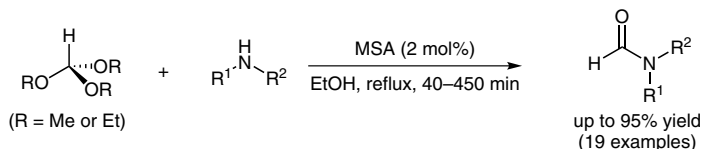


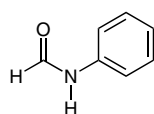
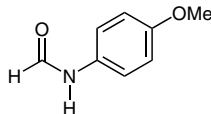
B. KARAMI,* M. FARAHI, F. PAM (YASOUJ UNIVERSITY, IRAN)

A Green Protocol for the N-Formylation of Amines Using Molybdate Sulfuric Acid as a Reusable Solid Catalyst
Tetrahedron Lett. **2014**, *55*, 6292–6296.

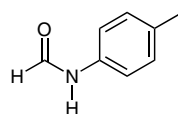
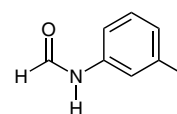
N-Formylation of Amines Using Molybdate Sulfuric Acid



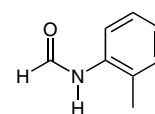
Selected examples:

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

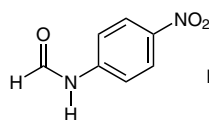
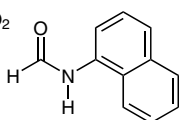
95% yield (R = Et)

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

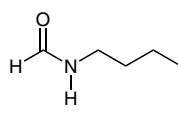
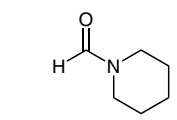
92% yield (R = Et)



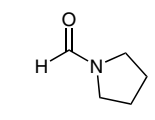
90% yield (R = Et)

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)

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).