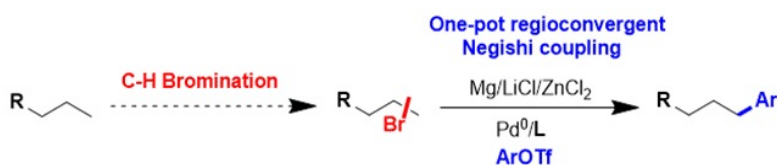


Terminal-selective arylation of alkyl chains by regioconvergent Negishi couplingK. ZHANG¹, S. DUPUY¹, A. GOUTIERRE¹, O. BAUDOIN^{1*}¹University of Basel

Palladium-catalyzed C(sp²)-C(sp³) cross-couplings are particularly valuable tools in synthetic chemistry and hence a great deal of interest has emerged in this area.^[1] Recently, our group has developed a new cross-coupling strategy based on the migration of an organopalladium species along an alkyl chain.^[2] Through experimental and theoretical mechanistic studies, we have shown that this migration occurs through a beta-H elimination/rotation/insertion sequence.^[3]

In this work, we have extended this migrative-coupling to simple and commercially available alkyl bromides. Under practical Barbier-type conditions involving magnesium insertion and transmetalation with ZnCl₂, a series of linear arylated products could be obtained in a regioconvergent manner with good to excellent linear/branched selectivities, thanks to the use of a suitable phosphine ligand. Moreover, this strategy could be coupled to a non-selective radical bromination process, which allowed the terminal-selective functionalization of simple alkanes in just two steps.^[4]



[1] a) Ranjan Jana, Tejas P. Pathak, Matthew S. Sigman, *Chem. Rev.* **2011**, 111, 1417-1492; b) Olivier Baudoin, *Chem. Soc. Rev.* **2011**, 40, 4902-4911.

[2] a) Alice Renaudat, Ludivine Jean-Gérard, Rodolphe Jazzar, Christos E. Kefalidis, Eric Clot, Olivier Baudoin, *Angew. Chem. Int. Ed.* **2010**, 49, 7261-7265; b) Sam Aspin, Anne-Sophie Goutierre, Paolo Larini, Rodolphe Jazzar, Olivier Baudoin, *Angew. Chem. Int. Ed.* **2012**, 51, 10808-10811; c) Anthony Millet, Paolo Larini, Eric Clot, Olivier Baudoin, *Chem. Sci.* **2013**, 4, 2241-2247; d) Anthony Millet, David Dailler, Paolo Larini, Olivier Baudoin, *Angew. Chem. Int. Ed.* **2014**, 53, 2678-2682.

[3] Paolo Larini, Christos E. Kefalidis, Rodolphe Jazzar, Alice Renaudat, Eric Clot, Olivier Baudoin, *Chem. Eur. J.* **2012**, 18, 1932-1944.

[4] Stéphanie Dupuy, Ke-Feng Zhang, Anne-Sophie Goutierre, Olivier Baudoin, *Angew. Chem. Int. Ed.* **2016**, 55, 14793-14797.