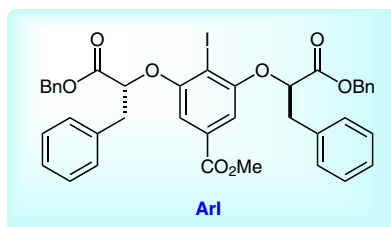
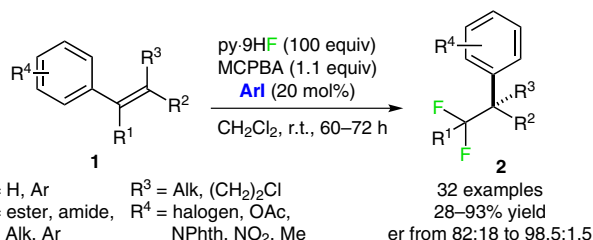
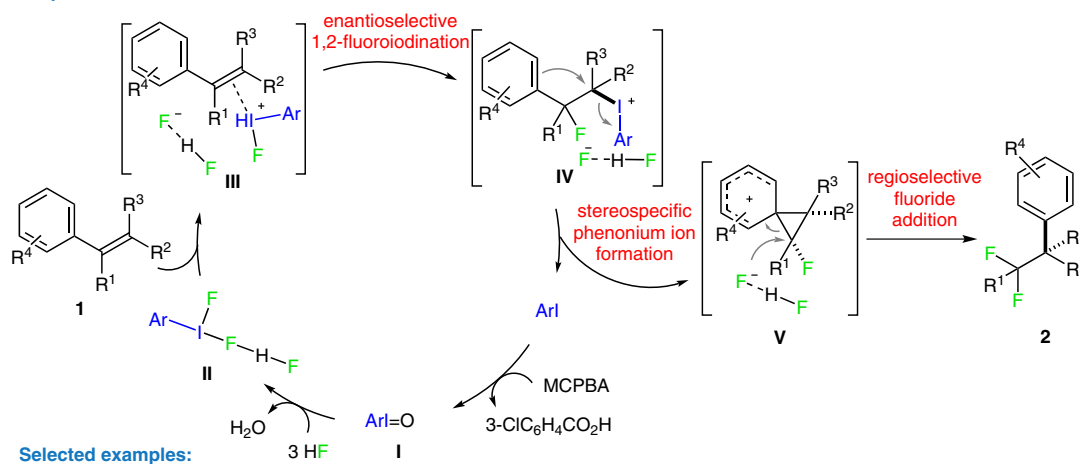


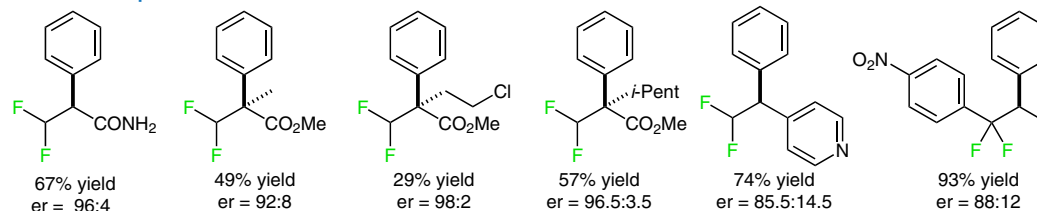
Catalytic Asymmetric Geminal Difluorination of β -Substituted Styrenes



Proposed reaction mechanism:



Selected examples:



Significance: Jacobsen and co-workers report a direct, catalytic, and highly enantioselective transformation of β -substituted styrenes to form difluoromethylated tertiary or quaternary stereocenters. The reaction starts with the oxidation of the aryl iodide catalyst to give iodoso arene **I**, which reacts with HF to give hypervalent iodine intermediate **II**. The catalytic cycle proceeds with an enantioselective 1,2-fluoriodination to give **IV**, followed by the stereospecific formation of phenonium ion **V**. The final regioselective fluoride addition leads to product **2** in high yield and high enantioselectivity.

SYNFACTS Contributors: Benjamin List, Francesca Mandrelli
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Comment: Geminal difluoro groups are important inert isosteres of polar functional groups such as alcohols and thiols. The authors recently reported a diastereoselective 1,2-difluorination of alkenes (*J. Am. Chem. Soc.* **2016**, 138, 5000), which occurs through anchimeric assistance by a carbonyl group, whereas here the 1,1-difluorination is achieved through skeletal rearrangement via phenonium ion intermediate **V**.