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Asymmetric Electrophilic Fluorination Using an Anionic Chiral Phase-Transfer Catalyst
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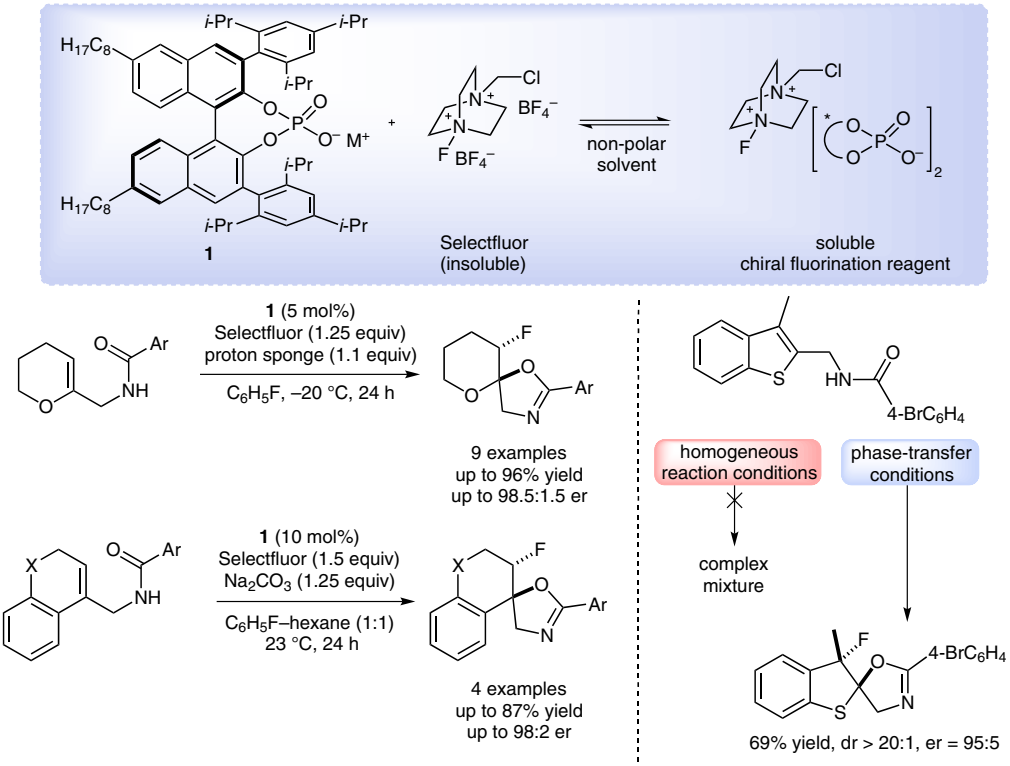
Asymmetric Counteranion Directed Phase-Transfer Catalysis



Significance: The Toste group reports an unprecedented catalytic asymmetric fluorocyclization of olefins to afford various fluorinated heterocycles in high yields and enantioselectivities. By using the liphophilic chiral phosphate anion **1**, a charge-inverted analogous of a phase-transfer catalyst, insoluble Selectfluor, can be converted into a soluble and chiral fluorination reagent in a non-polar solvent. This methodology can also be applied to less electron-rich alkenes in the presence of the inorganic base to afford fluorinated dihydronaphthalenes and chromenes. By observing negative nonlinear effects of the catalysis, the authors presumed that both BF_4 anions are exchanged for chiral phosphates before the reaction with the substrate takes place.

Comment: Asymmetric phase-transfer catalysis (PTC) has been utilized for various enantioselective organic transformations by using chiral cation salts to mediate the reaction of anionic substrates. Here, the authors describe an anionic PTC between solid/solution phases in an enantioselective electrophilic fluorination reaction. This highly enantioselective fluorocyclization using a commercially available fluorinating reagent and chiral phosphate anion emphasizes the applicability of the method to numerous enantioselective organic reactions, which involve cationic reagents or intermediates.

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fluorination
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