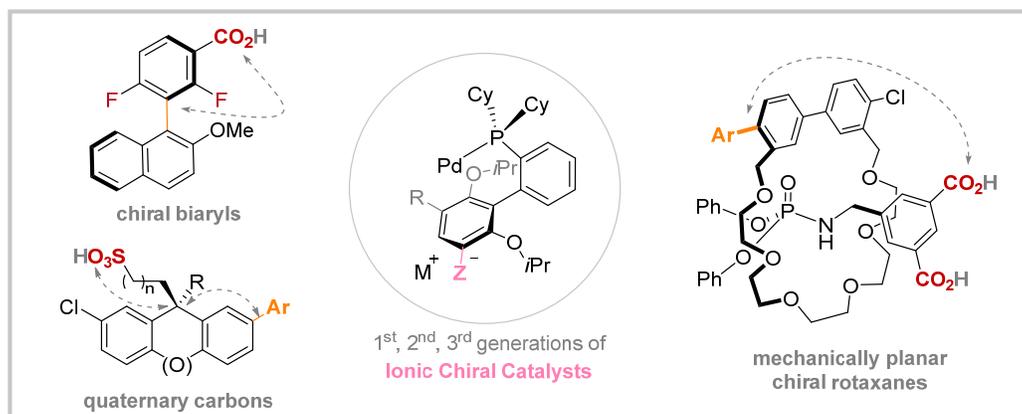


## Ionic ligand–substrate interactions enable electrostatic catalysis: long-range stereocontrol in palladium-catalyzed cross-coupling reactions

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Incorporating ionic groups into synthetic transition-metal catalysts represents a promising design element for enantioselective reactions. We hypothesize that reaction rate acceleration could be achieved through synergistic electrostatic steering and electrostatic catalysis by engaging ionic interactions between ligands and substrates. However, the nondirectional nature of ionic interactions presents a unique challenge in precise transmission of chirality from the catalysts to the prochiral substrates. Our recent work focuses on innovating three generations of phosphine ligands possessing nonligating ionic groups to exert long-range stereocontrol in Pd-catalyzed cross-coupling reactions. Applications of the ionic ligand–substrate interacting strategy in enantiotopic-group-selective reactions and atroposelective reactions to access quaternary carbon, triaryl phosphorus, axial biaryls, mechanically planar chiral rotaxanes, and inherently chiral cavitands will be discussed to illustrate the synthetic utilities. In addition, experimental and computational mechanistic studies reveal an unconventional combinations of electrostatic steering and electrostatic catalysis of the oriented internal electric field produced by the ionic ligand–substrate interactions.



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