
# Domino Reaction for the Controlled Functionalization of $sp^2$ Carbon Allotropes

Vincenzina Barbera

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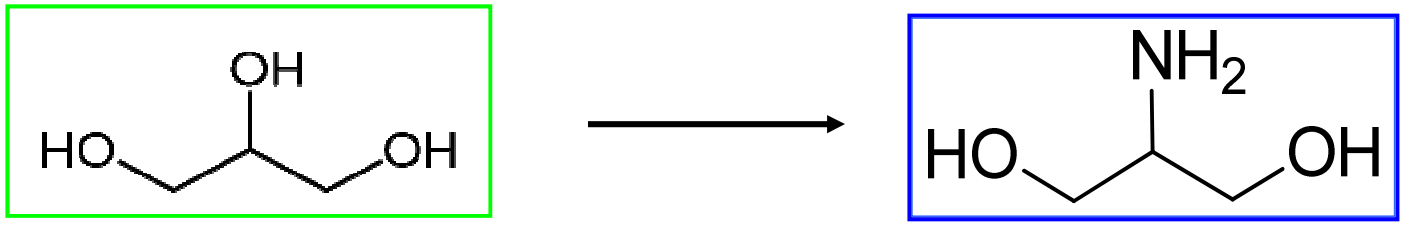
Innovative Sustainable Chemistry and Materials and Proteomics Group

# Chemistry from biobased C-3 platform



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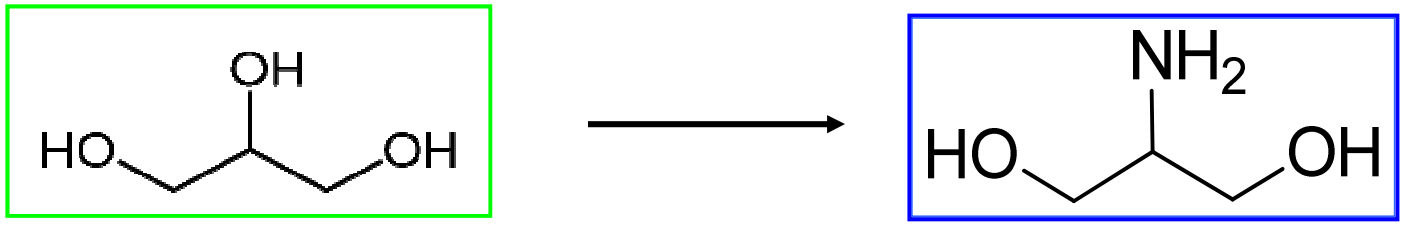
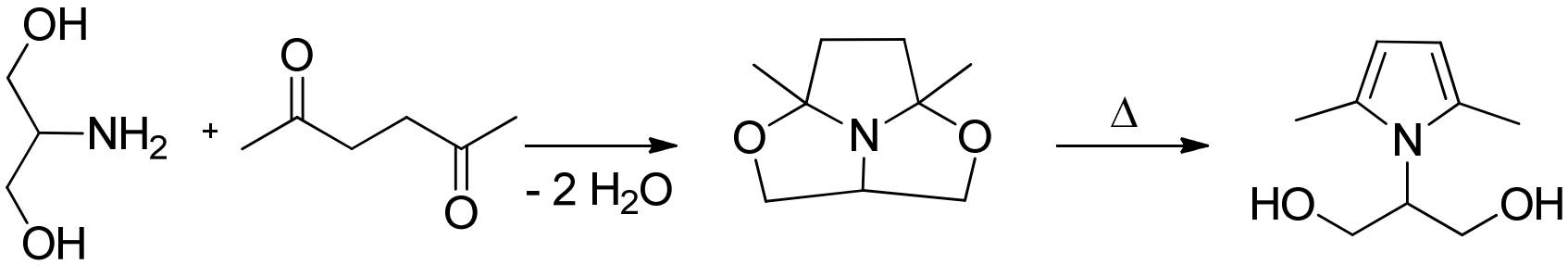


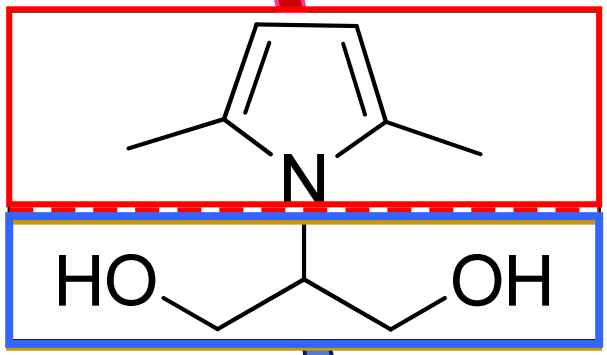




- Yield: at least 96%
- Atom efficiency: 85%
- Easy procedure
- No solvent
- By product: $H_2O$

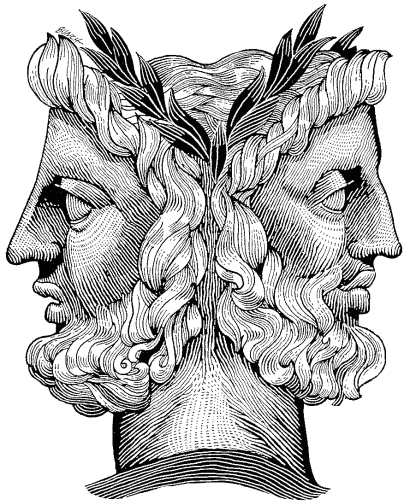
V. Barbera, A. Citterio, M. Galimberti, G. Leonardi, R. Sebastiano, S.U. Shisodia, A.M. Valerio. WO/2015/189411 A1 (2015)

# Serinolpyrrole: *Janus* molecule

INTERACTION WITH GRAPHITIC CARBONS




INTERACTION WITH POLAR SURROUNDING



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

graphene

stacked

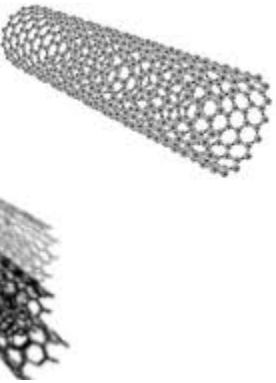
wrapped

stacked graphene layers

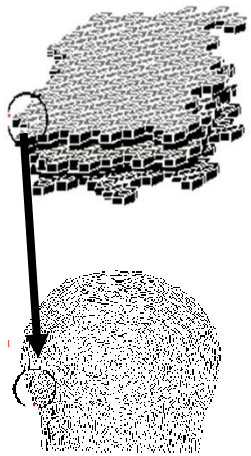
randomly arranged

with different shape anisotropy

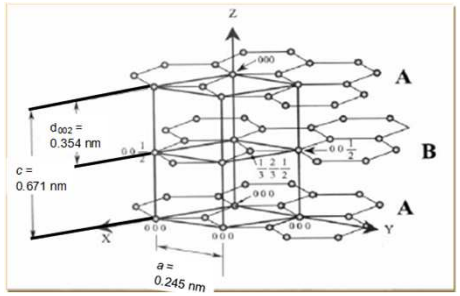
CNT



carbon black

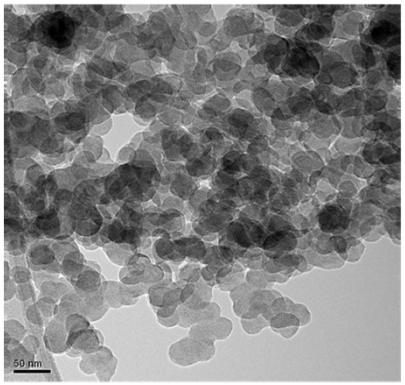


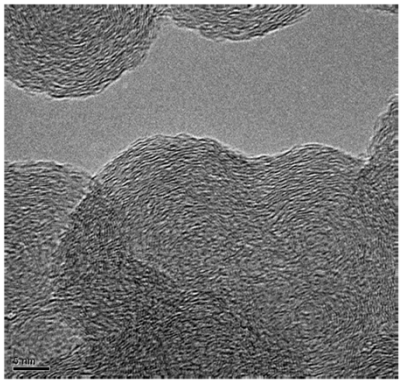
graphite,
nano-graphite,
graphene



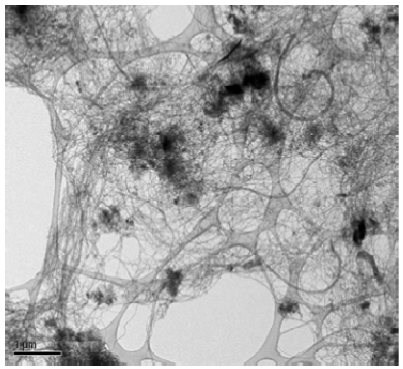
# Characterization of carbon allotropes (CA)

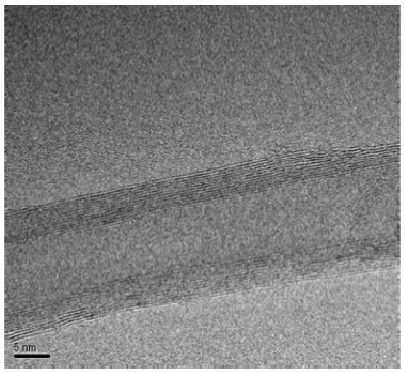
CB



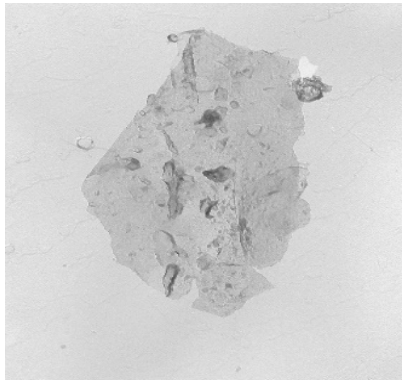


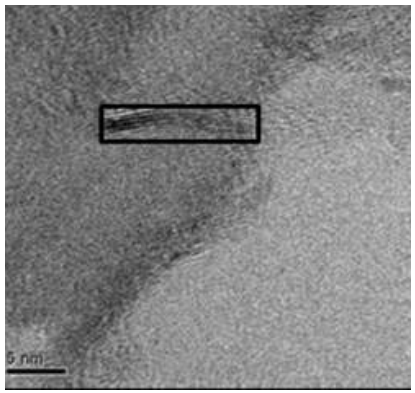
CNT





FEW LAYERS GRAPHENE





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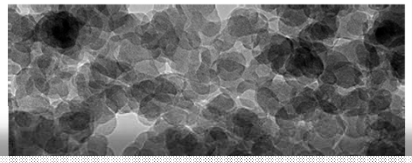

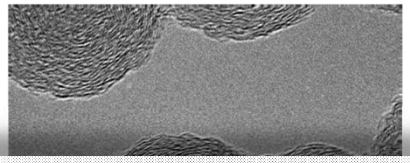

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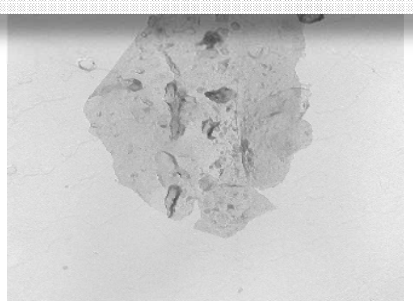
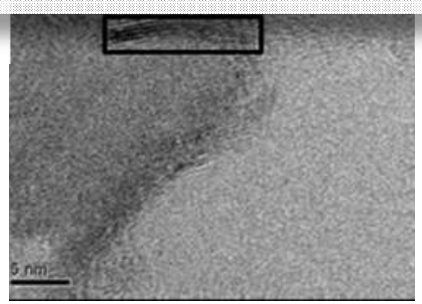





TGA, Elemental Analysis: carbon purity

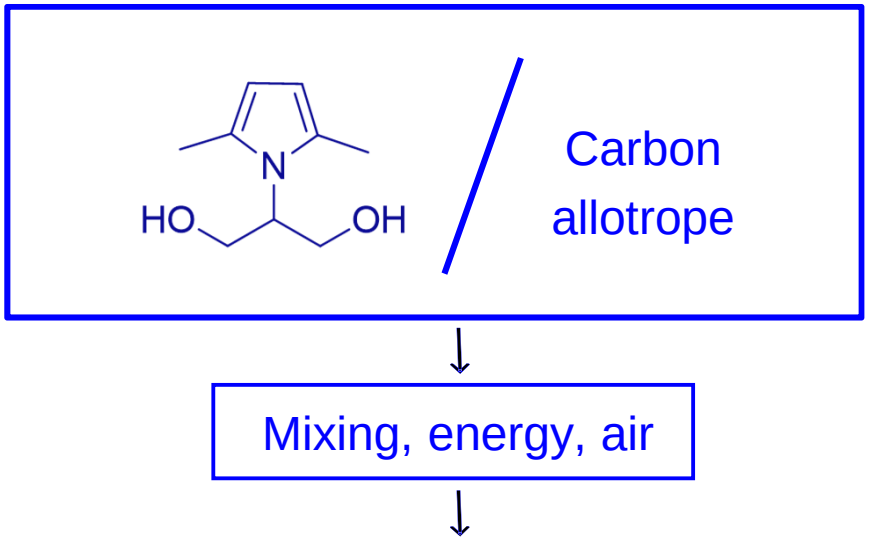
BET: surface area, activity

Infrared, XPS: functional groups

Raman, X-ray: bulk structure

TEM, HRTEM: morphology

# Facile functionalization of carbon materials




Oxygenated functional groups

on carbon allotrope surface

Bulk structure

substantially unaltered

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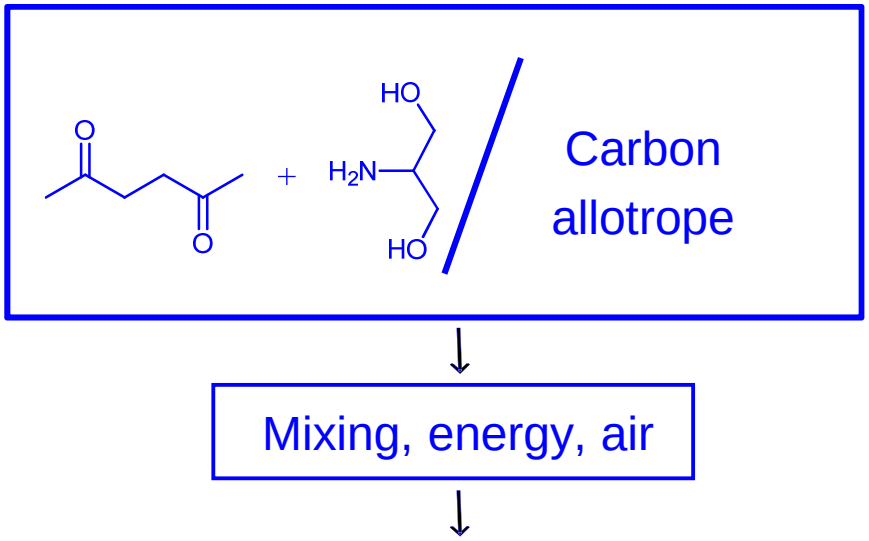


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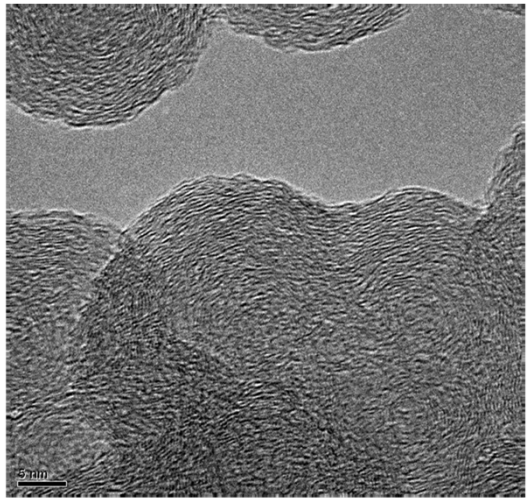
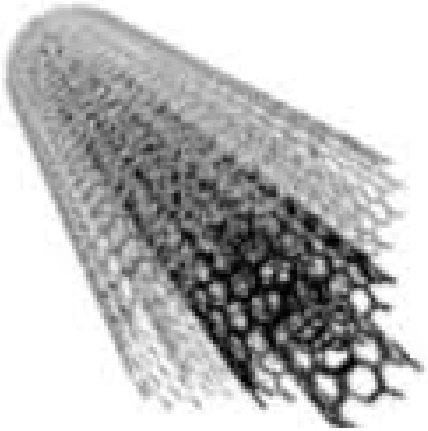
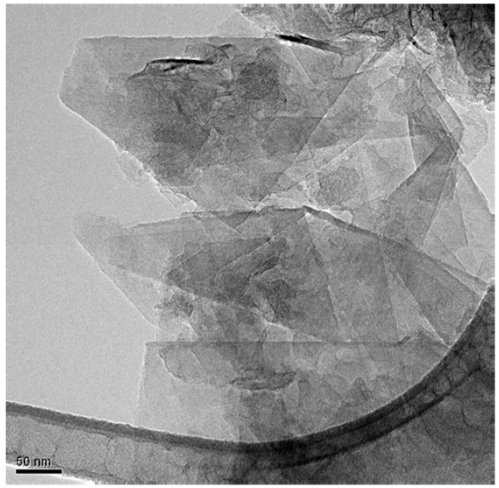
# High yield functionalization!

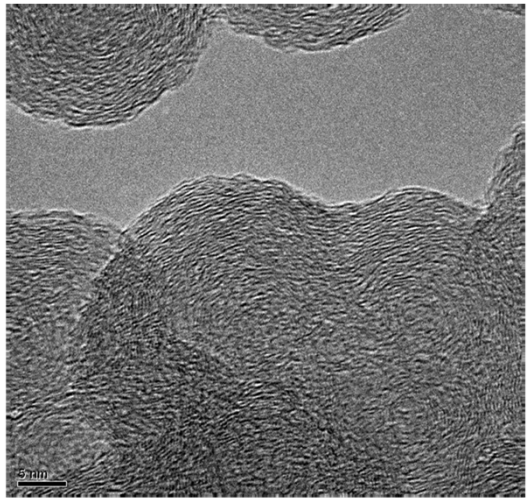


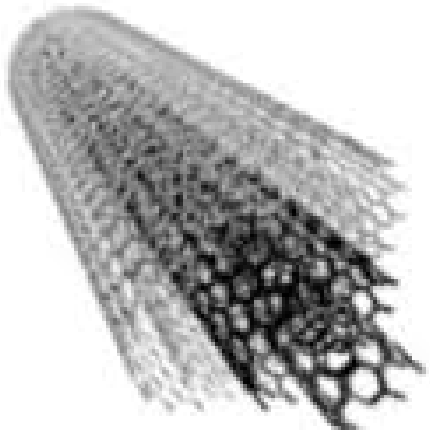


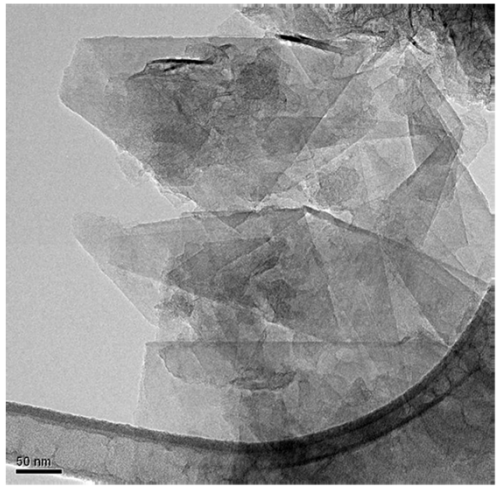


| | | | |
|---|---|---|---|
| Yield: | 86 % | 97 % | 98 % |
| BET Surface area: | 77 $m^2/g$ | 275 $m^2/g$ | 300 $m^2/g$ |

# High yield functionalization!







| | | | |
|---|---|---|---|
| Yield: | 86 % | 97 % | 98 % |
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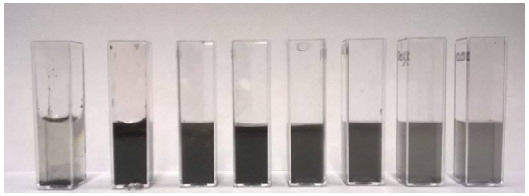
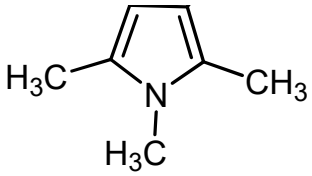
High surface area graphite

HSAG

HSAG water suspensions from 1 to 0.01 mg/mL

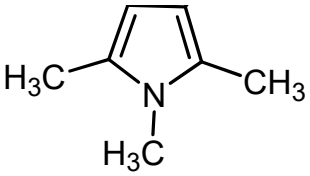


# Mechanistic investigation

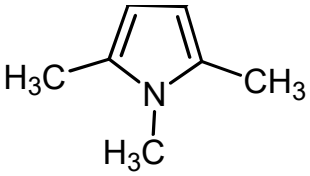



Model compound

# Mechanistic investigation

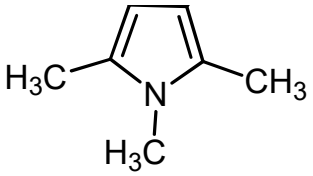



Model compound




In air

Thermal energy

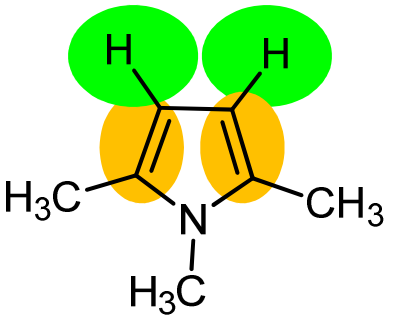


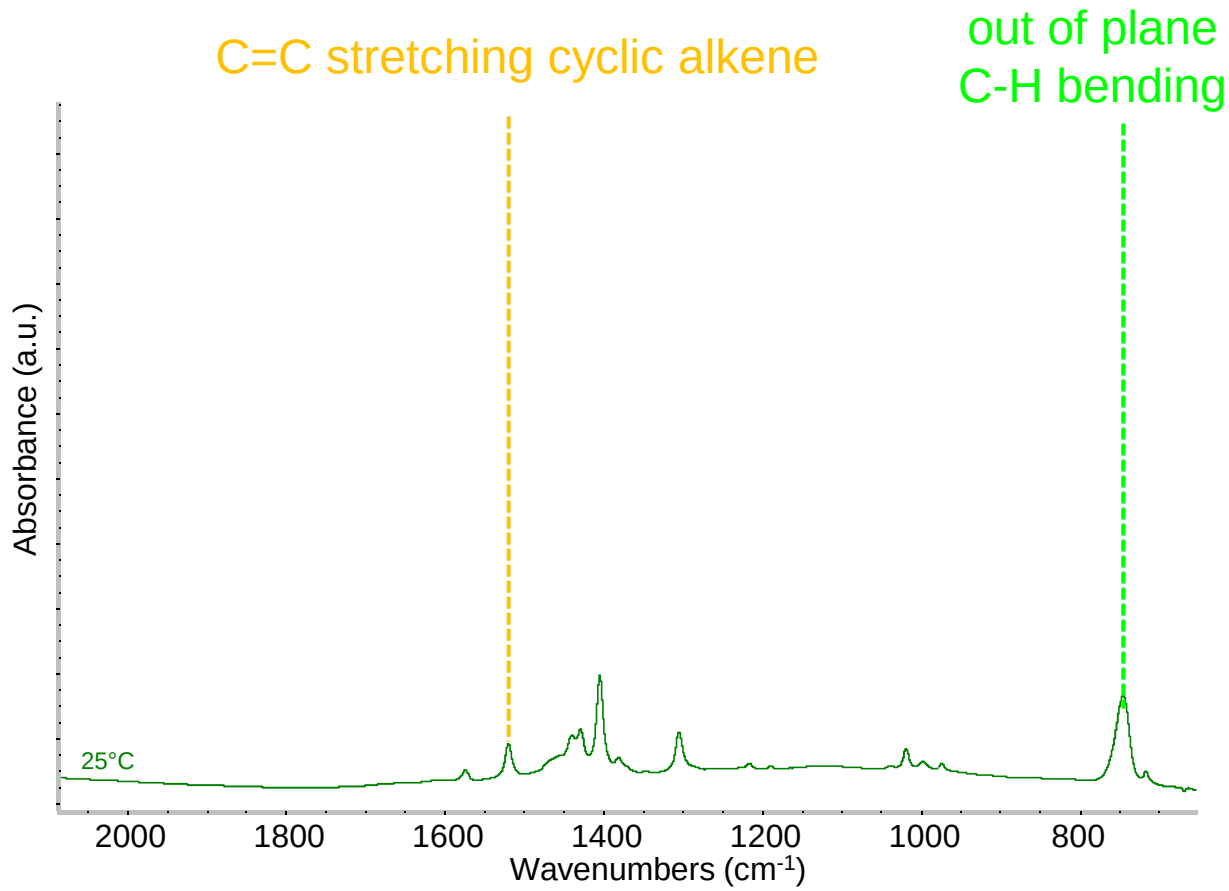

+ HSAG

In air

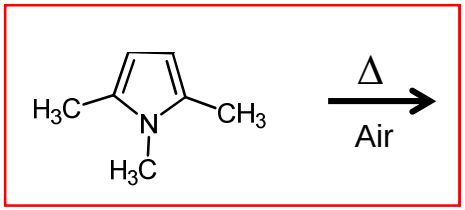
Thermal energy

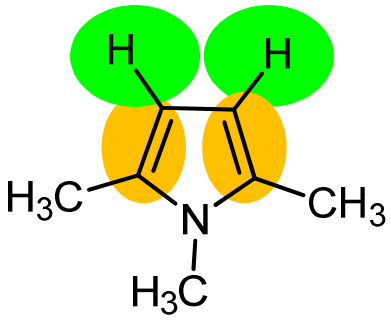
# 1,2,5-Trimethylpyrrole (TMP)

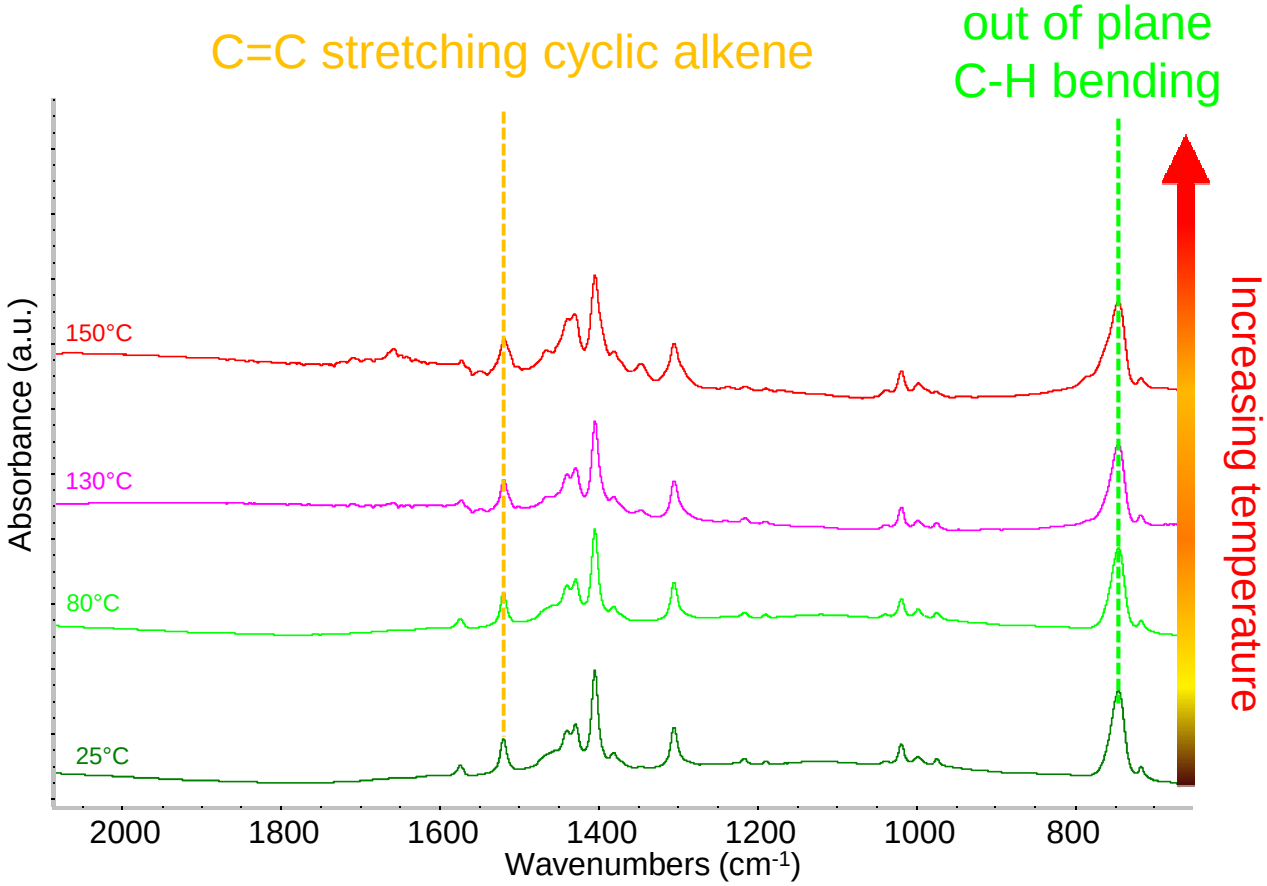


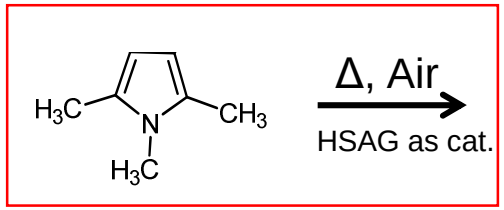
# TMP from 25 to 150°C

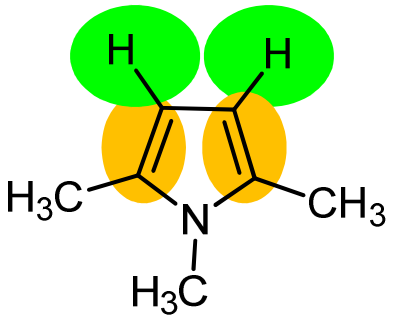


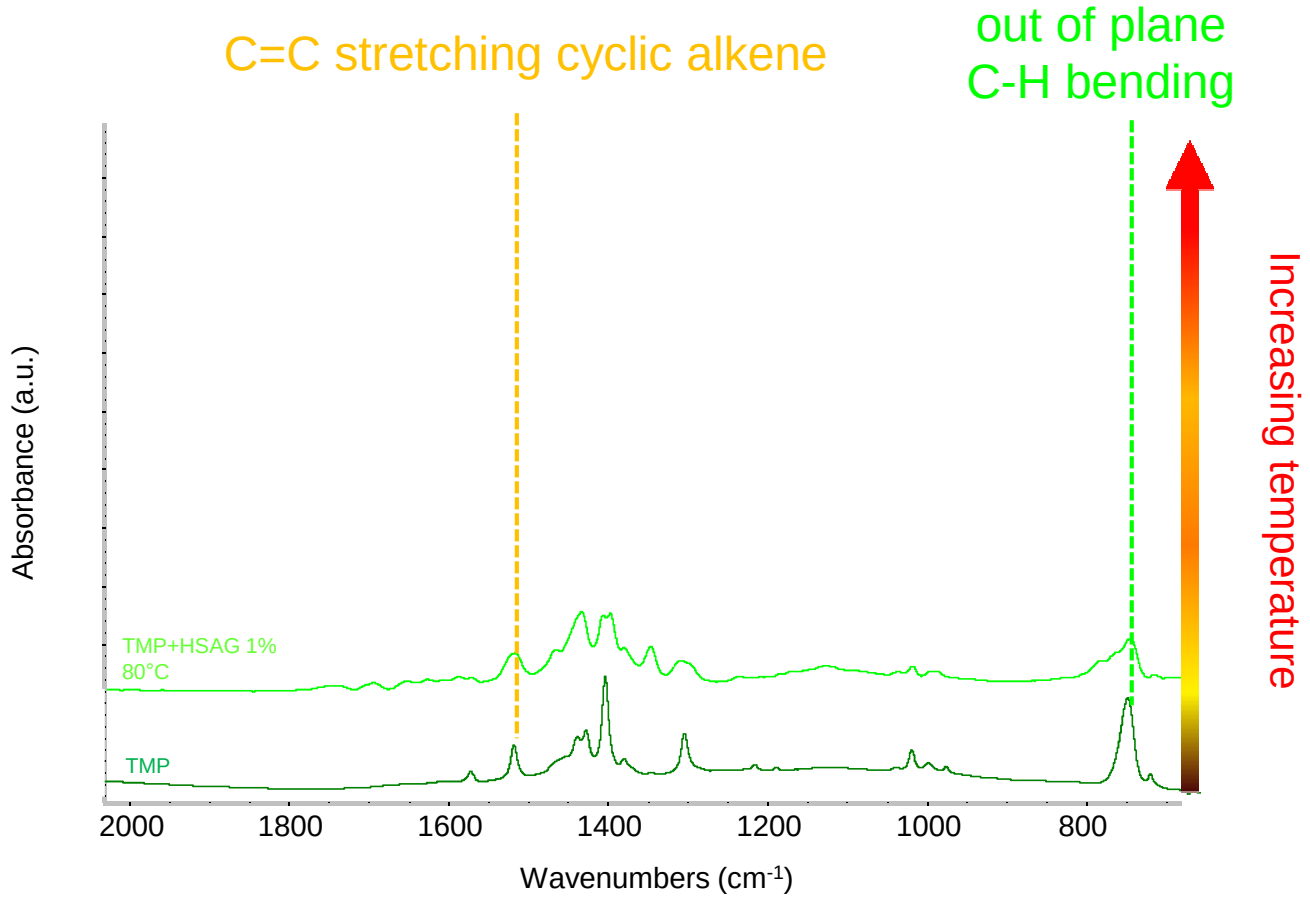



# TMP + HSAG cat. - from 25 to 150°C



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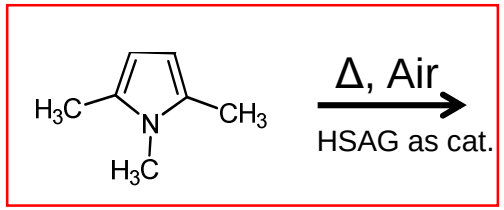


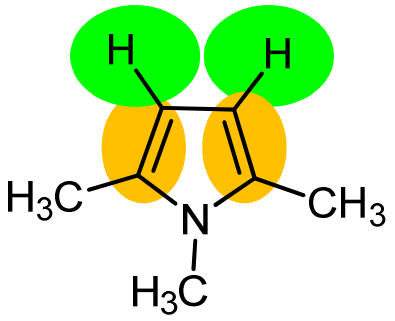


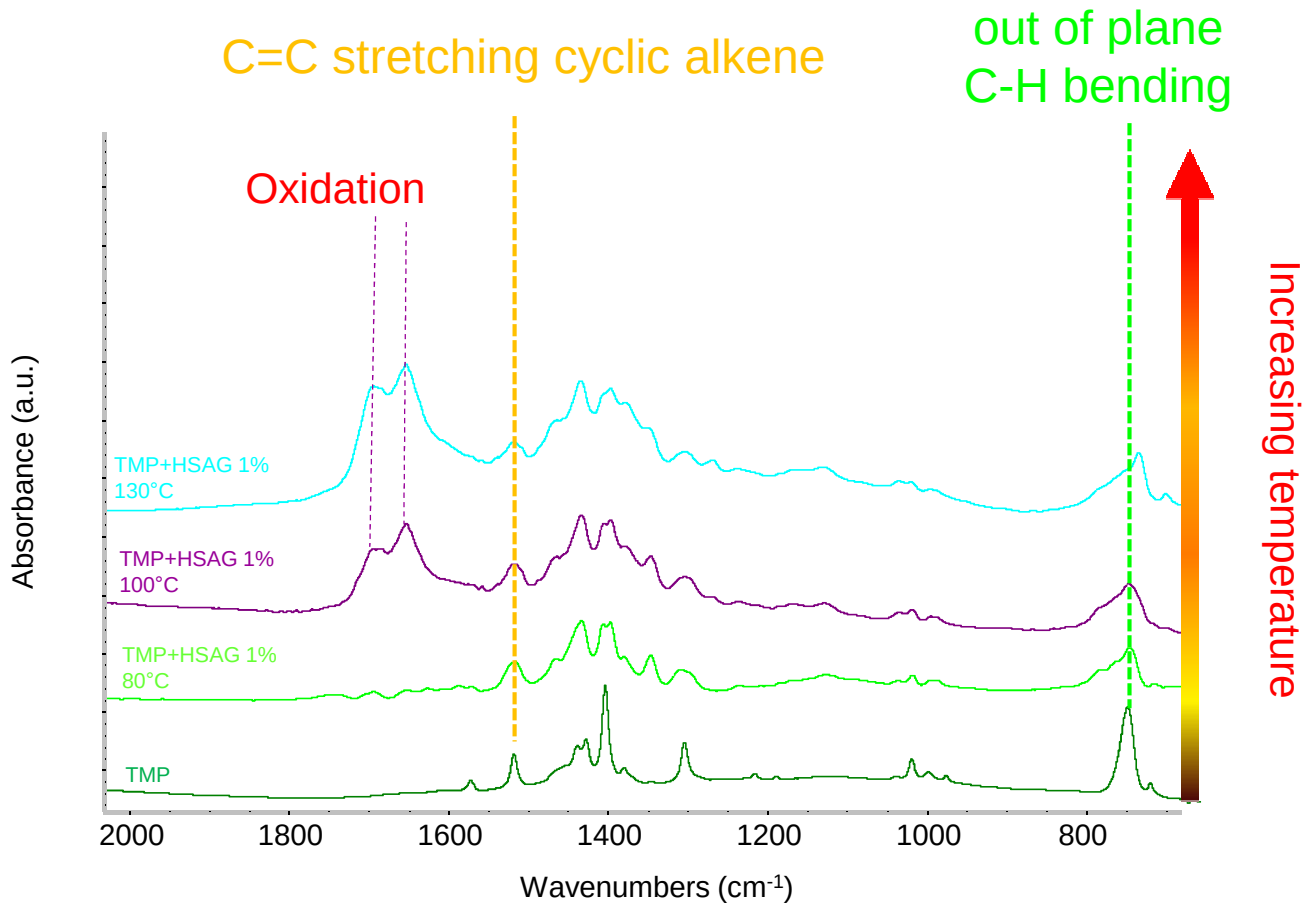

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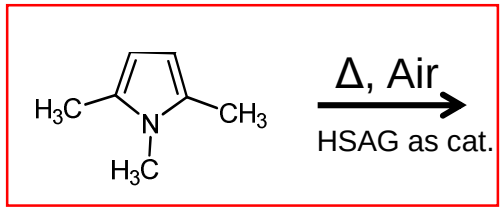
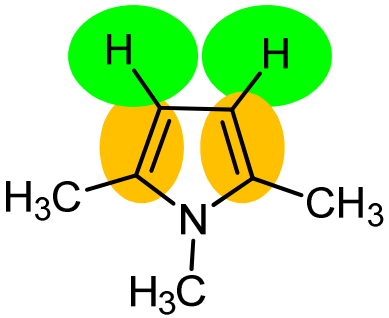
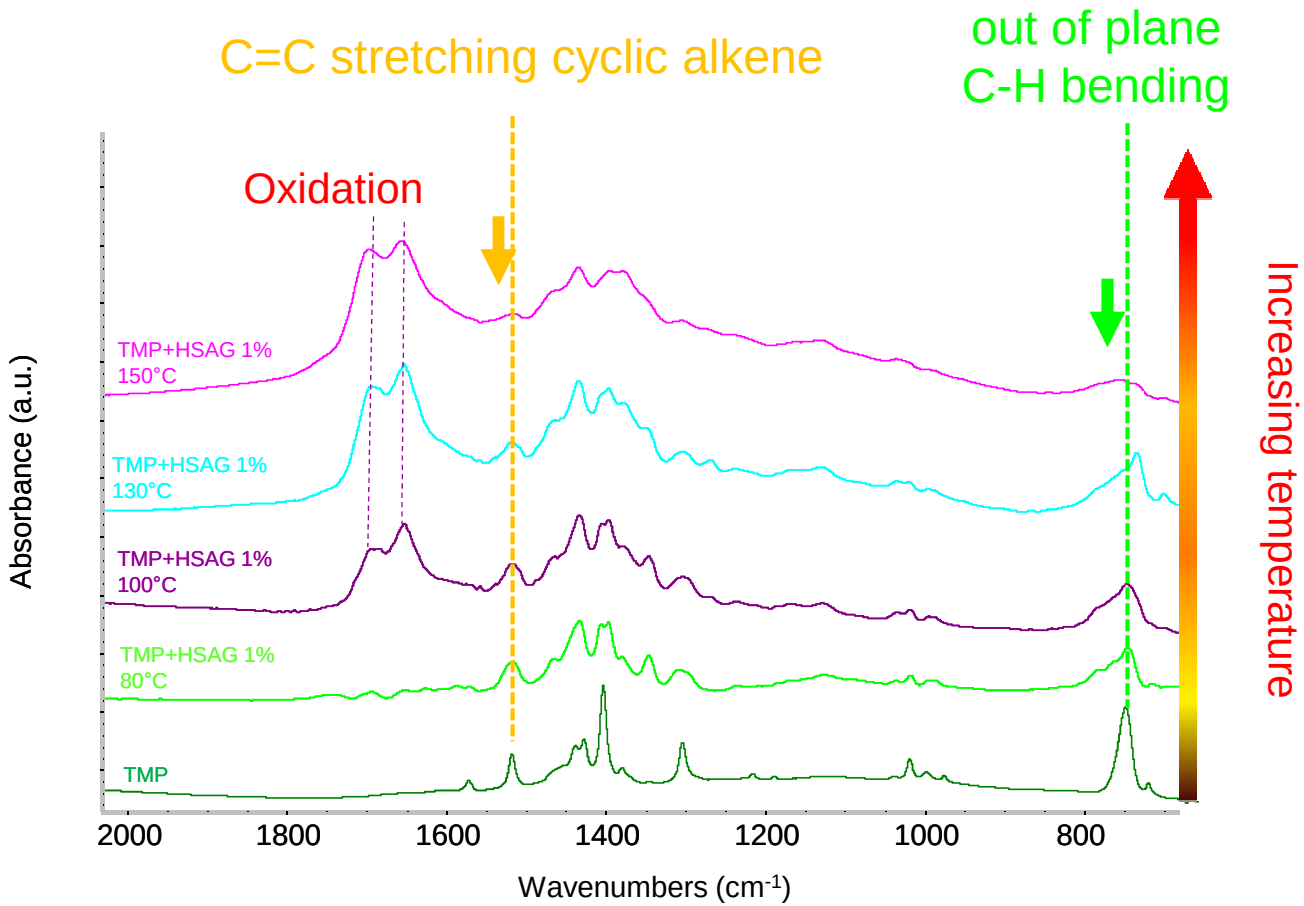
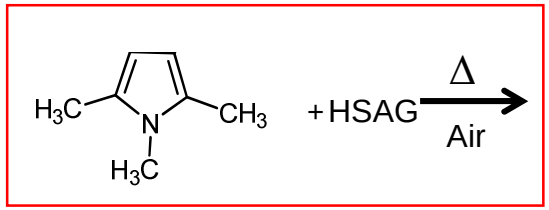
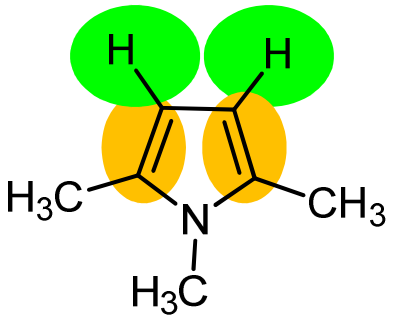


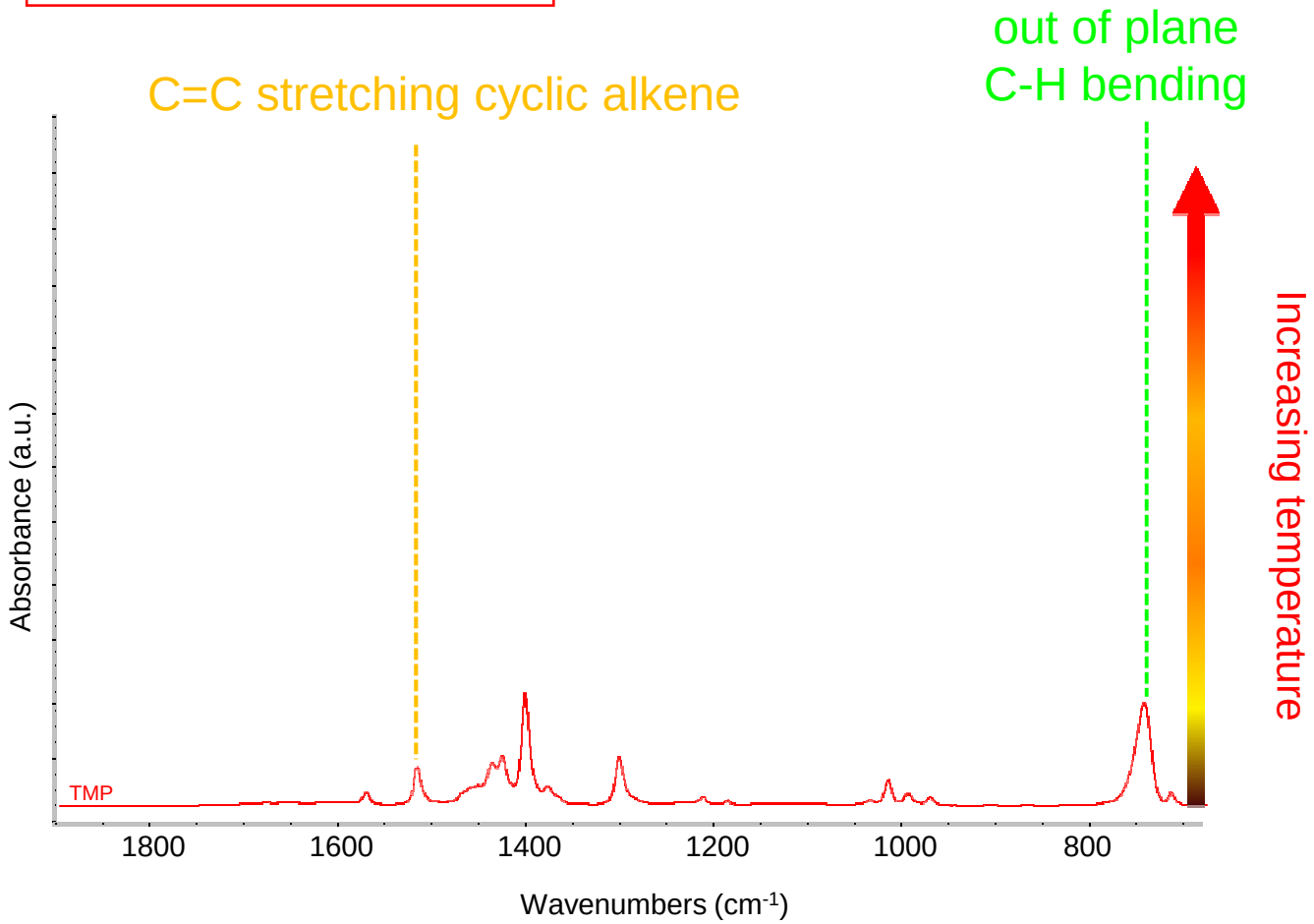



# TMP + HSAG 1/1 - from 25 to 150°C



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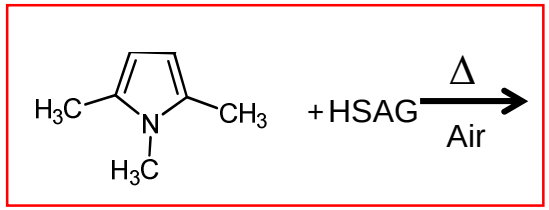


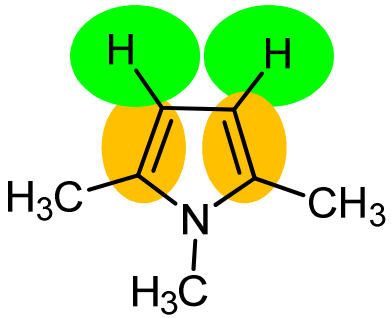


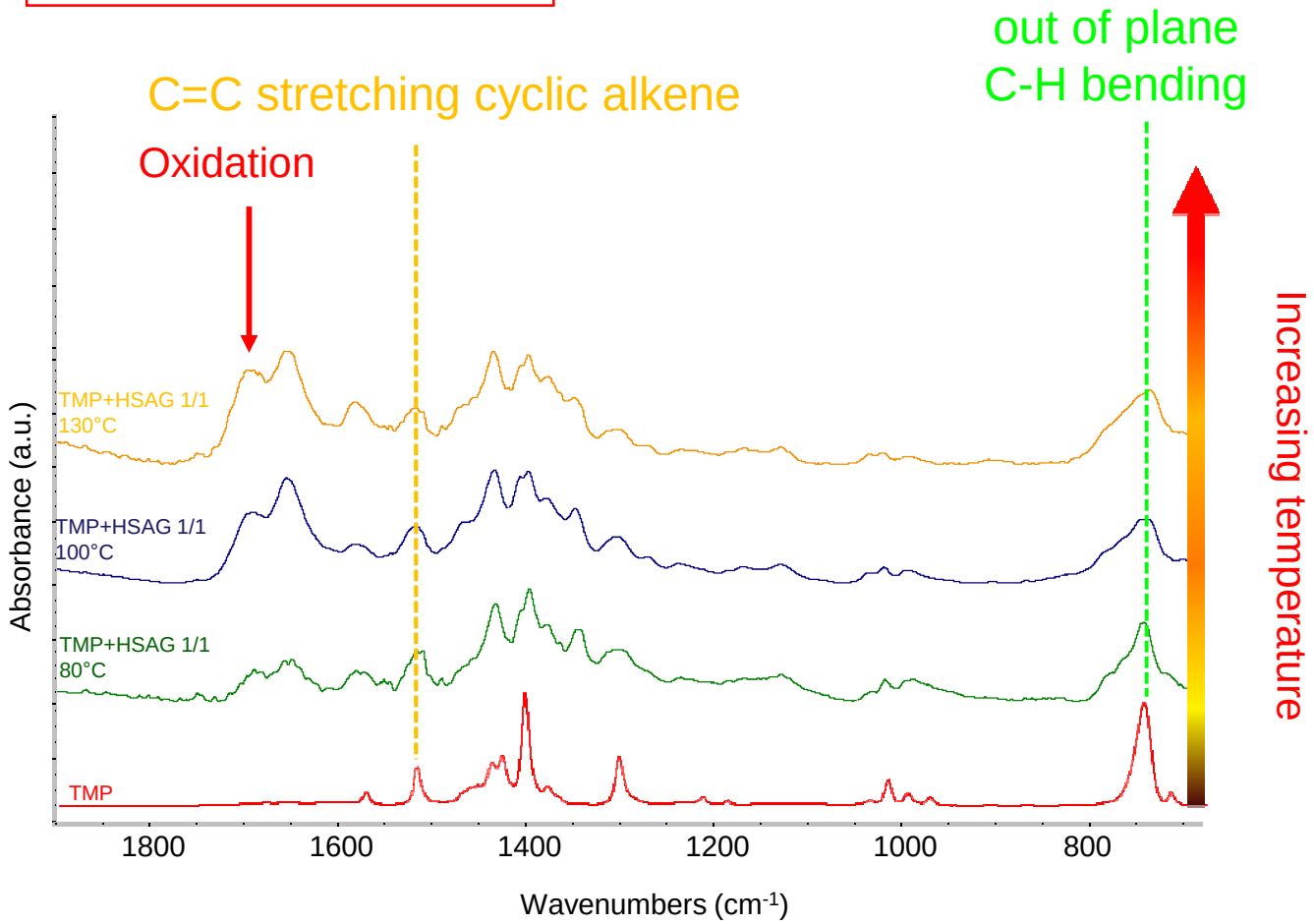

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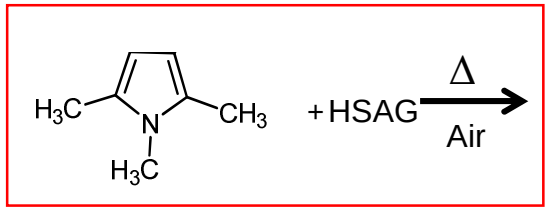
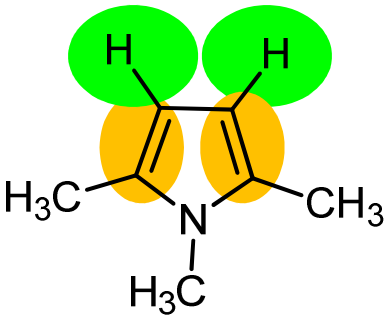
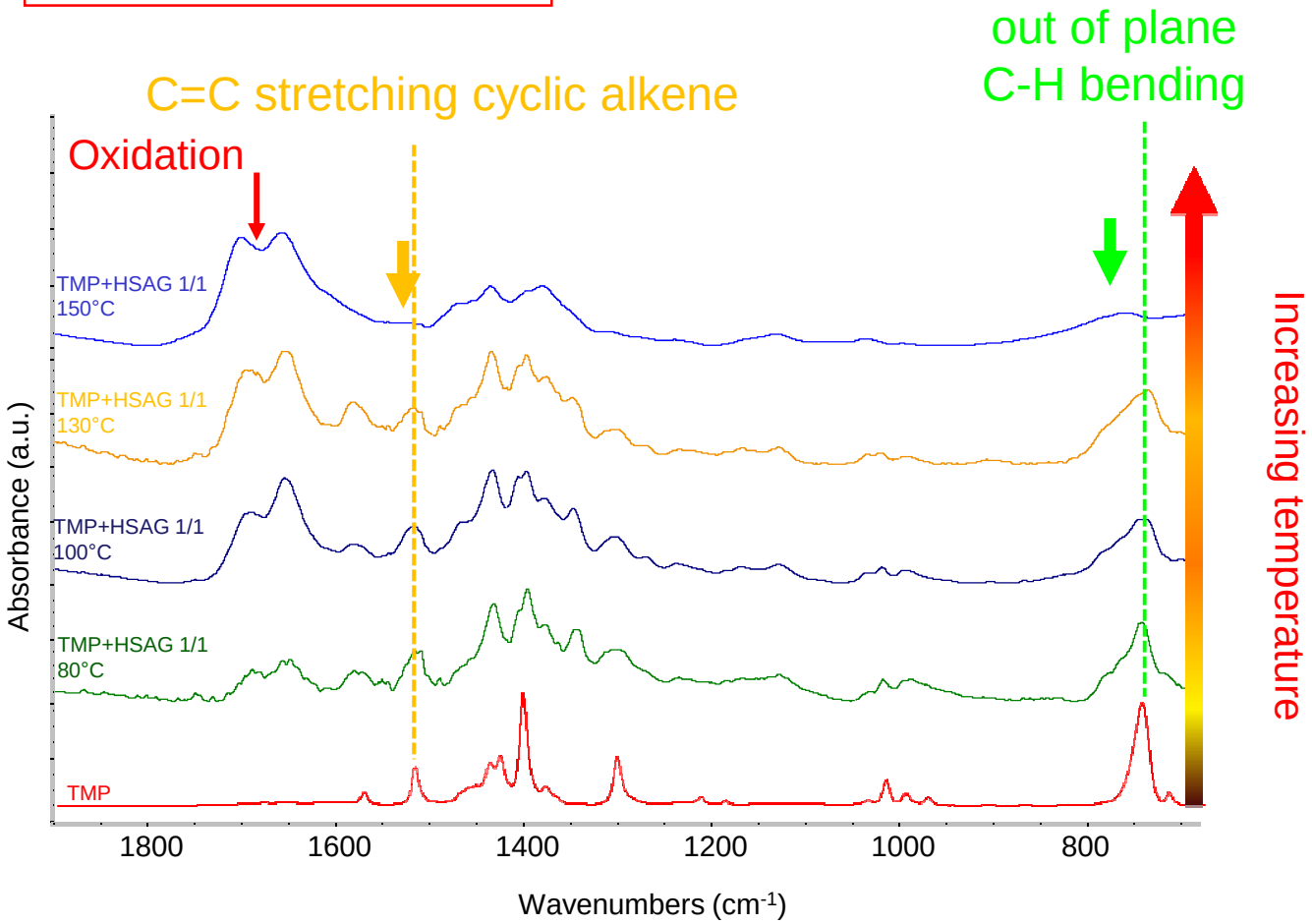
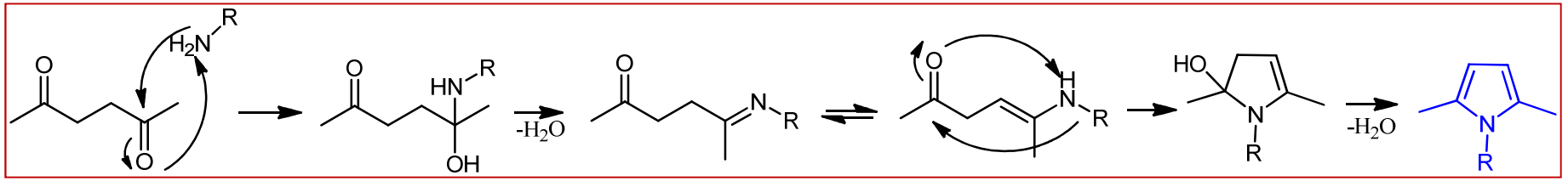


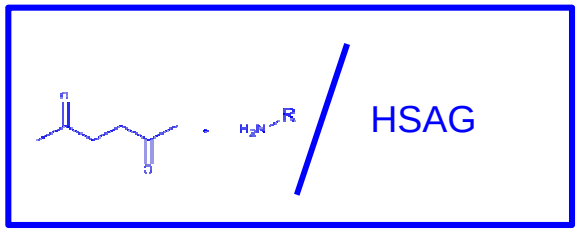



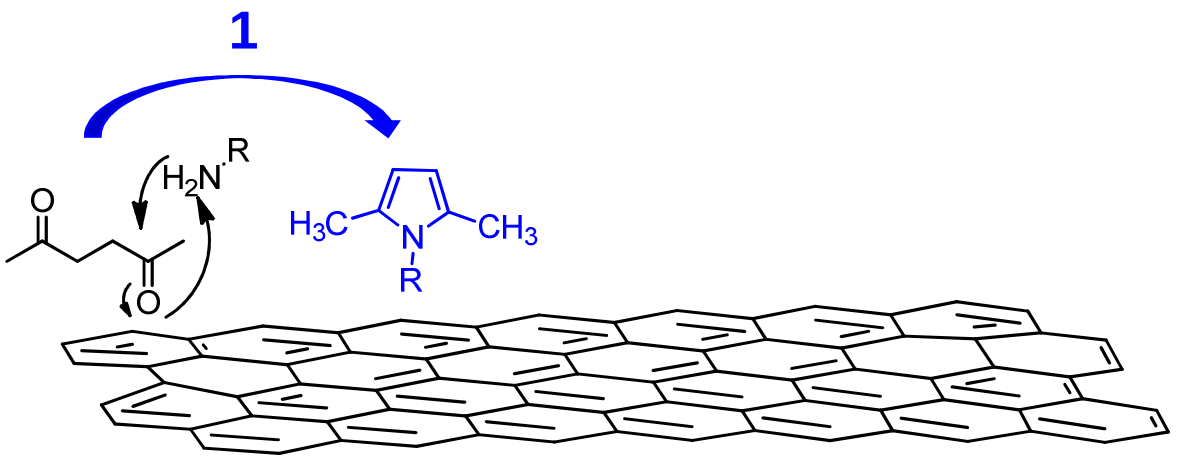



# Mechanistic path

## Paal-Knorr reaction

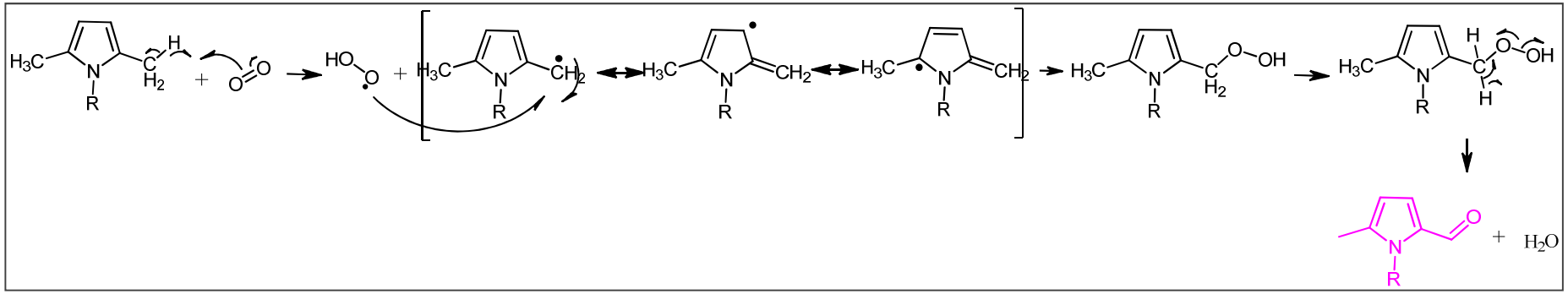


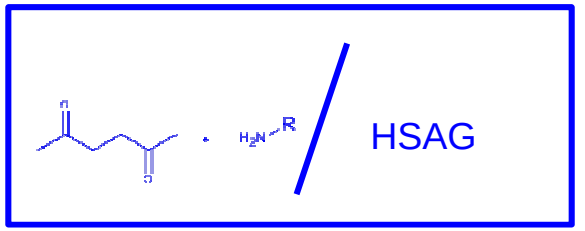



# Mechanistic path

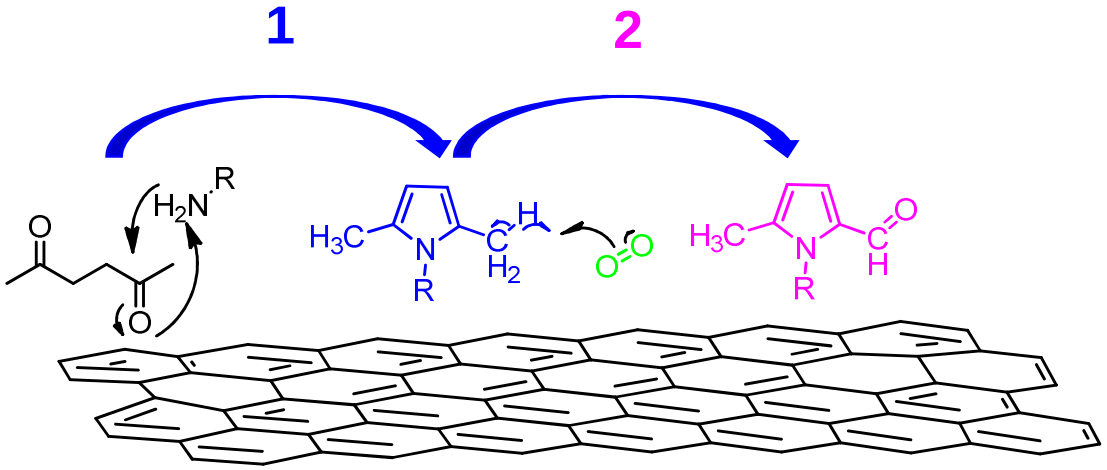
## Carbocatalyzed benzyl oxidation



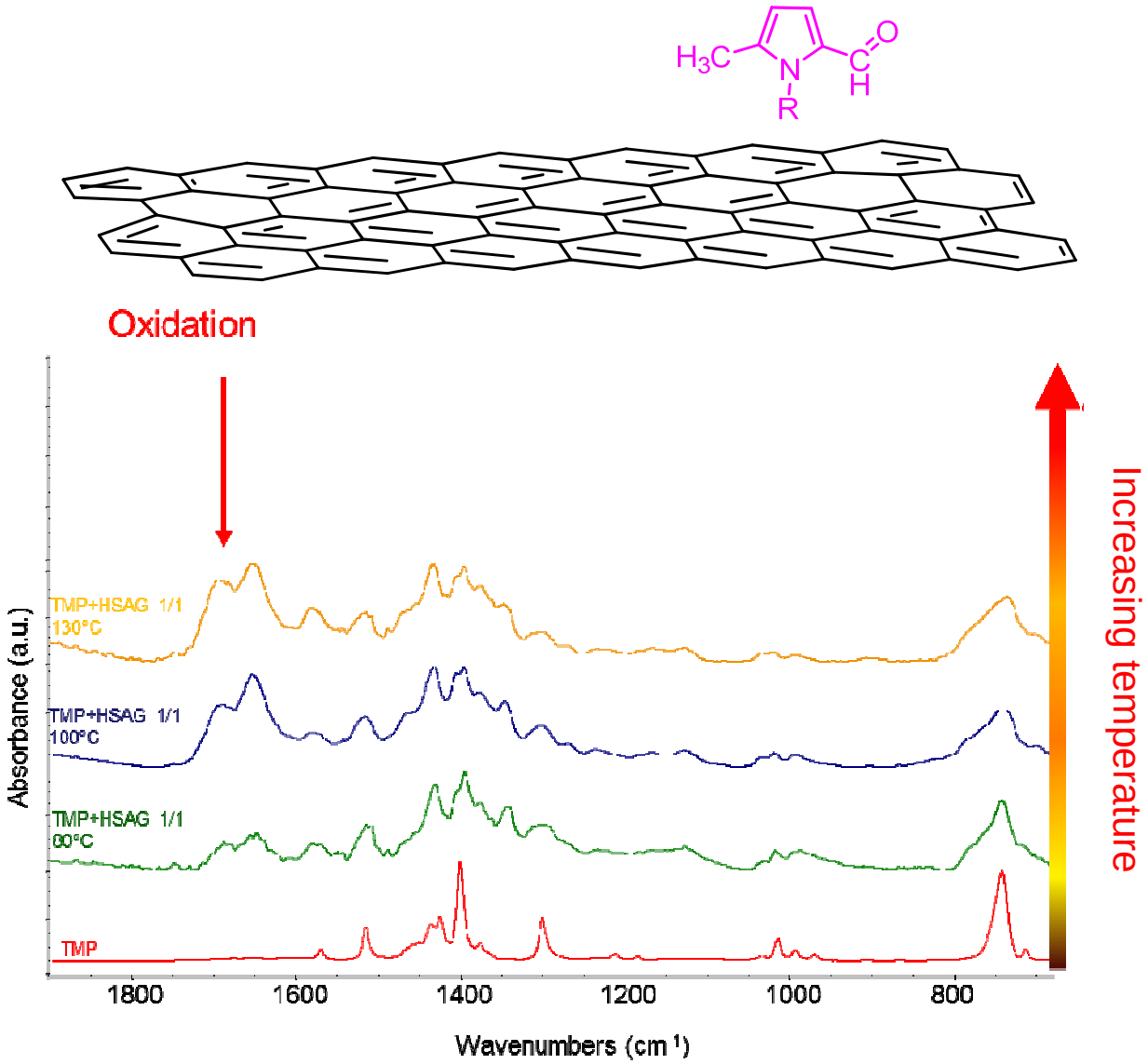



Paal – Knorr Reaction

Carbocatalyzed Oxidation

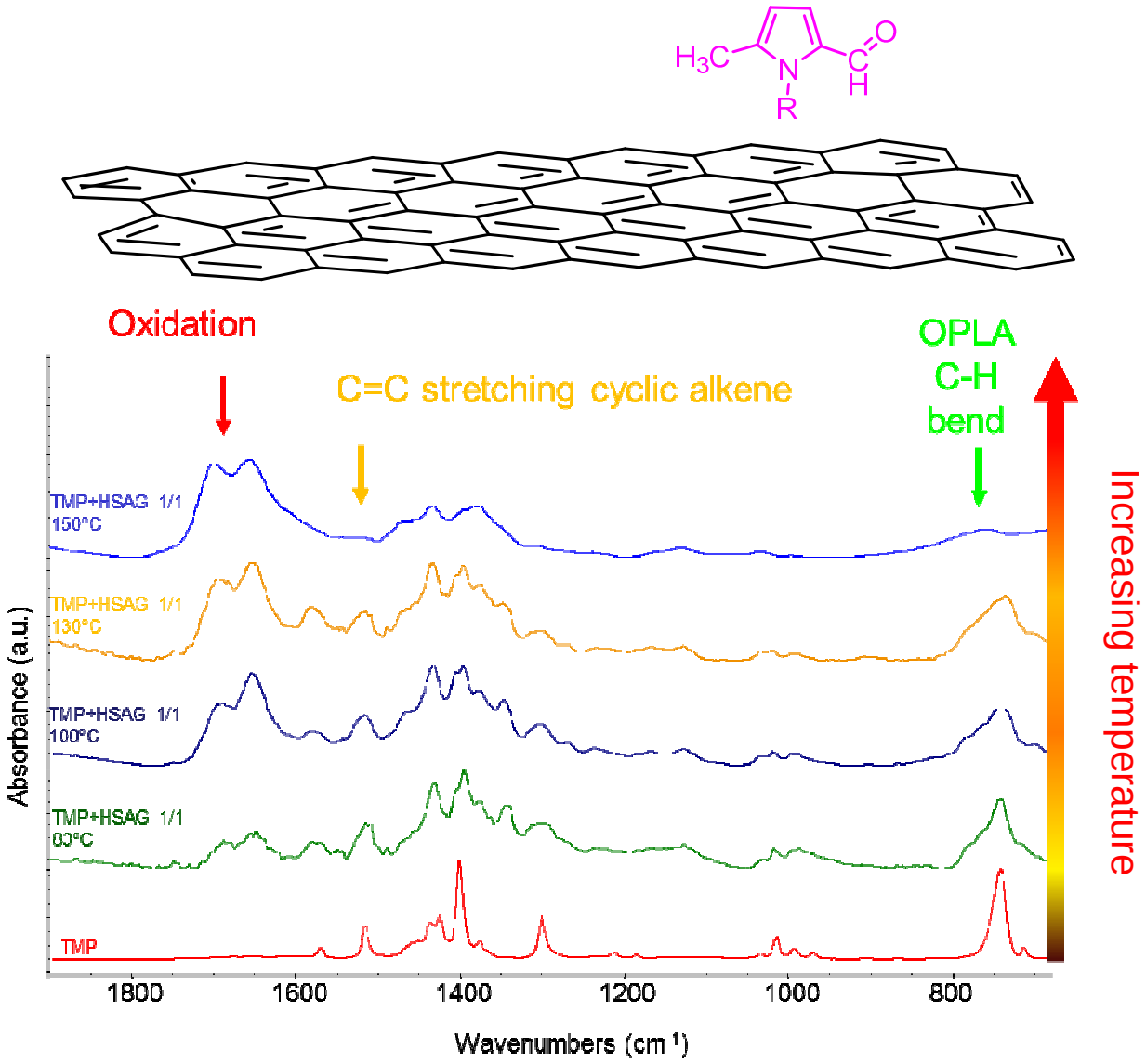


# Mechanistic path



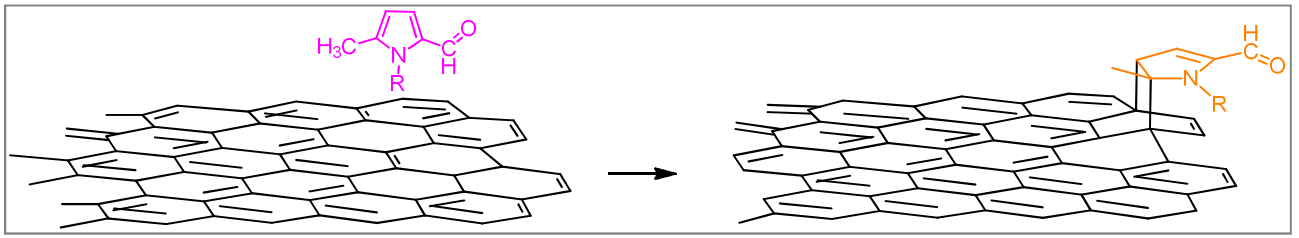

* Structure confirmed by means of NMR spectroscopy

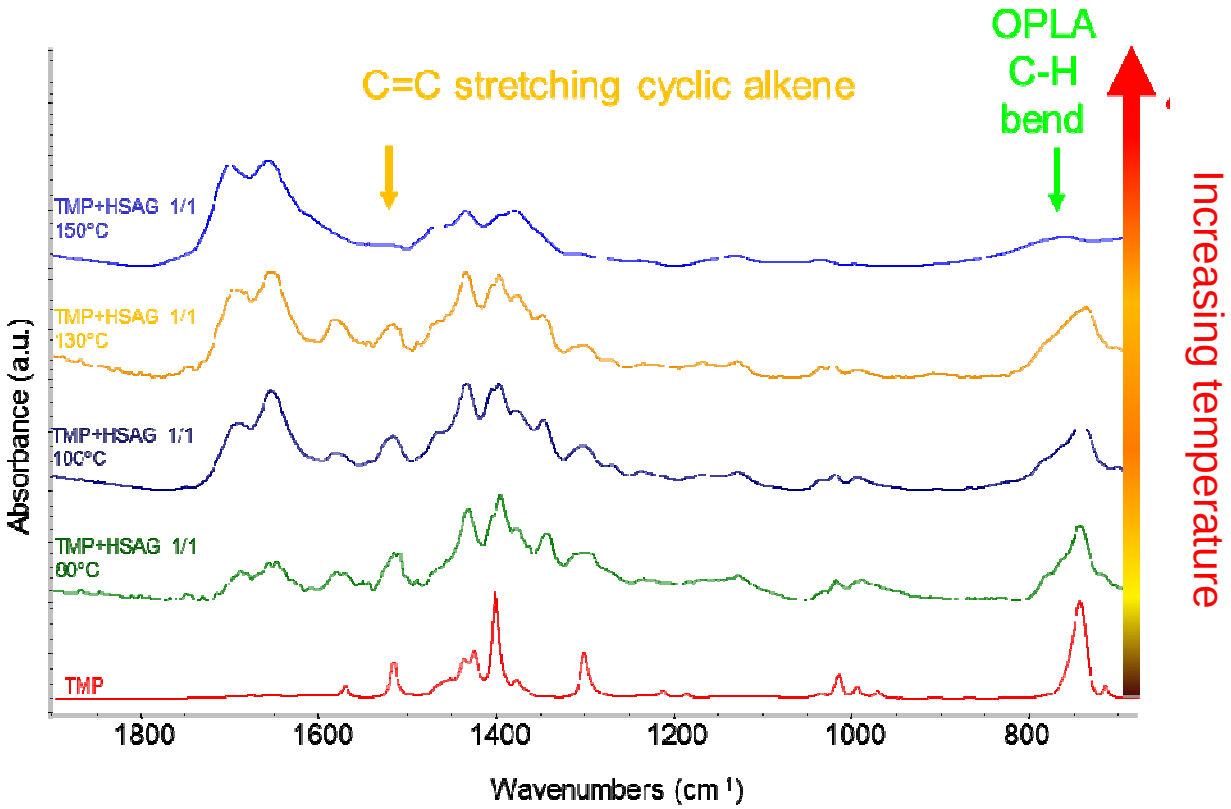
# Mechanistic path



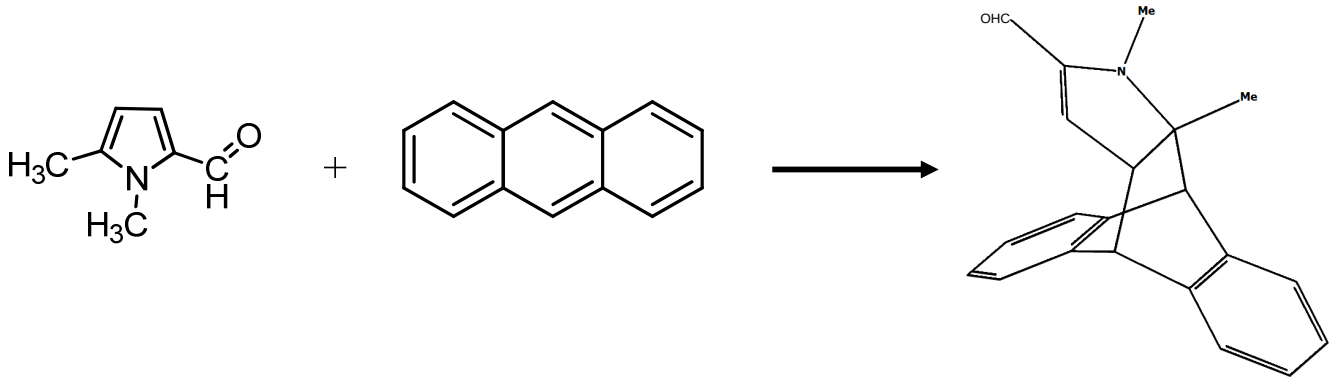

* Structure confirmed by means of NMR spectroscopy

# Mechanistic path



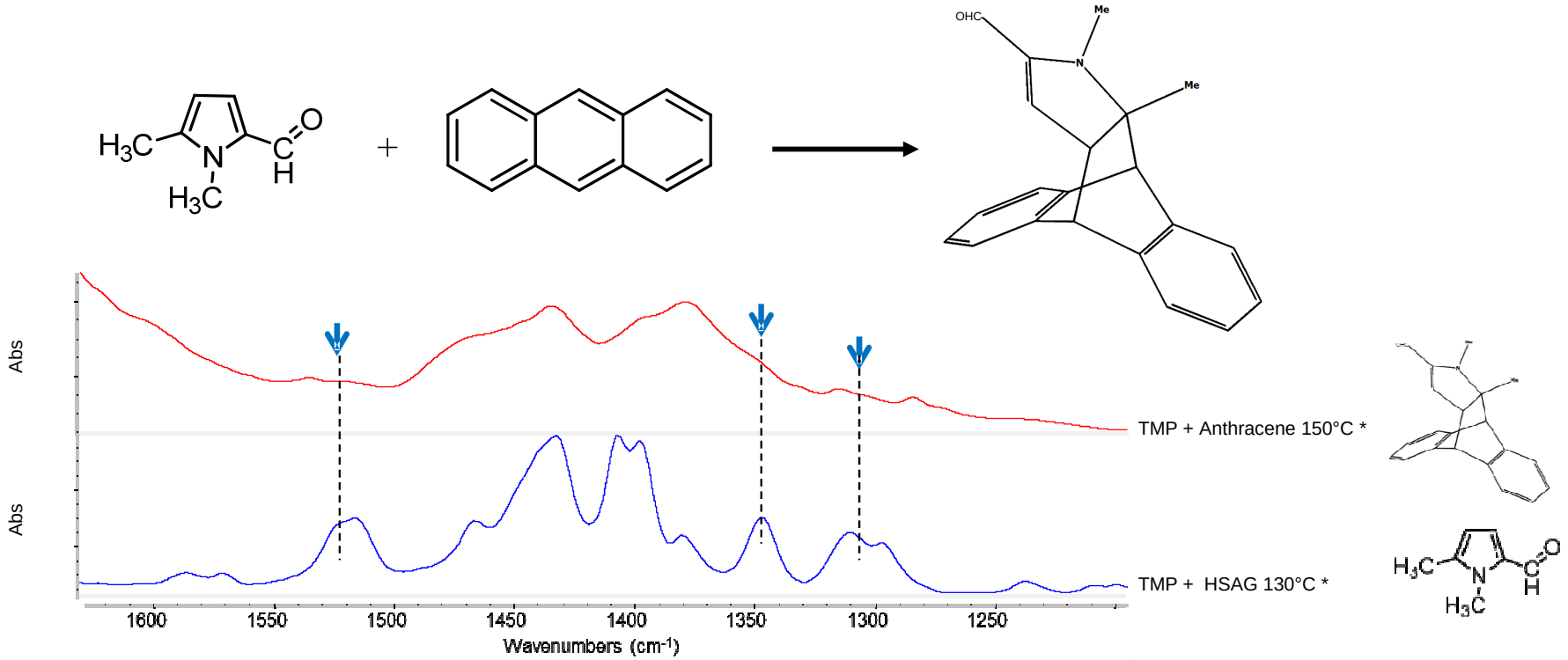
# Model reaction and DFT calculation




DFT (***B3LYP/6-311++G(d,p)***)

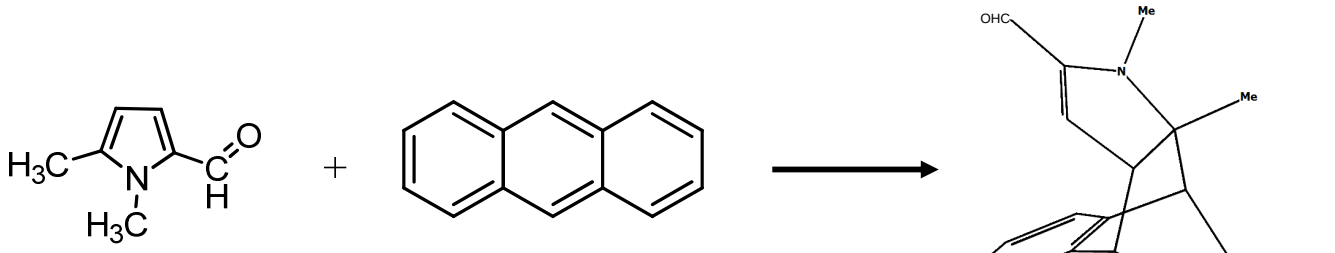
* Structure confirmed by means of FT-IR and NMR spectroscopy

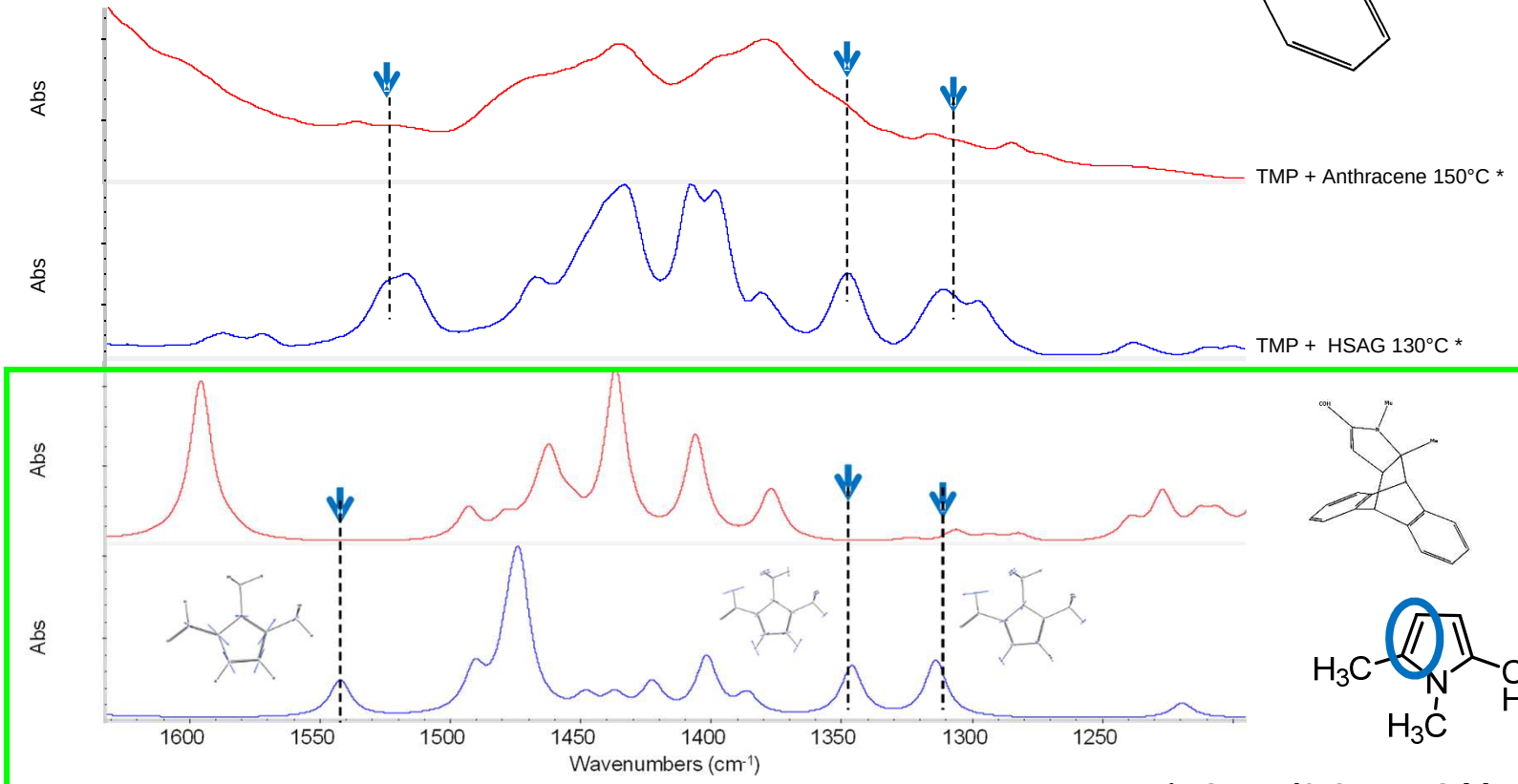
# Model reaction and DFT calculation




* Structure confirmed by means of FT-IR and NMR spectroscopy

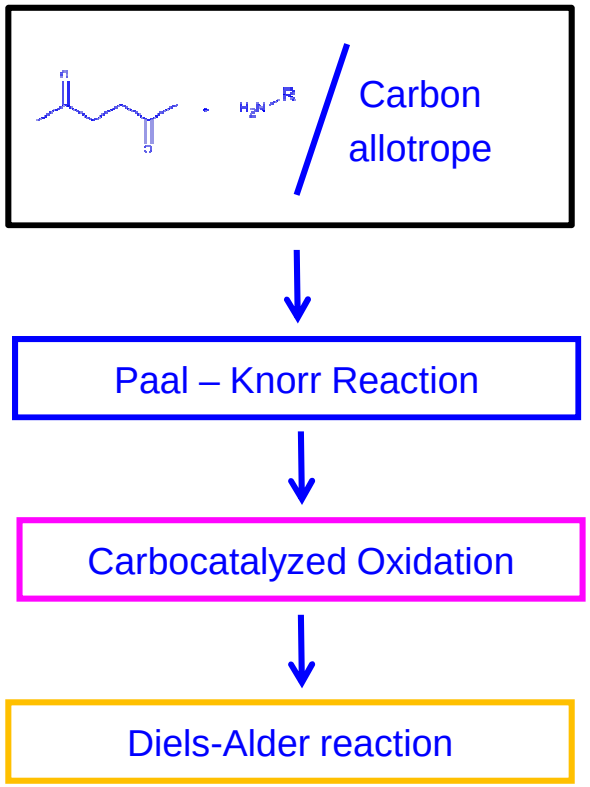
# Model reaction and DFT calculation

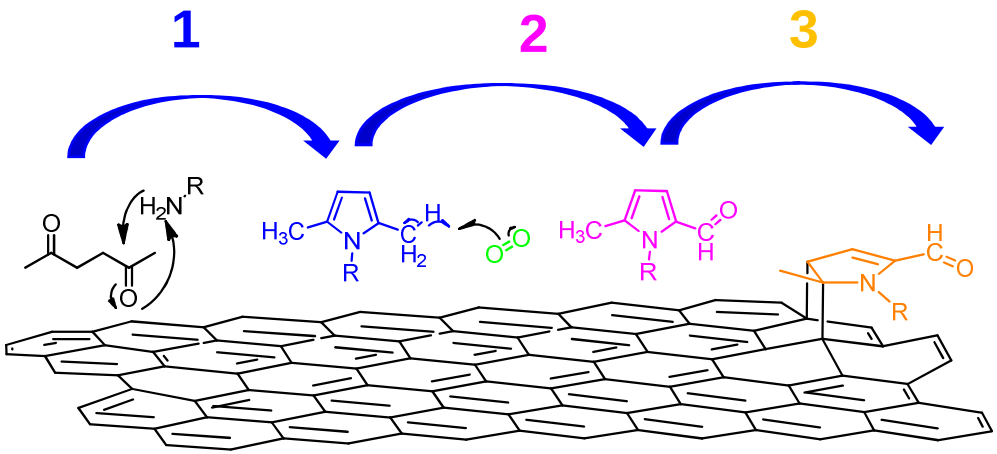


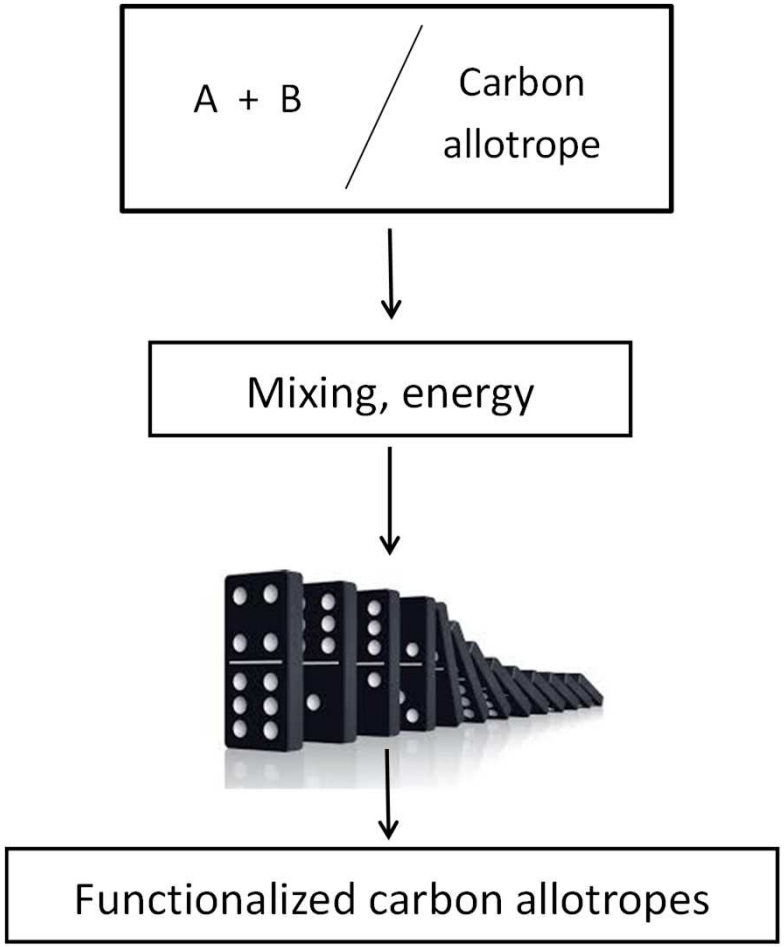
# Facile functionalization of carbon materials

## Hypothesis for the mechanism




# Facile functionalization of carbon materials



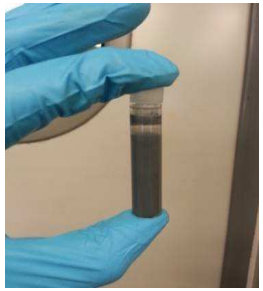

- Functional group:
  from few % to 20%
- Functionalization yield:
  from 85% to quantitative
- Covalent bond
  between functional group
  and graphene layer
- Bulk structure of graphitic materials:
  substantially unaltered

V. Barbera, A. Citterio, M. Galimberti, G. Leonardi, R. Sebastiano, S.U. Shisodia, A.M. Valerio. WO/2015/189411 A1 (2015)
M. Galimberti, V. Barbera, R. Sebastiano, A. Citterio, G. Leonardi, A.M. Valerio. WO/2016/050887 A1 (2016)
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)

# Nano-carbon Up

Polyol dispersions

Monolithic aerogel



Latex dispersions

Rubber nanocomposites

**Versatile Technology**


Polyurethane

Carbon papers

Conductive ink

Conductive coating

# Thanks for the Attention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