Supplementary Information

On the role of additive in alkyl-alkyl Negishi cross-coupling

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General Experimental

All reagents were purchased from commercial sources and used without further purification. 1,3-Dimethyl-2-imidazolidinone (DMI) was purchased from Fluka, stored over 4Å molecular sieves, and handled under Argon. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl radical prior to use. All reaction vials (screw-cap threaded, caps attached, 17 X 60 mm) were purchased from Fischer Scientific. Gas chromatography was rerecorded on a Varian Series GC/MS/MS 4000 System (Factor Four capillary column, VF-5MS, 5% phenyl 95% dimethylpolysiloxane; length: 30 m, diameter: 0.25 mm, film thickness: 0.25μm). The reported conversions are quantified over calibrated areas of undecane (internal standard), 3-bromo-1-phenylpropane and 1-phenylheptane.

Synthetic Procedures

Typical procedure for Table 1: In a glove-box, a 3 mL screw-cap threaded vial was charged with Pd-PEPPSI-IPr [(1,3-Diisopropylimidazol-2-ylidene)(3-chloropyridyl)palladium(II) dichloride] (3.4 mg, 0.6 mol%) and X mg of an additive (1.6 mmol, 2.0 equiv., see Table 1). The vial was sealed with a septum and removed from the glove-box. THF (2.0 mL) was added via syringe. After stirring for 5–10 minutes at room temperature (to maximize additive dissolution), *n*-butylzinc bromide (1.0 mL of a 0.8 M solution in DMI, 0.8 mmol, 1.0 equiv.) was added, followed immediately by 3-bromo-1-phenylpropane (76 μL, 0.5 mmol, 0.63 equiv.) and *n*-undecane (50 μL, GC/MS internal standard). The septum was replaced with a Teflon®-lined screw cap under a cone of argon and the reaction stirred at room temperature for 2 h.

Typical procedure for Figure 1: Reaction conditions and set-up are identical to those outlined above. The $ZnBr_2$ (2.0–X equiv., and/or LiBr (X equiv.) were stored and weighed in a glove box.

GC/MS analysis method: Approximately 200 μL of the reaction mixture were removed via syringe and passed through a plug of silica gel using hexanes as the eluent. The filtrate was collected and diluted with ethyl acetate (1 mL) and was subsequently analyzed by GC-MS.