D. DANG, P. WU, C. HE, Z. XIE, C. DUAN* (DALIAN UNIVERSITY OF TECHNOLOGY, P. R. OF CHINA)

Homochiral Metal-Organic Frameworks for Heterogeneous Asymmetric Catalysis
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Category

Polymer-Supported Synthesis

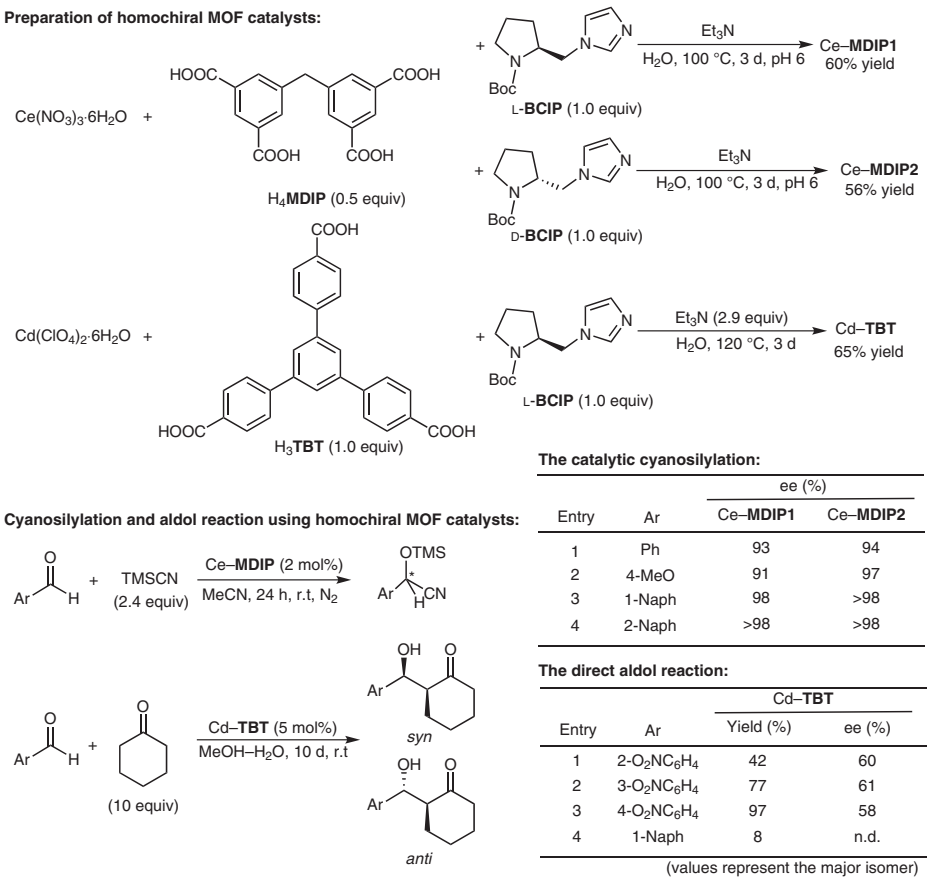
Key words

homochiral metal-organic frameworks

cyanosilylation

cerium

Asymmetric Catalysis with MOFs Prepared via Chiral Induction Effect



The catalytic cyanosilylation:

Entry	Ar	ee (%) Ce–MDIP1	ee (%) Ce–MDIP2
1	Ph	93	94
2	4-MeO	91	97
3	1-Naph	98	>98
4	2-Naph	>98	>98

The direct aldol reaction:

Entry	Ar	Cd–TBT Yield (%)	Cd–TBT ee (%)
1	2-$O_2NC_6H_4$	42	60
2	3-$O_2NC_6H_4$	77	61
3	4-$O_2NC_6H_4$	97	58
4	1-Naph	8	n.d.

(values represent the major isomer)

Significance: Homochiral metal-organic frameworks (MOFs) were prepared through the chiral induction effect. Thus, the homochiral crystallization of $Ce(NO_3)\cdot 6H_2O$ and H_4MDIP 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 $Cd(ClO_4)\cdot 6H_2O$ and H_3TBT 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.

SYNFACTS Contributors: Yasuhiro Uozumi, Yoichi M. A. Yamada, Yoshinari Yuyama
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