J. HE, Q. SHAO, Q. WU, J.-Q. YU* (THE SCRIPPS RESEARCH INSTITUTE, LA JOLLA, USA)  
Pd(II)-Catalyzed Enantioselective C(sp<sup>3</sup>)–H Borylation  

**Enantioselective Palladium(II)-Catalyzed Borylation**

Selected examples:

- **NHArF**
  - Bpin 78% yield, 95.6% ee (with L2)
  - Bpin 75% yield, 96.4% ee (with L1)
  - Bpin 75% yield, 99.8% ee (with L1)
  - Bpin 77% yield, 97.4% ee (with L1)
  - Bpin 52% yield, 88.3% ee (with L1)
  - Bpin (solvent = MeCN–DCE (4:1))

**Synthetic application:**

- **NHArF**
  - AgNO<sub>3</sub> (20 mol%) Selectfluor 53% yield, 95.6% ee cis-isomer
  - 50 °C, 6 h, TFA, CH<sub>2</sub>Cl<sub>2</sub>–H<sub>2</sub>O
  - Bpin 95.6% ee (with L1)
  - 0 °C to r.t., 2 h, H<sub>2</sub>O<sub>2</sub>, THF
  - NaH<sub>2</sub>P<sub>2</sub>O<sub>7</sub> (aq)
  - KHF<sub>2</sub> MeCN, r.t., 3 h
  - 95% yield

**Proposed asymmetric induction model:**

**Significance:** The authors developed a palladium(II)-catalyzed borylation of cyclic amides by using chiral bidentate ligands. A wide variety of borylated cyclobutanes bearing an amide group were obtained with high selectivities.

**Comment:** A transformation of the product, including the removal of the amide auxiliary, was accomplished to demonstrate the synthetic utility of the reaction. An asymmetric induction model is also proposed.