



# Highly Efficient and Selective Ruthenium Catalysts for the Synthesis of Enol Esters from Carboxylic Acids and Alkynes

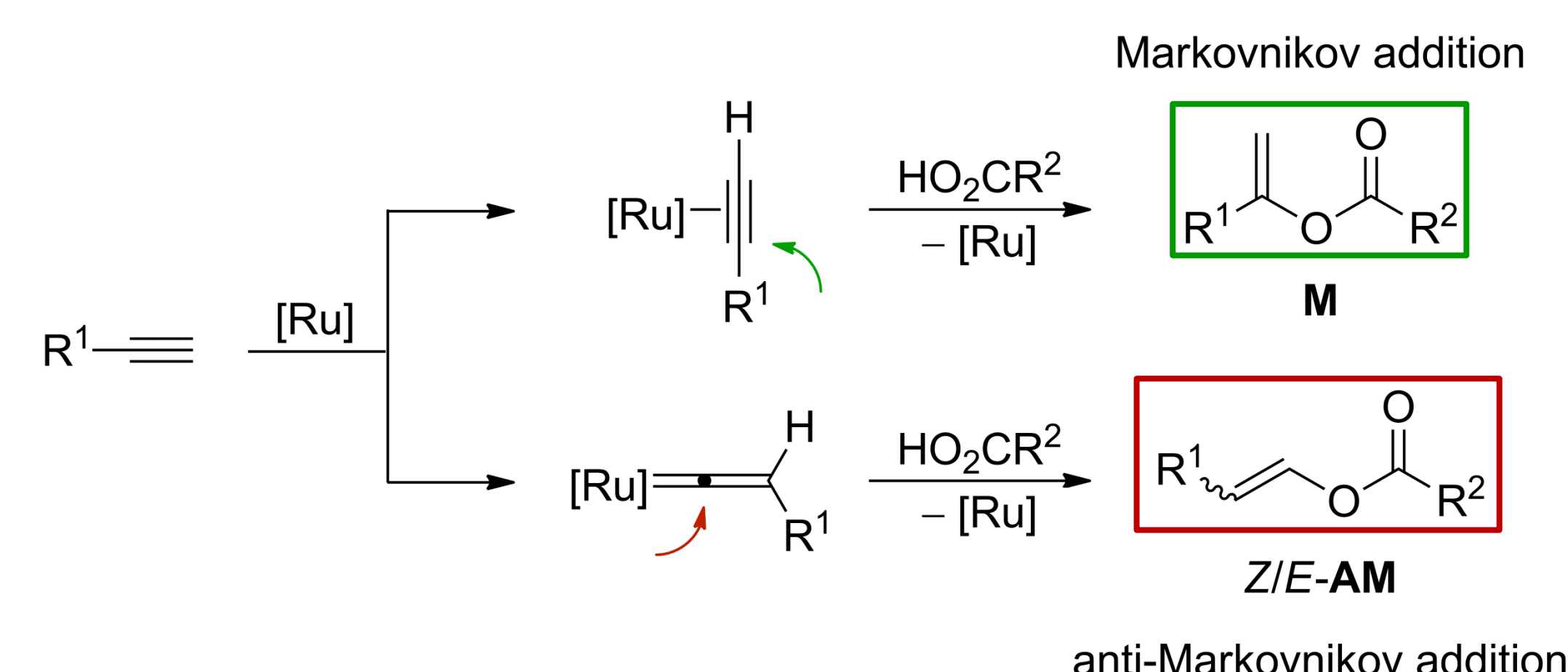
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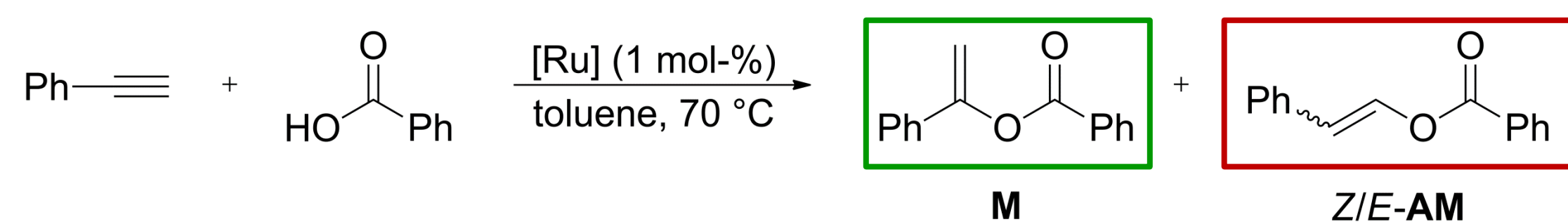
## Motivation

Enol esters are important monomers in olefin polymerization<sup>[1]</sup> (e.g. vinyl acetate) and intermediates in organic synthesis.<sup>[2,3]</sup> Since the first reports on the atom-economical Ru-catalyzed addition of carboxylic acids to alkynes in the 1980s<sup>[4-6]</sup>, a variety of Ru-catalysts has been developed.<sup>[7-9]</sup> Depending on the tautomerization between  $\eta^2$ -alkyne and vinylidene binding mode the Ru-catalyst either promotes the Markovnikov or anti-Markovnikov addition.<sup>[10,11]</sup> However, there are only few examples of catalysts that selectively promote the formation of the Markovnikov products.

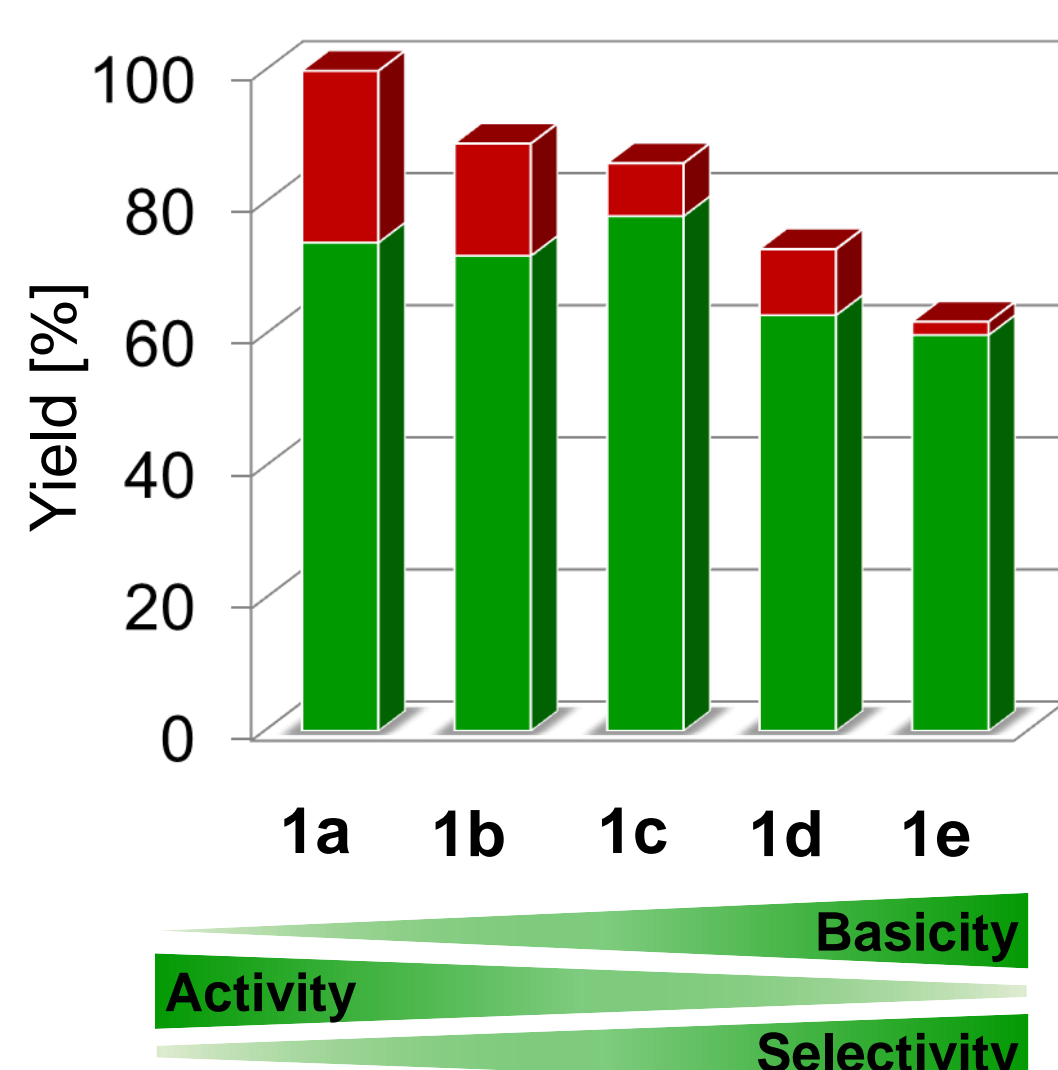
We present the application of Ru-complexes of type  $[\text{Ru}(\text{CO})_2(\text{P}(\text{p-C}_6\text{H}_4\text{-X})_3)_2(\text{O}_2\text{CPh})_2]$  (**1a**, X = CF<sub>3</sub>; **1b**, X = Cl; **1c**, X = H; **1d**, X = Me; **1e**, X = OMe) in the catalytic formation of enol esters under mild reaction conditions. These complexes have already demonstrated their suitability to selectively favor the Markovnikov products in the related synthesis of  $\beta$ -oxo esters by addition of carboxylic acids to propargylic alcohols.<sup>[12]</sup>



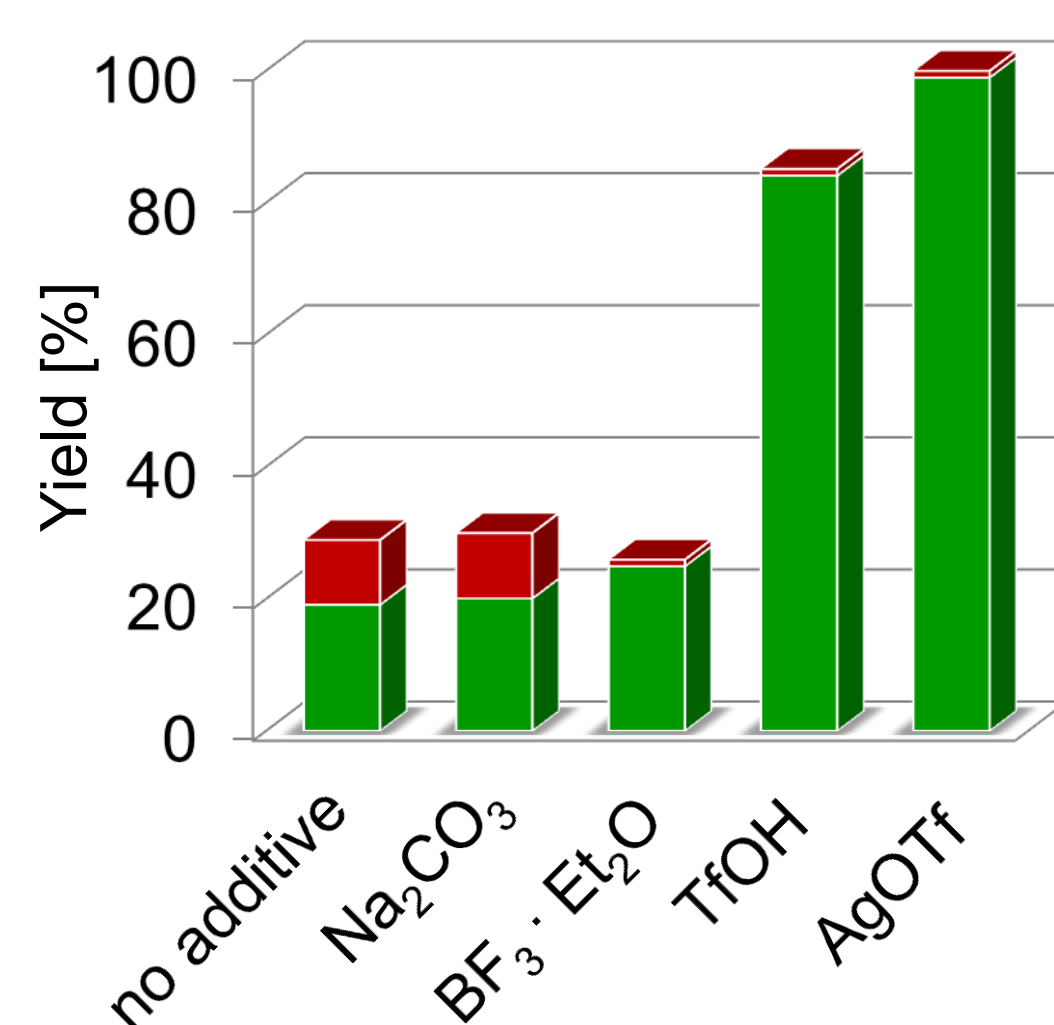
## Catalyst Screening & Optimization



### Catalyst Screening



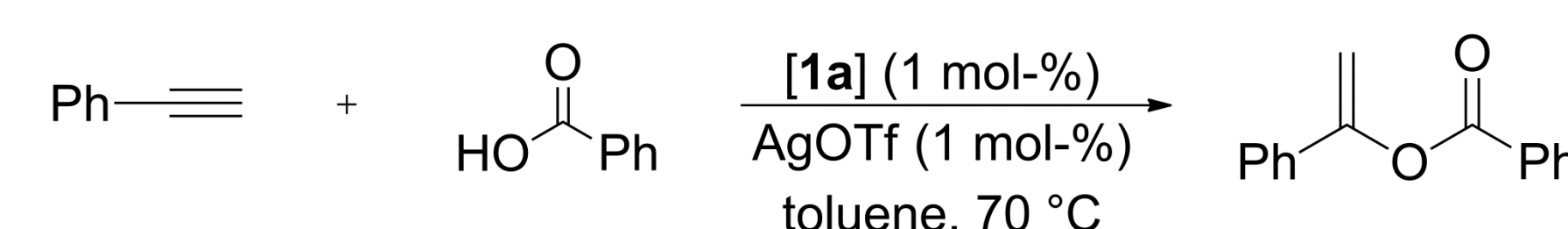
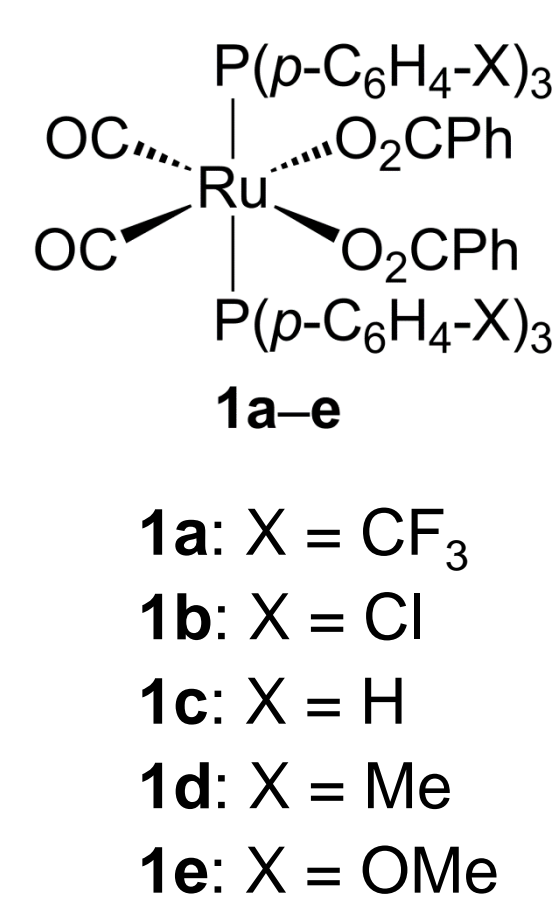
### Influence of Additives



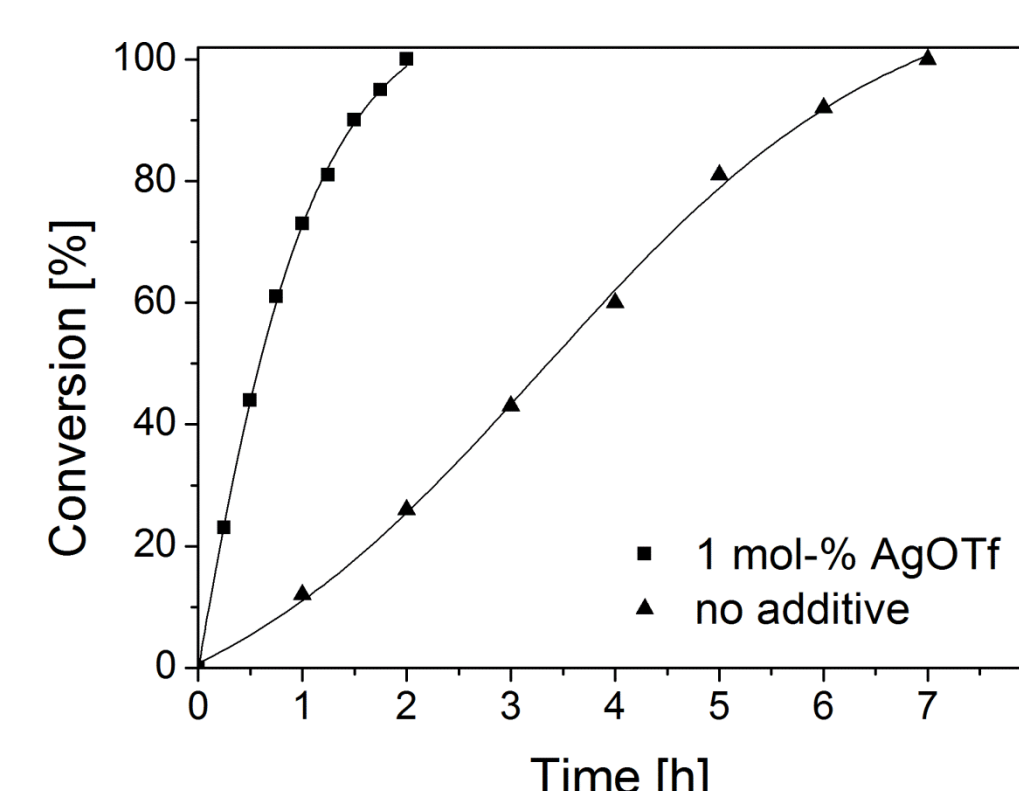
Markovnikov

anti-Markovnikov

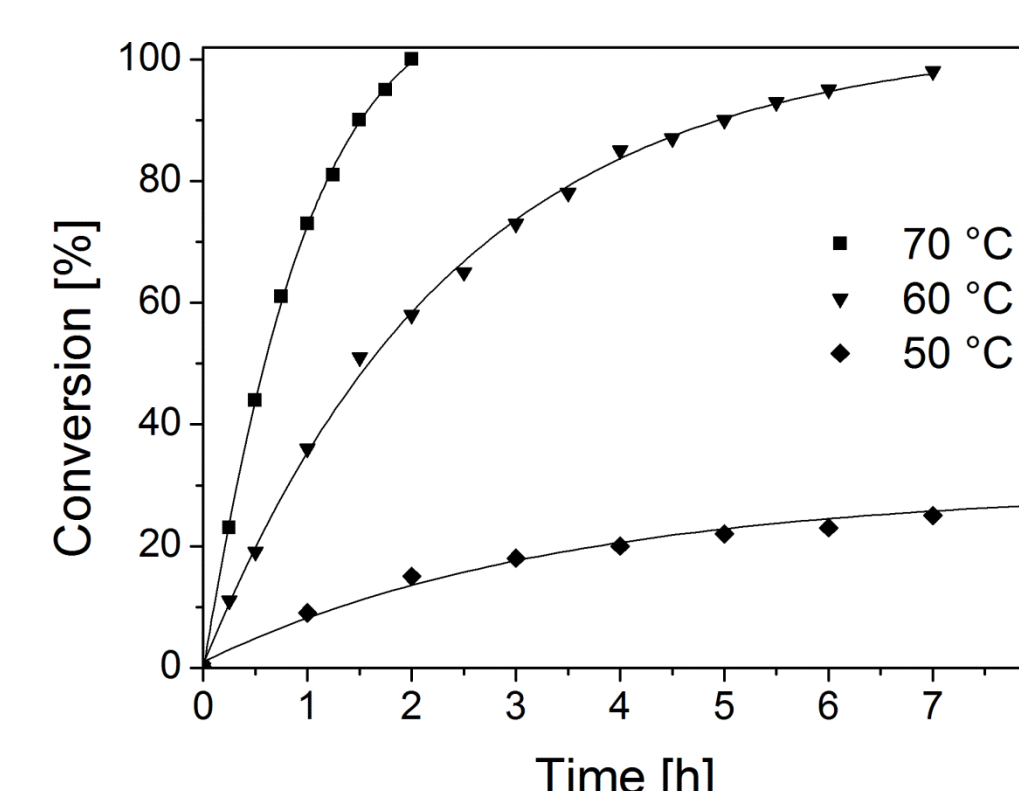
### Catalysts



### Reaction Profile – Addition of AgOTf –

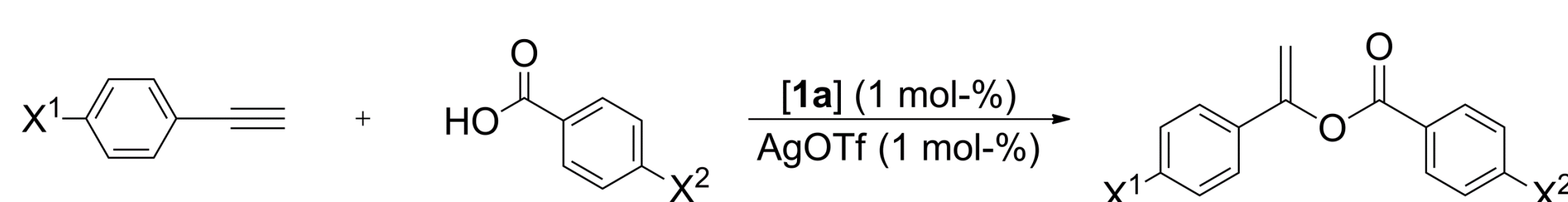


### Reaction Profile – Temperature –

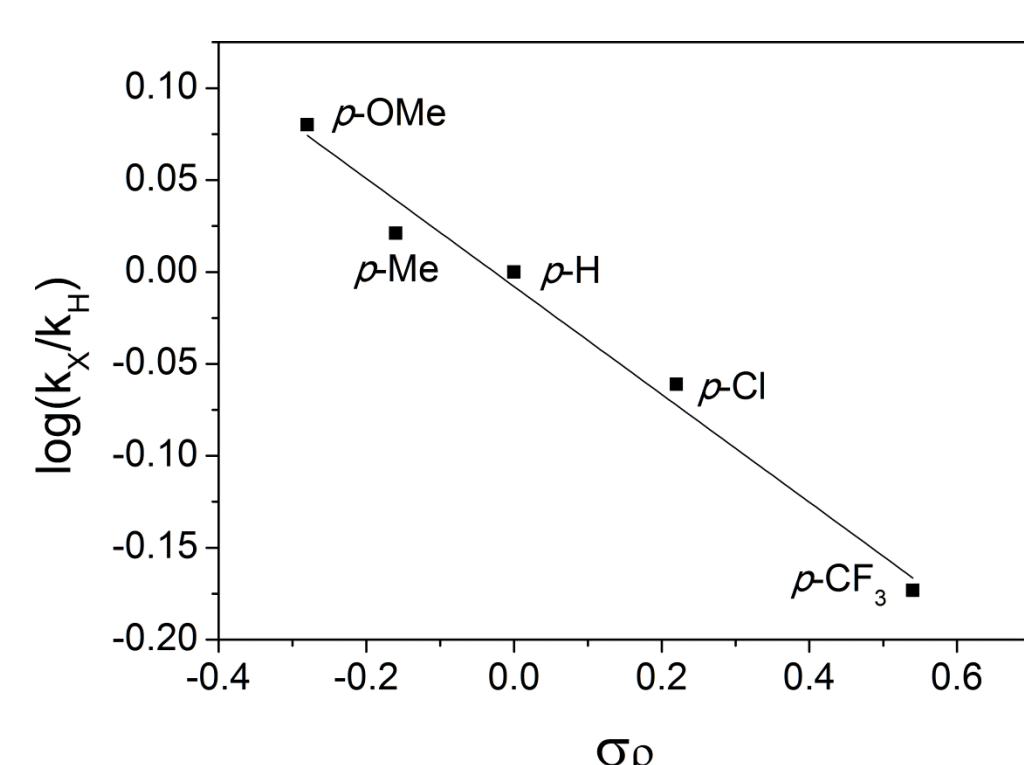


The reaction profiles demonstrate the increased activity of catalyst **1a** by the addition of catalytic amounts of AgOTf (■) compared to the abstinence of any additive (▲) at 70 °C.

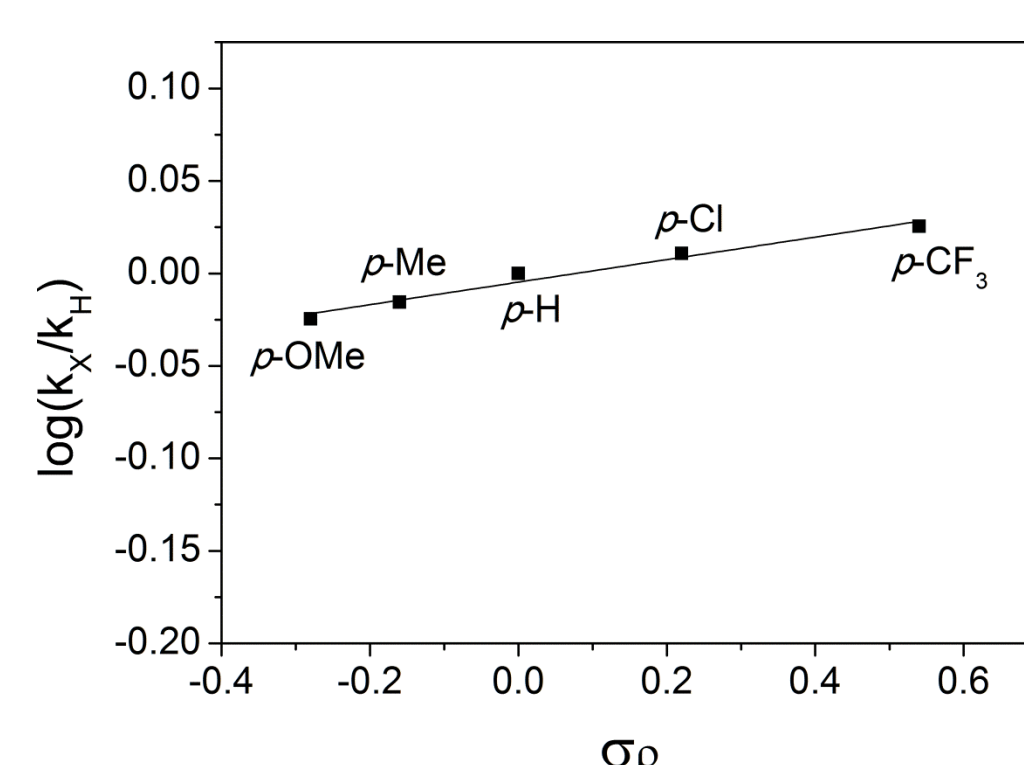
## Hammett Study & Substrate Screening



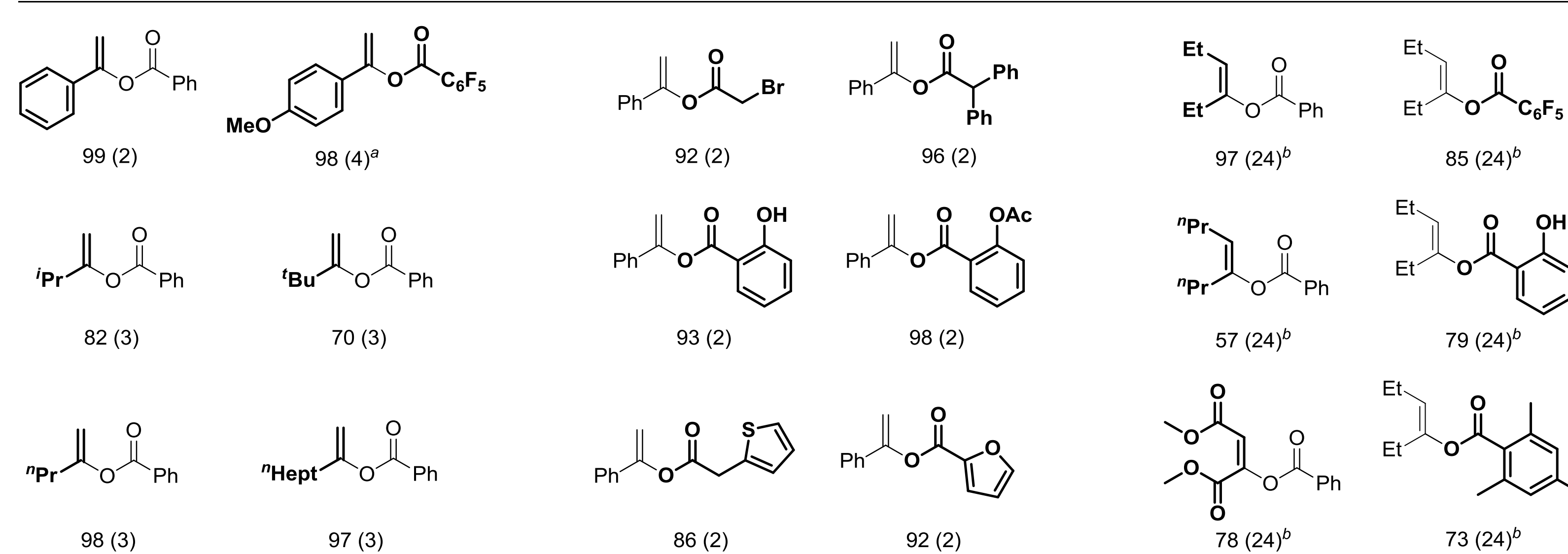
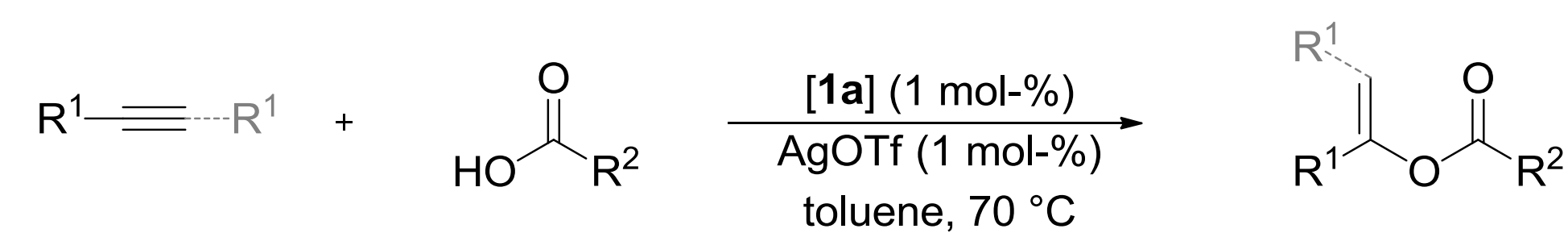
### Alkyne



### Carboxylic Acid



The Hammett study demonstrates that electron-donating groups at the phenylacetylene (X<sup>1</sup>,  $\rho = -0.29$ ) or electron-withdrawing groups at the benzoic acid (X<sup>2</sup>,  $\rho = +0.06$ ) increase the reaction rate.



Isolated yields. Optimized reaction times are given in parentheses. <sup>a</sup> Reaction performed at 25 °C. <sup>b</sup> Reaction performed at 140 °C.

## Summary

- ✓ Successful application of Ru-catalysts **1a-e** in the enol ester synthesis
- ✓ The addition of catalytic amounts of AgOTf increases activity and selectivity
- ✓ Selective formation of Markovnikov addition products (up to 99 %)
- ✓ Best reported activities and selectivities for the conversion of aromatic alkynes
- ✓ Mild reaction conditions (25–70 °C) for the conversion of terminal alkynes
- ✓ Successful conversion of internal alkynes

## References and Acknowledgements

[1] G. Roscher, *Ullmann's Encyclopedia of Industrial Chemistry*, Wiley VCH, Weinheim, **2002**. [2] H. Schröder *et al.*, *Adv. Synth. Catal.* **2013**, 355, 1799. [3] P. Kleman *et al.*, *ACS Catalysis* **2014**, 4, 4398. [4] M. Rotem, Y. Shvo, *Organometallics* **1983**, 2, 1691. [5] C. Ruppin, P. H. Dixneuf, *Tetrahedron Lett.* **1986**, 27, 6323. [6] Y. Hori, T.-A. Mitsudo, Y. Watanabe, *J. Organomet. Chem.* **1987**, 321, 397. [7] L. J. Gooßen, J. Paetzold, D. Koley, *Chem. Commun.* **2003**, 706. [8] F. Nicks, R. Aznar, D. Sainz, G. Müller, A. Demonceau, *Eur. J. Org. Chem.* **2009**, 5020. [9] C. S. Yi, R. Gao, *Organometallics* **2009**, 28, 6585. [10] V. Cadierno, J. Francos, J. Gimeno, *Organometallics* **2011**, 30, 852. [11] O. J. S. Pickup *et al.*, *Organometallics* **2014**, 33, 1751. [12] J. Jeschke, C. Gäbler, M. Korb, T. Rüffer, H. Lang, *Eur. J. Inorg. Chem.* **2015**, 2939.

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