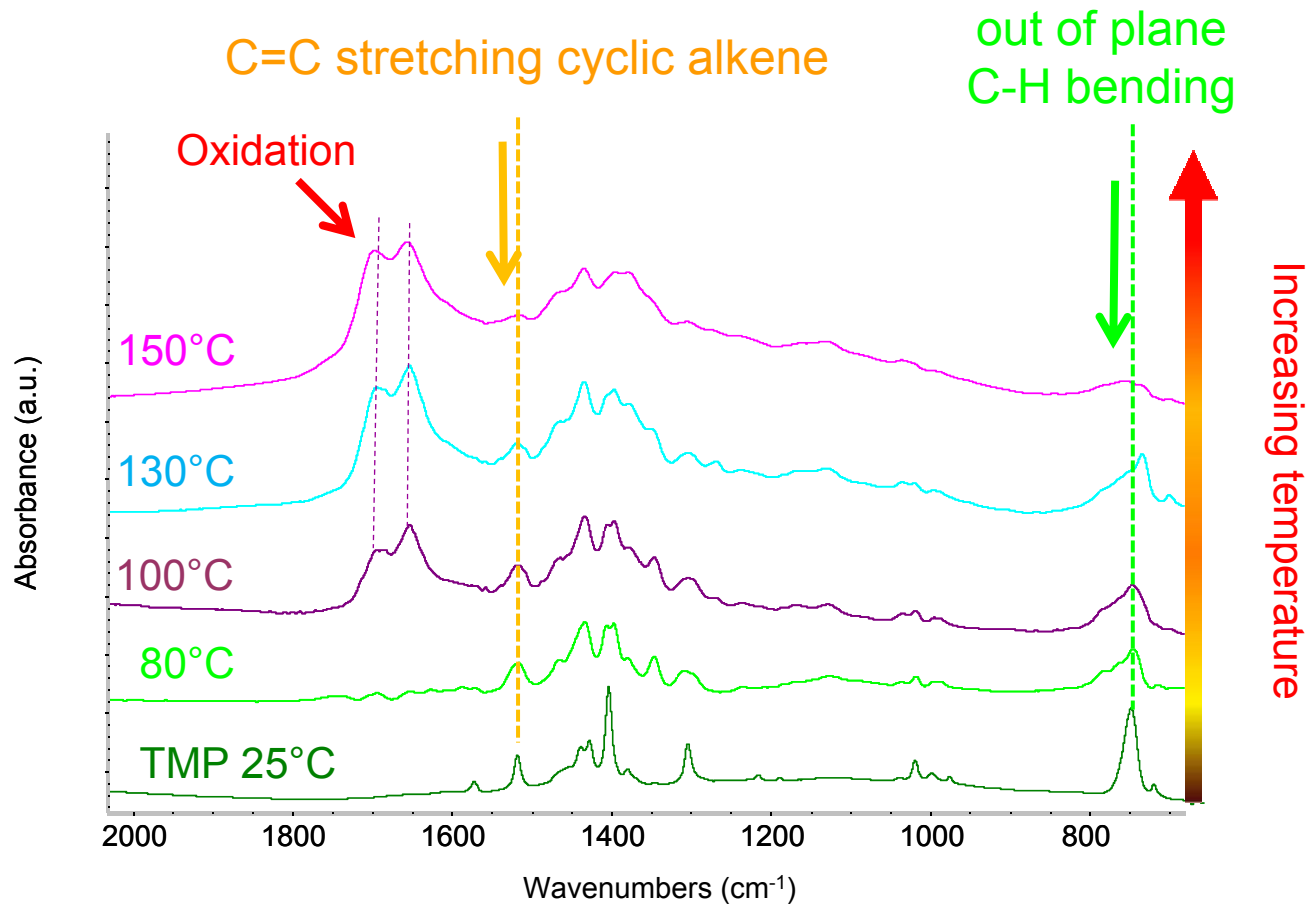
Isolated and characterized



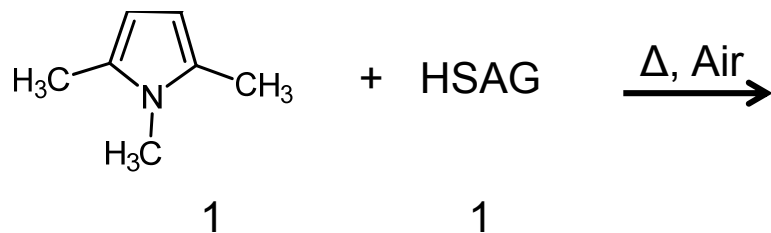
TMP + HSAG 1% - @ 150°C - Solid product



Reaction products of
intra-annular double bonds

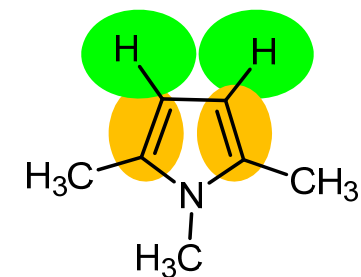
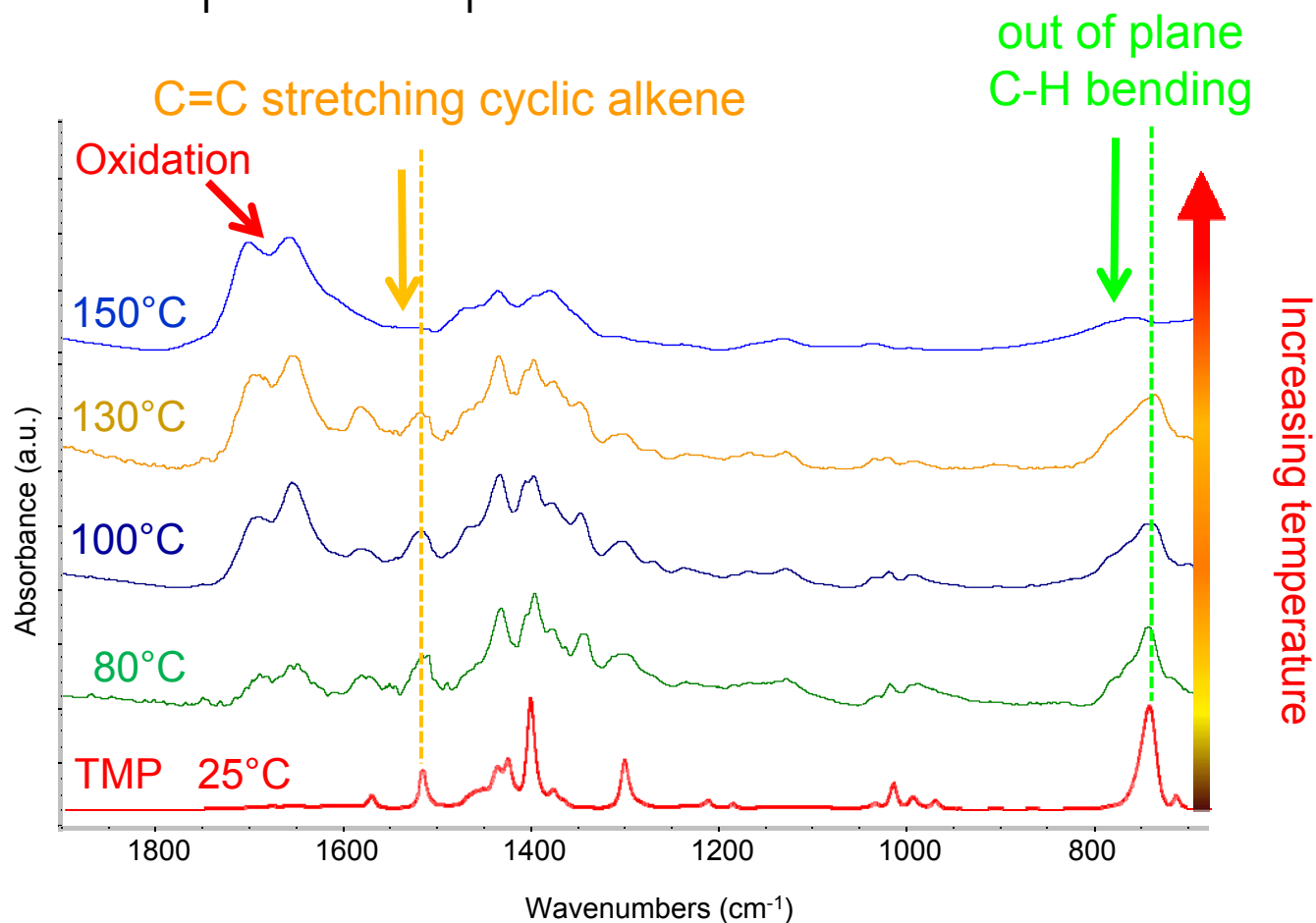


TMP + HSAG 1/1 - from 25 to 150°C - Solid product



Oxidation products

Reaction products of intra-annular double bonds



TMP + HSAG 1/1 - from 80 to 180°C - Solid product

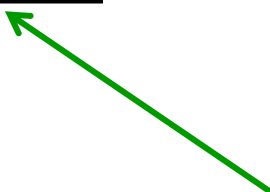
XPS

	C1s (at. %)	O1s (at. %)	N1s (at. %)
HSAG	95.8	4.2	0
HSAG/TMP 80°	81.8	10.8	7.4
HSAG/TMP 130°	76.6	15.9	7.5
HSAG/TMP 180°	87.9	6.5	5.6

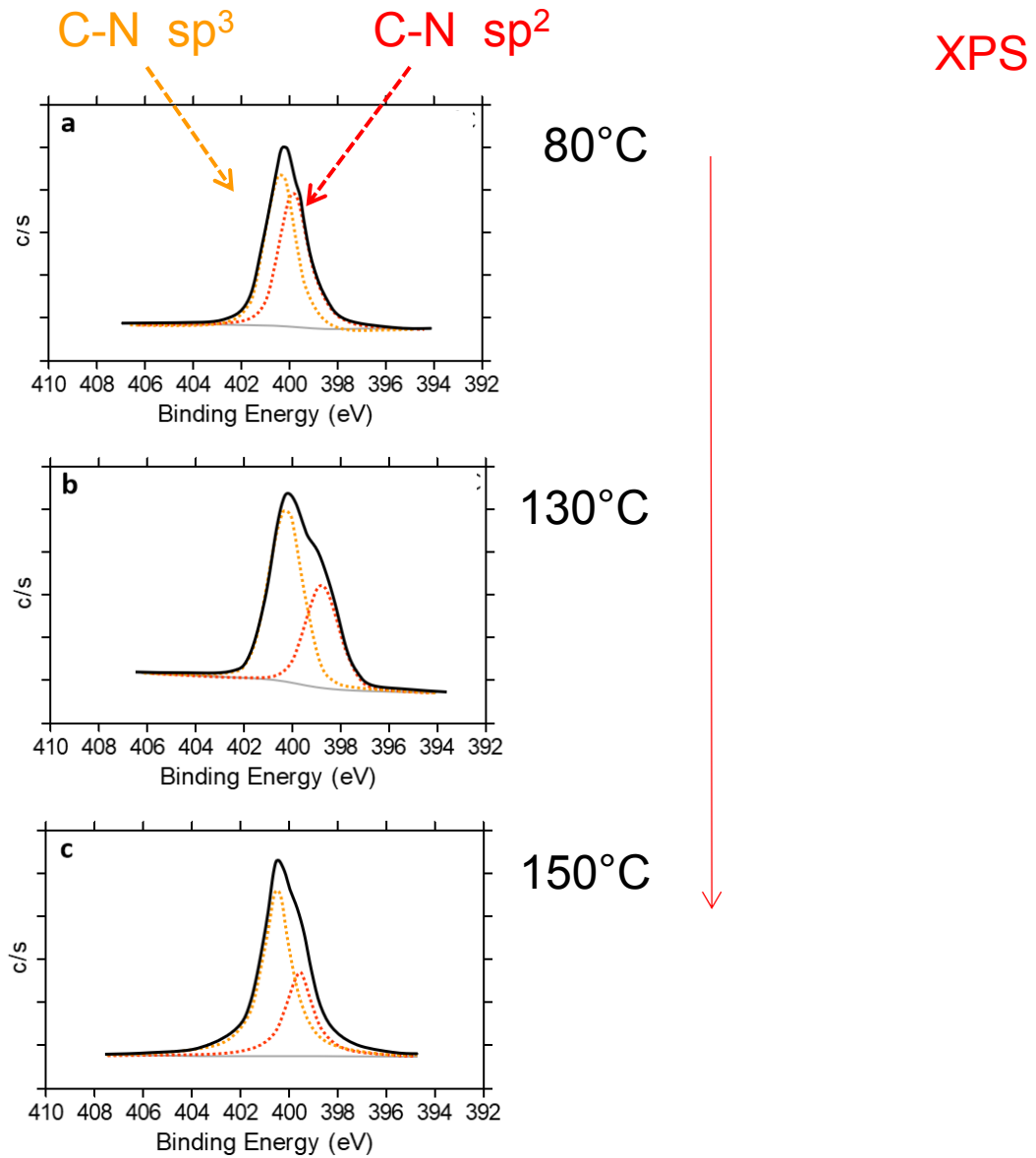
Oxidation products



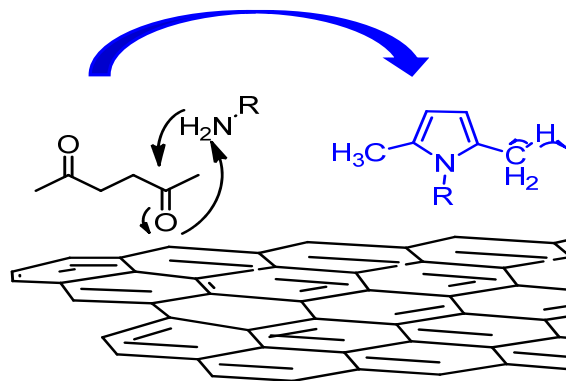
Nitrogen compound
in the adduct



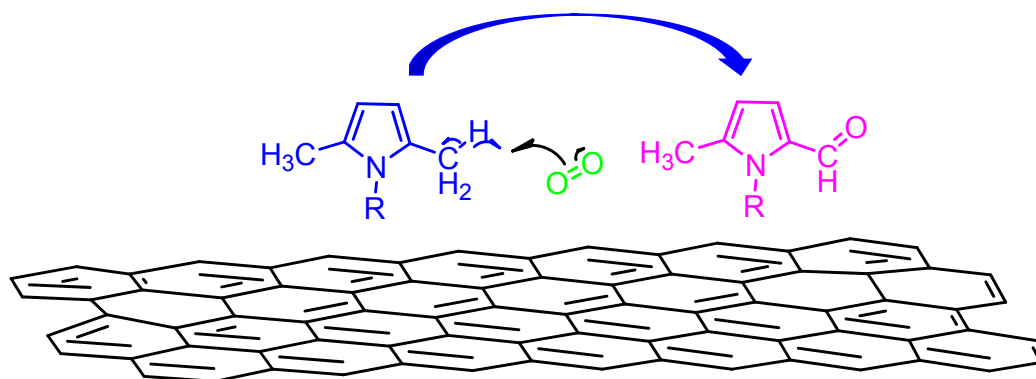
TMP + HSAG 1/1 - from 80 to 150°C - Solid product



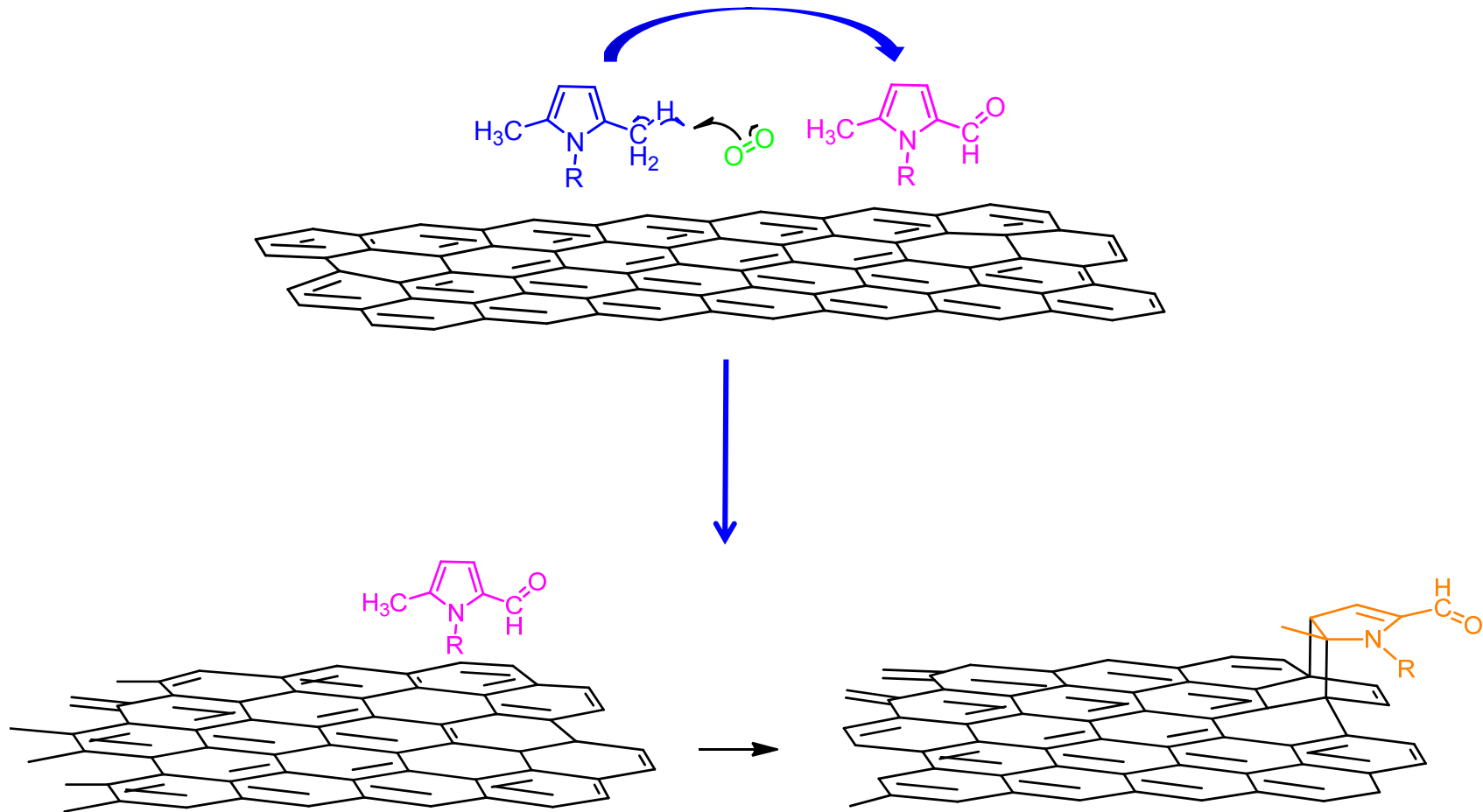
Hypothesis for the mechanism



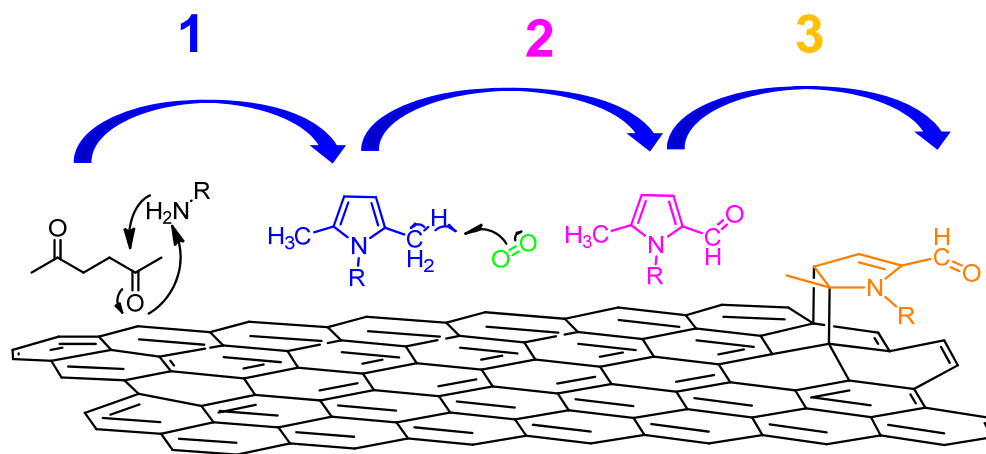
Hypothesis for the mechanism



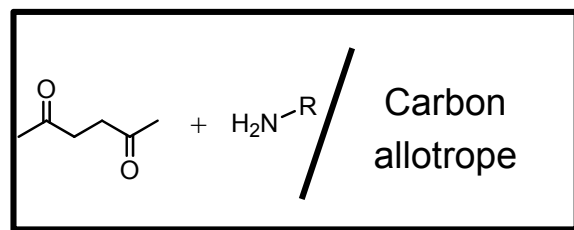
Hypothesis for the mechanism



Facile functionalization of carbon materials



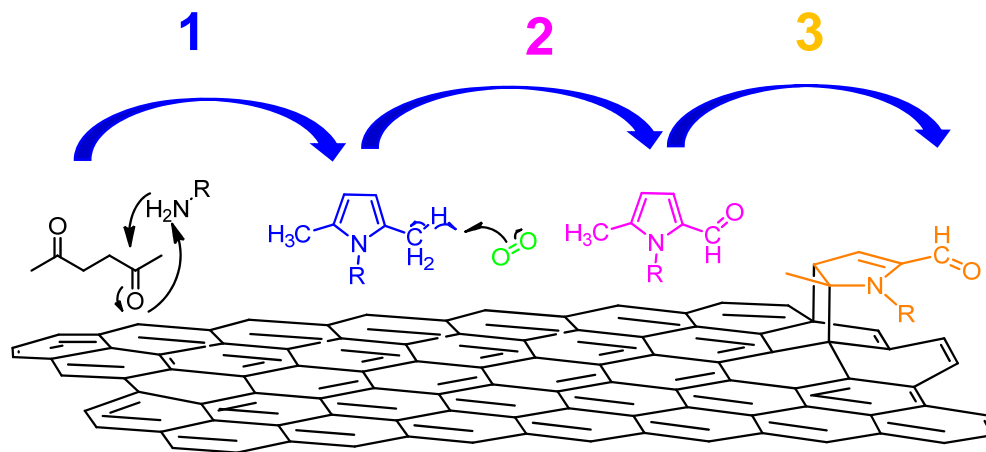
Facile functionalization of carbon materials



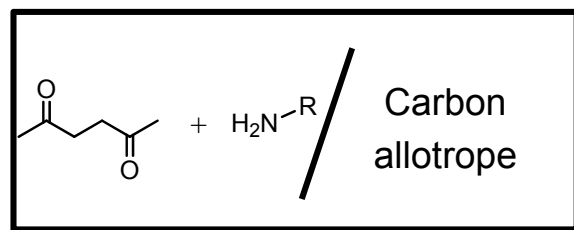
Paal – Knorr Reaction

Carbocatalyzed Oxidation

Diels-Alder reaction



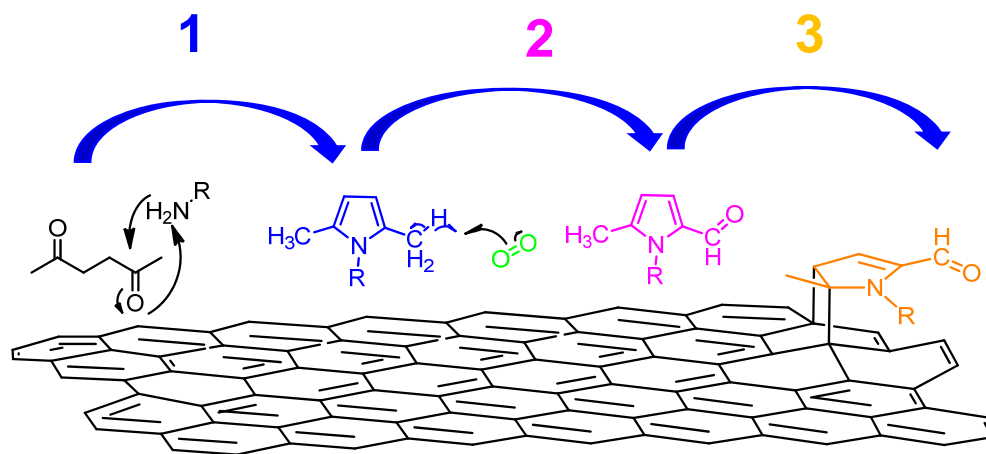
Facile functionalization of carbon materials



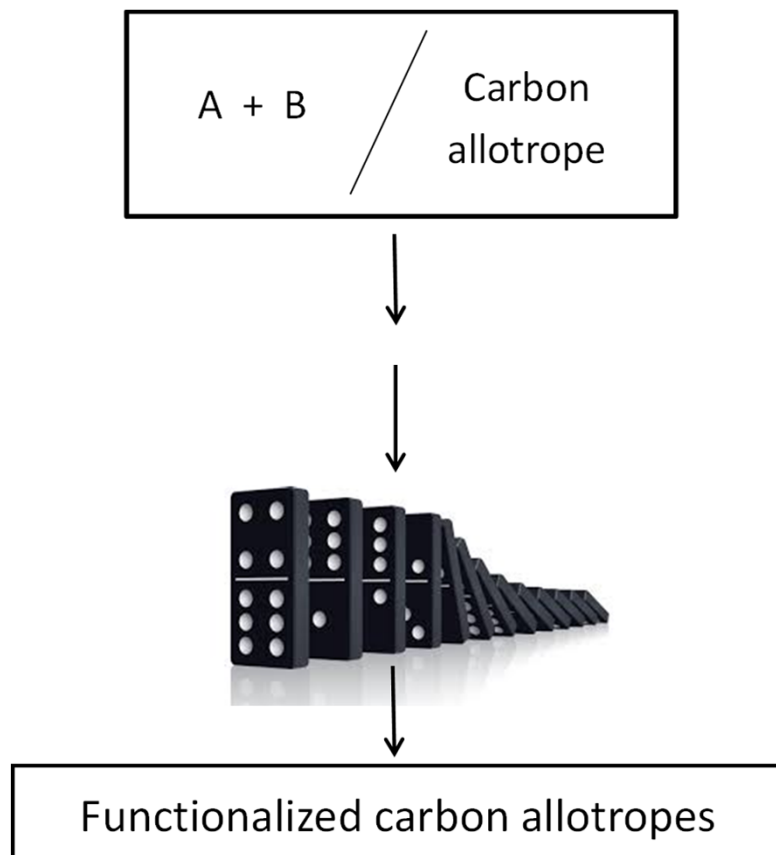
Paal – Knorr Reaction

Carbocatalyzed Oxidation

Diels-Alder reaction



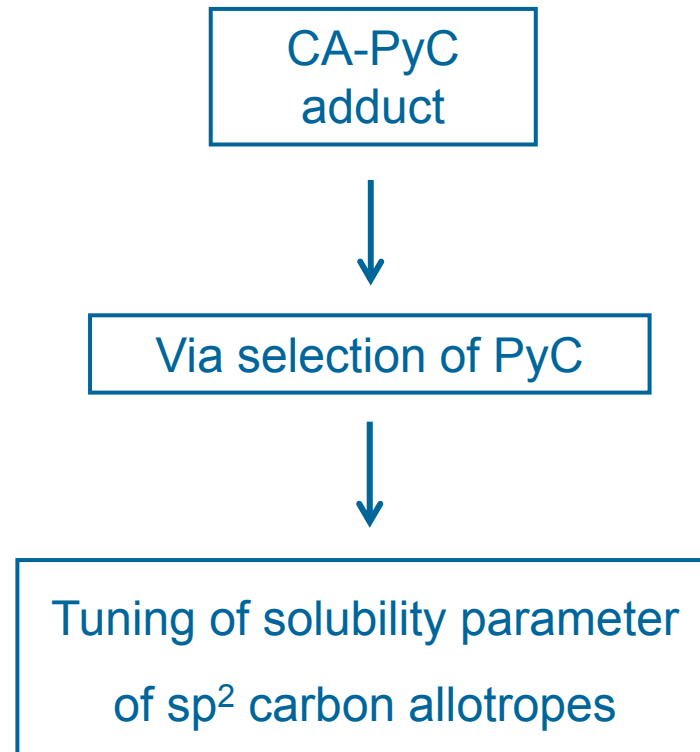
Facile functionalization of carbon materials



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

V. Barbera, A. Citterio, M. Galimberti, G. Leonardi, R. Sebastiano, S.U. Shisodia, A.M. Valerio. [WO/2015/189411 A1 \(2015\)](#)
Galimberti, M., Barbera, V., Sebastiano, R., Valerio A.M. Leonardi, G., Citterio, [EP 3209604 B1 - US 2017 0275169 A1](#)
M. Galimberti, V. Barbera, R. Sebastiano, A. Truscello, A.M. Valerio. [WO/2016/023915 A1 \(2016\)](#)
M. Galimberti, V. Barbera, [Italian Patent 102016000113012 \(2016\)](#)
M. Galimberti, V. Barbera, [Italian Patent 102016000113070 \(2016\)](#)

Tuning of solubility parameter of sp^2 carbon allotropes



CA / PyC adducts - Tuning of solubility parameters

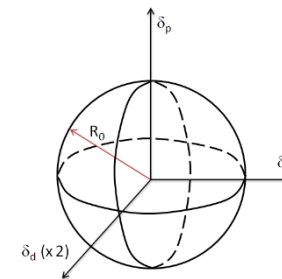
Experimental determination

Suspensions
in solvents
with different δ



Theoretical predictions

Computational model:
Hansen solubility parameters



Evaluation of solubility parameters of HSAG-PyC - Experiments

Adduct	solvents				
	water	isopropanol	ethyl acetate	toluene	heptane
TMP	bad (↓)	good	good	good	good
EP	bad (↑)	bad (↓)	good	bad (↓)	good
DDcP	bad (↑)	good	good	bad (↓)	bad (↓)
APTESP	bad (↑)	bad (↓)	bad (↓)	good	good
Gly	bad (↓)	good	good	good	bad (↓)
SP	good	good	good	bad (↓)	bad (↓)



No
suspension:
bad



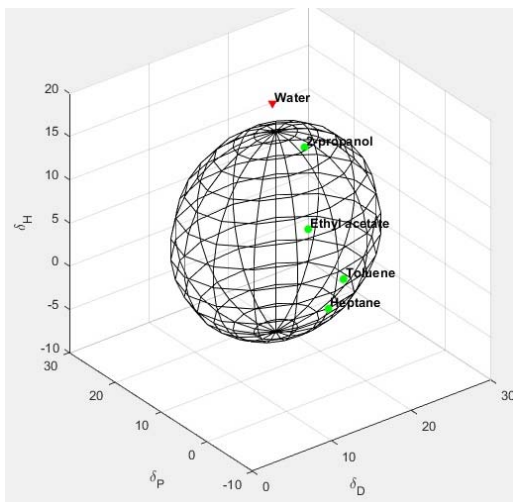
Unstable
suspension:
bad



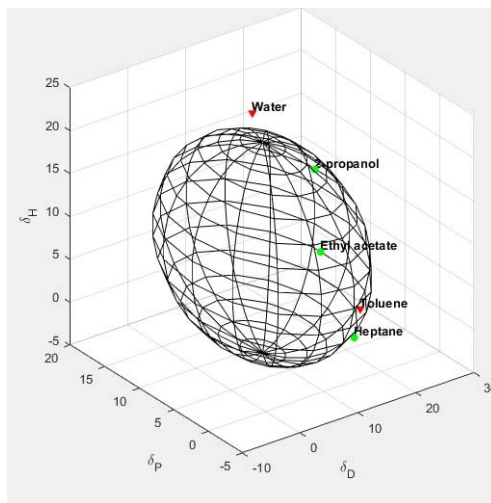
Stable
suspension:
good

Evaluation of solubility parameters of HSAG-PyC - Hansen sphere

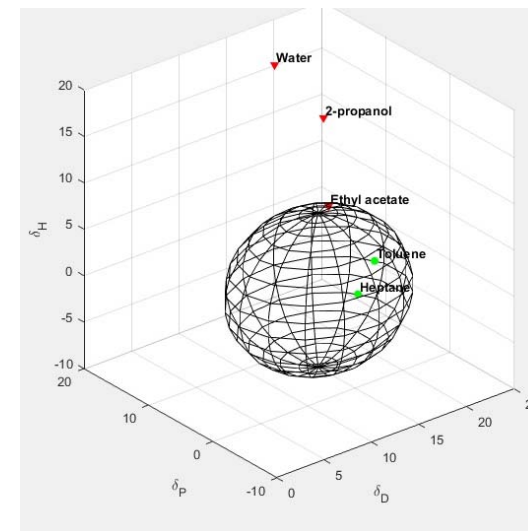
HSAG-TMP



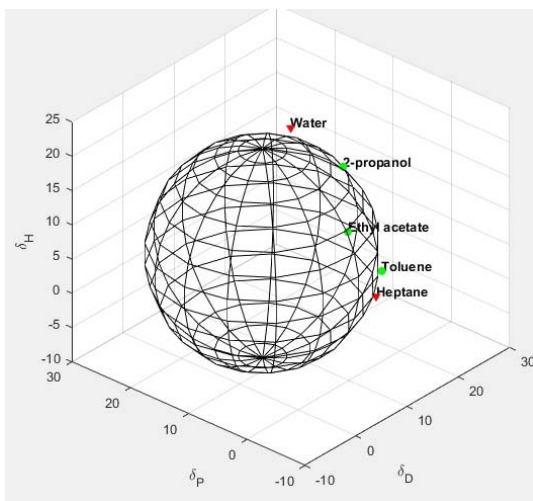
HSAG-DDcP



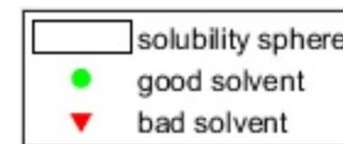
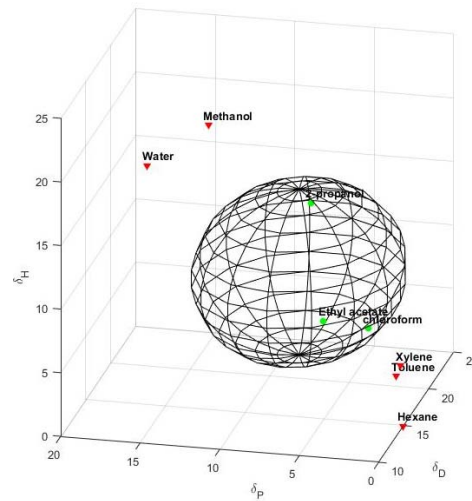
HSAG-APTESP



HSAG-GlyP



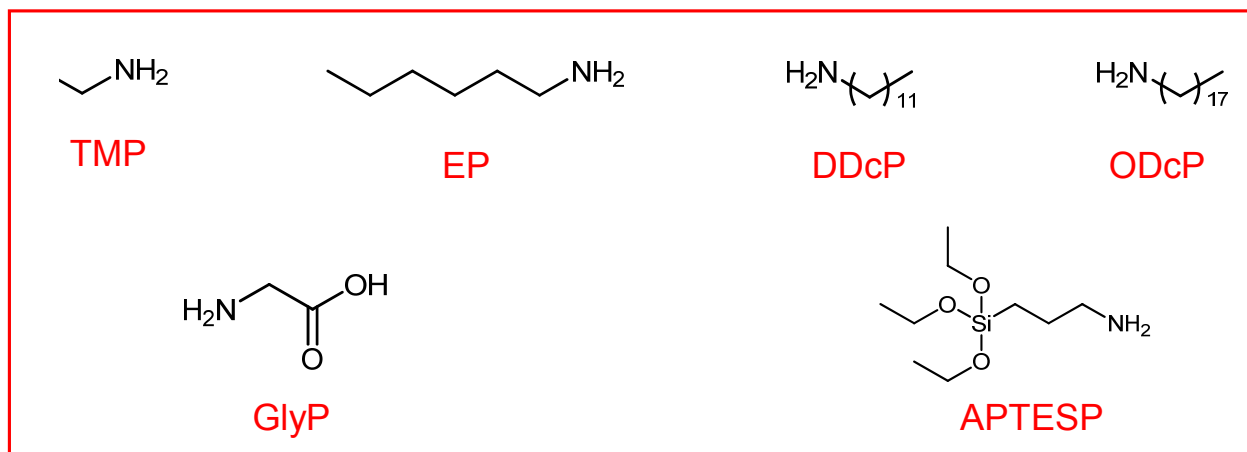
HSAG-SP



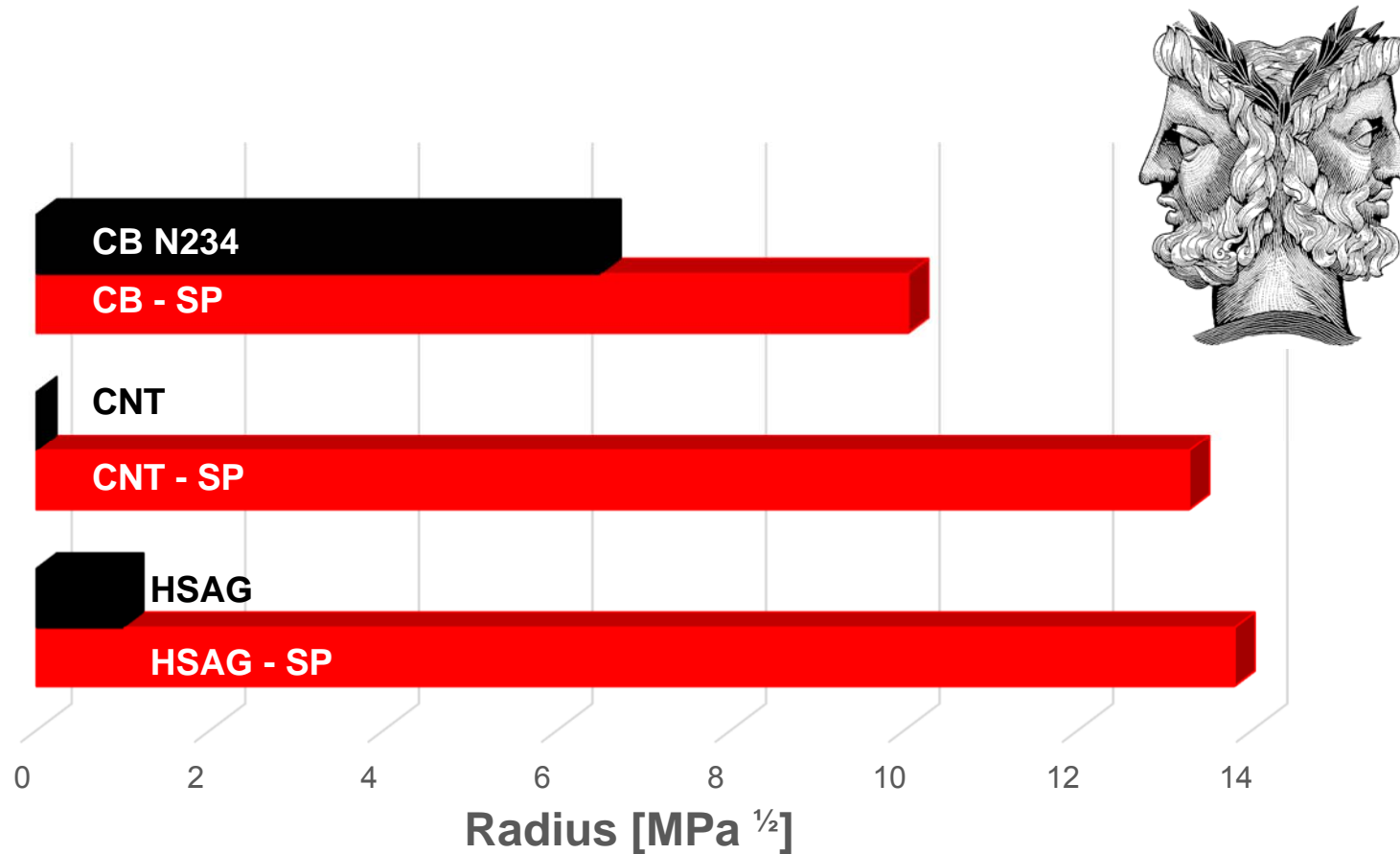
Evaluation of solubility parameters of HSAG-PyC - δ values

Sample	δ_D	δ_P	δ_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 CA-SP - Radius comparison

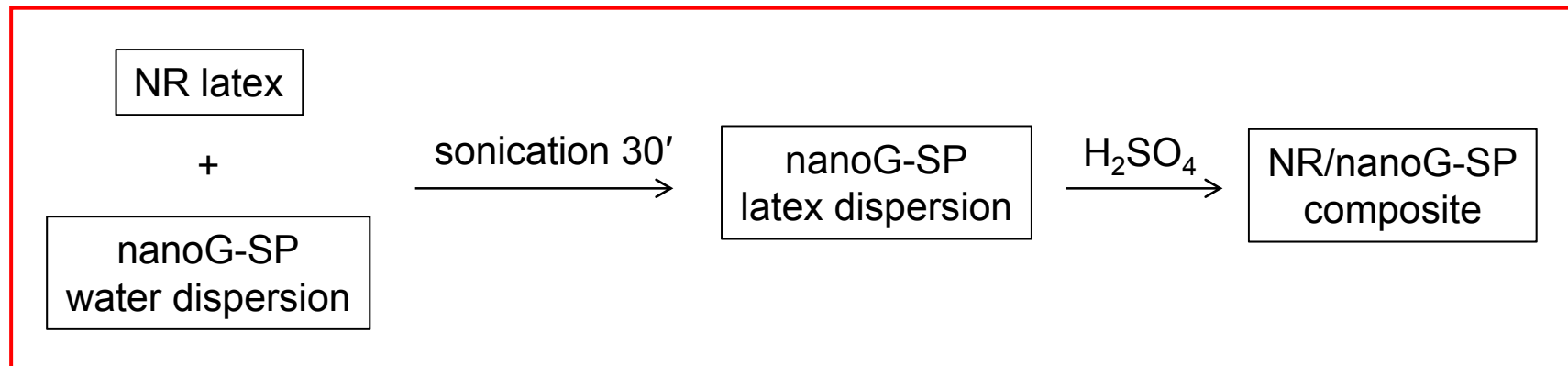


(*) Amount of SP on CA: 10 mass%

NR/HSAG-SP composites from NR latex

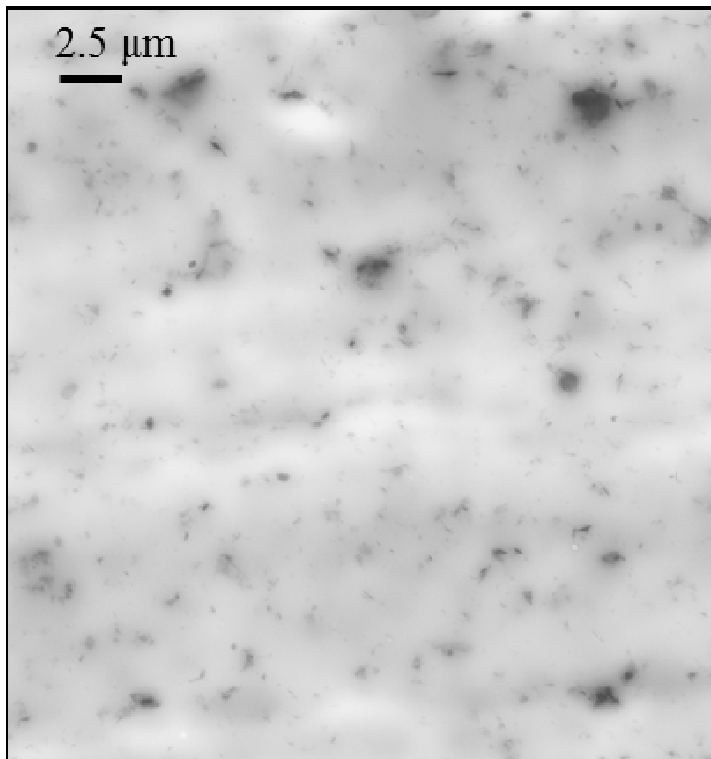


<i>Ingredients</i>	<i>phr</i>
NR	100
<i>HSAG-SP</i>	<i>10</i>

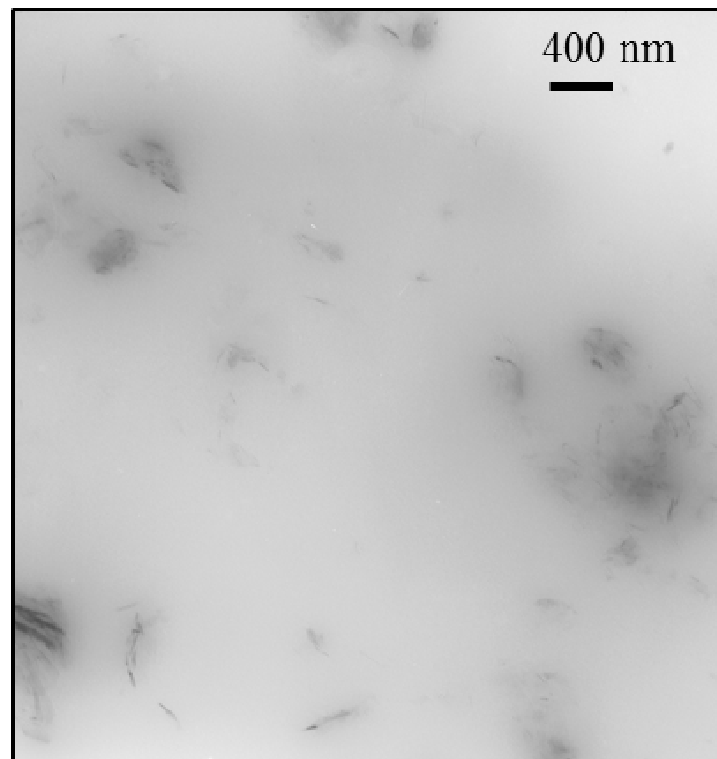


NR/HSAG-SP composites from NR latex

TEM Analysis



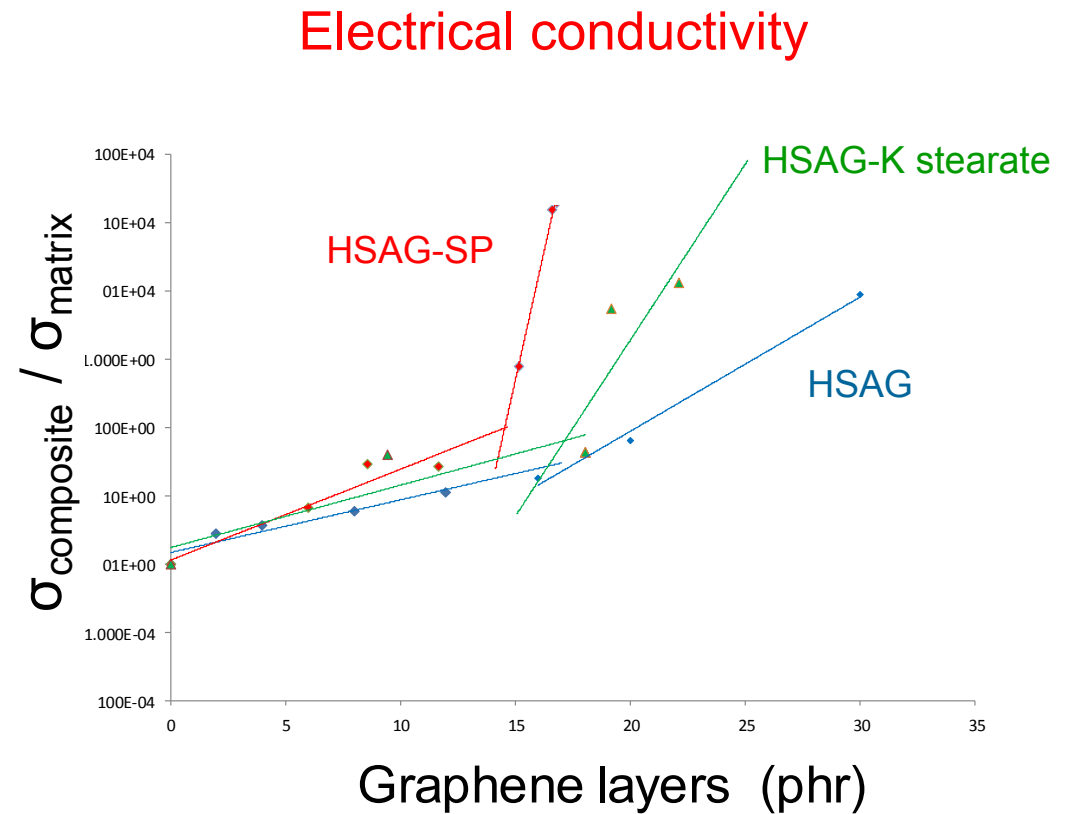
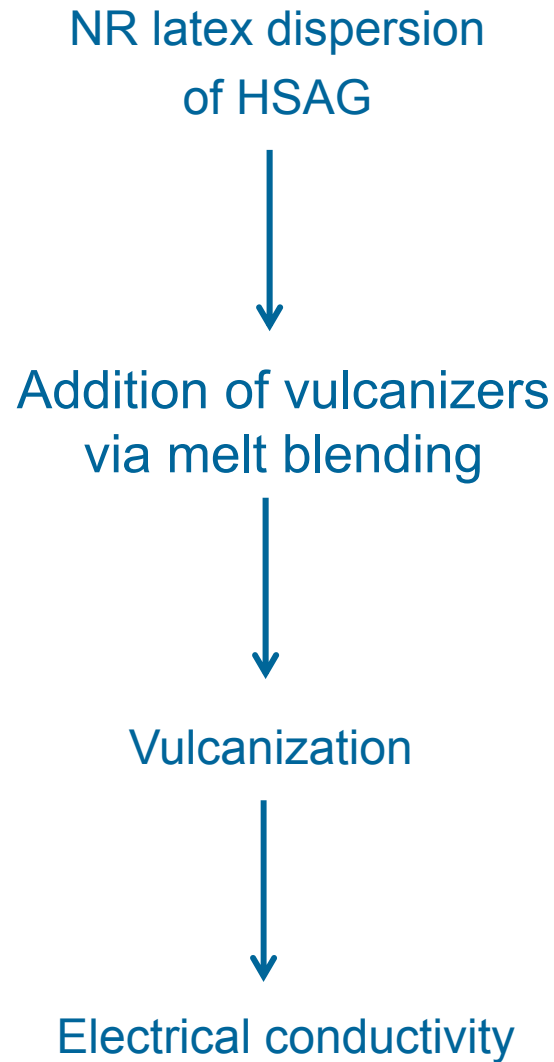
even distribution, fairly fine dispersion
No micrometric agglomerates



stacks of only a few nanoG layers,
isolated layers of nanoG



NR/HSAG-SP composites from NR latex



NanoCarbon Up Technology



V. Barbera, A. Citterio, M. Galimberti, G. Leonardi, R. Sebastiano, S.U. Shisodia, A.M. Valerio.
[WO/2015/189411 A1 \(2015\)](#)

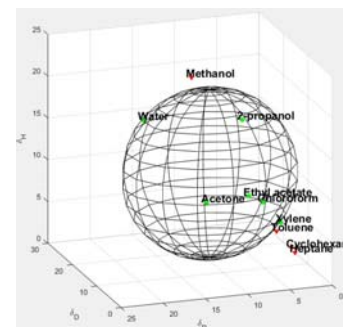
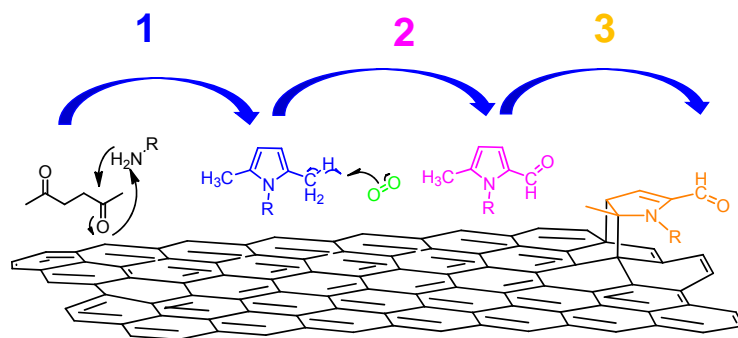
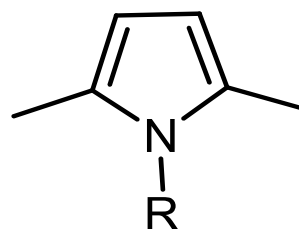
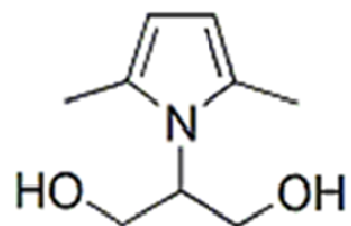
Galimberti, M., Barbera, V., Sebastiano, R., Valerio A.M. Leonardi, G., Citterio, [EP 3209604 B1 - US 2017 0275169 A1](#)

M. Galimberti, V. Barbera, R. Sebastiano, A. Truscillo, A.M. Valerio.
[WO/2016/023915 A1 \(2016\)](#)

M. Galimberti, V. Barbera,
[WO 2018/087685 A1](#)

M. Galimberti, V. Barbera,
[WO 2018/087688 A1](#)

Conclusions





*Thanks
for the attention!*



13th Kautschuk Herbst Kolloquium
Hannover, Germany, November 6-8, 2018