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A Green Protocol for the N-Formylation of Amines Using Molybdate Sulfuric Acid as a Reusable Solid Catalyst

**N-Formylation of Amines Using Molybdate Sulfuric Acid**

Significance: Molybdate sulfuric acid (MSA) catalyzed the N-formylation of amines with orthoformates to give the corresponding formamide derivatives in up to 95% yield (19 examples). In the N-formylation of aniline with triethyl orthoformate, the catalyst was recovered by filtration and reused three times with a slight loss of catalytic activity (1st reuse: 87% yield, 3rd reuse: 80% yield).

Comment: The catalytic activity of MSA was superior to that of the other catalysts (ZnO, ZrOCl₂, MgBr₂, ZnCl₂, and H₂SO₄). The authors have reported previously the preparation of molybdate sulfuric acid and its application to the synthesis of phenazines and quinoxalines (Polycycl. Aromat. Compd. 2011, 31, 97).

Selected examples:

- **90% yield (R = Et)**
- **85% yield (R = Me)**

- **95% yield (R = Et)**
- **90% yield (R = Me)**

- **95% yield (R = Et)**
- **92% yield (R = Et)**
- **90% yield (R = Et)**

- **67% yield (R = Et)**
- **70% yield (R = Me)**

- **87% yield (R = Et)**

- **80% yield (R = Et)**
- **80% yield (R = Me)**

- **65% yield (R = Et)**
- **73% yield (R = Et)**