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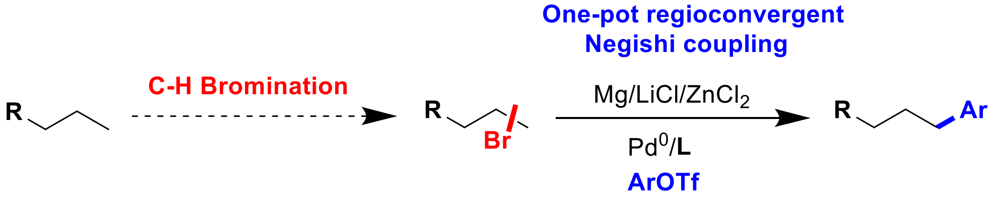
Terminal-selective functionalization of alkyl chains by regioconvergent cross-coupling

Ke-Feng Zhang, Stéphanie Dupuy, Anne-Sophie Goutierre, Olivier Baudoin*

Department of Chemistry, University of Basel, St-Johanns Ring 19, CH-4056, Basel, Switzerland
olivier.baudoin@unibas.ch

Palladium-catalyzed C(sp^2)-C(sp^3) 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 β-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 transmetallation with $ZnCl_2$, 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 flexible phosphine ligand. Moreover, this strategy could be coupled to a non-selective radical bromination process, which allowed the functionalization of simple alkanes in just two steps.[4]



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