Pd-Catalyzed Pyridine-Directed Aerobic Olefination of Unactivated sp<sup>3</sup> C–H Sites

**Significance:** A new palladium/polyoxometalate-catalyzed aerobic olefination of unactivated sp<sup>3</sup> 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, PtO<sub>2</sub>-catalyzed hydrogenation yields piperidines, and reduction with NaBH<sub>4</sub> gives 1,2,3,6-tetrahydropyridines. The pyridinium products can also be converted into the corresponding alkenes under basic conditions.

**Selected examples:**

![Selected examples](image)

**Equation:**

\[
\text{R}^1 \text{Me/C}_2\text{H}_4\text{CO}_2\text{Et} + \text{Me/C}_2\text{H}_4\text{CO}_2\text{Et} \xrightarrow{\text{air, AcOH, 110 °C, 18 h}} \text{Me/C}_2\text{H}_4\text{CO}_2\text{Et} \]

up to 92% yield

- **R<sub>1</sub>** = Ph, Me, OMe, CF<sub>3</sub>
- **R<sub>2</sub>** = CO<sub>2</sub>Et, CO<sub>2</sub>Bu, CO<sub>2</sub>Bn, CO<sub>2</sub>H, CONMe<sub>2</sub>, COEt
- **X** = OAc, OTf, BF<sub>4</sub>-