Asymmetric Miyaura–Michael Reaction with Polymeric Rh/Ag Catalysts

**Preparation of PI/CB Rh/Ag catalyst 2:**
1) carbon black (CB)
2) NaBH₄, diglyme

**Asymmetric 1,4-addition with PI/CB Rh/Ag catalyst 2:**

- **Significance:** Polystyrene-based polymer-incarcerated bimetallic rhodium nanoparticle catalysts PI/CB Rh/Ag 2a–b were prepared from co-polymer 1, carbon black (CB), [Rh(OAc)₃]₂, and AgSbF₆. Asymmetric 1,4-addition of arylboronic acids to enones was carried out with 2 and chiral ligand 3 to give the corresponding ketones in 70–99% yield with 74–98% ee without leaching of rhodium.

- **Comment:** Catalyst 2a was reused 13 times for the reaction of phenylboronic acid with 2-cyclohexenone. After the 10th use, the recovered catalyst was heated at 170 °C to regain its catalytic activity (1st–8th use: >94% yield, 9th use: 67% yield, 10th use: 60% yield, 11th–14th use: >90% yield, with 98% ee in all cycles).