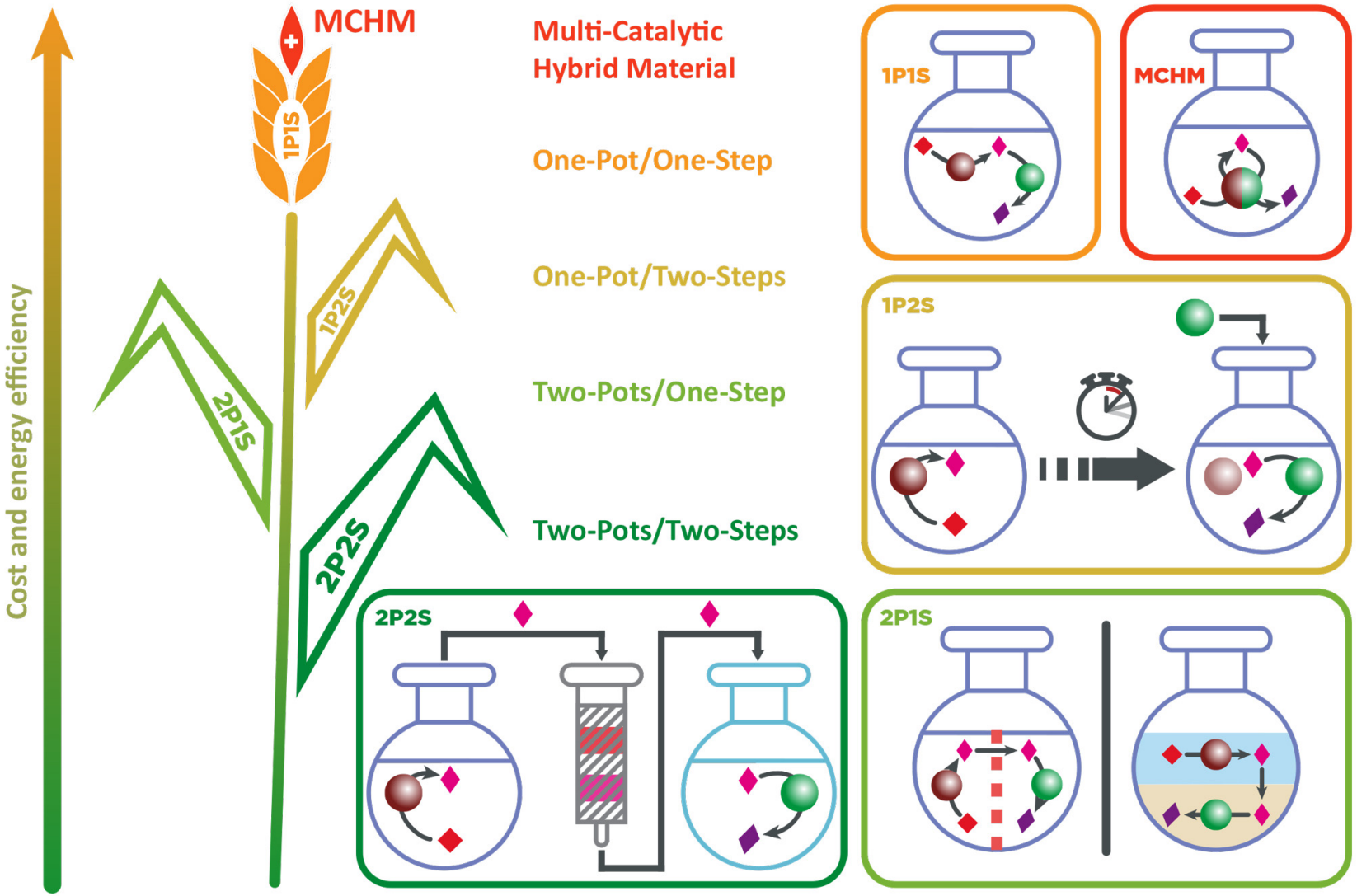
Hybrid catalysis: towards an optimal combination of catalysts
Application to HMF valorization

Antoine Lancien, Aurélie Fossey, Robert Wojcieszak, Renato Froidevaux, Anne Zaparucha, Egon Heuson

Heuson & Dumeignil, Catal. Sc. & Tech. 2020

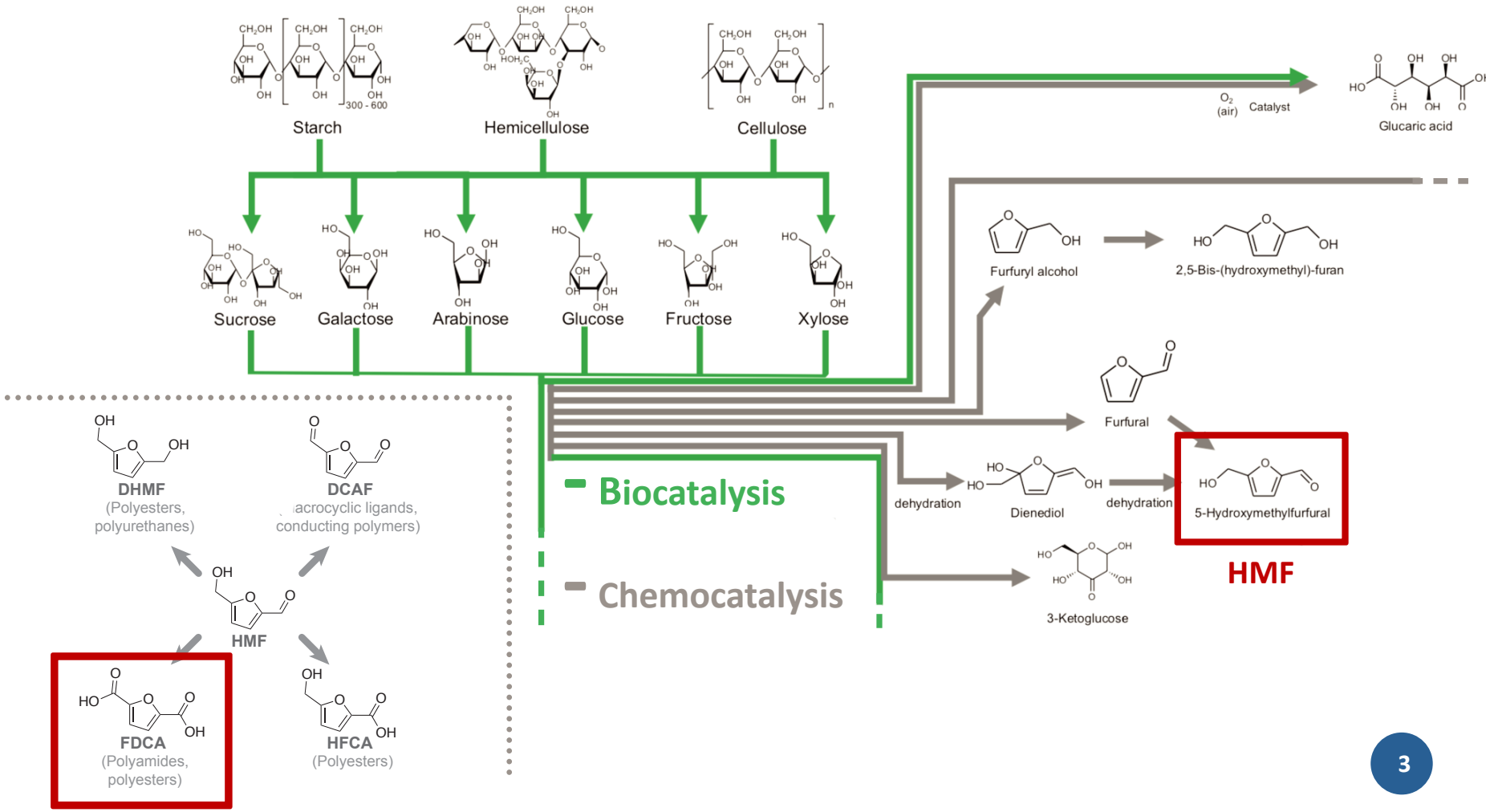
Towards maximum catalyst integration



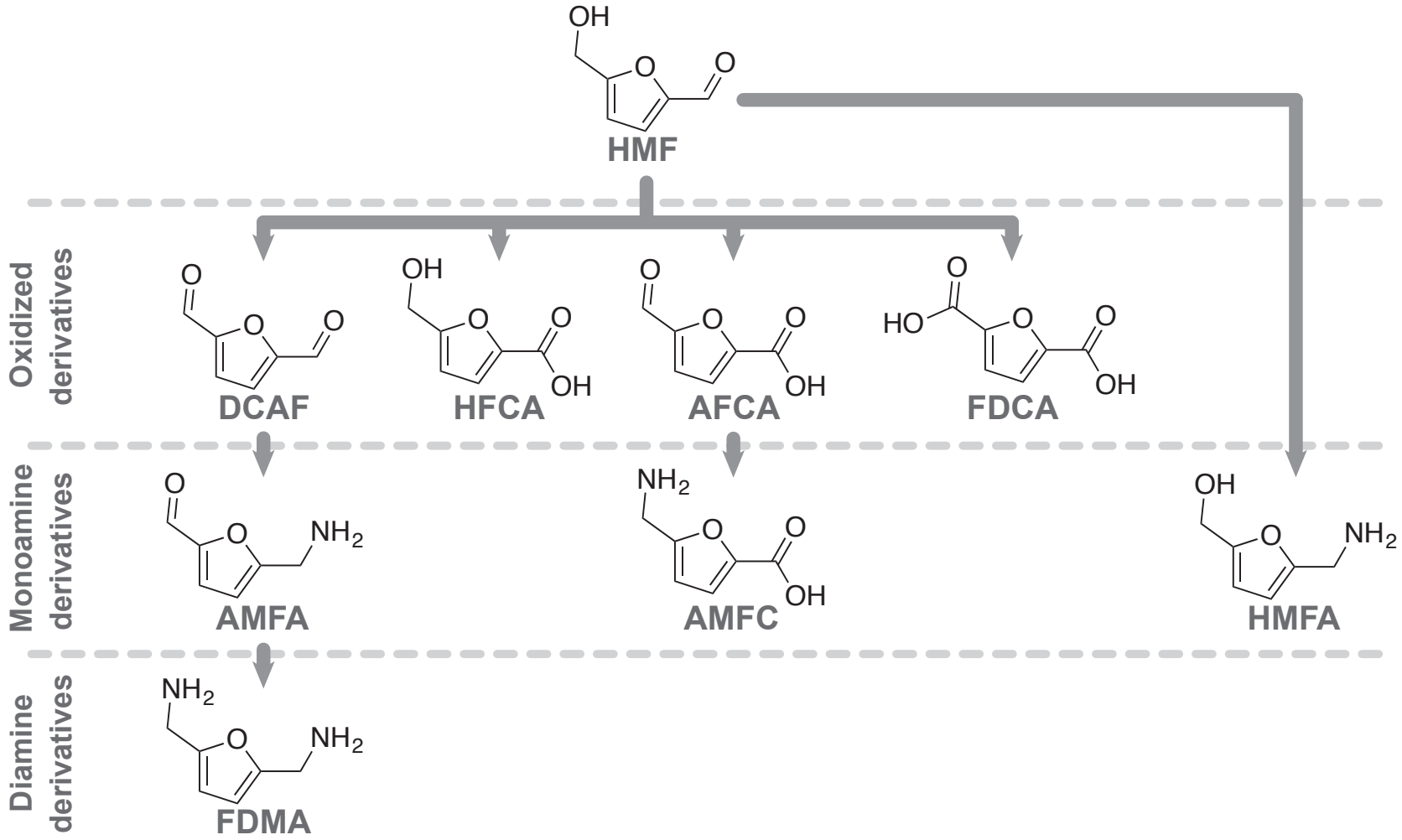
Valorization of HMF

5-hydroxymethylfurfural (HMF), a major bio-based building block

- Abundant by-product of lignocellulosic biomass
- Building block for the synthesis of many compounds of interest
- Direct source for the production of furan dicarboxylic acid (FDCA, among the DOE's 12)



Synthesis of Furfurylamines



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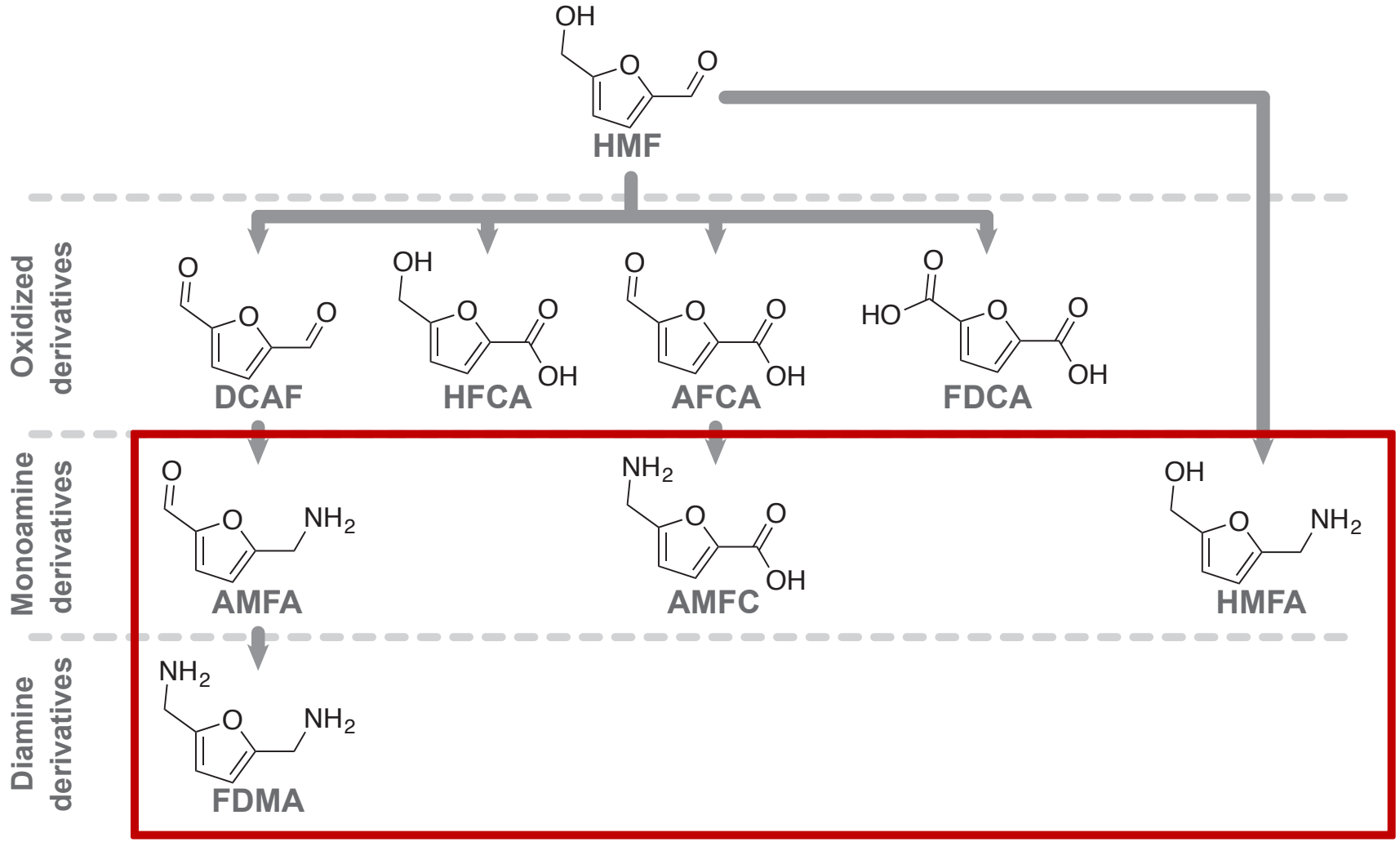

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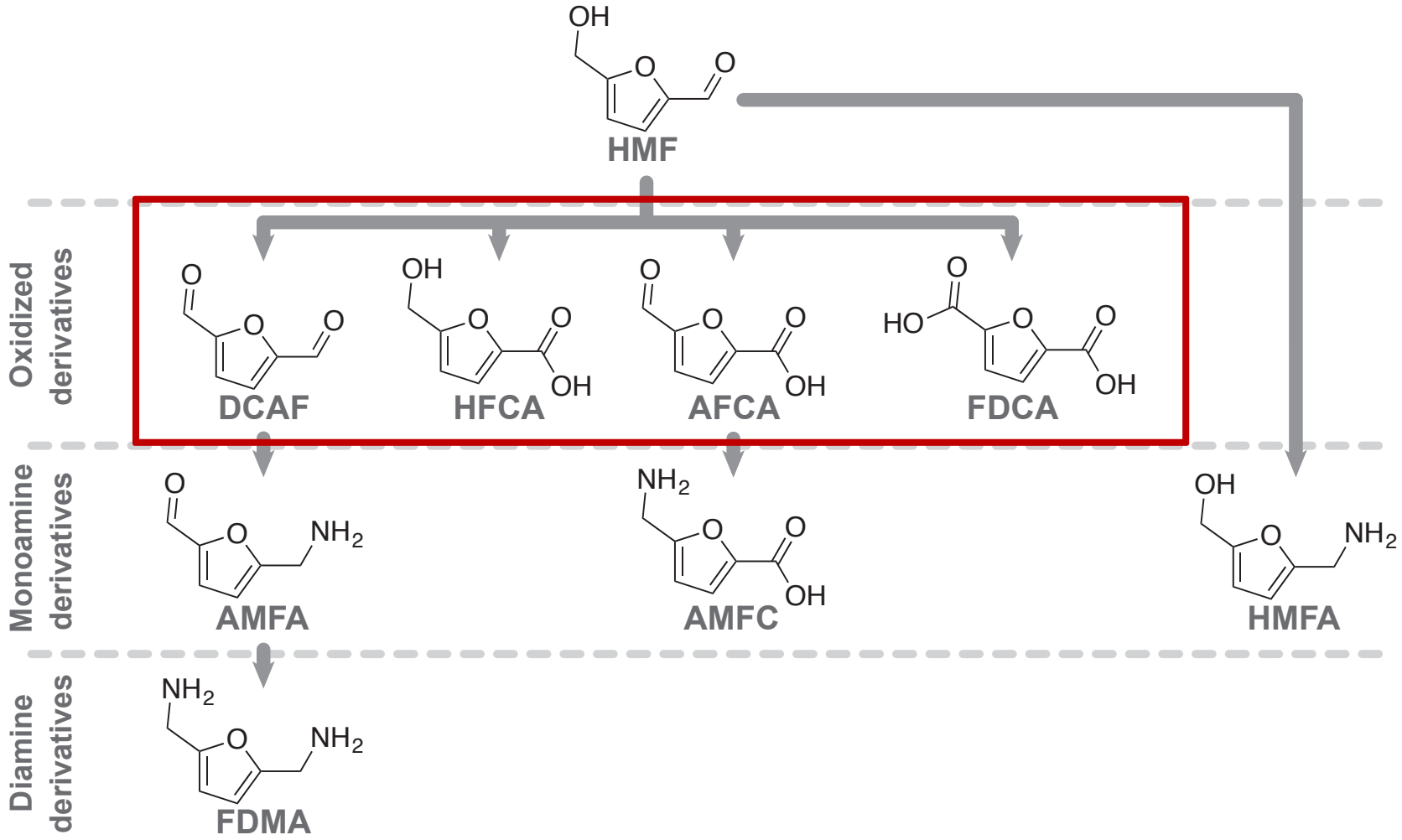

Synthesis of Furfurylamines

Synthetic pathways

- **Chemical reductive amination (requires numerous protections/deprotections)**
  - **Recent new methodology without protection (Lankenau *et al.* 2020)**
- **Biocatalytic (transamination)**
  - **Only two studies, no methodology for AMFC, AMFA, and FDMA (Dunbabin *et al.* 2017, Petri *et al.* 2018)**

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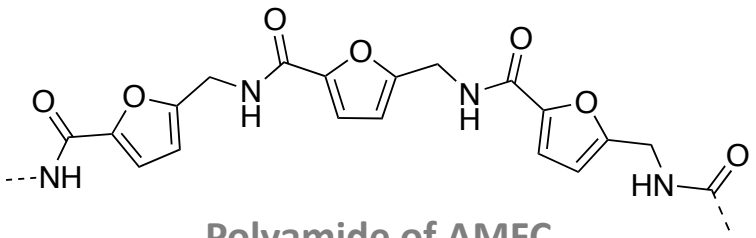
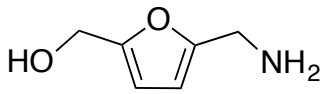
Applications

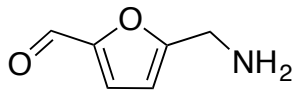
- **Very few applications described**
- **AMFC: Cyclic trimeric oligopeptide (Kchakraborty *et al.* 2002, Sharma *et al*. 2006)**
  - **Production of new polyamides/polyimines and other polymers**



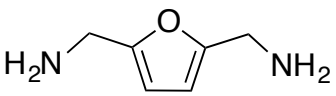
Polyamide of AMFC



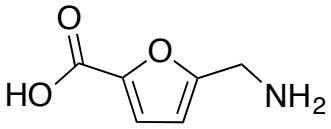
HMFA



AMFA

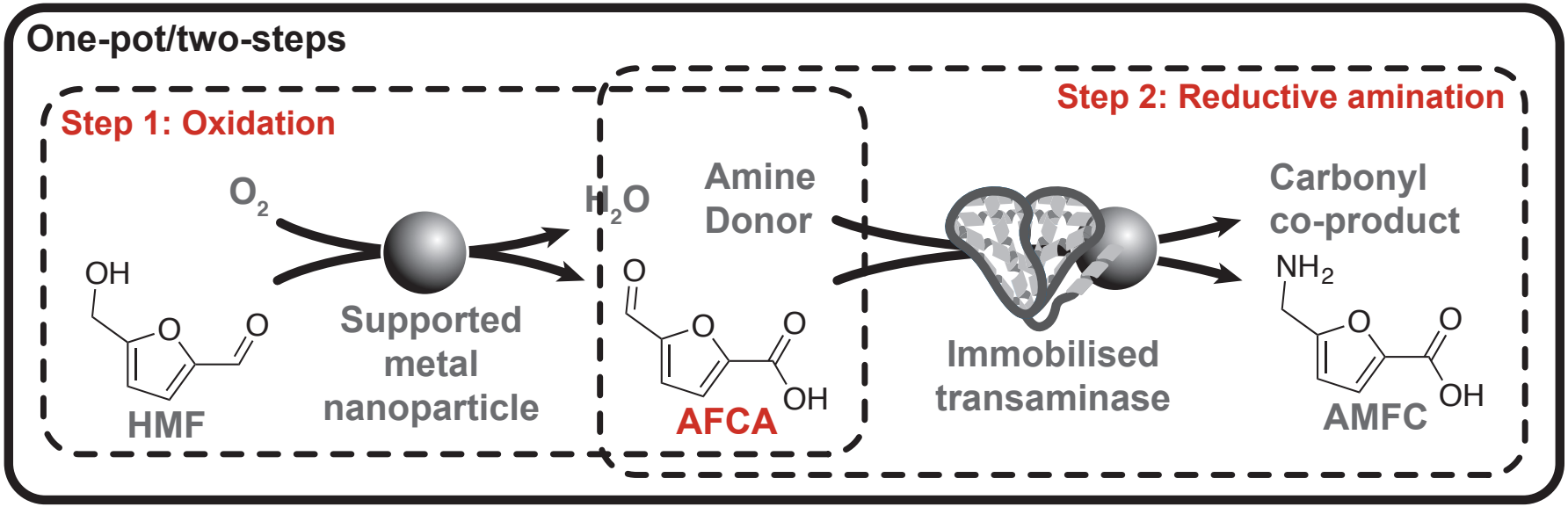


FDMA

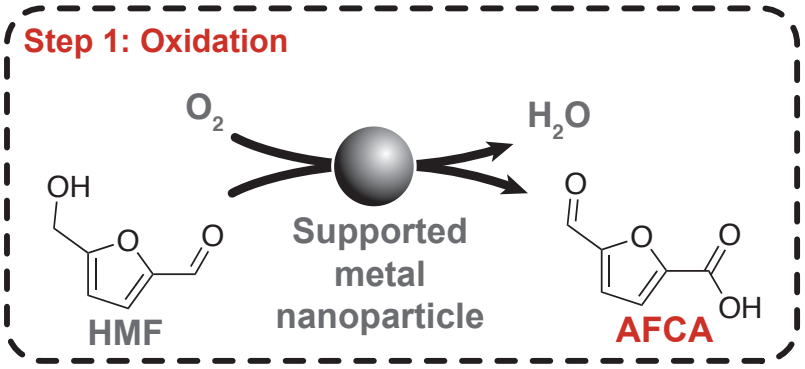


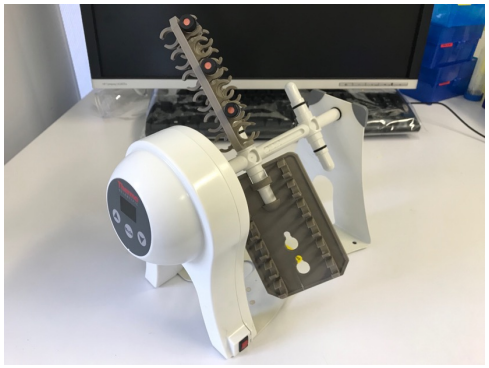
AMFC

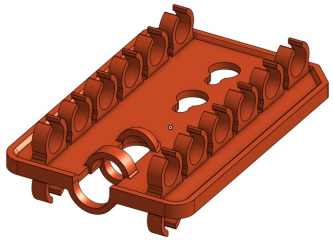
New hybrid route for AMFC

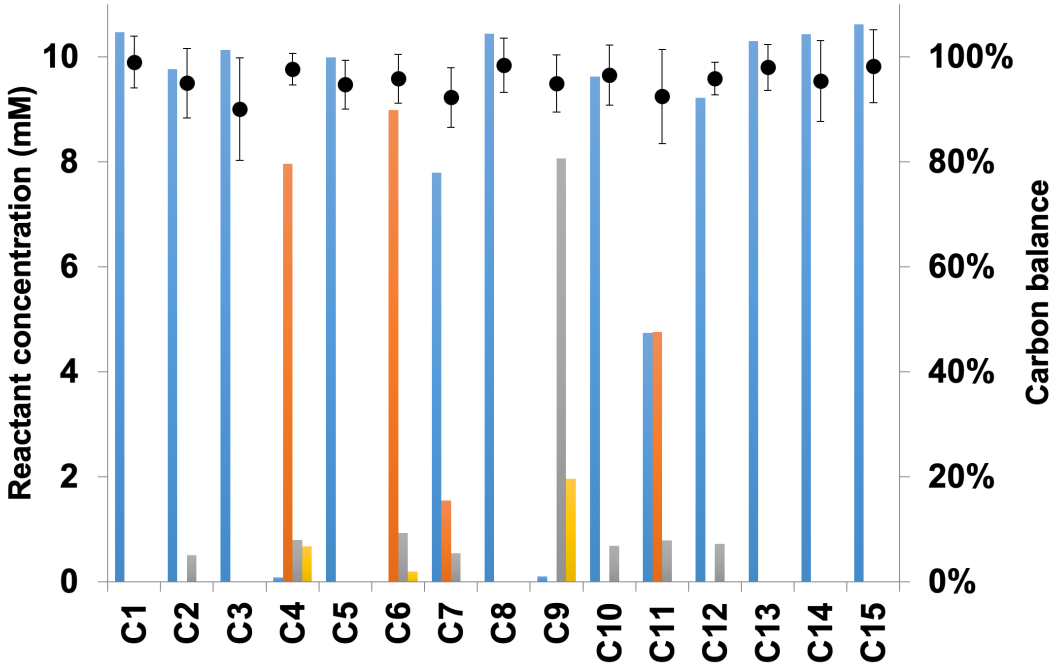


Screening of supported metal nanoparticles

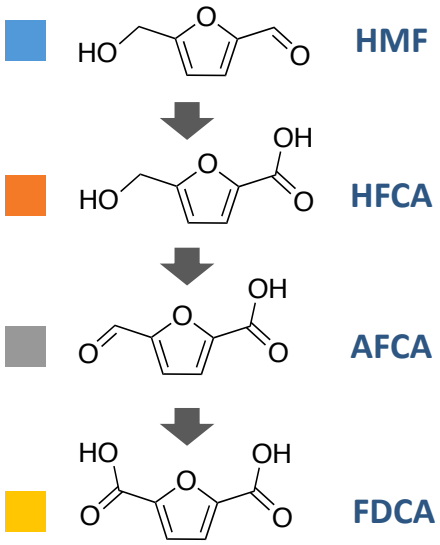






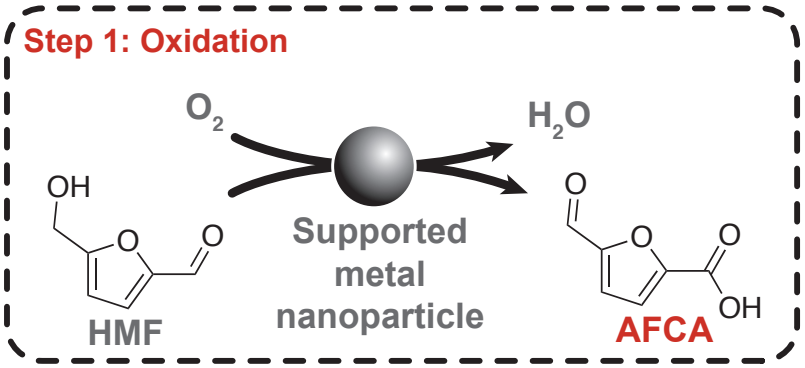


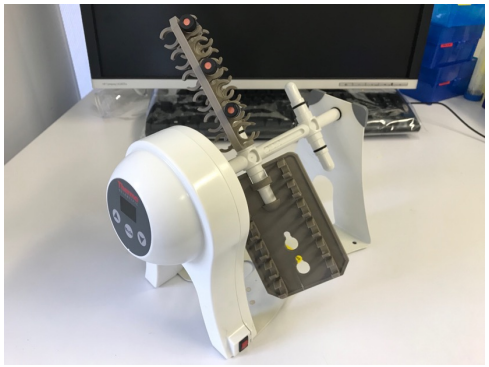
Results after 24 hours at 60°C

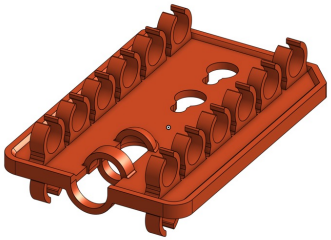


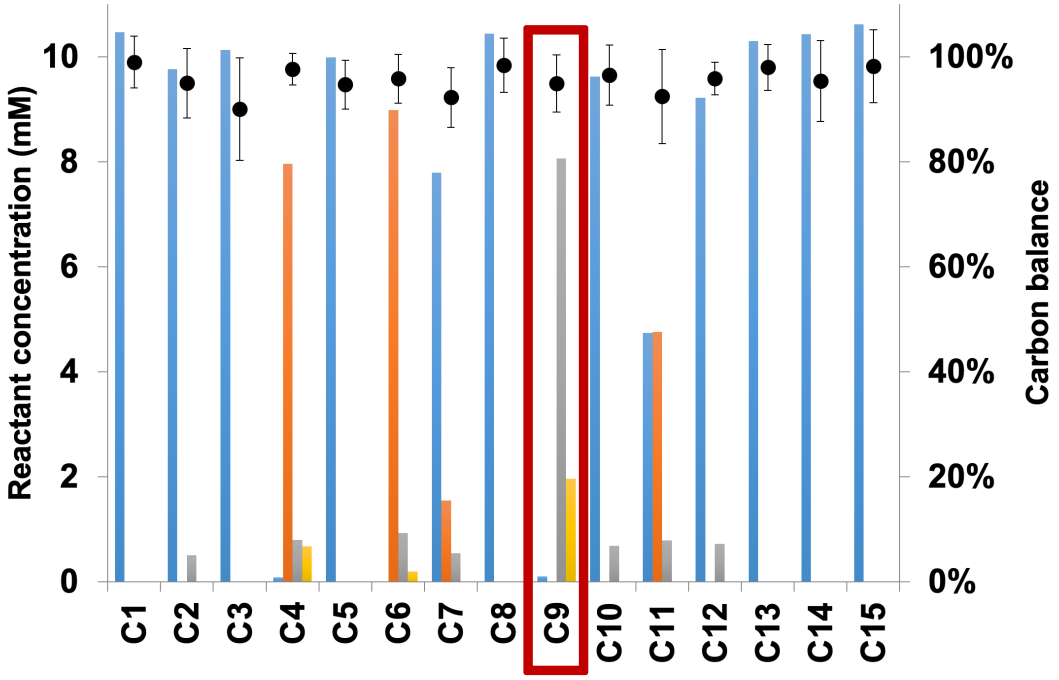
Very low activity detected at 30°C

Screening of supported metal nanoparticles









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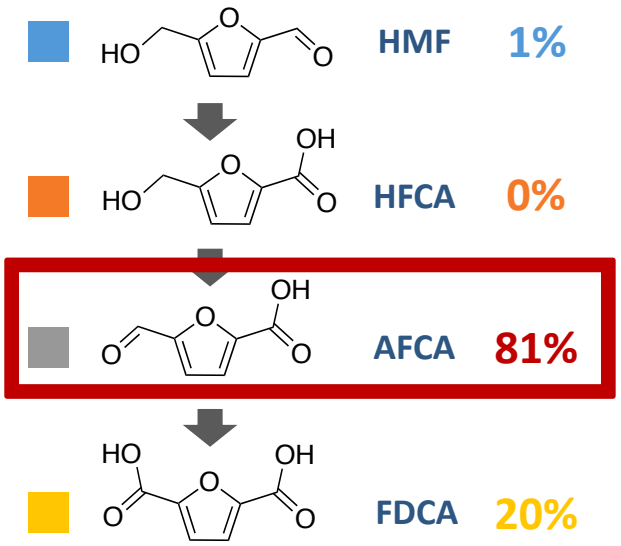
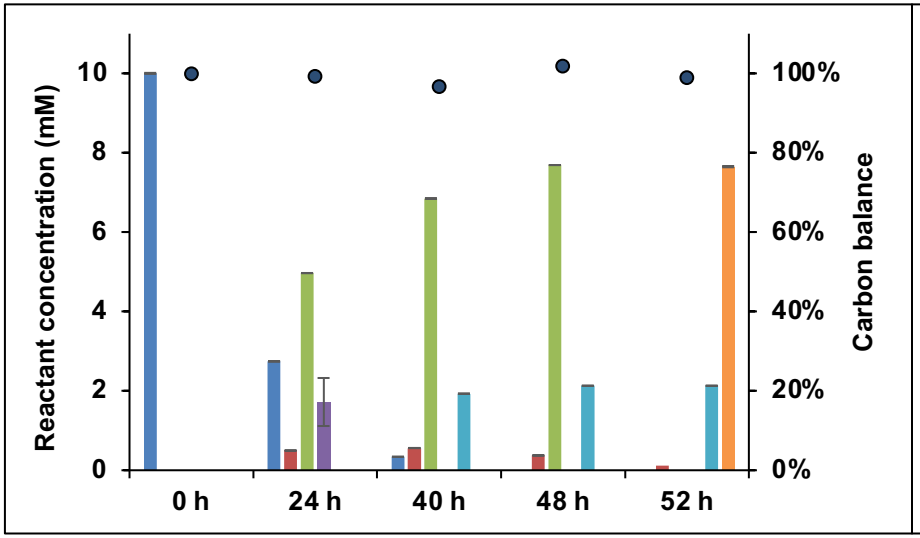


Pt/SiO_2

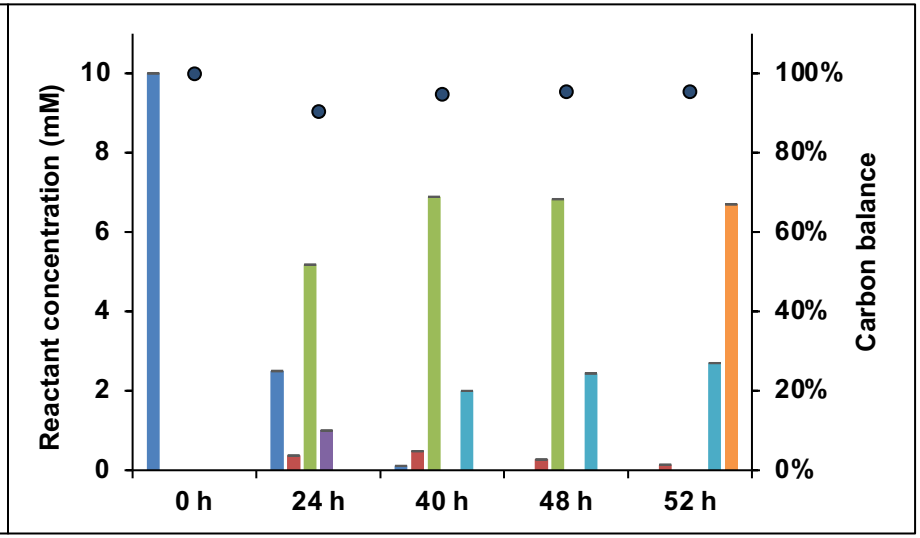
1P2S synthesis of AMFC

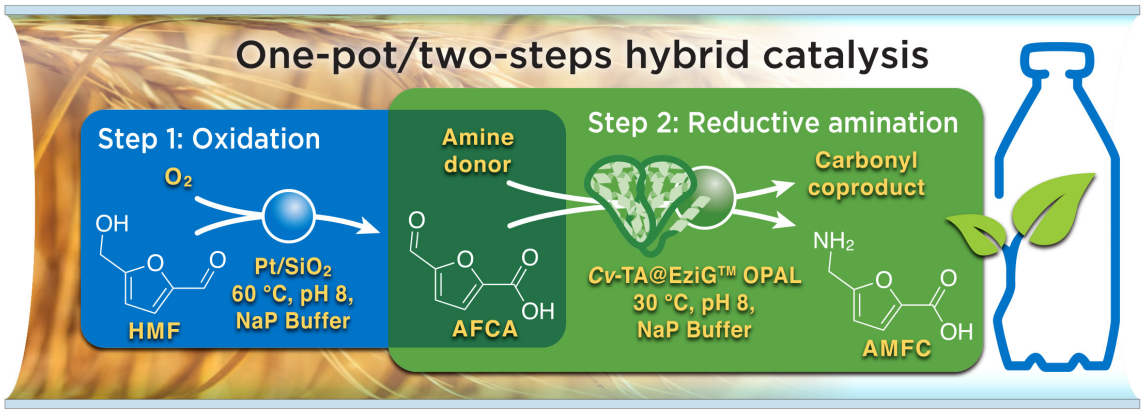
1P2S : Addition of *Cv*-TA@EziG™ OPAL after 48h reaction and cooling

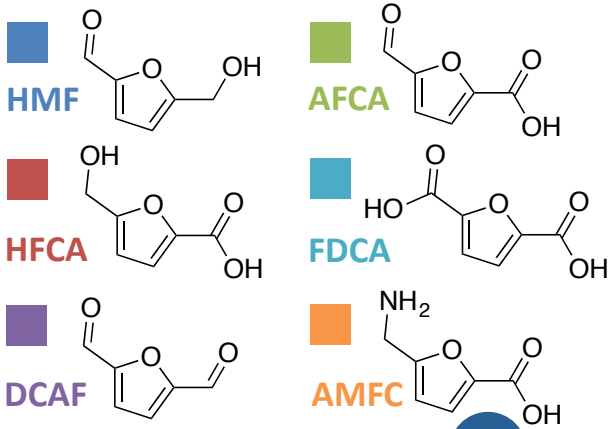
Donor : *(S)*-Methylbenzylamine (1:1)



Donor : Isopropylamine (10:1)

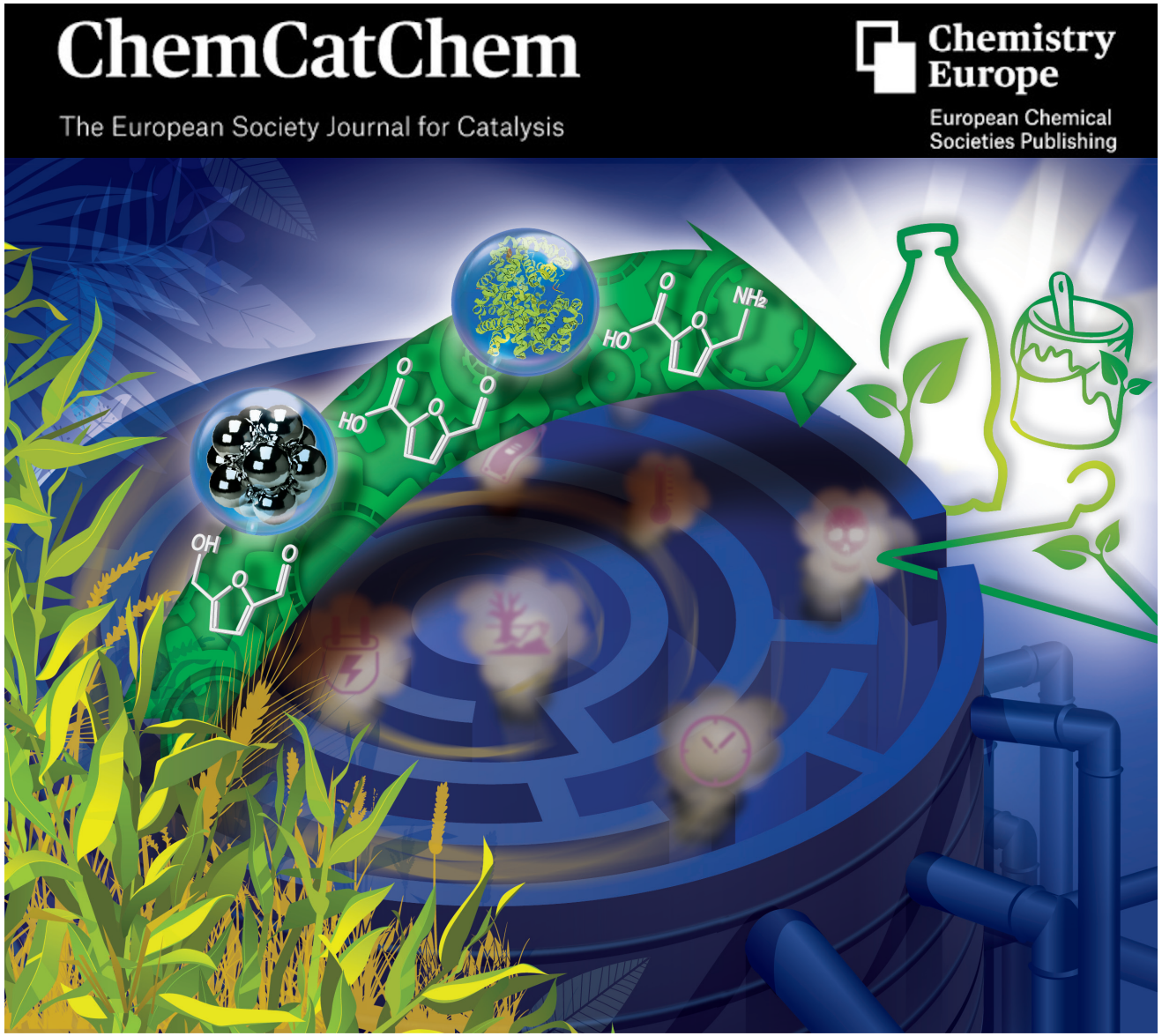






Lancien *et al.* ChemCatChem, 2021

1P2S synthesis of AMFC

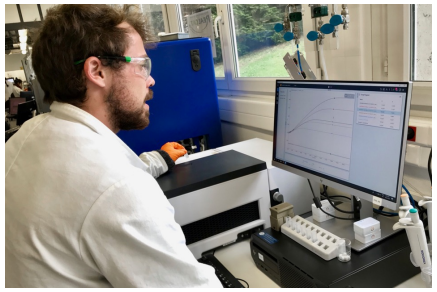


Lancien *et al.* ChemCatChem, 2021

Towards a 1P1S system

Seeking a thermostable TA

- **Attempted production of 5 new amine-TAs sent by the University of Greifswald**
  - **Efficient production of a single TA**
- **Testing the new TA on HMF and its derivatives**
  - **Higher activity for HMF and AFCA**



Antoine Lancien
PhD Student in
Hybrid Catalysis

Cary 3500 (Agilent)

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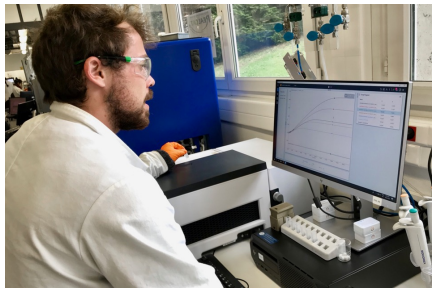
- **Thermostability/thermoactivity**



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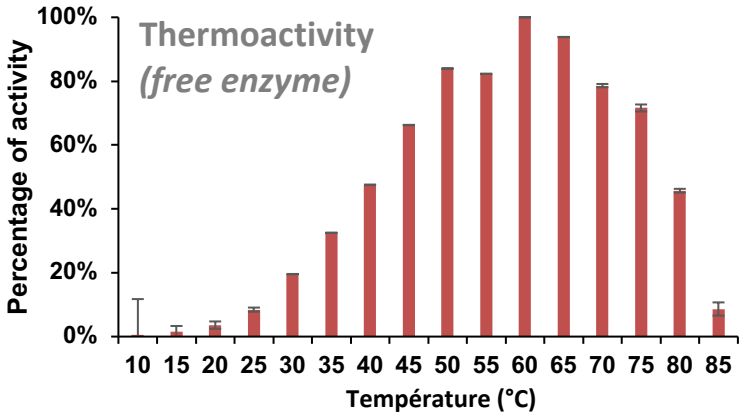
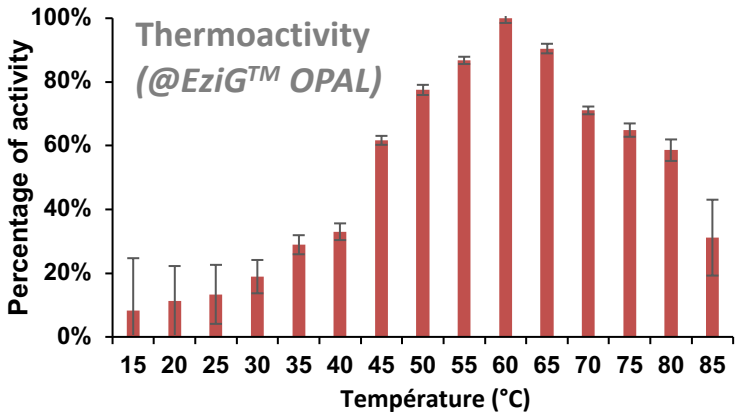
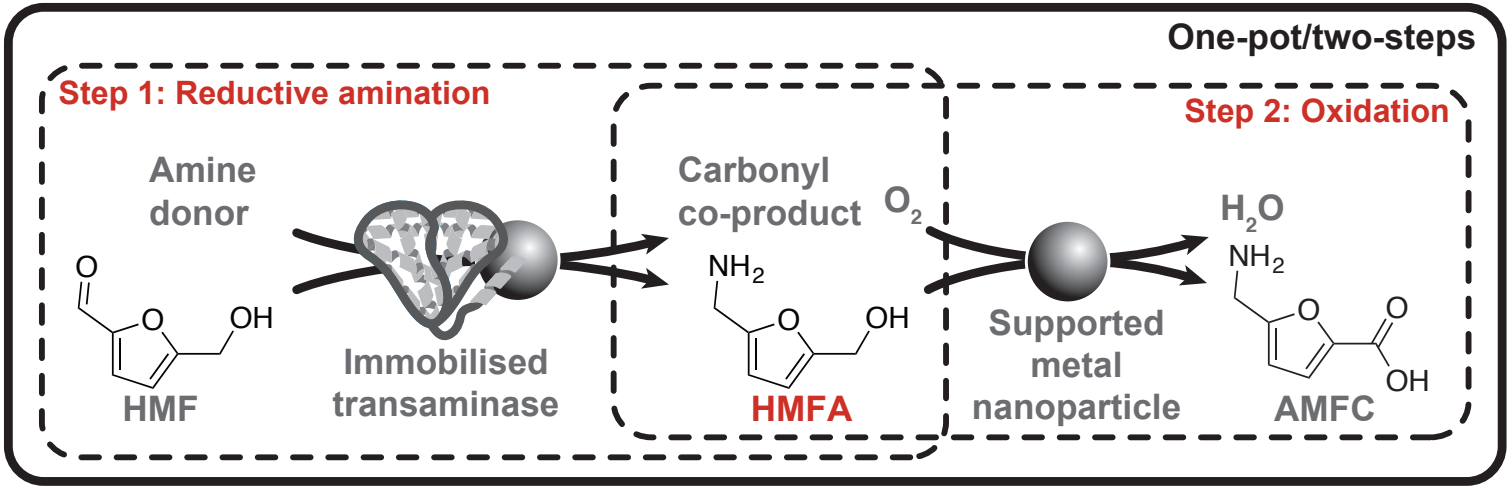
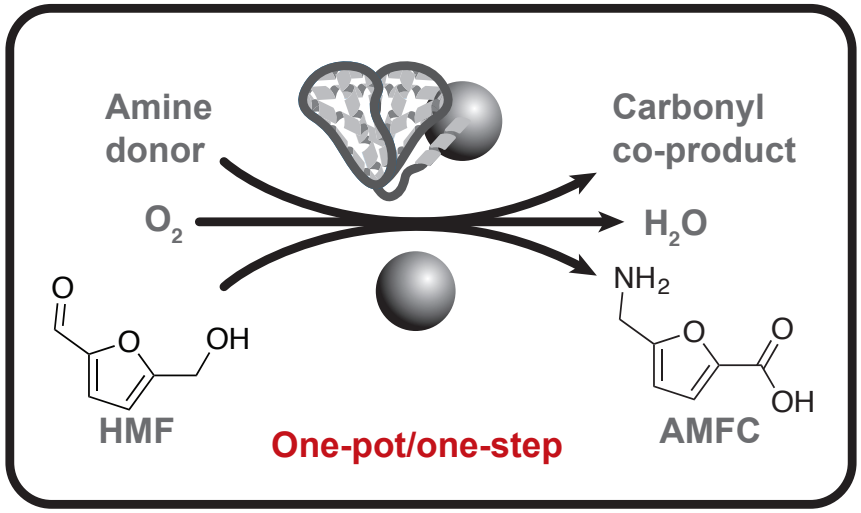




- **Thermostability at 60°C : 87% after 24h (free enzyme) – 55% after 24h (immobilized)**

Towards a 1P1S system

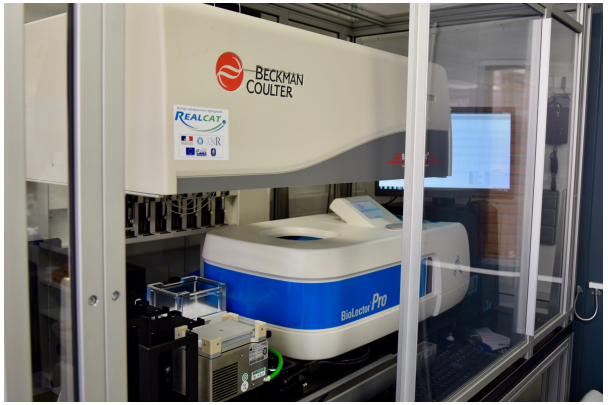




Towards a 1P1S system

Screening new chemocatalysts for HMFA oxidation

- **33 new catalysts tested (mainly Au based)**
- **300 combinations/conditions tested in 1 month**
  - **New screening methodology using the BioLector Pro**
- **Selection of $Au@TiO_2$, Au@CaO and $Au@UiO\text{-}66\_NH_2$**



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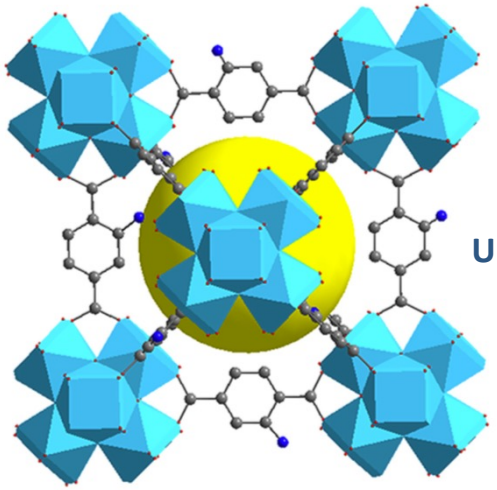
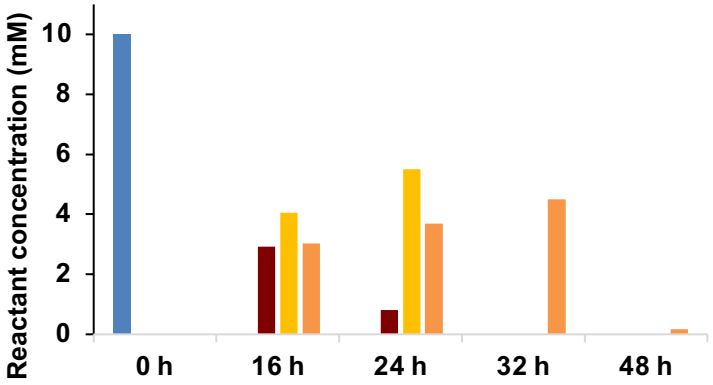


UiO-66_NH_2

First 1P1S system attempts

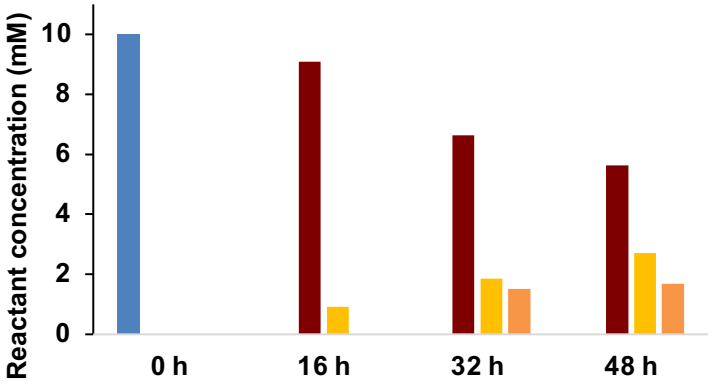
Au@CaO + TA@EziG™OPAL



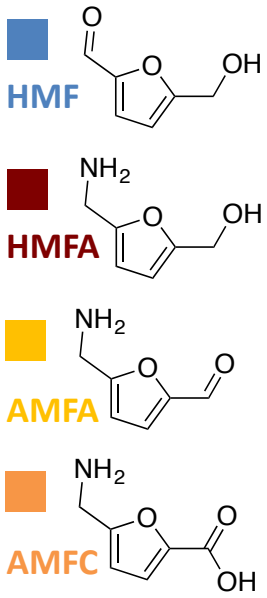
45% yield / 100% conversion

⇒ appearance of a precipitate

Au@UiO-66_NH_2 + TA@EziG™OPAL

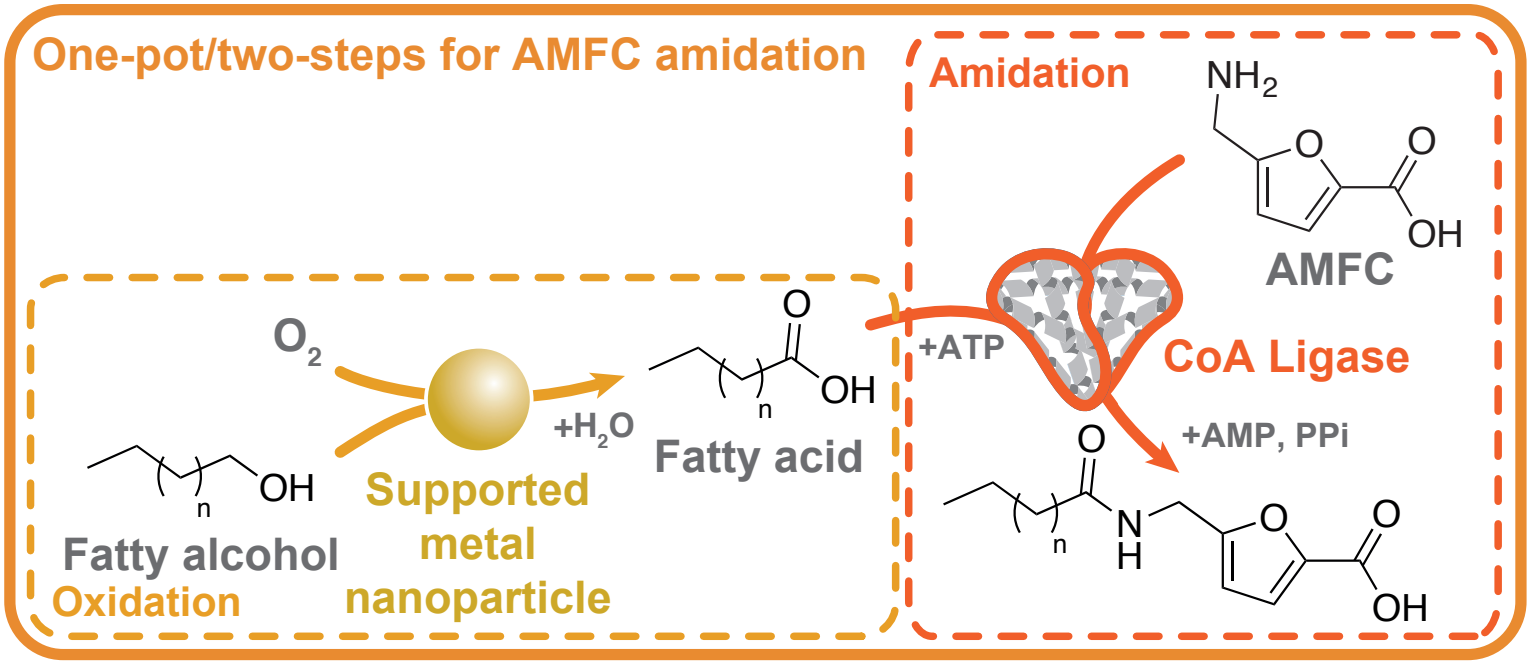


17% yield / 44% conversion



Expending the reaction scope: CoA Ligases

Production of amphiphilic molecules from alcohols derived from biomass

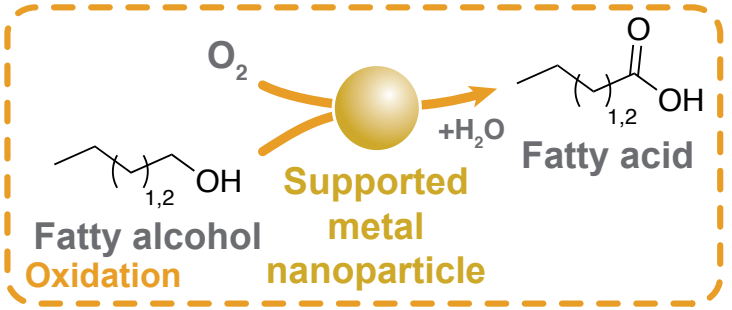


UMR GENOSCOPE
METABOLIC GENOMICS
Anne Zaparucha Aurélie Fossey

Expending the reaction scope: CoA Ligases

Screening new chemocatalysts for fatty alcohols oxidation

- Butanol and pentanol used as substrate
- 11 catalysts tested
- Selection of **Au@CaO**: **100% conversion** in 48h at 50°C



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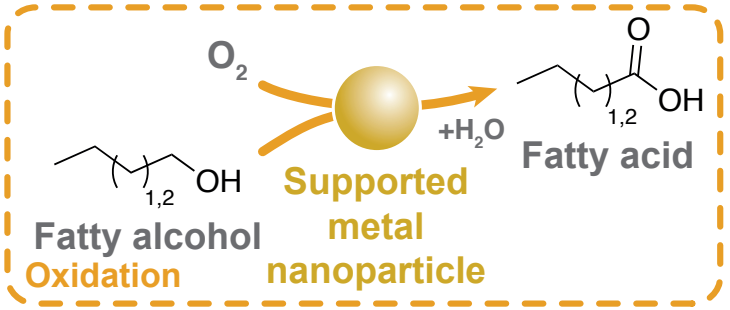
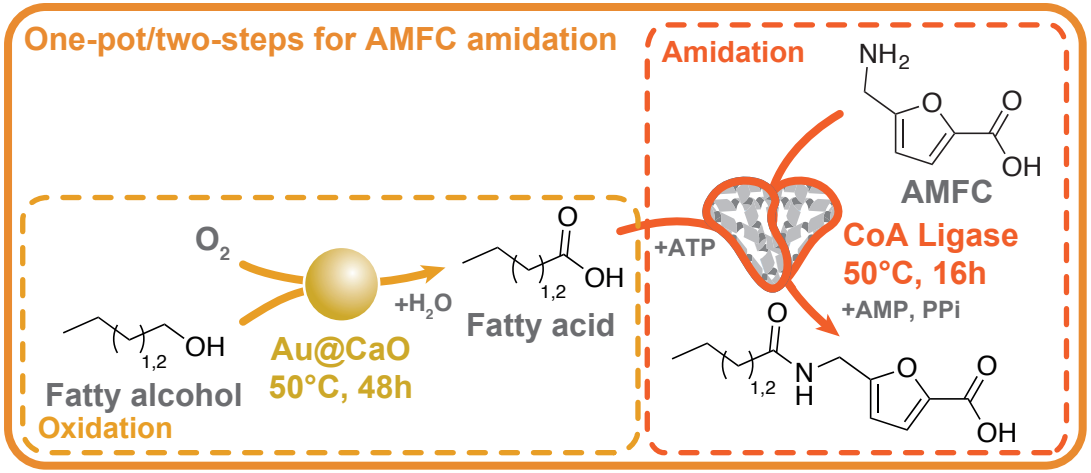
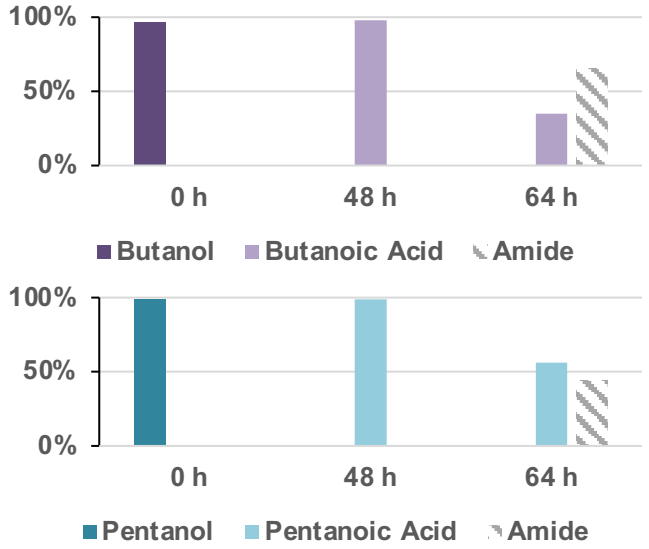


Promising preliminary results

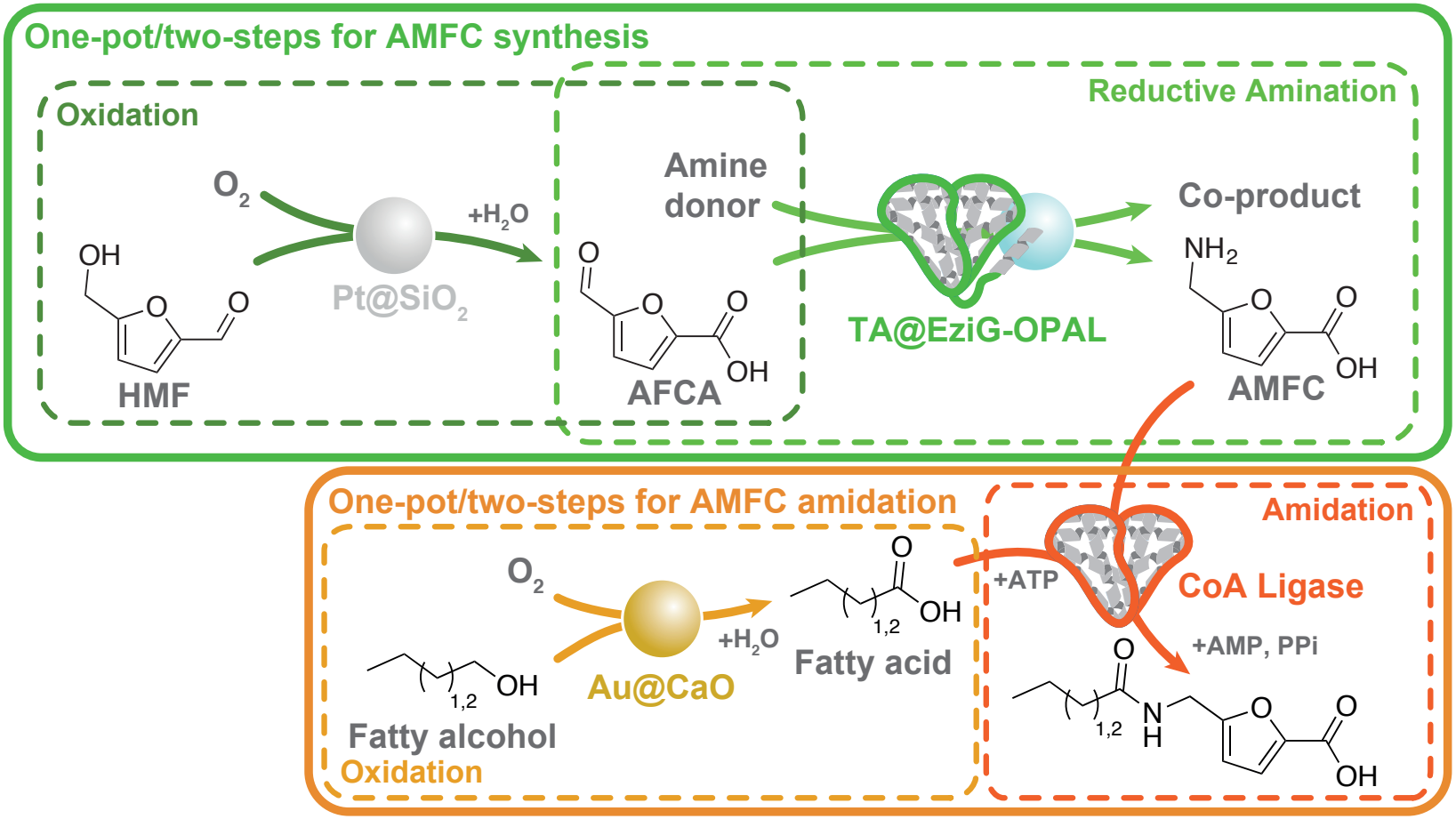




- **65%** and **54%** yield (100% conversion) for **butanol** and **pentanol** respectively
- Amide confirmed by NMR and Mass

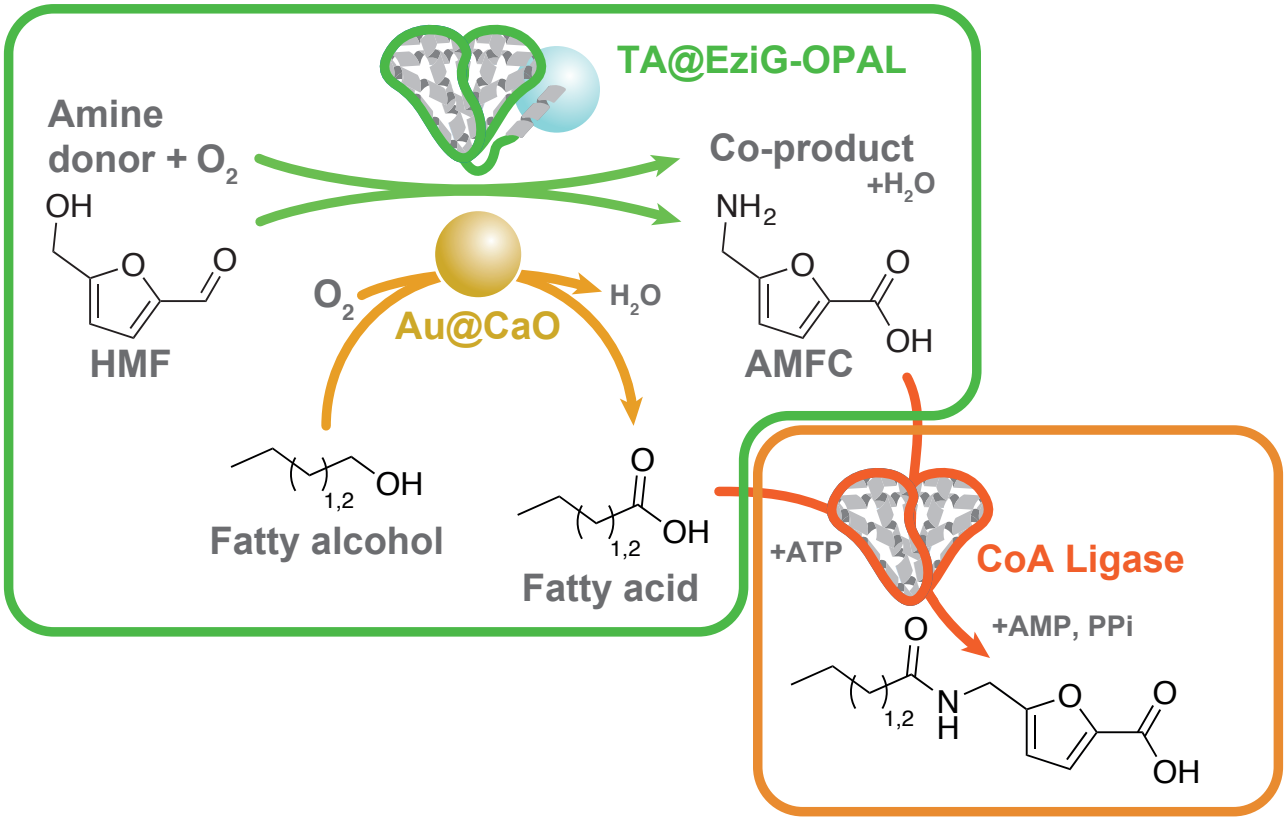
Expending the reaction scope: CoA Ligases

The next steps…



Expending the reaction scope: CoA Ligases

The next steps…



… toward a complete 1P1S system

Merci pour votre attention!

Brings catalysis over lightspeed

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… au Nord, c'étaient les Corons!

Antoine Lancien