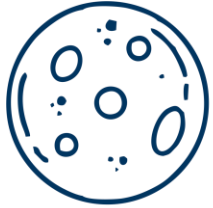


RUHR-UNIVERSITÄT BOCHUM

COMBINING RAM WITH DIFFERENT ACTIVATION MODES RESODYN'S TECHNICAL INTERCHANGE

Sven Grätz

“You can't get to the moon by climbing successively taller trees.”



Mo's Law of Evolutionary Development

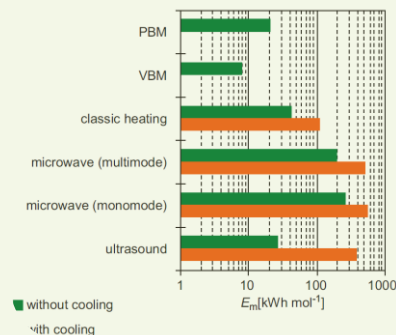




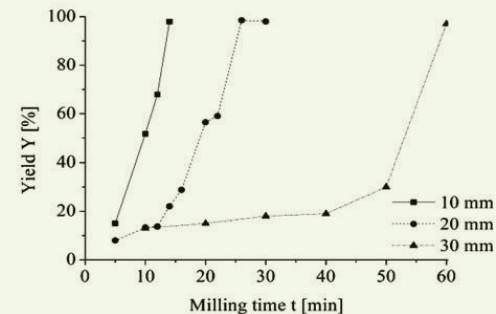
Solvent-Free



Energy Efficiency



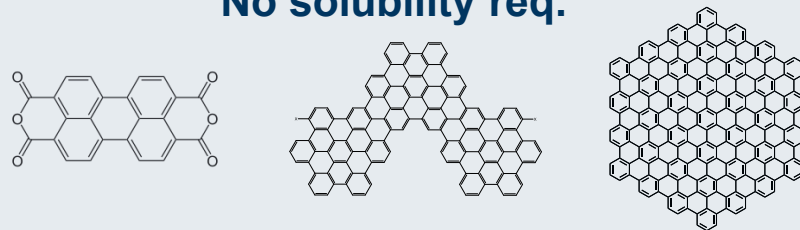
Time Efficiency



Ease of Use & Low Barrier of Entry



No solubility req.



Homogeneous Catalysis



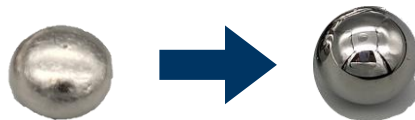
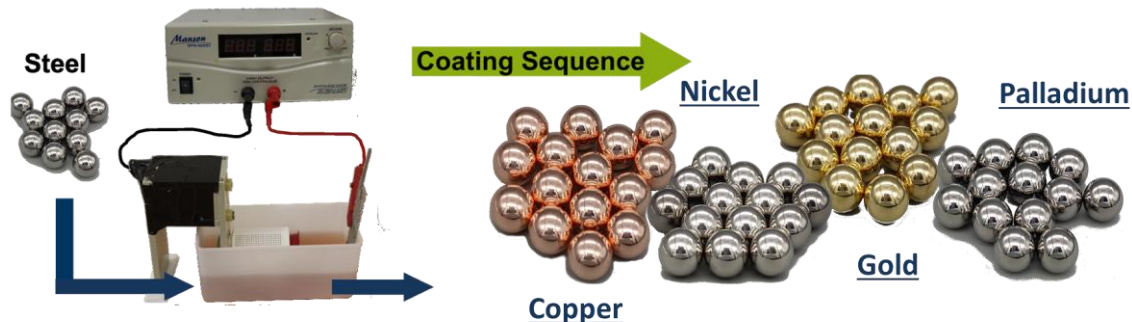
Heterogeneous Catalysis



Direct Mechanochemistry



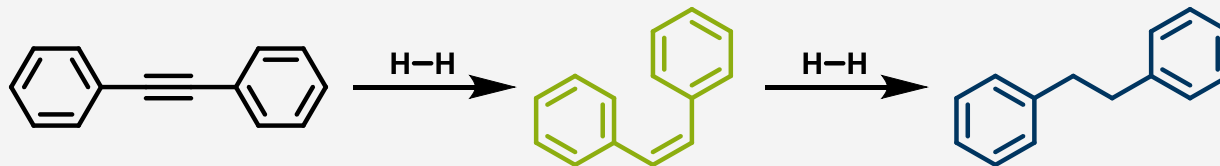
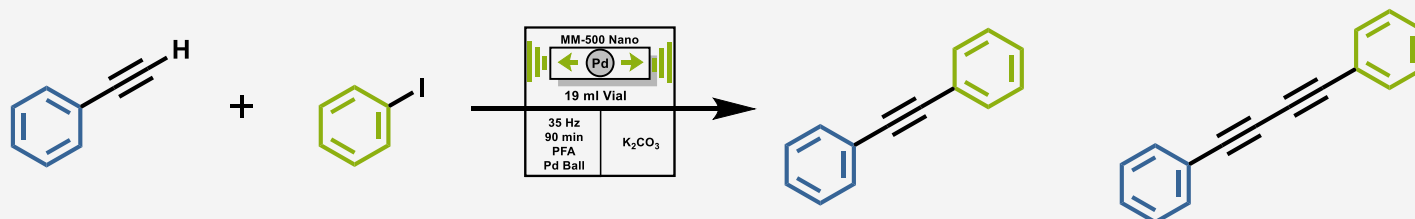
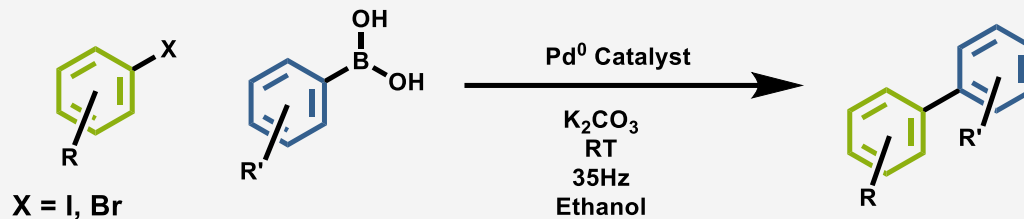
Electroplating



Cost per
ball: 450€

Cost per
ball: 11ct

Pickhardt, W., Grätz, S., Borchardt, L.; *Chem Eur. J.*, 2020
Hwang, S., Grätz, S., Borchardt, L. *Chem. Commun.* 2022



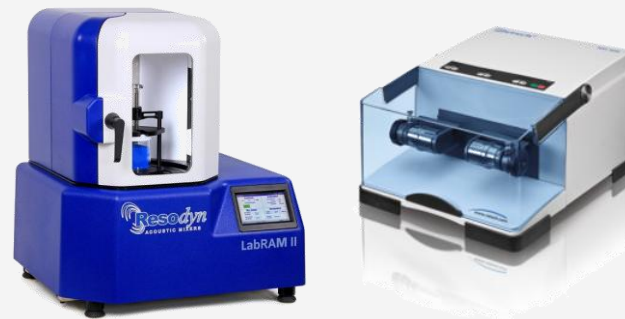
...”chemical transformation resulting from the absorption of mechanical energy.”

IUPAC Definition

TECHNOLOGY - CLASSICAL



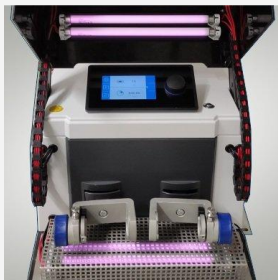
TECHNOLOGY – MEDIA-FREE



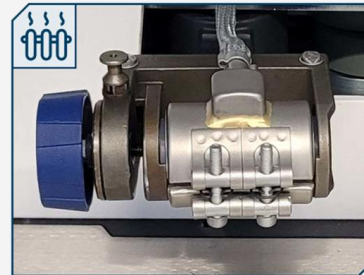
...”chemical transformation resulting from the absorption of mechanical energy.”

IUPAC Definition

PHOTON ENERGY



THERMAL ENERGY

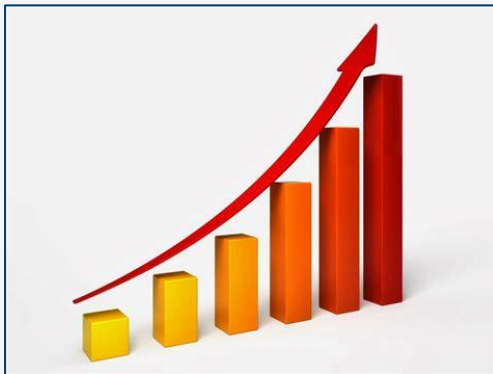


ABRASION



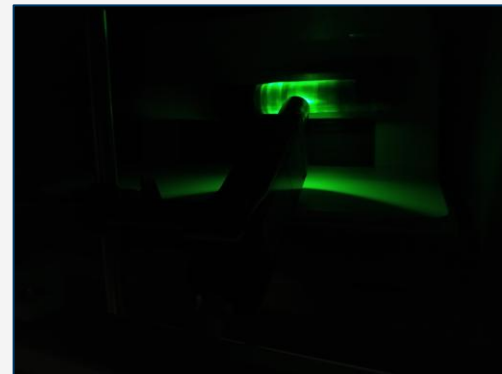
- Abrasion bad for applications
- Longevity of milling balls

SCALABILITY



- Bigger ball mills often unfeasible
- Other alternatives needed

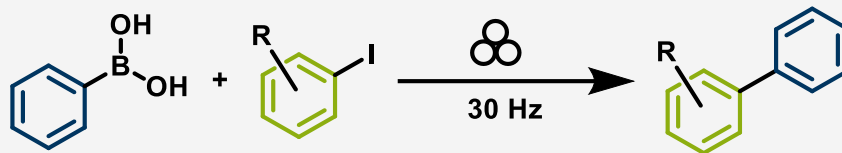
MONITORING



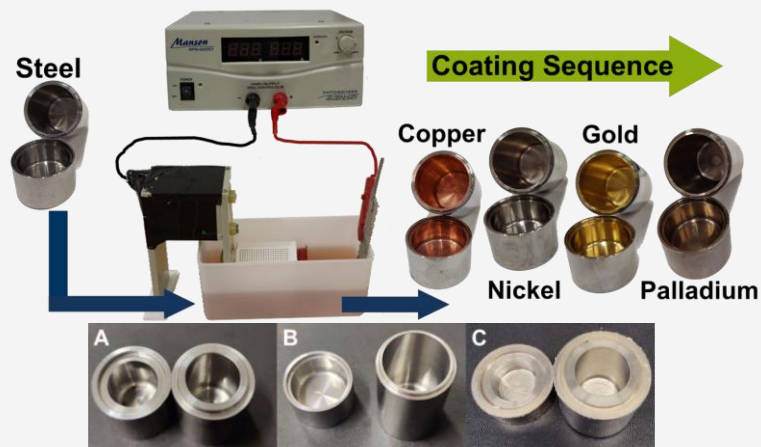
- Mills are often black boxes
- Media-free environment beneficial to monitoring

*1. How does Media-Free
Mechanochemistry compare?*

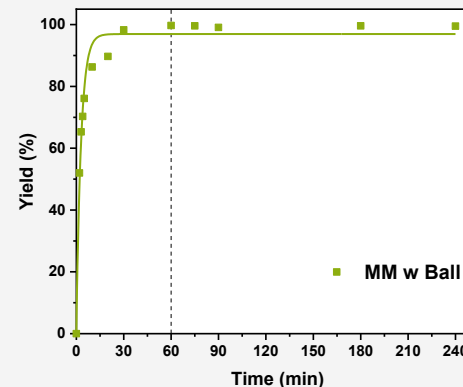
Direct Mechanochemical Suzuki Reaction



Ball = Cat. → Media-Free?

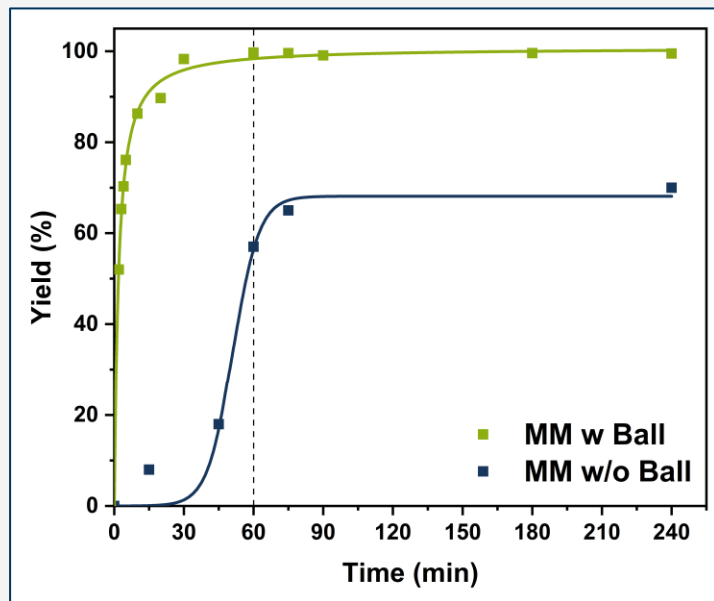


Vessel as good as ball?



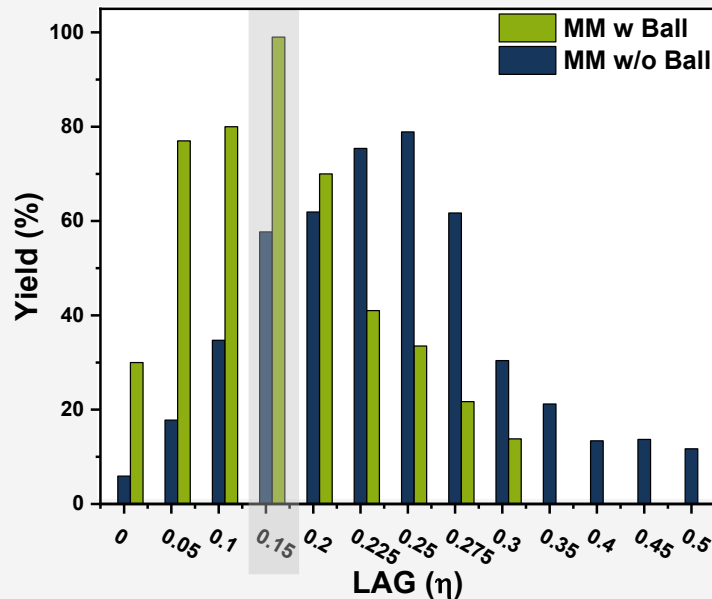
→ Reaction proceeds with coated vessels

Media-Free?



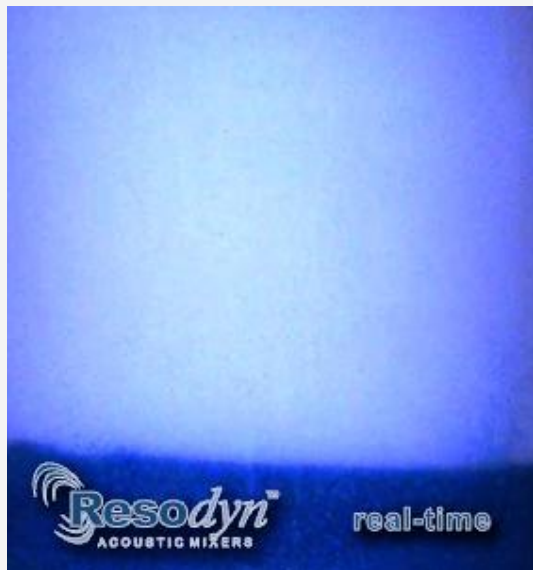
→ Reaction proceeds without milling balls

Diffusion or Particle Size?



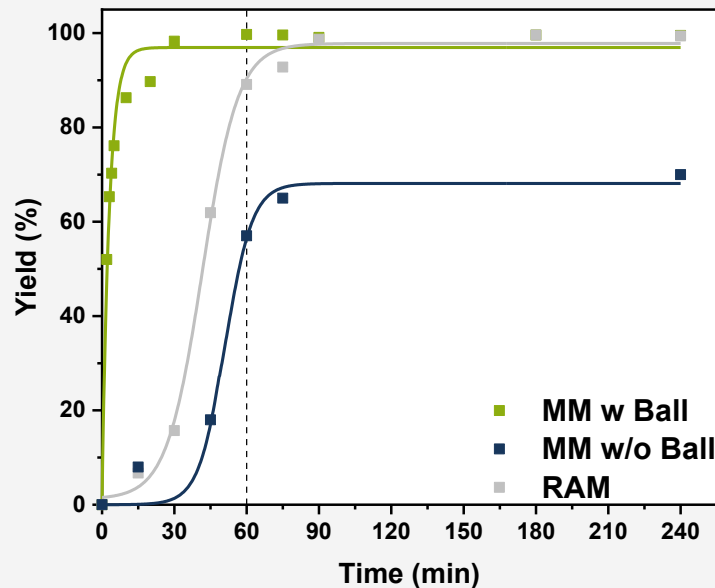
→ Probably both, more LAG helps

Can the we do better?



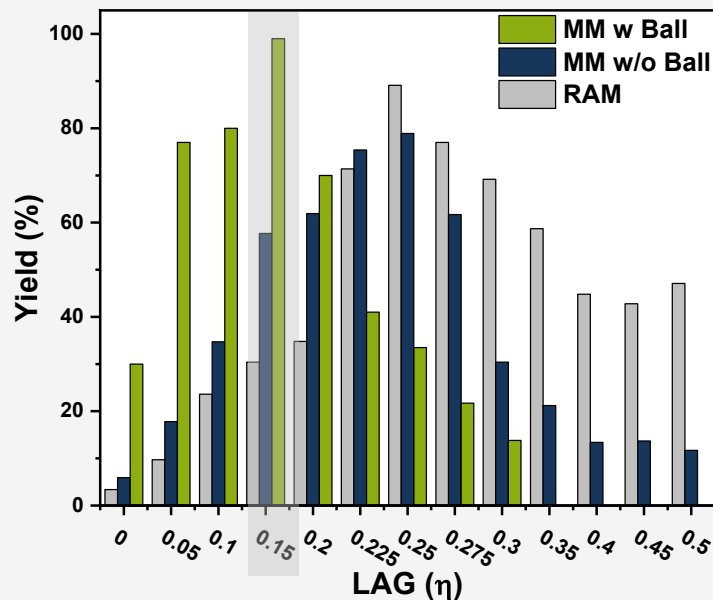
→ RAM delivers superior mixing

Can the RAM do better?



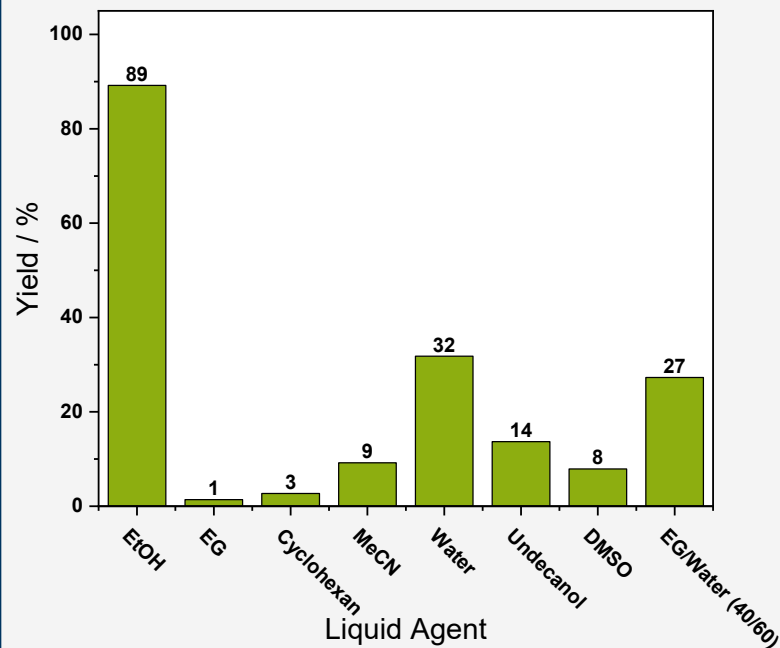
→ Fast and complete reaction

How about LAG@RAM?



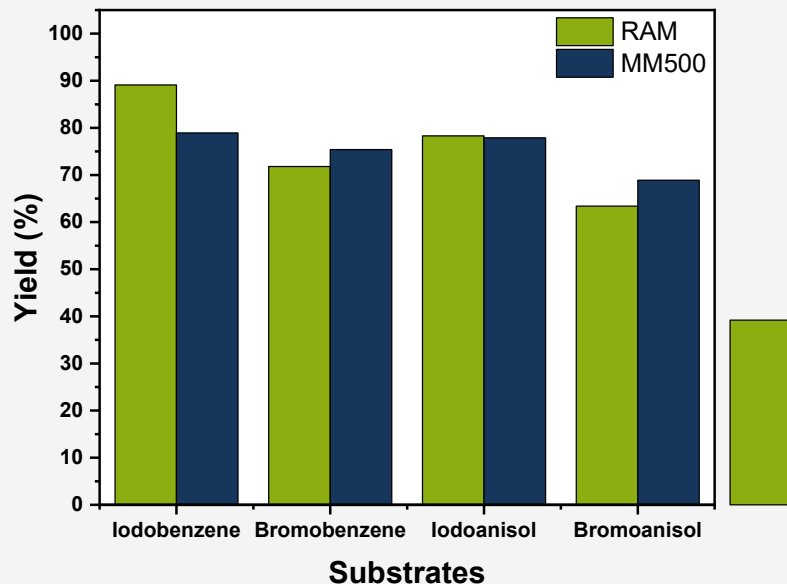
→ RAM and MM w/o balls comparable

Which LAG?



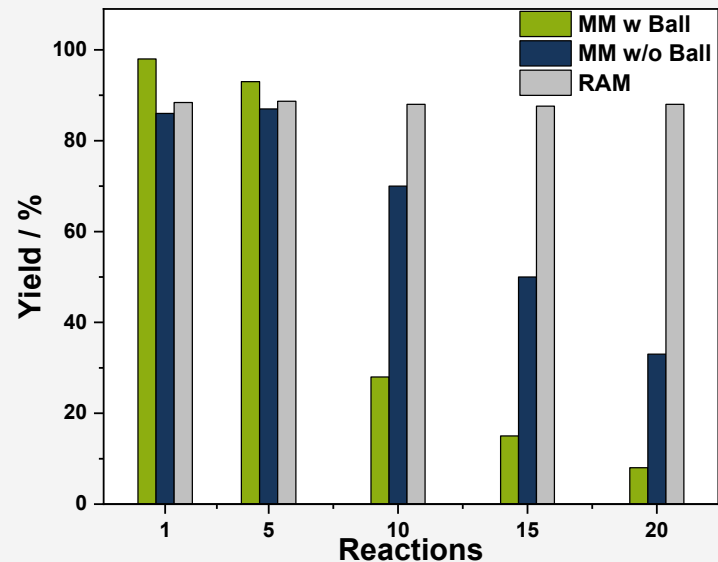
→ EtOH is not only LAG but a reagent

How does it compare?



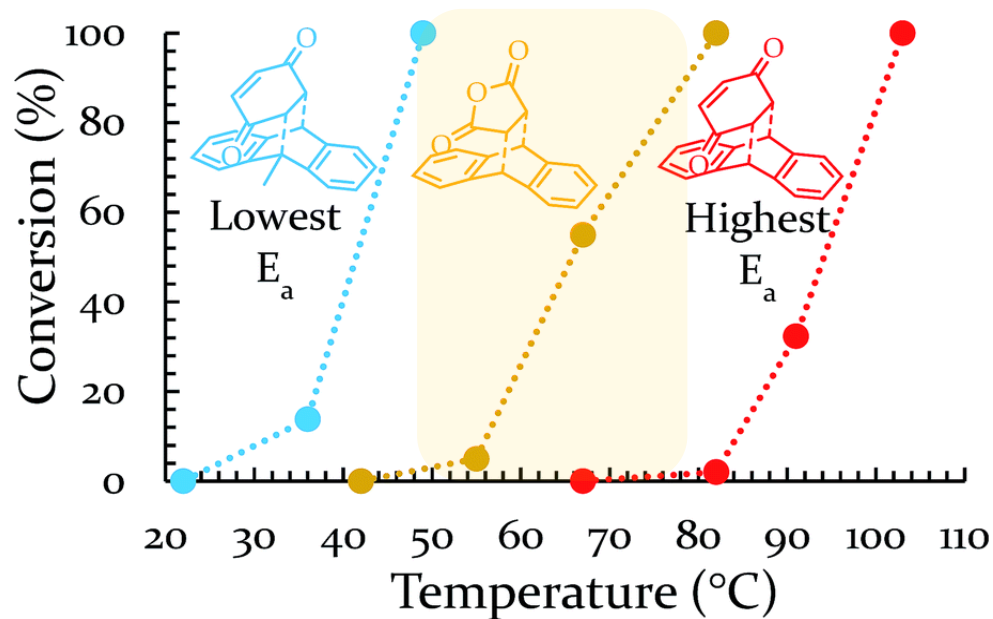
→ comparable to ball milling

Cycability?



→ Coating is more stable in RAM

2. Different Activation modes in the RAM?



- relation between frequency and activation energy by Arrhenius plot
- temperature-dependency

2. Understanding the RAM

HEATING

Nozzle-Heaters



→ stable reaction conditions

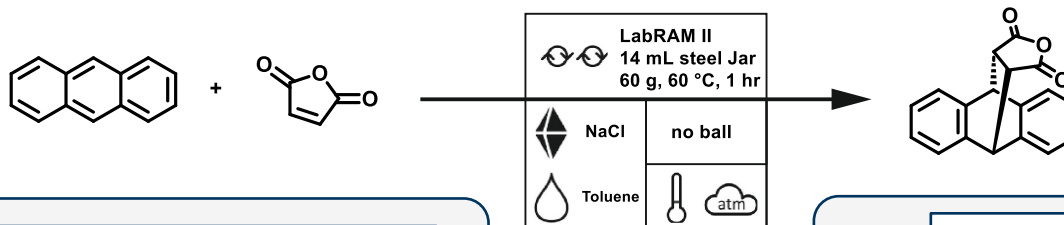
Nozzle-Heaters



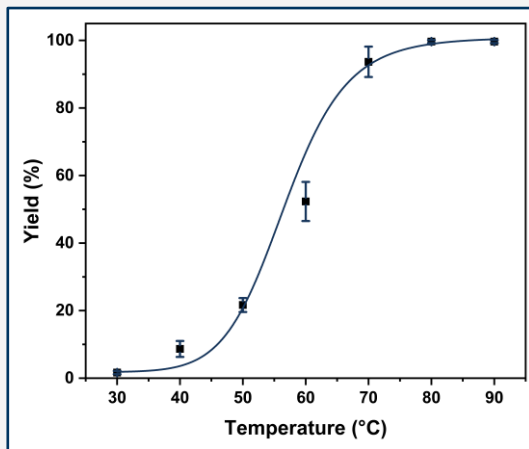
→ easily transferable

2. Understanding the RAM

PARAMETERS

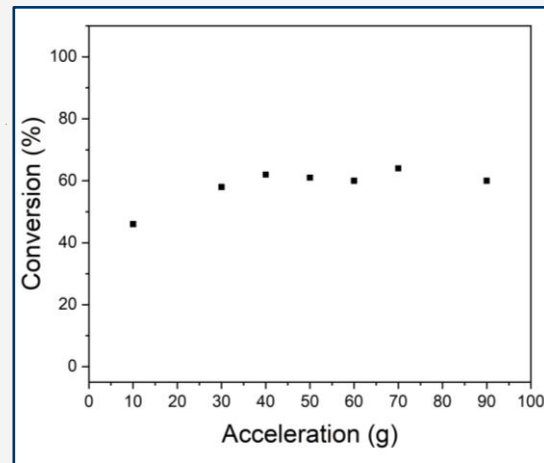


T



→ Temperature has huge impact

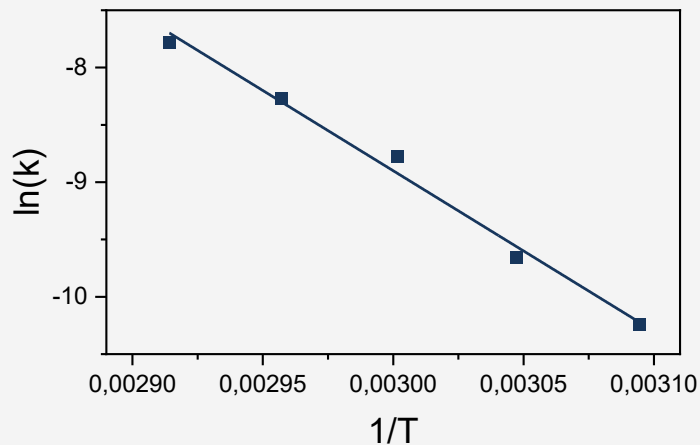
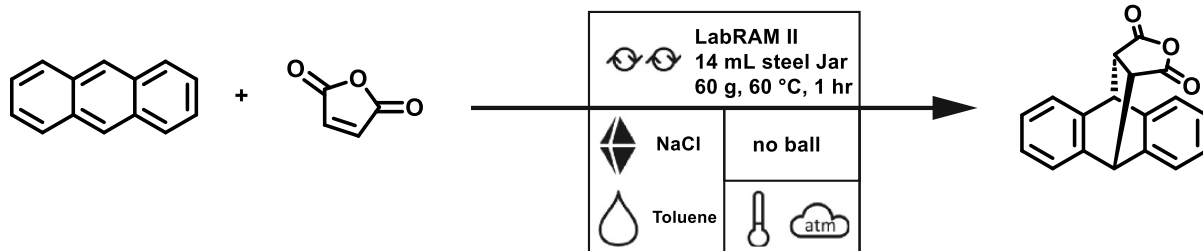
g



→ Acceleration is not important

2. Understanding the RAM

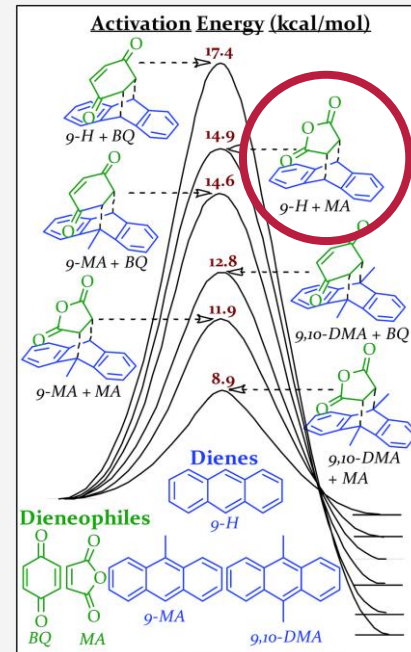
ARRHENIUS EQUATION



Arrhenius equation:

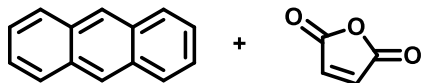
$$k = A \cdot e^{-\frac{E_a}{RT}}$$

$$E_a = 24.5 \text{ kcal/mol}$$

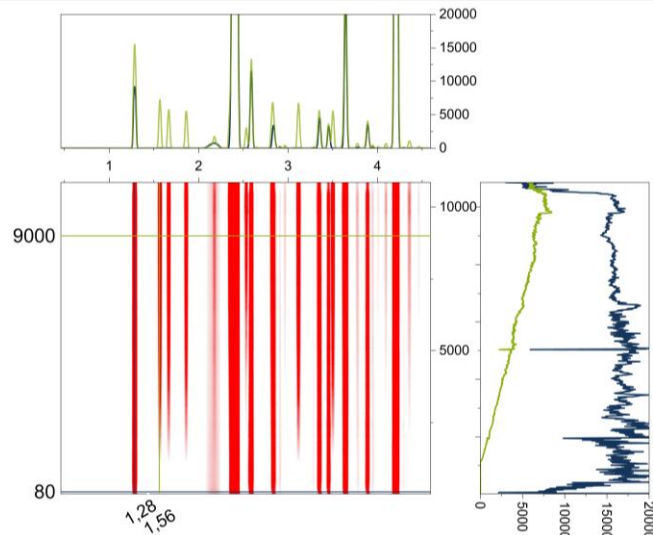
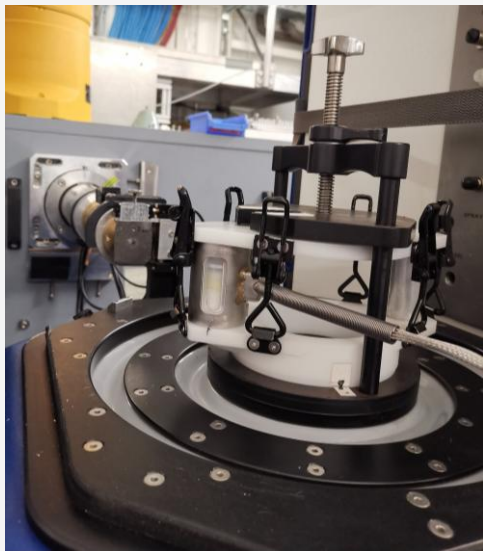
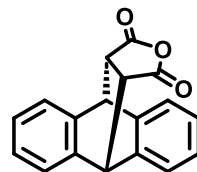


2. Understanding the RAM

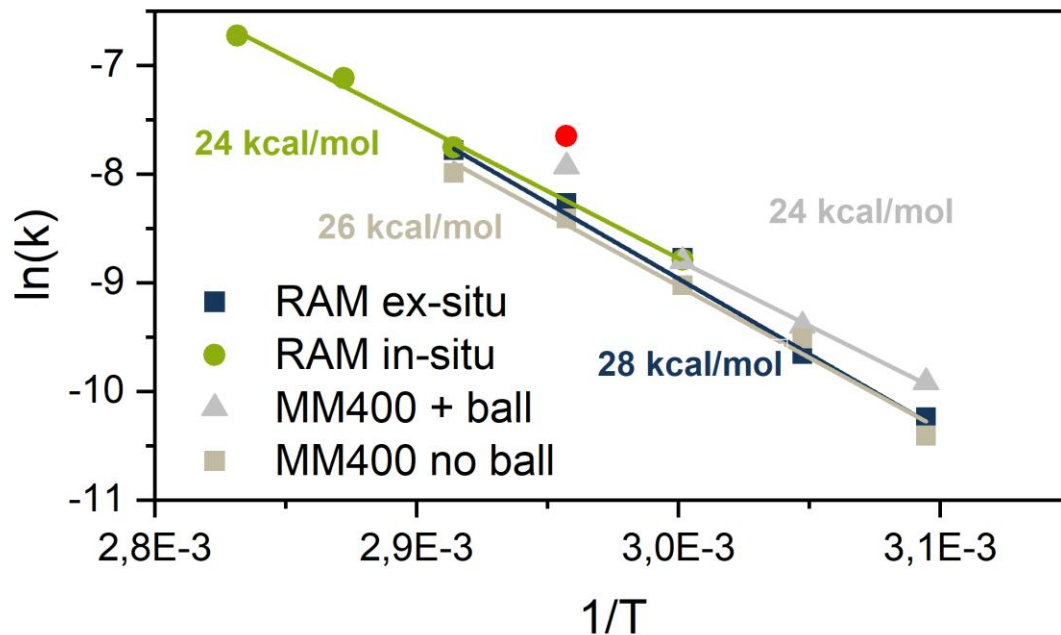
IN-SITU



LabRAM II 14 mL steel Jar 60 g, 60 °C, 1 hr	
NaCl	no ball
Toluene	atm

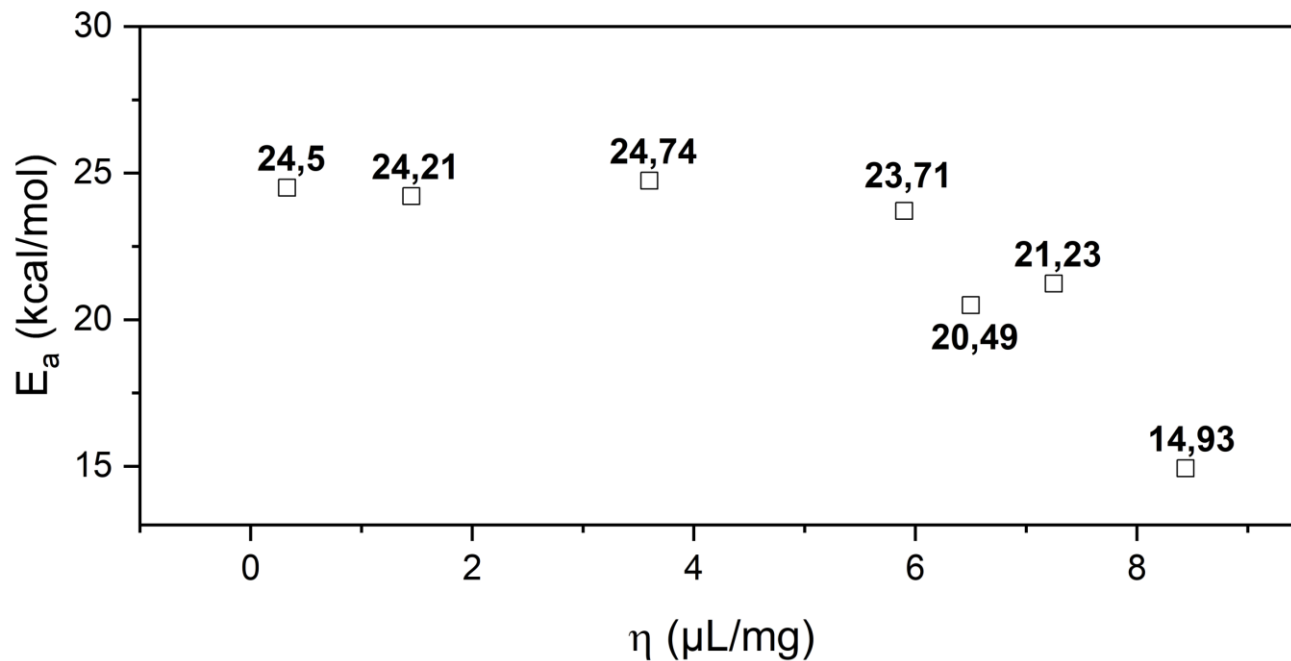


$$E_a = 23.96 \text{ kcal/mol}$$



→ RAM and ball mill are similar

→ Both techniques have higher apparent activation energies than solution-based reactions

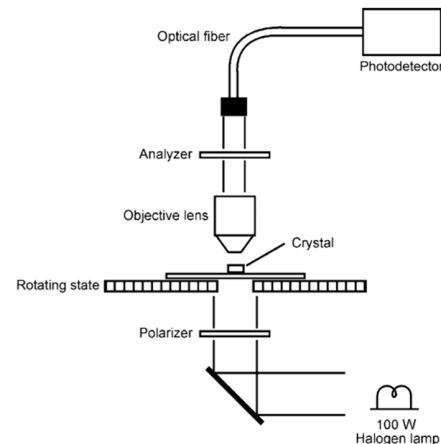


3. What else can we do with the RAM?



Solvent-based

- ✓ green, non-toxic energy source
- ☹ Poor penetration depth of light
- ☹ High dilutions = high amounts of solvents waste



Solid-state

- ✓ No solvent waste
- ☹ Stearic set-up
- ☹ Limited Diffusion
- ☹ Limited Scalality

M. Marimoto *et al.*, *CrystEngComm*, 2016,18, 7241-7248

Solvent-based

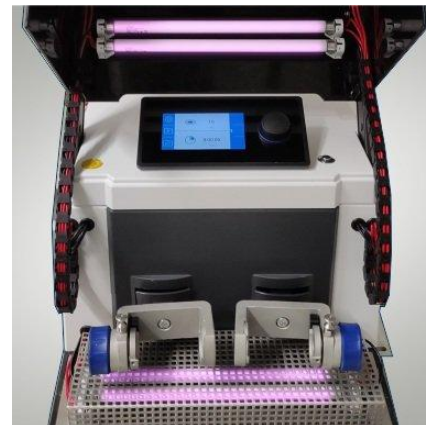
- ✓ green, non-toxic energy source
- ☹ Poor penetration depth of light
- ☹ High dilutions = high amounts of solvents waste

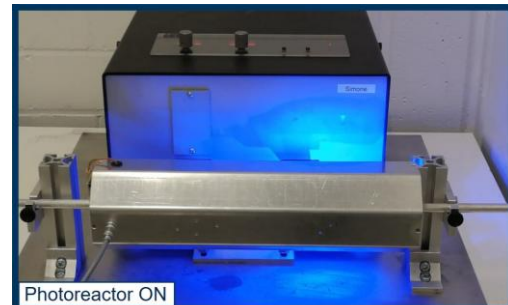
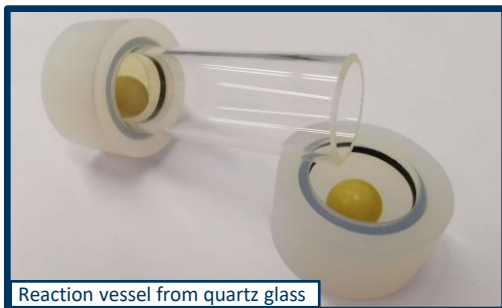
Solid-state

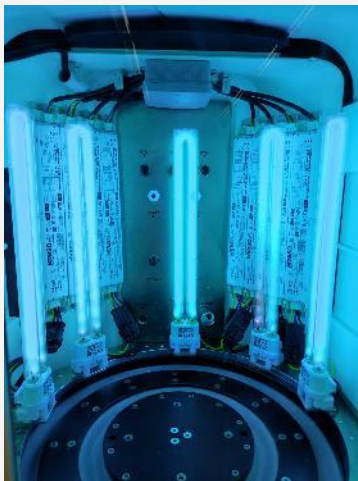
- ✓ No solvent waste
- ☹ Stearic set-up
- ☹ Limited Diffusion
- ☹ Limited Scalality

Mechanochemistry

- ✓ Solid-state technique
- ✓ Sufficient diffusion
- ✓ Renewing substrate surface
- ☹ No translucent milling vessel



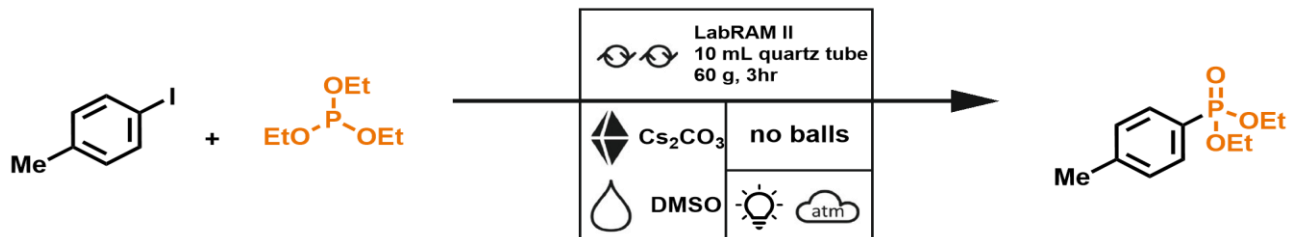




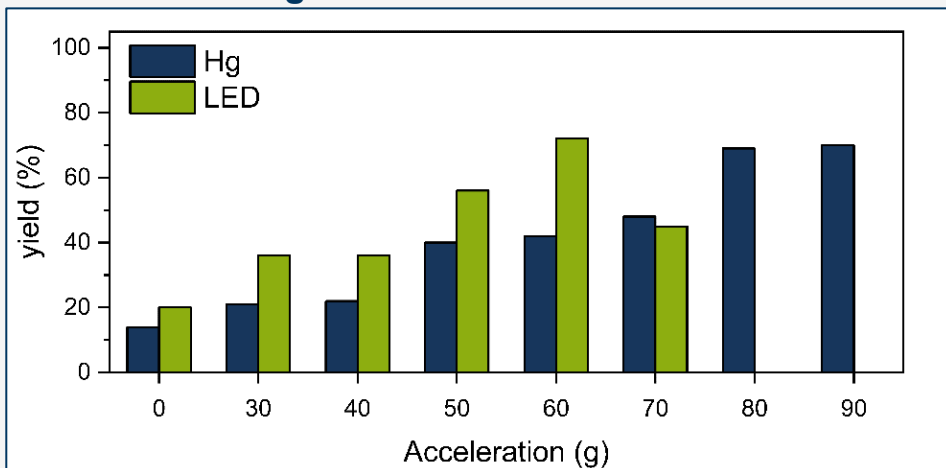
Fluorescent tubes ($\lambda=254\text{ nm}$)



LEDs ($\lambda=272\text{ nm}$)



Acceleration screening



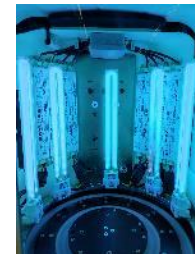
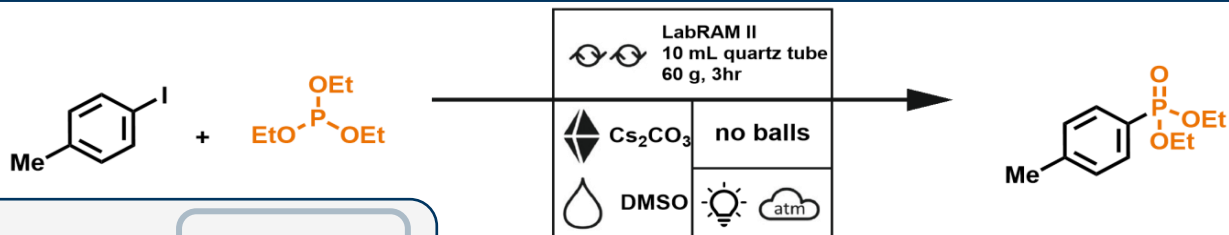
Hg lamps



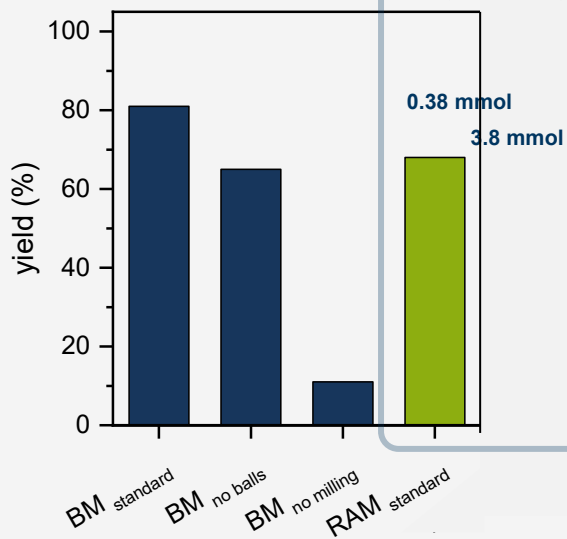
LEDs

Reaction parameter:

0.1 g 4-iodotoluene, 1 g SiO_2 , 3 eq. $\text{P}(\text{OEt})_3$, 2 eq. Cs_2CO_3 , LAG MeCN ($\eta=0.3$), under air, UVC, 3 h, 60 g



Hg lamps

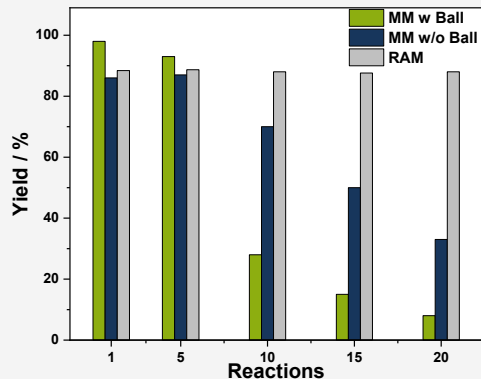


➤ Longer quartz glass tubes (x2)

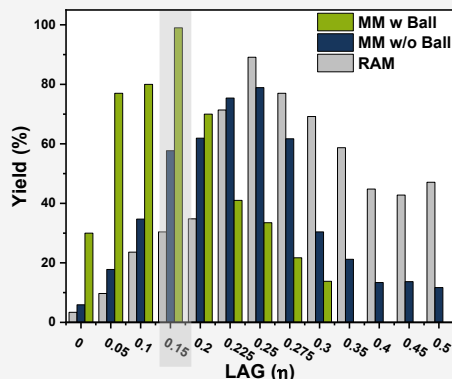
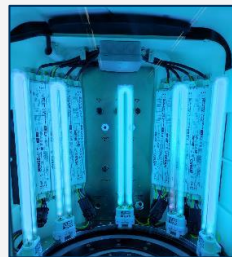
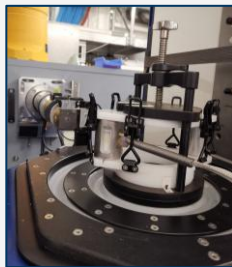


Reaction parameter:
 100 mg 4-iodotoluene, 3 eq. $\text{P}(\text{OEt})_3$, 2 eq. Cs_2CO_3 , DMSO ($\eta=0.15$), under air, 3 h, 60 g, fluorescent tubes ($\lambda=254 \text{ nm}$)

OPPORTUNITIES



CHALLENGES



OPTIONS



ACKNOWLEDGEMENT

THANK YOU



**Maximilian
Wohlgemuth**



Carolina Spula



THANK YOU FOR YOUR

ATTENTION

