Hydroamination of Nonactivated Alkenes

**Significance:** A catalytic amount of Brønsted acid enables high yielding intramolecular hydroaminations of electronically unactivated alkenes with basic amines. Screenings identified phosphoric acid 1 as the most active catalyst for this cycloisomerization. Substrates with ether, nitro, ester, or chloro functionalities are tolerated. By using enantiomerically pure phosphoric acid (R)-1a the authors show an unprecedented example of a metal-free asymmetric hydroamination of nonactivated alkenes, albeit with modest selectivity (er = 58.5:41.5).

**Comment:** This intramolecular addition of an amine to a C–C double bond depicts a direct and atom-economical access to N-heterocycles, which are ubiquitous in natural products as well as biologically active compounds. Most organocatalytic addition of N-nucleophiles to olefins require activation of the alkene functionality. The observed effectiveness of this addition might be due to the intramolecular nature of this cycloisomerization. A screening of different enantiopure phosphoric acids might result in higher enantiomeric ratios.

**Selected examples:**

- Ph1NPh Ph1NPh 93% yield
- Ph1NMe Ph1NPh 85% yield
- Ph1NMe Ph1NPh 53% yield
- Ph1NMe Ph1NPh 72% yield

**Selected examples:**

1: R = SiPh3
(R)-1a: R = 3,5-(F3C)2C6H3

N (R)-1a (20 mol%) Cl2HCCCHCl2, 130 °C, 23 h or 1,4-dioxane, 130 °C, 20 h

N Me Ph Ph N Me Ph Ph

N Me Ph Ph N Me Ph Ph

N Me Ph Ph N Me Ph Ph

N Me Ph Ph N Me Ph Ph

N Me Ph Ph N Me Ph Ph

N Me Ph Ph N Me Ph Ph

N Me Ph Ph N Me Ph Ph

N Me Ph Ph N Me Ph Ph

N Me Ph Ph N Me Ph Ph

N Me Ph Ph N Me Ph Ph