Many reports on water-compatible palladium catalysts have appeared in the recent literature. For hydrophobic substrates, mixtures with pure water are biphasic, and it is widely not regarded that the elusive locality of the catalytic process (in water, the organic layer, or at the phase boundary) has an important impact on the mechanism and efficiency of the reaction. In the present work, for the first time systematic variation of reaction parameters has been performed for Suzuki coupling experiments with chloro- and bromoarenes in pure water. The investigations are not only aimed at the factors influencing the catalytic activity, but also at the effects that may occur particularly in water/organic biphasic media, and on the question as to in which of the two liquid phases the reaction takes place. These investigations have revealed that dilution of the base (in the aqueous layer) and the Pd species (in the organic layer) are detrimental to the reaction, and that phase-transfer processes play a major role in the overall mechanism. A series of experiments with variation of parameters like precatalyst hydrophilicity, organic and water phase volume, additives, stirring rate, base concentration, and so forth, indicate that for the systems under study the reaction occurs in the organic layer. The water phase needs to be present to dissolve and provide polar reactants, and re-absorb side products. The results encourage to
pay more regard to the question of phase locality of coupling reactions in water in general.