**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.

**Equation:**

1) Pd(MeCN)₄(BF₄)₂ (10 mol%)  
H₂[PMo₁₁VO₄₀] (3 mol%)  
NaOAc (10 mol%) or NaOTf (1.1 equiv)  
air, AcOH, 110 °C, 18 h  
2) in some cases: aq NaBF₄

**Selected examples:**

- **89% yield**
- **71% yield**
- **75% yield**
- **69% yield**

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