Asymmetric Catalysis with MOFs Prepared via Chiral Induction Effect

**Significance:** Homochiral metal-organic frameworks (MOFs) were prepared through the chiral induction effect. Thus, the homochiral crystallization of Ce(NO₃)₃·6H₂O and H₂MDIP was performed with L- or D-BCIP as chiral inducers in water to give Ce-MDIP1 and Ce-MDIP2 (where no BCIP was installed), which exhibited Cotton effects exactly opposite to each other. Ce-MDIPs promoted the cyanosilylation to give the corresponding cyanohydrin derivatives quantitatively with 93 to >98% ee.

**Comment:** Ce-MDIP1 was reused twice without significant loss of catalytic activity. Cd-TBT was also prepared from Cd(ClO₄)·6H₂O and H₃TBT under similar conditions. Cd-TBT mediated the direct aldol reaction of aldehydes and cyclohexanone to afford the corresponding β-hydroxy ketones in 8–97% yield with 58–61% ee in ten days.

**Preparation of homochiral MOF catalysts:**

Ce(NO₃)₃·6H₂O + H₂MDIP (0.5 equiv) + L- or D-BCIP (1.0 equiv) H₂O, 100 °C, 3 d, pH 6 Et₃N

Ce-MDIP1 60% yield

Ce(NO₃)₃·6H₂O + H₂MDIP (1.0 equiv) L- or D-BCIP (1.0 equiv) H₂O, 100 °C, 3 d, pH 6 Et₃N

Ce-MDIP2 56% yield

Cd(ClO₄)·6H₂O + H₂TBT (1.0 equiv) + L-BCIP (1.0 equiv) H₂O, 120 °C, 3 d Et₃N (2.9 equiv)

Cd-TBT 65% yield

**Cyanosilylation and aldol reaction using homochiral MOF catalysts:**

Ar-H + OTMS + TMSCN + Ce-MDIP (2 mol %) MeCN, 24 h, r.t. N₂

Entry  Ar  Ce-MDIP1  Ce-MDIP2
1  Ph  93  94
2  4-MeO  91  97
3  1-Naph  98 >98
4  2-Naph >98 >98

**The catalytic cyanosilylation:**

Entry  Ar  Yield (%)  ee (%)
1  2-O₂N-C₆H₄  42  60
2  3-O₂N-C₆H₄  77  61
3  4-O₂N-C₆H₄  97  58
4  1-Naph  8  n.d.

(values represent the major isomer)