

## VIII-I Green and Risk-Free Catalysis

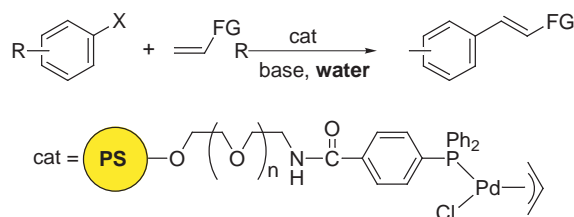
Catalytic organic transformations under mild, safe, and green conditions is an important goal in synthetic organic chemistry. We recently reported that several palladium-catalyzed reactions, including  $\pi$ -allylic substitution, carbonylation, the Heck reaction, and Suzuki-Miyaura cross-coupling, took place in water by use of palladium-phosphine complexes bound to an amphiphilic polystyrene-poly(ethylene glycol) graft copolymer (PS-PEG) resin. Rhodium-catalyzed hydroformylation, cyclotrimerization of alkynes, and Michael-type addition of arylboronic acids were also found to proceed smoothly in water. Here we wish to report that Heck reaction, Sonogashira reaction, Wacker reaction were successfully examined in water by use of PS-PEG resin-supported transition metal complexes.

### VIII-I-1 Heck Reaction in Water with Amphiphilic Resin-Supported Palladium-Phosphine Complexes

UOZUMI, Yasuhiro; KIMURA, Tsutomu

[*Synlett* 2045–2048 (2002)]

The Heck reaction of various aryl halides and alkenes took place in water in the presence of an amphiphilic polystyrene-poly(ethylene glycol) resin-supported palladium-phosphine complex to give the corresponding styrene derivatives in quantitative yields.



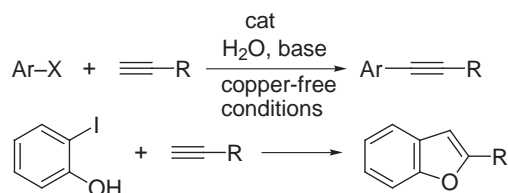
Scheme 1.

### VIII-I-2 The Sonogashira Reaction in Water with an Amphiphilic Resin-Supported Palladium-Phosphine Complex under Copper-Free Conditions

UOZUMI, Yasuhiro; KOBAYASHI, Yukinari

[*Heterocycles* 59, 71–74 (2003)]

The Sonogashira reaction of aryl halides with terminal alkynes was catalyzed by an amphiphilic polystyrene-poly(ethylene glycol) (PS-PEG) resin-supported palladium-phosphine complex in water to give the corresponding aryl-substituted alkynes in high yields under copper-free conditions. Reaction of *o*-iodophenol with terminal alkynes under Sonogashira conditions gave benzofuran derivatives in one step.



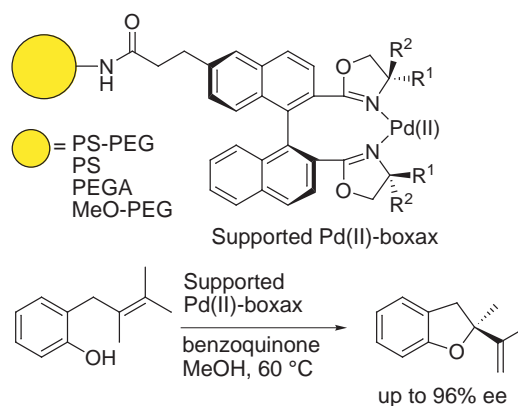
Scheme 1.

### VIII-I-3 Polymer-Supported 2,2'-Bis(oxazolin-2-yl)-1,1'-Binaphthyls (boxax): Immobilized Chiral Ligands for Asymmetric Wacker-Type Cyclizations

HOCHE, Heiko; UOZUMI, Yasuhiro

[*Synlett* 2049–2053 (2003)]

Homochiral 2,2'-bis(oxazolin-2-yl)-1,1'-binaphthyl (boxax) ligands were anchored on various polymer supports including PS-PEG, PS, PEGA, and MeO-PEG via selective monofunctionalization at the 6-position of the binaphthyl backbone. Palladium(II) complexes of the supported boxax ligands catalyzed Wacker-type cyclization of 2-(2,3-dimethyl-2-butenyl)phenol to give 2-methyl-2-isopropenyl-2,3-dihydrobenzofuran with up to 96% ee.



Scheme 1.