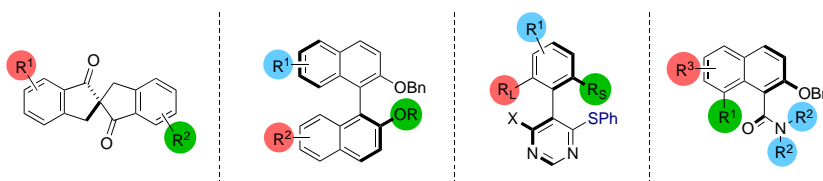


COUNTER-ION MEDIATED APPROACHES TO CONTROLLING AXIAL CHIRALITY

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Counter-ions affect both the reactivity and selectivity of anionic reactions. In this lecture I will describe my group's work on counter-ion-directed cyclization^[1] and mechanism and demonstrate how lessons learned in this area can be applied in the development of new enantioselective methods, with a particular focus on controlling axial chirality.^[2-5]



Extension of this chemistry to complexity-generating reactions will also be outlined.

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- [1] Catalytic enantioselective synthesis of indanes by a cation-directed 5-*endo-trig* cyclization, C. P. Johnston, A. Kothari, T. Sergeieva, S. I. Okovytyy, K. E. Jackson, R. S. Paton & M. D. Smith, *Nature. Chem.* **2015**, *7*, 171-176.
- [2] Catalytic enantioselective synthesis of atropisomeric biaryls: a cation-directed nucleophilic aromatic substitution reaction, R. J. Armstrong & M. D. Smith, *Angew. Chem. Int. Ed.* **2014**, *53*, 12822-12825.
- [3] Catalytic enantioselective synthesis of C_1 and C_2 -symmetric spirobiindanones through counterion-directed enolate *C*-acylation, B. F. Rahemtulla, H. F. Clark & M. D. Smith, *Angew. Chem. Int. Ed.* **2016**, *55*, 13180-13183.
- [4] Catalytic enantioselective synthesis of atropisomeric biaryls by a cation-directed *O*-alkylation, J. D. Jolliffe, R. J. Armstrong & M. D. Smith, *Nature Chem.* **2017**, *9*, 558-563.
- [5] Hydrogen bond enabled dynamic kinetic resolution of axially chiral amides mediated by a chiral counterion, A. J. Fugard, A. S. K. Lahdenperä, J. S. J. Tan, A. Mekareeya, R. S. Paton & M. D. Smith. *Angew. Chem. Int. Ed.* **2019**, *58*, 2795-2798.