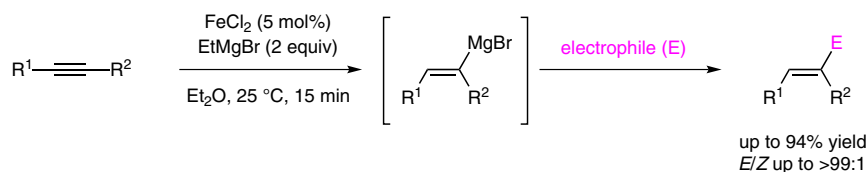


L. ILIES, T. YOSHIDA, E. NAKAMURA* (THE UNIVERSITY OF TOKYO, JAPAN)
Iron-Catalyzed Chemo- and Stereoselective Hydromagnesiation of Diarylalkynes and Diynes
J. Am. Chem. Soc. **2012**, *134*, 16951–16954.

Iron-Catalyzed Hydromagnesiation of Diarylalkynes and Diynes

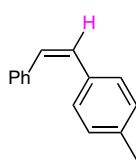


R¹ = Ph, 2-thienyl, 4-FC₆H₄, Tol, PMP

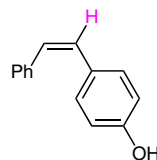
R² = Ar, HetAr, Alk, alkene, and alkyne substituents

E = H₂O, D₂O, allyl bromide, DMF, PhCHO, Ph₂SiHCl, PhI, *N*-ethyl-*N*-(2-iodobenzyl)ethanamine

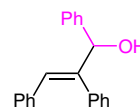
Selected examples:



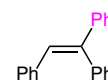
89% yield
E/Z = 4:96



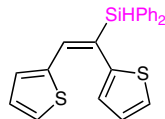
75% yield
E/Z = 11:89



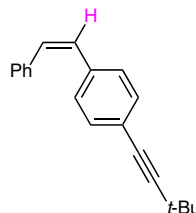
73% yield
E/Z > 99:1



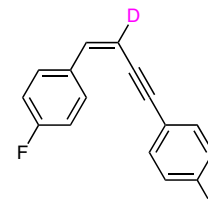
80% yield



38% yield
E/Z > 99:1



64% yield
E/Z > 1:99



63% yield
E/Z = 11:89

Significance: The authors report a novel iron-catalyzed hydromagnesiation of diarylalkynes in high yield with high stereoselectivity. Furthermore, alkenyl-magnesium compounds can be synthesized from diynes in a chemo-, regio- and stereoselective way.

Comment: The alkenylmagnesium intermediates can further be functionalized in a one-pot sequence. Reactions with allyl bromide, *N,N*-dimethylformamide and even nickel-catalyzed cross-couplings have been disclosed. The authors suggest a radical mechanism instead of a pure anionic mechanism.

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