Tuning Chemoselectivity in Iron-Catalyzed Sonogashira-Type Reactions Using a Bisphosphine Ligand with Peripheral Steric Bulk: Selective Alkynylation of Nonactivated Alkyl Halides Angew. Chem. Int. Ed. 2011, 50, 10973-10976.

Category

Alkyl———
up to $92 \%$ yield

Alkyl $=c$-Hept, Cy, substituted piperidines and aliphatics
$\mathrm{X}=\mathrm{Cl}, \mathrm{Br}, \mathrm{I}$
$\mathrm{R}=\mathrm{Cy}, o$-methylbenzyl, $\mathrm{C}(\mathrm{Me})_{2} \mathrm{OSiMe}_{2}(t-\mathrm{Bu}), \mathrm{Si}(i-\mathrm{Pr})_{3}, \mathrm{SiMe}_{2}(t-\mathrm{Bu})$


## Selected examples:


$88 \%$ yield

$86 \%$ yield

$81 \%$ yield

$68 \%$ yield

$73 \%$ yield

Significance: The authors report a novel coupling of primary and secondary alkyl halides with alkynylmagnesium reagents with iron catalysis. The use of a bisphosphine ligand bearing peripheral steric bulk as well as slow addition of the Grignard reagent suppress undesired side reactions.

Comment: By using starting materials with two potential reactive sites, for example $\mathrm{C}\left(\mathrm{sp}^{3}\right)-\mathrm{Br}$ and $\mathrm{C}\left(\mathrm{sp}^{2}\right)-O T f$, and applying the reported ironcatalyzed cross-coupling with an alkynyl Grignard reagent, the $\mathrm{C}(\mathrm{sp})-\mathrm{C}\left(\mathrm{sp}^{3}\right)$-coupled products are obtained in excellent yields.

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[^0]:    synfacts Contributors: Paul Knochel, Andreas K. Steib
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