## Asymmetric Allylic Substitution in Water with a Polymeric Pd Catalyst

## Category

Polymer-Supported Synthesis

## Key words

$\pi$-allylpalladium
asymmetric
aqueous media
PS-PEG polymer
supports



$0-17 \%$ yield

$+$



$43-64 \%$ yield, $90-99 \%$ ee

$+\begin{gathered}\text { ArOH } \\ (1.0 \mathrm{~mol} \text { equiv })\end{gathered}$
$\mathrm{Ar}=\mathrm{Ph}, 2-\mathrm{BnOC}_{6} \mathrm{H}_{4}, 2-\mathrm{ClC}_{6} \mathrm{H}_{4}, 2-\mathrm{BrC}_{6} \mathrm{H}_{4}, 2,6-\mathrm{diMeC} \mathrm{H}_{3}, 3-\mathrm{MeOC}_{6} \mathrm{H}_{4}, 4-t-\mathrm{BuC}_{6} \mathrm{H}_{4}$

 $\overline{\mathrm{Pd}}{ }^{*}$

Significance: Asymmetric $\pi$-allylic substitution of meso-1,4-diacetoxycycloalkenes was performed with an amphiphilic PS-PEG resin-supported chiral phosphine-palladium complex. Thus, the reaction of cis-1,4-diacetoxycyclopentene (meso-1) with diethyl malonate, dibenzylamine and phenols in water gave the corresponding 1 -acetoxy-4substituted cyclopentenes 2a-i with 90-99\% ee in 43-64\% yield. Cyclohexenyl ester (meso-4) also underwent etherification with phenol to give $\mathbf{5}$ in $37 \%$ yield ( $95 \%$ ee) and $11 \%$ of 6.

Comment: The authors have reported earlier the preparation and utility of the polymeric chiral phosphine-palladium complex used here (J. Am. Chem. Soc. 2001, 123, 2919; Org. Lett. 2004, 6, 281; Org. Lett. 2005, 7, 291; Tetrahedron: Asymmetry 2006, 17, 161; J. Org. Chem. 2006, 71, 8644). The reaction pathway giving high enantiomeric excess of the monosubstituted products includes kinetic resolution steps forming disubstituted 3.

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