Catalytic Asymmetric Geminal Difluorination of β-Substituted Styrenes

**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-fluoroiodination 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.

**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 $V$.