## Dibutyltin Dimethoxide and Ag(I)-BINAPCatalyzed Aldol Reactions of Ketones

## Key words

## aldol reaction

## ketones

## silver(I)-BINAP

tin

## Selected examples:


$86 \%$ yield, $\mathrm{dr}=83: 17,90 \%$ ee
(R)-BINAP (10 mol\%) AgOTf ( $20 \mathrm{~mol} \%$ )
$\mathrm{Bu}_{2} \mathrm{Sn}(\mathrm{OMe})_{2}(8 \mathrm{~mol} \%)$
MeOH (5 equiv)
THF, 3 A MS, $-20^{\circ} \mathrm{C}$


$58 \%$ yield, $d r=97: 3,89 \%$ ee

$38 \%$ yield, $\mathrm{dr}>99: 1,93 \%$ ee

Asymmetric aldol reaction of diketene with methyl benzoylformate:


Proposed catalytic cycle:



Significance: The authors have reported a new asymmetric aldol reaction of alkenyl trichloroacetates with $\alpha$-keto esters by using dibutyltin dimethoxide and $\mathrm{Ag}(\mathrm{I})$-BINAP complex in the presence of methanol. The aldol products were obtained in good to excellent yields and up to $93 \%$ ee. This methodology was further extended to the reaction of diketene with methyl benzoylformate.

Comment: Previously, the authors reported that dibutyltin dimethoxide acts as a catalyst in the aldol reaction of alkenyl trichloroacetates with aldehydes (Tetrahedron Lett. 2003, 44, 7163). In this paper, they have extended this method to $\alpha$-keto esters. It is interesting that the addition of a catalytic amount of silver(I) bidentate phosphine complex remarkably accelerated the aldol reaction.

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[^0]:    synfacts Contributors: Hisashi Yamamoto, Cheol Hong Cheon
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