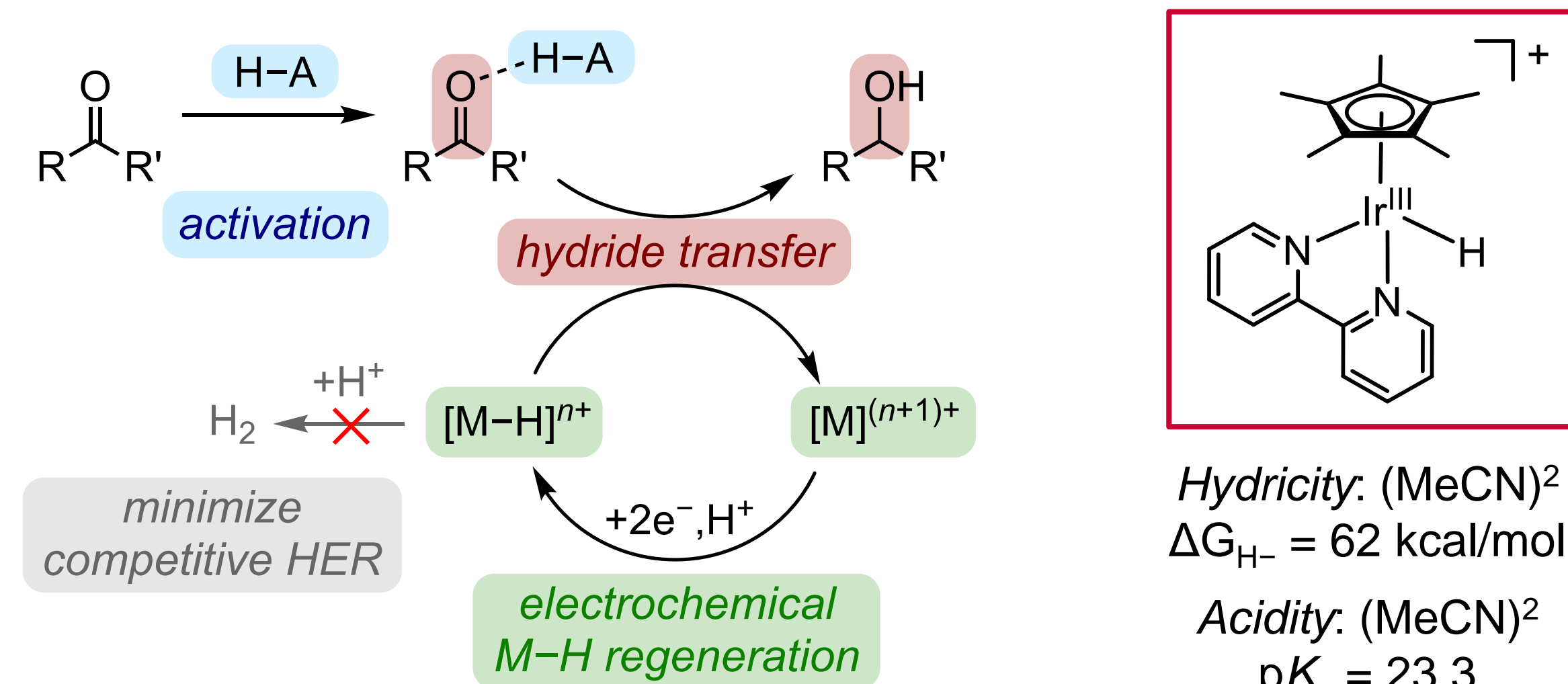




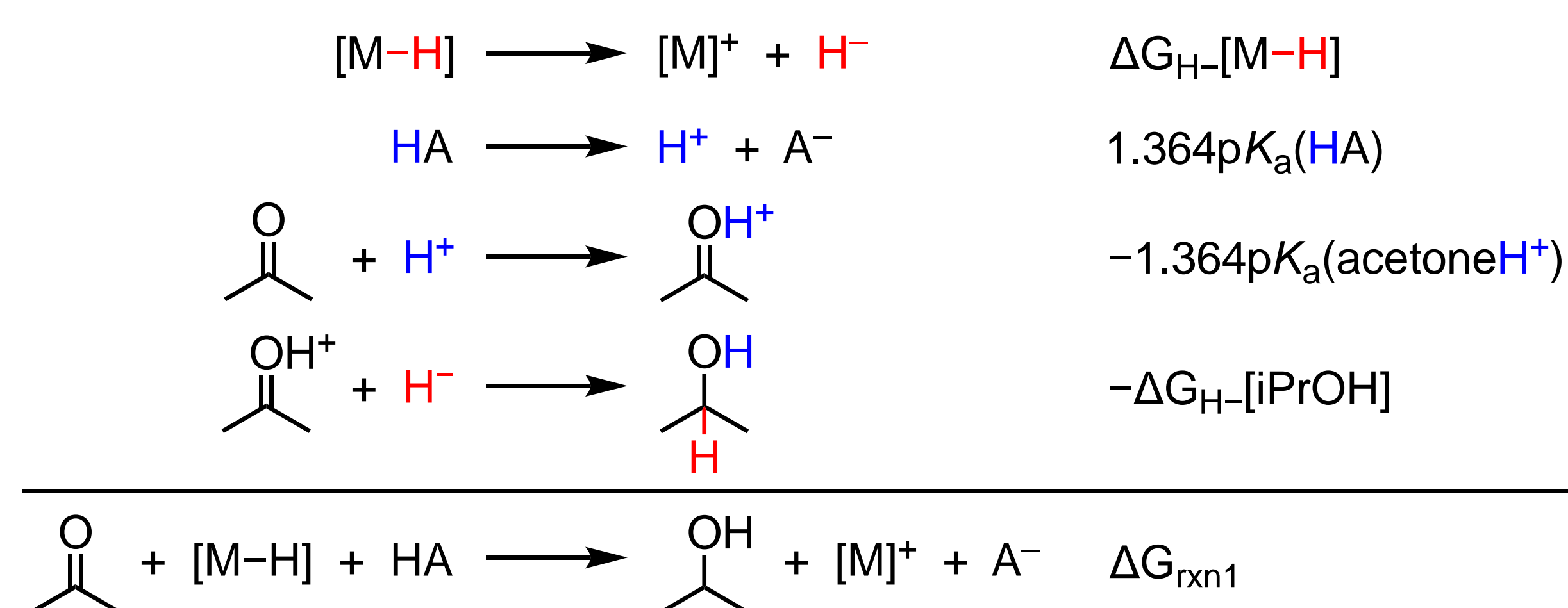
## Introduction and Motivation

Biomass is a renewable carbon source from which bio-oil can be produced via pyrolysis for sustainable fuel production. However, raw bio-oil must be upgraded to improve its shelf life for storage and transportation, as the presence of small carbonyl compounds leads to condensation and polymerization reactions that contribute to its chemical instability.<sup>1</sup> We aim to upgrade raw bio-oil by directly integrating renewable energy into electrochemical ionic hydrogenation using metal-hydride catalysts.



## Using Thermodynamics as a Guide

The favorability of carbonyl ionic hydrogenation is governed by hydricity ( $\Delta G_{H-}$ ) of the metal-hydride and the  $pK_a$  of the Bronsted acid.<sup>3,4</sup>

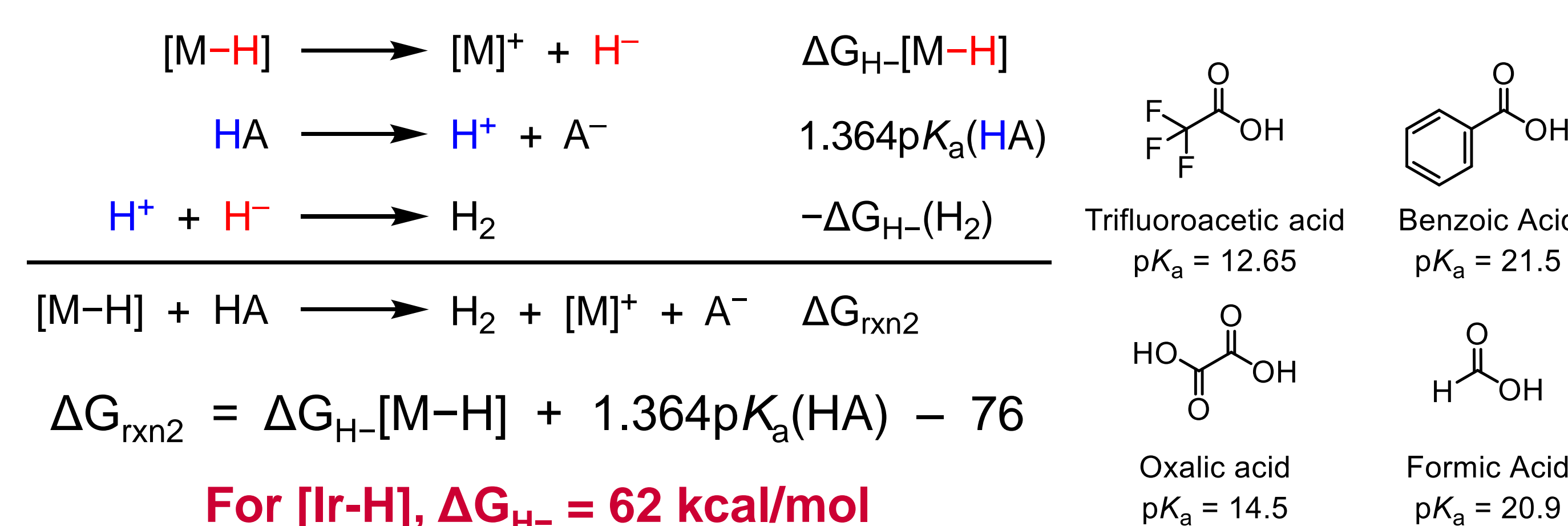


$$\Delta G_{rxn1} = \Delta G_{H-}[M-H] + 1.364pK_a(HA) - 88$$

For [Ir-H],  $\Delta G_{H-} = 62 \text{ kcal/mol}$

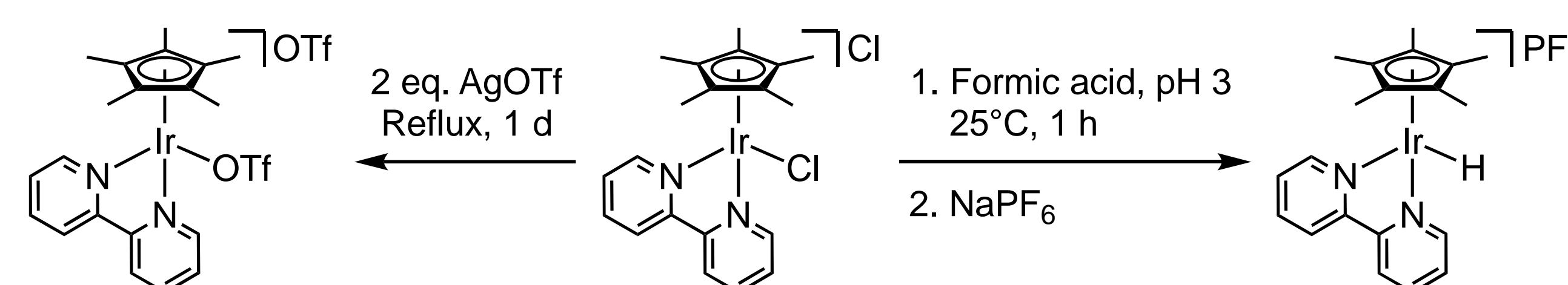
$\therefore pK_a(HA) < 19$  to favor hydrogenation

To avoid the competitive formation of H<sub>2</sub> gas, protonation of the [Ir-H] by the Bronsted acid must be thermodynamically unfavorable.<sup>2,3</sup>

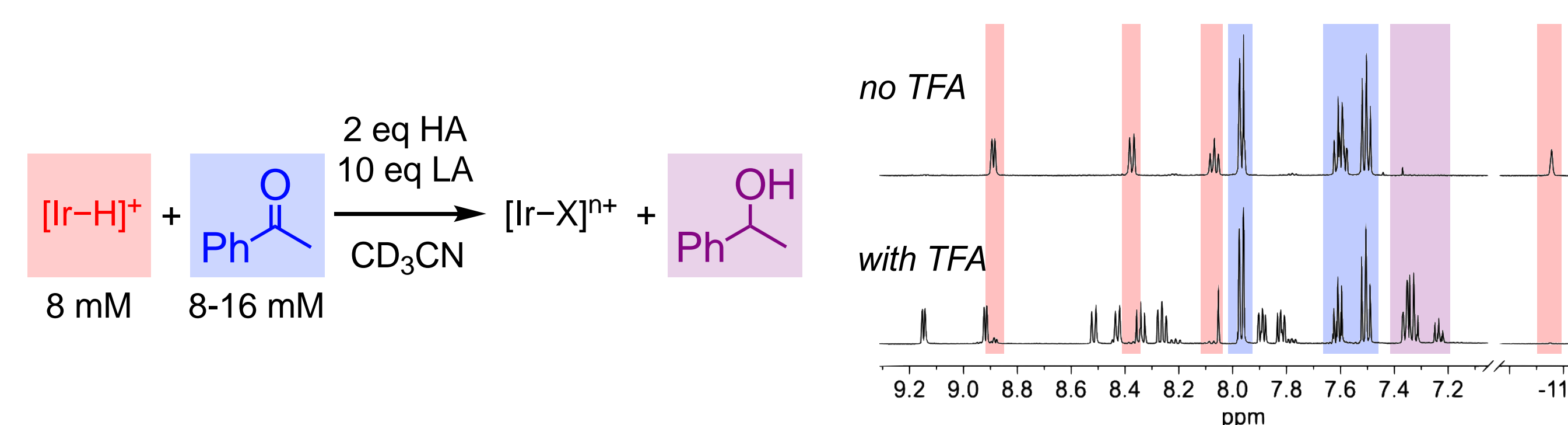


## Synthesis of Iridium Complexes<sup>5-7</sup>

The Ir-hydride complex is readily obtained from the Ir-chloride precursor. We have also prepared an Ir-triflate complex, which is converted into the Ir-MeCN species in acetonitrile solution (see below).

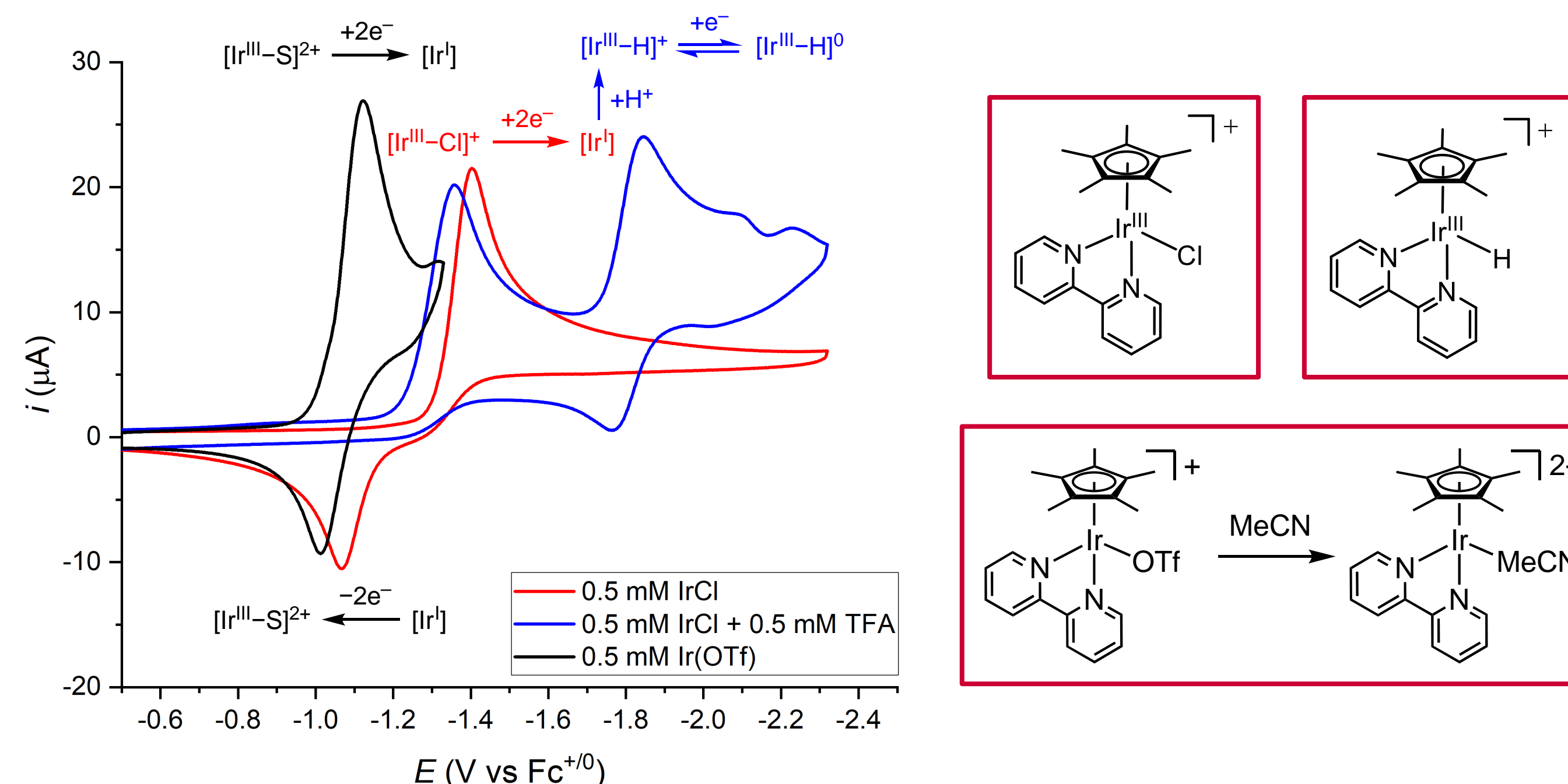


## Stoichiometric Reactivity Screening



LA	HA	[HA] (mM)	Time	[IrH] Conv. (%)	Alcohol Yield (%)
None	TFA	15	1 d	89	84
Zn(OTf) <sub>2</sub>	TFA	20	< 10 min	100	87
Zn(OTf) <sub>2</sub>	Oxalic	165	< 1 h	100	62
Zn(OTf) <sub>2</sub>	Benzoic	98	< 1 h	100	54
LiBF <sub>4</sub>	TFA	15	1 d	85	83
Mg(OTf) <sub>2</sub>	TFA	15	1 d	68	58
Ca(OTf) <sub>2</sub>	TFA	15	< 3 h	100	70
Ba(OTf) <sub>2</sub>	TFA	15	< 2 d	100	80
Sc(OTf) <sub>3</sub>	-	15	-	LA reacts directly with Ir-H	-
La(OTf) <sub>3</sub>	-	15	-	LA reacts directly with Ir-H	-
Al(OTf) <sub>3</sub>	-	15	-	LA reacts directly with Ir-H	-

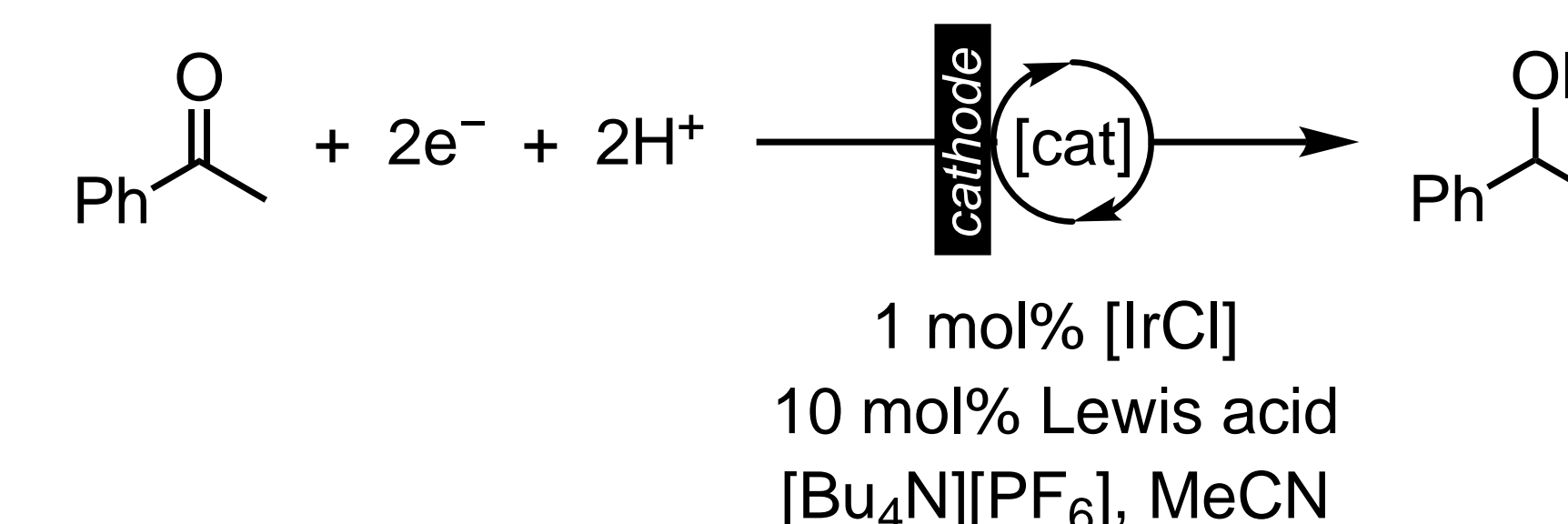
## Cyclic Voltammetry (CV) Studies



Conditions: 0.1 M TBAPF<sub>6</sub> in MeCN, glassy carbon WE, Ag/AgNO<sub>3</sub> RE, Pt wire CE

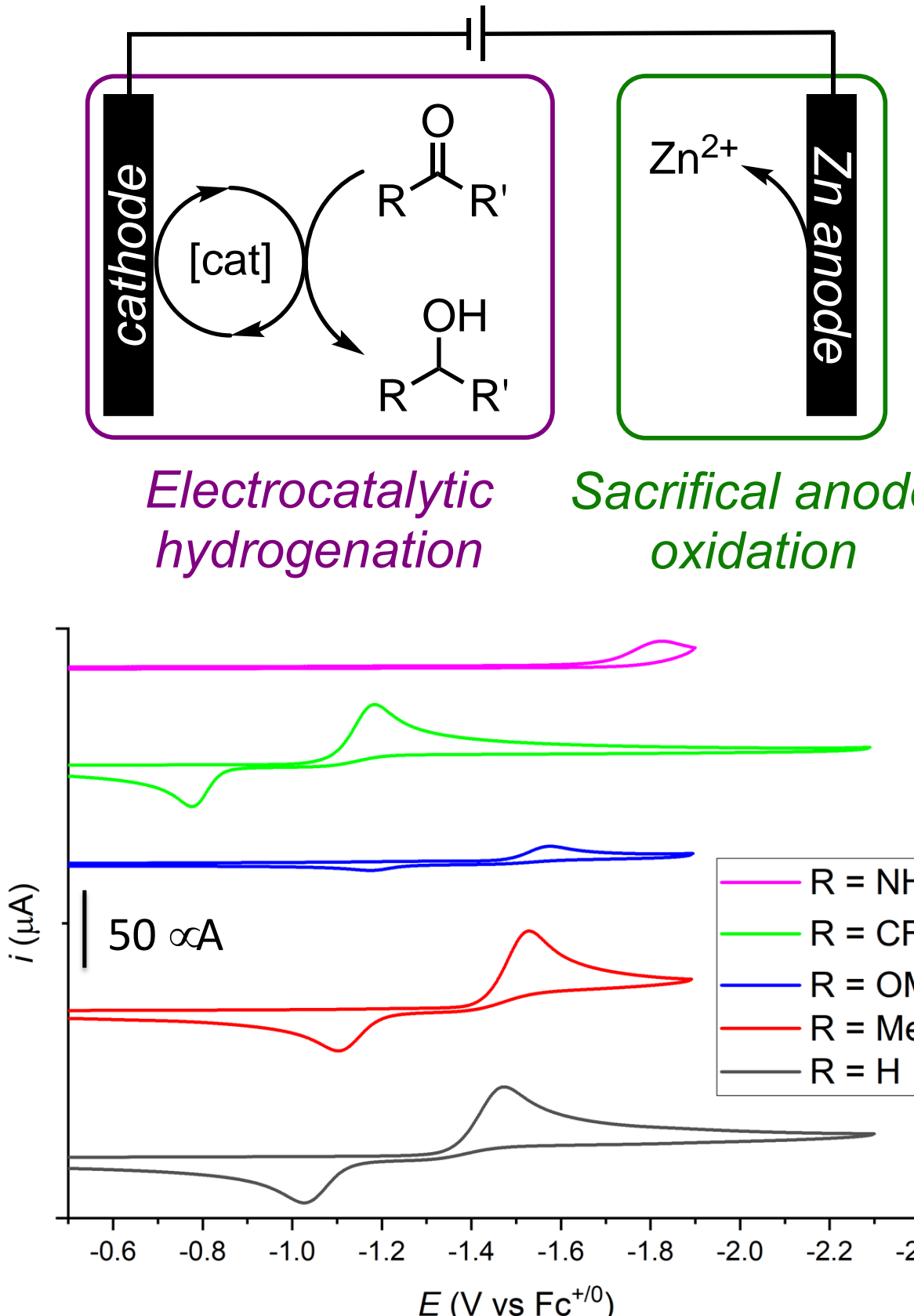
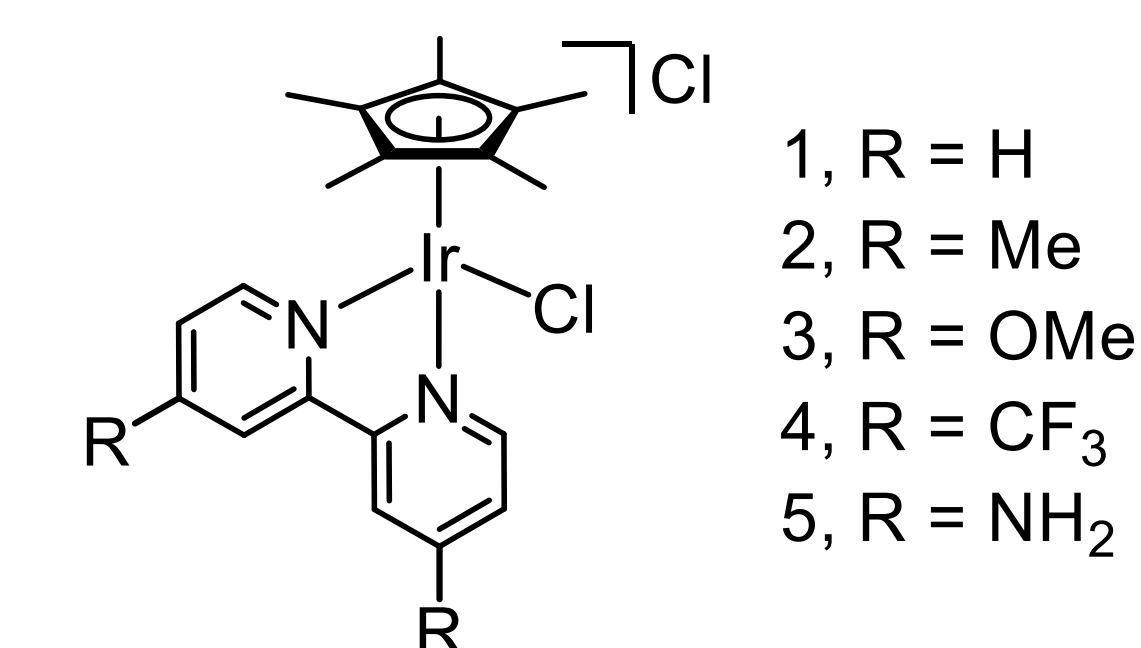
## Controlled Potential Electrolysis (CPE)

By CV, the Ir-hydride can be generated by 2e<sup>-</sup>/1H<sup>+</sup> reduction of the Ir-chloride or triflate at mild potentials. We are now using CPE to evaluate the electrocatalytic activity of this system for acetophenone reduction.<sup>8</sup> Stronger Brønsted acids result in significant H<sub>2</sub> evolution at the electrode surface. The combination of Lewis acids with milder Brønsted acids is promising for obtaining higher faradaic efficiencies.



LA	HA	[HA] (M)	E <sub>app</sub> (V)	Time (h)	Alcohol Yield (%)	FE <sub>alcohol</sub> (%)
None	TFA	1.0	-1.01	21	60	10
Zn(OTf) <sub>2</sub>	Benzoic	0.5	-1.01	3.5	18	54
Zn(OTf) <sub>2</sub>	Formic	0.5	-1.15	2.5	4.1	3.7

We are optimizing CPE conditions to achieve high conversion and faradic efficiency. Challenges include Zn metal plating at the cathode, poor solubility of zinc carboxylate salts in acetonitrile, and competitive HER. We are testing the Ir-triflate precatalyst with other Brønsted acids and electrode materials, and exploring catalyst modifications:



## References & Acknowledgements

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We thank Rutgers University and the National Science Foundation (CHE-2247645) for support of this project.

