Supporting Information
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Supporting Information

Rh-Catalyzed Cross-Coupling of Arylboronic Acids Using Vinyl Acetate as the Electrophilic Partner

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1. General considerations

Unless otherwise noted, all reagents were purchased from commercial suppliers and used without further purification. All air-sensitive reactions were performed in Rotaflo® (England) resealable screw cap Schlenk flask (approx. 8 mL volume) in the presence of Teflon-coated magnetic stirrer bar (3 mm × 10 mm). Thin layer chromatography was performed on Merck precoated silica gel 60 F\textsubscript{254} plates. Silica gel (Merck, 230-400 mesh) was used for flash column chromatography. Melting points were recorded on an uncorrected Büchi Melting Point B-545 instrument. \textsuperscript{1}H NMR spectra were recorded on a Varian (500 MHz) spectrometer. Spectra were referenced internally to the residual proton resonance in CDCl\textsubscript{3} (\(\delta\) 7.26 ppm), or with tetramethylsilane (TMS, \(\delta\) 0.00 ppm) as the internal standard. Commercially available CDCl\textsubscript{3} was stored under anhydrous K\textsubscript{2}CO\textsubscript{3} granules with 4Å molecular sieves in desiccators. Chemical shifts (\(\delta\)) were reported as part per million (ppm) in \(\delta\) scale downfield from TMS. \textsuperscript{13}C NMR spectra were recorded on a Varian 500 spectrometer and referenced to CDCl\textsubscript{3} (\(\delta\) 77.0 ppm). Coupling constants (\(J\)) were reported in Hertz (Hz). Mass spectra (EIMS and FABMS) were recorded on a HP 5989B Mass Spectrometer. High-resolution mass spectra (HRMS) were obtained on a Brüker APEX 47e FT-ICR mass spectrometer (ESIMS). GC-MS analysis was conducted on a HP 6890 system with a HP 5973N mass selective detector using a HP5MS column (30 m × 0.25 mm).
2. General procedures for Rh-Catalyzed Cross-Coupling of Arylboronic Acids with Vinyl Acetate

[Rh(COD)Cl]₂ (4.4 mg, 0.009 mmol), DPPB (8.4 mg, 0.019 mmol), 4-tert-butylboronic acid (53 mg, 0.3 mmol), K₃PO₄ (0.2 g, 0.9 mmol) and Teflon-coated magnetic stirrer bar (3 mm × 10 mm) were charged to a 8 mL screw capped Schlenk tube on bench-top at room temperature. These tubes were evacuated and backfilled with nitrogen (3 cycles), followed by the addition of vinyl acetate (0.6 mL, 6.0 mmol) and freshly distilled toluene (1.0 mL) under nitrogen and the reaction mixtures were magnetically stirred at a preheated 110 °C (± 3 °C) oil bath for 24 hours. The flasks were allowed to reach room temperature. Diethyl ether or ethyl acetate (~2 mL) was added. The crude reaction mixtures were purified by column chromatography on silica gel using pentane/ether as the eluent to afford corresponding vinylarenes.
3. Characterization data and NMR spectra of vinylarenes

![4-tert-Butylstyrene](image)

**4-tert-Butylstyrene**

Purified by column chromatography (2 cm diameter × ~20 cm height) on silica gel using pentane as eluent to obtain the title compound as colorless oil. 80% yield; $R_f = 0.7$ (pentane)

$^1$H NMR (CDCl$_3$, 500 MHz) $\delta$ 7.27 (s, 4H) 6.61 (dd, 1H, $J = 11.0$ Hz, 18.0 Hz) 5.63 (d, 1H, $J = 18.0$ Hz) 5.11 (d, 1H, $J = 11.0$ Hz), 1.24 (s, 9H)

$^{13}$C NMR (CDCl$_3$, 125 MHz) $\delta$ 150.8, 136.5, 134.8, 125.9, 125.4, 112.9, 34.5, 31.2

MS(EI) $m/z$ (relative intensity) 160 (M+, 40), 145 (100), 90 (25), 128 (15), 117 (40)

![4-Butoxystyrene](image)

**4-Butoxystyrene**

Purified by column chromatography (2 cm diameter × ~20 cm height) on silica gel using pentane as eluent to obtain the title compound as yellow oil. 55% yield; $R_f = 0.6$ (pentane)

$^1$H NMR (CDCl$_3$, 500 MHz) $\delta$ 7.24 (dd, 2H, $J = 2.0$ Hz, 7.0 Hz) 6.76 (dd, 2H, $J = 2.5$ Hz, 7.0 Hz) 6.56 (dd, 1H, $J = 11.0$ Hz, 18.0 Hz) 5.51 (d, 1H, $J = 17.5$ Hz), 5.03 (d, 1H, $J = 11.0$ Hz) 3.88 (t, 2H, $J = 17.0$ Hz) 1.66-1.69 (m, 2H) 1.40-1.42 (m, 2H) 0.89 (t, 3H, $J = 7.5$ Hz)

$^{13}$C NMR (CDCl$_3$, 125 MHz) $\delta$ 136.2, 130.2, 129.3, 127.3, 114.4, 111.3, 67.6, 31.3, 19.2, 13.8

MS(EI) $m/z$ (relative intensity) 176 (M+, 30), 120 (100), 91 (30)
4-(Dimethylamino)styrene\(^3\)

Purified by column chromatography (2 cm diameter \(\times\) ~20 cm height) on silica gel using pentane as eluent to obtain the title compound as brown oil. 60\% yield; \(R_f = 0.2\) (pentane)

\(^1\)H NMR (CDCl\(_3\), 500 MHz) \(\delta\) 7.22 (dd, 2H, \(J = 2.0\) Hz, 7.0 Hz) 6.59 (dd, 2H, \(J = 2.5\) Hz, 7.0 Hz) 6.55 (dd, 1H, \(J = 11.0\) Hz, 17.5 Hz) 5.45 (d, 1H, \(J = 17.5\) Hz), 4.93 (d, 1H, \(J = 11.0\) Hz) 2.87 (t, 6H, \(J = 6.5\) Hz)

\(^13\)C NMR (CDCl\(_3\), 125 MHz) \(\delta\) 150.2, 136.5, 129.0, 127.1, 112.6, 112.3, 109.3, 40.4

MS(EI) \(m/z\) (relative intensity) 146 (M\(^+\), 100), 131 (30), 103 (10) 77(15)

4-Phenylstyrene\(^4\)

Purified by column chromatography (2 cm diameter \(\times\) ~20 cm height) on silica gel using pentane as eluent to obtain the title compound as white solid. 69\% yield; \(R_f = 0.6\) (pentane)

\(^1\)H NMR (CDCl\(_3\), 500 MHz) \(\delta\) 7.60-7.65 (m, 4H) 7.53 (d, 2H, \(J = 8.0\) Hz) 7.46 (t, 2H, \(J = 7.5\) Hz) 7.37 (t, 1H, \(J = 7.5\) Hz), 6.79 (dd, 1H, \(J = 10.5\) Hz, 17.5 Hz) 5.83 (d, 1H, \(J = 17.5\) Hz) 5.31 (d, 1H, \(J = 11.0\) Hz)

\(^13\)C NMR (CDCl\(_3\), 125 MHz) \(\delta\) 140.6, 140.5, 136.5, 136.3, 128.7, 127.2, 126.9, 126.6, 113.8

MS(EI) \(m/z\) (relative intensity) 180 (M\(^+\), 100), 165 (30), 152 (20) 76(15)
2-Vinylnapthalene

Purified by column chromatography (2 cm diameter × ~20 cm height) on silica gel using pentane as eluent to obtain the title compound as colorless oil. 82% yield; $R_f = 0.4$ (pentane)

$^1$H NMR (CDCl$_3$, 500 MHz) $\delta$ 8.42 (d, 1H, $J = 8.5$ Hz) 8.14 (d, 1H, $J = 6.0$ Hz) 8.08 (d, 1H, $J = 8.0$ Hz) 7.92 (d, 1H, $J = 6.5$ Hz), 7.41-7.83 (m, 4H) 6.09 (d, 1H, $J = 17.5$ Hz) 5.78 (d, 1H, $J = 11.0$ Hz) 2.87 (t, 6H, $J = 6.5$ Hz)

$^{13}$C NMR (CDCl$_3$, 125 MHz) $\delta$ 135.5, 134.3, 133.5, 131.0, 128.4, 128.0, 126.0, 125.7, 125.5, 123.5, 117.0

MS(EI) $m/z$ (relative intensity) 153 (M+, 100), 76 (35)

2-Isopropenyl-4-phenylstyrene

Purified by column chromatography (2 cm diameter × ~20 cm height) on silica gel using pentane as eluent to obtain the title compound as colorless oil. 35% yield; $R_f = 0.4$ (pentane)

$^1$H NMR (CDCl$_3$, 500 MHz) $\delta$ 7.48-7.54 (m, 4H) 7.35-7.38 (m, 4H) 7.27-7.29 (m, 1H) 5.36 (s, 1H), 5.04 (s, 1H) 2.14 (s, 3H)

$^{13}$C NMR (CDCl$_3$, 125 MHz) $\delta$ 142.7, 141.2, 140.2, 128.7, 127.1, 126.9, 126.8, 125.9, 112.4, 104.7, 21.8

MS(EI) $m/z$ (relative intensity) 194 (M+, 100), 178 (45) 152 (15)
4. References


