Highly Stereo- and Chemoselective Iron-Catalyzed Alkenylation of Organomagnesium Compounds

**Synthesis 1998, 1199–1205.**

### Iron-Catalyzed Alkenylation of Organomagnesium Reagents

**Significance:** In 1998, Cahiez and Avedissian reported a general method for the iron-catalyzed cross-coupling between alkenyl halides (halide = Cl, Br, or I) and Grignard reagents in high yields and excellent diastereoselectivities (>99:1).

**Comment:** The approach significantly improved the cross-coupling between alkenyl halides and Grignard reagents using Fe(acac)₃ as catalyst. Additionally, it was found that the use of a polar co-solvent such as NMP was crucial for the cross-coupling to proceed in excellent yields. Furthermore, functional groups such as ketones were tolerated for the first time in these cross-coupling reactions (see Review below).


\[
\begin{align*}
R^1 & R^2 & X & \text{Fe(acac)}_3 (1 \text{ mol\%}) \\
& & (1.0 \text{ equiv}) & NMP (9.0 \text{ equiv}), \text{THF} \\
R^3 & R^4 & & -5 \text{ to } 0 \degree \text{C}, 15 \text{ min or } \\
& & (1.1 \text{ equiv}) & 20\text{–}25 \degree \text{C}, 15 \text{ min}
\end{align*}
\]

\[R^1, R^2, R^3 = \text{H, Alk, Ar} \]

\[X = \text{Cl, Br, I}\]

**Selected examples:**

- **Hex**
  - n-Bu
  - 75% yield, \(E/Z > 99:1\)
- **Hex**
  - **n-Bu**
  - 80% yield, \(Z/E > 99:1\)
- **Ph**
  - i-Pr
  - 73% yield
- **n-Bu**
  - 89% yield
- **C₈H₁₇**
  - 75% yield
- **n-Bu**
  - 84% yield
- **AcO**
  - i-Pr
  - 72% yield
- **O**
  - 80% yield
- **O**
  - 68% yield
- **n-Bu**
  - 79% yield
- **Cl**
  - 79% yield