

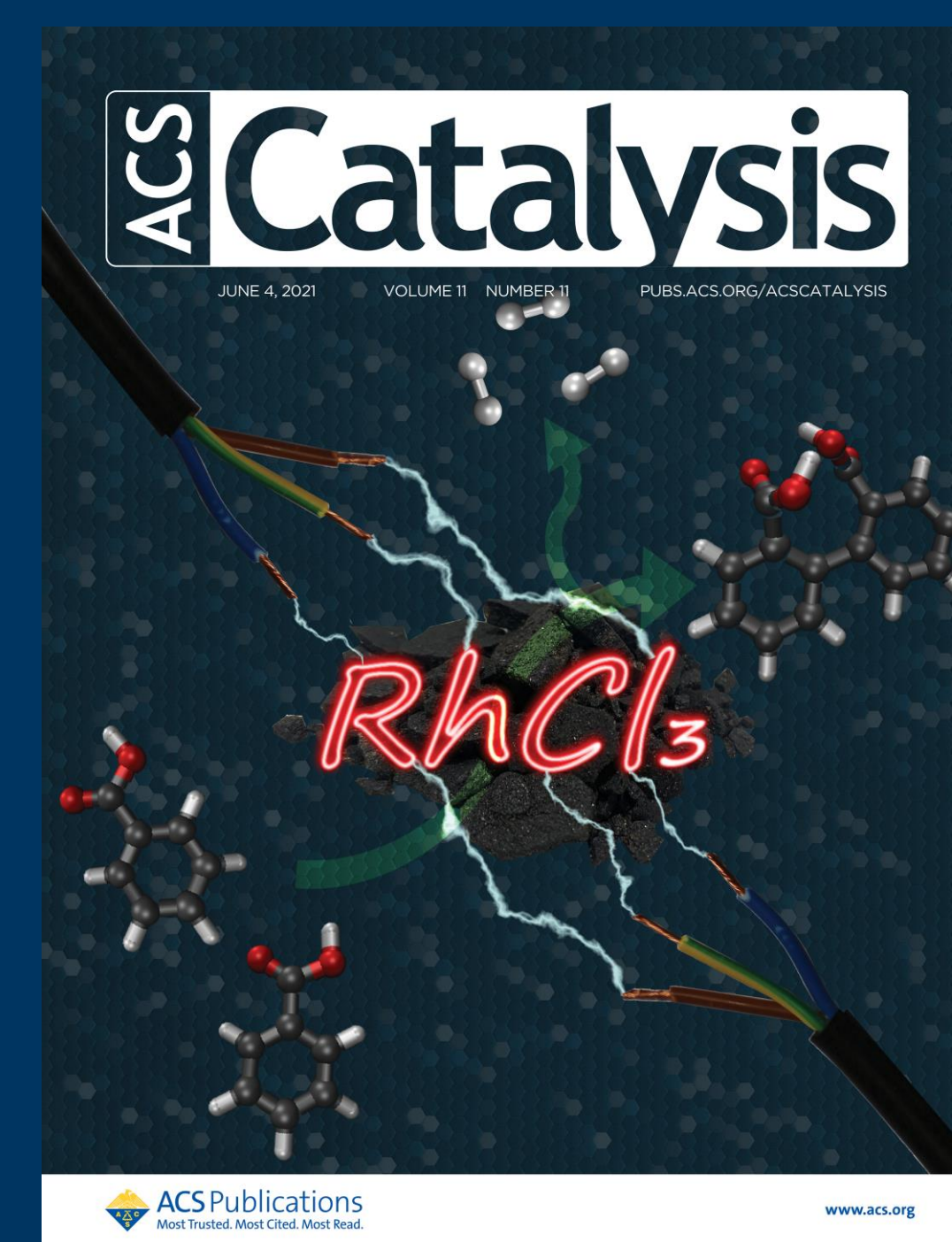
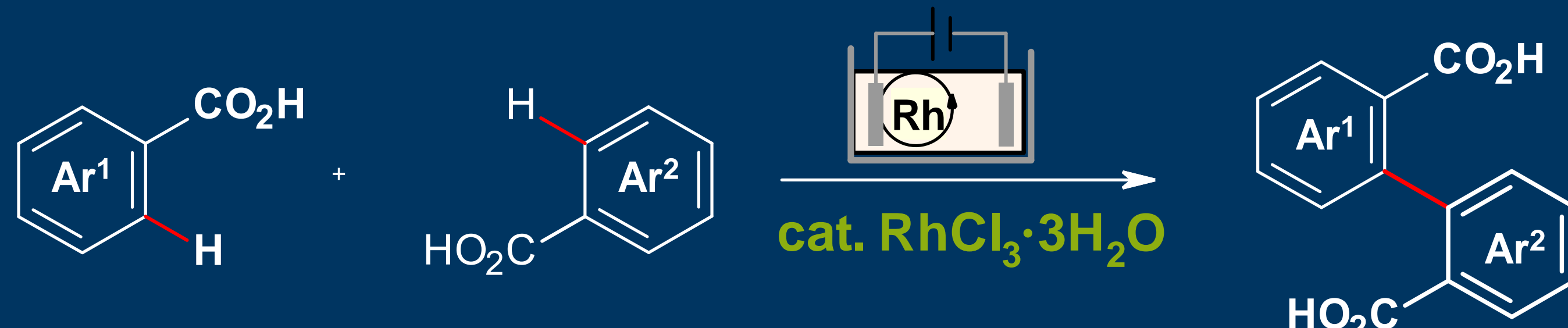
# 2,2'-Biaryldicarboxylate Synthesis via Electrocatalytic Dehydrogenative C–H/C–H Coupling of Benzoic Acids

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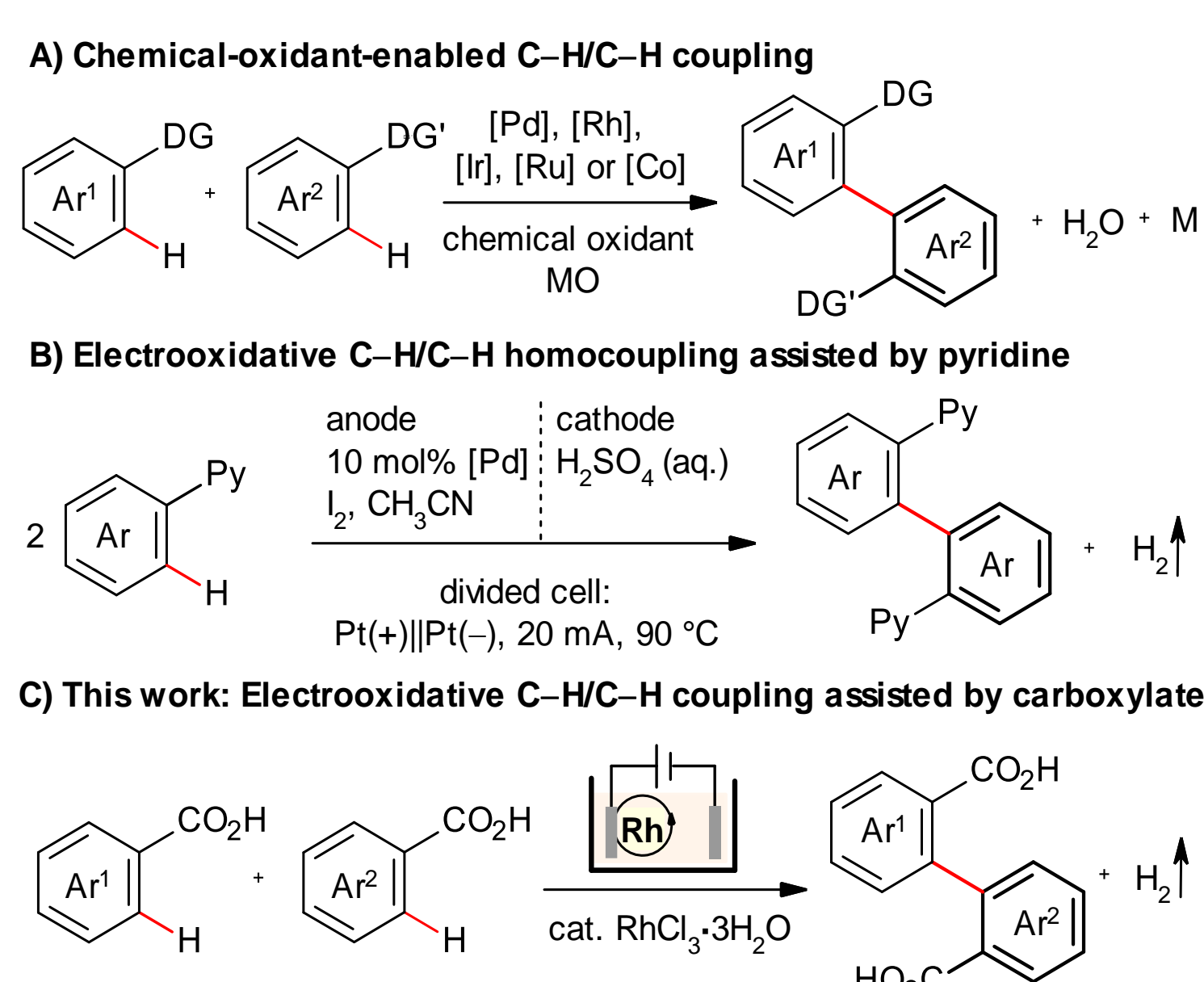


2,2'-Biaryldicarboxylates are important functionalities in bioactive compounds, functional materials, and chiral catalysts. These compounds have been found to be conveniently accessible from benzoic acids via Rh-catalyzed electrooxidative C–H/C–H couplings, giving valuable dihydrogen as the byproduct. In an undivided cell with Pt electrodes,  $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$  catalyzes the oxidative carboxylate-directed *ortho*-homocoupling of various aromatic acids with a current efficiency of 67%. The protocol is operationally simple, tolerates a wide variety of functional groups, and does not require the exclusion of air and moisture. Heterodimerizations via cross-dehydrogenative couplings of naphthyl-1-carboxylic acids with acrylic or benzoic acids have been proven to work as well.



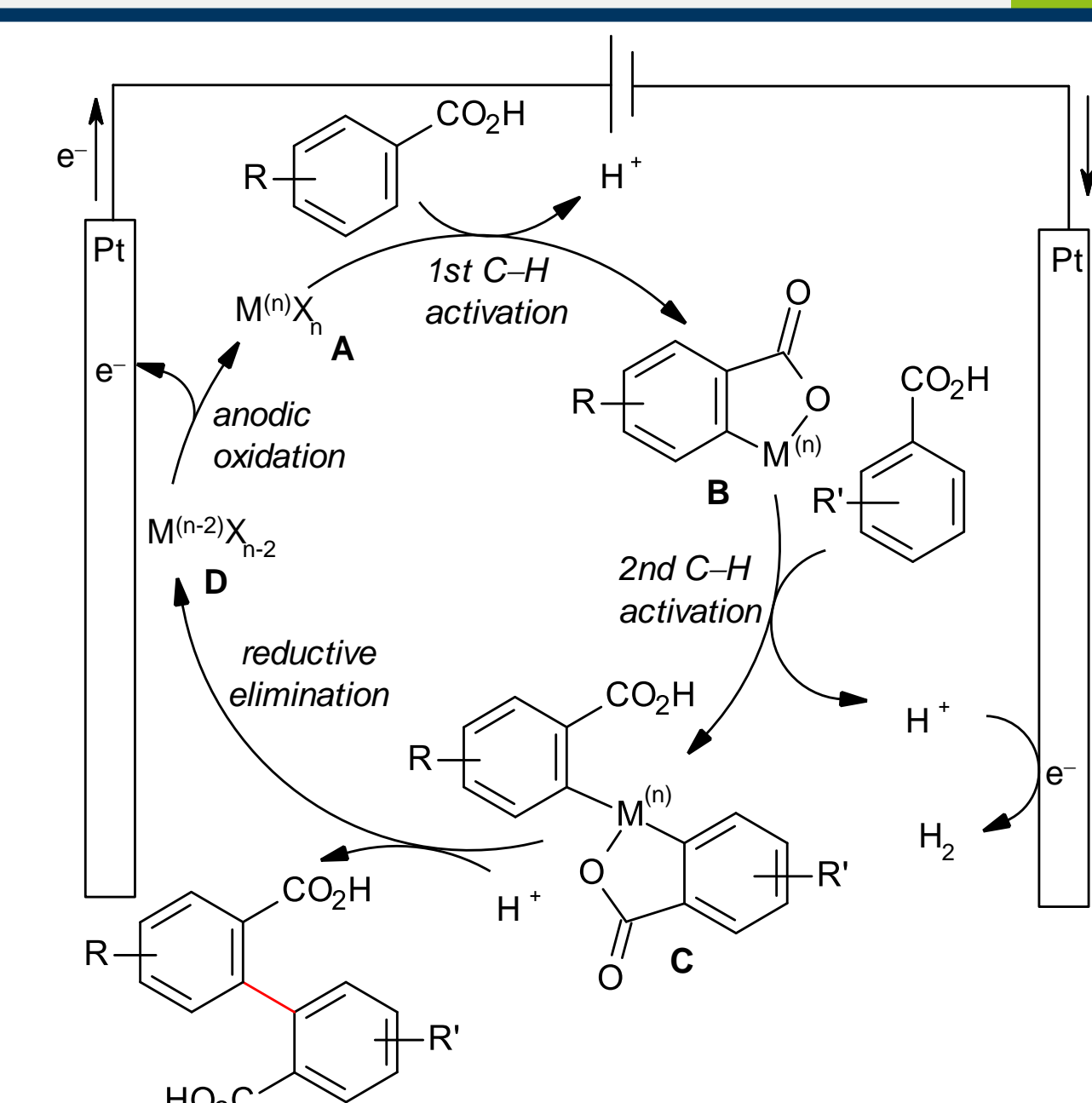
## Introduction

In chiral catalysis, bioactive compounds or functional materials, 2,2'-biaryldicarboxylates are often required as functional building blocks. However, conditions of biaryl synthesis usually require multistep prefunctionalization or wasteful oxidants.<sup>[1]</sup> The use of electricity as an inexpensive and waste-free oxidant opens new opportunities for the development of sustainable C–H biaryl syntheses.<sup>[2–4]</sup>



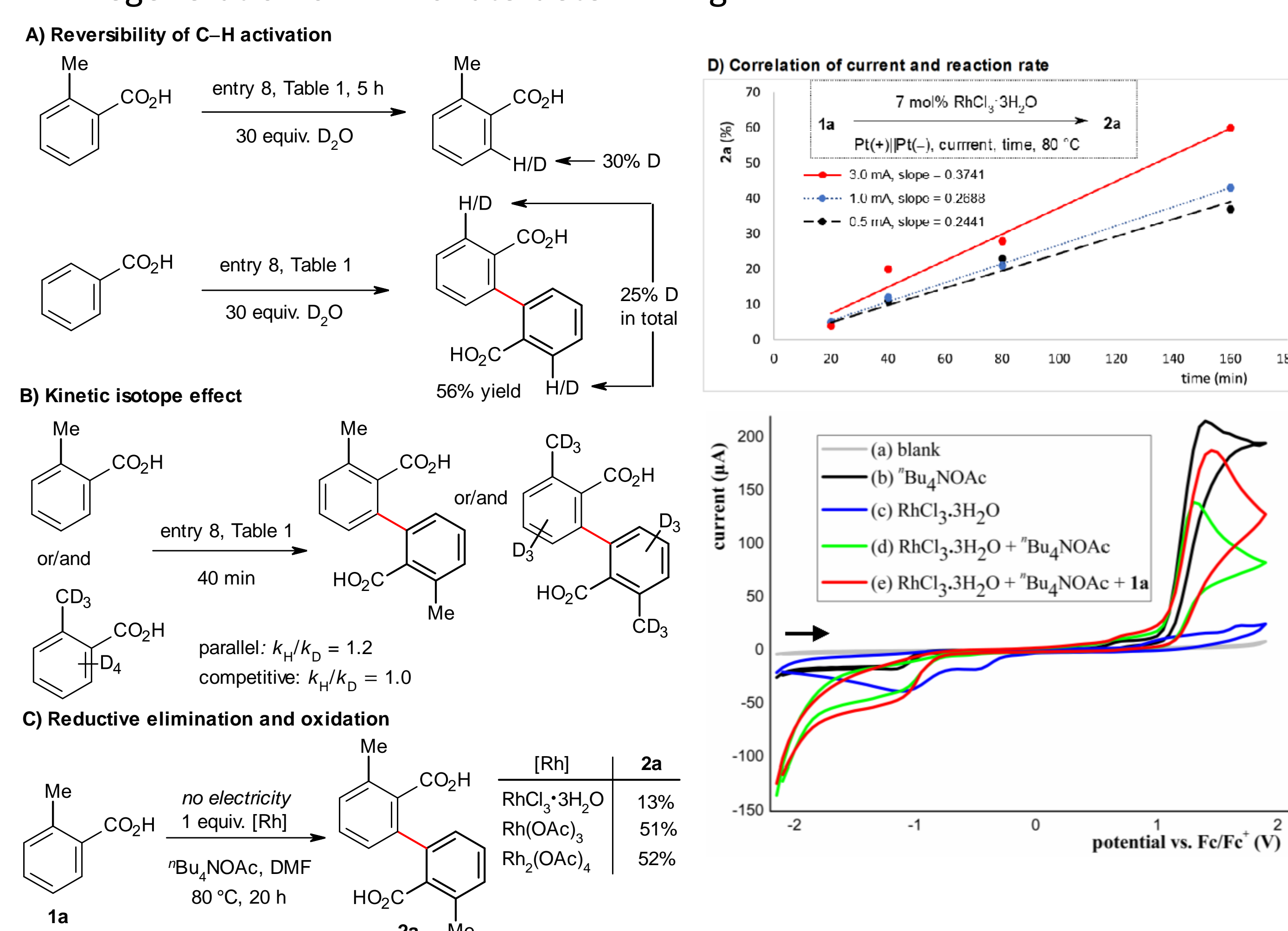
## Proposed Mechanism

- C–H /C–H activation
- Rhodium catalyst
- electricity as “green” oxidant
- valuable  $\text{H}_2$  as byproduct

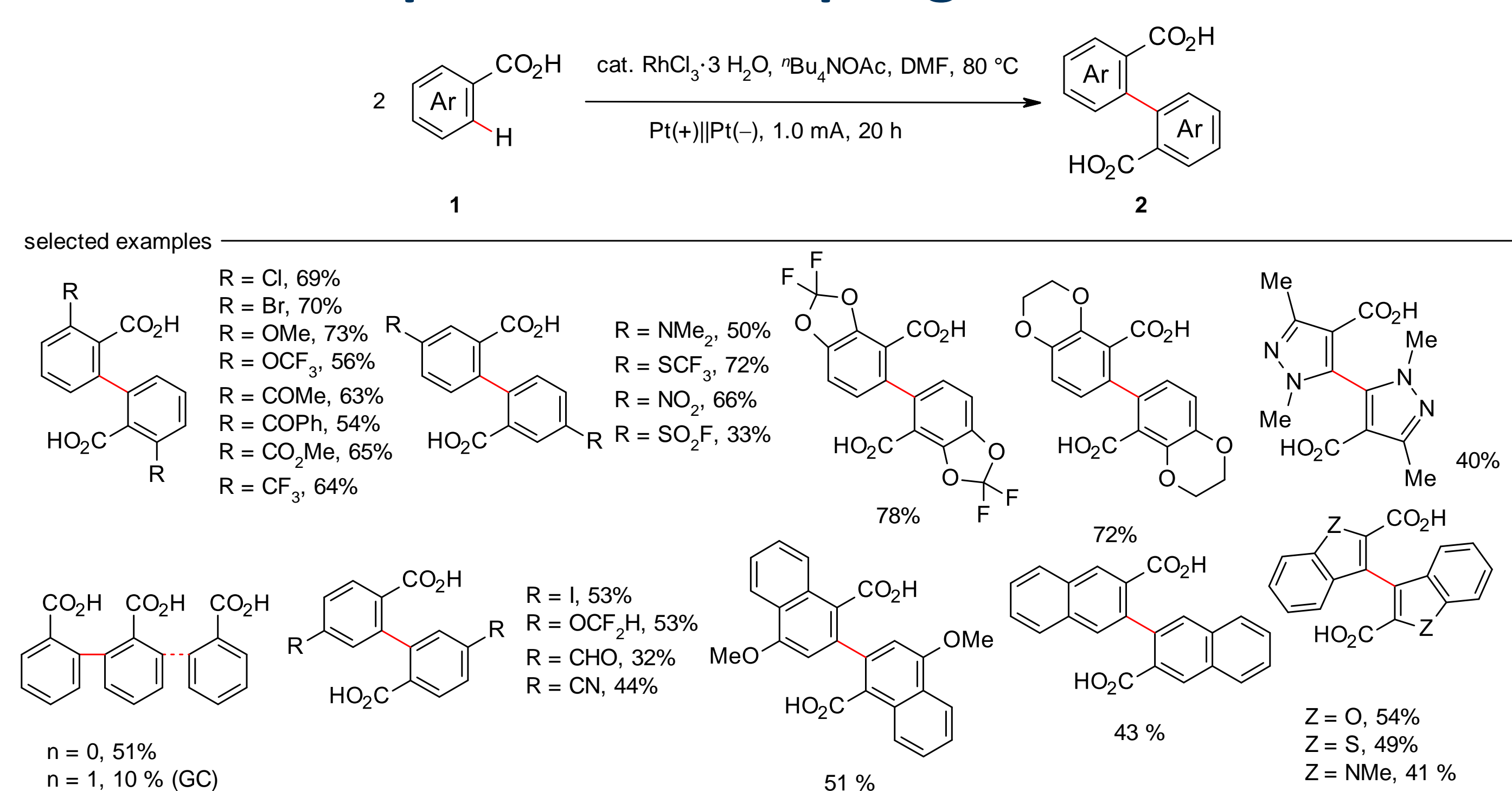


## Mechanistic Investigations

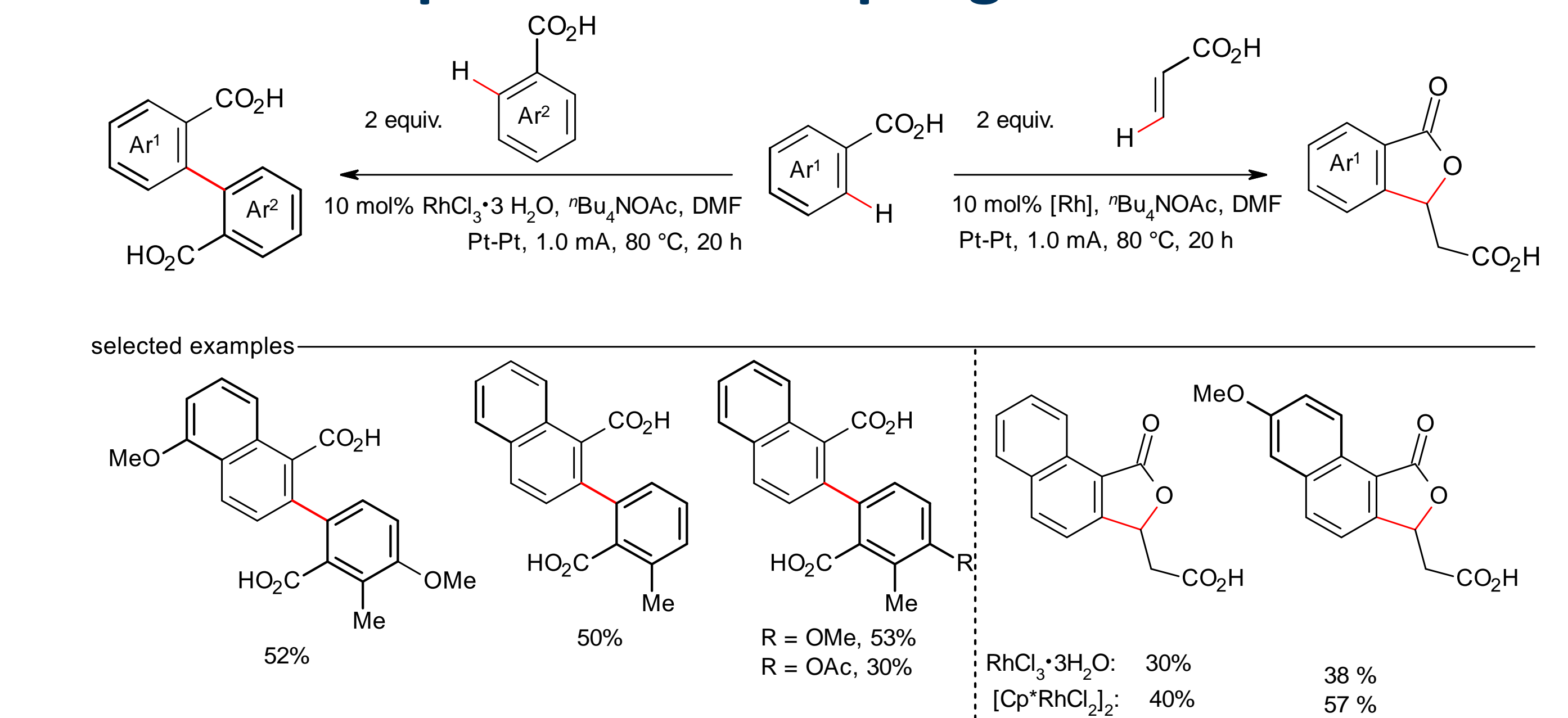
- rapid & reversible C–H metalation step
- kinetic isotope effect
- regeneration of  $\text{Rh}^{\text{III}}$  is rate-determining



## Substrate Scope – Homocoupling



## Substrate Scope – Cross-Coupling



## References

- [1] J. F. Goebel, Z. Zeng, L. J. Gooßen, *Synthesis* **2022**, *54*, 565.
- [2] Z. Zeng, J. F. Goebel, X. Liu, L. J. Gooßen, *ACS Catal.* **2021**, *11*, 6626.
- [3] C.-J. Li, *Acc. Chem. Res.* **2009**, *42*, 335.
- [4] N. Sauermann, T. H. Meyer, Y. Qiu, L. Ackermann, *ACS Catal.* **2018**, *8*, 7086.

## Conclusion

In conclusion, the newly developed electrocatalytic dehydrogenative C–H/C–H coupling allows for the formation of various biaryl dicarboxylates under mild conditions. The reaction is operationally simple and easily scalable, has an excellent functional group compatibility, and is orthogonal to common cross-coupling strategies.

We gratefully acknowledge financial support from:

