

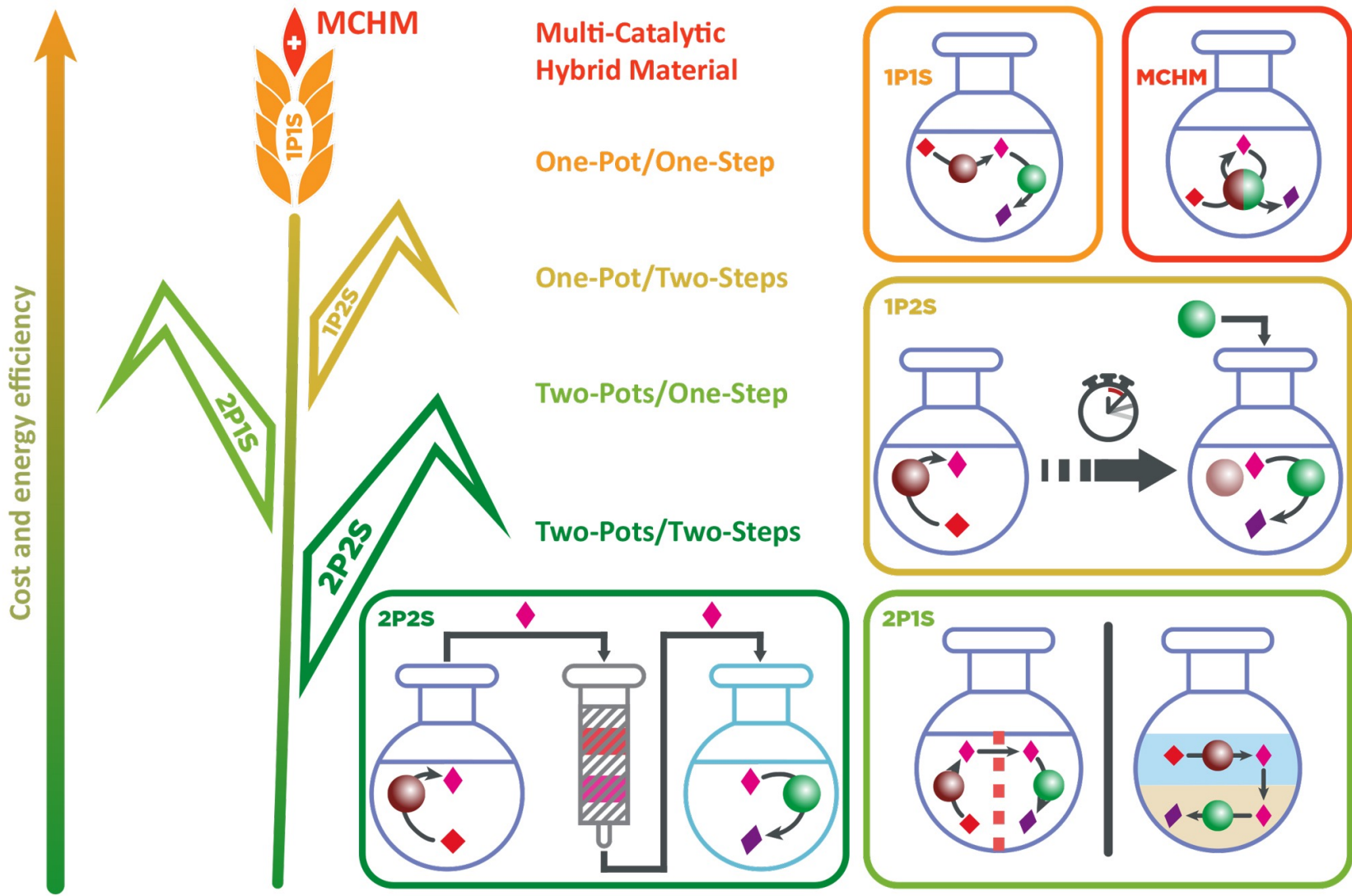
Hybrid catalysis: towards an optimal combination of catalysts

Application to **HMF** valorization

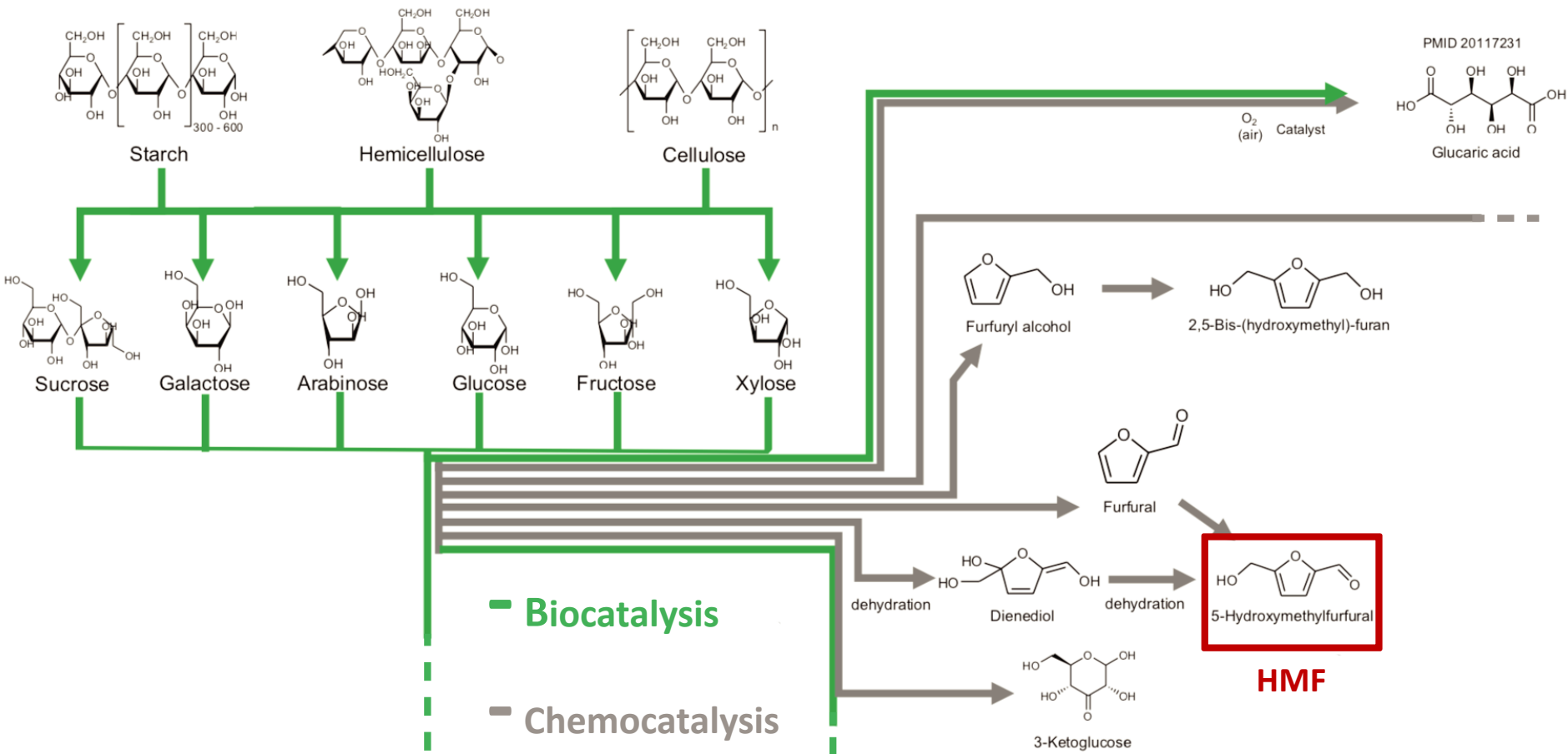


Antoine Lancien, Aurélie Fossey, Robert Wojcieszak, Renato Froidevaux, Matthias Höhne, Uwe Bornscheuer, Anne Zaparucha, Egon Heuson

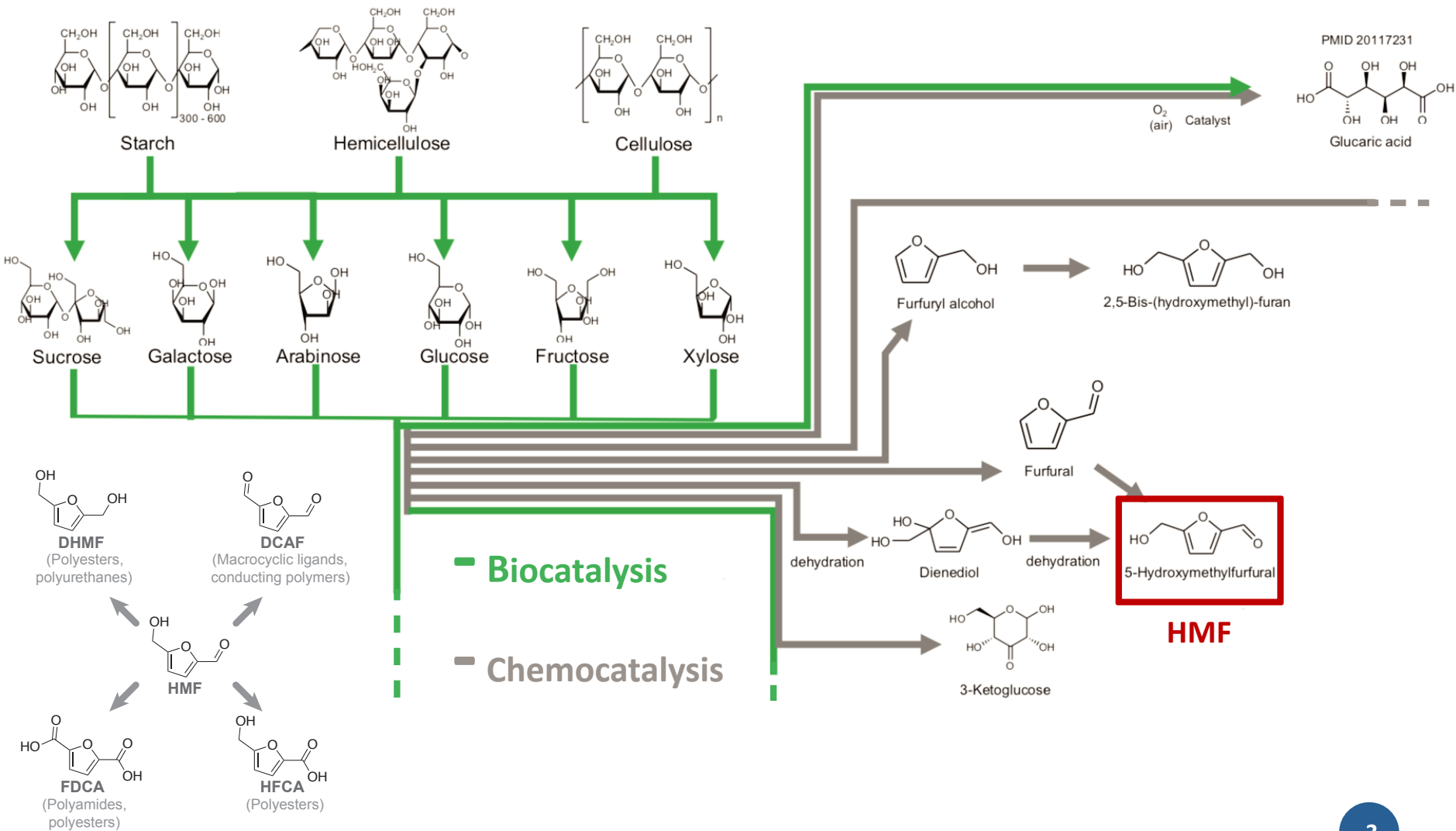
Towards maximum catalyst integration



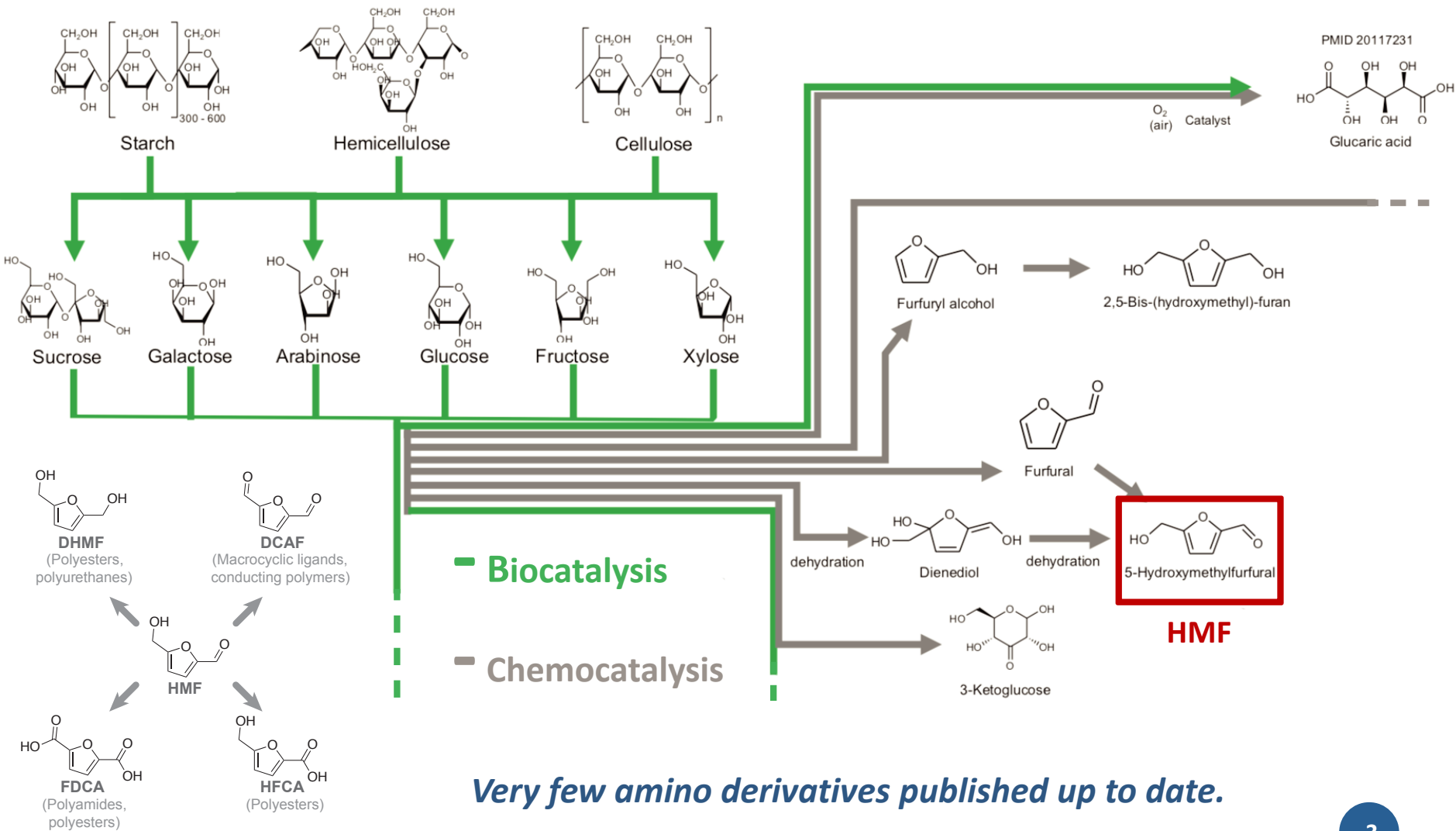
5-hydroxymethylfurfural (HMF), a major bio-based building block



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Very few amino derivatives published up to date.

Synthesis of Furfurylamines

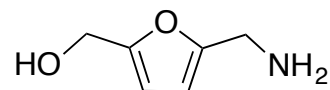
Synthetic pathways

- Mainly secondary amines from HMF derivatives

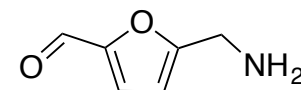
Synthesis of Furfurylamines

Synthetic pathways

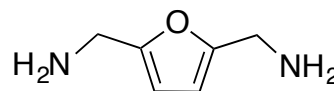
- Mainly secondary amines from HMF derivatives
- Chemical reductive amination (requires numerous protections/deprotections)
 - Recent new methodology without protection (Lankenau *et al.* 2020)
- Biocatalytic (transamination)
 - Only two studies, no methodology for direct synthesis of AMFC, AMFA, and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



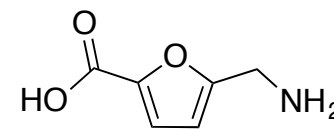
HMFA



AMFA



FDMA

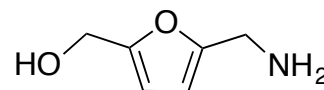


AMFC

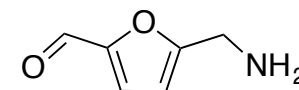
Synthesis of Furfurylamines

Synthetic pathways

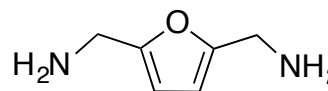
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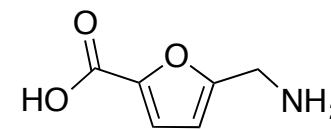
HMFA



AMFA



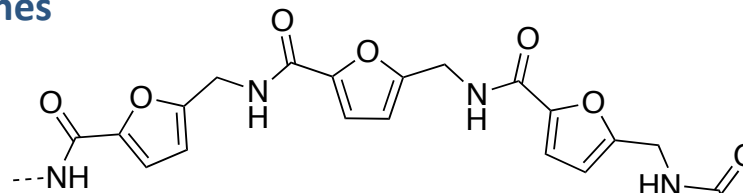
FDMA



AMFC

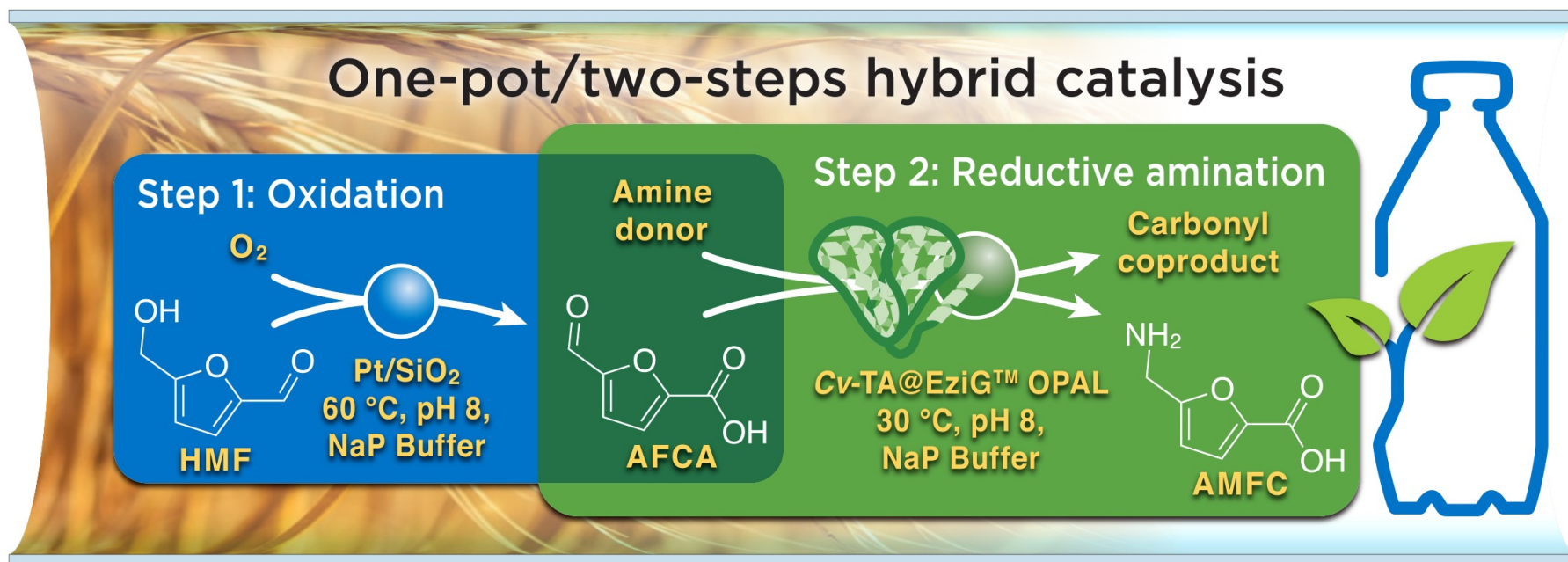
Applications

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

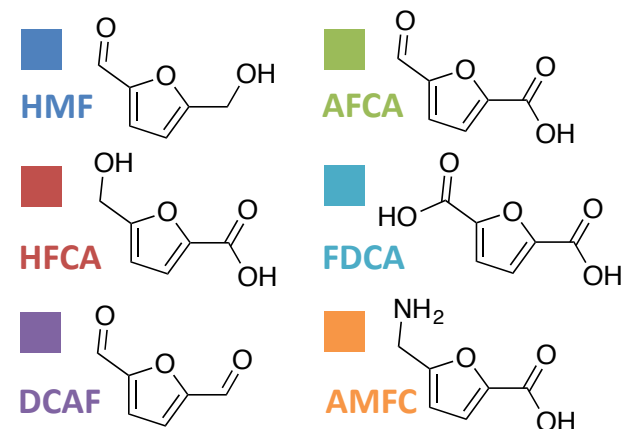
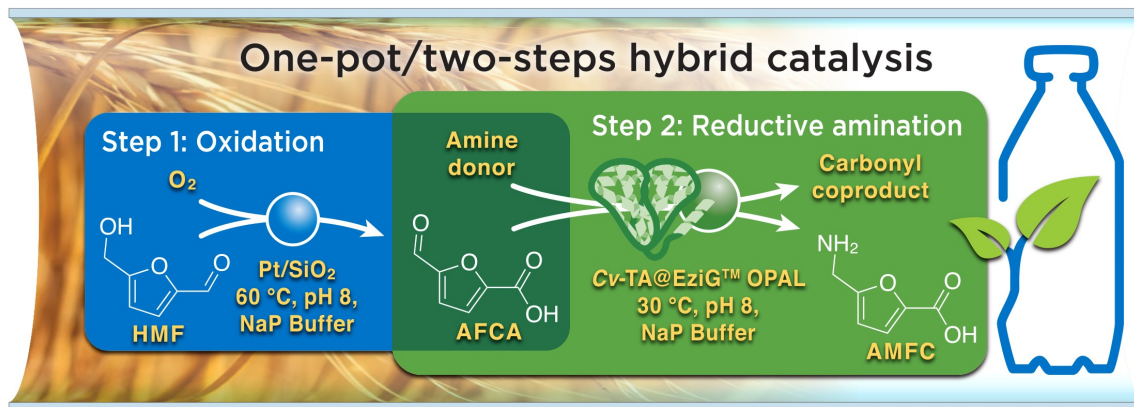


Polyamide of AMFC

One-pot/two-steps hybrid catalysis

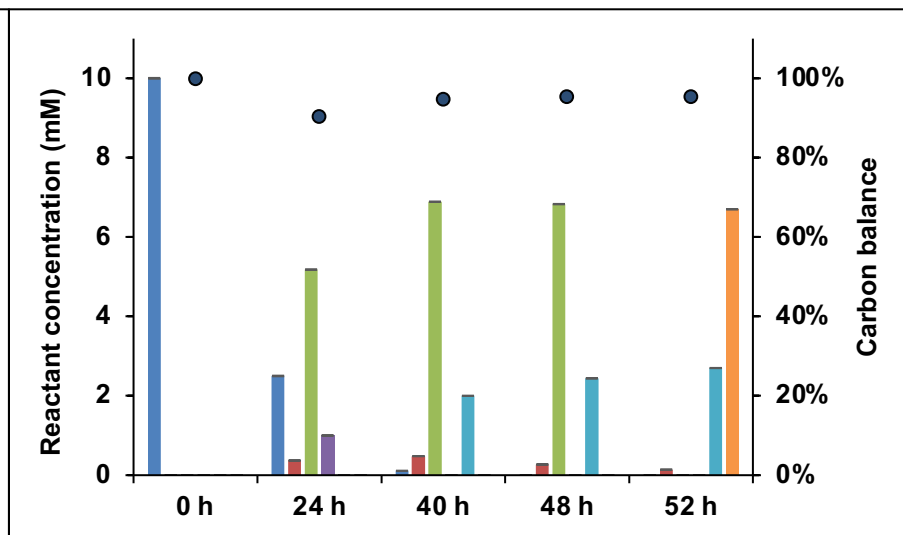
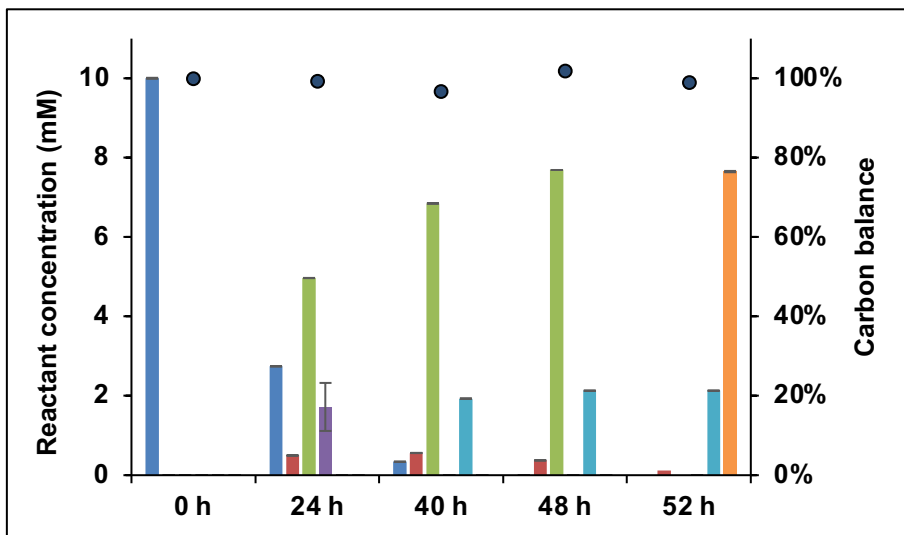


1P2S : Addition of the enzyme after 48h reaction and cooling



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

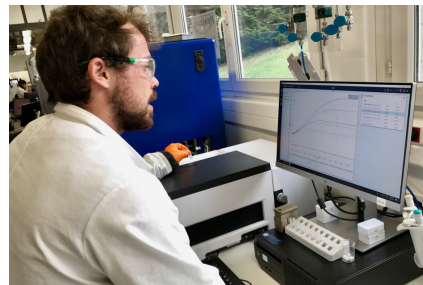
Donor : Isopropylamine (10:1)





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



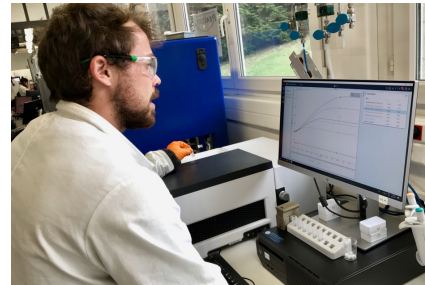
Antoine Lancien
PhD Student in
Hybrid Catalysis

Cary 3500 (Agilent)



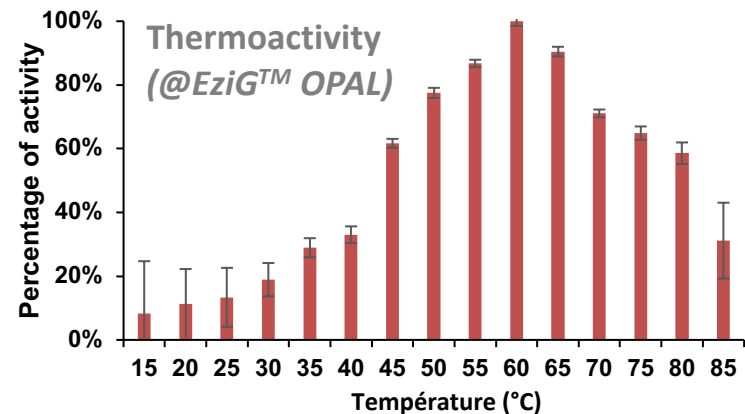
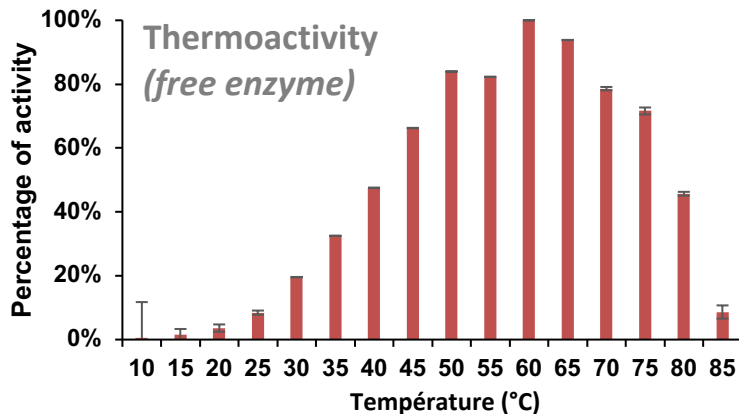
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 - Efficient production of a single TA
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 - Higher activity for HMF and AFCA
- Thermostability/thermoactivity



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PhD Student in
Hybrid Catalysis

Cary 3500 (Agilent)



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

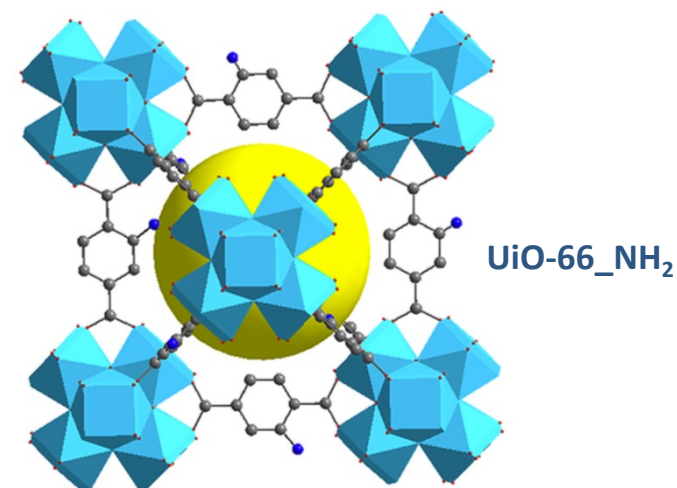
Screening new chemocatalysts for HMFA oxidation

- **33 new catalysts** tested (mainly **Au** based)
- **300 combinations/conditions** tested in **1 month**
 - New screening methodology using the BioLector Pro
- Selection of **Au@TiO₂**, **Au@CaO** and **Au@UiO-66-NH₂**



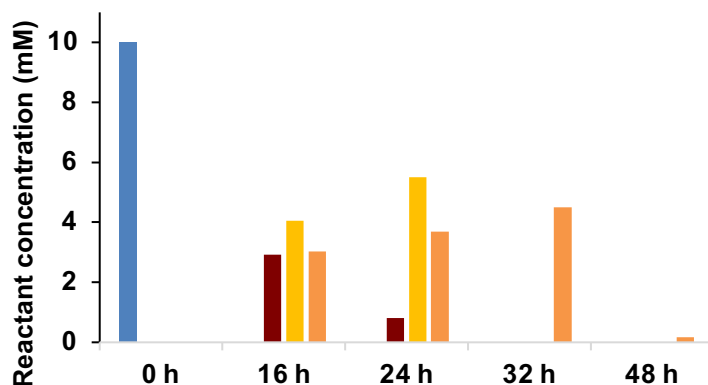
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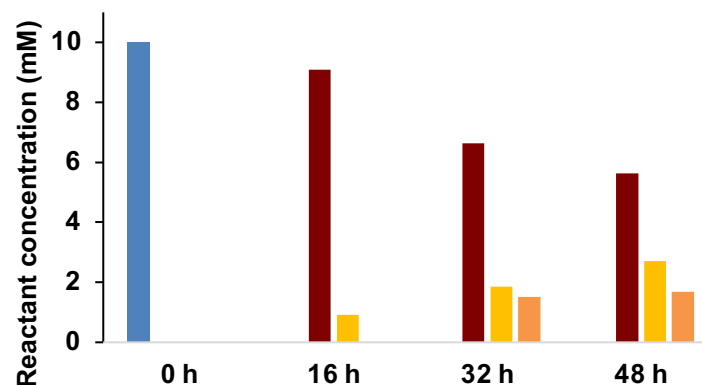
First 1P1S system attempts

Au@CaO + TA@EziG™OPAL

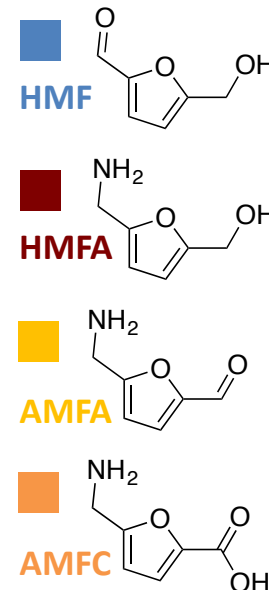


45% yield / 100% conversion
 ⇒ appearance of a precipitate

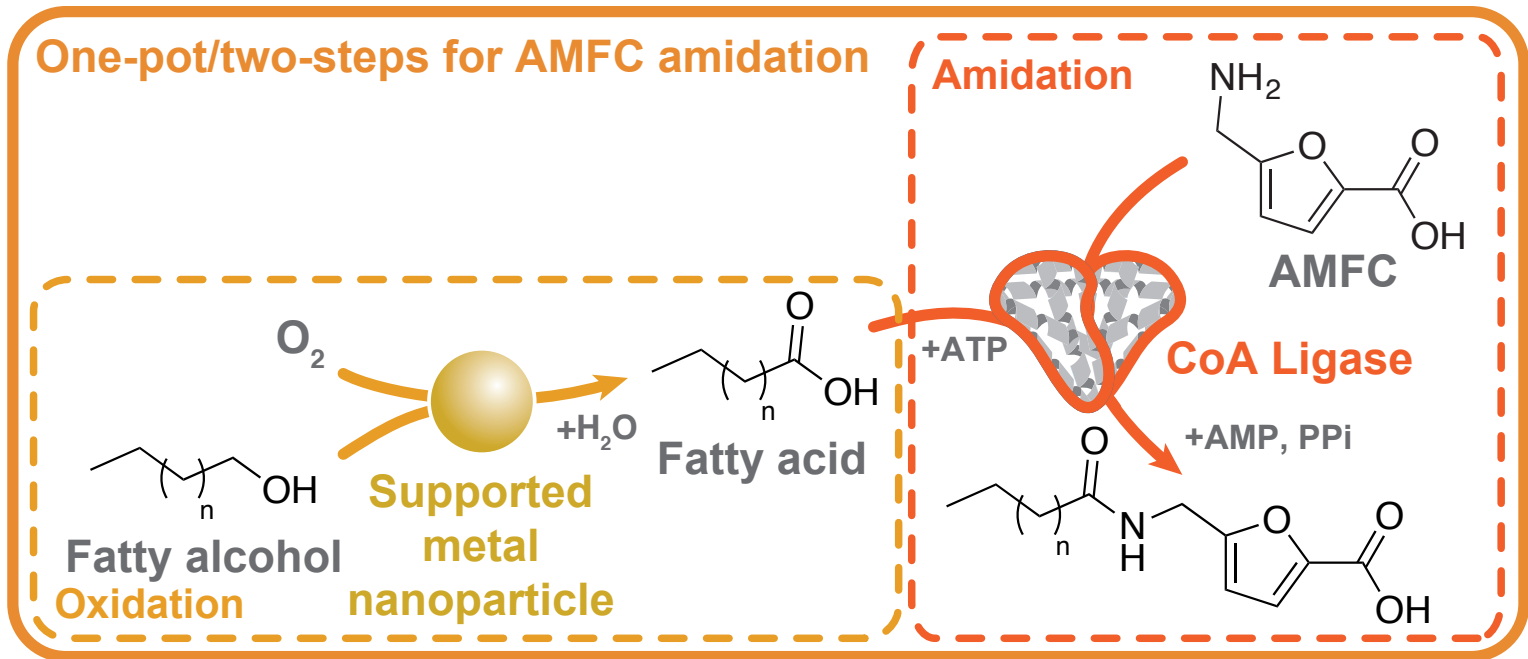
Au@UiO-66_NH₂ + TA@EziG™OPAL



17% yield / 44% conversion



Production of amphiphilic molecules from alcohols derived from biomass

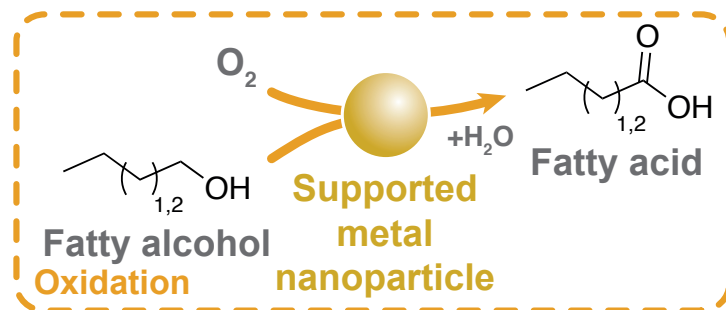


UMR GENOSCOPE
METABOLIC GENOMICS

Anne Zaparucha Aurélie Fossey

Screening new chemocatalysts for fatty alcohols oxidation

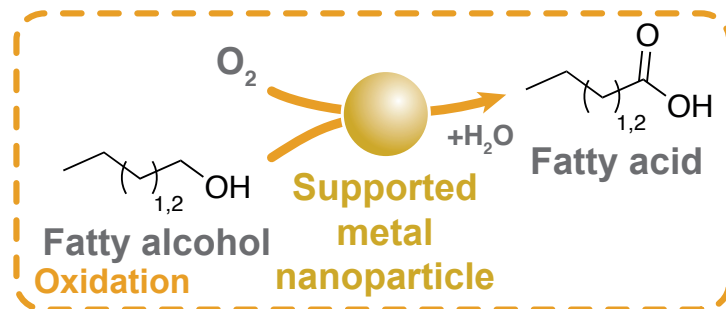
- Butanol and pentanol used as substrate
- 11 catalysts tested
- Selection of **Au@CaO**: 100% conversion in 48h at 50°C



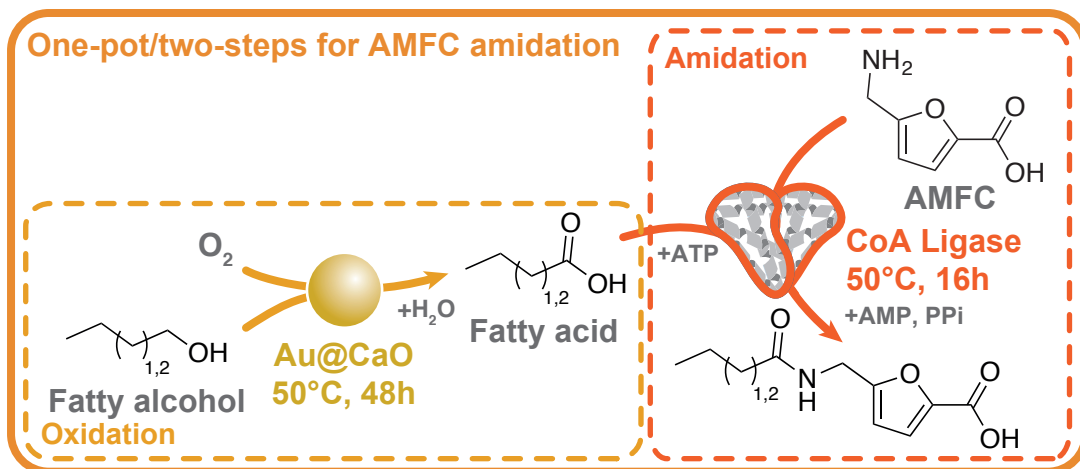
Expanding the reaction scope: CoA Ligases

Screening new chemocatalysts for fatty alcohols oxidation

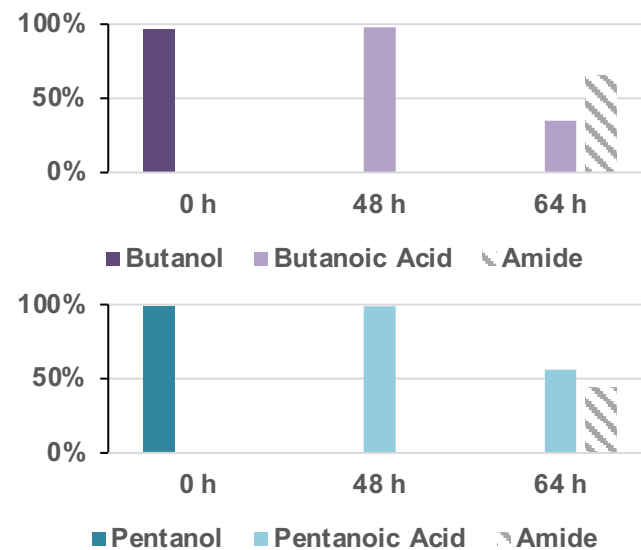
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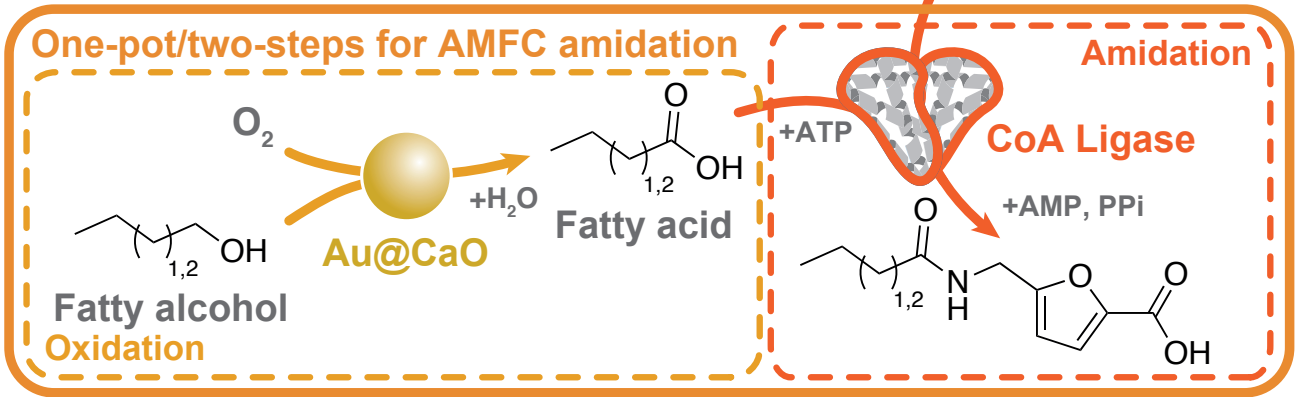
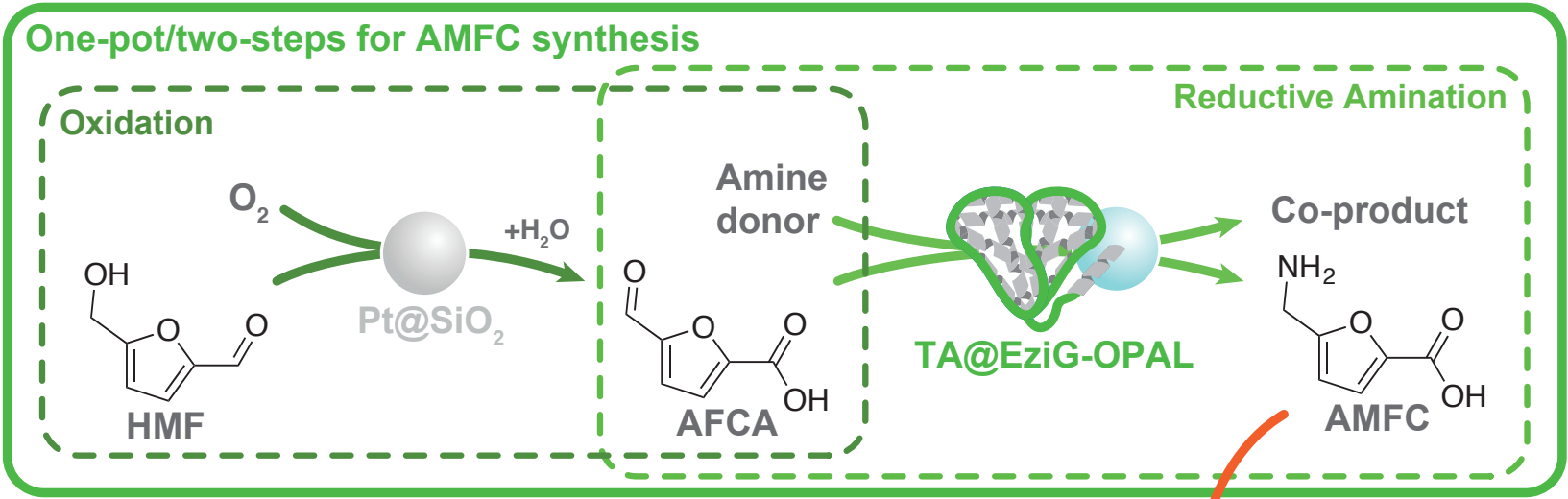
Promising preliminary results



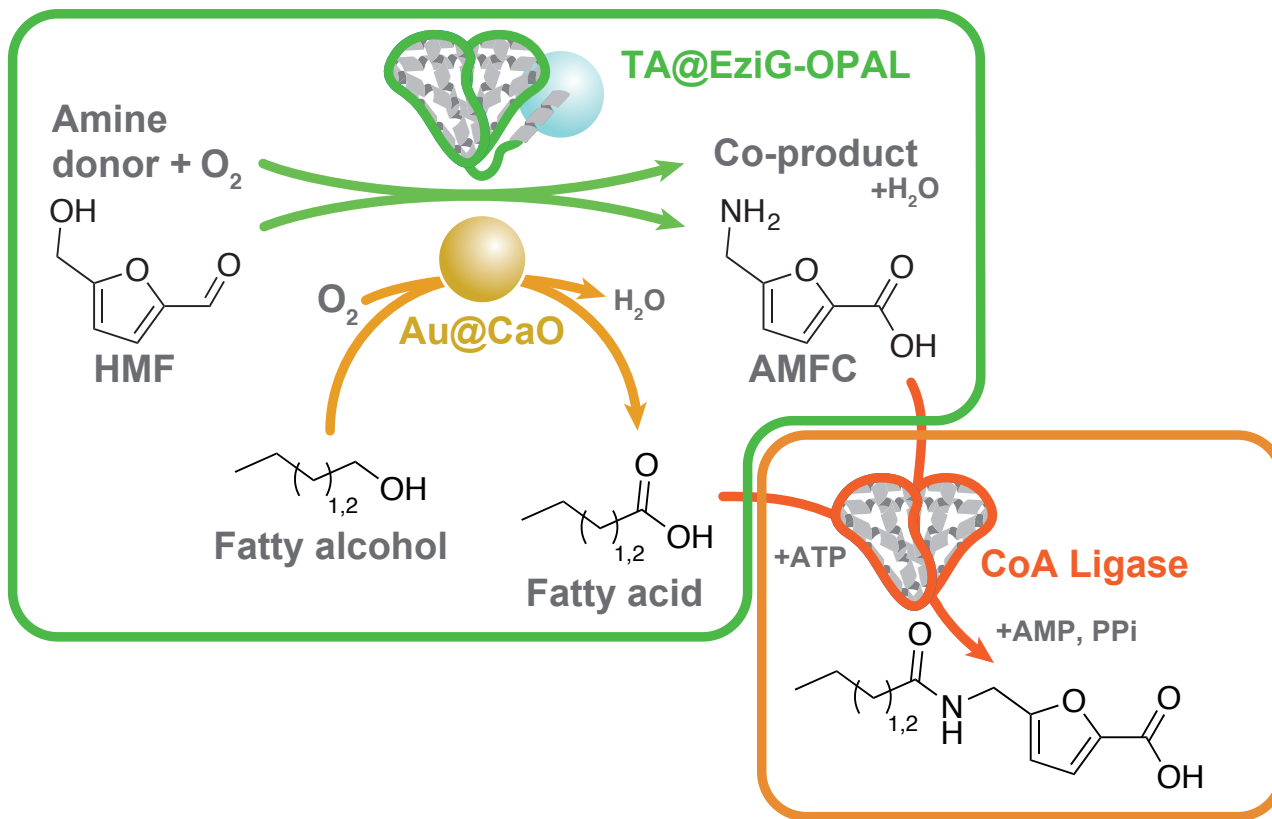
- 65% and 54% yield (100% conversion) for **butanol** and **pentanol** respectively
- Amide confirmed by NMR and Mass



The next steps...



The next steps...



... toward a complete 1P1S system

Merci pour votre attention!

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... au Nord, c'étaient les Corons!



Antoine Lancien