Iron-Catalyzed Alkenylation of Organomagnesium Reagents

\[ \text{R}^1 \text{R}^2 \text{R}^3 \quad \text{X} + \quad \text{R}^4 \text{MgCl} \quad \text{Fe(acac)}_3 (1 \text{ mol\%}) \]

\[ \text{NMP} (9.0 \text{ equiv}), \text{THF} \]

\[ \text{–5 to } 0 \text{ °C, 15 min or 20–25 °C, 15 min} \]

Selected examples:

- Hex\(\text{-}n\)-Bu: 75% yield, \(E/Z > 99:1\)
- Hex\(\text{-}n\)-Bu: 80% yield, \(Z/E > 99:1\)
- Ph\(\text{-}i\)-Pr: 73% yield
- \(n\)-Bu: 89% yield
- \(n\)-Bu: 82% yield
- \(n\)-Bu: 86% yield
- \(n\)-Bu: 84% yield
- \(n\)-Bu: 75% yield
- AcO\(\text{-}i\)-Pr: 72% yield
- O\(\text{-}n\)-Bu: 80% yield
- O\(\text{-}n\)-Bu: 68% yield
- O\(\text{-}n\)-Bu: 79% yield
- Cl\(\text{-}n\)-Bu: 79% yield

**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).