T. HATAKEYAMA, R. IMAYOSHI, Y. YOSHIMOTO, S. K. GHORAI, M. JIN, H. TAKAYA, K. NORISUYE, Y. SOHRIN, M. NAKAMURA* (KYOTO UNIVERSITY AND JAPAN SCIENCE AND TECHNOLOGY AGENCY, TOKYO, JAPAN)
 Iron-Catalyzed Aromatic Amination for Nonsymmetrical Triarylamine Synthesis
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Iron-Catalyzed Amination of Aromatic Bromides

Ar¹ = Me, OMe, NMe₂, Cl- and F-substituted (hetero)aromatics
 Ar² = Ph, 4-Tol, 3-Tol, 4-FC₆H₄
 R = Ph, 4-Tol, TMS

Selected examples:

Significance: A novel iron-catalyzed amination reaction of aryl bromides with in situ generated magnesium amides has been disclosed. This new protocol proceeds in xylene or dibutyl ether at elevated temperatures in the presence of lithium bromide and provides diaryl- and triarylamines without the use of expensive and/or toxic metals.

Comment: The authors propose the following mechanism: FeCl₂ reacts with two equivalents of magnesium amide to form monomeric and dimeric iron(II)–diamide complexes, which are in equilibrium with each other. The monomer undergoes an oxidative addition with the aryl bromide to form an iron(IV) intermediate. Reductive elimination affords the product and an iron(II)–monoamide complex. Regeneration of the active species via LiBr-assisted transmetalation with the magnesium amide completes the cycle.

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Category
**Metal-Mediated
 Synthesis**

Key words
 iron
 amination
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of the month