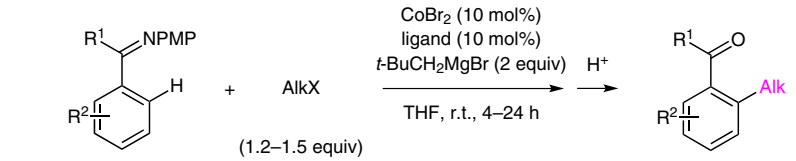
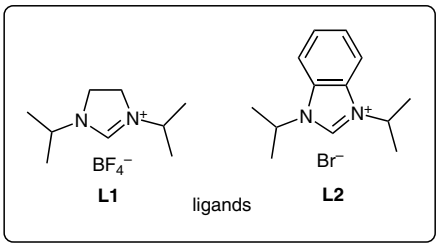
K. GAO, N. YOSHIKAI* (NANYANG TECHNOLOGY UNIVERSITY, SINGAPORE, SINGAPORE)
Cobalt-Catalyzed Ortho Alkylation of Aromatic Imines with Primary and Secondary Alkyl Halides
J. Am. Chem. Soc. **2013**, *135*, 9279–9282.

Cobalt–NHC-Catalyzed *ortho*-Alkylation of Aromatic Imines with Alkyl Halides

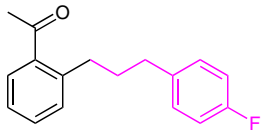


up to 86% yield

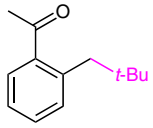
R^1 = H, Me, Et, Cy
R^2 = H, F, Cl, OMe, Ph, OCH_2O, Alk
X = Cl, Br



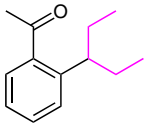
Selected examples:



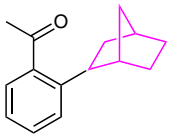
77% yield with **L2**



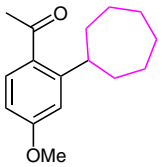
86% yield with **L1**



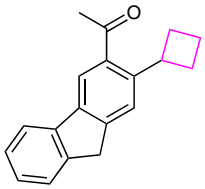
63% yield with **L1**



82% yield with **L1**



81% yield with **L2**



78% yield with **L1**

Significance: A novel method for the direct *ortho*-alkylation of aromatic imines has been disclosed. 10 mol% of cobalt(II) bromide ($CoBr_2$) in combination with an N-heterocyclic carbene (NHC) ligand catalyzes the reaction of an alkyl halide with the aromatic imine to deliver the corresponding *ortho*-alkylated ketones after acidic work-up.

Comment: The activation of the alkyl halide is proposed to occur through single-electron transfer from a cobalt species to generate an alkyl radical. Recombination of the cobalt and the radical centers may cause the C–C bond formation.

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Category
Metal-Mediated Synthesis

Key words
cobalt
alkylation
Grignard reagents

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