
Rhodium Catalyzed Cross-Coupling of Allyl Alcohols with Aryl- and Vinylboronic Acids in Ionic Liquids

George W. Kabalka, Gang Dong and Bollu Venkataiah

Departments of Chemistry and Radiology, The University of Tennessee, Knoxville, TN 37996-1600

Email Address kabalka@utk.edu

Supporting Information:

General Considerations: All glassware were oven dried at 120 °C and flushed with dry nitrogen. All reactions were carried out under a nitrogen atmosphere. All chemicals were purchased from commercial sources and used as received. Products were purified by flash chromatography using silica gel (60 Å, 230–400 mesh) with hexanes as eluent. Elemental analyses were performed by Atlantic Microlabs Inc., Norcross, GA. ¹H NMR and ¹³C NMR were recorded in CDCl₃ on a 250 MHz instrument with chemical shifts reported relative to TMS.

Representative procedure for the synthesis of (*E*)-1-phenyl-3-*p*-tolylpropene: cinnamyl alcohol (1 mmol) and *p*-tolylboronic acid (1.2 mmol) are dissolved in BmimPF₆ (1.5 ml) contained in a two-necked round-bottomed flask and RhCl₃·xH₂O (3 mole %) along with Cu(OAc)₂ (10 mole %) are added. The reaction mixture is allowed to stir for 2 hrs at 50 °C under a nitrogen atmosphere. The mixture is then cooled to room temperature and the product extracted into diethyl ether (4 x 3 ml). The combined extracts are dried over anhydrous MgSO₄, concentrated, and purified by flash chromatography using silica gel.

(*E*)-1-Phenyl-3-*p*-tolylpropene. ¹H NMR: δ 7.05–7.36 (m, 9H), 6.42 (d, 1H, *J* = 15.9 Hz), 6.30 (dt, 1H, *J* = 16Hz, *J* = 6Hz), 3.49 (d, 2H, *J* = 5.8Hz), 2.31 (s, 3H). ¹³C NMR: δ 137.5, 131.0, 130.6, 129.5, 129.1, 128.9, 128.5, 128.1, 127.0, 126.1, 38.9, 21.0.

(*E*)-1,3-Diphenylpropene. ¹H NMR: δ 7.12–7.38 (m, 10H), 6.46 (d, 1H, *J* = 15.75Hz), 6.36 (dt, 1H, *J* = 15.75, *J* = 6Hz), 3.52 (d, 2H, *J* = 6.25Hz). ¹³C NMR: δ 140.7, 138.0, 131.6, 129.7, 129.2, 129.0, 127.6, 126.6, 39.6.

(*E*)-1-Phenyl-3-*p*-methoxyphenylpropene. ¹H NMR: δ 6.80–7.36 (m, 9H), 6.43 (d, 1H, *J* = 15.9Hz), 6.33 (dt, 1H, *J* = 15.7Hz, *J* = 5.8Hz), 3.77 (s, 3H), 3.47 (d, 2H, *J* = 5.8Hz). ¹³C NMR: δ 137.5, 132.1, 130.7, 129.6, 128.4, 127.0, 126.1, 113.9, 55.2, 38.4.

(*E*)-1-Phenyl-3-*p*-chlorophenylpropene. ¹H NMR: δ 7.15–7.36 (m, 9H), 6.44 (d, 1H, *J* = 16Hz), 6.32 (dt, 1H, *J* = 15.9Hz, *J* = 6Hz), 3.51 (d, 2H, *J* = 6.2Hz). ¹³C NMR: δ 138.6, 137.2, 131.5, 130.0, 128.5, 127.2, 126.1, 38.8.

(*E*)-1-Phenyl-3-*p*-methylthiophenylpropene. ¹H NMR: δ 7.13–7.35 (m, 9H), 6.43 (d, 1H, *J* = 15.9Hz), 6.31 (dt, 1H, *J* = 15.8Hz, *J* = 6.2Hz), 3.48 (d, 2H, *J* = 6.2Hz), 2.45 (s, 3H). ¹³C NMR: δ 137.3, 137.1, 135.8, 131.1, 129.2, 129.0, 128.5, 127.9, 127.1, 126.1, 38.7, 16.2. Anal. Calcd for C₁₆H₁₆S: C, 79.95; H, 6.71; Found: C, 80.20; H, 6.78.

(*E*), (*E*) -1,5-Diphenyl-1,4-pentadiene. ¹H NMR: δ 7.10–7.39 (m, 10H), 6.47 (d, 2H, *J* = 15.9Hz), 6.29 (dt, 2H, *J* = 15.9Hz, *J* = 6.5Hz), 3.12 (t, 2H, *J* = 6.5Hz). ¹³C NMR: δ 137.6, 131.0, 128.5, 128.2, 127.1, 126.1, 36.2.

2-(3-Phenyl-allyl)thiophene. ¹H NMR: δ 7.18–7.39 (m, 8H), 6.47 (d, 1H, *J* = 15.9Hz), 6.29 (dt, 1H, *J* = 15.8, *J* = 6.3Hz), 3.13 (d, 2H, *J* = 6.3Hz). ¹³C NMR: δ 137.6, 131.0, 128.5, 128.2, 127.1, 126.1, 36.2.

(*E*)-1-Phenyl-3-*o*-tolylpropene. ¹H NMR: δ 7.11–7.37 (m, 9H), 6.40 (d, 1H, *J* = 15.9Hz), 6.33 (dt, 1H, *J* = 16Hz, *J* = 5.9Hz), 3.50 (d, 2H, *J* = 5.8Hz), 2.31 (s, 3H). ¹³C NMR: δ 138.2, 137.5, 137.3, 136.4, 135.6, 130.9, 130.2, 129.2, 128.5, 127.0, 126.4, 126.1, 38.9, 21.2.

(*E*)-1-Phenyl-3-*m*-tolylpropene. ¹H NMR: δ 7.03–7.36 (m, 9H), 6.39 (d, 1H, *J* = 15.8Hz), 6.33 (dt, 1H, *J* = 15.9Hz, *J* = 6Hz), 3.47 (d, 2H, *J* = 6Hz), 2.30 (s, 3H). ¹³C NMR: δ 138.2, 137.5, 137.0, 135.6, 130.8, 130.2, 129.5, 129.1, 128.5, 127.0, 126.2, 126.1, 38.9, 21.1.

(*E*)-2-Methyl-1-phenyl-3-(1-naphthyl)propene. ^1H NMR: δ 7.15–8.11 (m, 12H), 6.29 (s, 1H), 3.93 (s, 2H), 1.87 (s, 3H). ^{13}C NMR: δ 138.3, 137.7, 135.6, 133.9, 128.8, 128.6, 128.0, 127.3, 127.0, 126.0, 125.8, 125.5, 124.2, 43.8, 18.2. Anal. Calcd for $\text{C}_{20}\text{H}_{18}$: C, 92.98; H, 7.02. Found: C, 92.86; H, 7.18.

(*E*)-1,3-Diphenyl-3-*p*-tolylpropene. ^1H NMR: δ 7.12–7.37 (m, 14H), 6.66 (dd, 1H, $J = 15.8\text{Hz}$, $J = 7.5\text{Hz}$), 6.33 (d, 1H, $J = 15.8\text{Hz}$), 4.84 (d, 1H, $J = 7.5\text{Hz}$), 2.31 (s, 3H). ^{13}C NMR: δ 144.0, 140.5, 137.3, 135.9, 132.8, 131.2, 129.2, 128.6, 128.5, 127.2, 126.3, 53.8, 21.0. Anal. Calcd for $\text{C}_{22}\text{H}_{20}$: C, 92.91; H, 7.09. Found: C, 92.63; H, 7.24.

(*E*)-1,3-Diphenyl-3-*p*-methoxyphenylpropene. ^1H NMR: δ 6.79–7.33 (m, 14H), 6.62 (dd, 1H, $J = 16\text{Hz}$, $J = 7.5\text{Hz}$), 6.30 (d, 1H, $J = 16\text{Hz}$), 4.80 (d, 1H, $J = 7.4\text{Hz}$), 3.66 (s, 3H). ^{13}C NMR: δ 158.1, 143.7, 137.2, 135.5, 132.8, 131.1, 129.5, 128.4, 127.2, 126.2, 125.7, 113.8, 55.0, 53.2.
