N–C Aryl Transfer via Umpolung Carbolithiation of Vinyl Ureas

**Significance:** The umpolung carbolithiation of vinyl ureas was shown to result in an N–C aryl transfer allowing a fast access to tertiary alkyl amines. Notably, (E)- and (Z)-alkenyl ureas undergo this carbolithiation–rearrangement sequence diastereospecifically.

**Comment:** This novel tandem reaction represents an important achievement for the synthesis of heavily substituted tertiary amines. The reaction is general, allows the use of various organolithium reagents, and proceeds with electron-rich and electron-poor aryl moieties.

**Selected examples:**

1. **MeHN MeHN 1) RLi, THF, –50 °C 2) NaH, MeI 72–86% yield**

   - **Ar1**
   - **Ar2**

2. **MeHN MeHN 1) RLi, THF, –40 °C 2) MeOH or n-BuOH reflux 54–81% yield**

   - **MeHN**
   - **Ar1**

3. **MeHN MeHN 1) RLi, THF, –40 °C 2) DMPO 3) MeOH 54–75% yield**

   - **MeHN**
   - **Ar1**

4. **MeHN MeHN 1) RLi, PhMe, –40 °C 2) DMPU 3) MeOH 66–75% yield**

   - **MeHN**
   - **Ar1**

5. **MeHN MeHN 1) RLi, PhMe, –40 °C 2) DMPU 3) MeOH 67–70% yield**

   - **MeHN**
   - **Ar1**

**Proposed mechanism:**

- **Carbolithiation**
- **Configurationally stable**
- **Retentive migration**