

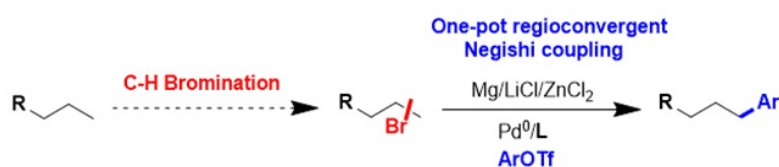
## Terminal-selective arylation of alkyl chains by regioconvergent Negishi coupling

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

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 ZnCl<sub>2</sub>, 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.<sup>[4]</sup>



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[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 Dailier, Paolo Larini, Olivier Baudoin, *Angew. Chem. Int. Ed.* **2014**, 53, 2678-2682.

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