

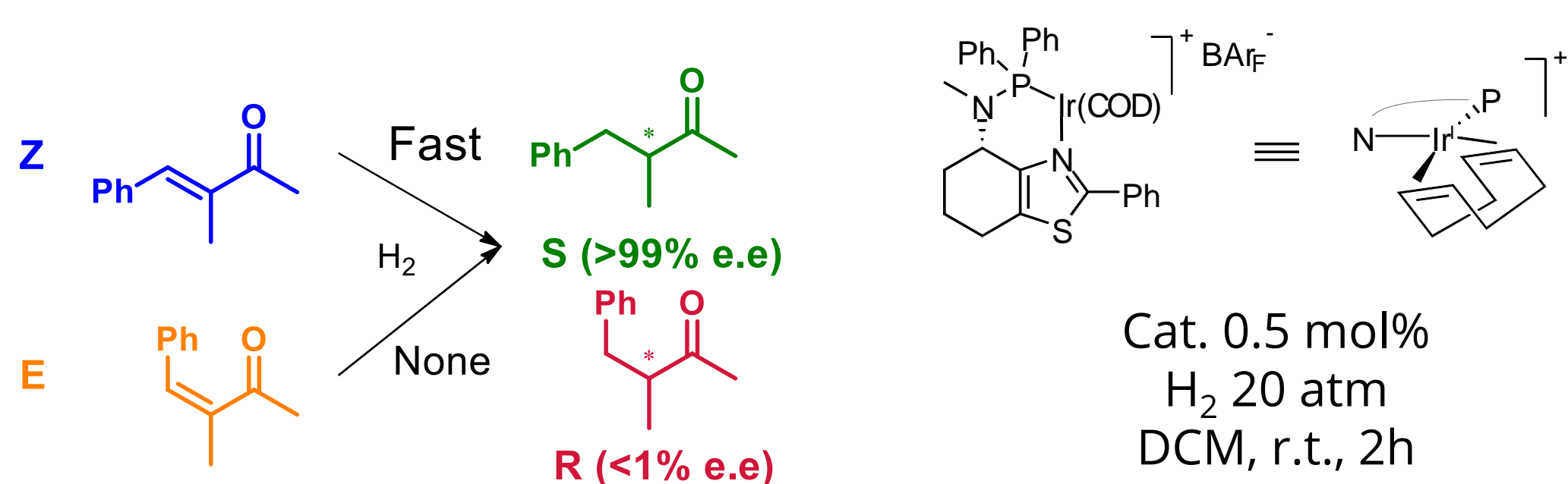
Reaction mechanisms for enantioconvergent hydrogenation of enones and alkenes

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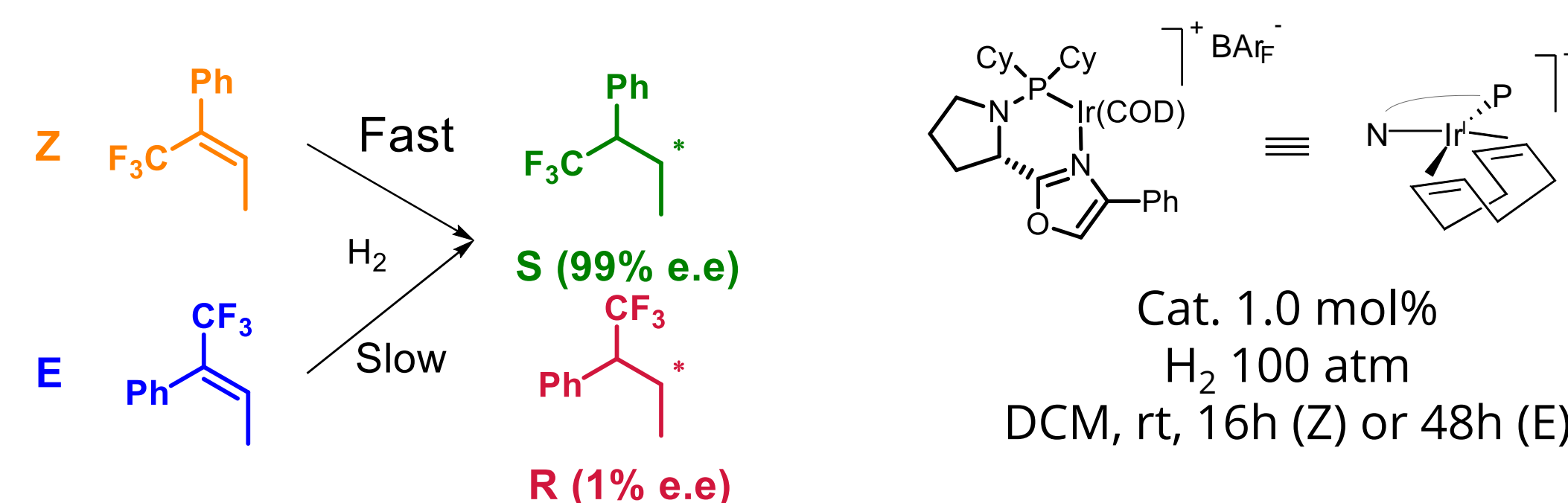
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Introduction

Enones

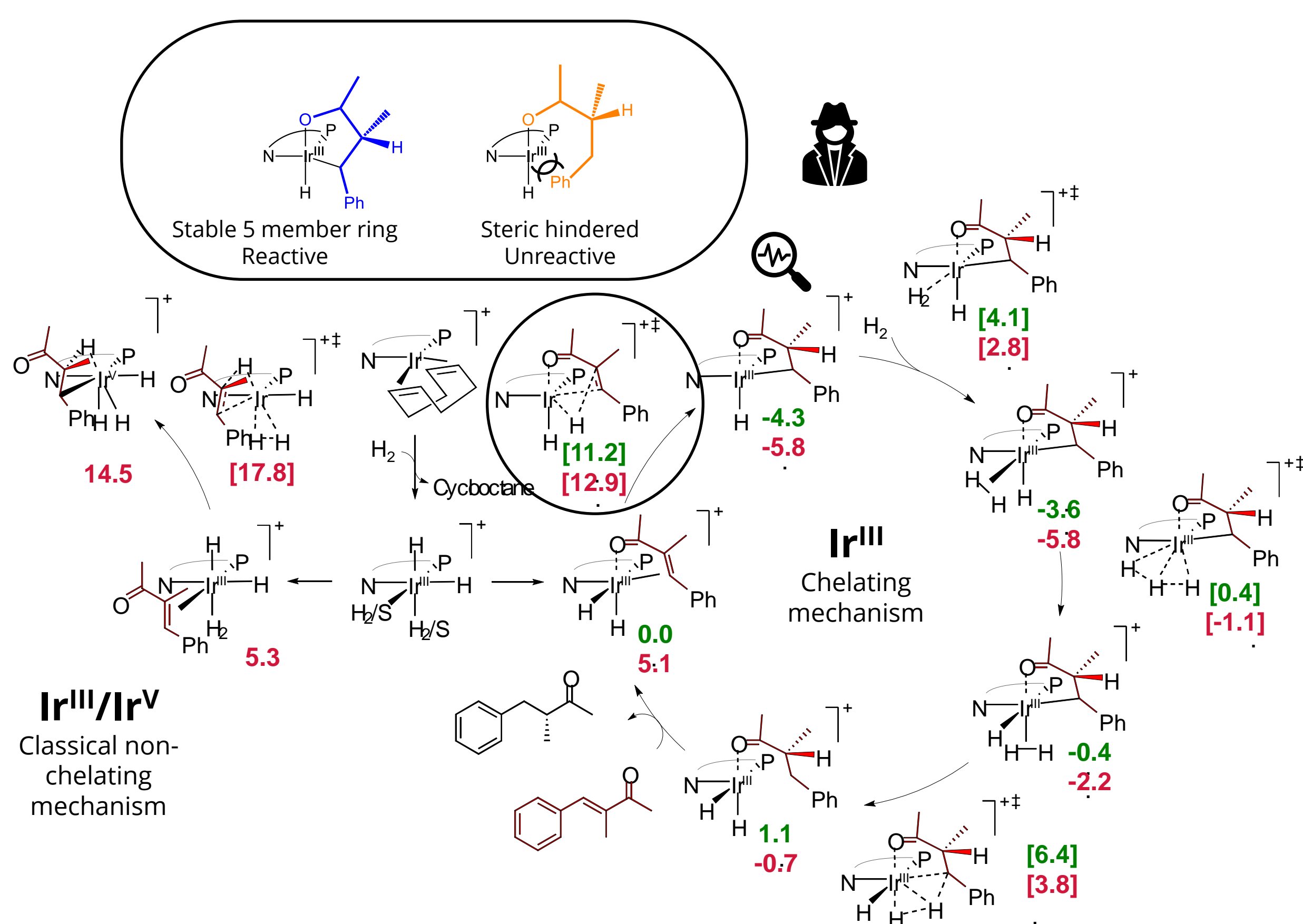


Alkenes

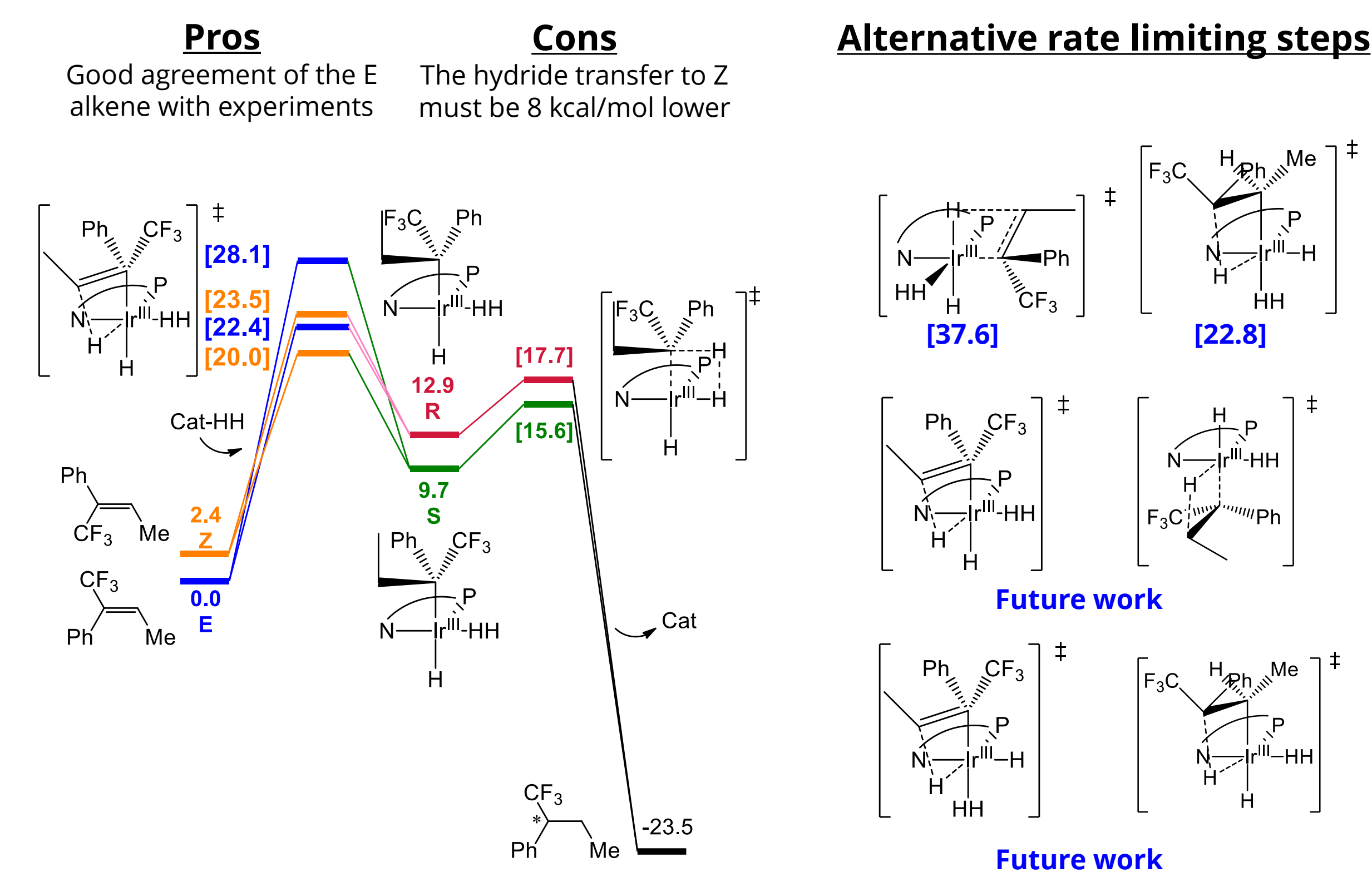


Results

Enones

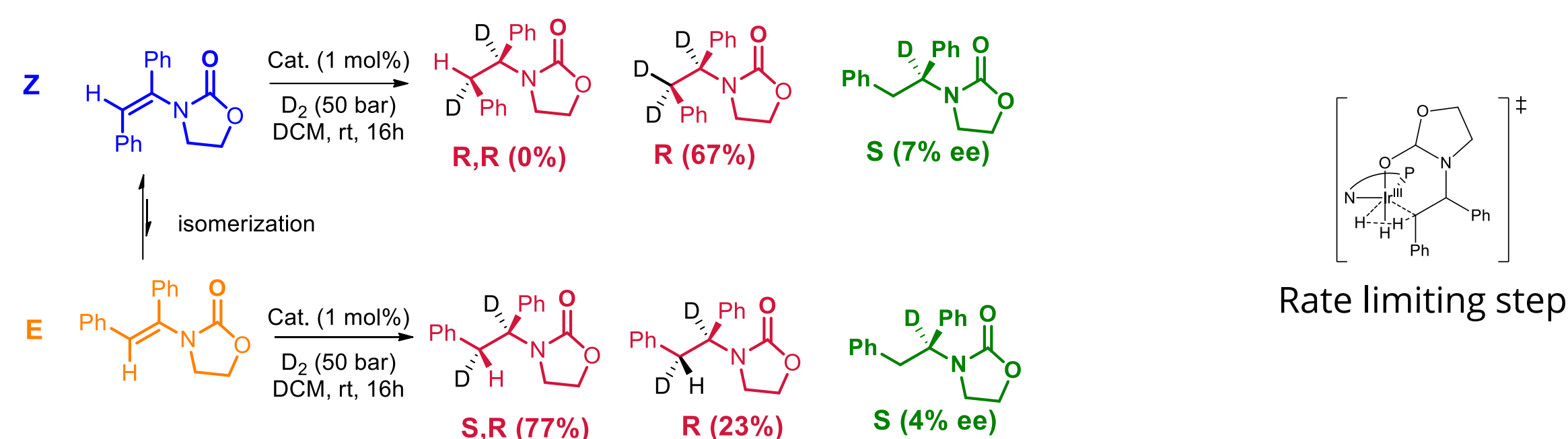


Alkenes



Precedents

Enamides



Our group has previously work with the also enantioconvergen hydrogenation of enamides with iridium catalysts of the same family as the ones in this study.[1] While also having chelating intermediates, the enamides formed 6 member rings instead of the enones 5 member rings. The stability and flexibility of the 6 member ring allowed E enamides to isomerize to the more stable Z isomer, thus explaining their enantioconvergency. Both enamides and enones follow the same 4 step reaction mechanism but with the proton transfer as rate-limiting step instead of the enones' hydride transfer.

Conclusion

Enones

The studied enone is hydrogenated through a four step mechanism: (1) chelating coordination of the enone to the catalyst active site, (2) hydride transfer to the beta carbon (rate-limiting step), (3) addition of dihydrogen to the catalyst and (4) proton transfer to the gamma carbon with concerted hydrogen-hydrogen bond breaking. The lack of reactivity of the E isomer is explained because of its inability to efficiently create a five member ring with the catalyst. The enantioselectivity is due to the sterics between the chiral ligand of the catalyst and the enone.

Alkenes

The reaction mechanism for the hydrogenation of the fluorinated alkene has only been elucidated. For the E isomer, which consist of a 3 step process: (1) hydride transfer to the alkene 2-carbon, concerted with the coordination of the alkene 3-carbon to the catalyst metal (rate-limiting step), (2) proton transfer to the 3-carbon with concerted hydrogen-hydrogen bond breaking and (3) catalyst hydrogenation. When the same mechanism was studied for the Z isomer, the expected product was the R alkene instead of the experimentally observed S alkene. There is work in progress with alternative conformations for the the hydride transfer tot eh Z isomer.

REFERENCES:

[1] J. Am. Chem. Soc. **2021**, 143 (51), 21594-21603

METHODS:

For enones
Jaguar 10.3
B3LYP-D3/psLACVP** + SM8 (dichloromethane) for optimizations and frequency calculations
B3LYP-D3/psLACVP**++ for single point calculations
For alkenes
Gaussian 16
B3LYP-D3/LANL2TZ for Ir and 6-311+G** + SMD (dichloromethane) for optimizations and frequency calculations

ACKNOWLEDGEMENTS: