SUPPORTING INFORMATION

Understanding Site-Selectivity in the Palladium-catalyzed Cross-coupling of Allenylsilanolates

Scott E. Denmark,* Andrea Ambrosi

Roger Adams Laboratory, Department of Chemistry, University of Illinois, Urbana, Illinois, 61801
sdenmark@illinois.edu

TABLE OF CONTENTS

1. General Experimental \( S2 \)
2. Synthesis of Silanols 5 and 9 \( S4 \)
3. Silanol Deprotonation and Cross-Coupling Experiments \( S12 \)
4. References \( S15 \)
5. NMR Spectra \( S16 \)
1. General Experimental

All reactions were performed in oven- (120 °C) and/or flame-dried glassware under an atmosphere of dry argon, unless noted. Reaction solvents tetrahydrofuran (Fisher, HPLC grade) and dichloromethane (Fisher, unstabilized, HPLC grade) were dried by percolation through two columns packed with neutral alumina under a positive pressure of argon. Reaction solvents hexanes (Fisher, OPTIMA grade) and toluene (Fisher, ACS grade) were dried by percolation through a column packed with neutral alumina and a column packed with Q5 reactant, a supported copper catalyst for scavenging oxygen, under a positive pressure of argon. Solvents for filtration and chromatography were certified ACS grade. “Brine” refers to a saturated solution of sodium chloride. All reaction temperatures correspond to internal temperatures measured with Teflon coated thermocouples unless otherwise noted.

$^1$H, $^{13}$C and $^{19}$F NMR spectra were recorded on Varian Unity 500, Varian VXR 500, Varian Unity Inova 500 NB, or Bruker Avance III HD 500 spectrometers (500 MHz, $^1$H; 126 MHz, $^{13}$C). Spectra are referenced to residual chloroform (δ 7.26 ppm, $^1$H; δ 77.0 ppm, $^{13}$C), residual benzene (δ 7.16 ppm, $^1$H; δ 128.0 ppm, $^{13}$C), or CFCl$_3$ (10% in CDCl$_3$) as an external reference for $^{19}$F NMR (δ 0.00 ppm $^{19}$F). Chemical shifts are reported in ppm, multiplicities are indicated by s (singlet), d (doublet), t (triplet), q (quartet), p (pentet), h (hextet), hept (heptet), m (multiplet) and br (broad). Coupling constants, $J$, are reported in Hertz. All assignments are corroborated by $^{13}$C APT and/or 2D experiments (COSY, HMQC, HMBC).

Mass Spectrometry was performed by the University of Illinois Mass Spectrometer Center. Electron Impact (EI) spectra were recorded on a Waters 70-VSE spectrometer. Electrospray Ionization (ESI) spectra were recorded on Waters Q-TOF Ultima or Waters Synapt G2-Si spectrometers. Data are reported in the form of m/z. Infrared spectra (IR) were recorded on a Perkin Elmer Spectrum Two ATR spectrometer using neat sample. Peaks are reported in cm$^{-1}$ with indicated relative intensities: s (strong, 67-100%); m (medium, 34-66%), w (weak, 0-33%). Kugelrohr distillations were performed on a Büchi GKR-50 Kugelrohr and boiling points correspond to uncorrected air bath temperatures (ABT). Analytical thin-layer chromatography was performed on Merck silica gel plates with QF-254 indicator. Visualization was accomplished with UV (254). Column chromatography was performed using 230-400 mesh silica gel purchased from Silicycle.
Analytical gas chromatography (GC) was performed using a Hewlett Packard 5890 Series II Gas Chromatograph fitted with a flame ionization detector (H₂ carrier gas, 1 mL/min). Injections were made on a Hewlett-Packard HP-1 (30 meter) capillary column. The injector temperature was 250 °C, the detector temperature was 300 °C, with a split ratio of 100:1. Retention times (t_R) and integrated ratios were obtained using Agilent Chemstation Software.

Dichlorodiethylsilane (Gelest), dichlorodiisopropylsilane (Gelest), mesyl chloride (Sigma-Aldrich), 2-butyn-1-ol (Sigma-Aldrich), triethylamine (Fisher), tetramethylethylenediamine (Sigma-Aldrich) were distilled prior to use. NaH and KH (Sigma-Aldrich, 30% in mineral oil) were washed repeatedly with hexanes and dried under vacuum prior to use. Commercial solutions of organometallic reagents were titrated prior to use according to the procedure described by Hoye et al.¹ HCl in Et₂O (Sigma-Aldrich) was titrated prior to use. All other reagents, metal catalysts and ligands were purchased from Sigma-Aldrich, Fisher, Oakwood, or Strem and used as received.

The following compounds were prepared according to published procedures: allylpalladium(II) chloride dimer,² L₁-3.³
2. **Synthesis of Silanols 5 and 9**

Chloro(2,4-dimethoxyphenyl)diethylsilane (1)

In a 250-mL, 3-necked, round-bottomed flask (equipped with an addition funnel, an Ar inlet and a septum), a solution of 1-bromo-2,4-dimethoxybenzene (3.6 mL, 25 mmol) in hexane (25 mL) at −78 °C was treated with 1.60 M t-BuLi in pentane (32.1 mL, 51.3 mmol, 2.05 equiv) and stirred for 30 min. TMEDA (3.9 mL, 26.3 mmol, 1.05 equiv) was slowly added and the resulting suspension was cannula-transferred into a solution of dichlorodiethylsilane (4.8 mL, 37.5 mmol, 1.5 equiv) in hexane (18 mL) at −78 °C. The original flask was rinsed with hexane (3 × 10 mL). The mixture was warmed to room temperature and stirred for 30 min. The resulting suspension was filtered on a medium glass frit to partially remove the Li salts. The solvent was removed under reduced pressure; the residual dichlorodiethylsilane and TMEDA were removed under vacuum over 2 h. The residue was purified by short-path distillation to afford 1 (6.47 g, 82%) as a colorless oil.

Data for 1:

bp: 122-124 °C (1 mmHg)

**1H NMR:**

δ 7.83 (d, J = 8.1 Hz, 1H, C(8)H), 6.40 (dd, J = 8.2, 2.1 Hz, 1H, C(7)H), 6.30 (d, J = 2.1 Hz, 1H, C(5)H), 3.30 (s, 3H, C(9)H₃ or C(10)H₃), 3.14 (s, 3H, C(9)H₃ or C(10)H₃), 1.16 – 1.05 (m, 10H, C(2)H₃ and C(1)H₂)

**13C NMR:**

δ 165.5 (C4 or C6), 164.1 (C4 or C6), 138.3 (C8), 113.3 (C3), 105.4 (C7), 98.2 (C5), 54.8 (C9 or C10), 54.6 (C9 or C10), 9.5 (C1), 7.2 (C2)

IR:

(neat)

3001 (w), 2930 (m), 2876 (w), 2876 (w), 1592 (s), 1569 (m), 1453 (s), 1396 (m), 1208 (s), 1164 (s), 1083 (s), 1030 (s), 918 (m), 842 (m), 740 (s), 700 (s)

**HRMS:**

(EI)

m/z: [M]+ Calcd for C₁₂H₁₉ClO₂Si: 258.0843; Found: 258.0848
1-((2,4-Dimethoxyphenyl)diethlysilyl)but-2-yn-1-ol (2)

In a 250-mL Schlenk flask, 1.52 M BuLi in hexane (14.1 mL, 21.4 mmol, 1.1 equiv) was added to a solution of 2-butyn-1-ol (1.46 mL, 19.5 mmol) in THF (30 mL) at −78 °C and the mixture stirred for 10 min. A solution of 1 (5.29 g, 20.4 mmol, 1.05 equiv) in THF (10 mL) was then slowly added via syringe. The resulting yellow solution was warmed to room temperature and stirred for 16 h. The mixture was then re-cooled to −78 °C and treated with 1.60 M t-BuLi in pentane (14.6 mL, 23.4 mmol, 1.2 equiv). The mixture was warmed to −45 °C and stirred for 2 h, then quenched by the addition of saturated aqueous NH₄Cl (10 mL). After warming to room temperature, the layers were separated and the aqueous layer was washed with Et₂O (2 × 20 mL). The combined organic extracts were washed with brine (20 mL), dried (Na₂SO₄), filtered and the solvent removed under reduced pressure. The residual oil was purified by silica gel column chromatography (pentane/Et₂O 75:25) to afford 4.38 g of an inseparable mixture of 2 (13.63 mmol, 70%) and 2a (1.64 mmol, 8%) as a colorless oil.

Data for 2:

**¹H NMR:** (500 MHz, CDCl₃)
- δ 7.36 (d, J = 8.1 Hz, 1H, C(12)H), 6.54 (dd, J = 8.1, 2.2 Hz, 1H, C(11)H), 6.45 (d, J = 2.1 Hz, 1H, C(9)H), 4.39 (dq, J = 5.3, 2.6 Hz, 1H, C(4)H), 3.82 (s, 3H, C(13)H₃ or C(14)H₃), 3.81 (s, 3H, C(13 or 14)H₃), 2.41 (d, J = 5.2 Hz, 1H, OH), 1.82 (d, J = 2.6 Hz, 3H, C(1)H₃), 1.12 – 0.88 (m, 10H, C(6)H₃ and C(5)H₂)

**¹³C NMR:** (126 MHz, CDCl₃)
- δ 165.4 (C8 or C10), 162.8 (C8 or C10), 137.4 (C12), 113.2 (C7), 105.3 (C11), 98.0 (C9), 83.4 (C3), 79.9 (C2), 71.6 (C4), 55.3 (C13 or C14), 54.9 (C13 or C14), 7.6 (C1), 2.8 (C6), 2.2 (C5)

**HRMS:** (ESI)
- m/z: [MH]⁺ Calcd for C₁₆H₂₅O₃Si: 293.1573; Found: 293.1574

**TLC:** R₂ 0.34 (pentane/Et₂O 75:25) [UV, p-anisaldehyde]
(2,4-Dimethoxyphenyl)diethyl(3-methyl-4-phenylbuta-1,2-dien-1-yl)silane (4)

In a 100-mL Schlenk flask, a solution of 2 (1.83 g, 6.25 mmol, actual 4.24 mmol of 2 based on $^1$H NMR integration) in CH$_2$Cl$_2$ (41 mL) at $-78$ °C was treated with Et$_3$N (1.2 mL, 8.43 mmol, 1.35 equiv) and MsCl (0.60 mL, 7.81 mmol, 1.25 equiv) and stirred for 30 min. The mixture was then warmed to room temperature and quenched with saturated aqueous NaHCO$_3$ (10 mL). The layers were separated and the aqueous layer was washed with Et$_2$O (2 x 50 mL). The combined organic extracts were washed with brine (30 mL), dried (Na$_2$SO$_4$), filtered and the solvent removed under reduced pressure. The resulting mesylate 3 was used in the next step without further purification.

In a 250-mL, 3-necked, round-bottomed flask (equipped with an addition funnel, an Ar inlet and a septum), 1.05 M BnMgCl in Et$_2$O (17.9 mL, 18.8 mmol, 3.0 equiv) was gradually added to a suspension of CuCN (1.68 g, 18.8 mmol, 3.0 equiv) and LiCl (1.59 g, 37.5 mmol, 6.0 equiv) in THF (32 mL) at $-78$ °C. The resulting suspension was warmed to room temperature to dissolve most of the solids, then re-cooled to $-78$ °C. A solution of the mesylate 3 in THF (32 mL) was then added via syringe and the reaction mixture stirred for 1 h. After warming to room temperature, the reaction was quenched by the addition of saturated aqueous NH$_4$Cl (20 mL). The mixture was filtered through a pad of Celite which was washed repeatedly with Et$_2$O (100 mL). The filtrate was washed with brine (50 mL), dried (Na$_2$SO$_4$), filtered and the solvent removed under reduced pressure. The residual oil was purified by silica gel column chromatography (pentane/CH$_2$Cl$_2$ 8:2) to afford 4 (1.38 g, 89% based on the actual amount of 2) as a colorless oil.

Data for 4:

$^1$H NMR: (500 MHz, CDCl$_3$)

$\delta$ 7.31 (d, $J = 8.0$ Hz, 1H, C(12)H), 7.27 (t, $J = 7.3$ Hz, 2H, C(18)H), 7.22 – 7.18 (m, 3H, C(17)H and C(19)H), 6.50 (dd, $J = 8.1$, 2.2 Hz, 1H, C(11)H), 6.42 (d, $J = 2.1$ Hz, 1H, C(9)H), 5.07 (h, $J = 3.6$ Hz, 1H, C(4)H), 3.83 (s, 3H, C(13)H$_3$ or C(14)H$_3$), 3.77 (s 3H, C(13)H$_3$ or C(14)H$_3$), 3.33 – 3.26 (m, 2H, C(15)H$_2$), 1.62 (d, $J = 3.7$ Hz, 3H, C(1)H$_3$), 0.97 – 0.92 (m, 6H, C(6)H$_3$), 0.88 – 0.82 (m, 4H, C(5)H$_2$)
**13C NMR:** (126 MHz, CDCl₃)

δ 210.2 (C3), 165.8 (C8 or C10), 162.4 (C8 or C10), 139.9 (C16), 137.2 (C12), 128.9 (C17), 128.1 (C18), 125.9 (C19), 115.8 (C7), 104.4 (C11), 97.5 (C9) 90.8 (C2), 78.1 (C4), 55.1 (C13 or C14), 54.9 (C13 or C14), 40.4 (C15), 17.5 (C1), 7.6 (C6), 5.0 (C5), 4.8 (C5’)

**IR:**

(neat)
2952 (m), 1944 (m), 1595 (s), 1570 (m), 1453 (m), 1299 (s) 1254 (s), 1156 (s), 1086 (s), 1034 (s), 917 (m), 834 (m), 731 (s), 698 (s)

**HRMS:** (EI)

m/z: [M]+ Calcd for C₂₃H₃₀O₂Si: 366.2015; Found: 366.2018

**TLC:** Rₜ 0.15 (pentane/CH₂Cl₂ 8:2) [UV, p-anisaldehyde]
\[^{13}\text{C}\text{ NMR:}\] (126 MHz, C\textsubscript{6}D\textsubscript{6})
\[\delta\] 210.9 (C3), 140.1 (C8), 129.3 (C9 or C10), 128.6 (C9 or C10), 126.6 (C11), 92.4 (C2), 80.0 (C4), 40.6 (C7), 17.7 (C1), 7.3 (C5), 7.2 (C5\textsuperscript{'}), 6.9 (C6), 6.9 (C6\textsuperscript{'}).

\[\text{IR:}\] (neat)
3277 (w), 2954 (m), 2876 (m), 1943 (m), 1494 (m), 1454 (m), 1358 (m), 1235 (m), 1009 (m), 829 (s), 750 (s), 727 (s), 697 (s).

\[^{1}\text{H}\text{ NMR:}\] (500 MHz, CDCl\textsubscript{3})
\[\delta\] 7.85 (d, \(J = 8.2\) Hz, 1H, C(6)H), 6.55 (dd, \(J = 8.2, 2.1\) Hz, 1H, C(5)H), 6.40 (d, \(J = 2.0\) Hz, 1H, C(3)H), 3.83 (s, 3H, C(7)H\textsubscript{3} or C(8)H\textsubscript{3}), 3.77 (s, 3H, C(7)H\textsubscript{3} or C(8)H\textsubscript{3}), 1.45 (hept, \(J = 7.3\) Hz, 2H, C(9)H), 1.06 (d, \(J = 7.3\) Hz, 6H, C(10)H\textsubscript{3}).

**Chloro(2,4-dimethoxyphenyl)diisopropylsilane (10)**

In a 500-mL, 3-neck, round-bottom flask (equipped with an addition funnel, an Ar inlet and a septum), a solution of 1-bromo-2,4-dimethoxybenzene (5.8 mL, 40 mmol) in hexane (60 mL) at −78 °C was treated with 1.52 M \(t\)-BuLi in pentane (55 mL, 84 mmol, 2.1 equiv) and stirred for 30 min. TMEDA (6.3 mL, 42 mmol, 1.05 equiv) was slowly added and the resulting suspension was cannula-transferred into a solution of dichlorodiisopropylsilane (10.8 mL, 60 mmol, 1.5 equiv) in hexane (30 mL) at −78 °C. The original flask was rinsed with hexane (3 \(\times\) 30 mL). The mixture was warmed to room temperature and stirred for 30 min. The resulting suspension was filtered twice on a medium glass frit to partially remove the Li salts. The solvent was removed under reduced pressure; the residual dichlorodiisopropylsilane and TMEDA were removed under high vacuum over 4 h. The residue was purified by Kugelrohr distillation to afford 10 (10.0 g, 87%) as a yellow oil.

**Data for 10:**

\[^{1}\text{H}\text{ NMR:}\] (500 MHz, CDCl\textsubscript{3})
\[\delta\] 7.85 (d, \(J = 8.2\) Hz, 1H, C(6)H), 6.55 (dd, \(J = 8.2, 2.1\) Hz, 1H, C(5)H), 6.40 (d, \(J = 2.0\) Hz, 1H, C(3)H), 3.83 (s, 3H, C(7)H\textsubscript{3} or C(8)H\textsubscript{3}), 3.77 (s, 3H, C(7)H\textsubscript{3} or C(8)H\textsubscript{3}), 1.45 (hept, \(J = 7.3\) Hz, 2H, C(9)H), 1.06 (d, \(J = 7.3\) Hz, 6H, C(10)H\textsubscript{3}).
0.94 (d, $J = 7.4$ Hz, 6H, C(10')H₃)

$^{13}$C NMR: (126 MHz, CDCl₃)

δ 164.7 (C2 or C4), 163.1 (C2 or C4), 138.4 (C6), 112.2 (C1), 104.9 (C5), 97.2 (C3), 55.2 (C7 or C8), 54.8 (C7 or C8), 17.4 (C9), 17.3 (C9'), 14.8 (C10)

1-((2,4-Dimethoxyphenyl)diisopropylsilyl)but-2-yn-1-ol (11)

In a 50-mL Schlenk flask, 2.38 M BuLi in hexane (3.0 mL, 7.30 mmol, 1.15 equiv) was added to a solution of 2-butyne-1-ol (0.47 mL, 6.34 mmol) in THF (9.5 mL) at −78 °C and the mixture stirred for 10 min. A solution of 10 (2.0 g, 6.97 mmol, 1.1 equiv) in THF (3.5 mL) was then slowly added via syringe. The resulting yellow solution was warmed to room temperature and stirred for 16 h. The mixture was then re-cooled to −78 °C and treated with 1.60 M t-BuLi in pentane (4.8 mL, 7.61 mmol, 1.2 equiv). The mixture was warmed to −45 °C and stirred for 2 h, then quenched by the addition of saturated aqueous NH₄Cl (5 mL). After warming to room temperature, the layers were separated and the aqueous layer was washed with Et₂O (2 × 20 mL). The combined organic extracts were washed with brine (20 mL), dried (Na₂SO₄), filtered and the solvent removed under reduced pressure. The residual oil was purified by silica gel column chromatography (pentane/Et₂O 75:25) to afford 1.18 g of an inseparable mixture of 11 (1.73 mmol, 25%) and 11a (2.33 mmol, 37%) as a colorless oil.

Data for 11:

$^1$H NMR: (500 MHz, CDCl₃)

δ 7.45 (d, $J = 8.1$ Hz, 1H, C(12)H), 6.55 (dd, $J = 8.2, 2.2$ Hz, 1H, C(11)H), 6.45 (d, $J = 2.1$ Hz, 1H, C(9)H), 4.56 (dq, $J = 5.4, 2.6$ Hz, 1H, C(4)H), 3.83 (s, 3H, C(13)H₃ or C(14)H₃), 3.80 (s, 3H, C(13)H₃ or C(14)H₃), 3.23 (d, $J = 5.6$ Hz, 1H, OH), 1.82 (d, $J = 2.7$ Hz, 3H, C(1)H₃), 1.55 – 1.36 (m, 2H, C(5)H), 1.15 (d, $J = 7.5$ Hz, 3H, C(6)H₃), 1.11 (d, $J = 7.5$ Hz, 3H, C(6')H₃), 1.08 (d, $J = 7.4$ Hz, 3H, C(6'')H₃), 1.07 (d, $J = 7.5$ Hz, 3H, C(6''')H₃)

TLC: $R_f$ 0.34 (pentane/Et₂O 75:25) [UV, p-anisaldehyde]
In a 50-mL Schlenk flask, a solution of 11 (1.18 g, 3.68 mmol, actual 1.73 mmol of 11 based on $^1$H NMR integration) in CH$_2$Cl$_2$ (25 mL) at –78 °C was treated with Et$_3$N (0.69 mL, 4.97 mmol, 1.35 equiv) and MsCl (0.36 mL, 4.60 mmol, 1.25 equiv) and stirred for 30 min. The mixture was then warmed to room temperature and quenched with saturated aqueous NaHCO$_3$ (5 mL). The layers were separated and the aqueous layer was washed with Et$_2$O (2 × 25 mL). The combined organic extracts were washed with brine (20 mL), dried (Na$_2$SO$_4$), filtered and the solvent removed under reduced pressure. The resulting mesylate 12 was used in the next step without further purification.

In a 100-mL, 3-neck, round-bottom flask (equipped with an addition funnel, an Ar inlet and a septum), 1.0 M BnMgCl in Et$_2$O (11.0 mL, 11.0 mmol, 3.0 equiv) was gradually added to a suspension of CuCN (989 mg, 11.0 mmol, 3.0 equiv) and LiCl (936 mg, 22.1 mmol, 6.0 equiv) in THF (18.5 mL) at –78 °C. The resulting suspension was warmed to room temperature to dissolve most of the solids, then re-cooled to –78 °C. A solution of the mesylate 12 in THF (18.5 mL) was then added via syringe and the reaction mixture stirred for 1 h. After warming to room temperature, the reaction was quenched by the addition of saturated aqueous NH$_4$Cl (10 mL). The mixture was filtered through a pad of celite which was washed repeatedly with Et$_2$O (70 mL). The filtrate was washed with brine (30 mL), dried (Na$_2$SO$_4$), filtered and the solvent removed under reduced pressure. The residual oil was purified by silica gel column chromatography (pentane/CH$_2$Cl$_2$ 9:1) to afford 13 (566 mg, 83% based on the actual amount of 11) as a colorless oil.

Data for 13:

$^1$H NMR: (500 MHz, CDCl$_3$)

δ 7.37 (d, J = 8.1 Hz, 1H, C(12)H), 7.34 – 7.28 (m, 2H, C(18)H), 7.28 – 7.22 (m, 3H, C(17)H and C(19)H), 6.52 (dd, J = 8.1, 2.0 Hz, 1H, C(11)H), 6.45 (d, J = 2.0 Hz, 1H, C(9)H), 5.08 (h, J = 3.4 Hz, 1H, C(4)H), 3.86 (s, 3H, C(13)H$_3$ or C(14)H$_3$), 3.79 (s, 3H, C(13)H$_3$ or C(14)H$_3$), 3.42 (dd, J = 14.6, 3.0 Hz, 1H, C(15)H), 3.31 (dd, J = 14.7, 2.9 Hz, 1H, C(15)H’), 1.67 (d, J = 3.8 Hz, 3H, C(1)H$_3$), 1.38 (hept, J = 7.4 Hz, 2H, C(5)H), 1.09 – 0.94 (m, 12H, C(6)H$_3$)
\[ ^{13}C\text{NMR:} \quad (126\text{ MHz, CDCl}_3) \]
\[ \delta 210.8 (C3), 165.7 (C8 or C10), 162.3 (C8 or C10), 139.9 (C16), 138.4 (C12), 128.9 (C18), 128.1 (C17), 126.0 (C19), 114.4 (C7), 104.3 (C11), 97.4 (C9), 90.23 (C2), 75.8 (C4), 55.1 (C13 or C14), 54.6 (C13 or C14), 40.5 (C15), 18.2 (C6), 18.1 (C6'), 18.1 (C6''), 17.5 (C1), 11.8 (C5), 11.7 (C5'') \]

\[ \text{TLC:} \quad R_f 0.23 \text{ (pentane/CH}_2\text{Cl}_2 9:1) \text{ [UV, } p\text{-anisaldehyde]} \]

**Diisopropyl(3-methyl-4-phenylbuta-1,2-dien-1-yl)silanol (9)**

In a 50-mL Schlenk flask, 2.08 M HCl in Et\(_2\)O (1.35 mL, 2.8 mmol, 2.0 equiv) was added dropwise to a solution of 13 (553 mg, 1.40 mmol) in CH\(_2\)Cl\(_2\) (14 mL) at room temperature. The mixture was stirred for 30 min, then cannula-transferred into a mixture of pH = 5, 1 M aqueous acetate buffer (28 mL) and CH\(_3\)CN (9 mL) at 0 °C, and stirred for 10 min. After diluting with Et\(_2\)O (20 mL), the layers were separated and the aqueous layer was washed with Et\(_2\)O (2 × 20 mL). The combined organic extracts were washed with saturated aqueous NaHCO\(_3\) (30 mL), dried (Na\(_2\)SO\(_4\)), filtered and the solvent removed under reduced pressure. The residue was purified by silica gel column chromatography (pentane/Et\(_2\)O 9:1) to afford 9 (325 mg, 85%) as a colorless oil.

**Data for 9:**

\[ ^1\text{H NMR:} \quad (500\text{ MHz, C}_6\text{D}_6) \]
\[ \delta 7.16 – 7.11 \text{ (m, 4H, C(9)H and C(10)H), 7.09 – 7.01 \text{ (m, 1H, C(11)H), 4.96 – 4.87 \text{ (h, J = 3.5 Hz, 1H, C(4)H), 3.24 – 3.07 \text{ (m, 2H, C(7)H}_2\), 1.57 \text{ (d, J = 3.8 Hz, 3H, C(1)H}_3\), 1.26 \text{ (s, 1H, OH), 1.07 \text{ (d, J = 7.1 Hz, 1H, C(6)H}_3\), 1.05 \text{ (d, J = 7.2 Hz, 1H, C(6')H}_3\), 1.03 \text{ (d, J = 7.0 Hz, 1H, C(6'')H}_3\), 1.02 \text{ (d, J = 7.0 Hz, 1H, C(6''')H}_3\), 0.99 – 0.88 \text{ (m, 2H, C(5)H)}}} \]

\[ ^{13}\text{C NMR:} \quad (126\text{ MHz, C}_6\text{D}_6) \]
\[ \delta 211.1 (C3), 140.1 (C8), 129.3 (C9 or C10), 128.63 (C9 or C10), 126.6 (C11), 92.1 (C2), 77.8 (C4), 40.6 (C7), 17.9 (C1), 17.4 (C6), 17.4 (C6'), 17.3 (C6''), 13.4 (C5), 13.4 (C5'') \]

\[ \text{TLC:} \quad R_f 0.45 \text{ (pentane/CH}_2\text{O 9:1) [UV, } p\text{-anisaldehyde]} \]
3. **Silanol Deprotonation and Cross-Coupling Experiments**

**General Procedure for the Deprotonation of Silanols 5 and 9**

 Cannizzaro and Ambrosi

A Schlenk flask was charged with the base and toluene (1.3 M). A solution of the silanol in toluene (0.6 M) was added at the indicated temperature. The reaction mixture was stirred for the indicated time (for NaH and KH, the reaction was interrupted when bubbling subsided). A 100-µL aliquot was taken via syringe and transferred into a vial containing a known amount of biphenyl. The resulting mixture was quenched with a few drops of acetate buffer, diluted with EtOAc (1 mL), filtered through a silica plug and analyzed by GC. The original reaction mixture was used in cross-coupling experiments after determining the title of the silanolate by integration of silanol and biphenyl GC peaks (see next section for GC method information).

**General Procedure for Cross-coupling Experiments (Tables 1 – 4)**

In a glove box, the Pd source and the ligand were added to an oven-dried 4-mL reaction vial containing a stir bar. A stock solution of 6 (0.05 mmol) and biphenyl in toluene (0.17 M) was added and the mixture stirred to homogenize. The vial was sealed with a septum screw cap, transferred outside the glove box and warmed to the indicated temperature. A solution of the silanolate in toluene (0.3 – 0.4 M) was then added via syringe. 50 µL aliquots were taken after the indicated time points, diluted with EtOAc (1 mL), quenched with a few drops of acetate buffer (pH = 5), filtered through a silica plug and analyzed by GC. The column oven temperature program was as follows: 125 °C for 1 minute, 125 °C to 260 °C at 30 °C/min, then 260 °C for 9.5 minutes (total run time: 15 minutes).
GC response factors were established by the following equation using biphenyl as the internal standard:

\[
\text{Response Factor} = \frac{\text{mmols of compound}}{\text{(area of compound)}} \times \frac{\text{mmol of biphenyl}}{\text{area of biphenyl}}
\]

Three samples containing a known amount of the desired compound and biphenyl were prepared and dissolved in EtOAc. An aliquot of each sample was injected into GC in triplicates. The average of 9 response factors was used to monitor cross-coupling reactions.

<table>
<thead>
<tr>
<th>compound</th>
<th>response factor</th>
<th>( t_R ) (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>0.849</td>
<td>6.60</td>
</tr>
<tr>
<td>9</td>
<td>0.610</td>
<td>7.37</td>
</tr>
<tr>
<td>6</td>
<td>1.912</td>
<td>3.02</td>
</tr>
<tr>
<td>7</td>
<td>0.633</td>
<td>7.08</td>
</tr>
<tr>
<td>8</td>
<td>0.638</td>
<td>6.99</td>
</tr>
<tr>
<td>biphenyl</td>
<td>-</td>
<td>4.88</td>
</tr>
</tbody>
</table>

1-(3-Methyl-4-phenylbuta-1,2-dien-1-yl)-4-(trifluoromethyl)benzene (7) and 1-(2-Methyl-1-phenylbut-3-yn-2-yl)-4-(trifluoromethyl)benzene (8)

A 10-mL Schlenk flask was charged with NaH (34 mg, 1.43 mmol, 1.1 equiv) inside a glove box. The flask was transferred outside the glove box and toluene (1.0 mL) was added. A solution of 5 (320 mg, 1.3 mmol) in toluene (2.0 mL) was added dropwise and the resulting suspension stirred until bubbling subsided (1 h). Stirring was interrupted to let the residual NaH settle.

In a separate 25-mL Schlenk flask, Pd(dba)\(_2\) (29 mg, 0.05 mmol, 0.05 equiv) and Ph\(_3\)As (31 mg, 0.1 mmol, 0.1 equiv) were combined and dissolved in toluene (7.0 mL). 6 (0.15 mL, 1.0 mmol) was added and the solution warmed to 40 °C. The decanted solution of Na\(^+\)5\(^-\) was added via syringe and the mixture stirred for 18 h. The reaction was quenched by adding acetate buffer (pH = 5, 1 M, 5.0 mL). The layers were separated and the aqueous layer was washed with pentane (2 × 10 mL). The combined organic extracts were treated with 30% H\(_2\)O\(_2\) (0.1 mL), followed by saturated aqueous Na\(_2\)S\(_2\)O\(_3\) (3.0 mL). The aqueous layer was removed and the organic layer was washed with brine (10 mL), dried (Na\(_2\)SO\(_4\)), filtered and the solvent removed.
under reduced pressure. The residue was purified by silica gel column chromatography (pentane) to afford 7 (115 mg, 40%) and 8 (37 mg, 13%) as colorless oils.

Data for 7:

\(^1\text{H NMR:}\) (500 MHz, CDCl\(_3\))
\(\delta\) 7.53 (d, \(J = 7.7\) Hz, 2H, C(7)H), 7.35 (d, \(J = 7.8\) Hz, 2H, C(6)H), 7.31 (t, \(J = 7.3\) Hz, 2H, C(13)H), 7.27 – 7.19 (m, 3H, C(12)H and C(14)H), 6.09 (br s, 1H, C(4)H), 3.51 – 3.37 (m, 2H, C(10)H\(_2\)), 1.80 (d, \(J = 2.4\) Hz, C(1)H\(_3\))

\(^{13}\text{C NMR:}\) (126 MHz, CDCl\(_3\))
\(\delta\) 204.6 (C3), 139.6 (C5), 138.9 (C11), 128.91 (C13), 128.4 (q, \(J = 32.3\) Hz, C8), 128.4 (C12), 126.6 (C6), 126.5 (C14), 125.4 (q, \(J = 3.8\) Hz, C7), 124.3 (q, \(J = 271.6\) Hz, C9), 103.9 (C2), 92.9 (C4), 41.0 (C10), 18.0 (C1)

\(^{19}\text{F NMR:}\) (470 MHz, CDCl\(_3\))
\(\delta\) –62.8

IR: (neat)
3029 (w), 2910 (w), 1953 (w), 1615 (m), 1494 (w), 1453 (w), 1391 (w), 1321 (s), 1161 (m), 1118 (s), 1065 (s), 853 (s), 732 (m), 697 (m)

HRMS: (Cl)
\(m/z: [M]^+\) Calcd for \(\text{C}_{18}\text{H}_{15}\text{F}_3\): 288.1126; Found: 288.1124

TLC: \(R_f\) 0.43 (pentane)

Data for 8:

\(^1\text{H NMR:}\) (500 MHz, CDCl\(_3\))
\(\delta\) 7.54 (d, \(J = 8.1\) Hz, 2H, C(8)H), 7.45 (d, \(J = 8.1\) Hz, 2H, C(7)H), 7.37 – 7.30 (m, 2H, C(13)H), 7.30 – 7.21 (m, 3H, C(12)H and C(14)H), 3.01 – 2.86 (m, 2H, C(1)H and C(4)H), 2.82 (dd, \(J = 12.6, 6.3\) Hz, 1H, C(4)H\(_1\)), 1.30 (d, \(J = 6.7\) Hz, C(5)H\(_3\))

\(^{13}\text{C NMR:}\) (126 MHz, CDCl\(_3\))
\(\delta\) 139.4 (C11), 131.7 (C7), 129.3 (q, \(J = 32.6\) Hz, C9), 129.3 (C13), 128.2 (C12), 127.8 (C6), 126.4 (C14), 125.1 (q, \(J = 3.8\) Hz, C8), 124.5 (q, \(J = 272.0\) Hz, C10), 96.8 (C3), 80.8 (C2), 43.0 (C4), 28.7 (C1), 20.4 (C5)

\(^{19}\text{F NMR:}\) (470 MHz, CDCl\(_3\))
\(\delta\) –63.2
IR:  (NaCl, CH$_2$Cl$_2$)
    2931, 2232, 1614, 1495, 1453, 1376, 1324, 1169, 1127, 1106, 1067, 1017
MS:  (EI)
    288 (M$^+$), 273, 233, 219, 197, 177, 128, 91
TLC:  $R_f$ 0.33 (pentane)

4. REFERENCES

5. NMR SPECTRA

![NMR Spectrum Image]
Denmark and Ambrosi
Denmark and Ambrosi