NHC-catalyzed ß-cyanation of enals via Electrochemistry

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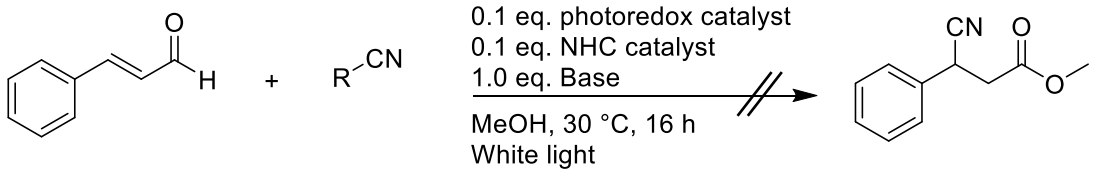
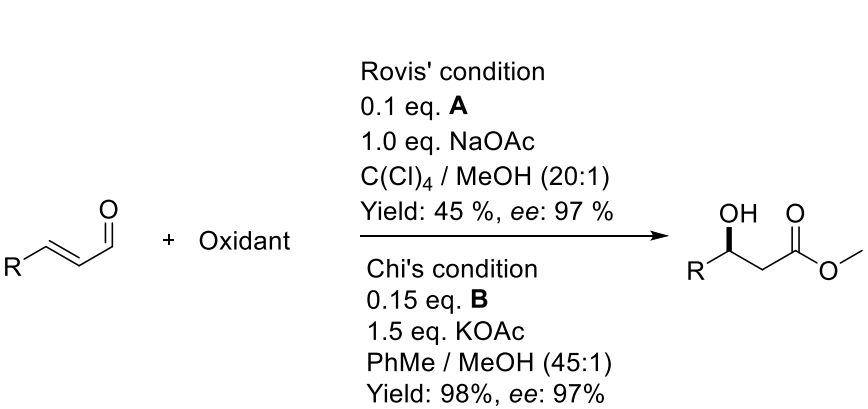
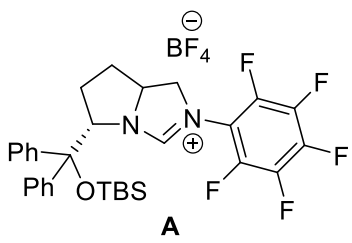
- Bachelor thesis:

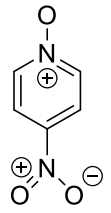


- Previous work: Enantioselective *ß*-hydroxylation of Enals

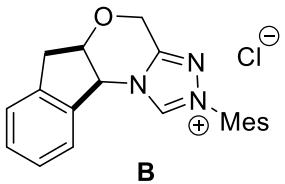




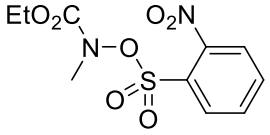
A



2a



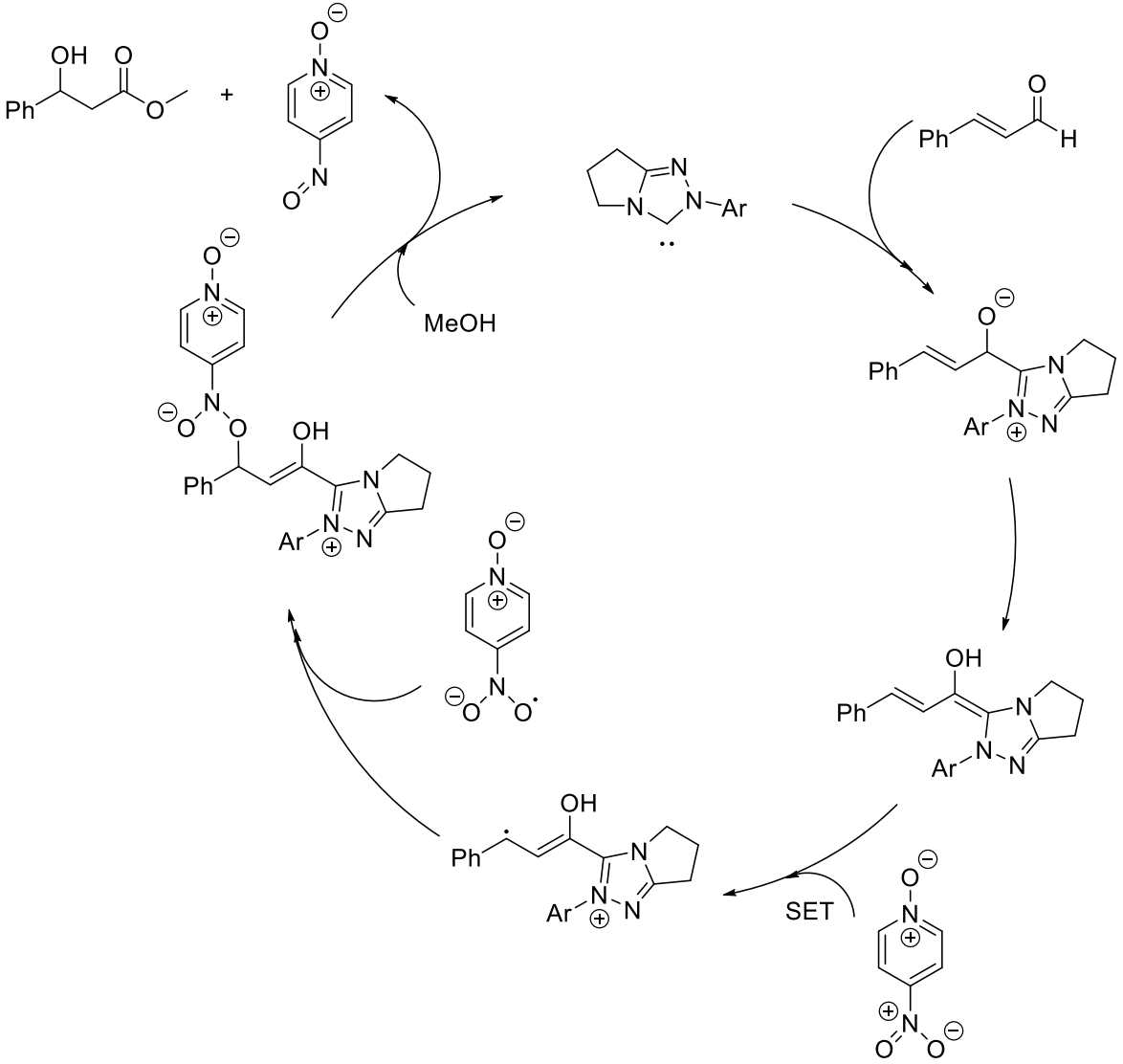
B



2b

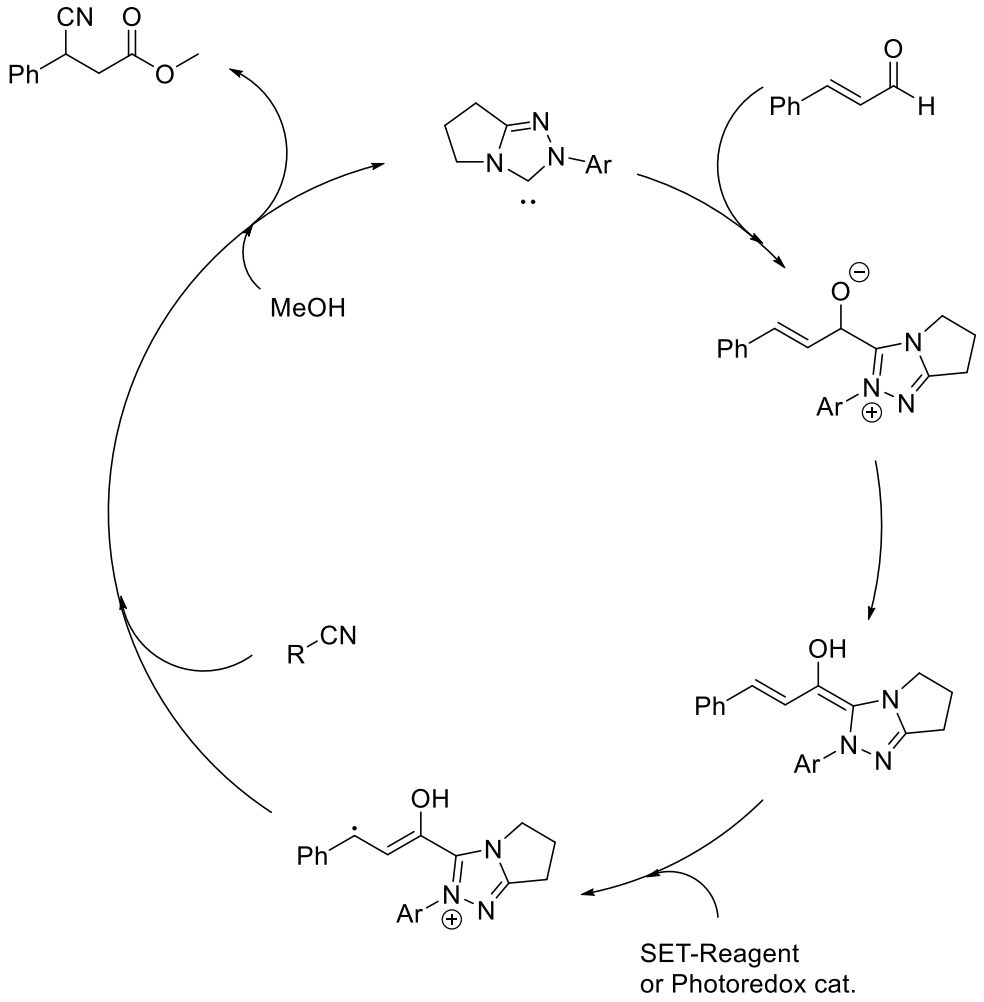
N. A. White, T. Rovis, *J. Am. Chem. Soc.,* **2014**, *136*, 14674−14677.
Y. Zhang, Y. Du, Z. Huang, J. Xu, X. Wu, Y. Wang, M. Wang, S. Yang, R. D. Webster, Y. R. Chi, *J. Am. Chem. Soc.,* **2015**, *137*, 2416−2419.

Postulated mechanism: *ß*-hydroxylation of Enals via single-electron-transfer

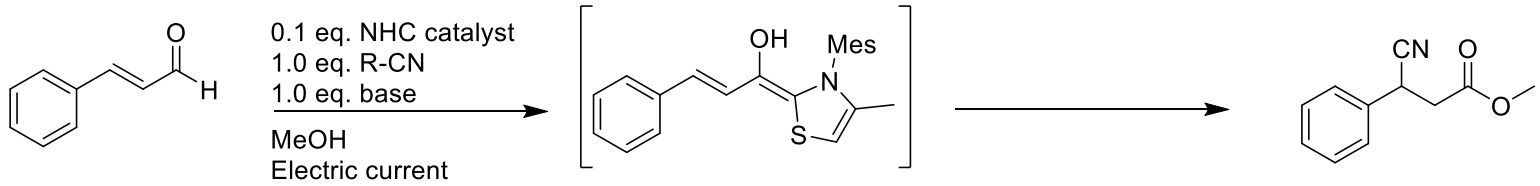


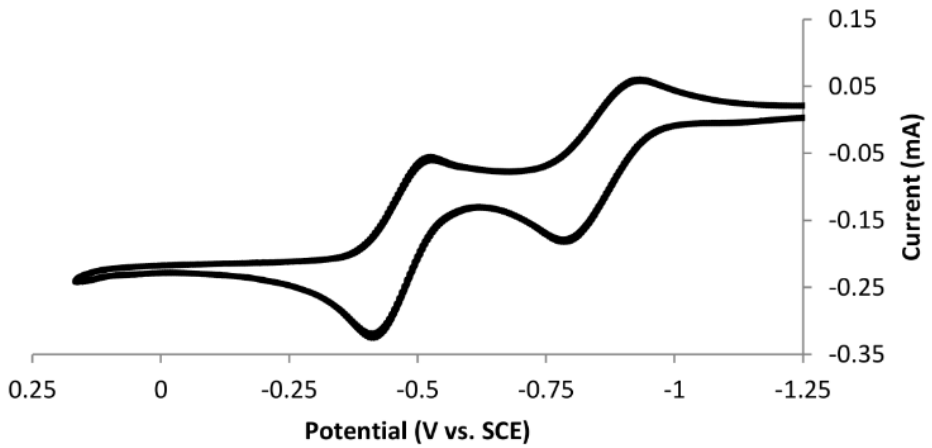
N. A. White, T. Rovis, *J. Am. Chem. Soc.,* **2014**, *136*, 14674−14677.

Working hypothesis: *ß*-cyanation of Enals via single-electron-transfer

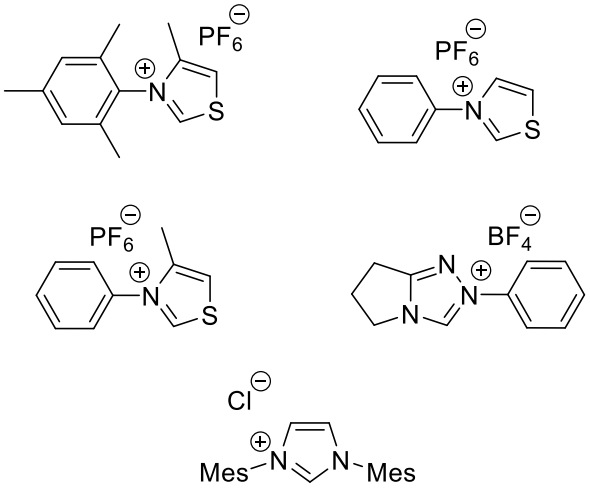


Motivation: Using electrical current to initilize the single electron transfer



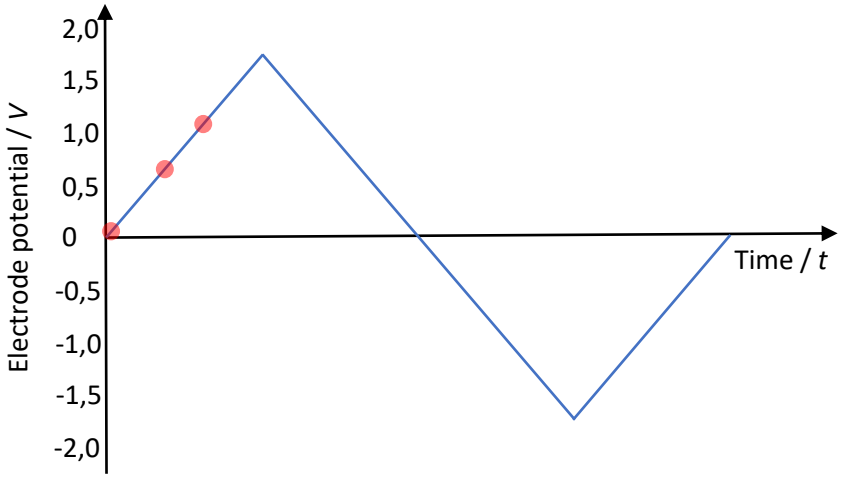


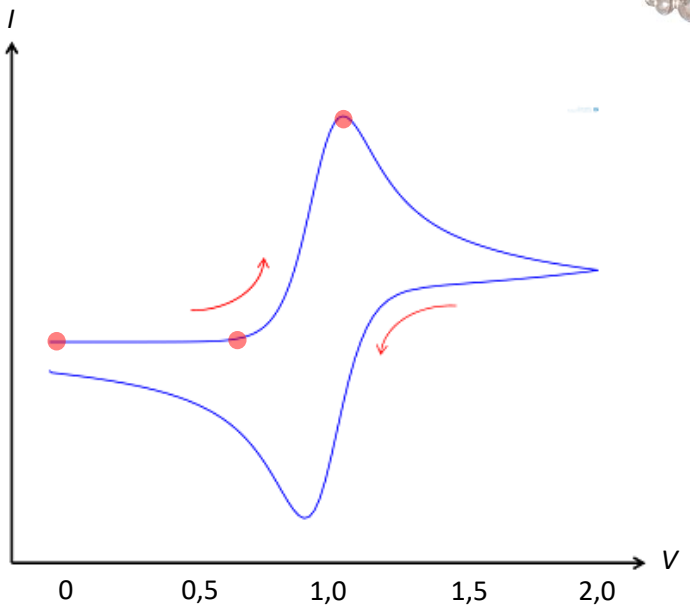
- Different NHC-catalysts to modify the required voltage

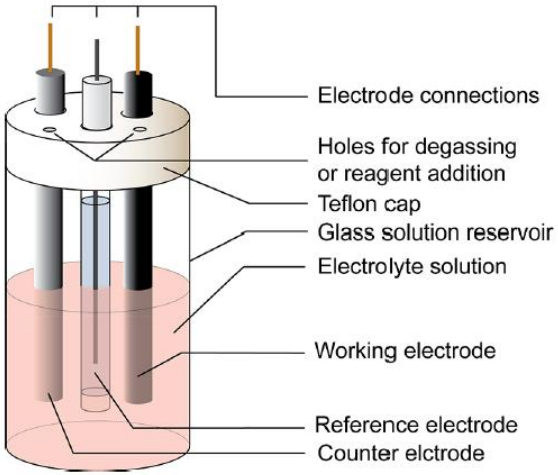


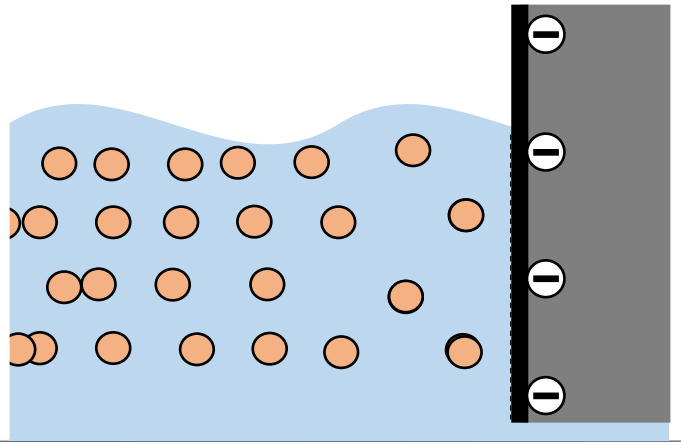
E. E. Finney, K. A. Ogawa, A. J. Boydston, *J. Am. Chem. Soc.,* **2012**, *134*, 12374–12377

Cyclic Voltammetry – The „duck-shape“





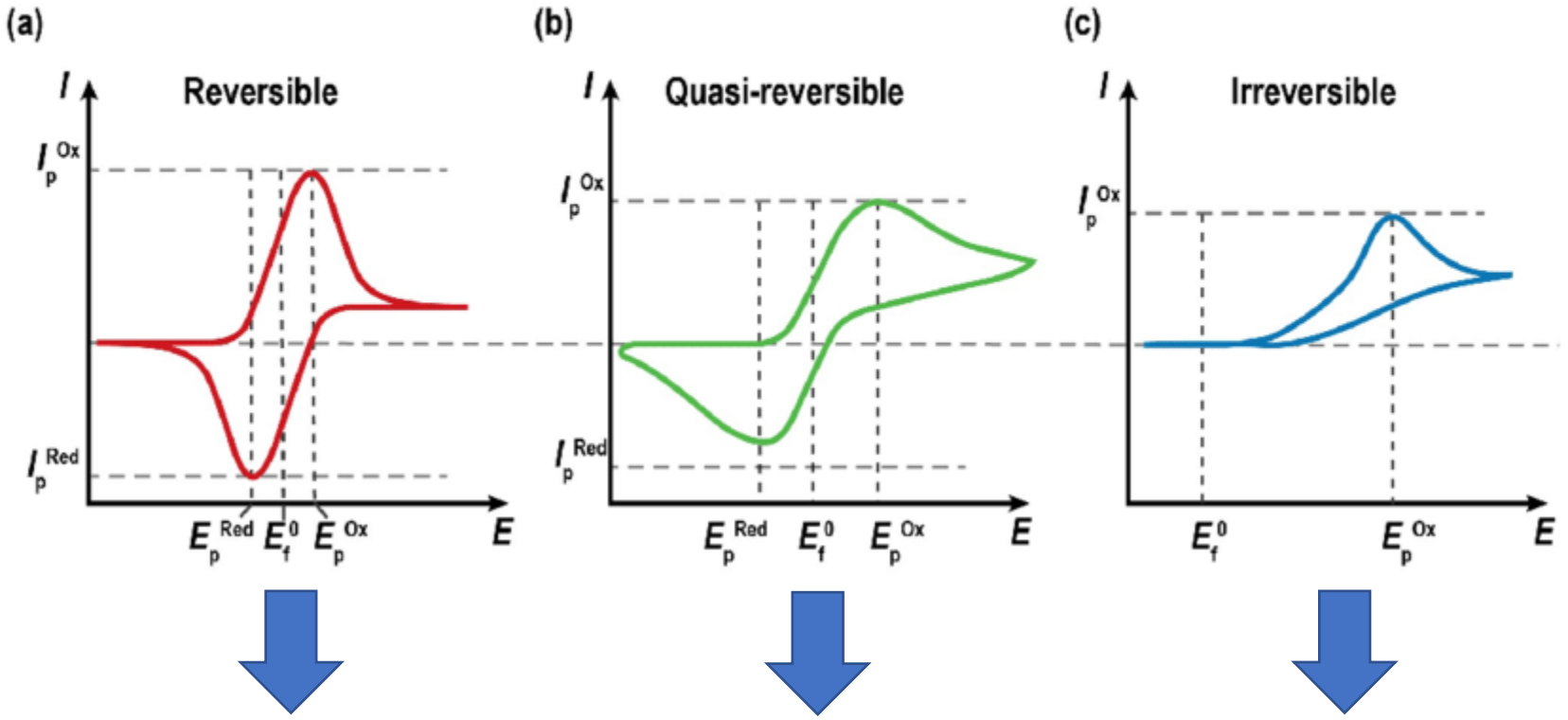




T. Kissinger, W. R. Heineman, *J. Chem. Educ.* **1983**, *60*, 702 – 706.

J. Heinze, *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 831 – 918.

N. Elgrishi, K. J. Rountree, B. D. McCarthy, E. S. Rountree, T. T. Eisenhart, J. L. Dempsey, *J. Chem. Educ.* **2018**, *95*, 197 – 206.



- Peak to Peak seperation: 57 mV

- Peak to Peak seperation: >57 mV
- May change with scan rate

- Only one Peak visible

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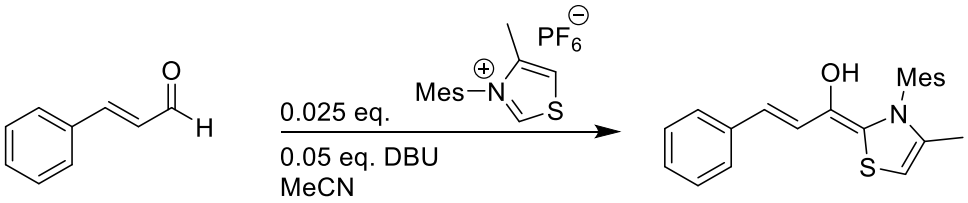
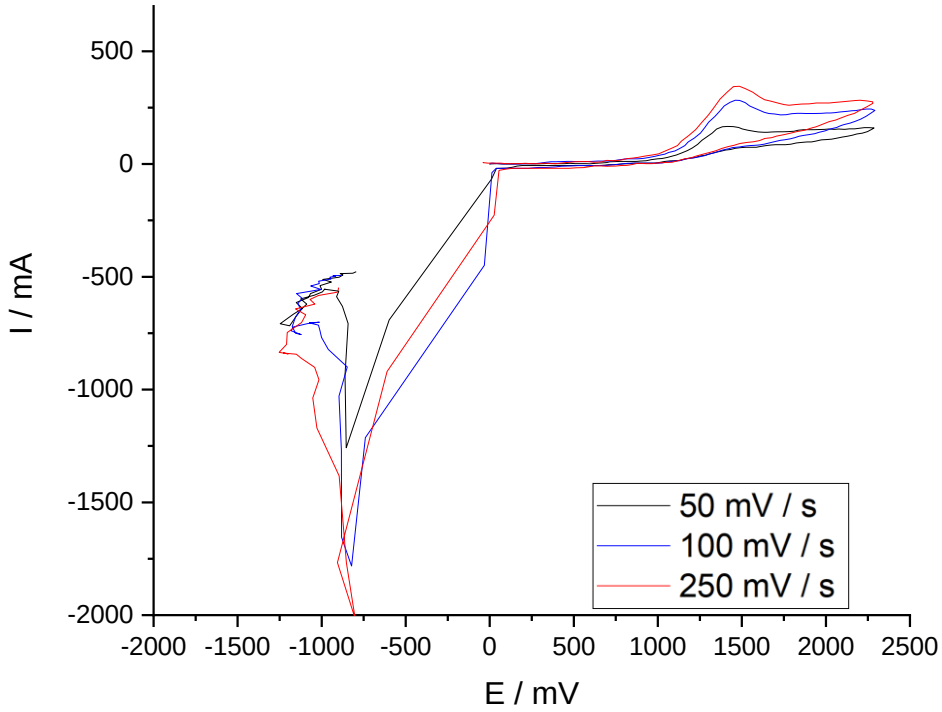
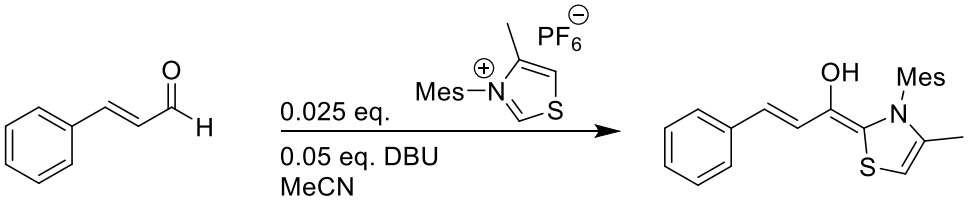
Cyclic Voltammetry: In situ investigation of breslow intermediat

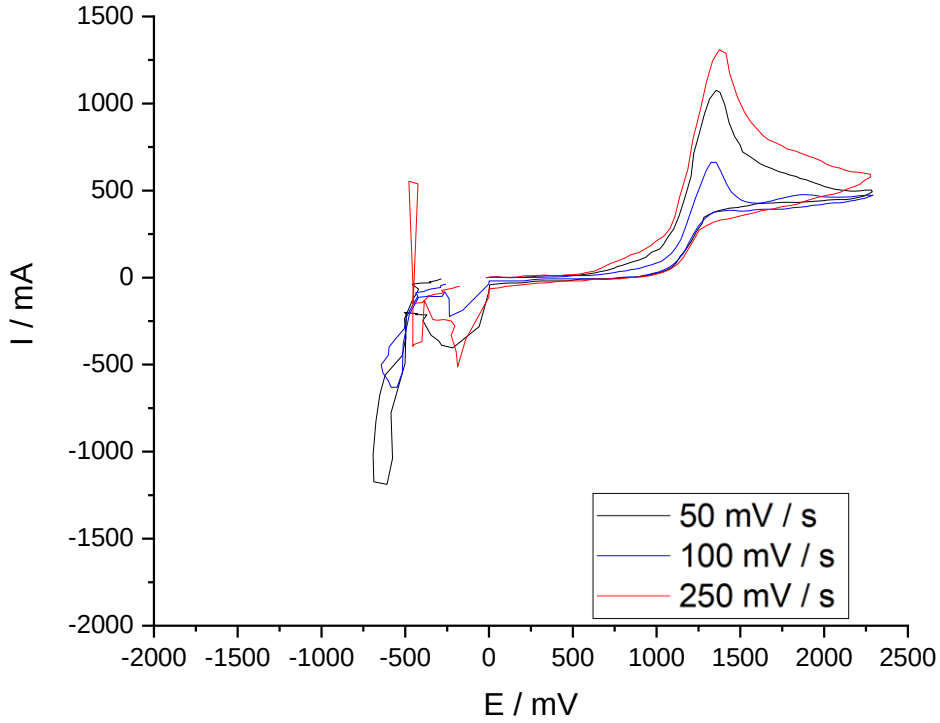




Data was recorded using 0.1 M TBA[PF_6] as Electrolyte and 0.25 M aldehyde. Potentials are reported against Ag/AgCl reference electrode

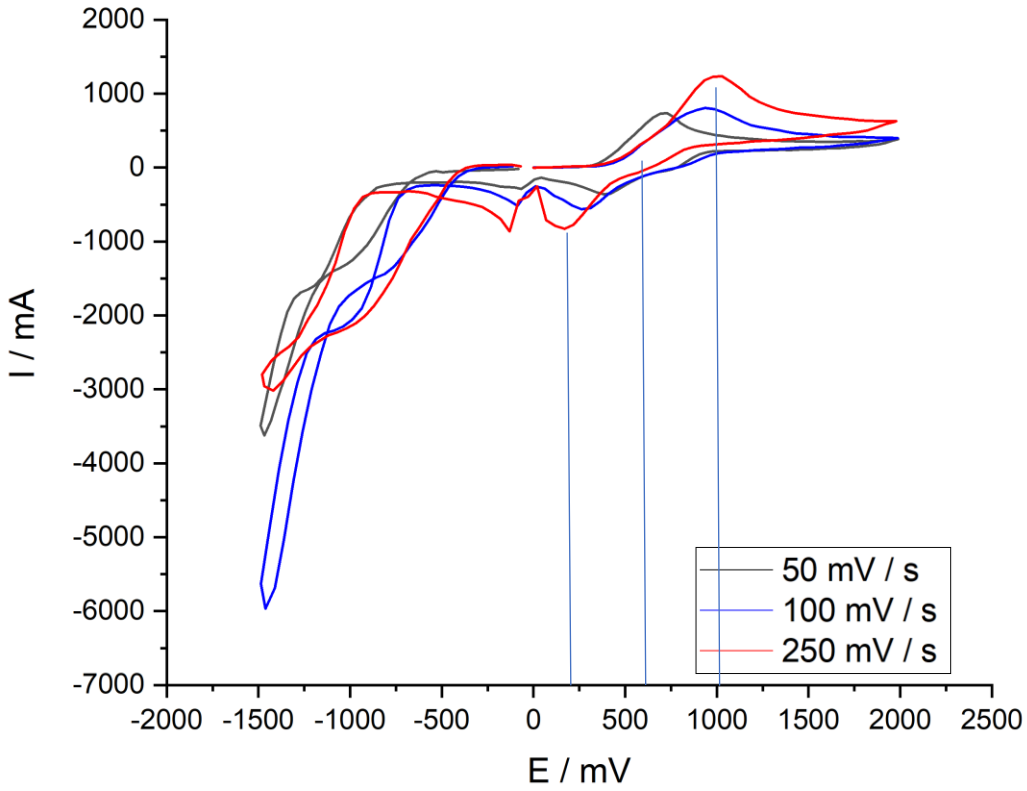
Cyclic Voltammetry: Replacing the Ag/AgCl reference electrode with $Ag/AgNO_3$





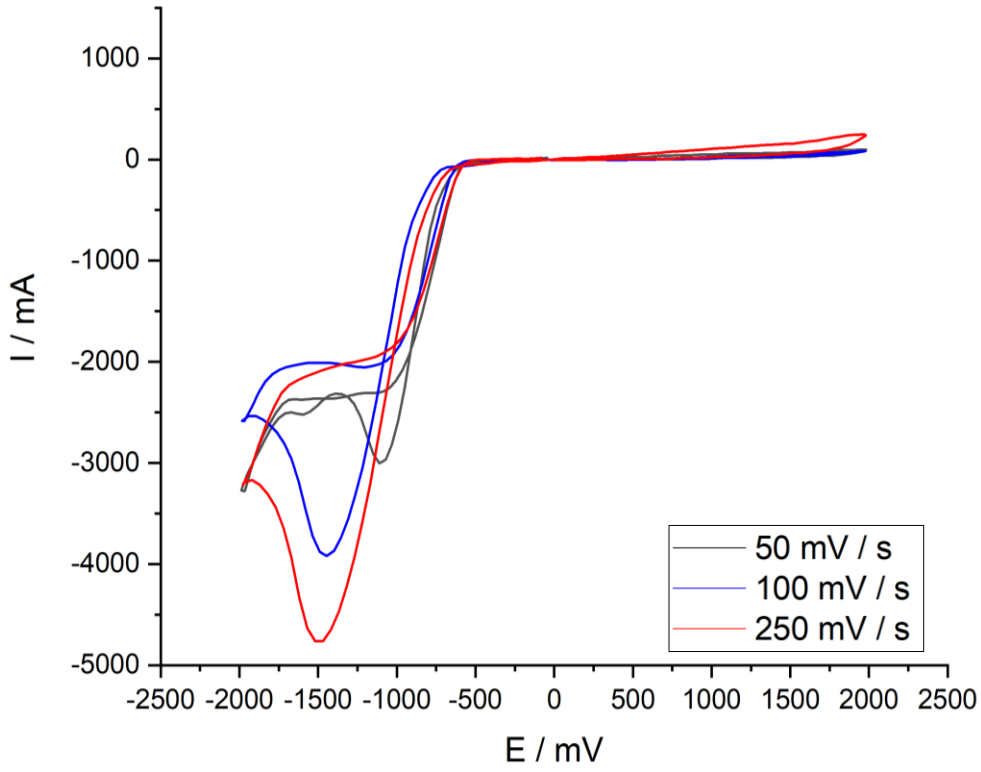
Data was recorded using 0.1 M TBA[PF_6] as Electrolyte and 0.25 M aldehyde. Potentials are reported against $Ag/AgNO_3$ reference electrode

- Meassuring ferrocene as reference sample: Peak to Peak seperation: 850 mV
  E_p^{Fc/Fc^+} = 620 mV



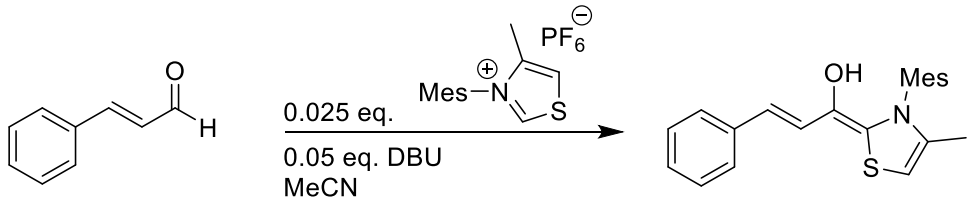
Data was recorded using 0.1 M TBA[PF_6] as Electrolyte and 0.25 M ferrocene. Potentials are reported against Ag/$AgNO_3$ reference electrode

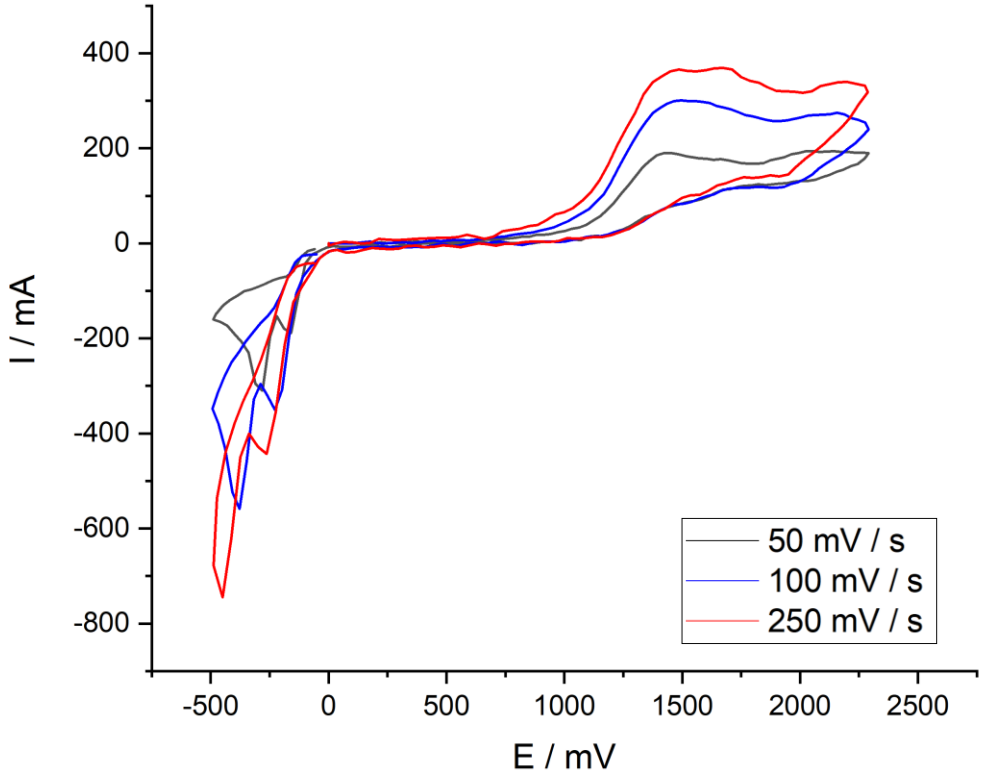
- Meassuring no sample at all!



Data was recorded using 0.1 M TBA[PF_6] as Electrolyte. Potentials are reported against Ag/$AgNO_3$ reference electrode

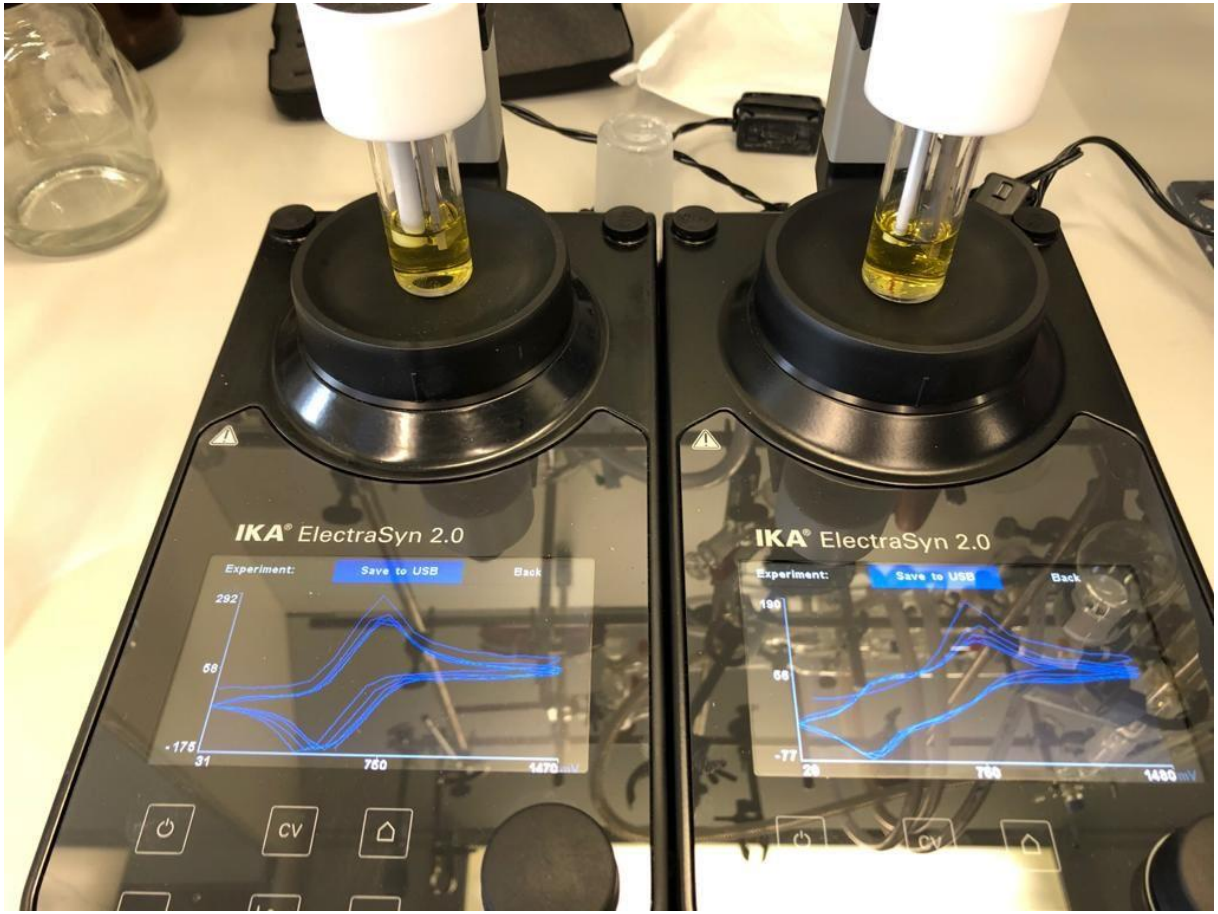
Cyclic Voltammetry: „Optimized conditions“ and 10 times higher sample amount.





Data was recorded using 0.1 M TBA[PF_6] as Electrolyte and 2.5 M aldehyde. Potentials are reported against Ag/$AgNO_3$ reference electrode

Cyclic Voltammetry – Comparing devices



Acknowledgement

- Prof. Dr. Peter R. Schreiner, PhD
- Frederik R. Erb
- Analytical department
- The whole PRS-Group!!