Asymmetric α-Arylation of Thioamides

**Significance:** α-Amine functionalization is a powerful practical tool for rapid access to substituted heterocycles common to many biologically active compounds. This work contributes to the large body of methods for α-functionalization, a process first rendered asymmetric through lithiation and electrophile trapping (P. Beak, S. T. Kerrick, S. Wu, J. Chu J. Am. Chem. Soc. 1994, 116, 3231), and later expanded to α-amino radical chemistry by Curran and Snieckus. These approaches, in addition to a broad variety of transition-metal-catalyzed processes, demonstrate the importance of the transformation to access value-added products (see Review). In the current report, aryl functional groups were installed with high levels of stereocontrol by coupling boronic acids with thioamides under palladium catalysis. Enantioselectivity was achieved by using a BINOL-derived chiral phosphoric acid.

**Comment:** In addition to the high enantioselectivity of the reaction, nonsymmetric substrates were functionalized with complete regioselectivity, in some cases giving different products to those that would be obtained by the lithiation approach. Speculation as to the basis for the observed regioselectivity would have been of interest. This work demonstrates a large scope for the α-arylation reaction, although it appears less effective for alkylation, thereby providing a complement to the Beak lithiation methodology.

**Review:** K. R. Campos Chem. Soc. Rev. 2007, 36, 1069–1094, and references therein.