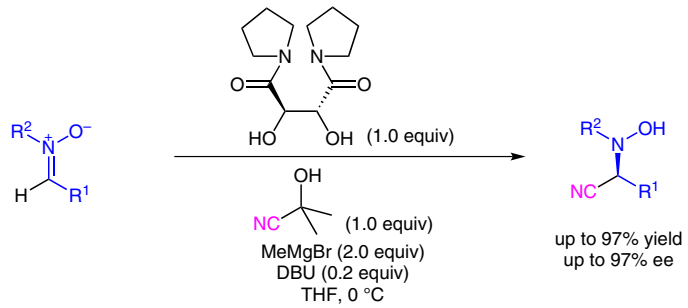
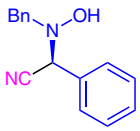
T. SAKAI, T. SOETA, K. ENDO, S. FUJINAMI, Y. UKAJI* (KANAZAWA UNIVERSITY, JAPAN)
Magnesium–Tartramide Complex Mediated Asymmetric Strecker-Type Reaction of Nitrones Using Cyanohydrin
Org. Lett. **2013**, *15*, 2422–2425.

Asymmetric Strecker-Type Reaction of Nitrones Using Cyanohydrin

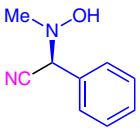


R^1 = Ph, PMP, 4-ClC_6H_4, 4-BrC_6H_4, 1-Naph, 2-Naph, Me, Cy, *t*-Bu
R^2 = Bn, Me, Ph, $CHPh_2$

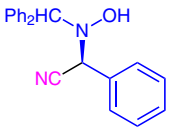
Selected examples:



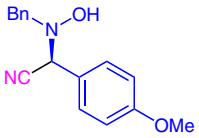
80% yield
89% ee



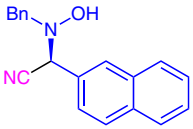
47% yield
72% ee



58% yield
96% ee

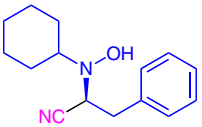


72% yield
90% ee



73% yield
96% ee

94% yield
97% ee



97% yield
73% ee

88% yield
93% ee

Significance: An asymmetric Strecker-type reaction of various nitrones with acetone cyanohydrin using a magnesium–(*R*,*R*)-tartramide complex was developed to successfully prepare optically active (*S*)-α-amino nitrile derivatives in excellent yield. Thereby, the acetone cyanohydrin serves as a less harmful and easy-to-handle synthetic equivalent of HCN and TMSCN.

Comment: The reaction mechanism is proposed to proceed as follows: first, the reaction of cyanohydrin and the (*R*,*R*)-tartramide with MeMgBr forms the corresponding bromomagnesium salts. The tartramide magnesium salt might be further deprotonated by DBU to form a magnesium ate-complex which coordinates the nitrone. Transfer of the cyano group from the cyanohydrin magnesium salt to the nitrone occurs from the *re* face, forming specifically the (*S*)-enantiomer.

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Category
Metal-Mediated Synthesis

Key words
magnesium
tartramide
Strecker reaction
nitrones
cyanohydrin