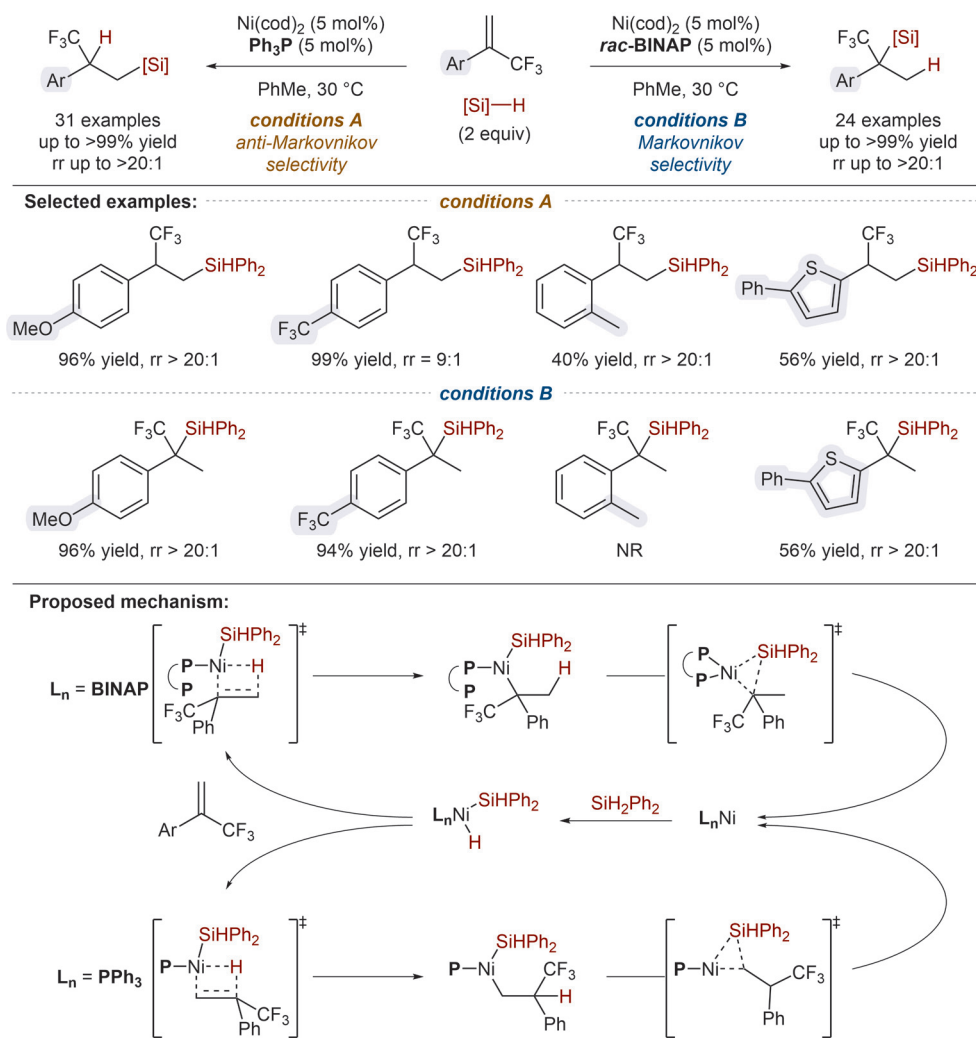


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Nickel-Catalyzed Regiodivergent Hydrosilylation of α -(Fluoroalkyl)styrenes without Defluorination

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Regiodivergent Nickel-Catalyzed Hydrosilylation of α -(Fluoroalkyl)styrenes



Significance: A regiodivergent hydrosilylation reaction of α -(fluoroalkyl)styrenes is reported to occur under mild conditions and with commercially available ligands providing both α - and β -trifluoromethyl-substituted scaffolds. With the bidentate ligand BINAP, the reaction proceeds via a Markovnikov pathway, selectively forming products with a quaternary center, without any by-products from β -F elimination. In contrast, use of the monodentate PPh₃ ligand promotes the traditional anti-Markovnikov addition pathway.

Comment: Experimental data support a polar mechanism involving the addition of a NiH species. Control experiments demonstrate that the trifluoromethyl group is essential for reactivity; in its absence, only anti-Markovnikov products are formed. DFT analysis confirms that a [1,2]-migratory insertion followed by reductive elimination (Path A) is favored in the presence of BINAP, which the authors attribute to the σ -withdrawing effect of the trifluoromethyl group.

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