

S09-2 Development of Site-Selective Cross-Coupling Using Oligoarene-Type Phosphines

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Site-selective reaction of halogenated benzene derivatives is one of the most powerful method for the practical synthesis of multisubstituted arenes. However, only a few examples of such reactions have been reported so far. In most of these cases, the site-selectivity is controlled by the electronic effect, and the reactions mainly occur at less electronically deficient carbon. For the site-selective reaction to proceed in no relation to the structure of the substrate and the electronic or steric property of the reaction site, the catalyst which binds the substrate and makes the desired position close to the catalytic center seems efficient. Therefore, we designed the ligand having both substrate binding part and transition metal binding part on the oligoarene chain. Oligoarene framework is expected to facilitate positioning the substrate properly and adjusting the catalytic activity. After investigation of several ligands, those remarkably accelerating the reaction of Br or Cl group at ortho position of phenols and anilines were identified. Kinetic studies indicate the reaction proceeds in Michaelis-Menten type mechanism, which is not observed in the reaction using the other simple phosphines such as PCy₃. We hope that this knowledge of catalyst-controlled site-selective reaction pave the way to the research on chemical syntheses.