

ENANTIOSELECTIVE SYNTHESIS OF FLUORADENES BY C(sp²)-H ARYLATION AND APPLICATION TO THE SYNTHESIS OF BUCKYBOWLS

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Enantioselective Pd⁰-catalyzed C-H activation reactions rely on the use of a chiral ancillary ligand and/or a chiral base [1]. Our group recently developed a new family of chiral bifunctional phosphine-carboxylate ligands for asymmetric C(sp²)-H arylation [2]. Application of this new approach to the preparation of enantioenriched fluoradenes and related structures is described herein.

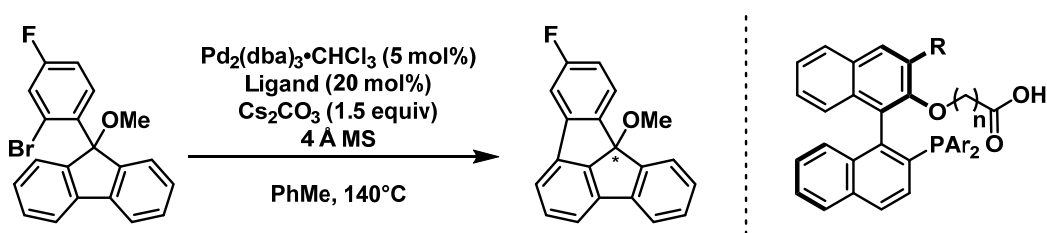


Figure 1 Enantioselective synthesis of fluoradenes

The reaction conditions and the ligand structure were optimized using the model substrate shown on Figure 1. These conditions were then applied to the preparation of other ring systems as shown on figure 2.

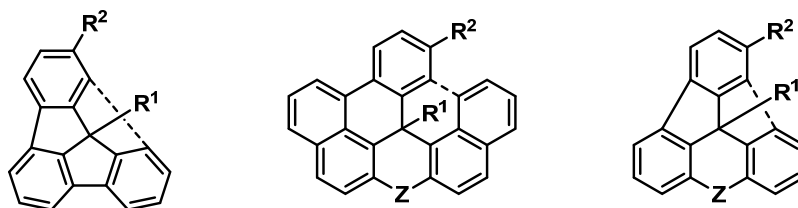


Figure 2 Examples of C-H activation products and targeted bowls (dashed bonds)

Starting from these C-H activation products a second cyclization reaction should allow the preparation of enantioenriched buckybowls and other bowl-shaped molecules from achiral building blocks. Efforts towards this goal are also discussed.

[1] a) P. M. Holstein, M. Vogler, P. Larini, G. Pilet, E. Clot, O. Baudoin *ACS Catal.* **2015**, 5, 4300–4308

b) L. Yang, R. Melot, M. Neuburger, O. Baudoin *Chem. Sci.* **2017**, 8, 1344–1349.

c) T. G. Saint-Denis, R.-Y. Zhu, G. Chen, Q.-F. Wu, J.-Q. Yu *Science* **2018**, 359, 759-770

d) C. G. Newton, S.-G. Wang, C. C. Oliveira, N. Cramer *Chem. Rev.* **2017**, 117, 8908-8976

[2] L. Yang, M. Neuburger, O. Baudoin *Angew. Chem. Int. Ed.* **2018**, 57, 1394–1398