**Organocatalytic Chemoselective Reduction of Phosphine Oxides to Phosphines**

**Significance:** Organophosphines represent valuable intermediates, catalysts, and ligands for transition-metal catalysis. Here, the authors report the utilization of inexpensive silanes by Bronsted acid catalysis, which shows broad functional group tolerance towards aldehydes, ketones, olefins, nitriles, and esters. Chemoselectivities of 99:1 for P–O double bonds and retention of the configuration at the P-center were achieved.

**Comment:** The catalytic chemoselective reduction of P–O double bonds (502 kJ/mol) is a formidable challenge in synthetic chemistry. This metal-free protocol under convenient, air-insensitive, and safe reaction conditions for aryl, alkyl, monodentate and bidentate phosphine oxides with its high functional group tolerance indicates possible applications in catalytic Wittig, Appel, and Staudinger reactions.