



POLITECNICO
MILANO 1863



The importance of being a *Janus* molecule: Performances and control of chemistry

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Alberto Palazzolo, Lucia Rubino, Simone Naddeo, Fatima Margani
and Maurizio Galimberti

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

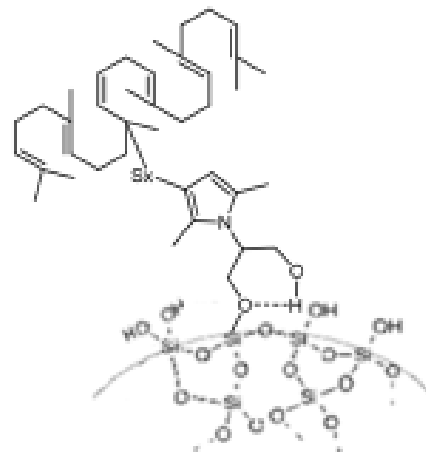
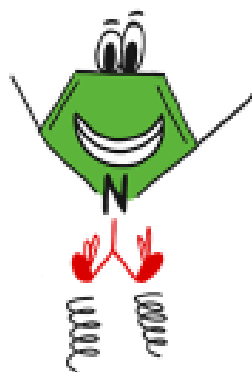
14th Fall Rubber Colloquium (KHK) ONLINE
Germany, November 2022, 8 - 10



Conclusions

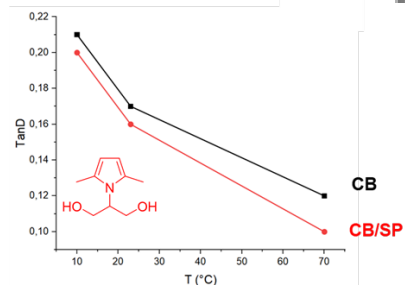


R = OH, SH



“Universal coupling agent for carbon black and silica”

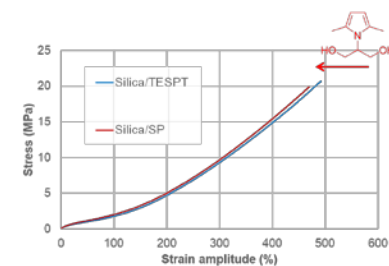
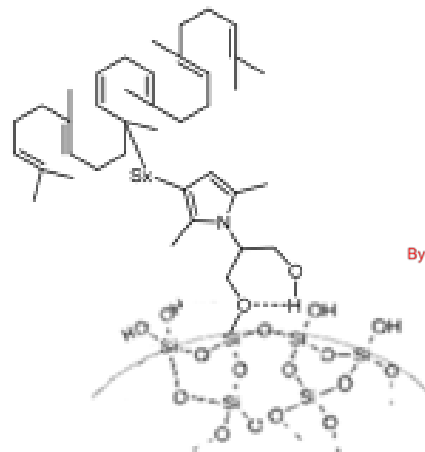
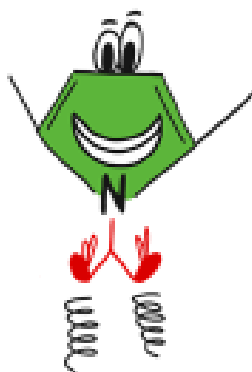
Conclusions



Rubber compounds based on CB/Silica with CB/SP

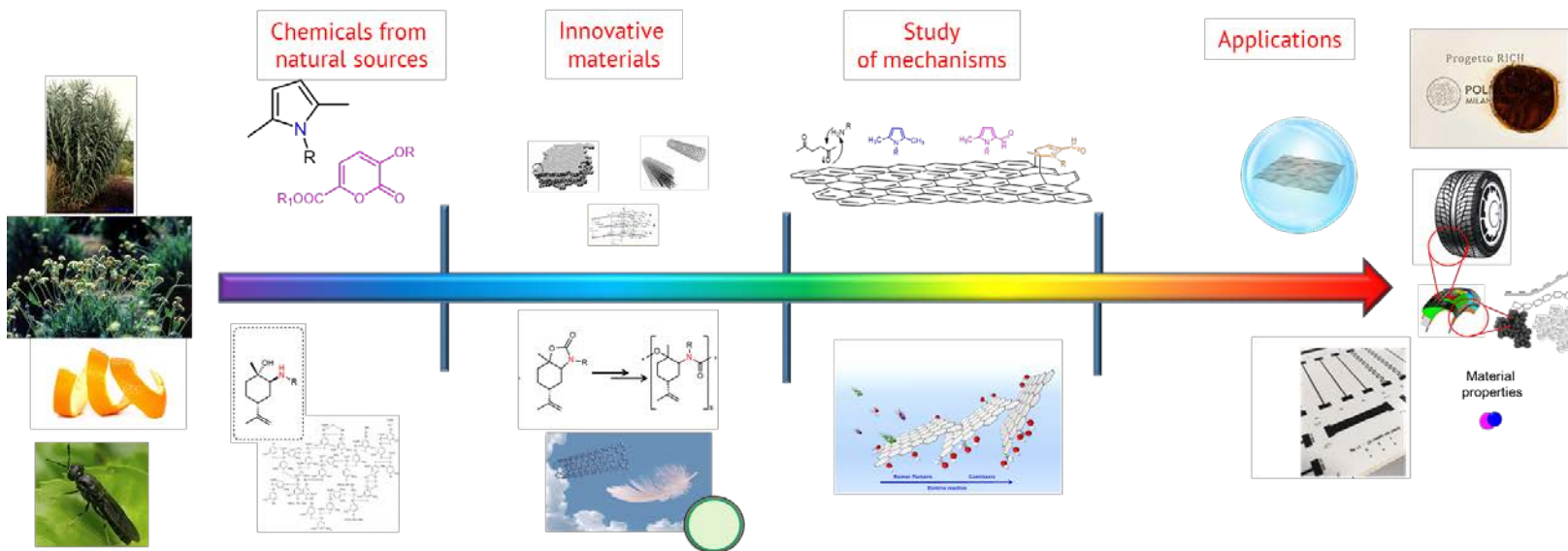


R = OH, SH

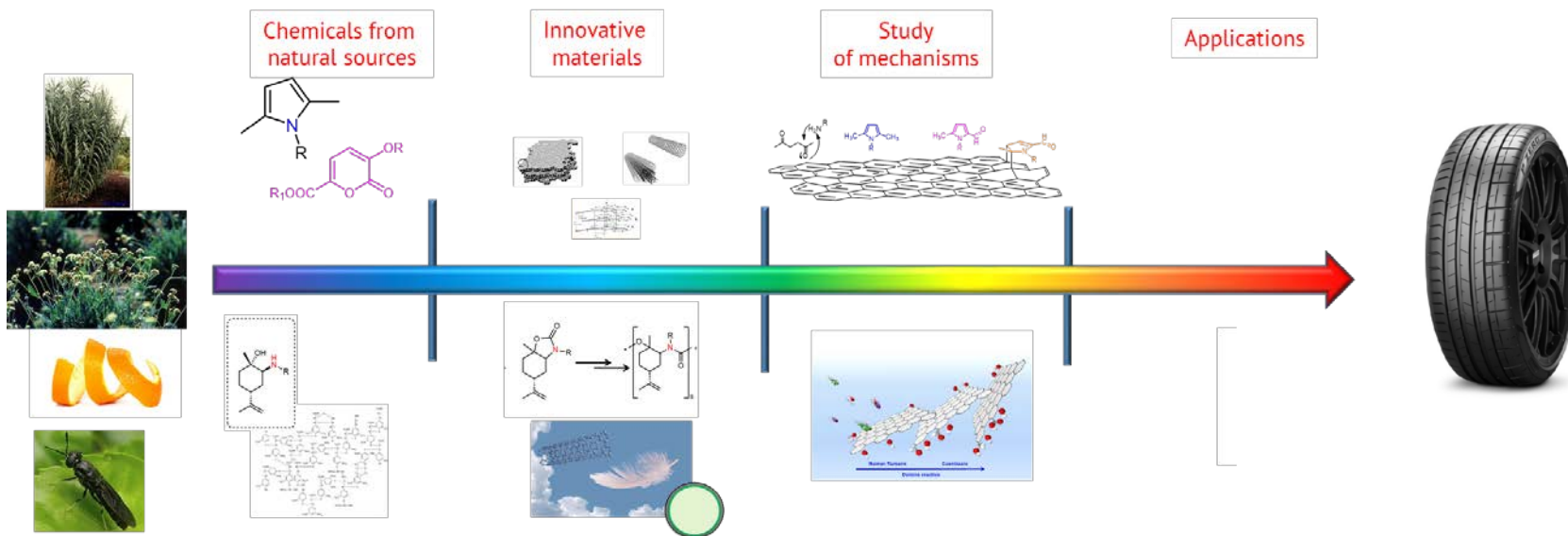


By modulating the amount of SP and of compound ingredients

“Universal coupling agent for carbon black and silica”

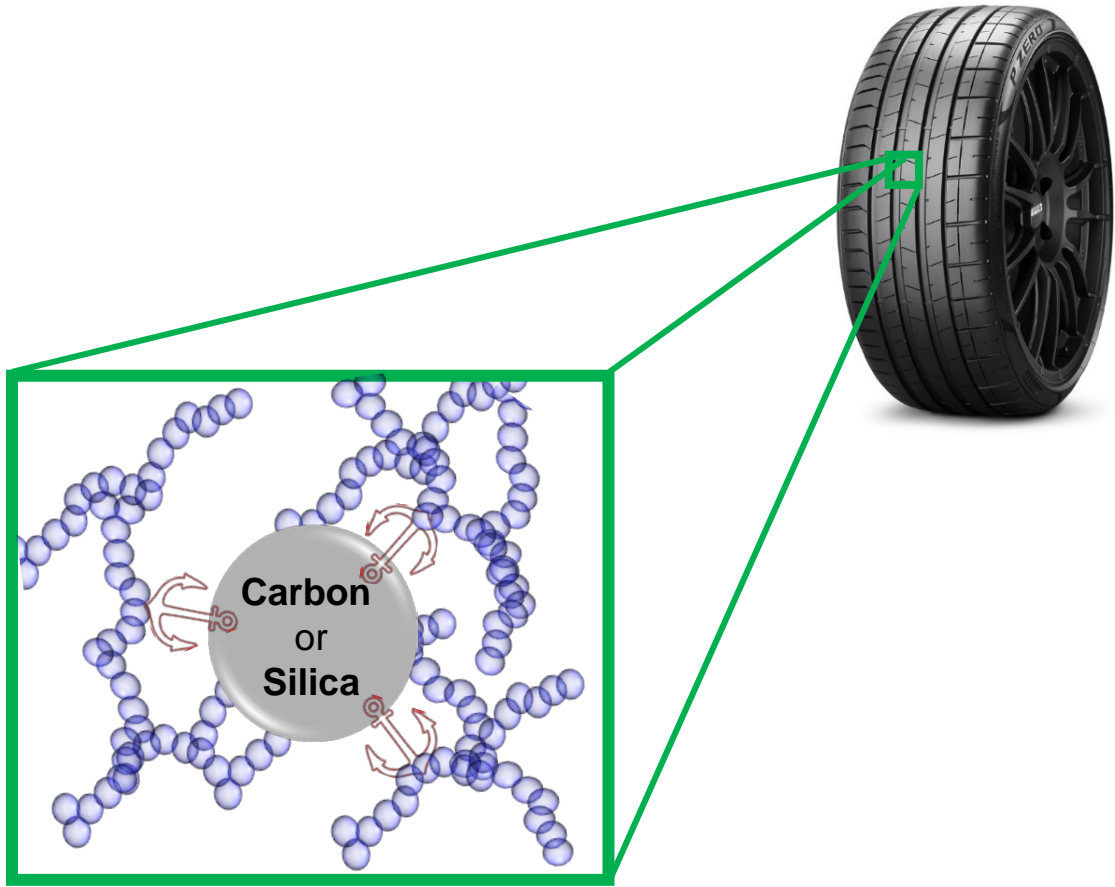


To prepare **tailor made materials**,
in view of the final application



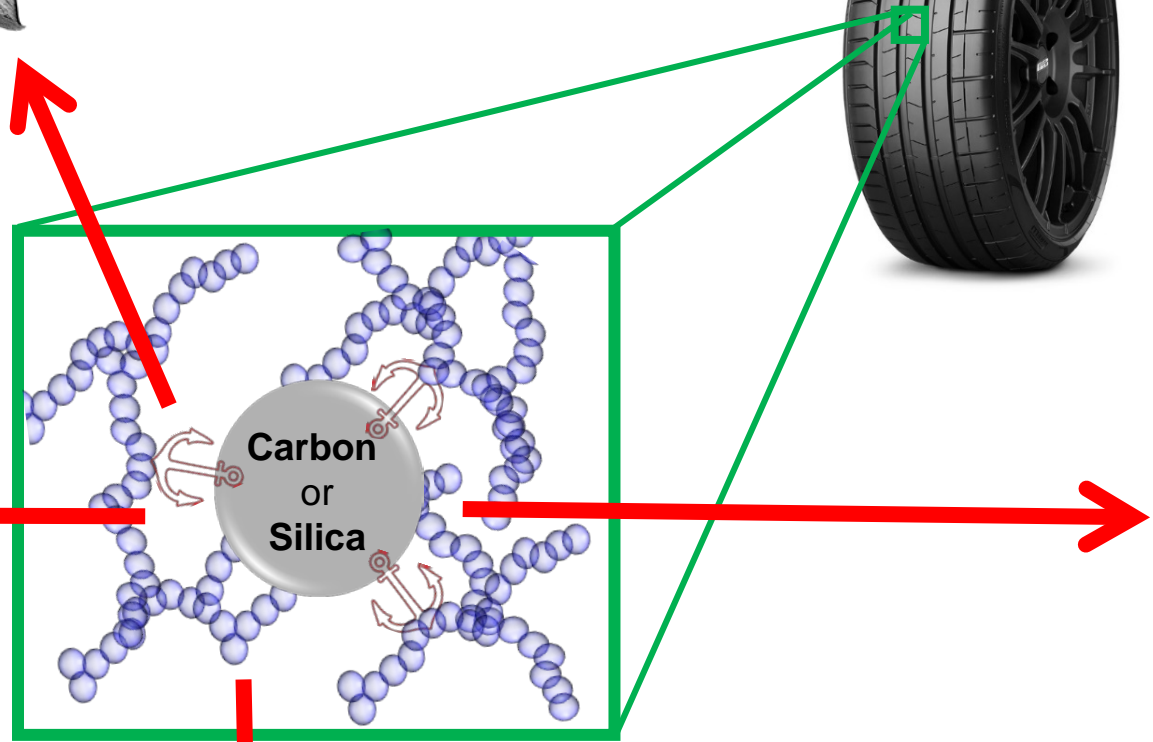
To prepare **tailor made materials**,
in view of the final application: **rubber composites**

Items of the presentation

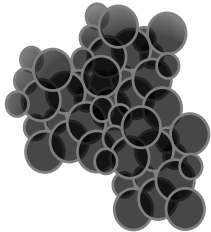


Items of the presentation

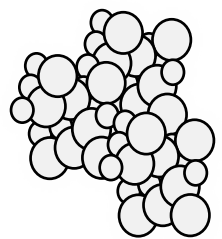
The anchor 



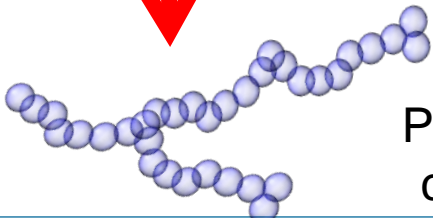
Carbon black



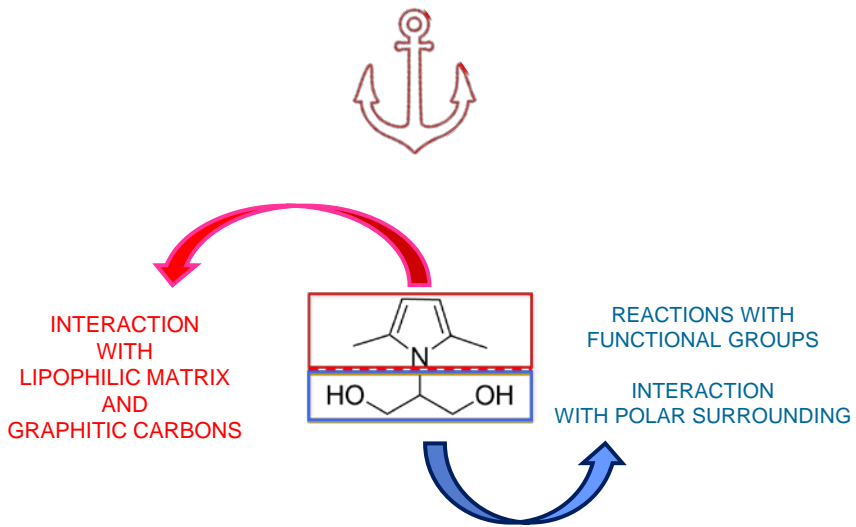
Silica



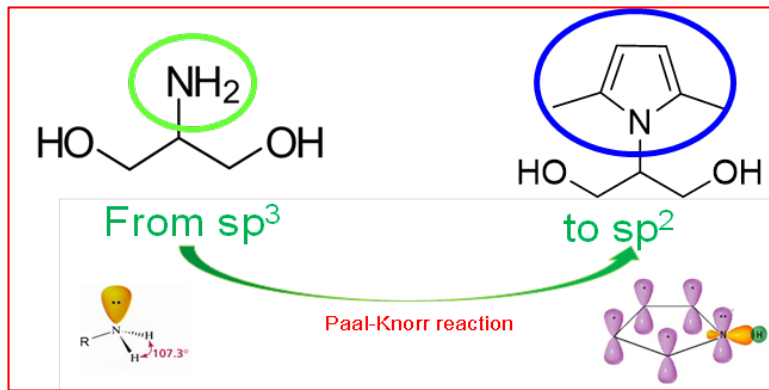
Polymer chains



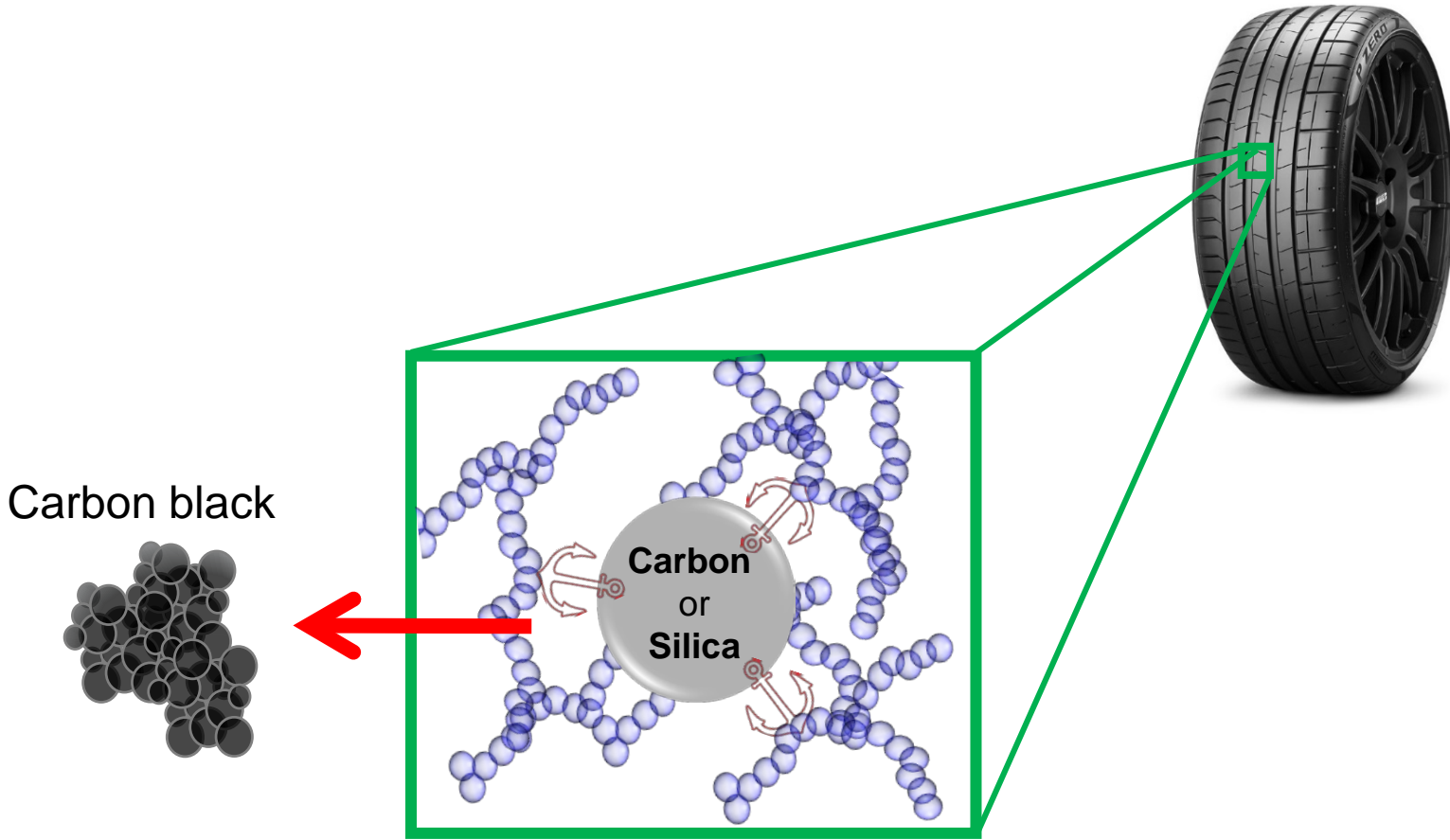
The importance of being a *Janus* molecule: Performances and control of chemistry



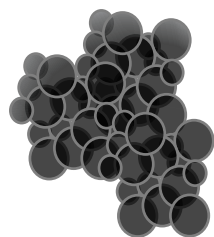
Serinolpyrrole: *Janus* molecule



Items of the presentation



Carbon black

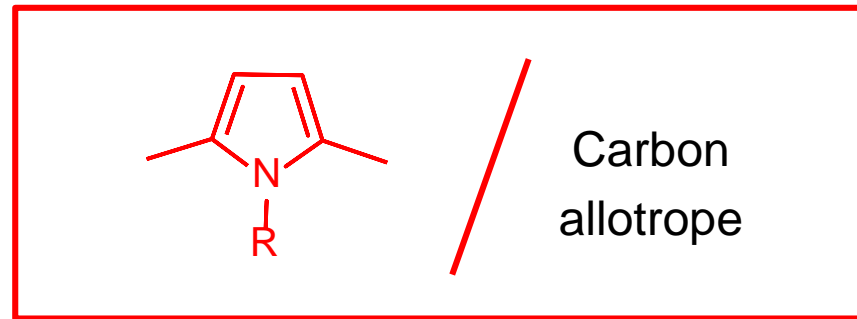


Reactive
Carbon black



Playing with chemistry on sp^2 carbon allotropes

Facile functionalization of carbon materials

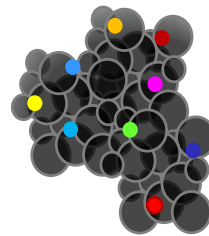


Mixing, energy, air

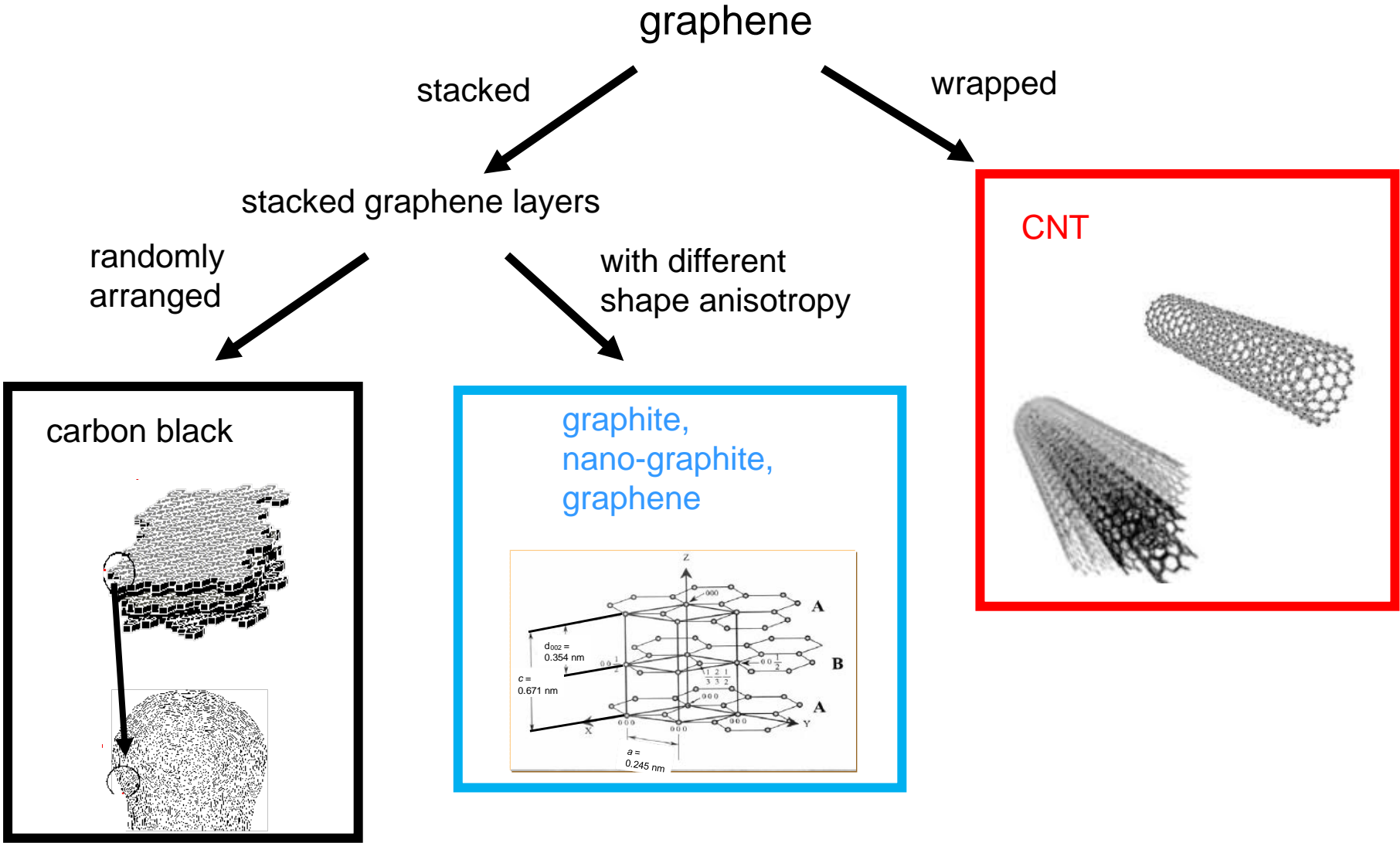
carbon allotrope

functional groups on surface

bulk structure substantially unaltered

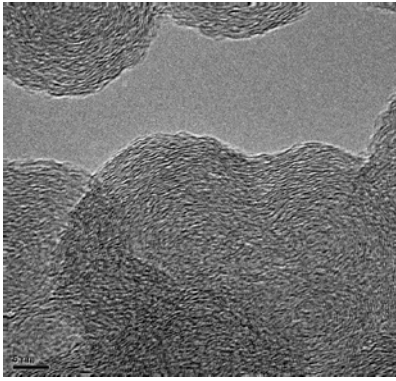
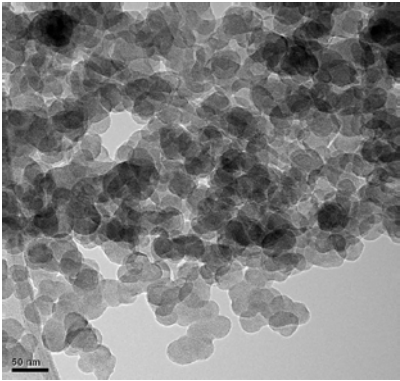


Carbon fillers from a layer of sp^2 -bonded carbon atoms

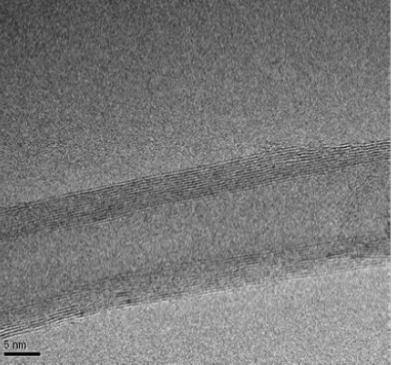
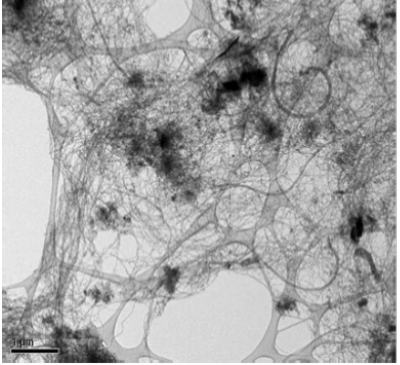


Carbon allotropes (CA)

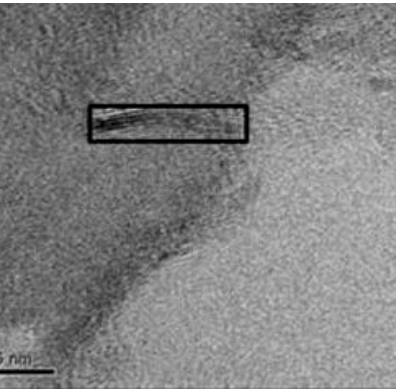
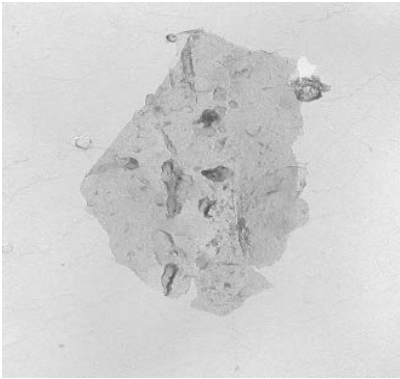
CB



CNT

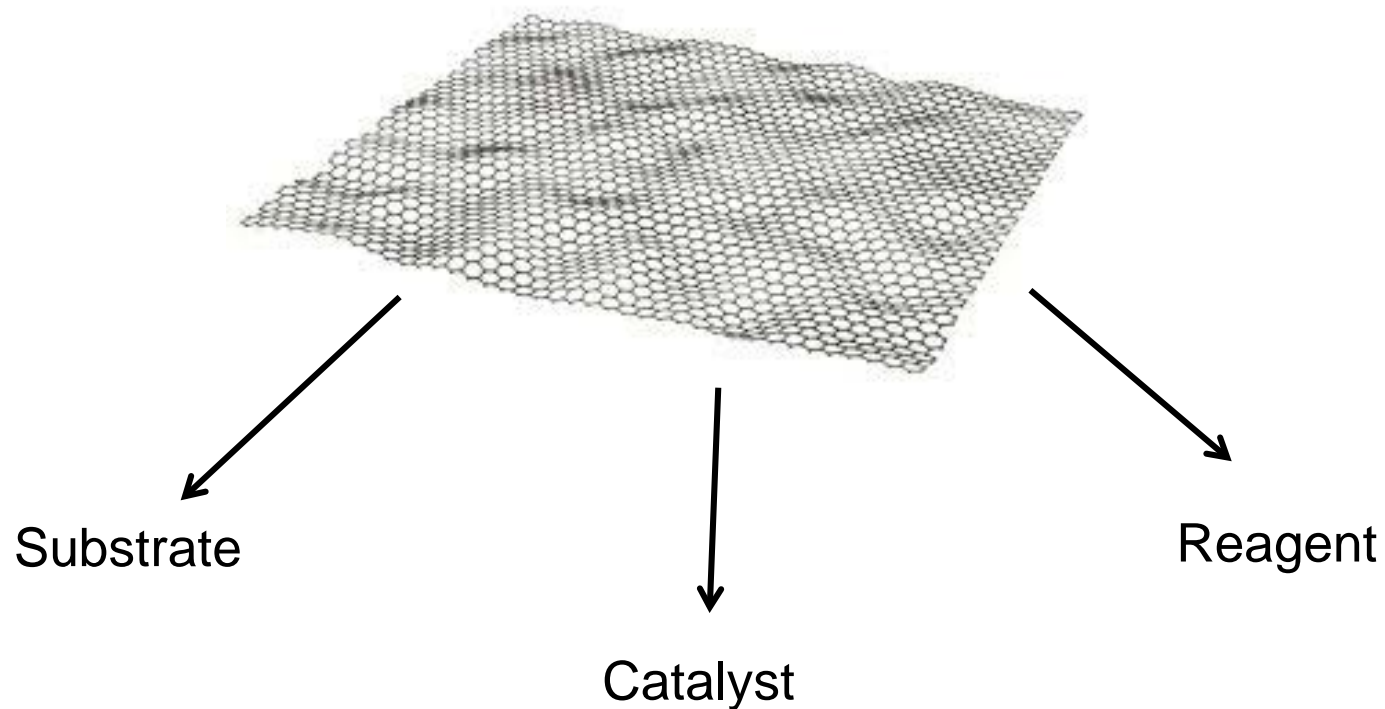


FEW LAYERS
GRAPHENE



Playing with chemistry on sp^2 carbon allotropes

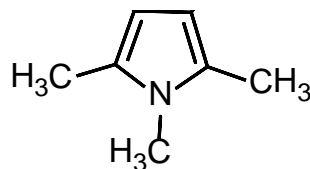
Manifold role for the carbon allotrope



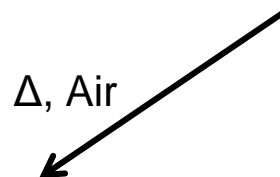
Investigation of mechanisms

Mechanism of the functionalization reaction

Investigation with a model compound

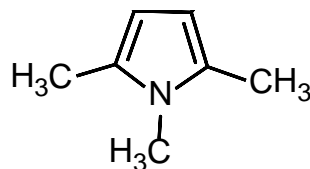


1,2,5-Trimethylpyrrole
(TMP)

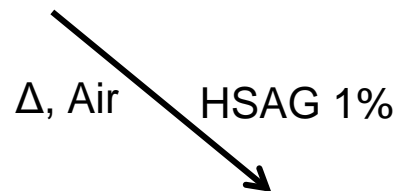
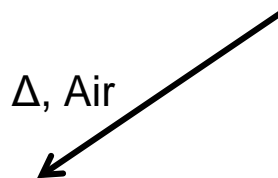


Mechanism of the functionalization reaction

Investigation with a model compound

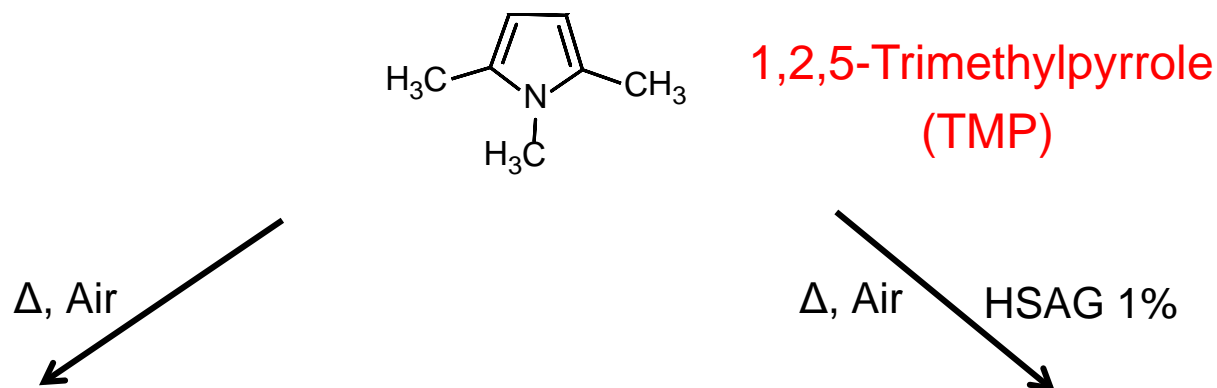


1,2,5-Trimethylpyrrole
(TMP)



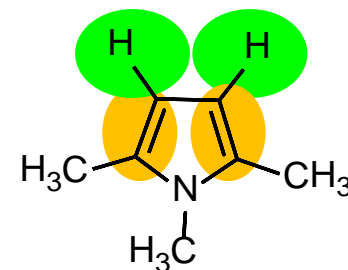
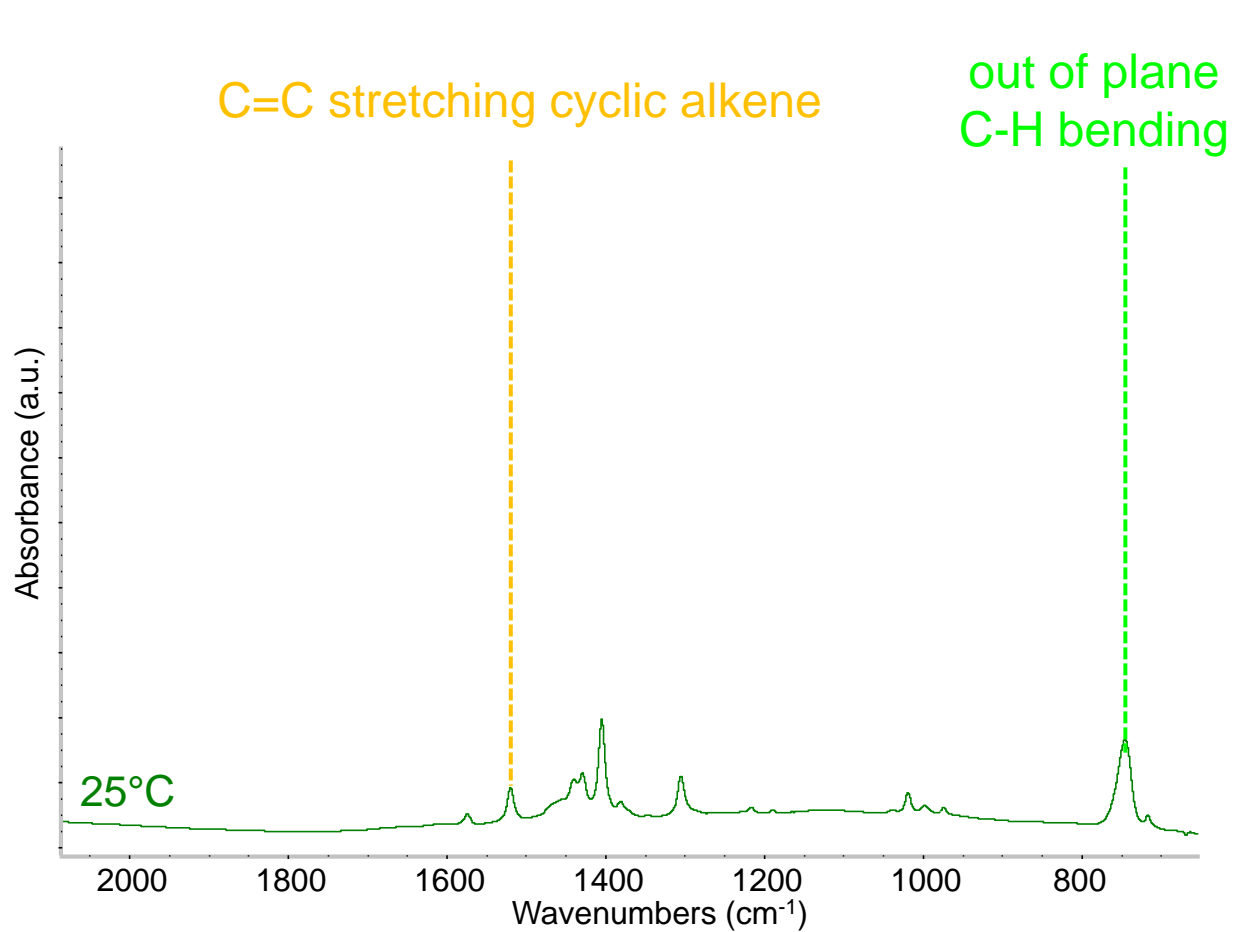
Mechanism of the functionalization reaction

Investigation with a model compound

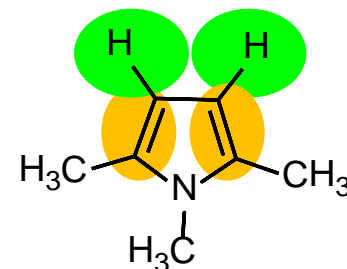
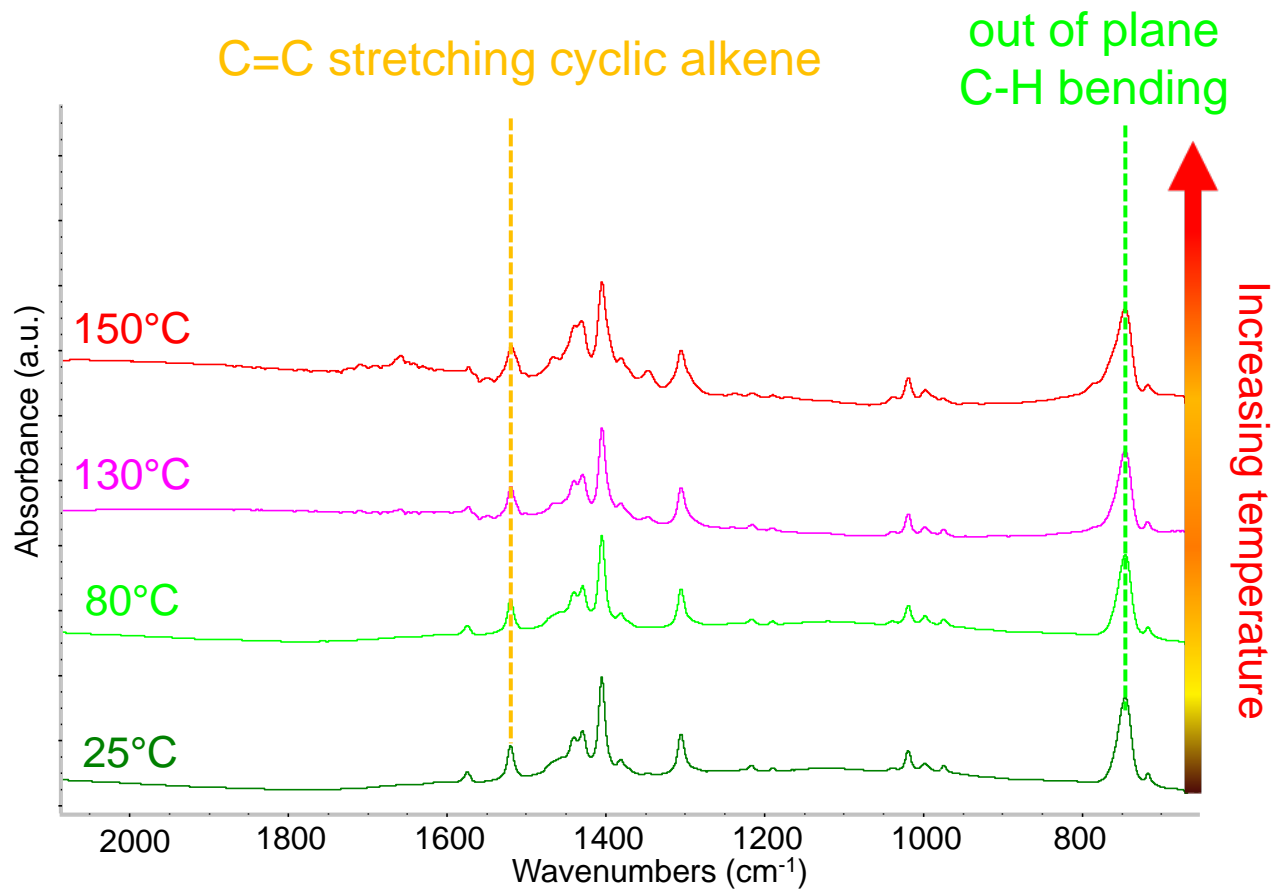
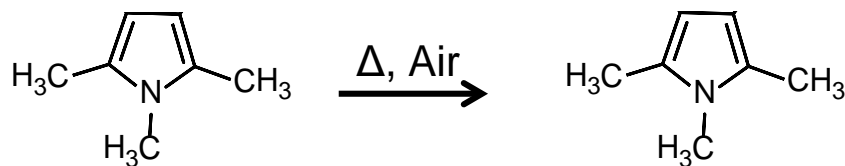


- ☞ Analysis of: liquids, HSAG/TMP adducts
- ☞ FT-IR and $^1\text{H-NMR}$ spectroscopies
- ☞ FT-IR spectra generation with Density Functional Theory (DFT) quantum chemical modelling.

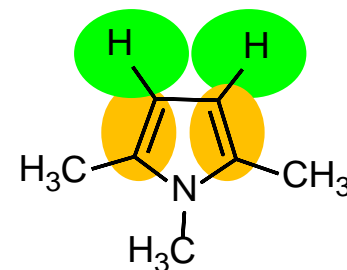
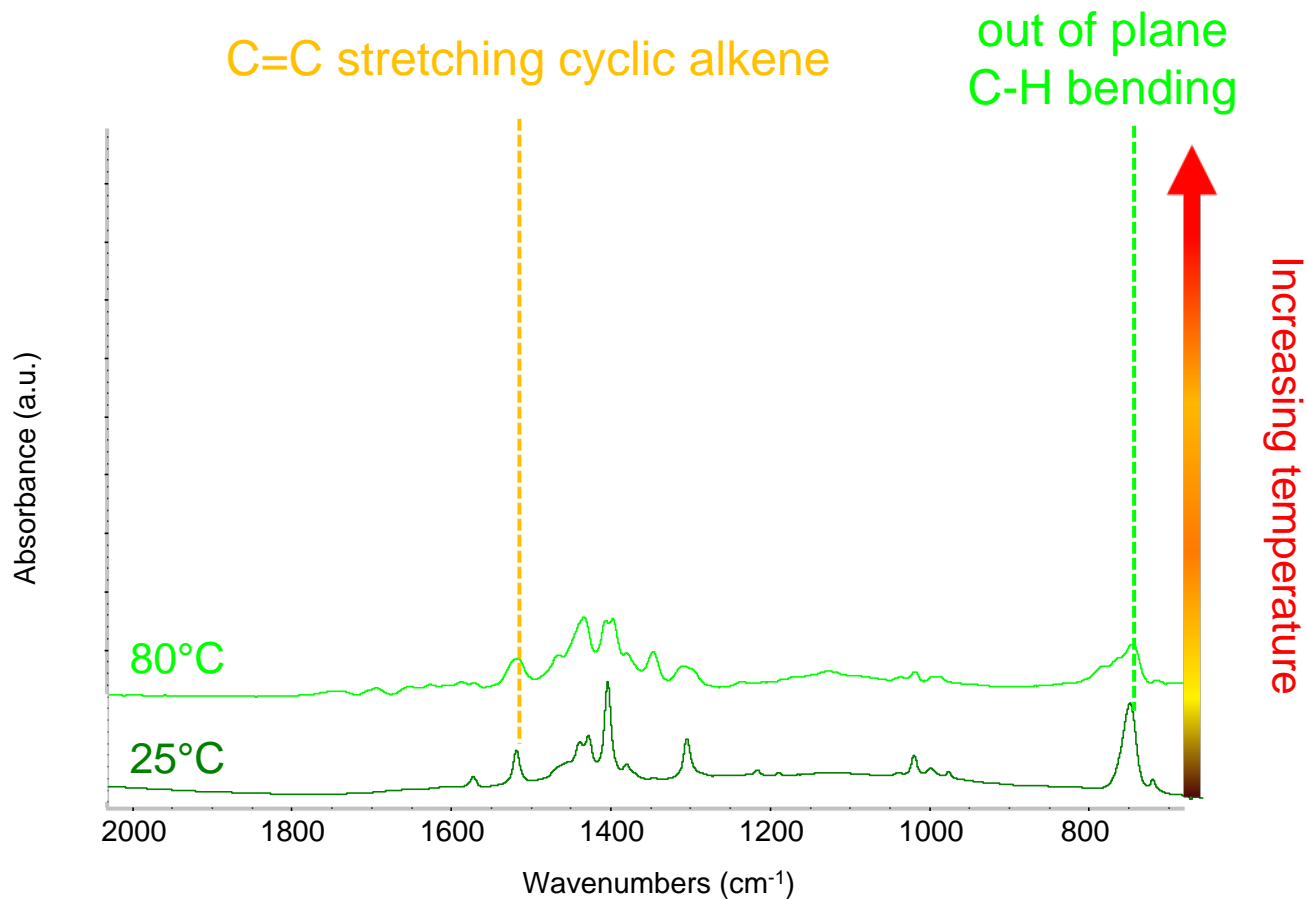
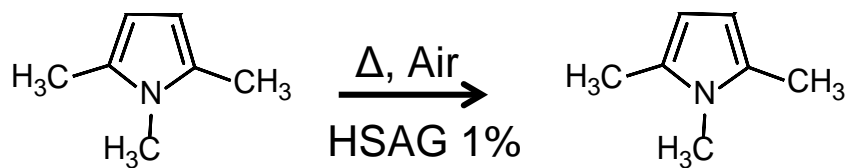
1,2,5-Trimethylpyrrole (TMP)



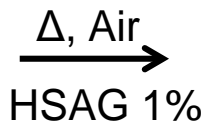
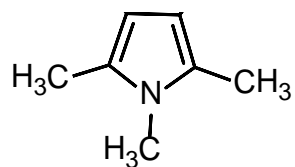
TMP + Air - From 25°C to 150°C



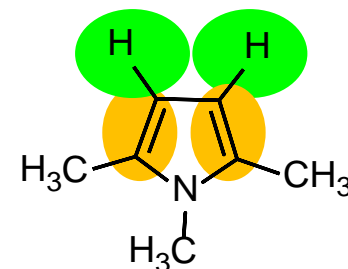
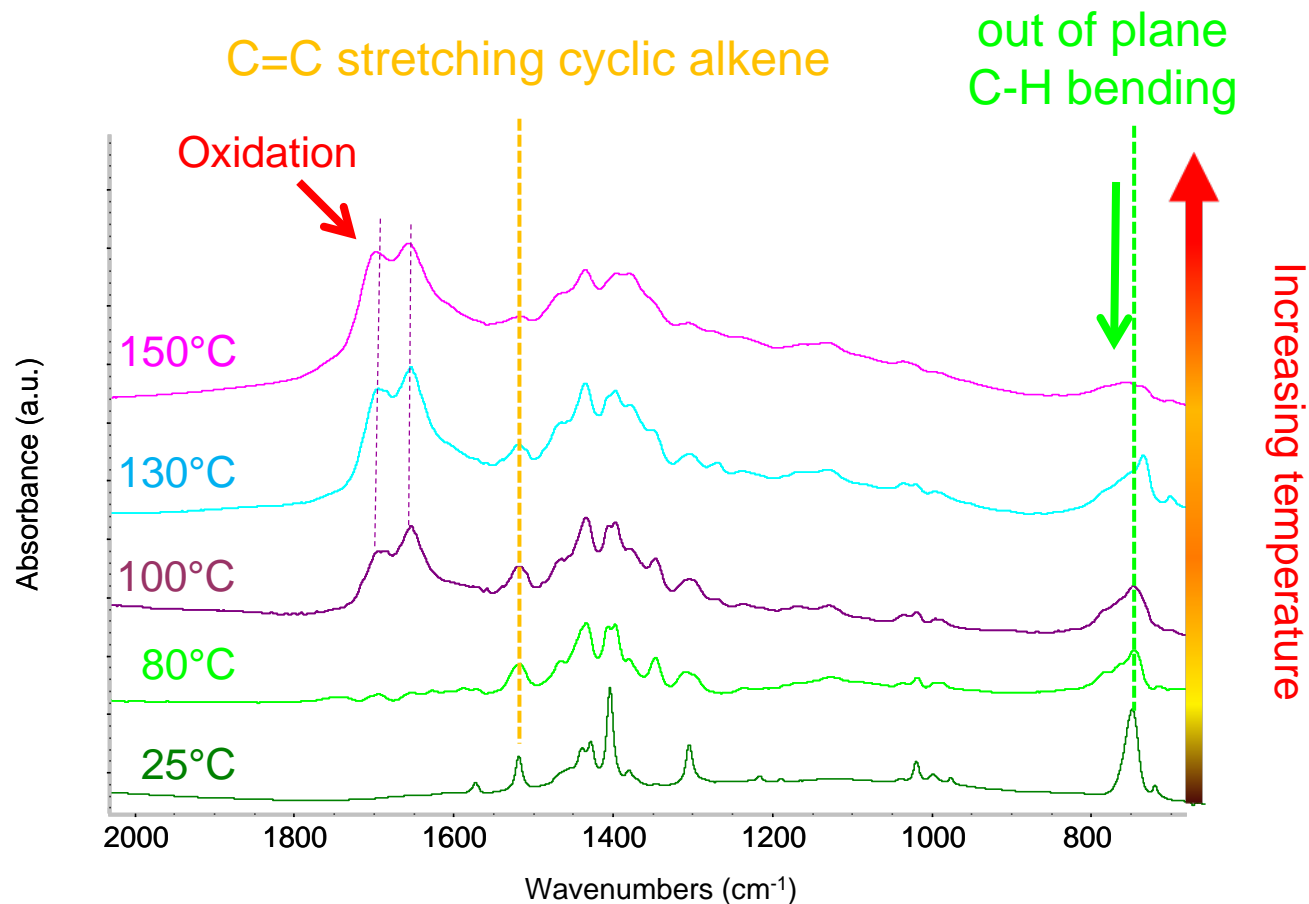
TMP + HSAG 1% / Air - From 25°C to 80°C



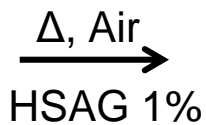
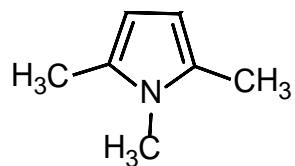
TMP + HSAG 1% - from 100°C to 150°C



Oxidation products

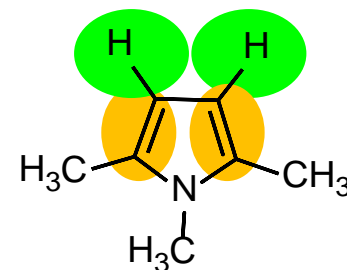
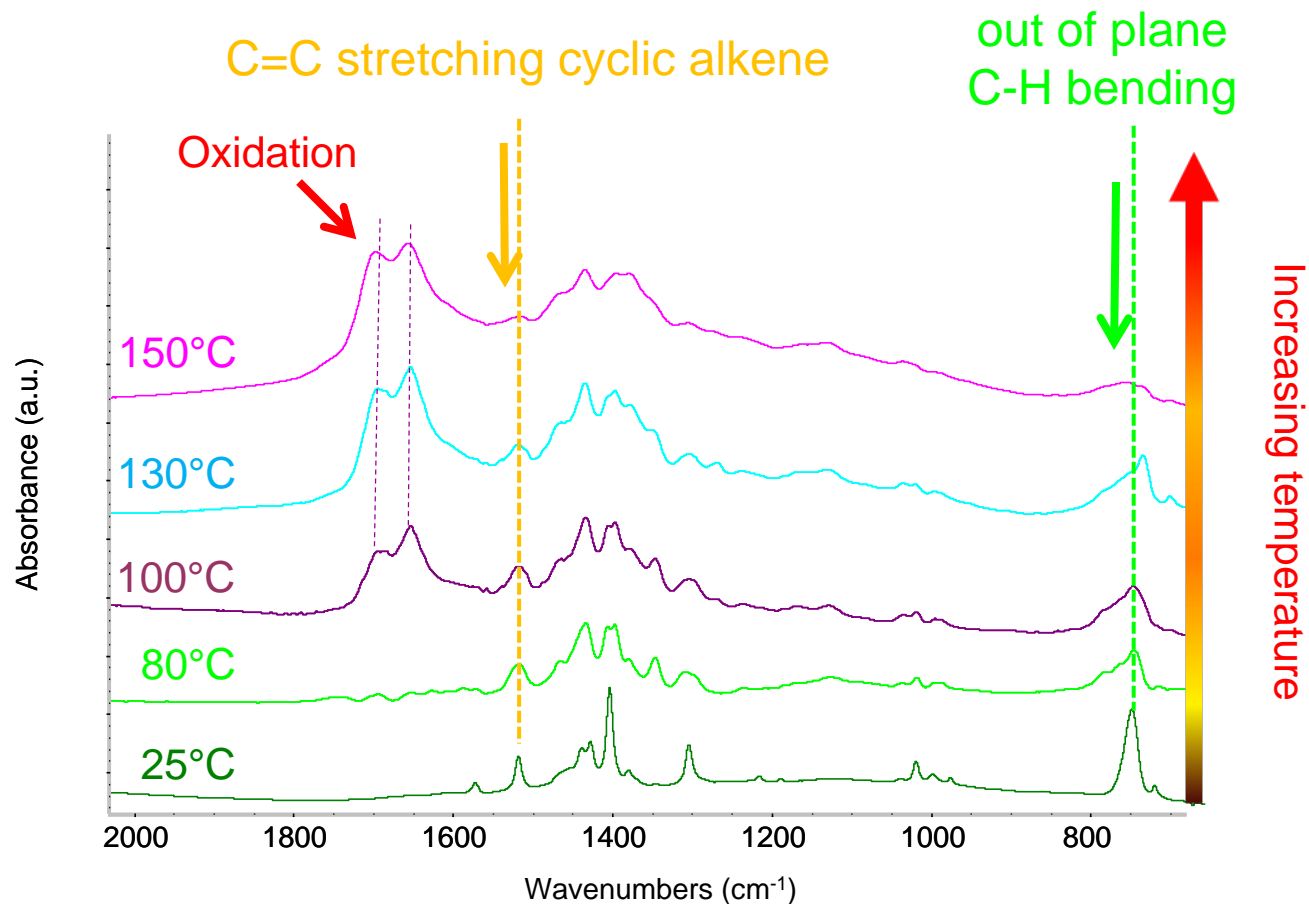


TMP + HSAG 1% - @ 150°C



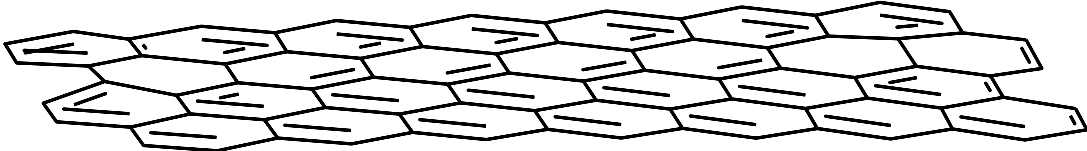
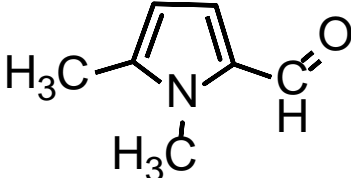
Oxidation products

Reaction products of intra-annular double bonds



TMP oxidation product

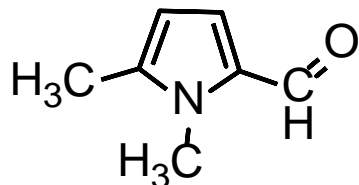
1,5-dimethyl-1*H*-pyrrole-2-carbaldehyde



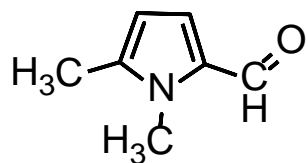
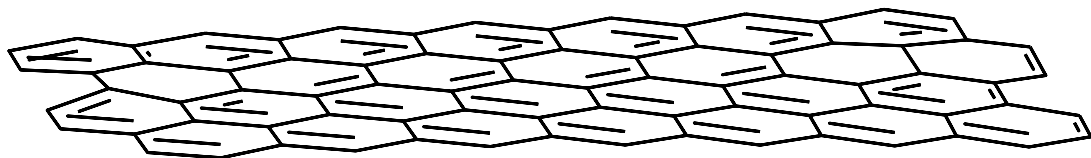
V. Barbera, L. Brambilla, M. Milani, A. Palazzolo, C. Castiglioni, A. Vitale, R. Bongiovanni, M. Galimberti, 2019. *Nanomaterials*, 9(1), p.44.

TMP oxidation product - Reaction with a model substrate

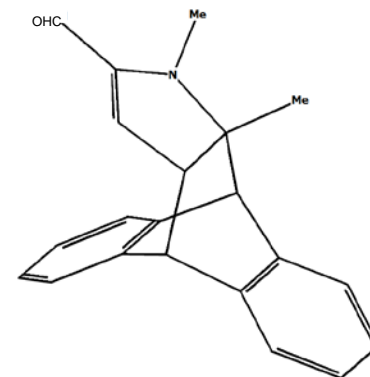
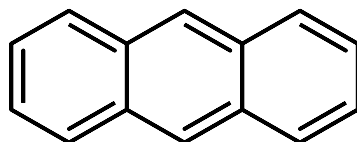
1,5-dimethyl-1*H*-pyrrole-2-carbaldehyde



?



+

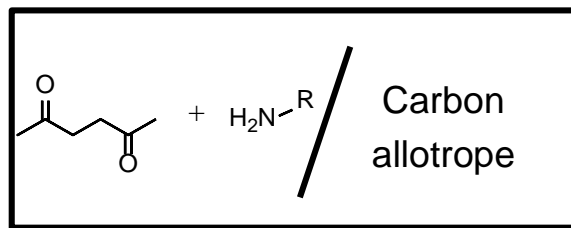


👉 FT-IR and ¹H-NMR spectroscopies

👉 FT-IR spectra generation with Density Functional Theory (DFT) quantum chemical modelling.

Facile functionalization of carbon materials

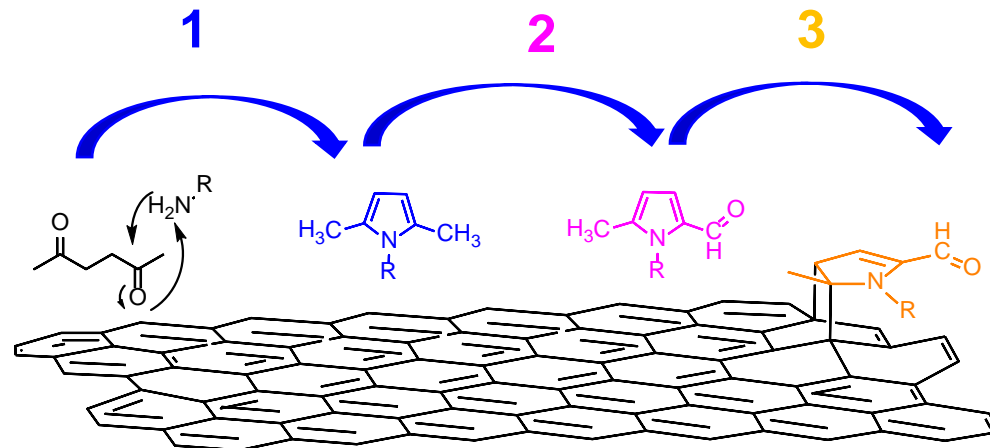
Hypothesis for the mechanism

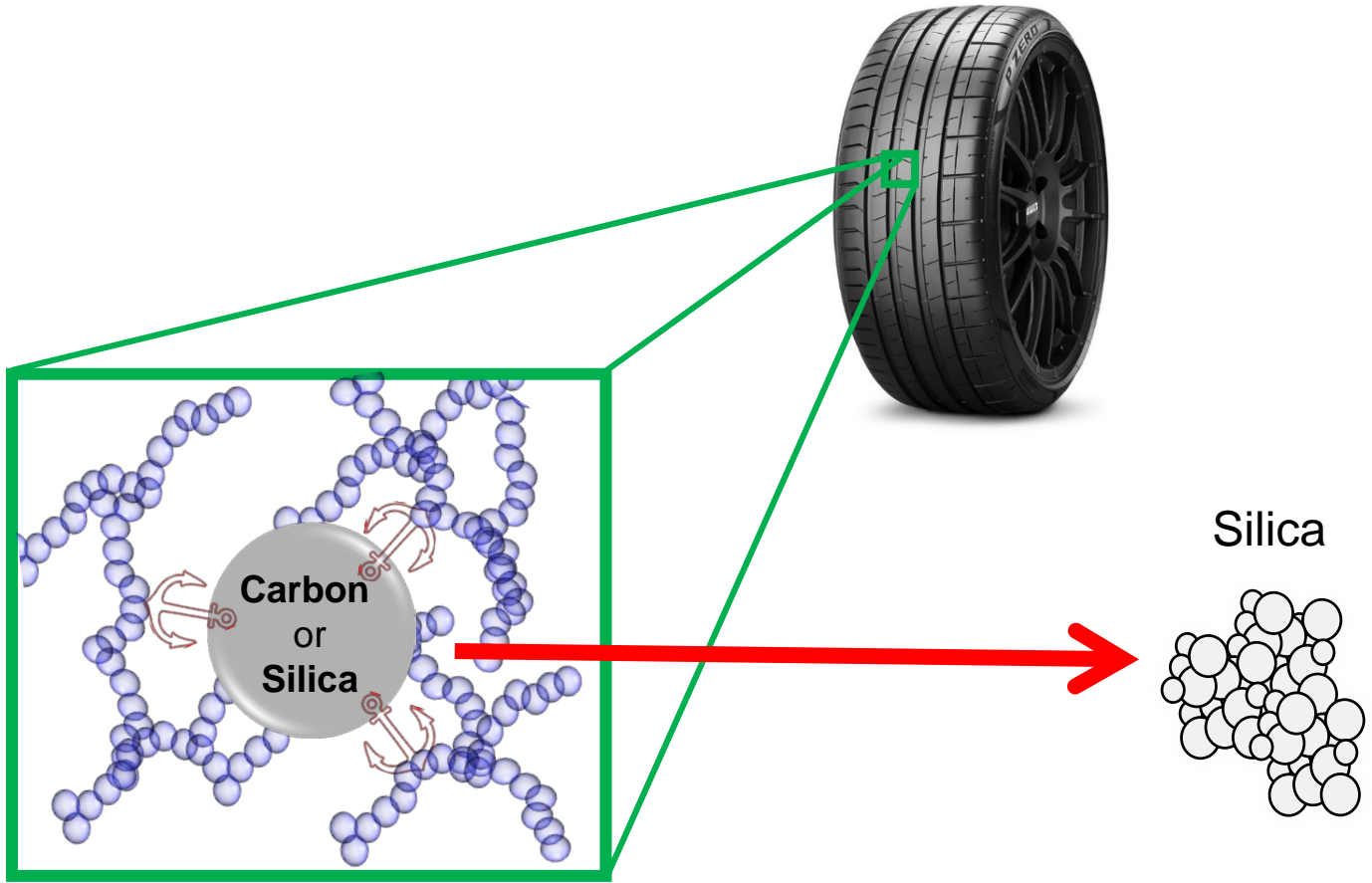


Paal – Knorr Reaction

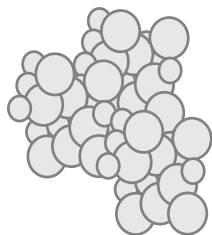
Carbocatalyzed Oxidation

Diels-Alder reaction

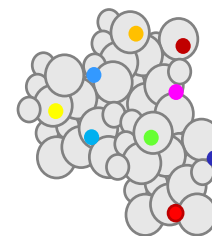




Silica

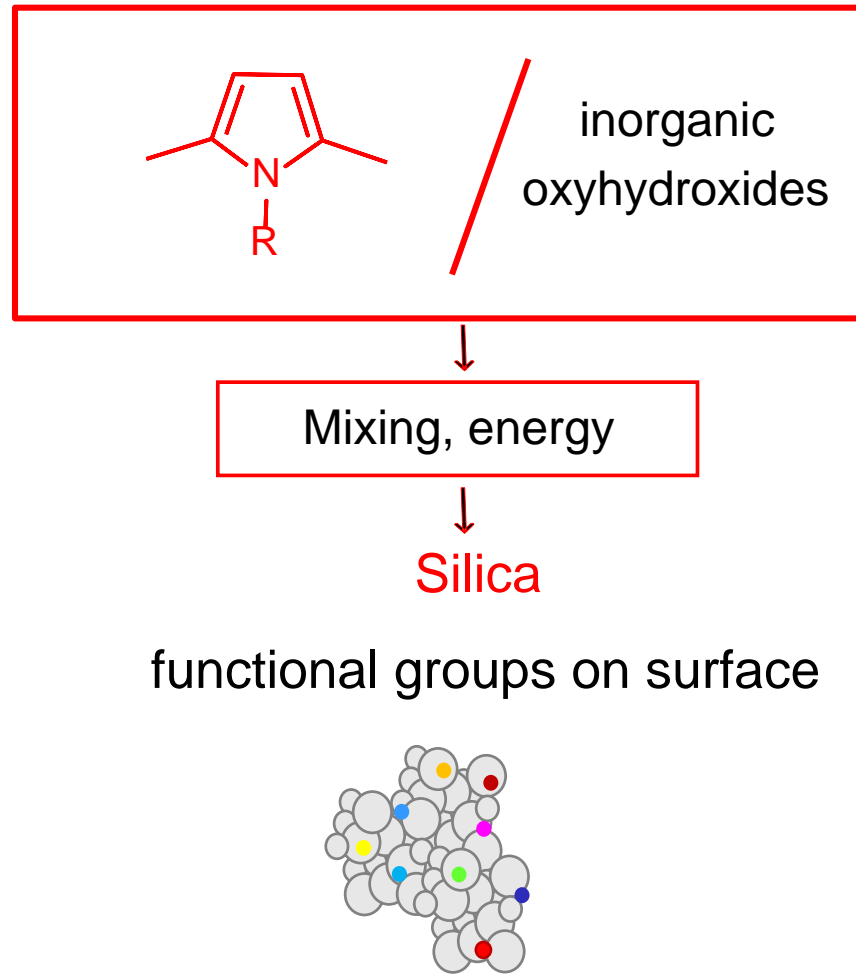


Reactive
Silica

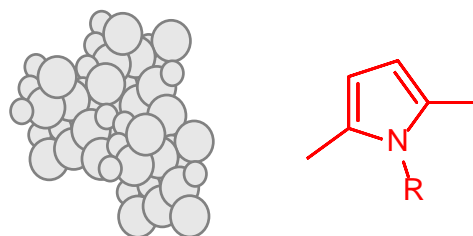


Playing with silanol chemistry

Facile functionalization of inorganic oxyhydroxides

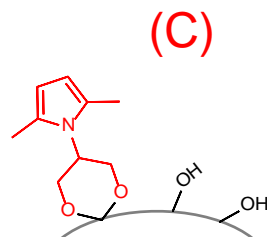
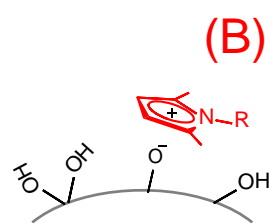
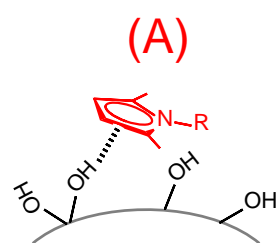


Mechanism of the functionalization reaction



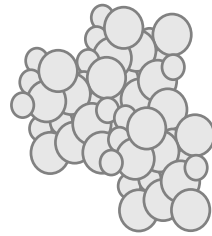
Silica

keep calm
and eat pizza

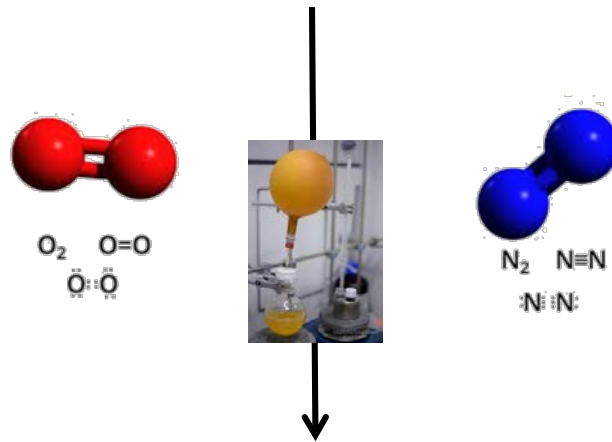
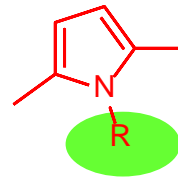


As a function of reaction temperature, time, and of reagents

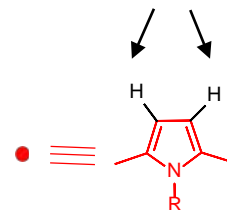
Mechanism of the functionalization reaction



Silica

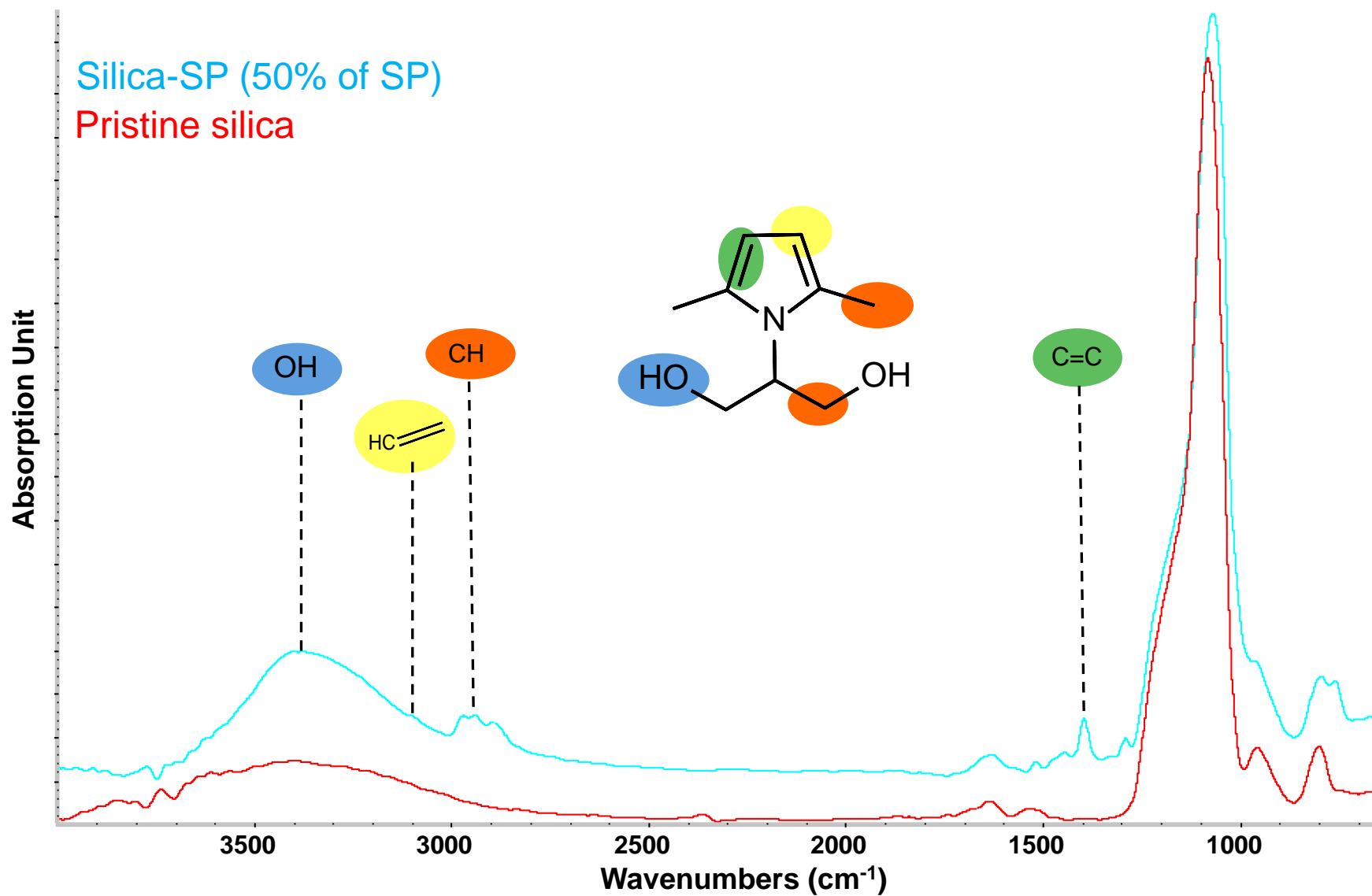


OPLA signals

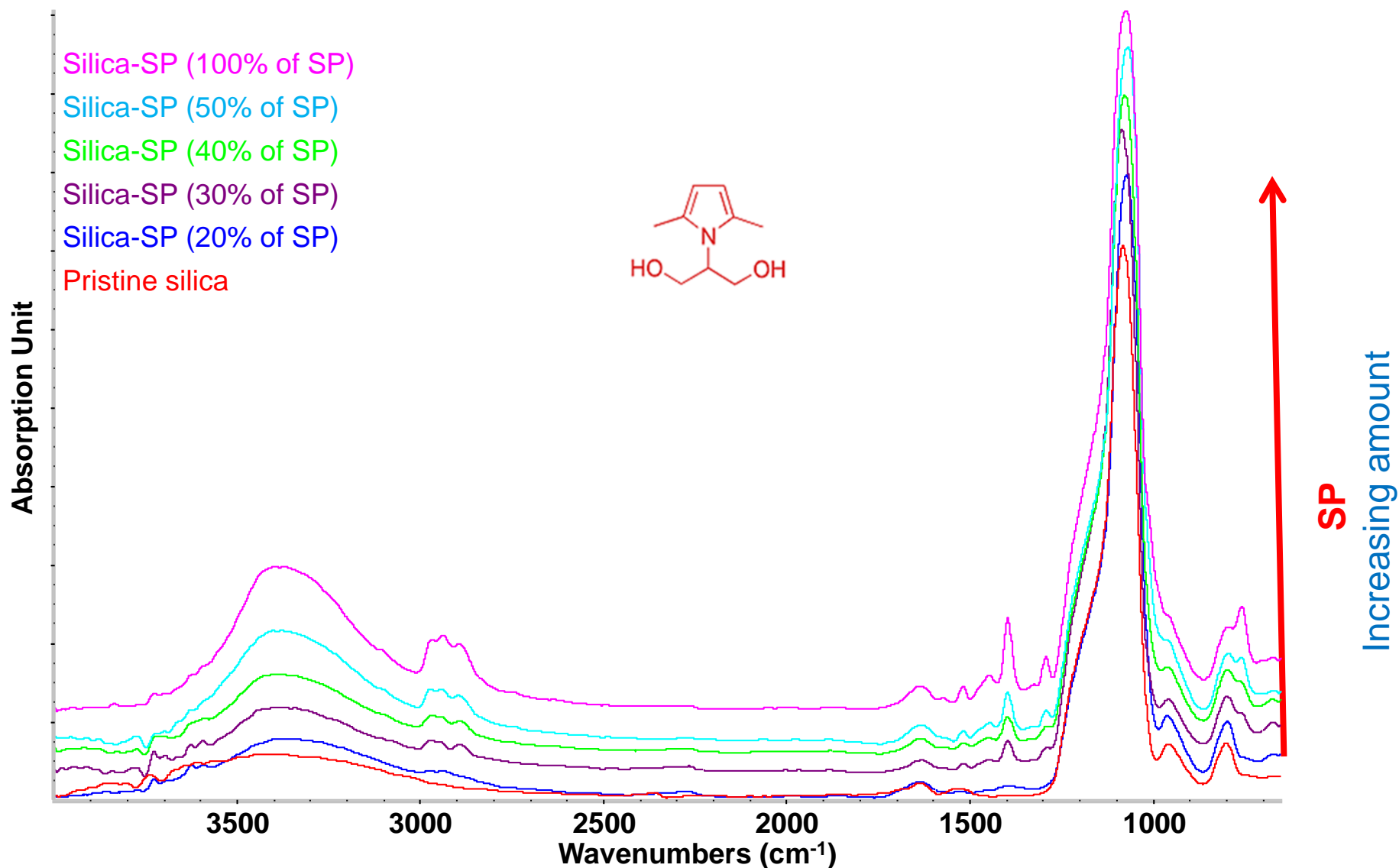


Marker bands

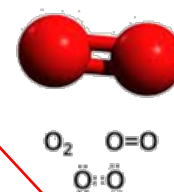
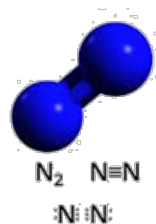
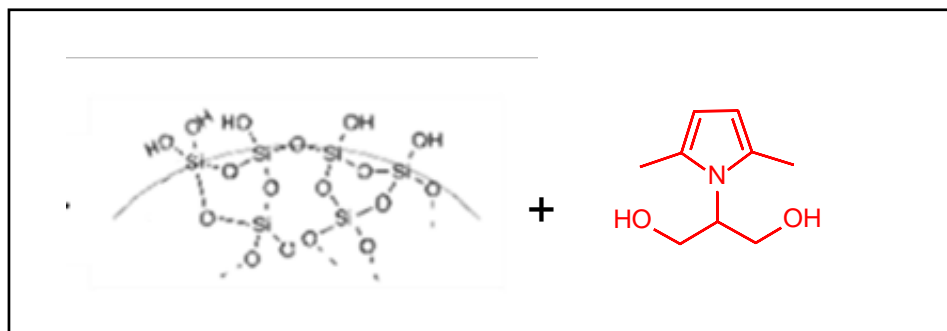
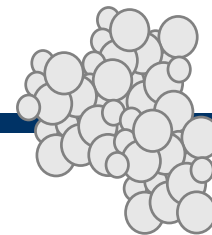
Silica + serinol pyrrole



Silica + serinol pyrrole - Physical mixture



Mechanism of the functionalization reaction



Analysis of:

☞ liquids
FT-IR, NMR, GS-MS and ESI-MS

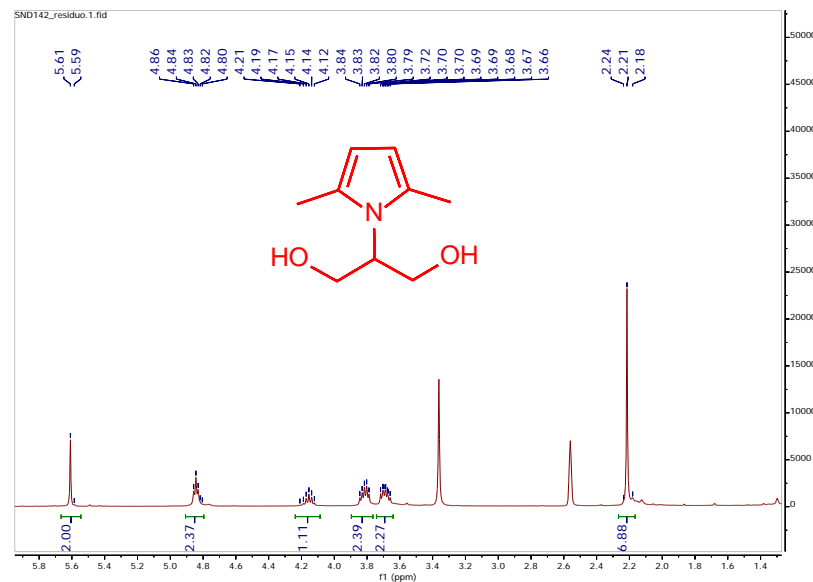
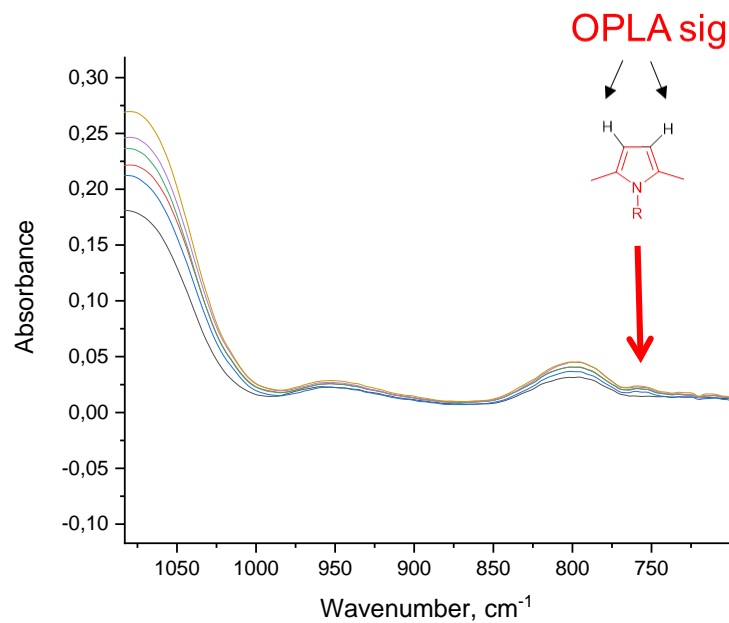
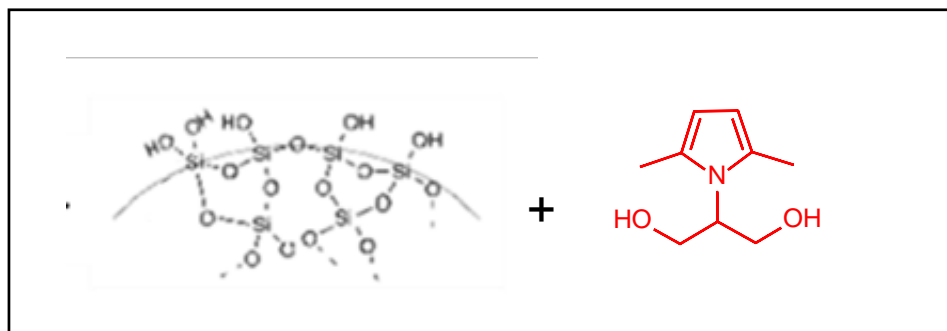
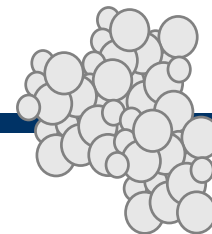
☞ Solids:
FT-IR and XPS

Analysis of:

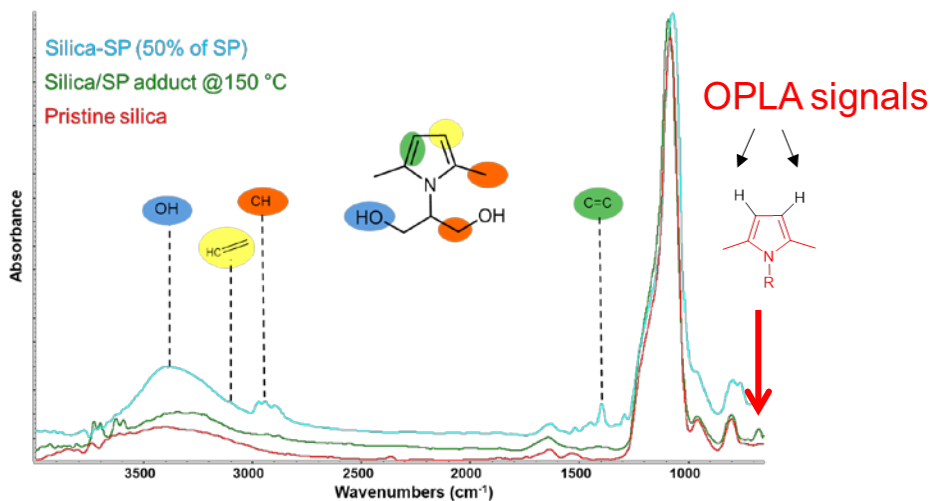
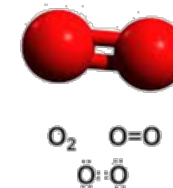
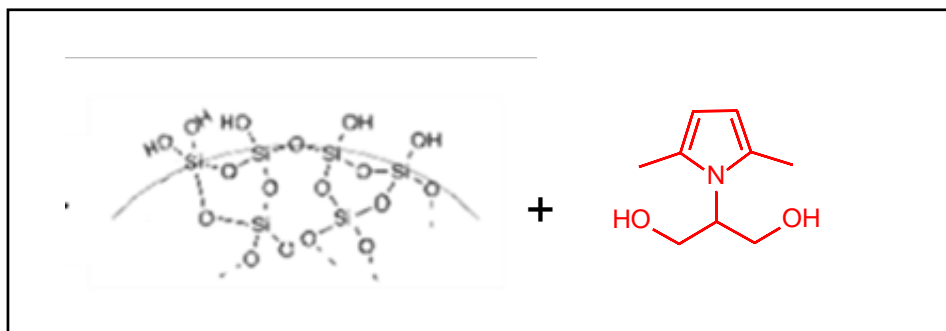
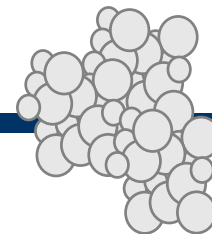
☞ liquids
FT-IR, NMR, GS-MS and ESI-MS

☞ Solids:
FT-IR and XPS

Mechanism of the functionalization reaction



Mechanism of the functionalization reaction

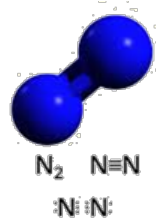
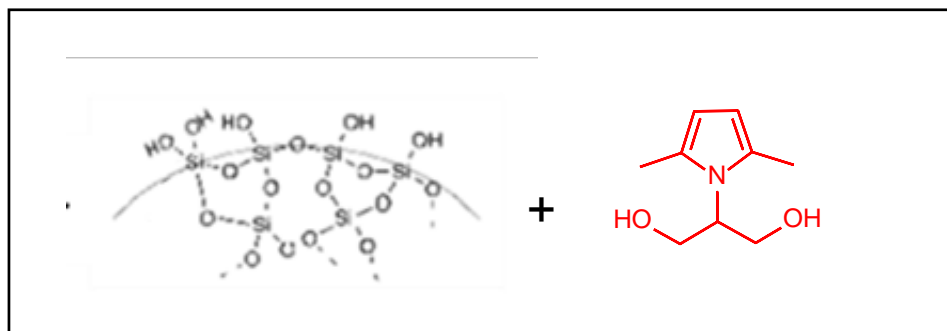
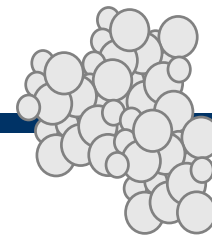


Data from high-resolution O1s spectra

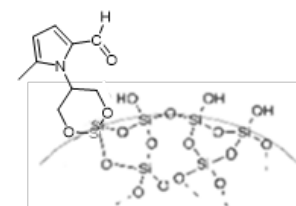
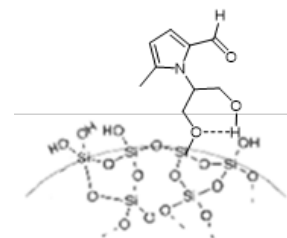
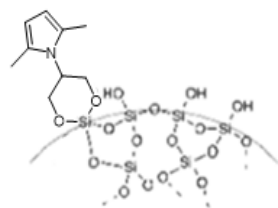
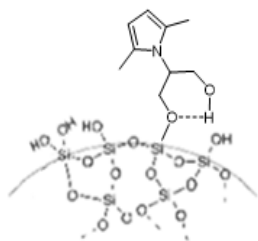
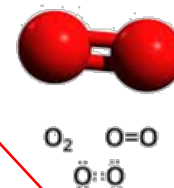
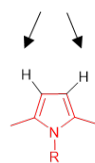
Sample	T (°C)	O ₁	O ₂	O ₃
Silica	-	11.7	88.3	0
silica/SP Adduct	150	2.7	95.0	2.3

By increasing the temperature (150 °C), the -O-H groups (O₁) decrease, the -O-Si and -O-C groups (O₂) increase. The O₃ at 530.2 eV attributed to O=C groups

Mechanism of the functionalization reaction

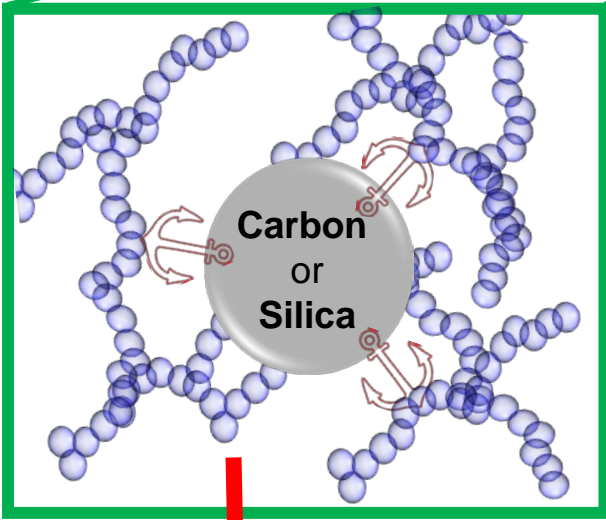


OPLA signals



Items of the presentation

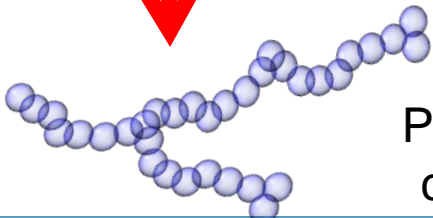
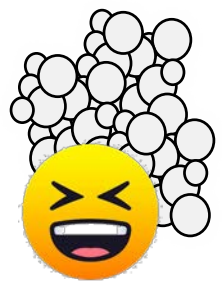
The anchor 



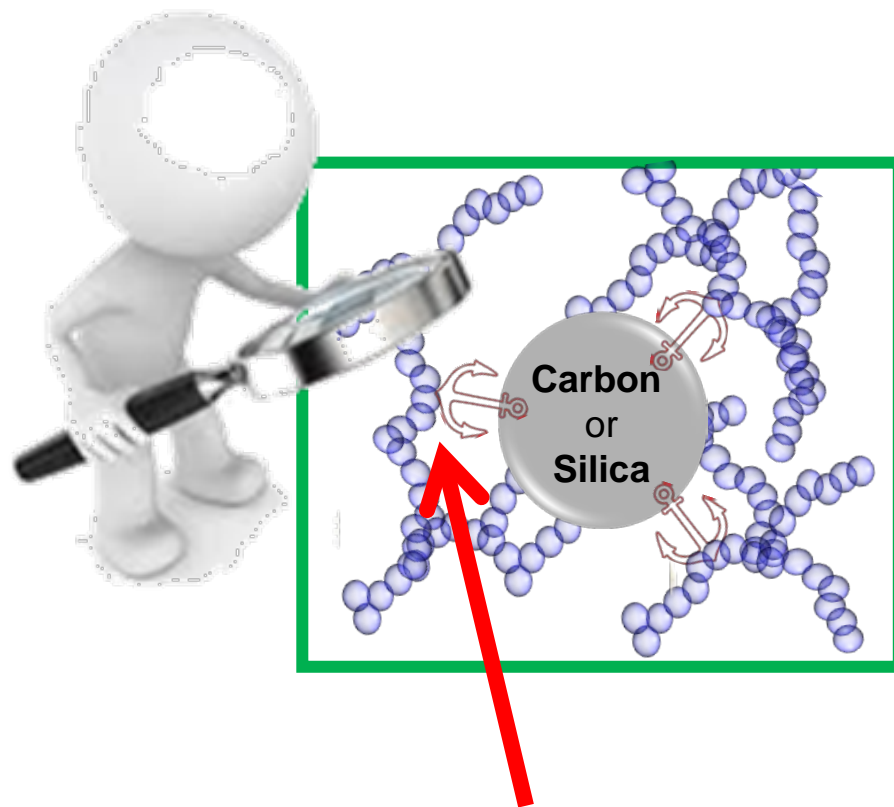
Carbon black



Silica

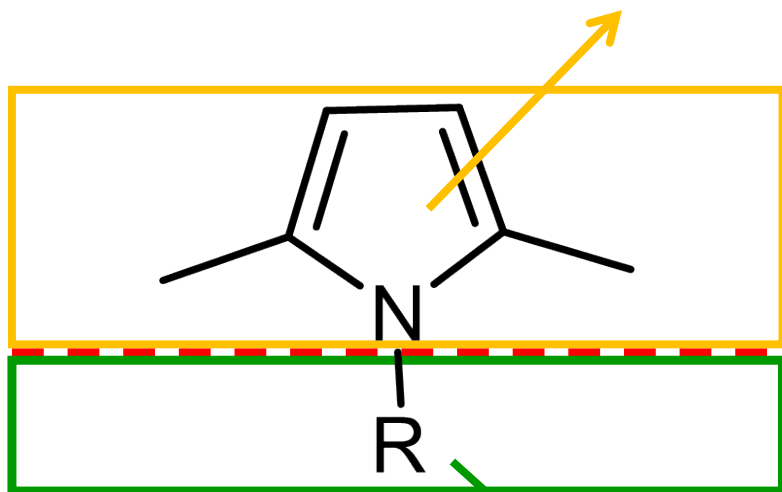
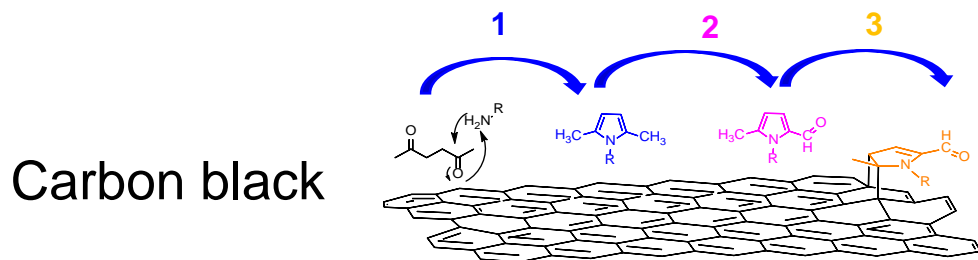


Polymer chains

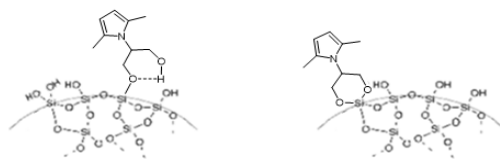


Study of the reactivity of the pyrrole ring
with sulphur, sulphur based chemicals and silanes

Reactivity of pyrrole compounds

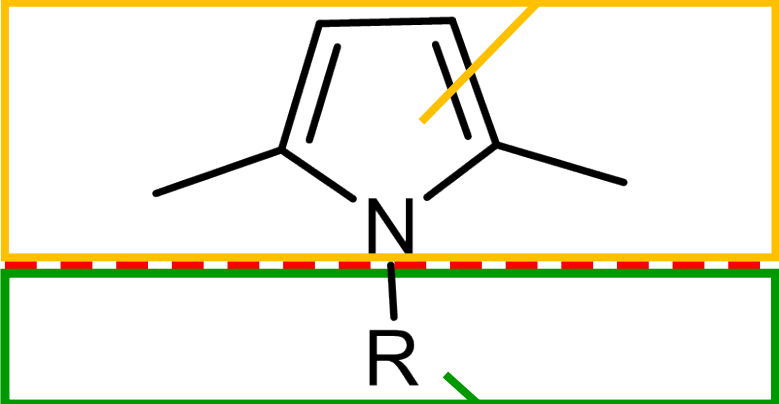
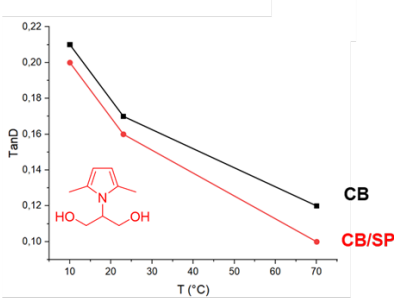
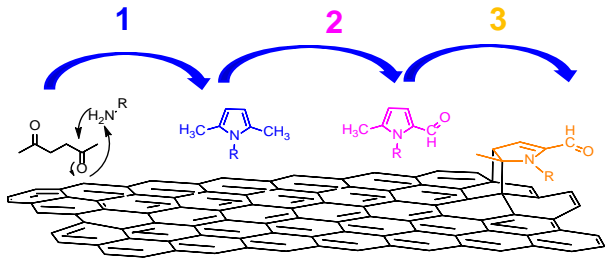


Silanols



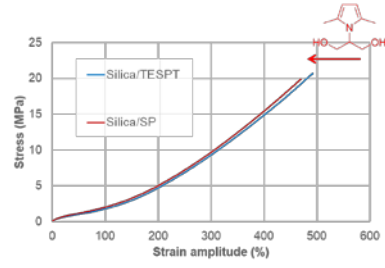
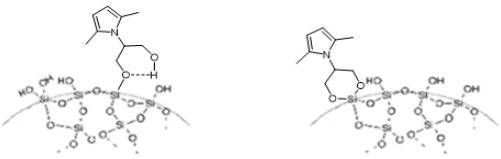
Reactivity of pyrrole compounds

Carbon black



with compound ingredients:
silanes, sulphur and sulphur based chemicals

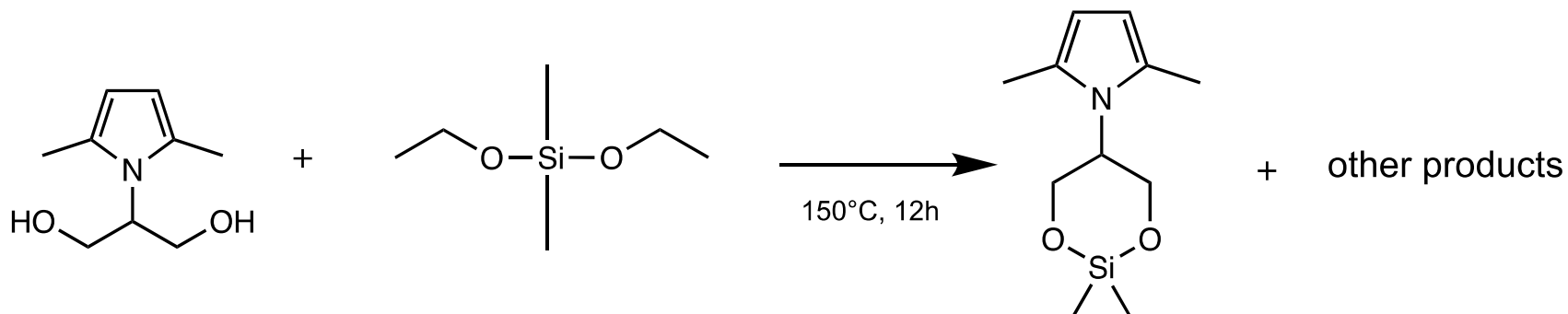
Silanols



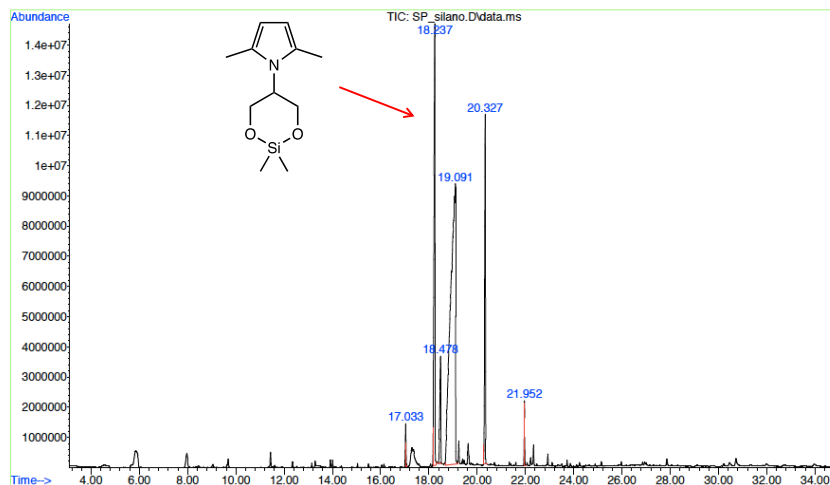
By modulating the amount of SP and of compound ingredients

Reactivity of pyrrole compounds with silanes

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



GC-MS

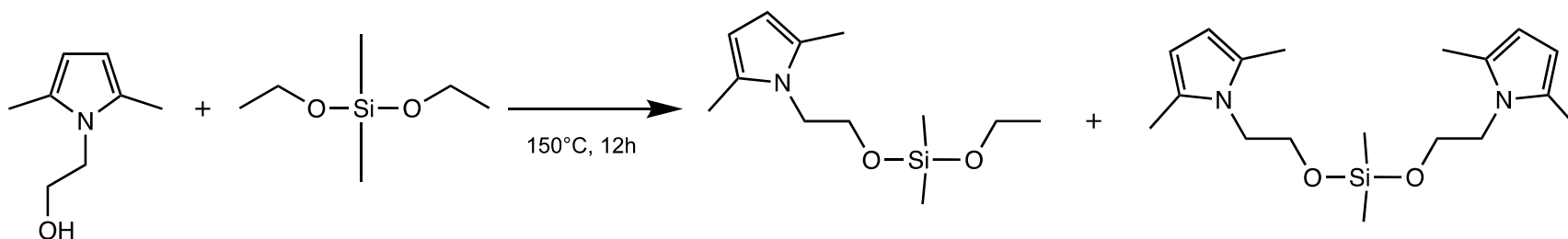


Synthesis of spiro-silicates directly from silica and ethylene glycol

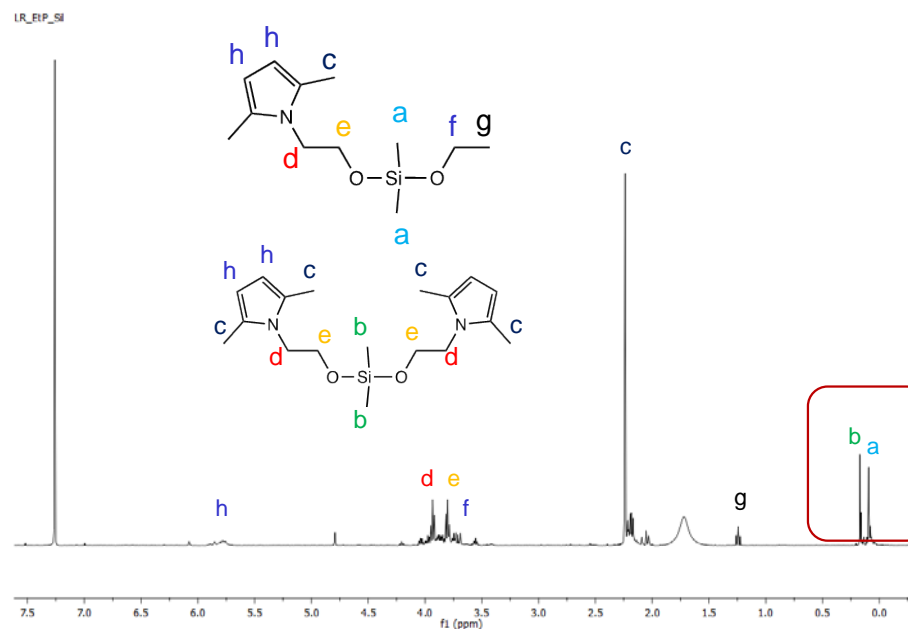
Jitchum, V., Chivin, S., Wongkasemjit, S., Ishida, H. (2001). *Tetrahedron*, 57(18), 3997-4003.

Reactivity of pyrrole compounds with silanes

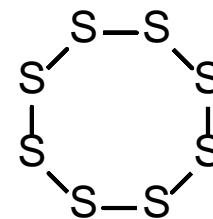
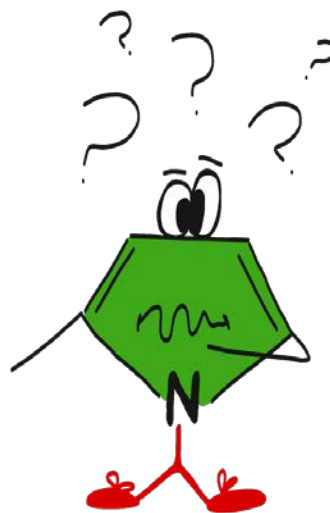
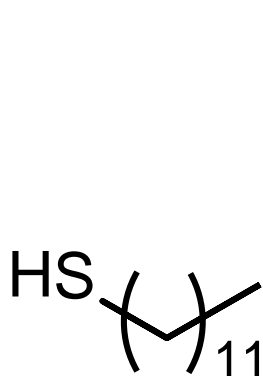
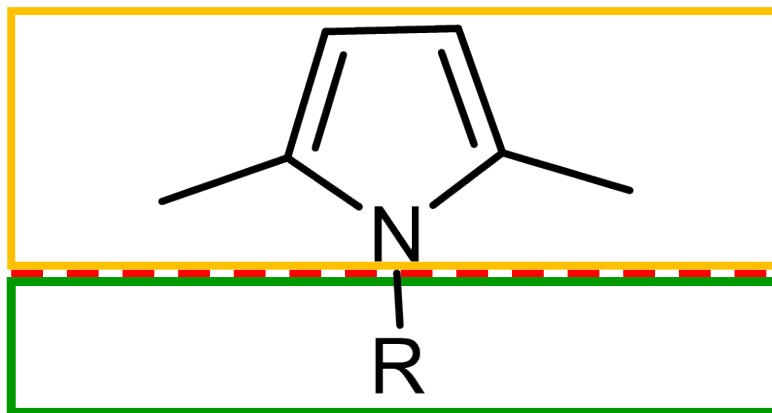
1-hexyl-2,5-dimethyl-1H-pyrrole + Diethoxydimethyl silane



1H-NMR

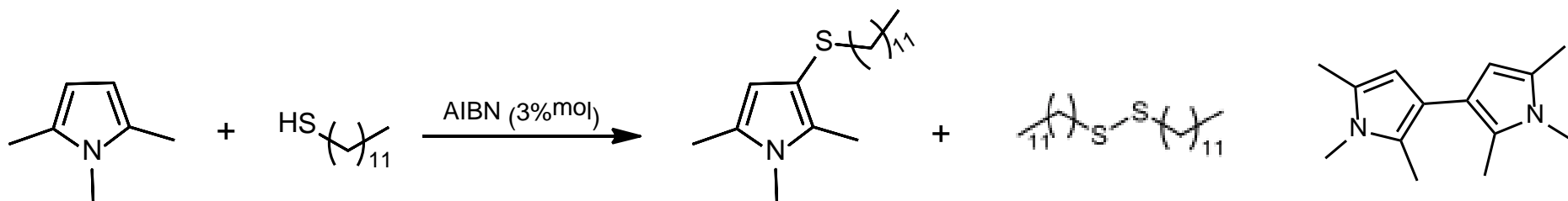


What about the reactivity with sulphur
and sulphur based chemicals?

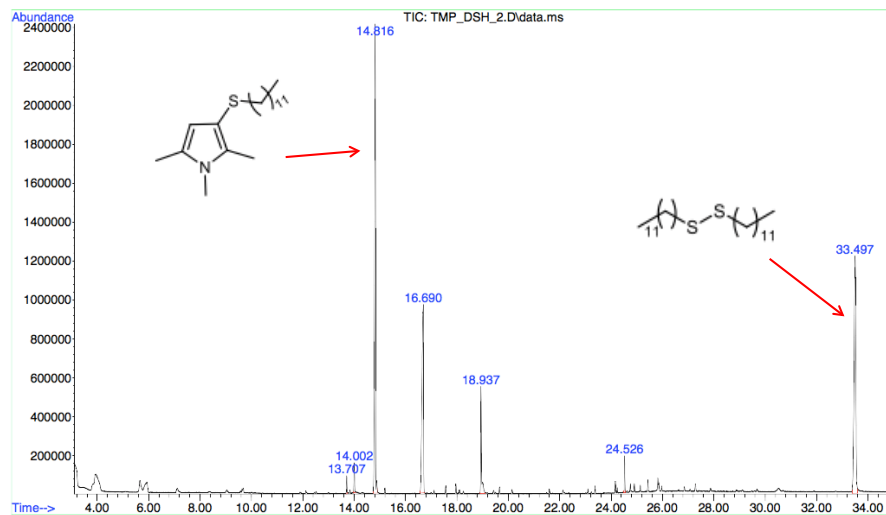


Reaction of a PyC with 1-dodecanthiol

1,2,5-trimethylpyrrole + 1-dodecanethiol

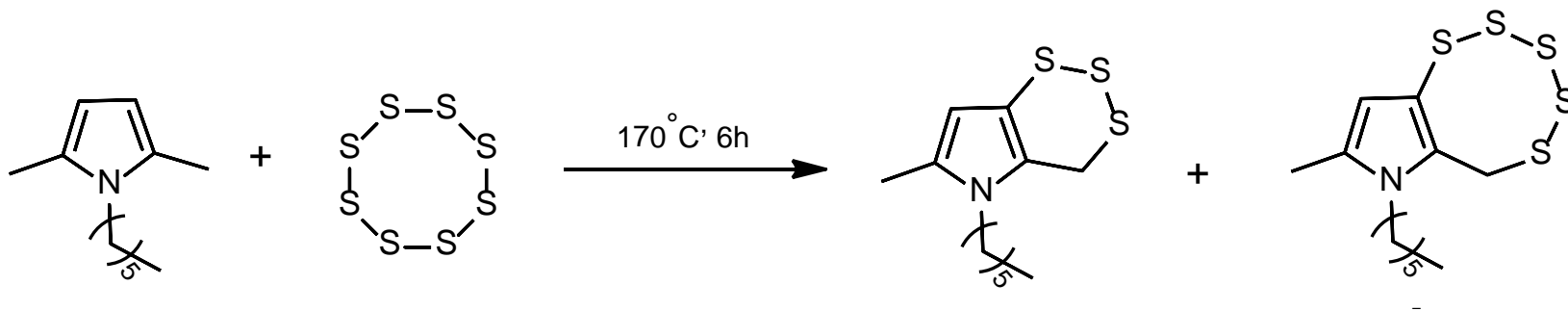


GC-MS

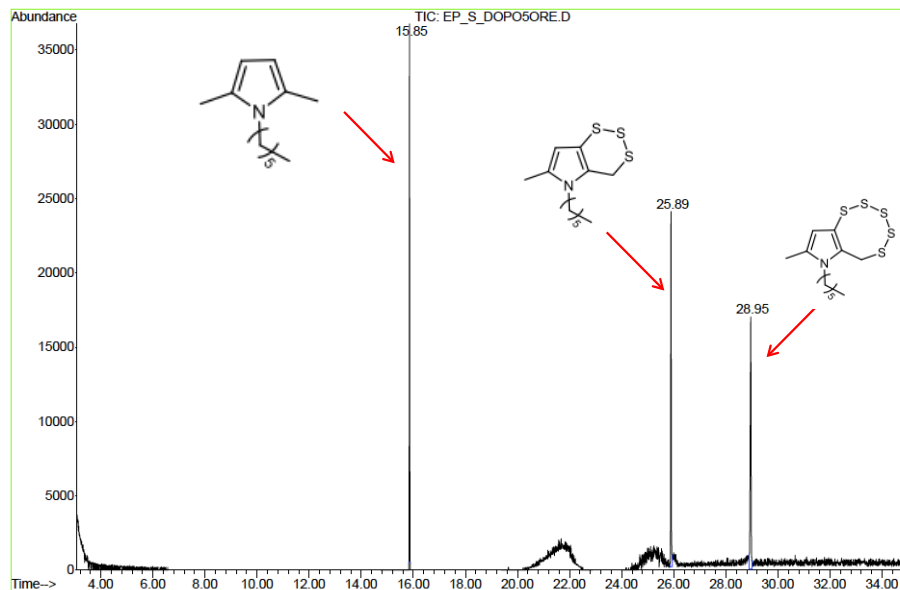


AIBN = 2-2'-azaisobutyronitrile

Reaction of a PyC with sulphur

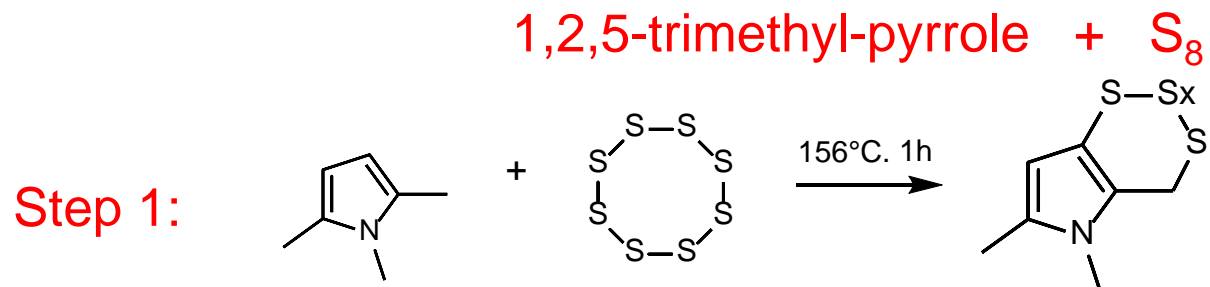


GC-MS



Zhang, J., Song, C., Sheng, L., Liu, P., & Sun, P. *The Journal of organic chemistry*, 84(4), 2191-2199 (2019).
Deng, J. C., Gao, Y. C., Zhu, Z., Xu, L., Li, Z. D., & Tang, R. Y. *Organic letters*, 21(2), 545-548 (2018).

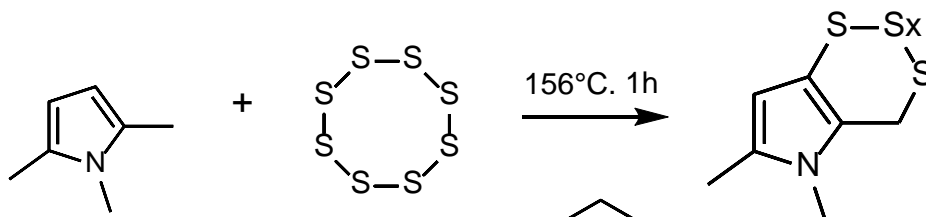
Reaction of a PyC with sulphur



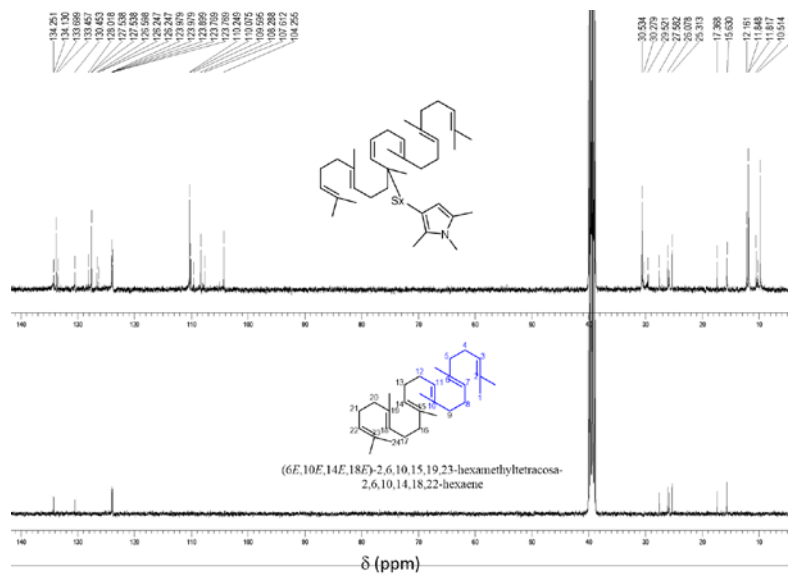
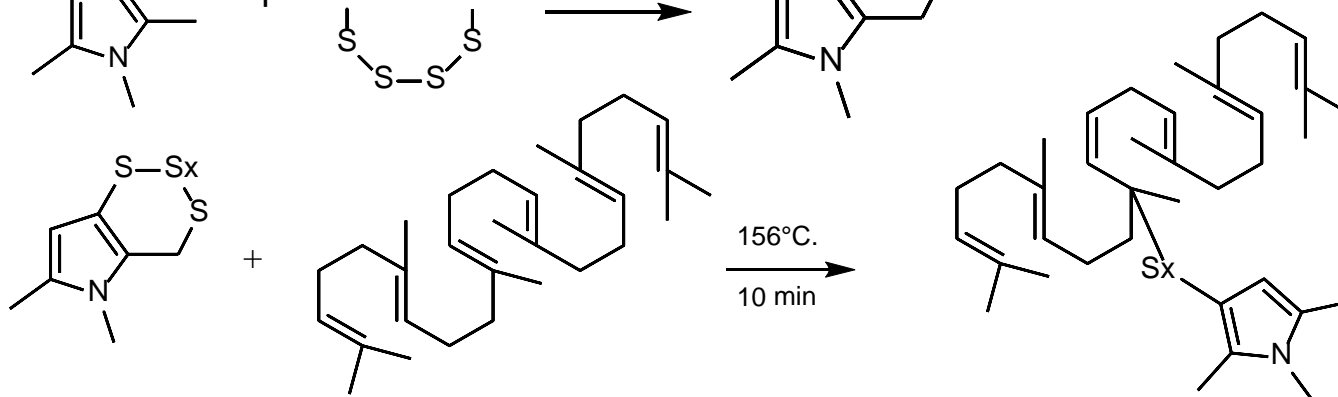
Reaction of a PyC with sulphur

1,2,5-trimethyl-pyrrole + S₈

Step 1:



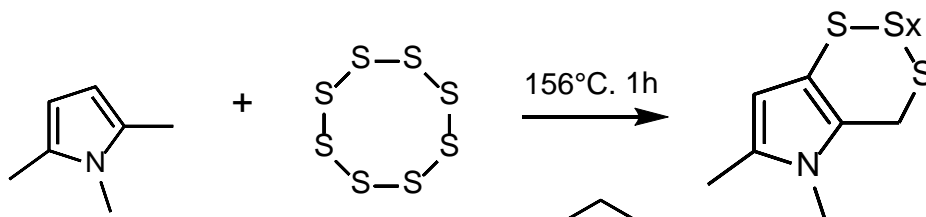
Step 2:



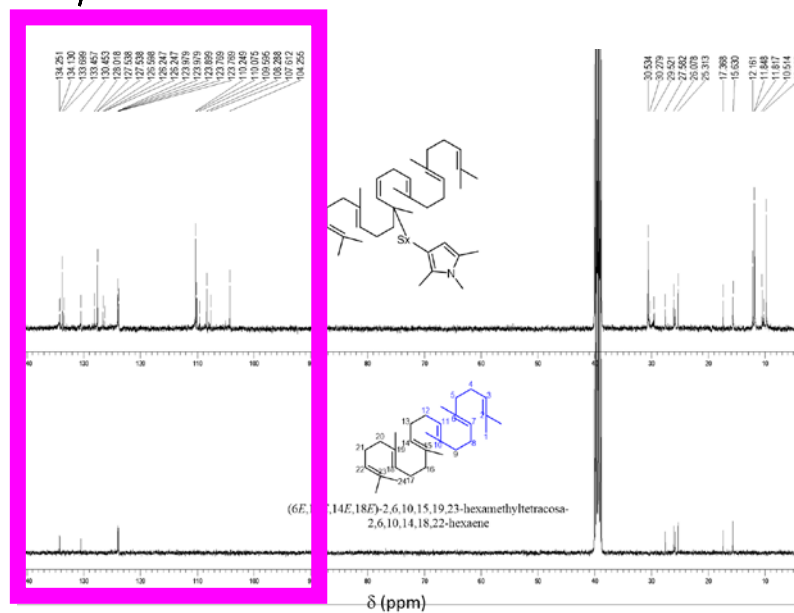
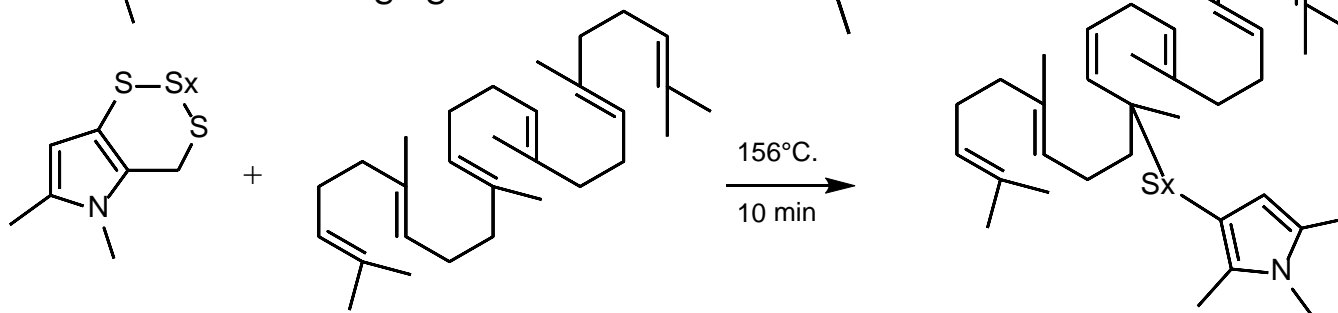
Reaction of a PyC with sulphur

1,2,5-trimethyl-pyrrole + S₈

Step 1:

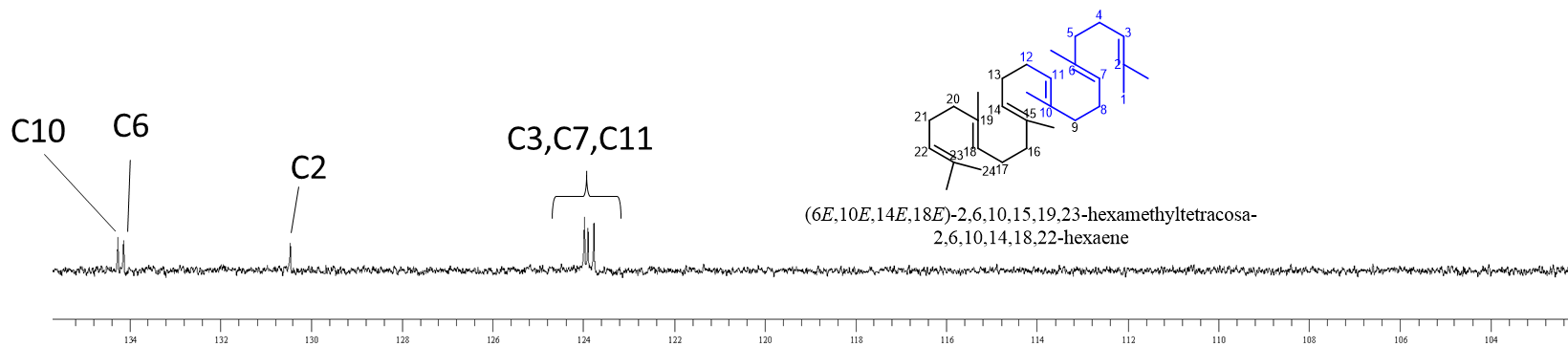


Step 2:



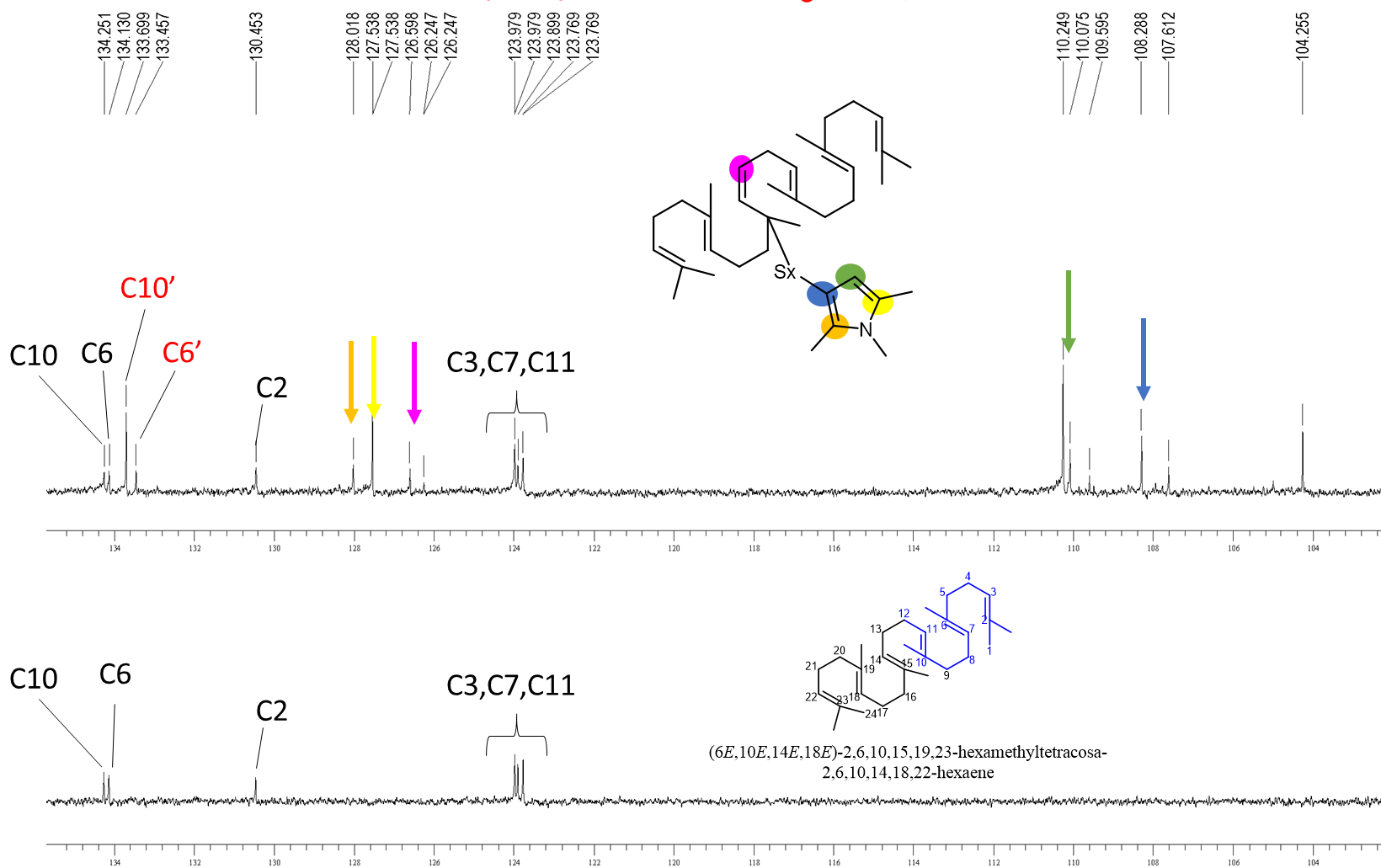
Reaction of a PyC with sulphur

1,2,5-trimethyl-pyrrole + S₈ + squalene

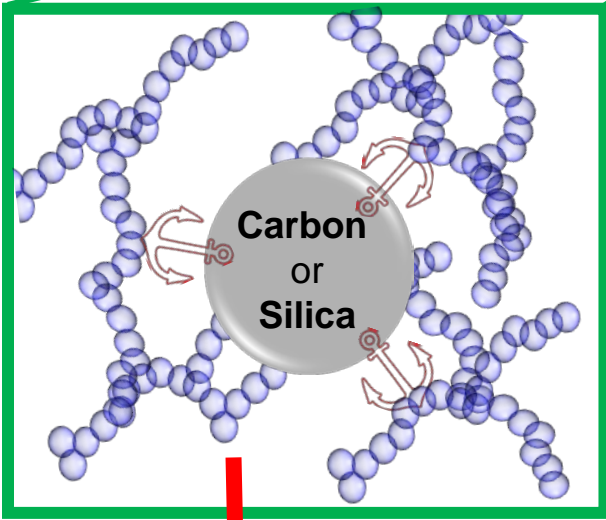


Reaction of a PyC with sulphur

1,2,5-trimethyl-pyrrole + S₈ + squalene



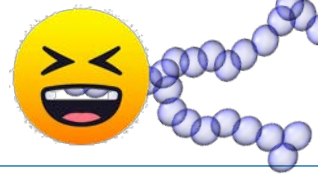
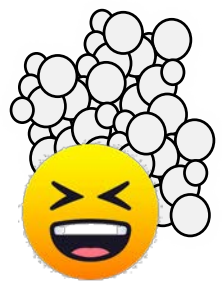
The anchor 



Carbon black



Silica

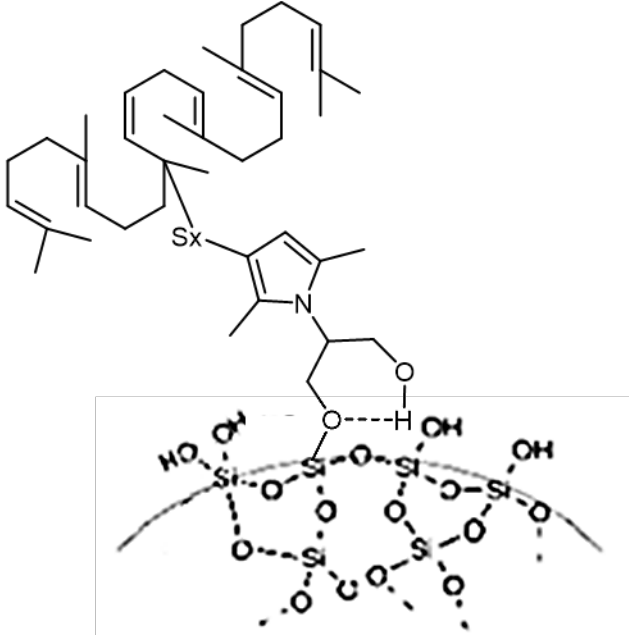
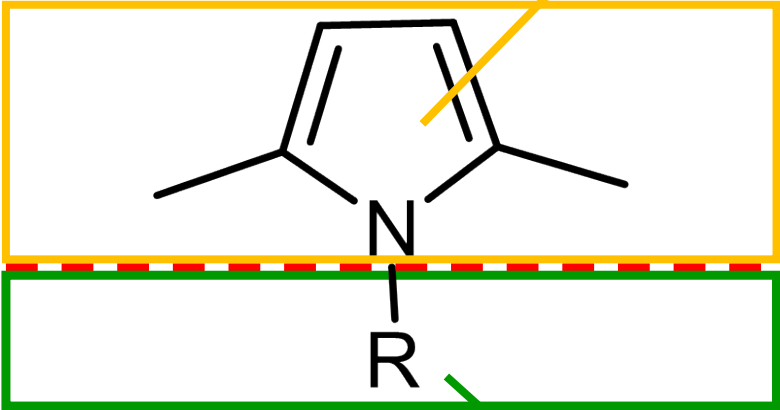
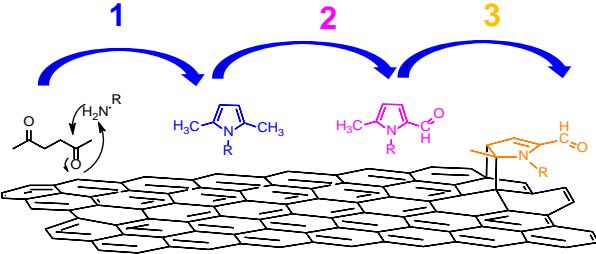


Polymer chains

Conclusions

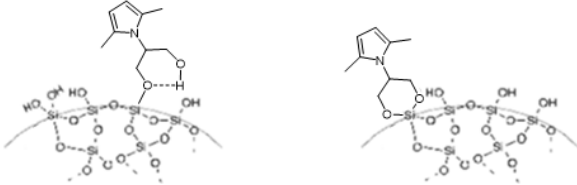


Carbon black



Coupling agent

Silanols



Acknowledgments

👉 **Pirelli Tyre for the financial support.**

Pirelli Tyre; Annual Report: The Human Dimension. 2020, 106.

https://corporate.pirelli.com/var/files2020/EN/PDF/PIRELLI_ANNUAL_REPORT_2020_ENG.pdf



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Germany, November 2022, 8 - 10

