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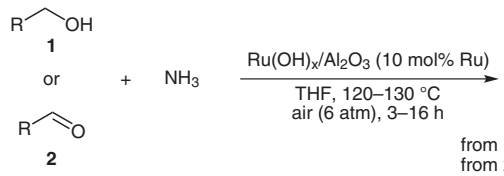
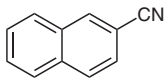
Catalytic Oxidative Synthesis of Nitriles Directly from Primary Alcohols and Ammonia
Angew. Chem. Int. Ed. **2009**, *48*, 6286-6288.

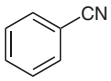
Synthesis of Nitriles from Primary Alcohols and NH_3 with $Ru(OH)_x/Al_2O_3$



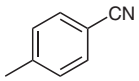
from **1**: 13 examples (65–96% yield)
from **2**: 7 examples (71–93% yield)



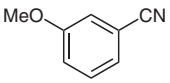
3a (from **1a**: 120 °C, 3 h, 96% yield)
(from **2a**: 120 °C, 3 h, 93% yield)



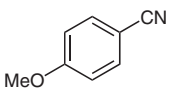
3b (from **1b**: 120 °C, 5 h, 72% yield)



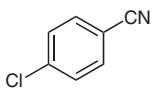
3c (from **1c**: 120 °C, 5 h, 80% yield)



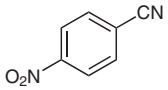
3d (from **1d**: 120 °C, 5 h, 85% yield)



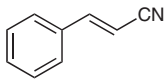
3e (from **1e**: 120 °C, 5 h, 83% yield)
(from **2e**: 120 °C, 5 h, 85% yield)



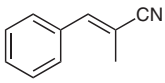
3f (from **1f**: 120 °C, 5 h, 92% yield)
(from **2f**: 120 °C, 5 h, 90% yield)



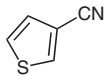
3g (from **1g**: 120 °C, 6 h, 82% yield)



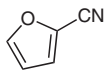
3h (from **1h**: 120 °C, 5 h, 82% yield)
(from **2h**: 120 °C, 5 h, 82% yield)



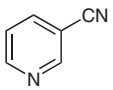
3i (from **1i**: 120 °C, 5 h, 76% yield)



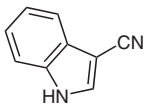
3j (from **1j**: 120 °C, 7 h, 80% yield)



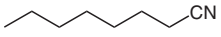
3k (from **1k**: 120 °C, 7 h, 67% yield)



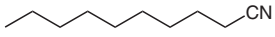
3l (from **1l**: 120 °C, 6 h, 81% yield)
(from **2l**: 120 °C, 6 h, 76% yield)



3m (from **1m**: 130 °C, 12 h, 65% yield)



3n (from **2n**: 130 °C, 16 h, 71% yield)



3o (from **2o**: 130 °C, 16 h, 81% yield)

Significance: An Al_2O_3-supported ruthenium hydroxide catalyst ($Ru(OH)_x/Al_2O_3$) promoted the reaction of primary alcohols **1** or aldehydes **2** with ammonia to give the corresponding nitriles **3** in 65–96% yield (from **1**, 13 examples; from **2**, 7 examples). No leaching of ruthenium was observed by ICP-AES analysis after the reaction.

Comment: The authors have previously reported the preparation and characterization of $Ru(OH)_x/Al_2O_3$ and its application to the aerobic oxidative dehydrogenation of alcohols (*Angew. Chem. Int. Ed*. **2002**, *41*, 4538; *Chem. Eur. J*. **2003**, *9*, 4353). The catalytic activity of $Ru(OH)_x/Al_2O_3$ was superior to that of the other supported catalysts for the formation of **3a** from **1a** [$Au(OH)_x/Al_2O_3$: 10%, $Pd(OH)_x/Al_2O_3$: <1%, $Pt(OH)_x/Al_2O_3$: <1%, $Rh(OH)_x/Al_2O_3$: <1%, Ru/C: 22%, RuHAP: 4%].

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Category
Polymer-Supported Synthesis

Key words
nitriles
primary alcohols
ammonia
ruthenium
aluminum oxide