Iron-Catalyzed Alkenylation of Organomagnesium Reagents

$$\text{R}_1^1, \text{R}_2^2, \text{R}_3^3 = \text{H, Alk, Ar}$$
$$X = \text{Cl, Br, I}$$
$$\text{R}_1^1 \text{R}_2^2 X + \text{R}_4^4 \text{MgCl} \xrightarrow{\text{Fe(acac)}_3 \ (1 \text{ mol} \%) + \text{NMP \ (9.0 \text{ equiv}), THF \ \sim -5 \text{ to } 0 \degree \text{C}, 15 \text{ min or } 20-25 \degree \text{C}, 15 \text{ min}}} \text{R}_1^1 \text{R}_2^2 \text{R}_3^3$$

**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).

**Selected examples:**

- 75% yield, $E/Z > 99:1$
- 80% yield, $Z/E > 99:1$
- 73% yield
- 89% yield
- 82% yield
- 86% yield
- 84% yield
- 75% yield
- 72% yield
- 80% yield
- 68% yield
- 79% yield
- 79% yield


**Key words**

- cross-coupling
- iron catalysis
- magnesium