Ruthenium-Catalyzed Lemieux–Johnson-Type Oxidation of Olefins

**Significance:** The authors report a ruthenium-based catalyst for the Lemieux–Johnson-type oxidation of olefins, providing, after carbon–carbon bond cleavage, the corresponding aldehydes or ketones. The key feature is the designed ruthenium complex which combines a dynamic donor ability, originating from the bisPYA ligand, with highly redox active ruthenium.

**Comment:** This method outperforms most of the state-of-the-art systems due to the exceptionally efficient ruthenium catalyst. This metal complex can achieve turnover frequencies of 1,000,000 h⁻¹, turnover numbers of several millions and is readily prepared in a four-step synthesis utilizing commercially available starting materials.

**Preparation of the ruthenium catalyst:**

1. diethyl oxalate (0.5 equiv) 150 °C, 1 h
2. MeI (3.6 equiv) MeCN, reflux, 18 h
3. KPF₆ (2.4 equiv) H₂O, 25 °C, 20 min

**Selected examples:**

- **100% conversion 100% selectivity**
- **100% conversion 100% selectivity**
- **100% conversion 87% selectivity**
- **100% conversion 76% selectivity**

**Selectivity towards carboxyl product (in %) vs. overoxidation to the corresponding acid.**