Oxidative Olefination of Polyfluoroarenes Catalyzed by Palladium

Overall transformation:

\[ \text{polyfluoroarene} + \text{Pd(OAc)}_2 (10 \text{ mol\%}) + \text{Ag}_2\text{CO}_3 (2 \text{ equiv}) + \text{PhSMe} (2.8 \text{ equiv}) \rightarrow \text{ArF} + \text{R} \]

DMF, 120 °C
0.1 mmol scale

Selected examples:

- 80% yield, E/Z = 20:1
- 80% yield, E/Z = 30:1
- 80% yield, E/Z = 20:1
- 72% yield, E/Z = 45:1
- 89% yield, E/Z = 30:1
- 74% yield, E/Z = 28:1
- 45% yield, E/Z = 13:1
- 40% yield

Competition experiment:

- 89% yield, E/Z = 30:1
- 74% yield, E/Z = 28:1
- 45% yield, E/Z = 13:1
- 40% yield

**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.

**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.