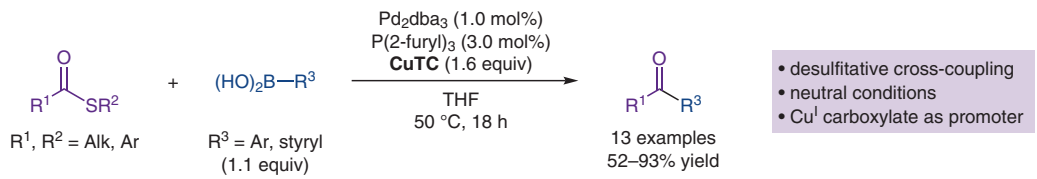
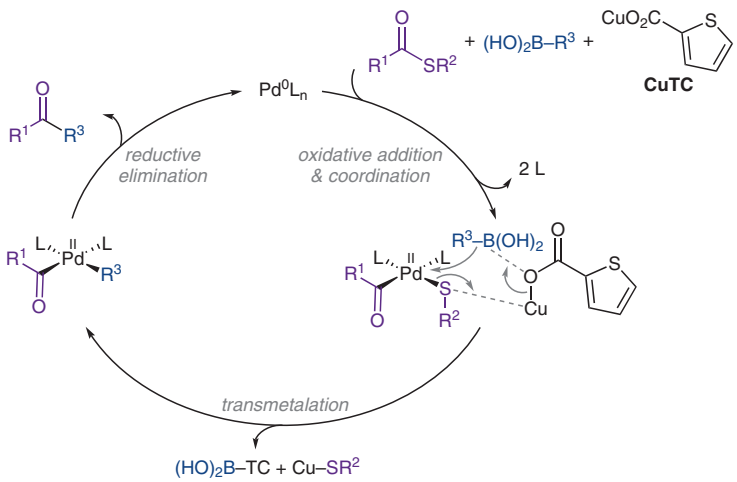
L. S. LIEBESKIND*, J. SROGL* (EMORY UNIVERSITY, ATLANTA, USA)

Thiol Ester–Boronic Acid Coupling. A Mechanistically Unprecedented and General Ketone Synthesis
J. Am. Chem. Soc. **2000**, *122*, 11260–11261, DOI: 10.1021/ja005613q.

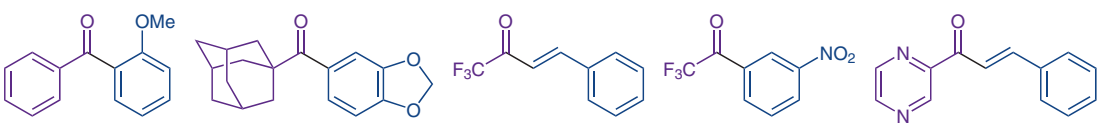
The Liebeskind–Srogl Cross-Coupling



Proposed mechanism:



Selected examples:



88% yield | 52% yield | 93% yield | 63% yield | 81% yield

Significance: In 2000, Liebeskind and Srogl disclosed a copper(I)-promoted palladium-catalyzed cross-coupling of thioesters and boronic acids for the synthesis of ketones under neutral conditions. This base-free desulfitative process is mediated by a palladium(0) catalyst and stoichiometric amounts of a copper(I) carboxylate salt.

Comment: The copper(I) carboxylate CuTC is a key feature of this transformation as it facilitates both the C(sp^2)–S bond cleavage via coordination of the copper center by the sulfur atom and the activation of the boronic acid through coordination of the carboxylate unit to the boron atom. Since its discovery, the Liebeskind–Srogl coupling has been thoroughly studied, and the scope of this transformation has been considerably extended.

Review: H. Prokopcová, C. O. Kappe *Angew. Chem. Int. Ed.***2009**, *48*, 2276–2286.

SYNFACTS Contributors: Martin Oestreich, Hendrik F. T. Klare, Lucie Finck
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Category
Metals in Synthesis

Key words
boronic acids
copper
cross-coupling
ketones
palladium catalysis
thioesters