Transition-Metal Free Suzuki –Type Coupling Reactions: Scope and Limitations of the Methodology

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SUPPLEMENTARY INFORMATION

General Experimental (S2-S3)

Analytical data for crude reaction mixture (S4-S5)

General experimental: All reactions were carried out in air and all chemicals were used as purchased. Microwave reactions were conducted using a focused microwave unit. The machine consists of a continuous focused microwave power delivery system with operator selectable power output from 0-300 W. Reactions were performed in glass vessels (capacity 10 mL) sealed with a septum. The pressure is controlled by a load cell connected to the vessel *via* a 14-gauge needle which penetrates just below the septum surface. The temperature of the contents of the vessel was monitored using a calibrated infrared temperature control mounted under the reaction vessel. All experiments were performed using a stirring option whereby the contents of the vessel are stirred by means of a rotating magnetic plate located below the floor of the microwave cavity and a Teflon-coated magnetic stir bar in the vessel. Conventional heating experiments were performed in an oil bath using identical reaction vessels to those used for the microwave experiments. The oil was pre-heated before placing the reaction vessel in. It is important that the reaction vessel is submerged in the oil bath to well below the surface of the reaction mixture to ensure as efficient heating as possible. As the reaction is in effect heterogeneous (the substrates are not soluble in water), it is very important that the reaction mixture is stirred rapidly throughout the reaction. The mixture is also shaken briefly prior to running the reaction. Reaction mixtures should be prepared freshly. Preparation the day before running the experiment has a considerably deleterious effect on the product yield. ¹H and ¹³C NMR spectra were recorded at 293 K. Product yields referring to isolated yields are those of compounds estimated to be ≥95% pure as determined by ¹H and ¹³C NMR analysis. Products were characterized by comparison of ¹H and ¹³C NMR data with that in the literature.¹

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ANALYTICAL REPORT ICP-AES

Date: 29 April, 2003

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Aqueous component of the entire product mixture formed in the reaction of 1 mmol 4-bromoacetophenone and 1.3 mmol phenylboronic acid using 1.0 mmol TBAB as phase-transfer catalysts, 3.7 mmol Na₂CO₃ as base, 2 mL water as solvent, 100 W microwave power, temperature ramped to 150 °C and held there for 5 min.

Element	Results	Units
B Na	4000+ 4000+	ppm ppm
K Ca	11 6.3	ppm ppm
Al Mg	3.8 3.5	ppm ppm
Fe Cu	1.4 0.35	ppm ppm
P Zr	0.33 0.30	ppm ppm
Ba Ti	0.20 0.08	ppm ppm
Zn	0.07	ppm
As, Se, Sm, Sn	<0.20	ppm
Be, Bi, Cd, Ce, Co, Cr, Dy, Eu, Gd	<0.10	ppm
Ge, Hf, Hg, Ir, La, Li, Mn, Mo, Nd	<0.10	ppm
Ni, Os, Pb, Pr, Pt, Re, Rh, Ru, Sb	<0.10	ppm
Sc, Tb, Th, Tl, Tm, V, Y, Yb	<0.10	ppm

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Organic component of the entire product mixture formed in the reaction of 1 mmol 4-bromoacetophenone and 1.3 mmol phenylboronic acid using 1.0 mmol TBAB as phase-transfer catalysts, 3.7 mmol Na₂CO₃ as base, 2 mL water as solvent, 100 W microwave power, temperature ramped to 150 °C and held there for 5 min.

Element	Results	Units
Na	0.44	%
B	0.16	%
Ca	3.7	ppm
Al	2.7	ppm
Ba	2.5	ppm
Fe	2.4	ppm
Mg	1.2	ppm
As, Bi, Mo, P, Pb Ru, Se, Sn	<1.0	ppm
Be, Cd, Ce, Co, Cr, Cu, Dy, Eu, Gd	<0.5	ppm
Ge, Hf, Hg, Ir, K, La, Li, Mn, Nd	<0.5	ppm
Ni, Os, Pr, Pt, Re, Rh, Sb, Sc	<0.5	ppm
Sm, Tb, Th, Ti, Tl, Tm, V, Y, Yb	<0.5	ppm
Zn, Zr	<0.5	ppm