A Practical Method for the Vinylation of Aromatic Halides Using Inexpensive Organosilicon Reagents

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The preparation of styrenes by palladium-catalyzed cross-coupling of aromatic iodides and bromides with divinyltetramethyldisiloxane (DVDS) in the presence of inexpensive silanolate activators has been developed. To facilitate the discovery of optimal reaction conditions, Design of Experiment protocols were used. By the guided selection of reagents, stoichiometries, temperatures, and solvents the vinylation reaction was rapidly optimized with three stages consisting of ca. 175 experiments (of a possible 1440 combinations). A variety of aromatic iodides undergo cross-coupling at room temperature in the presence of potassium trimethylsilanoate using $Pd(dba)_2$ in DMF in good yields. Triphenylphosphine oxide is needed to extend catalyst lifetime. Application of these conditions to aryl bromides was accomplished by the development of two complementary protocols. First, the direct implementation of the successful aryl iodide conditions at elevated temperature in THF provided the corresponding styrenes in good to excellent yields. Alternatively, the use of potassium tri*ethyl*silanolate and a bulky "Buchwald-type" ligand allows for the vinylation reactions to occur at or just above room temperature. A wide range of bromides underwent coupling in good yields for each of the protocols described.