Preparation of BMIM BF_4:

To a dry round-bottomed flask under nitrogen was added 40 mL (0.49 mol) of 1-methylimidazole and 51 mL (0.49 mol) *n*-butylchloride. The reaction mixture was stirred at 75-85 °C for 72 h. The resulting pale yellow, viscous liquid was washed with ethyl acetate (3*75 mL). The remaining ethyl acetate was removed by drying on a vacuum line overnight. The resultant white solid was dissolved in 250 mL of water and 79 mL (0.635 mol) of 50% aqueous HBF_4 was added dropwise over 60 min. The reaction was stirred for an additional 12 h at ambient temperature and was then extracted with CH_2Cl_2 (2*200 mL). The organic layer was washed with water (50 mL aliquots) until the aqueous washes were no longer acidic. The ionic liquid was dried in a vacuum oven overnight at 80-90 °C to afford 96.6 g (95%) of a pale yellow liquid that was used without further purification.

Representative procedures for Stille coupling:

Pd (II) catalyst system:

To a dry round-bottomed flask under nitrogen was sequentially added 235.9 mg (1.00 mmol) of 2-iodo-3-methyl-2-cyclohexen-1-one, 19.0 mg (0.100 mmol) of copper(I) iodide, 31.0 mg (0.100 mmol) of triphenylarsine, and 19.0 mg (0.0500 mmol) of bis(benzonitrile)palladium(II) chloride. This mixture was dissolved in 1mL of BMIM BF_4 and was immediately lowered into an oil-bath maintained at 80 °C. To this solution was added 0.35 mL (1.200 mmol) of tributylvinyltin. After stirring for 2 h, the reaction mixture was extracted with diethyl ether (10*10 mL). The combined organic layers were washed by saturated aqueous potassium fluoride (3*30 mL) The aqueous layers were combined and back-extracted with diethyl ether (2*20 mL). The combined organic layers were dried over magnesium sulfate, filtered, and concentrated *in vacuo*. The resulting oily residue was purified by flash column chromatography (5:95, then 1:9 EtOAc/Hexanes as eluent) to afford 90.3 mg (82%) of 3-methyl-2-vinylcyclohexenone as a pale yellow oil.

Pd (0) catalyst system:

To a dry round-bottomed flask under nitrogen was sequentially added 0.11 mL (1.0 mmol) of bromobenzene and 57.8 mg (0.050 mmol) of tetrakis(triphenylphosphine)palladium(0). This mixture was dissolved in 1 mL of BMIM BF_4 and was immediately lowered into an oil-bath maintained at 80 °C. To this solution was added 0.343 mL (1.05 mmol) of tributylphenyltin. After stirring for 18 h, the reaction mixture was extracted with diethyl ether (10*10 mL). The combined organic layers were washed by saturated aqueous potassium fluoride (3*30 mL) The aqueous layers were combined and then back-extracted with diethyl ether (2*20 mL). The combined organic layers were dried over magnesium sulfate, filtered, and concentrated *in vacuo*. The resulting oily residue was purified by flash column chromatography (hexanes as eluent) to afford 138.6 mg (90%) of biphenyl as a white solid.