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.

**Proposed mechanism:**

![Proposed mechanism diagram]

**Selected examples:**

1. **MeHN**
   - ![Example 1](image1)
   - 74% yield
2. **MeHN**
   - ![Example 2](image2)
   - 75% yield
3. **MeHN**
   - ![Example 3](image3)
   - 72% yield
4. **MeHN**
   - ![Example 4](image4)
   - 78% yield

**Selected conditions:**

1. **R Li, THF, –50 °C**
   - 72–86% yield
2. **NaH, MeI**
   - 1) R Li, THF, –40 °C
   - 2) MeOH or n-BuOH reflux
   - 66–75% yield

**Selected reactions:**

1. **Ar1 N Me Ar2**
   - **1) R Li, THF, –40 °C**
   - **2) MeOH or n-BuOH reflux**
   - 54–81% yield
2. **Ar1 N Me Ar2**
   - **1) R Li, THF, –40 °C**
   - **2) DMPU**
   - **3) MeOH**
   - 54–75% yield
3. **Ar1 N Me Ar2**
   - **1) R Li, THF, –40 °C**
   - **2) DMPU**
   - **3) MeOH**
   - 67–70% yield
4. **Ar1 N Me Ar2**
   - **1) R Li, THF, –40 °C**
   - **2) DMPU**
   - **3) MeOH**
   - 67–70% yield

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