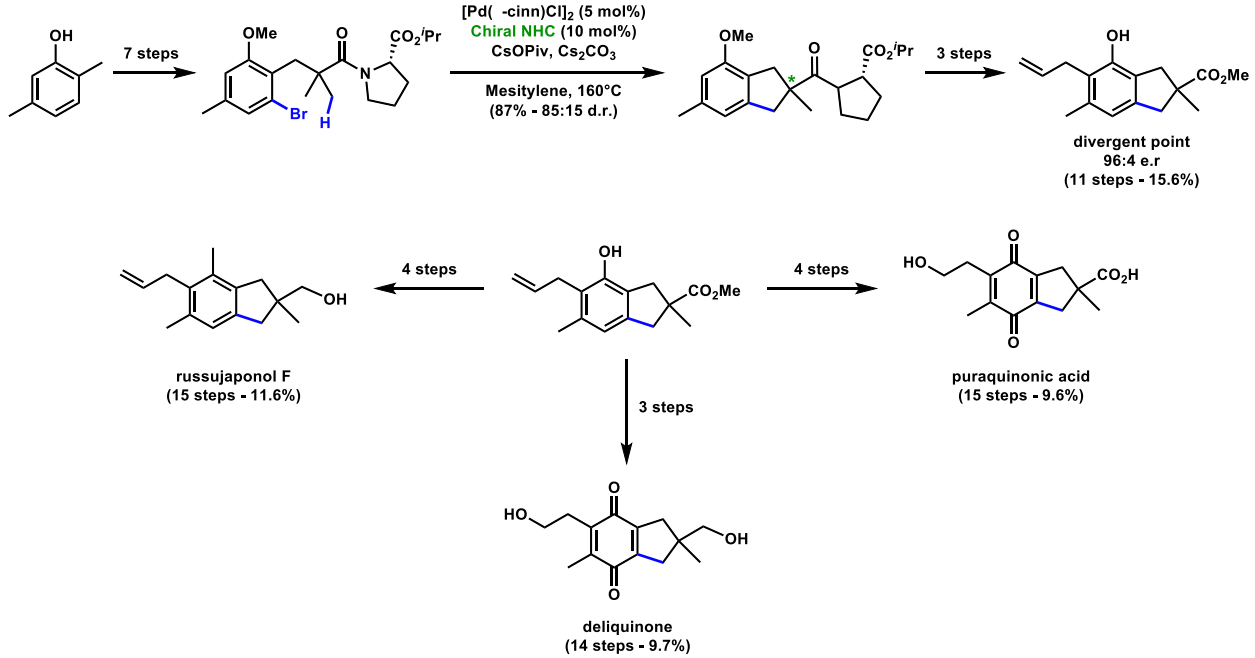
Total synthesis of illudane (nor)sesquiterpenes via Pd^0-catalyzed asymmetric C(sp^3)-H arylation

Romain Melot, Marcus Craveiro, Olivier Baudoin*

University of Basel St. Johanns-Ring 19 4056 Basel, Switzerland
romain.melot@unibas.ch

Higher fungi are sources of diverse bioactive illudalane and norilludalane sesquiterpenes such as the fused benzoquinones puraquinonic acid[1a] and deliquinone, [1b] and the indane russujaponol F.[1c] Due to the presence of a highly symmetrical quaternary stereocenter, the enantioselective total synthesis of these molecules proved to be challenging and lengthy.[2] To adress this problem, we planned to employ a Pd(0)-catalyzed intramolecular asymmetric C(sp3)-H arylation reaction. In the last decade, asymmetric C-H activation proved to be an efficient tool for the construction of tertiary and more recently quaternary stereocenters.[3] We recently developed a divergent total synthesis of puraquinonic acid, deliquinone, and russujaponol F from a common intermediate prepared by asymmetric C(sp3)-H activation using chiral NHC ligands developed by the Kündig group.[4]



[1] (a) U. Becker, G. Erkel, T. Anke, O. Sterner, *Nat. Prod. Lett.* **1997**, *9*, 229-236. (b) M. Clericuzio, F. Han, F. Pan, Z. Pang, O. Sterner, *Acta Chem. Scand.* **1998**, *52*, 1333-1337. (c) K. Yoshikawa A. Kaneko, Y. Matsumoto, H. Hama, S. Arihara, *J. Nat. Prod.* **2006**, *69*, 1267-1270.

[2] (a) D. L. J. Clive, M. Yu, *Chem. Commun.* **2002**, 2380-2381. (b) D. L. J. Clive, M. Yu, M. Sannigrahi, *J. Org. Chem.* **2004**, *69*, 4116-4125. (c) E. A. Tiong, D. Rivalti, B. M. Williams, J. L. Gleason, *Angew. Chem. Int. Ed.* **2013**, *52*, 3442-3445.

[3] For reviews, see (a) C. G. Newton, S.-G. Wang, C. C. Oliveira, N. Cramer, *Chem. Rev.* **2017**, *117*, 8908-8976. (b) T. G. Saint-Denis, R.-Y. Zhu, G. Chen, Q.-F. Wu, J.-Q. Yu, *Science* **2018**, *359*, 759-772.

[4] Melot, R.; Craveiro, M.; Baudoin, O. manuscript in preparation.