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Aerobic Pd-Catalyzed sp³ C–H Olefination: A Route to Both N-Heterocyclic Scaffolds and Alkenes


**Pd-Catalyzed Pyridine-Directed Aerobic Olefination of Unactivated sp³ C–H Sites**

**Significance:** A new palladium/polyoxometalate-catalyzed aerobic olefination of unactivated sp³ C–H bonds has been developed. Nitrogen-containing heterocycles act as directing groups and the products undergo reversible intramolecular Michael addition to form bicyclic nitrogen-containing scaffolds.

**Comment:** The cationic bicyclic products undergo further synthetic transformations. For example, PtO₂-catalyzed hydrogenation yields piperidines, and reduction with NaBH₄ gives 1,2,3,6-tetrahydropyridines. The pyridinium products can also be converted into the corresponding alkenes under basic conditions.

**Selected examples:**

<table>
<thead>
<tr>
<th>R¹</th>
<th>R²</th>
<th>X</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ph, Me, OMe, CF₃</td>
<td>CO₂Et, CO₂Bu, CO₂Bn, CO₂H, CONMe₂, COEt</td>
<td>OAc, OTf, BF₄⁻</td>
</tr>
</tbody>
</table>

Selected examples:

- **EtO₂C⁻**
  - **TIO⁻**
  - 89% yield
- **EtO₂C⁻**
  - **BF₄⁻**
  - 71% yield
- **EtO₂C⁻**
  - 75% yield
- **HO₂C⁻**
  - **BF₄⁻**
  - 69% yield

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