# Resin-Bound Pyrrolidine Catalysts for Enamine-Mediated Reactions 



2


3
a: $R^{1}=5-F, n=2$
b: $R^{1}=4-O E t, n=1$
c: $\mathrm{R}^{1}=4-\mathrm{OMe}, \mathrm{n}=2$
d: $R^{1}=4-F, n=2$
e: $R^{1}=6-O M e, n=1$
f: $R^{1}=5-E t, n=1$


5a-f
For 1:
5a ( $86 \%$ yield, $96 \%$ ee)
5b ( $78 \%$ yield, $97 \%$ ee)
5 c ( $71 \%$ yield, $95 \%$ ee)
5d ( $83 \%$ yield, $94 \%$ ee)
5 ( $86 \%$ yield, $93 \%$ ee)
5 ( $90 \%$ yield, $95 \%$ ee)


ent-5b-f

For 2:
ent-5b (83\% yield, 99\% ee) ent-5c (77\% yield, 96\% ee) ent-5d ( $81 \%$ yield, $98 \%$ ee) ent-5e ( $89 \%$ yield, $98 \%$ ee) ent-5f (83\% yield, $97 \%$ ee)


5g, h
For 1:
$5 \mathbf{g}$ ( $76 \%$ yield, $92 \%$ ee)
5h (89\% yield)

ent-5g, h
For 2:
ent-5g ( $80 \%$ yield, $95 \%$ ee) 5h (94\% yield)

Significance: Tentagel-bound asymmetric pyrrolidine catalysts $\mathbf{1}$ and $\mathbf{2}$ are reported for the preparation of optically active chromanones $\mathbf{5}$. The catalysts mediated the asymmetric tandem aldolMichael reactions with high enantioselectivity and complete diastereoselectivity. Thus, the reaction of $\mathbf{3}$ and cycloalkanones ( $\mathbf{4}$ and $\mathbf{6}$ ) was carried out with $\mathbf{1}$ in MeOH . The reaction mixture was then heated under microwave irradiation to give 5a-h in $71-90 \%$ yield with up to $97 \%$ ee (8 examples). The reaction with $\mathbf{2}$ under similar conditions afforded ent-5b-g and $\mathbf{5 h}$ in 77-94\% yield with up to $99 \%$ ee (7 examples).

Comment: The polymeric catalysts were also effective for kinetic resolution of racemic 3-methylcycloalkanones $\mathbf{4}$ with $\mathbf{3}$ (2 equiv) to give the unreacted 3-methylcycloalkanone in 35-43\% yield with 95-99\% ee. Enantioselective aldol, Michael, and Robinson annulations, as well as Mannich reactions with catalysts $\mathbf{1}$ and $\mathbf{2}$ are also described.

[^0]Polymer-Supported Synthesis

## Key words

organocatalysis


[^0]:    synfacts Contributors: Yasuhiro Uozumi, Yoichi M. A. Yamada, Hidetoshi Ohta
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