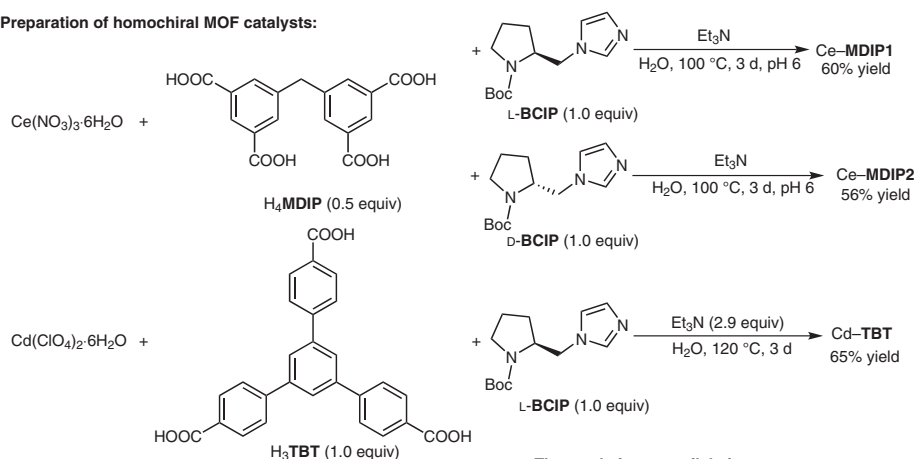
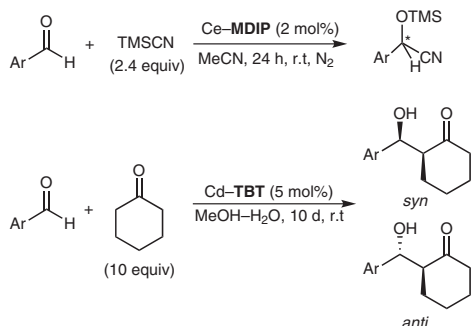


Asymmetric Catalysis with MOFs Prepared via Chiral Induction Effect

Preparation of homochiral MOF catalysts:



Cyanosilylation and aldol reaction using homochiral MOF catalysts:



The catalytic cyanosilylation:

Entry	Ar	ee (%)	
		Ce-MDIP1	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 (%)	ee (%)
1	2-O ₂ NC ₆ H ₄	42	60
2	3-O ₂ NC ₆ H ₄	77	61
3	4-O ₂ NC ₆ H 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 $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ 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 $\text{Cd}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ 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.

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