Plasma electrochemistry for organic synthesis: Pinacol coupling as a proof-of-concept

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Potential application space for atmospheric-pressure plasmas

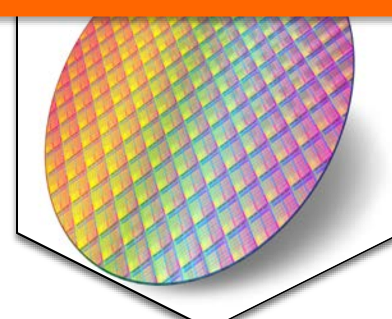
N_2 fixation
Food production

De-polymerization
Re/upcycling plastic waste

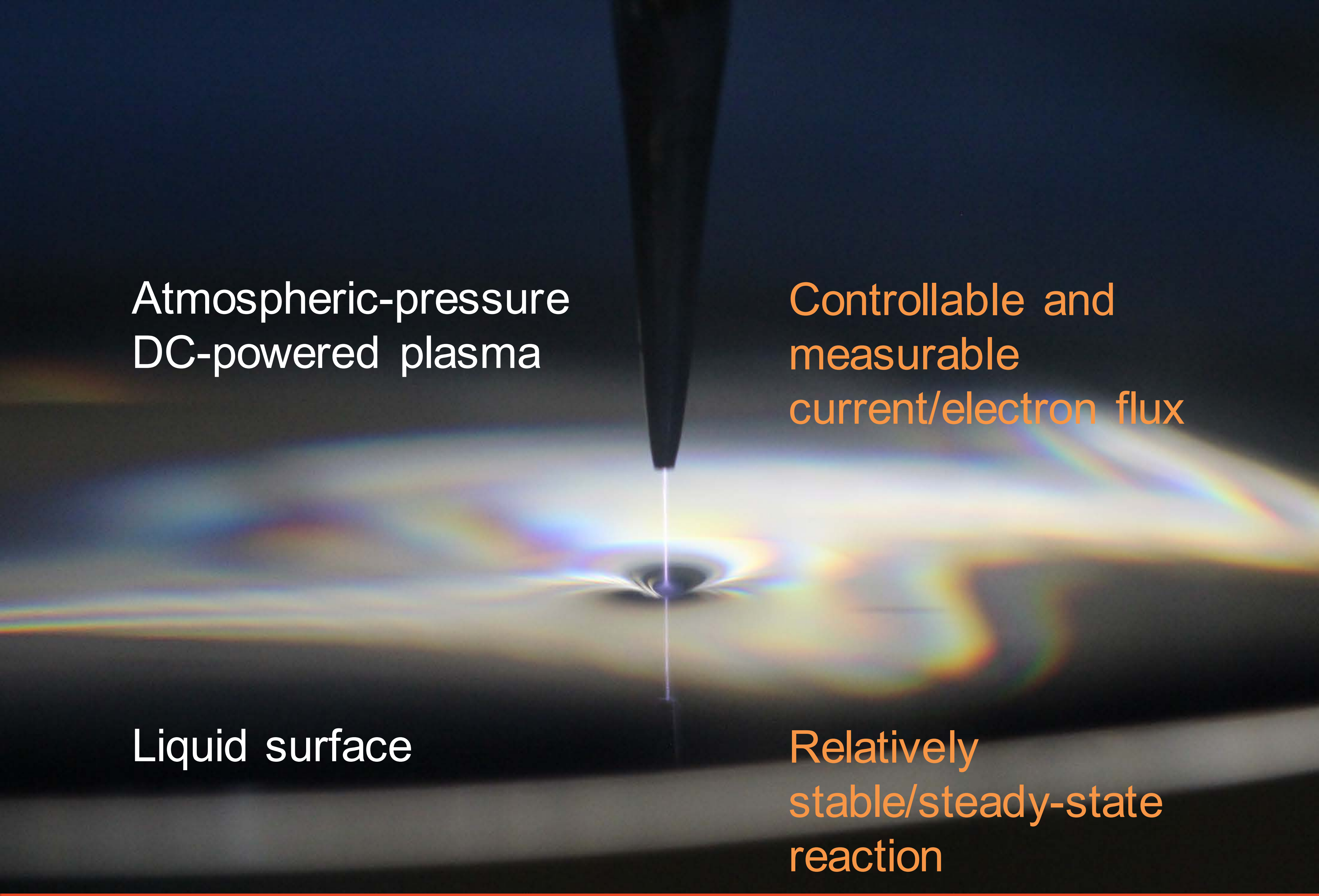
- Cost-effective (no vacuum)
- High throughput (high density)
- Compatible with high vapor pressure surfaces (polymers, liquids)
- Collisional environment promotes nucleation (for polymerization, nanoparticles)

Organic synthesis
Sustainable chemistry

nanoparticles
AM and resource recovery

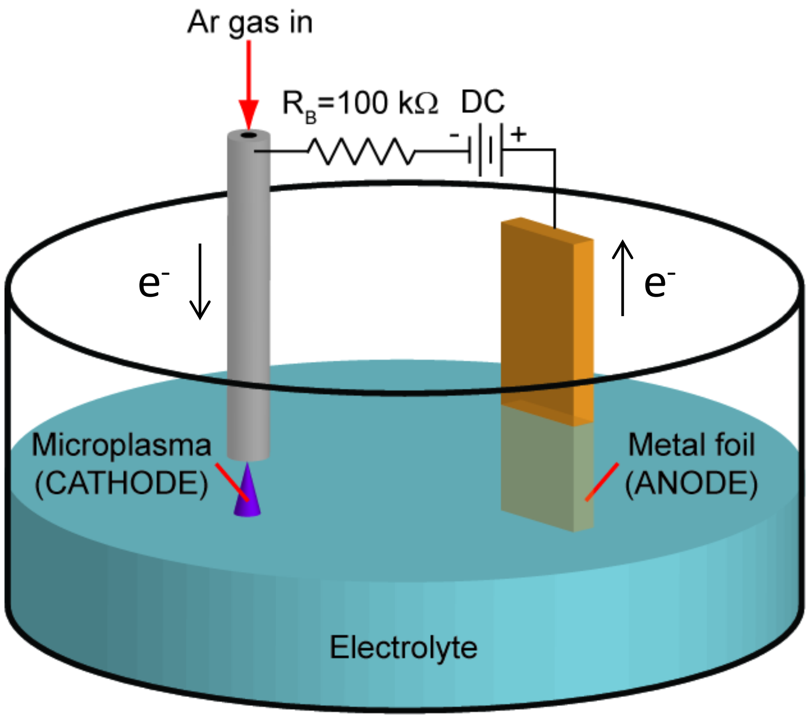


activation
Chemical-free cleaning


Atmospheric-pressure DC-powered plasma
Controllable and measurable current/electron flux
Liquid surface
Relatively stable/steady-state reaction

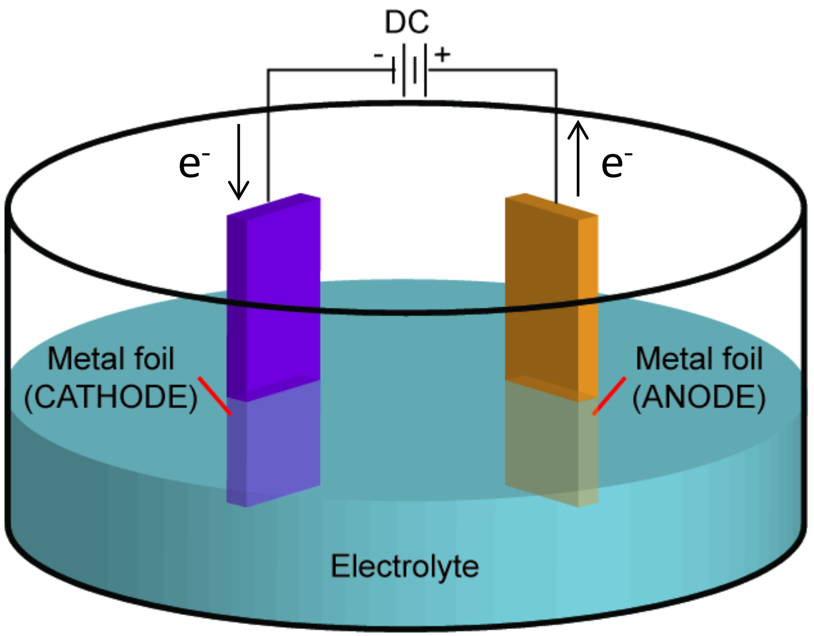
Plasma electrolytic cell vs. conventional electrolytic cell

Plasma electrolytic cell



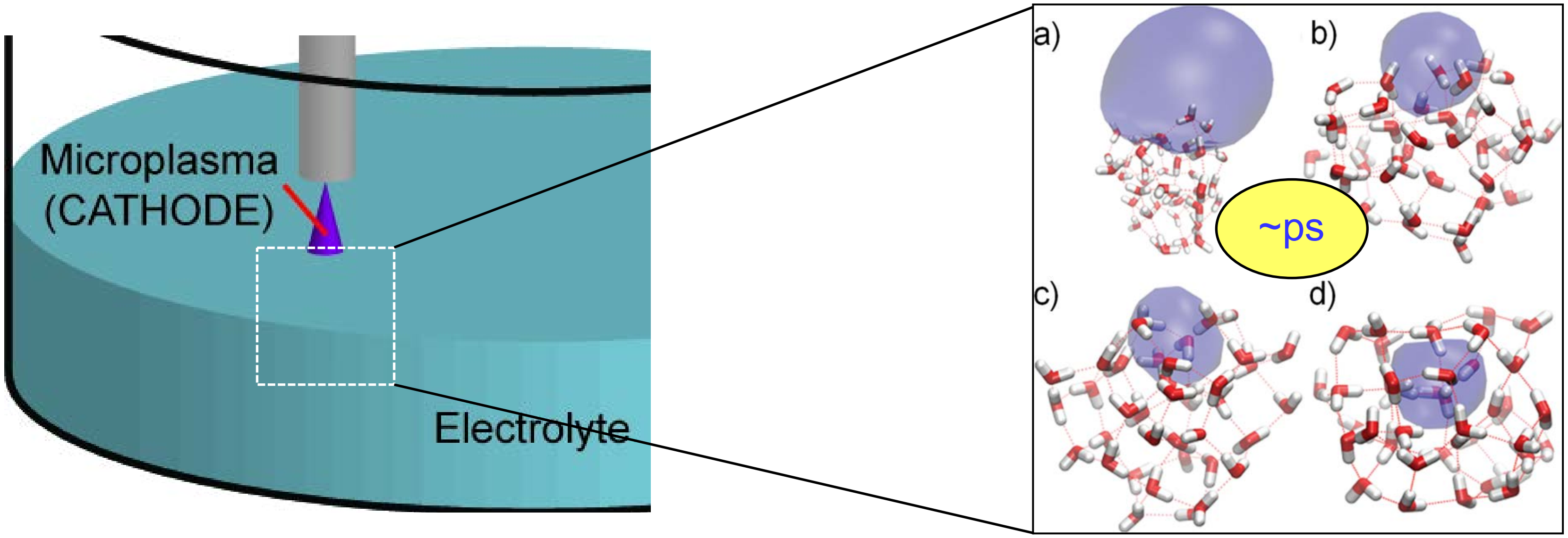
- Cathodic reactions at the plasma-liquid interface
- Electrons are injected from plasma (Ar dissociation)
- Total power – 1-5 W (~2 kV/400 V, 1-5 mA)

Conventional electrolytic cell

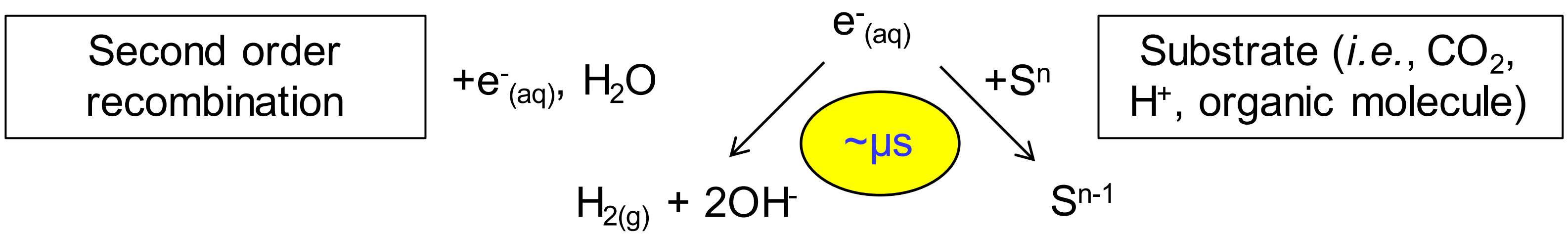


- Cathodic reactions at the solid-liquid interface
- Electrons are injected from metal
- Total power – 1-5 mW (1-5 V, 1-5 mA)

Hypothesis: electrons in plasma solvate in water, then react with everything (E^o=-2.77 V)



Young *et al.*, *Chem. Rev.* **112**, 5553 (2012).

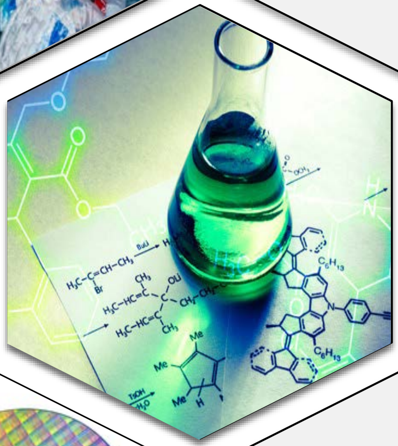


Potential application space for atmospheric-pressure plasmas

N_2 fixation
Food production and fuels

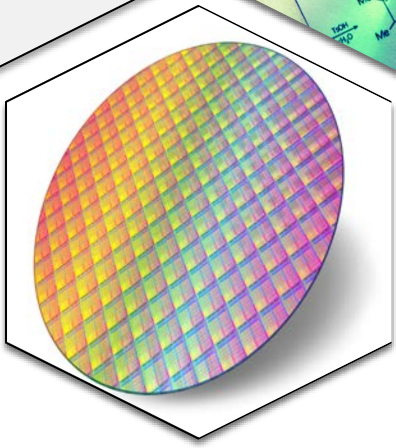
De-polymerization
Re/upcycling plastic waste

Organic degradation
Water treatment



Organic synthesis
Sustainable chemistry

Metal nanoparticles
AM and resource recovery



Solvent activation
Chemical-free cleaning

Our plasma organic chemistry team

Dr. Jian Wang, Chem

Prof. Necip Uner, ChE

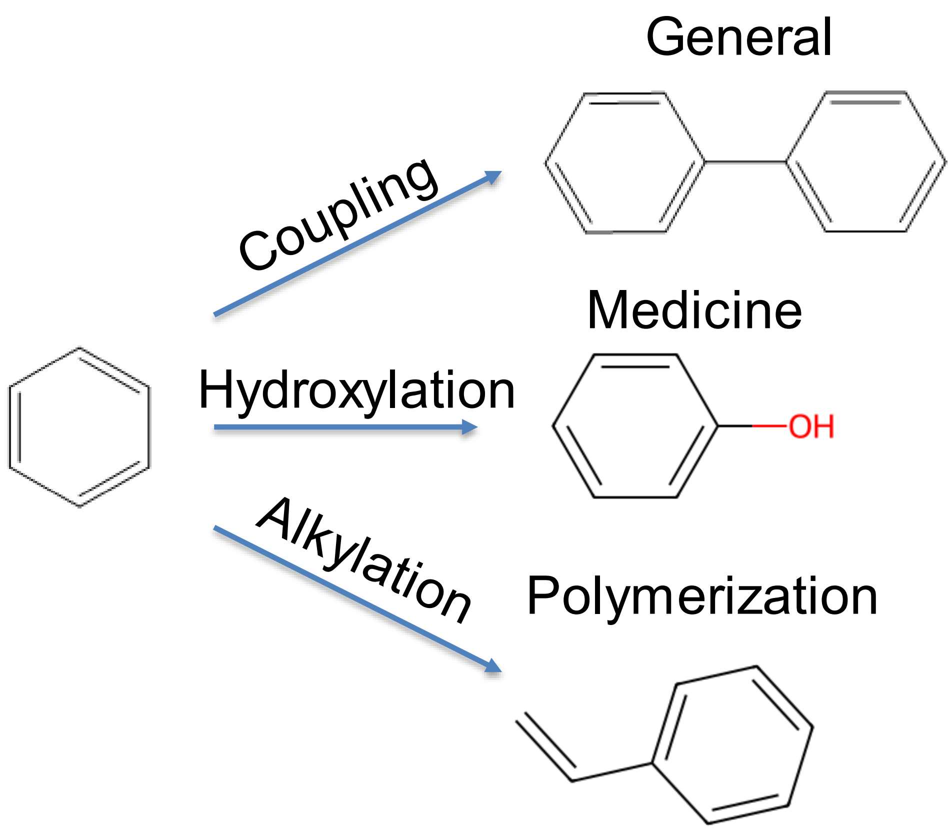
Dr. Scott Dubowsky, Chem

Dr. Matthew Confer, ChE

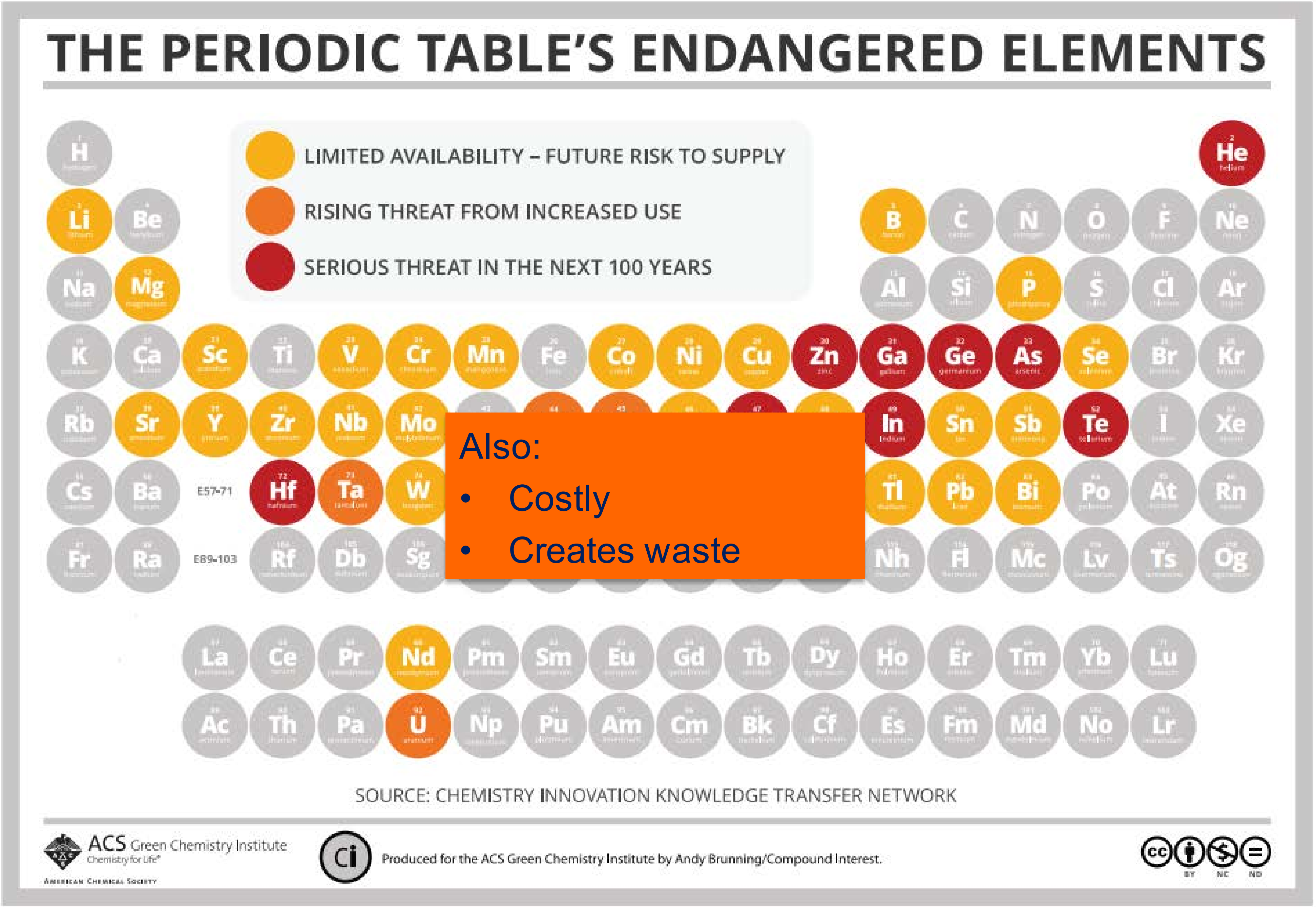
Prof. Rohit Bhargava, BioE

Prof. Jeffrey Moore, Chem

Organic chemistry



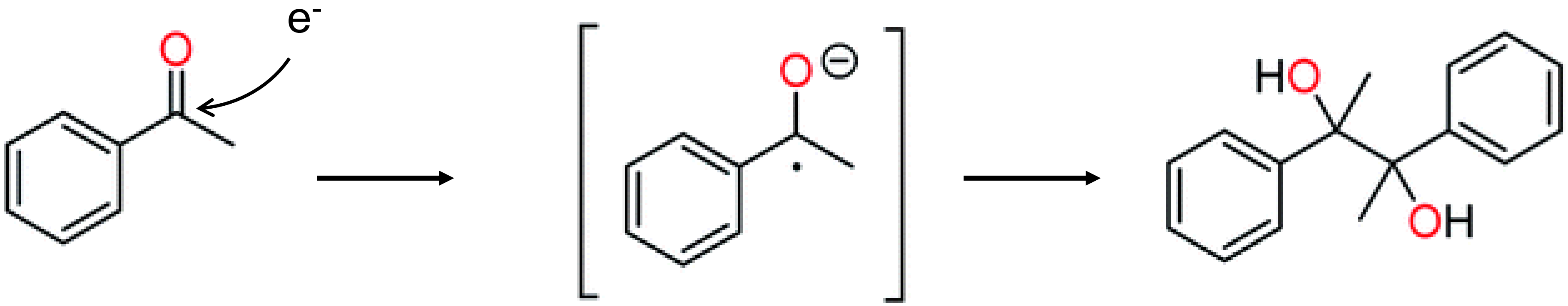
- ► Multistep
- ► Extreme reaction conditions (e.g., high P)
- ► Requires metal catalyst



Also:

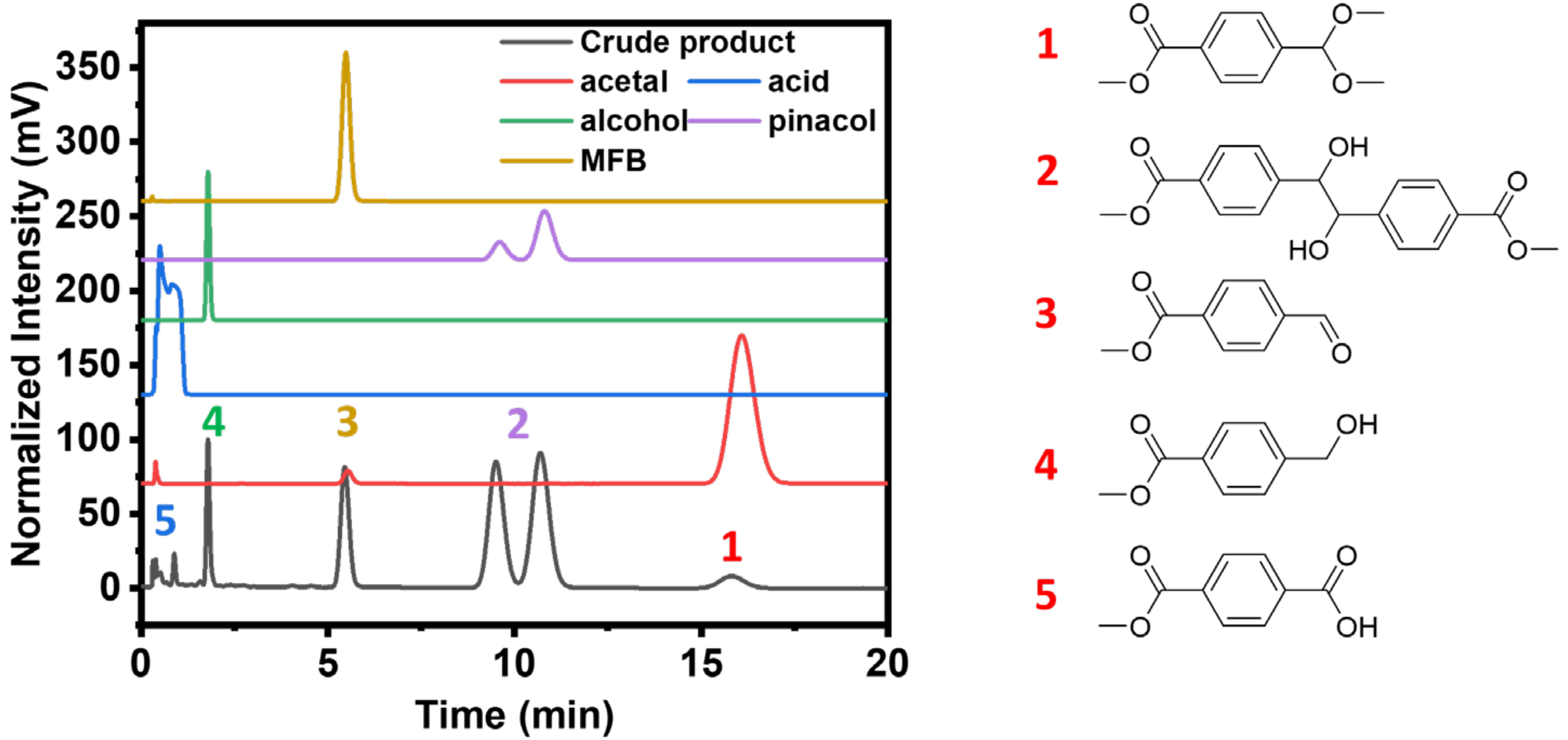
- Costly
- Creates waste

Example of carbon-carbon coupling: Pinacol coupling



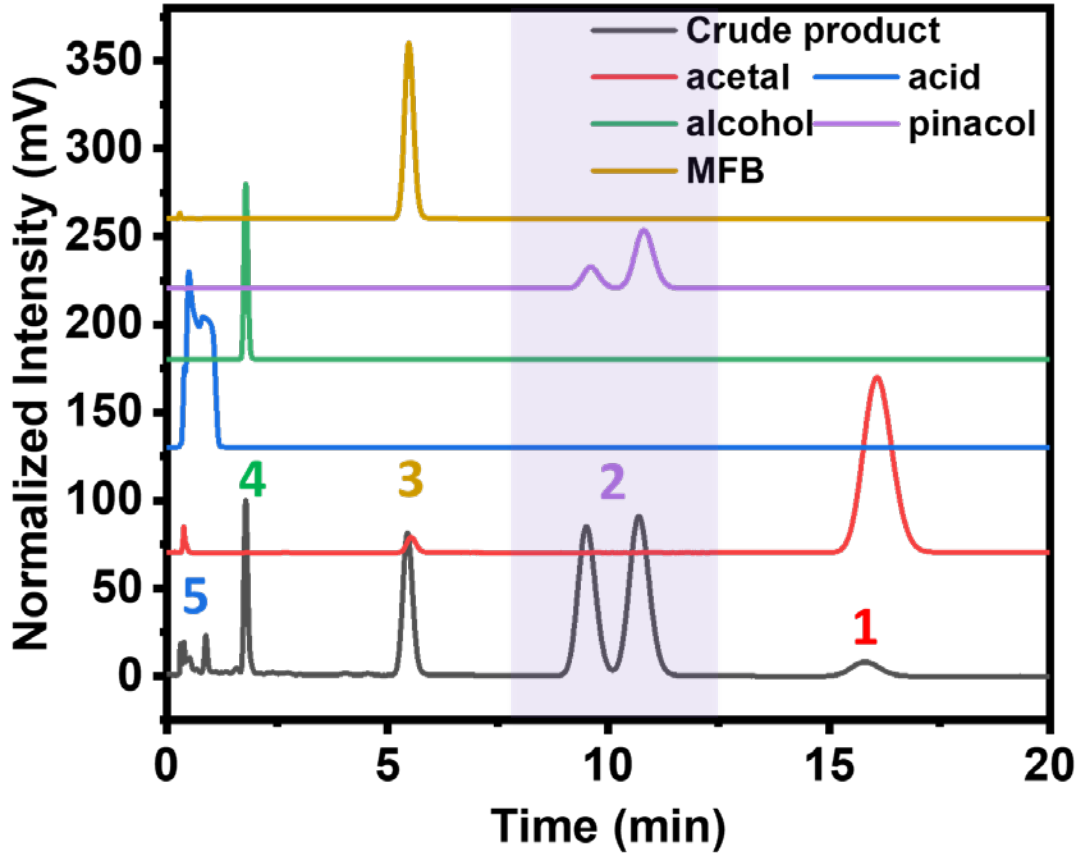
- ► Well-known reaction
- ► Single electron transfer reaction
- ► Should have a high-rate constant based on radiolysis of similar molecules

Initial evidence of products by high-pressure liquid chromatography

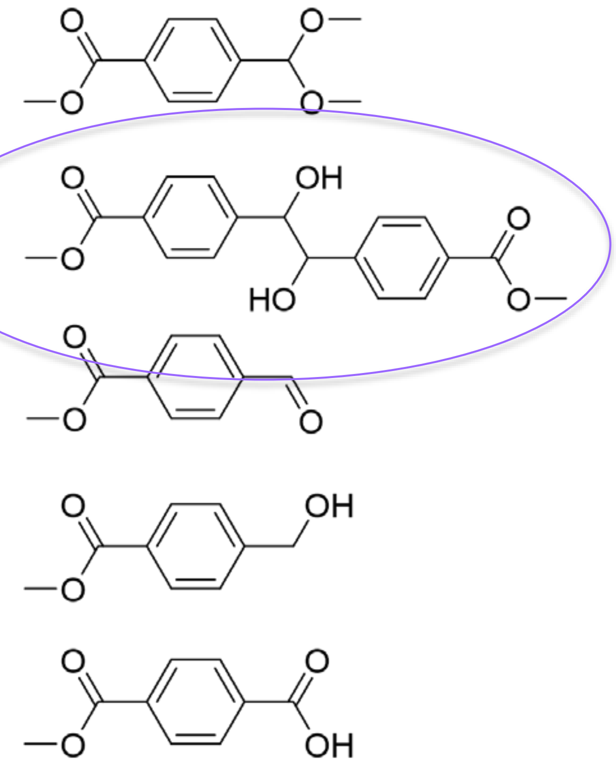


MFB = methyl-4-formylbenzoate
Solvent: MeOH + H_2O (5:1)

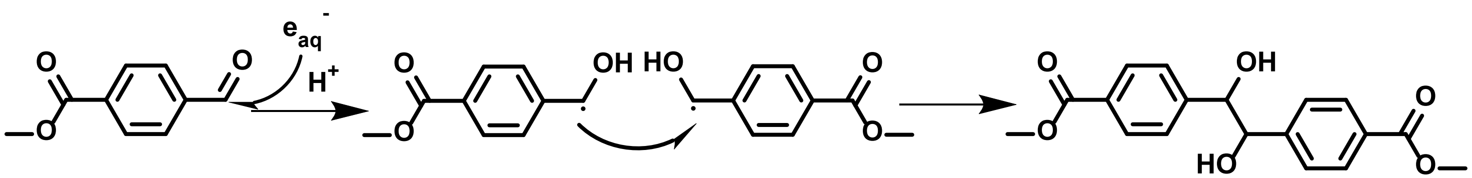
Initial evidence of products by high-pressure liquid chromatography



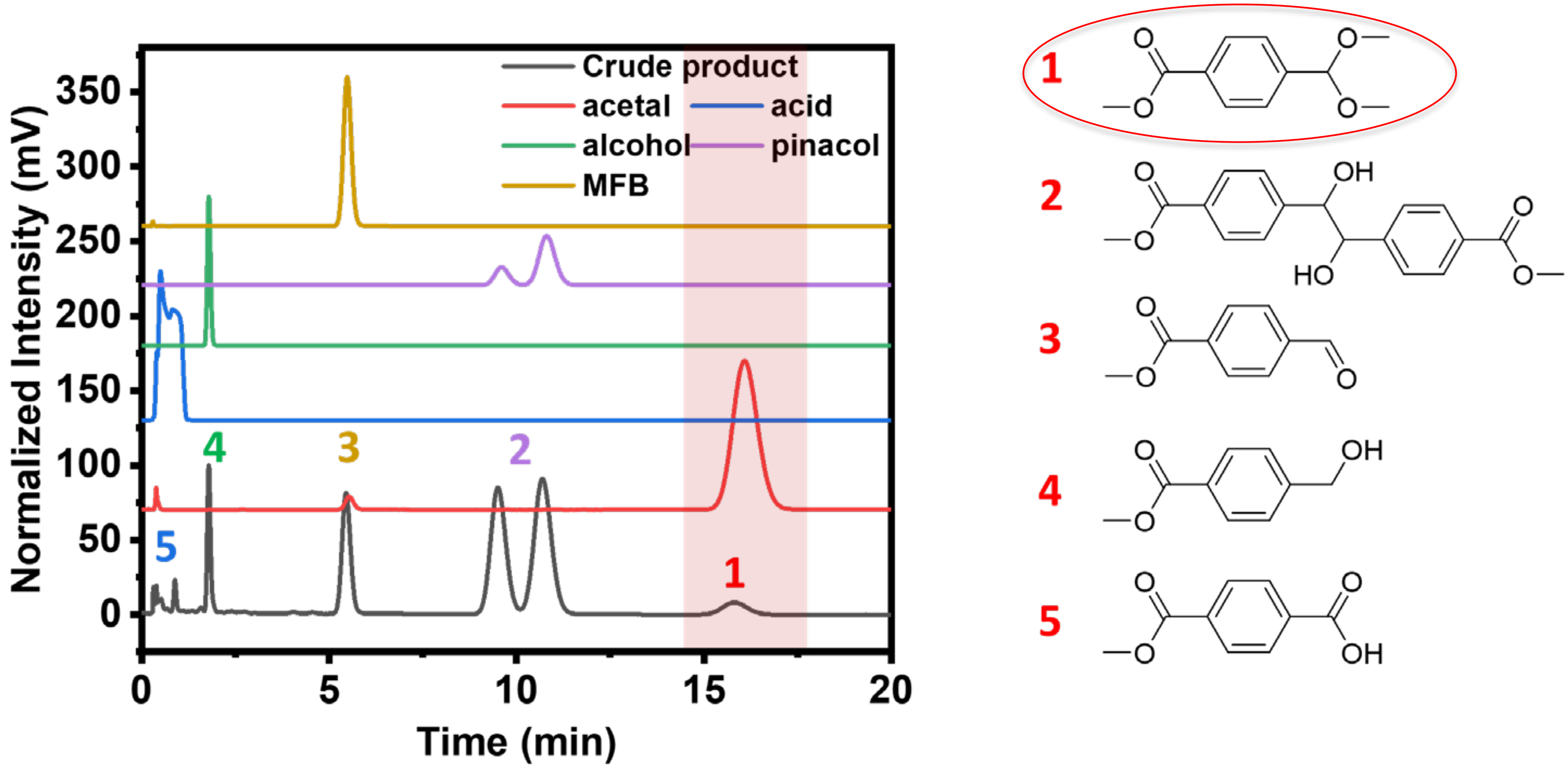
1
2
3
4
5



2) Pinacol:

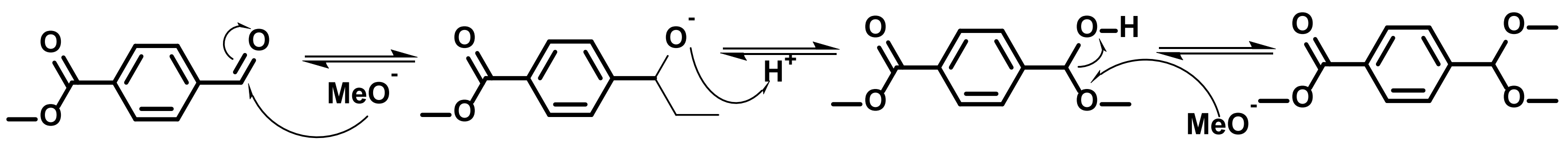


Initial evidence of products by high-pressure liquid chromatography

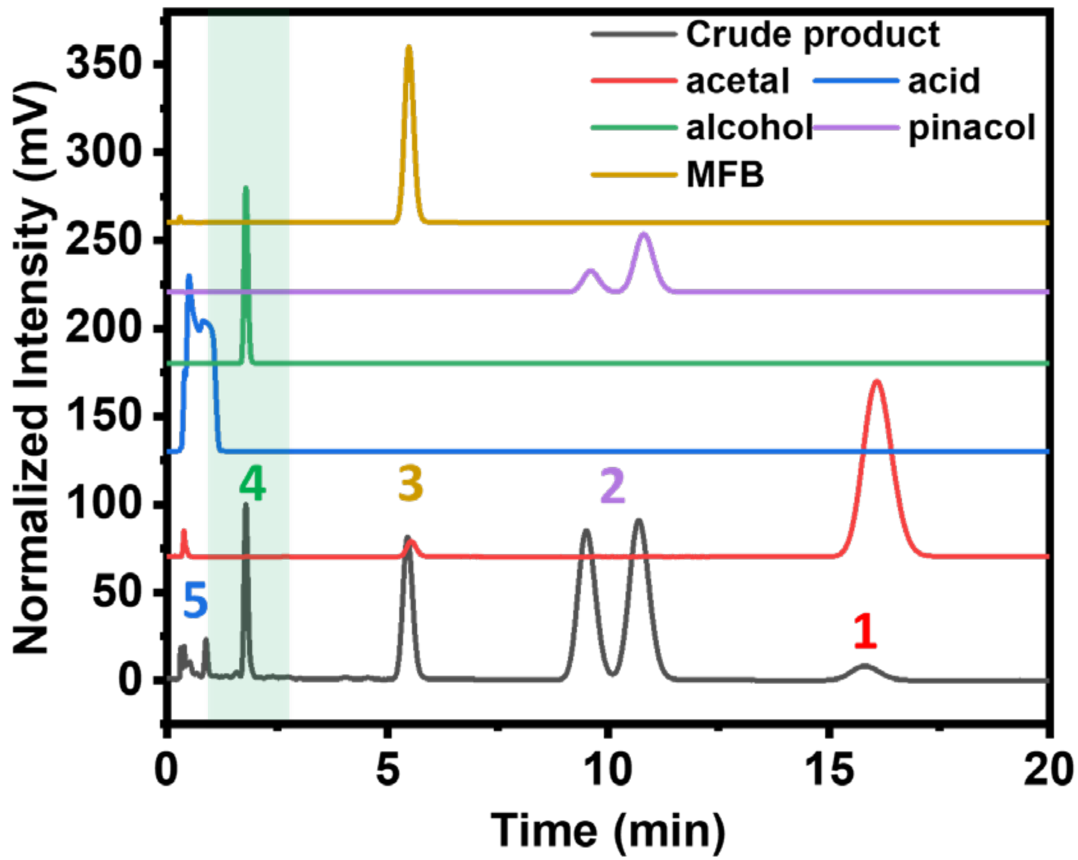


1) **Acetal:**

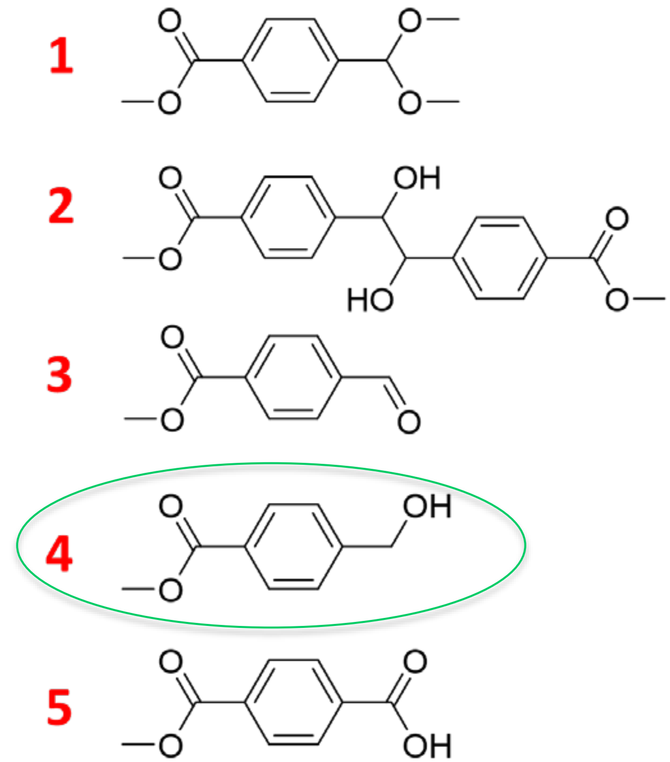
$e^{-}_{(aq)}$ + MeOH → MeO^{-} + H·



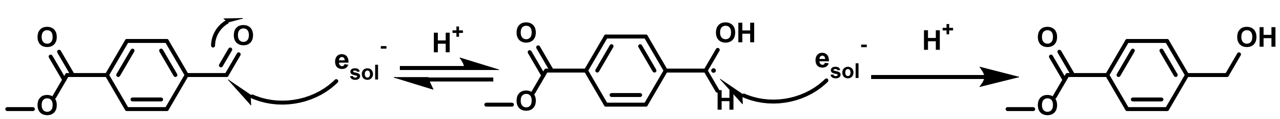
Initial evidence of products by high-pressure liquid chromatography



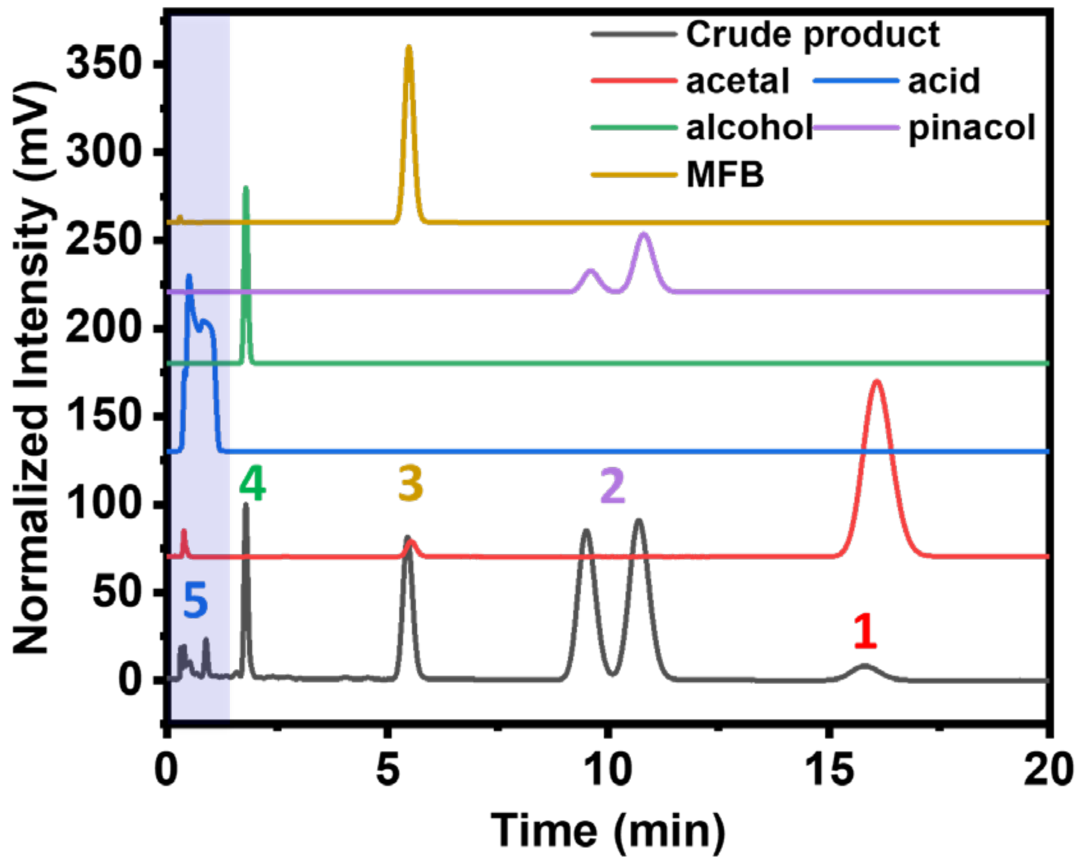
1 2 3 4 5

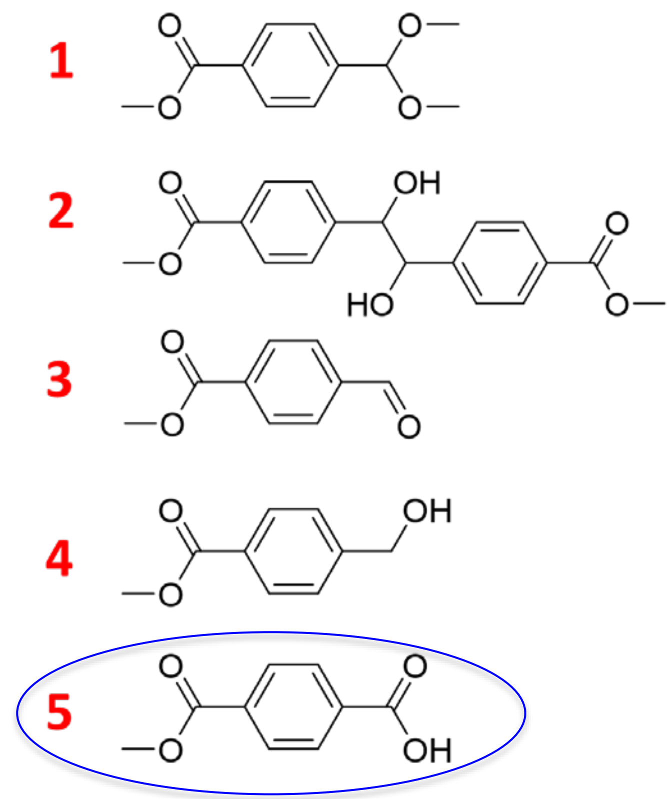


4) Alcohol:



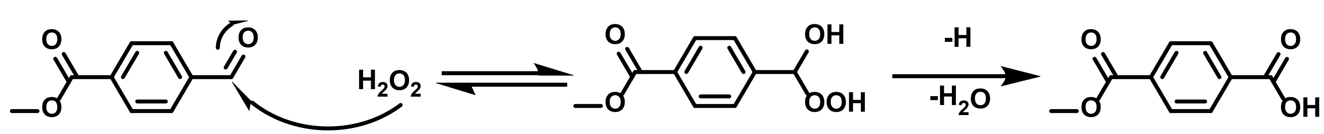
Initial evidence of products by high-pressure liquid chromatography



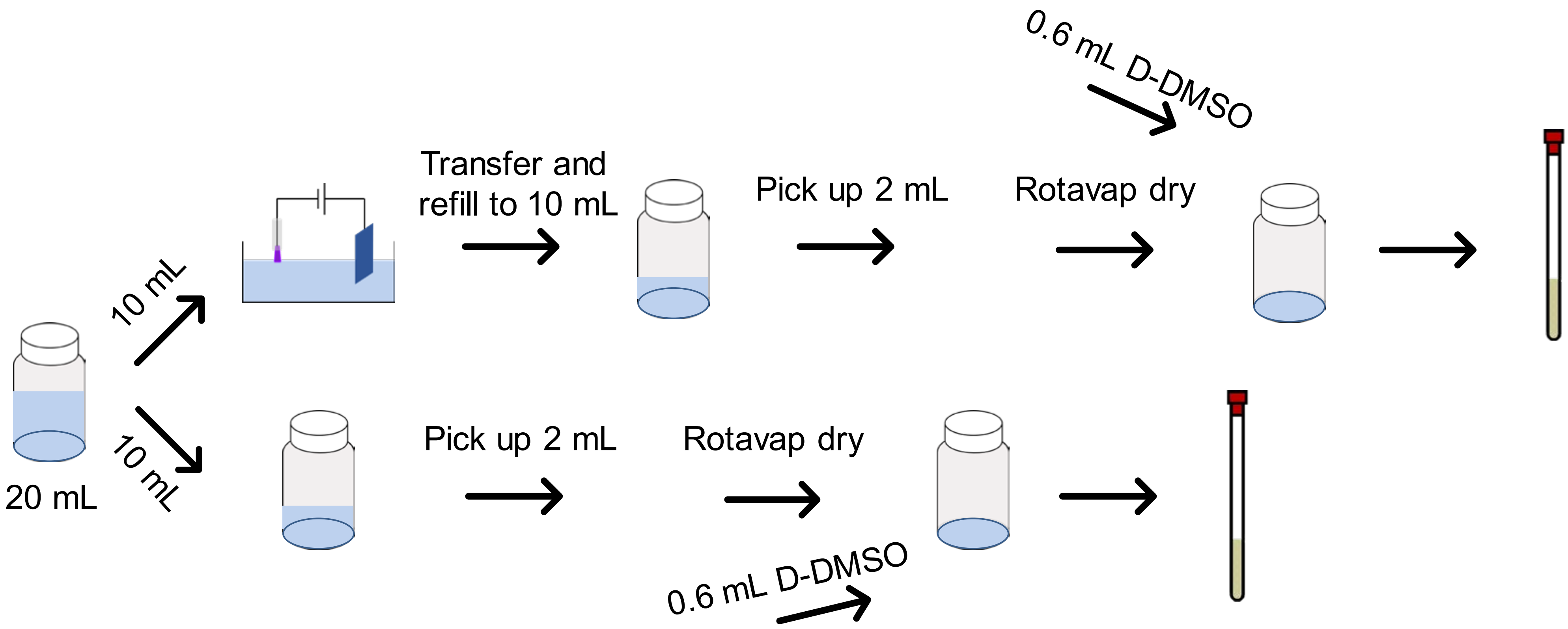


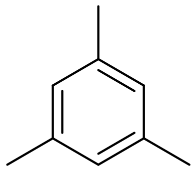
5) Acid:

$e^- + H_2O \rightarrow 2OH\cdot \rightarrow H_2O_2$



Procedure for quantitative analysis

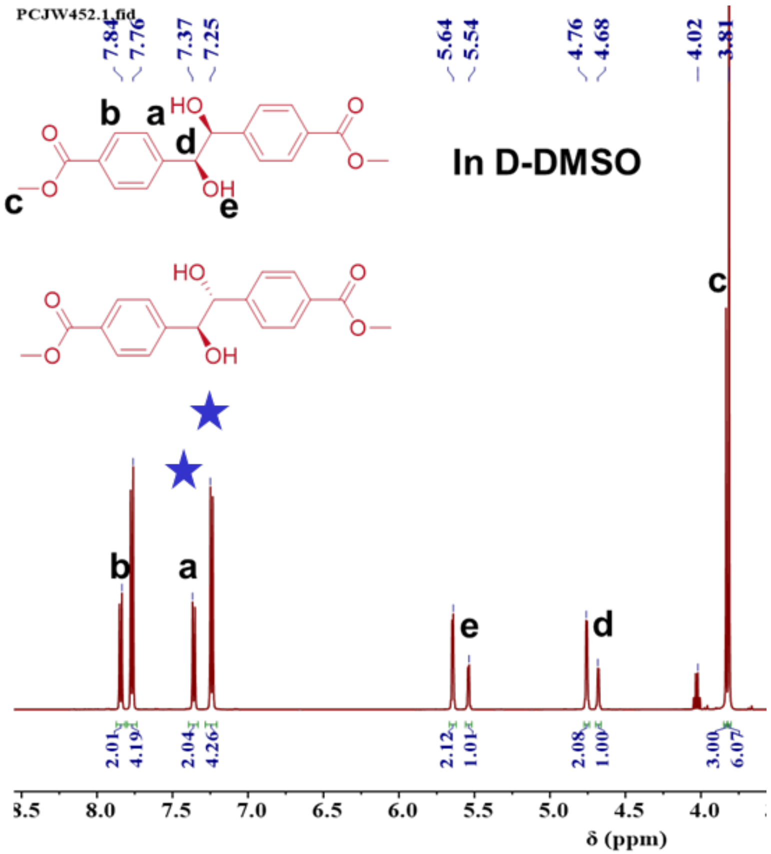




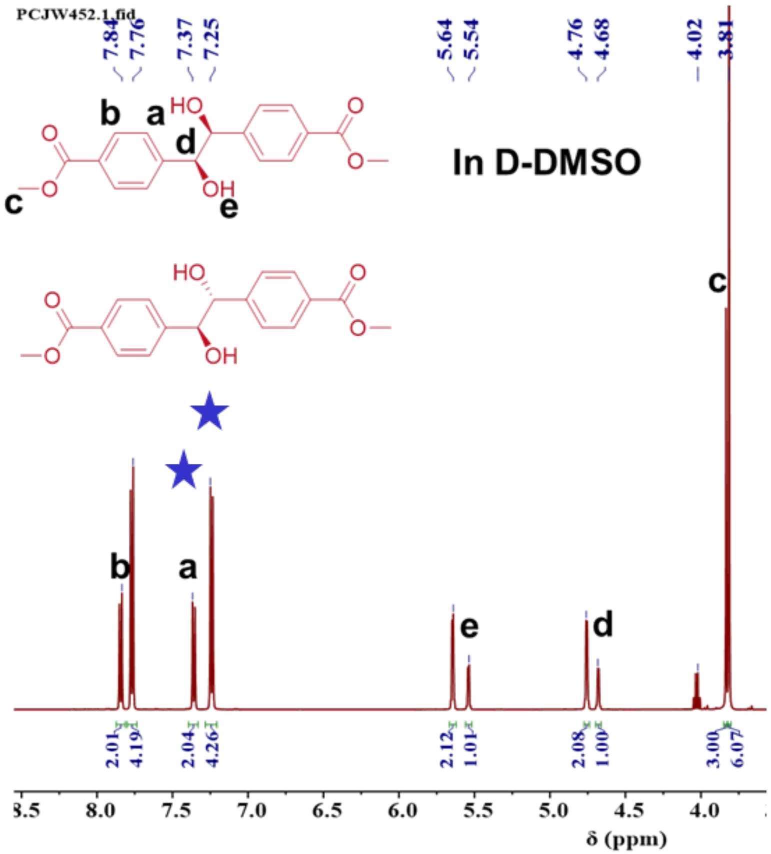
mesitylene

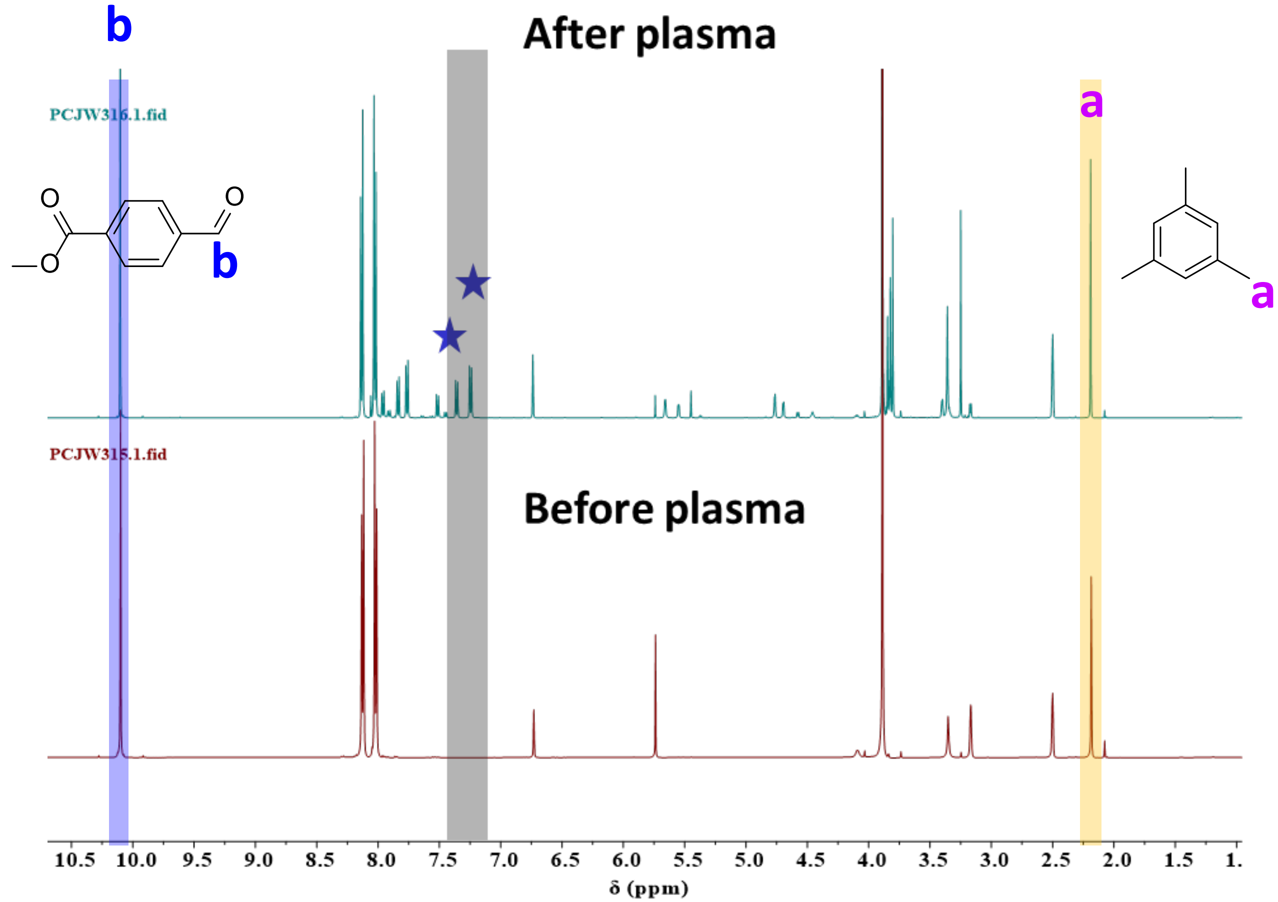
Internal standard in D-DMSO

Structural confirmation of pinacol product by NMR and assessment of yield/conversion

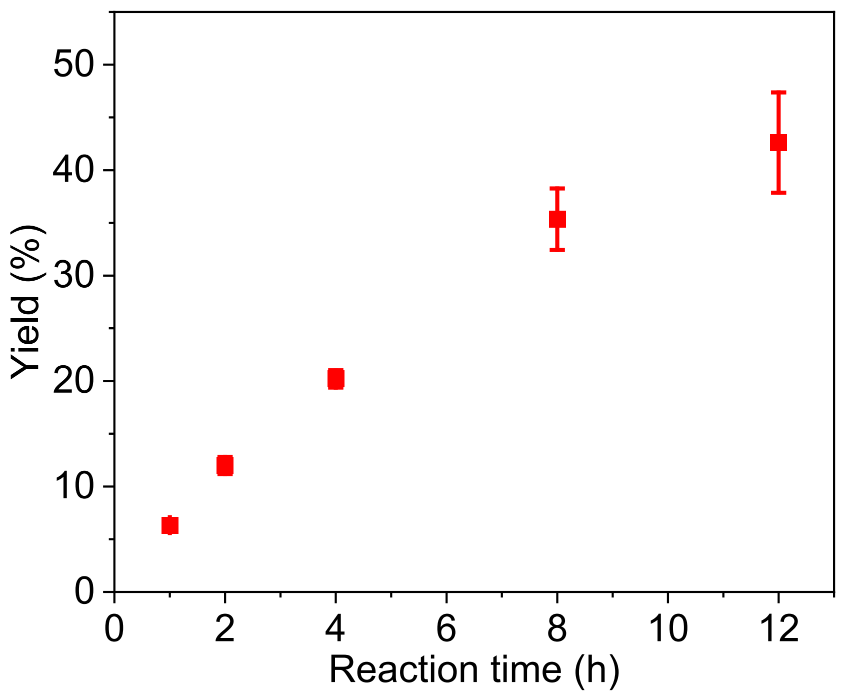


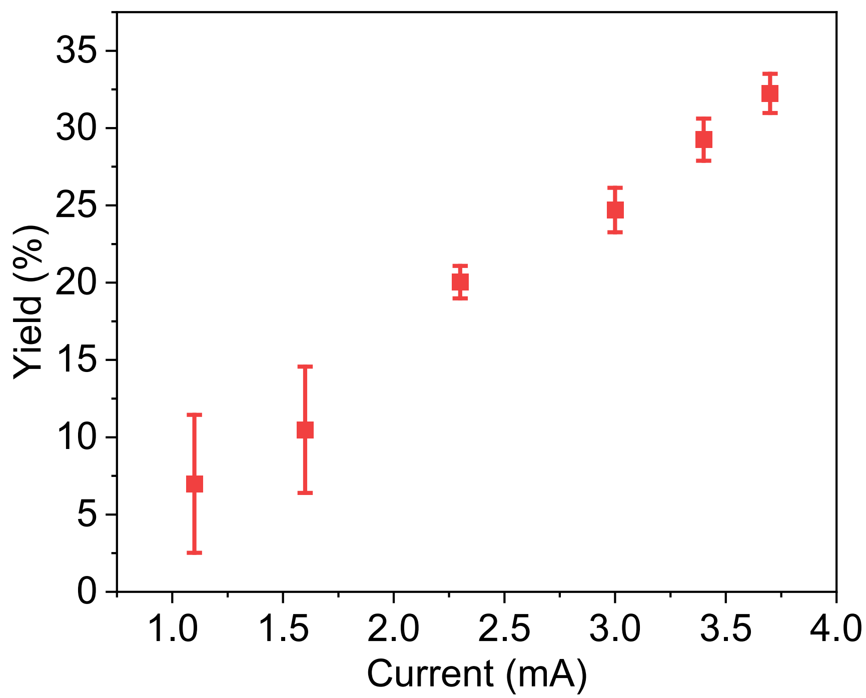
Structural confirmation of pinacol product by NMR and assessment of yield/conversion



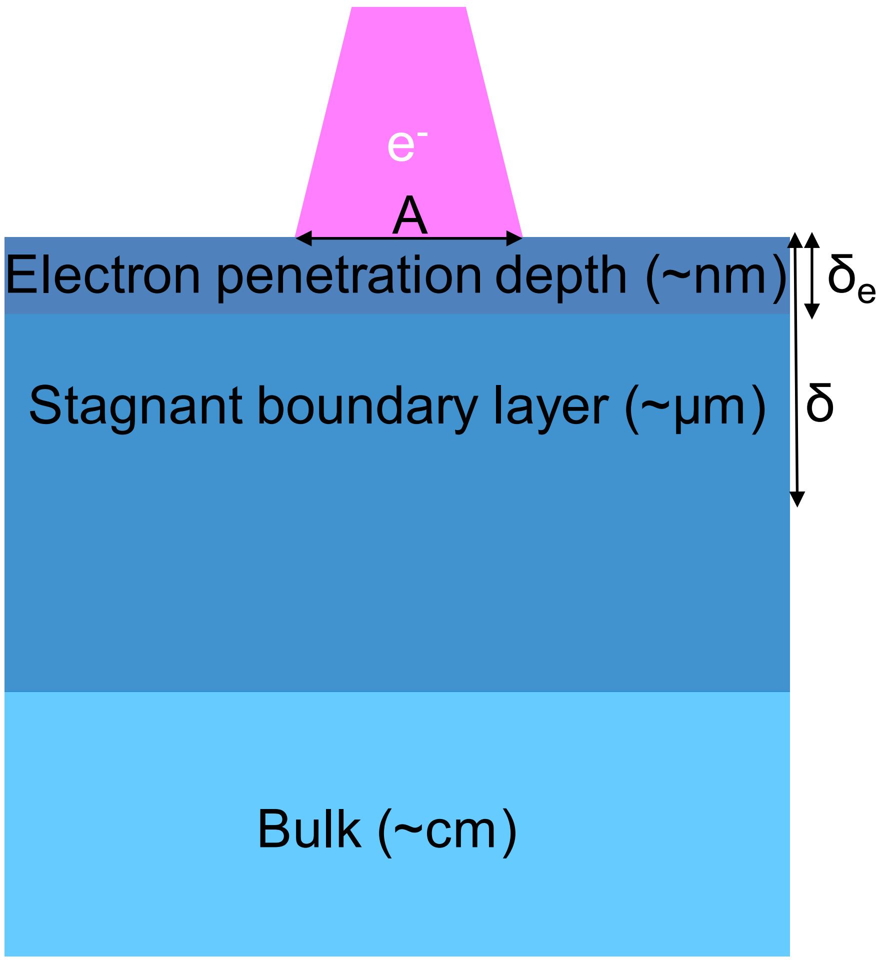


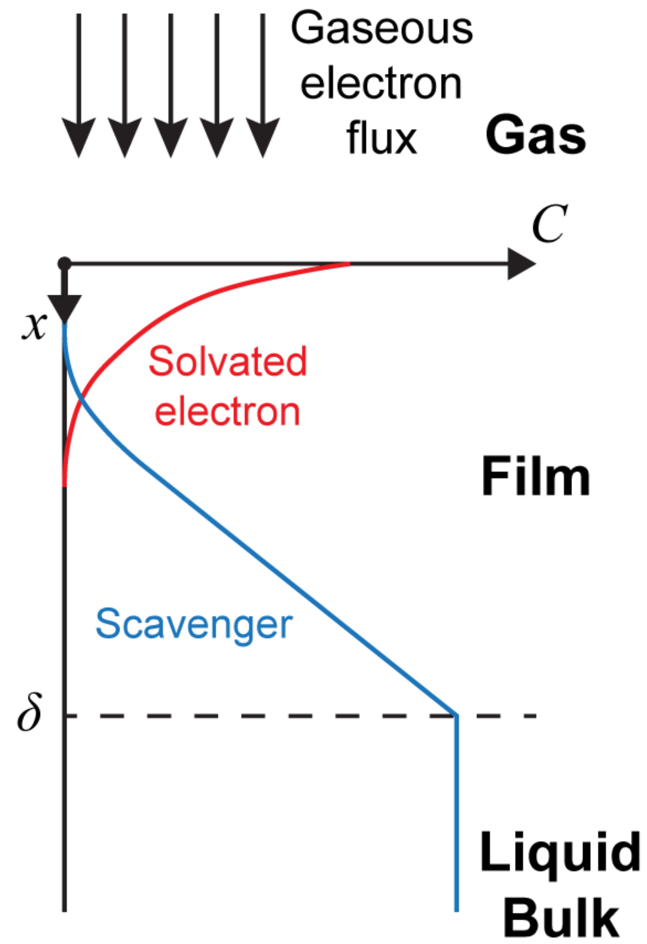
Reaction yield as a function of current and time





Reaction-diffusion model for plasma-liquid reactions

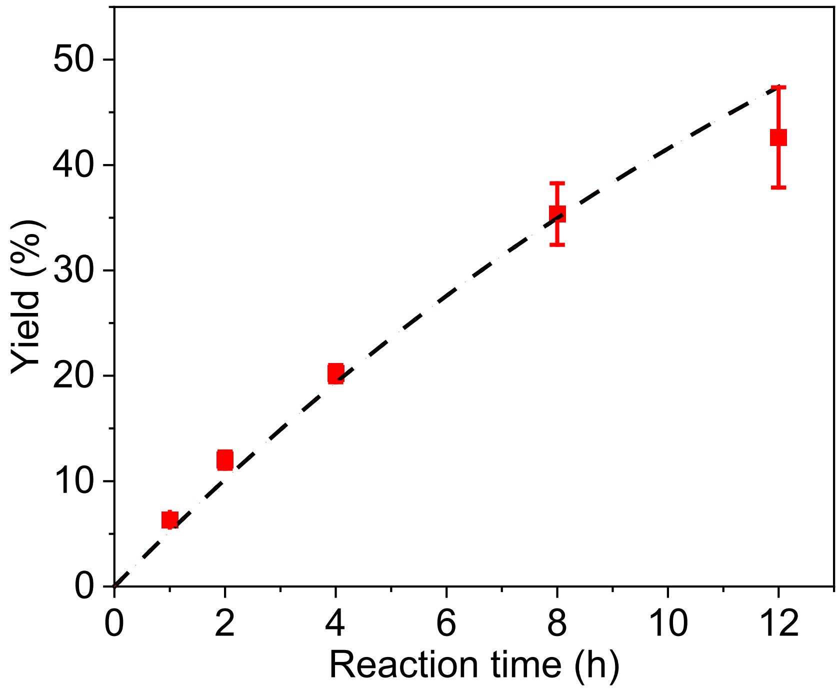


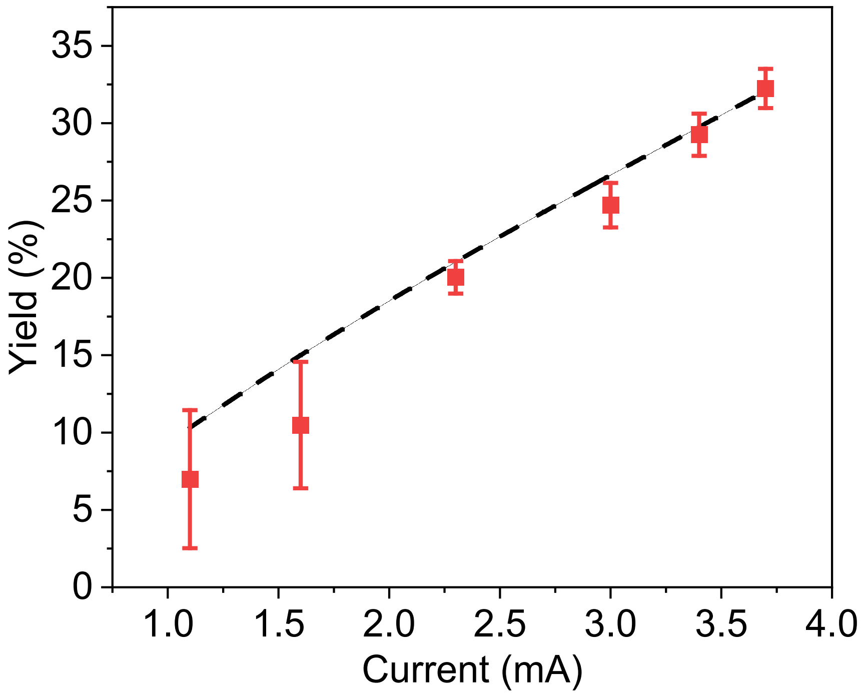


$$D_e \frac{d^2 C_e}{dx^2} - 2k_r C_e^2 - k_s C_e C_s - k_a C_e C_r = 0$$

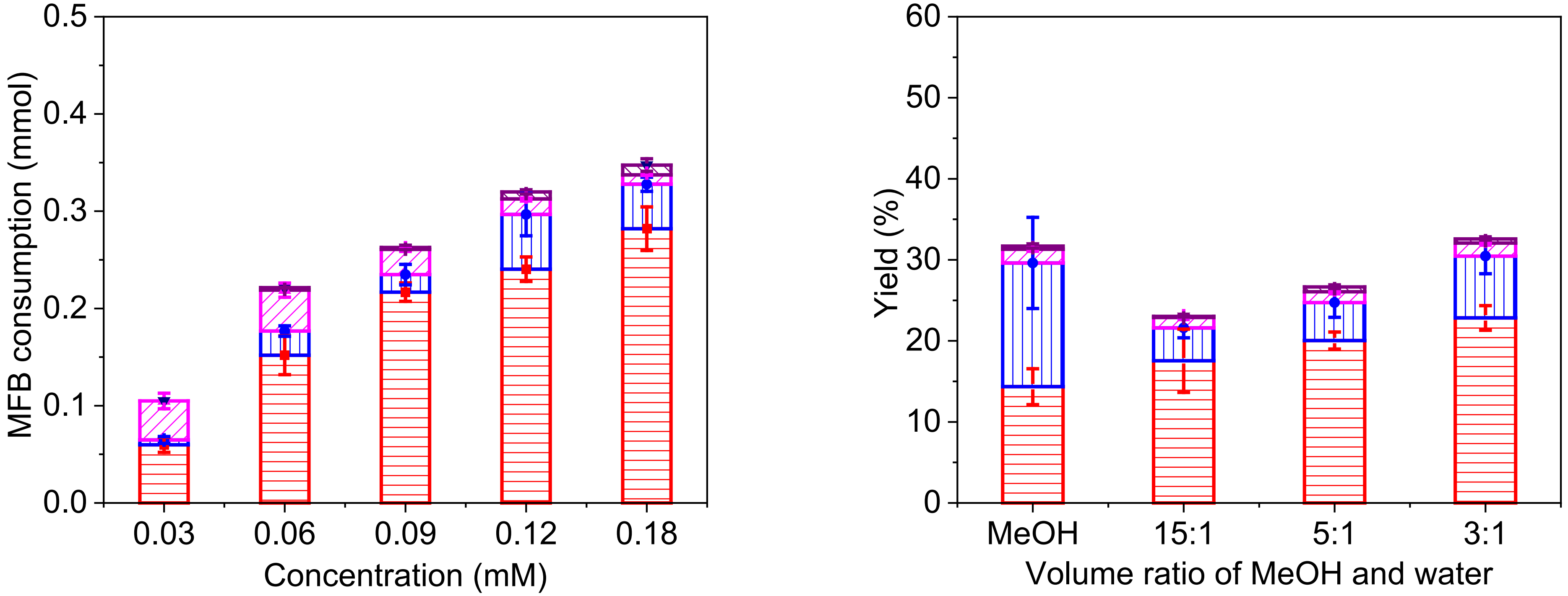
$$D_s \frac{d^2 C_s}{dx^2} - k_s C_e C_s = 0$$

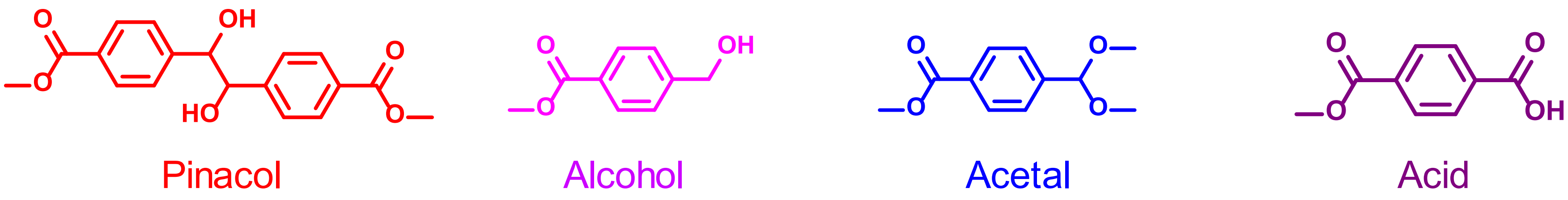
Reaction yield as a function of current and time



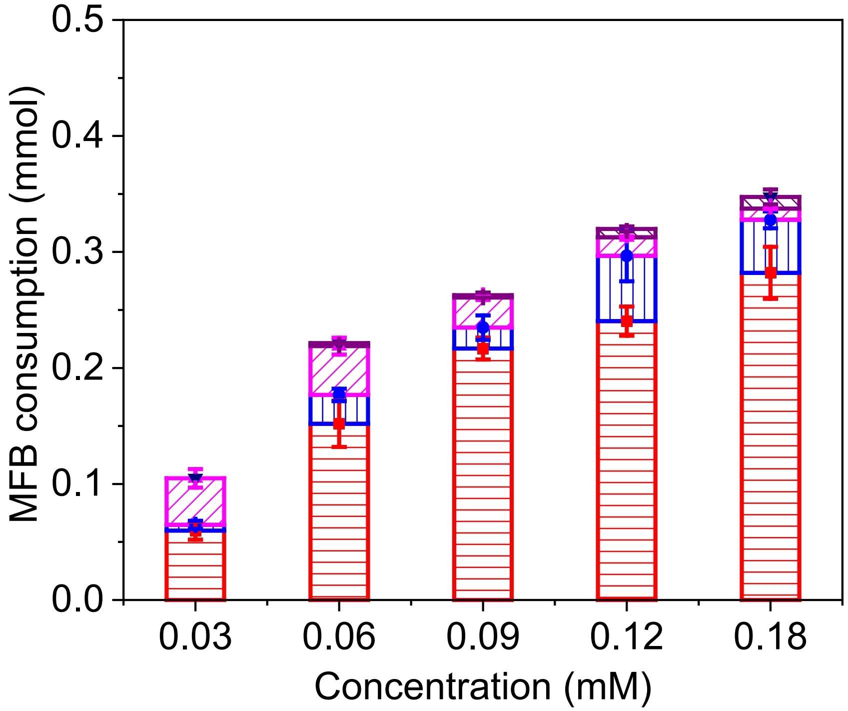


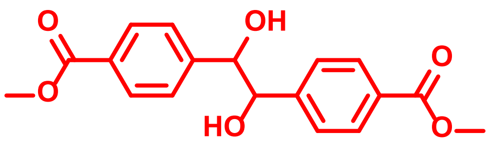
Effect of initial concentration and solvent composition

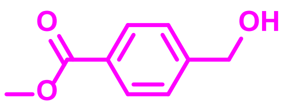


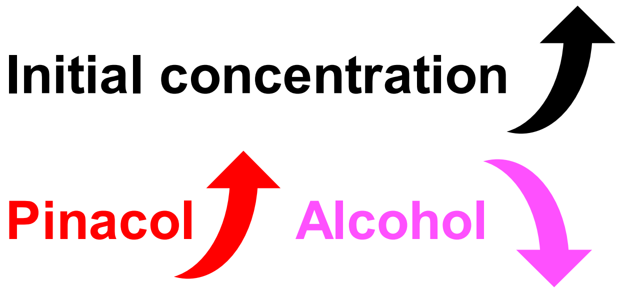


Effect of initial concentration





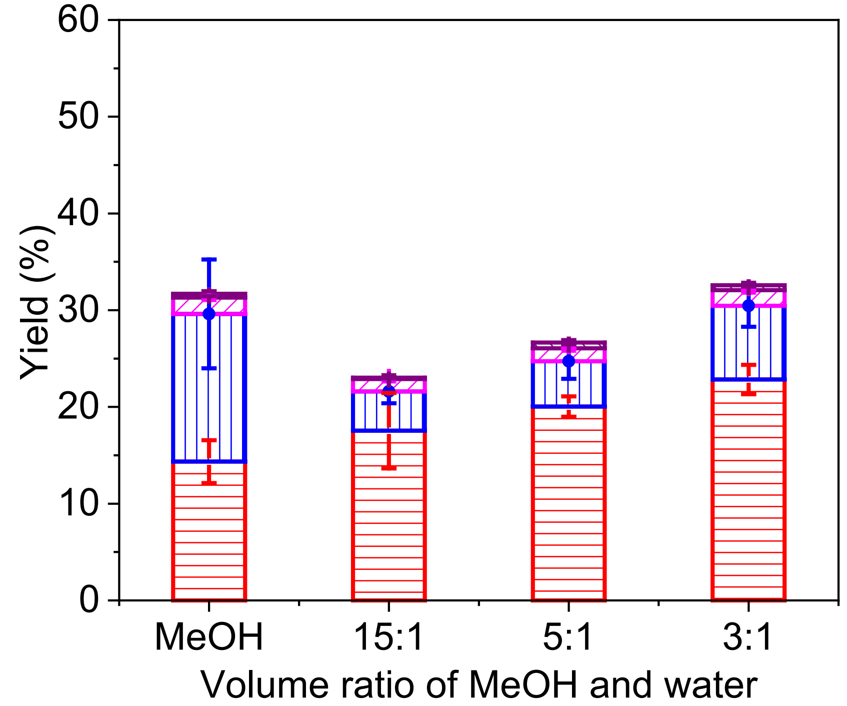


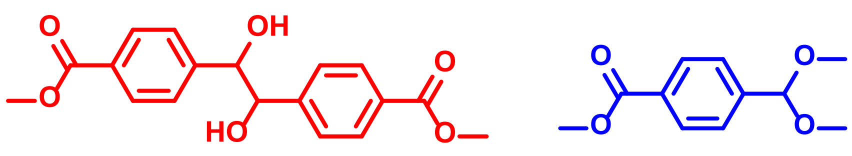


Effect of solvent composition

Water content ↑

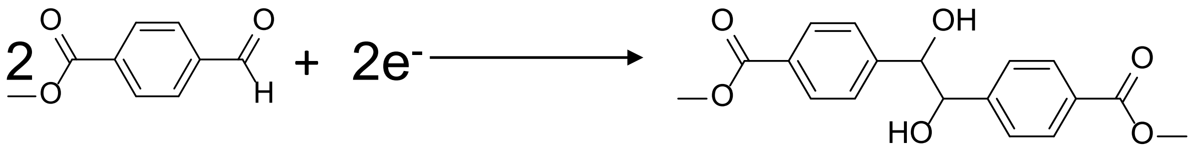
Pinacol ↑ **Acetal** ↓





Pinacol Acetal

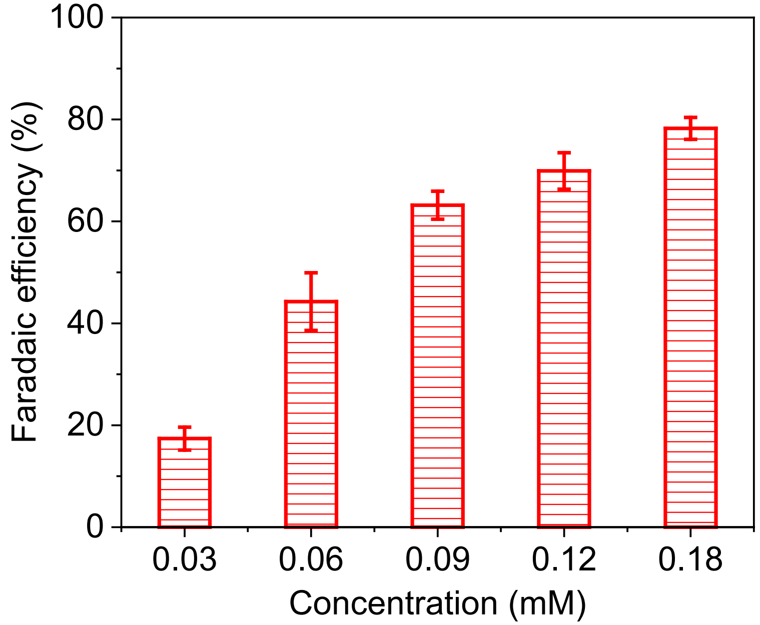
Effect of initial concentration and solvent composition

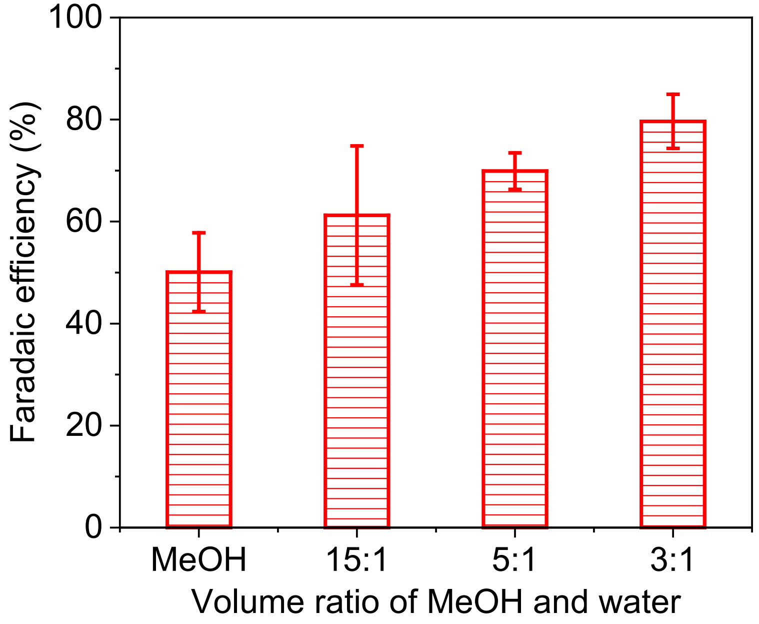


$$\text{Faradaic pinacol concentration} = \frac{Q}{FzV}$$

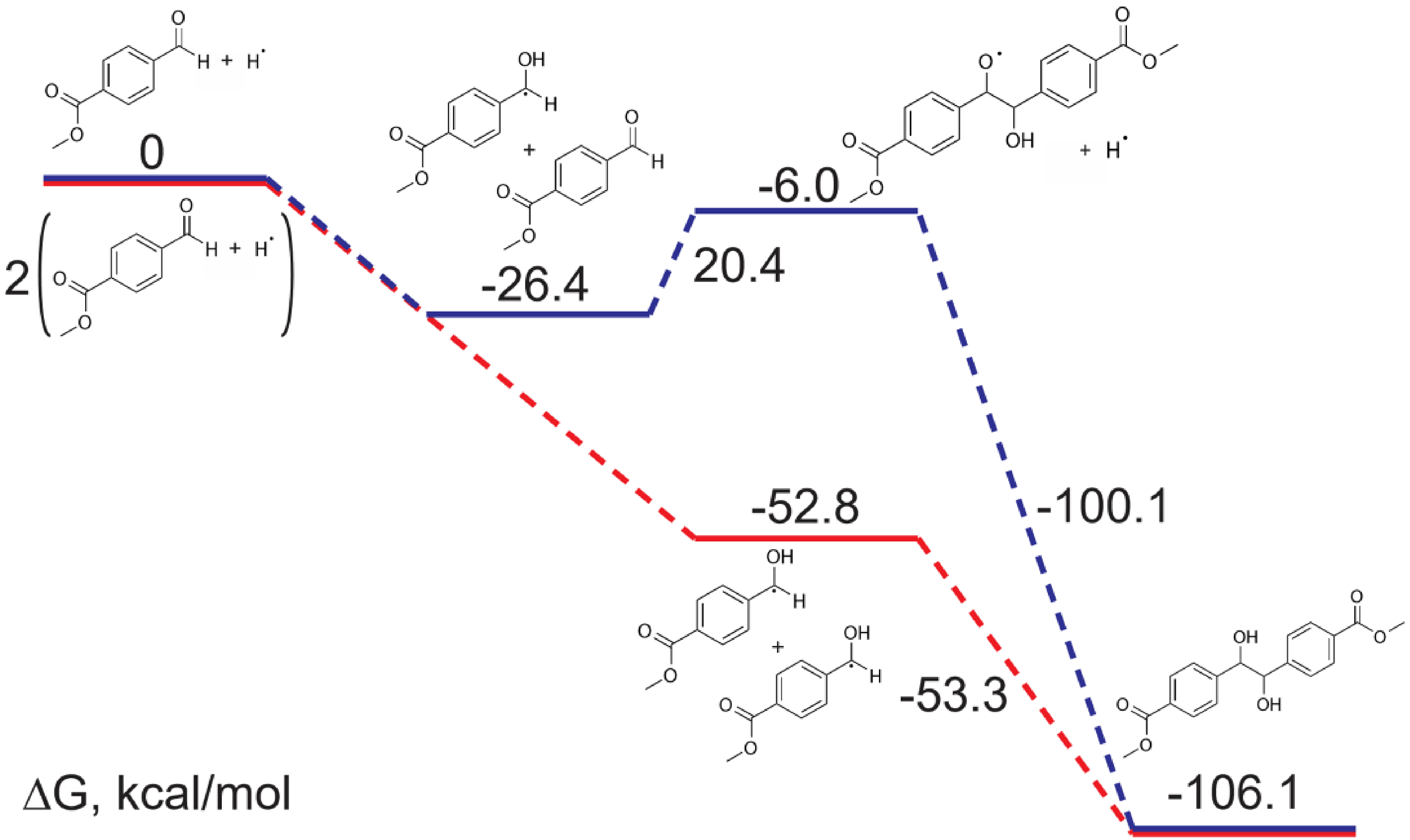
Q = total charge
F = Faraday's constant
$z = 2$ for *pinacol coupling* reaction
$V = 10$ ml for our experiments

$$\text{Faradaic efficiency (\%)} = \frac{\text{Experimentally measured } \textit{pinacol} \text{ concentration}}{\text{Faradaic pinacol concentration}} \, x\ 100$$



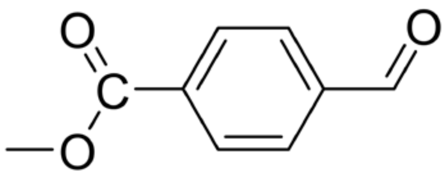


Density functional theory calculations of recombination vs. addition reactions



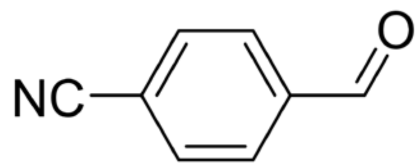
Extending to other substrates – ketones, aldehydes, and furfural

MFB



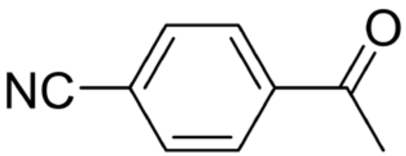
Yield: 46%

meso: dl= 53: 47



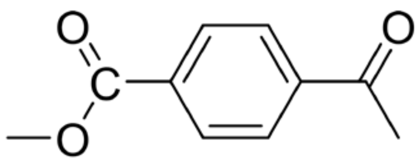
Yield: 54%

meso: dl= 57: 43



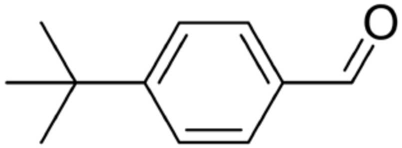
Yield: 57%

meso: dl= 71: 29



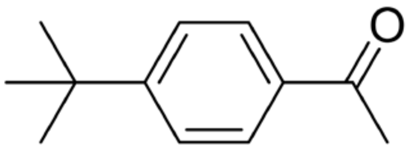
Yield: 36%

meso: dl= 71: 29



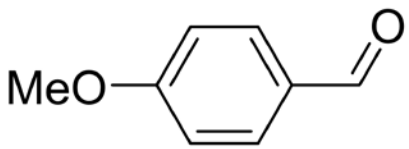
Yield: 50%

meso: dl= 59: 41



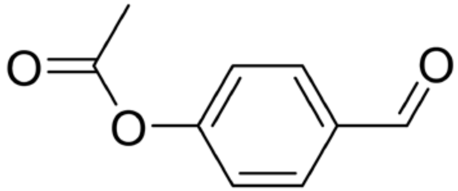
Yield: 44%

meso: dl= 56: 44



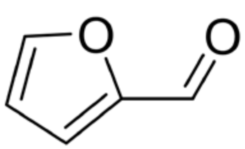
Yield: 38%

meso: dl= 55: 45



Yield: 23%

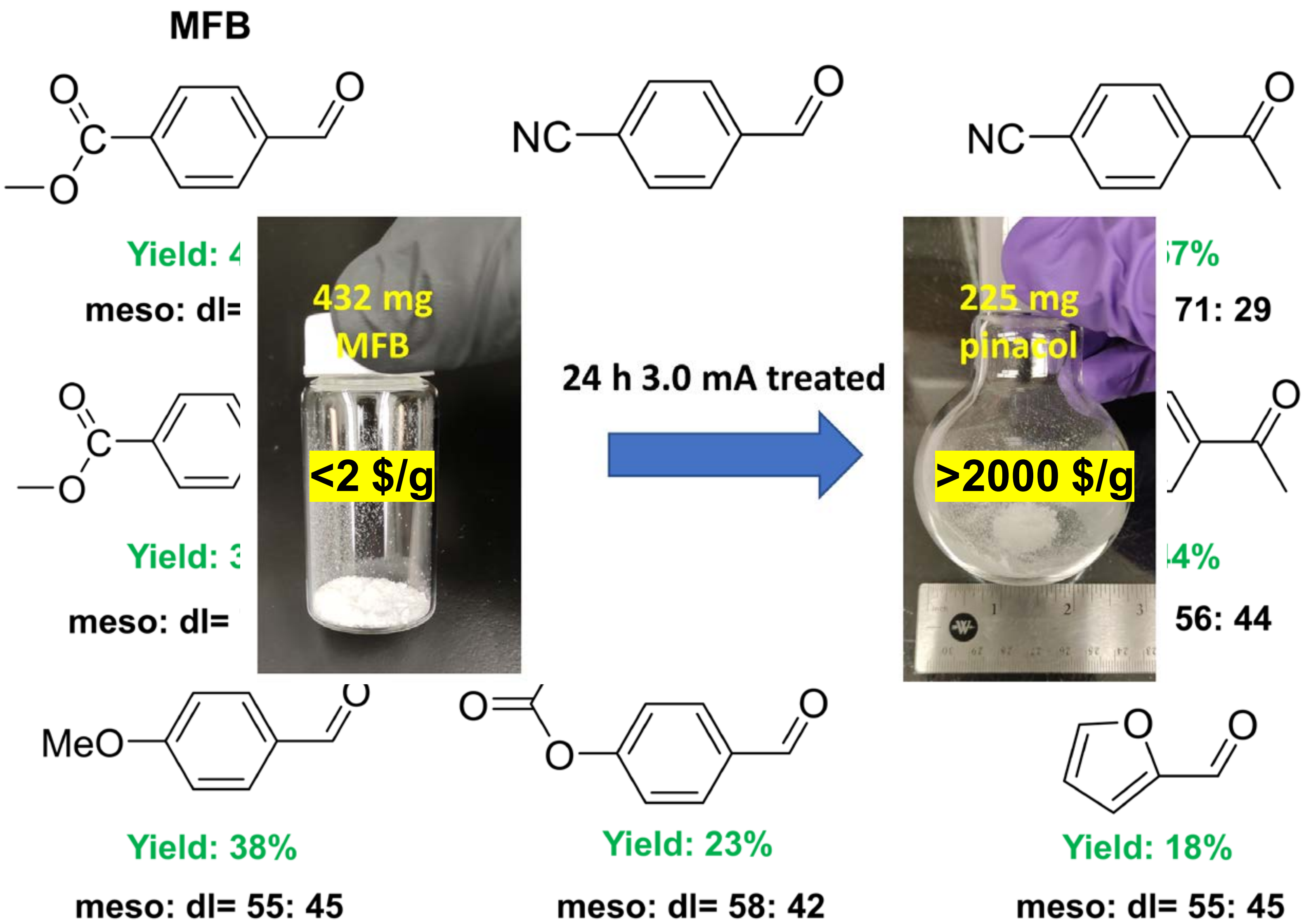
meso: dl= 58: 42



Yield: 18%

meso: dl= 55: 45

Extending to other substrates – ketones, aldehydes, and furfural



Acknowledgements

Reference:

J. Wang, N. Uner, S. Dubowsky, M. P. Confer, R. Bhargava, Y. Sun, Y. Zhou, R. M. Sankaran, and J. S. Moore, *J. Am. Chem. Soc.* **145**, 19, 10470 (2023).

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