Fe-Catalyzed Cross-Coupling of Alkyl Halides with Alkynyl Grignard Reagents

\[
\text{Alkyl} - X + \text{BrMg} - \text{alkynyl Grignard} \xrightarrow{\text{catalyst (3–5 mol\%)} \text{THF, 60 °C, 2–4 h}} \text{Alkyl} - \text{alkynyl} - \text{R, up to 92% yield}
\]

**Alkyl = o-Hept, Cy, substituted piperidines and aliphatics**

**X = Cl, Br, I**

**R = Cy, o-methylbenzyl, C(Me)2OSiMe2(t-Bu), Si(i-Pr)3, SiMe2(t-Bu)**

**Selected examples:**

\[
\begin{align*}
\text{88% yield} & & \text{86% yield} & & \text{68% yield} \\
\text{82% yield} & & \text{81% yield} & & \text{73% yield}
\end{align*}
\]

**Significance:** The authors report a novel coupling of primary and secondary alkyl halides with alkynyl-magnesium 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 C(sp^3)-Br and C(sp^3)-OTf, and applying the reported iron-catalyzed cross-coupling with an alkynyl Grignard reagent, the C(sp)-C(sp^3)-coupled products are obtained in excellent yields.