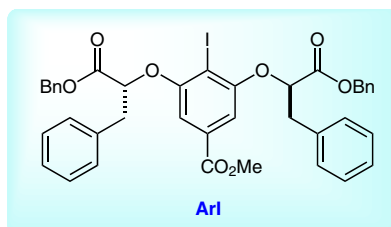
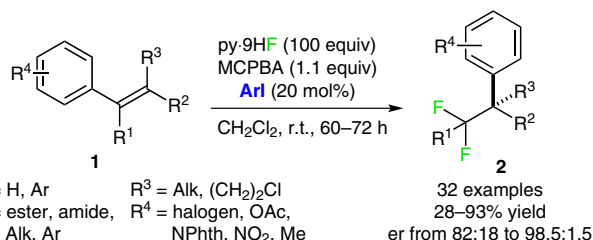
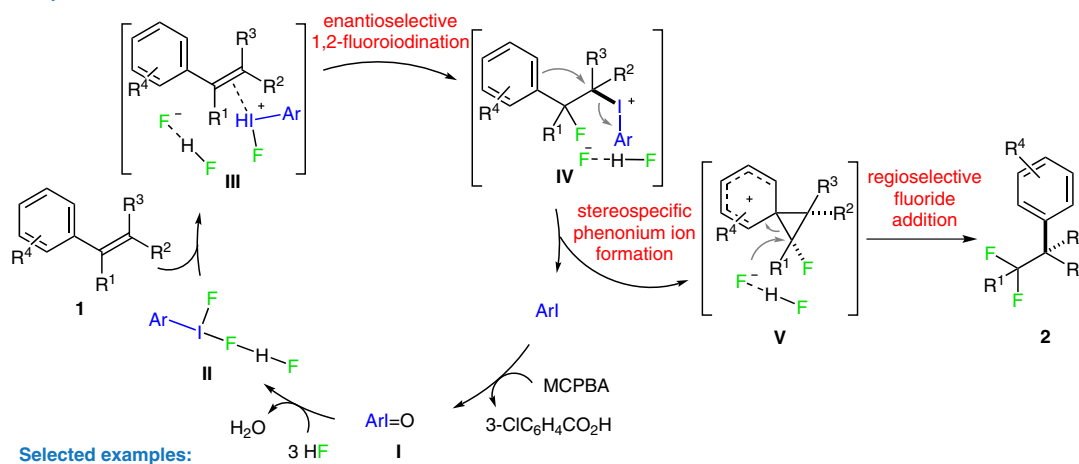


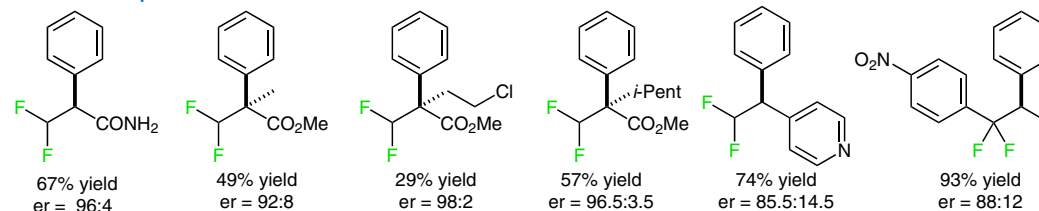
# Catalytic Asymmetric Geminal Difluorination of $\beta$ -Substituted Styrenes



## Proposed reaction mechanism:



## Selected examples:



**Significance:** Jacobsen and co-workers report a direct, catalytic, and highly enantioselective transformation of  $\beta$ -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  
*Synfacts* 2016, 12(10), 1085 Published online: 19.09.2016

**DOI:** 10.1055/s-0036-1589174; **Reg-No.:** B05716SF

**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**.