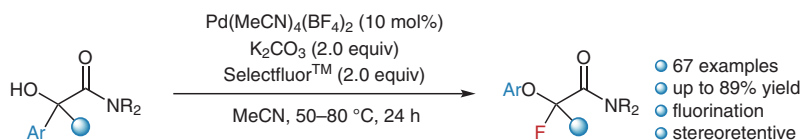
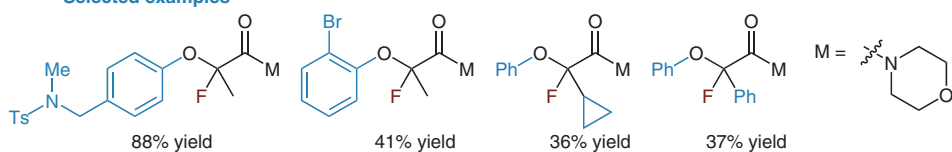


T. DELCAILLAU, B. YANG, Q. WANG, J. ZHU* (ECOLE POLYTECHNIQUE FÉDÉRALE DE LAUSANNE, SWITZERLAND)
 Editing Tetrasubstituted Carbon: Dual C–O Bond Functionalization of Tertiary Alcohols Enabled by Palladium-Based Dyotropic Rearrangement
J. Am. Chem. Soc. **2024**, *146*, 11061–11066, DOI: 10.1021/jacs.4c02924.

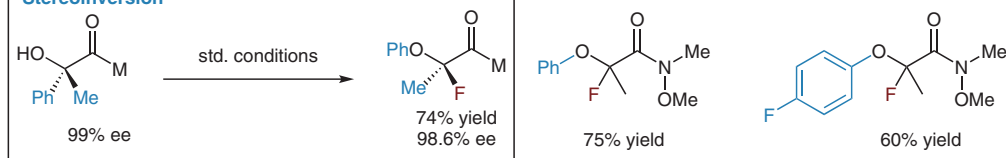
Dyotropic Rearrangement of Tertiary Alcohols for the Synthesis of Fluorinated Tetrasubstituted Carbons



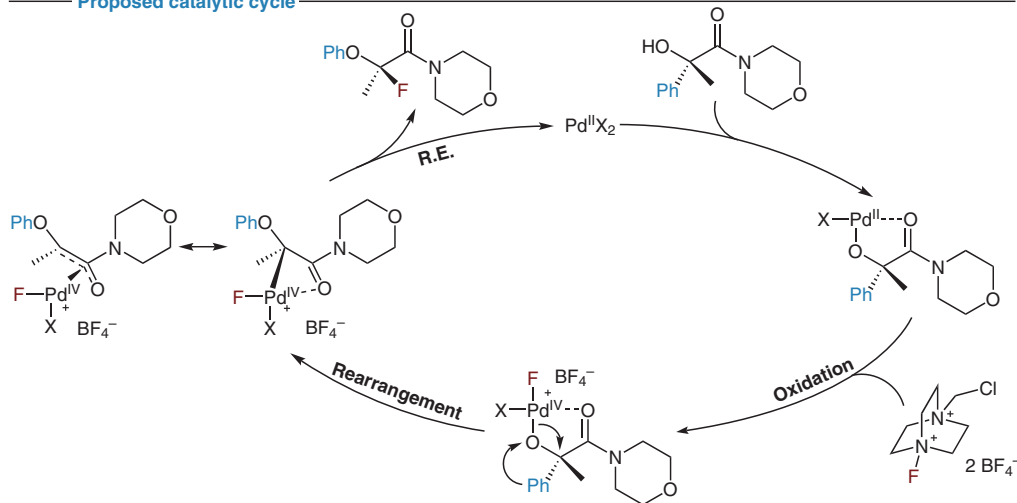
Selected examples



Stereoinversion



Proposed catalytic cycle



Significance: The authors report an unprecedented 1,2-aryl/ Pd^{IV} dyotropic rearrangement along a C–O bond to generate α -fluorinated tertiary ethers. The reaction proceeds with stereoinversion of absolute configuration of the tertiary alcohol center. It is hypothesized that the driving force for the 1,2-dyotropic rearrangement is the generation of a π -oxyallyl Pd^{IV} species.

Comment: Inclusion of a cyclopropyl group on the tertiary alcohol center indicated to the authors that radical intermediates are likely not involved. The authors were also able to carry out several post-transformations to generate a variety of fluorinated analogues of biologically active compounds.

SYNFACTS Contributors: Mark Lautens, Andrew G. Durant
 Synfacts 2024, 20(07), 0703 Published online: 14.06.2024
 DOI: 10.1055/s-0043-1775184; Reg-No.: L09124SF

© 2024, Thieme. All rights reserved.
 Georg Thieme Verlag KG, Rüdigerstraße 14, 70469 Stuttgart, Germany

Category

Metals in Synthesis

Key words

fluorination

palladium catalysis

dyotropic rearrangement

Synfact
of the
Month

This document was downloaded for personal use only. Unauthorized distribution is strictly prohibited.