C.-Z. WU, C.-Y. HE, Y. HUANG, X. ZHANG* (DONGHUA UNIVERSITY, SHANGHAI AND SHANGHAI INSTITUTE OF ORGANIC CHEMISTRY, P. R. OF CHINA)
Thioether-Promoted Direct Olefination of Polyfluoroarenes Catalyzed by Palladium
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Oxidative Olefination of Polyfluoroarenes Catalyzed by Palladium

Overall transformation:

Selected examples:

Competition experiment:

Significance: The dehydrogenative Heck reaction represents a more environmentally friendly variant of the classic Nobel prize winning transformation, as it makes use of non-prefunctionalized substrates. Polyfluoroarenes are important structural motifs, and the development of new methods to incorporate them in an efficient manner is an important endeavor. The report represents a rare example of a thioether promoted C–H functionalization of electron-deficient arenes.

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Comment: The authors report a palladium-catalyzed methyl phenyl sulfide promoted direct olefination of polyfluoroarenes. These previously 'unreactive' substrates undergo facile transformation with the specifically chosen sulfur-containing ligand. Products are obtained in good to excellent yields and with high E/Z selectivities. A competition reaction between pentafluorobenzene and both styrene and *tert*-butyl acrylate show that there is no bias between electron-rich and electron-deficient olefins under the reported conditions.