Construction of Quaternary Carbon Stereogenic Centers

**Significance:** The enantioselective construction of quaternary carbon stereogenic centers in acyclic systems remains one of the great challenges. A highly enantioselective rhodium-catalyzed allylic alkylation of allyl benzoate by α-substituted benzyl nitrile anions provides access to acyclic quaternary carbon stereogenic centers in good yields with excellent enantioselectivities.

**Comment:** Interestingly, 15-crown-5 was used as additive to provide a significant improvement in the enantioselectivity. The protocol provides a new approach for the construction of acyclic quaternary carbon stereogenic centers. Furthermore, the nitrile products can be easily transformed into a number of important derivatives.

**Selected examples:**

- **86% yield, 92% ee**
- **77% yield, 92% ee**
- **81% yield, 84% ee**
- **87% yield, 83% ee**
- **76% yield, 93% ee**
- **83% yield, 90% ee**
- **82% yield, 95% ee**
- **81% yield, 92% ee**

**Transformations of the enantioenriched nitrile:**

- **CHO**
  - **92% ee**
  - **84% yield**
- **NH₂**
  - **92% ee**
  - **89% yield**
- **CN**
  - **91% ee**
  - **90% yield**
  - **92% ee**
  - **86% yield**