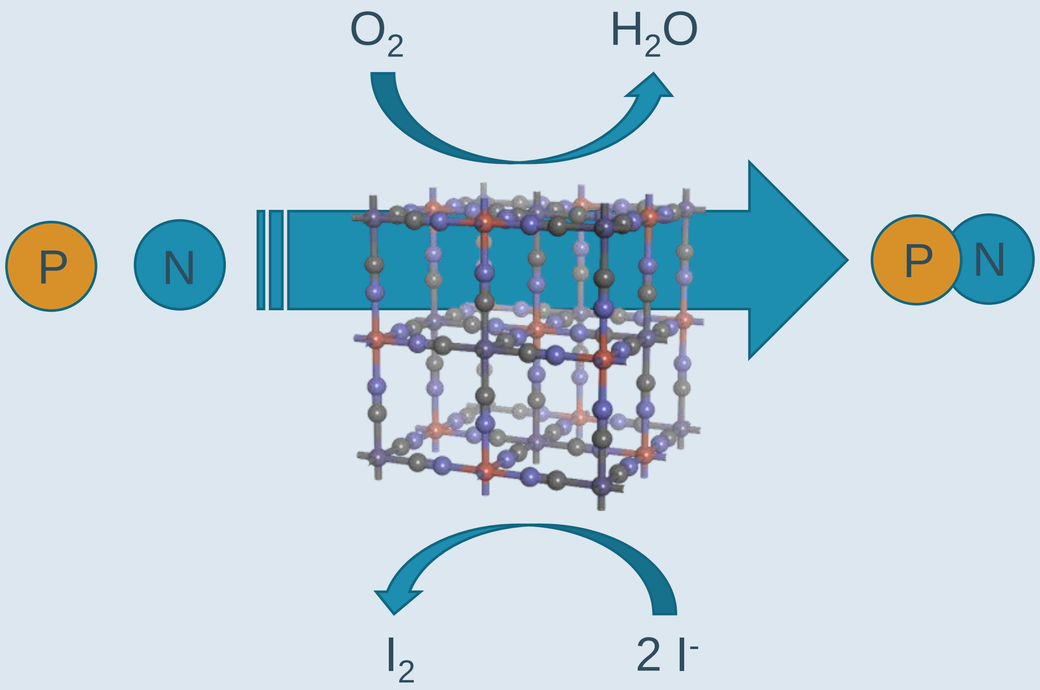
KU LEUVEN

Cu-Co double metal cyanides as green catalysts for phosphoramidate synthesis



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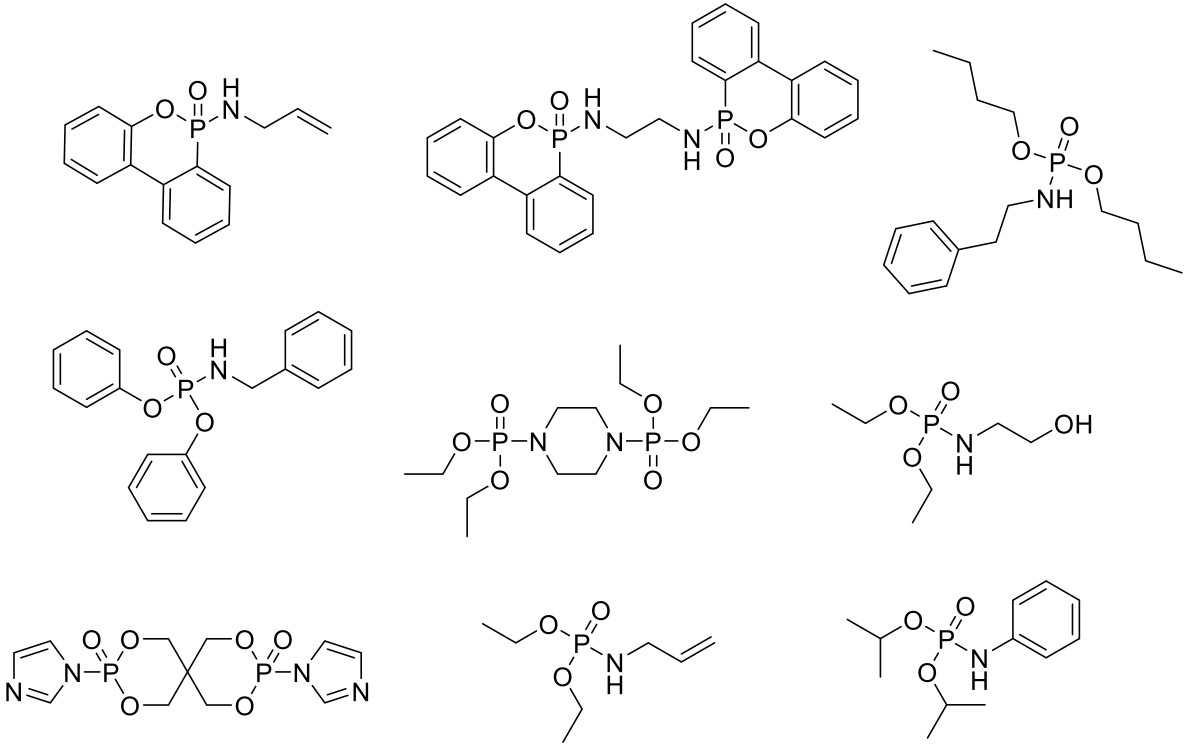
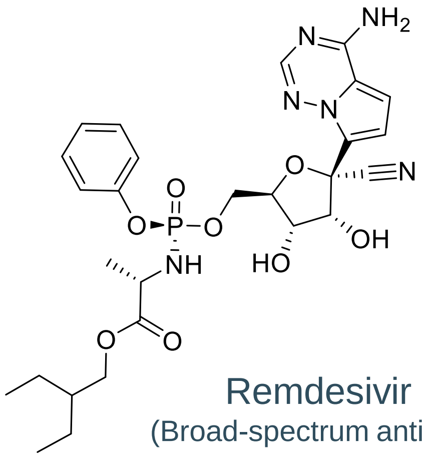
C-PlaNeT
CIRCULAR PLASTICS NETWORK FOR TRAINING

This Project has received funding from the European Union's Horizon 2020 research and innovation Programme under the Marie Sklodowska-Curie grant Agreement No.859885

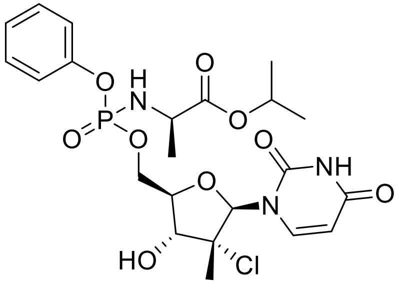
Relevance



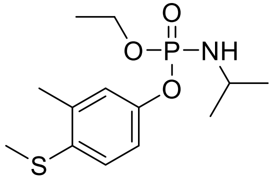
Phosphorus containing flame retardants



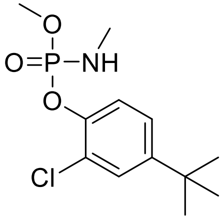
Remdesivir
(Broad-spectrum antiviral)



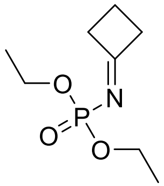
Uprifosbuvir
(Hepatitis C treatment)



Fenamiphos



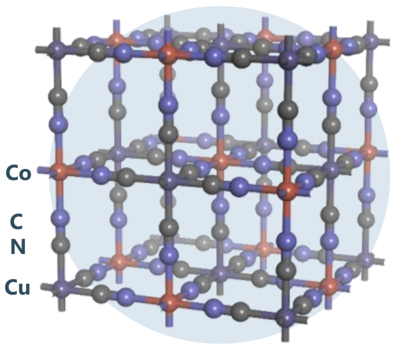
Crufomate



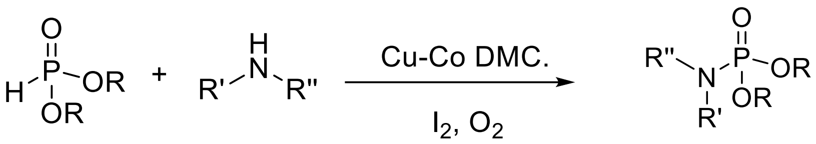
Fosthietan

(Insecticides)

Cu(II)-Co(III) double metal cyanide



This work:

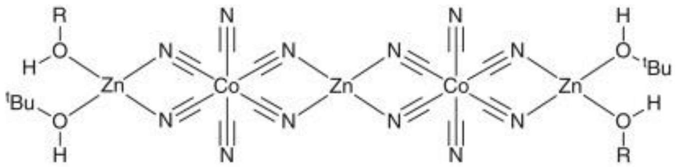


- Heterogeneous catalyst
- Recyclable after several iterations
- Simple preparation
- Air and moisture tolerant
- Atom economical

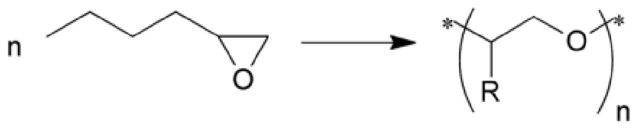
Cu-Co Double Metal Cyanide

Cu-Co DMC = **Co**pper-**Co**balt **D**ouble **M**etal **C**yanide

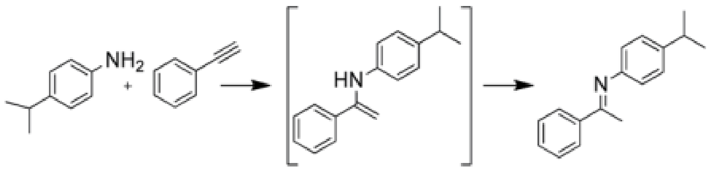
- A class of molecular salts made up of a crystalline metal cyanide framework
- Theoretical formula: $Cu_3[Co(CN)_6]_2$
- Other DMC with different metal combination exist: $Zn_3[Co(CN)_6]_2$ structure is very similar
- Synthetized using different additives and M[1] excess to increase the catalytic activity



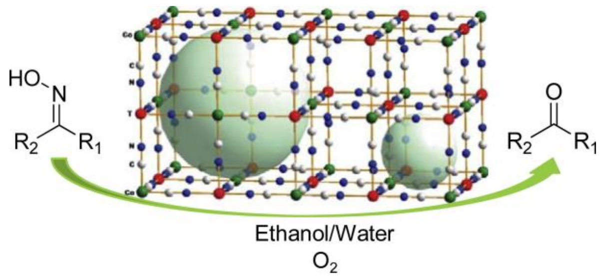
Applications:



Epoxide polymerization

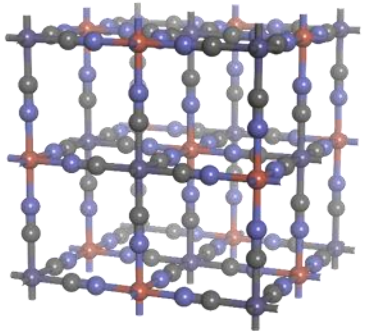


Hydroamination

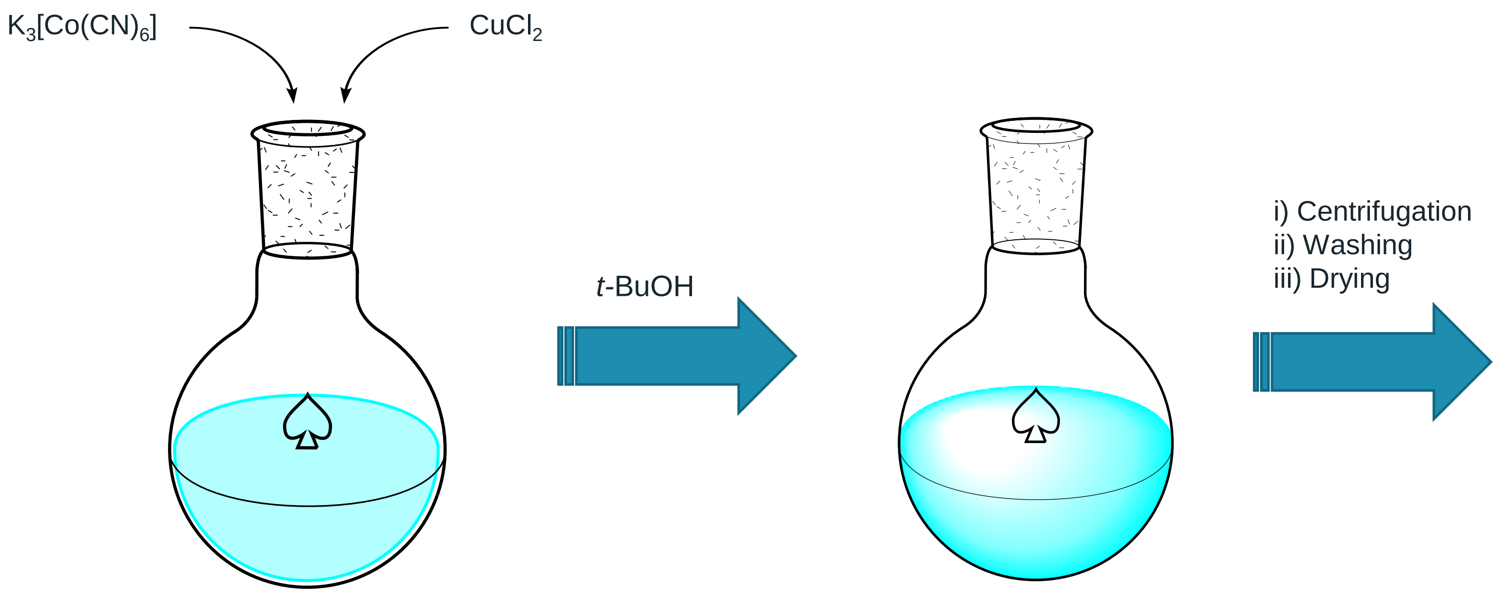


Oximes oxidation

Cu-Co Double Metal Cyanide

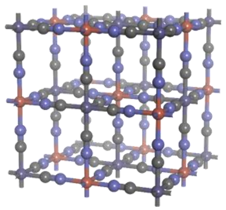


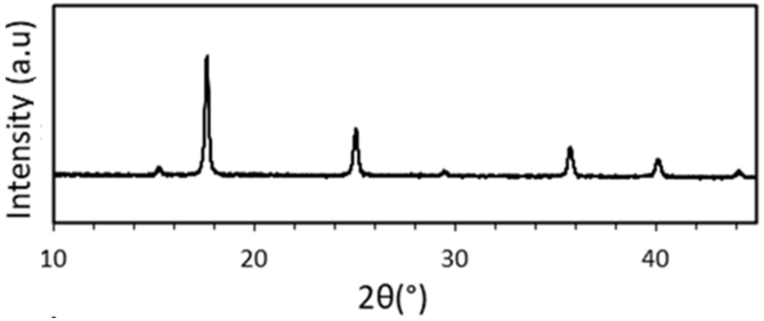
Preparation:



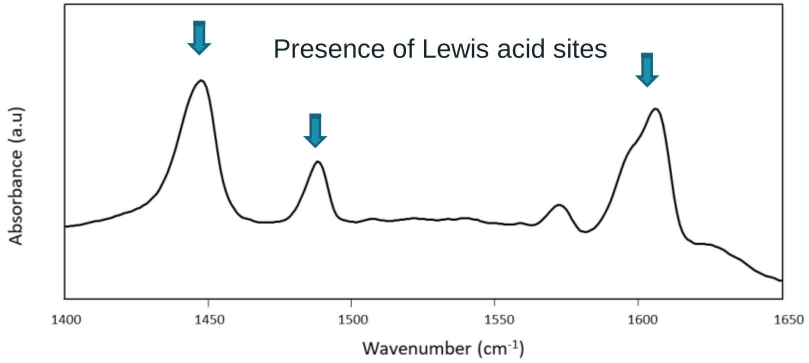
60% yield

Cu-Co Double Metal Cyanide

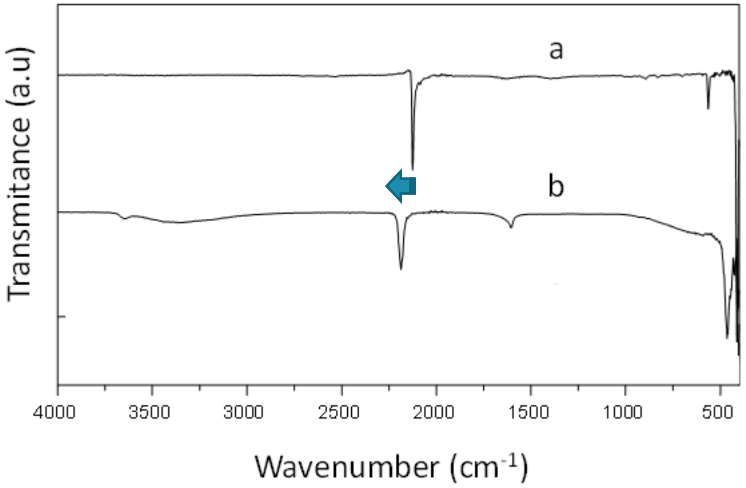




Crystaline solid with cubic lattice structure



Pyridine absorption.



a) $K_3[Co(CN)_6]$, b) Cu-Co DMC

Sample	S_{BET} (m^2/g)	S_{ext} (m^2/g)	V_{micro} (cm^3/g)	LAS (mmol/g)	APD
Cu-Co DMC	659	116	0.217	0.044	6.4 Å

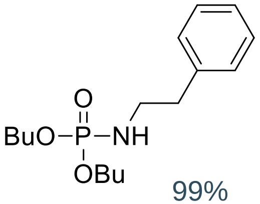
Textural properties

Reactivity

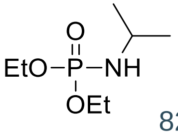
<u>Observations:</u>

- Iodine is necessary for the reaction to occur (**6% yield**)
- Without catalyst, stoichiometric yield is obtain with respect of I_2 added (**15% yield**)
- Increasing O_2 (balloon) p/p° accelerates the reaction (**3h on air**)
- Disappearance and reappearance of coloration in the reaction (Suggests consumption and formation of I_2)

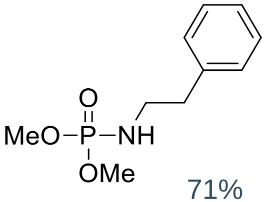
Scope



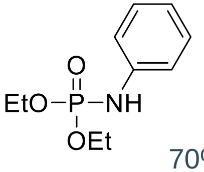
99%



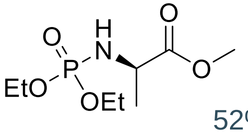
82%



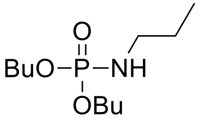
71%



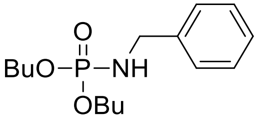
70%



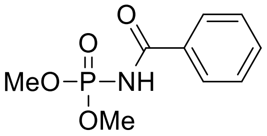
52%



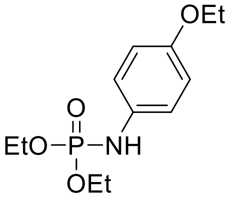
81%



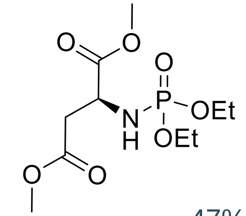
89%



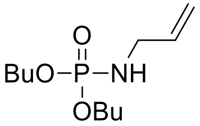
61%



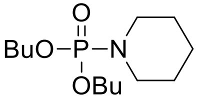
78%



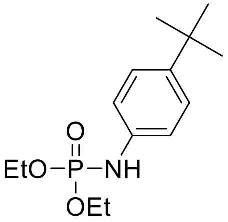
47%



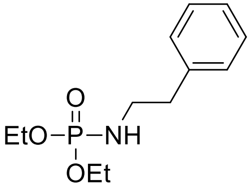
21%



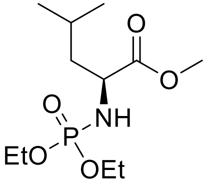
26%



63%

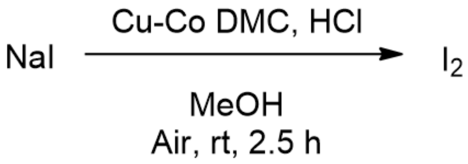


94%



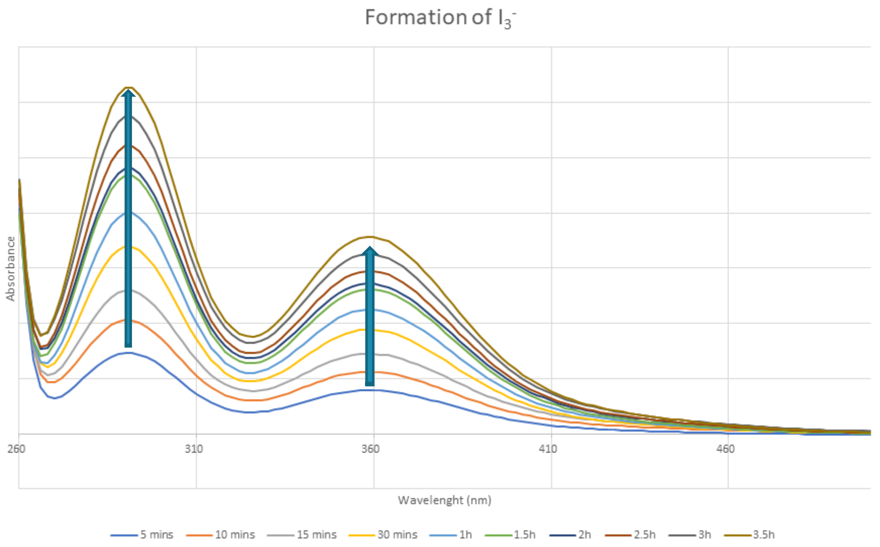
53%

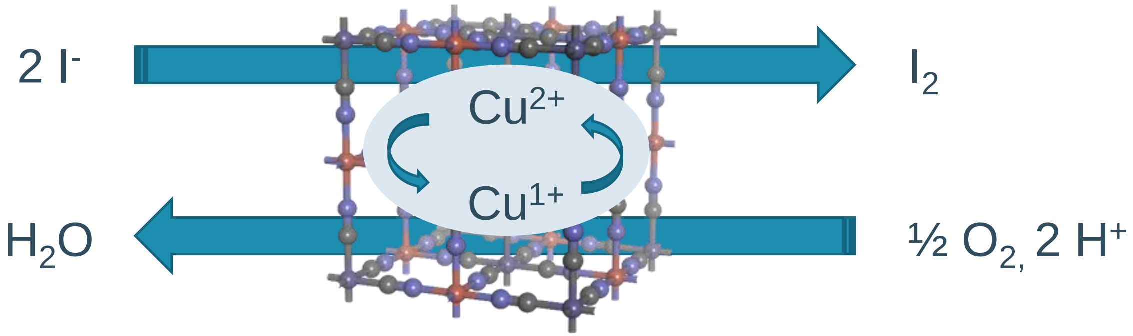
Oxidation of NaI by Cu-Co DMC



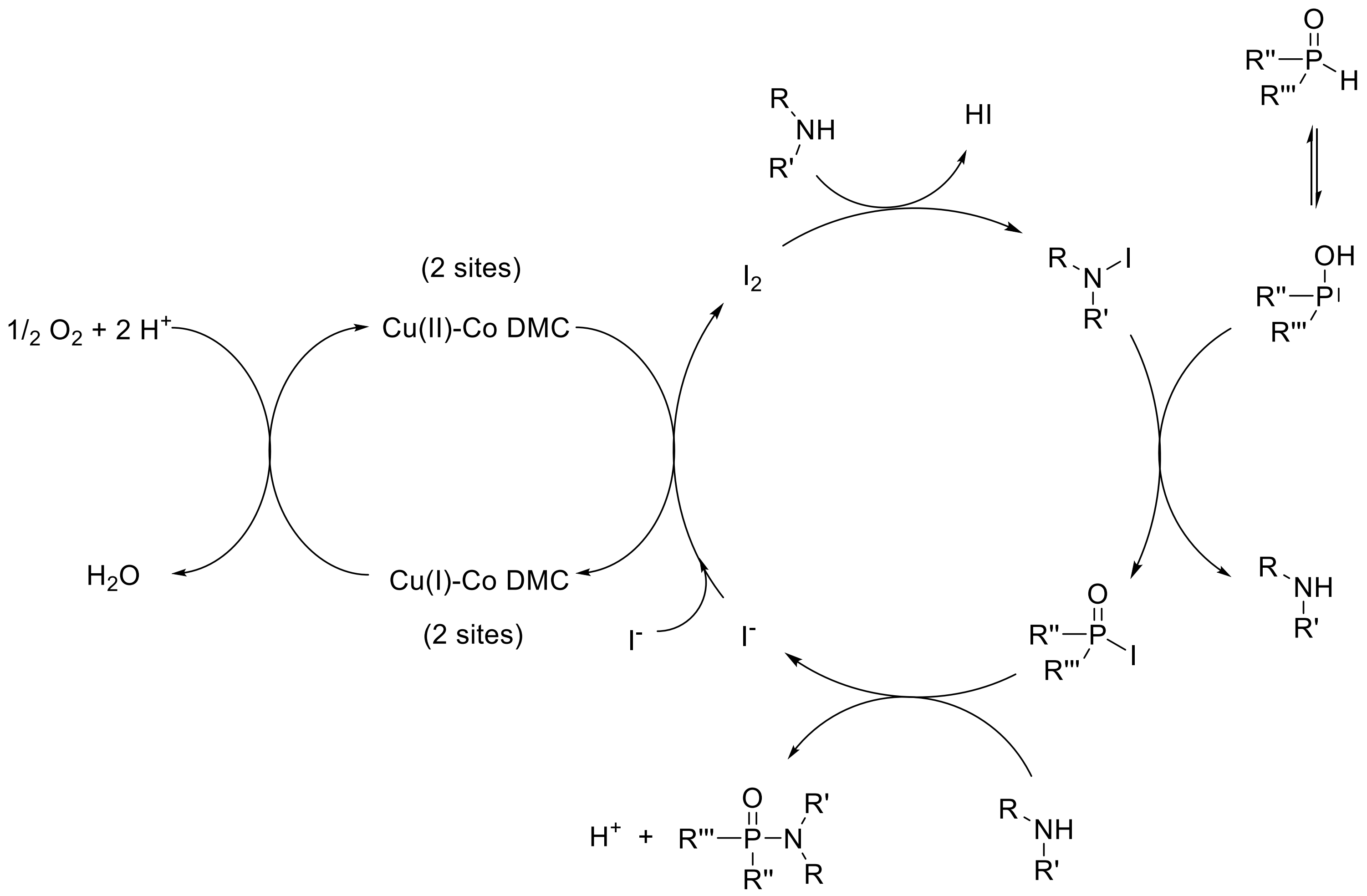
Entry	Cu-Co DMC (mg)	H^+ (mM)	Yield[b]
1	40	0	5%
2	40	75	20%
3	0	75	8%

[a]All reactions were performed using a scale of 2 mmol of NaI, catalyst, 37% HCl and methanol as solvent (4 ml) at room temperature, exposed to air, during 2.5 h. [b]Yields were determined by measuring I_3^- via UV-Vis measurements (λ = 360 nm) (Fig S1 and S3 SI).





Proposed mechanism



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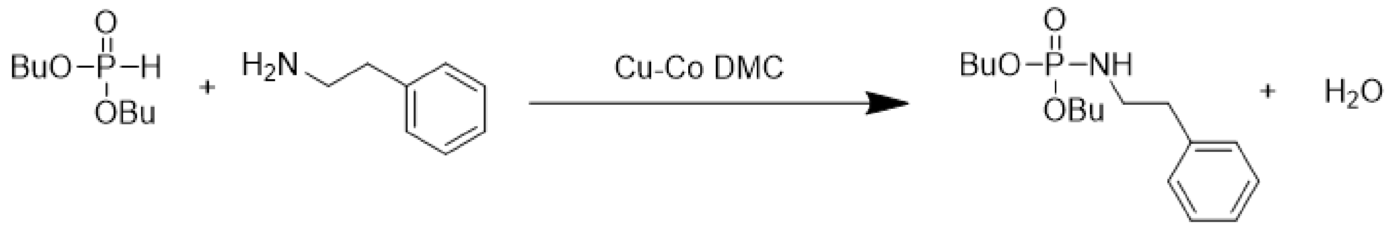
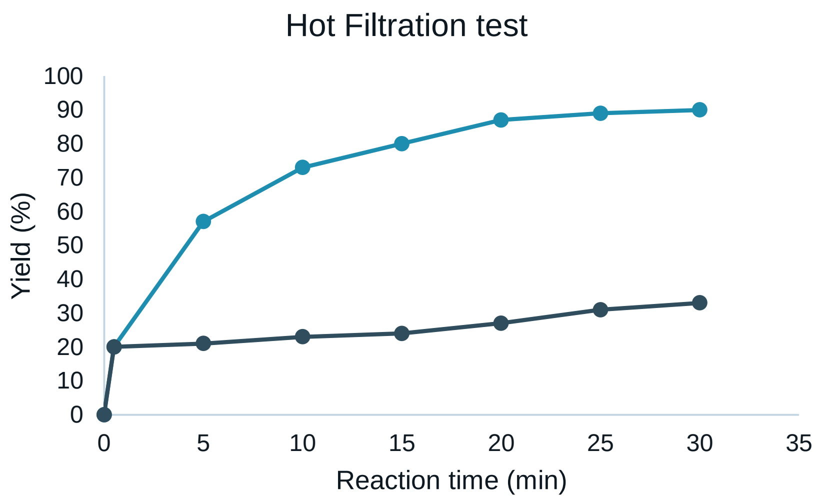
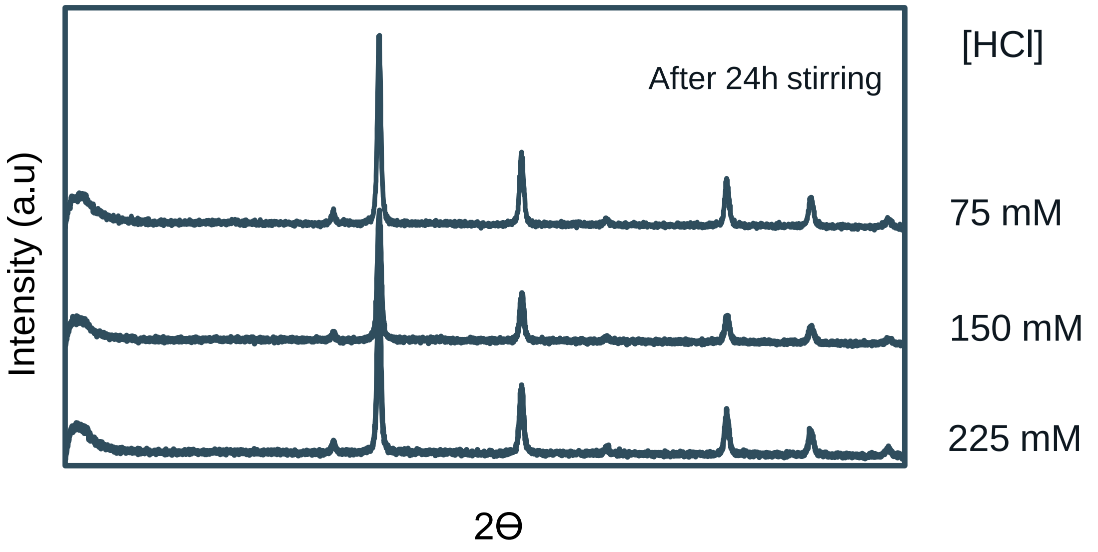
Stability



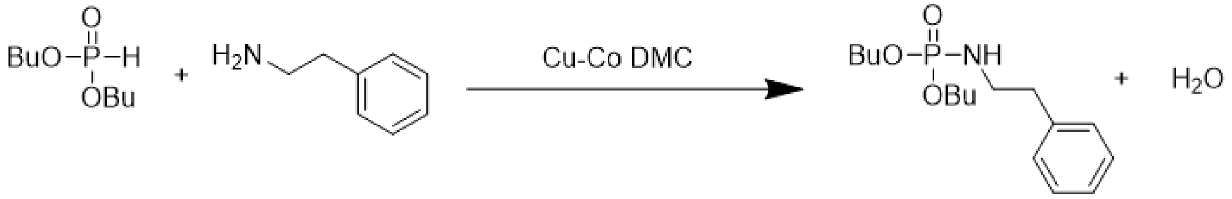


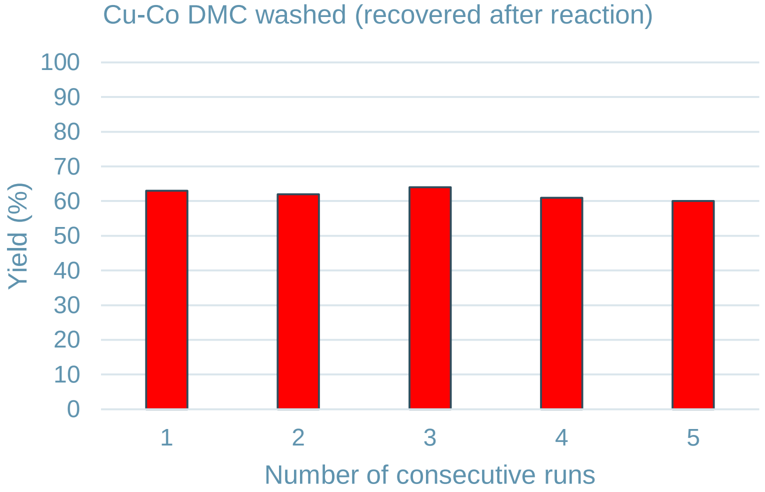


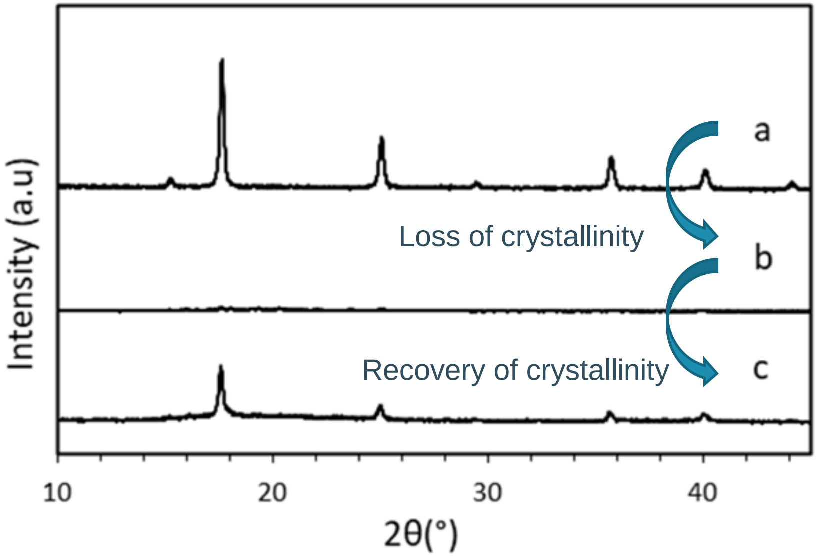
Sample	Cu mol%
Cu-Co DMC	1.6%

Cu leached after reaction

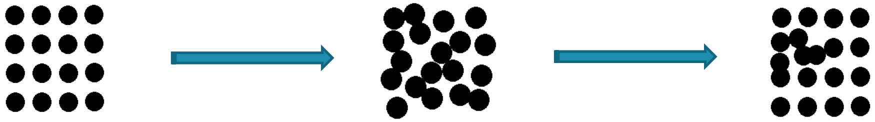
Recyclability





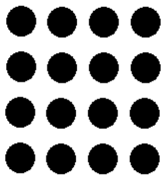


a) Pristine, b) Spent, c) Washed (recovered)



Local structure of the metal centers

Crystalline



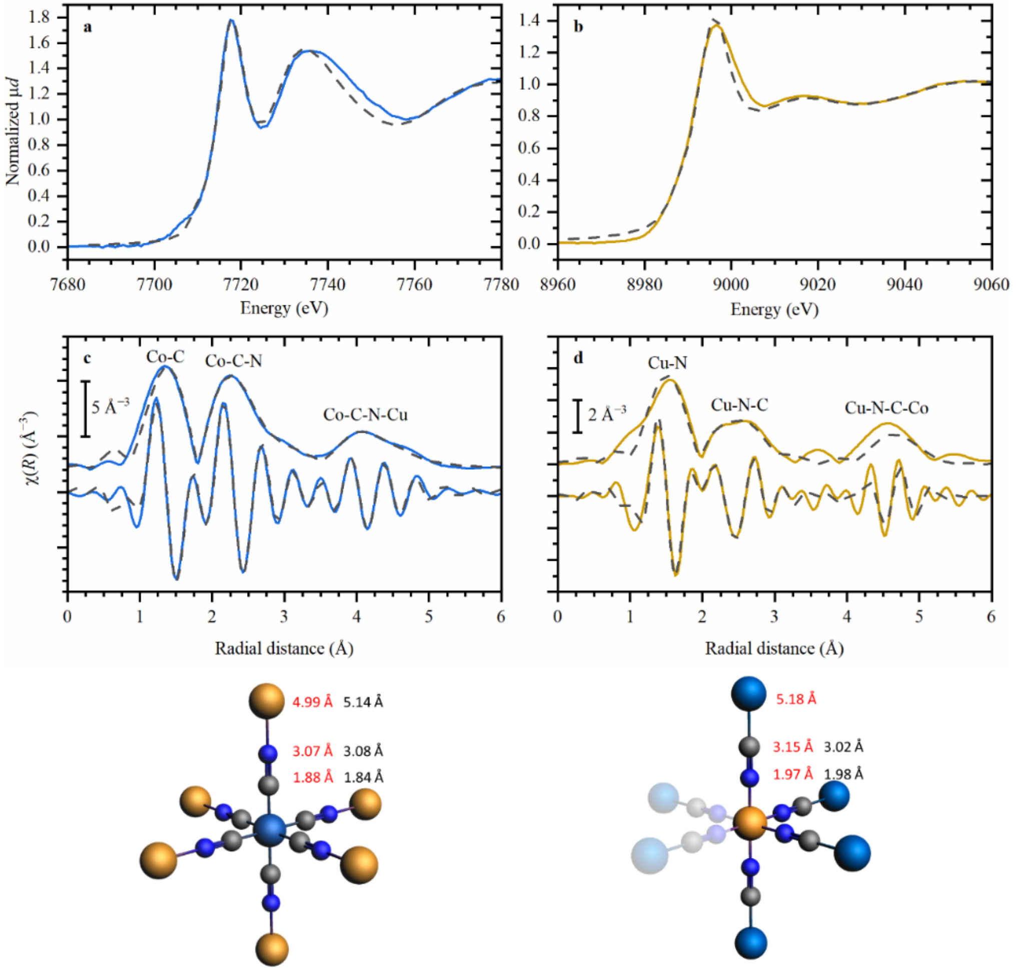
XAS spectroscopy → Allows us to know what atoms are near the metallic centers (Cu and Co) and their disposition in space

For the **pristine** Cu-Co DMC catalyst:

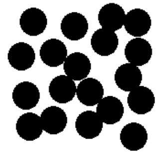
- Linear Co-N-C-Cu disposition
- Co octahedral geometry
- No free vacancies around Co atoms

- Cu octahedral geometry
- <u>But in this case, vacancies existed around Cu atoms!</u>

This vacancies correspond to the Lewis acid sites seen in IR.



Amorphous



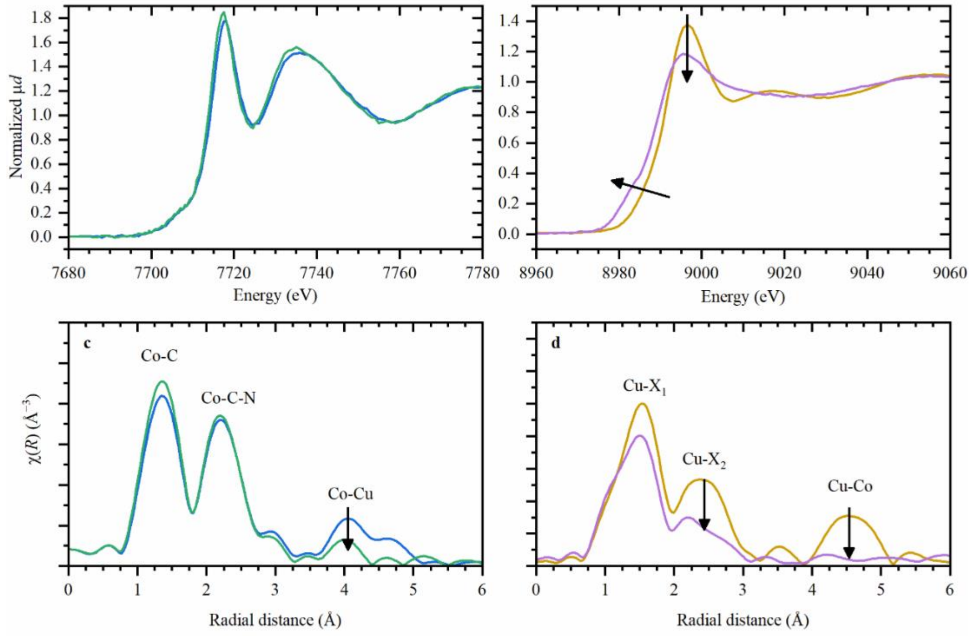
Catalyst characterization: Cu-Co DMC

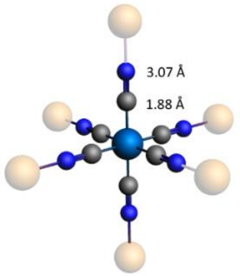
XAS spectroscopy → Allows us to know what atoms are near the metallic centers (Cu and Co) and their disposition in space

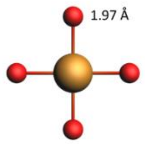
For the **spent** (just after reaction) Cu-Co DMC catalyst:

- Co atoms electronic and spatial structure was not changed
- However, Co-Cu long distance coordination was partially lost

- Cu appeared to exchange ligands
- Identifying this exact ligands is hard, possibly O and N atoms
- Cu adopts a newly square planar geometry

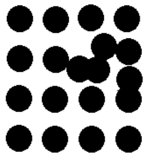






Catalyst characterization: Cu-Co DMC

Partial recovery of crystallinity

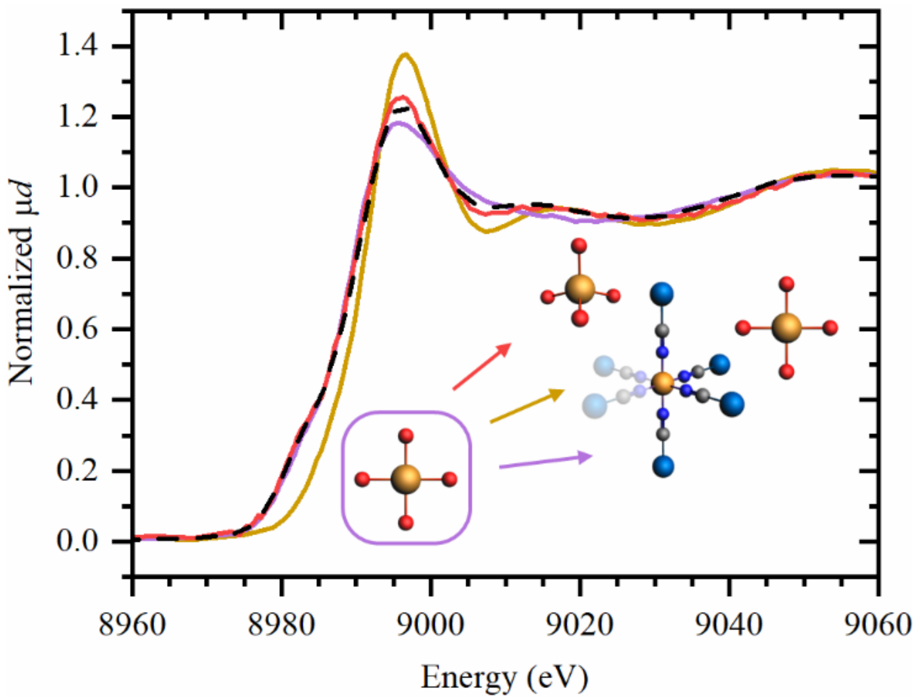


XAS spectroscopy → Allows us to know what atoms are near the metallic centers (Cu and Co) and their disposition in space

For the **recovered** Cu-Co DMC catalyst:

- Co atoms remain unchanged, but this time Co-Cu coordination was recovered

- Part of Cu atoms returned to their octahedral geometry
- Part of the Cu atoms stayed in the square planar geometry
- Part of the Cu atoms adopted a new tetrahedral geometry!



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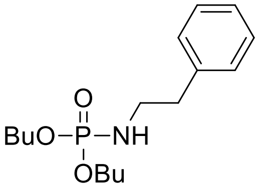
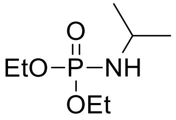
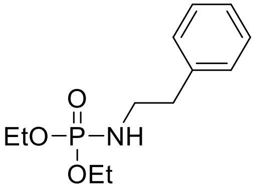
Testing on plastic



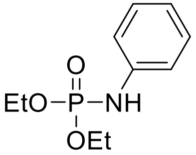
AF-A



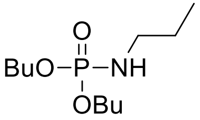
AF-B



AF-C



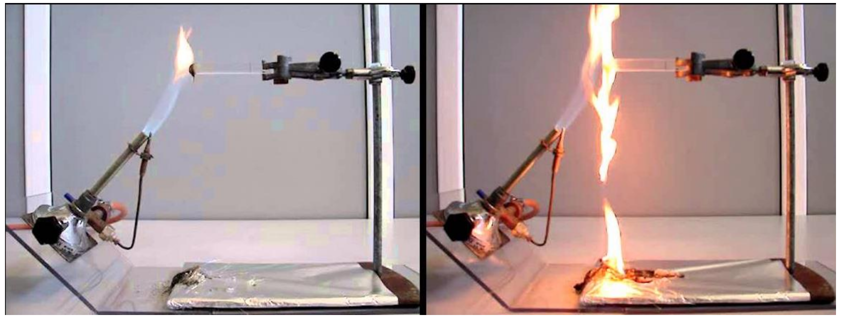
AF-D

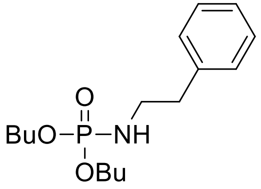


AF-E

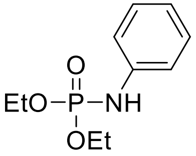
LDPE

- DSC
- TGA
- Viscosity
- Flammability test

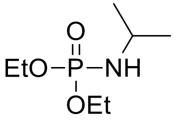




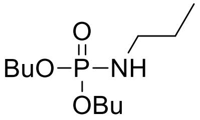
AF-A



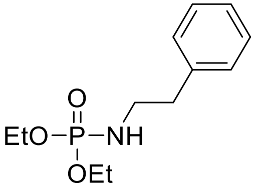
AF-D



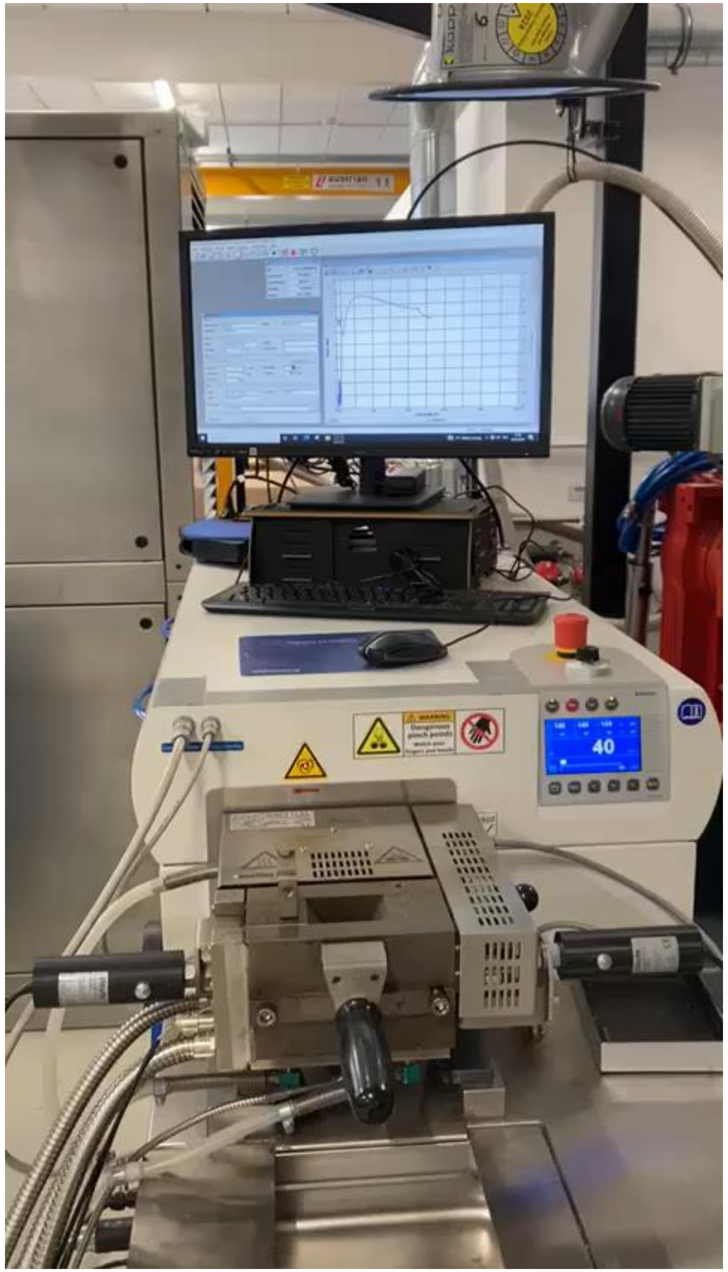
AF-B

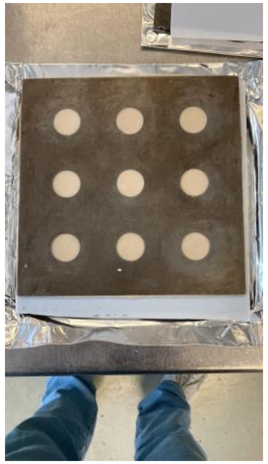


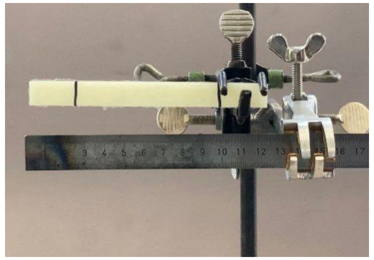
AF-E

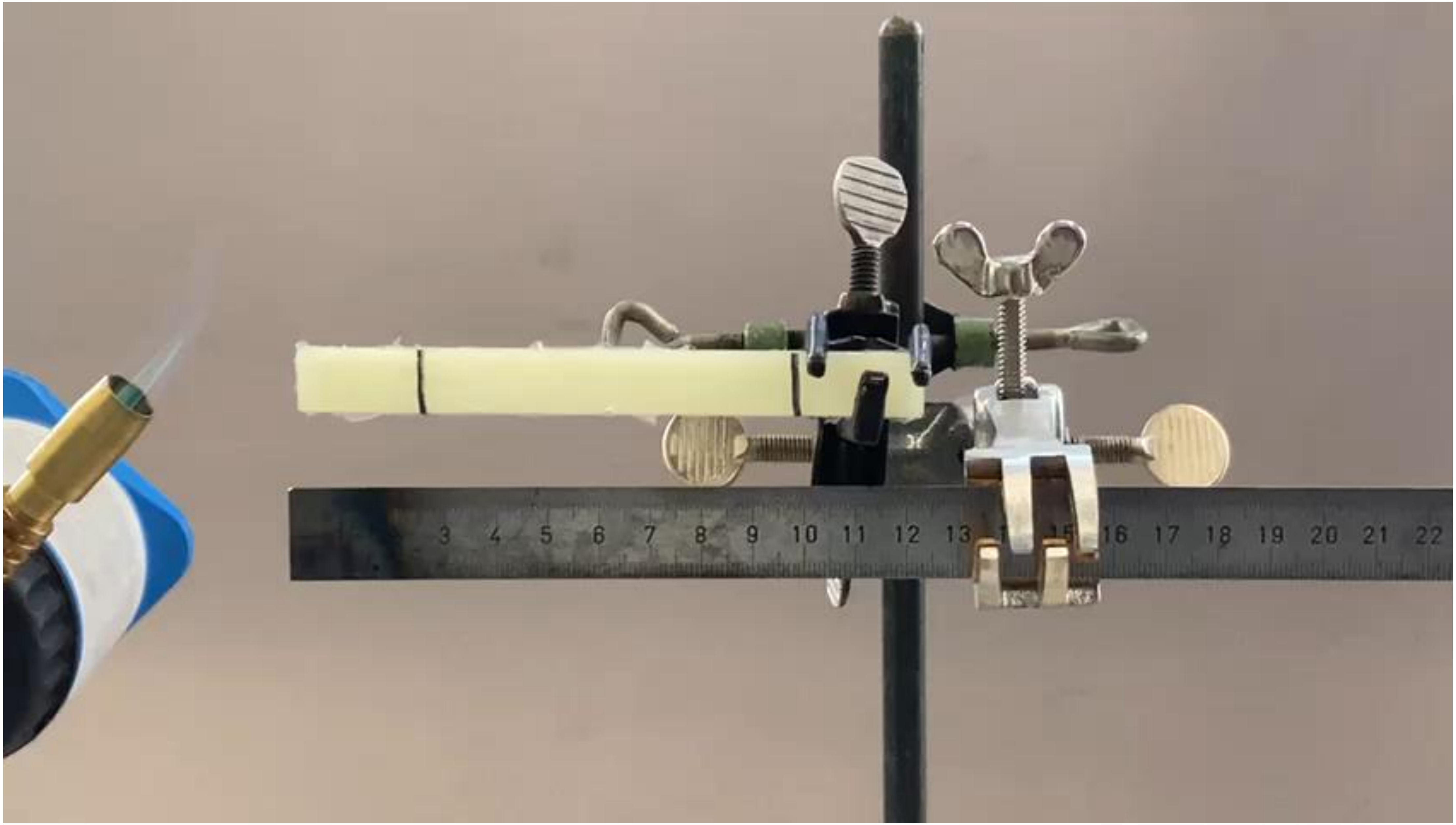


AF-C





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Thank you!

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