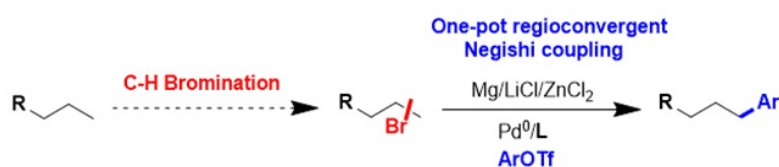


Terminal-selective arylation of alkyl chains by regioconvergent Negishi couplingK. ZHANG¹, S. DUPUY¹, A. GOUTIERRE¹, O. BAUDOIN^{1*}¹University of Basel

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]



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